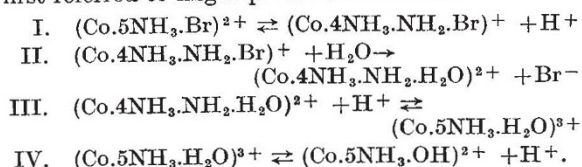


the general observation that diacido complexes undergo aquotization more rapidly than mon-acido complexes.

By analogy, then, the acido-hydroxo replacement first referred to might proceed as follows :



I, III, and IV represent instantaneously established equilibria, while II would be much more rapid than the 'spontaneous' aquotization of the bromo-pentamine ion. The whole process would give a velocity equation of the same form as that for the direct replacement by hydroxyl ion and would account for the unique behaviour of the latter in this respect.

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<sup>1</sup> Erlenmeyer and Gartner, *Helv. chim. Acta*, **17**, 1008 (1934); James, Anderson and Briscoe, *NATURE*, **139**, 109 (1937).

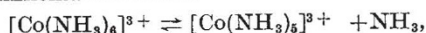
<sup>2</sup> Bronsted and Volquhartz, *Z. phys. Chem.*, **134**, 97 (1927).

<sup>3</sup> Bronsted and Livingstone, *J. Amer. Chem. Soc.*, **49**, 435 (1927).

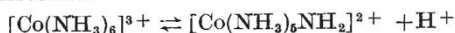
<sup>4</sup> Bronsted, *Z. phys. Chem.*, **122**, 383 (1926).

MR. GARRICK has very courteously allowed us to see the foregoing letter before publication, and indeed suggested that he would publish it only with our concurrence. This encourages us to give the following brief outline of certain results we have obtained during the last few months in our study of the rate of interchange between hexammine cobaltic chloride and heavy water, which have led us to precisely the same view of the basic reaction as that at which Mr. Garrick has independently arrived.

The direct exchange of covalently bound hydrogen for deuterium must necessarily involve high energies of activation. It must therefore be supposed that interchange reactions which proceed readily at room temperature proceed by way of the attachment of the deuterium ion, or of heavy water, to ions or co-ordinately unsaturated groups; in the latter case elimination of light water may complete the course of the reaction. In the case of hexammine cobaltic chloride, the nitrogen atoms of the ammonia groups are co-ordinately saturated, so that in our view interchange must pre-suppose either: (a) dissociation of an ammonia molecule:

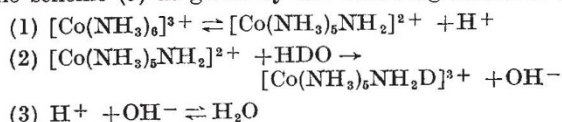


followed by interchange of the hydrogens of that ammonia through addition of water, or (b) an ionic dissociation



such as Mr. Garrick also supposes.

The great stability of the hexammine cobaltic ion toward acids rules out possibility (a), so that we envisage the mechanism of hydrogen interchange on the scheme (b) as given by the following reactions:



Reactions (1) and (3), as ionic equilibria are sensibly instantaneous; reaction (2) is the step determining the rate of reaction.

We are led on this basis to an expression for the velocity constant

$$K = \frac{1}{t} \cdot \frac{[\text{H}^+]}{[\text{A}]^{\frac{1}{2}}} \cdot \frac{[\text{HDO}]_{\infty}}{\xi_0} \cdot \log_e \frac{[\text{HDO}]_{\infty}}{[\text{HDO}]_{\infty} - [\text{HDO}]}$$

in which [A] = concentration of hexammine cobaltic chloride,

$\xi_0$  = initial 'heaviness' of the cobalt-ammine,

$[\text{HDO}]_{\infty}$  = concentration of heavy water after complete interchange,

[HDO] = concentration of heavy water at the time  $t$ .

This particular form of the expression is adapted to the conditions of our own experiments, in which we have found it convenient to reverse the normal procedure by measuring the rate of interchange between heavy cobaltamine and light water.

In agreement with the above expression, we find that (a) the rate of interchange varies inversely as the hydrogen ion concentration; (b) for constant [A], the rate of interchange is independent of the heaviness  $\xi_0$  of the salt; (c) for salt of a constant heaviness  $\xi_0$ , the rate of interchange varies inversely as  $[\text{A}]^{\frac{1}{2}}$ .

The underlying hypothesis of the ionic dissociation of the ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  appears therefore to be substantiated. Further aspects of this, and in particular the significance of the term  $[\text{A}]^{\frac{1}{2}}$  in the above expression, we hope to discuss in presenting our detailed results.

We would add that the velocity of interchange in unbuffered solutions indicates an acidity constant  $K_a$  about  $10^{-12}$ – $10^{-11.5}$  for the hexammine cobaltic ion.

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#### Calculation of Constants for Band Spectra

It has not infrequently proved difficult in the analysis of spectra to decide which of two or more sets of constants refer to the deepest-lying energy states: an example of this arose in my experience in the interpretation of Gale and Monk's work on the fluorine di-atom FF. Empirical methods of obtaining these numbers for ground states may therefore be useful. It is already possible on the basis of the periodic classification of di-atoms<sup>1</sup> to form estimates of such numbers in many cases. The fundamental nuclear vibration frequency  $\omega_e$  is one of the most important of these constants, since it enters into the expressions for other numbers. Methods by which the equilibrium internuclear distance  $r_e$  may be obtained from  $\omega_e$  have been recently improved<sup>2</sup>.

It has so far proved practicable to derive an empirical formula for  $\omega_e$ 's of di-atoms XX, XY and Y $\bar{Y}$ , so that if any two are known the third may be derived, but *only so long as X and Y contribute equal numbers of valency electrons to the shared group of XY*, or, in other words, so long as X and Y belong to the same atomic periodic group. In terms of the proposed classification, the di-atoms XY must be chosen from the *symmetrical* molecular groups designated II, IVs, VI, VIII, Xs, XII and XIV<sup>1</sup>. For such cases, Howell<sup>3</sup> and I<sup>1</sup> independently observed that  $a = \omega_e(\text{XY})$  is approximately the arithmetic mean of  $b = \omega_e(\text{XX})$  and  $c = \omega_e(\text{YY})$ , so that—

$$a = 0.500(b+c) \quad . \quad . \quad . \quad . \quad (1)$$