[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Conductance of Hydrogen Chloride and Ammonium Chloride in Ethanol–Water Mixtures

BY IRVING I. BEZMAN AND FRANK H. VERHOEK

The electrical conductivity of hydrogen chloride in ethanol–water mixtures has been investigated by several workers.[1] These results, however, were not obtained using experimental[2] and computational[3] techniques which are now available. This paper reports the results of a reinvestigation of the conductivity of hydrogen chloride in ethanol and in ethanol containing small amounts of water. For comparison, the conductivity of ammonium chloride in ethanol and in ethanol containing water was also determined; the only previous data for the conductivity of this salt in these solvents are those of Goldschmidt and Görbitz.[4]

Experimental

Materials.—Hydrogen chloride was prepared by dropping concentrated sulfuric acid on reagent grade sodium chloride, and passing the gas through drying tubes containing Drierite.

The ammonium chloride was a reagent grade recrystallized by precipitating from a water solution by adding alcohol, and dried over Drierite.

Ethyl Alcohol.—Absolute ethyl alcohol from The Ohio State University Laboratory Supply stores, prepared by distilling with benzene, was dried and distilled. For most of the experiments, drying was carried out by refluxing several hours over Drierite and distilling through a column 50 cm. long packed with glass helices, discarding the first and last third.

The water content of alcohol prepared in this manner was determined by the method of Smith[5] and found to be consistently of the order of 1.5 g. per liter. The specific conductivity was of the order of 10×10^{-9} to 50×10^{-9} reciprocal ohm, indicating that the presence of small amounts of water cannot be detected by conductivity measurements.

For the preparation of water-free alcohol, refluxing over lime for forty-eight hours and distillation, retaining the middle third, was used. This was found to be more successful in dehydrating the alcohol for conductivity measurements then the methods of Danner and Latimer,[6] or Lund and Bjerrum.[7] The specific conductivity of this alcohol was 7×10^{-9} reciprocal ohm.

The manipulative difficulties in the use of the Smith method for determining the water content of alcohol samples made the use of density measurements more satisfactory as a routine method for determining the composition of the solvent. In order that the measured density might be exactly related to the work being done, the densities of known mixtures of alcohol and water, in the range up to 41 g. of water per liter, were measured, and plotted against the water concentrations on a large-scale graph for interpolation. The alcohol used was that distilled from Drierite, with its water concentration determined in duplicate by the Smith method; additional amounts of water were added from a weight buret. The volume of the pycnometer was 36.4334 cc. at 25°. The densities obtained were found to lie on a smooth curve about 0.00020 unit below the values of Osborne, McKelvy and Bearce[8] for corresponding water concentrations.

Apparatus.—Conductivities were measured with a Jones bridge of the Dike[9] design powered by a Western Electric Type 8A oscillator; the signal was amplified and led into telephone receivers. For the measurements a frequency of 3000 c. p. s. was used, with occasional checks at other frequencies. These checks showed bridge balance to be independent of frequency.

The thermostat was an insulated cylindrical copper tank of 30 gallons capacity filled with high-grade transformer oil. To the inner wall of the tank was soldered 30 feet of $^1/_4''$ copper tubing through which water circulated at a constant rate and a constant temperature of 19° maintained by an auxiliary bath. Heating of the oil to 25° was carried out with three 75-watt light bulbs placed in different parts of the bath, actuated through a thyratron tube by a large mercury-in-glass thermoregulator. The temperature was measured by means of an 18–30° calorimetric thermometer calibrated by the Bureau of Standards and checked at the ice point twice during the investigation; control was accurate to 25 ± 0.003°.

The conductivity cell of Pyrex glass contained two bright platinum disks approximately 4 cm. in diameter held in a fixed position 5 mm. apart by three glass spacers. Platinum leads spot-welded to the centers of the disks were connected to mercury wells through lead glass seals. The cell carried a ground joint at the top for filling and a stopcock and ground joint at the bottom for emptying. Spacing of the leads was in accord with the recommendations of Jones.[10] The cell constant was so low that it was not feasible to determine it by measuring the resistance of a standard potassium chloride solution in it, and recourse was had to a step-down arrangement whereby the constant of a cell of higher cell constant was determined, using 0.1 *N* KCl, then the constant of a second cell by comparing the resistance of a dilute potassium chloride solution in the first and the second cells, and finally comparing the resistance of a still more dilute solution in the second cell with that in the cell used in the investigation. By this means the measured resistance was always within the range of accurate measurement on the bridge. The potassium chloride used was recrystallized several times from water and fused in platinum; the primary standard solution contained 7.4334 g. KCl in 1000 g. of a solution made with conductivity water, and the value 0.0128862 reciprocal ohm was used for its specific conductivity.[11] The constant for the cell used in the investigation was 0.02854; the volume of the cell was approximately 100 cc.

All the glass apparatus—alcohol still, alcohol storage flasks, solution and dilution flasks, weight burets, and the cell itself—were equipped with standard taper joints, to prevent exposure to air while transferring solution from one flask to another. Such transfer was made by forcing solution about under pressure of dried nitrogen.

Procedure.—The solutions containing hydrogen chloride were prepared by passing dried gas into prepared samples of solvent in a tared flask until the solution was approximately 0.1 *N*. During this time the solvent was chilled in ice to prevent any possible reaction. Samples were

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(1) Goldschmidt, *Z. physik. Chem.*, **89**, 131 (1914); **114**, 1 (1925); Thomas and Marum, *ibid.*, **143**, 191 (1929).

(2) Jones, et al., THIS JOURNAL, **50**, 1049 (1928); **51**, 2407 (1929); **53**, 411 (1931).

(3) Kraus and Fuoss, *ibid.*, **55**, 476 (1933); Fuoss, *ibid.*, **57**, 488 (1935).

(4) Goldschmidt and Görbitz, *Z. physik. Chem.*, **99**, 128 (1921).

(5) Smith, *J. Chem. Soc.*, 1284 (1927).

(6) Danner and Latimer, THIS JOURNAL, **44**, 2827 (1922).

(7) Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

(8) Osborne, McKelvy and Bearce, *Bull. Bur. Stds.*, **9**, 327 (1913).

(9) Dike, *Rev. Sci. Inst.*, **2**, 379 (1931).

(10) Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

(11) Jones and Prendergast, *ibid.*, **59**, 731 (1937).

withdrawn for analysis and density determinations, the remainder weighed and quickly diluted to 0.002–0.004 *M*. A portion of the diluted solution was forced into the conductivity cell, the latter placed in the thermostat and the resistance measured after temperature equilibrium had been established. The cell was then drained, refilled with solution, and the resistance measurement again made. This was continued until two successive fillings with the same solution gave the same resistance. This procedure corrected for changes in conductivity of the solutions on standing in the cell, due apparently to adsorption on the electrodes, which became more noticeable in the more dilute solutions. The solution remaining in the flask was weighed, and a weighed additional quantity of solvent added. The conductivity cell was drained, rinsed and filled with the diluted solution, and the resistance again determined.

For the salt solutions a solution 0.002–0.004 *M* was prepared by dissolving a known quantity of salt, weighed to the fifth place on a semi-micro balance, in a weighed quantity of solvent, after which resistance measurements and dilutions were carried out as before.

Weight concentrations were changed to volume concentrations using the density of the solvent except in concentrated solutions where the difference between solution and solvent densities was greater than the precision of the measurements; in these cases, solution densities were determined and used.

Results

When the observed equivalent conductances are plotted against the square root of the solute concentration, a straight line is obtained. In all except the highest water concentrations with hydrogen chloride, however, the slopes of these straight lines are greater than the expected slopes as calculated from the Onsager equation,[12] indicating ion-pair formation. For each solution and solute, therefore, values of the equivalent conductance at infinite dilution, Λ^0, and the dissociation constant, *K*, were calculated by the methods of Kraus and Fuoss.[3] In general two approximations were sufficient to establish the value of Λ^0. Values of dielectric constants[13] and viscosity[14] were obtained from the literature.

From the observed values of the dissociation constant and the values for the dielectric constants of the solvents, the distance of closest approach, *A*, of the ions was calculated. The treatment followed was that of Bjerrum.[15]

TABLE I

EQUIVALENT CONDUCTANCE OF HYDROGEN CHLORIDE IN ETHANOL–WATER MIXTURES AT 25°

		C, (m./liter × 10^4)	Λ
H_2O	0.000	1.548	80.94
κ	7.0×10^{-9}	4.212	77.97
Obs. slope	360	7.187	75.72
Calcd. slope	199	11.72	73.04
Λ^0	84.25	15.51	71.31
K	0.0113	19.50	69.54
A	3.99	23.50	68.11
		28.82	66.75
H_2O	0.005	2.789	73.47
κ	8.8×10^{-9}	4.204	72.41
Obs. slope	335	5.941	70.85
Calcd. slope	191	7.833	69.81
Λ^0	78.19	13.04	67.05
K	0.0109	19.34	64.64
		26.51	62.54
H_2O	0.030	7.513	64.10
κ	12.6×10^{-9}	10.51	62.65
Obs. slope	265	14.81	60.87
Calcd. slope	181	22.97	58.29
Λ^0	71.28	31.94	56.14
K	0.0142	46.01	53.62
H_2O	0.0833	1.940	57.32
κ	12.8×10^{-9}	3.090	56.41
Obs. slope	263	4.520	55.33
Calcd. slope	167	7.580	53.75
Λ^0	60.31	11.30	52.17
K	0.0131	17.30	50.29
A	4.52	27.50	48.18
H_2O	0.174	1.690	51.86
κ	12.8×10^{-9}	3.183	50.77
Obs. slope	216	4.611	49.95
Calcd. slope	158	6.401	49.18
Λ^0	54.28	9.994	47.84
K	0.0185	13.48	46.73
A	5.37		
H_2O	0.681	1.774	43.88
κ	37.8×10^{-9}	2.512	43.51
Obs. slope	160	3.971	42.84
Calcd. slope	143	6.351	41.83
Λ^0	45.52	9.553	41.00
K	0.0465	11.63	40.46
A	8.42	16.83	39.45
		21.79	38.47
		25.47	37.97
H_2O	1.40	2.758	43.18
κ	52.5×10^{-9}	6.153	42.01
Obs. slope	142	9.644	40.99
Calcd. slope	137	12.27	40.48
Λ^0	45.52	14.83	40.01
K	0.151	20.19	39.05
A	9.95	27.63	38.00
H_2O	2.39	2.004	43.89
κ	77.6×10^{-9}	3.694	43.18
Obs. slope	129	6.028	42.62
Calcd. slope	130	8.896	41.92
Λ^0	45.70[a]	11.88	41.26
K	. . .[b]	20.86	39.79
		29.29	38.75
		40.51	37.60
H_2O	5.82	3.884	48.87
κ	125×10^{-9}	5.330	48.54
Obs. slope	119	9.093	47.63
Calcd. slope	118	13.22	46.97
Λ^0	51.20[a]	17.93	46.18
K	. . .[b]	22.67	45.81
		28.86	44.91

[a] Extrapolated from conductance curves. [b] Completely dissociated.

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(12) Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1928).

(13) Akerlof, THIS JOURNAL, **54**, 4125 (1932).

(14) "International Critical Tables," Vol. V, p. 22.

(15) Bjerrum, *Kgl. Danske Viden. Selsk.*, VII, **9**, 2 (1926).

TABLE II

EQUIVALENT CONDUCTANCE OF AMMONIUM CHLORIDE IN ETHANOL-WATER MIXTURES AT 25°

		C, (m./l. × 10^4)	Λ
H_2O	0.000	1.963	40.51
κ	11.4×10^{-9}	2.829	39.98
Obs	209	3.887	39.34
Calcd.	144	4.884	38.86
Λ^0	43.05	7.095	37.80
K	0.0167	8.227	37.46
A	5.08	9.416	37.04
		12.08	36.21
H_2O	0.533	2.670	39.40
κ	31.1×10^{-9}	3.712	38.82
Obs.	193	5.206	38.23
Calcd.	138	6.849	37.54
Λ^0	42.11	9.096	36.75
K	0.0174	10.59	36.30
A	4.98	12.28	35.83
H_2O	0.587	3.499	39.13
κ	43.1×10^{-9}	4.369	38.61
Obs.	190	6.964	37.59
Calcd.	137	9.294	36.85
Λ^0	42.07	13.48	35.61
K	0.0205	17.94	34.70
A	5.53		
H_2O	1.171	5.671	37.89
κ	47.4×10^{-9}	6.950	37.47
Obs.	176	9.678	36.58
Calcd.	132	12.07	35.99
Λ^0	41.70	13.29	35.71
K	0.0227	17.17	34.79
A	5.61		
H_2O	4.41	2.340	40.26
κ	89.6×10^{-9}	3.654	39.68
Obs.	140	6.513	38.71
Calcd.	108	8.994	38.16
Λ^0	42.08	10.95	37.72
K	0.0340	14.64	37.00
A	5.32		

The experimental results are given in Tables I and II. The first columns give the molar concentration of water in the solvent and its specific conductivity in reciprocal ohms; the observed value of the slope of the curve when the equivalent conductance is plotted against the square root of the concentration, and the slope calculated from the Onsager equation; values of Λ^0 and K from the Fuoss calculations; and the values of the ionic separation, A, determined from the Bjerrum treatment, in Ångström units. The second and third columns give the equivalent conductance at the measured concentrations.

In Fig. 1 the values of Λ^0 are plotted against the water concentration, the larger figure representing the low concentrations and the insert the whole range studied. Figure 2 contains a large-scale graph of the Onsager slope plotted against the water concentration for hydrogen chloride at low water concentration and inserts for the whole range for both electrolytes. The scale of the two inserts is the same; the curves have simply been separated for clarity. In all three graphs in the figure, the lower curve represents the Onsager slope calculated from the properties of the solvent and the value of the conductance at infinite dilution from the Fuoss equation.

Discussion

For both the electrolytes investigated, the equivalent conductance at infinite dilution decreases as water is added to the alcohol and then increases again, though the minimum is much more pronounced with hydrogen chloride than with ammonium chloride. This is in accord with previous experience in ethanol-water mixtures.[16] The rapid change in the conductance of hydrogen chloride on the addition of small amounts of water is evidently the reason for the widely varying values of Λ^0 reported in the literature for hydrogen chloride in "anhydrous" alcohol. The change is explained as a change from conductivity involving proton transfer from the $C_2H_5OH_2^+$ ion to conductivity involving mass transfer of the H_3O^+ ion.[17]

Goldschmidt[1] and others[18] have calculated values of the equilibrium constant for the reaction $C_2H_5OH_2^+ + H_2O \rightleftarrows C_2H_5OH + H_3O^+$. On the assumption that the conductance due to chloride ion does not change with changing water concentration and that there is no molecular HCl present in the solution, the value of x, the fraction of protons present as H_3O^+, may be calculated from

$$\Lambda_0^0 - \Lambda_M^0 = x(\lambda^0_{\mathrm{EtOH_2^+}} - \lambda^0_{\mathrm{H_3O^+}})$$

Here Λ_0^0 represents the equivalent conductance at infinite dilution in pure alcohol and Λ_M^0 that at water concentration M moles per liter; $(\lambda^0_{\mathrm{EtOH_2^+}} - \lambda^0_{\mathrm{H_3O^+}})$ is the difference between the Λ^0 values in pure alcohol and the minimum value at $M \simeq 1.0$. Note that the Λ^0 values are those at infinite dilution, so that there is no question but that dissociation is complete. From x the equilibrium constant is obtained from $K = x/(1 - x)M$. The values obtained are given in Table III; they are in agreement with those reported by previous investigators.

TABLE III

M	Λ_M^0	K
0.005	78.2	37.3
.030	71.3	16.8
.083	60.3	19.4
.174	54.3	19.5

Comparison of the results for ammonium chloride and for hydrogen chloride show that although

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[16] See, for example, Goldschmidt, ref. 1.

[17] Hückel, *Z. Elektrochem.*, **34**, 546 (1928); Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933); Baker and LaMer, *ibid.*, **3**, 406 (1935); Longsworth and MacInnes, THIS JOURNAL, **59**, 1666 (1937).

[18] Deyrup, *ibid.*, **56**, 63 (1934).

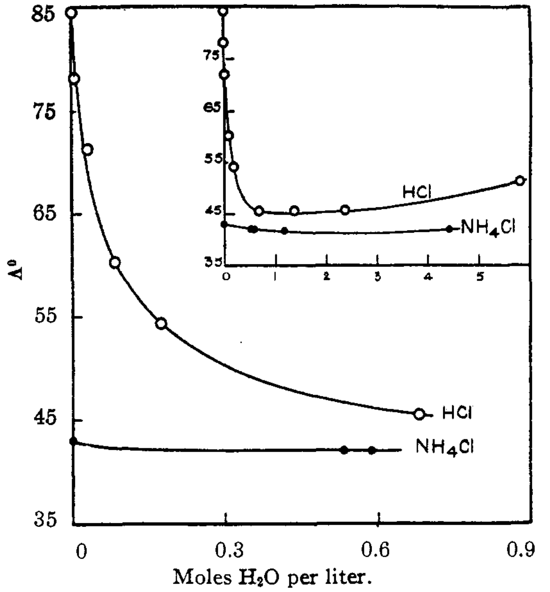

Fig. 1.—Equivalent conductance of hydrogen chloride and ammonium chloride in ethanol-water mixtures: circles, HCl; dots, NH_4Cl.

both are about equally associated to ion pairs in pure alcohol, the addition of water to the alcohol causes hydrogen chloride to become completely dissociated while the dissociation of ammonium chloride does not change appreciably. The change in the hydrogen chloride dissociation is illustrated in Fig. 2 by the approach of the observed Onsager slope to the calculated value with increasing water content of the solvent. The calculated values of K increase correspondingly (Table I) and become indeterminate at a water concentration above 2 M. With ammonium chloride, however, the slopes remain greater than the calculated slopes and the dissociation constant remains small out to 4 M H_2O. When ionic separations are calculated from these data it is seen that the value for hydrogen chloride is originally less than that for ammonium chloride, but increases to a value twice as great as that for the latter.

The value for the interionic separation of hydrogen chloride at the higher water concentration is much larger than the values calculated for water solution[19] and larger also than those obtained for dioxane–water mixtures.[20] It is to be noted, however, that Owen and Waters observed an increase in ion separation with increasing water concentration, corresponding to the increase observed here. To account for the larger ionic separation in water-containing solution than in pure alcohol, in spite of the smaller size of the water molecule compared to the alcohol molecule, it must be assumed that the solvent sheath of water molecules is several molecules thicker than the corresponding sheath of alcohol molecules. Perhaps the force field of the cation is transferred out through a chain of water molecules farther than through alcohol molecules with their terminal ethyl groups. The more symmetrical ammonium ion exerts a much smaller orienting effect than the hydronium ion, and is therefore but little solvated in any of the solvent mixtures,[21] or adds just enough more water molecules to the solvent sheath to compensate for lost alcohol molecules, as the water content of the solution increases. The larger size of the hydronium ion in alcohol solution 2 M in H_2O compared to its size in pure water is evidence for the sorting effect of ions in mixed solvents.

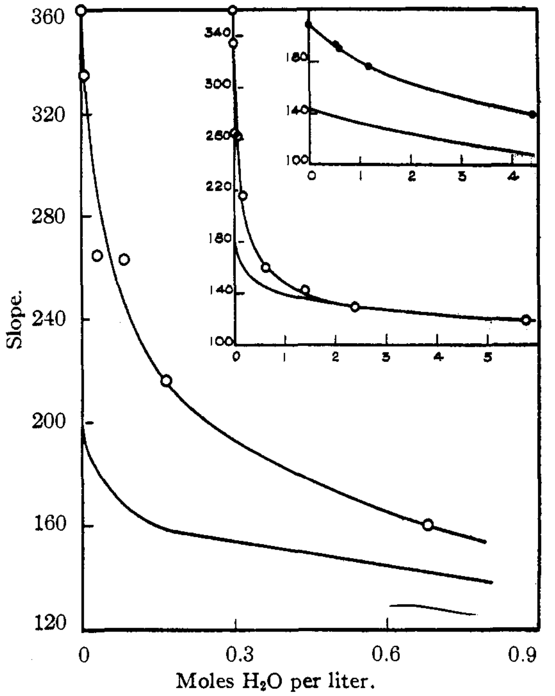

Fig. 2.—Change of Onsager slope with change in water concentration for hydrogen chloride and ammonium chloride in ethanol: circles, HCl; dots, NH_4Cl.

Summary

1. The conductivity of hydrogen chloride has been measured in ethanol containing small amounts of water, and values for the equivalent conductance at infinite dilution and for the dissociation constant have been calculated.

2. The equivalent conductance at infinite dilution passes through a minimum when the water concentration is approximately 1 M.

3. Values for the Onsager slopes are larger than the theoretical values in pure ethanol but approach and become equal to the theoretical value at approximately 2 M H_2O; correspondingly, association is large in pure alcohol, but dissociation rapidly becomes complete as water is added.

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[19] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933); Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936).

[20] Owen and Waters, *ibid.*, **60**, 2371 (1938).

[21] Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

4. The conductivity of ammonium chloride has been measured in ethanol containing small amounts of water, and values for the equivalent conductance at infinite dilution and for the dissociation constant have been calculated.

5. The equivalent conductance at infinite dilution undergoes a much smaller change than in the case of hydrogen chloride, passing through a shallow minimum at 2.5 M H_2O.

6. Values for the Onsager slopes are larger than the theoretical for all the solvent mixtures investigated; correspondingly, association is large in all the solvent mixtures, for ammonium chloride.

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[Contribution from the Chemical Laboratory of The Ohio State University]

Equilibrium Constants for the Formation of Ammine Complexes with Certain Metallic Ions[1]

By Gordon A. Carlson, James P. McReynolds, and Frank H. Verhoek

The study of the complexes formed between metallic cations and ammonia or amines has usually been directed toward the establishment of complex formation, or at most to a determination of the equilibrium constant for the over-all reaction

$$M + NA \rightleftharpoons MA_N \qquad (1)$$

Bjerrum,[2] however, has emphasized the importance of investigating the intermediate steps which enter into the over-all reaction

$$\begin{aligned} &M + A \rightleftharpoons MA \\ &MA + A \rightleftharpoons MA_2 \\ &\cdots\cdots\cdots\cdots \\ &MA_{n-1} + A \rightleftharpoons MA_n \qquad (2) \\ &\cdots\cdots\cdots\cdots \\ &MA_{N-1} + A \rightleftharpoons MA_N \end{aligned}$$

In these equations M represents the central ion, A the coördinating ligand and MA_N the coördinatively saturated complex ion. The concentration equilibrium constants for equations (2), written

$$k_n = [MA_n]/[MA_{n-1}][A] \qquad (3)$$

Bjerrum calls formation constants, while that for equation (1)

$$K_N = [MA_N]/[M][A]^N \qquad (4)$$

is called the complexity constant. Bjerrum shows how measurements of the hydrogen-ion concentrations of solutions containing amines and salts of complex-forming metals may be used to determine the successive formation constants and the composition of the coördinatively saturated complex ion.

This paper reports the results of a study of the formation of ethylenediamine and propylenediamine complexes of copper, nickel, cadmium and zinc ions and the complexes of silver ion with ethyl and diethyl-amine.

Calculation of the Constants

Since the maximum value of N for the systems investigated here is three, only the equations needed for those systems will be developed. The development is due to Bjerrum,[2] who has also treated the general case.

Let $\bar{n}$ be the ratio of the concentration of complex-bound ligand—for the moment not a basic substance—to the total concentration of central ion.

$$\bar{n} = \frac{C_A - [A]}{C_M} = \frac{[MA] + 2[MA_2] + 3[MA_3]}{[M] + [MA] + [MA_2] + [MA_3]} \qquad (5)$$

Here C_A is the total concentration of ligand, C_M the total concentration of metal ion, and [A] the concentration of free ligand. If equations of the type (3) are solved for $[MA_n]$ and substituted in (5), one obtains

$$\bar{n} = \frac{k_1[A] + 2k_1k_2[A]^2 + 3k_1k_2k_3[A]^3}{1 + k_1[A] + k_1k_2[A]^2 + k_1k_2k_3[A]^3} \qquad (6)$$

Bjerrum calls $\bar{n}$ the formation function of the system, and the curve obtained by plotting $\bar{n}$ against $-\log [A] = p[A]$ is called the formation curve.

If the ligand is basic, allowance also must be made for the fact that ligand is removed by reaction with hydrogen ion as well as with metal ion. For a monamine, for example, the total amine concentration is given by

$$C_A = [A] + [AH^+] + \bar{n}C_M \qquad (7)$$

Defining α as the fraction of the amine not complex bound which exists as free amine and $\bar{n}_A$ as the mean number of hydrogen ions bound to not-complex-bound amine, we have

$$\alpha = \frac{[A]}{[A] + [AH^+]} = \frac{k_{AH}}{k_{AH} + [H^+]} \qquad (8)$$

$$\bar{n}_A = \frac{[AH^+]}{[A] + [AH^+]} = \frac{[H^+]}{k_{AH} + [H^+]} \qquad (9)$$

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[1] From a dissertation submitted by Gordon A. Carlson to the Graduate School of The Ohio State University in June, 1944, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The problem was suggested by Professor James P. McReynolds; the major portion of the work was carried out after his death in June, 1943, under the direction of Professor Frank H. Verhoek.

[2] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941. A complete review is given in *C. A.*, **35**, 6527-6534 (1941).