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THE SOLUBILITY AND SURFACE ENERGY OF CALCIUM SULFATE

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It is well known in a qualitative way that the solubility of very fine particles is greater than that of coarse ones. This is exemplified in the ordinary custom of digesting precipitates in order to facilitate their filtration. The importance of having available some quantitative knowledge of just how solubility depends on size is very apparent. Such data are needed in elucidation of the surface-energy relations of solids such as are now involved in the study of the colloidal state. In spite of its importance, however, the only available experimental data in this field are those of Hulett[2] for calcium and barium sulfates, and for mercuric oxide, and even these are admittedly qualitative.

In the present paper and the one which follows,[2a] we have repeated some of Hulett's work and have extended his general experimental method to several other substances in an effort to obtain reliable values for their surface energy.

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[1] Grasselli Fellow, 1921–1922.

[2] Hulett, *Z. physik. Chem.*, **37**, 385 (1901); **47**, 357 (1904). It is true that Marian Jones and J. R. Partington [*J. Chem. Soc.*, **107**, 1019 (1915)] measured the increased solubility of small calcium sulfate particles. Sauer [*Z. physik. Chem.*, **47**, 160 (1904)] also mentions incidentally the increased solubility of finely pulverized calomel in connection with the use of a calomel electrode. But it is not reported in either of these papers that the size of the particles was measured. It should be noted also that F. C. Thompson [*Trans. Faraday Soc.*, **17**, 391 (1922)] by quenching an iron-carbon alloy at 780°, then tempering part of it at 500° and another part at 650°, obtained cementite grains of different sizes. He determined the concentration of the carbon dissolved in the iron in the two cases by measuring the electrical resistance, and calculated an interfacial tension of 1350 dynes/cm.

[2a] Dundon, THIS JOURNAL, **45**, 2658 (1923).

Theoretical Part

Surface energy, σ, has been calculated by Hulett and by Freundlich, by substitution in the Ostwald-Freundlich equation,[3]

$$\frac{RT}{M} ln \frac{S_2}{S_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad (1)$$

where R is the gas constant, T the absolute temperature, M the molecular weight of the solid in solution, ρ the density of the solid, σ the surface energy per unit surface between the solid and its solution, and S_2 and S_1 are the solubilities of the particles of radii r_2 and r_1, respectively. In the derivation of this equation it is assumed that the particles are spherical,[4] that the dissolved solid obeys the gas laws, and that σ and ρ are independent of the size of the particles. Equation 1 does not hold for dissociated substances. Jones[5] takes into account the dissociation of the dissolved substance by combining Equation 1 with the equation of Storch,[6] which is

$$\frac{(1 - \alpha)}{v} = K\left(\frac{\alpha}{v}\right)^m \qquad (2)$$

where α is the degree of dissociation, v is the dilution and K and m are constants. When m is 2, Storch's equation becomes the familiar Ostwald dilution equation. The equation which Jones derived, by a combination of Equations 1 and 2 and by integrating between the limits α_1 and α_2, is

$$\frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) = \frac{RT}{M}\left[(n - 1)(\alpha_1 - \alpha_2) - \frac{n}{m - 1} ln \frac{1 - \alpha_1}{1 - \alpha_2} + \frac{m}{m - 1} ln \frac{\alpha_1}{\alpha_2}\right] \qquad (3)$$

where n is the number of ions formed from the dissociation of one molecule. While this equation is theoretically sound, its practical application is complicated by the fact that concentrations are expressed only in terms of dissociation and the constant m in Storch's equation. Inasmuch as small differences in dissociation correspond to rather large changes of concentration, small errors in expressing dissociations are quite serious.

In these fundamental derivations the ordinary expression for osmotic work done is $\frac{RT}{M} ln \frac{p_2}{p_1}$ *for one mole* of dissolved solute. Then, if a substance is dissociated and we assume that this dissociation is constant during the process, Equation 1 becomes

$$(1 - \alpha + n\alpha)\frac{RT}{M} ln \frac{S_2}{S_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad (4)$$

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[3] First derived in its most general form by Willard Gibbs in 1876, "Scientific Papers," Longmans, Green and Co., **1906**, N. Y., vol. I, p. 315.

[4] William Jacob Jones [*Ann. Physik*, **41**, 441 (1913)] has considered the influence of various geometrical forms instead of the spherical particles assumed in the general equation.

[5] W. J. Jones, *Z. physik. Chem.*, **82**, 448 (1913).

[6] Storch, *ibid.*, **19**, 13 (1896).

Values obtained by this simple equation approximate closely to those calculated by means of the rigorous equation of Jones, the differences being very small in comparison with the errors inherent in the data.

There is another point in this connection which is important. In substituting numerical values for the radii in the expression $\frac{2\sigma}{\rho}\left(\frac{1}{r_2}-\frac{1}{r_1}\right)$, r_2 is the radius of the smaller and more soluble particles, and is, of course, measured by microscopic observation; r_1 represents the radius of a large particle, in equilibrium with its own saturated solution. In Hulett's work (and also in the present work) this saturated solution containing the large particles was simply a saturated solution of the substance in equilibrium with *large crystals*. Since the crystal surfaces were flat, $1/r_1$ is $1/\infty$. It is true that Hulett's results seemed to show that particles 2μ in diameter were also in equilibrium with the saturated solution of the crystals. But one cannot be absolutely certain of the equilibrium, and if it is a question of choosing between $1/\infty$ and $1/2\mu$ there can be no doubt that it is preferable to write $1/\infty$ into the equation. In this case, Equation 4 assumes the form

$$(1-\alpha+n\alpha)\frac{RT}{M}ln\frac{Sr}{S}=\frac{2\sigma}{\rho r} \tag{5}$$

and this is the equation which we have used throughout our work in calculating the surface energy.

In an interesting paper, Marian Jones and J. R. Partington[7] have attempted to test the validity of Equation 1 at 20°, 40° and 60°. Taking the known concentrations of saturated calcium sulfate solutions in equilibrium with gypsum crystals, they substitute these values for S_1 in Equation 1 and calculate S_2 for the respective temperatures and for various values of r_2, setting $r_1=\infty$, and making use of W. J. Jones' surface-energy value, 1050, calculated from Hulett's data. They have not measured the size of their particles, but have assumed a radius of 1μ, because their experimentally determined solubilities fit their calculated solubility curve for particles of this size. The surface-energy value, 1050, which takes into account the dissociation of the calcium sulfate, has unfortunately been substituted in Equation 1, which does not hold for dissociated substances. The result is that all of their calculated solubilities and radius values are much too high. This error is evident from the fact that their fine particles which give an increased concentration of 4.6% at 20° are considered to be of the same size as were found by Hulett to show no increased solubility, *although their own calculations are based on Hulett's data.*[8]

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[7] Jones and Partington, *J. Chem. Soc.*, **107**, 1019 (1915).

[8] It has seemed desirable to call attention to the difficulties with the conclusions reached by Jones and Partington, because the substance of their work has already been incorporated into two well-known chemical texts.

Experimental Part

The method we have employed in measuring the increased solubility of small particles of calcium sulfate is essentially the same as that of Hulett. Into a saturated solution of calcium sulfate in equilibrium at 25° with large crystals, a quantity of the finely powdered calcium sulfate was introduced. The increase in concentration, and the return to the original concentration were noted by conductivity measurements. In order to calculate the concentration of a solution of a dissociated substance from the conductivity by means of the formula, $\frac{\text{millimoles}}{\text{liter}} = \frac{k}{2\alpha\Lambda_\infty}$, it is necessary to know the degree of dissociation α. For strong electrolytes Storch's dilution law holds and can be applied to supersaturated solutions. That equation, however, contains two unknowns and cannot be solved for α, but corresponding values for concentration ($1/v$) and dissociation (α) may be determined by the method of trial and error. In this way values of $1/v$ and α corresponding to the conductivity of the solution in question are found. Λ_∞ at 25° was taken as 126. Concentrations of calcium sulfate can also be calculated from the conductivity value at 25° by the empirical formula[9] of Hulett, $\frac{\text{millimoles}}{\text{liter}} = -0.354 + 5211\ (k_{25}) + 841400\ (k_{25})^2$.

Calculations to millimoles per liter for two supersaturated solutions gave by the first method 15.59 and 48.84, and by Hulett's equation 15.54 and 49.35, respectively. In view of the evident agreement the simpler formula of Hulett was used in all subsequent calculations, for even though absolute values might be slightly different the percentage increase would be the same.

Preparation of the Salt.—Large crystals of calcium sulfate were prepared by allowing solutions of calcium chloride and of sulfuric acid to drop slowly into 3 liters of hot, well-stirred, distilled water. The precipitate was then thoroughly washed eight times, using 2 to 3 liters of distilled water each time. In this way a pure sample of crystals 20–50μ long was obtained. Analysis showed that its water content was 21.1%. A second analysis checked exactly with the first. The theoretical water content of the dihydrate, $CaSO_4.2H_2O$, is 20.93%.

The Kohlrausch type of conductivity cell with platinized electrodes that was used could be shaken violently by hand immediately upon addition of the powder.

Experiment 1.—Some of these large crystals were ground by hand in an agate mortar to a fairly uniform average size of 0.3μ. Part of this powder (0.4 g.) was added to about 40 cc. of the saturated solution in a conductivity cell and in one minute the conductivity rose from the original value of 2208×10^{-6} to 2616×10^{-6}. After two days it had returned

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[9] Hulett, *Z. physik. Chem.*, **42,** 581 (1903).

to 2276, and after six days to 2213 × 10^{-6}. The only large crystals, with which the final solution was presumably in equilibrium, were those large fragments introduced along with the fine powder. When calculated to concentration values, *the increase was about 24%.*

Analysis of a portion of the powder which had been ground in the agate mortar, showed that its water content was only 12%. Evidently, the grinding treatment had partially dehydrated it. This effect has been observed by Sullivan and Steiger,[10] who reduced the water in gypsum to about 5% by long grinding. Since it is well known[11] that dehydrated calcium sulfate is much more soluble than the dihydrate, it may be true that part, at least, of the observed increase in solubility noted in this experiment may have been due to the presence of the dehydrated material. Hulett, in fact, was careful to call attention to such a possibility. Practically the same result that has been noted in this experiment with precipitated calcium sulfate, has also been found with natural gypsum. With ground gypsum particles 0.3μ in diameter and a water content of 15%, *an increase in concentration of 28% was observed.*

Experiment 2.—The greater solubility of the dehydrated material may be shown in a very striking way. When calcium sulfate which has lost a few per cent. of its water content is added to a drop of water under the microscope, long needle-like crystals of the dihydrate form rapidly, thus showing a high degree of supersaturation. But the needles do not form if the added powder contains its full amount of water of crystallization, even though it be very finely divided.

Experiment 3.—To the same saturated solution in equilibrium with the large crystals used in Expt. 1, were added some of these same large crystals which had been *dehydrated by heating.* The crystals were not ground. The conductivity moved from the original value of 2208 × 10^{-6} to 2450 × 10^{-6} in one day, and in two days to 2520 × 10^{-6}. When filtered and seeded with the original hydrated crystals, the conductivity returned after four days to practically its original value. The question at once arose as to whether or not heating the crystals resulted in pulverization by decrepitation. Microscopic examination of the dry crystals failed to show the presence of fine particles, and the very slow rate of increase of the conductivity also indicated that small particles were not present.

This experiment shows that it is possible to *increase the concentration without powdering the calcium sulfate, if it is dehydrated.* It is interesting to note, incidentally, what happens to the dry crystals which have been dehydrated, when a drop of water is added to them on a microscopic slide.

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[10] This observation is given by W. F. Hillebrand, THIS JOURNAL, **30**, 1120 (1908). Compare John Johnston, *Rec. trav. chim.*, **42**, 850 (1923).

[11] Marignac, *Ann. chim. phys.*, (5) I, 274 (1874). Cavazzi, *Industria chimica*, **1906**, 366 (1906).

They are at once broken up into much smaller crystals, as though the water violently works its way with a disruptive force into porous places which have been produced in the crystals by the heat treatment.

Experiment 4.—It is evidently not at all an easy matter to grind calcium sulfate crystals without causing partial dehydration. An attempt was made to do this by grinding the precipitated crystals between two glass plates wetted with petroleum ether. The powder analyzed 21.1% water. Most of it was about 0.5μ in diameter, with very little smaller than that. *The increase in concentration obtained was 4.8%.*

The crystals can be ground between glass plates without the addition of petroleum ether and the powder will show by analysis its full water content, but it is difficult to obtain powder even as small as 0.5μ, because of the stickiness and the great resistance to rubbing.

Experiment 5.—In a further attempt to prevent dehydration on grinding, some clean natural gypsum crystals were ground in an agate mortar in a small room where the air was kept saturated by vapor from boiling water. The temperature was about 25°. Each lot of 0.1 g. powder was ground for 20 minutes. The powder so prepared showed a water content of 18.5%. It was then taken in small lots in the mortar, wet with conductivity water, ground until dry, and the resulting lumps were powdered. Analysis gave 21.0% water. Most of the particles were about 0.5μ in diameter, with a few 0.4μ. *An increase in concentration of 4% was found.*

Experiment 6.—It was observed, during examination of fine calcium sulfate particles under the microscope, that if water was used to wet the particles, a slight rubbing with the glass cover slip seemed to break them up into much smaller pieces. This suggested that the substance might be ground satisfactorily in the presence of water. Therefore, precipitated calcium sulfate crystals were wet with conductivity water and ground by hand in an agate mortar until dry. The resulting dry lumps were then ground until thoroughly powdered. The water content was 21.3%. The powder grains appeared very irregular in shape, and a large percentage of them were about 0.2μ, and some 0.3μ in diameter. *The increase in concentration, as shown by conductivity measurements, was 12.3%.*

Experiment 7.—Some of the ground powder used in Expt. 4, showing a water content of 21%, was heated at 100° for half an hour, until its water content had dropped to 15.5%. This powder when added to the saturated solution in the conductivity cell, *showed an increase of 257% in concentration.* There did not seem to be many smaller particles present after the heating than before, although, of course, there may have been a great deal of material too small to be visible in the microscope.

Discussion of Results

Examination of the results in Expts. 4, 5 and 6, shows that where precautions were taken to avoid dehydration, the increase in solubility due to the small size of the particles was not very great. In Expts. 4 and 5, where particles about 0.5μ in diameter were used, the average surface energy, calculated from Equation 5, taking i (that is, $1 - \alpha + n\alpha$) as 1.56, was 356 ergs per sq. cm. Calculation by Jones' Equation 3 gave 352 (a difference of about 1%), while an error of only 0.01μ in the diameter measurement would make a difference of 2% in the value for surface energy. In the microscopic estimation of the size of particles, the probable error is much greater than 0.01μ. It is more nearly 0.1μ. Thus it is clear that the simplified Equation 5 is amply sufficient for present needs. It is also clear that very little reliance should be placed on our present knowledge of the surface energy of solids.

In Expt. 6, where the particles were estimated at 0.2μ in diameter, the calculated value of the surface energy was 385. The average for the two sizes, 0.5 and 0.2μ, is then about 370.

The question now arises as to why the above result differs from that of Hulett, who found a much larger increase in solubility. The possibility of slight dehydration is suggested by the fact that he does not specifically mention any moisture determination on his fine powder. Moreover, gypsum crystals are transparent, and have a low refractive index, and when finely powdered are difficult to observe sharply in the microscope, so that it is very uncertain how many particles too small to be visible might be present in the powder. When the material was wet almost until the last stage of grinding, as in our own Expts. 5 and 6, the probability of the occurrence of invisible small particles would be greatly lessened.

We wish to express our gratitude to the Grasselli Chemical Company for the fellowship grant under which this investigation was carried on.

Summary

1. A brief discussion is given of errors which appear in the literature in the calculation of surface energy and size of particles of calcium sulfate based on Hulett's data.

2. On the basis of the simplifying assumption that the degree of dissociation does not change with small changes of concentration, the van't Hoff factor, i, is introduced into the Ostwald-Freundlich equation, to replace the complicated correction formula of W. J. Jones.

3. Experimental data have been produced which show the great tendency of gypsum and precipitated calcium sulfate, $CaSO_4.2H_2O$, to become dehydrated during grinding, and the importance of this factor in relation to experiments on the solubility of finely powdered calcium sulfate.

4. Working with particles 0.2μ and 0.5μ in diameter a value of about 370 ergs/sq. cm. has been calculated for the surface energy of the dihydrate of calcium sulfate.

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