CCLXV.—*A Simple Electrochemical Method for the Simultaneous Determination of the Constitution and Equilibrium Constant of Complex Ions in Solution. Application to Complex Silver Ions.*

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A PREVIOUS determination (J., 1928, 269) of the solution tension of silver in ten organic liquids showed that there was no simple relationship between this property and the dielectric constant of the solvent. In liquids whose molecules contained amino- or nitrile groups silver was found, however, to have a much higher solution tension than in those containing hydroxyl or ketonic groups. These facts indicated an interconnexion between solution tension, solvation, and complex formation, and led to the present investigation.

Consider the cell, $\mathrm{M}\begin{array}{|c:c|}\text{MS in} & \text{MS in}\\ \text{solvent B} & \text{solvent A}\end{array}\mathrm{M}$, where MS is a salt of the metal M. Then if c_A and c_B are the concentrations (or, more strictly, activities) of the metal ion M^{n+} in the solvents A and B respectively, according to the Nernst formula the *E.M.F.* (E) of this cell is given by

$$\begin{aligned} E - e &= (RT/nF) . \log_e P_A c_B / P_B c_A \\ &= (RT/nF) . \log_e c_B / \gamma_{AB} c_A \quad . \quad . \quad . \quad . \quad (1) \end{aligned}$$

where P_A and P_B are the respective solution tensions of the metal in the two solvents, $\gamma_{AB} = P_B/P_A$ is the ratio of these solution tensions, and e is the liquid-junction potential. It may be noted that γ_{AB} is identical with what Nernst has called the specific ionic distribution coefficient of the metal ion between two solvents; for, in the special case of distribution equilibrium, it is evident on thermodynamic grounds that $E = 0$ and equation (1) then reduces to

$$e = (RT/nF) . \log_e \gamma_{AB} c_A / c_B$$

which is the formula given by Nernst (*Z. physikal. Chem.*, 1892, **2**, 139) for the liquid-junction potential at distribution equilibrium.

The ratio γ_{AB} in equation (1) is in the nature of an activity coefficient, since it is evidently the factor by which the concentration of A-solvated ions must be multiplied in order to give the concentration at which B-solvated ions would have the same electromotive effect. When $\gamma_{AB} = 1$, equation (1) reduces to the formula for a concentration cell with a single solvent. For a solvent S compared with water, the ratio $P_W/P_S = \gamma_{SW}$, determined in the previous investigation (*loc. cit.*), may be called the "solvation activity coefficient" of a given ion in that solvent; γ_{AB} is therefore the ratio of two solvation activity coefficients. The further significance of this concept will be developed in a later paper.

Consider now the cell, $\mathrm{M}\left|\begin{array}{c}\text{MS in}\\ \text{solvent B}\end{array}\right\vdots\begin{array}{c}\text{MS in a mixture of}\\ \text{solvents A and B}\end{array}\left|\mathrm{M}\right.$, in which the pure solvent B contains B-solvated ions at concentration c_B, whilst the mixed solvent contains both A-solvated and B-solvated ions at the respective concentrations c_A' and c_B'. If it be assumed that the respective degrees of solvation of the ions in the mixture are the same as those in the pure solvents, then the *E.M.F.* (*E*) of the above cell will be given by

$$E - e = (RT/nF) \,.\, \log_e c_B/(c_B' + \gamma_{AB}c_A') \quad . \quad . \quad (2)$$

In a solution of the salt MS in the mixture of solvents A and B, the following equilibrium will exist between the metal ions and the solvent molecules

$$\mathrm{MA}_x^{n+} + i_B\mathrm{B} \rightleftharpoons \mathrm{MB}_y^{n+} + i_A\mathrm{A} \quad . \quad . \quad . \quad . \quad (3)$$

where x and y are the respective numbers (not necessarily integers) of molecules of A and B with which a single ion M^{n+} is solvated and i_A and i_B are the respective numbers of molecules of A and B in the mixture. If the concentration of salt present be very small compared with the concentration of either solvent, then

$$K_N = c_B' \,.\, N^x/c_A' \,.\, (1 - N)^y \quad . \quad . \quad . \quad . \quad (4)$$

where N is the mol. fraction of solvent A in the mixture and K_N is the equilibrium constant when the concentrations are expressed in mol. fractions. Eliminating c_B' between (2) and (4), we have

$$E - e = (RT/nF) \,.\, \log_e [\gamma_{AB} + K_N(1 - N)^y/N^x] - (RT/nF) \,.\, \log_e c_B/c_A' \quad . \quad . \quad (5)$$

If the proportion of A to B in the mixture be small, $(1 - N)^y$ can be regarded as unity, and the mol. fraction may be taken as proportional to the concentration (m) expressed in g.-mols./litre. Equation (5) thus becomes

$$E - e = (RT/nF) . \log_e(\gamma_{AB} + K_m/m^x) - (RT/nF) . \log_e c_B/c_A' \quad . \quad (5a)$$

where K_m is the equilibrium constant when the concentrations are expressed in g.-mols./litre.

In this last equation m and c_B can be arbitrarily chosen, γ_{AB} can be determined by a method previously described (*loc. cit.*), E can be measured, and e can be made negligibly small or estimated on the basis of an assumption such as that made in the previous work, but c_A' cannot, in general, be evaluated. The problem is, therefore, to choose conditions such that c_A' becomes approximately equal to some experimentally determinable quantity.

If to a solution of the salt MS in the solvent B, with which the metal ion forms relatively unstable solvates, there is added a second solvent A (in amount which is small compared with B, but large compared with MS), with which the metal ion forms relatively very stable solvates (*i.e.*, complexes), then practically all of the B-solvated ions originally present will be converted into A-complex ions. In this special case, which corresponds with the condition that K be very small, c_A' in equation (5*a*) may be replaced by c', the original concentration of B-solvated ions in the B-solution before addition of A. If, however, the salt MS is notably incompletely dissociated in B, it may be necessary to correct c' in order to allow for the change in the degree of dissociation caused by the addition of A.

In the above special case it is therefore possible to solve equation (5*a*) for K_m/m^x at any arbitrary value of m. By plotting $\log K_m/m^x$ against $\log m$, it is thus possible to determine K_m and x simultaneously.

By determining K_m at various temperatures and substituting $d(\log_e K_m)/dT$ in the van 't Hoff isochore,

$$-\Delta H_S' = RT^2 \,.\, d(\log_e K_m)/dT,$$

the heat of reaction (3), $\Delta H_S'$, may be determined. The free energy of this reaction is given by the van 't Hoff isotherm as $-\Delta A_S' = RT \,.\, \log_e K_m$.

It should be noticed (i) that conditions have been chosen so that it is unnecessary to know the value of y, and (ii) that if γ_{AB} be very small, equation (2) reduces to

$$E - e = (RT/nF) \,.\, \log_e c_B/c_B'$$

which is the expression ordinarily employed on the assumption that the complex ion MA_x^{n+} is electromotively inactive. In a number of cases γ_{AB}, in equation (5*a*), may actually be neglected in comparison with K_m/m^x.

EXPERIMENTAL.

Materials and Apparatus.—The purification of the reagents and the apparatus for the conductivity and $E.M.F.$ measurements have been previously described (*loc. cit.*; J., 1927, 647; 1928, 524).

Quadrant Electrometer as Null Instrument.—The Mudford's galvanometer (having an internal resistance of 10,000 ohms) was replaced by a Dolezalek quadrant electrometer, which was kindly lent by Professor H. B. Baker, F.R.S. This electrometer was used as a null instrument. One pair of quadrants was earthed and the other pair connected to the sliding contact of the potentiometer wire. One pole of the cell, the *E.M.F.* of which was to be measured, was earthed, and the other pole was connected to one end of the bridge wire. By moving the sliding contact, a point may be found for which the electrometer will show no deflexion. The second pair of quadrants will then be at earth potential and the potential drop along the part of the wire in this circuit will be equal to the *E.M.F.* of the cell. A condenser was inserted between the electrometer needle and the high-voltage battery in order to keep the potential on the needle steady and to prevent any chance short-circuiting. The instrument was encased in an earthed tin-box so that movement in its neighbourhood (causing capacity changes) should not produce unnecessary swinging of the needle. By using the finest and longest phosphor-bronze suspension available, and a potential of 108 volts on the needle, a deflexion of 0·7 mm. was obtained for a *P.D.* of 1 millivolt across the quadrants. The zero point was checked by earthing the second pair of quadrants both before and after each reading, since, although usually constant, it sometimes changed slightly.

This arrangement may be used with advantage (1) when measuring the *E.M.F.*'s of cells with a high internal resistance and (2) in cases where it is desirable that no current shall flow. It can, however, only be used when a greater accuracy than 1 millivolt is not required, and has the disadvantage that there is no damping.

In some of the later experiments, a Broca galvanometer (internal resistance 1000 ohms) was used.

Half Elements.—A thermometer was inserted into each of the half elements used for the determination of $d(\log_e K_m)/dT$. The liquid junction of the elements was disconnected during an alteration of temperature. For measurements at room temperature the thermometer was replaced by a second silver electrode, made by fusing about $\frac{1}{4}''$ of platinum wire between about $\frac{1}{2}''$ of silver wire and about 5″ of copper wire; the seal through the bottom of the glass tube is at the platinum, and any accidental leak would be noticed at once owing to the entry of liquid. None of the electrodes leaked even when heated to 80°. The electrodes were plated as before.

Solutions.—The solutions in the pyridine–water and pyridine–

ethyl alcohol mixtures, used for the determination of K_m, were made up by weight and weight dilution. A quantity of silver nitrate corresponding to a 0·1m-solution was weighed into a 100-c.c. graduated flask and made up to the mark with a weighed quantity of mixture. The 0·01m- and 0·001m-silver nitrate solutions were prepared from this by weight dilution. It seems, however, that volume dilution would have been sufficiently accurate, and in the other cases a given weight of silver nitrate and the complex-forming liquid were, therefore, weighed into a 100-c.c. graduated flask and made up to the mark with water. The aqueous ammonia was estimated with acid in the usual manner. In the tables the concentrations of the free complex-forming substance have been expressed in all cases as g.-mols./litre(m). For the above two series, the mol. fractions have been converted to g.-mols./litre by the formula $m = (1000\rho/M)N$ (where ρ is the density and M the molecular weight of solvent B); ρ has been taken as 1·0 and 0·79 for the pyridine–water and pyridine–ethyl alcohol mixtures respectively. Some values are recorded in the tables in which the concentration of silver nitrate is not negligible compared with that of the complex-forming substance A; in these cases the concentration of the latter has been corrected on the assumption that the complex ion is of the type AgA_2^+ (see later).

Except in the case of the pyridine–ethyl alcohol mixtures, measurements were made of cells of the type

$$\mathrm{Ag}\left|\begin{array}{c}\mathrm{AgNO_3\ in}\\ \mathrm{water}\ (c)\end{array}\right\vdots\begin{array}{c}\mathrm{AgNO_3\ in}\\ \mathrm{mixture}\ (c)\end{array}\left|\mathrm{Ag}\right.$$

where c is 0·1m, 0·01m, or 0·001m. Since silver nitrate in water at these concentrations can be regarded as almost completely dissociated, it may be assumed that the only effect of the complex-forming substance is the formation of complex ions, and that the degree of dissociation of the silver nitrate is not appreciably different from that in pure water. A change of 5% in the ionic concentration would, moreover, cause an error of only $\pm$ 0·058 $\log_{10}$ 1·05 = $\pm$ 1·2 millivolts in the measured $E.M.F.$

The $E.M.F.$ (E) of the above cell (the liquid-junction potential being negligible) is given by (5a) as

$$E = (RT/nF) \,.\, \log_e (\gamma_{AB} + K_m/m^x).$$

The values of γ_{AB} used to convert $\log_{10} (\gamma_{AB} + K_m/m^x)$ to $\log_{10} K_m/m^x$ are given in Table IV. The value of γ_{AB} for the silver ion for ammonia–water has not been determined. It will be observed that, except in the case of the acetonitrile–water mixtures, γ_{AB} is negligibly small compared with K_m/m^x.

The error which is characteristic of any individual value of the dissociation constant is eliminated in the determination of $d(\log_e K_m)/dT$ if the same cell is used for all temperatures (see results for pyridine–water, Fig. 2).

The convention has been adopted of giving the *E.M.F.* (*E*), which is in volts, the same sign as the electrode in the mixture.

Results.—The results for three pairs of solvents are given in Table I and those for pyridine–ethyl alcohol are recorded separately in Table II.

TABLE I.

Ammonia–water.

$0{\cdot}1m$-$AgNO_3$.			$0{\cdot}01m$-$AgNO_3$.		
m.	$-E$.	$-\log_{10}(\gamma_{AB} + K_m/m^x)$.	*m*.	$-E$.	$-\log_{10}(\gamma_{AB} + K_m/m^x)$.
0·037	0·252	4·34	0·047	0·256	4·40
0·274	0·356	6·12	0·094	0·302	5·20
0·747	0·407	7·01	0·217	0·340	5·85
1·694	0·445	7·68	0·454	0·374	6·42
			0·927	0·410	7·09
			1·874	0·455	7·81

Acetonitrile–water.

$0{\cdot}01m$-$AgNO_3$.

m.	$-E$.	$-\log_{10}K_m/m^x$.
0·0397	0·004	0·10
0·0995	0·012	0·24
0·219	0·018	0·35
0·458	0·028	0·53
0·936	0·041	0·85
1·892	0·070	1·97

Pyridine–water.

$0{\cdot}1m$-$AgNO_3$.

m.	$-E$.	$-\log_{10}K_m/m^x$.
0·0555	0·090	1·56
0·181	0·148	2·55
0·481	0·210	3·64

$0{\cdot}001m$-$AgNO_3$.

m.	$-E$.	$-\log_{10}K_m/m^x$.
0·0605	0·089	1·54
0·124	0·132	2·28
0·679	0·220	3·80

$0{\cdot}01m$-$AgNO_3$.

m.	$-E$.	$-\log_{10}K_m/m^x$.
0·00510	0·037	0·639
0·0191	0·053	0·919
0·0456	0·080	1·38
0·136	0·130	2·25
0·292	0·185	3·20
0·656	0·216	3·74

Pyridine–ethyl alcohol. Since the degree of dissociation of silver nitrate in ethyl alcohol cannot be regarded as remaining unaffected by the addition of pyridine, it is necessary to determine the ionic concentration in each case. This has been done, on the assumption that the ionic concentration may be deduced from conductivity data, by an inverse use of the method of determining the solution tension of metals in non-aqueous solvents previously described (*loc. cit.*). It has been shown that the *E.M.F.* (*E′*) of the cell

Ag | $AgNO_3$ in water ¦ $AgNO_3$ in a non-aqueous solvent | Ag is a linear function of $\log_{10} \kappa_W/\kappa_S$, where κ_W and κ_S are the specific conductivities of silver nitrate in the aqueous and the non-aqueous solvent respectively, *i.e.*,

$$E' = B + A \log_{10} \kappa_W/\kappa_S \quad . \quad . \quad . \quad . \quad . \quad (6)$$

A and B are constants connected by the equation

$$B = A \log_{10} P_W\Lambda_{\infty W}/P_S\Lambda_{\infty S} \quad . \quad . \quad . \quad . \quad (7)$$

where P_W and P_S are the solution tensions of silver and $\Lambda_{\infty W}$ and $\Lambda_{\infty S}$ are the molecular conductivities at infinite dilution of silver nitrate in water and in the non-aqueous solvent respectively. The values of A and B have thus been determined for a number of cells of the above type, pyridine–ethyl alcohol being the non-aqueous solvent, and the corresponding values of $e_W - e_M = (RT/nF) . \log_e P_W/P_S$ have been calculated; $(e_W - e_M)$ is the difference between the electrode potential of silver in the aqueous and the pyridine–ethyl alcohol solutions when the concentrations of silver ions in both solutions are the same. Since the previous investigation has shown that the difference in normal potential of silver in water and in ethyl alcohol is 0·126 volt, the substitution of ethyl alcohol for water in the left-hand side of the above cell would give

$$e_A - e_M = (RT/nF) . \log_e P_W/P_S - 0{\cdot}126$$

but by (5*a*) $e_A - e_M = (RT/nF) . \log_e (\gamma_{AB} + K_m/m^x)$

hence

$$(RT/nF) . \log_e (\gamma_{AB} + K_m/m^x) = (RT/nF) . \log_e P_W/P_S - 0{\cdot}126 \quad (8)$$

If $\Lambda_{\infty W}$ at 25° is taken as 134 and A as $-$ 0·065 (see below), the value of the term $A \log_{10} \Lambda_{\infty W}/\Lambda_{\infty S}$, in equation (7), is 0·018 volt when the non-aqueous solvent is pure ethyl alcohol ($\Lambda_{\infty S}$ at 25° $= 57{\cdot}4$), and 0·024 volt when the non-aqueous solvent is pure pyridine ($\Lambda_{\infty S}$ at 25° $= 71{\cdot}4$). The difference is thus only 0·006 volt, and therefore, since practically all the ions are pyridinated, the values of $\Lambda_{\infty S}$ for silver nitrate in these pyridine–ethyl alcohol mixtures have, for the purpose of this investigation, been taken as the same as that in pure pyridine.

In Table II, κ_S is the specific conductivity in mho/cm. at 25° ± 0·02° of silver nitrate in the pyridine–ethyl alcohol mixture. In the third, fourth, and fifth columns are given the *E.M.F.*'s (E_1, E_2, E_3) in volts of the mixture electrode measured against each of three standard aqueous silver nitrate electrodes (0·1*m*, 0·01*m*, and 0·001*m*) in whose solutions silver nitrate had specific conductivities (κ_W) at 25° of $9{\cdot}072 \times 10^{-3}$, $1{\cdot}035 \times 10^{-3}$, and $1{\cdot}118 \times 10^{-4}$ mho/cm. respectively. In the sixth column are given the values of B deduced from the linear plots of the *E.M.F.*'s against $\log_{10} \kappa_W/\kappa_S$ (three points). The mean slope (A) of the lines is $-$ 0·065, which is the same as that found previously for pure pyridine. In the seventh column are given the values of $\log_{10} K_m/m^x$ calculated by equation (8).

TABLE II.

Pyridine–ethyl alcohol.

m.	κ_S.	E_1.	E_2.	E_3.	B.	$-\log_{10} K_m/m^x$.
			$0·1m$-$AgNO_3$.			
0·0543	$1·270 \times 10^{-3}$	+0·008	+0·065	+0·125	+0·060	1·28
0·108	1·342 ,,	−0·031	+0·023	+0·082	+0·017	1·94
0·285	1·411 ,,	−0·084	−0·026	+0·035	−0·035	2·74
			$0·01m$-$AgNO_3$.			
0·0397	$2·215 \times 10^{-4}$	−0·030	+0·028	+0·090	+0·070	1·12
0·102	2·324 ,,	−0·078	−0·012	+0·050	+0·028	1·77
0·354	2·393 ,,	−0·147	−0·082	−0·017	−0·040	2·82
			$0·001m$-$AgNO_3$.			
0·0348	$3·316 \times 10^{-5}$	−0·098	−0·030	+0·036	+0·073	1·08
0·0594	3·332 ,,	−0·104	−0·045	+0·015	+0·048	1·45
0·199	3·372 ,,	−0·179	−0·115	−0·048	−0·012	2·38
0·374	3·640 ,,	−0·200	−0·141	−0·078	−0·048	2·94
0·629	3·758 ,,	−0·233	−0·166	−0·100	−0·068	3·25

TABLE III.

Variation of $\log_{10} K_m$ *with temperature.*

Ammonia–water			Pyridine–water.					
$0·01m$-$AgNO_3$; $0·3588m$-NH_3.			$0·01m$-$AgNO_3$; $0·4785m$-C_5H_5N.			$0·1m$-$AgNO_3$; $0·4956m$-C_5H_5N.		
Temp.	$-E$.	$-\log_{10} K_m$.	Temp.	$-E$.	$-\log_{10} K_m$.	Temp.	$-E$.	$-\log_{10} K_m$.
0°	0·372	7·77	0°	0·210	4·52	0°	0·195	4·60
18·5	0·366	7·24	17	0·202	4·16	18	0·180	4·13
25	0·363	7·03	30	0·190	3·80	40	0·166	3·66
30	0·359	6·86	40	0·184	3·60	50	0·157	3·44
40	0·349	6·49	50	0·174	3·35	60	0·146	3·20
52	0·338	6·16	70	0·156	2·93	70	0·137	3·02
			80	0·144	2·70	78	0·128	2·84

Independent Evidence of the Existence of Complex Ions.—Woodman and Corbet (J., 1925, **127**, 2461) have shown that the simple distribution law, $c_1/c_2 =$ constant, holds for the distribution of pyridine between benzene and water when there is less than 6% of pyridine in the system. In the following table are given some results now obtained for the distribution of pyridine between benzene and aqueous solutions of silver nitrate. The pyridine was estimated by titration with N-nitric acid, methyl-orange being used as indicator. The total available pyridine is 57·5 and 11·5 mols. per mol. of silver nitrate for the $0·02m$- and $0·1m$-silver nitrate solutions, respectively.

$AgNO_3$, g.-mols./l. (in water).	Pyridine, g.-mols./l. Water.	Benzene.	Mols. pyridine/ mols. $AgNO_3$.
0	0·303	0·847	—
0·02	0·331	0·818	1·9
0·10	0·451	0·699	2·0

The existence of the complex ion $AgPy_2^+$ in aqueous and alcoholic solution has also been deduced by Schmidt and Keller (*Z. physikal. Chem.*, 1929, *A*, **141**, 331) from conductivity and transport-number data. The existence of the complex ion $Ag(NH_3)_2^+$ in aqueous solution has been proved in several ways by Bodländer and Fittig (*Z. physikal. Chem.*, 1902, **39**, 597).

There is no recorded evidence of the existence of the complex ion $Ag(CH_3{\cdot}CN)_2^+$ in aqueous solution. The refractive index and density of a solution of silver nitrate in pure acetonitrile (in which it is as highly dissociated as in water) of concentration 0·63904 g.-mol. $AgNO_3$/1000 g. acetonitrile were found to be 1·35589 and 0·85835 at 25° ± 0·03° respectively. The refractive index and density of pure acetonitrile at 25° were 1·34169 and 0·77683 respectively. Hence the molecular refraction of silver nitrate in acetonitrile under these conditions is 17·3. The corresponding value for silver nitrate in water was found to be 16·0.

Discussion.

The Linear Relationship.—When $\log_{10} K_m/m^x$ is plotted against $\log_{10} m$ the points lie about a straight line of slope $x = 2$ (see Fig. 1), in accordance with the formula AgA_2^+. Table IV gives the values of K_m deduced from the graphs and of γ_{AB} found in the previous investigation (*loc. cit.*).

FIG. 1.

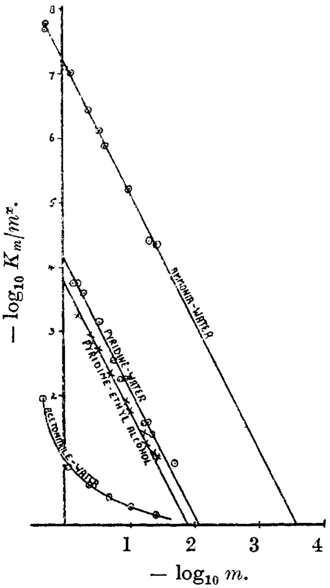


TABLE IV.

Equilibrium constants.

Solvent A.	Solvent B.	K_m.	γ_{AB}.
Ammonia	Water	$6{\cdot}3 \times 10^{-8}$	—
Pyridine	Water	$7{\cdot}1 \times 10^{-5}$	$2{\cdot}1 \times 10^{-6}$
Pyridine	Ethyl alcohol	$1{\cdot}6 \times 10^{-4}$	$1{\cdot}4 \times 10^{-8}$
Acetonitrile	Water	—	$5{\cdot}2 \times 10^{-2}$

The above value for K_m for the silver ion in ammonia–water is in good agreement with that given by Bodländer and Fittig (*loc. cit.*), *viz.*, $7{\cdot}88 \times 10^{-8}$. For the acetonitrile–water mixtures, the plot of $\log_{10} K_m/m^x$ against $\log_{10} m$ is not a straight line (see Fig. 1) and this must be due to the fact that the conditions for the determination of the equilibrium constant are not fulfilled. If a single measurement had been made in the usual manner, an erroneous value of the equilibrium constant would have been deduced.

The existence of the linear relationship is proof that the conditions are fulfilled. Conversely, when the linear relationship does not hold, the equilibrium constant cannot be deduced from *E.M.F.* data.

Thermodynamics of the Reaction $MA_x^{n+} + i_BB \rightleftharpoons MB_y^{n+} + i_AA$.—If in the above reaction, the x molecules of A were to redissolve in pure solvent A, and the y molecules of B in pure solvent B, then this reaction would be equivalent to the transference of the ion M^{n+} from pure solvent A to pure solvent B. When, however, the reaction takes place in a mixture of A and B containing a large excess of B, both the x molecules of A and the y molecules of B may be regarded as redissolving in pure solvent B.

If $\Delta A_S'$ and $\Delta H_S'$ are the free energy and heat of the above reaction in solvent B, then

$$- \Delta A_S' = RT \,.\, \log_e K_m \text{ and } - \Delta H_S' = RT^2 \,.\, d(\log_e K_m)/dT$$

and if ΔA_S and ΔH_S are the free energy and heat of transference of the ion M^{n+} from solvent A to solvent B, then

$$- \Delta A_S = RT \,.\, \log_e \gamma_{AB} \text{ and } - \Delta H_S = RT^2 \,.\, d(\log_e \gamma_{AB})/dT.$$

If in a special case the free energy and heat of solution of A in B were negligibly small compared with the free energy and heat of transference of the ion from A to B, K_m would be equal to γ_{AB}. Since it might be supposed that ionic-molecular forces are more powerful than intermolecular forces, a parallelism between the ionic distribution coefficient (γ_{AB}) and the equilibrium constant (K_m) might be expected. From the experimental results of Table IV it is evident, however, that the influence of intermolecular forces is by no means negligible.

There are, unfortunately, no data for $d(\log_e \gamma_{AB})/dT$, and values of ΔH_S cannot therefore be given. The differences $(\Delta A_S - \Delta A_S')$ and $(\Delta H_S - \Delta H_S')$ should, however, be independently calculable from the free energies and heats of solution of A in B. The values of $(\Delta H_S - \Delta H_S')$ (independent) given in the last column of the following table have thus been obtained by taking (from the "International Critical Tables") the heats of solution of 1 g.-mol. of pyridine in an infinite volume of water as 2·1 Cals., and in an infinite volume of ethyl alcohol as 0·13 Cal.

The free energies and heats (in Cals.) in the following table have been calculated from the experimental results set out in Tables III and IV. The slopes of the plots of $\log_{10} K_m$ against T are 0·0317 and 0·0225 for the ammonia–water and pyridine–water mixtures respectively (see Fig. 2).

Solvent A.	Solvent B.	$-\Delta A_S$.	$-\Delta A_S'$.	$-(\Delta A_S-\Delta A_S')$.	$-\Delta H_S'$.	$-(\Delta H_S-\Delta H_S')$ (independent).
NH_3	H_2O	—	9·6	—	12·3	—
C_5H_5N	H_2O	7·6	5·5	2·1	8·75	4·2
C_5H_5N	$C_2H_5{\cdot}OH$	10·5	5·1	5·4	—	0·26

Summary.

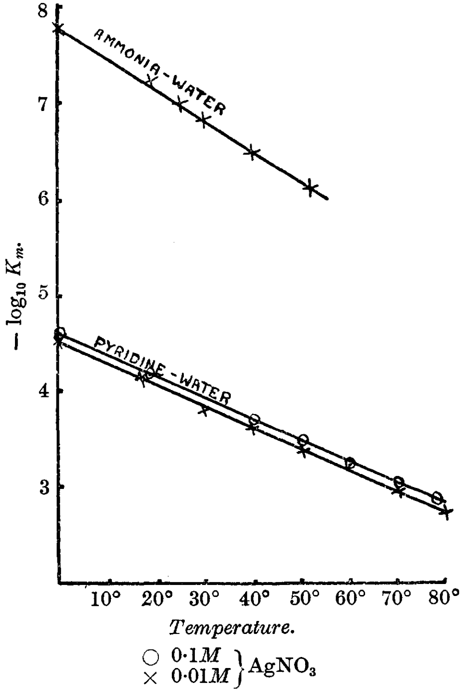
(1) A simple electrochemical method for the simultaneous determination of the constitution and equilibrium constant of complex ions in solution is given. It is shown that the equilibrium constant can only be deduced from *E.M.F.* data if it is small.

(2) The method is applied to the silver ion in ammonia–water, acetonitrile–water, pyridine–water, and pyridine–ethyl alcohol mixtures.

(3) The thermodynamics of the equilibrium between the solvated ions and the solvent molecules is discussed in relation to the experimental results.

(4) In developing the theory it was found useful to introduce a new concept called the "solvation activity coefficient."

FIG. 2.



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