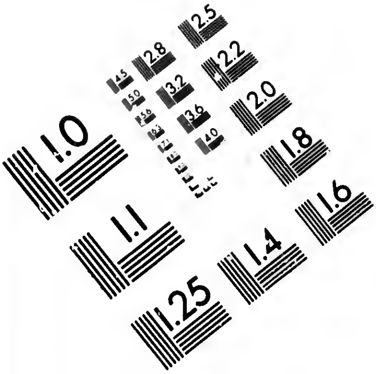

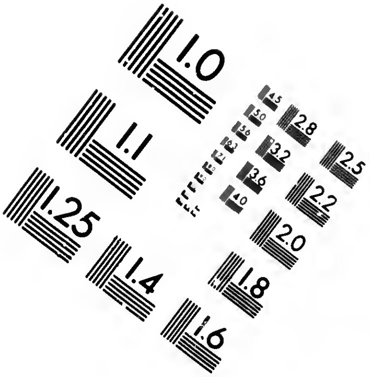

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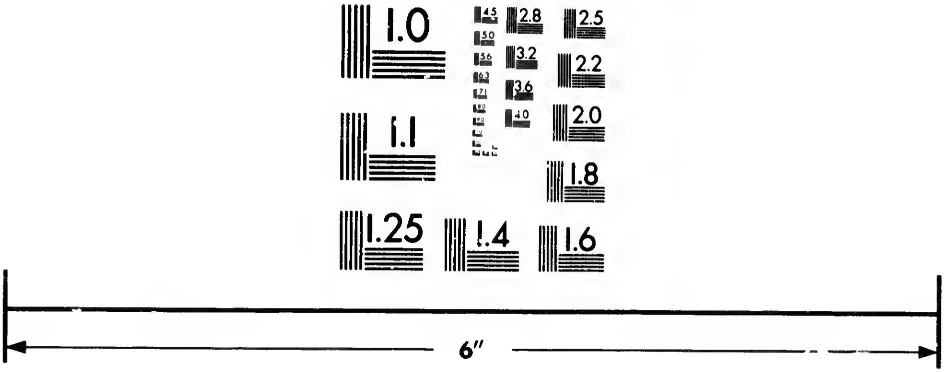

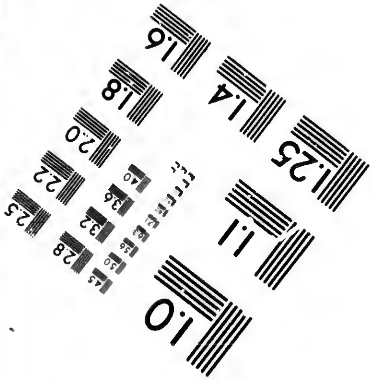

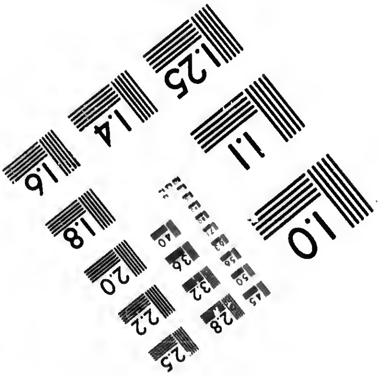

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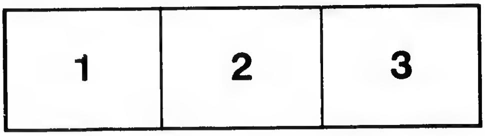

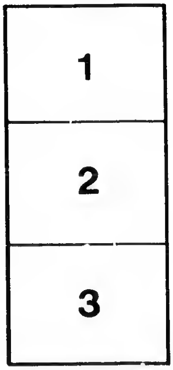

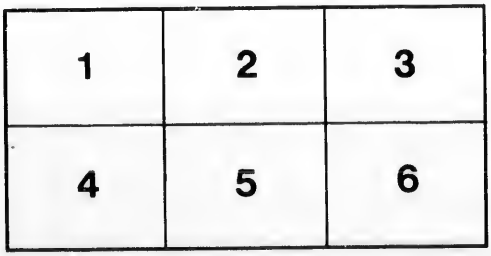

A

TEXT-BOOK OF CHEMISTRY

FOR

STUDENTS OF MEDICINE,

BY

W. L. GOODWIN, D.Sc. (EDIN.),
QUEEN'S UNIVERSITY, KINGSTON.

TORONTO:
THE COPP, CLARK CO., LIMITED, PRINTERS, COLBORNE STREET.
1887.

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PREFACE.

This book was written to meet a want in my own teaching, and is intended to give an outline of Chemistry, from the medical point of view, as far as possible. While no attempt has been made to treat the theory of chemistry exhaustively, I have tried to explain and apply the fundamental laws and principles of the subject in such a way as to render the mastering of the facts an easier task. The writers of text-books of chemistry have perhaps, in many cases, erred in arranging their matter *too* logically, e.g., adopting an invariable order in describing the compounds of the metals; while, in other cases, the error has been in the opposite direction. It has been my aim to steer a course between these two. The principle adopted has been to proceed from the known to the unknown, as far as is consistent with the limits of time and space imposed upon the teacher. Thus, *water* is studied before *oxygen* and *hydrogen* are introduced, the study of *air* precedes that of *nitrogen*, &c., &c. I have found it advantageous in teaching chemistry to medical students to let them make for themselves such experiments as those described in the text of this book. Nearly all the experiments described are such as can be made by students easily and with very simple apparatus. Class experiments have a rather limited value, and can be advantageously replaced in most cases by simpler experiments made by the students themselves. The compounds of carbon have been described along with that element, as there seems to be no longer any necessity for relegating them to the end of the book, as is generally done. In the Appendix is a *Table of solubilities*, which I have found very useful for reference. Tests are given at the end of the description of each acid, metal, &c., and are collected into analytical tables in the concluding chapter.

I wish to express my gratitude to my colleagues, Professors Dupuis and Shortt, and to my friend Dr. John Waddell, for valuable assistance in revising proofs.

W. L. GOODWIN.

Queen's University, Kingston, Ontario.
March 1st, 1887

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* This element has been lately prepared by the electrolysis of dry hydrofluoric acid. It is a gas having powerful chemism.

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CHAPTER XXIII.

ADDENDA ET CORRIGENDA.

Page 7, table, for 0.064 read 0,0648.
“ 7, table, for 28.3549 read 28.3495.
“ 11, l. 8, for 96 read 88,
“ 26, l. 18, for *no* read *not much.*
“ 35, l. 3, from bottom, for *is* read *was called.*
“ 48, l. 15, for *always* read *generally.*
“ 48, l. 15, for 6.6 read 6.3.
“ 48, ls. 19 and 20, for *specific* read *atomic.*
“ 53, last line, for HgO read $2HgO$,
“ 56, for *Experiment 28* read *Experiment 28 A.*
“ 57, l. 3, for *atomic* read *atom.*
“ 83, l. 16, for *red* read *blue.*
“ 122, l. 4 from bottom, for *that* read *the atom.*
“ 141, l. 8, for KOH read $NaOH$.
“ 145, l. 7, for *amphorous* read *amorphous.*
“ 154, last line, for $Ca_3(PO_4)_2$ read $3(Ca_3(PO_4)_2)$.
“ 163, first equation, for Na_2CO read Na_2CO_3.
“ 179, l. 3 from bottom, for 151 read 159.
“ 193, l. 6, after *absent,* insert, Fermentations are also caused by certain nitrogenous organic compounds called *unorganised ferments,* e.g. *diastase, synaptase,* &c.
“ 201, l. 4 from bottom, after *chlorine* read *by a series of reactions.*
“ 203, l. 17, for $C_3H_6O_3$ read $C_3H_8O_3$.
“ 209, l. 2, for *a solution of* read *sparingly soluble.*
“ 219, l. 15, omit *sparingly.*

CHEMISTRY

FOR

STUDENTS OF MEDICINE.

CHAPTER I.

INTRODUCTORY.

1. **Chemical Action.**—*Iron* rusts in air, and the rust differs in properties from the iron. Iron heated in air becomes changed to a black substance (as in a blacksmith's shop) unlike the iron in many respects. When placed in vinegar iron gradually disappears into the vinegar, *i. e. dissolves,* and a red liquid is formed, having the properties of neither vinegar nor iron. *Wood* burns, leaving only a small portion of ash, unlike the wood in colour, and other properties. The greater part of the wood has been changed into substances like air. A *plant* takes food from the soil and from the air in the form of water, carbonic acid, ammonia, and various mineral substances. From these it elaborates sugars, starch, gums, wood, &c., substances totally different from the original articles of food, and not to be found in the sources from which the plant gets its food. An *animal* brings about similar changes, forming out of its food substances quite

unlike that food, converting starch into sugar, albumin into fat, &c. In all these cases, substances undergo such changes that they become converted into other and different substances. Such processes are called *chemical actions*, and *Chemistry* is, for the most part, the study of chemical actions.

2. **Three States of Matter.**—All substances can be grouped into three classes, viz.: solids, liquids, and gases. *Solids* have a *definite form* and *volume*. *Liquids* have no definite form, but their volume does not tend to change. *Gases* are indefinite both in form and volume. They take the shape of the vessel in which they are confined, and readily undergo compression and expansion.

3. **Pure Substances.**—Simple inspection of granite shows it to contain more than one substance. It is a *mixture* or mixed substance. Soil, pudding stone, milk, and air, are other examples of mixtures. There are many methods of separating mixtures into their *ingredients*, and thus obtaining *pure substances*, or *chemical individuals*. The commoner methods are given in the following sections.

4. **Elutriation**, or "washing out," is a process used by the gold miner who washes away the *light* earth, sand, &c., from the *heavier* gold. Winnowing is a similar process.

5. **Filtration** is separating a liquid from a solid by allowing the former to flow through some porous substance which retains the latter. Thus, muddy water can be separated into mud and water. Unsized paper, called *filter paper*, is very commonly used.

6. **Solution.**—In this process, a liquid called a *solvent* is used to separate a *soluble* substance, sugar for instance, from an *insoluble* substance such as sand.

7. **Crystallisation.**—When all the ingredients of a mixture are soluble in some one solvent, *e. g.* in water, a separation can often be brought about by *evaporating* the solvent. When there is not enough of the solvent left to dissolve all the substances, that one which is most difficult to dissolve (or the least soluble), separates from the liquid, generally in regularly formed *crystals*. At another stage of the evaporation, the substance next in solubility *crystallises*, and thus a separation more or less complete is effected. It is by this process that common salt is separated from the other substances dissolved in sea water.

8. **Distillation.**—If a dish of alcohol and one of water be set side by side on a hot stove the alcohol begins to boil much before the water. Alcohol boils *at a lower temperature* than water, and a mixture of these two liquids can be separated by *distilling* them. For, when heat is applied to the vessel (the *boiler*, or *retort*,) containing the mixture, the alcohol is *first* changed to vapour, passes as vapour into the cold tube (or *condenser*), and is there cooled and condensed (or made liquid). Thence it runs into the *receiver*. Later, water begins to distil over and may be collected in a different vessel. In a similar way fresh water can be prepared from sea water, the pure water distilling, and the salt remaining in the boiler.

9. **Sublimation.**—This is distillation applied to solids which can be changed to gases by heat. Sulphur

is purified by heating it until it is changed to a gas which is then condensed in a clean vessel. The impurities remain, since they are *non-volatile.*

10. **Fusion.**—Some substances melt or *fuse* at lower temperatures than others. Thus, butter fuses at the temperature of the hand; while salt can be fused only by a strong, red heat. If a mixture of butter and salt be gently heated, the butter melts, the salt sinks to the bottom, and the liquid butter can be poured off. This is the pharmaceutical process of *clarification.* In some cases the impurities are lighter than the melted substance to be clarified. They, then, rise as a scum and are removed by skimming.

11. **Chemical Decomposition and Combination.**—In the processes described above, no permanent change is brought about in the pure substances which are separated out of the mixtures. They preserve their *identity.* In chemical actions substances lose their identity.

Experiment 1.—Heat a little *red oxide of mercury* in a tube of glass. The oxide disappears gradually, and a silvery liquid, quicksilver, gathers on the inside of the tube. Thrust a splinter of wood with its end still glowing into the tube. The splinter begins to burn very brightly.

Two substances have been formed from the oxide of mercury, viz., the liquid metal *quicksilver* or *mercury,* and the gas *oxygen,* which causes a live coal to burst into bright flame and therefore differs from ordinary air. This is an example of *chemical decomposition.* Red oxide of mercury has been *decomposed* by heat, and the *pro-*

ducts of its decomposition are mercury and oxygen. This process differs from the separation of a mixture into its ingredients, because the products of decomposition have not the properties of the substance decomposed. The chief agents which bring about chemical decomposition are heat, light, electricity, mechanical force (as in the explosion of dynamite), and contact with certain substances. Chemical decompositions are also brought about in some unknown way by living beings, as in fermentation.

Experiment 2.—Mix well four parts of flowers of sulphur with seven parts of very fine iron filings. A powder is obtained in which the presence of both iron and sulphur can be easily recognized. Shake up a little of the mixture with water in a test-tube. The iron sinks to the bottom more quickly than the sulphur and the two are separated. Move a magnet over another small portion of the mixture. The iron sticks to the magnet and the sulphur remains. The two substances were merely *mixed.* Now, heat the remainder of the mixture in a a small porcelain dish. It gets red hot, blackens, and becomes quite uniform in appearance. The closest examination does not show the presence of either sulphur or iron. Powder a little of the black substance and shake it up with water as before. No separation takes place. Move a magnet over another part. No iron sticks to it. The iron and sulphur have disappeared and this single black substance has taken their place.

This is an example of *chemical combination.* Iron and sulphur have *combined* to form sulphide of iron (ferrous sulphide), a substance differing altogether in properties from iron or sulphur. *Chemical combination* must be distinguished from *mixture.*

12. **Elements and Compounds.**—The majority of substances can be decomposed, but there are certain

which cannot, so far as known. Thus, it has been found impossible to obtain from a portion of pure mercury anything else; and the same is true of iron and sulphur. These substances will combine with others to form new substances, but from themselves, taken alone, nothing different has been obtained by any process yet tried. Such substances are called *Elements*, or *Simple Substances*. They unite to form *compounds*.

Definitions.—A *chemical action* or *reaction* is a change in which from one or more substances there are formed other substances differing from the original in essential properties, *e.g.* in colour, taste, smell, &c. In *chemical combination* simpler substances unite to form more complicated. In *chemical decomposition* complex substances are broken up into simpler. An *element* is a pure substance which has never been decomposed into substances differing from it in properties. A *compound* is a substance formed of two or more elements chemically combined.

There are at present sixty-seven elements known, and all the known substances on and in the earth consist of these elements and their compounds with each other. A list of the elements is given at page 39.

CHAPTER II.

WEIGHTS AND MEASURES—SPECIFIC WEIGHT.

13. **Weights and Measures.**—In order to study chemical actions completely the *quantities* of substances taking part in them must be known. The *metrical system* of weights and measures has been adopted by chemists everywhere. It involves very little calculation since its

units all increase in magnitude by *tens,* so that the operations of reduction can be performed by merely moving the decimal point. It is hence called the *decimal system* of weights and measures. The unit of length in this system is the *metre* intended to be equal to one ten-millionth part of a quarter of the earth's circumference through the meridian of Paris.

Linear Measures.—1000 millimetres (mm.) = 100 centimetres (cm.) = 10 decimetres (dcm.) = 1 *metre* (m.) = $\frac{1}{10}$ decametre = $\frac{1}{100}$ hectometre = $\frac{1}{1000}$ kilometre = 39.371 English inches.

Measures of Capacity.—1000 cubic centimetres (c.c.) = 1 cubic decimetre = 1 litre (l.) = 61.027 cubic inches = 1.761 pint.

Measures of Weight.—1000 milligrams (mgms.) = 100 centigrams (cgms.) = 10 decigrams (dgms.) = 1 *gram* (gm.) = $\frac{1}{10}$ decagram = $\frac{1}{100}$ hectogram = $\frac{1}{1000}$ kilogram = 15.43 grains.

1 gram = the weight of 1 cubic centimetre of pure water measured at 4° centigrade (its point of greatest density).

Relations of Pharmaceutical to Metrical Weights and Measures.

1 grain	=	0.064 gram.
1 ounce	=	28.3549 "
1 pound	=	453.5925 "

		CUBIC CENTIMETRE.
1 minim	=	0.059
1 fluid drachm	=	3.549
1 " ounce	=	28.396
1 pint	=	567.936
1 gallon	=	4543.487

or about 4½ litres.

Exercises.—1. In 1764 millimetres how many metres?

2. In 37 metres how many cms.?

3. How many litres capacity has a tank 2 metres long, 1.5 metres broad and 1.5 metres deep?

4. How many grams in a pound avoirdupois (= 7000 grains)?

5. What weight of water will fill the tank in (3)?

6. How many c. c. in a fluid ounce? (Note.—The fluid ounce is the volume of 1 ounce weight of water = 437.5 grains).

7. Reduce 38,674 cubic centimetres to litres.

8. In 1 kilogram how many pounds?

9. Find the number of kilometres in a mile.

10. How many inches in a kilometre?

11. Find the capacity in litres of a tank 4 feet long, 2½ feet wide and 3 feet deep.

12. What is the weight in grams of 8 fluid ounces of mercury? (mercury weighs 13.596 times as much as the same volume of water).

14. **Specific Weight.**—When it is said that lead is heavier than water it is meant that if equal volumes of lead and of water be weighed, the lead will be found to be heavier. Thus Specific Weights, or Specific Gravities, of substances are found by comparing the weights of equal volumes of the substances with that of the same volume of some substance chosen as a standard. For liquids and solids *water* has been chosen as the standard; and for gases, *air*, or *hydrogen*. For example, 1 cubic centimetre of water weighs one gram; and the same volume of mercury weighs 13.596 grams. Then, the specific weight of mercury is 13.596.

Definition.—The *Specific Weight* of a substance is a number expressing how many times heavier the substance is than an equal volume of some substance chosen as a standard.

15. **Specific Weights of Solids.**—If the solid is heavier than water it is first weighed in the air, and then hanging in water. Its weight in water (w) is less than its weight in air (W) by the weight of the water which it displaces, i.e., an equal volume of water. Or, if S represents the specific weight, then $S = \frac{W}{W - w}$.

16. **Specific Weights of Liquids.**—(1) Fill a weighed narrow-necked flask with water up to a mark on its neck, and weigh the full flask to determine the weight (W) of water. Fill the same flask with the liquid of which the specific weight is to be found and find the weight (W′) of the liquid. Then $S = \frac{W'}{W}$. (2) The *Hydrometer* or *Areometer* is a glass tube with a bulb blown on one end. In the bulb is a small quantity of mercury which causes the tube to swim upright in any liquid in which it is placed. The stem of the hydrometer is graduated and numbered. When placed in water it sinks until the water reaches a certain mark on the stem. When placed in a liquid heavier than water it does not sink so far. In a liquid lighter than water the instrument sinks farther than in water. Numbers marked on the stem indicate the specific weights of the liquids. This instrument in various forms is constantly used in medical practice.

17. **Specific Weights of Gases.** — These are found by methods the same in principle as the first

method for liquids (§ 16). A large glass globe, whose capacity is known, is made as nearly as possible empty of air by means of the air pump, and is then weighed. The gas of which the specific weight is to be determined is then allowed to flow in, and the flask is reweighed. The increase in weight is the weight of the flask full of gas. This weight divided by that of an equal volume of the standard gives the specific weight required. There are many minute precautions and corrections which cannot be described here.

18. In the following table are given the specific weights of some of the commoner solids and liquids, water at 4° centigrade being the standard :—

Platinum	22.069	Sodium	0.970
Gold	19.362	Ice at 0° C	0.918
Lead	11.352	Potassium	0.860
Silver	10.474	Mahogany	1.060
Copper	8.788	English Oak	0.970
Brass	8.383	Beech	0.852
Steel	7.820	Ash	0.840
Iron (wrought)	7.788	Yellow Pine	0.657
Iron (cast)	7.207	Cork	0.240
Tin	7.291	Mercury	13.596
Zinc	6.861	Oil of Vitriol	1.840
Diamond	3.531	Chloroform	1.525
Flint Glass	3.329	Nitric Acid	1.500
Marble	2.840	Hydrochloric Acid	1.220
Bottle Glass	2.600	Blood (human)	1.045
Plate Glass	2.370	Milk	1.030
Porcelain	2.300	Sea Water	1.028
Sulphur	2.030	Port Wine	0.990
Ivory	1.917	Castor Oil	0.970
Graphite	1.8 to 2.400	Linseed	0.940
Anthracite	1.800	Proof Spirit	0.930
Phosphorus	1.770	Oil of Turpentine	0.870
Magnesium	1.740	Brandy	0.837
Amber	1.080	Absolute Alcohol	0.780
Water at 4° C	1.000	Ether	0.720
White Wax	0.970		

QUESTIONS AND EXERCISES.

1. What is a *unit of measurement*? Why are there *many* units of length in use instead of only one?

2. A flask filled with water was found to weigh 72 grams, the flask alone weighing 22 grams. The same flask filled with oil of vitriol weighed 114 grams. Calculate the sp. wt. of oil of vitriol.

3. A piece of iron weighing 96 grams in air was found to weigh 76.5 grams in water. Calculate the sp. wt. of iron.

4. A flask filled with water weighed 153 grams; 25 *g*. of copper are dropped in. The flask and contents then weighed 175.19 *g*. What is the sp. wt. of copper?

5. "When a body is weighed in air its true weight is not found." Why not? How must it be weighed in order to find its real weight?

6. A man of 160 lbs. weight immersed his body completely in a bath 7 ft. long and 3 ft. wide. The water rose 1½ in. What was the sp. wt. of his body?

7. A piece of cork weighing in air 15 grams is immersed in a vessel of water 12 cm. long and 5 cm. wide. The water rises 1 cm. Calculate the sp. wt. of the cork.

8. What is the volume in cu. inches of a piece of lead weighing 10 lbs.?

9. Calculate the volume in cubic centimetres of 100 grams of copper.

10. What is the weight in grams of a gallon of pure water at 4° C.

11. What is the sp. wt. of a body which floats with one third of its bulk out of water?

12. When the lungs are inflated the specific weight of the human body is less than 1; but when the lungs are filled with water, it is greater than one. Explain this.

13. Write a short essay on the convenience of the metrical system.

CHAPTER III.

WATER—HEAT—SOLUTION.

19. **Water.**—About two-thirds of the weight of animals and a large fraction of the weight of plants consist of water. As it occurs in nature water is not a pure substance. This can be shown by *distilling* any sample of sea, river, lake, spring or rain water. A *solid residue* is left in each case. But if this distilled water (*aqua distillata*) be redistilled again and again no residue is left in the retort. *Distilled water* is a pure substance, a *chemical individual.* It is generally a liquid, but if sufficient *heat* be removed from it, it becomes solid (ice); and when heat is added liquid water is changed to a gas (water vapour, steam).

20. **Heat - Conduction.**—Heat and light were once thought to be substances. They are now known to be motion of some sort. When a body becomes hotter its particles move (*vibrate*) faster, and the motion is communicated to any other body in contact with it. Similarly, heat passes from a hot to a cooler part of a body without any movement of the body as a whole. This process is called *conduction* of heat.

Experiment 3.—Choose a piece of copper wire and another of iron wire of about the same size and length. Hold the end of each in the flame of a burner, and observe the time required for the heat to become unpleasant at the other end held between the fingers. The time is much longer for the iron than for the copper. Copper is a better conductor of heat than iron.

A glass rod may be heated at one end until it melts before the other end becomes warm. Glass is a poor conductor of heat. The metals generally are the *best conductors* of heat. Wool, feathers, asbestos, fur, air and gases generally, and most liquids are *bad conductors.* We use bad conductors, as clothing, to keep the heat from leaving our bodies ; but we also use them as packing for ice, &c., to keep the heat *out.*

Experiment 4.—Wrap a piece of copper wire round a small lump of ice and allow the ice to fall to the bottom of a test-tube full of cold water. Holding the test-tube aslant, heat the water *near the top* until it begins to boil. The ice at the bottom remains unmelted. Water is a bad conductor of heat.

21. **Radiation.**—Heat reaches us from the sun by a process different from conduction. It may warm the earth to 90° or 100° F., and still leave the air *through which it passes* cool. In this way, too, heat and light pass through space empty of everything as far as known. This movement of heat and light is called *radiation.* It is extremely rapid—about 186,000 miles per second.

22. **Relation of Light and Heat.**—Light and heat are related to each other just as the high notes of music are related to the low. Light consists of short waves, or rapid vibrations, which produce in the eyes the *sensation* ordinarily called *light.* Heat consists of the longer, slower waves which are not capable of exciting this sensation,—in *our* eyes at least. When light falls upon a body which is not a good reflector, it is *absorbed* and may be thus transformed into heat. It is in this way, principally, that the earth is heated by the sun.

23. Convection.

Experiment 5.—Fill a tall glass vessel (beaker) with water containing fine sawdust, and heat at the bottom. The movements of the sawdust show that the water as it is heated rises to the top, while the colder water sinks.

Thus, heat is *conveyed* from place to place by motion *en masse* of the substance which is being heated, *i. e.*, by *convection currents.* Winds are convection currents on a grand scale; drafts are the same on a smaller scale. From experiments 4 and 5 it is easily seen that a mass of water can be much more quickly heated by applying the heat at the bottom, than by applying it at the top.

24. Expansion by Heat.—In *Experiment* 5 the water rises as it becomes warm, because it is lighter than the cold water. Its volume has been increased. *Heat expands water.*

Experiment 6.—Fill a glass flask full with cold water, and heat the water to boiling. A small quantity runs over as the water becomes hot. Allow the water to cool. It sinks down the neck of the flask. Water expands when heated and contracts when cooled.

Other liquids expand when heated and contract on cooling, *but different liquids expand differently.* For example, mercury expands less than water for the same increase in degree of heat. Solids also expand when heated, but not so rapidly as liquids. It will be shown later on that gases expand when heated much more than either liquids or solids, and that *all gases expand almost exactly at the same rate.*

Experiment 7.—Fit a cork to a glass flask, bore a hole through the cork, and through the hole put a glass tube fitting tightly. Fill the flask with water, push in the cork tightly so as to cause the water to rise an inch or two in the tube. Pour hot water on the flask. The water in the tube at first sinks, but immediately afterwards begins to rise steadily. When it has stopped rising it begins to fall, and finally remains at about the same level as before the hot water was poured on the flask.

The flask expands *first* when the hot water is poured on and the contained water sinks down the tube. Then the heat penetrates to the water which expands *faster* than the glass, and therefore rises in the tube.—Builders of bridges allow for the expansion and contraction of iron with change of season, &c. In laying rails in cold weather the ends are not put close together, but space is allowed for the increased length in warm weather.

25. **Temperature**—If an instrument such as that described in *Experiment* 7 were put into a body of water which caused the water in the tube to rise, the conclusion drawn from such an experiment would be that the body of water was *hotter* than that in the flask. If, on the other hand, the liquid should fall in the tube, it would be concluded that the water under examination was *cooler* than that in the flask ; if no change were produced, the conclusion would certainly be that it was neither hotter nor colder. The *sense of touch* would confirm these conclusions in each case, if the hand were immersed successively in the two quantities of water.

Experiment 8.—Lay a piece of iron and a block of wood side by side on a table and after half an hour touch each of them with the hand. The iron *feels* colder than the wood ; and yet, if an instrument such as that used in *Experiment* 7 be touched first to one and then to the other it shows them to be exactly in the same state.

The sense of touch does not always give the same verdict regarding heat as the effect on volume does. The iron *feels* colder because it conducts heat away from the hand more rapidly, being a better conductor than wood. For the same reason blankets feel warmer than sheets. The words "hot" and "cold" do not convey a correct idea of the *state of a body with regard to its sensible heat.* Generally, bodies which have been in contact for some time are in the same state with regard to sensible heat, for, if they are at first in different states, heat *flows* from the hotter to the colder until they are, as it were, *at the same heat-level,* or at the same *temperature.*

Definition.—Temperature is the state of a body with regard to sensible heat; or temperature is heat-level.

26. **Thermometers.**—Temperatures are measured by *thermometers,* or *heat-measures.* In most thermometers the temperature is indicated by the amount of expansion of a liquid enclosed in a graduated glass tube with a bulb or reservoir at the lower end. The most convenient liquid for ordinary ranges of temperature is mercury. It expands regularly, freezes only at a low, and boils only at a high temperature. Alcohol is used for very low temperatures as it does not freeze until the temperature sinks much below any that occurs naturally. The thermometer is graduated by placing it first in a mixture of ice and water, then in steam at ordinary pressure, and marking on the stem or scale the level at which the mercury stands in each case. These are the

fixed points, and always when the thermometer is placed in melting ice the mercury stands at the *lower fixed point,* and when it is placed in water boiling under ordinary circumstances, the mercury remains stationary at the *higher fixed point.* Under the same circumstances water freezes always at the same temperature, and also boils always at the same temperature. It only remains to divide the interval between the fixed points into equal parts called *degrees,* and to number these in regular order. The numbers chosen are different in thermometers devised by different men. Any numbers may be chosen, according to taste or convenience. On the *Centigrade* or Celsius thermometer, the one always used for scientific purposes, the lower fixed point is marked 0°, the upper 100°, and the space between is divided into 100 degrees. On the *Fahrenheit thermometer,* generally used in this country, the two points are marked 32° and 212° respectively, so that the zero Fahrenheit is 32 degrees below the freezing point of water. On the Réaumur thermometer the space between the fixed points is divided into 80 degrees numbered from 0° to 80°. Thus, the degrees on the Réaumur scale are longer than on the Centigrade, which in their turn are longer than those on the Fahrenheit. The relations between the degrees are expressed as follows:—1 degree F. $= \frac{100}{180} = \frac{5}{9}$ degree C. $= \frac{80}{180} = \frac{4}{9}$ degree R. To change any temperature Fahrenheit to Centigrade (or Réaumur) subtract 32 and multiply by $\frac{5}{9}$ (or $\frac{4}{9}$). The 32 degrees between the Fahrenheit zero and the freezing point must be subtracted *first,* because the other thermometers reckon from the freezing point. To change any temperature Centigrade (or Réaumur) to Fahrenheit, multiply by $\frac{9}{5}$ (or $\frac{9}{4}$) and add 32. Or, if t represent any temperature Fahrenheit $(t - 32)\frac{5}{9}$ represents the same temperature Centigrade, and $(t - 32)\frac{4}{9}$ the same temperature Réaumur. Also let t be any temperature Centigrade, then $\frac{9}{5}t + 32$ represents that temperature Fahrenheit. Similarly for Rèaumur. Temperatures below zero are indicated by the minus sign (—).

27. Maximum Density Point of Water.

Experiment 9.—Bore a second hole in the cork in the apparatus of *Experiment* 8, fit a centigrade thermometer in it, and arrange the apparatus as in *Experiment* 8. Surround the flask with snow or ice. The water in the tube falls until the thermometer marks 4° C. It then begins to *rise*, and continues to do so until the temperature sinks to 0°.

Water has the smallest volume at 4° C., and has, therefore, the greatest specific weight at that temperature, which is for this reason called the *maximum density point* of water. Most liquids are densest at their freezing points. Water is exceptional in this respect. When a body of water cools at the surface, as a lake in autumn, the cooled water *sinks* until the whole lake is at the temperature 4° C. When the water at the surface is cooled below this it remains at the surface, because it expands and thus becomes specifically lighter than the warmer water below. As water is a very poor conductor of heat (see Experiment 4), the water below cools very slowly, even if the surface becomes changed into ice. Were it not for this exceptional feature in the effect of cooling on water, our lakes would become masses of ice every winter.

28. Freezing and Melting.

Experiment 10.—Heat slowly a vessel containing snow or ice, stirring constantly with a thermometer. The temperature of the whole mass remains at 0° C. until the last portion of snow or ice is melted. It then begins to rise.

Ice melts at 0° C. *always*, under ordinary circumstances. Other solids have different *melting points*, e. g. Lead melts at 300° C. The word *fuse* is used instead of *melt*, especially of solids which become liquid only at high temperatures. If a portion of water be cooled it begins to freeze at 0° C., and the temperature does not sink below that until the whole of the water is changed to ice. The *freezing point* of water is the same as the melting point of ice. This is true of most liquids, but not of all.

29. Change of Freezing Point by Pressure.

Experiment 11.—Support a slab of clear ice at either end and lay over it a thin clean wire having a weight attached to each end so as to cause the wire to press upon the ice. The wire gradually passes through the ice, but does not cut it in two.

The ice is melted by the pressure of the wire upon it, but solidifies again as soon as the pressure is removed by the onward movement of the wire. Ice at 0° C. can be melted by pressure, and cannot be frozen as long as the pressure continues, without reducing the temperature *below* 0° C. In other words *the freezing point of water is lowered* by pressure. Water is exceptional in this respect also; most liquids have their freezing points *raised* by pressure.

30. Change of Volume on Freezing.—Since ice floats on water it must be specifically lighter than water. *Water expands on freezing.* Most liquids contract on solidifying, e.g., solid lead sinks in liquid lead Water expands about one-eleventh of its volume on freezing. Enormous force is exerted during this expansion; hence the bursting of water-pipes, the splitting of rocks, the "heaving" of the foundations of buildings, &c.

31. **Latent Heat of Water.**—From Experimen 10 we learn that when ice is melting heat goes into i without raising its temperature. This heat become *latent* or hidden. In order to freeze the water again thi latent heat must be removed from it.

Experiment 12.—Mix 1,000 grams ice-cold water with 1,00 grams boiling water. The temperature of the mixture is 50° (Now, mix 1,000 grams ice with 1,000 grams boiling water, st well until the ice is melted. The temperature of the mixture only 10.5° C.

From these experiments it is plain that the hea rendered latent by melting 1,000 grams ice would war 2,000 grams water from 10.5° C to 50° C. If we tak as the *unit of heat* (or *thermal unit*) the quantity of hea required to raise the temperature of 1 gram of water degree Centigrade, then 2,000 × 39.5 = 79,000 uni of heat are rendered latent in melting 1,000 grams ic or 79 for 1 gram. *The Latent Heat of Water is 7 thermal units*; or, to change ice at 0° into water at 0 as much heat is rendered latent as would warm the san weight of water from 0° to 79°. The latent heat water is much greater than that of most substance That of mercury is only 2.28; that of molten lead 5. Ice is thus an excellent cooling agent.

32. Specific Heat.

Experiment 13.—Take equal weights of iron and lead, about 1,000 grams; cool them to 0° and immerse them in equal quantities of water (500 c. c.) at 50° C. After stirring for a moment note the temperatures. That of the water in which the iron is will be about 40° C.; of that in which the lead is, about 47° C.

The iron has taken more heat from the water than the lead has, and yet its temperature has not been raised so high. *Iron is harder to heat than an equal weight of lead*, i.e., requires more heat to raise its temperature, say, one degree. Different substances require different quantities of heat to raise the temperature of equal weights of them one degree.

Definition.—The *Specific Heat of a substance is the quantity of heat required to raise the temperature of unit weight (1 gram or 1 lb.) of the substance one degree (from 0° C. to 1° C.)*

The specific heat of water is of course the thermal unit. That of most other substances is much less. That of lead is only 0.031, of iron, 0.1137, and of copper, 0.095.

33. Evaporation and Ebullition.—Water in the state of gas (water vapour) is constantly escaping into the air from every exposed surface of water or ice; and, other things being equal, the hotter the water the more rapidly does it become changed to vapour. This process is called *evaporation*. Thus the air always contains water-vapour. At any particular temperature a portion of air is capable of containing only a certain quantity of water-vapour. When air contains as much water-vapor as it is capable of holding, it is *saturated*;

and if it be then cooled, some of the vapour is condensed; if it be heated, it becomes capable of containing more vapour. The air coming from our lungs is warm and saturated with water-vapour. When it comes in contact with cold air in winter some of the vapour is condensed and forms a "cloud." Dew, fogs, clouds, mists, &c., are explained similarly. Air is *moist* or *dry* according as it is near to, or far away from, its point of saturation. Thus, if moist air be heated it becomes dry, i.e., capable of receiving more water-vapour. Evaporation is hastened by heat, or by a current of dry air.

Experiment 14.—Heat some water in a glass flask until it begins to boil, observing the temperature by a thermometer in the water. The water begins to boil when the temperature rises to 100° C. Observe the temperature of the steam. It is also 100°. Use a larger flame so as to make the water boil more vigorously. The temperature does not rise. Now, close the flask with a cork through which the thermometer passes. Heat very carefully, and observe that the temperature rises *above* 100° and yet the water scarcely boils. Remove the lamp when the mercury has risen one or two degrees, otherwise the cork will be driven out by the *pressure* of the steam. Take out the cork, boil the water vigorously for a minute or two and while steam is still coming out put in a cork firmly at the same time taking the flask away from the lamp. Allow the water to cool a little, and then pour cold water on the flask. The water in the flask begins to boil.

Water in an open vessel boils at 100° C., and the temperature cannot be raised above that, unless the vessel be closed so as to *increase* the *pressure* on the surface of the water. When the pressure on the surface is lowered, as by condensing the steam—filling the closed flask in Experiment 14, water boils at temperatures below 100° C. The *boiling point* of water depends on the pressure on its surface, being higher the greater the pressure. On the top of a high mountain where the weight of air pressing on surfaces is less than it is lower down, water boils at so low a temperature that it can not *cook*.

Experiment 15.—Boil some alcohol in a flask, observing the temperature of the boiling liquid and of the vapour. If the alcohol is pure, the temperature in each case is 78.4° C. Try the boiling point of ether, heating it by means of hot water. Ether boils at 34.2°.

Every liquid boils at a particular temperature, just as every solid fuses at a particular temperature.

BOILING POINTS.

Nitrous oxide	—87.9	Ethylic Alcohol	78.4
Carbon dioxide	—78.2	Benzene	80.4
Ammonia	—33.7	Water	100.0
Sulphur dioxide	—10.5	Acetic Acid	116.9
Aldehyde	+19.8	Naphthalene	216.8
Ether	34.2	Phosphorus	290.0
Carbon Bisulphide	47.9	Mercury	350.0
Methylic alcohol	55.1	Sulphur	440.0
Chloroform	61.0	Cadmium	860.0
Bromine	63.0	Zinc	1040.0

34. **Latent Heat of Steam.**—From Experiment 14 we learn that the heat which goes into boiling water and changes it to steam does not cause any rise of temperature. This heat becomes latent, just as in the case of melting ice. The latent heat of steam is 536 thermal units; i.e., to change any weight of water at 100° C. to steam at the same temperature heat is required sufficient to raise the temperature of 536 times the weight of water one degree. The latent heat of steam is very great compared with that of other vapours. Water in evaporating from the earth's surface carries away a great

deal of heat. Wet clothes feel cold because of the heat consumed by the evaporating water. Much heat is lost to the body by the evaporation of water through the skin and lungs. The cooling effect of ether and other rapidly evaporating liquids is explained in the same way. Water can be frozen by rapidly evaporating ether. That such an enormous amount of heat is required to evaporate a liquid is accounted for by the great change of volume. For example, 1 cubic inch of water forms 1,700 cubic inches of steam.

35. Solution.

Experiment 16.—Mix 100 grams finely-powdered saltpetre with 100 grams distilled water in a beaker, stirring for some time with a glass rod. Part of the saltpetre disappears; the water has now the taste of saltpetre, and is colder. Apply heat, carefully stirring all the time. More of the saltpetre, and at length all of it, disappears. Allow the liquid to cool; some of the saltpetre reappears in long crystals which *grow* as the liquid cools. When quite cool, pour off some of the liquid into a small porcelain basin, boil away some of the water, and allow the remaining liquid to cool again. More saltpetre *crystallises out.* This process is called *concentration.* Repeat this experiment, using *washing soda* instead of saltpetre.

Experiment 17.—Carefully heat 300 grams saltpetre with 100 grams water. (Do not apply the flame to the beaker.) Only part of the saltpetre disappears even when the water begins to boil. Mix 10 grams of gypsum with 100 of water, and heat to boiling. The gypsum does not disappear. Filter some of the liquid into a porcelain basin and evaporate to dryness. A small quantity of white substance, *gypsum,* is left. Repeat this experiment, using clean white sand, and again with chalk. In each case little or nothing remains when the water is evaporated.

Saltpetre and washing soda *dissolve* readily in water, imparting their taste and other *properties* to the water. They are *soluble* in water, and form *solutions* from which they can be got again by evaporating the water.

Experiment 18.—Mix 10 c. c. hydrochloric acid with about four times as much water, pour it over three or four iron tacks in a porcelain basin, and warm gently. Bubbles rise from the tacks, which gradually disappear, giving a greenish color to the water. Evaporate the water. A solid remains, but it is not iron; it is ferrous chloride. Repeat the experiment, using marble instead of iron.

In Experiment 18 the process of solution is accompanied by chemical action. This kind may be called *chemical solution.*—Substances are generally more soluble in hot than in cold water.—Gypsum is much less soluble than saltpetre or washing soda. Sand and chalk are *insoluble.* A given quantity of water can dissolve only a certain maximum weight of each soluble substance at a given temperature, forming in each case a *saturated solution.* For example, 100 grams of water will *always* dissolve 13$\frac{1}{3}$ grams of saltpetre at 0° C., and *always* 250 grams at 100° C. These weights may be taken to represent the *solubility* of saltpetre at the two temperatures. (For *Table of Solubilities*, see Appendix.) To make a saturated solution of a substance at any temperature, either stir it up with water at that temperature until no more will dissolve (this requires much time and stirring), or heat the water to a higher temperature, dissolve in it as much as possible of the substance, cool, and decant or filter. Water saturated with one substance will still dissolve others. Solutions of solids in water are heavier than pure water and boil at higher temperatures. Heat is rendered latent when solids dissolve in liquids, and reappears when they become solids again (compare Art. 31).

Experiment 19.—Heat some sodic acetate in a flask with very little water until the salt is dissolved and steam issues from the flask. Put a plug of cotton wool, or a cork, in the mouth of the flask, and let cool. The solution remains liquid. Open the flask and drop in a small grain of sodic acetate. Crystals shoot out from the point where it falls, and soon the whole mass becomes solid. At the same time the flask becomes warm. (Why?) A solution of this sort is *supersaturated.* It contains more of the salt than can be dissolved at the lower temperature.

Water dissolves a great many substances, solids, liquids, and gases. It is a good *menstruum,* or *solvent.* Many substances insoluble in water will dissolve in other liquids. Thus, mercury dissolves most of the metals; alcohol dissolves resins; and ether dissolves fats; all insoluble in water. No heat becomes latent when one liquid dissolves another; there is no change of state.* When a liquid dissolves a gas the latent heat of the gas becomes sensible, but becomes latent again when the gas resumes its former state. This accounts for the coolness of effervescing drinks.

36. Freezing Mixtures.

Experiment 20.—Mix quickly and thoroughly 5 parts by weight of snow with 2 parts of salt. Observe the intense cold. Freeze some water in a test-tube. Note the melting of both snow and salt. The temperature can be reduced in this way to —20° C. What becomes of the heat? (See Art. 31 and Art. 35). Salt water will not freeze until the temperature sinks much below 0° C.

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* In some cases heat becomes sensible, as when alcohol and water are mixed.

Another freezing mixture is 16 parts water, 5 parts saltpetre, and 5 of sal-ammoniac.

37. **Crystallisation.**—*Crystals* are beautiful geometric forms, e.g., cubes, pyramids, in which solids can be obtained. They may be produced in several ways, particularly by cooling or evaporating solutions, as in the experiments with saltpetre (Art. 35). A substance is known to be at least nearly pure, if it consists of distinct and well-formed crystals. This is the reason for the care taken by manufacturers to prepare well-crystallised chemicals in particular cases where adulterations are common. Crystals are generally obtained by gradually cooling hot saturated solutions, or by slowly evaporating cold solutions. The impurities remain dissolved in the *mother-liquor*. Substances are often purified by crystallisation. Many substances combine with water as they crystallise. Washing-soda crystals contain 63% of *water of crystallisation*. The water is necessary to the form of the crystals. It is chemically combined, and is *solid*. If it be driven off by heat the crystals fall to powder. Many crystalline substances containing water of crystallisation lose this on exposure to air, and become powdery. This phenomenon is called *efflorescence*. Other solid substances attract moisture from the air and at last become liquid. This is called *deliquescence*.

38. **Infusion, &c.**—Water and other solvents are used to separate the soluble from the insoluble parts of medicinal plants, &c. *Maceration*, or *cold infusion*, is carried on at the ordinary temperature of the atmosphere. The substance to be macerated is ground up, or in some other way intimately mixed with the solvent, is

allowed to stand for some time, and the liquid is then strained or filtered off. An *infusion* (*hot infusion*) is made by pouring the boiling solvent on the substance, and allowing it to cool gradually. *Digestion* (or *simmering*) is the process of making a solution with the solvent kept just below its boiling point. The differences in these methods are mainly differences of temperature. When it is required to extract a substance which is decomposed at or below the boiling point of the solvent, or a substance which is very *volatile* (easily evaporated), the method of cold infusion or digestion is used. Tea should be infused, or at most digested, and never boiled, since boiling extracts a bitter and unwholesome principle, which is not dissolved in so great quantity by infusion or digestion. *Tinctures* are mostly macerations with alcohol as the solvent. *Percolation* has now largely superseded maceration in the preparation of tinctures. The substance is placed in a filter (*percolator*), and the solvent is poured upon it and allowed to *percolate* (run through) slowly. This method has the advantage of allowing a fresh portion of the solvent to be poured on the partially exhausted material; so that the extraction can be completed more quickly and thoroughly. (Why?) The same principle is employed in filtration when it is wished to wash away a soluble from an insoluble substance with as little as possible of the solvent. Very little is poured on at a time, and one portion is allowed to run through before another is added.

39. **Decomposition of Water.**—In Experiment 1 heat was the *kind of energy* used to decompose a compound. Very many chemical substances can be decomposed by heat, and under certain conditions water under

the action of heat breaks up into two different substances; but another kind of energy, *electricity*, is more convenient for showing the compound nature of water. It must be remembered that electricity is no more a substance than heat is. It is classed along with light, heat, &c., as a kind of energy, *power of doing work* of some kind. One kind of work for which electricity is specially suited is to separate compound into simpler substances. Chemical action is generally accompanied by the development of heat, and in the galvanic battery, a current of electricity takes the place of some of the heat which would be set free if the metal used were allowed to dissolve freely in the acid of the battery. Good conductors of heat are generally good conductors of electricity. Compounds which will not conduct electricity, i. e., through which it will not flow, are not decomposable by it. They may, however, become conductors by mixing with other substances, by melting, &c., and then, they may be decomposed. Water is a very bad conductor of electricity when it is pure, but when slightly acidified with sulphuric acid it conducts well.

Experiment 21.—Fasten two pieces of platinum foil or wire to the ends of the wires from a galvanic battery. Dip the foils in a vessel of distilled water, keeping them about an inch apart. Unless the battery is very powerful, there is no result. Add a few drops of sulphuric acid to the water. Bubbles of gas gather on the foil and rise. Collect the gases in two graduated tubes filled with water and inverted over the pieces of platinum foil *(electrodes)*. Observe that one tube fills faster than the other, and after some time the quantity in the one tube is seen to be double that in the other. Remove the tubes one at a time, closing them with the thumb, and put a lighted match into each. The larger quantity of gases catches fire and burns, putting out the match, but the smaller causes the match to burn more brightly. With a very powerful battery a small portion of pure water could be completely decomposed into these two gases differing in this and in other respects.

40. **Composition of Water.**—We thus prove water to be a chemical compound of two gases, *Hydrogen* and *Oxygen.* These gases have never been further decomposed and are therefore held to be elements. Water has been decomposed in a variety of ways, and always into these two gases; further, the volumes of the gases have always been in the ratio of *two* of hydrogen and *one* of oxygen. The next thing to discover is the *weights* of oxygen and hydrogen which form a given weight of water. In Experiment 21 water is *analysed*—its *composition* by *volume* has been found by *analysis*, i.e., by decomposing it into elements. It will be seen later that the word *analysis* is used also in a broader sense. In order to discover the *composition by weight*, the method of *building up*, or *synthesis*, is used. A current of hydrogen gas (How dried? See Sulphuric Acid.) is allowed to flow through a weighed tube containing black oxide of copper (a compound of oxygen and copper) heated to redness. The hydrogen takes away oxygen from this substance, forming water. This water is collected and weighed, and the tube of cupric oxide is re-weighed. The loss of weight in the latter case is the weight of oxygen consumed, and the difference between this and the weight of water collected gives the weight of hydrogen. (What law is assumed here?) This experiment has been made thousands of times and with the utmost nicety, and always with the same result—for every 8 parts by weight of oxygen taken away from the oxide of copper 9 parts of water are formed. Water is then composed

of the two gaseous elements, hydrogen and oxygen, united in the proportion of 1 of hydrogen to 8 of oxygen. (Deduce the relative weights of hydrogen and oxygen.)

QUESTIONS AND EXERCISES.

1. Is steam visible?

2. It is observed that arctic animals are generally white. Of what advantage is this to the animals?

3. Why does hot glass crack when a drop of water falls on it?

4. Change 10°, 32°, and — 40° Fahrenheit to centigrade.

5. At what temperature is the number on the Fahrenheit scale double that on the centigrade?

6. A Fahrenheit and a centigrade thermometer are placed side by side in a vessel of water. The centigrade thermometer reads 80°. What does the Fahrenheit read?

7. What is the latent heat of water if the Fahrenheit thermometer is the standard?

8. Twenty grams of ice at 0° C. is melted with 1,000 grams of water at 50°. What is the temperature afterwards?

9. What weight of water at 100° C. is required to melt 10 lbs. of ice at 0° C.?

10. Why does snow fall powdery in very cold weather, and in large flakes in mild weather?

11. If 100 grains of steam at 100° be condensed in 1 lb. of water at 0° C., what is then the temperature of the water?

12. A piece of silver weighing 120 grams is heated in boiling water and then put into a vessel containing 500 grams of water at 10° C. After stirring, the temperature of the water is found to be 11.2°. Calculate the specific heat of silver.

13. Why does stirring facilitate the solution of a substance?

14. How much steam must be condensed to heat 10 kilograms of water from 15° C. to 100° C.?

CHAPTER IV.

OXYGEN—COMBUSTION—CHEMISM—METALS AND NON-METALS.

41. **Discovery of Oxygen.**—Dr. Joseph Priestl was the father of *pneumatic chemistry*, or the *chemistr of gases*. He invented the *pneumatic trough* and devise the method of collecting gases over liquids. Simple a this method seems to us at this day, it required to b invented. The pneumatic trough is a vessel provide with a perforated shelf. The vessel is filled with wate or other liquid until the shelf is covered; jars or bottle are filled with the liquid in the trough, inverted, and se upon the shelf. These jars or bottles can be filled with an gas by allowing it to rise in bubbles through the liquid which it displaces downward. In 1744 (August 1st) Priestly heated a compound of mercury known as *re precipitate*, or *precipitate per se*, and collected a colourles gas which was driven off. (He called it an *air*, the nam *gas* not being used until later). He found that this ga had the remarkable property of causing a glowing coa to burst into flame. For reasons to be presently explaine it was afterwards called *oxygen*.

42. **Preparation of Oxygen.**—The most convenient way of preparing oxygen is by heating *potassi chlorate* mixed with a little *black oxide of manganese*.

Experiment 22.—Grind about 10 grams of potassic chlorat to powder in a mortar. Dry it by heating in a porcelain basin, taking care not to fuse it. It is best to stir constantly with glass rod while heating it. Dry in the same way about 1 gram manganese dioxide. Heat a small part of the potassic chlorate in a small glass tube closed at one end, until the salt-like substance fuses (melts), and bubbles of gas rise through it. Insert a small glowing splinter, and observe its bright flame. Mix the remainder of the chlorate thoroughly with the manganese dioxide, and put it in a larger hard-glass tube (test-tube size) provided with a *gas delivery tube* leading from the test-tube and dipping under the surface of water in the pneumatic trough. The tube passes tightly through a cork in the mouth of the test-tube. Arrange the test-tube, &c., conveniently, and heat at the bottom, applying the heat gradually, but not removing the lamp when once applied, unless the open end of the delivery tube is first lifted out of the water. Otherwise, as the heated gas in the retort (test-tube) cools, it will contract, and the cold water will run back into the retort, breaking it. Collect the gas which bubbles off, until about as much as would fill the retort and delivery tube is collected, then change the *receiver* (collecting vessel), and fill 5 small bottles with the gas. (Why reject the first portion?)

Oxygen can also be prepared by heating *black oxide of manganese* or *potassic bichromate*, either alone or with oil of vitriol. The black oxide of manganese used in *Experiment* 22 undergoes no change. It enables the oxygen to escape at a lower temperature. This is a case of so-called *contact-action*. When oxygen is prepared from potassic chlorate it is generally contaminated by the poisonous gas, *chlorine*, from which it should be freed by bubbling it through water, in which chlorine is very soluble. It is very necessary to do this when the oxygen is to be inhaled.

43. **Properties of Oxygen.**—Oxygen is an invisible gas, odourless, tasteless, and a little heavier than air. Below —130° C. it can be condensed to a liquid. There is a certain temperature for each gas, above which it

cannot be condensed to a liquid by pressure, below which it can. This is the *critical temperature*, about —130° C. for oxygen. Oxygen is a "supporter of combustion"—many substances burn in it. It is necessary to animal and, generally, to vegetable life. It is obtained from the air by animals when breathing, diffusing through the thin walls of the lungs into the blood. In the air, oxygen is *diluted* with four times its volume of another gas, *nitrogen*, so that its action is moderated. An atmosphere of pure oxygen would throw us into a state of excitement and fever, and would cause a vast conflagration over the surface of the earth. It was once often given as a stimulant. In cases of asphyxia and dyspnœa it is valuable. The patient obtains the necessary supply of oxygen in a much smaller space, therefore with less breathing. Oxygen is somewhat soluble in water, about 4 c. c. in 100 c. c. of pure water. When a glass vessel filled with water is heated slowly, bubbles of gas collect on the sides, and at length rise to the surface. These have been collected and proved to be largely oxygen. Fish obtain their oxygen by diffusion from the water. Hence, the necessity for a current of water, through the mouth and out over the gills. When fish are *drowned* they are in reality smothered. Water dissolves gases according to a certain *law*. *The quantity of any gas which is dissolved by a given quantity of water is proportional to the pressure and inversely as the temperature.* This law does not hold for gases which unite chemically with water, *e.g.*, ammonia, carbon dioxide.

44. **Combustion in Oxygen.**—When chemical action is accompanied by light and much heat it is called *combustion*. Flame also usually accompanies combus-

tion. Ordinary combustion takes place in an atmosphere which unites partially at least with the substance burned. It is a *supporter of the combustion.* Oxygen is the supporter of combustion in the case of wood and coal fires, lamps, &c.

Experiment 23.—Fasten a small piece of charcoal to the end of a copper wire; heat the charcoal until it glows, and then thrust it into a jar of oxygen. It glows more brightly and bursts into flame. Pour a few drops of *litmus solution* into the jar, close it with the hand and shake it. The blue litmus turns red.

Litmus is colouring matter extracted from a lichen. It turns red when acted on by sour substances (*acids*), e.g., citric acid, hydrochloric acid, and vinegar. We can conclude then that an acid is formed in this experiment. It is called *Carbonic Acid.*

Experiment 24.—Set fire to a piece of sulphur in a small long-handled iron cup, and then plunge it into a jar of oxygen. The sulphur burns with a dazzling purplish light, and suffocating fumes are formed. Shake up with a little water, and note the sourish taste. Add a few drops of litmus solution. It is reddened. *Sulphurous Acid* has been formed.

Experiment 25.—Cut off a *very* small bit of phosphorus under water, dry it carefully with blotting paper, put it in the small cup used before (*deflagrating spoon*), hold it in a jar of oxygen, and set fire to it with a hot wire. It burns with a bright white light, and white fumes are formed. Shake up with a little water, and note the sour taste. Test with litmus as before. Same result. *Phosphoric Acid* has been formed.

Certain substances burn in oxygen forming compounds which give a sour taste to water and turn blue litmus red. Oxygen is the *acid generator*; hence, its name, from the Greek. *To oxidise* is to combine with oxygen, as in the above three experiments. *Oxides* are compounds of oxygen with other elements. Thus, in the above experiments, oxides of carbon, sulphur, and phosphorus are formed. The greater part of the earth's crust is made up of oxides combined in various ways. Oxygen forms compounds with all the elements except *fluorine*. *To reduce* an oxide is to deprive it of a part or the whole of its oxygen, i.e., to *lead it back* to the original condition before oxidation.

Experiment 26.—Burn a small piece of the metal *sodium* in a jar of oxygen containing a little water, using the deflagrating spoon. It burns with a bright yellow flame forming white fumes and a grey substance which remains in the spoon. Wash the spoon in the water, and note the *soapy* feel and taste of the water. Add some of the litmus turned red in Experiments 25 and 26. It is turned *blue* again. The same results can be obtained by using the metal *potassium*.

The substances formed by burning these metals in oxygen in the presence of water have a character opposite to that of the acids. They are called *bases*. That formed from sodium is called *caustic soda*. Some other metals form soluble bases, but most bases are insoluble and can only be prepared indirectly from the metals.

Experiment 27.—Pour a few drops of litmus into a solution of hydrochloric acid so as to produce a distinct red colour. Then, add some solution of caustic soda, dropping it from a pipette gradually, and stirring, until the red just *begins* to turn blue, i.e., becomes purplish. Observe that the solution now tastes neither sour nor soapy, but salt. Both acid and base have disappeared; the colour is neither blue nor red; the solution is *neutral* in its action on litmus. Evaporate it in a porcelain dish. Crystals of common salt are obtained.

A similar result can be produced with sulphuric or nitric acid, and caustic potash. In each case, by mixing solutions of the acid and base in the right proportions a point is reached where the solution turns litmus neither blue nor red, both sour and soapy taste disappear, and a salt-like substance can be separated from the solution by evaporation. *Substances formed by the action of acids on bases are called salts.*

Experiment 28.—Make a bundle of thin strips of zinc foil, dip the ends in a little melted sulphur (Why?), set on fire and plunge into a jar of oxygen. The zinc burns with a white light, forming zinc oxide, or "philosopher's wool." Pour a little water into the jar, and observe that the oxide does not dissolve. Add a few drops of sulphuric acid; the oxide dissolves; evaporate in a porcelain dish; a salt, *zinc sulphate*, or white vitriol, remains. Burn some fine iron wire in the same way.

The oxide of zinc is a *base-forming oxide*, because it acts on an acid to form a salt; but it does not dissolve in water forming a base, as the oxides of sodium and of potassium do. But the corresponding base, known as *zinc hydroxide*, can be prepared in another way. It is insoluble in water, and does not turn red litmus blue, nor feel soapy when rubbed between the fingers, as the characteristic bases do. It is nevertheless called a base, because it forms salts with acids. Iron and other metals can be burned in oxygen. They all produce base-forming oxides; but it is to be noted that most bases have not the strongly marked characteristics of caustic soda. They are mostly insoluble in water, and do not turn red litmus blue, but *they are all acted on by acids, and thereby form salts.*

45. **Temperature of Ignition.**—It is necessary to heat combustible substances to a certain temperature before they will catch fire. This is called the *temperature of ignition.* It is very different for different sub-

stances. Thus, phosphorus catches fire in air below 100° C., carbon bisulphide at 150°, sulphur at 400°, while coal and wood begin to burn only at a red heat.

46. **Slow Combustion.**—Combustible substances often combine slowly with oxygen at temperatures below that of ignition. In such cases the more striking appearances of combustion are absent. Rusting of metals, respiration, decay of animal and vegetable substances, are processes of this kind, modified more or less by the action of water. Heat is produced in slow combustions (as in the heating of grain, of damp hay, &c.), but more slowly than in ordinary combustions, so that it is conducted away by surrounding objects and does not raise the temperature so much. In some cases, however, where the substance is finely divided, exposing a large surface to the action of the air, oxidation goes on so rapidly as to heat the mass up to the temperature of ignition. Thus occur cases of *spontaneous ignition and combustion.* Rags soaked with oil, and coal containing much sulphur, have been known to catch fire in this way.

47. **Chemism.**—That which causes oxygen to unite with carbon, sulphur, &c., is called *chemical affinity, chemical attraction,* or *chemism.* Oxygen may be compressed with a pressure of several tons to the square inch without liquefying it, and yet, when it combines with iron it becomes *solid.* Chemical attraction must be very powerful between oxygen and iron. Between some of the elements the attraction seems to be very slight or even wanting. Thus, oxygen forms no compound with fluorine, and cannot be got to unite directly with chlorine, bromine, iodine, or gold. As a rule elements

which are *unlike* have the greatest attraction for each other; for example, the metals and the non-metals.

48. **Metals and Non-Metals.** — All the substances described as burning in oxygen to form oxides are elements; observe that some of them, as sulphur, carbon, and phosphorus, produce acid-forming oxides, while others, sodium, potassium, zinc, iron, produce base-forming oxides. *Elements which have base-forming oxides are called metals; those whose characteristic oxides are acid-forming are called non-metals.* Of the 67 elements at present known,* 52 are metals and 15 non-metals; but some of the elements have the characters of both metals and non-metals, so that it is difficult to decide to which class they belong. Thus, antimony is classed by some chemists among the metals, by others with the non-metals.

TABLE OF THE ELEMENTS.

(Non-metals in **heavy type**, imperfect metals in *italics*.)

English Names.	Latin Names.	Symbols.	Atomic Weights.	† Specific Weights.	Remarks.
Aluminium. ..	Aluminium ...	Al^{iv}	27.3	2.6	Solid.
Antimony....	Stibium	$Sb^{iii\ v}$	122.	6.71	"
Arsenic	Arsenicum....	$As^{iii\ v}$	75 (74.9)	5.73	"
Barium	Barium	Ba^{ii}	136.8	3.75	"
Beryllium	Beryllium.....	Be^{ii}	9.	2.07	"
Bismuth......	Bismuthum...	$Bi^{iii\ v}$	210.	9.8	"
Boron	Borium........	B^{iii}	11.	2.5	Gas.
Bromine	Bromum	$Br^{i\ v}$	80 (79.75)	3.19	Liquid.
Cadmium.....	Cadmium	Co^{ii}	111.6	8.6	Solid.
Caesium......	Caesium......	Cs^{i}	132.56	1.88	" (melts at 32°)
Calcium......	Calcium.... .	Ca^{ii}	40.	1.57	"
Carbon	Carbo.........	C^{iv}	12 (11.97)	3.52 (diam'd)	"
Cerium.......	Cerium	Ce^{iii}	141.2	6.7	"
Chlorine	Chlorinum ...	$Cl^{i\ iii\ v}$	35.37	2.45	Gas.
Chromium....	Chromium....	$Cr^{ii\ iv\ vi}$	52.4	6.5	Solid.
Cobalt........	Cobaltum.....	$Co^{ii\ iv}$	58.6	8.5	"

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* New elements are discovered from time to time.

† For the specific weights of solids and liquids water at 4° C. is the standard; for those of gases, air.

TABLE OF THE ELEMENTS—*Continued.*

English Names.	Latin Names.	Symbols.	Atomic Weights.	Specific Weights.	Remarks.
Copper	Cuprum	$\mathrm{Cu}^{\mathrm{ii}}$	63.	8.88	Solid.
Didymium	Didymium	$\mathrm{Di}^{\mathrm{iii}}$	142.3	6.54	"
Erbium	Erbium	$\mathrm{Er}^{\mathrm{iii}}$	170.5	....	"
Fluorine	Fluorum	F^{i}	19.1	1.31	Gas prob'ly
Gallium	Gallium	G^{iv}	69.80	5.95	Solid (melt at 30
Gold	Aurum	$\mathrm{Au}^{\mathrm{i\ iii}}$	196.5	19.32	"
Hydrogen	Hydrogenum	H^{i}	1.	0.0692	Gas.
Indium	Indium	$\mathrm{In}^{\mathrm{iv}}$	113.6	7.42	Solid.
Iodine	Iodum	$\mathrm{I}^{\mathrm{i\ iii\ v}}$	126.5	4.948	"
Iridium	Iridium	$\mathrm{Ir}^{\mathrm{ii\ iv\ vi}}$	193.	22.42	"
Iron	Ferrum	$\mathrm{Fe}^{\mathrm{ii\ iv}}$	56.	7.86	"
Lanthanum	Lanthanum	$\mathrm{La}^{\mathrm{iii}}$	139.	6.1	"
Lead	Plumbum	$\mathrm{Pb}^{\mathrm{ii\ iv}}$	206.4	11.35	"
Lithium	Lithium	Li^{i}	7.	0.59	"
Magnesium	Magnesium	$\mathrm{Mg}^{\mathrm{ii}}$	24.	1.74	"
Manganese	Manganesium	$\mathrm{Mn}^{\mathrm{ii\ iv\ vi}}$	54.8	8.03	"
Mercury	Hydrargyrum	$\mathrm{Hg}^{\mathrm{ii}}$	200 (199.8)	13.596	Liquid.
Molybdenum	Molybdenum	$\mathrm{Mo}^{\mathrm{ii\ iv\ iv}}$	96.	8.6	Solid.
Nickel	Niccolum	$\mathrm{Ni}^{\mathrm{ii\ iv}}$	58.6	8.9	"
Niobium	Niobium	Nb^{v}	94.	7.06	"
Nitrogen	Nitrogenum	$\mathrm{N}^{\mathrm{iii\ v}}$	14 (14.01)	0.971	Gas.
Osmium	Osmium	$\mathrm{Os}^{\mathrm{ii\ iv\ vi}}$	199.	22.48	Solid.
Oxygen	Oxygenum	O^{ii}	16 (15.96)	1.105	Gas.
Palladium	Palladium	$\mathrm{Pd}^{\mathrm{ii\ iv}}$	106.2	11.4	Solid.
Phosphorus	Phosphorus	$\mathrm{P}^{\mathrm{iii\ v}}$	31.	1.83–2.2	"
Platinum	Platinum	$\mathrm{Pt}^{\mathrm{ii\ iv}}$	196.7	21.5	"
Potassium	Kalium	K^{i}	39.	0.87	"
Rhodium	Rhodium	$\mathrm{Rh}^{\mathrm{ii\ iv\ vi}}$	104.1	12.1	"
Rubidium	Rubidium	Rb^{i}	85.47	1.52	"
Ruthenium	Ruthenium	$\mathrm{Ru}^{\mathrm{ii\ iv\ vi}}$	103.5	12.26	"
Samarium	Samarium	Sm	150.	....	"
Scandium	Scandium	Sc	44.	....	"
Selenium	Selenium	$\mathrm{Se}^{\mathrm{ii\ iv\ vi}}$	79.	4.5	"
Silicon	Silicium	$\mathrm{Si}^{\mathrm{iv}}$	28.	2.39	"
Silver	Argentum	Ag^{i}	107.66	10.47	"
Sodium	Natrium	Na^{i}	23.	0.978	"
Strontium	Strontium	$\mathrm{Sr}^{\mathrm{ii}}$	87.2	2.54	"
Sulphur	Sulphurum	$\mathrm{S}^{\mathrm{ii\ iv\ vi}}$	32.	2.03	"
Tantalum	Tantalum	Ta^{v}	182.	10.4	"
Tellurium	Tellurium	$\mathrm{Te}^{\mathrm{ii\ iv\ vi}}$	125. ?	6.4	"
Terbium	Terbium	Tb	....	....	"
Thallium	Thallium	$\mathrm{Tl}^{\mathrm{i\ iii}}$	203.6	11.85	"
Thorium	Thorium	$\mathrm{Th}^{\mathrm{iv}}$	231.5	11.	"
Tin	Stannum	$\mathrm{Sn}^{\mathrm{ii\ iv}}$	117.8	7.29	"
Titanium	Titanium	$\mathrm{Ti}^{\mathrm{ii\ iv}}$	48.	....	"
Tungsten	Wolframum	$\mathrm{W}^{\mathrm{iv\ vi}}$	184.	19.12	"
Uranium	Uranium	$\mathrm{U}^{\mathrm{iv\ vi}}$	239.8	18.7	"
Vanadium	Vanadium	$\mathrm{V}^{\mathrm{iii\ v}}$	51.5	5.5	"
Yttrium	Yttrium	$\mathrm{Y}^{\mathrm{iii}}$	89.5	....	"
Zinc	Zincum	$\mathrm{Zn}^{\mathrm{ii}}$	65.	7.	"
Zirconium	Zirconium	$\mathrm{Zr}^{\mathrm{iv}}$	90.	4.15	"

CHAPTER V.

LAWS OF COMBINATION—ATOMIC THEORY.

49. **Conservation of Matter.**—In order to investigate fully the chemical actions described in connection with oxygen it is necessary to weigh and measure the substances. This has been done with the greatest accuracy, and the experiments have been repeated in a variety of ways with materials from different sources. The results which have been obtained are always the same for the same chemical action. Thus, 8 grams of oxygen and 1 gram of hydrogen are always obtained by the decomposition of 9 grams of water; 8 grams of oxygen and 100 grams of mercury, by the decomposition of 108 grams of red oxide of mercury; and 8 grams of oxygen and 40.8 grams of potassic chloride from 48.8 grams of potassic chlorate. We see that in chemical decompositions *the sum of the weights of the products of decomposition is always equal to the weight of the substance decomposed.* Again, 8 grams of oxygen burn 3 grams of charcoal to form 11 grams of carbon dioxide; 8 grams of oxygen burn 8 grams of sulphur to form 16 grams of sulphur dioxide; 8 grams of oxygen burn 6.2 grams of phosphorus to form 14.2 grams of phosphorus pentoxide; 8 grams of oxygen burn 39.1 grams of potassium to form 47.1 grams of potassic oxide; 8 grams of oxygen burn 23 grams of sodium to form 31 grams of sodic oxide; 8 grams of oxygen burn 32.5 grams of zinc to form 40.5 grams of zinc oxide. From this statement it

is seen that in chemical combinations, also, the sum of the weights of the substances combining is always equal to the weight of the substance formed. It may thus be stated generally that *in chemical actions no matter is lost—put out of existence; nor is there any gain of matter.* The weights of the elements entering into a chemical action remain the same at the end of the action; but the elements become differently arranged. This law, founded on experiments, is the *Law of the Conservation of Matter.* It is the fundamental law of the Science of Chemistry.

50. **Definite Proportions.**—Another law can be deduced from the facts stated in Art. 49. It is found that water is *always* composed of hydrogen and oxygen in the proportion of 1 to 8, that mercuric oxide is *always* composed of oxygen and mercury in the proportion of 8 to 100, and so with the others. Stated in general terms this is the *Law of Definite Proportions*: *Each chemical compound is always composed of the same elements and these are always in the same proportion in this compound.* In this respect chemical compounds differ from mixtures, which may be made in any proportions.

51. **Combining Weights--Equivalents.**—The weight [illegible]ygen which combines with 1 part by weight of h[illegible] to form water is called the *combining weight* o[illegible]n. *The weight of any element which combines w[illegible] 1 part of hydrogen is its combining weight*; but, as many of the elements do not form compounds with hydrogen, their combining weights must be ascertained, as it were, at second hand. Thus, the weight of zinc which combines with 8 parts by weight of oxygen (its

combining weight) is the combining weight of zinc. The expression *equivalent*, or *equivalent weight*, is used in exactly the same sense as *combining weight* when applied to the elements; but it is also applied to compounds. Thus, the *equivalent* of water is the quantity of water which will produce, when decomposed, 1 part by weight of hydrogen, i e., 9. Again the equivalent of zinc oxide is 40.5, since this weight of zinc oxide contains 8 parts (an equivalent) of oxygen. *The equivalent of an element or a compound is the weight of the element or compound equal in value in chemical action to 1 part by weight of hydrogen.* (Calculate the equivalents of all the substances mentioned in Art. 49.) Hydrogen is here, as in most cases, taken as the standard element.

52. **Multiple Proportions.**—When charcoal (carbon) burns in a free supply of oxygen, 8 parts of oxygen unite with 3 of carbon to form *carbon dioxide*; but if the supply be scant, as in the centre of a fire, only 4 parts of oxygen unite with 3 of carbon, and *carbon monoxide* is formed. Thus, carbon combines with oxygen in two proportions, and these are as 8 to 4, or as 2 to 1. When phosphorus burns in oxygen it also forms two compounds, the *pentoxide* when the oxygen is plentiful, and the *trioxide* when it is scant. In the pentoxide 6.2 parts of phosphorus (Why use this particular number?) are combined with 8 of oxygen; in the trioxide this weight of phosphorus is combined with 4.8 of oxygen. The quantities of oxygen are as 5 to 3. Sulphur also forms two compounds with oxygen, the relative quantities of which are as 2 to 3. Many other examples could be given of an element combining with another in two or more proportions; and it is noticed that in every such

case these proportions have a simple arithmetical relati to each other, as in the above cases. This is stated the *Law of Multiple Proportions: If two elements fo several compounds with each other, then the differe quantities of the first which combine with a fixed quanti of the second bear a simple ratio to each other, as 1 to 2 to 3, 3 to 5, &c.* (Apply this law to the exampl given.)

53. **The Atomic Theory.**—To explain these markable facts Dalton (1804 modified the atomic theo of ancient Greeks. According to this theory its modern form the elements are made up of *indivisi* extremely minute particles—*atoms*. (What is a theor The atoms of the same element are exactly alike, b those of different elements differ in weight, &c. T atoms of different elements unite to form *molecules* compounds, and this union always takes place 1 ato with 1 atom, 1 atom with 2, 2 with 3, &c. For e ample, when zinc burns in oxygen, 1 atom of zinc co bines with 1 atom of oxygen, 1,000 atoms of zinc wi 1,000 of oxygen and so on, until the whole of the zinc burned, when, of course, the oxide which is formed co tains equal numbers of atoms of zinc and of oxygen. follows from this that if the ratio of the weights of t atoms of zinc and oxygen are as 65 to 16, the ratio the whole quantities combining must be in this prop tion. As a matter of *fact*, zinc oxide is always co posed of the two elements in this ratio. In this w the atomic theory explains the *law of definite prop tions*. The explanation of the *law of multiple prop tions* is equally simple. For example, sulphur unit with oxygen in two proportions. According to t

atomic theory the addition of oxygen to sulphur takes place always by atoms, never parts of an atom; in the two compounds different *numbers of atoms* of oxygen unite with an atom of sulphur, in one case 2, and in the other 3. From this it follows that the *weights* of oxygen uniting with the *atomic weight* of sulphur are respectively twice and three times the atomic weight of oxygen.

54. **Avogadro's Law.**—If equal volumes of hydrogen, oxygen, marsh gas, and other gases generally are put in graduated tubes over mercury and heated equally, they are observed to expand equally, viz.: $\frac{1}{273}$ of their volume at 0° C. for every degree rise in temperature. Also, if the same increase of pressure be put on each gas, the volumes are diminished equally. These facts point to some close similarity in *equal volumes* of gases. The hypothesis put forward by Avogadro in 1811 is that *equal volumes of all gases under the same conditions of temperature and pressure contain the same number of particles (molecules).* This can also be deduced mathematically from the molecular theory of gases.

55. **Combination by Volumes.**—When water is decomposed by electricity (Art. 39) two volumes of hydrogen are set free for one of oxygen. If the gases be mixed and caused to unite again, water is formed, and none of either gas is left over. It has been found that in all cases where *gases* combine with each other, the *volumes combining have a simple ratio to each other, as 1 to 2, 2 to 3, &c.*

56. **Molecules and Atoms.**—Two litres of hydrogen unite with one litre of oxygen to form water. If the union takes place at, say 200° C., the water is in

the gaseous state. It is then found that the volume steam formed is the same as the volume of hydrog used, and according to Avogadro's law contains t same number of particles (Dalton's atoms). Let suppose that the two litres of hydrogen contain tw millions of particles; then one litre of oxygen contai one million particles, and two millions particles of stea are formed. Each particle of steam contains oxygen, that the oxygen must be divided into *two* millions parts when combination takes place. Therefore, t particles of oxygen must be *divisible*. They are n atoms, but *pairs* of atoms, which cannot be separat except by chemical action. They are called *molecul* (*little masses*). The molecules of elements consist (wi few exceptions) of two like atoms; and those of co pounds, of two or more unlike atoms. The molecules substances are imagined as in constant motion of son sort, the motion being different in solids, liquids, a gases. In solids the motion is mostly vibration, t molecules moving about particular points; in liquid there is a comparatively slow motion from place to plac and in gases this motion from place to place goes with great velocity, the molecules moving faster as t gases become hotter. It is the battering of the mol cules of an enclosed gas against the walls of the enclo ing vessel which produces pressure.

Definitions.—*A molecule is the smallest portion of any su stance which can exist by itself.* Imagine a drop of water divid and subdivided. A point is at last reached when no furth division is possible by mechanical means; and if the division forced by electricity or heat, it is no longer portions of wat which are obtained, but two different substances—oxygen a hydrogen. At this point we have reached the molecule water. *An atom is the smallest portion of an element which can exist in a molecule.* The atom cannot be divided even by chemical action ; it must enter into combination as a whole.

57. Molecular Weights of Gases.—Since equal volumes of gases contain the same number of molecules, it follows that the weights of equal volumes of gases are in proportion to the weights of single molecules. Thus, if a certain volume of hydrogen weighs 2 grams, if the same volume of oxygen weighs 32, of nitrogen 28, and of carbon dioxide 44, these numbers may be taken to represent the weights of the molecules, or the *molecular weights* of the gases. In the case of the elementary gases *half* the molecular weight gives the weight of the atom, or the *atomic weight* (why *half?*). In estimating the specific weights of gases, the weights of *equal volumes* are compared, one gas being taken as standard, and its weight taken as 1. Hydrogen is now usually taken as the standard gas, and it can readily be shown that the *specific weight of a gas is half its molecular weight.* (Explain this.)

58. Chemical Notation—Atomic Weights.—*Chemical symbols* are letters used to denote the *atomic weights* of the elements. They are the initial letters of the Latin names. Where two or more names begin with the same letter, a second is added to distinguish. For example H denotes 1 part *by weight* of hydrogen ; O, 16 parts by weight of oxygen ; C, 12 parts by weight of carbon ; Cl, 35.37 parts by weight of chlorine, &c. These numbers are obtained by experiments, by weighing and measuring. For example, it has been found that a litre of oxygen weighs 16 times as much as a litre of hydrogen, from which it is concluded that a molecule of oxygen weighs 16 times as much as a molecule of hydrogen (Art 54), and that the atom of oxygen must also weigh 16 time as much as the atom of hydrogen (why?). If, then, th atom of hydrogen be assumed to weigh 1 (1 what?), th atom of oxygen will weigh 16. Again, 16 parts o oxygen combine with 65 of zinc, and there is eviden that in this combination one atom of oxygen unites wit one of zinc. Hence it is concluded that the atomic weigh of zinc is 65. By similar methods the atomic weights o all the elements have been determined. There is a meth of determining the atomic weights which depends o measuring the specific heats of the elements. It was di covered by *Dulong and Petit that, if the atomic weight each element is multiplied by its specific heat, the produ is always the same number* (*nearly*), *that is, 6.6.* Fro which it follows that 6.6 divided by the specific he of any element gives its atomic weight. This number called the *specific heat of the elements*, and Dulong a Petit's law may be stated thus: *The specific heat of t elements is a constant quantity.*

The symbols of the atoms are combined into *formul* representing molecules. Thus (Art. 56), since the mol cule of water contains 2 atoms of hydrogen and 1 oxygen, its formula is H_2O. This formula is used express the following:—

1. Water is a compound of the two elements, hydrogen a oxygen, in the proportion by weight of 2 to 16. This is es lished by experiment.

2. The molecule of water is made up of 3 atoms, viz.: 2 of h drogen and 1 of oxygen. This is deduced from the ato theory, which is now strongly supported by experimental e dence.

Similarly, the molecule of oxide of sodium is represented by Na_2O; of oxide of zinc, by ZnO; of sulphuric acid, by H_2SO_4, and so on. In these formulas the small figure below the line multiplies the symbol immediately before it. Thus, the molecule of sulphuric acid contains 2 atoms of hydrogen, 1 atom of sulphur, and 4 atoms of oxygen. Very often the formulas are used loosely for the names of compounds, but it must be always remembered that they mean more than this. For example, H_2O means *18 parts by weight of water*, and not simply *water*, or *any quantity of water*. The formulas of substances are used to express their molecular weights, and, given the formula of a compound, its molecular weight is found by adding together the weights of all the atoms in the molecule. For example, the molecular weight of sulphuric acid is $(2 \times 1) + 32 + (4 \times 16) = 98$. To represent 2, 3, &c., molecules the number is prefixed to the formulas thus, $2ZnO$, $3H_2O$, $4H_2SO_4$, &c. Or, a formula may be multiplied thus, $(H_2O)_3$, $(NaCl)_5$.

59. **Chemical Equations.**—These are short-hand representations of the quantities of the substances taking part in chemical actions. Before they can be written, chemical actions must be studied by weighing and measuring. For example, the decomposition of water by electricity is represented as follows:—$2H_2O = 2H_2 + O_2$,* a short-hand method of stating that 36 parts by

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* It might be written more simply $H_2O = H_2 + O$, but since, according to theory, the molecule is the smallest portion capable of existing free, it is by many considered advisable not to represent single atoms in equations. However, where weights alone are being considered, this adherence to theory is unnecessary and often cumbrous; and, except when considering the volumes of gases, I shall always write the equations in the simplest form.

weight (or 2 molecules) of water decompose into 4 parts by weight (2 molecules) of hydrogen, and 32 parts by weight (1 molecule) of oxygen.

(1) The equation should represent all the substances taking part in the action, in the proportions in which they act on each other or are produced in the action. (2) The sum of the weights on the left side of the sign (=) should be equal to the sum of those on the right. (3) The number of atoms of each element represented on the left should be the same as that on the right.

The decomposition of potassic chlorate into oxygen and potassic chloride is represented by the followin equation :—$2KClO_3 = 3O_2 + 2KCl$. That is 2 × 122.6 grams of *potassic chlorate* decomposes into 3 × 22 grams of *oxygen* and 2 × 74.6 grams of *potassic chloride*. (Is it necessary then to use 245.2 grams of potassic chlorate in preparing oxygen ?)

60. **Chemical Calculations.**—From a chemical equation we can calculate readily the proportions of the substances represented in the equation ; and equations are useful as permanent records of chemical actions, to which we can refer when we wish to know in what proportions to use chemical substances in any reaction. Thus, suppose it is desired to prepare 100 grams o phosphorus pentoxide by burning phosphorus in air. The equation representing this action has been mad out as follows :—$2P + 5O = P_2O_5$. Referring to th table, p. 40, we see that P represents 31 parts b weight of phosphorus. Also, P_2O_5 represents 62 + 8 = 142 parts by weight of phosphorus pentoxide ; an 62 grams of phosphorus burn to form 142 grams

phosphorus pentoxide; and 142 : 100 : : 62 : 43.62, or 43.62 grams of phosphorus burn to form 100 grams of pentoxide.

Gases are usually *measured* instead of weighed. But, since equal volumes of all gases (at the same temperature and pressure) contain the same number of molecules, weights of gases in the ratio of the molecular weights are the weights of *equal volumes* of the gases. The molecular weights of hydrogen and of oxygen are 2 and 32 respectively; therefore, 2 grams of hydrogen will measure the same as 32 grams of oxygen; and so for other gases. The measurement has been made with the greatest care many times, and it is found that 2 grams of hydrogen gas measure (at 0° C. and 760 millimetres of mercury pressure) 22.33 litres. *The molecular weight in grams, or gram-molecule, of any gas measures, at 0° C. and 760 mm., 22.33 litres.*

Gas.	Formula.	Molecular Weight.	Volume of Gram-Molecule.
Hydrogen	H_2	2	22.33 litres.
Oxygen	O_2	32	
Nitrogen	N_2	28	
Ammonia	NH_3	17	
Carbon Dioxide	CO_2	44	
Marsh Gas	CH_4	16	
&c.	&c.	&c.	

Calculate the volume of oxygen formed by heating 50 grams potassic chlorate. The equation is:

$$\underset{\text{245.2 grams.}}{2KClO_3} = \underset{\text{149.2 grams.}}{2KCl} + \underset{3 \times 22.33 \text{ litres.}}{3O_2}$$

That is, 245.2 grams potassic chlorate give 66.99 litres of oxygen. Therefore, 50 grams give $\frac{50}{245.2} \times 66.99 =$ 13.66 litres.

In making such a calculation we simply assume that what is true for the *molecules* as represented in the equation, is true for *weights* which are taken proportionately to the weights of the molecules.

How much sulphur can be burned by 10 litres of oxygen measured at 0° C. and 760 mm. pressure? The equation is:

$$S + O_2 = SO_2$$

32 grams—22.33 litres.

That is, 32 grams of sulphur use up 22.33 litres of oxygen. Then, 22.33 : 10 : : 32 : 14.33; i. e., 14.33 grams of sulphur use up 10 litres of oxygen. What volume of sulphur dioxide is formed in this action? On looking at the equation we see that a molecule of sulphur dioxide is formed from a molecule of oxygen; therefore, the volume of sulphur dioxide is the same as that of oxygen, viz., 10 litres.

61. **Ozone.**—This is a peculiar modification of oxygen produced chiefly by the action of electricity. It is a gas of a penetrating odour. It is one and a half times as heavy as oxygen, and its molecule must therefore contain three atoms (O_3), if that of oxygen contains two (O_2). Ozone has very powerful oxidizing properties, destroying paper, india-rubber, &c., by rapid oxidation. It is slightly soluble in water, more so in turpentine. It is held to be a valuable means of disinfecting and deodorizing the atmosphere, and is supposed to exercise a bene-

ficial influence on the animal body. Of late, however, some investigators associate the prevalence of certain diseases of the respiratory passages with an excessive quantity of ozone in the air.

Ozone is produced by the passage of electricity through air (or oxygen)—for example, by flashes of lightning. It is more abundant in pure than in impure air; in the air of the country than in that of the towns; and in the higher than in the lower strata of the atmosphere. Its quantity is said to be smaller where cholera and other epidemics are prevalent. Ozone is also produced in small quantity during the electrolysis of water, and during the slow oxidation of phosphorus in moist air. It is also formed about an electrical machine when in motion.—If a strip of filter paper soaked in starch and solution of potassic iodide be brought into an atmosphere containing ozone, the paper turns blue. Iodine is set free by the ozone, and unites with the starch forming the blue *iodide of starch.*—When an element occurs in different modifications, these are called *allotropic* modifications. *Ozone is an allotropic form of oxygen.*

QUESTIONS AND EXERCISES.

1. What percentages of sulphur and oxygen are there in sulphur dioxide (SO_2), and in sulphur trioxide (SO_3)?

2. What are the molecular weights of the following: Chlorine, carbon monoxide (CO), ethylene C_2H_4), nitric acid (HNO_3), and cane sugar ($C_{12}H_{22}O_{11}$)?

3. What weight of mercuric oxide is required to give 20 litres of oxygen measured at 0° C. and 760 millimetres pressure? Equation: $HgO = 2Hg + O_2$.

4. Calculate the weights of 1 litre of the following gases measured at 0° C. and 760 millimetres of pressure: Oxygen, nitrogen, carbon dioxide (CO_2), ammonia (NH_3), acetylene (C_2H_2), and sulphur dioxide (SO_2).

5. What volume (at standard temperature and pressure) will 50 grams of oxygen occupy?

6. What weight of carbon dioxide will fill a vessel of 15 litres capacity?

7. Point out the errors in the following equation:—$2FeSO_4 = Fe_2O_3 + SO_3$.

8. The products of the combustion of a candle are collected, and are found to weigh more than the weight of candle burned. Is this contrary to the law of conservation of matter? Explain.

9. In what respects does a chemical compound of iron and sulphur differ from a mixture of these two substances?

10. 100 grams of oxygen combine with 393.75 grams of copper. What is the equivalent of copper?

11. Iron forms two basic oxides. The percentage composition of one is,—*iron*, 77.78%; *oxygen*, 22.22%; and of the other,—*iron*, 70%; *oxygen*, 30%. Apply the law of multiple proportions.

12. A litre of nitrogen unites with 3 litres of hydrogen. The molecule of the compound formed contains 1 atom of nitrogen and 3 of hydrogen. What is the change of volume when combination takes place?

13. What is the composition of the substances represented by the following formulas:—NH_3, H_3PO_4, $SO_2(OH)_2$, Fe_2Cl_6, $CO(NH_2)_2$, and $K_4Fe(CN)_6$? How many atoms in the molecules represented as follows:—$C_2H_4(OH)_2$, $(NH_4)_2SO_4$, $FeSO_4.7H_2O$, and $Fe_2(OH)_6$?

14. What weights of the following gases measure, at standard temperature and pressure, 22.33 litres, viz.:—*carbon monoxide* (CO); *ethylene* (C_2H_4); *hydric sulphide* (H_2S); *phosphine* (PH_3), and *methylamine* ($CH_3.NH_2$)?

CHAPTER VI.

HYDROGEN.

62. **Hydrogen.**—It was noticed by very early investigators that when metals dissolve in acids, an inflammable gas is given off, but the properties of this gas (*inflammable air*) were not fully investigated till the advance of pneumatic chemistry in the hands of Priestly and Cavendish towards the end of last century (1766 to 1781). Cavendish showed that when it burns in air it forms water; hence its name, which means, *water-generator*. Hydrogen is found uncombined only in small quantities, in volcanic gases, in the gas which occurs with petroleum, and in meteoric iron. In combination, however, it occurs in vast quantities, forming $\frac{1}{9}$th by weight of water, $\frac{1}{4}$th of marsh gas, and a considerable part of sugar, wood, starch, and animal and vegetable substances generally.

63. **Preparation of Hydrogen.**—Hydrogen can be prepared:

1. By the electrolysis of water:

$$H_2O = H_2 + O.$$

2. By the action of various acids on certain of the metals, particularly *sulphuric acid* (diluted) on zinc:

Zinc.		Sulphuric Acid.		Zinc Sulphate.		Hydrogen.
Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2
65		98		161		2

Hydrochloric acid may also be used:

$$\begin{array}{ccccccc} \text{Zinc.} & & \text{Hydrochloric Acid.} & & \text{Zinc Chloride.} & & \\ \mathrm{Zn} & + & \mathrm{2HCl} & = & \mathrm{ZnCl_2} & + & \mathrm{H_2} \\ 65 & & 73 & & 136 & & 2 \end{array}$$

and *iron* may be used as the metal:

$$\begin{array}{ccccccc} \text{Iron.} & & \text{Hydrochloric Acid.} & & \text{Ferrous Chloride.} & & \\ \mathrm{Fe} & + & \mathrm{2HCl} & = & \mathrm{FeCl_2} & + & \mathrm{H_2} \\ 56 & & 73 & & 127 & & 2 \end{array}$$

(If the weights of metals represented in these equations be taken *in grams*, what volumes of hydrogen will be produced?)

3. By decomposing water by metals. *Sodium* and *potassium* decompose water at ordinary, and even at very low, temperatures; *magnesium* begins to decompose it only at 100°C.; and *iron, copper*, and *silver*, only at a red heat.

Experiment 28.—Put some small pieces of zinc in a flask provided with a gas delivery tube, and pour over the zinc some sulphuric acid previously diluted with about five times its volume of water and cooled. Collect the gas which comes off, at first in an inverted test-tube filled with water, and test it from time to time with a match until it no longer explodes, but burns quietly (Why does it explode?) Then collect the gas in jars for further experiments. When the gas ceases to come off pour the liquid in the flask into a porcelain basin and set it to evaporate. Crystallised zinc sulphate, or *white vitriol* ($ZnSO_4.7H_2O$), is obtained. Repeat this experiment using iron (in the form of tacks) instead of zinc. Hydrogen is obtained as before, and on evaporating the liquid crystallised ferrous sulphate, or *green vitriol* ($FeSO_4.7H_2O$), is left. (How do these cases of solution differ from that of common salt in water?)

On consulting the equations representing these actions, it is seen that *one atom* of zinc sets free *a molecule* of hydrogen. In other words an atomic of zinc or of iron is *equivalent* to two atoms of hydrogen. (What are the *combining weights* of zinc and iron ?)

Experiment 29.—Dissolve scraps of zinc, iron, and tin, in small quantities of hydrochloric acid (diluted with four times its bulk of water), in test tubes ; and observe that an inflammable gas bubbles off. Evaporate the remaining liquids and examine the salts obtained (*zinc chloride*, $ZnCl_2$, *ferrous chloride*, $FeCl_2$, and *stannous chloride*, $SnCl_2$). (Write the equations).

If the same weights of zinc and iron were used in this experiment, as in Experiment 28, the same volume of hydrogen would be formed. *The volume of hydrogen evolved by dissolving any weight of a metal is not influenced by the acid, if there are no secondary actions.*

Experiment 30.—Stick a small piece of metallic sodium to the end of an iron wire and push the sodium quickly under an inverted test-tube filled with water (a small jar may be used). The sodium rises to the bottom of the tube disengaging a gas which pushes the water down. Closing the tube with the thumb, remove it, and touch its mouth with a flame. The gas burns ; it is *hydrogen*. Pour a few drops of red litmus solution into the test-tube and shake it up. The litmus turns blue, showing the presence of *caustic soda*

An atom of sodium *displaces* an atom of hydrogen from water :

$$\begin{array}{ccccccc} H_2O & + & Na & = & NaOH & + & H. \\ 18 & & 23 & & 40 & & 1 \end{array}$$

(Compare with zinc and iron. What is the equivalent, or combining weight, of sodium). The remaining atom of hydrogen can be driven out of the caustic soda by heating it with a second equivalent of sodium, when *sodic oxide* (Na_2O) is formed. (Write the equation for this action). Similar actions may be brought about with *potassium* (K) and water; and it is found that 39.1 grams of potassium decompose 18 grams of water, forming $\frac{22.33}{2}$ litres of hydrogen (1 gram), and 56.1 grams of caustic potash. (Write the equation).

64. **Hydroxides.**—Caustic soda and caustic potash are, in composition, midway between water and the oxides of sodium and potassium. They are called *hydroxides.* Other examples of hydroxides are *quick lime,* or *calcic hydroxide* ($Ca(OH)_2$), *magnesic hydroxide* ($Mg(OH)_2$), and *bismuthic hydroxide* ($Bi(OH)_3$). (How many atoms of bismuth, oxygen, and hydrogen in a molecule of the last of these?) The two atoms OH constitute a group, which, united with atoms of the metals, forms hydroxides of the metals. Such a group of atoms, *acting together as a single atom,* and being present in a series of similar compounds. is called a *compound radical* The name given to the compound radical OH is *hydroxyl* (= *hydr*ogen *ox*ygen radical).

65. **Properties of Hydrogen.** — (Symbol, H; atomic weight, 1; molecule contains 2 atoms (H_2); 1 litre weighs 0.0896 gram.) Hydrogen is an invisible gas, the lightest substance known. Air is 14.43 times as heavy as it.

Experiment 31.—Take a jar of hydrogen from the pneumatic trough, holding it upside and pour it carefully *upward* into another jar filled with air. To show that the hydrogen has risen into the second jar apply a flame to its mouth. (What properties of hydrogen does this experiment illustrate?)

Hydrogen is buoyant in air just as a cork is buoyant in water. It was formerly used for inflating balloons, but the cheaper coal gas has now largely taken its place. If soap bubbles be blown with hydrogen they rise rapidly, and can be set on fire while in the air.

Experiment 32.—Thrust up a burning pine splinter, or small taper, into a jar of hydrogen held upside down. The hydrogen catches fire and burns, but puts out the taper.

Hydrogen is not a supporter of ordinary combustion, but is itself combustible. Still, a jet of oxygen will burn in an atmosphere of hydrogen, just as a jet of hydrogen will burn in an atmosphere of oxygen. This shows that the terms *combustible* and *supporter of combustion* are only relative and would need to be reversed in their application if we happened to be living in an atmosphere of hydrogen.—When hydrogen burns in air it unites with the oxygen of the air to form water. It is a constituent of most kinds of fuel, as wood, coal, oils, &c., so that water is a constant product of fires and lights. (Account for the gathering of water on the bottom of a kettle of cold water set on the fire.)

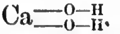
Experiment 33.—Fill an inverted test-tube one-third with oxygen (by pouring it *upwards* in the pneumatic trough) from a jar of the gas, and the remaining two-thirds with hydrogen. Close the tube with the thumb, remove it from the trough, turn it several times to mix the gases, and apply a flame to its mouth. The mixed gases explode with violence. Repeat the experiment using air and hydrogen in the proportions of 5 to 2 by volume. The explosion is less violent.

The mixture of 2 volumes of hydrogen and 1 of oxygen is known as *knall gas*. The gases may remain mixed for any length of time at the ordinary temperature without combining, but as soon as the temperature is made high enough at any point, combination begins at that point, water is formed, and enough heat is set free to raise the temperature of the surrounding uncombined gases to the point at which union takes place, so that the combination goes on spreading throughout the whole mass. This takes place with great rapidity, and an *explosion* results. (Why mix the gases in the proportions given, rather than in any other?) One gram of hydrogen in combining with oxygen liberates 34,462 heat units. (What is a heat unit?) Thus, in Experiment 33, the water formed by the combination of the gases is heated to a very high temperature; it expands suddenly, and, losing heat, contracts suddenly, making a disturbance in the air which reaches our ears as the *sound* of the explosion.—The flame of hydrogen is a very hot one. In the *oxyhydrogen blowpipe* a mixture of oxygen and hydrogen is used to give a flame of intense heat. When directed upon a piece of lime, this flame, although giving very little light itself, heats the lime to a bright white heat, producing the *lime-light*. Coal gas is often used instead of hydrogen.—Hydrogen can be condensed to a liquid by pressure at a very low temperature.—Although hydrogen and oxygen do not usually combine at the ordinary temperature of the air, yet in contact with certain substances which have the power of condensing gases on their surface, the two gases unite at the ordinary temperature. *Platinum* has this power very strongly, especially when in the finely divided conditions of *spongy platinum* and *platinum black*. If a coil of platinum wire is held in a flame of hydrogen until it is red hot so as to drive the condensed gases off its surface, it acquires the power of setting fire to a mixture of hydrogen and air, even after it has cooled. This property of platinum is utilised in heating a kind of surgical knife, which burns instead of cutting.—Hydrogen is very slightly soluble in water. It can be breathed, and then gives a high squeaking tone to the voice. It is not poisonous, but will not support animal respiration.—Hydrogen is evolved during the growth of fungi, and as it is being set free it has the power of converting arsenic, antimony, and sulphur into poisonous gaseous compounds. This accounts to some extent for the poisonous effects of arsenical dyes in wall papers and carpets.

66. **Valence.**—Two volumes of hydrogen unite with one of oxygen. This indicates a difference between hydrogen and oxygen atoms. We shall hereafter study cases in which gases unite with hydrogen in equal volumes, or, as is deducible, one atom with one atom. One atom of nitrogen is united with *three* of hydrogen to form ammonia; and one atom of carbon is united with *four* of hydrogen in the molecule of marsh gas. On referring to Art. 63 we find that while an atom of sodium displaces an atom of hydrogen, an atom of zinc displaces two.

The following formulas express some of these facts :—

Hydrochloric acid.	Water.	Ammonia.	Marsh gas.
HCl,	H_2O,	H_3N,	H_4C.

The atoms of chlorine, oxygen, nitrogen, and carbon differ in the number of atoms of hydrogen which they can take to form a molecule. The power, varying in this way, is called *atomicity*, *valence*, or *quantivalence*. It is measured for any element by the *number of atoms of hydrogen with which an atom of the element will combine*; *or by the number of atoms of hydrogen which an atom of the element will replace in a compound* (Art. 63). The words *bivalent*, *trivalent*, *quadrivalent*, *quinquevalent*, &c., are used to denote the valence of atoms which combine with or replace one, two, three, &c., atoms of hydrogen. The words *monad*, *dyad*, *triad*, *tetrad*, *hexad*, &c., are also used. It will be seen later that the valence of an element varies in different compounds, but it nearly always increases by *twos*. Thus, the valence of phosphorus is sometimes 3 and sometimes 5, e. g., PCl_3 and PCl_5. (Form a table of the elements mentioned in this article, writing the valence of each opposite its symbol). The valence of atoms is often indicated by Roman numerals attached to the symbols, as H^{I}, Na^{I}, Cl^{I}, O^{II}, Ca^{II}, Zn^{II}; N^{III}, Bi^{III}, P^{III}; C^{IV}, Si^{IV}; N^{V}, P^{V}, Sb^{V}, &c. In writing the formulas of compounds the valence of the atoms is often shown by lines joining the symbols. Formulas thus written are used to picture the knowledge we have of *the way in which the atoms are grouped in the molecule*, and are called *Graphic, or Constitutional Formulas.* For example, $H—O—H$, water; $Zn=O$, zinc oxide;  $N\begin{smallmatrix}-H\\-H\\-H\end{smallmatrix}$, ammonia;  $Ca\begin{smallmatrix}-O-H\\-O-H\end{smallmatrix}$, calcic hydroxide.

67. **Diffusion.**—If a lump of sugar be placed at the bottom of a glass of water, it dissolves; but the water is not at once sweetened, if it is kept still. After some time the taste of the sugar can be detected at the top, and the sugar will at length become evenly mixed with

the whole quantity of water, without the slightest apparent motion of the liquid. There must be some motion of the particles of sugar; in fact, the motion of molecules mentioned in Art. 56. It is supposed that the molecules of sugar, after dissolving, move about continually until they are evenly *diffused.* This change of place of substances by molecular movements is called *diffusion.* In one form or another it goes on in the most important processes of animal and vegetable life; e.g., digestion, assimilation, respiration, secretion, and excretion. Various words, *osmose, endosmose, dialysis,* &c., are used to describe diffusion under certain conditions, but the process is essentially the same in each case.

Experiment 34.—Fill a tall glass cylinder nearly full of water, and pour through a funnel with long *capillary* tube leading to the bottom a layer of saturated solution of *potassic bichromate.* If the cylinder be kept undisturbed, the red liquid will not be evenly diffused until several months have elapsed.

Diffusion of liquids is very slow. (Will solids diffuse?)

Experiment 35.—Fit with a bored cork a clean, dry, porous earthenware vessel (inner cell of a galvanic battery); push a long glass tube through the cork (it must fit tightly); and fix this apparatus so that the free end of the tube may stand in a vessel of some coloured liquid. Place over the cell a glass beaker or other convenient vessel bottom up, and fill the space between with hydrogen. The coloured liquid is at once forced down the tube, and bubbles of gas are driven out. Remove the outer vessel, and the liquid rises in the tube. (Coal gas answers in place of hydrogen.)

In the first part of the process, there is air inside and hydrogen outside the porous cell. Both find their way through the pores, but hydrogen diffuses faster than air, the volume of gases inside the tube is increased, and the liquid is forced down to make room. (Explain the second part of the experiment.) Diffusion of gases is a much more rapid process than that of liquids. (Why?) *Law of Diffusion of Gases* (Graham):—*Gases diffuse at rates (measured by volume) inversely proportional to the square roots of their relative weights.* For example, the relative weights of hydrogen and oxygen are 1 and 16. Their rates of diffusion are as $\sqrt{16}$ to $\sqrt{1}$, or as 4 to 1, i.e., hydrogen diffuses four times as fast as oxygen.

68. **Hydrogen Dioxide.**—(H_2O_2). This substance is also called *peroxide of hydrogen*, and *oxygenated water*. It is present in the air, and comes down with rain and snow, but only in minute quantities. It is a compound of hydrogen and oxygen in the proportion of 1 to 16 by weight. The simplest formula representing this composition is HO, but if we try to write this *graphically*, showing the atomicities, thus H—O, an anomaly appears; the oxygen atom must be represented as monad, and there is every reason to believe that it is dyad. From this and other considerations the formula is doubled,— H_2O_2, or H–O—O–H.

Preparation.—Mix *barium dioxide* with dilute sulphuric acid, allow to settle, and pour off the clear liquid. The substances formed in this reaction are hydrogen dioxide and baric sulphate:

$$H_2SO_4 + BaO_2 = H_2O_2 + BaSO_4.$$

(Put this equation into words, giving weights and names.)—In this action the hydrogen dioxide is obtained diluted with water, while the heavy, white, insoluble baric sulphate falls to the bottom. As the dioxide is decomposed by heat it cannot be separated from water by boiling away the latter; but the water can be removed by placing the solution under the receiver of an air pump along with a vessel of oil of vitriol, which is very *hygroscopic* (attracts moisture strongly). When the air is pumped out the water evaporates rapidly, and is absorbed by the oil of vitriol.

Properties.—A colourless, oily liquid, heavier than water (specific weight 1.452), soluble in water; very unstable, decomposing slowly at low temperatures, rapidly when heated, into water and oxygen. (Write the equation.) It easily parts with half its oxygen to oxidisable substances; i.e., it is an *oxidising agent.* For this reason it bleaches many colouring matters; e. g., that of the hair; and is commonly used for bleaching dark hair, old paintings, &c. It forms a froth when taken into the mouth, and excites the flow of saliva. It blisters when undiluted. Its principal use in medicine depends on its oxidising power.

Test.—Add a few drops of sulphuric acid to a solution of hydrogen peroxide, then a little ether, and a few drops of potassic bichromate solution. After being shaken the mixture turns deep blue. The ether takes up the colouring matter, and forms a layer at the top.

QUESTIONS AND EXERCISES.

1. Would you expect to find hydrogen uncombined in the air?

2. Calculate the percentage composition of water, i. e., the quantities of hydrogen and oxygen in 100 parts.

3. What volume of mixed gases, measured at 1000 mm. pressure and 10° C., is produced by the electrolysis of 100 grams of water?

4. 50 grams of zinc are put into a closed vessel of 10 litres capacity along with 1 litre of dilute sulphuric acid. What is the pressure of gas when the action is completed?

5. What weight of zinc must be dissolved in order to give 50 litres of hydrogen measured at 3 atmospheres pressure and 16° C.?

6. 20 grams of iron are dissolved in hydrochloric acid, and the evolved gas is measured at 750 mm. pressure and 20° C. What is its volume?

7. "One atom of zinc sets free a molecule of hydrogen." What evidence can you bring in support of this statement?

8. What is a *hydroxide*? Are there hydroxides of the non-metals?

9. Define *compound radical.* What is the meaning of the word *radical* as used here? Should it not be spelled *radicle*?

10. Calculate the weight of 20 litres of hydrogen measured at 25° C. and 1000 mm. pressure. What volume of oxygen has the same weight under the same conditions?

11. How does it happen that the atomic weight of hydrogen is 1?

12. Why does hydrogen explode less violently with air than with oxygen?

13. From the following formulas deduce the atomicity of bismuth (Bi), phosphorus (P), tin (Sn), and Sulphur (S): HCl, $BiCl_3$, PCl_5, H_2O, SnO_2, SO_3.

14. The specific weights of water vapour and oxygen are 9 and 16 (Hydrogen = 1). If 100 c.c. of water vapour diffuse into a vacuum in a certain time, what volume of oxygen will diffuse under the same conditions in the same time?

15. Hydrogen dioxide is sometimes called *hydroxyl.* Explain.

CHAPTER VII.

AIR.

69. **The Atmosphere.**—This is the gaseous ocean, supposed to be from 50 to 100 miles deep, at the bottom of which we are living. Spaces said to be empty are generally full of air.

Experiment 36.—Pass the tube of a small glass funnel through a bored cork having a short glass tube passing through a second hole (as in a *wash-bottle*). Fit the cork into a flask, close the glass tube with a finger and fill the funnel with water. A little runs into the flask; remove the finger from the tube, and the whole of the water runs in freely. If the tube have only a small opening, the water runs in slowly, and a flame held near the opening will be blown by a stream of air coming out.

(What conclusions do you draw from this experiment? Why is it necessary in filling a cask with water through a funnel, to bore a second hole in the cask?)

Air has *weight*, as can be shown by weighing a glass globe emptied by the air pump, then allowing the air to flow in, and weighing it again; a delicate balance shows an increase in weight. One cubic foot of dry air at standard temperature and pressure weighs 565½ grains (calculate the weight, in grams, of 1 litre).

Since air has weight, the atmosphere presses upon the surface of the earth, and upon every object on that surface. This pressure can be shown by the *barometer*. Fill a glass tube, closed at one end, and about 35 inches long, with mercury; close it with the thumb, invert it, and place the end beneath the surface in a dish of mercury. Remove the thumb, and the mercury after a few oscillations comes to rest at about 30 inches above the level of the surface in the dish (Torricelli, 1643). Some pressure on this surface balances the weight of the mercury in the tube, otherwise the mercury would fall. This pressure is the weight of the atmosphere. It is exerted in every direction on the surface of any body placed in it. (What is there inside the tube above the mercury?)

Experiment 37.—Make an experiment such as that described above, using water instead of mercury. The water does not fall at all when the inverted tube is opened under water. But if the tube were, say, 40 feet long the water would fall and remain at the height of about 34 feet.

An ocean of water 34 feet deep, or one of mercury 30 inches deep, would exert the same pressure upon the earth as the atmosphere does. (Calculate the specific weight of mercury). A column of mercury 30 inches high and 1 inch square in section weighs 14.7 lbs.; and the *pressure of the atmosphere is generally taken as 15 lbs. on the square inch.* When a barometer is carried up a tower (Blaise Pascal, 1648), or mountain, the mercury falls; if it is carried down a deep mine the mercury rises. (Explain). At the top of Mont Blanc it stands at 16 inches only. When any great portion of the atmosphere is heated, it expands and part of the air flows away over to colder regions. This diminishes the weight of the air in the heated region, and the barometer falls, until air rushes in from surrounding regions to equalise the pressure. (What natural phenomena does this explain?) Similarly, cooling causes rise of the barometer. These and other causes produce variations in the height of the mercury in the barometer, so that, in studying weather, careful attention must be given to the *readings* of the barometer. The average height at the sea-level is 30 inches, or *760 millimetres.* This is taken as the *standard pressure* in calculating volumes of gases.

70. **Boyle's Law** (1662).—If a quantity of air be confined and the pressure upon it increased, its volume is lessened; if the pressure be decreased the volume becomes greater. This can be shown by a cylinder closed at one end and provided with an air-tight piston. If one presses the piston down, one feels a *resistance*, but the volume is diminished; on the other hand, if the piston is raised above a certain distance, one feels that a weight is being lifted (What is the weight?) as the volume increases. The law of change of pressure with change of volume is as follows:—*The volume of any portion of air is inversely proportional to the pressure, the temperature being constant.* (Consult a work on Physics for the experimental demonstration.) When any portion of air is closed off from the rest of the atmosphere, the pressure upon it is that shown by the barometer at that moment, say 30 inches of mercury. If the pressure be doubled, the volume is reduced to $\frac{1}{2}$ the original; if the pressure be tripled, to $\frac{1}{3}$, &c. On the other hand, if the pressure is reduced to $\frac{1}{2}$, the volume is increased to twice the original and so on. Stated in general terms, $V : V^1 :: P^1 : P$, where V and V^1 represent volumes at pressures P and P^1. This law applies to *all gases far removed from their point of condensation.** It does not, for example, apply to water at 105° C.

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* At high pressures Boyle's Law is only approximately true.

71. Expansion of Air by Heat—Charles' Law.

Experiment 38.—Place a narrow-necked flask with its neck downwards and dipping under water. Pour hot water on the bottom of the flask; the air inside expands and part of it is driven out of the flask. Allow the flask to cool; the air contracts, and the water rises in the neck of the flask.

The amount of this expansion and contraction has been accurately measured for air and other gases. *It is almost exactly the same for all gases.* If we begin with a portion of gas at 0° C and heat it to 1°, its volume increases by $\frac{1}{273}$rd; at 2° its volume is greater than at 0°, by $\frac{2}{273}$rds, and so on. If the gas be cooled to — 1° its volume is less by $\frac{1}{273}$rd, at — 10° less by $\frac{10}{273}$rds, and at — 273° (if we could reach such a temperature) the volume would be 0. Hence — 273° C. is called the *absolute zero* of temperature, and temperatures reckoned from this point are called *absolute temperatures.* Evidently the absolute temperature corresponding to 0° C. is 273°, and generally any temperature t of the centigrade scale is $273 + t$ of the absolute scale. The *Law of Expansion of Gases* is as follows:—*The volume of any portion of gas is proportional to the absolute temperature, the pressure being constant.*[*]

Example.—A quantity of air measuring 10 litres at 20° C. is heated to 50° C. What is its volume?

$$273 + 20 : 273 + 50 :: 10 : x$$
$$x = \frac{3230}{293} = 11.02 \text{ litres.}$$

72. Measurement of Volumes of Gases.—In measuring the volume of any portion of gas at dif-

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[*] At high pressures, and near the points of condensation, Charles' Law is only approximately true.

ferent times, it nearly always happens that *both* pressure and temperature vary, so that it becomes necessary in comparing volumes to apply both Boyle's and Charles' laws.

Example.—20 litres of hydrogen at pressure 755 mm. and temperature 15° C. occupy what volume at 740 mm. pressure and 20° C.?

$$\left.\begin{array}{r} 740 : 755 \\ 273 + 15 : 273 + 20 \end{array}\right\} : : 20 : x$$

$$x = 20 \times \tfrac{755}{740} \times \tfrac{293}{288} = 20.7 \text{ litres.}$$

A good check on the correctness of the statement in such calculations is to remember the general effect of change of pressure and temperature on volume, and see if the fractional factors in the last equation increase or decrease the number of litres. Thus, in the above example, the pressure is lessened, and therefore the volume increased. I see that the factor $\tfrac{755}{740}$ is greater than 1, and its effect is to increase 20. Similarily with temperature.

Volumes of gases are best compared at the standard temperature and pressure (0° C. and 760 mm. of mercury); and calculations of volumes of gases produced in chemical actions are always based on the experimental facts that the *gram-molecule* of hydrogen (i. e., 2 grams of hydrogen) measures, at 0° C. and 760 mm. of mercury pressure, 22.33 litres, and that the gram-molecules of all other gases occupy the same space, under the same conditions. (Art. 60.)

Example 1.—What volume of oxygen measured at 15° C. and 740 mm. is formed by heating 100 grams manganese dioxide?

$$\text{Equation}: \underset{\substack{3 \times 86.8 \\ \text{grams.}}}{3MnO_2} = Mn_3O_4 + \underset{\substack{22.33 \\ \text{litres.}}}{O_2}$$

260.4 grams of the oxide give 22.33 litres oxygen measured at 0° C. and 760 mm. Thus, 100 grams give $\frac{100}{260.4} \times 22.33$ litres at 0° and 760; and $\frac{100}{260.4} \times 22.33 \times \frac{273 + 15}{273 + 0} \times \frac{760}{740}$ = the volume at 15° C. and 740 mm.

Example 2.—What weight of potassic chlorate, when decomposed, will give 10 litres of oxygen measured at 20° C. and 1000 mm. pressure?

$$\text{Equation: } \underset{\substack{2 \times 122.6 \\ \text{grams.}}}{2\,KClO_3} = 2\,KCl + \underset{\substack{3 \times 22.33 \\ \text{litres.}}}{3\,O_2}$$

i. e., 245.2 grams of the salt give 66.99 litres of oxygen *measured at 0° C.* and *760 mm.* In order to compare this volume with the volume required, they must be reckoned at the same temperature and pressure. It is well, to avoid confusion, to compare volumes of gases *always* at 0° and 760. In this case, then, we first reduce the 10 litres to the volume at 0° and 760:

$$10 \times \frac{273 + 0}{293 + 20} \times \frac{1000}{760} = \text{vol. at } 0° \text{ and } 760.$$

$$\text{Then, } 66.99 : 10 \times \frac{273}{293} \times \frac{100}{76} :: 245.2 : x$$

$$x = \frac{10 \times 273 \times 100 \times 245.2}{293 \times 76 \times 66.99}$$

73. Composition of Air.

Experiment 39.—Put a bit of phosphorus, dried on filter paper, into a small porcelain cup floated on a flat cork in a basin of water. Touch the phosphorus with a hot wire and immediately cover it with a beaker. It burns for some time, but at length goes out. As the enclosed gas cools, water rises in the beaker, showing a lessening of volume. Decant some of the gas into a test-tube (Art. 41), close the test-tube with the thumb, remove it, and thrust a burning match or splinter into the gas. The flame is put out.

Further examination of this gas has shown it to be an element, *nitrogen*. The combustion of phosphorus is due to the *oxygen* of the air. (What has become of these in the experiment?)—*Air is a mixture of the two elementary gases, nitrogen and oxygen.* That it is a mixture, and not a chemical compound, is seen from the following facts:—

1. If air be shaken up with water, oxygen dissolves in greater relative quantity than does nitrogen.

2. The two gases can be partially separated by *diffusion.* (Which gas diffuses faster?)

3. If nitrogen and oxygen be mixed in the ratio in which they are present in air, no heat is given out, and there is no other evidence of chemical action; but the mixture has the properties of pure dry air.

4. The volumes of the gases are not in any simple ratio. (What *law* is here referred to?)

VOLUMETRIC ANALYSIS OF AIR.—This analysis is made in a graduated glass tube called a *eudiometer.* The tube is closed at one end, at which two *platinum* wires are melted through the glass so as nearly to meet within the tube. The eudiometer is filled partly with mercury, inverted in a trough of the same liquid, and the volume of air thus closed off is noted, as well as the temperature and pressure. To this air is added about half its volume of pure hydrogen, and volume, temperature, and pressure are once more noted. The eudiometer is now tightly pressed down on a sheet of India-rubber, and an electric spark is passed between the platinum wires. An explosion takes place within the tube, and the volume of gas is seen to be much reduced. Volume, temperature, and pressure are once more read off. The remaining gas is a mixture of nitrogen and hydrogen. One-third of the loss of volume after the explosion is due to the disappearance of oxygen (What has become of it?); and the volume of oxygen being known, the remainder of the original volume of air is reckoned as nitrogen.

Example.—Volume of air enclosed, 20 c.c.; temperature, 15° C.; pressure, 750 mm.—Volume after addition of hydrogen, 32 c.c.; *t*, 16° C.; *p*, 718. Volume after explosion, 20 c.c.; *t*, 18° C.; *p*, 710 mm. Reduce these volumes to 0° C. and 760 mm., and find the decrease of volume after explosion to be 11.03 c.c. Calculate from this that 100 c.c. of air consist of 20.96 of oxygen and 79.04 of nitrogen.

COMPOSITION BY VOLUME.

Oxygen	20.96
Nitrogen	79.04
	100.00

ANALYSIS OF AIR BY WEIGHT.—Air is dried and purified, and then allowed to flow slowly through a weighed tube containing red hot copper filings. It loses oxygen, *cupric oxide* (CuO) being formed; and the nitrogen passes on into a weighed *vacuous* globe of glass. he increase in weight of the tube gives the weight of oxygen, and the increase in the globe the weight of nitrogen. The average of many careful experiments gives as the percentage composition of air *by weight*:

Oxygen	22.77
Nitrogen	77.23
	100.00

The composition of air is almost constant in all parts of the world, and in all situations. In towns and in foggy weather the percentage of oxygen, by volume, may sink to 20.8; and in crowded rooms it sometimes sinks much lower.—The oxygen of the air is necessary to support life, fires, decaying processes, &c. (What is the use of nitrogen?)

74. Other Substances in the Atmosphere.—

The atmosphere contains several substances besides oxygen and nitrogen, but in small and variable quantities.

CARBON DIOXIDE (CO_2).—Constantly present in air, from 4 to 6 volumes in 10,000. Its presence is of great importance, as it forms an essential constituent of the food of plants. The supply is kept up by the processes of combustion, respiration, and the decay of organic matter.

WATER (H_2O).—This is present in the air, in the form of vapour, in very variable quantities, depending on temperature and degree of saturation. A cubic metre of air at 25° C. contains when saturated 22.5 grams of water vapour; at 0° C., only 5.4 grams. *Dew* is formed by the condensation of aqueous vapour from the air by contact with cooled surfaces. Leaves radiate heat much faster than other objects, and therefore condense water vapour much more rapidly. (Why does not dew form on a cloudy or a windy night?) Aqueous vapour in the air tempers the heat of the sun, the rays of which would be unbearably hot, if a large fraction of the heat were not stopped on its passage through the atmosphere. Water vapour has in a very high degree the power of absorbing radiant heat.

COMPOUNDS OF NITROGEN. — Minute quantities of *oxides of nitrogen* are formed in the atmosphere by the action of electricity. (On what?) *Ammonia* (NH_3) is present in small proportions, generally as ammonic nitrite or nitrate. These substances are brought down to earth in rain and snow, and serve for plant food.

DUST, &c.—Under this head are included solid particles of all sorts, organic and inorganic. *Common salt* is always present in the air. If a little clean rain-water is evaporated on a microscope slide and the residue examined with the microscope, crystals of common salt ($NaCl$) can always be seen. *Spores*, or eggs of minute plants and animals, are constantly present. Many of them are the eggs of *ferments;* others are the cause, or at least the concomitants, of *diseases.* The object of the antiseptic spray in surgery is to kill such living dust; and it is important to note that disinfectants and antiseptics which are to purify air must (unless the air is drawn over them) be *volatile.* Air can be purified from dust by drawing it through cotton-wool, and other filters.

Ozone and *hydrogen dioxide* have been already mentioned.

75. **Combustion in Air.**—Substances which burn in oxygen usually burn in air, but not so rapidly. (Why?) The substances burned in lamps, candles, and fires are composed mostly of carbon and hydrogen, which unite with oxygen to form carbon dioxide and water. Thus, the oxygen of the air is used up, and in lamps and stoves, &c., provision must be made for a renewal of the supply of air,—in other words, there must be a draught.

The consumption of oxygen must be taken into account in considering questions of ventilation. An ordinary lamp consumes as much oxygen in 1 hour as a man does in 5. (How does a lamp or gas flame differ from a fire in a stove or grate in their effect on the air?)

76. **Respiration.**—In the air cells of the lungs the air is separated from the blood by a very thin membrane through which diffusion goes on readily and rapidly. The blood comes into the lungs charged with carbon dioxide, a waste product which it has gathered from the furnaces of the body,—the muscles, glands, &c. These need a continual supply of oxygen to feed the slow fires going on in them. Carbon dioxide passes outwards by diffusion, and is exhaled; oxygen diffuses inward and is carried away to the tissues. Thus, the air which returns out of the lungs contains less oxygen and more carbon dioxide than when it was inspired. In one hour an adult man consumes about 29 grams (how many litres?) of oxygen, and breathes out about 33 grams carbon dioxide. Besides carbon dioxide, water vapour and small quantities of complex organic compounds are exhaled. Both the organic compounds and the carbon dioxide are injurious to health; and therefore the necessity for renewing the air which is breathed. It is estimated that an average adult man requires 1500 cubic feet of fresh air per hour.

QUESTIONS AND EXERCISES.

1. A flask filled with water and closed with a cork through which passes a narrow tube open at both ends is held upside down. The water does not run out. Why?

2. Air is found to become less and less dense as we ascend. Account for this.

3. Why do men need to breathe faster at great elevations than lower down?

4. Why does blood burst through any place where the skin is thin, when a very great elevation is reached, as in balloons?

5. What is the pressure of the atmosphere in grams on every square centimetre?

6. The specific weight of alcohol is 0.784. What would be the average height of an alcohol barometer?

7. A quantity of air measures 264 c.c. at a pressure of 700 mm. What will it measure when the pressure is increased to 1000 mm.?

8. Calculate the weight of hydrogen in a vessel of 10 litres capacity, filled when the barometer reads 756 and the thermometer 18° C.

9. A quantity of air under a pressure of 32 inches of mercury undergoes a change of pressure and increases from 10 cubic feet to 12.4 cubic feet. What is the new pressure? (Temperature constant.)

10. What pressure must be used to compress 18 litres of oxygen into a vessel of 6 litres capacity, the oxygen being originally under a pressure of 785 mm.?

11. 150 c.c. of air at 50° C. is cooled to 10° C. Calculate the volume (pressure being constant).

12. A quantity of air measures 24 litres at 15°.; the temperature is reduced to — 16° C. What is now the volume? (Pressure constant.)

13. What volume of gas at 200° C. will measure 320 c.c. at 0° C.? (Pressure constant.)

14. What volume of oxygen measured at 2000 mm. and 12° C. is formed by the decomposition of 500 grams potassic chlorate?

CHAPTER VIII.

NITROGEN AND ITS COMPOUNDS.

Nitrogen—($N''' = 14$).

77. **Occurrence.** — Forms about four-fifths by volume of the atmosphere; in combination, it forms part of all living matter, and is therefore an essential constituent of plant and animal food. Other compounds occurring in nature are nitre (KNO_3), Chili nitre ($NaNO_3$), and ammonia (NH_3).

78. **Preparation.**—Nitrogen is most readily prepared from air (Exp't 39); see Art 73, "Analysis of Air by Weight." It can also be prepared from nitre (saltpetre).

Experiment 40.—Heat 10 grams iron filings in a hard-glass test-tube with ½ gram saltpetre. Collect the evolved gas in the usual way. It is nitrogen, the "*nitre-generator.*"

79. **Properties.**—An invisible gas, without smell or taste. It is 14 times as heavy as hydrogen and a little lighter than air. (Calculate its specific weight, air being standard.) It is incombustible and not a supporter of combustion (Make experiments to show this). It is remarkable for chemical inactivity, not entering readily into combination with other elements. Under the influence of electric sparks or flashes it unites with oxygen, and, in very small quantities, with hydrogen. It is

slightly soluble in water, about $1\frac{1}{2}$ vols. in 100 of water. It has been liquefied at — 146° C. by a pressure of 33 atmospheres.

Compounds of Nitrogen.

80. Ammonia.—($NH_3 = 17.$)

Experiment 41.—Heat a piece of dried meat in a glass tube closed at one end. It chars, and moisture collects. Wet a small strip of filter paper with red litmus and bring it in contact with this moisture. The litmus is turned blue. Same result, if a bit of coal, bread, or horn be heated.

The *alkaline reaction* of the moisture is due to the presence of a *volatile alkali*, ammonia. (What alkalis have already been noticed?) It is always formed when animal or vegetable bodies are *destructively distilled.* Coal, wood, bones, and other animal and vegetable substances are distilled on a large scale in the manufacture of gas, charcoal, bone-black, &c.; and the watery liquid (a by-product) contains much ammonia. From *gas liquor* ammonia is prepared by heating with lime and condensing the ammonia in cooled water. Formerly, it was prepared by distilling scraps of the horns of the hart; hence the popular name, "spirits of hart's horn." —Ammonia is always one product of the decay of animals and vegetables, excrement, guano, &c.

PREPARATION.—Ammonia is most conveniently prepared from one of its salts, *sal ammoniac* (NH_4Cl).

Experiment 42.—Mix thoroughly about 2 parts of dry powdered sal ammoniac with 1 of powdered quick-lime. Note the smell of ammonia. Put the mixture into a hard glass test-tube or flask, and arrange a gas delivery tube so as to collect the evolved gas in inverted bottles, to the tops of which the delivery tube must reach. (Why not over water?)

Equation:

Lime.		Ammonic Chloride.		Calcic Chloride.				
CaO	+	$2NH_4Cl$	=	$CaCl_2$	+	$2NH_3$	+	H_2O.
56 grams.		106.8 grams.		110.8 grams.		44.66 litres.		

Ammonia is generally used in water. To prepare the solution slaked lime is employed instead of quick lime, and the gas is passed into water, which must be kept well cooled. (Why?)

PROPERTIES.—Ammonia is an invisible gas, with a pungent smell, and a sharp alkaline taste. It is lighter than air. (How does Exp't 42 show this?) (Calculate its specific weight, air being standard; also when hydrogen is standard.) It is liquid at 15.5° C. under a pressure of 7 atmospheres (What is an *atmosphere of pressure*?), and at — 70° C. is solid. It is very soluble in water, 1148 vols. dissolving in 1 of water at 0° C. Much heat is given out during the process. (Account for this.) When a solution of ammonia is warmed the gas is driven off rapidly.

Experiment 43.—Fill a test-tube with ammonia gas (Experiment 42), close with the thumb, place the mouth under water, and remove the thumb. The water rises to the top, if there is no air in the tube. Close again with the thumb, remove the tube and examine the water in it, as to its smell, taste, feel, and action on red litmus.

The solution of ammonia in water (*liquor ammoniae*) has a strong alkaline reaction and probably contains *ammonic hydroxide* (NH_4OH). It neutralises acids, and thereby forms salts. The dry gas, also, combines with acids, and it is to be observed that no water is produced when ammonia unites with acids to form salts, e.g., $NH_3 + HCl = NH_4Cl$. These salts are called *ammonium* salts, since they contain the compound radical *ammonium* (NH_4) acting as a monad metal. Ammonia is not a supporter of combustion, and is incombustible in air; but a mixture of the gas and oxygen burns with a pale bluish flame, and forms water, nitrogen, and a little nitric acid.

Experiment 44.—Try the combustibility of ammonia gas by thrusting a burning match into a jar of it.

COMPOSITION OF AMMONIA.—The gas is decomposed by electric sparks. Two volumes of ammonia give one of nitrogen and three of hydrogen. That is, two molecules of ammonia decompose into one molecule of nitrogen and three of hydrogen. From this it is concluded that the molecule of ammonia contains an atom of nitrogen and three of hydrogen.

Liquor ammoniæ fortior is a nearly saturated solution of ammonia in water, prepared by distilling in an iron retort 3 lbs. ammonic chloride (NH_4Cl), with 4 lbs. slaked lime ($Ca(OH)_2$), and receiving the gas in water. It is lighter than water (sp. wt. 0.892), and contains 32.5 per cent. of ammonia. It must be kept well stoppered, otherwise the ammonia escapes. As ammonia is less soluble at high than at low temperatures this solution should not be allowed to get very warm. (What would happen ?)

Liquor ammoniæ or *aqua ammoniæ* is a weaker solution, made by mixing 1 pint of the stronger solution with 2 pints distilled water. It contains 10 per cent. of ammonia.

Ammonia has a strong inflammatory action on the respiratory and other mucous membranes. When breathed diluted with air, it stimulates; but its constant use may at length produce serious inflammation. Since it unites with acids to form mild salts, it is an antidote to acid gases. (What are antidotes for ammonia?).

Hydroxylamine (NH_3O) is a substance nearly related to ammonia. Its molecule contains hydroxyl (OH) instead of one of the atoms of hydrogen. If the molecule of ammonia is represented by  $N\begin{smallmatrix}H\\H\\H\end{smallmatrix}$, that of hydroxylamine is  $N\begin{smallmatrix}OH\\H\\H\end{smallmatrix}$. It is prepared by the action of *nascent* (just being set free) hydrogen on nitrogen dioxide (NO) :—$NO + 3H = NH_3O$.

81. Nitric Acid ($HNO_3 = 63$).

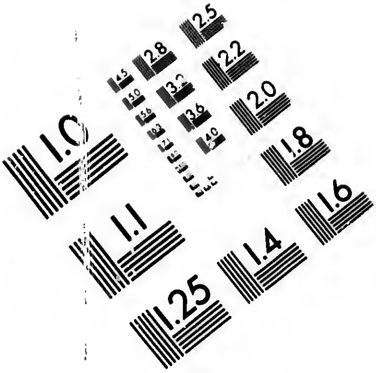
Experiment 45.—Put a little saltpetre in a test-tube, and drop on it from a pipette a small quantity of oil of vitriol. Heat very gently, and observe the drops of fuming liquid which gather on the sides of the tube. Gather them on a glass rod and try their action on red litmus.

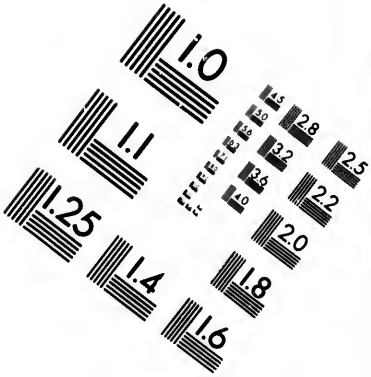
The acid liquid is *nitric acid*, or *aqua fortis*. Saltpetre is a salt of the base, potassic hydroxide, and nitric acid. When it is acted upon by the stronger acid, the weaker is displaced, and a new salt, *potassic sulphate*, is formed.

$$2KNO_3 + H_2SO_4 = 2HNO_3 + K_2SO_4.$$

Nitric acid occurs naturally only in small quantities; but its salts are found in large quantities. Chili saltpetre, or sodic nitrate ($NaNO_3$), is most plentiful, and is now used in preparing the acid.

PREPARATION.—Distil at a gentle heat, from a glass retort, equal weights of Chili saltpetre and oil of vitriol, keeping the receiver well cooled. Nitric acid distils, and a white salt remains in the retort. This salt has





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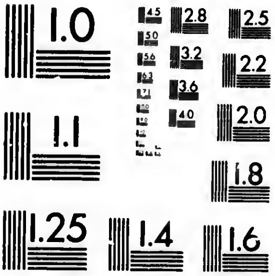

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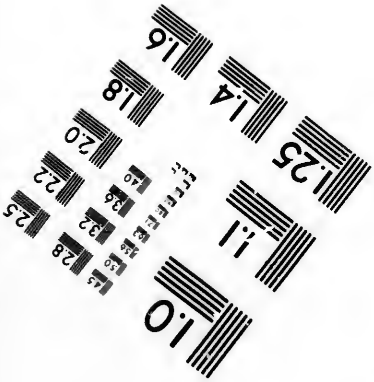

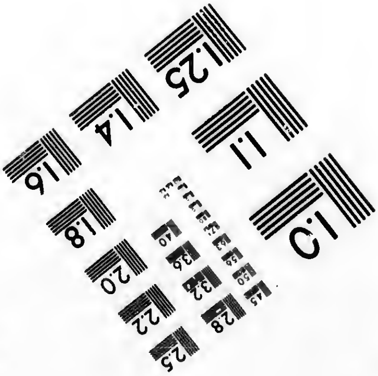

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acid properties. In fact it is still half acid, and is called *acid sulphate of sodium*, or *sodic hydric sulphate :*

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4.$$

Why not use double the quantity of sodic nitrate, as represented in the preceding equation? Because, in this case, the action would go on only at such a high temperature that the nitric acid would be partially decomposed.

PROPERTIES.—Pure nitric acid is a colourless fuming liquid of sp. wt 1.52. It has a strong attraction for water, and it is hard to prepare it free from water. The strong acid of commerce always contains about 10% of water, and is generally reddish or yellowish from impurities. *Red fuming nitric acid* is strong nitric acid coloured by nitrogen trioxide and tetroxide. When strong nitric acid is boiled it loses acid faster than it does water, until a liquid containing 70% of acid distils at 121° C. unchanged. If a weaker acid be boiled it loses water faster than acid until it contains 70°/₀ of acid.

Experiment 46.—Put a few cubic centimetres of strong nitric acid in a test-tube, and add an equal volume of water. Note the rise of temperature. (Account for it.) Pour the contents of the tube into about one litre of water, stir well, and taste.

Nitric acid is a powerful oxidising agent. (Calculate the percentage of oxygen which it contains).

Experiment 47.—Drop a little strong nitric acid on some powdered charcoal heated to redness in a deflagrating spoon. *N.B.*—The acid must contain very little water.

Experiment 48.—Very carefully drop a small piece of phosphorus into a little nitric acid in a small porcelain dish. It dissolves with the evolution of reddish fumes. If the acid is very strong, the phosphorus catches fire.

If the solution from Experiment 48 be evaporated, *phosphoric acid* is left. (How has this acid been before obtained?) Similarly, *sulphur* can be oxidised to *sulphuric acid* by boiling with nitric acid. *Turpentine* can be set on fire by [illegible] ixture of nitric and sulphuric acids.

Experiment 49.—Dilute a few cubic centimetres of nitric acid with about 4 times its volume of water, and pour it over a small bit of lead in an evaporating dish. The lead begins to dissolve, and red, strongly-smelling fumes come off. Apply heat to hasten the action, and when the lead is completely dissolved evaporate the solution on the water bath. Crystals of colourless *plumbic nitrate* ($Pb(NO_3)_2$) are left. Repeat the experiment, using copper instead of lead. Fine blue crystals of *cupric nitrate* are formed:

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O.$$

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

(Write down the *names* and *weights*.)

Nitric acid dissolves most metals, forming *nitrates* of the metals, *oxides of nitrogen*, and *water*. It dissolves silver, but not gold, and can thus be used to separate silver from gold. If the strong acid be used in dissolving metals, the gaseous product is nitrogen trioxide (N_2O_3); dioxide (NO), monoxide (N_2O), nitrogen, and even ammonia, are obtained at successive stages of dilution. As a rule, the more violent (rapid) the action of the acid, the less oxygen does it lose. Thus, the higher oxides of nitrogen are formed when the *acid is strong*, *the temperature high, or the metal easily oxidised.*—Nitric acid is a strong corrosive poison. It 'eats up' organic tissues when it is strong, and partially destroys them even when it is weak. The antidotes are mild alkaline substances, as *magnesia.* A drop of the weak acid left on the skin for a few moments colors it bright yellow (*Picric acid* is formed).

Nitro-glycerine and *gun-cotton* are chemical compounds of glycerine and cotton with nitric acid, in which the oxygen of the acid is ready to combine with the carbon and hydrogen of the glycerine and cotton. (Explain their explosiveness.) *Dynamite* is a commercial preparation of nitro-glycerine.

Tests.—1. Heat with some bits of copper. Red fumes are given off.

2. Colour light blue with a drop of *sulphate of indigo*, and heat. The colour disappears, because the indigo is oxidised.

3. Mix in a test-tube about equal volumes of strong sulphuric acid and solution of ferrous sulphate ($FeSO_4$), cool, and, holding the test-tube aslant, carefully pour down the side so as to form a layer on the top a dilute solution of nitric acid. Either at once or after a few moments a brown ring appears between the two layers. This is due to the formation of a brown compound of ferrous sulphate and nitrogen dioxide: $3H_2SO_4 + 2HNO_3 + 10\,FeSO_4 = 3Fe_2(SO_4)_3 + 2(FeSO_4)_2NO + 4H_2O$.

82. Nitrates.—Basicity.

Experiment 50.—Put a pipetteful of caustic potash solution in a porcelain basin, colour with litmus, and add *dilute nitric acid* (1 of strong acid to 4 of water) slowly with a pipette, stirring constantly, until the blue litmus turns purple. Taste the solution. Evaporate on the water bath. Long prismatic crystals of saltpetre are obtained.

If this experiment be made quantitatively it will be found that to get the neutral point, pure potash and pure acid must be mixed in the ratio by weight of 56.1 to 63. If any other ratio be used, some of the acid or of the base is left over :

$$\underset{56.1}{KOH} + \underset{63}{HNO_3} = KNO_3 + H_2O.$$

Base and acid give salt and water.

If a similar experiment be made with caustic soda, sodic nitrate, in cubical crystals, is formed; and it is found that in this case also the base and acid unite in *only one proportion*, viz., 40 to 63.

$$\underset{40}{NaOH} + \underset{63}{HNO_3} = NaNO_3 + H_2O.$$

40 g. of caustic soda are equivalent to 63 g. nitric acid (and to what weight of caustic potash?) Since nitric acid acts on these two bases in only one proportion for each, and forms only one salt for each, it is called a *monobasic acid*. The bases are *monacid* bases.

Experiment 51.—Put some dilute nitric acid in a porcelain dish, colour with litmus, and add dilute solution of ammonia until the litmus just turns blue. Then evaporate to dryness on the water bath, and preserve the crystals of *ammonic nitrate* for a later experiment :—

$$NH_3 + HNO_3 = NH_4NO_3.$$

Experiment 52.—Warm a little *plumbic oxide* (litharge) in a porcelain basin with dilute nitric acid. The oxide dissolves to a colourless solution. Evaporate on the water-bath. Colourless crystals of *plumbic nitrate* ($Pb(NO_3)_2$) are left :—

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Keep this salt for a later experiment.

The molecule of plumbic oxide is equivalent to *two* molecules of nitric acid. There is a corresponding base, plumbic hydroxide, $Pb(OH)_2$, the molecule of which is also equivalent to two of nitric acid. It is therefore called a *di-acid base.* We shall see later that there are also *di-basic acids.*

(We have observed three ways in which nitric acid forms salt. What are they ?)

The *nitrates* are, almost without exception, soluble in water. They can all be decomposed by heat. The nitrates of the *heavy metals* (copper, iron, lead, &c.,) give off a mixture of oxygen and oxides of nitrogen, when strongly heated. The nitrates of the *alkali metals* (sodium, potassium, &c.,) decompose slowly only at a bright red heat, giving off one-third of their oxygen and leaving nitrites :

$$KNO_3 = KNO_2 + O.$$

The nitrates are used in many operations as oxidising agents. *Gunpowder* is a mixture of potassic nitrate, charcoal, and sulphur (What becomes of the charcoal and sulphur during the explosion ?) Nitrates of barium, calcium, and strontium, are used to prepare coloured fires.

Tests.—Same as in Art. 81, but add *sulphuric acid* in (1) and (2). (Why ?) Try these tests with solution of saltpetre.

83. **Salts.**—The general nature of acids and bases can now be seen. They are opposite in properties, and, when brought together, tend to *neutralise* each other, i.e., destroy each other's distinctive properties. But only the stronger acids and bases do this completely. The substances formed when acids and bases act on each other

are mostly like common salt in their properties, and are thence called *salts*. Their relation in composition to the acids and bases from which they are formed can be best shown as follows :—

$H.NO_3$,	nitr*ic* acid.
$K.NO_3$,	potassic nitr*ate*.
$Na.NO_3$,	sodic "
$Pb(NO_3)_2$,	plumbic "
$Bi(NO_3)_3$,	bismuthic "
NH_4NO_3,	ammonic "

$K.OH$	potassic	hydroxide.
$K.NO_3$	"	nitrate.
$Na.OH$	sodic	hydroxide.
$Na.NO_3$	"	nitrate.
$Pb(OH)_2$	plumbic	hydroxide.
$Pb(NO_3)_2$	"	nitrate.
$Bi(OH)_3$	bismuth	hydroxide.
$Bi(NO_3)_3$	"	nitrate.

An inspection of these two lists shows that the nitrates differ from nitric acid by having *metal instead of hydrogen*, and from the bases by having NO_3 instead of OH (hydroxyl). Salts may be regarded as made up of two parts, *metal, and salt-radical.* The salt radical of the nitrates is then $—NO_3$, and we write the formula of any nitrate by adding to the symbol of the metal *n* times NO_3, *n* being the valence of the metal. Thus, for monad metals put NO_3 once; for dyads, NO_3 twice, and so on.

Names of salts are formed from the names of the metals (as adjectives), and those of the acids (as nouns). The syllabic *-ic* is generally added to the root of the name of the metal. In case the metal forms two bases, the salt of that containing the greater relative quantity of metal is distinguished by the ending *-ous.*[*] Thus, *ferrous nitrate*, $Fe(NO_3)_2$; and *ferric nitrate*, $Fe_2(NO_3)_6$. The names of acids generally end in *-ic*, and (with the exception of the *haloid acids* and a few others) this ending is changed to

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[*] Latin *osum*, abounding in.

-ate for the name of the salt. When the name of the acid ends in *-ous*, the name of the salt ends in *-ite*. Thus,

Nitr*ic*	acid	Nitr*ate*.
Sulphur*ic*	“	Sulph*ate*.
Nitr*ous*	“	Nitr*ite*.
Phosphor*ous*	“	Phosph*ite*.

There is a class of acids containing no oxygen, e.g., *hydrochloric acid* (HCl), *hydrobromic acid* (HBr), &c. The salts of these acids are called chlor*ides*, brom*ides*, &c. They are named in the same way as *oxides* and *sulphides*.

84. **Oxides of Nitrogen.**—Nitrogen and oxygen do not readily combine; but by indirect methods 5 compounds can be obtained. If electric sparks be passed through dry air, a red gas, *nitrogen tetroxide* (NO_2), appears, and this in presence of water and oxygen forms nitric acid. It is probable that considerable quantities of nitric and nitrous acids are formed in the atmosphere by lightning. The five oxides are as follows :—

Nitrogen monoxide	N_2O
“ dioxide	NO.
“ trioxide	N_2O_3.
“ tetroxide	NO_2 or N_2O_4.
“ pentoxide	N_2O_5.

If the formula of the second be doubled it will be easily seen that the proportion of oxygen increases regularly from 1 to 5. This is a good illustration of the Law of Multiple Proportions. (Apply it.)

85. **Nitrogen Monoxide** (N_2O)—Also called *laughing gas*, and *nitrous oxide*.

PREPARATION.—**Experiment 53.**—Dry some ammonic nitrate (Exp't 51) by fusing it in a porcelain dish. Break the dried salt into small lumps and heat some of it in a test-tube provided with a gas-delivery tube. The salt melts easily to a clear liquid, and a continuous stream of gas comes off. Collect 6 jars of the gas over *warm* water, and try its action on a glowing match and on burning phosphorus.

PROPERTIES.—Colourless gas, of ethereal smell and sweetish taste. (Try it.) (Calculate its specific weight.) At 0° C. it becomes liquid under a pressure of about 30 atmospheres. It is soluble in water to the extent of about $1\frac{1}{3}$ vols. in 1 of water (at 0° C.). (Try solubility in cold water.) It supports ordinary combustion better than air does. (Compare the percentages of oxygen in air and nitrogen monoxide). The whole of the oxygen is easily separated from the nitrogen by carbon, phosphorus, &c.:

$$C + 2N_2O = 2N_2 + CO_2$$
$$2P + 5N_2O = 5N_2 + P_2O_5.$$

(Translate these equations into ordinary language).

Experiment 54.—Set fire to a little sulphur in a deflagrating spoon, and *at once* plunge into a jar of nitrogen monoxide. The flame is extinguished. Light it again, and let it burn vigorously before putting it into the gas.

Nitrogen monoxide extinguishes a weak flame of sulphur, because the temperature is not high enough to *start* the action. Sulphur burning well in air, burns more brightly in nitrogen monoxide. The substances formed are *nitrogen* and *sulphur dioxide* (SO_2). (Write the equation.)

When breathed, nitrogen monoxide causes at first a peculiar intoxication with insensibility to pain. If mixed with about one-fifth of its volume of air it can be breathed for some time; but, as it diffuses into the blood, and cannot supply oxygen to the blood, symptoms of suffocation at length appear. When prepared for inhalation, it should be freed from acid fumes and nitrogen dioxide by bubbling it through solutions of caustic soda and ferrous sulphate.—Salts of an acid, *hyponitrous*, corresponding to this oxide, are known; e.g., KNO, *pot. hyponitrite.*

86. Nitrogen Dioxide.—NO. (Nitric Oxide).

PREPARATION—**Experiment 55.**—Mix 1 part strong nitric acid with 3 of water in a t. t. or flask, and add some scraps of copper. Heat gently and collect six jars of the gas over water

Other metals, as mercury, silver, iron, lead, &c., may be used. Nitrogen and the monoxide are always present as impurities.

PROPERTIES.—An invisible gas, a little heavier than air. (Calculate specific weight.) Smell and taste not known. (Why?) It can be condensed to a liquid at — 11° C. by a pressure of 104 atmospheres. It is the most stable of all the oxides of nitrogen. It is very sparingly soluble in water.

Experiment 56.—Set fire to a bit of phosphorus and plunge it *quickly* into a jar of the gas. It is extinguished. Try again, allowing the phosphorus to burn brightly before putting it in the gas. Try a lighted match, and sulphur burning strongly. They are both put out.

Experiment 57.—Pass up a little oxygen into a jar of the gas over water; red fumes appear and then disappear, the volume of gas being lessened:

$$NO + O = NO_2$$
$$3\,NO_2 + H_2O = 2HNO_3 + NO.$$

Nitrogen dioxide supports only very vigorous combustion. It combines with oxygen to form nitrogen tetroxide (NO_2). (What takes place on contact with air?)

Experiment 58.—Pour some solution of green vitriol into a jar of the gas, close, and shake up. The gas dissolves, giving a dark brown colour to the solution. A weak compound ($2FeSO_4 . NO$) is formed. This can be decomposed by heat, giving pure nitrogen dioxide. (In what former experiment was this compound obtained?)

In writing the graphic formula of nitrogen dioxide, either the nitrogen must be represented as dyad, $N=O$, or one *atomic bond* must be left unemployed, $-N=O$. In either case the compound seems anomalous. Other cases of this kind warn us that the idea of valence is one to be used cautiously, however convenient ordinarily.

87. **Nitrogen Trioxide.**—N_2O_3.

It is also called *anhydrous nitrous acid.*

PREPARATON.—Late experiments seem to show that this substance does not exist at ordinary temperatures, but decomposes above − 18° C. It can be prepared by mixing nitrogen dioxide with one-fourth its volume of oxygen, and cooling to − 20° C.

Experiment 59.—Heat a little starch with some nitric acid diluted with about one volume of water. Red vapours are evolved, said to be nitrogen trioxide. If these are cooled below − 18° C. they form a deep blue liquid.

PROPERTIES.—Nitrogen trioxide is a blue liquid which decomposes at − 18° C. into the dioxide and tetroxide:

$$N_2O_3 = NO + NO_2.$$

Experiment 60.—Repeat Experiment 59 on a larger scale and lead the red gas into a t. t. containing water and surrounded by ice and salt. A blue solution is formed, having *acid* properties. Add some caustic soda solution to this. The colour disappears. Evaporate on the water bath, and keep the remaining salt, *sodic nitrite.*

88. **Nitrous Acid.**—HNO_2. This is the blue solution of Experiment 60. It has not been obtained pure, and is easily decomposed. Its relation to nitrogen trioxide is seen thus:

$$N_2O_3 + H_2O = 2HNO_2.$$

It is a monobasic acid, and forms salts called *nitrites.* The "nitrous acid" of pharmacy is impure nitric acid.

NITRITES.—The nitrites are nearly all soluble in water, and quickly absorb oxygen to form nitrates :—$KNO_2 + O = KNO_3$. Nitrites are produced by the decomposition of animal matter, and their presence in water is an indication of pollution.

Tests.—1. Put a few drops of dilute sulphuric acid on a little of the salt from Expt. 60. Red fumes are evolved :

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + N_2O_3\ (?) + H_2O.$$

2. Add a little potassic iodide and starch paste to a solution of sodic nitrite; to this add a few drops of dilute sulphuric acid. The deep blue of *iodide of starch* appears.

3. Add a little potassic permanganate ($KMnO_4$) to solution of any nitrite; then some acetic acid. The colour of the permanganate dissappears. It is *reduced* by the nitrous acid. Try the acetic acid without the nitrite.

89. **Nitrogen Tetroxide**, NO_2 or N_2O_4.—This is also called *peroxide of nitrogen.*

PREPARATION.—**Experiment 61.**—Dry some plumbic nitrate (Expt. 52) by gently heating in a porcelain dish ; transfer to a hard-glass t. t. and heat gradually. Receive the red gas in a t. t. surrounded by a freezing mixture of snow and salt :

$$Pb(NO_3)_2 = PbO + N_2O_4 + O.$$

(What is the substance left in the t. t.? How can it be again converted into lead nitrate?) Nitrogen tetroxide can also be prepared by cooling a mixture of nitrogen dioxide and half its volume of oxygen : $NO + O = NO_2$.

PROPERTIES.—A colourless liquid at low temperatures, a reddish brown gas above 22° C., its boiling point. With cold water it forms nitric and nitrous acids : $N_2O_4 + H_2O = HNO_3 + HNO_2$. Similarly, with caustic soda or caustic potash it forms nitrate and nitrite (and water). (Write equations). It is irritating when breathed, and injures the mucous membranes of the respiratory passages.

90. **Nitrogen Pentoxide.** — N_2O_5. Also called *anhydrous nitric acid.*

PREPARATION.—By passing dry chlorine gas through a tube containing dry silver nitrate heated to 50° C.; or by distilling pure nitric acid with phosphorus pentoxide:

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$

PROPERTIES.—A white crystalline solid, beginning to decompose at 40° C. into tetroxide and oxygen. (Write the equation.) It is very hygroscopic, and rapidly deliquesces in moist air. It unites with water forming nitric acid :

$$N_2O_5 + H_2O = 2HNO_3.$$

QUESTIONS AND EXERCISES.

1. Calculate the weights of 1 litre of nitrogen and of ammonia, measured at 0° and 760.

2. Calculate the volume of air to give 20 litres of nitrogen.

3. What weight of ammonic chloride is required to give 5 litres of ammonia gas measured at 17° C. and 700 mm. pressure?

4. Calculate the volume of ammonia gas at 20° C. and 760 mm. formed by heating 100 grams ammonic chloride with lime.

5. Hold the moist stoppers of the ammonia and hydrochloric acid bottles near each other. Explain what you observe.

6. Warm some ammonic chloride solution with sodic hydroxide solution. Observe the smell. What substances have been formed? Write the equation.

7. In determining the composition of ammonia (Art. 80), how can the hydrogen be got rid of in order to measure the volume of nitrogen?

8. What weight of sodic nitrate ($NaNO_3$) is required to prepare 200 grams of nitric acid? How much sulphuric acid is used?

9. How much nitric acid can be obtained by the decomposition of 10 lbs. of saltpetre?

10. Lime water is an antidote to poisoning by nitric acid. Explain its action.

11. Calculate the weights of nitric acid required to neutralise 10 grams each of the following bases and oxides :—Sodic hydroxide ($NaOH$), potassic hydroxide (KOH), calcic hydroxide ($Ca(OH)_2$), magnesia (MgO), and litharge (PbO).

12. Write the formulas for nitrates of the following metals, referring to the table of elements for the valences:—Calcium, silver, iron, mercury, copper, cobalt, barium, magnesium, and aluminium.

13. What experiments already made illustrate the direct replacement of hydrogen by metals ?

14. How many litres of nitrogen monoxide, measured at 15° C. and 730 mm. pressure, can be prepared from 100 grams ammonic nitrate ? What weight of water is formed ? What volume will it occupy at 200° C. and 760 mm. pressure ?

15. How much ammonic nitrate must be used to fill a 10 gallon receiver with nitrous oxide under a pressure of 60 lbs. to the square inch when the thermometer reads 10° C. ?

16. What volume of nitrogen monoxide at 16° C. and 750 mm. will completely burn 1 gram carbon ?

$$C + 2N_2O = 2N_2 + CO_2.$$

17. What volume of air will convert 10 cubic inches of nitrogen dioxide into the tetroxide ?

CHAPTER IX.

THE HALOGENS.

91. **Sea Water.**—Sea water is a dilute solution o salts, some in much larger proportions than others. Th total quantity in 100 parts is about 3.5. The specifi weight of sea water at 0° C. is 1.03. *Common sal* (NaCl) is present in the greatest proportion ; next com *magnesic chloride* ($MgCl_2$), *magnesic sulphate* ($MgSO_4$) *calcic sulphate* ($CaSO_4$), *potassic chloride* (KCl), an *magnesic bromide* ($MgBr_2$). The bitter taste is due t the magnesic salts. *Magnesic iodide* (MgI_2) is presen in sea water in very minute quantity.

When sea water is evaporated, the sparingly solubl gypsum ($CaSO_4.2H_2O$) first crystallises out, and later *sodic chloride.* This latter salt is a compound of th metal *sodium* with a non-metal, *chlorine,* which i therefore called a *halogen,* or “salt generator.” Th “mother liquor,” an intensely bitter liquid (*bittern*) contains compounds of two elements very similar t chlorine, viz., *bromine* and *iodine*; and these three with a fourth, form the group of *halogens,* whic are peculiar among the elements, as *forming wit the metals salts which contain no third element,* e.g. NaCl, KBr, MgI_2, CaF_2, &c. (Compare with KNO_3 Na_2SO_4, &c.) Sea water is the principal source of th first three of the halogens.—(In the following section note resemblances and differences among the halogens.)

CHLORINE AND ITS COMPOUNDS.

92. **Chlorine.**—($Cl' = 35.37$). Very widely diffused in water and on land; never free, but in combination as chlorides.

PREPARATION.—**Experiment 62.***—Put a little sodic chloride mixed with manganese dioxide (MnO_2) in a t.t., pour some sulphuric acid in, and heat gently. Chlorine gas is set free. Note colour and smell (*cautiously*).

This chemical action is most clearly represented in three steps:

(1) $H_2SO_4 + NaCl = NaHSO_4 + HCl$.

(2) $MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$.

(3) $2HCl + O = H_2O + Cl_2$.

The substances ultimately formed are *sodic hydric sulphate* ($NaHSO_4$), *manganous sulphate* ($MnSO_4$), *chlorine*, and *water*. (Write a single equation representing the action. You know the formulas of all the substances. Remember that the equation must balance.)

Experiment 63.*—Heat gently a little manganese dioxide and *hydrochloric acid* in a test-tube. Chlorine is given off:

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O.$$

This is the method by which chlorine is generally prepared on the large scale.

Experiment 64.*—Warm a little hydrochloric acid with a small crystal of potassic chlorate ($KClO_3$), and note the evolution of chlorine: $KClO_3 + 6HCl = KCl + 3Cl_2 + 3H_2O$.

All these and similar methods may be considered as so many ways of oxidising hydrochloric acid:

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* Fill the test-tube with dilute caustic soda when the experiment is finished.

$$2HCl + O = H_2O + Cl_2,$$

and, indeed, chlorine is prepared on the large scale by passing a mixture of air and hydrochloric acid over hot bricks.

PROPERTIES.—A heavy, greenish yellow gas; is liquid at 0° under a pressure of six atmospheres; causes suffocation when breathed; has violent irritating action on mucous membranes, and may cause catarrh or ulceration; soluble in water, 3 vols. in 1 at 10° C.; the aqueous solution acts as a powerful irritant both externally and internally; antidotes are white of egg, milk, ammonia, lime water, soap, and other alkaline substances. Chlorine, both as gas and solution, is a powerful antiseptic and deodoriser; it is an antidote to poisoning by prussic acid (HCN), sulphuretted hydrogen (H_2S), and ammonic sulphide ($(NH_4)_2S$). The action on prussic acid has not been explained; that on sulphuretted hydrogen and ammonic sulphide is explained by the following equations:

$$H_2S + Cl_2 = 2HCl + S$$

$$(NH_4)_2S + 4Cl_2 = 8HCl + N_2 + S.$$

The substances formed are not poisonous.

Experiment 65.—Prepare a little chlorine as in Experiment 63, and hang a narrow strip of moist turkey-red cloth in the t.t. It is bleached white. Try other vegetable colours, e.g., a small flower. Try a mineral colour, e.g., red lead.

Chlorine and water bleach organic colouring matters, but not mineral. The presence of water is necessary. If dry chlorine be used, it does not bleach. A solution of chlorine in water gradually decomposes:

$$H_2O + Cl_2 = 2HCl + O.$$

This shows the nature of the bleaching action of chlorine. It is really an oxidation by means of the oxygen of water, the hydrogen combining with chlorine to form hydrochloric acid. The colouring matter is destroyed,—generally oxidised to carbon dioxide and water.

Experiment 66.—Prepare some *chlorine water*, by leading the gas prepared as in Experiment 63 into a bottle of water, using a gas-delivery tube bent twice at right angles and reaching to the bottom of the bottle. (This should be done under a hood or in a draught cupboard.) Note the colour of the solution. Try its effect on litmus. Explain.

Chlorine combines directly with most elements and thereby forms *chlorides*.

Experiment 67.—Prepare a little chlorine (Experiment 63) and drop some powdered *antimony* into the tube. It catches fire as soon as it falls into the gas: $Sb + 5Cl = SbCl_5$. Try a bit of phosphorus in the deflagrating spoon; and a lighted taper.

Chlorine supports the combustion of tallow, wax, turpentine, and other organic substances containing a large percentage of hydrogen. It combines with the hydrogen to form hydrochloric acid, setting the carbon free.

Test.—Add some starch paste to a dilute solution of potassic iodide (KI), and then a few drops of chlorine water. The deep blue iodide of starch is formed: $KI + Cl = KCl + I$.

Compounds of Chlorine.

93. **Hydrochloric Acid** ($HCl = 36.37$.)—Also called *muriatic acid*, and *spirit of salt*. If equal volumes of hydrogen and chlorine be mixed in the dark and then exposed to diffused daylight they combine without any

change of volume, forming a colourless gas, hydrochloric acid. If exposed to direct sunlight they combine with a violent explosion.

PREPARATION.—**Experiment 68.**—Put some dry sodic chloride in a t.t., pour strong sulphuric acid over it, fit the gas-delivery tube used in Experiment 66, warm gently, and collect a t. t. of the gas by displacing the air. (You can see when the t. t. is full by the fuming of the gas at the top; and by its overflowing on the fingers and making them feel warm.) Close with the thumb and open under water. Test, by taste and litmus, the water which rises in the tube.

Solution of hydrochloric acid is prepared in this way on the large scale as a by-product of the alkali manufacture:

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

(Write the names and weights. What remains in the t. t. in Experiment 68?)

PROPERTIES.—A colourless gas, soluble in water, 500 vols. in 1 at 0° C.; the solution is heavier than water. The saturated solution becomes weaker on boiling until it contains $20\frac{1}{4}$ p. c. of the acid, then distils unchanged at 110° C. The specific weight of this solution is 1.11. (What similar case has been studied already?) The specific weight of the gas is 1.269 (air = 1). At — 4° C. and with a pressure of 25 atmospheres it condenses to a colourless liquid.

Experiment 69.—Colour some solution of hydrochloric acid with litmus, and add to it a solution of caustic soda until the litmus begins to turn blue. Taste the solution. (What does it taste of?) Evaporate to dryness on the water bath. Crystals of common salt remain: $NaOH + HCl = NaCl + H_2O$. Try the same with potassic hydroxide.

Hydrochloric acid is a monobasic acid, as can be seen from its formula. Its molecule contains only *one* atom of hydrogen, which cannot be partially replaced by atoms of metals. It is called a *haloid acid* Its aqueous solution dissolves tin, iron, zinc, aluminium, and other metals.

CHLORIDES.—These are formed by replacing the hydrogen of the acid by metals, a monad replacing H, a dyad 2H, a triad 3H, &c. (Write the formulas for chlorides of silver, mercury, lead, copper, nickel, antimony, and tin.)

Experiment 70.—Drop a little hydrochloric acid solution into solutions of argentic nitrate ($AgNO_3$), mercurous nitrate ($Hg_2(NO_3)_2$), and plumbic acetate ($Pb(C_2H_3O_2)_2$). Precipitates are formed. Note any differences in their appearance.

Mercurous chloride, and the chlorides of silver and lead are insoluble in water (plumbic chloride, *sparingly* soluble); the chlorides of the other metals are soluble (but a few are decomposed on contact with water).

$$AgNO_3 + HCl = AgCl + HNO_3.$$

The silver and hydrogen atoms exchange places. (Write equations for the other two.)

Hydrochloric acid is irritating when breathed as a gas. The strong solution is a corrosive poison. (Alkaline substances are antidotes; magnesia, lime water, or soap may be used.) A very dilute solution is a tonic. Hydrochloric acid is secreted into the stomach during digestion, in which it plays an important part.

Tests.—Add a few drops of argentic nitrate ($AgNO_3$). A curdy white precipitate ($AgCl$) is formed, insoluble in nitric acid, soluble in ammonia solution. (Try with solution of hydrochloric acid, and also with a chloride.)

94. **Oxides of Chlorine.**—Chlorine and oxygen do not unite directly, but by indirect methods three compounds can be obtained, viz., chlorine monoxide, Cl_2O; trioxide, Cl_2O_3; and tetroxide, Cl_2O_4. They are dangerously explosive compounds of little importance.

95. **Chlorine Monoxide.**—Cl_2O. A yellow gas prepared by the action of dry chlorine on dry mercuric oxide:

$$2HgO + 2Cl_2 = HgCl_2.HgO + Cl_2O.$$

It dissolves in water forming *hypochlorous acid*:

$$Cl_2O + H_2O = 2HClO.$$

96. **Chlorine Trioxide.**—Cl_2O_3. A greenish yellow gas, of irritating action when breathed, dangerously explosive. Prepared by warming a mixture of nitric acid, potassic chlorate, and sugar: $2HClO_3 + N_2O_3 = Cl_2O_3 + 2HNO_3$. It dissolves in water forming *chlorous acid*:

$$Cl_2O_3 + H_2O = 2HClO_2.$$

97. **Chlorine Tetroxide.**—Cl_2O_4. Also called *peroxide of chlorine.* It is a yellow gas of not unpleasant odour. Very explosive when heated.

Experiment 71.—Put a small crystal of potassic chlorate in a t.t., held by the t.t. holder or a pair of forceps. Add a few drops of strong sulphuric acid, and heat gently, taking care that the mouth of the t.t. is directed away from everybody. The gas is evolved and quickly explodes with violence:

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + Cl_2O_4 + H_2O.$$

It dissolves in a caustic potash solution forming *chlorite* and *chlorate*. (What substance already studied is similar?):

$$Cl_2O_4 + 2KOH = KClO_2 + KClO_3 + H_2O.$$

98. **Oxygen Acids of Chlorine.**—Like nitrogen chlorine combines with hydrogen and oxygen in several proportions, forming a series of oxygen acids:

Hypochlorous acid	$HClO$
Chlorous acid	$HClO_2$
Chloric acid	$HClO_3$
Perchloric acid	$HClO_4$

The names of these acids illustrate very well the use of the terminations *-ic* and *-ous*; and of the prefixes *hypo-* and *per-*. *Hypo*chlorous acid is *below* chlorous acid in proportion of oxygen. *Per*chloric contains *more* oxygen than chloric.—These acids are all monobasic, and mostly unstable.

99. Hypochlorous Acid.—HClO.

PREPARATION.—By the action of chlorine water on freshly precipitated mercuric oxide:

$$HgO + H_2O + 2Cl_2 = HgCl_2 + 2HClO.$$

PROPERTIES.—It has never been obtained except as a dilute aqueous solution. It has a pleasant, somewhat chlorous, smell (that of bleaching powder), and bleaches powerfully.

HYPOCHLORITES.—The salts of hypochlorous acid are important, particularly *bleaching powder*:

$$(CaCl_2 \,.\, Ca(OCl)_2).$$

Experiment 72.—Generate some chlorine as in Experiment 62, and pass it for a short time into a beaker containing a very dilute solution of sodic hydroxide :

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O.$$

Sodic chloride, sodic hypochlorite, and water are formed. Keep the solution for further experiments.

Experiment 73.—Moisten a small piece of turkey-red cloth with acetic acid, and put it into a portion of the solution from Experiment 72. The colour is bleached.

Experiment 74.—Heat another portion of the solution nearly to boiling, and then try Experiment 73 with it. The colour is not bleached.

Hypochlorites are readily decomposed by heat into *chlorides* and *chlorates*, one portion giving up its oxygen to the other :

$$3KClO = KClO_3 + 2KCl.$$

Experiment 75.—Warm a third portion gently with a little hydrochloric acid and note the smell of chlorine :

$$KClO + HCl = HClO + KCl$$
$$HClO + HCl = Cl_2 + H_2O.$$

Hypochlorous acid is a very weak acid, its salts being decomposed even by carbonic acid. Hence the chlorous smell of bleaching powder. (Explain).

100. **Chlorous Acid.**—$HClO_2$. Cannot be obtained except as a solution in water (Art. 96). Its salts, the chlorites, are unstable and unimportant.

101. **Chloric Acid.**—$HClO_3$. There is no corresponding oxide known. (What would its formula be ? Compare with nitric acid.)

PREPARATION.—By action of *fluosilicic acid* on solution of potassic chlorate. An insoluble salt of potassium is formed (*precipitated*), and chloric acid remains in solution:

$$2KClO_3 + H_2SiF_6 = K_2SiF_6 + 2HClO_3.$$

PROPERTIES.—It forms a colourless, acid solution, of strong oxidising properties. It readily decomposes into chlorine, oxygen, and perchloric acid, and cannot be obtained free from water.

CHLORATES.—Chloric acid is monobasic, and its salts are all soluble in water. They can be prepared by dissolving the corresponding bases in chloric acid; but those of the stronger bases can be formed directly by the action of chlorine. Thus, when chlorine gas is passed into a *hot* solution of potassic hydroxide, chloride and chlorate are formed (Exp't 74):

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

Similarly with sodic, calcic, baric, and other hydroxides. The weaker bases, however, do not react in this way. Potassic chlorate is only sparingly soluble, and can thus be separated from the more soluble chloride. (How?)

Experiment 76.—Pass chlorine gas through a strong solution of caustic potash until it begins to smell of chlorine. Evaporate on the water bath until crystals begin to form, then set aside to cool. Pour off the liquor, dry the crystals on filter paper and keep them.

Tests.—1. Dry chlorates are known by the formation of chlorine tetroxide when acted on by strong sulphuric acid.

2. Colour with indigo sulphate, add a few drops of sulphuric acid, and boil. The colour disappears. (What other acid answers to this test? How would you distinguish?)

102. **Perchloric Acid.**—$HClO_4$. This is the most stable of all the oxygen acids of chlorine.

PREPARATION.—By distilling chloric acid :

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O.$$

Also, by the action of fluosilicic acid on solution of *potassic perchlorate* :

$$2KClO_4 + H_2SiF_6 = K_2SiF_6 + 2HClO_4.$$

(How are the two substances separated ?)

PROPERTIES.—It is a strong acid, of very great oxidising power, exploding violently when dropped on charcoal. It sets fire to wood, paper, &c. The acid and its salts are unimportant practically.

PERCHLORATES.—Potassic perchlorate is prepared by heating potassic chlorate until it fuses and at length becomes nearly solid again :

$$2KClO_3 = KClO_4 + O_2 + KCl.$$

(How can the two salts formed be separated ?)

BROMINE AND ITS COMPOUNDS.

103. **Bromine.**—($Br' = 79.75$.) Found as *bromides* in sea water, salt springs, and crude Chili saltpetre ; also as silver bromide (AgBr) in some silver mines. Certain sea-weeds extract bromine and iodine from sea water and store it up in their tissues. These two elements are prepared generally in one operation from the "mother liquor" of common salt, kelp (ashes of sea-weed), or Chili saltpetre.

PREPARATON.—A small sample of the liquor is first analysed and the quantities of iodine and bromine determined. Then enough manganese dioxide and sulphuric acid to set free the whole of the iodine is added to a large quantity of liquor: $2KI + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + I_2 + 2H_2O$. The iodine is distilled off, more manganese dioxide and sulphuric acid are added to set free the bromine, which is then distilled and condensed in separate receivers: $2KBr + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + Br_2 + 2H_2O$.

Experiment 77.—Mix about equal quantities of well powdered manganese dioxide and potassic bromide, put in a t.t., add a little sulphuric acid, and heat gently. Bromine is evolved, condensing on the sides of the t.t. as a dark reddish-brown liquid. Take care not to breathe the vapour. Pour some of the heavy vapour into a second t.t. containing a little water, and shake it up. The water dissolves the bromine.

PROPERTIES.—A heavy liquid (specific weight = 3.18), almost black when in mass; dark red, in thin layers. It is the only liquid element at ordinary temperature, excepting mercury. It freezes at — 22° C., and boils at 63° C., forming a reddish-brown vapour, which has a very unpleasant smell and an irritating action on the mucous membranes. On account of its low boiling point and corrosive action bromine should be handled very carefully. Its vapour should never be inhaled unless diluted with much air.

Experiment 78.—Try to bleach with *bromine water* made in Experiment 77.

Bromine is soluble in water to about 3%. It bleaches in the same manner as chlorine, but not so powerfully.

Experiment 79.—Dissolve a small crystal of potassic bromide (KBr) in a test-tube one-third full of water, and add a few drops of chlorine water. Bromine is set free. Add a few drops of carbon bisulphide, close with the thumb and shake the t.t. violently. Allow to stand a moment and observe. (What property of bromine is illustrated?)

Chlorine displaces bromine from combination with metals; in other words chlorine has greater chemical affinity (chemism) for the metals.

COMPOUNDS OF BROMINE.

104. Hydrobromic Acid.—HBr.

Preparation.—**Experiment 80.**—Add a few drops of strong sulphuric acid to a crystal of potassic bromide and warm. (What action would you expect? What do you observe?) Hydrobromic acid cannot be prepared in this way because of its decomposition by strong sulphuric acid:

$$H_2SO_4 + 2HBr = Br_2 + SO_2 + 2H_2O.$$

Compare hydrochloric acid.

Hydrobromic acid is prepared by the action of phosphorus and bromine on water. A bromide of phosphorus is first formed and this is then decomposed by the water:

$$\overset{\text{P. tribromide.}}{PBr_3} + 3H_2O = 3HBr + \overset{\text{Phosphorous acid.}}{P(OH)_3}.$$

To prepare it on the small scale, put a little bromine in the bottom of a t.t, then a layer of pieces of glass on which a few small bits of phosphorus are laid, cover this with an inch or two of small bits of glass, moisten with a drop or two of water, and distil with a gentle heat, receiving in a t.t. of water. A solution of hydrobromic acid is obtained.

Properties.—A heavy, fuming gas, very soluble in water, forming a solution similar to that of hydrochloric acid. It is a monobasic acid, and acts on bases to form salts called *bromides.*

BROMIDES.—These are very like the chlorides in appearance and properties. Bromine unites directly with nearly all metals. The bromides can all be decomposed by chlorine. The potassium salt (KBr) is the most important. It is much used in medicine. *Argentic bromide* ($AgBr$) is used in photography. *Ammonic bromide* (NH_4Br) is used as a medicine. Most of the bromides are soluble in water. A few are insoluble.

Experiment 81.—To a few drops of solution of potassic bromide add a drop of argentic nitrate. Argentic bromide is precipitated:

$$AgNO_3 + KBr = KNO_3 + AgBr.$$

Note its colour and try the action of ammonia solution and of nitric acid on it (dividing it into two portions). Make the same experiment with solutions of mercurous nitrate ($Hg_2(NO_3)_2$), and plumbic acetate ($Pb(C_2H_3O_2)_2$), instead of argentic nitrate. Write the equations.

Tests for Bromides.—Experiments 79 and 81. In the test with chlorine care must be taken not to use too much, as there is a colourless chloride of bromine. Except in weak solutions the bromine can be liberated by strong sulphuric acid. (Try it.) Free bromine colours starch-paste orange-yellow.

105. **Bromine and Oxygen.**—No compounds of bromine and oxygen are known, but two oxygen acids, *hypobromous* ($HBrO$), and *bromic* ($HBrO_3$), have been prepared. They and their salts (the hypobromites and bromates) are prepared by methods similar to those for the hypochlorites and chlorates. *Potassic hypobromite* ($KBrO$) is used in estimating *urea.* (Write equations

for the action of bromine on moist mercuric oxide, and on dilute and strong solutions of potassic hydroxide).

IODINE AND ITS COMPOUNDS.

106. **Iodine.**—($I' = 126.5$). Never found free in nature, but always as *iodides*, in small relative quantities, but widely diffused. Minute traces of iodides are present in sea-water. Certain plants (kelp and sponges) extract these and store them in their tissues. Some sea animals do the same, e.g., the cod. The ashes of kelp contain from 0.1 per cent. to 0.3 per cent. of iodine, and are the principal source of this element. The weed is washed up on the coasts of Ireland and Scotland in great quantities. It is gathered, dried, burned in shallow pits at a temperature not high enough to volatilise the iodides and bromides, and then lixiviated. The solution contains sodic carbonate (Na_2CO_3), chloride ($NaCl$), sulphate (Na_2SO_4), bromide ($NaBr$), iodide (NaI), &c. It is evaporated to crystallise the carbonate, chloride, and sulphate; and the iodine and bromine are prepared as described in Art. 103.

PREPARATION.—**Experiment 82.**—Mix well about equal quantities of *potassic iodide* (KI) and manganese dioxide, put in a t.t., add a little strong sulphuric acid, and heat very slightly for a few minutes. Violet vapour of iodine appears and condenses on the cooler parts of the tube, as a steely looking solid.

$$2KI + 3H_2SO_4 + MnO_2 = MnSO_4 + 2KHSO_4 + I_2 + 2H_2O.$$

PROPERTIES.—Blackish grey solid, somewhat *metallic* in appearance (compare *sulphur*, *selenium*, and *tellurium*), opaque and crystalline. Its odour suggests that of rotting sea-weed. The specific weight of the solid is 4.948 (calculate that of the gas). It melts at 114° C., and boils at 200° C., forming a splendid deep-blue vapour, which is purple when mixed with air. It volatilises slowly at ordinary temperatures and must therefore be kept in well stoppered bottles. Both iodine and bromine (as well as chlorine) corrode cork.

Experiment 83.—Put a few crystals of iodine in a t.t., fill half-full of water, shake for some time, and note that a little of the iodine dissolves. Add a small quantity of potassic iodide, and shake up. The whole of the iodine dissolves. A *tri-iodide* (KI_3) is formed.

Iodine is sparingly soluble in water, but freely so in solutions of certain salts, particularly potassic iodide.

Experiment 84.—To solution of potassic iodide in two test-tubes add respectively chlorine water and bromine water, then a few drops of carbon bisulphide (CS_2); shake well and allow to stand a moment. (What conclusions do you draw with regard to the relative *chemism* of the three halogens?)

Experiment 85.—Try the solubility of iodine in a mixture of equal volumes of alcohol and water, and in chloroform, using small quantities of each of the substances mentioned.

Iodine has an irritating action on the skin and mucous membranes, but not so violent as chlorine and bromine. It stains the skin yellow, but the stain disappears very soon, unless the iodine is applied often. It promotes absorption and thus reduces swellings, and is much used as an external application.

TINCTURE OF IODINE is a solution of iodine and potassic iodide in *rectified spirit* (alcohol and water)—1 pint of spirit to ½ oz. iodine and ¼ oz. potassic iodide.

SOLUTION OF IODINE.—Twenty grains of iodine, thirty grains of potassic iodide, dissolved in 1 oz. of distilled water.

Tests.—1. With chlorine water and carbon bisulphide as in Experiment 84.

2. Free iodine colours starch paste deep blue. (Try with *iodine water*).

COMPOUNDS OF IODINE.

107. Hydriodic Acid, HI.—

PREPARATION.—In the same way as hydrobromic acid (Art. 104). (Write the equation.) Hydrogen and iodine do not unite directly under ordinary circumstances.

It can also be prepared in solution by the action of iodine on sulphuretted hydrogen (H_2S) in presence of water.

Experiment 86.—Put a few small pieces of ferrous sulphide in a t.t. fitted with the gas-delivery tube of Experiment 66, add some sulphuric acid diluted with about five times its volume of water, and pass the evolved gas into a test-tube of water in which is some finely divided iodine. The iodine disappears and sulphur is precipitated :

$$H_2S + I_2 = 2HI + S.$$

Test a portion of the solution with litmus, add a little iodine water, shake up, and set aside for further experiments.

PROPERTIES.—A heavy gas (specific weight 4.416), colourless, fuming in moist air owing to its strong attraction for water, with which it forms minute drops of solution. It dissolves readily in water, forming a strongly acid solution similar to those of hydrochloric and hydrobromic acids. The gas is easily decomposed by heat, and the solution in water is decomposed by the oxygen of the air :

$$2HI + O = H_2O + I_2.$$

(Compare with the stability of hydrochloric acid.) It is a monobasic acid and unites with bases to form *iodides*, e.g.:

$$KOH + HI = KI + H_2O.$$

Iodides.—Of these the most important is potassic iodide (KI), of which very large quantities are used in medicine. The following iodides are insoluble in water and are bright in colour: *Argentic* (AgI), *mercurous* (Hg_2I_2), *mercuric* (HgI_2), *cuprous* (Cu_2I_2), and *plumbic* (PbI_2), the latter very sparingly soluble.

Experiment 87.—Put a little of the solution of hydriodic acid in four test tubes, and add a drop or two of argentic nitrate to one, of mercurous nitrate to a second, of mercuric chloride ($HgCl_2$) to a third, and of plumbic acetate to a fourth. Note the color, &c., of the precipitates formed :

$$AgNO_3 + HI = AgI + HNO_3.$$

Write equations for the other three. Try the same experiments with a dilute solution of potassic iodide (KI).

Tests.—These apply to both free acid and iodides.

1. Add to the solution a few drops of argentic nitrate solution. A yellow precipitate of argentic iodide is formed. Divide this into two portions. Test one part with ammonia solution ; it is whitened, but not dissolved. Test the other with nitric acid ; it is not dissolved.

2. Add some starch paste and a few drops of chlorine water to any solution containing an iodide. A blue colour appears. (Explain).

To test for chlorides, bromides, and iodides in a mixture—Distil a small portion of the carefully dried mixture with dry powered *potassic bichromate* ($K_2Cr_2O_7$), and strong sulphuric acid. (The apparatus must be dry.) Receive the distillate in a t. t. containing a little water, add caustic soda to it, until the colour of the bromine and iodine disappears. A yellow colour remains, that of sodic chromate. This proves the presence of a chloride in the mixture.—*Explanation*: A volatile compound, *chromic oxychloride* (CrO_2Cl_2), is formed, distils, and forms chromic acid with the water:

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

Dissolve a small quantity of the mixture in water in a t. t., add a few drops of carbon bisulphide, and then chlorine water drop by drop, shaking up after each addition and observing the colour of the carbon bisulphide. The violet of iodine appears first, but disappears on the addition of more chlorine owing to the formation of an almost colourless compound (ICl); afterwards, on the addition of more chlorine, the orange colour of bromine appears.

108. **Iodine and Chlorine.**—Two compounds are known, the *monochloride* (ICl), and the *trichloride* (ICl_3), formed by direct union of the elements. (What, then, is the valence of iodine?)

109. **Iodine and Oxygen.**—Only one compound of these two elements is known, viz., *iodine pentoxide* (I_2O_5), prepared by carefully heating the corresponding acid, *iodic acid* (HIO_3):

$$2HIO_3 = H_2O + I_2O_5.$$

When heated more strongly it decomposes into its elements. It is a deliquescent white solid, and unites with water to form iodic acid.

IODIC ACID, HIO_3.—Can be prepared by oxidising iodine with strong nitric acid, and evaporating the solution to dryness. It is a white crystalline solid, freely soluble in water, forming a strongly acid solution. It is a powerful oxidising agent. When mixed with hydriodic acid, it oxidises the latter, setting free iodine:

$$HIO_3 + 5HI = 3I_2 + 3H_2O.$$

IODATES.—Besides the normal iodates (KIO_3, &c.), there are peculiar acid iodates, e.g., $KIO_3.HIO_3$, and $KIO_3.2HIO_3$.

Tests—Add chlorine water and starch paste to a solution of an iodate. No blue colour appears. (What conclusion do you draw with regard to chemism of iodine and chlorine in oxygen salts?) Now add a little sodic sulphite or sulphurous acid. Blue colour appears: $KIO_3 + 3Na_2SO_3 = KI + 3Na_2SO_4$.

$$KI + Cl = KCl + I.$$

FLUORINE AND ITS COMPOUNDS.

110. **Fluorine** ($F' = 19.1$).—Is not known free, but only through its compounds, the *fluorides*. Many attempts have been made to prepare it, but with no success. It invariably attacks the vessels in which its preparation is attempted. It seems to have even stronger chemical affinities than chlorine.—The chief compounds of fluorine occurring in nature are *fluor spar* or *calcic fluoride* (CaF_2), and *cryolite* ($3NaF.AlF_3$).—Fluorine forms no compound with oxygen, and is the only element of which this is true.

111. Hydrofluoric Acid.—HF.

PREPARATION.—By distilling fluor spar with sulphuric acid in lead or platinum vessels and receiving in water:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4,$$

Glass or porcelain vessels cannot be used, as they are corroded by hydrofluoric acid. The pure acid is very dangerous, and is not often prepared. The aqueous solution is kept in leaden or gutta percha bottles.

PROPERTIES.—A colourless, fuming, acid liquid, boiling at 19.4° C. It is soluble in water, forming a strongly acid solution.

Experiment 88.—Put a little calcic fluoride in a small leaden dish, add some sulphuric acid and cover the dish with a piece of glass which has been coated with paraffin wax through which some word has been scratched with a knife or a pin. Set aside for a while, then warm the wax, and rub it off. The word has been etched into the glass.

Glass contains silica (SiO_2). This is acted on by the hydrofluoric acid with the formation of volatile compounds:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

Hydrofluoric acid is monobasic. It forms salts called fluorides, analogous to chlorides, bromides, and iodides.

FLUORIDES.—These are mostly colourless salts, soluble in water; but *calcic fluoride* (CaF_2), *baric fluoride* (BaF_2), and *strontic fluoride* (SrF_2) are insoluble. The fluorides have a tendency to unite with each other and with hydrofluoric acid forming *double fluorides*, e.g., $3NaF.AlF_3$ and $HF.KF$.

Test.—See Expt. 88.

QUESTIONS AND EXERCISES.

1. Compare the halogens (1) as to their chemism for metals, and (2) as to their chemism for oxygen.

2. What weight of manganese dioxide (MnO_2) must be used to prepare chlorine for the conversion of 10 lbs. of potassic hydroxide (KOH) into chlorate and chloride?

3. Calculate the specific weight of chlorine (air = 1). Calculate the weight of 1 litre at 0° and 760 mm.

4. Why cannot chlorine be collected over mercury or water?

5. What weight of pure hydrochloric acid is there in 1 litre of the solution of sp. wt. 1.11?

6. Compare the bleaching power of chlorine (and water), and hypochlorous acid.

$$\begin{aligned} Cl_2 + H_2O &= 2HCl + O. \\ HClO &= HCl + O. \end{aligned}$$

What weight of chlorine is equivalent to 100 grams of hypochlorous acid?

7. Compare the oxygen compounds of chlorine and of nitrogen.

8. What weight of sodium chloride must be used to prepare chlorine enough to set free the bromine from 100 oz. of potassic bromide (KBr)?

9. What weight of potassic chlorate ($KClO_3$) contains one equivalent (in grams) of oxygen?

10. Write the formulas of *magnesic*, *ammonic*, *ferric*, *cobaltic*, and *mercurous* chlorides; of *mercuric*, *argentic*, and *baric* iodides; and of *ferric* bromide.

11. Fluorine has never been prepared. How then has its atomic weight been determined?

12. Write the formulas of the chlorine acids and calculate the percentage of oxygen in each. Apply the Law of Multiple Proportions.

13. What weight of hydrochloric acid is equivalent to 100 grams sodic hydroxide (NaOH)? To 100 grams potassic hydroxide (KOH)? To 100 grams calcic hydroxide ($Ca(OH)_2$)?

CHAPTER X.

SULPHUR, SELENIUM, AND TELLURIUM.

112. **The Sulphur Group.**—The three elements mentioned here form a group closely related in their chemical and physical properties. Each unites with hydrogen to form a gas analagous to water in formula (H_2S, H_2Se, H_2Te). They unite with oxygen in two proportions (SO_2, SO_3; SeO_2, —; TeO_2, TeO_3); and each has two acids corresponding to the oxides. As in the case of the halogens, there are *gradations* in the properties in passing from one element to the next of this group of elements. Thus, while sulphur is a distinct non-metal, selenium is slightly metallic, and tellurium more so, in its appearance. The attraction for oxygen is stronger in sulphur, weaker in selenium and tellurium.

SULPHUR AND ITS COMPOUNDS.

113. Sulphur ($S^{ii, iv, vi} = 31.98$).

OCCURRENCE.—Found uncombined, in great masses in volcanic districts, particularly in Italy, Iceland, and Sicily. The compounds of sulphur found in nature are very numerous and abundant. There are two principal classes: (1) *sulphides*, including a great many ores of metals, e.g., galena (PbS), zinc blende (ZnS), cinnabar (HgS), and iron and copper pyrites; and (2) *sulphates*, e.g., gypsum ($CaSO_4.2H_2O$), heavy spar ($BaSO_4$), Epsom salts ($MgSO_4.7H_2O$), and green vitriol ($FeSO_4.7H_2O$). Sulphur also forms an essential constituent of animal and vegetable bodies.

PREPARATION.—(1) Crude sulphur is heated in shallow pits, and the melted sulphur is run off from the earthy impurities. It is further purified by distillation, the vapour being led into cool chambers where it solidifies and falls down as "flowers of sulphur." When the walls of the chamber become hot the sulphur remains liquid and is run off into moulds *roll brimstone*).

(2) Iron pyrites (FeS_2) when distilled gives off one-third of the sulphur:

$$3FeS_2 = Fe_3S_4 + S_2.$$

This can be condensed, &c., as above. (Try with powdered pyrites in a narrow glass tube sealed at one end.)

(3) Sulphur is also obtained as a by product in the process of purifying coal gas.

(4) The waste liquor from the alkali manufacture contains sulphur, and has been used as a source.

PROPERTIES.—Sulphur has three *allotropic* modifications, two *crystalline*, and one *amorphous* (formless). These differ in specific weight and other physical properties.

Experiment 89.—Heat carefully until completely fused some pieces of roll sulphur in a porcelain dish. Then take the burner away, and hold a cork in the liquid until a crust forms over the surface. Break two small holes in this crust on opposite sides, and pour out the liquid part into another dish.

(Why *two* holes?). Then cut out the crust with a knife, and, lifting it carefully by the cork, observe the beautiful crystals of sulphur. Lay aside for a day, and observe that the translucent amber solid becomes opaque and yellow.

Sulphur melts at 114.5° C. to a clear amber liquid; if allowed to cool at the ordinary temperature of the air it crystallises in needle-shaped crystals (*monoclinic*). These are unstable and gradually change to another crystalline form (*rhombic prisms*). Sulphur is therefore *dimorphous.* Each monoclinic crystal becomes transformed into a great number of minute rhombic crystals, and hence the opacity. This change goes on gradually, and its progress can be watched.

Experiment 90.—Melt some sulphur in a dry t. t. (using the holder), and continue heating it. The mobile amber liquid becomes (at 200° C.) dark and viscid (will not pour). Continue the heat. It becomes mobile again, and at length begins to rise as a heavy vapour. Now pour it in a thin stream into a beaker of cold water. *Plastic* sulphur is obtained. Keep and observe it.

Plastic sulphur is amorphous—has no particular form, as crystals have. It can be drawn out into threads, but slowly hardens and changes into rhombic sulphur. This latter is the permanent form of sulphur. Large crystals can be obtained by evaporating solutions of sulphur in carbon bisulphide.—Sulphur boils at 450° C., forming a dark red vapour. The specific weight of this vapour is peculiar. If determined at a temperature near its boiling point, it is 96 (hydrogen = 1). The molecule must then weigh 192 times that of hydrogen, and must contain 6 atoms, since the atomic weight of sulphur is 32. The formula for sulphur at temperatures not much above 450° C. is then S_6. The specific weight at 1040° C.

(boiling point of zinc) is, however, only 32. (How many atoms in the molecule at this temperature?)

Experiment 91.—Try the solubility of flowers of sulphur in water, alcohol, carbon bisulphide, and paraffin oil, by shaking in test tubes with a very large proportion of the solvent. Use a little heat also before deciding in the negative.

Sulphur burns in air with a pale blue flame forming *sulphur dioxide* (SO_2). It oxidises very slowly in moist air to *sulphuric acid* H_2SO_4).

MILK OF SULPHUR (*Lac sulphuris*).—This is sulphur in a very finely divided state suspended in water. When dried it is called *precipitated sulphur*.

Experiment 92.—Boil for some time in a t. t. a little of the flowers of sulphur (5 parts) with slaked lime (10 parts) and water (20 parts), filter, and divide the *filtrate* (the clear liquid which runs through) into two parts. To one part add dilute hydrochloric acid until the liquid is acid. Sulphur is precipitated as a white powder. Allow it to settle, collect it on a filter, wash (by pouring hot water on the filter), and allow it to dry. To the second portion add dilute sulphuric acid, until the liquid is faintly acid, and proceed as before. Compare the two specimens in appearance. Burn a small portion of each on a piece of mica. That prepared with sulphuric acid leaves a white residue ; the other leaves little or none. Test a few specimens obtained from druggists.

When sulphur and lime water are heated together a *persulphide* and *thiosulphate of calcium* are formed :

$$3Ca(OH)_2 + 12S = 2CaS_5 + CaS_2O_3 + 3H_2O.$$

The action of the acids is shown in the following equations :

$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 12S + 3H_2O.$$
$$2CaS_5 + CaS_2O_3 + 3H_2SO_4 = 3CaSO_4 + 12S + 3H_2O.$$

Prepared with sulphuric acid, precipitated sulphur is very impure. Calcic chloride ($CaCl_2$) is freely soluble in water and is washed away from the sulphur; while calcic sulphate ($CaSO_4$) being sparingly soluble, remains mixed with the sulphur. The impure precipitated sulphur has a glistening look, and feels slightly gritty.

SULPHUR AND OXYGEN.

114. **Oxides of Sulphur.**—Four oxides of sulphur are known. Their composition is represented as follows: SO_2, SO_3, S_2O_3, and S_2O_7. Of these only the first two are of importance.

115. **Sulphur Dioxide.**—SO_2.—Also called *sulphurous anhydride.* As has been seen, sulphur burns in oxygen forming an oxide which, dissolving in water, gives an acid substance. This oxide is sulphur dioxide.

PREPARATION.—Sulphur dioxide can be prepared (1) by burning sulphur in air (Is it obtained pure?); (2) by burning iron pyrites in air: $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$; (3) by heating strong sulphuric acid with charcoal: $2H_2SO_4 + C = CO_2 + 2SO_2 + 2H_2O$; and (4) by heating strong sulphuric acid with certain metals, e.g., *copper, mercury, silver.*

Experiment 93.—Heat a little iron pyrites on mica. Notice that it burns with a blue flame and the smell of "burning sulphur." (What action has taken place? What substance is left?)

Experiment 94.—Put a considerable quantity of scraps of copper in a small flask, or a large t. t. and pour in enough concentrated sulphuric acid to cover the metal. Fit with the delivery tube of Expt. 66, and heat carefully until a gas begins to bubble off. Collect three jars of it by displacement of air (downward or upward? Calculate the sp. wt.) Then, still heating very little, allow the gas to bubble through a bottle of distilled water cooled to 0° C. by snow or ice. After some time a white crystalline solid ($H_2SO_3 . 14H_2O$) is formed.

(Try preparation on a small scale with charcoal.)

PROPERTIES.—An invisible gas of suffocating smell ("burning sulphur"), about $2\frac{1}{4}$ times as heavy as air; soluble in water (at 0° C., 80 vols. in 1; at 20°, 40 in 1); condenses to a liquid at −8° and with ordinary atmospheric pressure.

Experiment 95.—Put a burning taper or match in a jar of the gas, and observe.

Experiment 96.—Hang a strip of moist turkey-red cotton in another jar, close it, and allow it to stand. The colour is bleached.

Sulphur dioxide bleaches only in presence of water; and its bleaching action is the reverse of that of chlorine. It is due to the action of *hydrogen* from water:

$$SO_2 + 2H_2O = H_2SO_4 + H_2.$$

The hydrogen unites with the colouring matter forming a colourless compound. In many cases the colour may be gradually restored by the oxidizing action of the air. The action of sulphur dioxide is not so destructive as that of chlorine, and it is therefore used for bleaching delicate materials, such as silk, wool, &c. Sulphur dioxide is a *reducing agent*, but most of the reducing actions take place in presence of water, which is decomposed under the double influence of sulphur dioxide attracting the oxygen, and some other substance attracting the hydrogen.

Experiment 97.—Test the action on litmus of the solution prepared in Experiment 94. It contains an acid, *sulphurous acid* (H_2SO_3). Note the smell and taste of the solution.

Sulphur dioxide forms a weak compound with water, which cannot be obtained free from water, except at low temperatures.

Experiment 98.—Mix some sulphurous acid with iodine solution until the colour is just discharged. Note that the odour of both is now absent. Test with litmus. The solution is still acid : $SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$. Do similarly with chlorine water.

Experiment 99.—Colour some sulphurous acid in a porcelain dish with litmus, add solution of caustic soda until the colour becomes blue, and evaporate to dryness on the water bath. A white crystalline salt, *sodic sulphite,* remains :

$$H_2SO_3 + 2NaOH = Na_2SO_3 + 2H_2O.$$

Sulphur dioxide is a good disinfectant and antiseptic.

Tests.—1. Wet a piece of filter paper with a mixture of *ferric chloride* (Fe_2Cl_6) and *potassic ferricyanide* ($K_3FeC_6N_6$) in solution, and hold it in an atmosphere containing sulphur dioxide. It turns blue. The ferricyanide is reduced to ferrous cyanide, and this forms *Prussian blue* with ferric chloride.

2. Mix a few drops of solution of sulphur dioxide with starch paste and solution of iodic acid (HIO_3). Blue iodide of starch is formed : $2HIO_3 + 5SO_2 + 4H_2O = 5H_2SO_4 + I_2$. If more sulphur dioxide be added the colour disappears. (Explain.)

116. Sulphur Trioxide SO_3. — Also called *sulphuric anhydride*, or *anhydrous sulphuric acid.*

Preparation.—(1) By passing a mixture of sulphur dioxide and oxygen over heated spongy platinum, or *platinised asbestos :*

$$SO_2 + O \quad SO_3.$$

(In what proportions by volume do the gases combine?) (2) By distilling pure sulphuric acid with phosphorus pentoxide (P_2O_5):

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

PROPERTIES.—A transparent white crystalline solid, melting at 16° C., boiling at 46° C. It readily combines with water, forming *sulphuric acid* (H_2SO_4). It hisses like red hot iron when thrown into water, and when exposed to the air it deliquesces. Its relation to sulphuric acid is seen thus:

$$H_2O + SO_3 = H_2SO_4.$$

117. Oxygen Acids of Sulphur.

— These are very numerous, but only two are of any importance as acids, viz., *sulphurous* and *sulphuric.* The others will be studied mostly through their salts.

*Hypo*sulphur*ous* acid	H_2SO_2	*Di*thionic acid....	$H_2S_2O_6$
Sulphur*ous* acid	H_2SO_3	*Tri*thionic acid...	$H_2S_3O_6$
Sulphur*ic* acid.......	H_2SO_4	*Tetra*thionic acid.	$H_2S_4O_6$
*Thio*sulphuric acid..	$H_2S_2O_3$	*Penta*thionic acid.	$H_2S_5O_6$

118. Hyposulphurous Acid, H_2SO_2.

—Also called *hydrosulphurous acid.* Prepared by the action of zinc on sulphurous acid solution in closed vessels:

$$H_2SO_3 + H_2 = H_2SO_2 + H_2O.$$

(What is the source of the hydrogen represented in the equation?) It is a strong reducing agent, and readily absorbs oxygen from the air. (What is formed?) It is a monobasic acid, and forms salts, the *hyposulphites,* in which half the hydrogen of the acid still remains. The second atom of hydrogen in the molecule cannot be replaced by metal.

SODIC HYPOSULPHITE ($NaHSO_2$), prepared by dissolving zinc in a solution of *sodic hydric sulphite* ($NaHSO_3$), is used to reduce indigo in calico printing.

119. **Sulphurous Acid,** H_2SO_3.—Has been already mentioned (Art. 115). The pure acid exists as a solid at low temperatures, and the solution of the dioxide in water has acid properties.

PREPARATION.—By heating in a glass flask 1 part of charcoal, broken in small pieces, with 7½ parts concentrated sulphuric acid. The sulphur dioxide is washed by passing through a small quantity of water, and is then dissolved in cold water to saturation. The solution must be kept well stoppered. It contains about 12 °/ₒ of sulphurous acid, and its specific weight is 1.04. For properties see Art. 115.

SULPHITES.—Sulphurous acid neutralises strong bases (Exp't 99) and forms salts, the *sulphites*. There are two classes of sulphites: (1) *normal sulphites*, containing no hydrogen, e.g., sodic sulphite (Na_2SO_3); and (2) *acid sulphites*, containing hydrogen, e.g., *sodic hydric sulphite* ($NaHSO_3$). Sulphurous acid is *dibasic*; it unites with bases in *two* proportions. This subject will be more fully discussed in treating of sulphuric acid.—The sulphites are generally colourless salts, not very stable, readily absorbing oxygen from the air to form sulphates. They are strong reducing agents, and are used as such in the arts. In medicine, sodic sulphites are administered to introduce sulphurous acid into the stomach. (What is the action?)

Tests.—See Art. 115. Sulphites can generally be known by giving the smell of sulphur dioxide when treated with sulphuric acid.

Experiment 100.—To a solution of sodic sulphite in a t. t. add a few scraps of zinc and some hydrochloric acid. Note the smell of the gas evolved. Dip a strip of filter paper in plumbic acetate solution and hold it over the mouth of the t. t. It blackens. By the reducing action of the nascent hydrogen, hydric sulphide (H_2S) is formed: $SO_2 + 3H_2 = H_2S + 2H_2O$. This acts on the lead salt to form *plumbic sulphide* (PbS), a black substance.

120. **Sulphuric Acid,** H_2SO_4. — Known commercially as "oil of vitriol," or simply "vitriol." It was formerly prepared by distilling green vitriol, and "fuming sulphuric acid" is still prepared in this way. It is the most important of all acids, and is used in the preparation of most other acids. About 850,000 tons are manufactured annually in Great Britain.

MANUFACTURE.—To form a molecule of sulphuric acid it is necessary only to unite a molecule of sulphur dioxide with an atom of oxygen and a molecule of water:

$$SO_2 + O + H_2O = H_2SO_4.$$

But this union does not take place directly except under the influence of platinum or some other "contact action" substance. In practice it is brought about by another chemical action. *Nitrogen dioxide* (NO) readily combines with the oxygen of the air and thus forms the tetroxide (NO_2). This as readily gives up half its oxygen to sulphur dioxide and water, and is ready to unite again with oxygen from the air. Thus, nitrogen dioxide acts as a "carrier of oxygen" from the air to sulphur dioxide and water. (Of course, this *carrying* goes on between molecules, and not between vessels or rooms!) Thus:

$$NO + O = NO_2.$$

$$NO_2 + H_2O + SO_2 = H_2SO_4 + NO.,$$

&c., &c.

Sulphur dioxide (from iron pyrites by burning), water, air, and nitric acid (from sodic nitrate and sulphuric acid), are brought together in large leaden chambers. The nitric acid immediately suffers reduction to nitrogen dioxide, and the actions described above go on continuously. Theoretically, one molecule of nitrogen dioxide would in time convert any quantity of the materials into sulphuric acid. In practice there is waste, so that a fresh supply of nitric acid is needed from time to time. (What is left in the chambers after the sulphuric acid is formed?) The sulphuric acid, as fast as it forms, falls in a fine shower to the floor of the chamber into a layer of water. It is drawn off and concentrated in leaden pans to 78% (sp. wt. 1.71), at which strength it is sold as "brown oil of vitriol". (B.O.V.) For special purposes it is further concentrated in glass or platinum vessels to 96% (sp. wt. 1.84).

PROPERTIES.—The pure acid free from water is a crystalline white solid below 10° C., a colourless oily liquid above this. It has such a strong attraction for water that it is impossible to keep it pure unless it is sealed up. Thus in practice we have to deal with an acid containing more or less water. The sp. wt. of the pure liquid acid is 1.85. With many of the properties of sulphuric acid the student has already become acquainted. It is the strongest of acids, and its powerful attraction for water enables it to decompose many substances which contain hydrogen and oxygen in the proportions to form water.

Experiment 101.—Pour some sulphuric acid on a little sugar in a porcelain dish. The sugar blackens after a few minutes. Put a drop of acid on a piece of paper; on a piece of cotton cloth.

Paper and sugar are composed of carbon united with hydrogen and oxygen in the proportions to form water. Sulphuric acid sets the carbon free by taking the hydrogen and oxygen as water. The dilute acid turns dyed cloth reddish. If ammonia be applied the colour is restored.*

Experiment 102.—Heat a drop of sulphuric acid on mica. Note that it disappears entirely, with "fuming."

Sulphuric acid boils at 338° C., but undergoes partial *dissociation* (temporary decomposition) into sulphur trioxide and water, recombination taking place in the air. Hence, the appearance of fumes.—With the exception of *gold, platinum,* and a few others, sulphuric acid dissolves all the metals, forming sulphates. When the concentrated acid is used it acts as an *oxidising agent* (Exp't 94), and sulphur dioxide is a by-product. Some metals, as *copper, silver, lead,* and *mercury,* are dissolved only by the strong hot acid:

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

Others, as *zinc, iron,* and *aluminum,* are dissolved by the strong acid with the evolution of sulphur dioxide, but can also be dissolved by the dilute acid, and in this case hydrogen is the gas evolved:

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

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* Sulphuric acid is a corrosive poison, charring the surfaces with which it comes in contact. It has often, owing to its oily appearance, been mistaken for castor oil. The antidotes are dilute alkalis.

Impurities in Sulphuric Acid.

PLUMBIC SULPHATE ($PbSO_4$) is very commonly present in the commercial acid. It comes from the leaden evaporating pans, which are attacked when the concentration is pushed too far. This salt is soluble in the concentrated acid, but is precipitated on diluting with water.

Experiment 103.—Pour a little commercial oil of vitriol into about four times its volume of distilled water. A white precipitate indicates the presence of plumbic sulphate.

ARSENIC, derived from the pyrites, is often present; and, as it forms many volatile compounds, it is a dangerous impurity. For example, when arsenical sulphuric acid is used in the preparation of hydrochloric acid, the arsenic distils over as trichloride ($AsCl_3$), and thus renders the hydrochloric acid highly poisonous. It can be tested for by diluting the sulphuric acid with water and adding *hydric sulphide* (H_2S), when the yellow *arsenic trisulphide* (As_2S_3) is thrown down.—The colour of B. O. V. is due to *organic matter.*—*Sulphur dioxide*, and *oxides of nitrogen* occasionally occur as impurities.

SULPHATES.—Sulphuric acid is a *dibasic* acid. Its molecule contains 2 atoms of hydrogen, and both of these, or one of them only, can be replaced by metal. Thus, there are *two series* of sulphates, *normal* and *acid*; e. g., K_2SO_4, *normal potassic sulphate*, and $KHSO_4$, *acid potassic sulphate*. The acid sulphates are often called *bisulphates* (Art. 121).—The following normal sulphates are insoluble or very sparingly soluble in water: *Plumbic* ($PbSO_4$), *baric* ($BaSO_4$), and *strontic* ($SrSO_4$). *Calcic* ($CaSO_4$), *argentic* (Ag_2SO_4), and *mercurous* (Hg_2SO_4) are sparingly soluble. The rest of the sulphates are soluble, mostly easily crystallisable salts.

Tests.—**Experiment 104.**—Add a few drops of solution of *baric chloride* ($BaCl_2$) or *nitrate* to dilute sulphuric acid. A white precipitate ($BaSO_4$) is thrown down. (Write the equation). This is insoluble in nitric acid. Try the same with solution of *magnesic* sulphate ($MgSO_4$).

121. Normal and Acid Salts.

Experiment 105.—Put one pipetteful of dilute sulphuric acid in a porcelain basin, colour with litmus, carefully add sodic hydroxide solution until neutral, and evaporate on the water bath. Repeat this operation, but after reaching the neutral point add a second pipetteful of the acid.

By these experiments two different salts are obtained. Their crystalline form and other physical properties differ; and that obtained in the second operation is acid in taste, &c. In fact, it is still half acid, as can be seen by referring to the equations:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$
$$NaOH + H_2SO_4 = NaHSO_4 + H_2O.$$

Sulphuric acid acts on caustic soda in two proportions, 98 to 80, and 98 to 40. With the larger proportion of the base a neutral salt is formed, and the *hydrogen of the acid is completely replaced by the metal.* With the smaller proportion an *acid salt* is formed, and only *half the hydrogen of the acid is replaced by metal.* Now, the term "neutral salt" applies as long as both acid and base are well marked, but, if either acid or base is weak, the properties of the other predominate, even in a salt formed with the largest proportion of the weak acid or base; so that a so-called *neutral* salt may turn blue litmus to red, or red to blue. It has been agreed to restrict the use of the term "neutral" to the action of substances on litmus; and to use the word *normal* instead.

Definitions.—A *normal salt* is one in which all the replaceable hydrogen is replaced by metal.

An *acid salt* is one containing replaceable hydrogen (i.e., replaceable by metal).

(Can monobasic acids form acid salts?)

122. **Fuming Sulphuric Acid,** or *Nordhausen sulphuric acid.*—This is of somewhat variable composition. It is sulphuric acid combined with the trioxide; generally $H_2SO_4 + SO_3$. It is prepared from *green vitriol* ($FeSO_4.7H_2O$) by roasting in air to drive off the water of crystallisation and oxidise the salt:

$$2(FeSO_4.7H_2O) + O = Fe_2O_3.(SO_3)_2 + 14H_2O,$$

and then distilling. Enough moisture is obtained from the air and the apparatus to form a certain proportion of sulphuric acid:

$$Fe_2O_3.(SO_3)_2 + H_2O = Fe_2O_3 + H_2SO_4.SO_3.$$

It is used to dissolve indigo, and in the manufacture of *alizarine.*

123. **Thiosulphuric Acid,** $H_2S_2O_3$.—Formerly called *hyposulphurous acid.* The name now in use means *sulpho-sulphuric acid,* and refers to the composition, the acid containing an atom of sulphur in place of one of the four atoms of oxygen. The acid itself cannot be isolated, as it decomposes quickly on being set free from its salts:

$$H_2S_2O_3 = H_2O + S + SO_2.$$

Experiment 106.—Add some dilute sulphuric acid to a solution of sodic thiosulphate ($Na_2S_2O_3$), and watch carefully. After a few seconds the solution becomes milky. Now note the odour. (Write the equation.)

THIOSULPHATES.—Thiosulphuric acid is dibasic, both atoms of hydrogen being replaceable by metal. The most important salt is sodic thiosulphate, prepared by combining sodic sulphite with sulphur :

$$Na_2SO_3 + S = Na_2S_2O_3,$$

or, in practice, by dissolving sulphur in sodic hydroxide solution and saturating with sulphur dioxide.

Experiment 107.—Boil a solution of sodic sulphite for some time in a porcelain basin with flowers of sulphur, filter, evaporate the filtrate to small bulk, and set aside to crystallise. Fine colourless crystals ($Na_2S_2O_3.5H_2O$) are formed. Collect and dry them on filter paper.

SODIC THIOSULPHATE readily absorbs oxygen from the air and becomes oxidised to sulphate. Its action on *iodine* renders it very useful in analytical chemistry.

Experiment 108.—Add a few drops of sodic thiosulphate solution to a solution of iodine. The colour of the iodine disappears :

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

Thus, by means of a solution of thiosulphate of known strength, the quantity of iodine in a solution can be determined. (How could a quantity of chlorine be measured indirectly by this reaction ?)

Experiment 109.—Prepare a little *argentic chloride* by mixing hydrochloric acid and argentic nitrate in solution. Shake up well, allow the chloride to settle, pour off the liquid carefully, add water, shake, &c., and repeat this operation three or four times. (This is *washing by decantation.*) Now, add some sodic thiosulphate solution to the argentic chloride. The latter is dissolved, forming a very sweet solution of the *double thiosulphate*, $NaAgS_2O_3$:

$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl.$$

If any of the argentic chloride has become darkened, it remains undissolved.

Sodic thiosulphate is used in photography to dissolve out the undarkened chloride, bromide, or iodide of silver, so as to *fix* the negative or print.—It is used in medicine to destroy certain organisms in the stomach (sarcinæ ventriculi). (What is the action of the gastric juice on it?)

SULPHUR AND HYDROGEN.

124. **Hydric Sulphide,** H_2S.—Commonly called *sulphuretted hydrogen.* It occurs in volcanic gases and in "sulphur springs." It is a product of the decay of animal and vegetable bodies, and is one cause of the attendant bad smell and poisoning of the air.

PREPARATION.—**Experiment 110.**—Pour a few drops of dilute sulphuric acid upon a little *ferrous sulphide* (FeS) in a watch glass. Note the odour of the gas given off. Repeat, with dilute hydrochloric acid and ferrous sulphide. Try also with *antimony trisulphide* (Sb_2S_3) and rather strong hydrochloric acid solution (1 vol. of the strong solution to 1 of water), warming them in a t. t.

The gas, kno [illegible] ts unpleasant smell, is hydric sulphide (H_2S) :

$$(1)\ FeS + H_2SO_4 = H_2S + \overset{\text{Ferrous sulphate.}}{FeSO_4}.$$

$$(2)\ FeS + 2HCl = H_2S + \overset{\text{Ferrous chloride.}}{FeCl_2}.$$

$$(3)\ Sb_2S_3 + 6HCl = 3H_2S + \overset{\text{Antimony trichloride.}}{2SbCl_3}.$$

Experiment 111.—Heat a little *paraffin wax* and flowers of sulphur together in a small porcelain dish. Hydric sulphide is evolved.

Paraffin wax is a mixture of *hydrocarbons*, or compounds of carbon and hydrogen. Hydric sulphide is prepared on the large scale in this way.—When hydric sulphide is prepared from ferrous sulphide it contains hydrogen, owing to the presence of uncombined iron in the ferrous sulphide of commerce. (What is the action?) The method with antimony trisulphide gives the pure gas.

PROPERTIES.—An invisible gas, of very unpleasant odour (that of rotten eggs), and of sweetish taste.

Experiment 112.—Prepare sulphuretted hydrogen with ferrous sulphide and dilute sulphuric acid, evolving it in a small flask or bottle, and bubbling it through a small quantity of water in a *wash bottle* (to wash it free from small drops of sulphuric acid carried up by the gas), and then through water in the reagent bottle provided. Gases are washed by passing them through a liquid in a bottle provided with a twice-bored cork. The tube from the generating flask passes through one hole and nearly to the bottom of the water. A second tube passes just throug' the other hole to lead the washed gas away. Note that after the air is driven out, most of the gas dissolves in the water. Some, however, escapes solution, and this experiment should be made in a draught cupboard or under a hood. After the gas has been running for a few minutes, bubble a little of it through test tubes containing solutions of *cupric sulphate* ($CuSO_4$), *tartar emetic*, and *stannous chloride* ($SnCl_2$). Then set fire to the gas and note its inflammability. Evaporate the solution remaining in the flask, and obtain crystals of green vitriol ($FeSO_4.7H_2O$).

Hydric sulphide is soluble in water, about 3 volumes in 1 of water. The solution has the smell, &c., of the gas. It slowly decomposes, absorbing oxygen from the air ($H_2S + O = H_2O + S$), and sulphur is deposited as a white powder. The gas burns in the air with a bluish flame and the formation of water and sulphur dioxide: $H_2S + 3O = H_2O + SO_2$.—It can be liquefied at — 70° C. under the ordinary pressure of the atmosphere.—Hydric sulphide is a valuable *reagent* (test substance) in analytical chemistry. Either as gas or in solution, it precipitates the sulphides of certain metals from solutions of their salts, while it does not precipitate others. It precipitates the sulphides of some metals in presence of a free acid, others only in the presence of a free alkali. Thus, all metals can be divided into *three groups:*

1. Those precipitated as sulphides in presence of a free mineral acid (Hg, Ag, Pb, Cu, Bi, Cd, Sb, Sn, As, Pt, Au, &c.)

2. Those precipitated only in presence of a free alkali (Fe, Ni, Co, Zn, Mn, Al, Cr, the last two as *hydroxides*).

3. Those not precipitated at all by hydric sulphide (Mg, Ca, Sr, Ba, K, Na, Li, &c.)

Hydric sulphide is very poisonous, even when largely diluted with air. It produces lassitude, headache, giddiness, fainting, and at last death. The best antidote is chlorine gas largely diluted with air. It can be administered by inhalation as evolved from a mixture of "chloride of lime" (bleaching powder) and vinegar.

Experiment 113.—Mix some chlorine water with solution of hydric sulphide in a t. t. Note that sulphur is precipitated. If the right proportions are used, the smell of both chlorine and hydric sulphide is destroyed:

$$H_2S + Cl_2 = 2HCl + S.$$

When hydric sulphide is taken as a medicine it is partially given off through the skin. Hence, its efficacy in skin diseases.

SULPHIDES OF METALS.—Sulphur combines directly with most of the metals, forming ***sulphides***. In these compounds the sulphur is *dyad*, as in hydric sulphide. The sulphides of the heavy metals can be formed by precipitation with hydric sulphide (see above); the sulphides of potassium, sodium, calcium, &c., can not be formed in this way, but are best prepared by reduction of the sulphates by heating with charcoal:

$$K_2SO_4 + 4C = K_2S + 4CO.$$

The sulphides run parallel with the oxides in composition, as the following formulas show:

$$H_2S,\ FeS,\ Fe_2S_3,\ Fe_3S_4,\ Ag_2S,\ Na_2S,\ As_2S_3,\ \&c.$$
$$H_2O,\ FeO,\ Fe_2O_3,\ Fe_3O_4,\ Ag_2O,\ Na_2O,\ As_2O_3,\ \&c.$$

Tests.—Free hydric sulphide blackens *lead paper*.

$$Pb(C_2H_3O_2)_2 + H_2S = PbS + 2C_2H_4O_2.$$

Most sulphides when treated with hydrochloric acid give the smell of hydric sulphide. Insoluble sulphides when fused on charcoal before the mouth blow-pipe with sodic carbonate, give a bead which stains silver black, when placed upon it and moistened with dilute hydrochloric acid.

HYDROGEN PERSULPHIDE.—The exact composition is unknown; perhaps H_2S_2, analogous to H_2O_2. It is prepared by pouring a strong solution of an alkaline persulphide (e. g., K_2S_5), into dilute hydrochloric acid. It is an oily liquid, readily decomposing into sulphur and hydric sulphide.

125. Sulphur and the Halogens.

—Sulphur unites directly with *chlorine* in several proportions (S_2Cl_2, S_2Cl_4, and SCl_4). The chlorides are all decomposable by water.—Sulphur combines with *bromine* in only one proportion (S_2Br_2); with *iodine* it forms two compounds (S_2I_2 and SI_6). The *moniodide* (S_2I_2) is prepared by heating together four parts of iodine with one of flowers of sulphur. It is a crystalline greyish-black solid, insoluble in water, but decomposed by boiling with it. It is soluble in glycerine. It is used in medicine in the form of an ointment.

126. **Selenium** ($Se^{ii, iv, vi} = 79$).—Rather rare, and found only in small quantities, in sulphur ores, &c. It was discovered by Berzelius (1817), in the deposit found in certain sulphuric acid chambers. Selenium has two allotropic forms, one of which is somewhat metallic in appearance.

COMPOUNDS.—These are similar in composition to those of sulphur; *seleniuretted hydrogen*, or *hydric selenide* (H_2Se); *selenium dioxide* (SeO_2); *selenious acid* (H_2SeO_3); and *selenic acid* (H_2SeO_4), are similar in properties to the corresponding compounds of sulphur; but no trioxide is known with certainty. Selenic acid differs from sulphuric acid in being easily reduced to selenious acid. Metallic selenium conducts electricity, and its conductivity is increased by exposure to light. It is so sensitive to the influence of light, that an electrical instrument has been constructed which shows the slightest variations in the intensity of the light falling on the surface of the selenium which is placed in the electric circuit.

127. **Tellurium** ($Te^{ii, iv, vi} = 128$).—This is also a rare element, being generally found combined with silver, gold, or bismuth. It forms compounds with hydrogen and oxygen, parallel with those of sulphur and selenium, but *tellurium dioxide* (TeO_2) has weak basic properties.

QUESTIONS AND EXERCISES.

1. Show how the oxides of sulphur illustrate the law of multiple proportions.

2. How much oxygen is there to 1 part by weight of hydrogen in each of the oxygen acids of sulphur? How much sulphur to 1 of hydrogen?

3. What weight of sulphuric acid is equivalent to 100 g. sodic hydroxide (KOH)? To 100 g. calcic hydroxide ($Ca(OH)_2$)?

4. 196 g. sulphuric acid in solution is mixed with 150 g. sodic hydroxide. Is the solution neutral, acid, or alkaline?

5. What is the valence of sulphur in sulphur dioxide? In sulphur trioxide? In hydric sulphide? In sulphur hexiodide (SI_6)? In Sulphuric acid ($SO_2 \begin{smallmatrix}-OH\\-OH\end{smallmatrix}$)?

6. What volume of chlorine is necessary to decompose 1 cubic foot of hydric sulphide gas?

7. Define normal and acid salts with regard to the equivalence of the acids and bases forming them.

8. Write the formulas for the following normal sulphates: *Sodic, argentic, ammonic, ferric, cupric, zincic, bismuth, chromic,* and *mercuric.*

9. Write the formulas for the following compounds: *potassic hydric sulphite, calcic thiosulphate, sodic argentic thiosulphate, zincic hyposulphite, mercuric sulphide,* and *argentic sulphide.*

10. Moisten a strip of filter paper with plumbic acetate and hold it in the mouth of the bottle of hydric sulphide solution. It is blackened. Explain.

11. What weight of ferrous sulphide (FeS) must be used to saturate 2 litres of water with hydric sulphide?

12. Balance the following equations:

(1) $SbCl_3 + H_2S = Sb_2S_3 + HCl.$
(2) $H_2SO_4 + Fe_2O_3 = Fe_2(SO_4)_3 + H_2O.$
(3) $SO_2 + I + H_2O = H_2SO_4 + HI.$
(4) $FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$

CHAPTER XI.

PHOSPHORUS AND ITS COMPOUNDS.

128. **Phosphorus** ($P^{\text{iii, v}} = 31$).—The name *phosphorus* (light-bearer) was at first given to substances which shone in the dark, particularly to *Bononian phosphorus* (barium sulphide). The substance at present called *phosphorus* was discovered about 1678 by an alchemist, Brandt, while distilling the residue left by evaporating urine. It created a great deal of interest on account of its luminosity and inflammability; and, besides, it was held to be a very valuable medicine. A few years after Brandt's discovery, Boyle discovered the secret of its preparation from urine, having had only the vague information that it was prepared from the human body. At present the phosphorus of commerce is prepared from bones and from mineral phosphates.

OCCURRENCE.—Phosphorus is never found in nature uncombined. (Why?) It occurs in *phosphates*, e. g., *phosphorite* ($Ca_3(PO_4)_2$), *apatite* ($3Ca_3(PO_4)_2 + CaCl_2$), and *coprolites*, or fossil dung of serpents. It is present in all fertile soils and is an essential constituent of the food of plants. Animals take it into their bodies along with their food and build it up especially into bones, which consist very largely of calcic phosphate ($Ca_3(PO_4)_2$). It is also found in sea-water, and in all parts of the earth's crust.

Preparation.—Bones are either distilled, *bone-black* and *bone-oil* being the products; or they are heated under pressure with water to extract the animal matter as gelatine. In the former case, the bone-black is used in sugar-refining and then burned to *bone-ash,* which is impure calcic phosphate. In the latter case the calcic phosphate is left from the extraction process. In either of these ways, then, or from some mineral source, calcic phosphate is obtained. This is treated with dilute sulphuric acid, when two-thirds of the calcium is precipitated as *calcic sulphate,* while an *acid phosphate* goes into solution:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

The solution is drawn off, evaporated to dryness, and strongly heated. It loses water, and calcic *metaphosphate* remains:

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O.$$

This is mixed with charcoal and sand (SiO_2), and strongly heated in earthenware retorts. The object of the charcoal is to remove oxygen from the phosphate; the sand forms a *silicate* of calcium, and thus aids in setting free the phosphorus, which distils, and is collected under water:

$$Ca(PO_3)_2 + 5C + SiO_2 = CaSiO_3 + 5CO + 2P.$$

It is purified by melting under water and pressing through chamois leather, or by oxidising the impurities by means of a mixture of *potassic bichromate* ($K_2Cr_2O_7$) and sulphuric acid.

Properties.—Phosphorus has several allotropic modifications, of which two only will be described.

(1) COMMON OR YELLOW PHOSPHORUS is a translucent, waxy solid, of sp. wt. 1.8. It melts at 44° C.

Experiment 114.—Put a small piece of phosphorus in a porcelain dish half-filled with water and heat the water. Notice that the phosphorus melts before the water becomes uncomfortably hot. Note the smell, &c., of the phosphorus. Is it heavier or lighter than water? Does it dissolve in water?

If heated in an atmosphere of some inactive gas (nitrogen) it boils at 290° C. The specific weight of its vapour is 4.3 (air = 1). (How many atoms in the molecule?) If heated in the air it catches fire at 60° C. It catches fire at lower temperatures if exposed to the oxidising action of the air for some time. Very slight friction often sets it on fire; and as it burns very vigorously, and causes frightful wounds if it comes in contact with the skin while burning, it should always be handled under water. It should be kept in well stoppered bottles of water in a cool, dark place.—Yellow phosphorus is soluble in carbon bisulphide (CS_2), in fats, oils, and slightly in ether and oil of turpentine. If the solution in carbon bisulphide be evaporated, crystals of phosphorus are obtained.—Yellow phosphorus is very poisonous, and as it is often used in making matches, phosphorus-poisoning cases are not rare. The fatal dose is as low as 1½ grains. The symptoms are pain in the stomach, nausea, vomit with garlic odour. The antidote is *blue vitriol* in 3-grain doses (dilute solution) every 5 minutes until vomiting ensues.

Experiment 115.—Put a bit of clear phosphorus in a small quantity of cupric sulphate solution. It is blackened.

When a poisonous substance is taken into the stomach it begins at once to pass into the circulation.

The object of an antidote is to prevent this, either by decomposing the poison (if it is a compound), or by rendering it insoluble, and therefore incapable of absorption into the circulation. In the present case, the phosphorus is combined with copper (Cu_3P_2), forming an insoluble black compound.

2. **Red or Amphorous Phosphorus** is prepared from common phosphorus by heating it for some time at 240°C., a small quantity of iodine being added to hasten the change. It is an amorphous red solid of specific weight 2.2 ; insouble in carbon bisulphide, &c.; does not fuse at 250°, catches fire only at 260°, and is not poisonous. It is prepared on the large scale in the manufacture of matches, to replace the poisonous common phosphorus.

Tests.—Phosphorus can be known by its odour of garlic, and by its luminosity in the dark. To detect small quantities, e.g., in cases of poisoning, the substance is distilled with water in a dark room, when the phosphorescence appears.

PHOSPHORUS AND OXYGEN.

129. Oxides of Phosphorus.—Two are known with certainty :

Phosphorus pentoxide.........	P_2O_5
Phosphorus trioxide...........	P_2O_3

and the existence of a third is probable :

Phosphorus monoxide........	P_2O (?)

Derived from these are three acids :

Phosphoric acid.............	H_3PO_4
Phosphorous acid	H_3PO_3
Hypophosphorous acid.......	H_3PO_2

130. **Phosphorus Pentoxide.** — P_2O_5. — Already noticed. Prepared by burning phosphorus in air. It is a snow-like solid, very hygroscopic, and hence used to dry gases, and in separating water from acids. In moist air it quickly deliquesces forming *metaphosphoric acid*:

$$H_2O + P_2O_5 = 2HPO_3.$$

If put into water it hisses and dissolves, forming at first metaphosphoric acid; but, gradually at ordinary temperatures, and quickly if heated, it combines with more water to form *orthophosphoric acid*:

$$HPO_3 + H_2O = H_3PO_4.$$

131. **Phosphorus Trioxide.** — P_2O_3. — Prepared by burning phosphorus slowly with a scant supply of air. If heated in air it combines with oxygen and forms the pentoxide:

$$P_2O_3 + O_2 = P_2O_5.$$

It combines with water to form *phosphorous acid*:

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$

132. **Phosphoric Acid.** — Phosphorus pentoxide unites with water in three proportions, forming three different acids, each of which is called *phosphoric acid*, but prefixes are used to distinguish them. The ordinary acid is that formed with the greatest proportion of water, and is called *ortho*phosphoric acid:

$$3H_2O + P_2O_5 = 2H_3PO_4.$$

(1) ORTHOPHOSPHORIC ACID, H_3PO_4. — This is generally called simply *phosphoric acid*.

Preparation.—Bone ash or mineral phosphate is dissolved in nitric acid :

$$Ca_3(PO_4)_2 + 4HNO_3 = CaH_4(PO_4)_2 + 2Ca(NO_3)_2.$$

Plumbic acetate ($Pb\bar{A}_2$) is added to the solution, when plumbic phosphate is precipitated :

$$CaH_4(PO_4)_2 + 3Pb\bar{A}_2 = Pb_3(PO_4)_2 + Ca\bar{A}_2 + 4H\bar{A}.$$

The object of the first reaction is to get the phosphate and impurities in solution ; that of the second is to remove the phosphoric acid from its impurities, and at the same time obtain a phosphate from which the acid can be easily obtained in one operation. The plumbic phosphate is washed, suspended in water, and decomposed by sulphuretted hydrogen :

$$Pb_3(PO_4)_2 + 3H_2S = 2H_3PO_4 + 3PbS.$$

Phosphoric acid dissolves, and plumbic sulphide remains undissolved. (How is the process completed ?)

Experiment 116.—Put a small piece of phosphorus in a porcelain dish and cover it with dilute nitric acid. Warm gently. The phosphorus melts and oxidises with the evolution of red fumes. (What are these ?) Evaporate to dryness, add a few drops concentrated nitric acid, and evaporate again to dryness. Phosphoric acid remains. Dissolve in water and keep.

Red phosphorus is better for this experiment, as it can be oxidised with concentrated nitric acid, which acts explosively on yellow phosphorus.

Properties.—A thick syrup, or hard, transparent, colourless crystals ; soluble in water, giving a strongly acid solution. (Try it by taste and litmus.) It is a *tribasic* acid, and forms three series of salts, e. g.:

(1) Na_3PO_4, trisodic phosphate.

(2) Na_2HPO_4, disodic hydric phosphate.

(3) NaH_2PO_4, sodic dihydric phosphate.

(To which of these classes do the phosphates mentioned in PREPARATION belong?)

Phosphoric acid is used in medicine in dilute solution as a tonic, &c.

PHOSPHATES (*orthophosphates*).—Of the *normal* and the *mon-acid* phosphates, only those of the alkali metals (Na, K, NH_4, &c.), are soluble in water. The *di-acid* phosphates are all soluble.

Tests.—1. Add a drop or two of argentic nitrate to a solution of sodic phosphate (Na_2HPO_4). A yellow precipitate is formed. Divide into 3 parts, and add to one part *ammonia*; to the second, dilute *nitric acid*; and to the third, *acetic acid*. The precipitate is soluble in each. (Could this test be used in a solution containing hydrochloric acid?).

2. Add ammonic chloride, magnesic sulphate, and ammonia to a solution of sodic phosphate, and stir with a glass rod. A granular white precipitate of *magnesic ammonic phosphate* ($Mg.NH_4.PO_4$) is formed:

$$Na_2HPO_4 + NH_3 + MgSO_4 = MgNH_4PO_4 + Na_2SO_4.$$

3. *Baric chloride* ($BaCl_2$) gives a white precipitate, soluble in nitric acid.

Phosphates are present dissolved in urine, and when the urine becomes *alkaline* by decomposition (Explain.) crystals of *microcosmic salt*, or *sodic ammonic hydric phosphate* ($Na.NH_4.H.PO_4$) are formed.

(2) METAPHOSPHORIC ACID.—HPO_3.—Formed when phosphorus pentoxide is dissolved in cold water; but is generally prepared by heating orthophosphoric acid to a red heat:

$$H_3PO_4 = HPO_3 + H_2O.$$

PROPERTIES.—It is a hard glassy colourless solid (*glacial* phosphoric acid)—the common phosphoric acid of commerce. It dissolves in water, but gradually combines with the water to form ortho-phosphoric acid.—It is a monobasic acid (To what acid is it similar in composition?), and forms salts called *metaphosphates*, e.g., $NaPO_3$, $Mg(PO_3)_2$, &c.

Tests.—1. Add argentic nitrate to a solution of the acid or a salt. A gelatinous white precipitate is formed. It is soluble in nitric acid.

2. Add some white of egg to a solution of metaphosphoric acid, or to a metaphosphate acidified with acetic acid. The white of egg is coagulated. Try with orthophosphate.

(3) PYROPHOSPHORIC ACID.—$H_4P_2O_7$ ($= P_2O_5 + 2H_2O$).

PREPARATION.—Heat orthophosphoric acid till the temperature rises to 215° C.:

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

PROPERTIES.—A soft glassy liquid; when heated with water, forms orthophosphoric acid. It is a *tetrabasic* acid. Its salts can be formed by heating acid orthophosphates of the class M_2HPO_4. (Write the equation.) The pyrophosphates are changed to acid ortho-salts when they are boiled with water.

Tests.—1. White precipitate with argentic nitrate, soluble in nitric acid.

2. Pyrophosphoric acid does not coagulate white of egg.

133. Phosphorous Acid.—H_3PO_3.

PREPARATION.—This acid is formed when phosphorus oxidises slowly in moist air; but it is best prepared by the action of phosphorus trichloride (PCl_3) on water:

$$PCl_3 + 3H_2O = P(OH)_3 + 3HCl.$$

This action of water on a chloride is a very frequent one. Observe that *hydroxyl* (— OH) replaces *chlorine* (— Cl).

PROPERTIES.—A white solid with garlic odour. Oxidises readily to phosphoric acid. When heated it decomposes into phosphoric acid and gaseous *phosphoretted hydrogen* (PH_3):

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

There are many decompositions of compounds containing oxygen, such that one part gains oxygen at the expense of another part. (Mention one already described.)—The *phosphites* are unimportant. Only *two* of the three atoms of hydrogen seem to be readily replaceable by metal.

Tests.—1. Add argentic nitrate to a solution of a phosphite. Metallic silver is precipitated.

2. Add solution of *baric chloride*. It gives a white precipitate soluble in nitric acid.

3. Heat a little of the substance on mica and smell. The odour of phosphoretted hydrogen is observed.

4. Add lime water to solution of phosphorous acid or a phosphite. A white precipitate is thrown down ($CaHPO_3$).

134. **Hypophosphorous Acid.** — H_3PO_2. — The acid itself is of little importance. It can be prepared from its barium salt by treating with sulphuric acid, (Why use the barium salt in particular?) It is a monobasic acid, of very strong reducing power, and quickly absorbs oxygen from the air.

HYPOPHOSPHITES.—**Experiment 117.**—Heat a small piece of phosphorus in a t. t. with milk of lime. Connect the t. t. with a gas-delivery tube dipping under water. A gas having the smell of decaying fish is evolved, and catches fire as soon as it comes in contact with the air. Continue the heating until the phosphorus is dissolved, and no more gas appears. The solution contains *calcic hypophosphite* ($Ca(H_2PO_2)_2$). Filter, pass into the clear solution a current of carbon dioxide to precipitate the uncombined calcic hydroxide as calcic carbonate ($CaCO_3$), then filter again.

The actions which take place are represented thus:

$$3Ca(OH)_2 + 8P + 6H_2O = 3Ca(H_2PO_2)_2 + 2PH_3.$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

The hypophosphites of sodium, potassium, barium, and strontium, may be prepared in the same way. The hypophosphites are powerful reducing agents. They must be kept out of contact with air, otherwise they become oxidised to phosphites and finally to phosphates. They are used in medicine, and are supposed to produce the same specific effects as free phosphorus; but this is very doubtful.

Tests.—1. *Argentic nitrate* gives a white precipitate which quickly turns brown and then black:

$$4AgNO_3 + H_3PO_2 + 2H_2O = 4HNO_3 + H_3PO_4 + 4Ag.$$

2. *Baric chloride* gives no precipitate,

3. Zinc and hydrochloric acid (nascent hydrogen) give the smell of phosphoretted hydrogen.

4. Evaporate to dryness, heat residue on mica ; odour of phosphoretted hydrogen :

$$2H_3PO_2 = PH_3 + H_3PO_4.$$

Note.—Try these tests with the solution of calcic hypophosphite (Experiment 117); also with a sample of "hypophosphites" from the druggist's.

The "hypophosphites" of medicine is a preparation of calcic hypophosphite.

135. **Phosphorus and Hydrogen.**—There are three compounds known :

Gaseous phosphoretted hydrogen, or phosphine	PH_3
Liquid " "	P_2H_4
Solid " "	P_4H_2

Only the first will be described.

136. **Phosphine** (*gaseous phosphoretted hydrogen*). PH_3.—Prepared as in Experiment 117, but better with a strong solution of potassic or sodic hydroxide :

$$3KOH + 4P + 3H_2O = 3KH_2PO_2 + PH_3.$$

It is formed by the decay of fish and other animal and vegetable bodies. It is supposed to be the cause of that dancing phosphorescent light which, under the name of *ignis fatuus*, or *will o' the wisp*, wanders over marshy and swampy places.

Properties.—An invisible gas, of strong smell (that of rotting fish), very poisonous, even when largely diluted with air. It readily burns in air (spontaneously inflammable when containing vapour of the liquid compound, as in Experiment 117) :

$$PH_3 + 2O_2 = H_3PO_4.$$

In chemical characters it resembles ammonia, uniting with acids to form salts, e. g. :

$$PH_3 + HI = \overset{\text{Phosphonium iodide.}}{PH_4I.}$$

PHOSPHORUS AND THE HALOGENS.

137. **Phosphorus and Chlorine.**—Two compounds are known :

Phosphorus trichloride............PCl_3
" pentachloride..........PCl_5

PHOSPHORUS TRICHLORIDE (PCl_3), is prepared by passing dry chlorine gas over heated amorphous phosphorus. It is a colourless liquid, fuming in moist air, decomposed by water (Art. 123). It boils at 76° C.

PHOSPHORUS PENTACHLORIDE (PCl_5), is prepared by treating amorphous phosphorus with dry chlorine at a low temperature, until no more is absorbed. It is a white solid, of pungent smell, fumes in moist air, being decomposed by water in two stages :

$$(1)\ PCl_5 + H_2O = \overset{\text{P. oxychloride.}}{POCl_3} + 2HCl.$$
$$(2)\ POCl_3 + 3H_2O = PO(OH)_3 + 3HCl.$$

In the first stage two atoms of chlorine are replaced by an atom of oxygen, and *phosphoryl chloride* (or phosphorus oxychloride), and hydrochloric acid are formed. This is the action with a small proportion of water. In the second stage the three remaining atoms of chlorine are replaced by three hydroxyl groups, and phosphoric acid is formed, along with a further quantity of hydrochloric acid. From this it is seen that phosphoric acid is the hydroxide of a trivalent radical *phosphoryl* ($PO\leqslant$). Oxygen acids generally can be represented as hydroxides, e.g.:

$$NO_2-OH,\ \ SO_2(OH)_2.$$

138. **Phosphorus and Bromine, &c.**—With the other halogens phosphorus combines forming compounds the formulas of which are:

$$PBr_3, PBr_5; P_2I_4, PI_3; \text{ and } PF_5.$$

These compounds, excepting the last, are prepared by direct union of the elements; and all are of great value in preparing halogen derivatives of carbon compounds. By means of these (as well as the chlorides), the oxygen and hydroxyl of carbon compounds can be replaced by the halogens. (Compare the action of phosphorus pentachloride on water.)

QUESTIONS AND EXERCISES.

1. Compare nitrogen and phosphorus, as to their compounds.

2. In what dehydrating processes is phosphorus pentoxide used?

3. When an orthophosphate of the class MH_2PO_4 is heated, water is driven off. What is left? Write the equation.

4. Mix a solution of sodic phosphate (Na_2HPO_4) with one of plumbic acetate. What result? Try with phosphite and hypophosphite.

5. When an orthophosphate of the class M_2HPO_4 is heated, water is driven off. What is left? Write the equation.

6. What is the basicity of phosphorous acid?

7. By what tests can the acids hypophosphorous, phosphorous, and phosphoric be distinguished from each other?

8. "The atomicity of phosphorus is 3 in some compounds and 5 in others." Apply this statement.

9. Calculate the wt. of 1 litre of phosphorus vapour at 400° C., and 760 mm. pressure.

10. Calculate the wt. of 1 litre of phosphorus vapour at 1040° C., and 760 mm. pressure.

11. What is the percentage of phosphorus in pure *apatite* ($Ca_3(PO_4)_2.CaCl_2$)?

CHAPTER XII.

ARSENIC AND ITS COMPOUNDS.

139. **Arsenic** ($As^{iii, v} = 75$).—Arsenic is found free in nature in crystalline masses. The ores from which the elementary substance is principally derived are *mispickel* ($Fe_2As_2S_2$), *arsenical iron* ($FeAs_2$), and arsenical ores of cobalt, nickel, and copper. Iron pyrites often contain arsenic.

PREPARATION.—Chiefly by sublimation from mispickel. The ore is heated in earthenware retorts, and the metal condensed in sheet iron and earthen cylinders :

$$Fe_2As_2S_2 = 2FeS + 2As.$$

It can be prepared on the small scale by heating the trioxide (As_2O_3) with charcoal.

Experiment 118.—Mix a small quantity of white arsenic (As_2O_3) with powdered charcoal, put in a narrow hard-glass tube closed at one end (matrass), drop in a small splinter of charcoal, and heat the tube slowly in the Bunsen flame, applying the flame first to the part of the tube in which the charcoal splinter is. A mirror of arsenic forms as a ring around the inside of the tube. The charcoal has reduced the oxide of arsenic :

$$As_2O_3 + 3C = 2As + 3CO.$$

PROPERTIES.—A steel grey solid, of somewhat metallic appearance. Sp. wt. = 5.727. It *sublimes* at 356° C. It can be melted by heating under pressure. Sp. wt.

of vapour = 10.2 (air = 1). (Calculate the number of atoms in the molecule.) It oxidises in moist air; and burns brightly when heated in air or oxygen, forming the trioxide (As_2O_3). Can also be oxidised by heating with nitric or sulphuric acid. It is not soluble in hydrochloric acid. Arsenic and all its volatile compounds are very poisonous. Lead is hardened in the manufacture of shot and bullets by alloying it with a small proportion of arsenic.

140. **Arsenic and Oxygen.**—Two oxides are known, viz.:

Arsenic trioxide	As_2O_3
Arsenic pentoxide	As_2O_5

They are both acid-forming oxides, and this marks arsenic as a non-metal, although it has some metallic characters.

141. **Arsenic Trioxide** (As_2O_3).—Also called (incorrectly) *arsenious acid.* This is the "white arsenic" of the shops.

PREPARATION.—By roasting arsenical pyrites and other ores of arsenic in a good current of air and receiving the fumes in cool chambers to condense them. These crude "flowers of arsenic" are purified by resublimation.

PROPERTIES.—A white solid, either a crystalline powder, or a porcelain-like cake; of *sweetish,* metallic taste; sparingly soluble in water. (Carefully study the appearance of specimens.) It is volatile, and sublimes readily. (Try a little in a t. t.)

Experiment 119.—Boil a little arsenic trioxide with distilled water in a t. t. It dissolves only to a small extent. Prove this by evaporating a little of the clear liquid in a watch glass. Add about $\frac{1}{5}$ of its volume of hydrochloric acid to the water, and heat again. The arsenic trioxide dissolves readily. Keep the solution.

Experiment 120.—Try the solubility of arsenic trioxide in solutions of sodic hydroxide, ammonia, nitric acid, and sulphuric acid.

Arsenic trioxide has very weak basic properties. It forms with acids no salts which are not decomposed by water. Its acid forming properties are distinct. (What proof of this have you had?) It is used in the manufacture of pigments, glass, &c., and in calico printing.—One grain (0.06 gram) of arsenic trioxide is a dangerous dose. Doses of 2 to 4 grains are nearly always fatal; but by use the system becomes able to withstand its action. In one case more than five grains were eaten without ill effect.

142. **Arsenic Pentoxide.**—As_2O_5.—Is unimportant. Can be prepared by heating arsenic acid (H_3AsO_4) nearly to a red heat: $2H_3AsO_4 = 3H_2O + As_2O_5$. (Compare with phosphoric acid). At a red heat it begins to decompose into oxygen and arsenic trioxide.—It is a deliquescent white solid, uniting with water to form *arsenic acid.*

143. **Arsenious Acid**—H_3AsO_3 (hypothetical).—This acid is known only in solution and through its salts. Its relation to arsenic trioxide is the same as that of phosphorous acid to phosphorus trioxide. It is a tribasic acid; but arsenites are known corresponding to a monobasic acid, $HAsO_2$. (Compare HNO_2).

ARSENITES.—**Experiment 121.**—Heat powdered arsenic trioxide with solution of sodic hydroxide until no more will dissolve, filter, dilute the filtrate, and preserve it for the following experiments.

This solution contains an *arsenite of sodium;* say Na_3AsO_3.

Experiment 122.—To a little of the solution add a few drops of solution of *ferric chloride* (Fe_2Cl_6). A reddish brown precipitate appears:

$$Fe_2Cl_6 + 2Na_3AsO_3 = Fe_2(AsO_3)_2 + 6NaCl.$$

Test its solubility in dilute hydrochloric acid, and in ammonia.

This precipitate of *ferric arsenite* is harmless when taken into the stomach, provided the contents of the stomach are not acid. Hence, *freshly precipitated ferric hydroxide* ($Fe_2(OH)_6$) is the best antidote to poisoning by arsenic. It unites with the acid of the stomach to form ferric chloride and precipitates the arsenic as arsenite. The ferric hydroxide can be prepared by the action of ammonia on ferric chloride, but must then be carefully washed, since ferric arsenite is somewhat soluble in ammonia. It is better prepared by the action of calcined magnesia on solution of ferric chloride; or a mixture of sodic carbonate and ferric chloride may be given.

Experiment 123.—Add some cupric sulphate solution to sodic arsenite in a t. t. A green precipitate (Scheele's green) is thrown down:

$$CuSO_4 + Na_2HAsO_3 = CuHAsO_3 + Na_2SO_4.$$

This green is often used for colouring wall papers, &c., and has been the cause of many cases of poisoning. *Schweinfurth green* is prepared from Scheele's green by boiling it with acetic acid. (Try it). *Paris green* is a variable mixture of these substances with others used merely as make-weights, or diluents.

Experiment 124.—Add a few drops of argentic nitrate solution to sodic arsenite. A yellow precipitate of argentic arsenite is formed. Test its solubility in nitric acid and in ammonia.

144. **Arsenic Acid.**—H_3AsO_4.—Prepared by action of oxidising agents and water on arsenic trioxide.

Experiment 125.—Put a little arsenic trioxide in a small porcelain basin, add a small quantity of strong nitric acid, and heat on the water bath. Red fumes are evolved (N_2O_3); evaporate to a syrup, and keep. This is arsenic acid containing a little water:

$$2HNO_3 + As_2O_3 + 2H_2O = 2H_3AsO_4 + N_2O_3.$$

Orthoarsenic acid (H_3AsO_4) is a strong tribasic acid. *Pyroarsenic* ($H_4As_2O_7$), and *metarsenic* ($HAsO_3$) acids can be prepared by heating the ortho-acid.

ARSENATES are very like the corresponding phosphates, being generally exactly the same in crystalline form (*isomorphous*). Disodic hydric arsenate ($Na_2HAsO_4.7H_2O$) is used in medicine. It is a white, crystalline, soluble salt, prepared by fusing together arsenic trioxide (10 parts), sodic nitrate (8½ parts), and dry sodic carbonate (5½ parts); dissolving in 35 parts of distilled water, filtering, and evaporating.

Experiment 126.—Dissolve the acid from Experiment 125 in a little water, colour with litmus, and add solution of caustic soda until neutral. With this solution make the tests for orthophosphoric acid (Art. 122).

Arsenates respond to the same tests as phosphates, but argentic nitrate gives a *chocolate* coloured precipitate (Ag_3AsO_4).

Experiment 127.—To solution of sodic arsenate add a little sodic acetate ($NaC_2H_3O_2$) and then ferrous sulphate ($FeSO_4$). A white precipitate of *ferrous arsenate* ($Fe_3(AsO_4)_2$) is thrown down. It quickly turns greenish owing to absorption of oxygen from the air:

$$2Na_2HAsO_4 + 2NaC_2H_3O_2 + 3FeSO_4 = Fe_3(AsO_4)_2 + 3Na_2SO_4 + \underset{\text{Acetic acid.}}{2HC_2H_3O_2}.$$

Ferrous arsenate is used in medicine. Ferrous phosphate ($Fe_3(PO_4)_2$) can be prepared in the same way from sodic phosphate. (Try.)

145. **Arsenic and Sulphur.**—Three sulphides are known:

Arsenic disulphide, or realgar	As_2S_2
Arsenic trisulphide, or orpiment	As_2S_3
Arsenic pentasulphide	As_2S_5

Experiment 128.—Treat some solution of arsenic trioxide in dilute hydrochloric acid with hydric sulphide. A yellow precipitate (As_2S_3) is formed:

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

Test its solubility in sodic hydroxide, in ammonic sulphide ($(NH_4)_2S$), and in strong hydrochloric acid.

Experiment 129.—Dissolve a little arsenic trioxide in sodic hydroxide and treat the solution with hydric sulphide. No precipitate is formed. (Why is arsenic trisulphide not formed, as in Experiment 128?)

Experiment 130.—Test some solution of sodic arsenate with hydric sulphide. No precipitate is formed. Acidify with hydrochloric acid and repeat the test. A yellow precipitate ($As_2S_3 + S_2$) is formed. Try its solubility as in Experiment 128.

Two of the sulphides of arsenic (As_2S_3 and As_2S_5) combine with the sulphides of the alkali metals to form soluble *sulphur salts*, in which sulphur plays the part of the oxygen of ordinary salts. This explains the solubility of these sulphides in alkaline sulphide solutions; for example, in Experiment 128, when arsenic trisulphide dissolves in ammonic sulphide, *ammonic sulpharsenite* ($(NH_4)_3AsS_3$) is formed.

146. **Arsenic and Hydrogen.**—*Arsine, or arseniuretted hydrogen* (AsH_3) is the only compound of importance.

Experiment 131.—Fit a 4-ounce wide-mouthed bottle with a cork twice bored and provided with a thistle funnel passing nearly to the bottom, and a hard glass tube passing just through the cork, both tubes fitting tightly. The hard glass tube must be bent at right angles and drawn out at the point. Cover the bottom of the bottle with granulated zinc, push in the stopper tightly, pour in through the funnel enough dilute sulphuric acid to fill the bottle about one-fourth. Be sure that the funnel dips below the surface of the acid. Hydrogen is evolved and issues from the glass jet. After two or three minutes wrap a towel around the bottle and light the hydrogen. (Why not at once?) Hold a piece of cold porcelain in the flame for a second or two and see if it is blackened. If it is, there is probably arsenic in the zinc. If not, pour through the funnel a few drops of aqueous solution of arsenic trioxide. The flame of hydrogen very soon becomes livid bluish. Try with the cool porcelain. A metallic spot is formed. Make several of these, and then set the apparatus in a draught or out of doors. Try the effect on the spots, of (1) ammonic sulphide, (2) hydrochloric acid, (3) bleaching powder solution. Results :

(1) (2)

(3)

This is *Marsh's test* for arsenic. For very delicate cases, the hydrogen should be dried by a *soda-lime tube. Explanation :* Nascent hydrogen reduces arsenic trioxide, forming arsine and water :

$$As_2O_3 + 6H_2 = 2AsH_3 + 3H_2O.$$

Arsine (an invisible gas) is decomposed by the heat of the hydrogen flame, and the metallic arsenic is condensed on the porcelain.

Arsine is formed in vegetable matters containing arsenic when certain minute fungi are growing in them, e.g., in arsenical wall papers. The air of a room may thus become contaminated by this intensely poisonous gas. One small bubble of the pure gas has been known to kill a man.

147. Arsenic and Halogens.

ARSENIC TRICHLORIDE ($AsCl_3$) is a colourless volatile liquid, formed by the action of sulphuric acid on a mixture of arsenic trioxide and sodic chloride. This explains its presence in hydrochloric acid prepared by means of arsenical sulphuric acid. It dissolves in water, at the same time decomposing:

$$2AsCl_3 + 3H_2O = As_2O_3 + 6HCl.$$

ARSENIC TRI-IODIDE (AsI_3) is used in medicine It is prepared by carefully heating arsenic and iodine together. (In what proportion?). In Donovan's solution, it is combined with mercuric iodide ($AsI_3 + HgI_2$), and forms a clear colourless solution. The other halogen compounds are of little importance ($AsBr_3$, AsF_3, and AsF_5).—Clemen's "bromide of arsenic" (so-called) is a solution of arsenic acid and hydrobromic acid, prepared by the action of bromine on arsenic trioxide.

148. Tests for Arsenic.—(See Experiments 118, 128, 130, and 131.)

1. To a solution of arsenic trioxide in dilute hydrochloric acid add a drop of *ammonio-cupric sulphate* (prepared by adding ammonia to cupric sulphate solution gradually, until the precipitate at first formed is just redissolved). A green precipitate (Scheele's green) appears.

2. *Reinsch's Test.*—Put a thin strip of bright copper in some hydrochloric acid solution of arsenic trioxide, and boil (in a t. t.). Arsenic is deposited on the copper. Remove the copper, wash it well (without rubbing), dry it by holding it over a flame

(not too near), put it in a narrow dry t. t. and heat it. Arsenic and the trioxide are sublimed upon the tube. Try this test with some green wall papers, by digesting them with strong hydrochloric acid, diluting with water, and then using the solution as directed above.

QUESTIONS AND EXERCISES.

1. Compare arsenic and phosphorus (*a*) as to physical properties, and (*b*) as to their compounds.

2. Show the analogy between oxygen and sulphur, as seen in the compounds of arsenic.

3. In what proportion should ferric chloride and sodic carbonate be mixed so as to produce ferric hydroxide :

$$Fe_2Cl_6 + 3Na_2CO + 3H_2O = Fe_2(OH)_6 + 6NaCl + 3CO_2.$$

4. What data have you for concluding that arsenic is triad and pentad ?

5. How much mispickel will (theoretically) give 10 lbs. of arsenic.

6. In what respect does the molecule of arsenic deviate from the general rule ? What other element shows the same deviation ?

7. Is arsenic a metal or a non-metal ?

8. What is the meaning of "isomorphous" ?

9. In testing for arsenic with hydric sulphide the solution is made acid. Why ?

10. In Marsh's test oxidising agents must be absent. Why ?

11. Balance the following equations :

(1) $As + HNO_3 = H_3AsO_4 + NO_2 + H_2O.$
(2) $As_2O_3 + HNaO = Na_3AsO_3 + H_2O.$
(3) $NH_4OH + Fe_2Cl_6 = NH_4Cl + Fe_2(OH)_6.$
(4) $Na_2HAsO_4 + AgNO_3 = Ag_3AsO_4 + NaNO_3 + HNO_3.$

12. Write the formulas for the following compounds : *Sodic dihydric arsenate, cupric hydric arsenite, sodic thioarsenite,* and *ammonic orthoarsenate.*

CHAPTER XIII.

CARBON AND ITS COMPOUNDS.

149. **Carbon** ($C^{iv} = 12$).—This element has three allotropic modifications: (1) *diamond*, (2) *graphite*, (3) *charcoal* (lamp black, &c.) Diamond and graphite are crystalline; charcoal is amorphous.

1. DIAMONDS are found in pebbly deposits of ancient rivers, in South Africa, Australia, South America, &c. It is the purest form of carbon, and its nature remained long unknown, until it was proved to be carbon by burning it in oxygen.—An impure black variety, *carbonado*, is used for polishing the diamonds.—Diamond is one of the hardest substances known. When pure it is colourless. Specific weight = 3.5 to 3.6. Its crystals are modifications of the cube. Its great lustre is due to its strong refractive power on light. At a high temperature it burns in air or oxygen forming carbon dioxide (CO_2). It has never been prepared artificially, although many attempts have been made.

2. GRAPHITE is found in lumps in granite, &c., well crystallised; or in obscurely crystalline masses of *plumbago*, or *black lead*. The best black lead is found in Cumberland, England. Graphite can be artificially prepared by crystallising carbon from molten iron. It often occurs in pig iron. It is not pure carbon, but leaves considerable ash on burning.—It is a black metallic-

looking substance, greasy to the touch; specific weight = 2 to 2.6. It burns with great difficulty at a high temperature to form carbon dioxide. It is used for lead pencils, crucibles, for polishing gunpowder grains, &c., and as a lubricant.

3. AMORPHOUS CARBON. — Lamp-black, gas-carbon, coke, charcoal, and animal black are impure amorphous carbon. *Lamp-black* is prepared by burning turpentine, &c., with a scant supply of air and collecting the soot on woollen cloths. It consists of particles of carbon covered with tar. It is used in the preparation of Indian ink, black paint, and printers' ink, and to give a grey shade to calico.—*Gas carbon* gathers in the upper part of the retorts in which coal is distilled in the manufacture of coal gas. It is very hard and resonant, and conducts electricity. It is used as the negative element in electric batteries, and in the manufacture of microphones.—*Coke* remains in the bottom of the gas retorts when the process of distilling is complete. It is hard and dense, and burns (at a high temperature) without smoke and giving an intense heat. It is used in smelting operations and as fuel in engines.—*Charcoal* is prepared by the destructive distillation of wood or bones. In the latter case it is called *animal charcoal*, or *bone black*.

Experiment 132.—Heat a small bit of dry wood in a mattrass, applying a match to the open end. A combustible *gas* is evolved, *tar* and *water* gather on the sides, and *charcoal* remains as the skeleton of the wood. Try the same experiment with a bit of bone, horn, or dried meat. Similar results are obtained.

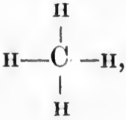
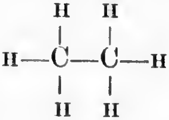
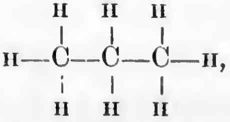
Charcoal has the power of absorbing gases and causing their oxidation when they are oxidisable. A piece of charcoal made from the shell of the cocoa-nut will absorb 171 times its volume of ammonia gas and 100 times its volume of hydric sulphide. It must first be heated to expel the gases already condensed in its pores. On account of this property it is used as a filter for air, being made into so-called "respirators." Evidently the charcoal in these respirators should be often renewed, or taken out and heated red-hot, in order to expel the condensed gases.

Experiment 133.—Fill a filter paper (placed in a funnel) about two-thirds full of bone-black. Colour some water with indigo, heat it, and pour it on the filter.

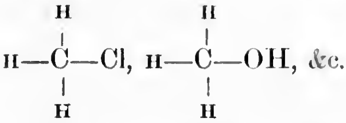
Charcoal has the property of extracting colouring matters from solution. Bone-black is used for this purpose in sugar refining.

Experiment 134.—Fill a filter with fresh ground charcoal, and pour some hydric sulphide water on it. If the smell has not been destroyed when the water runs through pour it on again.

Charcoal has the power of extracting offensive animal and vegetable matters from water. It is used for filtering water. Filters should be renewed very often. The charcoal should either be replaced or be taken out and heated red-hot to destroy the substances extracted from the water.—Charcoal poultices are used for purifying foul wounds. They are very efficacious.—*Coal* is impure amorphous carbon. It is the remains of primeval forests which have undergone a slow process of decay. This process is now going on in *peat bogs*. *Anthracite* is very pure, containing as high as 94 % carbon. *Bituminous, or soft coal* contains much hydrogen, oxygen, and nitrogen, and only up to 75 % carbon. *Lignite* is coal in the process of formation. It contains up to 70 °/$_0$ carbon. *Jet* is a hard variety of coal which takes a good polish.

150. **Compounds of Carbon.**—Carbon occurs in nature combined as well as free. As shown in Experiment 132, it forms an essential constituent of *animal and vegetable bodies.* In fact, it is *the* element of organic tissues.—It is found in vast quantities, as *carbonates,* e. g., *calcic carbonate* (limestone, marble, chalk, &c.), *magnesic carbonate* (in mountain limestone); also in the air as *carbon dioxide* (CO_2); in *marsh gas* (CH_4), *petroleum, shale,* &c.—The number of the compounds of carbon is so vast that a special branch of chemistry, *Organic Chemistry,* is devoted to their consideration. Many of them exist already formed in the bodies of plants and animals, and in the crust of the earth; but many are the product of the laboratory. The great number of the carbon compounds is due to the property which carbon atoms have of *uniting with each other* so as to form groups of carbon atoms capable of acting as the nuclei of molecules. Thus, carbon and hydrogen can unite in a great number of different proportions, the simplest compound being that having *one* carbon atom in the molecule,  $H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H$, the next containing *two,*  $H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H$, the next *three,*  $H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H$, and so on. The hydrogen atoms can be replaced by other atoms

and groups, and thus *derivatives* are formed. Thus,



$$H-\overset{\displaystyle H \atop |}{\underset{\displaystyle | \atop H}{C}}-Cl, \quad H-\overset{\displaystyle H \atop |}{\underset{\displaystyle | \atop H}{C}}-OH, \text{ \&c.}$$

151. **Sources of Carbon Compounds.**—*Plants* and *animals* supply compounds of carbon ready formed, and the most fruitful natural sources are the remains of organised bodies. In fact, if we exclude some of the naturally occuring carbonates, it may be stated that all carbon compounds not of artificial origin are the products of vegetable or animal organisms.

Petroleum supplies a great number of compounds of carbon and hydrogen, mostly belonging to the class of *paraffins* (C_nH_{2n+2}).—By the distillation of coal, *coal tar* is obtained. This once waste product has developed during the last 30 years into an almost inexhaustible source of new and valuable compounds. From it are manufactured the aniline and other beautiful colours, artificial essences and perfumes, and substances which in some degree serve as substitutes for quinine, &c. Lately, *saccharine*, said to be 220 times as sweet as sugar, has been made from coal-tar products.—*Bone-oil* and *wood-tar* are sources of organic compounds.

CARBON AND OXYGEN.

152. **Carbon Dioxide,** CO_2. — Commonly called *carbonic acid.*

OCCURRENCE.—Free in the air and in the crust of the earth, issuing from fissures, as in the celebrated Grotto del Cane. It is found combined in the carbonates. It is a product of the combustion, decay, and fermentation of organic substances. It is also given out by animals in respiration.

PREPARATION.—**Experiment 135.**—Put some lumps of marble or limestone in an 8-ounce bottle provided with a gas-delivery tube bent twice at right angles so as to collect a heavy gas by displacement of air. Fill the bottle about one-third with dilute hydrochloric acid, and collect several bottles of the gas by displacement of air, covering them with pieces of glass. Try to light the gas as it issues from the tube. Bubble some of it through blue litmus. Allow it to bubble through lime water. Evaporate the solution left in the bottle and get crystals of *calcic chloride* ($CaCl_2.6H_2O$).

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Carbon dioxide can also be prepared by heating limestone to a red heat:

$$CaCO_3 = CaO + CO_2.$$

PROPERTIES.—A heavy, invisible gas, of slightly pungent smell, and sharp, sour taste. Specific weight = . (Calculate.) It is not a strong poison, but has a *narcotic* action, and does not support animal life. It can be liquefied at —78.2° C. under the atmospheric pressure. At higher temperatures it can be liquefied by increased pressure; and when the pressure is removed the liquid boils, *part of it becoming frozen into a snow-like solid.* (Explain this.) It is somewhat soluble in water; at 0° C., 1.8 vols. in 1 of water; at 15° C., 1 vol in 1. The solution is slightly acid, and probably contains *carbonic acid* (H_2CO_3).

Experiment 136.—Put a lighted match into a bottle of carbon dioxide. Put another bottle, mouth downwards, in recently boiled cold water, and let it stand a few minutes with occasional shaking. Try the same experiment with solution of caustic soda. *Pour* a bottle of gas into a bottle filled with air, testing with a lighted match.

Experiment 137.—Bubble air from the lungs through clear lime water by means of a glass tube.

Carbon dioxide is absorbed by strong bases, with which it forms salts, the *carbonates.* It is being constantly given off into the air from the bodies of animals, but the quantity in the air does not increase. Vegetables use it as fast as animals excrete it. Carbon dioxide is present in the air to the extent of about 4 volumes in 10,000. In poorly ventilated rooms the proportion much exceeds this, and the relative quantity of gas is a good measure of the purity of the air. The danger, however, is not so much from carbon dioxide as from other waste products of the body expired with the air and exhaled from the general surface of the body. It is these which give the *stale* smell to a poorly ventilated room.—On account of its high specific weight carbon dioxide collects in depressions such as wells and cellars. Accidents often occur from workmen descending into wells and brewery vats filled with the gas. A good precaution is to lower a light before descending, although air which will support combustion often contains enough carbon dioxide to produce death.

153. **Carbonic Acid and Carbonates.**—The acid is not known except in solution. It is dibasic, and very weak, not forming salts with the weaker bases, such as ferric hydroxide, aluminic hydroxide, &c.—There are two series of *carbonates,* (1) *normal,* e.g., Na_2CO_3, and (2) *acid,* e.g., $NaHCO_3$. The carbonates of the alkali metals (K_2CO_3.Na_2CO_3, &c.) are soluble in water;

all other normal carbonates are insoluble. But many of the insoluble normal carbonates combine with carbonic acid to form unstable, sparingly soluble acid salts. Thus, calcic carbonate ($CaCO_3$), magnesic carbonate ($MgCO_3$), ferrous carbonate ($FeCO_3$), &c., dissolve in water containing carbonic acid. The solubility is increased by pressure of the gas.

Tests.—1. Carbon dioxide renders lime water turbid:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

2. Carbonates effervesce with hydrochloric acid. (Try with several of the carbonates.) If the evolved gas be poured into a t. t. containing clear lime water, it renders it turbid on shaking up.

154. Carbon Monoxide, CO.—Also called *carbonic oxide.*

PREPARATION.—**Experiment 138.**—Carefully heat a little dry powdered *potassic ferrocyanide* ($K_4FeC_6N_6$) with about 10 times its weight of concentrated sulphuric acid, and apply a light to the mouth of the tube. A gas is evolved which burns with a lambent blue flame:

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO.$$

Carbon monoxide is also formed when *oxalic acid* ($C_2H_2O_4$) is heated with sulphuric acid:

$$C_2H_2O_4 = CO + CO_2 + H_2O.$$

It is formed when carbon burns in a scanty supply of air, as in the inner parts of a fire.

PROPERTIES.—A colourless gas, of very faint odour; sp. wt. = 0.966. It burns with a pale blue flame

($CO + O = CO_2$), as seen on the top of a coal fire. It can be condensed to a liquid at —139.5° by a pressure of 35.5 atmospheres. It is sparingly soluble in water (3 in 100); easily in ammoniacal solution of *cuprous chloride* (Cu_2Cl_2). It is a deadly poison, combining with the hæmolglobin of the blood and thus preventing its aëration. As it often escapes combustion in coal and charcoal fires, it contributes greatly to the poisonous condition of ill-ventilated rooms. Open charcoal fires (braziers) are especially dangerous.

155. **Carbon Bisulphide**, CS_2.—

PREPARATION.—By passing sulphur vapour through long tubes filled with red hot charcoal.

PROPERTIES.—A mobile colourless liquid, of pleasant ethereal smell when pure, but generally having a disgusting odour due to impurities. Sp. wt. = 1.29. It does not mix with water.

Experiment 139.—Pour a little carbon bisulphide into a t. t. of water. Note the smell. Shake up with the water. Heat a few drops of carbon bisulphide gently in another t. t. It boils readily. Put a light to the mouth of the t. t.

Carbon bisulphide boils at 46° C., forming a heavy vapour, very explosive when mixed with air:

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

It evaporates quickly when exposed to the air and lowers the temperature. (Try a drop on the hand.) It mixes in all proportions with ether and alcohol; and dissolves fats, oils, india-rubber, phosphorus, iodine, bromine, &c.

A solution of india-rubber in carbon bisulphide is used for cementing rubber goods. Its vapour mixed with nitrogen dioxide (NO) burns with a dazzling white light used in photography. — Carbon bisulphide is poisonous. It is antiseptic, and is used for preserving meat, &c.

Sulphocarbonic acid, H_2CS_3.—Also called *thiocarbonic acid*. This acid and its salts are analogous to carbonic acid and the carbonates.

Potassic sulphocarbonate, K_2CS_3, can be prepared by dissolving carbon bisulphide in solution of potassic sulphide:

$$K_2S + CS_2 = K_2CS_3.$$

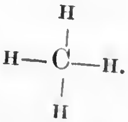
From this, sulphocarbonic acid can be separated as an unstable oily liquid by the action of hydrochloric acid:

$$K_2CS_3 + 2HCl = 2KCl + H_2CS_3.$$

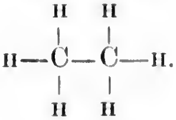
It soon decomposes into carbon bisulphide and hydric sulphide:

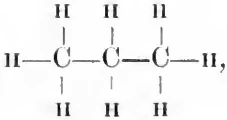
$$H_2CS_3 = H_2S + CS_2.$$

CARBON AND HYDROGEN.

156. **Hydrocarbons.**—The number of these is so great that only a very small proportion of them can be described.—The simplest compound of carbon and hydrogen is that containing 1 carbon atom and 4 hydrogen atoms in the molecule,  $\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$. A molecule containing 2 carbon atoms can have at most 6 hydrogen atoms, for each of the carbon atoms has 4 bonds, and 1 of these is

employed in holding the carbon atoms themselves together.

The graphic formula for this molecule is  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$.

The next would be  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$, and so on, the molecules increasing regularly by CH_2; so that a general formula, C_NH_{2N+2}, can be written. Very many members of this series are known. Most of them are found in petroleum oil and in the gas accompanying it. It is called the *Paraffin Series :*

Marsh gas, or methane....	CH_4	..... Gas
Ethane	C_2H_6	.... Gas
Propane.................	C_3H_8	..... Gas
Butane..................	C_4H_{10}	..... Boils at 1° C.
Pentane	C_5H_{12}	..... “ 38° C.
Hexane..................	C_6H_{14}	..... “ 70° C.
&c.	&c.	

The different members of this series resemble each other in chemical properties. *Paraffin oil* (kerosene) is a mixture of the liquid members. *Paraffin wax,* used in making candles, is a mixture of solid paraffins, the higher members. These substances are obtained by the fractional distillation of petroleum, which is a product of the decomposition of primeval forests.

Besides the paraffin series there are several other series of hydrocarbons containing a less proportion of hydrogen, the *Olefines* having the general formula C_NH_{2N}, — (C_2H_4, C_3H_6, &c.); the *Acetylene Series,* C_NH_{2N-2},

— (C_2H_2, &c.), and so on. In each of these series the difference between consecutive members is CH_2, and the members of one series have a general likeness to each other in chemical properties.

157. Marsh Gas, or Methane, CH_4.

OCCURRENCE.—In the mud of marshy and other stagnant pools, rising in bubbles when the mud is stirred. These bubbles can be collected in a bottle by displacement of water, and are found to be combustible. It is also found along with petroleum in vast quantities. The natural and artificial gas springs of America and Asia give off great quantities of a mixture of hydrogen, methane, and ethane, with small quantities of other hydrocarbons. In some parts of Pennsylvania, this natural gas is used for illuminating and other purposes. The sacred fires of Baku, in Persia, have been burning for ages. Marsh gas is the dreaded "fire damp" of coal miners. It is also present in considerable quantity in *coal gas.*

PREPARATION.—**Experiment 140.**—Mix well one part dried *sodic acetate* ($NaC_2H_3O_2$) with four parts *soda-lime* (a mixture of sodic and calcic hydroxides), and heat in a hard glass t. t., collecting the gas in the usual way over water. A mixture of lime and sodic carbonate remains:

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

PROPERTIES.—A colourless gas, inodorous, and harmless when breathed. Sp. wt. = 0.555. It burns in air with a pale blue flame, and does not support ordinary combustion.

Experiment 141.—Thrust a lighted match into a jar of the gas held upside down. Pour the gas from another jar upwards into a jar filled with air.

Methane is very explosive when mixed with air or oxygen :

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Frightful explosions occur in coal mines. For the protection of miners Sir Humphrey Davy invented the "Davy Lamp," in which the flame is surrounded by wire gauze. The metal conducts away the heat of the flame rapidly, and thus keeps the explosive mixture next to it below its point of ignition. The flame cannot pass through the gauze.

Experiment 142.—Hold a piece of wire gauze above a jet of gas, apply a light above the gauze and observe that the flame does not pass below.

Methane is sparingly soluble in water. It is very stable, like all the paraffins (*parum affinis* = having little affinity), resisting the action of nitric, sulphuric, and hydrochloric acids, and of other vigorous chemical substances. It cannot be got to unite with any element or compound, except by losing one or more of its atoms of hydrogen. The hydrogen can be replaced *in fourths* by the action of chlorine :

$$CH_4 + Cl_2 = \overset{\text{Monochlormethane.}}{CH_3Cl} + HCl.$$

$$CH_3Cl + Cl_2 = \overset{\text{Dichlormethane.}}{CH_2Cl_2} + HCl.$$

$$CH_2Cl_2 + Cl_2 = \overset{\text{Trichlormethane.}}{CHCl_3} + HCl.$$

$$CHCl_3 + Cl_2 = \overset{\text{Tetrachlormethane.}}{CCl_4} + HCl.$$

The molecule of marsh gas is incapable of taking up atoms except by replacement. It is a *saturated* compound, i.e., the carbon is saturated with hydrogen. *The paraffins are the saturated hydrocarbons.*

158. **Chloroform**, $CHCl_3$.—Formerly mentioned as *trichlormethane.*

PREPARATION.—By distilling at a gentle heat aqueous solution of bleaching powder with common alcohol (C_2H_6O).

Experiment 143.—Rub together one part bleaching powder and four of hot water, add one-tenth part strong alcohol and warm gently. Note smell, &c.

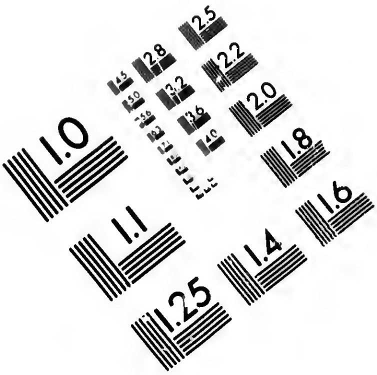
PROPERTIES.—A colourless liquid, of pleasant smell, and burning taste. It evaporates quickly when placed on the hand (Try it); and boils at 61° C. Sp. wt. = 1.525.

Experiment 144.—Put two or three drops of chloroform in a t. t. of water and shake. It dissolves, giving its odour to the water. Add a considerable quantity and try to dissolve it. Try with alcohol instead of water; also with ether.

Chloroform is slightly soluble in water, but mixes in all proportions with ether and alcohol. It is a good solvent for iodine, bromine, phosphorus, &c.—(Is it inflammable?)

When breathed as a vapour chloroform causes insensibility. It is an *anæsthetic.*—(Sir James Simpson, 1848.) It is now used in surgical operations very extensively, although ether is preferred by many surgeons. Its low boiling point renders it easy to administer as a vapour. It is also administered in the liquid form as a medicine.

IMPURITIES IN CHLOROFORM.—Great care should be taken in selecting chloroform for use as a medicine or an anæsthetic. The commercial article often contains deleterious substances, e.g., hydrochloric acid, chlorine, and chlorides of other organic compounds. *Pure chloroform* does not turn blue litmus red or give a precipitate with



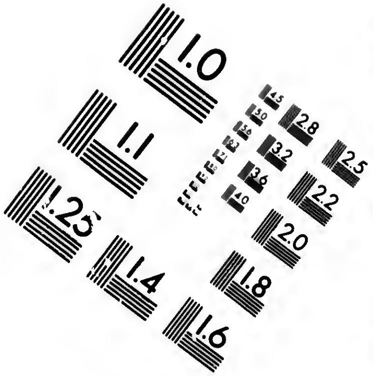
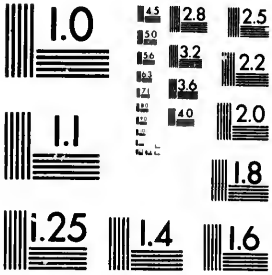
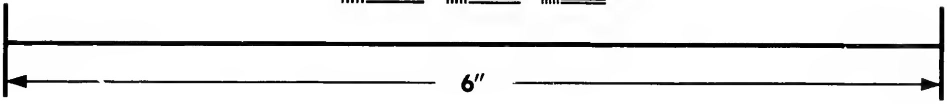
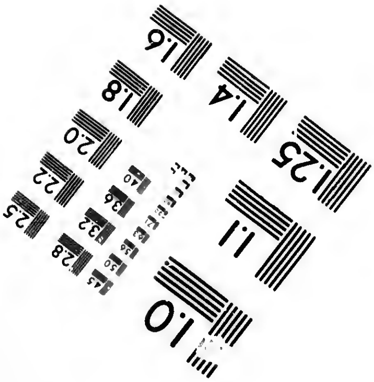
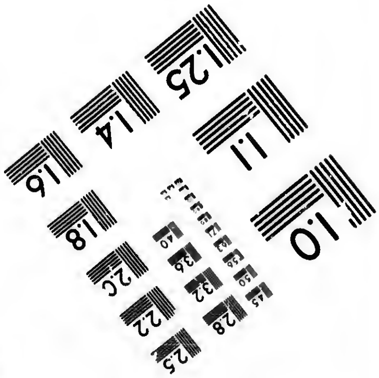


IMAGE EVALUATION
TEST TARGET (MT-3)









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argentic nitrate (impurities, HCl and Cl); it does not colour a mixture of potassic bichromate and dilute sulphuric acid green (alcohol, &c.); it is not coloured brown by potassic hydroxide or sulphuric acid; it does not cause bright sodium to tarnish, even when heated ($C_2H_4Cl_2$. &c.). If, when allowed to evaporate on a clean watch glass, chloroform leaves a strongly smelling residue, the alcohol from which it was prepared contained fusel oil.

Experiment 145.—Try these tests with samples from the druggists.

Iodoform (CHI_3) is a yellow crystalline solid prepared by adding iodine to a mixture of common alcohol and solution of sodic carbonate heated to 60°. It is insoluble in water, but soluble in alcohol and ether.

159. **Ethylene**, C_2H_4.—Also called "olefiant gas.' Is a constituent of coal gas.

PREPARATION.—By the action of potassic hydroxide on *monochlorethane* (C_2H_5Cl):

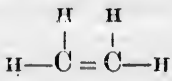
$$C_2H_5Cl + KOH = C_2H_4 + KCl + H_2O.$$

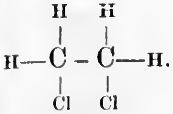
Or, by heating alcohol with strong sulphuric acid:

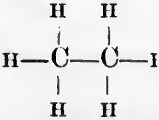
$$C_2H_6O = C_2H_4 + H_2O.$$

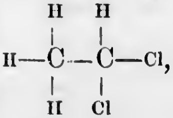
PROPERTIES.—It is the first member of the *olefine series.* It is a colourless gas, distinguished from the paraffins by the facility with which it unites directly with other substances, *without losing hydrogen.* Thus, it unites with an equal volume of chlorine to form *chloride of ethylene* ($C_2H_4Cl_2$), an oily liquid:

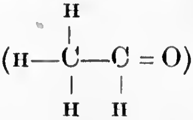
$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

Its molecule is *unsaturated*, and we express this fact by the graphic formula,  $H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H$, in which the carbon atoms are represented as united by two bonds. One of these can be divided so as to receive 2 atoms of chlorine,


$H-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C}}-H$. *The olefines are all unsaturated compounds.*

160. Isomerism.—As has been mentioned, methane is capable of entering into those chemical actions only in which its hydrogen atoms are *replaced* by other atoms or compound radicals. Thus, an atom of chlorine replaces one of hydrogen to form monochlormethane. This replacement has been made in a great many different ways, and the same substance is always obtained. It has been concluded that the four hydrogen atoms are exactly alike in relative position, so that it does not matter which is replaced. It is very important to get this idea clearly at the outset. It has been found also that only one *substitution product* of ethane having the formula, C_2H_5Cl, can be obtained; and it is therefore concluded that the six hydrogen atoms in ethane,  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$, are alike in position. But, when a second atom of hydrogen is replaced by chlorine, *two* substances are obtained, identical in chemical composition ($C_2H_4Cl_2$), but differing in properties. One of these is the substance mentioned in in Art. 151 as *ethylene chloride.* The only other different arrangement of the atoms is represented as follows:


$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-Cl$, both chlorine atoms being attached to

the same carbon atom. This second compound can be prepared from aldehyde ( $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\underset{\text{H}}{\text{C}}=\text{O}$), by replacing oxygen by chlorine; and it is distinguished from the first by the name *ethylidene chloride*. These two substances are *alike in composition, but different in properties*. This is a case of *isomerism*..

161. **Acetylene,** C_2H_2. — This compound is a colourless gas formed by the incomplete combustion of gases containing hydrocarbons. It has a strong disagreeable smell, which is easily observed in the smoke of a candle just blown out. It is produced in considerable quantity in a Bunsen burner "burning below." (Try it.) It can also be prepared by the action of alcoholic solution of caustic potash on ethylene chloride or bromide:

$$C_2H_4Cl_2 + 2KOH = C_2H_2 + 2KCl + 2H_2O.$$

It is poisonous when breathed, uniting with the hæmoglobin of the blood as carbon monoxide does. As it is formed by lamps when the flame is turned low, this practice should be discountenanced, especially in sick rooms.

Acetylene can be formed from the elements by passing a powerful current of electricity between carbon poles in an atmosphere of hydrogen. This is an important *synthesis*.

CARBON AND NITROGEN.

162. **Cyanogen Compounds.**—Nitrogen is present in all organised bodies. If nitrogenous matters such as horn, flesh, &c., be heated with sodium, a compound is obtained composed of sodium, carbon, and nitrogen ($NaCN$), and called *sodium cyanide.* When nitrogenous substances are heated with *potassic carbonate* (K_2CO_3), and iron scraps, a fused mass is obtained which yields on lixiviation a yellow crystalline salt, *potassic ferrocyanide* ($K_4Fe(CN)_6$). This salt gives a fine blue colour (Prussian blue) with ferric salts, and is the starting point in the preparation of the *cyanogen* (*blue-generating*) compounds. All these compounds contain the monad radical —CN, *cyanogen,* which can be set free, but, like an atom, unites immediately with another to form a molecule $(CN)_2$. The substance cyanogen (C_2N_2) can be prepared by heating *mercuric cyanide* ($Hg(CN)_2$). It is a very poisonous gas, having chemical properties like those of chlorine; and its compounds with metals are called *cyanides,* e.g.:

$$KCN,\ Fe\ CN)_2,\ Ca(CN)_2,\ \&c.$$

163. **Potassic Ferrocyanide.**—$K_4Fe(CN)_6.3H_2O$. Commercially known as *yellow prussiate of potash.*

PREPARATION.—Fuse refuse animal substances with potassic carbonate, and lixiviate the fused mass. A solution containing *potassic cyanide* (KCN) is obtained. To this add freshly precipitated *ferrous carbonate* ($FeCO_3$). It dissolves:

$$6KCN + FeCO_3 = K_4Fe(CN)_6 + K_2CO_3.$$

The solution is evaporated and the two salts separated by crystallisation, the potassic carbonate being much the more soluble of the two.

PROPERTIES.—A salt crystallising in large yellow prismatic crystals. (Examine a crystal, noting its "feel," taste, the ease with which a splinter can be split off, and the flexibility of the splinter.) It is soluble in about 4 times its weight of water. (Dissolve a small quantity and taste the solution.) It is not poisonous, and in large doses acts as a mild purgative.

Experiment 146.—Heat slightly a small crystal of potassic ferrocyanide in a t. t. It falls to a powder and water is condensed on the side of the tube. (From what source does the water come?) Heat more strongly, and the salt turns brown. It has been decomposed into potassic cyanide (KCN), *carbide of iron* (FeC_2), and nitrogen. (Write the equation.) Keep the residue.

Potassic ferrocyanide belongs to the class of *double cyanides*, and is composed of potassic and ferrous cyanides, $4KCN.Fe(CN)_2$. But these are so united that no ordinary test shows the presence of iron; and the salt does not possess the characters of a simple cyanide. It is a salt of *ferrocyanic acid* ($H_4Fe(CN)_6$). *All soluble simple cyanides are deadly poisons.*

161. **Hydrocyanic Acid,** HCN. — Originally called *prussic acid.* This is one of the most deadly and sudden poisons known. The vapour of the pure acid causes almost instant death, and even when largely diluted with air it causes headache and giddiness for some hours if inhaled for a few seconds. Unfortunately some persons are not able to detect its subtle odour—that of crushed cherry stones. Experiments with it must be

made very cautiously.—*Antidotes,—ammonia and chlorine water.*

PREPARATION.—Distil 2¼ oz. potassic ferrocyanide dissolved in 10 oz. water with 1 oz. sulphuric acid diluted with 3 oz. distilled water. Receive the distillate in 8 oz. distilled water until there is 17 fluid oz. Make up to 20 oz. with distilled water. This solution contains 2 % hydrocyanic acid; it is the *acidum hydrocyanicum dilutum* of the British Pharmacopœia.

$$2K_4Fe(CN)_6 + 6H_2SO_4 = 6KHSO_4 + \underset{\text{Everitt's Salt.}}{FeK_2.Fe(CN)_6} + 6HCN.$$

Experiment 147.—Add a little water to the residue from Experiment 146, and filter. To the filtrate add some very dilute sulphuric acid, and carefully smell. The peculiar odour of prussic acid can be noticed. (What is dissolved in the water? Write an equation showing the action of sulphuric acid.) Try solution of potassic ferrocyanide with the diluted sulphuric acid. Hydrocyanic acid is not set free.

PROPERTIES.—The pure acid is a colourless volatile liquid. The dilute solution has the smell of the acid, and is feebly acid in reaction. It gradually decomposes, the acid uniting with water and forming *ammonic formate* ($NH_4.CHO_2$):

$$HCN + 2H_2O = HCO_2.NH_4.$$

Another decomposition sometimes goes on in which an insoluble brown substance, *paracyanogen* (C_3N_3) is formed.

CYANIDES.—Hydrocyanic acid is a weak monobasic acid, very like hydrochloric acid in its chemical properties. The cyanides of the *alkali metals* (K, Na, &c.), of *barium calcium*, and *strontium*, and *mercuric cyanide*

($Hg(CN)_2$) are soluble in water. The other simple cyanides are insoluble in water, but dissolve in solutions of the alkaline cyanides to form *double cyanides.*

Experiment 148.—To a solution of argentic nitrate add a drop of solution of potassic cyanide. A white precipitate of argentic cyanide ($AgCN$) is thrown down:

$$AgNO_3 + KCN = KNO_3 + AgCN.$$

Add more potassic cyanide, and the precipitate is dissolved, owing to the formation of a soluble double cyanide ($AgCN.KCN$).

There are two classes of double cyanides: (1) those easily decomposed by dilute acids, and from which hydrocyanic acid is set free, and (2) those from which hydrocyanic acid is not set free by dilute acids. To (1) belong the double cyanides of potassium with silver, mercury, &c. To (2) belong the ferrocyanides, &c. *All the soluble simple cyanides and the double cyanides of class (1) are deadly poisons. The double cyanides of class (2) are not poisonous.*

Tests.—1. To a solution of hydrocyanic acid, or of a cyanide, add argentic nitrate. A white precipitate of argentic cyanide is formed. This is insoluble in nitric acid, and sparingly soluble in ammonia. (Compare $AgCl$.) (Why must a considerable quantity of argentic nitrate be added before a permanent precipitate is obtained with potassic cyanide?)

2. To a solution of the acid or of a cyanide add a few drops of ferrous sulphate solution, a drop or two of ferric chloride solution, and caustic soda (caustic potash, potassic carbonate, lime water, &c., will answer); warm gently, and acidify with hydrochloric acid. A blue colour or precipitate is formed (Prussian blue).

(1) $2KCN + FeSO_4 = Fe(CN)_2 + K_2SO_4.$

(2) $4KCN + Fe(CN)_2 = K_4Fe(CN)_6.$

(3) $3K_4Fe(CN)_6 + 2Fe_2Cl_6 = 12KCl + Fe_4(FeC_6N_6)_3.$

According to equations (1) and (2) potassic cyanide is converted into potassic ferrocyanide. This takes place best in presence of an alkali. When the alkali is neutralised by an acid, insoluble Prussian blue is formed. Both potassic ferrocyanide and Prussian blue are harmless.

3. To a drop or two of solution of potassic cyanide add a little ammonic sulphide (yellow), and evaporate to dryness in a porcelain dish on the water bath. Add a small quantity of ferric chloride solution. A blood red colour appears.

Explanation.—The sulphur in the yellow ammonic sulphide unites with potassic cyanide to form potassic sulphocyanate (KCNS). This, when treated with ferric chloride, forms *ferric sulphocyanate* ($Fe_2(CNS)_6$). The object of evaporating is to get rid of the excess of ammonic sulphide. (Add a drop of ammonic sulphide to solution of ferric chloride.)

165. **Cyanic Acid.**—HCNO. The potassium salt of this acid is formed along with potassic cyanide by the action of cyanogen gas on a solution of caustic potash:

$$(CN)_2 + 2KOH = K(CN) + K(CN)O + H_2O.$$

(Compare with *chlorine.*) It can also be prepared by oxidising potassic cyanide by fusing it with manganese dioxide (MnO_2): $KCN + O = KCNO$.

The acid itself is of little importance, but its ammonium salt ($NH_4.CNO$) possesses for us a great interest. It was from this salt that Wöhler, in 1828, first prepared *urea* artificially, and thus broke down the barrier between organic and inorganic chemistry. Previously to this, it was supposed that the chemical compounds associated with animal and vegetable life could not be made in the laboratory, and thus *organic* chemistry was a separate branch of the science.

Sulphocyanates.—These are salts of an acid ($HCNS$) which is related to cyanic in the same way as sulphocarbonic is to carbonic acid. The potassium salt ($KCNS$) is prepared by fusing potassic cyanide with sulphur. The ferric salt ($Fe_2(CNS)_6$) is of a blood red colour, seen when solutions of ferric chloride and potassic sulphocyanate are mixed. These salts are also called *thiocyanates*.

166. **Urea.**—$CO(NH_2)_2$. This substance is *isomeric* with ammonic cyanate; and if an aqueous solution of the latter be heated it is transformed into urea.

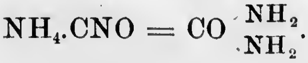
OCCURRENCE.—Urea is a waste product of the human and other animal bodies. It is the vehicle by which the waste nitrogen is carried out of the body in the urine.

PREPARATION.—**Experiment 149.** — Evaporate a small quantity of urine on the water bath to about one-third its bulk. Add to it about twice its volume of concentrated nitric acid. Pearly white scales of *nitrate of urea* are precipitated. Evaporate another small portion of urea to dryness, warm the residue with alcohol, filter, and evaporate the filtrate carefully to a small volume. On cooling, it deposits colourless needle-shaped crystals of urea.

Urea can be prepared artificially from potassic cyanide by oxidising it to cyanate ($KCNO$), from which ammonic cyanate is prepared by *double decomposition* with *ammonic sulphate* ($(NH_4)_2SO_4$):

$$2KCNO + (NH_4)_2SO_4 = K_2SO_4 + 2NH_4\,CNO.$$

Strong solutions of the salts are mixed, and the sparingly soluble potassic sulphate is precipitated. The solution at first contains ammonic cyanate, but this soon undergoes a change, especially if heated, by which the atoms in the molecule are rearranged, and urea results:



$$NH_4.CNO = CO\begin{matrix} NH_2 \\ NH_2 \end{matrix}.$$

PROPERTIES.—Urea is a colourless crystalline solid, soluble in its own weight of cold water, and in five parts of alcohol, but nearly insoluble in ether. It has a cooling taste like that of saltpetre. It unites with acids just as ammonia does, forming crystalline salts.

Experiment 150.—Heat a little pure urea with solution of caustic soda and note the smell, &c., of ammonia.

Urea is closely related to ammonia. It can be prepared by the action of ammonia on *chloride of carbonyl* ($COCl_2$), a substance formed by the direct union of chlorine and carbon monoxide :

$$COCl_2 + 2NH_3 = CO(NH_2)_2 + 2HCl.$$

In this action Cl is replaced by the monad radical $—NH_2$, called *amidogen.* Chloride of carbonyl is related to carbonic acid ($CO(OH)_2$), which may be looked upon as the *hydroxide of carbonyl.* Oxygen acids generally are the hydroxides of *acid radicals ;* and most acid radicals can be got combined with amidogen, thus forming a class of bodies called *am*ides from their relation to *am*monia. Urea is *carbamide.* Amides readily combine with water to form ammonium salts. Thus, when urea is heated above 100° C., with water, ammonic carbonate is formed :

$$CO(NH_2)_2 + 2H_2O = CO(ONH_4)_2.$$

This decomposition can be brought about more easily by heating with alkalis or acids. (Explain Experiment 150.) It goes on at the ordinary temperature during the fermentation of urine.

Tests.—1. Evaporate the liquid to small bulk, and treat with concentrated nitric acid as in Experiment 149. The crystals of urea nitrate ($CO(NH_2)_2.HNO_3$) are quite easily recognized.

2. Evaporate, and add a strong solution of oxalic acid ($C_2H_2O_4$). Crystals of oxalate of urea are formed ($2CO(H_2N)_2.C_2H_2O_4$).

Estimation of Urea.—The quantity of urea in urine can be readily determined by the Davy-Knop method, which depends on the fact that urea is decomposed by sodic hypobromite, and all its nitrogen set free:

$$CO(NH_2)_2 + 3NaOBr = CO_2 + N_2 + 3NaBr + 2H_2O.$$

This decomposition is brought about in an apparatus provided with a graduated tube in which the nitrogen is collected and measured. From the volume of nitrogen obtained from a given quantity of urine, the quantity of urea can be calculated.

167. **Uric Acid.**—$C_5H_4N_4O_3$. This substance is found in small quantities in human urine, but forms the principal part of the nitrogenous excrement of birds and reptiles. It occurs also in the human body as "chalk stones" in gout, and urinary calculi. *Guano* is the excrement of sea-fowl. It contains much *hydric ammonic urate* ($NH_4H.C_5H_2N_4O_3$), and from it large quantities of uric acid were formerly prepared for the manufacture of *murexide*, a red colouring matter, now superseded by aniline red.—If human urine be strongly acidified with hydrochloric acid and set aside for 24 hours small crystals of uric acid collect on the sides of the vessel. The buff-coloured sediment of urine is generally uric acid or the acid ammonium salt. As these compounds are about ten times as soluble in hot as in cold water, they disappear when the urine is heated.

Properties.—A crystalline solid, in small scales or plates, soluble at 20° C. in 14,000 parts of water; at 100° in 1,800 parts. It is insoluble in alcohol.

Urates.—Uric acid is dibasic, but the ordinary salts are the acid salts. *Sodic hydric urate* ($NaH\overline{Ur}$) is found in the urine and in gouty concretions. It is soluble at 15° in 1,100 to 1,200 parts of water, and at 100° in 123 to 125 parts.—The *potassium salt* ($KH\overline{Ur}$) dissolves at 20° in 700 to 800 parts, and at 100° in 70 to 80 parts of water. It is found as a urinary deposit in fevers.—*Acid lithium urate* ($LiH\overline{Ur}$) is more soluble than either of the above, dissolving at 20° in about 370 parts, and at 100° in 39 parts of water. The normal salts are freely soluble in water.—Solutions of urates deposit uric acid when acidified. This fact is of great importance in the treatment of uric acid stone, and gout. Both these diseases are due to excessive excretion of uric acid, and the treatment adopted is to transform the uric acid or acid salts into more soluble salts. The acidity of the urine is decreased by administering alkaline carbonates. As can be easily seen, lithium carbonate is the best.

Experiment 151.—Try to dissolve a little uric acid in water. Add some caustic potash or soda. The acid dissolves easily. Acidify the solution with hydrochloric acid.

Test.—To any substance containing uric acid add a few drops of strong nitric acid, and evaporate to dryness in a porcelain basin. (If the substance is a dilute solution it must first be evaporated to dryness.) The residue is *red*. Allow the basin to cool, and add a drop of ammonia solution. A fine, purple-red colour appears. This is the *murexide* test. Potash turns the red to blue.

CARBON, HYDROGEN, AND OXYGEN.

168. **Alcohols.**—Allied to the paraffins is a series of compounds which differ in composition from the paraffins by containing an atom of oxygen in the molecule.

Paraffins.		*Alcohols.*	
Methane	CH_4	Methyl alcohol	CH_4O
Ethane	C_2H_6	Ethyl "	C_2H_6O
Propane	C_3H_8	Propyl "	C_3H_8O
Butane	C_4H_{10}	Butyl "	$C_4H_{10}O$
Pentane	C_5H_{12}	Amyl "	$C_5H_{12}O$
&c.		&c.	

These alcohols can be prepared from the monochlorparaffins (CH_3Cl, &c.) by the action of water:

$$CH_3.Cl + H_2O = CH_3.OH + HCl.$$

Further, when they are acted on by phosphorus pentachloride (PCl_5), they lose an atom of oxygen and one of hydrogen, and gain one atom of chlorine:

$$CH_4O + PCl_5 = CH_3.Cl + POCl_3 + HCl.$$

From these facts it is concluded that the molecules of the alcohols contain the radical *hydroxyl* (— OH). They are thus *hydroxides* of the radicals, CH_3, C_2H_5, &c.

Methyl alcohol	$CH_3.OH$
Ethyl "	$C_2H_5.OH$
Propyl "	$C_3H_7.OH$
&c.	&c.

169. **Methyl Alcohol.** $CH_3.OH$.—Occurs in nature combined with acids, as in *oil of wintergreen* or

methyl salicylate. When wood is destructively distilled in the preparation of wood-charcoal, three other products are obtained: (1) A mixture of combustible gases (CH_4, &c.), (2) a watery liquid, and (3) a tarry liquid. From wood tar, *creosote* and other substances are obtained. The watery liquid (*pyroligneous acid*) is strongly acid, and from it is obtained *wood vinegar*, or impure acetic acid, and *wood spirit*, or methyl alcohol. The acid liquor is neutralized with lime, and the methyl alcohol is then distilled off and purified by fractional distillation, &c. It is also prepared in considerable quantities by distilling the waste ("vinasse") from the beet sugar industry.

PROPERTIES.—Pure methyl alcohol is a colourless liquid, similar to common alcohol in smell, and boiling at 55°.1. Specific weight = 0.8142. It mixes with water in all proportions, with contraction of volume and evolution of heat. It burns in air with a pale blue flame. It is a good solvent for fats, oils, resins, &c.

Experiment 152.—Mix a little methylic alcohol with an equal volume of water, and note the evolution of heat.

Experiment 153.—Set fire to a little methyl alcohol in a porcelain dish.

$$CH_4O + 3O = CO_2 + 2H_2O.$$

Commercial methyl alcohol is always impure, and has an unpleasant odour. It is used as a solvent, in the manufacture of aniline dyes, and in the preparation of *methylated spirit*, a mixture of common alcohol with a small percentage of crude methyl alcohol. This is unfit for use as a beverage, and is imported and manufactured free of duty in Great Britain. It is, however, often purified and used to adulterate liquors. It is probable that many of the cheaper sorts of strong liquors sold in this country are preparations of methylated spirit.

Methylic alcohol acts towards acids like a weak base, forming salts, which are unstable in presence of water. Thus, with hydrochloric acid it forms methyl chloride:

$$CH_3.OH + HCl = CH_3.Cl + H_2O.$$

Compare $K.OH + HCl = K.Cl + H_2O$.

The reaction is not complete unless the water be removed as fast as it is formed. The radical *methyl* (CH_3) thus plays the part of a monad metal. The salts of alcohol radicals are called *ethereal salts.* Many of them are volatile and have a pleasant ethereal smell.—When methyl alcohol is oxidised by a mixture of sulphuric acid and potassic bichromate ($K_2Cr_2O_7$) formic acid is produced:

$$CH_4O + O_2 = CH_2O_2 + H_2O.$$

170. **Ethyl Alcohol.**—C_2H_6O. This is *common alcohol,* the intoxicating principle of all spirituous beverages. It is also known as *spirits of wine.* It is prepared by the fermentation of sugar.

FERMENTATION.—This is a chemical action brought about by minute plants and animals, called *ferments,* which grow and multiply in the fermenting liquid. Certain conditions are necessary to the life of the ferments, and fermentation ceases when these conditions are absent. (1) The fermenting liquid must contain the elements of *food* for the ferment; a solution of *pure* sugar will not ferment. (2) The temperature must not be much above 40° C. nor much below 20° C. (3) There must be a proper proportion of water present. (4) The products of fermentation must not accumulate too much; and (5) certain substances called *antiseptics*, which are fatal to the life of the ferment, must be absent.—There are several kinds of fermentation:

1. *Alcoholic.*—Caused by yeast (*saccharomyces*), the products being *alcohol* and carbon dioxide:

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

2. *Acetous.*—Due to the vinegar plant (*mycoderma aceti*), which transforms alcohol by oxidation into *acetic acid.*

3. *Lactic.*—The lactic acid ferment has the power of transforming sugar into *lactic acid.* The ferment is present in sour milk.

4. *Butyric.*—Sugar is fermented into *butyric acid* by a ferment present in rotten cheese.

The germs, or *sporules*, of these ferments are present everywhere in the air, and wherever they find a suitable liquid they at once cause fermentation to begin.

Experiment 154.—Make a solution of commercial grape sugar in 40 or 50 times its weight of water. Put some yeast in the solution and fill three convenient dishes with it, also three test tubes. Invert the latter in the dishes. Keep No. 1 in a warm room. To No. 2 add a little carbolic acid and set it in the same room with No. 1, but not too near it. Set No. 3 in a cold place and surround it with snow or ice. Fermentation soon begins in No. 1, and bubbles of gas rise into the test tube. After a considerable quantity has collected, test it for carbon dioxide. Fermentation does not begin in Nos. 2 and 3.—Distil a few drops of alcohol from ale, receiving it in a cool test tube. Try taste and inflammability.

Alcohol is separated from fermented liquors by distillation. Common alcohol contains water, and often *fusel oil*, which consists principally of *amyl alcohol.* This is removed by fractional distillation and by filtering through charcoal. As it is poisonous it is important to have it absent from spirits of wine used in medicinal preparations.—*Absolute alcohol* is alcohol containing not more than 5 % of water. It is prepared by distilling the commercial article from quicklime, which holds the water. The last traces of water are very difficult to remove.—Much alcohol is now prepared from *glucose*, a sugar made from starch. When the glucose is made from potato-starch, the alcohol contains a large percentage of fusel oil and is highly poisonous.

PROPERTIES.—A colourless liquid of pleasant smell, boils at 78°.3, freezes at — 130°.5. When evaporated on the hand it leaves no unpleasant smell (if fusel oil is absent). It burns with a pale blue flame, forming carbon dioxide and water. (Write the equation.) It is a good solvent for organic substances, especially those insoluble in water; and is used extensively in the preparation of tinctures, &c.

Experiment 155.—Dissolve a litttle powdered resin in warm alcohol, and add water.

Beers contain from 2 % to 10 % of alcohol; *wines*, from 8 % to 30 %; *distilled liquors* (whiskey, brandy, &c.), up to 75 %. The different flavours are due to small quantities of substances present in the saccharine juice, formed during fermentation, dissolved out of the wood of the cask, or added by the manufacturer. *Proof spirit* contains 49 % by weight of alcohol.

In its chemical characters ethylic alcohol is like methylic. It is the hydroxide of ethyl (C_2H_5), and forms salts, e.g., *ethylic nitrate* ($C_2H_5.NO_3$), *chloride* ($C_2H_5.Cl$), *sulphate* ($(C_2H_5)_2SO_4$), &c. (Write equations showing the action of nitric, hydrochloric, sulphuric, and phosphoric acids on ethylic alcohol). *Sweet spirit of nitre* is a solution in alcohol of *ethyl nitrite* ($C_2H_5.NO_2$).

Experiment 156.—Mix some alcohol in a t. t. with one-tenth its volume of concentrated sulphuric acid, a little more of nitric acid, and some scraps of copper. Warm gently and note the smell. It is that of ethyl nitrite ("nitrous ether"). Attach a bent tube and distil a drop or two into a cool t. t.

Acetic ether is ethyl acetate ($C_2H_5.C_2H_3O_2$).

Experiment 157.—Pour a little rectified spirit (alcohol) on some dried sodic acetate in a t. t. Add a small quantity of concentrated sulphuric acid and distil into another t. t. kept cool. Note the smell, &c. of the acetic ether obtained.

Tests for Alcohol.—1. Heat a little alcohol (diluted with water) with a few drops of "bichromate mixture" ($4H_2SO_4 + K_2Cr_2O_7$). It is turned green, and the pungent odour of acetic *aldehyde* (C_2H_4O) can be observed:

$$3C_2H_6O + 4H_2SO_4 + K_2Cr_2O_7 =$$

$$3C_2H_4O + K_2SO_4 + \overset{\text{Chromic sulphate.}}{Cr_2(SO_4)_3} + 7H_2O.$$

2. Mix a little alcohol with solution of sodic carbonate, add iodine, and warm somewhat. Yellow crystals of iodoform (CHI_3) appear. This is a very delicate test.

171. **Higher Alcohols.**—*Propylic* ($C_3H_7.OH$), *butylic* ($C_4H_9.OH$), and *amylic* ($C_5H_{11}.OH$) alcohols are formed in small quantities during the fermentation of sugars. They boil at higher temperatures than does ethylic alcohol, and are partially separated from it in the process of distillation.

AMYLIC ALCOHOL ($C_5H_{11}.OH$) forms the greater part of "fusel oil." It is formed in large proportion by the fermentation of glucose prepared from starch (*amylum*). Hence its name. The quantity is especially large when the glucose has been manufactured from potato-starch; and amylic alcohol is sometimes called "potato-oil."

It is a colourless oily liquid of penetrating oppressive odour. It boils at 132° C. Specific weight = 0.818. When oxidised by bichromate mixture it forms first an *aldehyde* ($C_5H_{10}O$), and then *valerianic acid* ($C_5H_{10}O_2$). It is used to prepare *sodic valerianate* ($NaC_5H_9O_2$). It is highly poisonous, and its presence in cheap spirits is the cause of the furious intoxication often resulting from their use.

Amyl nitrite ($C_5H_{11}.NO_2$) is prepared by passing nitrogen tricxide (from nitric acid and starch) into amyl alcohol. It is a light yellow liquid, boiling at 99°. Specific weight = 0.902. It is insoluble in water, but soluble in alcohol. It has a peculiar action when inhaled, increasing the rate of the pulse and causing flushing of the face. If inhaled too long it causes suffocation by preventing the oxygen of the air from combining with hæmoglobin.

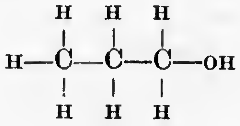
Experiment 158.—Dissolve a little amyl alcohol (or fusel oil) in an equal volume of concentrated sulphuric acid and cool. Add to this some solution of potassic or sodic nitrite in half its weight of water. Heat, and observe odour of amyl nitrite.

Several *artificial essences* are prepared from amyl alcohol, e.g., *essence of jargonelle pear* is *amyl acetate* ($C_5H_{11}.C_2H_3O_2$).

Test.—To detect amyl alcohol in spirits add a few drops of dilute acetic acid and *potassic permanganate* ($KMnO_4$) solution. The per-manganate is quickly decolourised if amyl alcohol be present. Or, shake with small crystals of *potassic iodide.* They are coloured yellow by amyl alcohol.

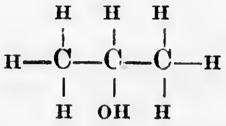
172. **Isomeric Alcohols.** — There is only one alcohol having the formula CH_4O, and one, C_2H_6O; but there are two propylic alcohols. One of them, when oxidised, gives first an aldehyde and then an acid—*propionic acid*—having the same number of carbon atoms in the molecule; the other gives a *ketone* and then breaks up into two acids having fewer carbon atoms in the molecule. For this and other reasons, it is believed that the hydroxyl is differently situated in the molecules of the two acids.

Primary propylic alcohol.....



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$$

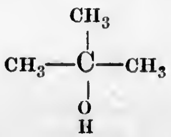
Secondary propylic alcohol ..



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-H}$$

A third kind of alcohols is known which, when oxidised, break up at once into acids having fewer carbon atoms in the molecule. These are *tertiary alcohols*; e.g.:

Tertiary butylic alcohol.........



$$\mathrm{CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3}$$

1. *Primary* alcohols are those in which the hydroxyl is attached to a carbon atom which is joined to only *one* other carbon atom.

2. *Secondary* alcohols have the hydroxyl attached to a carbon atom which is joined to *two* other carbon atoms.

3. *Tertiary* alcohols have the hydroxyl attached to a carbon atom which is joined to *three* other carbon atoms.

173. **Amines, or Substituted Ammonias.**—These are compounds related to the alcohols in the same way as urea is to carbonic acid (Art. 166); and they can be prepared by similar methods, viz., by the action of dry ammonia on the chlorides, bromides, or iodides of the alcohol radicals. Thus,

$$\underset{\text{Methyl chloride.}}{CH_3Cl} + NH_3 = \underset{\text{Methylamine.}}{CH_3.NH_2} + HCl.$$

They can also be regarded as derivatives of ammonia, formed by replacing a hydrogen atom by an alcohol radical. But a second, and a third hydrogen atom may be replaced, so that there are *three classes of amines, primary, secondary,* and *tertiary,* e.g., *mono-methyl-amine* ($CH_3.NH_2$), *di-methyl-amine* ($(CH_3)_2NH$), and *tri-methyl-amine* ($(CH_3)_3N$). Many of these compounds are found in nature. They resemble ammonia in their properties, uniting with acids to form salts, e.g , $C_2H_5.NH_3Cl$, *ethyl-ammonium chloride,* and dissolving freely in water to a strongly alkaline solution. They generally smell like ammonia.

174. **Ether.**—$(C_2H_5)_2O$. Also known as *sulphuric ether.* Ethers are *oxides of alcohol radicals,* and bear the same relation to alcohols as the oxides of the metals do to their hydroxides.

PREPARATION.—**Experiment 159.**—Mix 4 parts of alcohol with 9 of sulphuric acid and heat the mixture until it begins to boil (at 140° C.). Ether distils over. Note its odour.

On the large scale, as soon as the mixture begins to boil, a small stream of alcohol is allowed to flow into the still, and the temperature is kept at 140° C. Ether and water then distil over together continuously.

EXPLANATION.—Alcohol forms with sulphuric acid, *ethyl sulphuric acid*, or *ethylic hydric sulphate* ($C_2H_5.H.SO_4$):

$$C_2H_5.OH + H_2SO_4 = C_2H_5.H.SO_4 + H_2O.$$

The water distils as fast as it is formed. Alcohol decomposes ethyl sulphuric acid, forming ethyl ether and sulphuric acid:

$$C_2H_5.OH + C_2H_5HSO_4 = (C_2H_5)_2O + H_2SO_4.$$

The process is continuous, the alcohol being run in as fast as the ether and water distil. As far as the ultimate result goes, the action can be represented thus:

$$2C_2H_5OH = (C_2H_5)_2O + H_2O,$$

as a simple *dehydration* of alcohol.—It is purified by distilling from calcic chloride and lime to remove water and acids.

PROPERTIES.—A colourless liquid, bright and mobile. It boils at 34°.9, and the vapour forms an explosive mixture with air. Ether should never be boiled over a naked flame, but always in a hot water bath. Specific weight, 0.736.

Experiment 160.—Set fire to a little ether in a porcelain dish filled half-full of water.

Put some ether in a t. t. and immerse in water as hot as the hand can bear it. The ether boils.

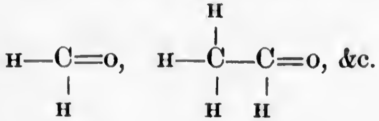
Ether is sparingly soluble in water, but mixes in all proportions with alcohol. It is a good solvent for fats and oils, resins, alkaloids, &c. Water is very slightly soluble in ether, and commercial ether generally leaves a wet stain when evaporated.—Ether is a good anæsthetic, but not so rapid in its action as chloroform. Its latent heat is high, and, as it evaporates so readily, an ether spray can be used to deaden by cold the sensibility of any part. Water can be frozen by the rapid evaporation of ether. (Try a drop or two of ether on the hand.)

Commercial ether generally contains considerable alcohol, which can be removed by washing with water. The presence of alcohol can be detected by finding the specific weight.

175. **Aldehydes.**—When primary alcohols are oxidised slowly, the first substances formed contain two atoms of hydrogen less than the alcohols. They are *Al*cohols *dehyd*rogenated, or aldehydes.

Alcohols.		*Aldehydes.*	
Methyl............	CH_4O	Formic............	CH_2O
Ethyl.............	C_2H_6O	Acetic............	C_2H_4O
Propyl...........	C_3H_8O	Propionic.........	C_3H_6O
&c.		&c.	

The atom of oxygen can be replaced by *two* atoms of chlorine; and from acetic aldehyde *chloride of ethylidene* ($C_2H_4Cl_2$) is thus formed. It is concluded that the atom of oxygen is not united with any of the hydrogen atoms, and the formulas of the aldehydes are written graphically thus:



$$\mathrm{H{-}\underset{\substack{|\\H}}{C}{=}O,\quad H{-}\overset{\substack{H\\|}}{\underset{\substack{|\\H}}{C}}{-}\underset{\substack{|\\H}}{C}{=}O,}\ \&c.$$

The group $-\underset{\substack{|\\ \mathrm{H}}}{\mathrm{C}}{=}\mathrm{O}$ is characteristic of the aldehydes.—(In what test already made was acetic aldehyde formed?)

Ketones are compounds analogous to the aldehydes, and are formed by the oxidation of secondary alcohols. Thus, *secondary propyl alcohol* ($CH_3.CHOH.CH_3$), yields on oxidation, *di-methyl ketone*, or *acetone* ($CH_3.CO.CH_3$). By further oxidation the ketones are broken up into acids having fewer carbon atoms in the molecule. In this they differ from the aldehydes.

176. **Chloral.**— $\mathrm{CCl_3{-}\underset{\substack{|\\H}}{C}{=}O}$. As can be seen by the formula, choral is derived from acetic aldehyde by the replacement of three atoms of hydrogen by chlorine; it is *trichloraldehyde*.

Preparation.—By the action of chlorine upon alcohol. Aldehyde is first formed:

$$CH_3.CH_2OH + Cl_2 = CH_3.COH + 2HCl.$$

Then, chlorine *replaces* hydrogen:

$$CH_3.COH + 3Cl_2 = CCl_3.COH + 3HCl.$$

Properties.—A colourless, somewhat oily liquid of pungent irritating odour. It boils at 94°. Specific weight

= 1.502. When mixed with $\frac{2}{3}$ its volume of water it unites with it, forming *chloral hydrate* ($CCl_3.CH(OH)_2$), a white crystalline solid.

Experiment 161.—Mix a drop or two of chloral on a watch glass with a drop of water. Crystallisation takes place. Dissolve these crystals in water, and note taste, &c.

Chloral hydrate is soluble in alcohol, water, and ether. By the action of strong bases it (as well as chloral) is converted into *chloroform* and *formic acid ;*

$$\overset{\text{Chloral.}}{CCl_3.CHO} + KOH = CHCl_3 + \overset{\text{Potassic formate.}}{HCO_2K}.$$

This explains the formation of chloroform by the action of bleaching powder on alcohol. Bleaching powder yields chlorine, and it always contains calcic hydroxide. —The substance generally sold as chloral is really the hydrate or its aqueous solution. It should give no precipitate with argentic nitrate, and should have an agreeable, somewhat aromatic, smell. Its taste is bitter and astringent.

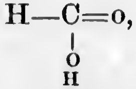
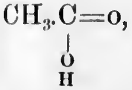
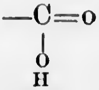
When chloral hydrate is injected under the skin it is decomposed by the alkali of the blood into chloroform and a formate, as shown in the above equation. Its effects are thus the same as those of chloroform. It is much used in cases of sleeplessness.

177. **Fatty Acids.**—By further oxidising the aldehydes a series of acids is obtained. They are called *fatty acids,* because the higher members are found combined in fats. They differ from the aldehydes by having one atom of oxygen more in the molecule.

Alcohols		*Aldehydes.*		*Acids.*	
Methyl....	CH_4O	Formic	CH_2O	Formic....	CH_2O_2
Ethyl......	C_2H_6O	Acetic......	C_2H_4O	Acetic.....	$C_2H_4O_2$
Propyl	C_3H_8O	Propionic...	C_3H_6O	Propionic.	$C_3H_6O_2$
&c.		&c.		&c.	

These acids are thought to contain hydroxyl, for, when they are treated with phosphorus trichloride (PCl_3), they yield substances in which Cl takes the place of OH, e.g.:

$$3C_2H_4O_2 + 2PCl_3 = 3C_2H_3O.Cl + P_2O_3 + 3HCl.$$

The expanded formulas of the acids are  $H-\underset{\substack{|\\O\\H}}{C}=o$,  $CH_3.\underset{\substack{|\\O\\H}}{C}=o$, &c., and the group  $-\underset{\substack{|\\O\\H}}{C}=o$ is characteristic. It is called *carboxyl*, and *the number of carboxyls in the molecule of an organic acid marks the basicity of the acid.*

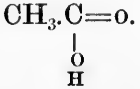
178. **Formic Acid.**—HCO.OH. First prepared by distilling the bodies of red ants; hence the name (*formica*, an ant). It can be prepared by careful oxidation of methyl alcohol; but more conveniently by distilling *oxalic acid* ($C_2H_2O_4$) with *glycerine* ($C_3H_6O_3$). The glycerine undergoes no change, and the oxalic acid is split into carbon dioxide and formic acid:

$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

PROPERTIES.—A colourless liquid, strongly acid, boiling at 99°.9. Specific weight = 1.22. When heated with concentrated sulphuric acid it breaks up into carbon monoxide and water. (Write the equation). It is a strong reducing agent, and when heated with argentic nitrate is oxidised to carbon dioxide, silver being set free.—It is a monobasic acid, and forms salts, the *formates*, all soluble in water, and all having the reducing properties of the acid.

Tests.—1. Neutral formates give a red colour with solution of ferric chloride.

2. Formates or formic acid, when boiled with solution of argentic nitrate, precipitate silver.

179. **Acetic Acid.** —  $\mathrm{CH_3.\underset{\substack{|\\ O\\ H}}{C}{=}O}$. Acetic acid is formed when acetic aldehyde (C_2H_4O) is oxidised; but its usual method of preparation is by the direct oxidisation of ethyl alcohol in the vinegar process.

Preparation.—1. By acetous fermentation of wines, beers, &c. In many cases sugar is the raw material, and it undergoes first alcoholic and then acetous fermentation:

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$

This gives a dilute solution.

2. By the destructive distillation of wood, a mixture of acetic acid, methyl alcohol, &c., is obtained. The watery acid liquid is neutralised with slaked lime ($Ca(OH)_2$), with which the acetic acid forms *calcic acetate* ($Ca(C_2H_3O_2)_2$):

$$2(H.C_2H_3O_2) + Ca(OH)_2 = Ca(C_2H_3O_2)_2 + 2H_2O.$$

The volatile liquids are distilled off, and the calcic acetate is purified by recrystallisation and then decomposed by sulphuric acid:

$$Ca(C_2H_3O_2)_2 + H_2SO_4 = CaSO_4 + 2C_2H_4O_2.$$

Sodic carbonate (Na_2CO_3) is often used instead of lime. (Write the equation for this.) (How can the acid be separated from the sodium salt?)

PROPERTIES.—A colourless liquid, of pungent, vinegary odour, and sharp acid taste. When free from water it boils at 119°. When pure, it acts upon the skin powerfully, causing blistering. It is solid below 16°.7, but may be cooled below 0° in closed vessels without causing it to solidify, being then in a state analogous to *supersaturation*. *Glacial acetic acid* is the solid acid. Of course, in warm weather it is not solid. The specific weight of the liquid is 1.08. Acetic acid dissolves in water in all proportions. *Vinegar* is an impure dilute solution (5 % to 10 %). *Sulphuric acid* is a frequent adulterant of vinegar, and can be detected by its giving a white precipitate with baric chloride. It sometimes contains *sulphurous acid*. (How test for this?).—The *acidum aceticum* of the B. P. contains only 33 % of the pure acid. A dilute solution ($4\frac{1}{2}$ %) is also used.

ACETATES.—Acetic acid, like all the acids of this series, is monobasic. Only *one* of the 4 atoms of hydrogen is replaceable by metal. The normal acetates are all soluble in water. (Of what other salts is this statement true?) *Sodic acetate* ($Na.C_2H_3O_2$), *zinc acetate* ($Zn(C_2H_3O_2)_2$), and *plumbic acetate* ($Pb.(C_2H_3O_2)_2$) are the most important.

Experiment 162.—To a solution of sodic carbonate in water coloured with a drop of litmus, add acetic acid (dilute) until the reaction is acid. Evaporate and obtain crystals of sodic acetate. This salt readily forms a supersaturated solution.

Experiment 163.—Dissolve a little *litharge* (PbO) in acetic acid, and evaporate to crystallisation. Examine the crystals as to taste, &c. Redissolve in water, and boil with some more litharge. It dissolves forming a *basic acetate* $\left(Pb\begin{smallmatrix}-OH\\-C_2H_3O_2\end{smallmatrix}\right)$.

Commercial acetate of lead (*sugar of lead*) often contains this basic salt.—*Verdigris* is *basic cupric acetate.* It forms as a green rust on copper or brass kitchen utensils when these are allowed to stand in contact with vinegary articles of food, &c. As it is very poisonous, cases of poisoning sometimes occur in this way.—Acetic acid dissolves many of the heavy metals, e.g., iron, zinc, lead, copper, &c., either unaided or aided by the oxidising action of the air. When it is formed in badly sealed cans of fruit, &c., it often dissolves the solder and thus renders the fruit highly poisonous.

Tests.—1. Warm some sodic acetate with sulphuric acid and observe the vinegary smell.

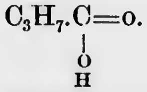
2. Heat a solution of an acetate with strong sulphuric acid and a little alcohol, and note the smell of acetic ether (ethyl acetate).

3. Add a few drops of neutral ferric chloride solution to neutral solution of an acetate. The blood-red colour of ferric acetate appears :

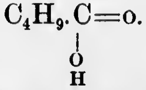
$$6NaC_2H_3O_2 + Fe_2Cl_6 = Fe_2(C_2H_3O_2)_6 + 6NaCl.$$

Add a few drops hydrochloric acid to a part of the solution ; the colour disappears. Boil the remainder for some time ; basic ferric acetate is precipitated :

$$Fe_2(C_2H_3O_2)_6 + H_2O = Fe_2(OH)_2(C_2H_3O_2)_4 + 2C_2H_4O_2.$$

180. **Butyric Acid.**—  $C_3H_7.\underset{\substack{|\\ O\\ H}}{C}{=}o.$ This acid is combined with glycerine in butter,—whence its name. When butter turns rancid, the characteristic odour is that of free butyric acid. It is prepared by the fermen-

tation of sugar by the *butyric acid ferment* of putrid cheese. It is an oily liquid with chemical characters similar to those of acetic acid. *Butyrate of sodium* ($Na.C_4H_7O_2$) is often present as an impurity in *valerianate of sodium*, being formed by the oxidation of the butylic alcohol of fusel oil.—*Ethyl butyrate* ($C_2H_5.C_4H_7O_2$) is the artificial *essence of pineapple.*

181. Valerianic Acid.— 
$C_4H_9.\underset{\substack{|\\ O\\ H}}{C}{=}o$. It is the acid of *valerian root.* It is now prepared from amylic alcohol (f[illegible] oil) by oxidising with bichromate mixture:

$$3C_5H_{11}OH + 2K_2Cr_2O_7 + 8H_2SO_4 =$$
$$3C_5H_{10}O_2 + 2K_2SO_4 + 2Cr_2(SO_4)_3 + 11H_2O.$$

Sodic Valerianate ($Na.C_5H_9O_2$) is prepared by neutralising the acid with sodic hydroxide. From this, *valerianate of zinc* is prepared by double decomposition with solution of *zinc sulphate* ($ZnSO_4$). The valerianate is sparingly soluble and separates out in pearly white scales:

$$ZnSO_4 + 2NaC_5H_9O_2 = Zn(C_5H_9O_2)_2 + Na_2SO_4.$$

182. Higher Fatty Acids.—Fats and oils are ethereal salts of glycerine (an alcohol) and the higher members of the fatty acid series. The acids of common fats and oils are:

Palmitic acid.	$C_{15}H_{31}.CO.OH$
Stearic acid	$C_{17}H_{35}.CO.OH$

In this connection may be mentioned *oleic acid* ($C_{17}H_{33}.CO.OH$) derived from the olefine series.—These acids are oily liquids or soft buttery solids. Their metallic salts are called *soaps*. *Hard soaps* are the sodium, and *soft soaps* the potassium salts. These are soluble in pure water. Other salts are mostly insoluble, e.g., the calcium, magnesium, and lead salts. (See *Glycerine.*)

183. **Glycol.**—$C_2H_4(OH)_2$. Prepared by the action of water on *ethylene bromide* ($C_2H_4Br_2$).

$$C_2H_4Cl_2 + 2H_2O = C_2H_4(OH)_2 + 2HBr.$$

(Are the hydroxyls attached to the same or to different carbon atoms?)—Glycol is a colourless liquid, of burning, sweet taste. It has the properties of an alcohol, forms ethereal salts, and when oxidised gives first an aldehyde, and then an acid (*oxalic acid.*) It unites with acids in *two* proportions, forming two series of ethereal salts: (1) Those in which one hydroxyl is replaced by salt radicals, e.g., $C_2H_4.OH.Cl$, $C_2H_4.OH.NO_3$, &c.; and (2) those in which both hydroxyls are replaced, e.g., $C_2H_4Cl_2$, $C_2H_4(NO_3)_2$, &c. It is thus analogous to diacid bases, such as calcic hydroxide ($Ca(OH)_2$); and is therefore called a *diacid alcohol.*

184. **Oxalic Acid.**—$C_2H_2O_4.2H_2O$.

OCCURRENCE.—In juices of wood sorrel, rhubarb, sour dock, &c., as *hydric potassic oxalate* (HKC_2O_4); in some plants and in urinary calculi, as *calcic oxalate* (CaC_2O_4); and in guano as *ammonic oxalate* ($(NH_4)_2C_2O_4$).

(What is the basicity of oxalic acid?)

PREPARATION.—Oxalic acid is formed when sugar, starch, &c., are oxidised with concentrated nitric acid; but is now made from pine sawdust by roasting at about

200° with a mixture of potassic and sodic hydroxides. The fused mass yields a solution of sodic oxalate ($Na_2C_2O_4$), which is decomposed by boiling with *milk of lime* (calcic hydroxide stirred up with water). Insoluble calcic oxalate is precipitated and sodic hydroxide remains in solution :

$$Na_2C_2O_4 + Ca(OH)_2 = CaC_2O_4 + 2NaOH.$$

The calcic oxalate is then drained, washed and decomposed by dilute sulphuric acid :

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4.$$

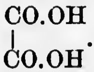
Calcic sulphate is only sparingly soluble, so that most of it remains undissolved. The solution of oxalic acid is drawn off, and evaporated to crystallisation. It is purified by re-crystallisation, and, if this is not done, it is contaminated by a small quantity of calcic sulphate.—The method of preparing organic acids by precipitating the calcium salt and then decomposing with sulphuric acid is very common. The object of the precipitation is twofold : (1) To separate the acid from the other substances dissolved along with it, and (2) to get it combined with a metal whose sulphate is insoluble. (Why is this advantageous ?)

Properties.—Oxalic acid is a white crystalline solid, of sharp acid taste. The crystals are long and pointed (prismatic), and somewhat resemble those of Epsom salts. The acid is soluble in 10 parts of water. It is a strong acid, and decomposes carbonates with effervescence. The pure acid is entirely decomposed and dissipated by heat. If any residue remains, it is impurity.

$$H_2C_2O_4 = H_2O + CO + CO_2.$$

Experiment 164.—Examine carefully some crystals of oxalic acid, noting shape, taste, &c., and comparing with Epsom salts. Heat a small quantity on mica. Dissolve a little in water, taste the solution, and try its action on sodic carbonate and on lime water.

Oxalic acid in large doses (60 grains and upwards) is, like all strong acids, a corrosive poison. In smaller doses it is a cumulative poison. The oxalates of the alkalis are also poisonous. The antidotes are chalk and water, magnesia, and lime water; their object being to form insoluble oxalates.

OXALATES.—Oxalic acid is dibasic. Its molecule is made up of two carboxyls,  $\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array}$.—There are two classes of oxalates, *normal* ($K_2C_2O_4$, CaC_2O_4, &c.), and *acid* (KHC_2O_4, &c.). Besides these there are salts composed of ordinary acid oxalates, combined with a further quantity of acid, e.g., *salt of sorrel* ($KHC_2O_4.H_2C_2O_4.2H_2O$). Of the normal oxalates only those of alkalis are soluble in water:

Experiment 165.—Prepare some *ammonic oxalate* by neutralising solution of oxalic acid with ammonia, filtering if necessary, and evaporating to crystallisation. Make a solution of this salt for the following experiments. (Write the equation.)

Experiment 166.—Add solution of calcic chloride ($CaCl_2$) to solution of ammonic oxalate. Calcic oxalate (CaC_2O_4) is precipitated. Test its solubility in acetic and in hydrochloric acids. Repeat with *baric chloride* ($BaCl_2$).

Experiment 167.—Add solution of ammonic oxalate to solution of ferrous sulphate ($FeSO_4$). Ferrous oxalate is precipitated. Note its colour, &c., and write its formula.

Tests.—1. (Experiment 166.)

2. Dry oxalic acid or an oxalate heated with concentrated sulphuric acid gives off a mixture of carbon monoxide and dioxide; the monoxide can be lighted, and burns with the characteristic bluish flame.

3. Argentic nitrate gives a white precipitate of argentic oxalate ($Ag_2C_2O_4$). This is soluble in nitric acid. (Can this precipitate be obtained with free oxalic acid?)

4. "With a solution of sulphate of lime, oxalic acid gives a white precipitate which is soluble in nitric acid, but insoluble in the vegetable acids." (B. P.)

5. Heat a little calcic oxalate in a small t. t., applying a light to the mouth. The flame of carbon monoxide is seen. Add a little hydrochloric acid to the cold, white residue. It effervesces.

$$CaC_2O_4 = CaCO_3 + CO.$$
$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

In this way insoluble oxalates can be tested for.

185. **Higher Dibasic Acids.**—Oxalic acid is the first member of a series:

Oxalic acid...............	$(COOH)_2$
Malonic acid..............	$CH_2(COOH)_2$
Succinic acid.............	$C_2H_4(COOH)_2$
&c.	&c.

SUCCINIC ACID is formed in small quantities during the alcoholic fermentation of sugar. It is found in the urine of the horse, and in the fluids of hydrocœle and hydatid cysts. It is prepared by distilling amber.

186. **Glycerine.**—$C_3H_5(OH)_3$. Glycerine forms the alcoholic (basic) part of the ethereal salts called fats and oils, and is prepared from them in the process of soapmaking.

SOAPS are made by boiling fats and oils with aqueous solutions of sodic hydroxide for hard soaps, and potassic hydroxide for soft soaps. The principal fats used are mixtures in various proportions of *stearin* $(C_3H_5(C_{18}H_{35}O_2)_3)$, *palmitin* $(C_3H_5(C_{16}H_{31}O_2)_3)$, and *olein* $(C_3H_5(C_{18}H_{33}O_2)_3)$. *Stearin* is the chief constituent of tallow. It is solid. *Palmitin* (a solid) is the chief constituent of palm oil, and *olein* (a liquid) of olive oil. Human fat consists mostly of palmitin. In the process of *saponification*, the glycerine is separated as indicated in the following equation, in which, for the sake of simplicity, $\overline{F}$ is put as a symbol for the salt radicals of the fatty acids:

$$\overset{\text{Fat.}}{C_3H_5\overline{F}_3} + 3NaOH = \overset{\text{Soap.}}{3Na\overline{F}} + \overset{\text{Glycerine.}}{C_3H_5(OH)_3}.$$

The soap is separated as a curd by the addition of common salt to the solution, and the glycerine is recovered from the mother liquor. In many factories the fats and oils are decomposed by heating under pressure with water and 2 to 3 per cent. of sulphuric acid. Aqueous solution of glycerine and fatty acids are obtained in separate layers. The glycerine is drawn off and purified by distilling with steam at 180° C. The acids are neutralised with caustic soda to form soap:

$$C_3H_5\overline{F}_3 + 3H_2O = C_3H_5(OH)_3 + 3H\overline{F}.$$
$$H\overline{F} + NaOH = Na\overline{F} + H_2O.$$

Sodium and potassium soaps are soluble in water and in alcohol. Most soaps are insoluble in salt water, but soap made from cocoanut oil and resin ("marine soap") is soluble in salt water. Lime and magnesium salts decompose ordinary soaps forming insoluble lime and magnesium soaps. Thus, in washing with hard water, there is always a waste of soap.—*Lead plaster* is a lead soap, made by heating litharge with olive oil (or lard) and a little water. It consists of *plumbic oleate* and *palmitate* principally, with some glycerine.

PROPERTIES OF GLYCERINE.—A thick, sticky, colourless liquid, of sweet and burning taste. Specific weight = 1.28. It dissolves in water in all proportions, and is hygroscopic. It mixes with alcohol in all proportions. It is a very good solvent for metallic oxides, salts, &c.; and is used in medicine in preparing *glyceritum acidi carbolici*, &c., which are solutions in 4 fluid ounces of glycerine, of 1 ounce of carbolic, gallic, and tannic acids. Glycerine has antiseptic properties, and *borate of glycerine* has been successfully employed in surgery.—Glycerine cannot be distilled alone, but decomposes at 280°, giving off pungent choking fumes of *acrolein* (C_3H_4O). If water be present part of the glycerine distils along with the water.—Glycerine is a triacid alcohol, and is analogous to triacid metallic bases, such as bismuth hydroxide ($Bi(OH)_3$). It forms three series of ethereal salts, in which one, two, and three hydroxyls respectively are replaced by acid radicals; e.g., $C_3H_5(OH)_2.NO_3$, $C_3H_5(OH).(NO_3)_2$, and $C_3H_5(NO_3)_3$, the three nitrates of glycerine. The latter, *trinitrate of glycerine*, is commonly called *nitro-glycerine*, and is prepared by the action of a mixture of concentrated nitric and sulphuric acids on cooled glycerine. When the resulting liquid is poured into water, nitro-glycerine separates out as a heavy oil:

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O.$$

Dynamite is made by absorbing glycerine in a porous siliceous sand. It is less dangerously explosive than nitro-glycerine.—On account of its attraction for moisture, glycerine is valuable in surgery as an emollient.

It is also used for preserving fruits, for making copying ink, and as a lubricator.

IMPURITIES.—Glycerine is often adulterated with cane sugar and glucose. To detect cane sugar, dissolve in water, add a few drops of sulphuric acid, and evaporate on the water bath. If cane sugar is present it is blackened. To detect glucose, heat with solution of caustic soda. If glucose is present the solution turns brown. (Try with samples of glycerine.) Glycerine should be neutral to litmus. Owing to imperfect purification it sometimes contains acids.

Test.—1. If a liquid containing glycerine be made slightly alkaline with caustic soda, a borax bead dipped in it will give a green colour to the Bunsen flame.

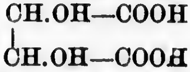
2. Heat a little glycerine with concentrated sulphuric acid, and note the smell of acrolein.

178. **Hydroxy-Acids.**—There are organic acids, the molecules of which have *alcoholic hydroxyl.* They partake of the nature of both alcohols and acids, but the acid properties predominate. They are called *hydroxy-acids.* Thus, *hydroxy-acetic acid* has the formula $CH_2OH.COOH$. There may be two hydroxyls in the molecule, as in the case of *tartaric acid,* which is *dihydroxy-succinic acid.*

188. **Lactic Acid,** $C_2H_4OH\text{-}COOH$.—This is *hydroxy-propionic acid.* Ordinary lactic is formed by fermentation of milk, which contains a fermentable sugar (*galactose*). It is present in the gastric juice, and in pickled cabbage and cucumber. It is generally prepared by the lactic fermentation of cane sugar, by means of putrid cheese. Zinc carbonate is added to neutralise the

acid as fast as it is formed.—It is a monobasic acid. *Ferrous lactate* ($Fe(C_3H_5O_3)_2$) is prepared by dissolving iron filings in warm dilute lactic acid. It is used in medicine.

189. **Tartaric Acid,** $C_4H_6O_6$.—This is *dihydroxy-succinic acid,* and its expanded formula is



$$\begin{array}{l}CH.OH—COOH\\ \mid\\ CH.OH—COOH\end{array}$$

It is at the same time a diabasic acid and a diacid alcohol. There are three isomeric tartaric acids, and our chemical theory is inadequate to explain their isomerism. Ordinary tartaric acid is found in the juice of grapes, berries of the mountain ash, cucumbers, potatoes, &c.

Ppeparation.—From *tartar* or *argol,* which is impure *potassic hydric tartrate* deposited in wine casks and vats during fermentation. (It is less soluble in alcohol than in water.) From this salt, purified by crystallisation, the acid is prepared as follows: "Boil 45 oz. cream of tartar (potassic hydric tartrate) with two gals. water; add 12½ oz. prepared chalk gradually, stirring constantly:

$$2KH\overline{T} + CaCO_3 = K_2\overline{T} + Ca\overline{T} + H_2O + CO_2.$$

($\overline{T} = C_4H_4O_6$.) Then add 13½ oz. calcic chloride in 2 pints of water:

$$K_2\overline{T} + CaCl_2 = Ca\overline{T} + 2KCl.$$

Allow the calcic tartrate to subside, pour off the liquid (What does it contain?), wash the precipitate with distilled water until tasteless, and pour on it 13 fluid ounces sulphuric acid diluted with 3 pints of water. Boil for half an hour and filter:

$$Ca\overline{T} + H_2SO_4 = CaSO_4 + H_2\overline{T}.$$

Evaporate the filtrate at a gentle heat to specific weight 1.21, allow to cool, and separate the deposited gypsum ($CaSO_4.2H_2O$). Again evaporate till a film forms on the surface, cool, and drain the crystals of tartaric acid which form." (B.P.) (Potassic hydric tartrate is sparingly soluble, the normal tartrate quite soluble, calcic tartrate insoluble in water. Explain the steps of the above process).

PROPERTIES.—Large colourless crystals or a white granular powder, of acid taste, soluble in water (2 parts in 1 of water), and in alcohol, but not in ether.

Experiment 168.—Examine the appearance and taste of a crystal of the acid, then heat on mica. It browns and chars with the smell of burning sugar; with a stronger heat it burns away completely.

Experiment 169.—Carefully add solution of tartaric acid to some solution of potassic carbonate (coloured with litmus) until the solution is neutral. (What salt is present?) Then add more tartaric acid, stirring all the time with a glass rod. A white granular precipitate of the acid tartrate forms. (Write equations.)

Experiment 170.—To a strong solution of hot sodic carbonate in a porcelain basin add, a little at a time, cream of tartar ($KH\overline{T}$) until it causes no effervescence. Evaporate to crystallisation. *Sodic potassic tartrate*, or *Rochelle salt* ($KNa\overline{T}$), is formed:

$$Na_2CO_3 + 2KH\overline{T} = 2KNa\overline{T} + H_2O + CO_2$$

Rochelle salt is one ingredient of *seidlitz powder*. The *blue* paper contains usually 3 parts Rochelle salt and 1 part sodic hydric carbonate; and the *white*, 1 part tartaric acid. When the solutions are mixed the tartaric acid decomposes the carbonate, while the Rochelle salt takes no part in the action :

$$2NaHCO_3 + H_2\overline{T} = Na_2\overline{T} + 2H_2O + 2CO_2.$$

(From this equation calculate the proportions of carbonate and acid which must be used in order that there may be excess of neither.)

TARTAR EMETIC *is antimonyl potassic tartrate* ($SbO.K.\overline{T}$), prepared by boiling cream of tartar with *antimony trioxide* :

$$Sb_2O_3 + 2KH\overline{T} = 2SbOK\overline{T} + H_2O.$$

The radical *antimonyl* (SbO) acts the part of a monad metal.

Tests.—1. To neutral solution of a tartrate add calcic chloride or to a solution of tartaric acid add lime water ; calcic tartrate ($Ca\overline{T}$) is precipitated. Wash the precipitate on a filter, break the filter, wash the precipitate into a t. t., and add sodic hydroxide ; the precipitate dissolves.

2. To tartaric acid or solution of a tartrate add acetic acid and potassic acetate and stir. Potassic hydric tartrate is precipitated as a white granular powder.

3. Tartaric acid or tartrates in solution, when heated with a considerable proportion of concentrated sulphuric acid, turn brown or black *at once.*

4. To neutral or alkaline solution of a tartrate add a few drops of potassic permanganate solution, and heat. The colour disappears.

NOTE.—Solution of tartaric acid in water undergoes slow decomposition owing to the growth of a fungus. Spirits of wine prevent this.

190. **Citric Acid**, $C_6H_8O_7.H_2O$. This is a tribasic acid and monacid alcohol, $C_3H_4.OH \left\{\begin{array}{l}COOH\\COOH.\\COOH\end{array}\right.$ It is found in the juices of limes, lemons, currants, raspberries, gooseberries, &c.

Preparation.—From the evaporated juice of unripe limes and lemons by almost the same method as that for tartaric acid. One hundred parts of lemon yield 5½ parts of acid.

Experiment 171.—Squeeze the juice of a lemon upon a filter and allow it to run into a porcelain basin. Heat to boiling and add prepared chalk by degrees until it does not cause effervescence :·

$$2H_3\overline{Ci} + 3CaCO_3 = Ca_3\overline{Ci}_2 + 3H_2O + 3CO_2.$$

Filter, wash the precipitate with hot water four or five times, break the paper and wash the precipitate through into a porcelain basin. Add a small quantity (2 or 3 c.c.) of sulphuric acid, boil gently for a little while, filter and concentrate the filtrate to crystallisation. Crystals of citric acid are obtained mixed with gypsum. The acid can be purified by recrystallisation from a small quantity of hot water.

Properties.—Usually sold as large, colourless, sharp-pointed crystals. These are soluble in ½ their weight of cold water, in ¾ of boiling water ; less soluble in alcohol ; still less in ether. Citric acid melts at 100° ; above this it loses water of crystallisation, then chars with the smell of burning sugar.

Experiment 172.—Heat a little solid citric acid in a t. t. by placing the t. t. in boiling water. The acid melts. Wipe the t. t. and heat it gently in the Bunsen flame. Note the water condensing. Heat more strongly. Note smell and charring. Heat a small crystal strongly on mica.

Experiment 173.—Put a pipetteful of citric acid solution in each of three porcelain dishes, and carefully neutralise with solution of potassic carbonate. To one add a second pipetteful of the acid, and to another two pipettefuls. Number and evaporate the three solutions on a water bath to a syrupy consistence, and then set aside to crystallise. Three salts are obtained, different in appearance. What are they? Taste them.

Experiment 174.—Dilute a little of the normal potassic citrate prepared in Experiment 172 and add to it about an equal volume of the reagent solution of calcic chloride. If no precipitate appears, boil. If a precipitate appears, gradually add distilled water and shake up until it is dissolved, and then boil. *Calcic citrate* ($Ca_3\overline{Ci}_2.4H_2O$) is less soluble in hot than in cold water. (Try with citric acid and lime water.)

MAGNESIC CITRATE ($Mg_3\overline{Ci}_2.4H_2O$) is a white sparingly soluble salt which can be prepared by the action of the acid on magnesium carbonate:

$$3MgCO_3 + 2H_3\overline{Ci} = Mg_3\overline{Ci}_2 + 3H_2O + 3CO_2.$$

Effervescing powders are made by mixing the substances in the solid state. Solids act on each other very slowly or not at all; but as soon as they are brought together in solution action begins. The more coarsely granular the solid ingredients are, the slower is the action between them. (Why?) "Granular effervescing citrate of magnesia" is a mixture of coarse granules of Epsom salts ($MgSO_4.7H_2O$), citric acid, tartaric acid, and hydric sodic carbonate ($HNaCO_3$). (What substances are formed when it is dissolved?)

Tests.—1. (Exp't 174.) The precipitate of calcic citrate is insoluble in sodic hydroxide.

2. Citric acid and citrates give no precipitate with acid solutions of potassium salts. (See tartaric acid).

3. Heat with concentrated sulphuric acid. The solution darkens only after some time.

4. To neutral or alkaline solution add a few drops of potassic permanganate solution and heat slowly. The permanganate is reduced to the green *manganate* (K_2MnO_4.)

5. All solid citrates are charred by heat.

Note.—Citric acid is sometimes adulterated with tartaric acid. This can be detected by the test with potassium salts. The addition of alcohol increases the delicacy of the test.

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191. **Carbohydrates.**—Under this head are included three groups of isomeric compounds, containing either 6 or 12 atoms of carbon in the molecule, together with hydrogen or oxygen *in the proportions to form water.* They are all naturally occurring substances, many of them being quite familiar vegetable products, e.g., sugar, starch, and cotton. (What compounds already discussed contain hydrogen and oxygen in the proportion to form water?).—The carbohydrates are in all probability *poly-acid alcohols,* and at the same time aldehydes or ketones. There are three groups :

1. SACCHAROSES ($C_{12}H_{22}O_{11}$).—Comprising cane sugar (saccharose), milk sugar, malt sugar (maltose), &c.

2. GLUCOSES ($C_6H_{12}O_6$).—Grape sugar (dextrose), fruit sugar (levulose), galactose, inosite, &c.

3. AMYLOSES ($C_6H_{10}O_5$).—Starch, dextrin, cellulose, glycogen, gums, inulin, &c.

192. **Saccharoses.** — $C_{12}H_{22}O_{11}$. The saccharoses seem to be analogous to ethers—they all unite with water to form glucoses :

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

(Compare this with the relation of ethyl ether to ethyl alcohol.) This takes place under the influence of ferments, and by boiling with dilute acids or alkalis.

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1. **Cane Sugar** ($C_{12}H_{22}O_{11}$).—Cane sugar is so called because of its manufacture from the juice of the sugar-cane. It is also now largely made from the sugar-beet. It is found also in the sugar-maple, sorghum, turnips, carrots, coffee, walnuts, hazelnuts, almonds, and in the blossoms of many plants along with more or less fruit-sugar.

Preparation.—The juice is expressed from sugar-cane or beet-root-pulp, and the solution of sugar is evaporated in "vacuum pans." It is necessary to evaporate at moderate temperatures in order to avoid the change into uncrystallisable members of the glucose group. The evaporated solution is allowed to crystallise, and the crystals are drained on "centrifugals," which are large revolving *sieves*. *Molasses* is the mother liquor drained from the raw cane-sugar. It is much used in the manufacture of rum, and lately a process has been devised to obtain more sugar from it. It contains cane-sugar, together with *inverted* sugar, or glucoses produced by the action of water on cane-sugar,—*inverted*, because the action on polarised light is the exact opposite. It must be remembered that beet-sugar and cane sugar, when pure, are the same substance. *Vinasses*, the mother liquor of beet-sugar, is evaporated to dryness, and distilled. A variety of useful products is obtained, viz., potassic carbonate, ammonia, methylic alcohol, trimethylamine, &c.

PROPERTIES.—A hard, colourless, crystalline solid of specific weight 1.593. It dissolves in about one-third of its weight of cold water, and in all proportions in boiling water. It is insoluble in absolute alcohol, and in alcoholic liquors is soluble in proportion to the water present. It melts at 160° C., and at 190° gradually loses water and darkens, forming a substance called *caramel* (*saccharum ustum*), much used for colouring wines and liquors. When heated more strongly it chars, giving off fumes having a characteristic odour.

Experiment 175.—Make a solution in water of pure cane-sugar, add to part of it a few drops of cupric sulphate solution, and then solution of caustic soda. A blue solution is formed. Heat this. If the sugar is pure no change takes place. Add a few drops of sulphuric acid to a little of the sugar solution and boil for some time in a porcelain dish; add water as it evaporates. Then repeat the test with cupric sulphate and caustic soda. A precipitate is formed on heating, at first yellow and then red. This precipitate is *cuprous oxide* (Cu_2O). (Fehling's test.)

As we shall see later this reduction of cupric sulphate solution is brought about by glucoses, but not generally by saccharoses. The cane-sugar has been inverted by boiling with an acid:

$$C_{12}H_{22}O_{11} + H_2O = \overset{\text{Dextrose.}}{C_6H_{12}O_6} + \overset{\text{Levulose.}}{C_6H_{12}O_6}.$$

This process goes on slowly in moist impure sugars (brown sugars). Cane-sugar does not at once undergo alcoholic fermentation when its solution is mixed with yeast. It must first be *inverted* by the action of the ferment.

Experiment 176.—To a dilute solution of pure sugar add some brewer's yeast, and set in a warm place for half an hour.

Then test the solution as in Experiment 175. It will be found to contain inverted sugar.

There are many ferments which cause the inversion of cane-sugar. The saliva has this power owing to the presence of a ferment, *ptyalin,* which however loses its power when the solution becomes acid, and, hence, as soon as it reaches the stomach. Oxidising agents convert cane-sugar into oxalic and other acids. Formerly oxalic acid was made by the action of nitric acid on cane-sugar.—Cane-sugar forms soluble compounds with many substances which are insoluble or sparingly soluble in water. It is thus useful for keeping in solution certain metallic compounds employed in medicine, e.g., slaked lime, calcic hypophosphite, &c.—*Oxymel* is a mixture of honey (80 %), acetic acid (10 °/₀), and water 10°/₀). The name means *acid-honey.*

Tests.—1. Fehling's test as in Experiment 175. *Fehling's solution* is made by dissolving 34.64 grams cupric sulphate (blue vitriol) in water, adding 200 g. Rochelle salt ($KNa\overline{T}$), 600 g. to 700 g. solution of caustic soda of specific weight 1.12, and making up to 1 litre with water. It must be kept well stoppered, and put in a cool, dark place.

2. Evaporate on the water bath with a few drops of sulphuric acid. Blackening shows the probable presence of cane-sugar. Grape sugar does not blacken.

3. Heat with solution of caustic soda, caustic potash, or potassic carbonate. Does not turn brown.

2. Milk Sugar (Lactose) ($C_{12}H_{22}O_{11}.H_2O$).—Milk sugar is found in the milk of all mammalia. Human milk contains 4 °/₀ to 5 °/₀, cow's milk 3 °/₀.

Preparation.—From whey, by evaporating and crystallising on threads or sticks.

PROPERTIES.—A hard, colourless crystalline solid, with one molecule of water of crystallisation. It is not so soluble in water as cane-sugar, dissolving in 6 parts of cold, or 3 of hot water. It is almost insoluble in alcohol. Its taste is less sweet than that of cane-sugar. Specific weight 1.534.—Milk-sugar does not ferment with yeast; but it undergoes another fermentation with the formation of alcohol and lactic acid, as in the preparation of the fermented liquor called *koumiss.* —Milk sugar is used to a considerable extent to increase the percentage of sugar in cow's milk for feeding infants. It is also used in the powdered state as a diluent of solid medicines, e.g., iodoform.

Experiment 177.—Try Fehling's test with milk-sugar. It differs from the other members of this group in that it reduces *cupric* to *cuprous* oxide.

Experiment 178.—Heat some solution of milk-sugar with an alkali. What result?

Experiment 179.—Add a few drops of argentic nitrate solution to a solution of milk-sugar, then some ammonia, and warm gradually. Silver is deposited as a mirror on the test.

Tests.—Distinguished from cane-sugar by Experiments 177 and 178; from glucose by not fermenting with yeast.

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3. MALT SUGAR (MALTOSE) ($C_{12}H_{22}O_{11}$).—This is also sometimes called starch-sugar.

PREPARATION.—By fermenting potato-starch with air-dried malt, and extracting the sugar with alcohol.

PROPERTIES.—A crystalline solid freely soluble in water, and to a considerable degree in alcohol. It can be transformed into grape-sugar by boiling with dilute sulphuric acid. It is used in the preparation of caramel.

193. **Glucoses.**—$C_6H_{12}O_6$. Glucoses are widely distributed in nature, occurring in both plants and animals. Fruits contain cane-sugar in the early stages of their ripening, but this gradually combines with water to form glucoses, generally equal quantities of dextrose and levulose. This mixture is called *invert-sugar.*

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1. DEXTROSE ($C_6H_{12}O_6$). — Also called *glucose* and *grape-sugar.*

OCCURRENCE.—In sweet fruits, almost always accompanied by an equal quantity of levulose, thus showing the origin of these sugars from cane-sugar. The latter is also generally present, until the fruit becomes fully ripe. Dextrose is also present in honey, and in the blood, liver, and urine of man. In cases of *diabetes mellitus* the quantity in the urine may reach 10 °/₀.

PREPARATION.—Dextrose can be prepared artificially from starch, dextrin, cellulose, &c., by the action of acids. It is manufactured on the large scale from corn and potato starch, by heating with dilute sulphuric acid, generally under pressure. Dextrin, isomeric with starch, is first formed, and this combines with water:

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

Experiment 180.—Boil some starch paste for half an hour with about one-fifth its volume of dilute sulphuric acid, replacing the water as it evaporates, and then test the solution for dextrose by Fehling's test. Try Fehling's test with starch.

The sulphuric acid is neutralised with chalk or limestone ($CaCO_3$), and the solution of dextrose is drawn off and evaporated to crystallisation. It is difficult to crystallise, as it tends to form supersaturated solutions.

Properties.—The *glucose* of commerce is either a thick syrup ("mixing syrup") or a hard, white solid ("grape sugar"). Specific weight = 1.825. It always contains dextrin, and other substances of unknown composition. The dextrin is harmless, but the unknown substances have an effect on the human system similar to that produced by fusel oil. Dextrose is not so sweet as cane-sugar, the sweetness being as 1 to 1.66 (or as 3 to 5). At 15° C. it dissolves in 1.2 parts of water. It is more soluble in alcohol than cane-sugar. It ferments to alcohol and carbon dioxide under the influence of yeast:

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O.$$

It also undergoes the lactic and butyric acid fermentations.—"Granulated grape sugar" looks very like cane-sugar, and is used to adulterate it. Many of the cheap sugars contain 10 °/₀ to 20 °/₀ of grape-sugar. It is used in the preparation of alcohol, artificial wines, &c. Wines and liquors made from such materials are poisonous.—Dextrose has the power of keeping in solution some substances which are insoluble in pure water.

Experiment 181.—Add a solution of sodic hydroxide to solution of cupric sulphate. *Cupric hydroxide* ($Cu(OH)_2$) is precipitated, and is not redissolved by excess of the precipitant. Repeat the experiment, with a solution of cupric sulphate containing grape-sugar. A blue solution is obtained. Heat the solution, and red cupr*ous* oxide is precipitated, the sugar undergoing oxidation. This explains Fehling's test.

Experiment 182.—Add a few drops of argentic nitrate solution to dilute solution of grape-sugar in a t. t. and warm gently. The inside of the t. t. is silvered.

Experiment 183.—Heat a solution of grape-sugar with sodic hydroxide. Try also with potassic hydroxide, and with sodic carbonate. The solution of sugar turns brown.

Tests.—Experiments 181 and 183 serve to distinguish from cane-sugar.

Note.—*Glucosides* are peculiar ethereal salts of glucose, which break up under the action of a ferment (or of dilute acids) into glucose and other substances, an aldehyde being very commonly among the number.

2. LEVULOSE, &c., $C_6H_{12}O_6$. *Levulose* is nearly as sweet as cane-sugar. It was at one time thought to be uncrystallisable, but it can be crystallised, although with difficulty. As has been previously observed, it occurs in ripe fruits accompanied by an equal quantity of dextrose. It is *fruit-sugar.*—*Galactose* is formed together with dextrose by the *inversion* of milk-sugar. It does not ferment with yeast, but reduces Fehling's solution.—*Inosite* ($C_6H_{12}O_6.2H_2O$) is found in the heart, lungs, &c., of the ox, and sometimes in the urine of man. It does not reduce Fehling's solution. It is soluble in 6 parts of water, and insoluble in alcohol.

AMYLOSES.

194. **Starch** (*amylum*).—$C_6H_{10}O_5$. Found in grain, potatoes, arrowroot, nuts, and very generally distributed throughout vegetable tissues. It is the form in which plants store up a reserve of food, just as animals store up fat.—Starch is manufactured from wheat, Indian corn, rice, and potatoes. The materials are ground up with water, strained through sieves, and treated with dilute caustic soda, or fermented. The starch is allowed

to settle, washed, &c. *Sago* is a starch made from the pith of the sago palm of the East Indies. *Arrowroot* is starch prepared from the roots of *Maranta arundinacea*, a West Indian plant. *Tapioca* is a similar preparation from *Jatropha manihot.*

PROPERTIES.—Starch is a white substance, forming granules of peculiar structure. Under the microscope these granules show concentric layers around a spot or *hilum.* The granules are different for different plants, and an examination by the microscope at once reveals the source from which any specimen of starch has come. —Starch is insoluble in water, but, when heated with it, swells up and forms a paste. Continued boiling, or the action of acids or alkalis, renders the starch soluble.

Experiment 184.—Scrape a piece of potato and place the pulp on a muslin filter. Pour a thin stream of cold water on it, catching the filtrate in a t. t. Allow the starch to settle, pour off some of the water, and then heat to boiling. Starch paste is formed.

Experiment 185.—To a little cold starch paste (*mucilago amyli*) add a few drops of iodine solution. A deep blue colour is produced. Heat, and the colour disappears. Allow to cool again.

Starch paste (or *mucilage of starch,* as it is called in medicine), changes gradually into a solution of dextrin. This change is hastened by boiling with dilute acids, or by the action of ferments (malt, &c.).—Starch is used in medicine as a vehicle for enemata, &c. The *blue starch* of the shops is coloured with indigo or smalt, and should not be used for medicinal purposes.

Test.—Experiment 185 is a very delicate test. The substance should be as cold as possible.

Inulin is a compound ($C_6H_{10}O_5$) which partially replaces starch in elecampane, the roots of dahlia, &c.

195. **Dextrin.**—$C_6H_{10}O_5$. Dextrin is prepared by heating starch to about 250° C. It is formed from starch at lower temperatures (up to 95° C.) by the action of the ferment (*diastase*) of malt, and also by boiling with dilute acids.

Experiment 186.—Boil in a t. t. for several minutes a little starch with water and a few drops of sulphuric acid. A clear solution is obtained. Cool this and test it with iodine.

Dextrin is soluble in water, but insoluble in alcohol. By the further action of malt or dilute acids it is changed first into maltose ($C_{12}H_{22}O_{11}$), and then into dextrose ($C_6H_{12}O_6$).—It is made on the large scale, and sold as *calcined farina*, or *British gum*, a cheap substitute for gum arabic.—Considerable quantities of dextrin are formed in the baking of bread. Toast is more easily digested, therefore, than bread. The first stage in the digestion of the insoluble starch is its transformation into soluble dextrin.

196. **Glycogen.**—$C_6H_{10}O_5$. This name means *sugar-generator*. Glycogen is found in the livers of most animals; it is also present in the blood and in muscles. Oysters contain a large percentage. It can be extracted from *fresh* liver by boiling with water or with alkalis. It is precipitated from its aqueous solution by the addition of alcohol, in which it is insoluble.

Properties.—A white amorphous powder, somewhat soluble in water. Under the action of malt, &c., it combines with water to form maltose and dextrose. It is generally supposed that the liver stores up the surplus sugar of the food in the form of glycogen. The liver contains a ferment which has the power of transforming glycogen into maltose or dextrose.

197. **Gums.**—$C_6H_{10}O_5$. These must be distinguished from resins, often called gums in this country. *Gum-arabic, gum tragacanth,* and *bassorin* are examples of true gums. They are non-crystalline, soluble in water, but insoluble in alcohol. They are converted into glucoses by boiling with dilute acids. *Vegetable mucilages,* e.g., that of linseed, are of a similar character.

198. **Cellulose.**—$C_6H_{10}O_5$. This is the groundwork of vegetable tissues, forming the walls of vegetable cells. Cotton, hemp, and flax are nearly pure cellulose. Paper is also very pure, especially when prepared from cotton. Woods consist in large part of cellulose.

PROPERTIES.—A white amorphous solid, insoluble in water, and in most chemical substances. It is, however, soluble in ammoniacal solution of cupric hydroxide (Schweizer's reagent), in strong, hot solution of caustic soda or potash, and in strong acids. These facts must be remembered in filtering processes. It can be converted into dextrose by dissolving in strong sulphuric acid, diluting, and boiling for some time.

riment 187.—Dissolve a piece of filter paper in a little ng sulphuric acid, dilute, boil for some time, and test with ehling's solution.

Gun-cotton, pyroxylin, or *nitro-cellulose,* is the *trinitrate of cellulose,* $C_6H_7O_2(NO_3)_3$, prepared by the action of a mixture of concentrated sulphuric and nitric acids on cotton or wood. It is very explosive, containing as it does an oxidisable and an oxidising part. (Explain).—*Celluloid* is a preparation of nitrates of cellulose and camphor, prepared by a method similar to that for gun-cotton. It softens when heated and can be moulded into any shape.—*Collodion* is a solution in alcohol and ether of nitrates of cellulose. It is used in photography.

QUESTIONS AND EXERCISES.

1. Compare carbon dioxide and carbon bisulphide, as to their compounds.

2. What causes the effervescence of soda water?

3. How would you prove by an experiment that carbon dioxide is formed by the burning of a candle?

4. Show that most of our materials for fires and lights are from a vegetable source.

5. Write a graphic formula for acetylene (C_2H_2). With how many atoms of chlorine would you expect its molecule to combine?

6. Show how green vitriol, ferric chloride, and sodic carbonate may be used as an antidote to poisonous cyanides.

7. Account for the smell of ammonia about stables and water closets.

8. A quantity of urine (70 c. c.) is decomposed by sodic hypobromite, and yields 8 c. c. of nitrogen. How many grains of urea per gallon?

9. Write formulas for *methyl nitrate, sulphate*, and *orthophosphate*; and for *ethyl bromide, acid sulphate*, and *sulphite*.

10. What is the practical distinction between primary, secondary, and tertiary alcohols?

11. Calculate the specific weight of ether vapour (air = 1).

12. Given *zincic carbonate* and *acetic acid*, prepare *zincic acetate*. Try it practically.

13. What chemical actions accompany the souring of milk?

14. What is "invert sugar"? Why so called?

15. Why is toast more easily digested than bread?

CHAPTER XIV.

CARBON AND ITS COMPOUNDS (CONCLUDED).

199. **Coal Tar.**—About thirty years ago coal tar was an offensive waste product of gas manufacture, and the problem was how to get rid of it. To-day it is the substance for which the coal is distilled in many factories; and the gas manufacturers regard it as one of the chief sources of their revenue. This change is due to the discovery of the *aniline dyes*, the raw materials for their manufacture being obtained from coal tar.—The tarry liquid which collects in the condensers of the gas-works is redistilled fractionally. There distils over first a *light oil* which floats on water; this contains benzene (C_6H_6), *toluene* (C_7H_8), *carbolic acid* (C_6H_7O), &c. Later there distils a *heavy oil* containing *xylene* (C_8H_{10}), *mesitylene* (C_9H_{12}), *cymene* ($C_{10}H_{14}$), *naphthalene*, *anthracene*, &c.

200. **The Benzene, or Aromatic, Series.**—We have already studied unsaturated hydrocarbons, such as ethylene and acetylene, the marked characteristic of which is the readiness with which they combine with such substances as chlorine to form saturated compounds. The benzene compounds are unsaturated as far as their composition goes, but they are characterised by the difficulty with which anything is added to their molecules. They yield *substitution*, rather than *addition*,

products, and in this respect resemble saturated hydrocarbons. The chief members of the series are as follows:

		Boiling points.
Benzene,	C_6H_6	81°
Toluene,	C_7H_8	111
Xylenes (3 isomers),	C_8H_{10}	about 140
Mesitylene	C_9H_{12}	163
Pseudocumene		151
Cumene		166

201. Benzene *(Benzol)*.—C_6H_6.

PREPARATION.—From the light oil of coal tar. This is washed first with caustic soda solution to dissolve out carbolic acid and other *acid* impurities, and afterwards with dilute sulphuric acid to remove *basic* substances. It is then distilled fractionally, and the part coming over between 80° and 90° is used for the preparation of benzene.—It can also be prepared by heating benzoic acid with lime:

$$C_6H_5.COOH + CaO = C_6H_6 + CaCO_3.$$

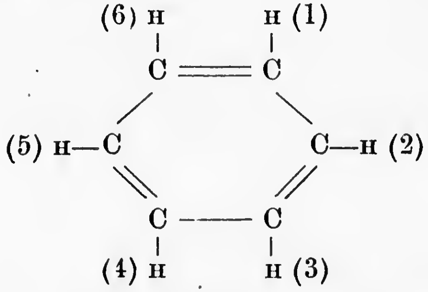
This method is analogous to that for the preparation of methane.

PROPERTIES.—A colourless liquid of specific weight 0.89. It boils at 80°.5, and has a pleasant *aromatic* odour. It burns with a brightly luminous flame.

Experiment 188.—Pour a little benzene into a basin of water and set fire to it.

Experiment 189.—Pour a few drops of benzene into a t. t. of water heated nearly to the boiling point. Observe that the benzene boils.

Benzene is solid at 0°C.—It is a good solvent for fats, oils, and resins.—When benzene is acted on by chlorine, substitution products are formed. There is only one *monochlor-benzene* (C_6H_5Cl). If the atoms of carbon in the molecule were connected as they are supposed to be in the hydrocarbons already studied, we should expect the hydrogen atoms to be differently situated and thus to permit the formation of isomeric derivatives by the replacement of the hydrogen atoms. Now *monochlor-benzene* has been prepared in a variety of ways, some of which lead to the conclusion that different hydrogen atoms have been replaced by chlorine; but the products are identical. It is plain, then that the six hydrogen atoms are similarly situated in the molecule. Kekulé, of Bonn, has devised a structural formula showing this. It is called the *benzol ring*, and although it only pictures an hypothesis, yet it has proved a powerful lever in the hands of experimenters.



The molecule is represented as being symmetrical, each carbon atom being united to a hydrogen atom, to another carbon atom by a single bond, and to a third by a double bond. (Study this formula, and observe that the hydrogen atoms are represented as similarly situated.)

When two hydrogen atoms of the benzene molecule are replaced, *three* isomeric *di-substitution* products are formed. If the hydrogen atoms represented in the above formula be numbered consecutively from 1 to 6, it is easily seen that (2) and (6) are similarly situated with regard to (1), so that replacing (1) and (2) with, say, Cl's, gives the same formula as is obtained by replacing (1) and (6). In the same manner (3) and (5) are similarly situated; but, with regard to (1), (4) is differently situated from (2), (3), (5), or (6). Only three different formulas of di-substitution products are possible, and this result is in accordance with the facts. By a series of beautiful experimental investigations, the relative positions of the substituted atoms have been determined, and names have been assigned accordingly. Thus (1) (2) (or (1) (6)) di-substitution products are called *ortho*, e.g., *ortho-dichlorbenzene*; (1), (3) products are called *meta*, and (1), (4) *para*.

202. **Nitro-substitution Products.** — When strong nitric acid acts on benzene, one or more of the hydrogen atoms are replaced by the monad radical —NO_2 (*nitroxyl*). Thus:

$$\begin{array}{ll}(1) & C_6H_6 + HNO_3 = C_6H_5.NO_2 + H_2O.\\ (2) & C_6H_6 + 2HNO_3 = C_6H_4.(NO_2)_2 + 2H_2O.\\ & \quad\&c. \qquad\qquad\qquad \&c.\end{array}$$

Only *one mononitrobenzene* is known, but *three* isomeric *dinitrobenzenes* have been obtained. (How many *trinitrobenzenes* are possible according to theory?)

MONONITROBENZENE ($C_6H_5.NO_2$) is manufactured on the large scale in the preparation of *aniline* ($C_6H_5.NH_2$). It is a yellow, oily liquid smelling like oil of bitter almonds. It is often sold as "artificial essence of mirbane," or "artificial oil of bitter almonds;" but as it is poisonous and different in its physiological action from the true oil, it should never be used in medicine in place of the true oil.—Mononitrobenzene boils at 205° C. Its specific weight is 1.2. It is insoluble in water. By the action of nascent hydrogen it is reduced to aniline ($C_6H_5.NH_2$):

$$C_6H_5.NO_2 + 3H_2 = C_6H_5.NH_2 + 2H_2O$$

Nitrobenzene is used to perfume cheap soaps and confectionery, as well as in the manufacture of aniline. It is sometimes mixed with oil of bitter almonds as an adulteration. Its presence can be detected by reducing to aniline by means of zinc and hydrochloric acid, and then treating with filtered solution of bleaching powder, with which aniline forms a beautiful purple colour.

Experiment 190.—Mix a few drops of benzene with a little concentrated nitric acid. Warm very gently and note the smell of nitrobenzene.

203. **Aniline** *(Phenylamine).* — $C_6H_5.NH_2$. Was first prepared from indigo (*anil*). It is found in small quantities in coal tar, wood tar, and bone oil.

PREPARATION.—By the action of nascent hydrogen on mononitrobenzene. The hydrogen is evolved from iron and acetic or hydrochloric acid. (Write the equations).

PROPERTIES.—Aniline is a colourless liquid of specific weight 1.036. It boils at 184°.5. It is soluble in 31 times its weight of water, and the solution has a weak alkaline reaction. It is more freely soluble in alcohol. —Aniline unites with acids to form salts:

$$C_6H_5.NH_2 + HCl = C_6H_5.NH_3Cl.$$

Compare with $NH_3 + HCl = NH_4Cl.$

Aniline is a substituted ammonia, or amine, of the aromatic series. Commercial aniline always contains *toluidine* ($C_7H_7.NH_2$), a higher member of the same series; and, when it is oxidised by means of arsenic acid or potassic chlorate, the beautiful colour *rosaniline* ($C_{20}H_{19}N_3$) is formed. This is the first of the *aniline dyes*, the discovery and manufacture of which have revolutionised the dyer's art. They are comparatively innocuous when pure, but arsenic acid is used in their manufacture, and through carelessness or ignorance it is sometimes imperfectly separated.

Tests.—1. To an aqueous solution of aniline add some filtered solution of bleaching powder. A purple colour results.

2. Dissolve a drop of aniline in strong sulphuric acid. (What is formed ?) Stir in a porcelain dish with a drop of potassic bichromate solution ($K_2Cr_2O_7$). A blue colour is produced.

204. **Carbolic Acid** *(Phenol).* — $C_6H_5.OH$. This is in reality a tertiary alcohol, but it has very weak acid properties.—It is found in small quantities in urine. It is a product of the distillation of wood, coal, bones, &c.

Preparation.—From the heavy oil of coal tar. This is treated with caustic soda solution, which dissolves the carbolic acid, forming *sodic carbolate*, or *phenolate*, ($C_6H_5.ONa$). The solution forms a layer separate from the oil. It is decanted, and is then decomposed by hydrochloric acid :

$$C_6H_5.ONa + HCl = C_6H_5.OH + NaCl.$$

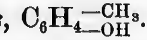
The carbolic acid is purified by distillation.

Properties.—A colourless, crystalline solid, crystallising in long needles. It has a strong, somewhat tarry smell, not unpleasant when the carbolic acid is pure. It melts at 35°, and boils at 180°. It is deliquescent, uniting with a small proportion of water to form a liquid. This liquid is sparingly soluble in water (1 in 15), but mixes with ether and alcohol in all proportions.

Experiment 191.—To a little solid carbolic acid add a drop or two of water. They combine to form an oily liquid. Add a little more water. The two do not mix. (Which is the heavier?) Now add much water, and the carbolic acid dissolves. Note taste and smell of this liquid.

It is very poisonous, and the strong solution burns the skin. It has a burning taste. The antidotes are olive oil, castor oil, and a mixture of slaked lime with 3 times its weight of sugar, rubbed up with a little water.—Carbolic acid is extensively used as an antiseptic in surgery, &c. It was introduced into general use by Lister, of Edinburgh, who devised a system by which surgical operations were carried on in an atmosphere containing no living putrefactive germs. The *antiseptic spray* was combined with a minute cleanliness hitherto unknown in surgery, and in all probability to this is due in a great measure the success of *Listerism.*

Test.—Mix the liquid with one-fourth its volume of ammonia solution and add a few drops of clear bleaching powder solution. The merest trace of carbolic acid will cause a blue colour to appear.

205. **Creosote.**—Pure creosote is obtained by distilling beech and other hard woods. It consists mostly of isomeric *cresols*,  $C_6H_4\begin{smallmatrix}-CH_3\\-OH\end{smallmatrix}$. It resembles carbolic acid in smell and taste. Carbolic acid is often sold as creosote; and the so-called "coal-tar creosote" is merely impure carbolic acid.

To distinguish carbolic acid from creosote:

1. Dissolve in glycerine and add water. *Carbolic acid* remains *dissolved.* *Creosote* is *precipitated* by the water.

2. Add to the liquid to be tested alcoholic solution of ferric chloride. *Carbolic acid* gives a *brown* colour; *creosote, green.*

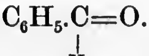
3. With aqueous ferric chloride, *carbolic acid* turns *blue*; *creosote* is *unchanged.*

206. **Picric Acid** (*Trinitrophenol,* or *Carbazotic Acid*).—$C_6H_2(OH).(NO_2)_3$.

PREPARATION.—**Experiment 192.**—Dissolve some carbolic acid in dilute nitric acid and add drop by drop about half the volume of strong nitric acid. Dilute with cold water, and picric acid is precipitated.

PROPERTIES.—A yellow crystalline solid sparingly soluble in cold, easily in hot water, and in alcohol or ether. It has a bitter taste and is poisonous. It explodes when heated rapidly. *Ammonic picrate* ($NH_4.C_6H_2N_3O_7$) is used as an explosive. Picric acid has strong colouring power, and is a good dye for silk and wool.

207. **Benzylic Alcohol.**—$C_6H_5.CH_2OH$. — Found in balsam of Tolu and Peru, and in storax, as ethereal salts of benzoic and cinnamic acids. When oxidised it gives first *benzoic aldehyde* ($C_6H_5.COH$), and then *benzoic acid* ($C_6H_5.COOH$).



208. **Benzoic Aldehyde.**—$C_6H_5.\underset{\substack{|\\ H}}{C}{=}O$. A component of *amygdalin,* a glucoside found in bitter

almonds, in laurel leaves, cherry kernels, &c. Amygdalin ferments under the influence of *synaptase* (a ferment present in the almond), forming benzoic aldehyde, hydrocyanic acid, and dextrose:

$$C_{20}H_{27}O_{11}N + 2H_2O = C_7H_6O + HCN + 2C_6H_{12}O_6.$$

Oil of bitter almonds is prepared by fermenting bitter almonds. The crude oil contains, besides benzoic aldehyde, hydrocyanic acid, and is therefore *very poisonous.* It is purified by distilling with milk of lime (to retain the prussic acid), and fused calcic chloride (to retain the water). Pure benzoic aldehyde is thus prepared.

PROPERTIES.—A colourless, bright liquid of pleasant aromatic odour. Specific weight = 1.054. It boils at 180° C. It dissolves in 30 times its weight of water, and mixes in all proportions with alcohol and ether.—It is not poisonous; but the so-called "artificial oil" (nitro-benzene) is poisonous. A delicate test for nitrobenzene in oil of bitter almonds is as follows:—Treat with zinc and dilute hydrochloric acid, filter, and add solution of potassic chlorate. A mauve colour appears, if nitro-benzene is present.—Benzoic aldehyde is easily oxidised to benzoic acid ($C_6H_5.COOH$).

209. **Benzoic Acid.**—$C_6H_5.CO.OH$. Benzoic acid is found in gum benzoin, in balsams of Peru and Tolu, &c. It is also present in the urine of some animals.

PREPARATION.—1. By sublimation from *gum benzoin*, formerly the chief source of benzoic acid.

2. From *hippuric acid* ($C_9H_9O_3N$), which can be obtained in large quantities from the urine of herbivorous animals. This, when boiled with a dilute acid, decom-

poses into benzoic acid and *amido-acetic acid*, or *glycocoll* ($NH_2CH_2.COOH$):

$$C_9H_9O_3N + H_2O = C_6H_5.COOH + NH_2.CH_2.COOH.$$

A considerable proportion of the benzoic acid of commerce is derived from this source.

3. A good deal of benzoic acid is now made by oxidising *toluene* ($C_6H_5.CH_3$):

$$C_6H_5.CH_3 + 3O = C_6H_5.COOH + H_2O,$$

also from naphthalene ($C_{10}H_8$), which, when oxidised, yields a dibasic acid, *phthalic acid* ($C_6H_4(COOH)_2$). This acid when heated with lime breaks up into benzoic acid and calcic carbonate:

$$CaO + C_6H_4(COOH)_2 = CaCO_3 + C_6H_5COOH.$$

Experiment 193.—Carefully heat a small bit of gum benzoin in a t. t. Benzoic acid sublimes and collects in feathery crystals on the cooler parts of the tube. Note the odour.

PROPERTIES.—A white solid in pearly scales or feathery needles, of aromatic odour. It melts at 121° C. It dissolves easily in alcohol.

Experiment 194.—Try to dissolve a little benzoic acid in a small quantity of water. Heat the water. Taste the solution. Test with litmus. Heat a small particle of benzoic acid on mica, and inhale the fumes.

BENZOATES.—Benzoic acid is monobasic, and its salts are mostly soluble in water.

Experiment 195.—Colour some solution of ammonia in a porcelain dish with litmus, and gradually add benzoic acid to it until it is neutralised. Evaporate on the water-bath. White crystals of *ammonic benzoate* ($NH_4.C_7H_5O_2$) are left. It is necessary to add a little ammonia from time to time during evaporation so as to keep the solution alkaline. When salts of ammonia are evaporating a little ammonia always escapes.

Ammonic benzoate is used in medicine. When taken into the system it is eliminated in the urine as *hippuric acid*, rendering the urine strongly acid.—*Sodic benzoate* ($Na.C_7H_5O_2$) can be prepared in the same way as ammonic benzoate. It is used as a medicine.

Experiment 196.—Dissolve in a little water the ammonic benzoate prepared in Experiment 195. To a small portion of the solution add dilute hydrochloric acid. Benzoic acid is precipitated. To another portion add neutral solution of ferric chloride. Ferric benzoate ($Fe_2\overline{Bz}_6$) is precipitated. Examine it carefully, noting its colour, &c.

Tests.—See last experiment.

210. Saccharine. $C_6H_4\begin{smallmatrix}-CO\\-SO_2\end{smallmatrix}>NH$. (*Benzoyl sulphonic imide.*—This substance is related to benzoic acid. *Benzosulphonic acid* has the formula $C_6H_4\begin{smallmatrix}-CO.OH\\-SO_2.OH\end{smallmatrix}$. If the two hydroxyls are replaced by the dyad radical $=NH$, the formula for saccharine is obtained.—This remarkable substance was discovered a few months ago by Dr. Fahlberg.

PROPERTIES.—A white crystalline solid, "220 times as sweet as cane-sugar." It has antiseptic properties, and is said to be harmless when taken into the system, passing away in the urine unchanged. It is difficultly soluble in cold water, more freely in hot water, in alcohol, and in ether. It is proposed to use it instead of cane-sugar in cases of diabetes mellitus.

211. **Salicylic Acid** *(Ortho-hydroxy-benzoic acid).* $C_6H_4\begin{matrix}-COOH\\-OH\end{matrix}$. Occurs in several plants, e.g., wintergreen, as *methyl salicylate* ($C_6H_4\begin{matrix}-CO.OCH_3\\-OH\end{matrix}$), or "oil of wintergreen." It is now prepared from carbolic acid, as well as by the oxidation of *salicin*, a glucoside.—It is a monobasic acid, powerfully antiseptic, preferable in some respects to carbolic acid, being not so injurious to the tissues.

212. **Gallic Acid** *(Trihydroxy-benzoic acid)*, $C_6H_2(OH)_3.COOH$. Is present as a glucoside in oak-galls, tea, various barks, &c.

PREPARATION.—From oak-galls, which are powdered, moistened with water, and fermented 5 or 6 weeks. The gallic acid is then dissolved out with boiling water.

PROPERTIES.—A light, white, crystalline solid. It dissolves in 100 parts of cold, and in 3 parts of hot, water; it is freely soluble in alcohol, and sparingly in glycerine and in ether. Gallic acid is a monobasic acid.

Tests.—1. With solution of ferric chloride it gives a blue-black precipitate, soluble in excess.

2. It does not coagulate solution of gelatine or white of egg.

213. **Tannic Acid.**—$C_{14}H_{10}O_9$. This is an *anhydride* of gallic acid, and its molecule is formed from two of gallic acid by the substraction of a molecule of water:

$$\underset{\text{Gallic acid.}}{2C_7H_6O_5} - H_2O = \underset{\text{Tannic acid.}}{C_{14}H_{10}O_9}.$$

PREPARATION.—From gall nuts by steeping them in water 3 or 4 days and then extracting with ether.

PROPERTIES.—A white or yellowish solid, of acid, astringent taste, soluble in water, and in a mixture of water with alcohol or ether.—*Tannin* is the glucoside, present in oak-galls, &c., which produces gallic and tannic acids by its decomposition. Glucose is formed at the same time, and commercial tannic acid generally contains glucose. Tannic acid forms gallic acid when boiled with dilute acids.

Tests.—1. With aqueous solution of ferric chloride, a black colour is produced (ink).

2. With ferrous sulphate, it slowly blackens.

3. Tannic acid coagulates solution of gelatine or white of egg. This illustrates the process of *tanning*.

NOTE.—Tannic acid is a good *local* astringent, while gallic acid is a *remote* astringent.

214. **Terpenes**.—$C_{10}H_{16}$. These form a series of isomeric hydrocarbons found in pines, firs, and other trees. —*Turpentine* is an oily liquid (like honey), which flows from incisions in firs, larches, &c. When distilled it yields "oil," or "spirits" of turpentine, and a rosin (resin) which remains in the retort. *Rectified oil of turpentine* is prepared by mixing the crude oil with caustic soda and distilling it. It is a limpid, colourless liquid of pungent smell and bitter taste. When exposed to the air it partly volatilises and partly oxidises to resin. It dissolves resins, and is hence used in preparing varnishes.—*Resins* are oxidation products of terpenes. *Balsams* are similar compounds. Resins consist largely of acids, and form soaps with alkalis. They are used in soap-making.

215. **Camphor.**—$C_{10}H_{16}O$. Is prepared by distilling camphor wood with water. The camphor laurel grows in China and Japan.

PROPERTIES.—A white, crystalline solid, melting at 175°. It volatilises slowly at ordinary temperatures. It is slightly soluble in water (40 grains in a gallon), freely in alcohol, and in oils. Specific weight = 0.98.—*Liquid camphor*, or *camphor oil* ($C_{20}H_{32}O$) is the essential oil of the camphor laurel. It yields camphor when oxidised by exposure to air.—*Borneo camphor* ($C_{10}H_{18}O$) is obtained from *Dryobalanops camphora.* "Oil of Borneo camphor" (so-called) is in reality a terpene.

216. **Cinnamic Acid.**—$C_6H_5 - CH{=}CH - COOH$, or $C_9H_8O_2$. Found in liquid storax, and in balsams of Peru and Tolu. It can be prepared by oxidation of *oil of cinnamon*, which consists largely of *cinnamic aldehyde* (C_9H_8O).

217. **Essential Oils** (*volatile oils*).—The essential oils are the substances which impart fragrance and flavour to different parts of plants. They generally contain compounds resembling camphor or turpentine, along with ethereal salts of benzoic, cinnamic, and other aromatic acids. They are obtained from the leaves, flowers, fruit, &c., of plants, by distilling with water, or by expressing. *Oil of cinnamon* and *oil of cloves* are good examples.

Experiment 197.—Distil some ground cloves with water and obtain oil of cloves. Receive in a cold t. t.

218. **Indigo Blue** *(Indigotin)*.—$C_{16}H_{10}N_2O_2$. Prepared from certain plants which contain a glucoside, *indican*. This yields indigo when fermented and oxidised by the air. Indigo is also made artificially by a complicated process, including the formation of cinnamic acid.

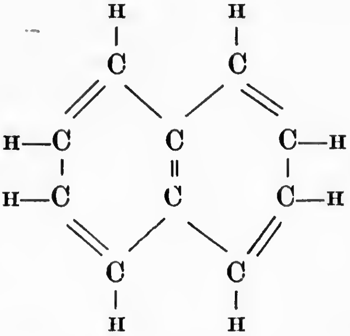
Properties.—A dark blue solid, insoluble in water, in dilute acids, alkalis, and ether; but soluble in paraffin oil and in hot alcohol. When indigo is heated it volatilises, forming a beautiful purple vapour. If it is pure (as it rarely is), there is no residue.—Indigo is soluble in concentrated sulphuric acid, forming *sulphindylic*, or *sulphindigotic* acid. A dilute solution of this is used as a test for nitric and chloric acids, which oxidise it and destroy the colour.—Indigo is reduced to *indigo white* by green vitriol and other reducing agents. Indigo white is soluble in water, a very important fact for the dyer. Calicos, &c., are printed or dyed with the colourless solution of indigo white and then exposed to the air. The oxygen of the air unites with the indigo white forming the insoluble indigo blue, and thus a *fast* colour is produced.—Indigo is often adulterated with Prussian blue, which leaves a bulky reddish residue when heated.

Experiment 198.—Heat a little indigo in a porcelain dish or on mica.

Experiment 199.—Try to dissolve a little indigo in water. Add some solutions of ferrous sulphate and caustic soda, and heat. Steep a piece of white cotton in the solution and expose it to the air for some time.

219. **Naphthalene.**—$C_{10}H_8$. Naphthalene is related

to benzene in the manner indicated by the structural formula:



It is prepared from the heavy oil of coal-tar by fractional distillation.—It is a colourless solid, crystallising in thin plates. It melts at 79°.2 and boils at 216°.6. It is insoluble in water, but soluble in alcohol. When oxidised it yields *phthalic acid*, $C_6H_4(COOH)_2$, from which benzoic acid is manufactured.

220. **Anthracene.**—$C_{14}H_{10}$. Is also obtained from the heavy oil of coal-tar. It is the starting point in the preparation of *alizarin*, or *artificial madder*.

221. **Glucosides.**—These are substances found in plants, which readily undergo fermentation, with a glucose as one product. The other products of the fermentation are various, but generally an aldehyde or an alcohol. The ferment is present in the same plant with the glucoside, but appears to be enclosed in separate cells, and thus does not set up fermentation until the cells are broken down by grinding, &c.

1. Amygdalin has been already described (Art. 205).

2. SALICIN ($C_{13}H_{18}O_7$). Found in willow bark and in poplar leaves and bark.

PREPARATION.—Boil willow or poplar bark with milk of lime, filter, decolourise with bone-black, evaporate the filtrate to dryness, and extract the salicin with alcohol.

PROPERTIES.—A white solid, soluble in alcohol and in hot water, but not in ether. It dissolves readily in solutions of alkalis or of alkaline carbonates.

Experiment 200.—Boil a little salicin for some time with water and a few drops of sulphuric acid, and then test for glucose.

When salicin ferments, it unites with water, thus forming *salicylic alcohol* and dextrose:

$$C_{13}H_{18}O_7 + H_2O = C_6H_4\left\{\begin{matrix}OH\\CH_2OH\end{matrix}\right. + C_6H_{12}O_6.$$

Experiment 201.—Dissolve a little salicin in solution of potassic carbonate. Neutralise with hydrochloric acid. The salicin is precipitated.

A solution of salicin with potassic carbonate is said to be valuable in cases of diabetes.

Tests.—1. Mix on a porcelain plate with concentrated sulphuric acid. A red colour is produced.

2. See Experiment 200.

3. Heat with potassic bichromate and dilute sulphuric acid, and observe the odour of salicylic aldehyde. It is like that of heliotrope.

3. DIGITALIN.—A mixture of several glucosides. It is the active principle of foxglove. When boiled with dilute acids it yields glucose and *digitaliretin.*—Digitalin is a white, inodorous solid, of very bitter taste. It is almost

insoluble in water and in ether, but soluble in alcohol and in acids. It leaves no residue when burned. It is poisonous, one-sixteenth of a grain being sometimes fatal.

Test.—Mix with weak aqueous solution of dried ox-bile, and add concentrated sulphuric acid. A deep red colour is formed.

4. JALAPIN ($C_{34}H_{56}O_{16}$), *glycyrrhizin* ($C_{24}H_{36}O_9$), and *helleborin* ($C_{26}H_{44}O_{15}$) are glucosides found in jalap, liquorice, and the hellebore respectively.—*Cerebrin* is a glucoside present in the brain and other nervous tissues.

222. **Alkaloids.**—As the name implies, alkaloids are substances having the properties of alkalis, i.e., of the volatile alkali, ammonia. They are, in fact, *amines* the molecules of which are of complex structure and in most cases not yet known. They are for the most part products of vegetable growth. Their names are generally derived from those of the plants from which the alkaloids are obtained, the terminations *-ine* and *-ia* being used interchangeably, e. g., *strychnine*, or *strychnia*, derived from *Strychnos nux vomica.*—The alkaloids all contain nitrogen, and many of them oxygen. in addition to carbon and hydrogen. Those which contain no oxygen are mostly liquids, which can be distilled ; those containing oxygen are crystalline solids and cannot be distilled. *Most of them are insoluble, or sparingly soluble, in water, but unite with acids to form soluble salts.* The alkaloids dissolve in alcohol, ether, chloroform, benzene, &c. Their taste is generally intensely bitter.—They are usually extracted from the plants with water or dilute acid; and the solution is then decomposed with an alkali. The volatile alkaloids are distilled, while the solid ones are filtered off.

General Tests.—1. All alkaloids give a precipitate with *phosphomolybdic acid.*

2. All alkaloids give a precipitate with solution of *potassic mercuric iodide* ($HgI_2.2KI$).

3. Most of the alkaloids give a precipitate with *potassic iodide solution of iodine.*

223. **Volatile Alkaloids.**—*Conine* ($C_8H_{14}.NH$) is the active principle of poisonous hemlock (*Conium maculatum*). It is a colourless liquid, boiling at 168° C. It dissolves in 100 parts of water, forming a strongly alkaline solution. It unites with acids, forming salts, e.g., $C_8H_{14}.NH_2Cl$. It is a narcotic poison. — *Nicotine* ($C_{10}H_{14}N_2$) is found in tobacco, from which it can be obtained by distilling with solution of caustic potash. It is a narcotic poison.

224. **Morphine.** — $C_{17}H_{19}NO_3.H_2O$. This is found in opium, associated with *narcotine* and other alkaloids. It is combined with *meconic acid.*

PREPARATION.—The meconate is dissolved out with water and treated with solution of calcic chloride. *Morphine chloride* remains in solution while *calcic meconate* is precipitated. From this solution the morphine is precipitated by ammonia.

PROPERTIES.—A white crystalline solid, insoluble in ether, sparingly soluble in water and in cold alcohol, and soluble in hot alcohol and in dilute acids. It unites with acids, forming crystallisable, soluble salts. The chloride (*hydrochlorate,* or *muriate*), sulphate, and acetate are used in medicine.—Morphine and its salts are narcotic poisons.

Tests.—1. If solid, add a little water; if liquid, evaporate nearly to dryness. Stir with a drop of neutral ferric chloride solution. A dirty blue colour appears.

2. Moisten the solid substance with strong nitric acid. It gives a bright orange-red colour.

225. The Alkaloids of Peruvian Bark (Cinchona).

1. Quinine ($C_{20}H_{24}N_2O_2.3H_2O$). The alkaloid itself is a white, crystalline powder. It is sparingly soluble in water (1 in 900), but easily soluble in alcohol and ether. The solutions have an alkaline reaction. *Sulphate of quinine* is the salt generally used in medicine, but preparations of *citrate* and *chloride* are also used. The sulphate is only sparingly soluble in pure water, but dissolves readily in water containing sulphuric acid (a soluble acid salt being formed).

Experiment 202.—Try to dissolve quinine or quinine sulphate in water. Add sulphuric acid. Note the *fluorescence* of the solution.

Experiment 203.—Add an alkali to a solution of quinine sulphate. What is precipitated?

Quinine and its salts are *antipyretic* (lower the temperature when taken internally); and also *antiperiodic* (prevent the return of periodic fevers, &c.)

Test.—Add chlorine water and then a considerable quantity of ammonia solution. A bluish-green colour appears. If potassic ferrocyanide be added before the ammonia, a red colour appears for a moment, but soon fades.

Note.—Quinine and its salts are sometimes adulterated with salicin.

2. Cinchonine ($C_{20}H_{24}N_2O$) is less soluble in alcohol than quinine, and is thus separated from it in the process

of preparation. It is similar to quinine in its properties, but is insoluble in ether. It is not so good a febrifuge as quinine.

Tests.—Cinchonine does not give the greenish-blue colour with chlorine water and ammonia. It is sometimes used to adulterate quinine. To detect it, make the following test: "Into a glass tube or bottle put ten grains of the suspected salt, dissolve in 10 minims of dilute sulphuric acid, and 60 minims of distilled water; to this add 150 minims of *pure* ether, 3 minims of spirits of wine, and 40 minims of a solution of soda (1 of caustic soda in 12 of water). Agitate well and set aside for 12 hours, when, if the slightest trace of quinidine or cinchonine be present, they will be seen at the line of separation between the ether and the solution of sodium sulphate."

3. QUINIDINE, cinchonidine, &c., are other alkaloids found in Peruvian bark.

226. **Strychnine.**—$C_{21}H_{22}N_2O_2$. Is found in *Strychnos nux vomica,* along with *brucine* ($C_{23}H_{26}N_2O_4$).—Strychnine is a white crystalline solid, sparingly soluble in water and intensely bitter in taste. It is soluble in spirits of wine, but not in absolute alcohol or ether. The solution generally used in medicine is made with hydrochloric acid, rectified spirits, and water. It is very poisonous.

Tests.—1. Dissolve the solid in pure sulphuric acid and stir with a drop of potassic bichromate solution. A violet colour is produced, which soon changes to red and yellow.

2. The solution, when treated with hydrochloric acid and *mercuric chloride* ($HgCl_2$), gives a clotted white precipitate.

3. Pure strychnine gives no colour with nitric acid. Brucine is turned deep red.

227. **Cocaine.**—$C_{17}H_{21}NO_4$. Obtained from cocoa leaves (*Erythroxylon coca*). The hydrochlorate ($C_{17}H_{21}$

$NO_4.HCl$) is used as a local anæsthetic. When a little of it is put into the eye, it causes insensibility to pain in that part, and operations can thus be performed without administering chloroform or ether.

228. **Atropine,** ($C_{17}H_{23}NO_3$), and **hyoscyamine** ($C_{15}H_{23}NO_3$), are poisonous alkaloids found in common plants; atropine in *belladonna,* the *thorn-apple,* &c., and hyoscyamine in *henbane.*

229. **Artificial Alkaloids.** — Several antipyretic alkaloids have lately been made by synthesis from coal-tar products. They promise to be very valuable as medicines.

1. KAIRINE ($C_{10}H_{13}NO$) is made from aniline by a series of rather complicated reactions. It unites with acids to form soluble salts. The *chloride* ($C_{10}H_{14}NO.Cl$) is sold as a substitute for quinine. It lowers the temperature in fevers, but this action is only of short continuance. On the other hand, it has none of those unpleasant effects associated with the antipyretic action of quinine.

2. ANTIPYRINE ($C_{11}H_{12}N_2O$) is also manufactured from aniline as a starting point. It is a powerful antipyretic, but *not* antiperiodic. It is a white, tasteless, odourless, crystalline solid, *easily soluble in cold water.* It is used uncombined with acids.

3. THALLINE ($C_{10}H_{11}NO_5$), a recently discovered artificial alkaloid, is said to be a specific for yellow fever.

There are many alkaloids prepared from coal-tar, the physiological actions of which have not been investigated. The results already obtained show the fruitfulness of a combination of the chemist's investigations with those of the physician. An illustration of the necessity for this is the fact that cocaine was known ten years before the peculiar power of its hydrochlorate was discovered.

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230. **Albuminoids, or Proteids.** — These are nitrogenous substances of a very complex character. They are the basis of all living matter. They are similar in composition, but vary slightly. They contain carbon, hydrogen, oxygen, nitrogen, sulphur, and, generally, phosphorus. Their percentage composition is as follows:

Carbon	from	51.5	to	54.5
Hydrogen	"	6.9	"	7.3
Oxygen	"	20.9	"	23.5
Nitrogen	"	15.2	"	17.0
Sulphur	"	0.3	"	2.0
Phosphorus	"	0.4		

The proteids are built up by plants out of the simpler compounds which form their food. Animals have no power of synthesising them, and must therefore obtain them ready-formed from plants.

Experiment 204.—Beat up the white of an egg with water, allow the solution to settle, and pour off the clear liquid. Heat a small quantity. It coagulates before it begins to boil. Try another portion after adding a little caustic soda. Test other portions with nitric, hydrochloric, and sulphuric acids, and with alcohol; also with acetic and tartaric acid. To another portion add a *very* small drop of cupric sulphate solution and then a large quantity of caustic soda. A purple colour is produced. This reaction is characteristic of proteids.

Experiment 205.—To small quantities of the solution of white of egg add solutions of plumbic acetate, cupric sulphate, and mercuric chloride (corrosive sublimate). Collect the precipitates on filters, and wash them three or four times by pouring distilled water on them. Then pour a little ammonic sulphide solution on each of them. They are blackened, showing the presence of the metallic salts. This explains the action of white of egg as an antidote.

Proteids are all colloid substances, and have very little power of passing through animal membranes. Hence, *albuminuria* indicates something radically wrong in the kidneys.—Many proteids are soluble in pure water, but others require a small quantity of sodic chloride to keep them in solution. After they have been coagulated, they can be dissolved by the action of dilute acids aided by a ferment, as in the process of digestion. Alkalis keep in solution many proteids insoluble in neutral or acid solutions. Thus milk, naturally alkaline, coagulates when it becomes sour.—Proteids are very unstable chemical compounds, readily undergoing fermentations and other chemical changes.

QUESTIONS AND EXERCISES.

1. Compare the preparation of benzene with that of marsh gas.

2. Explain the action of milk of lime in purifying oil of bitter almonds.

3. Write the formulas for chloride, sulphate, and acetate of morphia. (Its molecule is equivalent to one molecule of ammonia).

4. How would you test for salicin in a specimen of quinine?

5. How would you distinguish between specimens of morphine and brucine?

6. Calculate the percentage composition of acetylene (C_2H_2), and of benzene (C_6H_6).

7. Is carbolic acid a true acid? (Note.—Ethyl alcohol forms *alcoholates*, C_2H_5ONa, &c.)

8. The flowers, &c., of the Cherry Laurel contain amygdalin. Is that plant poisonous?

9. What is the relation of saccharine to benzoic acid? Would you expect it to be nutritive?

10. Why is indigo-blue reduced to indigo-white in dyeing? How is it re-oxidised?

11. Indigo is often adulterated with Prussian blue. How would you detect this?

12. How would you make an aqueous solution of quinine sulphate?

13. A specimen of urine gives a white precipitate with strong nitric acid. What is the cause of it?

CHAPTER XV.

SILICON AND BORON.

231. **Silicon** ($Si^{iv} = 28$).

Occurrence.—The greater part of the earth's crust is made up of compounds called *silicates*, composed of silicon, oxygen, and metals. Silicon is never found free in nature, but always in the form of *silica* (SiO_2), either uncombined (sand, quartz, &c.), or combined in silicates. Minute traces of combined silicon are present in the urine, blood, bones, &c., of man.

Preparation. — By heating *potassic fluosilicate* (K_2SiF_6) in iron tubes with potassium or aluminium. When potassium is used, the silicon is obtained as an amorphous powder; with aluminium, it crystallises:

$$2KF.SiF_4 + 4K = 6KF + Si.$$

Properties.—Two allotropic forms, one crystalline, the other amorphous. There is perhaps a third form resembling graphite. (Compare *carbon.*) Amorphous silicon burns readily in air, forming the dioxide (SiO_2); crystalline silicon oxidises only very slowly. Silicon resembles carbon in its chemical characters. Compounds with hydrogen, chlorine, bromine, and iodine are known, parallel with methane, &c. (SiH_4, $SiCl_4$, $SiBr_4$, SiI_4) also more complicated compounds (Si_2Cl_6, &c.); and silicon seems able to replace carbon to a certain extent in many organic compounds.

232. Silicon Dioxide.—SiO_2.

Also called *silica*, and *anhydrous silicic acid.* It is the only oxide of silicon known.

OCCURRENCE.—Quartz (rock crystal) is pure crystallised silica. Amethyst is coloured quartz. Sand, agate, flint, jasper, chalcedony, diatoms, opal, &c., are less pure forms. United with the oxides of metals, silica forms the great divison of minerals, the *silicates.*

PROPERTIES.—Pure amorphous silica, obtained by heating *silicic acid* (H_2SiO_3), is a light, white powder, insoluble in water and in all acids except *hydrofluoric* (HF). *It is easily soluble in alkalis*, even in ammonia. It decomposes sodic carbonate when heated with it either dissolved in water or solid. Various forms of silica are used in glass and soap manufacture, in mixing mortar and cements, for gems, &c. Agate is made into mortars and pestles used in triturating hard minerals.

233. Silicic Acid and Silicates.

Experiment 206.—Fuse a little clean white sand in a porcelain (or better, platinum) crucible with about 1½ times its weight of anhydrous sodic carbonate (Na_2CO_3). Continue heating until a clear liquid is obtained. Pour this out on a piece of clean iron, and, when it has cooled, break it up and dissolve it in water by boiling for some time.

In this experiment *sodic silicate* (Na_2SiO_3) is formed:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

(Have you observed the escape of the carbon dioxide?)

Experiment 207.—To a little of the solution of sodic silicate add dilute hydrochloric acid; collect the gelatinous precipitate on a filter and wash it with hot water. It is *silicic acid.* Heat a little of it on mica and obtain silica. Try the solubility of silicic acid in alkalis, and in acids. Write the equation for the decomposition of sodic silicate by hydrochloric acid.

SILICIC ACID has not been obtained of any definite composition free from water. There are numerous classes of silicates, corresponding to a great number of theoretical acids; e.g., *ortho-silicates,* salts of an acid, H_4SiO_4; and *meta-silicates,* from H_2SiO_3.—Silicic acid is insoluble in water, but an unstable solution, which easily gelatinises, can be obtained by careful manipulation (compare *dialysed iron*).—The silicates of the alkalis are soluble in water (*soluble glass*); all other silicates are insoluble. Mica, felspar, garnet, serpentine, and clays, are examples of natural silicates. *Felspar* is a double silicate of aluminium and potassium. By the action of air and water it is decomposed into potassic carbonate and *hydrated aluminium silicate,* or clay. In this way a fertile soil is gradually formed by the "weathering" of felspar.—The silicates are most conveniently represented as composed of oxides of metals united with one or more molecules of silica, e.g., $Na_2O.SiO_2$, $3MgO.2SiO_2$, &c.

Tests.—1. If the substance is solid, dissolve a little of it in a bead of molten borax on a small loop of platinum wire. The silica remains undissolved, floating in the clear bead.

2. Hydrochloric acid gives a gelatinous precipitate with solutions of silicates. If the solution is already acid, silica need not be tested for.

234. Fluosilicic Acid.—H_2SiF_6.

Preparation.—**Experiment 208.**—Mix some white sand with about twice its weight of powdered *fluor spar* (CaF_2), put the mixture in a t. t. or flask, pour some strong sulphuric acid over it, and immediately fit with a delivery tube dipping into a t. t. half-full of water. Heat gently. An invisible gas is evolved, bubbles through the water, and deposits a flaky white substance. Collect some of this and heat it on mica. It dries up to a light white powder. It is silica. Test the reaction of the water.—The delivery tube soon becomes choked up, and the experiment must then cease.

In this experiment, three chemical actions take place, as represented by the following equations:

$$(1)\quad H_2SO_4 + CaF_2 = CaSO_4 + 2HF.$$

$$(2)\quad 4HF + SiO_2 = \overset{\text{Silicon tetrafluoride.}}{SiF_4} + 2H_2O.$$

$$(3)\quad 3SiF_4 + 4H_2O = \overset{\text{Orthosilcic acid.}}{H_4SiO_4} + \overset{\text{Fluosilicic acid.}}{2H_2SiF_6}.$$

Silicon tetrafluoride is the gas which bubbles through the water. (What are the *final* products? Where are they at the end of the experiment?).—By filtering off the silicic acid, a solution of fluosilicic acid is obtained.

Properties.—A strong dibasic acid. Most of the *fluosilicates* are soluble in water, but *potassic fluosilicate* (K_2SiF_6), and *baric fluosilicate* ($BaSiF_6$) are only sparingly soluble. For this reason fluosilicic acid is used to separate these metals from others present with them in solutions.—*Fluo*silicic acid is silicic acid with fluorine instead of oxygen, 6 atoms of fluorine replacing 3 of oxygen.

235. **Boron** ($B^{iii} = 11$).—The chief compounds of this element occurring in nature are *borax* ($Na_2B_4O_7.10H_2O$), and *boric*, or *boracic, acid* (H_3BO_3). Borax is found principally in the plains of Thibet, and in the borax lakes of California. Boric acid issues along with steam from fissures in the sides of volcanic hills in Tuscany.—The element, boron, is of little importance. It can be prepared by methods similar to those used in the preparation of silicon, which element it resembles in its properties.

236. **Boric Acid.**—H_3BO_3. Derived from the lagoons of Tuscany, into which the boric acid comes from volcanic fissures or from holes bored for the purpose.

PREPARATION.—The water of these lagoons is evaporated by the heat of the steam which issues from the earth, until the acid crystallises out. The crystals are collected, dried, and purified by recrystallisation. Before the discovery of the presence of boric acid in the Tuscan lagoons, it was prepared from borax, by treating a hot saturated solution with strong hydrochloric acid. The boric acid crystallised out on cooling :

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

Since the discovery of the borax lakes of California, boric acid is again made in this way

Experiment 209.—Dissolve some borax in strong hydrochloric acid and cool. Boric acid crystallises out. Note the appearance of the crystals.

PROPERTIES.—A white solid, in small scales of a pearly lustre, and of somewhat soapy feel.

Experiment 210.—Heat a small quantity of boric acid in a dry t. t. It decomposes into water and *boron trioxide* (B_2O_3):

$$2H_3BO_3 = 3H_2O + B_2O_3.$$

Experiment 211.—Try the solubility of boric acid in water, cold and hot; also in alcohol. Pour the alcoholic solution into a porcelain dish and set fire to it. Note the green colour of the flame. Boric acid volatilises with alcohol, and is decomposed in the hot flame, imparting the green colour to it.—Taste the aqueous solution, and try its action on blue litmus.

Boric acid is tribasic, but the *borates*, like the silicates, are very various in their composition, and are best represented as compounds of *metallic oxides* with *boron trioxide*, e.g., $3MgO.4B_2O_3$.

237. **Borax**, or *Sodic Bi-borate*, $Na_2O.2B_2O_3.10H_2O$.—The crude salt, formerly largely imported into Venice and Amsterdam from Thibet, is called *tincal*. From this the borax of commerce was obtained by boiling with lime to rid it of grease, and then recrystallising the salt. Borax is now prepared mostly by fusing boric acid with sodic carbonate:

$$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2 + 6H_2O.$$

PROPERTIES.—Borax is generally sold in large colourless crystals. These effloresce in air. Borax is soluble in water, and the solution is alkaline. It is insoluble in alcohol.

Experiment 212.—Heat a small piece of borax in a dry t. t. Water condenses in the tube (Whence has it come?), and the borax swells up. Heat a little borax on a platinum wire, until it fuses to a clear bead, then allow it to cool, moisten it, touch it to some powdered cupric sulphate, fuse it again, and note the colour when it has cooled.

When borax is heated, it loses its water of crystallisation, and, if the temperature is high enough, fuses to a clear liquid. At high temperatures the *borax bead* dissolves metallic compounds, forming borates which give characteristic colours to the beads. Borax is used in this way to test small quantities of solid substances. —Borax is soluble in glycerine, and a *glycerine of borax* is used as a lotion and gargle.

Tests for Boric Acid and Borates.—1. Mix the substance with strong sulphuric acid and alcohol in a porcelain dish, and set the alcohol on fire. It burns with a green flame. Or, fuse some of the substance on a platinum wire, moisten it with strong sulphuric acid or glycerine, and hold it in the Bunsen flame. It gives a green colour to the flame.

2. Acidify the solution with hydrochloric acid, dip in it a strip of *turmeric paper*, and dry the paper at a gentle heat. It is turned brown.

3. Add a few drops of baric chloride ($BaCl_2$) to a solution of a borate. A white precipitate is formed. It is soluble in hydrochloric acid.

QUESTIONS AND EXERCISES.

1. Compare silicon and carbon, (*a*) with regard to chemical, and (*b*) with regard to physical, properties.

2. What is *soluble glass?*

3. Explain the term *fluosilicic acid*.

4. Balance the following equation:

$$K_2SiF_6 + Al = KF + Al_2F_6 + Si.$$

5. It is found that alkaline solutions eat away glass. Explain.

6. Mention an acid and a base which will dissolve sand.

7. How can it be proved that silica is an acid-forming oxide ?

8. With what does the delivery-tube become choked up in Experiment 208 ?

9. Boric acid (H_3BO_3) is tribasic. Write the formula for normal sodic borate. Is this the ordinary salt ?

10. Borax is an acid salt, and yet its solution is alkaline. Account for this.

11. How can borax be used to test for glycerine ?

12. In the preparation of boric acid from borax, sodic chloride is formed. How is the boric acid separated from it ?

CHAPTER XVI.

THE METALS.

238. **General Characters.**—The only characteristic common to all metals is the power of taking the place of the hydrogen of acids to form salts, or in other words, *the power of forming bases.* But most metals have a bright and peculiar appearance called *metallic lustre ;* as a rule, they are specifically heavier than water ; they are good conductors of heat and electricity ; and most of them are malleable and ductile.

239. **Ores of Metals.**—The *noble metals* (i.e., the least oxidisable) are generally found uncombined (*native*) ; native copper also occurs. Sometimes the baser metals are found free ; but in most cases they occur combined with other elements, from which they are separated by the processes of *metallurgy.* Common metals such as lead, iron, tin, &c., are found very gener-

ally as sulphides and oxides. In many cases salts of the metals are found in nature. If the metals of the alkalis be excepted, it may be stated as a general rule that metallic ores are insoluble in water.—The processes by which metals are obtained from their ores are various. A common way, applicable to oxides and some oxygen salts, is to heat to a high temperature with some form of carbon (coal, charcoal, &c.). In many cases sulphides are first roasted to convert them into oxides, and then reduced by means of coal or charcoal. In other cases sulphides are partially oxidised at a comparatively low temperature, and then heated to a higher temperature, at which the oxygen and remaining sulphur combine, setting the metal free. Lead and copper are obtained in this way:

$$(1)\ PbS + 3O = PbO + SO_2.$$

$$(2)\ PbS + 2PbO = 3Pb + SO_2.$$

1. *Metals reduced by heating the ores with coal, charcoal,* &c.: Na, K, Rb, Sn, Cd, Zn, Fe, Mn, Sb, Cr, Ni.

2. *By partial oxidation and subsequent fusion:* Pb, Cu, Bi.

3. *By heating with sodium or potassium:* Al, Mg, Ca, Be.

4. *By electrolysis of fused salts:* Ba, Ca, Sr, Li, Cs.

5. *By distilling in a current of air:* Hg.

6. *Native:* Cu, Ag, Au, Pt, Hg, &c.

This is only a general statement, and not intended to be exhaustive.

240. **Alloys.** — Metals usually combine with each other when fused together. In many cases the combina-

tion takes place in definite proportions, and chemical compounds are formed. In other cases, the proportions may be varied, and it is not easy to decide whether or not there is any chemical action. Compounds of metals with each other are called *alloys.* The properties of alloys are not the mean between those of the metals present. Alloys generally melt at lower temperatures than any of the constituents. Thus, *Rose's fusible metal* (tin, 1 part; lead, 1 part; and bismuth, 2 parts) melts at 95° C.; while tin melts at 235°, lead at 334°, and bismuth at 270°. Many alloys are in common use, e.g.

Solder, tin and lead in various proportions.

Brass, 65 parts zinc, and 137 parts copper.

Gold coin, 11 parts gold and 1 part copper.

Silver coin, 40 parts silver and 3 parts copper.

Gun metal, 9 parts copper and 1 part tin.

Bell metal, 4 parts copper and 1 part tin.

Type metal, 4 parts lead and 1 part antimony.

Britannia metal, copper, zinc, tin, antimony.

Pewter, 4 parts tin, and 1 part lead.

Bronze, tin, copper, and zinc.

German silver, 5 parts copper, 2 parts nickel, and 2 parts zinc.

Wood's fusible metal (melting at 68°), 8 parts lead, 5 parts bismuth, 4 parts tin, and 3 parts cadmium.

Amalgams are alloys of mercury with other metals.

241. **Compounds of Metals.**—The compounds of metals are classified into (1) *binary compounds,* including oxides, sulphides, chlorides, bromides, iodides, fluorides,

&c. (Note the ending—*ide*); and (2) *oxygen salts*, &c., such as sulphates, sulphites, nitrates, phosphates, &c.

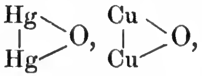
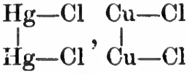
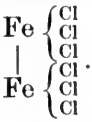
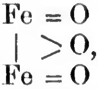
242. **Oxides of Metals.**—Each metal has at least one *basic oxide ;* several have *acid-forming oxides ;* and many have oxides which are neither base-forming nor acid-forming, hence called *indifferent oxides.*

1. BASIC OXIDES.—These may be classified as follows:

(a) *General formula* M_2O :—Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O ; Ag_2O, Hg_2O, Cu_2O ; Tl_2O, Au_2O.

(b) *General formula* MO :—CaO, SrO, BaO ; PbO, HgO, CuO, SnO ; FeO, MnO, ZnO, NiO, CoO, CrO ; PtO, &c.

(c) *General formula* M_2O_3 :—Sb_2O_3, Bi_2O_3, Au_2O_3, Tl_2O_3 ; Fe_2O_3, Al_2O_3, Mn_2O_3, Co_2O_3, Cr_2O_3.

This includes nearly all the basic oxides (the rarer metals being left out of consideration).—It will be observed that some metals have more than one basic oxide. Some dyad metals (Hg, Cu) have oxides in which they seem to play the part of monad metals. There is reason to believe, however, that the molecules of the corresponding chlorides must be represented as follows: Hg_2Cl_2, and Cu_2Cl_2. The metals must, then, be dyad in these compounds, and the structural formulas for the oxides and chlorides are  and  $\begin{array}{l} Hg-Cl \\ \vert \\ Hg-Cl \end{array}, \begin{array}{l} Cu-Cl \\ \vert \\ Cu-Cl \end{array}$.—Gold and thallium are monad and triad. Thus gold forms *aurous oxide*, Au_2O, and *auric oxide*, Au_2O_3.—Iron, cobalt, and manganese, have two basic oxides, e.g. *ferrous oxide*, FeO, and *ferric oxide*, Fe_2O_3. In the lower oxides these metals are dyad. The specific weight of ferric chloride in the gaseous condition shows that its formula is Fe_2Cl_6, or graphically  $\begin{array}{l}\mathrm{Fe}\begin{cases}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{cases}\\ \;| \\ \mathrm{Fe}\begin{cases}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{cases}\end{array}$. Ferric oxide must then be represented as  $\begin{array}{l}\mathrm{Fe}=\mathrm{O}\\ \;|\quad >\mathrm{O}\\ \mathrm{Fe}=\mathrm{O}\end{array}$, and in the ferric compounds iron is tetrad. So with manganese, cobalt, aluminium, and chromium, which have also basic *sesquioxides*. The first group of sesquioxides, Sb_2O_3, &c., correspond to chlorides, $SbCl_3$, &c., so that the metals must be represented as triad, e.g. $O=Sb-O-Sb=O$.—There are *hydroxides* corresponding to most of the basic oxides.

2. ACID-FORMING OXIDES.—The basic oxides of imperfect metals, such as antimony, have also weak acid characters; but there are also distinct acid-forming oxides of these metals, e.g. *antimony pentoxide*, Sb_2O_5. Chromium, manganese, &c., also form acids. The acid-forming oxides always contain a greater proportion of oxygen than the basic, and, as a rule, readily give up their oxygen to reducing agents, becoming transformed to basic oxides.

3. INDIFFERENT OXIDES.—These are such oxides as *manganese dioxide* (MnO_2), having neither acid nor basic properties. They generally contain a greater proportion of oxygen than the basic oxides, and are hence often called *per*-oxides.

243. **Sulphides of Metals.**—These correspond closely to the basic oxides of the metals, e. g., Li_2S, Na_2S, &c. The imperfect metals have sulphides corresponding to their acid-forming oxides, e. g., Sb_2S_5, SnS_2, &c. As a

rule, when a basic oxide of a metal is soluble in water, the corresponding sulphide is also soluble,—and so for insolubility. Thus, both the oxides and the sulphides of lithium, sodium, potassium, &c., are soluble in water.

244. **Chlorides,** &c. — There are chlorides corresponding to the basic oxides of the metals. In writing the formulas of chlorides, it must be remembered that 2 atoms of chlorine replace 1 atom of oxygen. Thus, given the formula of *aluminic oxide,* Al_2O_3, the formula for *aluminic chloride* is written, Al_2Cl_6. It could be written more simply, $AlCl_3$, but, for reasons similar to those stated above for ferric chloride, the simpler formula is doubled. The formula for *bismuth trioxide* is Bi_2O_3; replacing O_3 by Cl_6, we get as the formula for the chloride, Bi_2Cl_6, but its specific weight in the gaseous state shows that its molecule contains only half the number of atoms represented here, so that the formula for *bismuth trichloride* is $BiCl_3$.

245. **Oxygen Salts.** — The oxygen salts of the metals have been already noticed along with the various acids. To derive the formula of an oxygen salt from the formula of an oxygen acid, it is necessary to know the atomicity of the metal, and, also, whether or not two atoms of the metal play the part of a single atom as in the case of *mercurous salts* ($Hg_2(NO_3)_2$, &c.), and the *ferric* salts ($Fe_2(NO_3)_6$, &c.). For example, given the formula of sulphuric acid as H_2SO_4, and knowing the atomicity of calcium to be 2, it is easy to write the formula for calcic sulphate, viz,, $CaSO_4$. Again, bismuth is triad; and, therefore, 1 atom of bismuth replaces 3 of hydrogen. In order to replace the hydrogen of sul-

phuric acid by bismuth, we must take $3H_2SO_4$. The 6 atoms of hydrogen are equivalent to 2 of bismuth; and, therefore, the formula for *bismuth sulphate* is $Bi_2(SO_4)_3$. The atomicity of iron in the ferric salts is 4, but 2 atoms of iron are united in the molecules of ferric salts so that their joint atomicity is 6; i.e., Fe_2 replaces 6H. The formula for ferric sulphate is thus $Fe_2(SO_4)_3$. —To many oxygen salts there are corresponding *sulphur salts*, e.g., K_2CS_3.

246. **Classification of Metals — Analysis.** — The method of classification to be adopted here is that which is employed in the process of examining unknown substances to discover the elements of which they are composed. These processes constitute *analysis* in the broad sense of the term. The substances are not always —indeed, not generally—decomposed into their elements, but such evidence is obtained as enables the analyst to be certain of the presence of the elements. This is *qualitative analysis.* If the *quantities* of the elements in a compound, or the quantities of the elements and compounds in a mixture, are to be determined, this is done by *quantitative analysis.* A great deal of the work in both qualitative and quantitative analysis consists in preparing insoluble compounds of the metals (and acids) by *precipitation* from solutions. In order to understand the operations of analysis it is necessary to know the solubilities of chemical substances. Such knowledge is also of great importance to the prescriber of medicines. A physician who is not well acquainted with this part of chemistry is very likely to produce "muddy mixtures."

PRECIPITATION.—When two chemical compounds are brought together in solution, there is usually chemical action, consisting in exchange of parts of the molecules. If this exchange causes the formation of an insoluble substance, the latter is *precipitated*, or *thrown to the bottom.*

Experiment 213.—Mix solutions of *cupric sulphate* ($CuSO_4$) and *baric chloride* ($BaCl_2$). A white precipitate of *baric sulphate* ($BaSO_4$) falls, while *cupric chloride* ($CuCl_2$) remains in solution.

Such a chemical action is called a *double decomposition*, because the two salts decompose each other, the metals changing places :

$$\left.\begin{matrix} CuSO_4 \\ BaCl_2 \end{matrix}\right\} = \left\{\begin{matrix} BaSO_4 \\ CuCl_2 \end{matrix}\right.$$

GROUP REAGENTS.—Insoluble compounds can generally be obtained by precipitation. We have seen in studying groups of compounds, such as chlorides, sulphides, carbonates, &c., that each group may be classified into (1) *soluble*, and (2) *insoluble*. Thus, there are three insoluble chlorides ($PbCl_2$, $AgCl$, Hg_2Cl_2), and the rest are soluble. If a complex solution containing salts of all the metals were treated with hydrochloric acid, these three chlorides would be formed and precipitated. Thus, a separation would be effected of lead, silver, and mercury from the rest of the metals. Hydrochloric acid is a *group reagent*; and, in analysing substances, the first step is to determine by the use of group reagents to what group or groups the substances under examination belong.

GROUPS OF METALS.

I. *Lead*,* *silver*, and *mercury* (mercur*ous* salts). Chlorides precipitated by *hydrochloric acid.*

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* Plumbic chloride is sparingly soluble, so that lead appears in Groups and II.

II. *Lead, mercury* (mercuric salts), *copper, cadmium, bismuth, antimony,* [*arsenic*], *tin, gold, platinum,* and some rare metals. Sulphides precipitated by *hydric sulphide* from neutral or acid solutions.

III. *Iron, chromium, aluminium, zinc, manganese, cobalt,* and *nickel.* Sulphides precipitated only in presence of an alkali. *Ammonic sulphide* is the group reagent.

IV. *Calcium, strontium,* and *barium.* Precipitated as carbonates from solutions (in presence of ammonic chlorides) by *ammonic carbonate.*

V. *Magnesium.* Precipitated as phosphate, by *sodic phosphate.* Magnesium is often included in Group IV.

VI. *Lithium, sodium, potassium, ammonium, rubidium,* and *cæsium.* Salts mostly soluble.

Groups I., II., and III., include the common metals in everyday use. They are the *heavy metals.* Group IV. is made up of the *metals of the alkaline earths.* Group VI. includes the *metals of the alkalis.*

QUESTIONS AND EXERCISES.

1. Metals generally feel cooler than other substances. Why is this ?

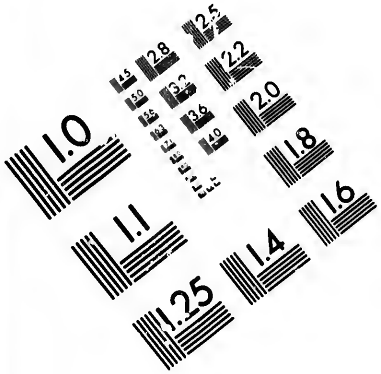
2. What is an *ore* ?

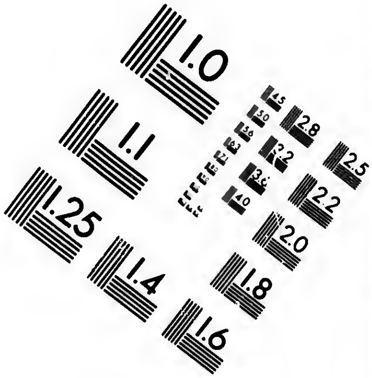
3. Are alloys compounds or mixtures?

4. What class of metallic compounds does the ending *-ide* mark ?

5. Why write the formula for chromic chloride Cr_2Cl_6, and not $CrCl_3$?

6. Mercury is a dyad metal, but it has an oxide Hg_2O. How is this explained ? What non-metal forms numerous compounds in the same way ?





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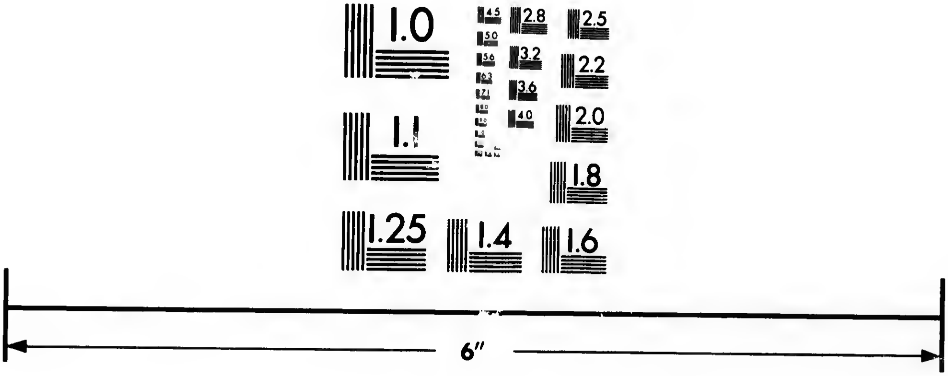

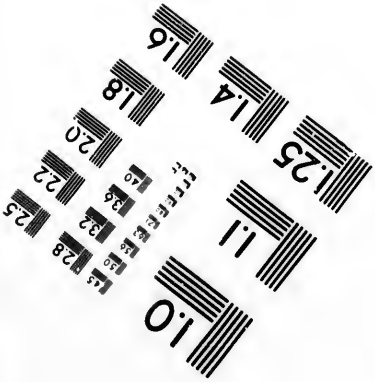

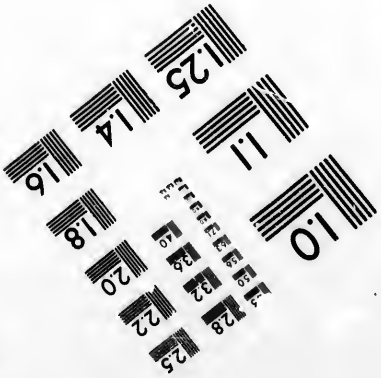

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7. Bismuth has an oxide, the formula of which is Bi_2O_3. Ferric oxide is represented by Fe_2O_3. The first is called *bismuth trioxide*; the second, *iron sesquioxide*. Is there any reason for this difference of momenclature?

8. Write the formulas for the chlorides corresponding to SnO, Cr_2O_3, K_2O, Bi_2O_3, BaO, CuO, Cu_2O, Ag_2O, and Au_2O_3.

9. The formula for oxalic acid is $H_2C_2O_4$. It is dibasic. Write the formulas for the normal oxalates of barium, sodium, ammonium, iron (ferrous and ferric), chromium, and copper.

10. Will the group reagent of Group II. precipitate the members of Group I. as sulphides? Try.

11. Have you observed any regularity in the atomicities of the groups of metals? Write the formulas for the oxides of Groups IV. and VI.

CHAPTER XVII.

METALS OF GROUP I.

Lead, Silver, and Mercury.

247. **General Characters.**—The metals of this group are heavy and soft (mercury is liquid). They are easily reduced from their ores by heating with charcoal. Their *sulphides* are black and insoluble in water and in dilute acids. The *oxides* are earthy compounds insoluble in water. The *chlorides* (except mercuric chloride), *bromides, iodides, carbonates*, and *phosphates,* are insoluble in water.

LEAD *(Plumbum).*

248. **Lead.**—(Pb^{ii} = 206.4. Specific weight = 11.352. Melting point = 334° C. Specific heat = 0.0315). The

chief ore of lead is *galena* (PbS). It is very common in Canada, occurring in crystalline masses, of a brilliant, metallic appearance.

Experiment 214.—Examine a specimen of galena, noting its colour, hardness (scratch with a knife), specific weight, &c. Mix a little of the powdered mineral with sodic carbonate, moisten, and heat it on charcoal before the blow-pipe, or on a charred splinter in the reducing flame of the Bunsen burner. Extract the metallic bead, and examine it carefully as to its hardness, malleability, &c. It is lead.

Galena generally contains silver, sometimes only in small traces, but often in considerable proportion.

PREPARATION.—The galena is partially oxidised by heating in air, and then more strongly heated to set the lead free. (Art. 239).

Experiment 215.—Put a piece of zinc in a solution of plumbic acetate, and allow it to remain for some time. Pour off the liquid, dry the metal which remains, and melt it by heating it in a closed porcelain crucible with a little charcoal dust. Examine it. It is lead.

PROPERTIES.—A heavy, dull metal, soft, tough, easily tarnished. A small quantity of antimony or arsenic alloyed with it renders it hard and brittle. Lead is easily set free from compounds in solution by the action of iron, zinc, &c., as in Experiment 215. This method is sometimes employed for impure ores.

Experiment 216.—Warm some small scraps of lead with dilute nitric, dilute hydrochloric, and dilute sulphuric acids. Divide the solution obtained with nitric acid into two portions. To one add some hydrochloric, to the other a little sulphuric acid. Heat bits of lead with strong hydrochloric and sulphuric acids.

Experiment 217.—Put pieces of bright lead into 4 test tubes, labelled (1), (2), (3), and (4). In (1) put distilled water, in (2) water containing ammonic nitrate, in (3) vinegar, and in (4) tap water. Set aside for a day and then test the liquid contents of the tubes for lead.

Lead is attacked and dissolved by distilled water (and rain water) owing to the action of the dissolved oxygen and carbonic acid. Water containing ammonium salts (especially ammonic nitrate) dissolves lead. Water contaminated by sewage generally contains ammonium salts, and is therefore dangerous on this account as well as on others. (Does vinegar dissolve lead?) Water containing lime and magnesia salts does not attack lead, so that ordinary river and well waters may be carried safely through lead pipes.

249. **Oxides of Lead.**—Lead forms several oxides (Pb_2O, PbO, Pb_2O_3, Pb_3O_4, PbO_2). Of these the important ones are *lead monoxide* (PbO), and *red-lead* (Pb_3O_4).

1. LEAD MONOXIDE (PbO).—Also called *litharge*, or *massicot*, according to the method by which it is prepared.

Experiment 218.—Heat some thin shavings of lead in an open porcelain crucible, They oxidise to a greyish yellow substance. This is the monoxide. Remove it and try the solubility of portions of it in dilute acetic, nitric, hydrochloric, and sulphuric acids. (Do you notice any change with hydrochloric and sulphuric acids ?)

Litharge is used for giving a glaze to earthenware, and in making flint glass. It is also used in preparing red-lead, lead acetate, nitrate, &c. "Drying oils" are prepared by boiling the raw oils with litharge.

Experiment 219.—Heat some lead monoxide with solution of sugar. It is dissolved.

Experiment 220.—Try the solubility of lead monoxide in water, and in solutions of sodic, potassic, and calcic hydroxides.

2. RED-LEAD, or MINIUM (Pb_3O_4).—This is prepared by heating litharge or massicot in air until it becomes further oxidised:

$$3PbO + O = Pb_3O_4.$$

It is a heavy red powder, used as a paint, and in the manufacture of flint glass. It is often adulterated with brick dust, ferric oxide, &c.

Experiment 221.—Heat a little red-lead in a porcelain dish and note any changes.

Experiment 222.—Warm a some red lead with dilute nitric acid to which a little sugar has been added. It is completely dissolved, if pure, a solution of plumbic nitrate being obtained. (What is the object of the sugar? What becomes of the oxygen in excess of 3PbO?)

250. **Salts of Lead.**—There are two basic oxides of lead, PbO and Pb_2O_3, but the sesquioxide forms unstable salts of no importance. The ordinary salts of lead are derived from the monoxide, PbO; and in these salts Pb takes the place of 2H. Moist lead oxide, as well as the hydroxide, turn red litmus blue. Salts of lead have a sweetish metallic taste.

251. **Plumbic Acetate, or Sugar of Lead,** $Pb(C_2H_3O_2)_2.3H_2O$. Prepared by dissolving litharge or massicot in acetic acid. (See Experiment 163.)

Experiment 223.—Examine carefully a specimen of sugar of lead. (Why called *sugar?*) Dissolve it in warm distilled water. (It is soluble in 1½ parts.) Test it with blue litmus. Note the odour of the solution. If the solution is turbid, add acetic acid until it is clear.

Goulard's Extract is a solution of *sub-acetate*, or *basic acetate*, of lead, $Pb(C_2H_3O_2)_2.PbO$, made by boiling solution of the normal acetate with litharge.

Experiment 224.—Boil some solution of plumbic acetate for some time with litharge in a porcelain dish. Filter, and test a little of the filtrate with red litmus. Leave the rest exposed to the air. It becomes turbid owing to the formation of plumbic carbonate. Try its action on gum arabic mucilage.

252. **Plumbic Nitrate,** $Pb(NO_3)_2$.—The nitrate of lead has already been prepared in several experiments.

Preparation—By dissolving litharge or massicot in warm dilute nitric acid, filtering, and evaporating to crystallisation :

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Properties.—A white crystalline solid, of astringent metallic taste. It dissolves in twice its weight of water, but is only sparingly soluble in alcohol.—It is an irritant poison. It has been used as a disinfectant and deodoriser. Its action as a deodoriser is due to the fact that it reacts with sulphuretted hydrogen to form the sulphide of lead (PbS). *Ledoyen's Disinfecting Fluid* contains a drachm of lead nitrate to an ounce of water.

Experiment 225.—Shake up a solution of plumbic nitrate with an equal volume of hydric sulphide water. Note the absence of bad smell in the solution. What is the black precipitate formed?

253. **White Lead.**—$2PbCO_3\,Pb(OH)_2$, a basic carbonate of lead.

Preparation.—1. *Dutch process.* Expose sheets of lead to the conjoint action of the fumes from vinegar and the carbon dioxide from decaying tan-bark. An acetate is formed first, and this is decomposed by carbon dioxide.

2. *Milner's process.* Grind litharge with common salt and water:

$$PbO + H_2O + NaCl = Pb\left\{\begin{matrix}Cl\\OH\end{matrix}\right. + NaOH.$$

Pass in carbon dioxide till the solution is neutral. The basic carbonate is formed.

PROPERTIES.—A soft, heavy, white powder, insoluble in water, but easily dissolved by dilute nitric or acetic acid with effervescence of carbon dioxide. It is poisonous.

Experiment 226.—Pour some hydric sulphide water on a little white lead in a porcelain dish. Explain the blackening.

Experiment 227.—Dissolve a little white lead in acetic acid. (What substances are formed? Write the equation.) To portions of the solution add hydrochloric acid, solution of potassic iodide, and dilute sulphuric acid respectively. (Note the appearance of the precipitates and write the equations.)

White lead is used as a paint. It is used in medicine in the form of an ointment *(unguentum plumbi carbonatis)*. It is very often adulterated with *baric sulphate* ($BaSO_4$), and gypsum; but, as both are insoluble in nitric or acetic acid, they are easily detected.

254. **Plumbic Chloride.** – $PbCl_2$. Occurs in nature as *horn lead.*

Experiment 228.—To a little solution of lead acetate add excess of hydrochloric acid. Plumbic chloride is precipitated. Filter, and transfer the precipitate to a t. t.; fill the t. t. half-full of pure water and heat to boiling. The chloride dissolves completely, if there is enough water. Allow to cool, and observe crystals.—Add to the solution a drop or two of hydrochloric acid to see that it gives no further precipitate. Now add a few drops of sulphuric acid, and white sulphate of lead ($PbSO_4$)

is precipitated. (What conclusion do you draw as to the solubility of plumbic chloride?)

Plumbic chloride is also sparingly soluble in pure water.

255. Plumbic Iodide.—PbI_2. (In what experiment has this been already formed?)

Experiment 229.—To some solution of plumbic acetate add solution of potassic iodide (KI), collect the precipitate of plumbic iodide on a filter, and wash it with cold water. Note its colour, &c. Transfer it to a t. t., fill half-full of water, boil, and allow to cool. The iodide dissolves in hot water, and crystallises beautifully on cooling.

Plumbic iodide is used in medicine in the forms of plaster and ointment.

256. Lead Plaster.—This consists of *oleate of lead* and lead salts of other fatty acids.

PREPARATION.—Boil at a gentle heat for 4 or 5 hours, 4 pounds of litharge with 1 gallon of olive oil and 3½ pints of water, adding water as it evaporates. The glycerine dissolves in the water, and the oleate of lead forms an insoluble gummy mass. Lard is sometimes used instead of olive oil.

257. Plumbic Sulphate.—$PbSO_4$.

Experiment 230.—Warm a little litharge with concentrated sulphuric acid. It dissolves. Cool the solution carefully and then dilute with water. Plumbic sulphate is precipitated.

Plumbic sulphate is soluble in strong, but insoluble in dilute, sulphuric acid.

Experiment 231.—Mix solutions of magnesic sulphate and plumbic acetate. Plumbic sulphate is precipitated:

$$Pb\bar{A}_2 + MgSO_4 = PbSO_4 + Mg\bar{A}_2.$$

Try its solubility in hot water, and in nitric and hydrochloric acids.

Commercial oil of vitriol often contains sulphate of lead. It is precipitated on dilution.

258. Commercial Preparations of Lead.

1. *Basic Carbonate.*—White lead, flake white, ceruse, mineral white, Newcastle white, and Nottingham white. Also some hair dyes.

2. *Sulphate.*—Miniature painter's white, white precipitate of lead.

3. *Chromates.*—Chrome yellow ($PbCrO_4$), chrome red ($PbCrO_4.PbO$).

4. *Basic Chloride.*—Turner's yellow, or Cassella yellow ($PbCl_2.7PbO$), and Pattinson's white ($PbCl.OH$).

5. *Litharge* and various salts of lead are constituents of hair dyes.

6. *Minium* (Pb_3O_4).—Red lead.

259. **Lead Poisoning.**—Nearly all compounds of lead are poisonous; but the insoluble compounds are at least very slow in their action. The soluble compounds are irritant poisons. The antidotes are soluble sulphates, such as Epsom salts. Lead is a cumulative poison. Minute quantities taken repeatedly remain in the system, and at length *accumulate* to such an extent as to produce symptoms of poisoning, as in *painter's colic.* The treatment in such cases is to administer antidotes and to remove the lead from the skin by repeated sulphur baths, which convert the soluble salts into plumbic sulphide, and this can be rubbed off the skin.

260. Tests.

1. If the solution is not too dilute, *hydrochloric acid* gives a white precipitate insoluble in a further quantity of the acid and unchanged by ammonia.

2. *Sulphuretted hydrogen* gives a black precipitate (PbS) insoluble in solution of ammonic sulphide, partly dissolved, partly whitened by strong nitric acid.

3. *Sulphuric acid* gives a white precipitate ($PbSO_4$).

4. *Potassic iodide* (KI) gives a yellow precipitate (PbI_2).

5. *Potassic bichromate* ($K_2Cr_2O_7$) gives a yellow precipitate ($PbCrO_4$).

6. Insoluble compounds are detected by reducing on charcoal with sodic carbonate, dissolving the metallic bead in nitric acid, and making the above tests.

SILVER *(Argentum).*

261. **Silver.** — ($Ag^{i} = 107.66$. Specific weight = 10.5. Melting point = 1040° C. Specific heat = 0.057.)

Occurrence.—Native, often in large masses; the principal ores are *silver glance* (Ag_2S), *ruby silver* (Ag_3SbS_3), *silver copper glance* ($Ag_2S.Cu_2S$), and *horn silver* (AgCl).

Preparation.—1. Silver is extracted from argentiferous lead by *Pattinson's process,* which consists in melting the lead and then cooling it slowly. Pure lead crystallises and sinks to the bottom. This is ladled out, until the remaining molten lead contains a considerable percentage of silver, when the process is finished by *cupellation.* The lead is melted in bone-ash *cupels,* or shallow vessels, and subjected to a blast which oxidises the lead and leaves the silver.

2. *Amalgamation Process.*—The silver is extracted with mercury, which is distilled, leaving the silver free.

3. The silver is dissolved out of its ores by acids, sodic thiosulphate, &c., and then precipitated by scraps of copper.

PROPERTIES.—A pure white metal, the best conductor of heat and electricity known; very tough and ductile; and very soft when pure.

NOTE.—Keep all residues from experiments with silver.

Experiment 232.—Cut small pieces of silver from a silver coin, and try their solubility in dilute hydrochloric, nitric, and sulphuric acids. Try the strong acids with the aid of heat.

Silver is soluble in nitric acid, argentic nitrate being formed. It is insoluble in hydrochloric, and in dilute sulphuric acid; but it dissolves in strong, hot sulphuric acid, with the formation of argentic sulphate (Ag_2SO_4) and sulphur dioxide:

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2.$$

Silver is easily reduced from its compounds.

Experiment 233.—Put a scrap of zinc in a small quantity of argentic nitrate solution in a porcelain basin. After a short time, a dark powder is formed in its place. Fuse this on charcoal with the blow-pipe. A bright silver bead is obtained. Dissolve it in nitric acid, and keep the solution to test.

Silver is much used for plating inferior metals. This is now generally done by means of electricity, in the process known as *electro-plating.* The object to be plated is fastened to the negative wire of a galvanic battery, and immersed in an aqueous solution of the double cyanide of silver and potassium (AgCN.KCN), through which the electric current is passed. The silver is deposited in an even layer on the object.—Silver is easily tarnished by sulphur or hydric sulphide, *argentic sulphide* (Ag_2S) being formed. This can be removed by washing with solution of ammonia, or of sodic thiosulphate.

262. **Oxides of Silver.**—There are three (Ag_4O, Ag_2O, Ag_2O_2), but only one of importance, viz., *argentic oxide*, Ag_2O.

Experiment 234.—To solution of argentic nitrate, add a little caustic soda. Argentic oxide is precipitated. Filter, wash, dry, and heat on mica. The oxygen is driven off and metallic siver remains:

(1) $2AgNO_3 + 2NaOH = 2NaNO_3 + Ag_2O + H_2O.$

(2) $Ag_2O = 2Ag + O.$

Argentic oxide is used in medicine. It is less liable than argentic nitrate to colour the skin.

263 **Salts of Silver.**—The only salt used in medicine is the nitrate.

Argentic Nitrate ($AgNO_3$), or *lunar caustic*, is prepared by dissolving pure silver in dilute nitric acid with the aid of a gentle heat, evaporating to dryness, and fusing.

Properties. — A colourless solid; sold either in sticks or as tabular crystals. It has a strong metallic taste, and is a violent, irritant poison. *Antidotes*—soluble chlorides, especially common salt.

Experiment 235.—To a little argentic nitrate solution add solution of common salt:

$$AgNO_2 + NaCl = AgCl + NaNO_3.$$

Test the solubility of the precipitate (AgCl) in nitric acid, and in ammonia.

Argentic nitrate is very soluble in water (2¼ parts in 1), and in alcohol. The solid substance is used as a caustic. If nitrate of silver be administered in small doses for a long time, it may produce permanent coloration of the skin. It darkens the skin when applied externally.

264. Tests.

1. To a small quantity of argentic nitrate solution add *hydrochloric acid.* A curdy white precipitate (AgCl) forms. Divide it into three portions. To one add nitric acid ; no change. To another ammonia ; dissolved. Let the third stand ; it darkens.

2. *Sulphuretted hydrogen* gives a black precipitate (Ag_2S), insoluble in ammonic sulphide

3. Heat with solution of *ferrous sulphate.* Metallic silver is precipitated. The ferrous sulphate is oxidised.

4. *Potassic bichromate* ($K_2Cr_2O_7$) gives a bright, reddish purple precipitate of argentic chromate (Ag_2CrO_4).

5. *Potassic iodide* (KI) gives a yellow precipitate of argentic iodide (AgI), insoluble in nitric acid, and whitened, but not dissolved, by ammonia. *Potassic bromide* (KBr) similarly. These salts of silver, especially the latter, are used in photography.

Note.—Many salts of silver are insoluble in water, and as they have characteristic colours and other properties, argentic nitrate is used as a group reagent in testing for acids.

MERCURY *(Hydrargyrum).*

265. **Mercury** ($Hg'' = 199.8$. Specific weight = 13.595. Melting point = − 39° C. Boiling point = 357° C. Specific heat = 0.0319.) The principal ore of mercury is *cinnabar* (HgS), from which the mercury is

obtained by roasting in a current of air and condensing the vapours of mercury in a series of cool chambers. It is purified by distillation.

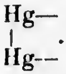
NOTE.—Keep all residues from experiments with mercury.

Experiment 236.—Put a little mercuric sulphide (vermilion) in a small hard-glass tube open at both ends. Hold the tube aslant and heat the sulphide until it disappears. Metallic mercury collects in the upper part of the tube :

$$HgS + O_2 = Hg + SO_2.$$

PROPERTIES.—Mercury is commonly called *quick silver*, which means *living* silver. It is brilliant when pure and does not readily tarnish in air. If it is impure (containing, lead, antimony, &c.), it soon gets a grey coating, and when allowed to run over white paper leaves a "tail."—When rubbed up with chalk, fats, and other substances, it becomes partially oxidised and very finely divided. It is in this way that mercury ointments and pills are made.—The specific weight of gaseous mercury is 6.93 (air = 1). (Calculate the number of atoms in the molecule). Mercury evaporates slowly even at low temperatures, and it should, therefore, always be kept in closed vessels.—On account of its high specific weight it is used for barometers, areometers, &c.

AMALGAMS.—Mercury unites with all metals but iron to form amalgams. From these the mercury can be driven off by heat. This property is utilised in *silvering* by means of a silver amalgam. *Cadmium amalgam* (Hg_2Cd) is very brittle, heavier than mercury, and has the property of hardening gradually. It is used for filling teeth. *Copper amalgams* are brittle at ordinary temperatures, but soften at 100° C. They are used for filling teeth and for sealing bottles, &c.

266. **Mercurous Compounds.** — In these compounds two atoms of mercury act as a dyad radical,  $\begin{array}{l}Hg-\\ |\\ Hg-\end{array}$. The salts are insoluble, or sparingly soluble, in water, and can be converted by oxidation, &c., to mercuric salts.

267. **Mercurous Nitrate.**—$Hg_2(NO_3)_2$.

Experiment 237.—Pour some dilute nitric acid over a globule of mercury, and allow it to stand for some time. The metal gradually dissolves, forming a solution of mercurous nitrate. Keep this for further examination.

Mercurous nitrate is soluble in water, but with a large proportion of water it is partially decomposed, with the formation of a yellow basic nitrate:

$$Hg_2(NO_3)_2 + H_2O = Hg_2.NO_3.OH + HNO_3.$$

268. **Mercurous Chloride** (Hg_2Cl_2). Also called *calomel.* This name is from the Greek, and means *beautiful black.*

Experiment 238.—To a small quantity of mercurous nitrate solution (Exp't 237) add hydrochloric acid. A white precipitate of mercurous chloride is thrown down:

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3.$$

To this add lime water until the chloride is blackened. This is the *black wash* of the Pharmacopœia:

$$Hg_2Cl_2 + Ca(OH)_2 = Hg_2O + H_2O + CaCl_2.$$

Calomel is usually prepared by subliming a mixture of *mercuric sulphate* ($HgSO_4$), mercury, and sodium chloride:

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4.$$

The sodic sulphate is not volatile.

PROPERTIES.—A white, tasteless, inodorous powder, insoluble in water, and in acids. (Try with a specimen of calomel.) It is turned black by alkalis, owing to the formation of *mercurous oxide* (Hg_2O), the active constituent of black wash. Precipitated calomel is more active as a medicine than that prepared by sublimation, owing to its finer state of division; but great care should be taken, in preparing it by precipitation, that no basic nitrate be present. This would dissolve readily in the acid juices of the stomach and might cause mercurial poisoning In order to guard against this, warm the precipitated calomel with dilute hydrochloric acid, filter, and wash well.—Calomel may be administered in doses up to 6 grains.

269. **Mercurous Iodide,** Hg_2I_2, *green iodide of mercury,* or *proto-iodide of mercury.*—A dull green powder, prepared by rubbing together iodine and mercury (In what proportions?), occasionally moistening with spirits of wine.

Experiment 239.—Add solution of potassic iodide to solution of mercurous nitrate. A greenish precipitate of mercurous iodide appears:

$$2KI + Hg_2(NO_3)_2 = Hg_2I_2 + 2KNO_3.$$

Mercurous iodide readily changes into *mercuric iodide* (HgI_2) and mercury. As the mercuric salt is more readily dissolved than the mercurous (and therefore more active as a poison), care should be taken that it be absent from the preparation. The mercurous iodide should be kept away from the light, which tends to bring about this decomposition:

$$Hg_2I_2 = Hg + HgI_2.$$

270. Tests for Mercurous Compounds.

1. White precipitate with *hydrochloric acid,* blackened by ammonia:

$$Hg_2Cl_2 + 2NH_3 = Hg_2Cl.NH_2 + NH_4Cl.$$

2. Insoluble compounds disappear when heated on mica, and are blackened by caustic soda.

271. Mercuric Compounds.

— In these compounds a single atom of mercury acts as a dyad ($Hg{=}$). They are more soluble than the mercurous compounds, and are generally deadly poisons.

272. Mercuric Nitrate,

$Hg(NO_3)_2$, is prepared by boiling mercury with excess of nitric acid until the solution no longer gives a precipitate with hydrochloric acid. (What is the precipitate?)

Experiment 240.—Heat a globule of mercury in a porcelain dish with nitric acid diluted with an equal volume of water. From time to time take out a drop of the solution with a glass rod, and mix it with a drop of hydrochloric acid. Continue heating, adding more acid if necessary, until the drop remains clear on mixing with hydrochloric acid. Evaporate to dryness. Examine the residue, dissolve part of it in water, and test it with lime water. It turns *yellow:*

$$Hg(NO_3)_2 + Ca(OH)_2 = Hg(OH)_2 + Ca(NO_3)_2.$$

Heat a little of the dry salt carefully in a dry porcelain capsule. Red fumes are evolved, and *red oxide of mercury,* or *mercuric oxide* (HgO), remains.

An acid solution of this salt is used in medicine as a caustic. It is an irritant poison.

273. Mercuric Sulphate,

$HgSO_4$, is prepared by dissolving mercury in hot, strong sulphuric acid:

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2.$$

(Calculate the proportions to be used.)

Experiment 241.—Heat a drop of mercury in a small porcelain vessel with about 7 or 8 times its volume of concentrated sulphuric acid, stirring constantly. The mercury dissolves. When cold, test a small portion of the salt with caustic soda. It is turned yellow :

$$HgSO_4 + 2NaOH = Hg(OH)_2 + Na_2SO_4.$$

Mercuric sulphate is used in the preparation of corrosive sublimate ($HgCl_2$).

274. **Mercuric Chloride**, $HgCl_2$, or *corrosive sublimate*, is prepared by subliming a mixture of mercuric sulphate and common salt, a little manganese dioxide being added to make sure of the absence of mercurous salts. (How ?) :

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$$

PROPERTIES.—Heavy colourless crystals, having a biting metallic taste (Examine a specimen); soluble in water (7 parts in 100), more so in alcohol, and still more so in ether. It volatilises more readily than calomel when heated. The medicinal dose is $\frac{1}{16}$ to $\frac{1}{8}$ of a grain. In larger doses it is a violent poison. The antidotes are white of egg, flour, &c. *Stannous chloride* ($SnCl_2$) may be given :

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$$

(How does this prevent the poisonous action ?)

Experiment 242.—Mix solutions of mercuric and stannous chlorides. What is the precipitate formed ?

Experiment 243.—To solution of corrosive sublimate add lime water. A yellow precipitate is formed :

$$HgCl_2 + Ca(OH)_2 = Hg(OH)_2 + CaCl_2.$$

This is the *yellow wash* of the Pharmacopœia.

Corrosive sublimate is an excellent antiseptic, even in very dilute solution, and is largely used instead of carbolic acid.

275. **Mercuric Oxide.**—HgO. There are two varieties, the differences depending on the fineness of division. *Red oxide of mercury* is prepared by heating mercury with mercuric nitrate:

$$Hg + Hg(NO_3)_2 = 2HgO + 2NO_2.$$

It is a heavy, red powder, soluble in those acids which form soluble mercuric salts. (What is the effect of a strong heat upon it?)—The *yellow oxide* is prepared by precipitation. A solution of mercuric chloride is treated with solution of caustic soda, and the precipitate of mercuric hydroxide ($Hg(OH)_2$) is washed, and dried at 100°. *This method of preparing the hydroxides and oxides of the heavy metals is very generally employed.* In several cases, the soluble base used as a precipitant is ammonia instead of soda.

276. **Mercuric Iodide,** HgI_2. Also called *red iodide of mercury*.

Experiment 244.—To solution of mercuric chloride add solution of potassic iodide drop by drop. A yellowish precipitate appears, but immediately turns red:

$$2KI + HgCl_2 = HgI_2 + 2KCl.$$

Add more potassic iodide. The precipitate of mercuric iodide redissolves, a soluble double salt ($HgI_2.2KI$) being formed This solution, with caustic soda added to it, constitutes *Nessler's reagent*, a very delicate test for ammonia, used in *water analysis*. Try it with a drop of ammonia dissolved in about half a litre of distilled water. A brown colour or precipitate appears:

$$NH_3 + 2HgI_2 + 3NaOH = NHg_2I + 3NaI + 3H_2O.$$

Mercuric iodide is a brilliant crystalline powder of a vermilion colour. It turns yellow when heated carefully. It is very slightly soluble in water, sparingly in alcohol, quite freely in ether and in aqueous solution of potassic iodide. It resembles corrosive sublimate in its poisonous action.

277. **Infusible White Precipitate,** or *mercuric ammonium chloride,* $NHgH_2Cl$.

Experiment 245.—Add ammonia solution to solution of mercuric chloride. A white precipitate falls :

$$HgCl_2 + 2NH_3 = NHgH_2Cl + NH_4Cl.$$

278. **Fusible White Precipitate,** or *mercuric diammonium chloride,* $Hg(NH_3Cl)_2$, is prepared by adding solution of mercuric chloride to a boiling solution of ammonic chloride and ammonia.—These two compounds differ as their names indicate. The infusible precipitate decomposes without fusing when heated; the fusible precipitate fuses and then decomposes.

279. **Mercuric Sulphide,** HgS, is found in nature as a heavy red mineral, *cinnabar.* It can be prepared by subliming mercury and sulphur together, when it is obtained as a red or black powder, *vermilion,* or *Æthiops mineral.* Or, it can be prepared as a black powder by precipitation.

Experiment 246.—Add hydric sulphide to solution of mercuric chloride. A white precipitate appears ($2HgS.HgCl_2$), but this rapidly passes through shades of colour until it becomes black (HgS). (Write the equation). Divide the precipitate into three parts and try its solubility (1) in ammonic sulphide, (2) in boiling dilute nitric acid, and (3) in *aqua regia.* Results (1) .... (2) ....
(3) ....

280. Tests for Mercuric Compounds.

1. See Experiment 246.

2. *Sodic hydroxide* solution gives with solutions of mercuric salts a yellow precipitate ($Hg(OH)_2$) not redissolved when more of the reagent is added.

3. *Stannous chloride* ($SnCl_2$) gives a white precipitate (Hg_2Cl_2), turning grey (Hg) with more of the reagent.

4. A bright *copper* wire is *silvered* when put in a mercuric solution. This applies to mercurous solutions also.

General Test for Insoluble Mercury Compounds.—Mix with dry sodic carbonate and charcoal powder, and heat in a matrass. Metallic mercury is obtained as a mirror in the tube.—All mercury compounds volatilise when strongly heated.

281. **Mercurial Poisoning.** — The soluble compounds of mercury are violent irritant poisons. A characteristic symptom is the increased flow of saliva (*salivation*). The insoluble compounds are not so poisonous, but are still dangerous. Even metallic mercury in a finely divided state will cause symptoms of poisoning, especially when it is breathed as a vapour. Therefore, it is dangerous to boil mercury, or to sublime compounds of mercury, into the atmosphere of an inhabited room. As mercury and its compounds are very extensively used in arts and manufactures, as well as in many patent and quack medicines, numerous cases of poisoning occur. The *antidotes* are albuminous substances, such as white of egg, flour, &c., and stannous chloride.

QUESTIONS AND EXERCISES.

1. Is there any reason why rain water should not be stored in lead-lined tanks ?

2. In what liquids is lead soluble, and in what insoluble ?

3. Mention some liquids which will, and some which will not dissolve litharge.

4. A white crystalline solid is given you. How would you determine whether it is sugar of lead?

5. What proportions of plumbic acetate ($Pb(C_2H_3O_2)_2.3H_2O$) and litharge (PbO) must be combined to form the subacetate of lead ?

6. Why should solution of subacetate of lead be kept well closed from the air ?

7. What chemical action takes place when white lead is taken into the stomach ?

8. In what acids is mercury soluble ?

9. Why is mercurous chloride called *calomel ?*

10. What chemical compounds are present in *black wash ?* In *yellow wash ?*

11. Write formulas for *mercurous sulphate, mercurous bromide,* and *mercuric cyanide.*

12. How would you prepare a specimen of *mercuric hydroxide*?

13. Black mercuric sulphide becomes red when rubbed. Can you account for this ?

14. Explain the action of stannous chloride as an antidote to poisoning by corrosive sublimate. Would stannic chloride ($SnCl_4$) do ?

15. Argentic cyanide is insoluble in water, but soluble in solution of potassic cyanide. What happens when a drop of argentic nitrate solution is added to a considerable quantity of potassic cyanide and shaken up with it ?

CHAPTER XVIII.

METALS OF GROUP II.

[*Lead, Mercury*], *Copper, Cadmium, Bismuth; Antimony, Tin,* [*Arsenic*], *Gold, Platinum, &c.*

282. **General Characters**.—The *sulphides* of these metals are precipitated from acid solutions by *hydric sulphide*, and also by ammonic sulphide, but some of them are redissolved by a further quantity of this latter reagent.—The *hydroxides* are precipitated from solutions of salts by *alkaline hydroxides*, e.g., sodic hydroxide.—The *oxides* can be prepared by heating the hydroxides. They are earthy substances insoluble in water, but soluble in acids.—The *carbonates* and *phosphates* are earthy substances insoluble in water.

This group is subdivided into two:

A. Metals having sulphides insoluble in solutions of alkaline sulphides: [*Lead*], *copper, cadmium*, and *bismuth*. In analysis, mercur*ic* salts are included in this class.

B. Metals having sulphides soluble in solutions of alkaline sulphides: *Antimony, tin,* [*arsenic*], *gold, platinum*, and some rare metals.

A.

COPPER *(Cuprum).*

283. **Copper** (Cu″ = 63.1. Specific weight = 8.92. Melting point = 1090° C. Specific heat = 0.0952).

Occurrence.—Free; sometimes in great masses. The ores of copper are very numerous. The commonest one is *copper pyrites*, or *chalcopyrite* ($CuFeS_2$). Copper is found in the liver and kidneys of man and of domestic animals.

Preparation.—The smelting of copper is a very complicated process, but it is the same in principle as that of lead, viz., a partial oxidation of the sulphide and subsequent fusion at a higher temperature. Poor ores are worked up by dissolving in acids and precipitating with iron.

Experiment 247.—Dip the point of a knife blade in a little solution of cupric sulphate. It becomes coated with copper:

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

Properties.—A red metal, heavy, very tough, malleable, and ductile. Next to silver it is the best conductor of heat and electricity. Its solubility in nitric and sulphuric acids has been already proved. (See Arts. 86 and 115).

Experiment 248.—Try the solubility of copper in hydrochloric acid, strong and dilute. Put a piece of bright copper wire in dilute acetic acid, so that it is half covered with the acid. Leave it for a day, and then examine it. Test the acid for copper. *Verdigris*, or *basic cupric acetate*, has been formed.

Experiment 249.—Put pieces of bright copper wire in test tubes or beakers containing (1) distilled water, (2) dilute solution of common salt, (3) butter or fat, and (4) solution of sugar. After 24 hours, examine the condition of the copper and test the solutions for copper.

Copper is gradually dissolved by water, especially when the water contains ammonium salts or chlorides. Vinegar, fats, oils, and syrups, with the aid of air and moisture, dissolve copper. Thus occur frequent cases of poisoning, from copper kitchen utensils, taps for liquors, &c.

284. **Compounds of Copper.**—Copper resembles mercury in forming two classes of compounds, (1) *cuprous*, in which two atoms of copper act as a dyad radical $\begin{array}{l}\mathrm{Cu}-\\ \,|\\ \mathrm{Cu}-\end{array}$, and (2) *cupric*, in which one atom of copper replaces two of hydrogen.—The *cuprous salts* are so easily oxidised that it is difficult to keep them. *Cuprous oxide* (Cu_2O) has been already noticed. (See *Sugars*). *Cuprous chloride* (Cu_2Cl_2) is remarkable as being a solvent for acetylene and carbon monoxide.

285. **Cupric Sulphate.**—$CuSO_4.5H_2O$. Also called *blue vitriol* and *blue stone.*

PREPARATION.—Copper pyrites is roasted so as to form cupric oxide (CuO) and ferric oxide (Fe_2O_3). The cupric oxide is then dissolved out by hot sulphuric acid, in which ignited ferric oxide is insoluble. The solution is evaporated, and the salt crystallised. The commercial salt always contains a little *ferrous sulphate* ($FeSO_4.7H_2O$). Blue vitriol is obtained as a secondary product in the refining of silver by precipitation on copper. (In what way has it been already prepared?)

PROPERTIES.—Cupric sulphate is generally sold in large blue crystals. These are soluble in water (2 parts in 5).

Experiment 250.—Carefully heat a crystal of cupric sulphate in a t. t. It turns white, and water gathers on the sides of the tube. The crystal falls to a powder, because it has lost its *water of crystallisation.* When the t. t. is cool, pour a few drops of water on the *anhydrous salt.* Note signs of heat.—Anhydrous cupric sulphate is used in testing liquids for water. It turns blue when acted on by water.

Experiment 251.—Dissolve a little cupric sulphate in water, and test the solution with blue litmus paper. The basic part of the salt is comparatively weak. Taste the solution. Test it for sulphuric acid.

Blue vitriol is used in medicine as a caustic, and also as an emetic. In small doses (up to 2 grains) it is not poisonous, but acts as a tonic and astringent. In larger doses it is *poisonous,* unless it exerts its emetic action. *Antidotes,* white of egg, &c. Cupric sulphate is an antidote to phosphorus.

286. Cupric Oxide.

—CuO. This is the *black oxide of copper.*

Experiment 252.—Heat a little powdered cupric sulphate strongly on mica. Black oxide of copper is left :

$$CuSO_4.5H_2O = CuO + SO_3 + 5H_2O.$$

Cupric oxide is a black hygroscopic powder, soluble in acids, insoluble in water. It is used in organic analysis to supply oxygen to oxidisable substances.

287. Commercial Preparations of Copper.

1. *Scheele's green.* (See *Arsenic.*)

2. *Schweinfurth green,* or *emerald green.* (See *Arsenic.*)

3. *Brighton green,* a mixture of impure cupric acetate and chalk.

4. *Brunswick green,* oxychloride of copper, or carbonate of copper mixed with chalk.

5. *Mountain green*, or *mineral green*, is a native carbonate of copper.

6. *Green verdites*, a mixture of cupric oxide and carbonate with chalk.

7. *Verdigris*, a basic acetate.

Many alloys of copper are used, e.g., brass, tombac, Muntz metal, bronze, &c. (See Art. 238.)

288. Tests.

1. Acidify a solution of cupric sulphate with hydrochloric acid, and add *hydric sulphide*. A black precipitate of *cupric sulphide* (CuS) falls:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

Filter, wash, and test the solubility of a portion of the precipitate in yellow ammonic sulphide. It is insoluble (in reality, sparingly soluble). Heat another portion in a porcelain dish with dilute nitric acid. It is dissolved. Heat a third portion with dilute sulphuric acid. It is undissolved.

2. Add *ammonia* solution gradually to cupric sulphate solution. A light blue precipitate is first formed. When more ammonia is added, this dissolves to a deep blue solution containing a compound, $CuSO_4.4NH_3$.

3. *Potassic ferrocyanide* gives a reddish-brown precipitate, or, with very dilute solutions, a reddish colour.

4. Insoluble compounds may be tested by heating a little of the substance on a platinum wire with a borax bead. The bead is green while hot, blue when cold. If it be moistened with solution of stannous chloride and heated in the inner (reducing) zone of the Bunsen flame, it becomes coppery red when cold.

CADMIUM.

289. Cadmium.—(Cd^{ii} = 111.6. Sp. wt. = 8.5. Melting point = 315°C. Boiling point = 860°C. Sp. heat = 0.0567).

Occurrence.—Along with zinc ores. In smelting zinc ores, cadmium volatilises first (Compare boiling points), burns when it reaches the air, and the oxide (CdO) collects as a brown dust in the flue of the furnace.

Preparation.—The impure cadmium oxide is dissolved in hydrochloric acid, and the cadmium is then precipitated as sulphide (CdS) by sulphuretted hydrogen, the zinc salt remaining in solution. The sulphide is dissolved in strong hydrochloric acid, and the carbonate ($CdCO_3$) is obtained by precipitating with sodic carbonate. By heating the carbonate, pure cadmium oxide is formed, and this is then reduced by heating in iron tubes with charcoal.

Properties.—A white metal, somewhat like tin. It crackles when bent. It is harder than tin, malleable and ductile, and takes a good polish. Cadmium is soluble in hot dilute hydrochloric acid, and in sulphuric acid. It is very easily dissolved by nitric acid.

(1) $Cd + 2HCl = CdCl_2 + H_2$
(2) $Cd + H_2SO_4 = CdSO_4 + H_2$
(3) $3Cd + 8HNO_3 = 3Cd(NO_3)_2 + 2NO + 4H_2O$.

290. **Compounds of Cadmium.**—Cadmium has only one oxide (CdO), a brown solid, mentioned above. The salts of cadmium are mostly colourless, and resemble those of zinc both in chemical properties and in physiological action. Solutions of the normal salts have an acid reaction.

291. **Cadmic Nitrate,** $Cd(NO_3)_2$, is prepared by dissolving the metal in nitric acid and evaporating the solution. It is a deliquescent white salt, used for preparing other salts, and in chemical experiments.

292. **Cadmic Sulphate,** $3CdSO_4.8H_2O$, is prepared from the nitrate or chloride.

Experiment 253.—Pour solution of cadmic nitrate or chloride into sodic carbonate solution :

$$Cd(NO_3)_2 + Na_2CO_3 = CdCO_3 + 2NaNO_3.$$

Filter off the precipitate of cadmic carbonate, wash it, and dissolve it in dilute sulphuric acid, taking care not to use too much. Evaporate to crystallisation, and examine the crystals :

$$CdCO_3 + H_2SO_4 = CdSO_4 + H_2O + CO_2.$$

This method of passing from one soluble salt of a metal to another is often employed. Sometimes the hydroxide is precipitated instead of the carbonate.

Sulphate of cadmium is a colourless salt, resembling sulphate of zinc in its physiological actions, but it is more powerful. It is used as a wash for diseases of the eye. It is soluble in about one and a half times its weight of water.

293. **Cadmic Iodide,** CdI_2, is prepared by digesting the metal with iodine and water, until the colour of the iodine disappears. A solution is obtained which, on evaporation, deposits thin pearly plates of the iodide. It is soluble in about an equal weight of water.—Cadmium iodide is used in medicine in the form of an ointment. It is also used in photography in preparing the sensitive plates, as it is one of the few iodides soluble in alcohol and ether. A solution in alcohol and ether is mixed with a collodion solution and spread in a thin layer upon the plate. The liquids quickly evaporate and leave a thin layer of collodion impregnated with cadmium

iodide. When this is dipped in a bath of argentic nitrate, double decomposition takes place:

$$CdI_2 + 2AgNO_3 = 2AgI + Cd(NO_3)_2.$$

This is the sensitive plate.

294. Tests.

1. To a cadmium solution add *hydric sulphide.* A yellow precipitate of *cadmic sulphide* (CdS) is formed. This is insoluble in yellow ammonic sulphide. It resembles arsenic trisulphide (As_2S_3) and stannic sulphide (SnS_2), but these are soluble in ammonic sulphide. Cadmic sulphide is soluble in hot dilute sulphuric and nitric acids.

2. To a solution of a cadmium salt add *ammonia* gradually. A white precipitate of *cadmic hydroxide,* $Cd(OH)_2$, appears, but redissolves in more of the reagent, forming a *colourless* solution.

BISMUTH.

295. Bismuth. ($Bi^{iii.\,v.} = 210$.—Sp. wt. = 9.8.—Melting point = 270°.—Sp. heat = 0.0305.)

OCCURRENCE.—Rather rare, chiefly in the free condition. It is found often with ores of cobalt.

PREPARATION.—Generally as a by-product in *smalt* works, being separated in the metallic state from the sulphide of cobalt by smelting with iron scraps. The commercial metal nearly always contains arsenic. For medicinal use it must be freed from this by melting with a little saltpetre, which oxidises the arsenic, but does not attack the bismuth.

PROPERTIES.—A hard, lustrous, brittle metal, of a reddish tint. It *expands* on solidifying, and gives this property to its alloys, some of which are used in stereotyping. It decomposes steam at a red heat. It oxidises slowly in the air. Bismuth is not dissolved by cold dilute hydrochloric or sulphuric acid.

Experiment 254.—Dissolve a little bismuth in hot, strong sulphuric acid:

$$2Bi + 6H_2SO_4 = Bi_2(SO_4)_3 + 3SO_2 + 6H_2O.$$

It dissolves easily in nitric acid and in *aqua regia.*—Alloys of bismuth, lead and tin, made to melt at particular temperatures, are used as safety plugs for boilers.

296. **Compounds of Bismuth.**—Bismuth unites with oxygen in four proportions (Bi_2O_2, Bi_2O_3, Bi_2O_4, Bi_2O_5), but only one of the oxides, viz., the *trioxide*, (Bi_2O_3) is of importance medicinally. It is a basic oxide. The pentoxide (Bi_2O_5) is acid-forming. The others are indifferent.

297. **Bismuth Trinitrate,** $Bi(NO_3)_3.3H_2O$. Also called *nitrate of bismuth.*

Experiment 255.—Dissolve a little bismuth in nitric acid diluted with about three-fourths its volume of water:

$$Bi + 4HNO_3 = Bi(NO_3)_3 + NO + 2H_2O.$$

Evaporate the solution to crystallisation. Colourless deliquescent crystals are obtained. Any arsenic present remains dissolved in the mother liquor.

298. **Bismuth Subnitrate,** or *basic nitrate of bismuth,* $BiNO_3(OH)_2$†. Also called *white bismuth.*

PREPARATION.—**Experiment 256.**—Add a *few* drops of water to the crystals of trinitrate obtained in Experiment 255, so as to form a solution, and pour it into a beaker of distilled water. A white precipitate falls:

$$Bi(NO_3)_3 + 2H_2O = BiNO_3(OH)_2 + 2HNO_3$$

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† The composition of this salt varies with the amount of water used in its preparation.

(Many salts of weak bases can be thus decomposed by water.) Filter off, wash, and dry the precipitate. Keep the filtrate.

PROPERTIES.—A heavy white powder, insoluble in water, but soluble in moderately strong nitric acid. It is again precipitated from this solution by the addition of water.

Experiment 257.—Dissolve a little bismuth subnitrate in a few drops of nitric acid and a drop or two of water. Then add more water.

Experiment 258.—Dissolve a little bismuth subnitrate in sulphuric acid diluted with an equal volume of water. To this add a few drops of ferrous sulphate solution. A black colour or precipitate is formed (Bi_2O_2).

Subnitrate of bismuth is much used in medicine. It is not poisonous, but it sometimes contains the tri-nitrate or arsenic compounds, and then gives rise to symptoms of poisoning. It should be carefully distinguised from the trinitrate. It is also used as a cosmetic, and to give an iridescent glaze to porcelain.

299. **Bismuth Trioxide,** Bi_2O_3, is prepared by boiling subnitrate of bismuth with solution of caustic soda:

$$2BiNO_3(OH)_2 + 2NaOH = 2NaNO_3 + Bi_2O_3 + 3H_2O.$$

The precipitate is collected on a filter, washed, and dried.

PROPERTIES.—A lemon-yellow powder, insoluble in water, but soluble in nitric and hydrochloric acids, with the formation of the trinitrate and the trichloride ($BiCl_3$) respectively. It is a basic oxide.—It is used instead of the subnitrate in many cases, and is to be preferred on account of its purity.

300. **Bismuthyl Carbonate.**—$2(BiO)_2CO_3 . H_2O$.

PREPARATION.—**Experiment 259.**—Pour solution of bismuth trinitrate into cold solution of ammonic carbonate. A white precipitate falls :

$$3(NH_4)_2CO_3 + 2Bi(NO_3)_3 = (BiO)_2CO_3 + 6NH_4NO_3 + 2CO_2.$$

Collect the precipitate on a filter and wash it.

PROPERTIES.—This salt, commonly called *carbonate of bismuth,* is a white powder, insoluble in water, but soluble in nitric acid *with effervescence.* It is also soluble in sulphuric acid, and the solution should not respond to the test for nitric acid. If it does, the carbonate has contained subnitrate. The carbonate of bismuth is often administered in place of the subnitrate, on account of its more ready solubility in the acid juices of the stomach, and also because of its *antacid* properties :

$$(BiO)_2CO_3 + 6HCl = 2BiCl_3 + CO_2 + 3H_2O.$$

In this salt the radical $-Bi=O$ plays the part of a monad metal. Other salts of bismuthyl are known, e.g., *bismuthyl chloride* ($BiOCl$), formed when the trichloride of bismuth is acted on by much water :

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

301. Tests.

1. To the filtrate from Experiment 256 add *hydric sulphide.* A brown-black precipitate of *bismuth trisulphide* (Bi_2S_3) falls :

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3.$$

It is insoluble in yellow ammonic sulphide, but soluble in hot dilute nitric acid.

2. Solutions of bismuth salts give with *ammonia* a white precipitate ($Bi(OH)_3$), not dissolved by more of the reagent. If this precipitate be filtered off and dissolved in as little as possible of

hydrochloric acid, the solution is turned milky on the addition of much water. This precipitate is not dissolved by tartaric acid.

3. *Potassic iodide* gives with bismuth solutions a brown precipitate (BiI_3).

4. *Caustic potash* gives a white precipitate ($Bi(OH)_3$), insoluble in excess.

5. Insoluble bismuth compounds can be tested by dissolving them in nitric acid and diluting with water. (Experiment 256.) The precipitate obtained is insoluble in tartaric acid. (Compare *Antimony.*)

B.

ANTIMONY (*Stibium*).

302. **Antimony** ($Sb^{iii.\,v.}$ = 120. Sp. wt. = 6.7 to 6.86. Melting point = 425°C. Sp. heat = 0.0523).—The chief ore of antimony is *stibnite* (Sb_2S_3). This occurs in black, shining, crystalline masses.

Preparation.—Stibnite, purified by fusion, is reduced by heating with iron:

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

Properties.—A silvery metal, generally in masses of laminated crystals, hard and brittle; it can be ground to a powder in the mortar. When heated in air, it burns, forming the *tetroxide* (Sb_2O_4). It is soluble in nitric acid and in *aqua regia.* It is also soluble in hot, strong sulphuric acid, *antimonic sulphate* being formed:

$$2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O.$$

In this salt antimony plays the part of a trivalent metal.—*Antimony black* is finely divided antimony prepared by reducing the metal from a solution of the chloride by means of zinc. It is used for giving to plaster casts, &c., the appearance of iron or steel.—Antimony is a constituent of many useful alloys. (Art. 240.)

303. **Compounds of Antimony.** — Antimony combines with oxygen in three proportions. The *trioxide* (Sb_2O_3) is both basic and acid-forming; the *pentoxide* (Sb_2O_5) is acid-forming, *antimonic acid* (H_3SbO_4) and the *antimonates* being similar to the corresponding compounds of phosphorus and arsenic; the *tetroxide* (Sb_2O_4) is also acid-forming.

304. **Antimony Trisulphide,** Sb_2S_3, is found in nature as *stibnite.* The mineral is purified by fusion, and is used as the starting point in the preparation of antimony compounds. It is also called *black antimony* and *crude antimony.*—It is a greyish-black crystalline powder, soluble in hot, strong hydrochloric acid, with evolution of hydric sulphide.

Experiment 260.—Heat a little black sulphide of antimony with strong hydrochloric acid. Keep the solution:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Experiment 261.—Boil a little sulphide of antimony with solution of sodic hydroxide. It dissolves:

$$2Sb_2S_3 + 4NaOH = NaSbO_2 + 3NaSbS_2 + 2H_2O.$$

Add dilute sulphuric acid until a precipitate appears:

$$NaSbO_2 + 3NaSbS_2 + 2H_2SO_4 = \\ 2Na_2SO_4 + 2Sb_2S_3 + 2H_2O.$$

The substances formed when antimony trisulphide is dissolved in caustic soda are *sodic antimonite* ($NaSbO_2$) and *sodic sulphantimonite* ($NaSbS_2$). When the acid is added the trisulphide is again precipitated, but it is *orange-red.* Prepared in this way it always contains a little of the trioxide, and is called *sulphurated antimony,* or *golden sulphide of antimony.*

305. **Antimony Trichloride** ($SbCl_3$) is prepared as in Experiment 260. By evaporating such a solution the trichloride is obtained as a crystalline, colourless, solid, melting at 72° ("butter of antimony"). It is very deliquescent.

Experiment 262.—Dilute a small part of the solution prepared in Experiment 260. A white precipitate of *antimonyl chloride*, or *powder of Algaroth* (SbOCl) is formed:

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

Filter, and test the filtrate for antimony and for hydrochloric acid. To two other portions add considerable quantities of strong hydrochloric acid and tartaric acid respectively, and dilute them as before. To a strong solution of antimony trichloride add a little dilute hydrochloric acid. A precipitate forms; the dilute acid has the same effect as water. Add more acid and the precipitate is redissolved.

Antimony trichloride is a powerful caustic. It is a corrosive poison, acting like a strong solution of hydrochloric acid. (Explain this.)

306. **Antimony Trioxide** (Sb_2O_3), also called *flowers of antimony*, is prepared by digesting powder of Algaroth (SbOCl) with sodic carbonate, and washing with hot water.—It is a greyish-white powder, insoluble in water, sulphuric and nitric acids, but readily soluble in alkalis, and in hydrochloric and tartaric acids:

$$Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O.$$

When heated strongly in air it fuses and, absorbing oxygen, becomes changed to the tetroxide (Sb_2O_4).—*Antimonial powder* is a mixture of 1 part of antimony trioxide with 2 parts of *calcic phosphate* ($Ca_3(PO_4)_2$).

307. **Tartar Emetic**, $SbO.K.C_4H_4O_6$, is *antimonyl potassium tartrate*, already mentioned (Art. 189).

Experiment 263.—Dissolve some tartar emetic in as little as possible of hot water. Dilute the solution. It does not turn milky. The explanation is as follows:—The antimony is already combined as a *soluble* antimonyl compound. (What experiment above does this explain?)

It will have been observed that antimony shares with bismuth the tendency to form so-called *oxysalts*, in which a radical, in this case, *antimonyl*, $-Sb=O$, acts the part of a univalent atom.

Experiment 264.—Examine a specimen of tartar-emetic carefully. Taste it. Heat a small portion on mica or platinum. It chars and burns, leaving a white solid.

In large doses tartar emetic is a poison. *Antidotes*, freshly precipitated ferric hydroxide, tannic acid, or any vegetable infusion containing tannin, e.g., tea.

308. Tests.

1. To a solution of an antimony salt, acidified with hydrochloric acid, add *hydric sulphide*. An orange precipitate falls. Filter off the precipitate and test the solubility of parts of it in yellow ammonic sulphide and in hot strong hydrochloric acid. It dissolves in both. Dilute the hydrochloric acid solution.—The ammonic sulphide solution contains *ammonic sulphantimonite* (NH_4SbS_2). Treat it with hydrochloric acid, and the sulphide is reprecipitated.

2. Test for antimony as in Marsh's test for arsenic (Art. 146). Antimony has a gaseous compound with hydrogen, *stibine*, or *antimoniuretted hydrogen* (SbH_3). Spots are obtained, similar to those of arsenic, but they are turned *orange* by ammonic sulphide, and are not dissolved by bleaching powder solution. (Compare *Arsenic.*)

3. Put a scrap of zinc in a solution of tartar emetic, collect the precipitated antimony, and test its solubility in hot hydrochloric acid. It is insoluble. (Compare *Tin.*)

4. Strong solutions of antimony trichloride give a white precipitate with water or dilute hydrochloric acid, soluble in tartaric acid; but this test does not answer with tartar emetic or alkaline solutions.

5. Insoluble antimony compounds can be dissolved in hydrochloric or nitric acid, and the solution then treated as above.

TIN *(Stannum).*

309. **Tin** ($Sn^{ii\,iv}$ = 117.8. Specific weight = 7.739. Melting point = 235°. Specific heat = 0.0548).—Tin is prepared almost exclusively from *tin-stone* (SnO_2), by smelting the purified ore in a blast furnace with anthracite:

$$SnO_2 + 2C = Sn + 2CO.$$

The impure metal is purified by *liquation*, i.e., by melting gradually. The pure metal melts first and flows away from its impurities. Commercial tin may contain arsenic, antimony, bismuth, zinc, lead, copper, and iron.

Properties.—A bright white metal, crackling when bent, harder than lead, softer than gold. It is malleable and ductile at 100° C. It does not tarnish readily in air, and is therefore used for covering sheet iron in the manufacture of "tin" utensils. It is soluble in hydrochloric and dilute nitric acids, and is oxidised, but not dissolved, by strong nitric acid.—Tin forms some useful alloys. (See *Alloys.*) *Tin amalgam* is used for silvering mirrors.

Experiment 265.—Put a bit of zinc in an alkaline solution of tin ($SnCl_2$ and NaOH). Tin is gradually deposited in crystals.

310. **Compounds of Tin.**—Tin forms two series of compounds: (1) Stann*ous* (SnO, SnS, $SnCl_2$, &c.) in

which the element is dyad; and (2) stann*ic* (SnO_2, SnS_2, $SnCl_4$, &c.), in which it is tetrad. *Stannous oxide* (SnO) is basic, forming salts with acids, e.g., $Sn(NO_3)_2$, $SnSO_4$, &c. *Stannic oxide* (SnO_2) is acid-forming (also weakly basic), and the *stannates* are analogous to the carbonates and the silicates, e.g., *sodic stannate*, Na_2SnO_3.

311. Stannic Oxide (SnO_2) is found in nature as *tin-stone.*

Experiment 266.—Pour some strong nitric acid on a few scraps of tin. Red fumes are evolved, and a white powder is formed. This is *stannic acid* (H_2SnO_3):

$$Sn + 4HNO_3 = H_2SnO_3 + 4NO_2 + H_2O.$$

Try its solubility in hydrochloric acid, and in caustic soda. It dissolves in both. forming *stannic chloride* ($SnCl_4$) and sodic stannate (Na_2SnO_3) respectively.—Heat a little stannic acid on mica. A white powder remains (yellow when hot). This is stannic oxide (SnO_2). Try its solubility in hydrochloric acid and in caustic soda.

312. Stannous Chloride ($SnCl_2$)

Experiment 267.—Dissolve some scraps of tin in hydrochloric acid diluted with an equal volume of water. Stannous chloride is formed:

$$Sn + 2HCl = SnCl_2 + H_2.$$

Put in more tin and evaporate on the water bath to crystallisation. "Tin Salt" ($SnCl_2.2H_2O$) is obtained.—Dissolve a little of this salt in a small quantity of water. It forms a clear solution. Add more water; it becomes turbid, owing to the formation of a basic chloride:

$$SnCl_2 + H_2O = SnCl.OH + HCl.$$

The same precipitate is formed when a solution of stannous chloride is exposed to the air:

$$3SnCl_2 + O + H_2O = SnCl_4 + 2SnClOH.$$

Stannous salts have an astringent metallic taste. They are easily oxidised, and must be kept from the air. They are powerful reducing agents, precipitating gold, silver, and mercury from their solutions.—The nitrate ($Sn(NO_3)_2$) and sulphate ($SnSO_4$) can be prepared by dissolving tin in the dilute acids. Solutions of stannous salts are acid in reaction. They are poisonous; *antidote,* solution of ammonic carbonate.

313. **Stannic Chloride** ($SnCl_4$) can be prepared by passing dry chlorine gas over tin foil, or by distilling tin with mercuric chloride ($HgCl_2$). It can also be prepared in solution as follows:

Experiment 268.—Boil solution of stannous chloride with nitric and hydrochloric acids, using only a small quantity of the substances. Keep the solution.

PROPERTIES.—A colourless, heavy, fuming liquid. It solidifies when mixed with one-third its weight of water, forming "butter of tin" ($SnCl_4.5H_2O$). With much water it is decomposed:

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$

Many compounds of tin are similar in composition to compounds of silicon, e.g., *potassic fluo-stannate* (K_2SnF_6), and the *stannates* (Na_2SnO_3, &c.).

Closely allied to tin are three rare metals, *titanium, zirconium,* and *thorium.*

314. Tests.

Stannic Salts.

1. To a solution of stannic chloride add *hydric sulphide.* A yellow precipitate (SnS_2) falls:

$$SnCl_4 + 2H_2S = SnS_2 + 4HCl.$$

This precipitate is soluble in ammonic sulphide and in strong, hot, hydrochloric acid. (Filter it off and try.)—*Stannic sulphide*(SnS_2) combines with alkaline sulphides to form *sulphostannates*, e.g.:

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

These are soluble salts, easily decomposed by acids. (Try with hydrochloric acid.)

2. Caustic soda gives with stannic salts a white precipitate (H_2SnO_3), soluble in excess of the reagent.

3. To a little stannic chloride solution in a porcelain dish add a scrap of zinc and warm. Wash the precipitated tin, dissolve it in warm hydrochloric acid, and add to the solution a drop of mercuric chloride. A white precipitate of calomel (Hg_2Cl_2) or a grey precipitate of mercury is formed:

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$
$$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

This test applies also to stannous salts.

Stannous Salts.

1. To solution of stannous chloride add *hydric sulphide.* A brown precipitate of *stannous sulphide* (SnS) is formed. Collect on a filter or wash by decantation, and test its solubility in yellow ammonic sulphide. It dissolves. To the solution add hydrochloric acid. Stannic sulphide is precipitated.—*Explanation:* Yellow ammonic sulphide contains a persulphide of ammonium $(NH_4)_2S_2$; this unites with stannous sulphide to form *ammonic sulphostannate:*

$$(NH_4)_2S_2 + SnS = (NH_4)_2SnS_3,$$

which is decomposed by hydrochloric acid as follows:

$$(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + SnS_2 + H_2S.$$

2. Caustic soda gives with stannous solutions a white precipitate ($Sn(OH)_2$) soluble in excess.

3. Same as for stannic salts; but stannous salts give a white (Hg_2Cl_2) or grey (Hg) precipitate with mercuric chloride, without the preliminary treatment with zinc, &c.

Insoluble tin compounds can be got into solution by reducing on charcoal and dissolving in hydrochloric acid.

GOLD (*Aurum*).

315. **Gold.** ($Au^{I.\,III.}$ = 196.2.--Sp. wt. = 19.265.—Melting point = 1037°.—Sp. heat = 0.03244.)

Occurrence.—Gold is usually found free or alloyed with silver, platinum, &c. It is found associated with quartz and pyrites mostly.

Preparation.—It is obtained from quartz by crushing, and washing away the lighter mineral. It is obtained from auriferous sand and gravel by simple washing. Gold is extracted from pyrites, &c., by treating with *aqua regia*, and precipitating the gold with green vitriol.

Properties.—Gold is of familiar appearance, and need not be described. It is softer than silver, and must be hardened by alloying with copper before it is suitable for use. It is the most malleable and ductile of all metals. A gold wire can be drawn so fine that 10,000 feet (about 1¾ mile) weigh only 15 grains. Gold is not attacked by any simple acid, excepting *selenic* (H_2SeO_4). It is attacked by caustic potash, caustic soda, and saltpetre. The best solvent for gold is *aqua regia*, which dissolves it as *trichloride* ($AuCl_3$). Gold is very easily precipitated from solutions by reducing agents such as stannous chloride, ferrous sulphate, oxalic acid, mercurous nitrate, &c. *Purple of Cassius* is formed by precipitating with stannous chloride. It consists of finely divided gold and some compound of tin.

316. **Compounds of Gold.** Gold forms two oxides, *aurous* (Au_2O), and *auric* (Au_2O_3). Both are decomposed into gold and oxygen at 250°C. Both are basic, but auric oxide is also a weak acid-forming oxide.—The aurous salts ($AuCl$, AuI, &c.) are very unstable,

readily decomposing into gold and auric salts. *Potassic aurous cyanide* (KCN.AuCN), is, however, quite stable, and is used in electro-gilding.—*Auric chloride* ($AuCl_3$) unites with hydrochloric acid to form *chlorauric acid* ($HAuCl_4$). This is the solution generally used and called *terchloride of gold.*

317. Tests.

1. Solutions of gold acidified with hydrochloric acid give a brown precipitate (Au_2S_2), soluble in ammonic sulphide.

2. Solutions containing gold give a purple colour or precipitate with stannous chloride or ferrous sulphate.

PLATINUM, &c.

318. **Platinum** ($Pt^{ii. iv.}$ = 196.7.—Sp. wt. = 21.5.—Melting point about 2600°.—Sp. heat = 0.03243).

Occurrence.—Platinum is found in the metallic state, alloyed with *palladium, osmium, iridium,* &c. It is found in the Ural Mountains, S. America, Australia, Borneo, and California. It has lately been discovered in British Columbia. It is generally present in small quantity in gold and silver.

Preparation.—The crude platinum is dissolved in aqua regia, and precipitated as ammonium chloroplatinate, $(NH_4)_2 PtCl_6$, by ammonic chloride. From this compound it is obtained by heating :

$$(NH_4)_2PtCl_6 = 2NH_4Cl + Pt + 2Cl_2.$$

It generally contains about 2 % of iridium.

Properties.—A tin-white metal, soft, very heavy and malleable. It fuses only at an intense white heat. It has the power of condensing gases on its surface, and, in the finely divided state of *spongy platinum* and *platinum black*, it is used to bring about the oxidation of alcohols to aldehydes, sulphur dioxide to trioxide, &c. Platinum is attacked by few chemical substances. It combines, however, with the halogens, and is dissolved slowly when heated strongly with caustic potash, caustic soda, potassic nitrate, or potassic cyanide. It is attacked by oxides and sulphides of easily reducible metals, such as lead, copper, bismuth, &c., as well as by these metals themselves. These substances should never be heated in a platinum crucible.

USES.—Platinum is of the greatest importance in chemistry. "Without platinum the composition of most minerals would have yet remained unknown."—(Liebig.) It is used for crucibles, as it resists the action of most chemicals. It is also used in the manufacture of chemical balances and many other instruments of precision. The surgeon employs it, heated by a current of electricity or by alcohol vapour, using it instead of a knife.

319. **Compounds of Platinum.** Platinum forms two series of compounds, *platinous* (PtO, $PtCl_2$, PtS, &c.), and *platinic* (PtO_2, $PtCl_4$, &c.). The platinous compounds are unimportant. When platinum is dissolved in *aqua regia* the solution contains *chloroplatinic acid* (H_2PtCl_6). This is the solution generally called "solution of *tetrachloride of platinum.*" It is a well-marked dibasic acid, and forms characteristic sparingly soluble salts (chloroplatinates) of potassium, ammonium, amines, and alkaloids. These salts are of a golden yellow colour, and are sparingly soluble in water.—As the sodium salt (Na_2PtCl_6) is very soluble in water, chloroplatinic acid is used in analysis to separate sodium from potassium.

320. Tests.

It is precipitated along with the other members of this group by *hydric sulphide*. *Platinic sulphide* (PtS_2) dissolves in ammonic sulphide.—A solution containing platinic salts gives a golden yellow precipitate with ammonic chloride.—Solid substances containing platinum are extracted with aqua regia and tested as above.

321. **Palladium** is similar to platinum, but is soluble in nitric acid. It is used instead of gold by dentists.—*Iridium* is alloyed with platinum to make standard weights and measures. The alloy is very hard, and as elastic as steel.—*Osmium* forms a remarkable acid-forming oxide (OsO_4), which is volatile and very poisonous. *Osmic acid* (H_2OsO_5) is much used in practical histology. It stains fats black. An alloy of osmium and iridium (*osmiridium*) is used for tipping gold pens. Osmium is the heaviest substance known (sp. wt. = 22.477). It has never been fused.—*Tungsten* and *molybdenum*, although not nearly allied to the metals of this group, are mentioned here because their sulphides are precipitated by hydric sulphide and dissolve in ammonic sulphide.

QUESTIONS AND EXERCISES.

1. "The hydroxides of Group II. are precipitated from solutions of salts by alkaline hydroxides." Illustrate this statement by examples.

Illustrate from the members of this group the *Law of Dulong and Petit.*

3. What experimental proof can you bring to show that iron has a stronger attraction for salt radicals than copper has, i.e., is a more positive radical?

4. How would you prepare crystals of *cupric nitrate?*

5. Why is it dangerous to eat food which has been for some time in contact with brass?

6. Is there any danger in using brass taps for vinegar and cider casks? Explain.

7. How can cadmic chloride be prepared from cadmic nitrate? (Both salts are soluble.)

8. The specific weight of cadmium vapour is 3.94 (air = 1). Calculate its molecular weight. How many atoms in the molecule of cadmium?

9. Why should we expect bismuth carbonate to be more soluble in the gastric juice than the subnitrate?

10. Compare bismuth and antimony (1) as to the properties of the elements themselves, (2) as to their compounds.

11. Bismuth trinitrate is poisonous, and large doses cause symptoms of nitric acid poisoning. Explain this.

12. How would you distinguish by a test bismuth subnitrate from bismuthyl carbonate?

13. Compare antimony and arsenic with regard to their compounds.

14. Balance the following equations:

(1) $SbCl_2OH + H_2O = Sb_2O_3 + HCl$.
(2) $Sb_2O_3 + KHC_4H_4O_6 = SbOKC_4H_4O_6 + H_2O$.
(3) $SbCl_3 + H_2S = Sb_2S_3 + HCl$.
(4) $Sb_2O_3 + H_2 = SbH_3 + H_2O$.

15. What substances are formed when tin is dissolved in very dilute nitric acid?

16. When solution of stannous chloride ($SnCl_2$) is added to auric chloride ($AuCl_3$), metallic gold is precipitated and stannic chloride remains in solution. Write the equation.

17. What is the chemical composition of "*butter of tin*," "*butter of antimony*," "*butter of arsenic*," and "*tin salt?*"

18. Why is it necessary to use ammonic sulphide containing excess of sulphur to dissolve stannous sulphide?

19. A solution of chlorauric acid in water oxidises ferrous sulphate. How is this possible? Does chlorauric acid contain any oxygen?

CHAPTER XIX.

METALS OF GROUP III.

Iron, Chromium, Aluminium; Zinc, Manganese, Cobalt, and Nickel. [*Rare metals of the Cerium class.*]

322. **General Characters.**—The metals of this group are mostly reducible from their oxides by smelting with charcoal, but are more difficult to reduce than those of the preceding group. With two exceptions (aluminium and zinc) they have two *oxides* having the general formulas MO and M_2O_3. Besides these, chromium and manganese have well-marked acid-forming oxides. Their *sulphides* are not precipitated by hydric sulphide from acid solutions; but are precipitated by alkaline sulphides (two exceptions will be noted further on). Both sulphides and oxides are insoluble in water, but soluble in dilute acids (nickel and cobalt sulphides with difficulty). The *hydroxides, carbonates,* and *phosphates* are insoluble in water, and can all be prepared by precipitation. The hydroxides are easily changed to oxides by heat. The *sulphates, chlorides, nitrates,* and *acetates* are soluble in water, and their solutions have an acid reaction. The sulphates form characteristic *double-sulphates* with those of the alkali metals, e.g., $K_2SO_4.FeSO_4.6H_2O$. The alums form an interesting group of these double sulphates.

For convenience of analysis this group is subdivided into: *A.* Metals forming stable hydroxides, $M_2(OH)_6$, insoluble in ammonia: *iron, chromium,* and *aluminium*;

and *B*. Metals, the most basic hydroxides of which have the general formula $M(OH)_2$ and are soluble in ammonia : *zinc, manganese, cobalt*, and *nickel*. In analysis the cerium metals, as well as uranium, zirconium, and thorium fall here.

A.

IRON *(Ferrum).*

323. **Iron** ($Fe^{ii\ iv}$ = 56.—Specific weight = 7.844. Melting point = 1600°. Specific heat = 0.11379).

OCCURRENCE.—Rarely free, and then generally of meteoric origin. Meteors composed mostly of iron have been found weighing several tons. The principal ores of iron are *red hæmatite* (Fe_2O_3), *brown hæmatite* ($2Fe_2O_3.3H_2O$), *magnetic iron ore* (Fe_3O_4), *spathic iron ore* ($FeCO_3$), *clay ironstone* ($FeCO_3$, with clay or sand), and *black band* ($FeCO_3$, with coal).—Iron is present in the sun and in many fixed stars.—Iron is an essential constituent of the bodies of plants and animals. In the latter it is chiefly found in the *hæmoglobin* of the blood.

SMELTING OF IRON. — The ores are first calcined, if necessary, to drive off water, &c., and then placed in a tall, somewhat spindle-shaped, furnace (*blast furnace*), with alternate layers of coal and limestone. The limestone combines with the siliceous impurities to form a fusible slag. The coal burning at the bottom of the furnace (where a blast of hot air feeds the combustion) forms carbon dioxide, which, passing upward, unites with carbon to form carbon monoxide. Ferric oxide (Fe_2O_3) is then reduced by the carbon monoxide :

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

This is repeated with the successive layers. The iron, as it falls toward the bottom of the furnace, combines with carbon and silicon and becomes more fusible. It melts and falls into the hearth of the furnace, the slag forming a layer above it. The molten iron is run off into channels made of sand, and solidifies into bars of *pig iron.* Pig iron contains from 76 % to 96 % of pure iron, from 1 % to 20 % of manganese, and from 1 % to 7 % of carbon. It melts with comparative ease, and is used in manufacturing stoves, &c., by the process of *casting.* It is hence called *cast iron.* It is more brittle than pure iron and lighter.—*Wrought iron* is prepared from cast iron by removing the carbon and silicon. This is done by subjecting the molten metal to a hot oxidising blast in the process of *puddling.* In the *Bessemer process* the iron is kept hot by the oxidation of its impurities. Wrought iron contains up to 0.3 % of carbon. It is heavier than cast iron and very tenacious and malleable. —Steel is intermediate in composition between cast and wrought iron. It is now generally prepared by the Bessemer process, modified more or less. The impurities are burned away until the composition is that of wrought iron. Then enough cast iron is added to bring up the percentage of carbon to about 1.5 %.—*Spongy iron,* the *ferrum redactum* of the Pharmacopœia, is prepared by heating pure ferric oxide in a current of hydrogen :

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O.$$

It is valuable as a medicine, and as a filter for water, since it possesses the power of destroying impurities.

Properties.—Pure iron is almost as white as silver. It is the most tenacious of all metals, except nickel and cobalt. Iron is soft at a red heat, and can be *welded* at a white heat. Borax, sand, &c., are used to clear away the oxide from the surfaces to be welded. This they do by uniting with it to form fusible slags (silicate and borate of iron), which are easily scraped off. Iron is attracted by magnets, and can be made magnetic by the influence of electricity or of other magnets. It does not rust in dry, but does in moist, air. The rust is a compound of ferric oxide with ferric hydroxide ($Fe_2O_3.Fe_2(OH)_6$). The rusting of iron can be prevented by coating it with tin, or with a layer of the black oxide (Fe_3O_4) by exposing it to the action of steam at 650° (Barff's process). *Galvanised iron* is covered with a layer of zinc, which protects the iron by rendering it *electro-negative.*—Iron dissolves in dilute acids, and thus forms ferrous salts and hydrogen (Expt's 28 and 29). It is also slowly eaten away by water in the presence of air. Part of the iron dissolves as acid carbonate, and part of it forms rust. Caustic soda and potash prevent this.

Experiment 269.—Put a piece of bright iron wire in a beaker of tap water, and another in water containing caustic soda. Examine after 24 hours.

324. **Compounds of Iron.** — Iron forms three oxides: *ferrous* (FeO), *ferric* (Fe_2O_3), and the *black* (Fe_3O_4), or *ferroso-ferric oxide* ($FeO.Fe_2O_3$). The latter is formed when iron is heated strongly in air, and is the chief constituent of the black scales of the smithy. It can also be prepared by adding caustic soda to a solution containing a ferrous and a ferric salt, and then applying heat. It then forms a black precipitate, attracted by the magnet. Ferrous and ferric oxides are basic, and thus

there are two classes of iron salts to be considered. In the Pharmacopœia, the names of the ferric salts are distinguished by the syllable *per-*, e. g., *perchloride of iron,* instead of *ferric chloride.*

1. *Ferrous salts* correspond to the oxide FeO, in which Fe takes the place of H_2. They are easily oxidised, and it is difficult to preserve them unchanged. They are light green, or colourless; have a sweetish, inky, astringent taste; and are powerful reducing agents.

2. *Ferric salts* correspond to the oxide Fe_2O_3, and are prepared mostly by the oxidation of the corresponding ferrous salts. They are colourless when anhydrous, but when hydrated they are yellow or brown. They have an astringent, *chalybeate* taste, and can be reduced to ferrous salts by the action of nascent hydrogen, &c.

FERROUS SALTS.

325. **Ferrous Sulphate** ($FeSO_4 . 7H_2O$). — Also called *green vitriol* and *copperas* (*copper rose,* from its supposed identity with the green rust of copper).

PREPARATION. — By slow oxidation of iron pyrites (FeS_2) piled in heaps and exposed to the weather:

$$FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4.$$

The acid drainage from these heaps is treated with scrap iron:

$$H_2SO_4 + Fe = FeSO_4 + H_2.$$

On evaporation, crystals of green vitriol are obtained.

Experiment 270.—Dissolve a few iron tacks in dilute sulphuric acid. (What is the black substance remaining?) Keep the solution for further experiments.

PROPERTIES.—A green crystalline substance (Examine a specimen carefully), often rust-coloured on the surface from the oxidising action of the air. It is soluble in water (70 parts in 100), insoluble in alcohol.

Experiment 271.—To a portion of the solution from Experiment 270 add caustic soda. A precipitate falls, which is at first white, but rapidly turns green. It is *ferrous hydroxide* ($Fe(OH)_2$):

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4.$$

Close the t. t. with the thumb, and shake vigorously. Note that the thumb is pushed inwards showing that the pressure inside has decreased, and that the hydroxide has become rust-coloured:

$$2Fe(OH)_2 + O + H_2O = Fe_2(OH)_6.$$

If ferrous hydroxide is precipitated in an atmosphere free from oxygen, it is white. When heated it loses water, and forms *ferrous oxide* (FeO), a black powder:

$$Fe(OH)_2 = FeO + H_2O.$$

Experiment 272.—Boil a little of the solution of ferrous sulphate with nitric acid. Red fumes are evolved, and the solution becomes red, owing to the formation of *ferric sulphate* ($Fe_2(SO_4)_3$) and *nitrate* ($Fe_2(NO_3)_6$):

$$6FeSO_4 + 8HNO_3 =$$
$$2Fe_2(SO_4)_3 + Fe_2(NO_3)_6 + 2NO + 4H_2O.$$

Add caustic soda to this solution; a red precipitate of ferric hydroxide is thrown down:

$$Fe_2(SO_4)_3 + 6NaOH = Fe_2(OH)_6 + 3Na_2SO_4.$$

Experiment 273.—Pour a small quantity of hot saturated solution of ferrous sulphate into an equal volume of alcohol. Shake or stir. Ferrous sulphate is precipitated in a granular condition (*Ferri sulphas granulata*).

Experiment 274.—Heat a crystal of green vitriol very gently in a t. t. It loses water of crystallisation and falls to a white powder (*Ferri sulphas exsiccata*).

In large doses ferrous sulphate may act as poison, but in smaller doses it is a useful medicine.—*Mohr's salt* is *ammonio-ferrous sulphate* $(NH_4)_2SO_4.FeSO_4.6H_2O$. It does not become oxidised as readily as green vitriol.

326. Ferrous Carbonate ($FeCO_3$).

Experiment 275.—Heat some solution of ferrous sulphate to boiling, and add to it solution of *ammonic carbonate* (best made with recently boiled water). A precipitate falls, which is at first white but rapidly becomes green by oxidation. It is *ferrous carbonate* ($FeCO_3$):

$$(NH_4)_2CO_3 + FeSO_4 = FeCO_3 + (NH_4)_2SO_4.$$

Ferrous carbonate is so easily oxidised that its preparation is attended with some difficulty. In medicine it is used mixed with sugar (*Ferri carbonas saccharata*). *Griffith's mixture* is another preparation of ferrous carbonate. They must be kept in well stoppered bottles. Ferrous carbonate, on account of its easy solubility in the gastric juice and its mild action, is a favourite prescription of iron.

327. Ferrous Arsenate ($Fe_3(AsO_4)_2$).

PREPARATION.—By adding solution of ferrous sulphate to one of sodic arsenate (Na_2HAsO_4) mixed with sodic acetate, ferrous arsenate is precipitated as a greenish readily oxidisable substance:

$$2Na_2HAsO_4 + 2NaC_2H_3O_2 + 3FeSO_4 =$$
$$Fe_3(AsO_4)_2 + 3Na_2SO_4 + 2HC_2H_3O_2.$$

It is always partially oxidised in the process of preparation.

328. Ferrous Phosphate ($Fe_3(PO_4)_2$).

PREPARATION.—This compound is prepared in much the same way as ferrous arsenate.

Experiment 276.—To solution of ferrous sulphate add some sodic acetate, and then sodic phosphate. Ferrous phosphate is precipitated. (Write the equation.)

The object of adding sodic acetate in these processes is to provide that the acid which is set free in the reaction shall not be a solvent for the phosphate. Note that, while sodic phosphate is an acid salt, the iron salt is normal. If the sodic acetate were not added, some of the phosphate would remain unprecipitated, being soluble in sulphuric acid. But it is insoluble in acetic acid.

PROPERTIES.—Similar in appearance to the arsenate (Art. 144), but inclining to blue in colour. It is insoluble in water, but soluble in hydrochloric acid.—To distinguish the phosphate from the arsenate, dissolve in hydrochloric acid and test with hydric sulphide. The arsenate gives a yellow precipitate, the phosphate none.

329. **Ferrous Iodide** (FeI_2).—This is the *green iodide of iron*, prepared by warming together 3 parts of of iodine, 1½ of iron, and 12 of water, until the iodine disappears, then boiling, filtering, &c. It is a deliquescent green salt.—*Ferrous Bromide* ($FeBr_2$) is prepared similarly.—*Ferrous Chloride* ($FeCl_2$) has been already noticed (Exp't 29).

FERRIC SALTS.

330. **Ferric Chloride** (Fe_2Cl_6).—Also called *perchloride of iron.*

PREPARATION.—**Experiment 277.** — Dissolve some iron tacks in dilute hydrochloric acid in a porcelain dish with the aid of a gentle heat. Let there be insufficient acid to dissolve the tacks completely. Filter the solution. (What is the black substance?) Add a small quantity of nitric acid and a little hydrochloric acid, and heat quickly until red fumes are evolved. Evaporate on the water bath.

Ferrous chloride ($FeCl_2$) is formed by dissolving iron in hydrochloric acid:

$$Fe + 2HCl = FeCl_2 + H_2.$$

This is changed to *ferric chloride* by the addition of chlorine produced by the action of nitric on hydrochloric acid:

$$6FeCl_2 + 6HCl + 2HNO_3 = 3Fe_2Cl_6 + 2NO + 4H_2O.$$

PROPERTIES.—The solution obtained in Experiment 277, when evaporated to a syrup and allowed to cool, solidifies to a yellowish mass of the hydrate, $Fe_2Cl_6.12H_2O$.—*Anhydrous ferric chloride* can be prepared as a steel-black deliquescent solid by heating iron in a current of dry chlorine gas.—Ferric chloride dissolves in water, forming a dark red solution which becomes yellow on dilution. The solution has an astringent taste. Ferric chloride is soluble in alcohol, but the solution (*tincture of iron*) tends to deposit ferric hydroxide, and has no virtues to recommend it above the cheaper aqueous solution.—Ferric chloride dissolves ferric hydroxide, and thus forms soluble basic salts, milder in their action than the normal salt. By dialysis of ferric chloride, *soluble ferric hydroxide (dialysed iron)* can be obtained. It is an excellent antidote for arsenic poisoning, and is the best preparation of iron for a delicate stomach. It unfortunately gelatinises after a time.

Experiment 278.—Make a small boat of parchment paper, fill it about one-fourth with dilute solution of ferric chloride, float it in a basin or beaker of distilled water, and leave it for 24 hours. Examine the water for hydrochloric acid, by taste, litmus, &c. Taste the iron solution. It has lost much of its astringency. Boil some of it in a t. t. Ferric hydroxide is precipitated.

In this experiment water decomposes ferric chloride:

$$Fe_2Cl_6 + 6H_2O = Fe_2(OH)_6 + 6HCl.$$

The *crystalloid* hydrochloric acid passes through the membrane, while *colloid* ferric hydroxide remains.

331. **Ferric Sulphate** ($Fe_2(SO_4)_3$).—This salt has been already noticed (Exp't 272). If it is desired to prepare the pure sulphate, sulphuric acid must be added according to the equation:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

It forms a reddish-brown solution, of strongly acid reaction.—Ferric sulphate unites with potassic sulphate and water to form *iron alum*, $K_2SO_4.Fe_2(SO_4)_3.24H_2O$.

332. **Ferric Nitrate** ($Fe_2(NO_3)_6$).—When iron dissolves in cold very dilute nitric acid, *ferrous nitrate* ($Fe(NO_3)_2$), and ammonic nitrate are formed:

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

But when the action is hastened by heat or by using a stronger acid, *ferric* nitrate is one product, and some oxide of nitrogen another, e.g.:

$$2Fe + 8HNO_3 = Fe_2(NO_3)_6 + 2NO + 4H_2O.$$

It forms a solution of a reddish-brown colour, the *ferri pernitratis liquor* of the Pharmacopœia.

333. **Ferric Hydroxide** ($Fe_2(OH)_6$). This is prepared as in the second part of Experiment 272, but ammonia is generally used instead of caustic soda. It is a reddish brown substance which gradually undergoes change even when kept in water. It loses water when dried in the air, forming a hydroxide of the composition $Fe_2O_3.H_2O$. The same decomposition goes on under water, and the dehydrated compound is less active, e.g. it does not combine with arsenic trioxide.

Experiment 279.—Heat a small quantity of ferric hydroxide on mica until it is converted into the oxide (Fe_2O_3). Try to dissolve this in hydrochloric acid. (Is the hydroxide soluble in hydrochloric acid?)

Experiment 280.—Add solution of sodic carbonate to one of ferric chloride. Ferric hydroxide is precipitated. It is so weak a base that it does not form salts with weak acids:

$$Fe_2Cl_6 + 3Na_2CO_3 + 3H_2O = Fe_2(OH)_6 + 6NaCl + 3CO_2.$$

(Did you observe the evolution of carbon dioxide?)

334. **Ferric Oxide** (Fe_2O_3). This compound has been already noticed several times.

Experiment 281.—Heat a few crystals of green vitriol strongly in a porcelain crucible. Ferric oxide remains as a red powder, called *colcothar*, *crocus*, *rouge*, or *venetian red*. Try to dissolve some of it in strong acids. It is insoluble.

Ignited ferric oxide should never be used in medicine instead of the hydroxide described in Art. 333, as it is insoluble in acids, and therefore useless for prescription as an iron preparation.

335. **The "Scale" Compounds of Iron.**—Certain organic acids (citric, tartaric, &c.,) prevent the precipitation of ferric hydroxide by ammonia.

Experiment 282.—To a solution of ferric chloride add tartaric acid, and then ammonia until the liquid is alkaline. No precipitate forms.

This is due to the formation of a soluble basic tartrate of iron and ammonium. If ferric hydroxide is dissolved in tartaric acid, *ferric tartrate* is formed. When ammonia is added to this and the whole evaporated to dryness, a basic salt is obtained in red amorphous *scales*. Similarly with citric acid. Quinine and other alkaloids are added to these scale preparations. They contain variable quantities of iron, and are rather difficult to prepare.

336. Tests.

Ferrous Salts.

1. Solutions of ferrous salts give with *ammonia* a greenish precipitate ($Fe(OH)_2$), turning rust coloured when shaken up with air.

2. *Ammonic sulphide* gives a black precipitate (FeS), soluble in dilute hydrochloric acid :

$$FeS + 2HCl = FeCl_2 + H_2S.$$

3. *Potassic ferrocyanide* ($K_4Fe(CN)_6$) gives a white or light blue precipitate of *potassic ferrous ferrocyanide* :

$$K_4.Fe(CN)_6 + FeSO_4 = K_2Fe.Fe(CN)_6 + K_2SO_4.$$

This quickly turns blue by oxidation, forming *Prussian blue.*

4. *Potassic ferricyanide* ($K_3Fe(CN)_6$) gives a deep blue precipitate (or colour, according to the strength of the solution) ($KFe.Fe(CN)_6$). (Turnbull's Blue.)

5. Ferrous solutions, when heated with *nitric acid,* turn red, and will then give a reddish-brown precipitate with ammonia.

Ferric Salts.

1. *Ammonia* gives a reddish-brown precipitate of ferric hydroxide, *insoluble in excess.*

2. *Ammonic sulphide* gives a black precipitate of ferrous sulphide mixed with sulphur :

$$Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$

This is soluble in dilute hydrochloric acid, the sulphur remaining undissolved.

3. *Potassic ferrocyanide* gives a deep blue precipitate of *Prussian blue.*

4. *Potassic ferricyanide* gives a greenish-brown colour, but no precipitate.

5. With *hydric sulphide* ferric salts give a white precipitate of sulphur. $Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S$.

6. Insoluble iron compounds are tested by the borax bead, which with iron is yellow in the oxidising, colourless or blue in the reducing flame.

CHROMIUM.

337. **Chromium** ($Cr^{ii, iv, vi} = 52.4$).—The metal itself is of no importance. The principal ore is *chrome ironstone*, or *chromite* ($FeO.Cr_2O_3$).—The name *Chromium* is derived from a Greek work meaning *colour*, because all chromium compounds are coloured. The metal is reduced from its ores with great difficulty. Chromium ores are sometimes added to iron ores, because chromium imparts great hardness to steel. *Chromium steel* requires to be worked at comparatively low temperatures.

338. **Compounds of Chromium.** — Chromium unites with oxygen in three portions, forming *two basic oxides,—chromous* (CrO), and *chromic* (Cr_2O_3); and one *acid-forming oxide,—chromium trioxide* (CrO_3).—The *chromous salts* ($CrCl_2$, $CrSO_4$, &c.) are very unstable, becoming oxidised even more readily than ferrous salts.—The *chromic salts* (Cr_2Cl_6, $Cr_2(SO_4)_3$, &c.) are similar to ferric salts in composition and properties. They are the

ordinary salts of chromium.—Besides these two series of compounds there are the *chromates*, salts of *chromic acid* (H_2CrO_4).

339. **Potassic Bichromate** ($K_2Cr_2O_7 = K_2O.2CrO_3$).—This salt is the starting point in preparing chromium compounds.

Preparation.—Chrome ironstone is roasted, ground, and heated with lime and potassic carbonate, with constant stirring so as to allow oxidation to go on. The object of the lime is to economise alkali, and to prevent fusion, so that the air may penetrate into the mass:

$$Cr_2O_3 + 2K_2CO_3 + 3O = 2K_2CrO_4 + 2CO_2.$$
$$Cr_2O_3 + 2CaO + 3O = 2CaCrO_4.$$

When oxidation is complete, the potassic and calcic chromates are dissolved in water, and to the solution potassic sulphate (K_2SO_4) is added to precipitate calcium:

$$K_2SO_4 + CaCrO_4 = CaSO_4 + K_2CrO_4.$$

To the strong solution of potassic chromate thus obtained sulphuric acid is added to form the *less soluble* bichromate:

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

The object of this operation is to separate the chromium salt from the impurities present in the solution.

Properties.—Potassic bichromate crystallises in large garnet red prisms, soluble in water (8 parts in 100). It is a strong oxidising agent, especially in the presence of acids. An instance of this has been already described (*Aldehyde*).

Experiment 283.—To a solution of potassic bichromate acidified with sulphuric acid add sulphuretted hydrogen. The red colour changes to green, and sulphur is precipitated:

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S.$$

In this action chromium trioxide is an oxidising agent, and the hydrogen of hydric sulphide is oxidised to water. Leaving the acid out of consideration the action can be represented more simply:

$$2CrO_3 + 3H_2S = Cr_2O_3 + 3H_2O + 3S.$$

Experiment 284.—To 50 c. c. of saturated solution of potassic bichromate add 5 or 10 drops of sulphuric acid, and then sulphurous acid until the colour is bright green. Evaporate to a small bulk and set aside. The solution contains *chrome alum* ($K_2SO_4.Cr_2(SO_4)_3.24H_2O$):

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4.Cr_2(SO_4)_3 + H_2O.$$

Potassic bichromate, on account of its oxidising power, is a corrosive *poison*. The *antidote* is ferric chloride, which forms the sparingly soluble ferric chromate. Alkaline sulphites should also be antidotal. (Why?)

Potassic bichromate is used in the preparation of other chromates. The following are insoluble in water but soluble in dilute acids: *baric* ($BaCrO_4$), *plumbic* ($PbCrO_4$), *argentic* (Ag_2CrO_4), *mercurous* (Hg_2CrO_4), *ferric* ($Fe_2(CrO_4)_3$), and others.

Experiment 285.—Add solution of potassic bichromate to solutions of the following salts, note the colour of the precipitates and test their solubility in acetic and nitric acids, viz., *baric chloride* ($BaCl_2$), *plumbic acetate* ($Pb(C_2H_3O_2)_2$), *argentic nitrate* ($AgNO_3$), and *mercurous nitrate* ($Hg_2(NO_3)_2$). *Normal chromates* are precipitated, and acid is set free in each case. (Write the equations.)

Plumbic chromate ($PbCrO_4$) is used as a paint (*chrome yellow*). *Chrome red* is a basic chromate of lead prepared by boiling the normal chromate with lime water.

Experiment 286.—Dip a piece of white cotton in dilute solution of plumbic acetate, soak it well, wring it, and then dip it in dilute solution of potassic bichromate. It is dyed yellow, and the colour is *fast*, being precipitated within the fibres of the cotton. Boil the cotton with lime water; it becomes orange red.

340. Chromic Acid.

Experiment 287.—To a cold saturated solution of potassic bichromate add one and a half times its volume of concentrated sulphuric acid, taking care to stir well. Set in a cool place. *Chromium trioxide* (CrO_3) separates out in beautiful red crystals.

Chromium trioxide dissolves in water, forming a strongly acid solution, but no definite acid has been separated from this. The normal *chromates* are analogous to the sulphates in composition, e.g. K_2CrO_4, $PbCrO_4$, &c., so that *chromic acid* may be supposed to have the formula H_2CrO_4. Potassic bichromate is then an *anhydrous acid salt.*

341. Chrome Alum ($K_2SO_4.Cr_2(SO_4)_3.24H_2O$).

This salt is prepared as in Experiment 284. It is a by-product in some operations in which potassic bichromate is used as an oxidising agent, e.g. in the manufacture of alizarine. It is soluble in water, and crystallises from cold solutions in violet crystals *isomorphous* with those of common alum. If a crystal of common alum be placed in a saturated solution of chrome alum it grows by addition of layers of the chrome alum. Solutions of chrome alum undergo a peculiar change on being heated. The colour changes from violet to green, and this solution does not crystallise. It slowly returns to its former condition. This property is common to all chromic

salts.—Chrome alum is used in tanning, dyeing, and calico-printing.

342. Chromic Hydroxide ($Cr_2(OH)_6$).

Experiment 288.—Add ammonia to a solution of chrome alum. Collect the precipitate of chromic hydroxide on a filter and wash it. Try the solubility of portions of it in hydrochloric acid, caustic soda, and ammonia. Heat part of it on mica.

Chromic hydroxide is of a dirty green colour. It dissolves in hydrochloric acid, forming *chromic chloride* (Cr_2Cl_6). It is also soluble in caustic soda, forming a green solution from which it is reprecipitated by boiling. When heated it loses water, and *chromium sesquioxide* (Cr_2O_3) remains. This oxide is used as a paint (*chrome green*). *Guignet's green* has the composition, $Cr_2O_3.2H_2O$. It is also sold as *chrome green.*

343. Tests.

Chromates.

1. *Baric chloride* gives a yellow precipitate insoluble in acetic acid, soluble in nitric acid.
2. Acidified solutions of chromates are turned green by *hydric sulphide.*
3. Solutions of chromates are reduced by *ammonic sulphide,* which precipitates chromic hydroxide, so that this group reagent is a test for chromates as well as for chromic salts.
4. Insoluble chromates can be tested for by the borax bead, to which they give an emerald green colour.

Chromic Salts.

1. *Ammonia* precipitates chromic hydroxide, insoluble in excess.
2. Ammonic sulphide gives a dirty green precipitate of hydroxide:

$$Cr_2(SO_4)_3 + 3(NH_4)_2S + 3H_2O = Cr_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S.$$

3. Caustic soda gives a green precipitate soluble in excess, reprecipitated by boiling.

4. Insoluble chromium compounds can be detected by the borax bead, or by heating in the oxidising flame with a sodic carbonate bead, to which they give a yellow colour, due to the formation of sodic chromate. If the bead be dissolved in water the yellow colour appears strongly.

ALUMINIUM.

344. **Aluminium** (Al^{iv} = 27.3.—Sp. wt. = 2.67.—Melting point = 700°.—Sp. heat = 0.2143).

OCCURRENCE.—Compounds of aluminium form a very considerable proportion of the earth's crust, being found in clay, granite, gneiss, mica, felspar, &c.

PREPARATION.—From *bauxite*, a hydroxide of aluminium and iron. *Aluminium chloride* (Al_2Cl_6) is obtained by a series of operations, and from this the metal is set free by sodium. Lately the metal has been obtained more economically by electrolysis.

PROPERTIES.—A light, tin-white metal, malleable, ductile, and sonorous. When pure it does not tarnish in air, but the impure metal soon tarnishes; and this is one difficulty in the way of the economical manufacture of the metal. It decomposes water at 100°, and dissolves easily in most acids and alkalis. Obviously, it cannot be used for cooking utensils. It is very useful wherever lightness and durability are required, as in optical instruments, &c. *Aluminium bronze* is an alloy of aluminium with 90 % of copper. It has the appearance and many of the qualities of gold.

345. **Alumina** (Al_2O_3). This is the only oxide of aluminium.

OCCURRENCE.—As corundum. ruby, sapphire, emery, &c.; and combined in many silicates, &c.

PREPARATION.—**Experiment 289.**—To a solution of alum add ammonia. Collect on a filter, and wash, the gelatinous precipitate of *aluminic hydroxide*, $Al_2(OH)_6$:

$$6NH_4OH + Al_2(SO_4)_3 = Al_2(OH)_6 + 3(NH_4)_2SO_4.$$

Heat a portion of the precipitate on mica. It decomposes into water and aluminic oxide:

$$Al_2(OH)_6 = Al_2O_3 + 3H_2O.$$

PROPERTIES.—A white powder, insoluble in acids after it has been ignited. Crystalline alumina is next to diamond in hardness, and in the form of *emery* is used in grinding and polishing hard substances.

Aluminic hydroxide, $Al_2(OH)_6$, is a weak base, and also a weak acid.

Experiment 290.—To a solution of alum add caustic soda, a little at a time. Aluminic hydroxide is precipitated and redissolved:

$$Al_2(OH)_6 + 6NaOH = Al_2(ONa)_6 + 6H_2O.$$

Aluminic hydroxide dissolves in solutions of caustic soda and caustic potash, forming *aluminates*. It does not dissolve in solution of ammonia.—It has the power of extracting colouring matters from solution, and is used as a clarifier, decolouriser, and as a *mordant* in dyeing.

346. **Aluminic Salts.** Aluminium salts are mostly colourless, and, when the acid is a strong one, of an astringent, acid taste. They resemble ferric and chromic salts in composition, e.g. Al_2Cl_6, $Al_2(SO_4)_3$, $Al_2(NO_3)_6$, &c.

Like chromium and iron (in ferr*ic* compounds), aluminium does not form salts of such weak acids as carbonic.

347. **Alums.** Aluminic sulphate ($Al_2(SO_4)_3$) combines with potassic sulphate (K_2SO_4) and water to form *potash alum*, $K_2SO_4.Al_2(SO_4)_3.24H_2O$. It also unites with ammonic sulphate to form *ammonia alum* $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$. The alums are a group of compounds similar in properties and composition, and exactly alike in crystalline form. A crystal of any one alum will increase in size when placed in a saturated solution of any other; the alums are *isomorphous*. A general formula may be written thus:

$$M_2SO_4.M'_2(SO_4)_3.24H_2O.$$

M = K, NH_4, Na, Rb, Cs, Ag, or Tl.
M' = Al, Fe, Cr, In, or Ga.

PREPARATION.—*Potash and ammonia alums* are the ones in common use. They are prepared mostly from *shale*, which contains clay (a silicate of aluminium) and iron pyrites (FeS_2). The shale is burned in heaps, when aluminic and ferrous sulphates are formed. By lixiviation a solution of aluminic sulphate is obtained. To this potassic or ammonic sulphate is added, and the alum is obtained by evaporation, and purified by recrystallisation.

PROPERTIES.—Potash and ammonia alums are colourless solids, generally sold in large crystals. They are exactly alike in appearance, and can only be distinguished by a chemical test. They have an acid, sweetish, astringent taste. They are soluble in water (12 parts in 100), the potash, a little more so than the ammonia, alum. They effloresce slowly in air, owing to the action of the ammonia of the air in forming basic salts.—Potash alum is now the one generally sold.

Experiment 291.—Heat a crystal of potash alum in a t. t., and observe the loss of water of crystallisation. The white powder which remains is anhydrous alum, or *burnt alum* (*alumen ustum*).

348. **Aluminic Sulphate** ($Al_2(SO_4)_3.18H_2O$). This salt, known as *concentrated alum*, or *alum cake*, is prepared on the large scale by the action of sulphuric acid on certain clays, the products being aluminic sulphate and silicic acid. It replaces the more expensive alum in many of the uses to which that substance has been put.

349. **Porcelain, &c.** Porcelain is made from a pure white clay (*kaolin, or china-clay*), a hydrated silicate of aluminium ($Al_2O_3.2SiO_2.2H_2O$). In the process of *burning*, the water is driven off. The *glaze* is felspar, borax, bone ash, or red lead.—*Stoneware, earthenware*, and common *pottery*, are made from impure clays.

350. Tests.

1. *Ammonia* precipitates aluminic hydroxide, insoluble in excess.

2. *Ammonic sulphide* gives the same precipitate :

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 3H_2O = Al_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S.$$

3. *Caustic soda* precipitates aluminic hydroxide, but redissolves it. (Experiment 290.) From this solution aluminic hydroxide is precipitated by *ammonic chloride* :

$$Al_2(ONa)_6 + 6NH_4Cl = Al_2(OH)_6 + 6NaCl + 6NH_3.$$

4. Insoluble aluminium compounds are detected by moistening with *cobaltous nitrate*, $Co(NO_3)_2$, and heating with the blowpipe on charcoal. A deep blue colour is imparted.

B

ZINC.

351. **Zinc** (Zn^{II} = 64.9.—Sp. wt. = 6.9.—Melting point = 433°.—Boiling point = 1040°.—Sp. heat = 0.09555).

Occurrence.—The principal ores of zinc are *calamine*, or *zinc spar* ($ZnCO_3$), *zinc blende* (ZnS), *franklinite* ($ZnO.Fe_2O_3$), and *red zinc ore* (ZnO).

Preparation.—The ore is roasted, and reduced by heating with pounded coal in clay retorts. The metal distils over and is condensed in iron tubes:

$$ZnO + C = Zn + CO.$$

Commercial zinc contains lead, carbon, iron, &c., as impurities. Arsenic is often present, a fact to be remembered in making Marsh's test.

Properties.—Zinc is of a bluish white colour when pure. When heated strongly in air it burns, forming zinc oxide (ZnO). Commercial zinc is brittle at ordinary temperatures, but is very malleable and ductile between 100° and 150°. It is easily oxidisable, and dissolves readily in acids. Alloyed with copper it forms brass.—Zinc is used in the manufacture of various utensils, in galvanizing iron, in generating electricity, in preparing hydrogen, &c.

352. **Zinc Oxide** (ZnO).—Zinc forms only one oxide, known in commerce as *zinc white.*

Preparation.—(1) By boiling zinc and burning its vapour.—(2) The British Pharmacopœia directs it to be prepared by heating *zinc carbonate* in a loosely covered crucible, until a portion taken out does not effervesce with acids :

$$ZnCO_3 = ZnO + CO_2.$$

This method of preparing oxides of metals is often employed.

PROPERTIES.—A soft, white powder, tasteless, and inodorous. It is insoluble in water. It is used in medicine and as a paint.

Experiment 292.—Heat a small quantity of zinc carbonate in a porcelain crucible for 15 minutes. Test a part of it with dilute sulphuric acid. Note that the oxide is yellow while hot.

353. **Zinc Salts.** The salts of zinc are colourless, unless the acid is coloured. The soluble salts have an acid reaction in solution, and a nauseous metallic taste. They are poisonous and act as emetics.

354. **Zinc Chloride** ($ZnCl_2$).—This salt is known as " butter of zinc."

PREPARATION.—The soluble salts of zinc are usually prepared from the commercial metal, and the method of preparation is similar for most of the pharmaceutical preparations.

Experiment 293.—Dissolve some granulated zinc in dilute hydrochloric acid by warming in a porcelain dish. Boil, filter, and add chlorine water to convert ferrous to ferric chloride. Add zinc carbonate until a brownish precipitate appears:

$$3ZnCO_3 + Fe_2Cl_6 + 3H_2O =$$
$$3ZnCl_2 + Fe_2(OH)_6 + 3CO_2.$$

Filter again, and evaporate until oily. Set aside for a day and observe.

PROPERTIES.—A white, fusible solid, very deliquescent. It has strong caustic properties, and the anhydrous salt chars sugar, &c. It dissolves easily in water, alcohol, and ether.—It is used for weighting cotton goods. In surgery it is employed as a caustic and antiseptic.—*Burnett's disinfecting fluid* is a solution of zinc chloride. It is very poisonous, and has sometimes been swallowed by mistake. The chemical *antidotes* are chalk, magnesia, sodic carbonate, &c. (Explain the action of these antidotes.)

355. **Zinc Sulphate** ($ZnSO_4.7H_2O$), — generally known as *white vitriol.*

Preparation.—Dissolve zinc in dilute sulphuric acid, and then proceed as with zinc chloride.

Properties.—A white crystalline salt, very much resembling Epsom salts ($MgSO_4.7H_2O$), with which it is isomorphous. (These two salts can be readily distinguished by their taste.) It effloresces when exposed to air. It is an irritant poison when taken in large doses. The *antidotes* are albumen, tannin solutions (tea, &c.), and sodic carbonate.—Zinc sulphate dissolves readily in water (1 part in 2 of water).

356. **Zinc Carbonate** ($ZnCO_3$). The normal carbonate of zinc is difficult to prepare. *Zinci carbonas* of the Pharmacopœia is a basic salt ($ZnCO_3.2ZnO.3H_2O$).

Experiment 294.—Add sodic carbonate to solution of zinc sulphate. Basic zinc carbonate is precipitated. Note its appearance. (What gas is evolved ?) Filter, wash, test solubility in acids. (Has this salt any taste ?)

357. **Zinc Acetate** ($Zn(C_2H_3O_2)_2.H_2O$).

Preparation.—**Experiment 295.**—Dissolve zinc carbonate in acetic acid until no more will dissolve, filter if necessary, evaporate to small bulk, adding a few drops of acetic acid from time to time, and set aside to crystallise.

PROPERTIES.—A colourless solid, crystallising in thin, pearly plates. It is soluble in water, and the solution has a sharp, unpleasant, metallic taste.

358. Tests.

1. *Ammonia* gives a white precipitate of *zinc hydroxide* ($Zn(OH)_2$), soluble in excess.

2. *Ammonic sulphide* gives a white precipitate of *zinc sulphide* (ZnS):

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4.$$

This is soluble in dilute hydrochloric acid.

3. *Caustic soda* precipitates zinc hydroxide, and then redissolves it:

$$ZnSO_4 + 2NaOH = Na_2SO_4 + Zn(OH)_2.$$
$$Zn(OH)_2 + 2NaOH = Zn(ONa)_2 + 2H_2O.$$

This solution gives no precipitate with ammonic chloride (because zinc hydroxide is soluble in ammonia), but gives a white precipitate of zinc sulphide when treated with hydric sulphide.

4. Zinc compounds insoluble in water can be dissolved in dilute sulphuric or hydrochloric acid, and tested as above.

MANGANESE.

359. Manganese ($Mn^{ii.iv.vi.} = 54.8$.—Sp. wt. $= 8$.—) Compounds of manganese are widely distributed in small quantities. They give the colour to many otherwise colourless minerals, e.g. many silicates; and are found in minute quantities in both plants and animals.—The chief ores of manganese are *pyrolusite*, or *black oxide of manganese* (MnO_2), *braunite* (Mn_2O_3), *hausmannite* (Mn_3O_4), *psilomelane* ($BaO.MnO_2$), and *rhodocrozite*

($MnCO_3$). The metal is of little importance. It can be prepared by reducing *manganous oxide* (MnO) with charcoal at a very high temperature. It decomposes warm water. Its presence in iron renders that metal very hard.

360. **Oxides of Manganese.** Manganese unites with oxygen in four proportion, forming two *basic,—manganous oxide* (MnO), and *manganic oxide* (Mn_2O_3); and two *indifferent oxides,—red oxide of manganese* (Mn_3O_4), and *manganese dioxide* (MnO_2). It unites with oxygen and hydrogen to form two *acids—manganic* (H_2MnO_4), and *permanganic* ($HMnO_4$). There is some evidence of the existence of an oxide (Mn_2O_7) corresponding to permanganic acid:

$$2HMnO_4 = H_2O + Mn_2O_7.$$

361. **Manganese Dioxide** (MnO_2). This substance is found in large quantities as the mineral *pyrolusite*, or black oxide of manganese. It is the most important compound of manganese, being used in the manufacture of bleaching powder and glass, and in the preparation of oxygen, chlorine, potassic permanganate, &c.

PROPERTIES.—A brownish black solid. When heated, it gives off one-third of its oxygen:

$$3MnO_2 = Mn_3O_4 + O_2.$$

Strong hot sulphuric acid causes it to lose half its oxygen:

$$MnO_2 + H_2SO_4 = MnSO_4 + O + H_2O.$$

The action of hydrochloric acid has been already studied. (Art. 92.)—Manganese dioxide is sometimes fraudulently mixed with coal dust and charcoal powder. This makes it explosive when heated :

$$2MnO_2 + C = 2MnO + CO_2.$$

362. **Manganous Salts.** In these salts manganese is bivalent ($MnCl_2$, $MnSO_4$, &c.). The soluble salts can be prepared by dissolving manganese dioxide or *manganous hydroxide* ($Mn(OH)_2$) in the acids; and the insoluble salts by precipitation. Manganous salts are usually pink or rose-coloured, and are not easily oxidised to manganic salts. (Compare with *ferrous* and *ferric* salts.)

Experiment 296.—Heat a little manganese dioxide with concentrated sulphuric acid. Observe the evolution of oxygen. A solution of *manganous sulphate* ($MnSO_4$) is obtained. There is usually a reddish residue of *ferric oxide*, nearly always present in manganese dioxide as an impurity. The solution contains ferric sulphate as an impurity. This can be removed by heating the impure manganous sulphate to redness, and thus decomposing the ferric sulphate. Manganous sulphate can then be dissolved out.

363. **Manganic Salts.** Unlike the corresponding salts of iron and chromium, manganic salts very readily lose oxygen, &c., and become converted into manganous salts. For example,

$$Mn_2(SO_4)_3 + H_2O = 2MnSO_4 + O + H_2SO_4.$$

364. **Manganates.** The manganates are similar to the sulphates and chromates in composition, and are also in many cases isomorphous with these salts. The most important manganates are *potassic* (K_2MnO_4), and *sodic* (Na_2MnO_4).

PREPARATION.—**Experiment 297.**—Fuse manganese dioxide in a porcelain basin with one and a half times its weight of caustic potash, and stir for some time with a glass rod so as to expose the mass to the oxidising action of the air :

$$2MnO_2 + O_2 + 4KOH = 2K_2MnO_4 + 2H_2O.$$

Lixiviate the blue mass with water. A solution of potassic manganate is obtained. (Keep the solution.) By using caustic soda a solution of sodic manganate can be prepared in the same way.

Properties.—The magnanates of potassium and sodium form dark green solutions from which the solid substances can be obtained by evaporation. They are stable only in the presence of free alkali. (See Exp't 298.)

Condy's green disinfecting fluid is an alkaline solution of sodic manganate, generally containing permanganate in small proportion. The manganates are powerful oxidising agents, and to this they owe their valuable disinfecting and deodorising properties.—*Manganic acid* (H_2MnO_4) is not known apart from its salts.

365. **Permanganates**. These are salts of *permanganic acid* ($HMnO_4$). The potassium and sodium salts are of most importance.

Preparation.—**Experiment 298.**—To the clear solution of potassic manganate (Exp't. 297) add carefully dilute sulphuric acid until the colour changes to purple. This takes place as soon as the free alkali is neutralised :

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

If this solution is evaporated, it deposits first potassic sulphate, and then *potassic permangandte* ($KMnO_4$).

Properties.—Potassic permanganate crystallises in needle-shaped crystals of a dark purple colour, and a somewhat steely lustre. It is soluble in water (1 part in 15) and has enormous colouring power.

The permanganates are strong oxidising agents, and are of great value as disinfectants and deodorisers. *Condy's red fluid* is a solution of more or less pure *sodic permanganate.* ($NaMnO_4$).

Experiment 299.—To a solution of potassic permanganate add sulphurous acid. The colour disappears :

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

Test this solution for sulphuric acid.—Decolorise acidified solutions of potassic permanganate with other reducing agents, e.g., *ferrous sulphate, hydric sulphide, ammonic sulphide,* &c. (Write the equations).

Potassic and sodic permanganates oxidise many organic substances, especially those which are offensive and noxious.

Experiment 300.—Bubble the air from the lungs through a dilute solution of potassic permanganate, using a glass tube. The purple colour disappears and a reddish precipitate of *hydrated dioxide of manganese* ($MnO(OH)_2$) is thrown down.—Repeat the experiment, first acidifying the solution with dilute sulphuric acid. The colour is discharged, and no precipitate appears.

366. Tests.

Manganous Salts.

1. *Ammonia* gives a white precipitate of *manganous hydroxide* ($Mn(OH_2)$), soluble in excess.

2. *Ammonic sulphide* gives a salmon-coloured precipitate of *manganous sulphide* (MnS), soluble in dilute hydrochloric acid.

3. *Caustic soda* gives a white precipitate of manganous hydroxide, insoluble in excess, and oxidising to brown *manganic hydroxide* ($Mn_2O_2(OH)_2$) when shaken up with air :

$$2Mn(OH)_2 + O = Mn_2O_2(OH)_2 + H_2O.$$

4. Insoluble compounds can be tested by heating with a *sodic*

carbonate bead in the oxidising zone of the Bunsen flame. The bead is coloured green by the formation of sodic manganate. The *borax bead* is coloured amethyst by manganese compounds.

Manganates and Permanganates.

1. *Hydric sulphide* reduces them, and precipitates manganous sulphide if the solution is alkaline.

2. *Ammonic sulphide* reduces them, and precipitates manganous sulphide.

COBALT.

367. **Cobalt** ($Co^{ii, iv}$ = 58.6.—Sp. wt. = 8.5.—Melting pt. = 1100°.—Sp. heat = 0.10696.)—Cobalt occurs combined with nickel, iron, arsenic, and sulphur. It is always accompanied by nickel. It is also found in meteoric iron, and is present in the atmosphere of the sun. It is an unimportant metal. Cobalt ores are used chiefly in the manufacture of *smalt*, a powdered blue glass used as a paint.

368. **Oxides of Cobalt.** Cobalt forms three oxides, parallel with those of iron. They are *cobaltous* (CoO), *cobaltic* (Co_2O_3), and *cobaltcso-cobaltic oxide* (Co_3O_4, or $CoO.Co_2O_3$). They are all stable.

369. **Salts of Cobalt.** There are two series of salts, *cobaltous* and *cobaltic*. The latter are very unstable, being readily reduced to the former.—*Cobaltous salts* ($CoCl_2$, $CoSO_4$, $Co(NO_3)_2$, &c.) are violet or blue when anhydrous, but rose coloured when hydrated.

370. **Cobaltous Nitrate** ($Co(NO_3)_2.6H_2O$) is a reddish, crystalline salt, prepared by dissolving cobaltoso-cobaltic oxide or cobaltous carbonate in nitric acid, and

evaporating the solution. It is freely soluble in water, and the solution has an acid, astringent taste.—Cobaltous nitrate is used in testing substances by means of the blowpipe. (Art. 350, 4). It is decomposed by a strong heat:

$$3Co(NO_3)_2 = Co_3O_4 + 6NO_2 + O_2.$$

371. **Cobaltous Chloride** ($CoCl_2.6H_2O$) is a rose-coloured salt prepared by the same method as that used for the nitrate. Its solution has an acid reaction, and is used as a *sympathetic*, or *invisible ink*.

Experiment 301.—Write with a solution of cobaltous chloride so dilute that the writing is invisible when dry. Hold the paper near a flame. The writing appears in blue characters. (Explain.)

372. Tests.

1. *Ammonia* gives a blue precipitate (basic salt) soluble in excess to a brownish solution.

2. *Ammonic sulphide* gives a black precipitate of *cobaltous sulphide* (CoS) * insoluble in cold dilute hydrochloric acid, but soluble in aqua regia.

3. *Caustic soda* gives a blue precipitate insoluble in excess and turning reddish when shaken up with air.

4. Insoluble compounds are tested by the *borax bead*, to which cobalt gives a deep blue colour.

NICKEL.

373. **Nickel** ($Ni^{ii.\ iv.}$ = 58.6. Specific weight = 8.9. Melting point = 1500°. Specific heat = 0.10863).

Nickel is found generally along with cobalt. The

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* In reality the *hydro-sulphide*, $Co(SH)_2$.

principal ore is *kupfer-nickel* (NiAs). *Nickel ores* generally contain cobalt, copper, iron, and arsenic.

It is a white metal, somewhat like steel in appearance, hard, ductile, and not easily oxidised by air. It decomposes steam slowly at a red heat, and is soluble in dilute acids. On account of its permanence in the atmosphere it is used for electroplating other metals.—*Nickel coins* are made of an alloy of 75 parts of copper with 25 of nickel. This alloy is hard and wears well.—*German silver* is an alloy of copper, nickel, and zinc in various proportions. It is harder than copper, but more easily attacked by acids.

374. **Oxides of Nickel.** Nickel forms two oxides, *nickelous* (NiO), and *nickelic* (Ni_2O_3). Nickelous oxide is basic, while nickelic is indifferent. (Compare with iron, &c.) The former occurs in nature as *Bunsenite.* It can be prepared by strongly igniting *nickel nitrate* ($Ni(NO_3)_2$):

$$Ni(NO_3)_2 = NiO + 2NO_2 + O.$$

It is a green powder, permanent in air, and soluble in acids.

375. **Salts of Nickel.**—There is only one series of nickel salts, and they are derived from the basic oxide, NiO. They are mostly green in colour, but are yellow when deprived of water of crystallisation. The soluble salts ($NiCl_2$, $NiSO_4$, $Ni(NO_3)_2$, &c.) form acid solutions of an astringent taste. They are prepared usually by dissolving the metal in dilute acids.

376. **Nickel Sulphate** ($NiSO_4.7H_2O$) is a green

salt, isomorphous with Epsom salts, prepared by dissolving nickel in dilute sulphuric acid:

$$Ni + H_2SO_4 = NiSO_4 + H_2.$$

It is soluble in water (2 parts in 5). It combines with ammonic sulphate to form *ammonio-nickel sulphate* ($NiSO_4.(NH_4)_2SO_4.6H_2O$), used in nickel-plating. In this compound, as in Mohr's salt, and other double sulphates of the same class, a molecule of alkaline sulphate replaces one of the seven molecules of water of crystallisation.

377. Tests.

1. *Ammonia* gives a green precipitate ($Ni(OH)_2$), soluble in excess of ammonia to a blue solution.

2. *Ammonic sulphide* gives a black precipitate of *nickel hydrosulphide* ($Ni(SH)_2$), insoluble in cold dilute hydrochloric acid. This precipitate is somewhat soluble in excess of ammonic sulphide, which should therefore be sparingly used in precipitating solutions containing nickel. It is better to use freshly prepared sulphide free from excess of sulphur.

3. *Caustic soda* gives a green precipitate of *nickelous hydroxide* ($Ni(OH)_2$) insoluble in excess.

4. Insoluble nickel compounds are tested by the *borax bead*, to which they give a reddish-brown tint. The test is, however, easily obscured by the presence of other metals.

378. **Cerium** ($Ce^{iii.} = 141.2$).—This is the most important of the *Cerite metals*, a group of rare metals, allied to the group under consideration. They have recently been discovered in large quantities and may assume considerable practical importance in medicine. Cerium forms two oxides (Ce_2O_3 and CeO_2), both basic. The *cerous salts* are of most importance in medicine. *Cerous*

nitrate $(Ce(NO_3)_3.6H_2O)$, and *cerous oxalate* $(Ce_2(C_2O_4)_3)$ are used. The nitrate is easily soluble in water, the oxalate very sparingly. They are both colourless.

QUESTIONS AND EXERCISES.

1. In what experiments already made has green vitriol been one product?

2. What weight of 70 % nitric acid is required to oxidise 1 ℔. green vitriol to ferric sulphate? How much pure sulphuric acid must be added?

3. Why would you expect ferrous carbonate to be less irritating to the stomach than ferrous sulphate?

4. How much iron in one-eighth of a grain of ferric arsenate? To what weight of ferric chloride is it equivalent?

5. What causes the red fumes in the preparation of ferric chloride?

6. Why must ferric hydroxide be freshly precipitated when used as an antidote to arsenic?

7. In what respects are iron and chromium alike? In what respects do they differ?

8. The third equation in Art. 339 represents *calcic sulphate* $(CaSO_4)$ as being precipitated from aqueous solution. Is this strictly correct?

9. Is there any resemblance between chromium and sulphur?

10. Chrome yellow dissolves in solution of caustic potash. What substances are formed?

11. Does *chrome alum* contain aluminum? Why is it called "alum"? Write the formulas of all the alums which have been mentioned.

12. Why cannot aluminium be used for making cooking utensils?

13. How would you distinguish aluminium bronze from gold?

14. Write the formula for *cæsium alum?*

15. What is the composition of *burnt alum?*

16. Can alums be represented by a simpler formula than that given in Art. 347?

17. Common alum is a good antidote to lead salts. Explain.

18. How would you distinguish a solution of aluminic from one of zinc sulphate?

19. What is *zinc white?*

20. What resemblance is there between manganese and sulphur?

21. Calculate the percentage of oxygen in potassic permanganate. What weight of potassic permanganate will oxidise the sulphurous acid obtained by burning 10 g. of sulphur?

22. Explain the explosive nature of a mixture of charcoal, manganese dioxide, and potassic chlorate?

23. Write a short essay on the general resemblances and differences among the metals of Group III. with regard to the salts which they form.

24. Explain the antiseptic properties of a solution of potassic permanganate. Will it disinfect the atmosphere?

25. How would you prepare cobaltous nitrate from cobaltous sulphate?

26. What differences have you noticed in the chemical characters of nickel and cobalt?

CHAPTER XX.

METALS OF GROUPS IV. AND V.

Calcium, Strontium, Barium; Magnesium.

379. **General Characters.**—Calcium, strontium, barium, and magnesium are the *metals of the alkaline earths.* Formerly, any insoluble earthy substance which

remained unchanged when heated was called an *earth;* so that substances such as lime, silica, phosphates, &c., were classed under this term. Then it was noticed that some of these earths, viz., *lime*, *strontia*, *baryta*, and *magnesia* were somewhat soluble in water, and had alkaline properties. They were therefore called *alkaline earths*, and were held to be elements until metals were obtained from them. The metals have very strong chemism and are difficult to separate from their compounds. Calcium, strontium, and barium are prepared by the electrolysis of their fused chlorides or cyanides. Magnesium can be prepared in the same way, but is prepared on the large scale by reducing its chloride by means of sodium. These metals oxidise so readily that they must be protected from the action of the air by naphtha. They are bright, easily fusible, and decompose water at ordinary temperatures. They are all dyad, and each has only *one basic oxide* (CaO, SrO, BaO, MgO). These oxides unite directly with water, forming sparingly soluble hydroxides ($Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, and $Mg(OH)_2$;—in the order of their solubility beginning with the most soluble). The *sulphides* (CaS, SrS, BaS, MgS) are decomposed by water, and cannot be prepared by precipitation. They are prepared by heating the sulphates with charcoal, e.g. :

$$CaSO_4 + 4C = CaS + 4CO.$$

The *carbonates* ($CaCO_3$, $SrCO_3$, $BaCO_3$, $MgCO_3$), *sulphates* ($MgSO_4$, $CaSO_4$, $SrSO_4$, $BaSO_4$, in the order of their solubility :—*magnesic sulphate* is freely soluble.), and *phosphates* ($Ca_3(PO_4)_2$, &c.) are insoluble (or sparingly soluble) in water. The *chlorides, nitrates*, &c., are soluble.

CALCIUM.

380. Calcium ($Ca^{II} = 40$).

OCCURRENCE. — Always in combination. Its compounds occur in vast quantities, and include limestone, marble, chalk, coral, dolomite, gypsum, apatite, &c. It is present in natural waters, in the bodies of plants and animals, and in the sun and fixed stars.

381. Calcic Oxide (CaO).

—Calcium combines with oxygen in two proportions (CaO, CaO_2), but the *monoxide* (CaO) is the only important oxide.

PREPARATION.—It is prepared on the large scale by strongly heating limestone. Impure calcic oxide (*quick lime*) is obtained:

$$CaCO_3 = CaO + CO_2.$$

Experiment 302.—Wrap several times around a small fragment of calc spar a platinum wire, one end of which is fastened in a handle of glass (by fusing the glass and sticking the wire into it). Thrust the calc spar into the centre of a Bunsen flame, and hold it for two or three minutes just above the point of the central bluish green zone. Remove it and observe the change in its appearance. Put a drop of water on it, and observe the change. Wash it into a t. t., shake it up with water, and add a little red litmus. See whether calc spar affects red litmus.

PROPERTIES.—Calcic oxide is a white solid, not fused by the intense heat of the oxy-hydrogen flame.

Experiment 303.—Place a lump of good quick lime on a clean iron or porcelain plate, and pour over it one-third its weight of water. Note the heating of the mass. Whence comes the heat? This process is called the *slaking* or *slacking* of lime:

$$CaO + H_2O = Ca(OH)_2.$$

(Keep the slaked lime for Experiment 305).

Experiment 304.—Leave a small lump of quick lime exposed to the air for two or three days. Note any changes in its appearance. Test it for carbonic acid.

Quick lime absorbs moisture and carbon dioxide from the air and becomes changed at length to calcic carbonate. Quick lime is often used to keep the air of an apartment dry and pure.

382 **Calcic Hydroxide** ($Ca(OH)_2$), also called *slaked lime*, is prepared as in Experiment 303. Much heat is given out during the combination of the lime and the water. Fires have been caused by the accidental slaking of large quantities of quick lime.

Experiment 305.—Put about equal quantities of recently slaked lime in two test tubes; to the one add about 100 parts of water, and to the other 100 parts of water and 2 of sugar. Shake both for some time and observe that the sweetened water dissolves much more slaked lime than the pure water does. Filter off the solution in pure water, and try its taste and action on red litmus.

Calcic hydroxide dissolves in water to the extent of 1 part in 700 of water. The solution is called *lime water.* Calcic hydroxide is more soluble in cold than in hot water. (Heat a little of the filtered solution prepared in Experiment 305.) Sugar increases the solubility of lime in water. *Saccharated solution of lime* contains about 1 part by weight of calcic hydroxide and 2 of cane sugar dissolved in 20 of water.

Experiment 306.—Leave a few cubic centimetres of lime-water in an open vessel for two or three days, stirring it from time to time. Then, try its action on red litmus. Pour off the liquid, add a few drops of hydrochloric acid to the sediment, and observe the result. What is the sediment?

Lime water is used in medicine as an *antacid*, &c., and as an antidote to poisoning by acids, particularly oxalic. —*Milk of lime* is water shaken up with more slaked lime than it can dissolve.

383. Calcic Carbonate ($CaCO_3$).

Occurrence.—*Calc spar* is nearly pure crystallised calcic carbonate. It is colourless and transparent. *Aragonite* is another crystalline form of calcic carbonate. This compound is therefore *dimorphous;* it crystallises in *two* forms. Calcic carbonate is found more or less pure, as marble, limestone, chalk, coral, &c. It forms a considerable part of the mass of egg-shells and of the shells of molluscs.

Preparation.—Calcic carbonate occurs so abundantly in nature that it is not necessary for most purposes to prepare it artificially. In medicine, however, it is prepared by precipitation (*calcis carbonas precipitata*) in order to obtain it in a fine state of division.

Experiment 307.—To a hot solution of calcic chloride ($CaCl_2$), add solution of sodic carbonate until no more precipitate is formed on further addition of the carbonate. Filter and wash the precipitate :

$$Na_2CO_3 + CaCl_2 = 2NaCl + CaCO_3.$$

Properties.—*Precipitated calcic carbonate* is a white powder, slightly granular, insoluble in water, soluble with effervescence in hydrochloric and other acids (Art. 152). Its solubility in water containing carbonic acid has been already referred to (Art. 153). It is used as an antidote to poisoning by acids, and also to correct acidity of the stomach.

384. Calcic Chloride ($CaCl_2.6H_2O$).

PREPARATION.—**Experiment 308.**—Dissolve in a porcelain dish a few fragments of calc spar in hydrochloric acid, and evaporate the solution on the water bath until it forms a pellicle on the surface. Then heat it over the Bunsen burner, placing the dish so far above the flame that it may not be touched by it. When the salt is quite dry, apply the flame to the dish until moisture ceases to come off. Leave this *fused calcic chloride* ($CaCl_2$) exposed to the air for 24 hours, and observe the result.

PROPERTIES.—Calcic chloride is a colourless salt very soluble in water. The fused chloride contains no water of crystallisation. It is very hygroscopic, and is used for drying gases. Solution of calcic chloride is used as a test reagent, and also as a medicine.

385. Calcic Sulphate ($CaSO_4$).

OCCURRENCE.—Crystallised as *gypsum, alabaster*, or *selenite* ($CaSO_4.2H_2O$), and *anhydrite* ($CaSO_4$). It is present in sea and other waters.

PREPARATION.—**Experiment 309.**—To solution of calcic chloride add dilute sulphuric acid, filter, and wash the precipitate with hot water. (Write the equation.) The precipitate is gypsum.

PROPERTIES.—Gypsum is a white solid of sp. wt. 2.3.

Experiment 310.—Heat a small quantity of gypsum in a t. t. and observe. Heat a larger quantity in a porcelain basin until moisture ceases to escape. Let cool, and mix the anhydrous salt with water on a piece of broken porcelain or smooth wood. (What proportion of water should be used to form gypsum?) Observe change after a few minutes.

Anhydrous calcic sulphate is called *plaster of Paris*, or sometimes simply *plaster*. It is used as a cement, for making plaster casts, &c., and in surgery for making stiff bandages.— Gypsum is less soluble in hot than in warm water. It is most soluble at 35°C.

Experiment 311.—Heat a saturated solution of gypsum to boiling.

One part of gypsum requires 500 of water to dissolve it.

386. **Bleaching Powder.** ("*Chloride of Lime.*") This substance has been already referred to at p. 105. It is probably a mixture of calcic hypochlorite and chloride in molecular proportions, $Ca\ OCl)_2 + CaCl_2$; but it always contains calcic hydroxide.

Preparation.—Slaked lime is spread on a series of shelves in large closed compartments, and exposed to the action of chlorine gas. The chlorine is generated by the action of crude hydrochloric acid on manganese dioxide:

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O.$$

Its action on the slaked lime may be represented as follows:

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2.CaCl_2 + 2H_2O.$$

Properties.—A white powder, having a chlorous smell. The odour is due to the liberation of hypochlorous acid by the action of the carbon dioxide and moisture of the air:

$$Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HClO.$$

It is one of the best known deodorisers and disinfectants, and is especially useful because of the volatility of hypochlorous acid, a substance which deodorises and disinfects the atmosphere into which it escapes.

Experiment 312.—Examine a specimen of bleaching powder, noting its colour and odour. Shake up about 10 grains of it with 50 to 100 cubic centimetres of water and filter. The filtrate contains calcic chloride and hypochlorite. It is the *Liquor calcis chloratæ* of the pharmacopœia. Add a few drops of it to a solution of sulphate of indigo. Try with acidified litmus solution, and with potassic bichromate solution.

Experiment 313.—Pour some dilute sulphuric and hydrochloric acid over small portions of bleaching powder in watch glasses, and note evolution of chlorine:

$$CaCl_2 + Ca(OCl)_2 + 2H_2SO_4 = 2CaSO_4 + 2Cl_2 + 2H_2O.$$
$$CaCl_2 + Ca(OCl)_2 + 2HCl = 2CaCl_2 + 2Cl_2 + 2H_2O.$$

When bleaching powder is heated, the hypochlorite is decomposed into chlorate and chloride:

$$6Ca(OCl)_2 = Ca(ClO_3)_2 + 5CaCl_2.$$

387. Calcic Phosphate ($Ca_3(PO_4)_2$).

This compound has been already studied. (Arts. 128 and 132.)

Occurrence.—It is found in the minerals *apatite* ($3Ca_3(PO_4)_2 + Ca[Cl_2, F_2]$*), *phosphorite* ($Ca_3(PO_4)_2$), *sombrerite* ($Ca_3(PO_4)_2.2H_2O$), &c., and in bones. Bone ash contains about 80 % of calcic phosphate.

Preparation.—**Experiment 314.**—Digest bone ash with dilute hydrochloric acid, filter, dilute to double volume, add ammonia to alkaline reaction, filter, and wash the precipitate with hot distilled water.

The hydrochloric acid acts on the phosphate to form calcic chloride and calcic tetrahydric phosphate:

$$Ca_3(PO_4)_2 + 4HCl = CaH_4(PO_4)_2 + 2CaCl_2.$$

The ammonia reprecipitates the calcic phosphate:

$$CaH_4(PO_4)_2 + 2CaCl_2 + 4NH_3 = Ca_3(PO_4)_2 + 4NH_4Cl.$$

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* When symbols are put within square brackets and separated by a comma, it signifies that the elements are present in varying proportions.

It is plain that any impurities in the bone ash which are soluble in hydrochloric acid may be precipitated along with calcic phosphate.

PROPERTIES.—A light, white powder, insoluble in water, soluble in dilute hydrochloric, nitric, or phosphoric acid. From this solution calcic phosphate is again precipitated when an alkali is added. (Experiment 314.) Thus, an acid solution of calcic phosphate might be mistaken for an aluminium salt; but the former gives a white precipitate (calcic oxalate) on the addition of sodic acetate and ammonic oxalate, while the latter does not.

388. **Mortars and Cements.**—Ordinary *mortar* is a mixture of slaked lime ($Ca(OH)_2$), sand (SiO_2), and water. It hardens by the formation of calcic carbonate, carbon dioxide being absorbed from the air. The process of hardening continues for years. There appears to be no combination of the lime with the silica.—*Hydraulic mortar*, or *Roman cement*, is prepared by carefully heating a mixture of lime and clay. It hardens under water, and the hardening seems to be due to the formation of silicate of lime and alumina. *Portland cement* is made by carefully heating a levigated mixture of clay and chalk. These cements deteriorate when kept exposed to the air, because the lime in them unites with carbon dioxide.

389. Tests.

1. Solutions of calcium salts give a white precipitate with *ammonic carbonate*. If the solution is acid it must be neutralised with ammonia. The precipitate is soluble with effervescence in nitric acid.

2. *Sodic phosphate* gives a white precipitate with neutral or

alkaline solutions of calcic salts (in practice the solution is made alkaline with ammonia):

$$3CaCl_2 + 2Na_2HPO_4 + 2NH_3 = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl.$$

3. *Ammonic oxalate* gives a white precipitate of calcic oxalate even with very dilute solutions of calcium salts:

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl.$$

This precipitate is soluble in dilute nitric or hydrochloric acid, but is insoluble in acetic acid.

4. Calcium compounds insoluble in water can be tested by dissolving in hydrochloric acid, adding sodic acetate (so that the acidity may be due to acetic acid), and then adding ammonic oxalate. Or, they may be tested by moistening them with strong hydrochloric acid and bringing them by means of a platinum wire into the Bunsen flame. A brick red colour is imparted to the flame by calcium compounds.

STRONTIUM.

390. **Strontium** ($Sr^{ii.} = 87.2$). — Compounds of strontium are found in considerable quantities in nature. The most commonly occurring are *celestine* ($SrSO_4$), and *strontianite* ($SrCO_3$). The metal is prepared by electrolysis.—Strontium compounds have not yet found a place in the pharmacopœia. The nitrate ($Sr(NO_3)_2$) and other salts are used in making fire-works. They give a fine red colour to flames.

Experiment 315.—Mix a little strontic nitrate with powdered charcoal and sulphur, put the mixture on a piece of mica or porcelain and touch it with a hot wire. (What causes the rapid combustion?)

The soluble salts are prepared by dissolving strontianite in the acids, or by reducing celestine to strontic sulphide (SrS), and dissolving this in the respective acids. Strontic *oxide* (SrO), and *hydroxide* ($Sr(OH)_2$) are similar to the corresponding calcium compounds, but the hydroxide is more soluble than calcic hydroxide. Strontium compounds are mostly colourless. The *sulphate* ($SrSO_4$) is less soluble than calcic, but more so than baric, sulphate.

391. Tests.

1. *Ammonic carbonate* gives a white precipitate ($SrCO_3$) with neutral or alkaline solutions of strontium salts. The precipitate is soluble with effervescence in dilute nitric acid.

2. *Sodic phosphate* (with ammonia) gives a white precipitate ($Sr_3(PO_4)_2$).

3. *Ammonic oxalate* gives a white precipitate of strontic oxalate (SrC_2O_4), soluble in nitric and sparingly soluble in acetic acid.

4. *Calcic sulphate* gives a white precipitate ($SrSO_4$) *after some time:*

$$CaSO_4 + SrCl_2 = SrSO_4 + CaCl_2.$$

5. Insoluble strontium compounds can be tested by moistening with strong hydrochloric acid and bringing on a platinum wire into the Bunsen flame. A carmine red colour is imparted to the flame. The test is more delicate if the substance be held for a few moments in the reducing flame, then moistened with hydrochloric acid, and held in the oxidising flame.

BARIUM.

392. **Barium** ($Ba^{II.}$ = 136.8).—The principal compounds of barium found in nature are *witherite* ($BaCO_3$), *heavy spar* ($BaSO_4$), and *psilomelane* ($[Mn, Ba]O.MnO_2$). The metal can be prepared by electrolysis of the fused chloride or cyanide.

393. **Oxides of Barium.**—Barium, like calcium and strontium, unites with oxygen in two proportions, forming the *monoxide* (BaO), and the *dioxide* (BaO_2).

1. *Barium monoxide* (BaO) is prepared by heating the nitrate :

$$Ba(NO_3)_2 = BaO + 2NO_2 + O.$$

It unites with water, and forms *barium hydroxide*, or *baryta* ($Ba(OH)_2$). This compound is more soluble than either calcic or strontic hydroxide. *Baryta water*, used in analysis, is a solution of barium hydroxide. The hydroxide is prepared on the large scale from heavy spar, for use in sugar refining. It forms an insoluble compound with cane sugar.

2. *Barium dioxide* (BaO_2) is a white solid prepared by heating the monoxide to a red heat in a current of oxygen. It is used in the preparation of hydrogen dioxide.

394. **Baric Chloride** ($BaCl_2.2H_2O$).

PREPARATION.—By dissolving baric carbonate or sulphide in hydrochloric acid :

$$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2.$$

It is also prepared from heavy spar, which is first reduced to sulphide (BaS), and then decomposed by hydrochloric acid :

$$BaSO_4 + 4C = BaS + 4CO.$$
$$BaS + 2HCl = BaCl_2 + H_2S.$$

PROPERTIES.—A white crystalline solid, soluble in water (35 parts in 100), sparingly soluble in alcohol.

Experiment 316.—Examine carefully a specimen of barium chloride, noting taste, &c. Dissolve it in a little distilled water, and to a small portion of the solution add about twice the volume of strong nitric acid. Baric chloride is only sparingly soluble in strong nitric acid. To another portion add magnesic sulphate. Baric sulphate is precipitated :

$$MgSO_4 + BaCl_2 = BaSO_4 + MgCl_2.$$

Baric chloride, in common with the other soluble compounds of barium, is very poisonous. Solution of magnesium sulphate is a good antidote. (How does it act?)

395. **Baric Nitrate** ($Ba(NO_3)_2$). Is prepared by the same methods as those used in preparing the chloride. It is much used in pyrotechny, being mixed with charcoal and sulphur to form "green fire."

Experiment 317.—Mix carefully with little friction small quantities of baric nitrate, sulphur, and ground charcoal. Put the mixture on a piece of mica, a flat stone, or a piece of porcelain, and touch it with a red hot wire.

396. Tests.

1. *Ammonic carbonate* gives a white precipitate ($BaCO_3$), soluble with effervescence in dilute nitric acid.

2. *Sodic phosphate* (with ammonia) gives a white precipitate ($Ba_3(PO_4)_2$).

3. *Ammonic oxalate* gives a white precipitate (BaC_2O_4), soluble in dilute nitric, sparingly soluble in acetic acid.

4. *Calcic sulphate* gives *at once* a white precipitate ($BaSO_4$). Baric sulphate requires 400,000 parts of water for its solution.

5. Insoluble compounds are tested for as in Art. 391 (5). Barium compounds give a greenish colour to the flame.

MAGNESIUM.

397. Magnesium. ($Mg^{II}=23.95$).

Occurrence.—Magnesium compounds are very abundant and widely distributed. Mountain limestone, or *dolomite*, ([Mg, Ca] CO_3.) forms whole ranges of mountains. Other commonly occurring compounds are *magnesite* ($MgCO_3$), *kieserite* ($MgSO_4.H_2O$), *carnallite* ($MgCl_2.KCl.6H_2O$), *spinelle* ($MgO.Al_2O_3$), *asbestos* ([Mg,Ca]SiO_3), *Epsom salts* ($MgSO_4.7H_2O$) &c. Magnesic phosphate ($Mg_3(PO_4)_2$) is found in the bones, &c., of animals.

PREPARATION.—By heating together a mixture of magnesium chloride, calcium fluoride, and sodium. The sodium displaces the magnesium :

$$MgCl_2 + 2Na = Mg + 2NaCl.$$

The metal is purified by distillation.

PROPERTIES.—A soft, silvery metal ; it tarnishes in moist air ; sp.wt.=1.75 ; melts at red heat, and boils above 1040° ; when heated in air it catches fire and burns with a dazzling white light. The *magnesium light* is used in photography, signalling, &c.

Experiment 318. Burn a piece of magnesium wire, dissolve the white ash (MgO) in a drop of dilute sulphuric acid, evaporate on a watch glass, and obtain crystals of Epsom salts.

398. **Magnesic Sulphate** ($MgSO_4.7H_2O$).—Magnesium sulphate is generally sold as Epsom salts, crystallised with seven molecules of water to the molecule of sulphate. It occurs in nature crystallised with one molecule of water, as *kieserite* ($MgSO_4.H_2O$.)

PREPARATION.—Epsom salts are now prepared mostly from kieserite, by heating in water. The sparingly soluble kieserite apparently combines with more water and becomes changed to the much more soluble heptahydrated salt. This is then purified by crystallisation.

PROPERTIES.—A colourless, crystalline solid, isomorphous with zinc sulphate ($ZnSO_4.7H_2O$), which it resembles very closely in appearance; it has an unpleasant bitter taste. It is soluble in water, 35 parts in 100.

Experiment 319. Compare specimens of Epsom salts and crystallised zinc sulphate, noting general appearance and taste. Dissolve them separately in water, and add ammonium chloride and a drop of ammonia to each.

Magnesium sulphate is used in medicine as a purgative. It is a "saline purgative," i.e., it acts by promoting the diffusion of water into the intestinal canal.

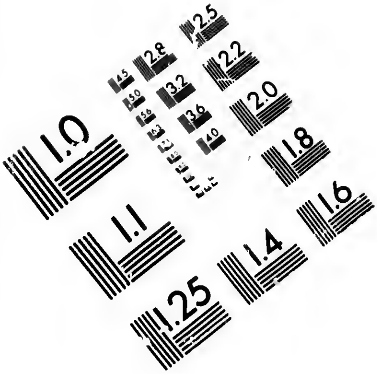
399. **Magnesic Carbonate** ($MgCO_3$).—Found in nature in large quantities, as *magnesite*. It was formerly used in preparing Epsom salts. The *carbonate of magnesia* of the pharmacopœia is a basic salt ($4MgO.3CO_2.5H_2O$).

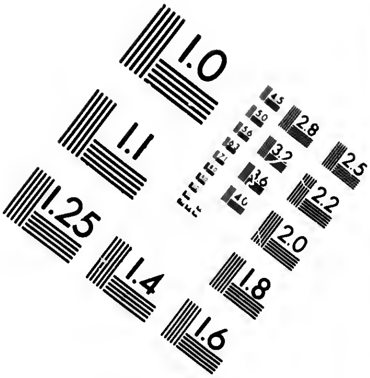
PREPARATION.—By the action of solution of sodic carbonate on solution of magnesic sulphate.

Experiment 320. To a hot solution of magnesium sulphate add hot solution of sodic carbonate. Basic carbonate of magnesium is precipitated. Filter, wash the precipitate, and dry it in a glass or porcelain dish. Note the appearance of the dried salt. It is the *heavy* carbonate of magnesia, or *magnesia alba ponderosa.* Repeat the experiment, but use cold solutions, and boil for a few minutes after precipitating. The dried precipitate is very *light*. It is *magnesia alba levis*.

PROPERTIES.—The carbonates of magnesia are white powdery solids insoluble in pure water, but soluble in dilute acids (with effervescence), in solutions of ammonium salts, and in water containing carbonic acid.

Experiment 321.—To solution of magnesic sulphate add ammonic carbonate; a white precipitate falls (unless the am-





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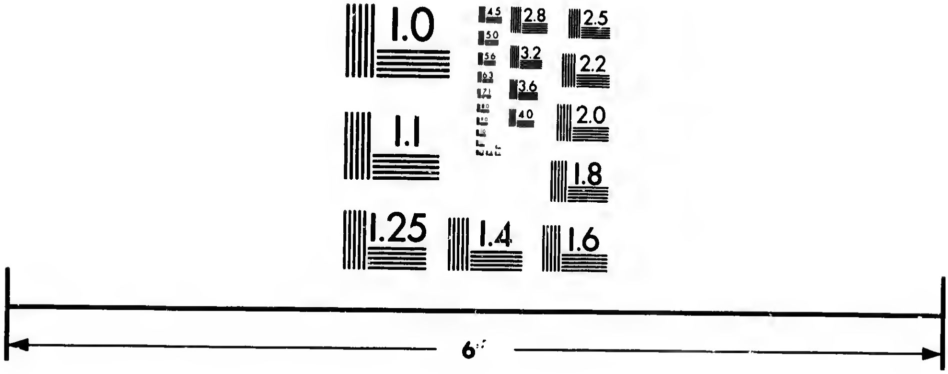

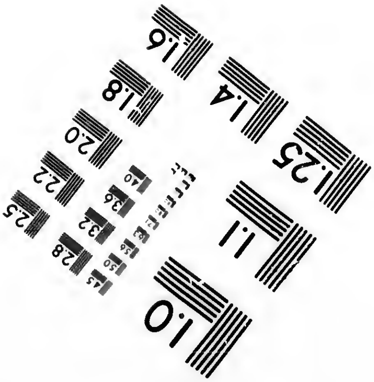

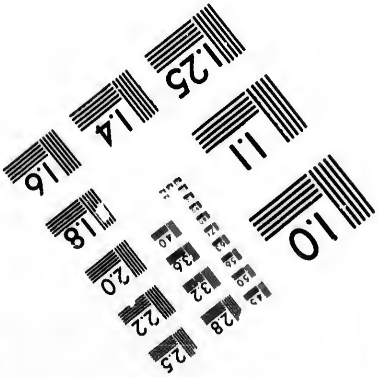

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monic carbonate consists mostly of the acid salt, in which case a little ammonia must be added). Add ammonic chloride; the precipitate is dissolved.

Experiment 322.—Put a little magnesia alba in a considerable quantity of distilled water in a flask or beaker, and pass carbon dioxide through the water for some time. If the carbonate does not dissolve completely, filter. Boil a little of the clear solution; it becomes milky owing to the precipitation of magnesic carbonate.

The solubility of magnesic carbonate increases with the pressure of the carbon dioxide. *Liquor magnesiæ carbonatis* is a solution made by using carbon dioxide under considerable pressure. It contains about 13 grains of "carbonate of magnesia" to the fluid ounce.

400. **Magnesic Oxide** (MgO).—Magnesium forms only one oxide. It is known in pharmacy as *magnesia*, or *magnesia usta*.

Preparation.—By heating strongly the carbonate of magnesia. A light or heavy magnesia is obtained corresponding to the carbonate used.

Experiment 323.—Heat a small quantity of magnesia alba for some time in a porcelain crucible. Try the action of hydrochloric acid on the residue. It dissolves without effervescence, if the heating has been continued long enough:

$$MgO + 2HCl = MgCl_2 + H_2O.$$

Properties.—A light white powder, almost insoluble in water (1 part dissolves in about 55,000); soluble in acids, salts of magnesium being formed; tasteless; when moistened, turns red litmus blue. It is thus a well-marked basic oxide. It is a good antidote to arsenic poisoning; it forms insoluble arsenite or arsenate, and neutralises the acid of the gastric juice.

401. Tests.

1. *Ammonic carbonate* gives a white precipitate, soluble in acids, and in solution of ammonium chloride. The carbonates of barium, strontrum, and calcium are not soluble in solution of ammonium chloride.

2. *Sodic phosphate* (with ammonia) gives a granular white precipitate ($Mg.NH_4.PO_4$), which forms in lines on the walls of the t. t. when the solution is stirred with a glass rod:

$$MgSO_4 + NH_3 + Na_2HPO_4 = Mg.NH_4.PO_4 + Na_2SO_4.$$

3. Compounds insoluble in water are dissolved in hydrochloric acid and tested by (1) and (2).

QUESTIONS AND EXERCISES.

1. In what way does calcic carbonate act as an antidote to acids? To zinc chloride?

2. What substances does quick lime absorb from the atmosphere?

3. What weight of water will 10 lbs. of quick lime absorb? What volume of air at 20°C saturated with water vapour will supply this amount of water?

4. Explain the "setting" of plaster of Paris.

5. Why does bleaching powder become moist when exposed to the air? Why must it be kept in well closed vessels?

6. Calculate the weight of limestone to furnish 1 ton of lime. What volume of carbon dioxide would be driven from it into the atmosphere in the process of burning?

7. What substances are formed by the action of hydrochloric acid on barium sulphide (BaS)? Write the equation.

8. How would you distinguish a specimen of zinc sulphate (white vitriol) from one of Epsom salts?

9. When potassic hydroxide solution is added to solution of magnesic sulphate a white precipitate falls. What is it? Write the equation.

10. How would you prepare baric nitrate from baric chloride?

11. Baric sulphate is often used by painters as a substitute for white lead. Why is it preferable?

12. What substances are formed when solutions of sodic sulphate and baric nitrate are mixed?

CHAPTER XXI.

METALS OF GROUP VI.

Lithium, Sodium, Potassium, Rubidium, Cæsium, [*Ammonium*].

402. **General Characters.** The metals of this group form freely soluble hydroxides, called *alkalis* (from *alkali*, the Arabic name for the plant from the ashes of which potash was first prepared). The *metals of the alkalis* form a series, similar in properties, but showing that gradation always found in chemical series. Thus the hydroxides increase in basic character from lithium to cæsium; the oxidisability of the metals increases in the same order, while their melting points increase from cæsium to lithium. The metals are all univalent, and are difficult to separate from their compounds. Each forms only one basic oxide (Na_2O, K_2O, Li_2O, &c.), which can be obtained by burning the metal in air. The oxides combine with water to form hydroxides ($NaOH$, KOH, &c.), from which the water cannot be driven off by heat. The salts of the alkali metals are mostly soluble in water. —The metals will be treated generally in the order of their importance.

SODIUM.

403. **Sodium** ($Na^{i} = 23$. Sp. wt. = 0.97. Melting point = 95°.6).

OCCURRENCE.—Compounds of sodium are universally diffused, so that it is very difficult to get any substance free from them. The compounds occurring in greatest abundance are sodic chloride ($NaCl$), and Chili nitre ($NaNO_3$).

PREPARATION.—By strongly heating in iron tubes a mixture of sodic carbonate, slack coal, and chalk:

$$Na_2CO_3 + 2C = 2Na + 3CO.$$

The sodium distils, is received in iron pots, and immediately sealed up to prevent oxidation.

PROPERTIES.—A bright, white metal, soft, and very easily tarnished. In moist air it remains bright only a few seconds. It readily burns in air, and forms sodium monoxide, Na_2O, along with some dioxide, Na_2O_2 (Exp't 26). It decomposes water, even in the form of ice, the products being sodic hydroxide and hydrogen (Exp't 30):

$$Na + H_2O = NaOH + H.$$

Sodium forms liquid and solid amalgams with mercury. A liquid amalgam is used in extracting gold from quartz.

404. **Sodic Chloride** ($NaCl$).

OCCURRENCE.—In masses in the earth, as *rock salt*; in sea-water to the extent of 2.6 %; in salt springs; and in small quantities very widely diffused.

PREPARATION.—(1) By mining, as in Poland, Germany, &c.; (2) by allowing water to run down shafts extending into the salt beds, and pumping up and evaporating the solution formed; (3) by evaporating the water from salt springs; and (4) by evaporating sea-water. This latter operation is often conducted in shallow bays (*salterns*) in which the water is left to evaporate by the heat of the sun; hence the name *bay salt.* The mother liquor (bittern) contains chloride, bromide, sulphate, and iodide, of magnesium, sodium, potassium, and calcium; and is used as a source of bromine and iodine. Common salt contains, as impurities, sodium and calcium sulphate, and magnesium chloride.

Properties.—Colourless cubical crystals. Specific weight = 2.16; melting point = 776°; soluble in water, the solubility increasing slowly with the temperature; 100 parts of water at 5°C dissolve 35.63 parts of the salt—at 50°, 37 parts—and at 100°, 39.16 parts.—Sodium chloride forms an essential constituent of blood and other animal liquids. It seems to be necessary to keep in solution certain albuminous compounds which are insoluble in pure water.—It is used in medicine as an antidote to nitrate of silver. (What is the action?)

405. **Sodic Sulphate** (Na_2SO_4).

Preparation.—From common salt by the action of oil of vitriol; enormous quantities are in this way prepared as "salt cake," in the manufacture of soda (sodium carbonate). Common salt is treated with sulphuric acid in furnaces so constructed that half the salt is decomposed at a comparatively low temperature:

$$2NaCl + H_2SO_4 = NaHSO_4 + HCl + NaCl.$$

and the remainder by transferring the mixed salts to a hotter part of the furnace:

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

The hydrochloric acid escapes up a flue, and is dissolved by water descending in a shower. Thus is obtained the impure hydrochloric acid of commerce.—Sodic sulphate is sometimes a by-product in the manufacture of nitric acid, but the acid sulphate ($NaHSO_4$) is generally obtained.

Experiment 324.—Warm a small quantity of common salt in a porcelain basin with about an equal weight of sulphuric acid, dissolve the residue in water, and evaporate to crystallisation. The crystals have the composition represented by $Na_2SO_4 . 10H_2O$. They are called *Glauber's salt.* Drain them and leave them exposed to the air for a day.

PROPERTIES.—Crystallised sodic sulphate ($Na_2SO_4 . 10H_2O$) is a colourless salt, of bitter saltish taste. It is efflorescent, and is soluble in water (35.96 parts in 100 at 15°). Its solubility is greatest at 34°C, and is only 42 in 100 at 100°. It is very sparingly soluble in alcohol.—Sodic sulphate is much used in Europe as a saline purgative. It is also used as an antidote in cases of poisoning by salts of lead and barium. (How does it act?)

406. Sodic Carbonate ($Na_2CO_3 . 10H_2O$).

Also called *carbonate of soda, soda,* and *washing soda.*

PREPARATION.—1. By LEBLANC'S PROCESS, in three stages:

(a) The *salt cake* process. (Art. 393.)

(b) The *black ash* process, in which the salt cake is strongly heated with limestone and slack coal. A certain proportion of quick lime is also generally added. The following equations represent the principal chemical actions which take place:

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

Calcic sulphide is insoluble, and the sodium carbonate is extracted from the "black ball" by

(c) *Lixiviation.* The strong solution thus obtained is evaporated and the soda allowed to crystallise. It may be purified by recrystallisation.

2. By the AMMONIA-SODA process. A saturated solution of common salt is saturated with ammonia, and then a current of carbon dioxide is passed through it. Sodic hydric carbonate is precipitated :

$$NH_3 + CO_2 + NaCl + H_2O = HNaCO_3 + NH_4Cl.$$

The ammonia is recovered by distilling the mother liquor with magnesia :

$$MgO + 2NH_4Cl = MgCl_2 + 2NH_3 + H_2O.$$

The magnesia is recovered (as hydroxide) by treating the chloride with superheated steam :

$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl.$$

Sodic hydric carbonate is easily converted into the carbonate by the action of heat :

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

PROPERTIES.—Sodic carbonate is sold in large crystalline lumps, or in the form of a white powder. The crystals are efflorescent, and are readily soluble in water (60 parts in 100). The solution is alkaline in reaction, and neutralises strong acids.

Experiment 325.—Heat gently a crystal of washing soda in a t. t. and note the escape of water. Dissolve a fragment in water and test with red litmus. Add sulphuric acid to a solution of washing soda.

Experiment 326.—Heat some washing soda in a porcelain capsule until the liquid at first formed dries up to a cake. This is *dried carbonate of soda.* Powder and preserve it in a stoppered bottle.

407. **Sodic Hydric Carbonate** ($NaHCO_3$). — Also called *bicarbonate of soda,* and *baking soda.*

Preparation.—By exposing washing soda crystals to the action of carbon dioxide evolved by the action of hydrochloric acid on marble or limestone:

$$Na_2CO_3.10H_2O + CO_2 = 2NaHCO_3 + 9H_2O.$$

It is also prepared from common salt by the ammonia soda process (Art. 406).

Properties.—A white powder, soluble in water, and in hydrochloric and other acids, with much effervescence. It is decomposed by heat (Art 406.) It is much less soluble in water than the normal carbonate, 100 parts of water at 15°, dissolving only 10.5 parts.

408. **Sodic Hydroxide** (NaOH). — Also called *sodium hydrate* and *caustic soda.*

Preparation.—**Experiment 327.**—Dissolve some washing soda in about six times its weight of water, heat to boiling in a porcelain dish, add, a little at a time, slaked lime equal to about half the weight of the washing soda, keeping the liquid at the boiling point, and adding water as it boils away. Allow to settle, pour off the clear liquor, and test it with hydrochloric acid. It should give no effervescence. Test the precipitate with hydrochloric acid. It effervesces:

$$Ca(OH)_2 + Na_2CO_3 = CaCO_3 + 2NaOH.$$

This solution (*liquor sodæ*) prepared on the large scale in this way is boiled down in iron pots until a red heat is attained, when the molten caustic soda is run into iron cylinders and sealed up.—Caustic soda is also formed when sodium decomposes water. (Exp't 30).

Properties.—A brittle white solid, of specific weight 2.13. It melts at a dull red heat, but is not decomposed until an intense white heat is attained. It is deliquescent, and when exposed to the air soon becomes changed to carbonate. It dissolves readily in water, with the evolution of heat.

Experiment 328.—Put a small piece of caustic soda in a porcelain dish, leave it a few days, and then test it with hydrochloric acid.

Experiment 329.—Pour a little water upon a piece of caustic soda in a t. t. Note the heat. Add more water, and note the taste and action on the skin of the resulting solution.

Caustic soda has a strong corrosive action on animal tissues. It is therefore very poisonous.—Solution of caustic soda dissolves glass and porcelain. This goes on gradually even with very dilute solutions.—Caustic soda has many uses. Combined with fatty acids it forms hard soaps; and on account of its solvent action on fats, &c., it is used in cleansing rags, grass, &c., in the manufacture of paper. In medicine caustic soda is used as an escharotic. In the chemical laboratory it is often used to precipitate insoluble metallic hydroxides.

409. **Sodic Nitrate** ($NaNO_3$).—Also called *cubic nitre* and *Chili saltpetre.* This salt is found in large quantities in Peru and Bolivia. It is obtained by mining, and purified by solution and crystallisation. Its crystals when perfect are nearly cubical. It is very soluble in water (84 parts in 100), and somewhat deliquescent. In dissolving, it renders much heat latent.

This accounts for its cooling taste. It is used as a fertiliser, and in the manufacture of nitric acid and inferior blasting powders.

410. Sodic Sulphite ($Na_2SO_3.7H_2O$).

Preparation.—Divide a solution of sodium carbonate into two equal parts. Saturate one with sulphur dioxide, add the other, and evaporate to crystallisation. *Sodic hydric sulphite* ($NaHSO_3$) is first formed:

$$Na_2CO_3+2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

This is then converted into the normal sulphate:

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + CO_2 + H_2O.$$

Properties.—A colourless crystalline salt, soluble in water (1 part in 4). The solution is alkaline. Both the normal and the acid sulphite are used in medicine. They are used especially to destroy *sarcinæ ventriculi*, minute parasitic plants sometimes present in the stomach. The acid of the gastric juice sets free sulphur dioxide, which has an antiseptic action:

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O.$$

Sodic sulphite must be kept well stoppered, as it absorbs oxygen from the air and becomes oxidised to sulphate.

411. Sodic Phosphate ($Na_2HPO_4.12H_2O$).

—This is the "*common*" or "*rhombic*" *phosphate of soda.* It was first prepared from urine, and is present in the blood and in other animal liquids.

Preparation.—Bone ash is decomposed with sulsulphuric acid:

$$Ca_3(PO_4)_2 +3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The solution of phosphoric acid is separated from the sparingly soluble gypsum, and treated with sodic carbonate:

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + H_2O + CO_2.$$

The solution is then evaporated to crystallisation.

PROPERTIES.—A colourless salt, soluble in water (14 parts in 100). Its solution is alkaline in reaction. Its taste closely resembles that of common salt.

Experiment 330.—Dissolve a little sodic phosphate in water. Note the taste of the solution. Test with red litmus. Add a few drops of argentic nitrate to a little of the solution. Note the yellow precipitate (Ag_3PO_4):

$$3Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 6NaNO_3 + H_3PO_4.$$

412. **Sodic Bromide** (NaBr).—This salt is prepared by dissolving bromine in solution of caustic soda:

$$6NaOH + 3Br_2 = 5NaBr + NaBrO_3 + 3H_2O.$$

evaporating to dryness, and heating with a little charcoal to decompose the bromate:

$$2NaBrO_3 + 3C = 2NaBr + 3CO_2.$$

It is a soluble, colourless, crystalline salt, similar to the potassium salt. It is proposed to use it in medicine in place of potassium bromide, since it is equally efficacious, and causes none of the unpleasant symptoms resulting from the continued use of the potassium salt.

413. **Sodic Sulphide** (Na_2S).—Can be prepared impure (*liver of sulphur*) by heating sodic sulphate with charcoal:

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

To prepare solution of sodic sulphide, take two equal quantities of a solution of caustic soda, saturate the one with hydrogen sulphide:

$$NaOH + H_2S = NaSH + H_2O,$$

and then add the other:

$$NaSH + NaOH = Na_2S + H_2O.$$

The same method is used for preparing solutions of potassium and ammonium sulphides.—Solution of sodium sulphide is used to precipitate and dissolve sulphides of heavy metals. It combines with the sulphides of arsenic, antimony, &c., to form soluble sulphur salts; e.g.:

$$3Na_2S + Sb_2S_5 = 2Na_3SbS_4.$$

414. **Glass.**—Glass is a mixture of silicates. The materials used are (1) *silica,* in the form of quartz, ignited flint, white sand, or red sand; (2) *alkali,* purified potashes, refined soda ash, or salt cake; and (3) *calcic carbonate,* &c.—calcspar, marble, chalk, or limestone, and, for flint glass, red lead or litharge. There are several varieties of glass:

1. *Bohemian Glass.*—Silicates of potassium and calcium. It fuses with difficulty and resists the action of chemicals better than the other kinds of glass.

2. *Window, or Crown, Glass.*—Silicates of sodium and calcium. It is more fusible than Bohemian Glass, and more easily acted on by chemicals.

3. *Bottle Glass.*—Silicates of sodium and calcium, but made from cheap materials. Its colour is due to iron compounds.

4. *Flint Glass, Crystal,* or *Strass.*—Silicates of potassium and lead. It is heavy, fusible, and has a bright

lustre. It is used for ornamental purposes, and one variety (*paste*) is used for imitating diamonds.

The properties of glass make it very useful in chemical operations. It is transparent, not readily fused, and only slowly and sparingly soluble in most chemical substances. It can be fused at a red heat, and can then be moulded into any desired form.

415. Tests.

Very few salts of sodium are insoluble, so that the tests are mostly negative. *Sodic metantimonate* is insoluble, and a solution of the potassium salt is sometimes used as a test for sodium; but the test chiefly relied upon in analysis is the exclusion of other metals, and the yellow colour given to the Bunsen flame when sodium compounds are brought into it.

POTASSIUM.

416. **Potassium** (K^1 = 39.04. Specific weight = 0.875. Melting point = 62°.5).

OCCURRENCE.—Is found almost universally, but always in combination. It forms from 1.5 to 3.1 % of granite, and occurs in many double silicates. *Potash felspar* is a double silicate of potassium and aluminium ($K_2O.Al_2O_3.6SiO_2$), which "weathers" and thus forms clay. The chief source of potassium compounds is the mineral deposits of Stassfurth, which contain *silvine* (KCl), *carnallite* ($KCl.MgCl_2.6H_2O$), &c. Potassium compounds are present in sea water, in soils, and in plants and animals.

PREPARATION.—In the same way as sodium, but special precautions must be taken on account of the formation of an explosive compound of potassium and carbon monoxide.

PROPERTIES.—A silver white metal, resembling sodium, but it is more easily oxidised. Its chemical properties are very like those of sodium, but more pronounced. It is used in preparing boron, silicon, magnesium, &c.

417. **Potassic Carbonate.**—(K_2CO_3). Also called *carbonate of potash*, *potashes*, and *salt of tartar* (was formerly prepared by igniting 'cream of tartar').

PREPARATION.—1. From potassic *chloride* (KCl), and *sulphate* (K_2SO_4), by the same process as that employed for sodium carbonate (p. 371).

2. From *wood ashes*, by leaching, evaporating, and calcining. The residue is impure potassium carbonate (potashes). It is purified by recrystallisation, and is then called *pearl ash.*

3. From the waste liquors of the *beet sugar* industry, by evaporation and repeated crystallisation.

4. From the washings of sheep's wool, technically called "suint." The washings are evaporated to dryness and distilled. An illuminating gas, and an ammoniacal liquor, are obtained. The fixed residue is lixiviated, &c., for potassium carbonate. Commercial carbonate of potash is rarely pure. It can be purified by treating a saturated aqueous solution with carbon dioxide, and collecting and heating the acid carbonate thus precipitated :

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3.$$

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

PROPERTIES.—A white granulated powder, or a pasty mass, very deliquescent, very soluble in water (106.4 parts in 100), sparingly soluble in alcohol. The aqueous solution has an alkaline reaction, the properties of the strong base being only partially neutralised by the weak acid. Potassic carbonate is used in medicine as an antacid, and to promote the solution of uric acid stones. Its taste is very disagreeable. It is also used in the manufacture of soft soap, crystal glass, potassium ferrocyanide, bichromate, and cyanide.

Experiment 331.—Scatter a few grains of dry potassium carbonate upon a sheet of paper and examine after a few hours. Make a solution, and try the taste and action on red litmus.

418. **Potassic Hydric Carbonate** ($KHCO_3$).—Also called *bicarbonate of potash.*

PREPARATION.—By passing a current of carbon dioxide for several hours through a cold saturated solution of potassium carbonate. The sparingly soluble acid carbonate is precipitated.

PROPERTIES.—Colourless crystals, of a saltish taste; soluble in water (25 parts in 100), giving a slightly alkaline solution, decomposed by heat, even when in solution:

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

This salt has none of the corrosive action of the normal carbonate. It is used as an antacid and antilithic. *Liquor potassæ effervescens*, or *potash water*, is a solution of potassium bicarbonate into which carbon dioxide has been introduced under a pressure of seven atmospheres.

419. **Potassic Hydroxide** (KOH), also called *potassium hydrate*, and *caustic potash.*—This compound is prepared from potassium carbonate by the same method

as that used for sodic hydroxide, which it resembles in its properties. It is, however, more strongly corrosive in its action on the skin &c. *Potash lye* is an aqueous solution of impure potassic hydroxide.

420.—Potassic Chlorate ($KClO_3$), also called *chlorate of potash.*

Preparation.—Milk of lime is saturated with chlorine, and part of the water is evaporated :

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

Potassium chloride is added (In what proportion ?), and the solution is boiled down and allowed to cool, when potassic chlorate crystallises out :

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3$$

In this way the whole of the potassium is obtained as chlorate. The old method is wasteful (Expt. 76).

Properties.—Colourless, flat crystals, or a white granular powder. It has a cooling acid taste, and is sparingly soluble in water (6 parts in 100). When heated to 352° C. it decomposes into oxygen, chloride, and perchlorate :

$$2KClO_3 = O_2 + KCl + KClO_4.$$

At a higher temperature the whole of the oxygen is driven off. It is a powerful oxidising agent, but is not capable of supplying oxygen to the blood.

Experiment 332.—Carefully mix some dry sugar with about one-fourth its weight of powdered potassic chlorate, place the mixture on a stone or a piece of porcelain and touch with a glass rod dipped in concentrated sulphuric acid. (Explain the action).

421. Potassic Nitrate, (KNO_3).—Also called *salt-petre,* and *nitre.*

OCCURRENCE.—As efflorescence on the soil in hot dry countries, such as Bengal and Egypt. Has been obtained by lixiviating certain porous rocks (hence the name, *sal petræ*). Its formation in the soil is due to the slow oxidation of nitrogenous matter in the presence of potassic carbonate or silicate. Nitric acid is first formed and this decomposes the potassium carbonate, &c.

PREPARATION.—It is prepared from the soil incrustation by lixiviation and crystallisation. Much saltpetre is now prepared from potassic chloride by dissolving along with an equivalent (Calculate the proportions) of sodium nitrate in hot water until the specific weight is 1.5. Sodium chloride is precipitated, and potassium nitrate separates out when the solution cools:

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

(Compare the solubilities of these four salts.)

PROPERTIES.—Long colourless crystals, of a cooling bitter taste, soluble in water (26 parts in 100). It is an oxidising agent and plays this part in gun powder and in many coloured fires. Its uses in medicine depend principally on its cooling properties.

422. Potassic Bromide, (KBr).

PREPARATION.—**Experiment 333.**—Gradually add dilute solution of potassic hydroxide to a drop of bromine under water, until the colour of the bromine disappears. Evaporate the solution to dryness in a porcelain dish and ignite the residue. Potassic bromide remains:

$$6KOH + 3\,Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

$$KBrO_3 = KBr + 3O.$$

Dissolve in a little hot water and crystallise.

PROPERTIES.—Translucent, colourless, cubical crystals, resembling those of potassic iodide, but not so porcelain-like; taste, sharp and saline; readily soluble in water, somewhat sparingly in alcohol.

423. Potassic Iodide, (KI).

Preparation.—**Experiment 334.**—Repeat Expt. 333, using iodine instead of bromine. Potassic iodide is obtained. (Write the equations).

Properties.—Potassic iodide is very like the bromide in its properties. It crystallises in cubes, which are opaque and porcelain-like when deposited from a hot solution, but clear when crystallised cold. It is very soluble in water (140 parts in 100). (Examine carefully and compare crystals of potassium bromide and iodide).

424. Tests.

1. *Tartaric acid* gives a white crystaline precipitate of potassic hydric tartrate, especially on stirring with a glass rod.
2. *Platinum tetrachloride* gives a yellow crystalline precipitate (K_2PtCl_6). Make this test by stirring together a drop or two of the solutions on a watch glass.
3. Potassium compounds give a violet colour to the Bunsen flame.

AMMONIUM.

425. Ammonium Salts.—These are compounds containing the radical *ammonium* (NH_4—), which acts the part of a monad atom. They are generally prepared by neutralising the appropriate acids with solution of ammonia. This solution may be supposed to contain *ammonium hydroxide* (NH_4OH), which acts towards acids as sodic hydroxide does, e.g.:

$$NH_4.OH + HCl = NH_4.Cl + H_2O.$$

Compare $KOH + HCl = K.Cl + H_2O.$

The ammonium salts resemble those of sodium and potassium, especially the latter, but can all be decomposed by heat.

426. Ammonic Sulphate, ($(NH_4)_2SO_4$).

Preparation.—By heating gas liquor with lime, and receiving the evolved ammonia in dilute sulphuric acid. The solution thus obtained is evaporated to crystallisation.

Properties.—A colourless salt, generally in small crystals, soluble in water (75.5 parts in 100). When heated strongly it volatilises completely.

Experiment 335.—Heat a little ammonic sulphate in a dry glass tube. Dissolve another portion in water and test it for sulphuric acid.

Ammonic sulphate is used as a fertiliser. It is the starting point in the manufacture of other ammonium salts.

427. Ammonic Chloride, (NH_4Cl), also called *sal ammoniac.*

Preparation.—**Experiment 336.** — Neutralise a small quantity of dilute hydrochloric acid with solution of ammonia and evaporate to dryness. Ammonium chloride remains: $NH_3 + HCl = NH_4Cl$.

Ammonic chloride is also prepared by subliming a mixture of the sulphate and common salt:

$$(NH_4)_2SO_4 + 2NaCl = 2NH_4Cl + Na_2SO_4.$$

It is purified by re-sublimation.

Properties.—Colourless crystals, either in tough masses of flexible fibres, or in grains. It has a sharp cooling taste, and is freely soluble in water (35 parts in 100). When the aqueous solution is boiled, ammonia escapes and the solution becomes acid. Ammonium chloride renders latent a great deal of heat when dissolving. It is an excellent cooling agent.

Experiment 337—Dissolve some ammonic chloride in a little water and note the low temperature produced. Heat a small quantity of the solid in a dry glass tube. It sublimes and leaves no residue, if it is pure.

428. **Ammonic Carbonate.**—The normal carbonate ($(NH_4)_2CO_3$) is difficult to prepare and keep. It loses ammonia and becomes converted into the acid carbonate (NH_4HCO_3). The "sesquicarbonate" of commerce is a compound of the acid carbonate with ammonium *carbamate* ($NH_4.CO_2.NH_2$).

PREPARATION.—By subliming a mixture of chalk and sal ammoniac or ammonium sulphate:

$$CaCO_3 + (NH_4)_2SO_4 = (NH_4)_2CO_3 + CaSO_4.$$

The salt which sublimes is, however, not the normal carbonate represented in the equation, but the "sesquicarbonate" (so called):

$$NH_4HCO_3.NH_4NH_2CO_2$$

Experiment 338.—Heat a mixture of ammonium sulphate and ground limestone in a dry test tube. Scrape out a little of the sublimate, observe its odour, and note that it effervesces with hydrochloric acid.

PROPERTIES.—Commercial carbonate of ammonia (*sal volatile*) is sold in hard translucent crystalline masses. It smells of ammonia, and, if exposed to the air, is soon changed to the acid carbonate by losing ammonia and gaining water:

$$NH_4.NH_2.CO_2 + H_2O = NH_4HCO_3 + NH_3.$$

It is soluble in water (27.5 parts in 100), and the solution is alkaline. *Aromatic spirit of ammonia* is a preparation of the carbonate

429. Ammonic Phosphate, $(NH_4)_2HPO_4$.

PREPARATION.—By neutralising solution of phosphoric acid with ammonia solution, and crystallising :

$$2NH_3 + H_3PO_4 = (NH_4)_2\ HPO_4$$

PROPERTIES.—Colourless crystals, soluble in water, insoluble in alcohol.

430. Microcosmic Salt.—Is *hydric sodic ammonic phosphate* $(H.Na.NH_4.PO_4.4H_2O.)$ first noticed as crystallising from concentrated urine. It is a colourless crystalline salt prepared by mixing hot strong solutions of sodium and ammonium phosphates and allowing to crystallise. By heat it decomposes as follows :

$$HNaNH_4PO_4.4H_2O = 5H_2O + NH_3 + NaPO_3.$$

The non-volatile sodic metaphosphate remains.

431. Ammonic Sulphide, $((NH_4)_2S.)$

PREPARATION.—In the some way as solution of sodic sulphide (Art. 413).

PROPERTIES.—Forms a colourless solution which gradually turns yellow, owing to the absorption of oxygen, which sets free sulphur. Ammonium sulphide solution dissolves sulphur, and thus forms "yellow ammonium sulphide," used in analysis to dissolve stannous sulphide.

Experiment 339.—Add hydrochloric acid to a few drops of yellow ammonium sulphide, and observe the precipitation of sulphur and the evolution of hydric sulphide :

$$(NH_4)_2S_x + 2HCl = 2NH_4Cl + H_2S + xS.$$

Ammonic sulphide is poisonous.

432. Tests.

1. Heat in a test tube with caustic soda solution, observe the odour, and hold over the mouth of the test tube a glass rod moistened with dilute hydrochloric acid. White fumes are formed :

$$NH_3 + HCl = NH_4Cl.$$

(What is the object of the caustic soda ?)

2. *Platinum tetrachloride* gives a yellow precipitate ($(NH_4)_2PtCl_6$). (Art. 424 (2)).

LITHIUM.

433. **Lithium** ($Li^1 = 7.01$.—Specific weight = 0.59.—Melting point = 180°.) The metal is prepared by electrolysing the fused chloride ($LiCl$). It resembles sodium and potassium in its properties, but is much lighter, and has not so strong an attraction for oxygen. Lithium compounds are widely diffused, but in small quantities. They are found in most mineral waters, and in river and spring water generally. The compounds of lithium resemble those of sodium and potassium, but the hydroxide ($LiOH$), carbonate (Li_2CO_3), and phosphate (Li_3PO_4), are much less soluble in water.

434. **Lithic Carbonate**, (Li_2CO_3).—This is the most important compound of lithium, as it is much used in medicine in treating gout, stone, &c.

PREPARATION.—**Experiment 340**.—To a small quantity of solution of ammonium carbonate in liquor ammoniæ add a small quantity of a strong solution of lithium chloride. Lithium carbonate is precipitated :

$$2LiCl + (NH_4)_2CO_3 = Li_2CO_3 + 2NH_4Cl.$$

Warm, filter, and wash with cold water.

PROPERTIES.—Lithium carbonate is a white crystalline powder, sparingly soluble in water (0.78 parts in 100). It is more soluble if carbonic acid be added, as the *bicarbonate* ($LiHCO_3$) is formed, of which 5.25 parts dissolve in 100 of water. When this solution is exposed to the air, it loses carbon dioxide and the normal carbonate is precipitated. (What other carbonates behave similarly?)

Lithium carbonate is prescribed for gout, stone, &c. It is preferable to the potassium salt. (Art. 167).

435. Tests.

Lithium compounds can be recognised by the spectrum of the beautiful red colour which they give to the Bunsen flame.

436. **Rubidium,** (Rb^I = 85.2).—Compounds of this rather rare alkaline metal are found in mineral springs, and in some minerals. The metal can be prepared by the same process as that for the preparation of sodium and potassium. It is like these in properties, but has greater chemism for oxygen than potassium has. Its compounds are similar in composition and properties to those of potassium, e.g., Rb_2O, $RbOH$, $RbCl$, &c.

437. **Cæsium** (Cs^I = 132.5).—Cæsium compounds were discovered in 1860 by Bunsen, by means of the *spectroscope*; and this discovery was the first fruit of *spectrum analysis.* When white light is passed through the edge of a wedge-shaped piece of glass (*prism*), it is spread out in such a way that the waves of different lengths fall on different parts of a retina receiving them. The sensation is one of a band of coloured lights ranging from red to violet. Such a band is called the *spectrum*

and in the spectrum each colour has its fixed place. Now, each element in the state of a hot vapour gives a light corresponding to particular lines in the spectrum; and if, when looking through a prism (appropriately arranged in a *spectroscope*), we see in a flame bands or lines, we can recognise these as being due to the presence of some known element. Bunsen, when looking at a flame in which was volatilising the solid residue of the water from a mineral spring, saw lines produced by no known element. He thus discovered the metals cæsium and rubidium.—Cæsium was prepared in 1881 by Carl Setterberg by electrolysing the fused cyanide (CsCN). It melts at the temperature of the hand, and exceeds rubidium in its chemism for oxygen. Its compounds are very like those of rubidium and potassium, e.g., Cs_2O, CsOH, CsCl, Cs_2CO_3, &c.

QUESTIONS AND EXERCISES.

1. Calculate the percentage of water in washing soda.

2. How much dried sodium carbonate is equivalent to 100 grains of washing soda?

3. What substances are antidotes to caustic soda and caustic potash?

4. "Sodium nitrate gives, weight for weight, more nitric acid than potassic nitrate does." Show the truth of this statement.

5. How would you distinguish (practically) sodium carbonate from potassium carbonate.

6. Solution of normal sodic sulphite is alkaline in reaction. How do you account for this?

7. Show that, weight for weight, lithium carbonate will dissolve a larger quantity of uric acid stone than will potassium carbonate.

8. How much potassium chlorate ($KClO_3$) can be obtained from 10 lbs. of caustic potash (KOH)—(1) by the method of Art. 101, and (2) by that of Art. 420?

8. What would you use as an antidote to poisoning by ammonium sulphide?

9. Arrange the metals of the alkalis (1) in the order of their atomic weights, and (2) in the order of their chemism for oxygen.

CHAPTER XXII.

ELECTRICITY.

438. **Voltaic Batteries.**—If a plate of copper held by a glass rod (an *insulator)* be touched by a zinc plate similarly held, and then withdrawn, the two plates will be found to be in a peculiar condition, such that they produce exactly opposite effects on electrified bodies. What the copper attracts the zinc repels, and *vice versa,*—the zinc is *positively*, the copper *negatively*, electrified. The condition is one analogous to a difference of temperature. If a drop of sulphuric acid be placed between the plates, a similar condition is produced. And, if the dry ends of the plates be now connected by a copper wire, so as to complete the circuit, the copper and zinc tend to assume the same electrical condition by a transference of electricity through the liquid from the zinc to the copper. At the same time sulphuric acid is decomposed into H_2 and SO_4, the hydrogen appearing at the surface of the copper plate, and the salt radical (SO_4) attacking the zinc plate and forming zinc sulphate. While this takes place in the liquid there passes round the rest of the circuit a disturbance of some sort, called, for lack

of a better term, a *current of electricity*. The source of this form of energy (which can be used to drive machinery, to heat a wire, &c.) is the chemical action between the zinc and acid. If no electricity were produced, *e.g.* if the zinc were put alone into sulphuric acid, an amount of heat equivalent to the electricity would appear in the liquid for the same amount of zinc dissolved. This is the simplest form of *voltaic cell*. The zinc is called the *positive element*, the copper, the *negative element*. As a rule, when any two substances are brought together in this way, the one assumes the positive condition and the other the negative. The chemical elements can thus be arranged in an *electro-chemical series*, beginning with the most positive, and ending with the most negative elements. In this series, any element is positive as regards succeeding, but negative as regarding preceding, elements.

Electro-chemical Series: Cs, Rb, K, Na, Li, Ba, Sr, Ca, Mg, Al, Mn, Zn, Fe, Ni, Co, Cd, Pb, Sn, Bi, Cu, Ag, Hg, Pt, Au, H, Si, Te, Sb, C, B, Cr, As, P, I, Br, Cl, F, N, Se, S, O.

439. **Electrolysis.**—Most compounds which can be got in the liquid condition, either by fusion or by solution, can be decomposed by a current of electricity allowed to pass through the liquid between two wires dipping into it. Compounds decomposable by electricity are called *electrolytes*. In such decompositions, one portion of the compound is set free at the wire (*the negative pole*) coming from the positive element of the battery, and the other at that *(the positive pole)* connected with the negative element. If the liquid is a metallic compound the metal always appears at the negative pole (Art. 261), and the non-metal, or *negative radical* (NO_3, SO_4, &c.) at the

positive pole. *The positive part of a compound goes with the current.* The wires or plates used for conducting the current into and out of the liquid are generally called *electrodes.* The positive electrode is often eaten away by the negative product of electrolysis. Platinum resists in most cases, but is attacked by chlorine, &c. Various *secondary actions* occur when solutions are electrolysed. For example, when a solution of sodium sulphate is electrolysed, sodium is set free at the negative pole, but immediately decomposes water, and thus hydrogen and caustic soda are the final products. At the negative pole, oxygen and sulphuric acid appear, since the radical SO_4 cannot exist by itself. Generally, when solutions of alkaline salts are electrolysed, an alkali and hydrogen appear at the negative electrode, while an acid and oxygen appear at the positive. The nascent hydrogen and oxygen may exert reducing or oxidising action on the other substances present in the solution.—The liquids of the human body contain salts of sodium and potassium, so that when a current of electricity passes through any part, alkali collects around the negative, and acid around the positive, needle. The alkali exerts its well-known solvent action on the tissues, while the acid coagulates the albuminous substances and thus causes the needle to become more or less firmly fixed in the tissues. Advantage is taken of these phenomena in the destruction of tumors, &c., by electrolysis of the diseased tissue.

CHAPTER XXIII.

ANALYSIS—TOXICOLOGY.

440. **Systematic Testing.** — Most of the substances which are met with in practice can be arranged under the three heads of *bases*, *acids*, and *salts*. In systematic testing of unknown substances, two cases may occur: (1) the substance may be *pure*—a chemical individual, or (2) it may be *mixed*—including two or more chemical individuals. The first case is the only one which admits of treatment here; the case of mixtures requires more space than we have at our disposal. For purposes of systematic testing, the metals are classified as at p. 270, and the first step is to determine, by the use of *group reagents*, to which of the six groups the metal whose base or salt is under examination belongs. This determined, further testing shows which metal of the group is present. The acids can be arranged in four groups:

1. Organic acids, which char when heated:—*Tartaric, citric, succinic, benzoic*, &c.

2. Inorganic acids, the *barium* salts of which are insoluble or sparingly soluble:—*Sulphuric, carbonic, phosphoric, oxalic, boric, sulphurous, chromic*, &c. The group reagent is *barium nitrate.*

3. Inorganic acids, the *silver* salts of which are insoluble: —*Ferrocyanic, ferricyanic, hydrocyanic, hypochlorous* (*chloride* precipitated), *hydriodic, hydrobromic,*

hydrochloric, *thiosulphuric*, *nitrous*, [*boric*, *oxalic*, *sulphurous*]. *Argentic nitrate* is the group reagent.

4. Acids which give no precipitate with the group reagents:—*Nitric*, *chloric*, *acetic*, and (in sufficiently dilute solutions) *oxalic*, *boric*, *sulphurous*, and *nitrous*.

NOTE.—In testing for the acids, the nature of the metal (already discovered) must be considered. For example, a solution of plumbic acetate might char on evaporation and ignition. On the addition of calcic chloride, a white precipitate would appear at once. This might lead to the conclusion that the acid is tarta[illegible] whereas the precipitate is plumbic chloride. In [illegible] cases, the metal must be removed as carbonate, by boiling with solution of sodic carbonate, filtering, and neutralising part of the filtrate with nitric acid, to test for all acids but nitric and chloric, and another with hydrochloric acid, to test for these two acids.

441. **Dissolving the Substance.**—Try the solubility of small portions of the substance in water, in hydrochloric acid, in nitric acid, and in aqua regia. If a solution is obtained in any of these solvents, make the analysis according to the following tables. If the substance is insoluble in water, but soluble in hydrochloric acid, it may be a phosphate, oxalate, or citrate, in which case it would be re-precipitated by ammonia (Table B), and might then be mistaken for alumina. In such cases, these three acids must be tested for separately (see articles 132, 184, 190). If the substance is insoluble in all the above-mentioned solvents, it is probably one of the following:—*Baric sulphate*, *strontic sulphate*, *silica*, *calcic fluoride*, *alumina*, *stannic oxide*, *argentic chloride*,

plumbic sulphate, carbon, ferric oxide. These are all white, excepting the last two. They may be tested for by special tests, described in the preceding pages (see *Barium*, &c.)

442. **Practical Hints.**—Use small quantities, both of reagents and of liquids, to be tested. Add the reagents a little at a time. Remember that in chemical actions, equivalents of the substances must be used in order to complete the actions.

Excess of a reagent means more than enough to complete the chemical action which the reagent brings about. It does not necessarily mean a large quantity. Chemical actions take time, and when solutions are very cold the time is longer. This is a matter to be considered in the more delicate tests.—Work slowly, and handle apparatus gently. Clean apparatus as soon as possible after using it, as it is more difficult to clean after standing for some time. Explain every test, and write equations where possible.

443. **Chemical Toxicology.** — Poisonous substances may be conveniently classified as follows :—

1. *Corrosives.*—Corrosive sublimate, concentrated acids (sulphuric, nitric, hydrochloric, oxalic, &c.), alkaline substances (caustic potash, caustic soda, ammonia, and the carbonates of these bases), acid, alkaline, and corrosive salts of the metals (potassium bi-sulphate, alum, antimony trichloride, silver nitrate, &c.), and carbolic acid.

2. *Irritants.*—Arsenic compounds, dilute acids, phosphorus, many metallic salts, e.g., those of antimony, lead, zinc, copper, and chromium, and many organic sub-

stances, e.g., elaterium, gamboge, aloes, colocynth, croton oil, cantharides, &c.

3. *Neurotics.*—Prussic acid, opium (including the opium alkaloids, e.g., morphine), strychnine, aconite, belladonna, &c.

4. *Gaseous Poisons.*—Chlorine, bromine, hydrochloric acid, hydrofluoric acid, sulphur dioxide, nitrogen oxides, ammonia, carbon dioxide, carbon monoxide, coal gas (carbon monoxide and acetylene), sulphuretted hydrogen, anæsthetics, vapours of hydrocarbons (e.g., of mineral naphtha).

Tests for most of these substances have been described in the preceding pages. These tests can be applied without any difficulty where a definite chemical substance is to be examined, but in many cases, the substance to be tested for poisons is a complicated mixture, such as the contents of a stomach, or some article of diet. In such cases, special methods must be used, in order to separate the poison from the organic matter which would obscure the tests. A very useful method is that of *dialysis*, since all poisonous substance diffuse through a moist membrane, while albuminous substances do not. The following method may be employed in testing for the common poisons. Boil with hydrochloric acid for some time, filter, and heat a portion of the clear filtrate for half an hour with a small piece of bright copper. Any *mercury*, *arsenic*, or *antimony* present will be deposited on the copper. Remove the copper, wash, and dry it carefully, and heat it in a narrow glass tube held aslant. *Mercury* forms a metallic coat on the tube, *arsenic* oxidises and forms a white crystalline deposit at some distance from the metal, while *antimony* forms a white deposit near the metal. Marsh's test (pp. 161 and 307) may be applied to other portions of the liquid. To test for *lead* and *copper*, pass sulphuretted hydrogen through the warm liquid for some time. A black precipitate may be PbS or CuS. Filter, wash, dissolve the precipitate in *aqua regia*, and test as at pp. 280 and 297. *Zinc* is tested for by treating the liquid with excess of ammonia, filtering, and adding sulphuretted hydrogen to the filtrate. A white precipitate (ZnS) indicates zinc. *Chromium* is detected as at p. 333.—*Acid* and *alkaline* substances can be tested for by observing whether a large quantity of alkali or acid is required to render the substance neutral. For *hydrochloric*, *nitric*, and *sulphuric* acids, see pp. 103, 86, and 133. As small quantities of the salts of these acids are naturally present in articles of food, &c., only large quantities should be looked upon as abnormal.—To test for *oxalic acid*, precipitate the clear liquid with lead acetate, collect the precipitate, wash, mix with water, decompose with sulphuretted hydrogen ($PbC_2O_4 + H_2S = PbS + H_2C_2O_4$), and test the filtered liquid for oxalic acid (p. 210).—*Prussic acid* can often be recognised by its smell, especially when the substance is treated with a little sulphuric acid. The tests at p. 184 can be made by mixing the suspected substance with sulphuric acid in small porcelain dishes, and placing over these inverted dishes or watch glasses moistened with argentic nitrate, caustic soda solution, and ammonium sulphide respectively. The acid is volatilised upon these, and the tests are completed as at p. 184.—Any substance containing free phosphorus is luminous in the dark. The luminosity is especially apparent when the substance is distilled along with water in the dark. A luminous ring appears in the neck of the condenser.—The examination of an organic mixture for poisonous alkaloids is a process too extensive for treatment here. They can be tested for separately as at pp. 250, 251, and 252.

NOTE.—The following ANALYTICAL TABLES are to be used in examining solutions containing not more than one metal and one acid.

Analytical Tables.

TESTING FOR THE METAL.

TABLE A.

N. B.—*O. S.* means *Original Solution.*

To O. S. add dilute HCl in excess.

<table>
<tr><td colspan="3">Wht. ppt. insoluble in excess.—Add NH_4OH.</td><td colspan="9">No ppt. (or wht. ppt. soluble in excess of the acid).*—Add H_2S.</td></tr>
<tr><td rowspan="5">No change
Pb
Confirm p. 280.</td><td rowspan="5">Dissolved
Ag
Confirm p. 283.</td><td rowspan="5">Blackened
Hg (-ous)
Confirm p. 287.</td><td colspan="4">Yellow or orange ppt.—Add $(NH_4)_2S_2$ to a part.</td><td colspan="5">Black or brown ppt.—Add $(NH_4)_2S_2$.</td></tr>
<tr><td colspan="3">Dissolved.—Add $(NH_4)_2CO_3$ to a second part.</td><td rowspan="4">Undissolved.
Cd
Confirm p. 300.</td><td rowspan="4">Dissolved
Sn (-ous)
Confirm p. 311.</td><td colspan="4">Undissolved.—Add a few drops H_2SO_4 to O. S.</td></tr>
<tr><td rowspan="3">Dissolved
As
Confirm p. 162.</td><td colspan="2">Undissolved.</td><td rowspan="3">Wht. ppt.
Pb
Confirm p. 280.</td><td colspan="3">No ppt.—Add NH_4OH to O. S.</td></tr>
<tr><td rowspan="2">Ppt. is yellow.
Sn (-ic)
Confirm p. 310.</td><td rowspan="2">Ppt. is orange.
Sb
Confirm p. 307.</td><td rowspan="2">Blue ppt. soluble in excess.
Cu
Confirm p. 297.</td><td colspan="2">Wht. ppt.—Add NaOH to O S.</td></tr>
<tr><td>Yellow ppt.
Hg (-ic)
Confirm p. 291.</td><td>White ppt.
Bi
Confirm p. 303.</td></tr>
</table>

If no ppt. with H_2S, pass to Table B.

* Indicating compounds of Sb, Bi, and Sn. A ppt. of sulphur appearing gradually indicates a *thiosulphate* or *persulphide.*

TABLE B.

To O. S. add NH_4Cl,* NH_4OH,† and $(NH_4)_2S$.						
Black ppt.—Add dilute HCl.			White or colored ppt.—Add NaOH to O. S.			
Dissolved. Fe To distinguish between *-ous* and *-ic*, test O. S. Confirm p. 328.	Undissolved.—Add to O. S. NH_4OH, drop by drop.		White ppt., soluble in excess. Divide the solution into two parts. To one part add H_2S, and to the other NH_4Cl.		Greenish ppt. soluble in large excess; re-precipitated on boiling. Cr Confirm p. 333.	Buff or skin-colored ppt., turning rust-colored when shaken up with air. Mn Confirm p. 345.
	Blue ppt. soluble in excess, giving a *brown* solution. Co Confirm p. 347.	*Green* ppt. soluble in excess, giving a *blue* solution. Ni Confirm p. 349.	Wht. ppt. with H_2S. Zn Confirm p. 341.	Wht. ppt. with NH_4Cl. Al Confirm p. 337.		

---

* To prevent the precipitation of magnesium compounds.

† To neutralise any acidity.

TABLE C.

<table>
<tr><td colspan="8">To O. S. add NH_4Cl,* NH_4OH,† and $(NH_4)_2CO_3$.</td></tr>
<tr><td colspan="3">Wht. ppt.—Add $CaSO_4$ to O. S.</td><td colspan="5">No ppt.—Add Na_2HPO_4, and stir.</td></tr>
<tr><td rowspan="4">No ppt.
Ca
Confirm p. 359.</td><td rowspan="4">Wht. ppt. after some time.
Sr
Confirm p. 361.</td><td rowspan="4">Wht. ppt. at once.
Ba
Confirm p. 363.</td><td rowspan="4">Wht. ppt.
Mg
Confirm p. 367.</td><td colspan="4">No ppt.—Add NaOH to O. S., and heat.</td></tr>
<tr><td rowspan="3">Smell of ammonia.
NH_4
Confirm p. 387.</td><td colspan="3">No smell of ammonia.—Add $H_2\bar{T}$, and stir.</td></tr>
<tr><td rowspan="2">Granular wht. ppt.
K
Confirm p. 383.</td><td colspan="2">No ppt.—Test O. S. by flame test.</td></tr>
<tr><td>Yellow.
Na</td><td>Colourless.
No common metal present.</td></tr>
</table>

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* To prevent the precipitation of magnesium compounds.

† To neutralise any acidity.

TESTING FOR THE ACID.

Evaporate a small quantity of the solution to dryness, in a porcelain capsule, and heat strongly. If it chars, proceed according to TABLE D; if not, pass on to TABLE E.

TABLE D.

<table>
<tr><td colspan="5">To the solution (made neutral, if necessary) add $CaCl_2$, and shake well for some time. If no ppt. appears, heat to boiling.</td></tr>
<tr><td rowspan="3">Wht. ppt. in cold, soluble in HCl.
Tartaric Acid.
Confirm p. 217.</td><td rowspan="3">Wht. ppt. on boiling, soluble in HCl.
Citric Acid.
Confirm p. 219.</td><td colspan="3">No ppt.—Add Fe_2Cl_6 to O. S.</td></tr>
<tr><td colspan="2">Light brown ppt.—Evaporate a little O. S. to dryness, heat, and smell.</td><td rowspan="2">Red colour.—No ppt.
Acetic Acid.
Confirm p. 206.
—
N.B.—Acetates char very little, and sometimes not at all.</td></tr>
<tr><td>Choking fumes.
Succinic Acid.
Confirm. No ppt. with HCl.</td><td>Tarry or aromatic fumes.
Benzoic Acid.
Confirm p. 242.</td></tr>
</table>

TABLE E.

Add $Ba(NO_3)_2$ to O. S. If no ppt., pass on to TABLE F.

Wht. ppt.—Add dilute HNO_3 to the ppt.						Yellow ppt. H_2CrO_4 Confirm p. 333.
Undissolved. H_2SO_4	Dissolved with effervescence. H_2CO_3 Confirm p. 171.	Dissolved without effervescence.				
		Add to O. S. NH_4Cl, NH_4OH, and $MgSO_4$. Stir well with a glass rod. Wht. ppt. H_3PO_4* Confirm p. 148.	Add $CaCl_2$ to O. S. Wht. ppt. insoluble in acetic acid. $C_2H_2O_4$ Confirm p. 211.	Evaporate some of O. S. to dryness, moisten some of the solid with H_2SO_4, and bring into the Bunsen flame on a platinum wire. Green flame. H_3BO_3 Confirm p. 262.	Add $AgNO_3$ to O. S.. and boil. Wht. ppt., turning grey. H_2SO_3 Confirm p. 129.	

* *Arsenic acid* gives same result. To distinguish, see p. 159.

TABLE F.

Add $AgNO_3$ to the solution (made neutral, if necessary).

<table>
<tr><td rowspan="7">Black ppt.
|
H_2S
Confirm p. 139.</td><td colspan="7">Wht. or yellowish ppt.—Add HNO_3.</td><td colspan="3">No ppt.—Test for HNO_3 (p. 86), and $HClO_3$ (p. 107).</td></tr>
<tr><td colspan="7">Not dissolved.—Add Fe_2Cl_6 to O. S.</td><td colspan="3">Dissolved.—Add dilute H_2SO_4, and warm.</td></tr>
<tr><td rowspan="5">Blue.
|
$K_4Fe(CN)_6$</td><td colspan="6">Not blue.—Add Fe_2SO_4 to same portion.</td><td rowspan="5">Ppt. of sulphur, and smell of SO_2.
|
$H_2S_2O_3$</td><td rowspan="5">Nitrous fumes.
|
HNO_2
Confirm p. 94.</td><td rowspan="5">No result. Test for *Boric* and *Oxalic* acids as solutions may have been too dilute to give ppt. with $Ba(NO_3)_2$.</td></tr>
<tr><td rowspan="4">Blue.
|
$K_3Fe(CN)_6$</td><td colspan="5">Not blue.—Add HNaO to some portion, warm, and acidify with HCl.</td></tr>
<tr><td rowspan="3">Blue on acidifying.
|
HCN.
Confirm p. 185.</td><td colspan="4">Not blue.—Add $Pb\bar{A}_2$, and boil.</td></tr>
<tr><td rowspan="2">Wht. ppt. turning black on boiling.
|
$HClO$
Confirm Expt. 75.</td><td rowspan="2">Yellow ppt. dissolved by heating with much water, and crystallising on cooling.
|
HI
Confirm p. 115.</td><td colspan="2">Permanent wht. ppt. dissolved on heating, &c. Add to O. S. MnO_2 and H_2SO_4, and heat.</td></tr>
<tr><td>Brown vapour.
|
HBr
Confirm p. 111.</td><td>Greenish yellow gas.
|
HCl
Confirm p. 103.</td></tr>
</table>

If no result so far, test for *Acetic* acid (p. 206), and for *Nitrous* (p. 94), *Boric* (p. 262), and *Oxalic* acids, as the solutions may have been too dilute for the discovery of these acids by the group reagents.

APPENDIX.

TABLE OF SOLUBILITIES.

100 parts (by weight) of water at 15°C dissolve of

NAMES.	FORMULAS.	PARTS.
Acetic Acid	$C_2H_4O_2$	all proportions.
Alcohol, amyl	$C_5H_{12}O$	25.00
" ethyl	C_2H_6O	all proportions.
" methyl	CH_4O	all proportions.
Alum, ammonia	$(NH_4.)_2 Al_2 (SO_4)_4. 24H_2O$	11.4
" chrome	$K_2 Cr_2 (SO_4)_4. 24H_2O$	14.3
" potash	$K_2Al_2 (SO_4)_4. 24H_2O$	12.3
Ammonia	NH_3	59.7
Ammonium carbonate	$N_3H_{11}C_2O_5$	27.5
Ammonic chloride	$NH_4.Cl$	35.
" chloroplatinate	$(NH_4)_2PtCl_6$	0.666
" nitrate	NH_4NO_3	200
" oxalate	$(NH_4)_2C_2O_4.H_2O$	4.22
" sulphate	$(NH_4)_2SO_4$	75.5
Antimony trichloride	$SbCl_3$	100†*
" trioxide	Sb_2O_3	0.001 (?)
Argentic chloride	$AgCl$	0.00
" nitrate	$AgNO_3$	100†
" oxide	Ag_2O	0.033
Arsenic acid	H_3AsO_4	100†
" trioxide	As_2O_3	3.33
Baric carbonate	$BaCO_3$	0.0071
" chloride	$BaCl_2.2H_2O$	45.
" fluosilicate	$BaSiF_6$	0.0263
" hydroxide	$Ba(OH)_2$	3.4
" nitrate	$Ba(NO_3)_2$	8.1
" phosphate	$Ba_3(PO_4)_2$	0.00
" sulphate	$BaSO_4$	0.00025
Benzene	C_6H_6	0.1 (?)
Benzoic acid	$C_6H_5.COOH$	0.5
" aldehyde	$C_6H_5.COH$	3.32
Bismuth trichloride	$BiCl_3$	100†
" trinitrate	$Bi(NO_3)_3.3H_2O$	100†
" subnitrate	$BiNO_3(OH)_2$	0.00
Boracic acid	H_3BO_3	3.00
Borax	$Na_2B_4O_7.10H_2O$	5.3
Bromine	Br	3.226
Cadmic chloride	$CdCl_2$	140
" sulphate	$CdSO_4$	58
Calcic carbonate	$CaCO_3$	0.0018
" chloride	$CaCl_2$	75.
" citrate	$Ca_3(C_6H_5O_7)_2.4H_2O$	0.1 (?)

* 100† means very soluble.

NAMES.	FORMULAS.	PARTS.
Calcic hydroxide	$Ca(OH)_2$	0.137
" oxalate	$CaC_2O_4.2H_2O$	0.00
" phosphate	$Ca_3(PO_4)_2$	0.00
" sulphate	$CaSO_4.2H_2O$	0.238
" tartrate	$CaC_4H_4O_6.4H_2O$	0.016
Camphor	$C_{10}H_{16}O$	0.1
Carbolic acid	$C_6H_5.OH$	6.67
Carbon bisulphide	CS_2	0.1
" dioxide	CO_2	0.19744
" monoxide	CO	0.00305
Chloral hydrate	$C_2HCl_3O.H_2O$	100 (?)
Chlorine	Cl	0.7515
Chloroform	$CHCl_3$	0.1 (?)
Citric acid	$C_6H_8O_7.H_2O$	133.00
Cobaltous chloride	$CoCl_2.6H_2O$	100†
" nitrate	$Co(NO_3)_2,6H_2O$	100†
" sulphate	$CoSO_4.7H_2O$	33.5
Cupric nitrate	$Cu(NO_3)_2.3H_2O$	100†
" sulphate	$CuSO_4.5H_2O$	39.5
Dextrin	$C_6H_{10}O_5$	100†
Ether (ethylic)	$(C_2H_5)_2O$	11.00
Ferric chloride	Fe_2Cl_6	100†
" sulphate	$Fe_2(SO_4)_3$	100†
Ferrous "	$FeSO_4.7H_2O$	70.
" ammonic sulphate	$Fe(NH_4)_2(SO_4)_26H_2O$	19
Gallic acid	$C_7H_6O_5.H_2O$	1.00
Glycerine	$C_3H_5(OH)_3$	all proportions.
Hydrochloric acid	HCl	75.72
Hydrocyanic "	HCN	all proportions.
Hydrogen	H	0.00017
" peroxide	H_2O_2	all proportions.
Iodine	I	0.182
Iodoform	CHI_3	0.01 (?)
Lithic carbonate	Li_2CO_3	0.8
" chloride	$LiCl$	78.
" urate	$Li_2C_5H_2N_4O_3$	10 (?)
Magnesic chloride	$MgCl_2$	130.
" oxide	MgO	0.0018
" am. phosphate	$MgNH_4PO_4.6H_2O$	0.0067
" sulphate	$MgSO_4.7H_2O$	67.5
Manganous carbonate	$MnCO_3$	0.013
" chloride	$MnCl_2.4H_2O$	200.00
" sulphate	$MnSO_4.4H_2O$	130.00
Marsh gas	CH_4	0.00286
Mercuric chloride	$Hg.Cl_2$	6.98
" oxide	HgO	0.00
Mercurous chloride	Hg_2Cl_2	0.00
" nitrate	$Hg_2(NO_3)_2$	100†
" oxide	Hg_2O	0.00
" sulphate	Hg_2SO_4	0.2
Morphine	$C_{17}H_{19}NO_3.H_2O$	0.05
" chloride	$C_{17}H_{19}NO_3.HCl$	5.00
Nickel sulphate	$NiSO_4.7H_2O$	67.0
Nitric acid	HNO_3	all proportions.
Nitrobenzene	$C_6H_5.NO_2$	0.1 (?)
Nitrogen	N	0.0023
" monoxide	N_2O	0.1533
Oxalic acid	$C_2H_2O_4.2H_2O$	11.

NAMES.	FORMULAS.	PARTS.
Oxygen	O	0.0057
Phosphoric acid	H_3PO_4	100†
Plumbic acetate	$Pb(C_2H_3O_2)_2.H_2O$	59.00
“ bromide	$PbBr_2$	0.05 (?)
“ carbonate	$PbCO_3$	0.002
“ chloride	$PbCl_2$	0.9
“ iodide	PbI_2	0.082
“ nitrate	$Pb(NO_3)_2$	53.00
“ sulphate	$PbSO_4$	0.0044
Potassic bichromate	$K_2Cr_2O_7$	10.3
“ bromide	KBr	100 (?)
“ carbonate	K_2CO_3	106.4
“ hydric carbonate	$KHCO_3$	25.00
“ chlorate	$KClO_3$	6.00
“ chloroplatinate	K_2PtCl_6	1.10
“ chloride	KCl	32.8
“ chromate	K_2CrO_4	62.0
“ cyanide	KCN	100†
“ fluosilicate	K_2SiF_6	0.12
“ ferricyanide	$K_3Fe(CN)_6$	40.5
“ ferrocyanide	$K_4Fe(CN)_6.3H_2O$	30.00
“ hydroxide	KOH	213.
“ iodide	KI	140.
“ nitrate	KNO_3	26.
“ oxalate	$K_2C_2O_4.H_2O$	33.
“ hydric oxalate	$KHC_2O_4.H_2O$	4.8
“ permanganate	$KMnO_4$	6.6
“ sulphate	K_2SO_4	9.2
“ tartrate	$K_2C_4H_4O_6$	151.5
“ hydric tartrate	$KHC_4H_4O_6$	0.453
“ sodic “	$KNaC_4H_4O_6.4H_2O$	59.
“ urate	$K_2C_5H_2N_4O_3$	2.24
“ acid urate	$KHC_5H_2N_4O_3$	0.125
Quinine	$C_{20}H_{24}N_2O_2.3H_2O$	0.05
“ sulphate	$(C_{20}H_{24}N_2O_2)_2.H_2SO_4$	0.14
“ bi-sulphate	$C_{20}H_{24}N_2O_2.H_2SO_4$	10.0
Salicylic acid	$C_7H_6O_3$	0.5 (?)
Sodic acetate	$NaC_2H_3O_2.3H_2O$	30.
“ carbonate	$Na_2CO_3.10H_2O$	60
“ hydric carbonate	$NaHCO_3$	10.5
“ chlorate	$NaClO_3$	95.
“ chloride	$NaCl$	35.76
“ hydroxide	$NaOH$	100†
“ nitrate	$NaNO_3$	84.
“ phosphate	$Na_2HPO_4.12H_2O$	14.
“ sulphantimonate	$Na_3SbS_4.9H_2O$	34.5
“ sulphate	$Na_2SO_4.10H_2O$	35.96
“ thiosulphate	$Na_2S_2O_3.5H_2O$	116.
Stannic chloride	$SnCl_4$	100†
Stannous chloride	$SnCl_2.2H_2O$	270.
Starch	$C_6H_{10}O_5$	0.00
Strontic carbonate	$SrCO_3$	0.00554
“ chloride	$SrCl_2$	50.00
“ hydroxide	$Sr(OH)_2$	0.457
“ nitrate	$Sr(NO_3)_2$	55.
“ phosphate	$Sr_3(PO_4)_2$	0.00
“ sulphate	$SrSO_4$	0.0145
Strychnine	$C_{21}H_{22}N_2O_2$	0.05

NAMES.	FORMULAS.	PARTS.
Strychnine chloride	$C_{21}H_{22}N_2O_2.HCl$	5. (?)
Sugar, Cane	$C_{12}H_{22}O_{11}$	300.
" Grape	$C_6H_{12}O_6$	75.
" Milk	$C_{12}H_{22}O_{11}.H_2O$	20.
Sulphur	S.	0.00
Sulphuretted hydrogen	H_2S	0.4918
Sulphur dioxide	SO_2	14.33
Sulphuric acid	H_2SO_4	all proportions.
Tartar emetic	$2(KSbOC_4H_4O_6).H_2O$	7.0 (?)
Tartaric acid	$C_4H_6O_6$	138-
Turpentine (oil)	$C_{10}H_{16}$	0.05 (?)
Urea	CON_2H_4	100.00
Uric acid	$C_5H_4N_4O_3$	0.0067
Zinc carbonate	$ZnCO_3$	0.00
" chloride	$ZnCl_2$	100†
" oxide	ZnO	0.00
" sulphate	$ZnSO_4.7H_2O$	50.5

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