stration of this since they both have the same number of valence electrons and the lattice constants are very close. Yet CeS which has one unbonded and unpaired "f" electron has a much lower lattice energy than ThS which has no "f" electrons and can contribute both of its extra electrons to metallic bonding.

The above consideration of bonding not only explains the relative stabilities of the sulfides, electrical properties, etc., but it also explains the abnormal behavior of the bond distances. Thus the bond distance in Å. between the metal ion and sulfide ion is as follows: BaS, 3.2; CeS, 2.88; ThS, 2.84; US, 2.74. The influence of the extra bonding due to the "d" electrons is clearly seen. In spite of the fact that Th is larger than Ce in normal compounds, the extra "d" electron available in ThS reduces the bond distance compared to CeS. A similar effect is seen when the bond distances for the tripositive sulfides are compared: La_2S_3, 3.01; Ce_2S_3, 2.98; Th_2S_3, 2.90; U_2S_3, 2.82. Comparison of these values with the crystal radii observed in compounds with no metallic bonding as given by Zachariasen[19] will emphasize the effect of metallic bonding.

Summary

The stable phase regions of the uranium and thorium sulfides have been determined. Methods of preparation of the pure compounds have been found. Many of the properties of these sulfides have been studied. Several of the sulfide phases show considerable promise for use as refractory containers. The distribution of "d" and "f" electrons is discussed and the types of bonding in the semi-metallic sulfides of two and three oxidation states are discussed.

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(19) W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).

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The Correct Application of the Gibbs–Helmholtz Equation to Reversible Galvanic Cells in which Several Phases Are in Equilibrium at One of the Electrodes

BY R. E. BARIEAU[1]

Some confusion exists in the literature concerning the application of the Gibbs–Helmholtz equation to reversible galvanic cells in which several phases are in equilibrium at the electrodes.

As Brickwedde and Brickwedde[2] have pointed out, saturated cells involving hydrated salts are either ignored or incorrectly treated in modern texts on thermodynamics. However, in the brief abstract of their correct application of the Gibbs–Helmholtz equation they state, "The Gibbs–Helmholtz equation relating the heat of the cell reaction to the free energy changes is not directly applicable to the electromotive force of cells in which the concentration of a solution entering the cell reaction changes with temperature." This statement is apt to leave the impression the Gibbs–Helmholtz equation is limited in its application. Such an interpretation would be unfortunate. The Gibbs–Helmholtz equation is derivable from very general principles, since it involves the relationship of the temperature coefficient of reversible work and the corresponding isothermal entropy change. For this reason, it may be stated with confidence that the Gibbs–Helmholtz equation is directly applicable to any reversible galvanic cell.

Confusion has arisen because of the failure to write correct cell reactions. As Lewis and Randall[3] have stated, "We cannot too strongly emphasize the importance of considering the electromotive force as a property, not of the cell, but of the reaction which occurs within the cell. Until that reaction is definitely known, measurements of electromotive force have no meaning. This is not a point of mere academic interest." It may be stated with confidence that one of the criteria that must be met, if the cell reaction presumably is known, is that the Gibbs–Helmholtz equation must be directly satisfied. If a reaction is written to represent a certain reversible cell reaction and it is then found that the Gibbs–Helmholtz equation is not applicable, this means that an incorrect cell reaction has been written.

The principle for writing complete cell reactions where several phases are in equilibrium at each electrode is the following: The processes that will take place between the phases in equilibrium are those that will maintain the phases in equilibrium. The application of this principle will be illustrated by developing the complete cell reaction for the Clark cell.

In the Clark cell, one electrode consists of mercury, mercurous sulfate, zinc sulfate heptahydrate and an aqueous solution saturated with respect to zinc sulfate heptahydrate and mercurous sulfate. The other electrode consists of zinc, saturated zinc amalgam, zinc sulfate heptahydrate and an aqueous solution saturated with zinc sulfate heptahydrate. We may start by writing the reaction

$$Zn(s) + Hg_2SO_4(s) = ZnSO_4 \text{ (in satd. soln.)} + 2Hg(l) \quad (1)$$

Here the reaction of zinc and mercurous sulfate

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[1] California Research Corporation, Richmond, California.

[2] Brickwedde and Brickwedde, *Phys. Rev.*, [II] **60**, 172 (1941).

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 400.

to produce mercury and zinc sulfate in a saturated solution is represented. Since the solution is saturated, on the application of the above principle, it is realized that zinc sulfate heptahydrate must be precipitated as the reaction proceeds. We can then write

$$\mathrm{Zn(s)} + \mathrm{Hg_2SO_4(s)} + 7\mathrm{H_2O(in\ satd.\ soln.)} = \mathrm{ZnSO_4{\cdot}7H_2O(s)} + 2\mathrm{Hg(l)} \quad (2)$$

But here water is being removed from a saturated solution, which will leave the solution supersaturated with respect to zinc sulfate, which must mean according to the above principle that more zinc sulfate heptahydrate will precipitate. We then finally write

$$\mathrm{Zn(s)} + \mathrm{Hg_2SO_4(s)} + \frac{7}{\mathrm{A} - 7}\mathrm{ZnSO_4{\cdot}AH_2O(satd.\ soln.)} = \frac{\mathrm{A}}{\mathrm{A} - 7}\mathrm{ZnSO_4{\cdot}7H_2O(s)} + 2\mathrm{Hg(l)} \quad (3)$$

where $\mathrm{ZnSO_4{\cdot}AH_2O}$ gives the composition of the saturated solution as A moles of water per mole of zinc sulfate.

The free energy changes of Reactions 1, 2 and 3 are the same at all temperatures, at which zinc sulfate heptahydrate is the solid phase in equilibrium with the saturated solution. However, the entropy changes of these reactions are not the same. As can be calculated from the results of Barieau and Giauque[4] and Giauque, Barieau and Kunzler,[5] the values of the entropy changes for Reactions 1, 2 and 3 at 25° are

$$\Delta S_1 = -20.4 \text{ E. U.}$$
$$\Delta S_2 = -43.3 \text{ E. U.}$$
$$\Delta S_3 = -61.9 \text{ E. U.}$$

These certainly differ by significant amounts. It is only the entropy change of Reaction 3 that can be calculated from the temperature coefficient of the Clark cell.

The proof that 3 is the complete cell reaction can be derived from either 1, 2 or 3. It will be derived in an exact manner starting with Equation 1. Using the nomenclature of Lewis and Randall[3]

$$\Delta F_1 = \bar{F}_2 + 2F_{\mathrm{Hg}} - F_{\mathrm{Zn}} - F_{\mathrm{Hg_2SO_4}} = \Delta F \text{ for Reaction 1} \quad (4)$$

where $\bar{F}_2$ is the partial molal free energy of $\mathrm{ZnSO_4}$ in the saturated solution.

$$\frac{\mathrm{d}\Delta F_1}{\mathrm{d}T} = \left(\frac{\partial \Delta F_1}{\partial T}\right)_{\mathrm{A}} + \left(\frac{\partial \Delta F_1}{\partial A}\right)_{\mathrm{T}}\frac{\mathrm{d}A}{\mathrm{d}T} \quad (5)$$

since A is a function of T, and where A again expresses the composition of the saturated solution as A moles of water per mole of zinc sulfate. Then

$$\frac{\mathrm{d}\Delta F_1}{\mathrm{d}T} = -\bar{S}_2 - 2S_{\mathrm{Hg}} + S_{\mathrm{Zn}} + S_{\mathrm{Hg_2SO_4}} + \left(\frac{\partial \bar{F}_2}{\partial A}\right)_{\mathrm{T}}\frac{\mathrm{d}A}{\mathrm{d}T} \quad (6)$$

where $\bar{S}_2$ is the partial molal entropy of $\mathrm{ZnSO_4}$ in the saturated solution. Along the saturated solution curve

$$\mathrm{ZnSO_4{\cdot}7H_2O(s)} = \mathrm{ZnSO_4(satd.\ soln.)} + 7\mathrm{H_2O(satd.\ soln.)} \quad (7)$$
$$\Delta F_7 = 0$$

But the condition that $\Delta F_7 = 0$ at all temperatures, requires

$$-\bar{S}_2 - 7\bar{S}_1 + S_{\mathrm{ZnSO_4{\cdot}7H_2O}} + \left[\left(\frac{\partial \bar{F}_2}{\partial A}\right)_T + 7\left(\frac{\partial \bar{F}_1}{\partial A}\right)_T\right]\frac{\mathrm{d}A}{\mathrm{d}T} = 0 \quad (8)$$

where $\bar{S}_1$ and $\bar{F}_1$ are the partial molal entropy and free energy of water in the saturated solution. From the Duhem equation

$$\left(\frac{\partial \bar{F}_2}{\partial A}\right)_T = -A\left(\frac{\partial \bar{F}_1}{\partial A}\right)_T \quad (9)$$

Substituting the value of $(\partial \bar{F}_1/\partial A)_T$ from (9) in (8) we have

$$\left(\frac{\partial \bar{F}_2}{\partial A}\right)_T \frac{\mathrm{d}A}{\mathrm{d}T} = \frac{A}{A - 7}\left[\bar{S}_2 + 7\bar{S}_1 - S_{\mathrm{ZnSO_4{\cdot}7H_2O}}\right] \quad (10)$$

Substituting (10) in (6) it follows

$$\frac{\mathrm{d}\Delta F_1}{\mathrm{d}T} = \frac{7}{A - 7}\left[\bar{S}_2 + A\bar{S}_1\right] - \frac{A}{A - 7} S_{\mathrm{ZnO_4{\cdot}7H_2O}} - 2S_{\mathrm{Hg}} + S_{\mathrm{Zn}} + S_{\mathrm{Hg_2SO_4}} \quad (11)$$

But $\bar{S}_2 + A\bar{S}_1 = S_{\mathrm{ZnSO_4{\cdot}AH_2O}}$ (satd. soln.) and therefore

$$\frac{\mathrm{d}\Delta F_1}{\mathrm{d}T} = S_{\mathrm{Zn}} + S_{\mathrm{Hg_2SO_4}} + \frac{7}{A - 7}S_{\mathrm{ZnSO_4{\cdot}AH_2O}}\ \text{(satd. soln.)} - 2S_{\mathrm{Hg}} - \frac{A}{A - 7}S_{\mathrm{ZnSO_4{\cdot}7H_2O}} = -\Delta S_3$$

and since

$$\frac{\mathrm{d}\Delta F_1}{\mathrm{d}T} = \frac{\mathrm{d}\Delta F_3}{\mathrm{d}T} = -\Delta S_3$$

Reaction 3 is the complete cell reaction. This has been known for a long time as Cohen[6] as early as 1900 had written Reaction 3 for the cell reaction of the Clark cell.

However, the principle of writing complete cell reactions has been overlooked in other cases. This is particularly true of cells in which a two phase amalgam is present at one of the electrodes. In 1902, Bijl[7] published a paper which gives the correct expression for the reaction in such a cell and this reaction has been correctly quoted by Jellinek.[8] However, the writer has failed to locate work by any other author which actually gives the equation for the chemical reaction occurring when such a cell is discharged reversibly and isothermally. It is to this equation, of course, that the Gibbs–Helmholtz equation is applicable. Consider a cell set up to measure the free energy:

$$\mathrm{Pb(s)} = \mathrm{Pb(2\ phase\ amalgam)} \quad (12)$$

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[4] Barieau and Giauque, unpublished.

[5] Giauque, Barieau and Kunzler, unpublished.

[6] Cohen, *Z. physik. Chem.*, **34**, 62 (1900).

[7] Bijl, *ibid.*, **41**, 641 (1902).

[8] K. Jellinek, "Lehrbuch der physikalischen Chemie," Verlag von Ferdinand Enke, Stuttgart, 1930.

This has recently been measured by Bates, Edelstein, and Acree[9] from 0 to 60°. They calculate an entropy change from their temperature coefficient and then state

$$\text{Pb(stick)} = \text{Pb (in saturated amalgam)} \qquad (13)$$

$$\Delta S_{13} = 0.93 \text{ cal./mole/°C.} \qquad (14)$$

Since Equation 13 is not the cell reaction, it is not legitimate to set ΔS of the cell equal to ΔS_{13}.

The saturated lead, two phase amalgam, is made up of a solid solution of mercury in lead and a liquid solution of lead in mercury. Let the composition of the solid phase be represented by $[\text{Pb}\cdot n_s\text{Hg}]$ (satd. solid) and the composition of the liquid phase by $[\text{Pb}\cdot n_l\text{Hg}]$ (satd. liquid), where n_s and n_l are the number of atoms of mercury per atom of lead in the solid and liquid, respectively. Then the complete cell reaction corresponding to 12 is

$$\text{Pb(s)} + \frac{n_s}{n_l - n_s}[\text{Pb}\cdot n_l\text{Hg}]\begin{pmatrix}\text{satd.}\\ \text{liquid}\end{pmatrix} = \frac{n_l}{n_l - n_s}[\text{Pb}\cdot n_s\text{Hg}]\begin{pmatrix}\text{satd.}\\ \text{solid}\end{pmatrix} \qquad (15)$$

and $\Delta S_{15} = 0.93$.

This can be proved in a manner similar to the development of the complete cell reaction for the Clark cell. Bates, Edelstein and Acree have also given a value for the ΔH of the reaction calculated from their observed electromotive force and its temperature coefficient. When the complete cell reaction has been written it is possible to see how the values derived from the electromotive forces may be checked. The ΔH of Reaction 15 may be determined by measuring the heat absorbed, when a known amount of lead is dropped into a calorimeter, containing sufficient amount of the two phase amalgam, so that after the reaction is complete two phases still remain. Under these conditions the reaction taking place is that expressed by Reaction 15.

As an example of where failure to write the correct cell reaction has led to incorrect thermodynamic calculations, consider a cell similar to the Clark cell but the zinc replaced with copper. The phase in equilibrium with the saturated copper sulfate solution is copper sulfate pentahydrate. This cell has been measured as a function of temperature by Oholm[10] and Obata.[11] Randall, Nielsen and West[12] have reviewed these data and give for the cell reaction

$$\text{Cu}\begin{pmatrix}\text{2 phase}\\ \text{amalgam}\end{pmatrix} + \text{Hg}_2\text{SO}_4\text{(s)} + 5\text{H}_2\text{O(in satd. soln.)} = \text{CuSO}_4\cdot 5\text{H}_2\text{O(s)} + 2\text{Hg(l)} \qquad (16)$$

The last authors have equated ΔH determined from the cell to the ΔH of Reaction 16. Bichowsky and Rossini[13] have taken ΔH of the cell as ΔH of Reaction 16 and used this incorrect value to calculate the heat of formation of copper sulfate pentahydrate. The complete cell reaction is

$$\frac{n_l}{n_l - n_s}[\text{Cu}\cdot n_s\text{Hg}]\begin{pmatrix}\text{satd.}\\ \text{solid}\end{pmatrix} + \text{Hg}_2\text{SO}_4\text{(s)} + \frac{5}{A-5}\text{CuSO}_4\cdot A\text{H}_2\text{O (satd. soln.)} = \frac{n_s}{n_l - n_s}[\text{Cu}\cdot n_l\text{Hg}]\begin{pmatrix}\text{satd.}\\ \text{liq.}\end{pmatrix} + \frac{A}{A-5}\text{CuSO}_4\cdot 5\text{H}_2\text{O(s)} + 2\text{Hg(l)} \qquad (17)$$

where $\text{CuSO}_4\cdot A\text{H}_2\text{O}$ (satd. soln.) gives the composition of the saturated solution, $[\text{Cu}\cdot n_s\text{Hg}]$ (satd. solid) gives the composition of the saturated solid solution of copper and mercury and $[\text{Cu}\cdot n_l\text{Hg}]$ (satd. liq.) gives the composition of the saturated liquid amalgam of copper and mercury. Disregarding any effect due to the amalgam and confining our attention to the rest of the reaction, using Equation 16 to incorrectly represent the cell reaction introduces an error of only 300 calories in the heat formation of copper sulfate pentahydrate. This is because of the small solubility of copper sulfate in water. However, if this same error were made in the case of the Clark cell, it would introduce an error of 5500 calories in the heat of formation of zinc sulfate heptahydrate.

Strickler and Seltz[14] have measured the electromotive force of cells of the type

$$\text{Pb(s)/PbAc}_2 + \text{NaAc(l)/Pb, Bi}\begin{pmatrix}\text{equilibrium liquid}\\ \text{and solid solutions}\end{pmatrix} \text{ from 120 to 200°}$$

and with the total mole fraction of the bismuth at the Pb–Bi electrode varying from 0.337 to 0.995. These cells were classified into two groups: one with a negative temperature coefficient of electromotive force and the other with a positive temperature coefficient. These authors were able to show that in the Pb–Bi system the eutectic temperature is 125° and the composition of the liquid is 54.4 mole per cent. bismuth. Above this composition they were able to show that the solid phase in equilibrium with the liquid was pure bismuth. The cell reaction for those cells with a positive temperature coefficient may then be written

$$\text{Pb(s)} + n_l\text{Bi(s)} = [\text{Pb}\cdot n_l\text{Bi}]\text{(satd. liq.)} \qquad (18)$$

where $[\text{Pb}\cdot n_l\text{Bi}]$ (satd. liq.) gives the composition of the liquid in equilibrium with solid bismuth. We may then use the temperature coefficients as determined by Strickler and Seltz to evaluate the change in entropy of Reaction 18. Approximately

$$(\text{d}E_{18}/\text{d}T)_{t = 125°\text{C.}} = 2.2 \times 10^{-4} \text{ volt/degree}$$

Then $(\Delta S_{18})_{t = 125°\text{C.}} = 4.6126 \times 10^4 \times 2.2 \times 10^{-4} = 10$ cal./mole/°C.,

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(9) Bates, Edelstein and Acree, *J. Research Natl. Bur. of Standards*, **36**, 159 (1946).

(10) Oholm, *Medd. Vetenskapsakad. Nobelinst.*, **5**, No. 4 (1919).

(11) Obata, *Proc. Phys. Math. Soc. Japan*, [3] **2**, 223 (1920).

(12) Randall, Nielsen and West, *Ind. Eng. Chem.*, **23**, 388 (1931).

(13) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

(14) Strickler and Seltz, THIS JOURNAL, **58**, 2084 (1936); Seltz, *Trans. Electrochem. Soc.*, **77**, 233 (1940).

at $t = 125°$

$$n_l = 54.4/45.6 = 1.19$$

Using the entropy of bismuth given by Kelley[15] and that of lead determined by Meads, Forsythe and Giauque[16] and the heat capacities as given by Kelley,[15] it is found

$$S_{\text{Pb}_{423.16°\text{K.}}} = 17.7 \text{ E. U.}$$
$$S_{\text{Bi}_{423.16°\text{K.}}} = 15.7 \text{ E. U.}$$

It then follows

$$S_{[\text{Pb}\cdot 1.19\,\text{Bi}]}\begin{pmatrix}\text{sat. eutectic}\\ \text{liq. } t = 125°\end{pmatrix} = (17.7) + (1.19 \times 15.7) + 10 = 46 \text{ E. U.}$$

Strickler and Seltz were also able to show that the composition of the solid solution in equilibrium with the eutectic liquid was 36.5 mole per cent. bismuth. The reaction may then be written for their cells with a negative temperature coefficient of electromotive force

$$\text{Pb(s)} + \frac{n_s}{n_1 - n_s}[\text{Pb}\cdot n_1\text{Bi}](\text{satd. liq.}) = \frac{n_1}{n_1 - n_s}[\text{Pb}\cdot n_s\text{Bi}]\ (\text{satd. solid}) \quad (19)$$

Using their temperature coefficients for these cells, it is found

$$(\Delta S_{19})_{t=125°} = -4.6 \times 10^4 \times 0.85 \times 10^{-4} = -3.9 \text{ E. U.}$$

at $t = 125°$

$$n_s = 36.5/63.5 = 0.575$$

and using the values of the entropy of lead and the eutectic liquid given above it is found

$$S_{[\text{Pb}\cdot 0.575\,\text{Bi}]}\begin{pmatrix}\text{satd. solid}\\ t = 125°\end{pmatrix} = \frac{1.19 - 0.575}{1.19}\left[(17.7 + \frac{0.575}{1.19 - 0.575}(46) - 3.9\right] = 29.4 \text{ E. U.}$$

Equation 19 may be subtracted from Equation 18 to give at the eutectic

$$n_1\text{Bi(s)} + \frac{n_1}{n_1 - n_s}[\text{Pb}\cdot n_s\text{Bi}](\text{satd. solid}) = \frac{n_s}{n_1 - n_s}[\text{Pb}\cdot n_1\text{Bi}](\text{satd. liq.}) \quad (20)$$

At the eutectic, $\Delta F_{20} = 0$ and

$$(\Delta S_{20})_{t=125°} = 10 + 3.9 = 13.9 \text{ E. U. and}$$
$$(\Delta H_{20})_{t=125°} = 423.16 \times 13.9 = 5880 \text{ cal.}$$

with $n_s = 0.575$ and $n_1 = 1.19$. Equation 20 is written for a total of 4.2 gram atoms. Dividing ΔH_{20} by 4.2, it is found

$$\Delta H_{\text{fusion, eutetic}} = 5880/4.2 = 1400 \text{ cal./gram atom}$$

This gives the absorption of heat that would take place if a lead–bismuth alloy containing 0.544 gram atom of bismuth and 0.456 gram atom of lead, were heated through the eutectic temperature under equilibrium conditions.

The above are typical of the calculations that can be made, once complete cell reactions have been written. One other equation will be given for a complete cell reaction that is believed to be new. If the electromotive force of a Clark cell unsaturated with respect to zinc sulfate, but saturated with respect to ice is measured, *i. e.*, ice is always present as a solid phase, the complete cell reaction may be written

$$\text{Zn(s)} + \text{Hg}_2\text{SO}_4\text{(s)} + A\text{H}_2\text{O(s)} = \text{ZnSO}_4\cdot A\text{H}_2\text{O}\begin{pmatrix}\text{satd.}\\ \text{H}_2\text{O(s)}\end{pmatrix} + 2\text{Hg(l)} \quad (21)$$

and the temperature coefficient of this cell would be a measure of the entropy change of Reaction 21.

Attention is called to the fact that when the complete reaction is written for cells in which several phases are in equilibrium at the electrode, total quantities (not partial molal quantities) appear in the equation.

It is recommended that in the future, complete cell reactions be written for such cells, even though incomplete reactions may adequately represent the free energy changes taking place. This will prevent misunderstanding of the significance and interpretation of the temperature coefficient of electromotive force of such cells.

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Summary

It is pointed out that confusion over the application of the Gibbs–Helmholtz equation has resulted from a failure to write correct cell reactions for cells involving several phases in equilibrium at the electrodes. The principle to be followed in writing the correct cell reaction for such cells is stated, and its application is demonstrated by developing the complete cell reaction for the Clark cell. Correct cell reactions are written for cells containing two phase amalgams at one of the electrodes.

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(15) Kelley, U. S. Bur. Mines, Bull. 434 (1941).

(16) Meads, Forsythe and Giauque, THIS JOURNAL, 63, 1902 (1941).