

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

A Thermodynamic Study of the Zinc-Antimony System. The Thermodynamic Properties of the Intermetallic Compounds: $ZnSb$, Zn_3Sb_2 and Zn_4Sb_3

BY BERNARD DEWITT AND HARRY SELTZ

In a previous paper¹ the authors have reported the results of an electromotive force study of mole fractions in Table II, and the activities are plotted in Fig. 1 and the \bar{L} and ΔH values in Fig. 2.

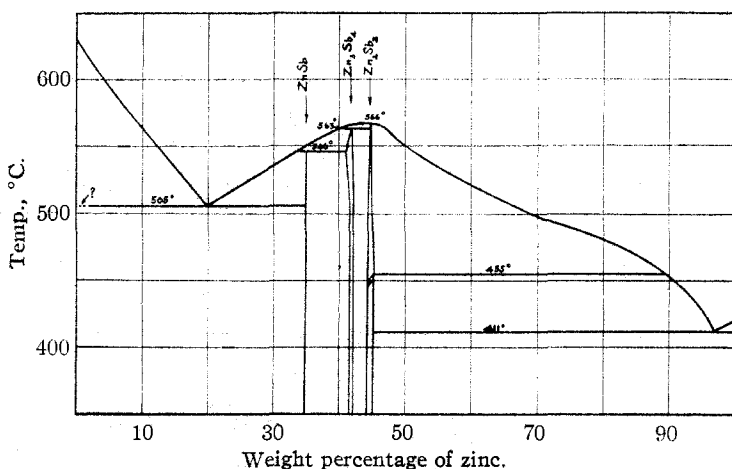


Fig. 1a.—Equilibrium diagram for the zinc-antimony system.

liquid cadmium-antimony solutions and have calculated the thermodynamic properties of the intermetallic compounds $CdSb$ and Cd_3Sb_2 . By similar methods, zinc-antimony solutions have now been investigated and the thermodynamic properties of the three intermetallic compounds, $ZnSb$, Zn_3Sb_2 and Zn_4Sb_3 , which appear as stable, solid phases, have been determined. The equilibrium diagram (Fig. 1a) for this system has been established accurately by the exhaustive studies of Takei,² and his solubility curves have been used in this work.

Experimental Results

The electromotive force measurements were made on evacuated cells of the type

$Zn(l)/ZnCl_2$ in $LiCl + KCl(l)/Zn$ (in $Zn-Sb$ liquid solutions)

and the results are given in Table I along with the calculated activities of zinc, a_1 , and relative heat contents, \bar{L}_1 .

From these a_1 and \bar{L}_1 values for zinc the corresponding a_2 and \bar{L}_2 values for antimony have been calculated along with the ΔH of formation of a mole of the liquid melts from the pure liquid metals. These results are given at round number

The activity curves show deviations from Raoult's law similar to those encountered in the cadmium-antimony system, except that here they are even more pronounced. The a_1 values at higher mole fractions of zinc exhibit definite positive deviations and at lower mole fractions very marked negative deviations. As stated elsewhere,³ in the binary systems of which antimony is a component there seem to be opposing influences at work, one tending to produce positive and the other negative deviations. A theoretical explanation of this behavior is not

as yet forthcoming. The abnormal forms of the \bar{L} and ΔH curves also are worthy of note.

TABLE I

| N_1 | E. m. f. at 823.1°K., mv. | a_1 823.1°K. | $dE/dT \times 10^4$ volt/°C. | \bar{L}_1 , cal. | Temp. range, °C. |
|--------|---------------------------|----------------|------------------------------|--------------------|------------------|
| 0.9198 | 1.68 | 0.954 | 0.58 | 142 | 480-560 |
| .7871 | 4.74 | .875 | 1.35 | 295 | 510-585 |
| .6973 | 9.49 | .765 | 3.91 | 1049 | 540-610 |
| .6451 | 14.67 | .661 | 4.60 | 1070 | 555-610 |
| .5826 | 25.23 | .491 | 4.18 | 425 | 565-620 |
| .4940 | 44.11 | .288 | 2.38 | -1031 | 565-620 |
| .3893 | 63.24 | .168 | 2.97 | -1788 | 535-595 |
| .2741 | 81.73 | .100 | 6.06 | -1468 | 530-590 |
| .1507 | 107.45 | .048 | 11.27 | -679 | 580-620 |

TABLE II

| N_1 | a_1 | At 823.1°K. | | a_2 | a_2/N_2 | \bar{L}_1 | \bar{L}_2 | ΔH , cal./mole |
|-------|-------|-------------|-------|-------|-----------|-------------|-------------|------------------------|
| | | a_1/N_1 | | | | | | |
| 1.0 | 1.0 | 1.0 | 0 | 0.400 | | 0 | 850 | 0 |
| .9 | 0.949 | 1.054 | 0.036 | .356 | | 140 | 400 | 166 |
| .8 | .883 | 1.104 | .053 | .264 | | 275 | -645 | 91 |
| .7 | .770 | 1.100 | .079 | .264 | | 1030 | -2870 | -140 |
| .6 | .525 | 0.875 | .152 | .381 | | 600 | -2205 | -522 |
| .5 | .292 | .584 | .324 | .647 | | -950 | -275 | -613 |
| .4 | .179 | .448 | .485 | .808 | | -1730 | 390 | -458 |
| .3 | .113 | .377 | .621 | .887 | | -1660 | 375 | -235 |
| .2 | .062 | .310 | .751 | .939 | | -960 | 150 | -72 |
| .1 | .024 | .240 | .884 | .982 | | -230 | 25 | 0 |
| 0 | .000 | .170 | 1.0 | 1.0 | | +220 | 0 | 0 |

(1) Seltz and DeWitt, *THIS JOURNAL*, **60**, 1305 (1938).(2) Takei, *Sci. Rep. Tohoku Univ.*, **16**, 1031 (1927).(3) Seltz and DeWitt, *THIS JOURNAL*, **61**, 2594 (1939).

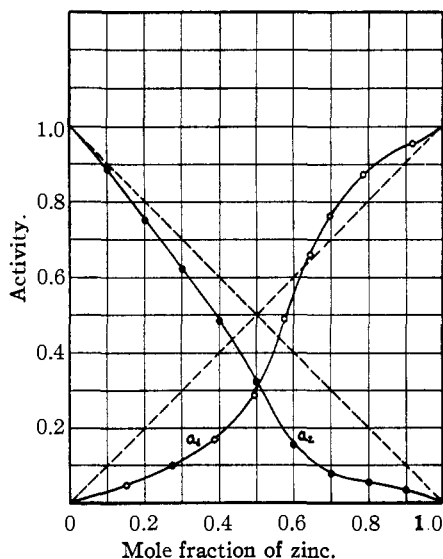
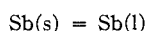


Fig. 1.—Activity curves at 823.1°K.: O, experimental; ●, calculated.

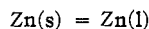
Calculations

In the calculations which follow, the heats and free energies of fusion of antimony and zinc at various temperatures are required. Equations for these quantities have been set up from the fusion and heat capacity data recommended by Kelley⁴ and are given below



$$\Delta H = 4015 + 1.64T - 0.89 \times 10^{-3}T^2 \quad (1)$$

$$\Delta F^\circ = 4015 - 1.64T \ln T + 0.89 \times 10^{-3}T^2 + 5.914T \quad (2)$$



$$\Delta H = 555 + 2.34T - 1.075 \times 10^{-3}T^2 \quad (3)$$

$$\Delta F^\circ = 555 - 2.34T \ln T + 1.075 \times 10^{-3}T^2 + 13.49T \quad (4)$$

The Solid Solubility of Zinc in Antimony.—

From equation 2 the activity of pure solid antimony, $a_2(s)$, relative to pure liquid as standard state, can be calculated at any temperature by the relation, $\Delta F^\circ = -RT \ln a_2(s)$. From the solubility or freezing point curve² the activity of antimony in the equilibrium liquid at a given temperature is calculated from the experimental a_2 and \bar{L}_2 values corresponding to this composition. The \bar{L}_2 values are considered constant over the temperature range. If the $a_2(s)$ and a_2 values thus determined are equal, the equilibrium solid phase is pure antimony. If, however, the value of a_2 is less than $a_2(s)$, the equilibrium solid must be a solid solution of zinc in antimony. For small solubilities the solid solution can be considered

(4) Kelley, Bureau of Mines Bulletins 383 (1935) and 393 (1936).

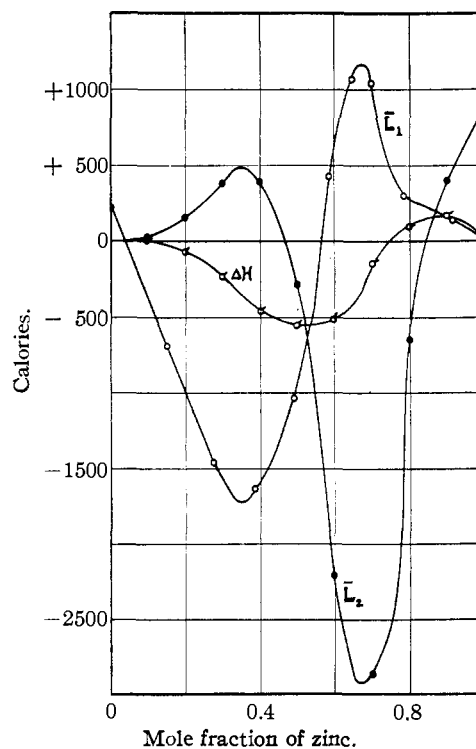


Fig. 2.—Relative heat content and heat of formation.

ideal, as shown for the Pb-Bi system,⁵ and the mole fraction composition, $N_2(s)$, is given by the relation $N_2(s) = a_2/a_2(s)$. In Table III the data and solubilities are given at temperatures between the melting point and the eutectic.

TABLE III

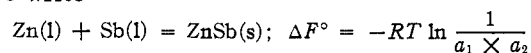
| Temp., °K. | N_2 Equil. liq. | $a_2(s)$ | a_2 | $N_2(s)$ Equil. solid soln. |
|------------|-------------------|----------|-------|-----------------------------|
| 865.1 | 0.900 | 0.890 | 0.883 | 0.992 |
| 823.4 | .800 | .773 | .751 | .972 |
| 784.6 | .800 | .670 | .627 | .936 |
| 778.1 | .682 | .653 | .609 | .933 |

(eutectic)

Thermodynamic Properties of ZnSb, Zn₃Sb₂ and Zn₄Sb₃.—At any temperature where a liquid phase is in equilibrium with a solid intermetallic compound such as ZnSb, we can write for the equilibrium constant

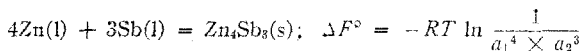
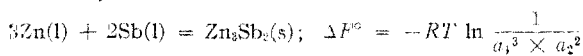
$$K_{\text{ZnSb}} = \frac{1}{a_1 \times a_2}$$

where a_1 and a_2 are the activities of zinc and antimony in the equilibrium liquid and where the activity of the solid is unity. Hence, for the formation of the compound from the two pure liquids, we write



(5) Strickler and Seltz, THIS JOURNAL, 58, 2084 (1936).

Similarly for the Zn_3Sb_2 and Zn_4Sb_3



Using the solubility curves of Takei and the experimental activities and relative heat contents from this investigation, the values of ΔF° of formation of the compounds at different temperatures are given in Table IV. For Zn_3Sb_2 and Zn_4Sb_3 the

TABLE IV

| Temp., °K. | Solubility N_1 | a_1 | a_2 | ΔF° |
|---|---------------------|-------|-------|------------------|
| Zn(l) + Sb(l) = ZnSb(s) | | | | |
| 778.1 | 0.318 | 0.117 | 0.609 | -4,085 |
| 791.4 | .375 | .153 | .528 | -3,957 |
| 804.1 | .425 | .195 | .452 | -3,881 |
| 810.3 | .450 | .225 | .410 | -3,838 |
| 816.7 | .475 | .259 | .369 | -3,815 |
| 3Zn(l) + 2Sb(l) = Zn ₃ Sb ₂ (s) | | | | |
| 837.1 | 0.610 | 0.551 | 0.152 | -9,243 |
| 823.1 | .655 | .682 | .103 | -9,314 |
| 806.0 | .700 | .780 | .076 | -9,449 |
| 774.2 | .800 | .892 | .052 | -9,625 |
| 760.1 | .850 | .938 | .045 | -9,762 |
| 4Zn(l) + 3Sb(l) = Zn ₄ Sb ₃ (s) | | | | |
| 819.1 | 0.485 | 0.272 | 0.350 | -13,604 |
| 823.1 | .502 | .300 | .317 | -13,515 |
| 826.1 | .513 | .320 | .298 | -13,445 |
| 829.4 | .525 | .341 | .283 | -13,335 |
| 832.3 | .538 | .362 | .266 | -13,294 |
| 836.1 | .558 | .410 | .233 | -13,183 |

slight solid solubilities are negligible; their activities are taken as unity at each temperature.

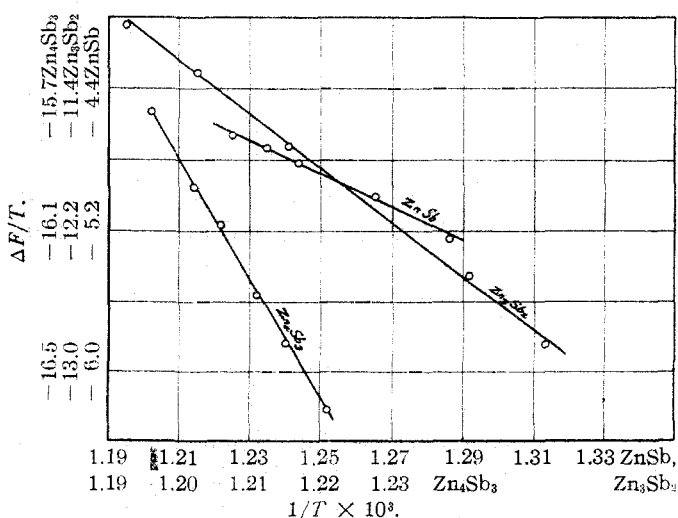
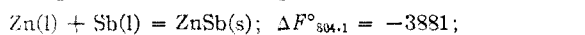


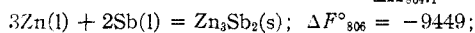
Fig. 3.—Plots of $\Delta F^\circ/T$ against $1/T$.

Plots of $\Delta F^\circ/T$ against $1/T$ for the three compounds are shown in Fig. 3, where it is seen that

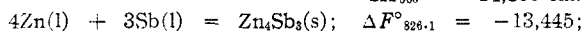
the points lie satisfactorily on straight lines, the slopes of which give directly the ΔH values of the reactions. Taking the mid-temperature for each compound the following relations obtain



$$\Delta H_{804.1} = -9570 \text{ cal.}$$

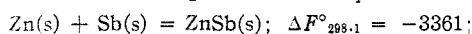


$$\Delta H_{806} = -14,800 \text{ cal.}$$

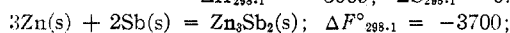


$$\Delta H_{826.1} = -34,400 \text{ cal.}$$

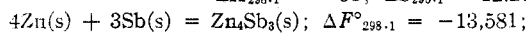
Combining these values with those calculated from equations (1), (2), (3) and (4) at the corresponding temperatures, and calculating to 298.1°K. by the usual thermodynamic methods, with the assumption that ΔC_p is zero, we obtain



$$\Delta H_{298.1} = -3069; \Delta S_{298.1} = 0.98 \text{ e. u.}$$



$$\Delta H_{298.1} = -51; \Delta S_{298.1} = 12.25 \text{ e. u.}$$



$$\Delta H_{298.1} = -13,095; \Delta S_{298.1} = 1.63 \text{ e. u.}$$

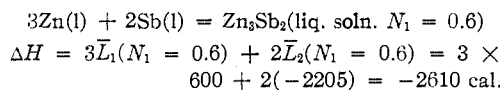
These values of $\Delta S_{298.1}$ with the entropies of Sb(s) and Zn(s)⁶ lead to the following entropies for the compounds

$$ZnSb(s), S_{298.1} = 21.43 \text{ e. u.}; Zn_3Sb_2(s), S_{298.1} = 63.65;$$

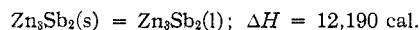
$$Zn_4Sb_3(s), S_{298.1} = 73.48 \text{ e. u.}$$

It should be noted that these thermodynamic quantities refer to the forms of the solid Zn_3Sb_2 and Zn_4Sb_3 as they exist at temperatures of the liquid-solid equilibria and do not consider any transformations which have been reported at lower temperatures. There is still some uncertainty as to the nature of these changes and no thermal data are available for them.

Of the three compounds, Zn_3Sb_2 is the only one which melts congruently and the heat of fusion can be evaluated from the \bar{L} values and the heat of formation. For the change



Combining this value with the ΔH of formation of the compound from the pure liquid metals, we obtain the heat of fusion



Summary

1. The activities and partial molal relative heat contents of zinc and antimony in their liquid melts have been determined over the entire concentration range.

(6) K. K. Kelley, Bureau of Mines Bulletin 394.

2. The solid solubility of zinc in antimony has been calculated.

3. The free energies and heats of formation and the entropies of ZnSb, Zn₃Sb₂ and Zn₄Sb₃

have been evaluated.

4. The heat of fusion of Zn₃Sb₂ has been calculated.

PITTSBURGH, PENNA.

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The Electron Diffraction Investigation of the Molecular Structures of the *meso* and Racemic 2,3-Dibromobutanes¹

BY D. P. STEVENSON² AND VERNER SCHOMAKER

The recent electron diffraction investigations of the structures of some ethylene halides by Beach³ and co-workers have provided considerable information regarding the magnitude of the repulsive forces acting between halogen atoms attached to adjacent carbon atoms. In order to extend the work of Beach to the study of the interactions of the methyl group with other methyl groups and with bromine atoms attached to adjacent carbon atoms, *meso* and racemic 2,3-dibromobutane were selected for electron diffraction investigation. It was hoped that the quite different chemical properties of this pair of molecules⁴ might result from an appreciable difference in the relative orientations of the "isopropyl bromide" groups about the 2,3 carbon-carbon single bond, inasmuch as these molecules would be expected to show structural differences in only this respect.

Experimental.—The *meso* and racemic 2,3-bromobutanes used in this research were portions of samples prepared for another investigation.⁵ It was estimated by Dr. Winstein that neither compound contained more than 2% of the other and that both were otherwise very pure. Inasmuch as the racemic and *meso* compounds are structurally very similar, such a quantity of one in the other would have no effect on the electron diffraction photographs.

The electron diffraction apparatus used in this investigation has been described by Brockway.⁶ The wave length of the electrons, determined in

the usual way from transmission photographs of gold foil, was 0.0611 Å. Photographs were taken with two camera distances, 10.86 and 20.21 cm.

As the compounds are not very volatile (b. p. *ca.* 150°), it was necessary to use the high temperature nozzle⁷ in order to obtain sufficient gas pressure. Photographs were taken with the liquid in the boiler at 100 to 130°.

Interpretation.—The photographs of each molecule showed 13 rings, and were practically identical qualitatively. Only small quantitative differences of doubtful reality were found. Curve C of Fig. 2, to be discussed below, gives a good representation of the appearance of the photographs. The observed values of s ($s_0 = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$) for the maxima and minima as well as the visually estimated intensities, I , are given in Table I.

Radial distribution functions⁸ were calculated using the formulas

$$D(l) = \sum_n C_n \frac{\sin s_n l}{s_n l} \quad (1)$$

$$C_n = f(I_n, s_n) \quad (2)$$

The values of C_n were chosen in accordance with the recommendations of Schomaker⁹ and are given in column 4 of Table I.

The curves of Fig. 1 are plots of the radial distribution functions calculated from the measurements of the maxima and the minima for the *meso* and the racemic compounds. The two curves for each compound are in satisfactory agreement with respect to the two peaks at ~ 2.8 and ~ 4.6 Å., the precise location being for the *meso*-maxima curve, 2.83 and 4.61 Å., the *meso*-minima 2.85 and 4.62, the racemic-maxima 2.82 and 4.58 Å., and the racemic-minima 2.87 and

(7) L. O. Brockway and K. J. Palmer, *THIS JOURNAL*, **59**, 2181 (1937).

(8) L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

(9) Verner Schomaker, A. C. S. meeting, Baltimore, Md., April, 1939.

(1) The results of this investigation were presented at the meeting of the A. A. A. S. in Stanford, June, 1939.

(2) National Research Fellow.

(3) (a) J. Y. Beach and J. K. Palmer, *J. Chem. Phys.*, **6**, 639 (1938); (b) J. Y. Beach and A. Turkevich, *THIS JOURNAL*, **61**, 303 (1939).

(4) The rates with which the *meso* and the racemic dibromobutanes react with iodide ion are very different: *cf.* Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930), and Young, Pressman and Coryell, *ibid.*, **61**, 1640 (1939).

(5) S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939).

(6) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).