

A Study on the Defect Structure of TiO₂ (Rutile) by Electrical Conductivity Measurements

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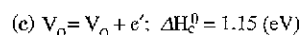
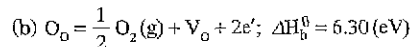
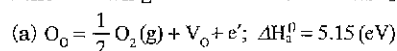
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The electrical conductivity of polycrystalline TiO₂ samples was measured over the temperature range 1000°-1400°C and from 0.21 to 10⁻¹⁶ atm of oxygen. Based on the excellent fit observed between the theoretically derived relation

$$\sigma^3 = (A\sigma + B)P_{O_2}^{-1/2} + D'\sigma^2$$

and the experimental conductivity data, the nonstoichiometric defect structure of TiO₂ was rationalized in terms of a defect model involving quasi-free electrons and both singly and doubly ionized oxygen vacancies

The standard enthalpy of formation for the following defect reactions in TiO₂:



were determined from the temperature dependence of A and B obtained from the above relation and from the experimental expression between the electron mobility and temperature. The electrical conductivity of TiO₂ in air below approximately 950°C appears, on the basis of this investigation, to be impurity controlled due to the presence of aluminum rather than intrinsic conduction.

Key words : Defect, Titanium dioxide, Electrical conductivity, Nonstoichiometry, Oxygen vacancy, Interstitial titanium

I. Introduction

TiO₂ is an n-type oxygen deficient semiconductor when nonstoichiometric(TiO_{2-x}). This oxygen deficient behavior may arise from the presence of a defect structure involving either anion vacancies or cation interstitials. However, in spite of all the scientific interest in this oxide, there has been no conclusive experimental evidence to indicate which of the above defect models predominates. Blumenthal and Whitmore¹⁾ studied the nonstoichiometry of TiO₂ and concluded from e.m.f and isopiestic measurements that the x value of TiO_{2-x} at 900°-1000°C is 0.01 in air. When the oxygen pressure dependence of x is expressed as P_{O₂}^{1/n}, it is found from considering all the available results²⁻⁷⁾ that n is a function of both temperature and the partial pressure of oxygen. Furthermore, plots of x vs. 1/T do not show a straight line relationships^{3,5,7)}. This suggests that the defect structure cannot be interpreted in terms of simple model in which either oxygen vacancies or interstitial titanium ions predominate. Both oxygen and interstitial titanium defects may be important depending on the temperature and partial pressure of oxygen. Kofstad⁸⁾ proposed that the defect structure is comprised simultaneously of doubly charged oxygen vacancies and interstitial titanium ions with three or four effective charges Blumenthal *et al.*⁹⁾ measured the con-

ductivity of rutile single crystals in the c direction at temperatures of 1000°-1500°C under partial pressures of oxygen from 10⁻¹⁶ to 1 atm. They found several oxygen pressure dependences of the electrical conductivity, characterized by $\sigma \approx P_{O_2}^{-1/1}$, $\sigma \approx P_{O_2}^{-1/5}$ and $\sigma \approx P_{O_2}^{-1/6}$, and interpreted the defect structures in terms of doubly charged oxygen vacancies or interstitial titanium ions.

Thus, in order to help elucidate the defect structure of TiO₂, work was initiated in this investigation on the electrical conductivity of TiO₂ as a function of temperature and partial pressure of oxygen, from 1000°C (between 0.1 and 10⁻¹⁶ atm of P_{O₂}) to 1400°C (between 0.1 and 10⁻¹² atm of P_{O₂}).

II. Experimental Section

1. Specimen preparation

The reduced polycrystalline pellet of TiO₂ was prepared by the following method. Rectangular bars are sintered at 1450°C using TiO₂ powder (Rutile, 99.9%) isostatically pressed. The pellet was given a light abrasive polish on one face and then turned over and polished until the voids of the interface region were fully eliminated. The pellet was etched in dilute-HNO₃, washed with distilled water and dried in a dry oven. The platinum electrode was then attached to the face of the pellet by holding for 15 min at

800°C.

2. Apparatus and procedure

After electroding, 0.5 mm in dia. standard grade platinum wire was wrapped around each end of the specimen to produce the current leads. The potential probes consisted of 0.25 mm in dia. standard grade platinum wire wrapped with a spacing of 8 mm between the current leads as shown in Fig. 1. Electrical conductivity measurements in the temperature range 1000°-1400°C were made in a Si₃N₄ heating-element furnace. The variation of oxygen partial pressure was obtained using the mixed gas of fine pure carbon dioxide (99%) and pure carbon monoxide (99.95%). The partial pressure of oxygen vs. the reciprocal of the absolute temperature for some of the gas mixtures is shown in Fig. 2. A standard four probe D.C. technique was utilized for the conductivity measurements. The specimen was equilibrated with the appropriate gas mixture at a given temperature and a small voltage impressed across the current probes of the specimen. The e.m.f. across the standard resistor and the e.m.f. across the potential probes were measured, the direction of the current reversed and the measurements repeated. The electrical conductivity was calculated from the average value of the e.m.f.s to reduce the effect of thermo-generated e.m.f.s and this procedure was repeated until a constant value of conductivity was obtained. The equilibration times were of the order of minutes over the entire range of

temperature and pressure. Measurements were taken at various temperatures between 1000° and 1400°C and

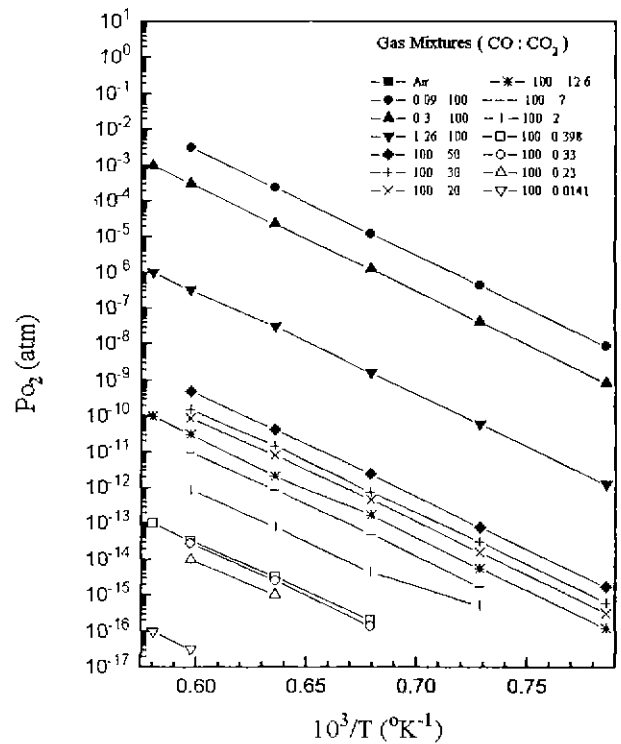


Fig. 2. The logarithm of the partial pressure of oxygen vs. the reciprocal of absolute temperature for gas mixture of CO and CO₂.

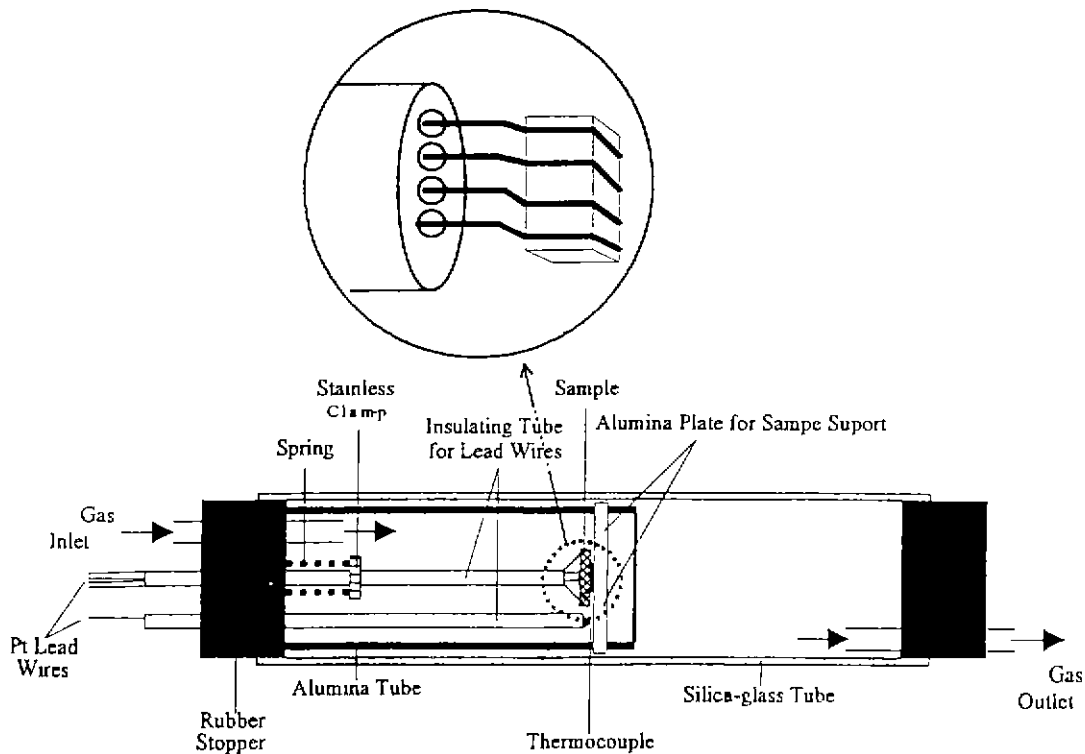


Fig. 1. The conductivity Jig.

fixed gas mixture for both increasing and decreasing temperature.

III. Results and Discussion

Results of the conductivity measurements as a function of temperature for various CO/CO₂ ratios are shown in Fig. 3 as a plot of logarithm of σ vs. $1/T$. The metal excess nature of nonstoichiometric rutile may arise from the presence of a defect structure involving either anion vacancies or cation interstitials. Using the law of mass action in combination with appropriate simplified electroneutrality equations, the concentration of conduction electrons can be obtained as a function of the partial pressure of oxygen. The electrical conductivity is, however, directly proportional to the concentration of conduction electrons. Consequently, if the assumptions made in deriving these equations are valid and the mobility is assumed to be a function of temperature only, theoretical equations for the pressure dependence of the electrical conductivity can be derived. Accordingly, for the defect reaction



the expression for conductivity is

$$\sigma = (K_2)^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} \tag{2}$$

or simply the pressure dependence is¹⁰⁾

$$\sigma \approx P_{O_2}^{-\frac{1}{4}} \approx P_{O_2}^{-\frac{1}{x}} \tag{3}$$

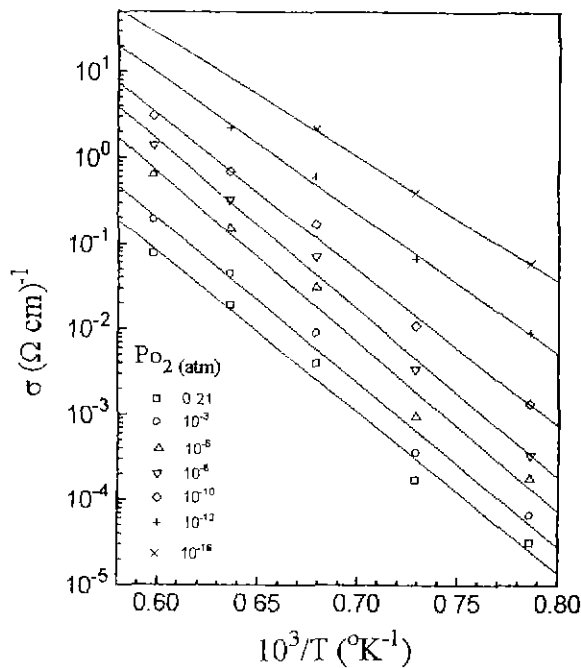


Fig. 3. The logarithm of the electrical conductivity as a function of reciprocal of absolute temperature for various oxygen pressures

where $x=4$; K_2' is the product of K_1 , the equilibrium constant for the formation of the oxygen vacancy; K_3 , the constant for the ionization of the first electron. The charge on an electron is given as e and μ is the electron mobility.

Similarly, for the defect reaction



the expression for conductivity is

$$\sigma = (2K_3)^{\frac{1}{3}} P_{O_2}^{-\frac{1}{6}} \tag{5}$$

or simply the pressure dependence is

$$\sigma = P_{O_2}^{-\frac{1}{6}} \approx P_{O_2}^{-\frac{1}{x}} \tag{6}$$

where $x=6$ and $K_4'=(K_1K_2K_3)$. K_3 is the equilibrium constant for the ionization of the second electron.

For the interstitial titanium defect model, $x=4$ for the case where the triply ionized interstitial titanium is the predominant defect and $x=5$ for the quadruply ionized interstitial titanium.¹¹⁾ Thus if the assumption made in deriving the above equations are valid, the defect structure in rutile can be determined from a plot of logarithm of vs. logarithm of P_{O_2} .

An experimental plot of $\log \sigma$ vs. $\log P_{O_2}$ was obtained in the following manner. Values of the conductivity were selected at 100°C intervals between 1000° and 1400°C from plots of $\log \sigma$ vs. $1/T$ (e.g. see Fig. 3). The partial pressure of oxygen corresponding to the above values of the electrical conductivity for various mixtures of CO and CO₂ were obtained from Fig. 2. The above values of conductivity were combined with their respective values of the partial pressure of oxygen to obtain the isothermal plots at 100°C intervals between 1000° and 1400°C of $\log \sigma$ vs. $\log P_{O_2}$ shown in Fig. 4.

It can be seen that the data in Fig. 4 is best represented by straight lines over the entire range of temperature and pressure with a two-slope behavior in evidence at the lower temperatures. The values of x calculated from the slopes are given and indicate that x depends both on temperature and the range of partial pressure of oxygen. For the purpose of convenience, the two slope behavior at lower temperatures will be divided into a low and a high oxygen pressure region.

Since the value of x is not an integer and varies from about 6.0 at 1400°C to 3.7 in the low oxygen pressure region and 6.6 in the high oxygen pressure region at 1000°C, the nonstoichiometric defect structure cannot be accounted for in terms of a point defect in a single predominant state of ionization. The electrical conductivity in the low oxygen partial pressure region appears to be controlled by nonstoichiometric defects while the higher oxygen pressure region at lower temperatures appears to be influenced by the presence of impurities. This result is consistent with the work the of Yahia¹³⁾ on

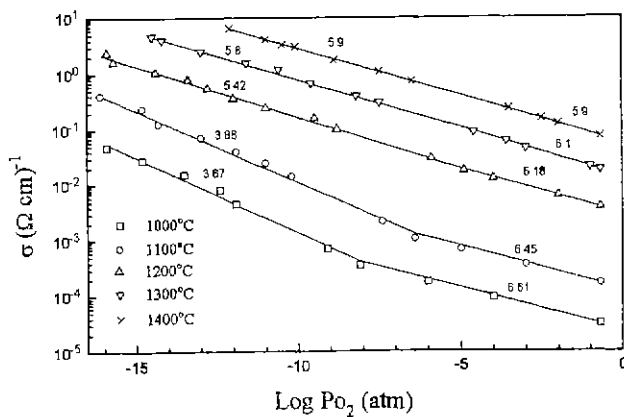


Fig. 4. Isothermal relation between the logarithm of the conductivity and the logarithm of P_{O_2} in the temperature range 1000°-1400°C.

single crystal of rutile doped with 0.5wt.% aluminum. The electrical conductivity of doped rutile reached a minimum at a characteristic partial pressure of oxygen for each temperature. The plot of the $\log \sigma$ vs. $\log P_{O_2}$ has a slope of $-1/4$ in the low pressure range and $+1/6$ in the high pressure range at 1000°-1100°C, $-1/6$ in the low pressure range and $+1/6$ in the high pressure range at 1200°-1400°C. The sign of the thermoelectric power determined in the same investigation changed at the value of P_{O_2} that was observed at the minimum of the conductivity (i. e. negative at lower pressures and positive at higher pressures).⁹⁾

Thus a qualitative explanation of the observed electrical conductivity data would be as follows:

1) The value of x at higher partial pressures of oxygen decreases with increasing temperature. This can be interpreted as the decreasing influence of impurities on the conduction process.

2) The value of x at lower partial pressures of oxygen increases with increasing temperature. This can be interpreted as an increased ionization of the non-stoichiometric defects as the temperature is increased.

Since the slopes at higher temperatures for both oxygen pressure regions approach the same value of x , approximately 6.0, it would appear that the defect structure in nonstoichiometric rutile can be rationalized on the basis of an oxygen vacancy model involving both singly and doubly ionized oxygen vacancies.

Therefore, an electroneutrality expression of the following type:

$$n = [V_O] + 2[V_{O'}] + D \quad (7)$$

where D is the concentration of ionized impurities which act as donors, should be employed to obtain a quantitative relation between σ and P_{O_2} , for a defect structure involving both singly ionized and doubly ionized oxygen vacancies.

From the mass action equations for defect equilibria,

an expression is obtained which relates the concentration of singly ionized oxygen vacancies to the concentration of conduction electrons and the partial pressure of oxygen; that is,

$$[V_O] = K_2' P_{O_2}^{-1/2} n^{-1} \quad (8)$$

where $K_2' = (K_1 K_2)$. The concentration of doubly ionized oxygen vacancies is,

$$[V_{O'}] = K_3' P_{O_2}^{-1/2} n^{-2} \quad (9)$$

where $K_3' = (K_1 K_2 K_3)$.

Substitution of equations (8) and (9) into equation (7) yields the expression

$$n = (K_2' n^{-1} + 2K_3' n^{-2}) P_{O_2}^{-1/2} + D \quad (10)$$

which relates the concentration of conduction electrons to the partial pressure of oxygen.

For extrinsic electronic conduction

$$\sigma = n e \mu \quad (11)$$

and

$$n = \sigma / C \quad (12)$$

where $C = e\mu$, and μ is assumed to be a function of temperature only.

By combining equations (10) and (12) and rearranging terms the following expression was obtained which relates the electrical conductivity to the partial pressure of oxygen:

$$\sigma^3 = (A\sigma + B) P_{O_2}^{-1/2} + D' \sigma^2 \quad (13)$$

where

$$A = K_1 K_2 C_2 \quad (14)$$

$$B = 2K_1 K_2 K_3 C^3 \quad (15)$$

and

$$D' = DC \quad (16)$$

Similarly, for a defect structure involving both triply and quadruply ionized titanium interstitials and ionized impurities which act as donor centers, the electroneutrality equation is

$$n = 3[Ti_3] + 4[Ti_4] + D \quad (17)$$

Accordingly,

$$\sigma^5 = (E\sigma + F) P_{O_2}^{-1} + D' \sigma^4 \quad (18)$$

where

$$E = 3K_4' C^4 \quad (19)$$

$$F = 4K_4' C^5 \quad (20)$$

and

$$D' = DC \quad (21)$$

Table 1. The Calculated Values of the Parameters A, B and D' in the Expression $\sigma^3 = (A\sigma + B)P_{O_2}^{-\frac{1}{2}} + D'\sigma^2$

Temp	A	Standard error of A(±)	B	Standard error of B(±)	D'	Standard error of D'(±)
1000°C	8.0864×10^{-11}	3.4102×10^{-14}	1.7238×10^{-13}	2.3192×10^{-15}	-1.181×10^{-2}	9.1021×10^{-4}
1100°C	2.4477×10^{-9}	1.0876×10^{-11}	3.2991×10^{-12}	4.0832×10^{-14}	-6.994×10^{-3}	3.2876×10^{-5}
1200°C	1.8587×10^{-6}	2.8608×10^{-8}	3.1655×10^{-7}	4.1329×10^{-8}	-2.283×10^{-1}	1.0871×10^{-3}
1300°C	6.5837×10^{-6}	1.9014×10^{-8}	2.0278×10^{-6}	5.6324×10^{-7}	2.1806×10^{-2}	2.3481×10^{-4}
1400°C	2.0989×10^{-4}	4.8913×10^{-7}	4.1701×10^{-4}	3.1011×10^{-6}	-1.3409×10^{-1}	1.0978×10^{-3}

A computer program was written for equations (13) and (18) and the values of σ and P_{O_2} obtained from the lines shown in Fig. 4 were used to calculate the values of the parameters in these equations at 100° intervals between 1000° and 1400°C. The calculated values of these parameters and their standard errors are tabulated in Table 1.

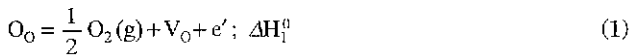
It is apparent from the values of the standard error of the parameter shown in Table 1 that equation (13) represents an acceptable fit of the experimental data; whereas equation (18) is not an acceptable representation of the data.

Thus, the excellent agreement between the expression

$$\sigma^3 = (A\sigma + B)P_{O_2}^{-\frac{1}{2}} + D'\sigma^2 \quad (13)$$

and the experimental data of the electrical conductivity as a function of the partial pressure of oxygen and temperature provides a quantitative confirmation of the qualitative interpretation of the data (which was rationalized in terms of a defect structure involving both singly and doubly ionized oxygen vacancies).

The standard enthalpy of formation for the non-stoichiometric defect reaction



is related to the thermodynamic equilibrium constant, K_2' , by the well-known expression

$$K_2' = e \left[\left(\frac{\Delta S_1^0}{k} \right) - \left(\frac{\Delta H_1^0}{kT} \right) \right] \quad (22)$$

but

$$A = K_1 K_2 C^2 \quad (14)$$

and according to Frederikse¹²⁾ μ is proportional to the $\exp(0.1/kT)$. Therefore, the slope of the line obtained from a plot of $\log A$ vs. $1/T$ would be equal to the expression

$$\frac{d(\log A)}{d\left(\frac{1}{T}\right)} = - \frac{(\Delta H_1^0 - 0.2)}{2.303k} \quad (23)$$

The result, $\Delta H_1^0 = 5.15$ (eV) was obtained by equating the right hand side of equation (23) with the slope of the

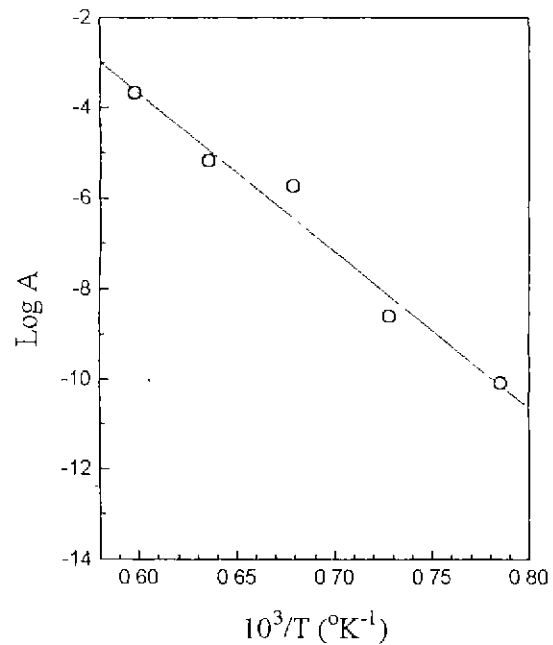
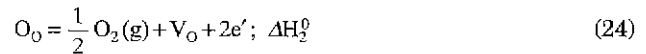


Fig. 5. The logarithm of A vs. the reciprocal of absolute temperature.

line shown in Fig. 5, where $\log A$ is plotted as a function of $1/T$.

In a similar manner, the standard enthalpy of formation for the nonstoichiometric defect reaction



was found to be equal to 6.30 (eV). This result was obtained by equating the relation

$$\frac{d(\log B)}{d\left(\frac{1}{T}\right)} = - \frac{(\Delta H_2^0 - 0.3)}{2.303k} \quad (25)$$

with the slope of the line shown in Fig. 6, where the $\log B$ is plotted as a function $1/T$.

The standard enthalpy of formation for the ionization reaction



can be calculated from the equation

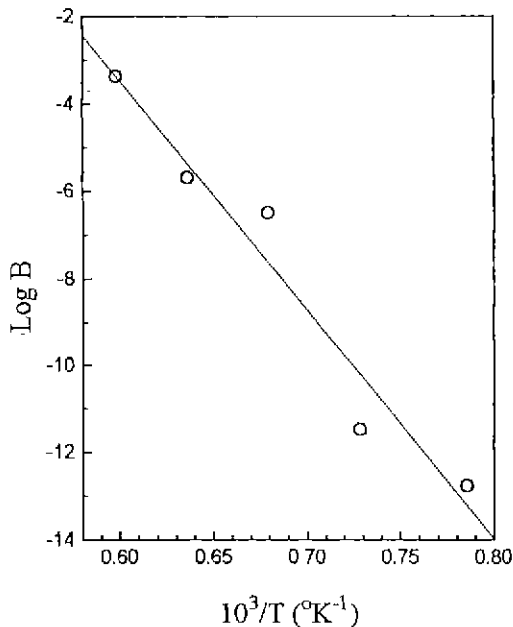


Fig. 6. The logarithm of B vs. the reciprocal of absolute temperature.

$$\Delta H_{1/2}^0 = \Delta H_2^0 - \Delta H_1^0 \quad (27)$$

Most of the previous investigators of the conductivity of rutile have attempted to relate the experimental activation energy (calculated from a plot of $\log \sigma$ vs. $1/T$ at constant oxygen pressure) to the energy of formation for some assumed nonstoichiometric defect reaction. Since the experimental data of this investigation can be represented by a defect structure involving more than one ionization state for the defect, the experimental activation energy cannot be simply related to a single nonstoichiometric defect reaction.

IV. Conclusions

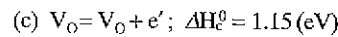
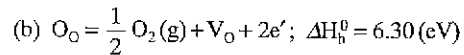
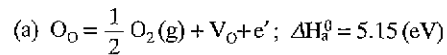
The nonstoichiometric defect structure of rutile was assumed to be a defect model involving quasi-free electrons and both singly and doubly ionized oxygen vacancies. In addition, donor type impurities are assumed to be present in rutile.

An experimental confirmation of this defect model is obtained from the excellent fit observed between the theoretical relation

$$\sigma^3 = (A\sigma + B) P_{O_2}^{-\frac{1}{2}} + D' \sigma^2$$

based on the above defect model, and the electrical conductivity data measured in the temperature range 1000°-1400°C and over the range of oxygen partial pressure from 10^{-15} to 0.21 atm.

The standard enthalpy of formation for the following defect reactions in rutile:



were determined from the temperature dependence of A and B obtained from the aforementioned relation and from the experimental expression between the electron mobility and temperature given by Frederickse.¹²⁾

The electrical conductivity of rutile in air at lower temperatures (i.e. below approximately 950°C in the as received condition) is interpreted, on the basis of this investigation, to be impurity controlled due possibly to the presence of aluminium rather than intrinsic conduction as proposed by Cronmeyer.¹⁴⁾

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