

The Mathematical Behavior of Extensive and Intensive Properties of Simple Systems

Thermodynamic properties are represented mathematically by certain specialized functions. These functions, which are subject to definite mathematical conditions, provide the relationships between the various forms of energy in macroscopic systems. It is the purpose of this paper to introduce the mathematical conditions which we require for intensive and extensive thermodynamic properties and to examine the consequences of these mathematical conditions.

Intensive and Extensive Properties

We speak of two types of thermodynamic properties—intensive (properties which are independent of any measure of the mass or the extent of the system under consideration) and extensive properties. The extensive thermodynamic properties are functions of state which are subject to the following mathematical conditions

- I They are functions which form exact differentials.
- II They satisfy Euler's formula for homogeneous functions of degree one.

While the intensive properties in addition to satisfying condition I,

- III Satisfy Euler's formula for homogeneous functions of degree zero.

A discussion of Euler's theorem for homogeneous functions and of exact differentials is given in Appendices A and B, respectively. For the development that now follows we shall merely note when we are invoking condition I, II, or III.

Only simple systems will be considered in this paper. We define a simple system to be one that is macroscopically homogeneous, isotropic, uncharged, sufficiently large that surface effects can be neglected, and one that is not acted on by electric, magnetic, or gravitational fields.

Differential Forms for the Functions U , H , A , and G

We shall now use the mathematical conditions just presented to develop the differential forms for the four fundamental property relations.

$$U = U(S, V, n_i) \quad i = 1, \dots, k \quad (1)$$

$$H = H(S, P, n_i) \quad i = 1, \dots, k \quad (2)$$

$$A = A(T, V, n_i) \quad i = 1, \dots, k \quad (3)$$

$$G = G(T, P, n_i) \quad i = 1, \dots, k \quad (4)$$

where A = Helmholtz free energy function, G = Gibbs free energy function, H = enthalpy function, n = mole number, P = pressure, S = entropy function, T = temperature, U = internal energy function, V =

volume, and subscripts i, \dots, k = refer to component i , etc.

Each of the functions given by eqns. (1) to (4) must satisfy condition I. Thus we can write

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_i} dV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j} dn_i \quad (5)$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P, n_i} dS + \left(\frac{\partial H}{\partial P}\right)_{S, n_i} dP + \sum_{i=1}^k \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j} dn_i \quad (6)$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V, n_i} dT + \left(\frac{\partial A}{\partial V}\right)_{T, n_i} dV + \sum_{i=1}^k \left(\frac{\partial A}{\partial n_i}\right)_{T, V, n_j} dn_i \quad (7)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \sum_{i=1}^k \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} dn_i \quad (8)$$

Introducing the following equations for the various partial derivatives which occur in eqns. (5) to (8)

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V, n_i} = \left(\frac{\partial H}{\partial S}\right)_{P, n_i} \quad (9)$$

$$P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S, n_i} = -\left(\frac{\partial A}{\partial V}\right)_{T, n_i} \quad (10)$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S, n_i} = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} \quad (11)$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V, n_i} = -\left(\frac{\partial G}{\partial T}\right)_{P, n_i} \quad (12)$$

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T, V, n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} \quad (13)$$

we find

$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i \quad (14)$$

$$dH = TdS + VdP + \sum_{i=1}^k \mu_i dn_i \quad (15)$$

$$dA = -SdT - PdV + \sum_{i=1}^k \mu_i dn_i \quad (16)$$

$$dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i \quad (17)$$

The set of eqns. (14) to (17) represent the differential forms for the internal energy, the enthalpy, the Helmholtz free energy, and the Gibbs free energy functions, respectively.

Explicit Expressions for U , H , A , and G

Having developed the differential forms for these functions, we now employ condition II to develop explicit expressions for the four fundamental property relations given by eqns. (1) to (4). Since each of the independent variables and the dependent variable, U ,

which appear in eqn. (1) are extensive variables, we have

$$U(\lambda S, \lambda V, \lambda n_1, \dots, \lambda n_k) = \lambda U(S, V, n_1, \dots, n_k) \quad (18)$$

for any scalar, λ . It is important to note that the intensive state of the system represented by eqn. (18) must remain constant, while the extensive variables are increased or diminished by the factor λ . Equation (18) clearly satisfies condition II, and we can write it in the following form

$$U(S, V, n_1, \dots, n_k) = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} S + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} V + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} n_i \quad (19)$$

The partial derivatives which are present in eqn. (19) have been introduced earlier in eqns. (9), (10), and (13) and if we substitute them into eqn. (19) we obtain

$$U = TS - PV + \sum_{i=1}^k \mu_i n_i \quad (20)$$

Equation (20) is the desired fundamental property relation for the independent variables of S , V , and n_i . If we repeat the above for the functions given by eqns. (2) to (4) we have

$$H(\lambda S, P, \lambda n_i) = \lambda H(S, P, n_i) \quad (21)$$

$$A(T, \lambda V, \lambda n_i) = \lambda A(T, V, n_i) \quad (22)$$

$$G(T, P, \lambda n_i) = \lambda G(T, P, n_i) \quad (23)$$

for any scalar, λ . As eqns. (21) to (23) satisfy condition II, we can write immediately

$$H(S, P, n_i) = \left(\frac{\partial H}{\partial S} \right)_{P, n_i} S + \sum_{i=1}^k \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_j} n_i \quad (24)$$

$$A(T, V, n_i) = \left(\frac{\partial A}{\partial V} \right)_{T, n_i} V + \sum_{i=1}^k \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j} n_i \quad (25)$$

$$G(T, P, n_i) = \sum_{i=1}^k \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} n_i \quad (26)$$

All of the partial derivatives which occur in eqns. (24) to (26) have been introduced earlier, and so we obtain

$$H = TS + \sum_{i=1}^k \mu_i n_i \quad (27)$$

$$A = -PV + \sum_{i=1}^k \mu_i n_i \quad (28)$$

$$G = \sum_{i=1}^k \mu_i n_i \quad (29)$$

Equations (20), and (27) to (29) represent the four fundamental property relations that we desired. It should be noted that once we had established eqn. (20) that eqns. (27) to (29) could have been obtained either directly from the definitions of H , A , and G

$$H \equiv U + PV \quad (30)$$

$$A \equiv U - TS \quad (31)$$

$$G \equiv U + PV - TS \quad (32)$$

or from Legendre transformations of the various independent variables which appear in eqn. (1). We chose the approach presented here to emphasize the beautiful symmetry which results from repeated application of condition II.

It is perhaps worthwhile to stop at this point and to comment on the validity of eqns. (20), and (27) to (29). We pointed out earlier that the intensive state of the given system was maintained the same on both sides of eqns. (18), and (21) to (23). If we choose to use T, P , and the composition variables to set the intensive state, as is common practice, we may then be *falsely* led to believe that eqns. (20), and (27) to (29) are valid only at constant T, P , and composition.

We must realize that eqns. (20) and (27) to (29) are explicit expressions for functions of state, and that the differential forms of these equations must satisfy condition I. Now one of the characteristics of an exact differential is that the line integral over a given path depends only on the initial and final states and not on the path between those states. As a result, in writing the differential form of eqns. (20) and (27) to (29) it is legitimate to allow variations in the intensive properties. We conclude that eqns. (20), and (27) to (29) are identities and are completely general for simple systems. They are not limited to the special cases of constant T, P , and composition.

The Constraints on the Intensive Properties—The Gibbs-Duhem Equation

If we differentiate eqn. (20) we obtain

$$dU = TdS + SdT - PdV - VdP + \sum_{i=1}^k \mu_i dn_i + \sum_{i=1}^k n_i d\mu_i \quad (33)$$

and comparing this expression with the one given in eqn. (14) we see that

$$SdT - VdP + \sum_{i=1}^k n_i d\mu_i = 0 \quad (34)$$

This equation, which is known as the Gibbs-Duhem equation, places a constraint on the possible variations of the *intensive* variables of the system under consideration. For the k component simple system we are treating, we have $k + 2$ intensive variables ($k \mu_i$ values and T and P). Equation (34) tells us that of these $k + 2$ intensive variables only $k + 1$ of them can vary independently.

If we repeat the sequence of steps just completed using eqns. (27) and (15), once again we obtain eqn. (34). The same statement can also be made if we select eqns. (28) and (16) and eqns. (29) and (17). In summary, there is one and only one Gibbs-Duhem equation and it is given by eqn. (34).

Partial Molar Properties

Partial molar properties play a vital role in the thermodynamic analysis of mixtures and solutions. References (1, 3, 7, and 9) provide descriptions of their uses and so they will not be repeated here. Partial molar properties are defined by

$$\bar{X}_i \equiv \left(\frac{\partial X}{\partial n_i} \right)_{T, P, n_j} \quad (35)$$

where X can be any one of the functions U, S, H, V, A , and G . (Actually eqn. (35) can be written for any extensive thermodynamic property as Guggenheim points out (4), but we shall limit our discussion to the six extensive properties mentioned above.) Also, it is

not necessary that the intensive variables selected be T and P . Any intensive variables which set the intensive state will do, we might select density and refractive index for example, but we have selected the conventional ones in our definition. From their definition the partial molar properties are seen to be intensive variables.

Writing eqn. (35) for the Gibbs free energy function, G , we have

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j, j \neq i} \quad (36)$$

and by comparing eqns. (36) and (13) we see that

$$\mu_i = \bar{G}_i \quad (37)$$

or the partial molar Gibbs free energy is equal to the chemical potential. Using the results of eqn. (37) in eqn. (29) we have

$$G = \sum_{i=1}^k \bar{G}_i n_i \quad (38)$$

We shall now show that we can write any extensive thermodynamic property in the form

$$X = \sum_{i=1}^k \bar{X}_i n_i \quad (39)$$

Writing

$$X = X(T, P, n_i) \quad i = 1, \dots, k \quad (40)$$

and noting that X is an extensive thermodynamic property we have

$$X(T, P, \lambda n_1, \dots, \lambda n_k) = \lambda X(T, P, n_1, \dots, n_k) \quad (41)$$

and by invoking condition II we obtain eqn. (39) immediately. As in the case with eqns. (20), and (27) to (29) this result is general for simple systems and is *not* limited to the case of constant T, P , and compositions.

We can use this result to obtain an additional relation which is analogous to the Gibbs-Duhem equation. Applying condition I to eqn. (40) we have

$$dX = \left(\frac{\partial X}{\partial T} \right)_{P,n_i} dT + \left(\frac{\partial X}{\partial P} \right)_{T,n_i} dP + \sum_{i=1}^k \bar{X}_i dn_i \quad (42)$$

and differentiating eqn. (39) we find

$$dX = \sum_{i=1}^k n_i d\bar{X}_i + \sum_{i=1}^k \bar{X}_i dn_i \quad (43)$$

Finally by comparing eqns. (42) and (43) we see that

$$\left(\frac{\partial X}{\partial T} \right)_{P,n_i} dT + \left(\frac{\partial X}{\partial P} \right)_{T,n_i} dP - \sum_{i=1}^k n_i d\bar{X}_i = 0 \quad (44)$$

Equation (44) is identical to the Gibbs-Duhem equation when it is written for the Gibbs free energy function, G . We see that eqn. (44) does play a similar role to the Gibbs-Duhem equation—it places constraints on the intensive variables in a thermodynamic system. The result shown in eqn. (44) is given in a very limited number of texts (2, 5, and 10). Because other texts (i.e., 6 and 8) explicitly state that eqn. (39) is valid only at constant T and P , they do not develop eqn. (44). This is unfortunate, for they fail to present the subject with the maximum clarity as a consequence.

Intensive Variables and Equations of State

We introduced the intensive variables T , P , and μ_i which were defined by eqns. (9), (10), and (13) and noted that they were the partial derivatives that occurred in eqns. (5) and (19). Inspection of eqns. (9), (10), and (13) shows that T , P , and μ_i are consequently also functions of S, V, n_i . Thus we must have a set of functional relationships

$$T = T(S, V, n_i) \quad i = 1, \dots, k \quad (45)$$

$$P = P(S, V, n_i) \quad i = 1, \dots, k \quad (46)$$

$$\mu_i = \mu_i(S, V, n_i) \quad i = 1, \dots, k \quad (47)$$

We shall call such relationships, which express intensive variables as functions of the independent extensive variables, equations of state. Our definition of an equation of state is thus seen to be more general than the common definition

$$P = P(V, T, n_i) \quad i = 1, \dots, k \quad (48)$$

Inspection of eqns. (45) and (46) shows that our definition of an equation of state includes the function given in eqn. (48).

The fact that the intensive variables are partial derivatives of homogeneous first-order functions has a direct bearing on the functional form of the equations of state. The equations of state must satisfy condition III—they are homogeneous zero-order functions. Expressing this condition mathematically we can write eqn. (45) for example, for any scalar λ .

$$T(\lambda S, \lambda V, \lambda n_1, \dots, \lambda n_k) = T(S, V, n_1, \dots, n_k) \quad (49)$$

Equation (49) tells us that enlarging or diminishing the extent of any simple system by a scalar λ , leaves the intensive variable temperature unchanged. This is in agreement with our intuitive feelings. The physical meaning of eqns. (46) and (47) can be treated in a similar fashion and the results are again in agreement with our intuitive feelings.

Literature Cited

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- (4) *Ibid*, p. 211.
- (5) *Ibid*, equation 5.08.2, p. 212.
- (6) KESTIN, J., "A Course in Thermodynamics," Blaisdell Publishing Co., Waltham, Mass., 1966, p. 327.
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Appendix A

If $\phi(x, y, z, \dots)$ satisfies the identity

$$\phi(\lambda x, \lambda y, \lambda z, \dots) = \lambda^n \phi(x, y, z, \dots) \quad (A-1)$$

where λ is any scalar, and n is fixed, then ϕ is said to be homogeneous in the variables, x, y, z, \dots and of degree n . Euler's theorem for homogeneous functions of degree n may be stated

$$x \left(\frac{\partial \phi}{\partial x} \right)_{y,z,\dots} + y \left(\frac{\partial \phi}{\partial y} \right)_{x,z,\dots} + z \left(\frac{\partial \phi}{\partial z} \right)_{x,y,\dots} + \dots = n\phi(x,y,z,\dots) \quad (\text{A-2})$$

The result shown in eqn. (A-2) is general. We had occasion to use special cases of Euler's theorem in this work in addition. For example, if

$$\phi(x,y,\lambda z,\dots) = \lambda^n \phi(x,y,z,\dots) \quad (\text{A-3})$$

then

$$z \left(\frac{\partial \phi}{\partial z} \right)_{x,y,\dots} + \dots = n\phi(x,y,z,\dots) \quad (\text{A-4})$$

The extensive thermodynamic properties are homogeneous functions of degree one and the intensive properties are homogeneous functions of degree zero.

Appendix B

The total differential of the function $\phi(x,y,z)$ is given by

$$d\phi = \left(\frac{\partial \phi}{\partial x} \right)_{y,z} dx + \left(\frac{\partial \phi}{\partial y} \right)_{x,z} dy + \left(\frac{\partial \phi}{\partial z} \right)_{x,y} dz \quad (\text{B-1})$$

Given a function $u(x,y,z)$ whose differential is given by

$$du(x,y,z) = M(x,y,z)dx + N(x,y,z)dy + P(x,y,z)dz \quad (\text{B-2})$$

we say that du is an exact differential if

$$M(x,y,z) = \left(\frac{\partial \phi}{\partial x} \right)_{y,z} \quad (\text{B-3})$$

$$N(x,y,z) = \left(\frac{\partial \phi}{\partial y} \right)_{x,z} \quad (\text{B-4})$$

$$P(x,y,z) = \left(\frac{\partial \phi}{\partial z} \right)_{x,y} \quad (\text{B-5})$$

A common test of an exact differential will now be given. Whenever,

$$\left[\frac{\partial M(x,y,z)}{\partial y} \right]_{x,z} = \left[\frac{\partial N(x,y,z)}{\partial x} \right]_{y,z} \quad (\text{B-6})$$

then du is an exact differential.

