

THE SURFACE-CHEMICAL STUDY OF THE SOLID TO WATER.

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Introduction.

The problem of the glass and other solids to get wet or not is considered one special case of the adhesion between substances. This adhesion between substances is connected with hydrostatic force, surface energy, friction and some other problems.

In Fig. 1, let ① represent air and ③ represent liquid in equilibrium on a solid

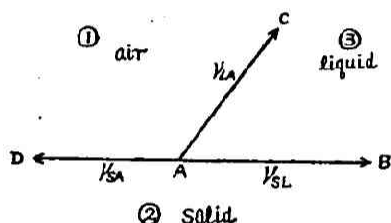


Fig. 1

②, AD the air-solid, AB the liquid-solid and AC the air-liquid interface, the line AC forming an angle θ with AB. This angle is called the angle of contact of the system. Then, since AC represents the equilibrium configuration of the system, we obtain

$$\nu_{SA} = \nu_{SL} + \nu_{LA} \cos \theta \quad (1)$$

where ν_{SA} represents the interfacial tension between the solid ② and the air ①, ν_{LA} the air-liquid interfacial tension, and ν_{SL} the interfacial tension between the liquid and the solid.

If W_{SL} denotes the work required to separate the liquid from the solid perpendicularly to the plane of contact, then

$$W_{SL} = \nu_{SL} + \nu_{LA} - \nu_{SA} \quad (2)$$

a relationship known as the equation of Dupré. From (1) and (2) we obtain the relationship proposed by Young;

$$W_{SL} = \nu_{LA} (1 + \cos \theta)$$

Then suppose fine drops of the liquid is put on the solid, and the system is

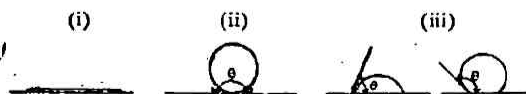


Fig. 2

	contact angle	example
(i) $\nu_{SA} - \nu_{SL} \gg \nu_{LA}$	$\theta = 0^\circ$	alcohol on the cleaned glass
(ii) $\nu_{SL} - \nu_{SA} \gg \nu_{LA}$	$\theta = 180^\circ$	mercury on the glass
(iii) $-\nu_{LA} < \nu_{SA} - \nu_{SL} < \nu_{LA}$	$180^\circ > \theta > 0^\circ$	

shown in Fig. 2. (in this case the gravity is neglected.)

Then in order to judge the problem to get wet or not and what degree to get wet between solid and liquid, it is enough to know the contact angle θ among three solid-liquid-gas systems. The investigation of the contact angle between solid-water system mentioned above is one important key to examine the wetness of the solid to water.

There are various methods to get the solid wet, for instance, with few large drops or many small drops. In this case, the problem to what degree the dew hinders the visibility according to the degree of the wetness of the solid when we see the substance through this solid, especially through glass is decided by the growth of the drops on the solid.

On the contract angle of the solids to the water.

§1 The method of the measurement.

There are many methods to measure the contact angle of the solid to the liquid,⁽¹⁻¹¹⁾ but we adopt the small drop method as a simple and fairly exact method in consequence of a few preliminary experiments, and we intend to take many data and to get fairly exact values statistically.

We make many drops on the solid using the spoit capillary to examine the contact angle to water, project the light to the drops and photograph that enlarged image. At the same time we insert the graduated plane in 1/10 m.m. for convenience to determine the drop size.

We photograph the drop immediately after placing it on the glass to prevent

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- 1) F. E. Bartell & A. D. Wooley, *J. Amer. Chem. Soc.*, **55**, 3518-27 (1933).
 - 2) G. L. Mack & D. A. Lee, *J. Phys. Chem.*, **40**, 169 (1936).
 - 3) Bashforth & Adam, *An Attempt to test the Theory of Capillary Action*, (1888).
Adam, *The Physics & Chemistry of Surfaces* 300-308 (1930).
G. L. Mack & Lee, *J. Phys. Chem.*, **40**, 169 (1936).
Hideo Akamatsu, Kagakuzikkengaku, physicochemical branch III, *The Chemistry of the thin film* 102-103 (1939).
 - 4) G. L. Mack, *J. Phys. Chem.*, **40**, 159 (1936).
 - 5) F. E. Bartell & Hatch, *J. Phys. Chem.*, **39**, 11 (1935).
 - 6) J. J. Bikerman, *Trans. Farad. Soc.*, **36**, 412 (1940).
 - 7) Kneen Eric & W. W. Benton, *J. Phys. Chem.*, **41**, 1195 (1937).
 - 8) A. K. Huntington, *Trans. Faraday Soc.*, **1**, 345 (1906).
N. K. Adam & G. Jessop, *J. Chem. Soc.*, **127**, 1863-8 (1925).
 - 9) A. H. Nietze, *J. Phys. Chem.*, **32**, 255-69 (1928).
Ablett, *Phil. Mag.*, **46**, 244 (1923).
 - 10) Lempei Goto, *This Journ.*, **7**, 138 (1934).
I. Langmuir *J. Am. Chem. Soc.*, **59**, 2400 (1937).
 - 11) Quincke, *Wied. Ann.*, **2**, 145 (1877), **52**, 1 (1894).
M. Pockel, *Phys. Z.*, **15**, 39 (1914).

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the change of its size according to the evaporation of water.

The height (h) and the base length ($2r$) of the drop on the photograph image are measured by means of a microscope.

Then the contact angle between water and solids is calculated by the following formula :

$$\tan \frac{\theta}{2} = \frac{h}{r}$$

§2 The method to make the sample.

We use some synthetic resin attaching half on the glass.

The glass is immersed in a solution of the completely dissolved synthetic resin in various solvents, and it is placed in a desiccator for two days and nights, then the synthetic resin on the glass is dried up. The glass takes up from the desiccator just before use.

§3 Results of the experiments and discussion.

An example of the results is shown in the following photograph.

Photograph of the Contact Angle.



"kuralugamu"—benzene 10%



vinylacetate—benzene 5%



vinylacetate—benzene 10%



ethylcellose—amylacetate 10%



benzylcellose—amylacetate 10%

The experimental results are tabulated in Table I.

Table I. Contact angle of the synthetic resin.

name of the synthetic resin	solvent	concentration	contact angle
"kuralugamu"	benzene	10%	68° 14'
vinylacetate	benzene	5 10	59° 0' 64° 48'
polystyrol	benzene	10	107° 28'
	xylene	10	78° 42'
	amylacetate	10	59° 52'
polyvinylalcohol	water	10	36° 44'
ethylcellose	amylacetate	10	72° 34'
benzylcellose	amylacetate	10	71° 34'

As seen in Table I, the contact angle of the polystyrol film is larger than 90° and that of the other films is on the whole 60° to 70°, and only that of the polyvinylalcohol is very small.

Difference of the contact angle in the case of the same synthetic resin dissolved in different

solvents may not be particularly large, though not decisive for lack of the experiments; the problem of such difference in the contact angle is not decided definitely, for the structure of the films used is not surely understood or the problem of the absorption to those films is not made clear.

Conclusion.

We have described first that the investigation of the contact angle in the solid-water system is one important key to examine the wetness of the solid to water.

We have adopted the small drop method as a simple and fairly exact method; for instance, the film of the thin synthetic resin is fixed on the glass and the contact angle of that film to water measured.

We have stated that the contact angle of the polystyrol film is larger than 90° and that of the polyvinylalcohol is very small.

We will state the problem of the wetness of the solids in other cases. But we will consider the relationship between the contact angle and the wetness of the solids.

It is interesting to mention that the size of the drop on the polystyrol-benzene is smaller than on the glass surface. The fact that the size of the drop is small, should be a matter of course, if we consider the contact angle of this film is greater than 90° .

On the other films the contact angle is smaller than 90° and the difference is very small. Then there may not be large difference in wetness.

Moreover, we should consider the problem that wetness is largely influenced by the water absorption of the film.

On wetness the water-polyvinylalcohol film shows the best result. One of the reasons of this result may be that this film easily absorbs water, then the dew attached on it diffuses into the film, not remaining on the film, and so not becoming large drop. (It means the degree of the size to hinder transparency.)

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