For further purposes of comparison, $\bar{L}_2$ at 25° has been plotted against $m^{1/2}$ over the entire concentration range in Fig. 3. The circles represent our results, the inked circles the results of Lange, Monheim and Robinson and the squares the values computed by Brönsted from electromotive force measurements. Since Brönsted's data were not determined in sufficiently dilute solutions for purposes of extrapolation, it was necessary to add 2530 cal. to each of his results. Our results and those of Brönsted[15] possess the same characteristics although the maximum deviation is of the order of 300 cal.

The Relative Partial Molal Heat Capacity of Sulfuric Acid in Aqueous Solutions.—By differentiation of equation (11) with respect to *t*, the relative partial molal heat capacity, $\bar{C}_p - \bar{C}_{p_0}$, is readily obtained. Thus

$$(\bar{C}_p - \bar{C}_{p0}) = \frac{d\bar{L}_2}{dt} = \alpha' + 2\beta' t = (\bar{C}_p - \bar{C}_{p0})_0 + 2\beta' t \qquad (12)$$

The constant α' is seen to equal the relative partial molal heat capacity at zero degrees, and $2\ \beta' t$ gives the variation of this quantity with the temperature. Since these values involve the second differential coefficient of the original electromotive forces we cannot give too much weight to their accuracy.

Summary

1. Measurements of the electromotive forces of the cells

$H_2 \mid H_2SO_4(m) \mid Hg_2SO_4 \mid Hg$ Type I

from 0.05 to 17.5 *M* and from 0 to 60° have been made.

2. From these and the cells

$H_2 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt$ Type II

the activity of water in sulfuric acid solutions has been evaluated and found to be in good agreement with values computed from the best vapor pressure measurements.

3. From the combined results of these cells the activity coefficient of sulfuric acid from 0 to 60° and from 0.0005 to 17.5 *M* have been calculated. In dilute solutions at 0°, the values obtained are in close agreement with the best freezing point data.

4. The normal potential of the mercurous sulfate–mercury electrode has been computed from 0 to 60°.

5. The relative partial molal heat content of sulfuric acid has been computed from 0 to 60° and from 0 to 17.5 *M*. The results at 25° agree very closely with the best heat of dilution data.

6. The relative partial molal heat capacity of sulfuric acid and its variation with temperature has been estimated over the above temperature and concentration ranges.

NEW HAVEN, CONN. RECEIVED AUGUST 30, 1934

[15] Brönsted, *Z. physik. Chem.*, **68**, 693 (1910); Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 95.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Molal Electrode Potentials and the Reversible Electromotive Forces of the Lead Accumulator from 0 to 60° Centigrade[1]

BY HERBERT S. HARNED AND WALTER J. HAMER

The present communication contains in a condensed and convenient form a summary of a very comprehensive study of the electrode potentials and reversible electromotive forces of the cells related to the lead accumulator. This will involve the employment of the measurements made by Hamer of the electromotive forces of the cells[2]

$$H_2 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt^+$$

and of the cells

$$H_2 \mid H_2SO_4(m) \mid Hg_2SO_4 \mid Hg^+$$

reported by Harned and Hamer.[3] The mercurous sulfate–mercury electrode was employed in place of the lead sulfate–two-phase lead amalgam electrode, since in solutions containing sulfuric acid the latter were found unreproducible. Even though the greatest precautions were taken to eliminate air by the use of a vacuum technique, errors as high as 2 mv. occurred in the moderately dilute solutions.

To circumvent this difficulty, measurements of

---

[1] This contribution is part of an investigation of the thermodynamic properties of the electrodes and electrolyte of the lead accumulator, and was aided by a grant from the Naval Research Laboratory, Anacostia Station, Washington, D. C., and is published with the permission of the Secretary of the Navy.

[2] Hamer, THIS JOURNAL, **57**, 9 (1935).

[3] Harned and Hamer, *ibid.*, **57**, 27 (1935).

the difference in electromotive force between the two-phase lead amalgam–lead sulfate electrode and the mercurous sulfate–mercury electrode will now be presented. Purified chemicals were employed and all precautions such as the elimination of air from the cells were taken.

Normal Cells and Electrode Potentials

1. Measurements from 0 to 60° at 5° intervals were made of the cells

$\text{Pb (2-phase amalgam)} \mid PbSO_4 \mid Na_2SO_4 \mid Hg_2SO_4 \mid Hg^+;\ E_1$

The experimental results were found to agree to within maximum limits of ±0.02 mv. with values calculable from the equation

$$E_1 = 0.96051 + 0.000155t + 0.00000038t^2 \qquad (1)$$

The numerical constants were obtained by the method of least squares.

2. The electromotive forces of the cells

$Pb \mid PbSO_4 \mid Pb^{++} \mid PbSO_4 \mid \text{Pb (2-phase amalgam)}^+;\ E_2$

were measured by Gerke[4] and may be expressed by the equation

$$E_2 = 0.00540 + 0.000016t \qquad (2)$$

3. Therefore

$Pb \mid PbSO_4 \mid Na_2SO_4 \mid Hg_2SO_4 \mid Hg^+;\ E_3$

is given by

$$E_3 = E_1 + E_2 = 0.96591 + 0.000171t + 0.00000038t^2 \qquad (3)$$

4. The normal potential of the cell, from 0 to 60°

$H_2\ \text{(1 atm.)} \mid H_2SO_4(m) \mid Hg_2SO_4 \mid Hg^+;\ E_4$

was computed by Harned and Hamer, and is given by

$$E_4 = 0.63495 - 0.00078144t - 0.0000004269t^2 \qquad (4)$$

which is a modified form of their equation (8). This is the electrode potential of the electrode, $SO_4^- \mid Hg_2SO_4 \mid Hg$, at unit activity of acid.

5. Upon subtracting E_4 from E_1, the normal electromotive force of the cell

$\text{Pb (2-phase amalgam)} \mid PbSO_4 \mid H_2SO_4(m) \mid H_2\ \text{(1 atm.)}^+;\ E_5$

is obtained. Therefore

$$E_5 = E_1 - E_4 = 0.32556 + 0.00093644t + 0.00000080689t^2 \qquad (5)$$

which is the normal potential of the Pb (2-phase amalgam) $\mid PbSO_4 \mid SO_4^-$ electrode.

6. Further, the electromotive forces of the cells

$Pb \mid PbSO_4 \mid H_2SO_4(m) \mid H_2\ \text{(1 atm.)}^+;\ E_6$

is given by

$$E_6 = E_3 - E_4 = 0.33096 + 0.00095244t + 0.000008069t^2 \qquad (6)$$

which is the normal potential of the $Pb \mid PbSO_4 \mid SO_4^-$ electrode.

7. The normal potential of the cell

$H_2\ \text{(1 atm.)} \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt^+;\ E_7$

was found by Hamer to be given by

$$E_7 = 1.67699 + 0.000285t + 0.0000012467t^2 \qquad (7)$$

8. Consequently, the normal electromotive force of the amalgamated lead accumulator or the cells

$\text{Pb (2-phase amalgam)} \mid PbSO_4 \mid H_2SO_4(m) \mid PbO_2 \mid PbSO_4 \mid Pt^+;\ E_8$

is given by

$$E_8 = E_7 + E_5 = 2.00265 + 0.00122144t + 0.0000205359t^2 \qquad (8)$$

9. The normal electrode potential of the lead accumulator

$Pb \mid PbSO_4 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt^+;\ E_9$

is given by

$$E_9 = E_7 + E_6 = 2.00795 + 0.00123744t + 0.0000025359t^2 \qquad (9)$$

All the equations are valid from 0 to 60° and represent experimental results determined at 5° intervals over this temperature range. The experimental accuracy was always of the order of ±0.1 mv. and these equations represent the results within these limits. The maximum uncertainty is in the value of normal potential of cell (7) since the extrapolation to zero concentration of acid was made from measurements of its electromotive force.

The Reversible Electromotive Forces of the Lead Accumulator from 0.05 to 7 M Sulfuric Acid Concentration and from 0 to 60°.—The electromotive forces of cells (4) and (7) have both been measured over the concentration range of 0.05 to 7 *M*, and 0 to 60°. Consequently, the open circuit electromotive forces of lead accumulator at different concentrations may be computed if we also employ cells (2) and (3). The result may be represented in a very convenient form by the quadratic equation

$$E = E_0^1 + at + bt^2 \qquad (10)$$

where E_0^1 is the electromotive force at 0° and a and b are constants. In Table I the values of these constants computed from our least squared equations have been compiled. Values at intermediate concentrations may be computed with high accuracy from graphs of E_0^1, a and b against m.

We have not made computations of the heat contents, entropies or heat capacities of the cell reactions. The material, however, is in such a form that such calculations can readily be made.

---

[4] Gerke, THIS JOURNAL, **44**, 1684 (1922).

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

Pb | $PbSO_4$ | $H_2SO_4(m)$ | $PbSO_4$ | PbO_2 | Pt^+ at 0° AND CONSTANTS OF EQUATION (10)—VALID FROM 0 TO 60°

m	E_0^1	$a \times 10^6$	$b \times 10^9$
0.05	1.76874	−310	134
.1	1.80207	−265	129
.2	1.83495	−181	128
.5	1.87910	− 45	126
1	1.91737	56.1	108
2	1.96637	159	103
3	2.00874	178	97
4	2.04789	177	91
5	2.08502	167	87
6	2.11910	162	85
7	2.15071	153	80

Our experience with the individual cells indicates that the cell reactions were those postulated and that the cell reaction corresponding to cell (9) is

$$PbO_2 + Pb + 2H_2SO_4(m) = 2PbSO_4 + 2H_2O$$

under conditions approaching reversibility which corresponds to the double sulfate theory first proposed by Gladstone and Tribe.[5]

Summary

1. Measurements of electromotive forces of the cells

Pb(2-phase lead amalgam) | $PbSO_4$ | Na_2SO_4 | Hg_2SO_4 | Hg^+

have been made from 0 to 60°.

2. The molal electrode potentials of the electrodes reversible to the sulfate ion and those related to the electrodes of the lead accumulator have been evaluated. The results are expressed as a function of the temperature by quadratic equations.

3. Electromotive forces of the cells

Pb | $PbSO_4$ | $H_2SO_4(m)$ | $PbSO_4$ | PbO_2 | Pt^+

through concentration and temperature ranges from 0.05 to 7 M and from 0 to 60°, respectively, have been expressed by quadratic equations. The constants of these equations are given in Table I.

[5] Gladstone and Tribe, "The Chemistry of the Secondary Batteries of Planté and Faure," The Macmillan Co., London, 1933.

NEW HAVEN, CONN. RECEIVED AUGUST 30, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Studies on Hydrazine: Heat Capacities of Aqueous Hydrazonium Salts at 20 and 25°[1]

BY ALAN W. COBB AND E. C. GILBERT

Search of the literature reveals that data on the thermodynamic properties of hydrazine and its salts are few and scattered. As the basis of an extensive investigation of these properties the heat capacities of solutions of certain hydrazonium salts have now been determined.

The choice of calorimetric design and procedure was governed by the necessity of using the same apparatus for widely varied types of determination, such as specific heat, heat of solution, heat of reaction, etc. An adiabatic calorimeter of the general type developed by Daniels and his co-workers[2] was finally adopted. The essential characteristics of this design are three: first, the adiabatic condition is maintained by electrolytic heating of the bath liquid; second, the temperatures are measured in the outer bath so as to eliminate thermal leakage along the platinum resistance thermometer to the calorimeter; third, the adiabatic control is made automatic by the use of a photo-electric cell.

Apparatus

The calorimeter resembled in design that of Urban,[2c] who gives an excellent diagram in his paper. The principles laid down by White and by Barry[3] were also applied in the details of construction. The innermost container which held the solutions was of copper, heavily gold plated inside and out, and coated with baked Bakelite lacquer inside. The capacity was 0.9 liter. It was supported on Bakelite pegs within another gold-plated vessel with an air gap of 11 mm. The lid of this larger vessel supported the gold-plated, lacquered stirrer upon two ball bearings, and also, in conical stuffing boxes, a heating element and one arm of a 17-junction thermel. The ground joint between the lid and can was lubricated with stopcock grease and held tightly closed by thumb screws. The chimney for the stirrer was lined with hard rubber, and the stirrer shaft had a 5-cm. insert of Bakelite to prevent excessive heat leakage.

The calorimeter assembly was supported below the water level on three Bakelite pegs in a well-lagged copper

---

[1] Taken from a thesis submitted by Alan W. Cobb in partial fulfilment of the requirements for the degree of Master of Science at the Oregon State College, June, 1934.

[2] (a) Daniels, THIS JOURNAL, **38**, 1473 (1916); (b) Williams and Daniels, *ibid.*, **46**, 903 (1924); (c) Urban, *J. Phys. Chem.*, **36**, 1108 (1932).

[3] (a) White, "The Modern Calorimeter," The Chemical Catalog Co., New York, 1928; (b) Barry, THIS JOURNAL, **44**, 899 (1922).