of the millicoulometer, it is evident that more accurate values of n are available when the diffusion current is relatively high, and the fact that the number of moles of material reduced is found from the difference between two current measurements means that the electrolysis should be allowed to proceed for as long a period of time as is convenient. From these considerations it can be deduced that the volume of solution should be very small and that the value of $m^{2/3}t^{1/6}$ should be fairly high. Increasing the concentration of the solution improves the accuracy of the millicoulometric measurements, but it correspondingly increases the time required for the deposition of a given fraction of the reducible material.

It can readily be shown that the diffusion current at the end of an electrolysis lasting for T seconds should be given by the equation

$$\log i_d = \log i_d^0 - \frac{4.403 \times 10^{-6}\, Im^{2/3}t^{1/6}\, T}{Vn} \qquad (1)$$

where i_d^0 is the diffusion current at the beginning of the electrolysis, V is the volume of the solution (ml.) and the other symbols have their ordinary polarographic significance. This relation is implicitly inherent in methods for the determination of n by the graphical integration of the current–time curve.

Typical diffusion current data for the electrolysis of a solution of 2.57 micromoles of lead(II) in 0.1 F potassium chloride 0.1 F hydrochloric acid are shown in Fig. 3. Under these conditions equation (1) becomes

$$\log i_d = 1.2711 - 2.009 \times 10^{-5}T \qquad (2)$$

In agreement with equation (2), the points are seen to fall very well on a straight line, but the slope of this line is found to be 1.82×10^{-5}. This gives a value of 2.21 for n, which is not in very good agreement with the theoretical $n = 2.00$ for the reduction of lead ion. The discrepancy is comparable with the errors found by Loveridge and Lingane[7] in their attempts to integrate the current–time curve, and it is directly attributable to the depletion of the solution around the capillary tip during the electrolysis.

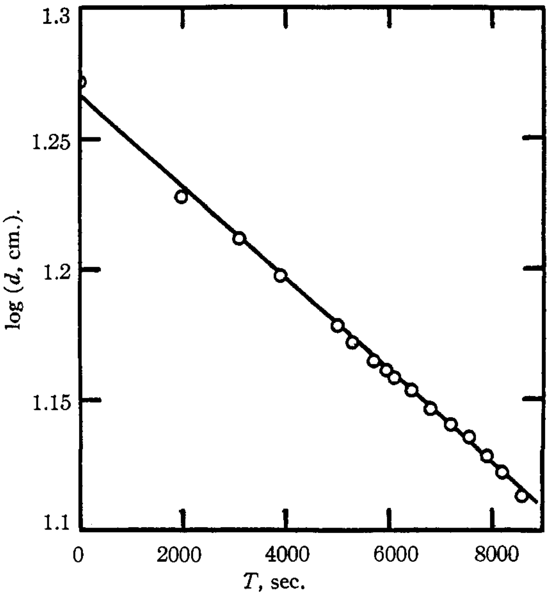

Fig. 3.—Current–time curve for the electrolysis of lead (II); see text for experimental details. Diffusion currents are in arbitrary units of galvanometer deflection, and have been corrected for the residual current.

From a number of electrolyses of solutions of thallium(I), cadmium(II) and lead(II), the average accuracy and precision to be expected from the method here described appears to be about 3%.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Heats of Formation of TiO, Ti_2O_3, Ti_3O_5 and TiO_2 from Combustion Calorimetry[1]

BY GEORGE L. HUMPHREY

A precise combustion calorimeter has been constructed to measure the heats of combustion of inorganic substances. Calculations from measured heats of combustion for titanium, titanium monoxide, titanium sesquioxide and titanium tritapentoxide have yielded the following values for the standard heats of formation ($-\Delta H_f^0$) in kcal./mole: TiO, $123.9_1 \pm 0.2_8$; Ti_2O_3, $362.9_3 \pm 0.4_8$; Ti_3O_5, $586.9_1 \pm 0.6_9$; TiO_2, $225.5_2 \pm 0.2_3$. Free energies of formation also are presented.

The facilities of this Laboratory for obtaining thermodynamic data for inorganic substances have been extended by the development of a precise combustion calorimeter. This calorimeter makes possible the determination of heats of formation of many substances that are not susceptible to the methods of solution calorimetry, either because of slow reaction rates or because of difficulties in obtaining unequivocal final solution states.

The heats of formation of the titanium oxides are important thermodynamic quantities in various metallurgical calculations of both research and industry. A survey of the literature shows large deviations among the existing values, or else the values are missing entirely. The only direct determination is the heat of formation of TiO_2 by combustion measurements, which yield values[2] ranging from 218.0 to 225.3 kcal. per mole for $-\Delta H_f^0$.

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(1) Article not copyrighted.

(2) (a) W. G. Mixter, *Z. anorg. Chem.*, **74**, 122 (1912); (b) W. A. Roth and G. Becker, *Z. physik. Chem.*, Ergänzungsband (1931) Bodenstein Festband; (c) A. Sieverts and A. Gotta, *Z. anorg. Chem.*, **199**, 384 (1931); (d) B. Neumann, C. Kröger, and H. Kunz, *ibid.*, **218**, 379 (1934); (e) W. A. Roth and U. Wolf, *Rec. trav. chim.*, **59**, 511 (1940).

Several reasons may be suggested for the apparent discrepancies in combustion measurements. Apart from systematic errors, variations may result from (1) impurities in the combustion samples, (2) incomplete combustions, (3) reaction of molten oxides with the crucible material, (4) ignition or kindling aids or (5) difference in combustion conditions between calibration and experiment. The investigations reported here have been carried out so as to eliminate, or correct for, as completely as possible the above-mentioned sources of error. Corrections for impurities in the combustion samples have been made from careful analytical data, and essentially complete combustions have been obtained. Fused quartz crucibles, heavily lined with pure TiO_2 (rutile), have been used when the heat liberated was sufficient to cause molten oxides, and no ignition aids other than the usual filter-paper fuse were used. The calibration of the calorimeter has been carried out in several different ways to reproduce as nearly as possible the actual combustion conditions, and reasonable corrections have been applied when this was not practicable.

The Apparatus and Method.—An ordinary non-adiabatic calorimeter of the type described by Dickinson[3] was designed and constructed. Minor changes were made in the calorimeter and constant-temperature jacket, but the shape and operation were essentially the same as the Bureau of Standards model. The opening around the calorimeter stirrer was closed by means of an oil seal,[4] and the water jacket was similar to that described by Hubbard,[5] *et al.* The water jacket was regulated at 30° (±0.001°) by means of a Precision Instrument Co. Magna-Set thermoregulator with suitable relays.

A double-valve Parr illium bomb having an effective gas volume of 355 ml. was used for combustions. The electrodes and crucible support of the original bomb were fitted with Hastelloy-C screw binding posts for making a reproducible contact with the electrical fuse wire, and the short metallic legs of the original bomb were replaced by bakelite supports about 12 mm. high.

The temperature rise in the calorimeter was measured by means of a platinum resistance thermometer, a type G-2 Mueller resistance bridge, and a high-sensitivity galvanometer, all supplied by the Leeds & Northrup Co. A change of 0.00005 ohm (0.0005°) in the resistance of the thermometer caused a 1 mm. shift in the reflection from the galvanometer mirror on the scale. The galvanometer was used as a null-point instrument, the time at which a predetermined resistance was reached being recorded on a Gaertner drum-type chronograph to a precision of 0.1 sec.

Samples were ignited by the platinum wire–filter paper fuse procedure of Huffman and collaborators.[6] The voltage, current and time were accurately measured to determine the electrical energy (*EIt*) introduced in the ignition process. An auxiliary electronic firing circuit facilitated control of the firing time, and, upon pressing a button to fire the charge, the current reached a steady value within a short time and was then automatically turned off. By maintaining constant voltage, identical current and time conditions were achieved from run to run, and thus the *EIt* correction was constant, amounting to 1.4 cal. Whatman ashless filter paper No. 42 was used as fuse material, and its heat of combustion was determined to be 3,898 cal. per gram (in air and at constant humidity).

The mass of calorimeter and water was determined to at least 0.1 g. on a torsion balance sensitive to 0.05 g. at 4 kg., and the mass of the samples was determined to 0.01 mg. on an assay balance.

Commercial tank oxygen was used in the combustions, and the bomb was flushed twice before final filling by admitting oxygen to 10 atm. and reducing to atmospheric pressure. The oxygen pressure used for combustion was either 30 or 40 atm., depending on the substance to be burned.

Nitric acid formed by small amounts of nitrogen in the tank oxygen was determined either by adding 1 ml. of water to the bomb before combustion and titrating the washings with dilute standard sodium hydroxide solution, using brom cresol green as indicator; or the gas from the bomb was passed through a scrubbing column containing a known amount of standard sodium hydroxide to absorb the acid, and the amount of nitric acid determined by titrating the excess base with standard nitric acid. The two methods gave results in good agreement, and the correction ranged from 0.0 to 0.4 cal., based on the value −13,960 cal. per mole for the heat of formation of nitric acid at constant volume.

The corrected temperature rise (in ohms) was calculated by the Dickinson[3] method, and the initial and final temperatures of the calorimeter were always the same within narrow limits. For convenience in attaining the same initial temperature, the calorimeter was equipped with a heater, and essentially constant final temperatures were obtained by adjusting the size of the samples burned.

Calibration.—Benzoic acid, N.B.S. Standard Sample 39 g, having an isothermal heat of combustion at 25° of 26.4338 abs. kj. per g. mass under standard bomb conditions[7] was used for determining the energy equivalent of the calorimeter.

As the heats of combustion per gram were expected to be rather low for some of the substances burned, the calorimeter was calibrated for two temperature intervals, one about half the other. For the larger temperature interval the deviation from the standard bomb process was small, amounting to −0.02%. When all corrections[8] were made for deviations from standard conditions, and for change in heat capacity of the initial and final systems the energy equivalent of the calorimeter remained constant, within experimental error, for both the large (2.2°) and small (1.1°) temperature intervals.

Twelve combustions of benzoic acid (using either 1.090- or 0.545-g. samples) yielded a value of 32366.6 cal./ohm for the energy equivalent of the calorimeter at 30°. The average deviation from the mean of these experiments was ±0.012% and the maximum deviation 0.03%. Fifteen additional calibrations of the calorimeter, made from time to time throughout this work, have further substantiated the value and precision given above for the energy equivalent.

Materials.—The titanium metal was obtained in the form of a pressed bar from the Boulder City Station of the Bureau of Mines. It was prepared for combustion by taking very thin lathe turnings from the interior of the bar with a carboloy cutting tool. The analysis was: Ti, 99.72; Fe, 0.022; Mg, 0.07; Cl_2, 0.065; Si, 0.002; N_2, 0.012; Mn, 0.008; O_2, 0.1 (est.).

The TiO was part of the sample used previously in low- and high-temperature heat-capacity measurements.[9,10] It was reheated in a vacuum at 325° and analyzed: TiO, 99.2; SiO, 0.7; TiC, 0.1.

New samples[11] of Ti_2O_3 and Ti_3O_5 were prepared according to the methods described previously.[9] The analyses were: (a) Ti_2O_3, 99.90; C, 0.06; SiO_2, 0.04. (b) Ti_3O_5, 99.95; C, 0.03; SiO_2, 0.02.

Prior to combustion, all samples were stored in a desiccator containing Dehydrite.

Units and Calculations.—The results of the combustion experiments and derived quantities are expressed in terms of the defined calorie,

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(3) H. C. Dickinson, *Bull. Bur. Standards*, **11**, 189 (1915).

(4) W. P. White, "The Modern Calorimeter," Chemical Catalog Co., (Reinhold Publishing Corp.), New York, N. Y., 1928, p. 150.

(5) W. N. Hubbard, J. W. Knowlton and H. M. Huffman, This Journal, **70**, 3259 (1948).

(6) (a) H. M. Huffman and E. L. Ellis, *ibid.*, **57**, 41 (1935); (b) R. D. Stiehler and H. M. Huffman, *ibid.*, **57**, 1734 (1935); (c) H. M. Huffman, *ibid.*, **60**, 1171 (1938).

(7) R. S. Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942); *ibid.*, **36**, 421 (1946); see also N. B. S. Certificate accompanying Standard Sample 39g.

(8) E. W. Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

(9) C. H. Shomate, This Journal, **68**, 310 (1946).

(10) B. F. Naylor, *ibid.*, **68**, 1077 (1946).

(11) Preparation and analyses of these compounds were made by K. R. Bonnickson, Chemist, Pacific Experiment Station, Bureau of Mines.

which equals 4.1840 absolute joules, and refer to weights *in vacuo*. For making the weight correction to vacuum, the densities given by Shomate[9] and Hoyt[12] were used (ref. Table I).

The heats of combustion per gram of substance burned under the conditions prevailing in the bomb, corrected to 30° and for impurities,[13] were converted to the isothermal heats of combustion per mole by multiplying by the molecular weights computed from the 1949 Table of International Atomic Weights. The corrections to unit fugacity were made by the equation,[14] $(\partial U/\partial P)_{301°\text{K.}} = -1.556$ cal. per atmosphere per mole for oxygen. (The correction to 303°K. for this equation is negligible.) To change to ΔH_{R}, the appropriate work function, $RT\Delta n$, was applied, and in correcting to standard temperature the equation $(\partial \Delta H/\partial T) = \Delta C_{\text{p}}$ was used. The values for computing ΔC_{p} were taken from Kelley.[15]

Combustion Data and Results.—Because of the low heats of combustion of Ti_2O_3 and Ti_3O_5, the temperature rise in the calorimeter was about one-quarter of the two-degree temperature rise obtained when the calorimeter was calibrated under nearly standard conditions. No attempt was made to calibrate the system for such a low temperature rise because of the difficulty in obtaining complete combustion of a small quantity of benzoic acid. Accordingly, the value obtained for the energy equivalent of the calorimeter in both the full and half temperature ranges was assumed to hold for an even smaller temperature rise.

For the titanium and TiO combustions, the intervals of temperature were two and one degree, respectively.

Combustions were made on turnings of titanium metal and the oxides in powdered form. Because of the formation of molten oxide in the combustion process, with subsequent attack of the crucible material, the titanium metal and the TiO were contained in quartz crucibles heavily lined with pure rutile. The slight sintering of the combustion product in the case of Ti_2O_3, and no change in the powder state of Ti_3O_5 during combustion, warranted the use of unlined quartz and platinum crucibles, respectively. The color of the TiO_2, formed in combustion, ranged from dark gray in the case of titanium metal to light yellow for Ti_3O_5, although no unburned material could be detected in either of these combustions.

The following methods were used to test for completeness of combustion: (1) the combustion product was finely ground in an agate mortar and ignited to constant weight; (2) the finely powdered combustion product was returned to the calorimeter with the correct amount of white oil ($-\Delta U_{\text{B}}/m$ = 10,681 ± 2 cal./g.) to give the required temperature rise and reburned to determine the additional heat not due to oil. Both of these tests proved negative in the case of Ti and Ti_3O_5, but a small increase in weight in the ignition test was detected in the case of TiO and Ti_2O_3. The increase in weight was taken as due to oxidation of the original oxide, and the combustion values were corrected accordingly. This method was chosen as the more reliable to correct for incomplete combustion because of the difficulty in measuring small quantities of heat from the unburned material in comparison with the large amounts due to oil when the former method was used.

The corrections for incomplete combustion applied to the individual values obtained for the heats of combustion per gram of substance burned in the bomb process, ranged from 3.08 to 5.87 cal./g. for TiO, and from 0.98 to 9.20 cal./g. for Ti_2O_3. No corrections were necessary for incomplete combustions in the case of Ti and Ti_3O_5.

Tests were made to determine the amount of oxidation of the substances prior to ignition in the oxygen atmosphere of the bomb. In all cases the amount of oxidation was found to be negligible.

The values from at least seven combustions for each substance were employed to compute average values for the heats of combustion per gram. The average values were then corrected for impurities in the samples. These corrections changed the measured heats of combustion by the following per cent.: Ti, +0.323; TiO, −0.420; Ti_2O_3, −0.608; Ti_3O_5, −0.478.

The final corrected values for the heats of combustion per gram at 30° are as follows: Ti, 4694.50 ± 1.33 cal./g.; TiO, 1584.56 ± 0.48 cal./g.; Ti_2O_3, 610.46 ± 0.08 cal./g.; Ti_3O_5, 399.46 ± 0.07 cal./g. (The indicated deviations are average deviations from the mean.)

All of the combustions included in the final values for the titanium compounds were made under 40 atm. oxygen pressure and with no water in the bomb. Appropriate corrections were applied to the standard energy equivalent of the calorimeter system for omission of 1 ml. of water, the increase in oxygen content from 30 atm., and differences in weights of crucible and lining. After each combustion, the interior of the bomb appeared clean and dry.

The titanium dioxide formed in the combustion process was examined by X-ray powder photographs and found to be rutile in all instances.

A summary of the derived data is presented in Table I. The quantities shown are $-\Delta U_{\text{B}}$, the actual heat evolved at 30° per mole of substance burned under bomb conditions, corrected for incomplete combustion and impurities; $-\Delta H_{\text{R}}$, the heat evolved for the reaction under standard conditions; $-\Delta H_{\text{f}}^0$, the standard heat of formation from the elements; and $-\Delta F_{\text{f}}^0$, the standard free energy of formation from the elements.[16]

The uncertainties given in Table I are the uncertainty interval of Rossini,[17] derived from considerations of the uncertainties in the heat of combustion of benzoic acid (± 0.010%), the calibration error (± 0.012%), the reaction errors that obtained in each case, and additional uncertainties for the impurities correction. The possibility

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[12] S. L. Hoyt, "Metals and Alloys Data Book," Reinhold Publishing Corp., New York, N. Y., 1943, p. 290.

[13] Values for the heats of combustion per gram of impurity were estimated from data given in the N. B. S. Tables of Selected Values of Chemical Thermodynamic Properties, U. S. Department of Commerce, for the heats of formation of logical combustion products.

[14] F. D. Rossini and M. Frandsen, *J. Res. Natl. Bur. Standards*, **9**, 733 (1932).

[15] K. K. Kelley, Bur. Mines Bull. 476 (1949).

[16] Entropy values for calculating free energies are from K. K. Kelley, Bur. of Mines Bull. 477 (1950).

[17] F. D. Rossini, *Chem. Revs.*, **18**, 233 (1936).

TABLE I

SUMMARY OF DERIVED DATA AT 25°[a]

Substance	Mol. wt.	Density	$-\Delta U_B$[b], kcal./mole	$-\Delta H_R$, kcal./mole	$-\Delta H_f°$, kcal./mole	$\Delta F_f°$, kcal./mole
Ti	47.90	4.51	224.86 ± 0.22	225.52 ± 0.23	225.52 ± 0.23[c]	212.33 ± 0.23[c]
TiO	63.90	4.92	101.25 ± 0.12	101.61 ± 0.12	123.91 ± 0.28	116.92 ± 0.28
Ti_2O_3	143.80	4.56	87.78 ± 0.10	88.11 ± 0.10	362.93 ± 0.48	342.31 ± 0.48
Ti_3O_5	223.70	4.15	89.36 ± 0.05	89.65 ± 0.05	586.69 ± 0.69	553.12 ± 0.69

[a] Errors are uncertainty interval. [b] At 30°. [c] Datum for TiO_2.

that the slight increase in weight on ignition of the combustion product (used to correct for incomplete combustion) was due to some higher oxide between the one burned and TiO_2 is not excluded by this work; consequently, the uncertainties in the final results have been increased when necessary to account for this.

The value 225.3 ± 0.3 kcal./mole obtained by Neumann, *et al.*,[2d] for the heat of formation, $-\Delta H_f°$, of TiO_2 from combustion measurements on titanium metal is in good agreement with the value obtained here. No combustion measurements for the other oxides of titanium appear in the literature. However, Nasu[18] determined the equilibrium H_2O/H_2 ratio for the reduction of TiO_2 in an iron tube and from his measurements calculated $-\Delta H_{298} = 388.1$ kcal./mole for the heat of formation of Ti_2O_3. Brewer[19] subsequently has used Nasu's data and other considerations in estimating the heats of formation at 298°K. of TiO, Ti_2O_3 and Ti_3O_5 as -127, -381 and -605 kcal./mole, respectively. The National Bureau of Standards[13] has also listed values for the standard heats of formation in kcal./mole as: Ti_2O_3, -367; Ti_3O_5, -584; TiO_2, -218. Although all of these values are of the correct order of magnitude, their accuracy is by no means comparable to that of the direct determinations reported here.

Using entropy data listed by Kelley,[16] free energies of formation from the elements at 1 atm. pressure and 298°K. were calculated (see Table I). Further calculations of free energy changes at ordinary temperatures show that both TiO and Ti_2O_3 are thermodynamically stable to disproportionation; the reaction, $Ti_3O_5 = Ti_2O_3 + TiO_2$, has a small negative ΔF; and decomposition of Ti_3O_5 into TiO_2 and TiO, or Ti, is precluded.

BERKELEY 4, CALIF. RECEIVED SEPTEMBER 18, 1950

(18) N. Nasu, *J. Chem. Soc. Japan*, **56**, 659 (1935).

(19) L. Brewer, "Thermodynamic Properties of the Oxides," University of California Radiation Laboratory Report-104, July 1948.

[CONTRIBUTION FROM THE ALUMINUM RESEARCH LABORATORIES]

Analogies in the Gallia and Alumina Systems. The Preparation and Properties of Some Low-Alkali Gallates[1]

BY L. M. FOSTER AND H. C. STUMPF

Gallium, appearing in Group III of the periodic table, shows great resemblance to aluminum in its chemical properties, and occurs to a very small extent in all natural aluminous materials. The similarity of the ionic radii of the two elements (0.57 Å. for aluminum, 0.62 Å. for gallium) permits mixed crystal formation, and a number of compounds, particularly oxides of gallium, have been observed which are isomorphous with the corresponding aluminum compounds.

In the aluminum system there are a considerable number of oxide and hydrated oxide phases. The older established forms are: alpha trihydrate (gibbsite), beta trihydrate (bayerite), alpha monohydrate (boehmite), beta monohydrate (diaspore), gamma alumina, and alpha alumina (corundum).[1] "Beta" alumina was originally thought to be another allotropic modification of anhydrous alumina, but it has since been found to be an alkali aluminate containing about 5% soda.[2]

Jellinek and Fankuchen[3] reported that the various X-ray powder diffraction patterns which can be obtained for gamma alumina can be interpreted as arising from specimens of different crystallite size, and that "gamma" represents a continuous transformation sequence in the nearly anhydrous alumina, ending in corundum at high temperature. Stumpf, *et al.*,[4] however, interpreted the patterns as arising from a number of discrete crystalline phases, the nature and proportion of which depend on the thermal treatment given the sample. These phases were arbitrarily designated gamma, delta, eta, theta, kappa and chi.

Striking analogies have been observed between the aluminas and gallias which contribute appreciably to our understanding of the two systems.

(1) Presented in part at the Seventh Annual Pittsburgh Conference on X-Ray and Electron Diffraction, November, 1948. The system of Greek letter designation used here is that introduced by J. D. Edwards, F. R. Frary and Z. Jeffries, "The Aluminum Industry, Vol. I—Aluminum and Its Production," McGraw-Hill Book Company, Inc., New York, N. Y., 1930.

(2) R. R. Ridgway, A. A. Klein and W. J. O'Leary, *Trans. Electrochem. Soc.*, **70**, 71–88 (1936).

(3) M. H. Jellinek and I. Fankuchen, *Ind. Eng. Chem.*, **37**, 158 (1945); **41**, 2259 (1949).

(4) H. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *ibid.*, **42**, 1398 (1950).