sponding mole fraction to the maximum extent of about 8% at the eutectic point. Judging from our present knowledge of such systems, geometrical isomers seem to show slight deviations from mutual ideality but not such as would indicate complex or mixed crystal formation.

It is possible that similar studies made on less polar isomers of this type may show them to be more nearly ideal than those discussed in this paper.

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[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF McGILL UNIVERSITY]

THE SURFACE ENERGY OF SOLID SODIUM CHLORIDE. III. THE HEAT OF SOLUTION OF FINELY GROUND SODIUM CHLORIDE

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In previous papers[1] it was shown that finely divided sodium chloride had a heat of solution different from that of coarsely ground sodium chloride. This difference was attributed to the energy bound up in the surface of the finely divided salt, and from the measurement of the difference in the heat of solution, the actual value of the surface energy of solid sodium chloride was calculated. In these experiments the finely divided salt had been obtained by sublimation.

In the present paper an account is given of similar measurements but here the finely divided salt is obtained by grinding. It has been found in this case also that the finely divided material had a lower (negative) heat of solution than the coarsely ground sodium chloride.

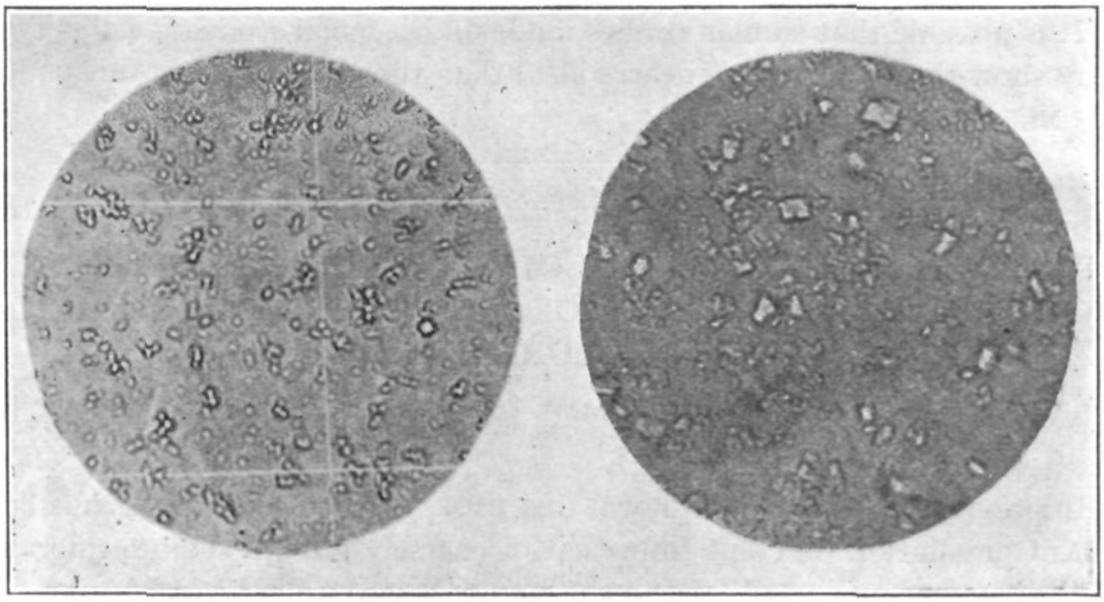
Experimental Procedure

Pure sodium chloride was ground in a mechanically driven agate mortar for fifteen minutes. The ground salt was then placed at the bottom of a vertical glass tube about 1 m. long and 4 cm. in diameter and dry air, at a constant pressure, was blown into the tube through a fine nozzle at the bottom. The air was admitted so as to impinge on the ground salt. The current of air carried up the fine particles of salt which then passed into a series of settling chambers[1b] where they were sorted out according to size. The vertical glass tube was jarred continuously by an automatic tapper to prevent salt from adhering to the walls of the tube. The salt in the tube was recharged every fifteen minutes.

In order to see whether the salt was contaminated by silica rubbed off the agate mortar, samples of the product were analyzed but no weighable amount of silica was found in them.

[1] (a) Lipsett, Johnson and Maass, THIS JOURNAL, 49, 925 (1927); (b) 49, 1940 (1927).

The heat of solution of the finely divided salt was determined using the apparatus described previously[1b] and the diameter of the particles was measured by means of photomicrographs.[1b]



Sublimed. Ground.

Fig. 1.—Finely divided sodium chloride. (805 diameters).

Experimental Results

The heat of solution was determined at 25° at a concentration of 4.62% with three different samples of salt. The results are given in Table I.

TABLE I

HEAT OF SOLUTION OF FINELY GROUND SODIUM CHLORIDE

Sample	Heat of soln., cal. per mole	Diff. in heat of soln., cal. per mole	Diameter of average particle, μ
I	−903.7	24.9	1.3
II	−903.6	25.0	1.2
III	−887.9	40.7	1.4

In Col. 3 is given the difference between the heat of solution of coarsely ground sodium chloride (−928.6 cal. per mole) and of the finely ground salt measured, of course, at the same temperature and concentration. This difference is far larger than that obtained with finely divided salt obtained by sublimation. It may be calculated from the previous work[1b] that sublimed salt whose particles were 1.3μ in diameter would have approximately a heat of solution only 11 cal. less than that of coarse salt. The exceptionally large difference obtained with the finely divided salt obtained by grinding is probably due to the uneven surface of the ground salt whereby the actual surface of the particles is much larger than the apparent surface.

The fine salt obtained by sublimation, when examined under the microscope, is seen to be definitely cubic in appearance. It is reasonable to suppose that crystals of salt formed by sublimation would have smooth surfaces and be fairly regular in shape. On the other hand, the fine salt obtained by grinding is distinctly irregular in appearance under the microscope and the crystals show many jagged fractures. This is shown in the accompanying photomicrographs of the finely divided salt prepared by the two methods. Calculation of the surface area of the finely divided ground salt from the measurement of the diameter of the particles, assuming that the particles are cubic in shape, will almost certainly give a result which is less than the actual surface, since no account will have been taken of the irregularities in the surface and the small projecting fragments which may be assumed to be present even when not visible under the microscope.[2]

For the above reason, the results obtained by using the ground material have been taken as more or less qualitative in nature and as supporting the previous work, but the actual calculation of the surface energy is believed best to be derived from the results obtained using the finely divided sublimed salt, since in the latter case the surface area is probably more accurately obtained.

The present work shows, however, that finely divided salt whether obtained by sublimation or by grinding has a lower (negative) heat of solution than coarsely ground salt.

Grateful acknowledgment is made to the National Research Council of Canada for a grant to aid in this work and also for a Studentship held by one of us, during the tenure of which this work was carried out.

Summary

The heat of solution of finely divided salt prepared by grinding has been determined and has been found to be less in magnitude than the heat of solution of coarsely ground sodium chloride.

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[2] D. Balarew, *Z. anorg. Chem.*, **154**, 170 (1926).