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VII. *The Density of the Vapours in Equilibrium with Water, Ethyl Alcohol, Methyl Alcohol and Benzene.*

By the Earl of BERKELEY, F.R.S., and E. STENHOUSE.

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Aim of the Research.—The ultimate aim of the research was to put the vapour pressure method of determining osmotic pressures on to a sound experimental basis. For that purpose it was necessary to investigate the following :—

- (1) The validity of DALTON'S law.
- (2) The extent of the association among vapour molecules.
- (3) The dependence of this association on temperature.

The agreement found by BERKELEY, HARTLEY and BURTON* between the osmotic pressures of aqueous solutions derived from the lowering of the vapour pressure and those directly observed shows, when it is remembered that their vapour pressure method is in reality a measurement of the relative vapour densities, that there is no great departure from DALTON'S law, nor any great change in association† with the relative concentration of vapour and air. Their experimental errors were of the order of 0·5 per cent., so that to obtain further light greater accuracy will be required.

For the investigation of DALTON'S law it was decided to (1) compare the vapour densities of two liquids, of as widely different molecular weights as possible at 0° C. in air, and (2) repeat the observations in argon, and (3), if possible, in helium.

Thus, if the departure from DALTON'S law is, as is generally supposed, due to mutual attraction between the molecules of the gas and vapour, and is, therefore, probably a function of the reacting masses, the wide range of the molecular weights of the gases should be sufficient to bring out the order of magnitude of the departure.

The choice of liquids to be used for this purpose is limited, partly on account of experimental difficulties and partly because the more accurate‡ formula for calculating the ratio involves a knowledge of the respective vapour pressures; it was decided therefore to compare water, ethyl alcohol, and methyl alcohol, although the range of molecular weights is not as great as could be wished.

* 'Phil. Trans.,' vol. 218, A, p. 295 (1919).

† Unless the two effects cancel out.

‡ The less accurate formula, which involves the assumption that the vapour densities are proportional to the vapour pressures, introduces an error of about 1 in 1000 in the ratio.

For the investigation of the association we hoped to be able to correct our vapour density ratios for any departure from DALTON'S law, and then compare them to the ratio of the respective vapour pressures (multiplied by the molecular weights). Then, using benzene, presumably a non-associating vapour, as the reference substance, it would be possible to calculate the average molecular weights of the other vapours. This has been done, but it emerges that benzene is associated and a highly speculative method, given at the end of this communication, had to be adopted.

For the investigation of the change in association with temperature, a direct method was found to be practicable and is applied to water and to EtOH at 0° C. and 30° C. The results are compared with the ratio of the vapour pressures and give the change in the association between these temperatures.

It was also thought advisable to determine the ratio of the vapour densities of water and EtOH at other temperatures as well as at 0° C. and 30° C. so as to deduce its value for any desired temperature lying between the limits.

Unfortunately the complete programme could not be carried out, for on proceeding to temperatures higher than 0° C., various experimental difficulties arose, the investigation of which took up a great deal of time and was barely finished before we had to give up work.

The Method.

On p. 316 of BERKELEY, HARTLEY and BURTON'S paper,* G. W. WALKER derives the equation

$$\frac{l_0}{l_1} = \frac{\rho_0}{\rho_1} \times \frac{B - \pi_1}{B - \pi_0}, \dots \dots \dots (1)$$

where l_0 and l_1 are the observed losses from the solvent and solution respectively; ρ_0 and ρ_1 are the vapour densities of the solvent and solution respectively; π_0 and π_1 are the vapour pressures of the solvent and solution respectively; and B is the mean barometric pressure during the experiment.

This equation applies to the particular arrangement of liquids given by the authors; but it is evident that had they modified their scheme so that the air entered the solution vessel, passed over sulphuric acid, then entered the solvent vessel and passed again over sulphuric acid (or even if the solvent and solution had been interchanged) WALKER'S analysis would still hold; and it still holds if we substitute, as in the method here used, two other liquids in place of the solvent and solution, the vapours of which are absorbed by sulphuric acid.

Obviously also the equation is valid if we substitute any non-absorbable gas in place of air, while a slight modification will make it applicable to the comparison of the vapour densities of the same liquid at different temperatures.

The apparatus used was that described in the paper mentioned. The authors of that

* *Loc. cit.*

communication had been content with results agreeing within about 1 part in 400 ; greater accuracy was not required for the object in view, *i.e.*, that of deducing the osmotic pressure from the vapour pressure, for, in that deduction, they had to assume that the ratio of the vapour pressures was equal to the ratio of the vapour densities ; while, on the other hand, the direct osmotic pressure did not seem to be of any greater accuracy.

A study of the conditions seemed to warrant the belief that greater accuracy was attainable ; indeed, at first sight it would be thought that it is only limited by the errors of weighing, and in fact the experiments at 0° C. on water and on EtOH came out satisfactorily close together ; later experiments at higher temperatures belied this and it was found necessary to investigate the cause of the discrepancies.

Before proceeding to describe this investigation it is advisable to give further details of the apparatus and method, and also enumerate the corrections which have to be applied.

The apparatus consists of five quartz glass vessels, preceded by one (No. 0) which always contains H_2SO_4 and serves to give a final drying to the entering air. Numbering the vessels from the entry end, Nos. 1, 2, 3 and 5 have four parallel branches, while No. 4 has only two. These branches are horizontal tubes each of which is charged with liquid (20 c.c.) until half filled ; they are joined together in such a way that the air enters the first branch through a vertical tube ; when it reaches the surface of the liquid it divides into two streams which travel to the ends where they pass into the second branch and converge towards the centre ; from the centre of the second branch the stream is led to the centre of the third branch where it again divides, travels to the ends, enters the fourth branch to reunite in the centre and pass to the next vessel through a removable inverted U-tube of some 12 c.c. capacity. (These U-tubes are themselves joined to the vessels by junction pieces also of about 12 c.c. capacity.) All the branches of all the vessels were made as closely alike as possible, as were also the vessels themselves, except that the second and third branches of No. 3 were spaced somewhat further apart so as to allow the bath stirrer to work between them.

The Corrections.

The procedure adopted was as follows. The vessels, after cleaning and drying out by a stream of warm dry air, were charged with the respective liquids. The outer surface was then washed with water, followed by pure alcohol, and wiped dry with fine linen dusters ; each vessel was weighed against a quartz glass sealed counterpoise which had been treated in the same way—the method of double weighing was employed and the weight deduced from the recorded decrement in the movement of the balance pointer. Care was taken to loosen the stoppers just before each weighing. The times of weighing, the temperature of the balance base, and the barometric pressure were noted.

Correction (1).—After weighing, the vessels were put by until they could be assembled

to form the train. During this period each liquid loses weight by diffusion past the stoppers. The hourly loss thus sustained was determined by separate experiments (unfortunately this precaution was omitted in the case of the MeOH, but it is interesting to note that the method of weighing was sufficiently accurate to enable us to calculate the time rate of loss for this substance). A similar loss occurs when the vessels are waiting to be weighed at the end of the experiment.

Correction (2).—We are concerned only with the loss of weight of the *liquid* during the period when the air current is passing, it is necessary therefore to include in the buoyancy correction the mass of air and vapour contained between the liquid and the stoppers—this gives us the vacuum weight of the liquid when on the balance. If the temperature of the balance is not the same at the beginning as at the end of the experiment (or should there be a fall in the barometric height) it is easy to see that there has been either a loss from or a gain by the liquid which is not caused by the air current. The method employed for calculating this correction is given under “2nd vessel losses.”

Correction (3).—When the vessels are joined together some vapour is given off sufficient to fill the U-tubes and junction pieces—on dismantling the train, this vapour is lost—hence the correction.

Correction (4).—During the run a quantity of vapour is transferred to the adjacent H_2SO_4 ; this is supplied by the liquid which in the case of EtOH loses some 10 to 20 c.c., but the vacated space is filled with vapour which is not a loss that can be charged to the air current, and must therefore be allowed for.

Correction (5).—In most of the experiments a deposit was found in the U-tubes—this deposit was weighed and an appropriate correction applied. The deposit was found even in the tube connecting two vessels charged with the same liquid—it was for a long time thought to be a temperature effect, but another more probable explanation will be given under “2nd vessel losses.”

It may be mentioned that the sum of the first four corrections, even in the case of EtOH rarely exceeds 0.0100 grammes, but it should be borne in mind that there is another source of error, the magnitude of which cannot be estimated; it lies in the fact that the vessels have to be handled (in “taking down”) both to disconnect the train and to wash and dry—this handling, if prolonged, may warm the contained liquid to such an extent that loss occurs by increased diffusion past the stoppers—obviously a liquid of low specific heat with a high ratio of change of vapour pressure will be most affected. To minimise this loss the vessels were never held with the bare hand.

Correction (6).—In this section it is convenient to discuss two sources of error since each is the result of changes in temperature and the method of calculating the correction is the same.

(a) The loss in the second vessel.—Before discussing this it is well to point out that the elucidation of the cause of the second vessel loss is of considerable importance; for should the magnitude of this loss turn out to be proportional to the total loss (as we at one time thought it to be) then our method of determining vapour densities

is limited in accuracy to about 1 per cent. (see the second vessel loss in the benzene experiments). In fact it was this fear that compelled us to devote a very large part of the time spent on this research to experiments devised to find out the cause.

When we have two vessels charged with the same liquid, the second vessel always lost weight. This phenomenon has already been reported to the society.* In the appendix to that communication it was tentatively ascribed to a local small difference in the temperature of the bath. Later experiments where the two vessels were placed in different positions in the train, and others with the direction of the air current reversed seemed conclusively to rule out a temperature gradient in the bath ; but it still remained possible that the air on leaving the first vessel is cooled by the latent heat of evaporation and only attains the bath temperature when it enters the second vessel. This hypothesis is negatived both by calculation and by experiments where the air speed is greatly reduced (indeed in the latter case the second vessel loss was markedly increased). There remained the possibility that the pressure gradient along the train was considerably greater than that shown by a manometer placed across the ends—in other words there might be local† differences of pressure which might cancel out before the air reached the exit. A great number of experiments with a sensitive manometer placed in various positions were made with negative results.

Moreover, an obvious modification of the analysis given later enabled us to calculate the effect of any small pressure gradient and it was at once apparent that the pressure difference required to explain our results was vastly higher than anything shown by the manometer. Other hypotheses, which, however, need not detain us, were considered ; as they seem all to be functions of the air speed they were ruled out by the results for slow air currents.

(b) The other error (which we will call the H and C loss) to be considered is manifest when we compare the vapour density ratio with water “leading” to that with EtOH “leading.” This discrepancy is shown even at 0° C., while at 30° C. it is much greater ; various hypotheses were adumbrated, of which the only one worth mentioning is the following.

When EtOH is treated with H_2SO_4 at temperatures higher than 30° C., ethylene is found ; now it is possible that small quantities are formed at lower temperatures,‡ if so, the ethylene may pass into the air stream and thus alter the volume of air passing over the comparison liquid. The change in the air speed can be calculated, and although the effect is in the right direction, yet the calculated result is only of the right order of number if we assume that the ethylene is itself reduced to carbon and hydrogen and the latter taken as the diluent of the air. In this connection it is worth noting that the quantity of alcohol vapour absorbed by the H_2SO_4 is always notably less than that lost by the liquid ; markedly so at 30° C.

* ‘ Phil. Trans., *loc. cit.*

† Caused by, say, the kinetic effect of accelerating the vapour from rest, etc.

‡ Our experiments take some days ; a minute effect thus prolonged might be manifest.

The explanation of these anomalies is as follows: We will begin with the H and C correction, for, as will be seen later, the calculated correction causes the discrepancy to vanish.

Consider a train of five vessels in which vessels 1, 3, and 5 contain H_2SO_4 and 2 and 4 contain water. Let the stopper be in the outer end of 1, and assume that the train, with its contents in equilibrium with the atmosphere through the open end of 5, is at a temperature T_0 . Neglect diffusion and let us confine our attention to the movements of the contained air.

Raise the temperature to T_1 ; clearly a certain volume, say A' c.c., leaves vessel 2, carrying with it approximately $A'(\rho_{T_0} + \rho_{T_1})/2$ grammes of vapour (where ρ is the vapour density of water) into the H_2SO_4 in vessel 3.

Simultaneously a volume $A' + B'$ c.c. of air leaves vessel 4, carrying with it approximately $(A' + B')(\rho_{T_0} + \rho_{T_1})/2$ grammes of vapour into the H_2SO_4 in vessel 5.

Thus vessel 4 loses more vapour than vessel 2.

Now lower the temperature to T_0 ; a volume of air, say, A'' c.c. leaves vessel 2 to enter vessel 1, and carries with it*

$$A''(\rho_{T_0} + \rho_{T_1})/2 \text{ grammes of vapour,}$$

and at the same time vessel 4 loses

$$(A'' + B'')(\rho_{T_0} + \rho_{T_1})/2 \text{ grammes of vapour.}$$

Again vessel 4 loses more vapour than 2, and it is readily seen that both losses are due to the fact that more air passes over the last vessel than over the first; so that if we had had vessel 4 charged with EtOH instead of water, the alcohol would have lost relatively more than the water; on the other hand, had vessel 2 contained the alcohol, the water in 4 would then have lost relatively more than the alcohol.

The discrepancies between the ratio of vapour densities when derived with water leading and with EtOH leading are thus qualitatively explained.

Turning now to correction 6 (a). If we apply the preceding discussion to the losses in two water vessels, which are joined together without any intervening H_2SO_4 , it is manifest that the second vessel will lose more than the first. If the dimensions of the two vessels are the same and if the rate of change of temperatures is slow and its range sufficiently restricted, the first vessel will on balance suffer no loss. This result is due to the fact that in the first operation (that of heating) the first vessel loses a quantity of vapour which during the subsequent cooling is returned to it by the air passing through vessel 2 provided that no condensation takes place in the connecting U-tubes.

The following considerations, which avoid the postulate that an air-vapour mixture obeys the gas laws give us a general method for calculating the maximum loss in any

* For simplicity we neglect the probability that the supersaturated vapour may carry with it condensed vapour.

vessel containing a volatile liquid—we say maximum advisedly—for, as far as we can see, any departure from the ideal conditions contemplated will reduce the loss.

Both the “2nd vessel”* and the “H and C” losses can be calculated thus:—

Consider the flask shown in fig. 1 where P_0 , P_1 and P_2 are the positions taken by a weightless, frictionless piston under conditions to be explained. The initial position is P_0 and the flask if it were cut off at this point would represent one of the vessels in the train. Let the flask be at T_0 and its contents in equilibrium. If the volume between the liquid and P_0 be A_0 c.c., and if ω be the weight of dry air in 1 c.c., b_0 the weight of vapour per gramme of air, then the weight of vapour enclosed by P_0 is $A_0 \omega_0 b_0$. Warm the flask to T_1 ; when equilibrium is reached the piston will have moved to P_1 ; the weight of vapour enclosed will be $A_1 \omega_1 b_1$.

Neglecting the expansion of the liquid, and the space vacated by the evaporated vapour, the loss sustained by the liquid is

$$-(A_1 \omega_1 b_1 - A_0 \omega_0 b_0) \quad \text{but} \quad A_1 \omega_1 = A_0 \omega_0$$

substituting; the loss is $-A_0 \omega_0 (b_1 - b_0)$. Suppose we had started at T_1 , with the piston at P_0 , and cooled to T_0 , the new position of the piston will be P_2 and the gain in weight by the liquid is $A_0 \omega_1 b_1 - A_2 \omega_0 b_0$.

To represent the actual circumstances obtaining in a vessel protected by H_2SO_4 on either side we must now imagine that the piston is furnished with a semi-permeable membrane, only permeable to air, and gradually cause the piston to be moved to its original position. Evidently now the liquid will lose the vapour required to saturate the space between P_2 and P_0 —this loss is $-(A_0 - A_2) \omega_0 b_0$, so that the total gain in the operation is $A_0 \omega_1 b_1 - A_2 \omega_0 b_0 - (A_0 - A_2) \omega_0 b_0$. The result for the two operations is a loss of $-A_0 b_1 (\omega_0 - \omega_1)$.

Evidently this method of calculating the H and C losses is based on the assumption of a close approach to equilibrium during the changes in temperature. In many of our experiments this condition was not satisfied, for we had plunged the train of vessels straight into the bath (the two being at different temperatures), hence the calculated correction could not be applied. In the later experiments, however, we placed the train in the bath, when both were at the temperature of the laboratory. The temperature was then gradually raised to $30^\circ C$. taking about 2 hours to get there—in some experiments the air current passed through the vessels during this period, while in others no air passed but the stopper was inserted at that end of the train which would cause the gaseous contents to move in the same direction as the subsequent air current. At the end of the constant temperature period the bath was slowly cooled to laboratory temperature. Having noted the bath temperature at intervals of 5 minutes and using the above exposition as a basis, it was possible to obtain

* In this case the whole of the loss is not accounted for—later on it is suggested that part is caused by diffusion.

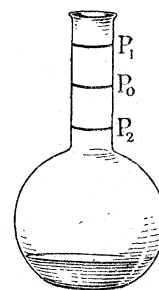


FIG. 1.

an approximate correction for the H and C losses. Even in the latter cases there are uncertainties in the tabulation of the quantity ω , but allowing for these we find that the calculated correction does not account for the whole of the second vessel loss—there must therefore be some other disturbing factor—this is discussed under the “diffusion hypothesis,” p. 277.

Analysis.

There seems to be some ambiguity in WALKER'S definitions of r (and ρ); it may mean either the number of cubic centimetres of air which pass a given point per second, or the number of cubic centimetres of space traversed by it; under the condition of the experiments contemplated by him either of these definitions will result in equation (1).

At the time of WALKER'S analysis we had no thought of a comparison between the losses from the same liquid in different experiments; and for that purpose and other reasons it is convenient to define the speed of the air, s ,* as the number of cubic centimetres of space it traverses in unit time, t .

A consideration of the suction device and associated mercury reduction valve shown in fig. 2, which is the arrangement in the experiments, suggests that the flow of air can be regarded as actuated by the piston and capillary represented in fig. 3.

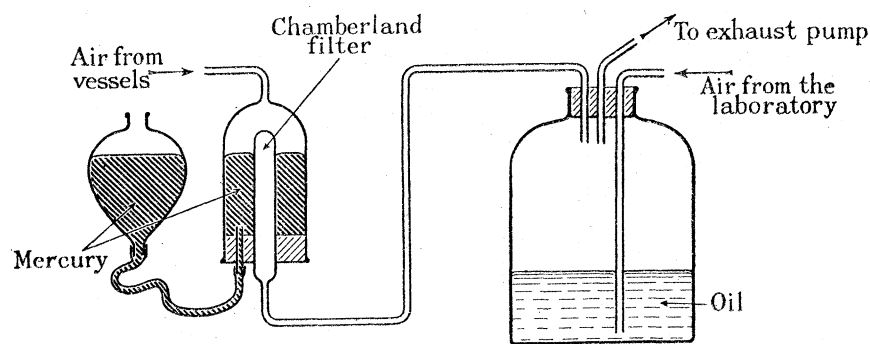


FIG. 2.

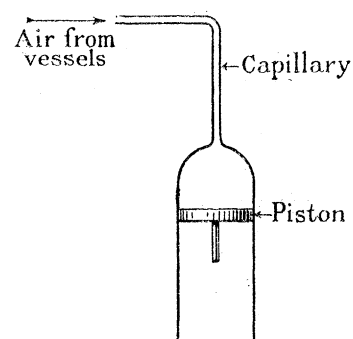


FIG. 3.

The piston is supposed to work without friction and is of a constant but negligible weight.

In these conditions, the temperature and setting of the mercury in the valve being constant, the piston moves at a speed which is uniform and independent of the barometer, consequently the volume of air entering the apparatus in unit time will also be constant and independent of the barometer.

If the bath be of a constant temperature differing from that of the remainder of the apparatus, the air entering the train of vessels will traverse a volume of s cubic centi-

* We use s instead of WALKER'S r so as to emphasise the definition.

metres (in unit time) which bears a constant relation to the speed of the piston ; the total space traversed by the air will be

$$\int_0^t s dt.$$

When the air mixes with the vapour it will then traverse a larger space in the proportion of B to $B - \pi$, and if ρ be the weight of vapour in each cubic centimetre of this space the total loss of vapour will be

$$l = \int_0^t \frac{sB\rho}{B - \pi} dt.$$

This equation leads to WALKER'S relation (1), but with liquids having a larger vapour pressure than water this relation may not be strictly accurate. The ratio of the vapour densities can, however, be calculated thus :

For example if the suffixes w and a relate to water and EtOH respectively, we have for the observed losses

$$l_w = \int_0^t \frac{sB\rho_w}{B - \pi_w} dt \quad \text{and} \quad l_a = \int_0^t \frac{sB\rho_a}{B - \pi_a} dt,$$

where s , ρ_w and ρ_a are constants, hence

$$\frac{l_w}{l_a} = \frac{\rho_w}{\rho_a} \int_0^t \frac{B - \pi_a}{B - \pi_w} dt \quad \dots \dots \dots (2)$$

and, knowing the variations of the barometer with time, the integral can be evaluated.

The foregoing is based on ideal conditions which are not readily realised in practice. To investigate the consequences of a departure from this ideal, and for other purposes, it may be necessary to compare the loss sustained by the same liquid when the laboratory is at different temperatures (*i.e.*, when the apparatus shown in fig. 3 or the mercury valve of fig. 2 is at different temperatures).

Consider two experiments, each carried out at the same bath temperature and with the same setting of the mercury valve.* Let the absolute temperature of the laboratory be K and the corresponding viscosity of the air be v ; then, using suffixes 1 and 2 to distinguish the quantities, we have for the losses from the same liquid

$$l_1 = \int_0^{t_1} \frac{s_1 B_1 \rho}{B_1 - \pi} dt$$

in the first experiment, and

$$l_2 = \int_0^{t_2} \frac{s_2 B_2 \rho}{B_2 - \pi} dt$$

in the second experiment.

* The quantity of air passing when the mercury is at different levels in the reduction valve was determined experimentally ; but the results were not concordant enough to apply equation (3) (*vide infra*).

Now consider fig. 3. As the variation in the temperature of the laboratory is only a matter of a few degrees, the change in the dimensions of the capillary (the capillaries of the Chamberland filter) may be neglected; so that the speed of the piston in the first experiment is to that in the second inversely as the respective air viscosities. Furthermore, as the density of the air enclosed by the piston is inversely proportional to the absolute temperature, we get

$$\frac{s_2}{s_1} = \frac{v_1}{v_2} \times \frac{K_2}{K_1}.$$

This relation makes it clear that if the laboratory temperatures are different the two experiments are carried out at different air speeds; and we get for the losses

$$l_1 = \int_0^{t_1} \frac{s_1 B_1 \rho}{B_1 - \pi} dt \quad \text{and} \quad l_2 = \int_0^{t_2} \frac{s_1 \times \frac{v_1 K_2}{v_2 K} B_2 \rho}{B_2 - \pi} dt.$$

Now the quantity $\frac{v_1}{v_2} \times \frac{K_2}{K_1}$ never varies more than 3 per cent., so during the run the mean value can be taken, and taking the mean barometer as sufficiently accurate, we get

$$\frac{t_2 l_1}{t_1 l_2} = \frac{\bar{B}_1}{\bar{B}_2} \times \frac{v_2}{v_1} \times \frac{K_1}{K_2} \times \frac{\bar{B}_2 - \pi}{\bar{B}_1 - \pi}. \quad \dots \dots \dots (3)$$

This equation* gives us a means of determining the experiment error.

On p. 261 we mentioned two methods by which it is possible to calculate the effects of bringing the bath from the laboratory to the desired temperature, and *vice versa*. As far as our experiments, which only reach 30° C., are concerned, we think it preferable not to pass the air current during this period; but if experiments are to be made with extremely volatile substance, or at higher temperatures (where obviously the time taken to reach the temperatures will be longer) it may be that the diffusion effects (see p. 277) will be greater, and it will then be necessary to start the air current when the train is at its initial temperature, and keep it running until this temperature is again reached at the end of the experiment. It has been shown, under correction (6), that the losses sustained on heating (apart from the possibility that the initial and final laboratory temperatures may not be identical) are not the same as when cooling, and they must therefore be separately calculated. To make them amenable to calculation, the procedure outlined on p. 261 was adopted, but it must be remembered that there may be an interval of some 9 days between the two operations of heating and cooling and the laboratory temperatures may differ considerably.

If $l_{\text{obs.}}$ be the loss observed, l_0 that sustained at constant temperature of 30° C., l_1

* We give the formula although there are no two experiments, with the same setting of the mercury valve, sufficiently good to apply it.

that while heating to 30° , and l_2 that while cooling from 30° to laboratory temperature, then

$$l_{\text{obs.}} = l_0 + l_1 + l_2 \\ = \int_0^{t_0} \frac{s_0 \bar{B}_0 \rho_0}{\bar{B}_0 - \pi_0} dt + \int_0^{t_1} \frac{s_1 \bar{B}_1 \rho_1}{\bar{B}_1 - \pi_1} dt + \int_0^{t_2} \frac{s_2 \bar{B}_2 \rho_2}{\bar{B}_2 - \pi_2} dt.$$

In this equation the only unknowns are the air speeds. To evaluate them approximately we can put for s_0 , its value, \bar{s}_0 at the mean laboratory temperature during the period of constant bath temperature (should the laboratory temperature have varied during that period). Thus when the train is first put into the bath we have

$$s_1 = s_0 \frac{v_1'}{v_0} \times \frac{K_0}{K_1} \times \frac{K_0}{K_2},$$

and when the bath has reached 30° C., $s = \bar{s}_0 \left(\frac{v_1}{v_0} \frac{K_0}{K_1} \right)$, similar relations hold for s_2 .

It will be noted that these values of s_1 and s_2 are those at the limits of the respective integrals; but the changing bath temperature not only affects the speed of the entering air but also that of the air leaving any vessel,*† and if we know the dimensions of the vessels, this effect, due to the expansion (or contraction) and readjustment of relative concentrations,‡ can be calculated and expressed in terms of \bar{s}_0 (the details need not be given here). Thus the s_1 's and s_2 's can be replaced by \bar{s}_0 , multiplied by known varying factors V; we then have

$$l_{\text{obs.}} = \bar{s}_0 \left(\int_0^{t_0} \frac{\bar{B}_0 \rho_0}{\bar{B}_0 - \pi_0} + \int_0^{t_1} \frac{V_1 \bar{B}_1 \rho_1}{\bar{B}_1 - \pi_1} dt + \int_0^{t_2} \frac{V_2 \bar{B}_2 \rho_2}{\bar{B}_2 - \pi_2} dt \right) \quad (4)$$

and all the terms inside the brackets can be evaluated and the value of \bar{s}_0 determined. The further procedure for calculating the ratio of the vapour densities of the two substances is readily seen.

It may be mentioned that subsidiary experiments designed to determine the sum of the last two integrals in equation (4) were made by noting the losses when the air passed only during heating and cooling (*i.e.*, there was no constant temperature period); but we were unable to secure the same conditions of laboratory temperatures and

* Note that therefore the speed of the air entering any one vessel is not the same as that entering another.

† Therefore for the integration, the function under the \int sign has to be multiplied by two varying factors: (1) a correction for the changing speed of the entering air; (2) a correction for the changing speed of the air leaving the vessel. The correction (1) is, as already indicated, $v_1/v_2 - K_0/K_1 = K_0/K_T$ (where the suffix 0 refers to the temperature of the bath when at laboratory temperature, while T is the temperature of the bath at the time t). The correction (2) is $K_0/K_1 = w_0/w_T$ (where W is the weight of air in 1 c.c. of mixture). These corrections apply to the leading vessel of the train, but for the air entering No. 4 a small correction depending on the expansions of the gaseous contents of the vessels must be applied after which (1) and (2) obtain as before.

‡ A change of 1° C. in the neighbourhood of 30° C., involves a gaseous expansion of 1 part in 300, but the change in the concentration is 1 in 100 for EtOH.

barometric pressures as in the experiments themselves, consequently the method of evaluating equation (4) has to be carried out.

The labour involved in calculating the H and C corrections from equation (4) is serious, and at the best only leads to an approximation. Prof. LINDEMANN suggested that the train should be placed in the bath when at laboratory temperature and raised to 30° C. gradually, then at the end of the run gradually cooled—both operations to be done without allowing the air to pass. The train should be stoppered at that end which causes the expanding (or contracting) air to move in the same direction as the air current, this is advisable both for the greater ease of calculation and for the purpose of avoiding the contamination of the anterior protecting H_2SO_4 .

This method, which we had already followed in one or two experiments without realising its full advantages, has the merit of lessening both the labour of calculation and the magnitude of the correction. On the whole we think it more accurate in despite of increased losses by diffusion.

Purification of Materials.

The concentrated H_2SO_4 used was KAHLBAUM'S purest—no test was applied, but the precaution of subdividing the contents of the main supply by pouring it into numerous small glass-stoppered bottles and keeping these in desiccators was made.

The EtOH was KAHLBAUM'S purest ; it was treated by standing over metallic calcium and, after redistilling, its density was determined—if the density differed too much from the accepted value, the purification was repeated. It may be mentioned that we were not satisfied that a pure substance is obtained by this method, and Sir H. HARTLEY kindly supplied us with a sample of the alcohol specially purified in his laboratory, he also gave us the specially purified MeOH and the charcoal used for absorbing the benzene. The latter was purified by the freezing method.

The Tables of Experiments.

The following tables give the experiments which were considered to be successful, together with others, which although defective, are noteworthy for special reasons.

The rejection of experiments was guided by four criteria :—

(1) Variation in the bath temperature during the run. If this variation took place during the night and was equal to or greater than 0·02° C., the experiment was rejected—a variation of 0·02° C. as a maximum would not affect the results to any great extent, but obviously we could not tell what took place at night. On the other hand if the variation took place during the day and the break down rectified within a reasonable time the experiment was accepted.

(2) A stoppage or leak in the air current. At first sight neither a stoppage nor a leak would be thought to affect the results, yet if it be remembered that the space above the liquids in the train is about 800 c.c. it is easy to see that differential movements in the

air contained therein may take place and cause one of the liquids to lose more than its share.

(3) A breakdown in the stirring mechanism. If this took place during the night the experiment was stopped, but once or twice the breakdown was noticed in time to effect repairs and the experiment was saved.

(4) Another criterion lies in the experiment itself. Clearly the success of an experiment depends on the complete absorption of the vapour from the "leading" liquid by the adjacent H_2SO_4 ; this is tested by comparing the loss from the "leading" liquid to the gain in weight of the acid.* Should the defect in "tot up" be unduly great it is to be presumed that the experiment is faulty, for, apart from weighing errors and leaks in the vessels, the defect means (a) that the air is not saturated and therefore the vapour density is not that sought for; or (b) the absorption by the acid is not complete and the speed of the air is no longer a constant, moreover some of the vapour carried forward may be absorbed by, and alter the weight of, the comparison liquid. A sufficient precaution against this source of error and indeed against others, which need not be recorded, was afforded by interchanging the positions of the comparison liquids and repeating the experiment. The "tot up" test also applies to the comparison liquid. Extra large deposits in the U-tubes were always viewed with suspicion.

In Tables I, II and III, column (11) gives the speed, in cubic centimetres per minute, of the air entering the vessel containing EtOH at the temperature of the experiment; it is derived from the equation

$$l_a = \int_0^t \frac{s\bar{B}\rho_a}{\bar{B} - \pi_a} dt.$$

As these speeds are required only for calculating correction (6), or for comparison (see diffusion hypotheses on p. 277) we have assumed that the ρ_w of LANDOLT and BORNSTEIN'S tables will give us a sufficiently accurate value of ρ_a when substituted in our experimentally determined ratio ρ_w/ρ_a . Column (13) gives the vapour density ratio calculated from equation (2).

In column (14) the same ratio ρ_w/ρ_a is calculated from the equation

$$\frac{\rho_w}{\rho_a} = \frac{l_w}{l_a} - \frac{\pi_w}{\bar{B}} \left(\frac{l_w}{l_a} - M \right), \quad \dots \dots \dots (5)$$

where M is the ratio of the molecular weights.

This equation is derived from equation (2), by assuming that

$$\frac{\rho_w}{\rho_a} = M \cdot \frac{\pi_w}{\pi_a},$$

and is the type of formula which would have to be used were we to determine the vapour pressures of (say) alcoholic solutions. Column (15) gives the observed density at 0°C . of the EtOH used; we were unable to get closer to YOUNG'S value (*i.e.*, 0.80625);

* A true comparison is only possible when the observed gain in the acid is corrected for volume changes caused by absorption of the EtOH (or water) vapour—these changes were determined by experiment and the corrections included in the buoyancy corrections.

TABLE I.—Experiments with Water and Ethyl Alcohol at 0° C.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
Date.	Corrected temperature of bath.	Maximum variation in temperature of bath.	Corrected mean barometer.	Vessel 1	Vessel 2	Vessel 3	Vessel 4	Vessel 5	Time of run in hours.	s in c.c. per minute.	$B - \frac{\pi_v}{\pi_a}$	$\frac{\rho_w}{\rho_a}$ from equation (2).	$\frac{\rho_w}{\rho_a}$ from equation (5).	Density of alcohol at 0° C.
Water Leading (in an air current).														
Nov. 15, 1922	0.35	None	761.3	Empty. Not weighed	Water. -1.1812	H ₂ SO ₄ . +1.1827	EtOH. -8.0405	H ₂ SO ₄ . +8.0359	137	28.77	1.0112	0.14854	0.14841	0.80630
Jan. 30, 1923	0.35	None	751.2	"	-1.1620	+1.1633	-7.9055	+7.9029	138.5	27.95	1.0113	0.14857	0.14852	0.80630
Mar. 1, 1923	0.35 ₅	0.05	743.9	"	-1.2526	+1.2537	-8.5183	+8.5124	139	29.99	1.0114	(0.14873)	—	0.80630
Nov. 1, 1922	0.55	None	739.5	"	-1.1925	+1.1954	-8.1209	+8.1184	136.25	32.90	1.0118	0.14857	0.14842	0.80630
Dec. 6, 1922	0.75	None	756.7	"	-1.2415	+1.2436	-8.4499	+8.4462	137.5	29.32	1.0116	0.14862	0.14848	0.80630
Feb. 14, 1923	0.75	None	740.8	"	-1.2270	+1.2306	-8.3584	+8.3516	139	28.67	1.0118	0.14853	0.14840	0.80630
Mar. 21, 1923	0.75	None	750.9	"	-1.2879	+1.2863	-8.7600	+8.7520	139	30.06	1.0116	0.14873	0.14859	0.80630
Alcohol Leading (in an air current).														
Dec. 11, 1923	0.35	0.02	757.8	Empty Not weighed	EtOH -8.4620	H ₂ SO ₄ +8.4589	Water -1.2440	H ₂ SO ₄ +1.2427	139.5	29.74	1.0112	(0.14866)	0.14852	0.80628
Oct. 26, 1923	0.75	None	746.4	"	-8.4429	+8.4429	-1.2422	Lost	140	28.76	1.0117	0.14885	0.14871	0.80628
Nov. 22, 1923	0.75	None	747.3	"	-8.9704	+8.9694	-1.3194	+1.3188	139.5	30.67	1.0117	0.14880	0.14860	0.80628
Oct. 22, 1926	0.75	0.01	740.3	EtOH -7.4923	-0.0040	+7.4905	-1.1019	+1.1170	114.75	31.16	1.0118	(0.14872)	†	†
Water Leading (in a current of Argon).														
June 26, 1924	0.75	None	748.5	Water -1.2163	H ₂ SO ₄ +1.2189	Empty +0.0019†	EtOH -8.2840	H ₂ SO ₄ +8.2862	140*	28.22	1.0117	0.14855	—	0.80628
Alcohol Leading (in a current of Argon).														
Apr. 20, 1924	0.35	None	737.5	EtOH -9.7136	H ₂ SO ₄ +9.7227	Water -1.4291	H ₂ SO ₄ +1.4299	Empty +0.0015†	116*	41.03	1.0115	0.14881	—	0.80628
May 20, 1924	0.75	None	742.1	-10.1655	+10.1642	-1.4931	+1.4958	+0.0011†	140.5*	34.50	1.0118	0.14861	—	0.80628
June 13, 1924	0.75	None	749.8	-9.3673	+9.3643	-1.3767	+1.3787	+0.0019†	140.5*	31.80	1.0117	0.14869	—	0.80628
Water Leading (in a current of Hydrogen).														
Feb. 7, 1928	0.75	None	745.1	Water -1.4518	H ₂ SO ₄ +1.4508	Empty +0.0010†	EtOH -9.8382	H ₂ SO ₄ +9.8352	140.25*	33.46	1.0117	0.14930	—	0.80621
Alcohol Leading (in a current of Hydrogen).														
Jan. 23, 1928	0.75	None	745.7	EtOH -8.6003	H ₂ SO ₄ +8.5958	Water -1.2697	H ₂ SO ₄ +1.2700	Empty +0.0005†	114.25*	35.90	1.0117	0.14936	—	0.80621

* During the last 2 hours of the run the gas was replaced by an air current.
 † The alcohol for this experiment was specially purified in Sir H. HARVEY'S laboratory.
 ‡ The inner surface of the vessel had been over-dried. There is no deposit if the vessel is not heated above 40° C.

except in the two experiments at the bottom of Table I where the alcohol was repeatedly treated with calcium.

The headings of the other columns explain the numbers tabulated. The figures given for the losses and gains have all (except where otherwise stated) been corrected for everything except the H and C.

Notes to Table I.—The experiments of March 1, 1923, and December 11, 1923, are included so as to show that at 0° C. somewhat large variations in the bath temperature may not cause large errors in the results.

The experiment of October 22, 1926, is rejected, the defect in the “tot up” between 4 and 5 is too great, but the experiment is of interest as there is a definite loss from the second alcohol vessel. The experiments with argon and hydrogen were carried out by passing these gases through the train (the rate being noted by means of a H₂SO₄ “bubbler” in which the gas bubbled through a depth of 1 to 2 cm. of acid), after they had passed through soda lime and over H₂SO₄. The argon was stated by the British Oxygen Company to be 90 per cent. argon, 1·6 per cent. oxygen and 8·4 per cent. nitrogen—the hydrogen was given as 99·9 per cent. pure. A difficulty arose with these gases in applying the buoyancy correction. It was impossible to get consistent results with argon filling the vessels; but it was found by experiment (the details need not be given) that if air replaced the argon 2 hours before “taking down” apparently all the argon was displaced. A similar procedure was adopted with hydrogen where, however, 2¼ hours were given; the weighings were consistent, and it is to be presumed that all the hydrogen had been removed. In calculating the ratios we have had to assume that the vapour pressures are the same in argon and in hydrogen as in air.

It will be noticed that the hydrogen results are somewhat higher than the previous numbers. It may be that this is a real effect, but we are inclined to think that the alcohol is at fault.

We would draw attention to the discrepancy between the results when water leads and when alcohol leads—the difference is small but marked. The discussion on p. 259 *et seq.* explains part of this, but unfortunately, as already stated, we are not in a position accurately to correct for the H and C losses.

The mean values of the ratio ρ_w/ρ_a are :—

$$\text{At } 0\cdot35^\circ \text{ C. with water leading in air } \rho_w/\rho_a = 0\cdot14855.$$

$$\text{At } 0\cdot75^\circ \text{ C. with water leading in air } \rho_w/\rho_a = 0\cdot14861.$$

$$\text{At } 0\cdot75^\circ \text{ C. with alcohol leading in air } \rho_w/\rho_a = 0\cdot14883.$$

If we assume that had we had successful alcohol “leading” experiments in air at 0·35° C. these would have been 0·00022 (the same difference as at 0·75° C.) in excess, then our mean value would come to :—

$$0\cdot14866 \text{ at } 0\cdot35^\circ \text{ C. in air.}$$

$$0\cdot14865 \text{ at } 0\cdot75^\circ \text{ C. in argon.}$$

$$0\cdot14877 \text{ at } 0\cdot75^\circ \text{ C. in air.}$$

$$0\cdot14933 \text{ at } 0\cdot75^\circ \text{ C. in hydrogen.}$$

$$0\cdot14881 \text{ at } 0\cdot35^\circ \text{ C. in argon.}$$

TABLE II.—Other Experiments at 0° in Air.

(1) Date.	(2) Corrected tempera- ture of bath.	(3) Maximum variation in bath tempera- ture.	(4) Corrected mean baro- meter.	(6) Number of vessel.					(10) Time of run (constant tempera- ture), in hours.	(11) Speed of air in c.c. per minute	(12) $\frac{B - \pi_w}{B - \pi_a}$	(13) Ratio of vapour densities from equation (2).	(14) Ratio of vapour densities from equation (5).	(15) Density of EtOH.
				1.	2.	3.	4.	5.						
Methyl Alcohol and Water (water "leading").														
Nov. 18, 1926	0.75	0.02*	724.1	Water -1.0883	H ₂ SO ₄ +1.0904	MeOH -13.4849	MeOH -0.0139	H ₂ SO ₄ +13.4831	115	30.72	1.0377	$\frac{\rho_w}{\rho_m}$ 0.08366	$\frac{\rho_w}{\rho_m}$ 0.08384	—
Methyl Alcohol and Ethyl Alcohol (EtOH "leading").														
Nov. 30, 1926	0.75	None	749.1	EtOH -4.2450	H ₂ SO ₄ +4.2438	MeOH -7.7263	MeOH -0.0116	H ₂ SO ₄ +7.7235	66.25	30.56	1.0245	$\frac{\rho_w}{\rho_m}$ 0.5620	$\frac{\rho_a}{\rho_m}$ 0.5623	0.80631
Ethyl Alcohol and Benzene (EtOH "leading").														
Oct. 13, 1927	6.43	0.07	747.8	Empty	EtOH -3.9460	H ₂ SO ₄ +3.9448	C ₆ H ₆ -14.0539	C ₆ H ₆ -0.1148	113.1	—	1.0273	(0.28612)	—	—
Nov. 3, 1927	6.45	0.05	738.1	—	-3.9450	—	-14.0502	-0.1137	114.3	—	1.0277	—	—	—
Nov. 25, 1927	6.45	None	756.5	—	4.3166	+4.3263	-15.4218	-0.1159	114	12.88	1.0269	0.28623	—	0.80621
Dec. 9, 1927	6.45	None	755.6	EtOH -4.6688	H ₂ SO ₄ +4.6689	C ₆ H ₆ -16.5961	C ₆ H ₆ -0.1707	Charcoal +16.05	117.25	13.05	1.0255	0.28587	—	0.80621

* Part of this variation took place in the daytime and the experiment was saved.

† These are the H and C corrections. The four benzene experiments were done by Prof. LINDEMANN'S method giving 2 hours to heat and cool without passing air. The first two are rejected on account of variations in bath temperature. There was a hitch in setting up on November 3, in that after putting the train into the bath it had to be withdrawn, the H and C correction cannot be properly applied; we give the experiment on account of the second vessel loss which is of the order of magnitude of the October experiment.

It is noteworthy that if we assume that the second vessel losses are caused by diffusion, and we neglect the hypothetical diffusion of the EtOH in vessel 1, as it will be the same in both experiments, the experiments of November 25 and December 9 agree. The numbers are: November 25, $\rho_w/\rho_a = 0.28885$, and December 9, $\rho_w/\rho_a = 0.28892$. Unfortunately we cannot apply the diffusion correction to any other experiment—the H and C data are lacking.

Notes to Table II.—In the experiments of November 18, 1926, and November 30, 1926, the air speed is calculated from the loss of water in the first experiment, and from the loss of EtOH in the second. Each experiment shows a loss in the second MeOH vessel; and although we cannot correct these for the H and C loss, yet it is interesting to calculate the ratio ρ_w/ρ_a and compare it with that found from the numbers in Table I. The calculated ratio comes to 0·14886, and compares favourably with the mean value 0·14877 found directly.

The experiments with benzene and EtOH do not seem to be so successful; here again there are second vessel losses, which are of a different order of number—they are discussed under “Diffusion hypothesis.” The two experiments of October 13 and November 3 are to be rejected on account of the large variation in the bath temperature. They are tabulated so as to show the magnitude of the “2nd vessel” losses.

It should be noted that in the November 25, 1927, experiment the benzene was absorbed by charcoal* in a glass tube placed outside the bath; while on December 13, 1927, the charcoal was in vessel 5 backed by charcoal outside.

The mean values are :—

$$\rho_w/\rho_m = 0\cdot08366 \text{ at } 0\cdot75^\circ \text{ C.}$$

$$\rho_a/\rho_m = 0\cdot5620 \text{ at } 0\cdot75^\circ \text{ C.}$$

$$\rho_a/\rho_b = 0\cdot2863 \text{ at } 6\cdot45^\circ \text{ C.}$$

* The charcoal was used more to protect the Fleuss pump oil, than with the intention of obtaining a satisfactory “tot up.” We were not sufficiently familiar with the manipulation to expect more than this.

TABLE III.—Alcohol and Water at other Temperatures.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
Date.	Corrected temperature of bath.	Maximum variation in bath temperature.	Corrected mean barometer.		Number of vessel.				Time of run in hours.	No. of c.c. of air passing per minute.	$\frac{B - \pi_w}{B - \pi_a}$	$\frac{\rho_w/\rho_a}{\text{from equation (2)}}$	$\frac{\rho_w/\rho_a}{\text{from equation (5)}}$	Density of alcohol.
	° C.	° C.			1	2	3	4	5					° C.
Experiments at 13° C. (with water "leading").														
Sept. 16, 1926	12.95	None	753.2	Water - 2.3498	Water + 0.0009	H ₂ SO ₄ + 2.3497	EtOH - 15.8045	H ₂ SO ₄ + 15.8018	116	29.56	1.0244	0.15233	0.15230	0.80630
Experiments at 13° C. (with alcohol "leading").														
Sept. 2, 1926*	12.95	None	752.0	EtOH - 15.7824	EtOH - 0.0121	H ₂ SO ₄ + 15.7765	Water - 2.3521	H ₂ SO ₄ + 2.3537	115	29.76	1.0244	0.15255	0.15252	0.80630
Experiments at 20° C. (with water "leading").														
Feb. 22, 1927	20.01	None	730.6	Water - 1.2220	Water - 0.0023	H ₂ SO ₄ + 1.2233	EtOH - 8.2375	H ₂ SO ₄ + 8.2335	66	17.65	1.0386	0.15437	0.15446	0.80631
Experiments at 20° C. (with alcohol "leading").														
Feb. 1, 1927†	20.01	None	758.6	EtOH - 14.2204	EtOH - 0.0050	H ₂ SO ₄ + 14.2099	Water - 2.1234	H ₂ SO ₄ + 2.1238†	113	17.84	1.0371	0.15481	—	0.80631
Experiments at 30° C. (with water "leading").														
Mar. 4, 1927	30.02	None	731.8	Water - 2.1585	Water - 0.0035	H ₂ SO ₄ + 2.1604	EtOH - 14.7810	H ₂ SO ₄ + 14.7770	64	17.94	1.0713	0.15670	—	0.80631
Apr. 17, 1928*	30.02	None	749.7	Water - 1.7465 0.0220	H ₂ SO ₄ + 1.7677‡	EtOH - 11.9275 0.1485	H ₂ SO ₄ + 13.9854‡	Empty *Not weighed	189.2	4.958	1.0694	0.15656	—	0.80629
Dec. 20, 1928	30.06	None	756.4	Water - 3.5756 0.0010¶	H ₂ SO ₄ + 3.5734	EtOH - 24.4256 0.0133¶	EtOH - 0.0152 0.0037¶	H ₂ SO ₄ + 24.4171	63	32.32	1.0687	0.15645	—	0.80630
				Water - 3.5746		H ₂ SO ₄ + 24.4123	EtOH - 0.0115							

* This experiment is viewed with suspicion, the defect in top-up of alcohol seems more than unduly large.

† This experiment is to be viewed with suspicion; the phenomenally large deposit of 0.0305 grammes was found in the U-tube joining 4 and 5; there were also some experimental troubles while cooling the bath down to the laboratory temperatures.

‡ These figures were not corrected for shrinkage; the vessels were required for an attempt to determine the actual loss incurred during the heating and cooling.

¶ These are the corrections of H and C with air passing.

¶ These are H and C corrections without air passing.

TABLE III.—Alcohol and Water at other Temperatures (continued).

(1) Date.	(2) Corrected temperature of bath.	(3) Maximum variation in bath temperature.	(4) Corrected mean barometer.	(5)-(9) Number of vessel.					(10) Time of run in hours.	(11) No. of c.c. of air passing per minute.	(12) $\frac{B - \pi_w}{B - \pi_a}$.	(13) $\frac{\rho_w/\rho_a}$ from equation (2).	(14) $\frac{\rho_w/\rho_a}$ from equation (5).	(15) Density of alcohol.
				1.	2.	3.	4.	5.						
Experiments at 30° C. (with alcohol "leading").														
Mar. 25, 1927*	30.02	None	731.8	EtOH -15.1317	EtOH -0.0079	H ₂ SO ₄ +15.1264	Water -2.2189	H ₂ SO ₄ +2.2199	66	17.83	1.0713	(0.15700)	—	0.80631
Sept. 1, 1927*	30.02	None	749.9	Lost	-0.0278	+12.7305	-1.8633	+1.8656	185.75	5.33	—	—	—	—
Sept. 15, 1927*	30.03	0.03	739.5	-12.9952	-0.0229	+12.9828	-1.8979	+1.9003	185.5	5.42	—	—	—	—
Mar. 16, 1928	30.02	0.01	741.1	EtOH -9.4042 0.1289	H ₂ SO ₄ +9.3930†	Water -1.3746 0.0191	H ₂ SO ₄ +1.3743†	Empty +0.0018	165.75	4.461	1.0704‡	0.15648	0.15672	0.80629
				-9.2753 +0.0033		-1.3555								
				-9.2720										

* These two experiments are included to illustrate the "second vessel loss" discussion.

† These figures were not corrected for shrinkage; the vessels were required for an attempt to determine the actual loss incurred during the heating and cooling.

‡ The number is referred to in the notes to the table.

|| These are the corrections for H and C with air passing.

Notes to Table III.—The experiments, the results of which are given in brackets, are included merely to illustrate the second vessel losses. These are higher at 30° C. than at other temperatures ; but as before stated most of them cannot be corrected for the H and C loss ; those that can be corrected have the corrections shown (the experiments of September, 1927, could be so corrected, but as they are rejected it was deemed not worth while doing so).

The experiment of March 16, 1928, is interesting because during the constant temperature period the barometer fell somewhat irregularly from 754·9 to 728·6. If we remember that the vapour pressure of EtOH at 30° C. is about 78 mm., the question arises as to whether the mean barometer is sufficiently accurate for evaluating the integrals. We were able to test this from the times and barometer readings taken during the run ; these were plotted and the value of B at the mid-time interval was assumed to be that operating during that interval ; from this we calculated $(B - \pi_w)/(B - \pi_a)$; which on comparing to that derived by taking the mean barometer was found to be 1·0704 instead of 1·0703. There is, however, another effect brought about by a large change in the barometer ; it arises thus : although the speed of the air is independent of the barometric pressure (and can be taken as constant at vessel 5) yet it is evident that the differential movements of the gaseous contents lying between 5 and 1 must follow the changes in the barometric pressure, and hence the air speed at 1 must vary. This effect is easily calculated (approximately) for the experiment under discussion and results in a correction of 0·0033 gramme to be added to the loss of alcohol observed. This correction is shown in the table.

The experiment of December 20, 1928, was carried out by Prof. LINDEMANN'S method where slow heating and cooling take place with the air current cut off. The positions of the stopper were in this case known and a fairly correct H and C loss could be calculated. It will be seen that the second vessel loss, even when corrected, is still large, and therefore there must be some other cause in operation.

A curious effect was noticed in the experiments at 30° C. ; on "taking down" there was always a marked orange colour to be seen in the H₂SO₄ of the second branch of the vessel which had received the alcohol vapour ; the first branch never showed more than the merest trace of discoloration ; the fact that this occurs in the second branch rules out the possibility that traces of rubber lubricant (this is used on the ground joints) have been carried forward with the alcohol—it seems a proof that a change has taken place in the reaction between EtOH and H₂SO₄.

The accepted results for ρ_w/ρ_a are :—0·15233 at 12·95° C. ; 0·15437 at 20·02° C. ; 0·15648 at 30·02° C., and 0·15645 at 30·06° C.

The two experiments of March 19, 1927, are not included as they could not be corrected for the H and C loss.

TABLE IV.—Experiments with the Liquids in separate baths—one at 0° C. and the other at 30° C.

(1)	(2)	(3)	Jena glass.		(6)	(7)	(8)	(9)	Quartz glass.			(14)	(15)	(16)		
			(4)	(5)					(10)	(11)	(12)					
Date.	Corrected temperature of bath.	Maximum variation in bath temperature.	Vessel I	Vessel 2	$\pi_{0.75}/\pi_{0.02}$	Mean barometer.	Corrected temperature of bath.	Maximum variation in bath temperature.	Vessel I	Vessel 2	Vessel 3	Length of run in hours.	δ at 30.02° in c.c. per minute.	$\frac{B - \pi_{0.02}}{B - \pi_a}$	Ratio of vapour densities.	
Nov. 8, '28	0.75	None	Water	H ₂ SO ₄	0.1518 _s	743.9	30.02	None	Water	Water	H ₂ SO ₄	h. m.	30.35	1.0380	0.16948	
			-1.3430	+1.3482					-0.0051	+9.1357	159					40
			0.0004†						0.0007†							
			1.3426					9.1318	-0.0044							
			0.0052‡													
			1.3478													
With Water.																
Nov. 28, '28§	0.75	0.10	EtOH	H ₂ SO ₄	0.1709 _e	758.5	30.02	None	EtOH	EtOH	H ₂ SO ₄	h. m.	26.55	1.0957	0.17839	
			-5.5896	+5.5811					-0.0166	37.972*	111					40
			0.0019†						0.0035†							
			5.5877					37.9832	-0.0131							
			0.0015‡													
			5.5892													
Dec. 11, '28§	0.75	0.04	-3.3574	+3.3513	—	748.0	30.02	None	-22.9092	-0.0013	22.8776	63	9	28.24	1.0972	(0.17801)
			0.0018†						0.0037†							
			3.3556						22.8959	+0.0024						

* This vessel was not weighed more accurately.
 † These corrections are the calculated values of the losses sustained while heating and cooling.
 ‡ The corrections marked thus are discussed in the notes.
 § Density of the alcohol in these two experiments was 0.80630, the same alcohol as in experiment of December 20, 1928, at 30° (Table III).

Notes to Table IV.—In this table we give the results obtained by comparing the vapour densities of the same liquid at two temperatures. The experiments were carried out as follows. Two baths were placed alongside one another; one, containing the quartz vessels was to be heated to 30° C.; the other, containing a train of Jena glass vessels was to be cooled to 0° C. At the beginning, these baths were at the temperature of the laboratory and the weighed vessels were placed in position—the baths were then simultaneously and slowly brought to the requisite temperature, 2 hours being taken over this operation. No air passed, but each train was closed at the proper end for the air movement to be in the direction of the subsequent air current. On reaching the temperature aimed at, the trains were joined together and the air current started; the air entered the 0° C. bath and then passed into that at 30° C. At the end of the experiment the air current was stopped, the trains disconnected and each stoppered at the appropriate end, and the baths slowly brought to the laboratory temperature. Again 2 hours were occupied in this operation.

Unfortunately three of these experiments suffer from defects. That of November 8, 1928, is somewhat vitiated by the accidental omission to charge the vessel anterior to Jena 1 with H₂SO₄—luckily this omission is not so serious as might be thought, for in all experiments we have had a protecting H₂SO₄ tube (*outside* the bath) containing glass beads moistened with the acid; obviously this protection is not perfect and the air entering Jena 1 was, towards the end of the experiment, slightly moist. In ordinary circumstances this experiment would be rejected, but as we are not in a position to repeat it it is included, and the gain in the adjacent H₂SO₄ (vessel 2) is taken as representing the loss that would have occurred had the air been dry (*i.e.*, the defect in “tot up,” which is 0·0052 gr., is added). On reference to other experiments at 0° C. (Table I) it will be seen that this procedure is justified; a further strengthening of the argument is afforded by an experiment made in January, 1929, which is rejected because the “tot up” for the 30° bath was largely in defect owing to a globule* of mercury (weighing about 1·56 grs.) which fell into the H₂SO₄ in vessel 5. This experiment without the H and C correction† gives a value for the vapour density ratio of 0·16950, agreeing closely with the result of November 8, 1928.

In the experiment of November 29, 1928, one of the heating lights burnt out, and the temperature dropped‡ from 0·75° to 0·65°; fortunately it could be proved that the temperature was normal 1 hour before. A simple calculation shows that the observed loss is in defect by 0·0030 gr. as a maximum—the more probable value is 0·0015, which is the correction we have applied. The change of temperature in the “nought” bath does not affect the air speed in the “thirty” bath.

* The mercury probably fell into the vessel when “taking down”; similar accidents have happened before.

† The H and C losses are, as seen in the No. 8 experiment, almost negligibly small.

‡ It will be realised that we have now lost the advantage given when the comparison liquids are in the same bath.

The experiment of December 11, 1928, was spoilt by persistent oscillations in the temperature of the "nought" bath; they ran from $0\cdot02^\circ$ above to the same below the mean. The experiment is interesting, however, on account of the second vessel loss which, on applying the H and C correction is turned into a small gain (see Diffusion hypothesis). We are left therefore with the two experiments of November, 1928, to give us the vapour density ratios for water and alcohol each compared between $0\cdot75^\circ$ C. and $30\cdot02^\circ$ C.

These ratios as given in column (16) are those calculated as in all previous cases from equation (I), but as the speed of the air in the "nought" bath is slower than in the "thirty" bath, the observed losses in the former have been multiplied by $303\cdot02/273\cdot75$, the ratio of the absolute temperatures.

If we take the experiment of December 20, 1928 (Table III), as giving the true* value for ρ_w/ρ_a at $30\cdot02^\circ$, namely $0\cdot15645$, and calculate ρ_w/ρ_a for $0\cdot75^\circ$, from the two experiments in Table IV, we get $0\cdot14867$; the mean of the observations at $0\cdot75^\circ$ in air (Table I) is $0\cdot14877$; the agreement is eminently satisfactory, and tends to prove that the method is susceptible of considerable precision.

The Diffusion Hypothesis.—On p. 347, paragraph (1) of B. H. & B.'s paper† an experiment is mentioned as disproving the diffusion hypothesis, but we know now that the H and C loss is responsible for part of the effect, so this hypothesis is still open to us.

Table V gives the results of experiments at 0° C. when no air passes through the train of vessels. The train was stoppered at both ends so as to avoid any differential

TABLE V.

Date.	Vessel 2.	Vessel 4.	Time.
	(Water)	(EtOH)	h. m.
November 12, 1924	—0032	—0048	42 40
November 17, 1924	—0057	—0101	91 0
December 17, 1924	—0006	—0048	43 0
December 20, 1924	—0050	—0099	91 45
April 7, 1925	—0053	—0109	91 30
	(EtOH)	(Water)	
November 27, 1924	—0165	—0033	91 0
December 3, 1924	—0078	—0015	43 40
January 13, 1924	—0082	—0010	43 45
January 17, 1924	—0174	—0037	91 0
March 28, 1925	—0160	—0036	91 30

The mean hourly loss from the water through U-tube 2/3 is $0\cdot455$ grammes.

" " " EtOH " 4/5 is $0\cdot3113$ "
 " " " water " 4/5 is $0\cdot36$ "
 " " " EtOH " 2/3 is $0\cdot183$ "

* The reason for choosing this experiment is given later on under the "diffusion hypothesis."

† *Loc. cit.*

movements due to changes of barometer ; and "handling" corrections, which unfortunately vary considerably, have been applied (details need not be given). The figures under the two headings of vessel 2 and vessel 4 are the losses for the "forward" diffusion only ; they are deduced by subtracting the gain in the last acid vessel from the loss in the adjacent vessel 4, and the difference, which is the back diffusion from 4 into 3 (containing H_2SO_4), when subtracted from the gain in 3 gives the forward diffusion from vessel 2.

Thus the "static" diffusion through U-tube 2/3, which is of slightly larger diameter than U-tube 4/5, is the greater ; and the mean rate for water as compared to EtOH is as 1 to 3.17, which is the same as the ratio of the vapour pressures multiplied by the inverse ratio of the viscosities, but as the latter differ by only 10 per cent. we may put the diffusion as proportional to the vapour pressures, and can then calculate the values for other temperatures and if necessary for MeOH (the viscosity of which is undetermined). Table VI gives the calculated values for the hourly rates at different temperatures.

TABLE VI.

Temperature.	Water.			EtOH.		
	Ratio of π_w .	U-tube 2/3.	U-tube 4/5.	Ratio of π_a .	U-tube 2/3.	U-tube 4/5.
° C.						
0.7	1	0.55	0.36	1	0.183	0.113
13.0	2.43	0.134	0.87	2.27	0.415	0.257
20.0	3.80	0.209	0.137	3.68	0.673	0.416
30.0	6.91	0.380	0.249	6.17	0.1129	0.697

Clearly these "static" diffusion rates are the upper limit to any diffusion that may be assumed to take place while the air is passing, and as they are much greater than any second vessel loss, such an assumption is not incompatible with the facts.

We will therefore assume that in the slow air currents of our experiments diffusion is still in operation. We are not concerned with back diffusion for even if such takes place, it is easy to see that it will not affect the losses sustained.* We will also make the further assumptions that this "dynamic" diffusion is inversely proportional to the air speed over the range of our experiments, and as already stated, it is proportional to the vapour pressure. It must however, be pointed out that these two assumptions can only be valid while the H_2SO_4 is still undiluted, and this qualification is the more important when it is remembered that four-fifths of the vapour is absorbed in the first

* It is obvious that when the posterior H_2SO_4 becomes diluted by the vapour carried forward by the air *ipso facto*, the forward diffusion tends to cease, but it may be argued that back diffusion, if any, into the anterior acid still goes on. Even if this be so, the air leaving the third branch of this vessel is dry and will thus dry the fourth branch, thus receiving precisely the amount lost ; but this may not apply to EtOH on account of chemical reaction.

branch of the sulphuric acid vessel. This latter fact, the effect of which cannot be calculated, prevents any other than rough qualitative results emerging from the analysis of such experiments as can throw light on the hypothesis. In this connection it should be borne in mind that in most cases we are dependent on the "handling corrections" which are far from accurate.

We must therefore be content to consider our hypothesis as probably true if the second vessel losses are found to run in the direction indicated, *i.e.*, that the loss is less the swifter the air current.

In Table VII all the second vessel losses are gathered together and numbered (first column) for convenience in reference. The losses are corrected for "handling" where a proper H and C correction was not known.

TABLE VII.

No.	Date.	Table.	Temperature.	Substance.	Second vessel loss.	Vapour pressure, mm. of mercury.	Speed of air.	Run in hours.	No. of vessel.	Second vessel loss reduced to 65 hours.
			°C.				c.c./min.			
(1)	Oct. 22, 1926	I	0	EtOH	-0026	12.8	31.16	115	2	0.0015
(2)	Nov. 18, 1926	II	0	MeOH	-0076	29.7	30.72	115	4	0.0041
(3)	Nov. 30, 1926	II	0	MeOH	-0050	29.7	30.56	65	4	0.0050
(4)	Sept. 16, 1926	III	13	Water	-0005	11.2	29.56	116	2	0.00028
(5)	Sept. 2, 1926	III	13	EtOH	-0052	28.9	29.76	115	2	0.0039
(6)	Feb. 22, 1927	III	20	Water	-0022	17.5	17.65	66	2	0.0022
(7)	Feb. 1, 1927	III	20	EtOH	-0018	44.0	17.84	115	2	0.0010
(8)	March 4, 1927	III	30	Water	-0032	31.9	17.94	64	2	0.0032
(9)	Dec. 20, 1928	III	30	EtOH	-0115	78.5	32.32	63	4	—
(10)	March 25, 1927	III	30	EtOH	-0049	78.5	17.83	66	2	0.0048
(11)	Sept. 1, 1927	III	30	EtOH	-0210	78.5	5.33	186	2	0.0073
(12)	Sept. 15, 1927	III	30	EtOH	-0161	78.5	5.42	186	2	0.0053
(13)	Nov. 8, 1928	IV	30	Water	-0044	31.9	30.35	160	4	0.0018
(14)	Nov. 29, 1928	IV	30	EtOH	-0131	78.5	26.55	112	4	—
(15)	Dec. 11, 1928	IV	30	EtOH	+0024	78.5	28.24	63	4	—

The experiments (9), (14) and (15) will not be included in our discussion; in all three the quantity of alcohol evaporated off was such as to leave the first branch dry.

The last column of the table gives the second vessel losses reduced to the same "run" of 65 hours—the loss has been assumed to be proportional to the time.

At the onset it seems clear that we cannot compare experiments carried out at different temperatures because we cannot even guess at the effect of the dilution of the acid, for this depends on factors such as diffusion in the acid and density changes which are totally unknown—on the other hand for different substances at the same temperature we may get some information.

For the same substance at the same temperature we have the following three sets of experiments (10), (11) and (12), where clearly the faster air current carries away less vapour from the second vessel.

(8) and (13) also follow the rule, but the figures are somewhat complicated by the fact that in (13) the water was in vessel 4, but we may assume that if the water had been in 2, the loss would have been $0018 \times 1.6 = 0029$.

(2) and (3) also follow the rule.

For different substances at the same temperature, we can compare (1) and (2). Here we have to bring (2) to the loss that would have occurred had the EtOH been in vessel 2, while (1) must be corrected in the ratio of the vapour pressures; the numbers are (1) losses $0.0015 \times 29.7/12.8 = 0035$, and (2) $0041 \times 1.6 = 0066$, these numbers follow the rule.

But if we compare (4) and (5); (6) and (7); and (8) and (10) the rule is not followed. An explanation of this is not far to seek, for on referring to the appropriate tables it will be seen that in these three cases the large transference of EtOH is sufficient to dilute the 20 c.c. in the first branch of the H_2SO_4 enough greatly to reduce the diffusion.

As to the benzene experiments—we must leave out of consideration the experiment of November 2 except to point out that the order of magnitude of the second vessel loss (at mean laboratory temperature of $12.8^\circ C.$) agrees with the others done under similar conditions, that is with the charcoal contained in a tube outside the bath; it is to be noted that the length of tubing* separating the charcoal from the benzene was about three times that on December 13 where the former is in vessel 5 *in* the bath.

In the October experiment the mean temperature of laboratory and charcoal is $12.7^\circ C.$; second vessel loss is 0.1137.

In the November 25 experiment the mean temperature of laboratory and charcoal is $11.0^\circ C.$; second vessel loss is 0.1228.

In the December 13 experiment the temperature of bath and charcoal is $6.45^\circ C.$; second vessel loss is 0.1701.

The losses are inversely as the temperature; this may be entirely fortuitous, but it may be, as generally supposed, that we here have evidence that charcoal is more absorbent the colder it is; on the other hand, the efficacy of charcoal is known to depend largely on its history, and our charcoal was not treated precisely in the same way each time so no great stress can be laid on the run of these figures, but in any event the magnitude of these losses can only be ascribed to diffusion.

On the whole the evidence seems to point to diffusion as operating when the air is passing slowly—a conclusion which ought not to be unexpected. Obviously the faster the current the less the diffusion, consequently it was decided to increase the speed (still keeping the pressure gradient along the train of vessels negligible), and in order

* Unfortunately no record was kept of the diameter of the tubing; but it was of the order of 5 mm., so that the square and not the fourth power of the diameter would enter as a factor in considering the viscosity.

to render some of the other corrections small as compared to the total loss, to run for as long as possible compatible with complete saturation. The result of this reversal of policy is shown in experiments (9), (14) and (15) where the second vessel losses, which are now relatively small, are no longer due to diffusion, but are doubtless the result of evaporating off too much EtOH with the consequence that the first branch of the first vessel is run dry, and, as the air current is rapid, the first branch of the second vessel is drawn upon to complete the saturation.

Thus these three experiments afford a strong confirmation of our hypothesis. Unfortunately it is impossible to calculate from theory or from the experiments the losses caused by diffusion where the air current is slow, hence we must regard the experiments at 20° C., and those at 30° C. except Nos. 9, 13, 14 and 15 as somewhat unreliable; on the other hand the air speed in the experiments at 0° and 13° was, it will be noticed, sufficiently rapid (*i.e.*, some 30 c.c. per minute) to make the diffusion effect negligible compared to the total loss.

Discussion of Results.

DALTON'S Law.—If we are to investigate the question of association by means of our results it is evident that we must form some idea as to how much they are affected by deviation from DALTON'S and BOYLE'S laws.

It is generally assumed that deviations from DALTON'S law are brought about by some interaction (not chemical) between the gas and vapour molecules which results in a certain percentage of vapour molecules adhering to the gas.

Two effects will ensue :—

- (1) The kinetic energy of the composite molecule as compared to that of the original gas molecule is increased, hence in a given space the total pressure will increase, but, in so far as it affects the conditions in our experiments the mixed air and vapour being open to the atmosphere can only be at atmospheric pressure, hence it is a fair inference that the vapour pressure in the air current is decreased as compared to the vapour pressure in a vacuum, or if it remains the same, then the air pressure is diminished.
- (2) In so far as a certain per cent. of vapour molecules are adhering to the gas, the gas on passing out of the vessel will carry away more vapour per cubic centimetre than is contained in the same space in a vacuum.

If, as suggested in (1), the vapour pressures in air and in a vacuum differ, then equation (1) becomes

$$\frac{l_0}{l_a} = \frac{\rho'_w}{\rho'_a} \cdot \frac{B - \pi'_a}{B - \pi'_w},$$

where π'_a and π'_w are the new vapour pressures and ρ'_w and ρ'_a the new vapour density in air.

Unfortunately we have no knowledge of the magnitude of the pressure coefficient in mixtures of air and vapour, but the experiments of Messrs. C. W. GIBBY, C. C. TANNER and I. MASSON* give “*b*” the pressure coefficient due to the departure from DALTON’S law of a 50 per cent. mixture of hydrogen and helium as about 1 part in 2000.

To form an estimate of how our air experiments differ from vacuum conditions, we may assume that the air-vapour coefficient is ten times that of the hydrogen helium mixture, *i.e.*, 1 part in 200, and to get the maximum deviation we will take the EtOH and water experiment at 30° C. (where $\pi_a = 78.5$) and assume that the alcohol mixture only is affected. Then $\pi'_a = 77.7$, $\pi'_w = \pi_w$. Putting these values in equation we find that ρ'_w/ρ'_a differs from ρ_w/ρ_a by 1 part in 1500—a quantity less than our experimental error.

As regards the change in the partial pressure of the air suggested in (1) : the arguments given in the following two paragraphs seem equally applicable here and rule out any change large enough to alter our results.

There are two sets of experiments which bear on the subject :—

- (a) Our own experiments in air and argon (we will refer to the hydrogen later) where the mass of the gases per cubic centimetre are as 28 to 40, and the weight of vapour as 0.18 gramme of water to 1 gramme of EtOH seem to give a range of operating masses large enough to have brought out any variation there may be in this part of the departure from DALTON’S law.
- (b) BERKELEY, HARTLEY and BURTON’S experiments on aqueous solutions of cane sugar and methyl glucoside and calcium ferrocyanide, where they compare the directly observed osmotic pressures to those calculated from the vapour density ratios, show no difference in the results greater than 0.5 per cent. In these experiments the maximum vapour density ratio is only 1.1, yet as the osmotic pressure is proportional to the logarithm of this number it is evident that a departure from DALTON’S law of 1 in 1000 would induce a discrepancy of 1 per cent. in the highly concentrated solutions, moreover if we remember that the relative departure from DALTON’S law would be more apparent for the high concentrations we should expect the latter to show larger discrepancies, all in one direction. As a matter of fact these discrepancies are somewhat less and are not in one direction.

As regards BOYLE’S law. Only a substantial departure therefrom will affect our results ; for it must be remembered that we are comparing one vapour with another, and presumably both will be similarly affected, hence the correcting factors will tend to cancel out because they will appear in the numerator and denominator of the right-hand side of equation (2).

Our experiments cannot show any such effect, except in so far as there is a difference

* ‘ Roy. Soc. Proc.,’ vol. 122, p. 283 (1929).

between the vapour density ratios given in columns (13) and (14). The former is calculated from equation (2), and the latter from equation (5), which is an equation derived from equation (2) by identifying the vapour density ratio with the rates of the vapour pressures multiplied by the ratio of the molecular weights of the normal molecules. But as this identity is only used in the nature of a correcting term, it does not enable us to calculate the full effect, nor as it embodies the departure from BOYLE'S law and the effect of association can we separate the two.

Dealing now with the values found when hydrogen was used. We have the following results :—

Temperature. °C.	In argon. ρ_w/ρ_a	In air. ρ_w/ρ_a	In hydrogen. ρ_w/ρ_a
0·35	0·14881	0·14866	—
0·75	0·14865	0·14877	0·14933

Although the three ratios at 0·75° are roughly inversely proportional to the molecular weights of the gases, yet as the two at 0·35° run in the contrary direction it is clear that the first sequence gives no information as to the divergence from DALTON'S law. On the other hand we view the hydrogen results with suspicion not only because the density of the EtOH differs considerably from that previously used (a difference which certainly means a different composition) but because, as is well known, hydrogen nearly always behaves in an abnormal manner.

Association in the Vapour.—From the preceding discussion we may therefore identify ρ_w/ρ_a with ρ'_w/ρ'_a , and for the discussion of the association it is convenient to reduce all our results to 0·75° C. so that we may compare the substances at the same temperature and pressure and in the same volume, for under these conditions we may assume that the same number of molecules are present.

In this discussion we will distinguish all quantities appertaining to the temperatures of 0·75° C., 6·45° C., and 30·02° C. by one, two and three dashes respectively.

We will take the case of EtOH at 0·75° and 30·02° as illustrative of the reduction.

Let the weight of vapour, in unit volume, when the temperature is 0·75° and the pressure π'_a be W'_a , while when at temperature 30·02° and π'''_a it is W'''_a . Then $W'_a/W'''_a = \rho'_a/\rho'''_a = 0·17839$.

Assuming that the vapour obeys the gas laws, then the weight of vapour, which was originally at π'''_a and 30·02° C., will, when reduced to π'_a and 0·75°, be

$$W'''_a \times \frac{\pi'_a}{\pi'''_a} \times \frac{303·02}{273·75} = W'''_a \times 0·18923 ; (\pi'_a = 13·42, \pi'''_a = 78·50).$$

Thus the ratio of the weights in the same volume, at the same pressure (π'_a) and the same temperature (0·75° C.), is 0·17839/0·18923, so that if \bar{M}'_a and \bar{M}'''_a are the mean molecular weights, then $0·17839/\bar{M}'_a = 0·18923/\bar{M}'''_a$, hence $\bar{M}'_a/\bar{M}'''_a = 0·9427$.

Using the same method, and remembering that in the case of EtOH and water at 30° both substances must be reduced to 0·75°, we get the equations given in the first half of the following table :—

For EtOH at 0·75° and 30·02° C.—

$$\bar{M}'_a/\bar{M}'''_a = 0\cdot9427 \quad (1) \quad \bar{M}'''_a = 47\cdot61.$$

EtOH and water at 30·02° C.—

$$\bar{M}'''_w/\bar{M}'''_a = 0\cdot43399 \quad (2) \quad \bar{M}'''_w = 20\cdot66.$$

EtOH and water at 0·75° C.—

$$\bar{M}'_w/\bar{M}'_a = 0\cdot41267 \quad (3) \quad \bar{M}'_a = 50\cdot48.$$

Water at 0·75° C. and 30·02° C.—

$$\bar{M}'_w/\bar{M}'''_w = 1\cdot0083 \quad (4) \quad \bar{M}'_w = 20\cdot83.$$

MeOH and EtOH at 0·75° C.—

$$\bar{M}'_a/\bar{M}'_m = 1\cdot2989 \quad (5) \quad \bar{M}'_m = 38\cdot88.$$

MeOH and water at 0·75° C.—

$$\bar{M}'_w/\bar{M}'_m = 0\cdot5372 \quad (6) \quad \bar{M}'_m = 38\cdot77.$$

EtOH and C₆H₆ at 6·45° C.*—

$$\bar{M}''_a/\bar{M}''_b = 0\cdot5948 \quad (7) \quad \bar{M}''_a = 47\cdot61 \quad (\bar{M}''_b = 83\cdot9).$$

Water and EtOH at 6·45° C.†—

$$\bar{M}''_w/\bar{M}''_a = 0\cdot4178 \quad (8) \quad \bar{M}''_a = 47\cdot61 \quad (\bar{M}''_b = 20\cdot77 \text{ assumed}).$$

We had hoped that benzene vapour would turn out to be unassociated, but, if we assume this, then, from Nos. (7) and (8), although the calculated molecular weight of EtOH is a possible one, that of water comes out less than 18·02—hence benzene must be an associating substance. By trial and error we can get a value for the molecular weight of EtOH at 0·75° which fits all the equations—this value is 50·5 and the results on this assumption are given on the same line as the equation for which it is derived. But it must be emphasised that values ranging from 50·5 to 51·0 also give a fairly good fit.

We may now speculate a little further and get plausible values for the relative concentrations of the normal and associated molecules in EtOH vapour at 0·75° and 30·02° C.

Theoretically all vapours should be made up of normal, double, treble and higher associated molecules in varying proportions, the law on which the variations depends being unknown. There seems to be a consensus of opinion that EtOH is not highly associated ; if we assume this to be true we can put for the vapour at 0·75° C.

$$\frac{C'_{a_1}}{18\cdot02} + \frac{C'_{a_2}}{2 \times 18\cdot02} = \frac{1}{50\cdot5}$$

* We have taken the $\rho''_a/\rho''_b = 0\cdot2889$; see Table IV notes.

† This value is derived from a curve plotting ρ_w/ρ_a against temperature.

where C'_{a_1} is the weight of normal EtOH molecules per gramme of vapour and C'_{a_2} the weight of the double molecule. Remembering that $C'_{a_1} = 1 - C'_{a_2}$, we get

$$C'_{a_1} = 0.8238, \quad C'_{a_2} = 0.1762.$$

And from the corresponding equation for EtOH at 30.02° C. we get

$$C'''_{a_1} = 0.9345 \quad C'''_{a_2} = 0.0655.$$

In the case of water our equations, as it is known that near the freezing point there must be normal, double and treble molecules, become

$$\frac{C'_{w_1}}{18.02} + \frac{C'_{w_2}}{2 \times 18.02} + \frac{C'_{w_3}}{3 \times 18.02} = \frac{1}{20.83}$$

$$\frac{C'''_{w_1}}{18.02} + \frac{C'''_{w_2}}{2 \times 18.02} + \frac{C'''_{w_3}}{3 \times 18.02} = \frac{1}{20.66}.$$

Clearly these two equations cannot be solved unless we make some further assumptions.

We will make two assumptions (1) that at 30.02° C., the term $\frac{C'''_{w_3}}{3 \times 18.02}$ is negligibly small compared to the other two; and having noticed that the ratio $C'''_{a_1}/C'_{a_1} = 1.134$ is a close approximation to $(243 - 0.75)/(243 - 30.02) = 1.137$, where 243° is the critical temperature of EtOH, we shall assume (2) that a similar relationship applies to water.

But with water we are dealing with three sets of molecules, so that with some plausibility, we will put

$$*(C'''_{w_1} + C'''_{w_2})/(C'_{w_1} + C'_{w_2}) = 1.0851,$$

which is the ratio $(374 - 0.75)/(374 - 30.02)$ where 374° is taken as the critical point of water.

Our first assumption enables us to calculate the concentrations for 30.02° C.; resulting in $C'''_{w_1} = 0.7444$ and $C'''_{w_2} = 0.2556$. And these figures, in conjunction with the second assumption, give, for 0.75° C.,

$$C'_{w_1} = 0.7554, \quad C'_{w_2} = 0.1662, \quad C'_{w_3} = 0.0784.$$

If our second assumption had been

$$\frac{C'''_{w_1}}{18.02} + \frac{C'''_{w_2}}{2 \times 18.02} = 1.0851 \left(\frac{C'_{w_1}}{18.02} + \frac{C'_{w_2}}{2 \times 18.02} \right)$$

it would give us

$$C'_{w_1} = 0.7753, \quad C'_{w_2} = 0.1677, \quad \text{and} \quad C'_{w_3} = 0.0570,$$

* The difference between these two assumptions is that in one case it is the sum of the concentration and in the other the sum of the number of molecules that is involved; with EtOH, the corresponding ratio, as the molecular weights are the same, may refer to either interpretation.

which, as C'_{w_2} is now considerably smaller, makes our first assumption, *i.e.*, that $C'''_{w_2}/18.02 = 0$, more plausible.

We attach no great importance to these figures; they are given here merely as a possible help to others working on the same subject.

Referring now to the experiments with MeOH. The large amount of association indicated by the figures given for \bar{M}'_w as compared to the normal molecular weight seems to show that this substance is even more highly associated than water, and as this probably involves the three sets of molecules, the equation for which cannot be solved, it is deemed not worth while to speculate thereon.

The experiments with benzene and EtOH could not be carried out at any lower temperature than 6.45°C .; hence we have no direct connection at 0.75°C .; but we may make an estimate of the mean molecular weight of benzene (M''_b) in the following way. We can derive a relation between EtOH and water at 6.45°C . from the curve of the variation in ρ_w/ρ_a with temperature—this relation, on reduction to 0.75° , can be solved approximately if we assume that $M''_w = 20.77$ is proportional to the temperature interval. This assumption seems justified if we remember that the numerical difference between M'_w and M'''_w is small, and it results in $M''_a = 49.72$, a value which also is approximately proportional to the temperature interval between M'_a and M'''_a . Inserting $M''_a = 49.72$ in equation (7) we get $M''_b = 83.9$, showing that benzene vapour is associated.

Then assuming that this association is confined to double molecules, we can calculate the relative concentration as before—giving us

$$C''_{b_1} = 0.8605, \quad C''_{b_2} = 0.1395.$$

Summary.

A precision method of determining the ratio of vapour densities in air and other gases is detailed. The results with water, EtOH, MeOH and benzene are given, so also is a direct comparison of the vapour density of EtOH at 0.75°C . to its vapour density at 30.02°C ., and a similar comparison with water. An analysis enabling the experimental error to be evaluated, and other analyses affording means for calculating the effects caused by changes in temperature or in the barometric pressure are also detailed. Numerous corrections, which must be considered if the highest accuracy is aimed at, are set out; and it is pointed out that diffusion is probably the cause of slight discrepancies, which, although not amenable to calculation, can be avoided when the experiments are conducted with a relatively rapid air current and for a sufficient time.

On certain assumptions it is shown that an approximate estimate of the concentrations of normal and associated molecules in the different vapours can be arrived at.

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