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Statistical Surface Thermodynamics of Simple Liquid Mixtures

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The surface properties of nonpolar liquid mixtures are derived from the application of the grand partition function to a cell model of the vapor-liquid interface. The surface tension and surface composition are expressed in terms of the activity coefficients in the bulk liquid and pure-component properties. The results are in excellent agreement with existing data for the surface tension of mixtures. This treatment provides a sound theoretical basis for the prediction of surface properties of other liquid systems and is especially applicable to cryogenic mixtures.

The surface tension of a liquid or liquid solution is a direct consequence of the molecular structure of the liquid phase and of the intermolecular forces operating within that phase; therefore better understanding of the surface tension is of physicochemical interest. In addition a better understanding of the surface properties of liquid mixtures also has engineering application; for example studies of vapor-liquid mass transfer in distillation columns (*13, 14, 33*) showed that the rate depends on whether the transfer tended to increase or decrease the surface tension of the liquid phase. Also it has been shown (*30*) that in extraction operations the presence or absence of interfacial turbulence is very much influenced by the variation of surface tension with composition. Finally the role of surface tension in heat transfer by nucleate boiling is now being recognized (*19*).

Although the treatment to be discussed is general, it is especially applicable to one class of mixtures, liquefied gases at low temperature. Surface tension data are available for most pure cryogenic fluids, but such data for cryogenic mixtures are very scarce. Since the possible number of mixtures is very large and since experimental measurements at low temperature are difficult to perform, it is of interest to develop a technique for calculating the surface properties of mixtures from more readily available thermodynamic data. Such a technique is provided through the methods of statistical mechanics. This work considers the application of molecular and statistical mechanical concepts to the derivation of a theoretical equation which relates the surface tension and the surface composition of a mixture to the surface energy of the pure components and to the excess free energy of the bulk solution. The final result is quite simple to use and gives excellent agreement between calculated and experimental surface properties.

The thermodynamic treatment of a surface liquid solution is considerably more difficult than that of a bulk liquid solution. Although the composition of the bulk solution is a known, independent variable, the composition of the surface is an unknown, dependent variable; as a result of preferential adsorption the mole fractions of the various components at the surface are quite different from those of the bulk. Therefore any attempt to calculate the surface tension of a mixture must be coupled with a calculation of the surface composition.

Previous attempts to apply statistical mechanics to the calculation of surface tensions of mixtures are due primarily to Guggenheim (*15*) and to Prigogine (*11, 12*). Guggenheim uses the lattice model for the liquid state, which necessitates some more or less arbitrary assumptions on the geometry of the liquid structure and which, when applied to mixtures, is valid only for components of very nearly the same size and shape. Prigogine approaches the calculation of the equilibrium surface tension of a mixture as a perturbation on the dynamic surface tension using a smoothed potential model; his technique is applicable only for mixtures which are very nearly ideal and requires the arbitrary choice of a reference substance, which can seriously affect the results. In the present work no lattice model is used, and the equilibrium surface tension is obtained by a minimization of the free energy without recourse to the dynamic surface tension. The picture of the liquid state as used here is strongly influenced by the ideas of Hildebrand (*16*) and is therefore most applicable to fluids composed of simple, nonpolar molecules. Because of the interest in cryogenic systems as well as the relative simplicity of the molecules involved the systems chosen for illustration are mixtures containing argon, methane, nitrogen, oxygen, and carbon monoxide.

PURE LIQUID

Before applying statistical mechanics to the surface of a liquid mixture one must first consider the case of the pure component. Adopting the Guggenheim version of the surface, wherein the surface layer or layers are a separate phase, one considers a system comprising the surface and bulk phases of a pure species consisting of N' and N molecules, respectively. The surface free energy σ of the system may be expressed as the difference between the actual free energy G for a system containing a surface of area Ω and the free energy of the same system were it to have zero surface:

$$\sigma\Omega = G - (N + N')\mu^o \tag{1}$$

The properties of the surface and bulk phases may both be described in terms of a cell model. In the cell model of a liquid the potential energy of a molecule is divided into two parts: first the potential energy required to take the molecule isothermally from infinite separation (the ideal gas) and place it at rest in the center of the cell and second the potential energy resulting from the molecule's displacement from the center of the cell. In using this model one ignores the interchange of cells by molecules, since this type of motion is negligible in liquids except at densities near the critical.

In terms of the partition functions of the cell model one may write the configurational Helmholtz free energy of the system as

$$F = -NkT \ln [q \exp (u_c/RT)] - N'kT \ln [q' \exp (u_c'/RT)] \tag{2}$$

Each partition function is expressed in terms of the product of the cell partition function which is related to potential energy changes within the cell and the exponential term which is the configurational effect of placing the molecule into the center of the cell. This term is positive because the configurational energy, or potential energy relative to the ideal gas, is an intrinsically negative quantity.

Now the excellent assumption is made that at low to moderate pressures the PV term for liquids is negligible, and the Helmholtz and Gibbs free energies are equivalent. Then the chemical potential of the bulk liquid is expressed as

$$\mu^o = -kT \ln [q \exp (u_c/RT)] \tag{3}$$

Then, still assuming the equivalence of F and G, one may combine Equations (1), (2), and (3) to give

$$\sigma\Omega = -kT\, N' \ln [q' \exp (u_c'/RT)] - N'\mu^o \tag{4}$$

which may be rearranged to yield

$$-\frac{\sigma\omega}{kT} = \ln q' + \frac{u_c'}{RT} + \frac{\mu^o}{kT} \tag{5}$$

Equation (5) is the basic equation which relates the pure-component surface tension to the statistical properties of the molecules. The thermodynamic reference state used in Equation (5), as well as in subsequent equations, is the ideal gas at the same temperature.

Before proceeding to use Equation (5) one must first write the partition function for the surface of a mixture.

GRAND PARTITION FUNCTION OF THE SURFACE

The cell model is also used to characterize the surface of binary mixtures. This treatment assumes that the part of the partition function pertaining to the motion within the cell is the same in the surface phase of a mixture as at the surface of the pure component. Such an assumption is valid in a great many cases, as for example the case of nonpolar species which interact with dispersion forces only.

In dealing with mixtures it is convenient to work with the grand canonical partition function in order to account for nonidealities in the bulk liquid. The surface tension of a mixture is related to Ξ', the grand canonical partition function of the surface phase (*15*)

$$\sigma\Omega = -kT \ln \Xi' \tag{6}$$

and the grand partition function for a binary mixture of 1 and 2 may be expressed in the form

$$\Xi = \sum_{N_1'} \sum_{N_2'} g(N_1', N_2')\ (q_1')^{N_1'}\ (q_2')^{N_2'} \exp\left(\frac{\mu_1' N_1'}{kT}\right) \exp\left(\frac{\mu_2' N_2'}{kT}\right) \exp\left[\frac{U_c'(N_1', N_2')}{kT}\right] \tag{7}$$

The double summation in Equation (7) is limited by the constraint

$$N_1' + N_2' = \text{constant}$$

This means that the total number of cells in the surface phase is fixed. The factor g, the combinatorial factor, represents the number of possible ways of placing the two types of molecules in their cells. If random mixing in the surface is assumed, the number of arrangements is

$$g(N_1', N_2') = \frac{(N_1' + N_2')!}{N_1'!\ N_2'!} \tag{8}$$

The cell partition functions of the surface molecules q_1' and q_2' are assumed to be the same in the mixture as in the pure-component surface phases. This does not say that the environment of a molecule is the same in the mixture as in the pure component, but rather that the changes in potential energy resulting from displacement of the molecule already within its cell are similar in the pure species and in the mixture. Such an assumption is quite good for nonpolar molecules, such as most cryogenic liquids.

The configurational energy U_c' represents the potential energy of taking the surface molecules of the mixture isothermally from the ideal gas state and placing them at rest in their cells. It is this which takes into account the effect of the different environment of a molecule in a mixture from its environment in the pure state.

For thermodynamic equilibrium the chemical potentials are equal in the surface and bulk phases:

$$\mu_i' = \mu_i \tag{9}$$

The activity of each species in the bulk mixture is given by

$$\mu_i - \mu_i^o = kT \ln a_i \tag{10}$$

If Equations (8), (9), and (10) are substituted into (7), the grand partition function becomes

$$\Xi' = \sum_{N_1'} \sum_{N_2'} \frac{(N_1' + N_2')!}{N_1'!\ N_2'!}\ (q_1' a_1)^{N_1'}\ (q_2' a_2)^{N_2'}$$

$$\exp\left(\frac{N_1'\mu_1^o}{kT}\right)\exp\left(\frac{N_2'\mu_2^o}{kT}\right)\exp\left[\frac{U_c'(N_1', N_2')}{kT}\right] \tag{11}$$

The double summation in Equation (11) can be replaced by a single summation, since for a binary mixture one may stipulate a single surface mole fraction that defines the composition of the surface. When one uses the surface mole fraction and applies Stirling's approximation to the combinatorial factor, Equation (11) becomes, for one mole of surface phase

$$\Xi' = \sum_{x_1'} \left(\frac{q_1'a_1}{x_1'}\right)^{x'_1\underset{\sim}{N}} \left(\frac{q_2'a_2}{x_2'}\right)^{x'_2\underset{\sim}{N}}$$

$$\exp\left(\frac{x_1'\underset{\sim}{N}\mu_1^o}{kT}\right)\exp\left(\frac{x_2'\underset{\sim}{N}\mu_2^o}{kT}\right)\exp\left[\frac{u_c'(x_1')}{kT}\right] \tag{12}$$

Finally Equation (5) for pure components may be written for each of the species in the mixture and solved for the q''s:

$$q_i' = \exp\left[-\frac{\sigma_i\omega_i + \mu_i^o}{kT} - \frac{u_c{}'_i}{RT}\right] \tag{13}$$

Combining Equations (12) and (13) one gets

$$\Xi' = \sum_{x_1'} \left(\frac{a_1}{x_1'}\right)^{x_1'\underset{\sim}{N}} \left(\frac{a_2}{x_2'}\right)^{x_2'\underset{\sim}{N}}$$

$$\exp\left(\frac{\Delta u_c' - \underset{\sim}{N}\,(x_1'\sigma_1\omega_1 - x_2'\sigma_2\omega_2)}{kT}\right) \tag{14}$$

The factor $\Delta u_c'$ represents the difference in configurational energy between the mixture and the pure components:

$$\Delta u_c' = u_c' - (x_1'u_c{}'_1 + x_2'u_c{}'_2) \tag{15}$$

Thus Equation (14) expresses the grand partition function of the surface phase of the mixture in terms of the bulk activities and pure-component surface tensions. However the surface composition has not yet been determined.

In order to ascertain the surface composition which is in equilibrium with the known bulk composition one employs the maximum-term method. The grand partition function is the sum of a series of terms t_i

$$\Xi' = \sum_{x_1'} t_i(x_1'{}_i) \tag{16}$$

wherein each term is a function of x_1' only. In the statistical treatment the series may be rigorously replaced by the maximum, or most probable, term in the series, as shown by Hill (17). Since the Helmholtz free energy is proportional to the negative logarithm of the partition function, this is equivalent to minimizing the free energy with respect to the surface composition. In other words the value of x_1' corresponding to the maximum term $t_{i\max}$ is the themodynamic equilibrium value of the surface composition. Therefore Equation (16) may be differentiated and set equal to zero

$$\frac{\partial[t_i(x_1'{}_i)]}{\partial x_1'} = 0 \tag{17}$$

in order to find x_1'.

However before the indicated differentiation may be carried out, it is necessary to define a functional form for the configurational energy difference $\Delta u_c'$.

THE CONFIGURATIONAL ENERGY

The factor $\Delta u_c'$ corresponds to the second part of the molecular potential energy, the energy required to place the molecules at rest in their cells. Furthermore, as is shown in Equation (15), $\Delta u_c'$ is the difference in potential energy between the mixture surface and the pure component surfaces.

Now one must define some form for the surface configurational energies of the pure components and the mixtures. This may be done in terms of the surface configurational energy density c':

$$c_{i'} = -u_{ci'}/\omega_i\underset{\sim}{N} \tag{18}$$

And in the mixture, for molecules interacting by primarily dispersion forces, one may sum over all possible pairs of molecules to get

$$u_c' = -\underset{\sim}{N}\left[\frac{x_1'^2\omega_1^2c_1' + 2x_1'x_2'\omega_1\omega_2\sqrt{c_1'c_2'} + x_2'^2\omega_2^2c_2'}{\omega_1x_1' + \omega_2x_2'}\right] \tag{19}$$

For convenience one defines a surface area fraction, or fraction of the surface occupied by a species

$$\zeta_i = \frac{x_i'\omega_i}{\sum_i x_i'\omega_i} \tag{20}$$

and a surface configurational energy density difference

$$\eta = c_1' + c_2' - 2\sqrt{c_1'c_2'} \tag{21}$$

Then combining Equations (18) to (21) with (15) one gets

$$\Delta u_c' = \underset{\sim}{N}\,(x_1'\omega_1 + x_2'\omega_2)\,\zeta_1\zeta_2\eta \tag{22}$$

The configurational energy of a pure species is defined as the difference in internal energy between the liquid and a state at the same temperature where the molecules are at infinite separation, that is the ideal gas. Therefore the molar configurational energy of a pure bulk liquid is given in terms of the heat of vaporization as

$$u_c = -\Delta h_{\text{vap}} - (h^{\text{id}} - h^{\text{s}}) + (RT - P^{\text{s}}v) \tag{23}$$

The second term on the right-hand side represents the enthalpy difference between the saturated vapor and ideal gas at the saturation pressure, and the last term represents the PV difference between the ideal gas and the bulk liquid.

The configurational energy difference between the bulk liquid and the surface phase is the internal energy of formation of surface. When one assumes for a macroscopic surface that the surface tension is independent of the surface area, the surface energy, relative to the bulk, is

$$\frac{U'}{\Omega} = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right) \tag{24}$$

The surface energy density is then the sum of the configurational energy of the bulk, converted to the proper units, plus the difference between the surface and bulk:

$$c' = -\left[\frac{u_c}{\underset{\sim}{N}\omega} + \frac{U'}{\Omega}\right] =$$

$$\frac{\Delta h_{\text{vap}} + (h^{\text{id}} - h^{\text{s}}) - (RT - P^{\text{s}}v)}{\underset{\sim}{N}\omega} - \sigma + T\left(\frac{\partial\sigma}{\partial T}\right) \tag{25}$$

The surface area per molecule ω is taken as the two-thirds power of the liquid volume per molecule and is assumed

TABLE 1. COMPARISON OF PREDICTIONS BY DIFFERENT METHODS

			Equimolar excess surface tension, dynes/cm.				Equimolar surface composition, x'_1	
System	σ_1, dynes/cm.	σ_2, dynes/cm.	Exptl. (*11*)	Guggenheim	Prigogine	Equation (29)	Guggenheim	Equation (28)
Carbon tetrachloride (1)-cyclohexane (2)	26.70	24.99	—0.54	—0.13	- 0.42	—0.36	0.467	0.495
Cyclohexane (1)-neopentane (2)	24.99	12.33	—1.50	—2.04	- 1.8	—1.32	0.242	0.224
Carbon tetrachloride (1)-neopentane (2)	26.70	12.33	—2.55	—2.60	—2.9	—2.47	0.217	0.211
Benzene (1)-neopentane (2)	28.90	12.33	—4.3	—3.87	—3.6	—4.32	0.167	0.174

to be the same in the mixture as for the pure species at the same temperature.

SURFACE COMPOSITION AND FREE ENERGY

Now that a functional form has been derived for the surface configurational energy difference, one may proceed with the solution for the equilibrium surface composition.

Equation (22) may be substituted into (14), and noting that for the bulk liquid

$$a_i = x_i\gamma_i \qquad (26)$$

one gets for the grand partition function Ξ' of the surface

$$\Xi' = \sum_{x}{}' \left(\frac{x_1\gamma_1}{x_1'}\right)^{x_1'\underset{\sim}{N}} \left(\frac{x_2\gamma_2}{x_2'}\right)^{x_2'\underset{\sim}{N}}$$

$$\exp\left[-\frac{\underset{\sim}{N}(x_1'\omega_1 + x_2'\omega_2)(\zeta_1\sigma_1 + \zeta_2\sigma_2 + \zeta_1\zeta_2\eta)}{kT}\right] \qquad (27)$$

The individual terms may now be differentiated and set equal to zero, as indicated in Equation (17). A transcendental equation which is a function of x_1' only results:

$$\frac{x_2'}{x_1'} = \frac{x_2\gamma_2}{x_1\gamma_1} \exp\left[\frac{\sigma_1\omega_1 - \sigma_2\omega_2 - (\zeta_1^2\omega_2 - \zeta_2^2\omega_1)\eta}{kT}\right] \qquad (28)$$

Using Equation (28) one may readily find the equilibrium surface mole fraction x_1' from the bulk activity coefficients in the mixture, the pure-component surface tensions, and the surface configurational energy density difference η.

Finally the surface tension of the mixture can be found by substituting the maximum term in (27), corresponding to the equilibrium value of x_1', into Equation (6), giving

$$\sigma = \zeta_1\sigma_1 + \zeta_2\sigma_2 + \zeta_1\zeta_2\eta + \frac{kT}{x_1'\omega_1 + x_2'\omega_2}$$

$$\left[x_1' \ln\left(\frac{x_1'}{x_1\gamma_1}\right) + x_2' \ln\left(\frac{x_2'}{x_2\gamma_2}\right)\right] \qquad (29)$$

A certain amount of physical significance may be attributed to the various terms in Equation (29) contributing to the surface tension of the mixture. The first two terms correspond merely to a surface area fraction average, and the third term corresponds to a surface energy difference between the mixture and the pure components. The last term includes both the effect of bulk nonideality in terms of the γ's and the entropic contribution of the composition variation in terms of the surface and bulk mole fractions.

A comparison of the above results with the Gibbs adsorption equation is presented in Appendix A.

COMPARISON WITH DATA

The results given in Equation (29) may now be used to calculate the surface tension of mixtures. It is first applied to the four systems quoted as examples by Englert-Chwoles and Prigogine (*11*) in order to compare the results of these methods with those given by other statistical thermodynamic approaches. Table 1 shows the results in terms of the excess surface tension

$$\sigma^e = \sigma - x_1\sigma_1 - x_2\sigma_2 \qquad (30)$$

Guggenheim's strictly regular solution model gives rather good agreement for the four systems quoted. However the molar volumes of the constituents involved are quite close in all cases, a maximum difference of less than 30% for benzene-neopentane, as is required to apply the Guggenheim method. Guggenheim's method, like the present development, requires the calculation of the surface composition, which is by no means the same as that in the bulk. The values of x' calculated by the strictly regular solution theory and by the present method are quite similar, but yet in three of the four cases well removed from the bulk mole fraction.

This points out the outstanding weakness in the approach of Englert-Chwoles and Prigogine, namely the assumption that the surface tension may be calculated as a small perturbation from a dynamic surface of composition equal to that in the bulk. Although they never calculate the surface mole fraction explicitly, these authors characterize the surface tension in terms of the ideal (or dynamic) case of equal surface and bulk mole fractions, plus the derivative of surface tension with surface mole fraction, dropping all terms of order 2 and higher. Therefore this approach must be better for more nearly ideal systems and of decreasing value as the surface mole fraction deviates from that in the bulk.

The mixture surface tensions predicted by Equation (29) are in excellent agreement with the data. The small deviations, of the order of 0.1 to 0.2 dynes/cm., are within the probable experimental uncertainties. The uncertainties in the calculation are a result of experimental errors in measuring the bulk activity coefficients (*21, 26*), the pure-component heats of vaporization (*26, 28*), and in the pure-component surface tensions.

MIXTURES OF CRYOGENIC FLUIDS

The approach presented here is most applicable to cryogenic mixtures since these contain small, nonpolar molecules. It has been applied to a number of binary systems for which there are sufficient pure-component data plus bulk free energy of mixing data. Pure-component data (bulk and surface configurational energies, surface tension, and surface area per molecule, over a wide range of temperatures) have been tabulated for five substances and have been deposited with the American Documentation

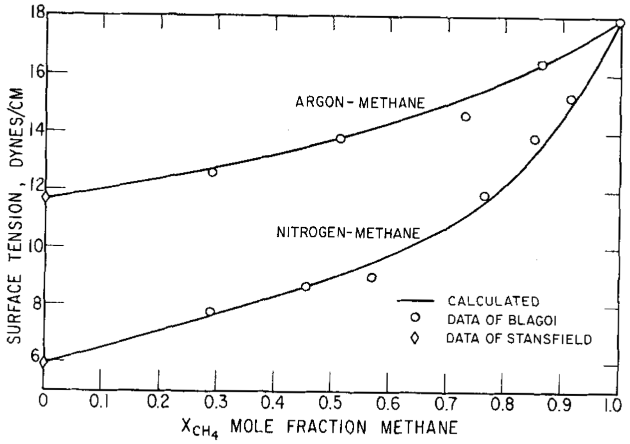

Fig. 1. Surface tension of methane mixtures at 91°K.

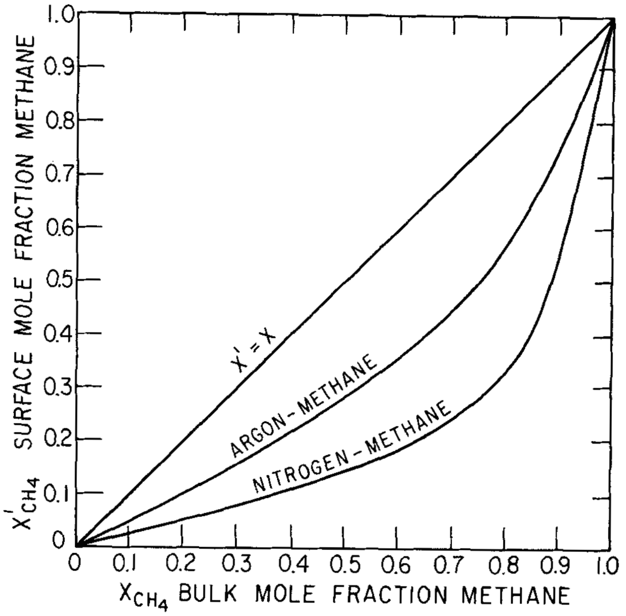

Fig. 3. Surface composition of methane mixtures at 91°K.

Institute.* These substances, with references for the pure-component data used, are argon (*6, 9, 29*), carbon monoxide (*8, 18*), methane (*3, 10, 26*), nitrogen (*29, 31*), and oxygen (*2, 23, 32*).

Figure 1 compares the experimental data of Blagoi (*3*) with the calculated surface tensions from Equation (29) for two relatively nonideal cryogenic mixtures, argon-methane and nitrogen-methane. The deviation from ideality may be shown more forcefully in terms of the large excess surface tensions shown in Figure 2. For these systems the agreement of the calculated surface tension with the experimental data is excellent, even for a mixture where the pure-component surface free energies differ by a factor of 3 (nitrogen-methane). The data used for the activity coefficients were taken from the work of Mathot (*20*) and Cinnes et al. (*5*).

The variation of the surface composition from that of the bulk is very important. Especially for relatively nonideal systems, the discrepancy can be quite significant (see Figure 3). For a true understanding of the molecular processes involved in the surface of a mixture, this composition change may not be neglected.

The available data on cryogenic systems are not only limited in quantity but also in quality. Most of the data on mixtures quoted are those of Blagoi (*3, 4*). These data show a great deal of general scatter, in addition to which the experimental methods used seem to indicate that uncertainties exist of the order of several tenths of a dyne per centimeter or even more. Blagoi reported no pure-component data except for methane, and his results for the surface tension of pure methane are lower than those of Rossini (*26*) by about 0.6 to 1.0 dynes/cm. The surface tension data of Saji and Okuda (*27*) for one system only are in excellent agreement with those of other authors for pure components, but still show some scatter for mixtures.

The calculational method may be applied to other cryogenic mixtures. Figure 4 compares the calculations with data for systems of nitrogen and oxygen with argon, with activity coefficients of Staveley et al. (*25*) used. Data (*1, 25*) exist over a fair temperature range for oxygen-nitrogen mixtures, and Equation (29) gives good predictions of the surface tension over the whole range, as shown in Figure 5.

No good data are available for the surface tension of mixtures including carbon monoxide, but from bulk free energy data (*22, 24, 25*) and pure-component properties one may estimate the variation of surface tension with composition. This is shown in Figure 6 for a relatively ideal mixture (carbon monoxide-nitrogen) and for a moderately nonideal mixture (carbon monoxide-methane).

Frequently it is useful to make estimates on the basis of ideal solutions. A discussion of the simplification of Equations (28) and (29) for various assumptions of ideality and estimates of the errors involved are given in Appendix B.

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* Tabular material has been deposited as document 8009 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or $1.25 for 35-mm. microfilm.

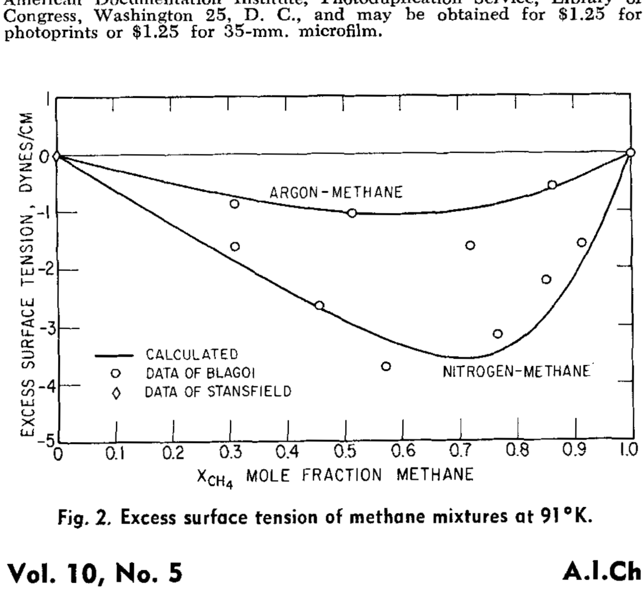

Fig. 2. Excess surface tension of methane mixtures at 91°K.

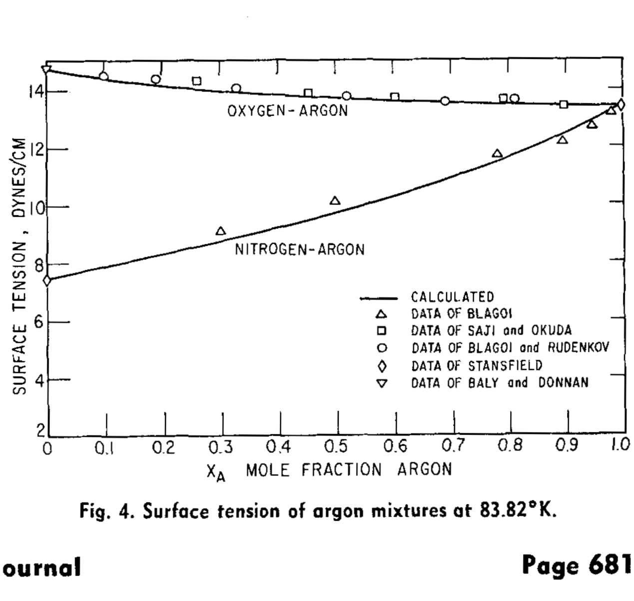

Fig. 4. Surface tension of argon mixtures at 83.82°K.

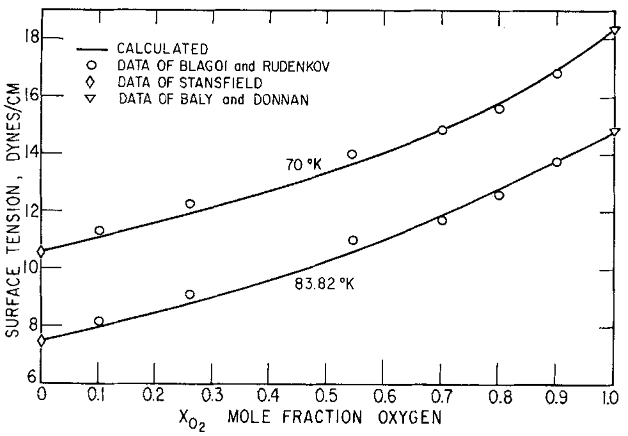

Fig. 5. Surface tension of oxygen-nitrogen mixtures.

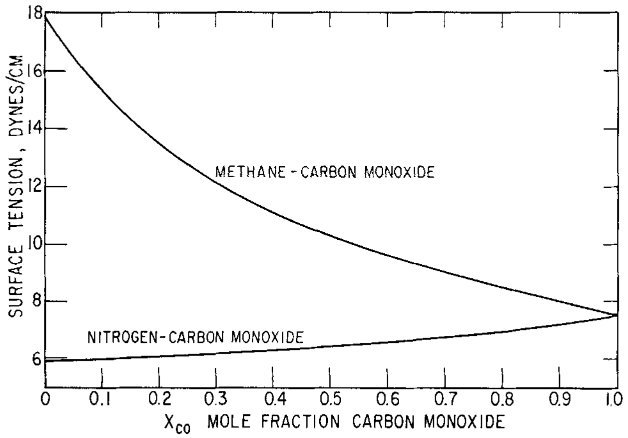

Fig. 6. Calculated surface tension of carbon monoxide mixtures at 91°K.

CONCLUSIONS

1. A theoretical treatment is presented wherein the surface tension of a binary liquid mixture is derived from a model of the surface by statistical mechanics. The surface tension of the mixture may be calculated from pure-component properties plus the activity coefficients in the bulk liquid.
2. The predictions made are in excellent agreement with the limited existing data.
3. This treatment provides a reliable and simple technique for determining surface tensions of cryogenic mixtures, for which data are scarce and difficult to obtain with accuracy.
4. The statistical method provides a sound theoretical basis for calculating the surface properties of mixtures; the method does not have some of the inherent limitations of previous methods. While this work has been restricted to binary systems, the methods used may readily be extended to mixtures containing more than two components. It is hoped that this study will contribute to a better understanding of molecular properties of fluids.

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NOTATION

a = activity
c = configurational energy density
F = Helmholtz free energy
g = combinatorial factor
G = Gibbs free energy
h = molar enthalpy
k = Boltzmann constant
N = number of molecules
$\underset{\sim}{N}$ = Avagadro's number
P = absolute pressure
q = cell partition function
R = gas constant
t = generalized term
T = absolute temperature
U = energy
u = molar energy
v = liquid molar volume
V = volume
x = mole fraction

Greek Letters

γ = activity coefficient
Γ = surface excess concentration per unit area
ζ = surface area fraction [Equation (20]
η = surface configurational energy density difference [Equation (15)]
μ = chemical potential
Ξ = grand canonical partition function
σ = surface tension
ω = surface area/molecule
Ω = total surface area

Subscripts

1 = component one
2 = component two
c = configurational
vap = vaporization

Superscripts

o = pure material
$'$ = surface
s = saturated
id = ideal
e = excess

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APPENDIX A

The Gibbs Adsorption Equation

The Gibbs adsorption equation, at constant temperature and pressure, is

$$d\sigma = -\Gamma_1\,d\mu_1 - \Gamma_2\,d\mu_2 \qquad \text{(A-1)}$$

This relationship is rigorous and can serve as a consistency check for any theory of the surface tension of a mixture.

In terms of the present development the surface excess for component i is

$$\Gamma_i = \frac{x_i' - x_i}{\omega_i \underset{\sim}{N}} \qquad \text{(A-2)}$$

and the differential of the chemical potential is

$$d\mu_i = RT\,d\ln x_i\gamma_i \qquad \text{(A-3)}$$

Upon substitution the Gibbs equation becomes

$$d\sigma = -kT\left[\frac{x_1' - x_1}{\omega_1}\,d\ln(x_1\gamma_1) + \frac{x_2' - x_2}{\omega_2}\,d\ln(x_2\gamma_2)\right] \qquad \text{(A-4)}$$

Although explicit evaluation of this equation in terms of Equations (28) and (29) is most tedious, numerical evaluation is quite straightforward. Equation (A-4) was evaluated numerically for the systems studied, and was satisfied in all cases within a few per cent. For the more nearly ideal systems the discrepancy vanished.

Such behavior is to be expected. The model of the surface, as a separate phase, is inherently inconsistent with the rigorous Gibbs equation. This occurs because one assumes a discontinuity of composition between the bulk liquid and the surface phase, whereas in fact none exists. However, the discrepancy is minor. Guggenheim (*15*, pp. 179-80) discusses this point in terms of his strictly regular solution theory and concludes that the error or inconsistency is small and vanishes for ideal solutions.

Defay and Prigogine (*7*) attempted to rectify the inconsistency by incorporating another phase into the model between the surface and bulk phases, intermediate in composition between the two. They found that this reduced the deviation from the Gibbs equation greatly and concluded that with a sufficient number of intermediate phases the discrepancy must vanish, since the discontinuity would disappear. Most important however was their finding that the incorporation of an extra phase had practically no effect on the calculated value of the surface tension.

Therefore one may conclude that the method presented in this work is substantially in agreement with the Gibbs adsorption equation, although it does exhibit small disagreements of a few percent for relatively nonideal systems. However such discrepancies are not significant, and the effect on calculated surface tensions should be extremely small.

APPENDIX B

The Ideal Surface of a Mixture

It is useful to estimate the size of the error involved in an engineering calculation if the assumption of ideality is made. However for the surface tension of a mixture there are several different possible concepts of ideality.

If one chooses the simplest definition of ideality, the surface tension is given by the bulk mole fraction average of the pure component surface tensions. In terms of the model presented herein this assumption is equivalent to neglecting three factors: the concentration difference between surface and bulk ($x_i' = x_i$) the surface configurational energy difference ($\eta = O$), and the nonideality of the bulk ($\gamma_i = 1$). For systems such as those considered here the result of such an assumption is a surface tension which is too large, possibly by as much as one-half the difference of the pure component surface tensions.

Of the three assumptions made in taking the mole fraction average by far the worst is the first, the equality of bulk and surface mole fractions. A much more realistic treatment for the ideal surface involves neglecting only the surface configurational energy difference ($\eta = O$). Then Equation (28) may be solved explicitly

$$x'_1 = \frac{1}{1 + \dfrac{x_2\gamma_2}{x_1\gamma_1}\exp\left(\dfrac{\omega_1\sigma_1 - \omega_2\sigma_2}{kT}\right)} \qquad \text{(B-1)}$$

and the result used in Equation (29). This procedure generally gives a value of the surface tension which is slightly too low but is a much closer approximation than the mole-fraction-average method.

If sufficient data on the activity coefficients in the mixture are not available, Raoult's law ($\gamma_1 = 1$) may be assumed in conjuncture with neglecting η without too great an error.

The errors involved in making the various assumptions are tabulated for a few representative systems in Table B-1. In these cases it is clear that the mole fraction average assumption is poor, whereas the assumption that $\eta = O$, with Equations (B-1) and (29) used, gives much better results. The effect of using Raoult's law varies, sometimes improving, sometimes decreasing the accuracy of the estimate.

TABLE *B*-1. ERRORS RESULTING FROM ASSUMPTIONS OF IDEALITY

System	T, °K.	Percent error in calculated equimolar surface tension from assuming: $\sigma = \sum_i x_i\sigma_i$	$\eta = 0$	$\eta = 0$, $\gamma_i = 1$
A-O_2	83.82	3.3	0.4	3.2
O_2-N_2	83.82	8.4	4.9	4.1
N_2-A	83.82	7.9	3.5	0.4
A-CH_4	91.00	7.7	1.3	5.5
N_2-CH_4	91.00	33.8	7.4	9.8