Standard Electrode Potential of Ag_2O/Ag Electrodes In Alkaline Solutions at 25° C.

THEDFORD P. DIRKSE, Calvin College, Grand Rapids, Mich.

IN 1957, Hamer and Craig (*5*) measured the electromotive force (e.m.f.) of the $Ag_2O/Ag/OH^-$ electrode *vs.* a $HgO/Hg/OH^-$ electrode. They developed a method for preparing Ag_2O/Ag electrodes which had a stable e.m.f. in alkaline solutions and pointed out that the generally accepted e.m.f. value for these electrodes (*8*) had not been determined potentiometrically. They reviewed the calorimetric data used to determine the electrode potential value and concluded that the standard e.m.f. of the electrode, $Ag_2O/Ag/OH^-$, must be measured *vs.* a hydrogen electrode.

EXPERIMENTAL

An H-type cell was constructed of borosilicate glass and had a Teflon needle valve in the cross piece to isolate the electrode compartments from each other, except when a voltage measurement was being made. It was desirable to prevent dissolved silver(I) oxide from diffusing to the hydrogen electrode compartment and possibly contaminating the hydrogen electrode. Each 40-ml. electrode compartment could be drained separately through Teflon stopcocks. Teflon stopcocks were used throughout the apparatus to eliminate the use of stopcock lubricant.

A stock solution of saturated potassium hydroxide for preparing the electrolyte was treated with a small amount of barium hydroxide to precipitate any carbonate. Laboratory distilled water was passed through an ion exchange column, and then distilled from alkaline permanganate in an all-borosilicate glass apparatus. Only the middle fraction was saved. The potassium hydroxide solution and the water were each in a polyethylene bottle and could be fed directly to the mixing flask through polyethylene tubing. They were protected from carbon dioxide contamination by Ascarite traps.

The electrolyte was prepared immediately before a run was made. Hydrogen was used to clear the mixing flask of air and the stock potassium hydroxide solution and water were then added and mixed by bubbling hydrogen through the mixture. Hydrogen was then used to pump the potassium hydroxide from the mixing flask into the cell. The first portion of electrolyte to enter the cell was drained out and then the cell was filled and the run started.

The Ag_2O/Ag electrodes were prepared according to the directions given by Hamer and Craig (*5*). Three such electrodes were used.

A new hydrogen electrode was used for every run. It consisted of a platinum wire which was cleaned in aqua regia and then thoroughly rinsed with distilled water. The platinum black was plated from a standard platinizing solution. After this, the electrode was rinsed in distilled water and stored in conductivity water until used. A dummy platinum electrode was made cathode in dilute potassium hydroxide solution and allowed to gas vigorously for at least half an hour to remove any impurities that might plate out on the platinum surface of the electrode to be used. The test electrode was then made cathode in the same way as the dummy electrode.

A high grade tank hydrogen was passed through silica gel, over heated copper shavings, through Ascarite, and finally bubbled through a dilute potassium hydroxide solution before it was bubbled into the cell. It was led into the hydrogen electrode compartment from the bottom, and passed upwards over the electrode.

The cell was immersed in a constant temperature bath kept at 25° ± 0.05° C. The thermometer used had been calibrated by the National Bureau of Standards. A portable potentiometer (Rubicon), used to make the voltage readings, was checked from time to time against a calibrated standard cell which was less than 1 year old. A run was not considered acceptable, if the total variation of cell voltage readings was more than 0.5 mv. over a 3-hour period, or if there was a constant, although small drift in voltage values during this time. Little difficulty was experienced in getting stable hydrogen electrodes. In one case, cell voltages were constant within 1 mv. for 48 hours. Figure 1 shows the results of a typical run. The silver oxide electrodes maintained their potential values for a period of months.

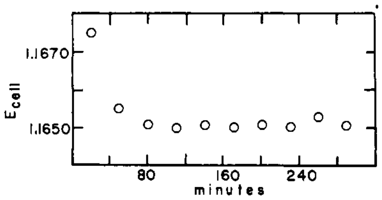

Figure 1. Variation of e.m.f. of the cell $Pt,H_2(g)/NaOH\ (0.19M)/Ag_2O(s), Ag(s)$ with time at 25° C.

The measurements with electrode C (Table I), extended over a period of about 3 months.

After a run, three samples of electrolyte from each electrode compartment were allowed to run into a hydrochloric acid solution, and the potassium chloride produced was weighed. The average deviation of the molalities so determined was less than 0.1%.

When a run was completed, the cell was rinsed several times with conductivity water and then filled with conductivity water. This was not drained out until just before the next run began.

RESULTS

Table I lists the results of cell voltage measurements and the analysis of the solutions in the electrode compartments. The electrode reactions were assumed to be:

$$Ag_2O + H_2O + 2e \rightarrow 2Ag + 2OH^- \qquad (1)$$

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e \qquad (2)$$

The equilibrium electrode potentials for each of these reactions as written are at 25° C.

$$E_{Ag} = E^0_{Ag_2O/Ag} - 0.05916 \log a_{OH^-} + 0.02958 \log a_{H_2O} \qquad (3)$$

$$E_H = 0.8282 - 0.05916 \log a_{H_2O} + 0.05916 \log a_{OH^-} + 0.02958 \log a_{H_2} \qquad (4)$$

The activity of the OH^- ions was calculated from the data of Akerlof and Bender (*1*). The activity of the water in these solutions was furnished by Bender (*3*). The a_{H_2} was taken to be equal to

$$(P_{bar,\ mm.} - a_{H_2O} \times 23.76)/760 \qquad (5)$$

As a first approximation, the cell voltage at equilibrium is the sum of Equations 3 and 4

$$E_{\text{cell}} = E_{\text{Ag}} + E_{\text{H}} \qquad (6)$$

This assumes no junction potential. However, in no instance was the composition of the solutions in the two electrode compartments exactly equal. The larger differences in the first measurements are due to the fact that a small amount of conductivity water remained in the cross piece of the cell and diluted the solution in the silver oxide electrode compartment. Subsequently, more thorough rinsing was used and then the solutions in the two electrode compartments had practically the same concentration at the end of the run.

Because of these differences in concentration, the possibility of a junction potential must be considered. It may be considered as due to the transfer of ions across the junction, and its value is then given by Equation 7

$$E = (2t^{-} - 1) \times 0.05916 \log a_{\text{OH Ag}}/a_{\text{OH H}} \qquad (7)$$

where $a_{\text{OH Ag}}$ and $a_{\text{OH H}}$ refer to the hydroxide ion activities in the silver and hydrogen electrode compartments, respectively. This junction potential is a maximum when t^{-}, the transference number of the OH^{-} ions, is unity. Equation 7 then becomes

$$E_{j_{\max}} = 0.05916 \log a_{\text{OH Ag}}\, a_{\text{OH H}} \qquad (8)$$

Equation 8 was used to calculate the $E_{j_{\max}}$ values in Table I.

The least precisely known values used in these calculations are the activities of the solute and solvent. This limits the number of significant figures in the final results to three. The $E^0_{Ag_2O/Ag}$ values in Table I are calculated from Equations 3, 4, and 5 and are based on the assumption of zero junction potential. The $E_{j_{\max}}$ values are within the range of deviation.

If the calculated $E_{j_{\max}}$ values are correct, then each $E^0_{Ag_2O/Ag}$ value would be larger by the amount of $E_{j_{\max}}$ where these junction potentials are negative. This brings the E^0 value calculated for the cell with the largest $E_{j_{\max}}$ into line with the other values. For the other cells, adjusting for the $E_{j_{\max}}$ value would make less difference than that of the experimental error.

These results give a standard electrode potential as follows.

$$Ag_2O + H_2O + 2e \rightarrow 2Ag + 2\,OH^{-} \quad E^0_b = +0.3384 \pm 0.0010 \text{ volt} \qquad (9)$$

Latimer (*8*) gives a value of 0.344 volt, based, in part, on calorimetric data. Hamer and Craig (*5*) derived a value of 0.342 volt by measurement against a $HgO/Hg/OH^{-}$ electrode. Both these values are slightly higher than the one reported here.

Table I. Electrolyte Concentrations and Cell Voltages at 25° C. for the Cell Pt , $H_2(g) | KOH(aq) | Ag_2O(s), Ag(s)$

E_{cell},	P_{bar},	$E_{j_{\max}}$,	Molalities at Electrode		Elec-	$E^0_{\text{calcd.}}$
Volts	Mm.	Volts	H_2	Ag_2O	trode	Volt
1.1664	739	−0.0011	0.939	0.904	C	0.3375
1.1659	743	+0.0001	0.533	0.536	C	0.3383
1.1662	740	−0.0023	0.670	0.612	C	0.3362
1.1656	742	−0.0003	1.516	1.500	C	0.3371
1.1671	740	−0.0003	1.665	1.646	C	0.3385
1.1665	736	−0.0003	0.784	0.773	C	0.3386
1.1670	749	−0.0003	0.598	0.591	B	0.3392
1.1668	749	−0.0003	0.598	0.591	A	0.3390
1.1668	741	−0.0001	0.444	0.441	B	0.3391
1.1665	745	−0.0002	0.294	0.292	A	0.3390
1.1660	745	−0.0002	0.294	0.292	B	0.3385
1.1659	740	−0.0003	0.367	0.363	B	0.3383
1.1651	746	−0.0002	0.192[a]	0.190[a]	B	0.3373
					Av.	0.3384[b]

[a] NaOH used as electrolyte in this cell.
[b] Exclusive of third cell listed.

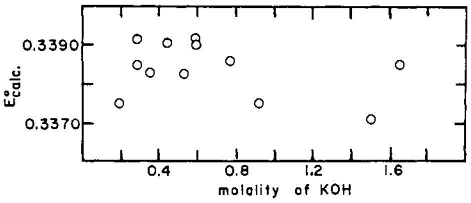

Figure 2. $E^0_{\text{calcd.}}$ for $Ag/Ag_2O/OH^{-}$ at various KOH concentrations

There appears to be no tendency of these calculated E^0 values to vary with potassium hydroxide concentration within the concentration range used in this work (Figure 2). Silver(I) oxide is soluble in these solutions. According to the work of Johnston, Cuta, and Garrett (*7*), the solubility of silver(I) oxide varies with the potassium hydroxide concentration and in the most concentrated solutions used in this work it would be 2.5×10^{-4} *M*. This is not sufficient to alter the ionic strength and activity coefficients of the solute and solvent. The steadiness of the cell voltages indicates that the dissolved silver oxide was insufficient to poison the hydrogen electrode. When these solutions were poured into hydrochloric acid for analysis, no precipitate of silver chloride was observed. Evidently, the amount of dissolved silver ion was too small to produce a precipitate of silver chloride under these conditions.

Hamer and Craig (*5*) noted that the voltage of the cell Hg(l), HgO(s) + NaOH(aq) + Ag_2O(s), Ag(s) varied with electrolyte concentration, although the equation for the total cell reaction shows no dependence on either hydroxide ions or water. This variation, however, is too small to account for the difference of 4 mv. between their E^0 value and the one reported here. Furthermore, the work of Chow (*4*) on the e.m.f. of the $HgO/Hg/OH^{-}$ electrode was recalculated using the activity of the water in the aqueous sodium hydroxide (*2*), but this correction amounted to less than 1 mv. Consequently, it cannot account for the difference either. No attempts were made to use electrolyte concentrations less than 0.2 *M* because then the experimental analysis error would become too great.

Another possibility for this discrepancy in E^0 values is in the electrolyte used. Hamer and Craig (*5*) used aqueous sodium hydroxide, while potassium hydroxide was used in this work. However, in the one case where sodium hydroxide was used in this work (Table I), the calculated E^0 was within the range of values for the cells which contained potassium hydroxide.

The results reported here show a variation of about 1 mv. This, however, is less than the difference between these results and those of other investigators (*5*). This experimental variation may be due in part to the variation in the Ag_2O/Ag electrodes. This is indicated especially by the differences between two electrodes used in the same solution (Table I). While the electrodes used in this work were reproducible within the experimental limits of the system studied, yet they did not appear to show as good reproducibility as those of Hamer and Craig (*5*).

It is possible also that the hydrogen electrode is not completely reproducible in highly alkaline solutions. While the cell voltages in each case were steady, it may be that each hydrogen electrode does not have precisely the same potential in these strongly alkaline solutions as every other such electrode. This, however, cannot account for the discrepancy in E^0 values noted above.

Another possible source of this discrepancy could lie in the values used for the activity of the solute and solvent. The values of Harned and Cook (*6*), however, led to a difference of only 0.1 to 0.3 mv. in the calculated E^0 values.

In conclusion, the E^0 for the Ag_2O/Ag electrode in alkaline solutions determined by direct measurement against the hydrogen electrode is somewhat lower than the E^0 value determined by indirect methods. An analysis of the experimental procedure shows that this difference is larger than the experimental errors associated with the method used in this work.

ACKNOWLEDGMENT

Thanks are given W.J. Hamer for this suggestions during the course of this work, and J.De Vries for his help in collecting some of the data.

LITERATURE CITED

(1) Akerlof, G.C., Bender, P., *J. Am. Chem. Soc.* **70**, 2366 (1948).
(2) Akerlof, G.C., Kegeles, G., *Ibid.*, **62**, 620 (1940).
(3) Bender, P., private communication, University of Wisconsin, February 7, 1950.
(4) Chow, M., *J. Am. Chem. Soc.* **42**, 488 (1920).
(5) Hamer, W.J., Craig, D.N., *J. Electrochem. Soc.* **104**, 206 (1957).
(6) Harned, H.S., Cook, M.A., *J. Am. Chem. Soc.* **59**, 496 (1937).
(7) Johnston, H.C., Cuta, F., Garrett, A.B., *Ibid.*, **55**, 2311 (1933).
(8) Latimer, W.M., "Oxidation Potentials," 2nd ed., p. 191, Prentice-Hall, New York, 1952.

RECEIVED for review November 30, 1960. Accepted March 8, 1961. Work sponsored by Office of Naval Research.

Densities of Some Salt Mixtures

$LiNO_3$-$LiClO_4$, KNO_3-$Ca(NO_3)_2$, KNO_3-$Sr(NO_3)_2$, and KNO_3-$Ba(NO_3)_2$

GUY F. PETERSEN, WILLIAM M. EWING, and G. PEDRO SMITH
Metallurgy Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

DENSITY DATA for molten salt mixtures are required for the computation of molar volumes which enter into the evaluation of many other physical properties.

EXPERIMENTAL PROCEDURES

The apparatus and general experimental procedures have been described in detail (*1*).

RESULTS AND DISCUSSION

The density data were fitted by the method of least squares to the equation $\rho = \alpha - \beta t$, where ρ is the density, and α and β are functions of composition, but not temperature. The results are given in Table I, which lists the composition in terms of the mole per cent of the specified nitrate, the constants α and β in the density equation, the standard deviation for the least squares fit, and the experimental temperature range. Each density equation is based on data taken at six to nine temperatures. The density equations for $LiNO_3$ and KNO_3 as previously measured by the authors (*1*) are included in Table I for convenience.

Table I. Density Equations

	$\rho = \alpha - \beta t$			
Compn., Mole %	α, g./cc.	$\beta \times 10^3$, g./cc./° C.	Std. Dev. × 10^3, G./Cc.	Exptl. Temp. Range, ° C.
KNO_3	KNO_3-$Ca(NO_3)_2$ System			
100.0	2.110	0.733	0.8	346–505
90.0	2.132	0.709	0.3	396–469
80.0	2.172	0.735	1.1	296–470
70.0	2.192	0.713	0.5	231–449
KNO_3	KNO_3-$Sr(NO_3)_2$ System			
90.0	2.218	0.740	0.5	361–501
80.0	2.316	0.737	1.4	348–497
70.0	2.403	0.721	0.2	421–452
KNO_3	$KNO_3Ba(NO_3)_2$ System			
90.0	2.305	0.773	0.3	324–520
80.0	2.475	0.795	0.8	377–518
70.0	2.629	0.805	0.4	438–517
$LiNO_3$	$LiNO_3LiClO_4$ System			
100.0	1.922	0.556	0.5	276–420
75.0	2.014	0.610	0.4	240–357
53.5	2.088	0.629	0.4	198–347
25.0	2.134	0.629	0.4	225–336
0	2.170	0.612	0.6	261–371

Molar volume calculations based on density equations show that the mixtures described here possess the property of volumetric additivity to within a very small error. Hence, this property may be used for precise interpolation of density at compositions intermediate to those which were measured.

The additivity of volumes of liquid $LiClO_4$-$LiNO_3$ mixtures was checked over the temperature range from the melting point of the eutectic (53.5 mole % $LiClO_4$) at about 172° up to 300° C. by extrapolating the density equations of the pure constituents into the supercooled liquid region as required. The deviations from volumetric additivity were negative and decreased with increasing temperature. The greatest deviations were for the eutectic mixture which was additive to within 0.4% at 172° C. and to within 0.2% at 300° C.

In the case of mixtures of KNO_3 and alkaline earth nitrates at 450° C., the volumes of the 10 and 20 mole % KNO_3 mixtures deviated from the additive volumes of pure KNO_3 and 30 mole % KNO_3, regarded as components, by about 0.2% for the KNO_3-$Sr(NO_3)_2$ system and by less than 0.1% for the KNO_3-$Ca(NO_3)_2$ and KNO_3-$Ba(NO_3)_2$ systems. These deviations are within experimental error.

LITERATURE CITED

(1) Smith, G.P., Petersen, G.F., J. CHEM. ENG. DATA **6**, No.4, 493 (1961).

RECEIVED for review February 6, 1961. Accepted May 25, 1961. The Oak Ridge National Laboratory is operated by the Union Carbide Corp. for the U.S. Atomic Energy Commission.