A Method of Solubility Measurement.   Solubilities in the System SrCl₂–H₂O from 20 to 200°

BY ALAN W. C. MENZIES

The method here described was devised primarily for measurement over a wide temperature range of solubilities of salts in deuterium water, a case in which economy of solvent is desirable. It soon became evident that the method was sufficiently simple and accurate to be used in more general cases. Brönsted has compiled for "International Critical Tables"[1] the aqueous solubilities of over 600 strong electrolytes. He estimates the degree of accuracy as ±1% or better in less than 7% of these cases. This degree of accuracy is improved in the present method, the use of which is here exemplified up to a temperature of 192.9°.

General Description.—In one form of the so-called synthetic method of solubility measurement, known weights of solvent and solute are sealed in a glass tube. This is slowly raised in temperature until the last crystal disappears. At this temperature the concentration of the saturated solution is known from the synthesis, and thus one point has been determined upon the solubility curve. The procedure is repeated for as many points as are desired. The method here described likewise employs a known weight of solute and a known weight of solvent contained in a sealed glass apparatus; but the amount of solvent admitted to the tube containing the solute may be varied at will without opening the apparatus. That part of the solvent which it is desired to keep out of use in any experiment is maintained apart from the rest of the material not by means of a stopcock, 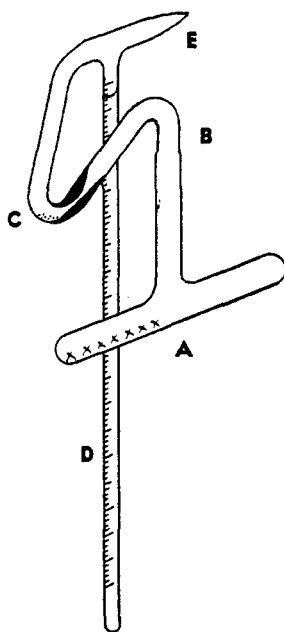which would leak, but by a trap which can be opened or closed by melting or freezing a sealing substance which can close a constricted connecting tube. The weight of the solvent used in any experiment is obtained by reading the volume of the unused portion, and deducting this from the total amount present. Correction, if necessary, may be made for the weight of solvent in the vapor phase.

Fig. 1.—Solubility apparatus.

The Apparatus as Used for Solubilities of Strontium Chloride in Ordinary Water.—Pyrex glass was used for the apparatus shown diagrammatically in Fig. 1. The tube A was of 6 mm. bore and 8 cm. length, and was sealed to an upright tube of 5 mm. bore extending to B. The anhydrous salt was weighed into the hammer-like portion which lies below B and there desiccated and reweighed before this portion was blown on to the rest of the apparatus. The trap C was made from 4 mm. bore tubing constricted to a bore smaller than 1 mm. with heavy walls at a point on one side of the U. Here was contained enough of a previously fused mixture of silver chloride and silver iodide near the eutectic composition[2] to fill the constriction when melted in the wider, unconstricted, portion of the U and caused to flow into the constriction by tilting. Before closing this trap, the apparatus was heated and washed out with dry air so as to remove moisture introduced in glass blowing, and evacuated. The graduated tube D, of 3 mm. bore and 17 cm. length, had a content of about 1 cc. covered by 100 graduations spaced as widely as 1.5 mm. for better precision in estimation of tenths. The water was introduced into this tube by distillation without ebullition, and in absence of air, from a bulb on the right of E where it had been freed from gases by repeated freezing by solid carbon dioxide and evacuating. The charged and completed apparatus was of such size as could be enclosed in a rectangular vessel of dimensions 18 × 8 × 5 cm.

Securing and Measuring Temperatures for Equilibrium.—For many of the experiments the glass apparatus was submerged in a four-liter beaker of oil, violently stirred, and heated by two knife-form resistance heaters with controllable wattage. The apparatus was affixed to a mechanical rocker which, by an eccentric device operated by a reducing gear driven by the stirring motor, caused the ends of the tube A to rise and fall alternately above and below its middle point which lay in the axis of rotation. This caused crystals of salt to slip about 30 times per minute from end to end of tube A. The crystals were rendered conspicuous by brilliant local illumination from the side of the beaker. For lower temperatures, mercurial thermometer threads were completely immersed; for higher temperatures, Anschütz thermometers were entirely immersed. Temperatures were in agreement to 0.1° with the Bureau of Standards scale, which was given by comparisons with certificated Allihn thermometers with zero points freshly redetermined after preheating. Although a vegetable oil containing 10% of beeswax smokes little at 200°, some experiments were run with conforming results in an electrically heated non-thermostated air oven of one cubic foot air volume with distributed heating elements, internal illumination and fan stirring. At 23° an ordinary water thermostat was used.

(1) Vol. IV, pp. 216–244.

(2) The eutectic temperature is given by Bergman and Genke as 264°, cf. C. A., 21, 523 (1927).

Procedure in One Experiment.—The water content of the graduated tube was adjusted to the desired value. For this purpose the trap was opened and water caused to distil without ebullition by placing the appropriate side of the apparatus in cold running water contained in a suitable vessel inside an air oven at about 50°. Alternatively, one side of the apparatus was warmed cautiously by running over it the flame of a Bunsen burner. The trap was sealed, and all liquid water in the graduated side of the apparatus was driven into the calibrated tube to form a coherent thread whose volume was read off at known (room) temperature. This volume was checked at the end of each experiment. No measurable leakage through the seal was found in any experiment save one above 180°, which was repeated successfully after more careful sealing. The apparatus was now fastened to the rocking device and immersed in the oil-bath, whose temperature was raised at first quickly but later more slowly when the quantity of salt remaining became small. The time required for equilibria varied with the temperature, an average run occupying two hours. With good mechanical arrangements, only a small portion of this time was occupied in actual observation.

Correction for Weight of Solvent in the Vapor Phase.— In these experiments, the volume of vapor above the saturated solution had a maximum value of 3.5 cc. The weight of this vapor was not negligible above 70°, and was corrected for by knowledge of the vapor pressures of the saturated solutions. These have been previously measured[3] up to 130°. Because of the anticipated uncertainty of extrapolation, further measurements were made to 200° over mercury in a closed U-tube, completely submerged in an oil-bath, where pressures of air-free saturated solution were opposed by those of a fixed quantity of permanent gas enclosed in the graduated opposite limb. The pressures thus found at 130, 150, 170, 190 and 200° were 1040, 1780, 2950, 4700 and 5720 mm., respectively, with an accuracy of a few per cent., which is amply adequate for the purpose. Contrary to expectation, these experimental values yielded corrections for weight of vapor not differing in any case by as much as one milligram from the values previously arrived at by extrapolation of the curve of relative molal vapor-pressure lowering against molality.

Particulars of the Work with Strontium Chloride.— Three solid hydrates come here in question, the hexahydrate passing to the dihydrate at 61.4° and the dihydrate to monohydrate at 134.4°. An excellent sample of DeHaën's reagent hexahydrate was fortunately available, which had been employed by Caley[4] in his work on the detection of calcium in presence of strontium and barium. The total amount of impurity present was probably less than 0.1%. An evidence of purity is found in the transition temperature determined by the intersection of solubility curves as 61.4 ± 0.2° as compared with 61.34° reported by Richards and Yngve.[5] Over four molecules of water were removed by a current of air from a sample of hexahydrate below 61° and most of the remaining water below 134°, after which the salt was desiccated at 180° in a current of dry filtered air. Analysis showed that hydrolytic decomposition was

negligible. Throughout all experiments the apparatus contained 0.5963 g. of strontium chloride. The total water within the apparatus was 1.097 g.

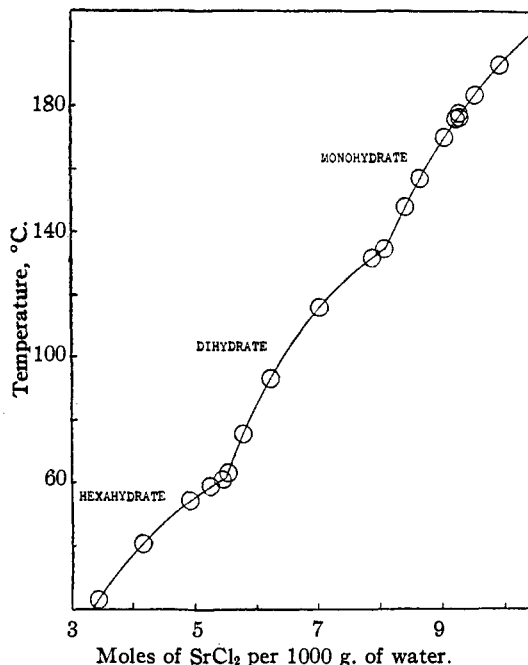Moles of SrCl₂ per 1000 g. of water.

Fig. 2.—Solubility of strontium chloride.

Nineteen points upon the solubility curves of the three hydrates were determined, from 22.9 to 192.9°, as noted in Table I and graphed in Fig. 2. These were graphed on a large scale, and the three curves drawn smoothly with the help of a celluloid lath held in curvature by applying torques at two points only. As read from these curves, the average divergence of a single observation was less than 0.2% of the solubility found.

TABLE I

OBSERVED SOLUBILITIES OF STRONTIUM CHLORIDE HYDRATES IN WATER

M = moles SrCl₂ (158.54) per 1000 g. of water

Temp., °C.	M	Temp., °C.	M
22.9	3.43	134.4	8.06
40.75	4.14	147.6	8.39
54.15	4.88	156.3	8.65
58.9	5.244	169.3	9.03
60.9	5.45	175.5	9.21
62.95	5.52	175.9	9.28
75.65	5.77	177.1	9.28
93.15	6.194	183.1	9.49
116.0	6.99	192.9	9.93
131.7	7.86		

Table II gives the molal solubilities for each five degrees from 20 to 200° as read from these curves, with extrapolated values in italics. The percentage correction that should be applied to the values in "International Critical Tables"[6] to

(3) Collins and Menzies, *J. Phys. Chem.*, **40**, 379 (1936).

(4) Caley, *Ind. Eng. Chem., Anal. Ed.*, **6**, 445 (1934).

(5) Richards and Yngve, THIS JOURNAL, **40**, 89 (1918).

(6) Vol. IV, p. 231.

yield the new values is also shown in Table II. From this it is apparent that the "I. C. T." values are in reality better than was estimated by Brönsted, who notes $\pm 2\%$ at 60° and below and $\pm 5\%$ at 70° and above. The 2% discrepancy as observed lies on each side of the 61.34° transition point of Richards and Yngve, in order to pass through which point Brönsted's curves were perhaps distorted injudiciously.

The two transition temperatures defined by the intersections of the curves lie at 61.4 and 134.4°, as compared with 61.34° as found by Richards and Yngve and 132° as reported by Collins and Menzies[3] from the rather small angle intersection of the log p versus $1/T$ equilibrium curves of the systems strontium chloride dihydrate–monohydrate–vapor, and dihydrate solid–saturated solution–vapor. If their values are graphed in the form of relative lowering of vapor pressure against temperature, the two curves intersect at a more favorable angle and at 134°.

TABLE II
SOLUBILITIES OF STRONTIUM CHLORIDE HYDRATES IN WATER

M = moles SrCl$_2$ (158.54) per 1000 g. water

Temp., °C.	M	% correction to "I. C. T." values	Temp., °C.	M
	S.6 Aq.			
20	3.33	0.0	110	6.74
25	3.50		115	6.95
30	3.69	.0	120	7.17
35	3.89		125	7.43
40	4.10	− .7	130	7.74
45	4.34			
50	4.62	− .7	S.2 Aq. + S.Aq.	
55	4.95		134.4	8.06
60	5.35	+2.1		
	S.6 Aq. + S.2 Aq.		S.Aq.	
61.4	5.50		135	8.08
			140	8.20
	S.2 Aq.		145	8.33
65	5.56		150	8.46
70	5.65	+1.9	155	8.60
75	5.76		160	8.74
80	5.86	+0.7	165	8.89
85	5.98		170	9.05
90	6.10	+ .3	175	9.21
95	6.24		180	9.39
100	6.39		185	9.58
105	6.56		190	9.79
			195	10.03
			200	10.29

Discussion of Error. (a) Quantity of Solid Phase.—One can confirm the statement of Kracek[7] that less than 0.1 mg. of crystalline mate-

(7) Kracek, J. Phys. Chem., 38, 417 (1934).

rial can be visually detected under our conditions of experiment. In every experiment the final disappearance of the hydrated material furnished by 0.6 g. of anhydrous salt was observed. If the visibility limit were even as great as 0.5 mg., an error below 0.1% could be introduced. (b) Quantity of Solvent.—The smallest quantity of water used to attain solution, at 192.9°, was 380 mg. If this were measured by naked-eye readings in error by 2 mg. over-all, an error of about 0.5% might be introduced. In later work, use of a simple reading telescope with ocular micrometer has made possible a five-fold improvement in dividing the scale interval etched upon the graduated measuring tube, improving accuracy also in original calibration of this tube. (c) A temperature error of 1° causes an error in solubility that varies according to the slope of the solubility curves. For the three curves here studied, this error runs from about 1.0 to 1.6% for the hexahydrate curve; from 0.4 to 1.0% for the dihydrate curve; and from about 0.3 to 0.6% for the monohydrate curve. If the temperature of complete solution can be determined to tenths of a degree, which is possible with patience, the greatest error due to inaccurate temperature would thus not exceed 0.2%.

Apart from systematic error, the combined errors would, therefore, be expected to fall within 1%. The fact that the average divergence of the nineteen observed points from smooth curves does not exceed 0.2% speaks for the liberality of this estimate. The most obvious discordance is shown by the three points at 175.5, 175.9 and 177.1°. The first two of these were determined using an oil-bath and the last, thirteen months later, using an air oven and modified thermometry. The departures in solubility from the smooth curve are −0.3, +0.4 and −0.1%, respectively.

Applicability of the Method in Special Cases. (a) Large Changes of Solubility with Temperature.—In the case of strontium chloride used here as an example, the increase of solubility in the temperature range studied was about three-fold. Where the data are available, more than half of the salts in Brönsted's table show a smaller increase than this. With a single charging of the apparatus described, one may perhaps deal with a five-fold increase. In order to widen this range, one would distil all the solvent into the measuring tube, close the trap and replace the salt tube with another containing five times as

much salt. In this way one could deal with a twenty-five-fold increase in solubility, which must be regarded as exceptional. Alternatively, five times as much solvent may be used at one filling without sacrifice of accuracy, if the lower end of the measuring tube is increased stepwise in volume by blowing a few bulbs separated by graduated necks. (b) **Low Solubilities.**—If we take 0.1 mg. as the limit of visibility for illuminated crystals, then 1% accuracy demands 0.01 g. of solute. Using 5 g. of solvent, a solubility as low as one part in 500 might thus be measured with 1% accuracy. (c) **Higher Temperatures.**—Kracek reports[7] that his Pyrex tubes of 11 mm. outside diameter and 1.2 mm. wall thickness were not attacked by water nor fractured up to 250°.

Economy of Solvent.—After the desired temperature range has been covered for one solute, the solvent may be distilled back into the gradu-

ated tube. After closing the trap, a fresh container with a new solute may be sealed on in readiness for some other study. Provision for exhaustion and desiccation may be furnished by a small side-tube, which is later sealed off.

Summary

1. A modification of the synthetic method has been described which permits solubilities of nonvolatile solids in volatile liquids to be measured with accuracy better than 1% over a wide temperature range, with complete recovery of the single cubic centimeter of solvent utilized.

2. This is illustrated by the determination of solubility curves in the system strontium chloride–water in the range 20–200° with accuracy better than 1% using 1.097 g. of water. The solubilities are tabulated for each 5° interval of temperature, and two transition temperatures are reported.
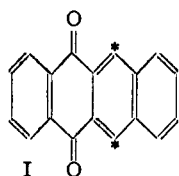
PRINCETON, N. J.   RECEIVED APRIL 2, 1936

A Synthesis of Rubrene

BY C. F. H. ALLEN AND LUCIUS GILMAN

In continuation of the investigation of the behavior of polynuclear ketones with the Grignard reagent[1] naphthacenequinone was selected for study. According to Fieser[2] this substance has the bond structure shown in I. In view of our previous work, in which it was shown that 1,4-addition to benzanthrones occurred, it seemed reasonable to expect that phenylmagnesium bromide should add to naphthacenequinone in a similar manner, the phenyl groups appearing in the starred positions. This was, indeed, found to be the case, as two stereoisomeric tetrahydroquinones II were obtained. In alkaline solution they were both easily dehydrogenated by atmospheric oxygen to give 6,11-diphenyl-5,12-naphthacenequinone III. The new quinone does not form a vat, in agreement with Fieser's observation[3] on naphthacenequinone; this behavior is also in accord with the effect of α,α'-substitution in the anthraquinone series.

The location of the phenyl groups in III was shown by the production of 1,4-diphenylnaphthalene-2-carboxylic and benzoic acids and 1,4-diphenylnaphthalene on alkaline fusion. The former acid was converted into the methyl ester and silver salt. The physical constants of all these substances agreed with those described in the literature.

The production of the diketones II and III affords experimental evidence of the correctness of Fieser's bond structure for naphthacenequinone. It also indicates that in the case of benzanthrone and other substances to which 1,4-addition involving a benzene ring takes place[1] the mechanism is exactly analogous to that observed with open chain conjugated systems of double bonds. The primary product is a saturated ketone, but since it is a dihydrobenzene it is easily dehydrogenated to the aromatic condition. In the case of naphthacenequinone, this intermediate is a tetrahydrobenzene and thus possible of isolation.

In October, 1935,[4] a short note appeared in which Dufraisse was recorded as being of the

(1) Allen and Overbaugh, THIS JOURNAL, **57**, 740, 1322 (1935).
(2) Fieser, ibid., **53**, 2329 (1931); Fieser and Martin, ibid., **57**, 1844 (1935).
(3) Fieser, ibid., **57**, 1846 (1935).
(4) Dufraisse, Velluz, Horclois, Étienne and Gerard, Bull. soc. chim., [5] **2**, 1546 (1935).