[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

SURFACE ENERGY OF SEVERAL SALTS

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Introduction.—In a previous article[2] the method of calculating surface energy from the increased solubility of fine particles was considered, and a value for the surface energy of gypsum calculated from new data. In the present work an attempt has been made to measure the change in solubility due to change in size of particles for several other substances. The best opportunity for such an investigation occurs with substances of small solubility, in which case equilibrium comes about with such slowness that it can be followed by frequent conductivity measurements. Such solubility equilibria must, however, be easily obtained, and continued hydrolysis or other decomposition in solution must not occur. With many of the substances considered, such as lead sulfate, mercurous chloride and magnesium fluoride, some interfering factor of this sort soon developed, which made it impossible to obtain data of use in this study. Of those substances which gave positive results and which are mentioned in this paper, lead fluoride, because of its many favorable properties, was investigated most extensively.

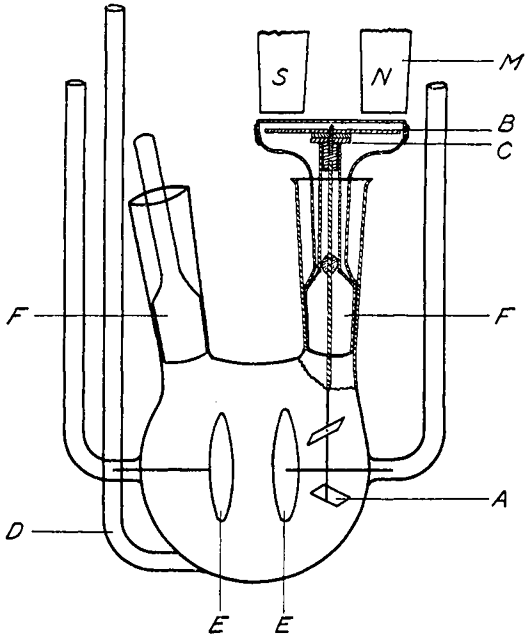

Fig. 1.—Conductivity cell

Experimental Method.—Fine powders have been obtained by hand-grinding in an agate mortar, with a mechanically operated mortar and pestle, or with a steel ball mill. Ordinarily, the powder was used directly, and the size of the smallest particles present in large numbers was the value recorded. Attempts were made to sort the particles into different sizes and to calculate the sizes by settling in water or alcohol, making use of Stokes' law. This method failed to yield satisfactory results because of the coalescence of the settling particles into clumps and also, no doubt, because of the adsorption effect at the surface of the small particles.[3] In the case of lead fluoride, how-

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[1] National Research Fellow, 1922–1923.

[2] Dundon and Mack, THIS JOURNAL, **45**, 2479 (1923).

[3] Williams, *Trans. Faraday Soc.*, **18**, 53 (1922).

ever, an air elutriation method was devised, of such a sort that the powder was carried upward through a long glass tower, and very uniformly sized particles, 0.3μ, were obtained, with no particles larger than 0.5μ. Consequently, a good deal of confidence may be placed in the results for lead fluoride.

Measurement of the size of particles was made with a calibrated scale in the eyepiece of a microscope having a magnification of 1800 diameters. Several conductivity cells were used, including the Kohlrausch type, some large flasks with suspended electrodes, and one cell especially designed for this work. This cell is shown in Fig. 1. The platinum paddle-wheel stirrer A can be operated by a magnet M outside the cell. The stirrer shaft of platinum was set into a brass plug at the top and had a drop of glass fused around it lower down to keep it in position. The steel bar B was fastened to the brass plug with a small screw which passed through the washers C. All metal parts other than the platinum were gold-plated. The glass cap above the bar is held in position by a rubber band. F is the ground-glass stopper.

The data for calculating concentrations from conductivity values, such as temperature coefficients, equivalent conductivities, etc., have been obtained in most cases from the work of Kohlrausch. A water correction has been applied to all conductivity values given.

Lead Fluoride

No crystallographic data concerning lead fluoride could be found in the literature and no crystals larger than a few microns were made. However, it was determined[4] that they belong to the orthorhombic system and have an average refractive index of 1.83 and a hardness of about 2.

Hydrolysis of the Solution.—Saturated lead fluoride solutions are distinctly acid, having a Sörensen value of about 1, and the acidity changes very little over a considerable range of dilution. Kohlrausch[5] found that in the variation of equivalent conductivity with dilution at 18° hydrolysis was not indicated, and his results on this point have been widely quoted. It was found in this investigation at 25° that, although a given solution remained constant, considerable hydrolysis took place on dilution, giving a value for the equivalent conductivity at infinite dilution which is much too high.

Calculation of Concentrations.—A carefully prepared saturated solution had a conductivity of 513×10^{-6} mhos, and gravimetric analysis showed the equivalent concentration to be 0.00555. Experimental data were then obtained from which a curve of equivalent conductivity against the cube root of the concentration was plotted. From this a second curve was plotted giving equivalent concentrations directly in terms of specific conductivity. Several gravimetric analyses of supersaturated solution prepared from fine powder checked this curve almost exactly.

Method of Obtaining Equilibrium.—A saturated solution was pipetted into the cell from a stock solution, powder added and the cell shaken

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[4] Thanks are due to Professor W. J. McCaughey of the Department of Mineralogy, Ohio State University, for assistance in making these determinations.

[5] Kohlrausch, *Z. physik. Chem.*, **64**, 134 (1908).

thoroughly, after which the maximum conductivity was reached in from two to ten minutes. The conductivity then gradually decreased for several days. Sometimes, in order to hasten the final equilibrium, the solution was carefully filtered and coarse crystals were added. In some cases also, a few drops of conductivity water were added to the supersaturated solution in order to hasten the final equilibrium. When too much water was added the conductivity again increased to approach the normal equilibrium. This change served as a means of determining whether a solution of conductivity higher than normal at the end of a test was still supersaturated, or whether the higher conductivity was due to impurities.

TABLE I

SOLUBILITY VALUES FOR LEAD FLUORIDE

At 25°. Size of particles 0.3μ except in No. 7 where it was about 0.2μ

	Conductivity × 10^6 [a]			High cond. corr. for return	High concn. $\times 10^3$	High concn. corr. for return[b] $\times 10^3$	Concn. from grav. analysis $\times 10^3$	% Increase		Wt. in g. added to 50 cc.
	Begin.	High	End					Uncorr.	Corr.	
1	513	547	523	536	6.02	5.88	..	8.5	6	0.06
2	513	555	524	544	6.14	5.99	..	10.6	8	0.05
3	513	549	515	548	6.07	6.03	..	9.4	8.7	0.1
4	513	547	...	...	6.03	..	5.99	8.7	..	...
5	513	545	...	...	6.00	..	6.00	8.1	..	...
6	(H_2O)	541	516	538	5.93	5.90	..	6.9	6.3	0.3
7	582	590[c]	538	565	..	6.28	..	..	13.1	0.025
8	543	557[c]	521	549	..	6.06	..	..	9.2	0.13
					(less than)			(less than)		
9	598	581[c]	543	550	6.32	6.07	..	13.8	9.4	0.3

[a] A water correction not greater than 2×10^{-6} was applied to the saturated solutions to bring them to the value determined gravimetrically as correct (0.00555 gram-equivalents per liter).

[b] When the supersaturated solution in contact with crystals failed to return to the conductivity value corresponding to a normal saturated solution, the presence of impurities was indicated. On this assumption, therefore, in columns marked "Corr. for return" a correction equal to the difference between the beginning and end solutions has been subtracted from the high value.

[c] Five minutes after adding powder.

In Table I are tabulated the most reliable data obtained on the increase in solubility of lead fluoride. In the first three experiments, the fine powder was added to the saturated solution and the solution kept until the conductivity had again decreased to a point where it was constant. In Expts. 4 and 5 the solution was filtered as soon as possible after the addition of the fine powder and the concentration also determined by gravimetric analysis. In No. 6 the powder was added directly to water and the solution observed until it had returned nearly to the saturated value. In Expt. 7 a supersaturated solution was prepared by heating a solution to boiling with an excess of crystals and filtering the liquid into the cell. Fine powder was then added and the conductivity found to increase slightly and then decrease to a value considerably below the starting point. This showed that the solution was not sufficiently concentrated to be in equilibrium with the finest particles present. The final conductivity when the solution became constant indicates considerable contamination, due either to increased hydrolysis at the higher temperature or to impurities acquired during the boiling and filtering. The increase calculated after applying corrections is high, but the powder was an unusually fine sample.

No. 8 is very similar to No. 7, except that the original solution was less concentrated and the maximum concentration reached was lower. In the case of No. 9, the original solution was more concentrated than a solution in equilibrium with the powder. This, therefore, sets an upper limit on the maximum increase in solubility for a powder of the size used. In a similar experiment not tabulated, an increased concentration of 20% was found to be much too high and a very rapid decrease occurred upon addition of the powder. It is interesting to note that the concentration reached five minutes after addition of the powder is approximately the same in No. 8 as in No. 9 although the point was approached from different directions.

Nine per cent. has been taken as the value representing the increased solubility of lead fluoride powder 0.3μ in diameter. Working with a saturated solution of lead fluoride in 95% alcohol, an effect of about the same magnitude was found.

Lead Iodide

Lead iodide gave a very small increased solubility effect. It is soft and flaky and is difficult to grind into a fine powder, even with the aid of fine quartz. The smallest particles were about 0.4μ in diameter. In two minutes an increase in concentration of about 2% was obtained.

Strontium Sulfate

Small particles added to solutions of strontium sulfate failed to disappear and allow the solution to return to the normal equilibrium. This may be due partially to a very slow rate of solution in this case, but similar difficulties occurred and are discussed in greater detail in connection with barium sulfate. While an initial increase as high as 25% was obtained for particles 0.3μ in diameter, there was never more than a 2% return from the maximum.

Silver Chromate

A precipitate composed of good orthorhombic crystals from 10 to 50μ in length was made by mixing very dilute hot solutions of silver nitrate and potassium chromate. The crystals were easily ground. The average size of the small particles was considered to be 0.3μ. The solutions were constant in cells with bare electrodes, but the conductivity of a saturated solution decreased when put into a cell with platinized electrodes. After adding 0.35 g. of powder to 500 cc. of solution and stirring the mixture with pure air, 24 hours was required to reach a maximum conductivity. The resulting solution when pipetted into another cell and stirred in contact with coarse crystals by means of a platinum paddle-wheel stirrer showed a decrease in conductivity for three days. After this time a slight but gradual increase set in, probably due to contamination of some kind. Two experiments at 26° agreed very closely, the fine powder causing an increase in equivalent concentration from 0.192×10^{-6} to 0.218×10^{-6}, or 13.5%, and the return in three days was 7%. In view of possible contamination or decomposition affecting the conductivity, 10% seems to be the most reasonable estimate of the real increase.

Calcium Fluoride

In one experiment pure mineral fluor spar was used. For the others, C. P. calcium fluoride was ground fine and digested several times with water until only coarse crystals remained. In some cases the powder was all added at once, and in other cases at intervals until no more effect was noticed on further addition. The time required for the powder to produce a maximum conductivity was usually from three to five minutes, but in one case was 24 minutes. This was followed by a decrease for about five days with all the solid added still present. With four experiments the increases were 24%, 19%, 32% and 29%, and the subsequent decreases were 10.5%, 15%, 12% and 17%. Considering the possible influence of impurities on the conductivity and the slow digestion back to the normal value the real increase in concentration for a given powder cannot be more than the original increase nor less than the return. Therefore, 18% is taken as the value for use in calculating the surface energy. The size of the finest powder was 0.2μ–0.3μ with some larger particles.

Barium Sulfate

The method used for strontium sulfate was not successful with barium sulfate, because of the failure of the fine particles in the solution to disappear or grow to a larger size in any reasonable length of time.

Instead, a highly supersaturated solution (at 30°) in which the barium sulfate did not precipitate was prepared by mixing approximately equivalent quantities of very dilute sulfuric acid and barium hydroxide. The conductivity of this solution was constant at 21.4×10^{-6}. Fine barium sulfate, 0.2μ in size, was added, whereupon the conductivity fell in five hours to 16×10^{-6} where it remained practically constant for three days. Some of the clear solution was then pipetted into another cell and large crystals, 2μ–20μ, were added. The change was slow, but in three days the conductivity fell to 12.9×10^{-6}. If it is assumed that the correction for water and impurities, such as excess acid or base, is 9.3×10^{-6} (the difference between the last value and the normal value for a saturated solution), the solubility of particles 0.2μ in diameter is 90% greater than that of the larger crystals.

Failure of Particles to Disappear or Grow

Attention has just been called to the failure of small barium sulfate particles to dissolve. This was also true of all the other substances studied, although to a more limited extent. Whenever, upon addition of a finely powdered substance to its saturated solution, the conductivity had gone up and then had slowly returned to its initial normal value, the expectation was that *all* of the smaller particles had dissolved and crystallized from the supersaturated solution onto the large crystals present. But this is not what happened. Particles were left in the solution at the end, which were just as small apparently as those present at the beginning, and these small particles, even though in intimate contact with large crystals, showed no tendency to dissolve. Frequently, large crystals formed in solution without seeding, starting with small uniform particles, as in the case of lead fluoride; but here, too, at the end of the process many small ones remained.

These facts indicate either that a large part of the increased solubility is due to particles in the powder too small to be seen and measured, or soon after entering the solution the increased solubility of the small particles is decreased by some adsorption effect such as the acquisition of a charge. The latter explanation seems more in harmony with the facts.

This effect was shown in a striking manner by the behavior of barium sulfate particles. Several very fine precipitates were made from barium hydroxide and sulfuric acid. One sample was made 0.1 N acid, one alkaline to the same degree, and the others were neutral. The precipitates were not retained by a filter, did not settle for several hours, and under the microscope most of the particles appeared to be 0.2μ–0.3μ or less in size. After standing for three months and being frequently shaken, they could be filtered, but under the microscope most particles still appeared to be as small as 0.3μ and certainly few, if any, were larger than 0.5μ. One of the samples was then boiled under a reflux condenser for a week with no visible change even when seeded with large crystals. The particles were found to have a negative charge as they migrated very definitely in a U-tube under a potential of 125 volts.

When 10 cc. of concd. hydrochloric acid was added to 100 cc. of the suspension and the boiling continued, a marked change took place. After a few hours particles several microns in length appeared, and after four days all particles were at least 1.5μ and some were as large as 3μ × 10μ.

If the growth of large particles at the expense of the smaller ones is a surface-energy effect, then the hydrochloric acid must act either to increase the surface energy at the solid-liquid interface, or else to remove those interfering factors which previously had prevented the normal surface energy from exerting its influence.

If we consider only the Ostwald-Freundlich equation, the calculated increase in solubility as particles become very small is so large that it seems improbable, and we are led to believe that some other factor enters to prevent actual attainment of the solubility predicted. W. C. M. Lewis[6] has proposed an expression, also independently developed and extended by Knapp,[7] which is based on the assumption that an electrical charge present on the surface of a small particle would decrease the solubility of such a particle. The curve plotted by Knapp from his equation shows that after a certain decrease in size a maximum solubility is reached, and for smaller particles the solubility is again diminished as we pass into the region of colloids. It seems probable that such a charge, by decreasing the surface energy and thus diminishing the increased solubility, may bring about a condition of equilibrium and prevent the further growth of particles at any size between those of a stable colloid and coarse crystals. If this is true, then the increased solubility for a definite size of particle would depend largely on conditions in the solution, and surface-energy calculations based on a solubility increase may be in error from this cause.

Calculation of Surface Energy.—By substituting the data giving the solubility of different sized particles in the equation[8]

$$\sigma = \frac{i\,RTr\,\rho\,ln\,\frac{Sr}{S}}{2M} \tag{1}$$

it is possible to calculate the surface energy at the solid-liquid interface. It is evident, however, that all data obtained so far, including those of the

TABLE II

CALCULATED VALUES FOR SURFACE ENERGY

Substance	Mol. wt.	Density	Mol. vol.	Diam. of particles μ	% Sol. increase	Temp. °C.	i	σ	Hardness
PbI_2	461.04	6.16	74.8	0.4	2	30	1.97	130	very soft
$CaSO_4.2H_2O$[a]	172.16	2.32	74.2	0.2–0.5	4.4–12	30	1.56	370	1.6-2
Ag_2CrO_4	331.76	5.52	60.1	0.3	10	26	1.95	575	about 2
PbF_2	245.20	8.24	29.7	0.3	9	25	1.70	900	about 2
$SrSO_4$	183.69	3.96	46.4	0.25	26	30	1.82	1400	3.0–3.5
$BaSO_4$[b]	233.43	4.5	52	0.1 (Hulett)	80	25	1.96	1250	2.5–3.5
	233.43	4.5	52	0.2	90	30	1.96	3000	2.5–3.5
CaF_2	78.07	3.18	24.6	0.3	18	30	1.97	2500	4

[a] See previous paper (Ref. 2) for discussion.

[b] The reason for the large difference in the two values of σ lies in the difference in the estimated size of the particles.

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[6] Lewis, *Kolloid Z.*, **5**, 71 (1909).

[7] Knapp, *Trans. Faraday Soc.*, **17**, 457 (1922).

[8] For a discussion of this equation see the previous paper, Ref. 2.

present paper, are liable to so many errors that such calculations cannot be made with any great degree of exactness. In fact, besides the charge effect, the unknown shape of the fine particles, the errors in measurement of their size, the different rate of solution of different crystal faces, and the influence of crystal habit on the immediate growth of the particles, are certainly factors which interfere very seriously with the applicability of an equation based on the assumption that particles are spherical with uniform surfaces. However, the values for surface energy in Table II are the most nearly correct that can be obtained from data available at this time.

It will be seen that there is a rough proportionality between surface energy and hardness, as might be expected. It is further evident from Equation 1 that, other things being equal, the surface energy should vary directly as the density and inversely as the molecular weight; in other words, the surface energy should vary inversely as the molecular volume. This general relation is indicated by the table. However, the solubility increase varies greatly with different substances, and it is evident that such a relation can hold only for substances of the same general type.

This inverse relation between surface energy and molecular volume is approximately true for the fused lithium, sodium, potassium, rubidium and cesium compounds of fluorine, chlorine, bromine and iodine, and their nitrates and sulfates. Of all these alkali salts[9] lithium fluoride has the smallest molecular volume and consequently the largest surface energy. At 1270° it is 201 ergs per sq. cm., at 1000° it is 237, and at 870° it is 250, making an extrapolated value of about 350 at 25°, for the supercooled liquid. By substituting 350 for σ in Equation 1 the calculated increase in solubility for particles of lithium fluoride 0.3μ in diameter would only be about 1%. As a matter of fact, it was not possible with the methods employed in this investigation to detect an effect with lithium fluoride as great as 0.5%, showing the very slightly increased solubility of fine powders with substances of small molecular weight.

This work was made possible through a National Research Fellowship. The author also wishes to thank Dr. Edward Mack, Jr., for his suggestions and encouragement.

Summary

1. A value for the surface energy has been calculated from the increased solubility of small particles for lead fluoride, lead iodide, silver chromate, strontium sulfate, barium sulfate and calcium fluoride.

2. It has been shown that a rough proportionality exists between surface energy and hardness, and the inverse proportion between surface energy and molecular volume, predicted by the Ostwald-Freundlich equation, has been indicated.

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[9] F. M. Jaeger, *Verslag Akad. Wetenschappen Amsterdam*, **17**, 555 (1914); *Z. anorg. allgem. Chem.*, **101**, 1 (1917).

3. It has been observed that fine particles may have their solubility diminished by an electrical charge or adsorption effect on the surface.

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[Contribution from the Chemical Laboratories of New Hampshire College]

THE PREPARATION OF DIPHENYL

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After the publication of a paper[1] in which the preparation of diphenyl was given, one of the present authors received several letters stating that the process failed to give good results. Since these statements were so contrary to those given in the original article, it seemed advisable to make a reinvestigation. A careful study of the faults of the first method revealed the fact that there were two striking difficulties which could be overcome only by bringing much sounder mechanical principles into play.

The first troublesome factor was the incessant short circuiting due to the expansion and sagging of the Nichrome ribbon filament, when heated. The second element of trouble was that due to superheating at the points where the filament came in contact with the means of support.

Description of the New Apparatus

As in the old, the new apparatus consisted of a 12-liter Pyrex flask, supported by a tripod. In the neck of the flask a tightly fitting stopper was inserted, through which a hole had been bored for the delivery tube of the inverted condenser. The latter was retained in a perpendicular position by means of an iron stand and clamp. In addition to the hole for the delivery tube, three symmetrically placed, very small holes were bored, through which passed the rods of the internal mechanism. Their purpose was to serve as threaded axes of the necessary binding posts for the essential electrical connections.

As has been previously mentioned, the problem was mainly one concerning an adequate filament support. After considerable experimentation, a type that was highly satisfactory was devised, all the faults of the old process being completely eliminated. The main supports consisted of two parallel steel rods, threaded on the ends that passed through the cork. These were securely retained in position by three steel cross-braces, two of which were held firmly in place by set screws.

Two larger blocks of steel were grooved on the edges and placed between the rods. This allowed the former to slide up and down, easily, as far as the cross-braces would permit. Between the middle cross-brace and upper block a powerful, arched strap spring of steel was inserted.

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[1] This Journal, 39, 933 (1917).