

655. *Structure and Reactivity of the Oxy-anions of Transition Metals. Part I. The Manganese Oxy-anions.*

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The electrode potential of the MnO_4^- - MnO_4^{2-} couple has been measured in aqueous alkaline solution at various ionic strengths, and the results extrapolated to give an E° value of 0.558 ± 0.002 v. The MnO_4^{2-} - MnO_4^{3-} couple has been studied in concentrated aqueous potassium hydroxide solution and a value of 0.285 ± 0.010 v found for the electrode potential adjusted to equal concentrations of the manganese ions at ionic strengths between 6 and 12. Some general observations on the reactivity of the manganate and hypomanganate ions are made, and the visible and ultraviolet absorption spectra of these ions in solution recorded.

ALTHOUGH considerable attention is being given to the structure and properties of complex compounds of the transition metals, the oxy-anions, in which the metal frequently shows its highest valency, have received little attention. This work will be concerned largely with transition-metal oxy-anions of general formula XO_4^{v-} , but condensed forms of these ions will also be considered, and later the work will be extended to anions in which the ligands are hydroxyl rather than oxide.

In considering structure it will be assumed that the ion XO_4^{v-} is tetrahedral and an endeavour will be made to throw light upon the electronic structure by detailed examination of electronic and paramagnetic resonance spectra.* In studying reactivity, attention will be confined to certain fundamental reactions for which, from measurements of electrode potentials, overall free-energy changes can be calculated. These reactions will be classified according to their mechanism either as electron-transfer or as displacement reactions with the aid of kinetic studies. Included in these reactions of transition-metal oxy-anions will be their oxidation and reduction by water and hydrogen peroxide, their disproportionation and condensation, and their ability to exchange oxygen.

In this paper we report measurements of the visible and ultraviolet absorption spectra of permanganate, manganate, and hypomanganate ions in aqueous solution, the electrode potentials of the permanganate-manganate and manganate-hypomanganate couples, and certain aspects of the reactivity of these ions. These topics are considered in turn.

Absorption spectra

Experimental.—Water used was doubly distilled from a concentrated alkaline solution of potassium permanganate, and glassware was cleaned with a similar solution. "AnalaR" reagents were used throughout.

* The paramagnetic resonance studies are being made in conjunction with Dr. D. J. E. Ingram.

Spectrophotometric measurements were made using a Unicam SP 600 spectrophotometer for the range 1000—360 $m\mu$ and a Unicam SP 500 spectrophotometer for the range 360—200 $m\mu$. Calibrated quartz cells of 1 mm. thickness and stoppered quartz cells of 1 cm. thickness were used. When necessary, test solutions were compared with solutions of potassium hydroxide of the appropriate concentration.

Potassium manganate was prepared by heating at 120° a solution of potassium permanganate in aqueous 8M-potassium hydroxide until a clear green colour was produced. The solid potassium manganate formed on cooling was recrystallised from the same solvent. Hydrated sodium hypomanganate was prepared by a modification of Lux's procedure.¹ Slightly less than 1 equiv. of powdered sodium sulphite was added to a solution of potassium manganate in aqueous sodium hydroxide (12M), and the solution cooled in ice until dark blue needles of the hydrated salt were deposited.

Potassium permanganate solutions were prepared by dissolving the solid in water containing a trace of perchloric acid to prevent decomposition. The concentrations were determined by titration with standard aqueous oxalic acid. These permanganate solutions were stable for many months if kept in the dark. Manganate solutions were prepared either by heating a permanganate solution of known concentration containing potassium hydroxide (4M), or by dissolving recrystallised potassium manganate in aqueous potassium hydroxide (4M). These solutions were stable in stoppered bottles for several weeks. Hypomanganate solutions were

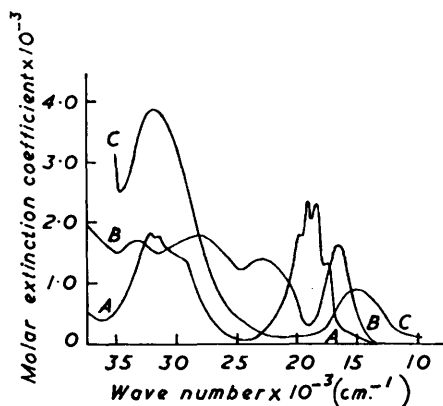


FIG. 1. Visible and ultraviolet absorption spectra of the manganese oxy-ions.

A, MnO_4^{2-} . B, MnO_4^{3-} . C, MnO_4^{-} .

prepared either by heating a permanganate solution of known concentration containing potassium hydroxide (12M), or by dissolving sodium hypomanganate in aqueous potassium hydroxide solution (12M). These solutions were stable for 2—3 days and then decomposed rapidly.

Neither addition of inert electrolytes nor temperature changes of the order of 50° had any noticeable effect on the permanganate spectrum. Further the spectra of the manganate and hypomanganate ions in solution were unaffected by limited changes in the concentration of alkali, and Beer's law was obeyed by solutions of both ions.

Attempts were made to estimate the concentrations of manganate and hypomanganate solutions by adding sufficient acid to cause complete disproportionation, centrifuging to remove manganese dioxide, and measuring the optical density of the remaining permanganate solution. This procedure gave low results, probably because the permanganate first formed decomposed slightly before all the alkali had been neutralised.

The spectra are shown in Fig. 1. These results were used for the estimation of mixtures of permanganate and manganate, spectrophotometric readings being taken at 417 $m\mu$ (23,980 cm^{-1}) and 500 $m\mu$ (20,000 cm^{-1}), and for the estimation of mixtures of manganate and hypomanganate, spectrophotometric readings being made at 434 $m\mu$ (23,050 cm^{-1}) and 715 $m\mu$ (13,980 cm^{-1}). Pairs of simultaneous equations involving these readings were solved to obtain the individual concentrations.

Discussion.—The absorption spectrum of potassium manganate in mixed crystals with potassium sulphate has been studied by Teltow² but we have found no record of its spectrum in solution. The spectrum of the hypomanganate ion has not been previously re-

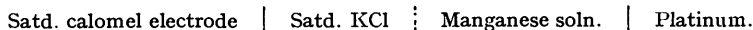
¹ Lux, *Z. Naturforsch.*, 1946, **1**, 281.

² Teltow, *Z. phys. Chem.*, 1939, **44**, B, 74.

corded. The measurements of the absorption spectrum of the permanganate ion in solution, shown in Fig. 1, are consistent with many earlier measurements and agree precisely with those made recently by Zimmerman,³ although the molar extinction coefficients are somewhat lower than those recorded by Lange and Schusterius.⁴ A discussion of the significance of these spectra to the electronic structure of the ions is deferred to a later paper.

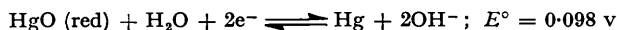
Electrode potentials

Experimental.—Potential measurements were made with the cell:



Oxygen-free nitrogen, previously passed over potassium hydroxide pellets, was bubbled continuously into the manganese half cell. The e.m.f. of the complete cell was balanced against that of a Weston standard cadmium cell by means of a Tinsley potentiometer and a sensitive spot galvanometer. Immediately after each e.m.f. measurement, the solution was analysed spectrophotometrically as described earlier, the estimated error being $\pm 1\%$. All e.m.f. measurements were made at $25^\circ \pm 0.5^\circ$ and were reproducible to within 0.5 mv.

It was observed that the e.m.f. fell several mv quite immediately after the calomel electrode was placed in a concentrated alkaline solution, indicating the presence of a significant liquid-junction potential. In an attempt to avoid the uncertainty introduced, measurements were made with a mercury-mercuric oxide half cell in place of the calomel electrode. The half-reaction for this electrode is



The electrode was made by placing freshly distilled mercury into a small glass cup with a fused-in tungsten-wire contact, the mercury being then covered with mercuric oxide thoroughly wetted with the appropriate alkaline solution. The inside of the cup was covered with a thin film of Silicone grease to prevent the solvent creeping past the mercury. Measurements made with this electrode indicated that in 1m-potassium hydroxide the error due to the junction potential is well within the limits of experimental accuracy quoted. In 10m-potassium hydroxide, however, the junction potential appears to be of the order 10 mv and in 10m-sodium hydroxide to be as high as 40 mv.

Since permanganate is unstable in alkaline solution, the relative concentrations of permanganate and manganate in a given solution were continuously changing. Under the conditions chosen this rate was very slow, and by following the reaction spectrophotometrically and by e.m.f. measurements it was possible to cover a large range of relative permanganate-manganate concentrations at a given ionic strength. The values of E_c , obtained from the measured potentials E (adjusted to the hydrogen electrode scale) by use of the expression

$$E_c = E - (RT/nF) \ln (\text{oxidised form/reduced form})$$

differed by less than 1 mv, and this is taken as good evidence for complete reversibility. Because of this reproducibility only one of the many values obtained at a given ionic strength is recorded in Table 1. Complete reversibility would be expected for this couple since the only act at the platinum electrode is gain or loss of an electron, and electron exchange between permanganate and manganate ions in solution is known to be extremely rapid.⁵ Similarly, the rapidity of the interaction between hypomanganate and permanganate ions in solution described later may be taken as evidence for reversibility of the manganate-hypomanganate couple, in accord with the fair reproducibility of results in solutions of high alkalinity.

In the study of the manganate-hypomanganate couple it was found that, after several hours, manganese dioxide was formed in the cell. It is thought that decomposition was induced by the platinum electrode, since comparable solutions in concentrated aqueous alkali kept in stoppered bottles were quite stable for several days. No measurements were considered under these conditions, and the marked drift in the e.m.f.'s which occurred was taken as a sensitive test for the formation of manganese dioxide.

Measurements of the permanganate-manganate and of the manganate-hypomanganate

³ Zimmerman, *J. Chem. Phys.*, 1955, **23**, 825.

⁴ Lange and Schusterius, *Z. phys. Chem.*, 1932, **159**, A, 295.

⁵ Sheppard and Wahl, *J. Amer. Chem. Soc.*, 1953, **75**, 5133.

potential are shown in Table 1. The ionic strength, μ , was varied by changing the concentrations of sodium and potassium hydroxide, the contributions of the manganese ions being neglected. The potential of the calomel electrode was taken as 0.242 v.

TABLE 1. *Electrode potentials: (A) Hg-HgO electrode used in place of the calomel electrode; (B) measured in aqueous solution of sodium hydroxide in place of potassium hydroxide.*

| MnO ₄ ⁻ -MnO ₄ ²⁻ couple | | | | MnO ₄ ²⁻ -MnO ₄ ³⁻ couple | | | |
|--|--|---|-----------|---|---|---|-----------|
| μ | 10 ⁴ [MnO ₄ ⁻] | 10 ⁴ [MnO ₄ ²⁻] | E_c (v) | μ | 10 ⁴ [MnO ₄ ²⁻] | 10 ⁴ [MnO ₄ ³⁻] | E_c (v) |
| 4.0 | 3.71 | 2.81 | 0.595 | 12.0 | 0.61 | 1.27 | 0.287 |
| 3.0 | 2.60 | 1.32 | 0.592 | 10.0 | 0.72 | 1.17 | 0.279 |
| 2.0 | 1.47 | 0.94 | 0.586 | 10.0 (A, B) | 0.58 | 1.64 | 0.370 |
| 1.0 | 3.54 | 4.97 | 0.583 | 10.0 (B) | 0.58 | 1.64 | 0.330 |
| 0.83 (A) | 2.96 | 2.31 | 0.580 | 8.8 | 0.38 | 0.91 | 0.282 |
| 0.75 | 6.80 | 2.70 | 0.579 | 7.5 (A) | 1.08 | 0.83 | 0.294 |
| 0.56 | 4.41 | 2.50 | 0.577 | 7.5 (A, B) | 0.65 | 1.50 | 0.310 |
| 0.32 | 2.30 | 1.94 | 0.575 | 6.0 | 2.75 | 0.13 | 0.285 |
| 0.24 | 1.70 | 1.54 | 0.573 | 4.0 | 1.77 | 0.22 | 0.301 |
| 0.06 | 0.46 | 0.82 | 0.567 | 3.0 | 5.07 | 0.42 | 0.303 |
| 0.02 | 0.79 | 0.69 | 0.565 | 2.0 | 0.87 | 0.21 | 0.328 |

Results and Discussion.—The value chosen for the permanganate-manganate couple is $E^\circ = 0.558 \pm 0.002$ v. In arriving at this value the graphical method of extrapolating

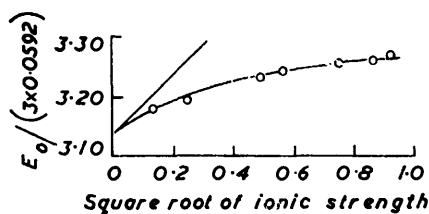


FIG. 2. $E_c / (3 \times 0.0592)$ for MnO₄⁻-MnO₄²⁻ couple, plotted against the square root of ionic strength.

potential measurements to zero ionic strength described by Randall and Vietti⁶ has been used. This method has the advantage that the curve should approach a limiting line of slope 0.505 as shown in Fig. 2. Because the assumptions made in this method of extrapolation may be considered somewhat arbitrary, we have also applied the method used by Schumb, Sherrill, and Sweetser.⁷ This gives an identical result within the limits quoted. Both these methods of extrapolation are described by Latimer,⁸ who has estimated a value of 0.564 v for this couple. This was derived from the results given by Schlesinger and Siems,⁹ using a value for the free energy of manganese dioxide which may be inappropriate since the thermodynamic properties of the dioxide vary with different samples. Our experiments are more direct, as they do not involve manganese dioxide, and therefore our value for E° will be used in preference to that of Latimer. The value of 0.58 v found by Miller and Rogers¹⁰ from a polarographic study in 0.1M-aqueous sodium hydroxide is in fair agreement with our results.

No attempt can be made to extrapolate the results obtained for the manganate-hypomanganate couple to zero ionic strength. As the concentration of alkali was reduced to below 6M, the values of E_c increased markedly although a decrease would be expected. This is probably a result of partial protonation of the hypomanganate ion which, we postulate, would have a basicity similar to that of the orthophosphate ion. It might be argued that, since the chromate ion is a far stronger base than sulphate,¹¹ the hypomanganate ion should be far stronger than phosphate. If this were so, then the blue ion studied in these measurements would be HMnO₄²⁻ and not MnO₄³⁻. However, it is possible that the relatively high basicity of chromate is a consequence of the associated condensation to

⁶ Randall and Vietti, *J. Amer. Chem. Soc.*, 1928, **50**, 1526.

⁷ Schumb, Sherrill, and Sweetser, *ibid.*, 1937, **59**, 2360.

⁸ Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1952.

⁹ Schlesinger and Siems, *J. Amer. Chem. Soc.*, 1924, **46**, 1965.

¹⁰ Miller and Rogers, *Science*, 1949, **109**, 61.

¹¹ Tong and King, *J. Amer. Chem. Soc.*, 1953, **75**, 6180.

dichromate and is thus apparent and not real. The constancy of our electrode-potential measurements in aqueous potassium hydroxide over a wide range of ionic strengths, and the fact that such hypomanganate solutions obey Beer's law, is evidence that MnO_4^{3-} is the only detectable species. Protonated species can only be present in minute concentrations.

The potentials measured in sodium hydroxide are consistently higher than in potassium hydroxide solution. This difference is also found in the relative reactivities of the two ions in sodium or potassium hydroxide solution, and is therefore real. However, as might be expected, the junction potential for the calomel electrode in aqueous sodium hydroxide appears to be large, whereas in potassium hydroxide solution it is always within experimental error. Therefore all the results obtained on using potassium hydroxide solutions in the range $\mu = 6-12$ have been averaged to give a value 0.285 ± 0.010 v, and, since the mercury-mercuric oxide electrode gave results somewhat higher than this, a value of 0.29 v is used for calculating the free energy of formation of the hypomanganate ion. This is used only when the free-energy change for a reaction involving manganate and hypomanganate in concentrated potassium hydroxide solution is being calculated. The value for the manganate-hypomanganate couple estimated by Miller and Rogers¹⁰ in 0.1M-sodium hydroxide is far higher than our value and is probably spurious since they state that manganese dioxide was deposited on the electrode.

Reactivity

Only recently has it been realised that the blue solutions which can be derived from Mn^{IV} or Mn^{VI} under certain conditions, contain MnO_4^{3-} ions.¹ The fact that hypomanganate solutions can be made simply by heating manganate in concentrated alkaline solution,^{12, 13} and that the resulting blue solutions may then be heated to high temperatures for a long time without further change, is clear evidence that this ion is remarkably stable. However, for reasons discussed below, it is important when studying the reactivity of the hypomanganate ion to use conditions that preclude protonation, since the protonated ion readily undergoes disproportionation, and once manganese dioxide is formed the remaining hypomanganate decomposes rapidly. The formula MnO_3^- is sometimes used for the oxy-ion of Mn^{V} . Lux¹ has however shown that salts containing Mn^{V} are isomorphous with phosphates and vanadates. Crystals containing orthophosphate and Mn^{V} have been prepared in these laboratories for paramagnetic resonance studies, thus confirming the similarity of the phosphate and hypomanganate structures. The ion MnO_3^- , if it did exist, would probably be polymeric, and the observation that Beer's law is obeyed by the hypomanganate solutions used makes the occurrence of any equilibria involving condensed species improbable.

Experimental and Results.—Water and all reagents were purified as already described. Hydrogen peroxide was prepared by suitable dilution of the 90% unstabilised product supplied by Laporte Chemicals Limited. When necessary, concentrations of manganese oxy-ions were estimated spectrophotometrically. Reactions in hot concentrated alkaline solution were

TABLE 2. *Estimated thermodynamic data for manganese oxy-ions.*

(S° values are calculated by means of Connick and Powell's formula.¹⁴)

| | ΔF° (kcal.) | ΔH° (kcal.) | S° (cal./deg.) |
|------------------------------|--------------------------|--------------------------|-----------------------|
| MnO_4^- aq. | -107.4 | -129.7 | 45.4 |
| MnO_4^{2-} aq. | -120.3 | -160.5 | 2.1 |
| MnO_4^{3-} aq. | -127.0 * | -185.8 | -44.6 |

* This value is not standard, but refers to MnO_4^{3-} in concentrated KOH solution.

carried out in Pyrex tubes and thus a certain amount of dissolved silicate must always have been present. This procedure was considered preferable to one in which nickel, platinum, or silver crucibles were used since it was invariably found that some oxidation of the metal occurred

¹² Symons, *J.*, 1953, 3956; 1954, 3676.

¹³ Scholder, *Angew. Chem.*, 1953, 65, 240.

¹⁴ Connick and Powell, *J. Chem. Phys.*, 1953, 21, 2206.

to give soluble salts. When oxygen-free conditions were required, the reactions were carried out *in vacuo*. However, it was generally found that simple heating in an open tube, in such a way that the upper part was filled with steam, was equally satisfactory.

Table 2 gives the estimated standard free energy, entropy, and heat-content values for the manganese oxy-anions. Table 3 shows the reactions under consideration, together with estimates for the overall free-energy and heat-content changes. Table 4 contains, in summary, the results found experimentally. These results will now be discussed in greater detail.

TABLE 3. Some possible reactions of the manganese oxy-ions.

ΔF_R° represents the free-energy change under standard conditions, with the one exception that ΔF° for MnO_4^{3-} is taken as -127.0 (see above). ΔF_R° and ΔH_R° are calculated for $n = 1$, not for the equations as written. Other values for ΔF° and ΔH° are taken from Latimer,⁸ except the value -37.4 for ΔH° for the ion HO_2^- , which has been estimated from the value for the entropy S° given by Evans, Hush, and Uri (*Quart. Rev.*, 1952, **6**, 186). The values for equation (3) are the experimental results of Schlesinger and Siems,⁹ and the ΔF° value for MnO_2 used in equation (4) has been derived from these results.

| | ΔF_R° | ΔH_R° |
|--|--------------------|--------------------|
| (1) $\text{MnO}_4^- + \text{MnO}_4^{3-} \rightleftharpoons 2\text{MnO}_4^{2-}$ | -6.2 | -5.5 |
| (2) $\text{MnO}_4^{2-} + \text{Mn}^{\text{IV}} \rightleftharpoons 2\text{MnO}_4^{3-}$ | | |
| (3) $3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_4^- + \text{MnO}_2 + 4\text{OH}^-$ | -0.82 | +7.3 |
| (4) $2\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{MnO}_4^{2-} + \text{MnO}_2 + 4\text{OH}^-$ | -14.0 | +3.5 |
| (5) $4\text{MnO}_4^- + 4\text{OH}^- \rightleftharpoons 4\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + \text{O}_2$ | -3.7 | -10.9 |
| (6) $4\text{MnO}_4^{2-} + 4\text{OH}^- \rightleftharpoons 4\text{MnO}_4^{3-} + 2\text{H}_2\text{O} + \text{O}_2$ | +2.6 | -5.4 |
| (7) $2\text{MnO}_4^- + \text{HO}_2^- + \text{OH}^- \rightleftharpoons 2\text{MnO}_4^{2-} + \text{H}_2\text{O} + \text{O}_2$ | -14.7 | -20.7 |
| (8) $2\text{MnO}_4^{2-} + \text{HO}_2^- + \text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_4^- + 3\text{OH}^-$ | -7.4 | +1.2 |
| (9) $2\text{MnO}_4^{2-} + \text{HO}_2^- + \text{OH}^- \rightleftharpoons 2\text{MnO}_4^{3-} + \text{H}_2\text{O} + \text{O}_2$ | -8.5 | -15.2 |
| (10) $2\text{MnO}_4^{3-} + \text{HO}_2^- + \text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_4^{2-} + 3\text{OH}^-$ | -13.6 | -4.4 |

TABLE 4. Observations on the reactions listed in Table 3.

| Forward reaction | | | Reverse reaction | | | |
|------------------|-----------------------|-------|--------------------|-----------------------|-------|--------------------|
| | Speed | Temp. | [OH ⁻] | Speed | Temp. | [OH ⁻] |
| (1) | Rapid | 20° | >6M | Not observed | | |
| (2) | Not observed | | | Not observed | | |
| (3) | Slow ^a | 20 | <1M | Rapid ^b | 120° | >10M |
| (4) | Slow ^a | 20 | <10M | Rapid | 100 | >10M |
| (5) | Rapid | 20 | >10M | Not observed | | |
| (6) | Slow | 120 | >10M ^c | Slow | 120 | >10M ^d |
| (7) | Rapid | 20 | >5M | Not observed | | |
| (8) | Not directly observed | | | Not directly observed | | |
| (9) | Rapid | 20 | >10M | Not directly observed | | |
| (10) | Rapid | 120 | >10M ^e | Not directly observed | | |

^a Induction period. ^b Reaction proceeds *via* MnO_4^{3-} . ^c Oxygen continuously removed. ^d In presence of oxygen. ^e KOH, not NaOH.

General Discussion.—Reaction (1) was postulated earlier¹² and is immeasurably fast at room temperature. Reaction (2) has not yet been observed, but since any monomeric form of Mn^{IV} is likely to be derived from MnO_4^{3-} simply by electron-, and possibly proton-, transfer reactions and since reaction (1) is so rapid, the great stability of solutions of hypomanganate in concentrated alkali may be taken as evidence that this equilibrium is also far over to the right. The forward reaction (3) can be totally suppressed provided that the ratio of the concentrations of permanganate and manganate is above a specific value depending only on the concentration of alkali. However, even when permanganate is initially absent, a long induction period occurs before manganese dioxide is formed. Duke¹⁵ studied this reaction kinetically but found somewhat shorter induction periods. This may have been because he prepared manganate by fusing permanganate with potassium hydroxide in a platinum crucible, a procedure which would almost certainly have yielded a considerable amount of hypomanganate. In discussing the mechanism of this reaction, both Duke¹⁵ and Abel¹⁶ appear to refer to manganese dioxide as if it could exist in solution as a monomer. It is far more likely that the formation of solid manganese dioxide is a polycondensation or displacement process, which, as in such reactions as polyesterification in

¹⁵ Duke, *J. Phys. Chem.*, 1952, **56**, 882.

¹⁶ Abel, *Monatsh.*, 1955, **86**, 461.

which the monomer has a functionality of three or more, would be expected to favour the ultimate separation of a closely knit three-dimensional polymer. This could then rearrange, at least in part, to give the more stable rutile structure characteristic of pyrolusite. It could also act as a reaction mediator for the equilibrium (3) or (4), since, provided the outermost manganese atoms retained their tetrahedral structure, the loss of permanganate ions from one site and the attachment of manganate ions at a different site should be rapid. Clearly, it is not necessary for monomeric Mn^{IV} to be formed before such condensation. If manganate resembles chromate, then some slight dimerisation would be expected at low alkaline concentrations, and ions such as $\text{Mn}_2\text{O}_7^{2-}$ might then act as centres of growth leading ultimately to the separation of manganese dioxide. This mechanism is still more probable for equilibrium (4), since hypomanganate will be a strong base and hence reactions of the type $2\text{HMnO}_4^{2-} \rightleftharpoons \text{Mn}_2\text{O}_7^{4-} + \text{H}_2\text{O}$ should occur more readily and at a higher pH. Also, this might be a cumulative process, since the highly charged ion $\text{Mn}_2\text{O}_7^{4-}$ should be a still stronger base, and hence such displacements will tend to occur preferentially on the growing polymer. At any stage in this process, manganate ions can split off, thus leaving Mn^{IV} in the polymer. There seems no compelling reason for postulating the formation of Mn^{III} .¹⁵ It is therefore suggested that the induction period of the forward reactions (3) and (4), besides being sensitive to the concentration of alkali, will also be strongly dependent upon the initial concentration of manganate or hypomanganate. This is found to be the case, and alkaline solutions of hypomanganate can be kept for many days at room temperature provided the concentration is low ($<10^{-4}\text{M}$).

A mechanism for the decomposition of permanganate in alkaline solution to give manganate and oxygen [reaction (5)] has already been presented,¹² but has been disputed by Abel¹⁶ and by Jezowska-Trzebiatowska, Nawojcka, and Wronska.¹⁷ For the present, however, this mechanism will still be used as a basis for discussion since the alternatives offered fail to explain certain characteristics of the reaction. Thus, by far the most striking feature of the kinetic results was the dependence of rate upon the initial concentration of permanganate. The mechanism suggested by Abel does not account for this dependence, which he suggests may be invalid. However, careful repetition has invariably given the same results. The relation derived by Abel from the results reported by Symons,¹² which shows that the initial velocity divided by the initial concentration of permanganate at a fixed concentration of alkali is a constant, is in fact in satisfactory agreement with both mechanisms. The rates reported by Jezowska-Trzebiatowska, Nawojcka, and Wronska¹⁷ are far higher than those observed under comparable conditions by Symons who, however, found that, unless very great care was observed in purifying the reagents and solvent, spurious kinetic results were obtained. Since these results were similar in form to those found by the Polish workers, it is tentatively suggested that this may account for the discrepancy. These authors also report kinetic results for the decomposition of manganate to hypomanganate and oxygen. Again the rates given are several orders of magnitude higher than we have observed. These authors conclude with a kinetic study of a reaction in which hypomanganate decomposes to give manganese dioxide and oxygen, but no evidence for this reaction has been obtained in these laboratories.

Reaction (6) has an unfavourable overall free-energy change and if it proceeds by a mechanism similar to that proposed for reaction (5),¹² it must also have a high energy of activation. It is therefore surprising that it may be induced to proceed in the forward direction. However, the reaction only occurs at high concentrations of alkali, under which conditions the reverse reaction is strongly inhibited, not only by the low solubility of oxygen in the medium but also because the relative concentration of water will be greatly diminished. (In 1M-alkali there are about four molecules of water to every hydroxide ion. Since the hydroxide ion will be strongly hydrated the effective concentration of water will be even smaller. The fact that sodium ions will be more strongly solvated than potassium ions may, in part, account for the marked differences observed for these ions.) Although reaction (8) is not directly observed, kinetic evidence for both the overall forward and the reverse step has been presented.¹²

¹⁷ Jezowska-Trzebiatowska, Nawojcka, and Wronska, *Bull. Acad. polon. Sci.*, 1954, **2**, 447.

The competing reactions (9) and (10) are the most interesting in this series. Since both reverse reactions are accompanied by a very large increase in free energy, they will be ignored. Two alternatives then arise. If the rate of (9) is much greater than that of (10), manganate will rapidly be converted into hypomanganate, and the hydrogen peroxide will then continue to decompose with no other apparent change. Conversely, if the rate of (10) is much greater than that of (9), then hypomanganate will at once be converted into manganate which will then catalytically decompose the peroxide. When a concentrated solution of sodium hydroxide is used as solvent, manganate is converted into hypomanganate under all conditions. Addition of further hydrogen peroxide merely results in rapid evolution of oxygen. If, however, a concentrated solution of potassium hydroxide is used, manganate is converted into hypomanganate at room temperature, but hypomanganate is converted into manganate at high temperatures, after which excess of hydrogen peroxide is catalytically decomposed without further change. That this remarkable difference is a function of temperature may be understood in terms of the estimated heat changes. Thus at low temperatures reaction (9) must be faster than (10). An increase in temperature favours the forward stage of reaction (10) more than that of reaction (9) so that at high temperatures reaction (10) dominates, and manganate is preferentially formed. The difference between the reactivity of manganate and hypomanganate in aqueous sodium or potassium hydroxide solutions parallels the differences found for the manganate-hypomanganate couple recorded above.

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