

PHYSICAL CHEMISTRY
An Advanced Treatise

VOLUME II / Statistical Mechanics

Edited by
HENRY EYRING

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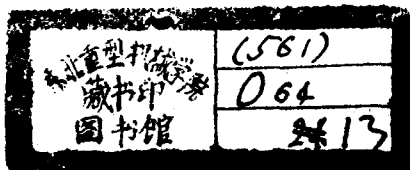
VOLUME II / Statistical Mechanics

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Foreword

In recent years there has been a tremendous expansion in the development of the techniques and principles of physical chemistry. As a result most physical chemists find it difficult to maintain an understanding of the entire field.

The purpose of this treatise is to present a comprehensive treatment of physical chemistry for advanced students and investigators in a reasonably small number of volumes. We have attempted to include all important topics in physical chemistry together with borderline subjects which are of particular interest and importance. The treatment is at an advanced level. However, elementary theory and facts have not been excluded but are presented in a concise form with emphasis on laws which have general importance. No attempt has been made to be encyclopedic. However, the reader should be able to find helpful references to uncommon facts or theories in the index and bibliographies.

Since no single physical chemist could write authoritatively in all the areas of physical chemistry, distinguished investigators have been invited to contribute chapters in the field of their special competence.

If these volumes are even partially successful in meeting these goals we will feel rewarded for our efforts.

We would like to thank the authors for their contributions and to thank the staff of Academic Press for their assistance.

HENRY EYRING
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Preface

Whether a chemist or physicist is concerned with the properties of a system, with an equilibrium constant, or with a reaction rate, the solution of the problem ultimately requires a knowledge of the partition functions of the constituents of the system. To understand such problems, one must know statistical mechanics. It is to meet this need that this book has been written. The authors of chapters are specialists in the phase of the subject they treat. They have each provided references to supplementary material which could not be included in the space available. We hope that what is lost in unity from looking through many eyes is more than compensated for by breadth and depth of coverage.

It is intended that the book be understandable without supplementary reading to graduate students in chemistry and physics, and that, together with the other nine volumes of the treatise, a student can obtain an overview of contemporary physical chemistry. However well we may have succeeded in presenting physical chemistry today, the field will have expanded by tomorrow. It is expected, nonetheless, that in large part what is new will simply add to what we now have rather than replace it. If the material presented here makes physical chemistry more generally accessible, we shall feel well repaid.

HENRY EYRING

December, 1966

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Chapter 1

Classical Statistical Thermodynamics

JOHN E. KILPATRICK

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I. Scope of Discussion

The goal of statistical thermodynamics is to demonstrate that the whole content of classical thermodynamics is a consequence of the laws of mechanics and to actually calculate the classical thermodynamic properties of any particular system from its mechanical specifications. We do not expect to accomplish such a sweeping program in the limited space we have here; in fact, it is not yet possible to carry out such a program complete in every detail. It does appear that eventually this will be done. Some of the difficulties are purely mathematical; some involve ambiguity as to just what some nonmechanical, gross properties of a system mean from a microscopic, detailed viewpoint.

One may assume the laws of mechanics to be either those of classical, Newtonian mechanics (which leads to classical statistical mechanics) or those of quantum mechanics (which leads to quantum statistical mechanics). We shall make the former assumption here; the second will be made in Chapter 2.

In addition one may calculate the properties of a system in a state of equilibrium or of a system in a state of flux. The former is by far the easier to do; the theory and practice are much more nearly complete. We shall confine ourselves strictly to equilibrium systems and to net changes between two states of equilibrium due to a relaxation of constraints. This is the attitude that is usually taken in classical thermodynamics. This division of statistical mechanics is usually called statistical thermodynamics.

Many approaches have been used in developing the theory of statistical mechanics. These approaches may be roughly classified as (1) those which attempt to find the most probable microscopic, detailed state of a system, then calculate the gross, macroscopic properties of interest for this state and finally identify the experimentally observable properties with these most probable values; and (2) those which attempt to find the probability of each macroscopic state, construct an average weighted with these probabilities and then identify the experimentally observable properties with these averages. Sometimes a combination of both techniques is used. Since the sort of probability distribution functions found in real systems are nearly always extremely sharply peaked at one place, i.e., are very nearly Dirac delta functions, there is very little practical difference in the results of the two approaches. In this chapter we shall use the average value approach.

II. Phase Space and Classical Mechanics

The detailed dynamic state of a mechanical system is specified in classical mechanics by giving the values of its n positional coordinates together with the values of the n corresponding conjugate momenta. A system consisting of one point mass molecule requires three positional coordinates, usually chosen to be three cartesian coordinates with respect to any convenient set of axes. A molecule formed from ν point mass atoms requires 3ν positional coordinates. If the molecule is non-linear, these are often chosen to be three center of gravity coordinates, three angular coordinates (such as Eulerian angles) to give its orientation in space and $3\nu-6$ internal or relative coordinates taken in such a way as to completely specify the relative positions of the constituent atoms.

Alternatively, 3ν cartesian coordinates, three for each atom, could be used. A system of N molecules, each formed from ν atoms, would require $3\nu N$ positional coordinates.

The original description of the mechanical system under discussion contains sufficient information to formulate the Lagrangian function for the system. The Lagrangian function, L , is a function of the positional coordinates, q_j , and their velocities or time derivatives, \dot{q}_j , and is equal to the difference between the kinetic energy of the system, $T(\dot{q}_1, \dot{q}_2, \dots, \dot{q}_n, q_1, \dots, q_n)$ and the potential energy, $U(q_1, q_2, \dots, q_n)$:

$$L = T - U. \quad (2.1)$$

In general, we shall be concerned with conservative systems (no dissipative forces) and with potentials which are not velocity dependent.

The momentum conjugate to the positional coordinate q_j is defined by the equation

$$p_j = \frac{\partial L}{\partial \dot{q}_j}. \quad (2.2)$$

In this differentiation, q_j and \dot{q}_j are to be treated as independent variables.

The Hamiltonian function for a conservative system is equal to the sum of the kinetic energy and the potential energy, written as a function of the q 's and p 's. That is to say, Eq. (1.2) must be used to eliminate all the \dot{q}_j from T , replacing them with the corresponding p_j . For example, a system consisting of two independent simple harmonic oscillators with positional coordinates q_1 and q_2 has the Lagrangian

$$L = \frac{1}{2}m_1\dot{q}_1^2 + \frac{1}{2}m_2\dot{q}_2^2 - \frac{1}{2}k_1q_1^2 - \frac{1}{2}k_2q_2^2. \quad (2.3)$$

From this we deduce $p_1 = m_1\dot{q}_1$ and $p_2 = m_2\dot{q}_2$. It follows that the Hamiltonian has the form

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{k_1q_1^2}{2} + \frac{k_2q_2^2}{2}. \quad (2.4)$$

The equations of motion of the system are given in the Lagrangian form by

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_j} - \frac{\partial L}{\partial q_j} = 0 \quad (j = 1, 2, \dots, n) \quad (2.5)$$

This consists of a set of n second-order differential equations. A particular solution of these equations gives the complete time dependence of each positional coordinate.

Alternatively, the equations of motion can be given in the Hamiltonian form

$$\dot{q}_j = \frac{\partial H}{\partial p_j}, \quad \dot{p}_j = -\frac{\partial H}{\partial q_j}, \quad (2.6)$$

a set of $2n$ first-order equations exactly equivalent to Eqs. (2.5).

For the example we considered above, the Lagrangian equations become

$$m_1 \ddot{q}_1 + k_1 q_1 = 0, \quad m_2 \ddot{q}_2 + k_2 q_2 = 0. \quad (2.7)$$

The Hamiltonian equations become

$$\begin{aligned} \dot{q}_1 &= p_1/m_1, & \dot{q}_2 &= p_2/m_2, \\ \dot{p}_1 &= -k_1 q_1, & \dot{p}_2 &= -k_2 q_2. \end{aligned} \quad (2.8)$$

Time differentiation of the first, followed by elimination of \dot{p}_1 with the second, yields Eq. (2.7).

The n positional coordinates and the n conjugate momentum coordinates that specify a particular configuration of our mechanical system can be used as the coordinates of a point in a $2n$ dimensional, orthogonal cartesian set of axes. The space spanned by these axes is called *phase space*. The range of each momentum coordinate is usually minus infinity to plus infinity; each space variable is allowed to cover its natural range in such a way that every distinct spacial configuration correspond to one and only one set of spacial coordinates.

There are two kinds of phase space commonly used. μ space (molecular) has a sufficient number of dimensions to give the configuration of one molecule. The state of a collection of N molecules will be given by N points in μ space. γ space (gas) has enough dimensions so that one point gives the configuration of all N molecules of a collection simultaneously.

Suppose we consider a system with n positional degrees of freedom. This could be one molecule, composed of $n/3$ atoms or it could be a collection of similar or different, interacting or noninteracting molecules or atoms. In any event, at any instant the configuration of the system is given by a point in γ space. The way that this point moves in time is given by the integrals of the equations of motion. If the system is at constant energy, all possible positions of the representative point will lie on a manifold of $n - 1$ dimensions. The equation of this manifold is

$$E = H(q_1, \dots, q_N, p_1, \dots, p_N). \quad (2.9)$$

In the subsequent discussion, we shall refer to the manifold of the whole of a phase space of n dimensions as a "volume" and to the manifold of $n - 1$ dimensions as a surface. Since our system is at constant energy, all of its particular integrals of the equations of motion lie in such surfaces.

III. Ensembles

A system consisting of a collection of molecules requires the specification of six coordinates (three positional and three momentum) for each elementary particule (usually an atom) in the system in order to fix its detailed, microscopic state. Usually we are concerned with the gross, macroscopic state only. To specify the macroscopic state one need only give three thermodynamic variables, if the system consists of only one type of molecule and one more parameter for each additional component. These are often taken to be the number of molecules of each sort, N_j , the internal energy, E , and the volume V . Other choices are possible but this is the only one that has a clear direct relation to the mechanical specifications of the system.

In order to apply statistical and probabilistic procedures to the calculation of gross, over-all or average properties, we need a *population* in the statistical sense. J. Willard Gibbs termed a population, consisting of an infinite collection of (grossly) identical system, each at the same N , E , and V and present in equal numbers for every distinct microscopic state, as a microcanonical or petit ensemble. A system drawn at random from such a population is a microcanonical or petit system.

If thermal contact or energy exchange is allowed between the members of this population, only the average energy of each member is fixed. Such a population is called a canonical ensemble. A canonical system drawn from this population is called a canonical ensemble. A canonical system drawn from this population has effectively been prepared by being in contact with a thermostat at a fixed temperature.

If the samples are not held at a fixed number of molecules but instead free, random flow of molecules between samples is allowed (in addition to thermal flow), we call the population a grand canonical ensemble.

In this chapter we shall take an even broader view, considering all possible types of contact and exchange between systems. It will not matter too much if there appear to be experimental difficulty in preparing some of the more generalized ensembles. Our view is that they are merely mathematical devices or tools used as intermediates in a practical calculation.

IV. Probability

There has been a great deal of discussion among mathematicians as to the proper way to define probability. In the following discussion we shall explain our attitude. The system under consideration will, in general, be able to exist in a wide variety of microscopic or detailed states. In classical mechanics these states usually vary continuously; in quantum mechanics they are more likely to be discrete and denumerable. The external parameters or constraints imposed on the system may drastically reduce the number of accessible states. For example, a particular system might, in general, be found in a state corresponding to any point in its phase space. If it were held at constant energy, only the points in a particular surface of constant energy would be possible. We shall postulate that, given a particular mechanical system, with no further information other than the system's over-all mechanical structure (i.e., the analytic form of its Hamiltonian function), all points in its phase space correspond to equally likely or probable states. That is to say, if we have no information as to the state of a system, including any useful information as to its past history, all states consistent with what we do know must be taken as equally probable. Of course, the real system, at a particular instant, exists in some definite state. We, however, are ignorant of just which one it is. If the system has additional constraints imposed upon it (such as the knowledge that it has a particular, constant energy), all points in its phase space consistent with these constraints are equally probable states while the remaining ones have zero probability.

We are using the term "probability" in the sense of "expectation." Our information about the structure and history of our system gives us no right to feel that were we to investigate and determine the actual state of the system (which would add a great deal of information to our store), one of the possible results of this determination would be more likely to be found than another.

Very often we shall be interested in a particular class of states which have some distinctive property A . It follows that we shall take the probability that our system has property A as the volume of phase space consistent with A out of the whole of the accessible, equally likely, phase space.

This attitude is exactly analogous to the view we take of the state of a die that has been rolled, out of our sight, across the floor. Our information is that the die is fair and unbiased. The die exists in any one of six equally likely states. From our point of view, with our *a priori* information, the probability that the digit "two" shows is $\frac{1}{6}$. It is immaterial that a friend may have peeked and know for sure which digit shows. Similarly, the probability that an even digit shows is $\frac{1}{2}$.

If the die were biased or loaded, unbeknownst to us, this would not affect our expectation as to the result of a roll. However, when after a number of rolls, the actual determination of the state of the die began to appear inconsistent with our expectations, we should probably begin to feel upset and either leave the game or provoke a fight. We should feel cheated in that our information as to the structure of the system appeared to be at variance with the facts. Our probability calculations are always made on an abstract model. We must make sure that our model corresponds to the real physical system that we are really interested in.

These statements must not be confused with predictions as to the results of a finite number of rolls and determinations. It can be shown that if the state A has the probability P and if we make N independent rolls, the fraction of the rolls having the result A is most probably P ; furthermore, as N increases without limit, that this most probable result becomes certainty. In addition, we can calculate the probability of any given deviation away from the most probable result of N rolls.

As an example of a system with continuous states, we could have a sphere, marked with one point on its surface and resting on a smooth plane. The state might be specified by the orientation of the radius vector from the center of the sphere to the special surface point. If the sphere were rolled out on a plane, all information as to its initial state would be quickly lost. All orientations after the sphere comes to rest would be equally probable. The probability that the radius vector would end up with a positive upward component would be exactly one half.

The basis of all probability calculations is the *a priori* assumption that there exists some collection of microscopic states that are equally likely. Very often we immediately collect these equally likely states into sets of varying size, with the members of each set having some special property in common. We then can construct a probability density function of the new parameter which gives the expectation that this parameter (or set of parameters) has a given value. For example, suppose we choose a point in a unit radius disk in a fair, random, unbiased fashion. The measure of the set of points at a distance r from the center is $2\pi r$. The probability that a randomly chosen point will lie at radius r is then proportional to r . The integral of the probability density over all possible values of r (0-1) must be unity, since by the rules of our game, the point must lie in the disk. Therefore,

$$P(r) = 2r \quad (4.1)$$

$$\int_0^1 P(r) dr = 1. \quad (4.2)$$

We see that $P(r) dr$ represents the infinitesimal probability that we shall find the value r within the range dr .

In general, if $P(x)$ is the probability of observing the value of x ,

$$\int P(x) dx = 1, \quad (4.3)$$

where the integration is taken over the entire possible range of x , i.e., at least over the range for which $P(x) \neq 0$. Furthermore, $P(x)$ is a strictly nonnegative function. As a corollary to these arguments, we define the average expected value of x as

$$\bar{x} = \int xP(x) dx, \quad (4.4)$$

and the average of any function of x , $f(x)$, as

$$\overline{f(x)} = \int f(x)P(x) dx. \quad (4.5)$$

In this sense, \bar{x} represents the limit of the average of all observed values of x as the number of samples from the distribution $P(x)$ increases without limit.

In statistical mechanics the probability density functions we deal with often are very sharply peaked, approaching the limit of a Dirac delta function. Under these circumstances it becomes almost a certainty that a single observation of $f(x)$ will have the result $\overline{f(x)}$. The distinction between the average value of $f(x)$, the most probable value of $f(x)$ and the value found for $f(x)$ in a single sampling essentially vanishes.

The n th moment of the probability function $P(x)$ is the average value of x^n :

$$\bar{x}^n = \langle x^n \rangle = \int x^n P(x) dx. \quad (4.6)$$

We can form a generating function for all the moments, $n = 0 - \infty$, if we multiply by $t^n/n!$ (t is a dummy variable) and sum over n :

$$\mathcal{M}(t) = \sum_{n=0}^{\infty} \frac{\bar{x}^n t^n}{n!} = \int e^{tx} P(x) dx. \quad (4.7)$$

It is frequently just as easy, if not easier, to evaluate the integral that defines \mathcal{M} and expand \mathcal{M} as a power series in t (thereby obtaining all the moments) as to evaluate directly just one moment.