

## CHAPTER III

### THEORY

It is known that titanium (Ti) can form a large number of addition compounds by coordination other substances such as hydrogen, nitrogen, boron, carbon, oxygen, and other systems. Titanium (IV) oxide is titanium compound that is the most important commercial form. Physical and chemical properties of titanium (IV) oxide have been studied to include preparation procedure and its advantages.

#### 3.1 Titanium (Ti)

Titanium (at no.22; ionization potentials: first 6.83 eV, second 13.67 eV, third 27.47 eV, fourth 43.24 eV) is the first member of Group IVB of the periodic chart. It has four valence electrons, and Ti (IV) is most stable valence state. The lower valence states Ti (II) and Ti (III) exist, but these are readily oxidized to the tetravalent state by air, water, and other oxidizing agents. The ionization potentials indicate that the  $Ti^{4+}$  ion would not be expected to exist and, indeed, Ti (IV) compounds are generally covalent. Titanium is able to expand its outer group of electrons and can form a large number of addition compounds by coordination other substances having donor atom, e.g., oxygen or sulfur. The most important commercial forms are titanium (IV) oxide and titanium metal.

#### 3.2 Thermochemical data

Thermochemical data of titanium (IV) oxide and other titanium compounds are described. Data relating to changes of state of selected titanium compounds are listed in Table 3.1. Table 3.2 gives values for heat of formation, free energy of formation, and entropy of a number of titanium compound at two temperature, 298 K and 1300 K.

**Table 3.1** Thermal data for changes of state of titanium compounds

Compound	Change	Temperature, K	$\Delta H$ , kJ/mol <sup>a</sup>
TiCl <sub>4</sub>	mp	249.05	9.966
	bp	409	35.77
TiCl <sub>3</sub>	sublimation temp	1104.1	166.15
TiCl <sub>2</sub>	sublimation temp	1591.5	248.5
TiI <sub>4</sub>	mp	428	19.83 ± 0.63
	bp	652.6	56.48 ± 2.09
TiF <sub>4</sub>	sublimation temp	558.6	97.78 ± 0.42
TiBr <sub>4</sub>	mp	311.4	12.89
	bp	504.1	45.19
TiO <sub>2</sub>	phase change (anatase to rutile)		ca -12.6

<sup>a</sup> To convert kJ/mol to kcal/mol, divide by 4.184

**Table 3.2** Thermochemical data for formation of titanium compounds

Compound	State	Heat formation		Free energy of formation		Entropy, S	
		$\Delta H_f^\circ$ , kJ/mol <sup>b</sup>		$\Delta G_f^\circ$ , kJ/mol <sup>b</sup>		J/(mol.K) <sup>b</sup>	
		at 298 K	at 1300 K	At 298 K	at 1300 K	At 298 K	at 1300 K
TiO	Crystal	-519.6	-515.9	-495.1	-417.1	50.2	127.0
TiO <sub>2</sub>	anatase	-933.0	-930.0	-877.6	-697.4	49.9	150.6
	rutile	-944.7	-942.4	-889.5	-707.9	50.3	149.0
TiC	crystal	-184.1	-188.2	-180.5	-169.1	24.2	92.25
TiN	crystal	-337.6	-337.6	-309.0	-215.0	30.2	100.8
TiCl <sub>2</sub>	crystal	-515.5	-504.2	-465.5	-314.8	87.4	204.2
TiCl <sub>3</sub>	crystal	-721.7	-698.2	-654.5	-445.9	139.7	290.9
TiCl <sub>4</sub>	liquid	-804.2	-771.4	-737.3	-604.6	252.4	431.2
TiCl <sub>4</sub>	gas	-763.2	-765.8	-726.8	-607.0	354.8	507.4
TiBr <sub>4</sub>	crystal	-618.0	-654.5	-593.3	-347.2	243.6	440.6
TiBr <sub>3</sub>	crystal	-550.2	-546.3	-525.6	-341.1	176.4	368.7
TiF <sub>4</sub>	crystal	-1649.3	-1611.1	-1559.2	-1290.3	134.0	338.7
TiI <sub>4</sub>	crystal	-413.4	-453.0	-370.7	-164.6	246.1	486.6
TiI <sub>3</sub>	crystal	-322.2	-385.7	-318.5	-149.2	192.5	368.5
TiI <sub>2</sub>	crystal	-266.1	-310.1	-258.9	-129.6	122.6	253.7

<sup>a</sup>  $H_f$  and  $G_f$  refer to the formation of the named substances in the named states at 298 K and 1300 K from their elements in the standard states of those elements at these temperatures.

<sup>b</sup> To convert J to cal, divide by 4.184

### 3.3 Titanium (IV) oxide

#### 3.3.1 Physical and Chemical properties

Titanium (IV) oxide occurs naturally in three crystalline forms: anatase, brookite, and rutile. These crystals are substantially pure titanium (IV) oxide but usually contain small amounts of impurities, e.g., iron, chromium, or vanadium, which darken them. A summary of the crystallographic properties of the three varieties is given in Table 3.3

Although anatase and rutile are both tetragonal, they are not isomorphous. Anatase occurs usually in near-regular octahedra, and rutile forms slender prismatic crystals, which are frequently twinned. Rutile is the thermally stable form and is one of the two most important ores of titanium.

The three allotropic forms of titanium (IV) oxide have been prepared artificially but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystals. The transformation from anatase to rutile is accompanied by the evolution of ca. 12.6 kJ/mol (3.01 kcal/mol), but the rate of

**Table 3.3** Crystallographic properties of anatase, brookite, and rutile

Property	Anatase	Brookite	Rutile
crystal structure	Tetragonal	Orthorhombic	Tetragonal
optical	uniaxial, negative	Biaxial, positive	uniaxial, positive
density, g/cm <sup>3</sup>	3.9	4.0	4.23
hardness, Mohs scale	5 1/2 – 6	5 1/2 – 6	7 – 7 1/2
unit cell	D <sub>4a</sub> <sup>19</sup> .4TiO <sub>2</sub>	D <sub>2h</sub> <sup>15</sup> .8TiO <sub>2</sub>	D <sub>4h</sub> <sup>12</sup> .3TiO <sub>2</sub>
Dimension, nm			
a	0.3758	0.9166	0.4584
b		0.5436	
c	0.9514	0.5135	2.953

transformation is greatly affected by temperature and by the presence of other substances which may either catalyze or inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is ca. 700°C, but this is not a transition temperature. The change is not reversible;  $\Delta G$  for the change from anatase to rutile is always negative (see Table 3.1 and 3.2 for thermodynamic data).

Brookite has been produced by heating amorphous titanium (IV) oxide, prepared from an alkyl titanates of sodium titanate with sodium or potassium hydroxide in an autoclave at 200 to 600°C for several days. The important commercial forms of titanium (IV) oxide are anatase and rutile, and these can readily be distinguished by X-ray diffraction spectrometry.

Since both anatase and rutile are tetragonal, they are both anisotropic, and their physical properties, e.g., refractive index, vary according to the direction relative to the crystal axes. In most applications of these substances, the distinction between crystallographic directions is lost because of the random orientation of large numbers of small particles, and it is mean value of the property that is significant.

Measurements of physical properties, in which the crystallographic directions are taken into account, may be made of both natural and synthetic rutile, natural anatase crystals, and natural brookite crystals. Measurements of the refractive index of titanium (IV) oxide must be made by using a crystal that is suitably orientated with respect to the crystallographic axis as a prism in a spectrometer. Crystals of suitable size of all three modifications occur naturally and have been studied. However, rutile is the only form that can be obtained in large artificial crystals from melts. The refractive index of rutile is 2.75. The dielectric constant of rutile varies with direction in the crystal and with any variation from the stoichiometric formula,  $\text{TiO}_2$ ; an average value for rutile in powder form is 114. The dielectric constant of anatase powder is 48.

Titanium (IV) oxide is thermally stable (mp 1855°C) and very resistant to chemical attack. When it is heated strongly under vacuum, there is a slight loss of oxygen corresponding to a change in composition to  $\text{TiO}_{1.97}$ . The product is dark blue but reverts to the original white color when it is heated in air.

Hydrogen and carbon monoxide reduce it only partially at high temperatures, yielding lower oxides or mixtures of carbide and lower oxides. At ca. 2000°C and under vacuum, carbon reduces it to titanium carbide. Reduction by metals, e.g., Na, K, Ca, and Mg, is not complete. Chlorination is only possible if a reducing agent is present; the position of equilibrium in the system is



The reactivity of titanium (IV) oxide towards acids is very dependent on the temperature to which it has been heated. For example, titanium (IV) oxide that has been prepared by precipitation from a titanium (IV) solution and gently heated to remove water is soluble in concentrated hydrochloric acid. If the titanium (IV) oxide is heated to ca. 900°C, then its solubility in acids is considerably reduced. It is slowly dissolved by hot concentrated sulfuric acid, the rate of solvation being increased by the addition of ammonium sulfate, which raises the boiling point of the acid. The only other acid in which it is soluble is hydrofluoric acid, which is used extensively in the analysis of titanium (IV) oxide for trace elements. Aqueous alkalis have virtually no effect, but molten sodium and potassium hydroxides, carbonates, and borates dissolve titanium (IV) oxide readily. An equimolar molten mixture of sodium carbonate and sodium borate is particularly effective as is molten potassium pyrosulfate.

### 3.3.2 Preparation procedure

Large surface area titanium (IV) oxide powders have been prepared by several methods. The physical and chemical properties of titanium (IV) oxides are quite different by the process of preparation.

### 3.3.2.1 Chemical vapor deposition (CVD) method

Chemical vapor deposition (CVD) is a process to deposit solids, in the form of a film or particles, using gaseous components. Extensive effort has been devoted to preparing ultrafine particles of metal, metal oxides and other inorganic compound. It is usual for the synthesis of particles by CVD method, to carry out the reaction at high temperatures in order to avoid incomplete reaction. Attempts were made to use metal organic compounds as the starting material in CVD, which may lower the reaction temperature. One of the attractive features of the low temperature CVD is the possibility of producing a material possessing a structure, which is unstable at high temperatures.

Ultrafine titanium (IV) oxide particles were prepared by chemical vapor deposition of titanium tetra isopropoxide. The particle formation reaction being catalyzed by titanium (IV) oxide deposit on the reactor wall, took place even at as low a temperature as 250°C, according to the stoichiometric relation as follow:



The titanium (IV) oxide particles were amorphous and porous, the specific surface area of which reached 300 m<sup>2</sup> g<sup>-1</sup>.

### 3.3.2.2 Chloride process

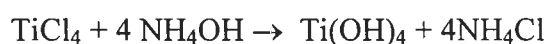
Ultrafine titanium (IV) oxide particles are produced routinely on a large scale by the oxidation of titanium tetrachloride (TiCl<sub>4</sub>) vapor, it is so called “chloride process”. Reactions in the gas phase at the temperature range 700 to 1400°C, according to the stoichiometric relation of  $\text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2 + 2\text{Cl}_2$ , result in the formation and growth of fine titanium (IV) oxide particles. Titanium (IV) oxide pigments that were produced by this method are used in coatings to provide maximum light scattering with actually no absorption.

Titanium (IV) oxide production from titanium tetrachloride vapor has been the focus of experimental studies. Akntar et al. prepared titanium (IV) oxide particles from the oxidation of  $TiCl_4$  in an aerosol reactor between 927 to 1450°C. The effect of process variables (reactor residence time, temperature and reactant concentration) on powder size and phase characteristics was investigated. They found that titanium particles were primarily anatase though the rutile weight fraction increase with increasing reaction temperature and the average particle size increased with increasing, inlet  $TiCl_4$  concentration, and residence time.

### 3.3.3.3 Precipitation method

Precipitation method involves the growth of crystals from a solvent of different composition to the crystals. The solvent may be one of the constituents of the desired crystals, e.g., crystallization of salt hydrate crystals using water as the solvent, or the solvent may be entirely separate liquid element or compound in which the crystals of interest are partially soluble, e.g.,  $SiO_2$  and various high melting silicates may be precipitated from low melting borate or halide melts. In these cases, the solvent melts are sometimes referred to as fluxes since they effectively reduce the melting point of the crystals by a considerable amount.

The method has recently been used to grow crystal of titanium (IV) oxide using titanium tetrachloride as starting material. Titanium tetrachloride is hydrolyzed in aqueous solution resulting in a precipitate of hydrated titanium (IV) oxide which, after washing and drying at 110°C, can be calcined at 800°C to remove combined water and chloride, according to the stoichiometric relation as follow:



This method used involves precipitation from titanium tetrachloride as hydrated titanium (IV) oxide conversion of the precipitate to the double oxalate, recrystallization of this from methanol and subsequent calcination.

### 3.3.3.4 Hydrothermal method

Hydrothermal methods utilize water under pressure and at temperatures above its normal boiling point as a means of speeding up the reactions between solids. The water performs two roles. The water –as liquid or vapor- serves as the pressure transmitting medium. In addition, some or all of the reactants are partially soluble in the water under pressure and this enables reaction to take place in, or with the aid of, liquid and/or vapor phases. Under these conditions, reactions may occur that, in the absence of water, would occur only at much higher temperatures. The method is therefore particularly suited for the synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arranging for a suitable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

Titanium (IV) oxide particles were prepared by hydrothermal method from titanium tetra ethoxide ( $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ). Kondo et al. reported that spherical amorphous monodispersed titanium (IV) oxide particles were synthesized by hydrolysis of titanium tetra ethoxide in dilute ethanol solution and were hydrothermally treated using an autoclave. The amorphous monodispersed titanium (IV) oxide particles were crystallized and many –sized particles of anatase single crystal produced in the particle by the hydrothermal treatment. The internal microstructure of the hydrothermally treated monodispersed titanium (IV) oxide had specific surface area  $113 \text{ m}^2 \text{ g}^{-1}$  and crystallite size which determined by XRD was 17 nm

### 3.3.3.5 Glycothermal method

Glycothermal method has been developed for synthesis of metal oxide and binary metal oxide by using glycol solvents such as 1,4 butanediol instead of water in hydrothermal method. The use of glycol instead of water in synthetic procedure, intermediate phase occurred to be different form and have found that stabilities of the intermediate phase by this method was not strong so, this intermediate phase was easily converted to product under quite mild condition.



Titanium (IV) oxide particles were prepared by glycothermal method from reaction of titanium tetrabutoxide with 1,4 butanediol at 300°C under autoclave condition yield nanocrystalline anatase titanium (IV) oxide with diameter of 17 nm and surface area  $> 90 \text{ m}^2 \text{ g}^{-1}$ . These titanium (IV) oxides were thermally stable.

As described above in literature review section, similar treatment in other organic solvents such as inert organic solvent and/or alcohol solvents gave nanocrystalline titanium (IV) oxide. The physical and chemical properties of this product depended on kind of organic solvents and reaction conditions.

### 3.3.3 Titanium (IV) oxide uses

#### 3.3.3.1 Pigment uses

**Titanium (IV) oxide pigment. Properties:** The high refractive index, lack of absorption of visible light, ability to be produced in the correct size range, and the stability and nontoxicity of titanium (IV) oxide are the reasons why it has become the predominant white pigment in the world. Titanium (IV) oxide pigments are produced in two forms, anatase and rutile. These names indicate that the pigments have the same crystal structure as the minerals of those names indicate but do not necessarily indicate that they have been made from those ores.

**Raw materials:** The raw materials in the manufacture of titanium pigments are ilmenite and rutile. Titanium (IV) oxide pigments are produced by two processes, i.e, the classical sulfate process and the chloride process. In the first, by which the bulk of the world's pigment is produced, the essential step is hydrolysis under carefully controlled conditions of an acid solution of titanyl sulfate, followed by calcination of the hydrous precipitate. In the second, the essential step is burning titanium tetrachloride in oxygen to yield titanium (IV) oxide and chlorine. These two routes make use of the two feasible methods in which titanium ores react by solution in sulfuric acid and by chlorination in the presence of a reducing agent.

### 3.3.3.2 Nonpigment uses

Large tonnages of titanium (IV) oxide are used in the vitreous enamel industry. The titanium (IV) oxide improves the acid resistance of the enamel and its excellent opacifying properties make it possible to use thinner coats, which result in improved resistance to flexure as well as savings in cost and weight. For improved ease of handling and decreased dusting, a coarse grade of titanium (IV) oxide is required. It is important also to specify carefully the concentration of elements, e.g., tungsten and niobium, which can produce pronounced color effects in the enamel. The opacity of the enamel does not result from the properties of the titanium (IV) oxide used, since a recrystallization process involved in producing the enamel.

A second important use for titanium (IV) oxide is in the production of components for electronic equipment. Its high dielectric constant and high resistance make it ideal for use in the miniaturization of capacitors. These are made by pressing high purity rutile into the desired shape and then heating the pressing until the particles sinter at ca. 1400 to 1450°C. Additions of materials, e.g., clay, assist in producing the mold and reduce the firing temperature. These additions must be kept small to avoid adverse effects on the electrical properties of the product.

Many substances have been added to titanium to improve or modify its electrical characteristics. Some of these, e.g., zirconium dioxide, simply act as diluents but others, e.g., barium oxide, form mixed oxides or titanates, which can also be manufactured and used independently.

Synthetic gems have been produced from rutile and strontium titanate. The high refractive index of these materials results in gems of high brilliance. The stones also provide a fine display of colors because of their high dispersion, which is superior to that of diamond; however, they are not very hard.

Mineral rutile is used as an ingredient of welding-rod coatings, for which impurities such as iron are acceptable.

Titanium (IV) oxide is used increasingly as a catalyst, either as an active agent or an inert support. The catalytic oxidation of o-xylene to phthalic anhydride using a mixture of titanium (IV) oxide and vanadium pentoxide as catalyst on an inert support is a well-established commercial process. The same agents have also been used for the reduction of nitrogen oxides in exhaust gases from internal combustion engines. Titanium (IV) oxide has also been used as an oxygen sensor to monitor automobile engine performance; the feedback from the detector controls the air-fuel ratio, giving optimum low pollution performance.

Titanium (IV) oxide impregnated with precious metals (e.g., platinum, rhodium, or ruthenium) or nickel is used in the Fischer-Tropsch synthesis for the production of hydrocarbons from carbon monoxide and hydrogen. There is much research interest in the photocatalytic splitting of water to give hydrogen, which is used as a fuel. Titanium (IV) oxide impregnated with platinum is used as the catalyst.

Numerous other reactions, which as yet are only of academic interest, have been studied in which titanium (IV) oxide is used as a catalyst. These include the oxidation of hydrogen sulfide to sulfur dioxide, the dehydration of alcohols, ammonoxidation, methylation, isomerization, and alkylation.