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Molecular Thermodynamics of Fluid-Phase Equilibria

Third Edition

International Series
in the Physical and Chemical
Engineering Sciences

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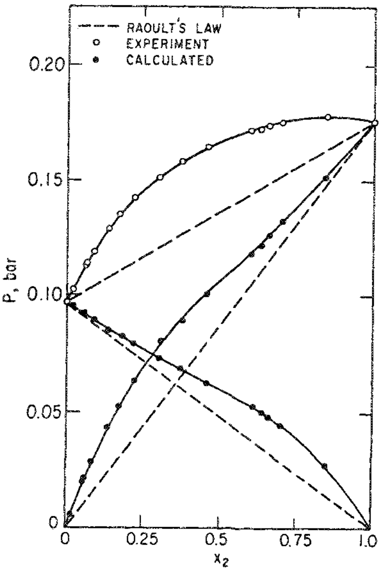

Figure 6-9 Total and partial pressures of toluene (1)/2,3-butanedione (2) at 45°C.

From P-x measurements for 14 binary systems at 30°C, constants A', B', and D' were obtained; results are shown in Table 6-4. The 14 systems represent a wide variety with some systems showing strong positive deviations from Raoult's law ($g^E > 0$) and others showing strong negative deviations ($g^E < 0$). One system (No. 6) exhibits ideal behavior.

Table 6-4 Excess Gibbs energy from P-x measurements at 30°C.* [Constants in Eq. (6-82)].

System (1)/(2)	A'	B'	D'
1. Carbon tetrachloride/THF†	-0.25704	-0.18188	0.04760
2. Chloroform/THF	-1.39352	-1.58092	0.58606
3. Dichloromethane/THF	-0.93341	0.87287	0.22232
4. Carbon tetrachloride/furan	0.28639	0.27034	0.01189
5. Chloroform/furan	-0.08350	-0.11890	0.02847
6. Dichloromethane/furan	0	0	0
7. THF/furan	-0.39970	-0.37125	-0.06410
8. Dichloromethane/methyl acetate	-0.42260	-0.63028	0.27851
9. Dichloromethane/acetone	0.58905	-0.76638	-0.11940
10. Dichloromethane/1,4-dioxane	-0.63128	-0.95516	-0.06863
11. Chloroform/1,4-dioxane	-0.75571	-1.58181	0.12739
12. Pyridine/acetone	0.19441	0.20447	0.02998
13. Pyridine/chloroform	-1.16104	-0.70714	0.37199
14. Pyridine/dichloromethane	-0.57919	-0.44873	0.03523

* Byer *et al.* (1973); † THF = tetrahydrofuran.

Figure 6-10 indicates a particularly convenient way to illustrate the nonidealities of the 14 systems; the coordinates of the plot are suggested by the Redlich-Kister expansion [Eq. (6-52)]: for simple mixtures, the plot gives a straight horizontal line; for slightly complex mixtures, the line is straight but not horizontal; and for complex mixtures, the line is curved. These three cases correspond, respectively, to those shown in Figs. 6-5, 6-6, and 6-7.

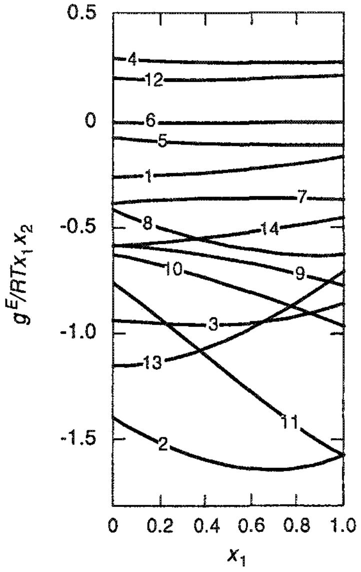

Figure 6-10 Excess Gibbs energies for 14 binary systems listed in Table 6-4.

6.8 Partial Pressures from Isobaric Boiling-Point Data

As indicated in the preceding section, the Gibbs-Duhem equation can be used to convert isothermal P-x data for a binary system into y-x data; similarly, it can be used to convert isobaric T-x data into y-x data. However, the latter calculation is often less useful because the Gibbs-Duhem equation for an isobaric, nonisothermal system (see App. D) contains a correction term proportional to the enthalpy of mixing and this correction term is not always negligible. The isothermal, nonisobaric Gibbs-Duhem equation also contains a correction term (that is proportional to the volume change on mixing), but in mixtures of two liquids at low pressures this term may safely be neglected.

Rigorous reduction of isobaric T-x data, therefore, requires data for the enthalpy of mixing at the boiling point of the solution. Such data are almost never at hand and if the object of a particular study is to obtain accurate isobaric y-x data, then it is usually easier to measure the y-x data directly in an equilibrium still than to obtain enthalpy-of-mixing data in addition to the T-x data. However, for approximate results, sufficient for some practical applications, boiling-point determinations may be useful because of experimental simplicity; it is a simple matter to place a liquid mixture in a manostated flask and to measure the boiling temperature. We now discuss briefly how isobaric T-x data may be reduced to yield an isobaric y-x diagram.

We assume that in the Gibbs-Duhem equation the correction term for nonisothermal conditions may be neglected. Further, we assume for simplicity that the gas phase is ideal and that the two-suffix Margules equation is adequate for the relation between activity coefficient and mole fraction:

$$RT \ln \gamma_1 = A x_2^2 \tag{6-83}$$

We assume that A is a constant independent of temperature, pressure, and composition. The Gibbs-Duhem equation then gives

$$RT \ln \gamma_2 = A x_1^2 \tag{6-84}$$

The problem now is to find parameter A from the T-x data. Once A is known, it is a simple matter to calculate the y-x diagram. To be consistent with the approximate nature of this calculation, we here use the simplified definition of the activity coefficient as given by Eq. (6-70).

To find A, we write

$$P = \text{constant} = x_1 P_1^s \exp\left(\frac{A}{RT} x_2^2\right) + x_2 P_2^s \exp\left(\frac{A}{RT} x_1^2\right) \tag{6-85}$$

From the T-x data and from the vapor-pressure curves of the pure components, everything in Eq. (6-85) is known except A. Unfortunately, Eq. (6-85) is not explicit in A but for any point on the T-x diagram, a value of A may be found by trial and error. Thus, in principle, the boiling point for one particular mixture of known composition is sufficient to determine A. However, to obtain a more representative value, it is preferable to measure boiling points for several compositions of the mixture, to calculate a value for A for each boiling point, and then either to use an optimum average value in the subsequent calculations or, if the data warrant doing so, to reject Eqs. (6-83) and (6-84) and, instead, to use a two- (or three-) parameter equation for relating activity coefficients to composition.

To illustrate, we consider boiling-point data for the diisopropyl ether/2-propanol system obtained at atmospheric pressure. Table 6-5 gives experimental boiling points. From Eq. (6-85) we find an average value of $A = (3.18 \pm 0.13)$ kJ mol^{-1}. When this average value is used, a y-x diagram is obtained, as shown by the line in Fig. 6-11. The points represent the experimental y-x data of Miller and Bliss (1940). In this case, agreement between the observed and calculated *y*-*x* diagram is good, but one should not assume that this will always be the case.

Table 6-5 Boiling points of diisopropyl ether/2-propanol mixtures at 1.013 bar.*

Mol % ether in liquid	Temperature (°C)	Mol % ether in liquid	Temperature (°C)
0	82.30	58.4	66.77
8.4	76.02	73.2	66.20
18.0	72.48	75.4	66.18
28.2	69.93	84.6	66.31
38.5	68.18	89.1	66.33
43.6	67.79	91.8	66.77
47.7	67.56	98.9	67.73
52.0	67.19	100.0	68.50

* Miller and Bliss (1940).

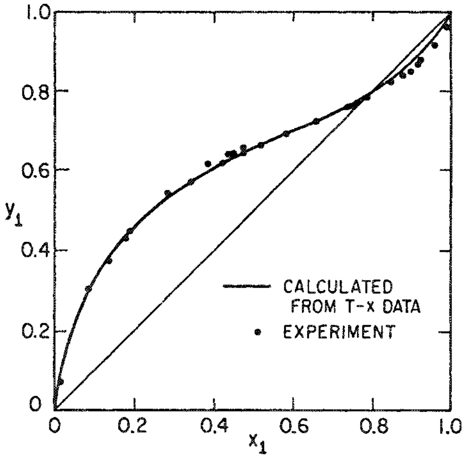

Figure 6-11 Vapor-liquid equilibrium for the diisopropyl ether (1)/2-propanol (2) system at 1.013 bar.

The method outlined above is rough and we can make many refinements; for example, we may use additional coefficients in the expressions for the activity coefficients or we may correct for vapor-phase nonideality (Adler and Adler, 1973). But these refinements are frequently not worthwhile when the temperature correction in the Gibbs-Duhem equation is neglected. It appears to be unavoidable that, unless the enthalpy of mixing can be estimated with at least fair accuracy, the boiling-point method for obtaining the *y*-*x* diagram is necessarily an approximation.

Techniques for estimating the isothermal or isobaric *y-x* diagram with the help of the Gibbs-Duhem equation have received a large amount of attention in the literature and many variations on this theme have been proposed. One particularly popular topic is concerned with the use of azeotropic data; if a binary system has an azeotrope, and if we know its composition, temperature, and pressure, we can compute the two constants of any two-constant equation for the activity coefficients and thereby calculate the entire *x-y* diagram (Miller and Bliss, 1940). This method assumes validity of the isothermal, isobaric Gibbs-Duhem equation. Good results are often obtained provided that the azeotropic mole fraction is in the interval 0.3 to 0.7.

While Van Ness (Byer *et al.*, 1973; Abbott and Van Ness, 1975) has stressed the relation between experimental *P-x* data and the Gibbs-Duhem equation, an interesting variation has been proposed by Christian *et al.* (1960), who describes apparatus and calculations for measuring *P-y* rather than *P-x* data to obtain the *y-x* diagram. A method for computing equilibrium phase compositions from dew point (*T-y*) data has been given by Bellemans (1959), and calculations using (*P-x*) data for ternary systems have been described by McDermott and Ellis (1965). All of these techniques have but one aim: To reduce the experimental effort needed to characterize liquid-mixture properties. Such techniques are useful but they have one serious limitation: Results obtained by data reduction with the Gibbs-Duhem equation cannot be checked for thermodynamic consistency because the method of calculation already forces the results to be thermodynamically consistent. Thus the Gibbs-Duhem equation may be used either to extend limited data or to test more complete data, but not both. In the next section we briefly discuss the basic principles for performing such tests.

6.9 Testing Equilibrium Data for Thermodynamic Consistency

The Gibbs-Duhem equation interrelates activity coefficients of all components in a mixture. Therefore, if data are available for all activity coefficients, these data should obey the Gibbs-Duhem equation; if they do not, the data cannot be correct. If they do obey the Gibbs-Duhem equation, the data are probably, although not necessarily, correct; it is conceivable that a given set of incorrect data may fortuitously satisfy the Gibbs-Duhem equation, but this is not likely. Unfortunately, there are many phase-equilibrium data in the literature that do not satisfy the Gibbs-Duhem equation and therefore must be incorrect.

To illustrate, we consider the simplest case: a binary solution of two liquids at low pressure for which isothermal activity-coefficient data have been obtained. For this case, the Gibbs-Duhem equation is Eq. (6-59).

A theoretically simple technique is to test the data directly with Eq. (6-59); that is, plots are prepared of $\ln\gamma_1$ versus x_1 and $\ln\gamma_2$ versus x_2 and slopes are measured. These slopes are then substituted into Eq. (6-59) at various compositions to see if the Gibbs-Duhem equation is satisfied. While this test appears to be both simple and exact, it is of little practical value; because experimental data inevitably exhibit some scatter, it is difficult to measure slopes with sufficient accuracy. Hence the "slope method" provides at best a rough measure of thermodynamic consistency that can only be applied in a semiquantitative manner. For example, if, at a given composition, $d\ln\gamma_1 / dx_1$ is positive, then $d\ln\gamma_2 / dx_2$ must also be positive, and if $d\ln\gamma_1 / dx_1$ is zero, $d\ln\gamma_2 / dx_2$ must also be zero. The slope method can therefore be used easily to detect serious errors in the equilibrium data.

For quantitative purposes it is much easier to use an integral rather than a differential (slope) test. While integral tests are popular and used often, unfortunately, they do not provide a stringent criterion for thermodynamic consistency. The most widely used integral test was proposed by Redlich and Kister (1948) and also by Herington (1947) and is derived below.

The molar excess Gibbs energy is related to activity coefficients by

$$\frac{g^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 \tag{6-86}$$

Differentiating with respect to x_1 at constant temperature and pressure gives

$$\frac{d(g^E / RT)}{dx_1} = x_1 \frac{\partial \ln\gamma_1}{\partial x_1} + \ln\gamma_1 + x_2 \frac{\partial \ln\gamma_2}{\partial x_1} + \ln\gamma_2 \frac{dx_2}{dx_1} \tag{6-87}$$

Noting that $dx_1 = -dx_2$ and substituting the Gibbs-Duhem equation [Eq. (6-59)], we obtain

$$\frac{d(g^E / RT)}{dx_1} = \ln\frac{\gamma_1}{\gamma_2} \tag{6-88}$$

Integration with respect to x_1 gives

$$\int_0^1 \frac{d(g^E / RT)}{dx_1} dx_1 = \int_0^1 \ln\frac{\gamma_1}{\gamma_2} dx_1 = \frac{g^E}{RT}(\text{at } x_1 = 1) - \frac{g^E}{RT}(\text{at } x_1 = 0) \tag{6-89}$$

If the pure liquids at the temperature of the mixture are used as the standard states,

$$\begin{aligned} \ln\gamma_1 &\to 0 \quad \text{as} \quad x_1 \to 1 \\ \ln\gamma_2 &\to 0 \quad \text{as} \quad x_1 \to 0 \end{aligned} \tag{6-90}$$

and

$$\begin{aligned} &\frac{g^E}{RT}(\text{at } x_1 = 1) = 0 \\ &\frac{g^E}{RT}(\text{at } x_1 = 0) = 0 \end{aligned} \tag{6-91}$$