which do not change more than 0.1 to 0.2 millivolt even after two hours' bubbling. Readings are reproducible to 0.01 *P*H.

The fact that the whole system is not at the same temperature should produce no appreciable error, since the liquid junction is at practically the same temperature as the electrodes and no potential can be produced by temperature variations in the bridge.

The "open stopcock" junction is subject to the usual errors.

Summary

A simple water-jacketed hydrogen electrode cell of the bubbling type is described which is accurately maintained at constant temperature with water from a bath, circulated by means of an air lift.

It gives accurate readings reproducible to 0.01 *P*H with 1 or 2 cc. of solution after three minutes' saturation with hydrogen, even with solutions of low conductivity.

It has a single stopcock which performs separately the following functions: It permits (1) bubbling of hydrogen gas through the solution; (2) drainage of solution; (3) drainage of potassium chloride solution from the salt bridge; (4) formation of liquid junction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE FREE ENERGY OF MERCURIDES

BY ROSCOE H. GERKE

RECEIVED MAY 26, 1923

Alloys and metallic compounds are important classes of substances for which there are few free-energy data. It is the purpose of this paper to collect available data on metallic compounds and solid solutions containing mercury, and incidentally point out that the method of calculating these quantities involves the use of partial molal free energy. Hitherto, the concept of partial molal free energy has not been used to split up the free energy of formation of a compound from its constituent elements into two parts, as has been done in this paper. In the case of the mercurides and other metallic compounds, it will be seen that the free energy of formation of the compound from its elements is equal to the sum of the separate free-energy changes which the elements undergo in the formation of the compound.

In the case of sodium mercuride, $NaHg_5$, the partial molal free energy $\bar{F}_2$,[1] of the sodium in the compound is measured by the electromotive force of the galvanic cell, Na(s) | Na^+ | Na in Hg + $NaHg_5$(s). The chemical equa-

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[1] The notation employed is that of Lewis and Randall, THIS JOURNAL, **43,** 233 (1921).

tions which represent the change of state attending the passage of electricity through the cell are as follows.

$$\text{Na(solid)} + 5\text{Hg from soln.} + x(\text{Na} + 5\text{Hg}) \text{ both in soln.} = (1 + x)\,(\text{NaHg}_5) \text{ solid}; \quad \Delta F = -\mathbf{n}\,\mathbf{E}\,\text{f}. \tag{1a}$$

$$\text{Na(s)} + 5\text{Hg}\ (N_1 \doteq 0.946) + x\text{Na}(N_2 = 0.054) + x(5\text{Hg})\ (N_1 = 0.946) = \text{NaHg}_5\text{(s)} + x\text{NaHg}_5\text{(s)};\ \Delta F = -\mathbf{n}\,\mathbf{E}\,\text{f}. \tag{1b}$$

$$5\text{Hg}\ (N_1 = 0.946) + x(5\text{Hg}\ N_1 = 0.946) = (1 + x)\ 5\text{Hg in NaHg}_5\text{(s)};\ \Delta F = 0 \tag{2a}$$

$$x\text{Na}\ (N_2 = 0.054) = x\text{Na in NaHg}_5\text{(s)};\ \Delta F = 0 \tag{2b}$$

$$\text{Na(s)} = \text{Na (in NaHg}_5\text{(s))};\ \Delta F = -\mathbf{n}\,\mathbf{E}\,\text{f}. \tag{3}$$

Equation 3 represents the sum of Equations 1b, 2a and 2b. It represents the change in state in the formation of one gram-atom of sodium in the compound and the corresponding change of free energy is equal to the partial molal free energy of one gram-atom of sodium, $\bar{F}_2$, in the compound, since the change of free energy in an equilibrium process is zero and the free energy of an element in its standard state is taken as zero.

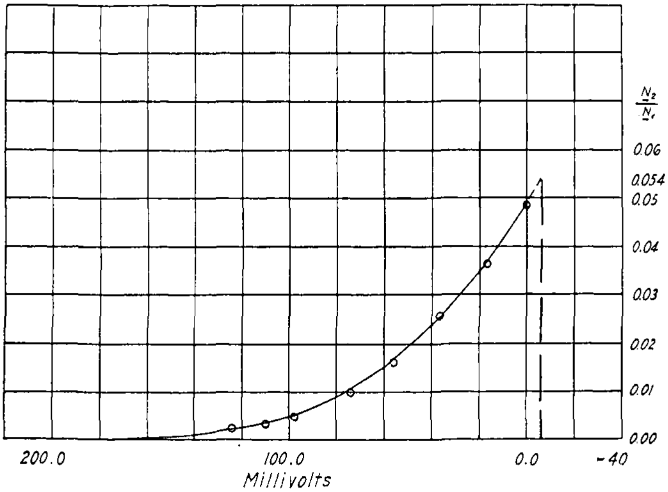

Fig. 1

If the free energy of dilution of the sodium in the mercury amalgam has been measured at various dilutions, then the partial molal free energy of the mercury, $\bar{F}_1$, in the compound may be determined with the aid of the Gibbs equation, $d\bar{F}_1 = -\frac{N_2}{N_1}\cdot d\bar{F}_2$, which when integrated takes the form,

$$\bar{F}_1 - F_{(\text{Hgl})} = \bar{F}_1 = +\text{nf}\int \frac{N_2}{N_1}\,d\mathbf{E},$$

where **E** is the electromotive force of galvanic cells similar to the one previously described, with different concentrations of electropositive metal in the dilute amalgams.

The integration is most conveniently carried out by plotting as ordinates the electromotive force and as abscissas the corresponding ratio, N_2/N_1 of the mole fractions of the constituents of the liquid amalgams. In Fig. 1

the data[2] for dil. sodium amalgams are plotted. A small extrapolation to the saturated amalgam, $N_2/N_1 = 0.054$, is indicated by the dotted line. The limits of the integration for N_2/N_1 are 0 and 0.054, respectively, and for **E** they are $+\infty$ and —6 millivolts, respectively. The area under the curve multiplied by the proper factor to convert to calories is equal to the change in free energy when one gram-atom of liquid mercury reacts to form one gram-atom of mercury in the liquid amalgam, which in turn is equal to the partial molal free energy of one mole of mercury in the compound, since the free energy of the liquid mercury is zero.

The free energy of sodium mercuride was calculated as follows,

$$\mathrm{Na(s)} = \mathrm{Na\ (in\ NaHg_5)};\ \Delta F = \bar{F}_2 \tag{4}$$

$$\mathrm{5Hg(l)} = \mathrm{5Hg\ (in\ NaHg_5)};\ \Delta F = 5\bar{F}_1 \tag{5}$$

$$\mathrm{Na(s)} + \mathrm{5Hg(l)} = \mathrm{NaHg_5(s)};\ \Delta F^\circ = \bar{F}_2 + 5\bar{F}_1 \tag{6}$$

In Table I are shown the free energies of formation of the mercurides of sodium and lead.

TABLE I

FREE ENERGY OF FORMATION OF MERCURIDES OF SODIUM AND LEAD

N_2 (sat.)	T °C.	E.m.f.	$\bar{F}_2$	$\bar{F}_1$	ΔF°	Compound
0.054[a]	25	0.7821[b]	−18,046	−61[c]	−18,351	$NaHg_5$[d]
0.017[e]	30	0.0058[f]	− 134	−12[g]	− 280	Pb_2Hg[e]

In Table I, *a* corresponds to References 3, 6; *b* to 2, 3, 4, 5; *c* to 2; *d* to 6; *e* to 7; *f* to 8; *g* to 9.

The mole fraction, N_2 (sat.), of the more electropositive metal in the liquid amalgam saturated with the compound is listed in Col. 1; the centigrade temperature in Col. 2; the electromotive force in volts of the galvanic cell, corresponding to Equation 1, in Col. 3; the partial molal free energy, $\bar{F}_2$, in calories of one gram-atom of the more electropositive metal in the compound in Col. 4; the partial molal free energy $\bar{F}_1$ in calories of one gram-atom of mercury in the compound, in Col. 5; and finally the free energy of formation ΔF°, of one mole of the compound in Col. 6. (The footnotes refer to the sources from which the data were taken.)

In Table II are collected the partial molal free energies of metals in the mercurides of lithium, potassium and rubidium. Since the free energies of dilution of these electropositive metals in mercury amalgams have not been measured, the partial molal free energy,[10] $\bar{F}_1$, of the mercury was

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[2] Richards and Conant, THIS JOURNAL, **44**, 601 (1922).

[3] Danner, *ibid.* **44**, 2832 (1922).

[4] Lewis and Kraus, *ibid.*, **32**, 1459 (1910).

[5] Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

[6] Smith and Bennett, THIS JOURNAL, **32**, 622 (1910).

[7] Fay and North, *Am. Chem. J.*, **25**, 216 (1901).

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

[9] Richards and Garrod-Thomas, *Z. physik. Chem.*, **72**, 165 (1910).

[10] It is nearer to the truth to make this assumption than to calculate this quantity from the equation $\bar{F}_1 = RT\ ln\ N_1$ assuming that Raoult's law is valid, since this calculation gives —30 calories as the value of the partial molal free energy of one mole of mercury in sodium mercuride, instead of the value —61 calories in Table I Since the

assumed to be the same as that in the case of sodium. Also, the liquid amalgams in the galvanic cells were not saturated with the solid compounds, as in the case of the sodium and lead mercurides. The small correction could be calculated and subtracted from the measured values, but since the measured values for the dilute amalgams are of such high precision, it may be well to insert them in the table as they appear in the literature.

TABLE II

PARTIAL MOLAL FREE ENERGY OF ALKALI METAL MERCURIDES AT 25°

N_2 (sat.)	N_2 (dil.)	E.m.f. (dil.)	$\bar{F}_2$	$\bar{F}_1$	Mercuride
0.02[11]	0.0087	0.9502[12]	−21,900	(−61)	$LiHg_3$[6]
.03[13]	.011	1.0481[14]	−24,200	(−61)	KHg_{12}[6]
.03[15]	.0054	1.0745[16]	−24,800	(−61)	$RbHg_{12}$[6]

In Table II are listed, respectively, N_2 sat., the mole fraction of the electropositive metal in the saturated amalgam; N_2 dil., the composition of the dil. amalgam actually employed in the cells; e.m.f. dil., the electromotive force, in volts, of the cell, the electrodes of which are solid electropositive metal and dil. amalgam; $\bar{F}_2$ and $\bar{F}_1$ are the approximate partial molal free energies in calories of one gram-atom of the electropositive constituent and of one gram-atom of mercury in the compound, respectively.

TABLE III

PARTIAL MOLAL FREE ENERGY OF METALS AND OF MERCURY IN MIXED CRYSTALS

N_2 (sat.)	T °C.	E.m.f.	$\bar{F}_2$	$\bar{F}_1$	Mixed crystals
0.07[g]	25	0.0047[h]	−215	− 35[i]	Zn in Hg
.10[j]	25	.0505[k]	−2330	− 77[l]	Cd in Hg
.43[m]	20	.0022[n]	− 51	−523[o]	Tl in Hg

In Table III, *g* corresponds to references 17, 18, 19; *h* to 20, 21; *i* to 22, 23, 24; *j* to 19; *k* to 19, 20, 22, 25, 26; *l* to 24, 27; *m* to 28; *n* to 28, 29, 8; *o* to 1, 28.

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mole fraction, N_1, of the mercury in these cases in Table II is greater than that in the case of sodium mercuride in Table I, the partial molar free energies, $\bar{F}_1$, of one mole of mercury in Table II are certainly not greater than, and in all probability are less than the value, —61 calories.

[11] Zukowsky, *Z. anorg. Chem.*, **71**, 409 (1911).

[12] Lewis and Keyes, THIS JOURNAL, **35**, 340 (1913).

[13] Janeke, *Z. physik. Chem.*, **58**, 245 (1907).

[14] Lewis and Keyes, THIS JOURNAL, **34**, 119 (1912).

[15] Kurnakow and Zukowsky, *Z. anorg. Chem.*, **52**, 427 (1907).

[16] Lewis and Argo, THIS JOURNAL, **37**, 1983 (1915).

[17] Puschin, *Z. anorg. Chem.*, **36**, 214 (1903).

[18] Cohen and Ginnekin, *Z. physik. Chem.*, **75**, 437 (1911).

[19] Cohen and Moesvald, *ibid.*, **95**, 285 (1920).

[20] Richards and Lewis, *ibid.*, **28**, 1 (1899).

[21] Cohen and Tombrock, *Verslag. Akad. Wetenschappen Amsterdam*, **18**, 17 (1909).

[22] Cohen, *Z. physik. Chem.*, **34**, 612 (1900).

[23] Crenshaw, *J. Phys. Chem.*, **14**, 158 (1910).

[24] Richards and Forbes, *Z. physik. Chem.*, **58**, 683 (1907).

[25] Hulett, *Trans. Am. Electrochem. Soc.*, **7**, 353 (1905).

[26] Obata, *Proc. Phys. Math. Soc. Japan*, [3] **3**, 64 (1921).

[27] Hulett and DeLury, THIS JOURNAL, **30**, 1812 (1908).

[28] Richards and Daniels, *ibid.*, **41**, 2452 (1919).

[29] Richards and Smyth, *ibid.*, **44**, 324 (1922).

In Table III are listed precise partial molal free energies of one gram-atom of the constituents of mixed crystals, in order to compare them with the partial molal free energy of the constituents of compounds.

Discussion

The conventions have been such that the free energy of formation, $\Delta F^0 = -18{,}351$ calories, means that there has been a decrease at 25° and 1 atm. of free energy attending the formation of one mole of $NaHg_5$ from one atom of sodium and 5 atoms of mercury. This decrease has been divided between the decrease for the sodium and the mercury respectively, such that $\bar{F}_2$ equals —18,046 calories and $\bar{F}_1$ equals 61 calories per atom. It is to be noted that the more electropositive the metal, the greater is the free-energy change, except in the case of lithium.

The most striking and unexpected conclusion which can be drawn from these data, is that the mercury does not greatly change in free energy, when it enters into chemical combination with a more electropositive metal. In other words, the vapor pressure of pure liquid mercury is only very slightly greater than the partial pressure of mercury from an amalgam saturated with a mercuride. On the other hand, the electropositive metal decreases in free energy more than the mercury in the formation of the compounds. In the case of the mixed crystals, thallium is an exception, which possibly may be due to the fact that it is so close to mercury in the periodic table of the elements.

Although the free energy of other metallic compounds and also compounds of the type represented by iodine chloride can be calculated by the above method, it does not seem feasible to make similar measurements for a simple compound such as sodium chloride, since it is not possible to have solid sodium chloride in equilibrium with its solution of sodium in liquid chlorine.

In conclusion, it may be stated that, if mercury reacts with a more electropositive metal to form a mercuride, the change in free energy for the mercury is small compared with that of the more electropositive metal.

The author wishes to express his appreciation for the helpful criticism of Dr. L. J. Gillespie and Dr. E. B. Millard.

Summary

1. The partial molal free energy of the electropositive atom in a mercuride or a mixed crystal containing mercury has been calculated from the measured value of the electromotive force of a galvanic cell, the electrodes of which consist of the electropositive metal and the liquid amalgam saturated with the mercuride or mixed crystal.

2. The values for the partial molal free energies of rubidium, potassium, lithium, sodium and lead in their mercurides have been found to be —24,800, —24,200, —21,900, —18,046 and —134 calories, respectively.

3. The partial molal free energy of mercury in some mercurides has been calculated from the measured values of the electromotive force of amalgam concentration cells.

4. The values for the partial molal free energy of mercury in sodium and lead mercurides were found to be —61 and —12 calories, respectively.

5. The free energies of formation of sodium and lead mercurides are —18,351 and —280 calories, respectively.

6. The partial molal free energies of the constituents of mixed crystals of zinc-mercury, cadmium-mercury and thallium-mercury crystals have been tabulated.

7. With the exception of thallium, it has been found in the case of the mercurides and the mixed crystals studied, that the change in free energy has been greater for the electropositive metals than for mercury.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. I. COPPER SALTS AS PROMOTERS IN THE IRON SALT CATALYSIS OF HYDROGEN PEROXIDE

BY VAN L. BOHNSON AND A. C. ROBERTSON

RECEIVED JUNE 11, 1923

The investigation described in this paper was an outgrowth of an earlier study[1,2] of the catalytic decomposition of hydrogen peroxide, during which it was noted that the rate of evolution of oxygen in the presence of a mixture of iron and copper salts is much more rapid than the rate which may be calculated on the assumption that each salt acts independently. This phenomenon is analogous to what has been known in cases of heterogeneous catalysis as "promoter action." The latter designation, first used in the patents of the Badische Anilin und Soda Fabrik, might well include, according to Pease and Taylor,[3] all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the assumption that each substance in the mixture acts independently. So defined, the term is applicable not only to cases of heterogeneous catalysis, to which it was first applied, but also to homogeneous catalysis, and in this sense it is used in this paper; such a use is no intimation that the mechanism of reaction in the two different systems is the same.

The known examples of promoter action have been reviewed and classified by Pease and Taylor,[3] and therefore will not be described here. Ex-

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[1] Bohnson, *J. Phys. Chem.*, **25,** 19 (1921).

[2] Bohnson and Robertson, THIS JOURNAL, **45,** 2493 (1923).

[3] Pease and Taylor, *J. Phys. Chem.*, **24,** 241 (1920).