[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, HARVARD UNIVERSITY]

Heats of Combustion and Formation of Metal Carbonyls. I. Chromium, Molybdenum and Tungsten Hexacarbonyls

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The heats of combustion of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ have been determined by direct calorimetric measurement. The values calculated for ΔHf°_{298} of the solid carbonyls are, respectively, −257.5, −234.8 and −227.2 kcal./mole. Sources of error are discussed and the results compared with those recently reported by Russian workers.

I. Introduction

This paper is the first of a series which is intended to provide reliable values of the enthalpies of formation of metal carbonyls and other thermodynamic properties derived therefrom. Such data for this class of compounds have been fragmentary and in the case of $Ni(CO)_4$ extremely discordant.

When the measurements on the hexacarbonyls of Cr, Mo and W were begun, no previous studies had been reported; during the course of this work the results of an investigation by Sharafov and Rezukhina appeared in abstract form.[2] It became apparent that no copy either of the paper or of the journal had reached the United States and that the English abstract was translated from the Russian abstract. A transcript of the paper was obtained.[3] In view of the inaccessibility of the original paper, and in order to provide a comparison with the present studies, a summary of important details not covered in the abstract is given here.

The Russian authors used a water-jacketed calorimeter with a mercury thermometer which could be read with an accuracy of ±0.0001° with temperature rises of $\sim 2°$. Thus, the final thermal effect cannot be expressed to more than four significant figures; the six figures in their report seem to be unjustifiably optimistic. The combustions were performed under a pressure of 40 atmospheres of oxygen to produce only Cr_2O_3 in the case of chromium carbonyl (however, *vide infra*), and to reduce the amount of unburned molybdenum and tungsten to a minimum. (The present work with $Cr(CO)_6$ revealed only a slight reduction in the amount of unburned chromium metal at 40 atmospheres of oxygen.) A collodion sack was used to contain the samples in order to eliminate volatilization loss after weighing; this necessitated a correction of unspecified magnitude for the heat of combustion of the collodion. Due to the presence of atmospheric nitrogen in the bomb, a correction for the heat of formation of nitrogen oxides was necessary. No data were given here, either. No water was used in the bomb. The solid combustion products were shown by X-ray diffraction to be essentially Cr_2O_3, MoO_3 and WO_3 with no traces of metals in the oxides. Unburned Mo and W were determined by dissolving the oxides in base and weighing the metallic residues. Thermal and analytical data for individual runs were, however, not listed, so that it is impossible to recalculate corrections for unburned metal by the use of the later values for the heats of formation of the metal oxides.

II. Experimental

A Parr Series 1300 plain calorimeter was used. The stirrer was driven at 150 r.p.m. and the temperature was measured by a Leeds and Northrup platinum resistance thermometer calibrated by the manufacturer in accord with the procedures of the National Bureau of Standards. With a Mueller bridge which had been newly reconditioned and recalibrated by the manufacturer, resistances were measurable to ±0.00003 int. ohm at a specified point in time by using the galvanometer as a null instrument. The cooling corrections were calculated by the method of Dickenson[4a] and the corrected resistances were used to calculate the temperatures by means of the Callander equation.[4b] The temperature rise can thus be measured to ±0.0006°.

The water equivalent of the calorimeter was determined by means of the combustion of National Bureau of Standards benzoic acid (sample No. 140) which had a heat of combustion of 6317.8 calories per g. *in vacuo* under the prescribed standard conditions. 1.1-g. pellets of the acid were weighed to ±0.05 mg. and placed in a platinum combustion cup. After closing, the bomb was flushed twice with oxygen at 30 atmospheres pressure before finally charging with oxygen to the same pressure in order to eliminate nitrogen and the subsequent need for a nitric acid correction. Eight cm. of No. 40 platinum wire served as a fuse when a 15-volt current was passed through it for three seconds. In preliminary tests the heating effect from the fuse raised the resistance of the thermometer an estimated 0.00006 ohm. The distilled water in the calorimeter bucket weighed 1,905.0 ± 0.1 g. Initial temperatures for the runs ranged from 25 to 28°.

The mean value of six runs was 438.8 g. with a standard deviation of the mean[5] of 0.7 g., giving a total water equivalent of 2343.8 ± 0.8 g. The estimated maximum random error is ±0.8 g. The accuracy of this calibration was checked for any gross systematic error by determining the heat of combustion of salicylic acid, whereby a value of 5247 calories per gram weighed in air was obtained, which may be compared with the value 5242 reported by Verkade and Coop.[6]

Purification of the carbonyls by triple sublimation *in vacuo* resulted in the formation of a compact mass on the cold-finger of the sublimer. The materials were used in this lump form directly. In each case the volatility is great enough so that the sample loses a significant weight between the time of weighing and the time when the bomb has been flushed and finally sealed. To eliminate unnecessary corrections, it was thought inadvisable to encase the sample in some foreign material to eliminate volatilization losses. To

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(1) (a) Chemistry Department, Massachusetts Institute of Technology, Cambridge 39, Massachusetts. (b) Chemistry Department, Imperial College of Science and Technology, London, England.

(2) K. A. Sharafov and T. N. Rezukhina, *Trudy Inst. Fiz. i Mat., akad. Nauk Azerbaidzhan, S.S.R., Ser. Fiz.*, **6**, 53 (1953); *Referat. Zhur. Khim*, No. 30309 (1954); *C. A.*, **49**, 2173 (1955).

(3) We are indebted to V. A. Getling, Secretary of the Division of Chemical Sciences of the Academy of Sciences of the U.S.S.R., for this courtesy. A translation of the paper is available in the library of the Chemistry Department, Harvard University.

(4) (a) H. C. Dickenson, *Bull. Bur. Standards*, **11**, 189 (1914). (b) See E. F. Mueller in "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 171.

(5) Standard deviation of the mean is taken as $\sqrt{\Sigma d_i/n(n-1)}$ where d_i is the deviation of the *i*th value from the arithmetic mean of *n* values. See, *e.g.*, Kolthoff and Sandell, "Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, pp. 273–274.

(6) P. E. Verkade and J. Coop, Jr., *Rec. trav. chim. Pays Bas*, **43**, 561 (1924).

make allowance for this loss factor, the loss in weight as a function of time was plotted for each sample. The relation is sufficiently linear to justify linear extrapolation over the 10-minute period from the time of the last weighing to the time of sealing of the bomb after the second oxygen flushing. A check was provided by preliminary experiments where the bomb was opened after the second flushing and the sample quickly weighed; 2.5-g. samples lost weight at the rate of 0.00004 g./min. for $Cr(CO)_6$, 0.00002 g./min. for $Mo(CO)_6$ and 0.00001 g./min. for $W(CO)_6$.

In all of the carbonyl runs, no water was placed in the bomb so that there would be no need to make corrections for the heat of solution of CO_2 in water, and to eliminate any possible heat of hydration of the metal oxides. In the case of chromium, this would also keep the Cr_2O_3 dry so there would be no weight error in the analyses due to hydration and/or adsorption of water.

With all of the carbonyls, the combustion is incomplete in respect to the metal, though it is reasonable enough to assume that all of the carbon monoxide is oxidized to carbon dioxide. Indeed, Sharafov and Rezukhina checked on the presence of carbon monoxide in the combustion products and found none. The Russian authors claim to have attained complete combustion of $Cr(CO)_6$ and almost complete combustion in the case of the other two carbonyls by using 40 atmospheres of oxygen. However, we found only slightly more nearly complete combustion by this means in the case of chromium, and the results for some reason became more discordant so these attempts were abandoned. No 40 atmosphere work was done with molybdenum and tungsten carbonyls. One factor in incomplete combustion is sometimes the use of too massive a combustion cup which transfers heat away from the sample so quickly that parts of the sample are kept below the necessary ignition temperature.[7] However, in the cases at hand, use of a lighter cup exposes one to the danger of melting the cup.

Comparison of the X-ray powder patterns of the bomb combustion products with known samples of the respective oxides showed that the oxides formed by the combustion of chromium, molybdenum and tungsten carbonyls are, respectively, Cr_2O_3, MoO_3 and WO_3. Lines indicative of formation of significant amounts of other oxides were not found. Our work is in agreement with that of Sharafov and Rezukhina on all points concerning the nature of the combustion products save one. In the combustion of $Cr(CO)_6$ at 40 atmospheres they reported a dark product in the cup, unlike the light green Cr_2O_3 found generally on the inner surfaces of the bomb, which they stated to be also Cr_2O_3. In the present work at 30 atm. the residue in the cup was clearly chromium metal and green Cr_2O_3.

The amount of unburned chromium metal was determined as follows. After the run, the platinum cup was removed from the bomb and the cup and contents were weighed and then transferred to a larger covered platinum crucible. Reagent grade sodium carbonate was placed in the crucible in an amount sufficient to cover the cup, and was then fused for 16 hours. This procedure served to convert all of the metal and oxide into sodium chromate which was obtained as a clear solution when the melt was dissolved in water. To ensure the presence of all of the chromium as chromate, the solution was oxidized with ammonium persulfate by heating in acid solution in the presence of a trace of $AgNO_3$. To $^1/_{10}$ aliquots of the cooled solution a weighed excess of Mohr's salt was added, and the excess ferrous salt titrated potentiometrically with standard ceric sulfate solution. The calculation of the amount of unburned chromium required using the assumption that all of the unburned chromium remained in the combustion cup. This was verified by analysis of material brushed from the bomb walls, which proved to be pure Cr_2O_3. The amount of unburned chromium in the cup was calculated by assuming that a fraction x of the cup contents was chromium and a fraction $1-x$ was Cr_2O_3. By equating total chromium titrated with total chromium as expressed in terms of x, and solving for x, the amount of unburned chromium was obtained. In an average run there was 0.04 g. of chromium metal left. The precision in this determination is ±0.3 to 1.0 mg. of Cr, which in the correction for incomplete combustion leads to an error of ±0.07 to 0.20 kcal./mole.

The determination of unburned molybdenum and tungsten was carried out by treating the combustion cup and its contents with 3 *N* NaOH, which dissolves the oxides but leaves any metal behind. Filtration on a weighed sintered glass filtering crucible gives the amount of metal directly. For the base treatment, a polyethylene beaker was used in the case of molybdenum in order to avoid errors from silica from a glass beaker. Overnight treatment with 100 ml. of base at 50° serves to dissolve the MoO_3 completely. For tungsten, the same procedure was used, except that a large nickel crucible was used instead of the polyethylene beaker. This was necessary because WO_3 is more difficult to dissolve than is MoO_3 at the temperatures to which one is limited by the softening of polyethylene. The WO_3 was dissolved in 50 ml. of base by leaving on the steam-bath overnight. The precision in this procedure is ±0.0005 g. of the metal, which leads to an error in the correction for incomplete combustion of ±0.10 kcal./mole for $Mo(CO)_6$ and ±0.07 kcal./mole for $W(CO)_6$. In an average run the amount of unburned metal is 0.01 g. of Mo, and 0.004 g. of W. The fact that all of the unburned metal remains in the cup was further confirmed in the $Mo(CO)_6$ and $W(CO)_6$ runs by applying to the bomb wall coatings the same procedure that was used on the cup.

III. Results

All essential experimental data for all runs not definitely known to be in error are presented in Tables I, II and III.

TABLE I

COMBUSTION OF $Cr(CO)_6$

Run	Vacuum wt. of sample, g.	Cor. temp. change, °C.	Uncor. heat of comb., kcal./mole	Cor. for incomplete comb., kcal./mole	Washburn cor., kcal./mole	Fully cor. heat of comb. kcal./mole, $\Delta E^{298°}_{\text{comb.}}$
1	3.07790	2.6150	−437.69	− 6.88	0.74	−443.83
2	2.74739	2.3227	−435.56	−11.07	.76	−445.87
3	2.20700	1.8586	−433.89	−12.22	.74	−445.37
4	3.09661	2.6261	−436.66	− 6.36	.77	−442.25
5	2.50068	2.1168	−436.12	− 8.52	.75	−443.89
6	2.82138	2.4000	−438.30	− 8.88	.76	−446.42
7	2.90630	2.4496	−434.30	− 9.59	.77	−443.12

TABLE II

COMBUSTION OF $Mo(CO)_6$

Run	Vacuum wt. of sample, g.	Cor. temp. change, °C.	Uncor. heat of comb., kcal./mole	Cor. for incomplete comb., kcal./mole	Washburn cor. kcal./mole	Fully cor. heat of comb. kcal./mole, $\Delta E^{298°}_{\text{comb}}$
1	2.82561	2.3081	−504.83	−8.24	0.66	−512.41
2	2.49599	2.0522	−508.18	−1.21	.65	−508.74
3	2.51345	2.0575	−505.92	−2.94	.65	−508.21
4	2.76289	2.2669	−507.12	−1.74	.66	−508.20
5	2.53736	2.0825	−507.22	−1.95	.65	−508.52
6	2.44063	2.0014	−506.84	−1.15	.65	−507.34
7	2.45742	2.0183	−507.66	−2.29	.65	−509.30

TABLE III

COMBUSTION OF $W(CO)_6$

Run	Vacuum wt. of sample, g.	Cor. temp. change, °C.	Uncor. heat of comb., kcal./mole	Cor. for incomplete comb., kcal./mole	Washburn cor., kcal./mole	Fully cor. heat of comb., kcal./mole $\Delta E^{298°}_{\text{comb}}$
1	2.46607	1.6116	−538.47	−0.76	0.63	−538.60
2	2.06405	1.3521	−539.76	− .22	.62	−539.36
3	2.62330	1.7148	−538.67	− .58	.64	−538.61
4	2.48060	1.6256	−539.97	− .31	.63	−539.65
5	2.76308	1.8027	−537.52	− .90	.64	−537.78
6	2.61154	1.7064	−538.46	− .38	.64	−538.20

The various corrections required to convert the measured heat into the heat at standard conditions, $\Delta E^{298°}_{\text{comb.}}$ (generally called Washburn corrections) were particularly simple in these runs, owing

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(7) Private communication from Dr. R. S. Jessup, National Bureau of Standards.

to the absence of water, and were made as prescribed by Washburn.[8] A correction for the heat of sublimation of the samples is negligible, amounting to ~0.005 kcal./mole.

Certain of the values given were rejected in computing the final averages using the rule that a result may be neglected if the ratio (deviation of doubtful result from mean of remaining values)/(average deviation of remaining values) is greater than 2.5. Hence for $Cr(CO)_6$, the results of runs 4 and 6 were discarded. The mean of the remaining values is -444.42 kcal./mole with a standard deviation of the mean of ± 0.51 kcal./mole. The heat of formation of Cr_2O_3 was taken to be -272.7 kcal./mole[9] in making the correction for incomplete combustion and in subsequent calculations.

By the same criterion for the $Mo(CO)_6$ determinations, the result of run no. 1 is discarded, the remaining six values having a mean of -508.38 kcal./mole with a standard deviation of the mean of ± 0.27 kcal./mole. The standard heat of formation of MoO_3 was taken here and throughout to be -178.00 kcal./mole.[10] The mean of the values for $W(CO)_6$ is -538.70 kcal./mole with a standard deviation of the mean of ± 0.29 kcal./mole. The heat of formation of WO_3 used in this work is -200.84 kcal./mole.[11] The temperature assigned to these combustion reactions is 25° even though the initial temperatures of the runs ranged from 22–24° since estimation from the available heat capacity data shows that ΔC_p is only about 0.007 kcal./deg. mole and 0.02 kcal./deg. mole for the Cr and Mo reactions, respectively.

The maximum random error to be expected in the value for the heat of combustion of $Cr(CO)_6$ calculated on the basis of the estimated errors in all measurements and analyses involved under the conditions of this work is ± 0.7 kcal./mole. Similarly, for $Mo(CO)_6$ and $W(CO)_6$ this expected maximum random error is ± 0.6 kcal./mole. It is to be emphasized that, (a) there may be systematic errors of which we are unaware, and (b) this maximum random error has been estimated as an upper limit and the true random error is doubtless less as indicated by the smaller standard deviations of the mean values.

By applying the ΔnRT correction, the above values of ΔE° were used together with supplementary data from the various sources cited (when not otherwise specified, the source is ref. 11) to calculate the standard enthalpies of the following reactions.

Standard enthalpies of combustion of carbonyls (in kcal./mole):

$$Cr(CO)_6(s) + 15/4O_2(g) = 1/2Cr_2O_3(s) + 6CO_2(g) \qquad \Delta H^\circ_{298^\circ} = -443.09 \pm 0.51$$

$$Mo(CO)_6(s) + 9/2O_2(g) = MoO_3(s) + 6CO_2(g) \qquad \Delta H^\circ_{298^\circ} = -507.52 \pm 0.27$$

$$W(CO)_6(s) + 9/2O_2(g) = WO_3(s) + 6CO_2(g) \qquad \Delta H^\circ_{298^\circ} = -537.81 \pm 0.29$$

Standard enthalpies of formation (in kcal./mole):

$Cr(s) + 6C(graphite) + 3O_2(g) = Cr(CO)_6(s)$ $\quad \Delta Hf^\circ_{298^\circ} = -257.57 \pm 0.51$[12]

$Mo(s) + 6C(graphite) + 3O_2(g) = Mo(CO)_6(s)$ $\quad \Delta Hf^\circ_{298^\circ} = -234.79 \pm 0.27$[12]

$W(s) + 6C(graphite) + 3O_2(g) = W(CO)_6(s)$ $\quad \Delta Hf^\circ_{298^\circ} = -227.34 \pm 0.29$[12]

Hieber and Romberg[13] studied the temperature dependence of the vapor pressures of the group VI carbonyls; from their data the values in Table IV for ΔH°, ΔF° and ΔS° of vaporization are calculated. It might seem a little surprising that the three quantities do not change more regularly, perhaps monotonically, but since the lattice parameters for the crystalline forms of the three substances[14] show a similar irregular behavior, the irregularity here is explicable.

TABLE IV

THERMODYNAMICS OF VAPORIZATION AT 298°K.

	ΔH°, kcal./mole	ΔF°, kcal./mole	ΔS°, cal./°mole
$Cr(CO)_6$	+17.18	+4.98	+40.94
$Mo(CO)_6$	+16.29	+4.99	+37.92
$W(CO)_6$	+17.71	+5.93	+39.52

Recently, the results of a spectroscopic study of $Cr(CO)_6$ and $Mo(CO)_6$[15] have been used to calculate entropies for the gaseous molecules. These results are not very certain since none of the low-lying frequencies which contribute heavily to the entropy were actually observed.[16] Nevertheless, using these entropy values together with the results of Hieber and Romberg in Table IV, the following free energies of formation are obtained

$Cr(s) + 6C(graphite) + 3O_2(g) = Cr(CO)_6(s)$ $\quad \Delta Ff^\circ_{298^\circ} = -232.16$ kcal./mole

$Mo(s) + 6C(graphite) + 3O_2(g) = Mo(CO)_6(s)$ $\quad \Delta Ff^\circ_{298^\circ} = -211.29$ kcal./mole

Appendix

In Table V a comparison of the results obtained here with those of Sharafov and Rezukhina is made. It may be noted first that for the reasons outlined in the Introduction the Russian work cannot have the high accuracy claimed. A rough error analysis indicates that the expected random error in their values is of the order of several kilocalories. In the second column we have listed values of $\Delta Hf^\circ_{298^\circ}$, recalculated from the Russian values utilizing the more recent values of $\Delta Hf^\circ_{298^\circ}$ for the metal oxides used throughout the present work. (Sharafov and Rezukhina used -288.0, -175.49 and -194.77, respectively, for Cr_2O_3, MoO_3 and WO_3.) Since the Russian workers found little or no oxide formation under their combustion conditions for $Mo(CO)_6$ and $W(CO)_6$ the values obtained by correcting

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

[9] A. D. Mah, THIS JOURNAL, **76**, 3363 (1954).

[10] B. A. Staskiewicz, J. R. Tucker and P. E. Snyder, *ibid.*, **77**, 2987 (1955).

[11] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular No. 500, Washington, D. C., 1952.

[12] The error specified includes only the error originating in the enthalpies measured here and not errors in other supplementary data.

[13] W. Hieber and E. Romberg, *Z. anorg. allgem. Chem.*, **221**, 332 (1935).

[14] W. Rudorff and U. Hofmann, *Z. physik. Chem.*, **B28**, 351 (1935).

[15] N. S. Hawkins, H. C. Matthew, W. W. Sabol and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955).

[16] Work is in progress by A. D. Liehr and F. A. Cotton with the assistance of the Spectroscopy Laboratory of M.I.T. to obtain further vibrational data on these molecules as well as $W(CO)_6$.

their reported values as described should be comparable to the ones determined in this research. It is seen in Table V that the differences are random, indicating a lack of systematic error in either set. The results for $Mo(CO)_6$ and $W(CO)_6$ agree surprisingly well whereas a considerable discrepancy exists for $Cr(CO)_6$. An error of more than ±1 kcal./mole is unlikely in our results, but a considerably larger error could have occurred in measurements made using a Beckman type thermometer. It may be recalled, however, that Sharafov and Rezukhina reported the formation of an appreciable amount of a peculiar dark chromium oxide which they presumably regarded as thermodynamically identical with ordinary Cr_2O_3.

TABLE V

COMPARISON OF PRESENT VALUES WITH THOSE OF SHARAFOV AND REZUKHINA[2]

Compound	ΔH°_{298} Sharafov and Rezukhina As reported	Corrected[a]	This research
$Cr(CO)_6$	−257.08	−249.4	−257.6
$Mo(CO)_6$	−233.12	−235.6	−234.8
$W(CO)_6$	−219.29	−225.3	−227.3

[a] Corrected as described in text by using more recent heats of formation of metal oxides.

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General Relation between Potential Energy and Internuclear Distance. II. Polyatomic Molecules[1]

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The simple form of a general relation between potential energy and internuclear distance derived from a quantum mechanical model is applied to the bonds of a large number of polyatomic molecules. The relation has the form $V = D_e[1 - \exp(-n\Delta R^2/2R)]$, where the parameter n is related to D_e by the equation $D_e = k_eR_e/n$. Using known values of bond stretching force constants as determined from molecular force models with known bond lengths, dissociation energies of bonds in polyatomic molecules have been calculated more accurately than was hitherto possible. One important feature of the method is that no empirically evaluated parameters are used. The relationship between bond dissociation energy and average bond energy as related to the derived potential function is discussed. For non-polar molecules or for polar molecules containing hydrogen or molecules with atoms of atomic number less than nine the calculated dissociation energies agree with the thermochemical bond energies with about 5% accuracy. A number of other applications of this function will be suggested. With due consideration to its limitations this function should be useful as a tool for elucidating other problems of bond formation and structure.

Introduction

Many attempts have been made to derive from quantum theory or to formulate empirically analytic relationships between potential energy and internuclear distance for diatomic molecules.[2] Except for the simplest systems such as the H_2^+ and H_2 molecules quantum theory has not given definite relationships,[3] while empirical internuclear potential functions have not correlated satisfactorily such bond properties as dissociation energy, bond lengths, bond stretching force constants and anharmonicity constants. In no case has it been possible to apply diatomic internuclear potential functions to the bonds of polyatomic molecules and obtain even a qualitative correlation of bond properties.

We have recently derived an internuclear potential function from a quantum mechanical model which has found extensive application in quantitatively predicting and correlating the bond properties of a large number of diatomic molecules.[4] It will be shown that this internuclear potential function can be used to predict and correlate the bond properties of a number of bonds in polyatomic molecules. One important feature of the method is that no empirically evaluated constants are used, since all necessary parameters have been evaluated from a quantum mechanical model.[4]

The form of the function which has been derived previously for diatomic molecules is

$$V = D_e[1 - \exp(-n\Delta R^2/2R)] \qquad (1)$$

where D_e bond dissociation energy referred to the bottom of the potential curve, $\Delta R = R - R_e$, and R_e = equilibrium bond length. The derivation of (1) shows that n may be obtained from the relation

$$n = n_0(I/I_0)_A^{1/2}(I/I_0)_B^{1/2} \text{ cm.}^{-1} \qquad (2)$$

where $(I/I_0)_A$ and $(I/I_0)_B$ are the ionization potentials of atoms A and B in the bond A–B, relative to those of the corresponding atoms in the same

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[1] Presented in part at the 125th Meeting of the American Chemical Society, Kansas City, March, 1954.

[2] P. M. Morse, *Phys. Rev.*, **34**, 57 (1929); Coolidge, James and Vernon, *ibid.*, **54**, 726 (1938); H. M. Hulburt and J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 61 (1941); M. L. Huggins, *ibid.*, **3**, 473 (1935); **4**, 308 (1936); R. Rydberg, *Z. Physik*, **73**, 376 (1932); M. F. Manning and N. Rosen, *Phys. Rev.*, **44**, 953 (1933); G. Poschl and E. Teller, *Z. Physik*, **83**, 143 (1933); E. A. Hylleraas, *ibid.*, **96**, 661 (1935); J. W. Linnett, *Trans. Faraday Soc.*, **36**, 1123 (1940); **38**, 1 (1942); G. B. B. M. Sutherland, *J. Chem. Phys.*, **8**, 161 (1940); *Proc. Indian Acad. Sci.*, **8**, 341 (1938); A. A. Frost and B. Musulin, THIS JOURNAL, **76**, 2045 (1954); *J. Chem. Phys.*, **22**, 1017 (1954).

[3] (a) E. Teller, *Z. Physik*, **61**, 458 (1930); (b) H. M. James and A. S. Coolidge, *J. Chem. Phys.*, **1**, 825 (1933).

[4] E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1131 (1955); E. R. Lippincott, *ibid.*, **23**, 603 (1955); E. R. Lippincott, to be published.