

“La différence entre les chaleurs moléculaires du sulfate et du chlorure de potassium est exactement la même que celle qu'on observe entre le sulfate et le chlorure de sodium.

“Il y a identité presque absolue de chaleur moléculaire pour les solutions de sulfate et de chromate de potasse, et de même pour celles d'acide sulfurique et d'acide chromique.” etc.¹

These quotations show that Marignac, while fully recognizing the possibility of occasional wide deviations, had considerable confidence in his final results, and thought them worthy of employment in parallel comparisons involving a number of data. I used Marignac's values (the best data available) for a kind of comparison not unlike that described in the above quotations, and in a spirit essentially in accord with his. I cannot help thinking that they still deserve this degree of confidence. It should be noted, also, that the special case cited by Dr. Bell is one of the very least significant of all those which I used. If all the cases had been so little decisive as this one, I should agree with Dr. Bell, and should never have drawn the conclusion in question. This is a case of statistical reasoning, which depends not upon a few cases, but rather upon the consensus of all.

Further discussion of the matter may well be postponed until Marignac's figures have been verified or disproved by new experimental determinations, already begun.

THEODORE W. RICHARDS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI.]

THE INFLUENCE OF PRESSURE ON SOLUBILITY.

BY HERBERT F. SILL.

Received September 8, 1916.

Introduction.

Experimental values for the terms involved in the equation $T dA/dT = Q$ have been applied with good agreement for the processes of fusion and of vaporization in one-component systems. The same is true for vaporization of mixtures (isothermal distillation).

For the important case of change of state in two-component solid-liquid systems (solution and precipitation) complete experimental data have heretofore been lacking.

When both the influence of pressure and of temperature on the solubility of a substance are known, as well as the volume change involved, the relationship dA/dT is obtainable as the product $ds/dT dp/ds (V_2 - V_1)$. The significance of these terms may be stated as follows:

Let a large amount of saturated solution at the temperature T be in contact with the solute at the pressure p . Then dp represents the increase in pressure necessary to cause one gram more of the solute to pass into

¹ Oeuvres Complet, II, 630, 632. *Ann. chim. phys.*, [5] 8, 421-425 (1876).

solution isothermally and dT represents the increase in temperature necessary to produce the same result at constant pressure.

Thus far the only accurate measurement of the influence of pressure upon solubility has been made by E. Cohen, Inouye, and Euwen,¹ in an apparatus designed by them and covering a range of 1500 atmospheres. The substances employed were sodium chloride and mannite and their solubilities in water were determined at the constant temperature 24.05° and pressures from one to 1500 atmospheres as follows:

Pressure (atmospheres).	Solubility in parts per hundred.	
	NaCl.	Mannite.
1	26.41	17.12
250	26.60	17.30
500	26.76	17.45
1000	27.02	17.63
1500	27.20	17.69

The values for the solubilities obtained by them, when plotted against the pressure, yield smooth curves, concave toward the pressure axis and indicating by their trend a point of maximum solubility for this temperature, at about 2500 atmospheres pressure.

It appears from the table that for these substances a considerable range of pressure is necessary in order that the solubility change may be sufficient to permit a satisfactory calculation of the value dp/ds .

These investigators did not attempt a comparison of these pressure solubility data, with any experimental values for the other thermodynamic factors

With view to establishing complete data for a case of solution the following experiments were made involving the design and construction of a new type of "pressure bomb" which is extremely simple in operation and permits the withdrawal of the sample for analysis without reducing or otherwise changing the pressure. This was not possible with the apparatus employed by Cohen, Euwen and Inouye, as it was necessary for them to relieve the pressure and open the bomb in order to take the sample for analysis. This was of no disadvantage for the systems employed by them, since during the few minutes required for the above manipulation the solution remained supersaturated to the full degree of the previous equilibrium conditions.

In the case of certain other systems such as ether-water, upon whose investigation the writer is now engaged, the composition of the layers would not remain unchanged during the time necessary to remove the sample after relieving the pressure.

The Pressure Bomb.

This was of the nature of a modified U-tube, the two arms of which were made from "Shelby Steel tubing" of 25 mm. bore and 63 mm. external diameter.

¹ *Z. physik. Chem.*, **75**, 291 (1910).

The left hand or "reaction chamber" (Fig. 1) was 30 cm. and the right hand or "mercury chamber" 28 cm. in length. These were filed at the ends to a hexagonal form to permit being held with a wrench when the screw-plugs were tightened.

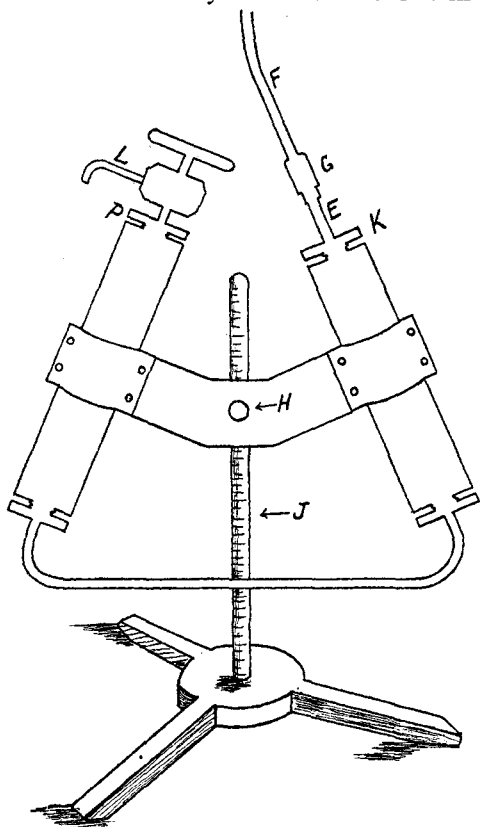


Fig. 1.

The ends of the capillary tubing are threaded and screwed into a steel disc, C, of the same dimensions as the washer and between the two is inserted a rubber washer, B, 3 mm. in thickness and forming a smooth cylindrical surface with the steel disc and washer.

The screw disc is slightly hollowed conically on its outer face to prevent trapping of air when inserted and rests on the shoulder D. When the plug is screwed tight the rubber is forced against the capillary tube and the wall of the bomb chamber.

Connection with the pump is made through the piece of steel capillary E joined to the $2\frac{1}{2}$ meter flexible copper capillary F by means of the brass coupling G. The bomb is supported in the thermostat by a clamping device so constructed that the whole can rotate freely on the adjustable axis arm H, which can be raised or lowered on the support J. The latter stands within and toward the left end of an oval tank. Through the use

Both chambers were reamed smooth on the inside and turned at each end on the inside for a distance of 40 mm. to a diameter of 31 mm., thus forming a 3 mm. shoulder at D (Fig. 2). These ends were threaded to a depth of 28 mm. for the reception of screw-plugs. The latter were 28 mm. long and provided with enlarged hexagonal heads. The connection between the two chambers and with the Cailletet pump and with the outlet valve is affected by means of capillary steel tubing of 1.5 mm. bore and 6 mm. external diameter. The steel tubing passes first through a 7 mm. hole in the center of the screw-plug, then through a steel washer, A, 6 mm. thick, which fits rather snugly but will slide readily.

The steel tubing passes first through a 7 mm. hole in the center of the screw-plug, then through a steel washer, A, 6 mm. thick, which fits rather snugly but will slide readily.

of the long flexible copper capillary F, which bends around in a large loop, the bomb can be rotated with little resistance through an angle of more than ninety degrees when connected with the pump, which stands to the right of the tank.

The Cailletet pump, together with its pressure gage, was one of those used in the numerous investigations on compressibility by T. W. Richards and others, and was kindly loaned to the writer for the purpose of the work here presented. The calibration of the gage is fully described in a recent article¹ on the "Compressibilities of Certain Hydrocarbons, Esters, Amines and Organic Halides," and is therein designated as Gage A.

The charging of the bomb is effected as follows:

The upper screw plugs P and K are removed and the apparatus—thoroughly cleaned and dried on the inside—is rotated so that the reaction chamber is in a vertical position and clean mercury is poured in to a depth of about 3 cm., after which the chamber is filled nearly to the top with saturated solution together with a suitable excess of the solid solute. The screw plug P, bearing the discs, outlet valve, etc., is then inserted with the valve closed and

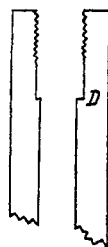
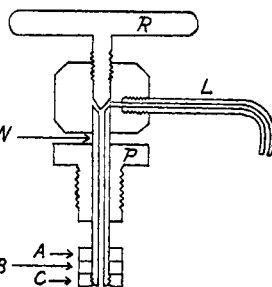


Fig. 2.

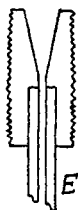
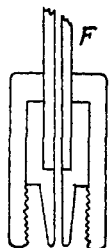


Fig. 3.

screwed down until mercury appears in the right-hand or mercury chamber. A further amount of mercury is then added, sufficient to half fill the mercury chamber, and the screw-plug P tightly screwed down with a wrench. The outlet valve R is now opened sufficiently to allow a few drops of the solution to escape and insure the expulsion of any air which may have been enclosed, whereupon the valve is tightly closed.

The apparatus is next rotated to the right to allow the mercury chamber to stand vertical and mercury is added to within a centimeter of the shoulder D.

Above the mercury is added a layer of the pump liquid (castor oil was employed in the measurements to be described) to a height about where the screw threads begin. The screw-plug K bearing the short piece of steel capillary E, with its discs and washer, is now inserted in the mercury chamber and screwed down tightly. This forces oil up the capillary and causes it to fill and overflow the conical cavity in the lower

coupling piece.

The upper coupling piece is then held above the lower one and oil from

¹ Richards, Stull, Matthews and Speyers, *THIS JOURNAL*, 34, 972 (1912).

the pump is forced through the long copper capillary and out of the conical tip, whereupon the coupling ring is tightly screwed down. Pressure is now applied from the pump in order to test for leaks and the joints further tightened if necessary.

The apparatus is again rotated to the right so as to place the reaction chamber in a horizontal position. The outlet tube L, made from the steel capillary tubing, is unscrewed, rinsed and dried, replaced and closed at the end by means of a piece of rubber tubing, plugged with a piece of glass rod. This is to prevent the entrance of water from the bath when the apparatus is submerged.

The mercury in the reaction chamber is caused to flow back and forth by means of a simple tilting mechanism. A pulley wheel is placed above the lower end of the horizontal reaction chamber and connected eccentrically with the latter through a brass strip which functions in the manner of a driving rod.

The pulley is so geared that the tilting occurs about every six seconds.

In the following measurements the thermal regulation and the stirring of the bath were connected in the manner described by T. W. Richards.¹

The regulator was adjusted to 25°, measured by means of a Reichsanstalt thermometer graduated in twentieths of degrees, of which the corrections were given to hundredths of degrees. By the use of a reading-lens readings accurate to this fraction could be readily made. A Beckman thermometer graduated in hundredths showed, during all the measurements made, which extended over some seventy hours, a fluctuation of two to three thousandths of a degree.

This excellent constancy is doubtless to be attributed to the use of the hydrogen generator which kept the mercury-platinum contact in an atmosphere of this gas and to the vigorous stirring which was employed.

The first system investigated was sodium chloride and water. This was done with a view to trying out the apparatus and also in order to obtain a comparison with the results obtained by Cohen, Euwen and Inouye.

C. P. sodium chloride was reprecipitated from a saturated water solution by means of HCl gas generated from C. P. acid by the addition from a dropping funnel of C. P. sulfuric acid. The precipitated salt was washed several times by decanting with small amounts of water, dried and heated for an hour at 350°. A solution containing about a gram of this product remained colorless on addition of phenolphthalein and turned pink on the addition of one drop of 0.05 *N* sodium hydroxide solution.

The bomb was charged in the manner described and the tilting mechanism set in operation.

In Expt. 1 no pressure was applied from the pump. The tilting was con-

¹ Stähler, "Handbuch der Arbeitsmethoden in der anorganischen Chemie," III,

tinued for two hours and the first sample withdrawn, after which the apparatus was tilted for an additional hour and the second sample taken. The identity in the analytical results on the two samples indicates that saturation was complete in the first case, hence in the following measurements on this system the tilting was suspended at the end of two hours.

In Experiments 2, 3 and 4, pressure was first applied to a point several kilograms beyond the final pressure desired. During the following two or three minutes the dissipation of the heat of compression caused the pressure indicated by the gage to slowly diminish.

When the gage reading had become practically constant the pressure was adjusted to the value given in the table and was maintained at this point throughout the experiment.

In Experiment 4, at 750 kg. pressure it was found that, owing to oil leakage at the pump connections, frequent manipulation of the pump was necessary in order to keep up the pressure. The measurements were, therefore, not carried beyond this point.

One of the samples from Expt. 4 became accidentally contaminated after its withdrawal and was not analyzed.

The procedure connected with the taking of the samples was as follows: After the tilting had been suspended the reaction chamber was placed in a vertical position and allowed to stand for fifteen minutes to permit the solid substance to settle. This step is probably not necessary since the slight loosening of the valve which permits the slow expulsion of the liquid would scarcely allow any solid particle to escape.

The bomb was next turned back to the position shown in Fig. 1. This left the end of the outlet tube sufficiently above the surface of the water in the bath to permit the attachment of the weighing bottle which was to receive the sample for analysis.

The outlet tube and the protective rubber tube were thoroughly dried with filter paper and the rubber tube removed.

The weighing bottle was provided, in addition to its glass stopper, with a flat one-hole rubber stopper about 1 cm. in thickness. This rubber stopper was slipped over the end of the outlet tube and the weighing bottle then pushed into the rubber stopper. By this means any loss by evaporation during the withdrawal of the sample was prevented.

The valve was now slightly loosened until the gage began to show a decrease in the pressure indicating the escape of liquid through the valve. The original pressure was at once restored by means of the pump and was kept up during the slow egress of the sample (about 20 drops per minute) into the weighing bottle. When 3-4 cc. of the solution had escaped the valve was tightened, the weighing bottle removed from the rubber stopper and its glass stopper at once inserted and the weighing made.

The analysis of the sample was effected without transferring from the

weighing bottle. The latter was placed in a tall beaker to protect it from the action of steam and the solution evaporated to dryness on the water bath, after which the residue was heated in an air bath for one hour at 350°, cooled in a desiccator, and weighed.

TABLE IV.—SOLUBILITY-PRESSURE DATA FOR SODIUM CHLORIDE AT 25°.

Expt. No.	Pressure kg. per sq. cm.	Wt. of sample.	% NaCl found.	% water.
1.....	I	4,100	26.44	73.56
	I	3,339	26.44	73.56
2.....	250	3,505	26.58	73.42
	250	3,408	26.58	73.42
3.....	500	3,629	26.76	73.24
	500	2,076	26.68	73.32
4.....	750	4,012	26.82	73.18

The divergence in the results of the analysis of the two samples for Expt. 3 cannot be accounted for.

If the average of the two values (26.72%) be taken, a smooth pressure-solubility curve results for the four points.

The accurate determinations by Andrea of the ordinary solubility (*i. e.*, at atmospheric pressure) of sodium chloride at different temperatures, resulted in the values 26.37% and 26.53% for the temperatures 20° and 30°, respectively. A straight line interpolation for 25° gives the value 26.45%, which is one point higher than the result contained in Table IV. The temperature coefficient of solubility ds/dt calculated from Andrea's data is therefore 0.16/10 or 0.016%.

From the data of Table IV it is seen that an increase in pressure of 249 kg. alters the solubility by only 0.14%.

In both instances it is apparent that a slight variation in the analytical results will produce an immense effect on the ratios ds/dt and dp/ds . A satisfactory calculation of the relation dA/dt as the product $ds/dt \cdot dp/ds$ ($V_2 - V_1$) is therefore not possible for this substance.

In considering the choice of a solute for which complete thermodynamic data could be readily established, barium hydroxide suggested itself on account of its moderate solubility, its much larger temperature coefficient of solubility than that of NaCl, and the ease and accuracy of its analysis by titration.

Moreover, being an alkaline substance, there is no danger of contamination of the solution through action on the iron.

Data for the heat of solution were found and for the temperature coefficient of solubility and for the specific volume of the solid substance, but owing to the absence of data for the specific volume of its solutions from which the volume change $V_2 - V_1$ could be calculated, it was not possible to estimate whether its pressure coefficient of solubility were large or small. Instead of first making the density determinations, the measurements with the pressure apparatus were carried out in the manner de-

scribed, except that the samples of solution withdrawn under pressure were titrated with 0.04 *N* hydrochloric acid carefully standardized against anhydrous sodium carbonate and with burets standardized by weight. The solution chamber was charged by preparing a hot solution of barium hydroxide of a concentration twice as great as that possessed by the saturated solution at twenty-five degrees. This hot solution was filtered (to remove carbonate) directly into the bomb and the screw-plug inserted. On cooling, the excess of solid solute separated. The material used was pure crystallized octohydrate and was not analyzed further.

The results are contained in Table V. The equilibrium for atmospheric pressure and for 250 kg. per sq. cm. (245 megabars)¹ was approached from both sides. In Expt. 1, hot water was added to the bath to bring it to a temperature of 30° and the bomb tilted for one-half hour. The bath temperature was then lowered to 25° (where it was maintained by the automatic regulation) and the bomb tilted for three hours at which time the sample was removed.

In Expt. 2 the bath was cooled to 20° and the bomb tilted for one-half hour, after which the temperature was raised to 25° and the tilting continued for three hours as before. The good agreement of the analyses shows that equilibrium was reached in both cases.

In Expts. 3 and 4 the same procedure was followed, except that the tilting at 25° was continued for 2 hours only. The difference in the analyses, although small, is somewhat beyond the probable analytical error and indicates that the tilting had not been quite long enough continued, hence in the subsequent calculation the average value, 8.791, is used.

In Expt. 5 the tilting was continued for 2.5 hours.

TABLE V.—SOLUBILITY OF $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ AT 25° AND VARYING PRESSURES.

Expt. No.	Pressure (megabars).	Wt. of sample.	% hydroxide.	% water.
1.....	1	6.179	8.304	91.696
2.....	1	5.228	8.295	91.705
3.....	245	10.523	8.779	91.221
4.....	245	6.481	8.802	91.198
5.....	490	6.320	9.366	90.634

The Heat of Solution.

The molar heat of solution of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in large amounts of water has been determined by de Forcrand and by Thomsen² as -14500 cal. and -15210 cal., respectively. These values correspond to -46.0 cal. and -48.2 cal. per gram of solute. On account of this divergence and the fact that the heat of solution of substances at or near the saturation point may be very different from the values for dilute solutions, two deter-

¹ Megabar = 10^6 dynes = 1.02 kilograms per sq. cm.

² Landolt-Börnstein Tabellen.

minations were made, the first starting with a solution already 54% saturated and using an amount of solute such as to bring its concentration to 64% saturated. The second determination continued from the latter point and brought the solution to 74% saturated.

The measurements were made in a Richards "adiabatic calorimeter."

During the process of solution the lowering of the temperature within the calorimeter vessel was kept pace with by the addition of colder water to the outside vessel whose contents were kept rapidly stirred.

At no time did the thermometer readings inside and outside differ by more than one-hundredth of a degree.

The initial solution (No. 1) was prepared by diluting a saturated solution and filtering into the calorimeter vessel after which a sample was pipetted out for analysis.

Barium hydroxide (150 g.) was dissolved at 60° and filtered clear into a flask which was then stoppered and allowed to cool. The fine crystals of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ separating out were quickly filtered in four Gooch crucibles and then rotated rapidly in a centrifuge until no more liquid could be separated. The upper portion of the contents of each crucible, which doubtless contained some carbonate formed during the rotating, was removed with a spatula and the remainder shaken out onto three thicknesses of filter paper and folded up in the latter to form a flat package. This was pressed vigorously between more sheets of filter paper and the contents of the package then transferred to a stoppered bottle. By this means the formation of carbonate was reduced to a negligible amount, as is shown by the fact that a sample of the product, dissolved in previously boiled water, left but a scarcely perceptible turbidity.

A sample of this product was transferred to a weighing bottle, weighed and titrated, with the result that the preparation was found to contain 6% of saturated solution which the treatment with the centrifuge and the filter paper failed to remove.

For each of the two measurements 3 g. of this preparation were roughly weighed into a small thin glass bulb which was sealed and placed in the calorimeter vessel along with the solution. When all was in readiness the bulb was broken by means of a stirrer. The time required for complete solution as indicated by the stationary temperature was eight to ten minutes, moderate stirring being employed.

A sample was withdrawn from the calorimeter vessel by means of a 10 cc. pipet, weighed and titrated. From the result of this titration the total increase in the octohydrate content of the solution was computed. From this amount was deducted the weight of octohydrate in the 6% of saturated solution which had been present in the sealed bulb and which had had no appreciable thermal effect. This correction amounts to $6\% \times 8.3\% = 0.5\%$.

The remainder gives the amount of solid octohydrate which had actually passed into solution during the calorimeter measurement.

These figures are contained in the fifth column of the following table:

TABLE V.

Solution No.	% hydrate.	Degree of saturation.	Grams of sol. used.	Grams solid hydrate dissolved.	Temperature change.
1.....	4.502	54%	360	2.948	-0.381°
2.....	5.280	64%	352	3.228	-0.437°
3.....	6.155	74%

The heat of solution per gram of solid hydrate added in bringing a 54% saturated solution to 64% saturation as calculated from these data is 48.3 calories and in bringing the latter solution to 74% saturation, 49.1 calories, account being taken of the heat capacity (10 cal.) of the calorimeter, stirrer, glass fragments, etc. A straight-line extrapolation gives the value 51.2 cal. for the heat of solution at the saturation point.

The heat capacity of the solutions may vary from that of water by 1-2%, but in the absence of any data no account could be taken of this possible difference.

The Volume Change.

A simple and accurate means of determining the volume change was suggested by the observations made in the course of the previous work that barium hydroxide solutions could be easily kept at a high degree of supersaturation. From this fact it appeared that a dilatometer measurement in which a supersaturated solution of known composition should be precipitated by inoculation would yield the desired value.

The successful use of mercury as a stirrer in the pressure-solubility experiments led to its adoption for the same purpose in hastening the approach to equilibrium in the dilatometer.

Fifty cc. of mercury were placed in a three and one-half liter round-bottomed flask whose neck was constricted at the opening to such a diameter as would accommodate a No. 1 one-hole rubber stopper. Through the stopper passed a glass tube of 5 mm. bore graduated in tenths of cubic centimeters. As the graduation marks were about six millimeters apart, hundredths of cubic centimeters could be readily calculated.

The octohydrate (400 g.) was dissolved in four liters of water by heating and the warm solution filtered into a four-liter flask which was stoppered and placed in the thermostat of 25° for several hours. The solution, which was calculated to be about 10% supersaturated at this temperature, remained perfectly clear. A sample (about 10 cc.) was pipetted out, weighed, and titrated and found to contain 9.199% of octohydrate.

The dilatometer flask containing the mercury, together with the rubber stopper and graduated tube, were counterpoised on a balance and the flask filled to the top with the supersaturated solution.

The rubber stopper was now inserted, causing a little of the solution to be expelled through the hole. The volumetric tube was then pushed through the stopper, the displacement of the liquid by the tube thereby raising the level to a convenient point on the scale.

The whole apparatus was weighed and found to contain 3540 g. of solution.

A small soda-lime tube was attached to the upper end of the volumetric tube and the flask immersed in the thermostat bath for half a day. During the last two hours of this period readings of the level in the tube were made and after each reading the mercury was swirled about in the flask.

The meniscus reading remained unchanged during the two hours and the solution entirely clear.

A minute particle of solid octohydrate about one-half millimeter in diameter was taken with a forceps and dropped down the tube and was seen to fall through the solution and rest on the bright mercury surface at the bottom of the flask. Flakes of octohydrate soon began to appear and the solution level to rise in the graduated tube. The process was hastened by agitating the mercury every few minutes.

At the end of six hours a large deposit of octohydrate had separated and an increase in volume of 1.28 cc. had taken place. No further rise in the meniscus level could be observed after an additional half hour.

Since the stirring had been only for a few seconds at intervals of from three to six minutes instead of being continuous as in the pressure-bomb experiments, it was not to be supposed that complete equilibrium had been established. The fact that no measurable increase in volume had occurred during half an hour indicated, however, that a sample of the solution could be safely removed for analysis.

The stopper and tube were accordingly removed and a sample drawn into a 10 cc. pipet, transferred to a weighing bottle, and weighed.

Although the solid octohydrate settles quickly, leaving the solution clear, the precaution was taken of attaching to the pipet a 5 cm. piece of glass tubing, constricted in the middle and packed below the constriction with a plug of cotton.

The titration analysis of the sample showed 8.487% of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

The total of the solid phase which had separated was accordingly

$$3540(0.09199 - 0.08487) = 25.205 \text{ grams,}$$

$$\text{and the specific volume change } (V_2 - V_1) \text{ was } \frac{1.28}{25.205} = 0.0508.$$

The Temperature Coefficient of Solubility.

This value was calculated from the solubility data of Rosenstühl and Rühlmann.¹ This table gives the percentage of BaO in the saturated

¹ Taken from the Landolt-Börnstein tables, 1912, p. 459.

solution for temperatures at intervals of 10° . The following table shows these values and equivalent values for $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$:

	BaO.	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.
10°	2.17%	4.46%
20°	3.36%	6.91%
30°	4.75%	9.77%
40°	6.85%	14.09%

When these four points are plotted and a smooth curve drawn, the curve-reading for the solubility at 25° is 8.30%, agreeing with the value obtained by direct measurement (Table V).

Hence the Rosenstühl-Rühlmann data may serve as a basis for the calculation,

$$\frac{ds}{dt} = \frac{9.77\% - 6.91\%}{10^\circ} = 0.288\%.$$

The application of the complete data to the equation

$$T \frac{(p_2 - p_1)(v_2 - v_1)}{t_2 - t_1} = Q$$

gives for the left-hand side

$$298 \times 0.288 \times \frac{244}{0.491} \times 10^6 \times 0.0508 = 2.16 \times 10^9$$

and for the right-hand side

$$51.2 \times 4.189 \times 10^7 = 2.14 \times 10^9.$$

The agreement is seen to be excellent.

The writer wishes to acknowledge his thanks to Prof. T. W. Richards, of Harvard University, for valuable advice and assistance in the devising of the pressure bomb employed in this investigation. This apparatus is owned by the Carnegie Institution of Washington and is now being used for other work under the auspices of the Institution.

COLUMBIA, MISSOURI.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

STUDIES ON THE COBALTAMMINES. I.

VARIOUS IONIZATION TYPES AS DETERMINED BY THE FREEZING-POINT LOWERING IN AQUEOUS SOLUTION, TOGETHER WITH CONDUCTANCE MEASUREMENTS.¹

BY WILLIAM D. HARKINS, R. E. HALL AND W. A. ROBERTS.

Received August 14, 1916.

The present investigation was undertaken as a starting point in the study of the structure of the cobaltammines. The first point necessary

¹ The temperature readings were taken to one-twenty thousandth of a degree by means of a 50 couple thermoelement, and a double combination potentiometer specially designed for this work by Dr. W. P. White, and we wish to express our indebtedness to him for this aid.