$PhSiCl_3$, 44 mole % Ph_2SiCl_2 and 5 mole % Ph_3SiCl. While this accounts for only 63% of the silicon, some definite statements concerning the reaction are still possible, on comparing the yield figures with the curves of Figs. 1 and 2. The reaction probabilities cannot be in the geometric ratio, because the yields of mono- and tri-chlorides are too low. It is clearly obvious that $\alpha > 1$; that is, unsymmetrical $RSiCl_3$ reacts much faster with Grignard reagent than symmetrical $SiCl_4$, despite the fact that the latter contains more halogen.

An interesting partially specialized case is obtained by setting $1:\alpha:\beta:\gamma = 1:3\gamma:{}^1/_2:\gamma$, *i. e.*, by setting the ratios of reaction probabilities for the pairs $AX_4 - R_2AX_2$ and $RAX_3 - R_3AX$ equal to their geometrical ratios, and leaving the relative probabilities for symmetrical and unsymmetrical compounds disposable as an arbitrary parameter. For this case

$$y_1 = (y_0 - y_0^{3\gamma})/(3\gamma - 1) \tag{16}$$

$$y_2 = [6\gamma/(6\gamma - 1)][2y_0^{1/2} + y_0^{3\gamma}/(3\gamma - 1) - (6\gamma - 1)y_0/(3\gamma - 1)] \tag{17}$$

$$y_3 = 3\gamma[y_0^{\gamma}/2\gamma(1 - 2\gamma)(1 - \gamma) - 4y_0^{1/2}/(6\gamma - 1)(1 - 2\gamma) + y_0^{3\gamma}/2\gamma(6\gamma - 1)(1 - 3\gamma) - y_0/(1 - 3\gamma)(1 - \gamma)] \tag{18}$$

$$4 - x = 3(4\gamma - 1)y_0^{3\gamma}/2(6\gamma - 1)(1 - 3\gamma) + 12\gamma(1 - 4\gamma)y_0^{1/2}/(6\gamma - 1)(1 - 2\gamma) + 3y_0^{\gamma}/2(1 - 2\gamma)(1 - \gamma) + (1 - 4\gamma)y_0/(1 - \gamma)(1 - 3\gamma) \tag{19}$$

Since (dy_0/dx) does not vanish for $0 < x < 4$, the maximum in y_2 is given by the root of $(dy_2/dy_0) = 0$. We find

$$y_2(\text{max.}) = 2(y_m^{1/2} - y_m) \tag{20}$$

where y_m is the value of y_0 at the x-value where the maximum in y_2 appears. The function

$$f(z) = 2(\sqrt{z} - z)$$

has a maximum of 0.5 when $z = 0.25$, so the yield of R_2AX_2 can never exceed 50% for the case considered in this paragraph.

For the general case, with α, β and γ arbitrary, the condition for a maximum in y_2 leads to

$$y_2(\text{max.}) = (y_m^{\beta} - y_m)/(1 - \beta) \tag{21}$$

where again y_m is the value of y_0 where y_2 is at its maximum. The maximum in y_2 depends only on β and the corresponding value of y_0; the latter, however, depends on α and γ in a complicated way. The function

$$\varphi(z) = (z^{\beta} - z)/(1 - \beta) \tag{22}$$

has a maximum when

$$z = \beta^{1/(1-\beta)}$$

The value of the maximum of $\varphi(z)$ is given by

$$\text{Max. } \varphi(z) = \Phi(\beta) = \beta^{\beta/(1-\beta)} \tag{23}$$

The following values give an estimate of the maximum possible yields of R_2AX_2, considered as a function of β, the relative probability of reaction of R_2AX_2 with Grignard reagent: $\Phi(0) = 1$, *i. e.*, if R_2AX_2 will not react, the final product is obviously R_2AX_2; $\Phi({}^1/_4) = 4^{-1/3} = 0.6300$, $\Phi({}^1/_3) = \sqrt{3}/3 = 0.5773$, $\Phi({}^1/_2) = {}^1/_2$, $\Phi(1) = e^{-1} = 0.3548$, $\Phi(2) = {}^1/_4$, $\Phi(3) = 3^{-3/2} = 0.1925$; and $\Phi(\infty) = 0$, *i. e.*, no R_2AX_2 can accumulate if it has zero relative probability of not reacting.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. VII. A Solubility Method for the Determination of Instability Constants in Solution and the Ammines of Nickel, Cadmium and Magnesium[1]

BY PAUL F. DERR AND W. C. VOSBURGH

To determine the instability constant of a complex ion it is necessary to measure the concentration or activity of one ionic or molecular species at equilibrium, in addition to the total amounts of the reactants. For a metal-ammonia complex ion, for example, the concentration or activity of the uncombined ammonia, of the uncombined (aquo) metallic ion, or of the complex ion may be determined. From one of these together with the total amounts of metallic ion and ammonia and suitable activity coefficients the equilibrium constant can be calculated.

If more than one complex ion is formed, several determinations on mixtures containing varying amounts of the reactants are needed. Simultaneous equations can then be set up which on solution will give the instability constants.

The activity of an aquo-ion in equilibrium with a complex ion can be determined by solubility[2] or electromotive force measurements[3] and that of the ammonia by distribution between the solution and either an immiscible solvent[4] or air.[5] Two spectrophotometric methods applicable in special cases have been described by Job.[6]

Bjerrum[7] has determined the stabilities of a number of metal ammines and ethylenediamine complexes by means of electromotive force measurements with a glass electrode. The electromotive force was related empirically to the concentration of free ammonia under the conditions of

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[1] Part of a thesis submitted by Paul F. Derr in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

(2) Randall and Halford, THIS JOURNAL, **52**, 178 (1930).

(3) (a) Bodländer and Fittig, *Z. physik. Chem.*, **39**, 607 (1902); (b) Job, *Ann. chim.*, [10] **9**, 166 (1928).

(4) Dawson and McCrae, *J. Chem. Soc.*, **77**, 1239 (1900).

(5) De Wijs, *Rec. trav. chim.*, **44**, 663 (1925).

(6) (a) Ref. 3b, 113; (b) Job, *Ann. chim.*, [11] **6**, 97 (1936).

(7) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941.

TABLE I

SOLUBILITY OF SILVER IODATE IN AMMONIA SOLUTIONS CONTAINING NICKEL NITRATE AND THE INSTABILITY CONSTANTS OF THE NICKEL-AMMINE IONS

NH_3, total, $m \times 10^3$	Ni, total, $m \times 10^3$	$AgIO_3$, $m \times 10^3$	NH_4NO_3, $m \times 10^3$	μ	NH_3, free, $m \times 10^3$	NH_3 in Ag complexes, $m \times 10^3$	NH_3 in Ni complexes, $m \times 10^3$	$k_1 \times 10^3$	$k_2 \times 10^3$	$k_3 \times 10^2$
5.28	9.97	0.806	116.1	0.1469	0.675	1.320	3.261	1.64	(9.0)	(2.0)
7.83	9.96	1.175	105.4	.1364	1.060	2.104	4.640	1.65		
10.41	9.97	1.597	107.7	.1392	1.478	2.973	5.92	1.64		
15.69	9.96	2.511	102.5	.1349	2.396	4.83	8.43	1.50		
21.13	9.96	3.643	100.9	.1344	3.52	7.11	10.45	(1.60)	8.5	
21.19	9.96	3.684	100.9	.1345	3.56	7.19	10.39		8.9	
21.00	9.96	3.591	70.5	.1039	3.62	7.05	10.27		9.6	
41.77	19.98	5.525	101.1	.1666	5.19	10.90	25.60		9.1	
31.27	9.96	5.956	101.0	.1369	5.80	11.75	13.68		8.7	
41.69	9.97	8.565	101.1	.1396	8.34	16.97	16.34		9.1	
42.73	9.97	8.822	101.1	.1398	8.59	16.52	16.63		8.7	
53.15	9.98	9.78[a]	101.2	.1512	13.44	19.45	20.23			2.4
64.50	9.97	14.29	109.7	.1539	13.73	28.43	22.32			1.5
71.1	9.98	16.17	110.6	.1567	15.5	32.2	23.4			1.6
96.5	9.98	23.34	107.5	.1608	22.3	46.5	27.6			1.6
128.2	20.00	25.60	115.7	.2013	23.4	51.1	53.7			2.1
128.1	9.99	32.91	104.6	.1675	31.2	65.7	31.2			1.6

[a] This solution contained 0.01014 *m* potassium iodate also.

the experiment. Bjerrum has discussed the theory of equilibrium in systems in which a series of compounds MA, MA_2, . . ., MA_n can be formed from the ion (or molecule) M by successive additions of the molecule or ion A. His experimental results are in agreement with the proposition that metallic ions generally add ammonia or ethylenediamine in steps of one molecule at a time. De Wijs[5] had previously found it necessary to postulate the existence of three different complex ions of nickel and ammonia, with two, four and six molecules of ammonia to one nickel ion. She postulated similar complex ions of cadmium and zinc with two and four molecules of ammonia to one cadmium or zinc ion. Bjerrum points out that the results of de Wijs could be interpreted just as well in term of the stepwise addition of one molecule at a time.

The purpose of this paper is to test a solubility method which differs a little from the solubility method previously used. The method has been applied to the determination of the instability constants of some of the complex ions formed from nickel, cadmium and magnesium ions and ammonia.

The solubility of silver iodate in water and ammonia solutions was first determined, and the results have already been published.[8] The solubility of silver iodate was then determined in solutions containing nickel ion and ammonia. From the results the concentration of free ammonia could be calculated, and with the total amounts of nickel ion and ammonia known, the ammonia bound in the nickel complexes could be calculated.

The method has been applied, in addition, to the complex ions of cadmium and ammonia and magnesium and ammonia. Also the solubility of barium iodate in some ammonia solutions has been determined.

Materials.—The silver iodate and ammonia solutions have been described.[8a]

Nickel, cadmium, and magnesium nitrate stock solutions, about 0.2 *M*, were prepared from chemicals of analytical reagent grade. The nickel nitrate concentration was determined by the dimethylglyoxime method, the cadmium nitrate by evaporation with an excess of sulfuric acid and weighing as cadmium sulfate, and the magnesium nitrate by means of 8-hydroxyquinoline.

Barium and calcium iodates were precipitated from solutions of reagent grade chemicals, digested at a high temperature, carefully washed, and preserved under water.

Ammonium nitrate of reagent grade was dried in a vacuum desiccator.

Nickel-Ammonia Ions.—The experimental procedure for the determination of the stability of the ions formed from nickel ion and ammonia was not much different from the procedure already described[8a] for the silver-ammonia ion. Solutions were prepared by dilution of a mixture of a measured volume of stock nickel nitrate solution, a roughly measured volume of stock ammonia solution and a weighed quantity of ammonium nitrate. In the finished solution nickel nitrate was about 0.01 *m* and ammonium nitrate about 0.1 *m*. Preliminary experiments had shown that this molality of ammonium ion prevented the formation of any hydroxide precipitate for at least a twenty-four-hour period. The solution was then saturated with silver iodate at 25° and samples taken as described in the previous paper. The total ammonia was determined by titration with standard acid. It was shown that the presence of the nickel ion in such a small concentration did not interfere. The total iodate was determined iodometrically.

The solubility of silver iodate in solutions of ammonia containing nickel nitrate is shown in Table I. The molalities in the first three columns are probably in error by not more than two parts in 1000. The ammonium nitrate molality may be somewhat more in error, but not enough to affect the results appreciably.

From the total iodate molality (assumed equal to the iodate ion molality) and from the ionic

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[8] (a) Derr, Stockdale and Vosburgh, THIS JOURNAL, **63**, 2670 (1941); (b) Vosburgh and McClure, *ibid.*, **65**, 1060 (1943).

strength and the solubility product for silver iodate, the silver ion molality was calculated as previously described.[8a] From the silver ion molality and an approximate value of the free ammonia molality obtained by a preliminary calculation, the molality of the monammine silver ion was calculated with the use of the instability constant[8b] $k_1 = 4.3 \times 10^{-4}$. The molality of the monammine silver ion was small and not far from constant, varying from 1 to 1.5×10^{-4} *m* in the various solutions. The remainder of the total silver, after subtraction of the silver ion and monammine molalities, was considered to be diammine silver ion. From its molality, together with that of the free ion and the instability constant of the diammine, the free ammonia molality was calculated. The instability constant[8b] used was $K_2 = 6.2 \times 10^{-8}$. The molality of free ammonia so calculated is given in the sixth column of Table I.

The ammonia bound in the complex nickel ions was calculated as the difference between the total ammonia molality and the sum of the molalities of free ammonia, ammonia in the complex silver ions, and a small amount assumed to be used in the hydrolysis of the nickel ion in accordance with the equation

$$Ni^{++} + H_2O + NH_3 \longrightarrow NiOH^{+} + NH_4^{+}$$

The hydrolysis of nickel salts has been measured by Denham[9] at 25° by means of hydrogen electrode measurements, Kullgren[10] at 85 and 100° by measurements of the rate of sugar hydrolysis, and Vesterberg[11] at 18° by distribution measurements. From the data of Vesterberg, the constant $K = [NiOH^+][H^+]f(\gamma)/[Ni^{++}]$ was calculated and found to be 4×10^{-10} at 18°. Kullgren found $K = 2.5 \times 10^{-9}$ at 100°, while Denham's value is much higher. Assuming $K = 5 \times 10^{-10}$ at 25°, the ratio of $[NiOH^+]$ to $[Ni^{++}]$ can be shown to be approximately equal to half the ratio of $[NH_3]$ to $[NH_4^+]$ at the ionic strength used in the present experiments. In the most dilute ammonia solution about 0.3% of the free nickel ion is hydrolyzed according to this method of estimation. Although neglect of this reaction would not affect the conclusions appreciably, the small amounts of ammonia and nickel ion calculated to take part in the hydrolysis were subtracted from the total ammonia and total nickel, respectively.

From the data in the second, sixth and eighth columns of Table I, the equilibrium constants were calculated. The assumption was first tried that the complex ion of smallest ammonia content was the diammine, in agreement with de Wijs.[5] This assumption failed, and it was necessary to assume with Bjerrum[7] that ammonia can add to nickel ion (or displace water molecules) in steps of one molecule at a time. It was possible by a system of rather laborious, but not difficult, approximations to calculate a set of equilibrium constants that are consistent with the data. The equilibrium constants are defined by the equations

$$[Ni(NH_3)_{n-1}^{++}][NH_3] = k_n\ [Ni(NH_3)_n^{++}]$$

in which *n* may vary from one to six and brackets indicate concentrations. Activity coefficients should cancel approximately. The values for the first three constants, k_1, k_2 and k_3, which were derived from the experimental results, are given in Table I. The assumed values $k_4 = 0.05$ and $k_5 = 0.07$ were found to give satisfactory constancy in k_1, k_2 and k_3. The sixth complex ion was not formed in large enough amount in the most concentrated solutions to allow an estimate of the sixth constant. The values in parentheses in the table are values assumed in the calculation of those not in parentheses. The method of approximation used required the assumption of instability constants for all but one of the complex ions present and the calculation of the constant not assumed from the data. This method was possible because two constants were sufficient for the most dilute solutions.

The constant k_1 is probably the most nearly correct. Errors in the other constants assumed in the calculation k_1 had little effect. The uncertainty was greater for k_2 and still greater for k_3, while the values for k_4 and k_5 were merely those which led to satisfactory results for k_1, k_2 and k_3.

The constants are to be considered at least in fair agreement with the constants of Bjerrum, for similar conditions (25° and 0.1 *m* ammonium nitrate) as the following comparison shows.

	$n = 1$	2	3	4	5	6
Bjerrum,[12] k_n	0.0019	0.0069	0.022	0.077	0.21	1.1
D. and V., k_n	.0016	.009	.022	(.05)	(.07)	...

Monammine Cadmium Ion.—The method was applied to complex ions formed from cadmium ion and ammonia also. In this case only a narrow range of dilute solutions could be measured, because a total ammonia concentration of more than 0.02 *m* led to a change in the solid phase. The results are given in Table II.

TABLE II

INSTABILITY CONSTANT OF THE MONAMMINE-CADMIUM ION[a]

NH_3, total, $m \times 10^3$	Cd, total, $m \times 10^3$	$AgIO_3$, $m \times 10^3$	NH_4NO_3, $m \times 10^3$	NH_3, free, $m \times 10^3$	NH_3 in Ag complexes, $m \times 10^3$	NH_3 in Cd complexes, $m \times 10^3$	$k_1 \times 10^3$
5.34	10.32	0.9185	99.6	0.840	1.70	2.80	2.74
7.95	10.32	1.370	104.3	1.279	2.59	4.08	2.67
10.55	10.32	1.847	107.3	1.741	3.55	5.26	2.66
20.87	10.32	3.942	97.3	3.83	7.74	9.30	2.74

[a] Constants k_2 and k_3 were assumed to be 0.010 and 0.025, respectively.

The experimental data are in accord with the assumption that monammine, diammine, and tri-

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[9] Denham, *J. Chem. Soc.*, **93**, 62 (1908).

[10] Kullgren, *Z. physik. Chem.*, **85**, 480 (1913).

[11] Vesterberg, *Z. anorg. Chem.*, **99**, 22 (1917).

[12] These values are actually the reciprocals of Bjerrum's stability or formation constants.

ammine cadmium ions exist in equilibrium with cadmium ion and ammonia in the concentration range investigated. By assuming instability constants for the diammine and triammine about 10% larger than those of the corresponding nickel ions, satisfactory constants were obtained for the monammine. These are given in the last column of Table II. In the calculations the hydrolysis of cadmium ion was neglected, since Kullgren[10] and Denham and Morris[13] found cadmium ion to be less hydrolyzed than nickel ion. Bjerrum[7] found 2.8×10^{-3} for k_1 as compared with 2.7×10^{-3} in this investigation.

Magnesium Ion and Ammonia.—Magnesium ion has only a small effect on the solubility of silver iodate in ammonia solutions, according to the results in Table III. A small amount of ammonia can be considered to have combined with magnesium ion, and assuming that only the monammine ion is formed, the instability constant is in the vicinity of unity. Bjerrum[7] found 0.59 at 23° and in 2 *M* ammonium nitrate solution.

TABLE III

INSTABILITY CONSTANT OF THE MONAMMINE MAGNESIUM ION

NH_3, total, $m \times 10^2$	Mg, total, $m \times 10^2$	$AgIO_3$, $m \times 10^2$	NH_4NO_3, $m \times 10^2$	NH_3, free, $m \times 10^2$	NH_3 in Ag complexes, $m \times 10^2$	NH_3 in Mg complex, $m \times 10^2$	k_1
3.561	1.005	1.165	3.89	1.234	2.317	0.010	1.2
8.09	4.028	2.780	7.94	2.485	5.54	.061	1.6
16.17	4.028	5.52	4.00	4.99	11.02	.16	1.2

Solubility of Calcium and Barium Iodates in Ammonia Solutions.—The solubilities of calcium and barium iodates are so small that the method described above could not be used to investigate ammine formation by these cations. Kolthoff and Stenger[14] found that calcium iodate is less soluble in 0.5 to 2 *M* ammonia solution than in water and concluded that there was no complex ion formation. However, Bjerrum[7] found that calcium ion forms a series of very unstable ammines. The decrease in solubility is probably the resultant of a small amount of ammine formation and a larger decrease in solubility than the apparent one.

In this investigation the apparent solubility product of calcium iodate was found to be unaffected by the presence of 0.1 mole per liter of ammonia but decreased when the ammonia concentration was larger. The solubility in water, 7.83×10^{-3} mole per liter, agreed excellently with the values of Kolthoff and Stenger[14] and Davies and Wise.[15]

The solubility of barium iodate in ammonia solutions was also determined. The results are given in Table IV. The activity solubility product, $K_{\text{S. P.}} = f^3[Ba^{++}][IO_3^-]^2$ where $f = 1.011\sqrt{\mu}/(1 + \sqrt{\mu})$, is shown to decrease as the ammonia concentration increases. This is in agreement with the observation of Hill and Zinc[16] that barium iodate is considerably less soluble in concentrated ammonia solution than in water. The decrease in the solubility product is roughly proportional to the ammonia concentration. If the same relationship holds in more dilute solutions, a 1% decrease would be caused by 0.03 to 0.04 *M* concentration of ammonia. If a little complex ion is formed, the true decrease in the solubility product is still larger than this.

The solubility of barium iodate in water agrees excellently with that found by Davies and MacDougall.[17]

TABLE IV

SOLUBILITY OF BARIUM IODATE IN AMMONIA SOLUTIONS

NH_3, total, *M*	$Ba(IO_3)_2$, $M \times 10^4$	NH_4^+ or OH^-, $M \times 10^3$	$\mu \times 10^3$	$K_{\text{S. P.}} \times 10^9$
....	8.09	..	2.43	1.53
....	8.47	2.29[a]	4.84	1.54
0.1682	8.24	1.74	4.21	1.46
.3912	8.30	2.66	5.16	1.44
.894	7.70	4.01	6.32	1.09
1.016	7.65	4.28	6.58	1.06

[a] Ammonium nitrate was added.

Summary

Instability constants for the complex ions formed from nickel, cadmium and magnesium ions and ammonia have been determined by measurements of the solubility of silver iodate in ammonia solutions containing the complex ions.

It was necessary to assume complex ions of the type $M(NH_3)_n^{++}$ where *n* can have any integral value up to a maximum, presumably six, which was not approached in the present experiments.

Instability constants were determined for monammine, diammine and triammine nickel ions, and monammine cadmium and magnesium ions.

The solubility of barium iodate in ammonia solutions was determined.

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[13] Denham and Morris, *Trans. Faraday Soc.*, **24**, 515 (1928).

[14] Kolthoff and Stenger, *J. Phys. Chem.*, **38**, 640 (1934).

[15] Davies and Wise, *J. Chem. Soc.*, 275 (1938).

[16] Hill and Zinc, THIS JOURNAL, **31**, 44 (1909).

[17] Davies and MacDougall, *J. Chem. Soc.*, 1418 (1935).