SURFACE TENSION AND THE PRINCIPLE OF CORRESPONDING STATES

James R. Brock and R. Byron Bird, University of Wisconsin, Madison, Wisconsin

Experimental surface-tension data for pure substances have been correlated successfully by the use of two recent modifications of the principle of corresponding states. The results are expressed in terms of simple analytical relations which allow one to calculate the surface-tension curves either from the critical constants P_c, V_c, and T_c or from P_c, T_c, and the boiling point T_b and also provide a method for estimating critical properties from surface-tension measurements. In addition, a method for estimating the surface tension of molten metals is suggested.

There is at present considerable interest in fluid mechanics problems involving free surfaces in connection with the reexamination of the unit operations in terms of the fundamental transport processes taking place. It is therefore important to have experimental data on surface properties or in the absence of such data to be able to make intelligent predictions of them.

The current status of the experimental data and the theory of surface tension is not too satisfactory. Many of the data in the standard handbooks are more than thirty years old and have never been corroborated by subsequent investigators. Also the discrepancies between measurements on a given substance by two different methods have not been properly explained. Considerable progress has been made, however, in developing the theory of surface tension in terms of intermolecular forces by means of statistical mechanics (*10*). Two main approaches have been used: the *free-volume* theories, based on an approximate evaluation of the partition function (*5, 15*), and the *radial-distribution-function* method (*2, 3, 13*). Thus far these theories have been developed only for monatomic substances, and much more needs to be done before the statistical theories will be generally useful for predicting surface tensions of complex compounds.

Hence the methods presented here, based on the principle of corresponding states (hereinafter abbreviated P.C.S.), are offered as an aid for practical calculations pending further experimental and theoretical developments. The results given here also serve as an additional test for the two modifications of the P.C.S. which are used.

PRINCIPLE OF CORRESPONDING STATES AND ITS MODIFICATIONS

The P.C.S. in its original form as enunciated by van der Waals was applied specifically to the equation of state in the form

$$P_r = P_r(V_r, T_r) \tag{1}$$

That is, for all substances the reduced pressure should be a universal function of the reduced volume and reduced temperature. This principle has been used in an alternate form by Hougen and Watson (*11*) in the preparation of their generalized compressibility chart, which is a graphical representation of the function

$$Z = Z(P_r, T_r) \tag{2}$$

In addition to the generalized compressibility chart (and the derived charts for the thermodynamic functions) charts have been prepared for two of the transport coefficients: viscosity (*11, 24*), for which $\mu_r = \mu_r(P_r, T_r)$, and thermal conductivity (*8, 12*), for which $k_r = k_r(P_r, T_r)$.

All these charts have been of considerable use for purposes of instruction and rapid calculation. It is, however, inherently assumed in these generalized representations that the constituent molecules of all substances are mechanically similar. This drawback led Kamerlingh Onnes to modify the original P.C.S. by suggesting that each group of mechanically similar substances—for example, the halogens, the alcohols, the straight chain paraffins—should obey a separate P.C.S. characteristic of its own group.

Actually very little has been done to modify the P.C.S. by the introduction of additional parameters to characterize the chemical structure of the constituent molecules. The reason for this is that an enormous amount of very accurate experimental data is required in order to deduce the effects of dipole moments, quadrupole moments, polarizabilities, and molecular shape on the bulk physical properties. Because of the impracticality of any such attempt at the present time, one might well ask whether some sort of empirical correlating parameter can be found—one which could be expected to work for a large number of substances. Recently two such empirical methods have been suggested, in which a single additional "correlating parameter" has been introduced:

1. Meissner and Seferian (*20*) have suggested that all substances with the same value of the parameter $Z_c = P_cV_c/RT_c$ obey the same P.C.S., that is, that Equation (2) be replaced by

$$Z = Z(P_r, T_r; Z_c) \tag{3}$$

indicating the explicit parametric dependence on Z_c. Similar expressions can be written for the transport coefficients and other properties. This modification of the P.C.S. has been used by Lydersen, Greenkorn and Hougen (*18*) to make a very extensive analysis of data on equation of state and thermodynamic properties of gases and liquids.

2. Riedel (*21*) has suggested that all substances with the same value of $Y_c = (d \ln P_V / d \ln T)_c$ follow the same P.C.S., that is, that Equation (2) be replaced by

$$Z = Z(P_r, T_r; Y_c) \tag{4}$$

with analogous relations for the other physical properties. Riedel has achieved particularly good suc-

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J. R. Brock is at present with Humble Oil and Refining Company, Houston, Texas.

cess with this method in the correlation of vapor-pressure data.*

The application of either of these methods raises the important question as to whether a single correlating parameter—such as Z_c or Y_c—can be expected to be sufficient for describing the behavior of many different physical properties. Recently Rowlinson(*23*) succeeded in showing theoretically that at least for certain types of molecular interactions a single correlating parameter is indeed adequate. To substantiate his theory he has studied the following properties of sixteen widely varying substances: second virial coefficients, vapor pressure of liquids, rectilinear diameters, Trouton's constants, heat capacities (at constant volume) of liquids, and surface tension. The success which the authors have had in correlating surface-tension measurements on the basis of methods 1 and 2 above can be regarded as an additional justification of Rowlinson's generalization of the P.C.S.

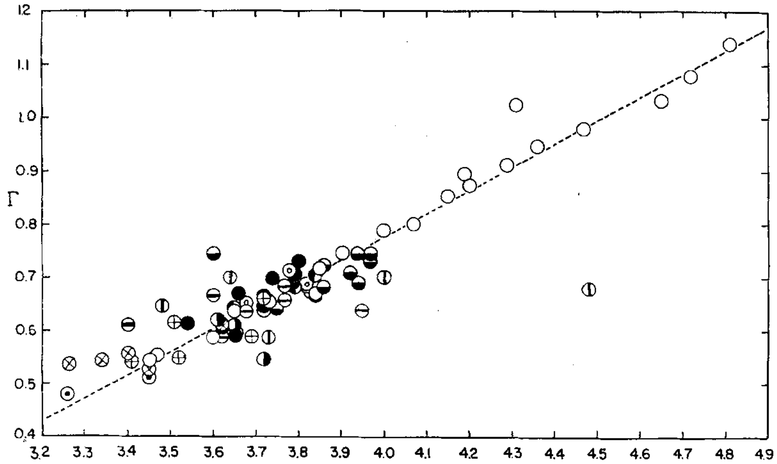

Fig. 1. Determination of the Function Γ (Z_c) in Equation (8). The Various Types of Chemical Substances Used in the Correlation Are Indicated by the Following Symbols:

- ⊙ noble gases
- ⊗ diatomic molecules
- ⊕ simple inorganic molecules
- ○ straight-chain paraffins
- ◐ alkyl benzenes
- ⌽ nitrogen-containing organic compounds
- ⊖ halogen-containing organic compounds
- ◎ miscellaneous organic compounds
- ● branched paraffins
- ◓ esters
- ◑ unsaturated hydrocarbons

The Dotted Line Represents the Least Square Fit, $\Gamma = -0.951 + (0.432/Z_c)$.

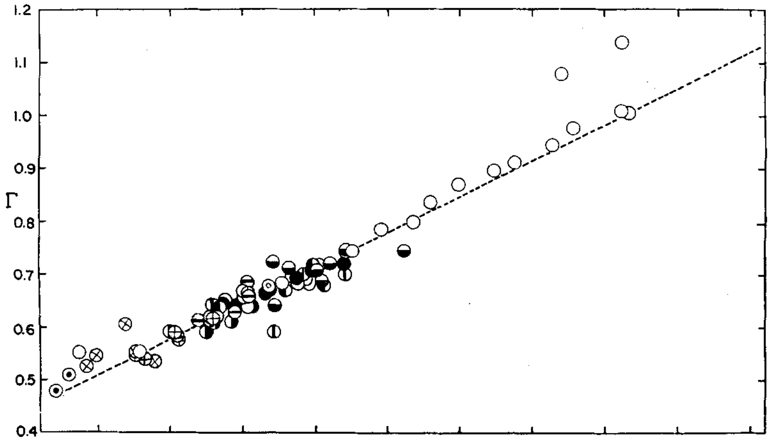

Fig. 2. Determination of the Function $\Gamma(Y_c)$ in Equation (9). The Symbols Used for the Various Types of Chemical Substances Are the Same as Those Given in Figure 1. The Dotted Line Represents the Least Square Fit, $\Gamma = -0.281 + 0.133 Y_c$.

APPLICATION OF THE MODIFIED P. C. S. TO SURFACE TENSION

Neither of the above discussed modifications of the P.C.S. has yet been fully examined as to how well various physical properties can be described. It is of interest to test these methods by applying them to the correlation of surface-tension data. For this property it is well known that the P.C.S. in its original form is definitely inadequate (*9*), probably because of the alignment effects at the interface, which are of course highly sensitive to the molecular shapes and molecular interactions. The surface tension of a pure substance is particularly easy to study, since it is a function of temperature but not of pressure.

For the purpose of this work a "reduced" surface tension has been defined by*

$$\gamma_R = \frac{\gamma}{P_c^{2/3}\, T_c^{1/3}} \qquad (5)$$

(It should be noted that the quantity $\gamma/P_c^{2/3}(\kappa T)^{1/3}$ is dimensionless but that quantity γ_R, defined in Equation (5), is not, because of the missing factor $\kappa^{1/3}$, which was omitted to simplify calculations.) According to the original P.C.S. one would expect γ_R to be a unique function of T_r for all substances.

According to the two modified P.C.S., however,

$$\gamma_R = \gamma_R\,(T_r; Z_c) \qquad (6)$$

$$\gamma_R = \gamma_R\,(T_r; Y_c) \qquad (7)$$

The temperature dependence of the surface tension for a great many substances has been shown(*9*) to be proportional to $(1-T_r)^{11/9}$. The assumption that this temperature dependence is universal allows one to rewrite Equations (6) and (7) thus

$$\gamma_R = \Gamma(Z_c)\,(1-T_r)^{11/9} \qquad (8)$$

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*The quantity here called Y_c, is given the symbol α_k by Riedel(*20*), but the present authors prefer not to use α since this letter is frequently used for the coefficient of expansion $(\partial \ln V/\partial T)_P$. Riedel has shown by a very careful analysis of vapor-pressure data that the quantity Y_c can be calculated from the boiling point T_b at a pressure P by means of the equation

$\ln P_r = Y_c \ln T_{br} - 0.0364(Y_c - 3.75)[(36/T_{br}) + 42 \ln T_{br} - 35 - T_{br}^{6}]$

in which T_{br} is the reduced boiling temperature corresponding to the reduced pressure P_r. If many values of Y_c are needed, they can be calculated quickly from tables prepared by Riedel(*21*).

*One might also define a reduced surface tension thus:

$$\gamma_R = \gamma V_c^{2/3} / \kappa T_c \qquad (5a)$$

This definition suffers from the disadvantage that V_c is not known accurately for many substances. Rowlinson(*23*) has, however, used this definition in his investigation.

$$\gamma_R = \Gamma(Y_c)\,(1-T_r)^{11/9} \qquad (9)$$

The experimental surface-tension data used for obtaining $\Gamma(Z_c)$ and $\Gamma(Y_c)$ are those given in Landolt-Börnstein's Physikalisch-Chemische Tabellen, the International Critical Tables, the Annual Table of Physical Constants, Tables Annuelles de Constantes et Données Numériques and the Tables of the American Petroleum Institute. For many substances it was not possible to find the surface tension of the pure substance against its own saturated vapor; it was necessary to use the value of surface tension against air or some inert gas. The error involved in the use of the latter data is believed to be quite small in comparison with the average deviation from the correlations based on the principle of corresponding states. The critical constants needed for the correlation were obtained from a recent compilation made by Lydersen *(17)* and from the extensive tabulation prepared by Kobe and Lynn *(14)*. Eighty-four substances of widely differing **character** were selected for which both surface-tension and critical data were available. These included two noble gases, five diatomic molecules, seven simple polyatomic inorganic substances, the first twenty normal paraffins, ten branched paraffins, five alkyl benzenes, six unsaturated hydrocarbons, eight esters, eight organic halogen compounds, six organic nitrogen compounds, and seven other organic compounds. The experimental values of $\gamma_R/(1-T_r)^{11/9}$ were plotted against $1/Z_c$ (as shown in Figure 1) and against Y_c (as shown in Figure 2). Through the point so plotted, the best straight lines were drawn by means of a least-squares fit. These linear relations then allow Equations (8) and (9) to be rewritten as

$$\gamma_R = (-0.951 + 0.432/Z_c)\,(1-T_r)^{11/9} \qquad (10)$$

$$\gamma_R = (-0.281 + 0.133\,Y_c)\,(1-T_r)^{11/9} \qquad (11)$$

which are the final generalized relations for surface tension based on the two modified P.C.S. described above.*

TABLE 1.—ANOMALOUS DEVIATION OF EXPERIMENTAL SURFACE TENSIONS FROM GENERALIZED EQUATIONS

Substance	Average % deviation from Eq. (10)	Eq. 11
Polar inorganic substances		
Water	+ 90.6	+ 44.0
Ammonia	+ 35.5	+ 6.2
Hydrogen chloride	+ 31.4	+ 13.2
Hydrogen bromide	+ 13.4	+ 5.0
Alcohols		
Methanol	+179	+ 58.2
Ethanol	+ 89	+117
Butanol	+ 39.4	+ 87
Carboxylic acids		
Acetic acid	+166	+ 70
Propionic acid	+ 88	+ 91
Butyric acid	+ 21	+115

GENERALIZED RELATIONS FOR SURFACE TENSION

Applicability. Over the temperature range of the available data for the eighty-four substances considered, it was found that the average error for Equation (10) is 6.2% and for Equation (11, 3.0%. The smaller deviation for the Y_c correlation does not necessarily indicate that Y_c is fundamentally a better choice of correlating parameter than Z_c. Many of the deviations in the Z_c correlation are quite likely due to erroneous values of Z_c (which in turn frequently can be traced to faulty V_c values).

Equations (10) and (11) are sufficiently accurate for most engineering calculations and provide a quick method for estimating surface tension from critical data. If experimental critical data are not available, they can be estimated by the group-contribution methods devised by Riedel *(21, 22)* and extended by Lydersen *(17)*. Lydersen has also given an empirical relation whereby Z_c may be estimated from heats of vaporization.

Equations (10) and (11) could be used for estimating critical constants from surface-tension measurements. If P_c and T_c are known, then V_c can be obtained from

$$V_c = 0.432\,(RT_c/P_c)\left[0.951 + \frac{\gamma/P_c^{2/3}T_c^{1/3}}{(1-T_r)^{11/9}}\right]^{-1} \qquad (12)$$

And if T_c and a boiling point are known, then P_c can be found from

$$P_c = \left[\frac{\gamma/T_c^{1/3}}{(-0.281+0.133Y_c)(1-T_r)^{11/9}}\right]^{3/2} \qquad (13)$$

A trial-and-error method has to be used to obtain P_c, as Y_c depends on P_c. Equation (13) is probably about as good for estimating P_c as is the group-contribution formula given by Lydersen *(17)*.

Limitations. The generalized relations for surface tension are reasonably successful for simple inorganic substances and for a wide variety of organic compounds. There are several groups of substances for which the correlations cannot be expected to hold: very light atoms and molecules (the isotopes of hydrogen and helium), molten metals, certain highly polar inorganic substances (H_2O, NH_3, HCl, HBr), associating substances (alcohols, carboxylic acids, etc.), and fused salts. The order of magnitude of the deviations of some of these substances from the generalized equations is indicated in Table 1.

The only class of substances listed above which has been successfully studied is the first one—the isotopes of hydrogen and helium—which exhibit quantum effects. These substances should always be excluded from generalized correlations inasmuch as there are other preferable ways to handle them. The first method was suggested by Byk *(4)*, who proposed a quantum mechanical modification of the original van der Waals' principle of corresponding states. A theoretically sounder method is the use of a quantum mechanical P.C.S. based on the reduction of variables with molecular parameters (rather than critical parameters), as proposed by de Boer *(7)* and discussed extensively by Lunbeck *(19)*. The application of this latter approach to surface tension has been carried out by one of the authors *(6)*. In this way the surface tension of He^3 and the various heavy isotopes of hydrogen. Recently the surface tension of He^3 was measured by Lovejoy *(16)* in the range 1.0° to 2.5°K. Above about 1.8°K. the experimental values agree almost exactly with the predicted curve. The discrepancy below 1.8°K. is undoubtedly due to statistics effects, which were not taken into account in the P.C.S. prediction. As yet no experimental values of the surface tension for the heavy isotopes of hydrogen are available.

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*The constants in Equations (10 and (11) are slightly different from those given previously[1], since only 30 substances were used in the original correlation.

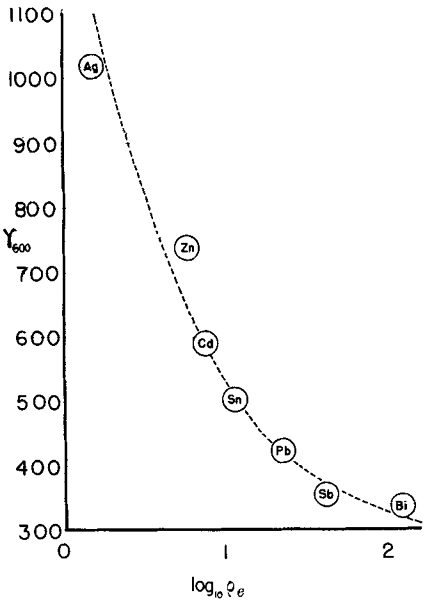

FIG. 3. SURFACE TENSION AT 600°C. IN DYNE CM.$^{-1}$ OF VARIOUS MOLTEN METALS PLOTTED AGAINST THE LOGARITHM OF THEIR ELECTRICAL RESISTIVITY AT 20°C. IN MICROHM CM.

Much needs to be done in connection with the other anomalous substances. For the molten metals there seems to be a relationship between the surface tension and the electrical resistivity, as can be seen in Figure 3. For the materials in the last three groups above, no workable generalizations have been obtained. It is not known at present whether Equations (10) and (11) apply generally to the fluorocarbons. The only one of these substances for which both surface-tension and critical data could be found was perfluoroheptane, for which the agreement was not particularly good. It will be interesting to see whether this class of compounds exhibits further deviations.

SURFACE TENSION AND THE PARACHOR

The calculation of the surface tension from the modified P.C.S. methods is not presented as a substitute for the method of calculating surface tension from the parachor. The latter calculation requires a knowledge of the liquid and vapor densities, whereas the former requires that one know either P_c, V_c, T_c or P_c, V_c, T_b. Thus the two schemes of estimating surface tension are complementary. Furthermore it is frequently useful to have two different methods available for estimating physical properties under unusual conditions. A P.C.S. approach to surface tension is in a sense more satisfying, in that the correlation is obtained by a general method, capable of being applied to a variety of properties as already discussed. The parachor, on the other hand, involves a specific method.

The parachor is far from being well understood theoretically. It was introduced as a useful empiricism by Sugden, and its use in structural determinations is well known. At the present time there is no satisfactory explanation of the fact that the parachor is very nearly constant over a wide range of temperature. Lennard-Jones and Corner(*13*) have shown that the parachor is given within about 4% for simple substances by the empirical relation:

$$[P] = (7.1 \times 10^3 \; \epsilon^{1/4} \sigma^{5/2} \tag{14}$$

in which σ and ε are the parameters in the Lennard-Jones potential (σ is the low-energy collision diameter in Ångström units and ε is the maximum energy of intermolecular attraction in ergs). This relation shows that the parachor is almost proportional to σ^3, which is in agreement with Sugden's contention that the parachor is some sort of modified molecular volume.

ACKNOWLEDGMENT

The authors are indebted to Aksel Lydersen for numerous interesting discussions and for the use of some of his unpublished work. They also wish to thank Arthur Stroud for performing some of the calculations. In addition, R. B. Bird wishes to acknowledge the financial support of the National Science Foundation.

NOTATION

k = coefficient of thermal conductivity
P = pressure
P_V = vapor pressure
R = gas constant
T = temperature
V = molar volume
Y = $(d \ln P_V / d \ln T)$
Z = compressibility factor, PV/RT
γ = surface tension
γ_R = "reduced" surface tension [*see* Equation (5)]
Γ = quantity defined in Equations (8) and (9)
κ = Boltzmann's constant
μ = coefficient of shear viscosity
ρ_e = electrical resistivity

Subscripts

b = quantity evaluated at the boiling point
c = quantity evaluated at the critical point
r = quantity made dimensionless by division by the corresponding quantity at the critical point

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