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°

BY KARL H. GAYER AND LEO WOONTNER

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.

TABLE I

Salt	NiCl₂							CoCl₂			
Vol. in liters/mole salt	4.4	8.8	17.2	35.2							
Moles H_2O/mole salt					2	8	32	16	32		
Molar concentration										0.05	0.01
Temperature, °C.	18	18	18	18	100	85.5	100	25	25	25	25
Hydrolysis, %	0.127	0.16	0.23	0.30	0.013	0.008	0.0019	0.11	0.17	0.12	0.53
$K \times 10^{-6}$	0.36	0.29	0.27	0.36	.....	.....	......	...	...	...	...
Investigator	3	3	3	3	5	5	5	4	4	4	4

TABLE II

HYDROLYSIS OF NICKEL CHLORIDE AT 25°

Mole $NiCl_2$/1000 g. of H_2O	Mole H^+/1000 g. of H_2O	$K_1 = \frac{a_{NiOH^+} \times a_{H^+}}{a_{Ni^{++}}} \times 10^{-11}$	
0.0156	4.6×10^{-7}	3.1	
.0312	5.6×10^{-7}	2.0	
.0625	7.2×10^{-7}	1.7	Calculated from previously published data, 1.5×10^{-11}
.1250	1.0×10^{-6}	1.6	
.250	1.6×10^{-6}	2.0	
.500	2.5×10^{-6}	2.6	
	Average	2.3	

TABLE III

HYDROLYSIS OF COBALT CHLORIDE

Mole of $CoCl_2$/1000 g. of H_2O	Mole H^+/1000 g. of H_2O	$K = \frac{a_{COOH^+} \times a_{H^+}}{a_{Co^{++}}} \times 10^{-13}$	
0.01	6.5×10^{-8}	5.6	
.02	9.6×10^{-8}	6.6	Calculated from previously published data, 4.0×10^{-13}
.05	1.2×10^{-7}	4.8	
.075	1.7×10^{-7}	7.1	
.1	2.0×10^{-7}	7.5	
	Average	6.3	

precipitating the nickel with alcoholic dimethylglyoxime as recommended by Treadwell and Hall.[7]

The Data.—Data are collected in Tables II and III. The generalized hydrolysis reaction and equilibrium expression for $NiCl_2$ and $CoCl_2$ is

$$M^{++} + HOH \rightleftarrows MOH^+ + H^+$$

$$K = \frac{a_{MOH^+} \times a_{H^+}}{a_{M^{++}}}$$

Conclusion

Hydrolysis Constant

$$Ni^{++} + HOH \rightleftarrows NiOH^+ + H^+ \quad K = 2.3 \times 10^{-11}$$

$$\Delta F^0 = 14000 \text{ cal./mole}$$

$$Co^{++} + HOH \rightleftarrows CoOH^+ + H^+ \quad K = 6.3 \times 10^{-13}$$

$$\Delta F^0 = 17000 \text{ cal./mole}$$

From the magnitude of the hydrolysis constants it can be concluded that $Ni(OH)_2$ and $Co(OH)_2$ are relatively strong bases. The hydrolysis data confirm the results obtained in solubility measurements of $Ni(OH)_2$ and $Co(OH)_2$.

[7] Treadwell and Hall, "Analytical Chemistry," John Wiley & Sons, Inc., New York City, 9th Ed., 1937–1942.

DEPARTMENT OF CHEMISTRY
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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

Polarographic Study of the Kinetics of Ionic Recombination and Comparison with Onsager's Theory

BY PAUL DELAHAY AND THOMAS J. ADAMS[1]

An equation for the rate constant of processes involving the recombination of two univalent ions is derived from Onsager's theory of ionic recombination. The temperature coefficient of the rate constant is essentially the same as for a diffusion process. The theoretical results are compared with polarographic data for the recombination of pyruvate and hydrogen ions. The dependence of the rate constant on ionic strength is studied experimentally, and the results are analyzed on the basis of the Debye–Hückel theory. Finally, the influence of the rate of the electrode process in polarographic studies of ionic recombination is discussed quantitatively.

The theory of ionic recombination which was developed by Onsager[2] has been verified by measuring the variations of the dissociation constant of weak electrolytes caused by the application of an electrical field of high intensity.[3] The implications of Onsager's theory with regard to the kinetics of ionic recombination have not been explored possibly because of the lack of an experimental method enabling one to verify the theoretical results. With the recent development of a polarographic method for the study of ionic recombination,[4,5,6] it becomes possible at the present to compare theoretical results on ionic recombination with the corresponding experimental data. Such a comparison is the object of the present investigation.

Kinetics of Ionic Recombination

Rate Constants for Ionic Recombination Processes.—The rate of recombination dC_{CA}/dt of

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[1] From a thesis to be submitted by T. J. Adams to the Graduate School of Louisiana State University in partial fulfillment of the requirements for the degree of Master of Science.

[2] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1950, pp. 216–222.

[4] R. Brdicka and K. Wiesner, *Collection Csechoslov. Chem. Commun.*, **12**, 138 (1947).

[5] J. Koutecky and R. Brdicka, *ibid.*, 12, 337 (1947).

[6] P. Delahay, THIS JOURNAL, 73, 4944 (1951). Note that K in equation (15) is in cm. sec.$^{-1}$ (moles per cc.)$^{-1}$.