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ENGINEERING AND INDUSTRIAL EXPERIMENT STATION

College of Engineering

University of Florida

Gainesville

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

Research Grant NGR 10-005-022

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ABSTRACT

Work during the first year of the grant has been concentrated in three areas: (1) measurement of the density and the vapor pressure of KOH solutions, (2) development of a method of concentrating dissolved gases before analysis, and (3) perfection of a steady state diaphragm cell for rapid measurement of diffusivities.

Densities of KOH solutions up to about 52 wt. per cent KOH and 150°C have been made using two techniques. Agreement with data available from other sources is satisfactory. A modified technique is being explored for measurements at higher temperatures and KOH concentrations.

Vapor pressures over KOH solutions have been measured for KOH concentrations up to about 53 wt. per cent and up to two atmospheres. Fairly satisfactory agreement with data reported in the literature has been obtained, but the method used does not appear to be suitable for measurements at very high KOH concentrations and temperatures. Other techniques are being explored.

A method for concentrating dissolved gases before analysis has been perfected and a few measurements of the solubility of oxygen in KOH solutions at 25°C have been made. These agree quite well with earlier data at low KOH concentrations and lie close to a straight line on a semi-log plot of solubility versus KOH concentration. Solubility data for 50°C also give a linear semi-log solubility versus concentration plot. The lines for the two temperatures are parallel, and the solubility of oxygen in KOH solutions at 50°C is about three-fourths as large as the solubility at 25°C.

A new steady state diaphragm cell method has been perfected for measuring diffusivities. It is capable of yielding reasonably accurate results rapidly but has not been used to measure the diffusivity of oxygen or hydrogen so far because of the unavailability of accurate solubility data. The adequacy of the method was shown by determining the diffusivity of several hydrocarbons and CO_2 in water, data for which were available from other workers. Agreement with earlier reported results was good.

1. INTRODUCTION

The paucity of data on the solubility and diffusivity of gases in fuel cell electrolytes has seriously hindered estimation of limiting current densities at fuel cell electrodes, and it has further interfered with studies of electrode kinetics. The principal work during the first year of this grant has been directed toward providing this information. To this end those data which were available in the literature have been assembled and correlated, and methods of measurement which appear to be suitable at high electrolyte concentrations and high temperatures have been devised. Since data on pertinent physical properties of the KOH-H_2O system were not available over the entire range of concentration and temperature, it has been necessary to make many of these measurements.

Earlier work by Gubbins and Walker (1) showed that both the solubility and diffusivity of oxygen in aqueous KOH solutions decreased sharply as the KOH concentration increased. It became clear from this work that accurate solubility data at high KOH concentrations would require modification of the techniques used in the earlier work. Moreover, Tobias (2) has observed that diffusion may not be the rate-limiting process in the electroreduction of oxygen in concentrated KOH solutions. Thus, the electrochemical method used earlier for determination of the diffusivity of oxygen in KOH solutions is not suitable for measurements at high KOH concentrations.

Another procedure for determining gas solubilities, especially suitable for low solubilities, has been developed, and a new method for measuring gas diffusivities has been devised and tested. These are described in detail in the appropriate sections of this report, and pertinent data are presented. The experimental methods which have been followed in measuring certain physical properties of the KOH-H_2O system are also discussed, as well as difficulties and limitations of technique which have been encountered. Pertinent physical property data are presented in both tabular and graph form.

It appears that the principal experimental difficulties in the measurement of gas solubility and diffusivity have now been overcome, and it is expected that these data can be generated at a relatively rapid rate during the second year of the grant.

2. PHYSICAL PROPERTY MEASUREMENTS FOR POTASSIUM HYDROXIDE SOLUTIONS

2.1 Materials

The potassium hydroxide used was Merck reagent grade, and contained approximately 1.2% of potassium carbonate. Solutions were standardized periodically, and both hydroxide and carbonate contents were determined. The figures given for weight percent KOH in the following sections do not include the carbonate impurity. The carbonate content of the solutions used was generally in the range 1.0 to 1.3% of total dissolved solids.

So far no attempt has been made to further purify the potassium hydroxide solutions. However, for certain of the property measurements test determinations will be carried out in which carbonate-free solutions will be used. Carbonate removal will probably be effected using ion-exchange resins as described by Davies and Nancollas (3).

2.2 Density Measurements

Experimental density measurements have been made for KOH concentrations in the range 0-52 wt. % for temperatures up to 150°C. Two different measuring procedures have been used:

a) a Westphal balance method

b) a pycnometer method

The procedure for method (a) has been described in a previous report (4); density determinations at temperatures up to 70°C have been made using this procedure.

In procedure (b) a glass pycnometer of the Lipkin type was used (5). The method was based upon the assumption that the rate of corrosion of the glass by KOH would not be so rapid as to invalidate the results, provided that the pycnometer was frequently recalibrated.

Pycnometers were calibrated using pure distilled mercury. The purity of the mercury was checked by determining its density at 25°C. Before a determination the pycnometer was weighed with mercury at three different levels in the capillary arms, the pycnometer being equilibrated in an oil bath controlled to ±0.02°C. The pycnometer was then cleaned, filled with the sample KOH solution, equilibrated in the oil bath, and then cooled and reweighed. Finally the pycnometer was recalibrated using mercury, to check for any possible volume change due to corrosion.

At temperatures up to 90°C no significant changes in volume were found for the pycnometers before and after a measurement. At the higher temperatures, however, measurable volume changes occurred during an experiment. Table 1 shows measured volumes before and after a density determination. Since the average of the two calibrations is used in calculating the density, the results suggest that the error due to volume changes during an experiment should not be greater than about 3 parts in 10,000.

TABLE 1

THE EFFECT OF KOH SOLUTIONS ON THE VOLUME OF GLASS PYCNOMETERS

	I	II	III
Temperature	110°C	110°C	150°C
Wt % KOH	43.99	52.60	52.60
Pycnometer volume before measurement	5.080 ml.	5.038 ml.	5.048
Pycnometer volume after measurement	5.083	5,041	5.056

The density measurements are given in Table 2, and are compared with densities reported by the Solvay Process Division of Allied Chemical Corporation (6). The latter measurements were made using a hydrometer.

TABLE 2

EXPERIMENTAL MEASUREMENTS FOR DENSITY OF KOH SOLUTIONS AT 1 ATM. PRESSURE

Temperature	Wt % KOH	Method	Measured Density	Solvay Values (6)
30°C	4.40	a	1.035 g./ml	1.034 g./ml
30	8.66	a	1.071	1.074
30	17.47	a	1.159	1.158
30	27.08	a	1.261	1.253
30	32.07	a	1.310	1.305
50	4.40	a	1.026	1.027
50	8.66	a	1.062	1.065
50	17.47	a	1.150	1.147
50	27.08	a	1.250	1.242
50	32.07	a	1.300	1.294
70	4.40	a	1.014	1.018
70	8.66	a	1.049	1.056
70	17.47	a	1.138	1.137
70	27.08	a	1.241	1.232
70	32.07	a	1.289	1.283
70	44.02	b	1.418	1.413
90	6.57	b	1.023	1.029
90	10.60	b	1.055	1.064
90	17.32	b	1.124	1.126
90	30.77	b	1.258	1.258
90	44.02	b	1.398	1.401
110	32.40	b	1.261	1.265*
110	43.99	b	1.389	1.387*
110	52.60	b	1.492	1.479*
150	52.60	b	1.472	

* Extrapolated values

2.3 Vapor Pressure Measurements

Experimental vapor pressure measurements have been made for KOH concentrations in the range 0-53.9 wt. % for vapor pressures up to 2 atm. (temperatures up to 170°C). The measurements were made by a static isoteniscope method which has been described in detail in a previous report (3).

Table 3 shows the results obtained together with values from International Critical Tables (denoted "Lit." in Table 3). The experimental results are plotted in Figure 1 as log p vs. T. Results obtained at constant wt. % KOH fall almost on a straight line when plotted in this way; the linearity appears to improve somewhat at higher concentrations of KOH.

For most of the results in Table 3 the agreement between experimental and literature values is moderately good (within a few percent). However the measurements of low vapor pressures reported here are generally several mm. below the literature values, and it seems likely that a consistent experimental error occurred in the experimental measurements at low pressures. Also, the measurements of vapor pressures above one atmosphere for 53.9 wt. % KOH solutions were not in agreement with measurements for lower temperatures at this concentration, and appear to be in error.

In view of the rather poor precision shown by the vapor pressure results, other methods of determining vapor pressures are being examined. The static method used to date has the advantage of simplicity, but has serious deficiencies when used for mixtures, and does not seem capable of yielding the desired accuracy.

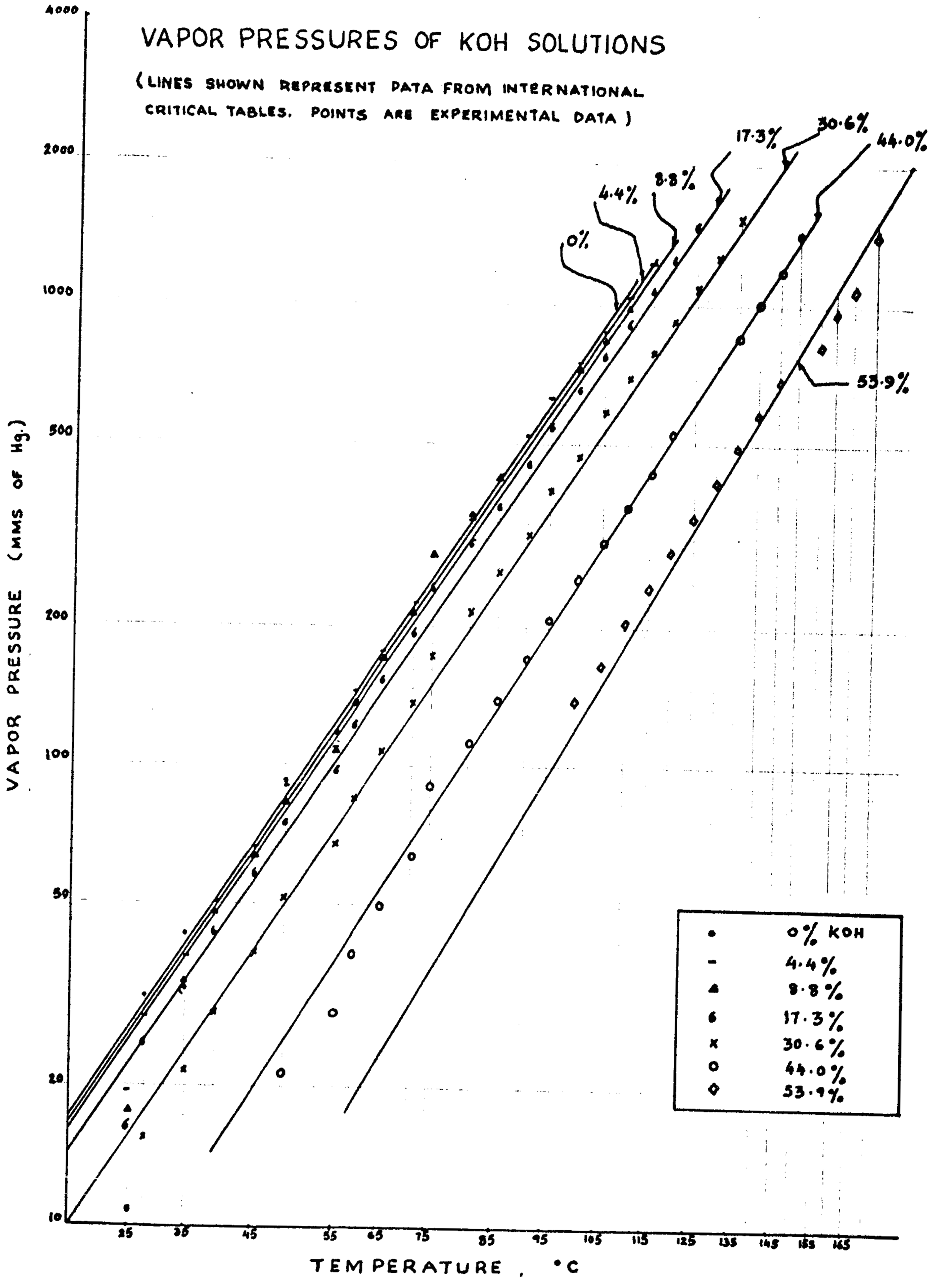
TABLE 3

VAPOR PRESSURE OF AQUEOUS POTASSIUM HYDROXIDE SOLUTIONS

Wt. % KOH	0		4.4		8.8		17.3		30.6		44.0		53.9	
T °C	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
20		17.54		17.02		16.31		14.55		10.1		4.51		1.38
25		23.7	19.1	23.0	17.4	21.8	16.1	19.3	10.6	13.7				
30	31.5	32.0	27.9	31.0	28.3	29.1	24.2	26.0	15.2	18.3				
35	43.0	41.3	38.0	41	33.2	38.5	32.5	34.4	21.3	24.5				
40		55.3	51.0	53.6	47.4	51.5	43.3	45.8	28.8	32.3		15.0		5.6
45		71	66.5	68	63.4	65.5	57.7	58.3	38.1	41.5				
50	92.8	93	90.0	90	83.5	85.4	74.5	76.5	50.8	54	21.2	25.9		
55	118.3	118	108.4	112	107.6	108	96.4	97	66.7	68	28.8	33.2		
60		149.5		144.6	138.0	139.1	121.9	124.2	85.0	88.0	38.3	43.0		18.5
65			177.1	181	171.0	171	152.5	155	108.2	110	49.7	55		
70			226.5	227	216.7	216	192.5	193	135.1	136	63.4	69		
75				278	289.4	264	245.7	238	174.6	170	90.1	87		
80		355.5	342.8	344	347.1	331	300.8	297	216.3	210	110.3	106		48
85			427.0	424	423.5	405	368.1	364	264.6	256	138.2	137		
90			520.3	517	512.3	495	448.5	438	322.8	312	169.2	168		
95			628.9	622	618.5	594	541.5	528	393.8	378	207.2	206		
100		760.0	751.8	736	730.6	708	651.5	632	470.0	450	250.5	251	139.6	126
105			868	880*	839	840*	766.2	758*	583.2	565*	300.3	305*	168.4	153*
110			1031	1050*	996	1000*	909	905*	690.6	655*	363.2	366*	203.7	187*
115			1211	1240*	1172	1180*	1073	1070*	784	770*	430.1	440*	242.8	230*
120							1253	1260*	923	905*	514.8	526*	288.7	280*
125							1474	1470*	1091	1075*			346.9	337*
130									1274	1250*			412.8	404*
135									1501	1460*	847	860*	486.1	485*
140											1002	1040*	576.9	580*
145											1186	1220*	680.1	690*
150											1413	1410*		810*
155													806	
160													967	
165													1166	
170													1409	

* Extrapolated values

FIGURE 1


VAPOR PRESSURES OF KOH SOLUTIONS
(LINES SHOWN REPRESENT DATA FROM INTERNATIONAL CRITICAL TABLES. POINTS ARE EXPERIMENTAL DATA)
VAPOR PRESSURE (MMS OF Hg.)
4000
2000
1000
500
200
100
50
20
10
TEMPERATURE, °C
25
35
45
55
65
75
85
95
105
115
125
135
145
155
165
0%
4.4%
8.8%
17.3%
30.6%
44.0%
53.9%
• 0% KOH
- 4.4%
▲ 8.8%
6 17.3%
x 30.6%
o 44.0%
◇ 53.9%

3. GAS SOLUBILITY IN AQUEOUS KOH SOLUTIONS

Up to the present time, all work has been directed towards measuring the solubility of oxygen in KOH solutions at various concentrations and temperatures. The solubility of hydrogen in KOH solutions will be studied as soon as the solubility of oxygen has been determined.

As noted earlier, Gubbins and Walker (1) had already found that the sharp decrease in oxygen solubility at increasing KOH concentration would soon lead to inaccurate solubility measurements with the method then in use. This method, which involved chromatography of the gas stripped from the solution by a stream of helium, has been described in detail by Gubbins, Carden, and Walker (7). The basic method appeared to be sound provided that a means could be devised for stripping larger volumes of saturated solution of the dissolved gas and concentrating the stripped gas in a manner which would permit its rapid introduction into the chromatograph. This proved to be a much more difficult and time-consuming task than had been anticipated, but it appears that a suitable technique has now been perfected; this is discussed below and new data presented.

3.1 Current Experimental Method

The principal difficulty with the original procedure was that the area of the peak recorded for oxygen was too small to measure accurately when the solubility decreased to only a few per cent of the solubility in water.

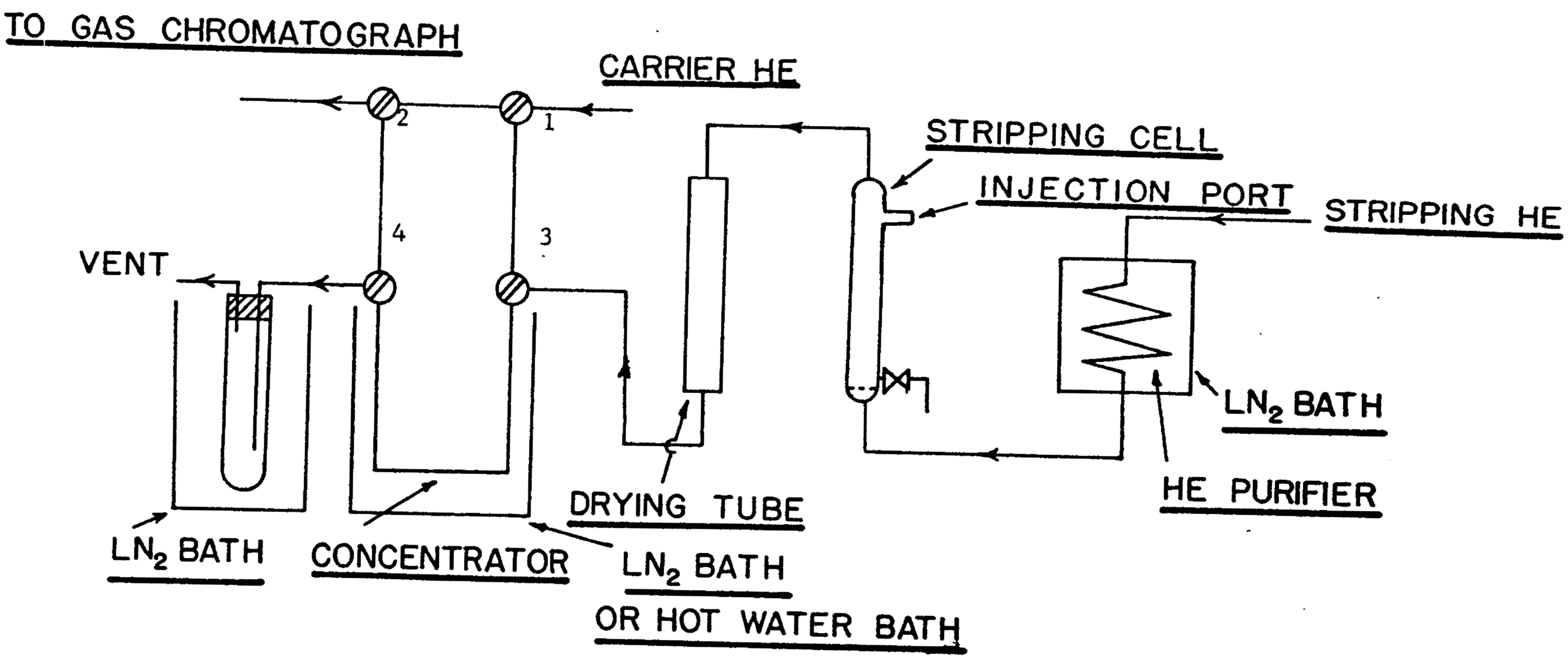
After testing numerous approaches, a satisfactory technique for stripping and concentrating dissolved gases was developed, and it is shown schematically in Figure 2. The saturator (not shown) is identical with that described in an earlier paper (7), as is the chromatograph.

The following procedure is used in making a measurement: Solenoid valves 1 and 2 are set to permit helium carrier gas to flow directly through to the sample column of the chromatograph, and the carrier helium flowrate is adjusted to the desired value. Solenoid valves 3 and 4 are set to permit stripping helium to flow through the system as shown in Figure 2. Liquid nitrogen baths are positioned as shown in Figure 2, and the stripping helium flowrate adjusted to the desired value (generally about 30 ml/min.).

Stripping helium passes first through an adsorption column at the temperature of liquid nitrogen for removal of all adsorbable impurities. It then flows to the stripping cell, which is merely an enlarged version of the one described in reference 7. Saturated KOH solution from the saturator is injected in any desired amount at the injection port. The fritted glass disc produces small bubbles which rapidly strip dissolved gases from the solution in the stripping cell. The stripping helium, now containing the stripped gas and water vapor, is first dried by passing through a column of Drierite (necessary because the molecular sieve used in the chromatograph adsorbs water vapor irreversibly), then it flows through Solenoid valve 3 to the concentrator, where the stripped gases are adsorbed. Stripping helium passes on through Solenoid valve 4 and the liquid nitrogen trap from which it is vented to the atmosphere.

Figure 2

DISSOLVED GAS STRIPPER AND CONCENTRATOR



NOTE: HE PURIFIER COLUMN AND ADSORPTION COLUMN ARE FILLED WITH ACTIVATED CHARCOAL

After the injected solution has been stripped for the desired time (usually about 5 min.), valves 3 and 4 are set to stop the flow of stripping helium and to connect to valves 1 and 2. The liquid nitrogen bath is removed from the concentrator and replaced by a bath of boiling water for a specified period (usually 5 min.), which causes essentially complete desorption of the adsorbed gases. Valves 1 and 2 are then set to direct the flow of carrier helium through the concentrator, and the desorbed gas sample is then swept into the chromatograph where the amount of dissolved gas in the injected sample of solution is measured in the manner described in reference 7.

3.2 Solubility of O_2 in KOH at 25°C

The experimental technique described in the previous section was perfected too late to permit many measurements. However, a few solubility data at 25°C were obtained and these are given in Table 4. These data, along with those reported earlier by Gubbins and Walker (1), and Geffcken (8), are shown in Figure 3, where log S is plotted versus wt. per cent KOH.

TABLE 4

SOLUBILITY OF O_2 IN KOH AT 25°C

(New UF data)

Wt/KOH	$S \times 10^3$	
6.5	0.788	g.mole/l.
10.2	0.588	
17.6	0.300	
43.99	0.044	

It may be seen that the new data lie along a straight line which is a fairly good average of the earlier data reported except for the high KOH concentration

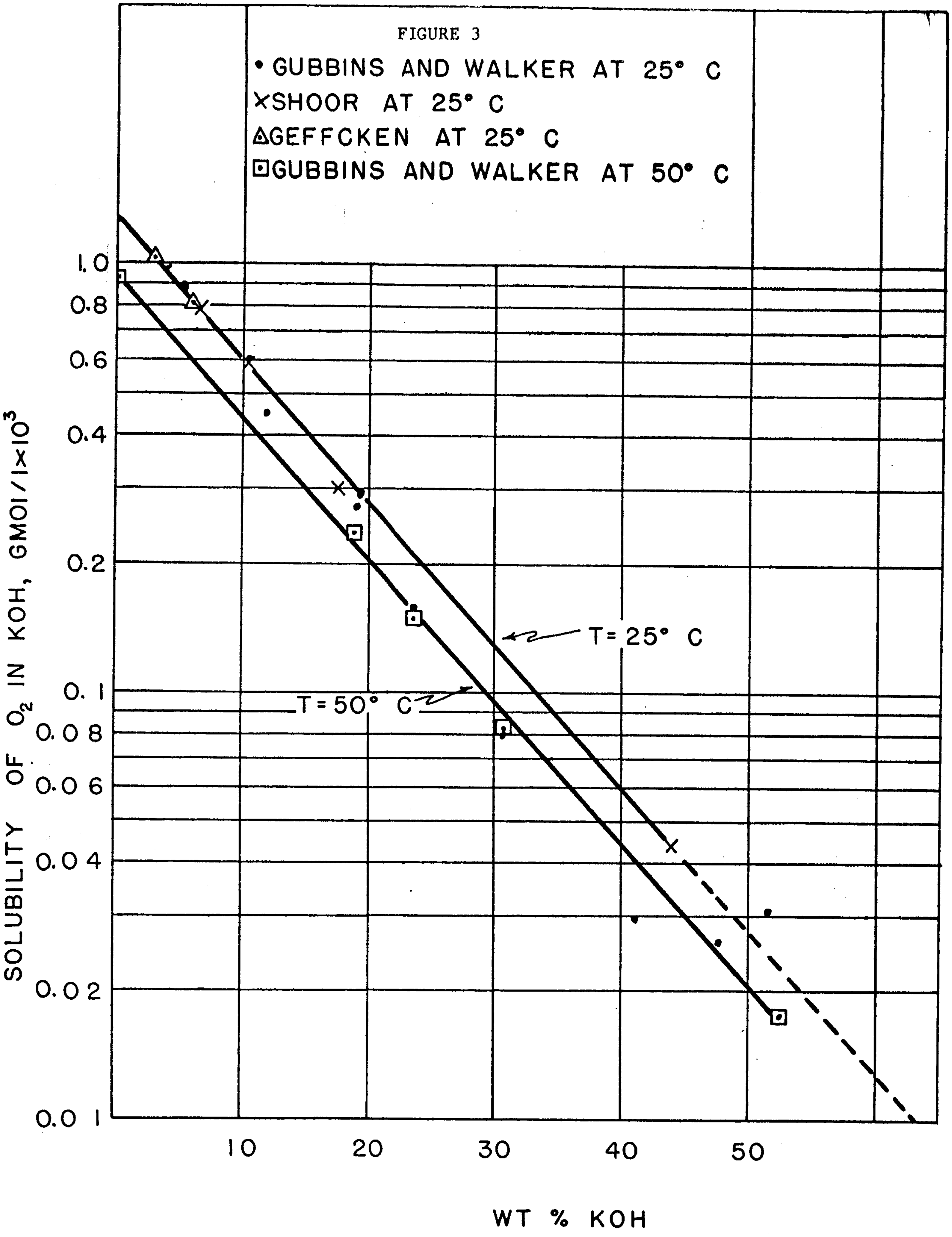


FIGURE 3

• GUBBINS AND WALKER AT 25° C
× SHOOR AT 25° C
△ GEFFCKEN AT 25° C
⊡ GUBBINS AND WALKER AT 50° C
T = 25° C
T = 50° C
SOLUBILITY OF O2 IN KOH, GMOl/l × 10^3
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
10
20
30
40
50
WT % KOH

values of Gubbins and Walker (1) which were suspected of being inaccurate. It also seems worth noting that the data of Knaster and Apel'baum (9) for the solubility of oxygen in KOH solutions at 21°C fall fairly close to the line of Figure 3 up to a KOH concentration of about 30 wt. per cent.

Also plotted on Figure 3 are the data of Gubbins and Walker (1) for the solubility of oxygen in KOH at 50°C. These data, too, lie close to a straight line on the semi-log plot which is parallel to the 25°C line and displaced towards lower solubilities. The ratio of the solubility at 50°C to the solubility at 25°C appears to be relatively constant at about 0.75 over the KOH concentration range studied.

A question may arise as to why the earlier data of Gubbins and Walker for solubility of oxygen in KOH at 25°C and high KOH concentrations scatter more than those for solubility at 50°C even though the solubility at 50°C is less than the solubility at 25°C and low solubility is judged to be a principal difficulty in making accurate measurements at high KOH concentrations. Frankly, it does not appear that sufficient data are available to substantiate any conclusions.

4. THE DIFFUSIVITY OF OXYGEN AND HYDROGEN IN KOH SOLUTIONS

Methods for determining the diffusion coefficients of oxygen and hydrogen in KOH solutions that have been considered include electrochemical methods and diaphragm cell methods. Experimental studies carried out to date have consisted of the development of a new steady-state diaphragm cell technique.

The commonly used diaphragm cell procedure (10,11) is attractive because of its simplicity, and the method is capable of giving quite accurate results. A drawback of the method is the considerable time, usually 2-3 days, required to obtain a measurement. Experimental studies of the diffusion of dissolved gases by the diaphragm cell method involve additional difficulties in the filling of the cell and subsequent analysis of the solutions (12). Analyses of the required accuracy are particularly difficult to obtain when the gases are very sparingly soluble, as is the case in the present work.

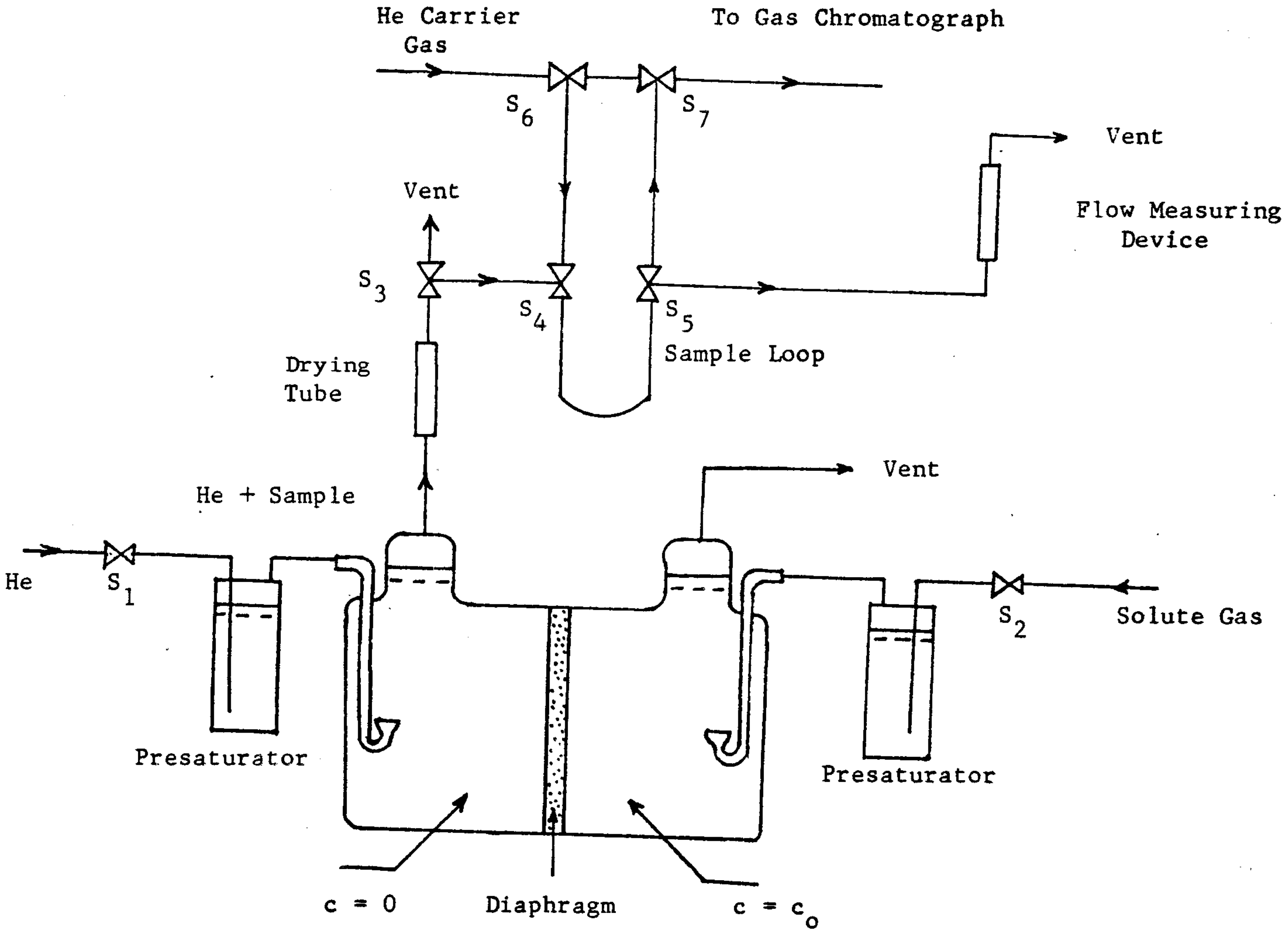
A more rapid and accurate measurement procedure has been developed in which the diaphragm cell is operated in steady state. In order to test the procedure, measurements of the diffusion coefficients of carbon dioxide and of several saturated hydrocarbon gases in water have been made; these systems were chosen to test the method since values of diffusion coefficients are available in the literature (15), and the gases readily lend themselves to analysis by gas chromatography.

4.1 Experimental

The diaphragm cell (Figure 4) was operated horizontally, with a gas space above the liquid in each compartment. A glass diaphragm having a diameter of 9 cm. and a mean pore size of about 5 μ was used,

Figure 4

SCHEMATIC DIAGRAM OF THE STEADY STATE DIAPHRAGM DIFFUSION CELL



and the cell compartments had a volume of approximately 350 ml. The cell was filled with solution under vacuum, and the last traces of air removed from the diaphragm in the following manner (11): The solution to be studied and the cell were connected with a stopcock and each evacuated about 20 min. with the stopcock closed. The stopcock was opened and the vapor pressure of the solution caused filling of the cells. When the upper compartment was almost filled with liquid, the last traces of gas contained in the frit were removed by varying the pressure differential to raise and lower the liquid level in the upper compartment. When no further bubbles appeared in the liquid the frit was assumed to be filled. The solute gas under study was passed slowly and continuously through the liquid in one of the compartments, keeping the concentration of dissolved gas close to the saturation value. A stream of helium was passed through the liquid contained in the other compartment, thus removing diffused solute gas from solution and keeping the concentration in this compartment close to zero. The flow-rates of both gas streams were controlled by very fine metering valves, S_1 and S_2, and the gases were presaturated with water before entering the cell. Both the diaphragm cell and presaturators were kept in a water bath controlled to $0.01^{\circ}C$. Gas flowrates of about 30 ml./min. were used; gas flowrates greatly in excess of this value were found to give rise to pressure fluctuations between the two compartments.

The concentration of diffused gas in the helium stream leaving the cell was determined by gas chromatography. A hydrogen flame ionization detector was used to determine hydrocarbon gases, and for measurements of carbon dioxide a hot-wire detector was used. After the steady-state condition had been achieved (usually between 1 and 2 hours) the helium gas flowrate was determined using a soap bubble meter, and a sample of the gas stream of known volume was trapped between the valves S_4 and S_5. The three-way solenoid valves S_4, S_5, S_6, S_7 were then so adjusted as to pass the sample to the gas chromatograph. At the end of the experiment samples of the liquid from each of the cell compartments were removed using a syringe and analysed for dissolved gas by gas chromatography. No measurable concentration of dissolved gas was found in samples taken from the helium side of the cell.

The diffusional resistance provided by liquid in the diaphragm may be considered equivalent to that of a cylinder of stagnant liquid of length L and cross-sectional area A, the volume of the liquid being equal to the volume of liquid contained in the frit. At steady state the total flowrate of diffusing material will be

$$N = \frac{Ac_oD}{L} = \gamma c_oD \tag{1}$$

where $\gamma = A/L$ is a cell constant. The cell was calibrated by obtaining the quasi-stationary cell constant β using 0.1N potassium chloride. The cell was completely filled with liquid and operated vertically, the liquids in each compartment being stirred with magnetic stirring bars. The procedure used was identical to that described by Robinson and Stokes (14). The quasi-stationary cell constant thus obtained is related to the steady state cell constant by

$$\beta = \frac{A}{L}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) = \gamma\left(\frac{1}{V_1} + \frac{1}{V_2}\right) \tag{2}$$

so that determinations of β and the volumes of the cell compartments were sufficient to determine γ. The cell constant was checked at frequent intervals; when not in use the diaphragm was filled with a solution containing 1 p.p.m. copper sulphate to prevent changes in the cell calibration due to the formation of algae.

Clearly, at high KOH concentrations and high temperatures a porous glass diaphragm will be unsuitable. Other materials are being investigated at the present time and it appears that one or more of these will prove satisfactory.

The gases used were obtained from the Matheson Company. The minimum purities were methane and ethane 99.0%; propane and butane 99.5%; carbon dioxide 99.99%.

4.2 Results and Discussion

Measurements of the diffusion coefficients of methane, ethane, propane, butane and carbon dioxide in water have been made. Table 5 compares the results obtained with values from the literature. The results reported are the mean values for about 5 measurements in each case; the values of precision shown are the standard deviations of the arithemetic mean. Literature values of diffusion coefficients reported by Witherspoon and Saraf (15) were obtained by the capillary cell method, and those of Unver and Himmelblau (16) were made by studying gas adsorption using a liquid jet. Several other workers have studied the diffusion of carbon dioxide in water (13), and at 25°C report values of D ranging from 1.74 to 1.92 x 10^{-5} cm.^{2} sec.$^{-1}$. At 40°C Ringbom (17) has reported a value of 2.75 x 10^{-5} cm.^{2} sec.$^{-1}$ for carbon dioxide diffusing in water. In view of the difficulties involved in making experimental determinations of the diffusion coefficient for sparingly soluble gases (13), the agreement shown in Table 5 appears to be quite good.

In summary, the principal advantage of the steady-state method over procedures previously described is the speed with which measurements may be made. For the cell used in this work a single measurement took about 2 hours. The steady state procedure is simpler and requires much less handling of liquids containing dissolved gases than the conventional diaphragm cell method. Since a measurement is not made until a steady state is reached, the possibility of adsorption of the diffusing gas on the diaphragm is not a problem, as it may be in the unsteady state diaphragm cell procedure.

TABLE 5

COMPARISON OF EXPERIMENTAL RESULTS WITH VALUES FROM LITERATURE

Gas	Temperature °C	Experimental Value $D \times 10^5$, cm.^{2}, sec.$^{-1}$	Literature Value $D \times 10^5$, cm.^{2}, sec.$^{-1}$	Reference
CH_4	25.0	1.99 ± 0.06	1.89	16
	40.0	2.36 ± 0.05	2.34	16
C_2H_6	25.0	1.53 ± 0.03	1.52	16
	40.0	2.02 ± 0.10	1.88	16
C_3H_8	25.0	1.27 ± 0.04	1.22	16
	40.0	1.63 ± 0.09	1.53	16
C_4H_{10}	25.0	0.97 ± 0.04	0.97	16
CO_2	25.0	1.89 ± 0.10	1.85	17
	40.0	2.81 ± 0.10	2.90	17
	60.0	4.15 ± 0.24	4.05	17

NOTATION

A = area of cylinder of stagnant liquid having resistance to diffusion equal to that of the diaphragm, cm.^{2}

c = concentration of dissolved gas, g.mole.cm.$^{-3}$

c_o = saturation concentration of dissolved gas, g.mole.cm.$^{-3}$

D = diffusion coefficient, cm.^{2} sec.$^{-1}$

L = length of cylinder of stagnant liquid having resistance to diffusion equal to that of diaphragm, and area A, cm.

N = total flowrate of diffusing gas, g.mole.sec.$^{-1}$

V_1, V_2 = volumes of cell compartments, cm.^{3}

β = cell constant for diaphragm cell operated using conventional quasistationary procedure, cm.$^{-2}$

γ = steady-state cell constant, cm.

5. FUTURE PLANS

Since the experimental methods which have been used for both density and vapor pressure measurements are proving unsatisfactory for high KOH concentrations and high temperatures, new techniques are being explored. A silver plummet has been procured for use with the Westphal balance, and it is expected that density measurements of adequate accuracy can be made with this equipment.

Two new techniques for measuring vapor pressure are being considered. These are (1), a static method in which the weight change of a KOH sample is measured when the vapor pressure of water around it is varied, and (2), a dynamic method in which the dewpoint of an inert gas is measured when it is in equilibrium with a KOH solution of known concentration and temperature.

A third graduate student is being assigned to these tasks, and it is expected that these physical property data will be available before the end of the next reporting period.

The newly developed method for determining gas solubility will be further applied to a study of oxygen dissolution in KOH solutions up to saturated KOH and 200°C. Determinations of the solubility of hydrogen in KOH solutions will be deferred until the data for oxygen are complete.

Since measurements of the diffusivity require a knowledge of the solubility of the gas at the KOH concentration and temperature in question, little additional work on the diffusivity is planned until most of the solubility data are in hand. At that time, efforts will be concentrated on the determination of the diffusivity of both hydrogen and oxygen in KOH solutions using the steady state diaphragm method described in this report.

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