

CLASSICAL SOLUTION THERMODYNAMICS

A Retrospective View

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THE PRIMARY VARIABLES of classical thermodynamics for fluid systems are temperature T , pressure P , and the molar properties volume V , internal energy U , and entropy S . Temperature is a primitive, having no definition in terms of anything simpler. Pressure and molar volume are defined directly by three other primitives: force, mass, and length. These primitives—temperature, force, mass, and length—are subject to direct sensory perception, and we have little difficulty accepting them as meaningful. Internal energy and entropy, however, are primitives not associated with direct detection by the senses. Nor are they directly measurable; we have no energy meters, no entropy meters. Energy and entropy are mental constructs which have meaning only as mathematical functions. Accepting this, we then need to know what they are functions of.

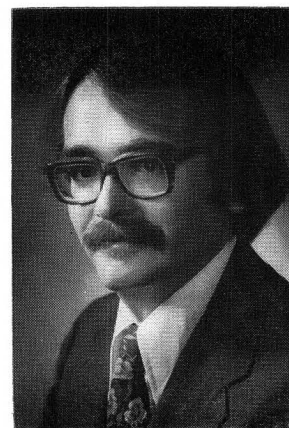
We find by experiment that the molar volume of a homogeneous phase is a function of its temperature, pressure, and composition. Generalizing, we postulate that the molar internal energy and entropy of a homogeneous phase are likewise functions of temperature, pressure, and composition. When this is true, the first and second laws lead to a fundamental property relation among the primary thermodynamic variables

$$d(nU) = Td(nS) - Pd(nV) + \sum \mu_i dn_i \quad (1)$$

The n_i are mole numbers of the species present,

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$n = \sum n_i$ is the total number of moles, and the μ_i are *chemical potentials*. Written for $n = 1$, Eq. (1) becomes

$$dU = TdS - PdV + \sum \mu_i dx_i$$

showing that

$$U = U(S, V, x)$$

Thus, in general, the natural independent (*canonical*) variables for U are entropy, volume, and composition.

New thermodynamic properties can be defined that are functions of alternative sets of independent variables. In particular, the enthalpy H and the Gibbs function G are defined as

$$H \equiv U + PV \quad (2)$$

and

$$G \equiv H - TS \quad (3)$$

Then

$$nG = nU + P(nV) - T(nS)$$

and

$$d(nG) = d(nU) + Pd(nV) + (nV)dP - Td(nS) - (nS)dT$$

Substitution for $d(nU)$ by Eq. (1) gives

$$d(nG) = - (nS)dT + (nV)dP + \sum \mu_i dn_i \quad (4)$$

This equation is equivalent to Eq. (1), and represents an alternative fundamental property relation. Written for one mole of material, it becomes

$$dG = - SdT + VdP + \sum \mu_i dx_i \quad (5)$$

whence

$$G = G(T, P, x)$$

Because temperature, pressure, and composition are subject to direct measurement and control, the Gibbs function is a defined thermodynamic property of great potential utility.

An equation such as Eq. (4) is too general for direct practical application. Its value is in storing much information. Thus, we write by inspection

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, x} \quad (6)$$

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, x} \quad (7)$$

and

$$\mu_i = \left(\frac{\partial (nG)}{\partial n_i} \right)_{T, P, n_j} \quad (8)$$

where the subscript n_j indicates that all mole numbers are held constant except n_i . Application of Eqs. (6) through (8) presumes knowledge of G as a function of T , P , and x ; given this, then Eqs. (6) and (7) yield S and V as functions of T , P , and x . Other properties come from defining equations; for example, by Eq. (3)

$$H = G + TS \quad (9)$$

Thus, if we know how G is related to its canonical variables, we can by simple mathematical operations evaluate all the other thermodynamic properties; given $G = G(T, P, x)$, we can also find S , V , μ_i , H , C_p , etc. as functions of temperature, pressure, and composition.

All this is the legacy of J. W. Gibbs and in principle nothing more is needed. An expression giving $G = G(T, P, x)$ is an example of a *canonical equation of state*. Such an equation serves as a generating function for the other thermodynamic properties, and implicitly represents complete property information.

For real-fluid mixtures, canonical equations of state are unknown. The problem is that such an equation must be based on experimental data. Unfortunately, there are no G meters and no convenient experimental measurements that lead easily to values of G . Without a canonical equation of state, we can make no direct practical use of a fundamental property relation. The slow evolution of solution thermodynamics since Gibbs' time has led to new formulations that relate much more directly to experiment. Our purpose here is

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In the early years of this century, G. N. Lewis introduced several concepts basic to all subsequent developments: the partial property, the fugacity, and the ideal solution.

A *partial property* is defined by the equation

$$\bar{M}_i \equiv \left(\frac{\partial (nM)}{\partial n_i} \right)_{T, P, n_j} \quad (10)$$

where M is the molar value of any extensive property. The simplest interpretation of Eq. (10) is that it apportions a mixture property among the constituent chemical species. Thus, \bar{M}_i has the characteristics of the property of species i in the mixture. Indeed, a mathematical consequence of Eq. (10) is the relation

$$M = \sum x_i \bar{M}_i \quad (11)$$

which shows that the partial properties combine in the simplest rational way to yield the mixture property. We see by comparison of Eq. (8) with Eq. (10) that

$$\mu_i = \bar{G}_i \quad (12)$$

Thus, the chemical potential is identified with the partial Gibbs function.

The *fugacity* is an auxiliary thermodynamic property related to the Gibbs function. Thus, for a mixture, the fugacity f is defined by the equations

$$dG = RT d \ln f \quad (\text{const } T, x) \quad (13)$$

and

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1 \quad (14)$$

For the special case of pure species i , these become

$$dG_i = RT d \ln f_i \quad (\text{const } T) \quad (15)$$

and

$$\lim_{P \rightarrow 0} \frac{f_i}{P} = 1 \quad (16)$$

For species i as a constituent of a mixture, the fugacity \hat{f}_i is defined by the equations

$$d\bar{G}_i = RT d \ln \hat{f}_i \quad (\text{const } T) \quad (17)$$

and

$$\lim_{x_i P \rightarrow 0} \frac{\hat{f}_i}{x_i P} = 1 \quad (18)$$

For an ideal-gas mixture one replaces V in Eq. (5) by RT/P ; then

$$dG' = RT d \ln P \quad (\text{const } T, x) \quad (19)$$

where the prime (') denotes an ideal-gas property. From Gibbs' theorem for such mixtures, we have

$$G' = \sum x_i G'_i + RT \sum x_i \ln x_i \quad (20)$$

By Eqs. (6), (7), and (9), we get

$$S' = \sum x_i S'_i - R \sum x_i \ln x_i \quad (21)$$

$$V' = \sum x_i V'_i \quad (22)$$

and

$$H' = \sum x_i H'_i \quad (23)$$

Each of these is implicit in Eq. (20). Moreover, Eq. (8) yields

$$\mu'_i = \bar{G}'_i = G'_i + RT \ln x_i$$

whence

$$d\bar{G}'_i = dG'_i + RT d \ln x_i \quad (\text{const } T)$$

By Eq. (19) written for pure species i , this becomes

$$d\bar{G}'_i = RT d \ln (x_i P) \quad (\text{const } T) \quad (24)$$

The actual properties of a fluid may be compared with the properties the fluid would have as an ideal gas at the same temperature, pressure, and composition. The comparison by subtraction gives rise to *residual properties*. Thus, by definition

$$M^R \equiv M - M'$$

and

$$\bar{M}_i^R \equiv \bar{M}_i - \bar{M}'_i \quad (26)$$

Applying this concept to the Gibbs function, we subtract Eq. (19) from Eq. (13)

$$d(G - G') = RT d \ln \frac{f}{P} \quad (\text{const } T, x)$$

or

$$dG^R = RT d \ln \phi \quad (\text{const } T, x) \quad (27)$$

where ϕ is the *fugacity coefficient*, defined as

$$\phi \equiv \frac{f}{P} \quad (28)$$

Integration of Eq. (27) gives

$$G^R = RT \ln \phi \quad (29)$$

The integration constant vanishes, because for $P = 0$, $G^R = 0$ by assumption and $\ln \phi = 0$ by Eq. (14). For the special case of pure species i , this becomes

$$G_i^R = RT \ln \phi_i \quad (30)$$

For species i as a constituent of a mixture, we subtract Eq. (24) from Eq. (17)

$$d(\bar{G}_i - \bar{G}'_i) = RT d \ln \frac{\hat{f}_i}{x_i P} \quad (\text{const } T)$$

or

$$d\bar{G}_i^R = RT d \ln \hat{\phi}_i \quad (\text{const } T) \quad (31)$$

where $\hat{\phi}_i$ is the fugacity coefficient of species i in the mixture, defined as

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{x_i P} \quad (32)$$

Integration of Eq. (31) gives

$$\bar{G}_i^R = RT \ln \hat{\phi}_i \quad (33)$$

Unlike a formulation based on a canonical equation of state, the residual-property formulation cannot provide complete property information. One needs in addition the heat capacities necessary for evaluation of properties for the ideal-gas state.

where again the integration constant vanishes.

An alternative form of Eq. (4) derives from the mathematical identity

$$d \left(\frac{nG}{RT} \right) \equiv \frac{1}{RT} d(nG) - \frac{nG}{RT^2} dT$$

Substituting for $d(nG)$ by Eq. (4) and for G by Eq. (3) gives

$$d \left(\frac{nG}{RT} \right) = \frac{-nH}{RT^2} dT + \frac{nV}{RT} dP + \sum \frac{\mu_i}{RT} dn_i \quad (34)$$

For the ideal-gas state, Eq. (34) becomes

$$d \left(\frac{nG'}{RT} \right) = \frac{-nH'}{RT^2} dT + \frac{nV'}{RT} dP + \sum \frac{\mu_i'}{RT} dn_i \quad (35)$$

With μ_i replaced by \bar{G}_i in Eq. (34) and μ_i' replaced by \bar{G}_i' in Eq. (35), we subtract these two equations:

$$d \left(\frac{nG^R}{RT} \right) = \frac{-nH^R}{RT^2} dT + \frac{nV^R}{RT} dP + \sum \frac{\bar{G}_i^R}{RT} dn_i \quad (36)$$

where the definitions of Eqs. (25) and (26) have been invoked. This is the fundamental property relation for residual properties. In view of Eq. (33), it may also be written

$$d \left(\frac{nG^R}{RT} \right) = \frac{-nH^R}{RT^2} dT + \frac{nV^R}{RT} dP + \sum \ln \hat{\phi}_i dn_i \quad (37)$$

Working relations for the residual properties can now be written by inspection

$$\frac{H^R}{RT} = -T \left(\frac{\partial (G^R/RT)}{\partial T} \right)_{P,x} = -T \left(\frac{\partial \ln \phi}{\partial T} \right)_{P,x} \quad (38)$$

$$\frac{V^R}{RT} = \left(\frac{\partial (G^R/RT)}{\partial P} \right)_{T,x} = \left(\frac{\partial \ln \phi}{\partial P} \right)_{T,x} \quad (39)$$

and

$$\ln \hat{\phi}_i = \left(\frac{\partial (nG^R/RT)}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial (n \ln \phi)}{\partial n_i} \right)_{T,P,n_j} \quad (40)$$

where the second form in each case follows from Eq. (29).

Equation (39) may be written

$$d \ln \phi = \frac{V^R}{RT} dP \quad (\text{const } T, x) \quad (41)$$

where by definition

$$V^R \equiv V - V' = V - \frac{RT}{P}$$

Values of V^R come directly from experimental PVTx data, and Eq. (41) then allows calculation of $\ln \phi$; Eqs. (38) through (40) yield other properties of interest. This close link to experiment is the major reason for a residual-property formulation of solution thermodynamics. Given a PVT equation of state

$$V = V(T, P, x)$$

we can evaluate all residual properties. Because of its direct relation to experiment, a PVT equation of state is far more easily developed than is a canonical equation of state. Furthermore, the principle of corresponding states allows the generalization of PVT data and the development of generalized correlations for the residual properties, thus greatly extending the usefulness of available experimental data. Unlike a formulation based on a canonical equation of state, the residual-property formulation cannot provide complete property information. One needs in addition the heat capacities necessary for evaluation of properties for the ideal-gas state.

In principle, PVT equations of state apply equally to gases and to liquids. In practice, however, the accurate representation of liquid properties proves much more difficult. Thus, an alternative formulation of solution thermodynamics has developed for liquids. The key idea is that of an *ideal solution*. By definition

$$\hat{f}_i^{id} \equiv x_i f_i \quad (42)$$

where the superscript *id* denotes an ideal-solution property. Expressions for all of the properties of an ideal solution follow from this equation.

Integration of Eq. (17) from the state of pure *i* to the state of *i* in solution at the same *T* and *P* gives

$$\bar{G}_i - G_i = RT \ln \frac{\hat{f}_i}{f_i} \quad (43)$$

For an ideal solution, this becomes

$$\bar{G}_i^{\text{id}} = G_i + RT \ln x_i \quad (44)$$

and by Eq. (11)

$$G^{\text{id}} = \sum x_i G_i + RT \sum x_i \ln x_i \quad (45)$$

Equations (6), (7), and (9) in this case yield

$$S^{\text{id}} = \sum x_i S_i - R \sum x_i \ln x_i \quad (46)$$

$$V^{\text{id}} = \sum x_i V_i \quad (47)$$

and

$$H^{\text{id}} = \sum x_i H_i \quad (48)$$

Just as we may compare the actual properties of a fluid with its ideal-gas-state properties, so may we compare the actual properties of a fluid mixture with its ideal-solution properties at the same temperature, pressure, and composition. Thus, we have definitions of *excess properties* quite analogous to those for residual properties

$$M^E = M - M^{\text{id}} \quad (49)$$

and

$$\bar{M}_i^E = \bar{M}_i - \bar{M}_i^{\text{id}} \quad (50)$$

Equation (49) applied in turn to the properties whose ideal-solution expressions are given by Eqs. (45) through (48) becomes

$$G^E = G - \sum x_i G_i - RT \sum x_i \ln x_i \quad (51)$$

$$S^E = S - \sum x_i S_i + R \sum x_i \ln x_i \quad (52)$$

$$V^E = V - \sum x_i V_i \quad (53)$$

$$H^E = H - \sum x_i H_i \quad (54)$$

The excess properties are closely related to *property changes of mixing*

$$\Delta M \equiv M - \sum x_i M_i \quad (55)$$

These quantities measure the changes that occur when one mole of mixture is formed from the pure constituent species by a mixing process at constant T and P. The definition of Eq. (55) allows Eqs. (51) through (54) to be written

$$G^E = \Delta G - RT \sum x_i \ln x_i \quad (56)$$

$$S^E = \Delta S + R \sum x_i \ln x_i \quad (57)$$

$$V^E = \Delta V \quad (58)$$

$$H^E = \Delta H \quad (59)$$

Thus, the excess properties are readily calculated from property changes of mixing and vice versa. Interest in property changes of mixing is focused on ΔV and ΔH , because these quantities can be experimentally determined by direct measurement.

Unfortunately, measurements of $\Delta V = V^E$ and of $\Delta H = H^E$ for liquid mixtures do not allow calculation of G^E . For this, we need vapor/liquid-equilibrium data, which are related to G^E as follows. Subtraction of Eq. (44) from Eq. (43) gives

$$\bar{G}_i^E = \bar{G}_i - \bar{G}_i^{\text{id}} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

or

$$\ln \gamma_i = \frac{\bar{G}_i^E}{RT} \quad (60)$$

where the *activity coefficient* γ_i is defined by

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} \quad (61)$$

In accord with Eq. (11)

$$\frac{G^E}{RT} = \sum x_i \frac{\bar{G}_i^E}{RT}$$

and by Eq. (60) this becomes

$$\frac{G^E}{RT} = \sum x_i \ln \gamma_i \quad (62)$$

Values of γ_i are calculated from experimental vapor/liquid-equilibrium measurements by the equation

$$\gamma_i = \frac{y_i P \Phi_i}{x_i P_i^{\text{sat}}} \quad (63)$$

Here, Φ_i is a secondary factor of order unity that can be readily evaluated from volumetric data for the equilibrium phases or from correlations of such data.

The fundamental property relation for the excess properties follows from Eq. (34). For an ideal solution, this equation is written

TABLE 1
Summary of key equations

$$d \left(\frac{nG}{RT} \right) = \frac{-nH}{RT^2} dT + \frac{nV}{RT} dP + \sum \frac{\mu_i}{RT} dn_i \quad (34)$$

$$d \left(\frac{nG^R}{RT} \right) = \frac{-nH^R}{RT^2} dT + \frac{nV^R}{RT} dP + \sum \ln \hat{\phi}_i dn_i \quad (37)$$

$$d \left(\frac{nG^E}{RT} \right) = \frac{-nH^E}{RT^2} dT + \frac{nV^E}{RT} dP + \sum \ln \gamma_i dn_i \quad (66)$$

$$\frac{G}{RT} = \sum x_i \frac{\bar{G}_i}{RT} = \sum x_i \frac{\mu_i}{RT}$$

$$\frac{G^R}{RT} = \sum x_i \frac{\bar{G}_i^R}{RT} = \sum x_i \ln \hat{\phi}_i$$

$$\frac{G^E}{RT} = \sum x_i \frac{\bar{G}_i^E}{RT} = \sum x_i \ln \gamma_i$$

$$d \left(\frac{nG^{id}}{RT} \right) = \frac{-nH^{id}}{RT^2} dT + \frac{nV^{id}}{RT} dP + \sum \frac{\mu_i^{id}}{RT} dn_i \quad (64)$$

With μ_i replaced by \bar{G}_i in Eq. (34) and μ_i^{id} replaced by \bar{G}_i^{id} in Eq. (64), we subtract these two equa-

$$d \left(\frac{nG^E}{RT} \right) = \frac{-nH^E}{RT^2} dT + \frac{nV^E}{RT} dP + \sum \frac{\bar{G}_i^E}{RT} dn_i \quad (65)$$

tions where the definitions of Eqs. (49) and (50) have been invoked. In view of Eq. (60), this equation may also be written

$$d \left(\frac{nG^E}{RT} \right) = \frac{-nH^E}{RT^2} dT + \frac{nV^E}{RT} dP + \sum \ln \gamma_i dn_i \quad (66)$$

Equation (66) is analogous to both Eqs. (34) and (37); analogous to Eqs. (38) through (40), we have

$$\frac{H^E}{RT} = -T \left(\frac{\partial (G^E/RT)}{\partial T} \right)_{P,x} \quad (67)$$

$$\frac{V^E}{RT} = \left(\frac{\partial (G^E/RT)}{\partial P} \right)_{T,x} \quad (68)$$

$$\ln \gamma_i = \left(\frac{\partial (nG^E/RT)}{\partial n_i} \right)_{T,P,n_j} \quad (69)$$

The formulation of solution thermodynamics through excess properties derives its usefulness from the fact that H^E , V^E , and γ_i can all be found by experiment. This relative abundance of experimental entries provides alternative measurements that yield property data. However, the excess-property formulation provides even less-complete property information than the residual-property formulation, because it tells us nothing about the properties of the pure chemical species.

In Table 1, we bring together for comparison the parent fundamental property relation for the Gibbs function and the two analogous property relations which follow from it for the residual and excess Gibbs functions. Included as well are the equations which relate the three mixture Gibbs functions to their respective partial properties. These are particular applications of Eq. (11). □

ChE books received

Fundamentals of Chemistry, Second Edition, James E. Brady, John R. Holm; John Wiley & Sons, Inc., New York; \$34.95 (1984)

Handbook of Powder Science and Technology, Edited by M. E. Fayed and L. Otten; Van Nostrand Reinhold, 135 West 50th Street, New York, 10020; 850 pages, \$79.50 (1984)

Analytical Pyrolysis: Techniques and Applications, Edited by Kent J. Voorhees; Butterworths, 80 Montvale Ave., Stoneham, MA 02180; 486 pages, \$69.95 (1984)

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