A SYMPOSIUM ON THERMODYNAMICS[1]

MODERN THERMOCHEMISTRY[2]

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I. INTRODUCTION

It is the purpose of this paper to present a picture of thermochemistry in relation to modern chemical thermodynamics, to discuss briefly the principles and methods of accurate thermochemical measurements, and to make certain suggestions and proposals for making the data of thermochemistry more uniform and reliable, and increasing their utility in chemical thermodynamics.

The aim of thermochemistry, which may be formally defined as that branch of chemical thermodynamics which treats of the changes in internal energy or heat content associated with chemical reactions, is to provide the experimental data for compiling a table of values from which may be calculated the heat of every possible chemical reaction. This table may be called the thermochemical table. The necessity of having accurate values of ΔH, the increment in heat content, for every process or reaction[3] is readily apparent to those engaged in almost any variety of calculation in chemical thermodynamics.

The ultimate end of chemical thermodynamics may be said to be the evaluation of the free energy of formation, from the appropriate fundamental units of matter, of every substance in all possible states, but the

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[1] This Symposium was held by the Division of Physical and Inorganic Chemistry at the Ninetieth Meeting of the American Chemical Society, in San Francisco, August 21, 1935, under the chairmanship of J. H. Hildebrand and with an introduction by Gilbert N. Lewis. The final paper in the Symposium, by Dr. Merle Randall of the University of California, entitled "Stoichiometry and the Correlation of Thermodynamic Data," was not submitted in time for inclusion in this publication.

[2] Publication approved by the Director of the National Bureau of Standards, United States Department of Commerce.

[3] The symbols and nomenclature used in this paper are those of Lewis and Randall (22). For any reaction, ΔH (or ΔF or ΔS) is equal to the sum of the heat contents (or free energies or entropies) of the products less the sum of the heat contents (or free energies or entropies) of the reactants, each substance being in a defined physical state at the given temperature.

attainment of this end will be made possible only by the utilization of many indirect methods of calculation, and the proper combination of what may at first sight appear to be only remotely related experimental data. From the standpoint of the compilation of the ultimate or master table of chemical thermodynamics, the most important thermodynamic properties, in addition to the free energy itself, are the heat content and the entropy; and the successful evolution of the master table is predicated upon the existence of accurate values of the heats of formation and of the entropies of formation.

In the master table there will appear for each substance values of ΔH, ΔS, and ΔF, the heat, entropy, and free energy of formation, respectively. For each temperature, all the values in the table should possess both "vertical" and "horizontal" consistency. "Vertical" consistency is assured when, at a given temperature, each value of ΔH (or of ΔS, or of ΔF) is in accord with all the other values of ΔH (or of ΔS, or of ΔF) with which it can be correlated by means of experimental data. With all the values in the table being "vertically" consistent, then the calculation of the values of ΔH (or of ΔS, or of ΔF) for any given reaction will be independent of the path (or the particular values which happen to be added or subtracted). "Horizontal" consistency in the table is assured when, for each temperature, the values recorded for ΔH, ΔS, and ΔF for each substance are in accord with the relation,

$$\Delta F = \Delta H - T\Delta S$$

This "horizontal" consistency will be automatic for all those substances for which independent values of only two of the three properties are available, but for the remainder this cross-checking will serve to increase the accuracy and reliability of the entire table. In order to facilitate the correlation, each value in the table should be written so as to indicate both its absolute and its relative accuracy.

The manner of assembling such a master table of chemical thermodynamics may be somewhat as follows: There will first be built up separate independent tables of values of ΔH, ΔS, and ΔF, for some selected standard temperature, say 25°C. The ΔH table will contain only values derived from calorimetric data on heats of reaction; the ΔF table will contain only values derived from data on equilibria; and the ΔS table will contain values derived from spectroscopic data, or from experimental data on heat capacities down to near the absolute zero, or from experimental data on the temperature coefficient of ΔF. The separate tables are, at this juncture, completely independent, and, after each table is made properly self-consistent "vertically," may be brought together to form the nucleus of the master table. It is at this point that the cross-checking for "horizontal" consistency will be made for all those substances for which there are independent values of all three properties. It is obviously necessary that the values of ΔH, $T\Delta S$, and ΔF be recorded in the same unit of energy if this cross-checking is to be significant, and therefore, all the original data must be accurately expressible in terms of fundamental units. When, by proper adjustment, the three columns have been brought into "horizontal" consistency, the value of the third property may be computed for those many substances for which there will be known the values of only two of the properties. There will be in the table a large number of substances for which the value of but one of the three properties is known; and, in addition, there will be a very large number of known substances not appearing in the table because no data at all are available. It will be the next order of business for the experimenters in chemical thermodynamics to supply these needed data.

The foregoing picture indicates the relation of thermochemistry to the general scheme of the data of modern chemical thermodynamics. Before the master table can be assembled, adequate and accurate tables of ΔH, ΔS, and ΔF must be prepared, and it is the work of thermochemistry to supply the fundamental data for the first of these.

II. THE RENAISSANCE IN THERMOCHEMISTRY

About fifteen years ago, thermochemistry began to undergo a sort of renaissance (33). In order to understand this phenomenon one must look back to the middle of the nineteenth century. At that time, Julius Thomsen at Copenhagen and Marcellin Berthelot at Paris were beginning their work in thermochemistry, and each independently announced the theorem that the heat of formation of a substance is a direct measure of the chemical affinity. Spurred on by this belief, Thomsen and Berthelot amassed an enormous amount of thermochemical data, their work reaching its zenith at about the time of the publication of Thomsen's monumental four volumes on thermochemistry, in 1882–86.

It was some years before this, however, that the second law of thermodynamics began to make its way into chemistry, and its true relation to chemical reactions was being developed by Clausius, Gibbs, Helmholtz, van't Hoff, and others. It was then shown that the true measure of the chemical affinity is not the heat content, H, but the heat content less the product of the entropy and the absolute temperature, $H - TS$, which function is now termed the free energy.

Before the close of the nineteenth century, both Thomsen and Berthelot reluctantly accepted the second law, which had caused the relegation of their great body of thermochemical data to a relatively minor place in the science, and experimenters turned their attention to those measurements which would yield true values of chemical affinity. The decline in thermochemical research continued with but minor halts until some ten or fifteen years ago, when two new developments brought about a radical change in the status of thermochemical data in relation to chemical thermodynamics. The developments which lifted the data of thermochemistry to a new position of importance in the science were: first, the determination of the entropies of substances by measurement of their heat capacities and latent heats down to low temperatures and utilization of the resulting data according to the third law; and, second, the calculation of certain thermodynamic quantities from a combination of statistical mechanics with the data of spectroscopy. With certain important limitations on the first, each of these methods yields values of the entropy independent of other experimental data; so that it is possible to compute values of ΔF by combining values of ΔS, obtained in the above manner, with values of ΔH, obtained from calorimetric data. There are a very great number of substances, especially among the organic compounds, for which values of the free energy can not be determined from equilibrium experiments. The methods of determining entropies by means of spectroscopic data and the third law are, therefore, extremely important; furthermore, they place a premium upon accurate thermochemical data, because, in most cases, the relative magnitudes and absolute accuracies of the values of ΔS and ΔH are such that the resulting uncertainty in ΔF is practically equal to the error in ΔH.

Now at this time the great body of thermochemical data was still founded upon the prodigious work of Thomsen, Berthelot, and their coworkers of the period before 1900, but their data, while more than accurate enough for the nineteenth century, fell far short of meeting the new requirements. This inadequacy of their data was no reflection upon the work of these pioneers in thermochemistry, who performed extraordinarily well with their meager apparatus in spite of considerable handicaps (such as the frequent lack of pure materials), but rather was evidence of the great advances which had taken place in chemical thermodynamics.

It is at this point that the renaissance in thermochemistry may be said to have begun. It became evident that the time was overdue for a redetermination of the important thermochemical values, in terms of a fundamental unit of energy, and with an accuracy as high as would be possible with the improved calorimetric apparatus and technique and the pure materials available today.

III. THE THERMOCHEMICAL TABLE

The ideal thermochemical table is one which will permit calculation of the heat of every chemical reaction. Obviously it would be impractical to list in a table the heat of every reaction, but the same end is accomplished by listing for each chemical substance its heat of formation from the elements in selected standard states. This is the scheme that has been used since the middle of the last century. It is evident that, by proper selection, the number of chemical reactions whose heats must be measured will be about the same as the number of substances listed in the table. Some saving in the number of reactions to be measured will occur among the organic compounds because of certain simplifying rules for the energy increment per CH_2 group in aliphatic radicals (34).

The value of the heat of formation of a given substance may be the result of the determination of the heat of one reaction, as for H_2O (liq.):[4]

$$H_2(\text{gas}) + \tfrac{1}{2}O_2(\text{gas}) = H_2O(\text{liq.})$$

For many other substances, however, the value will result from the measurement of the heats of a number of chemical reactions, as for NaOH(c):

$$\begin{array}{rcl}
Na(\text{c}) + H_2O(\text{liq.}) &=& NaOH(\text{aq.}) + \tfrac{1}{2}H_2(\text{gas}) \\
H_2(\text{gas}) + \tfrac{1}{2}O_2(\text{gas}) &=& H_2O(\text{liq.}) \\
NaOH(\text{c}) &=& NaOH(\text{aq.}) \\
\hline
\multicolumn{3}{c}{Na(\text{c}) + \tfrac{1}{2}O_2(\text{gas}) + \tfrac{1}{2}H_2(\text{gas}) = NaOH(\text{c})}
\end{array}$$

There will be certain basic values in the table which will be used very frequently in the derivation of other values. These basic values, which should be known with considerable accuracy, include the heats of formation of water, carbon dioxide, nitric acid, sulfuric acid, hydrogen chloride, hydrogen sulfide, and others. Because of this interdependence of many of the values of heats of formation, it is extremely desirable that values for the important thermochemical constants be carefully selected, and, when any change is made in any one of the basic values, corresponding changes should be made in all the values which depend upon it. It is for this same reason that the addition or subtraction of values of heats of formation from different tables is a very precarious undertaking. What is needed is one table of values that will be used universally.

In setting up the primary table of heats of formation, it is necessary to select a standard temperature for the entire table and a standard state for each substance. The most useful and convenient standard temperature is one at or near room temperature, and, following the convention already adopted for the standard free energy values by Lewis and Randall, one can select 25°C. as a desirable standard temperature. The standard state of each element, in which it will be assigned a reference heat content of zero for the purposes of this table, can be that state in which the element

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[4] The abbreviations used to indicate phases are as follows: c = crystal; liq. = liquid; aq. = aqueous.

naturally exists at the standard temperature and at a pressure of 1 atmosphere. For gases, the standard state would more exactly be that hypothetical standard state of unit fugacity (22), where the heat content is the same as that of the real gas at zero pressure at the given temperature. It is important to note that this hypothetical standard state of unit fugacity (1 atmosphere) is not that real state of the gas in which it has a fugacity equal to 1 atmosphere. For a large number of gases, at 25°C., the heat content at 1 atmosphere is not significantly (at present) different from its heat content at zero pressure.

IV. UNITS OF ENERGY

As pointed out in an earlier part of this paper, all thermodynamic values of ΔF, $T\Delta S$, and ΔH must be expressed in terms of a common unit of energy, otherwise the intercombination of values from the various sources will be inaccurate and may lead to disconcerting results. For a number of reasons, the logical and desirable unit of energy is the erg, the fundamental C.G.S. unit; particularly to be avoided are units of energy defined in terms of the properties of any substance, such as water. In order for it to have a real utility in chemical thermodynamics, a thermochemical value must therefore be expressible, so far as is significant, in terms of the fundamental unit of energy. This is easily accomplished today by using electrical energy, as from a lead or other storage battery, for comparison with the energy of the chemical reaction.

Electrical measurements of energy are based upon the second as the unit of time and upon working standards of electromotive force and resistance maintained at the various national standardizing laboratories. The working standards now universally used in these laboratories are wire (usually manganin) resistance coils and saturated cadmium (Weston) cells, which are calibrated in terms of the international ohm and the international volt. When originally established in 1908, the international units, defined in terms of the mercury ohm and the silver voltameter, were identical with the absolute units within the limits with which the latter could then be determined (15). Since that time, however, the accuracy of the absolute measurements has increased, and more accurate determinations of the absolute ohm and the absolute ampere have been made (10, 13, 40, 41). The results indicate that the international joule[5] is greater than the absolute joule (= 10^7 ergs) by about 0.04 per cent (6, 7, 10, 43).

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[5] It should also be pointed out that although the working standards (wire resistances and saturated cadmium cells) of the various national standardizing laboratories of England, France, Germany, and the United States were given the same values in 1910, the standards in the different countries have diverged a little since then. The international joule as derived from standards maintained at the National Bureau of Standards has differed from that of the other countries by amounts ranging from 0.006 to 0.014 per cent (44).

All measurements of electrical energy made since about 1910 by means of standard cells and standard resistances are actually in terms of the international joule. This is also true of all similar measurements that will be made until such time in the future as the various national standardizing laboratories begin to calibrate standard cells and resistances in terms of absolute units. It is the expectation of the Advisory Committee on Electricity of the International Committee on Weights and Measures that the old "international" standards set up in 1908, the mercury ohm and silver voltameter, will be discarded; that the working standards, saturated cadmium (Weston) cells and wire resistances, will be periodically calibrated in terms of the absolute units; and that all the national standardizing laboratories will adjust their units as soon as common international action can be obtained, to absolute values that will be decided upon by the International Committee from the results of the new determinations of the absolute ohm and absolute ampere that are now near completion in the various national laboratories (10, 43).

Values of ΔH, ΔF, and $T\Delta S$ will have their greatest utility in chemical thermodynamics if they are all expressible in the fundamental unit of energy, the erg (or the absolute joule $= 10^7$ ergs), or in terms of an arbitrary unit derived from the fundamental unit by pure definition.

The most accurate direct values of ΔH are today determined calorimetrically in terms of the international joule, which can be converted to the absolute joule by means of an appropriate factor.

Direct experimental values of ΔF can be determined from equilibrium measurements or from the electromotive force of cells. In the first case, ΔF is derived from the relation involving $RT\ln K$, and the value of ΔF depends upon the units of RT, the product of the gas constant and the absolute temperature. The product RT is equal to the product PV for an ideal gas at the given temperature, and, when P is expressed[6] in dynes per square centimeter and V in cubic centimeters, the unit of energy is the erg. In the second case, ΔF is derived from the relation involving $N\mathfrak{F}\mathfrak{E}$, and the value of ΔF depends upon the unit of the electromotive force $\mathfrak{E}$ and the Faraday constant $\mathfrak{F}$. At the present time, $\mathfrak{E}$ is measured in international volts. The value of $\mathfrak{F}$ is determined experimentally from the atomic weight of silver and the electrochemical equivalent of silver, the latter being defined as that mass of silver carried by 1 international ampere of current in 1 second. The quotient of the atomic weight and the electrochemical equivalent gives the value of $\mathfrak{F}$ in international joules/(international volt × equivalent). And the product of $N\mathfrak{F}\mathfrak{E}$ gives international joules, which can be converted to absolute joules by means of the appropriate factor.

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[6] It is true that P is not usually measured in dynes per square centimeter, but the unit ordinarily used can be converted to dynes per square centimeter with an accuracy of better than 0.001 per cent.

Independent values of $T\Delta S$ can be obtained in two ways. In the first place, the utilization of measurements of the heat capacity down to low temperatures according to the third law yields values of $T\Delta S$ in terms of international joules, which can be converted to absolute joules by means of the appropriate factor. In the second place, values of $T\Delta S$ can be calculated from spectroscopic data (and the Sackur-Tetrode-Stern equations) by statistical methods, and the value of $T\Delta S$ depends upon the units of RT. As before, this product is evaluated from a knowledge of the product PV for an ideal gas at the given temperature, and the energy is in ergs when P and V are in dynes per square centimeter and in cubic centimeters, respectively.

The foregoing discussion shows that values of ΔH, ΔF, and $T\Delta S$ are determined, independently of one another, in terms of the international or the absolute joule, and that, therefore, the values can all be expressed in terms of the absolute joule and combined with one another without fear of error due to inconsistent units. Since many thermodynamic calculations involve the combination of large numerical quantities to obtain a relatively small quantity, as for example,[7]

$$(\Delta F)_1 - [(\Delta H)_2 - T(\Delta S)_2] = (\Delta F)_3$$

it is imperative that all the quantities be expressed in units of the same size as well as the same name.

It would seem, therefore, that every branch of modern chemical thermodynamics is forced to accept the erg or absolute joule as the real unit of energy, and that all accurate thermodynamic values of energy, whether ΔH, ΔF, or $T\Delta S$, no matter how derived or in what units expressed, really arise from the absolute unit. This being the case, it is extremely desirable that chemical thermodynamics divorce itself completely from any unit of energy which is expressed as a property of some substance, such as that calorie which is defined in terms of the heat capacity of water.

About ten years ago, the late E. W. Washburn hoped that chemists might be prevailed upon to express their values of energy in terms of the absolute joule, and to that end F. R. Bichowsky used the absolute joule as the unit of energy in the thermochemical section of the International Critical Tables (16). But this change from calories to joules was apparently not received with favor by the great majority of chemists, and it appeared that the calorie would at least have to be retained as the name of the unit of energy. It was also realized that there would have to be separated from the new calorie every connection with the heat capacity of water, else one would have to change all the thermodynamic values every

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[7] The subscripts here indicate different reactions.

time someone determined the heat capacity of water with an accuracy greater than that already existing.

While there was justification in the time of Thomsen and Berthelot for using a unit of energy defined in terms of the heat capacity of water, the necessity for that awkward and not very accurate procedure disappeared about twenty-five years ago, when it became possible to measure quantities of energy much more accurately in terms of the absolute unit of energy by means of a potentiometer, standard cell, and standard resistances.

The situation with regard to the unit of energy in modern chemical thermodynamics may be summarized as follows: First, the actual unit of energy is the absolute joule, and all thermodynamic values should primarily be expressed in terms of that fundamental unit. Second, for historical, psychological, or other reasons, the values of chemical thermodynamics may be given also in terms of a unit of different size than the absolute joule having the name "calorie," which is derived from the absolute joule by means of an arbitrary factor set up by definition and universal agreement. The resulting calorie is a defined conventional unit bearing a constant unchanging relation to the absolute joule; and, furthermore, this calorie has no connection whatever with the heat capacity of water, although its numerical value is incidentally approximately equal to, and its name is historically derived from, the amount of heat energy required to raise the temperature of one gram of water through one degree Centigrade.

In 1930, the thermochemical laboratory of the National Bureau of Standards began to report thermochemical values having an estimated uncertainty as low as 0.02 per cent, and it was, therefore, necessary that a uniform policy for recording these values be established. Following the recommendation made at that time by the Division of Electricity at the National Bureau of Standards (43), the following was accepted as the true relation between the international joule and the absolute joule, with an error of less than 1 part in 10,000:

$$1 \text{ international joule} = 1.0004 \text{ absolute joules}^{8}$$

Then the following arbitrary definition of the calorie was made:

$$4.1850 \text{ absolute joules} \equiv 1 \textit{ calorie}$$

So that

$$4.1833 \text{ international joules} = 4.1850 \text{ absolute joules} \equiv 1 \textit{ calorie}$$

Since 1930, all the thermochemical values from this laboratory have been reported in the unit in which they were measured, the international joule,

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[8] See also references 6 and 7.

and converted to a conventional *calorie*, defined by means of the above relations. Fortunately, the other laboratories in the United States which are making energy measurements in chemical thermodynamics have accepted, by more or less tacit consent, the same relations, so that in this country at least there seems to be a uniformity of procedure in this regard.

It is suggested that, in order to avoid the confusion resulting from different sizes of units of energy with the same name, as has frequently occurred in the past history of thermodynamics and thermochemistry, all values of energy in chemical thermodynamics be reported in accord with the foregoing relations. When the national standardizing laboratories begin calibrating standard cells and resistances in absolute instead of "international" units, and when a more accurate relation between the international joule and the absolute joule is agreed upon by the national standardizing laboratories, the foregoing relations can be appropriately altered.

In the evaluation of free energies and entropies, the values assigned to the gas constant, R, the Faraday constant, $\mathcal{F}$, and the absolute temperature of the ice point, $T_{0°\text{C.}}$, should be consistent[9] with the best existing experimental values of $(PV)^0_{0°\text{C.}}$, $T_{0°\text{C.}}$, the atomic weight of silver, and the electrochemical equivalent of silver. As already pointed out, the energy units of R and $\mathcal{F}$ come out directly as absolute joules and international joules, respectively, and the conversion to the defined conventional *calorie* may be made by the relations given above.

It would be very desirable if a Committee on Chemical Thermodynamics were established to survey the existing data and establish values of R, $T_{0°\text{C.}}$, $\mathcal{F}$, and other pertinent constants that would be universally accepted. This would make for a uniformity in the data of chemical thermodynamics, which is now lacking.

V. REQUISITES OF THE CHEMICAL REACTIONS TO BE MEASURED

In order to determine the value of the heat of formation of a substance, one selects for measurement reactions in which all the reactants and products, save the given substance, have known heats of formation. In a few cases it is possible to utilize the direct reaction of synthesis of the given substance from its elements in their standard states.

The chemical reactions whose heats are to be measured must fulfill

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[9] For example, the values assigned to R and $T_{0°\text{C.}}$ must be such as to satisfy the relation:

$$RT_{0°\text{C.}} = (PV)^0_{0°\text{C.}} = (1{,}013{,}250)\ (22{,}414.1) = 2{,}271.11 \times 10^7 \text{ ergs} = 2{,}271.11 \pm 0.08 \text{ absolute joules.}$$

That is to say, while the uncertainty in the value of $T_{0°\text{C}}$. may be about 1 part in 14,000, the uncertainty (6) in the value of $RT_{0°\text{C}}$. is only 1 part in 28,000.

certain requirements under the conditions of the calorimetric experiment. First, each reaction must be one which proceeds to completion, and which is not significantly contaminated with side reactions, except so far as these can be accurately corrected for; and, second, each reaction must be one whose amount can be accurately measured.

VI. PRINCIPLE OF THE MODERN THERMOCHEMICAL METHOD

The principle of the modern experimental method in thermochemistry is to carry out the reaction to be studied in the calorimeter in such a manner that it will be possible to compare the heat evolved by the chemical reaction with the heat evolved by electrical energy, or by a measured amount of a standard chemical reaction, the heat of which has already been compared with electrical energy.

If the given reaction is one which evolves heat energy, then the comparison of the chemical energy with electrical energy can be made by performing two kinds of experiments: chemical reaction experiments and electrical energy experiments. In each of these experiments the calorimeter system is the same throughout. In the first kind of experiment, a measured amount of chemical reaction is used to bring the calorimeter system from an initial temperature T_A to a final temperature T_B. In an experiment of the second kind, a measured amount of electrical energy is used to bring the identical calorimeter system from the same initial temperature T_A to the same final temperature T_B. In this manner one obtains a comparison between a measured amount of chemical reaction and a measured amount of electrical energy, using the calorimeter as the absorber and comparator of the two kinds of energy.

This substitution method eliminates many of the usual calorimetric errors because of their cancellation in the two kinds of experiment, which are practically identical except that in one case the energy is electrical and in the other chemical. Furthermore, this method makes it unnecessary to know anything about the heat capacity of the calorimeter system or any of its parts, or to know the exact size of a degree of temperature, as is required in determinations of heat capacity. It is necessary only that the thermometric device used be sensitive enough to reproduce accurately and with sufficient precision the initial and final temperatures.[10] A knowledge of the actual temperature on the Centigrade scale is needed only to determine the temperature at which the reaction may be said to have taken place, and the absolute accuracy with which this reaction temperature

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[10] Actually, of course, it is necessary only that the initial and final temperatures in the different experiments be identical within a certain known small amount, because the subsequent small correction of the various initial (or final) temperatures to a common initial (or final) temperature can be made without loss of accuracy.

must be known depends upon the accuracy of the resulting thermochemical value and upon the magnitude of the temperature coefficient of the heat of the given reaction. Even for work of the highest accuracy and for reactions having a relatively large value of ΔC_p, the reaction temperature need be known only to about 0.01°C.

For reactions in which heat energy is absorbed, the comparison of the chemical energy with electrical energy may be made in the same experiment by adding to the calorimeter electrical energy at the same rate and of the same amount as is being absorbed by the reaction, so that the temperature of the calorimeter remains sensibly unchanged throughout the experiment. In this case, however, appropriate subsidiary observations must be made to determine the actual amount of the stirring energy, evaporation energy, etc.

Whenever it is not possible to determine an amount of electrical energy with the necessary accuracy and precision, one may utilize as the source of the "calibration" energy a "standard" chemical reaction, of the same type as the unknown, which has previously been accurately compared with electrical energy in a standardizing laboratory.

VII. TYPES OF REACTIONS

Nearly all the chemical reactions whose heats require measurement can be grouped into three classes according to the type of reaction and the corresponding calorimetric method which must be employed:[11]

1. Reactions substantially in the gaseous phase at constant pressure.
2. Reactions substantially in the liquid phase at constant pressure.
3. Reactions in a closed bomb at constant volume.

The reactions of the first class are carried out at constant pressure in a reaction vessel in the calorimeter, the reaction taking place in a flame or at the surface of a catalyst. Examples of this class include the following:

$$\begin{gathered}
\mathrm{H_2(gas)} + \tfrac{1}{2}\mathrm{O_2(gas)} = \mathrm{H_2O(liq.)} \\
\tfrac{1}{2}\mathrm{Cl_2(gas)} + \tfrac{1}{2}\mathrm{H_2(gas)} = \mathrm{HCl(gas)} \\
\mathrm{CH_4(gas)} + 2\mathrm{O_2(gas)} = \mathrm{CO_2(gas)} + 2\mathrm{H_2O(liq.)} \\
\mathrm{C_2H_4(gas)} + \mathrm{H_2(gas)} = \mathrm{C_2H_6(gas)} \\
\mathrm{O_2(gas)} + \mathrm{S(c)} = \mathrm{SO_2(gas)}
\end{gathered}$$

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[11] The present discussion does not include that class of reactions involving atomic energies, such as the dissociation of gaseous molecules into atoms, energies of excitation (rotational, vibrational, and electronic), and energies of ionization, which cannot be measured calorimetrically, except in isolated instances (5, 9, 29), but are determined by analyzing the appropriate experimental data of spectroscopy and electron bombardment measurements according to acceptable theories of atomic and molecular structure.

As actually carried out in the calorimeter, the second substance given in each of the first four of the foregoing examples is, for the practical purpose of obtaining completeness of reaction or accuracy in the determination of the amount of reaction, in excess of the stoichiometrical amount, except that in the first reaction hydrogen may be in excess without disadvantage. The last reaction is one in which, while the sulfur is in the solid state at the beginning and at the end of an experiment, the reaction actually occurs in a flame with oxygen burning in an excess of sulfur in the gaseous phase, in order to prevent the formation of sulfur trioxide (12).

The rate of evolution of heat energy in the above reactions as they proceed in the calorimeter is controlled by the rate at which the gas which is not in excess is fed into the reaction vessel, and can, therefore, be maintained practically constant at an appropriate value for the duration of an experiment.

The determination of the amount of reaction in the above reactions can usually be most accurately and conveniently made by determining the mass of one of the substances formed, rather than the mass of one of the substances used up.

The reactions of the second class are carried out at constant pressure in a reaction vessel which is usually itself the calorimeter, the reaction resulting from the mixing of two liquids, or of a solid and a liquid, or of a gas and a liquid. Examples of this class include the following:

$$\mathrm{HCl\cdot 100H_2O(liq.) + NaOH\cdot 100H_2O(liq.) = NaCl\cdot 201H_2O(liq.)}$$
$$\mathrm{HCl(gas) + 100H_2O(liq.) = HCl\cdot 100H_2O(liq.)}$$
$$\mathrm{NaCl(c) + 100H_2O(liq.) = NaCl\cdot 100H_2O(liq.)}$$
$$\mathrm{NaCl\cdot 100H_2O(liq.) + 100H_2O(liq.) = NaCl\cdot 200H_2O(liq.)}$$
$$\mathrm{NaCl(aq.) + AgNO_3(aq.) = AgCl(c) + NaNO_3(aq.)}$$
$$\mathrm{Na(c) + H_2O(liq.) = NaOH(aq.) + \tfrac{1}{2}H_2(gas)}$$

In some of the above reactions, the rate of evolution of heat energy can be controlled by the appropriate mixing of the two reacting substances, while in others the mixing is carried out at one stroke, in which case the heat energy is evolved or absorbed exponentially with time.

In reactions of this type, the amount of reaction is usually determined from the amounts of each of the initial substances. Because concentration is an important variable, this must be accurately known for all the reactants and the product. Furthermore, the extent of completion of the reaction must be ascertained from a knowledge of the free energies in the system formed in the reaction.

The reactions of the third class are carried out in a closed bomb at constant volume and, with a few exceptions, are all combustion reactions, in which a gas, liquid, or solid is burned with an excess of oxygen. Most of the substances so burned are organic compounds, and the main products of combustion are carbon dioxide and water. Because the reaction is in the nature of an explosion, the entire amount of heat is evolved in a very short period of time. While this type of reaction can be carried out quickly and simply with a bomb calorimeter, the calorimetric data can not always be interpreted with the highest accuracy because of the complex nature of the system existing in the bomb at the end of the experiment (see page 251).

VIII. THERMOCHEMICAL CALORIMETRY AND THERMOMETRY

Fortunately for present-day investigators in thermochemistry, the apparatus and technic of calorimetry have been developed to such a high degree of precision and accuracy that measurements of quantities of energy can be made with uncertainties as low as 0.01 or 0.02 per cent. The main calorimetric problem of the thermochemist, then, is to adapt the existing apparatus and technic to the determination of the heat of a particular chemical reaction.

The apparatus, technic, and procedure of modern calorimetry have been described at considerable length by a number of writers (11, 18, 28, 30, 46), to whose publications the reader is referred for detailed information on the subject of modern calorimeters and calorimetric thermometry. It is important to remember at this point that the investigator who is determining the isothermal heat of a chemical reaction has an advantage, in point of accuracy, over the one who is determining the heat capacity of a substance, or its increase in heat content between two temperatures. The former need only duplicate the apparent temperature rise of the calorimeter under the given conditions, while the latter must determine the true temperature rise of the calorimeter in absolute degrees.[12]

The type of calorimetric method to be used in a given thermochemical investigation is determined by the type of reaction to be studied. Nearly all the reactions susceptible of thermochemical measurement can be grouped into the three classes listed on page 244, and the different types of calorimetric apparatus and procedure may accordingly be said to fall into three classes.

Examples of modern calorimetric apparatus and procedure used in studying reactions of the first class, those occurring substantially in the gaseous

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[12] An exception is the determination, by the dropping method, of the decrease in heat content of a substance between a high temperature and that of the calorimeter (near room temperature), in which case the investigator can, as in the measurement of the heat of a reaction, duplicate the temperature rise of the calorimeter, whatever it may be, by means of electrical energy. While in this case the temperature rise of the calorimeter need not be known accurately, in absolute degrees, the difference between the initial and final temperatures of the substance under investigation must be so known.

phase at constant pressure, are those employed at the National Bureau of Standards and at several other laboratories (12, 20, 30). A detailed description of these assemblies and procedures is given in the papers cited.

For measuring the heats of reactions of the second class, those occurring substantially in the liquid phase at constant pressure, precise calorimetric apparatus and procedure have been developed in a number of laboratories (8, 21, 23, 25, 26, 28, 37, 39). Although extremely precise, some of these calorimetric assemblies have lacked an important feature of accurate modern thermochemical work, that of providing a means for reproducing, by means of electrical energy, the change in the calorimeter brought about by the energy of the chemical reaction.

The calorimetric apparatus for measuring the heats of chemical reactions of the third class, those occurring at constant volume in a closed bomb, is well standardized, and a detailed description of the modern apparatus and technic is given in a number of papers (11, 17, 18, 19, 27, 37, 38, 42). While the bomb calorimeter is susceptible of very high precision, approaching 0.01 per cent in some cases, two points in connection with the accuracy of the thermochemical values obtained should be noted. In the first place, if the assembly lacks an electrical energy circuit, the electrical energy equivalent of the calorimeter must be determined, as indicated on page 248, by means of a "standard" reaction carried out under certain given conditions. In the second place, the reaction which actually occurs in the bomb is never a completely clear cut one, and some very significant corrections to standard states must be made (see page 250).

IX. DETERMINATION OF THE ELECTRICAL ENERGY EQUIVALENT OF THE CALORIMETER

The electrical energy equivalent of the calorimeter is the amount of electrical energy required to bring the calorimeter from the initial temperature T_A to the final temperature T_B under the same calorimetric conditions as exist for the chemical reaction experiments, T_A and T_B being, respectively, the same in all the experiments.

Though the electrical energy equivalent of the calorimeter, per degree rise in temperature, approximates the heat capacity of the calorimeter, the latter term should be entirely avoided in experimental thermochemistry. There are several reasons for this. In the first place, the actual determination of the heat capacity of the calorimeter would require not only the accurate and precise calibration of the thermometer in terms of the true temperature scale, but also the definition of the physical limits of the system whose temperature is to be raised by the measured energy. Both of these requirements involve a considerable expenditure of effort and they are wholly superfluous, since the thermochemical values will in no way be made more accurate because of them. In the second place, the term "heat capacity of the calorimeter" carries, from the early days of thermochemistry, the implication that the value may be derived by summing the heat capacities of the parts of the system. Such a procedure is far too inaccurate for the requirements of modern thermochemistry, where it is desired to know accurately the energy required to take the calorimeter system from a given initial state to a given final state under the same calorimetric conditions as obtain in the reaction experiments.

The effect of possible calibration errors in the resistance thermometer and bridge, or in the thermoelement and potentiometer, can be entirely eliminated by using the same thermometric system in all the experiments and making both electrical energy and chemical reaction experiments over the same temperature interval.

Insofar as is possible, the rate of temperature rise should be made practically the same in both the experiments with electrical energy and those with chemical energy. This requirement is easily met in the experiments on reactions of the first class (see page 244), but with more difficulty for reactions of the second and third classes. The reactions occurring in the bomb calorimeter are probably the most difficult in which to match the rate of input of electrical energy with the rate of evolution of chemical energy. The more alike are the time–temperature curves in the two kinds of experiments, the less danger is there that errors in the corrections for heat flow into the calorimeter from the jacket and surroundings will fail to cancel.

The measurement of electrical power is most conveniently and accurately made by measuring the potential drop across the heating coil in the calorimeter and the current passing through it (the latter being determined by measuring the potential drop across a standard resistance in series with the heating coil). The accuracy of the measured value of the electrical energy then depends upon the accuracy of the device used for measuring the time of input of the electrical energy, and the accuracy of calibration of the electromotive force of the standard cell and the resistance of the coils of the potentiometer and the standard resistance.

When the necessary electrical and timing apparatus is not available for making a direct determination of the electrical energy equivalent of the calorimeter, a "standard" chemical reaction is used as the source of the calibrating energy. In the bomb calorimeter, for example, a standard sample of benzoic acid can be used, though it is important for accurate work that the benzoic acid be burned under the same conditions as in the standardizing laboratory. In a constant-pressure flame calorimeter the reaction between hydrogen and oxygen to form water may similarly be used to provide the "standard" energy (24, 30, 45).

X. EXAMINATION OF THE PURITY OF THE REACTION

One phase of thermochemical research that has often received too little attention in the past is the problem of examining the purity of the chemical reaction being studied. The investigator should demonstrate with reasonable certainty, by means of appropriate chemical or physical tests, that the reaction which actually occurs in the calorimetric reaction vessel is one which does not differ significantly, with regard to the evaluation of the given thermochemical constant, from the theoretically pure reaction. Or, if there is a side reaction, the amount and effect of it must be evaluated with the necessary accuracy.

Having first decided that the reaction being studied is reasonably complete and clear cut, one can investigate the purity of the reaction as it actually occurs, first by establishing the purity of the reacting substances, and second by examining the products of the reaction for the presence of possible foreign substances. The permissible amounts of impurities in the reacting substances, and the permissible amounts of side reactions, depend to a large extent upon the method by which the amount of the reaction is determined and upon the amount of heat energy contributed by the side reactions involved.

XI. DETERMINATION OF THE AMOUNT OF REACTION

One of the vital points in any thermochemical investigation is the method of determining the amount of chemical reaction which occurs in any given experiment. The method selected should be precise and accurate with respect to true mass in grams, and the amount should be accurately expressible in terms of moles. This latter requirement involves an accurate knowledge of the molecular weight of the substance whose mass determines the amount of reaction.

Suppose, for example, that the reaction being studied is

$$C_6H_{14}(\text{liq.}) + \tfrac{19}{2}O_2(\text{gas}) = 6CO_2(\text{gas}) + 7H_2O(\text{liq.})$$

Using the values given in the 1935 table of the International Committee on Atomic Weights (3), C = 12.00, H = 1.0078, and O = 16.0000, one obtains for the molecular weights of C_6H_{14}, CO_2, and H_2O, the values 86.109, 44.000, and 18.0156, respectively. In the past few years, however, a great deal of evidence has accumulated (2, 3) which indicates that the true atomic weight of carbon is somewhere between 12.007 and 12.009, and that of hydrogen is 1.0081. Using 12.007 and 1.0081, one obtains for the molecular weights listed above the respective values, 86.155, 44.007, and 18.0162. The change in the molecular weight of C_6H_{14} is 0.054 per cent, that in CO_2 is 0.016 per cent, and in H_2O 0.003 per cent.

It is obvious, therefore, that in this particular problem the substance whose mass should determine the amount of reaction in moles is, in order of preference, H_2O, CO_2, and C_6H_{14}, assuming, of course, that the true mass in grams of each substance is capable of being determined with about the same accuracy.

Another point which must be carefully considered, also, is that the determination of the amount of reaction from the mass of one substance, rather than that of another, may make permissible a greater amount of impurity in one of the reacting substances. An example of this situation is the combustion in oxygen of liquid ethyl alcohol. In such a case it would be unwise to determine the amount of reaction from the mass of ethyl alcohol without first establishing beyond doubt that the sample contained no water, whereas, the determination of the amount of reaction from the mass of carbon dioxide produced would make permissible the presence, in the ethyl alcohol, of a relatively large amount of water without introducing a significant error in the thermochemical value.

In general, it may be said that the "determining" substance should be one whose true mass can be accurately and readily measured. For example, carbon dioxide can be absorbed in ascarite (sodium hydroxide on asbestos) and water in anhydrous magnesium perchlorate (30, 31, 32). It should be emphasized that "weights in air" have no place whatever in accurate thermochemical work, because in chemical thermodynamics one must deal as accurately as possible in terms of moles, which can be derived only from true masses in grams. Where the substance determining the amount of reaction is absorbed in tubes to be weighed, the accuracy of the correction from apparent mass to true mass can be considerably increased by weighing the tube filled with hydrogen gas instead of the heavier oxygen, air, or nitrogen (30, 31, 32).

XII. CORRECTIONS TO STANDARD STATES

It frequently happens that the reactants and products of the chemical reaction as it takes place in the calorimeter are not in the accepted standard states. For this reason, it is imperative that significant data be recorded as to the phase, pressure, temperature, and concentration of the substances at the beginning and at the end of the reaction, so that the conversion to the standard states may be accurately made.

A study of each reaction will indicate with what significance the various properties must be recorded. In reactions involving aqueous solutions of strong electrolytes, for example, it is sometimes necessary to record the temperature to within 0.01°C., and similarly accurate information must be given as to the concentration. Absence of such information has made useless many thermochemical data obtained in the past.

The increasing accuracy and precision of thermochemical measurements has resulted in increasing the significance of information concerning the exact thermodynamic state of each substance participating in the chemical reaction. In former years, for example, the observed value of the heat evolved in the bomb calorimeter was taken as $-\Delta E$, the decrease in internal or intrinsic energy, for the pure reaction at 1 atmosphere. Several years ago, Washburn (45) investigated in considerable detail the reaction that actually occurs in the bomb calorimeter and showed that the value observed for the bomb reaction differs from $-\Delta E$ for the pure reaction at 1 atmosphere by amounts ranging from several hundredths to nearly 1 per cent.

That the reaction which actually takes place in the bomb calorimeter is a complex one is made evident by considering just what the initial and final states are. The following equation illustrates the nature of the bomb process for the combustion of benzoic acid when, as is usually done, a small amount of water is initially placed in the bomb;[13] the temperature and pressure of the initial state, T_A and P_A, usually will have values between 20° and 30°C., and between 30 and 40 atmospheres, respectively; the temperature and pressure of the final state will be $T_A + \Delta T$ and $P_A - \Delta P$, where ΔT will usually have a value from 1° to 4°C. and ΔP will usually be of the order of several atmospheres:

$$\begin{gathered} C_7H_6O_2(\mathrm{c}) + [(30 - a)O_2 + bH_2O]\ (\mathrm{gas}) + [(\tfrac{1}{18} - b)H_2O + aO_2]\ (\mathrm{liq.}) = \\ [(7 - f)CO_2 + (\tfrac{45}{2} - d)O_2 + eH_2O]\ (\mathrm{gas}) + [(3 + \tfrac{1}{18} - e)H_2O + \\ dO_2 + fCO_2]\ (\mathrm{liq.}) \end{gathered}$$

This complex actual reaction is to be compared with the simple reaction for which the thermochemical value is desired, the temperature and pressure of the reactants and products being, for example, 25°C. and 1 atmosphere:

$$C_7H_6O_2(\mathrm{c}) + \tfrac{15}{2}O_2(\mathrm{gas}) = 7CO_2(\mathrm{gas}) + 3H_2O(\mathrm{liq.})$$

To obtain the required thermochemical value for the simple reaction at 1 atmosphere, the observed value for the bomb reaction must be corrected with regard to the changes in internal energy with pressure of the initial oxygen and of the mixture of oxygen and carbon dioxide of the final state, the heat of solution of oxygen and carbon dioxide in water, and the heat of vaporization of water.

In a comprehensive study, Washburn (45) derived the complete and the approximate equations for correcting the heat of the bomb reaction to give

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[13] The presence of nitrogen in the oxygen used for the combustion further complicates the reaction through the formation of a significant amount of aqueous nitric acid:

$$\tfrac{1}{2}N_2(\mathrm{gas}) + \tfrac{5}{4}O_2(\mathrm{gas}) + \tfrac{1}{2}H_2O(\mathrm{liq.}) = HNO_3(\mathrm{aq.})$$

the heat of the pure reaction at 1 atmosphere, and proposed certain standard states for bringing uniformity in the data of bomb calorimetry. The important variables in this connection are the volume of the bomb, the mass of substance burned, the amount of water initially placed in the bomb, and the initial pressure. Washburn's recommendations concerning the standard conditions of the bomb process, and his equations for correcting ΔE of the bomb reaction to ΔE of the simple reaction at 1 atmosphere, have been accepted by the Commission Permanente de Thermochimie de la Union Internationale de Chimie (24).

In the case of the combustion of organic compounds containing sulfur or a halogen, the reaction is even more complicated than that described above. In each such combustion involving sulfur or a halogen, the investigator must determine, with an accuracy commensurable in significance with his calorimetric accuracy, just what the actual reaction is that occurs in the bomb. The observed heat effect must then be corrected by the appropriate amount necessary to give the heat of a reaction in which all the reactants and products are in definite known states (4, 14).

XIII. THE "PRECISION ERROR" AND THE ESTIMATED UNCERTAINTY OF THE FINAL EXPERIMENTAL VALUE

For the proper comparison, with respect to precision, of the values obtained at various laboratories for the thermochemical constants, it is necessary that the "precision error" assigned to the various values be determined in a uniform manner. This uniform comparison will, however, be concerned only with the precision of the various sets of data and not with their actual accuracy, because the accuracy will depend upon the magnitude of the unknown or unaccounted-for systematic errors, the control of which is the burden of the individual investigators.

Serious systematic errors may arise from the determination of the electrical energy equivalent of the calorimeter, from an impurity in the reaction, or from the determination of the amount of reaction; and it is the duty of each experimenter to investigate thoroughly his apparatus, reaction, and procedure with regard to these possible systematic errors.

For determining in a formal and uniform manner the "precision error" to be assigned to the values obtained by various investigators for a given thermochemical constant, the following procedure is proposed:

Case I. Where the investigator determines the energy equivalent of his calorimeter directly with electrical energy.

1. The experimenter performs *m* acceptable experiments to determine the energy equivalent of the calorimeter directly in terms of electrical energy. The *m* values so obtained are averaged arithmetically, and the

deviation of each of the m values from the mean is recorded. Then the "energy equivalent error" is

$$a = \pm(100) \frac{2\sqrt{\Sigma\Delta^2/m(m-1)}}{(\text{value of energy equivalent})} \text{ per cent}$$

where $\Sigma\Delta^2$ is the sum of the squares of the m deviations.

2. The experimenter performs n acceptable experiments to determine the heat of a unit amount of the given reaction. The n values so obtained are averaged arithmetically, and the deviation of each of the n values from the mean is recorded. Then the "reaction error" is

$$b = \pm(100) \frac{2\sqrt{\Sigma\Delta^2/n(n-1)}}{(\text{value of reaction energy})} \text{ per cent}$$

3. The final assigned "precision error" of the average value obtained by the investigator for the heat of the given reaction is

$$\text{"precision error"} = \pm\sqrt{a^2 + b^2} \text{ per cent}$$

Case II. Where the investigator determines the energy equivalent of the calorimeter by means of a "standard" or "calibration" reaction.

1. The thermochemical value of the "standard" or "calibration" reaction, which has been accurately measured in one of the standardizing laboratories, has an "assigned error" equal to $\pm e$ per cent.

2. The experimenter performs m acceptable "calibration" experiments with the "standard" reaction to determine the energy equivalent of the calorimeter. The m values so obtained are averaged arithmetically, and the deviation of each of the m values from the mean is recorded. Then the "calibration error" is

$$c = \pm(100) \frac{2\sqrt{\Sigma\Delta^2/m(m-1)}}{(\text{value of energy equivalent})} \text{ per cent}$$

3. The experimenter performs n acceptable "reaction" experiments to determine the heat of a unit amount of the given reaction. The n values so obtained are averaged arithmetically, and the deviation of each of the n values from the mean is recorded. Then the "reaction error" is

$$b = \pm(100) \frac{2\sqrt{\Sigma\Delta^2/n(n-1)}}{(\text{value of reaction energy})} \text{ per cent}$$

4. The final assigned "precision error" of the average value obtained by the investigator for the heat of the given reaction is

$$\text{"precision error"} = \pm\sqrt{e^2 + c^2 + b^2} \text{ per cent}$$

In connection with the foregoing proposed procedure, the following points should be noted: The "error" of the average value of n experiments made to determine a given quantity is $\pm 2\sqrt{\Sigma\Delta^2/n(n-1)}$. This formula yields a value of the "error" within whose limits the "true" value has a chance of about 21 to 1 of being. The foregoing "error" is three times as large as the usual "probable error" computed with the formula $\pm 0.67\sqrt{\Sigma\Delta^2/n(n-1)}$, which indicates a chance of 1 to 1 that the "true" value lies within the given limits. The use of the "21 to 1" formula, rather than the "1 to 1," seems better because it yields an "error" which is conservative and reasonable. When the number of experiments is in the range of about five to seven, the "error" so computed has usually about the same magnitude as the average deviation. The deliberate performance of a very large number of experiments in order to reduce the value of the computed "error," when the average deviation remains unchanged, should be avoided, because the resulting "error" may then be so small as to be comparable with a number of possible small systematic errors and would consequently lose real significance. In order to prevent the occurrence of this misleading situation, it is recommended that not more than twelve experiments be made in any one series. It is also recommended that not less than four or five experiments be performed in any one series, because the performance of a lesser number will decrease the certainty attainable with a given apparatus out of proportion to its possibilities. Acceptable experiments include all except those in which a mistake or gross error has obviously been made.

In addition to the foregoing "precision error," which is calculable in a uniform manner from the data of various investigators, it is also desirable to assign an "accuracy error" or estimated uncertainty to the final value. This may be done by assigning a reasonable value to the one or more possible but unaccounted-for systematic errors, say $\pm f$ per cent, and combining it with the "precision error" by taking the square root of the sum of the squares. The "accuracy error" for cases I and II above would then be, respectively, $\pm\sqrt{a^2 + b^2 + f^2}$ and $\pm\sqrt{e^2 + c^2 + b^2 + f^2}$, which should indicate the limits within which there would be a reasonable certainty that the actual true value of the thermochemical constant lies.

XIV. CONCLUSION

The contributions to thermochemistry which have been made in the United States in the past decade have been reviewed in the Annual Survey of American Chemistry (1), and most of the important modern thermochemical researches in both Europe and America have been reviewed in several articles by Roth (35, 36).

It is the opinion of the writer that the amount of work in thermochemistry that is being carried on in the laboratories of the world is entirely inadequate in view of its present-day importance to science. Thermochemical research is a field in which careful experimental work will not only yield important data for chemical thermodynamics, but will also produce data which can be utilized in conjunction with appropriate other values to obtain much needed information concerning the energies of formation of polyatomic molecules from atoms.

While it is true that research in thermochemistry has increased considerably in the past ten years, there is urgent need for more progress and expansion. It may be pointed out that even today there are a large number of chemical reactions for whose heats we depend upon the relatively uncertain data obtained nearly half a century ago. Some of these reactions are so important to both science and industry that the situation may be termed amazing.

Because the data of thermochemistry are of great importance to all branches of chemistry, to the theorists who are advancing our knowledge of molecular structure, and to all those industries whose processes are governed and controlled by the calculations and methods of thermodynamics, it is extremely desirable that every encouragement be given to thermochemical research, whether it be in the national standardizing laboratories, in the universities, or in the industrial laboratories, each of which will have its own particular part to play in the development of this important field.

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DISCUSSION

Dr. MacInnes: Has any account been taken of the slight difference between the value of the faraday obtained from the silver coulometer and that found with the iodine coulometer by Washburn and Bates and by Bates and Vinal?

Dr. Rossini: The present "best" value for the Faraday constant is based primarily upon the data from the silver coulometer (see Birge: ref. 6).