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Titanium(IV) Oxide Phase Stability in Alkaline Sodium Phosphate Solutions at Elevated Temperatures

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Titanium(IV) oxide is shown to transform to a sodium titanium hydroxyphosphate compound in concentrated sodium phosphate solutions at elevated temperatures via $TiO_2(s) + 4Na^+ + 2HPO_4^{2-} \rightleftarrows Na_4Ti(OH)_2(PO_4)_2(s)$. The thermodynamic equilibrium for this reaction was investigated in the system TiO_2–Na_2O–P_2O_5–H_2O for Na/P atom ratios between 2 and 3. On the basis of observed reaction threshold values for sodium phosphate concentration and temperature, the respective standard entropy and free energy of formation for $Na_4Ti(OH)_2(PO_4)_2$ were calculated to be 823.1 J/(mol K) and −4025.1 kJ/mol at 298 K.

Introduction

Natural titanium(IV) oxide exhibits three structural modifications: the rutile (tetragonal), brookite (orthorhombic), and anatase (tetragonal) minerals. In each of these compounds, the Ti(IV) ion is surrounded by an irregular octahedron of O^{2-} ions. The number of common edges shared by similar octahedra increases from two in rutile, to three in brookite, to four in anatase.[1] Brookite and anatase are known to transform exothermally and irreversibly to rutile over a wide range of temperatures so that rutile is the titanium(IV) oxide form expected to be present in hydrothermally grown corrosion films on titanium alloys.

Titanium dioxide (rutile) is known to exhibit limited phase stability in aqueous sodium hydroxide solutions.[2] At temperatures above 523 K and for NaOH concentrations between 3 and 10 wt %, sodium nonatitanate ($Na_2O{\cdot}9TiO_2$) is the stable titanium(IV) oxide phase in the TiO_2–Na_2O–H_2O system. At higher sodium hydroxide concentrations (10–20 wt %), the stable phase is sodium tetratitanate. As shown by Watanabe,[2] this phase exists as the monohydrate, i.e., $Na_2O{\cdot}4TiO_2{\cdot}H_2O$, for temperatures between 523 and 573 K. On the other hand, TiO_2 is also expected to have limited stability in aqueous phosphoric acid solutions. Einaga and Komatsu[3] have already obtained an equilibrium constant related to the precipitation of $Ti(OH)PO_4$ (i.e., $P_2O_5{\cdot}2TiO_2{\cdot}H_2O$) in the TiO_2–P_2O_5–H_2O system at ambient temperature. The similarity of this precipitate to that of zinc hydroxyphosphate, $Zn_2(OH)PO_4$, which exists in the ZnO–P_2O_5–H_2O system,[4] indicates that titanium hydroxyphosphate probably belongs to a family of metal oxide precipitates induced by the *triply* hydrolyzed phosphate ion:

$$TiO_2(s) + H_3PO_4(aq) \rightleftarrows Ti(OH)PO_4(s) + H_2O \quad (1)$$

Recently we investigated the solubility behavior of titanium(IV) oxide (rutile) in alkaline sodium phosphate solutions at elevated temperatures.[5] At high solution alkalinities in the presence of sodium phosphate, increases in TiO_2 solubility were observed due to formation of the $Ti(OH)_5^-$ ion and two of its phosphatocomplexes: $Ti(OH)_5(H_2PO_4)^{2-}$ and $Ti(OH)_5(HPO_4)^{3-}$. At elevated temperatures, the triply charged anion, $Ti(OH)_5(HPO_4)^{3-}$ (probably in the tetrahedrally symmetric form $TiO(OH)_2(PO_4)^{3-}$), became the predominant Ti(IV) species in solution. Since such phosphato complexes of the hydrolyzed Ti(IV) ion dominate the soluble titanium ion species in solution, the TiO_2 solid phase is expected to eventually give way to a precipitated sodium ion salt of a phosphatotitanate ion.

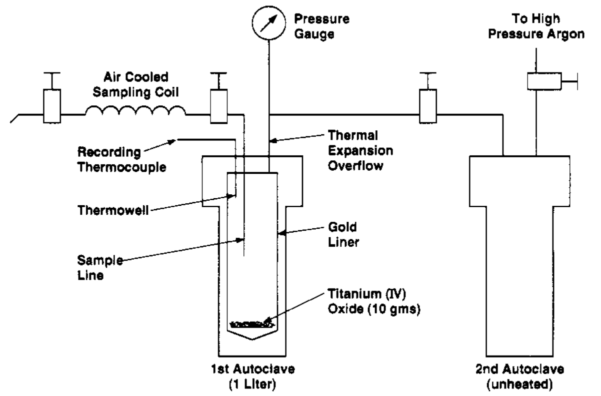

Figure 1. Schematic of autoclave arrangement used in titanium dioxide transformation study.

Previously we had reported the formation of $Na_2Ni(OH)PO_4$ from NiO and $NaZnPO_4$ from ZnO in alkaline sodium phosphate solutions at elevated temperatures.[6,7] The present work was undertaken to define TiO_2 stability limits in alkaline sodium phosphate solutions and to identify the precipitated sodium titanium (hydroxy) phosphate phase.

Experimental Section

Autoclave Tests. All tests were conducted in a 1-L, gold-lined autoclave vessel fitted with a platinum "dip" tube to permit hot sampling. A sketch of the apparatus is shown in Figure 1. The experimental methodology consisted of contacting a 10-g

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Table I. Titanium(IV) Oxide Decomposition Reaction Thresholds

	baseline[a]			final[b]		
test	phosphate molality	Na/P	threshold temp, K	phosphate molality	Na/P	indicated Na/P loss
1	0.5296	2.301	491.5	0.4233	2.380	1.99
2	0.2759	2.315	522.0	0.1664	2.533	1.98
3	0.1095	2.275	563.7	0.0569	3.526	2.00
4	0.2759	2.744	522.0	0.1916	3.071	2.01
5	0.6939	2.186	477.6	0.6560	2.200	1.95
6	0.1558	2.000	555.4	0.0737	1.990	2.01

[a] Solution composition in equilibrium with the two solid phases at the threshold temperature. [b] Solution composition at the final (highest) temperature.

charge of TiO_2 with a concentrated sodium phosphate solution in a static autoclave and incrementally elevating temperature until a phosphate loss occurred.

After adding the TiO_2 and deaerated test solution, the autoclave was pressurized to ~10.3 MPa with argon by means of an auxiliary vessel. This vessel also served to catch any overflow resulting from solution expansion during testing. Steady-state conditions were maintained for at least 4 h after the autoclave had been stabilized at a desired temperature (as measured by a platinum-sheathed thermocouple placed near the TiO_2 charge) before sampling took place through an air-cooled coil attached to the autoclave dip tube. A 15-mL aliquot was reserved for duplicate analysis after allowing a 6-mL line flush. The temperature controller setting was then increased to establish a new temperature. After an additional 4–16 h, the sampling procedure was repeated. This process of changing temperature, allowing time for equilibration and sampling, continued throughout each experimental run.

A typical phosphate inventory in the liquid phase was 50 g, i.e., 0.5 M. Approximately 10 g of phosphate was "consumed" during testing (5 g precipitated and 5 g was removed via sampling).

Reagents. All chemicals used (TiO_2(anhydrous), Na_2HPO_4(anhydrous) and $Na_3PO_4 \cdot 12H_2O$) were of analytical or equivalent grade obtained from the Fisher Scientific Co. Rutile was tested in its as-received condition.

Analytical Procedures. The total phosphate concentration of each sample aliquot was determined by a standard potentiometric titration procedure in which a known sample volume was diluted and titrated with 0.100 N HCl. The amount of titrant used between pH = 9.2 ± 0.1 (x) and 5.0 ± 0.1 (y), i.e., inflection points corresponding to orthophosphate dissociation equilibria, was taken to be the equivalent amount of phosphate. Solution density corrections were applied to convert to units of molality.

The sodium-to-phosphate molar ratio (Na/P) was then calculated by $\mathrm{Na/P} = (2y - x)/(y - x)$. The estimated precision in Na/P is calculated to be ±0.003 given a standard burette reading accuracy of ±0.02 mL and typical values of x and y (3, 13 mL).

Upon completion of each autoclave experiment, the platinum holder containing the reacted titanium dioxide powder was rinsed with deionized water and subjected to visual examination under a stereomicroscope. A portion of the reaction cake was then fractured and placed on a mount for high magnification viewing on a scanning electron microscope. By means of micromanipulators, i.e., needles and tweezers, the reaction product crystals were separated from the remaining mass of unreacted/reacted material. Samples isolated in this manner were subjected to X-ray diffraction (XRD) analyses. Powder XRD measurements were performed using a Model CN2155D5 Rigaku diffractometer (Bragg-Brentano geometry) and Cu Kα radiation (λ = 1.5417 Å). The X-ray tube was operated at 45 kV and 20 mA. Data were taken as a continuous scan from 8 to 92° (2θ) at a speed of 1°/min.

In an attempt to react to completion, test 5 was charged with 2 g of TiO_2, rather than the usual 10 g, and operated for a total of 10 days. The reaction product from this test was subjected to additional characterizations by infrared spectroscopy (IR), quantitative chemical, and transmission electron microscopic (TEM) analyses.

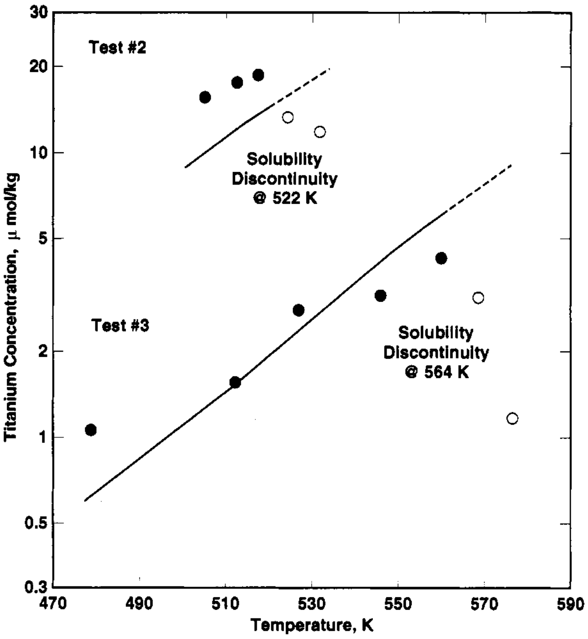

Figure 2. Soluble Ti(IV) levels measured during tests 2 and 3. Closed circles represent TiO_2 solubilities; open circles represent solubilities of the reaction product. Curves represent rutile solubility predictions based on ref 5.

Results

Titanium(IV) Oxide Phase Boundary. Threshold temperatures at which sodium phosphate precipitation was initiated were determined by reverse extrapolation of phosphate concentration versus temperature plots. At least three temperature points above the threshold level were included from each run. The threshold temperatures determined in this manner have an expected accuracy of ±1.5 K. Based on changes in the Na/P ratios of the depleted test solutions, compared with initial (baseline) values, indicated Na/P loss ratios were calculated. These values, along with the estimated TiO_2 transformation temperatures, are summarized in Table I.

The above results indicate that the titanium dioxide–sodium phosphate reaction product contains sodium and phosphate in a 2.0:1 molar ratio. Test 5, which decomposed the entire 2-g charge of TiO_2, precipitated 3600 ppm phosphate from approximately 1 L of test solution. This result indicates a reaction product composition of ~0.66 Ti/P.

Additional solution aliquots from tests 2 and 3 were analyzed for titanium by flameless atomic absorption spectrometry in order to (1) compare Ti solubilities with those previously reported[5] and (2) corroborate the reaction threshold temperature as a point of discontinuity in the slope of the TiO_2 solubility curve. Figure 2 confirms excellent agreement, both in measured versus predicted TiO_2 solubilities and in estimated threshold temperatures for TiO_2 decomposition.

Characterization of Decomposition Product. XRD analyses, as performed with monochromatic Cu Kα X-rays, revealed that the titanium dioxide decomposition products from all six tests had identical crystalline lattice configurations. That is, they were the same compound. The XRD pattern for this compound is summarized in Table II for reference purposes. A search of the JCPDS database[8] proved unsuccessful, indicating that the reaction product is a new crystalline phase. An indexing of the observed pattern and refinement of the unit cell constants, accom-

Table II. Indexed Powder X-ray Diffraction Pattern of Titanium(IV) Oxide–Sodium Phosphate Reaction Product

measd pattern		reflection plane indexes			calcd
d spacing, Å	rel int I/I_0	*h*	*k*	*l*	*d* spacing, Å
7.668	56	1	0	0	7.661
5.398	15	1	0	1	5.395
4.928	23	1	1	1	4.928
3.787	6	0	0	2	3.799
3.624	24	0	1	2	3.621
3.417	32	2	0	1	3.420
3.404	39	1	0	2	3.404
3.211	20	0	2	2	3.208
		1	3	1	
2.698	100	2	0	2	2.697
2.598	48	2	3	1	2.597
2.113	5	2	0	3	2.113
1.914	8	4	0	0	1.915
1.800	6	3	0	3	1.798
1.770	6	2	6	0	1.770
1.573	6	4	3	2	1.572
		3	6	0	
1.541	12	3	4	3	1.541
1.535	14	1	6	3	1.535

plished by means of the DICVOL computer code,[9] indicated that the reaction product possessed orthorhombic crystal symmetry with unit cell constants $a = 7.661 \pm 0.004$ Å, $b = 11.971 \pm 0.007$ Å, and $c = 7.598 \pm 0.004$ Å. The figure of merit[10] for this fit ($F_{17} = 5.0$) is consistent with an average discrepancy in 2θ of 0.024°.

The titanium dioxide decomposition product crystals, when viewed under the stereomicroscope at 50×, were white to transluscent in color. Although the individual crystals were very small, their presence was discernable by the "sparkle" produced by light reflection. Figure 3 shows two SEM photographs taken of the test 1 reaction product crystals at magnifications between 1000 and 3000×. These photographs reveal the reaction product crystals to have a flattened, whiskerlike appearance. In many instances the whiskers have grown into slabs or laths.

Infrared analysis of the test 5 reaction product, as obtained by the KBr pellet technique, indicates the presence of the hydroxyl ion. Absorption in the vicinity of 3490 cm^{-1}, which represents the stretching frequency of the O–H bond, establishes the presence of the hydroxyl ion group. Peak intensity, relative to normalized phosphate bond stretching frequencies, was approximately the same as that observed in the infrared spectrum of the $Na_2Ni(OH)PO_4$ reaction product.[6] This indicates that the reaction product has a OH/PO_4 molar ratio of unity.

Quantitative chemical analyses were employed to complete the characterization of the test 5 reaction product. Sodium and phosphorus were determined by atomic absorption and colorimetric analyses after acid digestion; titanium was determined by atomic absorption after persulfate fusion. The results are summarized as follows:

component	wt %	molar ratio of component to P
Na	25.01	1.97
P (as PO_4)	17.10 (52.44)	
Ti	13.42	0.51
OH, by difference	9.13	0.97

Complementary titanium and phosphorus analyses, obtained via the analytical TEM, verified a P/Ti molar ratio of 2/1. Assembly of the above information gives $Na_4Ti(OH)_2(PO_4)_2$ (i.e., $TiO_2 \cdot 2Na_2O \cdot P_2O_5 \cdot H_2O$) as the lowest whole number stoichiometry for the sodium–titanium–hydroxy phosphate reaction product.

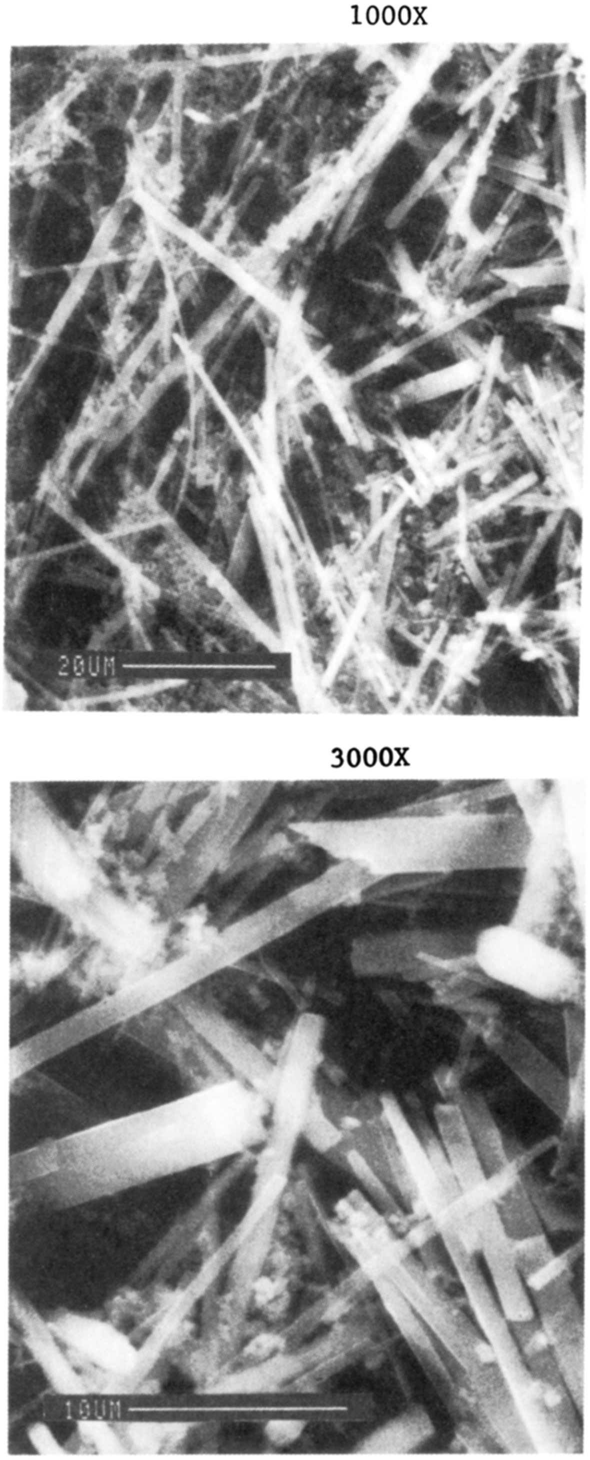

Figure 3. Scanning electron microscope photographs of titanium dioxide–sodium phosphate reaction products.

Discussion

The present work has demonstrated that concentrated alkaline sodium phosphate solutions chemically decompose titanium dioxide into a sodium titanium hydroxyphosphate compound at elevated temperatures. The existence of a reaction product with composition Ti/P ~ 0.5 indicates that the $Ti(OH)_2O(PO_4)^{3-}$ phosphato complex, previously identified as the predominant Ti(IV) species in concentrated alkaline phosphate solutions,[5] probably complexes with a second phosphate ion ligand

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(8) JCPDS Powder Diffraction File, International Centre for Diffraction Data: Swarthmore, PA, 1989; Sets 1–39.

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Table III. Dissociation Constants of Selected Compounds

dissociation constant	b_1	b_2	b_3	b_4	b_5	ref
K_w	31 286.0	−606.522	94.9734	−0.097 611	−2 170 870	12
K_1	17 655.8	−253.198	39.4277	−0.032 540 5	−810 134	13
K_2	17 156.9	−246.045	37.7345	−0.032 208 2	−897 579	13
K_3	−106.51	7.1340		−0.017 459		14

prior to precipitating as a sodium ion salt:

$$\mathrm{Ti(OH)_2O(PO_4)^{3-} + H_2PO_4^- \rightleftarrows Ti(OH)_2(PO_4)_2^{4-} + H_2O} \quad (2)$$

followed by

$$\mathrm{4Na^+ + Ti(OH)_2(PO_4)_2^{4-} \rightleftarrows Na_4Ti(OH)_2(PO_4)_2(s)} \quad (3)$$

It is noted that this behavior differs from that previously observed for divalent metal ions, since the latter precipitates contain only a single phosphate ligand.

By combining the various TiO_2 dissolution, complexing, and precipitation reactions, the overall solid-phase transformation may be written

$$\mathrm{TiO_2(s) + 4Na^+ + 2HPO_4^{2-} \rightleftarrows Na_4Ti(OH)_2(PO_4)_2(s)} \quad (4)$$

The equilibrium constant for the above reaction is defined by

$$K_{eq} = \frac{a_{\mathrm{Na_4Ti(OH)_2(PO_4)_2}}}{a_{\mathrm{TiO_2}}(a_{\mathrm{Na^+}})^4(a_{\mathrm{HPO_4^{2-}}})^2} \quad (5)$$

In the usual manner, activities (a_i) of the two solid phases were taken to be unity, while ionic activity coefficients (γ_i) were used to relate ionic concentrations [C_i] to thermodynamic activities. Marshall and Jones[11] have shown that an extended Debye–Hückel equation of the form

$$\log \gamma_i = -SZ_i^2\sqrt{I}/(1 + A\sqrt{I}) \quad (6)$$

gives reasonable approximations at ionic strengths typical of our tests. They also showed that an average value of $A = 1.70 \pm 0.05$ was observed over the temperature range 475–565 K. The Debye–Hückel limiting slope (S) was calculated from Sweeton et al.[12]

Combining eqs 5 and 6 yields

$$\log K_{eq} = \log Q + 12S\sqrt{I}/(1 + 1.70\sqrt{I}) \quad (7)$$

where

$$\log Q = -\log\,[\mathrm{Na^+}]^4[\mathrm{HPO_4^{2-}}]^2$$

An ion electroneutrality balance

$$[\mathrm{Na^+}] + [\mathrm{H^+}] = [\mathrm{OH^-}] + 3[\mathrm{PO_4^{3-}}] + 2[\mathrm{HPO_4^{2-}}] + [\mathrm{H_2PO_4^-}] \quad (8)$$

was employed to determine [H^+], hence [HPO_4^{2-}] at the measured threshold conditions. This quantity depended on the sodium phosphate molality, as well as the orthophosphate ion and water dissociation constants. These parameters, which are functions of solution temperature, are defined below in terms of thermodynamic activities and tabulated in Table III:

$$K_w = (a_{\mathrm{H^+}})(a_{\mathrm{OH^-}}) \quad (9)$$

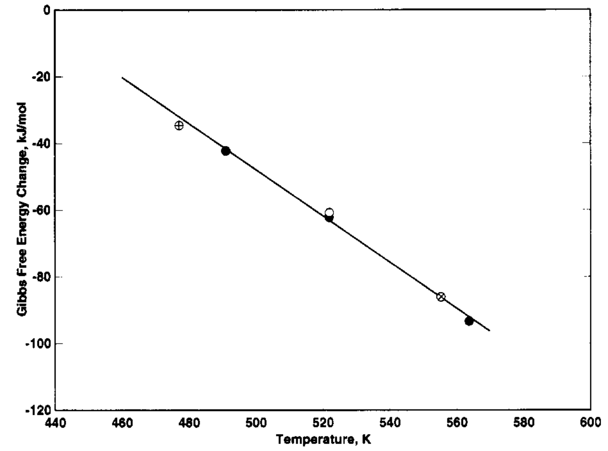

Figure 4. Free-energy changes determined for rutile transformation to sodium–Ti(IV)–hydroxyphosphate in alkaline sodium phosphate solutions. Solution compositions: ⊗, Na/P = 2.0; ⊕, Na/P = 2.2; ●, Na/P = 2.3; ○, Na/P = 2.7.

Table IV. Solution Chemistry Values Used To Describe the TiO_2–$Na_4Ti(OH)_2(PO_4)_2$ Phase Boundary

test	[Na^+], *m*	[HPO_4^{2-}], *m*	log *Q*	*I*	*S*	Δ*G*, kJ mol^{-1}
1	1.2187	0.5194	0.2254	1.7677	0.8672	−42.05
2	0.6386	0.2742	1.9029	0.9157	0.9840	−62.00
3	0.2491	0.1071	4.3549	0.3563	1.2242	−93.96
4	0.7570	0.2733	1.6103	1.0371	0.9840	−60.09
5	1.5168	0.6770	−0.3849	2.2433	0.8244	−34.68
6	0.3117	0.1459	3.6969	0.4561	1.1659	−86.07

$$K_1 = (a_{\mathrm{H_2PO_4^-}})/(a_{\mathrm{H_3PO_4}})(a_{\mathrm{OH^-}}) \quad (10)$$

$$K_2 = (a_{\mathrm{HPO_4^{2-}}})/(a_{\mathrm{H_2PO_4^-}})(a_{\mathrm{OH^-}}) \quad (11)$$

$$K_3 = (a_{\mathrm{PO_4^{3-}}})/(a_{\mathrm{HPO_4^{2-}}})(a_{\mathrm{OH^-}}) \quad (12)$$

with

$$\log K = b_1/T + b_2 + b_3 \ln T + b_4 T + b_5/T^2 \quad (13)$$

Dissociation constants K_w, K_1, and K_2 were corrected for ionic strength (to form equilibrium quotients) via literature correlations.[12,13] K_w was also corrected to a pressure of 9.0 MPa using the correlation presented in ref 12. Table IV summarizes all calculated values. Note that the inferred concentrations are specific to the solution model employed (i.e., Table III) and that other models may give different results.

Figure 4 demonstrates the linearity of the resulting ΔG versus T plot. A least-squares analysis yields

$$-RT \ln K_{eq} = \Delta G(T) = 297060 \pm 13665 - (689.69 \pm 26.11)T\ \mathrm{J/mol} \quad (14)$$

This fit provides free energy changes for eq 4 with an estimated standard deviation of ±1.62 kJ/mol over the temperature range 475–565 K.

Table V summarizes the aqueous sodium phosphate–titanium(IV) oxide system thermodynamics based on

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Table V. Thermochemical Parameters for Selected Species in the TiO_2–Na_2O–P_2O_5–H_2O System at 298.15 K

species	$C_p°$, J mol^{-1} K^{-1}	$S°$, J mol^{-1} K^{-1}	$\Delta H_f°$, kJ mol^{-1}	$\Delta G_f°$, kJ mol^{-1}	ref
H_2(g)	28.824	130.684	0	0	15
O_2(g)	29.355	205.138	0	0	15
H_2O	75.291	69.91	− 285.830	− 237.129	15
Na^+(aq)	117.4	36.8	− 240.12	− 261.905	15
H^+(aq)[a]	− 71	− 22.2	0	0	16, 17
PO_4^{3-}(aq)	−283	−153.6	−1277.4	−1018.8	15, 18
HPO_4^{2-}(aq)	−112	− 32.6	−1305.5	−1089.7	14, 18
$H_2PO_4^-$(aq)	37	72.4	−1308.8	−1130.8	13, 18
Na(s)	28.24	51.21	0	0	15
P(s)	23.84	41.09	0	0	15
Ti(s)	25.02	30.63 ± 0.21	0	0	15
TiO_2(s) rutile	55.02	50.33 ± 0.21	− 944.75 ± 1.67	− 889.5	15
$Na_2O\cdot TiO_2$(s)	125.73	121.75 ± 0.42	−1551.84 ± 2.09	−1456.87 ± 2.93	19, 20
$Na_2O\cdot 3TiO_2$(s)	229.16	233.88 ± 1.26	−3481.51 ± 3.76	−3279.42 ± 5.44	19, 20
$Na_2O\cdot 6TiO_2$(s)	397.23	398.61	−6317.84 ± 7.11	−5957.63	21, 20
$Na_4Ti(OH)_2(PO_4)_2$(s)		823.1	−4219.2	−4025.1	this work

[a] Values tabulated for $C_p°$ and $S°$ differ from the usual convention of zero due to conversion to an absolute scale of ionic properties.

literature values for the elements,[15] recent work at the U.S. Bureau of Mines,[19–21] and the present study. It is cautioned, however, that the elevated and limited temperature range covered by the present study makes estimation of thermochemical properties at 298 K very uncertain.

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Registry No. TiO_2, 13463-67-7; Na_2HPO_4, 7558-79-4; Na_3PO_4, 7601-54-9; $Na_4Ti(OH)_2(PO_4)_2$, 142982-14-7.

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