The Al-Si (Aluminum-Silicon) System

26.98154 28.0855

By J. L. Murray and A. J. McAlister
National Bureau of Standards

Equilibrium Diagram

Al-Si is a simple eutectic system with two solid solution phases, fcc (Al) and diamond cubic (Si). The assessed phase diagram is compared in Fig. 1, 2, 3, and 4 to the experimental data on which it is based, and its topological features are summarized in Table 1. The present diagram is calculated from Gibbs energies optimized with respect to thermochemical and phase boundary data. The reconciliation of phase diagram and thermochemical data is discussed in detail in the section entitled "Thermodynamics".

Al-Si alloys are among the most important commercial alloys when small additions (0.01 wt.%) of Na are made. These alloys are denoted "modified" and are greatly improved in microstructure and mechanical properties over the binary alloys. Cu or Mg is added for age-hardening. Much work has been done on solidification structures in Al-Si alloys as a function of composition, cooling rate, growth velocity, and ternary additions. [71Hel] provided an extensive review of this subject. Although this topic is beyond the scope of the phase diagram assessment, a list of solidification references was provided because of the importance of solidification processes.

Eutectic Reaction and Liquidus. The eutectic temperature is 577 ± 1 °C, based on [26Ota, 47Sin, 55Cra, 59Meu, 69Ber]. There is no significant disagreement in the literature on the eutectic temperature, although the eutectic reaction can be suppressed to about 10 °C below the equilibrium value by high cooling rates. The reaction temperature on heating is unchanged.

The eutectic composition is 12.2 ± 0.1 at.% Si, based on determinations of the composition of eutectic mixtures: 12.3 ± 1 at.% Si [59Meu] and 12.2 ± 0.1 at.% Si [65Ker]. This value is consistent with the liquidus data; [Hansen]'s value of 11.3 at.% Si was based on extrapolation to 577 °C of liquidus data now considered obsolete.

Liquidus points were determined by [08Fra, 14Rob, 26Ota, 29Ana, 31Los, 32Bro, 34Mat, 47Sin, 55Cra, 76Kob1, 76Kob2] using thermal analysis, and by [69Ber, 71Bat] using the electrochemical cell technique. All the data are plotted on Fig. 1 and 2 and selected data are listed in

Table 1 Al-Si Invariant and Congruent Transformations

Phase	Compositions, at.% Si			Temperature, °C	Reaction type
L ⇄ (Al) + (Si) ...	1.5 ± 0.1	12.2 ± 0.1	100	577 ± 1	Eutectic
Pure component transformations					
L ⇄ (Si)		100		1414	Melting
L ⇄ (Al)		0		660.452	Melting

Fig. 1 Assessed Al-Si Phase Diagram with Selected Liquidus Data

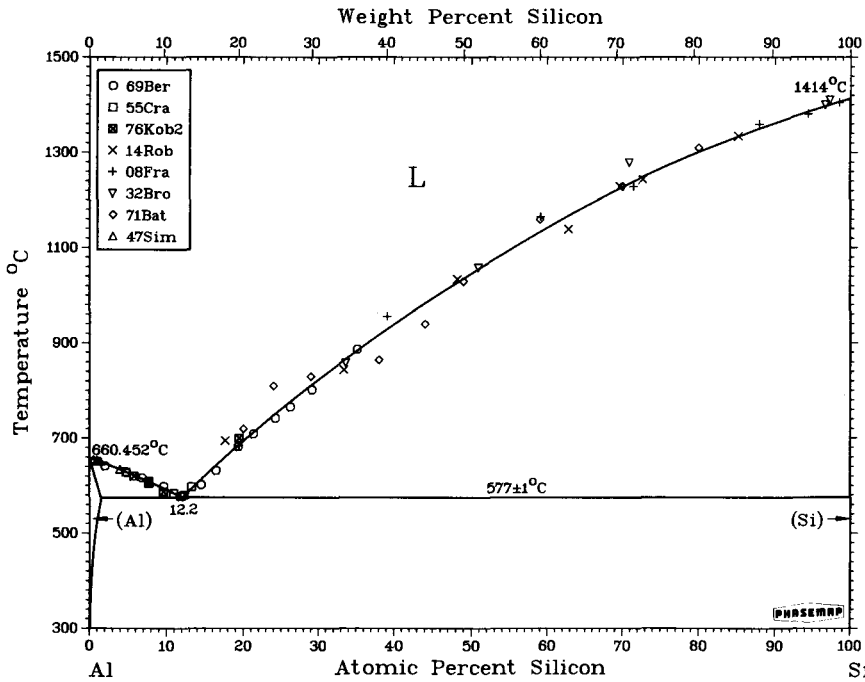

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Fig. 2 Enlargement of the (Al) Liquidus with Selected Data

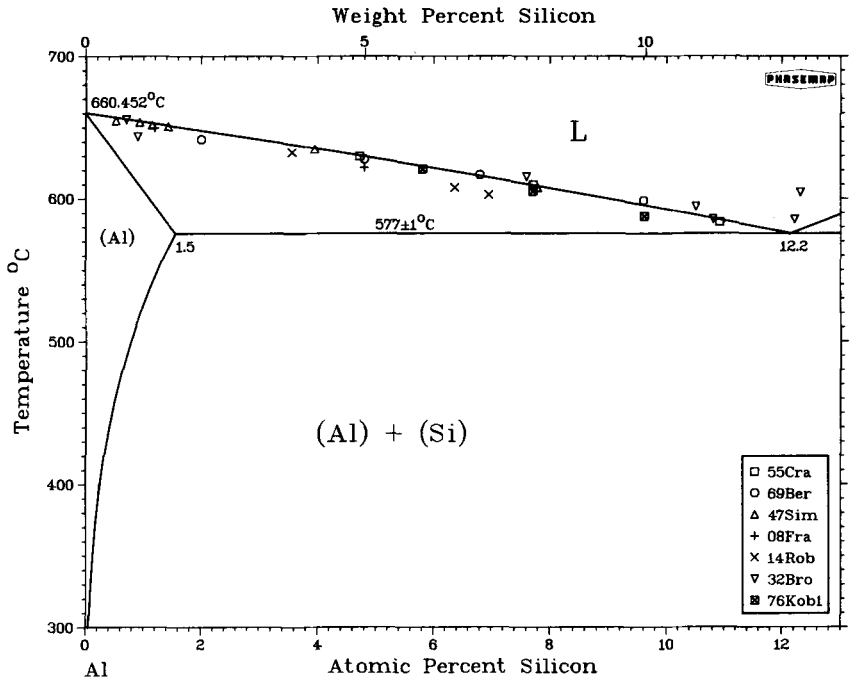

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Fig. 3 Al-Rich Solidus and Solvus with Selected Experimental Data

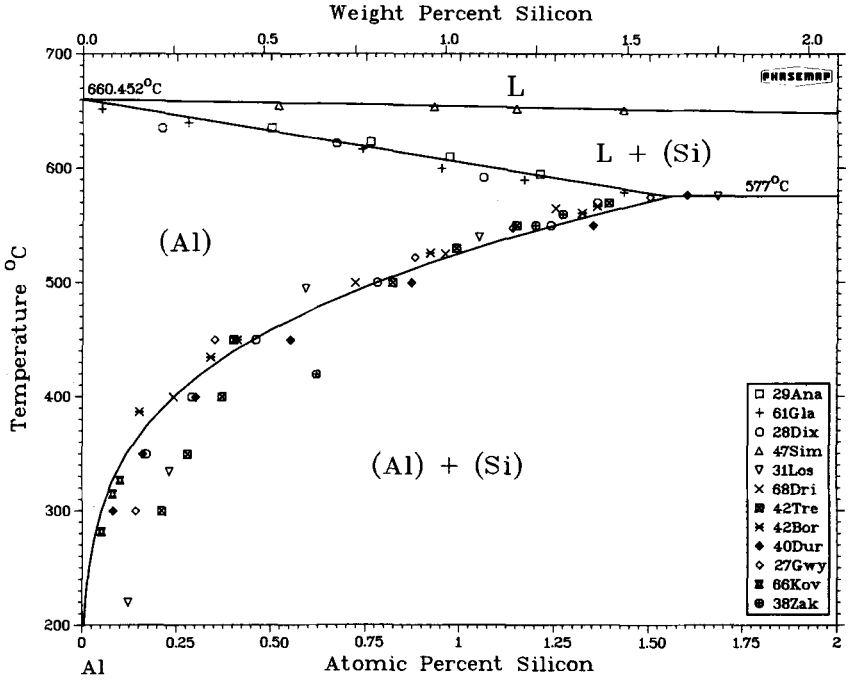

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Fig. 4 Si-Rich Solidus with Selected Experimental Data

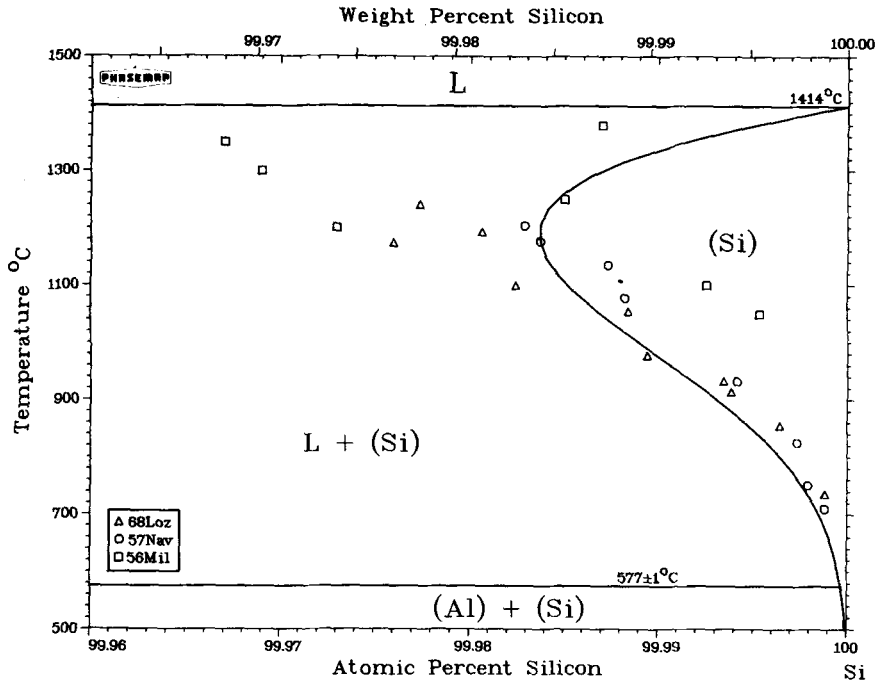

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Table 2 Experimental Al-Si Liquidus Data

Reference	Composition, at.% Si	Temperatures, °C Liquidus	Eutectic	Experimental method
[47Sin]	7.80	608	···	Thermal analysis
	7.42	···	574	
	3.94	635	···	
	3.75	···	575	
	2.01	···	577	
	1.44	651	···	
	1.15	652	···	
	0.93	654	···	
	0.52	655	···	
[55Cra]	13.23	598	578	Thermal analysis
	12.26	581	578	
	11.79	578	576	
	10.79	584	576	
	7.71	610	578	
	4.72	630	577	
[69Ber]	35.1	887	···	Electrochemical cell
	29.1	802	···	
	26.2	766	···	
	24.2	742	···	
	21.3	709	···	
	19.3	682	···	
	16.4	632	···	
	14.5	602	···	
	···	···	577	
	11.6	580	···	
	9.6	598	···	
	6.8	617	···	
	4.8	628	···	
	2.0	642	···	
[76Kob2]	5.8	621	···	DTA, cooling rate
	7.7	605.5	···	45 °C/min
	9.6	588	···	
[76Kob1]	19.4	700	···	DTA, end of melting
[34Mat]	7.7	605	···	Thermal analysis
	14.5	620	···	
	19.4	684	···	
	29.2	802	···	
	39.0	915	···	
	49.0	1005	···	
	59.0	1107	···	
	69.2	1200	···	
	79.4	1272	···	
	89.6	1367	···	

Table 2. Alloys used by [08Fra] and [14Rob] had significant impurity levels, particularly of Fe (0.3 wt.%). For Si-rich compositions, these studies comprise the only available data. For Al-rich alloys, later studies showed that impurities caused liquidus arrests to lie as much as 15 °C below the binary liquidus. The data of [31Los] also fell below the selected data, and the Si-rich data of [32Bro] and [71Bat] displayed considerable scatter. The data of [69Ber] and [55Cra] were weighted most heavily in the optimization calculation. All data are reproduced by the calculated diagram within the experimental errors.

(Al) Solidus and Solvus. The maximum solubility of Si in (Al) is 1.5 ± 0.1 at.% at the eutectic temperature, and it decreases to 0.05 at.% at 300 °C. The first definitive metallographic study of the solvus was made by [28Dix], and later work of [28Gwy, 31Los, 40Dur, 42Bor, 42Tre, 38Zak, 66Kov, 68Dri] corroborated their work within a scatter of

Table 3 Experimental (Al) Solvus Data in Al-Si

Reference	Composition, at.% Si	Temperature, °C	Experimental method
[27Gwy, 28Gwy]	1.50	575	Optical metallography
	1.14	548	
	0.88	522	
	0.35	450	
	0.14	300	
[28Dix]	1.36	570	Optical metallography
	1.24	550	
	0.78	500	
	0.46	450	
	0.29	400	
	0.17	350	
[66Kov]	0.05	282	Resistivity vs temperature
	0.08	315	
	0.1	327	
[68Dri]	0.24	400	Optical metallography, resistivity (quenched samples)
	0.72	500	
	0.96	525	
	1.25	565	
[31Los]	0.12	220	Dilatometry, hardness
	0.23	335	
	0.59	495	
	1.05	540	
	1.68	576	
[42Tre]	0.21	300	Optical metallography
	0.28	350	
	0.37	400	
	0.50	450	
	0.77	500	
	1.15	550	
[42Bor]	0.15	387	Dilatometry
	0.34	435	
	0.41	450	
	0.92	526	
	1.32	561	
	1.36	567	
[40Dur]	0.08	300	Thermoelectric measurements
	0.16	350	
	0.30	400	
	0.55	450	
	0.87	500	
	1.35	550	
	1.60	577	

±0.06 at.% Si. Data are summarized in Table 3 and compared to the result of the present thermodynamic optimizations in Fig. 3. Major sources of discrepancy among early determinations are high Fe contents and failure to achieve equilibrium at the lower temperatures. For this reason, the higher solubilities reported by [26Ota, 27Koe, 29Ana] are not tabulated or used for the diagram, and work prior to 1926 is considered obsolete.

The Al-rich solidus was studied by [26Ota, 29Ana, 28Dix, 47Sin, 61Gla]. These data, listed in Table 4 and shown in Fig. 3, are in accord with each other and with the present calculation of the diagram.

Si-Rich Solidus. The maximum solubility of Al in (Si) is 0.016 ± 0.003 at.% at 1190 °C—this temperature being the retrograde point of the (Si) solidus. Considerable disagreement exists regarding the Si-rich solidus. Conventional metallurgical studies were made by [60Gla, 81Ako] using microhardness, by [55Spe] using optical metallography, and by [55Obi, 57Got] using chemical analysis of separated (Si). These studies gave solubilities of Al in (Si) of as much as 1.0 at.% at 1000 °C, much higher than those observed by diffusion [56Mil] and temperature-gradient

Table 4 Experimental (Al) Solidus Data in Al-Si

Reference	Temperature, °C	Composition, at.% Si	Experimental method
[26Ota]	623	0.72	Electrical resistivity of heat treated and quenched samples
	608	1.10	
[28Dix]	635	0.35	Optical metallography of heat treated and quenched samples
	622	0.70	
	592	1.06	
[29Ana]	635	0.50	Electrical resistivity of heat treated and quenched samples
	623	0.76	
	610	0.97	
	595	1.22	
[47Sin]	644	0.096	Optical metallography of heat treated and quenched samples, mechanical properties
	641	0.19	
	621	0.67	
	604	1.06	
	578	1.54	
[61Gla]	652	0.06	Microhardness of heat treated and quenched samples
	640	0.29	
	617	0.74	
	600	0.96	
	590	1.18	
	579	1.44	

Table 5 Experimental (Si) Solidus Data in Al-Si

Reference	Composition, at.% Si	Temperature, °C	Experimental method
[56Mil]	99.987	1380	Diffusion
	99.967	1350	
	99.969	1300	
	99.985	1250	
	99.973	1200	
	99.9925	1100	
	99.9953	1050	
[57Nav]	99.9829	1204	Temperature gradient zone melting
	99.9837	1176	
	99.9873	1135	
	99.9882	1078	
	99.9941	933	
	99.9973	826	
	99.9979	752	
	99.9988	711	
[68Loz]	99.9774	1240	Temperature gradient zone melting
	99.9806	1193	
	99.9760	1173	
	99.9824	1100	
	99.9884	1055	
	99.9894	977	
	99.9934	934	
	99.9938	915	
	99.9964	856	
	99.9988	737	

zone melting [57Nav, 68Loz]. Solubilities according to [56Mil, 57Nav, 68Loz] were less than 0.035 at.% at all temperatures (see Table 5 and Fig. 4). The discrepancies are probably caused by lack of sensitivity of conventional tools, and the data of [56Mil, 57Nav, 68Loz] are preferred.

Effect of High Pressure. The effect of high pressure on alloys containing up to 15 at.% Si was studied by [71Fuj] at 28 kbar and [76Mii] at 54 kbar. In both investigations, temperature was varied and electrical resistivity was monitored *in situ*. Values for the melting point, liquidus, and solidus at these pressures are listed in Table 6. The solubility of Si in (Al) was raised to 7.0 at.% Si at 28 kbar

and above 15 at.% Si at 54 kbar. [76Mii] confirmed extended solubility in a 7 at.% Si sample quenched from 590 °C at 54 kbar by X-ray diffraction and hardness measurements. A thermodynamic analysis of high-pressure phase equilibria was made by [72Shi], based on volume changes estimated for the pure metals. They predicted that the eutectic point at 50 kbar is at 30 at.% Si and 677 °C.

Table 6 Al-Si Phase Diagram Under High Pressure

Pressure, kbar	Composition, at.% Si	Temperatures, °C Liquidus	Solidus	Solvus	Reference
28	0	840	...	...	[71Fuj]
	1.0	835	790	300	
	2.1	830	750	245	
	3.7	825	715	...	
	7.0	805	660	...	
	11.4	750	660	...	
	14.9	705	660	...	
54	0	970	...	...	[76Mii]
	3.7	940	910	280	
	7.0	930	820	320	
	11.4	900	790	380	
	14.9	890	700	420	

Metastable Phases

Solubility of Si in (Al) can be greatly extended by splat quenching of the liquid [68Ita, 73Bos, 73Shi, 80Ben, 73Aga]. Based on TEM observation of the absence of Si precipitation and lattice parameter measurements, [68Ita, 73Bos, 73Shi] placed the maximum extension of the solid solubility at 11 ± 1 at.% Si. Maximum extension of the solid solubility is based on TEM work, utilizing the thinnest, and hence most rapidly cooled, portions of the

Table 8 Al-Si Lattice Parameter Data

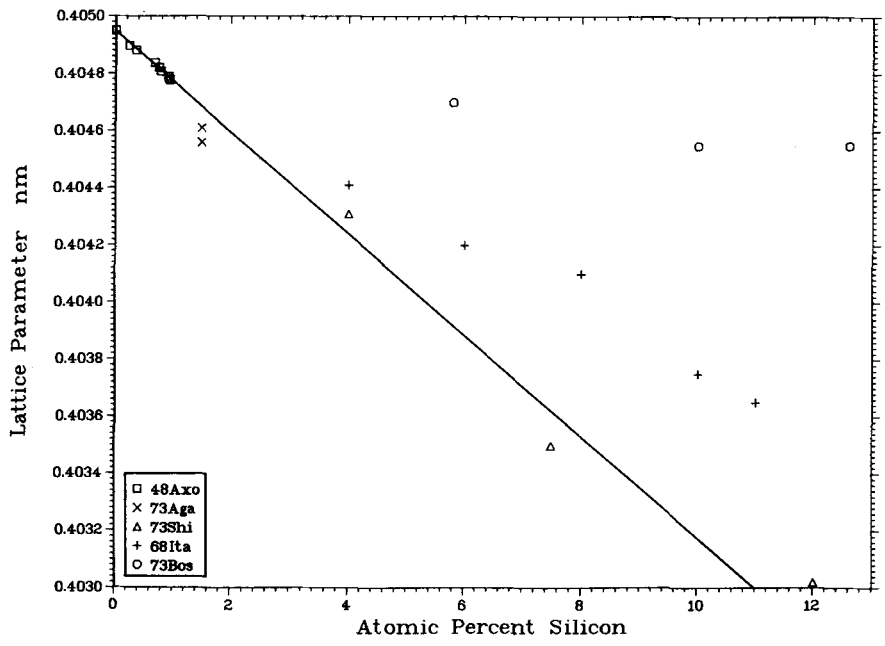
Phase	Composition, at.% Si	Lattice parameter, nm	Reference
(Al)	0	0.40495	[48Axo]
	0.23	0.404897	
	0.35	0.404881	
	0.67	0.404837	
	0.74	0.404820	
	0.78	0.404806	
	0.91	0.404789	
	0.92	0.404780	
	0.93	0.404776	
(Si)	100	0.54307	[Pearson]

Table 7 Al-Si Crystal Structure Data

Phase	Approximate composition(a), at.% Si	Pearson symbol	Strukturbericht designation	Space group	Prototype
(Al)	0 to 1.5	*cF*4	*A*1	*Fm*3*m*	Cu
(Si)	99.9984 to 100	*cF*8	*A*4	*Fd*3*m*	C (diamond)

(a) From the phase diagram.

Fig. 5 Lattice Parameters of Quenched (Al) Alloys



Alloys of [48Axo] and the higher lattice parameter alloy of [73Aga] were quenched from the single phase solid region; others were liquid-quenched.
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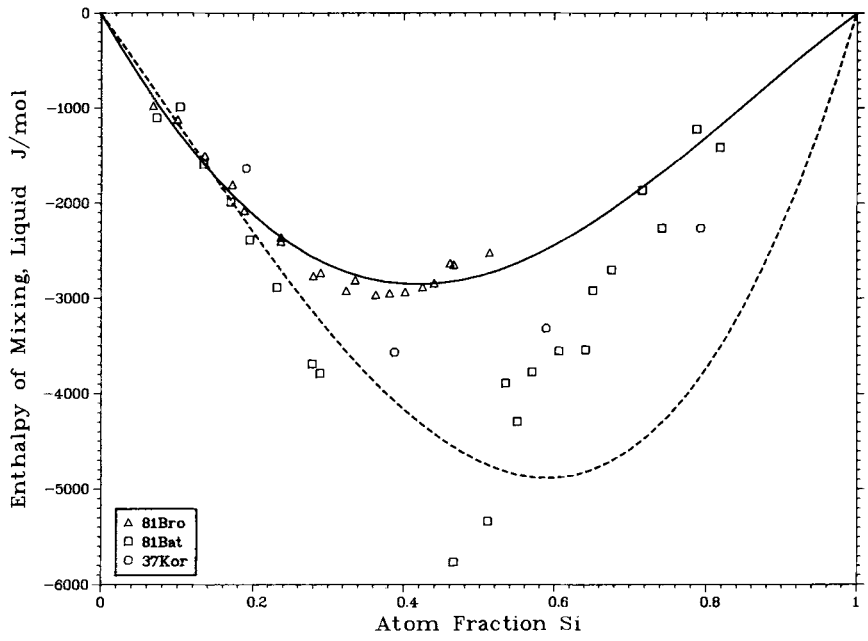
Fig. 6 Enthalpies of Mixing for the Liquid Phase and Calorimetric Data



_____ ≡ present calculation; ----- ≡ [80Dor]. J. L. Murray and A. J. McAlister, 1984.

Table 9 Liquid Integral Enthalpy of Mixing for Al-Si Alloys

Reference	Composition, at.% Si	Enthalpy, J/mol	Experimental method
[37Kor]	19.0	−1630	Heat content of alloys and pure metals from 0 to 1450 °C
	38.7	−3560	
	58.8	−3310	
	79.2	−2260	
[81Bro]	6.8	−971	Reaction calorimetry at 1104 °C; precision, 8%
	10.0	−1117	
	13.5	−1498	
	17.2	−1803	
	18.8	−2076	
	23.7	−2356	
	23.7	−2398	
	28.0	−2762	
	29.0	−2729	
	32.4	−2917	
	33.6	−2804	
	36.3	−2959	
	38.1	−2942	
	40.1	−2930	
	42.4	−2879	
	43.9	−2837	
	46.0	−2628	
	46.5	−2645	
[81Bro]	51.2	−2515	
[81Bat]	7.3	−1100	Reaction calorimetry; data digitized from figure
	10.3	−980	
	13.4	−1590	
	17.0	−1980	
	19.6	−2380	
	23.3	−2880	
	27.9	−3680	
	29.0	−3780	
	46.5	−5760	
	51.1	−5330	
	53.5	−3880	
	55.0	−4290	
	57.0	−3770	
	60.6	−3550	
	64.1	−3530	
	65.1	−2910	
	67.6	−2700	
	71.6	−1860	
	74.2	−2260	
	78.7	−1220	
	81.8	−1480	

sample. Lattice parameter measurements on splat-quenched samples do not allow an extrapolation of the lattice parameter vs composition relationship into the metastable regime. Various sets of lattice parameter data lie on approximately straight lines out to 11 at.% Si, but the slopes do not agree among themselves, nor with the slope for solid-quenched, dilute alloys.

Unlike Al-Ge alloys, Al-Si alloys have not been reported to form metastable intermetallic compounds or glassy alloys.

Crystal Structures and Lattice Parameters

Crystal structures and lattice parameters are given in Tables 7 and 8, respectively. Lattice parameters are taken from [48Axo]. Lattice parameters of the metastable (Al) solid solution also have been measured in splat-quenching experiments, but the agreement among these results prevents determination of a lattice parameter vs composition relationship. Lattice parameters are plotted in Fig. 5.

Table 10 Al-Si Electrochemical Cell Data on Liquid Partial Gibbs Energies

Reference	Temperature, °C	Composition, at.% Si	Partial Gibbs energy, J/mol
[79Sch]	827	0.9	−241
		2.9	−373
		3.7	−647
		6.4	−822
		7.4	−1221
		11.6	−1508
		12.7	−1682
		16.6	−1871
		18.7	−2803
		21.4	−3017
		26.8	−4095
		61.6	−4431
[69Ber]	580-980	2.0	$-100.4 - 0.151\ T$(a)
		4.8	$-309.7 - 0.226\ T$
		6.8	$-372.5 - 0.582\ T$
		9.6	$-405.9 - 0.901\ T$
		11.6	$-452.0 - 1.063\ T$
		14.5	$-556.6 - 1.373\ T$
		16.4	$-619.4 - 1.762\ T$
		19.3	$-845.4 - 2.130\ T$
		21.3	$-1050.4 - 2.176\ T$
		24.2	$-1242.9 - 2.544\ T$
		26.2	$-1365.9 - 2.616\ T$
		29.1	$-1640.5 - 3.812\ T$
		35.1	$-1741.0 - 4.959\ T$
[71Bat]	1423	10	−2469
		20	−4310
		30	−5020
		40	−5732
		50	−6318
		60	−6653
		70	−7615
		80	−9121
		90	−9791

(a) Temperatures in kelvin.

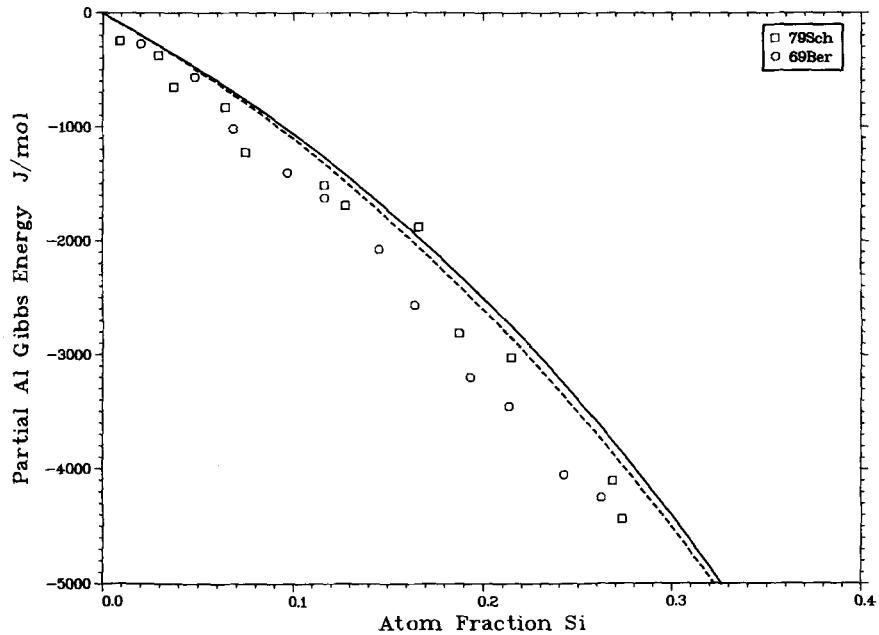
Thermodynamics

Experimental Work. Calorimetric studies of the liquid were made by [37Kor, 67Mat, 81Bro, and 81Bat]. Data are compared in Table 9 and Fig. 6. [81Bro] and [81Bat] measured the integral mixing enthalpy in the ranges 0 to 51.2 at.% Si and 0 to 100 at.% Si, respectively. The data of [81Bro] showed a sharp minimum at 40 at.% Si; the precision is estimated as ±8% and ±250 J/mol. Enthalpy data of [81Bat] are considerably more negative than the former and show a scatter of about ±1 kJ/mol. The present calculation of the phase diagram uses the data of [81Bro]. In addition, [67Mat] measured the partial mixing enthalpy $\Delta\overline{H}_{Si}$ in alloys containing up to 1.0 at.% Si at 689 °C. [37Kor] measured heat contents for six alloys, from which integral mixing enthalpies were computed. [37Kor] used commercially pure Si; large errors are attached to these data.

Electrochemical cell measurements of the partial Gibbs energy, $\overline{G}_{Al}$, of the liquid were made by [79Sch] at 827 °C from 0.5 to 27.6 at.% Si, by [69Ber] from 580 to 980 °C in the range 2.0 to 35.1 at.% Si, and by [71Bat] from 677 to 1377 °C in the range 9.6 to 79.3 at.% Si. Results are compared in Table 10 and Fig. 7. Although partial Gibbs energies are in reasonably good agreement, the separation into enthalpy and entropy contributions leads to discrepancies: [71Bat], for example, predicted positive integral heats of mixing in contradiction with direct measurements.

[67Mit] reported activities at 1200 °C, obtained from determination of the equilibrium constants of the reaction of Al-Si alloys with $AlCl_3$. [75Cha] determined both Al and Si vapor pressures at compositions spanning the diagram, at 1200, 1300, and 1427 °C. Si activities derived by Gibbs-Duhem integration from Al activities are more ideal than directly measured Si activities. Activity data of [67Mit]

Fig. 7 Partial Gibbs Energies, $\overline{G}_{Al}$, for the Liquid Phase by Electrochemical Cell Measurements



_____ ≡ present calculation; – – – – ≡ [80Dor].

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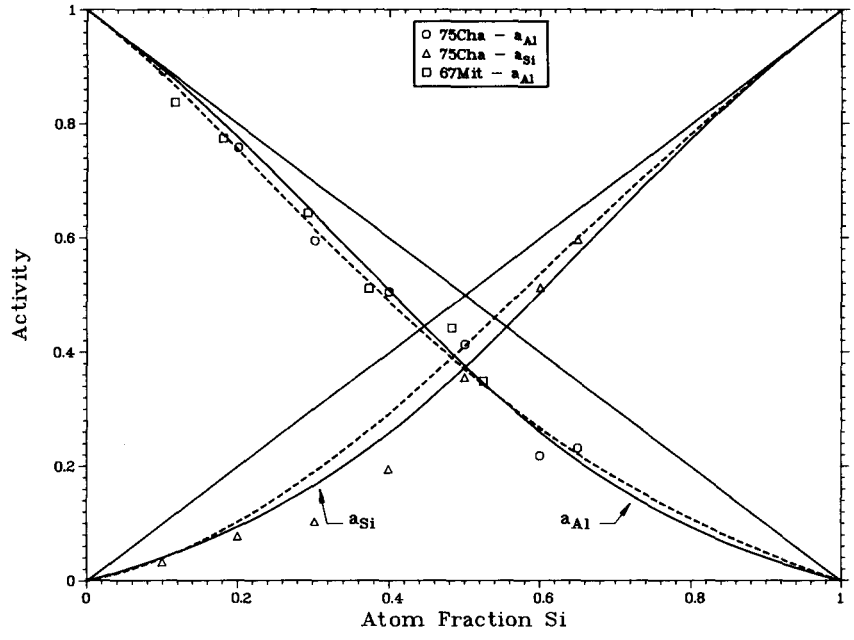
Fig. 8 Activity Data for the Liquid Phase



_____ ≡ present calculation; ---- ≡ [80Dor]. J. L. Murray and A. J. McAlister, 1984.

Table 11 Liquid Activities

Reference	Temperature, °C	Composition, at.% Si	Al activity	Si activity	Experimental method
[67Mit]	1200	74.0	0.275	...	Equilibrium constant
		70.0	0.250	...	of Al-Si + $AlCl_3$
		52.5	0.350	...	reaction
		48.3	0.443	...	
		37.3	0.512	...	
		29.3	0.644	...	
		18.0	0.775	...	
		11.5	0.838	...	
[75Cha]	1200	65.0	0.232	0.597	Vapor pressure
		60.0	0.219	0.513	
		50.0	0.414	0.356	
		39.9	0.506	0.196	
		30.3	0.595	0.104	
		20.0	0.759	0.078	
		9.9	0.893	0.033	
	1300	79.0	0.133	0.004	...
		70.0	0.212	0.080	
		60.0	0.315	...	
		50.0	0.427	...	
		39.9	0.503	0.360	
		30.3	0.595	0.508	
		20.0	0.795	0.637	
		9.9	0.876	...	
	1427	96.9	0.024	0.982	...
		94.1	0.040	0.412	
		90.2	0.089	0.914	
		50.0	0.430	0.973	

and [75Cha] are listed in Table 11 and compared with calculations in Fig. 8. Al activities obtained at 1700 and 1900 °C by [77Los], using a vapor-fluorescence technique, are in acceptable agreement with the results of [67Mit] and [75Cha].

Phase Diagram Calculations. The Al-Si system was calculated by [79Kau] using the subregular approximation with a positive enthalpy of mixing, based on the work of [71Bat]; and by [80Dor], using a polynomial expansion optimized to many of the data used here. The [80Dor] Gibbs energies

are compared to the present updated results in Table 12, and the differences in calculated thermodynamic functions are illustrated in Fig. 6, 7, and 8. The calculations by [80Dor] were made before enthalpy of mixing data [81Bro, 81Bat] were available. The phase diagram of [80Dor] is essentially indistinguishable from the present diagram. These figures illustrate the important contribution of the enthalpy of mixing data for Al-Si: whereas the phase diagram, partial Gibbs energies, and activities do not distinguish between these two calculations, the mixing enthalpies are quite different and the description of the system is now significantly improved. Differences in the [80Dor] and present values of solid-phase Gibbs energies reflect the fact that these coefficients are determined solely by phase diagram data for dilute alloys.

Table 12 Al-Si Thermodynamic Parameters, J/mol, T in K

Lattice stabilities of the pure components

${}^0G_{Al}^{fcc}$	$= -10\,792 + 11.56\,T$	${}^0G_{Al}^{L} = 0$
${}^0G_{Si}^{fcc}$	$= 12.12\,T$	${}^0G_{Si}^{L} = 0$
${}^0G_{Si}^{diamond}$	$= -50\,600 + 30.0\,T$	
${}^0G_{Si}^{diamond}$	$= 30.0\,T$	

Binary interaction parameters

	Present work	[80Dor]
A^L	$= -10\,695.4 - 1.823\,T$	$-18\,833.3 + 4.5988\,T$
B^L	$= -4\,274.5 + 3.044\,T$	$7\,464.6 - 6.8075\,T$
C^L	$= 670.7 - 0.460\,T$	0
A^{fcc}	$= -200 - 7.594\,T$	$-8\,120 + 1.448\,T$
$A^{diamond}$	$= 89\,138 - 31.445\,T$	$110\,556 - 45.553\,T$

Note: [80Dor] gave alternative sets of coefficients that include specific heat contributions. These additional contributions were not found to improve the optimizations. We cite this simpler representation for ease of comparison with the present results.

In the present calculations, the Gibbs energies of the (Al), (Si), and liquid phases are represented by polynomial expansions:

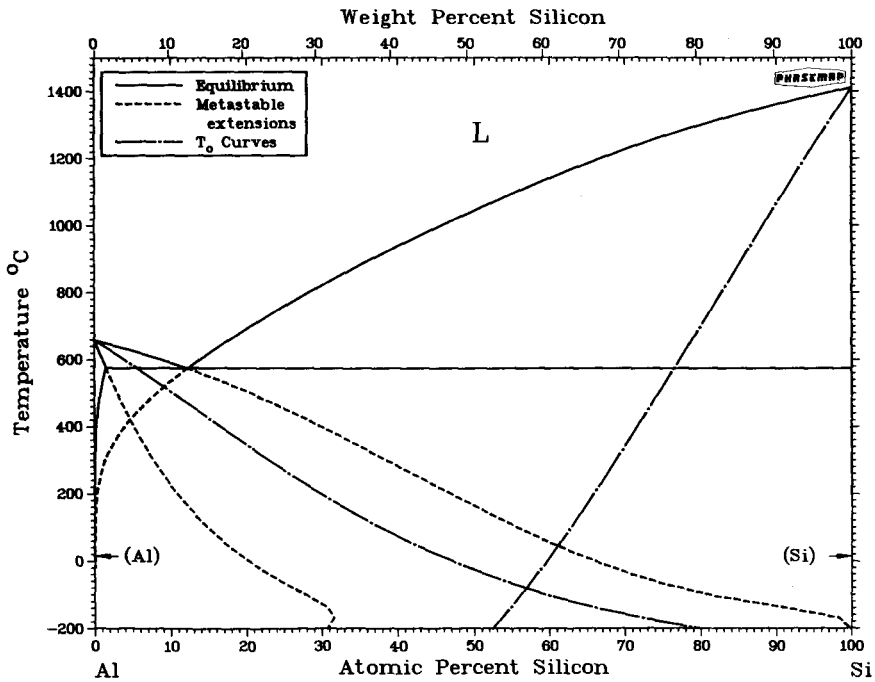
$$G^i = {}^0G_{Al}(1-x) + {}^0G_{Si}x + RT[x\ln x + (1-x)\ln(1-x)] + x(1-x)[A^i + B^i(1-2x) + C^i(1-6x+6x^2)]$$

where i designates the phase; x, the atomic fraction of Si; T, absolute temperature; ${}^0G^i$, the lattice stability terms of the pure elements; and A^i, B^i, and C^i, the interaction parameters. All coefficients are assumed to be linear in temperature. Lattice stabilities of the stable solid phases are taken from [Hultgren, Elements]; estimated lattice stabilities for fcc Si and diamond cubic Al are taken from [79Kau]. For this system, both solid phases behave as Henrian solutions.

After comparing a number of approaches similar to the previous work of [80Dor], we emphasized the following data: integral mixing enthalpy of [81Bro], the eutectic composition and temperature (±0.1 at.% and ±1 °C), the liquidus from the eutectic temperature to 900 °C, and the (Al) solvus. The starting point of the optimizations was the following expression for the liquid phase excess enthalpy, based on [81Bro, 75Cha, 69Ber]:

$${}^EH = x(1-x)[10\,695.4 - 4\,274.5(1-2x) + 670.7(1-6x+6x^2)]\ \text{J/mol}$$

Fig. 9 Full Calculated Diagram Including T_0 Curves and Metastable Extensions of the Phase Boundaries



J. L. Murray and A. J. McAlister, 1984.

The excess entropy of the liquid was determined from the liquidus data, with data near the eutectic temperature most heavily weighted. The Gibbs energy of (Al) was next determined by the solvus data and eutectic reaction, and the Gibbs energy of (Si) was determined by the (Si) solidus data. The calculated eutectic reaction occurs at 576 °C, with (Al) and liquid compositions 1.56 and 12.17 at.% Si, respectively. All the phase boundaries shown in the figures were calculated using the Gibbs energy expressions given in Table 12.

Metastable extensions of the equilibrium boundaries and T_0 curves of equal Gibbs energies are of interest for this system for interpreting the results of rapid solidification experiments [82Mur]. For Al-Si, the relevant quality seems to be the intersection of the (Al) T_0 curve and the extended (Si) liquidus; the extrapolation is less than 75 °C and can probably be made with relative safety. The full metastable diagram is shown in Fig. 9. In view of the sensitivity of the metastable extensions to the excess entropies and estimated lattice stabilities, the low-temperature portion of this figure should be understood as an illustration of the effect of the lattice stability parameters rather than a prediction of the phase relations.

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*Indicates key paper.

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