through the side-arm E. The point at which the galvanometer shows no deflection is then ascertained, and from the data the molecular weight is calculated in the usual manner.

The following determinations with the chloride, nitrate, and sulphate of potassium were made with water as solvent.

DETERMINATIONS (K = 510).

Salt.	Rise of B. P.	Molecular weight.	
		Potassium chloride.	
0.835	0.42	37.0	H_2O = 27.4 grams.
1.622	0.81	37.3	
2.295	1.19	35.9	
2.900	1.54	35.1	
		Potassium nitrate.	
1.691	0.54	58.3	H_2O = 27.4 grams.
2.207	0.67	61.3	
2.685	0.85	58.8	
		Potassium sulphate.	
0.887	0.28	82.4	
1.570	0.53	77.1	H_2O = 19.6 grams.
2.344	0.86	70.9	
2.960	1.08	71.3	
3.693	1.29	74.5	

The apparatus is convenient and in some ways much superior to that in which mercury thermometers are used, since neither adjustment for liquids having different boiling-points nor tapping device is necessary; changes in atmospheric pressure can introduce no error and the thermometers can be made of any degree of sensitiveness required.

McGILL UNIVERSITY, MONTREAL,
October, 1904.

THE SOLUBILITY OF GYPSUM AS AFFECTED BY SIZE OF PARTICLES AND BY DIFFERENT CRYSTALLOGRAPHIC SURFACES.

BY G. A. HULETT.

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IT HAS been shown[1] that the effect of the size of particles on the solubility of the solid is detectable and measurable; the smaller particles not only dissolve more rapidly, but have a greater solubility. The theoretical possibility of such a relation was pointed

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[1] Ostwald: *Ztschr. phys. Chem.*, **34**, 495 (1900); Hulett: *Ztschr. phys. Chem.*, **37**, 385 (1901).

out by P. Curie,[1] while Ostwald[2] has made use of the idea to explain the well-known fact that a precipitate in contact with its solution, will, in time, become coarse-grained. The explanation of the phenomenon is based on the following considerations: The boundary between a solid and a liquid is the seat of a certain amount of energy due to the surface energy of the liquid; if this surface is increased by powdering the solid, the total surface energy is correspondingly increased. Further, it is a generally observed fact that the form of a substance which has the greater free energy is the more soluble, has the greater vapor pressure, and is the least stable form,[3] *e. g.*, allotropic modifications of substances have different solubilities and the unstable form is always the more soluble. The phenomenon is hardly analogous to the well-known behavior of liquid drops of different sizes. Small drops in the vicinity of large ones grow smaller and disappear, while the large ones grow larger,[4] and the reason for this is quite clear. It is known that the curved surface of a liquid has a greater vapor pressure than a plain or less curved surface, therefore a distillation takes place. The similarity between the vapor pressure of liquids and the solution pressure of solids has suggested to some the analogy between the facts just mentioned and the behavior of solid particles of different sizes in contact with the solution. But we cannot assume that the surfaces of the particles of a powder are curved, or, if that is granted we do not know that a curved surface of a solid or a sharp edge, has a greater solution pressure than a plane surface of the same substance.

In order to get some idea of the energy on the surface between a solid and its solution, use was made of the previous work on gypsum.[5] A solution of gypsum saturated at 25° contains 2.080 grams $CaSO_4$ in a liter (0.01530 mol in a liter). If this solution is shaken with powdered gypsum, the concentration increases rapidly to a maximum, and then decreases and finally reaches the original concentration. The change can be easily and accurately followed by measuring the conductivity of the solution at intervals. In one experiment (*Loc. cit.*, p. 393) the concentration reached 2.542 grams $CaSO_4$ in a liter in a minute, and then began

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[1] *Bull. Soc. Min.*, **8**, 145 (1885).

[2] *Anal. Chem.*, pp. 15 and 23.

[3] Van't Hoff: *Vorlesungen*, II, 124; *Allgem. Chem.*, II, **2**, 860.

[4] Ostwald: *Grundriss d. allgem. Chem.*, pp. 152 and 318.

[5] *Ztschr. phys. Chem.*, **37**, 388 (1901).

to decrease, and finally reached the original value of 2.080 grams $CaSO_4$ in a liter. The powder used was ground as fine as possible in an agate mortar and contained many exceedingly fine particles, mere points under the highest magnification, while the powder obtained after nine days careful agitation at 25° showed no particles less than 1 μ (0.001 mm.) in diameter, but there were many of this diameter. It is to be noted that the smallest particles having proportionately the greater surface, as well as being the more soluble, will play the greatest rôle in the process of dissolving, and in dissolving become even smaller and more soluble. The effect is accumulative. All those particles below a certain size will completely disappear, supersaturating the solution, and finally be deposited on the larger particles. In view of this it is difficult to estimate the size of particles which would be in equilibrium with the above-observed solution containing 2.540 grams of $CaSO_4$ in a liter, certainly less than 0.1μ; but assuming that the particles which were in equilibrium with the solution were as large as 0.1μ, we can calculate the surface energy on a cubic centimeter of the gypsum powder (about 2.5 grams). A cubic centimeter with 6 sq. cm. surface if reduced to particles 0.1μ edge, would have a surface of 600,000 sq. cm. Increasing the surface of the gypsum solution by this amount would require about 4.8×10^7 ergs, since it requires about 80 absolute units to increase the surface of the solution 1 sq. cm. This is over a calorie in heat units and probably is under the true value that caused the 20 per cent. increase in the solubility. This is not much energy, but compares favorably with the difference in energy of allotropic modifications, and it is not unreasonable to assume that it is sufficient to account for the observed difference in solubility; however, in the absence of more exact proof, other possible causes have been considered, and especially the idea that different crystallographic planes may have different solubilities. If in powdering gypsum the more soluble planes predominate, an explanation of the observed facts is obvious.

In view of the different physical properties of different planes of a crystal it seems reasonable to assume that they also have different solubilities. There is an interesting article, by F. Rinne,[1] on "Richtungsverschiedenheiten bezuglich der Löslichkeit von Gypsspaltblättchen." The author prepared thin circular disks of gyp-

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[1] *Centrbl. f. Min. Geol. and Paleont.*, 1904, p. 116.

sum parallel to $_\infty P \grave{\infty}(010)$, and exposed these to the action of dilute hydrochloric acid, which is a good solvent for gypsum. It was observed that the circular disks, on dissolving, became elliptical, the edges in some directions dissolved *more rapidly* than in others, the action was greatest along $P\bar{\infty}(101)$, and least on $_\infty P\bar{\infty}(100)$.[1] Similar results are referred to under Coromila's Inaugural Dissertation, Tübingen, 1877. This work shows that the *rate* of solution is different in different directions. The existence of "Aetzfiguren" also proves[2] that there must be differences in the rate of solution for different planes of the same crystal; but have the different planes of a crystal different solubilities? The term solubility should be more clearly defined and entirely differentiated from any idea of rate. *Solubility is measured by the concentration of the solution which is in final equilibrium wth the solid,* and is independent of the rate at which this equilibrium is established.

In order to test the solubility of different planes of gypsum it seemed only necessary to determine whether a solution which was in equilibrium with one plane was also in equilibrium with another, and the conductivity of gypsum solutions affords such an exact and simple method of determining the concentration[3] that the determination seemed feasible, but no positive results were obtained, and in view of the exceeding slowness with which the system gypsum-solution comes to equilibrium[4] more evidence was sought.

In all the previous work the concentration of the solution in equilibrium with thin cleavage plates was taken as the measure of the solubility of gypsum; with such plates the clinopinacoid $_\infty P \grave{\infty}(010)$ so largely predominates that we can regard the 2.080 grams in liter as the concentration which is in equilibrium with (010) at 25°. Some exceedingly clear and perfect crystals of gypsum were procured on which the faces (010) formed only about one-third of the total surface, the other faces present being $_\infty P(110)$ and $-P(111)$. These crystals were rinsed with the abovementioned saturated solution, dried, weighed, and then the various diameters carefully measured with a micrometer caliper. The crystals with about an equal volume of the above solution, saturated in

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[1] See original.

[2] Nernst's "Theoretical Chemistry," 4th ed., p. 88.

[3] *Ztschr. phys. Chem.*, **37**, 385 (1901), and **42**, 577 (1903); This Journal, **25**, 667 (1902);
This Journal, **25**, 676 (190

respect to (010), were sealed off in a little Jena glass tube, placed in a thermostat (25°) and agitated from time to time. If the solution is not also in equilibrium with the faces (110) and (111), it will either dissolve from these faces or deposit on them, and will then no longer be in equilibrium with (010); in short, there will be a continual transference of material from the more soluble to the less soluble faces, and it will be merely a question of time until the effect on the different diameters becomes measurable. The tube with its contents remained at 25° ± 0.1 from April 7th to June 6th, with frequent gentle rotations. On opening the tube the solution had a conductivity $\lambda_{25} = 0.002210$, whereas the original solution was $\lambda_{25} = 0.002208$, and there was no detectable difference in the measurements of the various diameters of the crystals. There had, however, been a slight loss in weight of the solution ($\lambda_{25} = 0.002208$), and in a second similar tube some of the solution only. These tubes, frequently rotated, were maintained at three crystals of 1.4 mg. (their total weight being 9,2550 grams). The crystals were again sealed off in a tube with some gypsum 25° from June 6th to August 10th, when the solution from the crystals showed the conductivity $\lambda_{25} = 0.002209$, while the solution from the second tube without gypsum present showed $\lambda_{25} = 0.002191$. Evidently the Jena glass removed gypsum from solution, and the crystals had again lost about 1 mg. The various diameters were again very carefully measured and checked within the limit of error of measurement (±0.01 mm.) to the two previous measurements. The three crystals had been five months in contact with a solution which must have been in equilibrium with all the faces present and even a fracture on one of the crystals. The concentration of this solution was 2.080 grams n a liter and $\lambda_{25} = 0.002208$.

It can be concluded from the above that if there is a difference in solubility of the various planes it can not be detected by the above method, that it plays no rôle in the effect of size of particles on the solubility, and this constitutes a further proof that surface energy is the real cause.

The work so far has suggested some considerations in connection with solubility determinations that seem to deserve attention. If a solvent is to be saturated with a powdered substance, and the solubility is considerable, the finest particles and those that become fine by dissolving, will play the largest role in the process, as pointed out above. If after all these particles have disappeared the solution is still undersaturated, then the system slowly approaches the concentration that is in equilibrium with a plain surface from the undersaturated side. If, however, the solubility is small, say 1 per cent. or less, there may be a sufficient number of particles of 2 μ or less present, or produced, to rapidly bring the concentration above the normally saturated solution, and the system then approaches the concentration that is in equilibrium with a plain surface from the *supersaturated side,* while it has been generally assumed in such cases that the point was being approached from the undersaturated side. This is surely the case with gypsum, as the following experiments prove.

Fifty grams of clear, chlorine-free gypsum was powdered, and brought together with 500 cc. of conductivity water, all at 25°. The system was shaken and in three minutes a sample removed.

Time from mixing. Minutes.	Conductivity.	Concentration Gram $CaSO_4$ in L.
3	0.002350	2.254
25	0.002320	2.216
70	0.002301	2.192

From here on the decrease was continually slower, requiring seventeen days and careful handling to bring the system to final equilibrium. The previous work has shown that the conductivity is an exceedingly accurate measure of the concentration. The relation between concentration and conductivity has been carefully determined.[1] A few suspended particles between the electrodes play no role, while the heat of solution which might have affected the first determination is very small and negative. The system was in a tube some 20 x 5½ cm., drawn down and sealed off. Above the thermostat was a motor-driven shaft, and from the shaft little belts extended down into the bath. The above tube rested in the loops of these little belts, with rubber rings to keep the belts in place. Thus the tube was rotated around its longer axis in the bath and at any desired rate. The powdered gypsum was thus spread out in a long layer and slowly rolled "down hill" as the tube revolved. Previous work[2] has shown that this system, gypsum-solution, is one of the most difficult to bring to final equilibrium. With too

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[1] *Ztschr. phys. Chem.*, **42**, 581 (1903).

[2] *Ibid.*, **37**, 394.

rapid agitation the concentration may remain 5 per cent. too great, while on standing practically no change takes place. The above system required seventeen days of very slow rotation to come to final equilibrium. Two hundred cc. of the clear solution were finally removed, evaporated to dryness and the residue ignited, taking all precautions previously found necessary.[1] 0.4167 gram $CaSO_4$ was obtained (which, moistened with sulphuric acid and again ignited, gave the same weight). This is 2.083 grams $CaSO_4$ in a liter. Another experiment was tried where *only* 5 grams of finely powdered gypsum were shaken with 500 cc. of water (one-tenth the amount of powder used in the previous case).

Time for mixing. Minutes.	Conductivity.	Concentration. Grams $CaSO_4$ in L.
2	0.002290	2.167
8	0.002303	2.193
Hours.		
12	0.002241	2.112
198	0.002230	2.103

For lack of time this experiment was not carried further, but many experiments have shown that the concentration will finally decrease to 2.080 grams in a liter.

For inorganic substances gypsum is very exceptional in its behavior, requiring a half day or more to saturate the solution from the undersaturated side, where only plates of gypsum are used.[2] Under similar conditions most substances would saturate a solution in an hour or so. From the supersaturated side the system, gypsum-solution, exhibits an even more striking exception, requiring weeks and very careful handling to bring to final equilibrium, and in view of all the facts brought out it is not surprising that there have been great discrepancies in the solubility determinations of gypsum, as given by various investigators. Lately F. K. Cameron[3] has laid considerable stress on a value obtained by him of 2.120 grams $CaSO_4$ in a liter at 25° as the solubility of gypsum under ordinary conditions, while Droez,[4] working with equal care, obtained 2.180 grams $CaSO_4$ in a liter at 25°, etc. But it is to be concluded that the systems analyzed by these investigators were not in final equilibrium. With varying amounts of gypsum powder and solvent, different results will be obtained unless care is taken

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[1] This Journal, **24**, 672 (1902).

[2] *Ibid.*, **24**, 676 (1902).

[3] *J. Phys. Chem.*, **7**, 571.

[4] *Ber. d. chem. Ges.*, 1877, p. 330.

to bring each system to final equilibrium, and the solution then obtained contains only 2.080 grams $CaSO_4$ in a liter, from whichever side approached. The above sources of error should be guarded against in solubility work where the solubility is small. In attempting to approach the equilibrium from both sides, as is commonly done, it may happen that the point is *approached only from the supersaturated side,* as pointed out above.

If the bottom of an Erlenmeyer flask is covered with large particles or crystals of the solid, and the solvent rotated over these crystals by a motor-driven Schultz stirrer, none of the above difficulties will be encountered; further, the solution is always perfectly clear and free of particles, which is often a very considerable advantage. A supersaturated solution may also be rotated over the same crystals, and the equilibrium approached from both sides. By this method the solubility of gypsum from 0° to 100° has been determined by Hulett and Allen,[1] and the results in this paper show that the values obtained at that time, where the cleavage plane very largely predominated, are also the values for any plane of gypsum.

UNIVERSITY OF MICHIGAN
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THE ESTIMATION OF POTASH IN SOILS, PLANTS AND FERTILIZERS.

BY F. P. VEITCH.

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CONSIDERABLE interest has been displayed in improving standard methods for the estimation of potash in soils, plant substances and fertilizers during the past three or four years.[2]

It is now generally recognized that in the case of fertilizers, potash added in the form of salts is seldom entirely accounted for in the analysis of the completed mixtures, and this latter fact has led to much complaint from the manufacturers. It has been found

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[1] This Journal, **24**, 667 (1902).

[2] *Chem. News*, **79**, pp. 135-136; *J. Chem. Soc.* (London), **77**, 1076; *Stat. Spar. Agr. Itat.*, **33**, 454; *Ann. Chim. Anal. et. Appl.*, **5**, 289; *Ztschr. anal Chem.*, **39**, 481; **40**, 385; **40**, 569; *Chem. Ztg.*, **26**, 1014; **28**, 210; **28**, 36; *Ztschr. angew. Chem.*, **15**, 1263; *Ztschr. anorg. Chem.*, **36**, 323; **36**, 325; this Journal, **25**, 416; **25**, 491; **26**, 297.