[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Influence of Hydrogen Ion Concentration, Solubility, Rate of Precipitation and Relative Supersaturation on the Crystal Growth of Strontium Sulfate

BY S. Z. LEWIN AND JOHN E. VANCE

A new technique is described for the batch production of crystals of $SrSO_4$. By use of this technique, the size attained by the crystals and the crystal habit appear to be strongly influenced by the hydrogen ion concentration but not by the solubility, rate of precipitation or relative supersaturation. It is suggested that the rate-controlling step in the crystal growth is the transfer of ions from the adsorption layer to lattice positions.

In connection with other investigations, an effort was made to prepare relatively large and perfect crystals of $SrSO_4$. The purpose of the present paper is to report on a new technique for growing crystals of limited solubility and to note the effect of certain experimental conditions on the size of crystals obtained. In particular, the observations suggest that the hydrogen ion concentration of the medium in which crystals of $SrSO_4$ (and perhaps of other salts) are formed, may be a factor of primary importance in controlling crystal growth.

Experimental

The experimental arrangement consisted of a soxhlet extractor with the thimble replaced by glass wool packing which supported a bed of precipitated $SrSO_4$ of C.P. grade. The boiling flask was fitted with a stirrer through an ungreased ground-glass seal. Water solutions of various compositions were refluxed while being stirred rapidly; the condensed vapor percolated through the bed of $SrSO_4$ on its way back to the boiling flask. Consequently, a dilute solution of $SrSO_4$ was introduced continuously into the boiling flask while the solvent was vaporized, the net amount of liquid in the flask remaining more or less constant. The amount of $SrSO_4$ in the flask could thus be increased slowly and uniformly with time so that the processes of nucleation and growth set in and proceeded simultaneously after the salt concentration had increased to the requisite point. Efficient stirring was essential to prevent the solid from sticking to the walls and to ensure that all the crystals were in contact with the slightly supersaturated solution of $SrSO_4$.

With constant boiling HCl (about 6 N) as the solvent and with brisk ebullition, the yield of $SrSO_4$ was about 15 g. in 24 hours; under similar conditions, with water as the solvent, the yield was about 0.5 g. in the same period. The technique is referred to hereafter as "extractive crystallization."

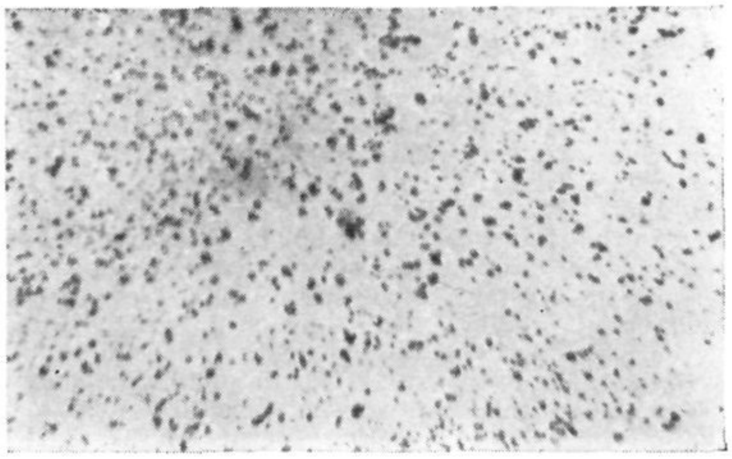
TABLE I

Exptl. group	Solvent	Solubility of $SrSO_4$ in relation to solubility in water	Approximate average value of greatest dimension, mm.
A	Water	Same	0.001
B	1 N NaCl, 5 N NaCl, 8 N LiCl, 8 N $MgCl_2$, 4 N $SrCl_2$, 6 N $CdCl_2$	Greater[a,b]	.001
C	5 N Na_2SO_4	Less[b]	.001
D	8 N H_3PO_4	Greater[b]	.001
E	8 N CH_3COOH	Greater[b]	.001
F	2 N H_2SO_4	Less[c]	.005
	4 N H_2SO_4	Less[c]	.01
	8 N H_2SO_4	Less[c]	.03
G	8 N HNO_3	Greater[b]	.01
H	2 N HCl	Greater[a,b]	.07
	6 N HCl	Greater[a,b]	.2–0.3

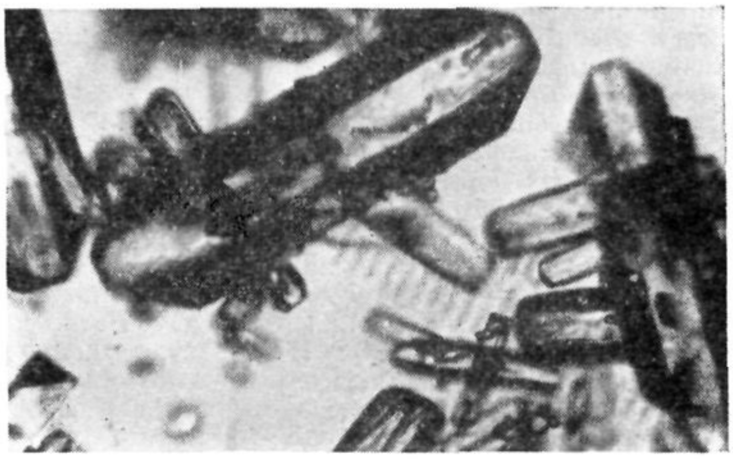
[a] See reference (1). [b] For effect of electrolytes on solubility see, for example, H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 51 ff. [c] By turbidimetric comparison.

Results

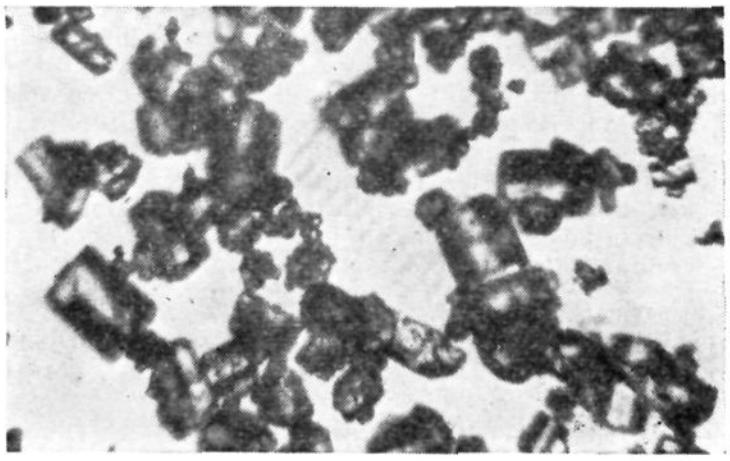
The size attained by the crystals was dependent on the solvent used in the boiling flask. Figure 1 shows the extremes of the sizes under 150× magnification and illustrates the orthorhombic development of the crystals obtained from 6 N HCl. The average greatest dimension of the crystals from 6 N HCl was up to 300 times as large as that of the crystals from water. The crystals obtained by this method, using water as the solvent, appeared to be



(a) From water or by direct precipitation.



(b) From 6 N HCl.



(c) From 8 N H_2SO_4.

Fig. 1.—Crystals under 150× magnification.

identical in size with those obtained by direct precipitation of $SrSO_4$. Table I summarizes the observations in relation to the solvents and the solubility of the $SrSO_4$ in the various media. In each case the rate of reflux was approximately the same but the durations of the experiments were not identical; for example, the experiment using 8 *N* HNO_3 lasted 4 hours while those with 4 *N* and 8 *N* H_2SO_4 lasted 8 hours. On the other hand, within rather wide limits, the duration of the experiment appeared to have no noticeable effect on the size distribution of the crystals and only increased the total yield; thus, the average size of crystals formed in water did not change detectably in runs ranging from 8 to 72 hours and that obtained in 6 *N* HCl after about 6 hours was not different from the average size of crystals from experiments of 24 hours duration.

The rate at which $SrSO_4$ was carried down to the boiling flask was the same (within the limits between which the rate of reflux could be controlled) in Groups A, B, C, D and F but was variable and much higher in Groups E, G and H because of the greater solubility of $SrSO_4$ in the latter condensates. This rate in itself appeared to have no direct bearing on the crystal size.

The solubility of $SrSO_4$ in the different media varied considerably. There is little quantitative information in this connection,[1] but the qualitative solubility relationships in Table I can be deduced from known principles. In addition, the solubility of $SrSO_4$ was shown to decrease in the order: water, 2 *N* H_2SO_4, 4 *N* H_2SO_4, 8 *N* H_2SO_4 by turbidimetric comparison of the $SrSO_4$ precipitated when the indicated amount of acid was added to a saturated solution of $SrSO_4$ in water; the relative turbidities were: H_2O, 1.0; 2 *N* H_2SO_4, 1.2; 4 *N* H_2SO_4, 1.6; 8 *N* H_2SO_4, 14.3; 12 *N* H_2SO_4, 16.2. The solubility of $SrSO_4$ in the medium was not related to the size of crystals obtained from that medium; for example, in Group F the solubilities were less than in water and the crystal size was from 5 to 30 times greater, while in Groups D and E, the solubility was greater than in water but the size of crystals was the same as that obtained from water. In Groups G and H, both solubility and crystal size were greater than the corresponding values with water as the solvent and the crystal size increased in Group H as the solubility was increased by the use of more concentrated HCl.

The effect of a variety of neutral salts was studied in Groups B and C and that of weak acids in Groups D and E; in every case, the appearance of the crystals was indistinguishable from that of crystals obtained from water or from direct precipitation.

The acid concentration of the solvent appeared to be related to the average size attained by the crystal. For example, in Groups D and E the weak acids had no effect noticeable under 150× magnification, while there was a steady increase in crystal size with H_2SO_4 concentration in Group F and again in Group H with HCl. Similarly, 8 *N* HNO_3 produced larger crystals than were obtained from water and mixed acids, *e.g.*, 6 *N* H_2SO_4 and 2 *N* HCl gave rise to crystals of about the same size as 8 *N* H_2SO_4. Some further indication of the effect of acid concentration was obtained in an experiment using a homogeneous precipitation procedure.

It is a commonly accepted hypothesis that the rate of precipitation of a sparingly soluble substance is related to the size attained by the crystals[2] and slow, controlled, homogeneous precipitation has been advocated frequently as a means of improving particle size in analytical chemistry.[3] The homogeneous precipitation technique has been applied to the precipitation of $SrSO_4$ by Elving and Van Atta[4] who utilized the hydrolysis of methyl sulfate to produce a slow and uniform increase of sulfate ion concentration throughout the solution; at the same time the hydrolysis causes a decrease in *p*H. In order to separate the effect of these factors, the homogeneous precipitation of $SrSO_4$ was carried out in accordance with the published procedure, both with and without the addition of sodium acetate to the solution. Although the precipitation proceeded at approximately the same rate in the two cases, the crystals of $SrSO_4$ obtained from the solution buffered with sodium acetate were not detectably larger than those obtained by direct precipitation (Fig. 1a). The unbuffered solution produced crystals which perhaps were not distinctly different under microscopic examination but which were judged to be larger or more dense on the basis of a considerably shorter settling time of the suspension.

The crystals obtained from the acid solutions differed in external habit; for example, the crystals from HCl (Fig. 1b) solutions appeared to exhibit another habit than those from HNO_3 and H_2SO_4 (Fig. 1c) and the habit also changed with the concentration of HCl. The refractive indices and interfacial angles of the specimens obtained from HCl, HNO_3 and H_2SO_4 solutions were measured by Professor L. E. Spock of the Department of Geology and found to be characteristic of celestite, naturally occurring $SrSO_4$.

Samples of the $SrSO_4$ obtained from 6 *N* HCl were analyzed in three ways: (a) by solution in concentrated H_2SO_4 and evaporation to constant weight; (b) by fusion with Na_2CO_3 and precipitation of $SrSO_4$ with weighing as $SrSO_4$; (c) by fusion with Na_2CO_3 and precipitation of SrC_2O_4 with weighing as SrO. The results, computed as per cent. $SrSO_4$ in the original sample were: (a) 100.05, 100.35; (b) 99.60, 99.88; (c) 99.92, 100.37; average 100.03 ± 0.19%.

Discussion

Crystals of $SrSO_4$, distinctly larger in size than those produced by direct precipitation, by homogeneous precipitation or by extractive crystallization from water, were obtained only from the following media: 2 to 8 *N* H_2SO_4, 8 *N* HNO_3 and 2 to 6 *N* HCl. The technique by which these crystals were obtained was quite different from previously reported experimental procedures for growing crystals, *e.g.*, the slow evaporation of a solution in which a crystal is suspended, or the gradual lowering of the temperature of a saturated solution. For this reason, a comparison of the present results with those obtained under very different experimental conditions is not easy, nor will theories devised to explain the usual type of experiments necessarily be directly applicable in the present case. However, since the basic process of enlargement of a crystal lattice is the same, it is useful to examine the effect of those factors which have been found to be dominant previously, since the use of a different experimental arrangement may reveal the importance of certain factors hitherto obscured and unrecognized.

The fact that the crystals obtained from 8 *N* H_2SO_4 were about 30 times the size of crystals from water, although the solubility was less by a factor of about 10, is noteworthy in itself since a direct correlation often has been noted between solubility and crystal growth.[5,6] This is reflected in all previously reported techniques for preparing macrocrystals of substances with low solubilities in water, which involve the use of media in which the solubility is enhanced, *e.g.*, the growth of quartz crystals from alkaline solutions at high temperatures and pressures, of silver chloride from ammonia, of lead sulfate from concentrated solutions of alkali salts. The present observations are also contrary to the predictions of the theories of Curie,[7] Marc and Ritzel,[8] and others who have considered solubility at the crystal–solution interface to be of primary im-

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(1) J. Wolfmann, *Oesterr-ungar. Z. Zuckerind.*, **25**, 986 (1897), gives the following data for 98°: 0.1789 g. $SrSO_4$ per 1000 g. H_2O; 0.6913 g. in 10% NaCl; 0.6694 g. in 10% (about 3 *N*) HCl; 0.2096 g. in 10% $SrCl_2$.

(2) W. D. Bancroft, *J. Phys. Chem.*, **24**, 105 (1920).

(3) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," 3rd Edition, D. Van Nostrand and Co., Inc., New York, N. Y., 1940.

(4) P. J. Elving and R. E. Van Atta, *Anal. Chem.*, **22**, 1375 (1950).

(5) P. H. Egli and S. Zerfoss, *Discussions Far. Soc.*, No. **5**, 64 (1949).

(6) E. Hofer, *Z. physik. Chem.*, **183A**, 455 (1939).

(7) P. Curie, *Bull. soc. franc. mineral.*, **8**, 145 (1885).

(8) R. Marc and A. Ritzel, *Z. physik. Chem.*, **76**, 584 (1911).

portance for crystal growth. In the present experiments, the solubility of $SrSO_4$ in the medium had no simple relationship to the size of crystals obtained.

Another factor, often assigned a predominant role in the rate of crystal formation and in crystal growth, is relative supersaturation at the instant of crystallization, defined as $(Q - S)/S$ by von Weimarn[9] where Q represents the concentration existing at the instant of mixing and S the equilibrium solubility of macro-crystals of the precipitate. The concept, as originally derived for solutions which are not stirred after the initial mixing of the reagents, is that the greater the value of $(Q - S)/S$, the higher the velocity of precipitation, the greater the number of nuclei and the smaller the size of the individual particles in the precipitate. Bancroft[10] has proposed that, in the case of vigorous stirring after initial mixing, the size of the crystals passes through a maximum with increasing supersaturation. In the present experiments, the $SrSO_4$ is introduced continuously into the stirred medium so that the conditions are significantly different from those of von Weimarn and of Bancroft; consequently, the application of their concepts must be made with some reservations but it is of interest to note the apparent effect of relative supersaturation on the results reported in Table I. In this work, the rate of precipitation was determined primarily by the rate of reflux (manually kept approximately constant in each experiment) so that, after an initial period, the degree of supersaturation reached a steady-state value as a result of a balance between the reflux rate and the precipitation process. No quantitative measure of the degree of supersaturation was possible, but one can discuss the data in terms of von Weimarn's definition of supersaturation if it is assumed that Q is proportional to the rate of reflux. To the extent that this assumption is justified, it would be concluded that in Group F the value of Q was constant while S decreased as the concentration of H_2SO_4 increased, *i.e.*, the relative supersaturation increased but the size of crystals increased, contrary to the idea that relative supersaturation favors the formation of new nuclei at the expense of the growth of existing nuclei.[11] In Group B, Q was again constant and S was larger in at least five of the solutions than in water, yet the smaller relative supersaturation did not lead to noticeably larger crystals than when pure water was the solvent.

In addition to the effect of solubility at the crystal–solution interface and of the relative supersaturation, several other factors have been assumed to exert a dominant influence on crystal growth,[12] including the rate of diffusion of ions to the crystal surface, the rate of deposition of ions after reaching the crystal surface, the rate of coalescence of crystal nuclei of submicron dimensions, the energy of adsorption of lattice ions on the crystal, and the energy of attachment of an ion in a lattice position. It is shown later that the experimental observations reported here appear to be explained best by the assumption that, for $SrSO_4$, the rate of deposition of ions from the liquid layer at the interface on to lattice positions is rate determining for the growth of the crystals.

The outstanding feature of the data is the fact that crystals larger than those characteristic of directly precipitated $SrSO_4$ were obtained only from solutions of strong acids. Solutions of H_2SO_4, HNO_3 and HCl gave rise to enhanced crystal growth while solutions of weak acids and of salts did not; further, the average size attained by the crystals increased with increasing concentrations of H_2SO_4 and HCl.

The effectiveness of hydrogen ions in promoting the growth of $BaSO_4$ crystals has been noted and applied by analytical chemists[13-16] though commonly the effect has been ascribed to increased solubility and consequent reduced relative supersaturation.[17] The usual gravimetric procedures involving $BaSO_4$, CaC_2O_4, ZnS and the R_2O_3 group (the latter by homogeneous precipitation) recommend precipitation at as low a *p*H as will result in quantitative separations; the precipitates thus obtained are coarser than those from solutions of high *p*H. Preliminary experiments applying the extractive crystallization procedure to $BaSO_4$, using HCl and H_2SO_4 solutions, have verified that the crystals so obtained are larger than those from neutral solutions.

The present results appear to justify the conclusion that the hydrogen ion concentration of the medium is a factor of primary importance in controlling the growth of $SrSO_4$ (and perhaps other) crystals in aqueous solutions and that under the experimental conditions it is predominant over the effects of solubility and relative supersaturation. The fact that the size of the crystals obtained was not determined principally by the rate of precipitation may indicate that the growth of these crystals is not a diffusion controlled process such as proposed in some theories[18,19]; nor does the action of hydrogen ions appear to consist in the discharging of the surface charge of colloidal particles since other ions (Group B, Table I) at comparable concentrations had no detectable effect on the size of the crystals of $SrSO_4$. Similarly, it is unlikely that the observed effects were the result of a change in the energy of adsorption of Sr^{++} or of SO_4^{--} on the lattice, brought about by adsorption of H^+, since no such effects were evident with other ions which could be adsorbed to comparable extents and with comparable energies. It must be noted, however, that surface adsorption effects are certainly involved since the crystal habit was affected by the different acids and by varying the concentration of

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[9] P. P. von Weimarn, *Chem. Revs.*, **2**, 217 (1925).

[10] W. D. Bancroft, *J. Phys. Chem.*, **24**, 105 (1920).

[11] In connection with the von Weimarn theory, see also T. B. Smith, "Analytical Processes. A Physico-chemical Interpretation," 2nd Ed., E. Arnold & Co., London, 1940.

[12] For a general discussion see H. E. Buckley, "Crystal Growth," John Wiley and Sons, Inc., New York, N. Y., 1951.

[13] F. W. Mar, *Am. J. Sci.*, **41**, 288 (1891).

[14] P. E. Browning, *ibid.*, **45**, 399 (1893).

[15] M. Huybrechts, *Bull. soc. chim. Belg.*, **24**, 177 (1910).

[16] J. Johnston and L. H. Adams, THIS JOURNAL, **33**, 829 (1911).

[17] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Ed., The Macmillan Co., New York, N. Y., 1943, chap. VII.

[18] A. A. Noyes and W. R. Whitney, *Z. physik. Chem.*, **23**, 689 (1897).

[19] W. Nernst, *ibid.*, **47**, 52 (1904).

the same acid; also, there was a considerable variation in the crystal size obtained from different acids of comparable strength.

The formation of larger crystals from solutions of strong acids could be the result either of the promotion of crystal growth or of the inhibition of nucleation by hydrogen ions. It is not difficult to visualize how enhanced solubility could inhibit nucleation and result in the production of larger crystals; however, the present experiments indicate that the average size of the $SrSO_4$ crystals is not related to the solubility in the medium. It appears reasonable to conclude that the hydrogen ions directly influence the rate of deposition of ions on the crystal lattice, though details of the mechanism can be learned only by further experiments which will be performed.

A tentative explanation which appears to be consistent with the observations is that the rate-controlling factor in the growth of a $SrSO_4$ crystal is the surmounting of an energy barrier involved in the displacement of an adsorbed water molecule by a lattice ion. It might then be expected that the rate of crystal growth in water solutions would be sufficiently slow so that the formation of new nuclei would be favored over the growth of existing nuclei; this would explain the occurrence of minute crystals of $SrSO_4$ from neutral solutions regardless of the rate of precipitation. On the other hand, hydrogen ions in aqueous solutions are unique with respect to their high mobility and the mechanism of their conduction[20] and in strongly acid solutions the protons may penetrate the adsorption layer with comparative ease and convert adsorbed H_2O molecules into H_3O^+. The energy barrier involved in the displacement of the hydronium ion would be much less than that involved in the displacement of a water molecule. In this way hydrogen ions could greatly facilitate the growth of the crystal lattice and an explanation could be given for the fact that larger crystals of $SrSO_4$ were obtained from strongly acid solutions than from water, regardless of solubility, relative supersaturation or rate of precipitation and that the crystal size increased with increasing acid concentration. On this basis it is suggested that the growth of $SrSO_4$ crystals is not diffusion controlled but that the rate determining step is the passage of ions from an adsorption layer to lattice positions.

Acknowledgment.—We are indebted to Professor L. E. Spock, Department of Geology, New York University, for measurement of the refractive indices and interfacial angles of the $SrSO_4$ specimens.

[20] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Hydrolysis of Cobalt Chloride and Nickel Chloride at 25°

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The purpose of this investigation was to obtain data on the magnitude of the hydrolysis reactions of the halides of cobalt and nickel. Such data make possible (1) the determination of the character of the ions in dilute solution, (2) the evaluation of the free energy of the reactions involved, (3) the evaluation of the amphoteric nature of the elements and (4) the hydrolysis constants will give check values for (by calculation) equilibrium constants obtained from solubility measurements of the hydroxides of these metals by Garrett and Gayer.[1,2] Previously published work on the hydrolysis of these metal chlorides is incomplete and shows considerable variation in the values obtained; furthermore, solubility measurements of the hydroxides indicate that these data are not reliable being in all cases too high.

This investigation was carried out to obtain data on the magnitude of the hydrolysis reactions of the halides of cobalt and nickel. Thus is possible (1) the determination of the character of the ions in dilute solution, (2) the evaluation of the free energy of the reactions involved, (3) the evaluation of the amphoteric nature of the elements and (4) the hydrolysis constants will give check values for (by calculation) equilibrium constants obtained from solubility measurements of the hydroxides of these metals by Garrett and Gayer.[1,2] Previously published work on the hydrolysis of these metal chlorides is incomplete and shows considerable variation in the values obtained; furthermore, solubility measurements of the hydroxides indicate that these data are not reliable, being in all cases too high. Table I is a summary of previous work by Denham,[3,4] Kullgren[5] and Althammer.[6]

Procedure.—The *p*H values of purified samples of cobalt chloride and nickel chloride were measured in salt concentrations up to about 0.1 molal.

Water.—Triply distilled water was used. It was boiled to free it from carbon dioxide and oxygen, then it was stored under nitrogen.

Preparation of Cobalt and Nickel Chlorides.—Reagent grade salts of both metals were recrystallized from dilute hydrochloric acid solutions. The crystals were then vacuum-dried for a day or two until a gram sample gave constant *p*H values.

Measurement of Hydrogen Ion Concentration.—The *p*H values were obtained by using a Beckman glass electrode. The meter was calibrated with disodium phosphate-monopotassium phosphate buffer at *p*H 7.

Gravimetric Analysis for Nickel.—The purity of nickel chloride and the concentration of the solution was checked by

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[1] K. H. Gayer and A. B. Garrett, THIS JOURNAL, **71**, 2973 (1949).

[2] K. H. Gayer and A. B. Garrett, *ibid.*, **72**, 3921 (1950).

[3] H. G. Denham, *J. Chem. Soc.*, **93**, 41 (1908).

[4] H. G. Denham, *Z. anorg. Chem.*, **57**, 378 (1903).

[5] C. Kullgren, *Z. physik. Chem.*, **85**, 466 (1913).

[6] W. Althammer, Dissert. Halle, 1913, p. 12.