Enthalpy of Formation of Gallium-Germanium-Tin Liquid Alloys: Evaluation of the Liquidus Surface of the Phase Diagram from Excess Functions of Mixing

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With a differential high temperature Calvet calorimeter, the enthalpies of formation of Ga-Ge-Sn liquid alloys have been measured at 703, 798, 895, 1000 and 1230 K in the whole concentration area. The experimental results are compared with those obtained by using an interpolation relation on the basis of the excess functions of mixing of the bordering binary systems. The interpolation relation is used to calculate the partial excess functions and to determine the position of the liquidus surface of the Ga-Ge-Sn phase diagram: the experimental and calculated values agree fairly.

1. Introduction

In the present work it is shown that, with a limited number of experimental data (mixing enthalpies, activities ...) and a suitable interpolation relation, it is possible to obtain a complete and satisfactory thermodynamical description — excess functions and equilibrium phase diagram — of some simple eutectic ternary alloys; previous studies on the systems Ga-Sn-Zn [1], Ga-In-Sb [2], and Al-Ga-Ge [3] proved that such a description requires a good knowledge of the bordering binary phase diagrams and the excess functions of mixing.

As an example, we have chosen the gallium-germanium-tin system. After compiling and criticizing the published thermodynamic data of the three binary systems, we have obtained a consistent set of enthalpies, free energies, entropies of mixing and phase equilibrium temperatures. From these it is possible to determine all excess functions of mixing and the position of the liquidus surface of the ternary system. A comparison between calculated and measured integral molar enthalpies of formation of some Ga-Ge-Sn liquid alloys allowed us to check the validity of the used hypothesis.

2. Excess Functions of Mixing of Ga-Ge, Ga-Sn and Ge-Sn Liquid Systems

In this paragraph a critical review of the thermodynamic data of the Ga-Ge, Ga-Sn and Ge-Sn systems is presented; much attention has been paid to obtain a consistent set of data for each binary system.

Gallium-germanium System

Phase Diagram

Several authors [4–10] have given the liquidus curve (Figure 1). The eutectic point is very close

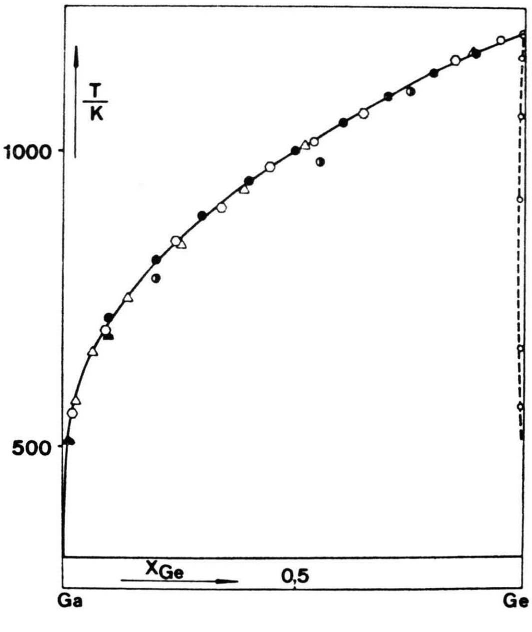

Fig. 1. Phase diagram of the Ga-Ge system:
△ Thurmond [5], ▲ Kech [8]
● Thurmond [6], ○ Greiner [9],
◑ Klemm [7], ⬡ de Roche [10].

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to pure gallium ($x_{\mathrm{Ge}}^{\mathrm{Eut}} = 5 \cdot 10^{-5}$ with a very small freezing depression $T_{\mathrm{Ga}}^{\mathrm{fus}} - T_{\mathrm{Eut}} = 0.007$ K). There seems to be no substantial range of gallium rich solid solutions. The maximum solubility of gallium in solid germanium, at 913 K, does not exceed 1.1 mole per cent.

Enthalpy of Mixing

By isothermal calorimetry, Predel and Stein [11], Bergman et al. [12] and Eslami et al. [3] have measured the integral enthalpy of formation of Ga-Ge alloys at 1273, 1270 and 1240 K, respectively.

From potentiometric measurements, Batalin et al. [13] have also obtained some values of the enthalpy of mixing. The two sets of data do not agree well (Figure 2). We have chosen Predel's and Eslami's results:

$$\Delta H_{\mathrm{Ga-Ge}} = x_{\mathrm{Ge}}(1 - x_{\mathrm{Ge}})(-612.24)\ \mathrm{cal\ mol^{-1}}.$$

Excess Entropy and free Energy of Mixing

A consistent set of experimental enthalpies of mixing, activities and equilibrium temperatures was not at our disposition, but using the equilibrium phase diagram and the preceding equation, we evaluated the excess entropy of mixing:

$$S_{\mathrm{Ga\text{-}Ge}}^{\mathrm{E}} = x_{\mathrm{Ge}}(1 - x_{\mathrm{Ge}})(-0.8636\, x_{\mathrm{Ge}}^2 + 1.4617\, x_{\mathrm{Ge}} - 0.0996)\ \mathrm{cal\ mol^{-1}\ K^{-1}}$$

and the excess molar free energy of formation, at 1240 K:

$$\Delta G_{\mathrm{Ga\text{-}Ge}}^{\mathrm{E}} = x_{\mathrm{Ge}}(1 - x_{\mathrm{Ge}})(+1070.9\, x_{\mathrm{Ge}}^2 - 1812.5\, x_{\mathrm{Ge}} - 488.8)\ \mathrm{cal\ mol^{-1}}.$$

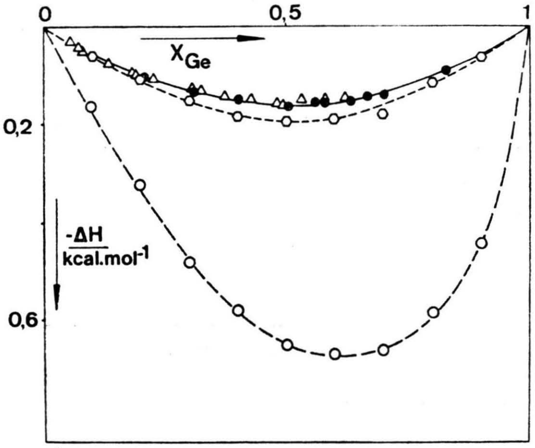

Fig. 2. Enthalpy of mixing of Ga-Ge liquid alloys:
△ Eslami [3], ⬡ Bergman [12],
● Predel [11], ○ Batalin [13].

Gallium-tin System

Phase Diagram

We selected the phase diagram published by Predel et al. [14, 15] and presented in Figure 3.

Enthalpy of Mixing

Between 400 K and 750 K, the enthalpy of formation of the liquid alloys has been determined in the whole concentration range by microcalorimetry [16]. The results, given by the relationship

$$\Delta H_{\mathrm{Ga-Sn}} = x_{\mathrm{Sn}}(1 - x_{\mathrm{Sn}})(893 - 124\, x_{\mathrm{Sn}}) \cdot \mathrm{cal\ mol^{-1}},$$

do not show any temperature dependence.

Excess Entropy of Mixing

The results obtained by Danilin et al. [17, 18] from e.m.f. measurements, on the one hand, and by Bergman [19] from vapor pressure measurements, on the other hand, do not agree well, though they both show a small deviation from Raoult's law at all compositions.

We have assumed the tin rich solid solution to be ideal and have obtained the excess entropy function from the preceding equation for $\Delta H_{\mathrm{Ga-Sn}}$ and the phase diagram:

$$S_{\mathrm{Ga\text{-}Sn}}^{\mathrm{E}} = x_{\mathrm{Sn}}(1 - x_{\mathrm{Sn}})\, 0.25\ \mathrm{cal\ mol^{-1}\ K^{-1}}.$$

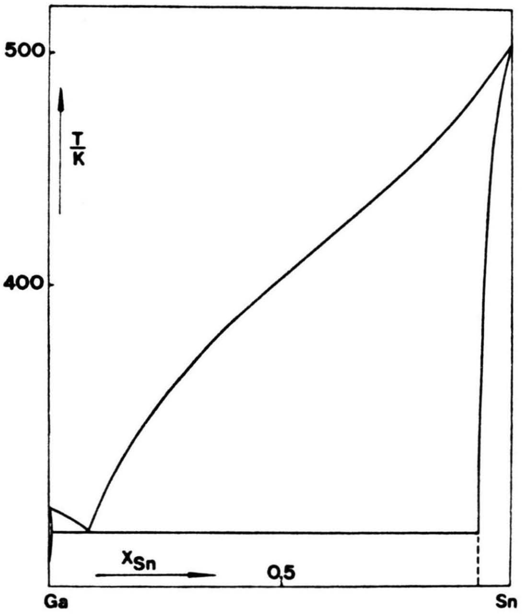

Fig. 3. Phase diagram of the Ga-Sn system.

Germanium-tin System

Phase Diagram

Several authors [7, 20–23] have determined the liquidus line of the Ge-Sn system. The eutectic point is very close to the melting point of pure

$$\mathrm{Sn}\,(T_{\mathrm{fus}}^{\mathrm{Eut}} = 505\ \mathrm{K} \quad \text{at} \quad x_{\mathrm{Ge}}^{\mathrm{Eut}} = 3 \cdot 10^{-3})$$

the solid solution range being very small (maximum solubility of Sn in solid Ge: $x_{\mathrm{Sn}} = 1.14 \cdot 10^{-2}$ at 673 K) (Figure 4).

Enthalpy of Mixing

At first, Predel and Stein [24] have given some values of the enthalpy of mixing. Then Mathieu [25] has determined the limiting partial enthalpy of solution of germanium in tin; these results confirm Predel's results. In 1978, Eslami [23] measured the enthalpy of mixing using a high temperature microcalorimeter. During our experimental work, we have also determined some values of this function. All these enthalpy data agree fairly and are expressed by

$$\Delta H_{\mathrm{Ge-Sn}} = x_{\mathrm{Ge}}(1 - x_{\mathrm{Ge}})\,(950.0 - 1793.8\,x_{\mathrm{Ge}} + 3291.7\,x_{\mathrm{Ge}}^2 - 2083.0\,x_{\mathrm{Ge}}^3) \cdot \mathrm{cal\ mol^{-1}}\,.$$

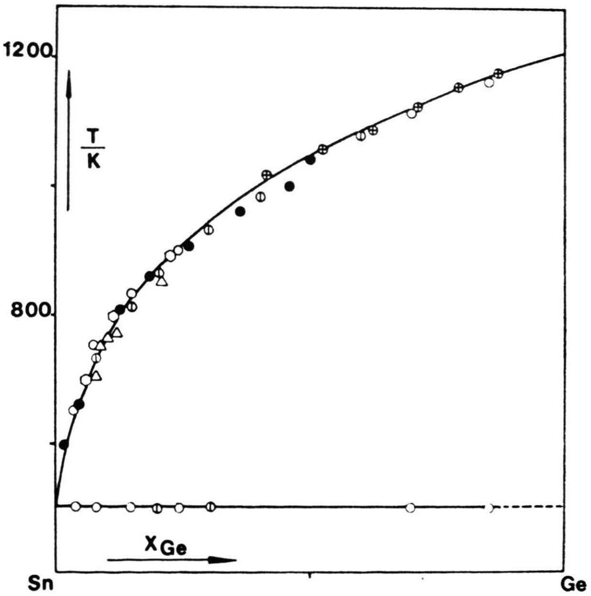

Fig. 4. Phase diagram of the Ge-Sn system:
● Thurmond [7], ⊕ Batalin [22],
○ Stohr [20], ⦶ Eslami [23].
△ Guertler [21],

Excess Entropy of Mixing

Both Howard and Hager [26] (by mass spectrometry) and Batalin et al. [27] (by potentiometry) obtained activities of Ge and Sn in their liquid alloys, but their results are quite different. So we preferred to calculate the S^{E} function from the phase diagram and the above equation for $\Delta H_{\mathrm{Ge-Sn}}$, to give

$$S_{\mathrm{Ge\text{-}Sn}}^{\mathrm{E}} = x_{\mathrm{Ge}}(1 - x_{\mathrm{Ge}})\,(-0.3461 + 1.3742\,x_{\mathrm{Ge}} - 2.7511\,x_{\mathrm{Ge}}^2 + 1.9274\,x_{\mathrm{Ge}}^3) \cdot \mathrm{cal\ mol^{-1}\ K^{-1}}\,.$$

3. Experimental Results

Using a differential high temperature Calvet calorimeter, we have measured the heat of formation of liquid alloys at constant pressure.

A detailed description of the apparatus and a critical study of the different devices used to prepare the liquid alloys in the calorimeter have already been published [3]. The main features are as follows.

Between 700 and 1200 K, most experiments have been performed with the "indirect drop method", which allows for the mixing of the liquid metals or alloys in the calorimeter cell at the experimental temperature. For the advantage of this method cf. [28]. All experiments are carried out under purified argon. A stirring device is used to mix the alloys thoroughly.

Calibration is performed by making use of the Joule effect or by dropping pieces of well known heat capacity (alumina*, gold, platinum ...).

The mixing enthalpies obtained have an accuracy better than 6%, the temperatures an error less than ±1.5 K.

The purity of the metals and their vapor pressure at different temperatures are listed in Table 1. The vapor pressures are not high enough to disturb the measurements.

The purpose of our calorimetric experiments was (i) to determine the function $\Delta H_{\mathrm{M}} = f(x_{\mathrm{Ga}}, x_{\mathrm{Ge}})$,

Table 1.

	Purity (moles per cent)	Pressure (atm) 1000 K	1200 K
Ga	99.9999	$6.22 \cdot 10^{-9}$	$1.77 \cdot 10^{-6}$
Ge	99.9998	$5.3 \cdot 10^{-13}$	$1.01 \cdot 10^{-9}$
Sn	99.9999	$8.5 \cdot 10^{-11}$	$3.09 \cdot 10^{-8}$

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* From Natural Bureau of Standard.

(ii) to beam about the influence of the temperature on the enthalpy of formation of the alloys and (iii) to obtain some points of the liquidus surface of the phase diagram.

Ge-Sn System

Our experimental values of the enthalpy of mixing at 703, 798 and 895 K are listed in Table 2. They are in fair agreement with those of Predel and Stein [24].

In a plot of the enthalpy of mixing at 798 K against the mole fraction of germanium (Fig. 5), the following two parts are showing up:

- for $0 < x_{\mathrm{Ge}} < 0.11$, the curved line corresponds to the formation of a single liquid phase;
- for $x_{\mathrm{Ge}} > 0.11$, a straight line is obtained: the resulting mixture is composed of a solid phase in equilibrium with a Ge-Sn liquid solution.

So the point (A) belongs to the liquidus line of the Ge-Sn phase diagram. The ordinate value of the intersection of the linear part of $\Delta H = f(x_{\mathrm{Ge}})$ with the $x_{\mathrm{Ge}} = 1$ axis corresponds to the enthalpy of solidification of germanium. Therefore the hypothesis is corroborated that the precipitation of almost pure germanium takes place [6].

From these calorimetric data, we deduced the following liquidus points:

$$T = 703\ \mathrm{K}, \quad x_{\mathrm{Ge}} = 0.06,$$
$$T = 798\ \mathrm{K}, \quad x_{\mathrm{Ge}} = 0.11,$$
$$T = 895\ \mathrm{K}, \quad x_{\mathrm{Ge}} = 0.22.$$

Table 2. Enthalpies of formation of germanium-tin alloys (experimental values expressed in calories per mole).

703 K		798 K		895 K	
x_{Ge}	ΔH	x_{Ge}	ΔH	x_{Ge}	ΔH
0.006	8	0.008	8	0.007	6
0.010	12	0.022	20	0.025	26
0.017	19	0.030	30	0.032	34
0.023	21	0.039	40	0.048	34
0.025	19	0.054	38	0.067	42
0.028	23	0.057	50	0.070	68
0.034	24	0.066	55	0.098	84
0.038	31	0.077	61	0.103	78
0.046	32	0.095	63	0.161	104
0.052	41	0.107	65	0.184	118
0.057	37	0.109	71	0.204	110
0.059	43	0.111	− 58	0.216	110
0.062	− 97	0.118	−180	0.220	0
0.063	−137	0.128	−340	0.234	−170
0.073	−180	0.138	−640	0.244	−150
0.077	−338				
0.092	−570				
0.102	−810				

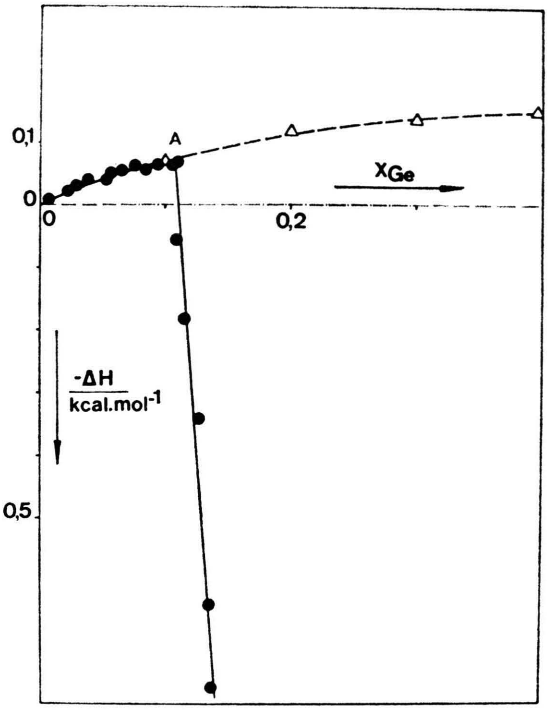

Fig. 5. Enthalpy of formation of the Ge-Sn system at 798 K:
△ Predel [24],
● our experimental results.

Ga-Ge-Sn System

The enthalpies of formation of ternary liquid mixtures have been determined at 703, 798, 895, 1000 and 1230 K by using the indirect drop method: solid germanium samples have been added to Ga-Sn liquid alloys.

The experimental conditions covered by Tables 3 to 7 are as follows:

Table No.	$\frac{T}{\mathrm{K}}$	$x_{\mathrm{Ga}}/x_{\mathrm{Sn}}$	x_{Ge}
3	703	1/1	0.004–0.099
3	703	3/1	0.003–0.098
4	798	1/3	0.012–0.197
4	798	1/1	0.012–0.176
4	798	3/1	0.032–0.211
5	895	1/1	0.045–0.366
5	895	3/1	0.018–0.330
6	1000	1/3	0.040–0.507
6	1000	1/1	0.061–0.622
6	1000	3/1	0.065–0.620
7	1230	1/3	0.035–0.721
7	1230	1/1	0.031–0.397
7	1230	3/1	0.050–0.491

Table 3. Enthalpies of formation of gallium-germanium-tin alloys at 703 K. (experimental values expressed in calories per mole).

$x_{Ga}/x_{Sn} = 1/1$		$x_{Ga}/x_{Sn} = 3/1$	
x_{Ge}	ΔH	x_{Ge}	ΔH
0	207	0	161
0.004	188	0.003	165
0.008	188	0.009	162
0.011	185	0.016	160
0.016	183	0.026	155
0.020	172	0.037	152
0.028	172	0.045	148
0.033	170	0.052	137
0.036	172	0.056	140
0.037	162	0.062	131
0.040	164	0.067	134
0.046	164	0.076	85
0.051	164	0.090	− 2
0.054	174	0.098	−44
0.058	164		
0.061	157		
0.067	35		
0.072	− 11		
0.078	−122		
0.091	−298		
0.099	−330		

Table 4. Enthalpies of formation of gallium-germanium-tin alloys at 798 K (experimental values expressed in calories per mole).

$x_{Ga}/x_{Sn} = 1/3$		$x_{Ga}/x_{Sn} = 1/1$		$x_{Ga}/x_{Sn} = 3/1$	
x_{Ge}	ΔH	x_{Ge}	ΔH	x_{Ge}	ΔH
0	150	0	207	0	161
0.012	170	0.012	207	0.022	155
0.022	165	0.023	206	0.035	145
0.029	175	0.031	205	0.052	143
0.036	176	0.038	202	0.068	135
0.050	165	0.046	199	0.077	121
0.059	176	0.054	199	0.087	128
0.070	175	0.066	194	0.095	120
0.079	173	0.075	192	0.104	108
0.086	180	0.083	180	0.114	105
0.088	165	0.092	184	0.120	91
0.096	168	0.101	180	0.132	85
0.102	164	0.107	168	0.146	80
0.113	170	0.115	165	0.156	77
0.123	75	0.122	165	0.162	75
0.162	−325	0.127	160	0.167	65
0.197	−550	0.135	150	0.177	61
		0.142	40	0.183	− 20
		0.148	− 35	0.189	− 95
		0.158	−135	0.198	−221
		0.167	−280	0.211	−280
		0.176	−330		

Table 5. Enthalpies of formation of gallium-germanium-tin alloys at 895 K (experimental values expressed in calories per mole).

$x_{Ga}/x_{Sn} = 1/1$		$x_{Ga}/x_{Sn} = 3/1$	
x_{Ge}	ΔH	x_{Ge}	ΔH
0	207	0	161
0.045	194	0.018	166
0.066	184	0.036	152
0.090	152	0.062	144
0.130	134	0.077	124
0.143	120	0.110	104
0.171	112	0.115	118
0.184	124	0.143	84
0.213	110	0.165	82
0.231	102	0.194	80
0.243	90	0.215	52
0.270	92	0.225	70
0.296	58	0.246	52
0.328	−300	0.260	36
0.341	−508	0.282	− 4
0.366	−542	0.283	− 70
		0.307	−250
		0.330	−440

Table 6. Enthalpies of formation of gallium-germanium-tin alloys at 1000 K (experimental values expressed in calories per mole).

$x_{Ga}/x_{Sn} = 1/3$		$x_{Ga}/x_{Sn} = 1/1$		$x_{Ga}/x_{Sn} = 3/1$	
x_{Ge}	ΔH	x_{Ge}	ΔH	x_{Ge}	ΔH
0	150	0	207	0	161
0.040	160	0.061	193	0.065	125
0.068	154	0.084	172	0.131	90
0.112	163	0.138	153	0.160	60
0.138	155	0.183	144	0.224	44
0.186	158	0.224	129	0.271	24
0.202	154	0.274	101	0.337	14
0.266	154	0.312	108	0.392	− 5
0.324	138	0.355	92	0.435	− 15
0.371	136	0.371	71	0.460	− 20
0.428	123	0.408	75	0.485	− 84
0.441	−178	0.436	75	0.514	−405
0.467	−289	0.450	66	0.532	−902
0.478	−725	0.471	−166	0.620	-2500
0.502	−820	0.498	−498		
0.507	−996	0.502	−662		
		0.622	-2505		

ΔH for the section $x_{Ga}/x_{Sn} = 1/1$ is shown in the Figs. 6 and 7. By the analysis of these results we obtained ternary liquidus points, the coordinates of which are given in Table 8.

Enthalpy of Mixing

The heats of formation of the liquid phase are calculated from an equation [29] already used for several ternary systems [30] (see Appendix 1).

For comparison, calculated and experimental enthalpies of mixing are given in Table 9 and, for the

Table 7. Enthalpies of mixing of gallium-germanium-tin alloys at 1230 K (experimental values expressed in calories per mole).

$x_{Ga}/x_{Sn} = 1/3$		$x_{Ga}/x_{Sn} = 1/1$		$x_{Ga}/x_{Sn} = 3/1$	
x_{Ge}	ΔH	x_{Ge}	ΔH	x_{Ge}	ΔH
0	150	0	207	0	161
0.035	153	0.031	188	0.050	133
0.067	154	0.046	180	0.071	108
0.069	158	0.049	182	0.073	121
0.120	156	0.060	173	0.102	109
0.143	160	0.084	178	0.165	88
0.155	160	0.094	171	0.169	63
0.173	156	0.110	159	0.172	69
0.175	160	0.130	150	0.219	53
0.195	159	0.139	156	0.260	28
0.220	157	0.163	146	0.276	15
0.228	154	0.202	122	0.279	27
0.234	154	0.204	132	0.328	12
0.275	153	0.207	102	0.328	2
0.280	153	0.275	106	0.340	− 9
0.305	150	0.333	85	0.385	− 9
0.355	142	0.336	93	0.386	−12
0.389	132	0.396	68	0.415	−26
0.403	140	0.397	76	0.430	−22
0.450	129			0.490	−36
0.460	121			0.491	−34
0.475	104				
0.530	109				
0.540	98				
0.558	90				
0.604	84				
0.664	71				
0.721	60				

Table 8.

$\frac{T}{K}$	$x_{Ga}/x_{Sn} = 1/3$	$x_{Ga}/x_{Sn} = 1/1$	$x_{Ga}/x_{Sn} = 3/1$
	x_{Ge}	x_{Ge}	x_{Ge}
703	/	0.06	0.07
798	0.09	0.14	0.18
895	/	0.28	0.30
1000	0.43	0.46	0.48

Table 9. Enthalpies of mixing of gallium-germanium-tin alloys at 1230 K. Comparison between calculated (a) and experimental (b) values expressed in calories per mole.

x_{Ge}	ΔH					
	$x_{Ga}/x_{Sn} = 1/3$		$x_{Ga}/x_{Sn} = 1/1$		$x_{Ga}/x_{Sn} = 3/1$	
	a	*b*	*a*	*b*	*a*	*b*
0	150	150	207	207	161	161
0.1	148	155	161	164	101	101
0.2	145	157	130	130	63	56
0.3	135	148	98	98	12	14
0.4	124	130	71	71	−20	−18
0.5	109	110	47	/	−42	−38
0.6	90	89	26	/	−52	/
0.7	70	68	9	/	−55	/
0.8	50	/	−2	/	−53	/
0.9	24	/	−9	/	−32	/
1	0	/	0	/	0	/

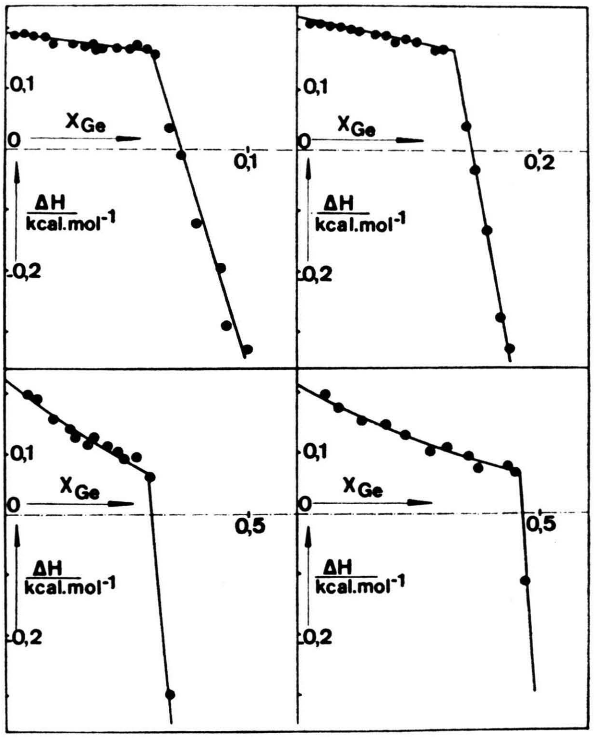

Fig. 6. Enthalpy of formation of the Ga-Ge-Sn system, $x_{Ga}/x_{Sn} = 1/1$: our experimental results

a	b
c	d

a) $T =$ 703 K,
b) $T =$ 798 K,
c) $T =$ 895 K,
d) $T =$ 1000 K.

section $x_{Ga}/x_{Sn} = 1/1$, are plotted against x_{Ge} in Figure 7. The two sets of data are in excellent agreement.

Our results allowed us to propose the mixing enthalpy surface of Ga-Ge-Sn liquid alloys (Figure 8).

Excess Entropy of Mixing

From the precedent results it is possible to conclude that no specific ternary interaction is occurring in the Ga-Ge-Sn system. So we have estimated the excess molar entropy of mixing (S^E) for the entire range of concentrations from the entropies of the bordering binary systems by using the relationship given in Appendix 1.

Partial Excess Functions

By applying the formula given in Appendix 2, $\Delta\bar{H}_{Ge}$ and $\bar{S}_{Ge}$ values have been calculated for the whole concentration range. Some results obtained for $\Delta\bar{H}_{Ge}$ and $\bar{S}_{Ge}$ are listed in Table 10.

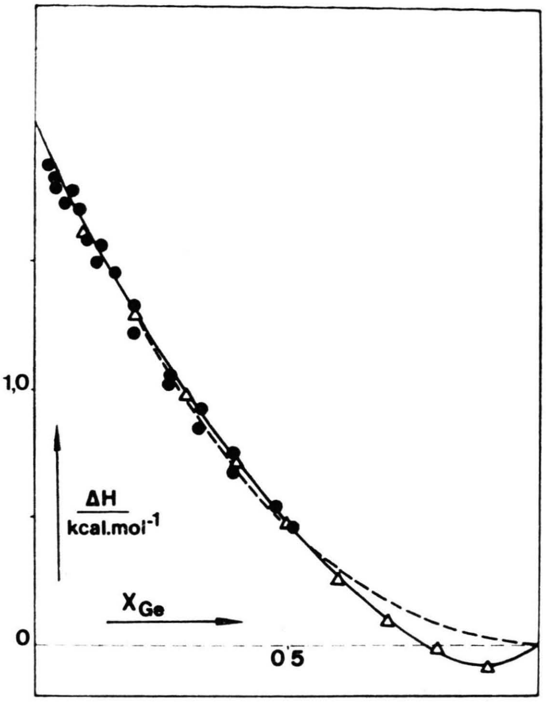

Fig. 7. Enthalpy of mixing of the Ga-Ge-Sn system at 1230 K, $x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 1/1$.
△ calculated values, ● experimental results.

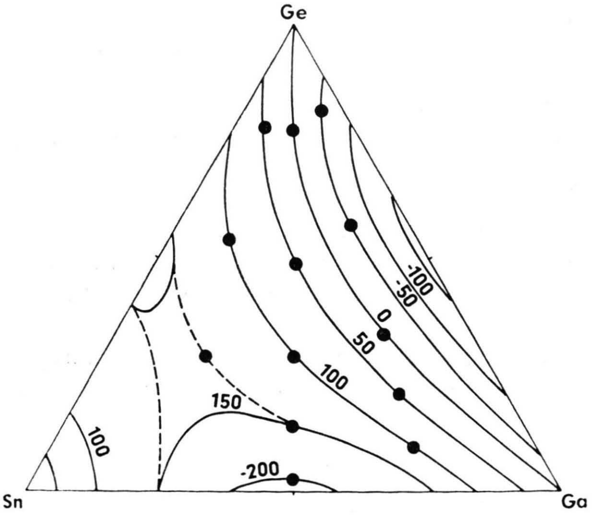

Fig. 8. Enthalpy of mixing of the Ga-Ge-Sn system (in calories per mole). Continuous line: calculated values; ● experimental points.

Table 10. Thermodynamic functions of some gallium-germanium-tin alloys along the sections $x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 1/1$, $3/1$. Calculated values expressed in calories per mole, and in calories per mole per Kelvin.

x_{Ge}	$x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 1/1$			$x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 3/1$	
	$\Delta\bar{H}_{\mathrm{Ge}}$	S^{E}	$\bar{S}_{\mathrm{Ge}}$	$\Delta\bar{H}_{\mathrm{Ge}}$	S^{E}
0.1	−178	0.0578	0.090	−357	0.0479
0.2	−144	0.0586	0.080	−305	0.0571
0.3	−109	0.0613	0.076	−235	0.0707
0.4	− 78	0.0634	0.072	−171	0.0834
0.5	− 59	0.0637	0.064	−125	0.0913
0.6	− 50	0.0614	0.040	− 82	0.0919
0.7	− 32	0.0558	0.030	− 46	0.0839
0.8	− 19	0.0425	0.010	− 24	0.0624
0.9	− 6	0.0278	0.005	− 10	0.0323

4. Calculation of the Liquidus Surface of the Equilibrium Phase Diagram

From the excess functions of mixing previously established, the calculation of the liquidus surface of the Ga-Ge-Sn phase diagram is possible; the following assumptions are needed:

- Trumbore et al. [4] and Thurmond [6], who have studied, respectively, the solubility of gallium and tin in solid germanium, proposed

  $$x_{\mathrm{Ga}} = 1.1 \cdot 10^{-2} \quad \text{at} \quad T = 923\ \mathrm{K}$$

  and

  $$x_{\mathrm{Sn}} = 1.14 \cdot 10^{-2} \quad \text{at} \quad 673\ \mathrm{K}\,.$$

  Therefore, during the freezing of Ga-Ge-Sn liquid alloys, it can be assumed that only pure germanium appears. So, at $T < T_{\mathrm{Ge}}^{\mathrm{fus}}$, the equilibrium

  $$\text{Ga-Ge-Sn}_{\text{liquid}} \rightleftharpoons \text{Ge}_{\text{solid}}$$

  is assumed.
- If the change of the heat capacities on melting is neglected, the temperature of the precedent equilibrium is given by the relation:

  $$T = \frac{\Delta\bar{H}_{\mathrm{Ge}} + \Delta H_{\mathrm{Ge}}^{\mathrm{fus}}}{\bar{S}_{\mathrm{Ge}} + S_{\mathrm{Ge}}^{\mathrm{fus}}}\,, \tag{1}$$

  where $\Delta H_{\mathrm{Ge}}^{\mathrm{fus}}$ and $S_{\mathrm{Ge}}^{\mathrm{fus}}$ are the enthalpy and entropy of fusion of the pure metal and $\Delta\bar{H}_{\mathrm{Ge}}$ and $\bar{S}_{\mathrm{Ge}}$ are the partial molar enthalpy and entropy of the solvent in the ternary solution. As an example, some calculated temperatures of this liquidus are listed in Table 11.

Table 11. Gallium-germanium-tin system. Equilibrium temperatures of the liquidus along the sections $x_{Ga}/x_{Sn} = 1/1$, 3/1 (calculated values).

x_{Ge}	$x_{Ga}/x_{Sn} = 1/1$ T (K)	$x_{Ga}/x_{Sn} = 3/1$ T (K)
0.1	724	/
0.2	822	812
0.4	953	950
0.6	1051	1052
0.8	1134	1138

Of course these assumptions introduce an uncertainty, all the more important since T is quite different from T^{fus}. But in the germanium rich region of this phase diagram, the uncertainty is probably of a minor order.

The projections of both the calculated and measured liquidus surface on the Gibbs triangle are given in Figure 10. Comparisons show quite small discrepancies between the experimental values and those obtained by using Eq. (1) on the one hand, and calculated by Ansara et al. [31] from the thermodynamic properties of the limiting binary systems, without ternary experimental data, on the other hand. These three sets of values are in good agreement except at low temperatures in the tin rich region. Indeed, in this region of the equilibrium phase diagram, the difference $T = T_{Ge}^{fus} - T_{eql}$ is too large, so that the previous assumptions are inadequate.

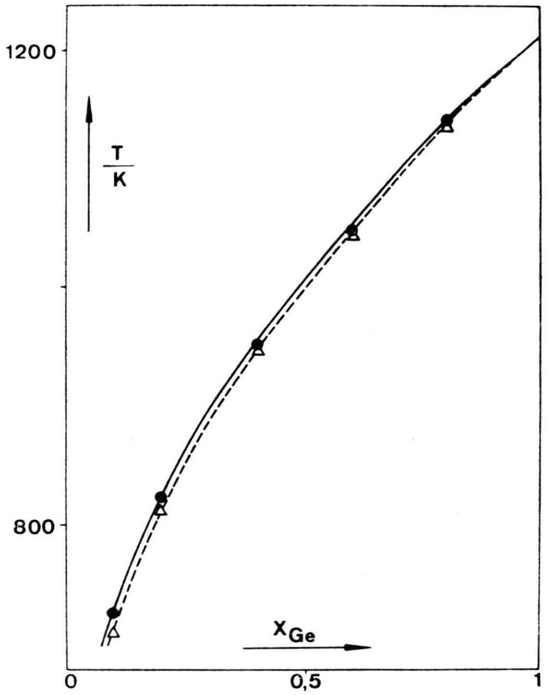

Fig. 9. Calculated curves of the liquidus along the sections:
● continuous line $x_{Ga}/x_{Sn} = 1/1$;
△ dotted line $x_{Ga}/x_{Sn} = 3/1$.

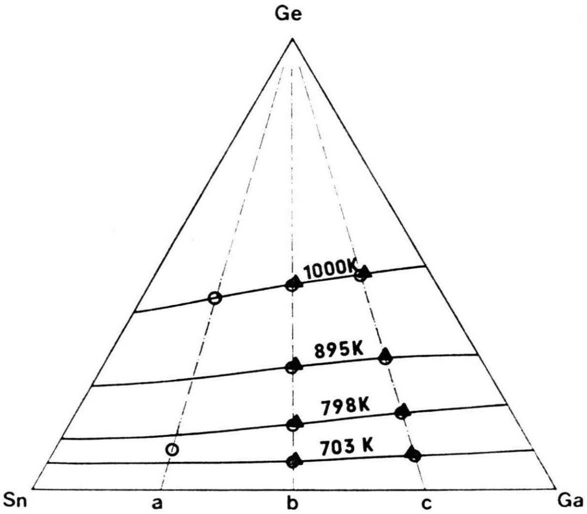

Fig. 10. Calculated liquidus surface of the Ga-Ge-Sn system:
▲ calculated points;
○ experimental points;
—— continuous line: Ref. [31].

5. Conclusion

From an empirical equation and some calorimetric values of the heat of formation of Ga-Ge-Sn liquid alloys we have calculated the enthalpy and entropy of mixing for the entire concentration triangle and the position of the liquidus surface of the phase diagram in good agreement with experimental data.

Moreover, the comparison between measured and calculated — from various empirical relations [29], [31] — enthalpies of mixing allows us to confirm the weakness of the ternary interactions between gallium, germanium and tin in the liquid state.

These results give further evidence of the feasibility of an empirical equation to calculate, from a set of consistent data of the bordering binary systems, excess thermodynamic properties of mixing and the liquidus of a simple ternary system like gallium-germanium-tin.

Appendix 1

In a A, B, C ternary system the molar excess function of mixing ΔF can be represented by

$$\begin{aligned}\Delta F_{(\mathrm{A-B-C})} = {} & \frac{X_\mathrm{A} X_\mathrm{B}}{(X_\mathrm{A} + \frac{1}{2} X_\mathrm{C})(X_\mathrm{B} + \frac{1}{2} X_\mathrm{C})} \cdot [\Delta F_{\mathrm{A-B}}]_{x_\mathrm{A} - x_\mathrm{C}} \\ & + \frac{X_\mathrm{B} X_\mathrm{C}}{(X_\mathrm{B} + \frac{1}{2} X_\mathrm{A})(X_\mathrm{C} + \frac{1}{2} X_\mathrm{A})} \cdot [\Delta F_{\mathrm{B-C}}]_{x_\mathrm{C} - x_\mathrm{B}} \\ & + \frac{X_\mathrm{C} X_\mathrm{A}}{(X_\mathrm{C} + \frac{1}{2} X_\mathrm{B})(X_\mathrm{A} + \frac{1}{2} X_\mathrm{B})} \cdot [\Delta F_{\mathrm{A-C}}]_{x_\mathrm{C} - x_\mathrm{A}}\end{aligned}$$

where $\Delta F_{\mathrm{A-B}}$ is the binary molar excess function of the A—B bordering system and x_A and X_A are the molar fractions of the A element in the binary and ternary alloy, respectively.

Appendix 2

The partial molar excess function of mixing of element A in the A, B, C ternary system is given by

$$\begin{aligned}\Delta \bar{F}_{\mathrm{A(ABC)}} = {} & \frac{4 X_\mathrm{B} X_\mathrm{C}}{(2 X_\mathrm{B} + X_\mathrm{A})(2 X_\mathrm{C} + X_\mathrm{A})} \cdot \left(\frac{X_\mathrm{B} - X_\mathrm{C}}{2 X_\mathrm{B} + X_\mathrm{A}} \Delta \bar{F}_{\mathrm{C(BC)}} - \frac{1}{2 X_\mathrm{C} + X_\mathrm{A}} \Delta F_{\mathrm{(BC)}} \right)_{x_\mathrm{C} = X_\mathrm{C} + \frac{X_\mathrm{A}}{2}} \\ & + \frac{4 X_\mathrm{C}}{(2 X_\mathrm{A} + X_\mathrm{B})(2 X_\mathrm{C} + X_\mathrm{B})} \cdot \left(\frac{X_\mathrm{B}}{2 X_\mathrm{A} + X_\mathrm{B}} \Delta F_{\mathrm{(AC)}} + X_\mathrm{A} \Delta \bar{F}_{\mathrm{A(AC)}} \right)_{x_\mathrm{A} = X_\mathrm{A} + \frac{X_\mathrm{B}}{2}} \\ & + \frac{4 X_\mathrm{B}}{(2 X_\mathrm{B} + X_\mathrm{C})(2 X_\mathrm{A} + X_\mathrm{C})} \cdot \left(\frac{X_\mathrm{C}}{2 X_\mathrm{A} + X_\mathrm{C}} \Delta F_{\mathrm{(AB)}} + X_\mathrm{A} \Delta \bar{F}_{\mathrm{A(AB)}} \right)_{x_\mathrm{A} = X_\mathrm{A} + \frac{X_\mathrm{C}}{2}} .\end{aligned}$$

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