A Method for Measuring the Surface Energy of Solid.

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It is well-known that the solubility of solid in liquid depends on the particle size of the solid. From this fact, we can calculate the surface energy of the solid which was studied by Hulett[1], Dundon[2], and other investigators. Dundon's method of measuring the dependence of solu-

(1) Hulett, *Z. physik. Chem.*, **37** (1901), 385.
(2) Dundon, *J. Am. Chem. Soc.*, **45** (1923), 2479, 2658.

bility on the particle size consists of observing the difference of electrical conductivities of the solutions which are in equilibrium with large crystals and with finely pulverized crystals, and of calculating the solubility from electrical conductivity, with some assumptions. The present author has measured the solubility, using a float-pycnometer, which is devised by Gilfillan and Polanyi(3) and modified by Toraisi and Outi(4). By this float-pycnometer, we can measure the density of solution at constant temperature by controlling the pressure with an accuracy of *ca.* 10 γ.

The measurement was carried out on $CaSO_4 2H_2O$. Pure crystals were obtained from $CaCl_2$ and H_2SO_4. The size of crystals obtained in this way was larger than 50 μ. Some of these crystals were ground by hand in an agate mortar. It is pointed out by several authors that crystals of $CaSO_4 2H_2O$ lose water by being ground in dry room. In this experiment, the agate mortar was always moistened with water vapour. The microscopic examination of the powder showed that the particles were fairly uniform, and the average size was 0.4 μ. The experimental procedure is as follows:—A measuring vessel is dipped in a thermostat, the temperature fluctuation of which is less than $\pm 0.01°$. The temperature of the thermostat is maintained at 33.30° throughout the experiment. About 5 g. of the large crystals are poured into the measuring vessel, filled with 50 c.c. of redistilled water. After violent agitation, the float is dipped, and then the pressure at which it is in equilibrium is read. Then 1 g. of the finely pulverized powder is added, and after violent agitation, the float is again dipped and the pressure is read. The results are shown in Table 1.

Table 1.

Exp.	Equilibrium Pressure in mm Hg		
	With large Crystals	With small Crystals	After 24 hours
I	596	686	600
II	593	699	598

From the table we see that, the pressure increases after the small crystals are added, and then it decreases gradually, and returns to the original value after 24 hours.

To calculate the increase of solubility from these data, we must know the relation between the density and the concentration of the solution. A general formula for electrolyte is given by Debye as follows:

$$D = D_0 + kc + k'c^{3/2},$$

where D and D_0 are the densities of the solution and water, respectively, c is the concentration of the solution in gram percent, and k, k' are constants. For a solution so dilute as that which is studied in our experiment,

(3) Gilfillan and Polanyi, *Z. physik. Chem.*, A. **166** (1933), 254.
(4) Toraisi and Outi, *J. Chem. Soc. Japan*, **55** (1935), 1325.

the third term in this equation can be neglected. The constant k is determined by experiment as follows:

The density of 0.200% solution at 33.30°	0.99624
The density of water at 33.30°	0.99463
The value of k calculated	0.805

From the compressibility of the float, the normal solubility of $CaSO_4 2H_2O$ at 33.30°, and from the above mentioned data, we obtain the solutibility of finely pulverized $CaSO_4 2H_2O$.

Normal solubility at 33.30°	0.210%
Solubility of fine powders at 33.30°	0.235% (mean value)

To calculate the surface energy, we use the following equation:

$$RT/M \ln S_2/S_1 = 2\gamma/\sigma\,(1/r_2-1/r_1)\,,$$

where σ and γ are the density and the surface energy of the solid, and S_1, S_2 are the solubilities of the spherical particles having radii r_1 and r_2, respectively. Putting the above values, we obtain 3.9×10^2 dyne/cm for the surface energy of $CaSO_4 2H_2O$. Although the applicability of this equation in this case is somewhat doubtful, the above value shows a satisfactory agreement with those of the prevalent experiments. (The value of Hulett is 1048 dyne/cm and that of Dundon is 370 dyne/cm.) The characteristic of this method is that it can be applied for measuring the surface energy of non-electrolyte, which is impossible with the conductivity method. Thus we can also measure the surface energies of organic substances with this method.

Summary.

(1) To measure the surface energy of soilds, a float-pycnometer method has been applied.

(2) By this method, the surface energy of $CaSO_4 2H_2O$ has been measured, and found to be 3.9×10^2 dyne/cm.

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