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Dissociation Pressures of Various Metallic Oxides

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Gases evolved during a vacuum heat treatment of various oxides were analyzed by means of an omegatron mass spectrometer. Carbon dioxide, carbon monoxide and water were detected as main gases evolved at lower temperatures. Oxygen due to thermal dissociation of ZnO, CdO, NiO, CuO, Cu_2O, and WO_3 was found at high temperatures. In the case of MoO_3, however, evolution of oxygen was not observed. The equilibrium pressures of the evolved gases over these oxides have been measured with a McLeod gauge and a Knudsen gauge. The oxygen dissociation pressures of ZnO, CdO, NiO, CuO, and Cu_2O were measured and compared with the calculated values.

The properties of metallic oxides were studied by many investigators from the various points of view. Especially, the semiconductivity of these oxides has been studied in relation to catalytic activities. However, the catalytic activity and the electrical conductivity of an oxide depend on the method of preparation and pretreatment.

In the case of *n*-type oxides (*e.g.*, ZnO, CdO, *etc.*), it is well known that the activity and conductivity are enhanced through a vacuum heat treatment. These effects may be attributed to the loss of oxygen from the stoichiometric composition. Baumbach and Wagner[1] found that the electrical conductivity of the oxides which were reduced by hydrogen or carbon monoxide depends on the equilibrium pressure of oxygen, and said that this is due to thermal dissociation accompanied with oxygen evolution represented by the following formula;

$$Zn^{2+}O^{2-} \rightleftarrows \frac{1}{2}O_2(g) + Zn^{+}(o) + e. \qquad (1)$$

However, thermal dissociation pressures of oxygen of these oxides are uncertain and few reports[2] have described the reason why non-stoichiometric oxides are produced at temperatures lower than their thermal decomposition temperatures.

Recently one of the present authors (I. K.)[3] pointed out that the loss of oxygen may be due to the reduction by impurity carbon contained in oxides, and in dirty vacuum the oxides may also be reduced by residual vapors of hydrocarbons. In the present work, we tried to obtain quantitative data about the dissociation pressures of oxygen of various oxides and to study the mechanism of dissociation.

The evolved gases during the heat treatment in vacuum were analyzed by an omegatron mass spectrometer. Up to the present, most of the investigators measured only the total pressure of the evolved gases, but it is very important to identify the gaseous species. In the present experiment, we found that carbon dioxide, carbon monoxide, and water were the main species evolved at lower temperatures, and that oxygen due to thermal dissociation of oxides such as ZnO, CdO, NiO, CuO, Cu_2O, and WO_3 was observed at higher temperatures.

Experimental

Figure 1 shows a schematic diagram of the apparatus, which is composed of two parts. Main part is made up of a decomposition cell made of fused quartz, and total pressure gauges. An omegatron mass spectrometer is in the other part. These parts are connected by a variable leak valve. The vacuum lines were constructed of molybdenum glass, and a copper sealed metal valve was used to cut off the main part from a pumping system. The apparatus was bakable at 450°C and its ultimate vacuum was 5×10^{-9} Torr. With liquid nitrogen traps no hydrocarbon was found in residual gases.

As a total pressure gauge a Knudsen gauge or a McLeod gauge was used. The Knudsen gauge of Klumb-Schwarz type was made in our laboratory[4] and calibrated with the McLeod gauge.

The omegatron tube, a modified simple box type with a rhenium electron emitter filament, was made by Mitsubishi Electronic Company. A large permanent magnet of about 4500 gauss with poles of 60 mm diameters and 35 mm gap was used. The resonance ion current of the omegatron was measured by a Takeda TR-84H vibrating reed electrometer. By combining these parts the following performance of the omegatron was obtained;

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1) H. H. v. Baumbach and C. Wagner, *Z. physik. Chem.*, **B22**, 199 (1933).

2) B. Arghiropoulos, J. Elston, P. Hilaire, F. Juillet and S. T. Teichner, Proc. 4th International Symposium on Reactivity of Solids, 525 (1960); K. Torkar and F. Mostad, *Monatschrift der Chemie*, **93**, 657 (1962).

3) M. Onchi and I. Kusunoki, *Nippon Kadaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **85**, 612, 617 (1964).

4) M. Onchi, K. Tominaga and N. Sasaki, *J. Vac. Soc. Japan*, **2**, 112 (1959); M. Onchi, Trans. 8th Natl. Vac. Symp. (1962, ed. L. E. Preuss, Pergamon Press), p. 544.

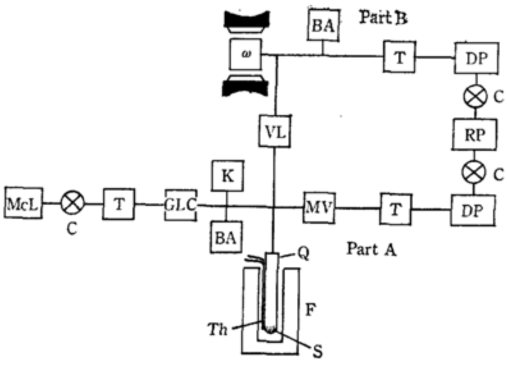

Fig. 1. Schematic diagram of the apparatus. (ω), omegatron; (BA), Bayard-Alpert gauge; (T), liquid nitrogen trap; (DP), oil diffusion pump; (RT), rotary pump; (VL), variable leak valve; (MV), metal valve; (K), Knudsen gauge; (GLC), greaseless cock; (McL), McLeod gauge, (C), cock; (Q), decomposition fused quartz cell; (Th), thermocouple; (F), furnace; (S), sample powder.

mass range: 1—500 a.m.u.,
resolution: 60 at $M/e = 60$,
measurable pressure range:
8×10^{-5}—5×10^{-10} Torr.

Samples of oxides were of extra pure grade and were used without further purification. In the decomposition cell 1 mmol of a powdered sample was placed and evacuated for a day in high vacuum at room temperature. After this treatment the main part of the apparatus, the volume of which is about 1 *l*, was cut off from the pump by the metal valve and the sample was heated in a furnace. The temperature was measured by a chromel-alumel thermocouple.

The total pressure of the evolved gases was measured by the McLeod gauge or the Knudsen gauge at regular intervals. Usually, after about a few hours it attained a stationary value. Then, the gas was introduced into the omegatron through the variable leak valve and analyzed. After the measurement, the apparatus was evacuated and the same procedure was repeated from room temperature up to 1200°C. The oxygen partial pressure evaluated from the omegatron measurement was taken to be the decomposition pressure of the oxide at the corresponding temperature. Confirmation of the equilibrium by varying the pressure or the temperature a little was not undertaken, because it would take unpractically long time for one run.

The oxide once heated to the highest temperature was cooled in vacuum and again the same procedure was repeated. In this second procedure, evolution of gases other than oxygen was reduced extremely, but the pressure of oxygen at the corresponding temperature was identical within the experimental error. This suggests that the equilibrium was not disturbed by the presence of the other gases.

Result and Discussion

Evolution of Carbon Monoxide and Carbon Dioxide.[3] All metallic oxides evolve large amount of carbon monoxide and carbon dioxide between 200 and 800°C. The gases adsorbed or combined with the oxides might constitute some fractions of the evolved gases. However, the main part of them seems to be produced by the reduction of metallic oxides by impurity carbon in them or by adsorbed or residual hydrocarbons on the oxide surface or in vacuum system, because the color and electrical conductivity of these oxides changed with carbon dioxide evolution. For example, the color of tungsten trioxide and molybdenum trioxide changed to dark gray after evolution of these gases. In our experiment performed in " hydrocarbon free " system, no hydrocarbon peak was observed in the spectra at any temperature. Therefore, the reduction by impurity carbon seemed to be more important than that by adsorbed or residual hydrocarbons, and the origin of non-stoichiometry of the metallic oxides should be attributed to the existence of some impurity carbon.

The Dissociation Pressure of Zinc Oxide. Mass spectra of evolved gases from zinc oxide at 600°C and 890°C are shown in Fig. 2. Above 750°C oxygen due to thermal decomposition begins to be observed. An example of the total equilibrium pressure of the evolved gases and its component is shown in relation to the temperature in Fig. 3. Above 900°C oxygen gas was a main component. In Fig. 4 the equilibrium pressures of oxygen are plotted

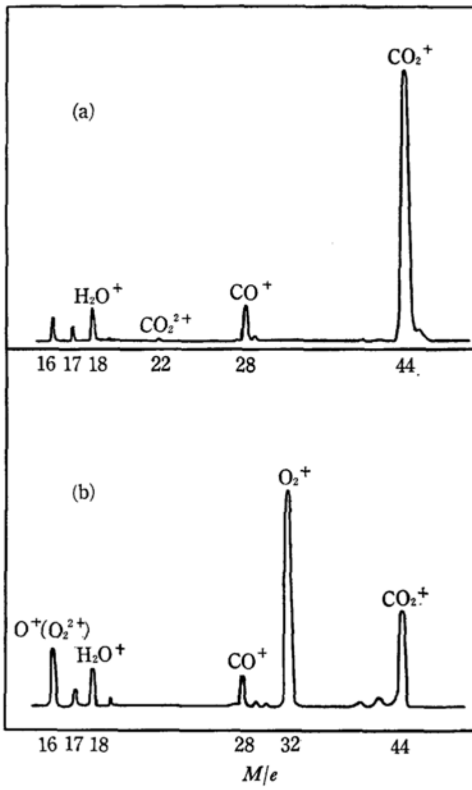

Fig. 2. Mass spectra of gases evolved from zinc oxide. (a) 600°C, (b) 890°C

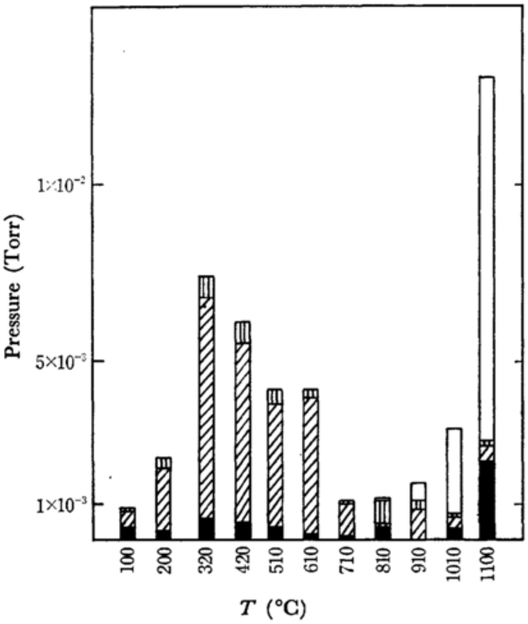

Fig. 3. Partial pressures of gases evolved from zinc oxide *versus* temperature.
☐, oxygen; ▥, carbon monoxide; ▨, carbon dioxide; ■, water

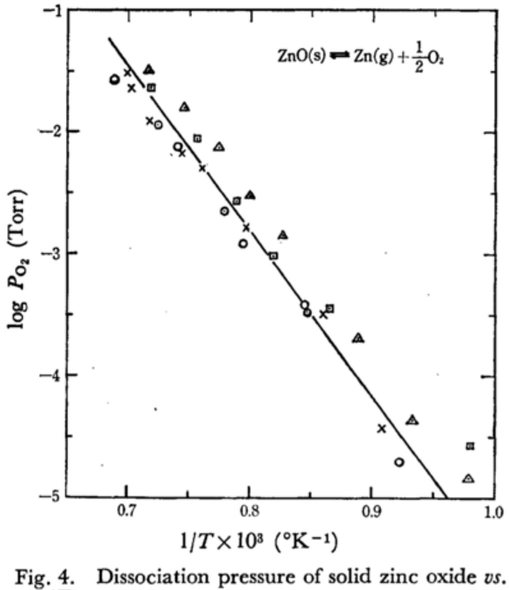

Fig. 4. Dissociation pressure of solid zinc oxide *vs.* $1/T$.
The values of different symbols show different runs.

against the reciprocal of the absolute temperatures. Then a good straight line, though the values by each run showed a little deviation from the line, was obtained. Over the range of 750—1200°C, the line is represented by the following equation;

$$\log P_{O_2}(\mathrm{Torr}) = -\frac{13500}{T} + 8.01 \qquad (2)$$

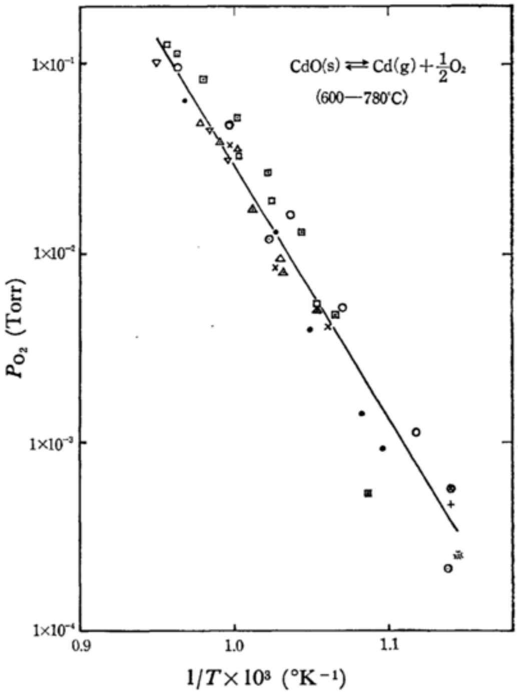

Fig. 5. Dissociation pressure of solid cadmium oxide *vs.* $1/T$.

If the following equilibrium is established at high temperature,

$$\mathrm{ZnO(s)} \rightleftarrows \mathrm{Zn(g)} + \frac{1}{2}\mathrm{O_2}, \qquad (3)$$

the equilibrium constant ($K_p = P_{Zn}\cdot P_{O_2}{}^{1/2} \simeq 2P_{O_2}$) is represented by the relation;

$$\log K_p(\mathrm{atm}^{3/2}) = -\frac{20250}{T} + 8.00, \qquad (4)$$

hence the value of standard free energy change, ΔG°, for the reaction, $\mathrm{ZnO(s)} \rightleftarrows \mathrm{Zn(g)} + \frac{1}{2}\mathrm{O_2}$, is given by;

$$\Delta G^\circ(\mathrm{cal}) = 92664 - 36.65T. \qquad (5)$$

On the other hand, the values of ΔG° for this reaction, which are obtained by combining the known values for other reactions, are as follows;

$$\Delta G^\circ(\mathrm{cal}) = 112170 - 49.03T \qquad (6)^{5)}$$

or; $$\Delta G^\circ(\mathrm{cal}) = 114640 - 51.65T. \qquad (7)^{6)}$$

The difference of these values are not so large in the temperature range of measurement.

This result conflicts with Seeco's report[7] that an equilibrium constant for the dissociation of solid zinc

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[5] E. C. Truesdale and R. K. Waring, *J. Am. Chem. Soc.*, **63**, 1610 (1961).

[6] J. A. Kitchener and S. Ignatowicz, *Trans. Faraday Soc.*, **47**, 1278 (1951).

[7] E. A. Seeco, *Can. J. Chem.*, **38**, 596 (1960).

oxide into the gaseous elements was greater than that calculated from Eq. (6) by a factor of 10^8. One possible reason of this discrepancy might be due to the existence of other gases than oxygen. Because no instrument such as mass spectrometer to identify gaseous species was used in Seeco's experiment, it is not unreasonable to suppose that Seeco considered all the evolved gases as oxygen and overestimated its pressure.

The Dissociation Pressure of Cadmium Oxide. At lower temperatures (20—500°C) main components of the evolved gases were carbon dioxide, carbon monoxide, and water. The oxygen gas due to thermal decomposition was found above 500°C. In Fig. 5 the measured equilibrium pressures of oxygen are plotted against $1/T$. The straight line obtained can be represented by the following equation;

$$\log P_{O_2}\,(\text{Torr}) = -\frac{13800}{T} + 11.6 \qquad (8)$$

The pressure of oxygen is about twenty times as large as those of the other author's,[8] which were obtained by flow methods or calculated from thermodynamical data. This discrepancy may be attributable to the inhomogeneity of temperature in the experimental system. That is, as the cadmium has larger vapor pressure compared to other metals its vapor was condenced at the cold part of the apparatus and removed quickly from the dissociation cell before the equilibrium of $CdO(s) \rightleftarrows Cd(g) + \frac{1}{2}O_2$ was attained.

The Dissociation Pressure of Nickel Oxide. Nickel oxide is one of the important p-type oxide-semiconductor. However, there are few reports[9] published about the thermal decomposition. Johnson and Marshall obtained a vapor pressure equation of nickel oxide by measuring the rate of vaporization from a metallic nickel ring slightly oxidized its surface to nickel oxide. The value for the vapor pressure of nickel oxide is somewhat larger than the calculated dissociation pressure of nickel oxide. Therefore, they concluded that the dissociation of solid nickel oxide was negligible between 1438 and 1566°K. On the other hand, Brewer and Mastick[10] criticized Johnson and Marshall's conclusion, and concluded that vaporization by dissociation is the major process in case of nickel oxide.

In the present experiment, oxygen gas produced by thermal decomposition was identified with the omegatron and the formation of thick nickel deposit was observed on the wall of the colder part of the cell. A thin film of nickel oxide was also observed at the part of higher temperature. This might be explained by oxidation of the deposited metal film, *i.e.*, the same phenomenon observed in case of zinc oxide.[11] In Fig. 6 the dissociation pressure are plotted against $1/T$. When an untreated sample was examined, abnormally large pressures of dissociation with a maximum was observed, shown as curve A. On the contrary, the sample which was treated in vacuum at 1100°C for a few hours gave normal dissociation pressures, shown as curve B. Curves C and D were obtained from the samples with longer heat treatment in vacuum at 1100°C (for about 40 hr). The following equation for the dissociation pressure is obtained from the curve C;

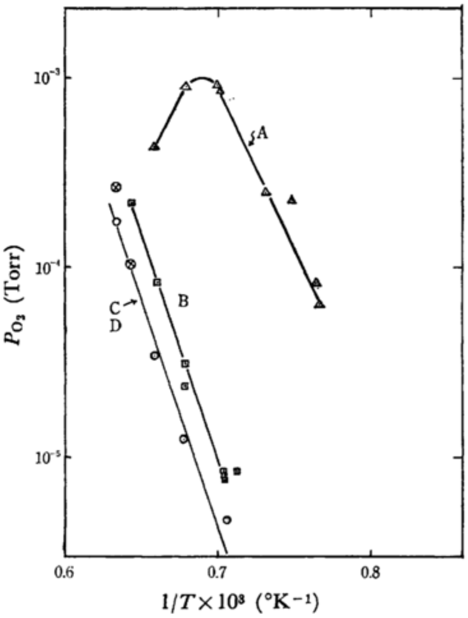

Fig. 6. Dissociation pressure of nickel oxide *vs.* $1/T$.
Curve A, from an untreated sample;
Curve B, C, D, from a vacuum-heat-treated sample.

$$\log P_{O_2}\,(\text{Torr}) = -\frac{23810}{T} + 11.33. \qquad (9)$$

Two processes of the dissociation of nickel oxide can be assumed as follows;

$$NiO(s) \rightleftarrows Ni(s) + \tfrac{1}{2}O_2,$$
$$Ni(s) \rightleftarrows Ni(g); \qquad (10)$$

or;

$$NiO(s) \rightleftarrows Ni(g) + \tfrac{1}{2}O_2. \qquad (11)$$

Equation (9) is in good agreement with the values calculated by the first process and not by the second process. Therefore, the standard free energy change

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[8] A. Krupkowski, *Hotnicke Listy* (*tschech*), **3**, 357 (1948); J. G. F. Gilbert and J. A. Kitchener, *J. Chem. Soc.*, **1956**, 3919; W. B. Hinche, *J. Am. Chem. Soc.*, **55**, 1751 (1933); K. Ueno, *Nippon Kwagaku Kwaishi* (*J. Chem. Soc. Japan*), **62**, 990 (1941); Von O. Glemser and U. Stöcker, *Ber. Bunsenges. Physik Chem.*, **67**, 505 (1963).

[9] J. Efemenko, *Chem. Abstr.*, **58**, 8612e (1963); H. W. Foote and E. K. Smith, *J. Am. Chem. Soc.*, **30**, 1344 (1908).

[10] L. Brewer and D. S. Mastick, *J. Chem. Phys.*, **19**, 834 (1951).

[11] K. Kodera, I. Kusunoki and S. Shimizu, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 814 (1965).

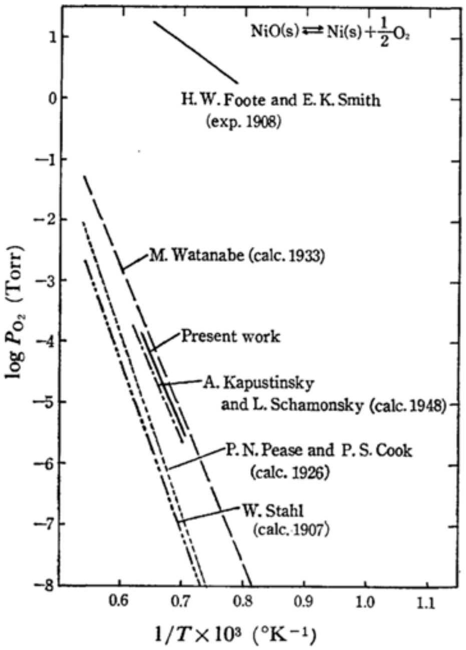

Fig. 7. Comparison of experimental and calculated pressures of oxygen in equilibrium with solid nickel oxide.

of $NiO(s) \rightleftarrows Ni(s) + \frac{1}{2}O_2$ is obtained from Eq. (9);

$$\Delta G^\circ(\text{cal}) = 54500 - 19.35T,$$
$$1400^\circ\text{K} \leq T \leq 1570^\circ\text{K}. \qquad (12)$$

In Fig. 7 the oxygen dissociation pressure is compared with literature data, most of which are calculated from the thermodynamical data obtained by the reduction of nickel oxide. Foote and Smith[12] reported very large value for the dissociation pressures of nickel oxide. However, as they did not analyze the gases, it is possible that they mistook other gases as oxygen. The values obtained by our experiment are in good agreement with the calculated ones. Therefore, the curve C in Fig. 6 shows that the sample treated in vacuum has a stoichiometric composition. The curve A shows that the untreated sample had excess oxygen over the stoichiometric component.

Molybdenum Trioxide. Main species of evolved gases were found to be carbon dioxide and carbon monoxide. The evolution rate of carbon dioxide increased considerably above 200°C and its color changed to gray. Moreover, it was observed that molybdenum trioxide sublimed above 630°C. However, we could not detect any oxygen gas due to thermal decomposition.

Tungsten Trioxide. It has not been reported that oxygen due to thermal decomposition of tungsten trioxide was observed. However, the origin of non-stoichiometry of the oxide is often considered to

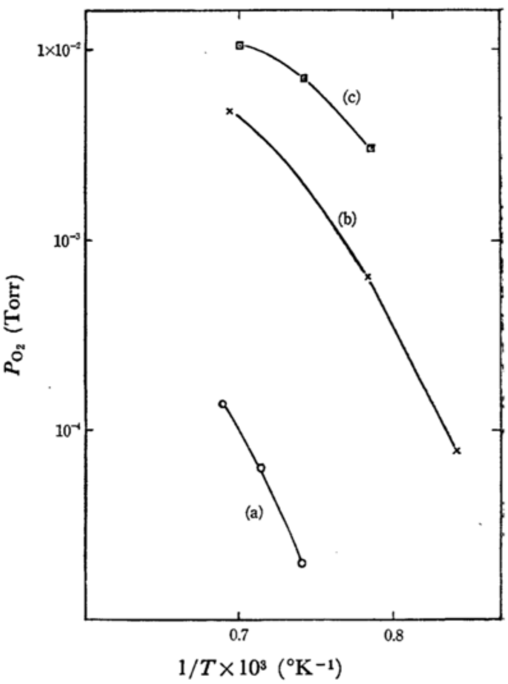

Fig. 8. Measured dissociation pressure in equilibrium with tungsten trioxide, (1), an untreated sample; (b), a sample treated in vacuum at 800°C for about 10 hr; (c), a sample treated in vacuum at 950°C for a couple of days.

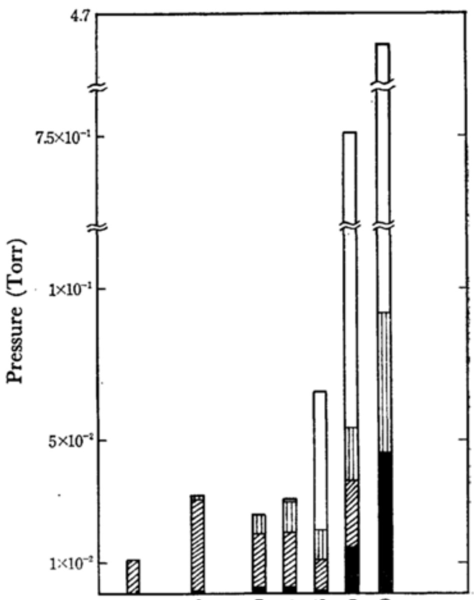

Fig. 9. Partial pressures of gases evolved from copper(II) oxide *vs.* temperature.
□, oxygen; ▥, carbon monoxide; ▨, carbon dioxide; ■, water

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[12] H. W. Foote and E. K. Smith, see Ref. 9.

be due to thermal dissociation.[13] In a previous paper, one of the authors (I. K.)[8] pointed out that the reduction of tungsten trioxide under vacuum heating at temperatures lower than 500°C was taken place by impurity carbon contained in the oxide.

In the present experiment, it was found that the sublimation of tungsten trioxide was accompanied with oxygen evolution above 950°C. Sometimes the oxygen dissociation pressure amounted to 1×10^{-2} Torr but the reproducibility of the measurement was not good among different runs. This may be due to the dissociation accompanied by sublimation. In Fig. 8 the examples of measured dissociation pressures are shown.

The Dissociation Pressure of Copper(I) and Copper(II) Oxides. In Fig. 9 the gaseous species evolved from copper(II) oxide are shown in relation to the temperature. Oxygen was observed above 590°C. Moreover, it was confirmed by X-ray analysis that copper(II) oxide transformed completely into cuprite (copper(I) oxide) under heat treatment in vacuum above 900°C. Therefore, the equilibrium of $2CuO(s) \rightleftarrows Cu_2O(s) + \frac{1}{2}O_2$ is only realized over the range of 600 to 900°C. In Fig. 10 the oxygen pressures are plotted against $1/T$. A good straight line is obtained over this range and the oxygen dissociation pressure is represented by;

$$\log P_{O_2}\,(\text{Torr}) = -\frac{14150}{T} + 12.61. \qquad (13)$$

Therefore, the free energy change for the reaction of $2CuO = Cu_2O + \frac{1}{2}O_2$ is given by;

$$\Delta G^\circ(\text{cal}) = 32400 - 22.28T,$$
$$870°\text{K} \leq T \leq 1170°\text{K}. \qquad (14)$$

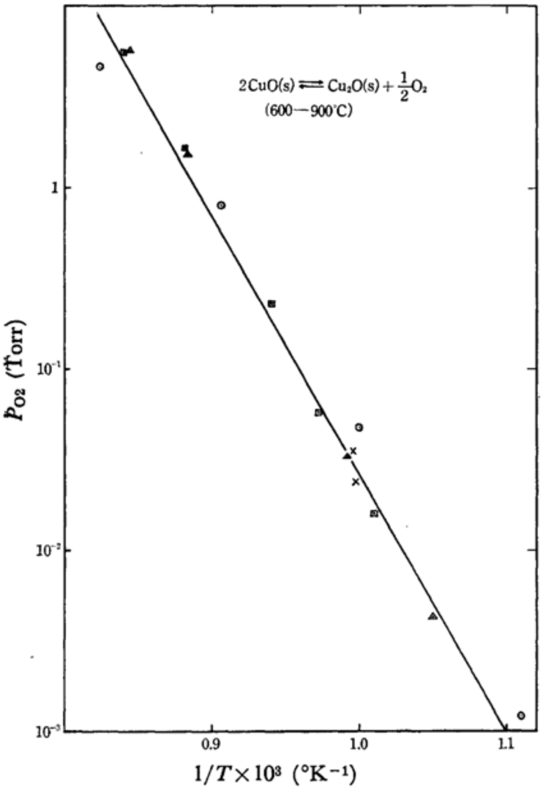

Fig. 10. Dissociation pressure of copper(II) oxide.

Brewer and Mastick[10] thought that the stability of gaseous copper(II) oxide is proved by the measurement of the vapor pressure of solid oxide by Mack, Osterhof, and Krauer.[14] The vapor pressures of gaseous copper(II) oxide between 873 and 1223°K were higher by factors of 10^6—10^8 than those of gaseous copper which is in equilibrium with solid copper(II) oxide. However, we found only the deposit of cuprite and not that of copper(II) oxide. This observation shows copper(II) oxide does not vaporize.

In the present experiment, the sample of cuprite was prepared by heating of copper(II) oxide in vacuum at 900°C for a couple of days, and identified by X-ray analysis. Above 900°C cuprite began to deposit on the hot wall and then decomposed with oxygen evolution. In Fig. 11 the dissociation pressures of oxygen are plotted against $1/T$, and expressed by;

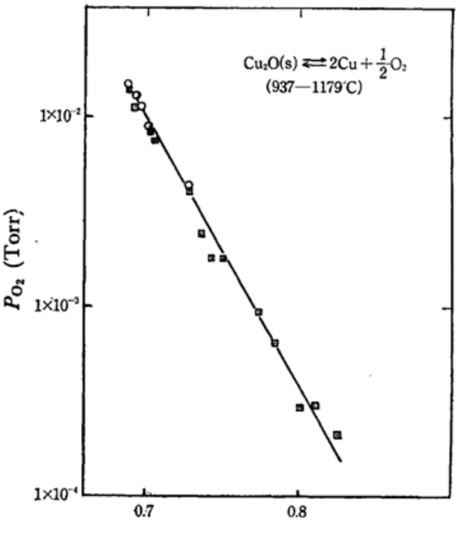

Fig. 11. Dissociation pressure of copper(I) oxide.

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[13] R. J. Ackermann and E. G. Rauch, *J. Phys. Chem.*, **67**, 2596 (1963).

[14] Mack, Osterhof and Krauer, *J. Am. Chem. Soc.*, **45**, 617 (1923).

[15] W. Stahl, *Berg. Hütt. Zty.*, **40**, 127 (1890); E. Heyn, *Z. anorg. Chem.*, **39**, 1 (1904); R. E. Slade and F. D. Farrow, *Proc. Roy. Soc.*, **87**, A524 (1912); H. S. Roberts and F. H. Smyth, *J. Am. Chem. Soc.*, **43**, 1061 (1921); O. Kubaschewski and E. L. L. Evans, Metallurgical Thermochemistry, London (1956); W. Hofman and H. J. Schneider, *Tech. Wiss. Beich. Giessereiw u. Metallk*, **28**, 1567 (1960); V. V. Kondakov, D. I. Ryzhonkov and I. A. Titova, *Chem. Abstr.*, **58**, 7408b (1963).

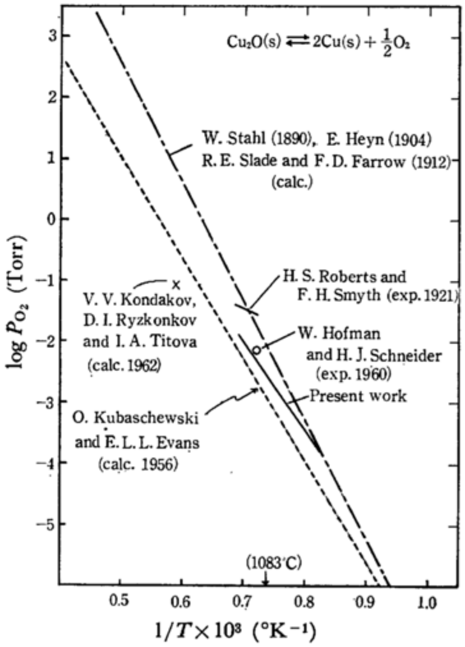

Fig. 12. Comparison of experimental and calculated pressures of oxygen in equilibrium with solid copper(I) oxide.

$$\log P_{O_2}\,(\text{Torr}) = -\frac{14100}{T} + 7.85. \tag{15}$$

The free energy change for the reaction of $Cu_2O(s) = 2Cu(s) + \frac{1}{2}O_2$ or $Cu_2O(s) = 2Cu(l) + \frac{1}{2}O_2$ was given by;

$$\Delta G^\circ(\text{cal}) = 32200 - 11.4T,$$
$$1200°\text{K} \leq T \leq 1420°\text{K}. \tag{16}$$

The melting point of copper is at 1083°C. However, we could not observe any change at this point. In Fig. 12 our result is compared with other author's values,[15] most of which were calculated from the thermodynamical data.

Summary

Carbon dioxide and carbon monoxide were often the main gaseous species evolved from various oxides at lower temperatures. Oxygen due to the thermal dissociation of tungsten trioxide was detected with the omegatron for the first time. In the case of nickel oxide, the excess oxygen contained in the p-type semiconductor was evolved at the first stage during a heat treatment in vacuum. Dissociation pressure of zinc oxide, cadmium oxide, nickel oxide copper(II) oxide, and cuprite were measured and were in good agreement with the calculated values from the standard free energy data.

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