Thermodynamic Consistency Test for Multicomponent Solutions

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In 1947 Herington (*1*) proposed a simple graphical method for testing the thermodynamic consistency of vapor-liquid equilibrium data for binary systems. Very shortly thereafter Redlich and Kister (*4*) independently proposed the same method. This convenient graphical test for thermodynamic consistency has won wide acceptance, and it is utilized with increasing frequency by workers in the field of phase equilibria.

Some years ago Herington showed how his consistency test might be applied to a ternary system (*2*, *3*). The purpose of this work is to show how the Herington-Redlich-Kister method may be generalized for application to a system of any number of components.

For a given solution the general technique of the consistency test is to plot a particular function of the activity coefficients of all the components in that solution against the mole fraction of one of the components. If the thermodynamic data are consistent, then the area under the resulting curve is equal to the excess free energy of a solution containing one component less than the number of components in the solution being tested. In the case of a binary the data for the two-component solution are related to the excess free energy of a one-component solution which is zero. In the general case data for a solution of n components are related to the excess free energy of a solution of $n - 1$ components.

A liquid-phase solution of n components is considered. The excess free energy for the solution is related to the activity coefficients by

$$\frac{\Delta G^E}{RT} = \sum_{i=1}^{n} x_i \ln \gamma_i \qquad (1)$$

M_i is defined by

$$M_i = \frac{x_i}{x_1} \qquad (2)$$

For a solution of n components $n - 2$ such parameters are required for components $i = 2$ to $i = n - 1$. In the discussion all M_i are constants, although not necessarily equal to one another.

Substituting (2) into (1) and noting that

$$x_n = 1 - x_1(1 + M_2 + M_3 + \cdots M_{n-1})$$

one obtains

$$\begin{aligned} \frac{\Delta G^E}{RT} &= x_1 \ln \gamma_1 + x_1 M_2 \ln \gamma_2 \\ &\quad + x_1 M_3 \ln \gamma_3 \\ &\quad + \cdots x_1 M_{n-1} \ln \gamma_{n-1} \qquad (3) \\ &\quad + [1 - x_1(1 + M_2 \\ &\quad + M_3 + \cdots M_{n-1})] \ln \gamma_n \end{aligned}$$

When Equation (3) is differentiated at constant temperature and pressure holding all M constant

$$\begin{aligned} &\frac{1}{RT}\left(\frac{\partial \Delta G^E}{\partial x_1}\right)_{T,P,M_i} \\ &= x_1 \frac{\partial \ln \gamma_1}{\partial x_1} + \ln \gamma_1 \\ &\quad + x_1 M_2 \frac{\partial \ln \gamma_2}{\partial x_1} \\ &\quad + M_2 \ln \gamma_2 + \cdots \\ &\quad + x_1 M_{n-1} \frac{\partial \ln \gamma_{n-1}}{\partial x_1} \qquad (4) \\ &\quad + M_{n-1} \ln \gamma_{n-1} \\ &\quad + [1 - x_1(1 + M_2 + M_3 \\ &\quad + \cdots M_{n-1})] \frac{\partial \ln \gamma_n}{\partial x_1} \\ &\quad - [1 + M_2 + M_3 \\ &\quad + \cdots M_{n-1}] \ln \gamma_n \end{aligned}$$

At constant temperature and pressure the Gibbs-Duhem equation is

$$\sum_{i=1}^{n} x_i \frac{\partial \ln \gamma_i}{\partial x_1} = 0 \qquad (5)$$

When one substitutes (5) into (4)

$$\begin{aligned} &\frac{1}{RT}\left(\frac{\partial \Delta G^E}{\partial x_1}\right)_{T,P,M_i} \\ &\quad = \ln \gamma_1 + M_2 \ln \gamma_2 \\ &\quad + M_3 \ln \gamma_3 \\ &\quad + \cdots M_{n-1} \ln \gamma_{n-1} \\ &\quad - (1 + M_2 + M_3 \qquad (6) \\ &\quad + \cdots M_{n-1}) \ln \gamma_n \\ &= \ln \gamma_1/\gamma_n \\ &\quad + M_2 \ln \gamma_2/\gamma_n \\ &\quad + M_3 \ln \gamma_3/\gamma_n \\ &\quad + \cdots M_{n-1} \ln \frac{\gamma_{n-1}}{\gamma_n} \end{aligned}$$

Equation (6) is now integrated with respect to x_1 holding all M constant. The integration is performed from $x_1 = 0$ to

$$x_1 = \frac{1}{1 + \sum_{i=2}^{n-1} M_i}$$

At constant M, when $x_1 = 0$, $x_n = 1$ and the solution consists of pure component n. At $x_1 = 0$ therefore $\Delta G^E = 0$.

When

$$x_1 = \frac{1}{\left(1 + \sum_{i=2}^{n-1} M_i\right)}$$

$x_n = 0$ and the solution of n components is in the special state where it contains only $n - 1$ components. When $x_n = 0$, ΔG^E is given by

$$\frac{\Delta G^E}{RT} = \sum_{i=1}^{n-1} x_i \ln \gamma_i = \text{function of a solution containing } n-1 \text{ components} \qquad (7)$$

Equation (6) therefore becomes

$$\sum_{i=1}^{n-1} x_i \ln \gamma_i = \int_0^{1/(1+\sum_{i=2}^{n-1} M_i)} \left[\ln \frac{\gamma_1}{\gamma_n} + M_2 \ln \frac{\gamma_2}{\gamma_n} + M_3 \ln \frac{\gamma_3}{\gamma_n} + \cdots M_{n-1} \ln \frac{\gamma_{n-1}}{\gamma_n} \right] dx_1 \qquad (8)$$

The consistency test is carried out by the arbitrary selection of a set of parameters and the numerical (or graphical) evaluation of the integral in Equation (8) with activity-coefficient data for the solution of n components utilized. This integral must then be equal to the excess free energy of a solution of $n - 1$ components having the composition

$$x_1 = \frac{1}{1 + \sum_{i=2}^{n-1} M_i} \; ; \quad x_2 = M_2 x_1 \; ;$$

$$\cdot x_3 = M_3 x_1 \; ; \cdots x_{n-1} = M_{n-1} x_1$$

If this equality is met, the data tested are thermodynamically consistent. To cover a large section of the data it will of course be necessary to repeat the calculation several times with new sets of parameters each time. For a system of many components the calculations are necessarily quite tedious. However the form of this consistency test is very well suited for programming on an electronic computer.

NOTATION

ΔG^E = excess free energy
M = parameter defined by Equation (2)
n = number of components in solution
R = gas constant
T = absolute temperature
x = mole fraction in the liquid phase
γ = activity coefficient

Subscript

i = component i
$1,2 \cdots n$ = component $1,2 \cdots n$

LITERATURE CITED

1. Herington, E. F. G., *Nature*, **160**, 610 (1947).
2. ———, *Research*, **3**, 41 (1950).
3. ———, *J. Appl. Chem.*, **2**, 11 (1952).
4. Redlich, Otto, and A. T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).

ERRATA

Vapor-Liquid Equilibria and Heat of Mixing: n-Octane-Ethylbenzene-Cellosolve System. P. S. Murti and Matthew Van Winkle.

Figure 4 of the above paper is in error. The corrected plot is presented below.
This article appeared on page 517 of the December, 1957, issue of the Journal.

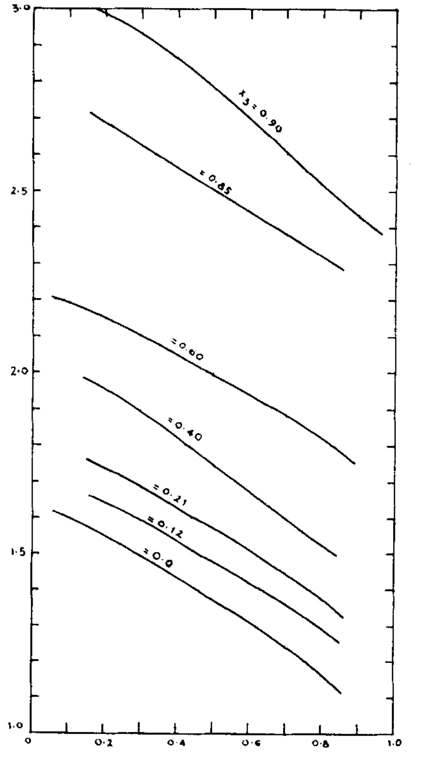

Fig. 4. Relative volatility parameter: mole fraction Cellosolve in ternary mixtures

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Liquid-Side Mass Transfer Coefficients in Packed Towers. Kakusaburo Onda, Eizô Sada, and Yasuhiro Murase.

Equation (3) of the above paper is in error. It should read

$$a_w/a_t = 1 - 1.02e^{-0.278(L/a_t\mu)^{0.4}}$$

This article appeared on page 235 of the June, 1959, issue of the Journal.

(*Continued from page 276.*)

Fluid Dynamics and Heat Transfer, James G. Knudsen and Donald L. Katz, McGraw-Hill Book Company, Inc., New York (1958). 576 pages. $12.50.

The need for solving problems concerned with fluid heat transfer has always faced many engineers. In the past, because of the complex nature of fluids in motion, solutions to these problems have been found by an approach which was basically empirical. One illustration of this approach is an early edition of McAdams's comprehensive book "Heat Transmission." However there has been a growing awareness that fluid heat transfer could best be understood by first understanding the

(*Continued on page 9S.*)