Thermodynamic Parameters of Liquid Gold-Aluminum Alloys

L. ERDÉLYI, J. TOMISKA, A. NECKEL, G. ROSE, E. S. RAMAKRISHNAN, AND D. J. FABIAN

Thermodynamic activities and enthalpies for Au-Al alloys have been measured by Knudsen-cell mass spectrometry, independently using closely similar techniques in laboratories in Vienna and Strathclyde. The results are consistent and indicate, for Au rich alloys, gold activities with positive deviations from Raoult ideality. This is in disagreement with EMF measurements of Au activity previously reported; the results also indicate endothermicities (of ~38 kJ/mol at x_{Al} ~ 0.5) that are some 5 to 6 kJ/mol larger than those indicated by the EMF measurements.

GOLD and aluminum form a series of interesting intermetallic compounds, $AuAl_2$, AuAl, Au_2Al, Au_5Al_2, and Au_4Al of varying stability and composition range. $AuAl_2$ is particularly strongly bonded in the solid, with high melting point (1333 K, close to that of pure gold) and heat of formation, is brittle and has a pronounced purple color; it has almost no solid solubility for gold or aluminum. The gold rich alloys are much less strongly bonded, with lower heats of formation and wide ranges of composition; Au_4Al, for example, melts at 818 K in a peritectic reaction, while a eutectic (798 K) forms at slightly lower gold concentration (~77.5 at. pct).

The liquid state Au-Al alloys have been studied thermodynamically by several investigators. Charquet *et al*[1] conducted EMF measurements of the activities of the two components, and observed large negative deviations from Raoult ideality over the entire composition range, with correspondingly large negative excess free enthalpies and heats of mixing. The general trend of these results was subsequently confirmed in further EMF studies, by Predel *et al*[2] and Yazawa *et al*[3], who adopted also a distribution method for the aluminum rich alloys, measuring the partition of gold between aluminum and lead.

In the investigations we report here activities and enthalpies were measured by Knudsen-cell mass spectrometry. The measurements were made independently with a single focusing VARIAN-MAT (Atlas) CH4 instrument at the Institut für Technische Elektrochemie, Technical University Vienna, and with a double focusing AEI MS702 at Strathclyde University, Glasgow. The experimental techniques were closely similar and we report the results together because they are consistent and indicate, for the gold rich alloys, activities of gold that are in some disagreement with the earlier EMF measurements cited.

EXPERIMENTAL

The Knudsen cell and mass spectrometric techniques adopted have been described in previous reports, *e.g.* Cuthill *et al*[4,5] and Neckel *et al.*[6,7] Similar precautions were taken in the present mass spectrometric investigations to achieve homogeneous furnace temperature for the Knudsen cell. The CH4 instrument employs electron bombardment heating, with two cathodes to diminish the temperature gradient, while the AEI MS702 cell furnace is heated by two independently controlled radiation elements. Temperature measurement in both instruments is made by pyrometer sighted through the Knudsen-cell orifice. The pyrometer is calibrated, for the CH4 instrument, at the melting points of copper and nickel; with the MS702 instrument, temperature monitoring is by thermocouple which is calibrated by the pyrometer at the melting points of pure gold, aluminum and silver. The temperature ranges covered in these investigations were 1420 to 1740 K with the Vienna instrument and 1320 to 1660 K with the Strathclyde instrument.

Cell liners for the Knudsen effusion studies were made chiefly from vitreous carbon, but also in some instances from high grade graphite that showed no reaction with the molten alloys; for the aluminum rich melts aluminia liners were used, which gave acceptable results with negligible contribution of Al^+ intensity from Al_2O resulting from reaction with Al_2O_3 and fragmentation. An extra Al^+ contribution from Al_2O was observed to interfere appreciably with the measurements of Al^+ originating from the gold rich alloys. The ionization energy employed in the Vienna instrument was 11 eV but with the Glasgow instrument was limited to higher electron energies ~70 eV.

With aluminum concentrations higher than 50 at. pct the measurements became increasingly difficult to make on account of the decreasing Au^+ intensity. For example, with the Vienna mass spectrometer, for aluminum concentrations from 75 to 85 at. pct the recorded Au^+ intensity was in the region of 10 mV compared with Al^+ intensities as high as 30 V or more. For this reason the ionizing beam, for measurements of Al^+ at these alloy concentrations, was lowered from 20 to 3 μA; then for comparison of intensities a ratio $(I_{Al^+})_{20\mu A}/(I_{Al^+})_{3\mu A}$ had to be applied.

The alloy samples were prepared by melting directly within the Knudsen cells of the mass spectrometers, by charging the cell-liners (or crucibles) with weighed amounts of the pure components. Overall masses from 300 mg, for the Al rich, to 850 mg for the Au rich alloys were prepared, at ~1400 K. Using cell liners of vitreous carbon, or of suitable graphite, no wetting of the crucible walls was observed up to Al contents of

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L. ERDÉLYI and J. TOMISKA are University Assistants, Technical University of Vienna. A. NECKEL is Professor, Technical University, University of Vienna. G. ROSE is Scientific Officer, AWRE, Dorset, England. E. E. RAMAKRISHNAN is Scientist, BHEL, Vikas Nagar, India. D. J. FABIAN is Reader, University of Strathclyde, Glasgow, England.

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50 at. pct. With alloys of Al content from 50 to 65 at. pct the degree of wetting increases, and finally a creeping of the melt out of the crucible, was observed—an effect that could not be avoided by use of less sample. Even when using corundum liners, alloys of aluminum content above ~50 at. pct showed a strong increasing tendency to wet the crucible or liner, but in this case the creeping-out of the melt could be avoided by restricting the sample charge to 300 mg. No dissolved carbon appeared to be present in the samples following a measurement (in the case of graphite liners) but its presence and a consequent lowering of vaporization rate cannot be completely excluded.

Evaporation loss during a measurement, especially when the alloy components have widely different partial vapor pressures, can lead to false concentrations. The mass loss m_i of component i during an effusion run at constant temperature T is given by the relation:

$$m_i = p_i t A \sqrt{M_i/2RT} \qquad [1]$$

where p_i is the partial vapor pressure of i, t is the measurement time, A is the orifice cross-section (cell orifice diam were typically from 0.7 to 0.9 mm with the Vienna instrument and from 0.75 to 1.0 mm with the Strathclyde instrument), M_i is the atomic weight of component i, R the gas constant, and T the absolute temperature. From this relation we obtain, for the binary alloys Au-Al, an expression for the ratio of masses evaporating:

$$\frac{m_{\mathrm{Al}}}{m_{\mathrm{Au}}} = \frac{p_{\mathrm{Al}}}{p_{\mathrm{Au}}} \sqrt{M_{\mathrm{Al}}/M_{\mathrm{Au}}} \qquad [2]$$

After each measurement the total weight loss of sample ($m_{\mathrm{Al}} + m_{\mathrm{Au}}$) could thus be ascertained, allowing for a corrected weight loss of the crucible, and then with the help of Eq. [2] the weight loss for each component could be determined. For calculation of the partial pressures p_{Al} and p_{Au} a medium temperature, 1600 K, was selected.

The partial vapor pressures, using vapor pressure data for the pure components from Nesmeyanov[8] and approximate values for the activities, were calculated. Total evaporation losses lay between 0.2 mg (gold rich alloys) and 1.7 mg (Al rich alloys). On the basis of the calculated weight losses the alloy concentrations were amended where necessary.

Evaluation of Thermodynamic Data

The partial pressure p_i of component i of the condensed phase in the cell, is related to the measured intensity I_i^+ of ion species of an isotope k of component i by the expression:

$$p_i = \frac{F}{\sigma_i \gamma_i N_i^k} I_i T \qquad [3]$$

where

F = geometric constant of the instrument,
σ_i = ionization cross-section for component i,
γ_i = ion-electron multiplier efficiency,
N_i^k = abundancy of isotope k of species i,
T = absolute temperature.

Direct determination of thermodynamic activities a_i, using,

$$a_i = p_i/p_i^o \qquad [4]$$

(where p_i^o = vapor pressure of pure component i) from measurements of p_i and p_i^o in separate experiments, is beset with difficulties associated with indeterminate changes in the instrument geometric constant F. To counter this, Belton and Fruehan,[9] and also Neckel and Wagner,[10] have proposed a method involving measurement of the ratio of intensities of ions of isotope species of the two components of the alloy. The method adopted by Neckel and Wagner[10] leads to a direct derivation of the excess molar Gibbs free energies ΔG^E by means of the expression:

$$\frac{\partial \Delta G^E}{\partial x} = RT \ln \frac{(1-x)I_2}{xI_1} + C_G(T) \qquad [5]$$

where x = mol fraction component 2.
The temperature dependent term $C_G(T)$ brings together all the concentration independent factors in the form:

$$C_G(T) = RT \ln \frac{\sigma_1 \gamma_1 N_1^k p_1^o}{\sigma_2 \gamma_2 N_2^l p_2^o} \qquad [6]$$

Then, $C_G(T)$ can be obtained by integration over the whole concentration range:

$$C_G(T) = -RT \int_{x=0}^{x=1} \ln \frac{I_2(1-x)}{I_1 x}\, dx \qquad [7]$$

while the excess molar Gibbs free energy is given by:

$$G^E(x) = RT \int_{x=0}^{x} \ln \frac{I_2(1-x)}{I_1 x}\, dx + C_G(T)x \qquad [8]$$

By similar reasoning, the temperature dependence of the ratio of the ion beams yields the partial derivative of the heat of mixing ΔH^E,

$$\frac{\partial \Delta H^E}{\partial x} = R\, \frac{\partial \ln (I_2/I_1)}{\partial (1/T)} + C_H \qquad [9]$$

where the integration constant C_H given by:

$$C_H = -R \int_{x=0}^{x=1} \frac{\partial \ln (I_2/I_1)}{\partial (1/T)}\, dx = H^o_{v,2} - H^o_{v,1} \qquad [10]$$

is effectively equal to the difference of heats of evaporation of the two pure components.[11] The heat of mixing can then be expressed as:

$$\Delta H^E(x) = R \int_{x=0}^{x} \frac{\partial \ln (I_2/I_1)}{\partial (1/T}\, dx + C_H x \qquad [11]$$

For evaluation of the experimental results an analytical technique, suitable for computer calculations, was employed. The temperature dependence of the ratios of intensities of the ion beams, for one particular concentration, was obtained through a linear regression in accordance with the expression:

$$\ln \frac{I_2(x)}{I_1(x)} = k(x)\frac{1}{T} + d(x) \qquad [12]$$

Further evaluations followed the technique described by Tomiska *et al*,[12] which uses a Redlich and Kister expansion[13] for a thermodynamic excess function of mixing, Z,

$$Z = (x - x^2) \sum_{n=1}^{N} B_n^Z (2x-1)^{n-1} \qquad [13]$$

(where $Z = \Delta G^E$, ΔH^E, ΔS^E, and N is the total number of Redlich-Kister parameters). Use of the Redlich-Kister expansion for $Z = \Delta G^E$ in Eq. [5] leads to the relation:

$$RT \ln \frac{(1-x)I_2}{xI_1} = B_1^{(\Delta G^E)}(1-2x) + \sum_{n=2}^{N} B_n^{(\Delta G^E)}(2x-1)^{n-2} \times [(2n+2)(x-x^2)-1] - C_G(T) \quad [14]$$

The technique is then to adjust the Redlich-Kister parameters $B_n^{(\Delta G^E)}$ and the constant $C_G(T)$, by means of a least square method, to fit as closely as possible the experimental values of $RT \ln (1-x)I_2/xI_1$. In an entirely analogous manner the Redlich-Kister parameters $B_n^{(\Delta H^E)}$ and the constant C_H for the heat of mixing are determined from Eq. [9]. The Redlich-Kister parameters for ΔG^E, ΔH^E, and ΔS^E are connected by the relation:

$$B_n^{(\Delta G^E)} = B_n^{(\Delta H^E)} - T\, B_n^{(\Delta S^E)} \quad [15]$$

from which, in agreement with Eq. [12], the parameters $B_n^{(\Delta H^E)}$ and $B_n^{(\Delta S^E)}$ emerge as temperature independent. For our present alloy results a satisfactory best-fit was achieved using a 3-parameter expansion ($N = 3$) for ΔG^E and ΔH^E.

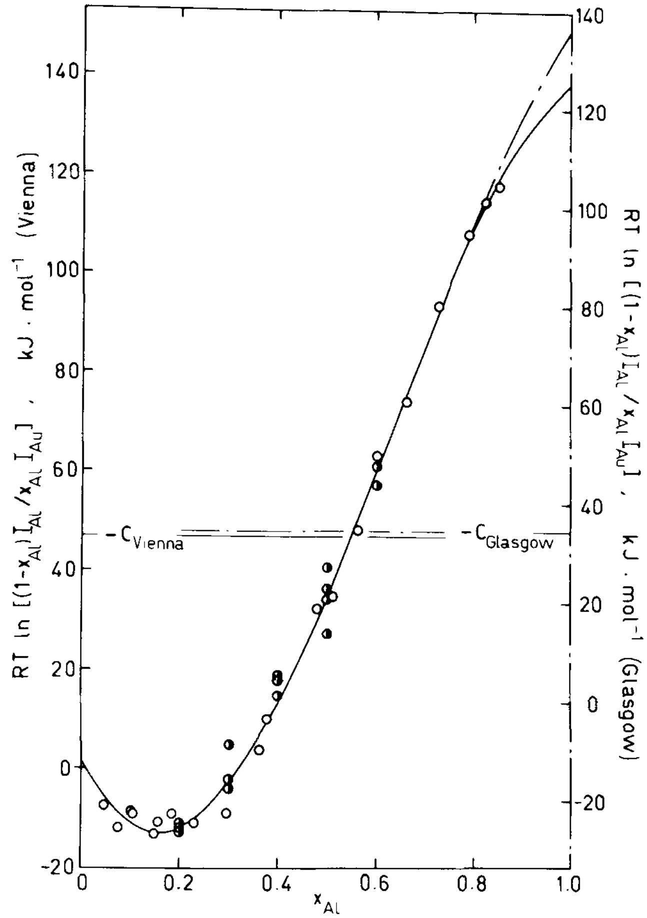

Fig. 1—$RT \ln [(1-x_{Al})I_{Al}/x_{Al}I_{Au}]$ as a function of the mole fraction of aluminum x_{Al} at 1540 K. ○, —: Vienna; ◑, —·—: Strathclyde.

RESULTS AND DISCUSSION

For each alloy concentration the ratios of the intensities of the ion beams were determined at about 15 different temperatures. Regression of the experimental data according to Eq. [12] yields the values for the slopes and intercepts, summarized in Table I.

In Fig. 1 we show the experimental values obtained for $RT \ln I_2(1-x)/I_1x$ as well as the 'best-fit' curve for these measurements at $T = 1540$ K. The lefthand ordinate applies to the Vienna measurements and the righthand ordinate to the Strathclyde measurements. A similar correspondence of the data was obtained at 1660 K.

Because of the higher electron energy applied in the Glasgow instrument, the ionization cross-sections σ_i are larger and the values of the constant $C_G(T)$ are therefore different from those for measurements with the Vienna instrument. However, the results from both laboratories follow practically the same curve of concentration dependence. The deviations observed for the Al rich alloys ($x_{Al} > 0.8$) are the result of the extrapolation necessary on account of the limited concentration range of the experimental data.

In Fig. 2 we compare, for $T = 1540$ K, our present results with those reported by other investigators; for

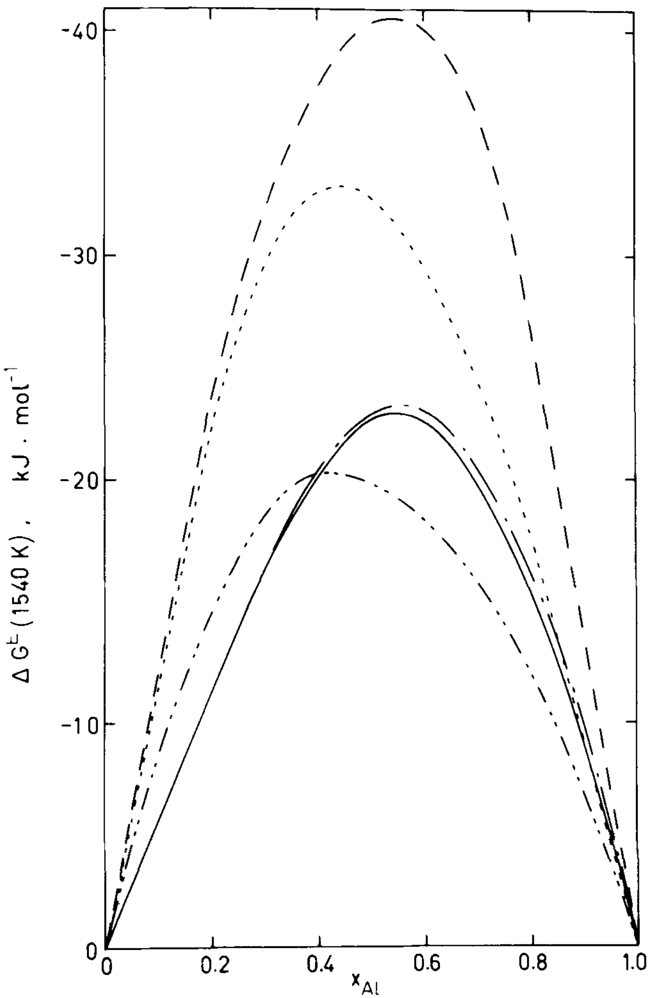

Fig. 2—Molar excess Gibbs energies ΔG^E of liquid Au-Al alloys at 1540 K. —: this work, Vienna; —·—: this work, Strathclyde; ····: Charquet *et al*[1] (recalculated from 1338 K); – – –: Predel *et al*[2] (recalculated from 1300 K); —··—: Yazawa *et al*[3] (recalculated from 1373 K).

this comparison the results obtained in other laboratories are extrapolated at 1540 K. The measurements at the Strathclyde and Vienna laboratories agree well, and for ΔG^E yield minimum values of respectively -23.8 kJ/mol ($x_{\text{Al}} = 0.54$) and -24.2 kJ/mol ($x_{\text{Al}} = 0.55$). The results reported by Yazawa *et al*[3] also agree satisfactorily with those of the present investigations, although with the minimum displaced to higher gold concentrations ($x_{\text{Al}} = 0.43$); however, the measurements reported by Charquet *et al*[1] and, above all, Predel *et al*[2] yield essentially more negative ΔG^E values. For $T = 1660$ K the ΔG^E values obtained in the Strathclyde and Vienna laboratories also agreed closely (as in Fig. 2 for 1540 K) across the whole composition range.

The ΔG^E values can be expressed by the Redlich-Kister parameters given in Table II; and are also summarized for $T = 1540$ K in Table III and for $T = 1660$ K in Table IV. The thermodynamic activities are summarized in Table V and Fig 3. In contrast to the findings reported by the other investigators cited, we observe gold activities of the Au rich alloys that show small positive deviations from Raoult ideality. Figure 4 shows the heats of mixing for the present work at 1600 K and compares these with those reported by Yazawa *et al*[3] (for 1373 K) and by Predel *et al*[2] (for 1300 K).

While the heats of mixing from the Vienna measurements were obtained through evaluation of Eqs. [9] to [11], those from the Strathclyde laboratory were determined as follows. First the excess entropies of mixing were calculated from the ΔG^E values at 1540 and 1660 K; then, using these ΔS^E values, the excess heats of mixing ΔH^E were determined from ΔG^E (1600 K).

The Vienna measurements for ΔH^E lead to a maximum exothermic value of -38.7 kJ/mol (at $x_{\text{Al}} = 0.52$) while the Strathclyde measurements yield an exothermic maximum of -37.2 kJ/mol (at $x_{\text{Al}} = 0.56$). The heats of mixing obtained by the other investigators indicate less exothermicity; however, in contrast to the

Table I. Slopes $k(x)$ and intercepts $d(x)$ of the Regression Lines $\ln[I_{\text{Al}}(x)/I_{\text{Au}}(x)] = k(x)/T + d(x)$ for the Experimental Data at Various Mole Fractions of Aluminum x_{Al}

Part A Laboratory Vienna

x_{Al}	$k(x)$	$d(x)$
0.0501	−10899.0	3.5115
0.0752	−10909.0	3.6343
0.1029	−8899.1	2.9228
0.1596	−9314.0	3.5477
0.1870	−8058.4	3.0188
0.2302	−7674.5	2.9474
0.2952	−5988.9	2.2862
0.3647	−3885.6	2.2632
0.3743	−2379.7	1.8262
0.4738	1690.9	1.3537
0.5044	2745.5	0.9779
0.5597	6005.5	0.1171
0.6005	6232.8	1.3015
0.6628	10180.6	−0.1022
0.7282	12160.5	0.4081
0.7891	15310.9	−0.1870
0.8274	14411.4	1.1832
0.8477	17944.0	−0.7296

Part B Laboratory Strathclyde

x_{Al}	$k(x)$	$d(x)$
0.1000	−61.0	−3.8617
0.1000	−2599.3	−2.1625
0.1500	−4005.8	−1.0829
0.2000	−2129.9	−1.9635
0.2000	−3042.6	−1.3710
0.2000	−8183.6	1.9259
0.3000	436.6	−2.3513
0.3000	107.2	−2.2604
0.3000	9159.0	−7.4560
0.4000	−11494.0	7.5072
0.4000	786.6	−0.7801
0.4000	1592.3	−1.9090
0.4000	−3627.6	2.3331
0.5000	15394.7	−8.1871
0.5000	−10559.0	7.9529
0.5000	−9309.7	7.6773
0.5000	17437.3	−9.1985
0.6000	−4157.0	6.8161
0.6000	16330.3	−6.7514

Table II. Redlich-Kister Parameters and Constants of Integration ($C_G(T) = C_H - TC_S$) of the Liquid System Au-Al

Parameter	Vienna	Strathclyde
$B_1^{\Delta H^E}$ [J/mol]	−154,607	−146,420
$B_2^{\Delta H^E}$ [J/mol]	−12,333	−41,810
$B_3^{\Delta H^E}$ [J/mol]	27,945	24,012
C_H [J/mol]	−27,235	
$B_1^{\Delta S^E}$ [J/mol·K]	−39.3459	−33.45
$B_2^{\Delta S^E}$ [J/mol·K]	7.1150	−9.35
$B_3^{\Delta S^E}$ [J/mol·K]	1.2607	1.77
C_S [J/mol·K]	12.8356	

Table III. Integral and Partial Excess Gibbs Energies of Liquid Au-Al alloys at 1540 K in kJ/mol.

Part A Laboratory Vienna (Redlich-Kister parameters:

$B_1^{\Delta G^E} = 94.014$, $B_2^{\Delta G^E} = 23.291$, $B_3^{\Delta G^E} = 26.004$;

Constant of Integration $C_G(1540) = -47.004$)

x_{Al}	ΔG^E	ΔG^E_{Au}	ΔG^E_{Al}
0.0	0	0	−44.72
0.1	−5.29	0.58	−58.09
0.2	−11.31	0.66	−59.18
0.3	−16.91	−1.69	−52.43
0.4	−21.20	−7.66	−41.50
0.5	−23.50	−17.68	−29.33
0.6	−23.43	−31.44	−18.10
0.7	−20.83	−47.86	−9.24
0.8	−15.78	−65.15	−3.44
0.9	−8.64	−80.73	−6.3
1.0	0	−91.30	0

Part B Laboratory Strathclyde (Redlich-Kister parameters:

$B_1^{\Delta G^E} = 94.894$, $B_2^{\Delta G^E} = 27.405$, $B_3^{\Delta G^E} = 21.276$;

Constant of Integration $C_G(1540) = -34.691$)

x_{Al}	ΔG^E	ΔG^E_{Au}	ΔG^E_{Al}
0.0	0	0	−46.21
0.1	−5.34	0.51	−58.03
0.2	−11.33	0.56	−58.86
0.3	−16.91	−1.65	−52.52
0.4	−21.25	−7.27	−42.23
0.5	−23.72	−16.87	−30.57
0.6	−23.89	−30.39	−19.55
0.7	−21.51	−47.15	−10.53
0.8	−16.59	−65.87	−4.27
0.9	−9.29	−84.67	0.91
1.0	0	−101.02	0

Table IV. Integral and Partial Excess Gibbs Energies of Liquid Au-Al Alloys at 1660 K in kJ/mol

Part A Laboratory Vienna (Redlich-Kister parameters:

$B_1^{\Delta G^E} = -89.293, B_2^{\Delta G^E} = -24.145, B_3^{\Delta G^E} = 25.853;$

Constant of Integration C_G (1660) = −48.542)

x_{Al}	ΔG^E	ΔG^E_{Au}	ΔG^E_{Al}
0.0	0	0	−39.30
0.1	−4.81	0.65	−53.89
0.2	−10.48	0.91	−56.04
0.3	−15.85	−1.15	−50.17
0.4	−20.02	−6.73	−39.97
0.5	−22.32	−16.29	−28.36
0.6	−22.34	−29.54	−17.54
0.7	−19.91	−45.44	−8.97
0.8	−15.12	−62.22	−3.34
0.9	−8.29	−77.36	0.61
1.0	0	−87.58	0

Part B Laboratory Strathclyde (Redlich-Kister parameters:

$B_1^{\Delta G^E} = -90.880, B_2^{\Delta G^E} = -26.283, B_3^{\Delta G^E} = -21.062;$

Constant of Integration C_G (1660) = −33.592)

x_{Al}	ΔG^E	ΔG^E_{Au}	ΔG^E_{Al}
0.0	0	0	−43.53
0.1	−5.07	0.52	−55.38
0.2	−10.80	0.60	−56.42
0.3	−16.17	−1.49	−50.41
0.4	−20.35	−6.90	−40.52
0.5	−22.72	−16.15	−29.29
0.6	−22.87	−29.16	−18.68
0.7	−20.58	−45.26	−10.01
0.8	−15.85	−63.14	−4.03
0.9	−8.86	−80.93	0.85
1.0	0	−96.10	0

strong differences in ΔG^E values observed among these various investigations, the maxima of the ΔH^E values obtained lie within a range of ~7 kJ/mol (Fig. 4).

The integration constant C_H is, in accordance with Eq. [10], effectively the difference of the heats of evaporation of the pure components, $\Delta H_v^0(\mathrm{Au}) - \Delta H_v^0(\mathrm{Al})$, at the temperature of measurement. Since the values given in the literature for heats of vaporization of gold and aluminum vary considerably, the difference in ΔH_v^0 for the two metals is subject to error. According to the data given in Codata[14] the difference amounts to 36.4 kJ/mol, for 1600 K; while the data of Stull and Sinke[15] give a difference of 30.7 kJ/mol for this temperature. The value of C_H obtained in the present investigations lies somewhat outside of this range (see Table II). However, it should be noted that even small deviations from the $R\ \partial\ln(I_2/I_1)/\partial(1/T)$ *vs* concentration curve lead to large variations in C_H.

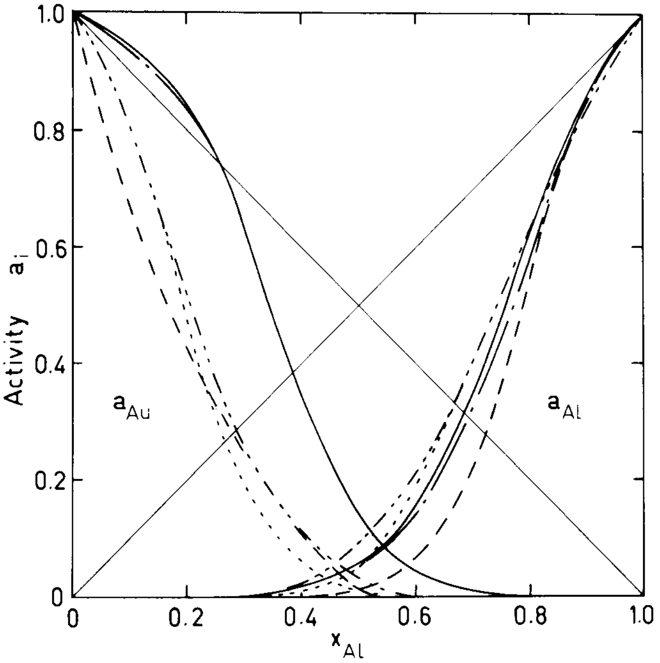

Fig. 3—Thermodynamic activities a_i of liquid Au-Al alloys. ——: this work, Vienna (1600 K); —·—: this work, Strathclyde (1600 K); .....: Charquet *et al*[1] (1338 K); – – –: Predel *et al*[2] (1300 K); —··—: Yazawa *et al*[3] (1373 K).

Just as for ΔG^E, we note large discrepancies in the values of ΔS^E obtained in the various investigations (Fig. 5). The ΔS^E values found in the present work, at 1600 K, were consistently negative with observed minima of −9.9 J/mol·K ($x_{\mathrm{Al}} = 0.47$; Vienna laboratory) and −8.5 J/mol·K ($x_{\mathrm{Al}} = 0.55$; Strathclyde laboratory). The results reported by Yazawa *et al*[3] are those in the best agreement with ours. Charquet *et al*[1] find almost ideal entropy of mixing, while the measurements of Predel *et al*[2] indicate a positive excess entropy.

The present results for ΔS^E (taken together with those of Yazawa *et al*[3]) are probably the more reliable. If it arises solely from a volume change, the value of ΔS^E for the 50-50 at. pct alloy (~ −10 J/mol·K, which corresponds to ~−1.2 k_B/atom) would represent an unusually large shrinkage on mixing (~ 15 pct; Young[16]); but this is entirely compatible with the large absolute value of the heat of mixing ΔH^E ~−40 kJ/mol (corre-

Table V. Activities a_i of Liquid Au-Al Alloys at 1600 K

	Vienna		Strathclyde	
x_{Al}	a_{Au}	a_{Al}	a_{Au}	a_{Al}
0	1.000	0.000	1.000	0.000
0.1	0.942	0.001	0.935	0.001
0.2	0.849	0.003	0.835	0.003
0.3	0.629	0.006	0.622	0.006
0.4	0.349	0.019	0.352	0.018
0.5	0.139	01057	0.145	0.053
0.6	0.040	0.157	0.043	0.143
0.7	0.009	0.353	0.009	0.323
0.8	0.002	0.620	0.002	0.586
0.9	0.000	0.859	0.000	0.842
1.0	0.000	1.000	0.000	1.000

Table VI. Integral Heats of Mixing ΔH^E and Integral Excess Entropies of Mixing ΔS^E of Liquid Au-Al Alloys at 1600 K

x_{Al}	ΔH^E [kJ/mol]		ΔS^E [J/mol · K]	
	Vienna	Strathclyde	Vienna	Strathclyde
0.0	0	0	0.00	0.00
0.1	−11.42	−8.78	−3.98	−2.24
0.2	−21.94	−18.03	−6.91	−4.35
0.3	−30.49	−26.43	−8.82	−6.18
0.4	−36.24	−32.90	−9.77	−7.56
0.5	−38.65	−36.60	−9.84	−8.36
0.6	−37.43	−36.92	−9.09	−8.46
0.7	−32.56	−33.45	−7.62	−7.75
0.8	−24.31	−26.06	−5.54	−6.15
0.9	−13.19	−14.80	−2.96	−3.58
1.0	0	0	0.00	0.00

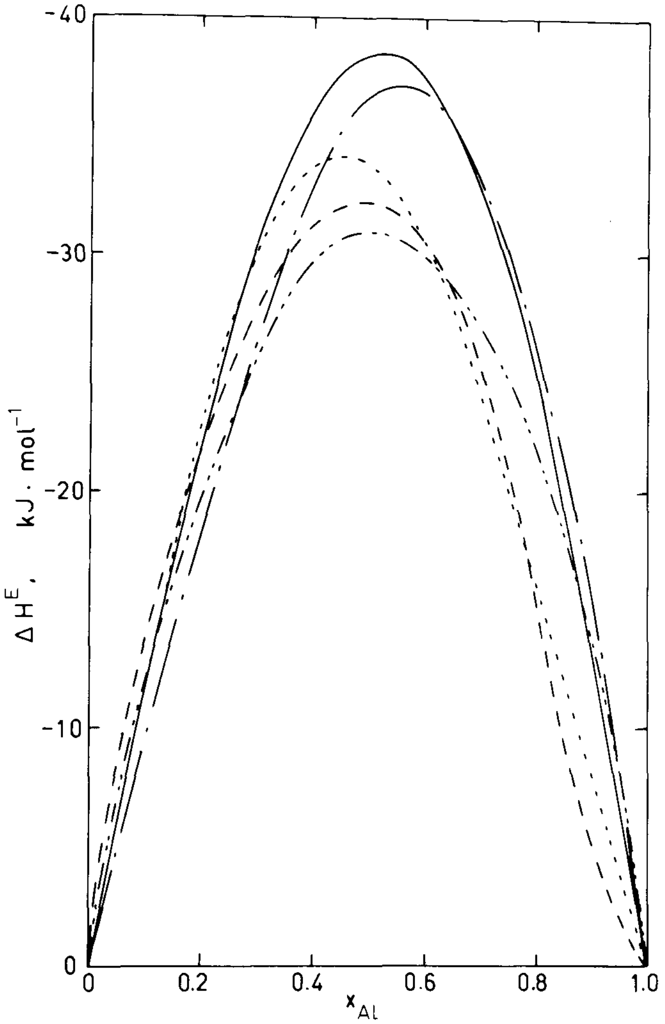

Fig. 4—Molar heats of mixing ΔH^E of liquid Au-Al alloys. —: this work, Vienna (1600 K); —·—: this work, Strathclyde (1600 K); .....: Charquet *et al*[1] (1338 K); – – –: Predel *et al*[2] (1300 K); —··—: Yazawa *et al*[3] (1373 K).

sponding to ~ -4 eV/atom) at this composition. Likewise we regard the hitherto unreported positive deviation of a_{Au} from Raoult ideality, for the Au rich alloys, as real. The eutectic for the Au rich alloys lies between the low melting intermetallics Au_4Al and Au_5Al_2, which each melt peritecticly, and it is in this region of composition that the positive deviation of a_{Au} is observed.

These aspects of the phase equilibrium diagram for the alloy system, as also the strong bonding in the intermetallic compound $AuAl_2$, are probably the result of the large difference in electronegativity between the Au and Al atoms. It is known for solid Au-Al alloys (see for example Fuggle *et al*[17]) that significant *s*- and *d*-electron transfer occurs between the component atoms. Likewise a very strong bond is known to exist in the gaseous molecule AuAl (Cuthill *et al*[5]). It would therefore not be unexpected, when a small proportion of Al atoms are introduced to a melt of Au atoms, if strong local groupings or clusters were to form in the liquid Au rich alloy with short range order consistent with the strongly bonded intermetallic $AuAl_2$. This would increase the activity of the atoms of gold in the liquid present in excess to the local groupings, causing their increased partial vapor pressure and the observed deviation of gold activity from Raoult ideality at high gold concentrations. Any such tendency for formation of local clusters of short range order would also lower the diffusion coefficient in the liquid alloy, for these Au rich compositions, which could correlate with the positive deviation from Raoult ideality (Shimoji[18]).

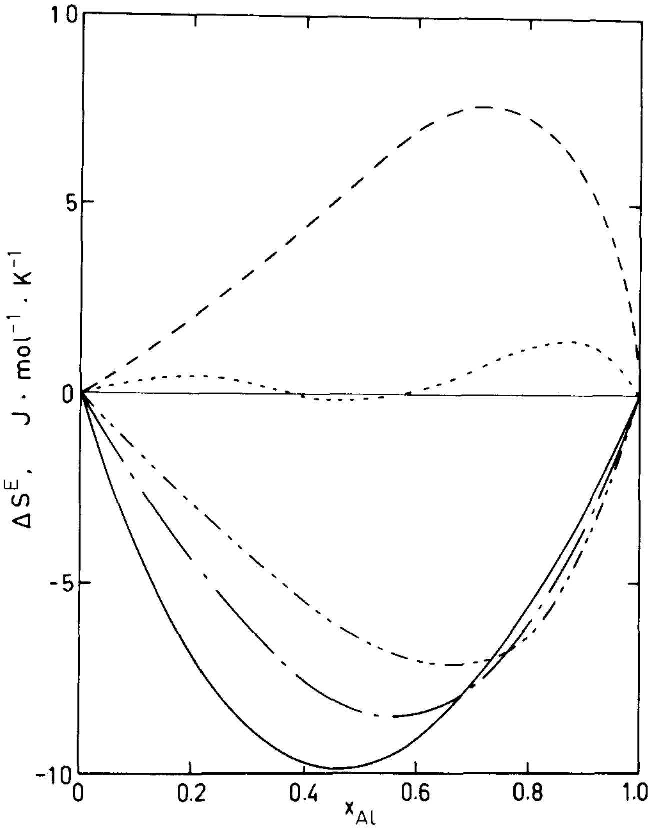

Fig. 5—Molar excess entropies ΔS^E of liquid Au-Al alloys.——: this work, Vienna (1600 K); —·—: this work, Strathclyde (1600 K); .....: Charquet *et al*[1] (1338 K); – – –: Predel *et al*[2] (1300 K); —··—: Yazawa *et al*[3] (1373 K).

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REFERENCES

1. D. Charquet, P. Desré, and E. Bonnier: *C. R. Acad. Sci. (Paris)*, 1967, vol. 264, pp. 1637-40.
2. B. Predel and U. Schallner: *Mater. Sci. Eng.*, 1969/70, vol. 5, pp. 210-19.
3. A. Yazawa and Y. K. Lee: *Trans. Jpn. Inst. Met.*, 1970, vol. 11, pp. 411-18.
4. A. M. Cuthill, P. B. Brown, and D. J. Fabian: *Proceedings International School of Mass Spectrometry*, J. Marsel, ed., pp. 243-258, J. Stefan Inst., Ljubljana, 1971.

5. A. M. Cuthill, D. J. Fabian, and S. Shu-Shou-Shen: *J. Phys. Chem.*, 1973, vol. 77, pp. 2008-11.
6. G. Sodeck, P. Entner, and A. Neckel: *High Temp. Sci.*, 1970, vol. 2, pp. 311-21.
7. A. Neckel, L. Erdelyi, E. Buschmann, and H. Nowotny: *Mh. Chem.*, 1975, vol. 106, pp. 355-67.
8. A. N. Nesmeyanov: *Vapor Pressure of the Chemical Elements,* Elsevier Publ. Comp., Amsterdam-London, New York, 1963.
9. G. R. Belton and R. J. Fruehan: *J. Phys. Chem.*, 1967, vol. 71, pp. 1403-9.
10. A. Neckel and S. Wagner: *Ber. Bunsenges. Phys. Chem.* 1969, vol. 73, pp. 210-17.
11. S. Wagner, G. Sodeck, and A. Neckel: *High Temp. Sci.*, 1971, vol. 3, pp. 481-90.
12. J. Tomiska, H. Nowotny, L. Erdelyi, and A. Neckel: *Z. Metallkde.*, 1977. vol. 68, pp. 350-65.
13. O. Redlich and A. T. Kister: *Ind. Eng. Chem.*, 1948, vol. 40, pp. 345-48.
14. Codata, NBSIR 75-968, 1975.
15. D. R. Stull and G. C. Sinke: *Thermodynamic Properties of the Elements,* Nat. Bureau of Standards, Washington, D.C. 1963.
16. W. H. Young: *Liquid Metals,* R. Evans and D. A. Greenwood, eds., Inst. Phys. Conf. Series. pl, 1976.
17. J. C. Fuggle, E. Källne, L. M. Watson, and D. J. Fabian: *Phys. Rev. B,* 1977, vol. 16, pp. 750-61.
18. M. Shimoji: *Liquid Metals,* Chapter 6, Academic Press, 1977.