

INTRODUCTION TO

CHEMICAL THERMODYNAMICS



REUBEN E. WOOD

Introduction to Chemical Thermodynamics

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THE GEORGE WASHINGTON UNIVERSITY



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Introduction to Chemical Thermodynamics

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Preface

Not the least difficult of the decisions I made in writing this book was the decision to use the word *Introduction* in the title. There was, of course, no doubt that the book would not be a comprehensive treatment of chemical thermodynamics. It was intended from the start to be a rather short textbook for use in a one-semester, upper undergraduate, or first-year graduate course of study. The problem is that most if not all of the readers of this book will have been already introduced to a number of aspects of chemical thermodynamics.

I have tried here to set forth the foundations of thermodynamics and to show how a number of principles, especially those useful in chemistry, can be built on these foundations. In some fields, admittedly somewhat arbitrarily selected, I have gone to considerable lengths in developing what approaches the fine structure of the field. This has been done on the premise that even though these detailed developments are only samples of a myriad of such specialized treatments, they do give the flavor of chemical thermodynamics and, hopefully, promote some mental agility that the student can transfer to other problems. It is in the sense of the above purposes that the book is called an introduction.

Because of the differing backgrounds of students in a first course in chemical thermodynamics, one can hope only to minimize the amount of material included in a textbook which is either too elementary for the ablest and most advanced students or which may seem unduly difficult for the least apt or least advanced students. Perhaps this problem is one of the chief reasons that live teachers are still standard equipment in the classroom. I have made an attempt to deal with this problem by literature citations. Perhaps all of the references given as footnotes fall into one of the three categories: (1) those given just properly to credit the source, (2) those given for the benefit of the student who may need help in an area (mathematical, for example) in which most of the students are already competent, and (3) those given for the benefit of the student who is interested to investigate a subject more extensively than it is treated in this book.

Probably teachers of chemical thermodynamics would agree almost unanimously that few students get a working grasp of the subject without solving a number of problems. In this book problems have been integrated into the text, a procedure that I first met in *Chemical Principles* by Noyes and Sherrill (Macmillan, 1938). Some additional problems are given at the ends of most chapters.

Nomenclature and notation are always problems. I have taken a permissive attitude. Although I have not ignored such recommendations as those of the International Union of Pure and Applied Chemistry, I have intentionally avoided complete uniformity. The student will undoubtedly use the chemical literature and will probably also consult other textbooks. It seems advantageous, therefore, that he should develop some familiarity with commonly-used variants. So, for example, I have used more or less interchangeably the symbols μ and \bar{G} to represent the chemical potential, and have tried to make it clear that the same property is commonly called by the various names: Gibbs energy, free energy, Gibbs free energy. One can only guess how far it is wise to go with this. What would be best for one student would probably not be best for another. I have, for example, not used the term free enthalpy which is a perfectly respectable one.

If this book is dedicated at all and if credit is given to those who have helped the author in learning thermodynamics or in the scientific aspects of writing this book, these things will be done in the second edition. Without implicating them in any responsibility for the treatments made, however, three people who gave me much help in preparing the typed manuscript can be mentioned with my thanks. This I do. They are Ava Fowler, Donna Allan, and Suzanne Froman.

R. E. W.

Introduction to Chemical Thermodynamics

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I

The First Law

ENERGY

Writing on pragmatism William James¹ said,

Metaphysics has usually followed a very primitive kind of quest. You know how men have always hankered after magic, and you know what a great part in magic *words* have always played. If you have his name or the formula of incantation that binds him, you can control the spirit, genie, afrit, or whatever the power may be. Solomon knew the names of all the spirits, and having their names, he held them subject to his will. So the universe has always appeared to the natural mind as a kind of enigma, of which the key must be sought in the shape of some illuminating or power-bringing word or name. That word means the universe's *principle*, and to possess it is after a fashion to possess the universe itself. "God," "Matter," "Reason," "the Absolute," "Energy," are so many solving names. You can rest when you have them. You are at the end of your metaphysical quest.

But if you follow the pragmatic method you cannot look on any such word as closing your quest. You must bring out of each word its practical cash-value, set it at work within the stream of your experience. It appears less as a solution, then, than as a programme for more work and more particularly as an indication of the ways in which existing realities may be *changed*.

Theories thus become instruments, not answers to enigmas in which we can rest.

Energy and its transformations is the grist of thermodynamics. But at the outset, energy is just a word, a name. A proper start in the study of thermodynamics is to identify this name and make of it an instrument.

¹ *Pragmatism*, 1907 p. 43 (Longmans, Green and Co., Inc., New York.)
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That it is a generic name is obvious from expressions such as kinetic energy, thermal energy, electrical energy, and others. Each of these expressions refers to quantities which can be defined and measured in terms of basic parameters. For example, translational kinetic energy is defined by the equation

$$E_{\text{Trans}} = \frac{mv^2}{2} \quad (1-1)$$

The electrical energy of a capacitor of capacitance C charged to a potential ε is

$$E_{\text{Stat}} = \frac{C\varepsilon^2}{2} \quad (1-2)$$

Gravitational energy:

$$E_{\text{Grav}} = mgh \quad (1-3)$$

The electrical energy corresponding to a current I flowing through a resistance R for the time t is

$$E_{\text{Current}} = I^2 R t \quad (1-4)$$

For the motion of a body through a distance dx against a force f

$$dE_{\text{Mech}} = f dx \quad (1-5)$$

The thermal energy corresponding to a temperature change from T_1 to T_2 of a body whose average heat capacity during the heating is C_P is

$$E_{\text{Therm}} = C_P(T_2 - T_1) \quad (1-6)$$

One may well ask, then, what do all these E 's have in common; why are they all called energy? An incomplete answer is that there exist interconvertibility relationships, that E_{Current} , for example, can be transformed into E_{Therm} . But a qualitative interconvertibility is an inadequate discriminator. Momentum is equal to mv . Any body which has a momentum has a nonzero value of E_{Trans} and is capable of producing heat. But momentum is not energy. The criterion is not interconvertibility but a kind of quantitative interconvertibility. Having said this, we have not quite stated but have come close to stating the First Law. In fact, the equation which is called the First Law equation is primarily a definition of energy in terms of measurable components, namely heat and the other particular kinds of energy such as those mentioned above.

James Joule, in a series of experiments carried out during the 1840's established the quantitative relationship between electrical and mechanical energy and the heating effects that these energies could produce. His experiments showed, for example, that when the temperature of a calorimeter (thermally insulated from everything except the heating coil) was made to rise by a passage of an electric current I through a heating coil of resistance R for a time t , the temperature rise from a constant starting temperature would be identical for all experiments in which the value of $I^2 R t$ was the same even though the values of I and R and t were varied. Likewise, it could be shown

that when a moving body of mass m and velocity v was brought to rest by impact or friction in the calorimeter, the temperature rise would be the same for all cases in which the quantity mv^2 had the same value, regardless of variations in the parameters m and v . Moreover, in the case of the electrical heating of an uncomplicated system such as a pail of water it would be found that over small ranges of temperature the temperature rise would be directly proportional to the value of I^2Rt . Thus, a proportionality^{2,3} has been shown among I^2Rt , mv^2 and $C_P(T_2 - T_1)$. One is justified, then, to consider these three expressions as different species of the same genus, and the name of the genus energy.

By similar experiments or by logical derivations, other members of the genus could be identified, the pretenders such as the momentum mv could be excluded. Moreover, by establishing a consistent set of units and by doing something about the fact that a given value of I^2Rt will produce different values of $T_2 - T_1$ in a small pail of water and in a large drum of kerosene, i.e., introducing the heat capacity parameter, we can develop expressions for these different manifestations of energy which can be summed to get the total energy change involved in a given experiment.

Before concluding the discussion of the equivalence (which we find to be limited by the Second Law) and additivity of the various forms of energy, two other ideas should be considered. These are the *system* and the *increment*.

The importance in thermodynamic derivations of distinguishing one or more *systems* from the *surroundings* can hardly be overstated. One chooses as a system something of particular interest. The system might be a mole of carbon dioxide—or it might be a steam engine. The surroundings are everything outside of the system or systems; but consideration has to be given only to those parts of the surroundings which interact in some way with the system(s).

Most commonly one deals with closed systems, which are those across whose boundaries matter is not allowed to pass. Less commonly but not infrequently one works with open systems. These can undergo gains or losses of substance. The reason that it is important to specify precisely, even though perhaps quite arbitrarily, the boundary of each system is that one of the most basic and fruitful operations of thermodynamics is the account-keeping of what kind of and how much energy—and in the case of open systems, matter—crosses this boundary during any process which occurs.

² Nothing in the proposed experiments would tell us that kinetic energy should be written $mv^2/2$ instead of mv^2 . The expression $mv^2/2$ comes from Newton's equation $f = ma$ together with the reasonable but nonetheless arbitrary convention that $dw = f dx$ and not $2f dx$.

³ At this point C_P may be considered just a property of the system. It will in general vary with the size and composition of the system and, indeed, with the temperature interval. But for a specified system undergoing changes within a specified small temperature interval, it will be a constant.

The bookkeeping is simple. There is a distinction, however, that should be explained. There are many things about systems that can be measured. Their pressures, volumes, temperatures, indexes of refraction, heat capacities, and other characteristics can be measured. Such things are the *properties* of a system. The *state* of a system is described by giving the values of its various properties. However, since these are interrelated, only a few of the properties of a system have to be specified in order to identify uniquely its state. For example, under ordinary conditions a mole of carbon dioxide at 25 °C having a dielectric constant of 1.00700⁴ can have only one particular value of each of its other properties including pressure and volume.

PROBLEM 1-1 Both the pressure and the dielectric constant of a gas are functions of temperature and volume. Should the pressure be considered a more fundamental property than the dielectric constant, or should it not? Why? What is the significance of the implied *caveat* “under ordinary conditions” in the statement that “under ordinary conditions a mole of carbon dioxide at 25 °C having a dielectric constant of 1.00700 can have only one particular value of each of its other properties including pressure and volume”? Could an electric or magnetic field affect the properties of the gas?



When a system undergoes a *change in state*,⁵ most of its properties change. The amount by which each property increases is called the increment in the property. If the change is finite, the increment is indicated by Δ . Thus, for example, $T_2 - T_1 = \Delta T$. If the change is infinitesimal, the usual calculus notation, for example dT , is used.

The distinction mentioned above is that between *properties* on the one hand and the quantities heat q and work w on the other. One cannot measure the heat of a system or the work of a system. Heat and work are transients and have significance only during processes. They are the amounts of energy which enter the system across its boundary in a particular form during a particular process.⁶ If the same change in state (transition from the same initial to the same final state) were to occur by a different process, the values of q and w could be quite different. An illustration of this fact, which we explore more fully later, is a comparison of two different processes of

⁴ Referred to some particular frequency.

⁵ This is a very general term meaning any change; it includes but is not limited to phase changes.

⁶ A partial analogy would be this: A system consists of a solution of sulfur in carbon disulfide. It was made up by adding A grams of rhombic sulfur and B grams of monoclinic sulfur to C grams of carbon disulfide. It is quite correct to say that A grams of rhombic sulfur *went into* the solution and that B grams of monoclinic sulfur *went into* it. But it is meaningless to say that the solution *contains* a certain number of grams of one form and certain number of grams of the other form. In the solution only the total quantity of sulfur can be specified. What form or how much of each form will crystallize out will depend upon the process or processes to which the solution is subjected.

doubling the volume of a gas at constant temperature. One process is to let the gas expand into a vacuum. In this case q is zero or nearly so. If the gas expands against an opposing pressure, q will not be zero or nearly zero.

The contrast, then, is this. Every time the same change in state occurs (as defined by specified initial and final values of a minimum number of properties) every *property* will have the same increment that it had every other time that change occurred even though the change may be carried out one time by one process and other times by different ones. But this is not in general true of *heat* and *work*; except in restricted cases such as we consider in the sections dealing with thermochemistry, there is no nonvariant relation between the initial and final states of a system and the values of q and w which pertain to the process of accomplishing the change from initial to final states. The *heat* and *work* depend on the *process* as well as on the *change in state*. The increments in *properties* depend only on the change in state and must be the same for all conceivable processes of carrying out the same change in state.

The language of mathematics is elegant—and to many, unexplanatory. Increments in properties such as dP , dV , etc. are exact differentials; dq and dw are not. The preceding sentence summarizes a number of the foregoing paragraphs. An equivalent summary is to say that pressure, volume, and others are properties whereas heat and work are not properties of systems.

We can now write a quantitative definition of the amount of energy put into a system. We anticipate our succeeding equations and use ΔE as the symbol for the total amount of energy put into a system during a particular change. The defining equation is

$$\Delta E \equiv q + w \quad (1-7)$$

where q is the amount of heat and w the total of all forms of work which enter the system from, or are done on the system by the surroundings.

At this point, in preparation for subsequent examination and use of 1-7, we recapitulate our basis for measurements and evaluations of q and w . Essentially, we start with some particular kind and scale of energy. Probably the classical starting point is the work associated with motion against a force

$$dE_{\text{Mech}} = f dx \quad (1-5)$$

and a useful secondary measuring stick is the electric energy associated with current flow through a resistance

$$dE_{\text{Current}} = I^2 R t \quad (1-4)$$

Then by definition and comparison we evaluate other forms of energy. The quantitative definition and measurement of heat energy illustrates this method. First, one thermally insulates a system from its surroundings and causes it to undergo some change by the introduction of a known amount of energy—the passage of a measured current for a measured time through a coil of

known resistance, for example. Then, after restoring the system to its initial state, the thermal insulation (adiabatic separator) is removed and the system is made to undergo the same change by thermal interaction with the surroundings—by heating with a flame, for example. The definition is, then, that the heat put into the system by the flame is the energy equivalent of the electric work required to produce the same effect in the experiment (adiabatic) in which the system was thermally isolated.

Figure 1-1 represents schematically the kinds of experiments that led to acceptance of the First Law. A system undergoes a change in state from state 1 to state 2. Equation 1-7 together with measurements of q and w

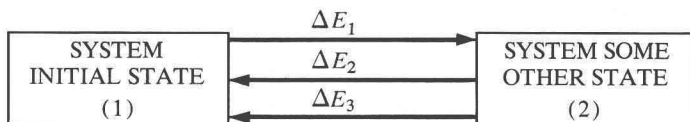


FIGURE 1-1

is used to evaluate ΔE_1 . Several different processes are now devised for accomplishing the reverse change in state. The ΔE 's for the reverse change are evaluated. The findings are, within the limits of experimental accuracy, (1) that ΔE_2 and ΔE_3 have identical values and (2) that the sums $\Delta E_1 + \Delta E_2$ and $\Delta E_1 + \Delta E_3$ are zero. This result has been found in every case in which such experiments have been done. The First Law of thermodynamics is the extremely useful hypothesis that such results will always be found and that the relationships represent an unqualified natural law.

It is the *unqualified* validity of the defining identity 1-7 for all closed systems together with the assertion that

$$\Delta E = E_{\text{final state}} - E_{\text{initial state}} \quad (1-8)^7$$

that is, that ΔE is dependent only on initial and final states, not on the process of transition, that permits us to view the First Law equation as:

$$\Delta E = q + w \quad (1-9)$$

Or we may write the First Law for the infinitesimal process

$$dE = dq + dw \quad (1-10)$$

in which the symbol dE represents an exact differential.

From the foregoing, it is clear that for an isolated system, since q and w are zero, ΔE must always be zero. One of the common verbal

⁷ Ordinarily one is concerned only with energy differences, and if values are assigned to the energy of a system in a particular state the values are with reference to an arbitrary zero level. These facts do not, however, invalidate the concept of energy as a property.

expressions of the First Law is that the energy of an isolated system remains constant.

Thermodynamics is founded on a few basic articles of faith, and the First Law is one of these. The meaning of that statement and the usefulness of that faith are illustrated in the discovery of the neutrino. Writing in *Nature*⁸ three years after they had first detected a free neutrino⁹ and twenty-three years after Wolfgang Pauli¹⁰ had first proposed the existence of the particle, Frederick Reines and Clyde Cowan introduce their paper with the following paragraph.

Each new discovery of natural science broadens our knowledge and deepens our understanding of the physical universe, but at times these raise new and even more fundamental questions than those which they answer. Such was the case with the discovery and investigation of the radioactive process termed 'beta decay.' In this process an atomic nucleus spontaneously emits either a negative or a positive electron, and in so doing it becomes a different element with the same mass number but with a nuclear charge different from that of the parent element by one electronic charge. As might be expected, intensive investigation of this interesting alchemy of nature has shed much light on problems concerning the atomic nucleus. A new question arose at the beginning, however, when it was found that accompanying beta decay, there was an unaccountable loss of energy from the decaying nucleus, and that one could do nothing to the apparatus in which the decay occurred to trap this lost energy. One possible explanation was that conservation laws (upon which the entire structure of modern science is built) were not valid when applied to regions of subatomic dimensions. Another novel explanation, but one which would maintain the integrity of the conservation laws, was a proposal by Wolfgang Pauli in 1933 which hypothesized a new and fundamental particle to account for the loss of energy from the nucleus. This particle would be emitted by the nucleus simultaneously with the electron, would carry with it no electric charge, but would carry the missing energy and momentum—escaping from the laboratory equipment without detection.

Except for tenacious faith in the "conservation laws," Pauli would have had no reason to propose the existence of his ghostly particle and Fermi¹¹ and Reines and Cowan and the others who developed the theory and experiments which ultimately led to the experimental proof of the existence of the neutrino would have had little reason to take the proposal seriously.

Of course, some of our surest and most useful science was at one time heresy to the tenets of the savants. But it seems most unlikely that one will successfully challenge such a reliable¹² science as thermodynamics—certainly, at least, until one has learned its precepts and lived by its discipline.

⁸ Frederick Reines and Clyde L. Cowan, Jr. *Nature*, **178**, 446 (1956).

⁹ F. Reines and C. L. Cowan, Jr., *Phys. Rev.*, **92**, 830 (1956).

¹⁰ W. Pauli in *Rapports du Septiem Conseil de Physique Solvay*, Brussels, 1933 Gautier-Villars, Paris (1934).

¹¹ E. Fermi, *Z. Physik* **88**, 161 (1934).

¹² See "Thermodynamics in Einstein's Thought" by M. J. Klein, *Science*, **157**, 509 (1967).