452. *Peroxy-complexes of Inorganic Ions in Hydrogen Peroxide–Water Mixtures. Part III.** *Decomposition by Molybdate Ions.*

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Measurements of pH and of optical absorption have shown that over a wide range of hydrogen peroxide–water composition and acidity the molybdate ion exists exclusively as two hydrolysis forms of a single peroxy-complex, probably $HMoO_8^-$ and MoO_8^{2-}. The acid dissociation constant of the $HMoO_8^-$ ion and the solvolysis constant of the MoO_8^{2-} ion have been measured at various hydrogen peroxide concentrations, and the latter figure has been shown to be less dependent on the solvent composition. Decomposition-rate studies have shown that catalysis is due entirely to a reaction between the MoO_8^{2-} ion and a water molecule.

Previous work in this field has been reviewed by Baxendale.[1] From an extensive kinetic and colorimetric study with dilute hydrogen peroxide, Spitalsky and Funck [2] postulated the existence of three permolybdates—a yellow compound formed in acid solution, which is catalytically inactive, and two red-brown compounds in neutral and alkaline solution, which are active; a maximum decomposition rate obtained in neutral solutions at very low hydrogen peroxide concentration was attributed to the preferential formation of the more active peroxy-complex. Jahr,[3] on the other hand, postulated only two peroxy-complexes, $HMoO_6^-$ (yellow) and $HMoO_8^-$ (red); he observed that the pH of an aqueous sodium molybdate solution was raised by addition of small amounts of hydrogen peroxide, and a maximum was reached at a 4 : 1 molar ratio of peroxide to molybdate, which he interpreted as being due to quantitative formation of red, undissociated $HMoO_8^-$. On repeating these experiments we found that the pH of a molybdate solution reaches a maximum as described by Jahr, but that the typical red colour of molybdate solutions in hydrogen peroxide is developed only at much higher peroxide concentrations. The simple picture given above cannot be completely correct, but the isolation from alkaline hydrogen peroxide by Jahr of red crystals of the formula K_2MoO_8, and of other permolybdates of similar composition by Kobosev and Sokolev [4] suggests that the red colour of the molybdate ion in hydrogen peroxide solution is probably due to a dissociated form of the acid H_2MoO_8. Consequently the one peroxy-complex which needs to be invoked to explain the results of the present investigation has throughout been assumed to have this formula.

EXPERIMENTAL

Materials.—" AnalaR " sodium molybdate, Na_2MoO_4, was used without purification. Other reagents have been described elsewhere.[5,6]

Units.—In conformity with Parts I and II, concentrations are expressed in mole fractions. Molarity has been retained in certain qualitative descriptive passages and in certain graphs where results obtained at more than one peroxide concentration are represented on the same figure.

Techniques.—Only minor variations in technique from that described in Parts I and II have been adopted. As before, each batch of solutions was prepared with varying acidity and constant hydrogen peroxide concentration. The ionic strength of the solutions was not controlled, but never exceeded 0·01. Owing to the weak catalytic power of the molybdate ion relatively high concentrations were used, normally 2×10^{-3}M, and, because of this, account

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* Part II, preceding paper.

[1] Baxendale, *Adv. Catalysis*, 1952, **4**, 80.
[2] Spitalsky and Funck, *Z. phys. Chem.*, 1927, **26**, 1.
[3] Jahr, *Ber. Ges. Freuden tech. Hochschule Berlin*, 1939, 91.
[4] Kobosev and Sokolev, *Z. anorg. Chem.*, 1933, **214**, 321.
[5] Part I, *J.*, 1963, 2434.
[6] Part II, preceding paper.

had to be taken of the pH changes produced by the hydrolysis of this ion. Spectrophotometric measurements at room temperature (22° ± 1°) and pH measurements at 25° were carried out as before. In the kinetic experiments at 22° the low decomposition rates called for particular care in measurement and in conditioning the reaction vessels. Samples (50 ml.) of hydrogen peroxide were run into Pyrex tubes which had been previously cleaned with hot concentrated nitric acid and washed three times with conductivity water and three times with the hydrogen peroxide–water mixture under test. The volume of oxygen evolved was measured during several hours, and, if this was negligible, the conditioning was regarded as satisfactory. Appropriate amounts of N-perchloric acid or N-sodium hydroxide were then added, with water, to give the same hydrogen peroxide concentration throughout the series of tests. The steady decomposition rates of these adjusted samples were measured after a few hours. Sodium molybdate solution was then added to each tube. Decomposition rates were found to be very erratic for several hours after the addition of catalyst, but steady, reproducible rates were obtained after 24 hr. Corrected rates were then obtained by subtracting from these final rates the rates observed with the pH-adjusted samples before the addition of molybdate. These corrections were normally significant only for samples to which sodium hydroxide had been added. Throughout the investigation the rates of oxygen evolution were obtained by using automatic, self-levelling gas-burettes.[7]

RESULTS

pH *Measurements.*—Addition of sodium molybdate to hydrogen peroxide–water mixtures decreases the acidity of the system owing to solvolysis of the molybdate ion. The acid dissociation constant, K, of the $HMoO_8^-$ ion and the solvolysis constant, K', of the MoO_8^{2-} ion can be calculated from the pH changes produced by the additions of perchloric acid to the alkaline molybdate solution.

If only one peroxide species is present—an assumption corroborated by spectrophotometric measurements—and this undergoes solvolysis:

$$MoO_8^{2-} + H_2O_2 \overset{K'}{\rightleftharpoons} HMoO_8^- + O_2H^- \qquad (1)$$

then, if the concentration of hydrogen peroxide is excluded, the solvolysis constant may be represented by

$$K' = a(a - x)/(A - a)$$

or

$$a - x = (K'A/a) - K', \qquad (2)$$

where A is the total molybdate concentration, a the concentration of the $HMoO_8^-$ ion, and x is the stoicheiometric concentration of perchloric acid added to the system. Hence a plot of $(a - x)$, the measured hydroperoxide-ion concentration of the system, against $1/a$, obtained from the measured value of $(a - x)$ and the known value of x, gives a straight line of intercept K' and slope AK'. In practice, the slope gave the more reliable figure for K'. In this treatment an accurate knowledge of the autoprotolysis constant $K_M = C_{H_3O^+}C_{H_2O^-}$ for the particular solvent concentration is essential in order that $C_{O_2H^-}$, which is $(a - x)$, can be calculated from the measured $C_{H_3O^+}$. The values given by Mitchell and Wynne-Jones [8] have been used.

It has been stated [9,10] that the permolybdate ion undergoes dimerisation with the loss of a water molecule. This cannot be so under the conditions of the present investigation. The MoO_8^{2-} ion cannot dimerise since it has no water to lose, and the observed pH data would not appertain to an equilibrium between this ion and the dimeric $Mo_2O_{15}^{2-}$.

The acid dissociation constant of the $HMoO_8^-$ ion as represented by the equation

$$HMoO_8^- + H_2O \xrightarrow{K} MoO_8^{2-} + H_3O^+ \qquad (3)$$

is given, if the water concentration is excluded as was the hydrogen peroxide concentration in equation (2), by

$$K = K_M/K'. \qquad (4)$$

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[7] Dedman, E.R.D.E. Technical Memorandum No. 1/M/62.

[8] Mitchell and Wynne-Jones, *Trans. Faraday Soc.*, 1956, **52**, 824.

[9] Souchay, *Bull. Soc. chim. France*, 1949, 122.

[10] Tridot, *Ann. Chim.* (*France*), 1955, **10**, 235.

Since the value of K_M changes by several powers of ten over the complete hydrogen peroxide-water range it is obvious that K and K' cannot both be independent of the solvent composition. In Parts I and II [5,6] interpretation of the results for the iron and the chromate system necessitated the assumption that dissociation constants analogous to K were unaffected by the concentration of hydrogen peroxide. In each case complications existed owing to the presence of more than one peroxy-complex and the dissociation constant of each species could be calculated only over a range of solvent compositions. In the molybdate system, only one peroxy-complex appears to exist and dissociation constants may be calculated for each solvent composition. The measured variation of K and K' with hydrogen peroxide concentration is therefore of extreme interest.

Fig. 1 shows typical plots of pH against added perchloric acid concentrations at constant molybdate and varying hydrogen peroxide concentrations. It can be seen that the neutral point of the system is always at an ~1 : 1 ratio of molybdate to perchloric added, indicating quantitative formation of the monohydrolysis product $HMoO_8^-$ in neutral solution. Fig. 2 shows $(a - x)$ plotted against $1/a$ for the curves of Fig. 1, and the Table lists the values of K and K' obtained by this method over the complete range of hydrogen peroxide concentrations. All figures, including the literature values of K_M, are quoted in mole fractions.

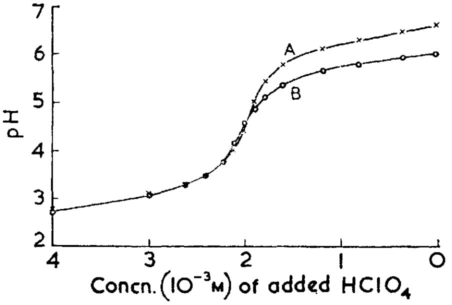

FIG. 1. Typical plots of pH against added perchloric acid.
[Molybdate] = 2×10^{-3}M. $C_{H_2O_2}$: A, 0·750; B, 0·433.

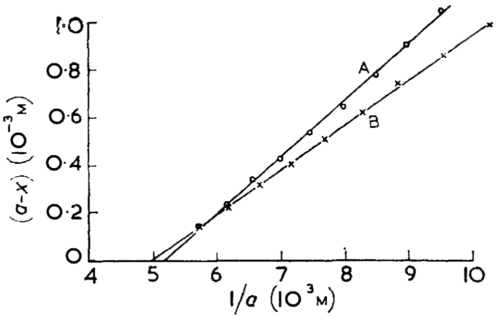

FIG. 2. Typical plots of $1/a$ against $(a - x)$. $C_{H_2O_2}$: A, 0·750; B, 0·433.

	pH method		pH and spectrophotometric method		Spectrophotometric method	
$C_{H_2O_2}$	10^8K	$10^5K'$	10^8K	$10^5K'$	10^8K	$10^5K'$
0·010			0·025	0·54	0·003	4·8
0·030			0·096	0·51	0·016	3·1
0·058	1·20	0·15	0·18	1·00	0·178	1·01
0·132	0·79	0·85	0·43	1·56	0·600	1·12
0·195	1·11	1·56	0·34	5·12	1·01	1·71
0·258	0·82	3·08	1·02	2·50	1·24	2·03
0·340	1·65	2·05	1·14	2·94	1·35	2·51
0·433	2·24	1·75	1·23	3·23	1·30	3·01
0·550	0·61	6·25	1·24	3·03	1·08	3·52
0·750	0·52	2·50	0·48	2·70	0·49	2·68
0·855	1·13	0·31	0·20	1·75	0·22	1·60
0·958	0·22	0·04				

Of the values of K' and K given by various methods (the Table), those by this method (pH) are the least accurate. The concentrations of $HMoO_8^-$, MoO_8^{2-}, and O_2H^- all depend on the one measurement of pH and on an accurate knowledge of the autoprotolysis constant K_M However, as a result of the pH experiments the charges on the peroxy-ions taking part in the solvolysis equilibrium have been determined and the order of magnitude of K and K' assessed. The curves of Fig. 1 are also necessary for the interpretation of the spectrophotometric data reported in the next section.

Spectrophotometric Measurements.—The red-brown colour of molybdate solutions in neutral and alkaline hydrogen peroxide was found to be due to a well-defined peak with a maximum at 450 mμ. No trace of such a peak could be found in solutions of the molybdate ion in water or in acidified hydrogen peroxide, and it may be assigned to the doubly charged peroxide species MoO_8^{2-}. All subsequent absorption measurements were made at 450 mμ, and the optical density was taken to be proportional to the MoO_8^{2-} concentration in the system.

If the equilibrium under investigation is $HMoO_8^- + H_2O \overset{K}{\rightleftharpoons} H_3O^+ + MoO_8^{2-}$ and the concentration of water is not included in the mass-action equation, then the concentration of the absorbing species, MoO_8^{2-}, is given by $C_{MoO_8^{2-}} = KA/(C_{H^+} + K)$, where A is the total concentration of molybdate added. Then the ratio of the optical density at hydrogen-ion concentration C_{H^+} to the standard optical density D_0 at hydrogen-ion concentration C_{H_0} is given by

$$D_0/D = (C_{H^+} + K)/(C_{H_0} + K), \qquad (5)$$

and a graph of D_0/D against C_{H^+} will have a slope equal to $1/(C_{H_0} + K)$ and an intercept of $K/(C_{H_0} + K)$. Because of the large release of hydroperoxide ion by solvolysis of the added molybdate, the C_{H^+} used in this graph is not the stoicheiometric concentration of added perchloric acid but the hydrogen-ion concentration of the system as recorded in the previous section. Therefore, each curve is derived from a combination of absorption and glass-electrode measurements.

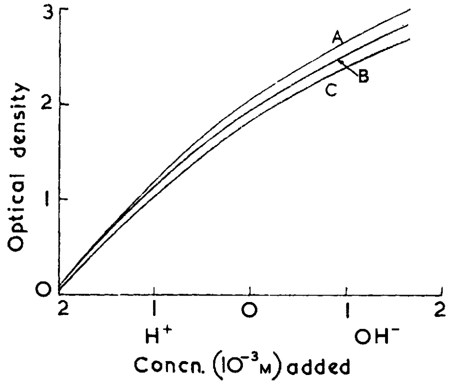

FIG. 3. Plots of optical density against concentration of added perchloric acid or sodium hydroxide.

[Molybdate] = 2 × 10^{-3}M. A, 40%; B, 60%; C, 86% H_2O_2.

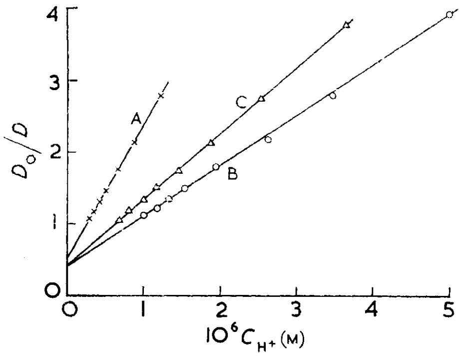

FIG. 4. Typical plots of D_0/D against C_{H^+}. $C_{H_2O_2}$: A, 0·750; B, 0·433; C, 0·258.

Fig. 3 shows the typical change in optical density on addition of perchloric acid or sodium hydroxide. The molybdate concentration is constant, and each curve represents one particular hydrogen peroxide concentration. The absorptions are very different from those of the chromate ion described in Part II.[6] In the case of chromate the absorptions, as they fall from their maximum limiting value in neutral and alkaline solution, are highly dependent on hydrogen peroxide concentration, whereas in Fig. 3 there is comparatively little separation between the three curves. It may be qualitatively deduced that the variation of K' with hydrogen peroxide concentration is not large. Fig. 4 shows the three curves of Fig. 3 treated as in equation (5), and the Table summarises the values of K and K' obtained by this method.

This method is the most accurate means of calculating the absolute values of K and K'. However, it still suffers from the disadvantage of being dependent on comparatively inaccurate pH measurements. The following method, which does not involve the measurement of pH, represents the most accurate calculation for the relative values of K and K'.

If D is the optical density obtained by addition of a total sodium molybdate concentration A to a neutral hydrogen peroxide–water mixture, and D_{sat} the optical density after further addition of sufficient sodium hydroxide to convert the molybdate completely into the MoO_8^{2-} ion, then

$$C_{MoO_8^{2-}} = DA/D_{sat}, \text{ and } C_{HMoO_8^-} = C_{O_2H^-} = (D_{sat} - D)A/D_{sat}$$

and

$$K' = DD_{sat}/(D_{sat} - D)^2A. \qquad (6)$$

Now, D_{sat} cannot be measured accurately because of the high rate of oxygen evolution in strongly alkaline solutions. A value was therefore selected which gave a series of K' values as close as possible to the scattered values obtained by the combined pH and spectrophotometric method. The value chosen corresponds to an extinction coefficient for the MoO_8^{2-} ion at the maximum (450 mμ) of 480. The values of K' and the corresponding values of K obtained by this method are listed in the Table.

The values of K' obtained by this method may be regarded as the most reliable listed in this paper. K is then obtained by multiplying K' by the autoprotolysis constant K_M. At low hydrogen peroxide concentrations (0·01 and 0·03) this may introduce large errors and at these concentrations the values of K given by the combined pH–spectrophotometric method are probably more correct. At higher peroxide concentrations greater reliance may be placed on K_M and then the K values of the relative spectrophotometric method are probably more accurate.

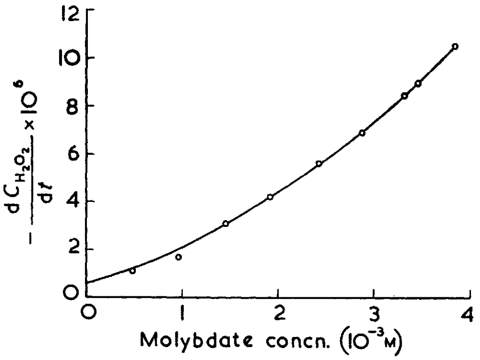

FIG. 5. Plot of rate against concentration of molybdate.
($C_{H_2O_2}$ = 0·750.)

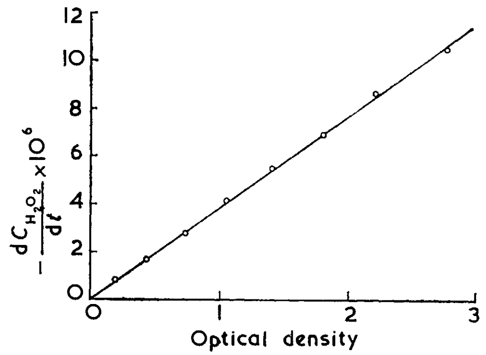

FIG. 6. Plot of decomposition rate against optical density for molybdate solutions of various concentrations.

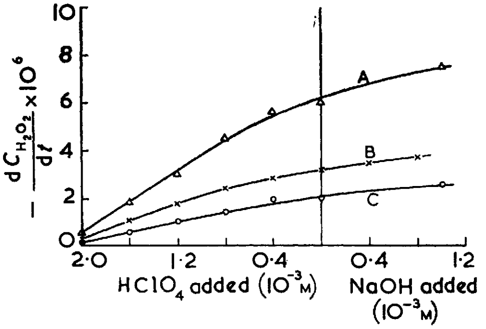

FIG. 7. Effect of added acid and alkali on molybdate-catalysed decomposition of hydrogen peroxide.
[Molybdate] = 2 × 10^{-3}M. $C_{H_2O_2}$: A, 0·058; B, 0·258; C, 0·750.

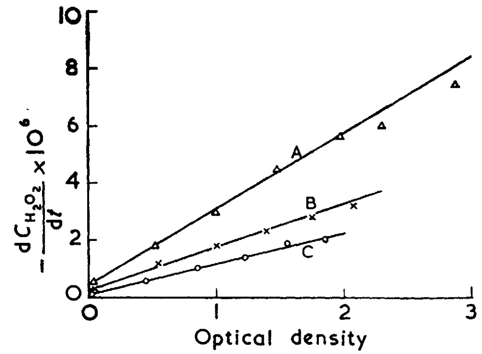

FIG. 8. Plot of rate of decomposition against optical density.
Details as for Fig. 7.

Decomposition-rate Experiments.—Even in alkaline solution the molybdate ion is not a powerful catalyst in the decomposition of hydrogen peroxide. Consequently rather higher concentrations, normally 2 × 10^{-3}M, were used than in the parallel chromate investigation.[6] The appreciable amount of perhydroxide ion liberated by this amount of catalyst by hydrolysis causes complications, and a careful check on the pH of the systems investigated is necessary.

Addition of varying amounts of sodium molybdate to neutral 86% hydrogen peroxide leads to a plot of decomposition rate against molybdate which is a smooth, concave-upwards curve (Fig. 5). This might be thought to contain a term that is of the second order with respect to molybdate, but it was noticed that these solutions deviate from Beer's law in a similar manner, and a graph of decomposition rate against optical density is a straight line (Fig. 6). Hence the rate is linearly proportional to that molybdate complex which is also causing the colour, previously shown to be MoO_8^{2-}, and deviation from linearity in Fig. 5 is due to the changing ionisation of the catalyst. Experiments described below allowed corrections to be made to Fig. 5 to bring all points to the same pH value. When this is done a linear relation between rate of decomposition and total molybdate concentration is observed.

The influence of pH on decomposition rate was studied over a wide range of hydrogen peroxide–water mixtures. Varying amounts of perchloric acid were added to solutions 2×10^{-3}M in partially hydrolysed sodium molybdate. A selection of these experiments is shown in Fig. 7. In every case the decomposition rate falls to zero as the neutral point of the peroxide is approached. The resemblance between Figs. 3 and 7 is apparent and it seems that once again the decomposition rate is proportional to the optical density of the solution, but that the proportionality constant is a function of the concentration of hydrogen peroxide. Fig. 8 shows decomposition rate plotted against optical density for a selected number of hydrogen peroxide concentrations. Straight lines are obtained. The slopes of these lines are then plotted in Fig. 9 against the water component of the solvent mixture. Although the slopes of Fig. 8 increase with increasing water concentration the results cannot be said to obey a simple kinetic formula. However, it is clear from these results that only one peroxy-complex is involved in the catalysis, namely, the MoO_8^{2-} ion, and to the first approximation and also by analogy with the kinetics of decomposition by the chromate ion, the decomposition due to the molybdate ion may be represented by the equation

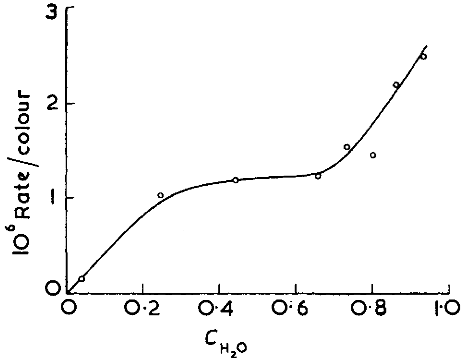

FIG. 9. The variation of the rate/colour with the water component of the solvent. [Molybdate] = 2×10^{-3}M.

$$MoO_8^{2-} + H_2O \xrightarrow{k} \text{Products}$$

If this is written

$$-dC_{H_2O_2}/dt = kC_{MoO_8^{2-}}C_{H_2O},$$

with all the concentration terms in mole fractions and t in minutes, then $k \approx 0{\cdot}3$. This is a power of ten lower than that of $k = 7$ obtained in Part II [6] for the analogous reaction between the $HCrO_5^-$ ion and water.

DISCUSSION

In Parts I and II the results could be interpreted only if the acid dissociation constants of the various peroxy-species present were independent of solvent composition. Although the results responded to this type of treatment the hypothesis could not be checked directly since the multiplicity of peroxy-species necessitated the calculation of dissociation constants averaged over a range of hydrogen peroxide concentrations. However, no such limitation besets the determination of the acid dissociation constant of the $HMoO_8^-$ ion, since it is the only peroxy-complex present in significant amounts under the conditions maintained in the present investigation.

The dissociation of the acid HA is generally represented by the equation

$$HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^-$$

although it is certain that the hydrogen ion is associated with a solvent molecule. In water this becomes

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

In simple solvents the activity of the solvent may be regarded as unity and ignored. K_a is then represented by

$$K_a = (C_{H_3O^+} C_{A^-})/C_{HA}. \qquad (7)$$

However, in mixed solvents where the hydrogen ion is known to react preferentially with one particular component—in hydrogen peroxide–water mixtures, with the water component—it might be expected that a true constant will only be obtained by introducing a water concentration into the equilibrium equation. Alternatively, if the concentration of water is ignored, K_a should vary inversely as the proportion of water in the solvent mixture. However, all indications point to the invalidity of this reasoning in the case of the peroxy-complexes present in hydrogen peroxide–water mixtures. Jones *et al.*[11] were the first to notice the lack of a solvent effect on the ionisation of certain ferric peroxy-complexes. Their explanation, that they are strong acids and completely ionised under all solvent conditions, becomes untenable on investigation of the effect of changing the hydrogen-ion concentration of the system. Parts I and II give very strong evidence that equations of the type (7) may be applied to the peroxy-complexes. Finally, although the constant K in the molybdate investigation cannot be said to be independent of solvent composition, no single trend with the water component is evident. No improvement will be made by the introduction of a water concentration term.

Equation (1) is an alternative way of representing the equilibrium between $HMoO_8^-$ and MoO_8^{2-} ions. In this case one might expect a term for hydrogen peroxide concentration to appear in the equilibrium equation, just as one might expect a water concentration term to appear in the equilibrium constant K. But K', which ignores the hydrogen peroxide concentration, is relatively independent of solvent composition and is certainly not improved by the introduction of such a term. There appears to be no less justification in ignoring the hydrogen peroxide concentration in the calculation for K' than in ignoring the water concentration in the calculation for K; neither assumption has theoretical backing. In this investigation, K' appears to be a much better constant than K, possibly because only in this investigation is the system on the alkaline side of the neutral point where an appreciable concentration of hydroperoxyl ions is present. The dynamic equilibrium between the $HMoO_8^-$ and the MoO_8^{2-} ion is then more likely to follow equation (1) rather than equation (3). The entire investigation of the ferric ion and that part of the chromate investigation in which assumptions concerning K were made were carried out in acid solution where the hydroperoxide concentration was negligible.

These results are particularly surprising in view of the basicity figures for hydrogen peroxide–water mixtures published by Beck and Wynne-Jones.[12] Their figures were obtained by using picric acid and other nitrophenols as indicators. The logarithm of the basicity decreased regularly as the hydrogen peroxide content of the mixture increased, and several powers of ten were involved over the solvent range covered in this investigation. The question of basicity in mixed solvents will be considered in a later paper.

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[11] Jones, Kitching, Tobe, and Wynne-Jones, *Trans. Faraday Soc.*, 1959, **55**, 79.

[12] Beck and Wynne-Jones, *J. Chim. phys.*, 1952, **49**, *C*97.