Modern Chemistry for the Engineer and Scientist

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Preface

Following the pattern of similar programs in physics and mathematics during the period 1952–1954, an extension course bearing the same title as this volume was given during the academic year 1954–1955 under the auspices of the Colleges of Engineering and the Departments of Chemistry of the University of California. Nineteen nationally known chemists, both academic and industrial, were invited, and each of these presented his initial lecture on the Los Angeles campus. Additional presentations were given at Corona, at the Naval Ordnance Test Station (China Lake), and at Berkeley, to accommodate the substantial number of professional workers at the more distant points. An essential feature of the plan required that each of the lecturers be a recognized research scholar, widely known as a contributor in his field. The lectures are published herewith in slightly abridged form.

Nominally these lectures were aimed at the graduate in physical science—perhaps a decade or more beyond his college graduation—for the purpose of bringing him up to date in a series of special chosen fields in chemistry. One may well concede that some of these chapters are sighted at a level somewhat above many of the auditors, whose formal education in chemistry did not go beyond conventional college courses in analysis, synthesis, etc. The editor has never been seriously concerned, however, over the predicament of a scientist or engineer listening to scholarly exposition a bit over his head. For example, there is no harm done when the industrious freshman listens to the Nobel laureate who has been invited to address the department seminar meeting on his special topic.

No attempt has been made to follow chronological order of the lecture schedule. Instead, the present work begins with fundamental principles of physical chemistry, gradually extended with industrial examples. Eventually the application of chemistry to life is treated, and this phase in one sense may be regarded as the highest development of the science.

Thanks of participants in the enterprise are offered to J. C. Dillon and Clifford Bell for their services in the management of the lecture series

and to Dean L. M. K. Boelter of the College of Engineering, Los Angeles, prime spark plug of the project. Gratitude is also expressed to Prof. Francis E. Blacet and the committee of chemists and engineers who gave critical consideration to the selection of the panel of lecturers. Last but not least do our thanks go to the lecturers themselves, for whom the project was a very great extra burden on top of an already busy professional life.

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1.1 Introduction

Although thermodynamics originally was just a theory of the maximum efficiency of a steam engine or a similar sort of heat engine, it has developed broad ramifications of great importance to chemistry. The most basic type of problem in chemistry is the production of a desired substance from readily available materials. Occasionally the optimum process can be predicted from thermodynamic considerations alone. More commonly, thermodynamics yields an outline of the reactions which are possible and a list of those that are impossible. Rates of reaction must be studied separately, and various possible catalysts must be tested. However, it is of immense value to know in advance the maximum possible yield of product, just as the engineer knows the maximum efficiency of a perfect heat engine working at a particular set of temperatures.

The presentation to follow will be in two general divisions. First, the basic principles and methods of thermodynamics will be reviewed, with emphasis on modern aspects which involve statistical probabilities. Second, there will be given a few examples of recent applications.

Space will not allow detailed discussions of engineering applications, but it will be apparent that the entropy and heat-content data are quite as appropriate for engineering design purposes as for the chemical equilibrium calculations.

PART I

1.2 Thermodynamics and Probability

The principle of conservation of energy, also called the first law of thermodynamics, is one of the most all-pervading principles of physical

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science.   Not only does it appear as one of the basic principles of classical Newtonian mechanics but it holds also in quantum mechanics and in relativity.   However, from the chemical viewpoint we must be sure to recognize the internal or latent energy stored within substances.   For many years scientists could only regard this energy as stored in a more or less mysterious fashion within the substance, but now we are in a position to give a detailed account of latent energy in terms of the motion of the atoms and of the forces operating between them.

The idea of the conservation of energy seemed intrinsically reasonable and was immediately accepted by the scientific world.   In its initial form, however, the second law seemed much less reasonable, as well as much more abstruse.   Thus it is not obvious why only a portion of the heat passing from the firebox into a steam boiler can be converted into mechanical work and why the remaining portion must pass as heat into the condenser water.   Initially, the second law was proved mainly by the failure of various efforts to disprove it.   Here it is particularly enlightening to examine phenomena in terms of the behavior of individual atoms and molecules, because in those terms the second law becomes merely the manifestation of probability.

If one tosses 100 pennies into the air, it is possible but very unlikely that all of them land heads up.   The probability is $(1/2)^{100}$, or approximately 1 chance in 1,000,000,000,000,000,000,000,000,000,000 or 10^{30}. The increase of the sample to merely 200 pennies decreases the chance of all heads to the square of the figure for 100 pennies, or to 1 in 10^{60}. Thus, as the numbers of particles become large, the results predicted by arguments of statistical probability become exceedingly accurate and reliable.   Thus also, the second law of thermodynamics reduces to the axiomatic statement that systems change spontaneously in the direction of increasing probability.

While the idea of applying probability to molecular behavior seems most reasonable and it is clear that this should have some relevance to the direction of chemical reactions, the relation to energy effects and to temperature needs further explanation.   Let us consider some gas in a cylinder, as in Fig. 1.1.   We may assume that this is a perfect gas, i.e., the molecules have negligible size and interact only in moments of collision.   Now it is clear that, if we open the valve in the bypass pipe, some of the molecules will flow around to the lower side of the piston until the concentration of molecules is uniform.   Here probability principles give the direction of a spontaneous process, but no mechanical work or other energy effects are involved.

Now suppose instead that the piston is allowed to move downward in the cylinder depicted in Fig. 1.1.   Thus mechanical work can be extracted from this system, and it will be found that the gas will cool off or else it

will absorb heat from the surroundings.   When the process is studied in sufficient detail, it is found that the available work for a constant-temperature process is given by the formula

$$w = kT \ln \left(\frac{V_2}{V_1}\right)^n = nkT \ln \frac{V_2}{V_1}$$

Here T is the absolute temperature; k is the Boltzmann constant, i.e., the gas constant on a molecular basis; and n is the number of molecules of gas present.   Also, V_1 is the initial volume above the piston, and V_2 is the final total volume after the piston has moved down.   The amount of heat absorbed from the surroundings is numerically equal to the mechanical work done in this process.

Here we have a process in which the internal energy of the substance does not change, and as a result the source of the work is purely the increase in statistical probability. We also note that the magnitude of the work available appears to be related to the thermal kinetic energy of the molecules.   Thermodynamicists discussed processes of this sort long before there were sound molecular models for them, and even today we wish to consider cases where we do not know all details

Fig. 1.1

about all the molecules present.   Consequently the quantity known as entropy was defined and is still of the greatest importance and usefulness. We shall best understand entropy if we realize that it is just a convenient measure of statistical probability.   The statistical definition of the entropy change in a process is

$$\Delta S = k \ln \frac{W_2}{W_1}$$

where W_2 and W_1 are the probabilities of the final and initial state, respectively.   In the case above, the probability of finding a given molecule in a portion of a space filled with gas is proportional to the volume selected.   Thus the probability of finding a molecule in the original volume after the piston has moved down is V_1/V_2.   The over-all probability of the original state compared with the final state is then $(V_1/V_2)^n$ for n
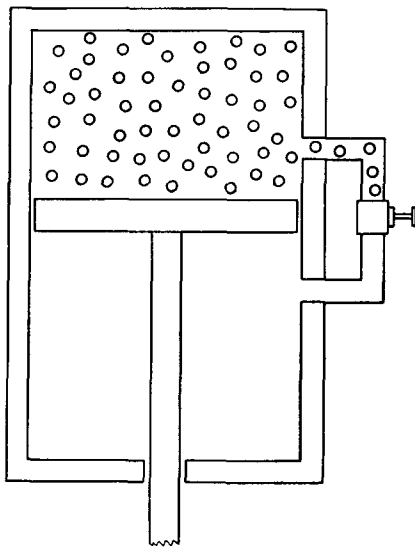
molecules, and the reciprocal of that quantity is introduced into the entropy equation, yielding

$$\Delta S = k \ln \left(\frac{V_2}{V_1}\right)^n = nk \ln \frac{V_2}{V_1}$$

The classical thermodynamic definition of the entropy change is the heat absorbed in a reversible process divided by the absolute temperature; thus,

$$\Delta S = \frac{q_r}{T} = nk \ln \frac{V_2}{V_1}$$

which is identical to the statistical result.

The equations given above relate to the entropy content of the substance itself—in this case, the gas in the cylinder. Actually the heat absorbed by the gas is furnished by some material surrounding the cylinder, and this material loses an amount of entropy equal to that gained by the gas itself in accordance with the formula given. We may now translate the second law in terms of entropy as follows: The total entropy change of the system and its surroundings increases in spontaneous processes and is zero for reversible process. We hasten to add that this is still a matter of probability and that exceptions may be expected unless the number of particles is exceedingly large.

1.3   The Third Law of Thermodynamics

The chemist who is interested in a process to produce some particular substance will want to know the entropy content of that substance. By classical methods he could measure this quantity only by finding some reversible reaction which yielded the substance. Then by measuring the heat absorbed in the reaction, he could calculate the entropy change. However, by the time the chemist had discovered a reversible reaction yielding the substance, he had partially solved his primary problem also, that of a practical production process. The knowledge of the precise thermodynamic properties involved in the reaction would be valuable in finding the optimum temperature, pressure, and other process conditions, but it would have been even more valuable to have had the thermodynamic data before the exploratory work on reactions was undertaken. During the last few decades two methods have been developed for measuring the entropy of a substance without the use of a reversible chemical reaction yielding the substance. Both methods depend on the concept of an absolute unit of statistical probability and therefore an absolute entropy. One method depends further on detailed data about the structure of the molecules and proceeds through statistical calculations. The

other method makes use of thermal measurements over the entire temperature range from near the absolute zero to the temperature of interest. Most of the entropy values for chemical substances now available come from one or the other of these methods.

To understand the third law of thermodynamics, with its ideas of absolute entropy and probability, one must consider the existence of quantum states. The sharp discrete lines in the atomic spectrum of hydrogen or sodium are interpreted to indicate that the atoms can exist only in discrete quantum states, or energy levels. By looking in the appropriate spectral region, one finds similar discrete spectra for virtually all atomic or molecular entities. Thus in the far infrared one finds a long series of sharp lines associated with the energy of rotation of the water-vapor molecules. Theory indicates that even the translational kinetic energy of molecules is quantized, although in that case the energy separating adjacent levels is exceedingly small.

One makes the simple and straightforward assumption that the probability of any one quantum state is the same as any other. Then we need only count the total number of quantum states in which a system might be in order to calculate its entropy. In this sense, entropy is a measure of our ignorance. The information that we have a gram of hydrogen gas at 0°C and 1 atm pressure is not sufficient to specify the quantum state for each molecule. The entropy is a measure of the number of combinations of molecular quantum states which are consistent with the specified temperature and pressure.

The third law of thermodynamics asserts that an absolute zero of entropy exists, and we now see that this will arise if the substance is entirely in a single quantum state. The relation between entropy and probability is

$$S = k \ln W$$

Hence, if W is unity, S will be zero. We now have the basis, in principle, for the two methods of determining the entropy of a substance. If we can calculate W by statistics, we may find the entropy. We shall return to the statistical method presently. We consider first the method based on thermal measurements over the temperature range from the absolute zero to the temperature of interest.

In almost all cases, a molecule has a single lowest-energy quantum state. Thus, if one could cool the substance sufficiently, each molecule would lose energy until it was in this lowest state. With every molecule in the same single quantum state, the entropy of the substance would be zero. Then one could measure the entropy increase on warming the substance by measuring the heat absorbed over each small temperature

increment.   The entropy is given by the integral

$$S_{T_2} = \int_0^{T_2} \frac{dq_r}{T}$$

where dq_r is the increment of heat absorbed reversibly at the absolute temperature T.   Usually the heat is introduced electrically in small increments, and the temperature is measured between each.

In practice it is not possible to reach the absolute zero of temperature, but it is usually possible to predict the behavior in the first few degrees if one has measurements over the entire remaining temperature range. Except at points of transition, fusion, or vaporization where isothermal absorption of heat occurs, one may write $dq_r = C \, dT$ and

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} C \, d \ln T$$

where C is the heat capacity (or specific heat).   A typical entropy calculation [14][1] by this method is given in Table 1.1.

Table 1.1   Entropy of Propane

0–15°K.	Extrapolation	0.25
15–85.45°K.	$\int C \, d \ln T$	9.702
Fusion	(842.2/85.45)	9.856
85.45–231.04	$\int C \, d \ln T$	21.063
Vaporization.	(4,487/231.04)	19.421
Entropy of real gas at boiling point.	. . . .	60.29
Correction for gas imperfection.	. . . .	0.16
Entropy of ideal gas at 1 atm and 231.04°K.	. . . .	60.45

This experimental method of entropy determination is as equally applicable to substances which are solid or liquid at the temperature of interest as it is to gases.   One must be sure, however, that the substance is in an ordered crystalline state at the lowest temperature of measurement so that one may calculate the entropy at that point.   This requirement excludes glasses, solid solutions, and certain unusual types of disordered crystals.

1.4   Molecular Statistics

We now return to the statistical method of calculation of entropy. To apply this method, it is necessary to have a complete catalogue of all the quantum states, or energy levels, for the molecule.   A complex theory is also required to predict the population of each energy level.

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[1] Numbers in brackets refer to the numbered list of references at the end of the chapter.

It is beyond the scope of this discussion to present these theories in detail; for that purpose the reader must look elsewhere [7, 11, 21]. Nevertheless we shall attempt to outline the nature of the theory and a few results.

Let us first suppose that we have just three diatomic molecules and confine our attention to the vibrational motion of the atoms toward and away from one another. Quantum theory gives an even spacing of energy levels for this vibration, and this is confirmed by experimental spectroscopy. Actually this result is only a first approximation but the refinements need not concern us. The energy interval between levels will be designated u. Thus any one molecule may have vibrational energy of 0, u, $2u$, $3u$, $4u$, etc. Suppose that our three molecules have exactly $3u$ of total vibrational energy. In the course of collisions, this energy may be transferred back and forth between the molecules. Consequently at one moment one molecule may have all $3u$ of this energy while a little later it may be distributed equally among all three molecules, i.e., energy u in each molecule. A third possible distribution is for one molecule to have $2u$, one to have u, and a third to have 0 vibrational energy.

We now set out the number of arrangements of three molecules a, b, c among these various energy levels in a diagram as follows:

Energy level:

$3u$	...	c	b	a	...	...	...	...	...	...	(3)
$2u$	...	...	...	...	c	b	c	a	b	a	(6)
u	abc	...	...	...	b	c	a	c	a	b	(9)
0	...	ab	ac	bc	a	a	b	b	c	c	(12)

First we note that there are 10 arrangements, and as a result the value of W is 10. Since any one of these 10 arrangements is just as probable as any other, we may expect each to occur one-tenth of the time. The relative population of each energy level may then be calculated from the total number of letters in that row which yields the values in the last column.

Actually, we are concerned with a much larger number of molecules than three. When the appropriate mathematical methods are applied, it is found that the relative population of a single quantum state of energy ϵ_i is given by the Boltzmann expression

$$n_i = (\text{const})e^{-\epsilon_i/kT}$$

where k is again the Boltzmann constant and T is the absolute temperature. The constant of proportionality is determined by the requirement

that all molecules must be accounted for, i.e., that the sum of all n_i's must equal the total number of molecules in the system.

In Table 1.2 we compare the relative population of various energy levels for the system of three molecules with that for a system of a large number of molecules of the same type and with the same average energy.

Table 1.2   Distributions of Molecules among Energy Levels

Energy level	3 molecules, per cent	Many molecules, per cent
$5u$	. . .	1.6
$4u$	. . .	3.1
$3u$	10	6.2
$2u$	20	12.5
u	30	25
0	40	50

The same methods that yield the Boltzmann factor for the population of an energy level give a formula for the total number of vibrational quantum states, W, in a system of many molecules. If x is the ratio of the energy-level spacing to kT (that is, $x = u/kT$), then the entropy contribution of this vibration for a mole of gas is

$$S_{\text{vib}} = R\left[\frac{x}{e^x - 1} - \ln\left(1 - e^{-x}\right)\right]$$

where R is the gas constant.

The complete calculations for a molecule must consider the translational motion and the rotational motion as well as the vibrational motion. These equations were developed by various authors and successfully applied first by Giauque [10] to such substances as hydrogen and the hydrogen halides.

Polyatomic molecules differ from diatomic molecules in that there are several different modes of vibrational motion. Also, in some cases there are other types of motion, such as rotation of one part of a molecule with respect to the remainder. The author has published a series of papers [22] on the application of these statistical methods to molecules with such internal rotational motions. These methods were needed for most organic molecules. Ring molecules also introduce complicated types of motion in some cases [2, 16].

Fortunately, the nature of these various motions is such that, in good approximation, one may simply sum up the entropy contributions of each motion to give a total for the whole molecule. Table 1.3 gives an example of an entropy calculation for propane [14]. This molecule has

also been studied by low-temperature specific-heat measurements, and the corresponding entropy calculation was given in Table 1.1.

In some cases the data on molecular energy levels cannot be completed from studies of the spectra. In such cases an independent value of the entropy, ordinarily from the low-temperature heat-capacity method, can be used to calculate a single final energy-level parameter. This situation has arisen rather commonly with internal rotational motions. These

Table 1.3   The Entropy of Propane by the Statistical Method
$T = 231.04°K$

Translation...................... 36.02
Rotation (external)............. 20.46
Vibration (25 modes)........... 1.05
Internal rotation............... 2.92
                              ────
                              60.45

motions frequently are inactive in the spectrum. Consequently, the measure of the energy-level spacing for such internal rotation is obtained from the entropy calculations. This was the case for propane as illustrated in Table 1.3. Thus thermodynamic methods have been of great value in determining molecular-structure data.

Much of the work in chemical thermodynamics in recent years has been concerned with entropy determinations by the two methods discussed here. The result is not only an extensive array of entropy values for a wide variety of substances but also a broad and thorough understanding of the quantum states of molecules and of the motions with which they are associated. This general understanding permits us to make quite reliable estimates for new substances, if measured values are available for substances of similar chemical constitution.

1.5   Equilibrium Constants and Electrode Potentials

Usually chemical reactions are carried out under constant-pressure and constant-temperature conditions. Thus one's ultimate objective is the prediction of equilibrium constants for chemical reactions under these conditions. Appropriate thermodynamic arguments show that

$$R \ln K = -\frac{\Delta F}{T} = \Delta S - \frac{\Delta H}{T}$$

where K = usual equilibrium constant
   R = gas constant
   ΔS = change in entropy with reaction
   ΔH = change in heat content (enthalpy) with reaction
The quantity ΔH is actually just the heat absorbed in the reaction. The new function ΔF is defined by this equation and is called the free energy.