

Classical Thermodynamics  
of Non-Electrolyte  
Solutions

H. C. Van Ness



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# Classical Thermodynamics of Non-Electrolyte Solutions

by

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## PREFACE

THE purpose of this monograph is to treat systematically and in depth that portion of classical thermodynamics which has to do with the properties of vapor and liquid solutions of non-electrolytes. This area has perhaps been too much neglected during the past several decades, with interest diverted to the developments of statistical thermodynamics, statistical mechanics, and molecular theory. However, such considerations are in no sense substitutes for classical thermodynamics, but are rather adjuncts through which one hopes to obtain added and perhaps more fundamental information.

The profound work of J. Willard Gibbs and the later contributions by G. N. Lewis and others put the classical thermodynamics of solutions on a firm base. Subsequent development has added to the structure, but it is even now by no means complete.

It should be remarked at the outset that this monograph is written from the viewpoint of an engineer. The ultimate aim of application to engineering problems has therefore had a vital influence on the content. To the engineer, thermodynamics has two faces. First is its application to the solution of practical problems from data at hand, and second is the calculation of the requisite data from experimental measurements. We shall be concerned here only with the latter. Many excellent texts are already available to point the way to the solution of engineering problems once the necessary data are available. But the general methods of developing such data from experimental measurements are not so well documented.

It is assumed that the reader is already well versed in the basic principles of classical thermodynamics. Nevertheless, an initial chapter on basic principles has been included for review purposes and as a summary. While disclaiming here any intention of writing a general textbook on advanced thermodynamics, I would not wish to deny the appropriateness of this material in advanced courses. This monograph has in fact been prepared from my notes for one term of a two-term course in thermodynamics for advanced students in chemical engineering.

This work is in no sense a record of the historical development of the thermodynamics of solutions, nor is it a compilation of pertinent material from the literature. It merely represents my own efforts to develop the known theory through concise derivation of the most general equations applicable to fluid systems. A knowledge of this material is usually assumed on the part of the reader by authors of works on statistical thermodynamics and molecular theory. Yet a convenient source from which to study it in depth

is not available. It is with the hope of satisfying this need that this monograph is written.

Where experimental data are not available to allow the accurate calculation of thermodynamic properties by the equations developed here, the engineer must have recourse to the various theoretical, semi-theoretical, and empirical correlations of thermodynamic data available. Although the existence of such correlations has been indicated from place to place, no attempt has been made to describe them in detail and no effort has been made to present a complete catalogue of them. In this regard there is no substitute for a familiarity with current literature. The general equations themselves are independent of such correlations, and remain valid as improvements are made to existing correlations.

Most of the material presented in this monograph was developed for courses of lectures to advanced students of chemical engineering. Some of it was first presented during 1958–1959 in England at King's College of the University of Durham and at the Houldsworth School of Applied Science of Leeds University. The opportunity provided by a Fulbright Grant to give attention to this subject while lecturing abroad is much appreciated. In addition, the support provided by the National Science Foundation for research in this area under my supervision has provided a stimulus for much concerted effort, and is gratefully acknowledged.

The constructive criticism of Professor J. M. Prausnitz, who reviewed the original version of this work, provided invaluable aid in the revision of the manuscript. Professor R. V. Mrazek not only made many useful suggestions but also wrote the computer programs and did many of the calculations upon which the numerical examples of this monograph are based. Finally, I would express my indebtedness to those students who by question and comment have contributed in no small measure to the final form of this monograph.

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## CHAPTER 1

# FUNDAMENTAL BASIS OF THERMODYNAMICS

CLASSICAL thermodynamics is a network of equations, developed through the formal logic of mathematics from a very few fundamental postulates and leading to a great variety of useful deductions. In the sense that mathematics is an exact system of logic, thermodynamics is an exact science. However, as with any deductive procedure, the derived conclusions are conditioned by the limitations imposed by the fundamental postulates and depend for validity upon the truth of these postulates within the imposed limitations. One might trace the historical development of the concepts necessary to the formulation of the fundamental postulates, but this does not seem appropriate to our purposes. Rather, we take advantage of the considerable benefits of hindsight, and present these concepts in such a way that they lead most directly to the basic postulates of classical thermodynamics.

**1.1. The Nature of a Function.** A variable  $F$  is said to be a *function* of  $x$  and  $y$ , i.e.,  $F = f(x, y)$ , if for every pair of values  $(x, y)$  there exists a value for  $F$ . An equation connecting  $F$  with  $x$  and  $y$  may or may not be known. The functional relationship may equally well be given graphically, for the nature of a function  $F = f(x, y)$  is obviously such that a definite value of the function  $F$  is associated with each point on a  $y - x$  plane.† The simplest means of representation is to show lines of constant  $F$  on a  $y - x$  plot, as illustrated in Fig. 1-1. For a given point  $(x_1, y_1)$  there is a particular value of  $F$ , namely  $F_1$ , and for another point  $(x_2, y_2)$  there is also a particular value of  $F$ , namely  $F_2$ . For a change in the variables  $x$  and  $y$  from  $(x_1, y_1)$  to  $(x_2, y_2)$ , no matter how accomplished, there is a particular change in  $F$ , given by  $\Delta F = F_2 - F_1$ . This constancy of  $\Delta F$  for a pair of points 1 and 2, regardless of the path connecting these points on a  $y - x$  plane, is a distinguishing characteristic which marks  $F$  as a function of  $x$  and  $y$  even though an equation relating  $F$  to  $x$  and  $y$  is not known.

†  $F$  may, of course, be a function of more than two independent variables. Although this renders graphical representation more difficult, the general nature of a function is the same regardless of the number of variables it depends on.

A simple example is evident if we regard Fig. 1-1 as a contour map.  $F$  then represents elevation, and  $x$  and  $y$  are the position coordinates. Clearly, if one travels from position 1 to position 2, the net change in elevation  $\Delta F$  is independent of the path taken. This immediately marks the elevation  $F$  as a function of the position coordinates  $x$  and  $y$ .

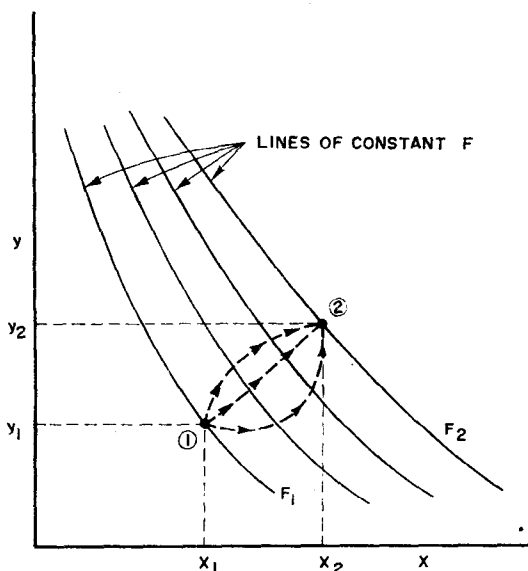


FIG. 1-1.  $F$  represented as a function of  $x$  and  $y$ .

We recognize the functional dependence of elevation on the position coordinates through experience. If we were interested in mathematics only, we could write a limitless number of equations expressing  $F$  as various functions of  $x$  and  $y$ , or alternatively we could draw an indefinite number of "contour maps" giving similar arbitrary relationships, and we might study their properties. But the problem of science and technology is to detect characteristics of our material world which are expressible as functions of measurable variables and to express these functional relationships in graphical, tabular, or equation form. The characteristic of elevation above a datum (sea level) is easily recognized, and has long been expressed as a function of position coordinates by means of contour maps.

**1.2. Properties of Simple Systems.** In the field of classical thermodynamics we are concerned with the macroscopic properties of matter and their relation to the measurable conditions of temperature, pressure, and composition. Experimentation with various materials leads us to believe that there is a large class of homogeneous fluids (both liquid and gas) whose



properties depend solely on these variables. We could observe, for example, that the density of pure liquid acetone is constant for a given temperature and pressure, regardless of the past history of the experimental sample. Similarly, we would find the specific volume of an equimolal mixture of gaseous oxygen and nitrogen to be fixed for a given temperature and pressure. Were we to change the temperature or pressure, or both, of these materials, we would find a fixed change in their properties, regardless of how the change was accomplished. These observations are quite general for single-phase fluids.

However, we might well note that in setting up our experiments we may well have eliminated the effects of certain extraneous influences. In all probability we would not carry out our experiments in the presence of a strong magnetic or electrostatic field. Our samples of material would be small enough so that the effect of the earth's gravitational field would not be detected in a variation of properties from top to bottom of the sample. The sample would be stationary, not subject to shear stresses, and samples would not be subdivided into small droplets or bubbles that would make surface-tension effects important. We would undoubtedly deal, quite naturally, with what have been called *simple systems*, and our equations would then be written to apply to fluids as they exist in such simple systems. In practice, these equations are often applied in cases where extraneous influences are not entirely absent but where their effect is considered to be negligible.

This discussion has been preliminary to the statement of our first fundamental postulate, which is that *the macroscopic properties† of homogeneous fluids can be expressed as functions of temperature, pressure, and composition only*. One must keep in mind that this is a postulate which contributes to the basis upon which our network of equations is founded, and is not an absolute law of nature. Thus the ensuing equations are restricted to applications where this postulate is essentially valid, i.e., to simple systems.

**1.3. The Special Functions of Thermodynamics.** We have taken temperature, pressure, and composition as basic thermodynamic variables for homogeneous fluids. These are not regarded primarily as properties of fluids but as *conditions* imposed on them, or manifested by them by virtue of their direct measurability. What *are* the properties that we recognize

† The simple term *property* as applied to a homogeneous material (here, a fluid) should not be ambiguous. It must obviously be independent of the amount of material; otherwise it would not be a property of the *material*. Specific or molal volume is such a property. Were we to speak of properties of a system, we would find it necessary to take into account the extent of the system. The total volume of a system is a property of the system, not of the material which constitutes it. Thus the common terms, intensive and extensive property, refer respectively to a material and to a system. Properties of systems generally depend not only on temperature, pressure, and compositions of the phases, but also on the extent of the phases.

as being functions of temperature, pressure, and composition? Specific or molal volume is certainly one; we know this from experience. For any homogeneous fluid of constant composition and existing as a simple system we can write:

$$V = v(T, P).$$

We know this functional relationship to exist, but its expression for a given material by means of a table, a graph, or an equation must be based on careful experimental measurements.

What other functions of constant-composition, homogeneous fluids can be expressed in terms of temperature and pressure? We could define *arbitrarily* any number of functions of  $T$  and  $P$ . For example, we might *define* a function  $X$  as

$$X = \frac{3P^2}{VT}.$$

We could give this function a name; call it *Xtropy*. We could show lines of constant Xtropy on a  $T - P$  plane for the given material. We could compute the values of  $\Delta X$  for the material which would result from given changes in  $T$  and  $P$ . The function  $X$  would satisfy all the mathematical requirements of a property of the material. But from the scientific, as opposed to the purely mathematical point of view, is  $X$  to be regarded as a *useful* property of the material? The scientist or engineer requires an affirmative answer to one or both of the following questions:

(a) Is  $X$  directly measurable, like specific volume, and thus capable of adding to our experimental knowledge of the material?

(b) Is  $X$  an *essential* function in that some generalization can be made concerning it which allows the prediction of the behavior of material systems? For example, are there common processes which occur at constant Xtropy? Since  $X$  was arbitrarily defined, the answer to both questions is probably negative, and we are unlikely to consider the function  $X$  a useful property of the material.

The only way to avoid completely arbitrary definitions of properties is to base their recognition on observations of the behavior of real materials. The most fundamental concept to arise from such observations is that of *energy*. The development of this concept took many centuries, and eventually led to one of the great generalizations of science: The law of conservation of energy. All this is discussed in detail in other books, and will not be further elaborated here. We merely list as postulates those principles pertinent to this work:

(a) There exists a form of energy, known as *internal energy*,  $U$ , which for homogeneous fluids existing as simple systems is a property of the material and is a function of temperature, pressure, and composition.

(b) The *total* energy of a system *and* its surroundings is conserved; energy may be transferred from a system to its surroundings and vice versa, it may be transformed from one form to another, but the total quantity remains constant.

The first of these postulates is requisite to the second, which through its universal acceptance has come to be known as the first law of thermodynamics. Its domain of validity has been circumscribed by the discovery of nuclear reactions in which mass is converted into energy and vice versa. Nevertheless, it remains a law valid for all other processes.

*Heat* is a word used to describe the process by which energy is transferred (“flows”) under the influence of a temperature difference between a system and its surroundings. Since internal energy is the only form of energy of which temperature is a manifestation, the notion of heat is inherently tied to the concept of internal energy. However, a quantity of heat,  $Q$ , represents merely an amount of energy crossing the boundary of a system, and thus cannot be a property of the system.

*Work* is a word used to describe the process by which energy is transferred between a system and its surroundings as the result of the displacement of an external force. A quantity of work,  $W$ , again represents an amount of energy crossing the boundary of a system, and is not a property of the system.

As applied to systems of constant mass (closed systems) for which the only form of energy to experience change is its internal energy, the first law takes the familiar form:

$$\Delta U = Q - W.$$

The usual sign conventions with regard to  $Q$  and  $W$  have been adopted: The numerical value of  $Q$  is taken as positive when heat is added to the system, while the numerical value of  $W$  is taken as negative when work is done on the system.

This equation cannot be regarded as giving an explicit definition of internal energy. In fact, no such definition is known. However, the postulated existence of internal energy as a property can be tested through the use of this equation as applied to experiments with homogeneous fluids.

Consider, then, the performance of a series of experiments with a constant-composition homogeneous fluid in a piston-and-cylinder assembly. Temperature and pressure are taken as the independent variables of the system. Changes are brought about in the system by alteration of its temperature and pressure. This is accomplished by the addition or extraction of heat and by displacement of the piston within the cylinder. In all experiments the temperature and pressure are changed from  $T_1$  and  $P_1$  to  $T_2$  and  $P_2$ , so that the properties of the system are altered by a constant amount. However, the *path* of the change, i.e., the relation between  $T$  and  $P$  during the process, is varied arbitrarily from run to run.

It is implicit in these discussions that there *be* a single value of  $P$  and a single value of  $T$  for the entire system at each stage of every process. The moment we write  $P$  and  $T$  for the system, we imply uniformity of temperature and pressure throughout the system. The only way we can ensure this uniformity during the course of our experiments is to carry them out slowly so as to avoid the generation of pressure waves in our fluids and so as to allow time for the thermal diffusivity of the system to smooth out even minute temperature variations. A system *within which* there are no non-uniformities which act as driving forces for change is said to be in a state of internal equilibrium. Processes that proceed so that displacements from internal equilibrium are always infinitesimal are said to be internally reversible. To carry out such processes in practice, we find it necessary also to keep the system very nearly in equilibrium with its surroundings. Processes that proceed so that displacements from both external and internal equilibrium are infinitesimal are called completely reversible, or more simply, reversible. The term arises from the fact that such processes can be reversed by a differential change in external conditions.

The experiments we are discussing are therefore conducted essentially reversibly. For each experiment we keep a careful account of the volume of the system,  $V$ , of the amount of heat,  $Q_{\text{rev}}$ , added or extracted, and of the work,  $W_{\text{rev}}$ , done on or by the system up to each intermediate set of conditions,  $T$  and  $P$ . We emphasize the restriction to processes that are reversible by writing  $Q_{\text{rev}}$  and  $W_{\text{rev}}$ .

We then examine the data, trying various combinations of the measured values and performing various numerical operations, to see what order, if any, can be brought out of the apparently disconnected sets of numbers.

For a given amount of material of given composition changed along various paths from a particular initial condition ( $T_1, P_1$ ) to a particular final condition ( $T_2, P_2$ ), we would first note, as would be expected, that  $\Delta V = V_2 - V_1$  is constant regardless of path. This serves to confirm our earlier observation that the volume of a given amount of a homogeneous fluid (or its specific or molal volume) is a function of temperature, pressure, and composition.

Our next observation would probably be that for the same set of experiments the difference  $Q_{\text{rev}} - W_{\text{rev}}$  is constant for the over-all change regardless of path. This result is expected provided our postulates regarding the existence of internal energy as a property and the conservation of energy are valid. This observation provides at least partial confirmation of these postulates, for the difference,  $Q_{\text{rev}} - W_{\text{rev}}$ , is seen to be the *measure* of a property change which has already been designated  $\Delta U$ . The restriction of reversibility here comes about from the nature of the experiments being considered, and not as a consequence of any limitation imposed by the basic postulates. The result obtained that  $\Delta U = Q_{\text{rev}} - W_{\text{rev}}$  is merely a special case of the more general equation for closed systems,

$\Delta U = Q - W$ , which applies for any two equilibrium states whether the process connecting them is reversible or not.

A further examination of the experimental data is then made to determine whether the existence of any additional properties is indicated. Certainly none is obvious, but if we evaluate the integral  $\int_1^2 dW_{\text{rev}}/P$  for each run, we find it to be constant and equal to  $\Delta V$ . Thus

$$\Delta V = \int_1^2 \frac{dW_{\text{rev}}}{P}.$$

This is actually a well-known equation, far more easily arrived at through the definition of work. As a result of this definition it is immediately deduced that for a reversible expansion or compression of a fluid

$$dW_{\text{rev}} = P dV.$$

Hence

$$dV = \frac{dW_{\text{rev}}}{P}$$

or

$$\Delta V = \int_1^2 \frac{dW_{\text{rev}}}{P}.$$

The point here is that we *could* establish the existence of the property,  $V$ , as a result of integrations of our experimental data as indicated. Once it is shown that a single value of the integral results, regardless of the path, for given initial and final states, it becomes clear that the integral is the measure of a property change. In this case we immediately recognize the property as already known through much more direct observations.

A similar integral is  $\int_1^2 dQ_{\text{rev}}/T$ . If we evaluate this integral for each run of our set of experiments, we again find a single value for all paths. Again we have evidence of the existence of a property. However, in this instance it is not recognized as being known. Nevertheless, once the existence of a property is indicated, it is natural to give it a symbol and a name. Thus we write

$$\Delta S = \int_1^2 \frac{dQ_{\text{rev}}}{T},$$

where  $S$  is called the *entropy*.

This result leads to an additional basic postulate: There exists a property of materials called *entropy*,  $S$ , which for homogeneous fluids existing as simple systems is a function of temperature, pressure, and composition. The integral given for  $\Delta S$  provides a means for the calculation of changes in this property.

Just as the equation  $\Delta U = Q - W$  does not explicitly define the property internal energy, so the equations  $\Delta V = \int_1^2 dW_{\text{rev}}/P$  and  $\Delta S = \int_1^2 dQ_{\text{rev}}/T$  cannot be considered to give explicit definitions of volume and entropy. But implicit in these three equations is the existence of three properties. This is obvious in the case of volume, for which an explicit definition in terms of directly measurable distances is known. With regard to internal energy and entropy, the situation is quite different. Classical thermodynamics furnishes no explicit definitions of these properties. Further insight can be gained only through study of statistical mechanics and molecular theory.

We have dealt so far with simple systems made up of a given amount of a homogeneous fluid. The reason for this is that the state of such systems is fixed by establishing the conditions of temperature, pressure, and composition. For *heterogeneous* simple systems made up of several phases, each in itself a simple system but existing in mutual equilibrium with the others, the state of the system depends on its temperature and pressure, on the composition of each of the phases, and on the relative amounts of the phases. It is clear that the total property of such a system is the sum of its parts. Thus one can ascribe a complete set of total properties to any equilibrium state of the system, and for a change in a closed system between two equilibrium states a unique set of property changes must result regardless of the path of the process connecting the two states. Experiments carried out on such systems yield exactly the same results as described for homogeneous fluids. It is simply more difficult to identify unique states of the system. The point of this is to generalize the equations presented for homogeneous fluids to apply to heterogeneous systems.

Thus for any closed system subject to the limitations already described, we may write the fundamental equations:

$$\Delta U = Q - W$$

and as a special case,

$$\Delta U = Q_{\text{rev}} - W_{\text{rev}}.$$

In differential form, this last equation is written:

$$dU = dQ_{\text{rev}} - dW_{\text{rev}}. \quad (1-1)$$

For reversible processes where the only force is that of fluid pressure

$$dW_{\text{rev}} = P dV. \quad (1-2)$$

For the calculation of entropy changes we have shown that

$$\Delta S = \int_1^2 \frac{dQ_{\text{rev}}}{T}.$$

It follows immediately from this that

$$dS = \frac{dQ_{\text{rev}}}{T}$$

or that

$$dQ_{\text{rev}} = T dS. \quad (1-3)$$

The methods of classical thermodynamics for the calculation of property values are based ultimately on Eqs. (1-1) through (1-3). This is not to suggest that direct use is commonly made of these equations for this purpose. Accurate measurements of heat and work effects in experiments such as those described are in fact very difficult. The actual methods used will be described in Chapter 3.

**1.4. The First and Second Laws of Thermodynamics.** The volume is an important thermodynamic property because it is directly measurable and can be used to provide experimental information about a system. Internal energy and entropy, on the other hand, can be determined only by indirect means. Nevertheless, these properties are essential to the science of thermodynamics, for without recognition of their existence the two great generalizations on which this science is based would be impossible.

The law of conservation of energy or the first law of thermodynamics could not be formulated without a prior postulate affirming the existence of internal energy as a property of materials. And internal energy is regarded as a property precisely for the reason that it allows this generalization to be made.

Once the existence of the entropy is postulated, it becomes necessary to determine whether any broad generalization based on this property is possible. Thus one calculates the entropy changes associated with various processes and examines the results to see whether some pattern emerges. The particular processes considered are not important, for one finds in every case that for reversible processes the *total* entropy change in system and surroundings resulting from the process is zero and for irreversible processes it is positive. Thus one is led to postulate that this is in general true, and we have for our final postulate a statement that has come to be known as the second law of thermodynamics: All processes proceed in such a direction that the *total* entropy change caused by the process is positive; the limiting value of zero is approached for processes which approach reversibility. Mathematically this is expressed as

$$\Delta S_{\text{total}} \geq 0.$$

It is one of the major triumphs of nineteenth-century science to have developed a principle, unsurpassed in conciseness of statement, that describes at once the directions of all processes in this vastly complex world.

The basic postulates upon which we build the science of thermodynamics are here recapitulated for convenience.

1. The macroscopic properties of homogeneous fluids existing as simple systems are functions of temperature, pressure and composition.
2. One such property is a form of energy known as internal energy.
3. Energy is conserved.
4. There exists a property called entropy. Changes in this property are calculable by the equation,  $dS = dQ_{rev}/T$ .
5. The total entropy change resulting from any real process is positive and approaches zero as the process approaches reversibility.

These postulates form the foundation for the development of a vast network of equations. All that is needed in addition is definition and deduction. The deductive process is purely mathematical. This deductive process and the postulates upon which it is based are ultimately subject to two tests. The network of equations which results must be internally consistent, and the consequences predicted must be in reality observed without exception. If these tests are met, then the system of logic employed and the postulates upon which it was based must be considered valid. Such tests have been applied for more than a century with complete success, so that now these postulates are regarded as laws of nature. As with all such laws, the proof of their validity lies in the absence of disproof, in the absence of contrary experience.



## CHAPTER 2

# THERMODYNAMIC PROPERTIES OF FLUIDS

**2.1. The Principal Thermodynamic Functions.** It was shown in the preceding chapter that for closed systems made up of phases which are themselves simple systems the following equations apply for an infinitesimal change of state of the system resulting from a reversible process in which the only force is fluid pressure.

$$dU = dQ_{\text{rev}} - dW_{\text{rev}}, \quad (1-1)$$

$$dW_{\text{rev}} = P dV, \quad (1-2)$$

$$dQ_{\text{rev}} = T dS. \quad (1-3)$$

Hence,

$$dU = T dS - P dV. \quad (2-1)$$

This is the basic differential equation relating the three thermodynamic properties considered so far. Since this equation relates properties only, it is not limited by the restrictions placed on the *process* considered in its derivation. However, the restrictions placed on the nature of the system still apply. Thus Eq. (2-1) is valid for *all* processes that result in a change of a *given mass of material* from one *equilibrium state* to another. Change of composition as a result of chemical reaction or mass transfer between phases is by no means excluded, provided equilibrium with respect to these processes is specified for the end states.

As a matter of convenience we now define several additional thermodynamic properties which are composites of the properties already discussed:

$$\text{Enthalpy:} \quad H = U + P V$$

$$\text{Helmholtz Function:} \quad A = U - T S$$

$$\text{Gibbs Function:} \quad G = H - T S.$$

For infinitesimal changes between equilibrium states of a given mass of material, simple differentiation gives:

$$dH = dU + d(P V)$$

$$dA = dU - d(T S)$$

$$dG = dH - d(T S).$$