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Author

Newman, John.

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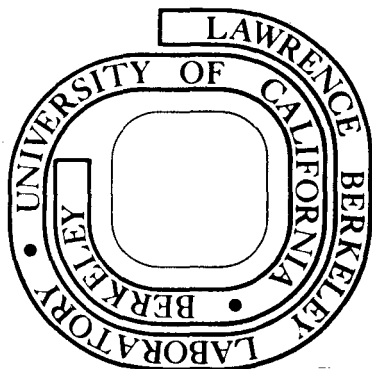
John Newman

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Integral Test for Consistency of
Vapor-liquid Equilibrium Data

John Newman

Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, and
Department of Chemical Engineering;
University of California, Berkeley 94720

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Abstract

This test can be used over a restricted range of composition, is essentially independent of the values used for the vapor pressures of the pure components, and avoids any differentiation of experimental data.

Scope

Thermodynamics is valuable because it tells us when a new quantity can be calculated from available experimental data. Alternatively, it provides a check on the accuracy of interdependent results. The individual components of vapor-liquid equilibrium data have been subjected to such tests for about thirty years. For example, from the total pressure over aqueous ammonia solutions of known compositions, it is possible to calculate the vapor-phase composition. If the latter is measured independently, the results are subject to rigorous thermodynamic test.

How can these tests be carried out most effectively, so as to give the best interpretation to expensive data? The basic thermodynamic relations involve differentials, but differentiation of numerical data magnifies errors and should be avoided if possible. It should also be possible to test data over a restricted composition range -- since many systems yield data over only such a range. A limited-range test can also give insight into the source of any discrepancy. Finally, a test should be independent of the vapor pressures of the pure components, since these values don't enter into determination of the binary data.

Conclusions and Significance

The calculation of the chemical potential of a second component from data on a first component, by means of the Gibbs-Duhem equation, typically can be restructured to avoid differentiation of data. This

concept provides the basis for developing a consistency test with desirable properties. The realization that it is unnecessary to extrapolate to the secondary reference states leads one to a test over the composition range of the experimental data, or a part of that range, with no dependence on the vapor pressures of the pure components. The test of Chueh et al. (1965) has most of these properties.

In application, one frequently finds that there are uncertainties in some of the quantities involved in a thermodynamic consistency test and that the redundant data could equally well be used to provide improved estimates of these quantities. We have in mind here vapor-phase fugacity coefficients and, in particular, the cross second virial coefficient B_{12} .

The Gibbs-Duhem equation

$$x_1 d\mu_1 + x_2 d\mu_2 = \tilde{V} dp \quad (1)$$

at constant temperature for a binary liquid mixture is the basis of many tests of thermodynamic consistency of vapor-liquid equilibrium data (Redlich and Kister, 1948; Redlich et al., 1968; Prausnitz, 1969). This equation is also the basis for calculating the activity coefficient of one component from data for the other component. For good data, equation 1 can be integrated numerically, with no need to fit the experimental data by an analytic expression over any extensive composition range. Alternatively, the data for one component are fit by an equation, such as that of van Laar, and chemical potentials or activity coefficients are predicted for the other component by means of an analytic integration of equation 1.

When data are available for the chemical potentials of both components of a liquid solution, these data are necessarily redundant, and the Gibbs-Duhem equation can be used to test the data for accuracy. This can be accomplished to advantage by calculating the logarithm of the activity coefficient of component 2 from data on component 1 and subtracting the result from the experimental value for component 2. This difference should be a constant, and consequently a graph of this difference versus composition will immediately provide quantitative insight into the consistency of the underlying data. In practice, the difference in the logarithms of the calculated and experimental activity coefficients (or a closely related quantity) is used because

this reduces or eliminates the effect of any uncertainty in the normalization of the activity coefficients.*

Let us assume that the data are given in the form of the partial pressures $p_i = py_i$ of the components in the vapor phase in equilibrium with the liquid of mole fraction x_i . Thus, the chemical potential of component i is

$$\mu_i = \mu_i^*(T) + RT \ln (p_i \phi_i), \quad (2)$$

where ϕ_i is the vapor-phase fugacity coefficient of component i .

Equation 1 becomes

$$x_1 d \ln (p_1 \phi_1) + x_2 d \ln (p_2 \phi_2) = \frac{\tilde{V}}{RT} dp. \quad (3)$$

This can be written in the equivalent form

$$x_1 d \ln \left(\frac{p_1 \phi_1}{f_1^o x_1} \right) + x_2 d \ln \left(\frac{p_2 \phi_2}{f_2^o x_2} \right) = \frac{\tilde{V}}{RT} dp, \quad (4)$$

where f_1^o and f_2^o are independent of pressure and composition.

The introduction of f_1^o and f_2^o is solely for convenience; by suitable selection of their values, the quantities in parentheses in equation 4 have a magnitude near unity and are, in essence, activity

*The term, secondary reference state, refers to this normalization and is synonymous with standard state. These terms are to be distinguished from the primary reference state, which relates to the condition defining the level from which the chemical potential is measured at other conditions of temperature, pressure, composition, and chemical form (if the primary reference state refers to the elements).

coefficients. One common convention is to set f_1^0 and f_2^0 equal to the vapor pressures of the pure components,* but in dilute solutions it is common to set f_2^0 equal to Henry's constant for component 2 in a solvent of component 1. It should be clear from the subsequent development that the choice of the values of f_1^0 and f_2^0 has no bearing on the outcome of the test of thermodynamic consistency. This is as it should be, since it should be possible to test data for consistency over a composition range which does not include any natural secondary reference state. (For example, for aqueous sulfuric acid solutions below 0°C, the vapor pressure or the freezing point provides a measure of the chemical potential of the solvent, and the electric potential of a lead-acid cell depends also on the chemical potential of the solute. However, pure H_2SO_4 seems far removed from the conditions of the system, and an infinitely dilute solution doesn't exist since the solvent freezes.) Furthermore, Van Ness et al. (1973) have criticized some integral consistency tests because of their sensitivity to values used for the vapor pressures of the pure components.

Next integrate equation 4, integrating the two terms on the left by parts, to obtain

$$x_1 \ln \left(\frac{p_1 \phi_1}{f_1^0 x_1} \right) + x_2 \ln \left(\frac{p_2 \phi_2}{f_2^0 x_2} \right) - \int^p \frac{\tilde{v}}{RT} dp + \int^{x_2} \ln \left(\frac{p_1 \phi_1 f_2^0 x_2}{p_2 \phi_2 f_1^0 x_1} \right) dx_2 = \text{constant} = C(x_2) \quad (5)$$

* Strictly speaking, the vapor pressure of the pure component should be multiplied by the fugacity coefficient of the pure equilibrium vapor.

This quantity should be a constant; we designate by $C(x_2)$ the evaluation of the left side of the equation from experimental data. (The lower limits of the integrals should be fixed but can be selected arbitrarily or for convenience.) A graph of C versus x_2 will be a horizontal line for consistent data. The data are also thermodynamically consistent over any composition range where C is constant. A step in the graph can be due to a change in the calibration base from one composition range to another (possibly due to data from two different sources for one component). A single bad data point will show up as a bad point on the graph, and it will also produce a step whose magnitude depends on the value of dx_2 associated with the bad point in the integration. A gradual but significant drift in C indicates a systematic error, and random deviations about a constant value suggest the magnitude of the experimental reproducibility. An error in the estimation of the fugacity coefficients (or of the liquid molar volume) would make excellent vapor-liquid equilibrium data appear to be inconsistent.

The consistency test of Redlich and Kister (1948) follows directly from equation 5. First, let the lower limits of integration correspond to $x_2 = 0$. The second term is thus zero, as well as the integrals, at $x_2 = 0$, and the first term will also be zero if one assumes that f_1^0 is the vapor pressure of pure component 1 and the fugacity component of pure component 1 is unity, or alternatively if one assumes that f_1^0 is the product of the vapor pressure and the fugacity coefficient of the pure equilibrium vapor. The constant $C(x_2)$ is now equal to

zero. Evaluation of $C(1)$, with similar assumptions for f_2^0 , yields

$$C(1) - C(0) = 0 = - \int_{x_2=0}^{x_2=1} \frac{\tilde{V}}{RT} dp + \int_0^1 \ln \left(\frac{p_1 \phi_1 f_2^0 x_2}{p_2 \phi_2 f_1^0 x_1} \right) dx_2 . \quad (6)$$

This is equivalent to the requirement of Redlich and Kister,

$$\int_0^1 \ln (\gamma_1/\gamma_2) dx_2 = 0 , \quad (7)$$

and the integral over pressure in equation 6 can be regarded as the result of the Poynting corrections so that the activity coefficients in equation 7 are at constant pressure as well as constant temperature.

Equation 5 has two significant advantages over equation 6 or 7. It can be applied and permit evaluation of consistency over any composition range for which data are available for both components, and the secondary-reference-state quantities f_1^0 and f_2^0 cancel and will not influence the constancy of the quantity $C(x_2)$ in equation 5. For example, a set of inconsistent data could appear consistent by equations 6 and 7 if the inconsistency integrates to zero over the composition range from zero to one. Also, a set of consistent data could appear inconsistent by equations 6 and 7 through an inadvertent choice of f_1^0 and f_2^0 . As Van Ness *et al.* state, this test places too much burden on values of p_i at the end points -- values which sometimes are obtained by interpolation of pure vapor pressures from the literature and which therefore are not part of the data set proper.

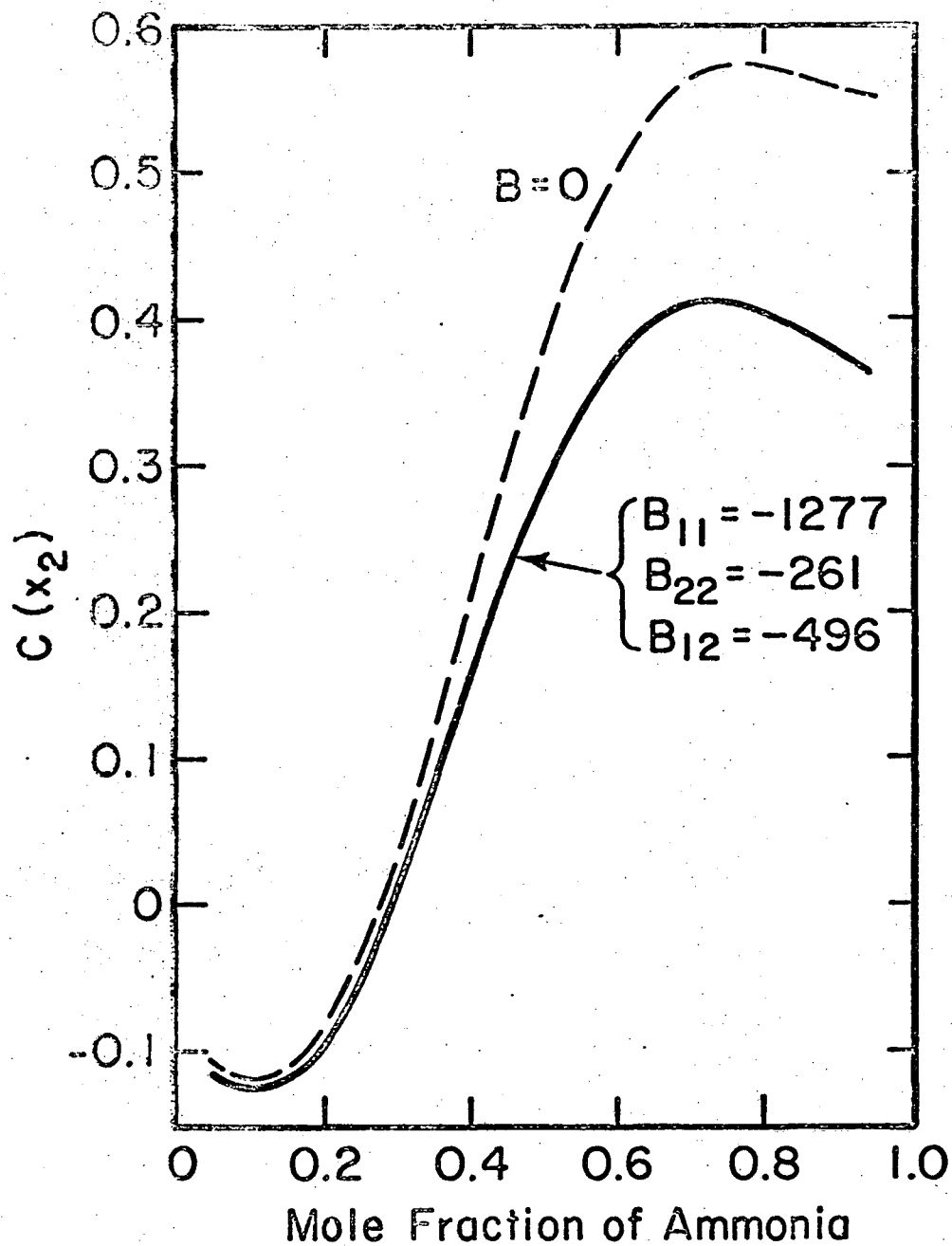
Chueh et al. (1965) present a test very similar to the one discussed here, and their method should be advocated more widely for low pressures as well as high pressures. However, the composition range is unnecessarily restricted by the use of $x_2 = 0$ for the lower limit on the integrals in equation 5, and an unnecessary dependence on a secondary reference state is introduced. In the interpretation, a percent deviation of the integral and nonintegral parts of equation 5 is less meaningful than the absolute variation of C with x_2 .

Ammonia-Water System

Let us now examine the data of Wilson (1925) for the ammonia-water system at 80°F (26.67°C). Figure 1 shows C plotted against x_2 , the mole fraction of ammonia. In evaluating C , the partial molar volumes of ammonia and water in the liquid phase were taken to be constant. The corresponding term, the first integral in equation 5, amounts to only 0.0084 over the concentration range from $x_2 = 0.05$ to $x_2 = 0.95$, within which the pressure rises from 0.1 to 10 bar. The effect of this term is to lower the ordinate more for higher mole fractions of ammonia.

For the dashed curve in figure 1, the fugacity coefficients were set equal to unity in equation 5. For the solid curve, the fugacity coefficients were calculated by means of the second virial coefficients according to the formula

$$RT \ln \phi_2 = p_2(2 - y_2)B_{22} + p_1 y_1(2B_{12} - B_{11}) \quad (8)$$



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Figure 1. Thermodynamic consistency function for water-ammonia data at 80°F (26.67°C). Liquid-phase partial molar volumes are taken to be 23.8 cm³/mol for ammonia and 18.2 for water.

Second virial coefficients of water and ammonia, taken from the compilation of Dymond and Smith (1969), were divided by the molar volumes at the critical points and plotted against the ratio of the temperature to the critical temperature. At the system temperature, the second virial coefficients were estimated to be $B_{11} = -1277$ for water and $B_{22} = -261 \text{ cm}^3/\text{mol}$ for ammonia. The same graph was used to estimate the cross virial coefficient B_{12} to be $-496 \text{ cm}^3/\text{mole}$ by using for the critical temperature the geometric mean of the values for ammonia and water and basing the critical molar volume on an arithmetic average of the cube roots of the values for ammonia and water (Prausnitz, 1969, p. 129). While this is a generally accepted procedure, the method is hardly considered reliable for polar substances like ammonia and water. The value of the second virial coefficient for water is also uncertain because the reduced temperature is low. However, changing the value to $-1000 \text{ cm}^3/\text{mol}$ has a negligible effect on the shape of the curve in figure 1 because the partial pressure of water is small over the entire composition range.

The curves in figure 1 show first the importance of fugacity-coefficient corrections in this system -- due to the moderately high pressures attained. Secondly, the curves suggest that the data are inconsistent. A possible source of error is the partial pressure of water in the vapor phase. The error appears to be gradual, but let us note that if the value of p_1 were too high by a factor of 2 for values of x_2 greater than 0.4, while being correct for values of x_2 less than 0.4, then the C curve would have a vertical step of 0.416 units at $x_2 = 0.4$.

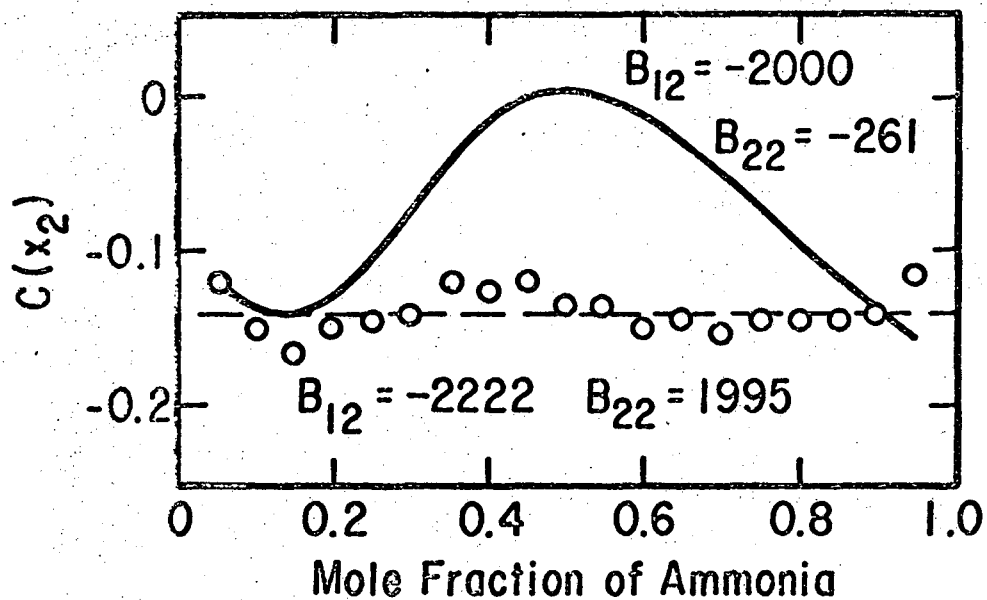
If one truly believed in the accuracy of the data, he would use the redundant data to calculate fugacity coefficients instead of testing for thermodynamic consistency. For example, the Gibbs-Duhem equation for the vapor phase, at constant temperature, reads

$$y_1 d \ln \phi_1 + y_2 d \ln \phi_2 = (Z - 1) d \ln p, \quad (9)$$

where Z is the compressibility factor ($p\tilde{V}/RT$) for the vapor phase. This could be substituted into equation 4 to eliminate the fugacity coefficient ϕ_2 . However, this procedure introduces the volumetric deviation $Z - 1$ from ideal-gas behavior, and volumetric data would be required in using the resulting equation to evaluate the variation of ϕ_1 from vapor-liquid equilibrium data. Furthermore, $Z - 1$, $\ln \phi_1$, and $\ln \phi_2$ are of the same magnitude and are intimately interrelated through the nonideal-gas behavior.

Consequently, a simpler alternative is to assume that virial coefficients beyond the second can be ignored and to regard B_{11} , B_{12} , and B_{22} as adjustable quantities whose values can be selected so as to fit best the data at hand. Since B_{11} and B_{22} are frequently known from volumetric measurements on the pure components, adjustments may be restricted to B_{12} . Literature values for B_{12} occasionally come by this route (rather than by means of volumetric data on vapor mixtures of components 1 and 2), particularly when one component is sparingly soluble in the liquid (Prausnitz, 1969, p. 171).

As shown by the solid curve in figure 2, a value of $B_{12} = -2000$ cm^3/mol considerably reduces the apparent departures from thermodynamic



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Figure 2. Effect of adjustment of cross virial coefficient B_{12} (solid curve) and of both B_{12} and the ammonia virial coefficient B_{22} (dashed line and data points).

consistency, although a systematic variation of C is still observed. This quite negative value of B_{12} points to a chemical reaction in the vapor phase such as



so that the apparent number of moles is reduced below the stoichiometric number.

The dashed line and the data points on figure 2 come from adjusting both B_{12} and B_{22} . (B_{11} was not changed from its value of $-1277 \text{ cm}^3/\text{mol}$ since it has a negligible effect on the results.) Systematic deviations are further reduced, and random deviations are beginning to show up. However, the value used for B_{22} is now $+1995 \text{ cm}^3/\text{mol}$, and this must be regarded as unreasonable in view of the direct experimental data on B_{22} and similar data on any pure component. We therefore conclude that the data show significant departures from thermodynamic consistency, at least those shown by the solid curve in figure 2, and that the value of B_{12} may be much more negative than we would predict.

Scatchard et al. (1947) present many thermodynamic properties for the ammonia-water system. However, they chose to calculate the amount of water in the vapor phase from the total pressure by means of the Gibbs-Duhem equation, saying that this method would be more accurate than the available experimental data. Consequently, their values for total pressure and vapor composition show excellent thermodynamic consistency (except for the first point) when we follow

Scatchard et al. and take B_{12} to be the arithmetic average of B_{11} and B_{22} .

Subsequently, Macriss et al. (1964) reported that ammonia-water refrigerators have been over or under designed depending on whether experimental vapor-liquid data or the calculated values of Scatchard et al. were used. Based on new dewpoint measurements of their own, Macriss et al. have revised the tables of thermodynamic properties. A value of $B_{12} = -1700 \text{ cm}^3/\text{mol}$ reduces the systematic variation when their vapor-liquid equilibrium tables are submitted to a thermodynamic consistency test, but there is still a variation of 0.16 in C.

Conclusions

An integral test can be used to evaluate the thermodynamic consistency of redundant vapor-liquid data over a limited composition range. Data at as few as two compositions can be tested. A definitive test requires an accurate method of estimating the fugacity coefficients.

Application of the test to ammonia-water data suggests that the data contain serious errors and also that the second cross virial coefficient B_{12} takes on a quite negative value characteristic of association of ammonia and water in the vapor phase.

Acknowledgment

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Notation

- B_{ij} second virial coefficient related to interactions between components i and j , cm^3/mol
- C thermodynamic consistency function
- f_i^0 fugacity of component i in the secondary reference state for the liquid phase -- or more generally, a quantity depending only on temperature, bar
- p total pressure, bar
- p_i partial pressure of component i in the vapor phase, bar
- R universal gas constant, $8.3143 \text{ J/mol-deg K}$
- T absolute temperature, deg K
- \tilde{V} molar volume (generally of liquid phase), cm^3/mol
- x_i mole fraction of component i in the liquid phase
- y_i mole fraction of component i in the vapor phase
- Z compressibility factor

Greek Letters

- γ_i liquid-phase activity coefficient of component i
- μ_i chemical potential of component i , J/mol
- μ_i^* chemical potential of component i in the ideal-gas secondary reference state, J/mol
- ϕ_i fugacity coefficient of component i in the vapor phase

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