

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Heat Capacities of Titanium Dioxide from 68–298°K. The Thermodynamic Properties of Titanium Dioxide

BY HUGH J. McDONALD¹ AND HARRY SELTZ

In an extension of a program of research in these Laboratories on the thermodynamic properties of metal systems, a low temperature calorimeter of the Nernst type has been constructed. In this paper, the results of heat capacity measurements on titanium dioxide from 68–298°K. are described and the entropy of this compound is calculated. From published heats of formation and heat capacities at higher temperatures, the complete thermodynamic properties of the oxide are derived.

Material.—The titanium dioxide used in these measurements was the purest that could be obtained commercially. Spectroscopic analysis showed that the only detectable impurity present was silica. Chemical analysis fixed the amount of this oxide at less than 0.4% and, as the difference between the heat capacity of titanium dioxide and silicon dioxide is small, the error thereby introduced is negligible. There are three allotropic modifications of titanium dioxide, rutile, anatase and brookite, and it was necessary to establish the form of the material used in this investigation from an X-ray powder photograph. Comparison of the X-ray pattern obtained with that of rutile showed perfect agreement for all the characteristic lines.

In order to get the greatest weight of the oxide, which was quite fluffy, into the calorimeter it was pressed into pellets which were ignited in a large platinum crucible for two hours and then broken into small pieces. The X-ray diffraction pattern was not altered by the ignition. The total charge of titanium dioxide used was 87.958 g. (*in vacuo*), or 1.1008 moles.

Apparatus.—The calorimeter used in these measurements was modeled after that described by Gibson and Giauque,² and since no significant modifications were made, it will not be described further. The calibrations of the calorimeter and shield windings were made by comparison with copper-constantan couples previously checked against a standardized couple, S-6, which was made available through the kindness of Professor J. G. Aston of Pennsylvania State College. This couple had been calibrated in terms of a helium thermometer.³ In comparing our couples with S-6 they were soldered with Wood's metal in deep holes in a copper cylinder and electromotive force readings were made with a White double potentiometer over the entire temperature range under conditions comparable to those in the actual measurements. These couples were then soldered in wells in the shield and in the

calorimeter and the resistances of the windings were calibrated against them. Frequent checks during specific heat runs have shown no significant variations in the resistances of these windings during the past year. The specific heat measurements were carried out as described by Gibson and Giauque² and the usual corrections for heat interchange between the shield and calorimeter were made. The free space in the calorimeter was filled with hydrogen during the measurements and rapid distribution of heat was achieved as indicated by a negligible temperature lag after introduction of the electrical energy. The over-all accuracy of the measurements of the heat capacities of titanium dioxide is believed to be $\approx 0.3\%$.

Experimental Results

In Table I, the experimental heat capacities for titanium dioxide are given. The conversion from electrical energy to defined calories was made on the basis of 1 calorie = 4.1833 international joules. The results are plotted in Fig. 1.

TABLE I
MOLAL HEAT CAPACITIES OF TiO₂ (RUTILE)

| Series I | | Series II | |
|----------|----------------|-----------|----------------|
| T, °K. | C _p | T, °K. | C _p |
| 85.40 | 3.58 | 68.78 | 2.67 |
| 89.15 | 3.87 | 73.06 | 2.85 |
| 93.23 | 4.20 | 77.80 | 3.09 |
| 106.02 | 5.04 | 82.10 | 3.29 |
| 112.09 | 5.33 | 86.13 | 3.60 |
| 119.50 | 5.87 | 90.05 | 3.89 |
| 128.35 | 6.40 | 94.32 | 4.19 |
| 137.52 | 7.00 | 105.60 | 5.01 |
| 153.80 | 7.89 | 109.69 | 5.21 |
| 163.53 | 8.49 | 134.65 | 6.73 |
| 174.28 | 9.06 | 146.68 | 7.53 |
| 184.36 | 9.57 | 277.09 | 12.95 |
| 194.77 | 10.07 | 286.40 | 13.23 |
| 215.08 | 10.98 | 291.90 | 13.36 |
| 224.70 | 11.34 | | |
| 234.22 | 11.70 | | |
| 244.20 | 12.01 | | |
| 264.22 | 12.66 | | |
| 274.23 | 12.98 | | |
| 295.07 | 13.44 | | |

Calculations

The Entropy of TiO₂.—The method suggested by Kelley⁴ was used to extrapolate the heat capacity values from 68–0°K. It was found that

$$C_p = D(306/T) + 2E(670/T)$$

fitted the experimental curve satisfactorily from

(4) Kelley, Bureau of Mines Bulletin 350, (1932), p. 8.

(1) Abstracted from a thesis presented by Hugh J. McDonald to the Committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science, June, 1939.

(2) Gibson and Giauque, *THIS JOURNAL*, **45**, 93 (1923).

(3) Aston, Willihnganz and Messerly, *ibid.*, **57**, 1642 (1935).

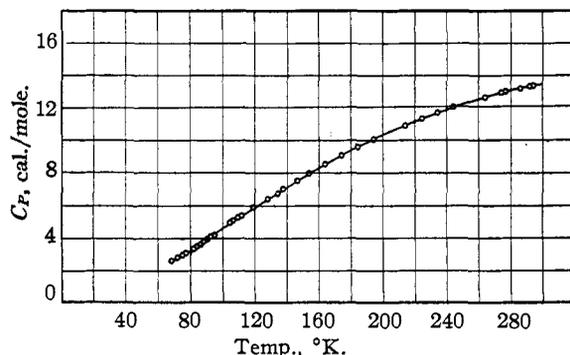
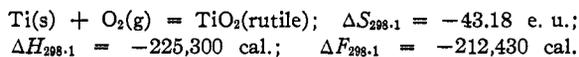


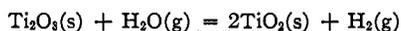
Fig. 1.—Molal heat capacities of TiO_2 .

68–175°K. At 68°K., the contribution of the Debye function to the entropy was 1.23 e. u., while that of the two equal Einstein functions was less than the probable experimental error. Between 68–298.1°K., the entropy change was evaluated graphically and amounted to 11.22 e. u. The sum of these values yields 12.45 e. u. for the entropy of titanium dioxide (rutile) at 298.1°K. The accuracy of this figure, with the small extrapolation, is estimated to be within ± 0.1 e. u.

Thermodynamic Properties of Titanium Dioxide.—Using accepted⁵ values for the entropies of the elements, $\Delta S_{298.1} = -43.18$ e. u. for formation of the oxide. The heat of formation of titanium dioxide has been determined by several investigators, and the latest and apparently most reliable value is that of Neumann, Kroger and Kunz.⁶ They find $\Delta H_{298} = -225,300 \pm 300$ cal. for formation of the oxide. From this value and the entropy of formation we calculate $\Delta F_{298.1}^\circ = -212,430$ cal., for the standard free energy of formation, and thus we can write



Nasu⁷ has studied the equilibrium



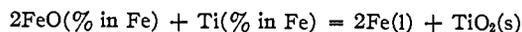
and has calculated from these equilibrium measurements, $\Delta H_{298.1} = -4700$ cal.; $\Delta F_{298.1}^\circ = -5280$ cal. Combining these data with those for TiO_2 and $\text{H}_2\text{O}(\text{g})$ we calculate for the entropy of $\text{Ti}_2\text{O}_3(\text{s})$; $S_{298.1} = 9.0$ e. u. This value appears much too low for an oxide of this type for which an entropy between 20 and 30 e. u. would be expected. This might indicate some serious error in the equilibrium measurements.

(5) Kelley, Bureau of Mines Bulletin 394, 1935, p. 35.

(6) Neumann, Kroger and Kunz, *Z. anorg. allgem. Chem.*, **218**, 379 (1934).

(7) Nasu, *J. Chem. Soc. Japan*, **56**, 542 (1935).

Deoxidation of Steel by Titanium.—Titanium is used occasionally as a deoxidizer in steel and Chipman⁸ has attempted to approximate the free energy equation for the deoxidation reaction



From the data on the formation of titanium dioxide, given above, it should be possible to arrive at a satisfactory free energy equation for this reaction applicable at liquid steel temperatures. From the tables by Kelley⁹ we find for the reaction: $\text{Ti(s)} + \text{O}_2(\text{g}) = \text{TiO}_2(\text{s})$, $\Delta C_p = -5.37 + 6.14 \times 10^{-3}T + 5.788 \times 10^5 T^{-2}$, and in the usual manner express the standard free energy change of the reaction

$$\Delta F^\circ = -222,030 + 5.37T \ln T - 3.07 \times 10^{-3}T^2 - \\ 2.894 \times 10^4 T^{-1} + 5.70T$$

In the temperature range, 1500–1800°C., this can be put in the linear form, approximately

$$\Delta F^\circ = -223,800 + 41.2T$$

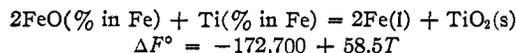
To convert from Ti(s) to Ti(l) , the melting point of titanium is taken as 2273°K. and the ΔH of fusion is estimated on the assumption that, like silicon, the entropy of fusion is 5.5 e. u./gram atom at the melting point, from which it follows

$$\text{Ti(s)} = \text{Ti(l)}; \Delta F^\circ = 12,500 - 5.5T$$

Evaluation of ΔF° for the change $\text{Ti(l)} = \text{Ti}(\% \text{ in Fe})$ presents some difficulty since a compound Fe_3Ti appears in the iron-titanium system and hence in dilute liquid solutions of titanium in iron marked negative deviations might be expected, and the limiting Henry's law value of the activity coefficient, a/N , for titanium must reach a value considerably less than unity. In the study of liquid metal systems from which intermetallic compounds appear as solid phases, one of the authors¹⁰ has shown that a reasonable estimate of the value of this coefficient is of the order of 0.2. Hence, we can write for low concentrations of titanium

$$\text{Ti(l)} = \text{Ti}(\% \text{ in Fe}) \\ \Delta F^\circ = -4.58T \log \frac{100 \times 47.9}{0.2 \times 55.84} = -9.5T$$

Chipman⁸ has determined the standard free energy change for the reaction: $\text{Fe(l)} + \frac{1}{2} \text{O}_2(\text{g}) = \text{FeO}(\% \text{ in Fe})$, for which in the steel-making temperature range: $\Delta F^\circ = -31,780 - 1.16T$. Combining the four equations



(8) Chipman, *Trans. Am. Soc. Metals*, **22**, 385 (1934).

(9) Kelley, Bureau of Mines Bulletin 371 (1932).

(10) Seltz and DeWitt, *This Journal*, **60**, 1305 (1938).

This equation indicates that titanium is somewhat more effective as a deoxidizer in steel than would be calculated from the equation of Chipman, which gives for the reaction

$$\Delta F^\circ = -151,000 + 57.3T$$

The deoxidation constants usually are expressed as the reciprocals of the constants of the deoxidation reactions; *i. e.*, $K = [\%Ti] \times [\%FeO]^2$. The values of these constants calculated from the authors' and from Chipman's equations are compared in Table II at several temperatures.

TABLE II
DEOXIDATION CONSTANTS

| Temp., °C. | 1500 | 1600 | 1700 |
|------------|----------------------|----------------------|----------------------|
| Chipman | 8.2×10^{-7} | 8.1×10^{-6} | 6.2×10^{-5} |
| Authors | 3.2×10^{-9} | 4.3×10^{-8} | 4.4×10^{-7} |

The authors wish to thank Professor J. G. Aston

of Pennsylvania State College who made available the standard couple, S-6, for calibration of our calorimeter; Dr. C. S. Barrett of the Metals Research Laboratory of this Institute for the X-ray photographs of the oxide used in this investigation; and Mr. J. W. Stewart, of the same laboratory, for the spectroscopic analysis.

Summary

1. The heat capacity of titanium dioxide (rutile) has been determined from 68–298°K.

2. The entropy of titanium dioxide has been computed from these measurements and found to be 12.45 e. u. at 298.1°K.

3. The thermodynamic properties of titanium dioxide have been evaluated, and applied to the problem of the deoxidation of steel by titanium.

PITTSBURGH, PENNA.

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[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Analytical Procedures Employing Karl Fischer Reagent. I. Nature of the Reagent

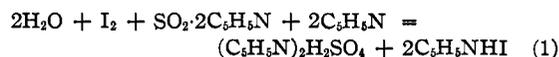
BY DONALD MILTON SMITH, W. M. D. BRYANT AND J. MITCHELL, JR.

The determination of water in mixtures by specific chemical methods has become an essential part of analytical chemistry. The senior authors¹ described such a procedure based on the hydrolysis of acetyl chloride in the presence of pyridine. Almost simultaneously another water method of unusual simplicity and range of application but based on a different chemical reaction was described by Karl Fischer.² The latter method involves a direct titration of the wet material with a solution of iodine, sulfur dioxide and pyridine in methanol, the reagent serving as its own indicator. The two methods have unique advantages in specific types of analysis, but the general analytical value of Fischer's method is sufficiently great to render desirable a detailed study of its underlying chemistry and a presentation of some of its significant applications.

Fischer has given a good practical discussion of the preparation and use of his reagent but has only briefly outlined the reactions involved. The latter, however, while partly correct as given, do not adequately explain the observed quantitative results. For example, his reaction

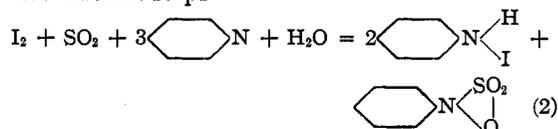
(1) Smith and Bryant, *THIS JOURNAL*, **57**, 841 (1935). This reference includes a brief review of earlier work.

(2) Karl Fischer, *Angew. Chem.*, **48**, 394 (1935).



calls for the removal of two moles of water for each mole of iodine introduced, while the writers find that actually about one mole or less of water is removed by the unmodified reagent. In order to shed more light on the mechanism and stoichiometric relations upon which Fischer's method is based, the present paper includes a study of the fundamental molal ratios of the various constituents of the reagent and their relation to water removal. By working with concentrated solutions, crystalline intermediates and products were isolated and identified by optical crystallographic methods. Other bases were substituted for pyridine and other solvents for methanol, and the effect of the various modifications noted.

One of the most interesting results was the discovery that the fundamental reaction occurs in two distinct steps:



and

