

EXCURSION IN CHEMICAL THERMODYNAMICS, FROM THE PAST INTO THE FUTURE

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INTRODUCTION

The title of this paper was chosen so as to provide an umbrella large enough to cover almost any topic in the field.

In view of the comprehensive nature of this Symposium the author decided to have a look at the science as a whole, see what it consists of and what its mission is, and discuss the auxiliary tools used in the science, particularly for purposes of communication. In this report, then, several topics that have been of particular interest and concern to the author over the years will be covered.

We who are in the field of thermodynamics and thermochemistry are most fortunate in working in a science that is basic to the behaviour of all matter in the universe. We have the privilege of working in a quantitative science, with the excitement of frequently doing something no man ever did before and learning something no man ever knew before. We can probe on the frontiers of our science and discover the great harmony of figures, formulae, and scientific laws.

In our world, science advances in a measure proportional to the extent to which we have knowledge of the rates at which phenomena occur, of the forces which hold entities together, and of the energies and arrangements of the components of the systems that constitute our world.

Science is based upon observation and measurement. The better and more precisely and accurately we can observe and measure, the better and more rapidly we can develop theories to explain the natural state of things and guide us to more fruitful observations and measurements.

As more knowledge comes to man, he is able to devise theories to correlate and explain hitherto unrelated observations. In time, as the theories are made more firm, mountains of observational data may be replaced with a few simple formulae.

BASIC THERMODYNAMIC PROPERTIES

The basic thermodynamic properties are pressure, volume, temperature, energy and entropy. Appropriately combined with the absolute temperature, values of energy and entropy yield quantitative information on the thermodynamic behaviour and stability of chemical substances. Important needs of science are therefore served by having available for chemical substances reliable values of entropy and of energy, the latter measured with respect to an appropriate reference state. The property of entropy is related

to the manner of arrangement of the entities that make up a given system, whereas the property of energy is related to the forces holding together the entities of the system. What have been the sources of these needed values of energy and of entropy?

ENTROPY

Let us consider first the property of entropy. The second law of thermodynamics, involving the property of entropy, was contained implicitly in the work of Carnot in 1824, but was first clearly enunciated by Clausius in 1850 and independently by Kelvin in 1851. Somewhat over half a century ago, it became possible to evaluate entropies of certain pure chemical compounds by way of calorimetric measurements, down to low temperatures, of heat capacities, heats of transition, heats of fusion, and heats of vaporization. These chemical compounds conformed to the requirements for the application of the third law of thermodynamics.

It was less than 40 years ago that chemists and physicists began to apply with much success the methods of statistical mechanics to calculate values of the thermodynamic properties of entropy, heat capacity, and heat content or enthalpy as a function of temperature, for simple gaseous molecules. Twenty-five years ago, such calculations became commonplace in chemistry and physics. Evaluations of entropy were made in this way for many molecules, including a large number of hydrocarbons having many atoms per molecule.

In general, such calculations required only a knowledge of the architecture and the simple energy levels of the given molecules, as given by appropriate spectroscopic and other molecular data. For the larger molecules, experimentally determined values of entropy for a few "key" compounds by way of the third law served to establish the values of one or more constants in the calculations. All this meant that values of entropy could be calculated for many molecules from a knowledge of the molecular architecture and the fundamental frequencies of vibration, and for other systems simply from a knowledge of the spatial arrangement. Thus the need for experimental measurement of entropies by way of the third law became less and less urgent.

ENERGY

On the other hand, what about values of the energy, or heat of formation, of the chemical substances? Here we find the picture quite different. The first law of thermodynamics, involving the property of energy, was contained implicitly in the work of Carnot in 1824 and of Mayer in 1842, but was first stated unambiguously by Helmholtz in 1847.

Until about 35 years ago most of the values of heats of formation of the chemical compounds were derived from the experimental work of Julius Thomsen at Copenhagen and Marcellin Berthelot at Paris. Thomsen's work began about 1850 and culminated in his famous four volumes entitled *Thermochemische Untersuchungen*, published in the years 1882 to 1886. Berthelot worked from about 1870 to several years beyond 1900, publishing many separate papers in *Annales de chimie et physique* and some in *Comptes rendus*. His book entitled *Thermochimie* was published in 1897.

Except for the work of some investigators like Matignon in France, Swietoslowski in Poland, Roth in Germany, and Richards in the United States—there were relatively few thermochemical investigations following Thomsen and Berthelot until about 30 years ago. The thermochemical data appearing in 1936 in the book of Bichowsky and Rossini, entitled *Thermochemistry of the Chemical Substances*, pointed clearly to two important facts: (i) there was a complete lack of data on the heats of formation of a number of important chemical substances; (ii) there were large uncertainties associated with many of the values of heats of formation then reported.

RENAISSANCE IN THERMOCHEMISTRY

Meanwhile, the requirements of basic science for pioneering investigations, and of applied science for industrial processes, were calling for data of increasing accuracy with respect to heats of reaction. Many values of heats of reaction calculated from the then existing data possessed uncertainties of one, two, or more kilocalories per mole. These figures loom large when one remembers that an error of about 2.7 kcal/mole in the heat of a reaction changes the calculated value of the equilibrium constant for that reaction at room temperature by a factor of 100.

In the old days, most of the industrial processes involved chemical reactions having extremely large values of the equilibrium constant, in the range 10^3 to 10^7 or more, so that large errors could be tolerated in the thermochemical data used in the calculations. However, with increasing precision of measurement and control of temperature and pressure in our research laboratories and in our industrial processes, it became possible to operate profitably with industrial processes having an equilibrium constant not far from unity. This placed a heavy burden on the accuracy required of the thermochemical data used in calculating the equilibrium constant for the given process.

It should be emphasized that, whereas values of the entropy of given systems could be calculated with adequate accuracy without recourse to experimental thermal measurements, the values of the energy of given systems could not be calculated with adequate accuracy, except for a few very special cases.

It was clear then that a renaissance in experimental thermochemistry was much needed, and a number of investigators set about to do something in the field, to obtain data leading to values of the heats of formation of the important chemical compounds.

CHEMICAL EQUILIBRIUM CONSTANT

To assess the relative importance of the change in energy and the change in entropy for a given reaction, it is well to look at our basic thermodynamic relations involving these properties with the equilibrium constant and the temperature.

We define the free energy or Gibbs energy as

$$G = E + pV - TS \quad (1)$$

where E is energy and S is entropy.

Since we also define the heat content or enthalpy as

$$H = E + pV \quad (2)$$

it follows that

$$G = H - TS \quad (3)$$

For a reaction taking place at constant temperature, with each reactant and product in its standard state, we may write

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

But we also have the relation

$$\Delta G^\circ = -RT \ln K \quad (5)$$

where K is the equilibrium constant, defined as the proper quotient of activities of the reactants and products at equilibrium.

Combination of equations (4) and (5) yields

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

or

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (7)$$

or

$$K = (e^{-\Delta H^\circ/RT})(e^{\Delta S^\circ/R}). \quad (8)$$

From this equation, we note that K increases with decrease in ΔH° and with increase in ΔS° . A decrease in ΔH° comes with increase in the energy of binding of atoms in the molecular structure, leading to greater "security" in the system. An increase in ΔS° comes with increase in the number of states of existence available, leading to greater freedom in the system. These are opposing factors in the evaluation of K . Hence the final state of equilibrium is a compromise between the "security" factor and the "freedom" factor.

Now let us look at this equation from the standpoint of its change with temperature. Note that the exponent $\Delta S^\circ/R$ does not contain the temperature explicitly and therefore will not change very greatly with temperature.

For very low temperatures, $\Delta H^\circ/T$ will be very large and K will be determined largely by ΔH° , the standard heat of reaction.

For very high temperatures, $\Delta H^\circ/T$ will approach zero, $e^{-\Delta H^\circ/RT}$ will approach unity, and K will be determined largely by ΔS° , the standard change of entropy for the reaction.

We have previously noted the sources of the values of ΔH° and ΔS° needed for the calculation of the equilibrium constant, K , for a given reaction according to equations (7) or (8):

ΔH° is usually evaluated from calorimetric measurements of the heats of appropriate reactions.

ΔS° is evaluated as the difference between the sum of the standard entropies of the products and the sum of the standard entropies of the reactants, for the given reaction:

$$\Delta S^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants}) \quad (9)$$

For each reactant or product, the standard entropy is usually evaluated in one of two ways:

(i) by application of the third law of thermodynamics to measurement of heat capacities, heats of transition, heats of fusion, and heats of vaporization, down to low temperatures;

(ii) from statistical calculations utilizing spectroscopic and other molecular data.

TEMPERATURE SCALE

In thermodynamics and thermochemistry, the temperature scale is a basic instrument. For experimental measurements of the thermodynamic properties of substances as a function of temperature, knowledge of the temperature scale and its realization is important in ascribing the measured values to the correct temperatures. For experimental measurements of heats of reactions or processes at essentially constant temperature, the precisely measured changes in temperature need not be known with reference to the temperature scale. For such investigations, the mean temperature of the experiment is required to be known only to the accuracy adequate to fix the temperature to which the measured heat of reaction is to be assigned. If the heat of the given reaction is measured precisely and has a very small temperature coefficient (with ΔC_p near zero), the mean temperature of the experiment does not need to be known at all accurately—perhaps 1° is adequate. On the other hand, if the heat of the given reaction is measured precisely and has a very large temperature coefficient, then the mean temperature may need to be known much more accurately, perhaps to 0.01° .

The thermodynamic scale of temperature is identical with what we may call the “zero-pressure” gas scale of temperature, which can be realized experimentally.

On this scale, we have, for one mole of gas,

$$(pV)_{T^p=0} = RT \quad (10)$$

The constant of proportionality in this equation may be evaluated in either of two ways: (i) by defining the number of degrees between two selected fixed points on the scale which are realizable in the laboratory; or (ii) by defining the absolute value of the temperature to be assigned to one fixed point realizable in the laboratory with reference to the non-realizable origin or zero on the scale of temperature. In the first method, the difference in the values of temperature between the two selected fixed points is defined and never changed, but the absolute values of the temperatures of the two points may change as the result of improvements in experimentation with the zero-pressure gas scale of temperature. In the second method, the absolute value of one fixed point with reference to the origin or absolute zero is defined and never changed, but the absolute value of the temperature of any other point may change as the result of improvements in experimentation. The second method above, involving only one realizable fixed point, was recommended by Kelvin in 1848 and again by Giauque in 1939.

However, until 1955, the International Temperature Scale was based on

two selected fixed points realizable in the laboratory: the ice point, the temperature of equilibrium of solid and liquid water saturated with air at 1 atmosphere; and the steam point, the temperature of equilibrium of liquid and gaseous water at a pressure of exactly 1 atmosphere. The difference in the temperature of these two selected fixed points was defined as 100 (exactly) °C, with the ice point labelled 0°C and the steam point 100°C.

To bring the basic temperature scale into the research laboratories, a practical or working temperature scale was needed, with an additional number of selected points for primary reference in addition to the two selected fixed fundamental points. The International (Practical) Temperature Scale was first adopted in 1927 at the Seventh General (International) Conference of Weights and Measures and was revised in 1948 at the Ninth General (International) Conference of Weights and Measures.

The International (Practical) Temperature Scale covered the range from -183°C to $+1063^{\circ}\text{C}$ using two selected fixed fundamental points and four selected primary reference points.

The two selected fixed fundamental points were:

Ice point	water, solid-liquid	0 (exactly)°C
Steam point	water, liquid-gas	100 (exactly)°C

The four selected primary reference points, and their assigned values (based upon experiment) were:

Oxygen point	oxygen, liquid-gas	-182.97°C
Sulphur point	sulphur, liquid-gas	444.60°C
Silver point	silver, solid-liquid	960.8°C
Gold point	gold, solid-liquid	1063.0°C

The thermometers used for interpolating between these points were as follows: from -183° to 0°C , a platinum resistance thermometer with an equation with four constants evaluated from measurements at the oxygen, ice, steam, and sulphur points; from 0 to 630°C , a platinum resistance thermometer with an equation with three constants evaluated from measurements at the ice, steam, and sulphur points; from 630 to 1063°C , a standard thermocouple of platinum and platinum-rhodium, with an equation of three constants, evaluated from measurements at the gold, silver, and antimony points, the value of the latter being determined with a platinum resistance thermometer.

Measurements of temperature above the gold point were made with optical thermometers using the radiation formula with measurements at the unknown temperature and the temperature of the gold point.

Currently, the Advisory Committee on Thermometry of the International Committee on Weights and Measures has six proposals relating to the International Practical Temperature Scale for presentation at the 1966 General (International) Conference of Weights and Measures. When adopted, these proposals will accomplish the following: (i) extend the use of the platinum resistance thermometer from the oxygen point down to the temperature of liquid hydrogen and from 630°C up to the gold point (this would give the platinum resistance thermometer the range from 20 (or less) °K up to 1337°K); (ii) substitute the zinc point (solid-liquid, near 420°C) for the sulphur point (liquid-gas, near 445°C); (iii) change the values of the silver

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and gold points by $+1.1$ and $+1.5^\circ$, respectively; (iv) adopt appropriate helium scales to cover the range 0.25 to 5°K .

With these changes, the International Practical Temperature Scale would be about as shown in *Table 1*.

Table 1

<i>Substance</i>	<i>Equilibrium</i>	<i>Temperature ($^\circ\text{K}$)</i>
Helium-4; helium-3	Liquid-gas	(0.25° to 5°)
Hydrogen	Liquid-gas	20.267
Oxygen	Liquid-gas	90.17
Water (ice point)	Solid-liquid	273.150
Water (triple point)	Solid-liquid-gas	273.16 (exactly)
Zinc	Solid-liquid	419.58
Silver	Solid-liquid	1235.05
Gold	Solid-liquid	1337.65

The International Practical Temperature Scale (IPTS) is gradually coming closer to the true Thermodynamic scale. As of several years ago, the difference between the two scales (Thermodynamic-IPTS) below 0°C was a maximum of about $+0.03^\circ$ near -90°C and -0.02° near -130°C . Between 0 and 100°C , the maximum difference was about -0.01° near 50°C . At the sulphur point, the difference was near 0.1° , while at the gold point more than 1° .

We can in due course look for very significant improvements in our temperature scale above the gold point. It should soon be possible to define a practical temperature scale above the gold point which will agree reasonably well with the thermodynamic scale, within a degree.

Very significant progress has been made in providing investigators in thermodynamics and thermochemistry with adequate scales of temperature from below 1°K up to near 3000°K , with some approach to satisfaction in the range to 4000°K . This is an enormous improvement over the situation existing not too many years ago.

FUNDAMENTAL CONSTANTS

An experimental investigator in his laboratory makes measurement of certain phenomena with instruments and apparatus calibrated in terms of the fundamental units of measurement—length, mass, and time. Frequently, the quantity reported by the investigator is not just precisely the quantities he has measured, but these combined with certain fundamental constants to obtain quantities for comparison with related observations of other investigators. For proper and convenient communication, it is desirable that the different investigators use the same values of the fundamental constants in reducing their respective sets of data, otherwise, the reported values will be different even though the quantities originally measured may actually have been in complete accord. It is important therefore for the entire field of science that there be available a currently acceptable self-consistent set of “best” values of the fundamental constants.

The need for fundamental constants was recognized in chemistry many years ago when there was established the chemists’ international scale of

atomic weights so that the chemists throughout the world might communicate their observations in a quantitative language that would be readily understood by other scientists. We now of course have the wonderful situation that the sciences of chemistry and physics are using one scale of atomic weights, the carbon scale, with twelve-carbon as the reference.

Since scientists engaged in thermodynamics and thermochemistry communicate largely in quantitative terms, the problem of having a self-consistent set of "best" values of the fundamental constants has always been very important to us.

We may simplify the problem by classifying the constants into three categories:

(i) the basic constants, the values of which are obtained from experimental measurement;

(ii) the defined constants, the values of which are fixed by definition; and

(iii) the derived constants, the values of which are obtained from the foregoing and appropriate physical relations.

Up to 1950, sets of fundamental constants which were more or less generally accepted in the United States, and to some extent in other countries, were provided by the International Critical Tables in 1926, followed by Birge with extensive reports in 1929, 1941, and 1945, and by DuMond and Cohen in 1948 and 1949.

In 1951, the Committee on Physical Chemistry of the National Research Council (U.S.A.) prepared a uniform set of fundamental constants for physical chemistry, based largely on the work of DuMond and Cohen.

This report was presented in such a way as to emphasize the fact that at that time, the purposes of physical chemistry, including thermodynamics and thermochemistry, were substantially fully served with a knowledge of six experimentally determined constants known as *basic constants*:

c , Velocity of light \mathcal{F} , Faraday's constant

N , Avogadro's number h , Planck's constant

$T_{0^\circ\text{C}}$ Absolute temperature of the ice point

$(pV)_{0^\circ\text{C}, p=0}$, Pressure-volume product for one mole of a gas at 0°C and zero pressure

Not to be confused with the foregoing basic constants are the fundamental units in terms of which all measurements are made—those of length, mass, and time.

Coupled with these basic constants were others mathematically related to them by way of known physical relations, known as *derived constants*:

e , Charge on the electron k , Boltzmann's constant

R , Gas constant per mole c_2 , Second radiation constant

Y , Constant relating energy and mass

Z , Constant relating wave numbers and energy

Actually, the picture is not quite as simple as displayed above in that some of the fundamental atomic constants are not uniquely determined independently of others. However, of the three constants, such as \mathcal{F} , e and N , which are related through the relation $\mathcal{F} = Ne$, we can place in the basic list the two which have the smaller percentage uncertainties and in the derived list the one with the largest percentage uncertainty.

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And, finally, there was the list of defined constants having the following exact values by definition:

g_0 , Standard acceleration of gravity	980.665 cm sec ⁻²
atm, Standard atmosphere	1,013,250 dynes cm ⁻²
cal, (thermochemical calorie)	4.184 joules
IT cal, International Steam calorie	4.1868 joules
B.t.u./lb.	(1/1.8) IT cal/g
in. inch	2.54 cm
lb. pound	453.59237 g

An important and most desirable change in one of the basic constants heretofore experimentally determined came about in 1955 when the International Committee on Weights and Measures approved the plan of defining the absolute temperature of the triple point of water. This meant moving to a temperature scale fixed with one experimentally realizable fixed point, the value for which is defined with respect to the non-realizable origin or absolute zero of temperature. The value selected for this was actually 0.01° less than the value extant in the tables most generally used in the United States. This was a change which would affect the value of the derived gas constant R ,

$$R = (pV)_{0^\circ\text{C}^p=0} / T_{0^\circ\text{C}} \quad (11)$$

by increasing it 1 part in 27316 or 37 parts per million.

Then in 1960 came another important and most desirable change when the scale of atomic weights was made common for both chemistry and physics by using, as the reference point, C-12 equal to 12.0000 (exactly). This change had the effect of decreasing the size of the mole by 43 parts per million from the chemists' scale and 318 parts per million from the physicists' scale.

This change has the effect of decreasing by 43 parts per million the values of those constants expressed in terms of the chemists' mole. Hence this change would decrease the value of the gas constant, R , by 43 parts per million. Since the change arising from the definition of the absolute temperature of the triple point of water increased the value of the gas constant, R , by 37 parts per million, the combined effect is to lower the value of the gas constant, R , by 6 parts per million—an almost negligible amount.

With the absolute temperature of the triple point of water now defined, we now have, in terms of our simple picture of presenting the fundamental constants, only five basic constants required to be determined experimentally:

$$c, N \text{ (or } e), \mathcal{F}, h, \text{ and } (pV)_{0^\circ\text{C}^p=0}$$

The difference between the ice point and the triple point of water has been determined experimentally quite precisely:

$$T \text{ (triple point)} - T \text{ (ice point)} = 0.0100 \pm 0.0001^\circ \quad (12)$$

This means that, with the triple point of water defined as 273.16 (exactly) °K, the absolute temperature of the ice point is 273.1500°K.

In the United States, the National Research Council enlarged its Committee on Fundamental Constants to cover all the sciences, and, after a delay

of several years, the Committee has this year been considering a proposed list of recommended constants. This list is also being considered by appropriate groups under the International Union of Pure and Applied Chemistry (I.U.P.A.C.) and the International Union of Pure and Applied Physics (I.U.P.A.P.). It is hoped that international accord will be reached between I.U.P.A.C and I.U.P.A.P. on these constants, in the same way that accord was reached on the scale of atomic weights.

For our five basic constants, we have the following recommended values:

c , Velocity of light	2.997925 ± 0.000003	10^{10} cm sec $^{-1}$
N , Avogadro's number	6.02252 ± 0.00028	10^{23} molecules mole $^{-1}$
\mathcal{F} , Faraday's constant	$96,487.0 \pm 1.6$	coulombs equivalent $^{-1}$
h , Planck's constant	6.6256 ± 0.0005	10^{-27} erg sec molecule $^{-1}$
$(pV)_{0^\circ\text{C}, p=0}$	2271.06 ± 0.04	joules mole $^{-1}$

From these, the values of the derived constants are easily obtained:

e , Charge on the electron, \mathcal{F}/N	4.80298 ± 0.00020	10^{-10} e.s.u.
R , Gas constant per mole, $(pV)_{0^\circ\text{C}, p=0}/T_{0^\circ\text{C}}$	8.31433 ± 0.00034	joules deg $^{-1}$ mole $^{-1}$
k , Boltzmann's constant, R/N	1.38054 ± 0.00011	erg deg $^{-1}$ mole $^{-1}$
c_2 , Second radiation constant, hc/k	1.43879 ± 0.00019	cm deg
Y , Constant relating mass and energy, c^2	8.987554 ± 0.000015	10^{13} joules g $^{-1}$
Z , Constant relating wave number and energy, Nhc	11.9626 ± 0.0011	joule cm mole $^{-1}$

With the changes now effected, regarding (i) the fixing of the absolute temperature of the triple point of water and (ii) the reference mass for the scale of atomic weights, it appears that the situation with respect to the values of the fundamental constants is in good shape as far as the needs of thermodynamics and thermochemistry are concerned. Of the five basic constants required to be determined experimentally, the present uncertainties are as follows, in parts per million: velocity of light, 1; Avogadro's number, 47; Faraday's constant, 17; Planck's constant, 75; pressure-volume product of one mole of a gas at 0°C and zero pressure, 18. Essentially all of these are known as well as needs for thermodynamics require for the present, and, most likely, for quite some time to come.

In this connection, it should be noted that setting the reference mass for the scale of atomic weights at 12 grams of carbon-12 as one mole fixes the number of molecules in a mole as the number of atoms of carbon-12 contained in a mass of 12 grams of pure carbon-12.

UNIT OF ENERGY

From about the year 1800 to 1900, the most convenient and readily applicable method of measuring quantities of heat arising from processes occurring at or near room temperature was to observe the rise of temperature produced in a known mass of water contained in a suitable vessel, or calorimeter. In this way, it was possible to measure a quantity of energy in terms of a given mass of water and its rise of temperature. The calorie was defined as the

quantity of heat required to raise the temperature of one gram of water through one degree Celsius. The experimenter was thus able to express the result in calories, obtained as the product of the mass of water in grams and the rise of temperature in degrees Celsius.

As the measurements increased in precision, it became necessary to do several things: (i) take proper cognizance of the heat capacity of the container, thermometer, stirrer, *etc.*; (ii) define the scale of temperature; and (iii) specify accurately the various conditions attending the absorption of the heat by the water, such as the mean temperature, the interval of temperature, *etc.* The specification of the mean temperature gave rise in itself to several calories, each representing a slightly different quantity of energy, such as the 0° calorie, the 4° calorie, the 15° calorie, the 18° calorie, the 20° calorie, and the mean (0° to 100°C) calorie. By about 1905, experimental calorimetry had advanced to a stage where measurements of heat energy in terms of the heat capacity of water could be made with a precision of about 1 part in 1000.

It was early recognized, however, that, notwithstanding the relative ease with which measurements of heat could be made in terms of the heat capacity of water, it was necessary to ascertain with appropriate accuracy what quantity of energy in absolute units, as ergs or joules, a given calorie was equivalent to. Investigations on this subject were carried out by a number of investigators, beginning with Joule about 1840, and continuing with Rowland, Reynolds and Moorby, Ames, and Barnes, to about 1900. Throughout all this work, the uncertainty of the value giving the number of joules equivalent to a given calorie was comparable with the uncertainty with which a given quantity of heat could be measured in terms of the heat capacity of water. Experimenters, therefore, continued up to about 1910 to use as the actual unit of energy the heat capacity of water under specified conditions.

Near the beginning of the present century, electrical standards of resistance and electromotive force became available with high precision and accuracy. Experimenters were then able to measure electrical energy with high precision. At this point, there was no longer any real need to retain the heat capacity of water as the unit of energy for calorimetric measurements. However, it was not until about 1930 that definite steps were taken to divorce the unit of energy in calorimetry from any connection with the actual heat capacity of water under specified conditions.

Electrical measurements of energy are based upon the mean solar second as the unit of time and upon highly precise and very stable working standards of electromotive force and resistance maintained at the several national standardizing laboratories. The working standards are saturated cadmium (Weston) cells and wire (usually manganin) resistance coils. When redefined in 1908, the international electrical units agreed upon were identical with the absolute units within the limits within which the latter could then be determined. Since then, however, the accuracy of the absolute measurements has increased. More accurate determinations of the relation between the absolute electrical units and the international electrical units were made. At the National Bureau of Standards, the chronology was somewhat as follows, for the number of absolute watts equivalent to one international

watt: in 1925, 1.00034; in 1930, 1.00036, rounded to 1.0004; in 1939, 1.00020 + 0.00005; in 1947, 1.000165 + 0.000025.

It is important to note that all measurements of electrical energy made from about 1910 to 1948 by means of standard cells and resistances were actually in terms of international joules. Beginning January 1, 1948, the several national standardizing laboratories began certifying standard cells and resistances in absolute volts and absolute ohms, so that the resulting power and energy are in terms of absolute watts and absolute joules, respectively.

Notwithstanding the fact that practically all accurate calorimetric measurements made after about 1910 were actually based on electrical energy, directly, or indirectly through standard calibrating substances, most investigators continued until about 1930 to express their final results in such a way as to make it appear that the unit of energy was in some way still related to the real heat capacity of water. Actually, what they did was to convert their values, determined in international joules, into one or more of the several calories based on the real heat capacity of water, usually for comparison with older values reported in the literature. This procedure should have been reversed, that is, the older data should have been converted to the modern unit of energy. However, the conversion to the older unit, one of the several calories, was favoured because most investigators were reluctant to change from their habits of thinking in terms of a unit of the size of a calorie.

An important effort to accustom scientists and engineers to the use of the joule as the unit of energy was made by Washburn in connection with many (but not all) of the tabulations of the data of thermodynamics and thermochemistry appearing in the International Critical Tables, of which he was Editor-in-Chief, and which were published in the period 1926 to 1930. This attempt to change over to the joule as the unit of energy was not popular. It appeared then that, at least for some time, the calorie would have to be retained as the name of the unit of energy, and that it should have a magnitude approximately the same as the traditional real calorie. It was also realized that there would have to be separated from any new calorie every association with the real heat capacity of water, otherwise all thermodynamic data would be subject to change every time someone determined the real heat capacity of water with an accuracy greater than that already existing.

The obvious solution was to have an artificial, conventional, or "dry" calorie, defined as equal to an arbitrary specified number of electrical joules. Investigators would then report their results in terms of electrical joules, the unit in which the calorimetric measurements are actually made, and, for the benefit of those who prefer to continue thinking in terms of a unit of energy having the name and magnitude of the calorie, would also give their values in terms of the defined calorie, using the conventional factor for the conversion.

In line with this development, there came into use independently about 1930 two different artificial, conventional, defined, "dry" calories—one for engineering steam tables and one for thermochemistry and chemical thermodynamics.

The artificial, conventional, defined, "dry" calorie for the engineering steam tables, designated as the IT calorie (International Table calorie),

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was agreed upon in 1929 by the International Steam Table Conference of that year. The definition was

$$1 \text{ IT calorie} = 1/860 \text{ international watt-hour.} \quad (13)$$

In terms of absolute electrical units, this relation becomes

$$1 \text{ IT calorie} = 4.1868 \text{ (exactly) joules.} \quad (14)$$

The British Thermal Unit (B.t.u.) is defined in terms of the IT calorie so as to retain the convenient relation

$$1 \text{ IT calorie/gram} = 1.8 \text{ B.t.u./lb.} \quad (15)$$

The artificial, conventional, defined, "dry" calorie for thermochemistry and chemical thermodynamics came into existence about 1930 by the author in the Thermochemical Laboratory at the National Bureau of Standards, and, by common consent, was used thereafter in practically all research laboratories in the United States dealing with thermochemistry and chemical thermodynamics. This calorie was defined as

$$1 \text{ calorie (thermochemical)} = 4.1833 \text{ international joules} \quad (16)$$

With the change to absolute electrical units in 1948, this calorie was re-defined in order to keep precisely the same the quantity of energy represented by it:

$$1 \text{ calorie (thermochemical)} = 4.184 \text{ (exactly) joules} \quad (17)$$

As has been emphasized, both the IT calorie and the thermochemical calorie are completely independent of the heat capacity of water.

Clearly now it is unfortunate that two different defined calories were established. With the greatly increasing number of contacts occurring between scientists and engineers, things would be much simpler with only one defined calorie to deal with and communication between scientists and engineers would be less complicated.

A possible solution to this problem is that in time, the scientists may see less and less point to the conversion of their values, measured in joules, into the defined thermochemical calorie, and they may be content to report and tabulate their data in joules, the actual unit of measurement. Such a change will require some reorientation of thinking but should not be too difficult to accomplish. When this occurs, then the engineers would be left with the way clear for only one defined calorie, their IT calorie. In due course of time, the engineers too may decide to deal directly with the actual unit of measurement of energy, the joule, and abandon their defined calorie.

It appears that we have made considerable progress over the years with respect to the problem of the unit of energy. The situation may now be described as good. We have passed from a plethora of calories to one real fundamental unit, the joule, with two associated defined calories which are really not necessary. There is a good chance that in due course of time one or both of the defined calories may disappear from the picture. Further,

we are in the fortunate situation of being able to measure quantities of energy electrically with very high precision and accuracy.

CALORIMETRIC METHODS

In the early days of calorimetry, apart from the problem of measuring the quantity of energy, difficulties were encountered in evaluating the heat capacity or energy equivalent of the calorimeter. It was not easy to specify the actual boundaries of the material system which would absorb the given heat energy nor to evaluate accurately the effective heat capacity of the calorimeter by summing the heat capacities of its parts.

These difficulties have been minimized by using substitution methods in which known quantities of energy are used to calibrate the calorimeter system under conditions substantially the same as those for the reaction or process whose heat is to be evaluated. The known quantities of energy may be provided electrically or by using the heat energy from a similar reaction or process whose heat is accurately known.

In the case of measurements of heats of reaction, the procedure is simply as follows: the thermochemical investigation consists of a chemical part and a calorimetric part. The chemical part involves accurate measurement of the quantity of chemical reaction taking place in the given experiment. The calorimetric part involves accurate measurement of the quantity of energy involved in the given experiment. The desired result is the ratio, in appropriate units, of the quantity of energy to the quantity of reaction. Using a "standard" calorimeter system, the heat evolved by a measured amount of the given chemical reaction is used to take the calorimeter system from an initial State A and Temperature T_A to a final State B and Temperature T_B . In another experiment, with the same calorimeter system, the heat evolved by a measured amount of electrical energy is used to take the calorimeter system from the same initial State A and Temperature T_A to the same final State B and Temperature T_B . In this manner, there is obtained a direct equivalence between the measured amount of chemical reaction and the measured amount of electrical energy, using the fixed calorimeter system as the absorber and comparator of the two kinds of energy. In such experiments, the over-all accuracy is usually limited by the chemistry of the investigation rather than the physics of it.

For reactions which absorb energy, the measured quantity of electrical energy can be introduced to balance the absorption of heat energy by the reaction, keeping the fixed calorimeter system at a constant temperature. Measurements of heats of transition, fusion, and vaporization have the advantage of this kind of system.

For measurements of heat capacity, or heat content or enthalpy, as a function of the temperature, the advantages of the substitution method are realized by making measurements with the sample container full, partially-full, and empty. Appropriate analysis of such data will permit elimination of constant errors affecting all the experiments.

Many novel calorimetric methods are coming into use, particularly for those reactions or processes which cannot be measured in the ordinary ways. Given a compound for which the heat of formation is to be determined, novelty in the selection of the reaction to be measured, and the type and

design of the reaction vessel to be measured, can frequently pay tremendous scientific dividends in the form of more accurate results with smaller uncertainties. The author feels certain that investigators will come up with many new and novel reaction vessels with which to measure heats of reaction.

ENERGIES OF NUCLEAR REACTIONS

In 1905, Einstein published his famous equation relating mass and energy:

$$E = m_0c^2/[1 - (v^2/c^2)]^{1/2} \quad (18)$$

For systems at rest, this relation simplifies to

$$E = m_0c^2 = Ym_0 \quad (19)$$

And for the difference in energy for a system going from State A to State B is

$$\Delta E = Y\Delta m_0 \quad (10)$$

where $Y = 8.987554 \times 10^{13}$ joules g^{-1} .

This equation received experimental verification about 30 years ago. Since then, this equation has been found most useful in calculating the energies of nuclear reactions from a knowledge of the masses of the reactants and products, and, conversely, for calculating one of the masses when the energy and all the masses but one are known.

With the extension of investigations on the determination of atomic masses, with respect to precision as well as the number of substances covered, many additional data on nuclear reactions will become available.

If it should happen some day that man can build a balance of sufficient sensitivity, say 10^{-10} g per g or better, then we may do away with nearly all of our calorimeters.

THEORETICAL CALCULATION OF ENERGIES

A number of investigators working in the field of quantum chemistry have been making calculations of the energies of molecular systems. Until recently, such calculations were not at all precise enough to be of much help for our needs in chemical thermodynamics. Now, several such investigators are stating that the precise and accurate evaluation of the energy of many molecular systems is just around the corner and that, in a few years, with the coming of bigger and better and faster computers, the progress made in this field will be astounding.

In connection with the problem of making such theoretical calculations of energy for large molecules, it is well to remember that, in general, we are not concerned with making a given large molecule from its elements, but rather we are concerned with studying its change to some isomeric form, or to a somewhat smaller molecule, or to a somewhat larger molecule. In these cases, the important thing to focus attention upon is the precise change in the structure of the given molecule, remembering the bulk of the structure of the molecule may remain unchanged. This mode of attack may make it possible to handle rather large molecular systems on a theoretical basis.

DATA OF CHEMICAL THERMODYNAMICS

For the proper and balanced advancement of the world today, we must maintain ourselves strong in science and technology. To do this requires an adequate system of communication in our scientific and technical community. This means information not only about current work and future plans, but also information on the results of past work.

The problem of storing and retrieving scientific data varies greatly in magnitude and complexity according to the nature of the data. Many simple facts are easily amenable to coding, storing, and retrieving by machines. But the problem of storing and retrieving quantitative scientific data is not so simple, because careful appraisal of much contextual information is required to recover the full significance and proper value of the data.

We use the term critical tables to mean tables of critically selected "best" values of properties, maintained substantially up to date by revision at appropriate intervals.

The problem is to critically collect, analyse, calculate, correlate, and compile data on the chemical thermodynamic properties of the chemical substances. In some cases, the selection of a best value involves only appropriate appraisal and weighting of different values of the same property. Sometimes, the several values for the same constant may all be in substantial accord within their respective limits of uncertainty. At other times, the numerical values reported for the same constant may be in considerable discord. At still other times, there is required to be created, by appropriate correlation with molecular structure, the value of a given property for a compound that has never been made, or if made, never measured.

In appraising the numerical data appearing in the literature, it is important to obtain a record of the experimental facts actually observed by the investigator, as distinguished from what he may have calculated or derived by combining his original data with those of other investigators or with stated values of the fundamental constants. Among such constants are values of the atomic weights as well as values of the fundamental physical constants.

Appraisal must be made of two features of a given recorded investigation: (i) the physical features; and (ii) the chemical features. Regarding the physical features, the work must be scrutinized as to the precision and accuracy of the physical quantities actually measured, the identification of the actual units of measurement, and the method of calibrating the measuring instruments. Regarding the chemical features, one is concerned with the purity of the substances measured and the purity of any reaction investigated. Categorical limits cannot be set as to permissible amounts of impurity, as these depend upon the character of the impurity and its properties in relation to the principal component. For some isomeric impurities, for example, relatively large amounts of impurity can sometimes be tolerated.

In retrieving data from the literature, it is important to recover the proper measure of the uncertainty associated with the values, and in some appropriate way to present this information in the final tables.

It is to be emphasized that the kind of appraisal we are discussing requires intellectual capacities of a high scientific level. It is not a matter of transcribing a number from the printed page of the original paper to the

printed page of the tables being compiled. The final selection of a "best" value involves keen scrutiny of frequently discordant facts, considerable judgment, and the application of what we may call inspired intuition.

Critical tables of chemical thermodynamic data are an important component of our system of communication in science. For quantitative information of the kind we are discussing, the entire communication process may be said to consist of five steps: (*i*) the generation and recording of the data by the original investigator; (*ii*) the catalogueing, indexing, and abstracting of the data by the documentalist; (*iii*) the critical appraisal of the numerical data and the production of selected "best" values by competent experts, to form our critical tables; (*iv*) the dissemination of the tables in appropriate forms; and (*v*) the utilization of the data by the end-using investigator. It is important that each of these steps be of appropriate high quality, and that all steps be appropriately co-ordinated and articulated to achieve the best results.

Because of the continually increasing quantity of data becoming available—said to be doubling every eight years—it is impossible and impractical for each end-using investigator to digest and critically appraise all the quantitative data pertaining to substances and properties of interest to him. Rather, the predigestion of the numerical data and the preparation of critical tables by competent experts reduces enormously the quantity of scientific literature that the end-using investigator himself must read. The aim of our system of communication in science is to make the proper information available to the user quickly and efficiently.

The problem of producing and maintaining critical tables has changed tremendously over the years. Up to about 1935, it was possible for dedicated scientists to do this as extracurricular work, in spare time, in evenings and on weekends. Then came a period of nearly three decades which saw the development of a number of different projects in different institutions engaged in producing critical tables of data in particular areas. Several years ago, it became evident that some co-ordination and over-all guidance and encouragement was needed for this work to proceed properly. This resulted in the establishment in the United States of the Office of Critical Tables of the National Research Council, which would not engage in any actual compilation work as such, but would do the following: (*i*) survey the needs of science and industry for critical tables; (*ii*) stimulate, encourage, and co-ordinate existing data-compiling projects; (*iii*) assist in establishing new data-compiling projects; (*iv*) promote uniform editorial policy and procedures and standards of high quality; (*v*) provide a continuing central indexing and directory service covering all appropriate tables.

The next stage which we are about to enter envisions the greater centralization of the data-compiling projects at the National Bureau of Standards with much larger resources to be made available by our government through the United States Department of Commerce to back up the enterprise, both with respect to existing projects, but also with respect to new projects which may be established at the National Bureau of Standards and elsewhere.

As the National Bureau of Standards proceeds on this work, the Office of Critical Tables of the National Research Council will serve to bring about

co-ordination with other organizations in the United States and to establish appropriate communication and co-ordination with data-compiling projects in other countries.

It is my feeling that we are finally on the verge of an enterprise which will begin to provide the kind of critical tables of thermodynamic data that are needed by scientists in today's world.

FUTURE DEVELOPMENTS

It is not difficult to extrapolate from the present-day trends in investigations in thermodynamics and thermochemistry to future developments: much more experimental data is becoming available on non-reacting mixtures of molecules and will lead to the information needed on intermolecular energies and forces and to further knowledge about molecules; many more investigators are working at high temperatures to learn what molecular systems are stable there; many more investigations at very high pressures are including the evaluation of thermodynamic properties as a function of pressure.

The author predicts also a renewed interest in the thermodynamics of systems in electrical fields, in magnetic fields, and in gravitational fields.

The great improvements in analytical thermochemistry will make it possible to reduce markedly the uncertainty of values from thermodynamic investigations, since the chemistry of the reaction or process may be more fully described and more accurately measured. The uncertainty in most thermodynamic investigations is limited by the chemistry of the process or reaction, not by the physics of it as previously said.

While many interesting and wonderful developments in thermodynamics and thermochemistry have been seen in our day, the new developments to come in the future will be surely outstanding and remarkable, far beyond anything that can be visualized today. These advances will be generated in the minds of scientists and in the minds of the young people who are being educated in schools today.

In conclusion the author expresses the wish that all of the laboratories in thermodynamics and thermochemistry will prosper with many fruitful investigations, and that, in particular, the Thermochemical Laboratory at the University of Lund will assume its now rightful place as the leading laboratory in this field in all of Scandinavia, taking over the position once held by Thomsen's Laboratory in Copenhagen.