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Oxygen-18 Isotope Effect in the Reaction of Oxygen with Copper

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The fractionation of oxygen-18 in the reaction of copper with oxygen of natural isotopic composition has been measured over the temperature range 68–256°C. The oxide films (estimated thicknesses varying from 150–2500 A) were removed for O^{18} assay by treatment with hydrogen at 350°C. Using the CO_2 equilibration technique, the O^{18}/O^{16} ratios for the resulting water samples were determined mass spectrometrically and compared with the ratio for a reference sample of water prepared from the original oxygen gas.

The direction of the fractionation indicated that O_2^{16} reacts preferentially compared to $O^{16}O^{18}$. The isotope effect appeared to be independent of the oxygen pressure over the limited range studied (2–25 cm Hg). The magnitude of the fractionation factor was 2.0% at 150°C, with a small negative temperature coefficient. From this it was possible to estimate a value of $\Delta E_{act} = 17$ cal/mole, which may be compared with the calculated isotopic zero-point energy difference of 64 cal/mole. The theoretical implications of the experimental results are discussed.

INTRODUCTION

A GREAT deal of experimental work on the kinetics of the reaction of oxygen with metals has appeared in the literature. A review of the experimental and theoretical aspects of this subject appears in the recent book by Kubaschewski and Hopkins.[1] Tylecote[2] has summarized the voluminous literature on the reaction of oxygen with copper.

Depending upon the extent of oxide film formation and the temperature, it appears that at least three oxidation mechanisms and rate laws apply to the oxidation of copper. In the case of low temperatures and very thin films (less than about 25 A) the logarithmic law is obeyed[3] as predicted from the Mott-Cabrera theory.[4,5] At higher temperatures and for films of intermediate thickness (up to about 10^4 A) the cubic law is observed,[3,6] as discussed by Cabrera.[7] For thicker films the familiar parabolic law describes the kinetics, as explained by the Wagner theory.[8]

It was thought that new and independent information bearing on the mechanism of the reaction of oxygen with metals could be obtained by a study of the oxygen isotope effect. For example, in the thick film region it is generally agreed that the rate-determining step is the diffusion of cuprous ions through the cuprous oxide lattice. At moderate pressures the reaction rate depends only very slightly upon the pressure[9] so that the surface may be considered to be saturated with an adsorbed layer of oxygen. Any O^{18} fractionation which might be observed in the course of the oxidation would then be associated with an isotope exchange equilibrium between gaseous oxygen and adsorbed atomic or molecular oxygen. In the case of adsorbed atoms this exchange would favor the concentration of the light isotope in the adsorbed layer; for adsorbed molecular oxygen the reverse would be expected. A possible rate-limiting step under certain conditions might involve an irreversible process such as the rupture of the $O-O$ bond; for example, the reaction $4e^- + O_2 \rightarrow 2O^=$. Here the effect would be such that O^{16} would tend to be concentrated in the oxide.

Dole and Lane[10] have reported some preliminary results on the fractionation of O^{18} during the chemisorption of oxygen on copper and steel at room temperature. The residual oxygen remaining unreacted after chemisorption was analyzed and found to be depleted in O^{16}, corresponding to a fractionation factor of about 1.05 for copper and 1.025 for steel.

The present report deals with a study of the O^{18} fractionation in the reaction of oxygen with copper for the case of oxide films of intermediate thickness. The method involves removal of the oxide film, measurement of its O^{18}/O^{16} ratio and comparison with the isotope ratio for the gaseous oxygen.

EXPERIMENTAL

Materials

The copper samples were prepared by hydrogen reduction of short lengths of CuO wire, Reagent Grade (General Chemical Company), stated to contain less than 0.01% of impurities. Samples ranging from 1–12 g were used. They were normally contained in small Pyrex boats which were perforated to allow gas circulation.

The oxygen used for most of the experiments was commercial tank oxygen (Bird Gas Division, Liquid Carbonic Corporation) purified by passage through silica gel, ascarite, P_2O_5, and a cold trap at $-78°C$. Mass spectral analysis showed it to contain only nitro-

[1] O. Kubaschewski and B. E. Hopkins, *Oxidation of Metals and Alloys* (Academic Press, Inc., New York, 1953).

[2] R. F. Tylecote, J. Inst. Metals 78, 259 (1950).

[3] T. N. Rhodin, J. Am. Chem. Soc. 72, 5102 (1950).

[4] N. F. Mott, Trans. Faraday Soc. 43, 429 (1947).

[5] N. Cabrera and N. F. Mott, Repts. Progr. Phys. 12, 163 (1948–1949).

[6] W. E. Campbell and U. B. Thomas, Trans. Electrochem. Soc. 91, 623 (1947).

[7] N. Cabrera, Phil. Mag. 40, 175 (1949).

[8] C. Wagner, Z. physik. Chem. B21, 25 (1933).

[9] C. Wagner and K. Grunewald, Z. physik. Chem. B40, 455 (1938).

[10] M. Dole and G. A. Lane, J. Chem. Phys. 22, 949 (1954).

gen and argon (totalling approximately 0.5%). A reference sample of some twenty grams of water was prepared from this oxygen by a nearly stoichiometric reaction with oxygen-free hydrogen at about 1000°C over a platinum gauze catalyst.[11] For certain check experiments oxygen was prepared by the electrolysis of a 40% NaOH solution using nickel electrodes. The electrolytic oxygen was purified by passage through a bubbler tube of 95% H_2SO_4 followed by ascarite, silica gel, and anhydrous $CaSO_4$. Mass spectrometric analysis showed it to be of greater than 99.9% purity.

Hydrogen from a commercial cylinder was purified by passage through a "De-Oxo" catalyst tube (J. T. Baker Chemical Company) followed by ascarite, silica gel, P_2O_5, and a cold trap at $-195°C$.

Carbon dioxide was obtained from two sources: either dry ice or a commercial tank (Matheson "Bone-Dry" grade). After passing through a train containing silica gel and P_2O_5, the gas was subjected to a trap-to-trap distillation from $-78°$ to $-195°C$. The mass spectrum of the resulting CO_2 revealed no significant impurities.

Apparatus, Procedure, and Analytical Method

The experiments were carried out in a conventional high vacuum apparatus. The Pyrex reaction vessel was enclosed in a specially constructed electric furnace provided with transparent Vycor walls, which permitted visual observation of the surface of the copper during the course of its oxidation. The extent of oxidation was monitored by means of a differential oil manometer as well as a mercury manometer. The decrease in oxygen pressure at constant temperature and at essentially constant volume could be related to the oxygen uptake by the copper. In certain experiments the weight increase of the metal sample was measured as a check.

In a typical experiment the copper sample was evacuated to 10^{-4} mm Hg, then heated (while continuously pumping) to the desired temperature, controlled to ±1°C. A calibrated Chromel-Alumel thermocouple was located directly on the outer wall of the reaction vessel to indicate the temperature of the sample. Oxygen was admitted and the rate of oxygen consumption followed manometrically. After reaction for a definite time the excess oxygen was pumped away. Hydrogen was then admitted and the sample was heated to 350°C for approximately 10 minutes (which was found to be sufficient to reduce the oxide quantitatively). The water was distilled (in vacuo) into a special weighing ampoule provided with a stopcock and $ joint. It was thus possible to measure the quantity of water formed in each run. In most of the experiments the water samples ranged from 5–25 mg, which were determined to ±0.1 mg.

The water sample was then distilled into an equilibration[12] tube of about 10 cc volume. A small quantity

of CO_2 was metered out from a standard volume and distilled into the equilibration tube. In order to minimize the correction for isotopic dilution the molar ratio of CO_2 to H_2O was usually kept less than 0.1.

After allowing the $CO_2—H_2O$ equilibration to proceed at room temperature for 2–5 days, the CO_2 was distilled from the equilibration tube at $-78°C$ into a sampling tube at $-195°C$.* In the case of the reference water, large samples (ca 250 mg) were used; since the CO_2/H_2O ratio was of the order of 0.005 no dilution correction was required.

An isotope-ratio mass spectrometer (Nier design) was used to determine the $C^{12}O^{16}O^{18}/C^{12}O_2^{16}$ ratio (m/e 46/44) for CO_2 from the reference water, CO_2 from the "unknown" water sample, and CO_2 from the storage bulb. From these ratios and the known value of the CO_2/H_2O molar ratio the isotopic enrichment may be calculated.

The exact expression for the dilution correction given by Dostrovsky and Klein[13] may be considerably simplified for the "tracer" case to give the following very good approximation:

$$N_0 = \frac{r_e}{K} + \frac{b}{a}(r_e - r_0), \tag{1}$$

where N_0 = atom fraction of O^{18} in "unknown" H_2O before equilibration; r_0 = 46/44 ratio for initial CO_2 (storage bulb), r_e = 46/44 ratio for equilibrated CO_2; b/a is the molar ratio, $(CO_2)/(H_2O)$; K is the isotope exchange equilibrium constant = 2.08 at room temperature.[12]

To establish confidence in the O^{18} analytical technique several samples of O^{18}—enriched water (Stuart Oxygen Company, stated to contain 1.4% O^{18}) were assayed and compared with distilled tap water. Normalizing these values, assuming 0.200% O^{18} in distilled H_2O, three independent determinations gave 1.42, 1.44, and 1.42% O^{18} for the enriched water.

The separation factor in the reaction of oxygen with copper is defined:

$$S = \frac{[(O^{18})/(O^{16})]_{\text{oxide film}}}{[(O^{18})/(O^{16})]_{\text{oxygen gas}}}. \tag{2}$$

Because of the negligible dilution correction for the reference water, Eq. (2) becomes:

$$S = \frac{\dfrac{r_m}{K} + \dfrac{b}{a}(r_m - r_0)}{\dfrac{r_g}{K}}, \tag{3}$$

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* At the suggestion of a referee, certain check experiments were performed which indicated that when tank CO_2 was equilibrated with distilled tap water and separated using the procedure described, the O^{18}/O^{16} ratio of the CO_2 showed an increase of about 1%. This effect introduces only a very slight error in the calculated fractionation factors, which involve essentially the *ratio* of the O^{18}/O^{16} ratios for CO_2 equilibrated with the unknown water sample compared to CO_2 equilibrated with the reference water sample.

[11] Anderson, Halford, and Bates, J. Chem. Phys. 2, 342 (1934).
[12] M. Cohn and H. C. Urey, J. Am. Chem. Soc. 60, 679 (1938); J. P. Hunt and H. Taube, J. Chem. Phys. 19, 602 (1951).
[13] I. Dostrovsky and F. S. Klein, Anal. Chem. 24, 414 (1952).

where $r_m=46/44$ ratio for CO_2 after equilibration with "unknown" water from the metal oxide, and $r_g=46/44$ ratio for CO_2 after equilibration with reference water prepared from oxygen gas. Defining the O^{16} enrichment

$$\epsilon \equiv 1-S, \qquad (4)$$

one obtains the expression:

$$\epsilon = \frac{r_g-r_m}{r_g} - 2.08\frac{b}{a}\frac{(r_m-r_0)}{r_g}. \qquad (5)$$

Equation (5) was used in all cases to calculate the enrichment factor from the four measured quantities r_g, r_m, r_0, and b/a.

In the course of this work a large number of intercomparisons of various isotope ratios were obtained; some of these results are summarized here. All values are normalized to the reference oxygen as standard.

A. Percentage difference, based on 46/44 ratios, corrected for CO_2 dilution effect.
    1. Reference H₂O from standard O₂   0.00 (assumed)
    2. Distilled tap water   −2.2±0.2

B. Percentage difference, based on 34/32 ratios.
    1. Reference O₂ (purified; tank No. 1)   0.00 (assumed)
    2. O₂ (tank No. 2, Matheson)   0.00±0.05
    3. O₂ (purified; tank No. 3, Bird)   0.00±0.05
    4. O₂, electrolytic (av of 4 analyses   −3.9±0.15
       for 4 different batches)

From the results of B 1, 2, and 3 it appears that there is no appreciable isotopic difference among the different tanks of oxygen. Experiments have also shown that the 34/32 ratios for tank oxygen and atmospheric oxygen differ by less than 0.2%. Thus the result A 2 is a measure of the so-called Dole effect,[14] i.e., the anomalous difference of 2.5% in the O^{18} ratio for atmospheric oxygen compared with oxygen from lake water.†

The O^{18} depletion of the electrolytic oxygen (B 4) was somewhat greater than anticipated. On the basis of the electrolytic fractionation, about 1%,[15] and the Dole effect, above, one would estimate a maximum depletion of about 3.5%, compared with the observed value of 3.9±0.15%. This difference may not be serious, however, in view of the large range of values reported for the electrolytic fractionation factor, from 1.008 to 1.035,[16] and its corresponding uncertainty.

The electrolytic oxygen served an important function in checking the direction and magnitude of the isotope effect in the oxygen-copper reaction, as it was initially depleted in O^{18} far below the level of either atmospheric

[14] M. Dole, J. Am. Chem. Soc. 57, 2731 (1935); Chem. Revs. 51, 263 (1952).

† Note added in proof.—2.2±0.2% is outside the range of values commonly reported for the Dole effect (2.5–2.8%), suggesting that fractionation might have occurred in the preparation of the reference water. If so, all fractionation factors, α, would be low by 0.3–0.6%. Experiments to check this point are now in progress.

[15] H. L. Johnston, J. Am. Chem. Soc. 57, 484 (1935); Selwood, Taylor, Hipple, and Bleakney, ibid. 57, 642 (1935); M. Dole, J. Chem. Phys. 4, 268 (1936).

[16] I. Kirshenbaum, Physical Properties and Analysis of Heavy Water (McGraw-Hill Company, Inc., New York, 1951), p. 243.

oxygen, water, or ordinary carbon dioxide. Thus any leak or contamination would tend to increase the O^{18}/O^{16} ratio. Since in the reaction with copper the O^{16} was found to concentrate in the oxide, the water obtained from the oxide should be further depleted in O^{18}. Experiments with the electrolytic oxygen therefore constituted a severe test of the validity of the experimental procedures.

The enrichments calculated according to Eq. (5) require small corrections to bring all data to the common basis of infinitesimal extent of reaction. The fraction of substrate (oxygen) consumed, represented by $f=\Delta P_t/P_0$, (where $P_0=$ initial oxygen pressure and $\Delta P_t=$ total pressure decrement in the course of the reaction) was usually less than 0.1. The standard logarithmic correction formula was employed.[17] For $f<0.1$ it was convenient to use the simplified formula:

$$\epsilon_0 = \epsilon(1+f/2). \qquad (6)$$

The corrected fractionation factor, α, is then defined:

$$\alpha \equiv 1+\epsilon_0. \qquad (7)$$

RESULTS

Certain preliminary experiments were carried out at 337° and 377°C using copper foil of known geometrical area. The total amount of oxygen reacted was, however, insufficient for isotopic analysis (for which a minimum of 3 mg of water is desirable), due to the small area of the sample. The oxidation followed the parabolic law after the first few minutes and the rate constants agreed (within a factor of 2) with the values calculated using the constants of the Arrhenius equation given in reference 1, p. 163. Other experiments with the high surface area copper wire over the temperature range 303–387°C also followed the parabolic equation. From these data it was possible to estimate the extent of available surface and thus the specific surface area, which was found to be about 500 cm²/g. Due to the difficulty in reproducibly reducing and annealing the specimens it was not possible to replicate the rate constants to better than a factor of 2. This difficulty was first pointed out by Dunn[18] in connection with his studies with active copper prepared by reduction of the oxide. It is possible therefore that the specific surface area varied from run to run by as much as a factor of two. However, assuming a constant value of 500 cm²/g, the estimated oxide film thickness corresponding to a given weight of oxygen reacted was calculated, using the method of Vernon.[19] Clearly these values are only indicative of the order of magnitude of the film thickness for any given run. Table I summarizes the reaction conditions and gross observations for all the experiments for which valid isotopic assays were carried out.

[17] W. G. Henderson, Jr., and R. B. Bernstein, J. Am. Chem. Soc. 76, 5344 (1954); Friedman, Bernstein, and Gunning, J. Chem. Phys. 23, 111 (1955).

[18] J. S. Dunn, Proc. Roy. Soc. (London) A111, 210 (1926).

[19] W. H. Vernon, J. Chem. Soc. 1926, 2273.

TABLE I. Summary of reaction data.

Run no.	Temp. (°C)	Oxygen pressure P_0 (cm Hg)	Wt. Cu (g)	Wt.[a] of O_2 reacted (mg)	Time (min)	Est.[b] oxide thick-ness (A)	Final appearance of oxide surface
11	203	18.0	2.185	13.0	55	1400	Black
12	201	1.9	2.185	11.4	110	1200	Black
13	155	16.3	2.185	3.4	355	360	Brown-black
14	155	4.6	2.185	3.35	400	360	Dark brown
15	256	2.9	2.185	7.0	12	750	Black
16	254	12.7	2.185	8.45	12	900	Black
17	183	9.8	2.185	6.6	240	700	Brown-black
18	133	21.5	11.485	15.2	69	400	Brown
19	100	20.5	11.485	12.8	80	330	Dark red-brown
20	100	23.2	11.485	12.7	35	330	Dark red-brown
21	99	10.3	11.485	9.8	40	260	Red-brown
22	77	18.7	11.485	9.2	175	240	Orange-red
23	135	16.2	11.485	23.8	90	620	Black
24	68	19.2	11.485	9.6	830	250	Red-brown
25	70	14.4	11.485	5.7	1300	150	Orange
26	120	12.8	11.485	9.7	25	250	Red-brown
27[c]	112	12.6	11.485	8.8	75	230	Brown-black
28[c]	128	10.5	11.485	8.8	60	230	Brown-black
30	229	8.3	1.671	13.8	7.5	2500	Black

[a] Weight of O_2 calculated from weight of H_2O recovered upon hydrogenation.
[b] Assuming a constant specific surface area of 500 cm²/g for the copper.
[c] Electrolytic oxygen used.

The appearance of the specimen may possibly give some indication of the extent of cupric oxide formation. It is of interest to note that Dighton and Miley[20] were able to measure the effective contribution of each of the oxides, Cu_2O and CuO, to the total film thickness. For one particular film formed at 180°C the ratio Cu_2O to CuO was 770 A/48 A = 16.0; for one produced at 221°C the same ratio was 2000/122 = 16.4. Even in the worst case of a film produced at 277°C the ratio was 5983/1016 = 5.9; it is believed therefore that in the present work the films consisted primarily of cuprous oxide even though the dark appearance of cupric oxide was observed for several of the thicker films.

For most of the experiments, carried out at temperatures below 250°C, the oxidation curves were not parabolic. Log-log plots showed that many of the curves followed the cubic law approximately. It appeared that the condition of the sample, affected by the treatment during a given run, seriously influenced the course of the oxidation in the subsequent run. Evans[21] has discussed the influence of physical factors upon the rate laws; such behavior for the irregular porous samples used is not unexpected.

The procedure for the measurement of the isotopic fractionation has been outlined in the previous section. Table II summarizes the O^{18} fractionation data. Examination of the data revealed no systematic dependence of α upon the pressure over the range of pressures investigated. All points were therefore plotted on the same graph in Fig. 1, which shows the dependence of α upon the reciprocal of the absolute temperature. The solid line represents the least-squares fit to the data. The

[20] A. L. Dighton and H. A. Miley, Trans. Electrochem. Soc. 81, 321 (1942).
[21] U. R. Evans, Trans. Electrochem. Soc. 91, 547 (1947).

fractionation factors for experiments performed with the electrolytic oxygen, of low O^{18} content, are seen to agree quite well with the rest of the results.

The average deviation of all the points from the line is ±0.0020, which is slightly greater than that anticipated on the basis of the analytical imprecision. The dotted line in Fig. 1 has been drawn through the data to extrapolate to an α of unity at $1/T=0$. The slope is 8.5 deg^{-1}, corresponding to an apparent activation energy of 17 cal/mole. The average deviation of the points with respect to this line is ±0.0022. Both lines pass through the point $\alpha = 1.020$ at 150°C.

Four additional experiments were carried out at considerably higher temperatures (300–400°C), where quite thick films were formed in very short times (<2 min). Because of the extremely high rate of oxygen consumption and the inadequacy of mixing in the reaction chamber the local oxygen isotopic composition in the region of the metal was probably not maintained that of the bulk of the oxygen supply. These results are therefore of very doubtful validity. The enrichment values obtained under these conditions were less than the experimental uncertainty of ±0.2%. It is planned to do further work in the high temperature region with a modified apparatus.

Several auxiliary isotope exchange experiments were performed, in which it was found that there was negligible O^{18} exchange between gaseous oxygen and bulk cupric oxide (wire) at 400°C (in agreement with the results of Allen and Lauder.[22]) Winter and co-workers[23] also showed, for a variety of metal oxides, that after the exchange of the first few surface layers of oxide the rate becomes extremely slow. Winter[24] also investigated the exchange of oxygen-18 with the growing

TABLE II. Summary of O^{18} fractionation data.

Run No.	T (°C)	f	ϵ	α
24	68	0.042	0.0197	1.0201
25	70	0.036	0.0231	1.0235
22	77	0.036	0.0198	1.0202
21	99	0.061	0.0237	1.0244
19	100	0.046	0.0215	1.0220
20	100	0.034	0.0220	1.0224
27*	112	0.055	0.0188	1.0193
26	120	0.059	0.0185	1.0190
28*	128	0.063	0.0179	1.0185
18	133	0.048	0.0190	1.0195
23	135	0.129	0.0208	1.0221
13	155	0.040	0.0249	1.0254
14	155	0.054	0.0174	1.0179
17	183	0.063	0.0225	1.0232
12	201	0.40	0.0169	1.0217
11	203	0.066	0.0185	1.0191
30	229	0.11	0.0155	1.0163
16	254	0.061	0.0152	1.0157
15	256	0.24	0.0154	1.0176

* Electrolytic oxygen used.

[22] J. A. Allen and I. Lauder, Nature 164, 142 (1949).
[23] G. Houghton and E. R. Winter, Nature 164, 1130 (1949); E. R. Winter, J. Chem. Soc. 1950, 1170.
[24] E. R. Winter, J. Chem. Soc. 1954, 3342.

FIG. 1. Temperature dependence of the O^{18} fractionation factor in the reaction of oxygen with copper. ○ Purified tank oxygen. ● Electrolytic oxygen. ———— Least-squares line through data. — — — — Line extrapolating to $\alpha=1$ at $1/T=0$.
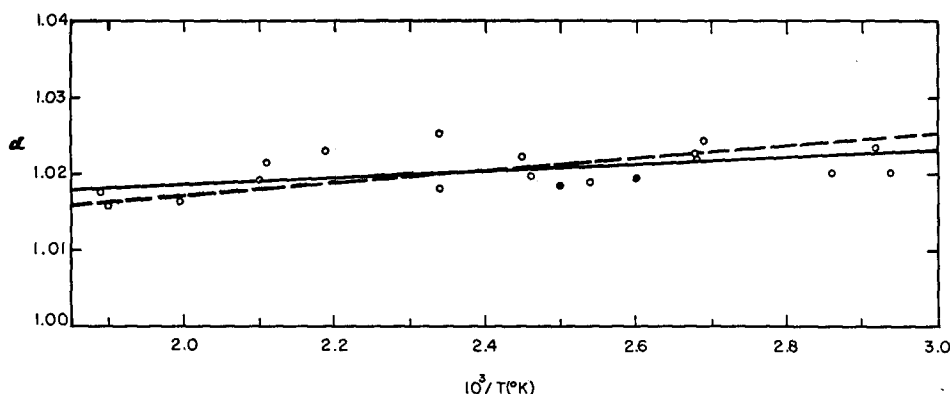
cuprous oxide film on copper at 50–110°C and pressures of 3 cm and found negligible exchange.

DISCUSSION

It is of interest to compare the fractionation factors obtained in the present investigation with the results of Dole and Lane[10] for the chemisorption of oxygen on copper at room temperature. Extrapolation of the dotted line of Fig. 1 to 25°C gives as an upper limit the value $\alpha=1.029$, which is significantly lower than the fractionation factor of 1.05 found by these authors.[25] The mechanism of the low temperature, very thin film chemisorption reaction is, of course, thought to be quite different than that associated with the formation of the films of intermediate thickness at elevated temperatures. Rhodin[3] was able to demonstrate for copper the transition at 80°C from the thin film (low temperature), logarithmic law to the intermediate thickness, cubic law of oxidation.

Any satisfactory explanation of the O^{18} fractionation data should therefore account for the following qualitative observations:

(1) The direction of the fractionation is such that O^{16} tends to concentrate in the oxide film.

(2) The fractionation factor appears to be essentially independent of pressure (for pressures exceeding a few cm Hg).

(3) The fractionation factor appears to be independent of the extent of oxide film formation in the intermediate thickness range (150–2500 A).

(4) The isotope effect for the chemisorption reaction is apparently larger than that associated with the formation of films of intermediate thickness.

Cuprous oxide is known to be a metal-deficit semiconductor. The oxidation theory of Cabrera and Mott[5] applied to the intermediate film thickness region makes use of the assumption that the cation transport (and thus the oxidation rate) is proportional to the number of cation vacancies/cm³, n_i, and the strength of the electrostatic field, F, established by the oxygen ions
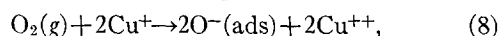
located at the oxide-oxygen interface. The field strength is, of course, V/X, where X is the oxide film thickness and V is the electrostatic potential set up across the oxide film; V is assumed independent of X. It is further hypothesized that the density of cation vacancies is proportional to the surface density of oxygen ions, N, which in turn is proportional to the field strength. Thus the oxidation rate, dX/dt, is found to be proportional to F^2 and is thus inversely proportional to X^2, in accord with the cubic law of oxidation. Here the rate should be independent of the oxygen pressure provided the surface is saturated with adsorbed oxygen.

According to this picture the isotopic composition of the oxide film would be identical with that of the surface layer of oxide ions. Any observed fractionation of O^{18} in the oxide would therefore reflect the fractionation associated with one of the possible steps in the establishment of the $O^=$ layer:

(1) $O_2(g) \rightleftharpoons O_2(\text{ads})$

(2) $O_2(\text{ads}) \rightleftharpoons 2O(\text{ads})$

(3) $O_2(\text{ads}) + 4e^- \rightarrow 2O^=$

(4) $O(\text{ads}) + 2e^- \rightarrow O^=.$

Since little or no isotopic fractionation would be associated with steps (1)‡ and (4) (the O–O bond is not ruptured), attention will be primarily centered on (2) and (3).

Winter's[24] results, which indicated no exchange between $O_2(g)$ and the growing film of cuprous oxide, suggest strongly that steps 3 and/or 4 are essentially irreversible (as indicated). His additional observation that the exchange reaction $O_2^{16}+O_2^{18} \rightleftharpoons 2O^{16}O^{18}$ does not occur in the course of the oxidation implies that the dissociative adsorption of oxygen on cuprous oxide under the conditions of his experiments is an irreversible process. Winter concurs with the mechanism of Garner et al.[26] and writes the slow step:

$$O_2(g)+2Cu^+ \rightarrow 2O^-(\text{ads})+2Cu^{++}, \qquad (8)$$

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[25] M. Dole, private communication, in which a more recent corrected value of α is given for the reaction of oxygen with copper at room temperature.

‡ For the equilibrium between gaseous and adsorbed O_2 molecules one anticipates a slight ($<0.3\%$) O^{18} enrichment in the adsorbed layer (based on the analogy with isotopic vapor pressure ratios).

[26] Garner, Stone, and Tiley, Proc. Roy Soc. (London) A211, 472 (1952).

followed by rapid changes including the gain of an electron by O^-, etc. Unfortunately this appears to be incompatible with the Cabrera-Mott concept of a quasi-equilibrium involving adsorbed atomic oxygen and oxygen ions, which is essential to the derivation of the cubic law of oxidation. Actually, this may be explained if one notes that the actual rate law observed by Winter (using very finely divided copper powder) was of the exponential type, $p/p_0 = \exp(-kt)$, rather than cubic. This kinetic behavior was first noted by Wilkins and Rideal,[27] at pressures below about 1 cm. Experiments of Garner et al.[26,28] with finely divided cuprous oxide powder showed that the rate of adsorption of oxygen (at low pressures) was proportional to the oxygen pressure. Thus the mechanism of Winter is self-consistent, but may not be relevant for the case of the usual cubic law oxidations carried out at moderate pressures.

Considering first the situation corresponding to the mechanism of Winter it is of interest to estimate the magnitude of the isotope effect for reaction of Eq. (8). Using the theory of Bigeleisen[29] the ratio of the isotopic rate constants for O_2^{16} and $O^{16}O^{18}$ would be

$$\alpha = \frac{k}{k^*} = \left(\frac{m^*}{m}\right)^{\frac{1}{2}} (1+\delta),$$

where

$$\delta = \sum G(u)\Delta u - \sum G(u^{\ddagger})\Delta u^{\ddagger},$$

m^*/m is the Slater[30] reduced mass ratio and the other quantities have their usual significance. The lower limit of α (corresponding to $T \rightarrow \infty$) is thus the Slater factor, calculated to be 1.029. The upper limit, calculated in the usual way for the case of the free atom activated complex is $\alpha = 1.080$ at 150°C. Since the observed fractionation at 150° lies well below the lower limit, this mechanism would seem to be eliminated. It should be noted however, that the high value of α obtained by Dole[25] may well be associated with this type of mechanism.

Next consider the fractionation associated with the isotopic exchange equilibrium between gaseous oxygen molecules and adsorbed oxygen atoms. The upper limit for the fractionation factor may be readily calculated from an examination of the case of equilibrium between gaseous oxygen molecules and free atoms:
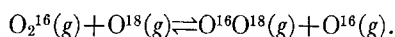
$$O_2^{16}(g) + O^{18}(g) \rightleftharpoons O^{16}O^{18}(g) + O^{16}(g).$$

The method of calculation is given by Bigeleisen and Mayer[31] and Urey.[32] Assuming $\nu(O^{16}-O^{16}) = 1580$ cm^{-1} and $\Delta\nu = 45$ cm^{-1} one obtains the value $\alpha = 1.050$ at 150°C. This result is consistent with the value of the appropriate partition function ratio (Q_2/Q_1) listed in Table X of reference 32. It may be of interest to compare the apparent activation energy for the fractionation factor, 17 cal/mole, with the theoretical upper limit as given by the isotopic zero point energy difference (for O_2^{16} and $O^{16}O^{18}$) of 64 cal/mole.

For the adsorption-exchange reaction:

$$O_2^{16}(g) + O^{18} - S \rightleftharpoons O^{16}O^{18}(g) + O^{16} - S,$$
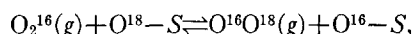
(where S represents an adsorption site), it is not possible to calculate the fractionation factor without some assumption as to the $O^{16}-S$ force constant or vibration frequency. However, by inverting the procedure, it is possible to estimate the frequency which would be required to account for the observed value of $\alpha = 1.020 \pm 0.002$ at 150°C. This was done, first, by assuming the ratio $\Delta\nu/\nu = 0.029$ (equivalent to an effective mass $m_s = 16$ awu). This gives a value for $\nu(O^{16}-S)$ of 1150 ± 50 cm^{-1}. The other extreme case, assuming $\Delta\nu/\nu = 0.061$ (equivalent to an effective mass $m_s = \infty$) gives the result $\nu(O^{16}-S) = 780 \pm 25$ cm^{-1}. The actual frequency would then be expected to lie within the range 780–1150 cm^{-1}, which does not seem implausible.

It is therefore suggested on the basis of the present results that the mechanism of the O^{18} fractionation observed in the oxidation of copper (under the conditions of these experiments) involves the isotopic exchange equilibrium between gaseous oxygen molecules and chemisorbed oxygen atoms§ which favors the concentration of O^{16} in the adsorbed layer. Then, in accord with the assumptions inherent in the Cabrera-Mott theory, it is expected that the isotopic composition of the oxide will be the same as that of the adsorbed layer. This interpretation appears to be consistent with the present observations.

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§ It should be pointed out that this exchange mechanism is not supported by the (low-pressure) experiments of Winter,[24] as previously discussed.