transition point. The problem yet to be solved is to determine the equilibrium concentrations of HCl, HgO and 2HgO·HgCl at the triple point.

Summary

The solubilities of mercuric oxide and of basic mercuric chloride, 2HgO·HgCl$_2$, have been measured in hydrochloric acid solutions. A break oc-

curs in the solubility relationships due to the formation of a new solid phase (2HgO·HgCl$_2$). This basic mercuric chloride, 2HgO·HgCl$_2$, has been prepared and identified; the water solubility is 11.4 × 10^{-4}. The relative distribution of mercury among several different ion species is indicated.

Adsorption and the Energy Changes[1] at Crystalline Solid Surfaces

BY G. E. BOYD AND H. K. LIVINGSTON[1a]

Theory

Adsorption is accompanied by a change both in the total and in the free surface energy of a surface. The classical relation of J. W. Gibbs[2] for interfaces between fluids has been used extensively and certainly must be regarded as valid when properly applied. The question of the applicability of the theorem to the interface between solids and fluids must be considered, and we are fortunate that Gibbs has discussed the problem in detail in the case in which the solid is anisotropic.

Thus, if the total surface energy, E_{so}; surface entropy, S_{so}; surface densities of chemical species, Γ_i; chemical potentials, μ_i; and temperature, T, are used, it is possible to define a quantity, ζ, for the arbitrarily restricted case of a system of two components by the equation[3]

$$\zeta = E_{so} - TS_{so} - \mu_1\Gamma_1 - \mu_2\Gamma_2 \qquad (1)$$

In Gibbs' words, "The quantity ζ evidently represents the tendency to contraction in that portion of the surface of the fluid which is in contact with the solid. It may be called *the superficial tension of a fluid in contact with a solid*. Its value may be either positive or negative.

"It will be observed for the same solid surface and for the same temperature but for different liquids the values of γ_{sf} (in all cases to which the definition of this quantity is applicable) will differ from those of ζ by a constant, *viz.*, the value of γ_{so} for the solid surface in a vacuum."

(1) Original manuscript received February 4, 1942.

(1a) Present address: Jackson Laboratory, E. I. du Pont de Nemours and Co., Deepwater, N. J.

(2) J. W. Gibbs, "Collected Works," Longmans, Green & Co., New York, N. Y., 1928, p. 314.

(3) It will be noticed that we have taken the liberty of modifying part of Gibbs' original nomenclature in order to bring it into approxi-

Obviously, ζ is defined by

$$\zeta = \gamma_{sf} - \gamma_{so} = -\pi \qquad (2)$$

or, the spreading pressure, π, is equal to the difference between the free surface energy of the clean solid surface (in a vacuum) and the free surface energy when in equilibrium with a chemically dissimilar fluid component (*i. e.*, gas or liquid).

Utilizing Gibbs' general thermodynamic methods, from equation (1), it is possible to obtain for a system consisting of a crystalline adsorbent and one adsorbate

$$d\pi = S_{so}dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \qquad (3)$$

If isothermal conditions are maintained, and if the Gibbs plane from which adsorption is reckoned is chosen so that the surface density of adsorbent, Γ_1, is zero, one may write

$$d\pi = \Gamma_2^{(1)}d\mu_2$$

or

$$\Gamma_2^{(1)} = \left(\frac{\partial\pi}{\partial\mu_2}\right)_{T, P, \mu_1} \qquad (4)$$

For the case in which the fluid contiguous to the solid surface is a gas or a vapor

$$d\mu_2 = RT\, d\ln f_2 \qquad (5)$$

where f_2 is the fugacity, and for vapors at low pressures

$$RT\, d\ln f_2 = RT\, d\ln p_2 \qquad (6)$$

is true with sufficient accuracy, so that equation (4) may be written as

$$d\pi = RT\Gamma_2^{(1)}d\ln p_2 \qquad (7)$$

where p_2 is to be taken as the equilibrium pressure of a gas or vapor above the crystal surface upon which adsorption has occurred.[4]

(4) Extensive calculations to establish the correctness of Equ.

Evidently, values of p_2 may range from zero to the saturation vapor pressure, p_2^0, of the pure liquid from which the vapor is formed. An integration of equation (7) gives

$$\int_0^\pi d\pi = \gamma_{so} - \gamma_{sv} = RT \int_0^{p_2} \Gamma_2^{(1)} \, d \ln p_2 \qquad (8)$$

where γ_{sv} represents the free surface energy of the solid in equilibrium with the vapor of the foreign component 2 at pressure p_2. The quantity $\gamma_{so} - \gamma_{sv}$ may be looked upon as either the two-dimensional spreading pressure of the adsorbed film on the solid surface,[5] or, as the free energy of immersion at constant temperature of a unit surface of clean solid in an infinite amount of vapor at pressure p_2. If the solid be immersed in a saturated vapor, of pressure p_2^0, equation (8) becomes

$$\gamma_{so} - \gamma_{sv^0} = RT \int_0^{p_2^0} \Gamma_2^{(1)} \, d \ln p_2 \qquad (9)$$

A determination of the important free energy of immersion of a solid in a saturated vapor is possible if the right-hand member of (9) can be integrated. This might be effected if an equation for the adsorption isotherm up to the pressure of the saturated vapor were known (i. e., $\Gamma_2^{(1)}$ as a function of p_2). Recent attempts[6] in this direction have been partially successful, but, for the
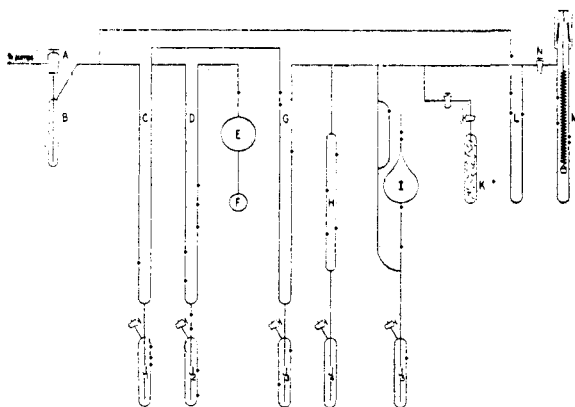

Fig. 1.—Vapor adsorption apparatus showing silica spring and platinum powder bucket. M; manometer. L; charcoal trap. K; McLeod gage. I; vapor compressing chamber, H; cutoffs. G. D and C; vapor pipets. E and F, and trap. B.

problem at hand, it was found that a graphical integration of (9) was the least time-consuming.

Two special points need be made concerning this procedure. From (9) it is evident that at $p_2 = 0$ the integrand approaches negative infinity, whereas, as $p_2 = p_2^0$, experimentally the adsorption, $\Gamma_2^{(1)}$, appears to increase without bound.

The first difficulty may be overcome by observing that

$$RT \int_0^{p_2''} \Gamma_2^{(1)} \, d \ln p_2 = RT \int_0^{p_2''} \frac{\Gamma_2^{(1)}}{p_2} \, dp_2 \qquad (10)$$

Since the ratio $\Gamma_2^{(1)}/p_2$ approaches a constant value (Henry's law for surfaces) for the adsorption of gases or vapors at low pressures, the integral may be evaluated at the lower limit. At the upper limit, the value of the integral is obtained by a short extrapolation when suitable methods are used.[7,8]

Experimental

In order to carry out the calculations described in the previous section it is necessary to have accurate adsorption data up to the saturation pressure of the vapor studied. An examination of the volumetric adsorption method as used in these laboratories[9] indicates that it is not a feasible technique to employ at pressures higher than half-saturation. Consequently, in these more recent studies the technique of McBain and Bakr[10] was used in which the amount of material adsorbed, q, is determined directly by the increase in weight of a given mass of crystalline non-porous adsorbent shown by the increased extension of a fine silica spring which supports the adsorbent, as in Fig. 1, M. The method has numerous advantages for this type of work, among which are: it is (1) rapid and accurate; (2) buoyancy corrections are small; and (3) organic vapors may be utilized without difficulty. Isotherms by this method are shown in Figs. 2–5.

It is important to make clear the connection between the adsorption experimentally meas-

(5) The concept that the molecules of a substance adsorbed on a crystal surface exert a two-dimensional spreading pressure was used first by Volmer. (Z. physik. Chem., 115, 253 (1925)) and arose quite naturally out of the researches on mobile films on solids. In this paper no assumptions are made concerning the physical state of the adsorbed films, but rather a thermodynamic viewpoint is maintained.

(6) Brunauer, Deming, Deming and Teller, This Journal, 62, 1723 (1940).

(7) See Appendix D of H. K. Livingston. Ph.D. Thesis. University of Chicago, 1941.

(8) Although the ideas presented in this section stem directly from the classic paper of J. W. Gibbs on the "Equilibria of Heterogeneous Substances," the authors wish to acknowledge the stimulation they have received from the very recent publications of Bangham and his co-workers (Bangham and Razouk. Trans. Faraday Soc., 33, 1459, 1463 (1937); Proc. Roy. Soc. (London). A166, 572 (1938)). The experimental work from the laboratory at Cairo has dealt so far only with a porous charcoal in which it is likely that the effects of capillary condensation were present.

(9) Gans. Brooks and Boyd, Ind. Eng. Chem.. Anal. Ed.. 14, 396 (1942).
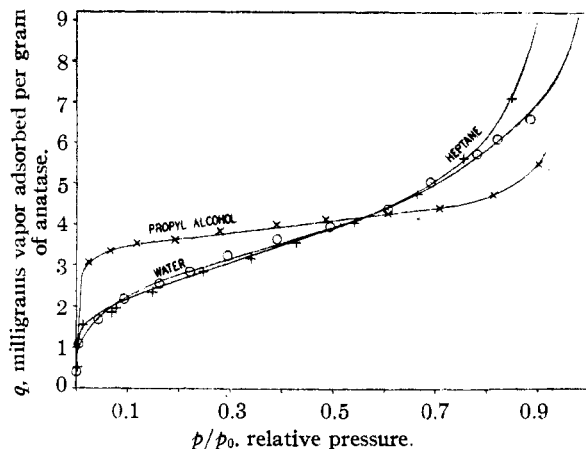
(10) McBain and Bakr. This Journal. 48, 690 (1926).

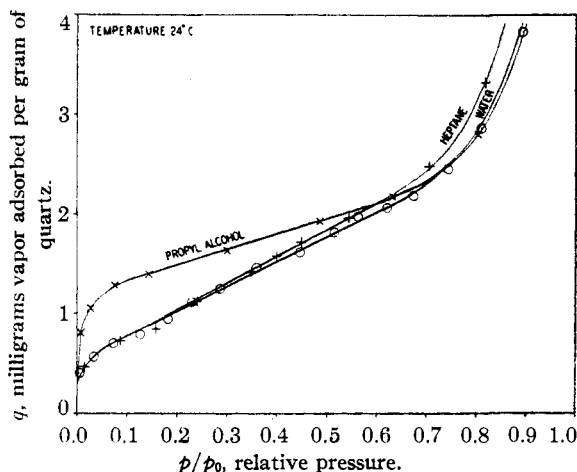Fig. 2.—Adsorption of water, propyl alcohol and heptane vapors on crystalline, non-porous TiO₂ (anatase).

Fig. 3.—Adsorption of water. propyl alcohol and heptane vapors on crystalline SiO₂ (quartz).
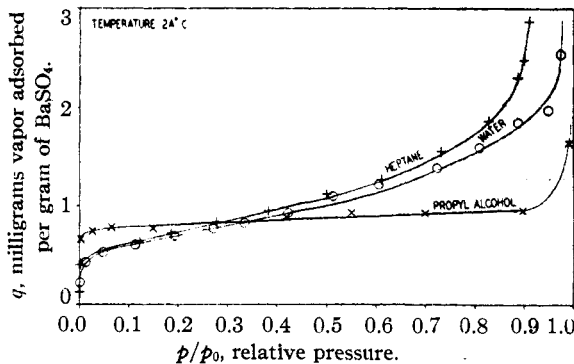

Fig. 4.—Adsorption of water, propyl alcohol and heptane vapors on crystalline BaSO₄ (X-ray grade).
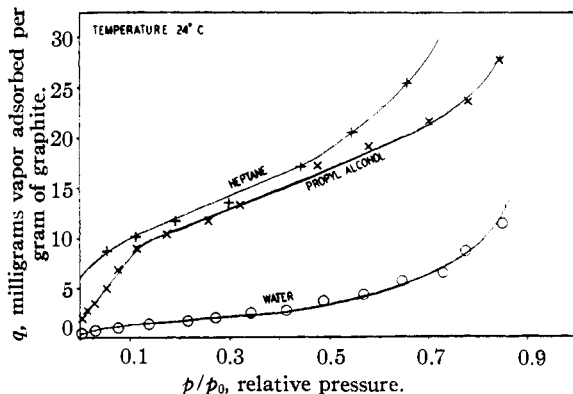

Fig. 5.—Adsorption of water, propyl alcohol and heptane vapors on graphite (Dixon 0708).

ured, expressed in milligrams (or micromoles) adsorbate per gram adsorbent, and the quantity, $\Gamma_2^{(1)}$, of equation (9). This latter adsorption has units of moles of adsorbate per sq. cm. adsorbent, and is defined by Gibbs[2] as, " . . . the surface density of fluid (in our case, vapor) component determined by the excess of matter in the vicinity of the surface over that which would belong to the solid if it were bounded by a vacuum in place of the fluid, and to the fluid, if it extended with a uniform volume–density of matter just up to the surface of the solid . . . . "

Thus, equation (11) serves to define $\Gamma_2^{(1)}$ experimentally

$$\Gamma_2^{(1)} = \frac{q}{M\Sigma} - \frac{\tau}{v_2} \qquad (11)$$

where q is the measured adsorption given in milligrams per gram of adsorbent, M the molecular weight of the vapor, Σ the area in sq. cm. per gram

of solid, τ the thickness of the surface region, and v_2 is the molal volume of the vapor. Since the vapor behaves as a perfect gas

$$v_2 = RT/p_2 \qquad (12)$$

so that

$$\Gamma_2^{(1)} = \frac{q}{M\Sigma} - \frac{\tau p_2}{RT} \qquad (13)$$

Substituting equation (13) into (9)

$$\gamma_{s\cdot} - \gamma_{svo} = \frac{RT}{M\Sigma}\left[\int_0^{p^0} \frac{q}{p_2}\,dp_2\right] - \left[\int_0^{p_2^0} \tau\,dp_2\right] \qquad (14)$$

A simple numerical computation shows that the term $\int_0^{p^0} \tau\,dp_2$ makes no significant contribution; therefore

$$\gamma_{so} - \gamma_{svo} = \frac{RT}{M\Sigma}\int_0^{p_2^0} \frac{q}{p_2}\,dp_2 \qquad (15)$$

If the adsorption isotherm for a vapor on a crystalline non-porous powder is obtained, and if the total area per gram of powder, Σ, is determined, it is possible to calculate the change in the free energy of a clean solid surface upon immersion in a saturated vapor. The surface areas em-

ployed in this calculation were determined by the method of Brunauer, Emmett and Teller.[11]

Table I summarizes the results of the graphical integrations carried out on the data obtained in this work, as well as on selected data from the literature.

TABLE I

FREE SURFACE ENERGY CHANGES UPON IMMERSION IN SATURATED VAPOR $(\gamma_{s_0} - \gamma_{sv_0})$ AT 25.0°

(ergs cm.$^{-2}$)

Values calculated from the data of (a) Gans, Brooks and Boyd, *op. cit.*; (b) Palmer and Clark, *Proc. Roy. Soc.* (London). **A149**, 360 (1935); and Palmer, *ibid.*, **A160**, 254 (1937).

Vapor	TiO$_2$-I	TiO$_2$-VI	SiO$_2$	BaSO$_4$	Graphite	SnO$_2$
Water	214^a	228	244	246	59	220*
n-Propyl alcohol	85^a	90	110	77	73	80^a
Acetone	...	...	85^b	...	...	...
Benzene	53^a	...	52^b	...	...	...
n-Heptane	...	38	39	38	56	...

The Change of the Free Energy of a Solid Surface upon Immersion in Bulk Liquid.[12]— In order to determine the magnitude of the free energy of immersion of a clean solid surface, $\gamma_{so} - \gamma_{sl}$, in a large amount of bulk liquid, it is necessary to find some relation of this quantity to the magnitude in Table I.

If a drop of liquid is placed upon a freshly cleaved crystal surface, in the absence of any other components, a number of possibilities arise: (1) the droplet will extend over the solid surface until it appears to cover the surface with an extremely thin film of uniform thickness; (2) the droplet flattens under gravity to an equilibrium shape in which an angle of contact is formed between the liquid and the crystal surface now covered with a film which may be monomolecular or of somewhat greater thickness as is shown in Fig. 6.[13]

According to Gibbs[2] the condition for the formation of an equilibrium contact angle is

$$\zeta_{sB} - \zeta_{sA} = \gamma_{AB} \cos \theta_E \qquad (16)$$

where ζ_{AB} and ζ_{sA} are quantities related to the film pressures π_{sB} and π_{sA} and θ_E is the equilibrium contact angle[14]

Since

$$\pi_{sB} = \gamma_{so} - \gamma_{sB} = -\zeta_{sB}$$

and

$$\pi_{sA} = \gamma_{so} - \gamma_{sA} = -\zeta_{sA}$$

equation (16) may be written

$$\pi_{sA} - \pi_{sB} = \gamma_{AB} \cos \theta_E$$

or

$$\gamma_{sB} - \gamma_{sA} = \gamma_{AB} \cos \theta_E$$

If fluid phase B is the saturated vapor and phase A the pure liquid with which the vapor is in equilibrium, then

$$\gamma_{sv_0} - \gamma_{sl} = \gamma_{lv_0} \cos \theta_E \qquad (17)$$

where γ_{sv_0} is the free surface energy for the interface between solid and saturated vapor, γ_{sl} for the solid-bulk liquid interface, and γ_{lv_0} for the bulk liquid and its own saturated vapor.

Equation (17) may be written as

$$(\gamma_{so} - \gamma_{sl}) - (\gamma_{so} - \gamma_{sv_0}) = \gamma_{lv_0} \cos \theta_E \qquad (18)$$

from which the free energy of immersion in bulk liquid may be computed if the quantities $(\gamma_{so} - \gamma_{sv_0})$, γ_{lv_0}, and θ_E are known.
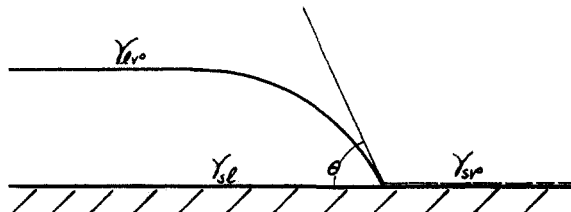

Fig. 6.—Equilibrium contact angle diagram: γ_{lv_0}, surface tension of pure liquid in equilibrium with its saturated vapor; γ_{sl}, interfacial tension between solid and liquid; γ_{sv}, surface free energy (or tension) of film covered solid in equilibrium with the saturated vapor of the pure bulk liquid.

In the special case in which $\theta_E = 0$, equation (18) assumes the form

$$(\gamma_{so} - \gamma_{sl}) - (\gamma_{so} - \gamma_{sv_0}) = \gamma_{lv_0} \qquad (19)$$

An examination of the relatively limited amount of reliable contact angle data[15–20] indicates that (a) clean polar solid surfaces are completely wet

(11) Brunauer, Emmett and Teller. THIS JOURNAL. **60**, 309 (1938).

(12) The material in the following section was given on September 24, 1941, in a paper read by G. E. B. at the Symposium on Surface Chemistry in celebration of the Fiftieth Anniversary of the University of Chicago under the title: Some Aspects of the Properties of Solid Surfaces. Subsequently, Professor W. D. Harkins has incorporated a portion of the data presented (Table II) and some of the conclusions in a recent publication. W. D. Harkins and H. K. Livingston. *J. Chem. Phys.*, **10**, 341 (1942).

(13) In his pioneering researches on this subject W. B. Hardy [*Phil. Mag.*, **38**, 49 (1919); Institut International de Chimie Solvay, Brussels (1925)] has described the diverse phenomena involved in the spreading and lens formation by liquids on clean solid surfaces. It is of interest that he remarks that mechanism (1) never occurs for a pure liquid and that the process whereby a film is built in (2) involves a transfer of molecules of liquid through the vapor phase from the lens to the solid (*i. e.*, "vapor spreading").

(14) This is the equilibrium value theoretically assumed by the angle between the solid and liquid surfaces when movement of the liquid over the solid surface is such as to alter this angle; *cf.* C. G. Sumner, "Wetting and Detergency," Chemical Publishing Co., New York, N. Y., 1937, p. 15.

(15) "International Critical Tables," **4**, 434 (1928).

(16) Richards and Carver, THIS JOURNAL, **43**, 827 (1921).

(17) Hunten and Maass, *ibid.*, **51**, 156 (1929).

(18) Carver and Hovorka, *ibid.*, **47**, 1325 (1925).

(19) Bartell, Culbertson and Miller, *J. Phys. Chem.*, **40**, 881 (1936).

(20) Bartell and Zuidema, THIS JOURNAL, **58**, 1449 (1936).

(*i. e.*, $\theta_E = 0$) by water and by polar and non-polar organic liquids,[21] (b) that non-polar liquids wet non-polar solids; but that generally, (c) polar liquids show finite angles with non-polar solids.[22]

The values of the free energy change upon immersion in bulk liquid, $\gamma_{so} - \gamma_{sl}$, calculated using (19) for the polar solids given in Table I are given in Table II. A comparison with the values for a non-polar solid, graphite, is included. In this case the free energy change was calculated from (18) using the measured contact angle of 85.7° with water taken from the work of Fowkes.[23]

The Work of Adhesion of a Liquid to a Solid. The Spreading of a Liquid over a Crystal Surface.—The work of adhesion[24] of a pure liquid to a clean solid surface is given by equation (20)

$$W_a = \gamma_{so} + \gamma_{lv0} - \gamma_{sl} \qquad (20)$$

and this quantity may be calculated from the previous value of the free energy of immersion in bulk liquid. These values are shown in Table II.

An important consequence of a knowledge of the free energy of immersion in bulk liquid, $\gamma_{so} - \gamma_{sl}$, is that a measure of the tendency of a bulk liquid to spread over an initially clean crystalline surface can be obtained. Although the spreading of liquids on clean crystalline surfaces bears an analogy to the spreading of immiscible liquids on water or mercury, a special consideration of the coefficients of spreading must be given in the light of the fundamental differences in mechanism in the two cases.[25]

For the spreading of a liquid as a *duplex* film over a solid surface, the initial spreading coefficient, $S_{lv0/so}$, may be defined by equation (21)

$$S_{lv0/so} = \gamma_{so} - \gamma_{sl} - \gamma_{lv0} \qquad (21)$$

and the final spreading coefficient, $S_{lv0/sv0}$, by equation (22)

$$S_{lv0/sv0} = \gamma_{sv0} - \gamma_{sl} - \gamma_{lv0} \qquad (22)$$

Combination of equations (22) and (17) yields

$$S_{lv0/sv0} = \gamma_{lv0} (\cos \theta_E - 1) \qquad (23)$$

which is a useful form for the purpose of calculation of the latter coefficient.

(21) However, mercury. a non-polar liquid. shows a large contact angle on glass. a polar solid. Published values of θ_E range from 128 to 148°. since effects of roughness and contamination of the solid or liquid surface all combine to cause angles greater than 90° to be too large: the value of 128° mgy be the more reliable.

(22) This generalization is again not without exception as has been shown by the work of Bartell and Zuidema (ref. 20) where zero angles for butyl acetate and amyl alcohol on talc are reported.

(23) F. M. Fowkes. Ph.D. Dissertation. University of Chicago. 1938.

(24) Dupré. "Théorie Mécanique de la Chaleur." 1869. p. 369.

(25) N. K. Adam. "The Physics and Chemistry of Surfaces." Oxford Press. New York. N. Y.. 1941. p. 215.

TABLE II

ENERGY RELATIONS WITH SOLIDS SHOWING ZERO CONTACT ANGLES AT 25°

(Values expressed in ergs cm.$^{-2}$)

Solid–Liquid[a]	$\gamma_{so} - \gamma_{sl}$	W_a	$S_{lv0/so}$	$S_{lv0/sv0}$
TiO_2–H_2O	300	370	228	0
TiO_2–C_3H_7OH	114	138	90	0
TiO_2–C_6H_6	85	114	56	0
TiO_2–C_7H_{16}	58	78	38	0
SiO_2–H_2O	316	388	244	0
SiO_2–C_3H_7OH	134	158	110	0
SiO_2–$(CH_3)_2CO$	109	133	85	0
SiO_2–C_6H_6	81	110	52	0
SiO_2–C_7H_{16}	59	79	38	0
$BaSO_4$–H_2O	318	390	246	0
$BaSO_4$–C_3H_7OH	101	125	77	0
$BaSO_4$–C_7H_{16}	58	78	38	0
SnO_2–H_2O	292	364	220	0
SnO_2–C_3H_7OH	104	128	80	0
Graphite–H_2O	64	136	− 8	−67
Graphite–C_3H_7OH	95	118	73	0
Graphite–C_7H_{16}	76	96	56	0
Hg–H_2O	101	174	32	0[b]
Hg–C_3H_7OH	108	132	85	0[b]
Hg–$(CH_3)_2CO$	86	110	62	0[b]
Hg–C_6H_6	119	148	90	0[b]
Hg–C_6H_{18}	101	123	79	0[b]

[a] Surface tensions of pure liquids and mercury were taken from "International Critical Tables." **4**, 436 (1928).
[b] *Cf.* Bartell. Case and Brown, THIS JOURNAL, **55**, 2769 (1933).

However, equations (21) and (22) refer to the tendency of the film of liquid to spread over the solid surface without change of the angle between solid and liquid at the line of contact, whereas θ_E of equation (23) refers to equilibrium conditions. Now this restriction may be satisfied if in spreading the movement of the liquid over the crystal surface is made to take place infinitely slowly, for then the contact angle would theoretically achieve its equilibrium value. Under these circumstances evaporation from the liquid and condensation on the crystal (*i. e.*, Hardy's secondary spreading) may be the actual physical process whereby the solid is covered. The final result at equilibrium in either case will be that the crystal face is covered with an exceedingly thin film, which is duplex if $\theta_E = 0$ and non-duplex for $\theta_E > 0$.

Equation (23) shows us that if $\theta_E = 0$, the final spreading coefficient vanishes or, that the free surface energy of the solid in equilibrium with a saturated vapor, γ_{sv0}, is equal to the sum for the surface tension of the bulk liquid against its own vapor, γ_{lv}, and the interfacial tension between

solid and liquid, γ_{sl}. This equality can be taken as the definition of a duplex film on a solid surface. Values for the initial and final spreading coefficients are included in Table II. Also it is instructive to note that combination of equations (19) and (21) gives

$$S_{lv^0/sv^0} = \gamma_{so} - \gamma_{sv^0} \qquad (24)$$

or, if a liquid forms a zero contact angle with a solid, the initial spreading coefficient of that liquid on the solid surface has the same value as the free energy change upon immersion in the saturated vapor of that liquid.

Energy Changes for Solids Showing Finite Contact Angles.—Inspection of equation (23) shows that S_{lv^0/sv^0} cannot be positive for finite values of θ_E. In such cases the final spreading coefficient is more appropriately a "recession coefficient," and measures the tendency of a *duplex* film, produced by some means over the surface, to contract. However, this does not mean that the withdrawal of the duplex film will denude the solid of molecules of the liquid substance. In fact, some evidence can be obtained that a non-polar crystalline surface is actually partially covered with a monolayer when a drop of liquid showing a finite contact angle rests upon another part of the surface.

The work of adhesion defined by equation (20) gives the amount of energy necessary to destroy one sq. cm. of liquid–solid interface and to form a unit area of liquid and of clean solid surface. However, since it is physically impossible to separate a solid and a liquid without leaving the solid covered with at least a monolayer in equilibrium with the vapor of the bulk liquid, it is convenient to define the work for such a process, W'_a, shown in equation (25)

$$W'_a = \gamma_{sv_s} + \gamma_{lv^0} - \gamma_{sl} \qquad (25)$$

Substitution of (25) into (17) gives the work of separation, W'_a, as

$$W_a = \gamma_{lv^0} (1 + \cos \theta_E) \qquad (26)$$

It is evident also that

$$W_a - W'_a = \gamma_{so} - \gamma_{sv^0} = S_{lv^0/so} \qquad (27)$$

Table III gives a summary of values for a number of liquids on a few hydrophobic solids compared with a value of mercury on glass.

TABLE III
ENERGY RELATIONS WITH SOLIDS SHOWING FINITE CONTACT ANGLES

Liquid–Solid	θ_E	S_{lv^0/sv^0}	W'_a	W_a	$W_c = 2\gamma_{lv^0}$
Mercury–glass[a]	90	476	476	...	952
Water–paraffin	109.0	– 97	17	48	144
Water–stibnite[c]	84.0	– 65	79	...	144
Water–graphite[c]	86.0	– 67	77	136	144
Water–talc[b]	88.0	– 69	75	...	144
CH_2I_2–talc[b]	53.0	– 20	80	...	100
CH_2Br_2–talc[b]	17.0	16	83	...	98
α Br. naphthalene talc.[b]	34.0	– 7.5	80	...	88
Benzyl alcohol–talc[b]	32.0	– 6.0	73	...	79
$C_2H_4Br_2$–talc[b]	26.0	– 3.8	72	...	76
C_6H_5Br–talc[b]	12.0	– 0.8	71	...	72
Water–TiO$_2$	0.0	0.0	144	370	144

[a] Bate. *Phil. Mag.*, **28**, 252 (1939).   [b] Bartell and Zuidema. ref. 20.   [c] Fowkes. ref. 23.

A deduction consistent with the data of Table III is that in separating bulk water from a non-polar solid, since the amount of work, W'_a, is considerably less than the work of cohesion, W_c, of water, the film left on the solid does not possess the properties of a liquid. It is possible that this film is even somewhat less than a complete monolayer.

Summary

1. The determination of the fundamentally important free energy change upon immersion in a saturated vapor for the non-porous crystalline solids, TiO$_2$ (anatase), SiO$_2$ (quartz), BaSO$_4$, SnO$_2$ and graphite has been made. This was accomplished through the graphical integration of vapor adsorption data utilizing the Gibbs adsorption relation.

2. The free surface energy change upon immersion in bulk liquid was obtained for these solid surfaces from the data of (1) combined with the correct equilibrium contact angle equation.

3. The data of (2) were employed to obtain the work of adhesion of a liquid to a solid surface, and to determine values of the changes in free energy associated with the spreading of a liquid as a duplex film over a crystal face.

4. An examination of the free energy changes for solids and liquids where the equilibrium contact angle is greater than zero indicates that, although a duplex film cannot exist, a monolayer may cover the solid surface.