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*Indicates key paper.
#Indicates presence of a phase diagram.

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The Ga-Zn (Gallium-Zinc) System

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Equilibrium Diagram

The Ga-Zn equilibrium phase diagram (Fig. 1) includes: (1) the liquid, L; (2) the hexagonal (Zn) terminal solid solution with a maximum solubility of 2.36 at.% Ga at 260 °C; and (3) the orthorhombic (Ga) solid solution with a maximum solubility of 0.8 at.% Zn at 20 °C.

The liquidus curve was established by [32Pus], using a cooling curve method, and [58Heu] used differential thermal analysis to determine the liquidus. Both sets of results show good agreement in the (Zn)-rich region. However, for alloys with less than 30 at.% Zn, the data of [32Pus] are several degrees lower, as shown in Fig. 1. [55Val] and [74Shu] also determined the liquidus curve in the same composition range. The data of [55Val] are close to those of [32Pus], whereas those of [55Heu] are close to the determinations of [74Shu]. [63Del] determined the liquidus in the composition range 0 to 8 at.% Zn by resistivity and thermal analysis measurements.

To explain the discrepancies observed between the previous experimental results and those derived from a thermochemical calculation, [62Cha] determined the liquidus for alloys containing up to 15 at.% Zn by thermal analysis. The alloys were made by dissolving high-purity Zn in Ga under an atmosphere of dry oxygen-

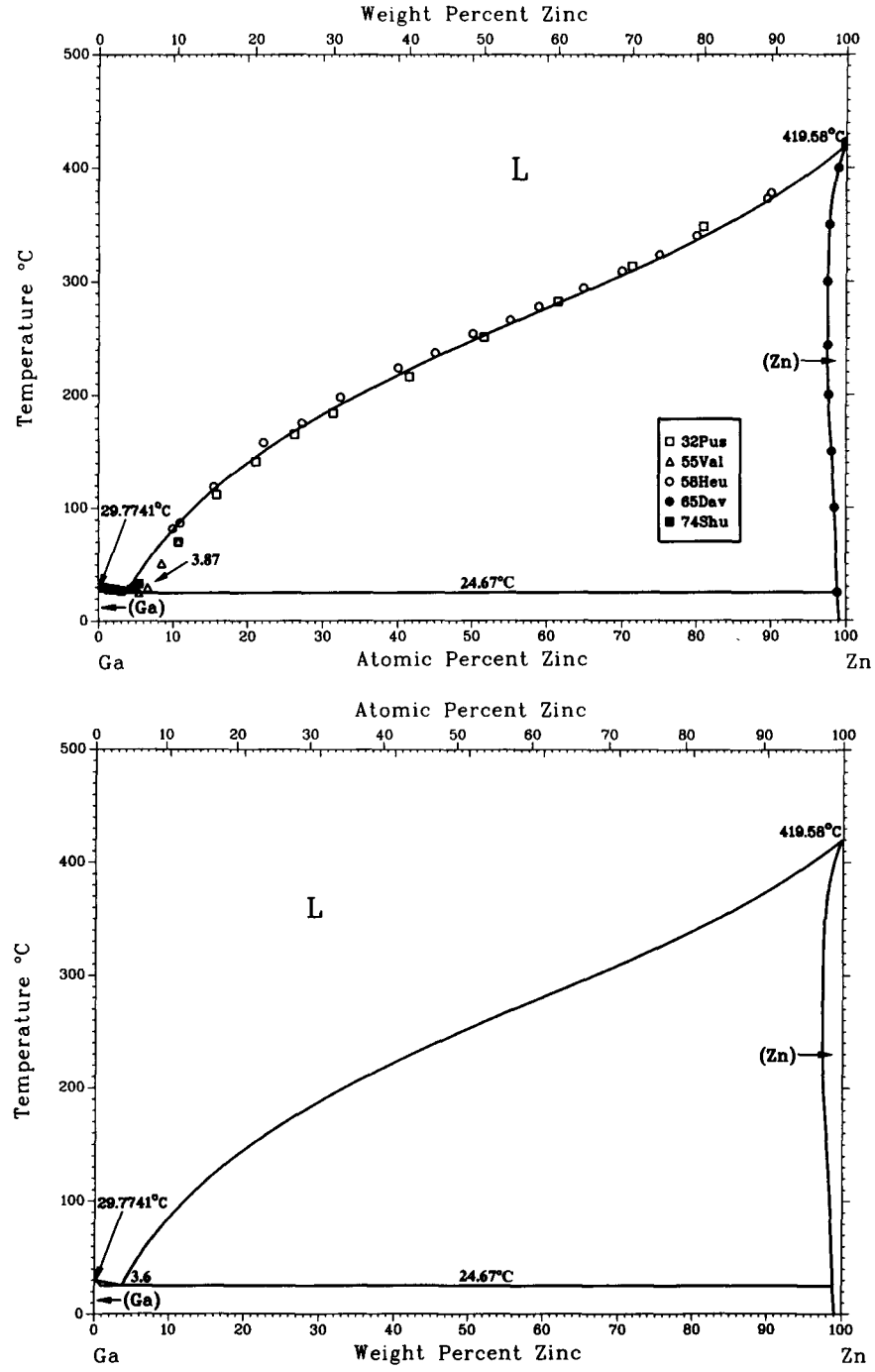
Table 1 Reported Temperatures and Compositions for the Ga-Zn Eutectic Reaction L ↔ (Ga) + (Zn)

Reference	Composition of L, at.% Zn	Temperature, °C	Method
[32Pus]	5.30	25.0	Thermal analysis
[58Heu]	3.70	25.4	Thermal analysis
[63Del]	3.70	25.0	Thermal analysis, resistivity
[74Shu]	3.70	25.0	Thermal analysis
This work	3.87	24.67	Calculated

free nitrogen between 30 and 50 °C above the liquidus. His results confirmed those obtained by the previous investigations for alloys with less than 15 at.% Zn, but produced values significantly higher than those determined previously for compositions between that of the eutectic and greater than 15 at.% Zn. These results are in close agreement with the thermochemical calculations of [64Kub].

The solubility of Ga in (Zn) was established previously with X-ray diffraction studies by [65Dav]. The solid solubility curve of Ga in (Zn) on the Zn-rich side is

Fig. 1 Assessed Ga-Zn Phase Diagram



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shown in Fig. 1. The maximum solubility of Zn in (Ga) was established by [58Heu] from hardness measurements as 0.8 at.% Zn at 20 °C. No data on the solid solubility curve are available.

The eutectic composition and temperature were reported by [32Pus] as about 5.3 at.% Zn at 25 °C, by [58Heu] as 3.7 at.% Zn at 25.4 °C, and by [74Shu] as 3.7 at.% Zn at 25 °C (Table 1). The Ga-rich region of the phase diagram is shown in Fig. 2.

Table 2 lists experimental liquidus and solidus data. The accepted phase diagram, shown in Fig. 1 and 2, results from the thermodynamic optimization.

Crystal Structures and Lattice Parameters

Table 3 lists crystal structure data for pure Zn and pure Ga; their lattice parameters and those of three Zn-rich quenched solid solutions are presented in Table 4. No data on the (Ga) solid solution lattice parameters are available.

Metastable Phases

Liquid Ga can be undercooled in the dispersed state to −122 °C, as shown by [65Bos]. Two metastable orthorhombic phases—βGa and γGa—were reported: βGa which melts at −16.3 °C and αGa at −35.6 °C. [65Bos] designates the two sorts of Ga by Ga_β and Ga_δ.

Ga_β and Ga_δ are similar to the modification GaII and GaIII obtained at high pressures.

[63Del] determined by resistivity and thermal analysis the metastable liquidus. At 10 ± 0.2 °C, a peritectic transformation occurs in which an unidentified compound is formed. The composition of the liquid is 0.06 at.% Zn. At lower temperatures, a eutectic transformation exists virtually at the melting temperature of Ga(II).

The position of the liquidus curve of the Ga-Zn system is very sensitive with respect to the cooling rate, as reported by [74Shu]. A cooling rate of 0.3 to 1 °C/min shifts the liquidus curve to lower temperatures by about 12 °C, these observations being made for alloy compositions between 0 to 5 at.% Zn.

As reported by [65Dav], (Zn) is retained only a few hours after quenching, then decomposition occurs.

Thermodynamics

The thermodynamic properties of liquid Ga-Zn alloys were studied by [55Gen], [62Svi], [66Ger], [67Pre], [71Rya], and [85Gir] using an emf method over the en-

Table 2 Experimental Liquidus and Solidus Temperatures of the Ga-Zn system

Composition, at.% Zn	Temperature, °C Liquidus	Solidus	Composition, at.% Zn	Temperature, °C Liquidus	Solidus
[32Pus]; l-(cph Zn); thermal analysis					
15.80	112.00	...	51.60	251.00	...
21.10	141.00	...	61.50	282.00	...
26.20	165.00	...	71.30	313.00	...
31.40	184.00	...	81.00	348.00	...
41.60	216.00	...			
[55Val]; l-(cph Zn); thermal analysis					
5.30	25.00	...	8.40	51.00	...
6.50	30.00	...	10.60	71.00	...
[58Heu]; L-(ortho Ga); differential thermal analysis					
1.00	...	29.00	3.10	...	26.40
2.10	...	27.60			
[55Heu]; l-(cph Zn); differential thermal analysis					
9.90	82.00	...	55.10	266.00	...
10.90	87.00	...	59.00	278.00	...
15.50	119.00	...	65.00	294.00	...
22.10	158.00	...	70.00	309.00	...
27.20	175.00	...	75.00	323.00	...
32.30	198.00	...	80.10	340.00	...
40.10	224.00	...	89.60	373.00	...
45.10	237.00	...	90.20	378.00	...
50.10	254.00	...			
[60Del]; l-(ortho Ga); thermal analysis, resistivity					
1.10	...	29.50	2.70	...	27.00
1.90	...	28.00	3.70	...	25.20
[60Del]; l-(cph Zn); thermal analysis, resistivity					
7.30	59.00	...	8.50	69.00	...

tire composition range and at temperatures from 693 K [62Svi] to 1033 K [71Rya]. The same technique was used by [59Kle] at x_{Zn} = from 0.606 to 0.908 and by [73Mos], who also analyzed dilute Zn solutions.

Vapor pressure measurements were performed by [73Pia] at 916 K in the composition range $0.191 < x_{Zn} < 0.795$. [58Kle] measured the enthalpies of formation of liquid alloys by calorimetry over the entire concentration range at 723 K, and [71Gam] did the same for alloys of $0 < x_{Zn} < 1$ at 723 and 873 K.

Figure 3 presents the data points of the partial excess Gibbs energy of Zn in liquid melts of various investigations, recalculated for 850 K, and the experimental values of the enthalpy of mixing from [58Kle].

Thermodynamic Calculations

An optimizing procedure developed by [77Luk] was used to evaluate the parameters of the liquid and (Zn) phases. Because a variation with temperature for the

Table 3 Ga-Zn Crystal Structure Data

Phase	Composition, at.% Zn	Pearson symbol	Space group	Strukturbericht designation	Prototype
Ga	0	*oC8*	*Cmca*	*A11*	Ga
βGa	0	*oC4*	*Cmcm*	...	Ga
Zn	100	*hP2*	$P6_3/mmc$	*A3*	Mg

From [Massalski].

Table 4 Ga-Zn Lattice Parameter Data

Phase	Composition, at.% Zn	Lattice parameters, nm *a*	*b*	*c*	Comment	Reference
Ga	0	0.45198	0.76602	0.45198	At 24 °C	[Pearson3, 65Bar]
βGa	0	0.29000	0.81300	0.31700	...	[Pearson3, 65Bar]
(Zn)	98.05	0.26484	...	0.49721	At 18 °C	[65Dav]
	99.05	0.26513	...	0.49123	At 18 °C	[65Dav]
	99.39	0.26520	...	0.49370	At 18 °C	[65Dav]
Zn	100	0.26535	...	0.49251	At 18 °C	[65Dav]

Fig. 2 Ga-Rich Region of the Ga-Zn Assessed Phase Diagram

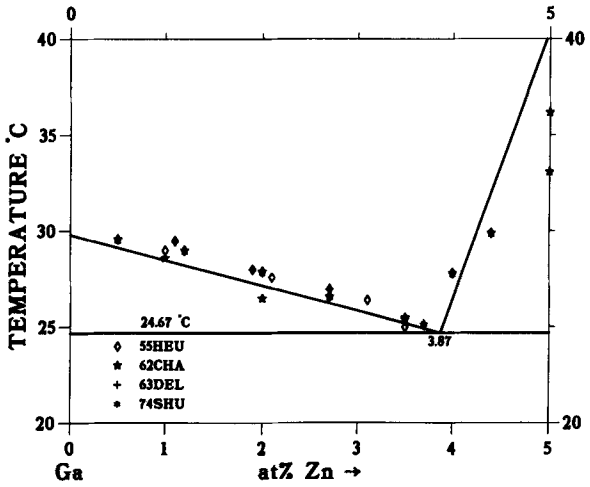

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Fig. 3 Experimental and Calculated Excess Partial Gibbs Energy of Zn at 850 K

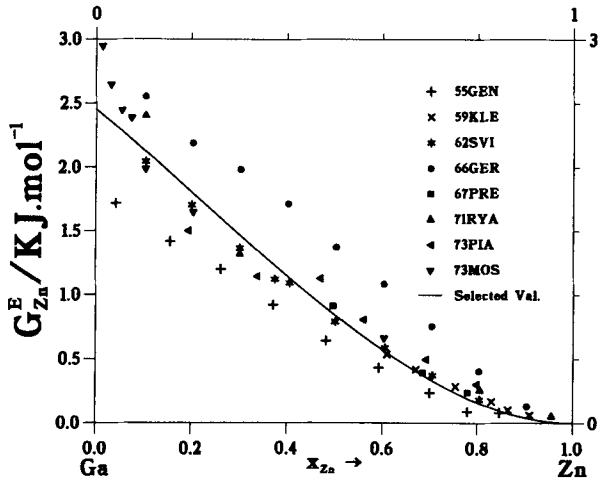

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Table 5 Thermodynamic Properties of Ga-Zn Liquid and cph Phases and Gibbs Energy of Transformation of the Pure Elements

Liquid

$G^{ex} = x(1-x)(3662.8 + 23.08629\,T + 4.20\,T(1-\ln T) - 464.2(1-2x))$

cph phase

$G^{ex} = 10\,744\,x(1-x)$

Pure elements

$G(Ga, orh) = 0$

$G(Zn, cph) = 0$

$G(Ga, L) = 5526.1 - 18.34017\,T - 0.020890\,T(1-\ln(T)) - 0.0000037\,T^2$

[86Sgt, 87Ans]

$G(Zn, L) = 7044.0 - 8.25629\,T + 0.370621\,T(1-\ln(T)) + 0.0002040\,T^2$

[86Sgt, 87Ans]

$G(Ga,cph) = 4500 - 9.5T$

[86Sau]

Note: Values in J/mol, T in K.

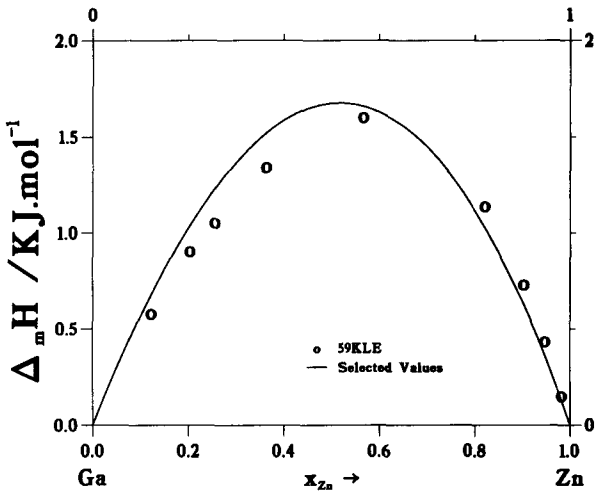
enthalpy of mixing of liquid alloys was observed experimentally, a term expressing ΔCp was included to reconcile the enthalpies of mixing and the partial Gibbs energies of Zn.

The data base included all the liquidus and (Zn) solidus data, the enthalpies of mixing, and partial Gibbs energies of the liquid solution. The results of the optimization show that the data were consistent within the experimental error of the various measurements.

The optimized expressions for the excess Gibbs energies of the liquid and (Zn) are given in Table 5, as well as the Gibbs energy of fusion of Ga and Zn. Figures 3 and 4 compare the calculated partial excess Gibbs energy of Zn and the enthalpy of mixing, due to [58Kle] with the experimental data.

The phase diagram calculated with these expressions is shown in Figure 1. The calculated eutectic composition and temperature agree very well with the experimental results, as shown in Table 1.

Fig. 4 Experimental and Calculated Enthalpy of Mixing Liquid Ga-Zn Alloys



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The Al-U (Aluminum-Uranium) System

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Equilibrium Diagram

Results of investigations of the U-Al phase diagram were published by [50Gor], [50Bit], [58Jep], [64Rus], [64Str], [63Kha], [55Cab], [65Par], [61Pet2], [58Abr], [61Sto], [64Roy], and [69Chi]. [50Gor] used thermal analysis, X-ray diffraction, and metallographic methods. [64Str] used thermal analysis, microprobe, and metallographic methods. [55Cab] used metallography; [65Par], [61Pet2], [58Abr], and [58Jep] used thermal analysis; [61Sto] used thermal analysis, resistance, and metallographic methods; [64Roy] used thermal and metallographic methods; and [64Rus] used optical metallography and electrical resistance measurements. These studies are in general agreement, although there are some differences. Previous reviews of the phase behavior of the U-Al system include [55Sal], [58Rou], [81Chi], [Elliott], [Shunk], [72Iva] and [Hansen].

The assessed U-Al phase diagram (Fig. 1), despite several modifications, is similar to that of [81Chi]. The [81Chi] diagram is essentially the [50Gor] diagram, with modifications suggested by [51Bor] and the above-mentioned investigations. The U-rich portion of the diagram is expanded in Fig. 2, and the special points of the diagram are shown in Table 1.

Al Solubilities in U Allotropes

The U-rich end of the phase diagram in Fig. 2 shows the results of the investigations by [50Gor], [55Cab], [59Bel], [64Str], [63Kha], [64Rus], and [65Par]. The precise solubilities of Al in (γU), (βU), and (αU) are not known, but estimates can be made. The temperature of the eutectic reaction L $\leftrightarrow$ (γU) + UAl_2 was estimated by [50Gor] as 1105 °C. These workers reported a maxi-