

# Thermodynamic description of metallization of oxides under pressure

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The possibility is discussed of chemical decomposition of oxides into a metal and oxygen gas under pressure as a probable alternative to metallization of oxides.

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1. On the basis of the established regularity<sup>[1]</sup> that governs the reversal of the sign of the thermal effect of reactions in open systems with unequal pressure on the solid and gas phases, it was suggested<sup>[2]</sup> that the resistance jump observed in metallization experiments may be due not to metallization of the oxide but to its decomposition (reduction) into a free metal and oxygen gas.

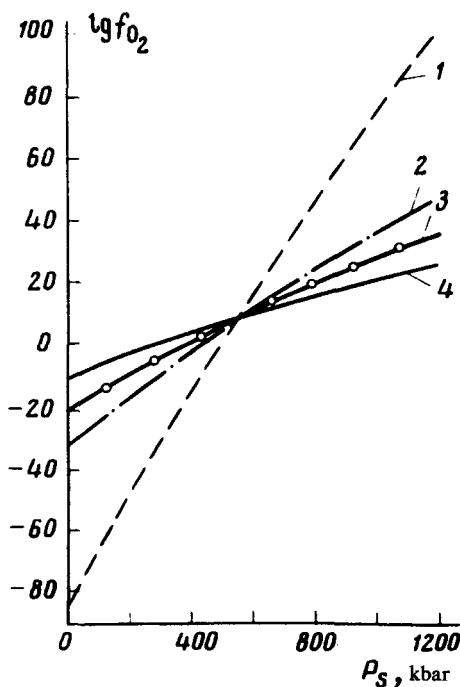


FIG. 1. Dependence of the fugacity of oxygen for the reaction  $\text{FeO}(\text{sol}) = \text{Fe}(\text{sol}) + \text{O}_2(\text{g})$  on the temperature and on the pressure. Isotherms: 1-298, 2-700, 3-1000, 4-1600 K.

For an open system with an equal pressure on the phases, where the independent variables are the temperature ( $T$ ), the pressure on the solid phase ( $P_s$ ), and the fugacity of the gas ( $f_i$ ), the equation of mixed equilibrium can be represented in the form<sup>[1]</sup>

$$\Delta H d\left(\frac{1}{T}\right) + \frac{\Delta V_s}{T} dP_s + R d \ln f_i = 0, \quad (1)$$

where  $\Delta H$  is the thermal effect of the reaction,  $\Delta V_s$  is the change of the volume of the solid phases (for example, for the reaction  $\text{SiO}_2 = \text{Si} + \text{O}_2$  we have  $\Delta V_s = V_{\text{Si}} - V_{\text{SiO}_2}$ ).

Inasmuch as in the system under consideration (oxide under pressure) the pressure on the solid phases and the pressure (fugacity) of the gas are independent thermodynamic parameters, it follows that  $P_s \neq P_{\text{O}_2}$ . The gas is under its own pressure and  $P_s > P_{\text{O}_2}$ —the case of osmotic thermodynamics. Thus, this system is regarded as open with respect to oxygen, i.e., the latter can exchange with the oxygen of the ambient. The reduction of the oxide to a metal and oxygen gas takes place at constant temperature and at that value of  $P_s$  at which the fugacity of the oxygen in the system exceeds the partial pressure of the oxygen in the ambient. Only in one case is the critical pressure ( $P_c$ ) of the reduction (decomposition) independent of the temperature—an illustration of this case is shown in Fig. 1. At the point of intersection of the curves, at  $P_s = P_c$ , the enthalpy of the reaction is equal to zero—the sign of the thermal effect is reversed.

At  $P_s = P_c$  the fugacity of the oxygen does not depend on the temperature and  $\Delta H = 0$ . The decrease of  $f_{O_2}$  with decreasing temperature at  $P_s > P_c$  (Fig. 1) indicates that the reduction reactions are accompanied by release of heat. Thus, endothermic reactions at pressures  $P_s < P_c$  become exothermic at  $P_s > P_c$  and conversely, exothermic reactions at pressures  $P_s < P_c$  become endothermic at  $P_s > P_c$ .

Consequently, the vanishing of the thermal effect of the reaction is an indicator of that critical pressure at which the oxide is reduced because at  $P_s = P_c$  the fugacity of the oxygen in the system becomes larger than the partial pressure of the oxygen in the air.

2. In their experiments on metallization, Vereshchagin *et al.*<sup>[3]</sup> heated electrically conducting  $\text{SiO}_2$ . It was noted that the resistance increased from  $\sim 10^2 \Omega$  to the initial value  $\sim 10^8\text{--}10^9 \Omega$ . In their opinion,<sup>[3]</sup> the return of the resistance of the oxide to the initial value is evidence either that  $\text{SiO}_2$  cannot be decomposed under pressure, or that the percentage of the decomposition is negligible, and they suggested that the jumplike increase of the resistance when conducting  $\text{SiO}_2$  is heated points to the existence of metastable conducting  $\text{SiO}_2$ .

Another explanation can be offered for this fact. At pressures  $P_s > P_c$  the decomposition of  $\text{SiO}_2$  (and of other oxides) becomes exothermic and, in accordance with the Le Chatelier principle, decomposition is aided not by an increase but by a decrease of the temperature. An increase of the temperature, on the other hand, takes it out of the stability region of the silicon (metal) into the stability region of the oxide (insulator), and consequently, the resistance should indeed increase. Figure 2 shows by way of illustration the calculations of  $f_{O_2}$  for the reaction of the decomposition reaction  $\text{SiO}_2(\text{sol}) = \text{Si}(\text{sol}) + \text{O}_2(\text{g})$  for two isobars,  $P_s < P_c$  and  $P_s > P_c$ , as well as the stability regions of  $\text{SiO}_2$  and Si.

Thus, from the experimental fact—the increase of the resistance of the oxide when heated—it is probably impossible to conclude that it becomes metallized at lower temperatures. Moreover, these experimental data confirm the possibility of decomposition of the oxides under pressure and of the reversal of the sign of the enthalpy

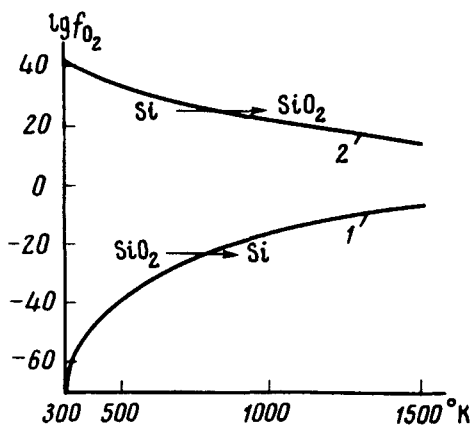


FIG. 2. Fugacity of oxygen for the reaction  $\text{SiO}_2(\text{sol}) = \text{Si}(\text{sol}) + \text{O}_2(\text{g})$ : 1—the isobar  $P_s = 800$  kbar; 2—isobar  $P_s = 2000$  kbar. The arrows mark the  $\text{SiO}_2$ —dielectric and Si—metal stability regions.

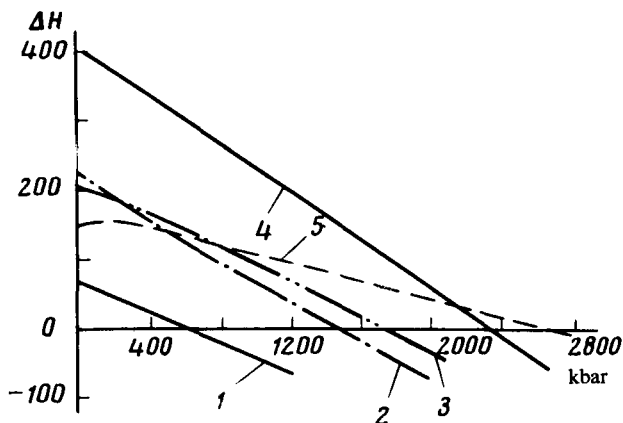
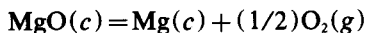
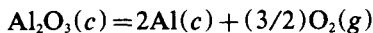
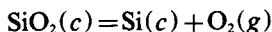
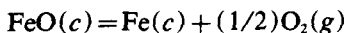


FIG. 3. Thermal effects of the reactions of the reduction of oxides ( $\Delta H_{298}^P$  kcal/mole): 1—FeO, 2—TiO<sub>2</sub>, 3—SiO<sub>2</sub>, 4—Al<sub>2</sub>O<sub>3</sub>, 5—MgO.

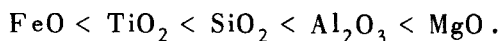
of the decomposition process as a result of the transition Si (metal)  $\rightarrow$  SiO<sub>2</sub> (insulator) with rising temperature.

3. The results of the calculation of the thermal effects of the reactions



by the procedure described in<sup>[1,2]</sup> are shown in Fig. 3. The equations of state of the oxides and of the element (with the exception of Mg) in the form  $\int VdP$  were calculated by us from the experimental data on the static and shock compression,<sup>[4-8]</sup> and the equation of state of Mg was calculated by the method of potentials.<sup>[9]</sup>

The calculations (Fig. 3) show that the general sequence of the decomposition of oxides under pressure is the following:



The decomposition (reduction) pressures for these oxides are respectively 550, 1450, 1700, 2300, and 2600 kbar.

This sequence can be compared with the sequence of the oxides that go over under pressure into the conducting state in accordance with the data of<sup>[10-12]</sup>: FeO  $<$  TiO<sub>2</sub>  $<$  SiO<sub>2</sub>  $<$  MgO and of the data of<sup>[13]</sup>: Al<sub>2</sub>O<sub>3</sub>  $<$  SiO<sub>2</sub>  $<$  MgO. It follows from the comparison that the order of the decomposition pressures of the oxides is practically

the same as that of the pressures of the dielectric-metal transition. Summarizing all the foregoing, we suggest that in experiments at high pressures the resistance jump can probably be attributed to the reduction of the oxides into a metal and oxygen gas.<sup>11</sup>

<sup>11</sup>We have decided also to verify the possibility of decomposition of oxides into solid phases in accordance with a reaction of the type  $\text{MeO}(\text{sol}) = \text{Me}(\text{sol}) + \text{O}(\text{sol})$ , using the equation of state of solid oxygen constructed by the method of potentials.<sup>9,14</sup> The calculations were carried out for a closed system with a total pressure of the phases 2 Mbar at 298 K. The free energy of the reactions at the given  $P$  and  $T$  was approximately 300 kcal/mole for the decomposition of  $\text{SiO}_2$  (stishovite) and 200 kcal/mole for the decomposition of  $\text{MgO}$  (periclase). It is clear therefore that decomposition of oxides into solid phases is thermodynamically forbidden.

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<sup>1</sup>O.L. Kuskov and N.I. Khitarov, Dokl. Akad. Nauk SSSR **231**, 1399 (1976).

<sup>2</sup>O.L. Kuskov and N.I. Khitarov, in: *Fazovye perekhody metall—dielektrik (Metal—dielectric phase transition)*, Moscow-L'vov, 31, 1977.

<sup>3</sup>L.F. Vereshchagin, E.N. Yakovlev, B.V. Vinogradov, V.P. Sakun, and G.N. Stepanov, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 472 (1974) [JETP Lett. **20**, 215 (1974)].

<sup>4</sup>Handbook of Physical Constants of Mineral Rocks (Russ. transl.), Mir, 1969.

<sup>5</sup>L.V. Al'tshuler and I.I. Sharipdzhanov, Izv. AN SSSR ser. Fiz. Zemli, No. **3**, 11 (1971).

<sup>6</sup>L.V. Al'tshuler, M.A. Podurets, G.V. Simakov, *et al.* Fiz. Tverd. Tela (Leningrad) **15**, 1436 (1973) [Sov. Phys. State **15**, 969 (1973)].

<sup>7</sup>O.L. Kuskov, Geokhimiya, No. **8** (1975).

<sup>8</sup>H.K. Mao and P.M. Bell, Preprint, Geophys. Lab. Carnegie Inst., USA, 1977.

<sup>9</sup>I.A. Ostrovskii, I.A. Tsarevskii, G.B. Bokiĭ, and G.P. Gorshkov, Izv. AN SSSR ser. geol. No. **6**, 18 (1977).

<sup>10</sup>N. Kawai and A. Nishiyama, Proc. Jpn. Acad. **50**, 634 (1974).

<sup>11</sup>N. Kawai and A. Nishiyama, *ibid.* **50**, 72 (1974).

<sup>12</sup>N. Kawai and S. Mochizuki, Phys. Lett. **36A**, 54 (1971).

<sup>13</sup>L.F. Vereshchagin, E.N. Yakovlev, Yu.A. Timofeev, B.V. Vinogradov, *op. cit.*,<sup>[2]</sup> **3**, 1977.

<sup>14</sup>V.N. Zharkov, V.P. Trubitsyn, I.A. Tsarevskii, Geodinamicheskie issledovaiya, No. 3, 5, M. Nauka, 1975.