An Electromotive-Force Study of the Activity of Aluminium in Al-Ga, Al-Ge and Al-Ga-Ge Systems

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The activities of aluminium in Al-Ga, Al-Ge and Al-Ga-Ge systems were measured between 933 K and 1273 K using an e.m.f. method with a molten salt electrolyte.

The results concerning Al-Ga and Al-Ge systems are in good agreement with those previously obtained.

The $E(T)$ curves of the 36 ternary alloys studied give also some liquid-solid equilibrium temperatures and allow isothermal curves of the ternary liquidus surface to be drawn.

Introduction

In the course of a general thermodynamic investigation on ternary liquid alloys, we are interested in the thermodynamic properties of aluminium alloys. We present in this article the results concerning the Gibbs function of Al in Al-Ga-Ge alloys, but also some results obtained simultaneously for Al-Ga and Al-Ge binary systems.

In a previous paper [1] we have reported enthalpies of formation of this ternary system obtained by microcalorimetric measurements: to complete this study we choose to determine aluminium activities from e.m.f. measurements of a galvanic cell; this method needs a lot of experimental care but, on a other hand, experimentals devices are simple; such a method was already developped by Wilder [2], Massart [3], and Girard [4] for binary alloys.
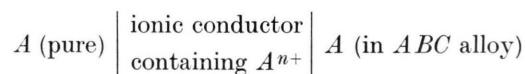
For this study, as for those already published [5, 6, 7], we begin by compiling and criticizing all thermodynamic data given in the literature on the three limiting binary systems Al-Ga, Al-Ge and Ga-Ge; they have the same characteristics: phase diagrams are reported on Fig. 1; the solid solubility range is generally very narrow and each eutetic point is quite near the more easily melted element. From Gibbs energy and enthalpy of mixing data we could recalculate the liquidus line of each binary phase diagram; so, for the three limiting binary systems, phase diagram and thermodynamic properties are in good agreement.

Principle

At constant pressure, the formation of a ternary alloy by a reaction of the type:

$$A + A_a\,B_b\,C_c \rightarrow A_{a+1}\,B_b\,C_c$$
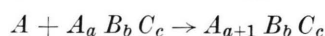
may be investigated by a concentration cell represented schematically by:

$$A \text{ (pure)} \left| \begin{array}{c} \text{ionic conductor} \\ \text{containing } A^{n+} \end{array} \right| A \text{ (in } ABC \text{ alloy)}$$

Electric conduction is due to A^{n+} ions.

From the knowledge of the e.m.f. value E at temperature T, the partial free energy ($\Delta \bar{G}_A$) and activity (a_A) of A in an alloy may be calculated using the equation

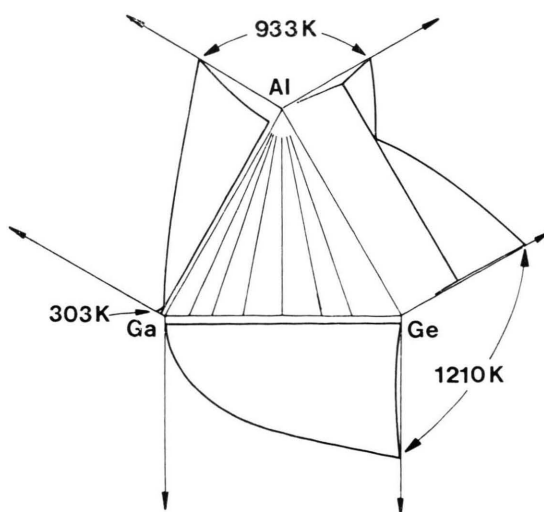$$-n\,F\,E = \Delta \bar{G}_A = R T \ln a_A\,,$$

Fig. 1. Phases diagrams of the binary systems.

where F is Faraday's constant and n is equivalent to the number of electrons given off when one mole of an element becomes a cation.

Since we have

$$\Delta \bar{G}_A = \Delta \bar{H}_A - T \, \Delta \bar{S}_A$$

with

$$\Delta \bar{S}_A = n \, F \, (\partial E / \partial T)_P$$

and

$$\Delta \bar{H}_A = - \, n \, F \, [E - T \, (\partial E / \partial T)] \, ,$$

the determination of $\Delta \bar{S}_A$ and $\Delta \bar{H}_A$ requires the measurements of the change in E with temperature.

If the e.m.f. of the cell is a linear function of T ($E = a \, T + b$), $\Delta \bar{S}_A$ and $\Delta \bar{H}_A$ do not vary perceptibly with temperature and they are proportional to the coefficients a and b.

Experimental

The cell used is represented schematically by

Al | Al^{+++} in molten LiCl + KCl | Al in Al-Ga-Ge .
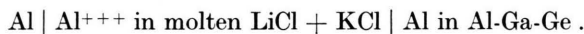
Electric conduction is due to ions Al^{+++} because this metal is more electropositive than gallium and germanium. In effect standard electrode potentials (ε^0) for aluminium and gallium in molten LiCl + KCl mixture at 723 K have been given by Laitinen [8]

$$\text{Al}^{\text{III}} - \text{Al}^0 \quad \overset{\circ}{\varepsilon}_{\text{Al}} = - \, 1.79 \, \text{Volt,}$$

$$\text{Ga}^{\text{III}} - \text{Ga}^0 \quad \overset{\circ}{\varepsilon}_{\text{Ga}} = - \, 0.88 \, \text{Volt.}$$

They have not measured the standard potential of germanium but, from the values of the free energy of formation of aluminium, gallium and germanium chlorides [9] listed in Table 1, we deduce than germanium is the least electropositive of these three metals.

In the temperature range 923—1273 K, the differences between the standard free energies of formation of aluminium, gallium, germanium,

Table 1.

Reaction	ΔG_f (kcal)	
	1000 K	1200 K
$K + 1/2 \, \text{Cl}_2 \rightleftharpoons \quad \text{KCl}$	− 81	− 76
$\text{Li} + 1/2 \, \text{Cl}_2 \rightleftharpoons \quad \text{LiCl}$	− 79	− 75
$1/3 \, \text{Al} + 1/2 \, \text{Cl}_2 \rightleftharpoons 1/3 \, \text{AlCl}_3$	− 42	− 41
$1/3 \, \text{Ga} + 1/2 \, \text{Cl}_2 \rightleftharpoons 1/3 \, \text{GaCl}_3$	− 33	− 32
$1/4 \, \text{Ge} + 1/2 \, \text{Cl}_2 \rightleftharpoons 1/4 \, \text{GeCl}_4$	− 21	− 20

Table 2.

Element	Vapour pressure (Pascal)	
	1000 K	1200 K
Al	$5.37 \cdot 10^{-6}$	$2.79 \cdot 10^{-3}$
Ga	$6.30 \cdot 10^{-4}$	$1.29 \cdot 10^{-1}$
Ge	$5.37 \cdot 10^{-8}$	$1.02 \cdot 10^{-4}$

lithium and potassium chlorides are large enough to avoid exchange reactions.

In addition, the vapor pressures of the three metals (Table 2) are small enough to keep the concentration of the alloys constant during the long high temperature experiments.

Galvanic Cell

Several authors [2, 3, 4] have devised useful techniques for the investigation of activities of liquid alloys. We have developed the apparatus previously described by Massart [3].

The general design of the galvanic cell is shown in Figure 2. All crucibles (A, B, C) and wire sheaths (D) are in pure alumina. The little electrode crucibles (C) ($\oslash$ 6 mm, length 30 mm) are wedged in place at the bottom of the crucible (B) by alumina pieces. Ten electrodes at a time were disposed in the cell: two are filled with pure metal — reference electrodes — the others with binary or ternary alloys.
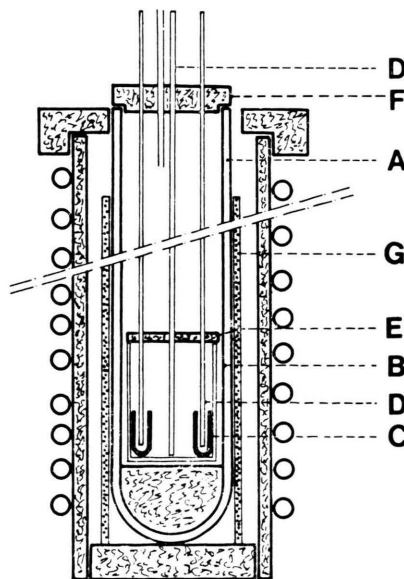

Fig. 2. Potentiometric cell.

Only the lower part of the electrode wire is unsheathed and immersed in the metal or alloy. Two covers (E, F) protect the cell and maintain electrodes, thermocouple Pt/Pt-Rh and gas tubes.

Several authors [10, 11] advocate the use of tantalum wire for electrodes while Batalin [12] employs tungsten wire. By spectroscopic analysis Massart [3] showed that tantalum metal is not corroded during such experiments up to 1373 K. We have used tantalum and tungsten wires between 933 K and 1273 K and obtained the same results.

A more uniform temperature distribution along the electrodes is obtained by enclosing the cell inside the furnace in a concentric refractory steel cylinder (G); this metallic tube keeps the same electric potential during the experiment.

Electrolyte Preparation

The preparation of the electrolyte mixture (eutectic mixture of lithium and potassium chlorides, 55.8 weight per cent LiCl, $T_{\text{fus}} = 623$ K) with a small amount of pure aluminium chloride (3 or 4 weight per cent of AlCl₃) needs a lot of care to avoid considerable trouble during experiment.

Potassium and lithium chlorides are dried at 523 K, under vacuum, during 48 hours, then melted under purified argon.

With a special glass apparatus, previously described [4], liquid electrolyte mixture is decanted; then aluminium chloride is added. A good dessication is obtained if dry hydrogen chloride flows through this ternary liquid mixture during 30 minutes. Afterwards this gas is replaced by pure argon, and the electrolyte mixture is quickly transferred into the cell after having put metals and alloys into the crucibles. After that, the cell is heated until 1100 K and stabilized during two hours at this temperature.

E.m.f. measurements, carried out at intervals of about 30 K between 923 K and 1273 K, after stabilisation of the cell, are made with the two following devices:

— a potentiometer* with a standard Weston Cell and a galvanometer (zero method),
— a digital millivoltmeter** with a large input impedance (10^{12} Ω).

We did not find any discrepancy between these two kinds of results.

* A.O.I.P. P12.   ** TACUSSEL, ARIES 20000.

The attainment of equilibrium by alloys after any change in temperature has been verified by observing the course of the e.m.f. over a large period of time; all requirements concerning the reversibility of the cell (a quasi null potential difference between the two electrodes, a good stability of e.m.f. values during the equilibrium period, the same e.m.f. values after heating and cooling) are observed.

Materials

99.9999% gallium rods donated by "Alusuisse France S.A."; 99.9999% germanium ingots and 99.995% aluminium wires supplied by Koch-Light Company. Lithium, potassium and aluminium chlorides were analytical grade salts (Merck and Prolabo).

Accuracy

It is difficult to make a general assertion about the accuracy of such measurements.

Several observations are significant:

— The e.m.f. between two reference electrodes was always lower than 0.0002 Volt at 950 K and 0.0003 Volt at upper temperatures.

— For each composition three independent experiments were carried out.

— Al-Ga and Al-Ge binary alloys were studied in the same cells and results were compared with published data to check the method.

— At fusion of the reference metal (Al), the slope change of the $E(T)$ diagram is proportional to the metal enthalpy of fusion:

$$\Delta H_{\text{fus}}(\text{Al}) = z \, F \, T_{\text{fus}} \left[\left(\frac{\partial E}{\partial T} \right)_{\text{Al(s)}} - \left(\frac{\partial E}{\partial T} \right)_{\text{Al(l)}} \right]$$

(generally accepted value for $\Delta H_{\text{fus}}(\text{Al})$: (2580 ± 30) cal mole^{-1}).

Results

a) Limiting Binary Systems

1. Aluminium-Gallium System

In Table 3 our experimental results obtained for $x_{\text{Al}} = 0.2, 0.4, 0.5, 0.6, 0.8, 0.9$ are listed. They are in good agreement with those already published by Yazawa [13], Predel [11] and Gaune [6]; a comparison of the different values obtained for $\Delta \bar{G}_{\text{Al}}$ at

Table 3. Aluminium-gallium system: $E(T/K)/mV$.

Reference: Al(liquid)		Reference: Al(solid)	
x_{Al}	$E(T)$	x_{Al}	$E(T)$
0.2	0.04903 T − 0.7944	0.2	0.09772 T − 45.5833
0.4	0.03025 T − 3.8282	0.4	0.07215 T − 42.5222
0.5	0.02170 T − 1.6875	0.5	0.06669 T − 43.1067
0.6	0.01697 T − 2.1776	0.6	0.06050 T − 42.2841
0.8	0.00878 T − 2.2962		
0.9	0.00375 T − 0.7977		

1023 K is possible in Figure 3. Moreover, our experiments provide also liquidus temperatures: the appearance of a solid phase changes the slope of $E(T)$ curves (Figure 4). These temperatures are compatible with Elliott's compilation [14].

2. Aluminium-Germanium System

Wilder [10] and then Batalin [15] determined the activities of aluminium by the same potentiometric method in the ranges (932−1258) K and (1070 to 1300) K. We reported all our results in Table 4 (see also Figure 5). The $\Delta \bar{G}_{Al}(x_{Al})$ curve does not show significant deviations from various results (Figure 6). Also for this binary system, the liquidus temperatures are in good agreement with the equilibrium phase diagram published by Elliott [14].

b) Ternary Aluminium-Gallium-Germanium System

Table 5 gives the composition of the thirty-six ternary alloys, the aluminium activity of which was measured in the temperature range (933−1273) K.

Experimental results are listed in Table 6.

In Figs. 7a−f the $E(T)$ curves are reported for these alloys disposed along six sections of the Al-Ga-Ge phase diagram. These e.m.f. values vary linearly across the one phase filled of the phase
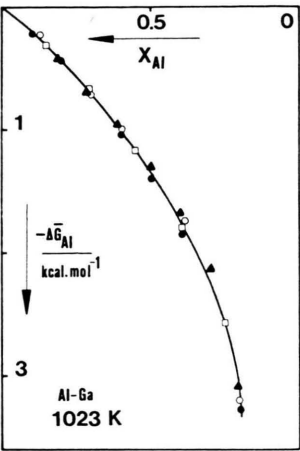

Fig. 3. Al-$\overline{G}$a system: $\Delta \bar{G}_{Al}(x_{Al})$ at 1023 K. ◇ Gaune (ref. [6]), ▲ Predel (ref. [11]), □ Yazawa (ref. [13]), ● our work.
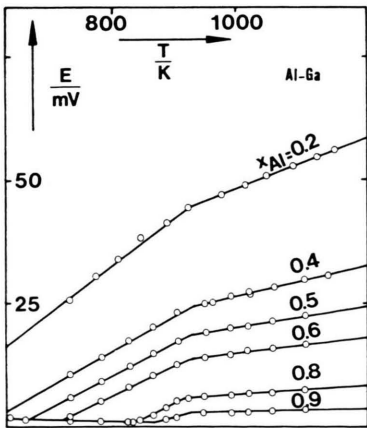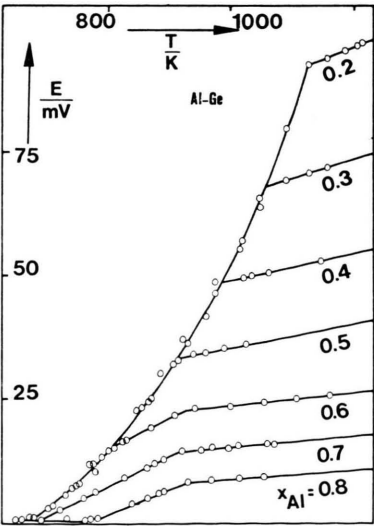

Fig. 4. Al-Ga system: $E(T)$, experimental points.

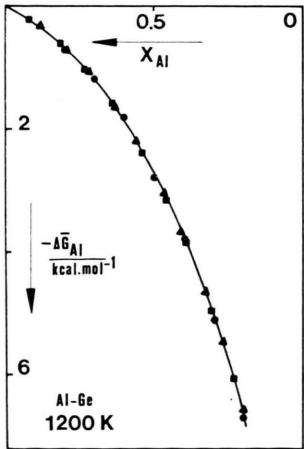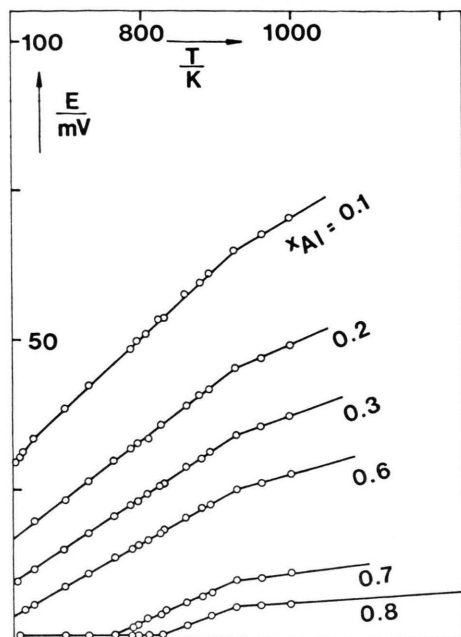Fig. 5. Al-Ge system: $E(T)$, experimental points.

Fig. 6. Al-Ge system: ▲$G_{Al}(x_{Al})$ at 1200 K. ▼ Wilder (ref. [10]), ■ Batalin (ref. [15]), ● our work.

Fig. 7. Al-Ga-Ge system: $E(T)$, experimental points. a: $x_{Ga}/x_{Ge} = 9/1$, b: 4/1, c: 2/1, d: 1/1, e: 1/2, f: 1/4.

e)

f)
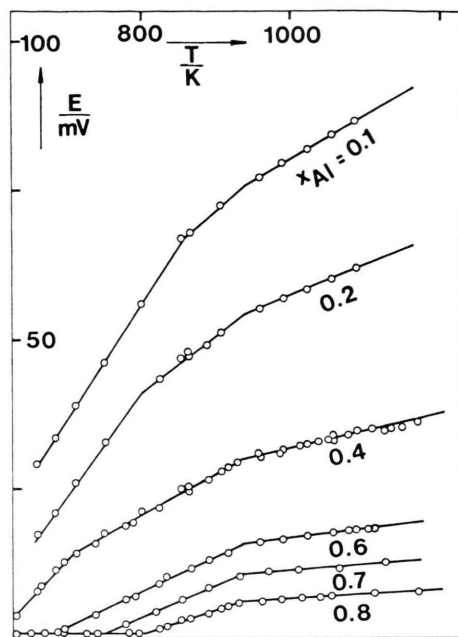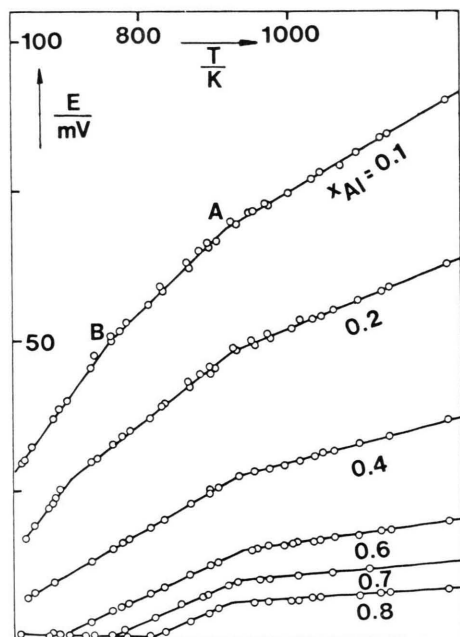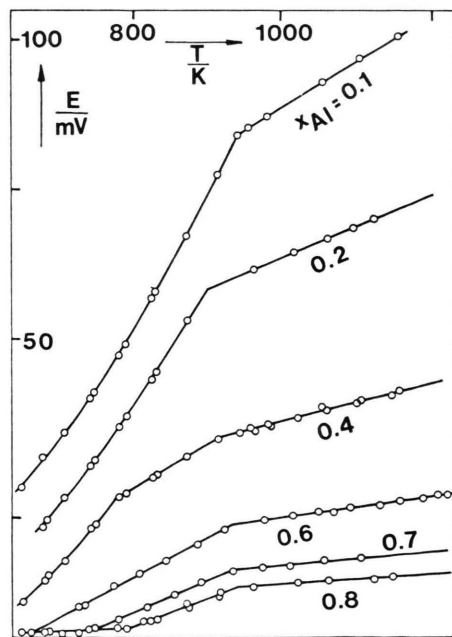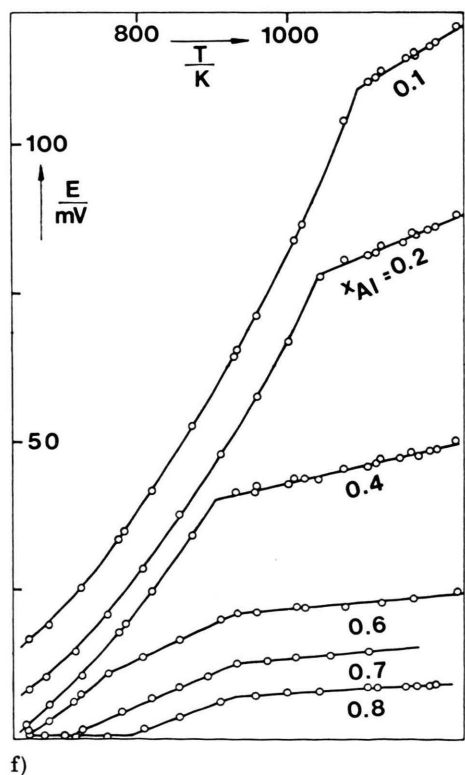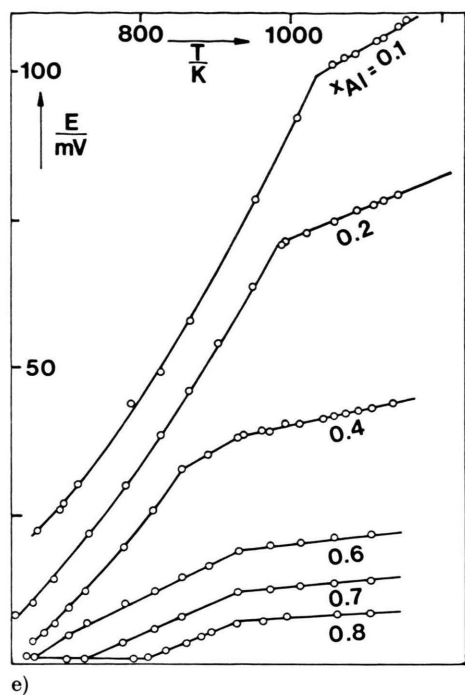
diagram. Some curves exhibit two sharp discontinuities:

— the first one corresponds to the solidification of the pure aluminium electrode, 933 K (A), and the slopes of each straight line before and after this point allow us to calculate the melting enthalpy of aluminium:

— the second discontinuity appears when the liquidus surface is reached (B).

Liquidus temperatures so determined are listed in Table 7 and plotted in Figure 8. By extrapolation, we obtained the position of the ternary eutectic valley and we can propose isothermal curves of the liquidus surface (Figure 9).

Fig. 8. Al-Ga-Ge liquidus Sections. a: $x_{Ga}/x_{Ge} = 1/4$, b: $1/2$, c: $1/1$, d: $2/1$, e: $4/1$, f: $9/1$.

Fig. 9. Isothermal liquidus curves of the ternary system.

Reference: Al(liquid)

x_{Al}	$E(T)$
0.2	$0.04927\ T + 37.4568$
0.3	$0.04000\ T + 25.8565$
0.4	$0.02777\ T + 21.4975$
0.5	$0.02484\ T + 10.6947$
0.6	$0.01512\ T +\ \ 8.5965$
0.7	$0.01166\ T +\ \ 3.7713$
0.8	$0.01041\ T -\ \ 1.5363$

Table 4. Aluminium-germanium system: $E(T/\mathrm{K})/\mathrm{mV}$.

Table 5. Composition of the studied ternary alloys.

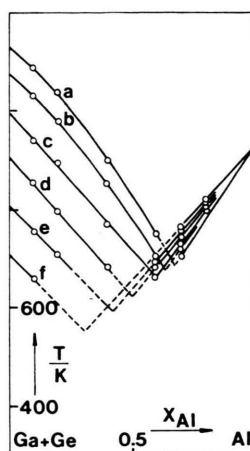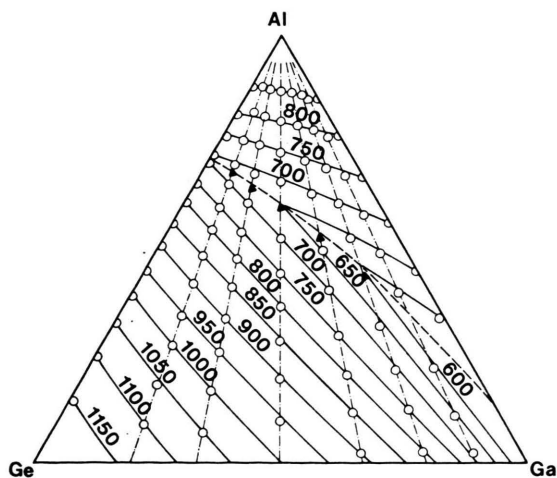| x_{Ga}/x_{Ge} x_{Al}	9/1	4/1	2/1	1/1	1/2	1/4
0.1	×	×	×	×	×	×
0.2	×	×	×	×	×	×
0.3	×					
0.4		×	×	×	×	×
0.6	×	×	×	×	×	×
0.7	×	×	×	×	×	×
0.8	×	×	×	×	×	×

Table 6. Aluminium-gallium-germanium system: $E(T/\mathrm{K})/\mathrm{mV}$.

$x_{Ga}/x_{Ge} = 9/1$, reference: Al(solid)

x_{Al}	$E(T)$
0.1	$0.11647\ T - 43.1846$
0.2	$0.09466\ T - 42.6122$
0.3	$0.08135\ T - 41.5329$
0.6	$0.06993\ T - 39.9416$
0.7	$0.05327\ T - 39.7344$
0.8	$0.04649\ T - 37.7562$

$x_{Ga}/x_{Ge} = 4/1$, reference: Al(solid)

x_{Al}	$E(T)$
0.1	$0.12122\ T - 42.2227$
0.2	$0.09544\ T - 39.8004$
0.4	$0.07155\ T - 39.0288$
0.6	$0.05758\ T - 38.7910$
0.7	$0.05283\ T - 39.2699$
0.8	$0.05008\ T - 40.0190$

$x_{Ga}/x_{Ge} = 4/1$, reference: Al(liquid)

x_{Al}	$E(T)$
0.1	/
0.2	/
0.4	$0.03287\ T - 3.2141$
0.6	$0.01757\ T - 1.4290$
0.7	$0.01137\ T - 0.6502$
0.8	$0.00823\ T - 1.3313$

$x_{Ga}/x_{Ge} = 2/1$, reference: Al(solid)

x_{Al}	$E(T)$
0.1	/
0.2	$0.09335\ T - 33.3728$
0.4	$0.06954\ T - 34.9808$
0.6	$0.05788\ T - 38.4246$
0.7	$0.05324\ T - 39.0323$
0.8	$0.03906\ T - 30.4388$

Table 6 (continued).

$x_{Ga}/x_{Ge} = 2/1$, reference: Al(liquid)

x_{Al}	$E(T)$
0.1	$0.07299\ T + 7.3206$
0.2	$0.05241\ T + 5.0766$
0.4	$0.02969\ T + 2.1732$
0.6	$0.01604\ T + 0.7840$
0.7	$0.01131\ T + 0.0309$
0.8	$0.00776\ T + 1.1335$

$x_{Ga}/x_{Ge} = 1/1$, reference: Al(solid)

x_{Al}	$E(T)$
0.1	/
0.2	/
0.4	/
0.6	$0.06708\ T - 43.6915$
0.7	$0.05357\ T - 38.6493$
0.8	$0.04701\ T - 35.7536$

$x_{Ga}/x_{Ge} = 1/1$, reference: Al(liquid)

x_{Al}	$E(T)$
0.1	$0.07619\ T + 12.2572$
0.2	$0.05232\ T + 11.2147$
0.4	$0.03188\ T +\ \ 4.2158$
0.6	$0.01783\ T +\ \ 2.2034$
0.7	$0.01164\ T +\ \ 0.4865$
0.8	$0.00807\ T +\ \ 0.9225$

$x_{Ga}/x_{Ge} = 1/2$, reference: Al(solid)

x_{Al}	$E(T)$
0.1	/
0.2	/
0.4	/
0.6	$0.06084\ T - 37.6553$
0.7	$0.05464\ T - 38.8219$
0.8	$0.04889\ T - 38.6350$

$x_{Ga}/x_{Ge} = 1/2$, reference: Al(liquid)

x_{Al}	$E(T)$
0.1	$0.07578\ T + 20.9210$
0.2	$0.05237\ T + 19.3345$
0.4	$0.02731\ T + 12.9637$
0.6	$0.01553\ T +\ \ 4.5526$
0.7	$0.01126\ T +\ \ 1.5777$
0.8	$0.00827\ T -\ \ 0.5784$

$x_{Ga}/x_{Ge} = 1/4$, reference: Al(solid)

x_{Al}	$E(T)$
0.1	/
0.2	/
0.4	/
0.6	$0.06008\ T - 34.7003$
0.7	$0.05454\ T - 37.9245$
0.8	$0.04873\ T - 38.1298$

$x_{Ga}/x_{Ge} = 1/4$, reference: Al(liquid)

x_{Al}	$E(T)$
0.1	$0.07569\ T + 26.8364$
0.2	$0.05193\ T + 24.2785$
0.4	$0.02941\ T + 13.7506$
0.6	$0.01220\ T +\ \ 9.6212$
0.7	$0.01148\ T +\ \ 2.1640$
0.8	$0.00752\ T +\ \ 0.1562$

Table 7. Liquidus Temperature.

x_{Al}	T/K					
	$x_{Ga}/x_{Ge} = 9/1$	4/1	2/1	1/1	1/2	1/4
0.1	665	765	858	943	1035	1093
0.2	/	708	803	898	983	1048
0.4	/	/	688	773	858	903
0.6	/	695	677	663	708	753
0.7	768	763	750	745	727	706
0.8	825	813	808	803	811	793

Conclusion

By potentiometric method, we have obtained activities of aluminium in aluminium-gallium, aluminium-germanium and aluminium-gallium-germanium systems in the whole range of composition between 933 K and 1273 K. $E(T)$ curves give also some liquid-solid equilibrium temperatures, these values are in good agreement with our microcalorimetric determinations. So enthalpies of mixing, partial free energies of aluminium and liquidus surface are well known and the thermodynamical description of the aluminium-gallium-germanium ternary system is complete.

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