

Contact Angles at Liquid-Liquid-Air Interfaces

William Fox

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zero distance from the irradiated zone, the volume of gas passing this point in 5 minutes is found (from the streaming velocity) to be 2.7×10^5 cc: the number of moles of CH_3 picked up in that time at that point is $4 \times 24 \times 10^{-6} / 207$ or 4.6×10^{-7} . The concentration of CH_3 is

therefore 1.7×10^{-12} mole per cc, or 2.1×10^{-13} mole percent in the gas.

Other examples of the usefulness of this method of counting free radicals will be given in forthcoming papers on the mechanism of the photolysis of propionaldehyde and of acetone.

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Contact Angles at Liquid-Liquid-Air Interfaces*

WILLIAM FOX

Department of Chemistry, Columbia University, New York, New York

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Angles at the points of contact of a number of liquid-liquid-air systems were measured. A new method of measuring the interfacial tension is presented. The work of adhesion between the phases is determined. A new theory of spreading is offered.

MEASUREMENTS of contact angles at liquid-liquid-solid and liquid-solid-air interfaces have been made by a number of workers. Difficulties due to poor reproducibility of solid surfaces and due to the effects of adsorbed and condensed layers on solid phases, however, markedly affect the experimental results.^{1,2} Notwithstanding these difficulties the measurements of contact angles have been of considerable value in both scientific and industrial investigations.

In view of the importance of this work it is perhaps surprising that no one has made use of the corresponding phenomenon at liquid-liquid-air interfaces. This phenomenon can be easily investigated by bringing an air bubble to a liquid-liquid interface and measuring the contact angles of the system. The surfaces involved are definite and reproducible. No condensed layers of an extraneous phase can be present under the condition of the experiment. In addition the systems involve surface energies for which values are known or can be determined. (The surface energies of solids cannot readily be determined.)

Such measurements at liquid-liquid-air inter-

faces can be used to determine the interfacial tension free from inexact assumptions concerning the value of the contact angles, and also to determine the values for the work of adhesion and the work of spreading of different phases. It is with this valuable and thermodynamically sound tool for the study of the energy relations at liquid-liquid interfaces that this paper will be concerned.

The method used is similar to that of Taggart *et al.* applied previously only to the measurement of contact angles at liquid-solid-air interfaces.³ An air bubble is brought by means of a curved pipette to a hollow glass tube (3-mm inside diameter) sealed to a glass rod. The air bubble is then brought down to the interface of the two liquids and the angles of contact at the points where the interfaces meet are determined. This simple apparatus can be easily refined in some such manner as indicated by Bartell² to allow for convenient measurement on either side of the interface. Photographs were made of the air bubble, the contact angles being determined by direct measurement with a protractor either upon the photograph itself or upon the ground glass focusing screen. The contact angles are sharply defined and reproducible, and are the same on approaching the interface

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¹ N. K. Adam, *Physics and Chemistry of Surfaces*, p. 180.

² F. E. Bartell and P. H. Cardwell, *J. Am. Chem. Soc.* 64, 494 (1942); 1530 (1942); 1641 (1942).

³ Taggart, Taylor, and Ince, *Trans. A.I.M.E.* 87, 285 (1930).

from either direction. Measurements made at different times agree with each other within the experimental precision of the measurement.

Equilibrium at the interfaces of the systems studied was obtained quickly and did not change with time. This is not unexpected as at the immediate vicinity of the surfaces of discontinuity the phases are quickly saturated with each other. It should be noted also that as predicted by the Gibbs relation all the interfaces (liquid 1-air, liquid 2-air, and liquid 1-liquid 2) will be richer in the material for which $-\partial\sigma/\partial c$ is greatest.

The only factors that can affect the angles are those which change the relations of the three interfacial tensions. As distortion of the air bubble at the interface can have no effect on the value of the interfacial tensions it is not possible for distortion to change the values of the angles. Therefore the size of the bubble and the manner in which it is held against the interface do not affect the values obtained.

Consider a system where the air bubble makes a definite contact angle with the liquid-liquid interface. On bringing an air bubble to a water-aniline interface equilibrium is established definitely and suddenly. When the points of contact of the three interfaces are in equilibrium the following relations may be written.⁴ (See Fig. 1.)

$$\sigma_{w,an} + \sigma_{w,A} \cos \theta + \sigma_{an,A} \cos \phi = \sigma_p = 0; \quad (1)$$

$$\sigma_{w,A} \sin \theta - \sigma_{an,A} \sin \phi = \sigma_p = 0. \quad (2)$$

From (1) and (2) we get

$$d\sigma_{an,w} = -\sigma_{w,A} [\sin(\theta + \phi)/\cos \phi] d\theta - [\cos(\theta - \phi)/\cos \phi] d\sigma_{w,A} - \left[\frac{\cos 2\phi}{\cos \phi} \right] d\sigma_{an,A}. \quad (3)$$

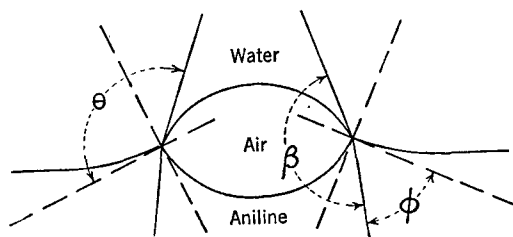


FIG. 1.

⁴ σ = interfacial tension; w = water; an = aniline; A = air; $\sigma_p = 0$ = tension at the points of contact at equilibrium.

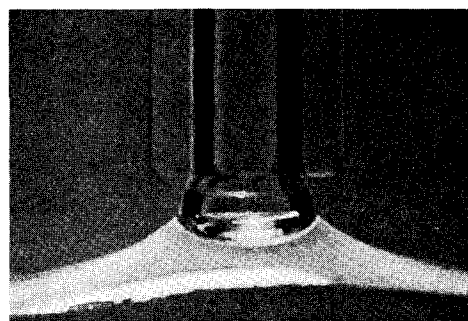


FIG. 2. Water-air-aniline; temperature 22°C.

Angle θ shall always be the angle measured through the top liquid, angle ϕ the angle through the bottom liquid, and angle β the angle through the gas phase.

Equation (3) will be discussed further in another paper.

The experimental procedure employed was to measure angle θ and then to calculate angles ϕ and β by the use of Eq. (2). Angles ϕ and β should not be measured directly as the image of the aniline-air interface is distorted by the curvature of the interfaces and by the difference in the refractive index of the different phases.

Reference to the photographs (Figs. 2 and 3) of the aniline-water-air systems⁵ show that $\theta = 131.1 \pm 3.0^\circ$.⁶

An air bubble when released below the interface in the aniline phase will rise to the interface and (if not too large) be held there showing the same relations of the angles within the experimental precision of the measurement.

It was observed that over a range of temperature from 20° to 50° there was no measurable change in the values of the angles.^{7,8}

Since a change in temperature over this range had no measurable effect on the values of the angles, we may therefore use the angles observed to determine the interfacial energies over the range of temperature for which the angles are constant.

⁵ The aniline was practically colorless. C. P. Bakers analyzed.

⁶ Result of twenty measurements. Mean = 131.1° a.d. 3.0°.

⁷ Investigations are now being made with systems in the region of critical mixing.

⁸ I. W. Wark and H. B. Cox [Trans. A.I.M.E. 112, 189 (1934)] report no measurable change in contact angles at liquid-solid-air interfaces for ΔT of 10 degrees.

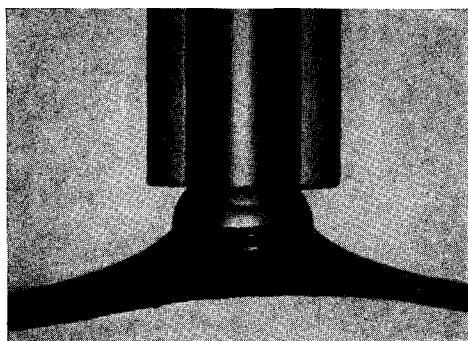


FIG. 3. Water-air-aniline; temperature 33°C.

By Eq. (2) using the surface tension values of Reynolds,⁹

$$0 = \sigma_{w,A} \sin \theta - \sigma_{an,A} \sin \phi,$$

$$\sin \phi = \frac{46.4}{42.2} \sin \theta$$

$$\phi = 56^\circ,$$

and by Eq. (1)

$$0 = \sigma_{an,A} \cos \phi + \sigma_{w,A} \cos \theta + \sigma_{an,w},$$

$$\sigma_{an,w_{26^\circ\text{C}}} = 6.9 \pm 0.6 \text{ erg/cm}^2.$$

This value although precise only to about 9 percent differs from the result predicted by Antonow's rule (which rests on the assumption that $\theta = 180^\circ$ and $\phi = 0^\circ$) by about 64 percent and from the value of Reynolds (who neglects consideration of the angle that the interface makes with the third phase) by about 44 percent.

In the case of the benzene-water-air (also ether-water-air) system the air bubble when brought down to the interface through the benzene is not held at the interface. If pressed against the interface the bubble will tend to distort and force the interface down. On the other hand when the bubble is brought up to the interface from the water layer the benzene enfolds the air bubble, i.e., the air bubble goes into the benzene layer immediately. If an air bubble is brought below the interface into the water layer and a drop of benzene placed in contact with the air bubble, the benzene spreads out over the gas phase replacing the water in

contact with the air so that the angle of the benzene-water interface against the benzene-air interface is 0° and that of the water-air interface against the benzene-air and the benzene-water interfaces is 180° . This behavior can be interpreted to mean that the air bubble is more easily "wetted" by the benzene than by water.

Considering the contact angles as the angles that the tangents to the curve (benzene-air and water-air) make with the liquid-liquid interface we have at the points of contact (Fig. 4) $\theta = 0^\circ$ and $\phi = 180^\circ$ and by Eq. (1)

$$0 = \sigma_{B,w} + \sigma_{B,A} \cos 0^\circ + \sigma_{w,A} \cos 180^\circ$$

and

$$\sigma_{B,w} = \sigma_{w,A} - \sigma_{B,A}. \quad (4)$$

The same relationship holds for the ether-water-air system. These results are those predicted by Antonow's rule. Antonow's rule is an empirical equation found to hold true for a number of systems. It can be seen that Antonow's rule is a special case resulting when $\theta = 0^\circ$ and $\phi = 180^\circ$ and Eq. (1) reduces to Eq. (4).

For the nitrobenzene-water (Fig. 5), carbon tetrachloride-water, chloroform-water, and malonic ester-water systems with air we have the condition that $\theta = 180^\circ$ and $\phi = 0^\circ$. Applying Eq. (1) we see that in all these cases (R = organic liquid)

$$\sigma_{R,w} = \sigma_{w,A} - \sigma_{R,A}$$

and Antonow's rule will also hold.

In all these systems an air bubble (if not too large) when released below the interface in the organic liquid will rise to the interface and be held there showing the same relations as above within the experimental precision of the measurement.

WORK OF ADHESION OF THE GAS PHASE AT THE INTERFACE OF TWO LIQUIDS

The work of adhesion between a gas and a liquid, both in contact with another liquid, at

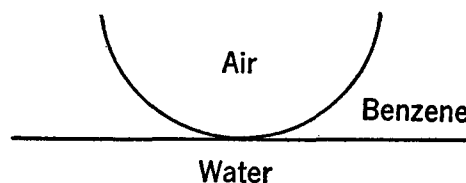


FIG. 4.

⁹ W. C. Reynolds, Trans. Chem. Soc. **119**, 461 (1921).

constant temperature and pressure is numerically equal to the free energy required to separate the gas phase from the liquid phase. This value can now be determined. Let 1 represent the top liquid; 2 the bottom liquid; σ_i the initial tension at the point of contact; $\sigma_e = 0$, the equilibrium tension at the points of contact.

As the air bubble is brought down to the interface, at the moment of contact $\theta_i = 0^\circ$; $\phi_i = 180^\circ$; $\beta_i = 180^\circ$.

$$(a) \quad \begin{aligned} \sigma_i &= \sigma_{2,A} + \sigma_{1,2} \cos \phi_i + \sigma_{1,A} \cos \beta_i, \\ \sigma_i &= \sigma_{2,A} - \sigma_{1,A} - \sigma_{1,2}. \end{aligned}$$

At equilibrium

$$(b) \quad \sigma_e = 0 = \sigma_{1,2} + \sigma_{1,A} \cos \theta_e + \sigma_{2,A} \cos \phi_e.$$

Solving for

$$\sigma_{1,2} = -[\sigma_{1,A} \cos \theta_e + \sigma_{2,A} \cos \phi_e]$$

and substituting in (a) we get

$$\sigma_i = \sigma_{2,A} - \sigma_{1,A} + \sigma_{1,A} \cos \theta_e + \sigma_{2,A} \cos \phi_e. \quad (5)$$

Since $dG = VdP - SdT - Ad\sigma$

$$dG_{T,P} = -Ad\sigma,$$

$$\Delta G_{T,P} = -A(\sigma_e - \sigma_i),$$

and since

$$\sigma_e = 0,$$

$$(\Delta G/A)_{T,P} = \sigma_i = -W/A = -\text{work of adhesion.}$$

In the benzene-water-air system and the ether-water-air system $\theta_e = 0^\circ$; $\phi_e = 180^\circ$; and $(\Delta G/A)_{T,P} = 0$. The work of adhesion of the air bubble to the water in the presence of the

organic liquid is zero and the air bubble will not be held by the water.

It is also necessary to consider the energy holding the gas phase to liquid 1. This can be calculated in the following manner.

If the air bubble approaches the liquid-liquid interface from below at the moment of contact $\phi_i = 0^\circ$; $\beta_i = 180^\circ$; $\theta_i = 180^\circ$.

$$(c) \quad \begin{aligned} \sigma_i &= \sigma_{1,A} + \sigma_{2,A} \cos \beta_i + \sigma_{1,2} \cos \theta_i, \\ \sigma_i &= \sigma_{1,A} - \sigma_{2,A} - \sigma_{1,2}. \end{aligned}$$

At equilibrium

$$(d) \quad \sigma_e = 0 = \sigma_{1,2} + \sigma_{2,A} \cos \phi_e + \sigma_{1,A} \cos \theta_e.$$

Solving for

$$-\sigma_{1,2} = \sigma_{2,A} \cos \phi_e + \sigma_{1,A} \cos \theta_e$$

and substituting in (c)

$$\sigma_i = \sigma_{1,A} - \sigma_{2,A} + \sigma_{2,A} \cos \phi_e + \sigma_{1,A} \cos \theta_e. \quad (6)$$

In the benzene-water-air and the ether-water-air systems $\phi_e = 180^\circ$; $\theta_e = 0^\circ$; $\beta_e = 180^\circ$ and from (6)

$$\sigma_i = -2(\sigma_{2,A} - \sigma_{1,A}).$$

$(\Delta G/A)_{T,P}$ will be negative and the gas phase will be held by the organic liquids (Table I).

In the carbon tetrachloride-water-air, nitrobenzene-water-air, chloroform-water-air and malonic ester-water-air systems $\theta_e = 180^\circ$; $\phi_e = 0^\circ$; $\beta_e = 180^\circ$. Applying Eq. (5)

$$\sigma_i = -2[\sigma_{1,A} - \sigma_{2,A}],$$

and from Eq. (6)

$$\sigma_i = 0.$$

The air bubble will thus be held by the bottom liquid but not by the top liquid (Table I).

In the aniline-water-air system by Eq. (5)

$$(\Delta G/A)_{T,P} = -11.1 \text{ ergs/cm}^2$$

and by Eq. (6)

$$(\Delta G/A)_{T,P} = -2.7 \text{ ergs/cm}^2.$$

These values are equal to the free energy required to separate the gas phase from the aniline phase (saturated with water) and from the water phase (saturated with aniline), respectively (Table I).

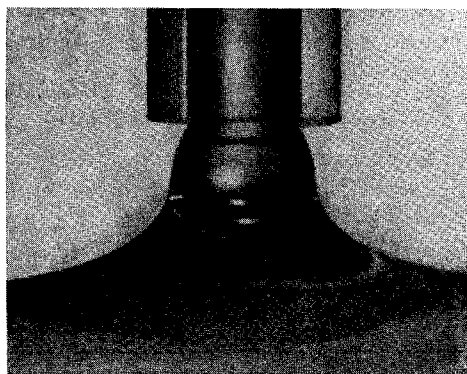


FIG. 5. Water-air-nitrobenzene; temperature 35°C .

TABLE I.*

Liquid 1 (saturated with liquid 2)	Liquid 2 (saturated with liquid 1)	Work of adhesion of liquid 1 (in contact with liquid 2) to air $=(-\Delta G/A)_{T,P}$	Work of adhesion of liquid 2 (in contact with liquid 1) to air $=(-\Delta G/A)_{T,P}$	Work of adhesion in air of liquid 1 to liquid 2 $=(-\Delta G/A)_{T,P}$	Temperature °C
Benzene	Water	68.8	0.0	57.6	19
Ether	Water	21.2	0.0	35.0	18
Water	Aniline	2.7	11.1	81.7	26
Water	Chloroform	0.0	66.8	52.8	18
Water	Carbon tetrachloride	0.0	87.0	53.4	17
Water	Nitrobenzene	0.0	49.4	86.4	18

* Units of Tables I and II = ergs/cm².

Values in Tables I and II based on surface tension data of Reynolds (see reference 9).

WORK OF ADHESION OF TWO-LIQUID PHASES AT A LIQUID-GAS INTERFACE

The work of adhesion between two liquids in contact with a gas phase at constant temperature and pressure is numerically equal to the free energy per unit area required to pull the liquids apart. This can also be calculated.

When a drop of the top liquid first touches the surface of the bottom liquid $\beta_i = 0^\circ$; $\theta_i = 180^\circ$; $\phi_i = 180^\circ$; and

$$(e) \quad \sigma_i = \sigma_{2,1} + \sigma_{1,A} \cos \theta_i + \sigma_{2,1} \cos \phi_i,$$

$$\sigma_i = \sigma_{2,1} - \sigma_{1,A} - \sigma_{2,A}.$$

At equilibrium

$$(f) \quad \sigma_e = 0 = \sigma_{2,1} + \sigma_{1,A} \cos \theta_e + \sigma_{2,A} \cos \phi_e.$$

Solving for

$$\sigma_{2,1} = -\sigma_{1,A} \cos \theta_e - \sigma_{2,A} \cos \phi_e,$$

and substituting in (e) we get¹⁰

$$\sigma_i = -\sigma_{1,A} - \sigma_{2,A}$$

$$-[\sigma_{1,A} \cos \theta_e + \sigma_{2,A} \cos \phi_e]. \quad (7)$$

In the benzene-water-air and the ether-water-air systems $\theta_e = 0^\circ$; $\phi_e = 180^\circ$; $\beta_e = 180^\circ$; and from (7)

$$(\Delta G/A)_{T,P} = -2\sigma_{1,A}.$$

In the nitrobenzene-water-air, carbon tetrachloride-water-air, chloroform-water-air, and malonic ester-water-air systems $\theta_e = 180^\circ$; $\phi_e = 0^\circ$; $\beta_e = 180^\circ$. $(\Delta G/A)_{T,P}$ will therefore be equal to

¹⁰ Compare with the Dupré equation, $W = \sigma_{2,A} + \sigma_{1,A} - \sigma_{2,1}$.

$-2\sigma_{2,A}$ (again twice the surface energy of the organic phase).

For the aniline-water-air system from Eq. (7) the work of adhesion of the two phases in the presence of air is found to be 81.7 ergs/cm² (Table I).

In the manner indicated above the value for the work of adhesion between any two liquids in the presence of a gas phase can be determined. The values thus obtained (Table I) do not agree with those given by Harkins¹¹ which are determined by measurements of the surface energies of the pure liquids, the interfacial tension between the saturated phases, and the application of the Dupré equation. If the surface tensions of each phase saturated with each other were determined, and the interfacial tension could be independently determined accurately, the application of the Dupré equation should then give the values as above calculated (Table I).

CONDITIONS WHICH WILL DETERMINE SPREADING

The theory of spreading which is commonly accepted states that spreading will occur if the work of adhesion between two phases is greater than the work of cohesion of the phase which is spreading.^{12,13} From Eq. (7) we can see that for the organic liquid-water-air systems where the contact angles are 0° and 180° the work of adhesion will be equal to twice the surface tension of the liquid which has the lower surface

¹¹ W. D. Harkins, J. Am. Chem. Soc., 356 (1917).

¹² W. D. Harkins, 6th Colloid Symposium Monograph, p. 23.

¹³ W. D. Harkins, J. Chem. Phys. 9, 552 (1941).

TABLE II.

Liquid 1 (saturated with liquid 2)	Liquid 2 (saturated with liquid 1)	$(-\Delta G/A)_{T, P}$ liquid 1 spreading on liquid 2 in air	"Spreading coefficient" (Harkins) $t=20^\circ\text{C}$	$(-\Delta G/A)_{T, P}$ liquid 2 spreading on liquid 1 in air	"Spreading coefficient" (Harkins) $t=20^\circ\text{C}$	Temperature $^\circ\text{C}$
Benzene	Water	57.6	8.86	-11.2	-78.92	19
Ether	Water	35.0	44.95	13.8	-66.35	18
Water	Aniline	70.6	-35.94	79.0	24.40	26
Water	Chloroform	-14.0	-78.25	52.8	12.99	18
Water	Carbon tetrachloride	-33.6	-89.35	53.4	2.83	17
Water	Nitrobenzene	37.0	-55.03	86.4	3.71	18

tension. Now the work of cohesion of a liquid in air is twice the surface tension. Therefore in considering the liquid with the lower surface tension as spreading, the "spreading coefficient" defined as $W_a - W_c$ (for the cases above mentioned where the contact angles are 0° and 180°) will not be greater than zero. When the liquid with the greater surface tension is considered in spreading the "spreading coefficient" as defined will always be negative.

This "peculiar restriction" in the instances where the empirical relation expressed by Antonow actually does hold true is realized by the proponents of that theory, in answer to which they express great doubt that the Antonow relation is a valid one.

Consideration of what happens when a liquid spreads makes it evident that to explain spreading in a specific gas phase, we need only compare the work of adhesion of the gas to the liquid on which the spreading is to occur with the work of adhesion of the two liquids in the presence of that same gas phase. If the free energy change at constant temperature and pressure is negative the action will be spontaneous, and spreading will occur in that direction which will give a negative free energy change. A direct comparison of the values of the free energy change for the systems involved will then give a thermodynamically exact measure of the tendency and direction in which spreading will occur (Table II).

This theory is equally well applied to the phenomena at liquid-solid-air and liquid-liquid-solid interfaces.

SUMMARY

1. A method is presented whereby it is possible to determine the interfacial tension between two liquids from the surface tensions.

2. Antonow's rule is shown to be a special case of the equation

$$0 = \sigma_{1,2} + \sigma_{1,A} \cos \theta + \sigma_{2,A} \cos \phi.$$

3. The Dupré equation is indicated as being a special case of the equation

$$\sigma_i = -\sigma_{1,A} - \sigma_{2,A} - [\sigma_{1,A} \cos \theta_e + \sigma_{2,A} \cos \phi_e].$$

4. The work of adhesion of a gas to each of the two liquids in contact with each other is calculated by the equations

$$\begin{aligned} \sigma_i &= \sigma_{2,A} - \sigma_{1,A} + \sigma_{1,A} \cos \theta_e + \sigma_{2,A} \cos \phi_e \\ \text{and} \\ \sigma_i &= \sigma_{1,A} - \sigma_{2,A} + \sigma_{2,A} \cos \phi_e + \sigma_{1,A} \cos \theta_e. \end{aligned}$$

5. The work of adhesion of two liquids in contact with air is determined by the equation

$$\sigma_i = -\sigma_{1,A} - \sigma_{2,A} - [\sigma_{1,A} \cos \theta_e + \sigma_{2,A} \cos \phi_e].$$

6. A new theory of spreading is offered.

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