

The TiO₂ Phase Explored by the Lattice Constant and Density Method*

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Samples of TiO₂ of various colours (bluish black to yellowish white) were obtained by heating TiO₂ at 1400 °C. under oxygen of increasing pressure. At that temperature the dissociation pressure is about 2/3 atm. (in oxygen). The homogeneity region of the phase extends from about TiO_{1.983} to TiO_{2.000} (39.845 to 40.05% b.w. of oxygen). The composition of the samples was determined from lattice parameter and density measurements. TiO₂ of stoichiometric composition has a sound lattice with $n' = 1.9999 \pm 0.0009$ molecules per unit cell. The structure of the grayish and deeper coloured samples is imperfect, caused by missing oxygen ions (up to 0.034 ions per unit cell or 0.85% of all oxygen positions are vacant at the left phase border).

The lattice constants of the tetragonal TiO₂-phase varied only slightly with increasing oxygen content (a increased and c decreased). The constants of stoichiometric TiO₂ were obtained by extrapolation: $a_{25} = 4.5937_3$ and $c_{25} = 2.9581_2$ (precision: ± 0.00005 Å); $c/a = 0.6439_5$; $v_{25} = 62.423 \pm 0.004$ Å³; the expansion coefficients between 10 and 60 °C. were $\alpha_a = 6.9 \times 10^{-6}$ and $\alpha_c = 9.9 \times 10^{-6}$ along the a - and c -axes respectively. The macroscopic density of TiO₂ was: $d_{25} = 4.2493 \pm 0.0005$ g.cm.⁻³. The density of the preparations decreased with decreasing oxygen content; their expansion coefficients were within the limits of error independent of composition.

Introduction

Ehrlich (1939, 1941) found that the narrow TiO₂ phase extends from 38.81 to 40.09% by weight of oxygen within the Ti-O system, that the phase is tetragonal and is equivalent to rutile in structure. Other authors reported a more extended homogeneity range (McQuil-lan). Lattice constant and density measurements were made by many authors, among whom were Ehrlich (1939), Schossberger (1942), Baur (1956), Andersson *et al.* (1957*a, b, c*). In comparing the results of these workers, there is some disagreement in the extent of the TiO₂ phase, in the magnitude of lattice parameters and in densities; the expansion coefficients and the perfection of the phase were not investigated at all. The aim of this publication is, therefore, to elucidate the two latter points, for which, of course, lattice parameter and density measurements of extreme precision are necessary. Again, it must be emphasized that the precision of the measurements attained concerns their reproducibility but not the absolute value (accuracy) of the final results. Efforts were made to estimate the systematic errors involved.

Experimental procedure and analyses

Preparation of samples

A transparent, yellowish rutile single crystal (sample I) made by a flame fusion process, was supplied by the Titanium Division of the National Lead Company. A yellowish powder was prepared by

heating TiO₂ under oxygen at 1400 °C. and then under fused NaCl at 1200 °C. according to Williamson (sample II).

Five further samples (III to VII) of increasing blackness (TiO_{1.990} down to TiO_{1.983}) were prepared as follows (for determination of composition see p. 496): An amount of dry titanium dioxide, 99.9% purity, supplied by the Baker Chemical Company, was compressed in a die under a pressure of 1500 psi. The resulting briquettes were heated in an alundum crucible in a vacuum resistance furnace at 1400 °C. for four or more hours. The charge, usually sintered to one solid piece of black color (with Ti/O = 1.98 and less), caused by oxygen loss due to dissociation of TiO₂, was reheated again under the same conditions for one hour and then a certain amount of oxygen gas was introduced into the system (by means of a special burette) and was held at 1400 °C. until equilibrium (four or more hours). Then the tube containing the sample was quenched in air to room temperature. The briquettes of different color, obtained at oxygen pressures between 360 and 0.005 mm. Hg were crushed, ground and stored in a dessicator. No change in oxygen pressure was found during heating of the samples at 1400 °C.

Composition and purity of the samples

Approximately one gram of sample was heated in a platinum crucible over a Bunsen burner for 20 min. in bright red heat, then cooled in a dessicator. Assuming that the final white product was TiO₂, the composition of the samples was estimated from their gain in weight. Four of the samples prepared in oxygen

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Table 1. Concentration of trace impurities in wt. % in samples I and III

Impurity	Sample	Sample	Impurity	Sample	Sample
	I	III		I	III
	less than			less than	
SiO ₂	0.06	0.06	Cu	0.0002	0.0002
Al ₂ O ₃	0.02	0.02	Pb	—	0.001
Fe ₂ O ₃	0.002	?	Mn	?	—
Sb ₂ O ₃	0.001	0.001	W	0.005	—
SnO ₂	0.001	0.001	Cr	0.001	—
Mg	0.0005	—	Ni	0.001	0.001

TiO₂ about 99.91(I) and 99.92(III) wt. %.

under reduced pressure did not show any weight change at all, except the darkest one (sample VII) obtained at 0.005 mm. pressure. A more exact determination of composition was made by the lattice constant and density method.

Spectrographic analyses were carried out for the estimation of trace impurity concentration (Table 1).

The powder patterns

Co K α_1 radiation ($\lambda = 1.78529$ kX.) was selected because the lines 042 and 150 appeared under high back reflection angles of 80 and 83 degrees. The indexing was made using the constants obtained by Schossberger for rutile ($a = 4.589$, $c = 2.954$ kX.). Rotating and scanning of the powder mounts during three hours of exposure developed the line doublets (α_1 , as well as α_2) to an intensity sufficient for accurate measurements.

To reduce the effect of the fluorescence radiation, thin aluminum foil was used to cover the film. The powder mounts were thin enough (0.12 mm. in diam.) to disregard the line shift due to absorption (Straumanis, 1959, 1960).

Lattice constants, coefficients of thermal expansion and densities of rutile

Thermal expansion coefficients between +10 and 60 °C.

Using the usual equations the a and c constants were calculated from the measured Bragg angles. The simple average of three (or more) values of the respective lattice constants obtained at a certain constant temperature was taken as a final value. Assuming a straight line relation throughout the temperature interval mentioned, the thermal linear expansion coefficients along the tetragonal a and c axes between 10 and 60 °C. for three TiO₂ solid solu-

Table 2. Thermal linear expansion coefficients of the tetragonal a and c constants between 10 and 60 °C.

Sample no.	α_a (in kX./°C. $\times 10^6$)	α_c (in kX./°C. $\times 10^6$)
I	6.5	9.7
IV	7.4	10.9
V	6.8	9.1
Average	6.9	9.9

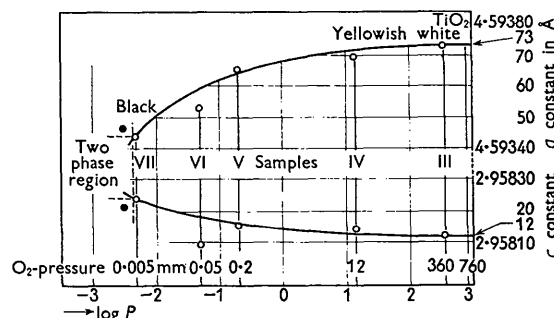
tions were computed (Table 2). As the linear expansion coefficients were very small and there was no systematic change with composition the average of the values was taken for pure TiO₂.

Lattice constants at 25.0 °C.

With the coefficients of Table 2 the values of the lattice constants obtained at different temperatures were reduced to 25.0 °C.

From the scatter of these values the standard deviation was calculated. The refraction correction of +0.00008 kX. for the a constant and +0.00005 kX. for the c constant was added. The final and corrected values of the lattice constants for each of the samples are given in Table 3.

Table 3 shows that except for samples I and II which were prepared by different methods, the a -constants decrease and the c -constants increase, but only very slightly, with the deepening of color of the samples, indicating a decrease in oxygen concentration (see also Fig. 1), and, hence, the changes in the lattice spacings.

Fig. 1. Variation of tetragonal lattice a and c constants of TiO₂ with equilibrium oxygen pressure (during heating).

It follows from Fig. 1 that the amount of oxygen uptake by the TiO₂ phase is dependent on pressure of oxygen. The results are similar to those observed by Kennedy *et al.* (1958).

The lattice constants at 25.0 °C. for pure TiO₂ were obtained by graphical extrapolation (see Fig. 1), and they are:

$$a = 4.5937_3 \pm 0.0000_5, c = 2.9581_2 \pm 0.0000_5 \text{ \AA}.$$

Table 3. *The final a and c constants in Å of TiO₂ preparations at 25 °C.*

Sample no.	Color	a (Å)	c (Å)
I	Yellowish	4.59356 ± 0.00004*	2.95820 ± 0.00002
II	V. l. yellow	4.59327 ± 0.00006	2.95833 ± 0.00011
III	Light yellow	4.59373 ± 0.00018	2.95812 ± 0.00015
IV	Silverish gray	4.59369 ± 0.00005	2.95814 ± 0.00005
V	L. gray	4.59365 ± 0.00007	2.95815 ± 0.00002
VI	Bluish gray	4.59353 ± 0.00016	2.95809 ± 0.00016
VII	Blue black	4.59344 ± 0.00007	2.95824 ± 0.00010

* Standard deviations at a confidence limit of 50%.

Table 4. *Axial ratio, c/a, volume of the tetragonal unit cell, etc. at 25.0 °C. of 7 TiO₂ preparations*

Sample no.	c/a _{25.0}	Coefficient of c/a × 10 ⁵	Volume in Å ³	β expansion coefficient × 10 ⁵
I	0.6439 ₅ ± 1*	3.5	62.420 ± 2*	2.3
II	0.6440 ₁ ± 3	—	62.415 ± 4	—
III	0.6439 ₅ ± 6	3.5	62.423 ± 8	2.6
IV	0.6439 ₆ ± 2	2.4	62.423 ± 2	2.3
V	0.6439 ₇ ± 2	—	62.422 ± 2	—
VI	0.6439 ₇ ± 2	—	62.417 ± 8	—
VII	0.6440 ₁ ± 2	—	62.418 ± 4	—
Average for TiO ₂		3.1†		2.4†

* Error in the last decimal place, standard deviation at 50% confidence error limits.

† Since no systematic change in the expansion coefficients with composition could be found, the average of the values was taken for pure TiO₂.

c/a ratio; the volume expansion coefficient

The axial ratios, the coefficient of change of these ratios with temperature, the volume of the tetragonal unit cell, and the thermal volume expansion coefficients are summarized in Table 4. The latter were calculated from

$$\beta = 2\alpha_a + \alpha_c \quad (1)$$

The *c/a* and the volume of the tetragonal unit cell at 25.0 °C. for pure TiO₂ was calculated from the extrapolated lattice constants and is:

$$c/a_{25} = 0.6439_5 \pm 0.00005 \quad \text{and} \quad v_{25} = 62.423 \pm 0.004 \text{ Å}^3.$$

Densities

The density of the samples was determined by the modified Baker & Martin method. The results obtained are summarized in Table 5.

Table 5. *Densities of TiO₂ preparations at 20.0 and 25.0 °C.*

Samples III to VII—decreasing oxygen content		
Sample no.	Density at 20.0 °C. (g.cm. ⁻³)	Density at 25.0 °C. (g.cm. ⁻³)
I	4.2498 ± 9*	4.2493 ± 9*
II†	—	—
III	4.2413 ± 6	4.2408 ± 6
IV	4.2388 ± 9	4.2383 ± 9
V	4.2372 ± 8	4.2367 ± 8
VI	4.2371 ± 14	4.2366 ± 14
VII	4.2361 ± 8	4.2356 ± 8

* Error in the last decimal place, standard deviation, 50% confidence error limits.

† Due to insufficient amounts of this sample, the density was not determined.

Discussion

The extent of the phase TiO₂

In the last few years, the existence of a new oxide phase Ti₁₀O₁₉(TiO_{1.9}) has been observed by Magnéli and his co-workers (1957*a, b, c*). In his report, it is also mentioned that the minimum oxygen content of the homogeneous phase TiO₂ is approximately of the composition TiO_{1.96}. However, it was not possible to prove the existence of a two-phase region between TiO_{1.90} and TiO_{1.96} by the experimental method used.

In the present investigation it was found that the first trace of a new phase appeared at the composition TiO_{1.983}, where the amount of missing oxygen could be estimated by complete burning of the sample (color changed from black to yellow). The intensities of the new lines increased with decreasing oxygen content of the sample (two phase region). These faint new lines escape observation if the powder mounts are not thin enough to produce sharp lines on the films. Thus, the homogeneity region of the TiO₂ phase is narrower than previously thought: it extends from TiO_{1.983} to TiO_{2.000} (see Table 6).

Chemical composition from X-ray and density measurements

Due to the insufficient accuracy of chemical analysis, it was not possible to determine the composition of the TiO₂ solid solutions the composition of which was varied in such a narrow range of homogeneity. However, the lattice constant and density method using the volume *v* of the unit cell and the macroscopic

density d , was well suited for this purpose. The number n of molecules present in the unit cell is:

$$n = N_0vd/M \quad \text{or} \quad nM = N_0vd, \quad (2)$$

where, the product N_0vd is known. M is the chemical molecular weight. If the solid solution consisting of elements of the atomic weights A and B is expressed by AB_x , then:

$$nM = n(A + xB) = N_0vd, \quad (3)$$

x being the atomic ratio.

In the event of loss in B , not detectable by normal chemical quantitative methods, it is assumed (see below) that $n = 2$ (for pure TiO₂). Thus,

$$nM = 2A + 2xB = N_0vd \quad (4)$$

or for the TiO₂ preparations

$$x = (N_0vd - 2A)/2B = (N_0vd - 2 \times 47.9)/2 \times 16. \quad (5)$$

The oxygen indices (x) of the solid solutions were calculated from (5), and are summarized in Table 6. Similar results are obtained calculating the loss of oxygen directly from the changes in density, assuming no alteration of the volume of the unit cell.

Table 6. Atomic ratios O/Ti of 7 preparations within the homogeneous phase TiO₂

Sample no.	Atomic ratio, O/Ti
I	1.999 ₅
II	—
III	1.990 ± 0.0020
IV	1.986 ₇
V	1.984 ₇
VI	1.984 ₃
VII	1.983 ₂

The calculations were made using $N_0 = 6.02403 \times 10^{23}$ for Avogadro's number (Straumanis, 1953a, b, 1954). However, if a smaller number is used e.g. 6.02368×10^{23} (Smakula *et al.*, 1955), the changes are insignificant. Values completely within the limits of error given are

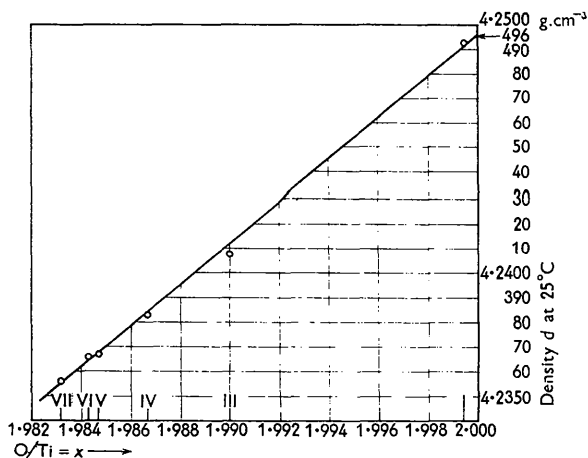


Fig. 2. Variation of density with composition within the titanium dioxide phase.

also obtained if instead of the normal atomic weight of Ti (=47.90) a larger value is used (47.905, due to the presence of heavy atoms in the TiO₂, see analyses). This investigation shows that on the oxygen rich border of the phase there is stoichiometric TiO₂, containing 40.05% by weight oxygen, but with a density slightly higher than that of prep. I, as it follows from the atomic ratio and macroscopic density plot (Fig. 2).

The method for the determination of the chemical composition is well founded and accurate (Straumanis, 1948, 1953a). However, in cases as the present it is necessary to know which element is in a non-stoichiometric quantity.

Imperfections within the TiO₂-phase

Since the molecular weights of the solid solutions could not be determined from chemical analysis, the number n' (actual number of molecules per unit cell) was found only for pure TiO₂, using the same equation as above:

$$n' = N_0vd/M, \quad (2a)$$

where M is the molecular weight of stoichiometric TiO₂. v was calculated from the extrapolated lattice constants (Fig. 1), and for d the density of sample I (at 25 °C.) was substituted, since the density of the preparations increased strongly (Table 5) with the index x of the preparations (or with their brightness, or increasing oxygen pressure during synthesis). A value of $n' = 1.9999 \pm 0.0009$ molec./u. cell was found, which compares favorably with the ideal value (2 for TiO₂) within the limits of error, meaning that the lattice at the composition TiO₂ is sound. However, this result is not self-evident at all, because a substance of stoichiometric composition like TiO shows 15.5% vacant sites with a $n' = 3.85$ (Ehrlich, 1939; Straumanis *et al.*, 1960), instead of 4 as required for the NaCl structure.

Hence, the other preparations within the TiO₂-phase prove to be of defect structure exhibiting less oxygen. The concentration of empty oxygen sites [=2(x-2)] at the left border of the phase (39.845% oxygen by weight) is then about 0.034 sites/unit cell, and it becomes zero at 40.050% O (stoichiometric TiO₂). To compensate for the loss of negative charges, an equivalent amount of Ti⁴⁺ should be in a Ti³⁺ state, which explains the dark color of the preparations. On the right side of the phase (containing 40.05% O b.w.) no excess oxygen was found, although there are some reports (Czanderna & Honig, 1959) showing that TiO₂, especially preparations of commercial grade absorb oxygen at elevated temperatures.

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The Crystal Structure of N-Benzyl-1,4-Dihydronicotinamide

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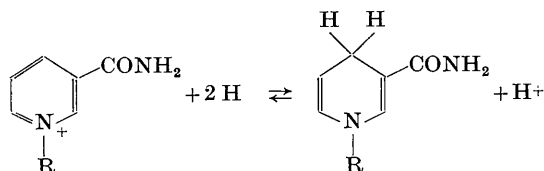
The structure of N-benzyl-1,4-dihydronicotinamide has been determined from three dimensional X-ray single crystal data. The space group is $P2_1/c$ and $Z=4$. The unit-cell dimensions are

$$a = 12.07, b = 5.86, c = 20.82, \beta = 129^\circ 30'$$

The structure was determined directly from the intensities by the application of probability methods to obtain the phases. The dihydronicotine ring is planar with $C=C = 1.32 \text{ \AA}$, $C-C = 1.51$ and 1.53 \AA , and $C-N = 1.43$ and 1.38 \AA . The amide group is nearly in the same plane as the dihydronicotine ring. The plane of the benzene ring makes an angle of 83° with the plane of the dihydronicotine ring. Hydrogen bonds connect pairs of molecules into centrosymmetrical dimers.

1. Introduction

Nicotinamide derivatives are essential dietary constituents for many animals. The nicotinamide residue performs an oxidation-reduction function:



When R is ribose pyrophosphate adenosine, we have the coenzymes DPN and DPNH, respectively. N-benzyl dihydronicotinamide, an analog of DPNH, serves as a good model for the DPN-DPNH transhydrogenase system (Mauzerall & Westheimer, 1955). The crystal structure of nicotinamide has been determined by Wright & King (1954). The particular

interest in the dihydronicotinamide derivative is whether the dihydronicotine ring is planar.

2. Experimental measurements

The crystals were yellow, transparent laths, with the b axis as the needle axis. They were very thin. Unit cell dimensions were obtained from rotation and precession photographs. The crystallographic data are:

$$a = 12.07, b = 5.86, c = 20.82, (\text{all } \pm 0.3\%), \\ \beta = 129^\circ 30' \pm 10', \text{ space group } P2_1/c, Z=4, \\ \rho(\text{X-ray}) = 1.252 \text{ g.cm.}^{-3}, \rho(\text{physical}) = 1.257 \text{ g.cm.}^{-3}.$$

Equi-inclination Weissenberg photographs were taken about the b axis, zero through the fourth layer. The shape of the crystals precluded obtaining good intensity data along the other axes. The zero layer about the a axis was used for those $0kl$ reflections