XXXVII.—*The Attractive Force of Crystals for Like Molecules in Saturated Solutions.*

By EDWARD SONSTADT.

ONE of the earliest experiments made with the object of tracing the effect of crystals on the strength of a solution was performed on considerably more than half a litre of solution of potassium platini-chloride standing in a beaker over a quantity of crystals of the salt which had been deposited from it by cooling. More than half of the solution (A) was poured into a separate beaker, and a trace of crystals of the same salt was added to it. The remainder of the solution (B) was left standing over the crystals. The two beakers, loosely covered with paper, were set in a cellar side by side, where the temperature varied but very slowly, and on the whole diminished. The first trial was made when the cellar temperature was 13.3° . A portion was placed in a tared porcelain dish, which was weighed, and set on the water-bath. In this and in all similar experiments, a certain fixed

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interval of time intervened after the drying before removing the dish from the bath, and a definite number of minutes was allowed to elapse before weighing, the conditions in all respects being strictly comparative. The platinichloride remaining was calculated as parts dissolved in 100 parts of water. The specimens were taken in immediate succession for each pair, as in all other cases.

	Temperature.	Pt salt to 100 aq. (A).	Pt salt to 100 aq. (B).
Sept. 16, 1897.....	13.3°	0.786 gram	0.775 gram

The experiment was started on the 14th September, 1897, and the lowest temperature attained in the two days' interval was 12.8°.

	Temperature.	Pt salt to 100 aq. (A).	Pt salt to 100 aq. (B).
Oct. 1, 1897	13.3°	0.790 gram	0.740 gram
„ 8, „	9.4	0.788 „	0.712 „
„ 15, „	11.1	0.759 „	0.696 „
Nov. 17, „	10	0.691 „	0.664 „

Crystals in beaker, 0.465 gram.   Crystals, 3.74 grams.

Thus, the differences between the quantity of the salt held in solution by 100 grams of water in the two beakers was: for two days, 0.011 gram; for sixteen days, 0.050 gram; for twenty-four days, 0.076 gram; for thirty-one days, 0.063 gram, and for forty-eight days 0.027 gram, the maximum difference being after twenty-four days. Obviously, the gradual accumulation of crystals in solution A, as time went on, would tend to diminish the difference.

In an experiment started November 3, 1897, about 50 c.c. of a solution of the platinum salt saturated at about 10° was put into each of two small flasks. To one flask (I), some minute particles of the solid salt were added, and about one gram of crystals of the salt was added to the second flask. Both flasks were stoppered lightly with cotton wool, and they were set side by side in the cellar.

	Temperature.	Pt salt to 100 aq. (I).	Pt salt to 100 aq. (II).
Nov. 9, 1897.....	10°	0.757 gram	0.672 gram
„ 15, „	8.8	0.706 „	0.649 „

Another experiment was made on a specimen of platinichloride specially crystallised in such manner as to produce crystals of comparatively large size. A saturated solution (167 c.c.) of these crystals was formed, a fourth part of which was put into each of four flasks. To one flask, 1.49 grams of platinum salt crystals were added; this flask was marked II. To the other three flasks, traces of the salt

were added, and into flask III were put 10·45 grams of glass beads (1494 beads having an estimated total surface of slightly more than 23 sq. inch). Flask IV was set on a layer of the platinum salt. All were plugged as usual and set in the cellar side by side. When tested after twenty-two days, at 5·5°, the results were :

Flask I	0·698	Flask IV	0·692
Flask III	0·667	Flask II	0·589

these numbers representing parts of platinum salt in 100 parts of water.

In this experiment, the difference between the solution contained in flask II, including the platinum salt crystals and the others, is well marked. But the influence of the beads is also noticeable, tending to show that the mere surface of indifferent substances exercises an influence on crystallisation. Hence, in such experiments, the vessels used for comparison of results should be as nearly alike in form and capacity as possible.

Test for Errors of Experiment.

From a solution of the platinichloride, four portions were successively taken for the trials. The portion first taken was weighed in the dish, evaporated, dried, and the residue weighed with the dish, precisely under the conditions observed in the previous experiments, and so in like manner with the three succeeding portions. The quantities taken varied from about 13 c.c. to 18 c.c. The results were, when calculated for each 100 parts of water, 0·5771, 0·5788, 0·5777, and 0·5783, showing a maximum difference, due to experimental errors, of 0·0017, or a mean error of 0·0009.

Potassium Chloride.—The potassium chloride had been several times crystallised. A part of a solution of the salt standing in a beaker over a considerable quantity of potassium chloride crystals was transferred to another similar beaker and some minute crystals were added to it. The two beakers, loosely covered with paper, were set side by side in the cellar. The next morning, the density of the solution in the first beaker (containing the crystals) was 1·1637 at 7·8°, and that of the second solution 1·1646, both uncorrected, the conditions being exactly the same in both cases.

Potassium Sulphate.—The salt employed was that commercially known as “pure.” A saturated solution of the salt was divided between two beakers, into the second (*B*) of which 10 grams of the crystallised salt were put, a minute portion being introduced into the first beaker (*A*). The beakers, covered by paper, were set side by side in the cellar. After four days (temperature 7·7°), the density of the solution in beaker *A* was 1·0690, and that of the solution in the second beaker (*B*) was

1.0709, that is, a higher instead of a lower density, as should have been the case had the salt been pure. To test this further, the solution in flask *B* was heated sufficiently to dissolve much of the salt contained in it, and the solution was again set to crystallise beside flask *A*. On testing two days afterwards, solution *A* gave, at 7.8° , the density 1.0687, and solution *B* 1.0716, showing a still greater difference on the wrong side, obviously due to the presence of impurities, probably in this case of a small proportion of sodium sulphate.

The crystals of potassium sulphate were then twice crystallised, and from the crystals thus obtained a saturated solution was formed and divided into two portions, *A* and *B*, to one of which, *B*, 11.17 grams of the crystals were added. After the usual procedure (temperature 6.1°), the trials were made after three days (the temperature having in the interval fallen to 5.5°). The solution in flask *A* (no added crystals, except the usual traces) had a density of 1.06850, whilst that in flask *B* (containing the added crystals) had a density of **1.06596**. The result in this case is therefore normal, showing that the salt used was, at least, approximately pure. The crystals which formed in flask *A* during the experiment were collected and dried, and weighed 0.637 gram. Of course, the crystals thus deposited also exercised attractive force in proportion to their quantity; and the ideal conditions for conducting such experiments would involve a minimum separation of crystals during their progress.

Boric Acid.—Equal parts of a solution of twice-crystallised boric acid (saturated at 17.2°) were placed in two small glass flasks, with addition to the solution in flask I of 2 grams of boric acid crystals. The second flask (II) was primed, other conditions being as usual (temperature, 13.9°). After eighteen days, with cellar and balance room temperatures of 14.4° and 16.1° respectively, the density for flask I (with the crystals) was **1.01494**, whilst that of flask II (no added crystals) was 1.01553. As the conditions were strictly comparable in both cases, no corrections were made.

Oxalic Acid.—This acid, after being twice crystallised from nitric acid solution and washed, was dissolved to form a saturated solution, of which equal portions were taken at 16.1° and placed in two similar flasks, to one of which (I) much crystallised oxalic acid was added, the solution in the other flask (II) remaining without addition beyond the priming. Portions were taken two days later with cellar and balance room temperatures of 13.9° and 15° respectively, when the density of the solution in flask I (with much solid acid) was **1.03055**, whilst that of the solution in flask II (solution only) was 1.0314.

Crystallised Copper Sulphate.—Equal portions of a saturated solution of this salt at 16.6° were placed in two small flasks, which were set in the

cellar under the usual conditions (temp. 14.4°). To the solution in the second of the flasks, 2 grams of the cupric sulphate crystals were added. After two days at 14.4° , the density of the solution in flask I was 1.1859, and that of the solution in flask II was 1.1832. A diminution of temperature from 16.6° to 14.4° caused considerable crystallisation in the solutions, which tended to diminish the difference which appeared. When the experiment was repeated under similar conditions (except as to temperature) at 11.1° , the densities of the solutions in flasks I and II were 1.1788 and 1.1740 respectively.

Potassium Ferrocyanide.—Thirty c.c. of potassium ferrocyanide solution saturated at 12.2° were put into each of three small flasks, together with a quantity of the crystals in flask I. The other two flasks were only primed. The trials were made eighteen days later, when the temperature both in cellar and balance room was 8.9° . The density of the solution in flask I (with crystals) was 1.1191, whilst those of the solutions in flasks II and III (solution only) were 1.1265 and 1.12615.

In the course of this experiment, the temperature increased a little after the commencement, thus necessitating slight addition of crystals to flasks II and III and frequent shaking of flask I to ensure saturation. The final temperature, however, was relatively low.

Ferrous Sulphate.—A saturated solution (25 c.c.) of the commercial "pure" salt at 9.4° was put into each of three small flasks, into the first of which 2.3 grams of crystals were added, the other flasks containing only the (primed) solution. The trials were made after two days at 8.9° . The density of the solution in flask I (with crystals) was 1.1949, whilst those of solutions II and III (solution only) were 1.1969 and 1.1964.

Borax.—A saturated solution of this salt was placed in each of three small flasks, into the first of which about 2 grams of the crystals were introduced (cellar temperature 7.2° , and varying subsequently between 9.4° and 4.4°). The trials were made forty-two days later, the temperatures in cellar and balance room being 4.4° and 5° respectively. The density of the solution in flask I (with crystals) was 1.0140, whilst those of solutions in flasks II and III were both 1.0155.

Potassium Iodate.—Thirty c.c. of a saturated solution of a highly purified specimen of this salt at 6.6° were placed in each of three small flasks, into the first of which about 2 grams of the crystals were introduced. The cellar temperature was 6.6° and during the experiment the temperature varied from 4.4° to 7.2° . The trials were made after four days at 7.2° . The density of the solution in flask I (with crystals) was 1.0317, whilst the densities of the other two solutions (without crystals) were 1.0338 and 1.0335.

Potassium Bromide.—Thirty c.c. of a solution of the commercial

salt saturated at about 7.7° were placed in each of three flasks, into the first of which about 2 grams of the crystals were placed, the solutions in the other flasks being primed only with traces of the crystals. The cellar temperature was 7.2° . The trials were made after six days, the temperature being 5.5° . The density of the solution in flask I (with the crystals) was **1.3431** whilst the densities of the two primed solutions were 1.3499 and 1.3502.

Thirty c.c. of a solution of recrystallised potassium bromide, saturated at about 5.5° , were placed in each of three flasks, into the first of which about 2 grams of the crystals of this salt were introduced, the solution in the other flasks being primed only; but in flask III about 2 grams of washed and ignited sand were placed. The trials were made after two days, the temperature being 5° . The density of solution with the crystals was **1.33655**, whilst the density of the solution in flask II (solution) was 1.3441, and that of the solution of flask III (solution and sand) was 1.3443.

It will be noted that the difference between the densities of the solutions with and without added crystals is sensibly greater with the recrystallised than with the ordinary bromide.

A number of experiments of a similar kind was made with potassium hydrogen and with sodium hydrogen carbonate, only to find that, notwithstanding the greatest care taken to work with the pure salts, and to ensure that these should be fully carbonated at the moment of use, the behaviour was always that of an impure salt. Either the portion of solution containing the added crystals proved to be of approximately the same density as that to which no crystals had been added, or the density of the former was even greater than that of the latter. I was forced to the conclusion that, under the conditions of the experiments, potassium hydrogen or sodium hydrogen carbonate was not stable; that, under ordinary atmospheric conditions, it parted with carbon dioxide, so as to become mixed with a small proportion of the neutral carbonate, a conclusion which I find has been independently arrived at by another investigator.

These experiments throw some light on the curious discrepancies existing between the solubilities of some well-known salts as determined by experimenters of unimpeachable skill and accuracy. While attending with the minutest care to the conditions which might be supposed to influence the results, there is no reason to suppose that attention was paid to the presence or otherwise in the solutions tested of a body of crystals. It is probable, also, that in exact determinations it may be advisable to work under certain standard conditions, as to the surface, relatively to the mass of the solution, exposed to the air, and the surface of the containing vessel in contact with the liquid. The experiment already recorded, in which a known surface

of glass beads was exposed to a solution, renders it at least probable that surfaces chemically inert may yet exercise a certain influence.

There is an obvious practical application of the property of crystals here described, in furnishing a very ready and reliable means of determining the purity of any given crystallisable salt. The test, if properly carried out, is capable of detecting a very small proportion of impurity, and the differences between saturated solutions depending on the presence or absence of a foreign salt are so considerable that very ordinary means suffice for their detection. In most cases, an experiment of the kind described need not be continued beyond two or three days.