Isothermal Enthalpy Difference for Saturated Liquid Mixture Via Isobaric Gibbs-Duhem Equation

BYUNG-IK LEE and WAYNE C. EDMISTER

Oklahoma State University, Stillwater, Oklahoma

The possibility of calculating the isothermal enthalpy difference for a saturated liquid mixture by applying the isobaric Gibbs-Duhem equation is attractive, until one has tried it. After working with this calculation for some time, we have experienced some difficulties and write this paper to share our experience with others who might be intrigued, as we once were, with this enthalpy calculation method.

Recent publications (*5*, *6*) have suggested the isobaric Gibbs-Duhem equation as a rigorous method for calculating the heats of vaporization of a mixture and then demonstrated the calculation via simplifying and nonrigorous assumptions.

For engineering design applications, the chemical engineer needs an analytical, as well as rigorous, method for calculating the enthalpies of coexisting equilibrium vapor and liquid mixtures. In other words, graphical differentiations and simplifying assumptions are not acceptable. From this point of view we looked at this method.

ISOBARIC GIBBS-DUHEM EQUATION

An exact and general form of the Gibbs-Duhem equation was derived by Van Ness (*7*). The isobaric form

$$\sum_1^n z_i(d\ln f_i/dT)_P = (H^o - H)/RT^2 \tag{1}$$

can be used to predict the isothermal enthalpy difference for a saturated vapor or saturated liquid mixture from temperature-composition data and the isobaric temperature derivative of log-fugacity.

Two other fugacity-enthalpy relationships of interest are

$$(\partial \ln f_i/\partial T)_{P,z} = (H_i^o - \overline{H}_i)/RT^2 \tag{2}$$

and

$$\sum_1^n z_i(\partial \ln f_i/\partial T)_{P,z} = (H^o - H)/RT^2 \tag{3}$$

Equations (1) and (3) differ in one small, but important detail; in Equation (1) the path of the derivative is an equilibrium isobar, while in Equation (3) the temperature derivative is at constant pressure and composition (liquid or vapor).

From a comparison of Equations (1) and (3) it is evident that

$$\sum_1^n z(d\ln f_i/dT)_P = \sum_1^n z(\partial \ln f_i/\partial T)_{P,z} \tag{4}$$

while:

$$(d\ln f_i/dT)_P \neq (\partial \ln f_i/\partial T)_{P,z}$$

In other words the derivative at constant pressure and composition equals minus the partial enthalpy difference divided by RT^2 while the derivation at constant pressure does not. This distinction is important in the present work.

The isobaric temperature derivative of log-fugacity can be evaluated graphically from plots of calculated $\ln f_i$ vs. temperature or it can be evaluated analytically. In both cases an equation of state is used, with the temperature-composition data, via a digital computer to find $\ln f_i$ or its temperature derivative. In view of this, the two methods should be equivalent in accuracy. For a few research type of calculations, the graphical differentiation of computed $\ln f_i$ values is an acceptable procedure. For repetitive applications, as in design work, analytical differentiation via a digital computer is the only acceptable technique and this is the method used in our work.

DERIVATIVES OF FUGACITY

The temperature derivatives of $\ln f_i$ that appear in Equation (1) were evaluated by using an equation-of-state and temperature-composition data. An expression for $(d\ln f_i/dT)_P$ will be derived from the definition of the fugacity coefficient, ϕ, that is $f_i = \phi_i P y_i$. Defining $\ln \phi_i$ as a function of P, T and y leads to the following

$$\left(\frac{d\ln\phi_i}{dT}\right)_P = \left(\frac{\partial\ln\phi_i}{\partial T}\right)_{P,y} + \left(\frac{\partial\ln\phi_i}{\partial y_i}\right)\left(\frac{dy_i}{dT}\right)_P + \left(\frac{\partial\ln\phi_i}{\partial y_j}\right)\left(\frac{dy_j}{dT}\right)_P + \cdots \cdots + \left(\frac{\partial\ln\phi_i}{\partial y_n}\right)\left(\frac{dy_n}{dT}\right)_P \tag{5}$$

By combining Equation (5) with $(d\ln f_i/dT)_P = (d\ln\phi_i/dT)_P + (d\ln y_i/dT)_P$ gives

$$\left(\frac{d\ln f_i}{dT}\right)_P = \left(\frac{\partial\ln\phi_i}{\partial T}\right)_{P,y} + \left(\frac{\partial\ln\phi_i}{\partial y_i}\right)\left(\frac{dy_i}{dT}\right)_P + \left(\frac{\partial\ln\phi_i}{\partial y_j}\right)\left(\frac{dy_j}{dT}\right)_P + \cdots \cdots + \left(\frac{\partial\ln\phi_i}{\partial y_n}\right)\left(\frac{dy_n}{dT}\right)_P + \left(\frac{d\ln y_i}{dT}\right)_P \tag{6}$$

The y derivatives of $\ln\phi_i$ are made with everything else constant, that is restricted as to all variables except the indicated value of y. This is the notation used by Van Ness (*8*).

The temperature derivatives of vapor composition must be evaluated from isobaric temperature-composition curves prepared from experimental data or from points obtained by calculations. This has been done by fitting a polynomial to a set of six or seven points to find the constants, by least square, in the equation

$$y_i = a_0 + a_1T + a_2T^2 + a_3T^3 + \ldots. \tag{7}$$

from which the derivative $(dy_i/dT)_P$ can be readily found for the middle range points, that is discarding the end points. Overlapping sets of temperature-composition values are processed in this way to obtain $(dy_i/dT)_P$ along the isobar. This must be done for all but one component of the mixture because

$$\sum_1^n \left(\frac{dy_i}{dT}\right)_P = 0$$

These temperature derivatives of the y's are very important derivatives in the calculation of enthalpies so they must be evaluated carefully.

The two derivatives of $\ln\phi_i$ must be found from an equation of state such as the Redlich-Kwong (*3*) or the Benedict-Webb-Rubin (*1*, *2*). Derivations have been made via both of these equations and programmed on the computer. The derivative $(\partial\ln\phi_i/\partial y_j)$ must be evaluated for each component of the saturated vapor mixture with each component as the variable, making a total of n^2 solutions for the derivative $(\partial \ln \phi_i / \partial y_j)$.

GIBBS-DUHEM ENTHALPY DIFFERENCE RELATIONSHIPS

For the vapor phase at constant pressure and composition $(\partial \ln f_i/\partial T)_{P,y} = (\partial \ln \phi_i/\partial T)_{P,y}$ so Equation (3) may be written as follows for a vapor mixture

$$\frac{H^o - H^V}{RT^2} = \sum_{i=1}^{n} y_i \left(\frac{\partial \ln \phi_i}{\partial T} \right)_{P,y} \tag{8}$$

Another expression can be obtained for the enthalpy difference of a saturated vapor mixture by combining Equations (1) and (6) to give

$$\frac{H^o - H^V}{RT^2} = \sum_{i=1}^{n} y_i \left(\frac{\partial \ln \phi_i}{\partial T} \right)_{P,y} + \sum_{i=1}^{n} \sum_{j=1}^{n} y_i \left(\frac{\partial \ln \phi_i}{\partial y_j} \right) \left(\frac{dy_j}{dT} \right)_P + \sum_{i=1}^{n} \left(\frac{dy_i}{dT} \right)_P \tag{9}$$

By comparing Equations (8) and (9), it can be seen that the last two terms in Equation (9) are zero for the saturated vapor state. Equations (8) and (9) are of theoretical interest only, as the best way to find the enthalpy difference for a vapor mixture is by the direct calculation applying an equation of state to the basic thermodynamics expression.

A similar expression to Equation (9) is obtained for the enthalpy difference of a saturated liquid mixture by combining Equations (1) and (6) to give

$$\frac{H^o - H^L}{RT^2} = \sum_{i=1}^{n} x_i \left(\frac{\partial \ln \phi_i}{\partial T} \right)_{P,y} + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i \left(\frac{\partial \ln \phi_i}{\partial y_j} \right) \left(\frac{dy_j}{dT} \right)_P + \sum_{i=1}^{n} \frac{1}{K_i} \left(\frac{dy_i}{dT} \right)_P \tag{10}$$

The derivatives of $\ln \phi_i$ in Equation (10) are the same as those in Equation (9), that is the derivatives in both expressions involve the saturated vapor compositions.

These derivatives of $\ln \phi_i$ should be evaluated via equation of state relationships. The third right hand term of Equation (10) is the ideal solution and perfect gas case. From this it is evident that the first and second right-hand terms of Equation (10) reflect the departure from perfect gases.

ILLUSTRATIONS

Equation (10) has been applied to the calculation of the liquid enthalpy differences for each of two ethane binaries to show the order of magnitude of the three right hand members. These calculations, which are given in Table 1, were made by using two equations of state (2) and (3) and Equation (7), fitted to the experimental temperature composition data. Equation of state calculations were made in the evaluations of the first and second right-hand members, while Equation (7) was used in the calculations of the second and third right-hand members.

TABLE 1. SOLUTION OF EQUATION (10) FOR TWO ETHANE BINARIES AND COMPARISON OF RESULTS USING ISOBARIC GIBB-DUHEM EQUATION

m.f C$_2$			Values of Terms in Equation (10)						Values of $(H^V - H^L)_{P,T}$ B.t.u./lb. mol		
			1st RHM × 10^3		2nd RHM × 10^3		3rd RHM × 10^3		This work		
x	y	T°R.	Via R-K	Via B-W-R	Via R-K	Via B-W-R	For R-K Calcs.	For B-W-R Calcs.	R-K	B-W-R	other work S&W (*4*)
ethane-n-butane system @ 350 lb./sq.in.abs.											
0.10	0.278	678.7	1.6583	2.1301	—0.4416	—0.6198	6.1958	6.2017	4721	4715	4860
0.30	0.680	612.0	1.8558	2.3880	—0.6184	—0.9042	8.2138	8.2028	4634	4654	4568
0.50	0.860	562.8	2.0456	2.6225	—0.4314	—0.6686	8.3843	8.3979	4262	4362	4528
0.70	0.943	528.4	2.1081	2.6660	—0.2610	—0.4213	8.8530	8.8545	4397	4499	4402
0.90	0.986	501.5	1.9916	2.4264	—0.1170	—0.1906	11.5287	11.2347	5623	5525	4062
ethane-n-pentane system @ 400 lb./sq.in.abs.											V&W (*9*)
0.10	0.300	769.8	1.8210	2.3690	—0.7945	—1.0245	5.3510	5.1069	4118	3838	3217
0.30	0.775	661.3	2.0191	2.6244	—0.8991	—1.3742	8.2255	8.5562	3866	4135	2663
0.50	0.919	588.7	2.4299	3.1647	—0.4562	—0.6272	6.8676	5.9098	2827	2480	3430
0.70	0.966	544.3	2.6308	3.4033	—0.2403	—0.3397	5.6070	4.7249	2503	2269	3721
0.90	0.992	514.3	2.3549	2.8947	—0.1621	—0.2723	10.8201	10.5689	5485	5452	3748

These calculations were made via a computer program, with print-out instructions to display the intermediate results. A few words of explanation about the third right-hand member will explain why two sets of values (headed *For R-K Calcs* and *For B-W-R Calcs*) are obtained from the same y-T data. Normally, the same data and curve-fit procedure should give the same values of this derivative term. The differences are very small for the ethane-*n*-butane system and of no significance, being due to slight variations in the two different computer runs of the curve fit, smoothing and differentiating operations. Equation (7) was used in the third-order form in these calculations.

For the ethane-*n*-pentane system, the differences between the two evaluations of the third right-hand member of Equation (10) are large and significant. These differences are due to using different forms of Equation (7) (that is fourth-order polynomial) in curve-fitting, smoothing and differentiating the y-T data for the solution of Equation (10) in the B-W-R calculations of liquid enthalpy difference.

Also included in Table 1 are values of $(H^V - H^L)_{P,T}$, found by two separate calculations in this work and by a different type of calculation by other workers (*4*, *9*). The H^V and H^L values are the enthalpies of the coexisting equilibrium vapor and liquid at the same pressure and temperature, both above the same datum ($H = 0$ at 0°R. and 0 lb./sq. in. abs.). In our own work the vapor enthalpies were found by a combination of equation of state calculations and ideal gas enthalpy values, while the liquid enthalpies were found by a combination of Equation (10) results and ideal gas state enthalpies.

DISCUSSION

From the results in Table 1 we can see that the values of $(\Delta H)_{P,T}$ found in this work were not in agreement with values obtained via another method by others. This, plus their unsmoothness makes the present values suspect.

Because of the relatively greater importance of the third right-hand member of Equation (10), compared to the first and second right-hand members, it seems obvious that the biggest weakness in the isobaric Gibbs-Duhem method for calculating liquid enthalpy of mixtures is in the handling of the temperature-composition data and obtaining derivatives. It also appears that the equation of state used is of lesser importance.

An alternate would have been to calculate $\ln f_i$ via an equation of state and the temperature-composition data, curve fitting these as a function of temperature and then differentiating. This alternative was not followed because of a desire to do as much of the calculation job as possible by already available equations, such as the equation of state, and to minimize the empiricism of curve fitting.

Another alternative would have been to use graphical differentiation with calculated $\ln f_i$ vs. T plots. This was ruled out as being impractical for design applications.

CONCLUSIONS

Theoretically, the isobaric Gibb-Duhem equation can be used to predict the enthalpy of saturated liquid mixtures from experimental temperature-composition data and an equation of state, using an expression presented herein. This method for computing saturated liquid enthalpies for mixtures is very sensitive to the input data, the equation of state, and the technique used in smoothing and differentiating the composition-temperature data, especially the latter.

From a practical viewpoint, this method cannot be recommended until a better method is found to evaluate the derivative $(dy_i/dT)_P$ for components of the mixture. Graphical methods are not acceptable.

NOTATION

x_i = mole fraction of i in liquid
y_i = mole fraction of i in vapor
z_i = mole fraction of i in system, liquid or vapor
f_i = the fugacity of component i in the mixture
$\overline{V}_i$ = partial molal volume of component i in mixture at T and P of the system
V = $\Sigma z_i \overline{V}_i$ = molal volume of mixture at T and P of the system
$\overline{H}_i$ = partial molal enthalpy of component i in mixture at T and P of the system
H = $\Sigma z_i \overline{H}_i$ = molal enthalpy of the mixture at system T and P conditions
H^o = $\Sigma z_i H_i^o$ = molal enthalpy of the mixture at the system temperature and the ideal gas condition of zero pressure
$(\Delta H)_{P,T}$ = $(H^V - H^L)_{P,T}$ = enthalpy difference for coexisting equilibrium vapor and liquid at P and T of system
H^V = enthalpy of saturated vapor mixture at dew point
H^L = enthalpy of saturated liquid mixture at bubble point
$H^o{}_{dp}$ = $\Sigma y_i H_i^o$ = ideal gas state enthalpy of dew point mixture
$H^o{}_{bp}$ = $\Sigma x_i H_i^o$ = ideal gas state enthalpy of bubble point mixture

LITERATURE CITED

1. Bendict, M., G. B. Webb, and L. C. Rubin. *J. Chem. Phys.*, **8**, 334 (1940).
2. Edmister, W. C., J. Vairogs, and A. J. Klekers. *AIChE J.*, **14**, 479 (1968).
3. Redlich, O., and J. N. S. Kwong, *Chem. Reviews*, **44**, 233 (1949).
4. Smith, L. C., and J. H. Weber, *J. Chem. Eng. Data*, **9**, No. 3, 349 (1964).
5. Tao, L. C., *AIChE J.*, **15**, 362 (1969).
6. *Ibid.*, **14**, 988 (1968).
7. Van Ness, H. C., *Chem. Eng. Sci.*, **10**, 225 (1959).
8. ———, "Classical Thermodynamics of Non-Electrolyte Solutions," MacMillan, New York (1964).
9. Vinnex, H. C., and J. H. Weber, *J. Chem. Eng. Data*, **7**, 169 (1962).

Correlation of Interphase Mass Transfer Coefficients for Transport of Gases through Insoluble Monolayers

DAVID H. T. CHEN

PMC Colleges, Chester, Pennsylvania

In a recent paper, Sada and Himmelblau (2) studied the transport of gases through insoluble monolayers and interphase mass transfer coefficients were reported for several gas-monolayer systems. However, the authors concluded that the mass transfer coefficients did not appear to be amenable to simple correlation as a function of the surface coverage of the monolayers. The purpose of this communication is to show that a correlation of the data is, indeed, possible and can be achieved through the use of a physical model.

THE MODEL

We may consider the transport of gases through an insoluble monolayer as a case of gas molecules diffusing through the void areas created by the compacting of monolayer molecules. If we neglect the interactions among the molecules, then the number of gas molecules diffusing through the film per unit time per unit area, or the interphase mass transfer coefficient (k_F), under steady state conditions, must be some functions of the void area and the radius of the gas molecule. Figure 1 is a plot of k_F vs. A on a semilogarithmic scale for the 1-hexadecanol monolayer system. Straight lines are obtained for each gas. Other gas-monolayer systems yield similar results. From the above observation, an equation of the following form is proposed to correlate the interphase mass transfer coefficients: