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A STUDY OF GAS SOLUBILITIES AND TRANSPORT PROPERTIES IN FUEL CELL ELECTROLYTES

Research Grant NGL 10-005-022

Ninth Semi-Annual Report

Period Covered: September 1, 1969 - February 28, 1970

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ENGINEERING AND INDUSTRIAL EXPERIMENT STATION

College of Engineering

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1.0 SUMMARY

Measurements of the diffusion coefficients of gases in LiOH solutions have been continued. No significant progress has been made in this direction due to instrumental problems. For the present, it is planned to use the dropping mercury electrode for measuring the diffusion coefficients of oxygen in LiOH solutions.

A modified Percus-Yevick theory for gases in electrolytes has been developed. This theory was based on sound theoretical background and gives better prediction than any other existing theory. Extensive calculations based on this theory are being planned.

The completion of the experimental laboratory for measuring partial molal volume allowed a few measurements on some controlled systems. Even though some unforeseen problems arose in the measuring procedure, it is expected that actual measurements can be started in the near future.

Experimental studies on the vapor pressure of LiOH solutions, and solubility of non-polar gases in LiOH have been completed. In addition, the diffusion coefficients of O_2 and H_2 in KOH were studied in the light of the free volume theory. This theory gives the correct qualitative trends of concentration dependence, but quantitative prediction cannot be made due to the presence of some unknown constants.

2.0 DIFFUSION OF OXYGEN IN LITHIUM HYDROXIDE SOLUTIONS

This work was undertaken in January, but no real progress can be reported at the end of this reporting period by reason of a series of instrumental problems. These have now been substantially overcome with the result that we expect to be able to make diffusivity measurements with the dropping mercury electrode in the immediate future.

Several attempts have been made to use the stagnant microelectrode technique for measuring the diffusivity of oxygen in LiOH solutions but these have not been successful. We have had great difficulty in obtaining reproducible currents and potentials. Since the dropping mercury electrode now seems to be giving reliable results, the stagnant microelectrode will be set aside for the time being.

3.0 PARTIAL MOLAL VOLUME OF GASES IN ELECTROLYTE SYSTEMS

Several improvements to both the experimental and theoretical developments on the partial molal volume of gases in electrolytes were begun during the last reporting period. Section 3.1 reviews the experimental developments for the determination of the partial molal volumes, section 3.2 briefly describes the recent theoretical results and section 3.3 describes the work being carried out on salting-in by complex ion electrolytes.

3.1 Experimental Measurements

The experimental laboratory for the determination of partial molal volumes of gases in electrolyte solutions is now complete. The major components of the system, as described in the last report (1) are performing according to specifications and the only major drawback has been the special glassware in which the actual measurement is made. Ace Glass Company has contracted to build the necessary glassware (dilatometers) which have now gone through several stages of refinement. The dilatometers made by Ace appear to be of satisfactory construction and preliminary runs on some control systems are now being evaluated.

Some experimental problems not originally envisioned have appeared. One of these concerned accurate temperature control but has been satisfactorily solved. The other concerns the actual measurement in the dilatometer. It was found that mercury of the highest purity possible was needed in order to adequately isolate the known volume of liquid in the dilatometer. Mercury of marginal purity caused it to adhere to the walls of the five capillary lines leading into the dilatometer bulb. Since the dilatometer is completely enclosed with only these capillary lines leading into it, it was further difficult to clean the apparatus after a run. These mercury purity and dilatometer cleaning problems have forced us to undertake some rather elaborate and time consuming procedures in order to insure accurate measurements.

3.2 Percus-Yevick Theory of Gas-Electrolyte Systems

Recent developments in an accurate equation of state for hard spheres (2) have modified the P-Y theory of gases in electrolytes accordingly. We have begun a rather extensive theoretical study of the salting-in and salting-out phenomena for a large number of gases and electrolytes using this modified P-Y theory. Calculations show that this theory is indeed an excellent one for concentrated electrolyte solutions. An abstract of this work has been accepted for presentation at the August, 1970 AIChE meeting in Denver (3). In this study we have included many alkali halide salts, some tetra-alkyl ammonium salts as well as the KOH system. We plan to give a complete account of this work in the next semi-annual report.

3.3 Salting-In by Complex Ion Electrolytes

In the last semi-annual report (1) we described some of the anomalous behavior exhibited by certain large tetra-alkyl ammonium salts. These systems were of interest both from a theoretical viewpoint since existing theories could not explain this phenomenon and an experimental viewpoint since these salts increased the solubility of solute gases with increased salt concentration.

One of the problems in using the present P-Y theory to study these systems is that certain of the molecular parameters are unknown. Especially troublesome is the energy parameter ε/k. In order to obtain this quantity the polarizability of the ion must be available. No such data exists and we have undertaken an experimental program to determine the ionic polarizabilities for a number of large tetra-alkyl ammonium bromides.

The relationship between the polarizability α and its molar refraction R is given by

$$\alpha = \frac{3}{4\pi} \left\{ \frac{V}{N} \right\} \frac{n^2 - 1}{n^2 + 2} = \frac{3R}{4\pi N} \qquad (3\text{-}1)$$

where N is the number of molecules in volume V and n is the index of refraction. Thus, it is possible to obtain α from refractometry measurements. We are using a method due to Böttcher (4) for the determination of both α and σ directly from measurements of the index of refraction as a function of ion concentration. The energy parameter ε is obtained from the experimentally obtained polarizabilities α from Mavroyannis-Stephen (5) theory for dispersion interactions and gives

$$\varepsilon = 3.146 \times 10^{-24} \frac{\alpha^{3/2} z^{1/2}}{\sigma^6} \quad \text{(ergs)} \qquad (3\text{-}2)$$

where z is the total number of electrons in the ion and σ is the size parameter.

Experimentally a Brice-Phoenix Differential Refractometer is used for the determination of the refractive index. An initial study on the system $(C_2H_5)_4N^+, Br^-$ has shown that the Böttcher method is extremely sensitive to small errors in n. We have concluded from this first set of experiments that better temperature control of the refractivity cell as well as better overall care in solution preparation and handling have become necessary in order to achieve the needed accuracy. A special refractivity cell has also been ordered which will enable us to make measurements over a wider concentration range.

4.0 SOLUBILITY OF NON-POLAR GASES IN LITHIUM HYDROXIDE SOLUTIONS

Experimental studies of solubilities of a series of non-polar gases in water and lithium hydroxide solutions over a range of temperatures and concentrations have been made. Vapor pressure of lithium hydroxide were also measured, because accurate data for vapor pressures at various temperatures and concentrations were needed for this study.

4.1 Material

Minimum purities for the gases used were helium and argon 99.99%, hydrogen 99.9% and oxygen 99.6%. Lithium hydroxide solutions were prepared from distilled and degassed water. Lithium hydroxide pellets used for preparing solutions were of 99.5% purity.

4.2 Vapor Pressure Measurements

The apparatus used in the measurements consists of a highly polished silver tube fitted with water circulating accessory. The silver tube was inserted into a glass vessel which contained the solution to be measured. The procedure consisted in first equilibrating the solution in a constant temperature bath, after evacuating it of any dissolved gas, then the temperature of the silver tube was lowered until traces of dew appeared on the silver surface. The temperature of the silver surface gives the dew point and thus the vapor pressure of the solution at that particular temperature. The results of the measurements are listed in Table 4-1.

To correlate these vapor pressure data, the Antoine equation was used.

$$\log_{10} P = A - \frac{B}{t+C} \tag{4-1}$$

Table 4-1

Comparison Between Experimental and Calculated Vapor Pressure of Lithium Hydroxide

wt% LiOH	Temperature	Experimental Value	Calculated		% error	
0.0	25	23.75	23.76		- 0.06	
	40	55.32	55.30		- 0.04	
	60	149.38	149.17		- 0.10	
	80	355.10	354.77		- 0.09	
	100	760.00	760.80		+ 0.1	
1.9	25	23.14	23.19		+ 0.2	
	40	53.88	53.85		- 0.05	
	80	346.08	343.89		- 0.6	
	100	731.92	736.08		+ 0.5	
3.85	25	22.57	22.60		+ 0.16	
	40	52.16	52.21		0.10	
	80	334.70	329.70		- 1.5	
	100	694.82	702.37		+ 1.0	
6.45	25	21.54	21.58	(22.03)*	+ 0.2	(2.3)
	40	50.42	50.34	(50.55)	+ 0.15	(0.26)
	60	136.9	136.2	(134.12)	- 0.5	(-2.0)
	80	323.63	324.75	(314.39)	+ 0.3	(-2.8)
	100	638.36	-	(665.6)	-	(+4.27)

Table 4-1 (continued)

wt% LiOH	Temperature	Experimental Value	Calculated		% error	
8.05	25	21.12	21.03	(21.43)	- 0.4	(+1.4)
	40	49.02	49.05	(48.84)	+ 0.6	(-0.4)
	80	317.4	316.4	(299.34)	- 0.3	(-5.6)
	100	601.89	-	(630)	-	(4.67)
10.1	25	20.3	20.09	(20.8)	- 0.9	(2.7)
	40	46.58	47.27	(47.27)	+ 1.48	(+1.48)
	60	129.13	129.13	(123.62)	0	(-4.2)
	80	311.87	310.5	(286.11)	- 0.4	(-8.25)
	100	549.71	-	(599.06)	-	(+8.98)

* Values using parameter by fitting data up to 100°C.

where P is vapor pressure in millimeters of mercury, t is temperature in degrees centigrade and A, B, and C are functions of concentrations.

As in the case of potassium hydroxide solutions (6), experimental results were used to fit equation (4-1) for each concentration. The procedure is as follows:

(1) The constant C for each concentration was calculated from the equation

$$\frac{\log_{10} P - \log_{10} P_1}{t - t_1} = \frac{A}{t_1 + C} - \frac{\log_{10} P}{t + C} \tag{4-2}$$

which was obtained by rearranging equation (4-1).

In equation (4-2), P_1 is the vapor pressure at arbitrarily chosen temperature t_1.

It turns out that, the best choice of C in the present case is the same as in the case of potassium hydroxide solutions at the same range of temperatures and concentrations (C was found to be 235).

(2) With known value of C, the constants A and B were obtained by least square fitting equation (4-1).

In Table 4-2, the values of the constants A, B and C for different concentrations are tabulated. Similar to the case of KOH solutions (1) there seems to be a discontinuity in the plot of $\log_{10} P$ vs $\frac{1}{t + C}$ at temperatures above 80°C and LiOH concentrations higher than 6.45 %. For these concentrations two sets of constants were given, one obtained by fitting data up to 80°C and the other up to 100°C. Since data above 100°C was not available, no attempt was made to separate the data into high and low temperature regions, and fitted them separately.

Table 4-1 shows the comparison between experimental and

Table 4-2

Antoine Coefficients for LiOH

wt % LiOH		A	B	C
0.0		8.0998	1748.2	235
1.9		8.0723	1743.8	235
3.85		8.0200	1733.1	235
6.45	up to 80°C	8.0776	1753.3	235
	up to 100°C	7.9543	1718.9	235
8.05	up to 80°C	8.0663	1753.3	235
	up to 100°C	7.8895	1705.2	235
10.1	up to 80°C	8.1124	1770.4	235
	up to 100°C	7.8321	1693.3	235

calculated vapor pressure. In most cases the agreement is within 1%. It can also be seen that better agreement was obtained when the points at 100°C were excluded from the data fitted for those concentrations above 6.45 wt %.

4.3 Solubility Measurements

The gas chromatographic method used in this research is essentially the same as that discussed by Gubbins, Carden and Walker (7) and further improved by Shoor, Walker and Gubbins (8). The method consisted of first preparing a saturated solution of the gas in the electrolyte by bubbling the gas through the saturating vessel. After reaching equilibrium, the solution was analyzed using a Perkin-Elmer gas chromatograph equipped with a thermal conductivity detector. Attainment of equilibrium was checked by analyzing the solution at constant time intervals until the composition remained the same for three successive measurements.

The solubilities of oxygen, hydrogen, helium and argon in lithium hydroxide solution were tabulated in Tables 4-3 and 4-4. These solubility data expressed in terms of activity coefficients may be used to calculate the partial molal heats of solution of these non-polar gases in LiOH solutions. The equation used is

$$\left(\frac{\partial \ln \gamma_1 K_1^o}{\partial T} \right)_{p,n_j} = \frac{-\bar{H}_1^L - h_1^G}{RT^2} = -\frac{\Delta \bar{H}_1}{RT^2} \qquad (4\text{-}3)$$

The trend of variation of $\Delta \bar{H}_1$ with concentration and temperature is similar to that in potassium hydroxide solutions. A typical plot of partial molal heat of solution is that for argon and is shown in Figure 4-1. These partial molal heats of solutions are large and negative for dilute solutions and become less negative as the LiOH concentration

Table 4-3

Activity Coefficients of Non-Polar Gases Dissolved in Aqueous LiOH Solutions

Activity Coefficient, γ_1

LiOH Concentration		Oxygen					Hydrogen				
Wt %	g mole/1.	25°C	40°C	60°C	80°C	100°C	25°C	40°C	60°C	80°C	100°C
0.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1.90	0.78	1.29	1.29	1.28	1.31	1.34	1.24	1.21	1.24	1.25	1.23
3.85	1.69	1.69	1.73	1.77	1.83	1.84	1.58	1.49	1.52	1.51	1.53
6.45	2.87	2.52	2.51	2.51	2.44	2.76	2.12	2.00	2.06	-	-
8.05	3.65	3.28	3.04	2.84	3.10	3.35	2.48	2.33	2.39	2.55	2.58
10.10	4.69	4.51	4.34	4.13	-	-	3.24	3.15	3.19	-	-

Table 4-4

Activity Coefficients of Non-Polar Gases Dissolved in Aqueous LiOH Solutions

Activity Coefficient, γ_1

LiOH Concentration		Helium					Argon				
Wt %	g mole/l.	25°C	40°C	60°C	80°C	100°C	25°C	40°C	60°C	80°C	100°C
0.00	0.00	1.00	1.00	1.00			1.00	1.00	1.00		
1.90	0.78	1.33	1.20	1.16			1.29	1.25	1.20		
3.85	1.69	1.46	1.56	1.42			1.73	1.61	1.61		
6.45	2.87	2.05	1.86	1.65			2.51	2.36	2.17		
8.05	3.65	2.46	2.17	1.96			3.21	3.03	2.67		
10.10	4.69	3.04	2.57	2.32			4.57	3.94	3.51		

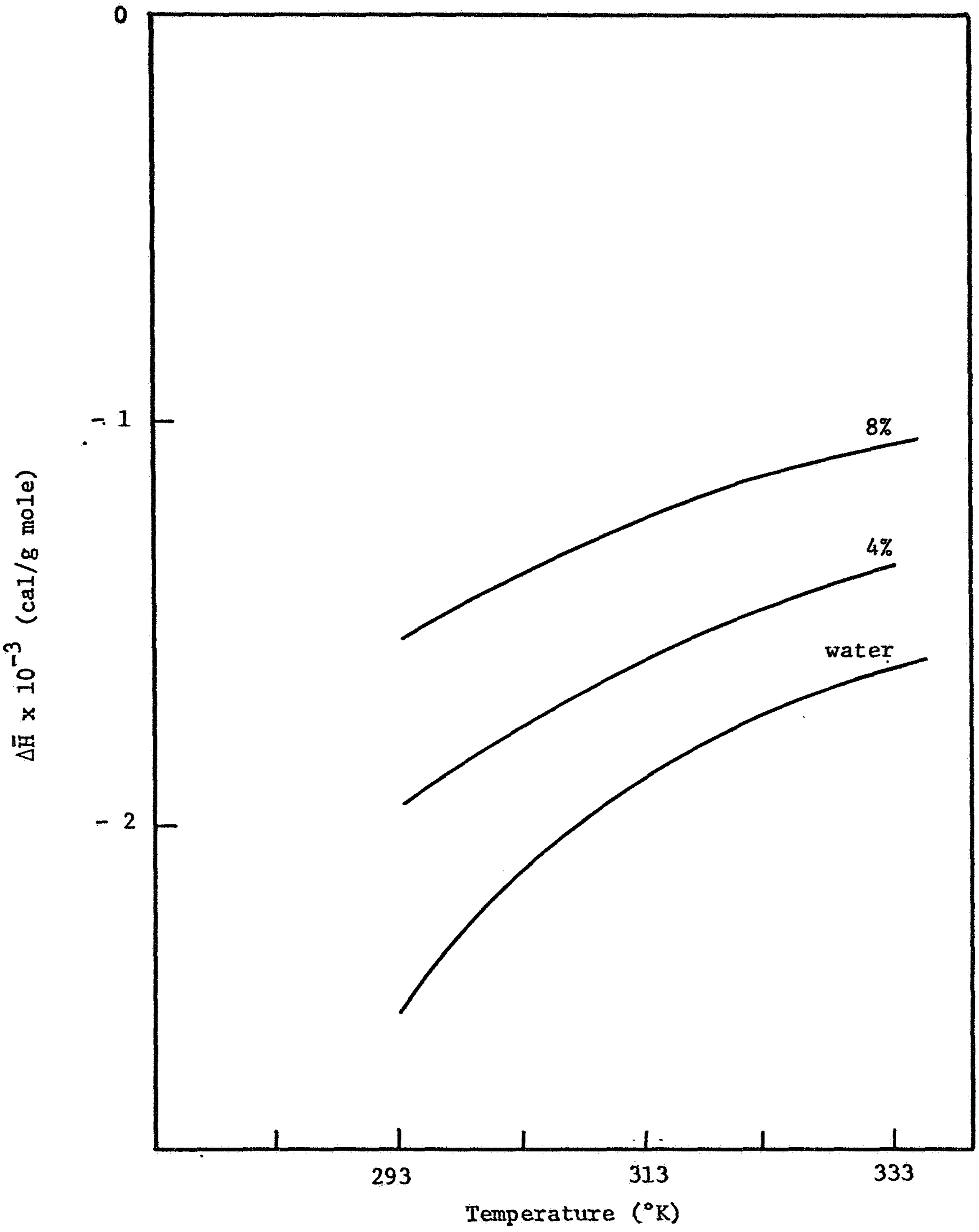

Figure 4-1 Partial Molal Heat of Solution for Argon

increases. Also at low temperatures, the heat of solution is more negative. It was also found that the absolute values of $\Delta\bar{H}_1$ are larger for larger molecules, and decrease with decrease in molecular size. A comparison between those of argon and helium at 60°C is shown in Figure 4-2.

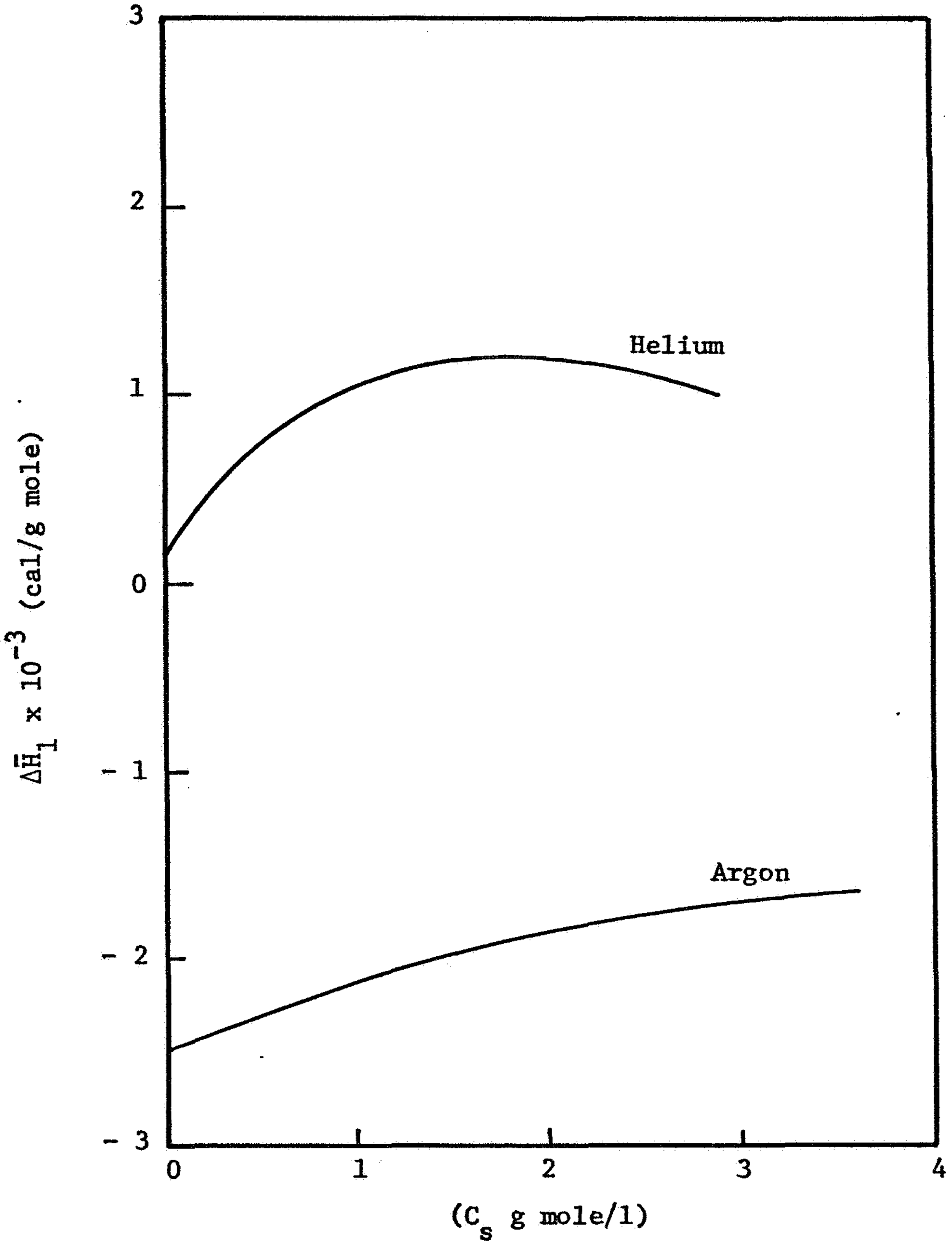

Figure 4-2 Partial Molal Heat of Solutions for Argon and Helium at 60°C.

5.0 DIFFUSION COEFFICIENTS OF OXYGEN AND HYDROGEN IN POTASSIUM HYDROXIDE SOLUTIONS

Diffusion coefficients of oxygen and hydrogen in potassium hydroxide solution were measured using the stagnant microelectrode method. The results were examined in relation to the modified Eyring theory and the free volume theory of Cohen and Turnbull.

5.1 Experimental

5.1.1 Materials

Potassium hydroxide pellets, containing a maximum of 1% K_2CO_3 were used. Solutions were prepared with doubly distilled water and stored in polyethylene bottles fitted with glass bulb containing Ascarite to minimize carbon dioxide absorption. Potassium ferrocyanide solution was prepared from analyzed reagent grade standard volumetric solutions.

5.1.2 Diffusion Coefficient Measurements

The method used was that of Laitinen and Kolthoff (9). The microelectrode used in the measurement consisted of a bright platinum disc cemented between two sections of precision bore capillary. A silver plate of 5.2 x 4.5 cm size was used as a counter electrode.

Gas, presaturated with water vapor was bubbled through a diffusion vessel until the solution was saturated with the gas. The temperature of the vessel and its contents was controlled within $\pm$ 0.01° in an oil bath. The microelectrode was filled with gas saturated solution by means of a syringe. A constant potential was then applied to the microelectrode and the current was measured as a function of time for 20 minutes. The diffusion limiting potentials used were - 0.4 to - 0.65 volt for oxygen, and 0.1 to 0.25 volt for hydrogen. Residual currents were measured in a similar way after stripping out dissolved solute gas with nitrogen.

Diffusion coefficients were calculated from the equation (9)

$$D = \left(\frac{i_t}{nFAS} \right)^2 \pi t \qquad (5\text{-}1)$$

where i_t is net diffusion current in amperes, n is number of electrons transferred, F is the Faraday, A is microelectrode area in cm^2, S in concentration of dissolved gas in g mole/ml, and t is time in seconds.

Calibration of the Microelectrode

The electrode area was determined by measuring the diffusion current vs time for the diffusion of 0.004 m potassium ferrocyanide in a supporting electrolyte of 0.1 N KCl.

5.2 Results

The experimental results are presented in Tables 5-1 and 5-2. Since the gas concentration is very low, the diffusion coefficients measured can be taken as the differential diffusion coefficients. Each datum is the arithmetic mean of five or six duplicate measurements. The estimated accuracy of the measurement is ± 10%. It is interesting to correlate these results in an analytical form for ease of interpolation and calculation. The equation fitted is of the Arrhenius type.

$$\ln D = A - E/RT \qquad (5\text{-}2)$$

where D is the mutual diffusion coefficient in the volume frame.

R is the gas constant in cal/g mole °K.

T is in °K.

A and E are functions of mass fraction of KOH.

Table 5-1

Diffusion Coefficients of Oxygen in Potassium Hydroxide Solutions in $cm^2/sec \times 10^5$

wt% KOH	25°C	40°C	60°C	80°C	100°C
3.5		2.45±0.02			
5.0			3.40±0.012	5.15±0.03	
6.0	1.45±0.018				
10.2	1.18±0.02	1.75±0.01			
13.0			2.45±0.021	3.70±0.035	
19.0	0.85±0.015	1.25±0.019	1.80±0.016		
24.0				2.22±0.031	3.70±0.045
26.0	0.60±0.018	0.90±0.01			
32.5			1.05±0.02	1.64±0.049	
40.2	0.40±0.01	0.57±0.02			
42.5			0.85±0.01	1.25±0.03	1.71±0.07
51.5	0.30±0.012	0.45±0.015	0.72±0.01	1.04±0.04	1.48±0.06

Table 5-2

Diffusion Coefficients of Hydrogen in Potassium Hydroxide Solutions in cm^2/sec x 10^5

wt% KOH	25°C	40°C	60°C	80°C	100°C
5.0	3.01±0.015	4.60±0.028	7.55±0.043	11.6±0.086	
13.0	2.36±0.02	3.60±0.017	5.82±0.06	8.70±0.054	
24.0	1.85±0.01	2.74±0.01	4.46±0.032	6.70±0.039	9.90±0.2
32.5	1.55±0.023	2.4 ±0.01	3.46±0.051	5.40±0.066	
42.5	1.25±0.01	1.95±0.02	2.89±0.11	4.40±0.095	
51.5	1.10±0.01	1.80±0.02	2.53±0.04	3.80±0.12	5.59±0.13

The coefficients A and E for O_2 and H_2 are given as follows:

Solute Gas	A	E
O_2	$8.434 - 5.531\ x + 3.475\ x^2$	$4580.4 - 64.02\ x$
H_2	$\exp^{(2.29 - 0.468\ x)}$	$5131.35 - 1154.21\ x$

where x is mass fraction of KOH. These parameters predict results well within ± 10% of the experimental results.

5.3 Discussion

There is no satisfactory theory available to describe the effect of ionic concentration on the diffusion coefficient of dissolved gases.

An approximate description of the variation of D with ionic concentration is obtained from a modification of the Eyring absolute rate theory, proposed by Ratcliff and Holdcroft (10). This theory predicts that $\ln D/D_o$ is a linear function of $\dfrac{C}{1000\ \rho - CM + 18\ C\ (\nu^+ + \nu^-)}$ where D_o is the diffusion coefficient of the gas in pure water, and C is the concentration. This relation was found to hold for several simple gas-electrolyte systems (10). For the present systems, linear behavior was observed up to moderate concentrations, while significant deviation from linear behavior was observed at higher concentrations.

An alternative framework for the discussion of diffusion is given by the free volume theory of Cohen and Turnbull (11). According to this theory the molecules may be thought of as hard spheres, and a diffusive jump will only occur if an adjacent hole is available for the molecule to move into.

Then

$$D = B\ P\ (r_c \geq \sigma) \tag{5-3}$$

where P $(r_c \geq \sigma)$ is the probability that a cavity of radius greater than or equal to σ is available for the diffusing molecules to move into. According to the Einstein theory of fluctuations, the probability $P(r_c \geq c)$ is given by

$$P\ (r_c \geq \sigma) = \exp\ [\ -\ g_c/kt\ ] \tag{5-4}$$

where g_c is the Gibbs free energy change needed to form a cavity.

$$\therefore \qquad D = B \exp\ [\ -\ G_c/Rt\ ] \tag{5-5}$$

where G_c is the Gibbs free energy change per mole of cavities. The latter can be calculated from the scaled particle theory of Reiss et al. (12,13). Table 5-3 compares values of $-\ (G_c - G_c^o)/RT$ with $\ln D/D_o$ for the systems studied here. The results lend qualitative support to the ideas of the Cohen-Turnbull theory. Thus, the number of cavities of suitable size decreases as the KOH concentration increases. This effect is common in most electrolytes, and evidence for this trend is also available from partial molal entropy measurement (14,15). It is also seen from Table 5-3 that the decrease in the number of cavities when electrolyte is added is more pronounced for oxygen than for hydrogen, and this trend parallels the greater decrease in D/D_o for oxygen. A more quantitative test of the

Table 5-3

Gibbs Free Energy for Cavity Formation at 25°C and Activation Energy of Diffusion (cal/g mole) for Oxygen and Hydrogen in KOH Solutions

C^1	$-(G_c - G_c^o)/RT^2$	$\ln (D/D_o)^3$	E
	O_2 Solute		
0	0	0	4700
2	- 1.12	- 0.541	4680
5	- 2.82	- 1.069	4740
10	- 5.70	- 1.627	4560
14	- 8.10	- 1.902	4580
	H_2 Solute		
0	0	0	5240
2	- 0.84	- 0.352	5010
5	- 2.06	- 0.655	4850
10	- 4.13	- 1.024	4810
14	- 5.82	- 1.197	4500

1 Molarity of KOH at 25°C.

2 Calculated from scaled particle theory (using the following parameters $\sigma_{H_2O} = 2.75$, $\sigma_{K^+} = 2.60$, $\sigma_{OH^-} = 3.30$, $\sigma_{O_2} = 3.46$, $\sigma_{H_2} = 2.87$ Å)

3 At 25°C.

Cohen-Turnbull theory is difficult because of the unknown concentration dependence of the term B.

Further work is being done on diffusion theory using the Kinetic theory. This theory was found to be quite successful in treating diffusion of organic liquids and gases in electrolytes (16).

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