

The thermodynamics of dilute liquid copper alloys

Abstract. The published data on the thermodynamics of dilute liquid copper alloys are reviewed. Selected thermodynamic values have been tabulated for binary and ternary alloys.

Résumé. Les auteurs font la critique des données thermodynamiques publiées des alliages liquides de cuivre en région diluée. Des valeurs thermodynamiques sélectionnées ont été classifiées pour les alliages binaires et les alliages ternaires.

In recent years considerable information on the thermodynamic behaviour of elements at dilute concentrations in liquid copper have been reported in the literature. However, this information is widely scattered and presented in a variety of ways. Some of this information has been compiled by Hultgren and Desai (1) in their survey of the thermodynamic properties of binary systems in which copper is one component. One also has the extended works on binary phase diagrams (2) by Hansen and Anderko, Elliott, and Shunk, as phase diagrams intrinsically are thermodynamic in character. In this contribution the available data on the behaviour of elements at dilute concentrations in liquid copper have been collected and summarized in a coherent and consistent form.

Three composition coordinates have been used in the literature reviewed in this work: atom fraction (X), atom per cent (a/o) and weight per cent (%). Table I shows the reference and standard states usually associated with these composition coordinates. The associated activity coefficients and means of designating them in this paper are also shown in the table. For simplicity, γ is the activity coefficient where the pure substance is used as the reference and standard states, and atom fraction is the composition coordinate. The symbol f is reserved for use when the infinitely dilute solution is the reference state. The composition coordinate used in each case is shown as the argument. It is to be noted that a "hypothetical" standard state results when one uses the infinitely dilute solution as the reference state. Unit activity at the "hypothetical" standard state is obtained by the relationship

$$\alpha_i = f_i^\circ \cdot \xi_i = 1; \text{ when } \xi_i = 1 \quad 1$$

ξ_i is the general composition coordinate and f_i° is the activity coefficient at infinite dilution. It is to be recognized that the *actual* activity of i at composition $\xi_i = 1$ is not necessarily equal to 1, since the *actual* activity coefficient, f_i , may no longer be equal to one.

Although data in the literature appear in several forms, only two are used in reporting the results of the study here. They are composition in atom fraction with the pure substance as the reference and standard states (a, Table I), and composition in weight per cent with the infinitely dilute solution as the reference state and the hypothetical 1 per cent solution as the standard state (d, Table I). By convention, the activity coefficient $\alpha_i/X_i = \gamma_i^\circ$ when $X_i \rightarrow 0$.

In preparing this material, it has been necessary in many instances to change the standard state for the data as reported in the literature. Because the reader may also want to alter the standard state for a set of data, a method for doing it is presented briefly. It is desired to calculate the change in standard Gibbs free energy for the reaction in a solution at constant temperature and one atmosphere pressure.

$$i(\xi_i') = i(\xi_i''); \Delta G_i^\circ = \mu_i^{\circ''}(\xi_i'') - \mu_i^{\circ'}(\xi_i') \quad 2$$

ξ_i' and ξ_i'' are the two composition coordinates involved in the transfer, and $\mu_i^{\circ'}(\xi_i')$ and $\mu_i^{\circ''}(\xi_i'')$ are the chemical potentials for the corresponding standard states. Within the solution, the chemical potential is μ_i regardless of the composition coordinate used. Therefore, by the definition of activity one may write

$$\mu_i = \mu_i^{\circ'} + RT \ln \alpha_i' = \mu_i^{\circ''} + RT \ln \alpha_i'' \quad 3$$

where α_i' and α_i'' are the activities of i in the solution in accordance with Equation 2. Equation 3 can be transformed simply to give for Equation 2

$$\mu_i^{\circ''} - \mu_i^{\circ'} = -RT \ln \alpha_i''/\alpha_i' \quad 4$$

The free energy change associated with a change in standard state as given by Equation 4 can be established if for a

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Table I. Reference and standard states used in this compilation.

Composition Coordinate	Reference State	Standard State	Activity Coefficient
(a) atom fraction, X_i	$\lim_{X_i \rightarrow 1} \frac{\alpha_i}{X_i} = 1$	$\alpha_i = 1, X_i = 1$	$\frac{\alpha_i}{X_i} = \gamma_i$
(b) atom fraction, X_i	$\lim_{X_i \rightarrow 0} \frac{\alpha_i}{X_i} = 1$	$\alpha_i = 1, X_i = 1^*$	$\frac{\alpha_i}{X_i} = f_i(X)$
(c) atom pct., a/o	$\lim_{a/o \rightarrow 0} \frac{\alpha_i}{a/o_i} = 1$	$\alpha_i = 1, a/o_i = 1^*$	$\frac{\alpha_i}{a/o_i} = f_i(a/o)$
(d) wt. pct., %	$\lim_{\%i \rightarrow 0} \frac{\alpha_i}{\%i} = 1$	$\alpha_i = 1, \%i = 1^*$	$\frac{\alpha_i}{\%i} = f_i(\%)$

*Hypothetical

Table II. Equations for changing standard states.

Change*	Standard Free Energy Change, $\Delta G^{\circ**}$
(a) $i(X, \text{pure } i \text{ ss}) \rightarrow i(X, \text{i.d.})$	$RT \ln \gamma_i^{\circ}$
(b) $i(X, \text{pure } i \text{ ss}) \rightarrow i(a/o, \text{i.d.})$	$RT \ln [\gamma_i^{\circ}/100]$
(c) $i(X, \text{pure } i \text{ ss}) \rightarrow i(\%, \text{i.d.})$	$RT \ln \gamma_i^{\circ} \cdot M_1/[100 \cdot M_i]$
(d) $i(X, \text{i.d.}) \rightarrow i(\%, \text{i.d.})$	$RT \ln M_1/[100 \cdot M_i]$
(e) $i(a/o, \text{i.d.}) \rightarrow i(\%, \text{i.d.})$	$RT \ln [M_1/M_i]$

*ss = standard state; i.d. - infinite dilution (unit concentration is hypothetical standard state)

** M_1 = molecular weight of solvent, M_i = molecular weight of species i

particular solution the activities, or activity coefficients, based on the two standard states are known. Usually this is true for the infinitely dilute solution. To illustrate, assume that $\xi_i'' = \text{wt. pct.}$ and $\xi_i' = X_i$ in Equation 2. Accordingly, Equation 2 can be re-written

$i(X_i, \text{pure } i \text{ is std. state}) = i(\%, \text{hyp. } 1\% \text{ } i \text{ is std. state})$

$$\Delta G_i^{\circ} = RT \ln \left\{ \gamma_i^{\circ} \cdot [M_1/100 M_i] \right\} \quad 5$$

using Equation 4. The activity coefficients are $\gamma_i = \gamma_i^{\circ}$ and $f_i(\%) = 1$ in this solution. M_i is the molecular weight of i , and M_1 is the molecular weight of the solvent. The term in the brackets expresses the ratio of $X_i/\%i$ at infinite dilution. Formulas for changing standard states that were used in this compilation are shown in Table II.

Interaction coefficients

There has been general adoption of free energy interaction coefficients in the literature to describe the behaviour of a solute element over a modest composition range. The interaction coefficient was introduced by Wagner (3), first used by Chipman (4), and later extended formally by Lupis and Elliott (5-10). The coefficients result from the Taylor

series expansion of the excess partial molar Gibbs free energy of mixing of component i , G_i^E . That is,

$$G_i^E = RT \ln \gamma_i \Big|_{T,P,X_1,X_2 \dots X_n} = RT \ln \gamma_i \Big|_{T,P,X_1 \rightarrow 1} + \sum_{j=2}^n RT \frac{\delta \ln \gamma_i}{\delta X_j} \Big|_{T,P,X_1 \rightarrow 1} [X_j] + \sum_{j=2}^n \frac{1}{2} RT \frac{\partial^2 \ln \gamma_i}{\partial X_j^2} \Big|_{T,P,X_1 \rightarrow 1} [X_j]^2 + \sum_{j=2}^n \sum_{k=2, k \neq j}^n RT \frac{\partial^2 \ln \gamma_i}{\partial X_j \partial X_k} \Big|_{T,P,X_1 \rightarrow 1} [X_j][X_k] + O(X^3) \quad 6$$

The solvent, liquid copper, has been designated as component 1 in our n -component system, and the pure substance 1 is used as the reference state. Using the notation of Lupis and Elliott, (5) Equation 6 becomes.

$$\ln \gamma_i = \ln \gamma_i^{\circ} + \sum_{j=2}^n \epsilon_i^j [X_j] + \sum_{j=2}^n \rho_i^j [X_j]^2 + \sum_{j=2}^n \sum_{k=2, k \neq j}^n \rho_i^{j,k} [X_j][X_k] + O(X^3) \quad 7$$

Third order terms are usually neglected, since the accuracy of the available data rarely permit their being calculated with any degree of certainty.

When atom per cent is employed, Equation 6 becomes:

$$\ln f_i(a/o) = \sum_{j=2}^n \dot{\epsilon}_i^j [a/o_j] + \sum_{j=2}^n \dot{\rho}_i^j [a/o_j]^2 + \sum_{j=2}^n \sum_{\substack{k=2 \\ j < k}}^n \dot{\rho}_i^{j,k} [a/o_j] [a/o_k] + O(a/o^3) \quad 8$$

The zeroth order term in Equation 8 vanishes since $f_i(a/o)$ at $a/o = 0$ is equal to one. The interaction coefficients in this coordinate system, $\dot{\epsilon}$, $\dot{\rho}$, etc., are related directly to those found when using mole fraction as a composition coordinate. That is:

$$\dot{\epsilon}_i^j = 10^{-2} \epsilon_i^j \quad 9$$

$$\dot{\rho}_i^j = 10^{-4} \rho_i^j \quad 10$$

and

$$\dot{\rho}_i^{j,k} = 10^{-4} \rho_i^{j,k} \quad 11$$

When the composition coordinate is weight per cent, the Taylor series expansion corresponding to Equation 6 is (5):

$$\log f_i = \sum_{j=2}^n e_i^j [\text{wt. } \%_j] + \sum_{j=2}^n r_i^j [\text{wt. } \%_j]^2 + \sum_{j=2}^n \sum_{\substack{k=2 \\ j < k}}^n r_i^{j,k} [\text{wt. } \%_j] [\text{wt. } \%_k] + O(\%^3) \quad 12$$

The relationships between interaction coefficients on mole fraction and weight per cent scales have been derived by Lupis and Elliott (5). Some of the more useful relationships are given below:

$$e_i^j = \frac{230}{M_1} M_j e_i^j + \frac{M_1 - M_j}{M_1} \quad 13$$

$$\rho_i^j = \frac{230}{(M_1)^2} [100 M_j^2 r_i^j + (M_1 - M_j) M_j e_i^j] + 1/2 \left[\frac{M_1 - M_j}{M_1} \right]^2 \quad 14$$

$$\rho_i^{j,k} = \frac{230}{(M_1)^2} [100 M_j M_k r_i^{j,k} + M_j (M_1 - M_k) e_i^j + M_k (M_1 - M_k) e_i^k] + \frac{(M_1 - M_k) (M_1 - M_j)}{(M_1)^2} \quad 15$$

Data

The available data on the thermodynamics of liquid copper alloys are summarized in Tables III, IV and V. Tables III and IV give selected thermodynamic values for binary copper-rich alloys. Atomic per cent has not been employed as a composition coordinate in this tabulation; those wishing to do so may use the conversion relationships given in Table II. Data for the ternary alloys Cu-i-H, Cu-i-O and Cu-i-S are summarized in Table V. In these tables interaction coefficients that have been italicized are experimentally determined values; others have been calculated by using Equations 13 to 15. Estimated values are shown in parenthesis. For example, the values for ϵ_{Ca}^{Ca} and ρ_{Ca}^{Ca} are based on experiments made at 877°C, and it is necessary to extrapolate to the supercooled liquid to determine the coefficients at infinite dilution. The temperature given indicates the experimental temperature used in the original determination of thermodynamic properties. A temperature range indicates that more than one temperature was employed in the original experiments, and that the values tabulated are valid for that range of temperature. Finally, the numbers of references which provide the results reported in Tables IV and V are italicized. When the authors have found it necessary to calculate (or recalculate) interaction coefficients from the data given in a study, an asterisk follows the corresponding reference number.

Unfortunately, it is not possible to indicate in a straight forward manner the accuracy of values tabulated in this study. Generally speaking, the error tends to increase with increased concentration of the solute element. It would be best, therefore, to consult the original works cited when second order terms become appreciable at the compositions encountered in a calculation. All references consulted are shown, and the ones used principally in determining the tabulated data are italicized.

The cross product second order terms, $\rho_i^{j,k}$ and $r_i^{j,k}$, have not been tabulated in this study. These terms are generally obscured by the errors inherent in the measurement of the tabulated interaction coefficients. Even so, when the inclusion of these terms is felt to be necessary, they often may be calculated from the reciprocal relations given by Lupis and Elliott (5):

$$e_i^j = \epsilon_j^i \quad 16$$

$$\rho_i^{j,j} + \epsilon_i^j = 2 \rho_j^i + \epsilon_i^i \quad 17$$

$$\rho_i^{j,k} + \epsilon_j^k = \rho_j^{i,k} + \epsilon_j^i = \rho_k^{i,j} + \epsilon_k^j \quad 18$$

and from Equation 15.

Table V. Interaction Coefficients in Ternary Alloys

Element, j	A. Cu-j-H Alloys						References
	ϵ_H^j	ρ_H^j	e_H^j	e_j^H	r_H^j	T(°C)	
Ag	-0.5	0	0.0006	-0.4	0	1225	50*
Al	6.2	3.4	0.0058	1.4	0	1225	50*
Au	-1.9	1.8	0.0003	-0.8	0	1225	50*
Co	-3.1	-0.2	0.015	-1.1	0	1150	48, 49, 57
Cr	-1.6	-0.3	0.0092	-0.7	0	1550	57
Fe	-2.9	-0.4	-0.015	-1.1	0	1150-1550	48, 49, 51, 57
Mn	-1.1	-1.9	-0.006	-0.6	-0.0001	1150	48*, 49*, 51
Ni	-5.5	-0.4	-0.026	-1.8	0	1150-1240	48, 49, 57
P	10.	5.	0.088	2.6	0	1150	48, 49, 57
Pb	21.	-50.	0.031	5.5	0	1100	57
Pt	-8.	14.	-0.0084	-2.5	0	1225	50*
S	9.	4.3	0.073	2.2	0	1150	48, 49
Sb	13.	-12.	0.031	3.2	0	1150	48, 49
Si	4.8	10.	0.042	1.1	0.0016	1150	48, 49, 57
Sn	6.0	5.6	0.016	1.4	0	1100-1300	48, 49, 50, 55
Te	-6.6	6.1	-0.012	-2.1	0	1150	48, 49
Zn	6.8	-0.2	0.029	1.6	0	1150	48, 49, 57
Element j	B. Cu-j-O Alloys						References
	ϵ_O^j	ρ_O^j	e_O^j	e_j^O	r_O^j	T(°C)	
Ag	-0.7	0.2	0	-0.025	0	1100-1200	70, 85*, 108, 109*, 110, 111, 112, 113
Au	8.6	-20.	0.015	0.14	0	1200-1550	84*, 112, 113
Co	-68.	450.	-0.32	-1.2	0.023	1200	83, 111, 114*
Fe	$-4.04 \times 10^6/T$ +2183	(200)	-20000/T +10.8	-70000/T +37.7	(0.01)	1200-1350	44, 72*, 77, 79*, 83*, 111, 114
Ni	$-36000/T$ +17.	(0)	-169/T +0.079	-621/T +0.292	(0)	1200-1300	69, 71, 83, 111, 112, 114, 115
P	$-700000/T$ +385.	-40.	$6230/T$ +3.43	-12100/T +6.63	0	1150-1300	87, 113, 116
Pb	-7.4	0	-0.007	-0.14	-0.0001	1100	81
Pt	38.	-81.	0.057	0.65	0	1200	111, 112, 113
S	-19.	(-9.)	-0.164	-0.33	(0)	1206	82, 120
Si	(-6300)	(-3500)	(-62)	(-110)	(0)	1250	122
Sn	-4.6	-6.	-0.009	-0.09	-0.0001	1100	70, 80, 82, 85*, 109, 110, 115, 117*, 118
Element, j	C. Cu-j-S Alloys						References
	ϵ_S^j	ρ_S^j	e_S^j	e_j^S	r_S^j	T(°C)	
Au	6.7	0	0.012	0.053	0.0001	1115-1200	97*
Co	-4.8	5.	-0.023	-0.046	0.0003	1300-1500	97*
Fe	$-25400/T$ +8.7	2.0	-125/T +0.042	-248/T +0.08	0.0002	1300-1500	97*
Ni	$-29800/T$ +13.	1.0	-159/T +0.069	-290/T +0.122	0.0001	1300-1500	97*
Pt	11.5	0	0.019	0.095	0.0001	1200-1500	97*
Si	6.9	0	0.062	0.055	-0.0008	1200	97*

Table III. The solution thermodynamics of elements in liquid copper.

Element, i	$\gamma_i^{\circ(a)}$ 1200°C	$\Delta G_i^{\circ(X)(b)}$ (cal/g-atom)	$\Delta G_i^{\circ(\text{wt.}\%)(c)}$ (cal/g-atom)	T (°C)	References Consulted
Ag(l)	3.23	3,900-0.32T	3,900-10.52T	1100-1200	1,11-20
Al(l)	0.0028	-8,630-5.84T	-8,630-13.84T	1100	1,14,18,20-26
As(v)	(4.8x10 ⁻⁴)	(-22,350 ⁽¹⁾)	(-22,350-9.44T ⁽¹⁾)	1000	27,28
Au(l)	0.14	-4,630-0.73T	-4,630-12.09T	1175-1325	1,14,18,29-32
Bi(l)	1.25	5,960-3.6T	5,960-15.1T	1100-1300	1,14,27,33,34
C(gr)	1.4x10 ⁵	8,550+17.8T ⁽²⁾	8,550+12.0T ⁽²⁾	1100-1300	35
Ca(l)	5.1x10 ⁻⁴	-22,200 ⁽¹⁾	-22,200-8.2T ⁽¹⁾	800-925	36,37
Cd(v)	15.6	-25,700+22.9T ^(1,3)	-25,700+12.7T ^(1,3)	-----	1,38-41
Cd(l)	0.53	-1,860 ^(1,3)	-1,860-10.2T ^(1,3)	-----	1,38-41
Co(s)	15.4	8,000 ⁽⁴⁾	8,000-9.0T ⁽⁴⁾	-----	11
Cr(s)	43	11,000 ⁽⁴⁾	11,000-8.72T ⁽⁴⁾	-----	2
Fe(s)	24.1	12,970-2.48T	12,970-11.34T	1460-1580	1,42,43,44
Fe(l)	19.5	9,300-0.41T	9,300-9.27T	1460-1580	1,42,43,44
Ga(l)	0.034	-10,800+0.61T	-10,800-8.68T	1100-1280	18,45,46
Ge(l)	0.009	-16,000+1.52T	-16,000-7.86T	1255-1545	18,45,46,119
1/2H ₂ (g)	-----	10,400+8.4T	10,400+7.5T	1100-1300	48-57
In(l)	0.41	-9,550+4.71T	-9,550-5.58T	700-1000	18,28,58
Mg(v)	0.08	-40,200+22.3T	-40,200+15.1T	650-927	59,60
Mg(l)	0.044	-8,670-0.31T	-8,670-7.53T	650-927	59,60
Mn(l)	(0.51)	(-1,950) ⁽¹⁾	(-1,950-8.83T) ⁽¹⁾	1244	1,61,62
Mn(s)	(0.53)	(1,550-2.31T)	(1,550-11.14T)	1244	1,61,62
Ni(l)	2.22	2,340 ⁽¹⁾	2,340-9.0T ⁽¹⁾	-----	1,11,63-69,71
Ni(s)	2.66	6,550-2.5T	6,550-11.5T	-----	1,11,63-69,71
1/2O ₂ (g)	-----	-20,400+10.8T	-20,400+4.43T	1100-1300	1,11,63-73
Pb(l)	5.27	8,620-2.55T	8,620-14.01T	1000-1300	1,14,27,88-94
Pd(s)	(1.3)	(800) ⁽¹⁾	(800-10.1T) ⁽¹⁾	1500-1600	95
Pt(s)	(0.05)	(-10,200+0.87T) ⁽³⁾	(-10,200-10.47T) ⁽³⁾	-----	1,2
1/2S ₂ (g)	-----	-28,600+13.79T	-28,600+6.03T	1050-1250	82,96-98,120,121
Sb(l)	0.014	-12,500	-12,500-10.4T	1000-1200	1,14,27,33,99
Se(v)	0.002	-18,200 ⁽¹⁾	-18,200-9.58T ⁽¹⁾	1200	88
Si(l)	0.006	-15,000 ⁽¹⁾	-15,000-7.5T ⁽¹⁾	1550	1,100,101,122
Si(s)	0.01	-2,900-7.18T	-2,900-14.68T	1550	1,100,101,122
Sn(l)	0.048	-8,900	-8,900-10.4T	1100-1300	1,14,18,30,63, 80,102,103
Te(v)	0.0328	-10,000 ⁽¹⁾	-10,000-10.53T ⁽¹⁾	1200	88
Tl(l)	8.5	6,730-0.31T	6,730-11.74T	1000-1300	1,90,93,94
V(s)	130	28,100-9.4T ^(2,5)	28,100-18.1T ^(2,5)	-----	2
Zn(l)	0.146	-5,640	-5,640-9.17T	1150	1,39,105,106

Notes: (a) For standard state shown in first column. Vapours and gases are at 1 atmosphere pressure.

(b) Change in standard state (a) in Table II.

(c) Change in standard state (c) in Table II.

(1) Regular solution assumed. (2) Calculated from solubility data. (3) Calculated from low temperature data and phase diagram.

(4) Calculated from phase diagram by assuming a regular solution. (5) Henry's law assumed in the solute-rich solid solution.

General remarks

Information on the behaviour of elements such as antimony, bismuth, selenium, and tellurium in copper is sparse or non-existent. Also, there is virtually no information about the effects of oxygen and sulphur on the behaviour of these elements in liquid copper alloys. Thus, it appears that there is still a considerable need for experimental work on the thermodynamic properties of liquid copper alloys.

References

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Table IV. Interaction coefficients in binary liquid copper alloys.

Element, i	ϵ_i^i	ρ_i^i	e_i^i	r_i^i	T(°C)	References
Ag	-2.5	1.3	-0.005	0	1150	1*, 12, 13, 16, 17*, 19*
Al	14.	-4.	0.14	-0.003	1100	1*, 23*, 24, 26
Au	3.7	-1.7	0.008	0	1277	1*, 29*, 30, 32*
Bi	-6800/T+1.65	3400/T-0.8	-9./T+0.0052	0.0001	1000-1200	1, 33*, 34
Ca	(20.)	(-10.)	(0.14)	(-0.0019)	877	36, 37*
Fe	-5.7	4.7	-0.029	0.0003	1550	1*, 42*
Ga	7.	(0)	0.028	(0)	1280	45*, 56
Ge	13.4	0	0.051	0.0001	1255	45*, 47*
H	(1.0)	(0.5)	(0)	(0)	1123	50*
Mg	(9.8)	(-4.9)	(0.1)	(-0.003)	927	59*, 60*
Mn	6.	-8.	0.03	-0.0005	1244	1*, 60*, 61
O	-24,000/T+7.8	0	-414/T+0.122	0.004	1100-1300	44, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87
Pb	-2.7	0	-0.0006	0	1200	1*, 89, 90*, 91, 93*, 94*
S	-20800/T	0	-179/T-0.004	1.8/T	1050-1250	82, 96*, 97*, 120, 121
Sb	(15)	(-7.5)	(0.04)	(0.0001)	1000-1200	33*, 99*
Sn	10.	-8.	0.025	0	1300-1320	30*, 102, 103
Tl	-4.8	+3.	-0.008	0	1300	1*, 93
Zn	4.	-2.	0.017	-0.0001	1150	39*, 105*

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