As the energy of the activated atom approaches thermal energies, the collisions become more inelastic in character[23] and result in epithermal reactions which form a variety of products which cannot be produced directly in the billiard-ball mechanism.

At energies not far above thermal, the recoil atom can effect various reactions, analogous to the hot reactions observed in photochemical systems.[24] Abstraction reactions of moderate activation energy such as

$$I\cdot + CH_3\text{-}CH_2I \longrightarrow CH_3I + \cdot CH_2I \qquad (2)$$

and

$$I\cdot + I\text{-}CH_2CH_3 \longrightarrow I_2 + CH_3CH_2\cdot \qquad (3)$$

are examples of this. The products observed from this type of reaction might be expected, at least as a first approximation, to be formed in a random statistical fashion.

The iodine atom, immediately after it has been fully thermalized, will begin diffusing through a medium in which there is initially an extremely high concentration of radicals which it itself has produced. It will have a high probability of reacting with these radicals to form both organic and inorganic (I_2) activity. Such reactions, although involving thermal atoms, will be peculiar to the nuclear process; *i.e.*, because the reactants are inhomogeneously distributed throughout the system, the reactions will not be subject to ordinary scavenging effects. In general the radicals produced along the track might be expected to resemble those observed in the radiation chemistry of the same system.[25] One would expect a relatively high yield of products which can be formed by low energy modes of radical decomposition.

Finally, after the unreacted iodine atoms have been thermalized and have diffused out of the zone of high radical concentration, they will be fixed as inorganic activity by exchange with the free iodine unavoidably present in the medium.

Inorganic activity will be formed by reactions of epithermal atoms with solvent molecules (such as 3), by reactions of the active atoms with iodine in the recoil track, and by atoms which have been thermalized without undergoing reaction.[26] Organic activity will be formed by billiard-ball processes (probably to a rather small extent), by reactions of epithermal atoms, and by thermalized atoms with radicals produced in their immediate vicinity. Although it is clearly difficult to distinguish between products formed in epithermal processes and those which result from random-fragmentation of the medium, details such as the relatively high methyl iodide yield from *n*-propyl iodide give considerable weight to the importance of the latter mechanism.

Acknowledgment.—We wish to thank the operating staff of the Brookhaven 60 inch cyclotron for their coöperation in making the necessary irradiations. We are indebted to Dr. A. O. Allen and Dr. R. W. Dodson for valuable discussions.

[23] The time required for a 10 e.v. iodine atom to pass through a butyl iodide molecule is of the order of 10^{-13} seconds. Time is available, therefore, for considerable vibrational energy to be transferred.

[24] W. H. Hamill, R. R. Williams, H. A. Schwarz and E. E. Voiland, Document AECU-1321, Technical Information Service, Oak Ridge, Tenn.

[25] Actually the energy loss processes are extremely different being due to ionization in the radiation chemical case and to knock-on effects in the recoil cases.

[26] By using dibromoethylene to scavenge thermal bromine atoms, it has been shown (ref. 15; R. R. Williams, Jr., W. H. Hamill, H. A. Schwarz, and E. J. Burrell, THIS JOURNAL, **74**, 5737 (1952)) in studies of (n,γ) activation of ethyl bromide that the inorganic bromine is produced both by thermal and hot processes.

JERSEY CITY, N. J.
UPTON, L. I., NEW YORK

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Oxygen Isotope Effects at Anodes

BY MICHAEL ANBAR AND HENRY TAUBE

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The isotope fractionation factor for O_2 liberated from water at an anode shows considerable variation with the nature of the electrode material, but is independent, at least over a limited range, of the current density. Mechanisms of the reaction are discussed. Tracer experiments using PbO_2 and MnO_2 as electrode material showed that none of the anode oxygen appears as O_2. They showed also that rapid exchange of the oxide electrode with water is induced when the material functions as an anode.

A study of oxygen isotope fractionation effects on the electrolysis of water would appear to have significance in relation to theories of the mechanism of oxygen evolution, quite apart from the usefulness the effects might have in separation of isotopes. Nevertheless a systematic exploration of the isotope fractionation effects seems not to have been reported in the literature. Individual values have been cited,[1] but the agreement among various authors is unsatisfactory, and certain of the values, in the light of experience subsequent to the early work, appear to be unreasonably high. We are reporting the results of an investigation in which attention was paid to the influence of the nature of electrode material, temperature and of certain other parameters, on the magnitude of the isotope fractionation, as well as the results of some tracer experiments using metal oxide anodes.

Procedure.—The solutions described in Table I as "acid" or "basic" contained 0.1 *M* $HClO_4$ or 0.1 *M* NaOH. The metal impurity content of the sample of Ni, Fe, Pd and Co used[2] did not exceed

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[1] The bibliography provided by L. Tronstad and J. Brun, *Trans. Faraday Soc.*, **34**, 766 (1938) is complete and still up to date.

[2] We are grateful to Prof. N. Nachtrieb for making certain of the electrode materials available to us.

0.001% (the samples were supplied as spectroscopically pure). The Co, however, did contain a small amount of oxide distributed throughout the sample. Cu, Mg, Si and Sn were analytical grade materials. Ag, Au, Pt, Pb and C were as supplied for electrode use. The oxides PbO_2 and MnO_2 were applied to Pt by anodic deposition from acid solutions containing the dipositive ions, and oxides on Co, Ni and Ag were formed by anodic oxidation in 6 *M* NaOH.

TABLE I

OXYGEN-ISOTOPE FRACTIONATION AT ANODES (ELECTRODE AREA, 1–3 CM.^{2})

No.	Electrode	Medium	Current density, m. amp. cm.$^{-2}$	Temp., °C.	Special conditions	$(1 - f) \times 100$
1	Pt	Acid	750	25	Bright	1.1_4
2	Pt	Basic	600	25	Bright	1.0_7
3	Pt	Basic	550	25	Bright	1.1_0
4	Pt	Basic	33	25	Black	1.2_7
5	Pt	Basic	200	25	Black	1.3_1
6	Pt	Basic	330	25	Black	1.3_5
7	Pt	Basic	500	25	0.5 *M* NaF	1.0_5
8	Pd	Acid	120	25	....	0.7_4
9	Pd	Basic	80	25	....	0.7_2
10	Ir	Basic	620	25	....	1.1_0
11	Au	Acid	24	25	....	0.5_1
12	Au	Basic	4	25	....	$.6_8$
13	Au	Basic	18	25	....	$.4_5$
14	Au	Basic	16	25	....	$.5_1$
15	Au	Basic	12	75	....	$.3_2$
16	Ag	Basic	60	25	....	1.8_0
17	Ag(oxide)	Basic	240	25	On Ag	1.3_1
18	Ag(oxide)	Basic	125	80	On Ag	0.9_9
19	Ag(oxide)	Basic	80	25	On Pt	1.1_8
20	Cu	Basic	17	25	....	0.7_2
21	Sn	Basic	5	25	....	0.3_5
22	Pb	Basic	35	25	....	1.0_5
23	PbO_2	Basic	80	25	On Pt	1.3_5
24	Ni	Basic	100	25	....	0.8_2
25	Ni	Basic	160	25	....	$.9_3$
26	Ni	Basic	350	75	....	$.7_7$
27	Ni(oxide)	Basic	300	25	On Ni	1.0_1
28	Co	Basic	22	25	....	1.6_7
29	Co	Basic	25	25	Used first as cathode. Polished with emery after pickling HNO_3	1.2_9
30	Co	Basic	24	25		1.4_9
31	Co	Basic	45	25		1.0_4
32	Co	Basic	45	25		1.0_4
33	Co(oxide)	Basic	80	25	On Pt	1.46
34	Fe	Basic	1	25	....	1.8_1
35	Fe	Basic	120	25	....	1.7_5
36	Fe	Basic	150	75	....	1.3_7
37	MnO_2	Basic	50	25	On Pt	1.4_0
38	MnO_2	Basic	40	35	On Pt	1.4_6
39	Ti	Basic	35	25	....	0.7_7
40	Si	Acid	18	25	....	1.2_3
41	Si	Basic	25	25	....	1.3_2
42	C	Basic	15	25	CO formed	1.5_3
43	Mg	Basic	100	25	....	0.8_3

The electrolyte solution was degassed before electrolysis, but it was nevertheless found necessary to reject the first 0.2–0.5 mmole of gas as containing excessive N_2. The gas was dried by passing it through a Dry Ice trap and the isotopic composition of the O_2 determined mass-spectrometrically. The isotopic composition of the water was determined[3] on the O_2 formed by oxidizing a portion completely with BrF_3. Because of the difficulty in making the analysis of the isotopic composition of water, the data in Table I are more reliable for intercomparisons than as absolute values. Thus as absolute values, the results in column 7 may be in error by a constant amount, which may be as great as 0.3. However, differences greater than 0.1 can be considered to arise from causes other than errors in the mass-spectrometric analysis.

The fractionation factor *f* is the isotope ratio O^{16}/O^{18} in the O_2 liberated on complete oxidation of water, divided by the ratio in the O_2 formed on electrolysis. The isotopic composition of the water is not changed significantly by the addition of the electrolytes, nor during the electrolysis.

Results

The results of the experiments on isotope fractionation are presented in Table I.

Table II contains a summary of some results of the tracer experiments.

TABLE II

OXYGEN EXCHANGE FOR METAL OXIDE ANODES IN ALKALINE SOLUTION

(Temp., 25°, in 0.1 *M* NaOH. The enrichment ratio (E.R.), is the ratio O^{18}/O^{16} in the material in question, compared to this ratio for normal water.)

Material	Amt. mol. $\times 10^5$	E.R. of oxide	E.R. of soln.	Amt. electricity, equiv.	Time, min.	E.R. of oxide final
PbO_2	2.0	1.000	7.20	None	60	1.014
PbO_2	4.0	6.20	1.000	2×10^{-4}	10	5.60
PbO_2	6.0	6.38	1.00	2×10^{-4}	10	4.62
Ag(oxide)	1.3	1.000	7.20	None	60	1.29
Ag(oxide)	1.3	6.49	1.000	2×10^{-4}	5	1.18
MnO_2	3.5	1.000	7.20	None	60	1.075
MnO_2	3.5	6.25	1.000	2×10^{-4}		1.045

For each oxide, using enriched oxide in normal water, the isotopic composition of the O_2 formed was indistinguishable, within the precision of the measurements, from that obtained using oxides of normal isotopic composition. This is as true for the smallest quantity collected (0.005 mmole from an anode containing 0.01 mmole of PbO_2) as for larger quantities.

Discussion

The data on fractionation factors reveal considerable differences for different electrode materials, from 0.3_5 as the percentage discrimination in the case of Sn to 1.8 for Fe. The values are reproducible for a given electrode material subjected to a fixed treatment and are little dependent on current density at least for certain electrodes (*cf.* data for Pt, Au, Fe) over a limited range of current density. The discrimination does depend on the treatment of the electrode (*cf.* 3 and 6, and 28–32 in Table I), and it is interesting that such differences for a given electrode material can persist over a considerable extent of electrolysis. At most, only a slight difference in isotopic discrimination between acid and basic solution is observed (*cf.* 1 and 2, 8 and 9, 11 and 12, 40 and 41, Table I), but certain inert materials can affect the discrimination (effect of NaF on Pt black, exp. 7 in Table I). The discrimination

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[3] We are indebted to Howard Baldwin for the determination of the isotopic composition of the water. The details of the method will be published elsewhere.

decreases as the temperature increases (*cf.* 14 and 15, 17 and 18, 25 and 26, 25 and 36).

A general conclusion which can be drawn from the results of Table I is that a mechanism in which electron removal and the subsequent acts take place out of contact with electrode material—as for example, a mechanism involving $OH_{aq.}$—cannot apply to all electrodes. The variations in isotopic discrimination for different electrode materials demonstrate that in most cases the electrodes are directly involved in the O–O bond formation. Reutchi and Delahay[4] in analyzing data on oxygen overvoltage already have concluded that the electrode material is involved as reactant in the rate-determining act. The experiments described in Table II suggest that at least the surface layer of oxide or hydroxide will be at exchange equilibrium with solvent. Accepting the view that Me–O bonds are formed as an intermediate step in the formation of O_2, the over-all isotope discrimination will then be composed of the equilibrium discrimination in the exchange reaction referred to

$$-\overset{|}{\underset{|}{\text{M}}}\text{OH} + \text{H}_2\text{O}^* \longrightarrow -\overset{|}{\underset{|}{\text{M}}}-\text{O}^*\text{H} + \text{H}_2\text{O} \qquad (1)$$

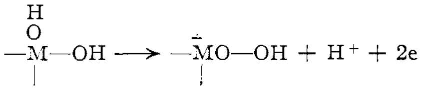
and the kinetic discrimination in the succeeding step, formation of the –O–OH bond. It can reasonably be supposed that once this bond is formed, under the oxidizing influence of the anode, the peroxide will proceed undirectionally to O_2.

Even though the fractionation effects expected on this mechanism cannot be calculated qualitatively, some additional comments on them seem worthwhile. Assuming[5] a frequency of 800 cm.$^{-1}$ for the oxygen bound to the metal on the surface, the formation of the bond between OH and the massive metal will contribute a factor of *ca.* 1.10 to the partition function ratio Q^{18}/Q^{16}. The O–H bond will also contribute to the isotopic discrimination, so that when the resultant is compared to the partition function ratio[6] for $H_2O_{liq.}$ of 1.07 at 25°, an equilibrium fractionation in reaction (1) of 3 to 5% can be expected (K of 1.03 to 1.05), with O^{18} concentrating in the surface layer. The small over-all discrimination is therefore caused by the fairly large equilibrium discrimination being opposed in sense to the kinetic one in the succeeding step. The latter, in certain cases, must be as large as 1.05.

Two distinct mechanisms exist for the formation of the O–OH bond, one in which solvent oxygen becomes attached to $-\overset{|}{\underset{|}{\text{M}}}\text{OH}$

$$-\overset{|}{\underset{|}{\text{M}}}\text{OH} + \text{H}_2\text{O} \longrightarrow -\overset{|}{\underset{|}{\text{M}}}\text{O}-\text{OH} + 2\text{H}^+ + 2\text{e}^- \quad (2)$$

another in which the terminal OH is taken from the surface



$$-\overset{\overset{\text{H}}{\text{O}}}{\underset{|}{\text{M}}}-\text{OH} \longrightarrow -\overset{-}{\underset{|}{\text{M}}}\text{O}-\text{OH} + \text{H}^+ + 2\text{e} \qquad (3)$$

Tracer experiments[7] on the reduction of H_2O_2 by Pb(II) show that when electrons are available on M, reduction of the O–OH bond can take place by rearrangement. It is not unreasonable to suppose then that withdrawing electrons from M in $-\overset{\overset{\text{H}}{\text{O}}}{\underset{|}{\text{M}}}\text{OH}$ can produce rearrangement as in equation 3. Mechanisms (2) and (3) require quite different variations in fractionation with surface material, but until the equilibrium fractionation in (1) can be calculated, the effects cannot be used to distinguish mechanisms. It is hoped to learn something about kinetic isotope discrimination in reactions such as (2) by the study of the reaction: $H^+ + H_2O_2 + I^- \rightarrow$ and others.

There is little correlation between the magnitudes of the isotope discrimination and of overvoltages. The order of increasing isotope fractionation for different metals is: Sn, Au, (Cu Pd Ni), Pb, Pt, $Pt_{bl.}$, Co, Fe(Ag?), of increasing overvoltage is: Co, Fe, Cu, Pb Ni Ag), Pd, Pt, Au. A close correlation need not be expected, since the isotope discrimination may not be restricted to the rate-determining step, which according to the analysis of Ruetchi and Delahay[4] is the formation of the M–OH bond. Persuasive though their analysis is, it seems remarkable that for the entire series considered by them the step

$$-\overset{|}{\underset{|}{\text{M}}} + \text{H}_2\text{O} \longrightarrow -\overset{|}{\underset{|}{\text{M}}}\text{OH} + \text{H}^+ + \text{e}^-$$

represents a higher potential energy increment than does a step such as (2) or (3). H_2O_2 is a stronger oxidizing agent than are many of the metal oxides presumably involved, at least when these are formed in bulk. For very active metals, such as Mg and Al, surely formation of the O–O bond, rather than of the M–O bond, is rate-determining.

The constancy of fractionation factor with acidity and current density implies that at least some features of mechanism are not altered by these changes. A change with current density can be expected where this does produce a difference in mechanism. The mechanisms were not always under control in our work; thus only one of the electrolytes with Ag (exp. 16) proceeded without formation of a visible layer of some oxide on the surface. The change in mechanism on Pt black produced by adding NaF to the solution is interesting in connection with the known effect of this electrolyte in changing[8] the course of electrolytic oxidation of acetate ion to that appropriate to shiny Pt.

For a number of reasons, the result that the O_2 liberated is not derived from the anode oxide cannot be taken as proving that Me–O bonds are not broken in forming O_2. The exchange of metal oxide with solvent induced by electrolysis is one such reason, and the effect, though it may be incidental to the mechanism of oxygen evolution, deserves further study.

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[4] Reutchi and P. Delahay, *J. Chem. Phys.*, **23**, 556 (1955).

[5] The symmetrical vibration frequency in $B(OH)_3$ is 875 cm.$^{-1}$, R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, **4A**, 74 (1936).

[6] The factor 1.068 for H_2O_g (H. C. Urey, *J. Chem. Soc.*, 562 (1947)) multiplied by 1.008, the isotopic fractionation liquefying.

[7] M. Anbar and H. Taube, to be submitted for publication.

[8] S. Glasstone and A. Hickling, *Chem. Revs.*, **25**, 407 (1939).

02026. The funds for the purchase of the mass spectrometer used in the research were supplied by the Atomic Energy Commission under Contract At(11-1)-92. We are grateful to Mr. Robert A. Silverman for help with some of the experiments.

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM WESTINGHOUSE RESEARCH LABORATORIES]

A Study of the $Li_xMn_{(1-x)}O$ System[1]

BY W. D. JOHNSTON AND R. R. HEIKES

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Compositions in the previously unreported system $Li_xMn_{(1-x)}O$ have been prepared by sintering Li_2O_2 and MnO at elevated temperatures. A study of the products of this reaction by X-ray diffraction has permitted a partial phase diagram to be constructed. Throughout a large range of composition single phase products having a sodium chloride structure may be obtained. At higher lithium compositions the compound $LiMnO_2$ is formed. It has been found to have orthorhombic symmetry with two formula weights per unit cell. The products having the sodium chloride structure have been studied magnetically. These data are discussed in terms of a double exchange interaction.

Introduction

Certain theoretical predictions can be made as to the electrical and magnetic properties of the system $Li_xMn_{(1-x)}O$. These predictions are based primarily on the interpretation by Zener[2] of the magnetic and electrical properties of the manganese perovskites. The manganese perovskites $(La_{(1-x)}A_x)MnO_3$ where A = Ca, Sr or Ba were found by Jonker and Van Santen[3] to be ferromagnetic where $0.2 < x < 0.4$. Further, in this composition range the compounds proved to be good electrical conductors. Zener explained this behavior on the basis of a ferromagnetic coupling of the 3d shell electrons of manganese by the double exchange mechanism. This mechanism is based on the degeneracy caused by the presence of manganese ions of two different valences in equivalent crystallographic sites. It involves an electron transfer from Mn^{+3} to an adjacent Mn^{+4} through an intermediate $O^{=}$. Such a transfer favors a parallel alignment of the manganese spin vectors which results in the observed ferromagnetism. The transfer of electrical charge in this exchange mechanism gives rise to the relatively high electrical conductivity found in these compounds.

In addition to the double exchange interaction expected in the $Li_xMn_{(1-x)}O$ system, super-exchange will also be present. This interaction, which arises from the deviation of the ground state from pure ionic character, can produce either a ferromagnetic or an antiferromagnetic spin alignment, depending on the number of electrons in the d shell. With less than five electrons in the d shell the simple theory of super-exchange predicts ferromagnetism, while with five or more d electrons antiferromagnetism is predicted. In terms of perturbation theory, the super-exchange is a higher order interaction than the double exchange. It would therefore be expected to be a weaker interaction than double exchange under similar conditions.

By writing a more complete formula for $Li_xMn_{(1-x)}O$ on the basis of lithium and oxygen having their usual valences of +1 and −2, respectively, *i.e.*, $Li_x^{+1}(Mn^{+2}_{(1-2x)}Mn_x^{+3})O^{-2}$, it can be seen that both Mn^{+2} and Mn^{+3} should be present in this system. If single phase structures are possible in which the Mn^{+2} and Mn^{+3} are randomly distributed over equivalent crystallographic sites, the requirements for double exchange are fulfilled. On this basis one might expect certain compositions of $Li_xMn_{(1-x)}O$ to be both ferromagnetic and good electrical conductors. The assumption that lithium has a plus one valence is easily justified by a consideration of the ionization potentials of the elements involved. Alternative possibilities exist, however, in the case of the valence of oxygen. If this system proved to consist of either manganese oxygen covalences or mononegative oxygen ions the double exchange requirements would not be satisfied and ferromagnetism would not result.

Verwey[4] and others[5-7] have prepared similar systems such as $Li_xNi_{(1-x)}O$, $Li_xCo_{(1-x)}O$ and $Li_xCu_{(1-x)}O$. In these systems the presence of lithium in normal cation sites of the crystal lattice causes the transition metal ions which also occupy normal cation sites, to take on both di- and trivalent oxidation states in the same way as was described for $Li_xMn_{(1-x)}O$. Lithium was chosen by these workers since it has nearly the same size as the transition metal and thus should be easily accommodated in the crystal lattice. It further has a fixed valence which differs from that of the transition metal in the parent oxide, *e.g.*, NiO, and hence requires the transition metal ion to exist in two valence states in compounds such as $Li_xNi_{(1-x)}O$. These compounds have been found to have much lower resistivities than the pure oxide (*i.e.*, 1 ohm cm. for $Li_{0.1}Ni_{0.9}O$ *vs.* 10^8 to 10^{12} ohm cm. for NiO) where the transition metal exists essentially in the divalent state. This behavior is in agreement with the present theories of double exchange. Unfortunately, however, no magnetic data are available on these compounds.

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[1] Work supported in part by Wright Air Development Center, U. S. Air Force.

[2] C. Zener, *Phys. Rev.*, **82**, 403 (1951).

[3] G. H. Jonker and J. H. Van Santen, *Physica*, **16**, 337 (1950).

[4] E. J. W. Verwey, P. W. Haayman, F. C. Romeijn and G. W. van Oosterhout, *Philips Res. Rpt.*, **5**, 173 (1950).

[5] P. J. Fensham, THIS JOURNAL, **76**, 969 (1954).

[6] (a) K. Hauffe and J. Block, *Z. physik. Chem.*, **196**, 438 (1951); (b) K. Hauffe and A. L. Vierke, *ibid.*, **196**, 160 (1950).

[7] H. Hauffe and H. Grunewald, *ibid.*, **198**, 248 (1951).