

ried on by Mr. H. E. Lloyd, of The Barrett Co., and the results obtained by him, although not conclusive, fully indicated the need for a more searching investigation into the problem.

One of the first things that attracted my attention while considering this problem was the mental haze of the practical employee when dealing with the simple mathematical relations involved in calculating coefficients of cubical expansion. I have found by personal observation and experience that very many chemists (strange to relate) do not relish the mental gyrations of the mathematician. Even engineers had been somewhat lax, for the trade had been making no correction for the coefficient of cubical expansion of the container and in consequence did not calibrate the container at any definite temperature.

Although it is a repeating of very elementary matter, I will give here the formulas which are used in determining and applying coefficients of cubical expansion.

The change in volume per unit volume per degree change in temperature is called the coefficient of cubical expansion.

Thus:

$$V_2 = V_1(1 + at)$$

in which a is the coefficient of cubical expansion.

Since in practice the container is always an expanding material, the apparent expansion is less than the real. The container expands, partly compensating for the expansion of the material.

The relations are generally expressed by the equation

$$A + C = T$$

in which A is the apparent coefficient of cubical expansion of the liquid, C is the coefficient of cubical expansion of the container, while T is the true coefficient of cubical expansion of the liquid.

This relation is strictly true only for the case where the container is always kept full, as in most specific gravity determinations with a pycnometer. When the liquid rises and falls in a steel container the deviation in the apparent coefficient from this relation can be shown mathematically to be about 3 parts in 100,000 per degree Centigrade.

This is of course much smaller than the errors of measurement in practice. Consequently the form given above (which is exceedingly simple) may be regarded as correct for all cases.

One of the first points considered was the relative effects of the variations in conditions in a large container, as for instance: stratification, sedimentation, inequalities of temperature, etc., which would not be pronounced in the small volume of a specific gravity bottle in which the previously used coefficient of cubical expansion of creosote oil had been determined. Accordingly, a hollow iron container with a capacity of about $2\frac{1}{2}$ gal. was fitted with a screw cap carrying a glass tube to serve as the neck of a pycnometer, and with three thermometers placed at different distances from the center. This was placed in a 50-gal. water bath provided with an agitator, and suitable burners, etc., for applying heat. A glass pycnometer was placed in the same bath in order to duplicate the work in a small volume. No essential difference in results was obtained, showing that the difficulty lay somewhere else.

The iron container was twice calibrated with water and the apparent coefficients of expansion of water in iron calculated over the ranges: $15.5\text{--}25^\circ\text{C.}$, $25\text{--}38^\circ\text{C.}$, $38\text{--}60^\circ\text{C.}$, $60\text{--}80^\circ\text{C.}$

These observed values were then subtracted from the true zero ones, giving by difference the coefficient of cubical expansion of iron. The mean of one set of experiments gave 0.000037 for this, while the mean of another set gave 0.000036. These results were considered very satisfactory, for the accuracy of 0.00001 to 0.00002 is from 5 to 10 times more than the previously accepted coefficient of cubical expansion of creosote oil (0.00079 per degree $C.$). The subsequent work with oils, however, was probably not quite so accurate, for the oils were much

harder to bring to a constant volume, probably because of a lower heat conductivity.

In the work with oils the container was filled at 80°C. and later made to the mark at about 60° , 38° , 25° , 15.5° , with weighed water. The pycnometer was made to mark with the oil when used with liquid oils. With solid oils it was filled at 80° , made to mark with oil at 60° , and then with water at temperatures below 60° .

Two creosote oils were examined: A refined liquid creosote oil, hereafter referred to as No. 1, which does not solidify in the range covered, and an oil representing a commercial grade of creosote oil according to the standard specifications of the American Railway Engineering Association, hereafter designated as No. 2, which gave a small amount of crystals at 15.5°C. The coefficients found for these oils checked very satisfactorily in duplicate experiments both in the large container and the small specific gravity bottle. The mean true coefficients found (0.000703 for No. 1 and 0.000724 for No. 2) were slightly lower than the previously accepted value (0.00079). The apparent coefficients in steel tank cars would be even lower. These findings, however, did not explain the discrepancies encountered in practice.

The thing which was especially interesting to me was the absence of variation in the coefficients with temperatures. The coefficient of cubical expansion of water shows a huge variation over the interval in question ($15\text{--}80^\circ\text{C.}$). This variation amounts to from 200 to 300 per cent.

The influence of salts upon the coefficients of cubical expansion of these oils was next studied by salting the same oils with pure naphthalene for a limpid point of about 40°C.

This mixture consisted of No. 1 oil 71.5 per cent and naphthalene 28.5 per cent by weight. A little more than 30 per cent distilled below 235°C. In the upper ranges this mixture contracted regularly with descending temperature and gave the coefficients found for the original No. 1 oil. At temperatures below 38°C. , however, the crystallization caused an enormous shrinkage. In one experiment the average coefficient between 38° and 25° was from 4 to 5 times as great as that for liquid creosotes. In a duplicate experiment the value was from 3 to 4 times as great. This abnormal behavior was always exhibited below 38° , that is, below the temperature at which crystallization became important. The expansion and contraction observed was of course the resultant of three factors: (1) The mechanical expansion or contraction of the liquid phase. (2) The mechanical expansion or contraction of the solid phase. (3) The volume change due to the solution or crystallization of the solid phase. Now it is very probable that the coefficient of cubical expansion of solid naphthalene is much less than that of the liquid creosotes. (Beilstein reports the density at 4° and 15°C. to have practically the same value.) Undoubtedly these huge and irregular coefficients are caused by the crystallization.

Naphthalene dissolves in creosote oil with an increase in volume; 1 qt. of naphthalene and 3 qts. of a salt-free creosote oil will make more than 1 gal. of mixture.

The magnitude of the volume change accompanying the solution or crystallization is unfortunately very large. Some of the experimental results obtained showed that an error of as much as 404 gals. per 10,000 gals. in a temperature interval from 110° to 70°C. might easily be possible, using the old coefficient of cubical expansion.

The word "unfortunately" is used advisedly. The process of crystallization and solution is very slow when contrasted with the mechanical expansion or contraction of the solid and liquid phases. In consequence, with varying temperatures there may be, and probably often will be, incomplete equilibrium between the two phases. Accordingly, the observed volume of the total will vary a great deal with the immediate past history

of the mixture. It is only to be expected, therefore, that the results obtained in measuring the coefficient of expansion of a partially solid oil will not check unless great care and a sufficiently long time is allowed to elapse at each temperature to insure that the crystallization or solution has attained equilibrium. Since in actual practice it is very often not desirable or even possible to maintain a tank or tank car at exactly the same temperature for a sufficiently long time to insure equilibrium between the solid and liquid phases before determining the volume, the practical value of such a coefficient, even when obtained with the greatest care, is very doubtful. Variations in the amount of crystallizable substances from time to time in the same grade of oil will seriously affect the coefficient.

Another possible complication is the variation in the character of the crystallizing solid. Suppose anthracene crystals appeared instead of naphthalene crystals, what would happen then?

This point was investigated by dissolving crude anthracene in the No. 1 oil. The work was abandoned, however, because of the extremely slight solubility of this compound in this oil; less than 5 per cent of the solid gave a limpid point of 40° C., while it took more than 28 per cent of naphthalene to give the same limpid point. With less than 5 per cent of anthracene present, it was not deemed worth while to examine the volume relations of the mixture.

Naphthalene is, of course, the most important solid. Moreover, its similarity in physical properties, composition, and structure to other coal-tar compounds leads one to believe that an analogous effect occurs when most of the other solids crystallize or dissolve.

The magnitude of the error, and the inherent insurmountable obstacles encountered when one attempts to predict the volume of an oil at a temperature at which it may be partly solid, may ultimately revolutionize the present practice of buying and selling oils by volume.

The simplest expedient, of course, is to buy and sell by weight.

At present, however, such a departure is so radical that it is practically impossible.

It is probable that a temperature of 100° F. will be widely adopted as the standard, displacing the 60° F. of the present, since at 100° F. the creosotes are liquid. The trade situation was somewhat amusing—we had been buying and selling gallons at 60° F. without knowing the volume relations which relate 60° F. to the customary temperatures of trade.

II—THE VAPOR DENSITIES OF COAL-TAR FRACTIONS

Although the composition of the higher fractions from the distillation of coal tar has long been a subject for study and speculation, and many of the compounds present have been isolated and identified, the quantitative composition of these interesting mixtures still remains a matter of mystery. It is probable, however, that the number of compounds present is very great.

This question was of especial concern to the engineering department of The Barrett Company in the design of large capacity condensing systems, since a knowledge of the exact composition would give by a simple calculation the vapor density of any fraction, and in turn a key to a design for a condenser embodying economical construction and efficient fractionation.

It fell to the lot of Mr. Gainey and myself to investigate these vapor densities which, of course, could be ascertained only by experiment.

Of all the methods for determining vapor densities, the Victor Meyer is the best suited for a problem of this kind, since it is applicable over a very wide range of temperatures and pressures and is equally useful for pure compounds and mixtures. Other methods afford some of these advantages but not all. Thus the Dumas could be used at the temperatures and pressures desired but, unfortunately, is inapplicable

to mixtures whose components have different boiling points. The Dumas, you will remember, calls for a light glass bulb drawn to a point and weighed. The substance under examination is introduced and the bulb is then placed in a constant temperature bath while a certain pressure is applied (generally atmospheric) until the bulb is completely filled with vapor and the excess vapor has been removed. The bulb is then sealed off and weighed. In this procedure, the lower boiling components would probably be removed from the bulb before the higher were completely vaporized, so we could not employ this to determine the vapor densities of fractions of the coal-tar distillate. The Gay-Lussac-Hofmann method, which consists in the introduction of the substance into the vacuum above an upright barometer, can be employed equally well for pure compounds or mixtures, but is unfortunately limited to temperatures where mercury exerts no appreciable vapor tension, that is, below 150° or 175° C., and could not be used for coal-tar fractions whose boiling points in some cases are higher than 400° C.

For the sake of a clear understanding of what follows, I will recall the principles which are involved in the Victor Meyer method of determining vapor densities by air displacement.

In its simplest form the apparatus for this method consists of a long "pear-shaped" glass tube provided with two side tubes near the upper end. One of these side tubes is connected through a rubber tube to a gas burette. The lower portion of the glass pear is brought to a temperature which is sufficiently high to insure complete volatilization of the test material. This material is then introduced through the stoppered opening in the top of the tube and dropped at the proper moment by withdrawing a glass rod thrust through one of the side tubes. Upon reaching the hot portion of the pear, the material vaporizes, driving up ahead of it and over into the gas burette, air, which, of course, does not condense and can be measured as soon as the system reaches equilibrium. From a knowledge of the weight of the material, the volume of the air driven over into the gas burette, and its temperature and pressure, it is possible to calculate the density of the test material in the vapor form.

A modification of the method consists in attaching the pear to a manometer and measuring the increase in pressure at constant volume caused by the volatilization of the test material. This modification is particularly useful when it is necessary to employ a diminished pressure to insure complete volatilization, since it is very difficult to measure an increase in volume in a system maintained at a very low pressure.

Such considerations are so preliminary and general that I feel compelled to apologize for presenting them to you.

The first consideration peculiar to the vaporization of these coal-tar distillates was the question of coking. To throw suddenly these hydrocarbon-containing mixtures upon glass surfaces heated to several hundred degrees Centigrade without cracking and coking them was indeed a problem, especially when the boiling point ranges ran above 350° and 400° C. Decomposition by cracking and coking had to be guarded against in the distillation which gave the test fractions also.

A composite oil typical of the distillate from coal tar, between first runnings and hard pitch, was distilled in the laboratory and cut to 50° C. fractions. This oil began boiling at 200° C. under atmospheric pressure, and the distillation was continued under atmospheric pressure for two fractions until the vapor temperatures reached 300° C. In order to forestall cracking, the distilling bulb was then allowed to cool and an absolute pressure of 50 mm. of mercury was then applied. The oil began to distill once more at 175° C. and continued to distill until a temperature of 370° C. was attained. Further heating only produced decomposition into non-condensing vapors. In all, 87 per cent of the oil distilled and five 50° fractions were obtained.

VAPOR DENSITY RESULTS

COMPOUND	Formula	B. P. at 760 mm.	Vapor density at 0° C. and 760 mm.		COAL-TAR FRACTIONS Boiling Point Ranges
			Calculated	G. per cc. Obtained	
Naphthalene di-hydride.....	C ₁₀ H ₁₀	200-210° C.	0.00579	0.00579	199-249° C. under 755 mm. Hg
Naphthalene.....	C ₁₀ H ₈	218° C.	0.00572		
Methyl naphthalenes.....	C ₁₁ H ₁₀	240-243° C.	0.00634		
Diphenyl.....	C ₁₂ H ₁₀	254° C.	0.00688	0.00667	249-296° C. under 755 mm. Hg
Acenaphthene.....	C ₁₂ H ₁₀	278° C.	0.00688		
.....	0.00691	180-229° C. under 50 mm. Hg
Anthracene.....	C ₁₄ H ₁₀	360° C.	0.00794	0.00867	229-276° C. under 50 mm. Hg
Methyl anthracene.....	C ₁₅ H ₁₂	Above 360° C.	0.00858	0.1047	276-322° C. under 50 mm. Hg
Chrysene.....	C ₁₆ H ₁₀	436° C.	0.00902

A number of preliminary experiments were made to fix a method of procedure. It was found advisable to confine the test fractions in Woods metal bottles which melted immediately and threw the entire contents in contact with the hot glass surface. Glass containers were unsatisfactory; the lower boiling material passed into the vapor form, reached the cool portion of the tube and condensed, before the higher boiling material was completely volatilized. Considerable time was spent investigating the possible coking of the fractions in the Victor Meyer pear. The criterion for coking was the appearance of the glass pear, which became badly discolored with carbon when the pear was heated much above 360° C. In a mercury vapor bath (giving a temperature of 357° C.), however, no coking occurred. This was extremely fortunate, for it permitted the use of this vapor bath as the heating agency, giving a temperature which remained constant without attention and was easily reproduced.

The discovery that coking became serious above some 360° or 370° C., coupled with the fact that two of the fractions had boiling point ranges higher than this when under atmospheric pressure, rendered it imperative that an apparatus capable of measuring vapor densities under diminished pressure be fitted up.

Accordingly a flexible mercury manometer made from two glass tubes, a rubber hose, and an upright meter stick was attached to the Victor Meyer tube and the tube evacuated to a low pressure by means of a vacuum pump, the fraction volatilized and the change in pressure noted. The calculations for this low pressure work involved a factor known as the tube constant. This constant depended upon the size of the tube; thus, when a tube of a certain size is used half as much pressure is developed by a given amount of vapor as is developed when a tube of only half that certain size is used, *i. e.*, in a tube twice as large, only half the pressure is developed.

The constant was determined by volatilizing in the tube at the temperature of the experiment a known amount of a compound possessing a known vapor density. The determination of this constant proved quite a bugbear to Mr. Gainey and myself. The slow deliveries on special glassware due to war conditions compelled us to blow our fragile tubes at the blast lamp. We would often carefully standardize a tube in duplicate (consuming several days in the operations) only to break it by some accident before we could use it for a determination. You can then imagine us sweating over the blast lamp in the heat of last August while we blew another tube, hoping for better luck the next time.

In the above table are given our vapor density results, compared with the calculated vapor densities of a few well-known hydrocarbons whose boiling points place them in the range of the appropriate fraction.

The vapor densities of the first two fractions were obtained by determining the volumes of air driven into a gas burette in the standard Victor Meyer method, the third was obtained by packing the tubes with hydrogen whose rapid rate of diffusion into the volatilizing oil insured complete vaporization, the last two were obtained by the use of the manometer and the low pressure system. Mercury vapor was used as the heating medium for all the experiments.

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The experimental material presented in this paper was obtained while I was engaged in physical chemistry research for The Barrett Company and is the product not only of my own efforts but also of the efforts of Mr. John Gainey, who so ably assisted me in the latter part of the work and who is now still engaged in extending it. My debt, however, is not limited to Mr. Gainey. It is owed to the administrative officers of the Research Department of The Barrett Company, to whom I extend my thanks for direction and advice.

It is my belief that physical chemistry is afforded no richer field for research and development than the coal-tar industry, so economically important to the country in peace and so prominent in the scheme of modern warfare. My short connection with this industry has led me to believe that it is only in its infancy and that many of its latent possibilities will be realized by the aid of physical chemistry.

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A MANUFACTURER'S EXPERIENCE WITH GRADUATE CHEMICAL ENGINEERS¹

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The writer has often objected to the term "Chemical Engineer." It seems to place chemical engineering alongside of civil, mechanical, and electrical engineering as one of the natural divisions of the engineering profession. We would define chemistry as the science of the composition of materials, and engineering as the science of works. Chemistry is therefore the fundamental science, as without some knowledge of the composition of materials an engineer will fail.

For the purpose of this paper the writer will consider that a chemical engineer means a graduate in engineering who has had at least four years of college training at an institution recognizing the engineer's need for knowledge of the composition of materials.

During the past two years we have employed in our General Manufacturing Department 100 student engineers. These men were employed, not to occupy at first a definite position, but to undergo a course of study in the Company's business and to fit themselves for positions in the engineering, operating or experimental departments of manufacturing, after a period of at least 6 months' training. In this training period the men receive instruction in the form of lectures on various products and processes by heads of the manufacturing and technical staff and are given special assignments for personal study of a product, process, manufacturing unit, laboratory, or works experiment, etc.

It is our purpose to have at all times about 10 to 20 men in the training period and at the end of about 6 months to assign a student to a definite position, or release him, or under certain conditions to continue his probationary period.

The men are in general selected with a view to their apparent fitness to become assistant superintendents or foremen, but in a

¹ Paper submitted for the Proceedings of the American Association for the Advancement of Science.