

2. It is pointed out that in the study of the V modifications of starch are to be sought important connections between iodine-color, Schardinger dextrin formation, and the behavior of starch molecules during the gelatinization process. Re-

lation of these properties to current ideas of straight-, branched-, and helical-chain starch molecules is briefly discussed with reference to the X-ray evidence.

CAMBRIDGE, MASS.

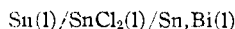
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

## A Thermodynamic Study of the Tin-Bismuth System

BY HARRY SELTZ AND F. J. DUNKERLEY

In previous publications<sup>1</sup> electromotive force studies of the thermodynamic properties of several lower melting binary metal systems have been described. In this paper the results of similar measurements on the tin-bismuth system are reported, with cells of the type



### Experimental

"Chempure" tin, containing less than 0.01% of impurities, and electrolytic bismuth<sup>2</sup> were used for the electrodes. The stannous chloride was prepared by passing dry hydrogen chloride over pure molten tin and then resubliming the solid chloride in a stream of carbon dioxide. Since stan-

nous chloride, boiling at 623°, has an appreciable vapor pressure at the temperature of the measurements and since, furthermore, this electrolyte should be entirely in the stannous state, a special design of Pyrex glass cell, Fig. 1, was used for all measurements. Tungsten lead wires were sealed at "A" into two 10-mm. glass tubes bent into the shape of a "J." The short arms of these tubes were connected by a 2-cm. length of tubing to form the electrolyte bridge "B" of the cell. A horizontal boat-shaped tube, "C," was sealed to one of the legs of the cell, and this was connected to a Hyvac pump. In setting up the cell about 2 g. of tin-bismuth alloy of the desired composition was fused under a degassed molten eutectic of potassium and lithium chlorides. After cooling and reweighing, to ensure that no loss had occurred, the alloy button was placed in leg "D" of the cell, which was then sealed at "E." Pure solid tin and solid stannous chloride were placed in the side tube "C" and the entire cell was thoroughly evacuated. Then heat was applied with a burner until they melted, and they were held at this temperature under vacuum for a sufficient time to degas and to ensure complete reduction of the tin in the electrolyte to the stannous condition. The cell was then tilted and the tin and stannous chloride were run into the heated leg "F" of the cell, and finally the electrolyte was run over on the alloy electrode, filling the cell to above the connecting arm. The vacuum was maintained until no further gassing occurred and then the side tube was removed by sealing at the constriction "G." By this technique the space above the electrolyte was filled with stannous chloride vapor and the electromotive force measurements were made with the cell immersed in a fused salt bath to a point above the top of the short legs.

The cells came to equilibrium rapidly at each temperature and the electromotive force was steady and reproducible to  $\pm 0.03$  millivolt. After completion of a run with an alloy it was removed from the cell and reweighed. The maximum loss in weight in the several runs was not greater than 1 mg. Measurements were made over a range of about 100°, this range being covered two or three times with each alloy.

In Table I the experimental electromotive force values at 608.1°K. are listed for the several compositions, along with the slopes of the e. m. f.-temperature curves. The activities,  $a_1$ , and the relative heat contents,  $\bar{L}_1$ , for tin, calculated from these data by the usual methods, are given in

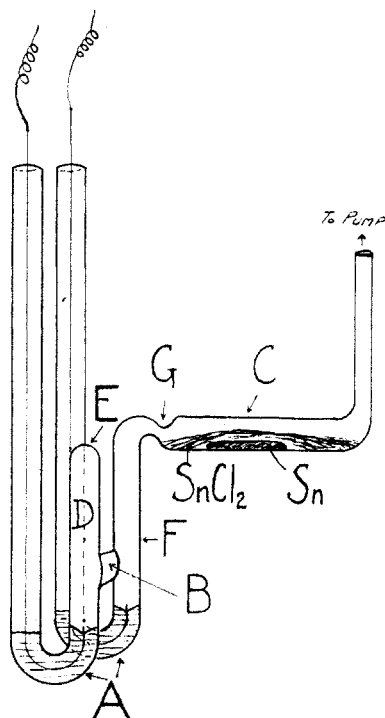


Fig. 1.

(1) Summarized by Seltz, *Trans. Electrochem. Soc.*, **LXXVII**, 233 (1940).

(2) Strichler and Seltz, *THIS JOURNAL*, **58**, 2084 (1936).

TABLE I  
EXPERIMENTAL DATA

$N_1$	E. m. f. at 608.1°K., mv.	$dE/dT$ , mv., °C.	$a_1$ (608.1°K.)	$\bar{L}_1$ , cal.
0.8942	2.80	0.0044	0.898	0
.8010	5.40	.0090	.814	0
.7029	8.40	.0142	.724	+10
.5974	12.20	.0206	.628	+15
.4989	16.49	.0278	.533	+20
.4011	21.66	.0364	.438	+30
.2974	28.79	.0488	.333	+40
.2419	33.64	.0572	.277	+55
.1034	55.47	.0940	.120	+80

heats of formation,  $\Delta H$ , of a mole of the liquid solutions from the pure liquid metals are given, where  $\Delta H = N_1\bar{L}_1 + N_2\bar{L}_2$ .

The activity curves for the two components are plotted in Fig. 2 and the  $\bar{L}$  values and  $\Delta H$  curves in Fig. 3. From these figures it is apparent that this system shows only slight positive deviations from ideal behavior. The symmetrical quadratic form of the  $\Delta H$  curve indicates a possible "regular" nature on the part of these solutions. This is confirmed by the fair agreement of the

TABLE II  
ACTIVITIES AND RELATIVE HEAT CONTENTS

$N_1$	$a_1$ (608.1°K.)	$a_1/N_1$	$a_2$ (608.1°K.)	$a_2/N_2$	$\bar{L}_1$	$\bar{L}_2$	$\Delta H$
1.0	1.000	1.000	0.000		0	110 <sup>a</sup>	0
0.9	0.905	1.006	.125	1.249	0	80	8
.8	.812	1.015	.231	1.157	0	60	12
.7	.720	1.029	.332	1.106	10	40	19
.6	.629	1.048	.426	1.066	15	30	21
.5	.532	1.064	.521	1.043	20	25	22
.4	.434	1.085	.616	1.026	30	15	21
.3	.334	1.113	.708	1.011	40	10	19
.2	.230	1.150	.802	1.003	60	5	16
.1	.114	1.140	.902	1.002	80	0	8
.0	.000	1.174 <sup>a</sup>	1.000	1.000	110 <sup>a</sup>	0	0

<sup>a</sup> Extrapolated.

columns 4 and 5. In Table II the activities and relative heat contents are tabulated for both components at round number mole fractions; the values for bismuth,  $a_2$  and  $\bar{L}_2$ , were determined by the usual graphical methods. In column 8 the

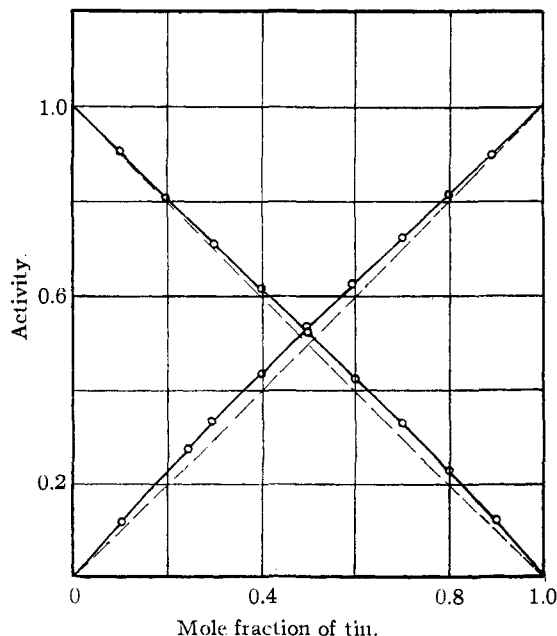


Fig. 2.

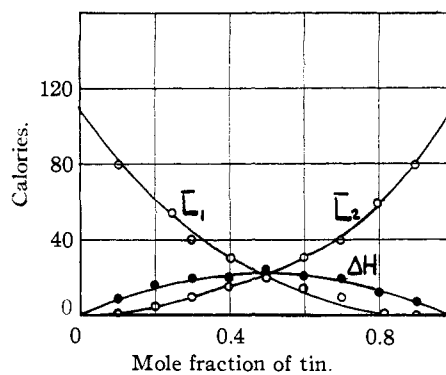


Fig. 3.

experimental values of  $\bar{S}_1 - S_1^0$ , calculated from the values of  $NF(dE/dT)$ , and the ideal entropy change of solution,  $-R \ln N_1$ , as shown in Table III.

TABLE III  
PARTIAL MOLAL ENTROPIES OF SOLUTION

$N_1$	$NF(dE/dT)$	$-R \ln N_1$
0.8942	0.20	0.22
.8010	.42	.44
.7029	.66	.70
.5974	.95	1.02
.4989	1.28	1.38
.4011	1.67	1.82
.2974	2.26	2.40
.2419	2.64	2.81
.1034	4.34	4.51

**Calculations of Solid-Liquid Equilibria.**—The phase equilibria in the tin-bismuth system have been studied by several investigators, and a critical analysis of these data has been made by Hansen.<sup>3</sup> The system shows a eutectic at 139°, at 42% of tin, ( $N_1 = 0.560$ ), and the solid eutectic phases are an  $\alpha$  solid solution of tin in bismuth and a  $\beta$  solid solution of bismuth in tin. For the  $\beta$  liquidus curve there is excellent agreement among the several investigators, while discrepancies of over 10° appear in the  $\alpha$  liquidus reported by Endo<sup>4</sup> and by Würschmidt.<sup>5</sup> Endo's work on the  $\beta$  solidus curve seems to be the most reliable, giving a solid solubility at the eutectic of about 16% of bismuth. The solubility of tin in the  $\alpha$  phase at the eutectic has not been definitely established; values of from zero to over 1% have been reported.

The thermodynamic data obtained in this investigation can now be compared with these equilibrium results. For these calculations the activities of pure solid tin and bismuth relative to the pure liquids are given by the equations

$$\text{Sn(s)} \log a^1 = -(338.5/T) + 0.780 \log T - 0.524 \times 10^{-3}T - 1.173 \quad (1)$$

$$\text{Bi(s)} \log a_2^1 = -(367.5/T) + 1.117 \log T - 0.284 \times 10^{-3}T - 2.226 \quad (2)$$

These equations were derived from the melting points, heats of fusion and heat capacities for the metals as given in Bulletins of the Bureau of Mines.<sup>6</sup>

Using the accepted  $\beta$  liquidus, at several temperatures between the eutectic and the melting point of tin, the activities of tin in the equilibrium liquids are taken from a plot of the activity data. These compositions and activities are given in (2) and (3) of Table IV. At the same tempera-

tures the activities of solid tin,  $a_1^1$ , are calculated from Eq. 1, and these values are listed in column (4). In column (5) the ratios,  $a_1/a_1^1$  are shown, and these ratios should give the mole fractions of tin in the equilibrium  $\beta$  solid solutions at each temperature, if these solutions can be assumed to obey Raoult's law over this short concentration range. In column (6) the corresponding values from a smoothed curve of Endo's results are given. The agreement here seems satisfactory, considering the uncertainties in the experimental determination of solidus temperatures. The agreement at the eutectic, corresponding to 20% of bismuth, which is the value accepted by Hansen, should be compared with 16% which Endo assigns from his measurements. From the form of the solidus curve, however, 16% seems too low, requiring a sharp break from the otherwise almost linear points.

As mentioned above there is considerable disagreement in the  $\alpha$  liquidus points except at the eutectic, where the composition seems well established at 42% of tin at a temperature of 139°. The  $\alpha$  solidus has not been investigated except at the eutectic, where uncertain values of from zero to 1% have been reported. In Table V the thermodynamic calculations on this side of the system are shown. In column (2) the mole fractions of bismuth,  $N_2$ , from Endo's liquidus are given at several temperatures between the eutectic and the melting point of bismuth, and in column (3) the corresponding activities,  $a_2$ , from a plot of the activity data. In column (4) the activities of solid bismuth,  $a_2^1$ , calculated from Eq. 2, are given at these temperatures. It can be seen that, except at the eutectic and at 420°K., the  $a_2$  values are greater than the  $a_2^1$  values, an impossible condition for equilibrium. Apparently Endo's liquidus points are low. At the well-established eutectic, however, the value of  $a_2/a_2^1$  is 0.959, which should correspond to the mole fraction of bismuth in the eutectic equilibrium  $\alpha$  solid solution. This value is equivalent to 2.4% of tin, which is appreciably higher than previously reported values. Assuming a straight line solidus from this point to the melting point of bismuth, a corrected liquidus curve can now be established. In Table V, column (5), the solidus compositions,  $N_2^1$ , are listed, and in column (6) the product  $N_2^1 \times a_2^1$ , which should equal the activity,  $a_2$ , of bismuth in the equilibrium liquidus. The corresponding mole fraction compositions are taken

TABLE IV

CALCULATION OF $\beta$ -SOLID SOLUTION COMPOSITIONS					
(1) Temp., °K.	(2) $N_1$	(3) $a_1$	(4) $a_1^1$	(5) $a_1/a_1^1$	(6) $N_1^1$
412	0.560	0.590	0.674	0.876	0.877
420	.605	.632	.703	.899	.884
440	.702	.722	.774	.932	.912
460	.790	.802	.845	.948	.938
480	.872	.880	.915	.962	.966
500	.974	.974	.984	.989	.994

(3) Hansen, "Die Aufbau der Zweistofflegierungen," Julius Springer, Berlin, 1936.

(4) Endo, *Sci. Rep. Tohoku Univ.*, **14**, 489 (1925).

(5) Würschmidt, *Z. Physik*, **5**, 39 (1921).

(6) Kelley, "Contributions to the Data on Theoretical Metallurgy," Bulletins 371, 383, 393, U. S. Department of the Interior, Bureau of Mines.

TABLE V  
 CALCULATION OF  $\alpha$ -SOLID SOLUTION COMPOSITIONS

(1) Temp., °K.	(2) $N_2$ (Endo)	(3) $a_2$	(4) $a_2'$	(5) $N_2'$	(6) $N_2'a_2' = a_2$	(7) $N_2$ (calcd.)	(8) $N_2$ (exp.)
412	0.440	0.465	0.485	0.959			
420	.485	.508	.513	.960	0.493	0.467	0.47
440	.587	.605	.584	.970	.566	.547	.55
460	.692	.705	.659	.955	.642	.628	.62
480	.755	.765	.736	.980	.721	.710	.70
500	.835	.840	.817	.987	.807	.800	.79
520	.915	.917	.898	.992	.891	.887	.89

from the activity curve and are shown in column (7). These values are in good agreement with Würschmidt's smoothed curve, column (8), which lies above that of Endo.

### Summary

1. The activities and relative heat contents of tin and bismuth in their liquid alloys have been determined from electromotive force studies.

2. These thermodynamic data have been compared with published equilibrium data for the system. The  $\beta$  solid solution at the eutectic has been calculated to contain 20% of bismuth, while the  $\alpha$  solid solution contains 2.4% of tin. The  $\alpha$  liquidus points obtained by Würschmidt are in good agreement with those calculated from these data, while Endo's curve seems to be too low.

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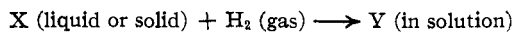
[CONTRIBUTION FROM THE HARVARD CHEMICAL LABORATORIES]

## Heats of Catalytic Hydrogenation in Solution. I. Apparatus, Technique, and the Heats of Hydrogenation of Certain Pairs of Stereoisomers

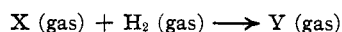
BY R. BRANSTON WILLIAMS

For some years past, Kistiakowsky and his co-workers<sup>1</sup> have been engaged in the direct measurement of the heats of certain catalytic reactions in the vapor phase. The application of the new method, however, is limited, being restricted to compounds which are appreciably volatile at the temperature at which the reactions are carried out and so it seemed desirable to attempt to extend the method to the liquid phase, where the same restriction as to the substances suitable for study does not hold.

The reactions studied have been of the type



and to obtain values applicable to the completely gaseous reactions



various corrections have to be applied. Thus the relationship between  $\Delta H$ , the molar heat of a reaction of the type studied, and  $\Delta H_g$ , the molar heat of the completely gaseous reaction, is given by

$$\Delta H_g = \Delta H - (xL_v - yL_v) - L_s \quad (1)$$

(1) Kistiakowsky, *et al.*, *THIS JOURNAL*, **57**, 65 (1935); **57**, 876 (1935); **58**, 137 (1936); **58**, 146 (1936); **59**, 831 (1937); **60**, 440 (1938); **60**, 2764 (1938); **61**, 1868 (1939); *Chem. Rev.*, **20**, 181 (1937).

when X and Y are both liquids at the temperature of the measurements, and by

$$\Delta H_g = \Delta H - (xL_v - yL_v) - (xL_t - yL_t) - L_s \quad (2)$$

when X and Y are both solids.  $xL_v$ ,  $xL_t$ ,  $yL_v$ , and  $yL_t$  are the molar latent heats of vaporization and fusion of X and Y, respectively, and  $L_s$  is the molar heat of solution of Y in the solvent used, all the terms being positive when heat is absorbed, and applying at the temperature of the measurements. In the present work, heats of solution have been determined directly, but latent heats have been taken from the literature.

The accuracy of the results yielded by the calorimeter has been tested by measuring the heat of hydrogenation of *n*-heptene-1, and comparing the result obtained with that yielded for the same substance by the vapor method.

### Method

The determinations of heats of hydrogenation and of solution involved in this investigation were carried out in the usual way by measuring the change in temperature of the calorimeter and contents due to the hydrogenation or solution of a known quantity of material, and then determining the electrical equivalent of the calorimeter and contents over the same temperature range.