MEASUREMENT
OF
BINARY GASEOUS DIFFUSION COEFFICIENTS
OF
POLAR SYSTEMS

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We accept this thesis as conforming to the required standard

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Dr. D.S.Scott, Associate Professor, Chemical Engineering;
Director of this investigation.

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ABSTRACT

This investigation was undertaken primarily for the purpose of collecting reliable experimental data on binary gaseous diffusion coefficients of polar systems. The binary gas pairs investigated were the $A - SO_2$, $A - HCl$, and $SO_2 - HCl$ systems. Diffusion through a porous solid in a flow apparatus was adopted for the diffusion measurement. The diffusion cell was standardized by making diffusion runs using the $N_2 - CO_2$ system at 5 different temperatures, room temperature, $70^{\circ}C$, $120^{\circ}C$, $200^{\circ}C$, and $250^{\circ}C$, and using also the $N_2 - H_2$ system at room temperature. Thermal conductivity cells and chemical methods, alone or in combination, were used for analysis of the gas streams.

The results in all these three systems could be represented by straight lines on logarithmic plots of diffusion coefficient against termperatures from $20^{\circ}C - 250^{\circ}C$. In the first two pas pairs, the experimental coefficients appeared to be 25.3% and 29.2% less at room temperature, and 20.0% and 12.1% less at about $250^{\circ}C$ than the respectively predicted values obtained by using the Stockmeyer potential function in the Hirschfelder diffusion equation. The slopes of the lines were 1.988 and 2.42, respectively. It was found that the $A - SO_2$ system could be represented by a potential function of the Lennard-Jones type, although the molecular force parameters determined from the diffusion data did not agree with those calculated from the pure component values and the usual empriical combining rules. The system $A - HCl$ could not be represented by a function of the Lennard-Jones type.

The third system, $SO_2 - HCl$, was also found to behave more or less the same way as $A - HCl$ system. However, the slope of the line obtained from a Log D vs Log T plot (2.22), was smaller than that of the $A - HCl$ system, although still greater than that predicted by using the Monchick and Mason (12-6-3) potential function. The magnitudes of the diffusion coefficients within the range of temperatures studied were found to be within 11.0% of the predicted ones. Nevertheless, the system did not conform completely to the Monchick and Mason

model.

Some qualitative reasons are given for the inadequacies of present potential functions and combining rules for use in predicting binary diffusion coefficients in mixtures containing polar molecules.

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INTRODUCTION

From the point of view of both applications in many engineering
operations and an understanding of the nature of the unlike molecular interact-
ions, it is important to have reliable values of the binary diffusion
coefficients of gases.

According to the rigorous kinetic theory of gases, the mutual diffusion
coefficients of gases in binary systems, in the first approximation, is
dependent only on the unlike molecular interaction. Hence, its accurate
determination is liable to give information about the force laws between
unlike molecules better than possibly any other property of gas mixtures.

Based on simplified assumptions Hirschfelder and others[1] have deduced a
mathematical expression for the prediction of binary gaseous diffusion
coefficients. This relationship has been found to be valid over fairly wide
ranges of temperature and pressure only for nonpolar, nearly spherical
molecules, that is, those molecules for which the Lennard-Jones potential
function might be adequate.

A modification of this function has been applied to predict the diffusion
coefficients of systems involving a nonpolar substance as one component and a
polar substance as the other. Unfortunately, the experimental data at
varying temperatures for such systems available in the literature are scanty
and often do not agree with the predicted values. Obviously, reliable
experimental data on diffusion coefficients of nonpolar - polar systems over
a reasonable range of temperature are needed to test the modified equation of
Hirschfelder and others.

Finally, for the prediction of diffusion coefficients of systems involving
polar molecules as both components, there exists no equation in the literature.
Furthermore, no attempt has yet been made for the experimental measurement of
the diffusion coefficients of such systems as a function of temperature.

It may be mentioned in this connection that, based on certain simplifying assumptions which though not rigorously justified are claimed by the authors to be physically reasonable, a theory has been worked out by Monchick and Mason[2] for the prediction of the transport properties of pure gases which have permanent dipole moments. An acid test for this theory lies in its simultaneous application to the viscosity and the self-diffusion coefficient data. Although reliable viscosity data of many polar gases are available in the literature, unfortunately, the data on the self-diffusion coefficients of such substances are almost negligible. Therefore, whether or not Monchick and Mason's model represents the true picture of polar molecules in so far as their transport properties are concerned, remains to be seen when reliable measurements of their self-diffusion coefficients are available.

Furthermore, this equation of Monchick and Mason is not adaptable as such to binary systems. Some combining rules, either purely empirical or based on some physical reasoning, are needed for the parameters of the proposed potential function for polar substances. Obviously, this requires reliable experimental data on binary diffusion coefficients of such systems if such rules are to be adequately tested.

The present investigation is therefore directed towards the measurement of binary diffusion coefficients of polar systems.

An outline of the plan of investigation is given in the next section.

METHODS OF APPROACH

As a first step toward the present investigation it was planned that a review of the pertinent literature be made for the purposes of the selection of systems of gas pairs and a method for the measurement of their diffusion coefficients, A brief account of this is given in the section, REVIEW OF LITERATURE.

To permit prediction of diffusion coefficients, two equations were selected, one based on classical kinetic theory and another based on modern kinetic theory. For the first, the Arnold equation was chosen, and for the second, that of Hirschfelder. An account of this is given in THEORY OF PREDICTION.

The systems selected for study were argon - sulphur dioxide, argon-hydrogen chloride, and sulphur dioxide - hydrogen chloride. The method chosen for the measurement of their diffusivities was by diffusion through a porous solid in a flow apparatus. An account of the design and construction of the apparatus is given in APPARATUS.

In order to obtain a methematical expression for the calculation of the diffusion coefficients of the selected systems from the measured data, it was decided to integrate the general diffusion equation under the conditions of the experiment. This is given in the THEORY OF MEASUREMENT.

For the purpose of the standardization of the apparatus it was planned that the diffusion cell be calibrated by making diffusion runs of a binary gaseous system whose diffusivities at various temperatures were fairly accurately known. The system selected for this purpose was nitrogen-carbon dioxide and the data to be used were those obtained by Walker and Westenburg[3]. Also, it was planned that the temperature dependence of the calibration factor, if any, be determined by repeating the calibration procedure at various temperatures ranging from room temperature to about 250°C. Further,

it was decided that the independence of the calibration factor of the particular binary system, be checked by repeating the calibration procedure with at least one different gas pair. The system selected for this purpose was the nitrogen - hydrogen system, and the data to be used were those obtained by Scott and Cox[4]. An account of the calibration procedure is given in the section entitled PROCEDURE while the results obtained therefrom are given in RESULTS.

Finally, the diffusion coefficients of the proposed systems obtained experimentally are presented in RESULTS.

REVIEW OF LITERATURE

Quite a few review articles on binary gaseous diffusion are available in the current literature. The one written by Westenburg[5] is fairly recent and comprehensive. However, a good deal of work has been done after this date by various workers including Walker and Westenburg themselves. For the purpose of the present investigation the original works of interest were all reviewed again. A bibliography is given in APPENDIX A.

From this review, it appeared that sulphur dioxide and hydrogen chloride would be a good choice for polar gases, as both of them have high dipole moments, and as their molecular structures do not deviate very much from the ideal spherical shapes. For making a nonpolar - polar combination with these polar gases, it was thought that an inert gas would be the best selection, as it would conform to the ideal molecule assumed in the ordinary kinetic theory of gases. It was found in the pertinent literature survey that no work had yet been done on argon - sulphur dioxide, argon - hydrogen chloride, and sulphur dioxide - hydrogen chloride systems. Consequently, these systems were selected for the purpose of the present investigation.

On the available methods for the measurement of the binary gaseous diffusion coefficients, a review has been made by Paul and Srivastava[6]. The so called "Point source technique" of Walker and Westenburg for the measurement of the diffusion coefficients in binary gaseous systems is particularly suitable for high temperature measurements with a high degree of precision. However, the apparatus is highly complicated, and difficult to duplicate with equal precision for work with corrosive gases. Diffusion through a porous solid as reported by Scott and Cox[4] appears to be a simple yet suitable method for fairly high temperature measurements. As far as the precision in this method is concerned, the authors have shown in at least one case i.e. in the case of nitrogen - hydrogen system, that the data

obtained by this method agree reasonably well with those obtained by Schafer and Moesta[7] , Schafer, Corte and Moesta[8], Jackmann[9], Waldmann[10], and Boardman and Wild[11], as well as with those predicted by the Hirschfelder equation using the Lennard-Jones potential function.

It was therefore decided that for the purpose of the present investigation the method of measuring diffusion through a porous solid in a flow system should be used. This method has the advantage over conventional types, like the Loschmidt Cell, in that it avoids the difficulties normally associated with heating a gas to high temperatures, in particular convection effects.

THEORY OF PREDICTIONS

Based on the early kinetic theory of gases, a number of equations were formulated for the prediction of binary gaseous diffusion coefficients. A critical review of this subject has been given by Reid and Sherwood[13]. It can be concluded from this review that the results from the semi-empirical Arnold equation appear to be less erratic for non-ideal systems than those calculated from other expressions. This equation is

$$D_{AB} = \frac{0.00837 \, T^{5/2} \left((M_A + M_B)/M_A M_B \right)^{\frac{1}{2}}}{P \left(V_{b_A}^{1/3} + V_{b_B}^{1/3} \right)^2 (T + S_{AB})} \tag{1}$$

where D_{AB} is the binary gaseous diffusion coefficient

M_A, M_B are the molecular weights of the respective

components,

T is the temperature,

P is the pressure

V_{b_A}, V_{b_B} are the molal volumes of the pure components

at their normal boiling temperatures,

S_{AB} is the Sutherland constant for the gas

mixture estimated by

$S_{AB} = F \sqrt{S_A S_B}$, or

$= 1.47 \, F \sqrt{T_{b_A} T_{b_B}}$ in cases where S_A, S_B

are not available,

F an empirical factor varying with the ratio,

V_{b_B}/V_{b_A}, as tabulated by Arnold.

The modern version of the kinetic theory of gases has led to the development of the Hirschfelder[1] equation which takes into account the forces

of attraction and repulsion between the molecules undergoing encounter.
His equation for binary systems is

$$D_{AB} = 0.0026280 \frac{T^{3/2} ((M_A + M_B)/2M_A M_B)^{\frac{1}{2}}}{P \; \sigma_{AB}^2 \; \Omega_{AB \; (T_{AB}^*)}^{(1,1)*}} \tag{2}$$

where σ_{AB} is the collision diameter or the distance
parameter of a potential function,

$\Omega_{AB(T_{AB}^*)}^{(1,1)*}$ is the collision integral that accounts
for the unlike molecular encounter; it is
a function of T_{AB}^* in the cases of nonpolar-
nonpolar, and nonpolar - polar systems
while it is a function of T_{AB}^* and a second
parameter σ_{AB}, in the case of polar-polar systems.

$T_{AB}^* = kT/ \epsilon_{AB}$

ϵ_{AB} is the depth of the potential well, or the
energy **parameter** of a potential function.

This equation (2) is perfectly sound and adaptable to any binary system,
i.e. it can be applied equally well to nonpolar-nonpolar, nonpolar-polar and polar-
polar systems, if a suitable potential function be available. A number of
potential functions are, in fact, available in the literature, but only one of
them has been used extensively to evaluate the collision integral and that
is the Lennard-Jones function[1], which is descriptive only of nonpolar -
nonpolar systems.

This function considers only the short range repulsive force and the long
range dispersion force which, therefore, covers only the encounter between two
isolated ideal molecules i.e. molecules with spherical shapes, electrically
neutral (i.e. having no charge or dipole or multipole moments) and which

undergo inelastic collisions. The first force has been approximated by an
inverse 12th power of the distance of separation, while the second has been
found to be proportional to the inverse 6th power of this distance. This is
expressed in the Lennard-Jones potential function as

$$\varphi_{(r)} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \tag{3}$$

The collision integrals both for like and unlike molecular encounters have
been calculated using this potential function. The parameters   and   for
pure components can be obtained from viscosity data, as this phenomenon
depends on like molecular interactions. The pure component parameters are
then combined by empirical rules suggested by Hirschfelder, that is

$$\left.\begin{array}{l}\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} \\[2mm] \sigma_{AB} = \dfrac{\sigma_A + \sigma_B}{2}\end{array}\right\} \tag{4}$$

and used in the Lennard-Jones potential function to permit prediction of
the behaviour of binary mixtures, and particularly the binary diffusion
coefficient, which depends on only unlike molecular interactions.

The diffusion coefficients calculated using this technique agree
fairly well with experiment for nonpolar - nonpolar systems as might be
expected.

In the case of nonpolar - polar systems, in addition to the above mentioned
two forces, a force of induction due to the interaction between the dipole
moment of one molecule and the polarizability of the other, comes into effect.
This force varies as the inverse 6th power of the distance of separation of
the point of action of the dipole and that of the polarizability. For this
purpose, therefore, the Stockmayer potential function rather than the Lennard-
Jones has been suggested for use. The Stockmayer potential function for
nonpolar - polar systems takes the same form as the Lennard-Jones with an

additional term to account for the primary induction effect, i.e.

$$\phi_{(r)} = 4\,\epsilon_{AB}\left[\left(\frac{\sigma_{AB}}{r}\right)^{12} - \left(\frac{\sigma_{AB}}{r}\right)^{6}\right] - \frac{\alpha_{np}\,\mu_{p}^{2}}{r^{6}} \qquad (5)$$

This expression neglects terms describing interactions between multipole moments. It has been shown by Hirschfelder that equation (5) can be written in the same mathematical form as the Lennard-Jones potential if it is assumed that the induction interaction is also from centre to centre i.e. the dipole is assumed to be a point dipole situated at the centre of the polar molecule and similarly, the polarizability situated at the centre of the nonpolar molecule. That is,

$$\phi_{(r)}_{np\text{-}p} = 4\,\epsilon'\left[\left(\frac{\sigma'}{r}\right)^{12} - \left(\frac{\sigma'}{r}\right)^{6}\right] \qquad (6)$$

where
$$\epsilon' = \epsilon_{AB}\left[1 + \frac{\alpha_{np}\,\mu_{p}}{4\,\epsilon_{AB}\,\sigma_{AB}^{6}}\right]^{2}$$

and
$$\sigma' = \sigma_{AB}\left[1 + \frac{\alpha_{np}\,\mu_{p}}{4\,\epsilon_{AB}\,\sigma_{AB}^{6}}\right]^{\frac{1}{6}}$$

Unfortunately, except for water in systems with a nonpolar substance, this potential function does not agree with the experimental results, giving values which are too high by up to 30%.

In the cases of polar - polar systems, neglecting induction forces between polarizability of one molecule and dipole or multipole moments of the other, and taking into account only the interaction between two dipole moments, the Stockmayer potential function assumes the form:

$$\phi_{(r)}_{p\text{-}p} = 4\,\epsilon_{AB}\left[\left(\frac{\sigma_{AB}}{r}\right)^{12} - \left(\frac{\sigma_{AB}}{r}\right)^{6}\right] - \frac{\mu_{A}\mu_{B}}{r^{3}} \qquad (7)$$

The last term i.e. the dipole-dipole interaction depends, apart from the distance of separation of the points of action of the dipoles, upon the orientations of the dipole moments of the molecules, i.e. it is an angle dependent force. On the assumption of centre to centre interaction i.e. the dipoles being assumed to be situated at the centres of the respective molecules, Monchick and Mason[2] have expressed the function in the form of Lennard-Jones potential function but with three terms and three parameters, i.e.

$$\phi_{(r) \atop p\text{-}p} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 - \delta\left(\frac{\sigma}{r}\right)^3 \right] \tag{8}$$

They have also calculated the collision integrals averaging over all orientations, and have applied their results to the viscosity data of some polar gases. However, this approach has not yet been tested for diffusion, as self-diffusion data of polar gases are not available. Further, in order to apply this function to binary systems, some combining rules for ϵ_{AB}, σ_{AB}, and δ_{AB} are necessary.

The parameter δ introduced by Monchick and Mason for a pure component can be related to those used in the Stockmayer potential function by combining equation (7) for a single component with equation (8) to give

$$4\epsilon\sigma^3\delta = 2\mu^2 \tag{9}$$

Assuming that Monchick and Mason's approach is valid for binary systems, the relationship between the binary parameters is

$$4\epsilon_{AB}\sigma_{AB}^3\delta_{AB} = 2\mu_A\mu_3 \tag{10}$$

If Hirschfelder's combining rules for ϵ_{AB} and C_{AB} are assumed to be still valid, then U_{AB} can be calculated from equation (10). However, no experimental data are available to test the validity of the combining rules. If values of the parameter U are available for the pure components, it can be proven that U_{AB} can be satisfactorily obtained from either the geometric or the arithmetic mean of these pure component values. This proof is given in Appendix E.

Both Hirschfelder's approach for nonpolar - polar systems, and Monchick and Mason's for polar - polar systems, suffer from limitations.

In the case of nonpolar - polar systems, in addition to the interaction between the point dipole of the polar molecule and the point polarizability of the nonpolar molecule, there might be (1) force contributions due to interactions between the permanent point dipole of the polar molecule and quadrupole or multipole moments of the nonpolar molecule if it happens to have one, (2) contributions due to the point-action assumption, that is, due to deviations (a) between the ideal point dipole and the real case for most polar molecules in which the effect spreads over the molecule (b) between the ideal point polarizability and the one non-uniformly distributed within the nonpolar molecule, and (c) caused by the non-coincidence of the centre of electric field with the centre of the polar molecule (in which case the distance of separation of the polar molecule from the nonpolar one at the point at which the potential function reduces to zero, i.e. as it appears in the Lennard-Jones potential, is not the same as the distance for induction interaction,) and (3) contributions due to chemical force (i.e. of the type of hydrogen bonding, or whatever causes association or cluster formation between molecules).

The first one represents angle dependent interactions, proportional to the inverse 4th and 5th powers of the distance of separation of the centres of electric fields in the two molecules, and their total effect may not be a

negligible quantity in all cases. However, there is no way, at least at this stage, to estimate this contribution to the potential function, because, first of all, the quadrupoles and higher multipole moments are not available and secondly, the collision integrals for this angle dependent function have not yet been evaluated.

It does not seem feasible at this stage to estimate by theoretical means the contributions mentioned under (2). Attempts have been made to calculate their effects on the Stockmayer potential parameters ϵ_{AB} and σ_{AB} in the cases of organic polar molecules interacting with nonpolar molecules by Blanks and Prausnitz[22], using the concept of homomorphs. Obviously, this approach is untenable in the cases of inorganic molecules as there exists no homomorph for them.

Finally, the estimation of the contribution due to chemical force, mentioned in (3), is beyond the present scope of the kinetic theory of gases and no clue is available as yet as to how it can be evaluated theoretically.

In the cases of polar - polar systems, apart from the point dipole - point dipole interaction which has been taken care of in the Monchick and Mason potential, there might be (1) contribution due to induction interaction between the point dipole of one and the ideal polarizability of the other, (2) contribution due to interaction between point dipole of one and quadrupole or higher moments of the other, (3) contributions due to deviations from ideal point dipole, central dipole, and from ideal polarizability, and (4) contribution due to chemical forces as mentioned in the case of nonpolar - polar systems.

The first and the second contributions are complicated by the factors discussed in the case of nonpolar - polar systems, whereas the third and the fourth contributions suffer from the same disadvantages of evaluation as mentioned above.

APPARATUS

The principles on which the apparatus was designed have been explained by

Scott and Cox[4]. They have also given a sketch of the apparatus.

The primary objective was to attain counter current ordinary diffusion

taking place through the pores of a properly selected solid, and then to

analyse the outgoing streams in order to calculate the diffusion coefficients

of the systems under investigation.

The solid selected for the purpose was a plug of pyrex fritted glass

cylindrical in shape, approximately 1 cm. in length and 1 cm. diameter, and

having a mean pore diameter of 4 to 5 microns (Corning "fine" grade). The

radius, therefore, was at least ten fold greater than the mean free path of

most gases and guaranteed predominantly ordinary diffusion. This plug was

fused in the middle of a pyrex glass tube 20 cms. in length and 1.25 cms. in

diameter. On each side of the porous solid the glass tube was provided with

an inlet and an outlet for the gas streams. The two sides of the porous solid

were also connected to a draft gauge in order to detect any inbalance of

pressure. A sketch of this diffusion cell is given in Figure 1.

For the purpose of metering the inlet gases, two flowmeters - one Matheson

rotameter type and the other a capillary type - were inserted, one on each

stream. The capillary flowmeter was constructed with three parallel capillary

tubes to give a wide range of flow rates of gases. and 3 rotameter tubes were used

For the analyses of the outgoing streams of gases, a number of methods were

tried to suit the specific systems. For nitrogen - carbon dioxide, nitrogen -

hydrogen and argon - sulphur dioxide systems, thermal conductivity cells were

used to analyse both the streams. For the argon - sulphur dioxide system, in

also a combination of thermal conductivity and chemical analysis was used,

the former for analysis of argon in a stream of sulphur dioxide, and the latter

for analysis of sulphur dioxide in a stream of argon. The combination method

was also used for the argon - hydrogen chloride system, whereas methods of chemical analysis were used for the sulphur dioxide - hydrogen chloride system. The thermal conductivity cells used for these purposes were Gow Mac Model NIS Diffusion Type. The T.C. Cells were thermostated in order to eliminate the effect of temperature variation during the day, or from day to day.

The gases employed were obtained in cylinders, and after being dried over anhydrous calcium sulphate, were used without further purification, except for hydrogen which was passed through a De-Oxo Converter prior to drying. The specifications for each gas are given below as guaranteed by the suppliers:

Nitrogen - 99.99% purity, Canadian Liquid Air

Hydrogen - 99.94%   "   Canadian Liquid Air

Carbon dioxide - 99.5% purity, Liquid Carbonic Co.

Argon   - 99.99% purity, Linde Co.

Sulphur dioxide - 99.92% Canadian Industries Ltd.

Hydrogen chloride - 99.0% purity, Matheson Co. Inc.

The temperature variation in the forced circulation hot air oven in which the diffusion cell was placed was $\pm 1^{o}C$ at $250^{o}C$.

For the inert gases, copper tubing was used for all lines except in the diffusion cell itself. For corrosive gases, all-glass equipment was employed with the exception of brass throttling valves and flow controller, and a few rubber sleeves.

Diffusion cell temperatures were measured by means of an iron-constantan thermocouple bead in contact with the outer glass surface of the diffusion cell.

A sketch of the lay-out of the apparatus is given in Figure 2 and the modifications made in using the combination method for analyses is shown in Figure 3.
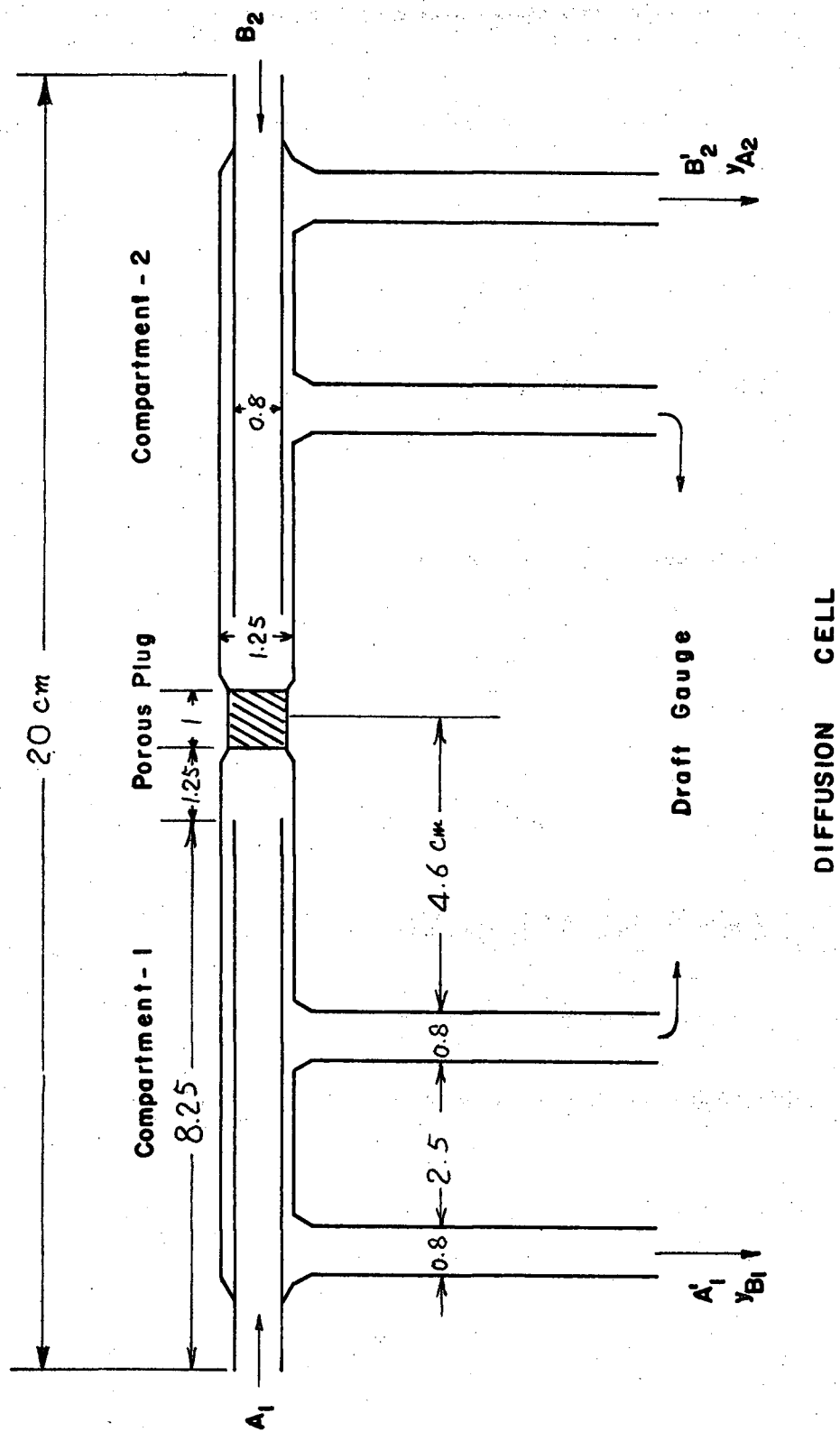
Figure 1   DETAILS OF THE DIFFUSION CELL
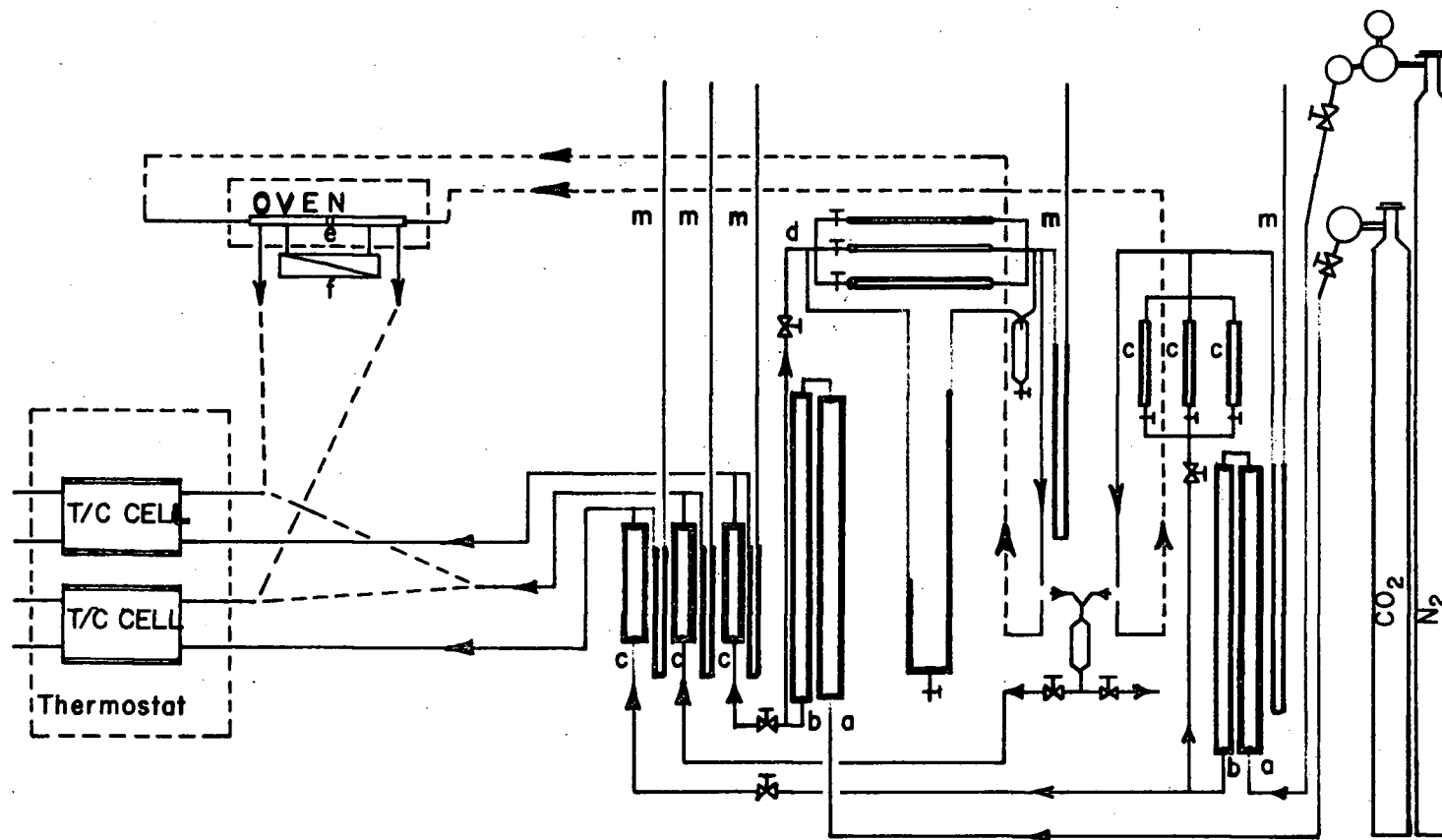
Figure 2   APPARATUS FOR DIFFUSION EXPERIMENT

a. Driers   c. Matheson Flowmeters   e. Diffusion cell
b. Filters   d. Capillary Flowmeters   f. Draft Gauge
                        m. Manometers
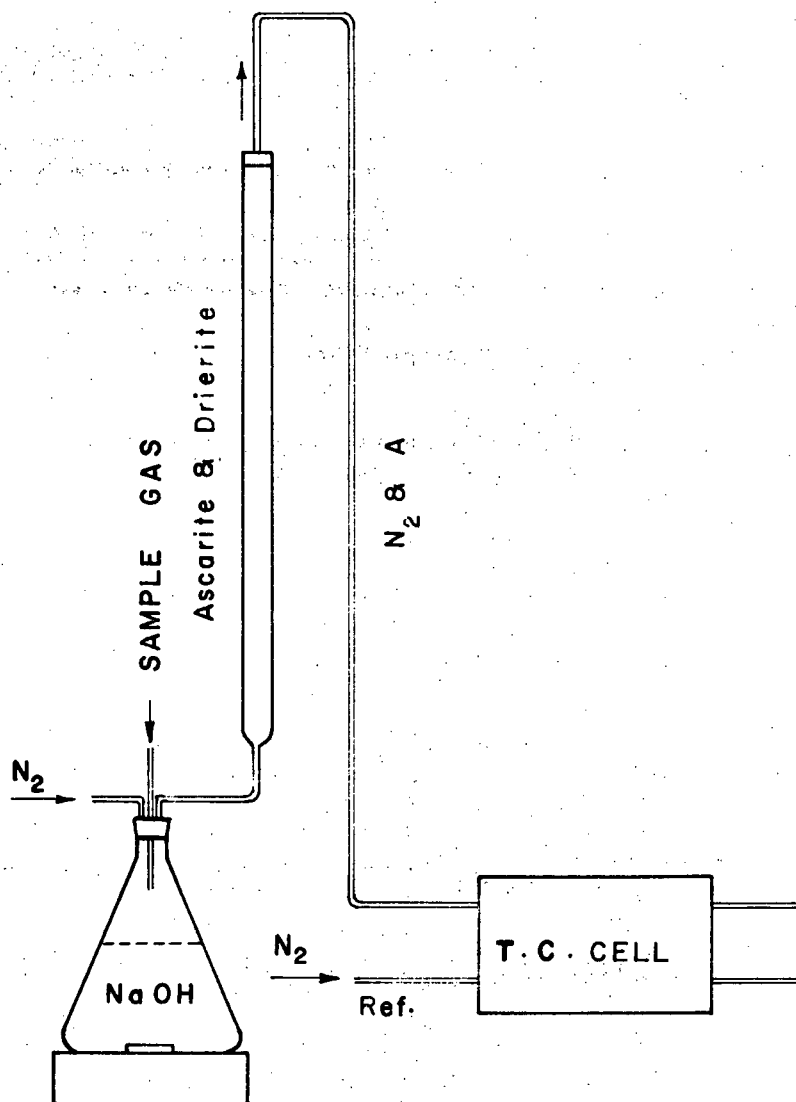
COMBINED CHEMICAL-T·C·CELL UNIT OF ANALYSIS

Figure 3   COMBINED CHEMICAL-T.C.CELL UNIT OF ANALYSIS

THEORY OF MEASUREMENT

A. Counter diffusion in a Flow System

Under the conditions of the experiment, a pure gas, A, is flowing through one compartment of the diffusion cell, while another pure gas, B, is flowing through the other, thus allowing counter current ordinary diffusion to take place through the pores of the glass plug separating the two compartments. Under these conditions of steady continuous flow of gases with steady states of temperature, pressure, and concentration at any point in the apparatus, the ordinary diffusion equation is given for fixed coordinates and perfect gases as

$$N_A = - D_{AB} S \frac{dC_A}{dz} + (N_A - N_B) \frac{P_A}{P} \tag{11}$$

where N_A, N_B are the total transfer of gases, A, and B, into streams

of B and A, respectively, moles/sec.

D_{AB} is the diffusion coefficient of gas, A into gas, B, cm^2/sec.

S is the area for diffusion, cm^2

z is the length of the diffusion path, cm.

C_A is the concentration of gas, A, in the bulk of gas, B, moles/cm^3

P_A is the partial pressure of gas, A, in the bulk of gas, B,; atm.

and P is the total pressure. atm.

On integration it gives the Sherwood and Pigford equation:

$$N_A = \frac{D_{AB} P S}{RTz(1 - \frac{N_B}{N_A})} \ln \frac{1 - (1 - \frac{N_B}{N_A}) y_{A_2}}{1 - (1 - \frac{N_B}{N_A})(1 - y_{B_1})} \tag{12}$$

where y_{A_2} represents the mole fraction of A in

compartment 2 i.e. in the outgoing stream

of gas, B,

and y_{B_1} represents the mole fraction of B in the

outgoing stream of gas, A.

The ratio, N_B/N_A, can be calculated if the total pressure is constant

from the relationship with the square-root of the inverse ratio of their

molecular weights as shown by Scott and Dullien (12), i.e.

$$\frac{N_B}{N_A} = \sqrt{\frac{M_A}{M_B}} \qquad (13)$$

where M_A, M_B are the molecular weights of A and B respectively. However, if

an experimental measurement of y_{A_2} and y_{B_1} is made, then it becomes possible

to calculate the exact value of N_B/N_A simply by means of a material balance

around the diffusion cell. Equation (12) is independent of variations in total

pressure because the product $D_{AB}P$ does not vary with pressure. Therefore, an

experimental determination of the ratio N_B/N_A means that the value of the

diffusion coefficient calculated from equation (12) is independent of experimental

errors in maintaining constant pressure across the diffusion cell.

B. Material Balance around the Diffusion Cell

Referring to Figure 1, let

A_1 be the flowrate of A in ccs/min. entering compartment 1,

B_2 be the flowrate of B in ccs/min. entering compartment 2,

A_1' be the flowrate of stream rich in A leaving the cell,

B_2' be the flowrate of stream rich in B leaving the cell,

y_{A_2} be the mole fraction of A in the stream B_2', and

y_{B_1} be the mole fraction of B in the stream A_1'.

Then by an over all material balance, assuming constant temperature and pressure,

$$A_1 \;-\; A_1' \;\;=\;\; B_2 \;-\; B_2' \tag{14}$$

by the balance of component A,

$$A_1 \;-\; A_1'(1 - y_{B_1}) \;\;=\;\; B_2' \, y_{A_2} \tag{15}$$

and by the balance of component b,

$$B_2 \;-\; B_2'(1 - y_{A_2}) \;\;=\;\; A_1' \, y_{B_1} \tag{16}$$

Therefore the total volume of component A entering into compartment 2 is

$$V_A \;\;=\;\; B_2' \, y_{A_2}$$

$$=\;\; \frac{B_2 y_{A_2} \;-\; (A_1 + B_2) \, y_{A_2} y_{B_1}}{1 - y_{A_2} - y_{B_1}} \tag{17}$$

and the total volume of component B entering into compartment 1 is

$$V_B \;\;=\;\; A_1' \, y_{B_1}$$

$$=\;\; \frac{A_1 y_{B_1} \;-\; (A_1 + B_2) \, y_{A_2} y_{B_1}}{1 - y_{A_2} - y_{B_1}} \tag{18}$$

Since these two gases are under identical conditions of temperature and pressure within the diffusion cell, V_B/V_A will be equal to N_B/N_A assuming that the gases behave ideally. However, V_A and V_B as expressed by equations (17) and (18), are under the conditions of room temperature and pressure rather than those at which the diffusion takes place. This does not alter the value of the ratio of N_B/N_A, nevertheless it changes the absolute values of both N_A and N_B. Thus,

$$N_A \;\;=\;\; \frac{V_A P_R}{RT_R} \;\;=\;\; \frac{V_A' P}{R\,T} \tag{19}$$

where V_A' is the new value of V_A measured at the conditions of temperature, T, and pressure, P, at which the diffusion actually takes place.

Therefore, from equation (19) and equation (12)

$$N_A RT \ = \ \frac{V_A' P_R T}{T_R}$$

$$= \ \frac{D_{AB} P \ S}{z(1 - V_B'/V_A)} \quad \ln \ \frac{1 \quad (1 \quad V_B/V_A) \ y_{A_2}}{1 \quad (1 - V_B/V_A)(1 - y_{B_1})}$$

On substitution of equations (7) and (8) and on subsequent simplification, this equation gives the following:

$$D_{AB} \ = \beta \frac{B_2 y_{A_2} - A_1 y_{B_1}}{1 - y_{A_2} - y_{B_1}} \quad / \quad \ln \ \frac{B_2 y_{A_2}}{A_1 y_{B_1}} \tag{20}$$

where $\beta = z/S$

i.e. a function of the geometry of the diffusion cell.

Therefore, the diffusion cell factor, β, can be determined by making a diffusion study of a gas system whose diffusion coefficients are known fairly accurately, and calculating from equation (20) using observed values of y_{A_2} and y_{B_1}.

PROCEDURE

The experimental procedure consisted of four phases:

(a) calibration of flowmeters for the gases to be used,

(b) calibration of equipment for the analysis of the outgoing

gases from the diffusion cell,

(c) calibration of the diffusion cell,

(d) diffusion measurements of the selected systems.

CALIBRATION OF FLOWMETERS:

The flowmeters, both Matheson rotameter and capillary types, were calibrated

for insoluble gases i.e. nitrogen, carbon dioxide, hydrogen, and argon - against

a wet test meter for large flow rates and against soap bubble flowmeters for

small flow rates, i.e., for flow rates less than about 200ccs/min.. For

hydrogen chloride and sulphur dioxide, the flowmeters were calibrated against

soap bubble flowmeters for both high and low flow rates. For this purpose, an

extra large soap bubble flowmeter with a capacity of 250cc measured at 20°C was

constructed.

The calibrations were expressed in terms of fluid properties and the

flowmeter characteristics, so that any effect due to changes of temperature

and pressure on the flow rates could easily be taken into account.

The derivation of the groups for calibration is given in APPENDIX B.

CALIBRATION OF THERMAL CONDUCTIVITY CELLS:

One of the thermal conductivity cells was calibrated for small percentages of gas,

B, in a mixture with gas, A, while the other for small percentages of gas, A,

in a mixture with gas, B.

For the first, 200 cc/min. of gas A was led through the reference side of

the thermal conductivity cell, and 100 cc/min. of the same gas led through the

sample side, in order to set the zero in the potentiometer connected to the

circuit. Then 100 cc/min. of a known mixture of a small percentage of gas B

in A was led through the sample side of the same thermal conductivity cell

instead of the 100cc/min. of pure gas used for setting the zero. The

corresponding millivolt changes were noted with the potentiometer, and plotted

against percentages of B.

The second thermal conductivity cell was calibrated also using the same

technique, but interchanging the gases.

CALIBRATION OF DIFFUSION CELL:

The diffusion cell was calibrated by making diffusion runs through the

apparatus using the system nitrogen - carbon dioxide. Nitrogen metered in a

in a Matheson rotameter entered one compartment of the diffusion cell at a

rate of 100 cc/min. while carbon dioxide metered in a capillary flowmeter

entered the other at about the same rate. Both the gases and the diffusion

cell were maintained at a constant temperature by placing the apparatus inside

an accurately temperature-controlled heated oven. The flow of the gases was

so adjusted that the pressure difference between the two compartments of the

diffusion cell was practically zero, with fluctuations of less than 2/100th

of an inch of the draft gauge oil (specic gravity 1.0). The two streams leaving

the diffusion cell were analysed by the two thermal conductivity cells previously

calibrated for the purpose. These data gave an effective diffusion coefficient

of the system at the particular temperature. This effective diffusion

coefficient, together with the known true diffusion coefficent of the system

at the same temperature, enabled the calculation of the characteristic

diffusion cell calibration factor, β , which is the ratio of the true

diffusivity to the effective diffusivity.

The calibration procedure was carried out at (1) room temperature, (2)

70°C, (3) 120°C, (4) 200°C, and (5) 250°C. The effective diffusion coefficients

obtained are plotted against temperature in Figure 4. The calculated

characteristic factor, β, of the diffusion cell are also plotted against temperature as shown in Figure 5.

The procedure was repeated at room temperature using the nitrogen - hydrogen system as well, in order to check the constancy of the calibration factor with respect to different systems. This result at room temperature is also shown in Figure 5.

MEASUREMENT OF DIFFUSION COEFFICIENTS OF THE SELECTED SYSTEMS:

Argon - Sulphur dioxide system: The same technique was employed for the diffusion runs as that used for the diffusion cell calibration, as well as the same method of analysis using the thermal conductivity cells for the diffused streams. The measurements were made at 5 different temperatures, room temperature, 70°, 120°, 200°, and 250°C. The diffusion coefficients were calculated using the known values of the diffusion cell calibration factors.

For the purpose of checking the results, the diffusion rates were measured once again using this time the chemical method of analysis for sulphur dioxide in the argon stream and a combined chemical and T.C. cell method for argon in the sulphur dioxide stream. The chemical analysis for sulphur dioxide consisted of taking a known volume of the gas mixture, dissolving it in 1/100 Normal iodine standard solution, and obtaining the amount of sulphur dioxide by back titration with 1/100 Normal sodium thiosulphate standard solution. Combined with a knowledge of total volume of sample, the concentration of sulphur dioxide was calculated. The combined chemical and T.C. cell method consisted of absorbing the bulk of the sulphur dioxide by passing it over a 10% solution of sodium hydroxide contained in a 250 cc flask agitated by a magnetic stirrer. In the flask, the small residue, principally argon, was diluted by nitrogen flowing at the rate of 50 cc/min. The mixture of argon and nitrogen was led through a tower containing a 50-50 mixture of Ascarite and Drierite, and then analysed in a T.C. cell previously calibrated for this purpose at a flow rate

of 50 cc/min. of both reference and sample gases.

Argon - Hydrogen chloride system: Using the same technique as before for diffusion runs, but only the chemical and combined chemical - T.C. cell method of analysis, the system, argon - hydrogen chloride, was studied also at the same 5 temperatures as argon - sulphur dioxide. In this case, the chemical method of analysis consisted of dissolving the hydrogen chloride contained in a known volume of the argon-rich gas leaving the diffusion cell in 50 cc of distilled water, and estimating the chloride ion by the Mohr method using 1/100 Normal silver nitrate standard solution. The combined chemical - T.C. cell method was exactly the same as before.

Sulphur dioxide - Hydrogen chloride system: This system was studied by using chemical analysis for both streams leaving the diffusion cell. For analysis of sulphur dioxide in the HCl-rich stream, a known volume of the gas sample was dissolved in a known amount of 1/100 Normal iodine standard solution, and back titrated with 1/100 Normal sodium thiosulphate standard solution. For the analysis of hydrogen chloride in the SO_2-rich stream, the known volume of the gas sample was dissolved in 50 cc of distilled water, and the sulphur dioxide was boiled off for half an hour, adding distilled water slowly in order to maintain the same constant volume of 50 cc.. After all sulphur dioxide had been expelled, the solution was cooled and titrated against 1/100 Normal silver nitrate solution. This technique, prior to its use, was tested with a known amount of hydrogen chloride. Mohr's method was followed in the silver nitrate titration and a blank test was always made.

The diffusion rates were measured for this system at the same 5 temperatures used for other systems.

RESULTS

NITROGEN - CARBON DIOXIDE SYSTEM

From the measured flow rates and concentrations of the inlet and outlet streams, the effective diffusion coefficients, D_E, for this system were calculated using equation (20), and are given in column 3 of Table 1. Column 1 represents the temperatures, expressed in $^\circ K$, at which the diffusion studies were made, while column 2 gives the ratio of the volume of carbon dioxide to the volume of nitrogen diffused at the corresponding temperatures.

Figure 4 represents a plot of Log D_E vs Log T as well as Log D_T vs Log T. Each point on the plot of Log D_E vs Log T represents an average of at least two runs. Individual runs differed from one another by not more than 2.4%. The best curve obtained from these data by the method of least squares is a straight line with a slope 1.624. The standard deviation is 0.89% and the maximum deviation is 3.02%.

TABLE 1

EFFECTIVE DIFFUSION COEFFICIENTS
OF
NITROGEN - CARBON DIOXIDE SYSTEM

Temperatures	Ratio, V_C/V_N [1]	Effective diffusion Coefficients, $cm^2/sec.$
$^{\circ}K$		D_E
296.5	0.5997 0.7000	0.0090
301.0	0.4304	0.0092
343.3	0.4354 0.5995	0.0110
393.0	0.4345 0.5692	0.0142
471.6	0.5907 0.6707	0.0183
525.0	0.5828 0.6227	0.0230

(1) Constant pressure value V_C/V_N = 0.789
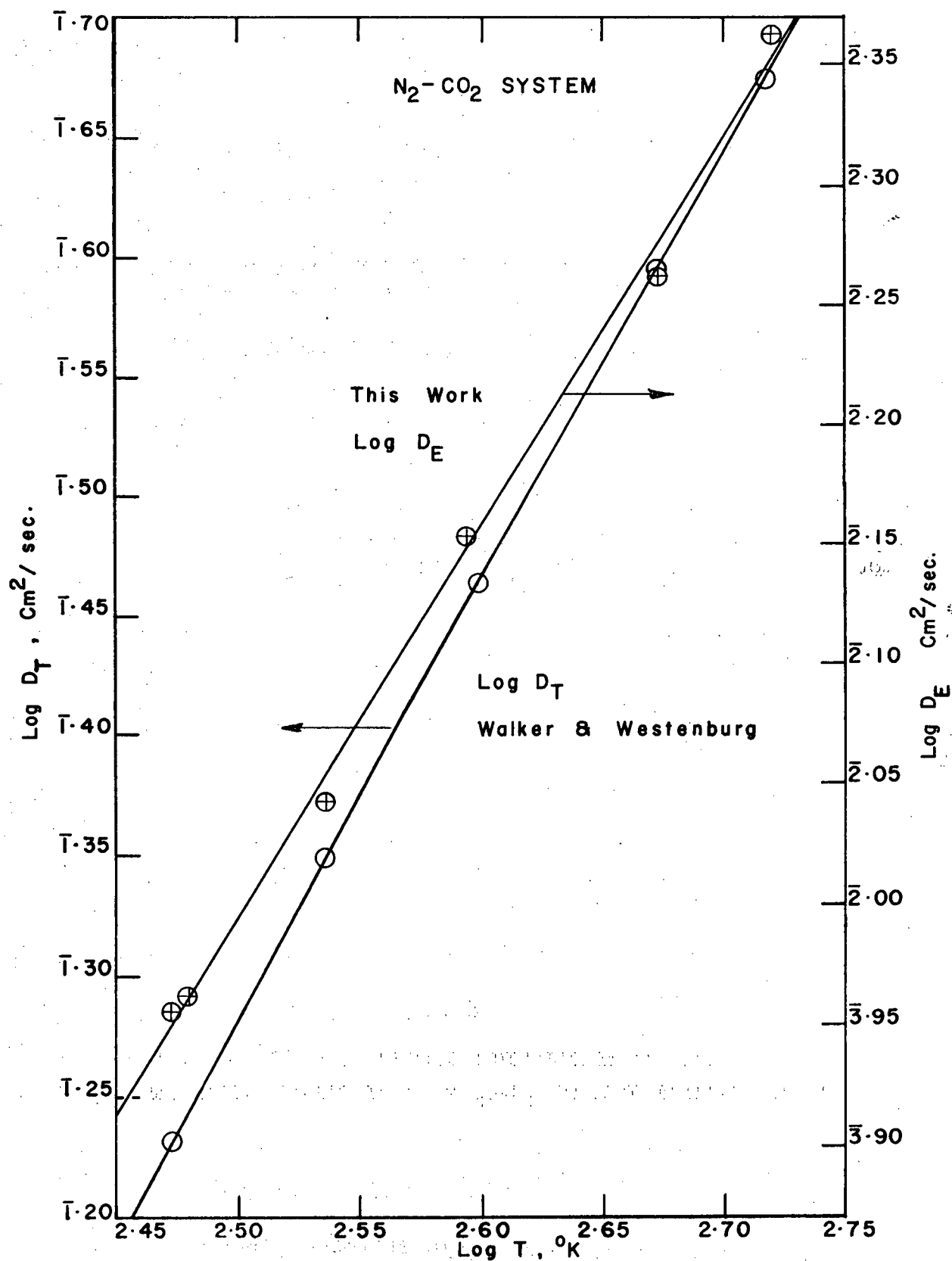
Figure 4   COMPARISON OF THE EFFECTIVE DIFFUSIVITIES WITH THE
TRUE DIFFUSIVITIES OF N_2-CO_2 AT VARIOUS TEMPERATURES

NITROGEN - HYDROGEN SYSTEM

The results obtained from the study of this system calculated as in nitrogen - carbon dioxide system, are given in Table 2 where the columns have the same significance as those of Table 1. In this case, the value given represents an average of two runs differing by 0.75%.

TABLE 2

EFFECTIVE DIFFUSION COEFFICIENT
OF
NITROGEN - HYDROGEN SYSTEM

Temperature $^{\circ}K$	Ratio, V_N/V_H [1]	Effective diffusion Coefficient, $cm^2/sec.$ D_E
298.2	1.95 1.91	0.0412

[1] Constant pressure values, V_N/V_H , = 0.267

DIFFUSION CELL CALIBRATION FACTORS

The diffusion cell calibration factor, β, calculated for the nitrogen - carbon dioxide system using the value of true diffusivity obtained from an equation representing the experimental data observed by Walker and Westenburg[14] within 1.2%, is expressed as a function of temperature in Table 3, and is plotted in Figure 5. The latter also shows β calculated from the nitrogen - hydrogen system results at room temperature, and identified by a cross within a circle.

TABLE 3

DIFFUSION CELL CALIBRATION FACTORS

Temperatures	Diffusion cell calibration factors
$^{\circ}K$	β
296.6	19.1506
343.3	19.7644
397.0	20.3077
471.0	20.8707
522.0	21.1596

33.
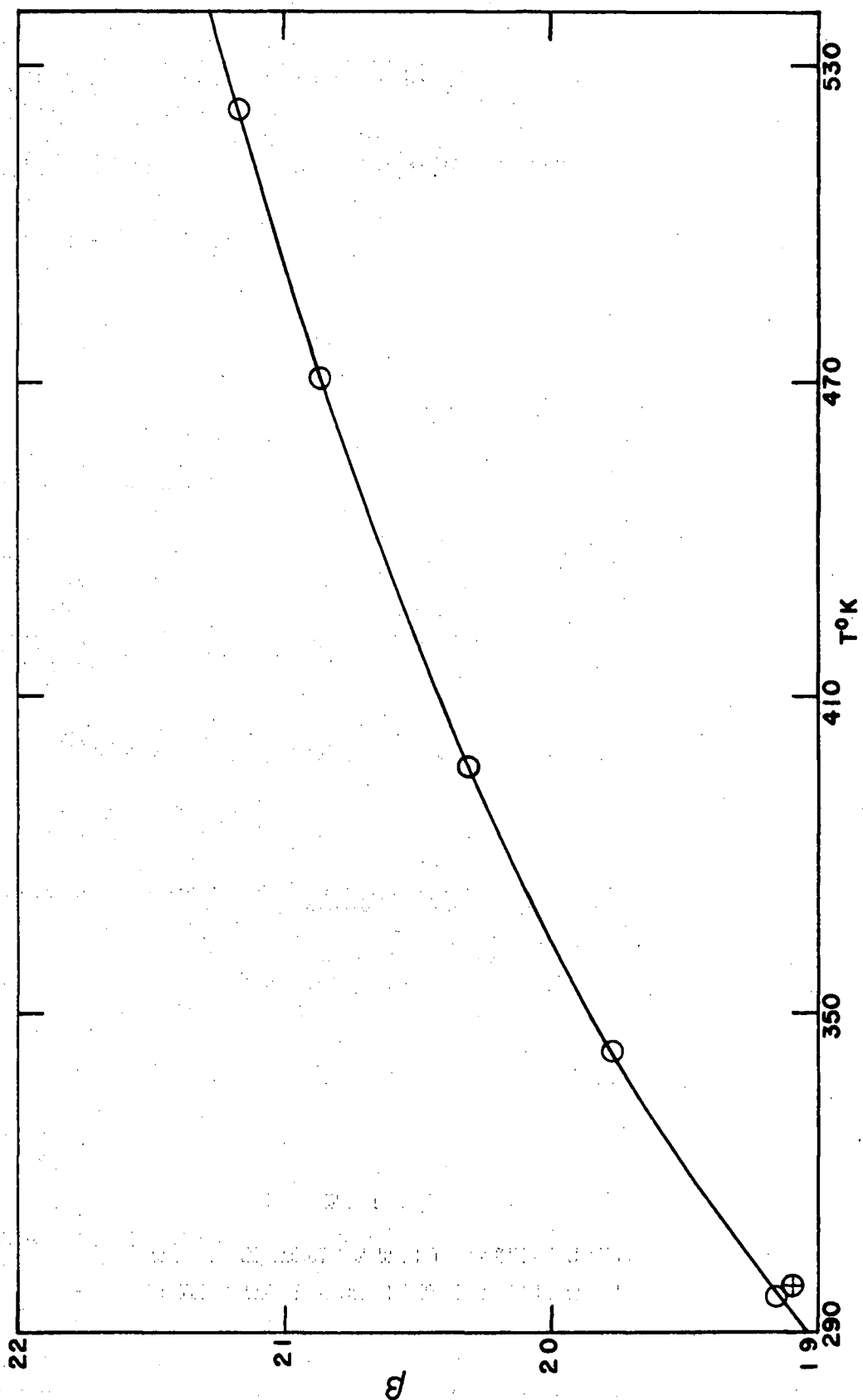
Figure 5   THE VARIATION OF THE DIFFUSION CELL CALIBRATION
FACTOR WITH TEMPERATURE

Circle - nitrogen-carbon dioxide system
Crossed circle - nitrogen - hydrogen system

ARGON - SULPHUR DIOXIDE SYSTEM

The results obtained from the study of the argon - sulphur dioxide

system as calculated using equation (20), and the diffusion cell calibration

factor, β, from Figure 5, are given in Table 4, and shown in Figure 6. Each

point again represents an average of at least two runs differing by a maximum

of 5.6% (only in one case). The best curve drawn through these points

by the method of least squares is a straight line with a slope, 1.988. The

standard deviation is 1.01% and the maximum deviation is 5.362%.

TABLE 4

DIFFUSION COEFFICIENTS

OF

ARGON - SULPHUR DIOXIDE SYSTEM

Temperatures $^\circ K$	Ratio V_A/V_S (1)	Diffusion coefficients, $cm^2/sec.$		
		Experimental (Ave.)	Arnold (Eqn.1)	Hirschfelder (polar-nonpolar)
522.0	1.004 0.919	0.2556 *	0.3445	0.3176
343.0	1.240 1.226	0.1120 *	0.1568	0.1461
298.8	1.304 1.093	0.0807 *	0.1194	0.1122
296.6	1.283 1.161	0.0828 *	0.1192	0.1111
294.0	6.019 4.888	0.0855	0.1162	0.1086
345.0	6.338 4.650	0.1087	0.1585	0.1487
397.0	6.468 4.385	0.1482	0.2072	0.1925
433.9	3.365 3.357 2.956	0.1734	0.2449	0.2270
471.0	4.518 4.041	0.2089	0.2852	0.2631
521.5	8.841 6.579	0.2515	0.3439	0.3170

* Indicates that the results were obtained by the combined chemical-T.C. cell
method of analysis.

(1) Constant pressure value $V_A/V_S = 1.268$ (Eqn. 13)
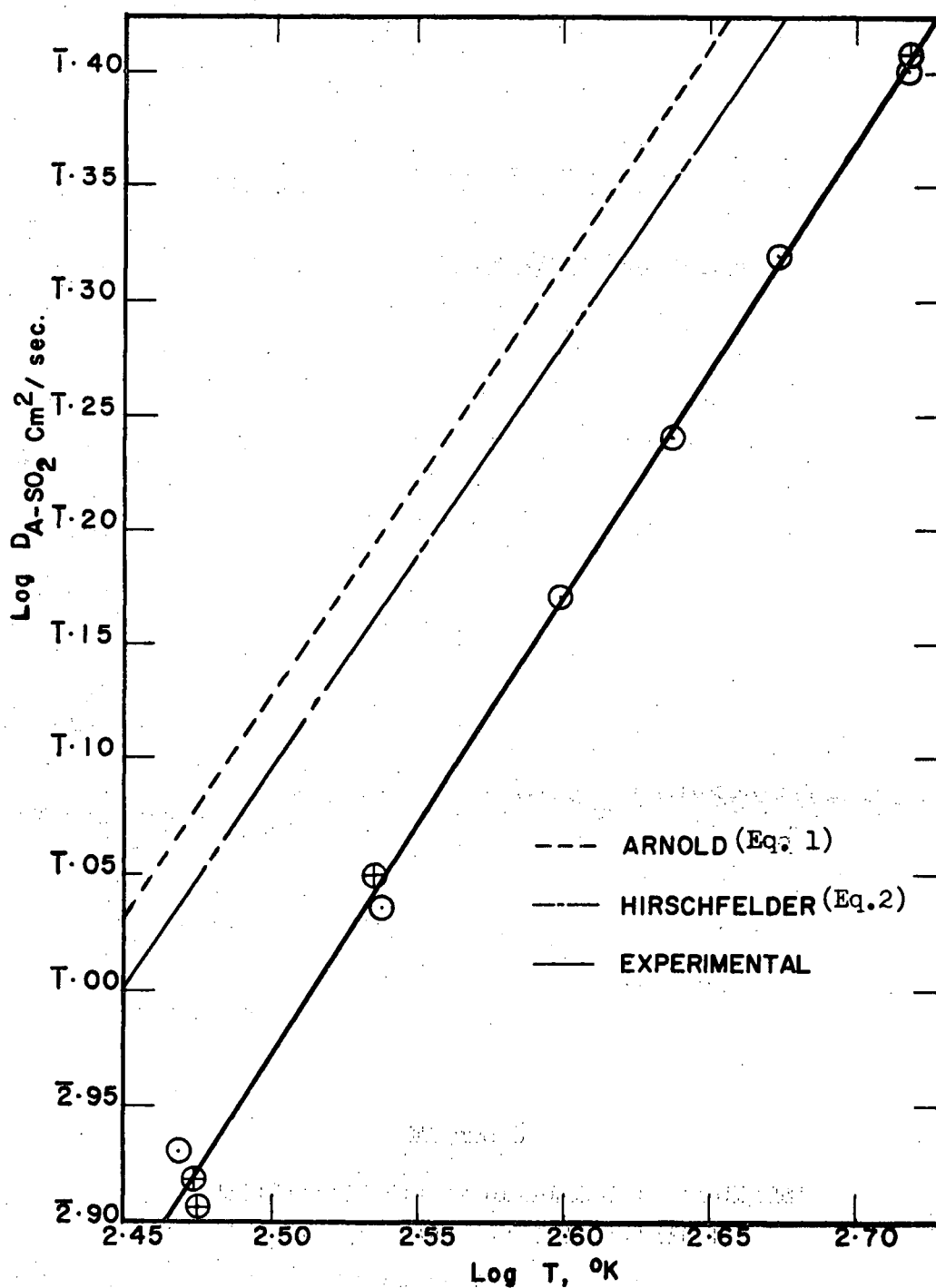
Figure 6   THE DEPENDENCE OF DIFFUSION COEFFICIENTS OF
A - SO$_2$ SYSTEM UPON TEMPERATURE
Circle - Analysis by T.C.cell alone
Crossed circle - Combined Chemical-T.C.cell
method.

ARGON - HYDROGEN CHLORIDE SYSTEM

The results obtained from this system, following the same procedure of calculation as for argon - sulphur dioxide, are presented in Table 5, and shown in Figure 7. Each point in this case is an average of at least two runs differing by not more than 2.7%. The best curve drawn through these points by the method of least squares is a straight line with a slope 2.424. The standard deviation is 1.265% and the maximum deviation is 4.713%.

TABLE 5

DIFFUSION COEFFICIENTS

OF

ARGON - HYDROGEN CHLORIDE SYSTEM

Temperatures °K	Ratio V_H/V_A (1)	Diffusion coefficients, $cm^2/sec.$		
		Experimental Ave.	Arnold (Eq.1)	Hirschfelder (polar-nonpolar)
297.0	1.057 1.098	0.0976	0.1589	0.1551
343.8	1.574 1.481	0.1506	0.2106	0.2053
393.0	1.654 1.690	0.2013	0.2711	0.2640
475.0	1.710 1.589	0.3055	0.3851	0.3733
523.0	1.815 2.016	0.3998	0.4588	0.4454

(1) Constant pressure value, $V_H/V_A = 1.046$ (Equation 13)
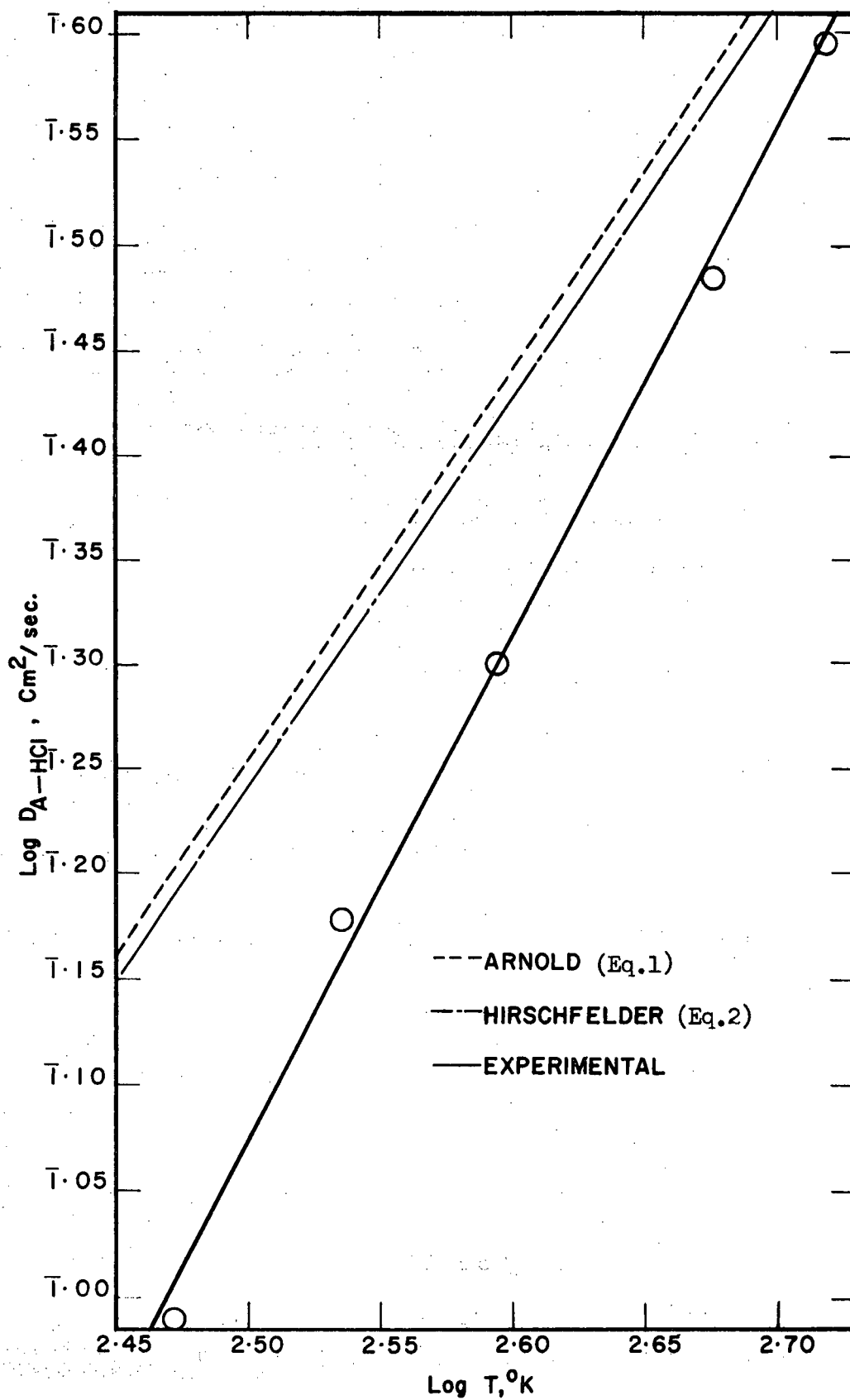
Figure 7 THE DEPENDENCE OF DIFFUSION COEFFICIENTS OF
A - HCl SYSTEM UPON TEMPERATURE

SULPHUR DIOXIDE - HYDROGEN CHLORIDE SYSTEM

The results from this system are given in Table 6 and shown in Figure 8. Each point represents an average of at least two runs differing by not more than 4.25%. The best curve drawn through these points by the method of least squares is a straight line with a slope, 2.22. The standard deviation is 0.707% and the maximum deviation is 4.456%.

TABLE 6

DIFFUSION COEFFICIENTS

OF

SULPHUR DIOXIDE - HYDROGEN CHLORIDE SYSTEM

Temperatures $^\circ K$	Ratio V_H/V_S (1)	Diffusion coefficients, cm^2/sec.		
		Experimental Ave.	Arnold (Eq.11)	Mason etc. (polar-polar)
296.5	1.822 1.396	0.0867	0.0882	0.0910
343.0	1.032 1.021	0.1240 *	0.1188	0.1225
393.0	1.678 1.472	0.1641	0.1561	0.1603
472.5	1.620 1.340	0.2490	0.2242	0.2301
523.0	1.660 1.470	0.2965 *	0.2727	0.2793
525.2	1.552 1.518	0.3250	0.2750	0.2815

* Indicates that the results were obtained by analyzing HCl in SO_2-rich

stream by solution of a gas sample, followed by evaporation of all the

SO_2 before titration with $AgNO_3$ standard solution. In all other cases

the SO_2 was oxidized by sodium peroxide,

(1) Constant pressure ratio V_H/V_S= 1.325 (Eqn. 13)

(1) Constant pressure ratio V_H/V_S = 1.325

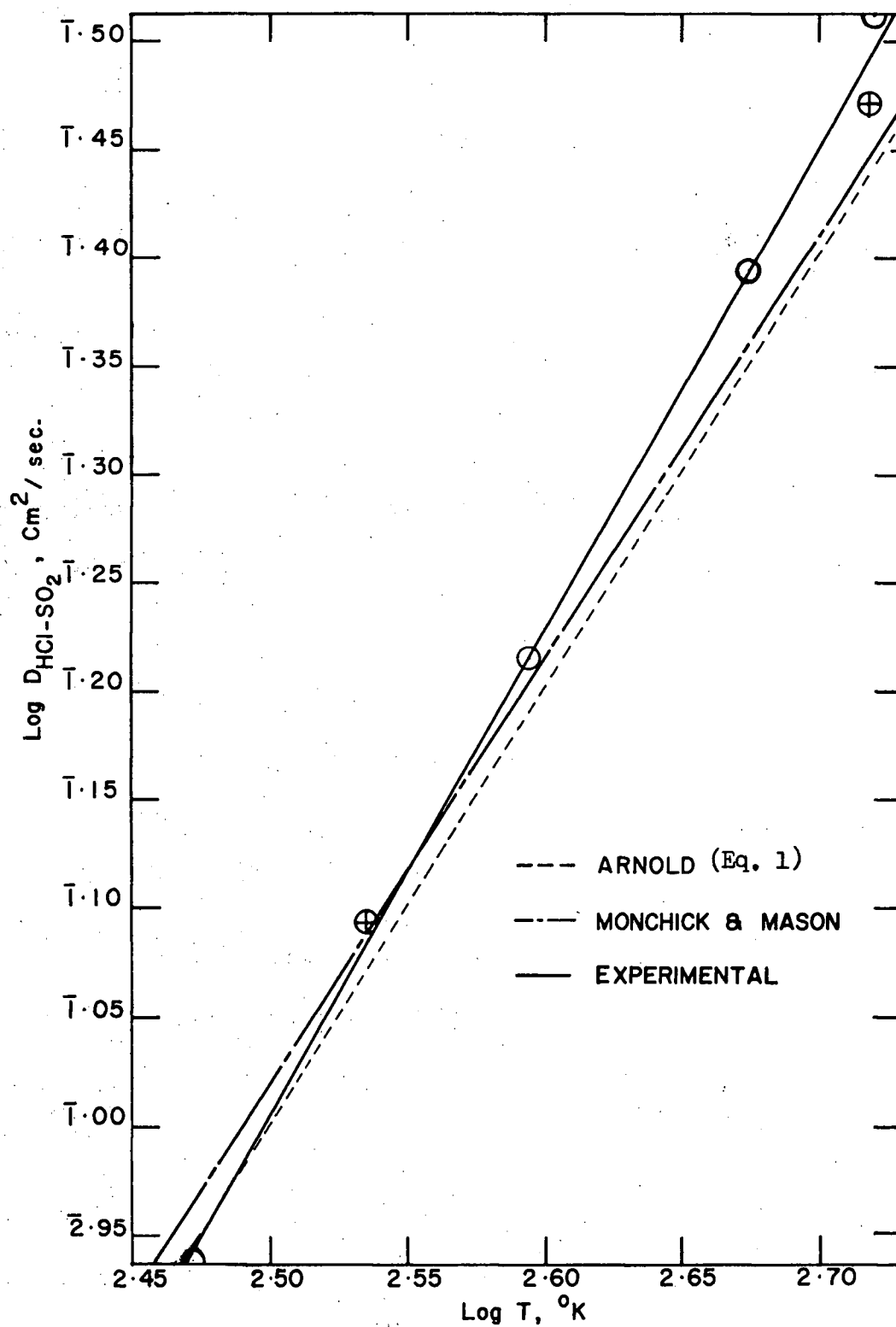Figure 8   THE DEPENDENCE OF DIFFUSION COEFFICIENTS OF
SO$_2$ - HCl SYSTEM UPON TEMPERATURE
Circle - Method 4-1, Appendix F
Crossed circle, 4-2, Appendix F

DISCUSSION

In summarizing the whole investigation, it may be mentioned that one major disadvantage of this method is that it requires large amounts of gases. One way of economizing the gas requirement would be to let one stream of gas act at first as reference in the T.C. cell, and later as inlet to the diffusion cell. The difficulty with this technique is that the T.C. cell reference side would always remain under pressure, which increases with increase of the temperature of the diffusion cell, whereas the sample side of the T.C. cell would always remain under atmospheric conditions. Whether this increasing pressure on the reference side of the T.C. cell would alter the calibration made under atmospheric conditions would need to be checked. On investigation, it was found that the T.C. cell calibration was indeed altered significantly, and that this alteration was not linear. Therefore, this method of gas economy could not be readily applied, and no other way to achieve gas economy appeared to be feasible. The flow measuring devices could have been operated under a constant positive pressure by using a suitable throttling valve, as was done by Cox[4], but the sensitivity of the thermal conductivity cell to slight changes in absolute pressure made this technique a difficult one in practice.

The increase in the diffusion cell calibration factors with temperature cannot be explained at the present time. Considerations of thermal expansion would lead one to expect a slight (less than one percent) decrease in the value of the calibration factor. On these grounds, Cox used the value measured at room temperature as a constant applying at all temperatures, at least up to 300°C. Further investigation of the flow and diffusive behaviour of porous solids as a function of temperature seems to be advisable in light of the results obtained in this work.

plug increased.

An estimation of probable error involved in this technique showed that in a typical diffusion run for the N_2-CO_2 system the maximum possible error was $\pm$ 14.13%. However, a large contribution to this error was due to the subtraction of logarithmic terms required in equation (20), amounting to $\pm$ 7.093%. A similar examination of N_2-H_2 system showed the maximum possible error to be $\pm$ 8.72% out of which $\pm$ 3.28% was the contribution due to the logarithmic terms. It was observed that the contribution to the error due to these terms depended on their magnitude. As long as this logarithmic term was away from unity - either greater or less than unity - the magnitude of error was reduced. Fortunately this source of error can be controlled. Depending on the molecular weights of the gases, M_A being greater than M_B, y_{B_1} is greater than y_{A_2} under equal pressure conditions, and vice-versa. Therefore, by adjusting the flow rates A_1 and B_2 properly, the logarithm of the ratio in equation (20) can be maintained at values either sufficiently greater than unity or sufficiently less than unity, so that the maximum possible error is minimized.

The results obtained from the study of the argon - sulphur dioxide system showed that the slope of the line obtained by a log-log plot of diffusion coefficients vs. temperature, was somewhat greater than that predicted by the use of the Stockmayer potential function and Hirschfelder's technique for getting the parameters. However, the magnitude of the diffusion coefficient was about 25.3% less at room temperature and 20.0% less at $250^{\circ}C$ than the Hirschfelder's prediction and 29.8% less at room temperature and 26.3% less at $250^{\circ}C$ than the prediction by Arnold's equation. An attempt to force the experimental data to conform to the Lennard-Jones potential function gave the values of the parameters, obtained by a graphical superposition method, (see Appendix D) as follows:

$$\frac{\epsilon_{A-SO_2}}{k} = 363.07^{\circ}k \qquad \text{and} \qquad \sigma_{A-SO_2} = 3.809 \text{ Å}$$

These values now correspond to the ϵ' and σ' defined by equation (6), and can be compared to results calculated from pure component values as outlined by Hirschfelder et al.[1] On this basis, the energy parameter appeared to be closer to that of SO_2 (using the pure component values from viscosity data listed by Hirschfelder et al[1]) than of argon, and to be much greater than the calculated value. The collision diameter found here, 3.809, was also greater than the calculated value.

The results of the argon-hydrogen chloride system showed a somewhat similar trend to those of the argon-sulfur dioxide system, in that the magnitudes of the diffusion coefficients were about 29.2% less at room temperature, and 12.1% less at about 250°C, than those predicted by equation (2), and 30.9% less at room temperature, and 14.7% less at 250°C than the prediction from the Arnold equation. The slope of the line from the log-log plot of diffusion coefficient vs. temperature was much higher than any of the predicted values. This system could not be represented by a potential function of the form of equation (6), inasmuch as collision integrals for the small values of T* are not available in the literature.

Monchick and Mason[2] have given values of the parameters ϵ and σ for both HCl and SO_2, calculated for the pure components from viscosity data, and applying the collision integrals for their potential model. These pure component parameters were combined using the customary combining rules to give binary parameters for use in the prediction of diffusion coefficients from equation (2), using Monchick and Mason's integrals. The results for the SO_2-HCl system showed that the magnitudes of the diffusion coefficients at room temperature and at 250°C were 3.3% less and 11.1% greater, respectively, than the prediction by the Monchick and Mason model, and 0.3% less and 13.8% more, than the prediction by the Arnold equation.

For the case of nonpolar-polar systems, qualitative reasons for their observed behaviour may be put forward. The possible forces of interaction are (1) short range repulsive forces (2) long range dispersion forces (3) dipole forces

(4) non-ideal and non-central dipole contribution

(5) chemical force contribution.

The first two have been taken care of in the Lennard-Jones potential function. The third one has been introduced into Stockmeyer potential, whereas the fourth and fifth are left unaccounted for. In the case of $A-SO_2$, an examination of the molecular model of SO_2 shows that its dipole-point is neither a point dipole nor is it situated on the centre of the mass. Whether or not SO_2 has the 5th contribution is not known with certainty. However, the effect of all these forces that are not accounted for in the Stockmeyer potential, on the $A-SO_2$ system appears, from experimental evidence, to be such as to increase the energy parameter ϵ_{12} considerably while decreasing the collision diameter parameter, σ_{12}.

In the case of A-HCl, apart from the above mentioned force contribution, there might be a contribution due to the specific nature of the HCl molecule. Experimental dipole moment determinations have shown that its molecular model is somewhere in-between a neutral form with the H-atom attached to the Cl-atom by a Co-valent bond, and a molecular form having the negative charge distributed within, a d the positive charge due to the separation of a H-nucleus after the H-atom has given off its electron to the Cl-atom, floating on the surface of the Cl-atom. These charges of the HCl-molecule while interacting with the Argon molecule may give rise to force contributions proportional to the inverse of the 1st, 2nd and 3rd power of the distance of separation of electric fields. This contribution is in no way a negligible quantity.

Finally, in the case of the SO_2-HCl system, the possible forces, apart from the Lennard-Jones potential forces, are:

(1) point dipole - point dipole interaction

(2) point dipole - induction interaction

(3) point dipole - multipole interaction

(4) contribution from non point dipole, noncentral dipole, non ideal polarizability etc.

(5) chemical forces contribution

(6) contribution arising from the special molecular model of HCl.

Monchick and Mason's potential function only takes care of contributions due to (1). All the other contributions are unaccounted for in their potential.

However, the prediction of diffusion coefficients by the Monchick and Mason potential using assumed combining rules for the parameters, are within 11% of the experimental data within the range of temperature up to 250°C. Therefore, this potential function as integrated by them represents the best presently available means of predicting diffusion coefficients in polar - polar systems.

CONCLUSIONS AND RECOMMENDATIONS:

In conclusion it may be mentioned that (1) Monchick and Mason (12-6-3) potential function appears to be promising for the prediction of diffusion coefficients of binary polar systems, although it seems to have some theoretical shortcomings as well; (2) Hirschfelder's approach with the Stockmayer potential function does not seem to describe adequately the interaction between nonpolar and polar molecules as evident from the experimental measurements of diffusion coefficients of such systems; and (3) results presented here, and by others, indicate that no suitable potential function exists for nonpolar - polar systems. Apparently, the dynamics of collisions between nonpolar and polar molecules are not yet adequately understood.

For the purpose of qualitatively explaining the above results, it is recommended that (a) similar experiments be carried out with the other members of the family of the halogen acids in combination with argon or any other inert gas.

If the reason for this peculiar behaviour lies in the chemical force contribution, then the above experiments would show some trend in the results. If, however, the reason lies in the noncentral placing of the dipole moments and not in the chemical force contribution, the results of the above experiments should agree with those of the A - HCl system.

For the purpose of further testing Hirschfelder's approach using the Stockmayer potential for nonpolar - polar systems, it may be further recommended that, (b) similar experiments be performed with polar molecules so chosen that their dipole moments are buried within and not on the surface of the molecules, for example, with H_2S.

Further work on the behaviour of diffusional and flow processes in porous solids as functions of temperature are indicated by the apparently anomalous results obtained here for the calibration factor.

TABLE OF NOMENCLATURES

N_A, N_B are the total transfer of gases, A, and B, into streams of B and A, respectively,

D_{AB} is the diffusion coefficient of gas, A, into gas, B,

S is the area for diffusion,

z is the length of the diffusion path,

c_A is the concentration of gas, A, in the stream rich in gas, B,

p_A is the partial pressure of gas, A, in the stream rich in gas, B,

P total pressure

M_A, M_B are the molecular weights of gases A and B respectively,

y_{A_2} is the mole fraction of A in the stream rich in B,

y_{B_1} is the mole fraction of B in the stream rich in A,

A_1, B_2 are the flow rates of A and B entering diffusion cell,

A_1', B_2' are the flow rates of streams rich in A and rich in B, respectively, leaving the diffusion cell,

V_A, V_B are respectively the volumes of A and B going into the streams rich in B and rich in A,

R is the universal gas constant,

T_R is the room temperature,

P_R is the atmospheric pressure,

T is the temperature at which the diffusion study was made,

P is 1 atmosphere,

V_A', V_B' are the values of V and V respectively at T and P,

β is the diffusion cell calibration factor,

V_{b_A}, V_{b_B} are the molal volumes of A and B at their normal boiling points,

S_{AB} is the Sutherland Constant for the gas mixture, estimated by

$$S_{AB} = F \sqrt{S_A \, S_B}$$

$$\text{or} \qquad = 1.47 \, F \sqrt{T_{b_A} T_{b_B}}$$

S_A, S_B are the Sutherland constants for A and B, respectively,

T_{b_A}, T_{b_B} are the respective normal boiling temperatures,

F is an empirical factor that depends on the ratio of V_{b_B}/V_{b_A} as tabulated by Arnold.

σ_{AB} is the collision diameter, or the distance parameter of the Lennard-Jones potential parameter,

ϵ_{AB} is the depth of the potential well, or the energy parameter of the Lennard-Jones potential parameters,

$\Omega_{AB}^{(1,1)*}$ is the collision integral for unlike molecular encounter,

T_{AB}^* kT/ϵ_{AB}

δ_A is the Monchick and Mason potential parameter for dipole-dipole interaction,

d_{oil}, d_{gas} are densities of manometer oil and the gas respectively,

μ_{gas} viscosity of gas,

μ_A, μ_B dipole moments of A and B,

Q_A, Q_B quadrupole moments of A and B.

BIBLIOGRAPHY

1. Hirschfelder, J.O., C.F. Curtis, and R.B. Bird: "Molecular Theory of Gases and Liquids", John Wiley & Sons Inc., New York, 1954.

2. Monchick, L., and Mason, E.A., The Journal of Chemical Physics, 35, 1676-1697 (1961).

3. Walker, R.E., and Westenburg, A.A., J.Chem.Phys., 29, 1139-1146, 1153 (1958).

4. Scott, D.S , and Cox, K.E., The Canadian Journal of Chemical Engineering, December, 1960. Cf. Cox, K.E., M.A.Sc. Thesis submitted to the department of chemical e gineering, University of British Columbia, January, 1959.

5. Westenburg, A.A., Combustion and Flame, 1, 346 (1957).

6. Paul, R., and Srivastava, I.B., J.Chem.Phys., 35, 1621-24 (1961).

7. Schafer, K., and Moesta, H., Z.Electrochem., 58, 743 (1954).

8. Schafer, K., Corte, H., and Moesta, H., Z.Electrochem., 55,662 (1951).

9. Jackman, W., International Critical Table, Vol.5, p.62.

10. Waldmann, L., Naturwissenschaften, 32, 223 (1944).

11. Boardman, L.E., and Wild, N.E., Proc. Roy. Soc. (London) A 162, 511 (1937).

12. Scott, D.S., and Dullien, F.A.L., J.A.I.Ch.E. 8, No.1, 113 (1962).

13. Reid, R.C., and Sherwood, T.K., "Properties of Gases and Liquids", McGraw Hill Book Company, Inc., New York, 1958, p.267. Cf. Arnold, J.H., Ind. Eng. Chem., 22, 1091 (1930).

14. Walker, R.E., and Westenburg, A.A., J. Chem. Phys., 31, 519-522 (1959).

15. Schafer, K., and Schuhmann, K., Z. Electrochem., 61, 247 (1957).

16. Amdur, I., and Schatzki, T.F., J.Chem.Phys., 27, 1049-1054 (1957).

17. Schwertz, F.A., and Brow, J.E., J. Chem. Phys., 19, 640-646 (1951).

18. Srivastava, B.N., and Srivastava, K.P., J. Chem. Phys., 30, 984 (1959).

19. Gilliland, Ind. Eng. Chem., 26, 681-85 (1934).

20. Walker, R.E., and Westenburg, A.A., J. Chem. Phys., 32, No.2, 436, (1960.)

21. Landolt-Bernstein, "Physikalish Chemisch Tablen".

22. Blank, R.F. and Prausnitz, J.M. J.A.I.Ch.E., Vol.8, No.1, p.86 (1962).

APPENDIX A

Temperature Dependence of Binary Diffusion Coefficients

BIBLIOGRAPHIC REVIEW OF PERTINENT LITERATURE

Systems studied		Temperature Range of diffusion study in ($^{\circ}$K)		Reference
Non polar - Non polar				
He	A	233.0 to 363.0		Schafer and others [7]
He	A	300	1100	Walker and Westenburg [14]
Ne	A	90	437	Schafer and others [15]
Ne	A	273	318	Srivastava and Srivastava [18]
Ne	Kr	273	318	Srivastava and Srivastava [18]
Kr	A	90	437	Schafer and others [15]
Kr	A	273	318	Srivastava and Srivastava [18]
Xe	A	194.7	378.0	Amdur and Schatzki [16]
He	N_2	300	1100	Walker and Westenburg [14]
A	N_2	233	363	Schafer and others [7]
Ne	H_2	253	341	Paul and Srivastava [6]
A	H_2	253	341	Paul and Srivastava [6]
X_e	H_2	253	341	Paul and Srivastava [6]
H_2	N_2	252	308	Schafer and others [7]
H_2	O_2	300	1100	Walker and Westenburg [20]
H_2	CO_2	252	308	Schafer and others [7]
N_2	CO_2	252	308	Schafer and others [7]
N_2	CO_2	300	1100	Walker and Westenburg [14]
O_2	CO_2	300	1100	Walker and Westenburg [20]
O_2	CH_4	300	1100	Walker and Westenburg [20]

APPENDIX A

Systems studied		Temperature Range of diffusion study in $(°K)$		Reference
Non polar - Polar				
He	H_2O	307.1 to 352.4		Schwertz and Brow[17]
O_2	CO	300	1100	Walker and Westenburg[20]
H_2	H_2O	307.1	352.4	Schwertz and Brow[17]
N_2	H_2O	307.1	352.4	Schwertz and Brow[17]
Air	H_2O	298.9	332.0	Gilliland[19]
O_2	H_2O	307.9	352.2	Schwertz and Brow[17]
H_2	CH_3OH	273	322.6	Landolt-Bernstein[21]
Air	CH_3OH	273	322.6	" "
H_2	C_2H_5OH	273	339.9	" "
Air	C_2H_5OH	298.9	332.0	Gilliland[19]
Air	Isopropyl alcohol	"	"	"
Air	Sec-Butyl alcohol	"	"	"
Air	n-Butyl alcohol	"	"	"
Air	Sec-amyl alcohol	"	"	"
Air	Ethyl-acetate	"	"	"
Air	Toluene	"	"	"
Air	Aniline	"	"	"
Air	Chlorobenzene	"		"
CO_2	H_2O	307	352.2	Schwertz and Brow[17]
CH_4	H_2O	307.5	352.1	" "
C_2H_4	H_2O	307.6	352.4	" "
CO_2	CH_3OH	273	322	Landolt-Bernstein[21]
CO_2	C_2H_5OH	273	339.9	" "
Polar - Polar				
None	---	---	---	

APPENDIX B

THE DERIVATION OF THE GROUPS

FOR

THE CALIBRATION OF FLOWMETERS

A. CAPILLARY FLOWMETERS:

In this case, pressure drop due to friction is equal to the hydrostatic pressure head of the oil in the manometer, i.e.

$$\triangle P = \frac{R(d_{oil} - d_{gas})g}{g_c} \qquad (a)$$

but

$$= \frac{2fu^2 d_{gas} L}{g_c D} \qquad (b)$$

or

$$f = \frac{RD(d_{oil} - d_{gas})g}{2 \mu^2 d_{gas} L} \qquad (c)$$

but

$$= f' \left(\frac{D u d_{gas}}{\mu_{gas}}\right) \qquad (d)$$

Equating (c) and (d),

$$\frac{R(d_{oil} - d_{gas})d_{gas}}{\mu^2_{gas}} = k \left(\frac{Q d_{gas}}{\mu_{gas}}\right)^n$$

Therefore, a plot of the group on left hand side vs the group on the right hand side would give a smooth curve.

APPENDIX - B

B. ROTAMETER TYPE FLOWMETER:

In this case, the drag coefficient is equated to a function of Reynold's number,

Drag force, $F = \dfrac{C\, d_{gas}\, A\, V^2}{2\, g_c}$ $\ldots$ $\ldots$ (1)

where C = drag coefficient

A = area of the solid (cross sectional area of the float)

V = relative velocity between the fluid and the float.

From a force balance on the float,

$F = \dfrac{v_f(d_f - d_{gas})\, g}{g_c}$ $\ldots$ $\ldots$ (2)

From (1) and (2)

$C = \dfrac{2 v_f(d_f - d_{gas}) g}{d_{gas}\, A\, V^2}$

Now $A = \dfrac{\pi\, D_f^2}{4}$ and $V = \dfrac{Q}{S_o}$

where Q = volumetric flow rate

S$_o$ = area of gas flow, constant for constant reading of the rotameter but varies with different reading.

D_f = diameter of the float.

Therefore

$C = \dfrac{2 v_f(d_f - d_{gas}) g}{d_{gas} \dfrac{\pi D_f^2}{4}\, \dfrac{Q^2}{S_o^2}}$

$ = \dfrac{8\, v_f(d_f - d_{gas}) g\, S_o^2}{\pi\, d_{gas}\, D_f^2\, Q^2}$

$ = f'\left(D_f V d_{gas}/\mu_{gas} \right) = f'\left(\dfrac{D_f\, Q\, d_{gas}}{S_o\, \mu_{gas}} \right)$

Since this function is known to be a logarithmic function,

$$\frac{v_f(d_f-d_{gas})g\,S_o^2}{Q^2\,d_{gas}\,D_f^2} = z\left(\frac{D_f\,Q\,d_{gas}}{S_o\,\mu_{gas}}\right)^m$$

where z and m are constants.

Multiplying both sides by $\left(\dfrac{D_f\,Q\,d_{gas}}{S_o\,\mu_{gas}}\right)^2$ and simplifying

$$\frac{v_f(d_f-d_{gas})\,d_{gas}}{\mu_{gas}^2} = k\left(\frac{D_f\,Q\,d_{gas}}{S_o\,\mu_{gas}}\right)^{m+2}$$

At a particular reading, R, in the particular rotameter D_f/S_o is constant.

Therefore, at constant R, (the reading in the rotameter),

$$\frac{(d_f-d_{gas})\,d_{gas}}{\mu_{gas}^2} \quad \text{is a function of} \quad \left(\frac{Q\,d_{gas}}{\mu_{gas}}\right).$$

Also $\left(\dfrac{Q\,d_{gas}}{\mu_{gas}}\right)$ is a function of R when d_{gas} and μ_{gas} are constants.

But when d_{gas} and μ_{gas} are constant, $\dfrac{(d_f-d_{gas})\,d_{gas}}{\mu_{gas}^2}$ is a constant.

Therefore, $\dfrac{Q\,d_{gas}}{\mu_{gas}}$ must be a function of $\dfrac{R\,(d_f-d_{gas})\,d_{gas}}{\mu_{gas}^2}$

when both R and $\dfrac{(d_f-d_{gas})\,d_{gas}}{\mu_{gas}^2}$ vary.

Consequently a plot of $\dfrac{Q\,d_{gas}}{\mu_{gas}}$ vs $\dfrac{R\,(d_f-d_{gas})\,d_{gas}}{\mu_{gas}^2}$

should give a smooth curve that would account for the variations of Q with

those of d_{gas}, μ_{gas} and R.

APPENDIX C

SAMPLE CALCULATION

System : SO_2 - HCl

	Run 1	Run 2
Flowmeter readings:		
Capillary flowmeter-2 (HCl)	27.2	27.2
Matheson rotameter, 203 (SO_2)	9.0	9.2
Gas sample bulb numbers:		
HCl-rich stream	VIII	III
	II	IV
SO_2-rich stream	VII	V
	I	VI

Titration for SO_2:

25cc of iodine standard solution = 24.05 cc of N/100 sodium thiosulphate solution

For sample No. VIII, thiosulphate required was 19.70 cc — Run 1
           II,   "   "   19.15 cc

           III,   "   "   19.25 cc — Run 2
           IV,   "   "   19.40 cc

Titration of HCl :

For blank test, the $AgNO_3$ standard solution required was 1.5 cc of N/100

For sample No.VII,   "   "   "   5.30 cc — Run 1
          I,   "   "   "   5.15 cc

          V,   "   "   "   5.30 cc — Run 2
          VI,   "   "   "   5.30 cc

Calculation of equivalent gas volume:

Example bulb VIII, volume of SO_2.

Bulb volume = 233.80 cc.

Density of SO_2 = 2.675×10^{-3} g/cc at 23.3°C (room temperature) and 754.1 mm Hg. (barometric pressure).

(Standard density taken from Handbook of Chemistry and Physics)

Iodine required for SO_2 = 24.05 - 19.70 = 4.35 cc

Equivalent volume of SO_2 = $\frac{4.35 (64.07)}{2 (1000)(100)(2.675 \times 10^{-3})}$

                = 0.521 cc.

Concentration of SO by volume = $0.521 \times 100/233.8$ = 0.2225% SO_2

Concentrations by Volume:	Run 1	Run 2
SO_2 in HCl rich stream	0.2225%	0.2475%
	0.246 %	0.2395%
HCl in SO rich stream	0.381 %	0.368 %
	0.369 %	0.377 %

APPENDIX C

SAMPLE CALCULATION

Experimental Data:

System : SO_2 - HCl

Room temperature, T_r, = 296.6°K

Atmospheric pressure, P_r, = 754.1 mm.Hg.

Diffusion temperature, T, = 393.0°K

Pressure, P, = 760.0 mm. Hg.

Diffusion cell calibration factor, β, = 20.28

		Run 1	Run 2
Flow rate of HCl, H_1,		122.2 cc/min.	122.2 cc/min.
Flow rate of SO_2, S_2,		119.5 cc/min.	123.5 cc/min.
Mole fractions of HCl in SO_2-rich stream, y_{H_2},		0.00375	0.00372
Mole fractions of SO_2 in HCl-rich stream, y_{S_1},		0.00234	0.00244

Calculation of terms in Equation (20)

		Run 1	Run 2
1.	$S_2 y_{H_2}$	0.44813	0.45942
2.	$H_1 y_{S_1}$	0.28595	0.29817
3.	$S_2 y_{H_2} - H_1 y_{S_1}$	0.16218	0.16125
4.	$1 - y_{H_2} - y_{S_1}$	0.99391	0.99384
5.	$\dfrac{S_2 y_{H_2} - H_1 y_{S_1}}{1 - y_{H_2} - y_{S_1}}$	0.16317	0.16224

6. $\dfrac{S_2 y_{H_2} - H_1 y_{S_1}}{1 - y_{H_2} - y_{S_1}} \times \dfrac{T}{T_r} \times \dfrac{P_r}{P}$

$= \dfrac{S_2 y_{H_2} - H_1 y_{S_1}}{1 - y_{H_2} - y_{S_1}} \times \dfrac{393.0}{296.6} \times \dfrac{745.1}{760.0}$

0.21452 0.21330

	Run 1	Run 2

7. $\dfrac{S_2 y_{H_2} - H_1 y_{S_1}}{1 - y_{H_2} - y_{S_1}} \times \dfrac{T}{Tr} \times \dfrac{Pr}{P} \times \beta$

$= \dfrac{S_1 y_{H_2} - H_1 y_{S_1}}{1 - y_{H_2} - y_{S_1}} \times \dfrac{T}{Tr} \times \dfrac{Pr}{P} \times 20.28$ 4.35047   4.32572

8. $\dfrac{S_2 y_{H_2}}{H_1 y_{S_1}}$ 1.56716   1.54079

9. $\ln$ $\dfrac{S_2 y_{H_2}}{H_1 y_{S_1}}$ 0.44926   0.43229

Substituting in equation (10),

$D_{H-SO_2} = \dfrac{S_2 y_{H_2} - H_1 y_{S_1}}{1 - y_{H_2} - y_{S_1}} \times \dfrac{T}{Tr} \times \dfrac{Pr}{P} \times \beta \Big/ \ln \dfrac{S_2 y_{H_2}}{H_1 y_{S_1}}$, $cm^2/min.$

$= \dfrac{\text{term 7.}}{\text{term 9.}}$, $cm^2/min.$

$= \dfrac{\text{term 7}}{60 \times \text{term 9}}$, $cm^2/sec.$ $\dfrac{4.35047}{60 \times 0.44926}$ $\dfrac{4.32572}{60 \times 0.43229}$

                           $=$ 0.16139 $=$ 0.16676

Average D_{H-SO_2} , $= 0.1641$ $cm^2/sec.$

Prediction of D_{HCl-SO_2} by Monchick and Mason method:

Data given by Monchick and Mason[2]:-

Dipole moment of SO_2, μ_{SO_2} , $= 1.63$ debye $= 1.63 \times 10^{-18}$ (stat-conlombs)(cm)

Dipole moment of HCl, μ_{HCl} $= 1.08$ debye $= 1.08 \times 10^{-18}$ "   "   "

$\dfrac{\epsilon_{SO_2}}{k} = 347^\circ K;$ $\sigma_{SO_2} = 4.04 \, \overset{o}{A}$: $\delta_{SO_2} = 0.42$

$\dfrac{\epsilon_{HCl}}{k} = 328^\circ K;$ $\sigma_{HCl} = 3.36 \, \overset{o}{A}$; $\delta_{HCl} = 0.34$

Calculation of terms in Hirschfelder equation (2)

Assuming the combining rules of Hirschfelder,

$$\frac{\epsilon_{HCl-SO_2}}{k} = \sqrt{\frac{\epsilon_{HCl}}{k} \times \frac{\epsilon_{SO_2}}{k}} = \sqrt{328 \times 347} = 337.3\,^{\circ}K$$

$$\sigma_{HCl-SO_2} = \frac{\sigma_{HCl} + \sigma_{SO_2}}{2} = \frac{3.36 + 4.04}{2} = 3.70\,\overset{\circ}{A}$$

Using equation (10)

$$\delta_{HCl-SO_2} = \frac{2\,\mu_{HCl}\,\mu_{SO_2}}{4\,\epsilon_{HCl-SO_2}\,\sigma_{HCl-SO_2}^3} = \frac{2 \times 1.08 \times 10^{-18} \times 1.63 \times 10^{-18}}{4 \times (337.3 \times 1.3803 \times 10^{-16})(3.70 \times 10^{-8})^3}$$

$$= 0.374$$

$$T^*_{HCl-SO_2} = \frac{kT}{\epsilon_{HCl-SO_2}} = \frac{393.0}{337.3} = 1.165$$

From tables of collision integrals given by Monchick and Mason,

corresponding to $\delta = 0.375$ and $T^* = 1.165$,

$$\Omega^{(1,1)*}_{HCl-SO_2} = 1.368$$

Substituting in equation (2)

$$D_{HCl-SO_2} = 0.0026280 \frac{393^{3/2} \left[\frac{36.47+64.06}{2 \times 36.47 \times 64.06}\right]^{\frac{1}{2}}}{1 \times (3.70)^2 \times 1.368}$$

$$= 0.1603 \quad cm^2/sec.$$

APPENDIX D

GRAPHICAL SUPERPOSITION METHOD

FOR

THE CALCULATION OF POTENTIAL PARAMETERS

(This method has been adopted from Mason and Monchick's technique for getting parameters of pure polar gases from viscosity data, on the assumption that σ is independent of ϵ .)

Writing the Hirschfelder equation for the binary gaseous diffusion coefficient in the form:

$$\frac{D_{12}P}{T^{3/2}\left[\frac{M_1+M_2}{2M_1M_2}\right]^{\frac{1}{2}}} = \frac{0.0026280}{\sigma_{12}^2\,\Omega_{12}^{(1,1)*}(T_{12}^*)}$$

the left hand side represents the experimental quantities while the right hand side, the theoretical quantities. Taking logarithms on both sides,

$$\log\frac{D_{12}P}{T^{3/2}\left[\frac{M_1+M_2}{2M_1M_2}\right]^{\frac{1}{2}}} = \log 0.0026280 - 2\log\sigma_{12} + \log\left[\Omega_{12}^{(1,1)*}(T_{12}^*)\right]^{-1} \quad \ldots(1)$$

Again, $\qquad T_{12}^* = \dfrac{kT}{\epsilon_{12}}$,

and taking logarithms on both sides

$$\text{Log } T_{12}^* = \text{Log } T - \text{Log }\frac{\epsilon_{12}}{k}$$

or $\qquad$ $$\text{Log } T = \text{Log } T_{12}^* + \text{Log }\frac{\epsilon_{12}}{k} \qquad\qquad (2)$$

Therefore a plot of $\text{Log }\dfrac{D_{12}P}{T^{3/2}\left[\frac{M_1+M_2}{2M_1M_2}\right]^{\frac{1}{2}}}$ vs $\text{Log } T$

should be superposable on a plot of $\text{Log }\left[\Omega_{12}^{(1,1)*}(T_{12}^*)\right]^{-1}$ vs $\text{Log } T_{12}^*$.

The translation of the experimental plot along the temperature axis over the theoretical plot until a good fit of the curves is obtained gives Log $\dfrac{\epsilon_{12}}{k}$. Similarly translation along the ordinat gives Log 0.0026280 - 2 log σ_{12}, from which σ_{12} can be calculated.

APPENDIX E

COMBINING RULE OF δ_{MAX} FOR BINARY SYSTEMS

The theoretical expression, given by equation (10), for

$$\left(\delta_{AB}\right)_{max} \quad \text{is} \quad 4 \; \epsilon_{AB} \; \sigma_{AB}^{3} \; \delta_{AB} \quad = \quad 2 \; \mu_A \; \mu_B$$

or

$$\delta_{AB} \quad = \quad \frac{\mu_A \; \mu_B}{2 \; \epsilon_{AB} \; \sigma_{AB}^{3}} \tag{1}$$

For pure components,

$$\delta_A \quad = \quad \frac{\mu_A^2}{2 \; \epsilon_A \; \sigma_A^3} \tag{2}$$

$$\delta_B \quad = \quad \frac{\mu_B^2}{2 \; \epsilon_B \; \sigma_B^3} \tag{3}$$

Assuming Hirschfelder's combining rules for ϵ and σ,

$$\epsilon_{AB} \quad = \quad \sqrt{\epsilon_A \; \epsilon_B} \tag{4}$$

$$\sigma_{AB} \quad = \quad \frac{\sigma_A + \sigma_B}{2} \tag{5}$$

Substituting equations (4) and (5) in equation (1)

$$\delta_{AB} \quad = \quad \frac{\mu_A \mu_B}{2 \sqrt{\epsilon_A \epsilon_B} \left(\dfrac{\sigma_A + \sigma_B}{2} \right)^3}$$

$$= \quad \frac{\mu_A^2 \left[\dfrac{\mu_B}{\mu_A} \right]}{2 \; \epsilon_A \sqrt{\dfrac{\epsilon_B}{\epsilon_A}} \; \sigma_A^3 \left(\dfrac{1}{2} + \dfrac{\sigma_B}{2\sigma_A} \right)^3}$$

$$= \quad \frac{\mu_A^2}{2 \; \epsilon_A \; \sigma_A^3} \; \frac{\dfrac{\mu_B}{\mu_A}}{\sqrt{\dfrac{\epsilon_B}{\epsilon}} \left(\dfrac{1}{2} + \dfrac{\sigma_B}{2\sigma_A} \right)^3}$$

$$= \quad \delta_A \; \frac{\dfrac{\mu_B}{\mu_A}}{\sqrt{\dfrac{\epsilon_B}{\epsilon_A}} \left(\dfrac{1}{2} + \dfrac{\sigma_B}{2\sigma_A} \right)^3} \tag{6}$$

Similarly, $\quad \sigma_{AB} = \delta_B \dfrac{\dfrac{\mu_A}{\mu_B}}{\sqrt{\dfrac{\epsilon_A}{\epsilon_B}} \left(\dfrac{1}{2} + \dfrac{\sigma_A}{2\sigma_B}\right)^3}$ $\hspace{2cm}$ (7)

Arithmetic average

Assuming that σ_{AB} be an arithmatic average of δ_A and δ_B, the necessary conditions can be derived as follows:

From equations (6) and (7), by adding

$$2\,\delta_{AB} = \delta_A \frac{\dfrac{\mu_B}{\mu_A}}{\sqrt{\dfrac{\epsilon_B}{\epsilon_A}}\left(\dfrac{1}{2}+\dfrac{\sigma_B}{2\sigma_A}\right)^3} + \delta_B \frac{\dfrac{\mu_A}{\mu_B}}{\sqrt{\dfrac{\epsilon_A}{\epsilon_B}}\left(\dfrac{1}{2}+\dfrac{\sigma_A}{2\sigma_B}\right)^3}$$

$$= \frac{\delta_A \dfrac{\mu_B}{\mu_A}\sqrt{\dfrac{\epsilon_A}{\epsilon_B}}\left(\dfrac{1}{2}+\dfrac{\sigma_A}{2\sigma_B}\right)^3 + \delta_B \dfrac{\mu_A}{\mu_B}\sqrt{\dfrac{\epsilon_B}{\epsilon_A}}\left(\dfrac{1}{2}+\dfrac{\sigma_B}{2\sigma_A}\right)^3}{\sqrt{\dfrac{\epsilon_B}{\epsilon_A}\dfrac{\epsilon_A}{\epsilon_B}}\left(\dfrac{1}{2}+\dfrac{\sigma_B}{2\sigma_A}\right)^3\left(\dfrac{1}{2}+\dfrac{\sigma_A}{2\sigma_B}\right)^3} \cdots$$

$$= \delta_A \frac{\dfrac{\sigma_A^3 \sqrt{\epsilon_A}}{\mu_A}\dfrac{\mu_B}{\sqrt{\epsilon_B}}}{\left(\dfrac{\sigma_A + \sigma_B}{2}\right)^3} + \delta_B \frac{\dfrac{\sigma_B^3 \sqrt{\epsilon_B}}{\mu_B}\dfrac{\mu_A}{\sqrt{\epsilon_A}}}{\left(\dfrac{\sigma_A + \sigma_B}{2}\right)^3} \hspace{1cm} (8)$$

Now assuming that $\quad \delta_{AB} = \dfrac{\delta_A + \delta_B}{2}$

$\hspace{3cm}$ or $\quad 2\,\delta_{AB} = \delta_A + \delta_B$,

Therefore, $\quad \dfrac{\dfrac{\sigma_A^3 \sqrt{\epsilon_A}}{\mu_A}\dfrac{\mu_B}{\sqrt{\epsilon_B}}}{\left(\dfrac{\sigma_A + \sigma_B}{2}\right)^3} \equiv 1 \equiv \dfrac{\dfrac{\sigma_B^3 \sqrt{\epsilon_B}}{\mu_B}\dfrac{\mu_A}{\sqrt{\epsilon_A}}}{\left(\dfrac{\sigma_A + \sigma_B}{2}\right)^3}$

or $\quad \dfrac{\sigma_A^3 \sqrt{\epsilon_A}}{\mu_A}\dfrac{\mu_B}{\sqrt{\epsilon_B}} = \left(\dfrac{\sigma_A + \sigma_B}{2}\right)^3 \hspace{2cm} (9)$

and $\quad \dfrac{\sigma_B^3 \sqrt{\epsilon_B}}{\mu_B}\dfrac{\mu_A}{\sqrt{\epsilon_A}} = \left(\dfrac{\sigma_A + \sigma_B}{2}\right)^3 \hspace{2cm} (10)$

In order that both equations (9) and (10) are simultaneously satisfied

$$\frac{\sigma_A^3 \sqrt{\epsilon_A}}{\mu_A} \quad \frac{\mu_B}{\sqrt{\epsilon_B}} \quad = \quad \frac{\sigma_B^3 \sqrt{\epsilon_B}}{\mu_B} \quad \frac{\mu_A}{\sqrt{\epsilon_A}}$$

or

$$\frac{\sigma_A^3 \; \epsilon_A}{\mu_A^2} \quad = \quad \frac{\sigma_B^3 \; \epsilon_B}{\mu_B^2}$$

i.e.

$$\frac{1}{\delta_A} \quad = \quad \frac{1}{\delta_B} \quad \text{or} \quad \delta_A = \delta_B .$$

But this is not **likely** to have equal δ_s for different polar gases.

Therefore the arithmatic average for pure component δ_s cannot be used for δ_{AB} of the mixture.

<u>Geometric average:-</u>

Assuming that δ_{AB} be a geometric average of δ_A and δ_B, the necessary condition can be derived as follows:

From equations (6) and (7), by multiplying

$$\delta_{AB} \times \delta_{AB} = \delta_A \frac{\frac{\mu_B}{\mu_A}}{\sqrt{\frac{\epsilon_B}{\epsilon_A}} \left(\frac{1}{2} + \frac{\sigma_B}{2\sigma_A} \right)^3} \times \delta_B \frac{\frac{\mu_A}{\mu_B}}{\sqrt{\frac{\sigma_A}{\epsilon_B}} \left(\frac{1}{2} + \frac{\sigma_B}{2\sigma_A} \right)^3}$$

$$= \delta_A \; \delta_B \quad \frac{\sigma_A^3 \; \sigma_B^3}{\left(\frac{\sigma_A + \sigma_B}{2} \right)^6}$$

Now assuming that

$$\delta_{AB} = \sqrt{\delta_A \; \delta_B}$$

or

$$\delta_{AB}^2 = \delta_A \; \delta_B$$

$$\delta_A \; \delta_B = \delta_A \; \delta_B \quad \frac{\left(\sigma_A \; \sigma_B \right)^3}{\left(\frac{\sigma_A + \sigma_B}{2} \right)^6}$$

The necessary condition, therefore, is that

$$\frac{\left(\sigma_A \; \sigma_B \right)^3}{\left(\frac{\sigma_A + \sigma_B}{2} \right)^6} = 1 \quad \text{or} \quad \left(\sigma_A \; \sigma_B \right)^{\frac{1}{2}} = \frac{\sigma_A + \sigma_B}{2} \quad \ldots (11)$$

i.e. the geometric average of C_A at C_B be equal to their arithmatic

average. This is possible only when $C_A = C_B$.

Although the exact equivalence of C_A and C_B is not likely, in

reality values of C do not differ very much. Therefore, if the values of

are pretty close to each other, a geometric average would be a close

approximation.

APPENDIX - F

METHODS OF ANALYSIS

METHOD - 1. COMBINED CHEMICAL - T.C.CELL ANALYSIS:

(a) Checking the accuracy of the method:

This analysis was carried out in the set of apparatus shown in
Figure 3. 50cc/min. of nitrogen gas was led through the apparatus, entering
into the flask containing 10% solution of NaOH, passing over the surface
and then through the vertical column containing a 50-50 mixture of Ascarite
and Drierite, and finally flowing through the sample side of the T.C.cell.
Another stream of 50cc/min. of nitrogen gas was flowing at the same time
through the reference side of the same T.C.cell. When steady state conditions
were reached, the electrical circuit of the T.C.cell was adjusted to give
no deflection in the galvanometer. After thus setting the zero of the T.C.
cell, 100cc/min. of SO_2 gas was introduced through another opening into
the same flask through which nitrogen was flowing. Most of the SO_2 was
dissolved in the NaOH solution and the remainder, if any, was swept away
by the nitrogen stream into the column of Ascarite and Drierite where it
was completely removed, together with any water vapour, before it entered
the T.C.cell. The electrical circuit showed no deflection in the galvanometer,
indicating that SO_2 was completely absorbed in the apparatus, and that
impurities in the SO_2 stream did not affect the T.C.cell.

The procedure was repeated three times using SO_2 and three times
using HCl gas, and the result was confirmed in all cases.

(b) Analysis of the stream out of the diffusion cell:

After setting the zero of the T.C.cell as described above, the T.C.
cell was calibrated for analysing argon in a stream of nitrogen by making
known mixtures of argon in nitrogen. Known mixtures were made by taking
about 1000cc/min. of nitrogen and from 5 to 20cc/min. of argon. 50cc/min.
of this mixture entered the sample side of the T.C.cell, after flowing through
the apparatus of Figure 3, and the corresponding millivolt changes were

noted in the potentiometer.

After the calibration was done, the stream of gas which came out of the diffusion cell, and which was to be analysed was introduced into the flask through the same opening which was previously used for letting in SO_2 or HCl gas.

The corresponding millivolt change was noted and converted into concentration units using the calibration chart.

METHOD - 2. ANALYSIS OF SO_2 IN ARGON-RICH STREAM:

(a) Checking the accuracy of the method:

A gas bulb of about 250cc. capacity and provided with stopcocks at each end, was filled with a known mixture of SO_2 in argon, and held in a slanting position with one end of the bulb dipped in 25cc of N/100 Iodine standard solution diluted upto 100cc, while the other end connected to a water reservoir by means of a rubber tube. The SO_2 was dissolved in water by letting it flow from the reservoir through the upper stopcock of the gas bulb a little at a time and shaking well. The solution of SO_2 in water was then allowed to flow down into the standard iodine solution by opening the lower stopcock, while keeping the lower end of the bulb dipped in iodine solution. This was repeated three times. The solution was then analysed for excess of iodine using N/100 Sodium thiosulphate solution and starch indicator.

The process was repeated three times and the results checked well.

(b) <u>Analysis of the sample stream:</u>

Exactly the same technique was used as described above except that the gas bulbs now contained sample gas rather than a known mixture. Duplicate gas samples were obtained in each run by allowing the outlet stream from the diffusion cell to flow continuously through two sample bulbs in series.

<u>METHOD - 3. ANALYSIS OF HCl IN ARGON-RICH STREAM:</u>

(a) <u>Checking the accuracy of the method:</u>

A gas bulb of about 250cc capacity, provided with stopcocks at each end, was filled with a known mixture of HCl in A and dissolved in water using the same technique as described in the analysis of SO_2 in argon-rich streams.

The solution of HCl gas in water was then netralised by using $NaHCO_3$ and the pH was adjusted by HNO_3 and $NaHCO_3$ to a value between 7 and 8. It was then titrated against N/100 $AgNO_3$ solution using potassium chromate indicator as indicator, i.e. using the Mohr's method for chloride estimation as given by Kolthoff and Sandell, "Quantitative Inorganic Analysis" McMillan and Co.(1936).

A blank test was simultaneously performed on the same volume of distilled water by adjusting the pH to the same value and titrating with the same $AgNO_3$ solution following the same technique.

The reading of the blank titration was subtracted from that of the sample titration, and the result was found to agree with the known mixture.

This check was also repeated three times.

(b) <u>Analysis of the sample stream:</u>

The same technique as described above was followed with the same gas, duplicate samples again being obtained for each run.

METHOD - 4. ANALYSIS OF HCl IN SO₂-RICH STREAM:

(a) Checking the accuracy of the method:

(1) A gas bulb, as described above, of known capacity was filled with SO₂ gas taken from the cylinder. The gas was then dissolved in an excess of approximately 1N-NaOH solution (about 200cc). 5 cc of N/100 HCl solution was then added and the solution was oxidised by sodium peroxide, adding a little at a time and stirring vigorously while keeping the solution sufficiently warm, until about twice the required amount of Na₂O₂ ~~were~~ *was* added. A spot test on a white surface with a drop of iodine solution and the oxidised solution was made to ensure the completion of oxidation.

The solution was then neutralized and brought to a pH between 7 and 8, and titrated using N/100 AgNO₃ solution with the Mohr method as described above. A simultaneous blank test was made on the same volume of water.

The check was repeated three times.

(2) Alternatively, the SO₂ gas sample taken in a gas bulb was dissolved in 50 cc of water by dipping one end of the gas bulb into the liquid and opening the lower stopcock. 5cc of N/100.HCl standard solution was added and the solution was boiled off, adding water gradually to keep the volume constant until all SO₂ was removed. The same spot test, as described above, was employed to ensure that no SO₂ was left. The solution was neutralized and titrated as described in (1) above.

(b) Analysis of the sample gas:

The same technique was employed as that used in checking the method except that the small amount of HCl was present in the gas sample.

METHOD - 5. ANALYSIS OF SO$_2$ IN HCl-RICH STREAM:

Except for the technique of dissolving the gas, this method is exactly the same as described in Method-2.

In this case the lower end of the gas bulb was dipped in a 25cc of N/100 Iodine solution diluted to 300cc and the lower stop-cock was opened. All the liquid sucked in and filled the bulb. After shaking several times, the solution was drained off and the bulb washed three times with distilled water.

The total solution was then titrated against N/100 Sodium thiosulphate solution as described in method-2.

APPENDIX F

METHODS OF ANALYSIS

METHOD 1.   COMBINED CHEMICAL - T.C. CELL ANALYSIS:

(a)   Checking the accuracy of the method:

This analysis was carried out in the set of apparatus shown in Figure 3.

50cc/min. of nitrogen gas was led through the apparatus, entering into the

flask containing 10% solution of NaOH, passing over the surface and then through

the vertical column containing a 50-50 mixture of Ascarite and Drierite, and

finally flowing through the sample side of the T.C. cell.   Another stream of

50cc/min. of nitrogen gas was flowing at the same time through the reference

side of the same T.C. cell. When steady state conditions were reached, the

electrical circuit of the T.C. cell was adjusted to give no deflection in the

galvanometer.   After thus setting the zero of the T.C. cell, 100cc/min. of SO_2

gas was introduced through another opening into the same flask through which

nitrogen was flowing.   Most of the SO_2 was dissolved in the NaOH solution and

the remainder, if any, was swept away by the nitorgen stream into the column of

Ascarite and Drierite where it was completely removed, together with any water

vapour, before it entered the T.C. cell. The electrical circuit showed no

deflection in the galvanometer, indicating that SO_2 was completely absorbed in

the apparatus, and that impurities in the SO_2 stream did not affect the T.C. cell.

The procedure was repeated three times using SO_2 and three times using

HCl gas, and the result was confirmed in all cases.

(b)   Analysis of the stream out of the diffusion cell:

After setting the zero of the T.C. cell as described above, the T.C. cell

was calibrated for analysing argon in a stream of nitrogen by making known

mixtures of argon in nitrogen.   Known mixtures were made by taking about 1000cc/

min. of nitorgen and from 5 to 20cc/min. of argon. 50cc/min. of this mixture

entered the sample side of the T.C. cell, after flowing through the apparatus

of Figure 3, and the corresponding millivolt changes were noted in the

potentiometer.

After the calibration was done, the stream of gas which came out of the diffusion cell, and which was to be analysed was introduced into the flask through the same opening which was previously used for letting in SO_2 or HCl gas.

The corresponding millivolt change was noted and converted into concentration units using the calibration chart.

METHOD 2.   ANALYSIS OF SO_2 IN ARGON-RICH STREAM:

(a)   Checking the accuracy of the method:

A gas bulb of about 250cc. capacity and provided with stopcocks at each end, was filled with a known mixture of SO_2 in argon, and held in a slanting position with one end of the bulb dipped in 25cc. of N/100 Iodine standard solution diluted up to 100cc., while the other end connected to a water reservoir by means of a rubber tube.   The SO_2 was dissolved in water by letting it flow from the reservoir through the upper stopcock of the gas bulb a little at a time and shaking well.   The solution of SO_2 in water was then allowed to flow down into the standard iodine solution by opening the lower stopcock, while keeping the lower end of the bulb dipped in iodine solution.   This was repeated three times.   The solution was then analysed for excess of iodine using N/100 Sodium thiosulphate solution and starch indicator.

The process was repeated three times and the results checked well.

(b)   Analysis of the sample stream:

Exactly the same technique was used as described above except that the gas bulbs now contained sample gas rather than a known mixture.   Duplicate gas samples were obtained in each run by allowing the outlet stream from the diffusion cell to flow continuously through two sample bulbs in series.

METHOD 3. ANALYSIS OF HCl IN ARGON-RICH STREAM:

(a) Checking the accuracy of the method:

A gas bulb of about 250 cc. capacity, provided with stopcocks at each end, was filled with a known mixture of HCl in A and dissolved in water using the same technique as described in the analysis of SO_2 in argon-rich streams.

The solution of HCl gas in water was then neutralized by using $NaHCO_3$ and the pH was adjusted by HNO_3 and $NaHCO_3$ to a value between 7 and 8. It was then titrated against N/100 $AgNO_3$ solution using potassium chromate as indicator, i.e. using the Mohr's method for chloride estimation as given by Kolthoff and Sandell, "Quantitative Inorganic Analysis" McMillan and Co.(1936).

A blank test was simultaneously performed on the same volume of distilled water by adjusting the pH to the same value and titrating with the same $AgNO_3$ solution following the same technique.

The reading of the blank titration was subtracted from that of the sample titration, and the result was found to agree with the known mixture.

This check was also repeated three times.

(b) Analysis of the sample stream:

The same technique as described above was followed with the same gas, duplicate samples again being obtained for each run.

METHOD 4. ANALYSIS OF HCl IN SO -RICH STREAM:

(a) Checking the accuracy of the method:

(1) A gas bulb, as described above, of known capacity was filled with SO_2 gas taken from the cylinder. The gas was then dissolved in an excess of approximately 1N-NaOH solution (about 200cc.) 5cc. of N.100 HCl solution was then added and the solution was oxidized by sodium peroxide, adding a little as a time and stirring vigorously while keeping the solution sufficiently warm, until about twice the required amount of Na_2O_2 was added. A spot test on a white surface with a drop of iodine solution and the oxidized solution

was made to ensure the completion of oxidation.

The solution was then neutralized and brought to a pH between 7 and 8, and titrated using N/100 AgNO$_3$ solution with the Mohr method as described above. A simultaneous blank test was made on the same volume of water.

The check was repeated three times.

(2) Alternatively, the SO$_2$ gas sample taken in a gas bulb was dissolved in 50cc. of water by dipping one end of the gas bulb into the liquid and opening the lower stopcock. 5cc. of N/100.HCl standard solution was added and the solution was boiled off, adding water gradually to keep the volume constant until all SO$_2$ was removed. The same spot test, as described above, was employed to ensure that no SO$_2$ was left. The solution was neutralized and titrated as described in (1) above.

(b) Analysis of the sample gas:

The same technique was employed as that used in checking the method except that the small amount of HCl was present in the gas sample.

METHOD 5. ANALYSIS OF SO$_2$ IN HCl-RICH STREAM:

Except for the technique of dissolving the gas, this method is exactly the same as described in Method 2.

In this case the lower end of the gas bulb was dipped in a 25cc. of N/100 Iodine solution diluted to 300cc. and the lower stop-cock was opened. All the liquid sucked in and filled the bulb. After shaking several times, the solution was drained off and the bulb washed three times with distilled water.

The total solution was then titrated against N/100 Sodium thiosulphate solution as described in Method 2.