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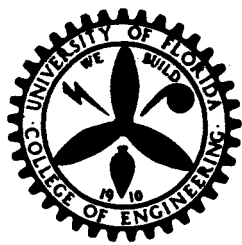
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GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 3.00

Microfiche (MF) .50

ff 853 July 65

**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

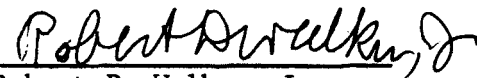
First Semi-Annual Report

Period Covered: September 1, 1965 - February 28, 1966

Prepared For

National Aeronautics and Space Administration  
Washington, D.C.

March 15, 1966



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## ABSTRACT

For the most part this period was utilized in the following manner:

- (1) Making a literature survey for pertinent data.
- (2) Planning and programming the most of the various tasks covered by the proposal.
- (3) Tooling up to conduct much of the experimental work.
- (4) Determining the density and vapor pressure of KOH solutions as required.

Data on the density and vapor pressure of aqueous potassium hydroxide solutions have been gathered from various literature sources and correlated. At the present time they are available only over a limited range of temperatures and concentrations, and it will be necessary to determine experimentally enough of the missing data to permit adequately accurate representation of the properties of the KOH-H<sub>2</sub>O system over the required range of temperatures, concentrations, and pressures.

A detailed program for the remainder of this year has been developed, and a fairly detailed plan for the second year of the grant. The first year plan involves (1) completion of vapor pressure and density measurements, (2) substantial progress, if not completion, of viscosity measurements, (3) a beginning on measurements of electrolytic conductivity, (4) completion of a substantial portion of the solubility measurements, and (5) a substantial beginning on diffusivity measurements with diaphragm cells.

Substantially all of the equipment for conducting the above-named experiments has been purchased, and much of it is set up and in operation.

Measurements of the density of aqueous KOH solutions have been completed at temperatures of 30°C, 50°C, and 70°C up to a concentration of 32 wt. per cent.

Vapor pressures have been measured for aqueous KOH solutions up to a temperature of 70°C and to a KOH concentration of 30 wt. per cent.



## 1. INTRODUCTION

Although a great deal of developmental research has been done on fuel cells and many significant advances have been made, many of the basic data for understanding the fundamentals of their operation are still lacking. A particular case in point is the estimation of the limiting current which can be supported at an electrode. Entirely aside from the question of transport within pores, adequate data do not exist to permit a calculation of the limiting currents for smooth electrodes. Few data exist on the solubility of gases in fuel cell electrolytes, especially if conditions far removed from room temperature and atmospheric pressure are involved. The situation is even worse when one examines the data for the diffusivity of gases which may be used in fuel cells. Since the limiting current density is proportional to the product of the solubility and the diffusivity, it is obvious that we are not in position to estimate confidently the limiting current density for even the simplest electrodes.

A few data on gas solubility in dilute electrolytes exist (1,2), and data for the diffusivity of hydrogen and oxygen in water are available over a limited range of temperatures (3). Virtually no data are available on the diffusivity of hydrogen and oxygen in strong alkaline electrolytes (4).

To make matters worse, present theories of the liquid state are in such a rudimentary stage of development that predictions of solubility and diffusivity in systems for which no experimental data are available are extremely hazardous. Indeed, it is not possible to extrapolate with confidence to greatly different conditions in systems for which experimental data are available. Semi-theoretical correlations, which are reasonably successful in predicting behavior in non-electrolytes, are of very limited

value at the present time in predicting the behavior of electrolyte systems.

This investigation, then, was undertaken with three purposes in mind:

1. To generate experimental data on the solubility and transport properties of hydrogen and oxygen in alkaline electrolytes. Since adequate data on other properties such as density, vapor pressure, viscosity, and the like do not exist over the range of temperatures and pressures of interest, some measurements of these, too, will be required.
2. To develop theories and/or correlations which afford a means of predicting behavior of systems for which there are inadequate experimental data, or to extrapolate to a different range of conditions.
3. To seek to understand more fully transport processes in fuel cells as these are affected by the various parameters involved.

## 2. SOLUBILITY OF OXYGEN AND HYDROGEN IN KOH SOLUTIONS

### 2.1 Experimental

The experimental method to be used consists of removing the dissolved gas from a sample of the solution, followed by quantitative analysis of the removed gas by gas chromatography. The method has been previously described in detail (5), and this paper is included in Appendix 2. The only modification to the procedure described there will be to design a sample cell in which the glass frit may be readily replaced; this is necessary since KOH solutions attack fritted glassware quite rapidly at higher temperatures.

During the period covered by this report the apparatus has been assembled, but no new measurements have been obtained as yet. A summary of the solubility measurements available in the literature is included in the next two sections.

### 2.2 Effect of Temperature and KOH Concentration on Solubility

Experimental measurements of the solubility of oxygen in potassium hydroxide solutions at 1 atmosphere partial pressure of oxygen have been reported by several workers. Geffcken (1) has reported data for KOH concentrations in the range 0-6.1 wt.%, and temperatures of 15 and 25°C; Knaster and Apel'baum (6) have given data for KOH concentrations up to 40.1% and temperatures in the range 21-75°C, and Gubbins and Walker (4) have reported measurements for the full concentration range at 25°C and 50°C. The solubility of hydrogen in KOH solutions has been reported by Geffcken (1) for the KOH concentration range 0-7.6% at 25°C, and by Knaster and Apel'baum (6) for the KOH concentration range 0-40.1% at 21°, 45° and 75°C.

The above solubility data is plotted in Figures 1 to 3 and tabulated in Appendix 1. The results of Geffcken and Gubbins and Walker (Figure 2) for oxygen are in good agreement, and also agree with measurements made by Lindstrom (see Section 2.3). These results agree less well with those of Knaster and Apel'baum (Figure 1), the latter results showing a less rapid decrease in solubility with rise in KOH concentration; however the discrepancies between the two sets of data amount to less than 20% of the solubility over the range of temperature and concentration studied. The results for hydrogen shown in Figure 3 also shows some disagreement between the data of Geffcken and Knaster and Apel'baum.

The data in Figures 1 to 3 show that the solubility decreases rapidly with rising KOH concentration at all temperatures; thus for oxygen at 25°C, using the data from Figure 2, the solubility in 50% KOH is only about 3% of the value for pure water. The temperature coefficient of solubility also varies rapidly with rise in KOH concentration; using the data in Figure 1, the temperature coefficient is approximately  $-0.015 \text{ g.mole.l.}^{-1}(\text{°C})^{-1}$  for pure water, but is only  $-0.00013 \text{ g.mole.l.}^{-1}(\text{°C})^{-1}$  for 40% KOH. The temperature coefficient also appears to decrease with rise in temperature.

### 2.3 Effect of Pressure on Solubility

Lindstrom (7) has made measurements of the variation of oxygen solubility with pressure for 23.1% KOH solutions at 25°C; the range of pressure covered was 0-10 atmospheres. The results are shown in Figure 4, and follow a straight-line relationship above 3 atm. Lindstrom reports that a consistent error may have been obtained in his results due to gas

that was not released from the liquid. A straight line through the origin of slope equal to the straight-line portion of the experimental curve is therefore probably a fairly good approximation to the true behaviour (this line is shown in Figure 4); this line is in excellent agreement with the data of Gubbins and Walker. As would be expected from theoretical considerations, these results indicate that the variation of solubility with pressure closely obeys Henry's Law for this system.

Figure 1. Solubility of  $O_2$  in KOH, Data of Knaster and  
Apel'baum (6)

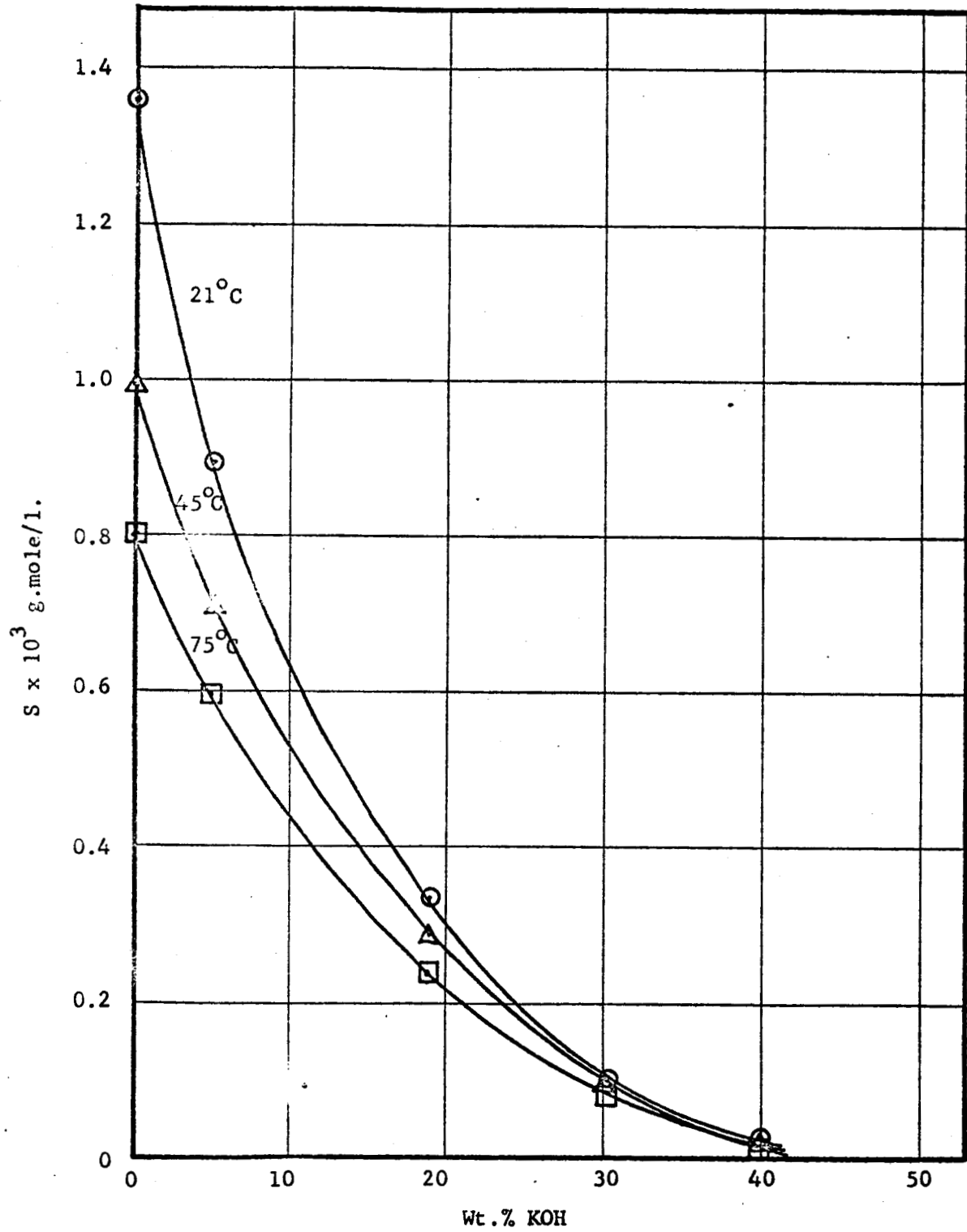


Figure 2. Solubility of  $O_2$  in KOH, Data of Geffcken (1) and Gubbins and Walker (4)

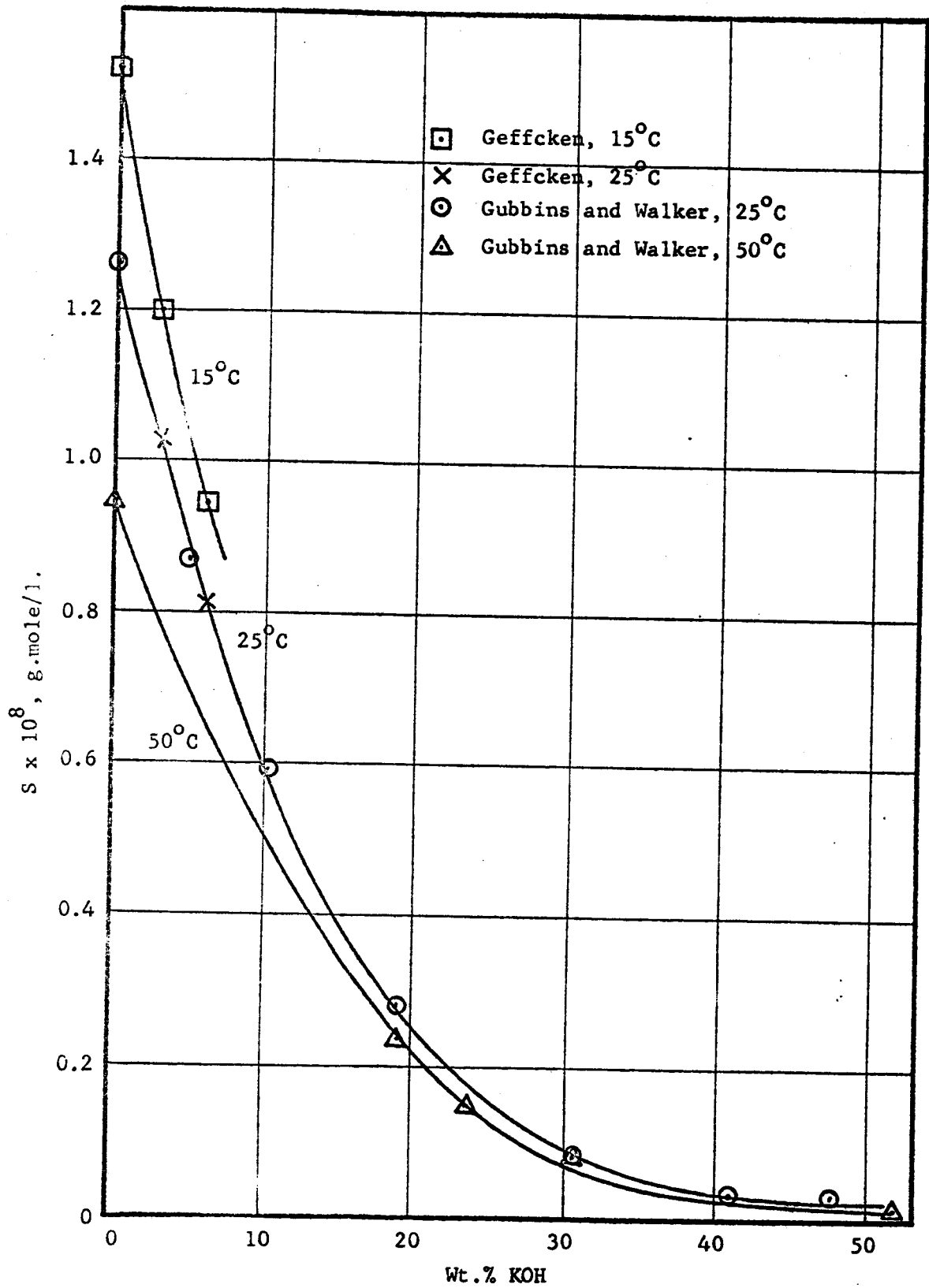


Figure 3. Solubility of  $H_2$  in KOH, Data of Geffcken (1) and Knaster and Apel'baum (6)

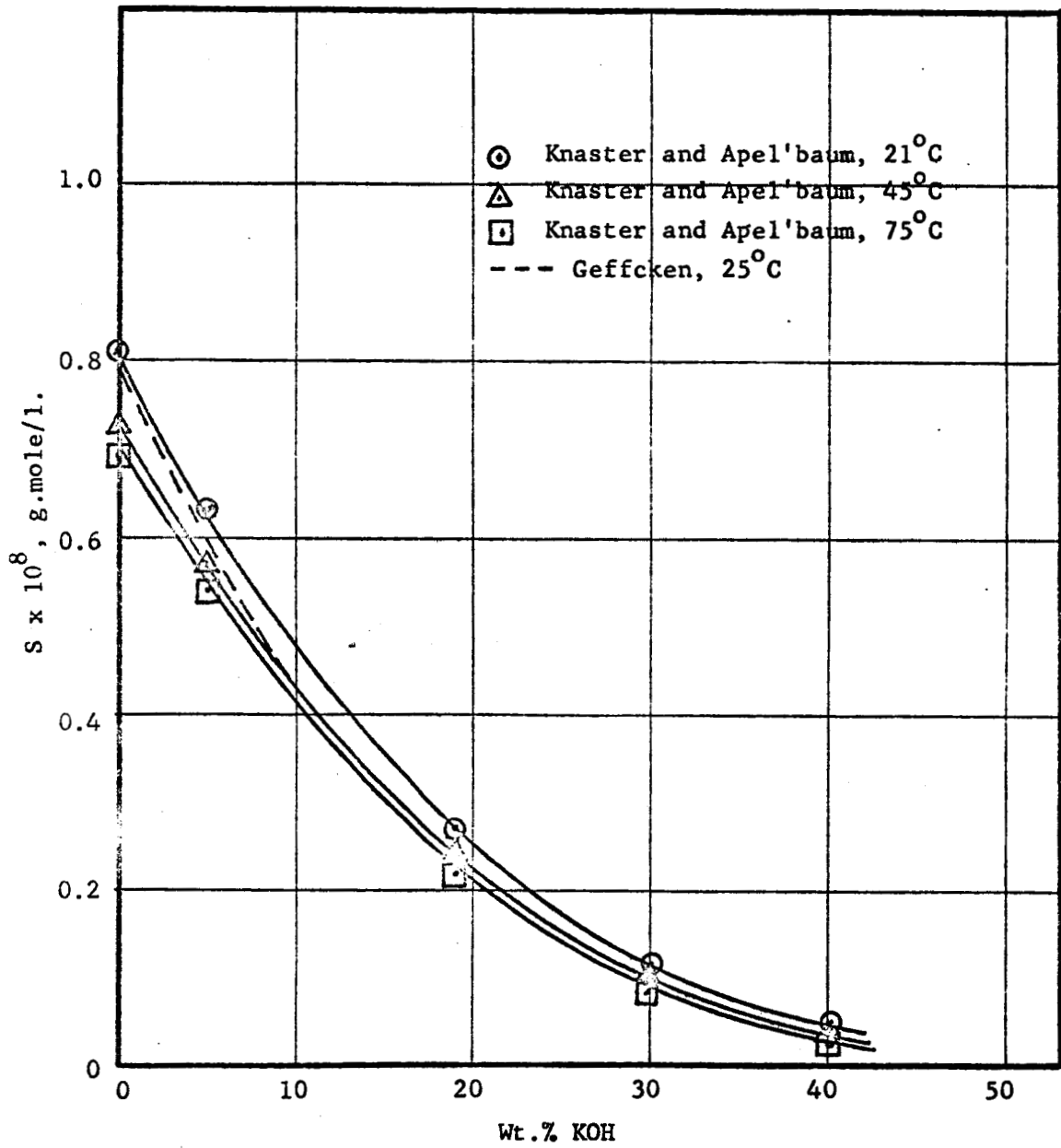
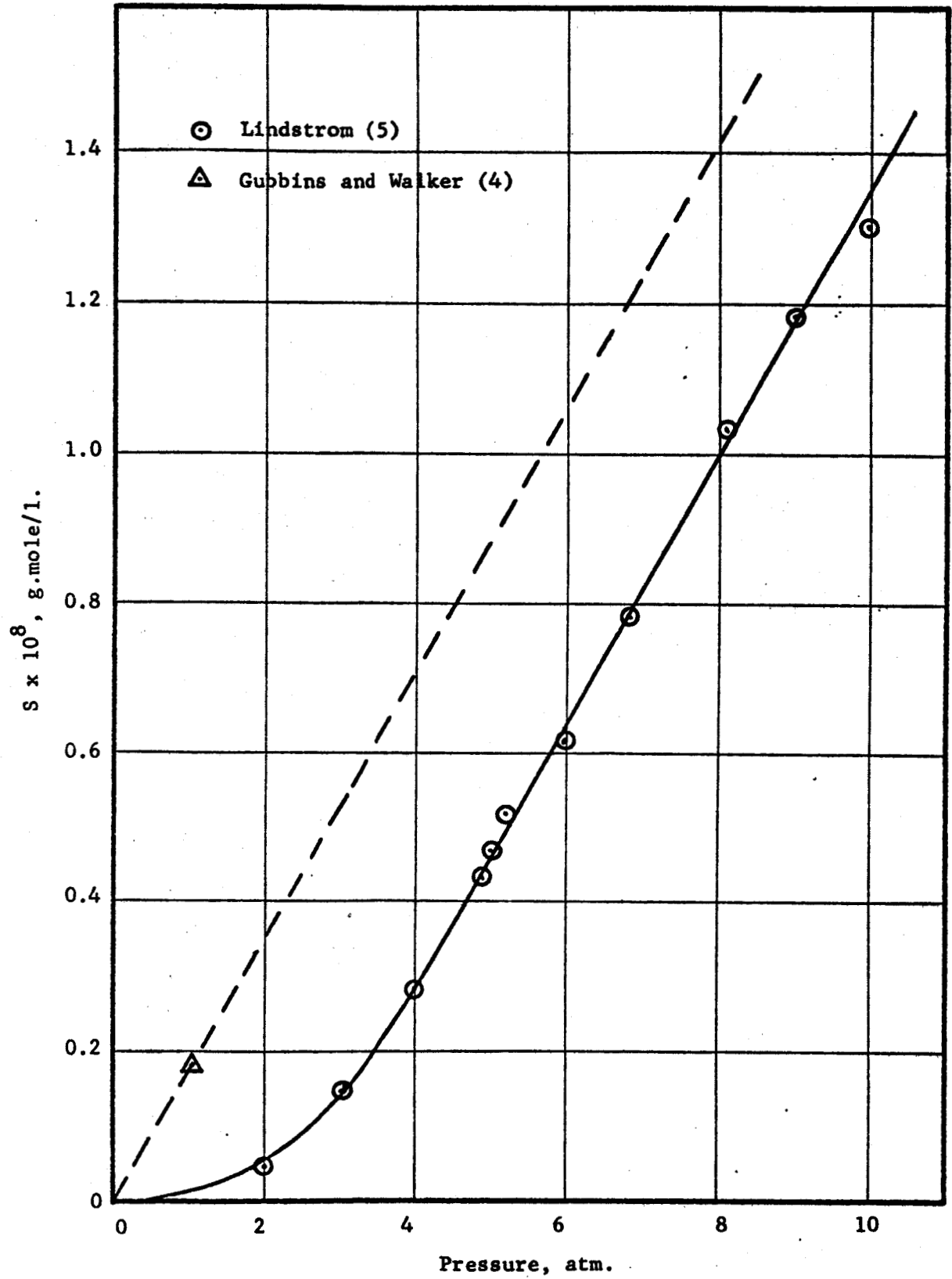




Figure 4. Variation of Solubility with Pressure for 23.1% KOH at 25°C, Data of Lindstrom (7)



### 3. THE DIFFUSIVITY OF HYDROGEN AND OXYGEN IN POTASSIUM HYDROXIDE SOLUTIONS

It was pointed out in the introduction that few experimental data exist on the diffusivity of gases in electrolytic solutions. One of the chief aims of this investigation is to provide some of these. Lightfoot (8) has recently reviewed the theory and techniques of measuring diffusivities. A considerable number of methods are available for experimental determination of diffusion coefficients. However, barring unforeseen circumstances, only two quite different techniques will be used in this work: (1) electrochemical methods, and (2) diaphragm cell methods. Each of these will be discussed briefly in following paragraphs.

#### 3.1 Electrochemical Methods

Basically, all electrochemical methods depend upon bringing about an electrochemical reaction at the interface between an electrode and an electrolyte in circumstances which permit a solution of the differential equations describing the transport processes. The diffusivity is then evaluated from the characteristics of the current-voltage or the current-time plot. Well-known variations are the dropping mercury electrode (DME), which has been thoroughly described by Kolthoff and Lingane (9), and the rotating disc electrode (RDE) described by Levich (10) and Riddiford (11). Recently Fatt (12) described a modification of a stationary electrode which appears to offer many possibilities. Each of these will be described more fully below.

##### 3.1.1 Polarography

Kolthoff and Lingane (9), among others, have described the theory and technique of polarographic measurements with the DME. Gubbins and Walker (4) used this technique to determine the diffusivity of oxygen in KOH

solutions. The modified Ilkovic equation (13,14) affords a means of calculating the diffusion coefficient if the solubility is known.

$$i_d = 607nD^{1/2}C_m^{2/3}t^{1/6} \left( 1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}} \right) \quad (3.1)$$

where  $i_d$  = the limiting diffusion current

$n$  = number of electrons involved in the reaction

$D$  = diffusivity

$C$  = concentration (solubility of reactant

$m$  = mass flow rate of mercury

$t$  = drop time of mercury

$A$  = a constant.

The value of the constant  $A$  is somewhat in question and the values derived from theory vary from 17 to 39. Experimentally, values for  $A$  appear to fall in the range 31.5 to 33.5 (15); a value of  $A = 31.5$  was used by Gubbins and Walker (4).

Polarography with the DME has the advantages of having been widely used and explored, and of a considerable range of equipments available. Moreover, the technique is relatively simple, and results are obtained rapidly. However, difficulties are experienced in obtaining the proper shape of the reduction wave, especially when the electrolyte is concentrated. These difficulties, as well as others, appear to limit the area of application of polarography to the study of oxygen reduction in not too concentrated solutions and at relatively low temperatures.

### 3.1.2 The Rotating Disc Electrode

Levich (10) showed that, under certain conditions, mass

transport from bulk fluid to a rotating disc electrode could be described quantitatively because mass transport was limited by diffusion across a thin layer of solution in contact with the electrode. Blurton and Riddiford (11) have extended and amplified the analysis to give a more detailed description of all of the phenomena involved. From a measurement of the limiting current density developed on these electrodes, the diffusion coefficient can be derived. The applicable equation is

$$i_{lim} = \pm 0.620zFD^{2/3}\gamma^{-1/6}\omega^{1/2}C(\infty) \quad (3.2)$$

where  $i_{lim}$  = the limiting current density for electrochemical reaction

$z$  = number of electrons involved in the electrode reaction

$F$  = the Faraday

$D$  = diffusivity of reacting species

$\gamma$  = kinematic viscosity =  $\mu/\rho$

$\mu$  = viscosity

$\rho$  = density

$\omega$  = angular velocity of electrode

$C(\infty)$  = bulk concentration of reactant.

Many investigators have made use of RDE techniques in recent years. It appears that the RDE will be quite suitable for measuring the diffusion coefficient of hydrogen in alkaline solutions. The diffusivity of oxygen may be measured in not too concentrated solutions of KOH, but Tobias (16) has reported difficulty at high concentrations of KOH which may be related to the electrode reaction itself (rather than diffusion) becoming rate-controlling. However, the RDE appears to hold sufficient

promise to warrant investigation for determining the diffusivity of hydrogen in KOH solutions.

### 3.1.3 The Modified Stationary Electrode

Both the DME and RDE require a knowledge of the solubility of a gas in the solution before one can evaluate the diffusivity. For diffusivity measurements this not only constitutes a problem of the additional required data, but it also introduces errors. Any error in the measured solubility is automatically carried over into the diffusivity. Thus, experimental diffusivities determined by DME and RDE techniques are distinctly limited as to their accuracy and precision. It is obviously desirable to utilize experimental methods which do not suffer from this disadvantage; and it appears that the method proposed by Fatt (12) enables one to do so. A schematic diagram of Fatt's modified stationary electrode is shown in Figure 5.

Fatt's modified stationary electrode is based on the demonstration by DeBoodt and Kirkham (17) that a disc electrode at the surface of a semi-infinite body "sees" only about six diameters into the body. Thus, if the electrode is very small, say one micron in diameter, only a relatively thin layer of liquid is required to provide a semi-infinite body. It is possible then to obtain a layer without convection currents and still have the electrode reaction affect it in a negligible manner. Under these circumstances the current is diffusion-controlled, and the diffusivity can be evaluated from the linear portion of a plot of  $\log I/I_0$  versus time. The diffusivity is calculated from the equation

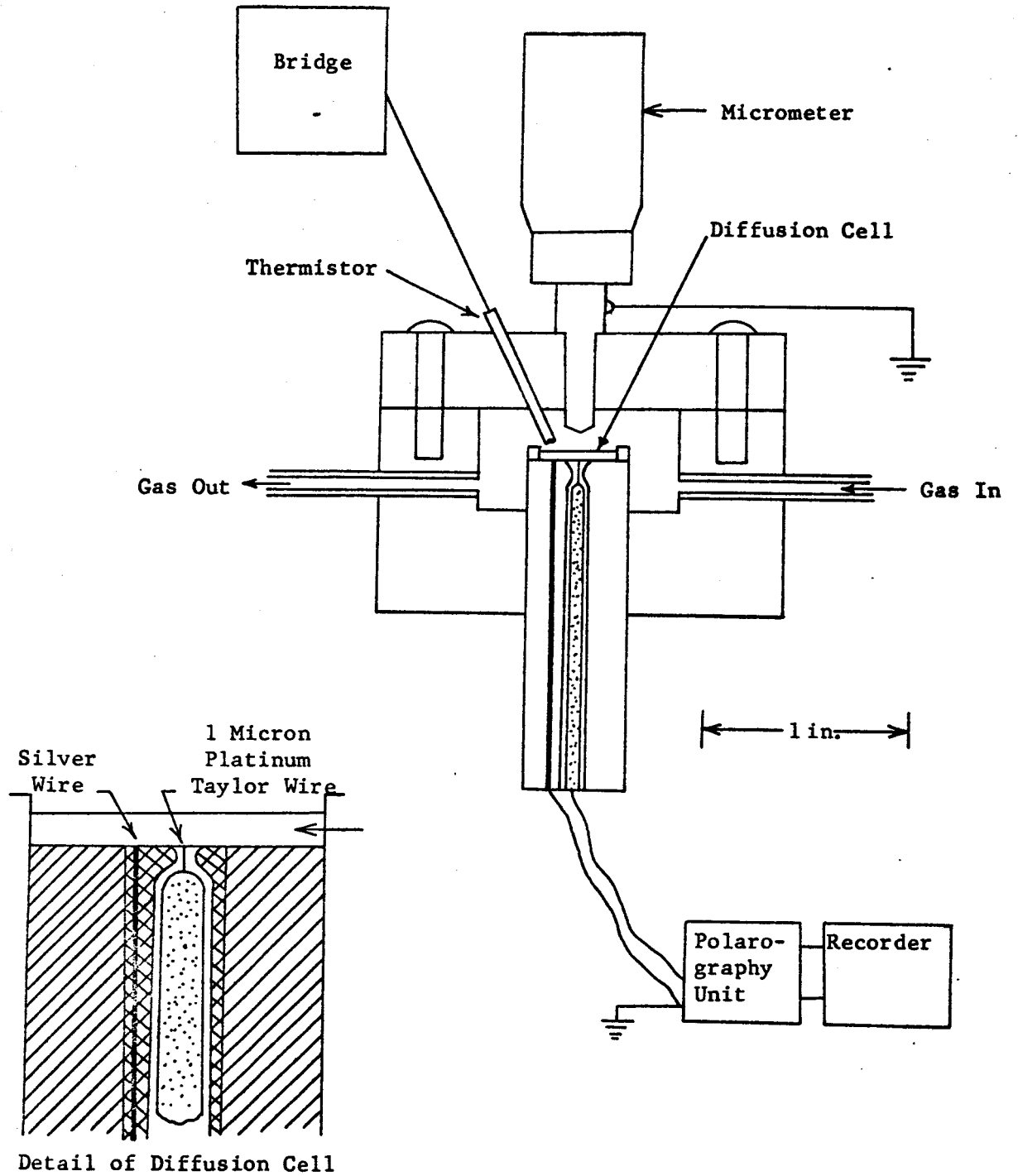


Figure 5. Apparatus of Fatt (12) for Studying Diffusion of Gases in Electrolyte Solutions

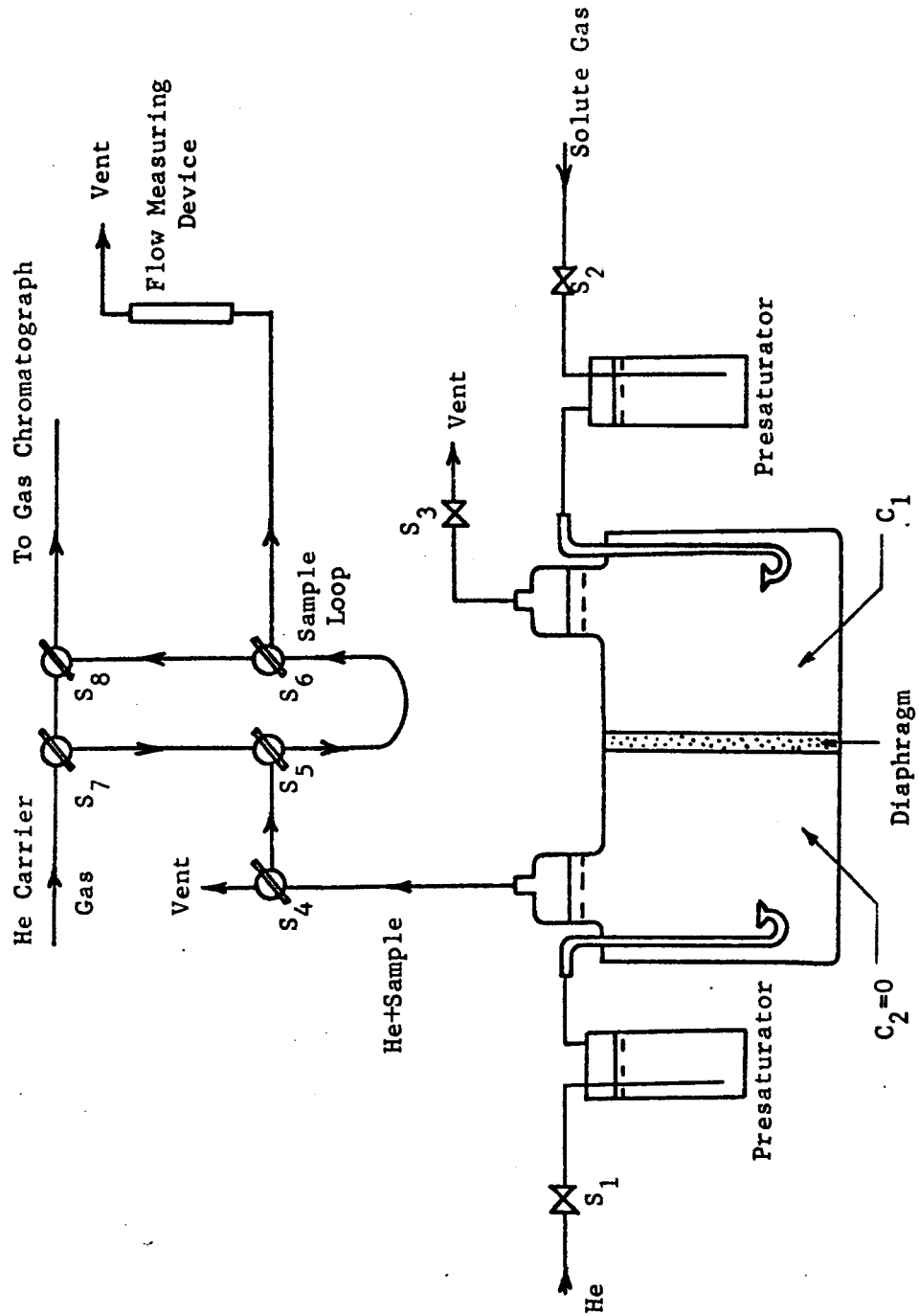


Figure 6. Steady-State Diffusion Apparatus

$$D = \frac{0.94 l^2}{t_1} \quad (3.3)$$

where  $I$  = current at any time  $t$

$I_0$  = current at time zero

$l$  = thickness of the diffusion layer

$t_1$  = time required for the linear portion of the  $\log I/I_0$  vs.  $t$  plot to decrease one logarithmic cycle.

### 3.2 Steady-State Diaphragm Cell Method (18)

The possibility of using a steady-state diaphragm cell method of measuring diffusion coefficients of gases in liquids has been examined. This work was originally initiated under a separate project as a general method of studying the diffusion of gases in liquids, but should be suitable to the study of oxygen and hydrogen in potassium hydroxide solutions.

A simplified diagram of the apparatus is shown in Figure 6. The diaphragm cell is operated horizontally, with a gas space above the liquid in each compartment. The solute gas under study is passed slowly and continuously through the liquid in one of the compartments, thus maintaining a concentration of gas close to the saturation value; a stream of helium is passed through the liquid contained in the other compartment, which effectively strips diffused solute gas from solution and maintains a concentration close to zero. After a suitable time period (about 1-1 1/2 hours for a medium porosity diaphragm) steady-state is attained. A sample of the gas issuing from the helium side is collected and analysed by gas chromatography. In Figure 6,  $S_1$  and  $S_2$  are fine metering valves, and the gases are presaturated by passing through the electrolyte solution under study.  $S_3$  provides a means of equalising the pressure above the compartments



(this is checked by a manometer not shown in the diagram).  $S_4$ - $S_8$  are three-way solenoid valves. When steady-state has been reached a gas-sample is trapped between  $S_5$  and  $S_6$ , and passed to the gas chromatograph. At steady-state the rate of diffusion of dissolved gas,  $N$ , is given by:

$$N = D \left( \frac{A}{l} \right) (c_1 - c_2) \quad (3.4)$$

where  $c_1$  and  $c_2$  are the concentrations of dissolved gas in the two compartments.  $\left( \frac{A}{l} \right)$  is a cell constant, and may be determined by a quasistationary experiment involving the diffusion of 0.1N KCl, using the standard procedure for diaphragm cell measurements (19).

The feasibility of this method has been studied using dissolved ethane diffusing in pure water at 25°C. The cell used for this study contained a porous glass diaphragm. The result obtained for the diffusion coefficient was  $1.62 \pm 0.01 \times 10^{-5} \text{ cm.}^2/\text{sec.}$ , the latter figure being the standard deviation for 5 determinations. This value is in quite good agreement with the value of  $1.52 \times 10^{-5} \text{ cm.}^2/\text{sec.}$  reported by Witherspoon and Saraf (20) and the value  $1.71 \times 10^{-5} \text{ cm.}^2/\text{sec.}$  given by Baird and Davidson (21).

This experimental method has the advantage that a diffusion measurement may be made within 2 or 3 hours; with the exception of electrochemical methods, other procedures require several days for a measurement. It is planned to construct a cell having a nickel or Teflon diaphragm for the study of potassium hydroxide solutions.

### 3.3 Diffusion Data

Up to the present time no new diffusion coefficient data have been generated; all efforts have been directed towards acquiring diaphragm cell

equipment, and setting it up. It is now possible to start experimental work on diaphragm cells. The application of electrochemical methods has been deferred for the present to afford an opportunity to make a reasonable number of measurements with diaphragm cells.

The only diffusion data available in the literature appears to be that of Gubbins and Walker (4) for the diffusion coefficient of oxygen in KOH solutions over the full concentration range at 25<sup>o</sup>C. These results were obtained by a polarographic method, and are shown in Figure 7, and tabulated in Appendix 1.

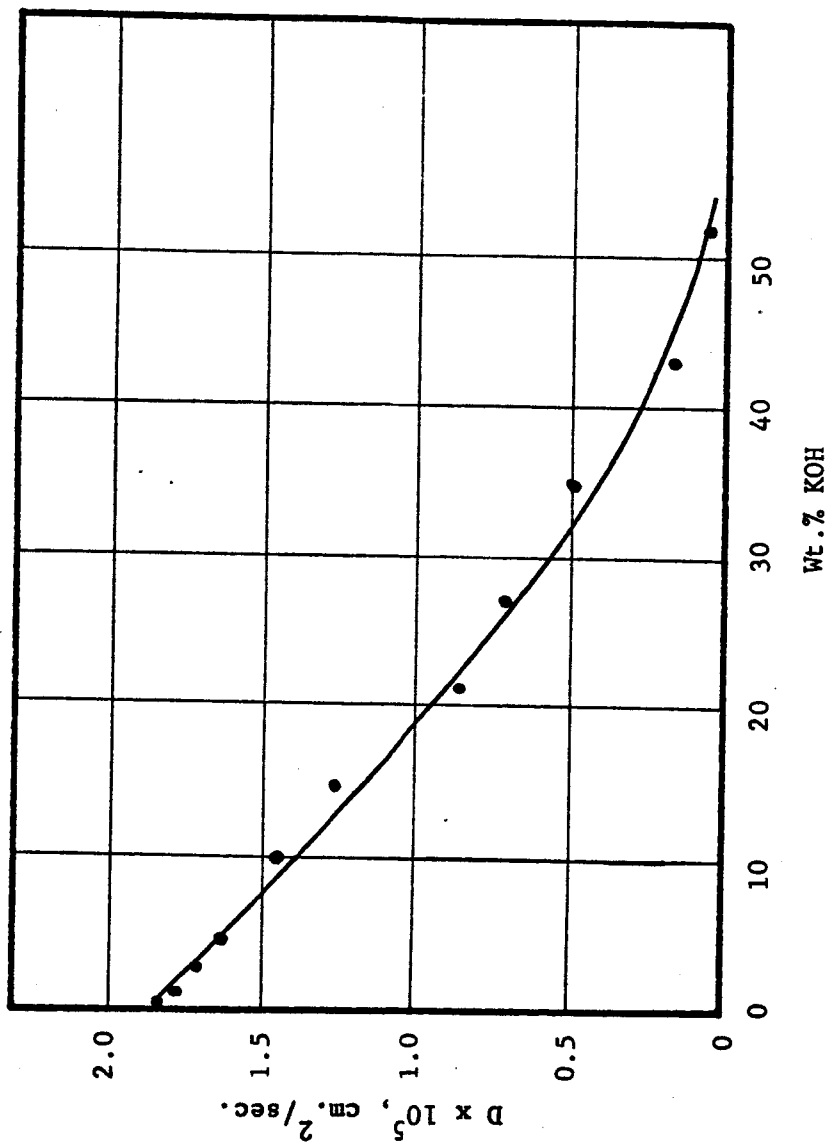


Figure 7. Diffusion Coefficients for  $\text{O}_2$  in KOH at  $25^\circ\text{C}$ ,  
Data of Gubbins and Walker (4)

#### 4. DENSITY OF KOH SOLUTIONS

##### 4.1 Experimental

Experimental density measurements have been made for KOH concentrations in the range 0-32 wt.% for temperatures of 30<sup>o</sup>, 50<sup>o</sup> and 70<sup>o</sup>C. The measurements were made using a Westphal balance having a glass plummet calibrated at 20<sup>o</sup>C; solution samples were equilibrated in a constant temperature water bath controlled to  $\pm 0.5^{\circ}\text{C}$ . Since the volume of the plummet varies with the operating temperature, and since KOH solutions may cause a slight decrease in plummet volume with time due to corrosion, the following procedure was employed. The manufacturer's calibration of the plummet was first checked at 20<sup>o</sup>C using pure distilled and de-ionised water, and found to be correct within experimental error. At each operating temperature (T), a measurement was first made using pure water, yielding an apparent density ( $\rho_{\text{app}}^{\text{w}}$ ) for water at that temperature. Apparent densities were then measured for KOH solutions of various concentrations ( $\rho_{\text{app}}^{\text{s}}$ ) at the same temperature, and finally the measurement for water was repeated to guard against the possibility of a volume change of the plummet due to corrosion. The actual density of a sample is then given by

$$\rho^{\text{s}} = \rho_{\text{app}}^{\text{s}} \left( \frac{V_1}{V_2} \right) \quad (4.1)$$

and

$$\rho^{\text{w}} = \rho_{\text{app}}^{\text{w}} \left( \frac{V_1}{V_2} \right) \quad (4.2)$$

where  $\rho^{\text{s}}$  = actual density of sample at temperature T

$\rho^{\text{w}}$  = actual density of water at temperature T

$\rho_{\text{app}}^{\text{s}}$  = apparent density of sample at temperature T, as indicated by Westphal balance

$\rho_{\text{app}}^{\text{w}}$  = apparent density of water at temperature T, as indicated by Westphal balance

$V_1$  = volume of plummet at 20°C

$V_2$  = volume of plummet at T

Equation (4.2) was used to determine the calibration constant ( $V_1/V_2$ ), using density values for pure water given in the literature. The sample densities were then evaluated from Equation (4.1). The calibration constant varied from unity at 20°C to 0.99715 at 70°C, and no measurable change in calibration was found to occur due to corrosion by the KOH solutions.

The above procedure has the advantage of providing rapid measurements, but cannot be used at temperatures above about 85°C, since pure water can no longer be used to calibrate the plummet. At high temperatures mercury is the only suitable calibration liquid, and has a density outside the measuring range of the Westphal balance. Density measurements at higher temperatures will be made using pycnometers, which will be calibrated at each temperature using pure mercury.

#### 4.2 Results

The density data obtained in this study is shown in Figure 8, and tabulated in Table 1; the error values shown in Table 1 are standard deviations from the arithmetic mean, about 6 measurements having been made at each condition. Density data available in the literature consist of data at 15°C from Lange (22), data for the temperature range -53.8°C to 0°C reported by Kelly (23), and data for the range 4.4°C to 98.9°C made available by the Solvay Division of Allied Chemical Co. (24). Some of this data is shown in Figure 9. A complete table of the literature data is

included in Appendix 1. The agreement of the experimental results with those provided by Solvay is generally good; however the differences between the two sets of results appear to exceed the limits of the expected experimental error. It should be noted that the Solvay data was obtained by hydrometer measurements, whereas the data reported here was obtained by Westphal balance. As noted earlier it is planned to make the high temperature measurements with a pycnometer. In view of the discrepancies noted above a few of the low temperature measurements will be repeated with the pycnometer as a check on the accuracy of the Westphal balance data.

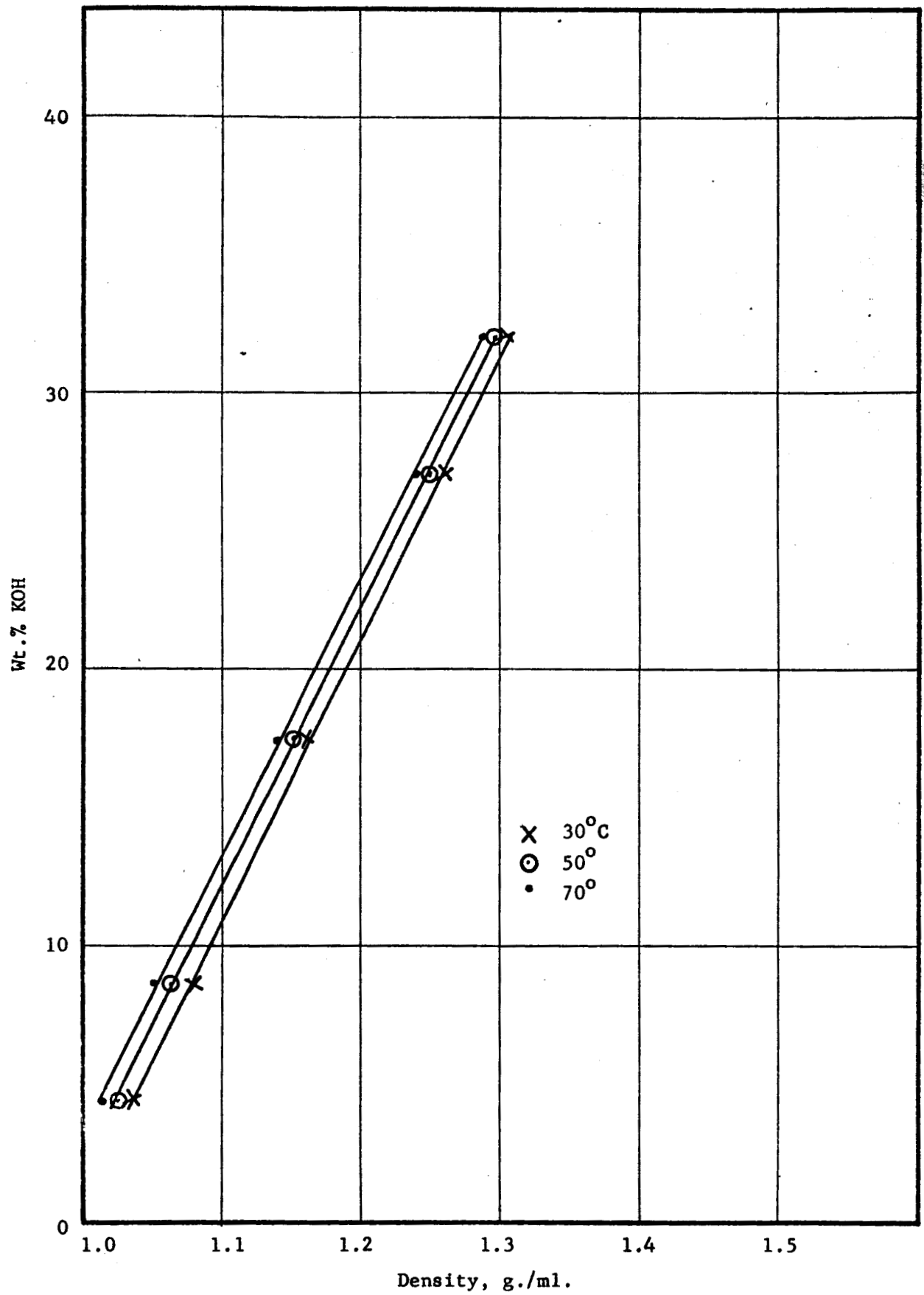


Figure 8. Experimental Density Measurements for KOH Solutions

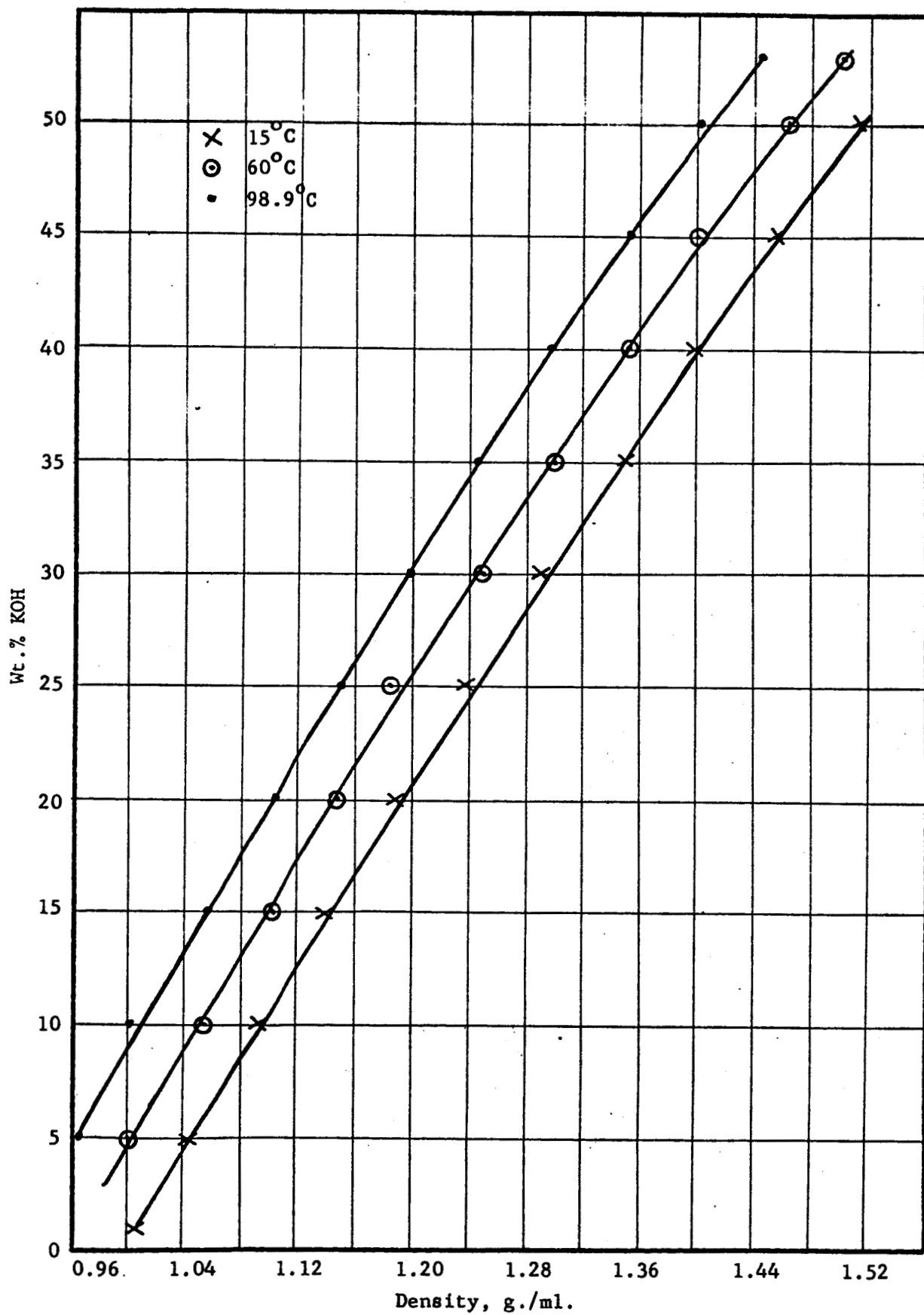


Figure 9. Density Measurements Available in the Literature



TABLE 1EXPERIMENTAL RESULTS FOR DENSITY OF KOH SOLUTIONS

<u>Temperature</u>	<u>Pressure</u>	<u>Wt. % KOH</u>	<u>Density (g./ml.)</u>
30°C	1 Atm.	4.40	1.0349 ± 0.000071
30°C	1	8.66	1.0709 ± 0.00005
30°C	1	17.47	1.1585 ± 0.0001
30°C	1	27.08	1.2611 ± 0.00011
30°C	1	32.07	1.3103 ± 0.00015
50°C	1	4.40	1.0263 ± 0.00015
50°C	1	8.66	1.0622 ± 0.00017
50°C	1	17.47	1.1495 ± 0.00015
50°C	1	27.08	1.2498 ± 0.00019
50°C	1	32.07	1.2999 ± 0.00019
70°C	1	4.40	1.0143 ± 0.00017
70°C	1	8.66	1.0485 ± 0.00011
70°C	1	17.47	1.1379 ± 0.00011
70°C	1	27.08	1.2407 ± 0.00007
70°C	1	32.07	1.2885 ± 0.00019

## 5. VAPOR PRESSURE OF KOH SOLUTIONS

### 5.1 Experimental

Experimental vapor pressure measurements have been made for KOH concentrations in the range 0-30.65 wt.%, over the temperature range 25-70°C. Measurements were made by the isoteniscope method, the procedure being essentially that described by Thompson (25) with minor modifications. This method of determining vapor pressure was found to be superior to the boiling-point method.

The apparatus used is shown in Figure 10. The isoteniscope consists of a bulb attached to a u-tube, both of which are partly filled with the liquid under study in such a way that a volume of vapor separates the two quantities of liquid. The isoteniscope was contained in a constant-temperature water bath, controlled to  $\pm 0.05^\circ\text{C}$ . A vacuum was first applied to the solution under study to remove all air and dissolved gases from the system. When this had been completed, air was introduced to the system using a needle valve, until the liquid level in the two legs of the u-tube was equalised. The vapor pressure of the solution was then read from a manometer. The isoteniscope used was provided with a spherical joint to facilitate cleaning, and an enlarged section to prevent loss of solution due to a sudden pressure change. To guard against the possibility of change in solution composition during the course of an experiment the KOH concentration was determined at the beginning and end of each experiment.

### 5.2 Results

The experimental results obtained are shown in Figure 11 and tabulated in Table 2. The results show a small departure from linearity at

the lower temperatures; this effect may be due to experimental errors, and these results are being rechecked. Figure 12 shows vapor pressure data taken from International Critical Tables; these values are tabulated in Appendix 1. The experimental vapor pressure results reported here agree with those in Figure 12 within about 3-4 mm. Hg over the range of conditions covered.

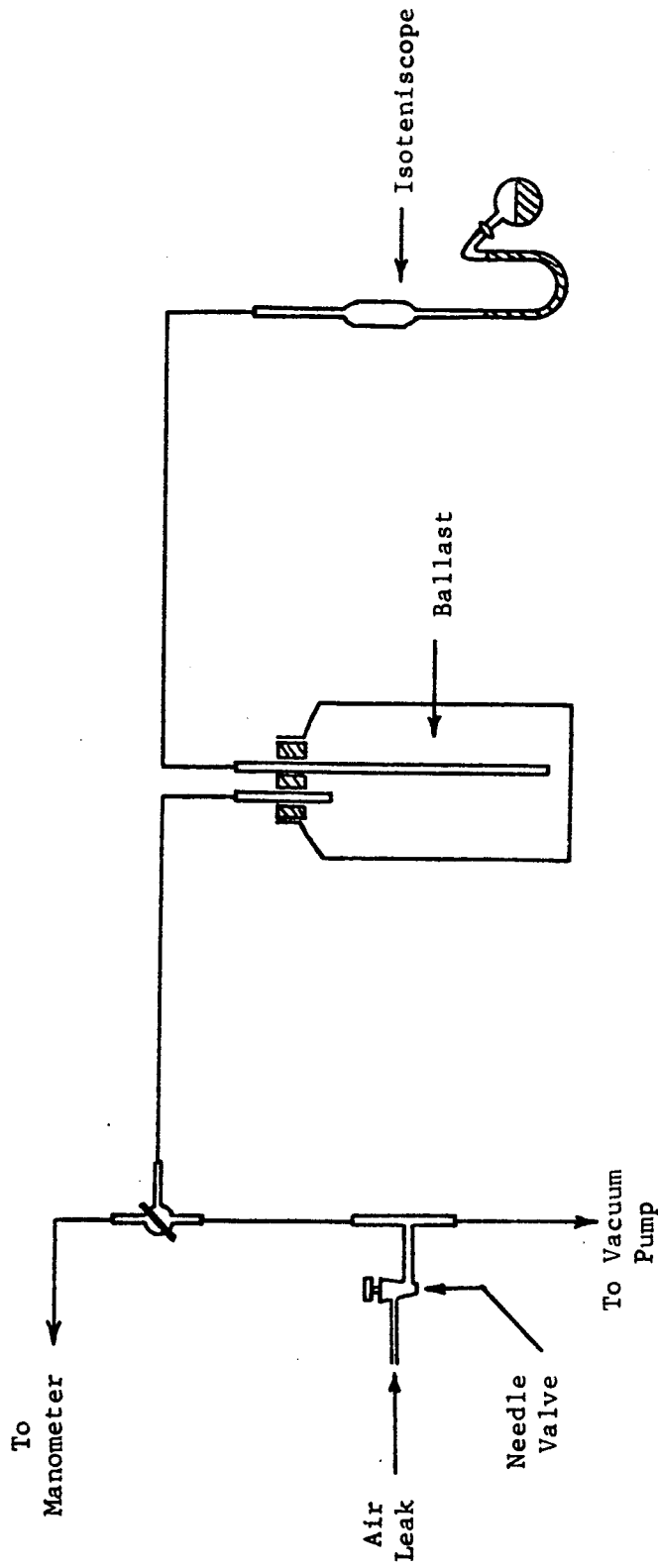


Figure 10. Vapor Pressure Apparatus

Figure 11. Experimental Vapor Pressure Measurements

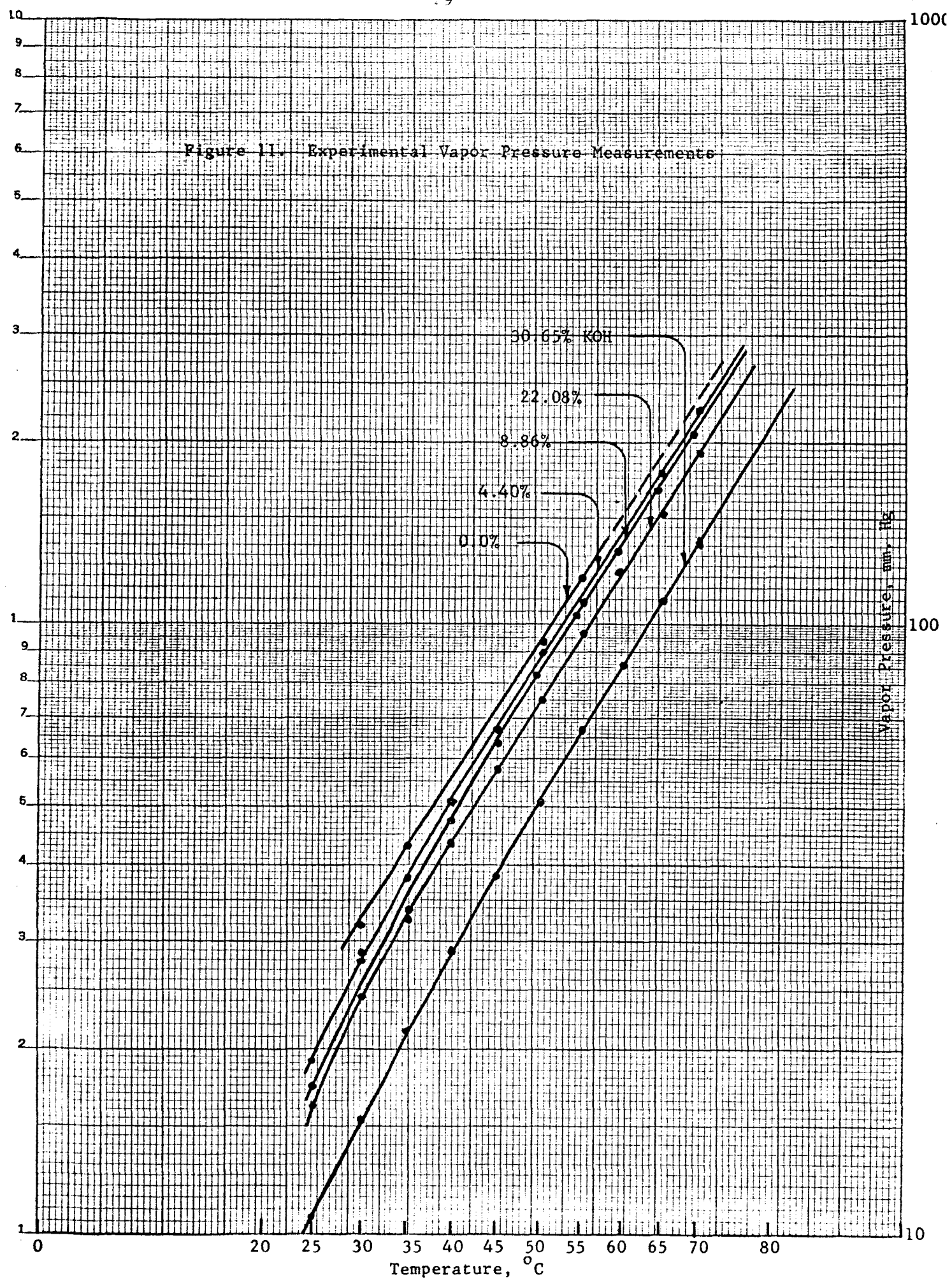


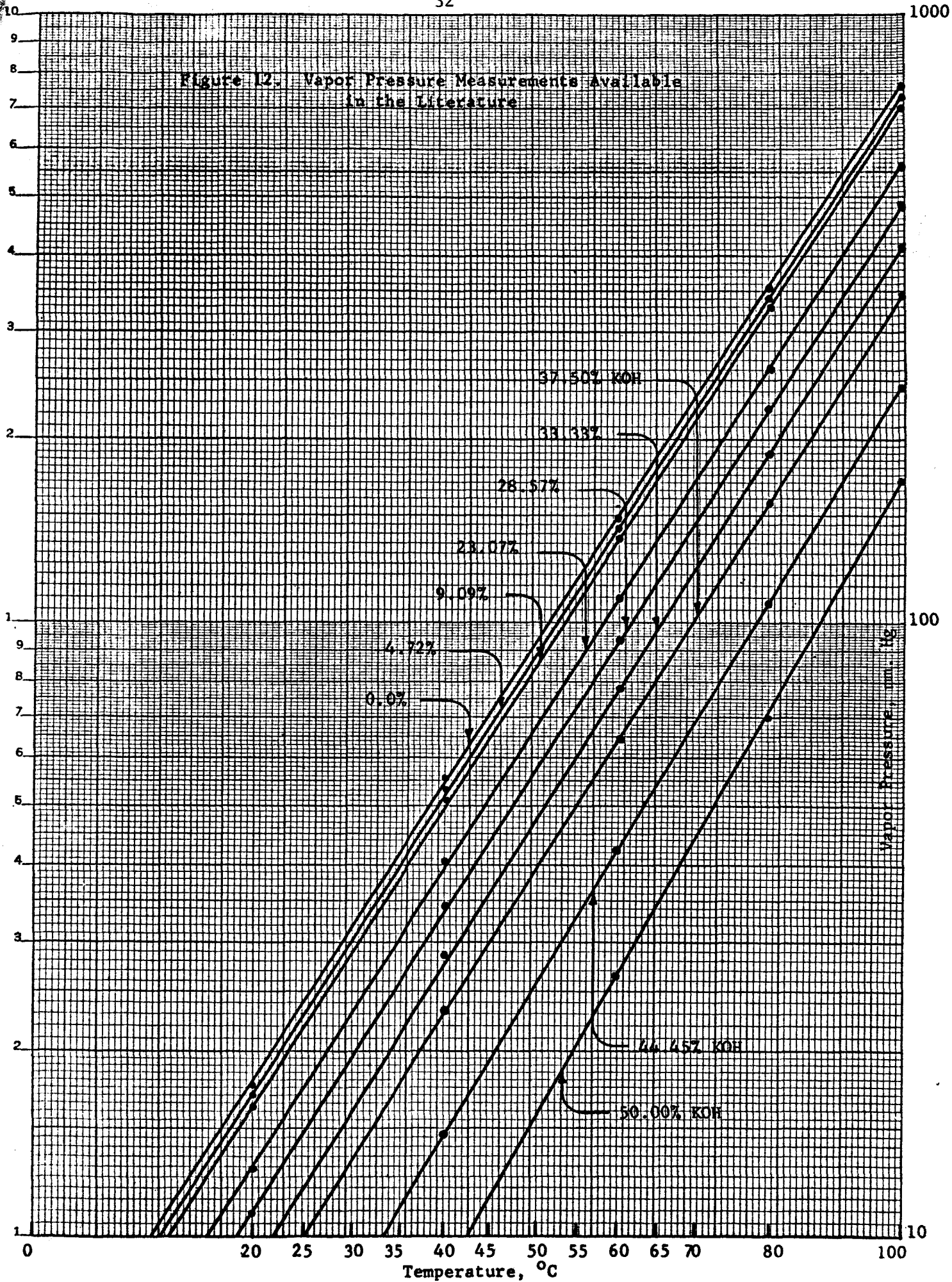
TABLE 2EXPERIMENTAL RESULTS FOR VAPOR PRESSURE OF KOH SOLUTIONS

<u>Temperature, °C</u>	<u>Wt.% KOH</u>	<u>Vapor Pressure mm Hg</u>
25°	4.40	19.1
	8.86	17.4
	22.08	16.1
	30.65	10.6
30°	0.0	31.5
	4.40	27.9
	8.86	28.3
	22.08	24.2
	30.65	15.2
35°	0.0	43.0
	4.40	38.0
	8.86	33.2
	22.08	32.5
	30.65	21.3
40°	4.40	51.0
	8.86	47.4
	22.08	43.3
	30.65	28.8
45°	4.40	66.5
	8.86	63.4
	22.08	57.7
	30.65	38.1
50°	0.0	92.8
	4.40	90.0
	8.86	82.1
	22.08	74.5
	30.65	50.8
55°	0.0	118.3
	4.40	108.4
	8.86	103.7
	22.08	96.4
	30.65	66.7

TABLE 2 (Continued)

<u>Temperature, °C</u>	<u>Wt. % KOH</u>	<u>Vapor Pressure mm Hg</u>
60°	8.86	132.1
	22.08	121.9
	30.65	85.0
65°	4.40	177.1
	8.86	165.7
	22.08	152.5
	30.65	108.2
70°	4.40	226.5
	8.86	213.4
	22.08	192.5
	30.65	135.1

Figure 12. Vapor Pressure Measurements Available  
in the Literature





## 6. CONCLUSIONS AND FUTURE PLANS

During this period experimental methods have been developed for measuring the density and vapor pressure of KOH solutions, and the solubility of  $O_2$  and  $H_2$  in KOH solutions over the required range of conditions. Experimental measurements of density and vapor pressure have been made for KOH concentrations in the range 0-32%, and for temperatures up to  $70^\circ C$ . Work has also been started on developing an experimental method for determining diffusion coefficients of oxygen and hydrogen in KOH solutions. A literature search has been made for values of density and vapor pressure, and values for the solubility of oxygen and hydrogen in KOH solutions; the results of this survey are contained in Appendix 1.

It is hoped that the solubility, vapor pressure and density measurements will be completed by September, 1966. It is also planned to start making measurements of viscosity and electrolytic conductivity during this period. A study of possible theoretical models for the prediction of transport coefficients for KOH solutions (diffusion coefficient, electrolytic conductivity, and viscosity) will also be undertaken; at present the hole and free volume models of liquid diffusion appear to provide the most fruitful starting point.

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## 8. APPENDICES

### 8.1 Appendix 1. Physical Property Values for KOH Solutions from the Literature

#### 8.1.1 Symbols and Units

The following notation and units will be adhered to:

Temperature will be expressed in °C.

KOH concentration will be in weight %.

Pressure will be in atm.

Vapor Pressure of KOH solutions will be in mm. Hg.

S = solubility of gas in KOH solution in g.mole/liter, with gas above solution at a partial pressure of 1 atm. (excluding vapor pressure of solution).

D = diffusion coefficient in cm.<sup>2</sup>/sec. referred to the center of volume.

$\rho$  = solution density in g./ml.

#### 8.1.2 Data for Solubility of O<sub>2</sub> and H<sub>2</sub>

##### 8.1.2.1 Data of Knaster and Apel'baum (6)

<u>Gas</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>S x 10<sup>3</sup></u>
H <sub>2</sub>	21° C	1 atm.	5.30	0.632 g.mole/l.
			19.10	0.273
			30.50	0.112
			40.10	0.0496
H <sub>2</sub>	45°	1 atm.	5.30	0.569
			19.10	0.239
			30.50	0.0952
			40.10	0.0361
H <sub>2</sub>	75°	1 atm.	5.30	0.542
			19.10	0.2325
			30.50	0.0884
			40.10	0.0328
O <sub>2</sub>	21°	1 atm.	5.30	0.897
			19.10	0.336
			30.50	0.102
			40.10	0.0232

<u>Gas</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Wt. % KOH</u>	<u>S x 10<sup>3</sup></u>
O <sub>2</sub>	45° C	1 atm.	5.30	0.712 g.mole/l.
			19.10	0.288
			30.50	0.0884
			40.10	0.0201
O <sub>2</sub>	75°	1 atm.	5.30	0.597
			19.10	0.244
			30.50	0.0812
			40.10	0.01835

8.1.2.2 Data of Geffcken (1)

<u>Gas</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Wt. % KOH</u>	<u>S x 10<sup>3</sup></u>
H <sub>2</sub>	25° C	1 atm.	2.70	0.700 g.mole/l.
			3.70	0.649
			5.50	0.581
			5.48	0.586
			7.60	0.505
O <sub>2</sub>	15°	1 atm.	3.0	1.200
			3.1	1.200
			6.0	0.945
			6.1	0.940
O <sub>2</sub>	25°	1 atm.	3.0	1.032
			3.1	1.026
			6.0	0.810
			6.1	0.807

8.1.2.3 Data of Gubbins and Walker (4)

<u>Gas</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Wt. % KOH</u>	<u>S x 10<sup>3</sup></u>
O <sub>2</sub>	25° C	1 atm.	5.2	0.874 g.mole/l.
			10.2	0.594
			11.8	0.444
			19.0	0.270
			19.1	0.290
			23.5	0.159
			30.8	0.0803
			41.0	0.0295
			47.5	0.0260
			51.5	0.0310
			O <sub>2</sub>	50°
23.7	0.149			
30.8	0.0833			
51.5	0.0174			

8.1.2.4 Data of Lindstrom (7)

<u>Gas</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>S x 10<sup>3</sup></u>
O <sub>2</sub>	25°C	2.0 atm.	23.1	0.049 g.mole/l.
		3.0	23.1	0.147
		4.0	23.1	0.282
		4.9	23.1	0.434
		5.0	23.1	0.470
		5.2	23.1	0.519
		6.0	23.1	0.618
		6.8	23.1	0.781
		8.1	23.1	1.035
		9.0	23.1	1.182
		10.0	23.1	1.305

8.1.3 Diffusion Coefficients of O<sub>2</sub> in KOH Solutions. Data of Gubbins and Walker (4).

<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>D x 10<sup>5</sup></u>
25.0°C	1 atm.	5.2	1.641 cm <sup>2</sup> /sec.
		10.2	1.457
		14.8	1.524
		21.2	0.867
		27.0	0.747
		34.8	0.575
		43.1	0.177
		52.0	0.037

8.1.4 Density of KOH Solutions8.1.4.1 Data from Lange (22)

<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>Density</u>
15°C	1 atm.	1	1.0083 g./ml.
		2	1.0175
		3	1.0267
		4	1.0359
		5	1.0452
		6	1.0544
		7	1.0637
		8	1.0730
		9	1.0824
		10	1.0918
		11	1.1013
		12	1.1108
		13	1.1203
		14	1.1299

<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>Density</u>
15°C	1 atm.	15	1.1396 g./ml.
		16	1.1493
		17	1.1590
		18	1.1688
		19	1.1786
		20	1.1884
		21	1.1984
		22	1.2083
		23	1.2184
		24	1.2285
		25	1.2387
		26	1.2489
		27	1.2592
		28	1.2695
		29	1.2800
		30	1.2905
		31	1.3010
		32	1.3117
		33	1.3224
		34	1.3331
		35	1.3440
		36	1.3549
		37	1.3659
		38	1.3769
		39	1.3879
		40	1.3991
		41	1.4103
		42	1.4215
		43	1.4329
		44	1.4443
		45	1.4558
		46	1.4673
		47	1.4790
		48	1.4907
		49	1.5025
		50	1.5143
		51	1.5262
		52	1.5383

#### 8.1.4.2 Data of Kelly (23)

<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>Density</u>
0.0°C	1 atm.	0.00	0.9998 g./ml.
0.0	1 atm.	10.04	1.0969
0.0	1 atm.	20.01	1.1955
0.0	1 atm.	25.19	1.248
0.0	1 atm.	31.53	1.3147

<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>Density</u>
0.0°C	1 atm.	35.43	1.3560 g./ml.
0.0	1 atm.	40.10	1.4088
0.0	1 atm.	45.72	1.4737
0.0	1 atm.	48.96	1.5131
-5.5	1 atm.	10.04	1.0979
-14.1	1 atm.	20.01	1.1959
-22.4	1 atm.	20.01	1.1966
-14.1	1 atm.	25.19	1.2508
-30.1	1 atm.	25.19	1.2542
-36.1	1 atm.	25.19	1.2554
-14.1	1 atm.	31.53	1.3180
-28.9	1 atm.	31.53	1.3213
-40.9	1 atm.	31.53	1.3240
-50.9	1 atm.	31.53	1.3262
-53.8	1 atm.	31.53	1.3270
-14.1	1 atm.	35.43	1.3577
-30.1	1 atm.	35.43	1.3598
-45.5	1 atm.	35.43	1.3619
-14.1	1 atm.	40.10	1.4093
-25.0	1 atm.	40.10	1.4104
-30.1	1 atm.	40.10	1.4109
-34.0	1 atm.	40.10	1.4113
-14.1	1 atm.	45.72	1.4858
-30.1	1 atm.	45.72	1.4939

8.1.4.3 Data from Solvay (24)

<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>Density</u>
4.40°C	1 atm.	5	1.048 g./ml.
4.40	1 atm.	10	1.096
4.40	1 atm.	15	1.147
4.40	1 atm.	20	1.193
4.40	1 atm.	25	1.246
4.40	1 atm.	30	1.298
4.40	1 atm.	35	1.351
4.40	1 atm.	40	1.406
4.40	1 atm.	45	1.461
4.40	1 atm.	50	1.523
4.40	1 atm.	53	1.561
15.6	1 atm.	5	1.045
15.6	1 atm.	10	1.091
15.6	1 atm.	15	1.140
15.6	1 atm.	20	1.188
15.6	1 atm.	25	1.239
15.6	1 atm.	30	1.291
15.6	1 atm.	35	1.344



<u>Temperature</u>	<u>Pressure</u>	<u>Wt. % KOH</u>	<u>Density</u>
15.6 °C	1 atm.	40	1.399 g./ml.
15.6	1 atm.	45	1.456
15.6	1 atm.	50	1.515
15.6	1 atm.	53	1.553
26.7	1 atm.	5	1.039
26.7	1 atm.	10	1.085
26.7	1 atm.	15	1.131
26.7	1 atm.	20	1.181
26.7	1 atm.	25	1.231
26.7	1 atm.	30	1.283
26.7	1 atm.	35	1.325
26.7	1 atm.	40	1.389
26.7	1 atm.	45	1.447
26.7	1 atm.	50	1.505
26.7	1 atm.	53	1.542
37.8	1 atm.	5	1.032
37.8	1 atm.	10	1.077
37.8	1 atm.	15	1.124
37.8	1 atm.	20	1.171
37.8	1 atm.	25	1.221
37.8	1 atm.	30	1.272
37.8	1 atm.	35	1.325
37.8	1 atm.	40	1.378
37.8	1 atm.	45	1.435
37.8	1 atm.	50	1.493
37.8	1 atm.	53	1.530
48.9	1 atm.	5	1.022
48.9	1 atm.	10	1.066
48.9	1 atm.	15	1.113
48.9	1 atm.	20	1.159
48.9	1 atm.	25	1.209
48.9	1 atm.	30	1.260
48.9	1 atm.	35	1.313
48.9	1 atm.	40	1.364
48.9	1 atm.	45	1.422
48.9	1 atm.	50	1.480
48.9	1 atm.	53	1.517
60.0	1 atm.	5	1.012
60.0	1 atm.	10	1.053
60.0	1 atm.	15	1.101
60.0	1 atm.	20	1.148
60.0	1 atm.	25	1.198
60.0	1 atm.	30	1.249
60.0	1 atm.	35	1.300
60.0	1 atm.	40	1.353
60.0	1 atm.	45	1.408
60.0	1 atm.	50	1.465
60.0	1 atm.	53	1.502

<u>Temperature</u>	<u>Pressure</u>	<u>Wt.% KOH</u>	<u>Density</u>
71.1 <sup>o</sup> C	1 atm.	5	1.000 g./ml.
71.1	1 atm.	10	1.044
71.1	1 atm.	15	1.089
71.1	1 atm.	20	1.136
71.1	1 atm.	25	1.185
71.1	1 atm.	30	1.235
71.1	1 atm.	35	1.287
71.1	1 atm.	40	1.340
71.1	1 atm.	45	1.394
71.1	1 atm.	50	1.451
71.1	1 atm.	53	1.488
87.8	1 atm.	5	0.9779
87.8	1 atm.	10	1.021
87.8	1 atm.	15	1.066
87.8	1 atm.	20	1.112
87.8	1 atm.	25	1.159
87.8	1 atm.	30	1.209
87.8	1 atm.	35	1.260
87.8	1 atm.	40	1.312
87.8	1 atm.	45	1.367
87.8	1 atm.	50	1.424
87.8	1 atm.	53	1.478
98.9	1 atm.	5	0.9665
98.9	1 atm.	10	1.011
98.9	1 atm.	15	1.056
98.9	1 atm.	20	1.102
98.9	1 atm.	25	1.150
98.9	1 atm.	30	1.199
98.9	1 atm.	35	1.245
98.9	1 atm.	40	1.297
98.9	1 atm.	45	1.352
98.9	1 atm.	50	1.409
98.9	1 atm.	53	1.444

#### 8.1.5 Vapor Pressures of KOH Solutions (26)

<u>Temperature, °C</u>	<u>Wt.% KOH</u>	<u>Vapor Pressure, mm Hg.</u>
0 <sup>o</sup>	0	4.579
	4.72	4.43
	9.09	4.25
	16.66	3.83
	23.07	3.35
	28.57	2.82
	33.33	2.30
	37.50	1.82
	44.45	1.08

<u>Temperature, °C</u>	<u>Wt.% KOH</u>	<u>Vapor Pressure, mm Hg.</u>
20°	0	17.539
	4.72	17.0
	9.09	16.3
	16.66	14.7
	23.07	12.9
	28.57	10.9
	33.33	8.9
	37.50	7.2
	44.45	4.4
	50.00	2.6
40°	0	55.34
	4.72	53.5
	9.09	51.4
	16.66	46.4
	23.07	40.7
	28.57	34.6
	33.33	28.6
	37.50	23.2
	44.45	14.6
	50.00	8.8
60°	0	149.46
	4.72	144.6
	9.09	138.9
	16.66	125.4
	23.07	110.1
	28.57	94
	33.33	78.6
	37.50	64.6
	44.45	42.6
	50.00	26.5
80°	0	355.47
	4.72	344
	9.09	331
	16.66	299
	23.07	263
	28.57	225
	33.33	190
	37.50	158
	44.45	108
	50.00	70.5
54.55	45.5	
58.33	29	

<u>Temperature, °C</u>	<u>Wt.% KOH</u>	<u>Vapor Pressure, mm Hg.</u>
100°	0	760.00
	4.72	735
	9.09	707
	16.66	639
	23.07	563
	28.57	485
	33.33	413
	37.50	348
	44.45	246
	50.00	172
	54.55	118
	58.33	81
	61.54	56
	64.03	40

# 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<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> 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 drain-

ing 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  $\pm 0.1^\circ\text{C}$ . A sample of distilled water was similarly equilibrated with the gas at 25°C and atmospheric pressure.

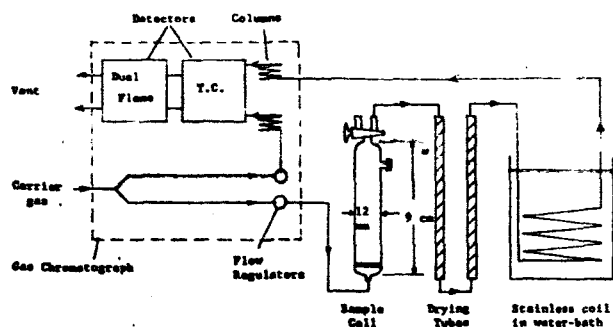


Figure 1. Apparatus for gas solubility determinations.

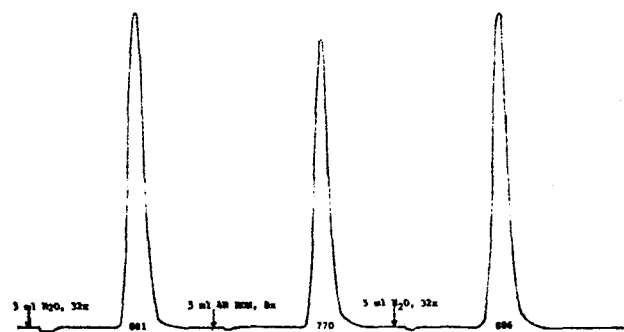


Figure 2. Peak obtained for  $O_2$  dissolved in 4N KOH at 25°C, compared with peaks for oxygen dissolved in water at 25°C. Figures beneath peaks are areas counted by disc integrator.

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

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

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.

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

$\pi$  = 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,  $\pi$  may be taken as 760 mm Hg with negligible error, thus eliminating the need to measure atmospheric pressure,

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

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.

### Acknowledgements

The authors wish to express their appreciation to the Harry Diamond Laboratories, U. S. Materiel Command, for sponsoring the work reported here. The encouragement and suggestions of Mr. Nathan Kaplan of the Harry Diamond Laboratories, and the assistance of co-workers in this laboratory are also gratefully acknowledged. ■

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Manuscript received Sept. 26, 1964.