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Thermodynamic Properties of Three Sodium Titanates

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THERMODYNAMIC PROPERTIES OF THREE SODIUM TITANATES

by

K. O. Bennington[1] and R. R. Brown[1]

ABSTRACT

Enthalpies of formation of three sodium titanates were determined by hydrofluoric acid solution calorimetry. The values obtained for formation from the elements at 298.15° K are -370.9±0.5 kcal/mole for Na_2TiO_3, -832.1±0.9 kcal/mole for $Na_2Ti_3O_7$, and -1,510.9±1.7 kcal/mole for $Na_2Ti_6O_{13}$.

Tables of enthalpies of formation and Gibbs energies of formation are given as a function of temperature both from the elements and from the component oxides for Na_2TiO_3 and $Na_2Ti_3O_7$.

INTRODUCTION

In the development of new processes for producing rutile from ilmenite it has been noted that important thermodynamic information on sodium titanates is lacking. As a result, the present Bureau of Mines experimental investigation was made to provide enthalpies of formation at 298.15° K of three sodium titanates--Na_2TiO_3, $Na_2Ti_3O_7$, and $Na_2Ti_6O_{13}$. A fourth titanate, $Na_2Ti_2O_5$, was not included, since its existence was not clearly established.

A solution calorimetric method was employed with a hydrofluoric-hydrochloric acid mixture as the solution medium. The enthalpy of formation results are expressed both in terms of the constituent elements and oxides. No similar data have been previously published.

MATERIALS

The sodium titanates were prepared by reacting stoichiometric mixtures of reagent-grade sodium carbonate (Na_2CO_3) and titanium dioxide (TiO_2). The TiO_2 consisted of a mixture of anatase and rutile, with anatase present as the primary phase. Neither preparation compound contained impurities in amounts greater than 200 ppm.

Sodium metatitanate (Na_2TiO_3) was synthesized by first fusing the carbonate-oxide mixture at 1,100° C. The product of this treatment was heated

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for 3 days at 980° C, followed by heating for 7 days at 910° C. During the heating periods there were several grindings, mixings, chemical analyses, and adjustments of composition. The X-ray diffraction pattern of the final material was similar to the one given in the ASTM catalog but matched more closely with the pattern reported by Batygin (2).[2]

Disodium trititanate ($Na_2Ti_3O_7$) was synthesized in the solid state by heating the stoichiometric mixture of Na_2CO_3 and TiO_2 for 17 hours at 850° C followed by 6 hours at 960° C. The heat treatment was repeated after grinding and mixing. No adjustments of composition ware necessary. The X-ray diffraction pattern agreed with the one given in the ASTM catalog.

Disodium hexatitanate ($Na_2Ti_6O_{13}$) was prepared by heating the proper mixture of carbonate and oxide for 3 hours at 1,000° C, 17 hours at 870° C, and 2 hours at 1,050° C. After grinding, chemical analysis, adjustment for slight sodium oxide loss, and mixing, the sample was heated for an additional 15 hours at 750° C, followed by 2 hours at 1,050° C. The X-ray pattern was in agreement with that in the ASTM catalog.

Efforts to prepare the compound $Na_2Ti_2O_5$ by procedures similar to those given above were unsuccessful. Both X-ray and microprobe analyses showed the product always to be a mixture in which $Na_2Ti_3O_7$ was the major phase. Chemical analyses of the three titanates are summarized in table 1.

TABLE 1. - Analysis of titanates

Compound	Weight-percent			Theoretical percent	
	Na_2O	TiO_2	CO_2	Na_2O	TiO_2
Na_2TiO_3	43.74	55.90	0.27	43.68	56.32
$Na_2Ti_3O_7$	20.51	79.36	[1].13	20.54	79.46
$Na_2Ti_6O_{13}$	11.43	88.55	.08	11.45	88.55

[1]Percent by difference.

The analysis of Na_2TiO_3 showed a slight excess of Na_2O. The excess, when combined with the CO_2, gives 0.65 percent Na_2CO_3 impurity, for which an appropriate correction was applied. No impurity corrections were made for either $Na_2Ti_3O_7$ or $Na_2Ti_6O_{13}$.

ENTHALPIES OF FORMATION AT 298.15° K

The enthalpies of formation were determined by solution calorimetry. The apparatus used was described by Torgeson and Sahama (16) with later modifications described by King (9). Some more recent alterations will be given in a later paper.

The aqueous solution medium was 948.7 grams of a mixture containing 10.05 weight-percent (HF) and 10.05 weight-percent of HCl. The acids were

[2]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

reagent-grade products that were used without treatment except for dilution to the proper strength. The quantities of the reacting substances were stoichiometric with 0.987 gram of TiO_2.

Weighed amounts of the substances to be dissolved were placed in paraffin-sealed Teflon[3] tape capsules and dropped at the appropriate time from room temperature into the calorimeter which was operated at 73.7° C. Each measured heat resulted from a process of converting a pure substance at 25° C to a solution product at 73.7° C. Combination of the heat measurements in accordance with reaction schemes resulted in the evaluation of a heat of reaction at 25° C (298.15° K) involving compounds in their standard states. Separate measurements provided corrections for the heat effects caused by the Teflon capsules and paraffin sealant. Electrical calibrations of the calorimeter were made following each individual heat measurement.

Throughout this report uncertainties were assigned to measured and derived heat values as follows: (1) When several individual heat values were measured for a reaction, the precision uncertainty was taken as $2\sqrt{\Sigma d_i^2/n(n-1)}$, where Σd_i^2 is the sum of the squares of the deviations from the mean value, and n is the number of determinations; (2) when the heats of two or more reactions were combined, the uncertainty was taken as the square root of the sum of the squares of the uncertainties for the individual reactions.

All results are expressed in defined kilocalories (1 kcal = 4,184.0 absolute joules). Weighings corrected to vacuum and molecular weights are in accordance with the 1969 Table of Atomic Weights (6).

Na_2TiO_3

The reaction scheme for obtaining the heat of formation of Na_2TiO_3 is given in table 2. The symbols c, l, and sol are used to denote substances that are crystalline, liquid, and in solution. The reactions are written in an abbreviated form sufficient to show that stoichiometry was maintained. This table also presents the average measured heat values and their precision uncertainties.

The heat of reaction 1 was measured previously by Kelley (8) under conditions identical to those used here. His value of -28.600±0.200 kcal/mole for the heat of solution of TiO_2 (rutile) was adopted.

Reaction 2 is a dilution of the final solution resulting from reaction 1. Before conducting this reaction, the stoichiometrically required amount of TiO_2 (0.987 gram) was dissolved in the acid mixture. Eight determinations of the heat of solution of H_2O gave 0.7471, 0.7406, 0.7444, 0.7436, 0.7414, 0.7429, 0.7470, and 0.7408 kcal/mole. The mean is 0.7435±0.0018 kcal/mole.

[3]Reference to specific makes and models of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 2. - Reaction scheme for Na_2TiO_3

Reaction	ΔH, kcal	Uncertainty, kcal
(1) TiO_2(c, 25°) + 6 HF(sol, 73.7°) = H_2TiF_6(sol, 73.7°) + 2 H_2O(sol, 73.7°)........	-28.600	±0.200
(2) 26.462 H_2O(l, 25°) = 26.462 H_2O(sol, 73.7°)......	19.674	±.048
(3) 2 NaCl(c, 25°) = 2 Na^+(sol, 73.7°) + 2 Cl^- (sol, 73.7°)...........................	2.782	±.012
(4) 2(HCl·12.731 H_2O) (l, 25°) = 2 H^+(sol, 73.7°) + 2 Cl^- (sol, 73.7°) + 25.462 H_2O(sol, 73.7°)....	22.066	±.038
(5) Na_2TiO_3(c, 25°) + 6 HF(sol, 73.7°) + 2 H^+(sol, 73.7°) = 2 Na^+(sol, 73.7°) + H_2TiF_6(sol, 73.7°) + 3 H_2O(sol, 73.7°).........	-70.293	±.041

$$\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$$

(6) 2 NaCl(c, 25°) + TiO_2(c, 25°) + 26.462 H_2O(l, 25°) = Na_2TiO_3 (c, 25°) + 2(HCl·12.731 H_2O) (l, 25°)

$$\Delta H_6 = 42.1 \pm 0.4 \text{ kcal at } 298.15^\circ \text{ K}.$$

Reaction 3, the solution of NaCl, was determined in the solution resulting from reaction 2. Eight measurements gave the heats 1.390, 1.379, 1.396, 1.403, 1.376, 1.395, 1.390, and 1.396 kcal/mole. The mean is 1.391±0.006 kcal/mole.

Reaction 4, the solution of HCl, was made in a fresh charge of acid. Seven determinations of the heat gave 11.032, 11.081, 11.021, 11.030, 11.002, 11.044, and 11.020 kcal/mole. The mean is 11.033±0.019 kcal/mole of HCl.

Reaction 5 represents the solution of one formula weight of Na_2TiO_3. The titanate, dissolved in the final solution of reaction 4, gave heats of solution of -70.325, -70.389, -70.270, -70.241, -70.324, -70.261, and -70.242 kcal/mole. The mean is -70.293±0.041 kcal/mole.

The final solution after conducting consecutive reactions 1, 2, and 3 is the same as that after conducting consecutive reactions 4 and 5. Consequently, the reactions and their heats can be combined ($\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$) to give 42.1±0.4 kcal for the overall calorimetric reaction at 298° K. The uncertainty assigned to reaction 6 contains, in addition to the precision uncertainties of the solution reactions, allowances for the uncertainties in the calibration measurements and the impurity corrections.

The enthalpy of formation of Na_2TiO_3(c) from the oxides is obtained by combining the heat for reaction 6 with the enthalpies of formation at 298° K of NaCl, water, HCl solution, and Na_2O. The enthalpy of formation of NaCl was taken from Stull and Prophet (15),

$$Na(c) + 1/2\ Cl_2(g) = NaCl(c),\ \Delta H^\circ_{298} = -98.26\pm0.08\ kcal, \tag{7}$$

the enthalpies of formation of water and of $HCl\cdot12.731\ H_2O(l)$ were from Wagman (17),

$$H_2(g) + 1/2\ O_2(g) = H_2O(l),\ \Delta H^\circ_{298} = -68.315\pm0.10\ kcal, \tag{8}$$

$$1/2\ H_2(g) + 1/2\ Cl_2(g) + 12.731\ H_2O(l) = HCl\cdot12.731\ H_2O(l), \tag{9}$$

$$\Delta H^\circ_{298} = -38.82\pm0.05\ kcal,$$

and the enthalpy of formation of Na_2O was from O'Hare (13),

$$2\ Na(c) + 1/2\ O_2(g) = Na_2O(c),\ \Delta H^\circ_{298} = -99.14\pm0.07\ kcal. \tag{10}$$

The combination of heats ($\Delta H_6 + 2\Delta H_7 + \Delta H_8 - 2\Delta H_9 - \Delta H_{10}$) gives $\Delta H^\circ_{298} = -46.0\pm0.5$ kcal for the formation of $Na_2TiO_3(c)$ from its component oxides,

$$Na_2O(c) + TiO_2(rutile) = Na_2TiO_3(c). \tag{11}$$

Calculation of the enthalpy of formation of $Na_2TiO_3(c)$ from the elements requires, in addition to some of the above supplementary data, the enthalpy of formation of rutile, for which the value of Mah (10) was adopted,

$$Ti(c) + O_2(g) = TiO_2(rutile),\ \Delta H^\circ_{298} = -225.8\pm0.1\ kcal. \tag{12}$$

The combination $\Delta H_6 + 2\Delta H_7 + \Delta H_8 - 2\Delta H_9 + \Delta H_{12}$ gives $\Delta H^\circ_{298} = -370.9\pm0.5$ kcal for the reaction

$$2\ Na(c) + Ti(c) + 3/2\ O_2(g) = Na_2TiO_3(c). \tag{13}$$

$Na_2Ti_3O_7$

The reaction scheme (table 3) used to derive the enthalpy of formation of $Na_2Ti_3O_7$ was nearly identical to the one used for Na_2TiO_3. The procedure and sequence of reactions were the same. The only changes were those of the quantities of materials dissolved. A weight of 0.987 gram of TiO_2 again served as the basis for the other substances in the scheme.

The solution process represented by reaction 14 is identical with reaction 1 and the same molal heat value, -28.6 kcal, is applicable.

Reactions 15 and 16, involving H_2O and NaCl, were successively conducted in the solution resulting from reaction 14. Seven determinations of H_2O gave 0.7457, 0.7443, 0.7428, 0.7445, 0.7437, 0.7476, and 0.7493 kcal/mole. The mean is 0.7454±0.0017 kcal/mole. Seven determinations of NaCl gave 1.398, 1.406, 1.411, 1.417, 1.422, 1.412, and 1.421 kcal/mole. The mean is 1.412±0.006 kcal/mole.

TABLE 3. - Reaction scheme for $Na_2Ti_3O_7$

Reaction	ΔH, kcal	Uncertainty, kcal
(14) 3 TiO_2(c, 25°) + 18 HF(sol, 73.7°) = 3 H_2TiF_6(sol, 73.7°) + 6 H_2O(sol, 73.7°)...........................	-85.800	±0.600
(15) 26.462 H_2O(1, 25°) = 26.462 H_2O(sol, 73.7°).....	19.725	±.045
(16) 2 NaCl(c, 25°) = 2 Na^+(sol, 73.7°) + 2 Cl^-(sol, 73.7°)...........................	2.824	±.012
(17) 2(HCl·12.731 H_2O) (1, 25°) = 2 H^+(sol, 73.7°) + 2 Cl^-(sol, 73.7°) + 25.462 H_2O(sol, 73.7°)......................	22.066	±.038
(18) $Na_2Ti_3O_7$(c, 25°) + 18 HF(sol, 73.7°) + 2 H^+(sol, 73.7°) = 2 Na^+(sol, 73.7°) + 3 H_2TiF_6(sol, 73.7°) + 7 H_2O(sol, 73.7°)...........................	-117.767	±.056

$$\Delta H_{19} = \Delta H_{14} + \Delta H_{15} + \Delta H_{16} - \Delta H_{17} - \Delta H_{18}$$

(19) 2 NaCl(c, 25°) + 3 TiO_2(c, 25°) + 26.462 H_2O(1, 25°) = $Na_2Ti_3O_7$(c, 25°) + 2(HCl·12.731 H_2O) (1, 25°)

$$\Delta H_{19} = 32.4 \pm 0.8 \text{ kcal at } 298.15° \text{ K.}$$

Reaction 17, the solution of HCl in a new acid solution, was identical to reaction 4. The value of 11.033±0.019 kcal/mole of HCl was adopted.

Reaction 18 represents the reaction of $Na_2Ti_3O_7$ in the final solution of reaction 17. Seven determinations of this heat provided -117.783, -117.659, -117.782, -117.811, -117.811, -117.853, and -117.670 kcal/mole. The mean is -117.767±0.056 kcal/mole.

Reaction 19, the overall calorimetric reaction, results from the proper combination of reactions 14-18,

$$\Delta H_{19} = \Delta H_{14} + \Delta H_{15} + \Delta H_{16} - \Delta H_{17} - \Delta H_{18}.$$

The enthalpy for this reaction is ΔH°_{298} = 32.4±0.8 kcal.

The enthalpy of formation of $Na_2Ti_3O_7$ from its component oxides is given by the combination $\Delta H_{19} + 2\Delta H_7 + \Delta H_3 - 2\Delta H_9 - \Delta H_{10}$, yielding ΔH°_{298} = -55.6±0.9 kcal for reaction

$$Na_2O(c) + 3\ TiO_2(\text{rutile}) = Na_2Ti_3O_7(c). \quad (20)$$

The standard enthalpy of formation from the elements is derived by the combination $\Delta H_{19} + 2\Delta H_7 + 3\Delta H_8 - 2\Delta H_9 + 3\Delta H_{12}$, from which $\Delta H^\circ_{298} = -832.1\pm0.9$ kcal for the reaction

$$2\ Na(c) + 3\ Ti(c) + 7/2\ O_2(g) = Na_2Ti_3O_7(c). \qquad (21)$$

$Na_2Ti_6O_{13}$

The reaction scheme for $Na_2Ti_6O_{13}$ (table 4) is similar to the two schemes already given. A weight of 0.987 gram of TiO_2 was adopted as the weight basis for dissolving the other substances in the reaction scheme. The molal heat for reaction 22 then is identical with that of reaction 1.

TABLE 4. - Reaction scheme for $Na_2Ti_6O_{13}$

Reaction	ΔH, kcal	Uncertainty, kcal
(22) 6 TiO_2(c, 25°) + 36 HF(sol, 73.7°) = 6 H_2TiF_6(sol, 73.7) + 12 H_2O(sol, 73.7°).........................	-171.60	±1.20
(23) 26.462 H_2O(1, 25°) = 26.462 H_2O(sol, 73.7°)....	19.630	±.066
(24) 2 NaCl(c, 25°) = 2 Na^+(sol, 73.7°) + 2 Cl^-(sol, 73.7°)..........................	2.824	±.050
(25) 2(HCl·12.731 H_2O) (1, 25°) = 2 H^+(sol, 73.7°) + 2 Cl^-(sol, 73.7°) + 25.462 H_2O(sol, 73.7°)......................	22.066	±.038
(26) $Na_2Ti_6O_{13}$(c, 25°) + 36 HF(sol, 73.7°) + 2 H^+(sol, 73.7°) = 2 Na^+(sol, 73.7°) + 6 H_2TiF_6(sol, 73.7°) + 13 H_2O(sol, 73.7°).........................	-202.32	±.022

$$\Delta H_{27} = \Delta H_{22} + \Delta H_{23} + \Delta H_{24} - \Delta H_{25} - \Delta H_{26}$$

(27) 2 NaCl(c, 25°) + 6 TiO_2(c, 25°) + 26.462 H_2O (1, 25°) = $Na_2Ti_6O_{13}$(c, 25°) + 2(HCl·12.731 H_2O) (1, 25°)

$$\Delta H_{27} = 31.1\pm1.5 \text{ kcal at } 298.15° \text{ K}$$

Reaction 23, the solution of water, was conducted in the solution resulting from reaction 22. Five determinations of reaction 23 yielded 0.7406, 0.7463, 0.7395, 0.7401, and 0.7423 kcal/mole. The mean is 0.7418±0.0025 kcal/mole.

Reaction 24 represents the solution of NaCl in the final solution of reaction 23. The stoichiometric sample size of NaCl was too small to obtain reliable heat results, so the heat for reaction 16 was adopted. The uncertainty in the heat value for reaction 24 was increased to 0.050 kcal to allow for the slightly different conditions of solution.

Reaction 25 is identical to reaction 4. The heat is 11.033±0.019 kcal/mole HCl.

Reaction 26, the solution of $Na_2Ti_6O_{13}$, was conducted in the solution resulting from reaction 25. The six values obtained for the heat are -202.36, -202.58, -202.61, -202.35, -201.91, and -202.14 kcal/mole. The mean is -202.32±0.22 kcal/mole. The summation of reactions, $\Delta H_{22} + \Delta H_{23} + \Delta H_{24} - \Delta H_{25} - \Delta H_{26}$, gives reaction 27 for which ΔH°_{298} is 31.1±1.5 kcal.

Proceeding as before, the enthalpy of formation from the oxides, $\Delta H_{28} = \Delta H_{27} + 2\Delta H_7 + \Delta H_8 - 2\Delta H_9 - \Delta H_{10}$, is $\Delta H^\circ_{298} = -56.9 \pm 1.6$ kcal/mole,

$$Na_2O(c) + 6\ TiO_2(\text{rutile}) = Na_2Ti_6O_{13}(c); \qquad (28)$$

and the enthalpy of formation from the elements, $\Delta H_{29} = \Delta H_{27} + 2\Delta H_7 + \Delta H_8 - 2\Delta H_9 + 6\Delta H_{12}$, is $\Delta H^\circ_{298} = -1{,}510.0 \pm 1.7$ kcal for the formation from the elements,

$$2\ Na(c) + 6\ Ti(c) + 13/2\ O_2(g) = Na_2Ti_6O_{13}(c). \qquad (29)$$

THERMODYNAMIC PROPERTIES ABOVE 298.15° K

The new experimental data for Na_2TiO_3 and $Na_2Ti_3O_7$ may be combined with published auxiliary data to give enthalpies of formation and Gibbs energies of formation as functions of temperature. Necessary auxiliary data are not available to do the same for the third titanate, $Na_2Ti_6O_{13}$. High-temperature enthalpy and entropy data for Na_2O and O_2 were from the JANAF tables (15). The value of S°_{298} for rutile was from Kelley and King (7). Enthalpy and entropy data above 298° K for rutile were taken from Arthur (1) and Naylor (12). The entropies at 298° K for Na_2TiO_3 and $Na_2Ti_3O_7$ were from Shomate (14). The entropy and enthalpy increments for the two titanates were from Naylor (11). All necessary enthalpy and entropy data for sodium were from Hultgren (5) as were the data for titanium (4).

Where warranted, auxiliary enthalpy and entropy data were corrected to the international temperature scale of 1968 (3).

Table 5 gives the high-temperature thermodynamic properties of Na_2TiO_3, including the enthalpy of formation and Gibbs energy of formation from the elements. Table 6 gives data for the energies of formation from the component oxides.

TABLE 5. - Thermodynamic properties of Na_2TiO_3

[Formation: $2\ Na(c, 1) + Ti(\alpha, \beta) + 3/2\ O_2(g) = Na_2TiO_3(\alpha, \beta, 1)$]

T, ° K	Cal/deg mole			Kcal/mole			Log Kf
	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	
298.15......	30.05	29.10	29.10	0	-370.9±0.5	-348.2±0.7	255.2
300.........	30.15	29.29	29.10	.06	-370.9	-348.0	253.5
371.........	32.67	36.01	29.79	2.31	-370.8	-342.6	201.8
371.........	32.67	36.01	29.79	2.31	-372.1	-342.6	201.8
400.........	33.70	38.51	30.33	3.27	-372.0	-340.3	185.9
500.........	35.71	46.26	32.77	6.75	-371.8	-332.4	145.3
560.........	36.73	50.36	34.43	8.92	-371.6	-327.7	127.9
560.........	34.87	51.08	34.43	9.32	-371.2	-327.7	127.9
600.........	36.00	53.53	35.63	10.74	-371.0	-324.6	118.2
700.........	38.05	59.24	38.60	14.45	-370.6	-316.9	98.9
800.........	39.54	64.42	41.51	18.33	-370.0	-309.3	84.5
900.........	41.00	69.16	44.32	22.36	-369.3	-301.7	73.3

TABLE 5. - Thermodynamic properties of Na_2TiO_3--Continued

T, ° K	Cal/deg mole			Kcal/mole			Log Kf
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
1,000.........	42.68	73.57	47.03	26.54	-368.5	-294.3	64.3
1,100.........	44.56	77.72	49.63	30.90	-367.6	-286.9	57.0
1,156.........	45.61	79.96	51.05	33.42	-367.0	-282.8	53.5
1,156.........	45.61	79.96	51.05	33.42	-368.0	-282.8	53.5
1,200.........	46.38	81.68	52.14	35.45	-365.0	-279.6	50.9
1,300.........	47.59	85.44	54.55	40.16	-366.2	-272.3	45.8
1,304.........	47.62	85.60	54.65	40.36	-366.1	-272.0	45.6
1,304.........	46.79	98.49	54.65	57.17	-349.3	-272.0	45.6
1,400.........	46.79	101.80	57.77	61.65	-348.2	-266.3	41.6
1,500.........	46.79	105.03	60.81	66.33	-	-	-
1,600.........	46.79	108.05	63.67	71.00	-	-	-

Phase changes: 371° K, melting point of Na;
560° K, α-β transition of Na_2TiO_3;
1,156° K, α-β transition of Ti;
1,304° K, melting point of Na_2TiO_3.

TABLE 6. - Enthalpy and Gibbs energy of the reaction $Na_2O(\alpha,\beta,\gamma,l) + TiO_2(\text{rutile}) = Na_2TiO_3(\alpha,\beta,l)$

T, ° K	Kcal/mole		T, ° K	Kcal/mole	
	ΔH°	ΔG°		ΔH°	ΔG°
298.15.........	-46.0±0.5	-45.7±0.7	1,100...........	-45.5	-45.5
300...........	-46.0	-45.7	1,200...........	-45.1	-45.5
400...........	-45.9	-45.6	1,244.4.........	-44.8	-45.6
500...........	-45.8	-45.6	1,244.4.........	-47.7	-45.6
560...........	-45.8	-45.5	1,300...........	-47.4	-45.5
560...........	-45.4	-45.5	1,304...........	-47.3	-45.4
600...........	-45.5	-45.5	1,304...........	-30.5	-45.4
700...........	-45.6	-45.5	1,400...........	-30.1	-46.6
800...........	-45.6	-45.5	1,406.7.........	-30.0	-46.6
900...........	-45.5	-45.5	1,406.7.........	-41.4	-46.6
1,000...........	-45.4	-45.5	1,500...........	-41.1	-47.0
1,023.7.........	-45.3	-45.5	1,600...........	-40.8	-47.4
1,023.7.........	-45.7	-45.5			

Phase changes: 560° K, α-β transition of Na_2TiO_3;
1,023.7° K, α-β transition of Na_2O;
1,244.4° K, β-γ transition of Na_2O;
1,304° K, melting point of Na_2TiO_3;
1,406.7° K, melting point of Na_2O.

Tables 7 and 8 provide similar data for $Na_2Ti_3O_7$.

TABLE 7. - Thermodynamic properties of $Na_2Ti_3O_7$

[Formation: 2 Na(c, l) + 3 Ti(α,β) + 7/2 O_2(g) = $Na_2Ti_3O_7$(c)]

T, ° K	Cal/deg mole			Kcal/mole			Log Kf
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
298.15......	54.77	55.90	55.90	0	-832.1±0.9	-783.8±1.3	574.5
300.........	54.99	56.24	55.91	.10	-832.1	-783.5	570.8
371.........	61.07	68.68	57.18	4.27	-832.0	-772.0	454.8
371.........	61.07	68.68	57.18	4.27	-833.2	-772.0	454.8
400.........	63.55	73.37	58.18	6.08	-833.1	-767.2	419.2
500.........	67.64	88.05	62.73	12.66	-832.5	-750.8	328.2
600.........	69.42	100.56	68.02	19.53	-831.7	-734.5	267.5
700.........	70.32	111.34	73.46	26.52	-831.0	-718.3	224.3
800.........	71.12	120.78	78.80	33.59	-830.2	-702.3	191.9
900.........	72.14	129.21	83.93	40.75	-829.5	-686.4	166.7
1,000.........	73.38	136.87	88.85	48.02	-828.8	-670.5	146.5
1,100.........	74.66	143.93	93.54	55.42	-828.0	-654.7	130.0
1,156.........	75.31	147.65	96.07	59.62	-827.6	-645.9	122.1
1,156.........	75.31	147.65	96.07	59.62	-830.7	-645.9	122.1
1,200.........	75.77	150.47	98.01	62.95	-830.2	-638.9	116.4
1,300.........	76.63	156.57	102.28	70.57	-829.2	-623.0	104.7
1,400.........	77.43	162.28	106.37	78.27	-828.2	-607.1	94.8
1,403.........	77.45	162.42	106.49	78.47	-	-	-
1,403.........	94.07	188.86	106.49	115.57	-	-	-
1,500.........	94.07	195.19	112.03	124.74	-	-	-
1,600.........	94.07	201.26	117.42	134.14	-	-	-
1,700.........	94.07	206.97	122.53	143.55	-	-	-

Phase changes: 371° K, melting point of Na;
1,156° K, α-β transition of Ti;
1,403° K, melting point of $Na_2Ti_3O_7$.

TABLE 8. - Enthalpy and Gibbs energy of the reaction
Na_2O(α,β,γ,l) + 3 TiO_2(rutile)
= $Na_2Ti_3O_7$(s, l)

T, ° K	Kcal/mole		T, ° K	Kcal/mole	
	ΔH°	ΔG°		ΔH°	ΔG°
298.15........	-55.6±0.9	-56.1±1.3	1,000...........	-56.7	-57.1
300...........	-55.6	-56.1	1,023.7.........	-56.8	-57.1
400...........	-55.6	-56.3	1,023.7.........	-57.2	-57.1
500...........	-55.5	-56.5	1,100...........	-57.4	-57.1
600...........	-55.6	-56.7	1,200...........	-57.5	-57.1
700...........	-55.8	-56.9	1,244.4.........	-57.6	-57.1
800...........	-56.1	-57.0	1,244.4.........	-60.4	-57.1
900...........	-56.4	-57.1	1,300...........	-60.5	-56.9

TABLE 8. - Enthalpy and Gibbs energy of the reaction $Na_2O(\alpha,\beta,\gamma,l) + 3\ TiO_2(rutile) = Na_2Ti_3O_7(s, l)$--Continued

T, ° K	Kcal/mole		T, ° K	Kcal/mole	
	ΔH°	ΔG°		ΔH°	ΔG°
1,400...........	-60.6	-56.6	1,406.7.........	-34.9	-56.7
1,403...........	-60.7	-56.6	1,500...........	-33.6	-58.2
1,403...........	-23.6	-56.6	1,600...........	-32.3	-59.9
1,406.7.........	-23.5	-56.7	1,700...........	-31.0	-61.7

Phase changes: 1,023.7° K, α-β transition of Na_2O;
1,244.4° K, β-γ transition of Na_2O;
1,403° K, melting point of $Na_2Ti_3O_7$;
1,406.7° K, melting point of Na_2O.

DISCUSSION

The two sodium titanates, Na_2TiO_3 and $Na_2Ti_3O_7$, for which complete thermodynamic data are now available, show considerable thermodynamic stability over a range of temperature with respect to their component oxides. The third titanate studied, $Na_2Ti_6O_{13}$, is also quite stable at 298° K.

The enthalpy and Gibbs energy of formation values for both Na_2TiO_3 and $Na_2Ti_3O_7$ are of similar magnitude and do not change greatly at temperatures below their melting points. With this evidence of small ΔS and ΔCp of formation from the oxides, it might be expected that for the reaction

$$Na_2Ti_3O_7(c) + 3\ TiO_2(rutile) = Na_2Ti_6O_{13}(c), \qquad (30)$$

the average change in the Gibbs energy would be around -2 kcal. From this estimate it appears doubtful that there are any titanates higher than $Na_2Ti_6O_{13}$. Other possible titanates in the series are $Na_2Ti_2O_5$, $Na_2Ti_4O_9$, and $Na_2Ti_5O_{11}$. We have already noted in the preparation section our inability to prepare $Na_2Ti_2O_5$. And Batygin (2) has reported that he was unsuccessful in attempts to synthesize either $Na_2Ti_4O_9$ or $Na_2Ti_5O_{11}$.

In summary, this work has determined standard enthalpies of formation for all of the undisputed compound members in the Na-Ti-O system.

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