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# Behavior of the Heat of Formation in the Bismuth-Antimony System

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Calorimetric studies on the behavior of the heat of formation in the bismuth-antimony system have been carried out at eight different compositions (10—80 at-% Sb). Values of the enthalpy and excess enthalpy at those compositions have been determined and tabulated at even temperature intervals of 10 °C in the range 50 to 650 °C. The heat of formation at 200 °C is given through the equation:

$$H^F = 11.658x_2 - 14.436x_2^2 + 2.778x_2^3$$

The heat of formation is positive and takes a maximum value (2556±11) J mol$^{-1}$ at 50 at-% Sb. The heat of formation is larger than the heat of mixing. The excess over the value of the heat of mixing is attributed to the larger excess volume in the solid state.

There has been considerable interest in the study of thermodynamic properties of binary systems of metals and metalloids. One such system, namely bismuth-antimony has been studied by some researchers e.g. phase diagram by Hansen and Anderko[1] and heat of mixing at 700 °C by Wittig and Gehring.[2]

The present study has been undertaken with the purpose of studying the behavior of the heat of formation in the bismuth-antimony system and of obtaining the ratio of the heats of formation to those of mixing. This would facilitate interpolation of the behavior of the heat of formation at positions having indefinite structures in other binary systems.

## Experimental

**Sample.** The samples were prepared at eight different mole fractions of antimony between 0.1 and 0.8. The metals in the form of bars were procured from E. Merck Company. These were of chemically pure grade. The alloy samples were produced in a melting device operating as "Zintl funnel" system (Fig. 1). By this melting device, while the clean liquid metal flows down into the lower tube of quartz, the oxide layer remains apart in the first one. The mixture of metals was stirred mechanically with a stirrer made of ceramic for 30 min at 700 °C. In order to reduce the effect of oxidation, argon gas was used as a protector during the melting process.

The samples of 10—40 at-% Sb were tempered for 70 h at 200 °C, those of 50—80 at-% Sb at 280, 300, 320, and 380 °C for 70 h at each temperature. The homogeneity of all the compositions studied was established through testing the polished pictures prepared as described by Czochralsky and Przyjemski.[3]

**Apparatus.** The measurements of enthalpies were carried out using the calorimeter described and utilized by Wittig and co-workers.[4] Modifications on the calorimeter, alteration to the suitable dimensions, regulation of the furnace temperature by means of a p-regulator[5] and using a digital millivoltmeter for measurement of the potential of the thermocouples, revealed satisfactory result.

**Procedure.** The procedure used depended on the method of primary indirect provision of energy under adiabatic conditions. (see Ref. 6).

The heat of formation can be computed through the equations:

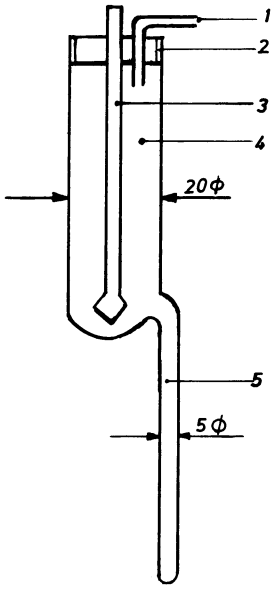


Fig. 1. Melting device.
1 : Gas supply, 2 : sealing, 3 : stirrer, 4 : quartz tube, 5 : quartz tube.

$$(1-x_2)\cdot Bi_{(l)} + x_2\cdot Sb_{(s)} \longrightarrow Bi_{1-x_2}Sb_{x_2(s)} - H^{F,M}$$
$$(1-x_2)\cdot Bi_{(s)} \longrightarrow (1-x_2)\cdot Bi_{(l)} - H_{Bi}^{s}$$

$$(1-x_2)\cdot Bi_{(s)} + x_2\cdot Sb_{(s)} \longrightarrow Bi_{1-x_2}Sb_{x_2(s)} - [H^{F,M} + (1-x_2)H_{Bi}^{s}]$$

$$H^F = H^{F,M} + (1-x_2)\cdot H_{Bi}^{s} \quad (1)$$

where $H^F$ is the heat of formation of solid bismuth and antimony, $H^{F,M}$ the heat of formation at the temperature of mixing, $H_{Bi}^{s}$ the heat of fusion of bismuth and $x_2$ the mole fraction of antimony. $H^{F,M}$ can be calculated with reference to the Helmholtz equation:

$$H^F(T_1) - H^F(T_0) = {}^eH(T_1) - {}^eH(T_0) \quad (2)$$

$T_0$ refers to the initial temperature, $T_1$ to any higher temperature and ${}^eH(T_1)-{}^eH(T_0)$ to the difference of the excess enthalpy which is given by

$${}^eH(T_1) - {}^eH(T_0) = [H_3(T_1)-H_3(T_0)] - (1-x_2)\cdot[H_1(T_1)-H_1(T_0)] - x_2\cdot[H_2(T_1)-H_2(T_0)] \quad (3)$$

Table 1. Enthalpy Values ($H_{50}{}^{t}$/J mol$^{-1}$) in the System Bi-Sb

| $t$/°C | At-% Sb | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |
| 60 | 258 | 258 | 250 | 260 | 270 | 250 | 250 | 250 |
| 70 | 522 | 522 | 513 | 522 | 540 | 513 | 488 | 501 |
| 80 | 782 | 782 | 771 | 791 | 808 | 771 | 752 | 798 |
| 90 | 1048 | 1038 | 1029 | 1058 | 1088 | 1038 | 1005 | 1008 |
| 100 | 1321 | 1300 | 1290 | 1318 | 1360 | 1290 | 1252 | 1260 |
| 110 | 1589 | 1569 | 1553 | 1592 | 1652 | 1553 | 1508 | 1518 |
| 120 | 1862 | 1840 | 1820 | 1860 | 1908 | 1820 | 1758 | 1782 |
| 130 | 2128 | 2100 | 2082 | 2134 | 2180 | 2108 | 2018 | 2041 |
| 140 | 2415 | 2375 | 2348 | 2408 | 2458 | 2375 | 2280 | 2305 |
| 150 | 2684 | 2654 | 2618 | 2685 | 2730 | 2644 | 2535 | 2558 |
| 160 | 2962 | 2922 | 2888 | 2948 | 3005 | 2912 | 2788 | 2835 |
| 170 | 3245 | 3203 | 3172 | 3228 | 3268 | 3180 | 3055 | 3092 |
| 180 | 3518 | 3473 | 3450 | 3500 | 3450 | 3328 | 3364 | 3364 |
| 190 | 3800 | 3750 | 3728 | 3777 | 3818 | 3720 | 3590 | 3618 |
| 200 | 4083 | 4033 | 4012 | 4058 | 4104 | 4002 | 3861 | 3888 |
| 210 | 4368 | 4308 | 4290 | 4340 | 4379 | 4268 | 4122 | 4160 |
| 220 | 4652 | 4600 | 4579 | 4618 | 4658 | 4548 | 4388 | 4421 |
| 230 | 4944 | 4884 | 4870 | 4900 | 4920 | 4832 | 4658 | 4690 |
| 240 | 5220 | 5167 | 5141 | 5179 | 5218 | 5101 | 4918 | 4957 |
| 250 | 5517 | 5456 | 5408 | 5472 | 5508 | 5379 | 5188 | 5228 |
| 260 | 5785 | 5760 | 5682 | 5748 | 5762 | 5171 | 5472 | 5505 |
| 270 | 6151 | 6048 | 5959 | 6039 | 6092 | 5959 | 5740 | 5775 |
| 280 | 9265 | 7025 | 6245 | 6325 | 6495 | 6285 | 6015 | 6055 |
| 290 | 13460 | 8450 | 6540 | 6620 | 6950 | 6640 | 6320 | 6330 |
| 300 | 16665 | 10085 | 7075 | 6910 | 7285 | 6950 | 6610 | 6600 |
| 310 | 17795 | 13740 | 7940 | 7240 | 7610 | 7300 | 6920 | 6890 |
| 320 | 18200 | 16040 | 10350 | 7620 | 8020 | 7680 | 7240 | 7180 |
| 330 | 18610 | 17530 | 12720 | 10020 | 8470 | 8050 | 7570 | 7480 |
| 340 | 19010 | 18500 | 14310 | 12160 | 9790 | 8430 | 7900 | 7790 |
| 350 | 19370 | 19220 | 15610 | 13770 | 11400 | 8950 | 8230 | 8100 |
| 360 | 19710 | 19810 | 16700 | 14960 | 12680 | 10080 | 8560 | 8410 |
| 370 | 20040 | 20330 | 17610 | 16010 | 13760 | 11210 | 8900 | 8710 |
| 380 | 20360 | 20790 | 18420 | 16790 | 14740 | 12160 | 9500 | 9010 |
| 390 | 20670 | 21220 | 19120 | 17920 | 15650 | 13050 | 10300 | 9310 |
| 400 | 20980 | 21620 | 19740 | 18850 | 16580 | 13900 | 11070 | 9610 |
| 410 | 21270 | 22000 | 20320 | 19700 | 17460 | 14730 | 11830 | 9940 |
| 420 | 21560 | 22360 | 20860 | 20480 | 18490 | 15560 | 12570 | 10380 |
| 430 | 21840 | 22720 | 21380 | 21200 | 19360 | 16440 | 13340 | 10910 |
| 440 | 22130 | 23070 | 21880 | 21830 | 20340 | 17320 | 14120 | 11490 |
| 450 | 22410 | 23410 | 22360 | 22420 | 21290 | 18370 | 14930 | 12120 |
| 460 | 22680 | 23750 | 22820 | 22990 | 22190 | 19320 | 15780 | 12790 |
| 470 | 22960 | 24080 | 23260 | 23530 | 23040 | 20540 | 16710 | 13490 |
| 480 | 23230 | 24410 | 23680 | 24070 | 23890 | 21610 | 17720 | 14260 |
| 490 | 23510 | 24720 | 24090 | 24570 | 24680 | 22790 | 18830 | 15080 |
| 500 | 23780 | 25010 | 24480 | 25060 | 25370 | 23930 | 20090 | 16000 |
| 510 | 24050 | 25280 | 24840 | 25520 | 25990 | 25020 | 21500 | 17010 |
| 520 | 24330 | 25650 | 25180 | 25940 | 26540 | 26020 | 23050 | 18170 |
| 530 | 24600 | 25910 | 25500 | 26320 | 27000 | 26910 | 24660 | 19460 |
| 540 | 24870 | 26170 | 25800 | 26640 | 27400 | 27710 | 26210 | 20830 |
| 550 | 25140 | 26420 | 26090 | 26930 | 27760 | 28410 | 27380 | 22500 |
| 560 | 25410 | 26680 | 26380 | 27230 | 28080 | 29020 | 28310 | 24270 |
| 570 | 25680 | 26940 | 26670 | 27510 | 28360 | 29560 | 29130 | 26110 |
| 580 | 25950 | 27190 | 26960 | 27790 | 28636 | 29990 | 29850 | 27690 |
| 590 | 26210 | 27450 | 27250 | 28070 | 28910 | 30330 | 30420 | 29190 |
| 600 | 26480 | 27710 | 27850 | 28350 | 29190 | 30590 | 30870 | 30450 |
| 610 | 26760 | 27960 | 27870 | 28360 | 29460 | 30850 | 31190 | 31500 |
| 620 | 27030 | 28220 | 28170 | 28910 | 29740 | 31110 | 31480 | 32320 |
| 630 | 27310 | 28470 | 28460 | 29190 | 30010 | 31360 | 31760 | 32980 |
| 640 | 27590 | 28730 | 28750 | 29470 | 30290 | 31610 | 23040 | 33430 |
| 650 | 27870 | 28980 | 29040 | 29760 | 30570 | 31870 | 32320 | 33760 |

Table 2. Excess Enthalpies ($^{e}H_{50}{}^{t}$/J mol$^{-1}$) in the System Bi-Sb

| $t$/°C | At-% Sb | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |
| 60 | 0 | 0 | −10 | 0 | 10 | 0 | −10 | −10 |
| 70 | 0 | 0 | −10 | 0 | 10 | 0 | −10 | −10 |
| 80 | 10 | −10 | −30 | 0 | 20 | 0 | −20 | −30 |
| 90 | 10 | −10 | −40 | 0 | 30 | 0 | −30 | −40 |
| 100 | 10 | −10 | −50 | 0 | 30 | 0 | −40 | −50 |
| 110 | 10 | −20 | −60 | 0 | 40 | 0 | −50 | −60 |
| 120 | 10 | −20 | −60 | 0 | 40 | 0 | −60 | −70 |
| 130 | 20 | −30 | −70 | 0 | 50 | 0 | −60 | −70 |
| 140 | 20 | −30 | −70 | 0 | 50 | 0 | −70 | −80 |
| 150 | 20 | −30 | −80 | 0 | 60 | 0 | −80 | −90 |
| 160 | 20 | −30 | −80 | 0 | 60 | 0 | −90 | −90 |
| 170 | 20 | −40 | −80 | 0 | 60 | 0 | −100 | −90 |
| 180 | 30 | −40 | −80 | 0 | 60 | 0 | −100 | −100 |
| 190 | 30 | −40 | −80 | 0 | 70 | 0 | −110 | −100 |
| 200 | 30 | −40 | −80 | 0 | 70 | 0 | −120 | −100 |
| 210 | 30 | −40 | −80 | 0 | 70 | 0 | −130 | −110 |
| 220 | 30 | −50 | −80 | 0 | 70 | 0 | −140 | −110 |
| 230 | 40 | −50 | −80 | 10 | 70 | 0 | −140 | −120 |
| 240 | 40 | −50 | −70 | 10 | 80 | 0 | −150 | −120 |
| 250 | 40 | −50 | −70 | 10 | 80 | 0 | −160 | −130 |
| 260 | 40 | −50 | −60 | −10 | 100 | 0 | −170 | −140 |
| 270 | −10120 | −9160 | −8020 | −6850 | −5560 | −4520 | −3580 | −2410 |
| 280 | −7100 | −8480 | −8010 | −6850 | −5510 | −4500 | −3580 | −2420 |
| 290 | −3210 | −7360 | −8000 | −6850 | −5440 | −4460 | −3570 | −2430 |
| 300 | −300 | −6100 | −7740 | −6850 | −5350 | −4400 | −3550 | −2430 |
| 310 | +540 | −2870 | −7170 | −6810 | −5250 | −4320 | −3530 | −2430 |
| 320 | 750 | −970 | −5060 | −6730 | −5120 | −4230 | −3430 | −2420 |
| 330 | 870 | +220 | −2980 | −4610 | −4960 | −4140 | −3450 | −2400 |
| 340 | 970 | +900 | −1680 | −2760 | −3920 | −4030 | −3400 | −2370 |
| 350 | 1040 | 1330 | −680 | −1440 | −2600 | −3850 | −3350 | −2340 |
| 360 | 1090 | 1640 | +120 | −530 | −1600 | −3000 | −3290 | −2320 |
| 370 | 1130 | 1860 | 740 | +220 | −780 | −2200 | −3220 | −2300 |
| 380 | 1160 | 2040 | 1270 | 900 | −110 | −1550 | −2930 | −2280 |
| 390 | 1190 | 2200 | 1670 | 1570 | +530 | −950 | −2410 | −2270 |
| 400 | 1200 | 2310 | 2010 | 2020 | 1150 | −380 | −1920 | −2240 |
| 410 | 1220 | 2410 | 2300 | 2770 | 1780 | +170 | −1450 | −2170 |
| 420 | 1230 | 2490 | 2560 | 3270 | 2430 | 710 | −990 | −2040 |
| 430 | 1230 | 2570 | 2790 | 3700 | 3120 | 1270 | −520 | −1790 |
| 440 | 1230 | 2630 | 3000 | 4050 | 3850 | 1850 | −40 | −1500 |
| 450 | 1230 | 2690 | 3200 | 4360 | 4480 | 2500 | +490 | −1150 |
| 460 | 1234 | 2742 | 3371 | 4642 | 5112 | 3252 | 1112 | −772 |
| 470 | 1234 | 2792 | 3532 | 4902 | 5702 | 4082 | 1820 | −355 |
| 480 | 1234 | 2845 | 3675 | 5120 | 6265 | 4965 | 2625 | +135 |
| 490 | 1234 | 2875 | 3805 | 5385 | 6765 | 5855 | 3525 | 665 |
| 500 | 1224 | 2885 | 3905 | 5595 | 7175 | 6685 | 4485 | 1295 |
| 510 | 1224 | 2885 | 3985 | 5765 | 7485 | 7435 | 5585 | 2015 |
| 520 | 1224 | 2875 | 4045 | 5905 | 7725 | 8095 | 6805 | 2885 |
| 530 | 1222 | 2865 | 4085 | 5995 | 7885 | 8665 | 8125 | 3885 |
| 540 | 1212 | 2840 | 4095 | 6035 | 7995 | 9165 | 9365 | 5115 |
| 550 | 1212 | 2825 | 4105 | 6045 | 8065 | 9575 | 10255 | 6335 |
| 560 | 1202 | 2805 | 4115 | 6055 | 8095 | 9905 | 10925 | 7755 |
| 570 | 1202 | 2785 | 4125 | 6045 | 8095 | 10105 | 11495 | 9205 |
| 580 | 1202 | 2765 | 4125 | 6045 | 8085 | 10245 | 11975 | 10635 |
| 590 | 1192 | 2745 | 4135 | 6035 | 8075 | 10215 | 12275 | 11745 |
| 600 | 1192 | 2725 | 4145 | 6035 | 8055 | 10185 | 12425 | 12805 |
| 610 | 1185 | 2705 | 4145 | 6025 | 8045 | 10155 | 12425 | 13485 |
| 620 | 1185 | 2685 | 4155 | 6025 | 8025 | 10125 | 12415 | 14085 |
| 630 | −815 | −1325 | −1795 | −1935 | −1955 | −1845 | −1535 | −1505 |
| 640 | −805 | −1355 | −1785 | −1945 | −1975 | −1875 | −1555 | −1395 |
| 650 | −805 | −1375 | −1785 | −1945 | −1995 | −1910 | −1575 | −1305 |

The indices 1, 2, and 3 indicate bismuth, antimony, and the alloy, respectively. The enthalpies of the alloys were measured at even temperature intervals of 10 °C in the region 50 to 650 °C. The enthalpy differences between $T_0$ and $T_1$ for bismuth and antimony are reported and tabulated (see Ref. 7). The heat of mixing values are reported by Wittig and Gehring.[2]

## Results and Discussion

Results of the enthalpy measurements are presented in Table 1 at even temperature intervals of 10 °C in the range 50 to 650 °C. The values of the excess enthalpy are listed in Table 2 at even temperature intervals of 10 °C in the same region of temperature.

The data in Table 3 represent the integral and partial heat of formation at 200 °C. The error of the individual measurement was found to be about 1%. The experimental result is in good agreement with the calculated value. Table 3, also illustrate the $\xi$-values. For $\xi(T)$, the following equation was used:

$$\xi(T) = H^F(T)/x_2 \cdot (1-x_2) \quad (4)$$

The experimentally determined $H^F$-values were used to obtain a polynomial function for $H^F(T)$. The $H^F(T)$ function was employed together with Eq. 4 to derive the following relation for $\xi$:

$$\xi = 11.658 - 2.778x_2 \quad (5)$$

Using the $\xi$-function (Eq. 5) and Eq. 4, the heat of formation is given as a function of $x_2$ through the equation:

$$H^F(200\,°C) = 11.658x_2 - 14.436x_2^2 + 2.778x_2^3 \quad (6)$$

This equation represents the curve shown in Fig. 3. Table 3 illustrate the $H^F$-values, calculated with the aid of Eq. 6. These values are presented in brackets.

Table 3. Integral and Partial Molar Heats of Formation; $\xi$-Values in the Bi-Sb System at 200 °C

| $x_{Sb}$ | $H^F$ kJ mol$^{-1}$ Found (Calcd) | $H_{Bi}{}^F$ kJ mol$^{-1}$ | $H_{Sb}{}^F$ kJ mol$^{-1}$ | $\xi$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| 0.1 | 1.035 (1.024) | 0.139 | 8.993 | 11.369 |
| 0.2 | 1.760 (1.770) | 0.533 | 6.750 | 11.119 |
| 0.3 | 2.294 (2.273) | 1.149 | 4.896 | 10.805 |
| 0.4 | 2.544 (2.531) | 1.954 | 3.398 | 10.531 |
| 0.5 | 2.556 (2.567) | 2.915 | 2.222 | 10.251 |
| 0.6 | 2.378 (2.398) | 3.997 | 1.335 | 9.972 |
| 0.7 | 2.056 (2.398) | 5.168 | 0.703 | 9.693 |
| 0.8 | 1.519 (1.501) | 6.394 | 0.294 | 9.453 |

The partial molar heats of formation of bismuth and antimony are given by

$$H_{Bi}{}^F = H^F - x_2 \cdot (\partial H^F/\partial x_2)_{T,p} \quad (7)$$

$$H_{Sb}{}^F = H^F - (x_2-1) \cdot (\partial H^F/\partial x_2)_{T,p} \quad (8)$$

Using Eq. 6, we obtain

$$H_{Bi}{}^F = 14.436x_2^2 - 5.556x_2^3 \quad (9)$$

$$H_{Sb}{}^F = 11.658 - 28.872x_2 + 22.778x_2^2 - 5.556x_2^3 \quad (10)$$

The calculated partial molar heats of formation of bismuth and antimony are presented in Table 3.

The data in Table 3 clearly indicate that the heat of formation in the bismuth-antimony system is positive and larger than the heat of mixing. This leads to the

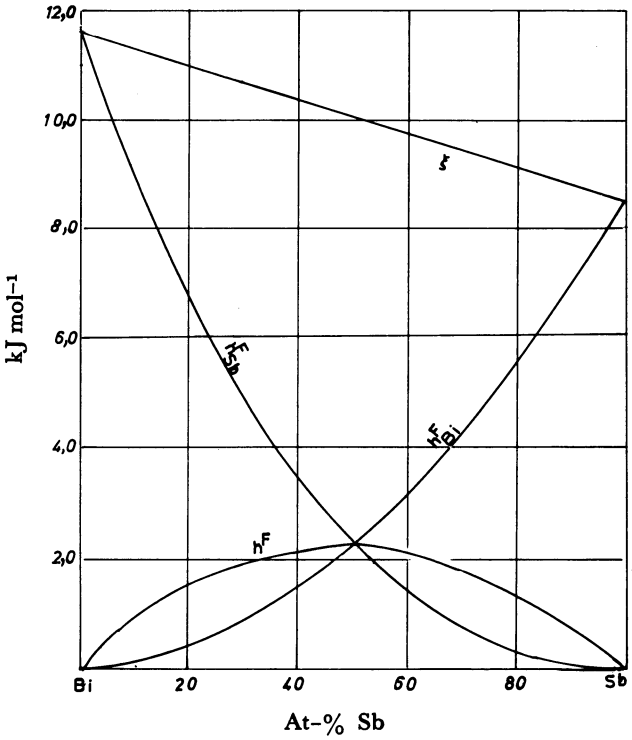


Fig. 2. The heat of formation, $\xi$-function and partial heats of formation of Bi and Sb in Sb-Bi system at 200 °C.

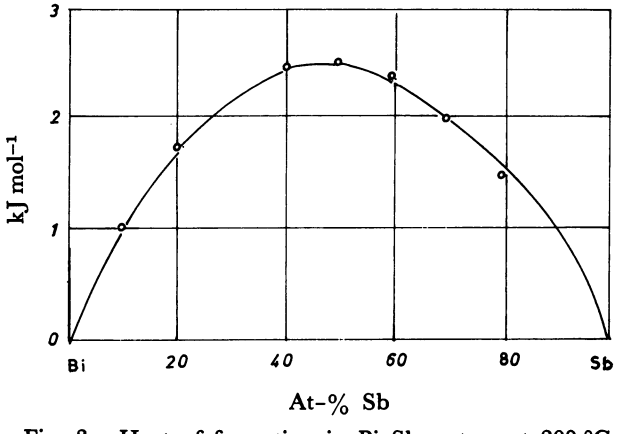


Fig. 3. Heat of formation in Bi-Sb system at 200 °C.

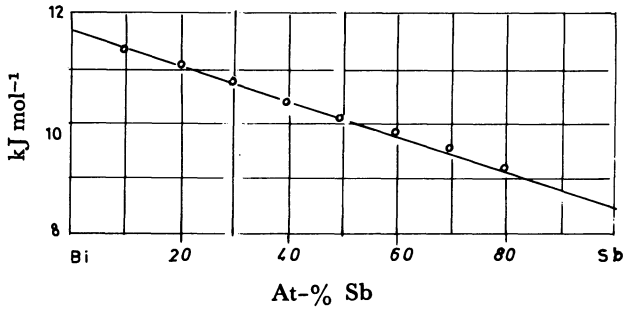


Fig. 4. $\xi$-Values in Bi–Sb system at 200 °C.

conclusion that there is a larger excess volume in the solid state. Bismuth expands more than antimony on solidification. As a result of this, the maximum of expansion lies at larger bismuth concentration.

Figure 2 shows the curves of the partial molar heats of formation of bismuth and antimony. These curves indicate that the partial heat of formation of bismuth is positive and increases with the increase of antimony mole fraction. The partial molar heat of formation of antimony is also positive but decreases with the increase of antimony mole fraction.

The heat of formation increases with the increase of the antimony mole fraction to reach a maximum at the point $x_{Sb}=0.5$ (Fig. 3); after that the heat of formation decreases with the increase of antimony mole fraction.

With reference to Eq. 5, $\xi$ (200 °C) exhibits a linear function of $x_2$. Figure 4 represents the experimentally determined $\xi$-values at 200 °C.

## References

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