2. The atomic radius calculated from these data is 2.171 Å. at room temperature.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICS, UNIVERSITY OF ILLINOIS]

PARTIAL MOLAL HEAT CAPACITIES AND RELATIVE PARTIAL MOLAL HEAT FUNCTIONS IN SOLUTIONS OF MOLTEN METALS

BY ALBERT N. GUTHRIE AND EARL E. LIBMAN

RECEIVED FEBRUARY 8, 1929 PUBLISHED JUNE 5, 1929

There exist in the literature no data on the partial molal properties of solutions of molten metals. There is likewise a great dearth of experimental work from which such data may be calculated. It seems worth while, therefore, to put on record the following results for the partial molal heat capacities and relative partial molal heat functions of Pb–Sb and Bi–Cd solutions calculated from the work of Wüst and Durrer.[1] By direct calorimetric measurements these investigators have determined the values of the specific heats of the above solutions at different concentrations from which the partial molal heat capacities may be determined. They have also obtained the heats absorbed per gram in going from the pure solid components to the liquid solution at the eutectic temperature, for different concentrations. From these data the relative partial molal heat functions may be calculated.

Relative Partial Molal Heat Functions

Consider a solution made up of components a and b. Let $H = E + PV$ be the total heat function of the solution. Then the partial molal heat function h_a of component a in the solution is defined as $(\mathrm{d}H/\mathrm{d}n_a)_{PTn_b}$ where the n's are the number of moles of the respective components in the solution. If h_a^0 is the value of h_a in some arbitrarily chosen reference state, $\bar{h}_a = h_a - h_a^0$ is called the relative partial molal heat function. It is convenient to choose for the reference state the infinitely dilute solution of a in b.[2]

Consider a system composed of some pure a and some solution. Let some of the a go from the pure phase into the solution. If Q is the heat absorbed by the system, then the molal heat of solution of a is defined as $l_a = (\mathrm{d}Q/\mathrm{d}n_a)_{PTn_b}$. Knowing l_a we may calculate $\bar{h}_a$ from the relation

$$\bar{h}_a = l_a - [l_a]_{n_a = 0} \tag{1}$$

Finally, when $\bar{h}_a$ is known, $\bar{h}_b$ can be calculated from

$$\int_{n_a = 0}^{n_a} \mathrm{d}\bar{h}_b = -\int_{n_a = 0}^{n_a} \frac{n_a}{n_b}\,\mathrm{d}\bar{h}_a \tag{2}$$

---

[1] "Forschungsarbeiten auf dem Gebiete des Ingenieurwesens," Heft 241 (1922).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, pp. 87–95.

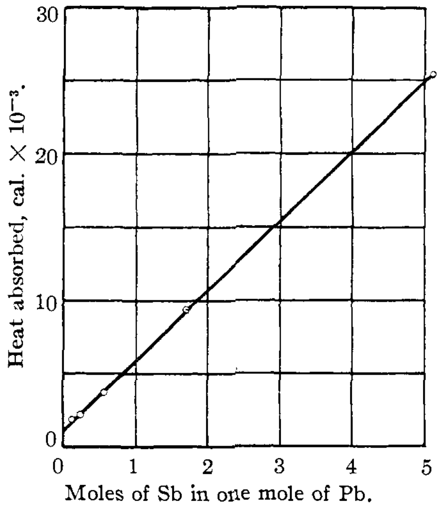

Fig. 1.—Relative partial molal heat functions in Pb–Sb solutions at eutectic temperature.

Let us now fix our attention upon a system of two components completely miscible in the liquid state, completely immiscible in the solid state. Such a system has a definite eutectic temperature. Let L be the heat absorbed when one mole of b and n_a moles of a go from the pure solid state at atmospheric pressure and eutectic temperature into the liquid state to form a solution. Then if λ_a and λ_b are the molal heats of fusion, at the eutectic temperature, of a and b

$$L = \lambda_b + \lambda_a n_a + \int_{n_a = 0}^{n_a} l_a \mathrm{d}n_a \qquad (3)$$

and

$$\left(\frac{\mathrm{d}L}{\mathrm{d}n_a}\right)_{PTn_b} = \lambda_a + l_a \qquad (4)$$

Values of L are given by Wüst and Durrer in the article mentioned, for different concentrations. Plotting L against n_a and drawing tangents, values of l_a may be determined by (4). As shown in Figs. 1 and 2, the L-n_a curves for the systems Pb-Sb and Bi-Cd are straight lines. Thus $(\mathrm{d}L/\mathrm{d}n_a)_{PTn_b}$ is, in each case, a constant, independent of the concentration, and by (4) the heats of solution for these systems are likewise constant, independent of the concentration. Then by (1) and (2) the relative partial molal heat functions at the eutectic temperature are strangely enough zero for these solutions at all concentrations (Tables I and II).

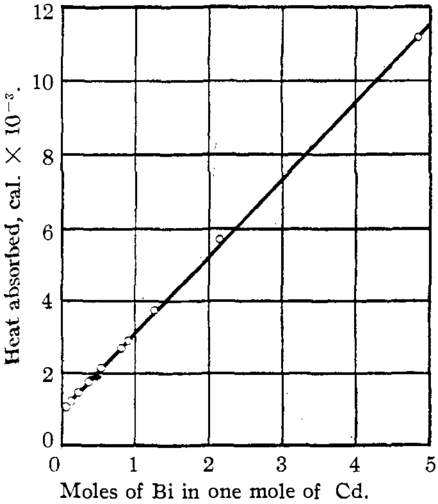

Fig. 2.—Relative partial molal heat functions in Bi–Cd solutions at eutectic temperature.

Partial Molal Heat Capacities

Let C_p be the total heat capacity of a solution of components a and b. Then the partial molal heat capacity of a is defined as $c_{p_a} = (\mathrm{d}c_p/\mathrm{d}n_a)_{PTn_b}$. The data of Wüst and Durrer give the specific heats for the solutions Pb–Sb and Bi–Cd

TABLE I

RELATIVE PARTIAL MOLAL HEAT FUNCTIONS IN PB–SB SOLUTIONS AT EUTECTIC TEMPERATURE

Sb, %	Mole frac. of Sb	G = gesamte Wärmeeffekte[a]	n_{Sb} = moles of Sb	Wt. of soln.	L = heat absorbed	$(dL/dn_{Sb})_{PTn_{Pb}}$	$\bar{h}_{Sb}$	$\bar{h}_{Pb}$
7	0.114	8.05	0.128	222.8	1794	4760	0	0
13	.203	9.08	.254	238.2	2165	4760	0	0
25	.362	13.40	.567	276.3	3705	4760	0	0
50	.630	22.76	1.70	414.4	9430	4760	0	0
75	.836	30.55	5.10	828.8	25300	4760	0	0

[a] Wüst and Durrer.

$L = G \times$ wt. of solution.

TABLE II

RELATIVE PARTIAL MOLAL HEAT FUNCTIONS IN BI–CD SOLUTIONS AT EUTECTIC TEMPERATURE

Bi, %	Mole frac. of Bi	G = gesamte Wärmeeffekte[a]	n_{Bi} = moles of Bi	Wt. of soln.	L = heat absorbed	$(dL/dn_{Bi})_{PTn_{Cd}}$	$\bar{h}_{Bi}$	$\bar{h}_{Cd}$
10	0.056	8.44	0.054	123.8	1045	2160	0	0
20	.118	8.61	.134	140.5	1210	2160	0	0
30	.187	8.98	.230	160.6	1443	2160	0	0
40	.263	9.47	.358	187.3	1775	2160	0	0
50	.350	9.47	.538	224.8	2130	2160	0	0
60	.446	9.69	.807	281.0	2695	2160	0	0
63	.477	9.55	.916	304.0	2900	2160	0	0
70	.556	10.02	1.257	374.7	3755	2160	0	0
80	.682	10.16	2.145	562.0	5705	2160	0	0
90	.828	9.92	4.850	1124.1	11150	2160	0	0

[a] Wüst and Durrer.

$L = G \times$ wt. of solution.

TABLE III

COMPARISONS OF DATA

Component		Bi		Cd		Pb	Sb
Temperature, °C.		300	1000	300	1000	700	700
Specific heat	Calcd.	0.0344	0.0416	0.0733	0.0823	0.0337	0.0547
	Obs. (ref. 4)	.0345	.0419	.0733	.0823	.0338	.0550

TABLE IV

PARTIAL MOLAL HEAT CAPACITIES IN PB–SB SOLUTIONS

Pb, %	25	50	75	87	93
Mole fraction of Pb	0.164	0.370	0.638	0.797	0.886
Sp. heat of the soln., 700°C.[a]	.0491	.0443[b]	.0387	.0367	.0351
Partial specific heat, 700°, all concns.		Pb,	.0337	Sb,	.0547
Partial molal heat capacity, 700°, all concns.		Pb,	6.98	Sb,	6.66

[a] Wüst and Durrer.

[b] In the original article some error was made in the calculation of this value and it has been recalculated from the experimental data.

for different weight per cents. These are plotted in Figs. 3 and 4. The tangents to these curves at any concentration intersect the axes at points representing the partial specific heats of the components.[3] For the systems considered the curves are straight lines and so the partial specific heats, and also the partial molal heat capacities, are constant, independent of the concentration and equal to the molal heat capacities of the pure components in the liquid state. This circumstance affords a means of checking the results by comparison with data obtained by Wüst, Meuthen and Durrer[4] from the pure components (Table III).

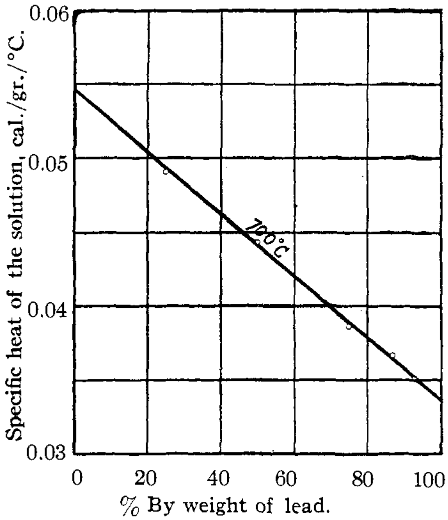

Fig. 3.—Partial molal heat capacities in Pb-Sb solutions.

In making use of the valuable data obtained by these investigators, it is to be noted that some errors have been made in the calculations. Thus Table 29 on the true specific heats of lead, above the melting point, is in error and should be recalculated directly from the experimental data given in the article. Unfortunately the errors noted have been reproduced in the "Handbook of Chemistry and Physics" published by the Chemical Rubber Publishing Co., the Smithsonian Physical Tables (7th edition), and perhaps elsewhere.

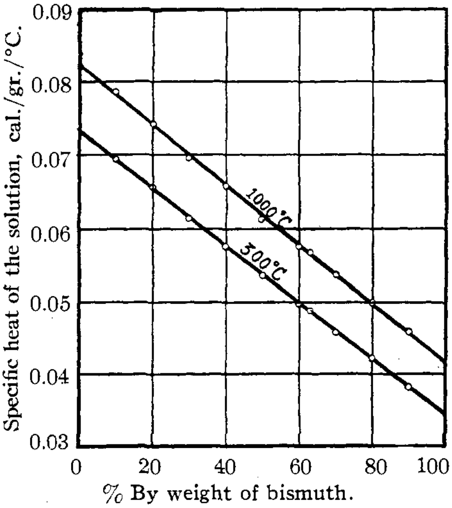

Fig. 4.—Partial molal heat capacities in Bi-Cd solutions.

We have seen that the partial molal heat capacities of Bi-Cd are constant and equal to the molal heat capacities of the pure liquid components both at 300 and 1000°. It is reasonable to assume that this is true for all temperatures. If we do so we may readily calculate the relative partial molal heat functions at temperatures other than that of the eutectic.

We have $(\mathrm{d}h_a/\mathrm{d}T)_p = c_{pa}$ and $(\mathrm{d}h_a^0/\mathrm{d}T)_p = c_{pa}^0$, so that $(\mathrm{d}\bar{h}_a/\mathrm{d}T)_p = [\mathrm{d}(h_a - h_a^0)/\mathrm{d}T]_p =$

---

[3] Lewis and Randall, ref. 2, p. 38.

[4] Ref. 1, Heft 204 (1918).

TABLE V

PARTIAL MOLAL HEAT CAPACITIES IN BISMUTH–CADMIUM SOLUTIONS

Bi, %	Bi, mole fraction	Sp. ht. of soln.[a] 300 °C.	1000 °C.
10	0.056	0.0695	0.0785
20	.118	.0656	.0743
30	.187	.0614	.0695
40	.263	.0576	.0659
50	.350	.0536	.0614
60	.446	.0499	.0576
63	.477	.0489	.0569
70	.556	.0459	.0537
80	.682	.0422	.0500
90	.828	.0382	.0459

[a] Wüst and Durrer.

Partial specific heat, all concentrations

Bi	300 °C.	0.0344
	1000 °C.	0.0416
Cd	300 °C.	.0733
	1000 °C.	.0823

Partial molal heat capacity, all concentrations

Bi	300 °C.	7.20
	1000 °C.	8.69
Cd	300 °C.	8.24
	1000 °C.	9.25

$c_{pa} - c^0_{pa}$. But on the assumption just made $c_{pa} - c^0_{ap} = 0$, and we have $(\mathrm{d}\bar{h}_a/\mathrm{d}T) = 0$. From this we see that $\bar{h}_a$ is independent of the temperature. Thus not only at the eutectic temperature but at all temperatures the relative partial molal heat functions of the components are zero at all concentrations.

Conclusions

1. The relative partial molal heat functions of the components of the systems Pb–Sb and Bi–Cd have been calculated for the eutectic temperatures. They are found to be equal to zero independent of the concentrations.

2. The partial molal heat capacities of the components of the system Pb–Sb have been calculated at 700° and have been found to be constant and equal to the molal heat capacities of the pure liquid components. The same calculation has been performed for the system Bi–Cd at the temperatures 300 and 1000° and in each case the partial molal heat capacities have been found to be constant, independent of concentration and equal to the molal heat capacities of the pure components.

3. Assuming that the partial molal heat capacities are the same as the molal heat capacities of the pure liquid components, not only at the temperatures for which this has been verified but at all others, it is shown that the relative partial molal heat functions are zero not only at the eutectic temperature but at all others.

URBANA, ILLINOIS