case, the dissociation constant of acetic acid was calculated from e.m.f. measurements at 25°. Formic acid was chosen as the acid of known strength. The buffer solutions were composed of sodium acetate and formic acid, each at molality *m*, and each solution was 0.005 molal with respect to potassium chloride. The calculation of $-1/2 \log K_AK_F$, where A represents acetic acid and F formic acid, is summarized in Table I. The extrapolation is shown in Fig. 1.

TABLE I

PRODUCT OF THE DISSOCIATION CONSTANTS OF FORMIC AND ACETIC ACIDS

m	$p_w\mathrm{H}$	$-{}^1/_2 \log (K_AK_F)'$ $a^* = 4$	$-{}^1/_2 \log (K_AK_F)'$ $a^* = 6$
0.04669	4.2384	4.2362	4.2363
.02993	4.2451	4.2419	4.2420
.02203	4.2490	4.2448	4.2450
.017426	4.2522	4.2471	4.2472
.014414	4.2522	4.2462	4.2463

$(\mu = 0)$; $-{}^1/_2 \log K_AK_F = 4.254$

The value of $-\log K_F$ is 3.751_5 at 25°.[7] Combination with the value of $-{}^1/_2 \log K_AK_F$, namely, 4.254, obtained by extrapolation gives 4.756_5 for $-\log K_A$ (acetic acid) at 25°. This result is in close agreement with 4.756 obtained by Harned and Ehlers[1] and with 4.755 from the conductance measurements of MacInnes and Shedlovsky[8] converted to the molal scale.

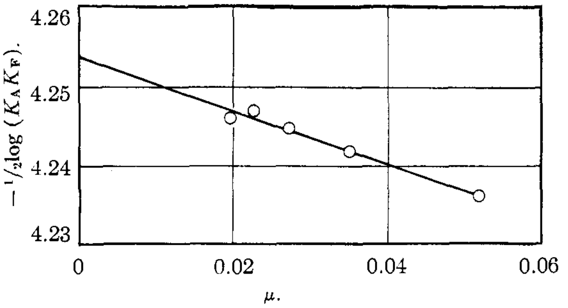

Fig. 1.—Extrapolation of $-{}^1/_2 \log (K_AK_F)'$ to zero ionic strength.

The results given in the last two columns of Table I show only a small uncertainty due to arbitrary choice of the ion size parameter in mixtures of formic and acetic acids. The error from this source increases, however, with the mean strength of the two acids concerned. If the two acids are phosphoric ($-\log K_1 = 2.14$) and formic ($-\log K_F = 3.75$) and $m_1 = 5m_2$, the value of $-{}^1/_2 \log K_1K_F$ in the limit is shifted by 0.0025 unit when $a^* = 6$ is chosen instead of $a^* = 4$. Hence, with increasing acid strength a threshold is reached, as also in the conventional method, above which this procedure is incapable of yielding accurate results.

WASHINGTON 25, D. C. RECEIVED DECEMBER 9, 1950

[7] H. S. Harned and N. D. Embree, THIS JOURNAL, **56**, 1042 (1934).

[8] D. A. MacInnes and T. Shedlovsky, *ibid.*, **54**, 1429 (1932).

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

The Heats of Combustion and Formation of Titanium Nitride (TiN) and Titanium Carbide (TiC)

BY GEORGE L. HUMPHREY

The heats of combustion of titanium nitride and titanium carbide were determined by burning the materials in a bomb containing oxygen. The standard heats of formation, calculated from the combustion data, are: TiN, $-80.4_7 \pm 0.2_7$; TiC, $-43.8_5 \pm 0.3_9$ kcal./mole. Free energies of formation also are listed.

Introduction

In continuation of a program of study of the thermodynamic properties of titanium compounds, the heats of combustion and formation of titanium nitride (TiN) and titanium carbide (TiC) were ascertained. This completes the basic information necessary for free energy calculations, since the entropies and high-temperature heat contents of these substances were reported in earlier publications[1-3] from this Laboratory.

The heat of combustion of titanium nitride was determined previously by Neumann, *et al.*,[4] resulting in −80.3 kcal. per mole for the heat of formation. No previous heat of combustion data for titanium carbide have been reported.

Experimental

The Calorimeter and Its Calibration.—The calorimeter and its general operation have been described[5] previously. A recalibration of the calorimeter was made using National Bureau of Standards benzoic acid, Standard Sample 39g, having for its isothermal heat of combustion per gram mass under standard conditions, at 25°, the value $-\Delta U_B/m = 26{,}433.8 \pm 2.6$ abs. joules. Under the conditions of the calibration experiments (volume of bomb, 355 ml.; water added, 1 ml.; oxygen pressure, 30 atm.; weight benzoic acid, 1.090 g.; temperature, 30°) $-\Delta U_B/m$ is 26,427.8 abs. joules. Conversion to calories was made by taking 1 cal. = 4.1840 abs. joules. The value obtained for the energy equivalent of the calorimeter was 32,369.5 cal./ohm, with an average deviation of ±0.02% and a maximum deviation of 0.03%, in good agreement with previous calibrations.[5]

Materials.—The titanium nitride and carbide were part of the samples used earlier[3] in the high-temperature heat-capacity measurements. The samples were reheated *in vacuo* at 325° and analyzed: (a) TiN, 99.60%; SiN, 0.40%; (b) TiC, 99.00%; Ti, 0.40%; Si, 0.26%; other impurities, 0.34%. The other impurities in the titanium carbide

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[1] K. K. Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944).

[2] C. H. Shomate, THIS JOURNAL, **68**, 310 (1946).

[3] B. F. Naylor, *ibid.*, **68**, 370 (1946).

[4] B. Neumann, C. Kröger and H. Kunz, *Z. anorg. Chem.*, **218**, 379 (1934).

[5] G. L. Humphrey, THIS JOURNAL, **73**, 1587 (1951).

TABLE I

EXPERIMENTAL DATA FOR HEATS OF COMBUSTION AT 30°

Weight of sample, g. in vac.	Cor. energy equiv. of cal., cal./ohm	Total heat evolved, cor. to 30°, cal.	Heat from *EIt*, fuse, HNO_3, cal.	$-\Delta U_B/m$, cal./g.	Cor. for incomp. comb., cal./g.	Heat of comb., cal./g.	Dev. from mean, cal./g.
Titanium nitride							
2.20228	32382.2	5181.11	23.97	2341.73	2.05	2343.78	+1.85
2.20231	32371.7	5176.71	19.92	2341.54	1.87	2343.41	+1.48
2.20129	32371.1	5170.04	21.02	2339.09	0.70	2339.79	−2.14
2.20198	32371.9	5168.58	16.26	2339.86	3.04	2342.90	+0.97
2.20189	32372.1	5168.58	19.76	2338.36	2.57	2340.93	−1.00
2.20159	32374.5	5166.57	17.16	2338.95	1.80	2340.75	−1.18
					Mean	2341.93	±1.44^a
			Mean corrected for impurities		(−0.195%)	2337.36	±1.44^a
Titanium carbide							
1.53136	32410.1	7037.07	18.75	4583.06	0.00	4583.06	−1.42
1.51183	32410.3	6914.43	24.21	4557.54	27.88	4585.42	+0.94
1.52971	32412.3	7026.11	17.61	4581.59	2.47	4584.06	−0.42
1.52982	32410.8	7010.75	20.69	4569.20	13.24	4582.44	−2.04
1.51037	32412.8	6906.03	23.03	4557.16	28.24	4585.40	+0.92
1.53112	32411.6	7012.96	16.50	4569.50	16.64	4586.14	+1.66
1.53004	32410.9	7032.51	19.80	4583.35	1.47	4584.82	+0.34
					Mean	4584.48	±1.11^a
			Mean corrected for impurities		(+0.138%)	4590.81	±1.11^a

^{a} Average deviation from mean.

sample were determined by spectrographic analysis[6] to be: Fe, 0.08%; Mn, 0.01%; Ni, 0.02%; CaO, 0.18%; Al_2O_3, 0.03%; MgO, 0.02%.

The experimentally determined densities,[3] TiC, 4.81 and TiN, 5.24 g./cc., were used in correcting weights to vacuum.

Combustion Data and Results

The precautions taken to avoid error in determinations of heats of combustion of inorganic substances were mentioned earlier[5] and followed in the present work.

The combustion experiments were carried out in quartz crucibles heavily lined with pure rutile. Samples were ignited by use of the usual filter paper fuse without the aid of any kindler. The oxygen pressure was 30 atm. Corrections were applied to the energy equivalent of the calorimeter for change in weight of crucible and lining and for the omission of 1 cc. of water when applicable.

Nitric acid formed in the combustion process was determined either by titrating the bomb washings with sodium hydroxide, if water had been added, or by passing the combustion gases from the dry bomb into excess sodium hydroxide and back-titrating with standard nitric acid. Brom cresol green was used as indicator. Substantially the same corrections for nitric acid were obtained by either method and amounted to approximately 0.3 cal. in the titanium nitride combustions and approximately 0.2 cal. in the titanium carbide combustions.

Tests[7] for nitrate and nitrite formation in the material from the titanium nitride combustions proved negative. No significant amount of carbon monoxide could be detected in the combustion gases from titanium carbide, using the method described by Cook.[8]

There was some spattering of titanium dioxide onto the walls of the bomb in both the nitride and carbide combustions. An examination of the combustion products by means of X-ray powder photographs showed that the portion of the material remaining in the crucible after combustion was rutile. Some lines that could be identified as due to anatase were evident on the photographs from the spattered material. A rough estimation, based upon the relative photographic intensities of the rutile and anatase lines and the amount of spattered material, indicated that less than 5% of the total titanium dioxide formed in combustion was anatase. No lines that could be identified as titanium nitride or carbide were found on the X-ray photographs of the spattered material.

Preoxidation of the materials in the oxygen atmosphere of the bomb proved negligible. A slight increase in weight upon strong ignition in air of the combustion product remaining in the crucible indicated that oxidation in the bomb process was not quite complete. The combustion values were corrected, therefore, by assuming the increase in weight as due to complete oxidation of any remaining original material.

The results of the individual combustion experiments are presented chronologically in Table I. The values listed in the column under $-\Delta U_B/m$ are the heats of combustion per gram measured in the bomb process and corrected to 30°. The next column shows the magnitude of the corrections applied for incomplete combustion to give the final values listed under heat of combustion. The average of the final values was corrected for impurities by calculating the heats of combustion of logical combustion products from data given by the National Bureau of Standards.[9] No corrections were made for the small amounts of anatase formed.

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(6) The spectrographic analysis was made by the Titanium Alloy Manufacturing Co.

(7) E. H. Swift, "System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1940, p. 486.

(8) F. Cook, *Ind. Eng. Chem., Anal. Ed.*, **12**, 661 (1940).

(9) N. B. S. Tables of Selected Values of Chemical Thermodynamic Properties, U. S. Dept. of Commerce.

The corrected mean heat of combustion of titanium nitride is 2337.36 cal. per gram for the sample burning at constant volume and in an initial oxygen pressure of 30 atm. The corresponding value for titanium carbide is 4590.81 cal. per gram. Molecular weights, computed from the 1949 Table of International Atomic Weights, were used to obtain, from the heats of combustion per gram, the values of the energy changes in the bomb ($-\Delta U_B$) for the combustion of one mole of titanium nitride, or carbide, to titanium dioxide (rutile) and nitrogen, or carbon dioxide.

To obtain the heats of combustion under standard conditions ($-\Delta H_R$), the value obtained for $-\Delta U_B$ must be corrected (1) to unit fugacity, (2) to a constant-pressure process and (3) to standard temperature. The values used for the intrinsic energy change of the gases with pressure were oxygen,[10] −1.56, nitrogen,[10] −1.43 and carbon dioxide,[11] −6.72 cal. per atm. per mole at 30°. The relation $\Delta H = \Delta U + RT\Delta n$ was used to compute the correction for the constant-pressure process, and values for computing ΔC_p to correct to standard temperature were taken from Kelley.[12]

The standard heats of combustion ($-\Delta H_R$) of titanium nitride and carbide are listed in Table II, together with the heats of combustion obtained under bomb conditions ($-\Delta U_B$), the standard heats of formation from the elements ($-\Delta H_f^0$), and the standard free energies of formation ($-\Delta F_f^0$). The deviations listed are the uncertainty interval of Rossini[13] and include, in addition to the respective precision errors taken for the heat of combustion of benzoic acid, the calibration experiments, and the combustion experiments on the nitride and carbide, reasonable values assigned to the possible errors in the corrections for impurities and incomplete combustion. In computing standard heats of formation, the value 225.52 ± 0.23 kcal./mole, obtained earlier[5] for the combustion of titanium metal to titanium dioxide, was used, as well as the value, 94,051.8 ± 10.8 cal./mole, for the heat of formation of carbon dioxide.[14] The entropy values listed by Kelley[12] were used to obtain the free energies of formation.

TABLE II

SUMMARY OF DERIVED DATA FOR TITANIUM NITRIDE AND TITANIUM CARBIDE[a]

Compound	$-\Delta U_B$ kcal./mole at 30°	$-\Delta H_R$ kcal./mole at 25°	$-\Delta H_f^0$ kcal./mole at 25°	$-\Delta F_f^0$ kcal./mole at 25°
TiN	144.70 ± 0.14	145.05 ± 0.14	80.47 ± 0.27	73.65 ± 0.27
TiC	275.04 ± .32	275.72 ± .32	43.85 ± .39	43.01 ± .39

[a] Errors are "uncertainty interval."

The value found here for the heat of formation of titanium nitride is in good agreement with that of Neumann.[4] Comparison with free energy values listed by Kelley[15] and Brewer, *et al.*,[16] indicates that titanium carbide and nitride are among the thermodynamically most stable carbides and nitrides.

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(10) F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

(11) E. W. Washburn, *ibid.*, **10**, 525 (1933).

(12) K. K. Kelley, *Bur. Mines Bull.*, 477 (1949).

(13) F. D. Rossini, *Chem. Rev.*, **18**, 233 (1936).

(14) E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Research Nat. Bur. Standards*, **33**, 447 (1944).

(15) K. K. Kelley, Bur. Mines Bull. 407 (1938).

(16) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "Chemistry and Metallurgy of Miscellaneous Materials," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 40-59.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

The Inductive Effect and Chemical Reactivity. I. General Theory of the Inductive Effect and Application to Electric Dipole Moments of Haloalkanes

BY RICHARD P. SMITH, TAIKYUE REE, JOHN L. MAGEE[1] AND HENRY EYRING

The inductive effect is discussed qualitatively in terms of bond orbital theory, and the main features of the effect are pointed out. A simple semi-classical model for the inductive effect is then introduced, and the analysis of this model leads to a method for calculating approximately net charges on atoms in molecules having no conjugation. All of the parameters are obtained from accepted longitudinal polarizabilities, screening constants, covalent bond radii and electric dipole moments. The method is checked by comparing calculated and observed electric dipole moments of some halogen substituted alkanes, and excellent agreement is found. The method will be shown, in succeeding papers, to be of great utility in understanding relative organic reaction rates and equilibria.

Introduction

The inductive effect has long been recognized as playing a prominent role in determining relative rates of organic reactions. The extent of this role has heretofore been impossible to determine, inasmuch as steric and resonance effects often overshadow—or have been thought to overshadow—the inductive effect, and lack of understanding of the nature of the effect has prohibited the calculation of its magnitude.

The successful correlation of relative amounts of ortho, meta and para nitration of substituted benzenes with empirically calculated charges[2] indicates that rough calculations of charges can be useful for discussing chemical reactivity semi-quantitatively. In this paper we propose to develop a general, approximate theory for calculating the magnitudes of charges on atoms in molecules having no conjugation. The theory will be checked by comparing a number of calculated and observed dipole moments. Succeeding papers in this series will show how reaction rates and equilibria may be semi-quantitatively correlated with charges calculated on the basis of our model for the inductive effect and improvements on it.

The principal inductive effect theories in existence are those of Branch and Calvin[3] and

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(1) Department of Chemistry, University of Notre Dame, Notre Dame, Ind.

(2) T. Ri (Ree) and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

(3) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 217ff.