

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Solubilities of Salts in Water at High Temperatures¹BY HAROLD SIMMONS BOOTH AND RICHARD MACPHERSON BIDWELL²

In the study of a solvent system, the solubilities of various substances in the solvent and their variations with temperature are among the first factors to be considered, as these determine, to a large extent, the possible reactions. For example, barium sulfate, due to its insolubility, reacts very little with aqueous sodium carbonate. In molten sodium chloride, however, both substances are soluble, and a good yield of barium carbonate is obtained on quenching.^{3,4} Similarly, while silver iodide and sodium chloride react in liquid ammonia solution to precipitate silver chloride, this reaction is reversed in aqueous solution.

Reactions may similarly be altered by merely changing the temperature of a solvent, as various solutes show widely divergent temperature coefficients of solubility, both positive and negative. Many otherwise impossible reactions may become practicable at higher temperatures and pressures, especially in the region beyond the critical temperature, where a highly mobile gaseous solution may exist. Solubilities in this region are not predictable from a simple consideration of low-temperature solubilities. Quartz, for instance, has a solubility in steam both above and below the critical point nearing or exceeding that of many salts, such as sodium sulfate, which are quite soluble at room temperature.^{5,6}

Among the most interesting and complex applications of a knowledge of solubility relations is the study of mineral formation, a field of great theoretical and practical importance now under investigation from several different viewpoints.^{5,7-12} Aside from the actual study of mineral deposition, this knowledge can be applied to the synthesis of pure mineral crystals for optical and other purposes. Minerals commercially grown from solution include quartz, beryl and willemite. It seems

likely that some of the other types of crystals now grown from melts may be more profitably synthesized by recrystallization from solution, possibly in the gas phase, under high pressure.

Aqueous Solubility Measurement at High Temperatures.—Solubility measurement and other operations in water at temperatures near and beyond its critical point are exceptionally difficult due to its abnormally high critical pressure and to its enhanced corrosive properties at higher temperatures. Glass and quartz, commonly used for such studies on other solvents, are too soluble in water above 300° to permit precise measurements, particularly on fluorides.^{5,13} Since conventional transparent apparatus is thus eliminated, it is necessary to determine solubilities at high temperatures either by physical measurements, such as electrical conductivity or electrode potentials, or by methods involving the separation of phases at near-equilibrium conditions.⁵ The new method described here for solubility measurements at high pressures combines features of the internal filter,^{5,14-17} sampling,^{5,18-20} and hydrothermal quenching methods.^{5,21} It is essentially a method for filtration of the solution inside a high-pressure bomb by the utilization of the vapor pressure of the solution itself as the driving force. The solid phase is confined to a cylindrical crucible equipped with a filter across its mouth. This crucible is attached inside the top of the bomb, and during a run is immersed in the liquid or in the super-critical gaseous phase. A forced filtration is effected by rapidly cooling the outer walls of the bomb, causing the still hot solution contained in the filter crucible to be forced out. Such rapid separation is, of course, necessary as a slower cooling would give a final solute concentration different from that at equilibrium at the experimental temperature.

Apparatus.—The solubilities were determined in a standard American Instrument Company Micro test bomb of Type 347 stainless steel with a rated strength of 6000 pounds per square inch. The capacity of the bomb when

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(3) H. S. Booth, U. S. Patent 2,112,903 (April 5, 1938).

(4) H. S. Booth and E. F. Pollard, *Ind. Eng. Chem.*, **40**, 1983 (1948).

(5) H. S. Booth and R. M. Bidwell, *Chem. Revs.*, **44**, 477-514 (1949).

(6) F. G. Straub, *Univ. of Illinois Bull., Eng. Expt. Sta. Bull. Ser.*, no. 364 (1946).

(7) E. Buehler and A. C. Walker, *Sci. Monthly*, **49**, 148-155 (1949).

(8) F. W. Clarke, *The Data of Geochemistry*, Bull. No. 695, U. S. Geological Survey, Washington, D. C. (1920).

(9) I. I. Friedman, *THIS JOURNAL*, **70**, 2649 (1948).

(10) E. Ingerson, *Am. Mineral.*, **32**, 375 (1947).

(11) O. F. Tuttle and I. I. Friedman, *THIS JOURNAL*, **70**, 919 (1948).

(12) E. G. Zies, *Chem. Revs.*, **23**, 47-64 (1938).

(13) G. W. Morey and N. L. Bowen, *J. Soc. Glass Tech.*, **11**, 97 (1927).

(14) J. Königsberger and J. W. Müller, *Zentr. Mineral. Geol.*, **A339** (1906).

(15) J. Königsberger and J. W. Müller, *Chem. Zentr.*, **II**, 268 (1906).

(16) J. Königsberger and J. W. Müller, *Zentr. Mineral. Geol.*, **A413** (1912).

(17) W. A. Tilden and W. A. Shenstone, *Trans. Roy. Soc. (London)*, **A175**, 23 (1885).

(18) C. H. Holder and O. Maass, *Can. J. Research*, **18B**, 293 (1940).

(19) W. F. Waldeck, G. Lynn and A. E. Hill, *THIS JOURNAL*, **54**, 928 (1932).

(20) W. C. Schroeder, A. Gabriel and E. P. Partridge, *ibid.*, **57**, 1539 (1935).

(21) G. W. Morey and E. Ingerson, *Am. J. Sci.*, **35A**, 217 (1938).

fitted with the special internal accessories was 138.6 ml. A cylindrical stainless steel crucible was screwed inside the top of the bomb as shown in Fig. 1. A Micro Metallic sintered stainless steel filter disk was fixed across the mouth of the crucible by a screw clamping ring.

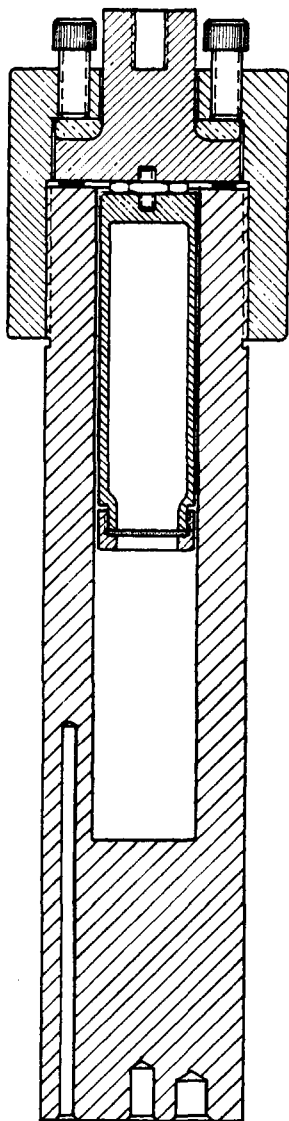


Fig. 1.—Section of bomb with filter crucible.

the bomb, thus decreasing the probability of leakage and contamination.

Experimental

Procedure.—A weighed amount of the salt to be investigated, usually 1 to 8 g., was placed in the filter crucible, and the desired amount of double-distilled water (40 to 70 ± 0.2 cc.) was pipetted into the bottom of the bomb. The air was blown out of both crucible and bomb by a stream of argon to evade corrosion due to atmospheric oxygen. The filter disk was clamped on the crucible, and the top with the crucible hanging from it was attached to the bomb and tightened down. The bomb was then inserted, still upright, into the furnace.

The bomb and contents were then heated as rapidly as possible to the equilibrium temperature. To minimize errors, the equilibrium temperature was ordinarily ap-

proached from the direction of lower solubility, *e. g.*, for the falling solubility-temperature curves observed for most of the systems studied, the bomb was heated rapidly to some 10 or 20° above the desired temperature, then cooled to that temperature. Ordinarily twenty to eighty minutes were required to attain the run temperature, and about two hours to become constant at that point.

When the equilibrium temperature had been reached, the furnace, containing the bomb, was inverted, thus immersing the filter crucible in the liquid phase. The assembly was then shaken periodically to facilitate saturation. To further encourage mixing, the furnace was occasionally returned to the upright position and agitated. Ordinarily a run lasted about twenty hours. At the end of a run, the furnace was turned to the upright position. The bomb was removed from the furnace and plunged, still upright, as rapidly as possible into cold water. The rapid diminution of water vapor pressure at the chilled outer walls of the bomb caused the portion of

The temperature of the furnace was recorded and controlled by a chromel-alumel thermocouple inserted into the wall of the bomb and connected through a Speedomax controller to relays operating a variable bank of resistors in series with the furnace. The maximum power input, when connected directly across a 110-volt line, was 2 kw. The thermocouples were calibrated at the freezing points of standard tin and zinc and of C. P. potassium dichromate, with the ice point as reference temperature at all times. The temperature of the bomb varied, in general, over a range of 2 to 10° during a run.

The entire furnace was mounted on a shaft and could be rocked by an electric gear-motor through cranks at 48 r. p. m. (Fig. 3). In this way the charge in the bomb was agitated without the use of stirrers or other devices entering

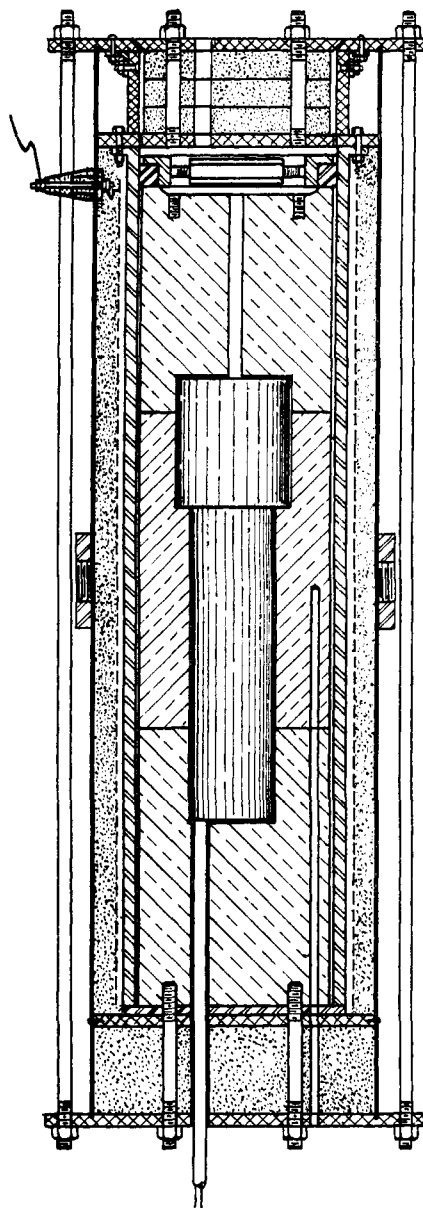


Fig. 2.—Section of furnace.

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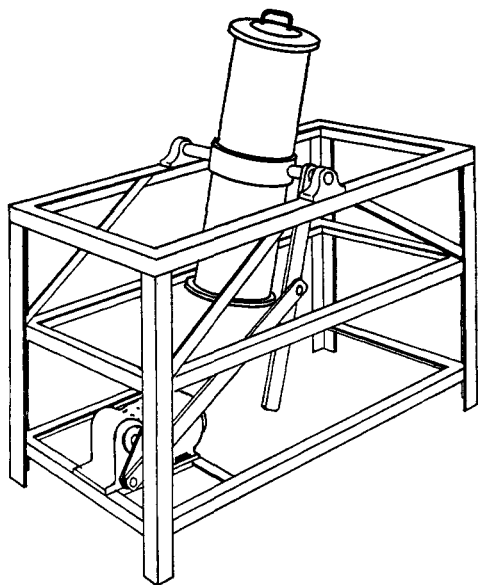


Fig. 3.—Diagram of furnace, frame and agitating apparatus.

the solution in the filter crucible to be driven out by its own vapor. Provided that very rapid precipitation or solution did not occur, solution of essentially the equilibrium concentration would thus be driven into the lower part of the bomb, and dry crystals would remain in the crucible. No plugging of the filter by fine particles of solute or other indication of precipitation has been observed, except for an occasional slight turbidity of a solution, which probably developed after filtration.

When cooled to a temperature below 100°, the bomb was removed from the water, dried, and opened. The solution or slurry in the bomb was poured into a graduate as a check for leakage in either direction. The bomb was

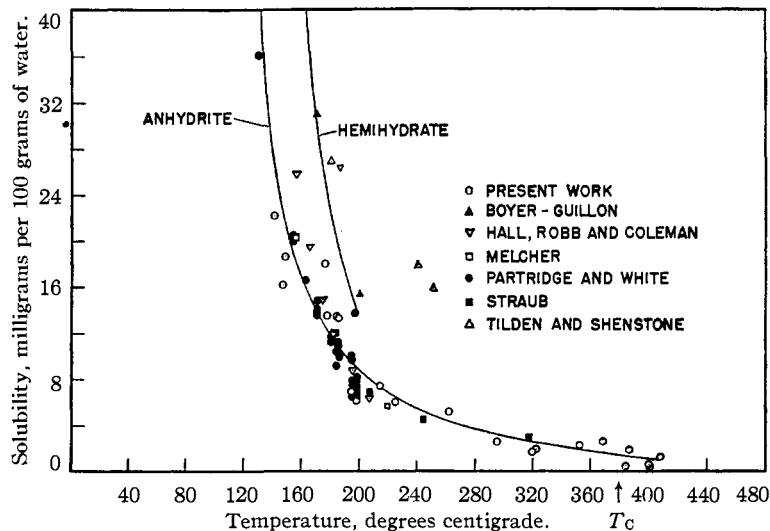


Fig. 4.—Solubility of calcium sulfate in water at 140–408°.

then thoroughly rinsed out, and the washings were added to the liquid measured. This entire liquid sample was then evaporated in a platinum crucible in an oven, and the residue was weighed to within 0.1 mg.

The solid residues from the evaporation of solutions appeared in general to be pure salts. In no solution tested

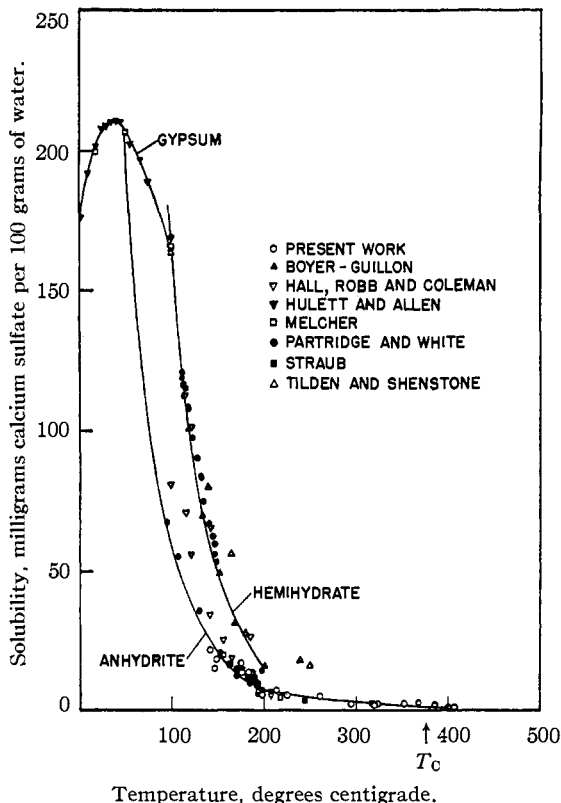


Fig. 5.—Solubility of calcium sulfate in water at 0–408°.

did a significant change in pH occur. Since no ions other than those of the salt and of water were present, a negligible amount of hydrolysis was indicated. Any contamination due to corrosion of equipment would manifest itself in colored solutions and residues. Unless the color in such a residue was only very faint, these results were rejected.

The crystals remaining in the filter crucible were carefully brushed out and weighed. Since some of the salt often adhered firmly to the walls of the crucible, the figures obtained from the loss of weight of the crystals were used only as a check.

The use of sintered metal filters did not permit precise solubility measurements to be made on fine powders, which were found to pass to an appreciable extent through the filters. Measurements were therefore made on pieces between 10 and 80 mesh, usually obtained from natural pure minerals or from a melt of the salt of interest. Lithium and calcium fluorides were fortunately available in optically pure form.^{21a} Calcium sulfate dihydrate, in the form of natural selenite, strontium sulfate as natural celestite, and sodium sulfate monohydrate crystals were used. It was necessary to melt the barium fluoride in an electric global furnace, in an inert atmosphere, the resulting product being fortunately a crystalline rather than a vitreous mass.

Calculations.—The principal assumptions made were that no changes in concentration occurred during or after

(21a) Supplied by the courtesy of the Harshaw Chemical Company.

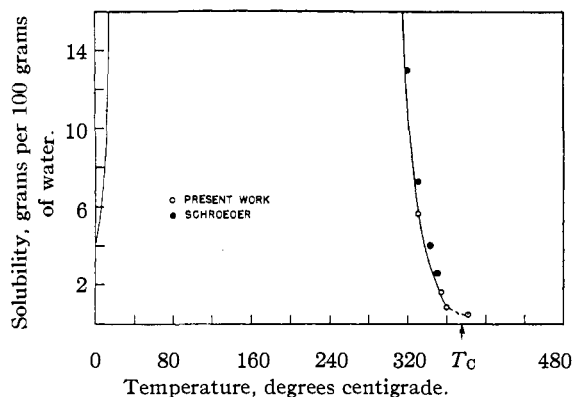


Fig. 6.—Solubility of sodium sulfate in water at 320–382°.

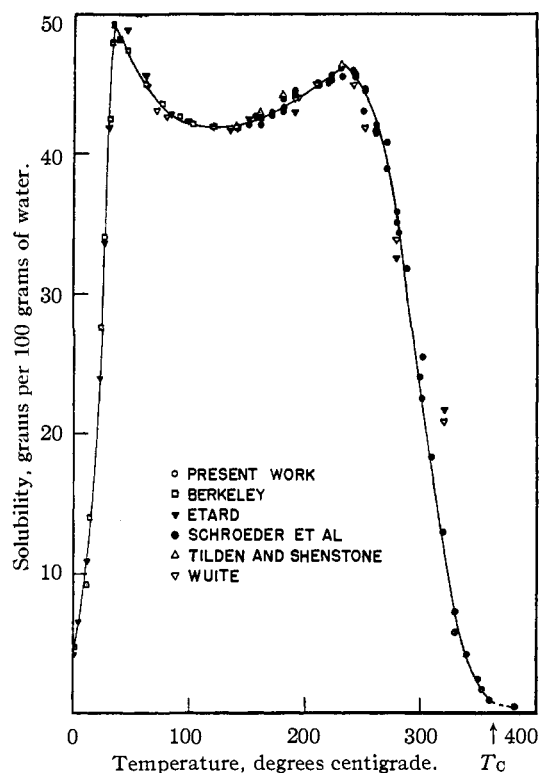


Fig. 7.—Solubility of sodium sulfate in water 0–382°.

filtration and that diffusion and flow through the filter was sufficient to permit saturation of the entire liquid phase, when present, outside as well as inside the filter crucible. That mixing was sufficient above 200° is indicated by the fact that runs varying from twenty to seventy hours in length gave consistent results. To check both assumptions, runs were made on calcium and sodium sulfates whose solubilities had previously been determined at high temperatures by other techniques.^{21,22} Agreement within approximately the precision of the earlier observations was obtained for both systems.

Since for most runs an appreciable proportion of the water was present in the vapor phase, corrections were applied to all results where two fluid phases had been present. It was assumed that the solubility in the vapor phase below the critical point was negligible as compared with that in the liquid phase. Although there is appar-

ently generally some small vapor-phase solubility, it has frequently been observed that solubilities in the liquid phase are by far the higher, especially for salts, except in the near vicinity of the critical point.^{5,6,18,23-25}

To minimize error due to solution in the vapor phase, the bomb was filled, for runs below the critical temperature, with as much water as possible, consistent with other experimental considerations. In this manner the bomb

TABLE I

SOLUBILITY OF CALCIUM SULFATE IN WATER		
Temp., °C.	Initial vol., ml.	Solubility, g./100 g. water
141 ± 4	50	0.0223
147	8	.0163
149	2	.0188
176	2	.0182
178	3	.0136
183	8	.0135
185	8	.0132
194	4	.0071
198	3	.0063
214	8	.0075
225	6	.0061
261	7	.0053
295	4	.0027
320	4	.0018
323	4	.0020
352	4	.0024
368	8	.0028
384	3	.0005
387	3	.0020
400	2	.0007
401	2	.0005
408	3	.0013

TABLE II

SOLUBILITY OF SODIUM SULFATE IN WATER		
Temp., °C.	Initial vol., ml.	Solubility, g./100 g. water
330 ± 1	72.5	5.74
354	2	1.65
360	3	0.900
382	2	0.377

TABLE III

SOLUBILITY OF STRONTIUM SULFATE IN WATER		
Temp., °C.	Initial vol., ml.	Solubility, g./100 g. water
194 ± 2	60	0.0032
203	1	.0025
208	1	.0031
259	2	.0026
284	5	.0029
293	4	.0017
307	4	.0022
333	2	.0013
339	2	.0018
348	1	.0016
381	2	.0009
401	3	.0003
426	2	.0005

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could be completely filled with a single phase, either liquid or gaseous, for runs above 369°.

The dissolved material present lowered the vapor pressure and therefore the proportion of the water in the vapor phase. The maximum effect of this phenomenon on the solubilities was calculated by Raoult's law and found negligible except for the most concentrated solution of sodium sulfate, to which a correction of 0.2% was applied.

The variations in the volume of the bomb due to elevated temperatures and pressures was calculated and considered in the reduction of data. A correction was also made for the estimated solid content of the distilled water.

TABLE IV
SOLUBILITY OF CALCIUM FLUORIDE IN WATER

Temp., °C.	Initial vol., ml.	Solubility, g./100 g. water
179 ± 3	50	0.0022
194 3	50	.0022
199 2	50	.0018
214 2	50	.0016
238 4	50	.0021
262 2	50	.0025
265 5	50	.0021
275 3	50	.0017
290 3	50	.0024
308 2	50	.0029
328 2	50	.0037
330 3	50	.0030
346 2	50	.0054
360 3	50	.0062
361 2	50	.0045
363 1	50	.0020
367 3	50	.0024
367 3	50	.0028
380 3	50	.0007
384 2	70	.0034
388 2	70	.0009
391 3	50	.0009
400 3	50	.0009
421 3	35	.0015

TABLE V
SOLUBILITIES OF BARIUM FLUORIDE IN WATER

Temp., °C.	Initial vol., ml.	Solubility, g./100 g. water
200 ± 2	65	0.0292
214 2	65	.0261
214 2	65	.0255
242 2	65	.0220
258 1	65	.0139
264 3	65	.0150
280 3	65	.0102
290 3	65	.0151
311 2	65	.0085
340 2	65	.0040
359 2	65	.0027
370 2	65	.0021
395 2	65	.0018

Discussion

Solubility measurements were made on six salts in water to temperatures above those previously reported, extending from about 200° to, or above, the critical temperature of water. The ranges of the results are summarized in Table VIII which

TABLE VI
SOLUBILITY OF LITHIUM FLUORIDE IN LIQUID WATER
198 to 375°

Temp., °C.	Initial vol., ml.	Solubility, g./100 g. water
198 ± 4	60	0.1081
202 4	60	.1118
222 2	60	.0726
232 2	60	.0718
235 3	65	.0605
243 4	65	.0726
252 3	65	.0582
269 2	65	.0477
272 3	60	.0566
290 3	65	.0471
300 3	65	.0493
313 5	60	.0475
322 4	65	.0452
330 2	50	.0445
331 3	65	.0459
332 3	65	.0489
340 3	65	.0388
343 3	65	.0437
345 3	65	.0404
349 3	65	.0357
350 5	65	.0370
351 5	50	.0340
353 2	60	.0333
362 5	65	.0262
368 4	65	.0243
369 5	60	.0235
374 5	65	.0208
375 3	60	.0222

TABLE VII
SOLUBILITY OF LITHIUM FLUORIDE IN WATER ABOVE THE
CRITICAL POINT

Temp., °C.	Solubility g./100 g. water	Temp., °C.	Solubility g./100 g. water
$D = 0.282$ ($v_0 = 40$ ml.)		$D = 0.423$ ($v_0 = 60$ ml.)	
380 ± 5	0.0075	375 ± 3	0.0222
421 2	.0042	409 4	.0086
437 2	.0026	$D = 0.459$ ($v_0 = 65$ ml.)	
448 3	.0044	379 3	.0181
$D = 0.353$ ($v_0 = 50$ ml.)		380 2	.0131
381 3	.0080	384 3	.0145
394 2	.0110	398 6	.0150
409 2	.0070	410 2	.0168
416 5	.0070	$D = 0.494$ ($v_0 = 70$ ml.)	
420 4	.0085	384 5	.0312
434 3	.0100	393 1	.0354
		394 2	.0149
		400 3	.0214
		403 4	.0209

also gives the upper temperature limits of previous investigations.

It is reasonable to expect solubility in gaseous phases at a given temperature to change with the density of the solvent, and therefore with the pressure, a hypothesis confirmed by experi-

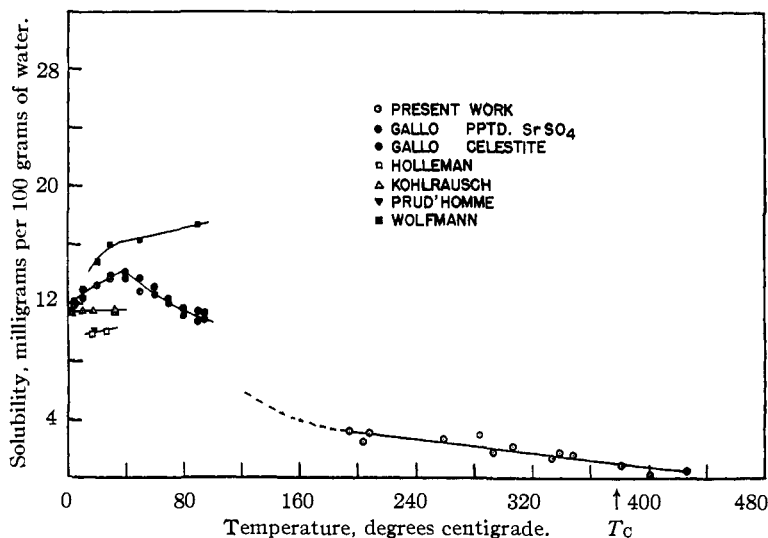


Fig. 8.—Solubility of strontium sulfate in water.

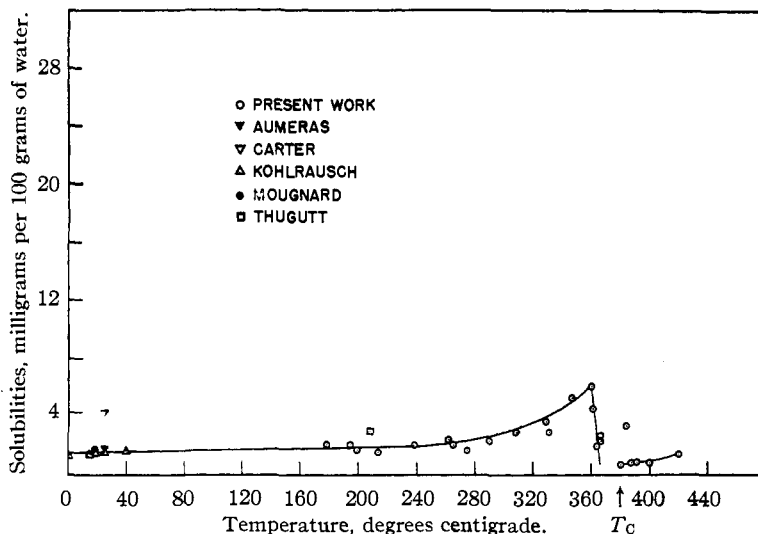


Fig. 9.—Solubility of calcium fluoride in water.

TABLE VIII

Salt	Temp. range, °C., present work	°C.	Previous limit, Ref.
CaSO ₄	141-408	318	22
Na ₂ SO ₄	330-382	350	20
SrSO ₄	194-426	95	26
CaF ₂	179-421	40	26, 207, 27 ^a
BaF ₂	200-395	30	26
LiF	198-448	35	26

^a Based on a single observation.

ence.^{5,6,23,28-30} A study was made here of the de-

(26) A. Seidell, "Solubilities of Inorganic and Metal-organic Compounds," D. Van Nostrand Company, New York, N. Y., 1940.

(27) S. J. Thugutt, *Arch. mineral Soc., sci. Varsovie*, **12**, 191-192 (1936).

(28) A. Smits, *Z. physik. Chem.*, **52**, 587 (1905).

(29) A. Smits, *Rec. trav. chim.*, **49**, 962 (1930).

(30) C. J. van Nieuwenberg and P. M. van Zon, *Rec. trav. chim.*, **54**, 129 (1935).

pendence of the solubility of lithium fluoride in water at a given temperature above the critical point of the solution on the density of the solvent. Densities were varied from 0.282 to 0.494, and the solubility measurements made at a number of temperatures for each density.

The variations in solubility with solvent density observed were very similar to those obtained by Tyrer,^{5,23} using the synthetic technique on salts in alcohols above their critical points. A plot of isothermal solubility curves for lithium fluoride in water as a function of pressure (Fig. 14) was of a different type than that of van Nieuwenberg and van Zon^{5,30} for silica in water above its critical point, indicating that the density dependence of solubility may depend to a larger extent on the nature of the solute than on that of the solvent. The well-known ether-anthraquinone system,^{5,23} which has a non polar

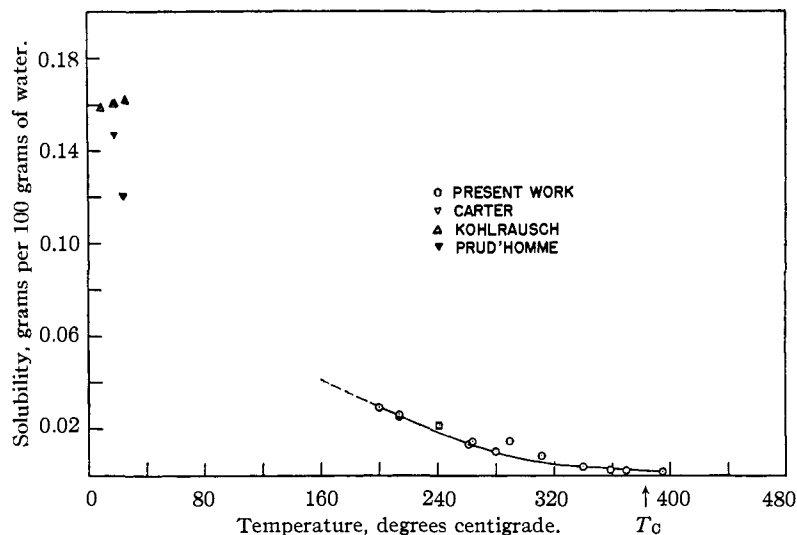


Fig. 10.—Solubility of barium fluoride in water.

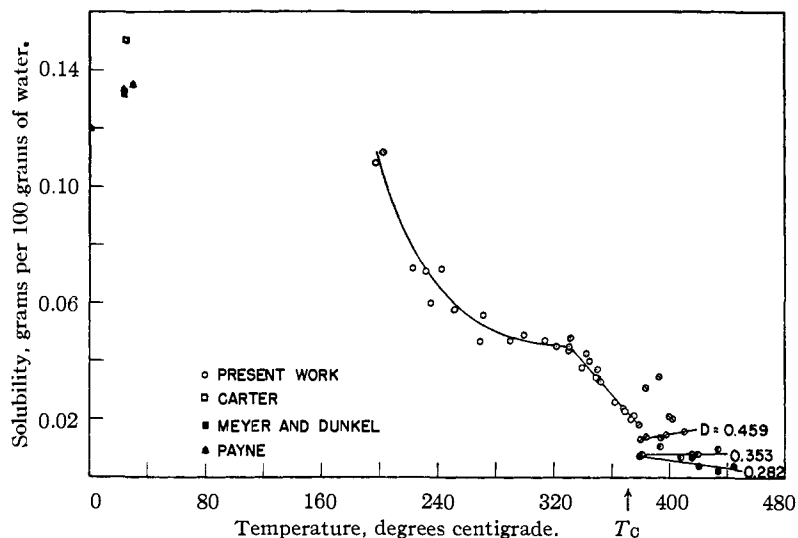


Fig. 11.—Solubility of lithium fluoride in water.

solute, resembles the silica-water system.²⁹

The solubility of lithium fluoride in water above its critical point was found to remain practically constant with temperature at a solvent density of about 0.36. It is interesting that this is close to the critical density. The solubility increased with temperature for higher densities and decreased with rising temperature for lower densities.

The solubilities of all substances tested, except calcium fluoride, were found to decrease toward higher temperatures, in the ranges observed, up to the critical temperature. The solubility measurements made on the previously investigated sodium²⁰ and calcium²² sulfates to check the method agreed well with published values. The observed solubility of calcium fluoride increased very slowly up to 300°, falling somewhat below Thugutt's value at 207°,²⁷ then increased more rapidly, breaking just below the critical temperature to

much lower values, to increase again in the gas-phase region.

The interesting break in the lithium fluoride solubility curve at about 332° indicates a possible polymorphic transition at this point.

The error in the recorded solubility due to temperature fluctuation during the run is estimated to be of the order of 3%. A greater uncertainty might be expected if the variation in temperature passed through the critical point. Odd mixing effects might result from repeated disappearances and reformations of the meniscus. This may be the explanation for the anomalous solubility observed for calcium fluoride at 384°.

To the error attributed to temperature variation must be added an absolute error of approximately ± 0.2 mg., or for most runs ± 0.3 mg. per 100 g., which can be considered due to weighing and other errors intrinsic in the technique.

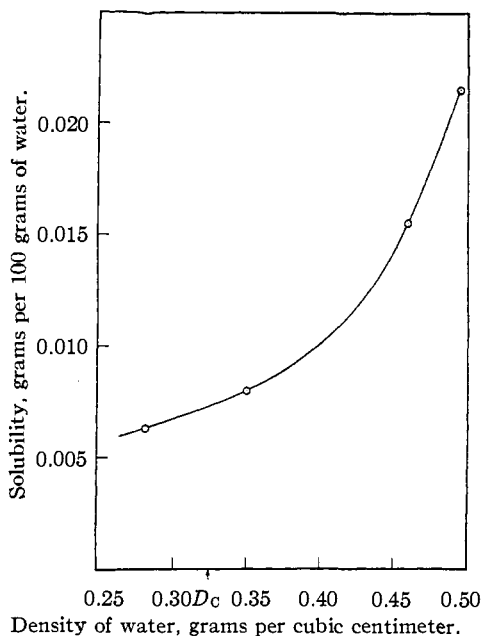


Fig. 12.—Solubility of lithium fluoride in water at 400° as a function of solvent density.

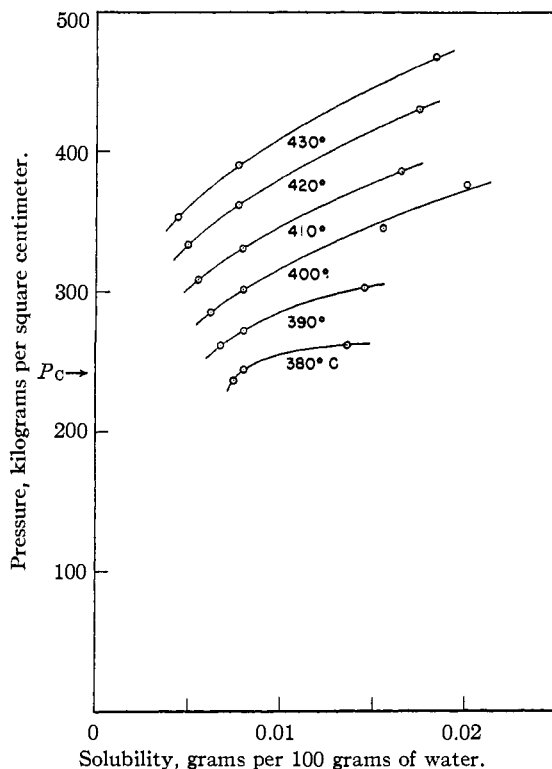


Fig. 14.—Isotherms for lithium fluoride in water above the critical point solubility as a function of pressure.

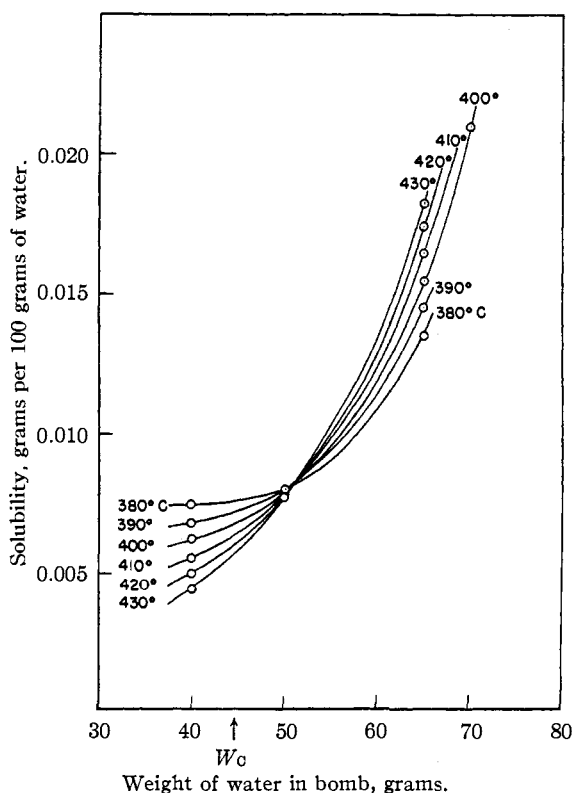


Fig. 13.—Isothermal solubilities of lithium fluoride in water at various temperatures above the critical point as a function of the weight of water contained in the bomb.

In the cases of sodium and calcium sulfates, as well as other substances not considered here, an

increasing solubility toward lowered temperatures indicates the incipient stability of a hydrated crystal form. We might therefore infer that the hitherto unobserved hydrates of strontium sulfate and lithium and barium fluorides might be stable in water, if it were supercooled to some distance below its normal freezing point.

The precision of the results is less than that of many solubility measurements below the boiling point of water. The results, however, compare favorably with those obtained by other, generally more complicated, methods in this region. Furthermore, the salts observed could be characterized in general as "very slightly soluble." The temperature limits of previous investigations listed in the above table are another measure of the limitation of most chemical thought to "beaker chemistry." Of the great number of sparingly soluble substances known, the solubilities of a mere half dozen have been measured to above 300°, and fewer yet in the gas phase.

One practical object of the present solubility measurements was to study the possibility of making synthetic optical crystals of calcium fluoride or other substances by recrystallization from solution near or above the critical temperature of the solution. It seems probable, however, that for the substances studied, some other solvent or solubilizing agent would probably be better than pure water for such a crystallization, as the solubilities near and above the critical point are so low

that even the highly enhanced mobility of the solution in that region would probably not make high temperature crystallization advantageous as compared with possible lower temperature crystallization. It is quite possible, of course, that at temperatures and pressures beyond the range of the present experiments, the solubility may increase to a value at which an excellent yield of crystals may be obtained. In this respect, it is encouraging that lithium fluoride at the higher solvent densities and calcium fluoride show increasing solubilities above the critical point.

Acknowledgment.—The generosity of the Harshaw Chemical Company, which made this investigation possible by the endowment of a fellowship and by supplying experimental materials, is gratefully acknowledged.

Summary

A technique for the measurement of solubilities at high temperatures and pressures has been developed, in which filtration of the saturated solution is effected by quenching the high-pressure vessel. The solubilities of four sparingly soluble

salts, calcium, barium, and lithium fluorides and strontium sulfate, formerly known only at low temperatures, were measured up to or past the critical temperature of water. The previously investigated solubilities of calcium and sodium sulfates at high temperatures were checked and extended.

The dependence of the solubility of lithium fluoride in water above its critical point on the density of the solvent was measured at several temperatures.

The very low solubilities of the salts investigated in the region of the critical point make it seem unlikely that the recrystallization from their pure aqueous solutions of these salts will be a practical method for the making of synthetic crystals of optical quality unless at appreciably higher temperature and pressure.

The precision of the results obtained compares well with other measurements in the same region, most of which required far more complex apparatus.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

Some Fluoride Complexes of Certain Bivalent and Tervalent Metal Ions in Aqueous Solution¹

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The purpose of this investigation was to determine the formulas for some fluoride complexes with metal ions in aqueous solution. Although complex fluoride compounds have been studied,³⁻⁸ the evidence for the existence of the complex ions is based mainly on the formation of solid compounds and on the behavior of the other halides, as pointed out by Ephraim⁴ on the existence of $\text{CrF}(\text{H}_2\text{O})_5^{++}$ and $\text{CrF}_2(\text{H}_2\text{O})_4^+$, similar to the ions $\text{CrCl}(\text{H}_2\text{O})_5^{++}$ and $\text{CrCl}_2(\text{H}_2\text{O})_4^+$. The complex $\text{FeF}_6^=$ is mentioned in most analytical texts. The literature shows a complex formed between manganese(III) and fluoride ion; however, if a specific complex is mentioned, it

is $\text{MnF}_5\text{H}_2\text{O}^=$ ⁹ and not $\text{MnF}_6^=$ as would seem logical considering the similarity between manganese(III) and iron(III).

In this investigation spectrophotometric methods were used to attain the evidence of complexing. There were limitations because of the presence of fluoride ions, which will combine with hydrogen ion to give hydrofluoric acid especially in solutions with a pH below 4. Hence, plastic optical cells were used in place of glass. Since all plastic materials absorb light in the ultraviolet as well as the near infrared only ions which give a color in the visible range were considered. Therefore, ions which are colored in the completely hydrated form offer the best starting point. Chromium(III), manganese(III), copper(II), cobalt II, nickel(II), vanadium(III) and titanium(III) are some of the possibilities which are colored and have been shown to complex. They were used to investigate the possibilities of complexing with fluoride ion.

Manganese(III) Fluoride Complexes

Of the various spectrophotometric methods presented in the literature the limiting density method developed by Bent and French¹⁰ was used

(9) The water molecules which are coordinated with the ions have been omitted from the formulas except where the discussion is clarified by including them.

(10) H. E. Bent and C. L. French, *THIS JOURNAL*, **63**, 568 (1941).

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(4) F. Ephraim, "Inorganic Chemistry," 4th ed. (translation Thorne and Roberts) Interscience Publishers, Inc., New York, N. Y., 1946.

(5) A. K. Babko and K. E. Kleiner, *J. Gen. Chem. (U. S. S. R.)*, **17**, 1259 (1947).

(6) R. J. MacWalter and S. Barrett, *J. Chem. Soc.*, 517 (1934).

(7) "Gmelins Handbuch der anorganischen Chemie," No. 5, Verlag Chemie G. m. b. H., Leipzig, 1926.

(8) R. Weinland, "Einführung in die Chemie der Komplex-Verbindungen," F. Enke, Stuttgart, 1924.