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Thermodynamics and Phase Diagram of the Gallium—Sodium System**

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A critical evaluation of the thermodynamic properties of liquid alloys was made. The *Gibbs* energies of formation of the solid compounds were derived from the original experimental data. Finally, calculations were carried out to match the thermodynamic description of the system to the known liquidus points.

(Keywords: Emf; Gallium alloys; Phase diagram; Sodium compounds; Thermodynamics)

Thermodynamik und Phasendiagramm des Gallium—Natrium Systems

Es wurde eine kritische Auswertung der thermodynamischen Eigenschaften von flüssigen Legierungen durchgeführt. Von den experimentellen Daten wurden die *Gibbs*'schen Bildungsenergien der festen Verbindungen abgeleitet. Letztlich wurden Berechnungen zur Anpassung der thermodynamischen Beschreibung des Systems mit bekannten Liquidus-Punkten durchgeführt.

Introduction

The earliest investigations on this system were reported in the thirties. The works of *Zintl* and *Kaiser* [1], *Gilfillan* and *Bent* [2] and of *Pushin, Stepanović* and *Stajić* [3] did not give any constitutional information except that the metals alloy easily and that a high melting compound forms. The systematic study of the Ga—Na system began with the work of *Feschotte* and *Rinck* [4]. They established the first known phase diagram with the two compounds: congruently melting Ga_8Na_5 and peritectically forming Ga_3Na. Their subsequent studies [5–8] confirmed the general

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** Dedicated to Prof. Dr. *Kurt L. Komarek* on the occasion of his 60th birthday.

features of the system except that the stoichiometry of the latter compound was to be Ga_4Na. The recent constitutional study by *Yatsenko* et al. [9] suggests the existence of a miscibility gap on the sodium-rich side and the formerly reported formula Ga_3Na.

The thermodynamic properties of liquid alloys were examined by *Lantratov* and *Tsarenko* [10] over the composition range from 10.8 to 79.64 at%. Na and within the temperature interval from 823 to 923 K. They employed an emf technique with the sodium glass as a solid electrolyte.

Tamaki and *Cusack* [11] used sodium beta-alumina as a solid electrolyte in the galvanic cells to determine the sodium activity in liquid Ga—Na solutions. Their experiment covered almost the whole concentration range at the temperatures up to 923 K. Finally, *Zabdyr* and *Fitzner* [12] employed the same experimental method for the determination of thermodynamic properties of solid compounds in the system. They obtained the *Gibbs* energies of formation from the liquid elements for both Ga_4Na and Ga_8Na_5, but the data for the second compound turned out to be wrong due to the non-equilibrium conditions during the solid state reaction in the cell:

$$2\,Ga_4Na(s) + 3\,Na(l) = Ga_8Na_5(s). \tag{1}$$

Hence, the *Gibbs* energy of formation due to the above reaction (1) had to be redetermined.

Experimental

The same experimental technique and cell arrangement was applied as in [12]. The cell:

$$Na(l) \mid \text{sodium beta-alumina} \mid Ga_8Na_5(s) + Ga_4Na(s)$$

was assembled by titrating the liquid sodium to the liquid gallium, lowering the temperature and then equilibrating for 24 hours to obtain the alloy electrode containing 21 at% Na. Emf measurements were taken within the temperature interval from 502 to 698 K. Afterwards the temperature was raised to reach the liquid phase and a titration was carried out again until 24 at% Na in the alloy electrode were obtained. The temperature was then lowered to solidify the alloy and additional emf measurements were taken.

The results are presented in Fig. 1; they were fitted by the least-squares method to give:

$$E(\pm 5.8) = 335.6(\pm 19.4) - 0.241(\pm 0.033)\,T\ \text{mV}. \tag{2}$$

Since the formation reaction of the solid Ga_8Na_5 from the liquid constituents:

$$8\,Ga(l) + 5\,Na(l) = Ga_8Na_5(s) \tag{3}$$

is the sum of the two reactions: a formation of two moles of the solid Ga_4Na from the liquid elements and of the reaction (1), the *Gibbs* energy change of the reaction (3) is equal to:

$$\Delta_r G(3) = 2\,\Delta_f G(Ga_4Na) + \Delta_r G(1).$$

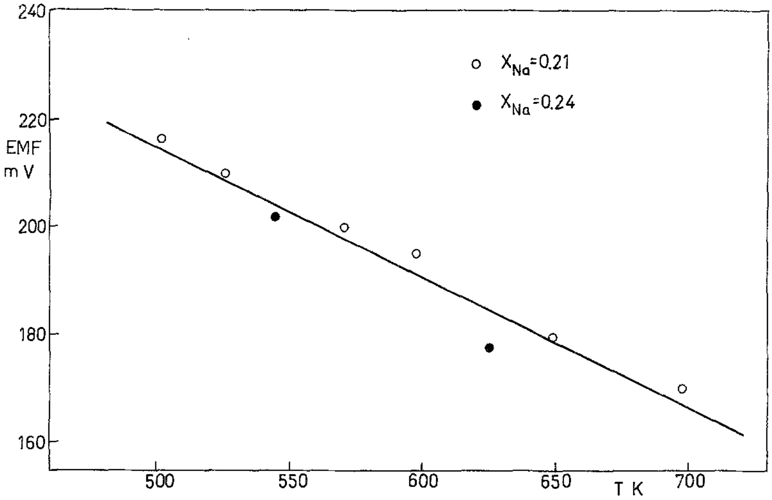

Fig. 1. Emf results plotted against temperature

The *Gibbs* energy of formation of the solid Ga_4Na from the liquid elements,-$\Delta_f G(Ga_4Na)$, was determined in [12] as:

$$\Delta_f G(Ga_4Na) = -104\,474 + 111.38\,T \text{ J/mol.} \tag{4}$$

The *Gibbs* energy change of the reaction (1) was calculated directly from the emf data, Eqn. (2), by means of the well-known relation:

$$\Delta_r G = -z\,n\,F\,E$$

where: $z = 1$; a valency of the sodium ions, $n = 3$; a number of the sodium ions involved, $F = 96\,497$ J/V; the *Faraday*'s constant, $E =$ the emf value in volts.

In result one obtains:

$$\begin{aligned}\Delta_r G(3) &= \Delta_f G(Ga_8Na_5)\\ &= -306\,101\,(\pm 10\,636) + 292.52\,(\pm 19.75)\,T \text{ J/mol.}\end{aligned} \tag{5}$$

To start the phase diagram calculation, a full thermodynamic description of the liquid and both the solid phases is needed.

Results and Discussion

Thermodynamic Properties

As mentioned above, only the two sets of thermodynamic data [10, 11] exist for the liquid alloys. They were carefully analyzed and then compiled using the *Pelton*'s polynomial description [13] as below:

$$G^{ex}_{Ga} = \sum_{2}^{9} A_i X^i_{Na};\; G^{ex}_{Na} = \sum_{0}^{9} B_i X^i_{Na};\; G^{ex} = \sum_{1}^{9} \varphi_i X^i_{Na} \tag{6}$$

where: G^{ex}_{Ga}, G^{ex}_{Na}, G^{ex} are the excess partial *Gibbs* energies of gallium and sodium and the excess *Gibbs* energy of mixing, respectively; the coefficients: A_i, B_i and φ_i are temperature-dependent as follows:

$$\begin{aligned}
A_2 &= -19\,339 + 1.300\,T \\
A_3 &= 221\,306 + 197.462\,T \\
A_4 &= -3\,120\,494 - 552.644\,T \\
A_5 &= 12\,142\,501 + 1\,673.383\,T \\
A_6 &= -23\,472\,403 - 3\,874.510\,T \\
A_7 &= 25\,890\,294 + 4\,673.093\,T \\
A_8 &= -15\,701\,395 - 2\,706.772\,T \\
A_9 &= 4\,058\,101 + 614.103\,T \\
B_0 &= -28\,452 + 28.193\,T \\
B_1 &= 38\,678 - 2.600\,T \\
B_2 &= -351\,298 - 294.893\,T \\
B_3 &= 4\,381\,965 + 934.321\,T \\
B_4 &= -18\,298\,614 - 2\,644.371\,T \\
B_5 &= 40\,309\,400 + 6\,322.772\,T \\
B_6 &= -53\,677\,760 - 9\,326.445\,T \\
B_7 &= 43\,834\,745 + 7\,766.545\,T \\
B_8 &= -20\,266\,753 - 3\,397.640\,T \\
B_9 &= A_9 \\
\varphi_1 &= B_0 \\
\varphi_2 &= -A_2 \\
\varphi_3 &= -110\,653 - 98.731\,T \\
\varphi_4 &= 1\,040\,164 + 184.214\,T \\
\varphi_5 &= -3\,035\,624 - 418.345\,T \\
\varphi_6 &= 4\,694\,482 + 774.899\,T \\
\varphi_7 &= -4\,315\,049 - 778.849\,T \\
\varphi_8 &= 2\,243\,056 + 386.680\,T \\
\varphi_9 &= -507\,262 - 76.763\,T \qquad \mathrm{J/mol.}
\end{aligned}$$

The values of G^{ex}_{Na} calculated from (6) at 898 K are compared with the corresponding experimental data of *Lantratov* [10] and *Tamaki* [11] in Fig. 2. The excess *Gibbs* energy functions calculated at the same temperature are shown in Fig. 3 while the enthalpies are presented in Fig. 4.

It has been observed during experiments with the solid compounds that the two-phase region (Ga_8Na_5 + Ga_4Na) begins at 20 at% Na and thus the stoichiometry of Ga_4Na has been confirmed.

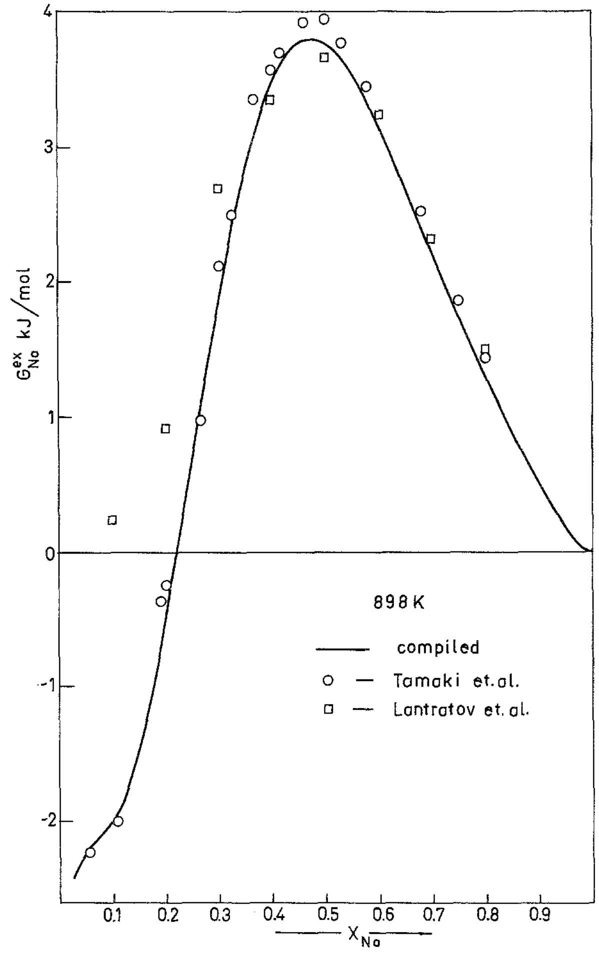

Fig. 2. Calculated G^{ex}_{Na} function compared with the experimental data of [10] and [11]

Phase Diagram

Calculations were divided into two parts: the sodium-rich side, 100 to 20 at% Na and the gallium-rich side, 20 to 0 at% Na, and the two liquidus equations were derived, respectively:

$$RT\ln[(1-X)^8 X^5] + 5\,G^{ex}_{\mathrm{Na}} + 8\,G^{ex}_{\mathrm{Ga}} - \Delta_f G(\mathrm{Ga_8Na_5}) = 0 \qquad (7)$$

$$RT\ln[(1-X)^4 X] + G^{ex}_{\mathrm{Na}} + 4\,G^{ex}_{\mathrm{Ga}} - \Delta_f G(\mathrm{Ga_4Na}) = 0 \qquad (8)$$

with $X = X_{\mathrm{Na}}$.

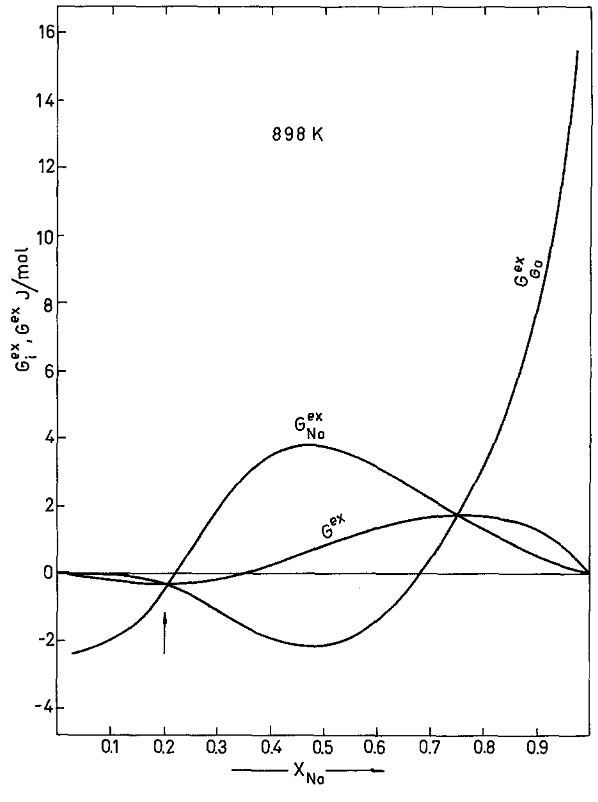

Fig. 3. Excess *Gibbs* energy functions calculated at 898 K

To match the experimentally determined points, the congruent melting, the peritectic and the gallium solubility in the liquid sodium, a slight correction was made in the relationship (4):

$$\Delta_f G(\mathrm{Ga_4Na}) = -106\,546 + 111.34\,T \quad \mathrm{J/mol} \qquad (9)$$

since the *Gibbs* energy of formation was the most prevailing term in the liquidus equation and the latter relation was used in the final calculation. The results confirmed the phase diagram established in [4] and corrected in [5–8]. Calculated temperatures of the congruent melting and of the peritectic are 2 K lower than those reported in [4–8].

The experimentally determined solubility data [5, 6] are compared with those calculated in Table 1.

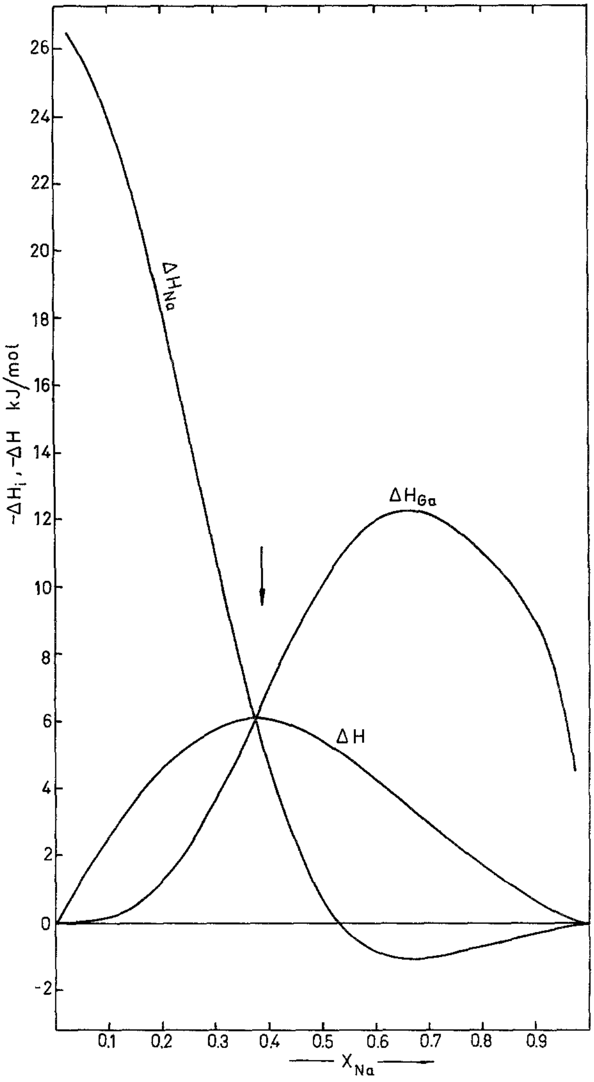

Fig. 4. Calculated enthalpies plotted against composition

Conclusions

The complete Ga—Na phase diagram is presented in Fig. 5: solid lines represent the results of [4–8] and points indicate the calculated values.

The suggestion of [9] on the existence of a miscibility gap in the sodium-rich region has not been confirmed. The flat part of the liquidus

Table 1. *Comparison of the observed [5,6] and the calculated solubilities of gallium in the liquid sodium*

T/K	at% Ga calculated	 observed
773	3.16	3
723	1.33	1.2
673	0.36	0.42
573	0.18	0.13
473	0.03	0.05
371	0.003	0.015

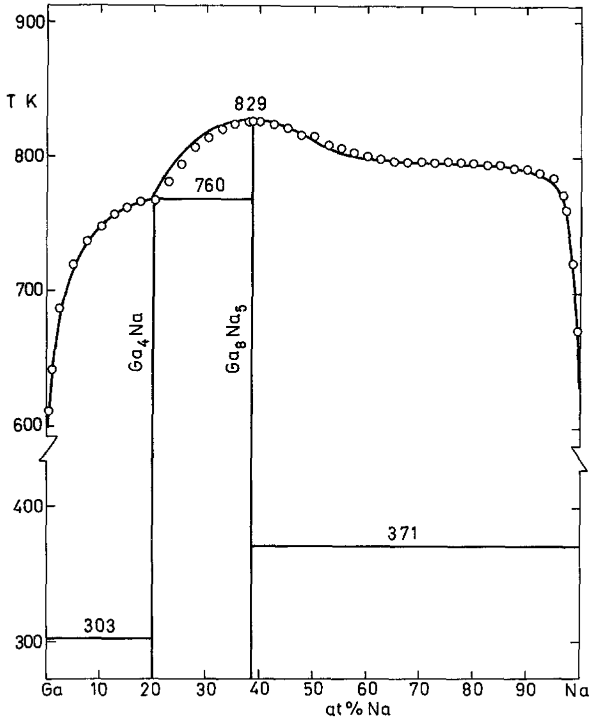

Fig. 5. The Ga—Na phase diagram; points indicate the calculated values

line reflects the presence of *A—A* interactions in the liquid which are not strong enough to cause an immiscibility.

The composition of the compound Ga_8Na_5 corresponds to a maximum in the heat of mixing curve while the lowest negative value of the excess *Gibbs* energy occurs at the composition Ga_4Na. Compound forming systems exhibit local changes of concentration fluctuations in the liquid phase which may appear as clustering tendency. The zero wavenumber component, $S_{cc}(0)$ of the concentration-concentration fluctuation derived by *Bhatia* and *Thornton* [14] is regarded to be a measure of such a tendency in the liquid alloys and is defined as follows:

$$S_{cc}(0) = RT(\partial^2 G/\partial X^2)^{-1}_{T,p} \tag{10}$$

where: G is the *Gibbs* energy of mixing and X is the composition in mole fraction.

The values of $S_{cc}(0)$ were calculated from (6) and (10) at 850 K and plotted against the composition in Fig. 6; the respective curve for the ideal mixing (the dashed line) is shown for comparison.

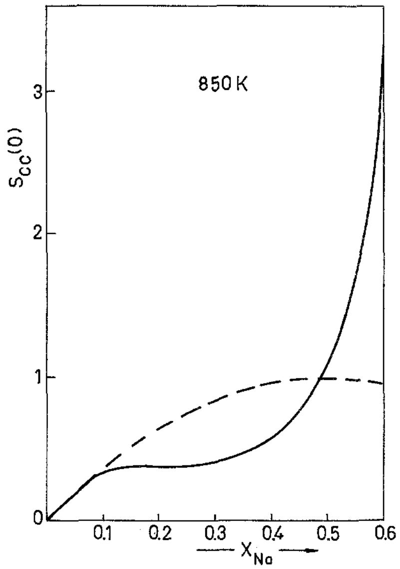

Fig. 6. The $S_{cc}(0)$ function calculated at 850 K versus a composition; a dashed line represents the ideal curve

In the liquid containing some amount of the undissociated compound molecules, $S_{cc}(0)$ is smaller than that for the random mixing and dissociation causes $S_{cc}(0)$ to increase. The values of $S_{cc}(0)$ within 0 to 0.5 mole fraction of Na indicate some degree of aggregation of the unlike atoms, whereas those larger than for the ideal mixing reveal a tendency to group the alike atoms together. It would be desirable to confirm the above conclusions by diffraction experiments.

References

[1] *Zintl E, Kaiser H* (1933) Z Anorg Chem 211: 121

[2] *Gilfillan ES, Bent HE* (1934) J Am Chem Soc 56: 1661

[3] *Puschin NA, Stepanović S, Stajić V* (1932) Z Anorg Chem 209: 333

[4] *Feschotte P, Rinck E* (1956) Comp Rend 243: 1525

[5] *Feschotte P* (1961) Ann Chim Paris 6: 1029

[6] *Rinck E, Feschotte P* (1960) Comp Rend 250: 1489

[7] *Rinck E, Feschotte P* (1960) Comp Rend 251: 869

[8] *Rinck E, Feschotte P* (1961) Comp Rend 252: 3592

[9] *Yatsenko SP, Chuntonov KA, Bushmanov VD, Diyeva EN* (1974) Diagrammy sostoyaniya sistem Ga—Na, Ga—K, In—K, In—Rb. In: *Ivanov OS, Alekseeva ZM* (eds) Struktura faz, fazovye prevrashcheniya i diagrammy sostoyaniya metallicheskikh sistem. Nauka, Moskva, p 198

[10] *Lantratov MF, Tsarenko EV* (1961) Zh Prikladnoi Khimii 34: 2435

[11] *Tamaki S, Cusack NE* (1979) J Phys F: Metal Phys 9: 403

[12] *Zabdyr L, Fitzner K* (1983) Archiw Hutn 28: 221

[13] *Pelton AD, Flengas SN* (1969) Can J Chem 47: 2283

[14] *Bhatia AB, Thornton DE* (1970) Phys Rev B 2: 3004