[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE SAN FRANCISCO JUNIOR COLLEGE]

Radioactive Manganese as an Indicator in Testing for Possible Equilibria between Several Valences of Manganese[1]

BY MILTON J. POLISSAR

Equilibria Assumed to Exist in a Permanganate–Manganic Oxalate Mixture.—The kinetics of the reaction between permanganate and oxalate ions was studied by Harcourt and Esson,[2] and later by Schilow[3] and Skrabal.[4] Recently Launer[5] has shown that Skrabal's mechanism for the reduction of manganic ion by oxalate ion is not in complete accord with experimental facts. Launer and Yost[6] have proved conclusively that the earlier mechanism for the reactions taking place in a permanganate–manganic oxalate complex mixture is incorrect.

Launer and Yost proposed another mechanism, based on the very plausible assumption that the following equilibria exist in a solution containing permanganate ion and manganic oxalate complex ion

$2MnO_4^- + 3Mn^{++}$ (always present in $KMnO_4$) $+ 16H^+ = 5Mn^{++++} + 8H_2O$ (rapid equilibrium or sum of equilibria) (1)

$Mn^{++++} + Mn^{++} = 2Mn^{+++}$ (rapid, reversible) (2)

$Mn^{+++} + 2C_2O_4^{--} = Mn(C_2O_4)_2^-$ (rapid, reversible) (3)

A little later, Polissar[7,8] has shown that the immeasurably fast reaction taking place on mixing permanganate, oxalate and manganous ions is in need of a new interpretation. He showed that the mechanism of this reaction may be explained with the use of the equilibria assumed by Launer and Yost.

Until very recently there was no other evidence as to the reversibility of reaction (1) in acid solutions. With the discovery of radioactive manganese,[9] it became possible to test for the existence of such equilibria, using marked manganese atoms. The present paper deals with the method of attack used by the writer in carrying out such tests.

The Use of Marked Atoms in Testing for Equilibria.—The method of attack will be illustrated by means of a concrete example. Assuming that it is possible to trace the identity of atoms, one can rewrite equation (1) as follows

$2MnO_4^- + 3{}^*Mn^{++} = 2Mn^{IV} + 3{}^*Mn^{IV}$ (rapid, reversible) (4)

The marked substances are contaminated with radioactive substances chemically identical with them. For the sake of simplicity, the equation is not completely balanced. In this and in the following equations the substances whose exact formulas are not known will be indicated simply by the valence number of the manganese in them. Precipitated manganese dioxide will be represented by the formula MnO_2, even though it is known that the latter is hydrated.

If we start with ordinary permanganate and marked manganous ion, then, provided equilibrium (4) actually exists, the radioactivity should spread into the permanganate, through the operation of the reverse of reaction (4). Thus, we have a means of carrying out a crucial test for the existence of this equilibrium. (1) Mix a *small* amount of marked manganous ion with a *large* amount of ordinary permanganate ion in acid solution. (2) After allowing the mixture to stand for the desired length of time, add enough sodium hydroxide to make the mixture neutral or slightly basic. Filter off the manganese dioxide from the large excess of permanganate ion. If there is a rapid equilibrium, then *most* of the radioactivity should be found in the *filtrate*. On the other hand, if there is no exchange, then *none* of the activity should be found in the filtrate.

All the experiments in this investigation were carried out in the same manner: a highly radioactive filtrate indicates an exchange reaction; an inactive filtrate indicates the absence of an exchange reaction.

Experimental Procedure and Results

The Preparation of Marked Manganous Ion. Analysis for Radioactivity.—Radioactive manganese was prepared by bombarding metallic manganese for about forty-five minutes with a 4-microampere beam of 5.8 m. v. deuterons

$$25^{Mn^{55}} + 1^{H^2} = 25^{Mn^{56}} + 1^{H^1} \qquad (5)$$

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[1] This work is part of a project supported by a grant from the National Research Council.

[2] Harcourt and Esson, *Phil. Trans. Roy. Soc.* (London), **156**, 193 (1866).

[3] Schilow, *Ber.*, **36**, 2735 (1903).

[4] Skrabal, *Z. anorg. Chem.*, **42**, 1 (1904).

[5] Launer, THIS JOURNAL, **54**, 2597 (1932).

[6] Launer and Yost, *ibid.*, **56**, 2571 (1934).

[7] Polissar, *J. Chem. Ed.*, **13**, 40 (1936).

[8] Polissar, *J. Phys. Chem.*, **39**, 1057 (1935).

[9] Amaldi *et al.*, *Proc. Roy. Soc.* (London), **A149**, 522 (1935).

The radioactive layer was dissolved in a solution containing perchloric acid and ordinary manganous sulfate. The solution so obtained was analyzed for its total content of manganous ion. Enough sodium hydroxide, ordinary manganous sulfate, and water was added to give 50 cc. of 0.01 M $^*MnSO_4$.

The preparation of the various reaction mixtures and the methods of precipitating out one of the valences will be described in connection with the respective experiments. The precipitated manganese dioxide was in each case filtered off rapidly through asbestos, in a Gooch crucible. After separation, the solid phase and the filtrate were each treated with 25 cc. of buffered hydrogen peroxide (approx. 4 M NaAc + 2 M HAc + 0.25 M H_2O_2). The resulting solutions were accurately diluted to 100 cc., a 20.0-cc. portion was removed, and a 20.0-cc. portion of 1 M $MnSO_4$ was added. Thus, all solutions to be tested for radioactivity had approximately the same concentrations of manganous ion, sodium acetate, acetic acid and hydrogen peroxide; they differed only in the concentration of radioactive manganous ion.

The solutions were tested for radioactivity in a special apparatus.[10] If the solution to be tested was found to be too active for measurement, it was diluted with another one containing the proper concentrations of manganous sulfate, sodium acetate, acetic acid and hydrogen peroxide. Frequent measurements were made to check the "background" count of the apparatus.

The experimental results are shown in Fig. 1. The ordinates in the diagram show the number of counts per minute given by each individual solution, corrected for the "background" of the Geiger counter, and for dilution. The abscissas give the time of day at which the respective measurements were made. The four circles marked with short arrows give the measurements on a control solution containing as much marked manganous sulfate as was used in every experiment. The heavy line is the best semi-logarithmic line drawn through these four points, with a slope corresponding to the half-life of radioactive manganese (two hours and forty min.). The lines running parallel to it across the diagram correspond to 80%, down to 0.1% of the activity of the control solution. They make it possible to estimate directly the fraction of the original activity present in a given solution.

The tie lines each connect the two points obtained from a single experiment. In each case the circle corresponding to the filtrate is plain. The circle corresponding to the precipitate is blackened. The radius of each circle is drawn approximately to scale, to indicate the maximum error in the measurement of the radioactivity.

Shortly before 10 P. M. the amplifying circuit of the counter stopped functioning. The last five measurements were made by placing each solution, in an Erlenmeyer flask, over the aluminum window of an electroscope. All five values of the activity, expressed in divisions per minute, were multiplied by a constant factor, selected in such a way as to bring the third control point (11:05 P. M.) on the 100% line.

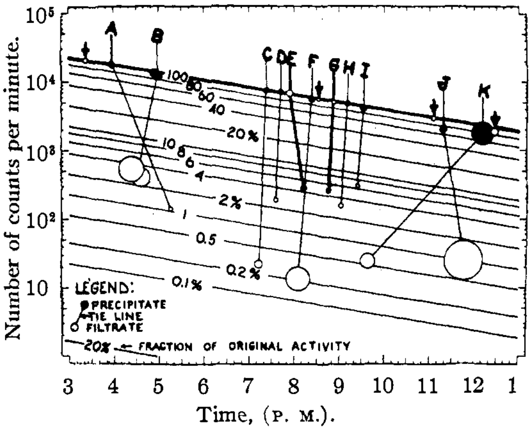

Fig. 1.—Complete record of radioactive measurements. The activities of the solutions obtained from the precipitates (blackened circles) and from the filtrates (plain circles). A very active filtrate indicates an exchange reaction. An inactive filtrate indicates the absence of exchange. Exchange reactions evident in Experiments E and G. In all other experiments no exchange took place. In experiment I the filtrate contained 6.7% of the original activity because of the use of an excess of marked manganous ion in the preparation of the manganese dioxide. The small activity of the filtrates in A, B, C, D, F, H, J and K was due to imperfect filtration.

It will be seen that in all experiments, but J, the sum of the activities of the filtrate and the precipitate was equal to the activity of the control solution, within the experimental accuracy of measuring the activity. In experiment J the deficiency was large, for some unexplained reason. Inspection of the results in experiment K and of Fig. 2 will show, however, that this slight uncer-

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[10] Olson, Libby, Long and Halford, THIS JOURNAL, 58, 1313 1936).

tainty does not invalidate the conclusions to be drawn from experiment J.

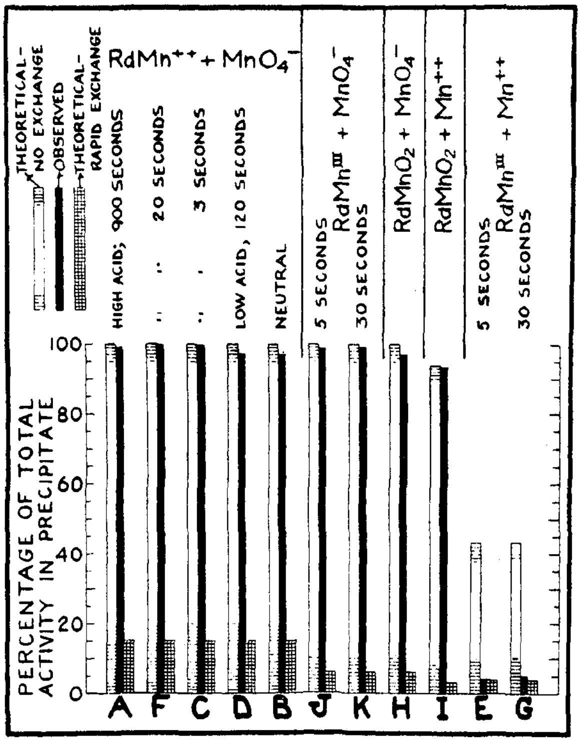

Fig. 2.—Observed activities of the precipitates (black bars) compared with the theoretical values for complete absence of exchange (shaded bars) and for complete exchange (cross-hatched bars). This diagram exhibits more clearly the complete exchange in a solution containing manganic complex and manganous ions (Experiments E and G) and the absence of exchange in the other nine mixtures.

Description of Individual Experiments

Experiments C, F, A, D, B. Marked Manganous and Permanganate Ions.—*Experiment C.*—(10.0 cc. of 0.02 *M* $KMnO_4$ + 1.0 cc. 1 *M* $HClO_4$) was added to (2.0 cc. 0.01 *M* $MnSO_4$ + 10 cc. H_2O). Three seconds later, with the solution still clear and violet, 10.0 cc. of 0.1 *M* NaOH was added. The manganese dioxide precipitated at once. Filtration started about two minutes later. 100% (±6%) of the original activity was found in the precipitate; 0.3% (±0.05%) in the filtrate. (The small amount of radioactivity found in this and in some of the other filtrates is probably not due to a slow exchange. The weight of the precipitated manganese dioxide did not exceed 4.4 mg. in any of the experiments. From visual observations, the writer is inclined to ascribe small activities of the filtrates to imperfect filtration.)

Experiment F.—The same mixture as in C quenched forty seconds after mixing. Just before quenching, the solution was still clear, but definitely reddish, because of the small amount of manganese dioxide formed; 100% (±8.5%) of the original activity found in the precipitate; 0.2% (±0.1%) in the filtrate.

Experiment A.—The same mixture as in C allowed to stand for fifteen minutes. By this time the spontaneous formation of manganese dioxide was practically complete, and it was unnecessary to add sodium hydroxide: 100% (±8%) of the original activity in the precipitate; 1% (±0.05%) in the filtrate.

Experiment D.—(10.0 cc. of 0.02 *M* $KMnO_4$ + 0.1 cc. 1 *M* $HClO_4$) was added to (2.0 cc. 0.01 *M* $MnSO_4$ + 10 cc. H_2O). In this experiment the initial acid concentration was one-tenth as large as in experiment C. The spontaneous formation of manganese dioxide was much faster. In three to four seconds the mixture was definitely red, and in a few more seconds it was opaque. No sodium hydroxide was necessary. Filtered five minutes after mixing: 100% (±6.5%) of the original activity in the precipitate; 3% (±0.18%) in the filtrate.

Experiment B.—The perchloric acid was omitted. The precipitation of manganese dioxide took place on mixing; filtered two minutes later. In this experiment the activities of the two solutions were measured twice: 95% (±6%) of the original activity in the precipitate; 3% (±0.3%) in the filtrate.

Experiments J and K Marked Manganic Oxalate Complex Ion and Permanganate Ion.—*Experiment J.*—Ten cc. of 0.002 *M* potassium permanganate was added to (2.0 cc. 0.01 *M* $^*MnSO_4$ + 10.0 cc. 0.5 *M* $H_2C_2O_4$). Manganic oxalate complex formed on mixing. The solution contained a slight excess of permanganate ion. Two seconds after mixing, 25.0 cc. of 0.02 *M* potassium permanganate was added. Five seconds later the following quenching mixture was added: (5 cc. 3 *M* NH_4OH + 10 cc. 0.5 *M* $CaCl_2$). (The calcium chloride was added to facilitate the decomposition of the manganic oxalate complex into manganese dioxide and manganous ion.) Filtered about two minutes later. In this experiment, and in experiment K, after treating the precipitate with the buffered hydrogen peroxide, it was necessary to carry out a second filtration, since calcium oxalate does not dissolve in the acetic acid buffer solution: 75% (±10%) of the original activity found in the precipitate; 1% (±1%) in the filtrate.

Experiment K.—The same as in J, except that the manganic complex-permanganate mixture was allowed to stand for thirty seconds before adding the quenching mixture: 80% (±24%) of the original activity found in the precipitate; 1% (±1%) in the filtrate.

Experiments E and G. Marked Manganic Oxalate Complex and Manganous Ions.—*Experiment E.*—(2.4 cc. 0.002 *M* $KMnO_4$ + 10 cc. H_2O) was added to (2.0 cc. 0.01 *M*$^*MnSO_4$ + 10.0 cc. 0.5 *M* $H_2C_2O_4$). Marked manganic oxalate complex formed on mixing. Two seconds later 25.0 cc. 0.01 *M* $MnSO_4$ was added. Five seconds later (5 cc. 3 *M* NH_4OH + 5 cc. 2.5 *M* $(NH_4)_2SO_4$) was added. Manganese dioxide precipitated at once; the manganous ion remained in solution. The mixture was filtered two minutes later: 105% (±8%) of the original activity found in the *filtrate;* 4.5% (±0.5%) in the precipitate.

Experiment G.—Procedure the same as in E, except that the quenching mixture was added thirty seconds, instead of five seconds, after the addition of the manganous sulfate: 95% (±7%) of the original activity was found in the filtrate; 5% (±0.25%) in the precipitate.

Experiments H and I. Marked Manganese Dioxide and Permanganate Ion. Marked Manganese Dioxide and Manganous Ion.—*Experiment H.*—(7.0 cc. 0.002 *M* $KMnO_4$ + 10 cc. H_2O) was added to 2.0 cc. 0.01 *M* $^*MnSO_4$. Manganese dioxide formed at once. In this case the excess of permanganate was used advisedly. Two minutes later 25.0 cc. of 0.02 *M* $KMnO_4$ was added. The mixture was shaken and filtered two minutes later: 100% (±6%) of the original activity was found in the precipitate; 3.3% (±0.6%) in the filtrate.

Experiment I.—(6.25 cc. 0.002 *M* $KMnO_4$ + 10 cc. H_2O) was added to 2.0 cc. 0.01 *M* $^*MnSO_4$. Manganese dioxide formed at once. Two minutes later 10.0 cc. 0.1 *M* $MnSO_4$ was added. The mixture was shaken and filtered two minutes later: 95% (±7%) of the original activity was found in the precipitate; 6.7% (±0.35%) in the filtrate.

Attention should be called to the fact that in the preparation of the manganese dioxide a slight excess of the marked manganous ion was used. This accounts for practically the entire activity of the filtrate. Assuming that there is no exchange, the theoretical distribution would be 93.76% in the precipitate and 6.24% in the filtrate.

Sample Calculations

In the following calculations all the amounts have been multiplied for the sake of convenience by the factor 10^6.

Experiments C, F, A, D, B.—The original solution contained 20 moles of marked manganous ion and 200 moles of permanganate ion. The final mixture contained 33.33 moles of manganese dioxide and 186.67 moles of permanganate ion in solution. If there were a rapid exchange between the manganous and permanganate states in the original solution, then the radioactivity of the two ultimate phases would have been proportional to the manganese content of each, namely, 15.1% in the precipitate and 84.9% in the filtrate. In the absence of any interchange, the precipitate should contain all the radioactive manganese.

Experiments E and G. Marked Manganic Oxalate Complex and Manganous Ions.—Subsequent experiments with ordinary manganese yielded the following information, essential for the calculation of the theoretical distribution of radioactivity. (a) In the instantaneous reaction in which manganic oxalate complex was formed, 10% of the oxidizing titer was lost through oxidation of oxalic acid. (b) After this initial reduction, the further reduction of manganic ion was extremely slow, both before and after the addition of the large amount of manganous ion.

The mechanism of the initial 10% reduction is not sufficiently well understood. For this reason it is impossible at present to decide whether the manganous ion formed in this process originated from the marked manganous ion, from the permanganate ion, or from both. The last assumption was made in carrying out the calculation of the theoretical distribution of activity. In other words, it was assumed that the oxidation of the oxalic acid took place *after* the instantaneous formation of trivalent manganese. It should be emphasized, however, that this uncertainty is only of secondary importance. It does not in any way invalidate the conclusions to be drawn from the experimental results, namely, that there is a rapid exchange between the bivalent and trivalent states. On the contrary, if it is assumed that the oxalic acid was oxidized by the permanganate only, the evidence for rapid exchange is strengthened, but only to a small extent.

The mixture was prepared from

$$4.8 \text{ moles } MnO_4^- + 20 \text{ moles } ^*Mn^{++}$$

On mixing, the solution contained the following substances

$$4.8\ Mn^{III} + 19.2\ ^*Mn^{III} + 0.8\ ^*Mn^{++}$$

After the 10% reduction, the mixture contained

$$4.32\ Mn^{III} + 17.28\ ^*Mn^{III} + 2.72\ ^*Mn^{++} + 0.48\ Mn^{++}$$

To this was added 250 moles of ordinary manganous ion. After precipitation, the mixture contained

$$2.16\ MnO_2 + 8.64\ ^*MnO_2 + 11.36\ ^*Mn^{++} + 252.64\ Mn^{++}$$

The preceding material balance was carried out on the assumption that there was no exchange between the bivalent and trivalent states. Under such conditions, the precipitate should contain 8.64/20.0, or 43.2% of the original activity.

On the other hand, if there is a complete exchange between the two valence states, the precipitate must contain only 10.80/274.8, or 3.93% of the original activity.

Discussion of the Experimental Results

The experimentally observed activities are shown in Fig. 1. The fraction of the original activity present in the precipitate and in the filtrate, respectively, can be read directly, with the use of the reference semi-logarithmic lines.

In Fig. 2 the same data are presented in the form of a bar diagram. Before plotting, each pair of activities was multiplied by the same factor, to normalize the total activity to 100%. In each case the observed value of the activity of the precipitate is flanked on both sides by the two theoretical values corresponding to complete exchange and to complete absence of exchange, respectively.

An inspection of the diagram will show that there was no exchange between the two valence states in the first nine experiments. In the last two experiments there was a complete exchange between the two valence states.

The evidence seems to be conclusive that the equilibrium postulated in equation (1) does not actually exist. It does not follow, however, that no other equilibrium exists between permanganate and manganous ions in the same solution. It is possible to postulate other equilibria which would not be in disagreement with the experimental results obtained in the present investigation. The following two will serve as illustrations

$$MnO_4^- + {}^*Mn^{++} = Mn^{VI} + {}^*Mn^{III} \text{ (rapid, reversible)} \quad (6)$$

$$\text{or } 2MnO_4^- + {}^*Mn^{++} = 2Mn^{VI} + {}^*Mn^{IV} \text{ (rapid, reversible)} \quad (7)$$

An inspection of the two equations will show that the radioactivity cannot spread from the bivalent to the permanganate state, provided there is no exchange between Mn^{VI} and Mn^{III}, or between Mn^{VI} and Mn^{IV}, respectively.

The rapid exchange between the manganous and manganic states can be explained easily with the use of the well-known equilibrium shown in equation (2). However, the observed exchange cannot be considered as additional evidence for such an equilibrium. The exchange may have been taking place through the operation of an entirely different reversible reaction, involving no quadrivalent manganese, but involving a direct transfer of an electron from one ion to another

$$^*Mn^{III} + Mn^{++} = {}^*Mn^{++} + Mn^{III} \quad (8)$$

The absence of exchange in experiment I (manganese dioxide and manganous ion) is probably due to the fact that only the surface atoms of the precipitate can be affected by the exchange reaction.

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Summary

1. Radioactive manganese was used as a "tracer" in a search for possible equilibria existing in solutions containing manganese in two valence states.

2. It was found that no exchange takes place in the following pair-systems: (a) permanganate ion–manganous ion; (b) permanganate ion–manganic oxalate ion; (c) permanganate ion–solid manganese dioxide; (d) solid manganese dioxide–manganous ion.

3. A rapid and complete exchange was found to take place in the system (e) manganic oxalate ion–manganous ion.

4. The absence of exchange in system (a) offers conclusive evidence against the existence of a rapidly established equilibrium between permanganate and manganous ions on one hand and some *one* substance of intermediate valence on the other.

5. The absence of exchange in system (a) cannot be taken as evidence against the existence of a rapidly established equilibrium between permanganate and manganous ion on one hand and *two* substances of intermediate valence on the other, provided there is no exchange between the latter two substances.

6. The rapid exchange in system (e) is in agreement with the known existence of an equilibrium between manganic oxalate ion, manganous ion and quadrivalent manganese. However, it may be due to yet another rapid reversible reaction involving the transfer of an electron from a manganous to a manganic ion.

7. The apparent absence of exchange in system (d) is probably due to the fact that only the surface atoms on the solid manganese dioxide can be affected by such an exchange.

8. Work on the mechanism of reduction of permanganate ion is to be continued.

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