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AN EXPERIMENTAL EVALUATION OF THE THERMODYNAMIC PROPERTIES OF CONCENTRATED AQUEOUS POTASSIUM HYDROXIDE SOLUTIONS

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AN EXPERIMENTAL EVALUATION OF THE THERMODYNAMIC PROPERTIES OF CONCENTRATED AQUEOUS POTASSIUM HYDROXIDE SOLUTIONS

Final Report

February 1985

by

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ABSTRACT

The thermodynamic activity of water in a binary KOH H_2O system has been measured using an electrochemical cell, Cell A, in the concentration range between 1 and 8 molal and the temperature range of 0-80°C.

$$H_2(Pt) \ / \ KOH \text{ in } H_2O \ / \ Hg, HgO(Pt) \qquad (A)$$

From the equilibrium voltage of cell (A), the activity of water can be directly calculated without making assumptions about the degree of dissociation of the solute or any other solution parameters. The measured values of activity are greater than those found in previous vapor pressure studies, but are consistant with previous EMF measurements of KOH concentration cells at 25°C. These values are invariant with temperature for concentrations up to 4.0 molal but between 6.0 and 8.0 molal the H_2O activity first decreases by ∿10% and then increases by ∿15% as the temperature is increased. The general activity trend is consistant with, though smaller than, the results in the higher concentration ranges of the previous vapor pressure studies.

The values of activity of water reported here can be used to refine previous calculations of Macdonald and coworkers (see LBL Final Report 4505110) on the theoretical efficiencies of alkaline battery systems. Since the measured activity values of water are within ∿10% of those used in the previous calculations, the major conclusions of that study are not significantly affected.

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Section 1

INTRODUCTION

The thermodynamic parameters for concentrated potassium hydroxide solutions have been experimentally determined in this work. Calculations of pH and cell potentials as a function of concentration and temperatures carried out under a previous study (1) suffered from inaccuracies due to limitations of availaible thermodynamic input data. The principal sources of error are considered to be :

(i) Uncertainty in the activity of water, particularly in the case of concentrated KOH solutions.
(ii) Uncertainty in the dissociation constant for water in concentrated alkaline solutions.
(iii) Uncertainty in the degree of association of cations with hydroxide ions in concentrated alkaline solutions.

The values for activity of water have previously been calculated from measured vapor pressures, and activity coefficients of KOH by integration of Gibbs Duhem equation. In this study the activity of water in concentrated KOH solutions has been directly measured as a function of concentration and temperature so that improved thermodynamic calculations are possible.

The thermodynamic properties of strong electrolytes in highly concentrated solutions over a large temperature range may conceivably be obtained by a number of different methods (2). In most cases, however, the methods applicable narrow down to a single one, the determination of the vapor pressure of the solution. The alkali hydroxides and hydrochloric acid belong to the few electrolytes forming exceptions to this general rule, since it would appear to be possible to study their solutions using an electromotive force method.

Chemical reactions in which there is a change in the valence of reactants are known as oxidation-reduction reactions (3). In each of such reactions, some reactants give up their electrons (oxidize) and others receive electrons (reduce). Correspondingly, the oxidation reduction reaction is usually separated into two half reactions. For comparison of two different electrodes (half reactions) with each other, there are values of electrode potentials. The electrode potential E of the electrode is its potential with relation to the standard ($pH=0$, $pH_2=1$) hydrogen electrode which is defined as equal to zero and is used as a reference or standard state. The International Union of Pure and Applied Chemistry in 1953 defined electrodes having higher oxidation states than the hydrogen electrode to have a positive sign, and those having higher reduction states to have a negative sign.

Electrode potentials are related to the free energy change corresponding to the chemical reaction associated with equation 1

$$\Delta G = -nFE \tag{1}$$

where n is the number of electrons taking part in the reaction.
F is the Faraday number, corresponding to the amount of electricity required to separate from solution one gram equivalent of substance. Its value is 96489 Couloumbs/mol.

The standard state potential E° can be determined at any temperature from equation 1 and the standard state Gibb's free energy function. This function can be obtained using the relation between the standard state heat capacity, enthalpy, entropy, and Gibb's free energy given by equation 2 :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2}$$

where ΔH° is the change in the standard state enthalpy of the reaction
ΔG° is the change in the standard state free energy of the reaction
ΔS° is the change in the standard state entropy of the reaction.

The relation between the real heat capacity and temperature is usually expressed as an empirical equation

$$Cp = a + bT + cT^{-2} + \ldots \tag{3}$$

where a, b, and c are constants characteristic of the substance being considered.

The change in heat capacity as a result of a chemical reaction, $\Delta Cp°$, is the difference between the heat capacities of the product and reactant substances.

$$\Delta Cp° = \sum Cp° \text{ (products)} - \sum Cp° \text{ (reactants)} \tag{4}$$

$$\Delta Cp° = \Delta a + \Delta bT + \Delta cT^{-2} + \ldots \tag{4a}$$

For enthalpy, the relation is determined from equation 5

$$\Delta H_T° = \int \Delta Cp° \cdot dT = \Delta aT + \frac{1}{2} \Delta bT^2 - \Delta cT^{-1} + x \tag{5}$$

For entropy

$$\Delta S_T° = \int \frac{\Delta Cp°}{T} \cdot dT = \Delta a \ln T + \Delta bT - \frac{1}{2} \Delta cT^{-2} + y \tag{6}$$

where x and y are constants of integration which can be determined knowing values for $\Delta H°$ and $\Delta S°$ at any single temperature, for instance, 298.15°K.

$$x = \Delta H°_{298.15} - \Delta a(298.15) - \frac{1}{2} \Delta b(298.15)^2 + \Delta c(298.15)^{-1} \tag{5a}$$

$$y = \Delta S°_{298.15} - \Delta a \ln(298.15) - \Delta b(298.15) + \frac{1}{2} \Delta c(298.15)^{-2} \tag{6a}$$

The relation between the free energy and temperature can be obtained by substituting the above equations into equation 2.

$$\Delta G^\circ_T = x + (\Delta a - y)T - \Delta a T \ln T - \frac{1}{2}\Delta b T^2 - \frac{1}{2}\Delta c T^{-2} \qquad (7)$$

Under equilibrium conditions, the Nernst Equation relates the desired thermodynamic parameters to the measured cell potential for any general reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b} \qquad (8)$$

where R is the universal gas constant equal to 8.3143 Joules/°Kmol.
T is the temperature of the reaction in °Kelvin.
a is the activity or the active mass of the species which appears in the subscript.

Then an equilibrium measurement of E would yield values of activities of different species involved in the reaction, since E° can be evaluated from equations 1 and 7.

In the present study, an attempt has been made to experimentally measure the thermodynamic properties of the binary potassium hydroxide-water system. Three different classes of electrochemical cells were selected which would yield values of activity of water and activity of potassium hydroxide in concentrated solutions. A new design of the reaction vessel was employed, which incorporated all these cells in the same unit, along with providing concentration cells between corresponding pairs of electrodes. These concentration cells serve as an internal check on the values of activity of water and potassium hydroxide generated by the three different cells mentioned earlier.

A detailed description of each cell is given in the Experimental System and Procedures Section. The literature review details some background information about related work done earlier to determine the thermodynamic properties of binary H_2O - KOH system. The data obtained in the present research is reported in the Results Section and compared with previous studies. The concluding section of this report discusses the failures and successes of the experimental work done and the relevant conclusions which can be drawn from them.

Section 2

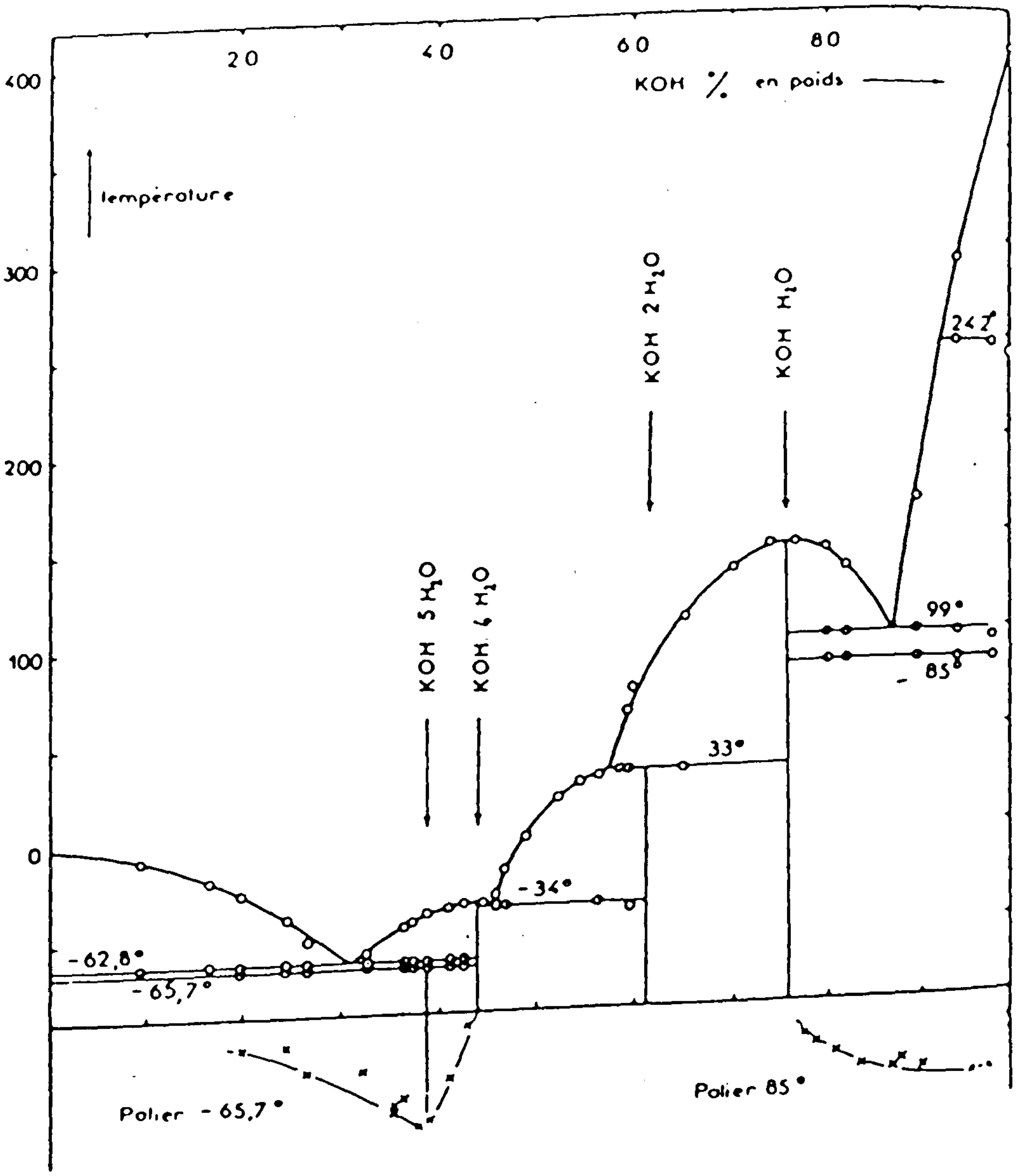
LITERATURE REVIEW

2.1. The $KOH-H_2O$ Binary System: This system has not been studied extensively. The measurements made by Pickering (4) in mixtures with less than 65% weight percent KOH show the existence of three hydrates of potassium which crystallize with 4, 2 and 1 molecules of water. The diagrams drawn by different authors show several gaps due to the different experimental methods used. They do not report a combination hydrate $KOH \cdot 5H_2O$ which appears in mixtures very rich in potassium. Pickering measured the temperature at which crystals disappeared in mixtures of known composition. Cohen-Adad and Michaud (5) have given a modified equilibrium diagram based on thermal analysis using heating curves after thermal treatment leading to crystallization. They also used solubility measurements to get more precise knowledge of liquidus lines. The diagram is shown in Fig. 1 and characterized by eutectic points whose coordinates are also given. The transition from $KOH \cdot 2H_2O$ to $KOH \cdot H_2O$ occurs at 33°C and 58.1 wt % KOH.

For mixtures less than 44% in weight, different thermal treatment shows a new transformation line at -65.7°C, which is clearly distinguished from eutectic transformation at -62.8°C. It refers to a new chemical species $KOH \cdot 5H_2O$ formed by a solid-state reaction. For mixtures with concentration greater than 76% the heating curves show two transformation lines at 85°C and 99°C. The transformation at 99°C corresponds to a eutectic at 87% KOH. The transformation at 85°C shows the existence of a new solid phase, whose nature has not been determined as yet.

2.2 Activity Determination by Vapor Pressure Studies: The activity of the solvent can be determined from its vapor pressure by the relation

$$a_w = \frac{p}{p°} \tag{9}$$



Voici les coordonnées des points d'eutexie :
Glace — KOH, $4H_2O$ (— 62°,8 et 30,9 % KOH en poids);
KOH, $4H_2O$ — KOH, $2H_2O$ (— 34°,0 et 45,2 %);
KOH, H_2O — KOH (— 99° et 87 %).
L'hydrate KOH, $4H_2O$ présente une fusion congruente à — 33°,7.

Figure 1. The KOH-H_2O binary equilibrium diagram. (The concentration range of the present study is between 0.053 wt% KOH and 30.97 wt% KOH.)

where p is partial vapor pressure of water in KOH solution of concentration m (in mole/1000 g. water), and p° is vapor pressure of pure water.

A "practical" activity coefficient, ie. the mean ionic activity coefficient, γ, is defined by the equation 10.

$$\bar{G} = \bar{G}^\circ_m + \nu RT\ln\gamma m \tag{10}$$

where: $\bar{G}$ is partial molal free energy/mole electrolyte,
$\bar{G}^\circ_m$ is free energy in a standard state such that $\gamma \rightarrow 1$ as $m \rightarrow 0$,
ν is number of ions into which one molecule of electrolyte dissociates.

The practical osmotic coefficient, ϕ ,is defined by equation 11.

$$\bar{G}_{H_2O} = \bar{G}^\circ_{H_2O} - \phi RT\frac{m\nu}{55.51} \tag{11}$$

where $\bar{G}_{H_2O}$ is partial molal free energy of the solvent,

$\bar{G}^\circ_{H_2O}$ is free energy of solvent in the standard state.

The activity of water a_w can be defined by equation 12.

$$\bar{G}_{H_2O} = \bar{G}^\circ_{H_2O} + RT\ln a_w \tag{12}$$

Then by comparing equations 11 and 12 we get:

$$\phi = -\frac{55.51 \ln a_w}{m} \tag{13}$$

From vapor pressure determination, a_w and thus ϕ can be determined. The activity of the solute can be found by integration of a form of Gibbs-Duhem equation given by Lewis and Randall (6). They define a divergence function h which rapidly approaches zero at infinite dilution.

$$h = \frac{\ln a_1}{r} + 1 \tag{14}$$

where r = Moles of Solute/Moles of Solvent
$= (N_2/N_1) = (m/55.51)$.

The Gibbs-Duhem equation can be written as (7):

$$d\ln a_1 = -(N_2/N_1)d\ln a_2 = -r d\ln a_2 \tag{15}$$

On differentiating equation 14 equation 16 is obtained

$$dh = \frac{d\ln a_1}{r} - \frac{\ln a_1}{r^2}\, dr \tag{16}$$

Combining equations 15 and 16 and adding dlnr to both sides gives

$$-d\ln(a_2/r) = dh + h\, d\ln r \tag{17}$$

Integrating to infinite dilution

$$\ln(a_2/r) = -h - \int_0^r (h/r)\, dr \tag{18}$$

Then by choosing the standard state of the solute X_2 such that $(a_2/m_2) = 1$ when $m_2 = 0$, equation 18 becomes

$$\ln(a_2/m) = - h - \int_0^m (h/m).dm \tag{19}$$

where $h = (55.51 \ln a_1/m) + 1$.

This treatment was given for the activity coefficient of non-electrolytes in aqueous solution. However, for an electrolyte, Randall and White (8) argue that since one molecule of the solute dissociates into molecules or ions, the rate of decrease of the activity of solvent (a_1) as the mole fraction of the solute is increased, is ν times the rate if there were no dissociation. The divergence function is accordingly modified as:

$$h = (55.51 \ln a_1/\nu_m) + 1 \tag{20}$$

Comparing equation 13 and 20 gives the following relation

$$h = 1 - \phi \tag{21}$$

Equation 19 then reduces to equation 22.

$$\ln \quad = -(1-\phi) - \int_0^m (1-\phi)/m \, dm \tag{22}$$

Then by plotting $(1-\phi)/m$ against m, the area under the curve can be obtained, from which the activity coefficient of the solute is calculated with a high degree of accuracy.

In general, values of ϕ are obtained by isopiestic vapor pressure measurements (9). The experimental results of this method are expressed as pairs of molalities of solutions of equal vapor pressure, one solution being that of the electrolyte being studied and the other of reference electrolyte. If the isopiestic measurements are made, and m_R is the molality of the solution of the reference electrolyte and m that of the salt being considered, a plot of the isopiestic ratio $R = (m_R/m)$ against m can be made. From this, values of R at round values of m can be read, and the osmotic coefficient of the solution can be calculated by the equation 23.

$$\nu\phi = \nu_{ref} R \phi_{ref} \qquad (23)$$

The reference solution chosen is such that ϕ_{ref} and ν_{ref} are accurately known over a wide concentration range.

Bro and Kang (10) manometrically measured the vapor pressure of water between -40°C and 25°C for concentrations between 2M KOH and 15M KOH. Their results showed that the vapor pressure of the solutions decreased markedly with temperature in accordance with Clapeyron equation. As expected they also decreased with an increase in KOH concentration. Anisimov (11) measured vapor pressure of aqueous KOH solutions to temperature and concentration in the ranges 0-200°C and 60 wt% KOH respectively. An equation of the type

$$\log P = A - (B/T) - C \log T \qquad (24)$$

was fitted to the experimental data, and good agreement with the literature values was observed.

Macdonald et al (1) performed a statistical analysis of the vapor pressure data of Bro and Kang and Anisimov to obtain the most appropriate polynomials to describe the variation of activity of water with concentration at each temperature. They used a computer program, "Statistical Analysis of Systems," which yielded values for the coefficients in equation 25. These coefficients are listed in the Appendix.

$$a_{H_2O} = (p/p°)A(i)m^{i} \qquad (25)$$

Thus values for activity of water based on vapor pressure studies have been generated for a wide range of concentrations and temperatures.

2.3. Activity Determination of H_2O and KOH in the Binary System by Electromotive Force Measurements

The studies for activity determination have been carried out by several researchers in the past. The earliest known was done by Ming Chow (12), who measured the elctromotive force attending the transfer of potassium hydroxide in aqueous solution from one concentration to another. He used flowing potassium amalgam and mercury-mercuric oxide electrodes at 25°C. His results were considered unreliable by Knobel (13) who repeated the work using hydrogen electrodes instead of the mercury-mercuric oxide type. However neither of them accounted for different activity of water in solutions of different concentrations. Subsequently Harned (14) made similar kinds of measurements for NaOH at 25°C, which were followed by measurements of Harned and Hecker (15) in a range of temperatures from 0°C to 35°C. Here they outlined more precise procedures to evaluate the activity coefficients. This work was extended by Harned and Cook (16) for concentrated KOH solutions up to 4M. Akerlof and Bender (17) made their E.M.F. measurements for a wider range of concentrations up to 17 Molal. Based upon the work of Harned and Cook and Akerlof and Bender, Robinson and Stokes (9) have compiled values for activity coefficient of KOH and osmotic coefficient of solvent at 25°C.

The experimental procedure employed by all these researchers has remained basically the same. The two cells containing solutions of different concentrations were connected by means of capillary tubes joined to a reservoir containing the dilute alkali amalgam. Each cell had platinum electrodes fitted to them, over which hydrogen could be bubbled. Solutions were prepared by gravimetric dilution of one of the strong solutions with hot conductivity water. Great precautions were taken to remove all dissolved air from the solutions and the apparatus. Solutions were filled in each cell under an atmosphere of nitrogen and hydrogen was bubbled until the electrodes were in equilibrium. Then stopcocks were opened to allow amalgam to drop through the capillary tubes into the lower part of each cell and then overflow into a vessel open to atmosphere. Measurements were taken between the two hydrogen electrodes during the time that the amalgam was flowing.

The cells measured had the composition :

$$\mathrm{Pt,H_2\ /\ KOH(m)\ /\ K_xHg\ /\ KOH(m_r)\ /\ H_2,Pt.}$$

The half-cell reactions and the resulting E.M.F. expressions are given respectively by :

$$\begin{array}{llllll}
2K^+ & +\ 2H_2O(m_r) & +\ 2e & \rightleftharpoons & H_2(m_r) & +\ 2KOH(m_r) \\
2K^+ & +\ 2H_2O(m) & +\ 2e & & H_2(m) & +\ 2KOH\ (m) \\
\hline
\end{array}$$

$$2H_2O(m_r) + H_2(m) + 2KOH(m) \longrightarrow H_2(m_r) + 2KOH(m_r) + 2H_2O(m)$$

$$E = \frac{2*2.303\ RT}{F} \log \frac{a_{H_2O\ (m_r)}\ a_{KOH\ (m)}\ P^{0.5}_{H_2\ (m)}}{a_{H_2O\ (m)}\ a_{KOH\ (m_r)}\ P^{0.5}_{H_2}} \qquad (26)$$

where m_r refers to the concentration of reference solution.

Chow(12) and Knobel(13) did not account for different activity of water in concentrated and reference solution, nor was the correction for unit fugacity of hydrogen made. Thus in equation 26 they evaluated the ratio of activity coefficients of test and reference solution. Then activity coefficients were obtained by assuming that the activity is equal to concentration in the most dilute reference solution (0.001 M).

Harned and Cook(16) represented equation 26 in the following form:

$$\log(\gamma/\gamma r) = E/2k - \log(m/m_r) - (1/2)\log(P_r/P) \qquad (27)$$

where P_r is vapor pressure of the reference solution,
P is vapor pressure of KOH at the concentration m.

The last term in this equation refers to water transfer potential ignored by Knobel and Chow.

The Gibbs-Duhem equation may be converted to the form given in equation 28.

$$-d\log P = (2/55.51x2.303).\ dm + (2/55.51)m.d\log \gamma \qquad (28)$$

Since $\log\gamma_r$ is a constant, $d\log\gamma$ in the last term may be written as $d\log(\gamma/\gamma_r)$. Making this substitution in equation 28 and integrating gives the following equation:

$$(1/2)\log(P_r/P) = \frac{1}{55.51}\int_{m_r}^{m_1} m.d\log(\gamma/\gamma_r) + \frac{m-m_r}{55.51*2.303} \qquad (29)$$

The first term is evaluated by calculating the area under the curve $\log(\gamma/\gamma_r)$ (obtained from equation 27 by neglecting the last term) plotted against m. The value of $(1/2)\log(P_r/P)$ calculated is substituted into equation 28 and a better estimate of $\log(\gamma/\gamma_r)$ obtained. These two equations are solved iteratively until both are satisfied. Thus correct values of $\log(\gamma/\gamma_r)$ are now available. Based upon Debye Huckel theory $\log(\gamma/\gamma_r)$ is extrapolated as a function of concentration and temperature whose precise form is known. From this extrapolation the values of activity coefficient of KOH are calculated. The activity of solvent was obtained earlier from equation 30.

Akerlof and Bender (17) corrected their data for E.M.F. measured to one atmosphere partial hydrogen pressure in each cell by adding the correction term based on literature values of solution vapor pressures. They then processed equation 26 using a form of Gibbs Duhem equation which yielded water transfer potentials given in equation 30.

$$E_{H_2O} = \frac{-RT}{F} \ln \frac{a_{H_2O(m)}}{a_{H_2O(m_r)}} = \int_{m_1}^{m_2} \frac{m}{55.51+m} \frac{dE}{dm} dm \qquad (30)$$

To obtain the coefficients dE/dm needed for application of equation 30, the corrected data for E was plotted and least squared at each temperature with respect to m. Thus E was obtained as a function of m in different concentration ranges and E_{H_2O} values calculated .

Equation 31 now reduces to a ratio of activity coefficients of test and reference solutions.

$$E = \frac{2RT}{F} \ln \frac{a_m}{a_r} = \frac{2RT}{F} \ln \frac{\gamma_m m}{\gamma_r m_r} \qquad (31)$$

The values of activity coefficient of solute and activity of solvent were computed from empirical relations which are a function of concentration (17).

The results of Akerlof and Bender(17) are in good agreement with those obtained by Harned and Cook(16) over the entire range of concentrations. A summary of work done by different researchers, along with the details of the present study are given in Table 1.

Table 1

COMPARISON OF WORK DONE BY DIFFERENT AUTHORS.

Author	Experimental Approach	Concentration Range	Temperature Range	Comments
Bro and Kang (10)	Measured Vapor Pressures	2 M to 15 M	-40°C to 25°C	Gave Values for low Temperatures
Anisimov (11)	"	0 to 60 wt % KOH	0°C to 200°C	Gave Values for high Temperatures
Macdonald et.al. (1)	-	1 M to 8 M	-10°C to 120°C	Collated data of (10, 11)
Ming Chow (12)	Used HgO/Hg Electrodes in KOH Concentration Cells.	0.0013 M to 1.00 M	25°C	Ignored Water Transfer Potentials.
Knobel (13)	Used H_2(Pt) Electrodes in KOH Conc. Cells.	0.01 M to 3.0 M	25°C	"
Harned and Cook (16)	"	0.05 M to 4.0 M	0 to 35°C	Measured a_{H_2O} indirectly by using mean ionic activity coefficients of KOH considered reliable.
Akerlof Bender (17)	"	0.225 to 17.0 M	0 to 70°C	"
Robinson Stokes	-	0.1 to 16.0 M	25°C	Collated data of (16),(17)
Present Work	Used HgO/Hg and H_2 (Pt) Electrodes	1.0 to 8.0 M	0 to 80°C	Directly measured values for a_{H2O} .

Section 3

EXPERIMENTAL SYSTEM AND PROCEDURES

3.1. Experimental Cells

Three different classes of electrochemical cells were selected, each of which is described in detail here.

3.1.1. Type I: $H_2(Pt)/KOH/Hg,Hgo(Pt)$.

Half-cell reactions and the overall reaction are:

$$\begin{array}{ll} HgO + H_2O + 2e^- \rightleftharpoons Hg + 2OH^- & \text{R.H.S} \\ 2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- & \text{L.H.S} \\ \hline HgO(s) + H_2(g) \longrightarrow Hg(l) + H_2O(l) & \end{array}$$

According to the Nernst Equation we have:

$$E_{R.H.S.} = E^\circ_{R.H.S} - \frac{2.303RT}{2F} \log \frac{a_{Hg}\ a^2_{OH}}{a_{HgO}\ a_{H2O}}$$

$$E_{L.H.S.} = E^\circ_{L.H.S.} - \frac{2.303RT}{2F} \log \frac{f_{H_2}\ a^2_{OH}}{a^2_{H_2O}}$$

$$E_1 = E_{cell} = E^\circ_{R.H.S.} - E^\circ_{L.H.S.} - \frac{2.303RT}{2F} \log \frac{a^2_{H_2O}}{a_{H_2O}\ f_{H_2}}$$

$$E_1 = E^\circ_1 - \frac{2.303RT}{2F} \log \frac{a_{H_2O}}{P_{H_2}} \qquad (32)$$

The standard states for water, mercury and mercuric oxide are that they are in their pure form. Therefore the activities of pure mercury and mercuric oxide are unity and hence have been dropped from the Nernst equation. The standard state for H_2 is unit fugacity of hydrogen.

The value of E_1° can be evaluated from the standard-state free energy of the cell reaction using equation 7. The thermodynamic data required for calculating E_1° is presented in Table 2. The values for HgO, Hg, H_2 and H_2O are from G.B.Naumov et. al. Handbook (3), while values for KOH are from Fredrick D.Rossini et. al. (18). The E_1° values at different temperatures are listed in Table 3. These values are in close agreement with those calculated by Macdonald and McKubre in a previous study(19).

Here an assumption is made that within the cell, the hydrogen entering is in equilibrium with the water vapor of the solution and each exerts its equilibrium vapor pressure. Then

$$P_{H_2} = P_{Total} - P_{H_2O}$$

To ensure that this assumption is satisfied, the hydrogen was preequilibrated by bubbling it through a KOH solution of the same concentration and temperature as that in the cell. Using the definition of activity of water given by equation 9, one obtains

$$P_{H_2O} = a_{H_2O} * P^\circ_{H_2O}$$

$$P_{H_2} = P_{Total} - a_{H_2O} * P^\circ_{H_2O} \qquad (33)$$

The experimental conditions used are such that $P_{Total} = 1$. The values for vapor pressure of pure water $P^\circ_{H_2O}$ are taken from the C.R.C. Handbook (20). Then subsituting equation 33 in equation 32 yields the following expression for the activity of water :

Table 2

THERMODYNAMIC DATA USED FOR CALCULATING STANDARD STATE CELL POTENTIALS

Chemical Composition	$\Delta H^\circ_{f(298.15)}$ Kcal/mole	$S^\circ_{(298.15)}$ cal/mole degree	$C^\circ_{p(298.15)}$ cal/mole degree	Coefficients of the equation $C_p=a + bT\times10^{-3} - cT^{-2}\times10^{5}$		
				a	b	c
KOH	-115.29	21.9	-30.3	--	--	--
HgO (Yellow)	- 21.68	16.8	10.53	8.33	7.37	--
Hg	--	18.17	6.69	6.44	--	-0.19
H_2	--	31.208	6.89	6.52	0.78	-0.12
H_2O	- 68.315	16.71	17.995	12.65	11.38	1.73

Note: Values for KOH are at infinite dilution standard state.

Table 3

CALCULATED STANDARD STATE POTENTIALS E_1° FOR TYPE I CELL AT DIFFERENT TEMPERATURES

T(°C)	T(°K)	ΔG_1° (CALS/MOL)	E_1° (V)
0	273.15	-43,052.64	0.9338
10	283.15	-42,919.24	0.9309
20	293.15	-42,786.71	0.9281
30	303.15	-42,655.53	0.9252
40	313.15	-42,525.35	0.9224
50	323.15	-42,396.24	0.9196
60	333.15	-42,268.21	0.9168
70	343.15	-42,141.76	0.9141
80	353.15	-42,016.07	0.9114

$$E_1 = E°_1 - \frac{2.303\ RT}{2F} \log \frac{a_{H2O}}{1- a_{H_2O} * P°_{H_2O}} \quad (34)$$

Thus, the measured cell potential, E_1, gives a self consistent activity of water at any given different temperature from the known values of $E_1^°$ and $P^°_{H_2}O$.

3.1.2. Type II: $K_{(Hg)}(Pt)/KOH/Hg,Hgo(Pt)$

$K_{(Hg)}$ represents potassium in the form of amalgam.
Half-cell reactions and the overall reaction are:

$$HgO + H_2O + 2e^- \rightleftharpoons Hg + 2OH^- \qquad R.H.S.$$

$$2K^+ + 2e^- \rightleftharpoons 2K_{(Hg)} \qquad L.H.S.$$

$$HgO(s) + H_2O(l) + 2K_{(Hg)}(l) \rightleftharpoons Hg(l) + 2KOH(l)$$

According to the Nernst Equation:

$$E_{R.H.S.} = - \frac{2.303RT}{2F} \log \frac{a^2_{OH}}{a_{H_2O}}$$

$$E_{L.H.S.} = E^°_{L.H.S.} - \frac{2.303RT}{2F} \log \frac{a^2_{k(Hg)}}{a^2_{k+}}$$

$$E_2 = E_{cell} = E^°_{R.H.S.} - E^°_{L.H.S.} - \frac{2.303RT}{2F} \log \frac{a^2_{OH}\ a^2_{K+}}{a^2_{K(Hg)}\ a_{H_2O}}$$

$$E_2 = E^°_2 - \frac{2.303RT}{2F} \log \frac{a^2_{\ KOH}}{a_{H_2O}\ (wt\ \%\ K)^2} \quad (35)$$

The standard states for KOH and K(Hg) are:

$$\text{KOH: Dilute solution standard state ie. } \lim_{C_{KOH} \to 1} \frac{a_{KOH}}{C_{KOH}} = 1$$

$$K_{(Hg)}\text{: Dilute solution standard state ie. } \lim_{\% K \to 1} \frac{a_K}{\text{wt } \% K} = 1$$

Standard states for all other species are as defined earlier.

The weight percent of potassium in the amalgam is less than 0.4 wt.% (mole fraction of potassium, X_K, less than 0.02). Hence the activity of potassium in the amalgam can be replaced by its weight percent. The standard state free energy for formation of potassium in amalgam is taken from Gmelin's Handbook (21). The value used for the experimentally known concentration of potassium in the amalgam is -24,906 calories/mole. Consequently the values calculated for E_2° are represented in Table 4. Since the activity of water is known from Type I cell, measurement of Type II cell potential in the range of 0°C to 80°C would give values for activity of KOH at different temperatures.

3.1.3. Type III: $H_2(Pt)/KOH/K_{(Hg)}(Pt)$

Half cell reactions and the overall reaction are:

$$2K^+ + 2e^- \rightleftharpoons 2\underline{K}_{(Hg)} \qquad \text{R.H.S.}$$

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad \text{L.H.S.}$$

$$2KOH(l) + H_2(g) \rightleftharpoons 2K_{(Hg)}(l) + 2H_2O(l)$$

$$E_{R.H.S.} = E^\circ_{R.H.S.} - \frac{2.303RT}{2F} \log \frac{a^2_{K(Hg)}}{a^2_{K+}}$$

Table 4

CALCULATED STANDARD-STATE POTENTIAL E_2° FOR TYPE II CELL AT DIFFERENT TEMPERATURES

T(°C)	T(°K)	ΔG_2° (CALS/MOL)	E_2° (V)
0	273.15	-98,460.50	2.1357
10	283.15	-98,798.02	2.1430
20	293.15	-99,111.97	2.1498
30	303.15	-99,394.76	2.1559
40	313.15	-99,653.82	2.1615
50	323.15	-99,883.59	2.1665
60	333.15	-100,100.51	2.1712
70	343.15	-100,280.51	2.1751
80	353.15	-100,444.09	2.1787

$$E_{L.H.S.} = E^{\circ}_{L.H.S.} - \frac{2.303RT}{2F} \log \frac{f_{H_2} a^2_{OH}}{a^2_{H_2O}}$$

$$E_3 = E_{cell} = E^{\circ}_{R.H.S.} - E^{\circ}_{L.H.S.} - \frac{2.303RT}{2F} \log \frac{a^2_{K(Hg)} a^2_{H_2O}}{a^2_{KOH} f_{H_2}}$$

or
$$E_3 = E^{\circ}_3 - \frac{2.303RT}{2F} \log \frac{(\text{wt \% K})^2 a^2_{H_2O}}{a^2_{KOH} P_{H_2}} \tag{36}$$

The values of E°_3 are listed in Table 5. Measurement of E_3 would serve as a check on the values of activity of water and potassium hydroxide obtained from E.M.F. measurements of all three types of cells being mutually consistent with one another.

3.2 Experimental Procedure

3.2.1. Cell Design: A new design of the reaction vessel was employed, which incorporated all three types of cells within the same unit. This has not been done before in the previous studies. The unit consists of two identical cells made of teflon. The height and diameter of the cylindrical cells are both three inches. The cell cover has four openings. Two larger ones accomodate hollow quarter-inch outer-diameter teflon tubes for the flow of hydrogen into and out of the cell. The mercury, mercuric oxide electrode consists of a mixture of Hg, HgO and KOH in a hollow cylindrical teflon container, threaded and tightened into the cell cover. There is a hole in the bottom of this container, which is sealed tightly with a porous Zirconia plug. This plug permits a contact between the Hg, HgO mixture and the KOH solution inside the cell, without allowing them to mix. A Platinum wire inserted inside the container forms the electrode for E.M.F. measurements. The fourth opening accommodates the Platinum foil, which serves as the hydrogen electrode. To establish equilibrium, hydrogen must bubble along the

Table 5

CALCULATED STANDARD STATE POTENTIALS E_3° FOR TYPE III CELL AT DIFFERENT TEMPERATURES

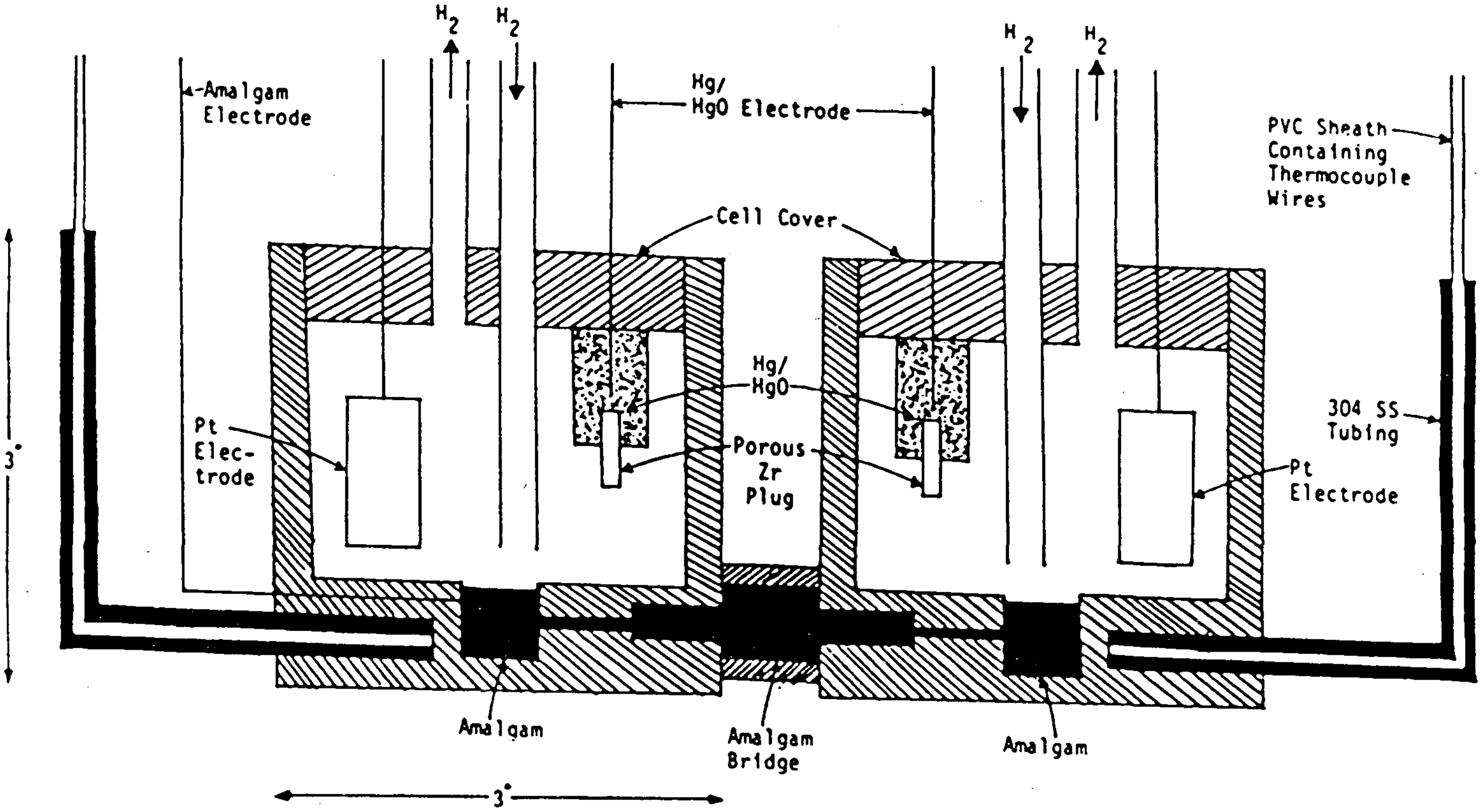
T(°C)	T(°K)	ΔG_3° (CALS/MOL)	E_3° (V)
0	273.15	55,408.01	-1.2018
10	283.15	55,878.93	-1.2120
20	293.15	56,325.42	-1.2217
30	303.15	56,739.39	-1.2307
40	313.15	57,128.60	-1.2391
50	323.15	57,493.02	-1.2471
60	333.15	57,832.48	-1.2544
70	343.15	58,138.93	-1.2611
80	353.15	58,428.21	-1.2673

foil. To facilitate this, the foil was aligned to lie flat along the tube bringing in hydrogen. Very small holes were made along the tube in the region where the foil and the tube overlap. The flow pattern was studied for this arrangement by immersing the tube and the foil in a beaker of water and passing Argon. Fine bubbles emerge from the tiny holes, impinge normally on the surface and then travel upwards along the foil.

The bottom of the cell has a small recess in which potassium amalgam is contained. The two cells are connected by means of an amalgam bridge. A platinum wire inserted into the pool of amalgam forms the amalgam electrode. One cell contains the N molal test solution while the other is a standard cell with 1.0 Molal KOH solution. Thus by measuring the E.M.F. between corresponding H_2/Pt electrodes of the two cells, we set up a concentration cell of the kind described earlier by equation 26. This set up also accentuates the change in the properties of KOH solution with concentration, since all other parameters remain the same for two solutions inside their respective cells.

The temperature of the solution inside the cell would be different from the bath temperature since teflon is a poor conductor of heat. The actual solution temperature is monitored by inserting a 'J' type Iron-Constantan thermocouple in the wall of the cell, close to the solution. The thermocouple wires are within a PVC sheath, which in turn is enclosed in a 304 stainless steel tubing. A schematic representation of the two-cell teflon unit is shown in Figure 2.

3.2.2. Preparation of the solutions and amalgam. For preparing the KOH solutions, reagent grade potassium hydroxide was used. A carefully weighed quantity of potassium hydroxide was dissolved in the required amount of pure double-distilled water. The true concentration of the prepared solution was determined by titrating it against standard HCl of known concentration using Phenolphthalein as an indicator. All volumes



Test Cell with N Molal KOH Solution

Standard Cell with 1.0 Molal KOH Solution

Figure 2. Schematic representation of the two-Cell Teflon unit.

were corrected to 20°C, and the concentrations determined to three decimal places. The solutions were stored in polyethylene bottles.

The amalgam was prepared in a dry box under one atmosphere of nitrogen. One pound of mercury was mixed with 1.0655 grams of pure potassium, giving the composition of amalgam as 0.234 weight percent or 0.012 mole fraction of potassium. The amalgam was sealed in an air-tight flask before removal from the dry box.

3.2.3 Preparation of the electrodes. The mercury, mercuric oxide electrode is prepared by first mixing the two together thoroughly until the yellow color of HgO turns to dull brown. This mixture is placed in the container and packed closely with free mercury interspersed in between. Finally it is saturated with the potassium hydroxide solution which it will contact in the cell. The platinum wire is firmly embedded in this mixture to form the Hg, HgO electrode.

In order for the H_2(Pt) electrode to attain equilibrium, the surface of the platinum foil must be in a finely divided state (22). The platinization of the foil is done by first cleaning it in hot aqua regia (75% HCl, 25% HNO_3 by volume). The platinizing solution was made by adding 8.47 mgm of lead acetate and 1.0 gm of platinic chloride to 32.1 millilitres of water. The two platinum foils are immersed in this solution and connected to the leads of a platinizing kit. The current is set to 50 milliamperes and the polarity is reversed every 30 seconds. The platinizing is done for five minutes, at the end of which the foils are covered with an adherent uniform coating of platinum black. After being thoroughly washed in distilled water, the foils are immersed in 0.75 Molar H_2SO_4 and electrolysis is done in a similar way of reversing polarity every 30 seconds for the same length of time. This ensures that residual Cl^- ions clinging to the surface of the foil are removed, at the same time providing some pre-saturation of foils with hydrogen evolved at the electrodes. The foils are once again washed thoroughly and stored in a beaker of distilled water.

3.2.4 The Experimental Arrangement. The experimental arrangement is schematically illustrated in Figure 3. Before being introduced into the cell, the gas is passed through a saturator bottle containing the same concentration of KOH solution as that contained in the cell. This is to ensure that the hydrogen enters the cell at the same temperature and vapor pressure saturation conditions as that existing within the cell. The gas is bubbled out against a very small head of water into the cell atmosphere. The total pressure inside the cell is assumed to be one atmosphere.

The cell and the saturator are placed in a ethylene glycol bath, which can be heated by coils or cooled by circulation through a pump. The bath has an attached temperature controller and a separately immersed thermometer. However the actual temperature of the solution within the cell is monitored by using the thermocouples. The junction reference temperature must be known if the solution temperature is to be determined, since the thermocouple voltage is a function of the difference between the two temperatures (23). To obtain a constant temperature the reference junction is maintained in a bath of melting crushed ice and water, well stirred and contained in a Dewar Flask. The leads from the electrodes are connected to a Keithley 179A TRMS Multimeter, which measures voltage to fourth decimal place in the required range.

The cell is assembled inside a dry box to prevent the oxidation of potassium in amalgam. The connections are made as in Figure 3. The gas flow is adjusted by means of the valve on the regulator of the gas tank to about one bubble every second. E.M.F. measurements can be recorded to a precision of ± 0.1mV after the steady state has been acquired at each temperature from 0°C to 80°C at ten degree intervals. This procedure is repeated for each of the five concentrations, namely 1.007 M, 2.000 M, 4.001 M, 6.005 M and 8.017 M KOH solutions.

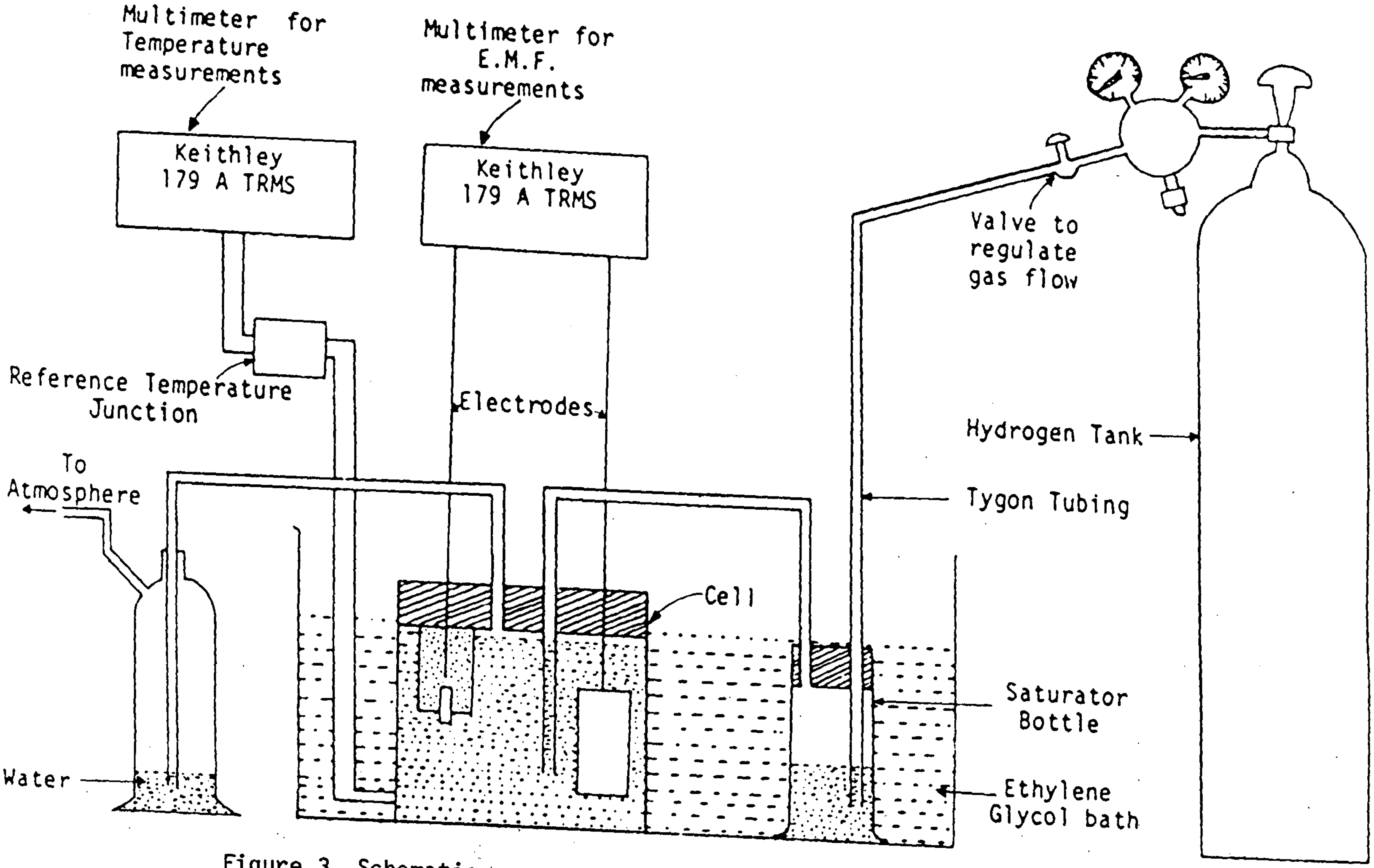


Figure 3. Schematic representation of the experimental set-up.

Section 4

RESULTS

4.1 Type II and Type III Cells : All the three proposed cells were contained in the same reaction chamber as described earlier. Experimentation was done with the 2.0 M solution in the test cell and 1.0 M solution in the standard cell. Even after hydrogen was bubbled into the solutions for 48 hours, no definite end point or steady state equilibrium could be attained. The E.M.F. measurements for all the three types of cells were not near the respective E° values. Repeating the experiment with new solutions also did not produce any meaningful results. The reasons for the failure of simultaneous E.M.F. measurements of all the three cell is discussed in the next section. Subsequently it was decided to measure only the Type I cell and to remove the amalgam electrode and the amalgam bridge from each cell.

4.2 Type I Cell: After the cell was loaded and gas flow started the E_{cell} rose rapidly and reached a limiting value within 30 minutes. Generally steady state was acquired for successful runs in one hour. The E.M.F. measurements were started from 0°C onwards. The temperature was held constant until a steady E.M.F. value was obtained, before being increased again. The test runs in which stable values were not obtained were discarded. Values of partial pressure of hydrogen in the cell are given in Table 6 . The results are presented in Tables 7,8,9,10 and 11 for 1.007 M, 2.000 M, 4.001 M, 6.005 M and 8.017 M solutions respectively. Similar data is not available in literature for comparison with these measured E.M.F. values. However Donnan and Allmand (24) comment that values for the temperature coefficients of the electrodes Hg/HgO, normal KOH and Hg/HgO, normal NaOH should ideally be identical. They measured the temperature coefficient of the cell Hg/HgO, N-NaOH/H_2 to be -0.00031 volt/degree in the range 0 to 25°C, a value which agrees well with that obtained in the present work.

The values of activity of water generated by Macdonald et al(1) are presented in Table 12. At each concentration and temperature, they are lower than the values obtained in the present study. This is

Table 6

PARTIAL PRESSURES OF HYDROGEN INSIDE THE CELL AS A FUNCTION OF CONCENTRATION AND TEMPERATURE

Temperature		Partial Pressure of H_2 (atm)				
t(°C)	T(°K)	1.007 M	2.000 M	4.001 M	6.005 M	8.017 M
0	273.15	0.9941	0.9944	0.9951	0.9959	0.9965
10	283.15	0.9882	0.9887	0.9901	0.9916	0.9931
20	293.15	0.9776	0.9785	0.9805	0.9835	0.9862
30	303.15	0.9592	0.9607	0.9645	0.9692	0.9734
40	313.15	0.9288	0.9317	0.9384	0.9457	0.9528
50	323.15	0.8814	0.8851	0.8969	0.9065	0.9169
60	333.15	0.8083	0.8178	0.8357	0.8496	0.8713
70	343.15	0.7001	0.7169	0.7486	0.7756	0.8079
80	353.15	0.5439	0.5698	0.6189	0.6613	0.7254

Table 7

VARIATION OF MEASURED EMF OF TYPE I CELL AND ACTIVITY OF WATER WITH TEMPERATURE FOR 1.007 MOLAL KOH SOLUTION

t(°C)	T(°K)	(1/T)x1000	E(v)	a_{H_2O}	$\log a_{H_2O}$
0	273.15	3.66	0.9340	0.97736	-0.009945
10	283.15	3.53	0.9311	0.97215	-0.012265
20	293.15	3.41	0.9282	0.96991	-0.013267
30	303.15	3.30	0.9250	0.97401	-0.011435
40	313.15	3.19	0.9217	0.97824	-0.009554
50	323.15	3.09	0.9182	0.97459	-0.011179
60	333.15	3.00	0.9141	0.97551	-0.010769
70	343.15	2.91	0.9092	0.97519	-0.010909
80	353.15	2.83	0.9025	0.97615	-0.010484

Table 8

VARIATION OF MEASURED E.M.F. OF TYPE I CELL AND ACTIVITY OF WATER WITH TEMPERATURE FOR 2.000 MOLAL KOH SOLUTION

t(°C)	T(°K)	(1/T)X1000	E(v)	a_{H_2O}	Log a_{H_2O}
0	273.15	3.66	0.9346	0.92906	-0.031955
10	283.15	3.53	0.9316	0.93356	-0.029856
20	293.15	3.41	0.9287	0.93308	-0.030079
30	303.15	3.30	0.9255	0.93887	-0.027392
40	313.15	3.19	0.9223	0.93860	-0.027517
50	323.15	3.09	0.9187	0.94416	-0.024952
60	333.15	3.00	0.9150	0.92703	-0.032906
70	343.15	2.91	0.9104	0.92070	-0.035882
80	353.15	2.83	0.9041	0.92063	-0.035913

Table 9

VARIATION OF MEASURED E.M.F. OF TYPE I CELL AND ACTIVITY OF WATER WITH TEMPERATURE FOR 4.001 MOLAL KOH SOLUTION

t(°C)	T(°K)	(1/T)X1000	E(v)	a_{H_2O}	Log a_{H_2O}
0	273.15	3.66	0.9362	0.81156	-0.090681
10	283.15	3.53	0.9332	0.81997	-0.086202
20	293.15	3.41	0.9300	0.84361	-0.073857
30	303.15	3.30	0.9269	0.84684	-0.072197
40	313.15	3.19	0.9238	0.84594	-0.072660
50	323.15	3.09	0.9204	0.84684	-0.072197
60	333.15	3.00	0.9168	0.83573	-0.077932
70	343.15	2.91	0.9128	0.81743	-0.087547
80	353.15	2.83	0.9072	0.81562	-0.088511

Table 10

VARIATION OF MEASURED EMF OF TYPE I CELL AND ACTIVITY OF WATER WITH TEMPERATURE FOR 6.005 MOLAL KOH SOLUTION

t(°C)	T(°K)	(1/T)X1000	E(v)	a_{H_2O}	Log a_{H_2O}
0	273.15	3.66	0.9382	0.68526	-0.164142
10	283.15	3.53	0.9352	0.69705	-0.156736
20	293.15	3.41	0.9321	0.71654	-0.144757
30	303.15	3.30	0.9288	0.73574	-0.133274
40	313.15	3.19	0.9256	0.74604	-0.127238
50	323.15	3.09	0.9219	0.76845	-0.114383
60	333.15	3.00	0.9183	0.76529	-0.116173
70	343.15	2.91	0.9150	0.72979	-0.136801
80	353.25	2.83	0.9100	0.72498	-0.139673

Table 11

VARIATION OF MEASURED EMF OF TYPE I CELL AND ACTIVITY OF WATER WITH TEMPERATURE FOR 8.017 MOLAL KOH SOLUTION

t(°C)	T(°K)	(1/T)X1000	E(v)	a_{H_2O}	Log a_{H_2O}
0	273.15	3.66	0.9403	0.57368	-0.241332
10	283.15	3.53	0.9376	0.57345	-0.241505
20	293.15	3.41	0.9344	0.59892	-0.222633
30	303.15	3.30	0.9308	0.63407	-0.197861
40	313.15	3.19	0.9276	0.64812	-0.188344
50	323.15	3.09	0.9237	0.68302	-0.165567
60	333.15	3.00	0.9209	0.65483	-0.183869
70	343.15	2.91	0.9179	0.62479	-0.204262
80	353.15	2.83	0.9146	0.58780	-0.230770

Table 12

RESULTS OF ACTIVITY OF WATER COMPUTED BY MACDONALD *ET.AL.* FROM VAPOR PRESSURE STUDIES.

Temperature		Molal concentration				
t(°C)	T(°K)	1.00	2.00	4.00	6.00	8.00
0	273.15	.9690	.9110	.7950	.6800	.5640
10	283.15	.9660	.9080	.7920	.6765	.5605
20	293.15	.9630	.9050	.7890	.6730	.5570
30	293.15	.9610	.9047	.7910	.6770	.5600
40	313.15	.9620	.9080	.7990	.6900	.5810
50	323.15	.9640	.9100	.8010	.6925	.5840
60	333.15	.9660	.9120	.8030	.6950	.5870
70	343.15	.9660	.9120	.8050	.6985	.5920
80	353.15	.9650	.9120	.8070	.7020	.5970

graphically represented in Figs. 4 to 13 for each temperature. Robinson and Stokes collated data of other workers and gave values for osmotic coefficients of H_2O at 25°C. From these, activity of water values have been calculated. These values are compared with Macdonald et al and the present work in Table 13 and represented graphically in Fig 7. Robinson and Stokes(9) values lie between those of Macdonald et al and the present work.

The studies of Harned and Cook (16) showed that logarithm of activity of water changes only in the fourth decimal place between the limits 0 and 35°c up to 4.0 M. This was confirmed by Akerlof and Bender (17) in their studies. To compare the results of present work regarding variation of activity of water with temperature, log a_{H_2O} was plotted against 1/T. The plots are shown in Figs 14 to 18 for each concentration. Up to 4.0 M the variance of log a_{H_2O} is not very great. This is in accordance with the results of earlier studies. However deviation is seen to occur for 6.0 M and 8.0 M solutions.

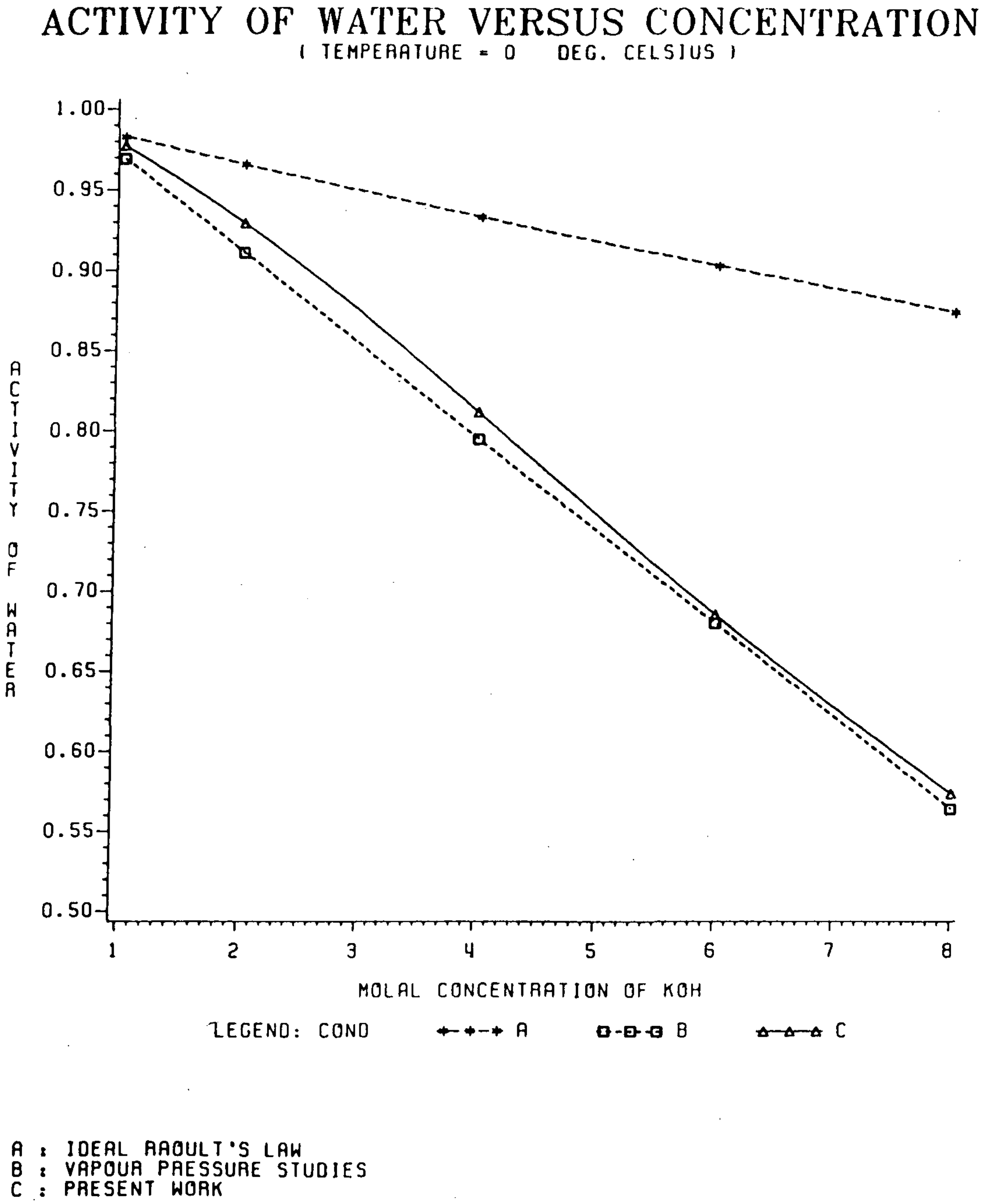


Figure 4. Activity of water versus concentration at 0° Celsius.

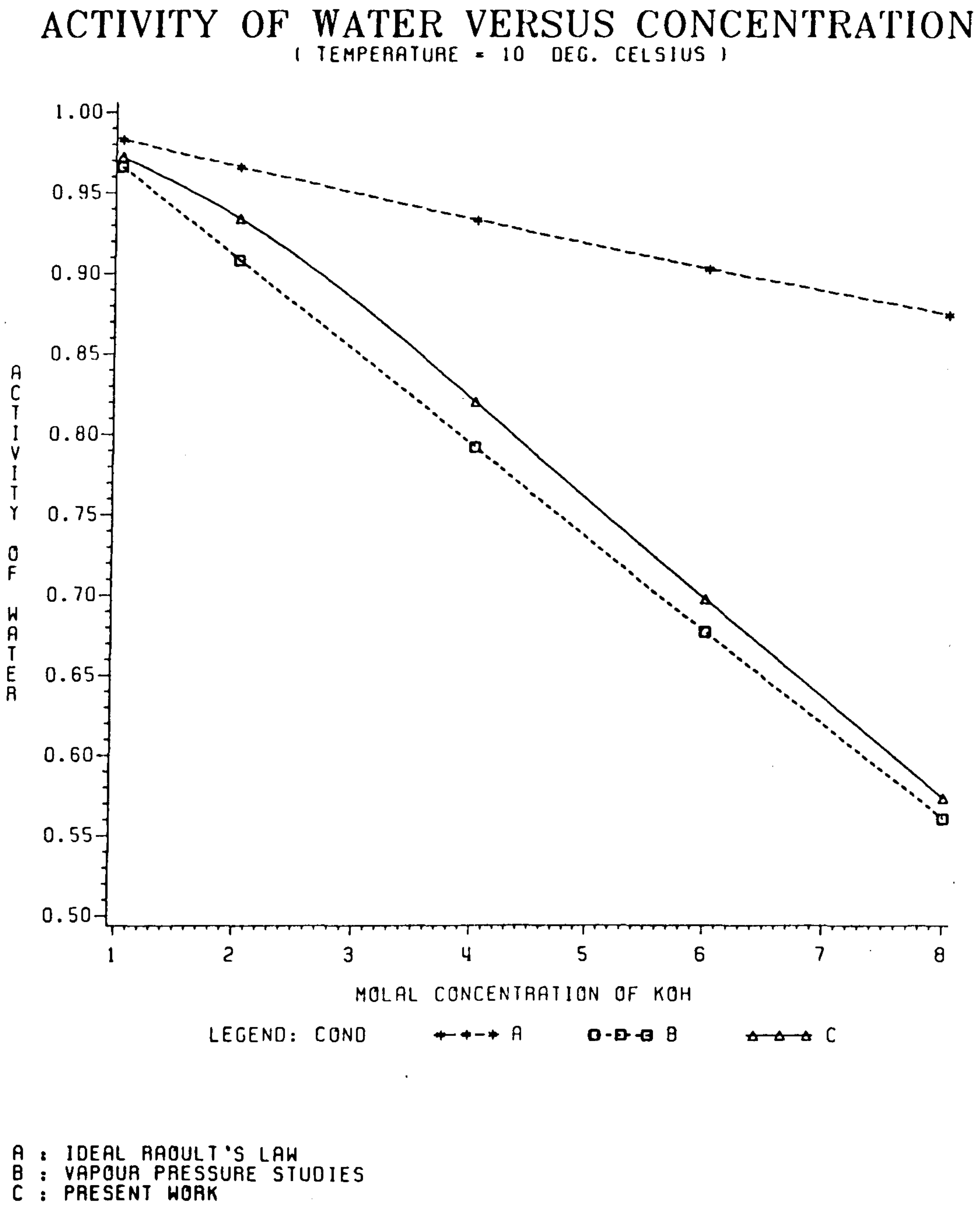
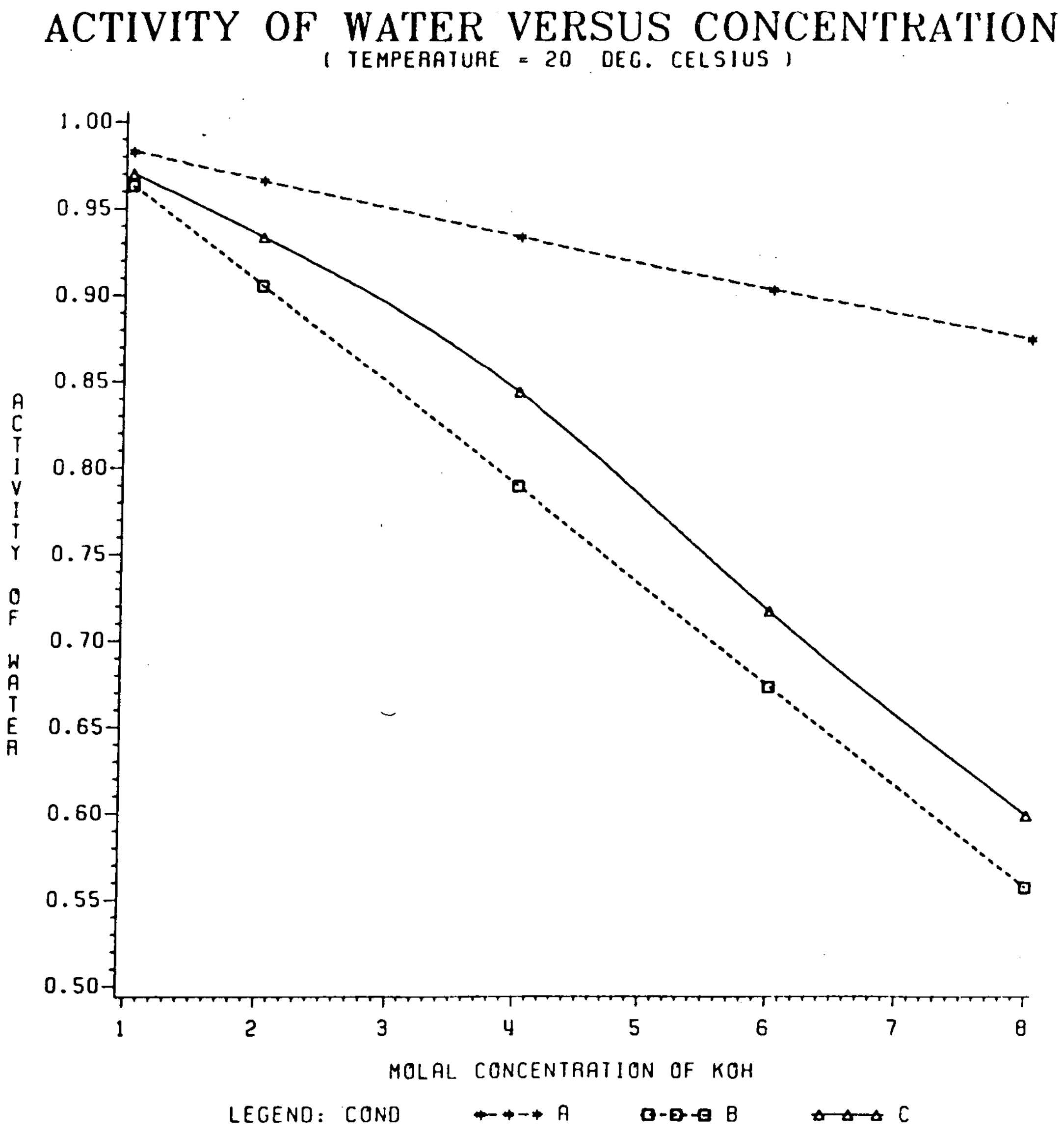


Figure 5. Activity of water versus concentration at 10° Celsius.



A : IDEAL RAOULT'S LAW
B : VAPOUR PRESSURE STUDIES
C : PRESENT WORK

Figure 6. Activity of water versus concentration at 20° Celsius.

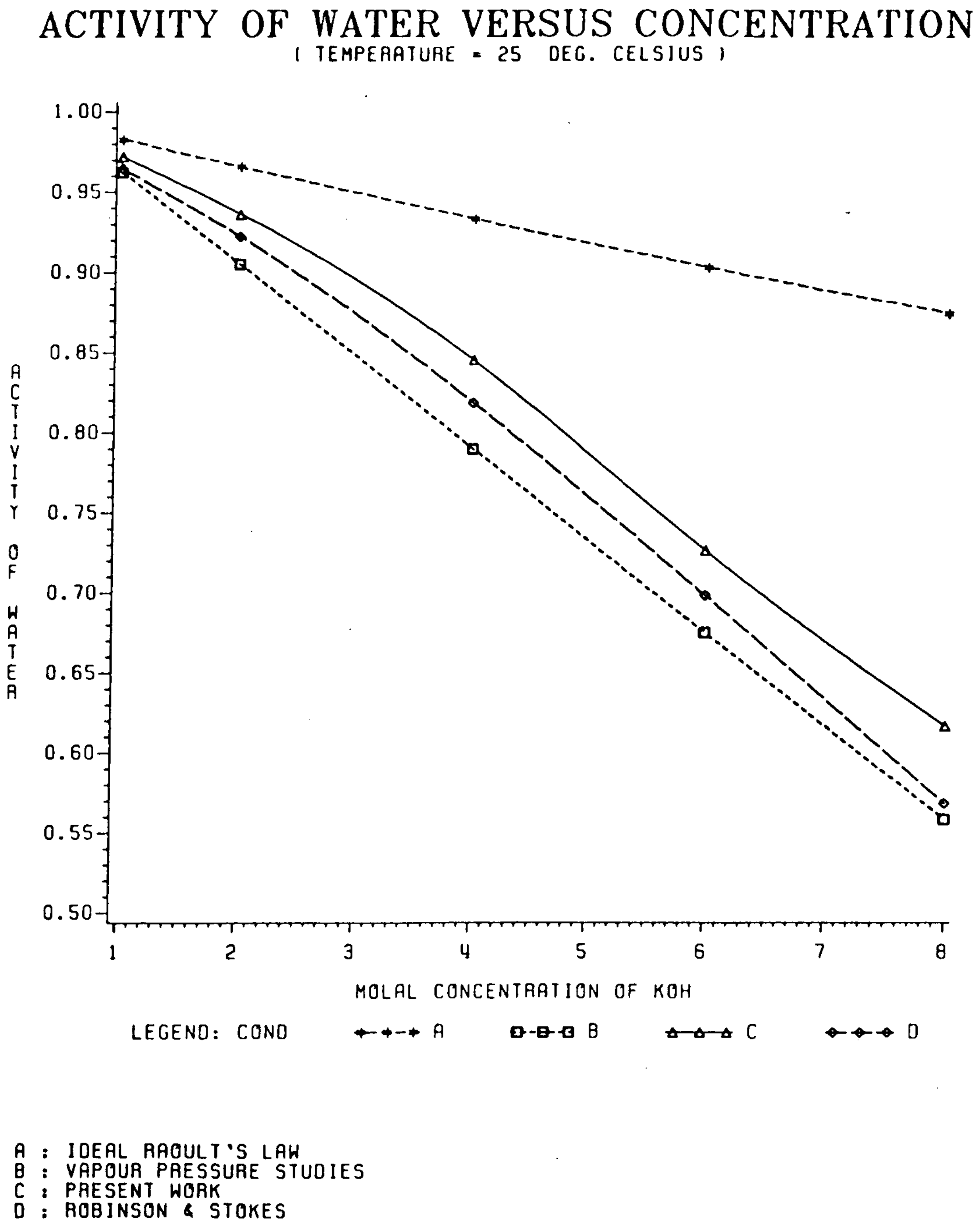


Figure 7. Activity of water versus concentration at 25° Celsius.

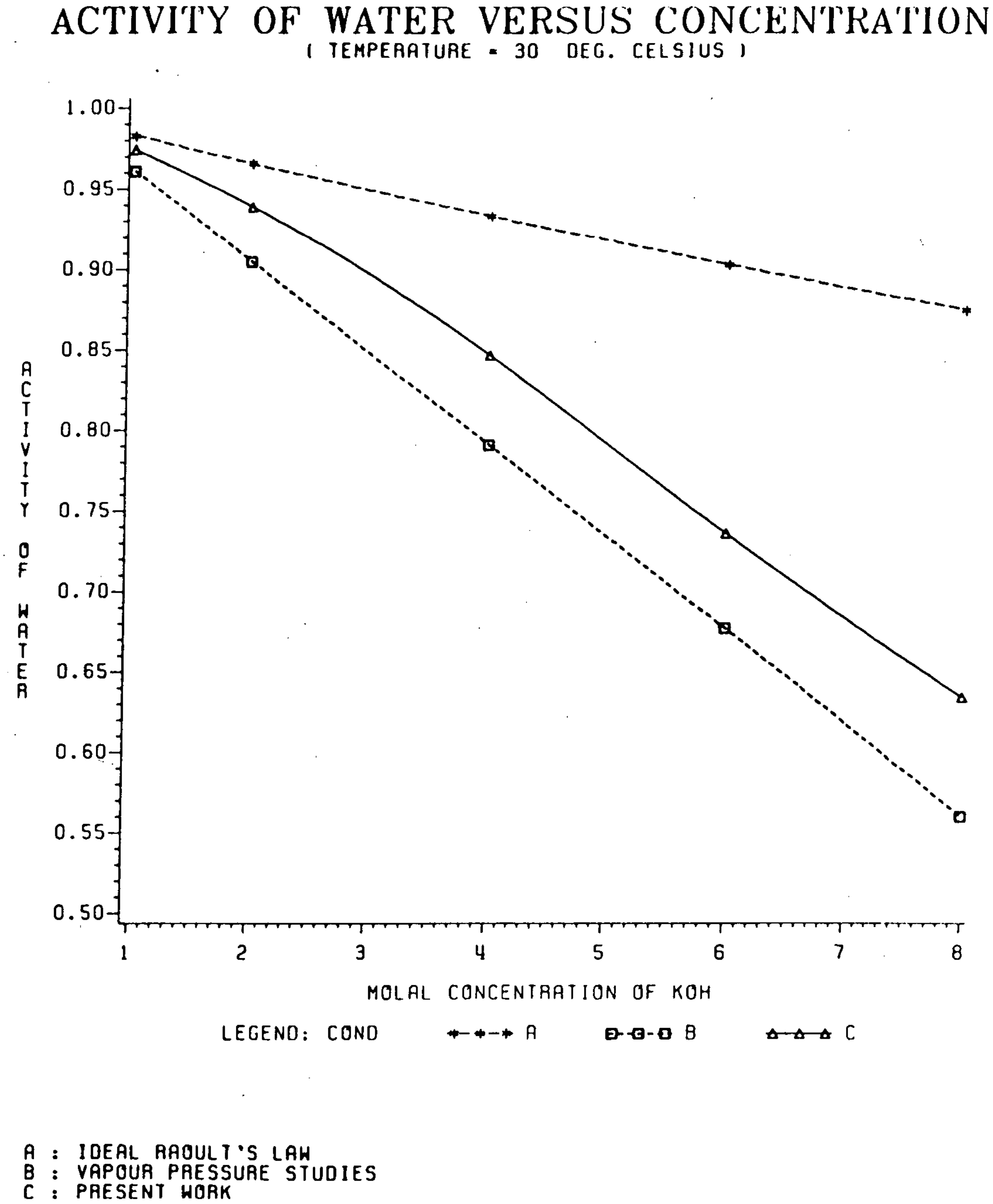
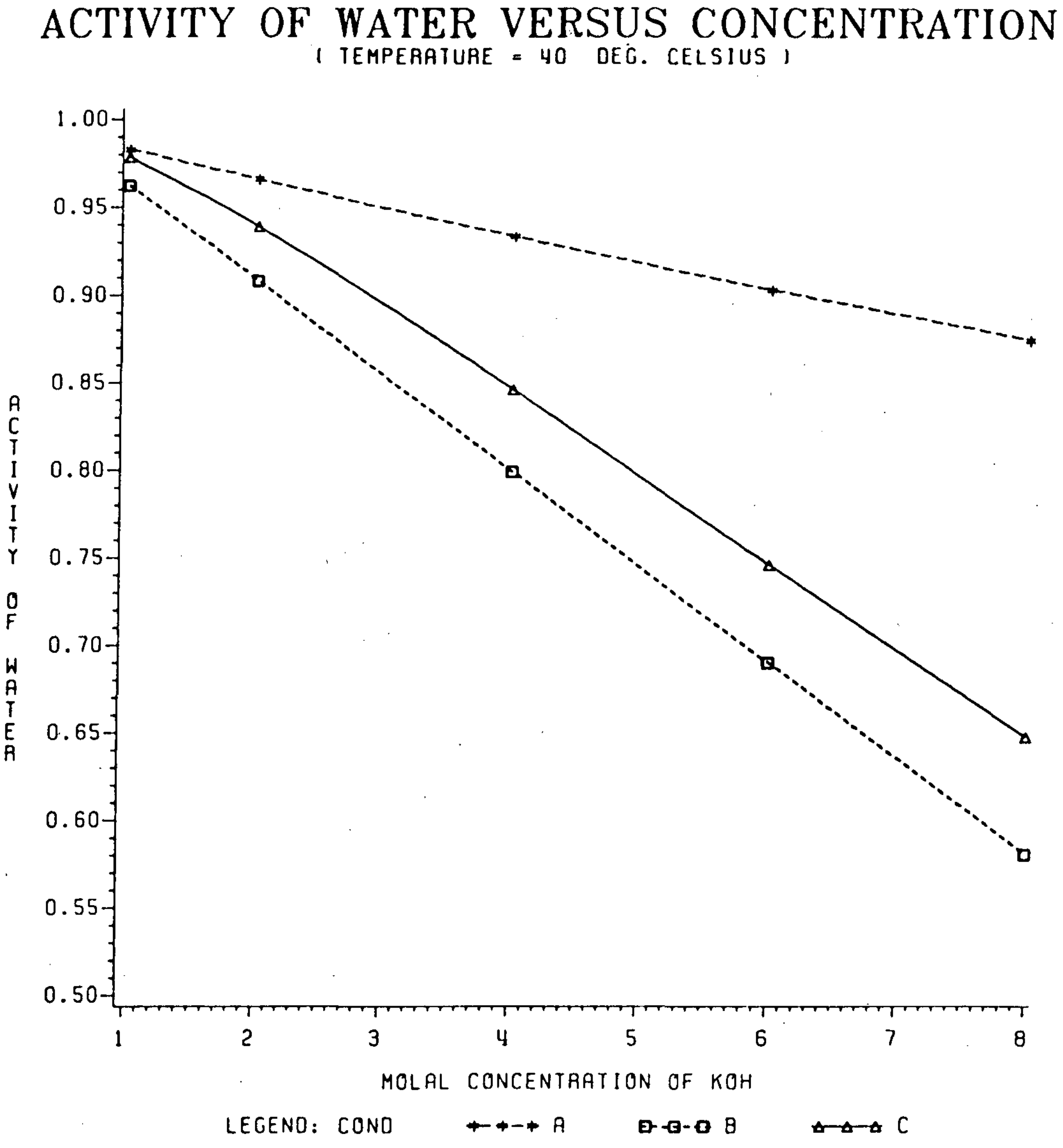


Figure 8. Activity of water versus concentration at 30° Celsius.



A : IDEAL RAOULT'S LAW
B : VAPOUR PRESSURE STUDIES
C : PRESENT WORK

Figure 9. Activity of water versus concentration at 40° Celsius.

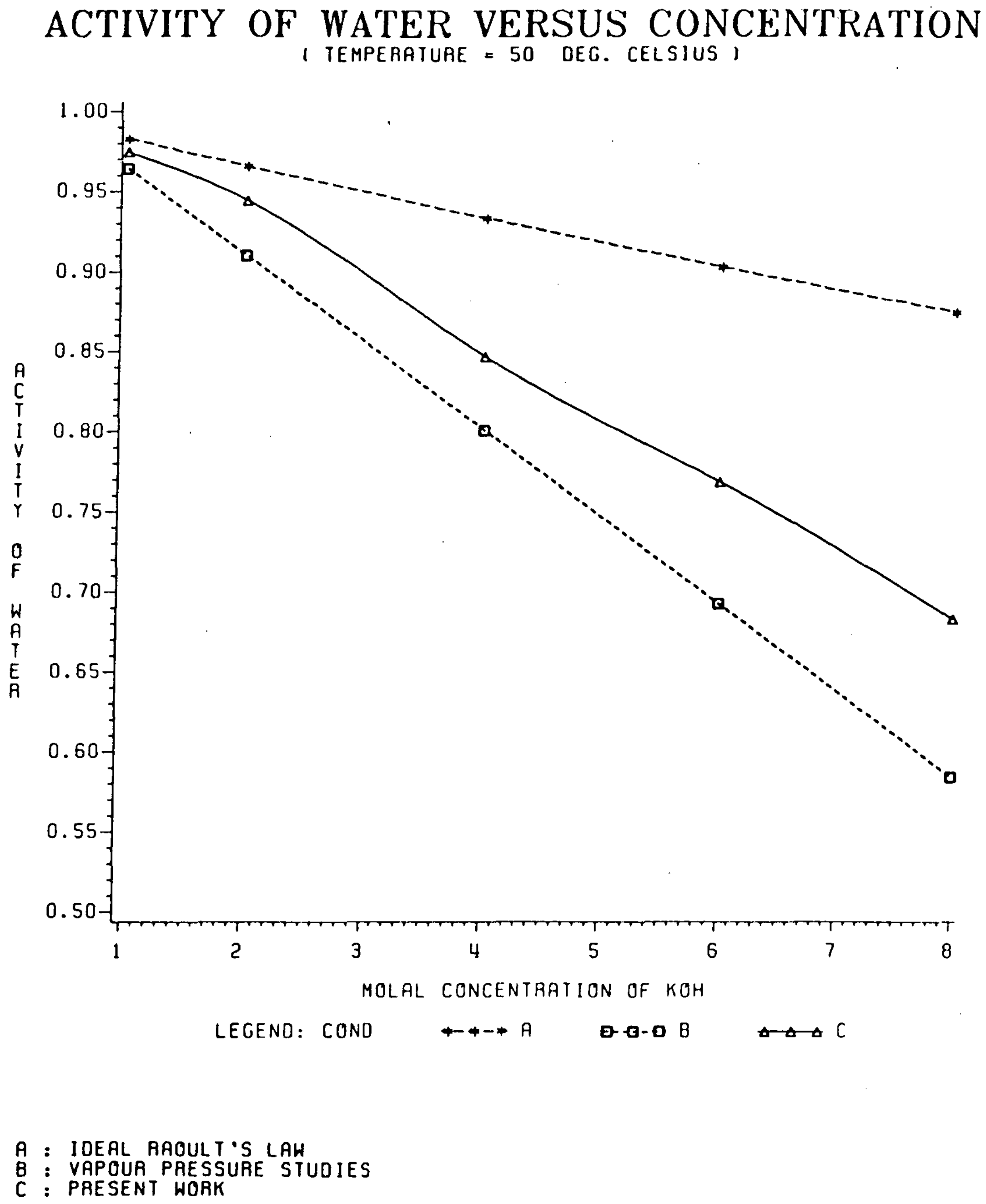


Figure 10. Activity of water versus concentration at 50° Celsius.

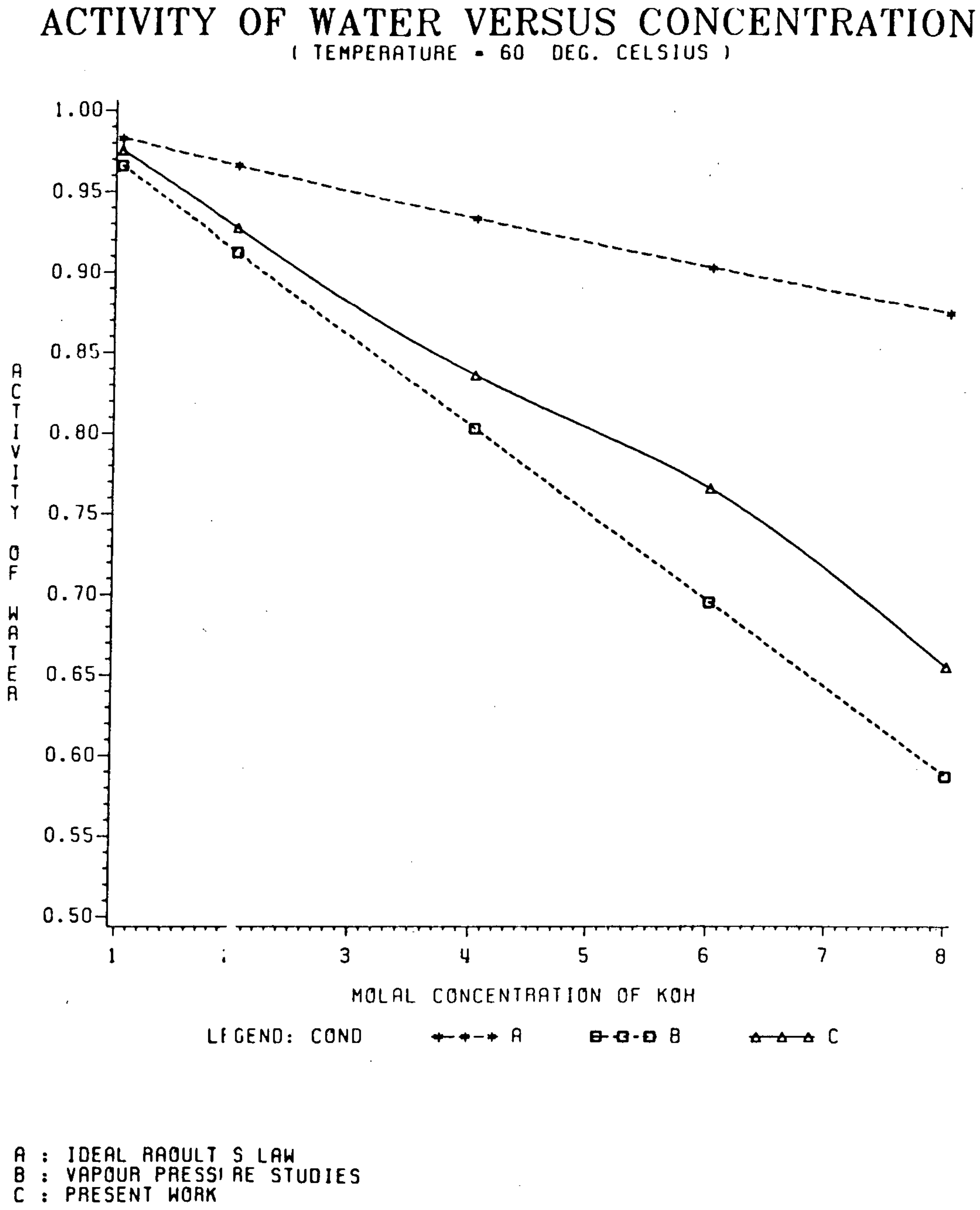


Figure 11. Activity of water versus concentration at 60° Celsius.

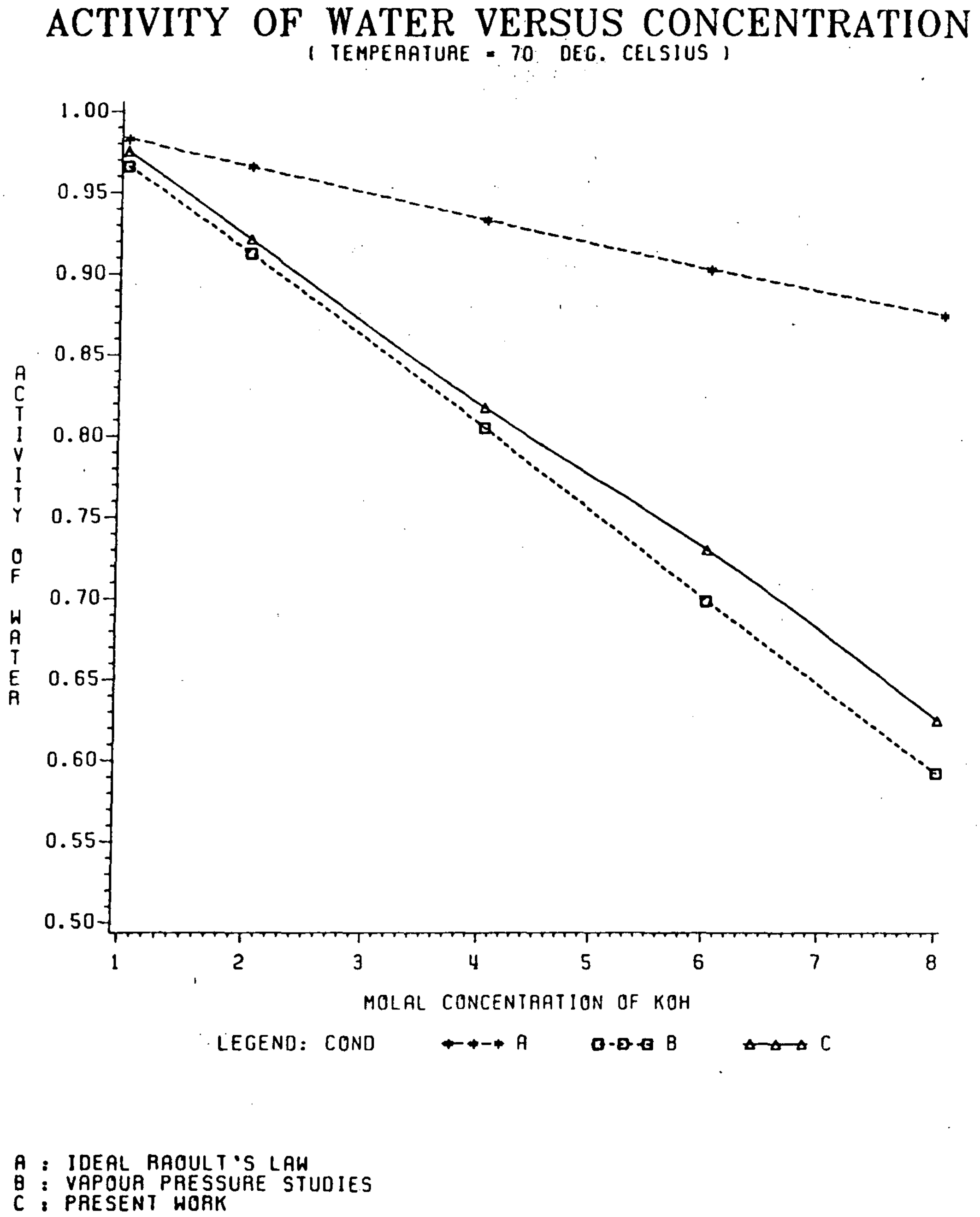
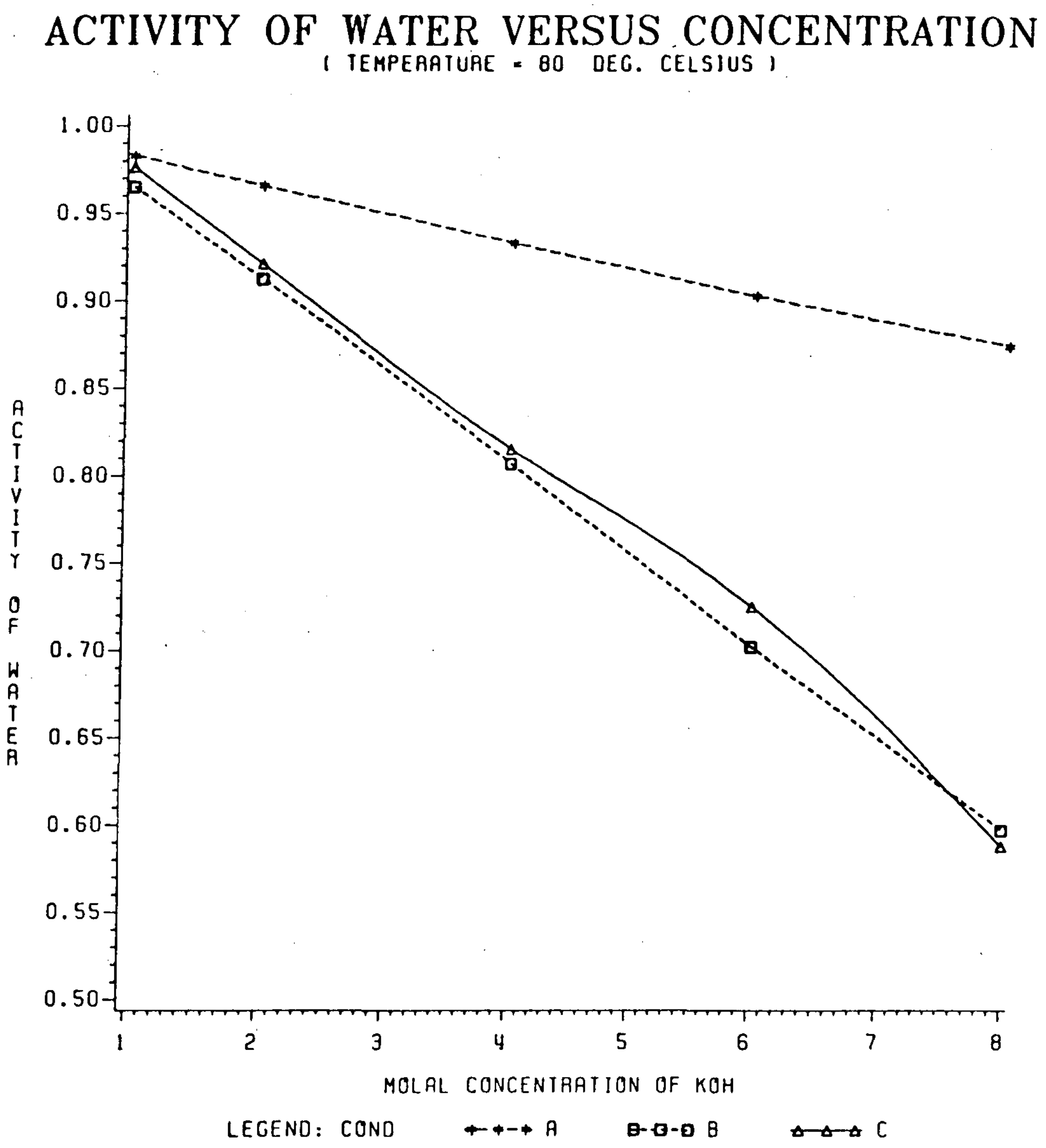


Figure 12. Activity of water versus concentration at 70° Celsius.



A : IDEAL RAOULT'S LAW
B : VAPOUR PRESSURE STUDIES
C : PRESENT WORK

Figure 13. Activity of water versus concentration at 80° Celsius.

Table 13

COMPARISON OF VALUES OF ACTIVITY OF WATER AT 25° CELSIUS FROM DIFFERENT SOURCES.

Concentration	Ideal	Vapor Pressure Studies(10,11)	Present Work	Robinson Stokes(9)
1.00	.9823	.9620	.97196	.9645
2.00	.9653	.9048	.93598	.9220
4.00	.9328	.7900	.84523	.8188
6.00	.9025	.6750	.72614	.6983
8.00	.8741	.5585	.61649	.5683

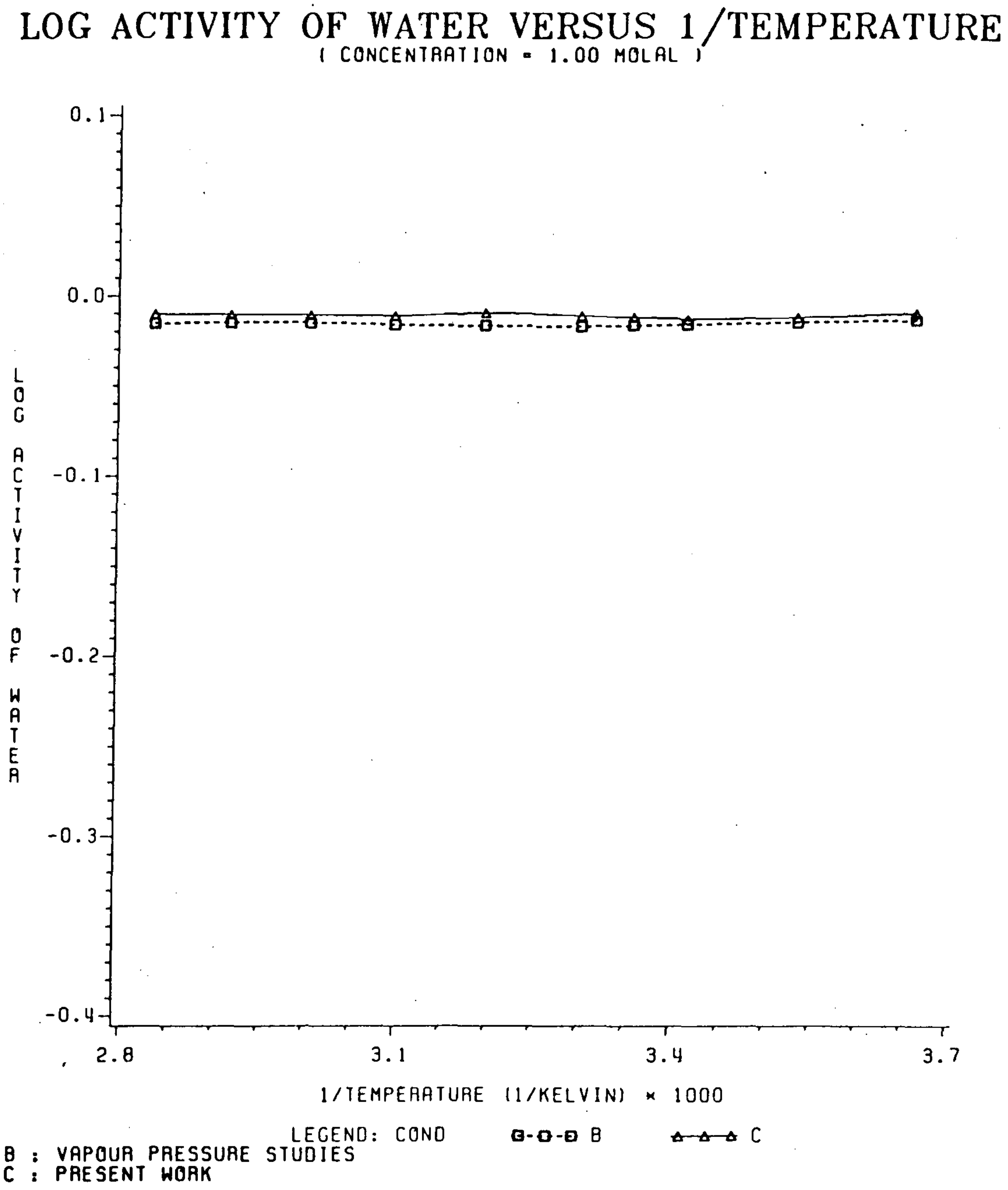


Figure 14. Log activity of water versus 1/temperature for 1.00 Molal KOH solution.

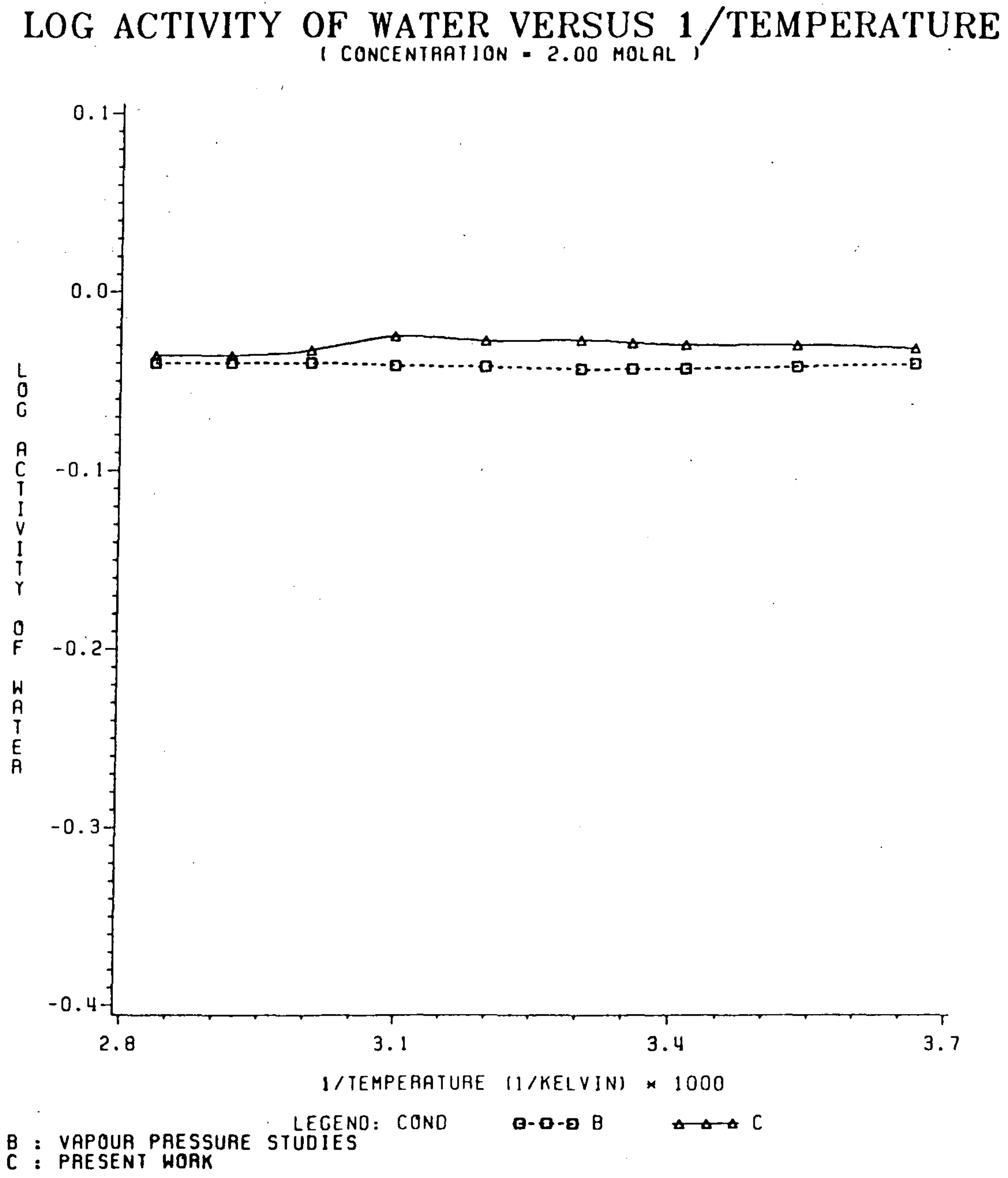


Figure 15. Log activity of water versus 1/temperature for 2.00 Molal KOH solution.

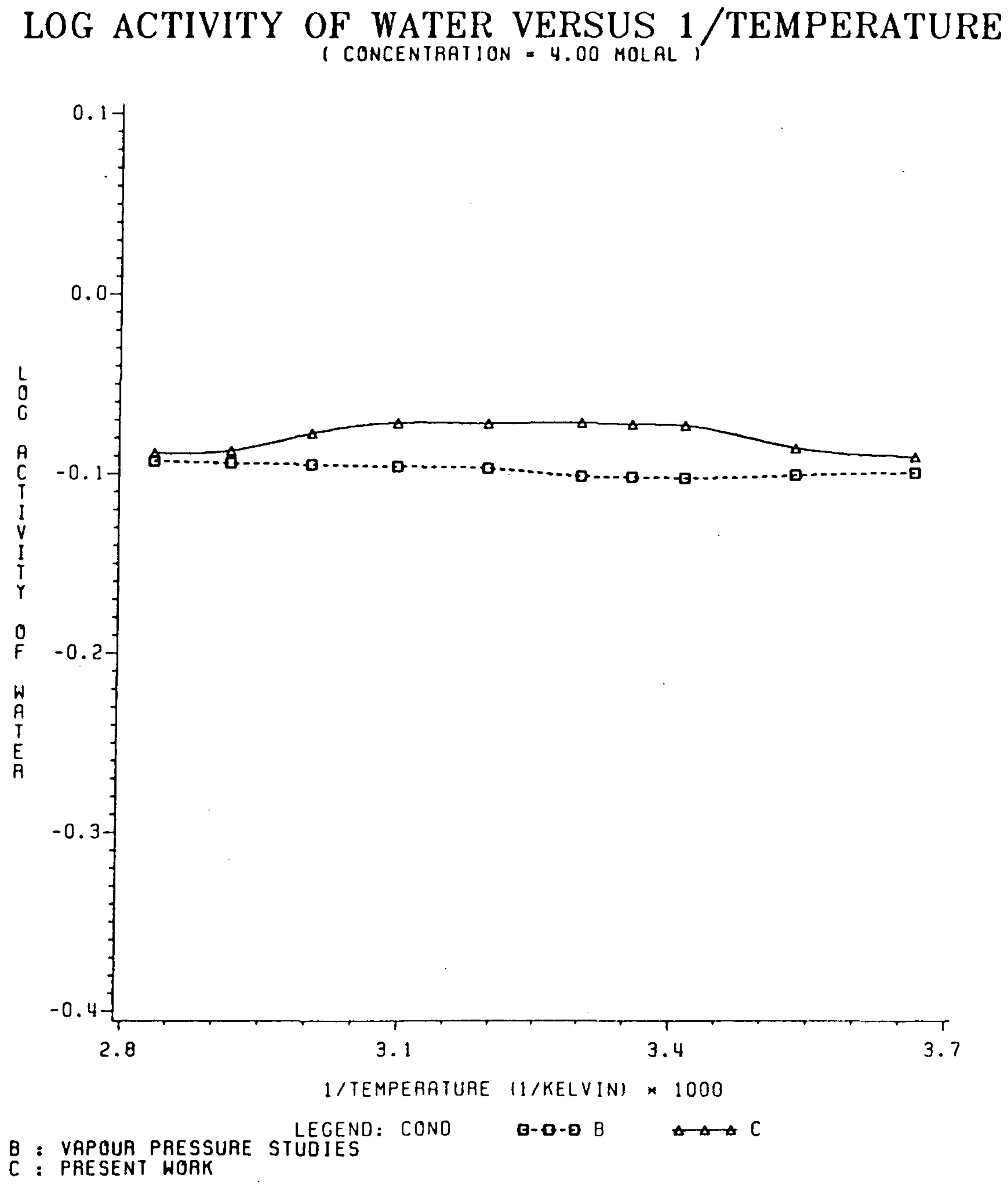


Figure 16. Log activity of water versus 1/temperature for 4.00 Molal KOH solution.

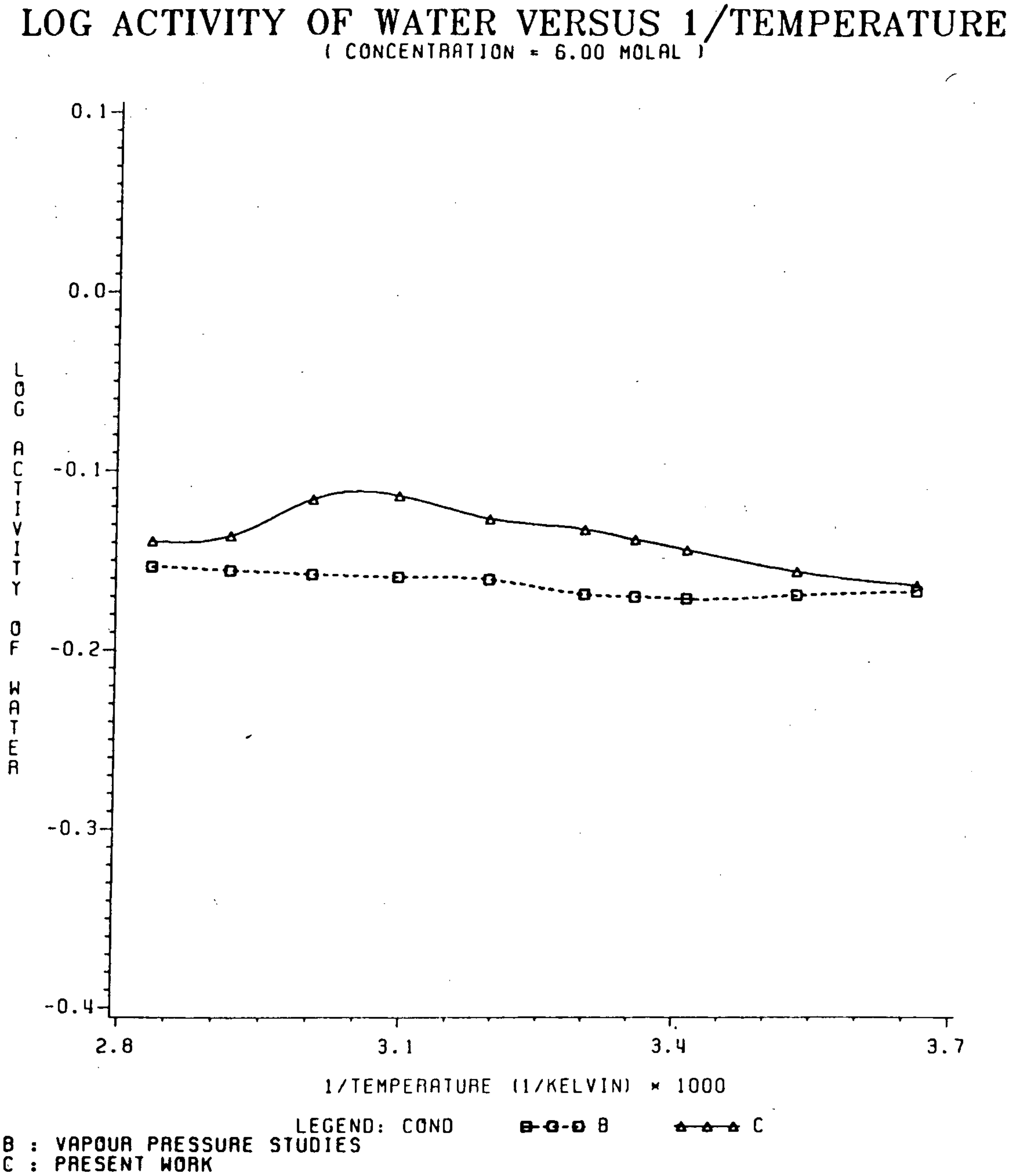


Figure 17. Log activity of water versus 1/temperature for 6.00 Molal KOH solution.

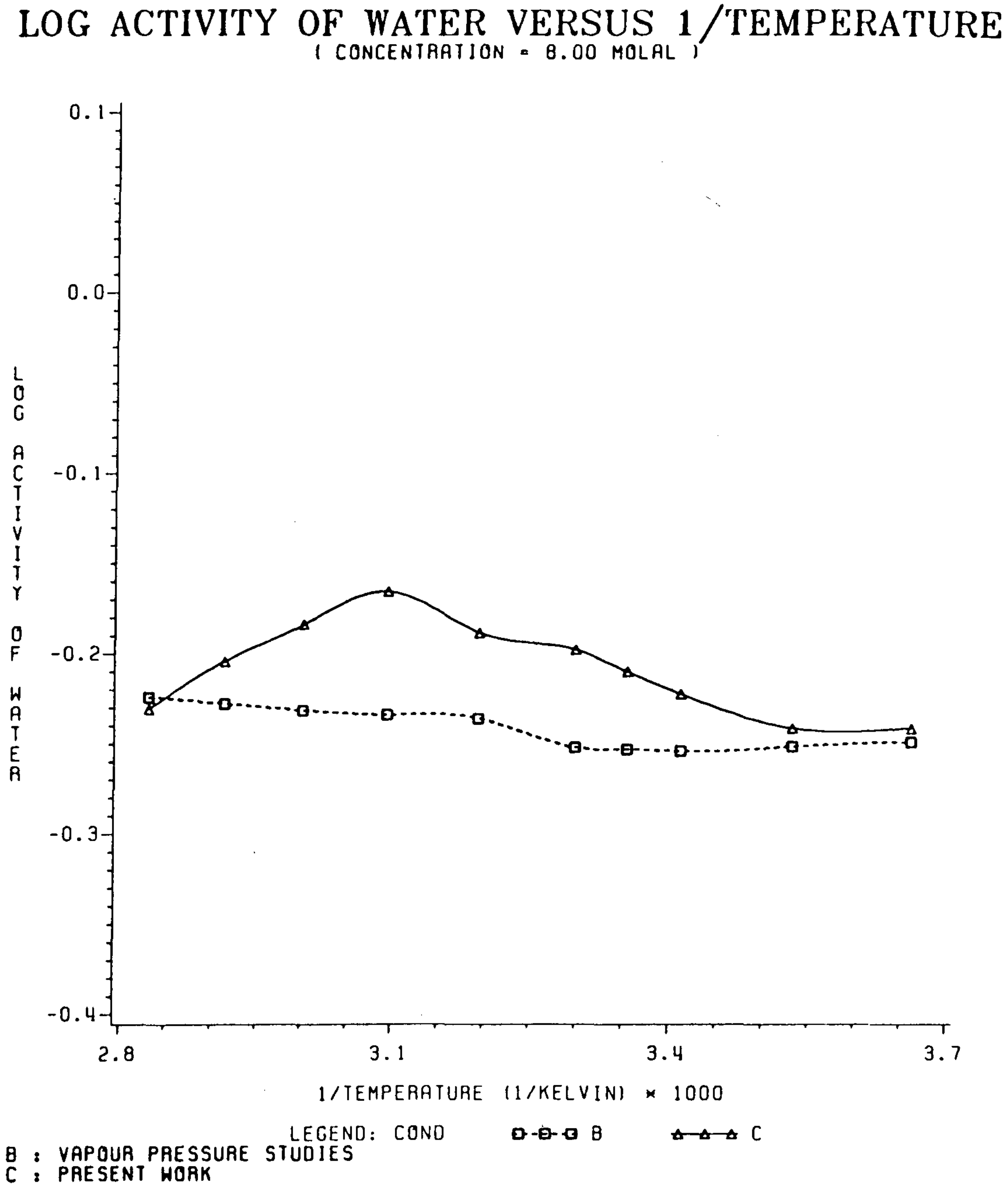


Figure 18. Log activity of water versus 1/temperature for 8.00 Molal KOH solution.

Section 5

DISCUSSION

5.1 Type II and Type III Cell: The failure of simultaneous E.M.F. measurements of all the three cells can be attributed mainly to the fact that the continuous exposure of the amalgam to aqueous KOH solution resulted in the potassium in amalgam reacting with water to form the hydroxide solution. Vigorous evolution of hydrogen is seen to occur when the KOH solution covers the amalgam in the ports. The local pH around the platinum foil increases, thereby leading to erroneous E.M.F. values for the pH-dependent hydrogen electrode. It is exceedingly important to have no dissolved oxygen in the solution, for oxygen reacts with the potassium of the amalgam, decreasing its concentration and at the same time increasing the concentration of the solution. However in the existing cell design, the solutions cannot be introduced into the cell without exposure to air first. This further accelerates the rate of removal of potassium from the amalgam.

Once the potassium in amalgam goes into solution, the pool of mercury does not function as an electrode. It is conjectured that mercury may subsequently physically adsorb on to the platinum foil and thus poison the hydrogen electrode. It is obvious then that no true equilibrium is possible in such a situation. In all the previous studies, flowing amalgams were used so that their contact with aqueous KOH solution is reduced to a minimum.

5.2 Type I Cell: The measurement of the equilibrium potential of Type I cell directly measures the activity of water. In all the previous studies involving electromotive force method, the activity coefficient of KOH was measured. Subsequently using mathematical techniques, the activity of water was calculated as a related parameter. Thus the results obtained in the present study can be considered more reliable.

The accuracy with which the activity of water can be determined depends upon the equilibrium potentials that are established in the system and the preciseness with which they can be measured. Some of the factors which may affect the accuracy of the results obtained are discussed below.

The HgO/Hg electrode has been subject of controversy regarding its reproducibility and reversibility. There are two forms of mercuric oxide - red and yellow. It is generally considered that the only difference between them is that the yellow form has smaller grains(25). In discussing preparation of electrodes, Gmelin's Handbook (21) says that HgO in coarse particle form must be present in excess. This is made possible by careful heating of $Hg_2(NO_3)_2$ or $Hg(NO_3)_2$ in a porcelain crucible under constant stirring, with occasional cooling and grinding, until all oxides of nitrogen are removed. The product so obtained is bright reddish brown in color, and contains only a very few particles of very small grain size so that quick accomplishment of equilibrium is guaranteed.

Considerable experience with red and yellow mercury oxide produced by various different techniques shows that the potential of the electrode varies with the grain size. Cohen (26) has found that there is a difference of 0.685 millivolts when the two forms of the oxide are made into electrodes of the form HgO/Hg, KOH. This is to be expected since finely divided substances have greater solubility than coarsely crystalline ones. Knobel (13) considered Chow's (12) results unreliable because of use of HgO/Hg electrode instead of hydrogen electrode. Akerlof and Bender (17) have also suggested that at higher concentrations the HgO/Hg electrode may not function reversibly,thereby giving erroneous results.

Reagent-grade yellow mercuric oxide of very fine grain size was used in the present work. The extent of deviation from true equilibrium due to its solubility in the alkaline solution cannot be estimated. However the maximum error introduced is estimated to be on ythe order of 1 mV, which is approximately 0.1% of the measured EMF (1 mV out of $\sim$900).

Strong alkaline solutions absorb carbon dioxide from the atmosphere. In all the previous studies carbonate present was precipitated using barium hydroxide and then filtered out. The solutions were boiled to expel all air and always kept under a nitrogen atmosphere to prevent contamination. Such procedures were not followed in this study since the effect of CO_2 pick-up on the results was not considered significant. Carbon dioxide is only 0.033% of air and its solubility in water is 1.45 gm/liter at 25°C(20). This would change the concentration of the KOH solution by only 0.04 percent. The actual figure would be less than this since saturation can only be achieved under conditions of vigorous stirring. Here the exposure to air occurs only when the solutions are transferred from the container to the cell, and the kinetics of equilibriation are not sufficiently fast to reach an equilibrium saturation value under the existing experimental conditions. Furthermore, the agreement between the results of this study at 25°C and the previous studies at the same temperature indicate that the carbonate concentration does not significantly affect the measured activity values.

From the expression for E.M.F. of the cell, it can be readily seen that the activity of water depends upon the partial pressure of hydrogen inside the cell. It has been assumed that the water vapor and hydrogen exert their equilibrium partial pressures inside the cell. This assumption is reasonable because the gas first passes through a pre-saturator and thus acquires the same temperature and water vapor saturation as that existing within the cell. For this to occur slow flow rates of gas are essential, so that the process of gaseous equilibriation is not controlled by diffusion of hydrogen through the KOH solution. Experimentally the flow rates were monitored carefully to obtain steady E.M.F. values.

5.3 Significance of the present study: The direct measurement of the activity of water in concentrated KOH solutions can be used to calculate several related parameters which are important in battery technology. The details of such calculations will not be given here as a complete description and computer programs of their implementation have been previously presented (1). Rather, examples of the types of refinements which are possible from the current measurements will be illustrated in this section. Furthermore, since the measured activity values of water are within ∿10% of those used in the previous calculations (1) the major conclusions of that study are not significantly affected.

Using equation 22, the mean ionic activity coefficient of KOH can be evaluated. The osmotic coefficient has already been defined in terms of the activity of water by equation 13. Then the graphical integration of Gibbs-Duhem equation yields values for the activity coefficient of the solute with a high degree of accuracy.

In the previous study (1) pH of the solution was defined as $-\log(a_{H^+})$ for the concentrated hydroxide system, with the understanding that it is a purely formal relationship requiring a_{H^+} itself to be specified. The dissociation constant of water can be defined by equation:

$$K_w = \frac{a_{H^+} \, a_{OH^-}}{a_w} \tag{37}$$

where a_w is activity of water.

An expression for K_w as a function of temperature is given by Naumov et.al. (3). Using this and rearranging after accounting for ion pairing leads to the following expression for the pH of the solution

$$\mathrm{pH} = \log \frac{m}{a_w} + \frac{4466.2}{T} - 5.941 + 0.016638\ T \tag{38}$$

where m = stoichiometric concentration of KOH solution.

The thermodynamic properties of metals in aqueous media can be derived for reactions having the general form

$$aA + xH^+ + ne^- = bB + cH_2O \tag{39}$$

The Nernst equation for this reaction can be written as:

$$E = E^{o} + \frac{2.303\ RT}{nF}(\ a \log a_A - b \log a_B - c \log a_W\ ) - \frac{2.303RTx}{nF} \text{pH} \quad (40)$$

Under equilibrium conditions this equation reduces to:

$$x\text{pH} = \frac{-\Delta G^{o}}{2.303RT} + a \log a_A - b \log a_B - c \log a_W \quad (41)$$

Since the pH of the solution and activity of water is now known,the equilibrium potentials for each reaction at various stoichiometric concentrations of KOH can be calculated. Programs have been generated which make these computations for each specific metal/water equilibrium system (1). They can also handle mixed oxidation products which may be produced in an actual battery system. Using these programs, equilibrium potentials for selected reactions in the systems of interest can be recalculated by substitution of water activity and pH data into the appropriate potential vs pH equations. Subsequently the voltage efficiency of a cell at open circuit which is defined by the following equation

$$e_{Cell} = \frac{E_{Test}}{E_{Cell}} \quad (42)$$

where E_{Test} is the open circuit potential for a practical cell

E_{Cell} is the computed thermodynamic value

can be obtained more accurately due to the more accurately known value of the activity of water.

Section 6

CONCLUSIONS

The principal conclusions which can be derived from this study are:

- The equilibrium E.M.F. measurements of stationary amalgam electrodes in aqueous alkali solutions is not possible due to potassium in amalgam reacting with the KOH solution.

- The values of activity of water obtained in this work are greater than those found by vapor pressure studies. However they are closer to the values of water activity found by E.M.F. measurements of KOH concentration cells at 25°C.These measurements directly measure the water activity and thus need make no assumptions regarding the electrolyte behavior as in the previous electrochemical studies. Therefore, these results present more accurate data for water activity in concentrated KOH solutions.

- The logarithm of activity of water is fairly invariant with 1/Temperature for concentrations up to 4.0 M. For higher concentrations of 6.0 M and 8.0 M, the activity first decreases by $\sim$10% and then increases by $\sim$5% as the temperature is increased. This general activity trend in the higher concentrations is consistant with previous studies.

- The values of activity of water obtained here from direct E.M.F. measurements can be used to improve the calculations of equilibrium cell voltages and theoretical efficiencies of battery systems.

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APPENDIX

POLYNOMIAL COEFFICIENTS FOR BEST FIT OF p/p^* VS CONCENTRATION FOR POTASSIUM HYDROXIDE

		p/p^*		
T/°C	A(0)	A(1)	A(2)	A(3)
- 10	0.98215	-0.05855	0.0	0.0
0	1.026269	-0.05775	0.0	0.0
20	1.01106	-0.05547	0.0	0.0
25	1.018776	-0.05803	0.0	0.0
40	1.01683	-0.05451	0.0	0.0
60	1.01961	-0.05404	0.0	0.0
80	1.01700	-0.05248	0.0	0.0
100	1.01504	-0.05095	0.0	0.0
120	1.01196	-0.04924	0.0	0.0

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