PART (B) - EXPERIMENTAL -

MEASUREMENT OF MUTUAL DIFFUSION COEFFICIENTS.
INTRODUCTORY NOTE.
INTRODUCTORY NOTE

The experimental technique used for the determination of the coefficient of diffusion of a gaseous system has been restricted so far to one of several basic methods, all of which involve the measurement of time, temperature, pressure and concentration. An experimental arrangement, adequate for the measurement of gaseous diffusion, which readily suggests itself, consists of a rather long tube of not too large diameter, separated into two halves by means of a stopcock of bore equal to the diameter of the tube. The tube is kept vertical with the heavier component in the lower half of the tube. After each half of the tube has been filled with a different gas or with gas mixtures differing in concentration, the experiment is started by opening the stopcock. Convection in the gas may cause considerable error in diffusion measurements and therefore the temperature of the tube has to be kept quite constant over its whole length. In some cases it has been considered advantageous to maintain a slight temperature gradient (of the order of $10^{-3}$ °C/cm) to preclude the possibility of convection. While several modifications have been used, the techniques developed by the early workers in this field still form the basis for most modern investigations.

EARLY INVESTIGATIONS

Diffusion coefficients for a number of gas pairs were measured by Loschmidt in 1870. He took the two gases in a
uniform symmetrical cell separated into two equal portions by a stopcock having a bore equal to the diameter of the tube. The two halves were filled with different pure gases, the heavier being in the lower half, and diffusion was allowed to start by opening the stopcock; the whole length of the tube being maintained at a constant temperature. After the diffusion has proceeded for a given time, the stopcock was closed and the gas in the two halves allowed to reach equilibrium. The gas in each half of the cell was then analysed. A very elaborate apparatus, employing this principle, has been described by Obermayer. One aim of these measurements was to find the correct law for the temperature dependence of $D$. Since all theories lead to a relation of the form $D = f \frac{\eta}{\rho}$, where $f$ is a factor of the order unity, $\eta$ the viscosity coefficient and $\rho$ the density (varying at constant pressure as $T^{-1}$), the temperature dependence of $D$ ought to be greater than that of the viscosity by a factor $T^{+1}$, which within the limits of experimental error, was verified by Obermayer. Both Loschmidt and Obermayer were able to verify the fundamental dependence of the diffusion coefficient on temperature and pressure as predicted by the kinetic theory.

A series of investigations was carried out at Halle under the direction of Dorn, cf. Lonius, in order to determine the dependence of the diffusion coefficient on the concentration ratio of the two inter-diffusing gases (Schmidt, 1904; Jackmann, 1906; Deutsch, 1907). Loschmidt's method of the vertical tube, divided into two separate parts by a stopcock, was employed by all of them for the above determination. Schmidt and Lonius determined the dependence on concentration more carefully by...
using gas mixtures of different concentrations instead of the pure components. The results of Lonius showed a variation of the diffusion coefficient with concentration up to 2%. A review of these early investigations has been given by Trautz.

Another basic technique is due to Stefan who studied the evaporation of a volatile liquid contained at the bottom of an open cylinder communicating with the atmosphere. This was used for determining the diffusion coefficient of vapours in air or in other gases. The diffusion cylinder should be sufficiently long so that observations on the rate of evaporation of the liquid could be taken without the vapour being able to reach the open end during that time, otherwise any accumulation of the vapour near the open end will disturb the process of diffusion, and an end correction has to be applied for it. A stream of air or other gas is sometimes passed (flow system) across the open mouth of the tube to wash away the accumulated gas. The experiments showed that the rate of evaporation was inversely proportional to the height of air through which the vapour has diffused. As with the Loschmidt technique, this method has also been employed with minor modifications by a large number of workers such as Trautz, Winklemann, Le Blanc and Wuppermann, Hack, Tropley and Whytlaw-Gray, Gilliland, Klotz and Miller, and Mullaly and Jacques. Of the early workers Trautz and Winklemann employed the Stefan's technique quite extensively. Winklemann performed a number of experiments and was the first to develop the flow system mentioned above.
Later on Le Blanc and Wuppermann showed that the results of Winklemann were too low because of the effect of supercooling at the vapour - liquid interface. More recently Mack and Tropley and Whytlaw - Gray have employed this method for the determination of the coefficient of diffusion of iodine vapour in air. Both Jost and Partington are excellent sources for references and reviews of those early experimental studies.

MODERN INVESTIGATIONS

The modern methods for the determination of diffusion coefficient differ essentially from the older ones in the manner of analysing the mixture. The early workers used the methods of chemical analysis but modern investigators have employed more accurate physical methods of analysis such as mass - spectrometry, interferometry, radio-active tracers, thermal conductivity, viscosity, ultrasonic waves etc.

(a) EXPERIMENTS BASED ON STEFAN'S TECHNIQUE.

In modern investigations, attempt is made to refine the original Stefan's method by trying to eliminate or correct for the various sources of error such as the end correction, the supercooling at the vapour - liquid interface etc. Among these the recent investigation of Lee and Wilks is noteworthy for its attention to experimental details and thorough mathematical analysis. Both Arnold and Wilks have discussed the general limitations of analysis by the Stefan's method. Extensive tables
of diffusion data have been given by Trawt and Muller,5 (1936) who used long diffusion paths rather than a flow technique.

Fairbanks and Wilke12 have determined the diffusion coefficient of toluene and ethyl propionate into multicomponent gas mixtures of air, argon and hydrogen. They have utilised the volume of gas displaced in a semi-infinite column by the vaporization of a liquid as means of determining the diffusion coefficients.

Schwartz and Brow15 have used the Stefan's technique in measuring the diffusivity of water in some common gases and recently Raw20 has measured the coefficient of diffusion for boron-trifluoride and boron-trichloride in carbon tetrachloride vapour. Klirnova21 and his coworkers have essentially used Stefan's technique for determining the diffusion coefficient of air - CO and air-H2O over a temperature range from 0° to 1260°C. The only fundamental improvement introduced in the Loschmidt method to this date, is the elimination of the stopcock by the use of two ground discs, rotating upon each other and each connected to one tube. Boardman and Wild22 were the first to utilise this shear technique for the determination of diffusion coefficient for the gas pairs N2O - CO2. They selected these systems because for them the mutual diffusion coefficient will closely approximate to the coefficient of self diffusion for each component as both components have the
same molecular weight and approximately the same molecular
diameter and intermolecular field. They measured the average
concentration in the cell after the experiment, from the thermal
conductivity of the mixture. Wall and Kidder23 also took gases
of same molecular weights but used interferometric method of
analysis. From their studies on propane, carbon-di-oxide,
nitrous oxide and ethylene oxide (all of the same molecular
weight) they concluded that the difference in the observed
effects could be attributed primarily to size. Wintergerst24
also utilised an interferometer to measure the concentration
change by withdrawing samples and finding out the refractive
index of the mixture.

The basic equation for determining the diffusion coefficient
from the foregoing experiments is the following:

$$\Psi_2 = \frac{1}{2} + \frac{2}{\kappa} \sum_{K=1}^{\infty} \frac{L}{K} \frac{K^2}{2} \cos \frac{K\pi z}{L} \cdot e^{-D_{12} (\pi^2 L^2)}$$

where $\Psi_2$ is the mole fraction of the heavier gas filled in
the lower half cell, $t$ is the time in seconds, $L$ is the overall
cell height in cm, $z$ is the distance from bottom at which the
change in concentration is observed and $D_{12}$ is the coefficient
of mutual diffusion of the binary system in cm²/sec. The above
equation is based on the assumptions that $D_{12}$ is constant over
the entire composition range and the gases are ideal (no
pressure change in mixing).
In the case where one measures the average concentration in the lower half of the cell, equation (1) yields on integration between the limits 0 to 1/2:

$$
\bar{Y}_L = \frac{1}{2} + \frac{4}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \sin \frac{k\pi}{2} e^{-D_{12}(\frac{k\pi}{L})^2 t}
$$

where $\bar{Y}_L$ is the average mole fraction of the heavier gas in the lower half of the cell. Under the conditions when $D_{12}(\gamma/\alpha)^2 t \leq 0.7$, the second and higher terms of the series are always less than 0.2% of the first of the first term and can therefore be neglected. Equation (2) then yields

$$
D_{12} = \frac{1}{4\pi^2} \log \left[ \frac{4}{\pi^2} \left( \frac{1}{\bar{Y}_L} - \frac{1}{\gamma} \right) \right]
$$

for average analysis in the bottom half.

Drickamer$^{25-27}$ and his coworkers have applied the Loschmidt technique in specially designed cells and have measured the self-diffusion of carbon-di-oxide up to 150 atmospheres and the mutual diffusion coefficient for mixtures of carbon-di-oxide-methane up to 225 atmospheres. They used radio-active tracers and employed a scintillation counter for analysing the gas mixture. Amdur$^{28}$ and his coworkers also used radioactive tracers and employed ionization technique to determine the diffusion coefficients of CO$_2$ - CO$_2$ and CO$_2$ - N$_2$. (Recently Amdur and Schatzki$^{29}$ have determined the diffusion coefficient of the system Xe-Xe and Ar-Xe using Loschmidt technique in which saturation ionization currents were used as a measure of tracer concentrations.)
In the foregoing experiments with the Loschmidt cell, the average concentration in one cell was measured but on account of the large area of diffusion cross-section, errors are likely to arise due to turbulence at the shear interface or the valve opening and convection within the cell (in the vertical cells). Convection is usually minimised by maintaining the upper half cell at a slightly higher temperature than the lower half and keeping the heavier gas in the latter.

Strehlow\textsuperscript{30} tried to carry out a point analysis, using the thermal conductivity of a horizontal wire placed at a height equal to one-sixth of the over-all cell height, and studied the temperature dependence of the diffusion coefficient of systems He-A, H\textsubscript{2}-A, H\textsubscript{2}-n\textsubscript{2}, and H\textsubscript{2}-SF\textsubscript{6}. Thermal conductivity is practically the only means available for analysing a gas mixture of ortho and para-hydrogen and has consequently been utilised by Hartsock and Schmidt\textsuperscript{31} and Heath, Ibbs, and Wild\textsuperscript{32} for this purpose using the Loschmidt technique. Bunde\textsuperscript{33} and Rumpel\textsuperscript{34} have also carried out a point analysis by a complicated interferometer arrangement and obtained fairly reliable and reproducible results. They studied the systems H\textsubscript{2}-N\textsubscript{2}, H\textsubscript{2}-NH\textsubscript{3}, N\textsubscript{2}-NH\textsubscript{3} and He-H\textsubscript{2}, He-N\textsubscript{2}. In the case of point analysis, at $z = 1/6$, equation (1) can be shown to yield:

$$P_{12} = \frac{1}{t} \left( \frac{11}{12} \right)^{2} \ln \left[ \frac{\frac{t}{2} \left( \frac{1}{\gamma_{1}} \right)}{\gamma_{2} - \frac{1}{\gamma_{2}}} \right]$$

The above equation holds good only when $t$ is large enough so that the fifth and higher terms of equation (1) become negligible.
Another technique which stems from the Loschmidt method is the use of a cell composed of two bulbs connected by a narrow tube or capillary with a valve in between to start or stop the diffusion run. This type of apparatus has been used extensively in studies of self and thermal diffusion for a wide range of experiments. Nobody however, appears to have used it for mutual diffusion experiments but it seems to possess several advantages over the usual Loschmidt type of cell. It is free from errors due to convection, turbulence etc. Further, the progress of diffusion can be easily studied at different intervals of time and the usual methods of analysis by mass-spectrometer, tracer technique, interferometer, thermal conductivity etc. can all be conveniently employed. Analysis by mass-spectrometer has been employed by a large number of workers such as Watson and Woernley, Murphy, Ney and Winn, Ney and Armistead, Winn and Winter for the determination of self-diffusion and thermal diffusion of gases. In addition to the work previously mentioned utilizing radioactive tracers, mention may be made of the study of thermal diffusion in mixtures containing radon by Harrison and the measurements of the self-diffusion of argon by Hutchinson, Schafer, Corte and Moesta have recently tried to find the concentration dependence of the diffusion coefficient by using a two-bulb-capillary technique and thermal conductivity method of analysis. They
have studied the systems, hydrogen - carbon dioxide, hydrogen-nitrogen and carbon dioxide-nitrogen and have reported a dependence of as much as twenty percent in some cases, which however seems doubtful, and has not been confirmed by any other investigator. Recently Srivastava and others have determined the binary diffusion coefficients of rare gas pairs using thermal conductivity analyser.

(d) OTHER METHODS.

Kinetic theory of gases predicted that diffusion thermo-effect must exist as the inverse effect of thermal diffusion. This was first observed by Clausius and Waldmann. Thus inter-diffusion of gases produces a temperature difference which provides us with a new method of determining the diffusion coefficient. Waldmann was the first to tackle this problem and employing platinum resistance thermometry, he was able to determine both thermal and ordinary diffusion coefficients from observations of the diffusion thermo-effect in flow and nonflow systems. This method is particularly advantageous in studying thermal diffusion on account of the positive assignment of the temperature. However, the method is not free from trouble as it requires a knowledge of the thermal conductivity of the mixture.

Nettley has devised an altogether new method of determining ordinary diffusion coefficient by studying the approach to equilibrium in thermal diffusion experiments. This method is
suitable for determination of relative diffusion coefficients as a function of concentration. Nettlows results for hydrogen and nitrogen agree reasonably well with those of Schafer. The theory of the method has been treated in detail by Saxena and Mason. They have also performed some experiments, but the accuracy attained is not high. Recently, Walker and Westenberg have used a point source technique to measure diffusion coefficients of various gas pairs at high temperature. Walker, de Haas and Westenberg have used the same technique to study multicomponent diffusion in the system CO₂-H₂-N₂. Very recently, McCarty and Mason, and Mason, have tried to use Kiskendall effect in gases as a device to measure the diffusion coefficient of gases.

(e) PRESENT WORK.

In the present investigations, we have utilised the two-bulb method for determining the mutual diffusion coefficients of some binary gas mixtures. Diffusion is allowed to take place between two diffusion bulbs through a precision capillary tube and samples of gas are withdrawn from one bulb (analysis bulb) at different times and analysed by a differential conductivity analyser. A general theory of this method of determining the diffusion coefficient has been given in considerable detail by Ney and Amistead. We shall formulate it for our present case. For the sake of ready reference all the symbols employed are collected below:
\[ V_1 = \text{Volume of the bulb I (analysis bulb) in cc.} \]
\[ V_2 = \text{volume of the bulb II in cc.} \]
\[ c_1^t = \text{Concentration in grams/cc. of the heavier gas in bulb I at time 't' sec.} \]
\[ c_2^t = \text{Concentration in grams/cc. of the heavier gas in bulb II at time 't' sec.} \]
\[ D = \text{Coefficient of diffusion in cm}^2/\text{sec.} \]
\[ l = \text{Effective length of the connecting tube.} \]
\[ A = \text{Effective area of the connecting tube.} \]
\[ c_1^\infty = \text{Equilibrium value of the concentration of the heavier component in bulb I after complete mixing.} \]
\[ c_1^0 = \text{Initial value of the concentration of the heavier component in bulb I.} \]
\[ V_0 = V_1 + V_2 \]

The simplest case of the diffusion problem will be worked out first and the necessary corrections developed later. The simple theory is based on the following assumptions:

(a) The concentration gradient is linear throughout the connecting tube.

(b) The concentration gradient is only confined to the connecting tube.

(c) The volume of the connecting tube is negligible compared with the volume of the bulbs.
Under these conditions we can write the equation for $Q$, the rate of transfer of the heavier component (filled in bulb I) by diffusion to bulb II as

$$Q = -DA \text{ grad } C \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3)$$

From the above assumptions (a) and (b) we get

$$Q = -\frac{DA}{\ell} \left( c_2^t - c_1^t \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4)$$

The rate of transfer of the heavier component can also be given in terms of time as

$$Q = -V_1 \frac{dc_1^t}{dt} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5)$$

Equating (4) and (5), we get the differential equation

$$\frac{dc_1^t}{dt} = -\frac{DA}{\ell V_1} \left( c_1^t - c_2^t \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6)$$

Now in view of the following relation

$$V_1 c_1^t + V_2 c_2^t = V_0 c_1^\infty \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7)$$

we get $c_2^t = \frac{V_0 c_1^\infty - V_1 c_1^t}{V_2}$ \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (8)

Substituting the above value of $c_2^t$ in equation (6) we get
Let us introduce two constants $\alpha$ and $\beta$ defined by the relations

$$\alpha = \frac{DA}{\ell} \frac{V_0}{v_1 v_2}$$

$$\beta = \frac{DA}{\ell} \frac{V_0}{v_1 v_2} c_1^\infty$$

Equation (9) then reduces to

$$\frac{dc_1^t}{dt} = - \alpha c_1^t + \beta$$

$$= - \alpha (c_1^t - \beta/\alpha)$$

Therefore

$$\frac{dc_1^t}{c_1^t - \beta/\alpha} = - \alpha \ dt$$

Integrating the above we get
\[ \log \left( \frac{c_1^t - \beta}{\beta} \right) = -\beta t + \text{const} \]

or \[ c_1^t = \frac{\beta}{\beta} = Ae^{-\beta t} \] ... (10)

We also have the following boundary conditions:

1. \[ c_1^t = c_1^0 \quad \text{at} \quad t = 0 \]
2. \[ c_1^t = c_1^\infty \quad \text{at} \quad t = \]

with these boundary conditions, equation (10) becomes

\[ c_1^0 - \frac{\beta}{\beta} = A \]

and \[ c_1^\infty - \frac{\beta}{\beta} = 0 \]

Equation (10) then yields

\[ c_1^t - c_1^\infty = (c_1^0 - c_1^\infty) e^{-\beta t} \] ... (11)

Equation (11) is the simple solution of the diffusion equation.

It can be written in the more convenient form

\[ \frac{c_1^t - c_1^\infty}{c_1^0 - c_1^\infty} = e^{-\beta t} \] ... (12)

In order to apply the above equation (12) to our geometry it is necessary to modify it by making proper corrections for the assumptions (a), (b) and (c).
CORRECTIONS FOR THE ABOVE THREE ASSUMPTIONS.

(a) In practice the tube joining the two bulbs may have stop-cock and end pieces of different cross-sections. It is therefore not strictly correct to put $A \text{ grad } C = A(c_1 - c_2)/l$. If, however, the concentration gradient is assumed to be linear in each element of length $l_j$ with cross-section $A_j$, it can be easily shown that $l/A$ may be taken to be equal to mean $\sum l_j/A_j$; provided $D$ is assumed to be independent of composition. The dependence of $D$ on composition is however too small and has not been experimentally established with any certainty as to its magnitude, it has therefore been neglected in these experiments.

(b) Since in our experiment, the $l/A$ for the bulbs was less than one-tenth of one percent of the $l/A$ for the connecting tube, the assumption that the gradient is all in the connecting tube is justified. A very small end correction would, however, be necessary which, in the case of cylindrical bulbs, was found by Rayleigh to cause an increase in the effective length of the tube at each end by about 0.82 times the radius of the tube. This additional length is to be considered only in $\sum l_j/A_j$. It has however been neglected in the present case.

(c) The connecting tube possesses a volume which cannot always be neglected. It can be taken into account in the following way. Let the average concentration in the connecting tube, $c_L$, be at any time the mean of the concentrations at the ends of the connecting tube i.e.
Equation (7) must be replaced by

\[ \bar{v}_1 c_1^t + \bar{v}_2 c_2^t + \bar{v}_L A \ell = (V_0 + A \ell) c_1^\infty \]  \hfill (14)

From equations (13) and (14) we get

\[ (V_1 + A \ell/2) c_1^t + (V_2 + A \ell/2) c_2^t = (V_0 + A \ell) c_1^\infty \]

Equation (8) can be made consistent with this condition if one replaces \( V_1 \) by \( (V_1 + A \ell/2) \), \( V_2 \) by \( (V_2 + A \ell/2) \) and \( V_0 \) by \( (V_0 + A \ell) \).

In the light of all the above three corrections, the quantity defined previously can now be written in the form

\[ \kappa^{(\text{corrected})} = \frac{D}{\sum_j \left( \frac{\ell_j}{A_j} \right)} \left( \frac{V_0 + A \ell}{(V_1 + A \ell/2)(V_2 + A \ell/2)} \right) \]

\hfill (15)

In our actual experiments, the contribution of the correction for (c) was negligible, and equation (15) was therefore used in the form

\[ \kappa^{(\text{corrected})} = \frac{D}{\sum_j \left( \frac{\ell_j}{A_j} \right)} \frac{V_0}{V_1 V_2} \]

\hfill (16)

In the second chapter of this thesis, two additional corrections due to diffusion coefficient varying with concentration and non-attainment of quasi-stationary state have been considered in detail.
CALCULATION OF THE DIFFUSION COEFFICIENT

The time derivative of the logarithm of equation (12) gives,

\[
\frac{d}{dt} \ln (c_1^t - c_1^\infty) = -\kappa
\]

A plot of \(\log_2(c_1^t - c_1^\infty)\) versus \(t\) gives a straight line the slope of which determines \(-\kappa\). The quantity \(D/\kappa\) is precalculated from the measured geometric constants of the apparatus with the help of equation (16). The diffusion constant was then obtained by multiplying this \(D/\kappa\) by the experimental \(\kappa\) obtained from the graph.

In the following three chapters, the binary diffusion coefficient of monatomic - diatomic gas pair measured at four different temperatures are given.

Chapter III deals with the measurement of mutual diffusion coefficient of the gas pairs \(\text{H}_2-\text{Ne}, \text{H}_2-\text{A}\) and \(\text{H}_2-\text{Xe}\) at \(-30^\circ\text{C}, 0^\circ\text{C}, 30^\circ\text{C}\) and \(60^\circ\text{C}\). The experimental data have been used to calculate the force parameters on Lennard-Jones (12:6) model by least square fitting. Also the experimental values of the mutual diffusion coefficient, thermal conductivity and viscosity of pure components have been combined to calculate the thermal conductivity of the corresponding binary mixtures and a good agreement with the experimental data has been obtained. In chapters IV and V the same procedure has been followed with \(\text{O}_2-A, \text{O}_2-\text{Xe}\) and \(\text{O}_2-\text{He}\) trio and \(\text{N}_2-A, \text{N}_2-\text{Xe}\) and \(\text{N}_2-\text{He}\) trio respectively.
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