The Prediction of K_{sp}'s.—These relationships can be used to predict the K_{sp}'s of unknown substances or substances for which the K_{sp}'s are not known. For example from (1) we calculate the pK_{sp} for AuS to be 78. The upper limit of the oxidation potential for the Au–Au^{++} couple calculated from this agrees well with the potential estimated from Taube's[5] values for the chloro complexes. Some other calculated values are shown in Table II.
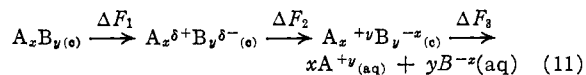
TABLE II
CALCULATED pK_{sp}'s

AuS	78	Au₂S₃	113	Ag(OH)₃	50
AgS	62	Mn₂S₃	47	Cu(OH)₃	48
TlS	38	Cr₂S₃	55	Au(OH)₂	39
CrS	14	V₂S₃	39	Ag(OH)₂	36
VS	− 2	Ti₂S₃	35	InI	8
TiS	−10	Sc₂S₃	30	InCl	1

Discussion

A justification for this relationship may be developed as follows.

Let the process of dissolution of a completely covalent substance A_xB_y to give ions A^{+y}(aq) and B^{-x}(aq) be represented as

$$A_xB_{y(c)} \xrightarrow{\Delta F_1} A_x{}^{\delta+}B_y{}^{\delta-}{}_{(c)} \xrightarrow{\Delta F_2} A_x{}^{+y}B_y{}^{-x}{}_{(c)} \xrightarrow{\Delta F_3}$$
$$xA^{+y}{}_{(aq)} + yB^{-x}(aq) \quad (11)$$

where $(\Delta F_1 + \Delta F_2)$ is the total ΔF required for transition from the completely covalent crystalline state to the completely ionic crystalline state, and where $A_x{}^{\delta+}B_y{}^{\delta-}$(c) represents the actual state of a substance for which the electronegativities of A and B are not the same. Let us further note that the free energy of dissolution of the completely covalent substance

$$\Delta F_0 = \Delta F_1 + \Delta F_2 + \Delta F_3 \quad (12)$$

and that the free energy of dissolution of the actual substance

$$\Delta F_{sp} = \Delta F_2 + \Delta F_3 \quad (13)$$

and

$$\Delta F_0 = \Delta F_1 + \Delta F_{sp} \quad (14)$$

It easily can be seen that the degree of ionic nature of A_xB_y is

$$I = \frac{\Delta F_1}{\Delta F_1 + \Delta F_2} \quad (15)$$

or for single covalent bonds, according to Hannay and Smyth[6]

$$I = 0.16\Delta x + 0.035(\Delta x)^2 \quad (16)$$

or

$$I \approx 0.16\Delta x \text{ for } \Delta x < 0.5 \quad (16')$$

Let us now consider the cases of highly covalent substances, for which $\Delta x < 0.5$. For these cases it will also be true that $\Delta F_2 \gg \Delta F_1$ and, therefore

$$I \approx \frac{\Delta F_1}{\Delta F_2} \quad (15')$$

Combining (15') and (16') and substituting an indefinite constant a for the coefficient 0.16 because of the many bonds involved

$$a\Delta F_2\Delta x = \Delta F_1 \quad (17)$$

Now combining (14) and (17)

$$\Delta F_0 = a\Delta F_2\Delta x + \Delta F_{sp} \quad (18)$$

Now noting that when $\Delta F_2 \gg \Delta F_1$, the percentage change in Δx will be much greater than the percentage change in ΔF_2, it can be seen that ΔF_2 is relatively constant, and, therefore

$$\Delta F_0 = b\Delta x + \Delta F_{sp} \quad (19)$$

or

$$\Delta F_{sp} = \Delta F_0 - b\Delta X$$

Since $\Delta F = 1.364 \, pK$, then

$$pK_{sp} = pK_0 - C\Delta x_0 \quad (20)$$

(5) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

(6) N. B. Hannay and C. P. Smyth, This Journal, **68**, 171 (1946).

LAFAYETTE, INDIANA

Preparation of Highly Purified TiO₂ (Anatase)

BY A. W. CZANDERNA, A. F. CLIFFORD AND J. M. HONIG

Spectroscopically pure TiO₂ has been prepared by dissolving silica-free titanium metal in an ammoniacal solution of 90% H₂O₂. Common impurities, such as Fe, Mn, Mg, Sn, Ni, Al, Ag were quantitatively removed by filtration. Care was taken to avoid contamination with Si, which could not be removed by this procedure. Upon driving off the peroxide, titania gel formed, from which crystals of TiO₂ 3 mm. on each edge were obtained by heating to 200°. The sample composition was established by titration of Ti³⁺ ion with ferric ammonium sulfate. X-Ray diffraction results showed that samples prepared in this manner were of the anatase structure.

Introductory Comments

In the course of research on properties of TiO₂, it became necessary to prepare this material in highly pure form. Several preparative methods have been described in the literature. Work up to 1950 has been summarized in Gmelin.[1] Since then, some additional work has been described.[2-4] The meth-

ods of procedure may be classified broadly as follows: (1) direct combination of titanium and oxygen; (2) treatment of titanium salts in aqueous solution; (3) reaction of volatile, inorganic titanium compounds with oxygen; (4) oxidation or hydrolysis of organic compounds of titanium.

Regarding method 1, the stoichiometry of the final product is likely to be indefinite and non-uni-

(1) "Gmelins Handbuch der Anorganischen Chemie," 8th Ed., Vol. 41, Gmelin Institut; Verlag Chemie. Weinheim, Germany, 1951, pp. 226–232.

(2) S. Teichner, *Compt. rend.*, **237**, 900 (1953).

(3) F. Trombe and M. Foëx, *ibid.*, **238**, 1419 (1954).

(4) S. Taki and M. Kunitomi, *J. Chem. Soc. Japan; Ind. Chem. Sect.*, **57**, 534 (1954).

form. Furthermore, any non-volatile metal oxide impurities initially present will remain in the product. Trombe and Foëx[3] claim to have removed trace impurities by heating TiO_2 beyond its melting point in a solar furnace. At such high temperatures a partial reduction of TiO_2 cannot be avoided. If methods 2 and 3 are used, there is likelihood of contamination due to incomplete removal of anions and other cationic constituents. In method 4 the presence of carbon due to incomplete reaction is a distinct possibility.

In an attempt to circumvent these difficulties, the following procedure was used. Titanium metal powder was dissolved in an ammoniacal solution of 90% hydrogen peroxide at a pH greater than 11. Spectroscopic analysis indicated that the common impurities Fe, Mg, Mn, Sn and Ni, Al, As, V in trace amounts could be removed essentially by filtration. Upon evaporation of the filtrate on a steam-bath, spectroscopically pure TiO_2 was formed.

All attempts to remove Si have failed to date; consequently it was necessary to use silica-free titanium metal as starting material. The latter, containing no more than 5 p.p.m. of silica[5] is commercially available from the Electrometallurgical Company. If desired, specific impurities can be introduced in controlled amounts just prior to the precipitation of the gel.

Using standard analytical procedures, the product was found to have a composition ranging from $TiO_{1.98}$ to $TiO_{2.01}$, which lies within experimental error of the stoichiometric ratio TiO_2. Using a Geiger Counter X-ray diffractometer, the crystal structure of the samples dried below 200° was found to correspond to that of anatase.

Method of Preparation.—In view of the difficulty encountered in the removal of silica, all reactions were carried out in polyethylene vessels and in platinum dishes. The latter required scrupulous cleaning in 48% HF containing one drop of H_2SO_4. Freshly prepared conductivity water was used throughout. In order to check on the possibility of Si contamination, the "molybdenum blue test"[6] was employed at every step in the procedure; the presence of $0.1\mu g$. of silicic acid is said to be detectable in this manner. Before testing the H_2O_2 solutions the peroxide was decomposed. Ninety per cent. H_2O_2 solutions, were found to be suitable for use, whereas the 30% solutions gave rise to a yellow coloration when the molybdenum blue test was applied, probably due to the presence of a phosphate stabilizer.

The procedure consisted of placing a weighed amount of titanium powder in a polyethylene container, adding 90% H_2O_2, and adding gaseous NH_3 by gentle warming of concentrated NH_4OH. The latter step required care, since if the distillation was allowed to proceed too rapidly, a positive molybdenum blue test for Si was obtained. As the solution became basic, a vigorous reaction ensued. It was necessary to dilute the solution with conductivity water and to use an ice-bath to control the reaction rate. The reaction in all probability is represented by

$$Ti + 3H_2O_2 + 2OH^- \longrightarrow TiO_4^- + 4H_2O$$
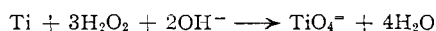
After all the solid had dissolved, the solution was filtered, more H_2O_2 being added, if needed, to prevent precipitation of titania gel at this stage. The filtrate was collected in a platinum evaporating dish and the excess H_2O_2 and NH_3 were driven off over a steam cone. (If desired, the sample can be doped just prior to this stage, by addition of measured amounts of the desired impurities in appropriate solu-

tions). Titania gel began to form after all the H_2O_2 was eliminated.

If drying was allowed to proceed for several hours, yellow crystals, approximately 3 mm. on each edge, were obtained. These, upon heating at 100–200°, assumed an ivory appearance. (Whenever the procedure was carried out with 30% H_2O_2 solutions, the final crystals exhibited yellow tinges in varying degrees of intensity.)

Purity of Samples.—The titanium powder was subjected to analyses using "spec pure" carbon electrodes in a Baird spectrograph. One of the commercial titanium powders used as a starting material for the synthesis of TiO_2 contained Fe (0.048%) as the chief impurity, and small amounts of Mg, Sn, Ni, Al, Ag and a trace of B. A molybdenum blue test for silicic acid carried out on the dissolved sample was negative, indicating the almost complete absence of Si. A second commercial sample contained Fe (0.2%), Mg (0.02%) and Si as the chief impurities; small amounts of Mg and Sn, and traces of Ni, Al and Ag were observed.

The corresponding oxide samples revealed Si lines at their original intensity, as well as the principal Fe and Mg lines at the very faint intensities of blank runs. This indicates that, with the exception of Si, all the common impurities in Ti powder can be eliminated by this procedure.

Composition of the Oxide.—The composition of the oven dried oxide produced was determined by dissolving the oxide in sulfuric acid, containing ammonium sulfate. Prolonged heating was required to dissolve the solid oxide. The solution was then reduced over zinc amalgam and the Ti^{3+} ion was titrated with ferric ammonium sulfate solution to a thiocyanate end-point. The ferric ammonium sulfate in turn had been standardized previously by reduction with zinc amalgam, followed by oxidation using a standardized permanganate solution.

Three distinct samples obtained from different preparations were analyzed. Their compositions, after correcting for a residual moisture content of $2.05 \pm 0.03\%$ as determined by vacuum drying at 450°, were found to be $TiO_{1.98}$ $TiO_{2.01}$, $TiO_{2.01}$. These values lie within the expected experimental error ($\pm 1\%$) of the composition TiO_2.

X-Ray Analysis.—A sample of pure TiO_2 and a second sample containing 0.1% by weight of barium oxide were subjected to an X-ray analysis. The samples were ground to a sufficiently small particle size and suspended in a collodion solution on a glass plate, as directed by Swanson and Tatge.[7] The samples were mounted on a North American Philips Company Geiger Counter X-ray diffractometer with a maximum sweep of 0 to 150°. The instrument was equipped with current and voltage stabilizers, counters and a strip chart recorder. A nickel filter was employed with copper $K\alpha$ radiation to give an incident wave length of 1.5405 Å. The diffractometer was calibrated with silicon powder. The accuracy and reproducibility of this instrument has been discussed by Klug and Associates.[8]

Table I

X-Ray Data for TiO₂

Sample	2θ (degrees)	d calcd., Å.	d (Anatase) (NBS values) Å.	Relative intensities This work	Relative intensities NBS	d (Rutile) (NBS values), Å.
Pure TiO_2	25.30	3.515	3.51	3.4	100	3.245
	37.90	2.370	2.379	1.0	22	2.489
	48.15	1.885	1.891	1.3	33	2.188
	54.05	1.695	1.699	1.0	21	1.687
	55.10	1.665	1.665	1.0	19	1.624
$TiO_2 + 0.1\%$ Ba(OH)₂	25.25	3.515	3.51	3.3	100	3.245
	37.95	2.370	2.379	0.8	22	2.489
	48.20	1.885	1.891	1.0	33	2.188
	54.10	1.695	1.699	0.7	21	1.687
	55.30	1.660	1.665	0.7	19	1.624

(5) Personal communication from the Electrometallurgical Company, Niagara Falls, New York.

(6) F. Feigl, "Spot Tests," 3rd English Edition, Elsevier Publishing Co., Inc., New York, N. Y., 1946, p. 252.

(7) H. E. Swanson and E. Tatge, "Standard X-Ray Diffraction Powder Patterns," N.B.S. Circular 539, Vol. 1, U. S. Government Printing Office, Washington, D. C., 1953, pp. 44–47.

(8) H. P. Klug, *Anal. Chem*, **25**, 704 (1953); H. P. Klug, L. Alexander and E. Kummer, *ibid.*, **20**, 607 (1948).

Absorption peaks at 2θ angles were recorded on the strip chart and the d values were calculated from the Bragg diffraction law. The results are shown in Table I.

There is excellent agreement in the d values obtained in this study with those previously reported.[7] Likewise, the relative peak intensities match as well as might be expected. No significant difference was found in the results obtained with the pure and the doped sample. The last column of the table shows that no confusion with the rutile pattern is possible. Neither the principal nor the second strongest rutile lines (at $d = 3.245$ and 1.687 Å., respectively) were found.

On this basis it is concluded that the above samples were both of the anatase structure.

Additional Observations.—An attempt was made to obtain larger single crystals of TiO_2 by dissolving the latter in a NaF–KF eutectic melt at high temperatures followed by very slow cooling. The melt was leached in conductivity water; the TiO_2 thus obtained was snow-white, but nevertheless contained considerable quantities of the alkali metal and fluoride ions. We were unable to obtain highly purified single crystals. Doped samples containing barium were much whiter than purified TiO_2. This shows again that the absence of color is not a suitable criterion of sample purity.

Upon heating the purified TiO_2 in air with a Meker burner, no color change was observed, even in the temperature range where a reversible white to yellow transition with commercial samples has been reported.

Heated *in vacuo* at $1000°$, the sample sustained a slight irreversible loss of oxygen. This was accompanied by the appearance of a greyish-black cast on the surface of the crystals.

Preparation and X-Ray Study of Niobium Pentaiodide

BY ROBERT F. ROLSTEN

Crystalline niobium pentaiodide was prepared by reaction of pure niobium and resublimed iodine at 250–285°. X-Ray diffraction data have been obtained.

Introduction

Niobium pentaiodide was first prepared[1] by the reaction between hydrogen iodide and niobium pentabromide. The stable product was not free from bromine and, therefore, was not analyzed. Körösy[2] prepared the pentaiodide by direct reaction of gaseous iodine and an electrically heated (1300–1500°) niobium filament. The red-to-brown colored solid could not be purified. Iodine was not eliminated at 200°, while at 300–400°, the pentaiodide dissociated into a lower iodide and iodine. His observed analytical values of 11.7% Nb, 88.3% I compared to the calculated values of 12.77% Nb, 87.23% I indicate that either niobium was not quantitatively precipitated or the pentaiodide was contaminated with free iodine. Alexander and Fairbrother[3] prepared well-defined, brass-like crystals of pentaiodide by the direct reaction of inductively heated 4–6 mil niobium sheet and excess iodine at 1–2 atmospheres pressure. Repeated attempts were made to analyze these crystals with somewhat inconsistent results arising from the difficulty of separating them quantitatively from traces of metal, lower iodides and from their reactivity on exposure to air. Their results, however, suggest that the crystals were essentially NbI_5.

Preparation

The Pyrex glass apparatus contained 1.8 g. of 5 mil acid-cleaned, acetone-dried niobium sheet contained in a 20 mm. tube (14–16 inches long) and resublimed iodine, 10 g. in excess of stoichiometry. The vacuum tight system, with the iodine reservoir cooled in Dry Ice, was heated to 500–

550° to outgas the metal and reaction bulb. A system pressure of less than 10^{-5} mm. was maintained for 48 hours. The reaction tube was cooled to room temperature, iodine sublimed from the reservoir was condensed as a solid in the reaction bulb and this bulb was then hermetically sealed. The temperature of the entire bulb was maintained at 265–271°. As the reaction progressed, the active niobium surface was reduced by the condensed, plate-like pentaiodide, which appeared to be black although individual platelets were bronze colored. The unit was slowly cooled to the melting point of I_2 (114°) and the excess iodine condensed at one end of the tube which was cooled in an air blast. The iodine removal operation was of 72-hour duration, necessitated by the low temperature level required to prevent disproportionation, or reduction by the residual niobium, of the pentaiodide to lower iodide. The reaction tube was opened in an argon-purged dry box and the lumps of pentaiodide stored in weighing tubes.

Although the above-mentioned preparation is quite satisfactory, it does have the disadvantage that all the available niobium is not transformed to pentaiodide. Therefore, in new experiments, the niobium sheet was supported on a flared and slotted Pyrex tube located in the center of the 20 mm. Pyrex reaction tube. The reaction was again carried out at 280–290° under a partial pressure of iodine to stabilize the temperature sensitive pentaiodide. The large bronze colored crystals were then collected in a very compact form at the bottom of the tube. The unit was opened in a dry box and the pentaiodide stored in weighing bottles. Niobium was determined as Nb_2O_5 by dissolving the sample in freshly filtered NH_4OH, evaporating to dryness, and heating in air in a platinum crucible. Iodine was determined by the modified Volhard[4] technique.

Anal. Calcd. for NbI_5: Nb, 12.77; I, 87.23. Found: Nb, 12.81, 12.70, 13.1, 12.70; I, 87.33, 87.55, 87.52, 87.24, 87.17.

X-Ray Study.—The solid pentaiodide was pulverized in an agate mortar cooled by Dry Ice inside an argon-purged dry box. The CO_2 provided both a protective atmosphere and permitted the crystalline NbI_5 to be pulverized easily. Samples hermetically sealed in 0.2 mm. Lindemann glass

(1) W. M. Barr, THIS JOURNAL, **30**, 1668 (1908).

(2) F. Körösy, *ibid.*, **61**, 834 (1939).

(3) K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, 2472 (1949).

(4) J. R. Caldwell and H. B. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).