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Quantitative Correlation of Interfacial Free Surface Energies*

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In the earliest work done in this Laboratory on adhesion tension measurements it was observed that the order of increasing adhesion tension for liquids against carbon was exactly the reverse of the order of increasing adhesion tension for the same liquids against silica.[1] Later measurements on other solids have shown that some of them have wetting properties intermediate between those of carbon and silica; and that, as was predicted from the earliest work, there seems to be a definite relationship between adhesion tension values and wetting properties of a series of such solids against a given liquid.[2] No quantitative relationship has heretofore been derived, however, correlating adhesion tension measurements and wetting characteristics.

Those solids which are more readily wet by water than by organic liquids, or from which water will displace organic liquids herein will be designated as hydrophilic solids. Those solids which are more readily wet by organic liquids, or from which organic liquid will displace water will be designated as organophilic solids. Not all hydrophilic solids are hydrophilic to the same degree, however. Solids on which the interface water–organic liquid forms an angle (measured through the water phase) of less than 90° are all hydrophilic; solids giving interfacial angles greater than 90° are organophilic; while solids giving interfacial angles of 90° would be preferentially wetted neither by water nor by organic liquid and may, therefore, be said to have neutral wetting characteristics. The diagram shown in Fig. 1 indicates the approximate interfacial angles obtained with water and an organic liquid against silica (hydrophilic) carbon (organophilic) and Prussian Blue (neutral). On this diagram the interfacial angle formed on silica is shown to be close to 0° or cos Θ = +1 and the carbon angle to be close to 180° or cos Θ = −1, while the Prussian Blue angle is close to 90° or cos Θ = 0.

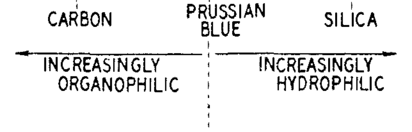

Fig. 1.

It is apparent that the "wetting characteristics" of a solid may be indicated by the interfacial contact angle (or the cosine of that angle)

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* Presented at the Chicago meeting of the American Chemical Society, September, 1933.

(1) F. E. Bartell and H. J. Osterhof, "Colloid Symposium Monograph," 5, 113 (1927); *Ind. Eng. Chem.*, 19, 1277 (1927); *J. Phys. Chem.*, 37, 543 (1933).

(2) F. E. Bartell and C. W. Walton, *ibid.*, 38, 503 (1934).

formed between water and an organic liquid in contact with the solid. Having no better measure of the "wetting characteristics" of a solid we may tentatively accept the cosine of the interfacial angle value as such a measure. This wetting characteristics value represents, then, the degree of hydrophilic or organophilic nature of the surface of a given solid, and is definite for that surface.

Values for the cosines of the interfacial angles formed by water and alpha bromonaphthalene on various solids have been determined in this Laboratory. Most of the determinations were made by the pressure of displacement method using the Bartell–Osterhof cell. The adhesion tensions of water and of alpha bromonaphthalene against these solids have also been measured. Adhesion tension is a measure of the energy change which occurs when a given liquid completely wets a given solid surface and gives the value for the degree of wetting of the solid by the liquid.[3] In Table I the data for these measurements on a series of solids are given, together with references to the papers in which the data were published. The solids listed in the table have been chosen so that almost the whole range of the cosine scale, from cos 0° = +1 to cos 180° = −1, is covered.[4]

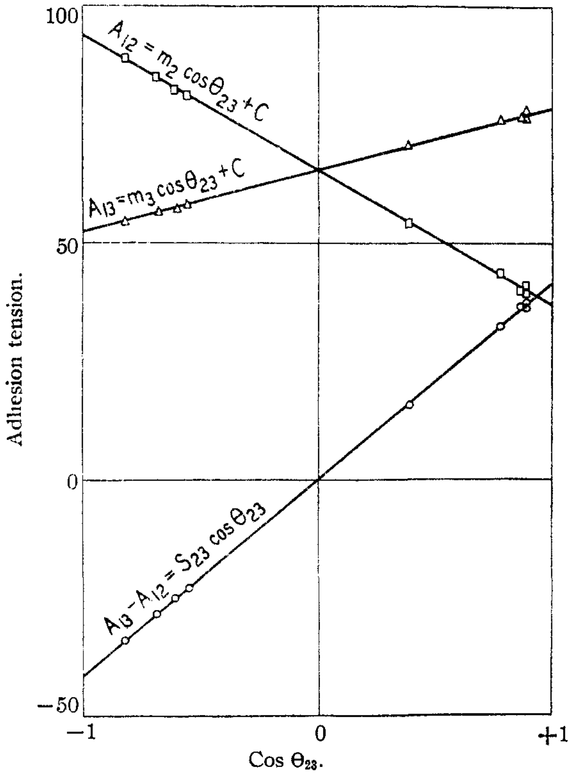

Fig. 2.

TABLE I

ADHESION TENSION DATA FOR WATER AND FOR α-BROMONAPHTHALENE AGAINST DIFFERENT SOLIDS

Solid	Cosine interfacial contact angle Cos θ_{23}	Adhesion tension water–solid A_{13} (dynes)	Adhesion tension α-bromonaphthalene solid A_{12} (dynes)	$A_{13} - A_{12}$
Carbon (1)[a]	−0.819	54.7	88.8	−34.1
Stibnite A(2)	− .686	56.5	85.0	−28.5
Stibnite B(2)	− .605	57.2	82.4	−25.2
Stibnite C(2)	− .555	58.1	81.2	−23.1
Stibnite G(2)	+ .386	70.5	54.5	+16.0
Stibnite H(2)	+ .780	76.0	43.5	+32.5
Silica (10)	+ .870	76.6	40.1	+36.5
Al_2O_3 (2)	+ .884	76.7	40 1	+36.7
Stibnite I(2)	+ .891	77.1	40.0	+37.0
Barite (9)	+ .883	76.4	39.9	+36.7

[a] Number in parentheses refers to reference giving data.

An interesting relationship will be observed if a graph is constructed plotting cosine of interfacial contact angle values as abscissas against adhesion tension values as ordinates.

From the data in column 2 (Table I) we will indicate the position of the solids on the horizontal cos θ_{23} axis and will plot the corresponding adhesion tension data for water, A_{13}, on the vertical. This has been done in the graph in Fig. 2. It will be observed that the points so determined lie on a straight line. This straight line may be called the A_{13} or water line. In like manner ordinates were measured off for each solid equal to the A_{12} value for that solid. It will be noted that these points lie on another straight line, the A_{12}, or alpha bromonaphthalene line. The A_{12} line intersects the A_{13} line at a point with an ordinate value of about 65 (dynes), and a value on the horizontal cosine scale where cos θ_{23} = 0. Taking the point cos θ_{23} = 0 as the origin and putting through it a vertical adhesion tension axis; one can write an equation for A_{13} or A_{12} in terms of cos θ_{23}; thus $A_{13} = m_3 \cos \theta_{23} + c$ and $A_{12} = m_2 \cos \theta_{23} + c$. This relationship is rather surprising in view of the fact that A_{13} involves only the solid and water, A_{12} involves only the solid and alpha bromonaphthalene, while cos θ_{23} involves the two liquids and the solid.

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(3) H. Freundlich, "Colloid Chemistry," 1926, p. 157.

(4) The symbols used in this paper are the same as those used in recent papers from this Laboratory, namely: S represents surface tension, interfacial tension or free surface energy; A represents adhesion tension and θ the contact angle. Subscripts 1, 2 and 3 refer to the solid, organic liquid and water phases, respectively. For example, the symbol S_{13} refers to the interfacial tension or free surface energy existing at a solid–water interface.

The adhesion tension water–solid, A_{13}, is defined by the equation $A_{13} = S_1 - S_{13} = S_3 \cos \Theta_{13}$,[3,5] in which S_3 is the surface tension of water, $\cos \Theta_{13}$ is the cosine of the angle of contact made by water on the solid in air, S_1 is the surface tension of the solid and S_{13} is the interfacial tension solid–water. In like manner $A_{12} = S_1 - S_{12} = S_2 \cos \Theta_{12}$ where S_2 is the surface tension of alpha bromonaphthalene, $\cos \Theta_{12}$ is the cosine of the contact angle made by alpha bromonaphthalene on the solid in air, S_{12} is the interfacial tension solid–alpha bromonaphthalene and S_1 has the same significance as in the previous equation. A vector equilibrium equation relating the interfacial contact angle with the different interfacial tension values may be written.[5,6,7] $S_{12} - S_{13} = S_{23} \cos \Theta_{23}$, where S_{23} is the interfacial tension water–alpha bromonaphthalene and all other terms have the same significance as before. If now A_{12} be subtracted from A_{13}

$$A_{13} - A_{12} = (S_1 - S_{13}) - (S_1 - S_{12}) = S_{12} - S_{13} = S_{23} \cos \Theta_{23} \text{ or}$$
$$A_{13} - A_{12} = S_{23} \cos \Theta_{23}{}^1$$

The difference between A_{13} and A_{12} is then a linear function of $\cos \Theta_{23}$, but no evidence of a simple relationship between $\cos \Theta_{23}$ and either A_{13} or A_{12} alone has been observed heretofore.

The fact that such a relationship exists will not seem so surprising if one remembers that when the solids were arranged on the horizontal $\cos \Theta_{23}$ axis in the order of their increasing $\cos \Theta_{23}$ values (*i. e.*, decreasing angle, measured through the water phase, formed by the interface water–alpha bromonaphthalene on the solid surface), or, in other words, in the order of their increasing preferential wetting by water; they were at the same time arranged in the order of their increasing $\cos \Theta_{13}$ values (*i. e.*, decreasing angle of contact formed by water on the surface of solid in air), or in the order of their increasing degree of wetting by water. It is apparent from the equation $A_{13} = S_3 \cos \Theta_{13}$ that A_{13} is a straight line function of $\cos \Theta_{13}$; and since the order of arrangement of the solids is the same for $\cos \Theta_{23}$ as for $\cos \Theta_{13}$ one would expect some simple relationship between A_{13} and $\cos \Theta_{23}$. That the latter turns out to be a straight line relationship makes it possible to write a very simple equation relating $\cos \Theta_{13}$ to $\cos \Theta_{23}$. Thus

$$A_{13} = S_3 \cos \Theta_{13} = m_3 \cos \Theta_{23} + c, \text{ or}$$
$$\cos \Theta_{13} = (m_3/S_3) \cos \Theta_{23} + (c/S_3)$$

It follows then that one can indicate on the horizontal axis either the $\cos \Theta_{23}$ values or the corresponding values of $\cos \Theta_{13}$. This has been done in Fig. 3. In like manner for alpha-bromonaphthalene

$$\cos \Theta_{12} = m_2/S_2 \cos \Theta_{23} + c/S_2$$

and one can indicate on the horizontal axis either $\cos \Theta_{23}$ values or the corresponding $\cos \Theta_{12}$ values, as is shown in Fig. 3.

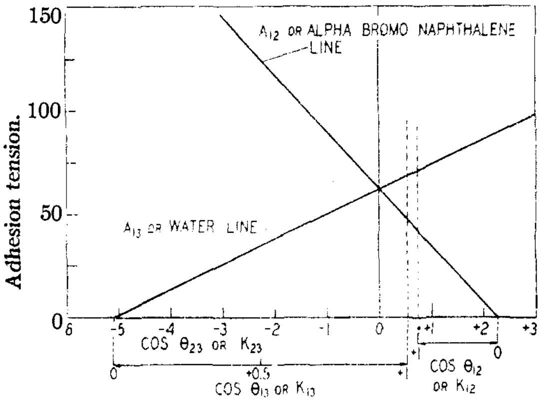

Fig. 3.

A study of Fig. 3 will bring out many interesting points. It will be observed that the interfacial angle (water–organic liquid) is a much more sensitive measure of the wetting properties of a solid than is the contact angle made by water on the solid in air. The length of the horizontal axis between the values $\cos \Theta_{23} = -1$ to $\cos \Theta_{23} = 0$ is small as compared to the length between $\cos \Theta_{13} = 0$ to $\cos \Theta_{13} = +1$. While the interfacial angle is going from 180 to 90° ($\cos \Theta_{23} = -1$ to $\cos \Theta_{23} = 0$) the water contact angle goes only from about 43 to 25° ($\cos \Theta_{13} = 0.726$ to $\cos \Theta_{13} = 0.904$).

The equation $A_{13} = m_3 \cos \Theta_{23} + c$ obviously holds only between the limits $\cos \Theta_{23} = -1$ to $\cos \Theta_{23} = +1$. Beyond these limits the $\cos \Theta_{23}$ has no physical meaning. $\cos \Theta_{13}$ has a physical meaning beyond the limit of $\cos \Theta_{23} = -1$, however, and measurements of A_{13} for solids on which water makes a contact angle greater than 43° ($\cos \Theta_{13} = 0.726$) have been made, and such values fit the diagram. The usefulness of the equation $A_{13} = m_3 \cos \Theta_{23} + c$ can be extended by substituting a K_{23} value which is equal to $\cos \Theta_{23}$ between the limits -1 and $+1$, and which takes on values less than -1 (as indicated). This makes pos-

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(5) Thomas Young, *Trans. Roy. Soc.* (London), 65 (1805).

(6) G. Quincke, *Ann. Physik*, **139**, 1 (1870); Rhumbler (Des Coudres), *Arch. Entwicklungsmech. Organ.*, **7**, 103 (1898).

(7) Hofmann, *Z. physik. Chem.*, **83**, 390 (1913).

sible the use of a single equation with K_{23} as the independent variable for the whole length of the A_{13} line. This K_{23} value has a physical meaning when expressed in terms of the water contact angle.

The same thing can be done for the A_{12} line by using K_{23} values greater than $+1$ which have physical meaning in terms of the alpha bromonaphthalene contact angle. For values of A_{12} where K_{23} takes on values less than -1 the situation is a little more complicated. Where K_{23} is less than -1 neither the cos Θ_{23} nor the cos Θ_{12} has a physical meaning. Yet the adhesion tension of alpha bromonaphthalene against solids in this region has a definite value $= S_1 - S_{12}$, and it will be seen later that the use of K_{23} less than -1 in calculating A_{12} in this region gives values which are in agreement with the properties of such solids and which seem to justify such use of K_{23}. Similar arguments hold for the A_{13} line in the region beyond $K_{23} = +1$, where neither cos Θ_{23} nor cos Θ_{13} has a physical meaning.

Such diagrams as have been given for water and alpha bromonaphthalene can be drawn for water and any other organic liquid for which data have been obtained. Similar equations can be derived for each diagram, since in each case the A_{13} values and the A_{12} values (or A_{1n} values where the subscript n is used to refer to any organic liquid) show a straight line relation to the corresponding values of the cosine of the interfacial angle. But a further and quite important property of the interfacial angle has been brought out by a study of all the data on interfacial angles obtained in this Laboratory in the past ten years. The data on the interfacial angle show that the cosine of the angle formed by the interface between water and *any* organic liquid on the surface of a given solid is always the same (or so nearly the same that it appears justifiable to assume that any very appreciable difference is due to experimental error), *no matter what organic liquid is used.* This means that the K_{n3} values for all organic liquids (*i. e.*, all that have been tested in this Laboratory) on the same solid are the same, and lines for all the organic liquids under consideration may be drawn on the same set of coördinates.

In Table II are given data for several organic liquids on different solids together with references to the papers in which the data appear. Most of these data were obtained by the pressure of displacement method, but a few values were obtained by direct measurement of angles. Column two in Table II gives the average K_{n3} values for the various solids. These average values were obtained by averaging the interfacial angle determinations for all the organic liquids used on a given solid. The figures in the following columns are all experimentally determined values.

TABLE II

ADHESION TENSION DATA FOR SIX DIFFERENT LIQUIDS AGAINST A NUMBER OF DIFFERENT SOLIDS[a]

Solid	Average K_{n3}	Water A_{13}	Isoamyl alcohol A_{1n}	*n*-Butyl acetate A_{1n}	Benzene A_{1n}	Acetylene tetrabromide A_{1n}	α-Bromo-naphthalene A_{1n}
Carbon (1)	−0.806	54.7	58.8	65.8	81.1		88.8
Stibnite A(2)	− .661	56.5	59.9	66.1	78.4	81.1	85.0
Stibnite B(2)	− .623	57.2		66.4	76.6		82.4
Stibnite C(2)	− .555	58.1		65.8	76.0		81.2
Stibnite D(2)	− .387	60.3		65.8	72.6		76.4
Stibnite E(2)	− .10	64.2					
Stibnite F(2)	+ .08	66.5					
Stibnite G(2)	+ .418	70.5		65.0	55.0		54.5
Soda Lime Glass (11)	+ .75					45.7	44.0
Stibnite H(2)	+ .826	76.0		64.8	47.0		43.5
Pyrex (11)	+ .869					42.2	41.2
Pyrex (10)	+ .87						40.1
Silica (10)	+ .87	76.6					40.1
Al_2O_3 (2)	+ .897	76.7	73.9	64.5	45.0	43.0	40.1
Stibnite I(2)	+ .904	77.1	74.0	64.9	45.4	43.4	40.0
Barite (9)	+ .905	76.4		64.6	44.3	40.5	39.9

[a] The adhesion tension data given in this table are experimental values. The average K_{n3} for each solid was calculated from a number of different liquids. This average K_{n3} gives the degree of hydrophilic or organophilic nature of the solid and, being an average, may be more nearly correct than the cos Θ_{n3} determined for the given solid by using only one organic liquid. If the K_{n3} values given in the table are used for calculating adhesion tension values, these calculated values will not be, in every case, identical with the experimental values.

If we accept as fact that the K_{n3} value for all the different organic liquids on a given solid is always the same, it becomes possible to obtain the equation for the adhesion tension of any organic liquid whose interfacial tension against water is known. All the A_{1n} lines will intersect at a common point where $K_{n3} = 0$. Here the adhesion tension is the same for all liquids. This seems to be the case with Prussian Blue. This adhesion tension value is the c in our A_{13} and A_{12} equations. Now since $A_{13} - A_{1n} = S_{n3} \cos \Theta_{n3}$ we can write

$$(m_3 \cos \Theta_{n3} + c) - (m_n \cos \Theta_{n3} + c) = S_{n3} \cos \Theta_{n3}, \text{ or}$$
$$m_3 - m_n = S_{n3}$$

Then m_n (the slope of any organic liquid line) $= m_3 - S_{n3}$. m_3, the slope of the water line, has been determined by the method of least squares to be 12.8. The value of c, the intercept on the adhesion tension axis, has been determined to be 65.2 dynes. Using these values and using K_{n3} instead of $\cos \Theta_{n3}$ the water line equation becomes

$$A_{13} = 12.8\,K_{n3} + 65.2$$

The equation for any organic liquid becomes

$$A_{1n} = (12.8 - S_{n3})\,K_{n3} + 65.2$$

In Fig. 4 lines of slopes thus calculated, representing several organic liquids, are shown. The experimental data given in Table II have been placed upon this diagram. The agreement between the calculated lines and the experimental data is close.

In the region where $K_{n3} > +1$ no solids have been examined as yet, but certain carbons in the region where $K_{n3} < -1$ have been examined. Work on these carbons was done by means of the pressure of displacement method. This work was done before such relationships as are herein presented had been discovered, and no explanation of their anomalous behavior could then be offered. Two carbons, carbon "G" and carbon "C," had been tested.[8] Their A_{13} values were determined by water–air pressure of displacement measurements. Both A_{13} values were less than 52.4 degrees, which places the two carbons in the region where $K_{n3} < -1$. The A_{13} value for carbon "G" was lower than the A_{13} value for carbon "C." When interfacial pressure of displacement measurements were made using benzene and water, both carbons gave the same $A_{13} - A_{1n}$ value. For both carbons this value was the $-S_{n3}$ value to be expected when $\cos \Theta_{n3} = -1$, since $A_{13} - A_{1n} = S_{n3} \cos \Theta_{n3}$ (or $S_{n3}K_{n3}$). When the A_{13} values already determined for the two carbons were substituted in this equation, it was of course found that A_{1n} for carbon "G" was lower than A_{1n} for carbon "C." This seemed wrong at the time since for all other solids those having lower A_{13} values had higher A_{1n} values. Moreover, qualitative tests such as rate of imbibition in the loose powder showed that carbon "G" was more readily wet by benzene than was carbon "C." In the light of the present developments it would seem that the explanation for the behavior of the carbons is as follows. For solids in the range where $K_{n3} < -1$ the interfacial pressure of displacement method is no longer applicable. Since no angle greater than 180° can be measured by the method, for solids in this range the $-S_{n3}$ value will always be obtained for $A_{13} - A_{12}$. The A_{13} measurement can be made and by means of this measurement the place of the solid on the diagram can be determined. From the A_{1n} equations the A_{1n} values can then be calculated. Figure 5 shows the carbons placed on the diagram by means of their A_{13} values. On the solid A_{1n} lines are the "true" calculated values for A_{1n}. On the broken lines paralleling the A_{13} line are indicated the values that were obtained for the carbons when the interfacial liquid–liquid measurements were made.

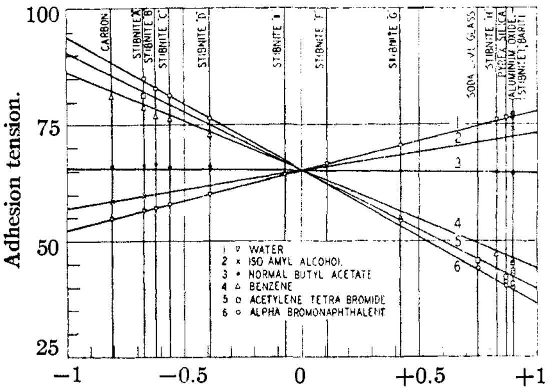

Fig. 4.

The wetting characteristics of solids, then, can be definitely indicated in the terms of K_{n3} (or K_{23}) values; and these K_{n3} values do have a meaning beyond $K_{n3} = +1$ and $K_{n3} = -1$.

The fundamental equations so far developed in this paper, expressed in terms of K_{n3} values, are brought together in the following list.

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(8) F. E. Bartell and C. N. Smith, *Ind. Eng. Chem.*, **21**, 1102 (1929).

$$A_{13} - A_{1n} = S_{n3}K_{n3} \tag{1}$$
$$A_{13} = 12.8\,K_{n3} + 65.2 \tag{2}$$
$$A_{1n} = m_n K_{n3} + 65.2 \tag{3}$$
$$m_n = 12.8 - S_{n3} \tag{4}$$
$$A_{13} = S_3 K_{13} \tag{5}$$
$$A_{1n} = S_n K_{1n} \tag{6}$$
$$K_{13} = 0.178\,K_{n3} + 0.904 \tag{7}$$
$$K_{1n} = [(12.8 - S_{n3})K_{n3} + 65.2]/S_n \tag{8}$$

On the positive side of the K_{n3} axis, where $K_{n3} = 0.54$, $K_{13} = 1$. This means that water forms a zero angle on a solid of $K_{n3} > +0.54$.

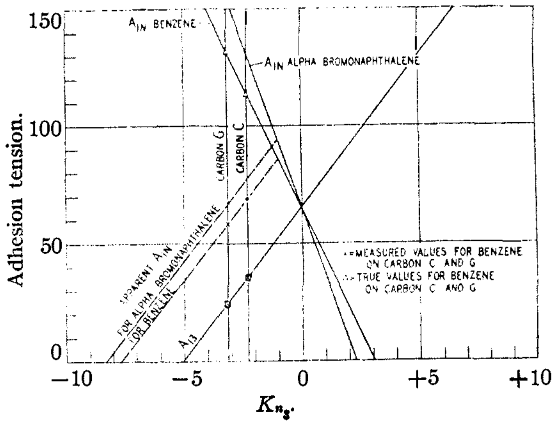

Fig. 5.

All solids with $K_{n3} > +0.54$ are completely wet by water and must tend to adsorb water films upon their surfaces. As K_{n3} approaches +1, the solids in this range probably have increasingly thick (or more nearly complete) films of water upon their surfaces.[9] When $K_{n3} = +1$, from equation (5), $A_{13} = 77.96$. The value for the surface tension of supercooled water, as given in the "International Critical Tables," can be as high as 77 dynes. As the water cools and approaches the solid crystalline state, the molecules probably become oriented. The value for the surface tension of ice, or of a plane surface of water with oriented molecules, probably is then close to 77 dynes. The interfacial tension of water in bulk against oriented water, or of water against ice, should be close to zero. Then since $A_{13} = S_1 - S_{13}$ and since S_{13} should be close to zero, A_{13} for a plane surface of oriented water may be taken to be 77.96. When $K_{n3} = +1$ we are probably dealing, then, with a plane surface of oriented water molecules, in effect with solid water, or with a solid covered by a complete film of oriented water which is of sufficient thickness to mask entirely the surface of the underlying solid and to act with the surface characteristics of a plane surface of solid water.

Summary

1. A straight line relationship between the cosine of the interfacial angle and the adhesion tension of any given liquid for a series of solids has been demonstrated, and the equation for this relationship has been derived. The relationship between such an equation for water and the equation for any organic liquid, as well as equations relating interfacial angle to the air contact angle, have also been derived.

2. The use of the symbol, K_{n3}, rather than the cosine of the interfacial angle, has been explained, and the usefulness of K_{n3} to extend the derived equations beyond values of the cosine of the interfacial angle = ±1 has been shown.

3. By means of the equations presented in this paper it is possible, after making only one accurate determination of adhesion tension or of contact angle of a given liquid for a given solid, to calculate the adhesion tension of this solid for water or for any other liquid whose interfacial tension against water is known.

ANN ARBOR, MICHIGAN RECEIVED JANUARY 13, 1934

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(9) F. E. Bartell and H. Y. Jennings, *J. Phys. Chem.*, **38**, 495 (1934).