When samples that had been stored for a long time over phosphorus pentoxide were sublimed, however, appreciable amounts of a white, vesicular, relatively non-volatile residue were obtained. This may be identical with the residual traces noted by Curtius and Rissom.[5c] It was at first surmised that this residue might be the long-sought isomer predicted by Mendeléeff.[7] Analysis by the Pregl method, however, proved that the substance was not a hydronitrogen, but rather, in all probability, an ammonium salt of hypophosphorous acid. It is interesting to note, further, that storage of ammonium trinitride over phosphorus pentoxide, calcium chloride or any other desiccant capable of absorbing ammonia but not hydrogen trinitride, soon results in the accumulation of considerable amounts of the latter substance in the vapor phase. The reverse is true for alkaline desiccants that selectively absorb hydrogen trinitride.

Summary

The solubility of ammonium trinitride (1) in water, methanol, ethanol, benzene and ether has been determined quantitatively and (2) in numerous organic liquids has been studied qualitatively. The specific gravity of solid ammonium trinitride and of various saturated solutions has been determined. The vapor tension of the solid has been measured over a temperature range of 15 to 134°.

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Solid-Liquid-Air Contact Angles and their Dependence upon the Surface Condition of the Solid

BY F. E. BARTELL AND ALLAN D. WOOLEY

Introduction

Several investigators[1] have observed that the angle formed when a contact angle forming liquid has advanced to rest over a dry solid surface is larger than the angle formed when the liquid has receded to rest from a wetted surface. Sulman[1d] called this phenomenon "hysteresis of contact angle," which term was used to imply that advancing and receding contact angles are unstable forms of a definite equilibrium contact angle. Later workers,[1e,2] holding similar views, have attempted to evaluate equilibrium contact angles by relating them mathematically to the advancing and receding contact angles. Thus Ablett, believing that the so-called

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[1] (a) Edser, Fourth Report of Colloid Chem., 284 (1922); (b) Rayleigh, *Phil. Mag.*, **30**, 397 (1890); (c) Pockels, *Physik. Z.*, **15**, 39 (1914); (d) Sulman, *Trans. Inst. Min. & Met.*, Nov. (1920); (e) Adam and Jessop, *J. Chem. Soc.*, **127**, 1865 (1925).

[2] Ablett, *Phil. Mag.*, **46**, 244 (1923); Nietz, *J. Phys. Chem.*, **32**, 255 (1928).

hysteresis of contact angle is due to adsorption of the liquid by the solid, concluded that the "stationary angle" is the arithmetical mean of the dynamic advancing and receding contact angles. Adam and Jessop consider that the difference between advancing and receding contact angles lies in a "simple friction" effect between the liquid and the solid, and assume that the cosine of the equilibrium angle is equal to the mean of the cosines of the advancing and receding angles. Others have expressed the view that with proper precautions "equilibrium" contact angles can be obtained directly and measured as such.[3] Proof of the existence of a single and definite equilibrium contact angle, however, has not been given, nor has any definite relationship between the theoretical equilibrium contact angle and the observed static advancing and receding angles been established.

The purpose of the present investigation was to study the characteristics of static advancing and receding contact angles and to determine if possible their relation to the "equilibrium" contact angle. The results obtained indicate that both the advancing contact angle and the receding contact angle may exist as stable and characteristic angles for the precise system in question.

Experimental

The general capillary formulation used for calculation of surface tension values in cases in which the liquids form a contact angle with the walls of the capillary is $S = rhdg/2 \cos \Theta$, in which S represents the surface tension of the liquid, r the radius of the capillary, h the height of liquid ascension, d the density of the liquid, g the gravitational constant, and Θ the contact angle. Thus, by measurement of the capillary rise of a liquid forming a contact angle in a capillary of known radius, the contact angle can be calculated if the true surface tension of the liquid can be obtained by some method which gives true values independent of the contact angle. The only method independent of contact angle which seemed sufficiently accurate for this purpose was the drop weight method as developed and standardized by Harkins and co-workers. Accordingly, that method was adopted for this investigation. The liquids selected were α-bromonaphthalene and acetylene tetrabromide. The solids selected were "Pyrex" and silica.

Apparatus

The Capillary Height Method.—The details of apparatus and operation necessary to obtain results of high accuracy with the capillary height method are fully discussed by Richards and Coombs,[4] Richards and

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[3] Langmuir, *Trans. Faraday Soc.*, **15**, 62 (1920); Bartell and Merrill, *J. Phys. Chem.*, **36**, 1178 (1932).

[4] Richards and Coombs, THIS JOURNAL, **37**, 1656 (1915).

Carver[5] and Harkins and Brown.[6] The apparatus used by us is illustrated in Fig. 1.

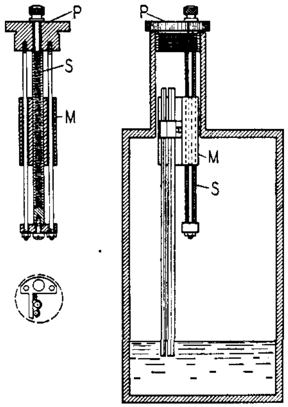

Fig. 1.—Capillary height apparatus.

The apparatus used for the determination of the drop weight was modeled, in its essential details, after that described by Harkins and Brown.[6] It was used in an air thermostat which made some minor alterations advisable (see Fig. 2).

The air thermostat was used with both methods. During the time of a series of observations the temperature of the liquid under measurement never varied more than 0.03°.

Density Determinations.—The density data appearing in the literature for α-bromonaphthalene and acetylene tetrabromide show such discrepancies[7] that densities of these liquids were determined. Values were determined over small temperature ranges so that the density at the working temperature could be obtained by linear interpolation. A new pycnometer was devised which greatly reduced the labor necessary in determining a series of densities over a given temperature range.

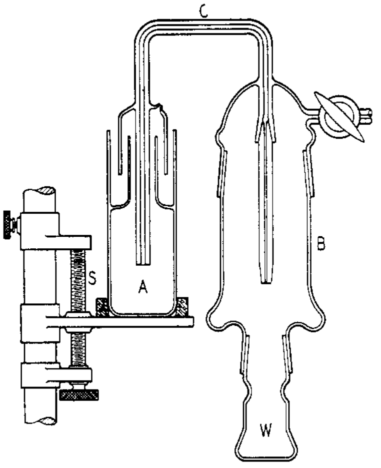

Fig. 2.—Drop-weight apparatus.

The details of the pycnometer are shown in Fig. 3. The new feature of the pycnometer is that it can be tightly closed so as to eliminate evaporation losses. This is effected by the use of copper-to-glass seals upon the inlet and outlet tubes which makes it possible to use screw-caps fitted with lead gaskets. The pycnometer is used as a constant-weight volume-determining apparatus

Procedure and Measurements.—It was our belief that in former investigations the pretreatment of the solid surface upon which contact angle measurements were made had not been sufficiently investigated, and that the cause of apparent anomalies and of the so-called "hysteresis contact angle" might lie therein.

The preliminary work indicated that although the magnitude of the advancing contact angle was dependent upon the precise pretreatment of the solid surface upon which it was measured, the magnitude of the receding contact angle was largely independent of the pretreatment of the solid surface. This suggested that it might be possible by proper pretreatment to obtain a solid surface

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(5) Richards and Carver, This Journal, **43**, 827 (1921).

(6) Harkins and Brown, *ibid.*, **41**, 499 (1919).

(7) Patterson and Thompson, *J. Chem. Soc.*, **93**, 366 (1908); Walden and Swinne, *Z. physik. Chem.*, **82**, 271 (1913); Harkins, Clark and Roberts, This Journal, **42**, 700 (1920); Harkins and Feldman, *ibid.*, **44**, 2665 (1922).

TABLE I

DENSITY AND SURFACE TENSION DATA FOR α-BROMONAPHTHALENE AND ACETYLENE TETRABROMIDE

α-Bromonaphthalene			Acetylene tetrabromide		
Temp., °C.	Density, d_4^t	Surface tension, dynes/cm.	Temp., °C.	Density, d_4^t	Surface tension, dynes/cm.
17.4	1.4854	44.88	20.0	2.9638	49.44
20.1	1.4826	44.53	23.0	2.9571	
25.23	1.4774	43.89	25.4	2.9518	48.65
25.24	1.4773		27.3	2.9479	
26.3	1.4763				
30.02	1.4726	43.28			

upon which the advancing contact angle would be equal to the receding contact angle. Such surfaces were finally produced.

The capillaries used were first given a rigorous acid cleaning with concentrated nitric acid, were then washed with a large quantity of distilled water (steamed with water for at least three hours), dried and calibrated, again treated with nitric acid and washed. After this second acid cleaning, acid was never used again in recleaning the capillaries. After use the capillaries were cleaned each time by drawing liquids through them. The order of treatment was first, ether or benzene, then benzene and then acetone. Usually about 100 cc. of each liquid was used, after which a quantity of distilled water was drawn through.

After being cleaned as described above, the capillaries were given one of the following pretreatments: (1) steamed with water for one hour. Heated in a current of clean, dry air at a certain temperature (shown in the data) for a given time. (2) Flushed with benzene vapor for one hour. Heat treated at a known temperature for a given time in a current of clean, dry air.

After the capillaries had been heat treated at an elevated temperature (425°),[8] the furnace was slowly cooled over a period of one hour (to 300°), after which it was disconnected and allowed to cool fairly rapidly. As soon as the capillary had reached the temperature of the thermostat (one-half to one hour) it was lowered into the liquid very slowly to avoid wetting above the meniscus. The height of the large meniscus was taken and subsequently the height of the lowest point of the small meniscus. The capillary was then lowered further into the liquid and the meniscus caused to advance up the dry capillary. Again, after equilibrium had been reached, the capillary height was measured. Usually six such advancing heights, and then a series of six receding heights, were measured. Each series of six measurements was averaged to give a single advancing or receding capillary height. At least three series of measurements were run for both advancing and receding heights for each method of pretreatment. Corrections were made for meniscus effects when determining capillary height values.

Before confidence could be placed in the values of the contact angles calculated by comparison of the apparent surface tension

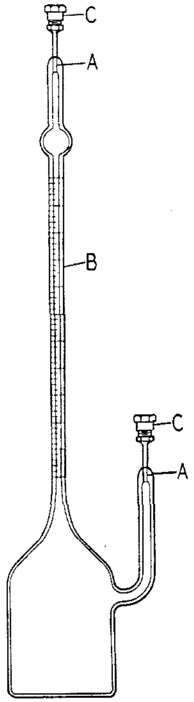

Fig. 3.—Pycnometer: A, copper-to-glass seals; B, tube graduated to 0.01 cc.; C, metal cap with lead jacket.

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[8] Careful investigation showed that the radii of both Pyrex and silica capillaries remained unchanged even after heating the capillary for one hour at 450°.

as measured by the capillary height method with the true surface tension as measured by the drop-weight method, it was necessary to prove that the two apparatuses gave the same surface tension value when a zero contact angle liquid was used. For this purpose benzene was selected.

The surface tension at 25.23° of very carefully purified benzene was determined by the capillary height method using both Pyrex and silica capillaries. The capillaries were carefully cleaned, flushed with benzene vapor for one hour and finally heated for one hour at 425°. Advancing and receding capillary heights were measured. The values obtained in the Pyrex capillary were as follows: the average of all the advancing heights gave 28.165 dynes/cm.; the average of receding heights gave 28.16 dynes/cm.; the average of advancing heights in the silica capillary gave the value 28.18 dynes/cm., and the average of receding heights gave 28.16. The mean of these values gives the surface tension of benzene at 25.23° as 28.166. The drop-weight method using a dropping tip having a radius of 0.29835 cm. gave 28.175 dynes/cm. as an average value of the surface tension of the same sample of benzene at 25.23°.

Discussion of Results

Influence of Pretreatment.—Tables II and III give, respectively, the advancing and receding contact angle values obtained for the systems α-bromonaphthalene–Pyrex (and silica)–air, and acetylene tetrabromide–Pyrex (and silica)–air by measurements in capillaries treated in the manner indicated in the tables as "Pretreatment." Inspection of the tables shows that for a particular vapor treatment such as steaming with water, the magnitude of the advancing contact angle depends upon the temperature and duration of heat treatment. Taking the results in Table II as typical, it is seen that the advancing contact angle of α-bromonaphthalene in a Pyrex capillary which had been steamed with water and heat treated at 115° for fifteen minutes is 24°. If during pretreatment the capillary is heated at 125° for one hour, an angle of 18° is obtained. Heating for twenty-four hours at 125° gives an angle of 16°. With longer heating of the capillary at 125° during pretreatment, the contact angle remains sensibly constant. If the capillary is pretreated by heating for one hour at 425°, the advancing angle becomes zero. The calculated cosine of the angle (0.99946) is equivalent to an angle of 1°53′, but since the error of measurement for an angle of zero degrees magnitude is equivalent to a 3° angle, the angle 1°53′ is sensibly zero. The advancing contact angle of α-bromonaphthalene on a Pyrex surface pretreated by steaming with water and subsequently by heat treating at 425° for one hour has been proved by us (using the Richards and Carver test) to be a zero contact angle. Pretreatment of the capillary at elevated temperatures tends to cause a decrease of the advancing contact angle. Heat treatment of a capillary at a given temperature lowers the advancing contact angle rapidly during the first hour, after which longer times of heating leave it sensibly constant.

The same generalizations apply if the capillary is vapor-flushed with benzene rather than with water. It should be noted, however, that a Pyrex capillary steamed with water and heated at 125° for one hour gives

TABLE II

ADVANCING AND RECEDING CONTACT ANGLES FOR THE SYSTEMS α-BROMONAPHTHALENE–PYREX–AIR AND α-BROMONAPHTHALENE–SILICA–AIR

t, 25.23° $S = 43.89$ dynes/cm. $(D^t_4 - d) = 1.4762$

Advancing Capillary Heights

Pretreatment			Pyrex		Silica	
Vapor treatment of capillary steamed for 1 hr.	Heat treatment temp., °C.	Time of heating	Av. corr. height, cm.	θ_a	Av. corr. height, cm.	θ_a
Water	115	15 min.	2.740	24°	1.809	24°
Water	125	1 hr.	2.86	18°	1.828	22° 30′
Water	125	24 hr.	2.903	16°		
Water	425	1 hr.	3.010	0°[b]	1.967	6°[a]
Benzene	125	1 hr.	2.910	15°	1.907	15° 30′
Benzene	125	24 hr.			1.915	14° 30′
Benzene	425	1 hr.	3.010	0°[b]	1.969	5° 30′[a]
		Receding Capillary Heights				
				θ_r		θ_r
Water	115	15 min.	2.977	8° 23′	1.956	8° 30′
Water	125	1 hr.	3.008	0°[b]	1.969	5°[a]
Water	125	24 hr.	3.009	0°[b]		
Water	425	1 hr.	3.011	0°[b]	1.969	5° 30′[a]
Benzene	125	1 hr.	3.010	0°[b]	1.960	7° 30′[a]
Benzene	125	24 hr.			1.971	5°[a]
Benzene	425	1 hr.	3.011	0°[b]	1.969	5°[a]

[a] Proved to be finite by Richards and Carver method.

[b] Proved to be zero by tests made with the Richards and Carver method.

an advancing contact angle of 18° with α-bromonaphthalene, while an angle of 15° is obtained if the capillary is flushed with benzene and heated under the same conditions. The data show similar results for the systems α-bromonaphthalene–silica–air, acetylene tetrabromide–Pyrex–air and acetylene tetrabromide–silica–air.

The receding contact angles for the same systems and for the same pretreatments are also given in the tables. Taking the data for the receding contact angles of α-bromonaphthalene–silica–air as typical (Table II), one observes that the receding contact angle is largely independent of the pretreatment. Even insufficient drying (25°) was shown to have comparatively small effect upon the magnitude of the receding contact angle.

The data show that for the system α-bromonaphthalene–Pyrex (and silica)–air the same or very nearly the same advancing and receding contact angles are obtained, if the capillaries are pretreated by steaming with water or flushing with benzene and heat treated at 425° for one hour. This contact angle must be characteristic of the system, for it fulfils the most rigid requirement for an equilibrium contact angle—namely, that the same angle be obtained when the liquid advances to, and recedes to, equilibrium. The advancing contact angle of a system can, then, become equal to the receding contact angle, which is independent (apparently) of pretreatment; the receding contact angle must, therefore, be the most characteristic contact angle of a system.

Table III shows that for the systems acetylene tetrabromide–Pyrex (or silica)–air, the advancing and receding contact angles are not quite equal when the capillaries are heated during pretreatment for one hour at 425°. Subsequent experiments, in which silica tubes were heated to 600° for one hour in their pretreatment, gave for advancing and receding contact angles for the system silica–acetylene tetrabromide–air values which were sensibly the same.

TABLE III

ADVANCING AND RECEDING CONTACT ANGLES FOR THE SYSTEMS ACETYLENE TETRABROMIDE–PYREX–AIR AND ACETYLENE TETRABROMIDE–SILICA–AIR

t, 25.04° S = 48.72 dynes/cm. $(D^t_4 - d) = 2.9513$

Advancing Capillary Heights

Pretreatment			Pyrex		Silica	
Vapor treatment of capillary steamed for for 1 hr.	Heat treatment temp., °C.	Time of heating	Av. corr. height, cm.	θ_a	Av. corr. height, cm.	θ_a
Water	25	15 min.	1.495	27°	1.063	15°
Water	140	3 hr.	1.546	21°	1.072	12°
Water	425	1 hr.	1.609	15°	1.0853	10°
Benzene	140	24 hr.	1.617	14°	1.046	18°
Benzene	425	1 hr.	1.622	13°	1.0651	14°
		Receding Capillary Heights				
				θ_r		θ_r
Water	25	15 min.	1.660	7°	1.079	11°
Water	140	3 hr.	1.647	10°	1.086	9°
Water	425	1 hr.	1.6496	9° 15′	1.0866	9° 30′
Benzene	140	24 hr.	1.649	9° 30′	1.086	9°
Benzene	425	1 hr.	1.6486	9° 30′	1.0862	8° 30′

The dependence of the advancing contact angle upon the treatment history of the solid surface suggests that in an advancing contact angle we have a very sensitive criterion of the surface condition of a solid.

During the course of the investigation the question arose—will a capillary which has been well wetted with a liquid and then drained by gravity, give an advancing height with that liquid equivalent to the receding height in the wetted capillary? This was tested for the systems α-bromonaphthalene–Pyrex–air and α-bromonaphthalene–silica–air as follows. The capillaries were cleaned in the usual manner, steamed for one hour with water, heated at 125° for one hour, cooled and then wetted with α-bromonaphthalene. The capillaries were then allowed to drain for twelve hours in an atmosphere saturated with α-bromonaphthalene. The advancing height of the liquid was then measured in the capillaries. It was found that advancing heights in capillaries treated in this manner were easily reproducible. The advancing contact angle for α-bromonaphthalene in a

Pyrex capillary treated as described was found to be 13°, and for α-bromonaphthalene in a silica capillary treated in an identical manner, 21°. Comparison with the corresponding receding contact angles, 0 and 5°, respectively, shows the advancing contact angles to be considerably larger in magnitude.

Theoretical Considerations.—The magnitude of the contact angle which a given liquid will form with a solid surface depends upon the relative values of the existing interfacial tension forces of the system. For any given set of interfacial energies there is a corresponding equilibrium configuration for the system; the contact angle formed may be either zero or finite. If any one of the free surface energies be changed, the contact angle (if finite) will change to a new characteristic value. This will be readily understood by considering Young's[9] equation[10] $S_1 - S_{12} = S_2 \cos \Theta$, for a drop at rest and in equilibrium upon a solid surface. It is seen that the magnitude of the contact angle is dependent upon the relation of the interfacial tensions at the solid–air (S_1), liquid–air (S_2) and solid–liquid (S_{12}) interfaces. If contamination of the system is prevented, the interfacial tensions of the solid–liquid and liquid–air interfaces remain constant. A difference in magnitude between an advancing contact angle and a receding contact angle for two different samples of the same uncontaminated system is indicative that the free surface energy of the solid (against air) is different in the two cases.

In explanation of the results obtained in this investigation the problem to be dealt with seems to be the cause of the free surface energy changes in the solid–air interface The particular pretreatment methods used in preparation of the solid surfaces were of such nature that two closely related processes undoubtedly contributed to the final state of the solid surface, namely, sorption and change in surface structure. By the term "sorption" is meant the collective result of the processes of adsorption and persorption. There is evidence that the processes of adsorption and persorption are accompanied by a change in structure of the sorbent solid.[11] Moreover, there can be little doubt that solids subjected to heat treatment at elevated temperatures undergo a change in surface structure.[12] The precise condition of a solid surface depends in fact upon every process to which it has been subjected during its preparation.

Penetration of gases or liquids to a finite distance into a solid surface (termed "persorption"[13]) must result in a change in the free surface energy

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(9) Young, *Phil. Mag.*, 165 (1805).

(10) The symbols S_1, S_{12} and S_2 represent, respectively, the surface and interfacial tension values of the solid–air, solid–liquid and liquid–air interfaces. Since free surface energy values are numerically equal to surface tension values, the relations of the equation are fulfilled equally well by free surface energy values.

(11) McBain, "The Sorption of Gases by Solids," Routledge, London, 1932; Bangham, *Phil. Mag.*, [7] **5**, 737 (1928).

(12) Beilby, "Aggregation and Flow of Solids," The Macmillan Company, New York, 1921.

(13) McBain and Britton, THIS JOURNAL, **52**, 2198 (1930).

of the solid–air interface by alteration of the forces of adhesion and by modification of the intermolecular cohesive forces existing between the molecules of the solid. The processes of sorption and of structural change are in most cases so intimately related that the individual effects cannot be isolated.

It has been shown,[14] by investigations on the adsorption of gases, that the surface of a solid in the amorphous form possesses a more intense field of surface force and a greater free surface energy than a crystalline form of the solid. Further, Beilby[12] has shown that the condition of a solid surface can be altered greatly by very simple treatments, such as heat treatment and subjection to solvents.

An advancing contact angle formed by a given liquid upon such an amorphous surface of a given solid would tend toward a minimum value for that solid–liquid system. A silica or Pyrex surface which has been subjected to sorption processes possesses a lower free surface energy, and as a result the advancing contact angle formed upon it by a given liquid would tend toward a maximum value.

The solid surface upon which a receding contact angle is formed is one which has had, in effect, an additional (and final) pretreatment process included in its preparation, namely, it has been wetted by the liquid under measurement. The independence of the receding contact angle from the initial pretreatment of the solid surface becomes more readily understood by consideration of this fact, for the final pretreatment process of a surface upon which a receding contact angle is formed is always the same. Wetting a solid surface by a liquid is apparently a very powerful pretreatment process, for it alters the effects of such other pretreatment processes as vapor flushing and low temperature heat treatment. Sorption and change in surface structure processes may occur when the solid surface is wetted by the liquid. The wetting liquid probably causes desorption of previously sorbed molecules. Likewise, the wetting liquid may cause a change in surface structure of the solid by exerting orientational and adhesional forces upon the surface molecules of the solid. The constancy of the receding contact angle of a given solid–liquid–air system suggests that a solid surface which has been wetted by a liquid is left in a definite condition with its characteristics determined by the wetting liquid used.

To account for the difference between advancing and receding angles in a single system one may conclude then that the advancing angle is dependent upon the precise condition (*i. e.*, the pretreatment) of the unwetted solid surface upon which the liquid is advancing, while the receding angle is largely independent of the pretreatment (*i. e.*, of the type described herein) of the solid surface. The liquid as it recedes leaves the solid surface in a definite and characteristic condition.

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(14) Langmuir, *Phys. Rev.*, **8**, 149 (1916); Kuster, "Lehrbuch d. allg. Physik," 1916, p. 189; Pawlow, *Z. physik. Chem.*, **88**, 316 (1920).

When the advancing and receding angles in a system are found to be the same, it must be that the pretreatment of the surface has been so adjusted (through changes in sorption and orientation) as to give to the solid surface approximately the same characteristic condition as that imparted to it by wetting by the liquid in question.

The apparent anomalies and the so-called hysteresis of contact angles have caused certain investigators to propose concepts which describe the contact angle as an unstable configuration of a solid-liquid-air system. To the authors it seems that a careful consideration of the free surface energy relationships of such a system (particularly of the changes which may occur in the existing value of the solid-air interfacial free surface energy) explains the phenomena which seem to present anomalies and "hysteresis effects." To us it seems that a contact angle formed by a system whether advancing or receding is in effect an equilibrium contact angle and is characteristic of the system precisely as it then exists.[15] The contact angle formed by a system is then an extremely sensitive criterion of the energy relations existing in the system. Any variation in its magnitude points to the occurrence of some process which has caused a change in one or more of the interfacial energy values.

Summary

Certain conclusions which seem justifiable can be drawn from the data obtained in this investigation.

1. The magnitude of the advancing contact angle is intimately related to the treatment history of the solid surface upon which it is measured. A standard method of treatment of a solid surface results in a characteristic reproducible advancing contact angle with a given liquid. Because of the reproducibility and apparent stability of such contact angles they are in effect equilibrium angles. Advancing contact angles are very sensitive criteria of the condition of a solid surface.
2. The magnitude of receding contact angles is largely independent of the treatment history of the solid surface upon which they are formed. Receding contact angles are equilibrium angles and are the most characteristic of contact angles for a given solid-liquid pair.
3. A characteristic equilibrium contact angle exists for the system α-bromonaphthalene-silica-air and acetylene tetrabromide-Pyrex (or silica)-air which can be approached from either direction, *i. e.*, advancing liquid or receding liquid. This is the most characteristic contact angle for a given solid-liquid pair and is equivalent to the receding contact angle.

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(15) The advancing contact angle may not represent a true equilibrium angle in the strict sense of that term, but does represent a relatively stable angle which will not change appreciably with time. Its tendency to change is dependent upon the tendency of the solid phase (or surface) to pass to a more stable form (or condition) which can exist at a lower energy level.