Surface Segregation and Surface Tension of Liquid Mixtures

T. UTIGARD and J. M. TOGURI

A model has been developed in which surfaces are treated as separate phases with a thickness corresponding to a monolayer. It is argued that the surface tension of liquids is a measure of the excess surface chemical potential of the surface atoms relative to the bulk atoms. Equations for the calculation of the surface composition and surface tension of liquid mixtures are developed. Using only the surface tension and molar volume data of the pure components, excellent correspondence between calculated and experimental surface tension values was obtained. The method was also tested on liquid systems showing immiscibility. The surface coverage calculated from the present model is compared with that calculated using Gibbs adsorption equation. The surface coverage of the solute species increases with increasing solute concentration. However, depending on the surface properties of the system, the excess surface coverage may pass through a maximum value and then decrease with increasing solute concentration.

I. THERMODYNAMICS OF LIQUID SURFACES

SURFACE energy is the reversible work required to extend a surface by a unit area at constant temperature, pressure, and composition. Consequently, surface energy is the Gibbs energy per unit surface area. In creating a surface, atoms or molecules must be transferred from minimum potential energy positions in the interior of the bulk phase to an interface with an asymmetrical potential energy field. Since the surface species are in a state of higher Gibbs energy than those in the bulk, the tendency of the system is to reduce the number of atoms in the surface, *i.e.*, to minimize the surface area. This tendency results in the so-called surface tension or surface energy.

The Gibbs energy of a one component, two phase system is:

$$G = n\mu + \gamma A \qquad [1]$$

where A is the surface area, γ is the surface tension, n is the number of mols, and μ is the chemical potential. At equilibrium the Gibbs energy has its lowest value. Guggenheim[1] treated a planar interface as a surface phase between two bulk phases. From thermodynamic considerations, he developed the following expression for the Gibbs energy of the surface phase for a two component system:

$$G = n_A\mu_A + n_B\mu_B + \gamma A \qquad [2]$$

where n_A and n_B are the number of mols of components A and B in the surface phase, respectively.

In the following model the liquid/gas interface is treated as a separate phase, in a manner similar to Guggenheim.[1] By assuming that it consists of a single monolayer to which all the surface properties are ascribed, the Gibbs energy of a one component, two-phase system becomes:

$$\begin{aligned} G &= n_t\mu + \gamma A = n_t\mu + n_s\gamma/\Gamma \\ &= (n_t - n_s)\mu + n_s(\mu + \gamma/\Gamma) \end{aligned} \qquad [3]$$

where n_t is the total number of molecules, n_s is the number of molecules in the monolayer, and Γ is the surface coverage ($\Gamma = n_s/A$) calculated from the following equation:

$$\Gamma = \mathrm{N_A}^{-1/3}V^{-2/3}(\mathrm{mol/m^2}) = 1.18V^{-2/3}10^{-8}(\mathrm{mol/m^2}) \qquad [4]$$

where $\mathrm{N_A}$ is the Avogadro number and V is the molar volume of the pure component. At constant temperature, pressure, and composition, the apparent chemical potential of the surface molecules becomes:

$$\mu_s = \delta G/\delta n_s = \mu + \gamma/\Gamma \quad \text{and}$$
$$\mu^{xs} = \mu_s - \mu = \gamma/\Gamma \qquad [5]$$

The difference in chemical potential between two phases is the reversible work of transferring a molecule from one phase to another. From the present definition of a surface phase, the net transfer of a molecule to the surface phase leads to an increase in the surface area and the difference in the chemical potential is given by Eq. [5]. It is concluded that the surface tension is a measure of the excess Gibbs energy of the surface molecules relative to the bulk molecules. A corollary of this definition of surface energy is that when the Gibbs energy of an interface between two phases is zero, they are completely miscible and no interface is discernible.

It must be noted that treating the surface as a separate phase consisting of a single monolayer is thermodynamically questionable. It will, however, be shown that this model is useful in explaining the behavior of the surface tension of liquid mixtures.

II. BULK-SURFACE EXCHANGE REACTION

Using the surface chemical potential of each of the species in the mixture, the surface composition of any alloy A_xB_y can be calculated from the equilibrium constant of the following equation:

$$A(s) + B(b) = A(b) + B(s) \qquad [6]$$

where (s) and (b) represent surface and bulk species, respectively. By applying the surface excess chemical potential (Eq. [5]) to this exchange reaction, the equilibrium constant becomes:

T. UTIGARD is Metallurgical Engineer, Falconbridge Ltd., Falconbridge, ON, Canada, P0M 1S0. J. M. TOGURI is Professor, Department of Metallurgy and Materials Science, University of Toronto, Toronto, ON, Canada, M5S 1A4.

Manuscript submitted February 24, 1987.

$$K = \exp(-(\mu_B^{xs} - \mu_A^{xs})/\mathrm{R}T)$$
$$= \exp(\gamma_A/\Gamma_A - \gamma_B/\Gamma_B)/\mathrm{R}T = \frac{a_{A(b)}a_{B(s)}}{a_{A(s)}a_{B(b)}} \qquad [7]$$

The surface activity of species A and B is assumed to be $(1 - \theta)$ and θ, respectively, when the fractional surface coverage of species B is θ. The following expression is obtained for the surface coverage of element B:

$$\theta = 1/(1 + a_{A(b)}/Ka_{B(b)}) \qquad [8]$$

where $a_{A(b)}$ and $a_{B(b)}$ are the activities of A and B, respectively. For an ideal solution the activity can be replaced by the mol fraction. The average molar surface chemical potential becomes:

$$\mu_{\mathrm{avc}}^{xs} = (1 - \theta)\mu_A^{xs} + \theta\mu_B^{xs} = (1 - \theta)\gamma_A/\Gamma_A + \theta\gamma_B/\Gamma_B \qquad [9]$$

The molar surface area of the alloy will vary with composition according to:

$$1/\Gamma = \theta/\Gamma_B + (1 - \theta)/\Gamma_A \qquad [10]$$

The surface tension of the alloy is calculated from the average surface chemical potential and the molar surface area as shown in Eq. [11].

$$\gamma = [(1 - \theta)\gamma_A/\Gamma_A + \theta\gamma_B/\Gamma_B]/[(1 - \theta)/\Gamma_A + \theta/\Gamma_B] \qquad [11]$$

For a multi-component system, Eq. [11] can be extended as follows:

$$\gamma = \Sigma(\theta_i\gamma_i/\Gamma_i)/\Sigma(\theta_i/\Gamma_i) \qquad [12]$$

III. SURFACE TENSION OF BINARY MIXTURES

The surface tension of liquid mixtures is generally not expected to be an additive quantity as given by the relation

$$\gamma = x_A\gamma_A + x_B\gamma_B \qquad [13]$$

where x_A and x_B are the mol fractions and γ_A and γ_B are the surface tension of the pure components, respectively. The commonly observed negative deviation from this relation is explained by the surface enrichment of the component of lower surface tension.

According to Guggenheim,[1] the surface tension of an ideal solution of two components can be calculated from the following equation:

$$\exp(-\gamma a/\mathrm{R}T) = x_A\exp(-\gamma_A a/\mathrm{R}T) + x_B\exp(-\gamma_B a/\mathrm{R}T) \qquad [14]$$

where a is the surface area per mol which is assumed to be equal for the two components. It has been found, however, that the surface tension of many mixtures deviates more negatively than that predicted by Eq. [14]. Another limitation is that this method can not be used to predict the surface tension of liquid mixtures which are not completely miscible. In both Guggenheim's and the present model, only data for the pure components are necessary to perform the calculations. The first step in the present model is to calculate the surface coverage (Eq. [8]) and then the surface tension (Eq. [11]).

Eberhart[2] assumed the surface tension to be a linear function of the surface mol fractions. He obtained the following expression for the surface tension of mixtures:

$$\gamma = (Sx_A\gamma_A + x_B\gamma_B)/(Sx_A + x_B) \qquad [15]$$

where S is a surface enrichment factor determined by fitting the surface tension-composition curve to this equation. This method is therefore an interpolation formula and can not be used to predict the surface tension of mixtures when data are not available.

The present method was applied to the same four systems (H_2-D_2, Cu-Ni, $RbNO_3$-KNO_3, and C_6H_6-C_8H_{18}) used by Eberhart[2] to test his equation. The physical properties used are given in Table I. For these calculations, it was assumed that the activity of the species in the mixture is equal to the respective mol fraction. The experimental and calculated surface tension values for these four systems are shown in Figure 1. A good fit is observed between the experimental and calculated surface tension values for the H_2-D_2,[3] Cu-Ni,[4] and $RbNO_3$-KNO_3 systems. However, the experimental surface tensions[6] of C_6H_6-C_8H_{18} mixtures deviate negatively (a maximum of 6 pct) from the predicted values. This may be due to the large difference in the geometry of C_6H_6 and C_8H_{18}.

To test the model further, the calculated surface tension values are compared with the experimental for the following six systems: Cu-Sn, Cu-Sb, Pb-Bi, Ag-Ge, Ag-Sb, and Fe-Sn. These results are shown in Figure 2 for the Cu-Sn and Cu-Sb[7] systems, in Figure 3 for the Pb-Bi system,[8] in Figure 4 for the Ag-Ge and Ag-Sb systems,[7,9] and in Figure 5 for the Fe-Sn system.[10] Satisfactory fit is observed. The largest discrepancy occurs for the Ag-Sb system with the calculated values being lower than the experimental values by 10 pct. However, scatter in the experimental surface tension data is not uncommon. For example, the reported surface tension of copper varies from 1018 to 1390 mN/m.[11]

For the Fe-Sn system (Figure 5), the surface tension calculated by the present model is lower than that predicted by Guggenheim's equation. This is the case for most systems. Based on the present model, the surface tension of a mixture will never be smaller than the smallest of the surface tension of the pure components. For systems such as Fe-Cr, where both components have approximately the same value, a straight line will be obtained. This is confirmed experimentally.[10]

IV. SURFACE TENSION FOR LIQUID SYSTEMS WITH IMMISCIBILITY

Considering the mercury-water system, Gibbs[12] reasoned that on a clean mercury surface, water will be adsorbed as the mercury becomes saturated with water, and may reach such a thickness that the interior of the water layer behaves as if it were a bulk liquid water. If this is the case, the surface tension of the saturated mercury should be the sum of the surface tension of water and the interfacial tension between mercury and water, *i.e.*,

$$\gamma_{\mathrm{Hg(Sat.\,H_2O)}} = \gamma_{\mathrm{H_2O}} + \gamma_{\mathrm{Hg/H_2O}} \qquad [16]$$

The surface tension of water saturated with Hg is not expected to be very different from that of pure water. Thus,

Table I. Physical Properties of Liquids Used to Test the Proposed Surface Tension Model. Series A: Mixtures with Complete Miscibility

Mixture			V (cm^3/mol)		γ (mN/m)		
A	*B*	Temp. (K)	*A*	*B*	*A*	*B*	Ref.
D_2	H_2	20.4	23.7	28.2	3.45	1.93	3
Ni	Cu	1823	7.54	8.36	1730	1260	4
KNO_3	$RbNO_3$	623	48.9	53.8	111.1	105.0	5
C_6H_6	C_8H_{18}	303	153.9	114.2	17.8	27.5	6
Cu	Sn	1373	7.94	18.5	1337	488	7
Cu	Sb	1373	7.94	19.5	1337	349	7
Pb	Bi	75	20.7	19.9	436	371	8
Ag	Ge	1273	11.6	13.0	915	585	7,9
Ag	Sb	1273	11.6	19.3	903	344	9
Fe	Sn	1823	7.92	19.8	1929	460	10

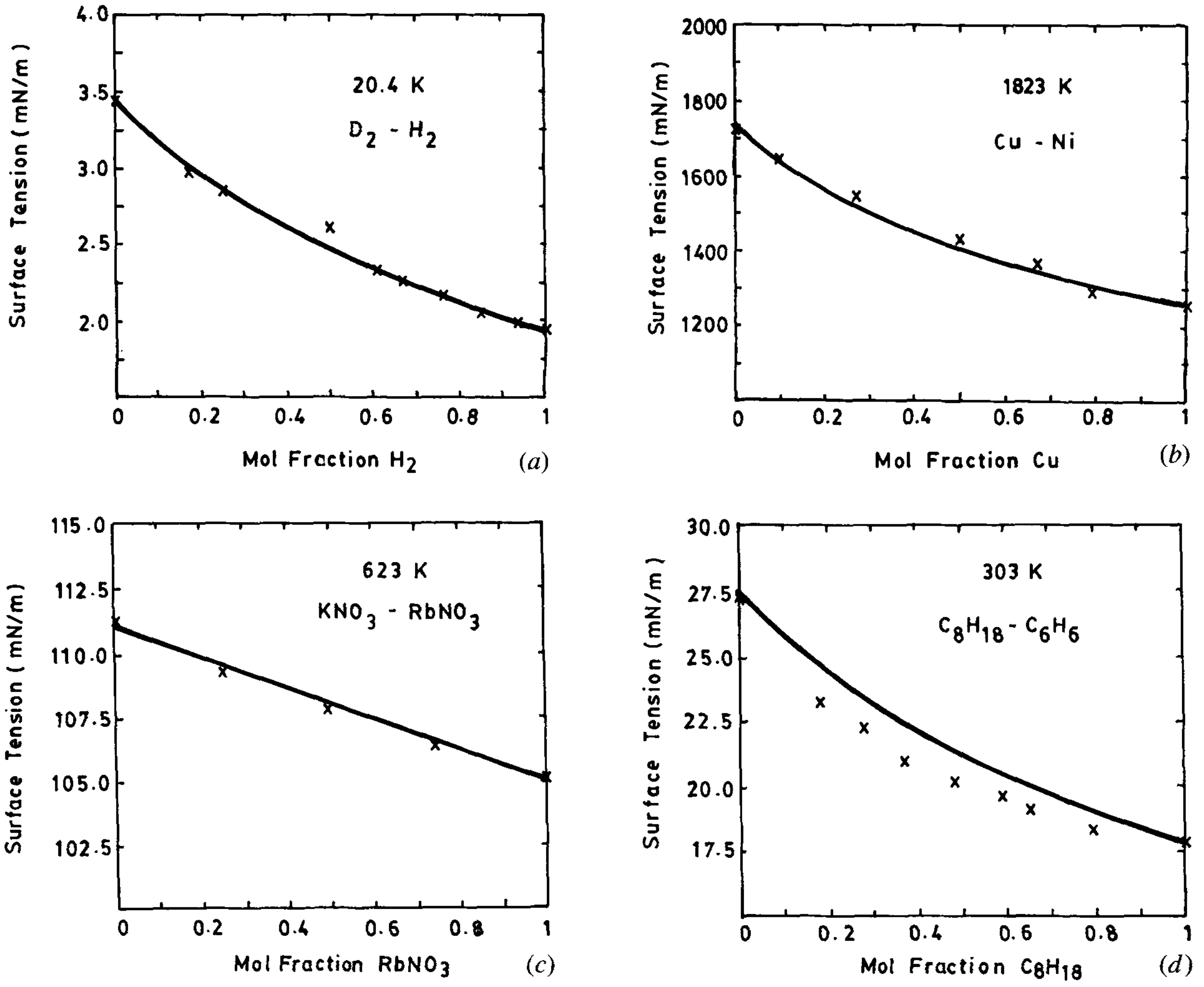


Fig. 1—Calculated and experimental surface tensions of deuterium-hydrogen (*a*),[3] nickel-copper (*b*),[4] potassium nitrate-rubidium nitrate (*c*),[5] and benzene-isooctane (*d*)[6] mixtures.

to calculate the surface tension of Hg saturated with water, it is necessary to estimate the interfacial tension between Hg and H_2O.

The interfacial tension is the result of the attraction of the molecules at the interface to the bulk of the two phases. This pulling force depends on intermolecular forces within the bulk liquid and on the interaction between the two phases. Berthelot[13] proposed the following relation for the attractive constant a_{AB} between like molecules:

$$a_{AB} = (a_{AA}a_{BB})^{1/2} \qquad [17]$$

Girifalco and Good[14] set up a corresponding relation involving the energies of adhesion and cohesion of two phases, and obtained Eq. [18].

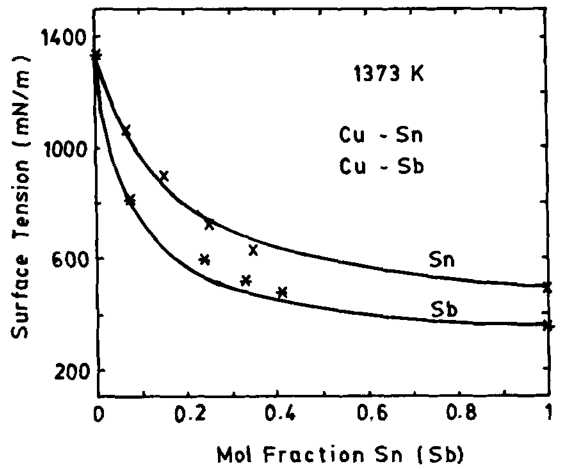


Fig. 2—Calculated and experimental surface tensions of copper-tin and copper-antimony alloys.[7]

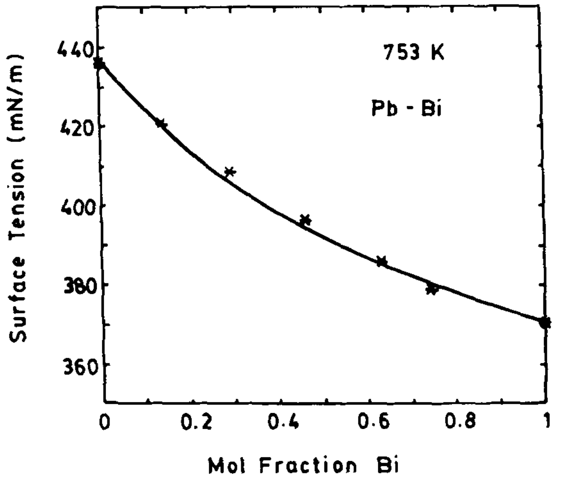
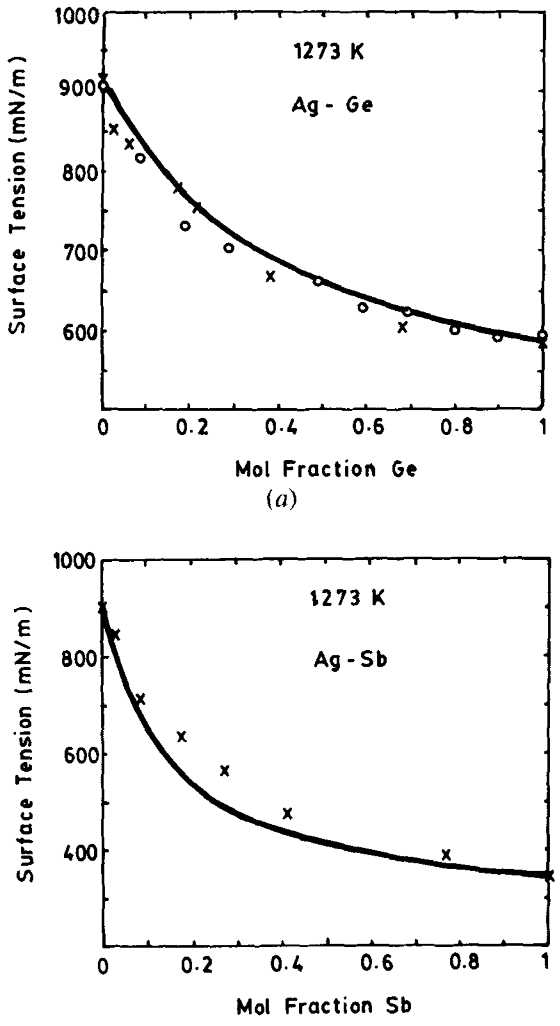


Fig. 3—Calculated and experimental surface tensions of lead-bismuth alloys at 753 K.[8]



(a)

(b)

Fig. 4—Calculated and experimental surface tensions of silver-germanium[7,9] and silver-antimony[9] alloys.

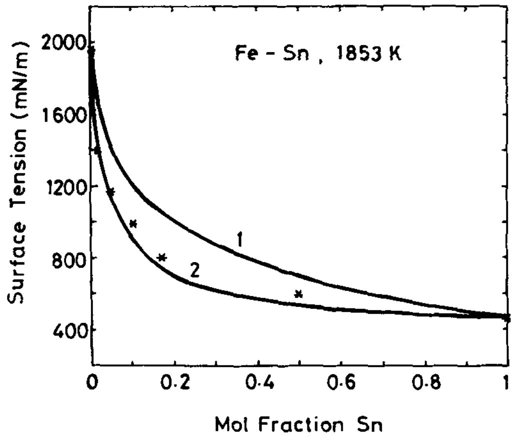


Fig. 5—Calculated surface tensions of iron-tin alloys on the basis of (1) Guggenheim and (2) present model based on the experimental data of Nogi *et al.*[10]

$$\gamma_{AB} = \gamma_A + \gamma_B - 2\phi(\gamma_A\gamma_B)^{1/2} \qquad [18]$$

ϕ is a constant which depends on and represents the interaction between the two liquids. If $\phi = 0$, there is no interaction between the two phases and the interfacial tension is the sum of the surface tensions. The larger ϕ is, the larger the interaction between the two phases. For liquids of high mutual solubility, the interaction parameter is generally[14] close to unity due to the strong interaction between the two phases and due to similar bonding types.

The surface tension of a liquid where the surface layer consists only of the solute species (B) is given by combining Eqs. [16] and [18].

$$\gamma_{A(\mathrm{Sat.}B)} = \gamma_A + 2\gamma_B - 2\phi(\gamma_A\gamma_B)^{1/2} \qquad [19]$$

This dependency is illustrated in Figure 6 for different values of Good's interaction parameter. Assuming that a solute B has a lower surface tension than A and that it has a limited solubility in A, the lowest possible surface tension of liquid A with additions of B is one-half the value of pure A. This occurs when the surface tension of pure B is one-fourth that of pure A and when the interaction parameter is unity. Experimentally, this has been observed for additions of different elements to aluminum[15] and iron.[16] It is interesting to note that this also occurs for the surface and grain boundary energies of solid Cu-Sb alloys,[17] indicating that this treatment may be applied to solids as well.

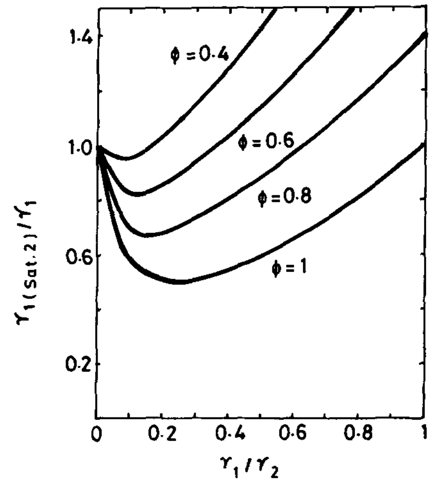


Fig. 6 — Surface tension of a liquid saturated with an immiscible solute, as a function of Good's parameter and the surface tensions of the pure liquids.

If the solubility of species B in A is very low, it can be assumed that the activity of solvent A is unity and that the activity of solute B increases linearly from zero in pure A to unity at saturation. However, when activity data are known they can be used directly in Eq. [8] to calculate the surface coverage. Because the surface tension of A with a complete surface layer of B is equal to $\gamma_{A(\mathrm{Sat}.B)}$ and not to that of pure B, Eq. [11] is rewritten in the following form:

$$\tau = \frac{(1 - \theta)\gamma_A/\Gamma_A + \theta\gamma_{A(\mathrm{Sat}.B)}/\Gamma_B}{(1 - \theta)/\Gamma_A + \theta/\Gamma_B} \qquad [20]$$

To test this equation, the following systems were investigated: Al-Pb, Al-Bi, Zn-Pb, Zn-Bi, Fe-FeO, Cu-Cu_2S, and solid mixtures of Sb in Cu. The physical properties used for these calculations are given in Table II. As shown in Figure 7 for the Al-Pb, Al-Bi, and Zn-Pb metallic systems, the present model predicts slightly higher values than those experimentally[18] obtained. For the Zn-Bi system, the experimental data from two different investigations[18,19] deviate considerably. The model calculations are lower than those obtained by Okajima and Sakao[19] while they are higher than those reported by Goumiri *et al.*[18]

The surface tension of Fe and Cu depends strongly on the oxygen and sulfur content[20,21,22] The same procedure as used for the metallic binaries was adopted. The experimental[20] and calculated surface tensions of iron and copper are shown as a function of mass pct oxygen and log (mass pct oxygen) in Figure 8. The only assumptions made in the calculation are that the interaction parameters between Fe and FeO and between Cu and Cu_2S are unity. The data used for the pure species are given in Table II.

The calculated surface tensions of solid copper with additions of Sb compare excellently with the experimental data[17] as shown in Figure 9. The fractional surface coverage of Sb is also calculated. To perform these calculations, the same assumptions as applied to liquid mixtures were used. Good's interaction parameter between the Cu-rich phase and the Sb-rich phase was assumed to be unity. The surface tension and density of Sb used in the calculation were the values for pure liquid Sb (see Table II).

V. SURFACE COVERAGE

Surface active elements concentrate on the surface of the liquid solvent and lower the surface tension. To calculate the excess surface concentration of these elements, Gibbs adsorption equation is often used.

$$RT\Gamma^{xs} = -d\gamma/d \ln a_{\mathrm{solute}} \qquad [21]$$

By plotting the surface tension as a function of the logarithm of the activity of the surface active element, the excess surface concentration is given by the slope of the curve. At the point where the slope becomes independent of the activity, it is commonly assumed that a complete monolayer of the surface active element is formed.[24] Several investigators[20,25-27] have found that the slope decreases beyond the point of maximum slope. No simple interpretation has been given for this behavior, but it has been suggested that it might be due to the formation of multi-molecular layers. However, it is unlikely that the surface tension continues to decrease at the same rate with increasing activity of the surface active element, after a complete monolayer has been formed.

Considering a mixture A_xB_y, the excess fractional coverage of solute B becomes:

$$\theta^{xs} = \theta - y \qquad [22]$$

where y is the mol fraction of B in the bulk phase. This is illustrated in Figure 10 for the Fe-Sn system. The surface concentration of Sn increases continuously with increasing content of Sn. However, the excess surface coverage goes through a maximum at about 20 mol pct Sn and then decreases and becomes zero at pure Sn.[28]

The surface coverage for the Fe-O, Cu-S, and Co-O systems using Gibbs adsorption equation (Eq. [21]) was calculated from the shape of the surface tension curves obtained from the present model. These values are compared in Table III with the literature values and with those calculated from the molar volumes on which the present calculations were based. The surface coverages obtained by using these three different methods do not differ very much when taking into consideration the experimental errors.[20] Using the present model, it was assumed that the respective surface layers consisted of FeO, Cu_2S, and CoO. It was further assumed that these surface layers had the same properties as if they were bulk liquids.

VI. CONCLUSIONS

Surfaces were treated as separate phases with a thickness corresponding to a monolayer. It was argued that the surface tension of liquids is a measure of the excess surface chemical potential of the surface atoms relative to the bulk atoms. From the surface tension and the molar volumes of pure liquids, surface chemical potentials were calculated. The surface composition of liquid mixtures was calculated based on the following exchange reaction:

$$A(s) + B(b) = A(b) + B(s)$$

The surface coverage of solute species increases with increasing solute concentration. A complete monolayer may

Table II. Physical Properties of Liquids Used to Test the Proposed Surface Tension Model. Series B: Mixtures with Immiscibility

Mixture		Temp. (K)	V (cm^3/mol)		γ (mN/m)		Sol Mol Pct	Ref.
A	*B*		*A*	*B*	*A*	*B*		
Al	Pb	1173	11.6	20.9	836	399	1.2	18
Al	Bi	973	11.4	21.9	860	348	0.8	18
Zn	Pb	760	9.96	19.7	775	440	1.0	18
Zn	Bi	760	9.96	21.3	775	363	2.5	18
Zn	Bi	823	10.1	21.5	815	300	3.0	19
Zn	Bi	903	10.2	21.8	800	280	miscible	19
Fe	FeO	1823	7.92	16.4	1800	570	0.21 mass pct	20
Cu	Cu_2S	1473	8.65	30.4	1120	380	2.2 mass pct	21
Cu	Sb	1173	7.14	19.3	1770	351	1.6 mass pct	17

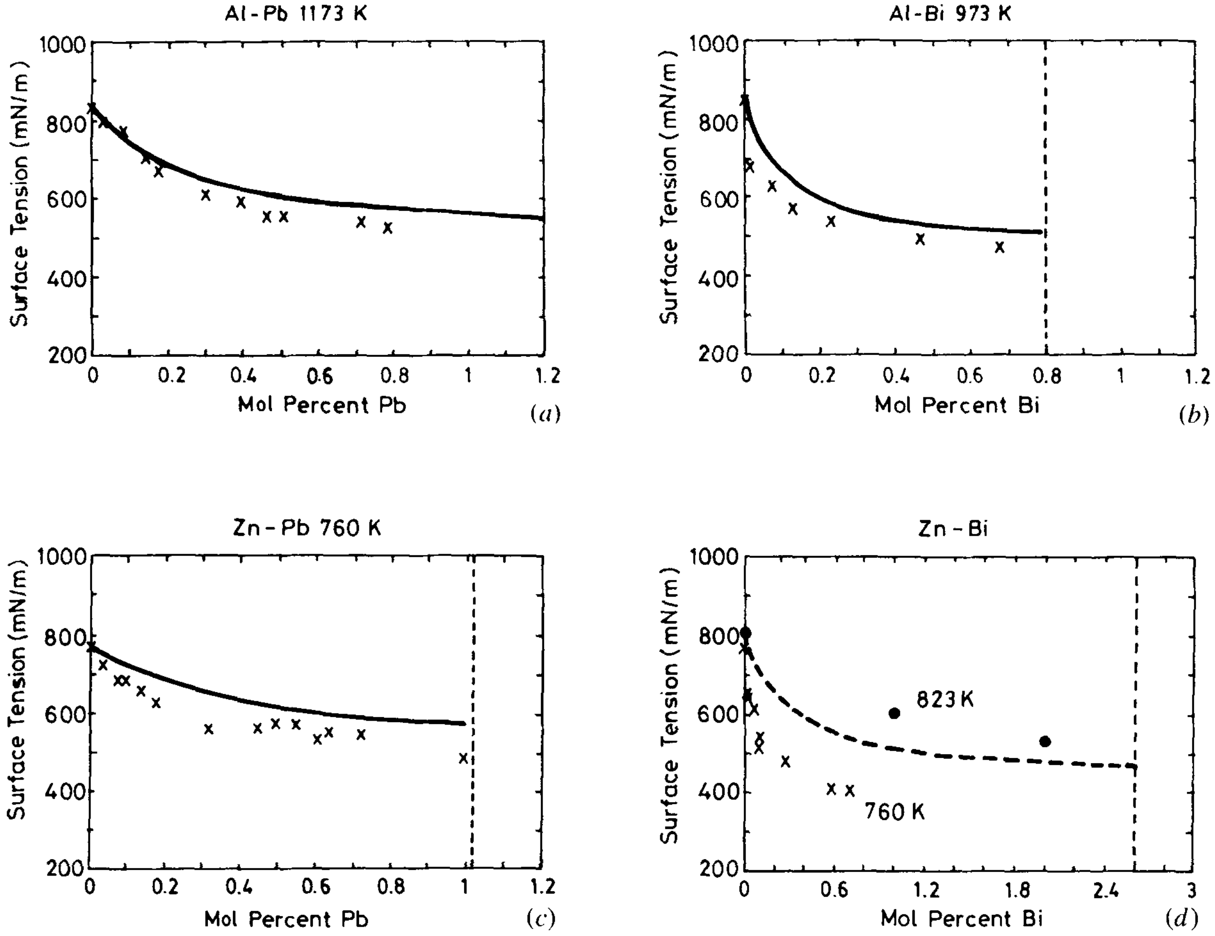


Fig. 7—Calculated and experimental[18,19] surface tensions of aluminum-lead, aluminum-bismuth, zinc-lead, and zinc-bismuth alloys.

form only at solute saturation. However, depending on the surface properties of the system, the excess fractional surface coverage may have a maximum value within the binary system.

Equations for the calculation of the surface tension of liquid mixture were developed. The surface tension of a liquid with the surface layer covered by a solute was found to be equal to the interfacial tension between the two phases plus the surface tension of the pure solute. Applying Girifalco and Good's equation to these systems, expressions for the surface tension of mixtures with limited miscibility were developed.

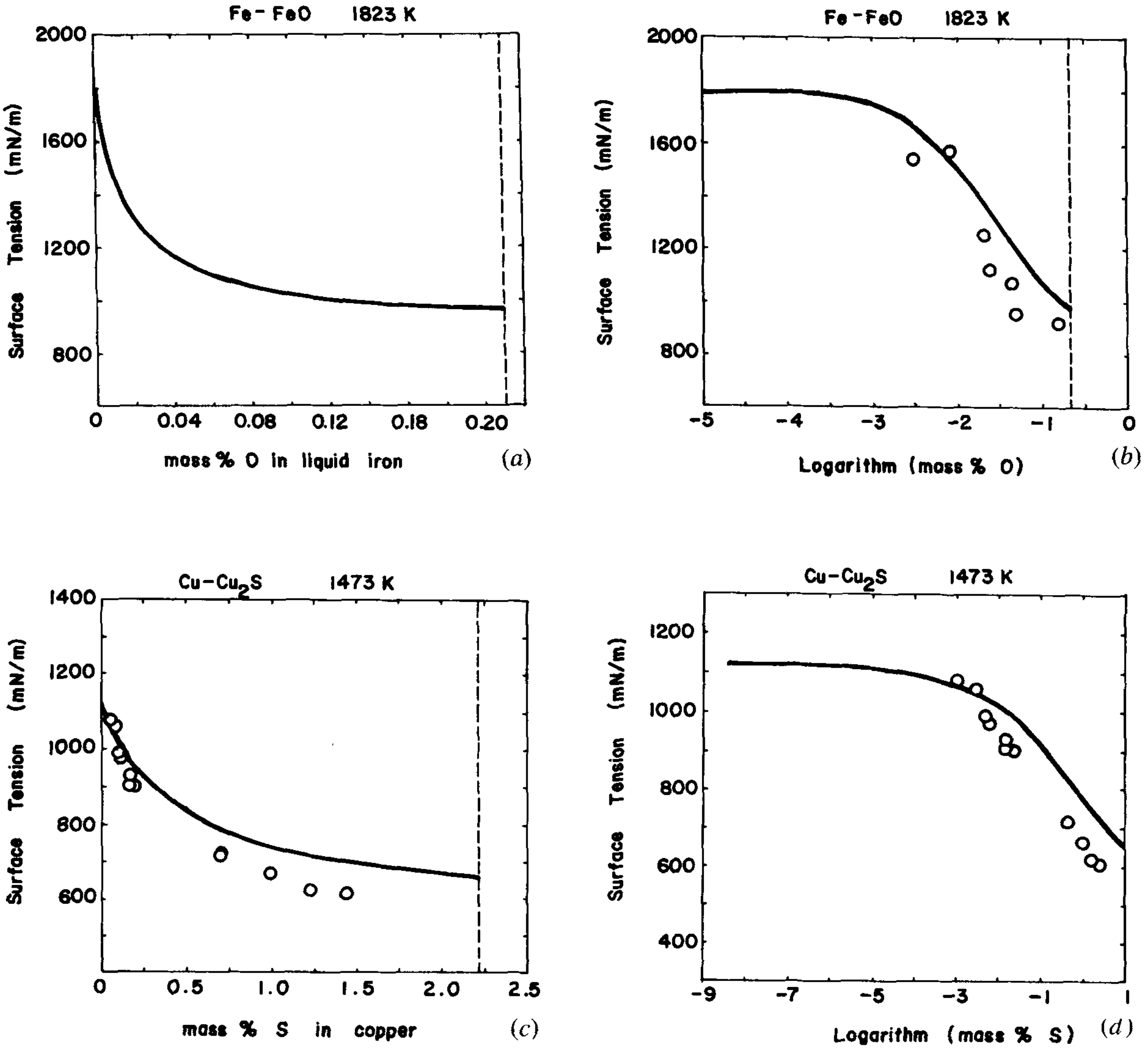


Fig. 8 — Surface tensions of iron as a function of oxygen content and of the logarithm of oxygen content.[20] Surface tension of copper as a function of sulfur content and the logarithm of sulfur content.[21]

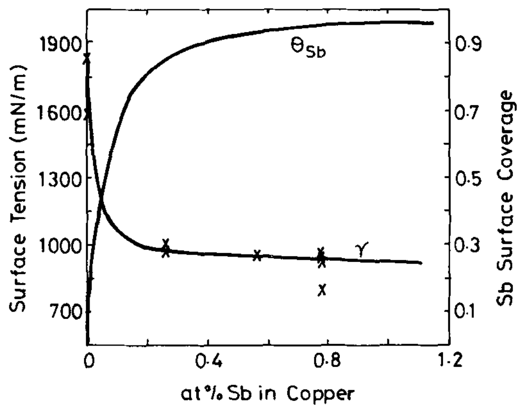


Fig. 9 — Calculated and experimental[17] surface tension of copper as a function of the antimony content at 1173 K.

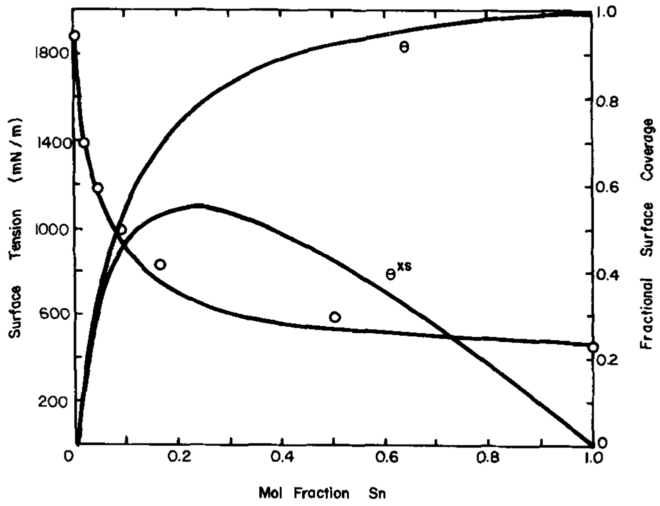


Fig. 10 — Calculated surface tensions of Fe-Sn alloys, the excess surface, and the surface concentrations of Sn.

Table III. Excess Surface Coverage for the Fe-O, Cu-S, and Co-O Systems. Excess Surface Coverage ($10^5 \cdot \mathrm{mol} \cdot \mathrm{m}^{-2}$)

		Gibbs Adsorption Equation	
	Mol. Vol.	Calc. Curve	Exp. Curve
Fe-O	1.83	1.64	2.0 (20)
Cu-S	1.21	1.41	1.56 (21)
Co-O	1.83	1.58	1.7 (25)

ACKNOWLEDGMENTS

This work was financially supported by the Natural Sciences and Engineering Research Council of Canada. One of the authors (T. Utigard) wishes to thank the University of Toronto and the Royal Norwegian Council for Scientific and Industrial Research (NTNF) for financial support.

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