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MEASURED BATTERY VOLTAGES -
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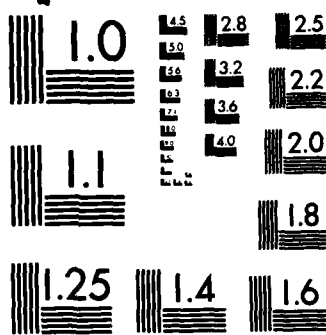
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CALCULATED AND MEASURED BATTERY VOLTAGES— THERMODYNAMICS AIDS IN IDENTIFYING ELECTROCHEMICAL REACTIONS

BY LARRY E. DeVRIES

RESEARCH AND TECHNOLOGY DEPARTMENT

FEBRUARY 1985

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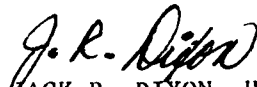
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Both the open and closed circuit voltages of a battery depend on the thermodynamic conditions inside the cell. When the actual electrochemical reaction of a particular battery is unknown, thermodynamic calculations can help to identify it. Using thermodynamic data, the open circuit voltages for alternative electrochemical reactions can be calculated. When accurate data are available, the calculated voltage for the correct electrochemical reaction will agree to within millivolts with the measured value. For the Cl_2 -Li molten salt system, the calculated and measured values are both 3.612V at 773K. For alkaline zinc batteries, the data indicate that ZnO is the discharge product at the anode under ambient conditions. For the acidic MnO_2 -Zn system, under the thermodynamic conditions, a two electron reduction of MnO_2 occurs. Initially, in the alkaline MnO_2 -Zn system, $\text{Mn}(\text{OH})_2$ is the discharge product at the cathode.					
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FOREWORD

Batteries serve as the chemical source of electrical energy. The voltage of a battery cell is determined by the thermodynamic conditions within the cell. Thermodynamics can be used as an aid in distinguishing between electrochemical reactions proposed for the reaction which sets the voltage of the cell. In this report thermodynamic data are used to select the electrochemical reaction in each of eight systems.

The author wishes to thank I. David Yalom and Phil B. Cole for the initial support in gathering the data, Donald L. Warburton for information supplied on most of the systems presented here, and Benjamin F. Larrick for many discussions on thermodynamics and battery reactions.

Approved by:

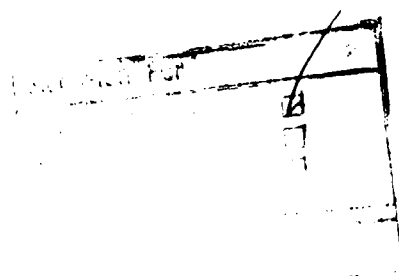

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CONTENTS

	<u>Page</u>
INTRODUCTION	1
THE THERMODYNAMIC DATA	1
BATTERY REACTIONS WITHOUT CONTROVERSY	2
BATTERY REACTIONS WITH CONTROVERSY	3
SUMMARY	7
REFERENCES	13

TABLES

<u>Table</u>		<u>Page</u>
1	STANDARD GIBBS ENERGY OF FORMATION (ΔfG°) AT 298.15K IN kJ/MOLE - BATTERY ACTIVE MATERIALS	9
2	ELECTROLYTES	10
3	ACTIVITY DATA AT 298.15K	11



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INTRODUCTION

For some batteries there has been little controversy concerning the actual electrochemical reactions. For others there is still much debate about what reactions produce the currents and give the observed potentials. One needs to know what these reactions are if the capabilities of the batteries are to be determined from a theoretical standpoint. Once the theoretical capabilities are known a comparison with the actual performances can be made.

Various measurements made on the anode, cathode, and complete cell can be used to determine the electrochemical reaction actually taking place in a battery. Among these are the constancy and changes in voltage during discharge, the determination of the products formed, the variation of voltage with changes in the electrolyte's composition, and the consumption or production of water during discharge. However, both the open circuit voltage (OCV) and closed circuit voltage are determined by the thermodynamic conditions in the battery's cells. The most useful method for determining the correct electrochemical reaction is to calculate the OCV from thermodynamic data and compare it with the measured OCV.

Three requirements for having the calculated OCV (V_c) agree with the measured OCV (V_m) for a cell are: (1) equilibria exist in the system, (2) the chemical composition for the V_m is known, and (3) the standard Gibbs energies of formation and activities are known with sufficient accuracy for the V_c . When these requirements are met, the V_c for the correct electrochemical reaction will agree to within millivolts of the V_m confirming that the reaction is correct.

THE THERMODYNAMIC DATA

A number of typical batteries and one experimental cell are considered. The data are for 298K except where indicated. Table 1 lists the standard Gibbs energies of formation, $\Delta_f G^\circ$. Table 2 lists the electrolyte compositions of battery cells for the V_m 's where the electrolyte enters into the electrochemical reaction. Table 3 lists the activities used in calculating the V_c 's. The standard Gibbs energy of reaction is $\Delta_r G^\circ$, and E° is the corresponding voltage. The Gibbs energy for the reaction under cell conditions is $\Delta_r G$.

BATTERY REACTIONS WITHOUT CONTROVERSY

Some of the systems for which there is presently no controversy concerning the electrochemical reactions include both primary and secondary systems, molten salt, aqueous, and solid electrolyte systems. For the $\text{Cl}_2\text{-Li}$ molten salt system the reaction is (1) with the V_c equal to the V_m



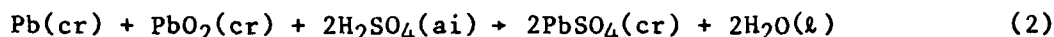
$$\Delta rG^\circ = -685.44 \text{ kJ}$$

$$V_c = 3.612\text{V}$$

$$E^\circ = 3.552\text{V}$$

$$V_m = 3.612\text{V}$$

at 773K.¹⁵ The anode is a Li-B alloy, and the electrolyte is a molten LiCl-KCl eutectic. For the secondary $\text{PbO}_2\text{-Pb}$ system with a sulfuric acid electrolyte, (2), the V_c and V_m agree to within 0.1%. The values given with



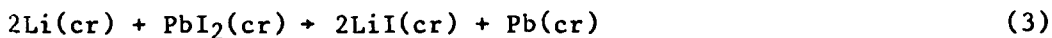
$$\Delta rG^\circ = -394.148 \text{ kJ}$$

$$V_c = 2.123\text{V}$$

$$E^\circ = 2.042\text{V}$$

$$V_m = 2.125\text{V} \text{ (16)}$$

(2) are for a 37.4% electrolyte. Since the electrolyte enters into the reaction, the voltage changes with its composition. For a 33.8% electrolyte the V_c is 2.093V and the V_m is 2.095V¹⁶ again agreeing to within 0.1%. The agreement between the V_c and V_m for the solid electrolyte system of $\text{PbI}_2\text{-Li}$,¹⁷ (3), is within 0.5%. For the system $\text{Ag}_2\text{O-Pb}$ with an



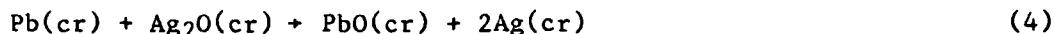
$$\Delta rG^\circ = -366.94 \text{ kJ}$$

$$V_c = 1.901\text{V}$$

$$E^\circ = 1.901\text{V}$$

$$V_m = 1.892\text{V}$$

alkaline electrolyte, (4), there is exact agreement between the V_c and V_m .



$$\Delta rG^\circ = -176.69 \text{ kJ}$$

$$V_c = 0.916\text{V}$$

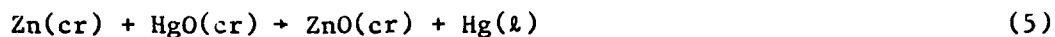
$$E^\circ = 0.916\text{V}$$

$$V_m = 0.916\text{V}^*$$

*Unpublished data, Chreitzberg, A. M.

BATTERY REACTIONS WITH CONTROVERSY

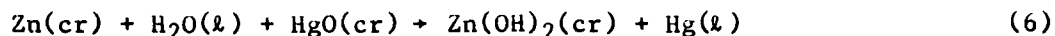
In all zinc anode batteries with an alkaline electrolyte the possibility exists that Zn(OH)_2 , rather than ZnO , is the anodic discharge product. The available thermodynamic data for determining $\Delta_r G^\circ$ for the dehydration of Zn(OH)_2 to ZnO as a function of temperature^{1,2,18} indicate that Zn(OH)_2 is not stable above 287K. For the HgO-Zn system with the alkaline electrolyte saturated with respect to ZnO and HgO , (5),



$$\Delta_r G^\circ = -259.761 \text{ kJ} \quad V_c = 1.346\text{V}$$

$$E^\circ = 1.346\text{V} \quad V_m = 1.346\text{V}$$

the V_c equals the V_m . Taking the anodic discharge product as Zn(OH)_2 , (6), the V_c is too low.

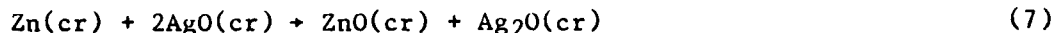


$$\Delta_r G^\circ = -259.402 \text{ kJ} \quad V_c = 1.328\text{V}$$

$$E^\circ = 1.344\text{V} \quad V_m = 1.346\text{V}$$

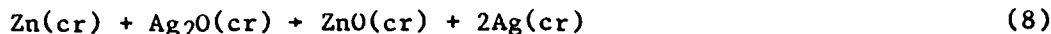
Although Zn(OH)_2 is unstable at ambient conditions, it is slow to dehydrate. Experiments indicate that alkaline systems saturated with Zn(OH)_2 give a Zn(OH)_2 voltage initially^{19,20} and those saturated with ZnO give a ZnO voltage.¹⁹ Using a hydrogen electrode with Zn , ZnO , the V_c (for ZnO , -0.4207V) agrees with the V_m to within 0.2% (-0.4197V) in a 0.1212m Ba(OH)_2 electrolyte; and with Zn , Zn(OH)_2 in a 0.2262m Ba(OH)_2 electrolyte the V_c (for Zn(OH)_2 , -0.4185V) and V_m (-0.4136V) agree to within 1.2%.¹⁹ Using the HgO-Zn system with a 1m NaOH electrolyte saturated with Zn(OH)_2 , the V_c (for Zn(OH)_2 , 1.3435V) and the V_m (1.3434V) agree to within 0.01%.²⁰ For (6) the V_m was for a 40% KOH solution saturated with respect to ZnO . The activity for H_2O in the saturated, concentrated KOH is less than 1/3 that for the saturated 1m NaOH system; and the V_c for (6) (Zn(OH)_2 , 1.328V) will not be the same as the V_c for 1m NaOH (Zn(OH)_2 , 1.3438V). Since many of the alkaline zinc batteries are saturated with ZnO and since it is stable with respect to hydration at ambient conditions, ZnO is the expected discharge product of Zn anodes.

Two reactions, (7) and (8), occur in the AgO-Zn system with an alkaline



$$\Delta_r G^\circ = -357.72 \text{ kJ} \quad V_c = 1.854\text{V}$$

$$E^\circ = 1.854\text{V} \quad V_m = 1.856\text{V}^{21}$$



$$\Delta_r G^\circ = -307.1 \text{ kJ}$$

$$V_c = 1.591\text{V}$$

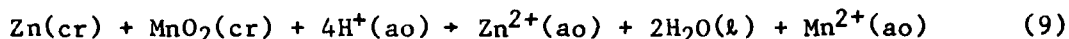
$$E^\circ = 1.591\text{V}$$

$$V_m = 1.602\text{V}^{21}$$

electrolyte saturated with respect to ZnO and silver ions. The V_c and V_m for reaction (7) agree to within 0.1%. A closed circuit voltage plateau for (7) does not exist too long before (8) starts occurring probably because AgO becomes coated with Ag_2O .²² Reaction (8) is not controversial, but the V_c is lower than the V_m . Cells starting with AgO were partially discharged to give Ag_2O for which the V_m is given for (8).²¹ It is tempting to say that a pure reaction (8) was not occurring resulting in a V_m higher than the V_c by 0.7%.

One of the oldest commercial batteries, the Leclanche battery, is the one for which the most controversy exists about the actual electrochemical reaction. A large number of electrochemical reactions have been proposed for the MnO_2 -Zn system with an NH_4Cl - ZnCl_2 electrolyte. The initial conditions prior to discharge are the conditions which can be used to calculate the OCV. After discharge has progressed, the composition of the system is often not known for an OCV measured by interrupting the discharge; and a V_c corresponding to the V_m cannot be given.

A two, rather than a one, electron reduction of MnO_2 occurs for the initial electrolyte conditions that exist in most commercial cells. Reaction (9) is one of those that can be written for a two electron



$$\Delta_r G^\circ = -384.278 \text{ kJ}$$

$$V_c = 1.603\text{V}$$

$$E^\circ = 1.991\text{V}$$

$$V_m = 1.598\text{V}$$

reduction of MnO_2 . The agreement between the V_c and V_m is 0.3%. Where various reactions occurring in a system are interrelated through equilibria, reactions giving the same calculated voltage can be written. Equilibria exist in the system so that reactions (10) and (11) can be used to generate

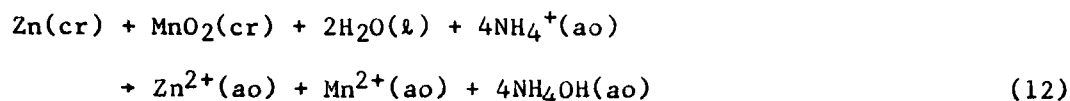


$$\Delta_r G^\circ = 79.885 \text{ kJ}$$



$$\Delta_r G^\circ = 27.096 \text{ kJ}$$

data for (12) by which NH_4OH is produced. The V_c 's for (12) and (9) should



$$\Delta rG^\circ = -173.122 \text{ kJ} \quad V_c = 1.604 \text{ V}$$

$$E^\circ = 0.897 \text{ V} \quad V_m = 1.598 \text{ V}$$

be identical and are within 1 mV.

Additional information supports a two electron reduction of MnO_2 . Under acid conditions ($\text{pH} < 5$) only Mn^{2+} ions are formed during discharge.²³ Under the initial electrolyte conditions the slope of the potential versus pH curve indicates a two electron reduction.²⁴ If the initial electrolyte conditions (thermodynamic conditions) are maintained, the capacity of an MnO_2 cathode approaches that of a two electron reduction on discharge. The initial thermodynamic conditions can be maintained by using a flowing electrolyte²⁵ or a large volume of electrolyte.²⁶

An alternate source of Mn^{2+} ions could be (13) implying a one electron



$$\Delta rG^\circ = -45.5 \text{ kJ} \quad \Delta rG = -21.8 \text{ kJ}$$

reduction of MnO_2 by (14). The V_c is too low for (14) to be the initial

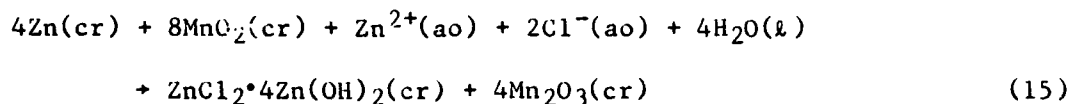


$$\Delta rG^\circ = -338.8 \text{ kJ} \quad V_c = 1.491 \text{ V}$$

$$E^\circ = 1.756 \text{ V} \quad V_m = 1.598 \text{ V}$$

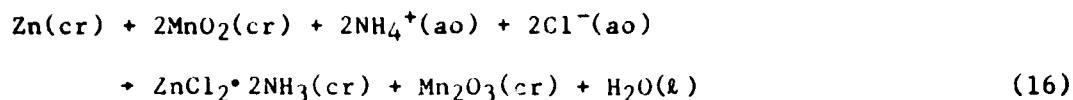
electrochemical reaction. The Gibbs energy for (13) (-21.8 kJ) at a pH of 4.65 indicates that the electrolyte would not be saturated with MnOOH . When the pH becomes higher (> 7) as the cell is discharged, the slope of the potential versus pH curve approaches that for a one electron reduction of MnO_2 .^{24,27}

Three other reactions (15), (16), (17) involving a one electron reduction of MnO_2 are given to show what their calculated voltages are under the initial cell conditions. Reactions (15) and (16) are written with Mn_2O_3 , rather



$$\Delta rG^\circ = -1098.2 \text{ kJ} \quad V_c = 1.453 \text{ V}$$

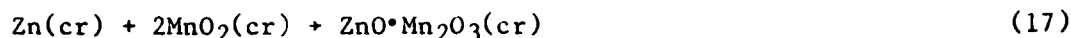
$$E^\circ = 1.423 \text{ V} \quad V_m = 1.598 \text{ V}$$



$$\Delta rG^\circ = -270.073 \text{ kJ} \quad V_c = 1.480\text{V}$$

$$E^\circ = 1.400\text{V} \quad V_m = 1.598\text{V}$$

than MnOOH - the "hydrated" form. The V_c for MnOOH would generally be about 0.019V higher. For (17) the V_c is higher than for any other one electron



$$\Delta rG^\circ = -295.72 \text{ kJ} \quad V_c = 1.532\text{V}$$

$$E^\circ = 1.532\text{V} \quad V_m = 1.598\text{V}$$

reduction of MnO_2 , but the V_c is still 4.3% lower than the V_m . For all of the one electron reductions of MnO_2 , (14) - (17), the facts are the same. Under the initial electrolyte conditions a one electron reduction of MnO_2 can not be taking place because the V_c is too low, the slope of the potential versus the pH curve is wrong, and the electrolyte is unsaturated. The thermodynamic data indicate that all of the Mn^{3+} products would react to form Mn^{2+} ions, MnO_2 , and H_2O . Not until a pH > 7 would any of them become stable.

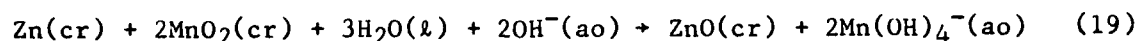
A one electron reduction of MnO_2 occurs initially for the alkaline electrolyte MnO_2 -Zn system. This is expected since even for the Leclanche battery a one electron reduction occurs when the pH > 7. In addition, the V_c is too low compared with the V_m for reaction (18), the two electron



$$\Delta rG^\circ = -231.03 \text{ kJ} \quad V_c = 1.189\text{V}$$

$$E^\circ = 1.197\text{V} \quad V_m = 1.54 \text{ (29)}$$

reduction, to be the initial electrochemical reaction. In commercial cells the alkaline electrolytes are usually saturated with ZnO , but they would not become saturated with complexed Mn^{3+} ions until after discharge has occurred for a while. Before saturation, reaction (19) would be expected.



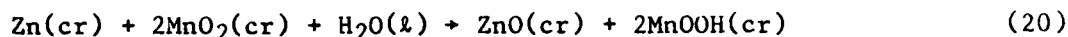
$$\Delta rG^\circ = -228.145 \text{ kJ} \quad V_c = 1.534\text{V}$$

$$E^\circ = 1.182\text{V} \quad V_m = 1.54\text{V}^*$$

*Warburton, D. L., personal communication.

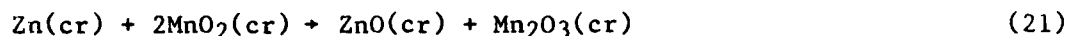
The V_c is based on 1% of saturation with complexed Mn^{3+} ions in a 30% KOH solution saturated with ZnO. The V_m is for a commercial cell with that electrolyte.

After saturation with respect to complexed Mn^{3+} ions, a reaction such as (20) or (21) probably occurs. The MnO_2 discharge product for (22)



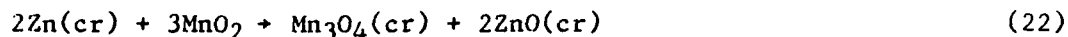
$$\Delta rG^\circ = -272.9 \text{ kJ} \quad V_c = 1.406V$$

$$E^\circ = 1.414V \quad V_m = 1.54V^*$$



$$\Delta rG^\circ = -269.12 \text{ kJ} \quad V_c = 1.395V$$

$$E^\circ = 1.395V \quad V_m = 1.54V^*$$



$$\Delta rG^\circ = -524.38 \text{ kJ} \quad V_c = 1.359V$$

$$E^\circ = 1.359V \quad V_m = 1.54V^*$$

contains both Mn^{2+} and Mn^{3+} , and reaction (22) has the lowest V_c . Of course (20) - (22) all have much lower V_c 's than the initial V_m . This is to be expected. The electrolyte is not initially saturated so no solid product containing Mn^{3+} can form. Even if a solid solution of $MnOOH$ and MnO_2 is formed,²⁸ it will not be formed initially. As indicated earlier if the exact cell conditions in a partially discharged cell are not known when OCV's are measured by interrupting the discharge no exact comparison can be made between the V_m and a V_c .

SUMMARY

The data given here conclusively demonstrate that the V_c for the correct electrochemical reaction will agree to within millivolts of the V_m when:

1. The cell composition is known for the V_m .

*Warburton, D. L., personal communication.

2. The activities and standard Gibbs energies of formation are known with sufficient accuracy for the V_c .

3. Equilibria exist in the system.

Using such information the thermodynamic data indicate:

4. At ambient conditions, in the normal commercial alkaline systems with zinc anodes, ZnO is the anodic discharge product.

5. In the "acid" MnO_2 -Zn system the initial electrochemical reaction involves a two electron reduction of MnO_2 .

6. In the alkaline MnO_2 -Zn system a one electron reduction of MnO_2 forming an aqueous solution of complexed Mn^{3+} ions accounts for the initial V_m .

TABLE 1. STANDARD GIBBS ENERGY OF FORMATION (ΔfG°)
AT 298.15K IN kJ/MOLE - BATTERY ACTIVE MATERIALS*

SUBSTANCE	ΔfG°	REFERENCE	COMMENTS
PbO ₂ (cr)	-217.33	1, p. 119	
H ₂ SO ₄ (ai)	-744.53	1, p. 58	
PbSO ₄ (cr)	-813.14	1, p. 120	
H ₂ O(l)	-237.129	1, p. 38	
PbI ₂ (cr)	-173.64	1, p. 120	
LiI(cr)	-270.29	1, p. 293	
Ag ₂ O(cr)	-11.20	1, p. 160	
PbO(cr), yellow	-187.89	1, p. 119	
HgO(cr), red	-58.539	1, p. 150	
ZnO(cr)	-318.30	1, p. 138	
Zn(OH) ₂ (cr), ε	-555.07	1, p. 138	
MnO ₂ (cr)	-465.14	1, p. 191	
Zn ²⁺ (ao)	-147.06	1, p. 138	
Mn ²⁺ (ao)	-228.1	1, p. 191	
OH ⁻ (ao)	-157.244	1, p. 38	
NH ₄ OH(ao)	-263.65	1, p. 65	
NH ₄ ⁺ (ao)	-79.31	1, p. 65	
Cl ⁻ (ao)	-131.228	1, p. 47	
Mn ₂ O ₃ (cr)	-881.1	1, p. 191	
ZnCl ₂ ·2NH ₃ (cr)	-503.2	1, p. 141	
Mn(OH) ₂ (am)	-615.0	1, p. 191	
Mn ₃ O ₄ (cr)	-1283.2	1, p. 191	
LiCl(l)	-342.721	2, ---	At 773K, Calculated
AgO(cr)	14.11	3, pp. 612-615	Calculated
ZnCl ₂ ·4Zn(OH) ₂ (cr)	-2653.	4, pp. 935-940	Estimated
ZnO·Mn ₂ O ₃ (cr)	-1226.	5, pp. 209C-214C	Estimated
Mn(OH) ₄ ⁻ (ao)	-933.	6, pp. 405-409	Calculated
Mn(OOH)(cr)	-561.	7, pp. 959-963; 8, pp. 262-265	Selected

*For substances in reactions not listed here, $\Delta fG^\circ = 0$.

TABLE 2. ELECTROLYTES

SUBSTANCE	WEIGHT PERCENT	MOLALITY	REACTION NUMBER
a. LiCl	44.7	19.0641	1
b. H ₂ SO ₄	37.4	6.0914	2
c. KOH	40.0	11.8814	

After Saturation*

ZnO	6.60**	1.3518	
d. NH ₄ Cl	26.0	7.4551	
ZnCl ₂	8.8	0.9904	
MnCl ₂		4.65 x 10 ⁻⁶	

The ionic strength was 10.426. The pH was measured as 4.65 9-16

e. KOH	30.0	7.6381	
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After Saturation***

ZnO	4.13**	0.7251	
-----	--------	--------	--

*The ionic strength was 13.2333.

6

**Based on recalculated data of Reference 9.

***The ionic strength was 8.3631.

18-20

TABLE 3. ACTIVITY DATA AT 298.15K*

SUBSTANCE	ACTIVITY	ACTIVITY COEFFICIENT	REACTION NUMBER	REFERENCE NUMBER
a. LiCl	0.4063 (At 773K)	---	1	10, p. 49
b. H ₂ SO ₄	14.061	0.2946	2	11, p. 797
H ₂ O	0.6176	---	2	11, p. 797
c. H ₂ O	0.2868	2.6192**	6	12, p. 1075
d. CL ⁻	5.331	0.565	15,16	12, p. 1085
H ₂ O	0.953	---	9,10,12,13,15,16	
Mn ²⁺	7.89 x 10 ⁻⁶	1.0694	9,12,13	13, p. 1028
NH ₄ ⁺	4.210	0.565	11,12,16	12, p. 1085
Zn ²⁺	0.451	0.2870	9,12,14,15	14, p. 10-11
H ⁺	10 ^{-4.65}	MEASURED	9,10,13,14	
OH ⁻	4.30 x 10 ^{-10***}	---	10,11	1, p. 38
NH ₄ OH	1.01 x 10 ^{-4***}	---	11,12	1, p. 65
e. H ₂ O	0.5460	2.0085**	18-20	12, p. 1075
OH ⁻	26.709	3.885	19	12, p. 1075
Mn(OH) ₄ ^{-****}	1.2 x 10 ^{-5***}	---	19	6, pp. 405-409; 12, p. 1070; 12, p. 1075

*For substances not listed, the activity is one.

**Osmotic Coefficient

***The activity was calculated from the equilibrium constant.

****Solubility data⁶ were combined with activity data for water and the hydroxide ion¹² (p. 1075) and activity data for the perchlorate ion¹² (p. 1070) which was used for Mn(OH)₄⁻.

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