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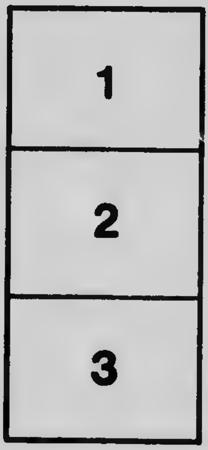
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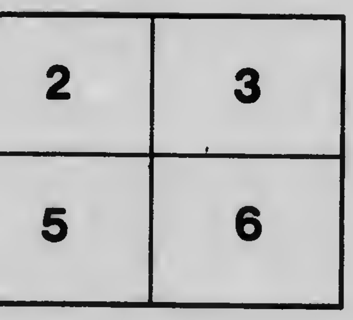
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PAPERS
FROM THE
CHEMICAL LABORATORY.

No. 20.—Chemical and Physical Reactions.

BY

W. LASH MILLER, Ph.D., [illegible].S.C.

Reprinted from the Journal of the Ontario Educational Association,
April, 1902.

TORONTO, 1902.

CHEMICAL AND PHYSICAL REACTIONS.

By W. Lash Miller, Ph.D., F.R.S.C., Toronto.

A Paper Read Before the Educational Association, Wednesday, April 2nd, 1902.

In the last few years it has become quite the fashion for physicists and chemists to write books on the philosophy of their respective sciences, and last year the climax was reached when f the best known of the German Professors of Chemistry, in ic, having been granted a year's holiday by the University orities, spent it in preparing and delivering a course of lec- s on philosophy.* My friend, Dr. J. J. Mackenzie, who was present at some of the lectures, informs me that they were delivered in the largest lecture-room in the University, and were regularly attended by an audience of between three and four hundred; so that, whether the philosophy was good or bad, we may be sure that the lectures were interesting.

There are two matters, rather obvious perhaps, but very important, on which all these amateur philosophers agree. The first is: That the nomenclature, the theories, and the general trend of thought common among scientific men at any time, depend not only on the facts of the science which are known at that time, but also, and in a much greater degree, on the order in which these facts have been discovered and interpreted. The theories put forward to explain the phenomena first studied are retained, and patched, and added to, and forced to explain the new facts as they are brought to light.

We are all such conservatives at heart—whatever we may call ourselves for political purposes—that the mere fact that a theory is an old one, and has been taught us when we were students, seems to be an argument in its favor; whereas, in reality it only proves that the theory in question was invented in the old days, when a great many facts now familiar had not yet been discovered. And the consequence of this conservatism is that when the time has come for the old theory to step aside—when in the struggle for existence it has been defeated by a younger rival—

Published as "Vorlesungen ueber Naturphilosophie, von W. Ostwald." Leipsic: Veit & Comp. 1902.

there are always men to be found who will range themselves resolutely on the side of the old against the new—men who genuinely *believe* in the theory in which they have been brought up, and who may be relied upon to advance and defend any absurdity, if only it afford a chance of escape from the logic of their opponents.

An excellent example is afforded by the contest between the Phlogiston theory and the present theory of combustion, which took place at the end of the eighteenth century. In spite of the advantages of the modern view, obvious enough now, the Phlogiston theory died hard. Some of its adherents pooh-poohed all arguments based on the use of the balance, on the ground that this was a "physical" instrument, and ought not to be brought into a purely chemical controversy. Others endowed Phlogiston with negative gravity, others again identified it with hydrogen—anything but give it up. Priestly, the discoverer of oxygen, remained steadfast to the last: a Phlogistonist he was born, and a Phlogistonist he died.

The second point made by our philosophers is: That the order of discovery, on which so much depends, though settled in some cases by chance, and in many cases by pecuniary and economic conditions, in general follows this law, namely, that the most striking, the most wonderful, phenomena are taken up first; the commonplace and the uninteresting have to wait.

Of all chemical phenomena the most striking are certainly those of combustion with the evolution of flames, light and heat; and, accordingly, we find that the first chemical theory was the Phlogiston theory, or Flame theory. Its downfall was brought about by the study of comparatively obscure reactions of mercury and lead.

After combustion, the reaction between acids and bases has attracted the attention of chemists perhaps more than any other. In this jar I have a mixture of sulphuric acid and water, some litmus, a stirrer, and the bulb of a thermometer; in the burette is ammonia. As the ammonia runs into the jar its smell and taste and the sharp taste of the acid disappear; the thermometer rises, the liquid expands (two pints do not make a quart when one is ammonia and the other sulphuric acid): in short, a "chemical reaction" is taking place. Suddenly the red color of the litmus changes to blue, the smell of ammonia is noticeable, and the thermometer ceases to rise, although ammonia is still flowing into the cylinder—the reaction is over.

The more this reaction was studied the more wonders were discovered. We began with ammonia gas and water, and (liquid) sulphuric acid and water; if water be removed from the contents of the cylinder a solid will remain. Measurement of the quantities of acids and alkalies which react together led to the law of combination in reciprocal proportions; the law of combination in multiple proportions soon followed, to explain which the schoolmaster of Manchester set up his Atomic theory, one hundred years ago—an extraordinary theory, based on extraordinary facts.

Originally invented to explain the law of multiple proportions, the Atomic theory soon became the fundamental doctrine of chemistry. The highest aim of chemistry was to become the "mechanics of the atoms." In the cylinder we saw the bubbling liquid, the rising thermometer, the change of color. We are invited to believe that what was "really" there was: a whirl of atoms and molecules, attracting and repelling one another, rushing past one another, colliding, uniting together. A little universe in the cylinder: an astronomical system on the small scale.

You have read, no doubt—perhaps in some Commentary on the Book of Joshua—of the tremendous quantity of heat that would be generated if this earth should suddenly stand still: or, worse, should collide with some other planet. The heat of combustion of dozens of earths of coal would be nothing to it. When the ammonia planet collides with the acid planet in the astronomical system in the cylinder, a similar quantity of heat must obviously be generated; it is only because these planets are as small as the others are large, that we have escaped with our lives!

Thomsen, of Sweden, and Berthelot, of Paris, were the first to call attention to this consequence of the "mechanics of the atoms." "Every genuine chemical reaction must be accompanied by evolution of heat"—using words borrowed from the science of mechanics, Berthelot baptized this principle the "Law of Maximum Work."

Now, Thomsen was a Northern chemist: but Berthelot lives in Paris, were it is execrably hot in the summer time, and every time he put a bottle of champagne on ice he must have been reminded that there are reactions which are accompanied by a very considerable—and a very grateful and comforting—*absorption* of heat. Lest it should escape his notice, this fact was repeatedly pointed out to him by others, some of whom were perhaps a little too much inclined to jeer at his law of maximum work. But Berthelot had a reply. He silenced all criticism by distinguishing between "chemical" and "physical" reactions. Such reactions as the change of ice into water, of water into steam, and of salt and water into brine, do not come into the province of the law of combination in multiple proportions, and they are in flat opposition to the law of maximum work; so Berthelot read them out of the party, and denied their right to be called chemical.

When we speak of this celebrated chemist "silencing all opposition" to his law of maximum work, these words may be taken, I am sorry to say, in a very literal sense. Besides being a chemist, this remarkable man was a politician, and has occupied the position not only of head of the Department of Education, but of Minister of Foreign Affairs of the French Republic. His word was law in all that concerned appointments in chemistry in the University of France, and more than one French chemist has found that opposition to the scientific views of the powerful Minister meant exile from Paris. For them, the law of maximum work read "Maximum Work and Minimum Pay" in a distant part of the provinces, far from the boulevards of Paris where we have pictured the Head Chemist of France keeping himself comfortable during the hot weather by the help of a heat-absorbing—and therefore non-chemical reaction.

Under somewhat similar circumstances Galileo recanted, consoling himself with the reflection that his words would not affect the motion of the earth. But these men were teachers; a single perfunctory recantation would not serve in their case; they were called upon to *teach* what they believed to be false. If they had consented the motion of the world would have been perceptibly retarded.

Leaving the chemists and returning to chemistry, Berthelot's views met with fair success. Everywhere we find the majority agreed that to boil water is not a "chemical" process, neither is it to dissolve sugar in one's tea. Ice and water, water and steam, are "the same thing," and in the brine both salt and water are present "unchanged." Can one not *see* the water? and *taste* the salt?

The physicists, too, were satisfied. The reactions ejected from the "official tabernacle" of chemistry found a good reception. Regnault, the celebrated experimentalist had made an exhaustive study of the conditions under which water, ice, and steam may be converted one into the other, and finally Clausius perfected the theory of these reactions. Rejected by the chemists and adopted by the physicists, surely these reactions have a good right to be called "physical."

Clausius' theory was a non-chemical theory, there were no atoms in it; and, still more characteristic, it involved the use of the calculus At that time the calculus was a distinctive tool of the physicist, just as previous to Lavoisier the balance was: and the sign *dx* was as characteristic of a work on physics as H_2O is of one on chemistry. How much the times have changed can be seen from this lantern-slide.* This change came about in a very natural manner. Some level-headed manufacturers in place of setting their chemists at work discovering new compounds, which might or might not prove serviceable to them when discovered, set them instead to find the best methods of making products already known, for which there was already a market. And thus a new problem arose in chemistry; to be solved only by studying the influences that modify the nature and quantities of the products of chemical reactions, and the rates at which they take place:—for time is money in a chemical factory as well as elsewhere.

This was the very problem that Regnault and Clausius had solved for the change of water into steam.

One of the most famous of the early experimenters in the new direction, was a chemist who studied the behavior of a great many substances at very high temperature; his faverite piece of apparatus was a white-hot platinum tube. This man went by the appropriate name of Deville. His most important discovery was, that many substances, water for instance, which are readily formed from their elements at ordinary temperatures, are decomposed into their elements again at a white heat. That, in fact, the reaction $2H_2 + 2O_2 = H_2O$ is a "reversible" reaction in the same sense that the reaction "water = steam" is reversible: the one substance turns into the other, or the other into the one, depending on the temperature.

This discovery was a staggerer to the law of maximum work. When water is formed from its elements heat is given out; when it is decomposed heat is absorbed. If both phenomena were to be regarded as "chemical" reactions the law had to be repealed.

I shall not go into details as to the determined attempts that were made to uphold the majesty of this particular law: the last struggles of the phlogistonists a hundred years ago were not

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* Photograph of a page of van Laar's "Mathematische Chemie."

more ingenious and persistent. But the new facts brought to light in the course of the argument have gradually made it clear to every one that the reactions studied by Deville are not isolated, exceptional cases; but that, under suitable circumstances many of the best known "genuine chemical" reactions are as capable of taking place in either direction as are the physical reactions: Water = ice; water = steam; water + salt = brine.

The factors that determine the direction of the reaction—temperature, pressure, concentration—are the same that affect the physical reactions just enumerated; and lastly, while the theory of Clausius has proved capable of predicting the direction and the yield of particular reactions under given circumstances, the Atomic theory cannot even "explain" the formulas and equations by which this result is accomplished. This seems to me a very striking circumstance; every one who has used a "key" knows how easy it is in general to solve a problem when the answer is supplied.

And so, with heavy hearts, perhaps, and some of them later than others, the chemists took to buying Clausius' works and then books on the calculus, as a preliminary to understanding him; a bitter dose for those among them who had all their lives "thrown physics to the dogs," and whose higher mathematics were limited to the expression *D*— x. But, needs must! and now they are writing books on the same lines themselves. You remember the lantern slide?

Naturally enough an "anti-atom" party has arisen. "The mechanics of the atoms raised a barrier where none should exist," they say, "*A la lanterne* with the mechanics of the atoms!" Of course, it is possible to go too far in this direction also, and perhaps the Germans need to be reminded of their own proverbs: "When emptying the bath don't throw out the baby," and "The scum is at the top, and the dregs at the bottom, but the beer is in the middle." The past history of the science however encourages us to hope that if there is any baby at all, or any beer, the chemists will succeed in finding them.

I have endeavored to give a short account of the history of the distinction between chemical and physical reactions. There was thought to be a difference of kind, it is now known to be one of degree only.

At the close of the paper an experiment* was shown, illustrating the reversibility of the reaction,

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$$

An antimony solution was prepared by dissolving 2 grammes of tartar-emetic in 20 cc. of hydrochloric acid sp. gr. 1.148, and diluting with 80 cc. of water.

(*a*) Passed a little H_2S into 5 cc. antimony solution - →
(*b*) Added 15 cc. hydrochloric acid (sp. gr. 1.148) - - ←
(*c*) Added 5 cc. antimony solution - - - - - - - - - →
(*d*) Heated over a Bunsen burner - - - - - - - - - ←
(*e*) Cooled again in a dish of water - - - - - - - →
(*f*) Added 10 cc. hydrochloric acid - - - - - - - - ←
(*g*) Saturated with H_2S under 4 atmospheres pressure →
(*h*) Reduced the pressure to 50 mm. (by a filter pump) ←

NOTE.—The arrows indicate the direction of the reaction ; → meaning precipitation of Sb_2S_3, and ← formation of antimony chloride from the sulphide and hydrochloric acid.

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* W. Lash Miller and F. B. Kenrick, Lecture Experiments, Reversible Chemica Reactions. *Jour. Amer. Chem. Soc.* xxii. 291 (1900).