

# Thermodynamic Properties of Selected Binary Aluminum Alloy Systems

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This work reviews the data and information available through March 1985 on the various thermodynamic properties of five binary aluminum alloy systems: Al-Fe, Al-Mn, Al-Ni, Al-Si, and Al-Ti. The thermodynamic properties covered in this work are heat capacity, Gibbs energy, enthalpy, and entropy of formation. Existing data have been evaluated and analyzed. The values for heat capacity and room-temperature enthalpy of formation for a large number of alloys have been generated. For each of the binary alloy systems, the recommended values for integral Gibbs energy, enthalpy, and entropy of formation as well as the partial quantities, activity, and activity coefficients for each component covering the entire composition range have been reported. These values are reported for both solid and liquid alloys.

Key words: activity; activity coefficient; aluminum-iron; aluminum-manganese; aluminum-nickel; aluminum-silicon; aluminum-titanium; enthalpy; entropy; Gibbs energy; heat capacity; phase diagram.

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## 1. Introduction

The principal objective of this work was to critically evaluate and analyze data on the thermodynamic properties of five binary alloy systems: Al-Fe, Al-Mn, Al-Ni, Al-Si, and Al-Ti.

The general background information for these properties is reported in Sec. 2. Discussion of the thermodynamic properties and the details of data analysis are reported in Secs. 3-8. For the Al-Fe alloy system, heat capacity values are reported for  $x_{\text{Fe}} = 0.15-0.95$  and cover the temperature range from 1.4 to 1400 K. The room-temperature integral enthalpies of formation,  $\Delta H$ , are reported for  $x_{\text{Fe}} = 0.1-0.75$ . The integral Gibbs energies of formation, the partial Gibbs energies of formation, and the activities and activity coefficients for solid alloys are reported for  $x_{\text{Fe}} = 0.243-0.90$  at 1173 K. For liquid alloys at 1873 K, the integral and partial Gibbs energies, enthalpies, entropies, activities, and activity coefficients for Al and for Fe are reported for  $x_{\text{Fe}} = 0.0-1.0$ .

For the Al-Mn alloy system,  $C_p^\circ$  values from below 1 to 4.5 K are reported for  $x_{\text{Mn}} = 0.00045-0.167$ . The integral Gibbs energy, enthalpy, and entropy of formation for solid alloys at 980 K are reported. For liquid alloys at 1600 K, the integral and partial Gibbs energy, enthalpy, entropy, activity, and activity coefficients for Al and for Mn are reported for  $x_{\text{Mn}} = 0.0-1.0$ .

For all Al-Ni alloy system, low-temperature  $C_p^\circ$  values are reported for  $x_{\text{Ni}} = 0.25-0.90$ . High-temperature  $C_p^\circ$  values are reported for  $x_{\text{Ni}} = 0.5$  from 400 to 1500 K. The

room-temperature  $\Delta H$  are reported for  $x_{\text{Ni}} = 0.25-0.90$ . The recommended integral Gibbs energy of formation for solid alloys as well as other quantities are reported at 1273 K. For liquid alloys at 1873 K, integral  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$ , as well as partial quantities and the activity and activity coefficients for  $x_{\text{Ni}} = 0.0-1.0$  have been reported.

For the Al-Si alloy system, the integral and partial Gibbs energies, enthalpy, and entropy of formation for liquid alloys and the activity and activity coefficients are reported at 1700 K for the entire range of composition.

For the Al-Ti alloy system,  $C_p^\circ$  values are reported for several alloys and cover the temperature range from 1.4 to 1700 K. The room-temperature enthalpy of formation,  $\Delta H$ , is reported for  $x_{\text{Ti}} = 0.25-0.89$ . Integral and partial Gibbs energies of formation along with activities and activity coefficients for solid alloys are reported at 973 and 1780 K for  $x_{\text{Ti}} = 0.5-1.0$ . For liquid alloys at 2000 K, integral and partial enthalpies of formation covering the entire range of composition are also reported.

Units used are  $\text{J mol}^{-1}$  for the thermodynamic functions; the composition is expressed in mole fraction  $x$ .

## 2. General Background

To understand the nature of the metallic chemical bond in an alloy, knowledge of the electronic contribution to  $C_p^\circ$  is essential. A few such measurements, mainly those near liquid helium temperature, have been reported. The Kopp-Neumann additivity law usually supplies a reasonably good approximation a few hundred degrees above room tempera-

ture, except in the region near the curie temperature or at order-disorder transition in the alloy.

The relative partial molar Gibbs energy  $\Delta G_A$  of one of the components is frequently measured by the emf, vapor pressure, chemical equilibria, or distribution coefficients method. If  $\Delta G_A$  is known over a range of compositions which includes one composition where  $\Delta G_B$  of the other component is independently known, then  $\Delta G_B$  and the integral molar free energy  $\Delta G$  can be calculated over the entire composition range by the use of Gibbs-Duhem integration. If  $\Delta G_A$  is known over a temperature range, relative partial molar entropy can be calculated:  $\Delta S_A = -(\partial G_A / \partial T)_x$  at constant  $x = x_A$ , the atom fraction of A in the alloy. Thus partial and integral molar entropies and enthalpies can also be calculated. It is worth noting that errors in  $\Delta G_A$  measurements are multiplied when temperature coefficients are taken. Seemingly reliable  $\Delta G_A$  values may, therefore, produce erroneous  $\Delta S_A$  values. It is common practice to derive entropy values by combining the Gibbs energies with calorimetric enthalpies of formation ( $\Delta H$  values), which are measured from direct reaction of the metallic components in the calorimeter. Liquid metal solution calorimetry has had great success, but the accuracy of acid solution calorimetry has been disappointing. Combustion calorimetry presents formidable difficulties and, therefore, has not been often tried successfully.

### 3. Evaluation of Data

Knowledge of the functional form of the temperature dependence of a measured property is essential for the comparison of the same property values measured at different temperatures. Enthalpies and entropies can be assumed independent of temperature over moderate temperature range. Gibbs free energy values reported by different sources at different temperatures are difficult to compare in the absence of reliable entropy values.

All experimental results of the same property at various temperatures are plotted as a function of temperature after the properties have been reduced, wherever possible, to a single evaluating temperature. The best results are obtained if the data are expressed in the form of a function which varies comparatively slowly with composition. The  $\alpha$  function has proven satisfactory for partial molar free energies:

$$\alpha_A = \Delta G_A^{\text{ex}} / (1 - x_A)^2.$$

If  $\Delta G_A$  (or  $\alpha_A$ ) is known over a range of concentration and  $\Delta G_B$  (or  $\Delta G_B^{\text{ex}}$ ) is known independently at one concentration  $x_0$ , then  $\Delta G_B$  can be calculated over the entire range of concentration by the following equation derived from the Gibbs-Duhem relation:

$$\begin{aligned} \Delta G_{B,x}^{\text{ex}} &= \Delta G_{B,x_0}^{\text{ex}} + x_0(1 - x_0)\alpha_{A,x_0} \\ &\quad - x(1 - x)\alpha_{A,x} + \int_{x_0}^x \alpha_A \, dx. \end{aligned}$$

For  $\Delta G_B^{\text{ex}} = 0$  at  $x_0 = 0$ ,

$$\Delta G_{B,x}^{\text{ex}} = -(1 - x)\alpha_{A,x} + \int_0^x \alpha_A \, dx.$$

The  $\beta$  function has similar advantages:

$$\beta_A = \Delta S_A^{\text{ex}} / (1 - x_A)^2.$$

The Gibbs-Duhem integration can be carried out by substituting  $\beta_A$  for  $\alpha_A$  in the above equation to obtain  $\Delta S_B$ . From  $\Delta G$  and  $\Delta S$  of the two components, it is easy to calculate partial enthalpies and other integral quantities.

For analyzing measured enthalpies by calorimetry, the  $Q$  function is useful:

$$Q = \Delta H / x(1 - x).$$

Partial quantities can be derived from the  $Q$  function:

$$\Delta H_A = x_B^2 \left( Q - x_A \frac{dQ}{dx_B} \right),$$

$$\Delta H_B = x_A^2 \left( Q - x_B \frac{dQ}{dx_A} \right).$$

Entropies calculated from these enthalpies and Gibbs energies from equilibrium measurements are normally more accurate than those derived solely from the temperature coefficients.

## 4. Thermodynamic Properties of Al-Fe Binary Alloy System

### 4.1. Phase Diagram and Structures

The phase diagram shown in Fig. 1 was taken from Kubaschewski<sup>1</sup> without further evaluation. The main characteristics are a wide ( $\alpha$ -Fe) solid solution and five stable phases with homogeneity ranges. The ordered  $\beta'$ (AlFe) region is now divided into two additional fields, namely, high-

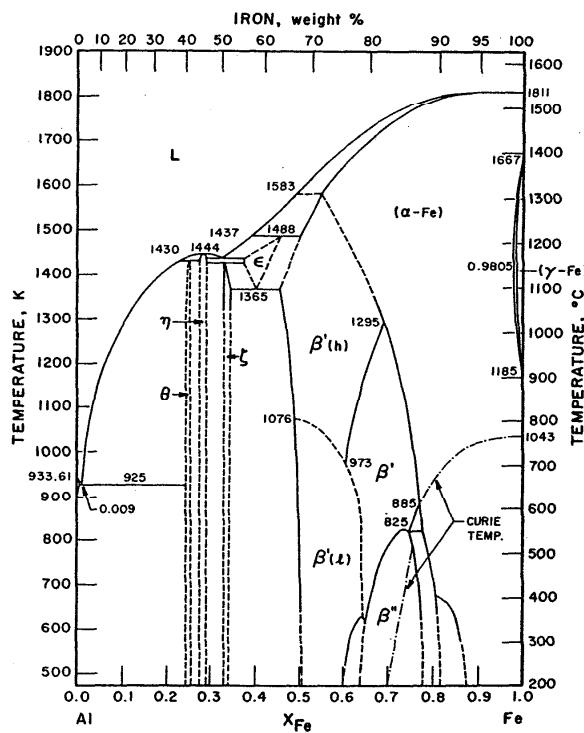


FIG. 1. Aluminum-iron phase diagram.

temperature  $\beta'$ (h) and low-temperature  $\beta'(\ell)$ . Transformation between these three phases is reversible. The aluminum-rich region below 1000 K is extremely complicated and many features reported so far are not completely resolved. Pearson<sup>2,3</sup> lists the following phases:

$\theta$ , " $\theta$ -Al<sub>3</sub>Fe," with a very complex end-centered monoclinic structure.

$\eta$ , " $\eta$ -Al<sub>5</sub>Fe<sub>2</sub>," with an end-centered orthorhombic structure.

$\beta'$ , "AlFe," with an ordered bcc (B2) structure isotropic with CsCl.

$\beta''$ , "AlFe<sub>3</sub>," with an ordered bcc (DO<sub>3</sub>) structure isotropic with BiF<sub>3</sub> (confirmed by Lesoille and Gielen<sup>4</sup>).

"Al<sub>6</sub>Fe," with an orthorhombic structure isotropic with Al<sub>6</sub>Mn. This is a metastable phase (not shown on the phase diagram).

Hansen<sup>5</sup> reported structures for the following phases:

$\zeta$ , " $\zeta$ -Al<sub>2</sub>Fe," with a complex rhombohedral structure.

$\epsilon$ , with a complex bcc structure (nearly hexagonal with parameters very similar to those of  $\zeta$ -Al<sub>2</sub>Fe according to Taylor and Jones<sup>6</sup>).

du Chatenier and Goedemoed<sup>7</sup> found from  $C_p^{\circ}$  measurements that a very small amount of Fe ( $x_{\text{Fe}} = 0.001$ ) raised the superconducting transition temperature of Al from 1.16 to 1.5 K.

#### 4.2. Solid Alloys

The  $C_p^{\circ}$  values of Table 1 were taken from the data of Cheng *et al.*<sup>8</sup> The data for  $x_{\text{Fe}} = 0.50$  showed a marked "upturn anomaly," which was explained as being due to the formation of magnetic clustering and was confirmed by Pakchanin *et al.*<sup>9</sup> A series of investigations by Pakchanin *et al.*<sup>9-11</sup> for  $x_{\text{Fe}} = 0.5-0.88$  and Okamoto and Beck<sup>13</sup> for  $x_{\text{Fe}} = 0.75$  indicated a decrease in the electronic specific heat  $\gamma$ , and the Debye temperature  $\theta_D$ , with an increase in the degree of short or long range ordering and some uncertainty in the derived  $\gamma$  value. These  $\gamma$  values are in generally fair agreement with those of Cheng *et al.*<sup>8</sup> except for the lower value of  $x_{\text{Fe}} = 0.50$  alloy. Electronic specific heat coefficient values from these and other investigations are also reported in Table 2.

Table 1. Low-temperature data for solid Al-Fe alloys

$x_{\text{Fe}}$	Phase	$T, \text{K}$				$\gamma \times 10^3$	$\theta_D, \text{K}$
		1.4	2	3	4		
		$C_p^{\circ} \times 10^2, \text{J mol}^{-1}\text{K}^{-1}$					
0.512	$a_2(\ell)$	3.18	3.95	5.27	6.61	12.76**	440
0.5914	$a_2(\ell)$	1.88	2.75	4.32	6.15	13.18	242
0.6392	$\beta''$	1.81	2.65	4.15	5.82	12.89	262
0.6977	$\beta''$	1.93	2.78	4.24	5.81	13.68	334
0.7547	$\beta'$	1.41	2.03	3.07	4.13	10.08	500
0.7547	$\beta''$	1.10	1.58	2.42	3.32	7.79	395
0.7547	( $\alpha$ -Fe)	1.38	1.99	3.06	4.20	9.79	353
0.7672	0.829	1.20	1.84	2.54	5.86	401	
0.8391	0.726	1.06	1.69	2.42	5.06	314	
0.8989	0.759	1.09	1.65	2.24	5.40	540	
0.9232	0.758	1.09	1.68	2.32	5.36	414	
0.9488	0.736	1.07	1.65	2.30	5.19	382	
1.000*	( $\alpha$ -Fe)	0.697	1.00	1.53	2.10	4.94	465

\* From recommended values for Fe.<sup>14</sup>

\*\*Anomalous behavior at lowest temperatures.

Table 2. Electronic specific heat coefficients of Al-Fe alloys

Source	$x_{\text{Fe}}$	Phase	$\gamma$ $\text{mJ mol}^{-1}\text{K}^{-2}$
Desai <sup>14</sup>	1.00	( $\alpha$ -Fe)	4.94
Shinozaki <sup>12</sup>	0.99	( $\alpha$ -Fe)	4.88
	0.98	( $\alpha$ -Fe)	4.95
Cheng <i>et al.</i> <sup>8</sup>	0.95	( $\alpha$ -Fe)	5.15
	0.92	( $\alpha$ -Fe)	5.36
	0.90	( $\alpha$ -Fe)	5.40
Pakchanin <i>et al.</i> <sup>9</sup>	0.88	( $\alpha$ -Fe)	4.98
	0.84	( $\alpha$ -Fe)	5.08
Cheng <i>et al.</i> <sup>8</sup>	0.84	( $\alpha$ -Fe)	5.06
	0.77	( $\alpha$ -Fe)	5.86
	0.75	( $\alpha$ -Fe)	9.79
Pakchanin <i>et al.</i> <sup>11</sup>	0.75	$\beta''$	8.74
Cheng <i>et al.</i> <sup>8</sup>	0.75	$\beta''$	7.79
Pakchanin <i>et al.</i> <sup>11</sup>	0.75	$\beta'$	9.63
Cheng <i>et al.</i> <sup>8</sup>	0.75	$\beta'$	10.08
	0.70	$\beta''$	13.68
Pakchanin <i>et al.</i> <sup>11</sup>	0.65	$\beta''$	12.80
Cheng <i>et al.</i> <sup>8</sup>	0.64	$\beta''$	12.89
	0.59	$\beta'(\ell)$	13.18
	0.512	$\beta'(\ell)$	12.76
Okamoto and Beck <sup>13</sup>	0.51	$\beta'(\text{h})$	10.71
	0.51	$\beta'(\ell)$	11.55

Minayev and Iveronova<sup>15</sup> graphically reported  $C_p^{\circ}$  data for alloys in the complex region of the phase diagram ( $x_{\text{Fe}} = 0.734-1.00$ ) where fully unresolved order-disorder transformations are occurring. These transformations produce  $\lambda$ -type anomalies, often with some first-order latent heats. Kinetic factors will displace these to higher temperatures and probably alter their shape. The  $C_p^{\circ}$  values reported in Table 3a are taken from these measurements. It is worth noting that superimposed ferromagnetic anomalies may depend on the degree of order present at the time of measurement in some compositions. Hence,  $C_p^{\circ}$  values from Table 3a may not represent equilibrium values for  $x_{\text{Fe}} = 0.734$  and 0.808. Minayev and Iveronova<sup>15</sup> and Iveronova *et al.*<sup>16</sup> found a dip in the  $C_p^{\circ}$  curve between 450 and 550 K for quenched alloys in the range  $x_{\text{Fe}} = 0.84-0.74$ . Similar behavior was observed by Troschkina and Kutcherenko<sup>17</sup> for FeAl( $\beta'$ ) alloy. The  $C_p^{\circ}$  values from Table 3b were taken from the data of Orehotsky and Schroder.<sup>18</sup> The data of Eguchi *et al.*<sup>19</sup> for  $x_{\text{Fe}} = 0.75$  yielded higher  $C_p^{\circ}$  values.

$\Delta H$  values in Table 4 were taken from the direct reaction calorimetry of Kubaschewski and Dench.<sup>20</sup>  $\Delta H$  values of Oelsen and Middell<sup>21</sup> were more exothermic than the tabulated values by about 400-2400 J mol<sup>-1</sup>, and those of Ferro<sup>22</sup> for  $x_{\text{Fe}} = 0.50$  were slightly less exothermic. Acid solution calorimetry of Biltz<sup>23</sup> for  $x_{\text{Fe}} = 0.75$  yielded values less exothermic by about 2000 J mol<sup>-1</sup>. These investigators did not make any attempt to establish the final state of the alloys they studied. Gorenkin *et al.*<sup>24</sup> measured the  $\Delta H$  for a number of aluminum alloys using an isothermal calorimetric technique. Their  $\Delta H$  value for  $x_{\text{Fe}} = 0.75$  is  $-30.96 \pm 8.4$  kJ mol<sup>-1</sup>, for  $x_{\text{Fe}} = 0.5$  is  $40.79 \pm 6.3$  kJ mol<sup>-1</sup>, and for  $x_{\text{Fe}} = 0.33$  is  $-18.83 \pm 6.3$  kJ mol<sup>-1</sup>.

The recommended  $\Delta G_{\text{Al}}$  values of Table 6 agree ( $+3200$  J mol<sup>-1</sup>) with the emf measurements of Radcliff *et al.*<sup>25</sup> and the vapor pressure measurements of Gross *et al.*,<sup>26</sup>

Table 3a. High-temperature heat capacity of solid Al-Fe alloys

T, K	$x_{\text{Fe}}$					
	0.734	0.808	0.837	0.851	0.887	1.000
	$C_p^0, \text{ J mol}^{-1}\text{K}^{-1}$					
350	27.68	28.54	27.79	28.32	27.95	27.54
400	27.68	28.92	27.87	28.33	28.07	27.77
500	27.74	29.73	28.36	28.79	28.57	28.47
600	29.54	30.74	29.69	30.34	29.92	30.00
640	30.89	32.13	30.90	31.26	30.90	31.04
650	31.13	32.79	32.14	31.50	31.19	31.35
700	32.40	37.14	34.73	32.89	32.92	32.98
729	33.40	40.31	35.43	33.88	34.04	34.03
750	34.28	39.40	35.84	34.70	34.88	34.81
775	35.58	39.11	36.30	35.74	36.02	35.77
800	37.73	40.05	36.75	36.90	37.19	36.95
838	43.83	41.79	37.39	38.73	39.48	39.24
880	36.82	43.90	38.42	40.88	42.54	42.29
900	37.21	44.96	30.35	41.94	44.14	43.82
920	37.73	46.01	45.10	43.06	45.76	45.39
935	38.20	45.62	53.56	44.00	47.03	46.67
950	38.74	45.24	49.08	45.14	48.39	48.04
992	40.67	44.68	44.12	58.77	54.30	52.97
1000	41.08	44.69	44.00	50.75	56.37	54.41
1021	42.28	45.01	44.11	47.60	69.04	59.95
1050	44.10	46.12	45.13	46.22	56.18	76.45
1053	44.31	46.28	45.30		55.82	79.12
1060	44.80	46.62	45.78		55.13	64.90
1080	46.24		47.48		53.79	56.41
1100	47.79		49.64		52.77	56.71
1110	48.62		50.81		52.31	56.88
1130	50.30		53.35		57.28	

Table 3b. High-temperature heat capacity of solid Al-Fe alloys

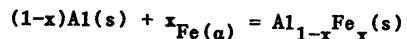
T, K	$x_{\text{Fe}}$			T, K	$x_{\text{Fe}}$		
	0.90	0.79	0.75		0.90	0.79	0.75
	$C_p^0, \text{ J mol}^{-1}\text{K}^{-1}$						
550	30.12	29.67		950	48.67	38.18	
600	31.50	31.34		975	51.43	38.96	
650	32.93	33.62		1000	56.52	37.37	
700	34.50	36.80		1017	61.35		
725	35.35	38.80		1025	50.73		
750	36.25	36.25	41.31	1050	46.05		
775	37.24	37.24	44.83	1075	43.13		
795	38.09	38.09	50.48	1100	41.73		
800	38.31	38.31	43.50	1150	40.36		
825	39.54	39.54	37.72	1200	39.50		
850	40.92	41.08	36.78	1250	38.91		
875	42.42	43.47	37.70	1300	38.47		
890	43.45	45.62	37.08	1350	38.14		
900	44.18	41.60	35.98	1400	37.89		
925	46.22	38.96					

except that the latter's value near  $x_{\text{Fe}} = 0.94$  is considerably less exothermic ( $16 \text{ kJ mol}^{-1}$ ). Isopiestic measurements of Eldridge and Komarek<sup>27</sup> are within  $\pm 8000 \text{ J mol}^{-1}$  of the recommended values. Vapor pressure measurements of Gulbransen and Andrews<sup>28</sup> at  $x_{\text{Fe}} = 0.894$  yielded much lower values of  $a_{\text{Fe}}$  than those recommended. Other quantities of

Table 4. Enthalpies of formation for solid Al-Fe alloys at 298.15 K<sup>a</sup>

$x_{\text{Fe}}$	Phase	$\Delta H$		$x_{\text{Fe}}$	Phase	$\Delta H$	
		$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$			$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$
0.25	$\theta$	-27.91		0.50	$\beta'$	-25.10	
0.333		[ $-18.83 \pm 6.3$ ]				[ $-40.79 \pm 6.3$ ]	
0.335		-26.15		0.60	$\beta'$	-19.98	
				0.70	$\beta'$ or $\beta''$	-15.73	
				0.75	$\beta''$	[ $130.96 \pm 8.4$ ]	
				0.80	( $\alpha\text{-Fe}$ ) <sup>b</sup>	-11.00	
				0.90	( $\alpha\text{-Fe}$ ) <sup>b</sup>	-5.77	

<sup>a</sup>Values in brackets are from Gorelkin et al.<sup>24</sup>  
<sup>b</sup>Final state uncertain.

Table 5. Recommended integral quantities for solid Al-Fe alloys at 1173 K<sup>a</sup>

$x_{\text{Fe}}$	Phase	$\Delta G$	$\Delta G^{\text{ex}}$
		$\text{J mol}^{-1}$	$\text{J mol}^{-1}$
0.243 <sup>b</sup>	$\theta$	0.716	0.946
0.257 <sup>b</sup>	$\theta$	0.228	0.306
0.274 <sup>b</sup>	$\eta$	0.228	-14435
0.290 <sup>b</sup>	$\eta$	0.128	-20083
0.320 <sup>b</sup>	$\zeta$	0.128	-20083
0.342 <sup>b</sup>	$\zeta$	0.073	-25522
0.48 <sup>b</sup>	$\beta'(\text{h})$	0.073	-25522
0.50		0.061	-27263
0.60	$\beta'(\text{h})$	0.022	-37094
0.70	$\beta'$	0.006	-49420
0.80	( $\alpha\text{-Fe}$ )	0.001	-64240
0.90	( $\alpha\text{-Fe}$ )	0.000	-82923
1.00	( $\alpha\text{-Fe}$ )	0.000	-

<sup>a</sup>Note standard states.

<sup>b</sup>Phase boundaries.

Tables 5 and 6 were calculated from the recommended ones using the Gibbs-Duhem relation.

### 4.3. Liquid Alloys

The recommended  $\Delta G_{\text{Al}}$  values of Table 8 are in general based ( $\pm 1500 \text{ J mol}^{-1}$ ) on the values calculated from the distribution of Al between  $\text{Ag}(\ell)$  and  $\text{Fe}(\ell)$  by Chipman and Floridis<sup>29</sup> and on the emf data of Batalin et al.<sup>30</sup> Woolley and Elliott<sup>31</sup> calculated  $\Delta G_{\text{Al}}$  values from the data of Chipman and Floridis,<sup>29</sup> which are about  $2700 \text{ J mol}^{-1}$  less exothermic. The values of Vachet et al.<sup>32</sup> from their data of distribution between  $\text{Ag}(\ell)$  and  $\text{Fe}(\ell)$  are  $500 \text{ J mol}^{-1}$  less exothermic for  $x_{\text{Fe}} > 0.8$  and up to  $2400 \text{ J mol}^{-1}$  more exothermic than the recommended values for  $x_{\text{Fe}} < 0.8$  with the largest deviation occurring at  $x_{\text{Fe}} = 0.5$ . The following lower temperature measurements were corrected to 1873 K using the recommended  $\Delta S_{\text{Al}}$  values which compare with the recommended  $\Delta G_{\text{Al}}$  values as follows. The emf studies of

Table 6. Recommended partial molar quantities for solid Al-Fe alloys at 1173 K<sup>a</sup>

$x_{\text{Fe}}$	Phase	$\text{Al}$ component $\text{Al}(s) = \text{Al}(\text{alloy})(s)$			$\text{Fe}$ component $\text{Fe}(\text{a}) = \text{Fe}(\text{alloy})(s)$		
		$\gamma_{\text{Al}}$	$\Delta G_{\text{Al}}$	$\Delta G_{\text{Al}}^{\text{ex}}$	$\gamma_{\text{Fe}}$	$\Delta G_{\text{Fe}}$	$\Delta G_{\text{Fe}}^{\text{ex}}$
		$\text{J mol}^{-1}$	$\text{J mol}^{-1}$	$\text{J mol}^{-1}$		$\text{J mol}^{-1}$	$\text{J mol}^{-1}$
0.243 <sup>b</sup>	$\theta$	0.716	0.946	-3255	-540	0.000	0.001
0.257 <sup>b</sup>	$\theta$	0.228	0.306	-14435	-11538	0.005	0.020
0.274 <sup>b</sup>	$\eta$	0.228	0.314	-14435	-11312	0.005	0.019
0.290 <sup>b</sup>	$\eta$	0.128	0.180	-20083	-16743	0.022	0.077
0.320 <sup>b</sup>	$\zeta$	0.128	0.190	-20083	-16177	0.022	0.068
0.342 <sup>b</sup>	$\zeta$	0.073	0.111	-25522	-21440	0.067	0.197
0.48 <sup>b</sup>	$\beta'(\text{h})$	0.073	0.140	-25522	-19145	0.067	0.140
0.50		0.061	0.122	-27263	-20503	0.081	0.162
0.60	$\beta'(\text{h})$	0.022	0.056	-37094	-28158	0.184	0.307
0.70	$\beta'$	0.006	0.021	-49420	-37678	0.364	0.520
0.80		0.001	0.007	-64240	-48544	0.603	0.754
0.90		0.000	0.002	-82923	-60466	0.843	0.936
1.00	( $\alpha\text{-Fe}$ )	0.000	0.000	-	-72200	1.000	1.000

<sup>a</sup>Note standard states.

<sup>b</sup>Phase boundaries.

Table 7. Recommended integral quantities for liquid Al-Fe alloys at 1873 K  
 $(1-x)Al(\infty) + xFe(\infty) = Al_{(1-x)}Fe_x(\infty)$

$x_{Fe}$	$\Delta G$	$\Delta H$	$\Delta G^{\text{ex}}$	$\Delta S$	$\Delta S^{\text{ex}}$
	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
0.1	-10012	-8383	-4949	0.870	-1.833
0.2	-16293	-14291	-8500	1.069	-3.092
0.3	-20319	-17997	-10806	1.240	-3.839
0.4	-22483	-19740	-12002	1.465	-4.131
0.5	-22990	-19742	-12196	1.734	-4.029
(±1.00)	(±1.700)	(±2.5)	(±21.00)	(±2.5)	
0.6	-21964	-18175	-11484	2.023	-3.573
0.7	-19390	-15265	-9877	2.202	-2.876
0.8	-15210	-11165	-7418	2.160	-2.001
0.9	-9183	-6029	-4121	1.684	-1.018

Ichise *et al.*<sup>33</sup> (1673 K) are up to 1900 J mol<sup>-1</sup> less exothermic, except their values are 800 J mol<sup>-1</sup> more exothermic for  $x_{Fe} = 0.9$ , while those of Mitani and Nagai<sup>34</sup> (1473 K) are up to 3800 J mol<sup>-1</sup> less exothermic. Vapor pressure studies of Coskum and Elliott<sup>35</sup> (1588 K) are up to 500–4500 J mol<sup>-1</sup> more exothermic, while those of Gross *et al.*<sup>26</sup> (1573 K) are about 2100 J mol<sup>-1</sup> less exothermic. Mass spectrometric vapor pressure measurements of Belton and Fruehan<sup>38</sup> yielded  $\Delta G_{Al}$  values 400–6000 J mol<sup>-1</sup> less exothermic than the recommended values for  $x_{Fe} < 0.8$ , the largest deviation occurring at high Fe contents. The emf studies of Fruehan<sup>39</sup> for  $x_{Fe} = 0.97$ –0.9996 and those of Sudavstova and Batalin<sup>40</sup> for  $x_{Fe} = 0.90$ –0.98 yielded considerably more exothermic  $\Delta G_{Al}$  values.

The recommended  $\Delta H$  values of Table 7 are primarily based on the direct reaction calorimetry of Woolley and Elliott<sup>31</sup> (90–980 J mol<sup>-1</sup> more exothermic) and the high-temperature isothermal calorimetric values of Petrushevskii *et al.*<sup>41</sup> (150 J mol<sup>-1</sup> less exothermic for  $x_{Fe} \geq 0.8$  and up to 1300 J mol<sup>-1</sup> more exothermic for  $x_{Fe} < 0.8$ ). Jounel *et al.*<sup>36</sup> and Mathieu *et al.*<sup>37</sup> reported a value of -128.4 kJ mol<sup>-1</sup> at 971 K for  $\Delta H_{Fe}$  at  $x_{Fe} = 0.0$ , while Dannoh and Lukas<sup>42</sup> reported a value of -121.8 kJ mol<sup>-1</sup> at 1023 K. These values compare with the recommended value of -97.4 kJ mol<sup>-1</sup> at 1873 K and 95.19 kJ mol<sup>-1</sup> reported by Petrushevskii *et al.*<sup>41</sup> Other quantities from Tables 7 and 8 are calculated from the recommended  $\Delta G_{Al}$  and  $\Delta H$  values using the Gibbs–Duhem relation.

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Table 8. Recommended partial molar quantities for liquid Al-Fe alloys at 1873 K  
 $Al(\infty) + Fe(\infty) = Al_{(1-x)}Fe_x(\infty)$

Al Component			$Al(\infty) = Al$ (in alloy)( $\infty$ )				
$x_{Al}$	$*_{Al}$	$\gamma_{Al}$	$\Delta G_{Al}$	$\Delta G_{Al}^{\text{ex}}$	$\Delta H_{Al}$	$\Delta S_{Al}$	$\Delta S_{Al}^{\text{ex}}$
			J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.859	0.954	-2367	-727	-1292	0.574	-0.302
0.8	0.673	0.841	-6167	-2692	-4754	0.755	-1.101
0.7	0.488	0.697	-11170	-5616	-9946	0.654	-2.312
0.6	0.331	0.551	-17235	-9280	-16381	0.456	-3.791
0.5	0.209	0.418	-24594	-13600	-23805	0.315	-5.449
	(±0.027)	(±0.053)	(±21.00)	(±2.5)	(±35.00)	(±2.5)	(±2.5)
0.4	0.122	0.304	-32791	-18522	-31813	0.522	-7.096
0.3	0.064	0.212	-42882	-24132	-39999	1.539	-8.471
0.2	0.028	0.141	-55534	-30470	-48320	3.851	-9.530
0.1	0.009	0.090	-73369	-37511	-56473	9.020	-10.124
0.0	0.000	0.055	∞	-45290	-64300	0.000	-10.149

Fe Component  $Fe(\infty) = Fe$  (in alloy)( $\infty$ )

$x_{Fe}$	$*_{Fe}$	$\gamma_{Fe}$	$\Delta G_{Fe}$	$\Delta G_{Fe}^{\text{ex}}$	$\Delta H_{Fe}$	$\Delta S_{Fe}$	$\Delta S_{Fe}^{\text{ex}}$
			J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
0.0	0.000	0.026	∞	-57053	-97400	∞	-21.541
0.1	0.006	0.063	-78813	-42956	-72195	3.533	-15.611
0.2	0.026	0.130	-56796	-31733	-52442	2.325	-11.057
0.3	0.069	0.230	-41665	-22915	-36782	2.507	-7.403
0.4	0.142	0.356	-30352	-16086	-24779	2.977	-4.641
0.5	0.250	0.500	-21586	-10791	-15680	3.153	-2.610
	(±0.032)	(±0.062)	(±21.00)	(±2.5)	(±35.00)	(±2.5)	(±2.5)
0.6	0.388	0.647	-14746	-6791	-9083	3.023	-1.224
0.7	0.550	0.785	-9322	-3768	-4665	2.487	-0.479
0.8	0.719	0.899	-5129	-1654	-1876	1.737	-0.118
0.9	0.877	0.974	-2052	-411	-424	0.869	-0.007
1.0	1.000	1.000	0	0	0	0.000	0.000

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## 5. Thermodynamic Properties of Al-Mn Binary Alloy System

### 5.1. Phase Diagram and Structures

The phase diagram shown in Fig. 2 was taken from Gedecke and Koster.<sup>1</sup> It differs from the previously reported phase diagram in the following respects: the high-temperature modification of  $\text{Al}_{11}\text{Mn}_{4\text{H}}$  has an extended range of homogeneity and the room-temperature modification  $\text{Al}_{11}\text{Mn}_{4\text{K}}$  is a single phase, while  $\gamma_2(\text{AlMn})$ -phase has two high-temperature modifications,  $\gamma$  and  $\gamma_1$ . Metastable  $\text{Al}_{10}\text{Mn}_3$  appears at moderate cooling rates. Rao *et al.*<sup>2</sup> identified several other intermediate metastable phases by annealing the rapidly quenched Al-rich commercial Al-Mn alloys. Refinement of the phase diagram and the identification of new metastable phases have been reported, e.g., Shechtman *et al.*,<sup>3</sup> Varich *et al.*,<sup>4</sup> Gorichok and Vengrenovich,<sup>5</sup> Teplova *et al.*,<sup>6</sup> Vintainkin *et al.*,<sup>7</sup> and by Sakamoto *et al.*<sup>8</sup> Gedecke and Koster<sup>1</sup> and Pearson<sup>9</sup> report the following intermediate phases:

$\epsilon$ , "Al<sub>6</sub>Mn," with the orthorhombic ( $D_{2h}$ ) prototype structure.

$\zeta$ , "Al<sub>4</sub>Mn," with a hexagonal structure.

$H$ , "Al<sub>11</sub>Mn<sub>4H</sub>," with an orthorhombic structure.

$\lambda$ , "Al<sub>11</sub>Mn<sub>4R</sub>," with a triclinic structure.

$\gamma$ , " $\eta$ -Al-Mn," with a hexagonal structure.

$\gamma_2$ , with a bc rhombohedral structure.

$\epsilon$ , with a hexagonal structure.

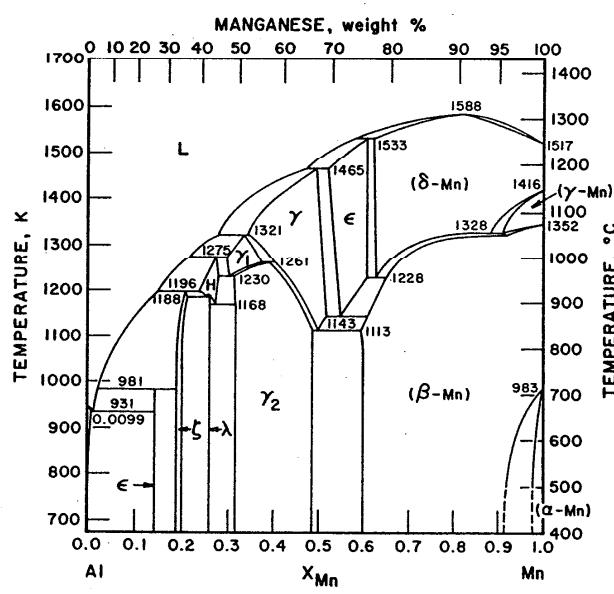


FIG. 2. Aluminum-manganese phase diagram.

Table 9. Low-temperature heat capacity of solid Al-Mn alloys

T, K	$x_{\text{Mn}}$			
	0.00045	0.001	0.004	0.167
	$C_p^{\circ}, \text{J mol}^{-1}\text{K}^{-1}$			
0.4	0.00054 <sup>a</sup>			
0.5	0.00103 <sup>a</sup>			
0.84	0.00270 <sup>a</sup>			
1.0	0.00139			
1.4	0.00215	0.00206	0.00207	0.00197
2.0		0.00306	0.00304	0.00286
3.0		0.00500	0.00484	0.00449
4.0		0.00744	0.00699	0.00635
4.5				0.00739
	$\gamma \times 10^3$ $\text{J mol}^{-1}\text{K}^{-2}$	1.42	1.45	1.38

<sup>a</sup>Superconductor.

### 5.2. Solid Alloys

$C_p^{\circ}$  values of Table 9 were taken from the data of Martin.<sup>10</sup> He found that the electronic specific heat term  $\gamma$  is the same for aluminum and the single alloy ( $x_{\text{Mn}} = 0.00045$ ), which he measured in the normal state, and that the superconducting transition temperature  $T_c$  dropped to 0.84 K from 1.160 K for pure aluminum. However,  $C_p^{\circ}$  measurements of Aoki and Ohtsuka<sup>11</sup> for  $x_{\text{Mn}} = 0.001$  and 0.004 indicated an increase in  $\gamma$  with composition.  $C_p^{\circ}$  values for  $x_{\text{Mn}} = 0.167$  were taken from the data of Dunlop *et al.*<sup>12</sup>

The  $\Delta G$  values in Table 10 were based on the emf studies of Samokhval and Vecher,<sup>13</sup> who reported only integral quantities.  $\Delta H$  values were based on the temperature coefficients of Samokhval and Vecher,<sup>13</sup> which were referred to Al(s) assuming  $\Delta_{\text{fus}}S^{\circ} = 11.337 \text{ J mol}^{-1}\text{K}^{-1}$  for Al invariant with  $T$ . Reaction calorimetry of Kubaschewski and Heymer<sup>14</sup> yielded values in fair agreement with those report-

Table 10. Integral quantities for liquid Al-Mn alloys at 980 K<sup>a</sup>

$x_{\text{Mn}}$	Phase	$\Delta G$ $\text{J mol}^{-1}$	$\Delta H$ $\text{J mol}^{-1}\text{K}^{-1}$	$\Delta S$ $\text{J mol}^{-1}\text{K}^{-1}$
0.142	$\epsilon$		-15750	
0.190	$\zeta$		-20050	
0.20	$\zeta$		-20900	
0.267	$\lambda$		-22050	
0.32	$\gamma_2$		-22920	
0.40		-21070	-24080	-3.071
0.45		-20640	-24410	-3.847
		(±3000)	(±3000)	(±3.00)
0.485	$\gamma_2$		-24500	
0.60	( $\beta$ -Mn)		-24000	
0.68		-18410	-22710	-4.388
0.75		-16030	-19950	-4.000
0.80		-13830	-17250	-3.490
0.85		-11170	-13810	-2.694
0.90	( $\beta$ -Mn)		-9680	

<sup>a</sup>Note standard states.

Table 11. Recommended integral quantities for liquid Al-Mn alloys at 1600 K  
 $(1-x)Al(\text{L}) + xMn(\text{L}) = Al_{(1-x)}Mn_x(\text{L})$

$x_{\text{Mn}}$	$\Delta G$	$\Delta H$	$\Delta G^{\text{ex}}$	$\Delta S$	$\Delta S^{\text{ex}}$
	J mol $^{-1}$	J mol $^{-1}$	J mol $^{-1}$ K $^{-1}$	J mol $^{-1}$	J mol $^{-1}$ K $^{-1}$
0.1	-7322	-6392	-2997	0.581	-2.122
0.2	-11986	-11901	-5329	0.053	-4.108
0.3	-15462	-15414	-7034	-0.126	-3.230
0.4	-17216	-16908	-8263	0.192	-5.403
0.5	-18521	-16848	-9300	1.046	-4.718
(±0.000)	(±4000)	(±3000)	(±2.50)	(±2.50)	
0.6	-19232	-15470	-10279	2.350	-3.244
0.7	-18979	-13171	-10853	3.630	-1.449
0.8	-16998	-10048	-10342	4.344	0.184
0.9	-12217	-5687	-7893	4.081	1.379

ed by Samokhval and Vecher<sup>13</sup> except at  $x_{\text{Mn}} = 0.50$ , where they were about 3000 J mol $^{-1}$  less exothermic. Most of their measurements were in questionable one-phase regions. Although Kubaschewski and Heymer<sup>14</sup> claimed that they checked the completeness of alloy formation, they failed to give the structure and phases to which their alloys belong.

### 5.3. Liquid Alloys

The recommended  $\Delta H$  values in Table 11 were based on the calorimetric measurements of Esin *et al.*,<sup>15</sup> who measured  $\Delta H_{\text{Al}}$  from  $x_{\text{Mn}} = 0.4$ –1.0 and  $\Delta H_{\text{Mn}}$  from  $x_{\text{Mn}} = 0.0$ –0.4. They did not report experimental data; instead, smooth values of partial and integral enthalpies covering the entire composition range were reported. A consistency check of their partial quantities using the Gibbs–Duhem relation failed to produce reasonably close  $\Delta H_{\text{Mn}}$  from  $\Delta H_{\text{Al}}$  values. Therefore,  $\Delta H_{\text{Al}}$  and  $\Delta H_{\text{Mn}}$  values in Table 12 were recalculated from their  $\Delta H$  values.  $\Delta H_{\text{Al}}$  values reported by Esin *et al.*<sup>15</sup> are up to 3300 J mol $^{-1}$  (at  $x_{\text{Mn}} = 0.5$ ) less exothermic and  $\Delta H_{\text{Mn}}$  are up to 4450 J mol $^{-1}$  (at  $x_{\text{Mn}} = 0.3$ ) more exothermic than the recommended values.

The recommended  $\Delta G_{\text{Mn}}$  values in Table 12 are based on the tabulated  $\Delta G_{\text{Al}}^{\text{ex}}$  values of Batalin *et al.*<sup>16</sup> derived from their measured emf data and the calculated  $\Delta G_{\text{Al}}^{\text{ex}}$  and  $\Delta S_{\text{Al}}^{\text{ex}}$  values. It is worth noting that the emf data, which they reported graphically, failed to reproduce their tabulated partial quantities, especially for low Mn concentrations. Other quantities in Tables 11 and 12 were calculated from the recommended  $\Delta G_{\text{Mn}}$  values, using the Gibbs–Duhem relation, the partial and the integral enthalpy values.

### 5.4. References

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Table 12. Recommended partial molar quantities for liquid Al-Mn alloys at 1600 K

$x_{\text{Al}}$	$a_{\text{Al}}$	$\gamma_{\text{Al}}$	$\Delta G_{\text{Al}}$	$\Delta G_{\text{Al}}^{\text{ex}}$	$\Delta H_{\text{Al}}$	$\Delta S_{\text{Al}}$	$\Delta S_{\text{Al}}^{\text{ex}}$
			J mol $^{-1}$	J mol $^{-1}$	J mol $^{-1}$	J mol $^{-1}$	J mol $^{-1}$ K $^{-1}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.878	0.975	-1735	-333	-202	0.958	0.082
0.8	0.725	0.906	-4286	-1318	-2691	0.997	-0.858
0.7	0.570	0.814	-7488	-2744	-8244	-0.473	-3.438
0.6	0.445	0.741	-10775	-3980	-14200	-2.141	-6.388
0.5	0.365	0.731	-13396	-4175	-20707	-4.569	-10.322
(±0.110)	(±0.053)	(±1000)	(±1000)	(±1000)	(±1000)	(±2.50)	(±2.50)
0.4	0.274	0.685	-17222	-5033	-26968	-6.091	-13.709
0.3	0.142	0.474	-25941	-9925	-31413	-3.420	-13.430
0.2	0.042	0.212	-42047	-20636	-39840	1.379	-12.002
0.1	0.004	0.040	-73340	-42709	-50738	14.126	-5.018
0.0	0.000	0.000	∞	-121272	-63800	=	35.920

$x_{\text{Mn}}$	$a_{\text{Mn}}$	$\gamma_{\text{Mn}}$	$\Delta G_{\text{Mn}}$	$\Delta G_{\text{Mn}}^{\text{ex}}$	$\Delta H_{\text{Mn}}$	$\Delta S_{\text{Mn}}$	$\Delta S_{\text{Mn}}^{\text{ex}}$
			J mol $^{-1}$	J mol $^{-1}$	J mol $^{-1}$	J mol $^{-1}$	J mol $^{-1}$ K $^{-1}$
0.0	0.000	0.082	—	-33300	-64600	—	-19.562
0.1	0.013	0.132	-57604	-26973	-62103	-2.812	-21.956
0.2	0.040	0.201	-42786	-21376	-48739	-3.721	-17.102
0.3	0.083	0.278	-33068	-17052	-32144	0.578	-9.433
0.4	0.133	0.332	-26877	-14688	-20970	3.692	-3.926
0.5	0.169	0.338	-23646	-14425	-12988	6.661	0.898
(±0.044)	(±0.088)	(±4000)	(±4000)	(±4000)	(±4000)	(±2.50)	(±2.50)
0.6	0.213	0.355	-20571	-13776	-7806	7.978	-3.731
0.7	0.300	0.429	-15995	-11250	-5353	6.651	3.686
0.8	0.446	0.558	-10736	-7168	-2600	5.085	3.230
0.9	0.665	0.739	-5425	-4024	-681	2.965	2.089
1.0	1.000	1.000	0	0	0	0.000	0.000

<sup>11</sup>R. Aoki and T. Ohtsuka, J. Phys. Soc. Jpn. **26**, 651 (1969).

<sup>12</sup>J. B. Dunlop, G. Gruner, and A. D. Caplin, J. Phys. F **4**, 2203 (1974).

<sup>13</sup>V. S. Samokhval and A. A. Vecher, Izv. Akad. Nauk SSSR Met. **2**, 75 (1971).

<sup>14</sup>O. Kubaschewski and G. Heymer, Trans. Faraday Soc. **56**, 473 (1960).

<sup>15</sup>Yu. O. Esin, N. T. Bobrov, M. S. Petrushevskii, and P. V. Gel'd, Russ. J. Phys. Chem. **47**, 1103 (1973).

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## 6. Thermodynamic Properties of Al-Ni Binary Alloy System

The phase diagram shown in Fig. 3 was taken from the preliminary investigation of Singleton *et al.*<sup>1</sup> In general, this

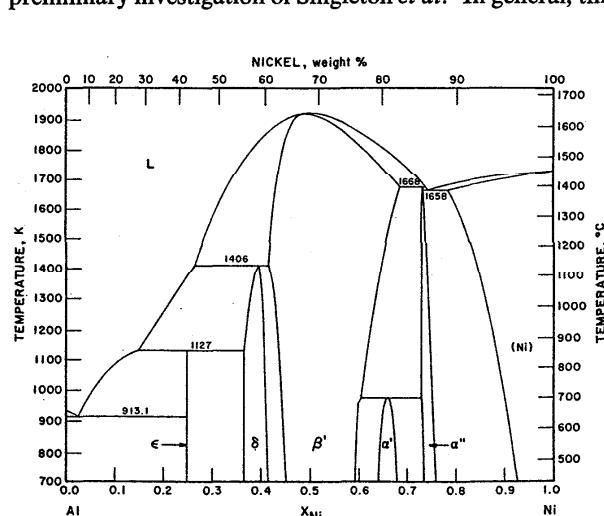


FIG. 3. Aluminum–nickel phase diagram.

Table 13. Low-temperature heat capacity of solid Al-Ni alloys

T, K	$x_{Ni}$									
	0.25	0.46	0.49	0.51	0.53	0.56	0.75	0.90	1.00	
$C_p^o, J \text{ mol}^{-1} \text{ K}^{-1}$										
1.5		0.0018	0.0020							
2	0.0027	0.0025	0.0027	0.0031	0.0034	0.0039	0.0177	0.0150	0.0142	
3	0.0043	0.0038	0.0043	0.0048	0.0054	0.0062	0.0266	0.0228	0.0217	
4	0.0064	0.0054	0.0062	0.0069	0.0078	0.0090	0.0355	0.0315	0.0295	
5						0.0129	0.0447		0.0381	
6							0.0543		0.0477	
7							0.0645		0.0583	
8							0.0756		0.0698	
9							0.0877		0.0826	
10							0.101		0.0963	
11							0.116			
12							0.133			
13							0.153			
14							0.178			
	$\gamma$	1.24	1.19	1.31	1.37	1.50	1.52	6.50	6.82	7.055
	$\text{mJ mol}^{-1} \text{ K}^{-2}$									

phase diagram is similar to the one assessed by Hultgren *et al.*,<sup>2</sup> although a new phase,  $\text{Al}_3\text{Ni}_5$  ( $\alpha'$ ), has been added. Singleton *et al.*<sup>1</sup> lists the following intermediate phases:

$\epsilon$ , "Al<sub>3</sub>Ni" has an orthorhombic (DO<sub>11</sub>) isotypic with CFe<sub>3</sub>.

$\delta$ , "Al<sub>3</sub>Ni<sub>2</sub>" has an ordered trigonal (D5<sub>13</sub>) prototype structure.

$\beta'$ , "AlNi" has an ordered bcc (B<sub>2</sub>) structure isotypic with CsCl. At high temperatures it probably transforms to a disordered phase (see Sec. 6.2).

$\alpha'$ , "Al<sub>3</sub>Ni<sub>5</sub>" has an orthorhombic structure isotypic with Ga<sub>3</sub>Pt<sub>5</sub>.

$\alpha''$ , "AlNi<sub>3</sub>" has an ordered fcc (L1<sub>2</sub>) structure isotypic with AuCu<sub>3</sub>.

## 6.2. Solid Alloys

The  $C_p^o$  values of Table 13 were taken from the data of

Table 14. High-temperature data for the ordered Al-Ni  $\beta'$ -phase,  $x_{Ni} = 0.50$ 

T K	$C_p^o$		T K	$C_p^o$	
	J $\text{mol}^{-1} \text{ K}^{-1}$	J $\text{mol}^{-1} \text{ K}^{-1}$		J $\text{mol}^{-1} \text{ K}^{-1}$	J $\text{mol}^{-1} \text{ K}^{-1}$
60	5.52		298.15	23.98	
80	8.97		300	23.01	
100	12.09		400	24.25	
120	14.47		500	24.84	
140	16.37		600	25.19	
160	17.93		700	25.51	
180	19.17		800	26.19	
200	20.16		900	27.42	
220	20.94		950	28.25	
250	21.89				

Gupta *et al.*<sup>3</sup> ( $x_{Ni} = 0.90$ ), of de Dood and de Chatel<sup>4</sup> ( $x_{Ni} = 0.75$ ), and of Dunlop *et al.*<sup>5</sup> ( $x_{Ni} = 0.25$ ), respectively.  $C_p^o$  values for other compositions were taken from Galli *et al.*,<sup>6</sup> who observed upturns in  $C_p^o/T$  versus  $T^2$  plots at the lower temperatures for alloys  $x_{Ni}$  compositions  $> 0.50$  which were confirmed by two other investigators. This behavior was partially attributed to the formation of magnetic clusters. de Dood and de Chatel<sup>4</sup> also measured  $C_p^o$  of several alloys in the range of existence of the AlNi<sub>3</sub> phase,  $\alpha''$  ( $x_{Ni} = 0.73-0.76$ ), and concluded that the most nearly ferromagnetic sample ( $x_{Ni} = 0.748$ ) had the highest heat capacity ( $\gamma = 7.77 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ).

$C_p^o$  values of Table 14 for  $x_{Ni} = 0.50$  were taken from the data of Sandakova *et al.*<sup>7</sup> and of Kucherenko and Troshkina.<sup>8</sup> Sandakova *et al.*<sup>7</sup> have reported

Table 15. High-temperature data for Al-Ni  $\alpha'$  phase,  $x_{Ni} = 0.766$ 

T K	$C_p^o$	
	J $\text{mol}^{-1} \text{ K}^{-1}$	J $\text{mol}^{-1} \text{ K}^{-1}$
400	24.40	
500	25.62	
600	26.55	
700	27.26	
800	27.96	
900	28.95	
1000	30.33	
1100	32.40	
1200	34.20	
1300	35.47	
1400	36.41	
1500	36.12	

Table 16. Enthalpies of formation for solid Al-Ni alloys at 298.15 K  
 $(1-x)Al(s) + xNi(s) = Al_{1-x}Ni_x(s)$

$x_{Ni}$	Phase	$\Delta H$ $J \text{ mol}^{-1} \text{ K}^{-1}$
0.25	$\epsilon$	-37850
0.368 <sup>a</sup>	$\delta$	-55500
0.40		-59050
0.415 <sup>a</sup>	$\delta$	-60500
0.451 <sup>a</sup>	$\beta'$	-66650
0.500		-71650 (+2000)
0.592 <sup>a</sup>	$\beta'$	-57100
0.640 <sup>a</sup>	$\alpha'$	-54000
0.680 <sup>a</sup>	$\alpha'$	-48050
0.734 <sup>a</sup>	$\alpha''$	-41000
0.759 <sup>a</sup>	$\alpha''$	-37550
0.930 <sup>a</sup>	(Ni)	-10950

<sup>a</sup>Approximate phase boundaries.

$H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 4320 \text{ J mol}^{-1}$  and  $S^\circ(298.15 \text{ K}) = 27.0 \text{ J mol}^{-1} \text{ K}^{-1}$  for this alloy.  $C_p^\circ$  measurements of Kucherenko and Troshkina,<sup>8</sup> Troshkina and Khomyakov,<sup>9</sup> and of Kucherenko *et al.*<sup>10</sup> on quenched and annealed samples indicated an order-disorder transformation in the  $\beta'$ -phase region. Moreover, Kucherenko *et al.*<sup>10</sup> reported that the disordering temperatures for nickel-rich alloys ( $\beta'$ -

Table 17. Recommended integral quantities for solid Al-Ni alloys at 1273 K<sup>a</sup>

$x_{Ni}$	Phase	$\Delta G$ $J \text{ mol}^{-1}$	$\Delta G^{\text{ex}}$
0.375 <sup>b</sup>	$\delta$	-47164	-40162
0.403 <sup>b</sup>	$\delta$	-49353	-42217
0.429 <sup>b</sup>	$\beta'$	-50791	-43562
0.45		-51938	-44654
0.50		-53931	-46595 (+8000)
0.55		-51810	-44527
0.60		-47869	-40746
0.631 <sup>b</sup>	$\beta'$	-44842	-37878
0.728 <sup>b</sup>	$\alpha$	-35392	-29200
0.742 <sup>b</sup>	$\alpha$	-33934	-27891
0.864 <sup>b</sup>		-20477	-16268
0.90	(Ni)	-16095	-12655
0.95		-8890	-6788

<sup>a</sup>Note standard states.  
<sup>b</sup>Phase boundaries.

phase region) were higher than those for  $x_{Ni} = 0.50$ . Additionally, Pop and Ilonca<sup>11</sup> have reported  $C_p^\circ$  data for  $x_{Ni} = 0.766$ . The  $C_p^\circ$  values of Table 15 were taken from the measurements of Kovaleav *et al.*<sup>12</sup>

$\Delta H$  values of Table 16 were essentially based on the calorimetric measurements of Oelsen and Middel<sup>13</sup> except in the  $\beta'$ -phase region, where more weight was given to the data of Henig and Lukas<sup>14</sup> and of Dannoehl and Lukas.<sup>15</sup> The data of Kubaschewski,<sup>16</sup> especially in the  $\beta'$ -phase region, are as much as 13  $\text{kJ mol}^{-1}$  less exothermic than the tabulated values. The data of Eskov *et al.*<sup>17</sup> and of Sandakova *et al.*<sup>7</sup> for  $x_{Ni} = 0.50$  are less exothermic by as much as 12  $\text{kJ mol}^{-1}$  and 10  $\text{kJ mol}^{-1}$ , respectively. The value reported by Bokshtein *et al.*<sup>18</sup> at  $x_{Ni} = 0.748$  from their temperature coefficients of vapor pressure measurements is in fair agreement with the tabulated value.

$\Delta G_{Al}$  values of Table 18 were based on the isopiestic measurements of Steiner and Komarek,<sup>19</sup> emf studies of Malkin and Pokidyshev,<sup>20</sup> of Schaefer and Gokcen,<sup>21</sup> and of Schaefer.<sup>22</sup> Other quantities in Tables 17 and 18 were calculated from  $\Delta G_{Al}$  values using the Gibbs-Duhem relation. Hanneman and Seybolt<sup>23</sup> carried out the Gibbs-Duhem integration of the data of Steiner and Komarek<sup>19</sup> without having access to the data of Malkin and Pokidyshev.<sup>20</sup> Their

Table 18. Recommended partial molar quantities for solid Al-Ni alloys at 1273 K<sup>a</sup>

Al component		$Al(s) = Al(\text{in alloy})(s)$		$\Delta G_{Al}$ $J \text{ mol}^{-1}$	$\Delta G_{Al}^{\text{ex}}$
$x_{Al}$	Phase	$\gamma_{Al}$	$\gamma_{Al}$		
0.625 <sup>b</sup>	$\delta$	0.446	0.714	-8544	-3569
0.597 <sup>b</sup>	$\delta$	0.0775	0.130	-27062	-21602
0.571 <sup>b</sup>	$\beta'$	0.0775	0.136	-27062	-21131
0.55		0.0704	0.128	-28090	-21762
0.50		0.0125	0.0250	-46400	-39064
		(+0.007)	(+0.013)	(+8000)	(+8000)
0.45		0.000197	0.000438	-90300	-81849
0.40		0.000068	0.000169	-101600	-91902
0.369 <sup>b</sup>	$\beta'$	0.000043	0.000117	-106322	-95780
0.272 <sup>b</sup>	$\alpha$	0.000043	0.000159	-106322	-92552
0.258 <sup>b</sup>	$\alpha$	0.000018	0.000069	-115780	-101441
0.136 <sup>b</sup>		0.000018	0.000131	-115780	-94664
0.10	(Ni)	0.0000031	0.000031	-134106	-109735
0.05		0.00000031	0.0000061	-158733	-127026
0.00		0.000	0.000	-∞	-144930
Ni component		$Ni(s) = Ni(\text{in alloy})(s)$		$\Delta G_{Ni}$ $J \text{ mol}^{-1}$	$\Delta G_{Ni}^{\text{ex}}$
$x_{Ni}$	Phase	$\gamma_{Ni}$	$\gamma_{Ni}$		
0.375 <sup>b</sup>	$\delta$	0.000027	0.000071	-111530	-101149
0.403 <sup>b</sup>	$\delta$	0.000416	0.00103	-82374	-72755
0.429 <sup>b</sup>	$\beta'$	0.000416	0.00097	-82374	-73417
0.45		0.000471	0.00105	-81085	-72634
0.50		0.00301	0.00601	-61462	-54126
		(±0.002)	(±0.003)	(±8000)	(±8000)
0.55		0.147	0.267	-20319	-13991
0.60		0.320	0.354	-12049	-6642
0.631 <sup>b</sup>	$\beta'$	0.432	0.684	-8890	-4017
0.728 <sup>b</sup>	$\alpha$	0.432	0.593	-8890	-5530
0.742 <sup>b</sup>	$\alpha$	0.596	0.803	-5476	-2317
0.864 <sup>b</sup>		0.596	0.690	-5476	-3928
0.90	(Ni)	0.754	0.838	-2983	-1868
0.95		0.910	0.957	-1003	-460
1.00		1.000	1.000	0	0

<sup>a</sup>Note standard states.  
<sup>b</sup>Phase boundaries.

Table 19. Recommended integral quantities for liquid Al-Ni alloys at 1873 K  
 $(1-x)Al(\ell) + xNi(\ell) = Al_{(1-x)}Ni_x(\ell)$

$x_{Ni}$	$\Delta G$	$\Delta H$	$\Delta G_{ex}^{ex}$	$\Delta S$	$\Delta S_{ex}^{ex}$
	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
0.1	-14737	-13637	-9675	0.587	-2.116
0.2	-25964	-26850	-18172	-0.473	-4.633
0.3	-34734	-38379	-25222	-1.946	-7.025
0.4	-40773	-46796	-30292	-3.216	-8.812
0.5	-42858	-50003	-32054	-3.815	-9.583
	(±8000)	(±1500)	(±8000)	(±4.270)	(±4.270)
0.6	-40326	-46960	-29855	-3.537	-9.133
0.7	-34745	-39589	-25232	-2.586	-7.665
0.8	-26362	-28874	-18569	-1.341	-5.502
0.9	-15122	-15460	-10060	-0.180	-2.883

$\Delta G_{Ni}$  values in most cases are as much as 2800 J mol<sup>-1</sup> less exothermic than the  $\Delta G_{Ni}$  values of Table 18.

### 6.3. Liquid Alloys

Vachet *et al.*<sup>28</sup> measured the distribution of Al between Ag( $\ell$ ) and Ni( $\ell$ ). They gave their results at 1873 K for  $x_{Ni} = 0.60\text{--}0.96$  in terms of  $\Delta G_{Al}$  only, which were calculated using Wilder and Elliott's<sup>29</sup> data for Ag-Al. Schaefer and Gokcen<sup>21</sup> and Schaefer<sup>22</sup> reported  $\Delta G_{Al}$  values from the emf studies. Their measurements covered the temperature range of 950–1200 K for  $x_{Ni} = 0.005\text{--}0.205$ . Therefore, the recommended  $\Delta H_{Al}$  values of Table 20 were combined with  $\Delta G_{Al}$  values and  $\Delta S_{Al}^{ex}$  values were calculated for each of these measurements. The recommended  $\Delta S_{Al}^{ex}$  values of Table 20, with the exception of the values for  $x_{Ni} = 0.2\text{--}0.6$  which were interpolated, were based on these calculated values. The  $\Delta S_{Ni}^{ex}$  values were calculated from the recommended  $\Delta S_{Al}^{ex}$  values using the Gibbs-Duhem relation. Other quantities of Tables 19 and 20 were calculated from the recommended  $\Delta H$  and  $\Delta S^{ex}$  values using the standard procedure. Mass spectrometric Knudsen-cell measurements of Johnston and Palmer<sup>30</sup> yielded  $\Delta G_{Al}$  values, which are up to 10 kJ mol<sup>-1</sup> less exothermic than the recommended values.

Sandakov *et al.*<sup>24</sup> measured  $\Delta H_{Al}$  for  $x_{Ni} = 0.40\text{--}1.00$  and  $\Delta H_{Ni}$  for  $x_{Ni} = 0.0\text{--}0.55$ . The partial molar enthalpies of other components were calculated by means of the Gibbs-Duhem equation. In order to obtain a consistent set of  $\Delta H_{Al}$  and  $\Delta H_{Ni}$  values, the Gibbs-Duhem calculations of  $\Delta H_{Al}$  values were carried out to obtain  $\Delta H_{Ni}$  values using the equation reported by Woolley and Elliott.<sup>25</sup> The  $\Delta H_{Al}$  and  $\Delta H_{Ni}$  values thus obtained are reported in Table 20, and  $\Delta H$  values calculated from these partial values are reported in Table 19.  $\Delta H$  values reported by Sandakov *et al.*<sup>24</sup> and by Bobrov *et al.*<sup>26</sup> are up to 400 J mol<sup>-1</sup> more exothermic for  $x_{Ni} > 0.6$  and up to 1600 J mol<sup>-1</sup> less exothermic below  $x_{Ni} = 0.6$ .  $\Delta H_{Al}$  and  $\Delta H_{Ni}$  values at infinite dilution reported in Table 20 are in fairly good agreement with those reported by Sandakov *et al.*,<sup>24</sup> Bobrov *et al.*,<sup>26</sup> and by Gorokhov *et al.*<sup>27</sup>

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Table 20. Recommended partial molar quantities for liquid Al-Ni alloys at 1873 K

Al component			$Al(\ell) = Al_{(in \ alloy)}(\ell)$				
$x_{Al}$	$\Delta G_{Al}$	$\Delta G_{Al}^{ex}$	$\Delta H_{Al}$	$\Delta S_{Al}$	$\Delta S_{Al}^{ex}$		
	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>		
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.868	0.964	-2204	-563	-18	1.167	0.291
0.8	0.680	0.851	-5996	-2521	-1684	2.302	0.447
0.7	0.458	0.654	-12172	-6618	-7605	2.439	0.527
0.6	0.222	0.371	-23413	-15458	-21936	0.788	-3.459
0.5	0.0561	0.112	-44858	-34064	-50500	-3.012	-8.775
	(±0.022)	(±0.044)	(±8000)	(±8000)	(±1500)	(±4.5)	(±4.5)
0.4	0.0152	0.0381	-65168	-50899	-79488	-7.646	-15.264
0.3	0.0046	0.0154	-83728	-64979	-103782	-10.707	-20.717
0.2	0.0012	0.0060	-104641	-79578	-126208	-11.515	-24.896
0.1	0.0002	0.0024	-130072	-94214	-146448	-8.744	-27.888
0.0	0.000	0.0010	-	-100840	-	-	-29.610

Ni component

Ni component			$Ni(\ell) = Ni_{(in \ alloy)}(\ell)$				
$x_{Ni}$	$\Delta G_{Ni}$	$\Delta G_{Ni}^{ex}$	$\Delta H_{Ni}$	$\Delta S_{Ni}$	$\Delta S_{Ni}^{ex}$		
	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>		
0.0	0.000	0.0013	-	-103971	-136400	-	-17.314
0.1	0.0003	0.0028	-127536	-91679	-136208	-4.630	-23.774
0.2	0.0011	0.0056	-105838	-80775	-127512	-11.571	-24.953
0.3	0.0037	0.0122	-87379	-68630	-110186	-12.177	-22.187
0.4	0.0137	0.0342	-66813	-52544	-84087	-9.223	-16.841
0.5	0.0726	0.145	-40838	-30044	-49506	-4.628	-10.391
	(±0.029)	(±0.058)	(±8000)	(±8000)	(±1500)	(±4.5)	(±4.5)
0.6	0.217	0.362	-23781	-15826	-25275	-0.798	-5.045
0.7	0.413	0.591	-13752	-8198	-12077	0.894	-2.071
0.8	0.647	0.808	-6792	-3317	-4540	1.202	-0.653
0.9	0.860	0.955	-2350	-709	-906	0.771	-0.105
1.0	1.000	1.000	0	0	0	0.000	0.000

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## 7. Thermodynamic Properties of Al-Si Binary Alloy System

### 7.1. Phase Diagram and Structures

The simple eutectic phase diagram with two solid solutions, (Al) phase with fcc and diamond cubic (Si) phase shown in Fig. 4 and similar to the one reported by Hultgren *et al.*,<sup>2</sup> was taken from Murray and McAlister.<sup>1</sup>

### 7.2. Liquid Alloys

The recommended  $\Delta H$  values of Table 21 agree within  $\pm 225 \text{ J mol}^{-1}$  with the reaction calorimetry of Bros *et al.*<sup>3</sup> Enthalpies reported by Korber *et al.*<sup>4</sup> are about  $900 \text{ J mol}^{-1}$  more exothermic than the recommended values. The reaction calorimetric values of Batalin *et al.*<sup>5</sup> agree within  $\pm 600 \text{ J mol}^{-1}$  except for  $x_{\text{Si}} = 0.25-0.7$ , where their values are as much as  $3000 \text{ J mol}^{-1}$  more exothermic than the recommended values. Recent measurements of Gizenko *et al.*<sup>6</sup> yielded up to  $500 \text{ J mol}^{-1}$  more exothermic values. They also reported  $\Delta H_{\text{Al}}$  and  $\Delta H_{\text{Si}}$  values which appeared to be inconsistent with one another. Therefore, less weight was given to these measurements. The recommended  $\Delta H$  values of Murray and McAlister<sup>1</sup> are up to  $90 \text{ J mol}^{-1}$  more exothermic below  $x_{\text{Si}} = 0.2$  and about  $30-50 \text{ J mol}^{-1}$  less exothermic above. The direct reaction calorimetry of Mathieu *et al.*<sup>7</sup> at  $962 \text{ K}$  for  $x_{\text{Si}} = 0.000-0.0095$ , yielded a value of about  $-10500 \text{ J mol}^{-1}$  for  $\Delta H_{\text{Si}}$  at  $x_{\text{Fe}} = 0.0$ , which compares with the recommended values of  $-11200 \text{ J mol}^{-1}$ .  $\Delta H_{\text{Al}}$  and  $\Delta H_{\text{Si}}$  from Table 22 were calculated from the recommended  $\Delta H$  value using the Gibbs-Duhem relation.

Although there have been several measurements from which Gibbs energy values can be derived, they were at different temperatures, making it difficult to compare them on the same basis. Therefore, the recommended  $\Delta G_{\text{Al}}$  values from Table 22 were combined with  $\Delta G_{\text{Al}}^{\text{ex}}$  values from each of these measurements, and  $\Delta S_{\text{Al}}^{\text{ex}}$  values were calculated. The recommended  $\Delta S_{\text{Al}}^{\text{ex}}$  values of Table 22 were based on the results of Berthon *et al.*<sup>8</sup> and Chatillon *et al.*<sup>9</sup> The values of Schaefer and Gokcen<sup>10</sup> are up to 0.35 e.u. higher than the

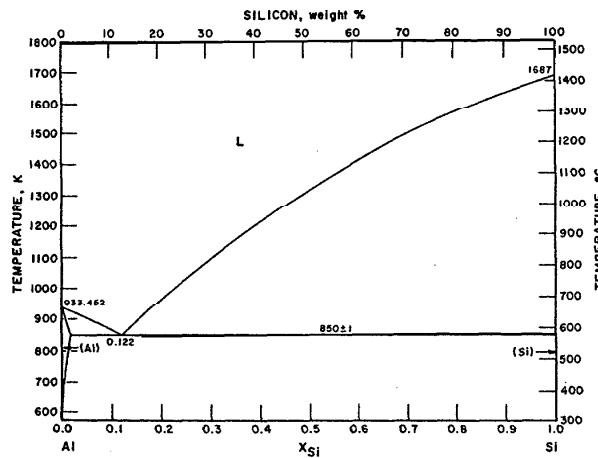


FIG. 4. Aluminum-silicon phase diagram.

Table 21. Recommended integral quantities for liquid Al-Si alloys at 1700 K

$$(1-x) \text{Al}(\ell) + x\text{Si}(\ell) = \text{Al}_{(1-x)}\text{Si}_x(\ell)$$

$x_{\text{Si}}$	$\Delta G$	$\Delta H$	$\Delta G^{\text{ex}}$	$\Delta S$	$\Delta S^{\text{ex}}$
	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
0.1	-3568	-1154	-973	2.596	-0.106
0.2	-8691	-2080	-1618	3.889	-0.272
0.3	-10616	-2657	-1982	4.682	-0.397
0.4	-11615	-2883	-2102	5.136	-0.459
0.5	-11807	-2809	-2010	5.293	-0.470
( $\pm 700$ )	( $\pm 500$ )	( $\pm 700$ )	( $\pm 700$ )	( $\pm 706$ )	( $\pm 706$ )
0.6	-11255	-2484	-1743	5.159	-0.436
0.7	-9977	-1960	-1344	4.716	-0.362
0.8	-7966	-1326	-893	3.906	-0.255
0.9	-4981	-664	-387	2.539	-0.163

recommended values.  $\Delta G_{\text{Al}}$  values thus obtained from the recommended  $\Delta H_{\text{Al}}$  and  $\Delta S_{\text{Al}}^{\text{ex}}$  values compared with the measured data when corrected to 1700 K using the recommended  $\Delta S_{\text{Al}}^{\text{ex}}$  values as follows:

Source	Deviation, J mol <sup>-1</sup>
Berthon <i>et al.</i> <sup>8</sup>	$\pm 100$
Chatillon <i>et al.</i> <sup>9</sup>	$\pm 900$
Schaefer and Gokcen <sup>10</sup>	-500
Mitani and Nagai <sup>11</sup>	-700 ( $x_{\text{Si}} < 0.5$ ) 4000 ( $x_{\text{Si}} > 0.5$ )
Loseva <i>et al.</i> <sup>12</sup>	up to -6000

The data of Batalin *et al.*<sup>13</sup> are as much as  $9900 \text{ J mol}^{-1}$  more exothermic than the recommended values. Other quantities from Tables 21 and 22 are calculated from the recommended  $\Delta H_{\text{Al}}$  and  $\Delta S_{\text{Al}}^{\text{ex}}$  values using the Gibbs-Duhem relation.

Table 22. Recommended partial molar quantities for liquid Al-Si alloys at 1700 K

Al Component		$\text{Al}(\ell) = \text{Al}(\text{in alloy})(\ell)$					
$x_{\text{Al}}$	$a_{\text{Al}}$	$\gamma_{\text{Al}}$	$\Delta G_{\text{Al}}$	$\Delta G_{\text{Al}}^{\text{ex}}$	$\Delta H_{\text{Al}}$	$\Delta S_{\text{Al}}$	$\Delta S_{\text{Al}}^{\text{ex}}$
			J mol <sup>-1</sup>		J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.889	0.988	-1661	-172	-82	0.929	0.053
0.8	0.766	0.958	-3767	-613	-550	1.892	0.037
0.7	0.640	0.914	-6313	-1272	-1478	2.844	-0.121
0.6	0.518	0.864	-9291	-2071	-2613	3.928	-0.319
0.5	0.406	0.812	-12737	-2940	-3844	5.231	-0.532
( $\pm 0.019$ )	( $\pm 0.039$ )	( $\pm 700$ )	( $\pm 700$ )	( $\pm 500$ )	( $\pm 706$ )	( $\pm 706$ )	( $\pm 706$ )
0.4	0.306	0.765	-16743	-3792	-5090	6.855	-0.764
0.3	0.219	0.730	-21458	-4441	-6146	9.007	-1.003
0.2	0.146	0.730	-27196	-4448	-6572	12.131	-1.250
0.1	0.075	0.749	-36628	-4082	-6640	17.640	-1.505
0.0	0.000	0.773	--	-3642	-6642	--	-1.765

Si Component  $\text{Si}(\ell) = \text{Si}(\text{in alloy})(\ell)$

$x_{\text{Si}}$	$a_{\text{Si}}$	$\gamma_{\text{Si}}$	$\Delta G_{\text{Si}}$	$\Delta G_{\text{Si}}^{\text{ex}}$	$\Delta H_{\text{Si}}$	$\Delta S_{\text{Si}}$	$\Delta S_{\text{Si}}^{\text{ex}}$
			J mol <sup>-1</sup>		J mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	
0.0	0.000	0.460	--	-10980	-11200	--	-0.130
0.1	0.056	0.560	-40729	-8183	-10801	17.605	-1.540
0.2	0.134	0.671	-28388	-5640	-8202	11.874	-1.507
0.3	0.232	0.773	-20656	-3639	-5409	8.969	-1.041
0.4	0.344	0.859	-15100	-2149	-3288	6.948	-0.670
0.5	0.463	0.927	-10876	-1079	-1773	5.355	-0.408
( $\pm 0.022$ )	( $\pm 0.044$ )	( $\pm 700$ )	( $\pm 700$ )	( $\pm 500$ )	( $\pm 706$ )	( $\pm 706$ )	( $\pm 706$ )
0.6	0.584	0.974	-7597	-377	-746	4.030	-0.217
0.7	0.699	0.999	-5057	-16	-166	2.877	-0.088
0.8	0.800	1.000	-3158	-4	-14	1.849	-0.006
0.9	0.902	1.002	-1465	24	0	0.862	-0.014
1.0	1.000	1.000	0	0	0	0.000	0.000

### 7.3. References

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## 8. Thermodynamic Properties of Al-Ti Binary Alloy System

### 8.1. Phase Diagram and Structures

The phase diagram shown in Fig. 5 was taken from the preliminary investigation of Murray.<sup>1</sup> Loiseau and Lasalmonie<sup>3</sup> have recently reported the existence of an additional three phases around equiatomic composition: Ti<sub>46</sub>Al<sub>54</sub> and Ti<sub>42</sub>Al<sub>58</sub> corresponding to an ordered superstructure of an fcc type different from AuCu. The transformation between them can be achieved by introducing periodic antiphase boundaries. The third phase, "Ti<sub>2</sub>Al," is of complex structure. Murray<sup>1</sup> and Pearson<sup>2</sup> list the following intermediate phases:

$\gamma$ , "Al<sub>3</sub>Ti," has the tetragonal (DO<sub>22</sub>) prototype.

$\delta$ , has the tetragonal (DO<sub>23</sub>) structure isotropic with Al<sub>3</sub>Zr.

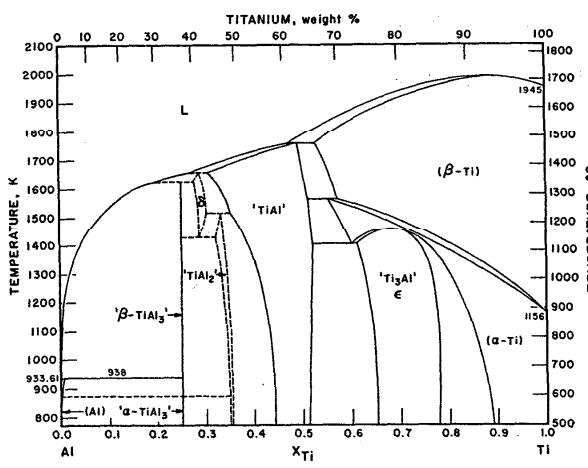


FIG. 5. Aluminum-titanium phase diagram.

Table 23. Low-temperature heat capacity of solid Al-Ti alloys

T, K	$x_{\text{Ti}}$					
	0.0 'Al'	0.25 ' $\gamma$ '	0.75 ' $\epsilon$ '	0.914 '(a-Ti)'	0.95 '(a-Ti)'	1.00 'Ti'
	$C_p^{\circ}, \text{J mol}^{-1}\text{K}^{-1}$					
1.4			0.0027		0.0050	0.006473
2	0.0029		0.0039		0.0073	0.00687
3	0.00472		0.0060		0.0113	0.01068
4	0.00699		0.0082	0.0164	0.0159	0.0149
5	0.0096	0.005		0.0212		0.0198
10	0.0359	0.021		0.0604		0.0623
15	0.0982	0.048		0.145		0.147
20	0.223	0.095		0.322		0.338
25	0.456	0.189		0.613		0.661
30	0.837	0.356		1.100		1.172
40	2.064	0.992		2.503		2.665
50	3.827	2.029		4.352		4.690
60	5.800	3.420		6.399		6.918
80	9.690	6.642		10.340		11.030
100	12.996	9.832		13.650		14.388
120	15.637	12.615		16.228		16.862
140	17.615	14.874		18.164		18.788
160	19.190	16.694		19.731		20.255
180	20.439	18.148		20.838		21.423
200	21.435	19.320		21.436		22.338
220	22.203	20.240		22.174		23.088
240	22.828	21.004		22.728		23.734
260	23.358	21.652		23.235		24.286
280	23.832	22.207		23.696		24.762
298.15	24.225	22.620				25.142
	$x_{\text{Ti}} = 1 - x_{\text{Al}}$	0.00135		0.00192	0.00374	0.00354
	$C_p^{\circ}(298.15 \text{ K})$	28.35	23.10			30.67

"TiAl<sub>2</sub>" has the tetragonal structure isotropic with HfGa<sub>2</sub>.

"TiAl" has the tetragonal structure isotropic with AuCu.

$\epsilon$ , "Ti<sub>3</sub>Al," has an ordered hexagonal (DO<sub>19</sub>) structure isotropic with Ni<sub>3</sub>Sn.

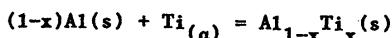
### 8.2. Solid Alloys

The  $C_p^{\circ}$  values of Table 23 for  $x_{\text{Ti}} = 0.25$  were taken from the data of Stuve and Ferrante,<sup>4</sup> for  $x_{\text{Ti}} = 0.75$ , and  $x_{\text{Ti}} = 0.95$  from the data of Ho *et al.*,<sup>5</sup> and for  $x_{\text{Ti}} = 0.914$  from those of Ilyicv *et al.*<sup>6</sup> The  $C_p^{\circ}$  values for Al and Ti were taken from the recommended CINDAS values.<sup>7,8</sup> The  $C_p^{\circ}$  values of Table 24 were taken from the plane temperature waves

Table 24. High-temperature heat capacity of solid Al-Ti alloys

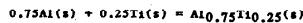
T, K	$x_{\text{Ti}}$			
	0.787	0.92	0.936	0.97
	$C_p^{\circ}, \text{J mol}^{-1}\text{K}^{-1}$			
298.15	21.85			
300	21.90			
400	23.68			
500	25.09			
600	26.29			
700	27.74			
800	29.55	35.02	32.63	30.13
900	31.69	36.89	33.99	31.78
1000	34.02	38.49	35.85	33.76
1100	40.84	38.55	35.95	
1180		42.65	39.60	36.80
1200		42.91	39.55	36.65
1240		43.10	38.35	34.75
1300		39.81	33.65	30.80
1320		37.26	33.40	30.35
1400		35.92	33.37	30.83
1500		36.79	34.40	32.26
1600		37.87	35.85	33.82
1700		39.11	37.57	35.45

Table 25. Enthalpies of formation for solid Al-Ti alloys at 298.15 K



$x_{Ti}$	Phase	$\Delta H^{\circ}$ $J \text{ mol}^{-1}$
0.25	$\gamma$	-36800 $\pm$ 2100
0.349	TiAl <sub>2</sub>	-40100 $\pm$ 2100
0.355	TiAl <sub>2</sub>	-40200 $\pm$ 2100
0.444	TiAl	-39200 $\pm$ 2100
0.513	TiAl	-38000 $\pm$ 2100
0.653	$\epsilon$	-31000 $\pm$ 2100
0.778	$\epsilon$	-23000 $\pm$ 2100
0.892	( $\alpha$ -Ti)	-12000 $\pm$ 2100

Table 26. High-temperature data for solid Al-Ti alloys as a function of temperature,  $x_{Ti} = 0.25^a$



T K	$C_p^o$ $J \text{ mol}^{-1} \text{ K}^{-1}$	$\Delta E_p^o$ $J \text{ mol}^{-1} \text{ K}^{-1}$	$H_T^o$ $J \text{ mol}^{-1}$	$\Delta H_T^o$ $J \text{ mol}^{-1} \text{ K}^{-1}$	$\Delta G_T^o$ $J \text{ mol}^{-1} \text{ K}^{-1}$	$S_T^o$ $J \text{ mol}^{-1} \text{ K}^{-1}$	$\Delta S_T^o$ $J \text{ mol}^{-1} \text{ K}^{-1}$	$-(G^o - H^o_{298.15})$
								T
298.15	22.62	-1.960	0	-36800	-35061	0.000	-5.834	23.096
300	22.67	-1.946	42	-36804	-35050	0.140	-5.846	23.096
400	24.17	-1.786	2393	-36985	-34435	6.890	-6.374	24.006
500	25.07	-2.128	4858	-37178	-33773	12.38	-6.811	25.763
600	25.70	-2.730	7398	-37419	-33076	17.02	-7.239	27.782
700	26.19	-3.522	9993	-37730	-32321	21.01	-7.727	29.832
800	26.63	-4.574	12635	-38131	-31525	24.54	-8.257	31.840
900	27.06	-6.070	15319	-38659	-30677	27.71	-8.869	33.775
1000	27.52	-4.510	18047	-39279	-29745	30.57	-9.434	35.627
1100	28.04	-4.442	20825	-39623	-28779	33.22	-9.858	37.384
1200	28.67	-2.372	23659	-40961	-27741	35.69	-11.017	39.068
1300	29.43	-1.825	26564	-41169	-26619	38.01	-11.192	40.679

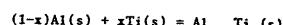
<sup>a</sup>Note standard states.

<sup>b</sup>Values for  $T \geq 1000$  K are referred to Al( $\epsilon$ ).

with the modulated electronic heating technique of Zaretskii and Peletskii.<sup>9</sup>

The recommended  $\Delta H$  values of Table 25 were based on the direct reaction calorimetry of Kubaschewski and Dench<sup>10</sup> and of Kubaschewski and Heymer.<sup>11</sup> The recommended  $C_p^o$  values of Table 26 were based on the copper-block drop calorimetry of Stuve and Ferrante.<sup>4</sup> Other thermodynamic functions were calculated by integrating the  $C_p^o$  values and by combining the entropy and enthalpy data with the standard enthalpy of formation at 298.15 from Table 25.

Table 27. Recommended integral quantities for solid Al-Ti alloys at 973 K<sup>a</sup>



$x_{Ti}$	Phase	$\Delta G$	$\Delta G^{ex}$
		$J \text{ mol}^{-1}$	
0.500	$\theta$	-31513 ( $\pm 2000$ )	-25906 ( $\pm 2000$ )
0.513 <sup>b</sup>	$\theta$	-31197	-25592
0.649 <sup>b</sup>	$\epsilon$	-25918	-20675
0.700	$\epsilon$	-23312	-18371
0.779 <sup>b</sup>	$\epsilon$	-18056	-13784
0.870 <sup>b</sup>	( $\alpha$ -Ti)	-11521	-8395
0.900	( $\alpha$ -Ti)	-9255	-6626

<sup>a</sup>Note standard states.

<sup>b</sup>Phase boundaries.

The necessary thermodynamic functions needed for these calculations were taken from Desai.<sup>7,8</sup>

The recommended  $\Delta G_{Al}$  values of Table 28 were based on the emf studies of Samokhval and Vecher<sup>12</sup> and Samokhval *et al.*<sup>13</sup>  $\Delta G_{Al(s)}$  values obtained from their reported emf values were transformed to  $\Delta G_{Al(\epsilon)}$  by applying the required standard state correction:  $(T_m - 973) \times \Delta_{\text{fus}} S^{\circ} = -446 \text{ J mol}^{-1}$ .  $\Delta G_{Ti}$  and other quantities of Table 28 were calculated from the recommended  $\Delta G_{Al}$  values using the Gibbs-Duhem relation. The recommended  $\Delta G$  and  $\Delta G^{ex}$  values of Table 27 were calculated from partial quantities of Table 28.

The recommended  $\Delta G_{Al}$  values of Table 30 were taken from the mass spectrometric vapor pressure coupled with a triple Knudsen cell measurement of Hoch and Usell.<sup>14</sup> Their  $a_{Al}$  values had a considerable scatter. The recommended  $\Delta G_{Al(\epsilon)}$  values obtained from their  $a_{Al(\epsilon)}$  were converted to  $\Delta G_{Al(s)}$  by applying the required standard state correction:  $(T_m - 1780) \times \Delta_{\text{fus}} S^{\circ} = -9550 \text{ J mol}^{-1}$ .  $\Delta G_{Ti}$  and other values of Table 29 and 30 were calculated using the method discussed above.

### 8.3. Liquid Alloys

The recommended  $\Delta H_{Al}$  values of Table 31 were based on the high-temperature vacuum calorimetric measurements of Esin *et al.*<sup>15,16</sup> The recommended  $\Delta H_{Ti}$  values of Table 31 were calculated from  $\Delta H_{Al}$  values and the Gibbs-Duhem relation.  $\Delta H_{Al}$  and  $\Delta H_{Ti}$  values were combined to yield  $\Delta H$  values of Table 31.

Table 28. Recommended partial molar quantities for solid Al-Ti alloys at 973 K<sup>a</sup>

$x_{Ti}$	Phase	Al(s) = Al(in alloy)(s)				Ti(s) = Ti(in alloy)(s)			
		$a_{Al}$	$\gamma_{Al}$	$\Delta G_{Al}$	$\Delta G_{Al}^{ex}$	$a_{Ti}$	$\gamma_{Ti}$	$\Delta G_{Ti}$	$\Delta G_{Ti}^{ex}$
				J mol <sup>-1</sup>				J mol <sup>-1</sup>	
0.500		0.01203 ( $\pm 0.003$ )	0.0241 ( $\pm 0.005$ )	-35760 ( $\pm 2000$ )	-30153 ( $\pm 2000$ )	0.0344 ( $\pm 0.021$ )	0.0687 ( $\pm 0.053$ )	-27266 ( $\pm 2000$ )	-21659 ( $\pm 2000$ )
0.513 <sup>b</sup>	$\theta$	0.00180	0.0037	-51110	-45289	0.219	0.427	-12293	-6893
0.649 <sup>b</sup>	$\epsilon$	0.00180	0.0051	-51110	-42640	0.219	0.337	-12293	-8796
0.700		0.00032	0.0011	-65050	-55310	0.511	0.730	-5425	-2540
0.779 <sup>b</sup>	$\epsilon$	0.00011	0.00050	-74000	-61788	0.763	0.980	-2185	-165
0.870 <sup>b</sup>	( $\alpha$ -Ti)	0.00011	0.00082	-74000	-57495	0.763	0.877	-2185	-1058
0.900		0.00005	0.0005	-80350	-61722	0.846	0.940	-1356	-504
1.000	( $\alpha$ -Ti)	0.000	0.00017	$\infty$	-70300	1.000	1.000	0	0

<sup>a</sup>Note standard states.<sup>b</sup>Phase boundaries.Table 29. Recommended integral quantities for solid Al-Ti alloys at 1780 K<sup>a</sup>

$$(1-x)Al(s) + xTi(s) = Al_{1-x}Ti_x(s)$$

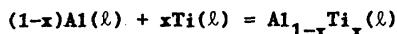
$x_{Ti}$	$\Delta G$	$\Delta G^{ex}$
	J mol <sup>-1</sup>	
0.493 <sup>b</sup>	-25187 ( $\pm 2000$ )	-14930 ( $\pm 2000$ )
0.548 <sup>b</sup>	-24552	-14362
0.6	-23726	-13765
0.7	-20860	-11819
0.8	-16262	-8857
0.9	-9719	-4908

<sup>a</sup>Note standard states.<sup>b</sup>Phase boundary.Table 30. Recommended partial molar quantities for solid Al-Ti alloys at 1780 K<sup>a</sup>

$x_{Ti}$	Al(s) = Al(in alloy)(s)				Ti(s) = Ti(in alloy)(s)			
	$a_{Al}$	$\gamma_{Al}$	$\Delta G_{Al}$	$\Delta G_{Al}^{ex}$	$a_{Ti}$	$\gamma_{Ti}$	$\Delta G_{Ti}$	$\Delta G_{Ti}^{ex}$
			J mol <sup>-1</sup>				J mol <sup>-1</sup>	
0.493 <sup>b</sup>	0.124 ( $\pm 0.015$ )	0.245 ( $\pm 0.031$ )	-30881 ( $\pm 2000$ )	-20814 ( $\pm 2000$ )	0.271 ( $\pm 0.024$ )	0.549 ( $\pm 0.048$ )	-19332 ( $\pm 2000$ )	-8865 ( $\pm 2000$ )
0.548 <sup>b</sup>	0.124	0.275	-30881	-19114	0.271	0.494	-19332	-10430
0.6	0.089	0.221	-35881	-22320	0.348	0.580	-15622	-8062
0.7	0.042	0.141	-46851	-29032	0.519	0.741	-9721	-4442
0.8	0.017	0.085	-60363	-36544	0.702	0.877	-5237	-1935
0.9	0.005	0.048	-78878	-44801	0.871	0.968	-2034	-475
1.0	0.000	0.026	$\infty$	-53775	1.000	1.000	0	0

<sup>a</sup>Note standard states.<sup>b</sup>Phase boundary.

**Table 31.** Enthalpies of formation for liquid Al-Ti alloys at 2000 K



$x_{Ti}$	$\Delta H$	$\Delta H_{Al}$	$\Delta H_{Ti}$
		$J \text{ mol}^{-1}$	
0.0		0	-114136
0.1	-11158	-557	-106566
0.2	-11949	-6155	-75126
0.3	-25274	-13941	-51717
0.4	-27669	-23104	-34516
0.5	-27710	-32725	-22695
	(±2000)	(±2000)	(±2000)
0.6	-25752	-43060	-14214
0.7	-21908	-51773	-6795
0.8	-16275	-67827	-3387
0.9	-8978	-82280	-833
1.0		-98000	0

#### 8.4. References

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