# Standard States and the Gibbs-Duhem Equation for Nonisothermal or Nonisobaric Phase Equilibria

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During the last decade attention has been drawn to the fact that the Gibbs-Duhem equation, as originally formulated many years ago, is not applicable to a two-phase, two-component system since it is impossible to vary the composition of such a system without simultaneously changing either the temperature or the total pressure. Ibl and Dodge (*1*), and more recently Van Ness (*3*), have derived a generalized Gibbs-Duhem equation which, unlike its historical antecedent, does not specify both constant temperature and constant pressure. In its most useful form the Gibbs-Duhem equation is expressed in terms of activity coefficients. The above-named authors both present equations in terms of activity coefficients, but both of them have restricted themselves to the case where the activity coefficients refer to the pure components in the same phase and at the same temperature and pressure as those of the solution. The purpose of this note is to show that this is not an essential restriction but that it is possible to derive a generalized Gibbs-Duhem equation for any set of convenient standard states.

It is frequently convenient to choose a standard state other than that specified by Ibl and Dodge and Van Ness. For example if one is concerned with a solution of a gas (or a solid) in a liquid, it is common to use a standard state for the solute referred to either the infinitely dilute solution or the saturated solution under specified conditions (*2*). Below is given a brief derivation of a generalized Gibbs-Duhem equation which permits use of any suitable standard states for the activity coefficients of both solute and solvent. The standard states may be, but need not be, the same for both components, although they must each be at some fixed composition. The only other restriction is that the standard state should always be at the same temperature as the solution. This is a necessary restriction if one wishes to use activity coefficients which are consistent with the isothermal definition of the activity function in terms of chemical potential.

Van Ness has shown (*3*) that the generalized Gibbs-Duhem equation in terms of fugacities is

$$\frac{v\,dP}{RT} - \frac{\Delta h^*}{RT^2}\,dT = \sum_i x_i\, d\ln f_i \quad (1)$$

where

$$\Delta h^* \equiv h - \sum_i x_i\, h_i^*$$

To express Equation (1) in terms of activity coefficients substitute

$$f_i = \gamma_i\, x_i\, f_i^{\circ}$$

Equation (1) then becomes

$$\frac{v\,dP}{RT} - \frac{\Delta h^*}{RT}\,dT = \sum_i x_i\, d\ln\gamma_i + \sum_i x_i\, d\ln f_i^{\circ} \quad (2)$$

Two cases may now be considered. The standard state should be at the same temperature as the solution, but it can be defined either at a fixed pressure or at some variable pressure.

*Case 1*: The standard state fugacity is defined at a fixed pressure, fixed composition, and at the temperature of the solution. This case is most useful for isothermal data but is not restricted to such data. A common example of such a case occurs in treating isothermal data for a mixture of liquids where the standard state fugacity may be taken as that of the pure liquid at the temperature of the solution and under its own vapor pressure. Another example is the case of a gas dissolved in a nonvolatile liquid; the standard state fugacity of the solute may be taken as the fugacity of the gas in a solution saturated at the temperature of the solution and at some arbitrarily fixed pressure. Finally, a frequently used standard state for isothermal data is to refer to the infinitely dilute solution at the temperature of the solution and at the vapor pressure of the solvent; the standard state fugacity for a gaseous solute (component 2) in a liquid is given by the Henry's law constant $H$ as determined by

$$H = \lim_{x_2 \to 0} \left(\frac{f}{x}\right)_2$$

When the standard state fugacity is independent of pressure, substitute into Equation (2) the common thermodynamic relation valid at constant pressure

$$d\ln f_i^{\circ} = \left(\frac{h_i^* - h_i^{\circ}}{RT^2}\right) dT$$

which yields

$$\frac{v\,dP}{RT} - \frac{\Delta h\, dT}{RT^2} = \sum_i x_i\, d\ln\gamma_i \quad (3a)$$

where

$$\Delta h \equiv h - \sum_i x_i\, h_i^{\circ}$$

In Equation (3*a*), as well as in (3*b*) below, $\Delta h$ is the enthalpy change which is observed when all the components in their standard states are mixed isothermally to form one mole of solution. For example in a solution of solute and solvent, if the standard state for the solute is referred to the infinitely dilute solution, whereas the standard state for the solvent is the pure liquid, then $\Delta h$ is the heat of dilution (to infinite dilution) multiplied by minus 1.

*Case 2*: The standard state fugacity is defined at a fixed composition, at the temperature of the solution, and at a pressure which varies in some arbitrary way with the composition. Usually the pressure chosen is the total pressure which corresponds to a given composition, but this choice is strictly one of convenience, not of thermodynamic necessity. The standard state which is most frequently employed by chemical engineers in the thermodynamic treatment of phase-equilibrium data is the pure component at the temperature and total pressure of the solution and in the same phase as the solution. (A disadvantage of this choice is that it unavoidably introduces hypothetical standard states.) However sometimes it is more convenient to use other standard states. For example for isothermal data for gas-liquid solutions at advanced pressures it is useful to refer the standard state for the solute to the infinitely dilute solution at the temperature and total pressure of the solution. In that case the fugacity of the standard state for the solute (component 2) is given by

$$f_2^{\circ} = H \exp \frac{1}{RT} \int_{P_1^s}^{P} \bar{v}_2^{\infty}\, dP$$

where $H$ is as defined above and is a function only of temperature.

(*Continued from page 562*)

## INFORMATION RETRIEVAL

**Key Words:** Equilibrium-8, Thermodynamics-8, Solutions (Mixtures)-8, Estimating-8-Predicting-8, Fugacities-9, Activities-9, Properties (Characteristics)-9, Physical Properties-9, Chemical Properties-9, Phases-9, Vapor Phase-9, Liquid Phase-9, Mixtures-9, Equation of State-9, Ideal-9.

**Abstract:** A new ideal K value is defined which does not depend on the Lewis and Randall ideal solution rule but is derived only from composition dependent pseudocritical constants and the corresponding states principle. Methods of estimating mixture properties are discussed. The derivation of an improved pseudocritical expression which is applicable to liquids composed of simple molecules is presented. Calculated and experimental K values for mixtures of simple molecules are compared.

**Reference:** Leland, Thomas W., Patsy S. Chappelear, and Bernard W. Gamson, **A.I.Ch.E. Journal, 8,** No. 4, p. 482 (September, 1962).

**Key Words:** Compression-8, Agglomeration-8, Powders-1, Sodium Chloride-1, Sucrose-1, Quartz-1, Tablets-2, Pellets-2, Pressure-6, Particle Size-6, Density-7, Porosity-7.

**Abstract:** Pressure-volume measurements in the compression of closely sized powder fractions of sodium chloride, sucrose, and quartz showed that in each case the decrease in volume for a given pressure increase was greater for small particles than for large. This was attributed to the completion of the slippage phase of compression at relatively lower pressures for the larger particles. Data for all sizes of the three materials and for mixed sizes of sodium chloride indicated that the pressing modulus proposed by Bal'shin was a simple exponential function of particle size, with specific constants for each material.

**Reference:** Huffine, Coy L., and Charles F. Bonilla, **A.I.Ch.E. Journal, 8,** No. 4, p. 490 (September, 1962).

**Key Words:** Adsorption-5, Methane-1, Hydrogen-1, Activated Carbon-4, Diffusion-1, Mass Transfer-8, Flow-, Fixed-, Beds-, Rate-, Internal-, External-.

**Abstract:** The adsorption of methane from mixtures of methane and hydrogen on fixed beds of activated carbon at — 115°F. and 1 atm. has been studied. The external diffusion of adsorbate to the surface can be correlated by the usual mass transfer expressions for packed beds. An equation for internal particle diffusion is developed. It is not a mass transfer model in the usual sense but a convenient correlating expression.

**Reference:** Geser, John J., and Lawrence N. Canjar, **A.I.Ch.E. Journal, 8,** No. 4, p. 494 (September, 1962).

**Key Words:** Upper Velocity Limit-7, Ignition-8, Butane-Air-1, Composition-6, Turbulent Intensity-6, Pressure-6, Pilot Stabilized Flame-4, Cold Stream Velocity-6, Combustion Chamber-6, Air-5, Combustion-8, Quenching-6, Turbulent Boundary Layer-6.

**Abstract:** The upper velocity limit for the ignition of butane-air mixtures was determined for compositions up to the stoichiometric mixture and turbulent intensities up to 7.0% at a pressure of 0.2 atm. A pilot stabilized flame was used to initiate and maintain the ignition. Cold stream velocities up to 666 ft./sec. and turbulent intensities as high as 7.0% in three different sizes of combustion chambers were investigated.

**Reference:** Griskey, Richard G., and David H. Archer, **A.I.Ch.E. Journal, 8,** No. 4, p. 498 (September, 1962).

**Key Words:** A. Thermodynamics-5, Solubilities-7, Equilibrium-10, Vapor-5, Liquid-5, Low Pressure-6. B. Nonpolar-6, Polar-6, Associated-6, Nonassociated-6.

**Abstract:** The Hildebrand regular-solution theory is extended to binary systems consisting of a nonpolar and a polar, nonassociated liquid. Based on a general equation of Hildebrand and Wood and the Stockmayer potential function, an equation is derived in this paper to express the partial molar internal energy of mixing for the nonpolar component in such a system. This equation is applied to gas-liquid solutions according to the two-step dissolution process of Prausnitz and Shair. Because of our limited knowledge of liquid and of solution the resulting theoretical equation cannot be used for the prediction of gas solubilities using only data for the pure components. However it provides the thermodynamic framework for a single semiempirical correlation to estimate low-pressure gas solubilities in polar, nonassociated liquids.

**Reference:** Yen, Lewis Chinsun, and J. J. McKeffa, Jr., **A.I.Ch.E. Journal, 8,** No. 4, p. 501 (September, 1962).

(*Continued on page 566*)

Since the standard state fugacity is now a function of pressure as well as of temperature, the appropriate relation which must be substituted into Equation (2) is

$$d \ln f_i^\circ = \left(\frac{h_i^* - h_i^\circ}{RT^2}\right) dT + \frac{v_i^\circ}{RT} dP^\circ$$

If $P^\circ$ is chosen to be the total pressure $P$, substitution yields

$$\frac{\Delta v \, dP}{RT} - \frac{\Delta h \, dT}{RT^2} = \sum_i x_i \, d \ln \gamma_i \quad (3b)$$

where

$$\Delta v \equiv v - \sum_i x_i \, v_i^\circ$$

Equations (3*a*) and (3*b*) are useful forms of the Gibbs-Duhem equation in terms of activity coefficients for equilibria under nonisothermal or nonisobaric conditions. The activity coefficients may refer to any suitably chosen standard state which may or may not be the same for all components in the solution. Equation (3*a*) considers the case where each standard state is taken at some fixed pressure. Equation (3*b*) considers the case where all the standard states are taken at the total pressure of the solution. In both Equations (3*a*) and (3*b*) all the standard states should be taken at the temperature of the solution in order to retain the thermodynamic significance of activity coefficient which is based on the isothermal definition of activity in terms of the chemical potential.

There are two important advantages which are obtained when the standard state chosen is not the pure component in the same phase and at the same temperature and pressure as those of the solution. One advantage is that hypothetical standard states are thereby avoided, and thus the problem of evaluating self-consistent thermodynamic properties of nonexisting substances is eliminated. The other advantage, which is not generally appreciated, is that by appropriate choice of standard states the correction terms on the left-hand side of Equation (3*b*) can be made sufficiently small to be negligible; when this is the case, testing data for thermodynamic consistency or representing activity coefficient data in terms of simple empirical equations are both very much simplified. For example consider the case of a gas—liquid solution where isothermal data are taken at variable (and high) pressures. If the standard state for the heavy component 1 is the pure liquid, but that for the light component 2 refers to the infinitely dilute solution, both at the total pressure of the solution, then

(*Continued on page 566*)

(*Continued from page 564*)

## INFORMATION RETRIEVAL

**Key Words:** Vapor-Liquid Equilibrium Data-1, Methane-9, Ethane-9, Propane-9, Liquid Phase Activity Coefficients-2, van Laar Constants-2, Standard State Fugacities-2, Hypothetical Liquid-9, Vaporization Equilibrium Constants-2, Solubility Parameters-2, Generalized Correlations-10.

**Abstract:** Vapor-liquid equilibrium data for binary systems where the more volatile components are methane, ethane, or propane have been studied. Liquid phase activity coefficients of the less volatile component of each system were calculated, and van Laar constants were determined. From these constants, liquid phase activity coefficients for the more volatile component of each system were calculated, and they were used to evaluate the standard state fugacities of the more volatile components in their hypothetical liquid state. Coincident values of vaporization equilibrium constants and solubility parameters were evaluated. Generalized correlations of the results were obtained.

**Reference:** Hoffman, Dwight S., J. Reed Welker, Rowland E. Felt, and James H. Weber, **A.I.Ch.E. Journal, 8,** No. 4, p. 508 (September, 1962).

**Key Words:** Flow-8, Fluid Flow-8, Boundary Layers-8, Momentum Transfer-8, Heat Transfer-8, Convection-8, Stability-9, Stagnation-9, Force (Energy)-6, Gravity-6, Acceleration-6, Fields-6, Distribution-7, Temperature-7, Velocities-7.

**Abstract:** The effect of body forces perpendicular to the direction of flow has been investigated for fully developed and boundary-layer flows. Exact solutions for fully developed flow between parallel plates with a linear axial temperature distribution are obtained, and the criterion for stagnation at the walls is presented. Similarity substitutions are given for horizontal boundary-layer flows, and the resulting differential equation is solved for selected cases. The constant temperature flat plate is discussed briefly using the Karman-Pohlhausen integral method.

**Reference:** Gill, William N., and Eduardo del Casal, **A.I.Ch.E. Journal, 8,** No. 4, p. 513 (September, 1962).

**Key Words:** Enthalpy-7, Solution-5, Equilibrium-8, Vapor-5, Liquid-5, Pressure-6, Methane-9, Decane-9, Nonideality-6, Solubility-8.

**Abstract:** A general expression is derived for calculating the heat of solution of a gas in a liquid from solubility and PVT data. Various approximate forms are discussed. The heat of solution of methane in decane is calculated at several temperatures, and it is shown that nonidealities in the vapor and liquid phases can make significant contributions to the calculated heat of solution.

**Reference:** Sherwood, A. E., and J. M. Prausnitz, **A.I.Ch.E. Journal, 8,** No. 4, p. 519 (September, 1962).

**Key Words:** Predicting-8, Estimating-8, Transport Properties-8, Properties (Characteristics)-8, Physical Properties-8, Viscosity-9, Self-Diffusion-9, Thermal Diffusion-9, Gases-9, Intermolecular Potentials-9, Potential Energy Functions-9, Argon-1, Xenon-1, Nitrogen-1, Hydrogen-1, Deuterium-1, Scattering-10, Molecular Beams-10, Kinetic Theory of Gases-10.

**Abstract:** Calculation of transport properties of dilute gases at very high temperature is discussed in terms of limitations in knowledge of appropriate intermolecular potentials, and limitations in existing dynamical theory of gases. It is shown that the scattering of high energy neutral beams can provide necessary potential energy information so that reliable calculations can be made for a number of properties with existing kinetic theory. Illustrations are given for viscosity, self-diffusion, and isotropic thermal diffusion for normal argon, xenon, and nitrogen. Extension to systems containing ionic, atomic, excited, and metastable species is discussed.

**Reference:** Amdur, I., **A.I.Ch.E. Journal, 8,** No. 4, p. 521 (September, 1962).

(*Continued from page 564*)

$$\Delta v = v - (x_1 v_1^{\circ} + x_2 \bar{v}_2^{\infty}) =$$

$$x_1 (\bar{v}_1 - v_1^{\circ}) + x_2 (\bar{v}_2 - \bar{v}_2^{\infty})$$

Now if all the data are remote from the critical conditions, then it is often a good approximation to assume that $\bar{v}_1$ and $\bar{v}_2$ do not vary significantly with composition, in which case $\Delta v = 0$. Hence, even though the pressure may be quite large, it becomes a good approximation in this case to apply the simple Gibbs-Duhem equation

$$x_1 \, d \ln \gamma_1 + x_2 \, d \ln \gamma_2 = 0$$

By proper choice of standard states then, it is frequently possible to simplify thermodynamic treatment of nonisobaric or nonisothermal solution data.

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## NOTATION

$f_i$ = fugacity of component $i$ in solution
$f_i^{\circ}$ = fugacity of component $i$ in standard state
$H$ = Henry's law constant
$h$ = molar enthalpy of the solution
$h_i^{*}$ = molar enthalpy of component $i$ in ideal gas state
$h_i^{\circ}$ = molar enthalpy of component $i$ in standard state
$P$ = total pressure of solution
$P^{\circ}$ = pressure of standard state
$P^{s}$ = saturation (vapor) pressure
$R$ = gas constant
$T$ = absolute temperature
$v$ = molar volume of the solution
$v_i^{\circ}$ = molar volume of component $i$ in standard state
$\bar{v}_i$ = partial molar volume
$\bar{v}_i^{\infty}$ = partial molar volume of component $i$ at infinite dilution
$x_i$ = mol fraction of component $i$
$\gamma_i$ = activity coefficient of component $i$

## LITERATURE CITED

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2. Mauser, H., and G. Kortüm, *Z. Naturforsch.*, **10a**, 42 (1955).
3. Van Ness, H. C., *Chem. Eng. Sci.*, **10**, 225 (1959).