Thermodynamic Study of Al-Ge-Sn Ternary Alloys by E.M.F. Measurements

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An electrode potential study of liquid Al-Ge-Sn alloys has been conducted with the cell

$$Al \mid Al^{3+} \text{ in } KCl + LiCl \mid Al \text{ in Al-Ge-Sn}$$

in the temperature range 683 K $\leqq T \leqq$ 1273 K.

Aluminium partial mixing functions were determined for alloys. These measurements allow us to give the surface corresponding to aluminium partial free energy at 1273 K and the liquidus surface of the Al-Ge-Sn phase diagram.

Introduction

Part of the experimental work in our laboratory is aimed at the determination of the thermodynamic properties of binary and ternary alloys. For this purpose several devices for measurements of the enthalpies and free energies of mixing in a large temperature range are available.

It is the purpose of this paper to give a short description of the potentiometric method and to present for the Al-Ge-Sn system the partial free energy of aluminium and the liquidus surface of the ternary phase diagram. The equilibrium phase diagrams of the limiting binary systems Al-Ge, Al-Sn and Ge-Sn, shown in Fig. 1, have eutectic points, the generally adopted coordinates of which being

for Al-Ge:

$$x_{Ge}^{Eut} = 0.303, \quad T^{Eut} = 697 \text{ K}, \qquad [1]$$

for Al-Sn:

$$x_{Sn}^{Eut} = 0.978, \quad T^{Eut} = 501.3 \text{ K}, \qquad [1]$$

for Ge-Sn:

$$x_{Sn}^{Eut} = 3.10^{-3}, \quad T^{Eut} = 505 \text{ K}. \qquad [1]$$

The eutectic compositions of Al-Sn and Ge-Sn are near Sn, the most fusible metal. The terminal solid solubilities are small and the liquidus curve of the Al-Sn system exhibits an inflexion point indicating a tendency for demixing in the liquid phase.

The form of the three limiting binary phase diagrams allows us to predict a very simple liquidus surface of the Al-Ge-Sn system with an eutectic valley going from $x_{Ge} = 0.303$, $T = 697$ K to pure tin.

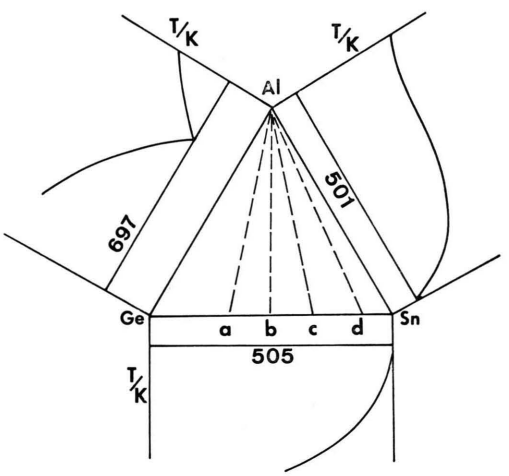

Fig. 1. Phase diagrams of the three limiting binary systems and studied ternary alloys compositions:

	a)	b)	c)	d)
x_{Ge}/x_{Sn}	2/1	1/1	1/2	1/7

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Experimental

Several techniques are available to determine the activity of a metal in a liquid alloy [2]; we have chosen the potentiometric method because the standard potentials of aluminium, germanium and tin are very different.

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At constant pressure ($P = 1$ Atm) and molar fraction (x_{Al}, x_{Ge}) the electromotive force (E) of the concentration cell

$$Al \,|\, Al^{3+} \text{ in } KCl + LiCl \,|\, Al \text{ in } Al\text{-}Ge\text{-}Sn$$

at several temperatures allows us to calculate the partial molar thermodynamic functions of formation of the ternary alloys Al-Ge-Sn by using the following relations:

$$\Delta\bar{G}_{Al} = -ZFE = RT \ln a_{Al},$$
$$\bar{S}_{Al} = ZF(\partial E/\partial T),$$
$$\Delta\bar{H}_{Al} = -ZF[E - T(\partial E/\partial T)],$$

where F is Faraday's constant, a_{Al} the activity of aluminium and $Z = 3$ the valency of aluminium.

Electric conduction is assured by Al^{3+} because this element is more electropositive than germanium and tin; the standard electrode potentials (ε°) of Al and Sn were measured by Laitinen [3] in a lithium chloride-potassium chloride melt at the eutectic composition, at 723 K. They have found $\overset{\circ}{\varepsilon}_{Al^{3+}/Al^\circ} = -1.79$ V, $\overset{\circ}{\varepsilon}_{Sn^{2+}/Sn^\circ} = -1.08$ V. ε° of Ge has not been determined, but from the values of the free energy of formation of aluminium, tin and germanium chlorides — see Table 1 — we can deduce that germanium is the least electropositive of these three elements.

The standard free energies of formation of the cholrides gathered in Table 1 are large enough to avoid exchange reactions in the experimental temperature range.

Apparatus

We have used an apparatus, formerly described by Massart [4], Gaune [5], Girard [6], Wilder [7], Hayer [8].

A schematic design of the cell is shown in ref. [12]. Briefly, the apparatus consists of

— a large external crucible ($\Phi = 55$ mm).

— a second crucible ($\Phi = 46$ mm) containing the molten electrolyte and ten electrode crucibles ($\Phi = 7$ mm) in which pure metal and the alloys are placed.

— ten electrode wires and a thermocouple (Pt/Pt-Rh 10%).

Table 1. Free energy of formation of chlorides.

Reaction	ΔG^f/kcal mol^{-1}	
	500 K	1000 K
$K + 1/2\ Cl_2 \rightarrow KCl$	− 93	− 81
$Li + 1/2\ Cl_2 \rightarrow LiCl$	− 88	− 79
$1/3\ Al + 1/2\ Cl_2 \rightarrow 1/3\ AlCl_3$	− 45	− 41
$1/2\ Sn + 1/2\ Cl_2 \rightarrow 1/2\ SnCl_2$	− 33	− 26
$1/4\ Ge + 1/2\ Cl_2 \rightarrow 1/4\ GeCl_2$	− 13	− 11

Covers, gas tubes for inert gas and a refractory steel cylinder complete this apparatus.

The galvanic cell is maintained at constant temperature ($632\ K < T < 1200\ K$) by means of a cylindrical vertical furnace and an electronic regulator device.

The output of the electrodes of the different crucibles is fed directly into a digital millivoltmeter with a large input impedance ($10^{12}\ \Omega$).

Samples and Materials

Aluminium, germanium and tin of 99.999 mole per cent purity were used without further purification.

Lithium, potassium and aluminium chlorides were analytical grade salts (MERCK) and kept under an inert atmosphere.

During the experiments the galvanic cell was supplied with purified argon (Air Liquid C°); at the top of the apparatus a suitable pipe allows to maintain an argon flow.

Crucibles, covers, wire sheaths and thermocouple sheath are pure alumina (Al 23 DEGUSSA).

Tantalum and tungsten wires were employed with identical experimental results. This finding is in good agreement with those [9] and [10].

Cell Preparation

The eutectic mixture of lithium and potassium chlorides (55.8 weight per cent of LiCl, $T_{fus} = 623$ K) was dried at 523 K for 24 hours under dynamic vacuum and molten under a flow of purified argon. After addition of aluminium chloride (5 weight per cent), kept under vacuum at 383 K, the decanted mixture was transferred into the experimental cell in which the alloys have previously been placed in little crucibles.

Accuracy

During the experiments we took the following precautions:

— Two crucibles at least contain pure metal (Al): the difference between these two reference electrodes must be lower than 0.0002 V at

Table 2. Al-Ge system: potentiometric results.

x_{Al}	Ref.	$E/mV = f(T/K)$	1273 K				
			a_{Al}	γ_{Al}	$-\Delta\bar{G}_{Al}$	$\Delta\bar{H}_{Al}$	$\bar{S}_{Al}$
					cal mol^{-1}	cal mol^{-1}	cal mol^{-1}
0.2	$Al_{(l)}$	$0.04927\,T + 37.4568$	0.065	0.323	6931	− 2592	3.409
0.3		$0.04000\,T + 25.8565$	0.122	0.408	5312	− 1789	2.767
0.4		$0.02777\,T + 21.4975$	0.211	0.528	3933	− 1487	1.922
0.5		$0.02484\,T + 10.6947$	0.314	0.629	2928	− 740	1.719
0.6		$0.01512\,T + 8.5965$	0.467	0.778	1926	− 595	1.047
0.7		$0.01166\,T + 3.7713$	0.601	0.859	1288	− 261	0.807
0.8		$0.01041\,T + 1.5363$	0.726	0.907	810	106	0.720

moderate temperatures and 0.0003 V at the highest temperature.

- After each change in temperature, the equilibrium is verified by observing the variation of the e.m.f. The equilibrium temperature is generally reached after one or two hours.
- All e.m.f. measurements are repeated many times, on heating and cooling , to check the reproducibility. For each concentration three e.m.f. determinations were carried out.
- At the temperature of fusion of aluminium (reference metal) the change in the slope of the $E = f(T)$ diagram must be proportional to the enthalpy of fusion of the metal:

$$\Delta H = ZFT_{fus}\left[\left(\frac{\partial E}{\partial T}\right)_s - \left(\frac{\partial E}{\partial T}\right)_l\right].$$

The heat of fusion of aluminium generally accepted is (2580 ± 30) cal mol^{-1} [11].

Experimental Results

Our activity measurements of aluminium in Al-Ge-Sn liquid alloys are a continuation of former records on Al-Ga-Ge mixtures [12]; for each study, the activities of aluminium in Al-Ge liquid alloys have been carried out to check the method.

Al-Ge System

In Table 2 are gathered experimental results. They are in good agreement with those of Wilder ($932\ K < T < 1258\ K$) [10] and of Batalin and Beloborodova ($1070 < T < 1300$ K) [13].

These experimental values and the enthalpies of formation previously published [14] form a self consistent set of data: the liquidus temperatures derived from the combination of these data are in good agreement with the equilibrium phase diagram [1].

Al-Sn System

From the critical study by Slough [15] we have selected the values determined by Batalin [16] et al. and confirmed by Massart [4] (see Table 3).

Al-Ge-Sn System

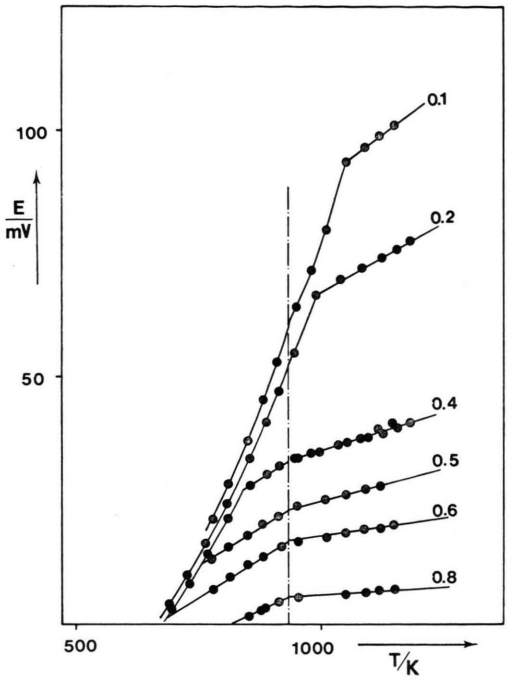
E.m.f. measurements have been performed for 24 ternary alloys lieing on four lines $x_{Ge}/x_{Sn} = $ Constant on the Gibbs triangle. The composition investigated are:

x_{Ge}/x_{Sn}	x_{Al}					
2/1	0.1	0.2	0.4	0.5	0.6	0.8
1/1	0.1	0.2	0.4	0.5	0.6	0.8
1/2	0.1	0.2	0.4	0.5	0.6	0.8
1/7	0.1	0.2	0.4	0.5	0.6	0.8

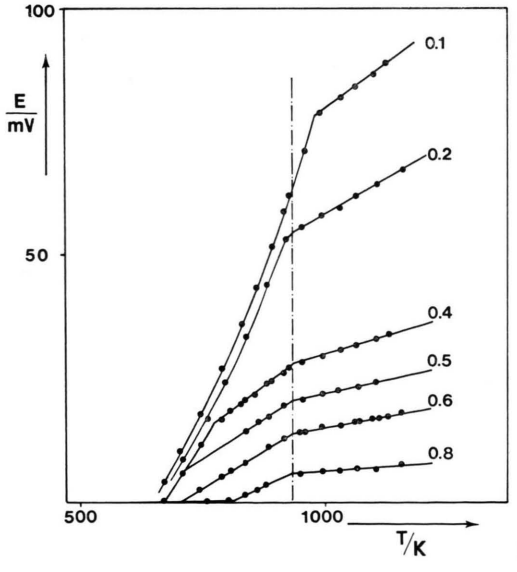
The experimental results are listed in Table 4. Figure 2 shows $E = f(T)$ curves. For all alloys, $E(T)$ is linear at the upper temperatures and shows a break at the temperature of fusion of aluminium

Table 3. Al-Sn system: potentiometric results (Ref. [4]).

x_{Al}	Ref.	$E/mV = f(T/K)$
0.05	$Al_{(l)}$	$0.1023\,T - 45.38$
0.10		$0.0840\,T - 45.20$
0.20		$0.0591\,T - 36.35$
0.30		$0.0464\,T - 31.66$
0.40		$0.0403\,T - 29.88$
0.50		$0.0278\,T - 20.29$
0.60		$0.0215\,T - 15.36$
0.75		$0.0112\,T - 7.35$
0.90		$0.0046\,T - 2.59$



(a)



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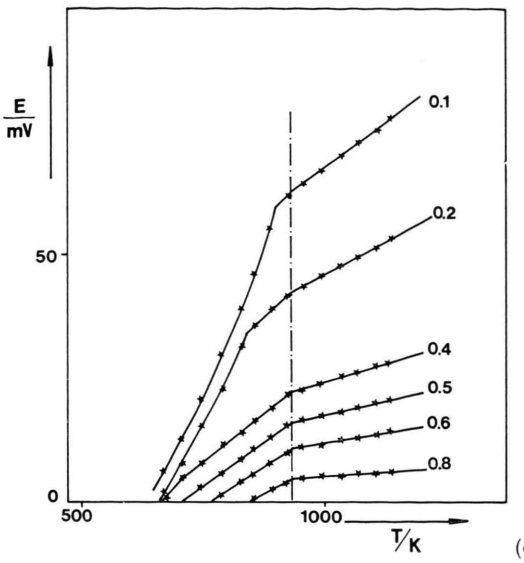

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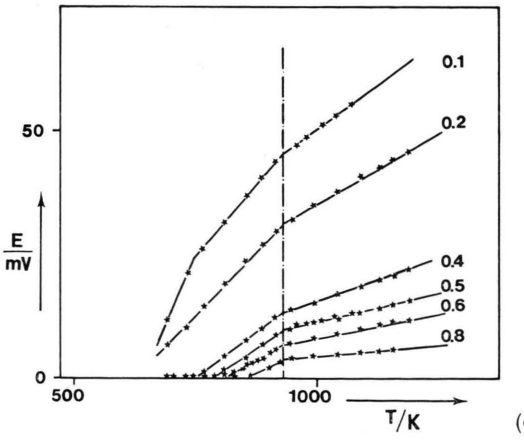

(d)

Fig. 2. Experimental values of the e.m.f. (in mV) versus temperature (in Kelvin)

a) $x_{Ge}/x_{Sn} = 2/1$ and $x_{Al} = 0.1, 0.2, 0.4, 0.5, 0.6, 0.8$;
b) $x_{Ge}/x_{Sn} = 1/1$ $x_{Al} = 0.1, 0.2, 0.4, 0.5, 0.6, 0.8$;
c) $x_{Ge}/x_{Sn} = 1/2$ $x_{Al} = 0.1, 0.2, 0.4, 0.5, 0.6, 0.8$;
d) $x_{Ge}/x_{Sn} = 1/7$ $x_{Al} = 0.1, 0.2, 0.4, 0.5, 0.6, 0.8$.

(933.25 K [11]). A second discontinuity appears on the (E vs. T) plots when the liquid solid equilibrium is reach; so, some liquidus temperatures have been obtained (Table 5 and Figure 3).

From the experimental results we have calculated the activity, the activity coefficient and the partial free energy of aluminium at 1273 K (see Table 4). Fig. 4 gives the general shape of the $\Delta\bar{G}_{Al}$ vs. x_{Al} curves.

Using the liquidus temperatures listed above, the position of the eutectic valley has been determined by extrapolation (Figure 3).

Table 4. Al-Ge-Sn system: potentiometric results.

x_{Ge}/x_{Sn}	x_{Al}	Ref.	$E/mV = f(T/K)$	1273 K a_{Al}	γ_{Al}	$-\Delta\overline{G}_{Al}$ cal mol^{-1}	$\Delta\overline{H}_{Al}$ cal mol^{-1}	$\overline{S}_{Al}$ cal mol^{-1}
2/1	0.1	$Al_{(l)}$	$0.075585\,T + 14.18590$	0.049	0.488	7638	− 982	5.230
	0.2		$0.055148\,T + 12.30958$	0.105	0.523	5708	− 852	3.816
	0.4		$0.031198\,T + 4.07337$	0.302	0.755	3029	− 282	2.159
	0.5		$0.026605\,T - 1.53490$	0.413	0.826	2237	− 106	1.841
	0.6		$0.016834\,T + 1.17723$	0.539	0.898	1564	− 81	1.165
	0.8		$0.007811\,T - 1.78263$	0.800	1.000	565	123	0.541
	0.4	$Al_{(s)}$	$0.068012\,T - 30.10778$	0.213	0.534	3907	2083	4.706
	0.5		$0.068827\,T - 40.48878$	0.276	0.551	3260	2802	4.763
	0.6		$0.064077\,T - 42.61378$	0.345	0.574	2695	2949	4.434
	0.8		$0.063094\,T - 43.54907$	0.518	0.648	1663	3013	3.674
1/1	0.1	$Al_{(l)}$	$0.073054\,T + 6.45773$	0.066	0.659	6881	− 447	5.055
	0.2		$0.056717\,T + 1.60730$	0.133	0.664	5106	− 111	3.925
	0.4		$0.032098\,T - 2.25345$	0.348	0.870	2671	156	2.221
	0.5		$0.022177\,T - 0.08443$	0.463	0.926	1947	6	1.535
	0.6		$0.185031\,T - 3.30179$	0.575	0.958	1401	228	1.280
	0.8		$0.008014\,T - 1.69461$	0.792	0.990	589	117	1.554
	0.4	$Al_{(s)}$	$0.071867\,T - 39.40307$	0.241	0.602	3603	2727	4.973
	0.5		$0.065247\,T - 39.81669$	0.306	0.613	2991	2755	4.515
	0.6		$0.061789\,T - 43.40918$	0.381	0.636	2439	3004	4.276
	0.8		$0.052488\,T - 42.58681$	0.515	0.644	1676	2947	3.632
1/2	0.1	$Al_{(l)}$	$0.074015\,T - 6.09628$	0.106	1.058	5681	422	5.122
	0.2		$0.054706\,T - 8.65738$	0.189	0.943	4219	599	3.785
	0.4		$0.032563\,T - 8.44755$	0.405	1.014	3384	585	2.253
	0.5		$0.025509\,T - 7.99580$	0.512	1.024	1694	553	1.764
	0.6		$0.018184\,T - 6.39790$	0.632	1.054	1159	443	1.258
	0.8		$0.007962\,T - 2.80702$	0.818	1.023	507	194	0.551
	0.2	$Al_{(s)}$	$0.099002\,T - 49.71445$	0.124	0.620	5280	3440	6.851
	0.4		$0.074756\,T - 47.77388$	0.274	0.684	3279	3306	5.173
	0.5		$0.067758\,T - 47.50104$	0.374	0.693	2681	3287	4.689
	0.6		$0.061874\,T - 47.41179$	0.424	0.707	2169	3281	4.281
	0.8		$0.050413\,T - 42.56619$	0.554	0.692	1495	2945	3.488
1/7	0.1	$Al_{(l)}$	$0.079077\,T - 28.71370$	0.140	1.397	4978	1987	5.472
	0.2		$0.057935\,T - 22.48860$	0.246	1.230	3546	1556	4.009
	0.4		$0.034951\,T - 19.39457$	0.503	1.258	1736	1342	2.418
	0.5		$0.022631\,T - 11.04749$	0.615	1.230	1229	764	1.566
	0.6		$0.019195\,T - 10.91521$	0.691	1.151	935	755	1.328
	0.8		$0.007322\,T - 2.66320$	0.834	1.042	461	184	0.507
	0.1	$Al_{(s)}$	$0.119680\,T - 65.30283$	0.092	0.925	6022	4519	8.282
	0.2		$0.100551\,T - 62.15277$	0.165	0.826	4556	4301	6.959
	0.4		$0.073957\,T - 55.54189$	0.348	0.870	2671	3843	5.117
	0.5		$0.061759\,T - 48.53092$	0.439	0.878	2082	3358	4.274
	0.6		$0.056273\,T - 45.64969$	0.491	0.819	1798	3159	3.894
	0.8		$0.047285\,T - 40.54578$	0.584	0.730	1359	2805	3.272

Table 5. Al-Ge-Sn system: equilibrium temperatures of the liquidus (in Kelvin).

x_{Al}	T/K \ x_{Ge}/x_{Sn}	2/1	1/1	1/2	1/7
0.1		1045	978	920	745
0.2		990	915	840	/
0.4		838	770	700	755
0.5		755	715	710	790
0.6		685	705	765	815
0.8		805	815	850	870

From the binary phase diagrams and our experimental results we have deduced some isotherms of the Al-Ge-Sn phase diagram (Figure 5).

Outlook

Measurements of the heat of formation using a high temperature microcalorimeter will complete our thermodynamic study of the Al-Ge-Sn ternary system.

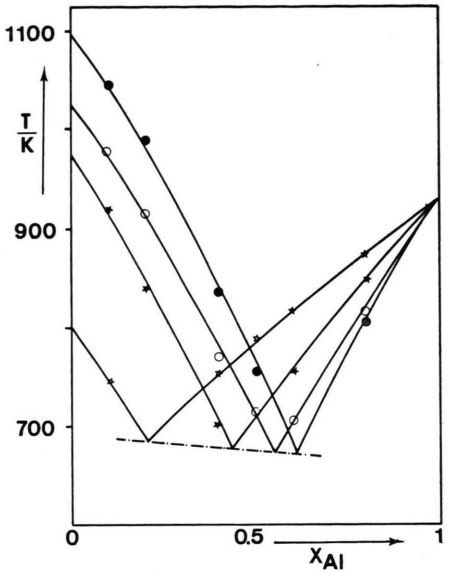

Fig. 3. Liquidus lines for the following quasi-binary alloys ● $\left(\text{Al-}\frac{\text{Ge}}{\text{Sn}}=\frac{2}{1}\right)$, ○ $\left(\text{Al-}\frac{\text{Ge}}{\text{Sn}}=\frac{1}{1}\right)$, ✱ $\left(\text{Al-}\frac{\text{Ge}}{\text{Sn}}=\frac{1}{2}\right)$, ⁘ $\left(\text{Al-}\frac{\text{Ge}}{\text{Sn}}=\frac{1}{7}\right)$.

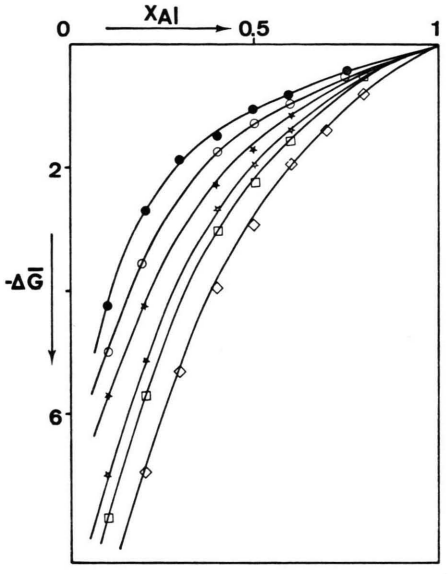

Fig. 4. Partial free energy of Al ($\bar{G}_{Al}$) (in 10^{-3} cal mol^{-1}) at 1273 K for:

◇ Al-Ge, □ Al-$\frac{\text{Ge}}{\text{Sn}}=\frac{2}{1}$, ✱ Al-$\frac{\text{Ge}}{\text{Sn}}=\frac{1}{2}$.

● Al-Sn, ⁘ Al-$\frac{\text{Ge}}{\text{Sn}}=\frac{1}{1}$, ○ Al-$\frac{\text{Ge}}{\text{Sn}}=\frac{1}{7}$,

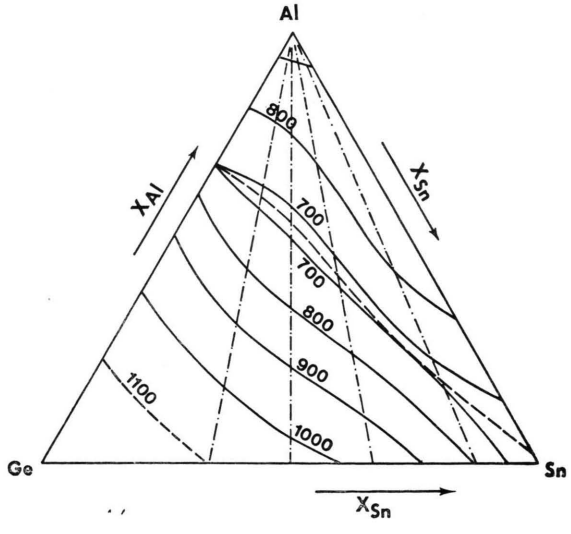

Fig. 5. Isothermal sections of the Al-Ge-Sn equilibrium phase diagram (in Kelvin). --- eutectic valley.

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