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COMPUTING SURFACE TENSIONS OF BINARY AND TERNARY ALLOY SYSTEMS WITH THE GIBBSIAN METHOD

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ABSTRACT

The surface tension in metallic alloy systems is modelled by applying direct Gibbs energy minimisation technique to the surface monolayer model. The model results are compared with previously published experimental values for Bi-Sn system as well as surface tension values determined by the authors using the sessile drop method for the ternary Ag-Au-Cu system.

Keywords: surface tension, Gibbs energy minimisation, metal alloys

1. Introduction

Information about the surface tension of metal alloy systems is essential for understanding and prediction of things such as wettability, crystal growth or phase properties of nanoscale particles. A commonly used assumption is that the surface can be modelled as a single monolayer. The purpose of this work is to show how the monolayer model can handled by normal thermodynamic equilibrium programs based on the minimisation of the total Gibbs energy of the system. The model results are compared with experimental data in two example cases.

2. Experimental

Experimental surface tension values for the Ag-Au-Cu system were determined by the sessile drop method at 1381 K. The shape of a metal alloy drops of about 6-8 mm in equatorial diameter and 4-6 mm height was determined using a CCD camera and image analysis software and the drop shape was used to calculate the surface tension of the alloy. Detailed description of the experimental procedure can be found in reference [1]

3. Theory

3.1 Basic thermodynamic relations

If a system containing a surface is considered being comprised of two parts (phases), a surface layer (s) and an isotropic bulk (b), the total Gibbs energy of the system can be written as:

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$$G = \sum_i n_i \mu_i + A\sigma = \sum_i n_i^b \mu_i + \sum_i n_i^s \mu_i + A\sigma \qquad (1)$$

where n_i is the molar amount and μ_i the chemical potential of species i, σ the surface tension in the system and A the surface area. If the surface phase is considered to be of a monolayer thickness, the equation (1) can be rewritten in a form

$$G = \sum_i n_i^b \mu_i + \sum_i n_i^s \left(\mu_i + A_i \sigma \right) \qquad (2)$$

where A_i is the molar surface area of the species i. The chemical potential of species i in the bulk phase can be written as

$$\mu_i = \mu_i^0 + RT \ln a_i^b \qquad (3)$$

and in the surface phase as

$$\mu_i = \mu_i^{0,s} + RT \ln a_i^s - A_i \sigma \qquad (4)$$

By applying equations (3) and (4) for the case of pure one component system, a relationship between the standard states of the bulk and surface phase can be derived

$$\mu_i^{0,s} = \mu_i^0 + A_i \sigma_i \qquad (5)$$

By combining equations (1), (3) and (4), the total Gibbs energy of the system can be given in a simple form that does not explicitly include the surface tension term:

$$G = \sum_i n_i^b \left(\mu_i^0 + RT \ln a_i^b \right) + \sum_i n_i^s \left(\mu_i^{0,s} + RT \ln a_i^s \right) \qquad (6)$$

while from equations (3), (4) and (5) one receives

$$\mu_i^0 + A_i \sigma_i + RT \ln a_i^s - A_i \sigma = \mu_i^0 + RT \ln a_i^b \Rightarrow \sigma = \sigma_i + \frac{RT}{A_i} \ln \frac{a_i^s}{a_i^b} \qquad (7)$$

equation first derived by Butler [2], and used extensively in calculating surface tension in various mixtures, including metal alloy systems[3].

3.2 Use of Gibbs energy minimiser for surface equilibria calculations

When a Gibbs energy minimiser is used to solve chemical equilibrium states, the total Gibbs energy is usually calculated as:

$$G = \sum_\alpha \sum_i n_i^\alpha \mu_i \text{ (over all phases (}\alpha\text{) and species (}i\text{) present in the system) } (8)$$

where the chemical potentials of the species are calculated from supplied thermodynamic data using an equation of the type or equivalent to:

$$\mu_i^\alpha = \mu_i^{0,\alpha}(T,p) + RT \ln x_i^\alpha \gamma_i^\alpha \qquad (9)$$

Comparing equations (2), (4) and (9) one can see that the chemical potential for a species in the surface phase as calculated by a Gibbs energy minimiser would really be the total molar Gibbs energy of the surface species, marked here with μ_i^*

$$\mu_i^* \equiv \mu_i + A_i \sigma \qquad (10)$$

For a traditional chemical equilibrium calculation the mass balance relations restricting the possible states can be given in the form

$$\sum_\alpha \sum_i v_{ik} n_i^\alpha - b_k = 0 \text{ (for all components k)} \qquad (11)$$

where b_k is the total molar amount of component k and v_{ik} the stoichiometric coefficient between species i and component k. The condition of constant total surface area can be stated in a similar form as

$$\sum_i A_i n_i^s - A = 0 \qquad (12)$$

or alternatively as

$$\sum_\alpha \sum_i A_i^\alpha n_i^\alpha - A = 0 \qquad (13)$$

where the molar surface for any species in any non-surface phase α is zero. A is the total surface area of the system. As the constant surface area condition (equation 13) is of the same form as the traditional mass balances (equation 11), it can for the mathematical handling of the system be combined with them by considering the surface area as a new component in the system. In the Table 1 this is presented in a matrix form; the species in the system are presented as rows and the conserved components as columns.

In Table 1 A_0 is a normalization constant with dimensions of m^2/mol. The numerical value of A_0 is in principle arbitrary, but for the best numerical performance of Gibbs energy minimisers it is generally best to chose the value so that the resulting A_i / A_0 values are fairly near to unity.

In a chemical equilibrium state, in addition to species and phases chemical potentials can also be defined for the different components in the system[4]. The chemical potential of individual species are related to the chemical potentials of the components by equation (14)

$$\mu_i = \sum_k v_{ik} \pi_k \qquad (14)$$

where π_k is the chemical potential of the component k, and v_{ik} the stoichiometric coefficient between species i and component k.

Applied to the surface system, equation (14) can be stated for a bulk species as

$$\mu_i = \sum_{k=1}^{M+1} v_{ik} \pi_k = \sum_{k=1}^{M} v_{ik} \pi_k \qquad (15)$$

and for the surface species as

$$\mu_i^* = \sum_{k=1}^{M+1} v_{ik} \pi_k = \sum_{k=1}^{M} v_{ik} \pi_i + \frac{A_i}{A_0} \pi_{area} \qquad (15)$$

where π_{area} is the chemical potential of the new component defined to fix the total surface area of the system

Finally, from equations (15) and (10) we have the equalities

$$\pi_{area} / A_0 = \left(\mu_i^* - \mu_i \right) / A_i = \sigma \qquad (16)$$

The chemical potential (divided by the normalization constant A_0) of the new 'area' component is equal to the surface tension of the system.

4. Results

As examples we consider a binary and a ternary alloy system in the liquid state. The method described above is applied to calculate the surface tension and composition of Bi-Sn and Ag-Au-Cu melts in temperatures were experimental surface tension data is available for these mixtures.

4.1 Bi-Sn liquid binary system at 608 K

Thermodynamic and other physical data required to do the calculations in the Bi-Sn system are presented in Table 2.

The molar surface areas are calculated from the molar volume data using equation (17) where N_a is the Avogardo's number.

$$A_i = 1.091 \cdot N_a^{1/3} V_i^{2/3} \tag{17}$$

The resulting surface areas at 608 K are A_{Bi} = 70028 m2/mol and A_{Sn} = 64499 m2/mol. By choosing the value 10 000 m^2/mol for the normalization factor A_0 the stoichiometric definitions for the system at 608 K are as presented in Table 3.

Normal standard state values can be used for the bulk phase (although for the purpose of calculating surface tension and equilibrium composition they could also be set to zero), while the standard state values for the surface phase need to be adjusted using the equation (5). The excess Gibbs energy for the bulk is calculated as given in Table 2, but the excess energy for the surface phase is modified by using equation (18)

$$G_{surface}^{Excess} = \beta \cdot x_{Bi}^s x_{Sn}^s L \tag{18}$$

where the factor β with a numerical value of 0.83[3] is used to approximate the effect that the reduced coordination number of metal atoms on the surface as well as that of reconfiguration has on the excess Gibbs energy.

The calculation results for the example system are as shown in Table 4 and in Figure 1. The calculations were done using the ChemSheet program[7] that is based on the ChemApp[7] thermodynamic program library.

4.2 Ag-Au-Cu liquid ternary system at 1381 K

Molar volume and surface tension data required for the calculations in the Au-Ag-Cu system are presented in Table 5.

The excess Gibbs energy values for the bulk phase are calculated using the equation (19) [10]

$$G^{Excess}(J/mol) = \sum_i \sum_{j>i} x_i x_j L_{i,j} + x_i x_{j>i} x_{k>j} L_{i,j,k} \tag{19}$$

The binary and ternary interaction parameters have a Redlich-Kister type dependency on the composition (equations (20-21)

$$L_{i,j} = \sum_v \left(x_i - x_j \right)^v {}^v L_{i,j} \qquad (20)$$

$$L_{i,j,k} = x_i\, {}^0 L_{i,j,k} + x_j\, {}^1 L_{i,j,k} + x_k\, {}^2 L_{i,j,k} \qquad (21)$$

The interaction parameters are listed in Table 6.

For the surface phase the excess Gibbs energy is modified as in previous example by multiplying the excess energy expression with $\beta = 0.83$. Modelled surface tension values are compared with experimental results in Figure 2. There is a fairly large amount of scatter in the experimental surface tension results. More precise measurements are currently being conducted in Osaka University using the constrained drop method [13]. Also modelled dependencies of surface mole fraction of copper from the bulk fraction are shown for different Ag/Au ratios.

5. Conclusions

The stoichiometric conservation matrix of a Gibbs energy minimising program can be extended to include a surface monolayer as a separate phase while the constraint of constant surface area is included by adding a new component in the system. A single equilibrium calculation then results the equilibrium composition of the bulk and surface phases. The surface tension of the mixture is obtained from the chemical potential of the new area component. The model is consistent with the Butler monolayer model for surfaces while the use of a general Gibbs energy minimiser makes it easier to handle systems with multiple components and complex non-ideal mixing energies. The example cases considered in the paper are metal alloy systems with a particularly simple relation between the expressions of excess Gibbs energies in the bulk and in the surface, but the method is directly extendable also to other systems where more complex relations for Gibbs excess energies for the surface layer have been derived, such as ionic melts [14].

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Figure 1. Calculated surface tension values (left) and surface layer composition (right) as a function of bulk composition in the Bi-Sn system. Experimental surface tension values are from reference[8]

Figure 2. Calculated surface tension values compared to experimental values measured by the authors (left) and the dependency of the surface molar fraction of copper from bulk composition (right) in the Ag-Au-Cu ternary system.

Table 1. Presentation in a matrix form of stoichiometries in a system with a bulk phase and a surface phase, N species and M components

		Component(1)	Component(2)	...	Component(M)	Area
bulk	Species (1)	v_{11}	v_{12}	...	v_{1M}	0
	Species (2)	v_{21}	v_{22}	...	v_{2M}	0
	⋮	⋮	⋮	⋱	⋮	⋮
	Species (N)	v_{N1}	v_{N2}	...	v_{NM}	0
surface	Species (1)	v_{11}	v_{12}	...	v_{1M}	A_1/A_0
	Species (2)	v_{21}	v_{22}	...	v_{2M}	A_2/A_0
	⋮	⋮	⋮	⋱	⋮	⋮
	Species (N)	v_{N1}	v_{N2}	...	v_{NM}	A_N/A_0

Table 2. Required data for calculations in Bi-Sn binary system from references [4-5].

V_{Bi} (m³/mol)   = 0.0000208*(1+ 0.000117*(T/K- 544))   [5]

V_{Sn} (m³/mol) = 0.000017*(1+ 0.00087*(T/K - 505))   [5]

σ_{Bi} (N/m)   = 0.378 - 0.00007*(T/K - 544) [5]

σ_{Sn} (N/m)   = 0.56 - 0.00009*(T/K - 544) [5]

G^{Excess} (J/mol) =$x_{Bi}\,x_{Sn}$ L   [6]

L (J/mol) = 490 + 0.97T + (xBi - xSn)(-30-0.235T)

Table 3. Stoichiometry of the Bi-Sn system at 608 K

		Bi	Sn	area
bulk	Bi(l)	1	0	0
	Sn(l)	0	1	0
surface	Bi(l)	1	0	7.0028
	Sn(l)	0	1	6.4499

Table 4. Calculated chemical potentials of the surface component and the surface tensions as a function of Sn content of the Bi-Sn binary alloy.

$x(Sn)$	π_{area} (J/mol)	$\pi_{area}/A_o = \sigma$ (N/m)
0	3736.71	0.3737
0.05	3769.70	0.3770
0.1	3803.93	0.3804
0.15	3839.54	0.3840
0.2	3876.66	0.3877
0.25	3915.50	0.3915
0.3	3956.28	0.3956
0.35	3999.33	0.3999
0.4	4045.01	0.4045
0.45	4093.82	0.4094
0.5	4146.41	0.4146
0.55	4203.61	0.4204
0.6	4266.53	0.4267
0.65	4336.72	0.4337
0.7	4416.33	0.4416
0.75	4508.53	0.4509
0.8	4618.17	0.4618
0.85	4753.25	0.4753
0.9	4928.10	0.4928
0.95	5171.49	0.5171
1	5542.38	0.5542

Table 5. molar volume and surface tension data for the Ag-Au-Cu system

V_{Au} (m^3/mol)	= 11.3*(1+0.8/10000*(T/K-1337.33))/1000000 [5]
V_{Ag} (m^3/mol)	= 11.6*(1+0.98/10000*(T/K-1234.93))/1000000 [9]
V_{Cu} (m^3/mol)	= 7.94*(1+1/10000*(T/K-1357.77))/1000000 [9]
σ_{Au} (N/m)	= 1.33 - 0.00014*T/K [5]
σ_{Ag} (N/m)	= 1.207 - 0.000228*T/K [9]
σ_{Cu} (N/m)	= 1.585 - 0.00021*T/K [9]

Table 6. Interaction parameters for the Ag-Au-Cu system

${}^0L_{Ag,Au} = -16402 + 1.14T\,/\,K$ [11]		
${}^0L_{Ag,Cu} = 17384.37 - 4.46438T\,/\,K$ [10]	${}^1L_{Ag,Cu} = 1660.74 - 2.31516T\,/\,K$ [10]	
${}^0L_{Au,Cu} = -27900 - T\,/\,K$ [12]	${}^1L_{Au,Cu} = 4730$ [12]	${}^2L_{Au,Cu} = 3500 + 3.5T/K$ [12]
${}^0L_{Ag,Au,Cu} = 10000$ [10]	${}^1L_{Ag,Au,Cu} = -105000 + 30T/K$ [10]	${}^2L_{Ag,Au,Cu} = -1000$ [10]

Surface tension (N/m)

0.6
0.55
0.5
0.45
0.4
0.35
0.3

0   0.5   1

x(Sn) bulk

Calculated
experimental

x(Sn) surface

1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

0   0.2   0.4   0.6   0.8   1

x(Sn) bulk