

The Defect Structure of Rutile

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The defect structure of rutile (TiO_2) has been studied by equilibrium measurements in the temperature region 934–1194°C and at partial oxygen pressures in the region 10^{-7} – 10^{-16} atm.

At temperatures above 1100°C the weight loss is proportional to $P_{\text{O}_2}^{-1/2}$, and the defects consist of oxygen vacancies and electrons not associated with the vacancies.

The highest percentage of oxygen vacancies obtained is 0.384 % at 1194°C and $P_{\text{O}_2} = 10^{-13.4}$ atm.

The enthalpy of vacancy formation is calculated to be 130 kcal/mole in the temperature region 1099–1194°C.

I. INTRODUCTION

For many years rutile is known to be a semiconductor of the n -type. This has been confirmed by investigation of the conductivity of titanium dioxide as a function of the oxygen pressure in the temperature range 800–1000°C by Hauffe and co-authors.¹

Several authors have studied the variation of the oxygen content in rutile with the temperature and/or the oxygen pressure. Andersson, Magnéli and co-authors² have carried out X-ray studies over oxide phases in the composition region $\text{TiO}_{1.75}$ – $\text{TiO}_{1.90}$. Structures with formulas $\text{Ti}_n\text{O}_{2n-1}$ (where n is an integer) up to $\text{Ti}_{10}\text{O}_{19}$ were determined. It was indicated that the homologous series may extend up to $\text{TiO}_{1.96}$, but with the experimental method used it was not possible to prove the existence of a two-phase region beyond $\text{TiO}_{1.9}$.

Czanderna and Honig³ studied the weight loss of TiO_2 by heating in vacuum and the subsequent oxygen uptake of the vacuum heated samples. Highly purified and doped TiO_2 samples showed no oxygen uptake after heating at pressures 10^{-4} Torr or lower at temperatures up to 1000°C, while commercial TiO_2 powders showed a reversible oxygen uptake at a temperature of 500°C and higher. The experiments were carried out using a thermobalance.

Using samples of highly pure titanium dioxide, Brauer and Littke⁴ studied the variation of the melting point and the composition of the melt with oxygen pressure. At an oxygen pressure of 10^{-3} Torr the titanium dioxide melted at 1795°C and the composition was $\text{TiO}_{1.969}$, at 15 Torr oxygen pressure it melted at 1820°C with a composition $\text{TiO}_{1.990}$, and at 159 Torr oxygen pressure

it melted at 1830°C with a composition $\text{TiO}_{1.996}$. The oxygen content was determined by reheating the cooled and pulverized melt to 1300°C in pure oxygen.

Straumanis and co-authors⁵ studied the composition of rutile samples after heating at 1400°C under different oxygen pressures. They determined the homogeneity region of the TiO_2 phase to extend from $\text{TiO}_{1.983}$ to $\text{TiO}_{2.000}$. The homogeneous $\text{TiO}_{1.9832}$ was obtained at an oxygen pressure of 0.005 Torr, and an oxygen pressure of 12 Torr corresponded to a composition $\text{TiO}_{1.9867}$. The composition of the samples was determined from lattice-parameters and density measurements on the quenched samples.

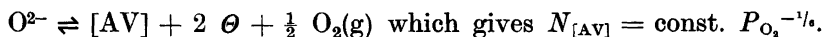
While conductivity measurements indicate a change in the composition of the rutile below 1000°C,¹ measurements of the oxygen uptake show no change in the composition below 1000°C.³ Measurements carried out on cooled samples^{2,4,5} do not give conclusive evidence on the behaviour of rutile at elevated temperatures. To obtain more reliable information on what is occurring in the high temperature region it is necessary to perform measurements at elevated temperatures. An investigation of the variations of the weight of rutile when varying the temperature and the oxygen pressure was expected to give more reliable information on the defect structure.

If only ideal non-stoichiometric defects are formed in the lattice (*i.e.* as long as the concentration of defects is small and they do not interact) one should expect the weight loss of rutile at a given temperature to vary linearly with the oxygen pressure in some particular power. The power of the oxygen pressure would be determined by the type of defects. Further, it is reasonable to assume that infinite oxygen pressure should correspond to the perfect TiO_2 crystal.

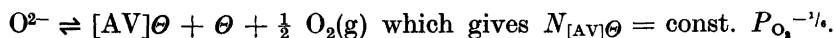
The following examples of ideal equilibrium equations illustrate the possibilities, assuming small percentages of lattice defects.

I. The point defects consist of vacant oxygen positions. In the following equations O^{2-} denotes an oxygen in a normal lattice position, $[\text{AV}]$ denotes a vacant oxygen position and Θ denotes an excess electron.

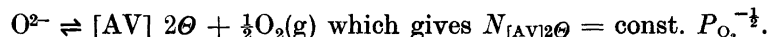
(a) The electrons are not associated with the vacant oxygen position:



(b) One electron is associated with each vacant oxygen position:



(c) Two electrons are associated with each vacant oxygen position:



II. The point defects consist of titanium in interstitial positions. In the following equation TiO_2 denotes titanium and oxygen in normal lattice positions $\text{Ti}_{\text{IP}}^{n+}$ denotes titanium in an interstitial position, and Θ as before denotes an excess electron.

$\text{TiO}_2 \rightleftharpoons \text{Ti}_{\text{IP}}^{n+} + n\Theta + \text{O}_2(\text{g})$ which gives $N_{\text{Ti}} = \text{const. } P_{\text{O}_2}^{-1/(1+n)}$ where N_{Ti} is the fraction of $\text{Ti}_{\text{IP}}^{n+}$. The number of excess electrons, n , may be 0, 1, 2, 3, or 4, corresponding to the exponent -1 , $-1/2$, $-1/3$, $-1/4$, or $-1/5$ for the oxygen pressure.

Mutual interaction of the defects, combinations of two or more defect types, or stoichiometric defects should be expected to give correlations different from those above, and in such cases one would probably not obtain linear variations of the weight loss *versus* oxygen pressure in any power. Phase changes should be expected to be indicated by discontinuous losses of weight at particular temperatures and oxygen pressures. Impurities in the rutile should be expected to influence the results, particularly impurities introducing ions of valences different from those of the host lattice.

While the present investigation was under way, similar experiments were started and carried out by Kofstad.⁶ He studied the non-stoichiometry of rutile by means of a thermobalance very similar to the one used in the present investigation, in the temperature range 1200–1500°K. He found oxygen vacancy concentrations proportional to $P_{O_2}^{-1/2}$, and calculated the enthalpy of oxygen vacancy formation in rutile to be $\Delta H^\circ = 131$ kcal/mole.

Tannhauser⁷ studied the electrical conductivity of rutile in the temperature region 1388–1740°K and the oxygen pressure region $1-10^{-14}$ atm. He found the electrical conductivity to be proportional to $P_{O_2}^{-1/2}$.

II. EXPERIMENTAL

The present investigation was carried out by measuring the weight changes of a rutile sample in a thermobalance in the temperature region 934 – 1194°C, and at oxygen partial pressures in the region $10^{-7}-10^{-16}$ atm.

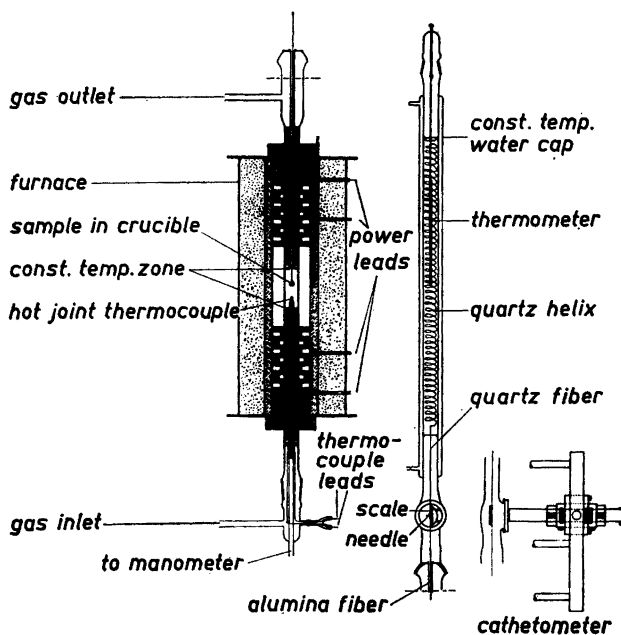


Fig. 1. The thermobalance used in the investigations.

The *material* used was Standard Sample 154a from U.S. Department of Commerce, National Bureau of Standards, consisting of 99.6 % TiO_2 (dried at 105°C). The following data on the analysis of the sample are given by National Bureau of Standards: "Loss on ignition — 0.23, SiO_2 — 0.01, Fe_2O_3 — 0.004, P_2O_5 — 0.05. Spectrographic analysis indicates the presence of Al, Ba, Ca, Cu, Mg, Pb, and Sb in amounts probably less than 0.01 % each. These values have not been established with sufficient certainty to warrant certification and are given only as a matter of general information". The weight of the sample used was 0.84310 g.

Experimental procedure. Fig 1. shows the construction of the balance used. The weight change was found by measuring the elongation of a silica glass helix from which the sample was suspended. The sample was placed in a zirconium dioxide crucible in the center of an electric furnace. The crucible was suspended from a thin alumina fiber connected with the quartz glass helix by means of a silica fiber.

The temperature of the sample was measured with a Pt-Pt 10% Rh thermocouple placed close to the sample in the furnace room. The heating current of the electric furnace was adjusted to give no significant temperature difference between the sample and the hot joint of the thermocouple.

The desired oxygen pressures were obtained by passing proper mixtures of carbon monoxide and carbon dioxide of atmospheric pressure over the sample. The oxygen pressures of the different mixtures at the different temperatures were calculated by means of data for the equilibrium $\text{CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2$ given by Coughlin,⁸ Kelly,⁹ and Kelley and King.¹⁰

The weight measurements were equilibrium measurements. When prolonged heating at constant oxygen pressure and constant temperature gave no weight change, the sample was supposed to be in equilibrium with the oxygen atmosphere. It was checked that equilibrium could be reached both from the side of increasing weight and from the side of decreasing weight.

A detailed description of the construction, operation and calibration of the experimental equipment and its limitations will be given elsewhere.¹¹

Before the measurements were carried out the sample was preheated at 1200°C for several days in oxygen pressures ranging from 1 atm to $10^{-13.5}$ atm to insure that no irreversible weight loss should occur during the measurements.

III. EXPERIMENTAL RESULTS

Table 1 shows the temperatures of measurements, the ranges of oxygen pressures and the logarithm of the weight loss *versus* the logarithm of the

Table 1. The temperatures of the measurements ($t^\circ\text{C}$), the ranges of oxygen pressures (P_{O_2} , atm) and the logarithm of the weight loss *versus* the logarithm of the oxygen pressure ($\log_{10}w/\log_{10}P_{\text{O}_2}$).

$t^\circ\text{C}$	P_{O_2} , atm	$\log_{10}w/\log_{10}P_{\text{O}_2}$
934	$10^{-11.1} - 10^{-16.1}$	-1/6.68
995	$10^{-10.9} - 10^{-15.1}$	-1/6.40
1051	$10^{-9.9} - 10^{-15.2}$	-1/6.39
1099	$10^{-9.3} - 10^{-14.1}$	-1/6.06
1151	$10^{-7.2} - 10^{-13.7}$	-1/6.03
1194	$10^{-6.8} - 10^{-13.4}$	-1/6.01

oxygen pressure, which represents $-1/a$ in the equation $\text{weight loss} = \text{const. } P_{\text{O}_2}^{-1/a}$. The values of $\log_{10} w / \log_{10} P_{\text{O}_2}$ were calculated by the method of least squares.

Only at the higher temperatures the weight loss is clearly proportional to $P_{\text{O}_2}^{-1/6}$ which is in agreement with eqn. Ia (p. 1268). As the other equations correlating weight loss and oxygen pressure give proportionalities with $P_{\text{O}_2}^{-1/a}$ where $a < 6$, the equilibrium equation Ia was adopted, and the weight change *versus* $P_{\text{O}_2}^{-1/6}$ was studied. The elongation of the helix was plotted *versus* $P_{\text{O}_2}^{-1/6}$ at different temperatures. Extrapolation of the best fitting straight lines through these points showed that the lines met at the same point at infinite pressure. This point was assumed to represent the ideal TiO_2 lattice, and the percentages vacant oxygen positions at the different temperatures and oxygen pressures were calculated on this assumption.

Fig. 2 shows the percentage vacant oxygen positions as a function of $P_{\text{O}_2}^{-1/6}$ at different temperatures. The slopes, k , of the lines at the different temperatures were calculated by the method at least squares.

$$\% [\text{AV}] = k \cdot P_{\text{O}_2}^{-1/6}$$

The equilibrium constant for reaction Ia:

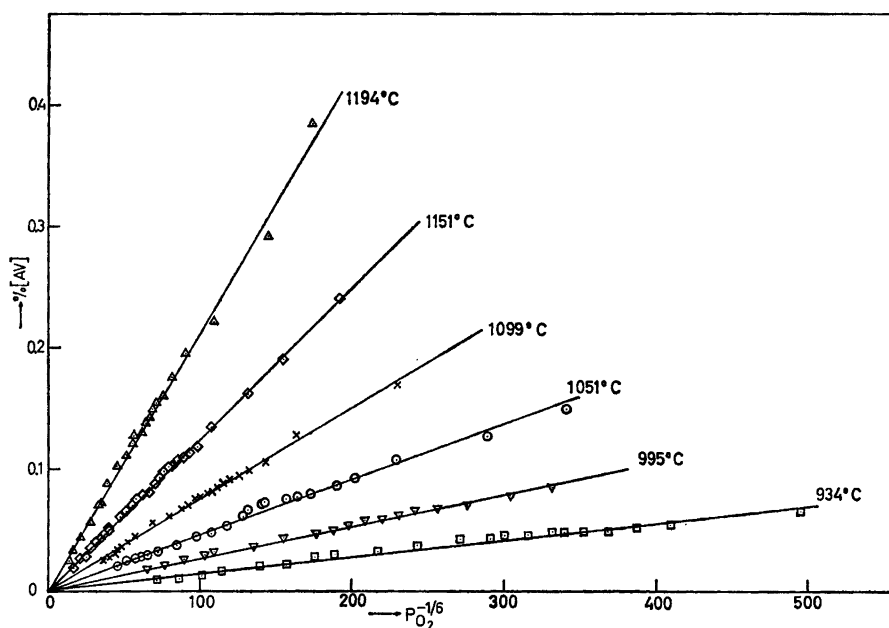


Fig. 2. Percentage vacant oxygen positions *versus* $P_{\text{O}_2}^{-1/6}$. \square 934°C; ∇ 995°C; \circ 1051°C; \times 1099°C; \diamond 1151°C; \triangle 1194°C.

Table 2. The slopes of the lines in Fig. 2 (k), the standard deviation of the percentages vacant oxygen positions (St.d. % [AV]), the equilibrium constants (K), the Gibbs free energy divided by the absolute temperature ($-R \log_e K$), the inverse absolute temperatures ($1/T$) at the different temperatures of measurements ($t^\circ\text{C}$).

$t^\circ\text{C}$	k	St.d.%[AV]	K	$-R \log_e K$	$1/T$
934	1.389×10^{-4}	0.0005	1.072×10^{-17}	77.65	8.234×10^{-4}
995	2.635×10^{-4}	0.0004	7.318×10^{-17}	73.83	7.888×10^{-4}
1051	4.575×10^{-4}	0.0007	3.830×10^{-16}	70.54	7.555×10^{-4}
1099	7.537×10^{-4}	0.0004	1.713×10^{-15}	67.57	7.290×10^{-4}
1151	1.240×10^{-3}	0.0004	7.630×10^{-15}	64.60	7.024×10^{-4}
1194	2.127×10^{-3}	0.0014	3.850×10^{-14}	61.38	6.816×10^{-4}

is

$$K = \frac{N_{[\text{AV}]} N_{\Theta}^2 P_{\text{O}_2}^{+1/2}}{N_{\text{O}^{2-}}} = 4 \times 10^{-6} k^3$$

where $N_{\Theta} = 2 N_{[\text{AV}]}$.

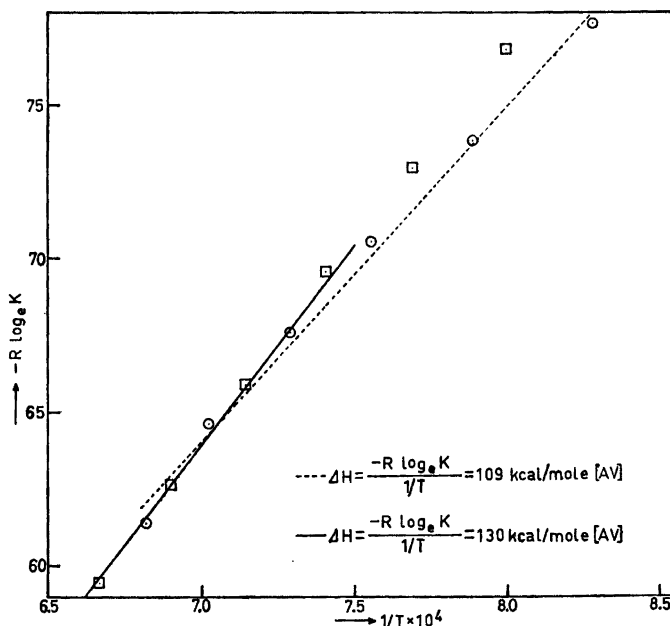


Fig. 3. $-R \log_e K$ versus $1/T \times 10^4$. \circ The present investigation; \square Kofstad.⁶

The enthalpy of oxygen vacancy formation may be determined from the equations:

$$\Delta G^\circ = RT \log_e K$$

and

$$\left(\partial \frac{\Delta G^\circ}{T} / \partial \frac{1}{T} \right)_P = \Delta H^\circ$$

The slope of the dotted line in Fig. 3 gives the average enthalpy of oxygen vacancy formation in rutile in the temperature interval 934–1194°C:

$$\Delta H^\circ = 109 \text{ kcal/mole.}$$

The slope of the solid line in Fig. 3 gives the average enthalpy of oxygen vacancy formation in rutile in the temperature interval 1099–1194°C, where the weight loss is clearly proportional to $P_{O_2}^{-1/2}$:

$$\Delta H^\circ = 130 \text{ kcal/mole}$$

IV. DISCUSSION

The best fitting curve for $-R \log_e K$ versus $1/T$ for the temperature range 934–1194°C would have a slight bend indicating that the enthalpy of oxygen vacancy formation increases with temperature (Fig. 3). At the higher temperatures 1099–1194°C the values obtained in the present investigation are in a very good agreement with the values obtained by Kofstad.⁶

At the lower temperatures 934–1051°C $a > 6$ for the weight loss versus $P_{O_2}^{-1/2}$. This does not fit with any of the ideal equations for defect formation. An absorption of surface oxygen at the higher pressures and mutual interaction of the defects might explain these results, but the weight changes at temperatures up to 1050° are too small to permit any conclusions on the mutual interaction of defects.

At these small defect concentrations one would also expect small amounts of impurities to affect the shape of the curves. Kofstad's measurements⁶ showed a shape of the curves at 977°C and 1027°C different from the shapes obtained at the lower temperatures in the present investigation. The cause of this discrepancy may be the use of different raw materials not containing identical impurities in the two investigations.

The highest percentage of oxygen vacancies obtained is 0.384 % at 1194°C and $P_{O_2} = 10^{-13.4}$ atm, which correspond to $TiO_{1.99232}$. Thus the present measurements do not overlap the measurements by Andersson, Magnéli and co-authors.²

Czanderna and Honig³ found no subsequent oxygen uptake in TiO_2 at temperatures up to 1000°C after treating pure TiO_2 at a pressure 10^{-4} Torr or lower. According to the present measurements the weight loss from an ideal TiO_2 crystal would be extremely low at 10^{-4} Torr oxygen pressure. At 995°C the weight loss would be less than 0.01 % at oxygen pressure 10^{-8} Torr.

To compare the results with those obtained by Brauer and Littke⁴ the present data were extrapolated to much higher temperatures using the value

Table 3. The composition found by Brauer and Littke ⁴ (B and L) compared with the compositions at the same temperatures and oxygen pressures extrapolated from the results of the present investigation (F).

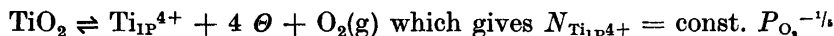
Oxygen pressure (Torr)	Temperature (°C)	Composition	
		B and L	F
10 ⁻³	1795	TiO _{1.989}	TiO _{1.979}
15	1820	TiO _{1.990}	TiO _{1.993}
159	1830	TiO _{1.996}	TiO _{1.995}

$\Delta H^\circ = 130$ kcal/mole. This is stretching the data far beyond the measuring range. The results, however, are in good agreement with the results obtained by Brauer and Littke; see Table 3.

The values obtained in the present work do not agree so well with the values obtained by Straumanis and co-authors.⁵ Extrapolations to 1400°C using the value $\Delta H^\circ = 130$ kcal/mole, gives the composition TiO_{1.9995} at an oxygen pressure of 12 Torr compared with the value TiO_{1.9876} obtained by Straumanis and co-authors. At 0.005 Torr the composition will be TiO_{1.9981} compared with the value TiO_{1.9832} obtained by Straumanis and co-authors.

Straumanis and co-authors carried out their experiments heating the titanium dioxide in an alundum crucible. During the experiments leading to the present results, it was found that the choice of crucible material was important. A crucible of pure aluminium oxide, *e.g.*, led to continuous weight loss with time at temperatures even below 1000°C. This weight loss may be caused by a reaction between the crucible and the sample. A crucible of pure zirconium dioxide appeared not to interfere with the measurements, the original weight of the sample could be reproduced repeatedly by increasing the oxygen pressure to one atmosphere. At present, investigations are being carried out by the author to study the effects of small amounts of aluminium oxide in titanium dioxide.

The results obtained in the present investigation are not in agreement with those obtained by Tannhauser.⁷ His results agree best with the equation:



With reference to the work by Kofstad⁶ Tannhauser points out that a very small shift in the assumed stoichiometric weight of the sample will change the exponent from $-1/6$ to $-1/5$.

The most important evidence for the exponent $-1/6$ in the present investigation is the determination of the stoichiometric weight. When plotting the elongation of the helix *versus* $P_{\text{O}_2}^{-1/6}$, the extrapolations of the best fitting straight lines met at the same point at infinite pressure. On the other hand there are some uncertainties connected with the determination of defects from electrical conductivity measurements, the method used by Tannhauser.⁷

Contact resistance, variations in electron mobilities, and, for polycrystalline material, grain boundary conductivity may influence the results.

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