# 94. *Interchange of Hydrogen Isotopes with Complex Salts. Part I. Kinetics of the Interchange with the Luteocobaltic Complex.*

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The hydrogen of hexamminocobaltic chloride and of trisethylenediaminocobaltic chloride undergoes isotope exchange with heavy water in solutions. The interchange reaction in buffered solutions proceeds at measurable speed, according to a pseudo-unimolecular law, the reaction rate being inversely proportional to the hydrogen-ion concentration, but practically independent of the concentration of ammine, or of the proportion of deuterium that it contains. The interchange mechanism is interpreted on the basis that a metal ammine group $M-NH_3$ can ionise as an acid, forming a metal amide-group, $M-NH_2$, and hydrogen ion. There is thus a parallelism with the properties of the aquo-ammines, which form hydroxo-ammines by dissociation. There is some evidence that the ease of acid dissociation runs parallel to the stability of the ammines.

ERLENMEYER and GARTNER (*Helv. Chim. Acta*, 1934, **17**, 1008) observed that the hydrogen contained in the ammonia molecules of typical cobaltammines interchanged with deuterium when the salts, *e.g.*, hexamminocobaltic nitrate, $[Co(NH_3)_6](NO_3)_3$, were dissolved in heavy water. From their approximate measurements of the extent of interchange, it appeared that all the hydrogen atoms of the ammine were involved. Bankowski (*Monatsh.*, 1935, **65**, 262), however, claimed that only one atom in diaquotetramminocobaltic chloride and three atoms in carbonatotetramminocobaltic chloride underwent interchange. This inherently improbable conclusion was criticised by Erlenmeyer, and disproved by Horiuti and Okamoto (*Sci. Papers Inst. Phys. Chem. Res. Japan*, 1937, **31**, 205), who showed, for ammines of various types, that all aquo- and ammino-hydrogen is replaceable.

Anderson, James, and Briscoe (*Nature*, 1937, **139**, 507; J., 1937, 1492) had already reached the same conclusion, and had shown further that the interchange of deuterium with complex salts in partly heavy water is slow, recording some preliminary observations on the velocity of the process. Since the typical cobaltammines are remarkably stable compounds (*e.g.*, hexamminocobaltic chloride may be warmed with concentrated hydrochloric acid for long periods without undergoing any decomposition), it is plain that the interchange of hydrogen for deuterium cannot take place by way of an initial dissociation of ammonia, followed by the equilibrium of ammonia with the heavy water. As the interchange reaction promised to be of considerable interest in relation to the general theory of the co-ordinated complex, its kinetics were investigated (during 1936—37), hexammino- and trisethylenediamino-cobaltic chlorides being used.

## EXPERIMENTAL.

In the work of Anderson, James, and Briscoe, as in the other investigations cited, the general method of experiment had been to dissolve the cobaltammine in partly heavy water, and to observe the decrease in density of that water consequent upon the exchange of hydrogen for deuterium. For the study of reaction kinetics, this method is disadvantageous. Small changes in deuterium content, such as attend interchange reactions in dilute solutions, are most accurately and conveniently determined in solutions of low deuterium content, where the flotation method (cf. J., 1934, 1207; 1937, 1492) of determining the " heaviness " of water can be applied. In the present work, therefore, the usual procedure was reversed. Hexamminocobaltic chloride was first converted into the " heavy " salt by suitable treatment with concentrated deuterium oxide; this salt was then dissolved in normal (" light ") water, and the isotope interchange followed by observing the rate at which deuterium appeared in the solvent. The maximum final concentration of deuterium oxide encountered in the experiments was about 1·4%, corresponding to a flotation temperature of 24·01° with the float used (flotation temperature in standard water = 16·80°). This procedure had the further advantages (*a*) that the deuterium content of the solvent remained small throughout the reaction, which therefore proceeded practically to completion, and (*b*) that systems of very high deuterium content could be investigated by using relatively small amounts of heavy water.

*Preparation of Materials.*—Hexamminocobaltic chloride, prepared essentially by Jörgensen's method (*Z. anorg. Chem.*, 1898, **17**, 455), was rigorously purified from unchanged aquopentammine and chloropentammine: the former was converted into the latter by 3 hours' heating in a vacuum at 100°, and the chloropentammine was removed by repeated fractional precipitation with hydrochloric acid.

Trisethylenediaminocobaltic chloride was obtained by the action of ethylenediamine hydrate (30 g.) upon chloropentamminocobaltic chloride (19 g.) in water (150 c.c.) at 100°. The salt was precipitated with alcohol, and finally purified by recrystallisation, as the trihydrate, $[Co\,en_3]Cl_3,3H_2O$, from water.

*Conversion of the ammines into the " heavy " salts.* All manipulations involving the distillation of heavy water or the transference of samples in the course of a determination were carried out by means of vacuum apparatus of the type described previously. For the preparation of the heavy ammines, approximately 10 g. of heavy water (containing 50—100% of $D_2O$, according to the experiment) were distilled on to a weighed sample of the pure, thoroughly dehydrated, light salt, contained in a 50-c.c. flask attached to the apparatus by means of a standard ground joint. The salt taken did not quite saturate the solution at 60°. To facilitate interchange a small quantity of heavy ammonia was introduced into the solution by adding about 0·1 g. of calcium nitride to the heavy water just before the distillation. The flask containing the salt and heavy water was then capped and heated at 60° during 2 hours, to ensure attainment of interchange equilibrium. The heavy water was then distilled off from the salt in the vacuum apparatus, leaving the salt in the form of a hard cake. The neck of the flask was cut off, and this cake removed, and the heavy salt was finally dried in a vacuum desiccator over phosphoric oxide.

*Interchange Experiments.*—Preliminary measurements by Dr. F. W. James had shown that the rate of interchange was a function of the hydrogen-ion concentration of the solution. All experiments of the present series were therefore carried out in buffered solution. The choice of buffer mixture demanded consideration, in that any possibility of slow interchange of hydrogen and deuterium between the buffer and the solvent must be avoided (cf. the slow interchange reactions of acetates). Fortunately, the range of hydrogen-ion concentration covered by Sörensen's $Na_2HPO_4-KH_2PO_4$ buffer extended sufficiently far into the acid range for our purpose, and it seems to be free from any objection on the above grounds. The buffer solutions were prepared from M/15-solutions of the pure anhydrous salts in carbon dioxide-free distilled water, according to the usual procedure.

A suitable amount of the dry, powdered, heavy salt was weighed into a 50-c.c. flask fitted with a standard ground joint and cap. The flask was immersed in a thermostat at 20°, and 30 c.c. of the buffer solution, previously brought to the same temperature, were pipetted as rapidly as possible on to the salt. The flask was well shaken (in the thermostat), and the stop-clock started simultaneously : this addition took about 7 secs., and in no case did the time required for the salt to dissolve exceed 30 secs. The zero time of the reaction is considered to be known within ±10 secs.

The dissolution of the salt marked the commencement of the exchange reaction, and samples (4—5 c.c.) were removed at definite intervals of time to determine the progress of the reaction : the times were so chosen as to bracket the time of half-change. A final residual sample, after standing for 24 hours, or being warmed for a short time, gave the equilibrium concentration of heavy water at $t = \infty$, from which the quantity of deuterium contained in the original salt could be calculated. Each sample withdrawn was immediately transferred to a test-tube containing a suitable excess of solid precipitant, whereby the complex cation was thrown out of solution, and the interchange sharply arrested. Anderson, James, and Briscoe used for this purpose mercuric chloride, which precipitated hexamminocobaltic mercurichloride, $[Co(NH_3)_6](HgCl_4)Cl$. In this series of experiments, it was found preferable to precipitate the hexammine salt as its sparingly soluble iodide, by running the sample of solution on to about 0·5 g. of dry powdered potassium iodide, which dissolved so quickly as to arrest the interchange almost instantaneously. As the iodide of the trisethylenediamine compound was too soluble for this device to be used, this complex was precipitated as the mercurichloride, a large excess of mercuric chloride being used. This precipitation, which required about 30 secs. for completion, was less satisfactory than that described for the hexammine, and the results are therefore less trustworthy. After precipitation, the sample was immediately filtered by means of the device shown in Fig. 1 (essentially a modified Pregl microfilter) into a flask fitted with a standard ground joint. Since no further interchange was possible, the sample could at this stage be put aside for purification.

FIG. 1.

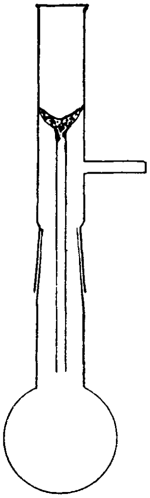
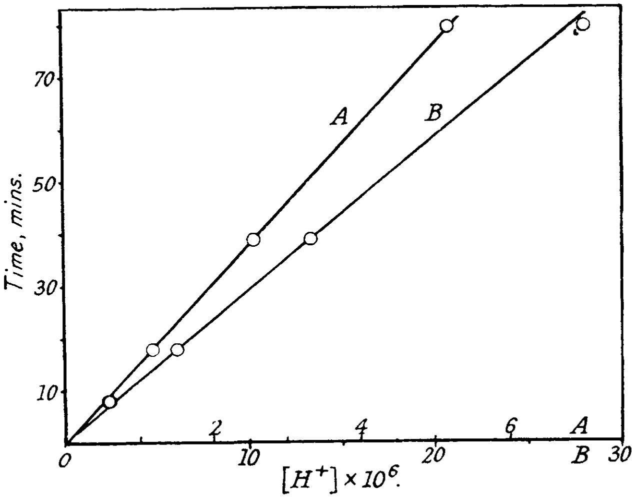


FIG. 2.



The purification of samples, and micro-flotation temperature measurements followed the lines of earlier work in these laboratories. Each sample was purified by three distillations in the vacuum apparatus described previously (J., 1937, 1492, Fig. 2). Much time was saved by distilling, at each stage, only about 90% of the water out of each specimen. With samples containing less than 1·5% of deuterium oxide—as in this work—the fractionation of isotopes resulting from this procedure is negligible when the subsequent density determinations are made only to ±2*γd*. The original volume of filtrate was about 4 c.c.; density determinations were ultimately made on a sample of about 2·5 c.c. In the first-stage distillation (A), water was distilled from the filtrate sample (containing phosphates from the buffer mixture + excess precipitant) into a second similar 10-c.c. flask. With the trisethylenediamino-salt, to obviate the tendency of the excess of mercuric chloride to sublime over at this stage, each sample was treated with an excess of solid potassium iodide just before the distillation, thereby fixing the mecury as the non-volatile $K_2HgI_4$. The distillate from process (A) was boiled for 10 secs. with about 0·05 g. of sodium peroxide and 0·5 g. of potassium permanganate, cooled rapidly to 0°, and redistilled in the same apparatus. This distillate (B) was treated with about 0·05 g. of phosphoric oxide (to fix any ammonia arising from slight decomposition during the interchange reaction itself), and finally distilled into the flotation vessel (*loc. cit.*, Fig. 5). This third distillation was performed in a second vacuum apparatus reserved exclusively for this purpose. The specimen of water was poured into the flotation tube, the vessel capped with tin foil, and the flotation temperature then determined by the rapid float-velocity method already described (*loc. cit.*, p. 1497).

*Results.*—The interchange reaction followed a pseudo-unimolecular law, in that, for each experiment,

$$\log [HOD]_\infty / ([HOD]_\infty - [HOD]_t) = kt,$$

where [HOD] is the excess concentration of heavy water in the solution at the times $t$ and $\infty$. The velocity constant $k$ is a function of $[H^+]$, and possibly also of the concentration of ammine and the " heaviness " of the ammine.

(a) *Effect of hydrogen-ion concentration.* A series of experiments was carried out with hexamminocobaltic chloride, the same concentration of the same batch of salt (0·300 g. of 53% heavy salt, in 30 c.c. of buffer solution), being dissolved in four different buffer mixtures, of original pH = 5·29, 5·59, 5·91, and 6·24 severally at 20°. The plot of the time of half-change, $t_{\frac{1}{2}}$, against the hydrogen ion activities corresponding to these values is linear. When these experiments were carried out, the authors were not cognisant of the very large effect of cobaltammine salts, with their high valency type, upon the hydrogen-ion activity of phosphate buffer mixtures. Curve *A*, Fig. 2, is plotted from the uncorrected figures, whereas curve *B* is obtained after correcting the hydrogen-ion activity of the buffers for the effect of the salt, according to the measurements of Cobb and Anderson (in the press). Neglect of the correction, although it gives incorrect numerical values for the velocity constant $k$, does not, in this series of measurements, invalidate the conclusions. It would appear, then, that the rate of interchange is inversely proportional to the activity of the hydrogen ion. These results are given in Table I. The velocity constants in this and the following table are the observed first-order velocity constants multiplied by $[H^+]$.

TABLE I.

| Run. | Nominal pH. | True pH. | $[H^+] \times 10^6$. | $t_{\frac{1}{2}}$, mins. | $k \times 10^7$ | Run. | Nominal pH. | True pH. | $[H^+] \times 10^6$. | $t_{\frac{1}{2}}$, mins. | $k \times 10^7$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 5·28 | $4{\cdot}54_8$ | 28·3 | 79 | 2·48 | A3 | 5·89 | $5{\cdot}21_0$ | 6·2 | 18 | 2·39 |
| A2 | 5·59 | $4{\cdot}87_1$ | 13·5 | 39 | 2·40 | A4 | 6·20 | $5{\cdot}59_4$ | 2·55 | 8·5 | 2·08 |
| | | | | | | | | | | | Mean 2·34 |

(b) *Effect of concentration of deuterium in the salt.* For this series of measurements, samples in which 88%, 60%, 16%, and 12% severally of the hydrogen was replaced by deuterium were prepared by dissolving equal weights (0·45 g.) of the 88% heavy salt in $H_2O$–$D_2O$ mixtures of suitable concentration, according to the procedure used in the preparation of heavy salt (see above). The interchange experiments were then carried out in the vessel used for the preparation of each sample of salt, without transference, the same buffer solution of initial pH 5·59 being used throughout at 20°. By this technique molecularly equivalent quantities of the salt of varying molecular weight were taken, without prior knowledge of the degree of heaviness of each, which was subsequently calculated in each case from the final concentration of heavy water in the interchange experiments. The results are collected in Table II. It is clear that the rate of interchange is practically independent of the heaviness of the salt. The theoretical considerations detailed below suggest that the interchange in 12% heavy salt should take place about 1% slower than in 88% heavy salt. The precision of this series of experiments does not suffice to decide whether the rate of reaction is appreciably dependent on the deuterium content, or whether the low velocity constants found for the heavier salts (runs B1, B2) are significant. We may return to this point in a later investigation.

TABLE II.

| Run. | Percentage heaviness ($= \xi$). | True pH. | $[H^+] \times 10^6$. | $t_{\frac{1}{2}}$, mins. | $k \times 10^7$. | Run. | Percentage heaviness ($= \xi$). | True pH. | $[H^+] \times 10^6$. | $t_{\frac{1}{2}}$, mins. | $k \times 10^7$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| B1 | 88 | $4{\cdot}78_0$ | 16·6 | 49 | 2·35 | B4 | 30 | $4{\cdot}77_3$ | 16·9 | 39·5 | 2·97 |
| B2 | 60 | $4{\cdot}77_7$ | 16·7 | 44 | 2·63 | B5 | 16 | $4{\cdot}77_2$ | 16·9 | 42 | 2·79 |
| B3 | 48 | $4{\cdot}77_5$ | 16·8 | 40 | 2·91 | B6 | 12 | $4{\cdot}77_0$ | 17·0 | 42·5 | 2·77 |
| | | | | | | | | | | | Mean 2·74 |

(c) *The effect of varying concentration of ammine in solution.* Before Cobb and Anderson (*loc. cit.*) had measured the effects of varying concentrations of ammines on the hydrogen-ion activities of phosphate buffer solutions, this factor constituted a very puzzling feature of the investigation. Two series of measurements were made at 20°: (C) hexamminocobaltic chloride (65% heavy) and (K) trisethylenediaminocobaltic chloride (80% heavy). In series C, the salt concentration was varied from 2·1 to 20 g./l. in a buffer solution of original pH 5·59; in series K, concentrations were varied from 6·7 to 34 g./l. in a buffer solution of original pH 5·29. Both sets of results are in Table III.

TABLE III.

| Run. | Concn. of salt, g./l. | $t_{\frac{1}{2}}$, mins. | True pH. | $[H^+] \times 10^6$. | $k \times 10^7$. | Run. | Concn. of salt, g./l. | $t_{\frac{1}{2}}$, mins. | True pH. | $[H^+] \times 10^6$. | $k \times 10^7$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C1 | 20·0 | 57 | $4{\cdot}70_1$ | 19·9 | 2·42 | K1 | 34·4 | 66·5 | $4{\cdot}40_0$ | 39·0 | 4·15 |
| C2 | 13·0 | 45 | $4{\cdot}80_2$ | 15·8 | 2·43 | K2 | 26·7 | 58·5 | $4{\cdot}44_0$ | 36·3 | 4·30 |
| C3 | 8·5 | 34 | $4{\cdot}90_7$ | 12·4 | 2·53 | K3 | 17·9 | 44·5 | $4{\cdot}52_9$ | 29·6 | 4·61 |
| C4 | 4·2 | 23·5 | $5{\cdot}08_4$ | 8·24 | 2·43 | K4 | 13·4 | 39·5 | $4{\cdot}59_5$ | 25·4 | 4·45 |
| C5 | 2·1 | 14·5 | $5{\cdot}26_9$ | 5·34 | 2·57 | K5 | 6·7 | 27·5 | $4{\cdot}75_5$ | 17·6 | 4·43 |
| | | | | | Mean 2·48 | | | | | | Mean 4·38 |

No simple relation between velocity and concentration is apparent, but when $t_{\frac{1}{2}}$ is plotted logarithmically against [ammine], a good linear relation is found, indicating apparently that: for series C, $k \propto [\text{ammine}]^{-0{\cdot}56}$; for series K, $k \propto [\text{ammine}]^{-0{\cdot}54}$. This peculiar dependence upon concentration at once finds its explanation in the measurements of hydrogen-ion activity (see p. 362), for this increases with the concentration of ammine according to exactly the same laws. The true pH of the solutions in each case, the actual hydrogen-ion activity, and the velocity constant calculated after correction for the variations in $[H^+]$ are recorded in cols. 4, 5, and 6 of Table III. Within the limits of error of the measurements, the velocity of interchange is independent of the concentration of ammine in the solution.

(d) *The influence of added electrolytes.* The presence of the Brönsted secondary kinetic salt effect is evident from the large effect of the complex salt on the pH of the phosphate buffer mixtures. No systematic investigation of the Brönsted primary salt effect was made, but the possibility of direct participation of ammonium and chloride ions in the reaction mechanism was eliminated by appeal to experiment. Interchange measurements were made with hexamminocobaltic chloride at 22°, 0·400 g. of 58% heavy salt in 30 c.c. of solution (original pH of buffer 5·59) being used in the presence of one molecular proportion of ammonium nitrate or of potassium chloride. The results are in Table IV.

TABLE IV.

Solution containing 13·33 g./l. of 58% heavy $[Co(NH_3)_6]Cl_3$ at 22°. True pH $4{\cdot}81_0$ throughout.

| | | | |
|---|---|---|---|
| Run ............................................ | D1 | E2 | E3 |
| Addition to solution ........................ | None | $NH_4NO_3$, 1 mol. | KCl, 1 mol. |
| $t_{\frac{1}{2}}$, mins. ........................................ | 29·5 | 30·25 | 29·75 |

(e) *The temperature coefficient of the reaction.* Measurements on both ammines were carried out at 22°, 15°, 8°, and 0°, equimolecular concentrations of the same batch of heavy salt and buffer mixtures of the same pH being used throughout each series. It has been shown by Walbum (*Biochem. Z.*, 1920, **107**, 219) and by Hastings and Sendroy (*J. Biol. Chem.*, 1924, **61**, 693) that the pH of phosphate buffer mixtures is almost independent of temperature. Hence the measurements recorded in Table V represent the true variation of reaction velocity with temperature at constant hydrogen-ion activity.

TABLE V.

| Run. | Temp. | $t_{\frac{1}{2}}$, mins. | $k \times 10^7$. | | Run. | Temp. | $t_{\frac{1}{2}}$, mins. | $k \times 10^7$. | |
|---|---|---|---|---|---|---|---|---|---|
| D1 | 22° | 29·5 | 3·64 | $k_{20°}/k_{10°} = 5{\cdot}4_7$<br>$k_{10°}/k_{0°} = 6{\cdot}4_4$<br>$E = 28{,}400$ cals. | L1 | 22° | 33 | 6·27 | $k_{20°}/k_{10°} = 5{\cdot}4_3$<br>$k_{10°}/k_{0°} = 6{\cdot}4_1$<br>$E = 28{,}100$ cals. |
| D2 | 15 | 92 | 1·17 | | L2 | 15 | 102 | 2·03 | |
| D3 | 8 | 322 | 0·333 | | L3 | 8 | 357 | 0·58 | |
| D4 | 0 | 1400 | 0·0707 | | L4 | 0 | 1500 | 0·148 | |

## DISCUSSION.

If we assume that all the hydrogen atoms in the ammine are equivalent, *i.e.*, that the partial deuteration of any one ammonia group in no way affects the probability of further interchange, we may symbolise the light hexamminocobaltic cation as $[CoN_6H_{18}]^{+++}$, and a heavy ammine cation in which $x$ atoms of hydrogen are replaced by deuterium can be represented as undergoing interchange according to the equation

$$[CoN_6D_xH_{18-x}]^{+++} + xH_2O \longrightarrow [CoN_6H_{18}]^{+++} + xHOD$$

In dilute solutions, this reaction, as has been shown, is pseudo-unimolecular; the rate of the reaction is inversely proportional to the activity of hydrogen ions. This implies either (*a*) that hydroxyl ions participate as a reactive species in the rate-determining step, or (*b*) that the true reactive species and hydrogen ions are present in dissociative equilibrium, which is therefore shifted by changes in the hydrogen ion activity of the solution—*e.g.*, an ionic dissociation of the ammine ion, such as

$$[Co(NH_3)_5NH_3]^{+++} \rightleftharpoons [Co(NH_3)_5NH_2]^{++} + H^+$$

Such an ionisation reaction, which Garrick (*Nature*, 1937, **139**, 507) has postulated independently, is indeed essential at some stage in the interchange, in order that hydrogen may be transferred from the ammine ions to the water molecules or *vice versa*. The hexamminocobaltic cation is a co-ordinatively saturated entity, not only as far as the metal is concerned, but also with respect to the nitrogen atoms of the ammonia groups. Each of these completes its stable co-ordination number (4) by combination with the central metal atom. The actual mechanism of interchange must, however, involve at some stage the addition of hydrogen ions or water molecules to a co-ordinatively unsaturated molecule, such as is provided by the dissociation mechanism shown. As one of us has indicated elsewhere, this conception is of considerable interest in relation to the theory of co-ordination compounds, and of weak acids generally.

The heavy ammine used is, of course, a mixture of all the various possible deuterated types, *e.g.*, $x$ (above) may have all values from 0 to 18, and the replacement of deuterium by hydrogen is brought about by a complex series of consecutive reactions. In interpreting the kinetic data, we have therefore first to establish the relation between the deuterium lost to the solution and that remaining in the salt. By a method exactly similar to that employed by Ives (J., 1938, 91) in considering the interchange of deuterium with glutaconic acid, it can easily be shown that, at equilibrium, the concentration of the deuterated ammine containing $j$ atoms of deuterium is related to the concentration of completely light ammine by

$$c_j = \frac{\underline{|18}}{\underline{|j}\,\underline{|18-j}} \cdot f^j[CoN_6H_{18}], \text{ where } f = \frac{k_{rH} \cdot k_{aD}}{k_{aH} \cdot k_{rD}} \frac{\{\alpha[HOD][HOH] + [HOD]^2\}}{\{[HOH]^2 + (1-\alpha)[HOD][HOH]\}}$$

In this expression, $k_{aH}$, $k_{rH}$ are respectively the rates of the reactions by which hydrogen is added to or removed from the ammine; $k_{aD}$, $k_{rD}$ are the similar constants relating to deuterium; $\alpha$ is the probability that a molecule HOD will react in such a way as to add on a deuterium atom to the ammine complex; $1 - \alpha$ is the probability that HOD will so react as to add on a hydrogen atom, and [HOD] is the concentration of HOD in the solution in equilibrium with the ammine.

The total concentration of ammine in the solution $= C = \sum_{j=0}^{j=18} c_j$. As a further simplifying assumption, it will be taken that $k_{aH} = k_{aD}$, $k_{rH} = k_{rD}$, $\alpha = 1 - \alpha = \frac{1}{2}$. These simplifications, which are not vital to the interpretation of the results, are justified since the partition of deuterium between ammine and water is nearly uniform. It follows from the foregoing that if we define a quantity $\xi$, the statistical mean heaviness of the ammine, by $\xi = \Sigma jc_j/18C$, then the isotopic composition of the material in equilibrium—*i.e.*, the initial salt and the final state—is completely defined when $\xi$ is known.

The rate of formation of heavy water is given by the relation

$$-d[HOD]/dt = \sum_{j=0}^{j=18} j \, . \, dc_j/dt$$

If the further approximation is introduced that the back reaction—regeneration of deuterated ammine by interchange with HOD—can be neglected (as is nearly true in our experiments, where the molar fraction of HOD was in all cases very small at the conclusion of the reaction), one can proceed at once to set up an approximate differential equation for the reaction. For, in this case, the ammine with $j$ atoms of deuterium *disappears* solely by conversion into ammine with $j - 1$ atoms of D, and is *formed* only by interchange from the ammine with $j + 1$ atoms of D, while the probability that it will react so as to exchange D for H is given by the statistical weight $j$; *i.e.*,

$$dc_j/dt = -kjc_j + k(j + 1)c_{j+1}$$

In this equation, the velocity constant $k$ is a composite quantity, in which the experimentally found dependence of rate upon $[H^+]$ is implicit. Its nature will be subsequently evaluated when the particular mechanism of the reaction is considered. Then,

$$\frac{1}{k} \cdot \frac{d[HOD]}{dt} = \sum_{j=0}^{j=18} j\{jc_j - (j + 1)c_{j+1}\} = + \sum_{j=0}^{j=18} jc_j$$

Hence,

$$(1/k)d[HOD]/dt = 18\xi C$$

At any time $t$, the concentration of HOD present in the solvent is related to the decrease in heaviness of the salt by $[\mathrm{HOD}] = 18(\xi_0 - \xi)C$, where $\xi_0$, $\xi$, represent the statistical mean heaviness initially and at the time $t$ respectively. Substituting for $\xi$ in the above differential equation, we have that

$$(1/k)\mathrm{d}[\mathrm{HOD}]/\mathrm{d}t = 18\xi_0 C - [\mathrm{HOD}]$$

Integrating this, and setting $[\mathrm{HOD}] = 0$ at $t = 0$, we obtain the unimolecular expression

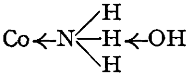
$$k = (1/t)\ \ln 18\xi_0 C/(18\xi_0 C - [\mathrm{HOD}]).$$

The foregoing formal treatment of the system of consecutive reactions establishes the pseudo-unimolecular nature of the kinetics. For the explicit evaluation of $k$, we must consider the experimental results in relation to a particular mechanism of interchange. As was indicated above, the dependence upon hydrogen-ion activity is compatible with either of the schemes (A) or (B).

$$\text{(A)}\qquad \begin{aligned} [\mathrm{CoN_6D_{\mathit{x}}H_{18-\mathit{x}}}]^{+++} &\rightleftharpoons [\mathrm{CoN_6D_{\mathit{x}-1}H_{18-\mathit{x}}}]^{++} + \mathrm{D^+} \\ [\mathrm{CoN_6D_{\mathit{x}-1}H_{18-\mathit{x}}}]^{++} + \mathrm{HOH} &\rightleftharpoons [\mathrm{CoN_6D_{\mathit{x}-1}H_{18-\mathit{x}}HOH}]^{++} \\ [\mathrm{CoN_6D_{\mathit{x}-1}H_{18-\mathit{x}}HOH}]^{++} &\longrightarrow [\mathrm{CoN_6D_{\mathit{x}-1}H_{19-\mathit{x}}}]^{+++} + \mathrm{OH^-} \\ \mathrm{D^+} + \mathrm{OH^-} &\rightleftharpoons \mathrm{HOD} \end{aligned}$$

$$\text{(B)}\qquad \begin{aligned} [\mathrm{CoN_6D_{\mathit{x}}H_{18-\mathit{x}}}]^{+++} + \mathrm{OH^-} &\rightleftharpoons [\mathrm{CoN_6D_{\mathit{x}}H_{18-\mathit{x}}OH}]^{++} \\ [\mathrm{CoN_6D_{\mathit{x}}H_{18-\mathit{x}}OH}]^{++} &\rightleftharpoons [\mathrm{CoN_6D_{\mathit{x}-1}H_{18-\mathit{x}}}]^{++} + \mathrm{HOD} \\ [\mathrm{CoN_6D_{\mathit{x}-1}H_{18-\mathit{x}}}]^{++} + \mathrm{H^+} &\longrightarrow [\mathrm{CoN_6D_{\mathit{x}-1}H_{19-\mathit{x}}}]^{+++} \end{aligned}$$

These schemes are equivalent, and must lead to similar kinetic expressions. The following is based on the set of reactions (B), which readily lends itself to expansion. The transition complex may be considered as formed by the hydroxyl-bond union of hydroxide ion with ammonia hydrogen, *e.g.*, as inset, enabling the group to revert either to ammine or to amino-ion (and water) by fission at the appropriate linkage. We revert to the discussion of this idea in a later paragraph. From the partly heavy ammine, two types of complex may be formed—to be formulated as



$[\mathrm{CoN_6D_{\mathit{x}-1}H_{18-\mathit{x}},DOH}]^{++}$, formed with statistical weight $\xi$,
and $[\mathrm{CoN_6D_{\mathit{x}}H_{17-\mathit{x}},HOH}]^{++}$, ,, ,, ,, ,, $1 - \xi$.

We denote the concentration of the former as $c_1$, the rate of formation of transition complex as $k_1$, the rate of fission to give ammine + OH⁻ as $k_2$, and the rate of fission to give amino-ion + water as $k_3$. By reaction with OD⁻ ions from the HOD present in solution, we shall have similar complexes $[\mathrm{CoN_6D_{\mathit{x}-1}H_{18-\mathit{x}},DOD}]^{++}$, concentration $c_3$, and $[\mathrm{CoN_6D_{\mathit{x}}H_{17-\mathit{x}},HOD}]^{++}$, concentration $c_4$, formed respectively. Then

$$\begin{aligned} \mathrm{d}[\mathrm{HOD}]/\mathrm{d}t &= k_3(c_1 + c_4 + 2c_3) + k_2(c_3 + c_4) - k_1 K_w[\mathrm{HOD}]C/[\mathrm{H^+}] \\ {}^*\ \mathrm{d}c_1/\mathrm{d}t &= \xi k_1 K'_w[\mathrm{H_2O}]c/[\mathrm{H^+}] - (k_2 + k_3)c_1 \end{aligned}$$

Taking $c_1$, $c_3$, $c_4$ as stationary concentrations, we have

$$\begin{aligned} c_1 &= K'_w[\mathrm{H_2O}]\xi C k_1/[\mathrm{H^+}](k_2 + k_3) \\ c_3 &= K'_w[\mathrm{HOD}]\xi C k_1/[\mathrm{H^+}](k_2 + k_3) \\ c_4 &= K_w[\mathrm{HOD}](1 - \xi)C k_1/[\mathrm{H^+}](k_2 + k_3) \end{aligned}$$

Hence,
$$\begin{aligned} \frac{k_2 + k_3}{k_1 K_w}\frac{[\mathrm{H^+}]}{C}\frac{\mathrm{d}[\mathrm{HOD}]}{\mathrm{d}t} &= k_3\xi[\mathrm{H_2O}] + k_3(1 + \xi)[\mathrm{HOD}] + k_2[\mathrm{HOD}] - (k_2 + k_3)[\mathrm{HOD}] \\ &= k_3\xi([\mathrm{H_2O}] + [\mathrm{HOD}]) \end{aligned}$$

Making for $\xi$ the same substitution as before, $\xi = \xi_0 - [\mathrm{HOD}]/(18C)$, we have

$$18\frac{k_2 + k_3}{k_1 k_3}\frac{[\mathrm{H^+}]}{K_w}\frac{\mathrm{d}[\mathrm{HOD}]}{\mathrm{d}t} = (18\xi_0 C - [\mathrm{HOD}])([\mathrm{H_2O}] + [\mathrm{HOD}])$$

On integrating the above equation between the limits 0 and $t$, and setting $[\mathrm{HOD}] = 0$ at $t = 0$, we obtain the final relation

$$\frac{k_1 k_3}{18(k_2 + k_3)}\frac{K_w}{[\mathrm{H^+}]} = \frac{1}{t}\frac{1}{18\xi_0 C + [\mathrm{H_2O}]}\log_e\frac{18\xi_0 C([\mathrm{H_2O}] + [\mathrm{HOD}])}{[\mathrm{H_2O}](18\xi_0 C - [\mathrm{HOD}])}$$

This gives for the time of half-change

$$t_{\frac{1}{2}} = \frac{18(k_2 + k_3)}{k_1 k_3}\frac{[\mathrm{H^+}]}{K_w}\frac{1}{18\xi_0 C + [\mathrm{H_2O}]}\log_e\left[2 + \frac{18\xi_0 C}{[\mathrm{H_2O}]}\right]$$

According to this, $t_{\frac{1}{2}}$ will not be quite independent of either the concentration or the heaviness of the ammine

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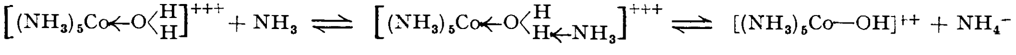
* We take the dissociation constant of water, $K'_w = [\mathrm{H^+}][\mathrm{OH^-}]/([\mathrm{H_2O}]$ for the sake of homogeneity with the subsequent equations involving ionisation of HOD.

if the back reaction is detectable; since $C$ is small compared with the mole-fraction of water in the system, the effect is not appreciable experimentally.

The formation of a transition complex of the type indicated appears to us a plausible hypothesis, since the reciprocal acid–base pairs (ammino-group + hydroxide ion) and (amino-ion + water) parallel exactly the state existing in solutions of aquo- or hydroxo-pentammine salts, as Garrick (*loc. cit.*) has pointed out. We venture the above rather concrete formulation of the transition state because it can be correlated with Nakatsuka's observations (*Bull. Chem. Soc. Japan*, 1936, **11**, 629) on molecular association in these precisely analogous systems, in the presence of ammonium hydroxide: he found that, whereas addition of alkalis (sodium hydroxide or carbonate, etc.) to solutions of aquopentammine cobaltic salts caused immediate and quantitative formation of hydroxopentammine salt, yet addition of aqueous ammonia, or solutions of amines (pyridine, alkylamines, etc.) led to the formation of a new type of compound, which, although not isolable, was clearly characterised by its absorption spectrum. That the appearance of this spectrum was attended by an association of the ammine with ammonia was well attested by cryoscopic measurements. The process as interpreted by Nakatsuka can be formulated as the analogue of that which we have postulated in this discussion as leading to ionisation of the ammine, and isotope exchange:



$$\left[(NH_3)_5Co\leftarrow O\langle{}^{H}_{H}\right]^{+++} + NH_3 \rightleftharpoons \left[(NH_3)_5Co\leftarrow O\langle{}^{H}_{H\leftarrow NH_3}\right]^{+++} \rightleftharpoons [(NH_3)_5Co{-}OH]^{++} + NH_4^{+}$$

The displacement of equilibrium in the above system, and consequent quantitative formation of hydroxopentammine salt, takes place only when the solubility of the latter is sufficiently lowered by the addition of alcohol. That the association product in Nakatsuka's reaction is formed fairly quantitatively, whereas the transition complex, postulated as formed by the hexammine cation with hydroxide ions, is formed in infinitesimal concentration, is compatible with the relatively high acidity of the aquopentammine.

The foregoing kinetic analysis has been worked out for the particular case of the hexamminocobaltic cation. A general expression for the velocity constant, applicable to any ammine, would be $k_1k_3K_w/N[H^+](k_2 + k_3)$, where $N$ is the number of interchangeable hydrogen atoms. We may proceed to compare the product $k_1k_3/(k_2 + k_3)$ for different ammines, and for ammines of different metals. In this expression, the factor $k_3/(k_2 + k_3)$ represents the probability that ionisation will follow the formation of the transition complex. Hence, $k_1$, the rate of formation of the transition complex, appears as the true rate-determining factor. Considering, now, the critical increments and the true velocity constants for the two salts discussed here, it is possible to make only reasonable conjectures as to the significance of the several factors. The reaction constant $k_1$ should not be markedly affected by substitution of a primary amine group for an ammonia molecule. On the other hand, the probability term, $k_3/(k_2 + k_3)$, is a measure of the readiness with which the co-ordinated ammino-group $Co\leftarrow NH_3$ passes over into the covalent amino-group $Co{-}NH_2$. The greater stability of co-ordination compounds containing ethylenediamine as against those containing ammonia may be correlated with a higher velocity constant of hydrogen isotope interchange. Constants obtained by multiplying the velocity constants found in this work by the number of interchangeable hydrogen atoms are: for $[Co(NH_3)_6]^{+++}$, $4{\cdot}54 \times 10^{-6}$; for $[Co\,en_3]^{+++}$, $5{\cdot}27 \times 10^{-6}$. We suggest that this variation from one ammine to another can be taken as reflecting principally the variation in the probability of acidic ionisation. If this be so, a new method becomes available for comparing semiquantitatively the co-ordinating powers of ammines, and the influence of the structure of the co-ordinated complex upon its stability.

To the critical increment for the interchange, the factors considered will contribute severally, and the rather high temperature coefficient is therefore comprehensible. It is noteworthy that Nakatsuka (*loc. cit.*) found that the formation of the association complex between ammonia and the aquopentammine cation is strongly dependent upon temperature. By analogy, this would indicate that the rate-determining factor $k_1$ in our interchange mechanism is also to be attributed a high temperature coefficient. Allowance being made for the temperature coefficient of $K_w$, it is clear that the factors $k_1k_3/(k_2 + k_3)$ together have a critical increment of about 14,500 cals.

*The Acid Dissociation of Metal Ammines.*—The conception of an acid dissociation of the ammines introduced in the foregoing discussion is not entirely novel, since for one particular class of compound—the ammines of quadrivalent platinum—the formation of aminoammines (corresponding to the hydroxoammines) had already been established by the preparative investigations of Tschugaev (*Z. anorg. Chem.*, 1924, **137**, 1; *Compt. rend.*, 1915, **160**, 840; 1915, **161**, 699), and investigated further by Grünberg (*Z. anorg. Chem.*, 1924, **138**, 333; Grünberg and Faermann, *ibid.*, 1930, **193**, 193). These workers showed that acidopentammino- and diacidotetrammino-platinic salts, *e.g.*, $[Pt(NH_3)_5Cl]Cl_3$, $[Pt(NH_3)_4(NO_2)Cl]Cl_2$, were converted in mildly alkaline solutions into the corresponding aminoammino-salts, such as $[Pt(NH_3)_4(NH_2)Cl]Cl_2$, which as Tschugaev showed, is a base slightly weaker than aqueous ammonia. Although the corresponding amino-compound appears not to have been isolated, it is evident from pH measurements on its solutions, and from the colour change of those solutions on lowering the hydrogen-ion concentration, that $[Pt(NH_3)_6]Cl_4$ similarly furnishes an aminoammine, *viz.*, $[Pt(NH_3)_5NH_2]Cl_3$. The hexammine appears to be the strongest acid of this type; the acidity constants decrease progressively in the series $[Pt(NH_3)_6]^{4+} > [Pt(NH_3)_5Cl]^{3+} > [Pt(NH_3)_4Cl_2]^{2+}$, largely, no doubt, because of the decreasing repulsion between the hydrogen ion and the residual anion as the valency of the latter is diminished. This effect is observed in the analogous ionisation of aquo-compounds. Because of the lower positive charge of the central atom of the complex, both ammines and aquo-compounds of the tervalent metals are inherently weaker acids than those of quadrivalent platinum. Grünberg and Faermann showed, however that in each of the pairs of analogous acids

$$[Pt(NH_3)_5NH_3]^{4+} \text{ and } [Pt(NH_3)_5H_2O]^{4+}$$
$$[Rh(NH_3)_5NH_3]^{3+} \text{ and } [Rh(NH_3)_5H_2O]^{3+}$$

the dissociation constant of the aquo-complex is about $10^{-5}$ that of the ammine. On the basis of measurement by Brønsted and Volquartz on aquopentamminocobaltic chloride, the dissociation constant of $[Co(NH_3)_6]^{3\cdot}$ should be about $10^{-11}$, a value compatible with our measurements.

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