

**CIHM
Microfiche
Series
(Monographs)**

**ICMH
Collection de
microfiches
(monographies)**



Canadian Institute for Historical Microreproductions / Institut canadien de microreproductions historiques

© 1999

The Institute has attempted to obtain the best original copy available for filming. Features of this copy which may be bibliographically unique, which may alter any of the images in the reproduction, or which may significantly change the usual method of filming are checked below.

- L'Institut a microfilmé le meilleur exemplaire qu'il lui a été possible de se procurer. Les détails de cet exemplaire qui sont peut-être uniques du point de vue bibliographique, qui peuvent modifier une image reproduite, ou qui peuvent exiger une modification dans la méthode normale de filmage sont indiqués ci-dessous.

- This item is filmed at the reduction ratio checked below /
Ce document est filmé au taux de réduction indiqué ci-dessous.**

10x 14x 18x 22x 26x 30x

										✓							
12x		16x				20x				24x		28x				32x	

The copy filmed here has been reproduced thanks to the generosity of:

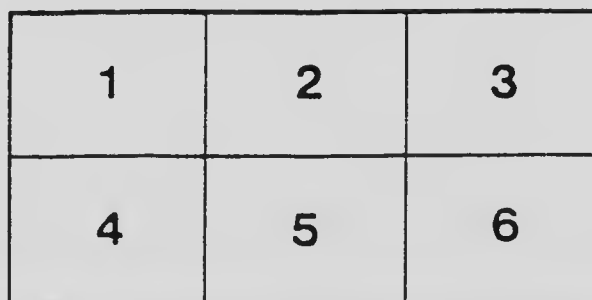
National Library of Canada

The images appearing here are the best quality possible considering the condition and legibility of the original copy and in keeping with the filming contract specifications.

Original copies in printed paper covers are filmed beginning with the front cover and ending on the last page with a printed or illustrated impression, or the back cover when appropriate. All other original copies are filmed beginning on the first page with a printed or illustrated impression, and ending on the last page with a printed or illustrated impression.

The last recorded frame on each microfiche shall contain the symbol $\longrightarrow$ (meaning "CONTINUED"), or the symbol ∇ (meaning "END"), whichever applies.

Maps, plates, charts, etc., may be filmed at different reduction ratios. Those too large to be entirely included in one exposure are filmed beginning in the upper left hand corner, left to right and top to bottom, as many frames as required. The following diagrams illustrate the method:



L'exemplaire filmé fut reproduit grâce à la générosité de:

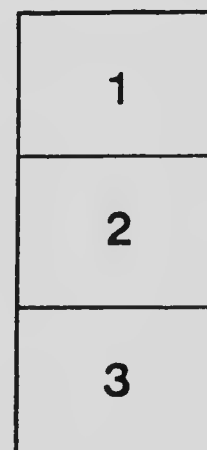
Bibliothèque nationale du Canada

Les images suivantes ont été reproduites avec le plus grand soin, compte tenu de la condition et de la netteté de l'exemplaire filmé, et en conformité avec les conditions du contrat de filmage.

Les exemplaires originaux dont la couverture en papier est imprimée sont filmés en commençant par le premier plat et en terminant soit par la dernière page qui comporte une empreinte d'impression ou d'illustration, soit par le second plat, selon le cas. Tous les autres exemplaires originaux sont filmés en commençant par la première page qui comporte une empreinte d'impression ou d'illustration et en terminant par la dernière page qui comporte une telle empreinte.

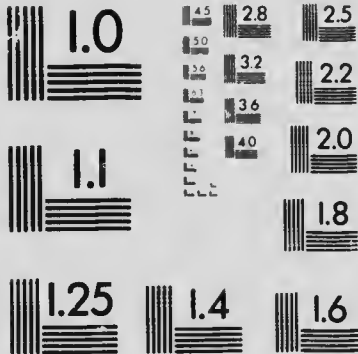
Un des symboles suivants apparaîtra sur la dernière image de chaque microfiche, selon le cas: le symbole $\longrightarrow$ signifie "A SUIVRE", le symbole ∇ signifie "FIN".

Les cartes, planches, tableaux, etc., peuvent être filmés à des taux de réduction différents. Lorsque le document est trop grand pour être reproduit en un seul cliché, il est filmé à partir de l'angle supérieur gauche, de gauche à droite, et de haut en bas, en prenant le nombre d'images nécessaire. Les diagrammes suivants illustrent la méthode.



MICROCOPY RESOLUTION TEST CHART

(ANSI and ISO TEST CHART No. 2)



APPLIED IMAGE Inc

1653 East Main Street
Rochester, New York 14609 USA
(716) 482 - 0300 - Phone
(716) 288 - 5989 - Fax

~~NR 22~~
NR 25
DOMINION OF CANADA
THE HONORARY ADVISORY COUNCIL FOR SCIENTIFIC
AND INDUSTRIAL RESEARCH

REPORT No. 2

THE RECOVERY OF VAPOURS FROM GASES

Particularly of Benzene and Toluene
from Coal Gas

By
HAROLD S. DAVIS, M.A., Ph. D.,
and
MARY DAVIDSON DAVIS, B.A.



Canada

Published by the authority of the Sub-Committee of the Privy
Council for Scientific and Industrial Research

OTTAWA, 1918

DOMINION OF CANADA
THE HONORARY ADVISORY COUNCIL FOR SCIENTIFIC
AND INDUSTRIAL RESEARCH

REPORT No. 2

THE RECOVERY OF
VAPOURS FROM GASES

Particularly of Benzene and Toluene
from Coal Gas

By
HAROLD S. DAVIS, M.A., Ph. D.,
and
MARY DAVIDSON DAVIS, B.A.



Canada

Published by the authority of the Sub-Committee of the Privy
Council for Scientific and Industrial Research

OTTAWA, 1918

TABLE OF CONTENTS.

	PAGE.
I PREFACE.....	3
II INTRODUCTION.....	3
Destructive Distillation of Coal.....	3
Recovery of " Light Oils " from Coal Gas.....	4
The Relation between Maximum Enrichment and the Composition of the Oil.....	6
The Extraction of Toluene only from Coal Gas.....	9
III A NEW METHOD FOR THE QUANTITATIVE ESTIMATION OF VAPOURS IN GASES.....	10
Theory of Method.....	10
Experimental Part.....	11
Efficiency of Method.....	13
The Estimation of the Benzene Content of Coal Gas....	13
Contents of the Rich and Poor Washing Oils.....	14
IV CONCLUSION.....	14
V LIST OF PREVIOUS PUBLICATIONS ON THE SUBJECT BY THE AUTHORS.....	15

00937797

I. PREFACE.

This bulletin is not intended to be a comprehensive treatise on "benzol recovery." It embodies the main results of research carried out for two sessions, 1916-18, in the University of Manitoba, with some reference to practical tests carried out on the Light Oil Recovery Plant of the Toronto Chemical Co., at Sault Ste. Marie, Ont. Most of the results of this research have already been published with fuller details in the papers listed on page 15, but it is hoped in this bulletin to present the conclusions and their significance in a brief collected form.

We wish to acknowledge the substantial grant given by the Advisory Council to aid the prosecution of this work during the session 1917-18. This grant was used to secure as a research assistant Mr. Donald G. MacGregor, who has been intimately associated with the work.

II. INTRODUCTION.

The number of problems arising from the tremendous impetus given the production of benzene and toluene since the year 1914, led to the investigations outlined in this paper.

Benzene is a colourless liquid boiling at about 80° and freezing at about 5.5° , with a specific gravity of 0.87. On account of its theoretical and practical importance, it holds a place almost unique among organic compounds. It is the basic substance from which the greater part of organic compounds constituting what is known as the aromatic series, may be considered to be derived. Many of these compounds such as phenol and aniline are actually synthesized from it on a commercial scale, while great quantities are used in the manufacture of high explosives. It makes an excellent motor fuel, particularly when certain suitable organic liquids are dissolved in it, lowering its freezing point and also preventing the deposition of carbon in the cylinders. Commercial fuels such as "bengas" are formed in this way.

Toluene is also a liquid, of a somewhat higher boiling point and lower freezing point than benzene. It is used in large quantities in the manufacture of the high explosive, trinitrotoluene.

The increase in the number of industries concerned with the manufacture of these substances since the beginning of the war has led to an overproduction of benzene in America; the supply of toluene, however, is still quite inadequate.

These two substances, benzene and toluene, are mainly obtained as by-products from the destructive distillation of coal.

THE DESTRUCTIVE DISTILLATION OF COAL.

When coal is heated in a closed space with air excluded, it undergoes decomposition and a great many chemical substances are formed. At ordinary temperatures some of these are solids, others liquids, and many gases. A great deal of solid material remains in the oven and constitutes *coke*. The mixture of other substances formed

in great volume is drawn off from the coke ovens. The greater part of this gas mixture is composed of such permanent gases as methane and carbon monoxide, but it also contains small quantities of a large number of liquids and solids of various boiling points. As it is cooled, partial condensation takes place, and one or more complex solutions appear. At ordinary temperatures, at least two solutions separate out, one composed largely of water, known as *ammoniacal liquor*, the other made up of a great number of organic substances and known by the general name, *tar*.

It would be a fundamental mistake, however, to suppose that some substances completely condense into the solution while others pass along in the gas. Rather, each substance distributes itself in a certain ratio between the gaseous and liquid phases.

About 1-2 p.c. by volume of the gases from the coke ovens is composed of compounds of the aromatic series, chiefly the hydrocarbons, such as benzene and toluene. They are the chief constituents of what is technically called the "light oil."

Of course a certain amount of these substances stays in the tar, especially if it is separated from the gas at a low temperature; indeed for many years tar was their chief source. But by far the greater quantity of the light oils remains in the coal gas, even after it has been washed with water or otherwise purified. The ratio of the amounts in the gas and in the tar is 20-40: 1.

The amount of each of these vapours in the gas is far below its saturation concentration, i.e. the concentration in equilibrium with the pure solid or liquid substance at that temperature. To separate these vapours from the gas, two main methods have been employed:—

1. The gas is cooled and compressed so that the concentration of the vapours is brought above saturation and they separate out as liquids.

2. The vapours are absorbed into a high boiling oil, from which they are subsequently separated by distillation.

The first method has never been a success commercially: the latter is the one universally employed.

THE RECOVERY OF "LIGHT OILS" FROM COAL GAS.

The theory of the washing process may perhaps be more readily understood if we consider the extraction of one vapour only, e.g. benzene, from a mixture of permanent gases.

Consider a bubble of gas at a definite pressure and temperature, surrounded by a pure washing liquid. The benzene vapour in the gas will dissolve in the oil until the vapour pressure of benzene from the surrounding oil is equal to that in the gas. So the maximum content of benzene which can be absorbed by the oil from the gas is that which gives a vapour pressure of benzene from the solution equal to the vapour pressure of benzene in the gas. Consider a counter-current washing system, such as is represented in Fig. 1, for washing the gas continuously with oil. The gas passing through the system meets the oil travelling in the opposite direction. Fresh oil takes out the last traces of benzene from the gas, since such oil has no vapour pressure of benzene. The oil thereby acquires a vapour pressure of benzene proportional to

its benzene content, and in passing through the scrubbers it continuously meets gas with a higher vapour pressure of benzene until it could leave with a vapour pressure of benzene equal to that in the rich gas entering. The benzene is separated by distillation from the oil and the pure oil re-enters the absorption column.

To ensure complete removal of the benzene from the gas there are two necessary conditions:—

1. The contact between gas and oil in the scrubbers must be sufficiently good to maintain equilibrium at every point.
2. The rate of flow of the oil must be so regulated that the quantity of benzene, carried from the washers per second, shall be equal to the quantity brought in by the gas.

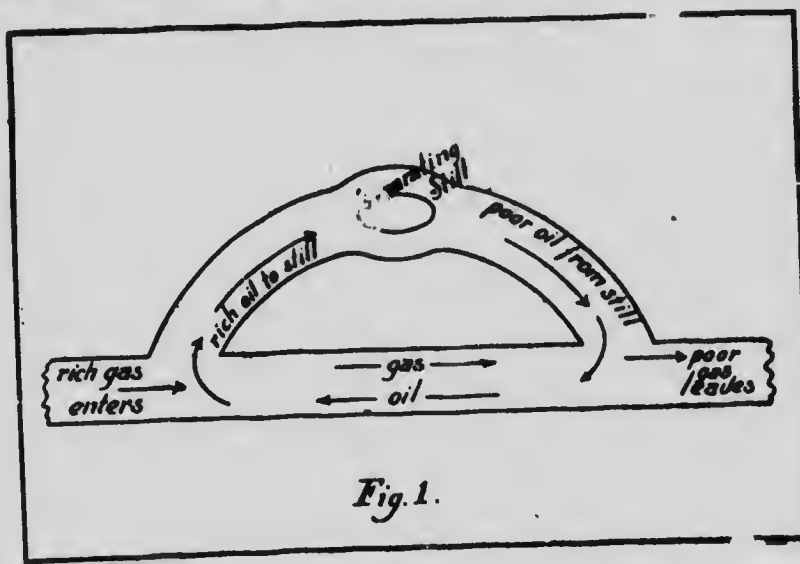


Fig. 1.

Several important points should be noted here:—

1. If just that amount of oil is passed through the washers, which is necessary to completely remove all the benzene from the gas, the vapour pressure of benzene from the oil emerging from the scrubbers (technically the "rich oil") will be equal to that in the rich gas, and all the benzene will have been washed from the poor gas. If less oil than necessary is passed through the washers, the rich oil will be saturated as in the first case. Some of the benzene, however, will pass through in the poor gas, since there is not sufficient oil to remove it. Finally, if more oil than necessary is used, all the benzene will be removed from the poor gas, but the vapour pressure from the rich oil will never be equal to that in the rich gas.

2. If it is desired to completely remove all the benzene from the gas, the flow of oil should be somewhat greater than the amount theoretically necessary, so that the vapour pressure of benzene in the gas will always be greater than its vapour pressure from the oil. This gradient of vapour pressure will tend to dissolve the benzene from the gas into the oil. The more nearly perfect the washing system the smaller

this gradient need be. On the other hand, a very inefficient washing system will extract all the benzene if sufficient oil is passed through the scrubbers. However, since the chief cost in benzene recovery is concerned with the separation of the benzene from the rich oil, it is desirable to use as little washing oil as possible.

3. In order to completely remove the benzene from the gas, the poor oil which enters the scrubbers must be completely free from benzene, *for no amount of washing will ever lower the vapour pressure in the poor gas below that of the poor oil with which it is finally washed.* The presence of benzene in the poor oil means that the steam distillation is inefficient, and does not completely separate the benzene from the washing oil. Such inefficiency may cause a very serious loss to the plant, for the fraction of benzene lost will be the ratio of the vapour pressure of benzene from the poor oil to that in the rich gas. Later in this paper, methods of measuring this ratio will be described.

THE RELATION BETWEEN MAXIMUM ENRICHMENT AND THE COMPOSITION OF THE OIL.

From what has preceded it will be plain that the maximum enrichment of benzene which the oil can assume is the quantity which will give a vapour pressure of benzene equal to the vapour pressure of benzene in the gas. Hence the maximum enrichment will depend upon the content of the gas and the pressure upon it. In order to determine the other factors governing this maximum enrichment, we carried out a series of experiments in which we measured the vapour pressure of benzene from solutions in washing oil, using different concentrations and different temperatures. The results obtained may be summarized as follows:—

1. The vapour pressure of benzene at 33.2° from two solutions in oil, one of approximately double the concentration of the other, was directly proportional to the concentration. That is to say, the vapour pressure of benzene from a solution in oil, and the concentration of benzene in the oil are related according to Henry's Law for the solubility of gases in liquids—a result of great theoretical and practical importance.

2. The ratio of the vapour pressure of benzene from a solution of definite concentration to its saturation pressure was independent of the temperature. (Von Babo's Law.)

It is thus possible to calculate the vapour pressure of benzene from a solution of any particular concentration at any temperature, since the vapour pressure of pure benzene is known at that temperature and also the ratio borne to it by the vapour pressure from a 1 p.c. solution in oil.

The amount of fresh washing oil required for any particular rate of flow of gas depends only on the temperature of washing. The benzene content of the gas does not affect it; for if this content is increased, then the maximum content in the rich oil is increased in the same proportion.

Now the efficiency of an oil for absorbing benzene from gases is determined by the magnitude of the vapour pressure of benzene from its solution in the oil, or to look at it from another point of view, the efficiency of an oil is determined by its power to lower the vapour

pressure of benzene when dissolved in it. For dilute solutions in common solvents, this power of lowering the vapour pressure is inversely proportional to the molecular weight of the dissolved substance, so that if the molecular concentration of the solution is known, the proportional lowering of the vapour pressure of the solvent can be calculated from a well-known formula. Since benzene and the washing oil used were soluble in all proportions we suspected that this relation might hold for very concentrated solutions; results confirmed this supposition.

The average molecular weight of the oil determined by the freezing point method was found to be 205. From this, the vapour pressure from a 99 p.c. solution of oil in benzene, i.e. a 1 p.c. solution of benzene in oil, was calculated to be 0.0263, in excellent agreement with the experimental result 0.026.

The determination of the molecular weight of an oil when dissolved in benzene seems therefore to afford a good method for testing the efficiency of the oil for absorbing benzene or other vapours from gases; the lower the molecular weight, the greater the efficiency.

A few tests were made on absorbing oils used at a light-oil recovery plant, in order to ascertain if this method of standardization would hold. In general it was found that oils of low molecular weight, 200-230, were good absorbers in practice, while an oil with a much higher molecular weight, 280, had been rejected as inefficient. It is hoped that research may lead to the development of washing media with lower molecular weights than those of the present absorbers, which at the same time will have the desired qualities of fluidity, boiling point, etc.

So far we have considered the removal of one vapour only from the gas. Similar considerations apply to the removal of a mixture of vapours such as those which make up the "light oils."

In considering the process of absorption of light oils into washing oil, account must be taken of the following premises, experimental confirmation of which is cited further on in the paper:—

1. Each separate vapour contained in the gas dissolves in the washing oil, independently of the other vapours present, until equilibrium is reached between its vapour pressure in the gas and its vapour pressure from the oil solution.

2. When washing of moderate efficiency is employed, equilibrium between the oil and each of the light oil vapours is reached much more quickly than has often been supposed.

Of course each of the constituents of the gas, other than the light oils, also dissolves in the washing medium until corresponding equilibrium is reached, but the amount dissolved is so small that its effect may be neglected.

Now, although the oil constantly absorbs vapours from the gas, equilibrium between the vapour pressures of each substance in the gas and from the oil being closely maintained at every stage, it does not follow that the oil becomes saturated with every vapour at the same stage of washing. Rather, the stage at which the oil becomes saturated with respect to any one vapour is determined by the saturation pressure of the pure liquid of the same composition as the vapour in question.

Consider now the absorption of benzene and toluene vapours from the gas into the washing oil. The benzene content in the rich oil will be at its maximum when it gives a vapour pressure of benzene equal to that in the rich gas. At this stage the dissolved toluene only gives a pressure from the oil equal to a fraction of the toluene pressure in the rich gas. This fraction can be shown to be equal to the ratio of the saturation pressure of pure toluene to that of pure benzene, so that when the oil is saturated with benzene it is only $\frac{1}{10}$ saturated with toluene. Any attempt to obtain a higher percentage of toluene in the rich oil will result in loss of benzene, for some will pass now through unabsorbed.

If by the maximum enrichment of the washing oil is meant the maximum quantity of light oil which it can contain, without any light oil passing through unabsorbed, then it is reached when the vapour pressure from the washing medium of the lowest boiling compound in the light oil, in this case benzene, is equal to its pressure in the rich gas.

From the equation for the lowering of the vapour pressure referred to above, using an oil with an average molecular weight 205, the following calculations can be made for a gas with a vapour pressure of benzene of 0.6 cm. and of toluene of 0.15 cm.:—

1. The possible concentration in oil at 26° for benzene is 2.3 p.c. and for toluene 2.3 p.c.

2. When the oil is saturated with benzene, it will have taken up only 0.68 p.c. of toluene.

The addition of the toluene (mol. wt. 92) will also lower the average molecular weight of the solution in which the benzene is dissolved, thereby increasing the possible concentration of benzene.

Similar considerations apply to the small quantities of high-boiling compounds which exist in the gas and which are soluble in the oil. These factors would result in a steady slow increase in the amount of the total hydrocarbons absorbed, over a comparatively long period.

To test these conclusions, the following experiments were carried out:—

1. Two flasks were filled with known weights of absorbing oil, and illuminating gas was passed through them for a period of two months, the gain in weight being recorded daily.

2. Two flasks filled with absorbing oil were connected in series to the gas supply, and the gain in weight of each recorded at certain equal intervals.

In the case of 1 the following results were obtained:—

- (a) The curves plotted to represent the gain in weight of the flasks rose quite sharply at first, then gradually fell off. At the end of the time the greatest gain in weight of the oil was 5 p.c., with the curve still rising.

- (b) After the curves began to fall off, due undoubtedly to the fact that the benzene was no longer being absorbed from the gas, they began to fluctuate with changes in atmospheric pressure. A low pressure would lessen the concentration of benzene in the gas, so that the oil would give up some of its benzene to the gas. When this amount was greater than the amount of higher-boiling compounds still being absorbed from the gas, the result was a loss in weight of the oil.

The same result would follow a rise in temperature of the absorbing flasks.

In the case of 2 the results were:—

(a) The second flask did not begin to gain in weight until there was a perceptible vapour pressure of the light oils from the first flask.

(b) When the pressure on the second flask was increased, an immediate gain in weight was recorded. When the extra pressure was taken off, the weight immediately fell off again.

To sum up, our experiments showed:—

1. Equilibrium was closely maintained between the vapour pressure from the oil and that from the gas, although the washing was not particularly efficient.

2. The oil continued to gain in weight long after it had reached its maximum benzene content, and this increase in weight continued over a very long period.

THE EXTRACTION OF TOLUENE ONLY FROM COAL GAS.

The shortage of toluene and the overproduction of benzene have brought up in this country the question raised some time ago in Europe as to whether it is possible to obtain all the toluene from the gas without extracting all the benzene. As has been pointed out already, it is theoretically possible to extract any of the constituents from the gas, provided the proper amount of oil is used.

In any washing system the absorption process is really selective, some of the constituents being wholly extracted, others only partially. The rich oil is always saturated with respect to the latter. Since the vapour pressure of pure toluene is considerably less than the vapour pressure of pure benzene, it follows that much less oil is required to completely remove the toluene than to completely remove the benzene. It is only necessary to have that quantity of oil which will give a vapour pressure of toluene equal to that in the rich gas. This quantity of oil will also remove all the xylenes and other high-boiling constituents, but will only partially extract the benzene.

Experiments conducted at absorption plants, however, have shown that if the flow of oil is much below that required to nearly extract all the benzene, the toluene yield of the plant is decreased. The following reasons may be given for this decrease in the yield of toluene:—

1. If the scrubbing system is inefficient, a considerable excess of oil over the amount theoretically required is necessary in order to provide a solution gradient for the toluene, as previously described for benzene.

2. The steam stills for separating the light oils may not be efficient and may leave a certain vapour pressure of toluene in the poor oil. As has already been pointed out in the case of benzene, the proportion of toluene lost will be in the direct proportion of the vapour pressure of toluene from the poor oil to that in the rich gas. Now, the time occupied by any quantity of oil in passing down the steam still is fixed, as is the amount of heating and the quantity of steam to which it is exposed. We may therefore assume that as the amount of toluene in the rich oil is decreased, the amount left in the poor oil will also be

decreased. Hence, with an excess of oil, the poor oil coming from the still will contain but little toluene, so that the amount left in the poor gas will be correspondingly small. The result is a comparatively high yield of toluene. The steam distillation still is therefore a very important part of a light-oil recovery plant; nothing can compensate for its inefficiency.

III. A NEW METHOD FOR THE QUANTITATIVE ESTIMATION OF VAPOURS IN GASES.

A great need has been felt, by those engaged in the commercial production of light oils, for methods of gas analysis requiring only small samples and giving a rapid estimation of the content of these vapours either collectively or individually. Such methods would make it possible to find the conditions of production necessary to obtain the maximum concentration of each aromatic substance, and would also permit the efficiency of absorption processes to be checked at every point.

Methods at present employed require the absorption of the light-oil vapours from the gas over a comparatively long period, so that the results represent the average values for this period. Such a method is wholly unsuitable for checking the efficiency of the different parts of the washing system, since conditions such as the rate of flow of the gas, its composition, the temperatures of the washing towers, etc., are continually changing.

We have developed a new method for the quantitative estimation of vapours in gases, which requires only a small sample of gas, 150-350 cc. and which can be carried to completion in $\frac{1}{2}$ -1 hr.

THEORY OF METHOD.

It is a generally accepted principle that the vapour pressure from a liquid is independent of the kind of gas above it, provided the gas is inert. Deviations from this law are well known, but it holds with surprising accuracy in the case of a mixture of benzene and air at atmospheric pressure.

Consider two closed flasks, as in Fig. 2, connected by a manometer and filled with air at atmospheric pressure. If now a small sealed bulb containing a volatile liquid be broken in each, the liquid will partially evaporate, and if the temperatures of the flasks remain the same, the same additional pressure will be developed in each, so that the manometer connecting them will register no difference in pressure. Even if the temperatures of the flasks do vary, no difference in pressure will be recorded until there is a relative difference in temperature between them.

Now, suppose that one of the flasks had contained a certain quantity of the vapour of the volatile liquid corresponding to a pressure less than the saturation pressure. When the small bulb of liquid was broken in this one, the liquid would not add all its vapour pressure to the pressure already in the flask, for part of that was already due to its vapour. It would add only the amount of pressure necessary to bring its pressure up to saturation, and since the total saturation pressure

was added to the pure air in the other flask, the manometer connecting the two would register a pressure equal to the pressure of vapour in the original gas. The following points are of especial importance:—

1. Each of the sealed bulbs must contain considerably more liquid than is required, at the temperature of the experiment, to saturate the atmosphere of the flask into which it is broken with the vapour in question.

2. It is essential that the substances remaining in the bottoms of the flasks after the bulbs are broken shall have the same composition and shall give the same pressure of the vapour in question, and that this pressure shall be greater than the original pressure of the vapour in the gas.

3. A solid can be used in the bulbs in place of a liquid, if the substance exists as a solid at the temperature of the experiment.

4. A solution containing the liquid of the vapour to be measured can be used in the bulbs provided there is sufficient of this liquid to give a pressure greater than the pressure in the gas. A solution will offer advantages over the pure liquid if less total pressure is developed from it, so that the danger of leakage from the flasks is decreased. Further, if a solution is used which gives partial pressures of two or more separate substances, and if these substances were contained in the original gas as vapours, then the differential pressure developed between the two flasks will be equal to the sum of the original partial pressures of these vapours in the gas.

5. The partial pressure of any particular vapour in a sample of gas is independent of the temperature of the gas, provided that the total pressure on the gas remains constant while the volume can change with the temperature, and provided the vapour remains always unsaturated and obeys the simple gas laws. An apparatus constructed on this principle will, therefore, measure a definite quantity: viz., the pressure of the vapour in a gas at atmospheric pressure. This measurement can easily be reduced to standard pressure.

6. Though the partial pressure of a vapour is independent of the temperature, the actual weight of the vapour contained in unit volume of the gas depends on the temperature. For one vapour, this weight may be calculated from the partial pressure, on the assumption that the vapour gives the same partial pressure as it would if it were a true gas at that temperature and molecular concentration. In the case of two or more vapours, the actual weight of each vapour cannot be so calculated, unless the relative proportions of the vapours are also known. This, however, does not impair the usefulness of the method for comparative tests on the total quantities of several vapours, e.g. light oils, in different samples of gas.

EXPERIMENTAL PART.

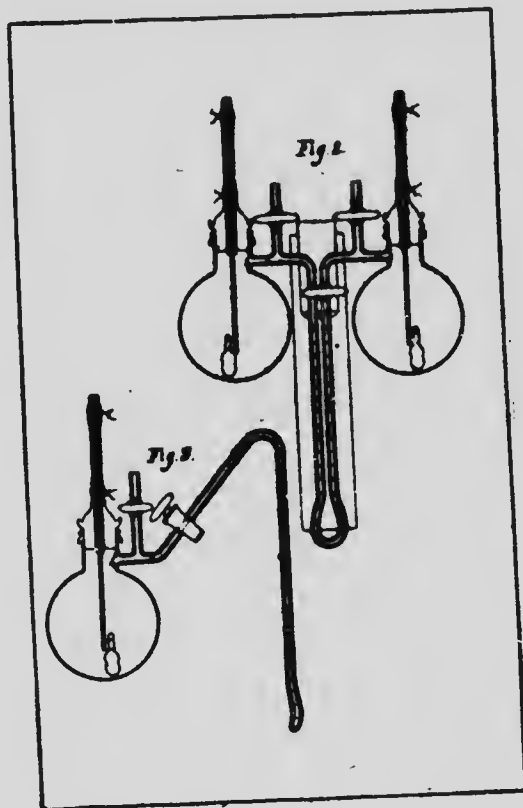
The apparatus used is of the form shown in Fig. 2. Details of the apparatus can be obtained by reference to Paper No. 2 listed on page 15.

The essential features are:—

1. Two compensating flasks connected by a manometer.
2. That these flasks be air tight, but that they can be opened to atmospheric pressure.

3. That when the flasks are closed the bulb of liquid (or solid) can be easily broken.

A modified form of apparatus is shown in Fig. 3. This form is so arranged that the flasks are close together and the manometer tube is led out from them, so that they may be placed in a bath of any kind, while the manometer remains outside.



The procedure is as follows:—

- (a) Attach the bulbs filled with the desired liquid (or solid).
- (b) Evacuate the flask which is to be filled with the gas sample, i.e. the flask on the same side of the manometer as the stop-cock. We have evacuated by means of a water pump, which rapidly reduced the pressure to less than 1 cm. of mercury.
- (c) Fill this flask with the gas sample and close the outlet stop-cock. We have found small gas holders (about 300 cc.) with stop-cocks at both ends most satisfactory for collecting gas samples. The gas is displaced from them into the apparatus by means of mercury. Samples of gas should not be allowed to stand over water, as the solubility of the light oils in water is quite large for small samples of gas.

(d) Let the apparatus stand until equilibrium is reached. Open the stop-cock in the manometer, equalize the pressures by bringing each flask to atmospheric pressure. Close both outlets.

(e) Break the bulbs, preferably the one on the gas side first, as the pressure will develop the other way.

(f) Let stand until equilibrium is reached; 10-15 min. and 30-60 min. for flasks of 150 and 350 cc. capacity, respectively.

(g) Clean and dry the apparatus. We have done this by drawing warm air through each side.

Considerable care must be taken with blowing the bulbs, which *must* have thin bottoms. A person with ordinary laboratory technique, however, can easily prepare a large number in a short time. Details of the procedure we found most satisfactory are given in Paper No. 2 listed below.

While determinations can be made quite successfully in a room moderately free from draughts, more accurate work requires a water bath, kept stirred. For the latter, the modified form of apparatus is required.

EFFICIENCY OF THE METHOD.

In order to check the method we ran a series of experiments in which different known quantities of benzene in air were estimated. The results were very satisfactory, the average agreement of the known and measured values for thirteen experiments being within 1.5 p.c.

When, however, the air contained toluene vapour in addition to the benzene, it was found that the toluene rapidly dissolved in the liquid benzene in the bottom of the flask. As a result, the differential pressure recorded was not the pressure of benzene, but the pressure of benzene plus the pressure of the toluene dissolved out. If sufficient liquid benzene was used all the toluene dissolved out, and the differential pressure then represented the sum of the benzene and toluene pressures in the original sample of air.

It was found experimentally that any one of the following liquids used in the bulbs gave the total light-oil content of illuminating gas, the results agreeing satisfactorily:—

1. Benzene only (under certain conditions).
2. A solution of equal volumes of benzene and toluene.
3. A solution of equal volumes of benzene, toluene, and xylene.

In the first case, the toluene and xylene from the gas dissolve in the benzene. In the second case, the pressures of both the toluene and benzene from the solution are greater than their original pressures in the gas, and they are estimated by the same principle. In the third case all three vapours are estimated in this way.

THE ESTIMATION OF THE BENZENE CONTENT OF COAL GAS.

It has already been pointed out that the amount of benzene in a sample of air can be accurately determined by the Differential Pressure Method, using bulbs of liquid benzene. On the other hand, when the sample in question is illuminating gas, which also contains toluene and other light oils, the following factors must be considered:—

1. The toluene and other light oils dissolve in the liquid benzene so that their pressures are almost entirely removed from the gas,

while, at the same time, these dissolved substances lower the vapour pressure of the benzene.

2. A less serious error is caused by the gases other than the light oils dissolving in the liquid benzene.

In order to eliminate these sources of error, we have conducted investigations on gases by the Differential Pressure Method, using bulbs filled with solid benzene, and immersing the apparatus in a bath below the freezing point of benzene, 5.48° . It is well known that the solubility of permanent gases in a solid, such as frozen benzene, is vanishingly small, so that the second source of error mentioned above is completely removed.

Again, the vapour pressure from the solid benzene is, at any fixed temperature, independent of the solution by which it is surrounded, so that while the solid benzene is present at equilibrium there can be no lowering of the vapour pressure.

The experiments were highly successful. It was found possible to determine the benzene content of a gas in this manner with considerable accuracy, even when fairly large quantities of toluene and xylene were present in the gas.

It is quite easy to keep a bath for the apparatus at a temperature near 0° with ice and water. The chief difficulty we experienced was in freezing the small bulbs of benzene, for they could be enormously supercooled. The best method is to freeze them in the escaping stream of liquid and gas from a carbon dioxide cylinder. Once frozen, they are of course quite stable for several degrees above zero.

As far as we know this is the only method by which the benzene content only can be found accurately in a small sample of gas which contains also its homologues.

CONTENTS OF THE RICH AND POOR WASHING OILS.

In order to measure the vapour pressures of the light oils from the rich and poor washing oils, we have used two methods:—

1. A small amount of air was shaken up with a large amount of washing oil until equilibrium was reached. The quantity of oil must be so large that its concentration of light oils is not appreciably affected by the amount which evaporates into the air. The air was then drawn into a Differential Pressure Apparatus and analysed for its total light-oil content.

2. About 5 gm. of the oil was sealed up in a thin-bottomed bulb. The bulb was then placed in a Differential Pressure Apparatus whose flasks had a small capacity. After equilibrium was reached, the bulb was broken and the pressure of light oils from the washing oil measured directly.

By means of these measurements, and those previously described in this paper, a close check can be kept on the efficiency of the washing system, and on the steam distillation stills of a light-oil recovery plant, and this in general will lead to an increased production.

IV. CONCLUSION.

It is possible that the methods outlined in this paper may be of use in other fields besides light-oil recovery. In natural processes and

in many industries it often happens that large quantities of gas mixtures are produced which contain the vapours of valuable liquids. Thus, natural gas often contains, as vapours, quantities of the substances which constitute gasolene, while methyl alcohol and acetone vapours exist in the gases given off during the destructive distillation of wood. The method may also prove useful for the quick estimation of the water content of air.

Finally, it is hoped that by this method of analysis it will be possible to obtain more precise knowledge concerning the effect of conditions of coking on the production of light oils. We have done some preliminary work on the variation of the light-oil content in illuminating gas with the different stages of coking, but extensive research with good equipment is needed in this field from which so much information of great economic value is still to be obtained.

V. PREVIOUS PUBLICATIONS ON THE SUBJECT BY THE AUTHORS.

1. The Extraction of Aromatic Hydrocarbons from Gases by means of Liquid Absorbents, by Harold S. Davis. University of Manitoba publications, 1917.
2. A new Method for the Estimation of Vapours in Gases, by Harold S. Davis and Mary Davidson Davis. J. Ind. and Eng. Chem. (In Press).
3. The Application of the Differential Pressure Method to the Estimation of the Benzene and of the total Light Oil Content of Gases, by Harold S. Davis, Mary D. Davis and Donald G. MacGregor. J. Ind. and Eng. Chem. (In Press).
4. Studies on the Absorption of Light Oils from Gases, by Harold S. Davis and Mary D. Davis. J. Ind. and Eng. Chem. (In Press).
5. "A Process for the Quantitative Estimation of Vapours in Gases." U.S.A. Patent No. 1,272,922, July 16, 1918.

CLIFTON, COLCHESTER CO.,
Nova Scotia.

