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ENGINEERING AND INDUSTRIAL EXPERIMENT STATION

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SOLUBILITY AND DIFFUSIVITY OF HYDROCARBONS AND OXYGEN IN FUEL CELL ELECTROLYTES

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SUMMARY

Experimental measurements of the solubility of oxygen in KOH, H_2SO_4 and H_3PO_4 solutions, and of straight-chain, saturated hydrocarbons in phosphoric acid have been made over the full electrolyte concentration range. The diffusion coefficient of oxygen in KOH solutions at 25°C and in 85% H_3PO_4 solutions at 60° and 80°C are also reported.

A correlation for the solubility of gases in phosphoric acid solutions has been derived by dimensional analysis, and shown to fit the measured values within the limits of experimental error. The correlation presented should enable the solubility of oxygen and hydrocarbons in 85-105% H_3PO_4 to be predicted with reasonable accuracy.

The values of the diffusivity of oxygen in KOH have been shown to obey the theory of Ratcliff. A correlation for the diffusion coefficient of gases in phosphoric acid solutions has been derived, but insufficient experimental data was obtained for a test of the correlation to be made.

1. INTRODUCTION

It seems probable that in some cases the current obtainable from fuel cells is limited by diffusion of the reacting gas (or liquid) through the liquid (electrolyte) phase to active sites on the surface of the electrode. Under these conditions it follows from Fick's Law that the limiting current that may be drawn from a given electrode will depend on the concentration of the reacting substance in the bulk electrolyte and on its diffusivity. A knowledge of the magnitude of both of these properties is needed before any estimate of mass transfer limitations may be made.

The work reported here has been aimed at making experimental measurements of the solubility and diffusivity of fuel cell gases in suitable electrolytes, and at developing theoretical or empirical methods of estimating these properties for systems that have not been studied experimentally. The correlations available for the prediction of gas solubilities and diffusivities in pure liquids are not generally applicable to electrolyte solutions, and a modified approach is necessary.

Previous workers have estimated the rate of mass transfer at fuel cell electrodes using the values of the solubility and diffusivity of the gas in pure water. According to Fick's Law the rate of mass transfer is proportional to the product of the solubility and diffusivity. Experimental measurements on fuel cell electrolytes have indicated that this product may be as low as 1% of the value in pure water. Calculations of the current expected from a mass-transfer limited fuel cell in which data for pure water are assumed will therefore give current values that are much too high.

2. SOLUBILITY STUDIES

2.1 Theory

2.1.1 Variables Involved

The solubility of a gas in electrolyte solution may be expected to vary with the properties of the solute gas, concentration of the electrolyte, temperature and pressure. The system is a complex one, since the electrolyte solution is itself a mixture of chemical species; in the case of phosphoric acid the solution composition varies with the temperature. Because of this, attempts to provide a sophisticated theoretical treatment by analysis of the intermolecular forces involved or along the lines adopted by Hildebrand and Scott (1) appear likely to prove difficult. For the purpose of predicting solubility data for engineering use an empirical method of correlation has been selected.

Although empirical correlations may be necessary to predict the solubility, the variation in solubility of a given solute with temperature and pressure will follow well-known thermodynamic laws. Thus the variation in solubility (s_A) with temperature will be given by,

$$\left(\frac{\partial \ln s_A}{\partial T}\right)_{p,c_B} = \frac{\Delta H}{RT^2} \tag{2-1}$$

where c_B is the concentration of electrolyte and ΔH represents the differential heat of solution per mole of gas. Equation (2-1) may be integrated, if ΔH may be assumed independent of temperature, to get

$$(\ln s_A)_{p,c_B} = -\frac{\Delta H}{RT} + I \tag{2-2}$$

where I is an integration constant. A positive heat of solution will therefore produce a decrease in solubility with rise in temperature, and vice versa. Although most systems show the former type of behavior, there are also cases in which solubility may increase with rise in temperature. While equation (2-1) will be true in all cases, the integrated equation (2-2) will hold only if the heat of solution is independent of temperature. Since the chemical composition of phosphoric acid changes with temperature, the heat of solution may well vary with temperature, so that equation (2-2) may not hold in this case.

The effect of pressure on the solubility of gases in liquids is described quantitatively by Henry's Law, which states that solubility is directly proportional to the partial pressure of the gas above the liquid,

$$\left(\frac{s_A}{p_A}\right)_{T,c_B} = h \qquad (2\text{-}3)$$

where h is the Henry's Law constant. Henry's Law has been found to hold well for gases of low solubility at pressures such that fugacities may be replaced by pressures (2); thus it may be expected to hold satisfactorily at pressures up to a few atmospheres. Deviations from Henry's Law may be expected for high pressures, low temperatures, or cases where the solute and solvent interact chemically. It therefore seems likely that the pressure effect of solubility of oxygen and hydrocarbon gases in electrolyte solutions should be quite well described by equation (2-3) at pressures up to 4 or 5 atmospheres. Paynter and McDonald (3) have reported data for the solubility of propane in phosphoric acid at various partial pressures which appear to obey Henry's Law up to 1000 mm. H_g.

For solutions of gas mixtures, Henry's Law may be applied independently to each gas irrespective of the pressures of the others, provided that the conditions noted in the previous paragraph are fulfilled. Thus the solubility of each component of the mixture should be directly proportional to its partial pressure. The solubility of gases and hydrocarbons in electrolytes is so low that the assumption of each solute acting independently appears valid.

For a gas mixture containing components 1, 2, ...i..., at partial pressures p_1, p_2.....p_i..., the solubilities of the various components will be given by the set of equations of general form,

$$(s_i)_{p=p_i} = p_i(s_i)_{p=1} \tag{2-4}$$

where $(s_i)_{p=1}$ is the solubility of the pure component gas i at a partial pressure of one atmosphere. If solubility data are available for the pure component gases contained in the mixture the solubility of any mixture may be readily obtained from the set of equations (2-4). The above discussion assumes that Henry's Law holds for each component of the gas mixture. If Henry's Law is found by experiment to hold for oxygen and hydrocarbons in electrolyte solutions, it should be possible to predict the solubility of any gas mixture from experimental data for the pure component gases.

Several workers have considered the solubility of gases in aqueous salt solutions (4,5), and an empirical correlation of the form,

$$\log \frac{s_A}{s_A^o} = kc_B \qquad (2\text{-}5)$$

has been used, where s_A^o represents the solubility in pure water, and c_B is the concentration of salt. The Debye-Huckel theory has been used to predict theoretically the salting-out coefficient k; however this treatment applies only to dilute solutions of completely ionized electrolytes, and so may not be expected to apply to phosphoric acid solutions or to concentrated strong electrolytes.

2.1.2 Dimensional Analysis of Solubility

As discussed in the previous section, the solubility of gas mixtures may be obtained from equation (2-4) provided that data for the pure component solubilities are available and that Henry's Law holds. For phosphoric acid electrolytes, the solubility of any pure component gas will be a function of temperature, pressure, concentration of phosphoric acid, and the properties of the solute gas. If all the variables that affect the solubility can be suitably defined, dimensional analysis may be used to simplify the correlation of the variables. The problem is thus reduced to finding suitable parameters to define the properties of the solute and the solvent. A possible choice for a parameter characterizing the solute is the molal volume of the solute at the normal boiling-point (V_A), since this has been successfully used to correlate other solution properties.

If the solution obeys Henry's Law, equation (2-3) states that $\frac{s_A}{p_A}$ should be independent of pressure. The effect of the solvent (phosphoric acid) on the solubility will depend on the temperature and composition of the solvent. Under these conditions we may expect the solubility to be a function of the following variables:

$$\frac{s_A}{p_A} = f(T, V_A, R, c_{B_1}, c_{B_2} \ldots\ldots c_{B_i}) \qquad (2\text{-}6)$$

where R is included as a dimensional constant and $c_{B_1} \ldots\ldots c_{B_i}$ are the independently variable concentrations of the chemical species present in phosphoric acid; the latter will include water, various ions, H_3PO_4, a number of polyphosphoric acids, etc. In view of the large number of chemical species present in phosphoric acid, a dimensional analysis of equation (2-6) would yield expressions which are too cumbersome to be of practical value. In addition, the composition of phosphoric acid solutions over the range of temperature and concentration of interest is uncertain.

Because of the complexity of equation (2-6), a property of the solvent that would summarize the effects of the various concentration terms on solubility was sought. Hildebrand and Scott (1) have obtained good results using a solubility parameter involving the energy of vaporization of the solvent. Unfortunately extensive data for the latent heat of vaporization of phosphoric acid solutions is not available. However, thermodynamic considerations suggest that the latent heat and vapor pressure of a multicomponent solution are closely related. Extensive experimental measurements of the vapor pressure of phosphoric acid have been reported (6,7,8,9). If solvent vapor pressure is a sufficient variable to characterize the effect of solvent, the solubility may be written as

$$\frac{s_A}{p_A} = f(T, V_A, R, p_B^{\,o}) \tag{2-7}$$

where $p_B^{\,o}$ is the solvent vapor pressure. A dimensional analysis of equation (2-7) yields a functional relation between two dimensionless groups,

$$\left(\frac{s_A V_A p_B^{\,o}}{p_A}\right) = f\left(\frac{RT}{V_A p_B^{\,o}}\right) \tag{2-8}$$

or, since R is constant,

$$\left(SV_A p_B^{\,o}\right) = f\left(\frac{T}{V_A p_B^{\,o}}\right) \tag{2-9}$$

so that a plot of $(SV_A p_B^{\,o})$ vs. $(T/V_A p_B^{\,o})$ should correlate all gas solubilities on a single curve. In equation (2-9), $\frac{s_A}{p_A}$ has been replaced by the solubility measured experimentally with the gas at one atmosphere. In view of the somewhat intuitive deviation and of the assumptions made, equation (2-9) should be regarded as tentative.

2.2 Experimental Approach

The general experimental procedure for the determination of dissolved gases in electrolytes has been previously described (10). This paper is included in Appendix 1, and the method described there has been used to determine the solubility of oxygen and hydrogen in several electrolyte solutions (11).

In the determination of oxygen solubilities in phosphoric acid solutions at higher temperatures the procedure was modified in order to overcome corrosion difficulties. Above 100°C phosphoric acid rapidly attacks stainless-steel syringe needles. In these experiments the syringe was filled with sample using a Teflon needle; the gas-stripping cell used was equipped with a Hamilton Teflon valve in place of the rubber septum, and the sample was injected directly into the cell without the aid of a needle. Samples of phosphoric acid were equilibrated with oxygen gas in an oil bath controlled to 0.05°C.

Because the above procedure leads to errors in transferring the sample to the gas chromatograph, the apparatus was modified in order to determine hydrocarbon solubilities in phosphoric acid. A flow diagram of the apparatus is shown in Figure 1. The solvent was equilibrated with the gas in a gas-lift device (C). The vessel was filled with solvent (phosphoric acid) and brought to the required temperature; gas introduced at the base of the vessel lifted slugs of solvent up to the disengaging section, causing continual circulation of the liquid. This method of achieving equilibrium avoided the possibility of supersaturation, whereas dispersion of the gas through the liquid in the form of small bubbles may cause a high value to be obtained because of the Thomson effect. The volume of liquid contained in vessel C was approximately 50 ml., and equilibrium was reached after bubbling for about 15 minutes. Before entering C the gas was passed through a preheating coil (A) and two presaturators (B) containing the solvent. From a knowledge of the vapor pressure of the solvent, the partial pressure of the gas contacting the solvent in C may be estimated. A condenser (F) was provided for the collection of readily

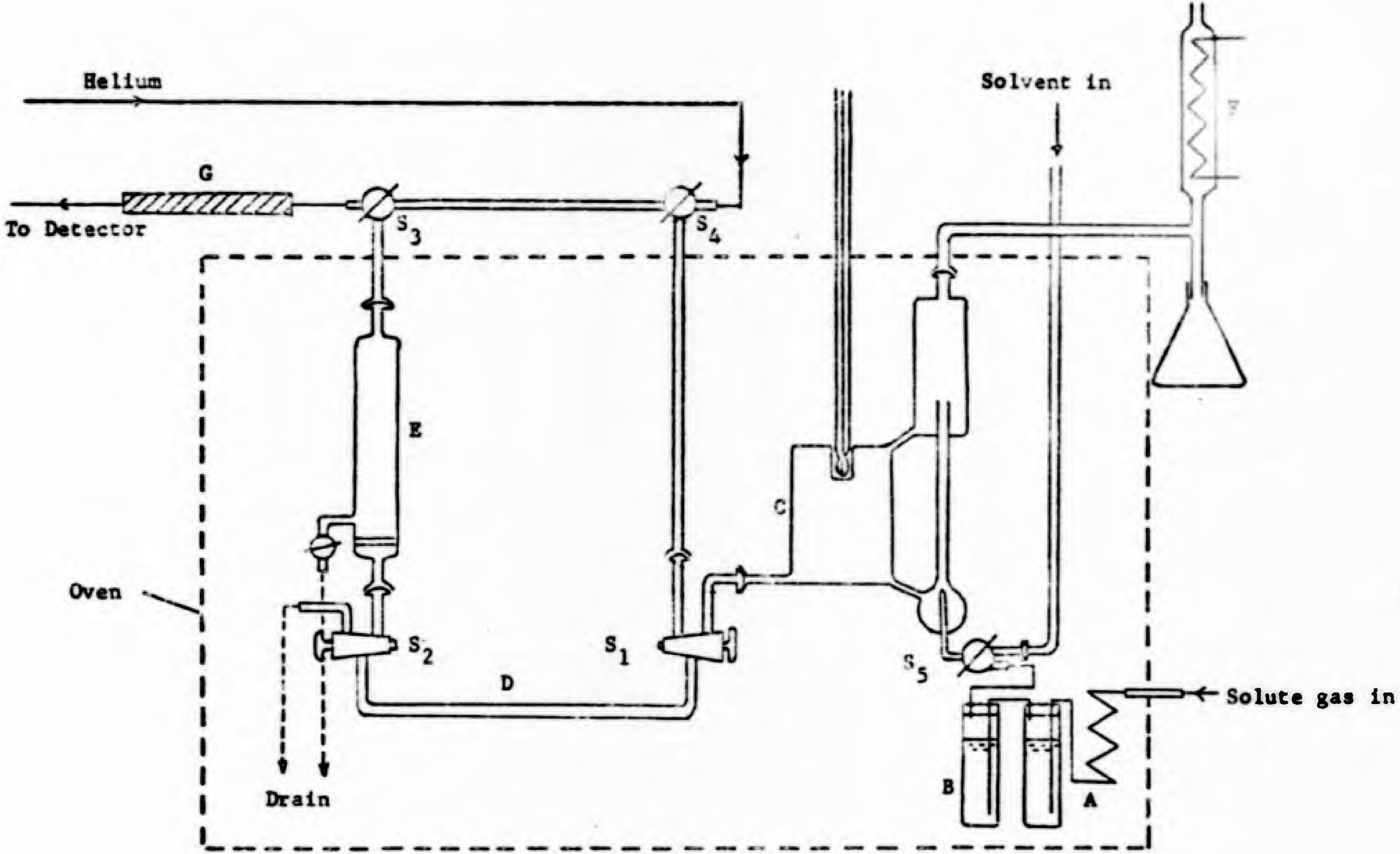

Figure 1. Apparatus for Determination of Hydrocarbon Solubilities in Phosphoric Acid

condensable hydrocarbon solute gases.

During the equilibration period stopcocks S_3 and S_4 were adjusted so that the helium carrier gas bypassed the solubility apparatus and passed directly to the columns and detector. When saturation was complete, stopcocks S_1 and S_2 were adjusted to allow solution to flow by gravity into a sample tube (D) of known volume. Stopcocks S_3, S_4, S_1 and S_2 were then adjusted to allow the helium stream to push the liquid contained in D into a gas-stripping cell (E). The gas-stripping cell was equipped with a coarse-porosity frit which served to disperse the helium through the liquid sample. Dissolved gas was rapidly stripped from the sample by the helium stream and passed to the detector via a drying-tube (G) which served to remove solvent vapor. Sample tubes (D) having volumes in the range 1-5 ml. have been used.

For the determination of the solubility of permanent gases in aqueous solutions Drierite effectively removes water vapor before passing the gas stream to the detector. In the case of hydrocarbons, a drying-tube containing calcium chloride has been used, since hydrocarbon gases are readily adsorbed by Drierite and silica gel. A tube containing Ascarite was also included to remove phosphoric acid vapor.

The apparatus was assembled using ball-and-socket joints sealed with a silicone grease (Dow Corning 11 Compound) having a very low vapor pressure. Controls were provided so that the stopcocks S_1 and S_2 could be operated from outside of the oven.

2.3 Results

The solubility data obtained are presented in Tables 1-5. The solubility values (S) quoted are expressed as g.moles of gas/liter at

TABLE 1

SOLUBILITY OF O_2 IN H_2SO_4 SOLUTIONS

Temperature	Electrolyte Concentration	Wt. % H_2SO_4	$S \times 10^3$
-30°C	3.69 g.mole/l.	29.9	1.136
-30	5.30	39.9	0.889
-30	7.25	50.6	0.828
-30	10.30	65.1	0.506
-30	12.10	72.4	0.430
-30	17.00	91.5	0.766
25°C	0.10	1.0	1.229
25	0.30	2.2	1.183
25	1.00	9.4	1.014
25	2.00	17.2	0.824
25	3.00	25.0	0.721
25	4.00	32.0	0.657
25	6.00	44.1	0.601
25	8.00	54.5	0.550
25	10.00	64.0	0.489
25	12.50	74.0	0.451
25	13.70	78.5	0.452
25	15.00	83.4	0.492
25	15.65	86.0	0.568
25	16.95	91.5	0.860
25	17.65	95.0	1.105

TABLE 2

SOLUBILITY OF O_2 IN KOH SOLUTIONS

Temperature	Electrolyte Concentration	Wt. % KOH	$S \times 10^3$
25°C	1.0 g.mole/l.	5.2	0.874 g.mole/l.
25	2.0	10.2	0.594
25	2.35	11.8	0.444
25	3.96	19.0	0.270
25	4.00	19.1	0.290
25	5.15	23.5	0.159
25	7.07	30.8	0.0803
25	10.30	41.0	0.0295
25	12.55	47.5	0.0260
25	14.00	51.5	0.0310
50	3.96	19.0	0.239
50	5.15	23.7	0.149
50	7.07	30.8	0.0833
50	14.00	51.5	0.0174

TABLE 3

SOLUBILITY OF O_2 IN H_3PO_4 SOLUTIONS

Temperature	Electrolyte Concentration	Wt. % H_3PO_4	S x 10^3
-30°C	8.42 g.mole/l.	58.5	0.787 g.mole/l.
	9.97	65.8	0.706
25	0.332	3.6	1.236
25	0.41	4.4	1.231
25	0.68	6.9	1.151
25	1.19	11.1	1.065
25	1.81	16.5	1.024
25	2.00	18.0	0.976
25	4.16	33.8	0.769
25	8.42	58.4	0.513
25	9.97	65.8	0.426
25	14.33	84.3	0.276
120		85.54	0.423
120		96.07	0.307
120		100.02	0.347
120		105.36	0.349
120		105.36	0.385
130		85.54	0.446
150		85.54	1.126*
		85.54	1.003*
		90.61	0.487
		95.90	0.374
		100.02	0.313
		105.36	0.384

*These results are probably too large because of inefficient oxygen presaturation.

TABLE 3 (Continued)

Temperature	Electrolyte Concentration	Wt. % H_3PO_4	S x 10^3
180°C		95.90	0.415 g.mole/l.
		100.02	0.355
		105.36	0.364

TABLE 4

SOLUBILITY OF H_2 IN H_3PO_4 SOLUTIONS

Temperature	Electrolyte Concentration	Wt. % H_3PO_4	$S \times 10^3$
25°C	0	0	0.783 g.mole/l.
25	0.332	3.6	0.744
25	0.68	6.9	0.679

TABLE 5

SOLUBILITY OF HYDROCARBONS IN H_3PO_4 SOLUTIONS

Solute	Temperature	Wt. % H_3PO_4	$S \times 10^3$
n-C_5H_{12}	130°C	85.54	0.0749 g.mole/l.
	130	104.4	0.348
	150	104.4	0.153
	180	104.4	0.0787
n-C_6H_{14}	130	85.54	0.0392
n-C_7H_{16}	130	85.54	0.0210
	130	104.4	0.190
	150	104.4	0.148
	180	104.4	0.0517
n-C_8H_{18}	130	85.54	0.015

one atmosphere pressure. Henry's Law was assumed in adjusting the solubility values to 1 atmosphere pressure. The results for the solubility of oxygen and hydrogen in H_2SO_4, KOH and H_3PO_4 at temperatures up to 50°C were generally reproducible to ±4%. The relative accuracy of the measurements for the solubilities in concentrated phosphoric acid (oxygen and hydrocarbons) at high temperatures (Tables 3 and 5) is estimated to be within ±10%; the possibility of errors was increased in these measurements because of the difficulty of working with phosphoric acid.

The results for the solubility of oxygen in sulfuric acid at 25°C are in good agreement with data given by Bohr (12); the minimum exhibited in the plot of solubility against concentration is also shown by Bohr's results. Geffcken (13) has reported measurements of oxygen solubility in dilute potassium hydroxide solutions at 25°C, and his results are in good agreement with those in Table 2.

The results given in Tables 1-5 are plotted in Figures 2 to 6. In Figure 5 the data point for propane was supplied by General Electric Co. (3).

2.4 Discussion

Figures 3 and 4 show that the solubility of oxygen falls off continuously with increasing electrolyte concentration for potassium hydroxide and phosphoric acid solutions; the decrease in solubility is particularly marked in the case of KOH solutions. The minimum in the solubility curve in the case of sulfuric acid has been discussed by Bohr (12). The form of Figure 3 suggests that an equation similar to equation (2-5) should apply to the solubility in KOH solutions, and

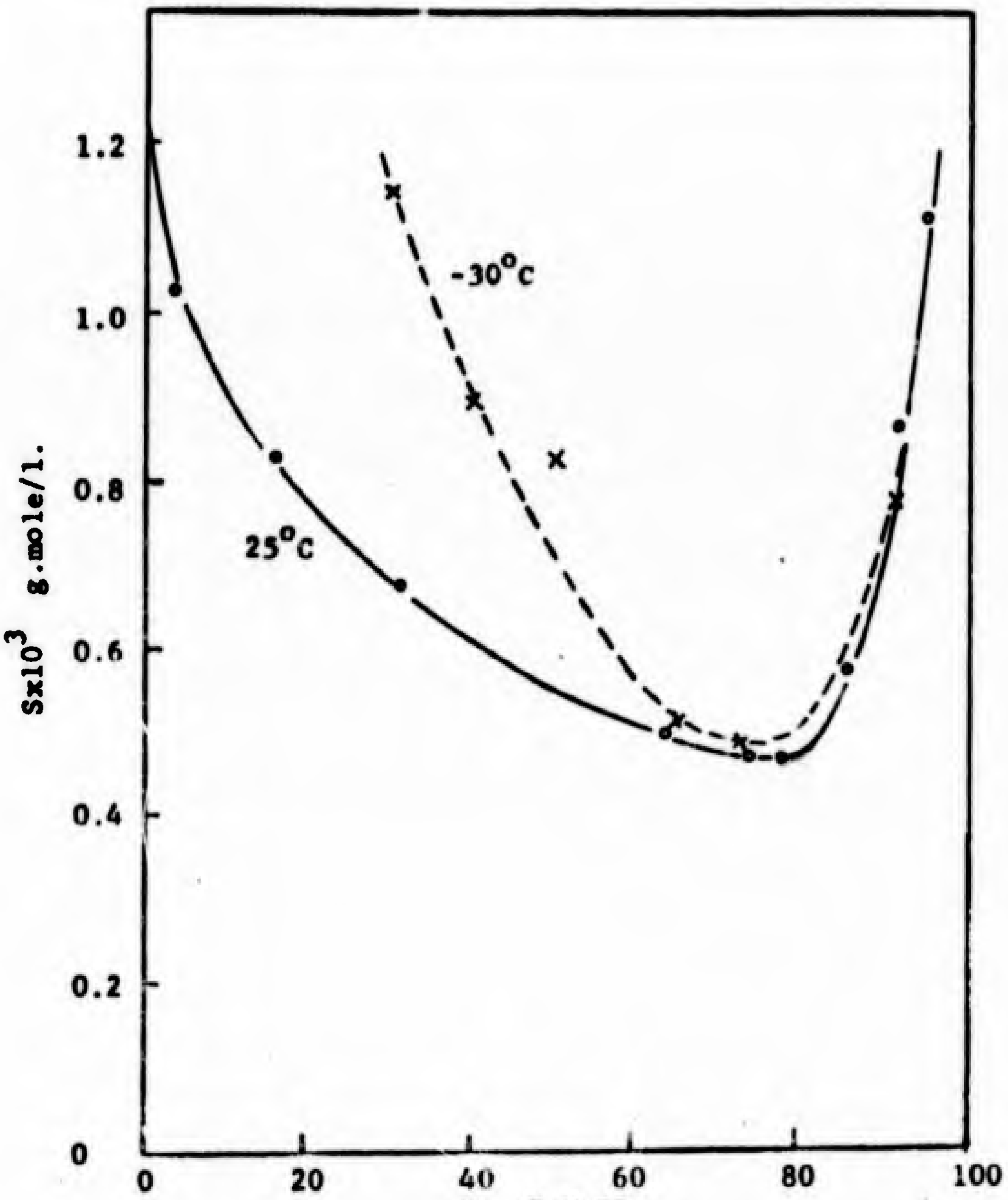

Figure 2. The Solubility of O_2 in H_2SO_4 Solutions

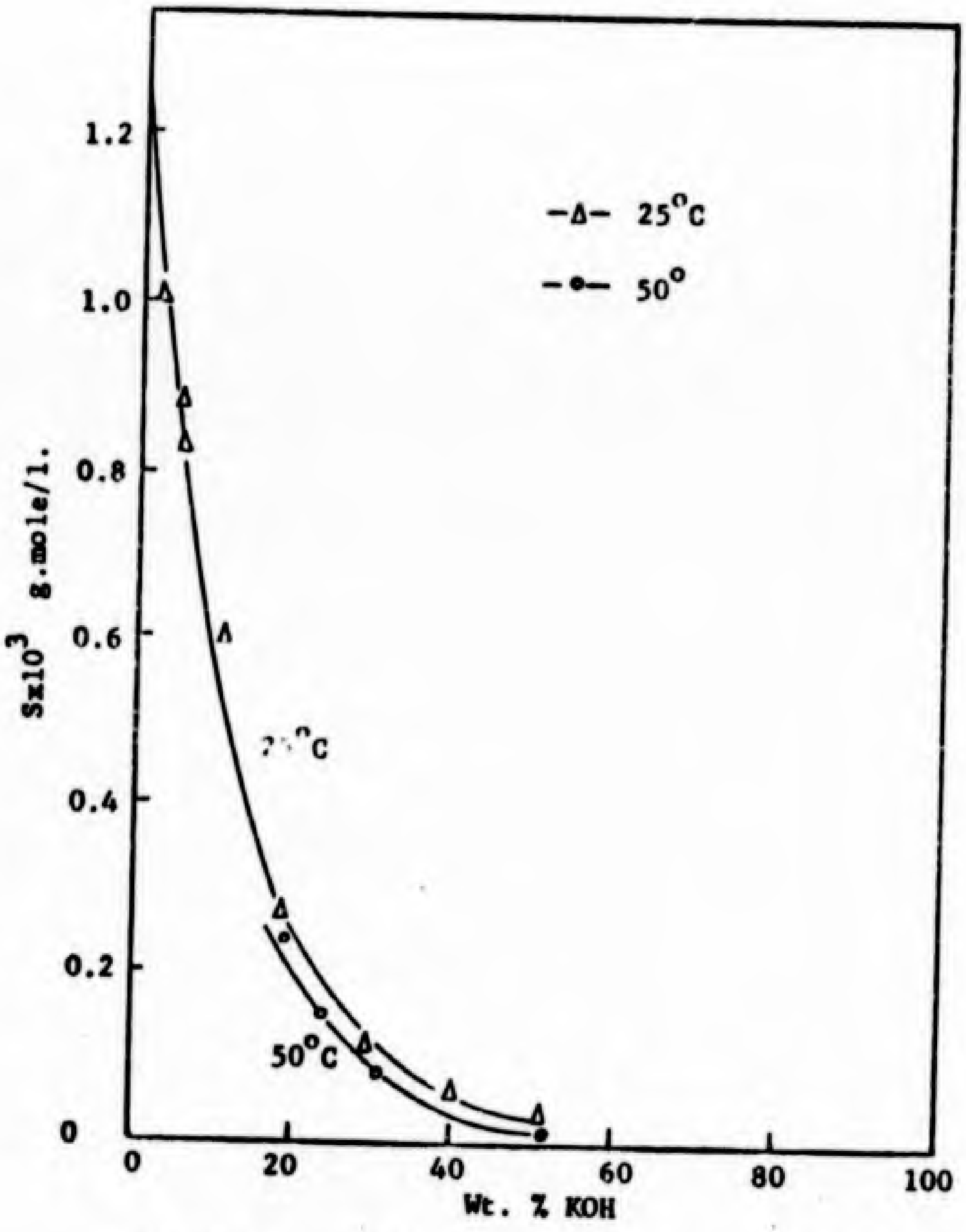

Figure 3. The Solubility of O_2 in KOH Solutions

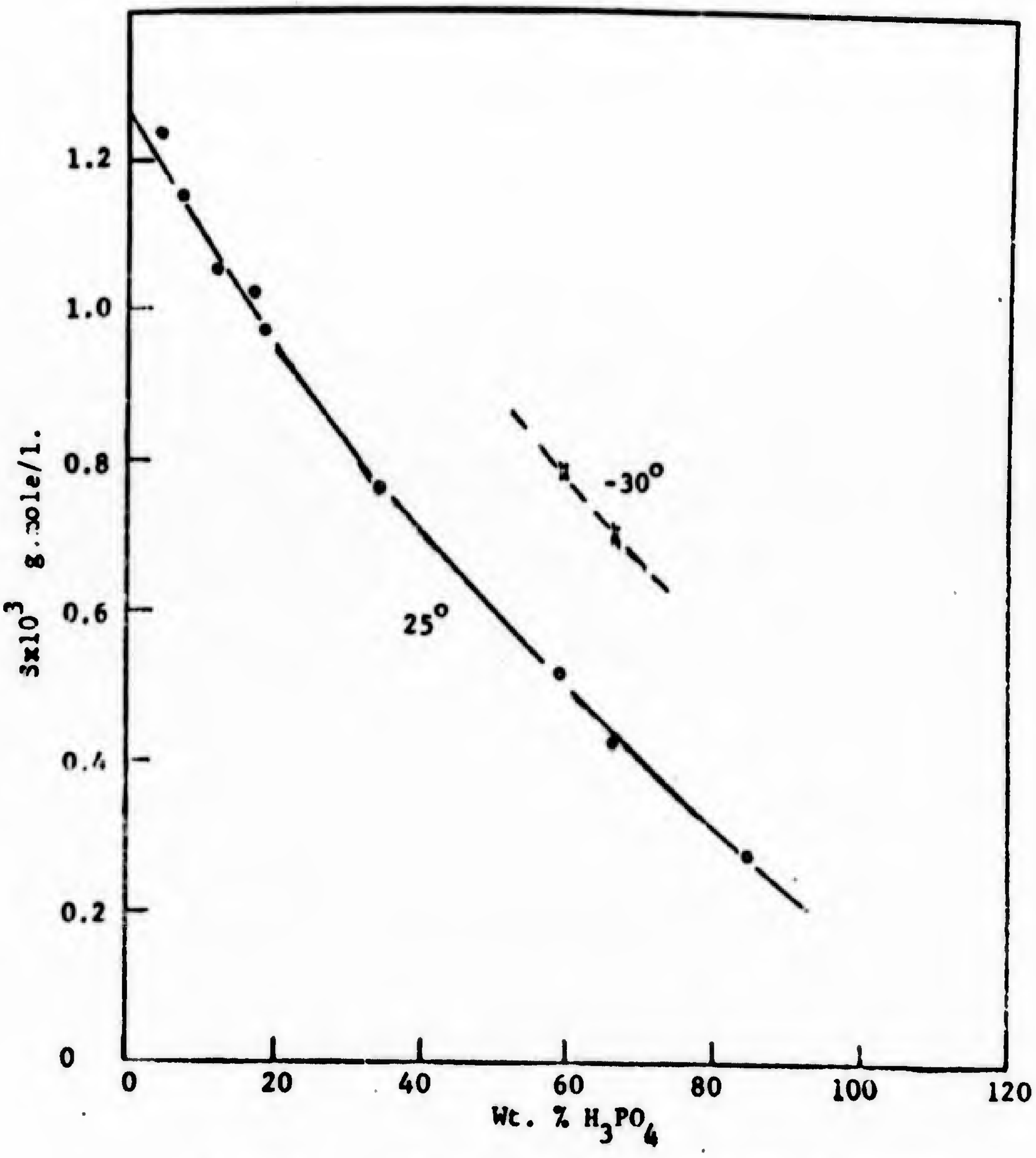

Figure 4. The Solubility of O_2 in H_3PO_4 Solutions

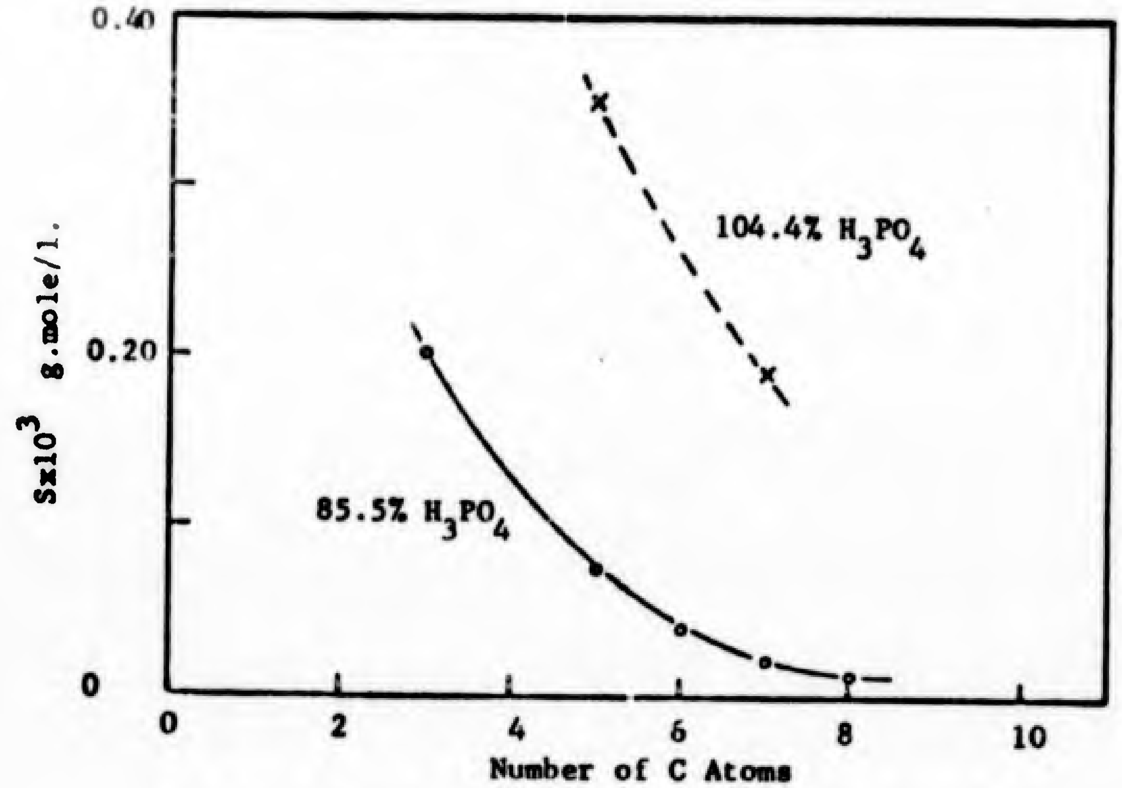

Figure 5. Solubility of n-Hydrocarbons in H_3PO_4 at 130°C

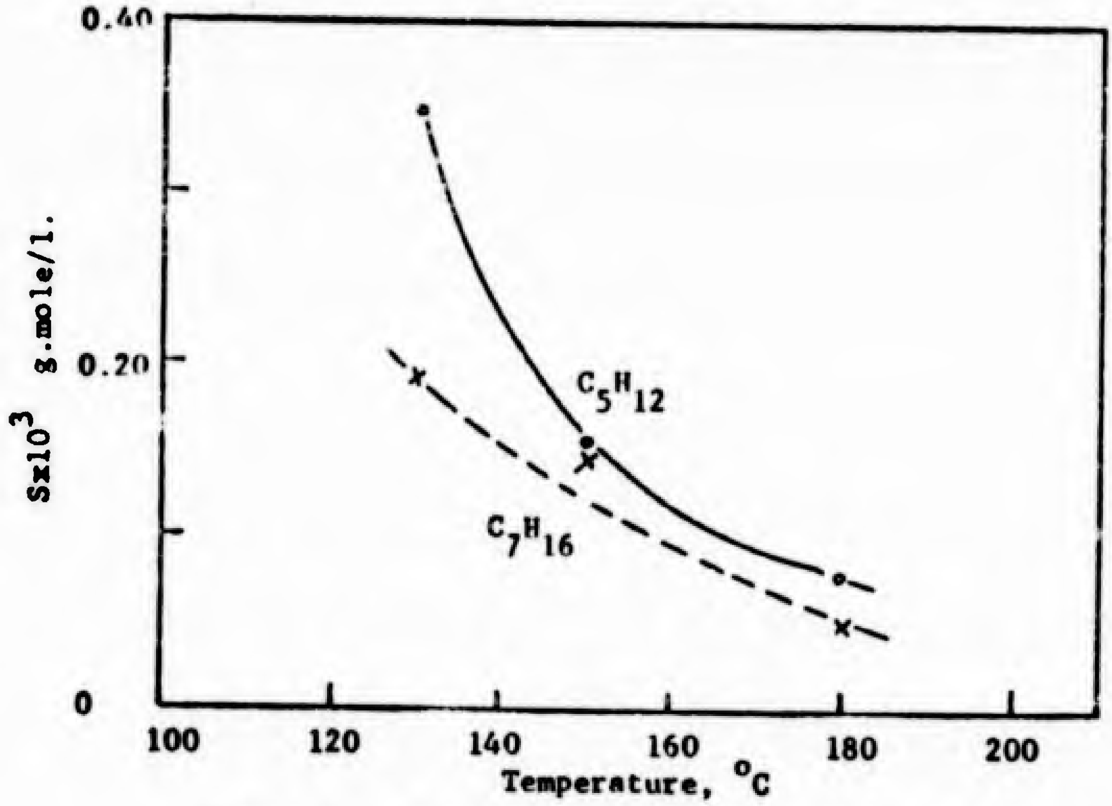

Figure 6. Solubility of n-Pentane and n-Heptane in 104.4% H_3PO_4

probably to other completely dissociated electrolytes. For electrolytes of this type it seems likely that the effect of electrolyte on solubility could be separated into terms representing the effect of the individual ions; this approach has been used successfully in the study of viscosity and diffusion in strong electrolytes (14,15,16).

Equation (2-9), developed in section 2.1.2, has been applied to the experimental results for the solubility of oxygen and hydrocarbons in phosphoric acid. The necessary calculations are presented in Table 6. The vapor-pressure data for phosphoric acid (p_B^o) were obtained from references (6,7,8,9). The molal volume of the solute at its normal boiling-point (V_A) was estimated by the atomic group contribution method of Le Bas (17). Values of V_A calculated in this way for oxygen and normal, saturated hydrocarbons in the range C_1 to C_{10} are presented in Table 7. The resulting dimensionless groups are plotted in Figure 7. Experimental data are included for oxygen, propane, pentane, hexane, heptane and octane for the phosphoric acid concentration range 85-105 wt. %. The solubility data for propane in phosphoric acid were those given by H. R. Maget (9).

The hydrocarbon data appear to fall on a smooth curve as shown. The scatter observed in these results may be due to experimental errors, which may be appreciable for the low solubilities exhibited by hydrocarbons. In addition, the scatter in the results do not show a progressive trend with temperature, phosphoric acid concentrations or solute. The results for oxygen do not fall on the same curve as those for hydrocarbons, and are better fitted by the curve shown. The oxygen results show less scatter than do the results for hydrocarbons. This

TABLE 6

SOLUBILITY DATA FOR H_3PO_4

Solute	Wt. % H_3PO_4	(°K) T	(g.mole/cc.atm) $S \times 10^6$	(cc./mole) V_A	(mm.) P_B^o	$\left(\frac{mm.}{atm.}\right)$ $(SV_AP_B^o) \times 10^3$	$\left(\frac{K^o\ g.mole}{cm.^3\ mm.}\right)$ $\left(\frac{T}{V_AP_B^o}\right) \times 10^2$
n-C_5H_{12}	85.54	403°K	0.0749	118.4	335 mm.	2.97	1.015
	104.4	403	0.348	118.4	1.25	0.0568	272
	104.4	423	0.153	118.4	3.65	0.0662	97.9
	104.4	453	0.0787	118.4	14.0	0.1306	27.3
n-C_6H_{14}	85.54	403	0.0392	140.6	335	1.847	0.857
n-C_7H_{16}	85.54	403	0.0210	162.8	335	1.144	0.739
	104.4	403	0.190	162.8	1.25	0.0386	198
	104.4	423	0.148	162.8	3.65	0.0880	71.2
	104.4	453	0.0517	162.8	14.0	0.118	19.9
n-C_8H_{18}	85.54	403	0.015	185.0	335	0.929	0.650
n-C_3H_8*	85.8	298	0.194	74.0	1.9	0.027	212
	96.6	298	0.144	74.0	~0.1	~0.001	~4,000

*Data provided by H. R. Maget, General Electric Co., private communication

TABLE 6 (Continued)

Solute	Wt. % H_3PO_4	T	S x 10^6	V_A	P_B^o	$(SV_AP_B^o)$ x 10^3	$\left(\frac{T}{V_AP_B^o}\right)$ x 10^2
n-C_3H_8* (Cont.)	85.8	323°K	0.181	74.0	8.7mm.	0.117	50.1
	96.6	323	0.160	74.0	1.5	0.0178	291
	85.8	373	0.207	74.0	88	0.135	5.72
	97.9	373	0.170	74.0	7.3	0.0918	69.0
	97.4	403	0.159	74.0	45.0	0.530	12.1
	97.2	423	0.183	74.0	99.0	1.34	5.77
	99.3	443	0.160	74.0	93	1.10	6.43
O_2	97.6	403	0.296	25.6	42	0.32	37.5
	97.7	423	0.340	25.6	85	0.74	19.5
	85.54	393	0.423	25.6	237	2.56	6.48
	96.07	393	0.307	25.6	45	0.35	34.2
	95.9	453	0.415	25.6	333	3.54	5.30
	100.0	393	0.347	25.6	10	0.089	153.5
	100.0	423	0.313	25.6	33	0.254	50.0
	100.0	453	0.355	25.6	100	0.91	17.68
	105.4	393	0.367	25.6	0.45	0.004	3,410
	105.4	423	0.384	25.6	2.40	0.0197	826
	105.4	453	0.364	25.6	9.0	0.084	196.3

*Data provided by H. R. Maget, General Electric Co., private communication

TABLE 7

VALUES OF MOLAL VOLUME AT THE NORMAL BOILING POINT

Solute	V_A
O_2	25.6 cc./g.mole
n-CH_4	29.6
n-C_2H_6	51.8
n-C_3H_8	74.0
n-C_4H_{10}	96.2
n-C_5H_{12}	118.4
n-C_6H_{14}	140.6
n-C_7H_{16}	162.8
n-C_8H_{18}	185.0
n-C_9H_{20}	207.2
n-$C_{10}H_{22}$	229.4

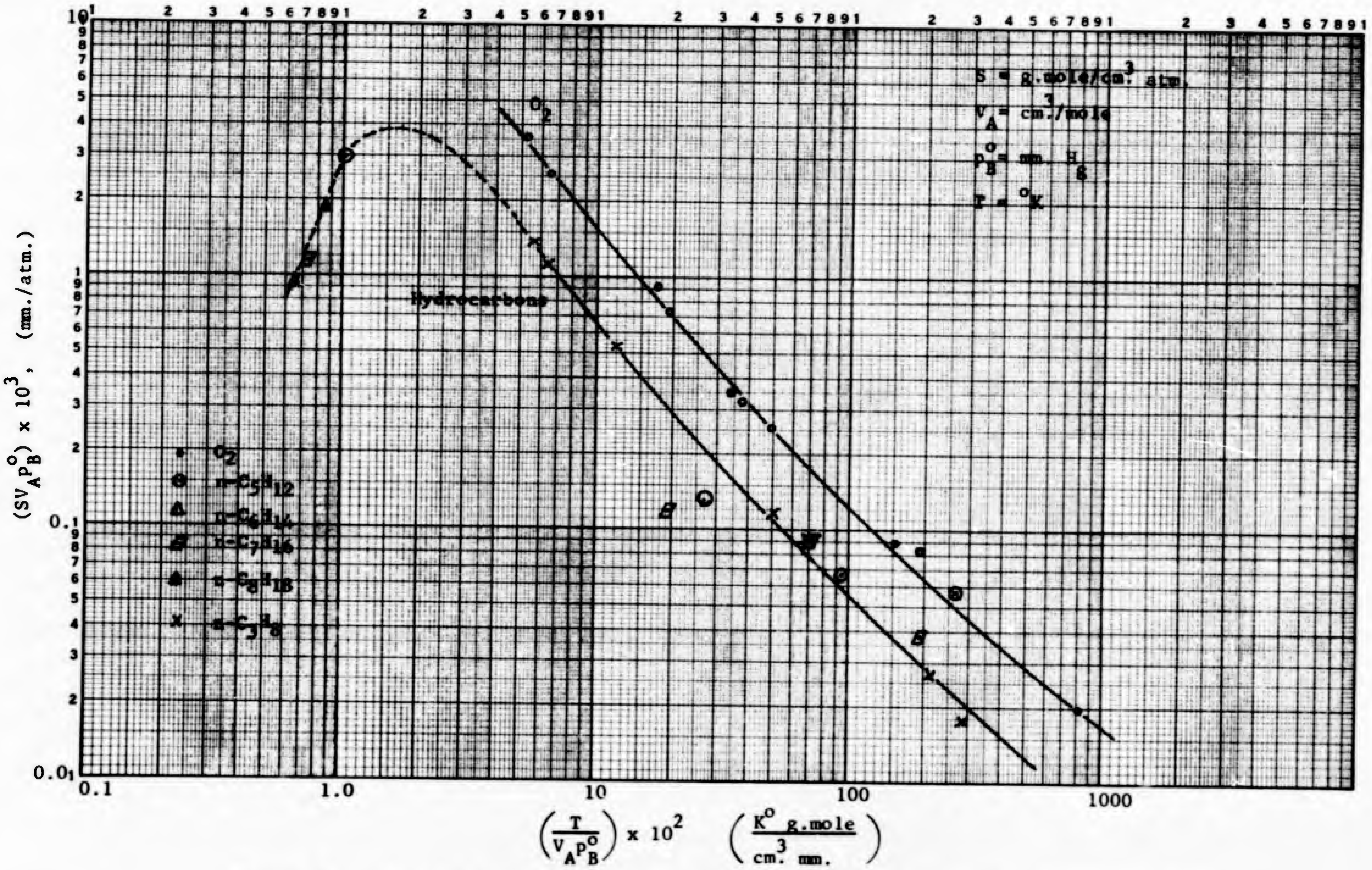

Figure 7. Dimensionless Plot of Solubility of O_2 and Hydrocarbons in Phosphoric Acid

may be attributed to the fact that the experimental accuracy was greater for these measurements because of the higher solubility of oxygen. The dotted part of the hydrocarbon curve is tentative due to the small amount of data in this region.

The fact that the results for oxygen and hydrocarbons do not fall on the same curve emphasizes the limited nature of the correlation, and the assumptions involved. The curves presented in Figure 11 may not apply to other solutes which are chemically dissimilar to hydrocarbons. However, the good agreement shown for the results obtained so far strongly suggests that the curves presented may be used to obtain reasonable estimates of the solubility of oxygen and hydrocarbons in phosphoric acid for systems that have not been studied experimentally.

2.5 Conclusions

Measurements have been made of the solubility of oxygen in KOH, H_2SO_4, and H_3PO_4 solutions, and of the solubility of hydrocarbons in phosphoric acid. A dimensional analysis of the solubility problem gave a relationship between two dimensionless groups. When the solubility data for hydrocarbons in phosphoric acid were plotted in this way the data were found to fall close to a single smooth curve; a similar correlation was obtained for the oxygen results. These two curves should enable the solubility of oxygen or any saturated hydrocarbon solute in phosphoric acid to be predicted with reasonable accuracy in the concentration range 85-105% H_3PO_4. Some additional experimental solubility data would be useful in further defining certain parts of the dimensionless plot.

3. DIFFUSION STUDIES

3.1 Theory

3.1.1 Variables Involved

The diffusion coefficients of gases in electrolyte solutions may be expected to vary with temperature, pressure, concentration of phosphoric acid and solute properties. Up to the present time little progress has been made in deriving statistical or kinetic theories capable of predicting liquid diffusion coefficients. The most successful methods for predicting liquid diffusion coefficients presently available are the Eyring absolute rate theory, the hydrodynamic theories, and engineering correlations such as the Wilke-Chang equation.

The temperature dependence of the diffusion coefficients in liquids is usually described by a relation of the form

$$D_{AB} = K \exp(-E_d/RT) \tag{3-1}$$

where E_d is generally referred to as the activation energy of diffusion, and is obtained experimentally by plotting log D vs. 1/T. Equation (3-1) has been verified experimentally for a large number of liquid systems.

Comparatively little work has been done on the pressure dependence of diffusion in liquids. Johnson and Babb (18) have reviewed liquid diffusion data up to 1956, and report several instances in which D_{AB} has been measured at various pressures. In all cases the effect of pressure on the diffusion-coefficient is very small except for pressure changes of the order of hundreds of atmospheres. Thus Drickamer (19) reports that the self-diffusion coefficient of water at

$25^{\circ}C$ increases by about 9% when the pressure is increased from 1 to 245 atm. It therefore seems very likely that the diffusion coefficients of oxygen and hydrocarbons in electrolytes will be virtually independent of pressure over the range 0-5 atm.

When several concentration gradients exist in the electrolyte due to the simultaneous diffusion of a multicomponent mixture of dissolved gas or liquid solutes, the diffusion coefficient of any one solute species will in general be affected by the presence of the others. The liquid diffusion coefficient is determined by the nature and strength of the intermolecular forces existing between the diffusing molecule and the molecules through which it passes. For oxygen and hydrocarbons dissolved in phosphoric acid the solubility ranges from about 0.3×10^{-3} g.mole/l. for propane to about 1×10^{-5} g.mole/l. for octane (3). Thus the concentration of solute is less than 1 solute molecule in 10^5 solvent molecules. The effect of intermolecular forces between two diffusing solutes of different species should therefore be quite negligible, and the diffusion coefficient for each diffusing species should be independent of the presence of other solutes.

3.1.2 Recommendations for Predicting Diffusivity

While no satisfactory theory is available for predicting diffusion coefficients even in simple liquid systems, a number of semiempirical relations have been found useful in practice. Equation (3-1) provides a satisfactory means of predicting the diffusion coefficients for a particular solute-solvent system over a temperature range from only two experimental measurements. This equation has been shown to be closely obeyed by a large number of gas-electrolyte systems (14).

A number of liquid diffusion theories predict that the group $D_{AB}\eta_B/T$ should be constant for a particular solute-solvent system,

$$\frac{D_{AB}\eta_B}{T} = \text{constant} \qquad (3\text{-}2)$$

For solvents consisting of a pure component, equation (3-2) appears to hold within fairly narrow limits. For gases diffusing in electrolyte solutions the group $D_{AB}\eta_B/T$ has been found to vary somewhat with electrolyte concentration (14); however its use should enable D_{AB} to be predicted within about 30-40% from a knowledge of the diffusion coefficient of the gas in water at one temperature. Although equation (3-2) may provide a means of approximately estimating D_{AB} for strong electrolyte solutions, its application to strong phosphoric acid solutions is of doubtful validity, since the concentration of polyphosphoric acids increases markedly as the concentration approaches 100%. Experimental measurements would be required to test the accuracy of equation (3-2) in this case.

Hildebrand (20) has recently reported measurements of the diffusion coefficients of a large number of gases in several liquids. His results closely obey the equation,

$$D_{AB}\sigma^2 = \text{const.} \qquad (3\text{-}3)$$

where σ represents the diameter of the molecule, and may be taken as the Lennard-Jones 6-12 diameter for neutral molecules. Since this equation appears to be of general validity, a measurement of the diffusion coefficient of a single solute gas in a particular electrolyte (of given concentration) should provide sufficient information for the estimation of D_{AB} for any other solute gas.

In summary, equations (3-1) and (3-3) provide a fairly reliable means of extrapolating existing diffusion data to other temperatures and solutes. The prediction of the variation in diffusion rate with electrolyte concentration is considerably more difficult; equation (3-2) should provide a rough guide to the variation in D_{AB} with electrolyte concentration for strong electrolytes, but may not apply to concentrated phosphoric acid solutions.

3.1.3 A Theory of Diffusion in Strong Electrolytes

According to the Eyring reaction-rate theory, the binary diffusion coefficient in dilute solution is given by,

$$D_{AB} = k_d \lambda^2 e^{-\Delta G_d^*/RT} \qquad (3\text{-}4)$$

where k_d is approximately constant and involves the average distance between liquid molecules, λ represents the average distance moved by the diffusing molecule for each jump, and ΔG_d^* is the free energy of activation for diffusion. The diffusion coefficient for the process is determined primarily by the activation energy and the temperature.

Using equation (3-4) Podolsky (15) has derived an expression for the fluidity of an electrolyte solution, and Ratcliff (16) has proposed a corresponding equation for the diffusion coefficient of neutral molecules in electrolytes.

The presence of ions in the solution is assumed to cause changes in the free energy of activation of the process; changes in the lattice spacing λ due to the presence of ions are assumed to have a negligible effect on the transport coefficient as compared to the effect of changes in free energy of activation. The free energy of activation in equation (3-4) is replaced by a free energy of activation which is averaged over all possible configurations of the molecule undergoing diffusion.

A solute molecule is assumed to interact with n surrounding solvent molecules; on replacing one of the surrounding water molecules by an ion of type i, the free energy of activation is supposed to be perturbed by an amount δ_i, so that the free energy of activation for diffusion becomes $(\Delta G_d^* + \delta_i)$ where ΔG_d^* represents the free energy of activation for pure water. If it is assumed that the distribution of ions in the neighborhood of the solute molecule is the same as that in the bulk solution, the average free energy of activation is given by,

$$\left\langle \Delta G_d^* \right\rangle = \Delta G_d^* + \frac{18c_B n(\nu_1\delta_1 + \nu_2\delta_2)}{1000\rho - c_B M + 18c_B(\nu_1 + \nu_2)} \qquad (3\text{-}5)$$

where C_B is the concentration of the electrolyte in g.mole/l., ρ is the solution density, M the molecule weight of the electrolyte, and ν_i is the number of g. ions of ions of type i for each g. mole of electrolyte. The second term in equation (3-5) represents the change in free energy of activation for the solute molecule in water due to electrolyte. Combining equations (3-4) and (3-5), and assuming the second term is small and that λ is not affected appreciably by the presence of electrolyte,

$$D = D_o \left[1 - \frac{c_B n(\nu_1 \delta_1 + \nu_2 \delta_2)}{55.5\ RT} \right] = D_o(1 - ac_B) \qquad (3\text{-}6)$$

where D_o is the diffusion coefficient of the solute in pure water. A plot of D against concentration of electrolyte should therefore be a straight line of slope a. Equation (3-6) has been shown to hold for a variety of electrolytes up to quite high concentrations (14,16). The term a may be split into effects characteristic of the individual ions, so that data from experiments performed on a relatively small number of electrolytes may be used to predict diffusion coefficients for electrolytes on which no measurements have been made.

3.1.4 Dimensional Analysis of Diffusion

If the diffusion coefficient may be assumed to be independent of pressure, D_{AB} should be a function of temperature and the properties of the solute and solvent. As in section 2.1.2, the molal volume at the normal boiling-point (V_A) may be taken as characterizing the solute species. The effect of the solvent will depend on a number of factors such as the type and concentration of the various chemical species present. It is well-known that for liquids D_{AB} is closely correlated with the liquid viscosity. For a particular electrolyte, such as phosphoric acid, it may be possible to correlate D_{AB} with the viscosity (η_B) of the solution. Using this assumption D_{AB} would be given by

$$D_{AB} = f(T, V_A, \eta_B, R, g_c) \qquad (3\text{-}7)$$

where R and g_c are dimensional constants. Dimensional analysis yields

$$\left[\frac{D_{AB}}{(RT)^{3/2} g_c} \right] = f \left[\frac{V_A \eta_B}{(RT)^{3/2} g_c} \right] \qquad (3\text{-}8)$$

or,

$$\frac{D_{AB}}{T^{3/2}} = f\left[\frac{V_A \eta_B}{T^{3/2}}\right] \qquad (3\text{-}9)$$

Equation (3-9) suggests that a plot of ($D_{AB}/T^{3/2}$) against ($V_A \eta_B/T^{3/2}$) should yield a single curve for a variety of solute-solvent systems. The result is rather tentative in view of the assumptions, but might be expected to apply to a variety of solutes diffusing in phosphoric acid solutions of variable concentration and temperature.

3.2 Experimental

A review of the possible experimental methods for the determination of diffusion coefficients in liquids (18,21) indicated that the polarographic method and the diaphragm cell method appeared most promising. In addition an attempt has been made to develop a steady-state method which would enable data to be obtained rapidly whilst providing an approach that would be generally applicable to all gas-liquid systems. The principal difficulty in all liquid diffusion measurements arises from the slowness of the diffusion process as compared to convection due to thermal and density gradients or vibration.

3.2.1 Polarographic Method

Reduction of the diffusing species at the dropping mercury electrode (DME) provides a simple and relatively rapid means of determining the diffusion coefficient. The method is capable of an accuracy of about ±4%. Its principal disadvantage is that its use is restricted to gases that react suitably at the DME to produce a current limited by the rate of diffusion rather than reaction rate.

This method was used to determine the diffusion coefficient of oxygen gas in aqueous potassium hydroxide solutions over the concentration range zero to saturated at 25°C. The electrolyte solution to be studied was saturated with oxygen in a polarograph cell of standard H-form. The resulting polarogram showed a horizontal limiting-current portion over the voltage range -0.2 to -1.0 V. vs. saturated calomel; this region corresponded to the reduction of oxygen to hydroxyl ion,

$$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$$

The second wave, corresponding to reduction of the peroxide, was less well-formed, and the first wave was used in all determinations. The procedure, and recommendations for the care and use of the DME given by Kolthoff and Lingane (22) were used.

The diffusion coefficient was calculated from the modified Ilkovic equation,

$$i_d = 607nD_{AB}^{1/2}cm^{2/3}t'^{1/6}\left(1 + \frac{A'D^{1/2}t'^{1/6}}{m^{1/3}}\right) \qquad (3\text{-}10)$$

where A' = constant
n = number of electrons in reaction
c = concentration of gas
t = drop time of DME, sec.
m = drop rate of DME, mg./sec.

The drop-rate (m) was determined electrically for each run by the method of Lingane (23). The gas concentration was found by gas chromatography.

Different workers have given somewhat different values for the constant A, ranging from 17 to 39. The value of 31.5 given by Meites and Meites (24) was chosen in using the Ilkovic equation since it seems to fit experimental evidence somewhat better than the other values. Under normal experimental conditions the value obtained for D is not highly sensitive to changes in the value of A; thus changing the value of A from 31.5 to 39 produces a change in the value of D of only about 4%.

3.2.2 The Diaphragm Cell Method

Although the polarographic method is simple and rapid it is unsuitable for the study of some gases, notably hydrocarbons. The porous diaphragm cell method of Liu and McBain (25) has the advantage of simplicity and is generally applicable to all systems. The apparatus and theory has been thoroughly reviewed by Gordon (26).

The apparatus consists of a cell having two compartments separated by a porous frit or diaphragm; solution is placed in one compartment, and pure solvent in the other (Figure 8). The solutions in both compartments are stirred by magnetic stirrers so that concentrations are uniform in each compartment (27). In this way a relatively large concentration gradient is confined to a relatively small frit thickness. After a suitable time (usually 24 hours or more) the cell is removed and samples taken from each compartment for analysis. The use of a diaphragm ensures that mass transfer may only occur by diffusion, and the possibility of convection is eliminated.

The system may be regarded as a quasi-stationary state, and

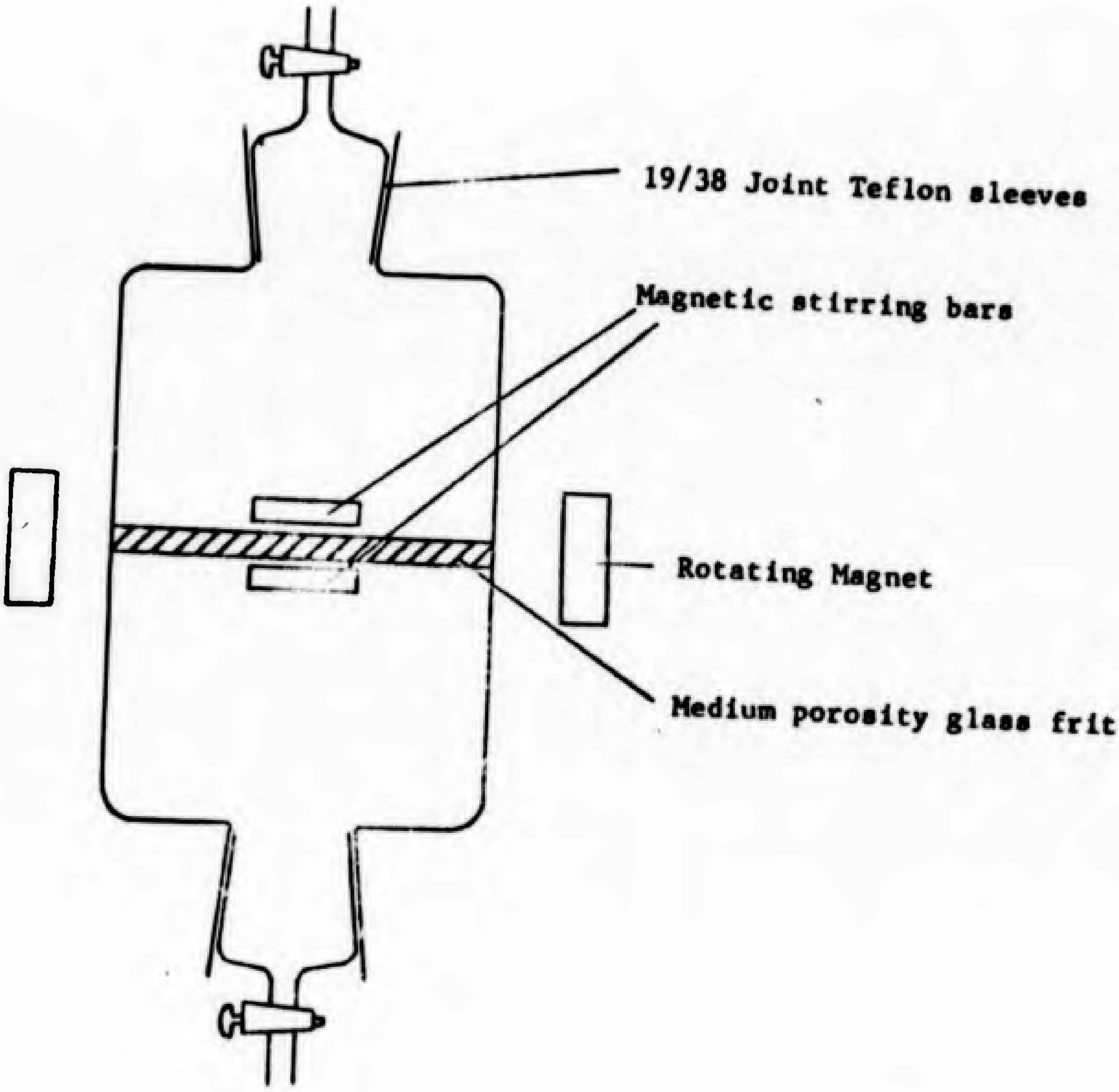

Figure 8. Diaphragm Cell

Fick's law of diffusion may be solved to give (26)

$$\bar{D}_{AB} = \frac{1}{\beta t} \ln \frac{c_1 - c_2}{c_3 - c_4} \qquad (3\text{-}11)$$

where β is the cell constant, t the time of diffusion, and $\bar{D}$ is the integral diffusion coefficient; c_1 and c_2 are the initial concentrations of gas in the high and low concentration compartments of the cell respectively, and c_3 and c_4 are the final concentrations.

A glass cell having compartments of about 25 ml. was used. The solutions were stirred by magnetic stirrers at a rate of 100 r.p.m. Failure to stir the solutions was found to result in errors of about 3%. Experiment indicated no detectable streaming of the solution through the diaphragm due to density gradients.

The cell was calibrated using 0.1 N KCl solution, for which accurate values of the differential diffusion coefficient are available (26). In performing experiments on the gases, the cell was filled with electrolyte that had been freed from dissolved gases by refluxing under vacuum. The electrolyte in the upper compartment was then saturated with the gas under study, and the time of diffusion was measured from the start of saturation. Experiments were conducted in a water-bath controlled to 0.05°C. Since the solubility of the gases studied was of the order 10^{-3} molar or less, the diffusion coefficient given by equation (3-11) may be regarded as the differential coefficient at infinite dilution. At the end of the experiment, samples were taken from each compartment and analysed by gas chromatography.

The usual procedure in measuring diffusion coefficients by the diaphragm cell method is to allow diffusion to occur until a linear concentration gradient has been established across the diaphragm. The solution in the compartment of lower concentration is then replaced by fresh solvent, and the time of diffusion under quasistationary conditions is measured from the time of replacement. This procedure is unsatisfactory when studying the diffusion of gases in liquids because of the difficulty of replacing the solution on one side of the diaphragm with gas-free solvent. In addition it is difficult to avoid creating temperature fluctuations in the cell when replacing solutions; this effect is particularly liable to lead to difficulties when measurements are made at temperatures appreciably different from ambient.

To overcome this difficulty the time of diffusion was measured from the time at which the cell was filled with the gas-saturated solution. At the end of the experiment a correction was applied for the initial period of unsteady-state operation. The required correction may be estimated with sufficient accuracy by solving the diffusion equation with the following initial and boundary conditions:

$$\begin{array}{lll} c = 0 & t \leqslant 0 & 0 \leqslant x \leqslant L \\ c = c_o & t > 0 & x < 0 \\ c = 0 & t > 0 & x > L \end{array}$$

The solution of the diffusion equation is (28),

$$c = c_o - \frac{c_o x}{L} - \frac{2}{\pi} \sum_{j=1}^{\infty} \frac{c_o}{j} \sin \frac{j\pi x}{L} \, e^{-j^2 D \pi^2 t/L^2} \qquad (3\text{-}12)$$

where c is the concentration of gas at position x, c_o is the initial gas concentration, t is time, and L is the length of a cylinder of stagnant liquid having a resistance to diffusion equal to that of the diaphragm. From a knowledge of the cell constant the necessary correction to be applied for the unsteady-state period was obtained from equation (3-12).

3.2.3 Steady-State Diffusion Cell

In an effort to obtain diffusion data more rapidly, a steady-state diffusion method has been developed; the apparatus is shown in Figures 9 and 10. A thin film of the liquid to be studied was held between two porous Teflon plates; in the case of aqueous solutions, pore penetration does not occur. The gas to be studied was passed through one side of the cell, and pure helium through the other side. After a sufficient time had elapsed (about 1 hour), a linear concentration gradient of the diffusing gas was established across the liquid film. The helium gas leaving the lower side of the cell then contained a constant concentration of the diffusing gas. Measurement of this concentration, together with a knowledge of the helium flow rate, is sufficient to determine the diffusion coefficient from the equation

$$N_A = AD_{AB}\left(\frac{c}{l}\right)$$

where N_A is the diffusion rate in g.mole/sec., A and l are the cross-section and length of the liquid film respectively, and c is the concentration of diffusing gas in the liquid surface in contact with pure diffusing gas in g.mole/cm^3.

The cell is shown in Figure 10. The liquid film was held

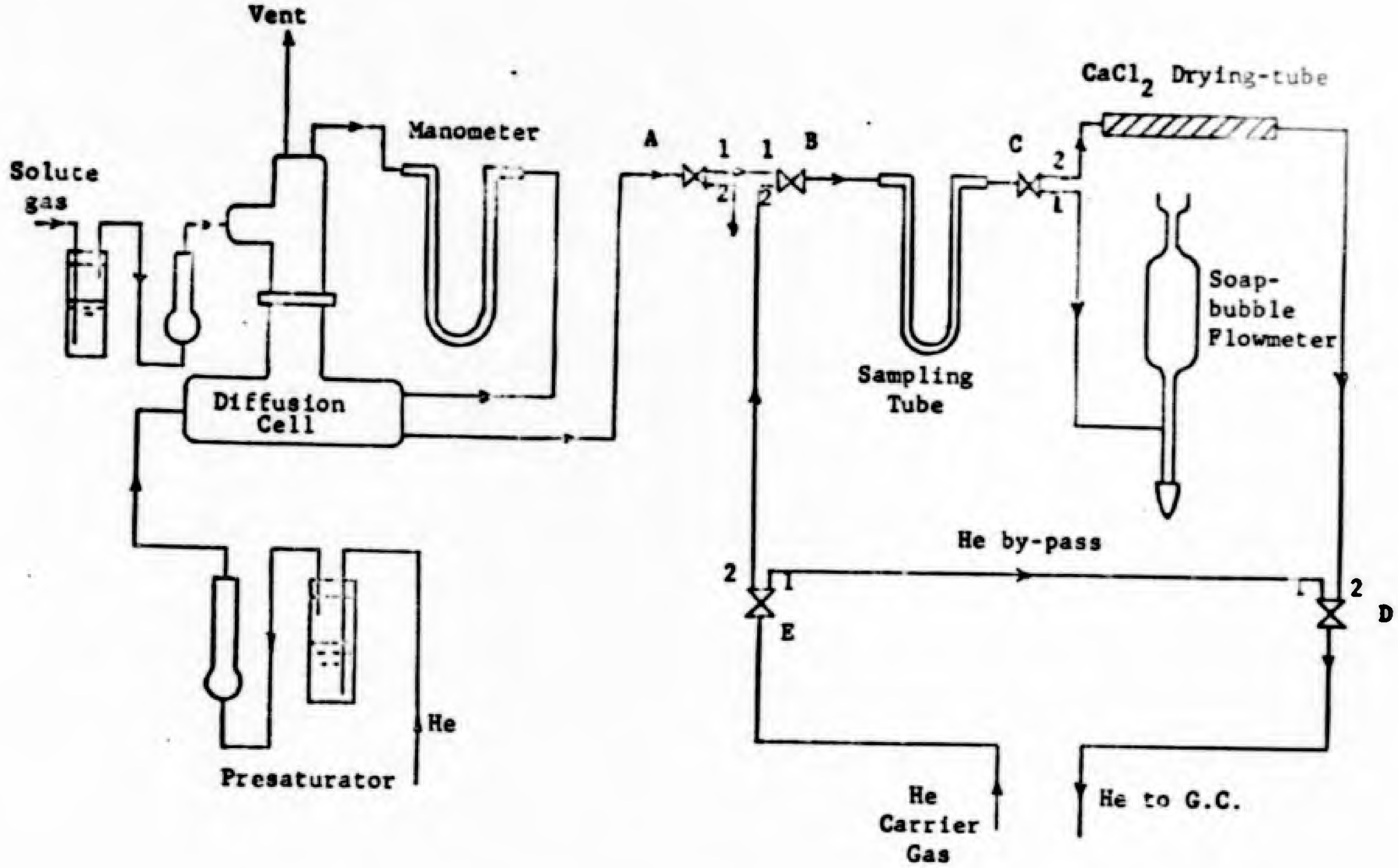

Figure 9. Steady-State Method for Measuring Diffusion Coefficients

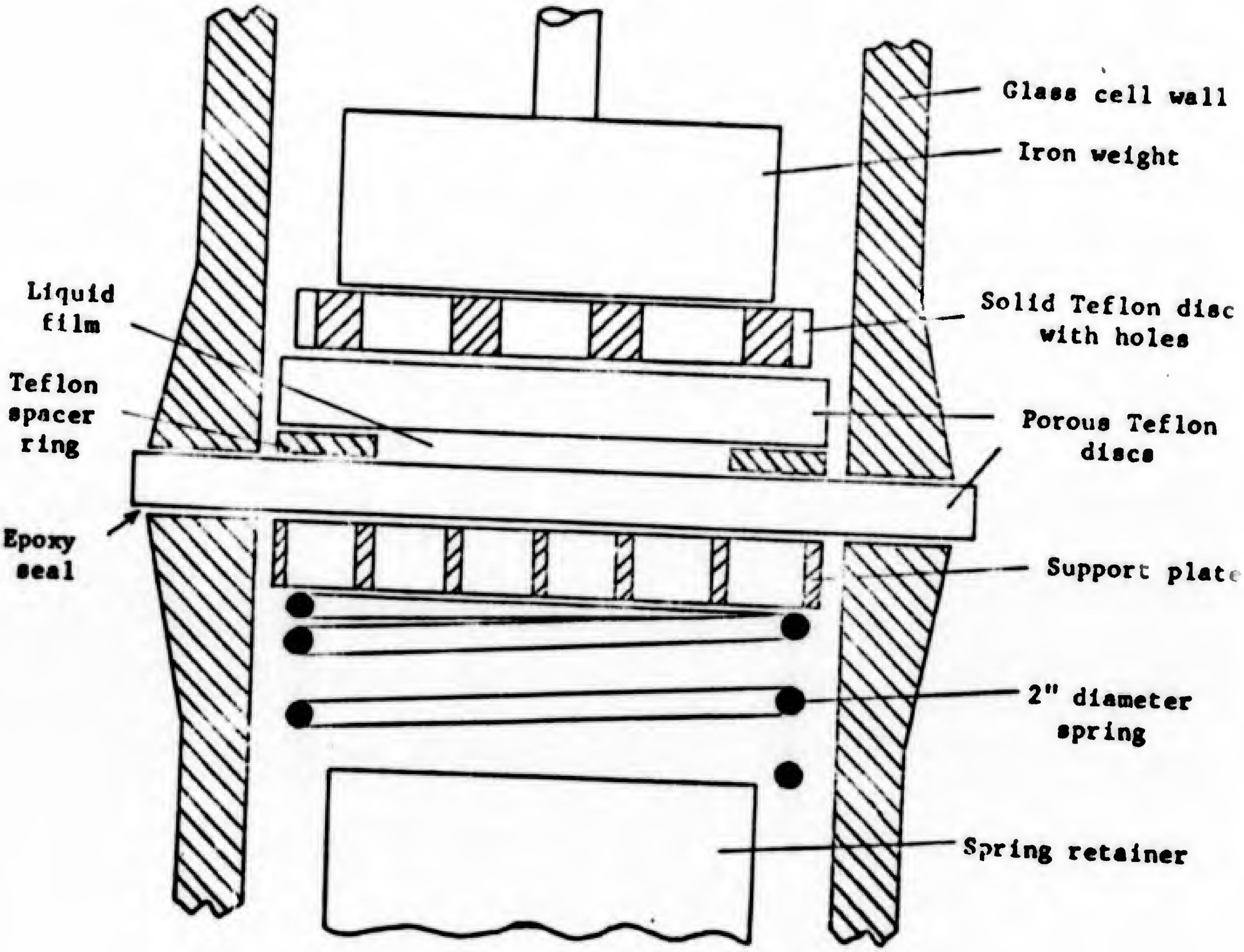

Figure 10. Steady-State Diffusion Cell

between Teflon discs separated by a Teflon spacer ring of about 0.020" thickness. A liquid film of reproducible thickness (1) was obtained by holding the assembly together using a spring and weight as shown.

A flow diagram of the complete apparatus is shown in Figure 9. The solute gas was passed through a pre-saturator containing the liquid studied, followed by a trap, before entering the upper compartment of the diffusion cell. The helium entering the lower compartment was also presaturated. A, B, C, D and E in Figure 9 represent 3-way stopcocks. These were set in position 1 during the period of approach to steady-state. When steady-state conditions had been attained, these stopcocks were turned to position 2. The gas sample, containing helium and the diffusing gas, was swept from the sample tube into the gas chromatograph, and analyzed using a flame ionization detector. A calcium chloride drying tube was used to remove water vapor. The flow-rate of both gases was controlled using metering valves, and the helium flow rate was measured with a soap-bubble flowmeter. Pressures in the upper and lower cell compartments were equalized by adjusting the flow rates of the two gases. A sample tube of about 5 ml. volume was sufficient to provide a large signal on the gas chromatograph.

In principle the values of A and 1 could be determined by direct measurement Since the porous Teflon discs are not perfectly flat, however, it is necessary in practice to calibrate the cell using a gas-liquid system for which D_{AB} is accurately known; since the diffusion data for gas-liquid systems reported by various workers generally show rather poor agreement (21), this is a disadvantage of the method. The principal advantages of the technique are the rapidity with which data may be obtained, and the relatively large sample of diffusing gas available for analysis due to the large value of A and small value of l.

3.3 Results

The results obtained for the diffusion coefficient of oxygen in potassium hydroxide solutions at 25°C are given in Table 8 and plotted in Figure 11. These results were obtained by the polarographic method. Taking into account the uncertainty in the value of the constant A, and experimental errors in the measurement of the variables in the Ilkovic equation, it is estimated that the maximum error of the diffusivity values reported is about ±6%.

Extrapolation of the curve in Figure 11 back to zero concentration gives a value of 1.90×10^{-5} cm.^{2}/sec. for the diffusion coefficient of oxygen in water at 25°C. This is in good agreement with values determined by other workers (21); thus Kreuzer (29) gives 1.90×10^{-5}, Semerano (30) gives 1.87×10^{-5}, and Jordan (31) gives 2.12×10^{-5}.

Table 9 presents results obtained for the diffusion coefficient of oxygen in 85% phosphoric acid solution at two temperatures. These measurements were made by the diaphragm cell method using a glass diaphragm having a pore size of about 10μ. At these temperatures the glass diaphragm was attacked only very slowly by the phosphoric acid, and the cell constant did not change during the experiments. Because of the high viscosity of the solutions diffusion was very slow, and each experiment took about 6 days. As a result of the experimental difficulties

TABLE 8

DIFFUSION COEFFICIENT OF O_2 IN KOH SOLUTIONS, 25°C

Electrolyte Concentration	Wt. % KOH	D_{AB}
1.00 g.mole/l.	5.2	1.641×10^{-5} cm.^{2}/sec.
2.00	10.2	1.457×10^{-5}
3.00	14.8	1.524×10^{-5}
4.50	21.2	0.867×10^{-5}
6.00	27.0	0.747×10^{-5}
8.25	34.8	0.575×10^{-5}
11.00	43.1	0.177×10^{-5}
14.26	52.0	0.037×10^{-5}

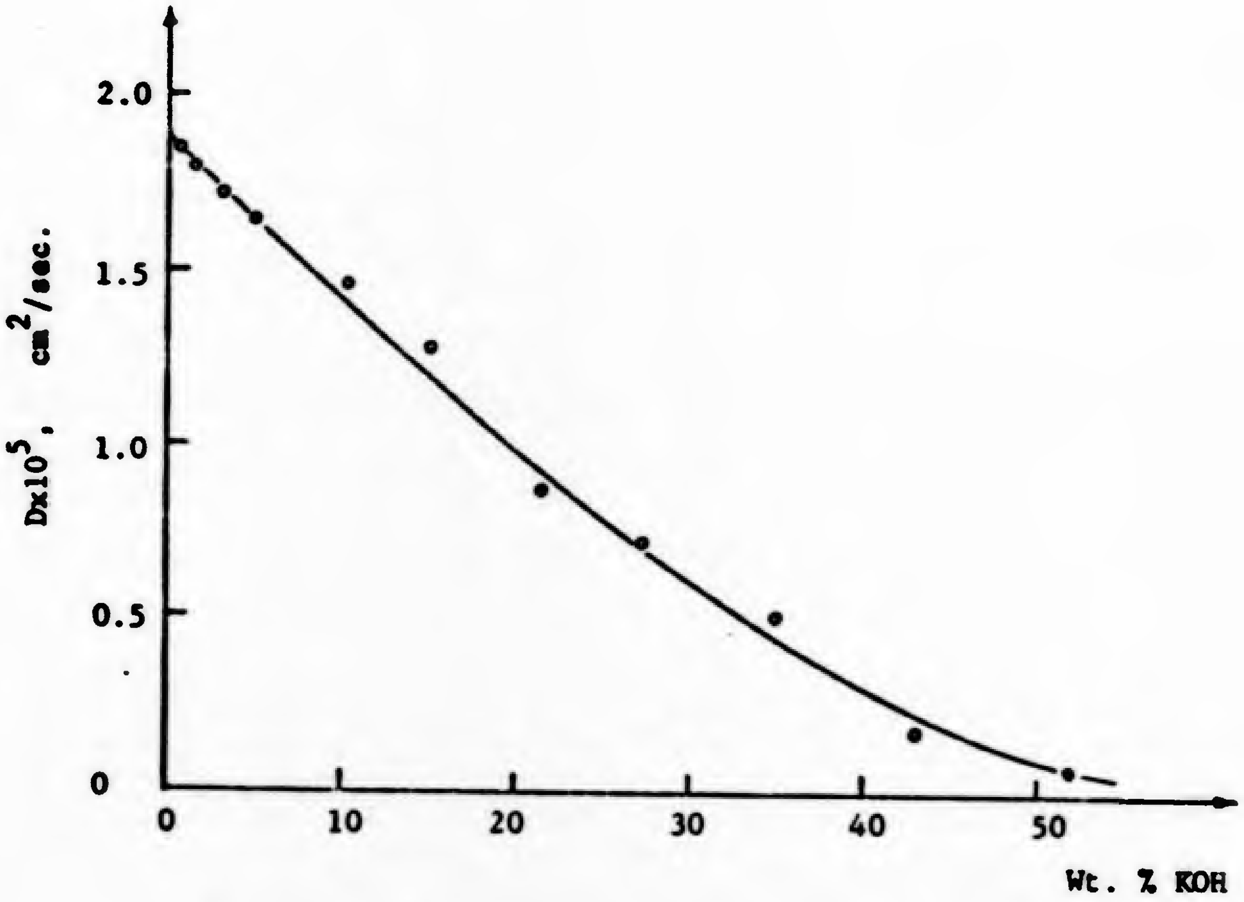

Figure 11. The Diffusion Coefficient of Oxygen in KOH Solutions at 25°C

chromatography.

TABLE 9

DIFFUSION COEFFICIENT OF O_2 IN H_3PO_4 SOLUTIONS

Temperature	Wt. % H_3PO_4	D_{AB}
60°C	85.0	2.2×10^{-6} cm.^{2}/sec.
83°C	85.0	4.2×10^{-6} cm.^{2}/sec.

The system may be regarded as a quasi-stationary state, and

---

involved the estimated accuracy of the data is only about ±15%.

Attempts to obtain data for diffusion coefficients in 85% phosphoric acid at temperatures much above $80^{\circ}C$ using a glass diaphragm cell were unsuccessful, because of the rapid corrosion of the diaphragm. In addition, measurements at higher phosphoric acid concentrations were impractical due to the inordinate time needed for each measurement. This situation arises from the rapid increase in viscosity with concentration.

The steady-state method described in section 3.2.3 has been tested using the system ethane-water at $25^{\circ}C$. Although the results obtained were not in very good agreement with those reported by others (32), the method appears worthy of further investigation.

3.4 Discussion

The diffusion coefficients for oxygen in potassium hydroxide shown in Figure 11 give an almost linear plot against concentration up to about 40 wt. % KOH. This suggests that equation (3-6) should apply to this system; studies for a number of strong electrolytes should provide sufficient data to enable diffusion coefficients to be predicted for gas-electrolyte systems that have not been studied experimentally. The slope of the plot of $\frac{D}{D_o}$ vs. concentration (a in equation (3-6) appears to be almost independent of the solute gas (14).

For diffusion in phosphoric acid, insufficient data was obtained to make possible a test of the dimensional equation (3-9) derived in section 3.1.4 For the two experimental results reported in Table 9 for oxygen, the group $D_{AB}\eta/T$ was constant within 6% (well within the limits of experimental error) for this phosphoric acid concentration. It is possible to extrapolate these two results to other temperatures using the constant group $D_{AB}\eta/T$ or equation (3-1). Extrapolations were performed by both methods; the values obtained for D_{AB} by the two methods agreed within 15% over the temperature range 0-100°C; the agreement was somewhat poorer over the range 100-150°C Table 10 shows the results of this extrapolation; the values of D shown there are the mean of the values predicted by the above two extrapolation methods. The accuracy of these predicted values is probably of the order ±30%.

Equation (3-3) may be applied to the data of Table 9 to give a rough estimate of D_{AB} for other solute gases in 85% phosphoric acid. The values of D_{AB} predicted in this way are shown in Table 11. Values of σ used were the Lennard-Jones 6-12 parameters (33). The predicted data are tentative, and are probably accurate to within 40-50%.

It may be possible to estimate the variation of D_{AB} with phosphoric acid concentration for a particular solute by assuming that the group $D_{AB}\eta/T$ remains constant, as suggested in section 3.1.2. Since experimental data is available at only one concentration there is no means of checking the correctness of this assumption, and this extrapolation method has not been attempted.

3.5 Conclusions

Diffusion coefficients have been measured for oxygen in KOH solutions at 25°C over the full concentration range of KOH. The

TABLE 10

PREDICTED VALUES OF D_{AB} FOR OXYGEN DIFFUSING IN 85% PHOSPHORIC ACID

Temperature	D_{AB}	
0°C	0.25×10^{-6}	cm.²/sec.
25	0.70×10^{-6}	
50	1.7×10^{-6}	
75	3.4×10^{-6}	
100	6.0×10^{-6}	
125	9.9×10^{-6}	
150	15.4×10^{-6}	

TABLE 11

VALUES OF D_{AB} PREDICTED FROM EQUATION (3-3) FOR VARIOUS SOLUTES IN 85% PHOSPHORIC ACID

Solute	σ	D_{AB} at 60°C	D_{AB} at 83°C
O_2	3.487 Å	2.2×10^{-6} cm.^{2}/sec.	4.2×10^{-6} cm.^{2}/sec.
CH_4	3.809	1.8×10^{-6}	3.5×10^{-6}
C_2H_6	4.418	1.4×10^{-6}	2.6×10^{-6}
C_3H_8	5.061	1.0×10^{-6}	2.0×10^{-6}
n-C_4H_{10}	4.997	1.0×10^{-6}	2.0×10^{-6}
n-C_5H_{12}	5.769	0.80×10^{-6}	1.5×10^{-6}
n-C_6H_{14}	5.909	0.77×10^{-6}	1.4×10^{-6}
n-C_8H_{18}	7.451	0.48×10^{-6}	0.92×10^{-6}

results appear to support the theory of Ratcliff (16). Two measurements have been made of the diffusion coefficient of oxygen in 85% phosphoric acid. These results have been used to predict values of D_{AB} for oxygen in 85% H_3PO_4 at other temperatures, and values of D_{AB} for other solutes in 85% H_3PO_4. Considerable experimental difficulties were encountered in measuring diffusion coefficients in concentrated phosphoric acid because of corrosion problems and the high viscosity of the phosphoric acid. A steady-state method for measuring diffusion coefficients has been developed which should enable diffusion data to be collected more rapidly for these systems.

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5. SYMBOLS

a = constant in equation (3-6)

A = area of liquid film in steady-state diffusion experiment

A' = constant in Ilkovic equation

c = concentration of solute gas in electrolyte solution

c_o = initial concentration of solute gas in concentrated side of diaphragm cell

c_B = electrolyte concentration

D_{AB} = mutual diffusion coefficient of solute in electrolyte solution

D_o = diffusion coefficient of solute in pure water

$\bar{D}_{AB}$ = integral diffusion coefficient

E_d = experimental activation energy for diffusion

g_c = gravitational constant

ΔG_d^* = free energy of activation for diffusion of solute in water

$\langle \Delta G_d^* \rangle$ = average free energy of activation for diffusion of solute in electrolyte solution

h = Henry's Law constant

ΔH = differential heat of solution

i_d = limiting polarographic diffusion current in Ilkovic equation

I = integration constant in equation (2-2)

k = constant in equation (2-5)

k_d = constant in Eyring rate equation

K = constant in equation (3-1)

l = liquid film thickness in steady-state diffusion experiment

L = diaphragm thickness in diaphragm cell

m = mass flow rate of mercury in Ilkovic equation

M = molecular weight of electrolyte

n = average number of nearest neighbor molecules to diffusing molecule

n = number of electrons involved in electrochemical reaction, equation (3-10)

N_A = rate of diffusion of solute, g.mole/sec.

p = pressure

p_A = partial pressure of solute gas

p_i = partial pressure of solute species i

p_B^o = vapor pressure of electrolyte

R = gas constant

S = solubility of gas in electrolyte

t = time

t' = mercury drop-time in Ilkovic equation

T = temperature

V_A = molar volume of solute at its normal boiling-point

x = distance in direction of diffusion in diaphragm cell

<u>Greek Letters</u>

β = cell constant for diaphragm cell

δ_i = perturbation of free energy of activation for diffusion due to an ion of type i

η_B = viscosity of electrolyte

λ = average distance moved by diffusing molecule in each jump in Eyring rate equation

ν_i = number of g. ions of ions of type i/g.mole of electrolyte

ρ = density of electrolyte solution

σ = diameter of solute molecule (using Lennard-Jones 6-12 potential)

Subscripts

A = solute

B = solvent (electrolyte solution)

i = chemical species i

1,2 = upper and lower compartments of diaphragm cell at start of experiment

3,4 = upper and lower compartments of diaphragm cell at end of experiment

APPENDIX 1

Determination of Gas Solubilities in Electrolyte Solutions

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Abstract

A procedure is described for the determination of gas solubilities. It has been applied to the determination of the solubility of oxygen and hydrogen in KOH, H_2SO_4 and H_3PO_4 electrolytes over the temperature range −55°C to +70°C.

Of the analytical methods available for the quantitative determination of dissolved gases, gas chromatography is particularly suitable because it provides rapid analyses and has the necessary versatility. Chemical and electrochemical methods, on the other hand, are restricted in application since they are not easily applicable to determinations of gases in liquids of widely variable composition.

The method described has been used in this laboratory for the determination of the solubility of oxygen and hydrogen in electrolytes commonly used in fuel cells (3), including KOH, H_2SO_4 and H_3PO_4 solutions over the temperature range −55°C to +70°C. The method is similar in principle to that described by Swinnerton (4), but some modifications to the procedure were found to be necessary.

Procedure

An F & M Model 700 gas chromatograph was used, modified so that thermal conductivity and flame ionization detectors could be used in series. The carrier gas used was helium (except for measurements of hydrogen, when nitrogen was used as carrier gas) and the column consisted of a 3 meter length packed with molecular sieve MS 13X.

The solution sample to be analyzed was injected into a glass stripping cell outside the chromatograph (Figure 1). The carrier gas flowing through the sample line of the chromatograph was diverted through this cell and its associated equipment before re-entering the sample column. Cells of various size were used, but a cell having a volume of about 7 ml. was found to be most satisfactory for general purposes. The glass cell had a medium porosity glass frit (fine frits were found to give rise to excessive pressure-drop when wetted), and was equipped with a rubber septum for injection of the sample, and a two-way glass cock to facilitate draining of the cell.

A solution sample of known volume, usually 5 ml., was injected using a syringe equipped with Chaney adapter. Carrier gas, dispersed by the frit, rapidly removed dissolved gases and carried them into the chromatograph column. Before returning the gases to the column they were passed through two drying tubes containing Drierite, followed by a stainless steel coil immersed in a water-bath. The latter served to bring the gases to ambient temperature before returning them to the column; this was particularly important when determining solubilities at very low or high temperatures, since the sudden cooling or heating of the gas stream caused baseline instability. Care was taken to keep all tubing (especially the drying tubes) of small diameter to prevent back-mixing and broadening of the peaks.

In order to determine a gas solubility, a sample of the required electrolyte solution was equilibrated with the gas at atmospheric pressure and the desired temperature in a water-bath controlled to ±0.1°C. A sample of distilled water was similarly equilibrated with the gas at 25°C and atmospheric pressure.

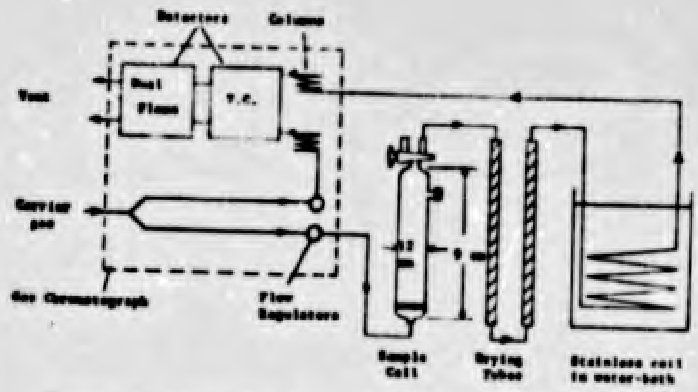

Figure 1. Apparatus for gas solubility determinations.

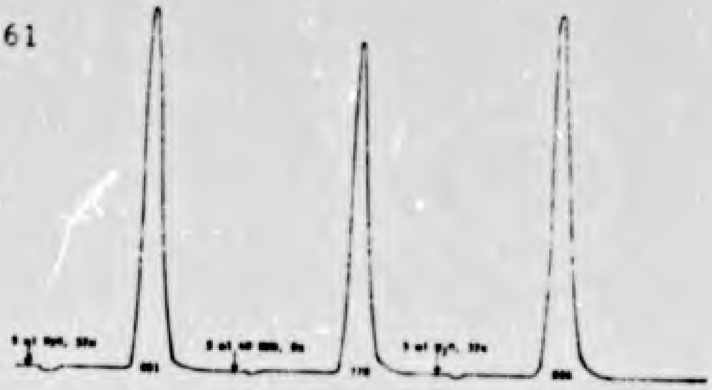

Figure 2. Peak obtained for O_2 dissolved in 4N KOH at 25°C, compared with peaks for oxygen dissolved in water at 25°C. Figures beneath peaks are areas counted by disc integrator.

Since the solubility of most common gases in water at 25°C is accurately known from chemical analysis, the water sample served as a standard for calibration purposes. Identical volumes (5 ml.) of the saturated water and saturated sample solutions were injected into the chromatograph, and the peak areas due to dissolved gases were compared. This procedure eliminated errors resulting from changes in instrument sensitivity over extended periods of time.

Results and Discussion

The solubility of the gas in the sample was calculated from the equation

$$S_s = x\,S_w \left(\frac{\pi - p'}{\pi - p}\right) \qquad \text{Eq. 1}$$

where

S_s = g.mole/liter of gas in sample solution equilibrated with gas at 1 atmosphere partial pressure (excluding partial pressure of water) at temperature T.

S_w = g.mole/liter of gas in distilled water solution equilibrated with gas at 1 atmosphere partial pressure (excluding partial pressure of water) at 25°C.

$$x = \frac{\text{Peak area for sample at T°C}}{\text{Peak area for water at 25°C}}$$

π = atmospheric pressure

p' = vapor pressure of pure water at 25°C

p = vapor pressure of sample solution at T°C

Equation 1 assumes Henry's Law in order to correct for the effect of solution vapor pressures; for fairly low temperatures where p and p' are small the error in making this assumption will be negligible. At low temperatures, when the vapor pressures are small, π may be taken as 760 mm Hg with negligible error, thus eliminating the need to measure atmospheric pressure,

$$S_s = x\,S_w \left(\frac{760 - p'}{760 - p}\right) \qquad \text{Eq. 2}$$

Figure 2 shows a peak obtained for oxygen dissolved in 4N KOH at 25°C compared with the peak for water at 25°C. The peaks obtained are broadened because of the time required to completely strip the gas from solution, and also because of back-mixing in the external part of the flow circuit; with electrolyte solutions at low temperatures (about −55°C) it was impossible to inject the sample rapidly because of very high viscosity of the solution. Even for solutions containing very little dissolved gas, however, the carrier gas rapidly and completely stripped gas from solution, and there was no pronounced peak tailing. With the 5 ml. sample used the peak broadening was not excessive, and the 3 m. MS 13X column gave complete separation of oxygen and nitrogen peaks at all temperatures. Very little precise data is available in the literature for gas solubilities in electrolytes; the results obtained by the above technique have been in good agreement with data obtained by Bohr (1) and Geffcken (2) using manometric methods.

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