

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE UNIVERSITY OF MICHIGAN]

THE SOLUBILITY OF CALCIUM SULFATE FROM 0 TO 200°

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The Literature on the Solubility of Calcium Sulfate

A search of the literature, complete up to May, 1928, covering references to the solubility of any of the various forms of calcium sulfate, was made and the original data abstracted from these articles were compared. Such as seemed significant have been utilized in conjunction with the determinations described in the present paper.

For the purposes of this paper all concentrations have been expressed in parts of CaSO_4 per million parts of solution. Conversion from original data has been carried out with the use of the density measurements of Hulett and Allen³ on calcium sulfate solutions, although in view of the low solubilities encountered this is a refinement well within the experimental error.

The Solubility of Gypsum.—The lower curve of Fig. 1 represents the solubility of gypsum as determined by the values of Raupenstrauch,⁴ Hulett and Allen,³ Melcher,⁵ and Cavazzi.⁶ The excellent agreement of the four sets of data is checked by individual determinations at various temperatures made by other recent investigators.

It should be noted here that Raupenstrauch has never received the credit due him for the first accurate determination of the gypsum solubility curve. His article antedates the well-known and equally excellent work of Hulett and Allen by seventeen years but it has been quite generally ignored.

The Solubility of Calcium Sulfate Hemihydrate.—Marignac,⁷ Potilitzin⁸ and Cavazzi⁶ found the solubility of dehydrated gypsum at room temperature to be approximately five times that of fully hydrated gypsum. That these values represent the solubility of calcium sulfate hemihydrate

¹ This paper forms part of the dissertation submitted by Dr. Partridge in partial fulfillment of the requirements for the Ph.D. degree at the University of Michigan. Acknowledgment is made to The Detroit Edison Company which sustained this work through a fellowship.

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³ G. A. Hulett and L. E. Allen, *THIS JOURNAL*, **24**, 667-669 (1902).

⁴ G. A. Raupenstrauch, *Monatsh.*, **6**, 563-569 (1885).

⁵ A. C. Melcher, *THIS JOURNAL*, **32**, 50-66 (1908).

⁶ A. Cavazzi, *L'Industria Chimica*, **6**, 366-368 (1904); *Chem. Centr.*, [5] **9**, 1693-1694 (1905).

⁷ C. Marignac, *Ann. chim. phys.*, [5] **1**, 274-282 (1874).

⁸ A. Potilitzin, *J. Russ. Phys.-Chem. Soc.*, **26**, 170, 221-229 (1894); *Ber.*, **27**, 613-616 (1894); *Chem. Centr.*, 515 (1894).

seems apparent from the values published by Chassevent,⁹ in 1926, for this substance. The upper curve of Fig. 1 represents the solubility of the hemihydrate as determined by the data of the latter investigator, and shows the individual points previously reported. Chassevent found that hemihydrate solutions were very unstable at lower temperatures but were relatively stable for a short range below 100°.

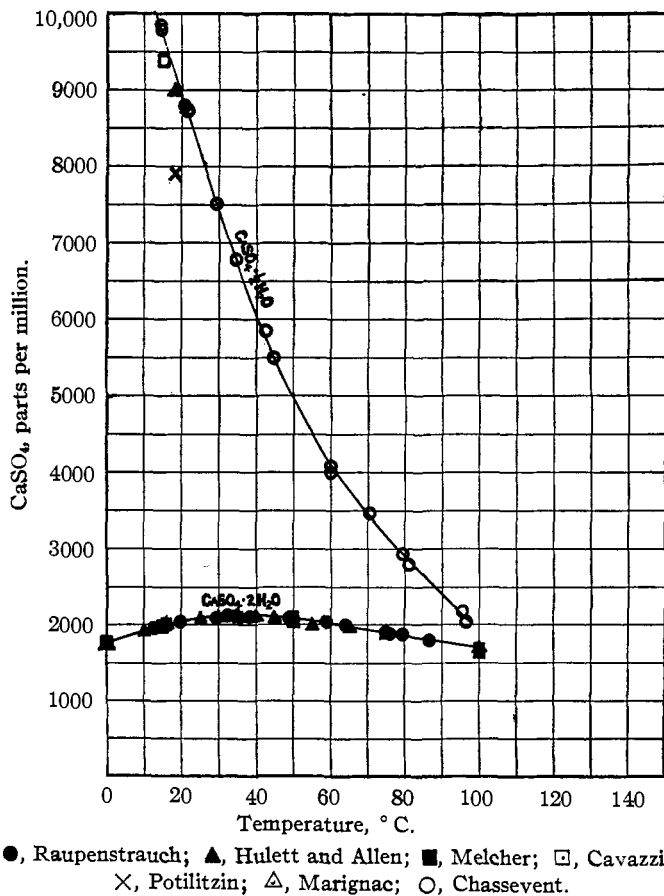


Fig. 1.—Solubility of gypsum and hemihydrate at temperatures from 0–100° C. expressed in parts per million of CaSO₄.

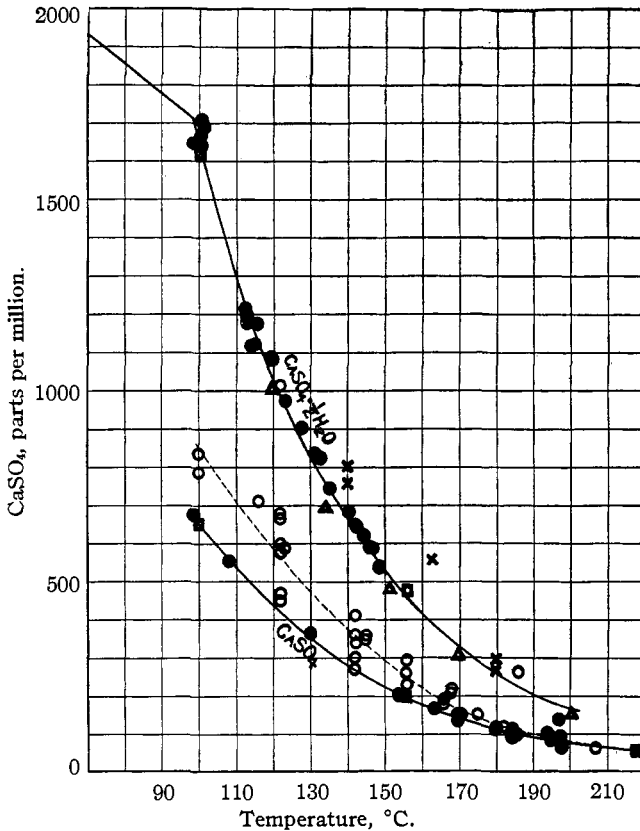
The Solubility of "Soluble Anhydrite."—It seems probable, at the present time, as a result of a series of investigations culminating in the work of Linck and Jung¹⁰ and of Jung alone,¹¹ that only three crystal forms of

⁹ I. Chassevent, *Bull. soc. encour. ind. nat.*, 789–803 (1926); *Ann. chim.*, [10] 6, 313–351 (1926).

¹⁰ G. Linck and H. Jung, *Z. anorg. Chem.*, 137, 407–417 (1924).

¹¹ H. Jung, *ibid.*, 142, 73–79 (1925).

calcium sulfate exist and that "soluble anhydrite," long a mystery, possesses the crystal structure of calcium sulfate hemihydrate. Evidence confirming this statement will be presented in the near future by Ramsdell and Partridge in a crystallographic study of the forms of calcium sulfate produced at various temperatures between 100 and 200° in contact, re-



X, Tilden and Shenstone; Δ , Boyer-Guillon; \square , Melcher;
 O, Hall, Robb and Coleman; \bullet , White and Partridge.

Fig. 2.—Solubility of gypsum, hemihydrate and anhydrite from 100 to 220° C. expressed in parts per million of CaSO₄.

spectively, with water and with dry air. Additional circumstantial evidence will be shown in the present article from the fact that the solubility curve for hemihydrate below 100° found by Chassevent is continuous with the solubility curve above 100° previously ascribed to "soluble anhydrite."

When gypsum is the initial solid phase in contact with water, the solubility at temperatures above 100° is shown by the upper curve of Fig. 2,

which is determined by the data of Boyer-Guillon,¹² Melcher⁵ and Hall, Robb and Coleman¹³ on "soluble anhydrite," and of the authors of this paper on calcium sulfate hemihydrate. The less accurate values of Tilden and Shenstone¹⁴ are also shown.

This solubility curve for hemihydrate intersects that for gypsum at a temperature of approximately 98°, which is in excellent accord with the observation made by Davis,¹⁵ and checked by the authors of this paper, that gypsum crystals in contact with water at 100° are gradually converted to hemihydrate.

The Solubility of Anhydrite.—Melcher⁵ calculated the solubility of anhydrite at 100, 156 and 218° from conductivity measurements carried out with solutions of calcium sulfate in a platinum-lined bomb, using as solid phase either an initial addition of anhydrite or anhydrite formed from an initial addition of gypsum by maintaining the bomb at 218° for several hours. Hall, Robb and Coleman¹³ made a series of direct determinations in a small laboratory boiler, using solutions of calcium sulfate in contact with a solid phase of anhydrite prepared by burning gypsum at a dull red heat in a muffle furnace for several hours. The dotted line of Fig. 2 is determined by the average values of the individual determinations of the latter investigators, while the bottom curve, determined by the authors of this paper, passes through the points found by Melcher.

Experimental Work

General Method.—Solubility values at intervals in the temperature range 100–200° were obtained by analysis of the sulfate content of samples removed from an experimental boiler housed in a thermostat which could be maintained for any desired period of time at a temperature constant to within 0.5°. This boiler was initially charged for each series of determinations with 10 liters of a solution of calcium sulfate saturated with gypsum at room temperature, to which solution was added 10 g. of precipitated gypsum powder. Solution samples were removed through a filter within the boiler and were cooled to 14–16° in a cooling coil while still subjected to boiler pressure. The sulfate concentration of these samples was found gravimetrically by precipitation as barium sulfate.

Apparatus.—A photograph of the experimental boiler unit used in the authors' work is shown in Fig. 3. This was used for the solubility work here described and also for a series of scale formation tests which will be described in the future. For the determinations of solubility the unit consisted essentially of the boiler proper, suspended within an *air thermostat*, fed by a small *pump*, and equipped with an *internal filter* connected to a *cooling coil* outside of the thermostat.

¹² A. Boyer-Guillon, *Ann. conserv. arts metiers*, [3] 2, 187–211 (1900).

¹³ R. E. Hall, J. A. Robb and G. E. Coleman, *THIS JOURNAL*, 48, 927–938 (1926).

¹⁴ W. A. Tilden and W. A. Shenstone, *Phil. Trans. Royal Soc. London*, I, 175, 23–36 (1884).

¹⁵ Davis, *J. Soc. Chem. Ind.*, 26, 727–738 (1907).

The *boiler* was a two-foot length of six-inch steam pipe, fitted with companion flanges. The boiler feed line and an exhaust line were tapped into the top flange, while the bottom flange carried a special plug which served to introduce the internal filter and to make connection between this filter and the external cooling coil.

The *air thermostat* was made of sheet steel with two spaced linings of transite to cut down heat radiation. It was heated by Chromel A resistance coils and rapid circulation of the air was maintained by a motor-driven fan. The temperature of the thermostat was controlled by a mercury column, the expansion of which operated a relay controlling the current through the heating coils. The fluctuation of the thermostat air temperature was rapid and was less than 0.5° . Such a fluctuation was considered negligible in view of the relatively great heat capacity of the boiler and its contents.

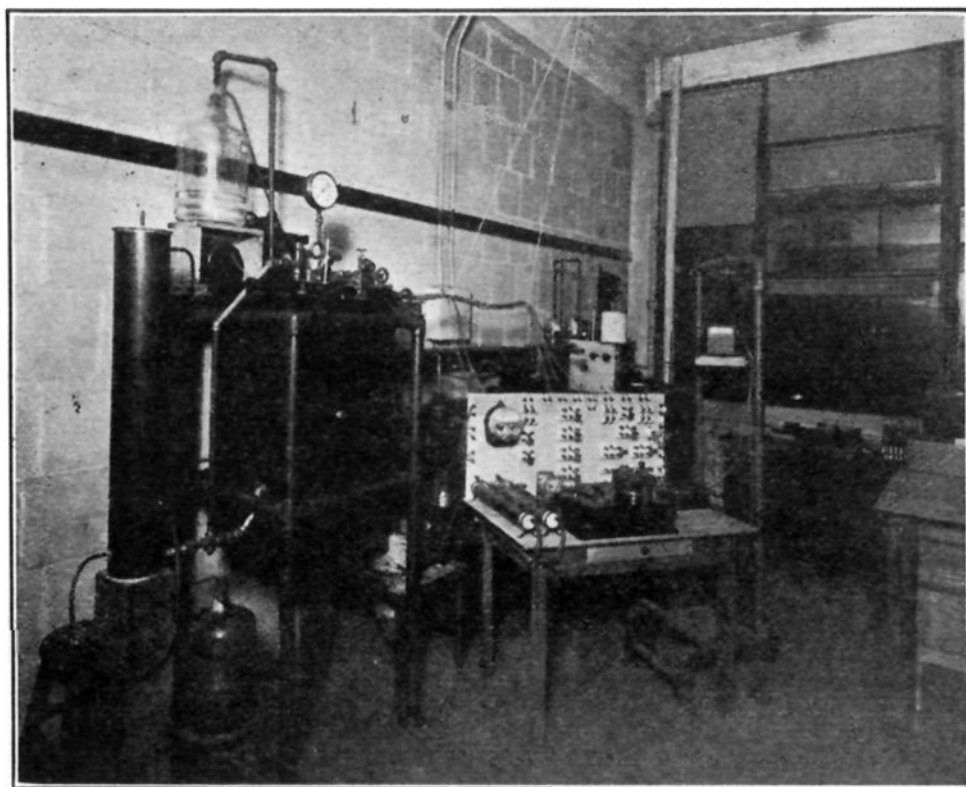


Fig. 3.—Equipment used in determining solubilities of calcium sulfate at temperatures above 100°C .

The *pump*, used for introducing solution into the boiler under pressure during an extended series of determinations, was loaned to the authors by Dr. R. E. Hall. It has previously been described by him elsewhere.¹⁶

The *internal filter* consisted of fifteen layers of very finely-woven cotton cloth supported between fine copper gauze and perforated metal plates and mounted in a cylindrical cup. Since this was mounted vertically within the boiler, a deposit of solid material accumulated in the cup during each run and served not only as an additional filter medium but also as a safeguard against the passage of supersaturated solution.

The *cooling coil* was made from twenty feet of $1/8$ " galvanized iron pipe bent in a spiral and suspended in a container through which tap water was rapidly circulated. The flow of solution samples was continuously downward from the internal filter to the discharge from the cooling coil. This discharge was regulated by a small needle valve just above the outlet.

¹⁶ R. E. Hall and others, *Carnegie Inst. of Tech. Bull.*, 24, 145 (1927).

The measurement of temperatures was carried out with copper-nickel thermocouples, since it was necessary to use this pair of elements in the scale formation tests also conducted in this boiler. For the solubility work the temperatures of the solution within the boiler and of the air thermostat were measured with a Leeds and Northrup Type K potentiometer and a galvanometer of the enclosed lamp-and-scale type, using ice in a thermos bottle for a cold junction. The thermocouples used were calibrated directly against a standardized thermometer in the vapor of boiling liquids. Distilled water, ethylene bromide, bromobenzene, aniline and nitrobenzene were used to establish the calibration curve between 100 and 200°. This curve was almost a straight line, with a slight concavity downward.

Experimental Procedure.—During the early part of the solubility determinations it was discovered that hemihydrate remained apparently stable for periods up to forty-eight hours when held at temperatures between 100 and 130° but at temperatures above the latter value the solubility values gradually dropped toward the anhydrite curve. In the neighborhood of 200° this change took place within a few hours. Advantage was taken of this natural establishment of equilibrium with anhydrite in determining the solubility curve for this form, instead of using a solid phase of anhydrite prepared by the ignition of gypsum.

At the start of each series of determinations, the boiler was filled with 10 liters of a solution saturated with respect to gypsum at room temperature, with a concentration very close to 2000 parts per million of CaSO_4 . Ten grams of gypsum powder was introduced with the solution. The air thermostat was heated up to the temperature at which the first sample was to be taken and temperature readings were taken at occasional intervals until the boiler solution had become constant at this value. The first samples were taken at from two to twelve hours after this attainment of the steady state, longer intervals being used in the later series of determinations. Second samples were taken after a similar interval and in some cases third samples after another interval. The temperature of the air thermostat was then changed and the same procedure repeated at the new temperature. When the solution level in the boiler had dropped to that of the internal filter, a fresh charge was pumped in. During the early runs the stock solution of saturated calcium sulfate solution was used for refilling; during the later runs, distilled water, because it was found by experience that less time was lost in coming to equilibrium from a condition of undersaturation than from one of supersaturation. This was particularly noticeable in the case of determinations with anhydrite, so that points for this curve were obtained with successively decreasing temperatures in order to prevent the possibility of supersaturation.

Duplicate 250-cc. portions of solution were obtained at each sampling. The temperature of the cooled sample was measured and always fell between 14 and 16°. From this temperature and the calibration for the volumetric flask used in measuring the samples, the mass of the sample was obtained. The sample and the washings from the volumetric flask were acidified with 0.5 cc. of concentrated hydrochloric acid, and were evaporated on a hot-plate to a volume of approximately 200 cc. The sulfate was then precipitated with 20 cc. in excess of the calculated amount of a solution of barium chloride containing 20 g. per liter of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. The solution then was returned to the hot-plate and again evaporated to 150–200 cc. (one to two hours). It was then filtered through an alundum crucible and the precipitate was washed thoroughly with hot water. The crucible was ignited in an electric muffle furnace at approximately 850° for one hour and was cooled in a desiccator.

Experimental Data and Discussion

The experimentally determined solubilities are given in Table I. Values representing pre-equilibrium conditions at various temperatures have been omitted, as have been values representing transition from hemihydrate to anhydrite in the range above 130°. The data of Table I are presented also in Fig. 2 as the solid circles. From Fig. 2 it is readily evident that the data of the authors for the hemihydrate curve check excellently with

TABLE I
EXPERIMENTAL SOLUBILITY DATA

Run no.	Time at temp., hrs.	Temp., °C.	Sol., parts per million		Run no.	Time at temp., hrs.	Temp., °C.	Sol., parts per million	
			Hemi-hydrate	An-hydrate				Hemi-hydrate	An-hydrate
1	10.0	144.3	620			10.5	112.4	1216	
2	10.5	100.8	1709			22.5	112.5	1198	
	4.0	119.4	1088			22.5	112.5	1202	
	10.0	119.8	1072			34.5	112.9	1179	
	9.0	123.2	976			34.5	112.9	1177	
	10.0	123.2	972			9.0	114.0	1117	
	2.5	131.2	835			9.0	114.0	1119	
	1.0	132.7	827		6	1.5	197.0	139	
	3.0	142.2	645		7	2.5	193.8		98
	4.0	142.2	644			2.5	193.8		102
	4.5	145.8	590			1.5	180.0		119
	1.0	148.9	532			1.5	180.0		114
	3.0	148.9	535		8	4.5	195.2		80
	3.0	163.3		167		2.0	198.2		79
3	1.0	100.3	1666			6.5	184.5		111
	5.0	100.3	1640			6.5	184.5		114
	1.5	101.3	1690		9	4	198.4		80
	2.5	101.4	1690			4	198.4		74
	3.0	127.8	902		10	18	197.9		76
	12.0	140.1	683			18	197.9		83
	3.0	146.6	586			10	185.6		101
	6.0	195.2			10	185.6		102	
	2.0	197.9			24	184.2		105	
	4.0	197.6			24	184.2		93	
4	11.0	98.5	1648			8	169.6		152
	11.0	98.5	1640			8	169.8		136
	2.5	100.3	1667			9	169.5		137
	2.5	100.3	1667			9	169.5		140
	16.0	112.7	1182			20	169.6		137
	16.0	112.7	1178			22	153.9		201
	4.0	115.5	1175			22	153.9		206
	4.0	115.5	1177			12	108.0		555
	8.0	135.1	745		11	11	197.6		94
	8.0	135.1	744			11	197.6		64
	2.5	170.5				12	98.6		677
	2.5	170.5				12	98.6		677
5	10.5	112.4	1217			9	130.0		362

the previously published values of Boyer-Guillon, Melcher, and Hall, Robb and Coleman. In the case of the anhydrite curve, however, the authors' points check identically with those of Melcher and determine a curve which falls 200 parts per million below that of Hall, Robb and Coleman at 100°, approaching the latter as the temperature increases, until they attain an identical value at 200°.

It is the belief of the authors that the lowest points obtained by Hall, Robb and Coleman at each temperature for the solubility of anhydrite represent the most accurate determinations, and that the higher values indicate that complete conversion to anhydrite was not obtained in the preliminary burning of gypsum for their experiments. The variation between different determinations at the same temperature is easily accounted for by the assumption that varying amounts of hemihydrate were still present in the anhydrite added to their experimental boiler as the solid phase. This assumption is supported by the note appearing in their data to the effect that crystallographic examination of the solid phase from their boiler during one experiment showed material with refractive indices between 1.550 and 1.600. The alpha index of hemihydrate has been determined as 1.550, while the alpha index for anhydrite, its lowest index, is 1.571.¹⁷

At this time it is not possible to define with certainty the equilibrium diagram for the various forms of calcium sulfate in contact with water. The authors suggest the system shown in Fig. 4, in which the solubility curves of Figs. 1 and 2 are combined. Use has here been made of a solubility value for anhydrite at 33° given by Haddon and Brown,¹⁸ which indicates the course of the anhydrite curve below 100°. This portion of the curve requires accurate determination before the intersection of the anhydrite and gypsum curves can be known with any certainty, but at present it appears to be at 38-39°, which is the maximum of the gypsum solubility curve.

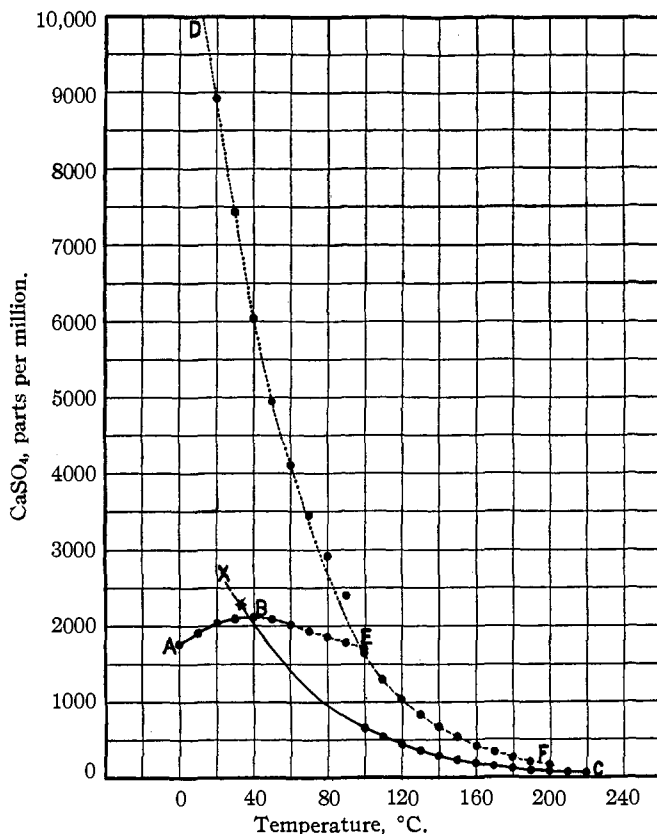
The transition temperature from gypsum to anhydrite given by van't Hoff¹⁹ is 66°. This value was obtained by two separate methods, one depending on vapor pressure and dilatometer measurements on concentrated salt solutions containing calcium sulfate, the other depending on a thermodynamic treatment of solubility data. The latter method is in error, since the solubility data of Boyer-Guillon were used under the misconception, common at the time, that they referred to anhydrite. The former method presents experimental difficulties which made van't Hoff consider it less certain than the latter. This transition temperature of 66°, therefore, is not securely founded.

¹⁷ E. S. Larsen, *Proc. Am. Soc. Testing Materials*, **23**, 236 (1923).

¹⁸ G. L. Haddon and M. W. A. Brown, *J. Soc. Chem. Ind.*, **43**, 11-16T (1924).

¹⁹ Van't Hoff and others, *Z. physik. Chem.*, **45**, 257-306 (1903).

From work of the authors on calcium sulfate scale formation, which will be described in the future, it appears that while anhydrite should apparently be the stable solid phase formed from solution over the whole range of boiler temperatures, hemihydrate is actually formed in the range of 100–130°. This apparent anomaly requires further study, as does the



●, From Figs. 1 and 2; *, Haddon and Brown. ABE, gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; DEF, hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$; XBC, anhydrite, CaSO_4 .

Fig. 4.—Equilibrium diagram of the system calcium sulfate-water at temperatures from 0–220°C.

fact that gypsum is not converted to anhydrite when in contact with water between 39 and 98° but does change rapidly to hemihydrate at some temperature between 98 and 100°. Incomplete experiments indicate that hemihydrate is converted very slowly to anhydrite at this latter temperature.

Table II gives the values at 10-degree temperature intervals of the solubilities of hemihydrate and of anhydrite in the range from 100 to 220°. These values are taken from the curves of Fig. 2.

TABLE II
SOLUBILITIES OF HEMIHYDRATE AND ANHYDRITE AT ROUNDED TEMPERATURES FROM
100 TO 220°

Temp., °C.	Sol. as parts of CaSO ₄ per million parts of soln.		Temp. °C.	Sol. as parts of CaSO ₄ per million parts of soln.	
	Hemihydrate	Anhydrite		Hemihydrate	Anhydrite
100	1645	650	170	325	140
110	1290	535	180	255	112
120	1030	435	190	205	92
130	830	350	200	165	76
140	665	280	210	..	64
150	530	222	220	..	55
160	415	176			

Conclusions

The solubilities of hemihydrate and of anhydrite have been studied in the temperature range 100–200°. The values for the solubility of hemihydrate check those of earlier investigators commonly referred to as the values for the solubility of "soluble anhydrite." The values found for anhydrite are lower than the accepted values up to 200°, approaching the latter with increase in temperature and coinciding with them at 200°.

The solubility curve previously designated as that of "soluble anhydrite" between 100 and 200° has been shown to be a prolongation of the solubility curve for hemihydrate below 100°. Evidence that "soluble anhydrite" is identical in crystal structure with calcium sulfate hemihydrate has been advanced by other investigators and support of this view will be presented in a future paper by L. S. Ramsdell and E. P. Partridge.

A tentative equilibrium diagram for the system calcium sulfate–water is proposed, which indicates that the temperature of transition from gypsum to anhydrite lies slightly below 40° and that the temperature of transition from gypsum to hemihydrate lies at 98°.

Hemihydrate exists in contact with water only as an unstable phase over the entire temperature range 0–200°. In the range 90–130°, however, it is apparently metastable for periods up to forty-eight hours. Incomplete experiments indicate that gypsum is converted into hemihydrate in less than one day when in contact with water at 100°, and that the hemihydrate thus formed is subsequently transformed into anhydrite over longer periods of time.

Summary

Values for the solubility of calcium sulfate between 100 and 200° have been redetermined. The whole system of calcium sulfate and water up to 200° has been reviewed, with the conclusion that gypsum and anhydrite are the only stable phases within this range. The transition temperature of gypsum into anhydrite lies near 40°. Hemihydrate is the only other

form of calcium sulfate which has existence in the range 0–200°. “Soluble anhydrite” is identical in crystal form with hemihydrate, and the solubility curve formerly given as that of “soluble anhydrite” is the curve for hemihydrate. Hemihydrate is metastable in the approximate range 90–130°, showing decreasing stability with decrease of temperature below 90° and with increase of temperature above 130°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

OXIDATIONS PROMOTED BY ULTRASONIC RADIATION

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During the course of an investigation of the effects of ultrasonic radiation on certain photosensitive reactions, it was found that iodine was liberated from an aqueous solution of potassium iodide by such radiation. It was subsequently discovered that other reactions were sensitive to this agency; indeed Richards and Loomis,² using a 2-kilowatt oscillator, have reported two cases in which they observed some stimulation.

Experimental Methods

The high-frequency mechanical vibrations were generated in a manner already described.³ The electrical oscillations were produced by a single 250-watt tube tuned to the natural frequency of the quartz crystal, which was about 750 kilocycles per second. In the cases of almost all reactions reported in the present paper, the reactants were contained in a test-tube dipping into the liquid dielectric immediately over the crystal. In this way the energy was transmitted to the solution in the test-tube, resulting in vigorous cavitation of any dissolved gas, the escaping bubbles being momentarily caught in the nodes of the standing wave system. In certain reactions it was desirable to render the liquid free, to all practical purposes, of dissolved gases before radiation. This was accomplished by boiling for three or four minutes in a test-tube fitted with a valve. On cooling the tube the valve closed, excluding the air indefinitely. In other reactions in which the presence of only one gas was desired, the liquid was rendered air-free in the manner already described; the valve was removed and a layer of mineral oil laid over the surface; the gas to be dissolved was then bubbled in from a fine jet. The use of oil had certain disadvantages and it was never employed unless absolutely essential. In order to ascertain whether electrical oscillations were responsible for the observed effects, a test-tube containing the reactants was placed above

¹ Fellow in Medicine of the National Research Council.

² Richards and Loomis, *THIS JOURNAL*, 49, 3086 (1927).

³ Schmitt, Olson and Johnson, *Proc. Soc. Exptl. Biol. Med.*, 25, 718 (1928).