

A New Test for the Thermodynamic Consistency of Vapor-Liquid Equilibrium

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A new thermodynamic consistency test of vapor-liquid equilibrium data at low pressure has been proposed based on the equation that describes the bubble point of the mixture. The test can be used in a point-to-point or area manner and requires knowledge or estimation of the heat of vaporization of the pure components. The point-to-point mode is applicable to binary and multicomponent data and simplifies the locating of experimental errors.

The Gibbs-Duhem equation imposes a general coupling among the partial properties of the components in a mixture and is generally the basis of most methods to test their thermodynamic consistency, i.e., that they obey relations from thermodynamics.

The general form of the Gibbs-Duhem equation is (Van Ness, 1964)

$$\sum x_k d \ln \gamma_k = -\frac{\Delta V}{RT} dP + \frac{\Delta H}{RT^2} dT \quad (1)$$

where ΔV and ΔH represent, respectively, the molar volume and molar enthalpy of mixing.

For a binary system the integrated form of eq 1 becomes

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = -\int_{P_2^*}^{P_1^*} \frac{\Delta V}{RT} dP + \int_{T_2^*}^{T_1^*} \frac{\Delta H}{RT^2} dT \quad (2)$$

At constant temperature and pressure eq 1 may be written

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0 \quad (3)$$

Equation 3 establishes a simple relationship between the slopes of the plots of $\ln \gamma_k$ vs x_k which can be used to test the thermodynamic consistency of each experimental point. This point-to-point test is unfortunately of little practical importance because of the difficulties in measuring slopes with enough accuracy. In addition, vapor-liquid equilibria data are normally measured at either constant temperature or constant pressure; hence conventional consistency tests make use of particular forms of eq 2.

For the special case of constant pressure and temperature eq 2 becomes

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \quad (4)$$

Equation 4 means that, in the plot of $\ln \gamma_1/\gamma_2$ vs x_1 , the areas above and below the x -axis must be equal. This is the so-called area of Redlich-Kister test (1948). The actual difference in the areas may be accounted for by analyzing either the isothermal case

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = -\int_{P_2^*}^{P_1^*} \frac{\Delta V}{RT} dP \quad (5)$$

or the isobaric one

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = \int_{T_2^*}^{T_1^*} \frac{\Delta H}{RT^2} dT \quad (6)$$

In most cases the right-hand-side integral of eq 5 can be safely neglected so that in practice the thermodynamic consistency test is performed according to the Redlich-Kister method. For isobaric nonisothermal data the right-hand-side integral of eq 6 cannot be neglected, and its evaluation requires data on the variation of the heat of

mixing with temperature and composition. This information is rarely available, and to overcome this difficulty Herington (1951) has proposed an empirical test that estimates the value of the right-hand-side integral by using the total boiling-point range of the mixture as the only parameter. The Herington test is very simple to use, but the constants that appear in the equations were obtained from the analysis of only 15 systems and have never been the subject of a more comprehensive review.

Recently Kojima et al. (1990) have proposed a more comprehensive test that combines the point test and the area test with a new infinite dilution test based on the plot of (G^E/RTx_1x_2) vs x_1 . According to Kojima the comprehensive test offers the advantage of selecting the reliable data among several data sets. Nevertheless its use requires availability of information on the heat of mixing.

A different approach can be developed based on a thermodynamic relationship linking the excess of the Gibbs function of a mixture, G^E , with its boiling point. The general scheme is that developed by Malesinski (1965) and the modification proposed by Wisniak and Tamir (1976).

The excess of the Gibbs function for a multicomponent mixture is given by

$$G^E = RT \sum x_k \ln \gamma_k \quad (7)$$

If we assume that all nonidealities are concentrated in the liquid phase, the activity coefficients are given by

$$\gamma_k = \frac{y_k P}{x_k P_k^*} \quad (8)$$

If it is further assumed that the heat of vaporization of each component is constant in the range of boiling points under consideration (or an average value is used) and that the liquid molar volume is negligible compared to that of the vapor, we can apply the Clausius-Clapeyron equation to estimate the ratio P/P_k^* as follows:

$$\ln \frac{P}{P_k^*} = \frac{\Delta h_k^*(T_k^* - T)}{RT_k^* T} = \frac{\Delta s_k^*(T_k^* - T)}{RT} \quad (9)$$

where T_k^* , Δh_k^* , and Δs_k^* are the boiling point, heat of vaporization, and entropy of vaporization of pure component k at the operating pressure P , and P_k^* is the vapor pressure at temperature T .

Replacing eqs 8 and 9 in eq 7 yields

$$G^E = \sum x_k \Delta s_k^*(T_k^* - T) + RT \sum x_k \ln(y_k/x_k) \quad (10)$$

Defining

$$\Delta s = \sum x_k \Delta s_k^* \quad (11)$$

$$w = \sum x_k \ln(y_k/x_k) \quad (12)$$

we obtain the following expression that describes the

Table I. Results of Thermodynamic Consistency Test L - W of Isobaric Vapor-Liquid Equilibrium Data and Comparison with the DECHEMA Tests

system	this work			DECHEMA ^a		system	this work			DECHEMA ^a	
	L	W	D	T1	T2		L	W	D	T1	T2
acetone + carbon tetrachloride (1) ^b	6.10	6.29	1.5	+	+	methanol + ethyl acetate (19)	5.76	6.23	3.9	-	+
benzene + acetonitrile (10)	5.78	6.11	2.8	+	+	methanol + methyl ethyl ketone (9)	6.23	5.89	2.8	-	+
benzene + 2,3-dimethylpentane (24)	3.85	4.19	4.2	+	+	methanol + toluene (3)	18.72	20.92	5.5	-	+
benzene + 2-propanol (18)	7.39	7.75	2.4	+	+	pentane + acetone (13)	10.54	10.59	0.24	-	+
butanol + benzene (15)	10.60	11.78	5.3	+	+	propanol + heptane (5)	10.41	10.98	2.7	-	+
butanol + chlorobenzene (25)	6.10	5.94	1.3	+	+	propanol + toluene (14)	8.19	8.99	4.7	-	+
chloroform + methanol (17)	7.11	7.21	0.70	+	+	2-propanol + carbon tetrachloride (29)	8.41	8.73	1.9	-	+
2,3-dimethylbutane + chloroform (28)	2.50	3.09	11	+	+	2-propanol + methylcyclohexane (18)	10.43	10.83	1.9	-	+
ethanol + methyl ethyl ketone (7)	3.46	3.70	3.4	+	+	toluene + acetonitrile (10)	9.17	10.55	7.0	-	+
hexane + benzene (22)	2.65	2.73	1.5	+	+	<i>p</i> -xylene + furfural (23)	9.54	8.45	6.1	-	+
hexane + benzene (6)	2.92	2.95	0.51	+	+	carbon tetrachloride + cyclohexane (29)	0.72	0.81	5.4	+	-
methanol + methyl isobutyl ketone (9)	16.77	18.21	4.1	+	+	pyridine + benzene (27)	3.90	4.05	1.9	+	-
methanol + ethyl acetate (17)	5.85	6.39	4.4	+	+	acetone + 1,1,2-trichloroethane (26)	6.73	7.75	7.0	-	-
propanol + chlorobenzene (25)	10.68	10.54	0.66	+	+	benzene + propanol (22)	9.13	9.63	2.7	-	-
2-propanol + methyl isobutyl ketone (2)	5.96	6.46	4.0	+	+	carbon tetrachloride + 2-propanol (18)	8.22	8.41	1.1	-	-
2-propanol + methyl propyl ketone (2)	3.37	5.56	25	+	+	cyclohexane + 2-propanol (29)	10.08	10.19	0.54	-	-
cyclohexane + 2-propanol (18)	9.86	10.28	2.1	-	+	2,3-dimethylbutane + methanol (28)	15.79	16.74	2.9	-	-
cyclohexane + 2-propanol (16)	9.91	10.25	1.7	-	+	ethanol + acetone (7)	4.57	5.12	5.7	-	-
2,3-dimethylbutane + acetone (28)	9.38	9.76	2.0	-	+	ethanol + nitromethane (21)	8.89	9.98	5.8	-	-
ethanol + benzene (12)	9.03	9.48	2.4	-	+	ethanol + methyl propyl ketone (7)	7.59	7.31	1.9	-	-
ethanol + cyclohexane (29)	12.73	12.98	0.97	-	+	methanol + butanol (8)	4.94	11.63	40	-	-
ethanol + nitromethane (21)	11.65	12.06	1.7	-	+	methanol + methyl propyl ketone (9)	11.1	13.77	11	-	-
ethanol + toluene (12)	12.66	13.31	2.5	-	+	methanol + pentanol (8)	7.48	20	46	-	-
ethanol + water (4)	8.16	9.77	9.0	-	+	methanol + water (4)	7.50	7.46	0.27	-	-
ethylbenzene + furfural (23)	8.90	8.93	0.17	-	+	pyridine + water (27)	7.28	7.61	2.2	-	-
hexane + propanol (22)	13.88	14.62	2.6	-	+	methanol + water (11)	7.71	7.79	0.52	na	na
methanol + anisole (20)	34.03	31.58	3.7	-	+	methylcyclohexane + 2-propanol (16)	11.04	11.43	1.7	na	na
methanol + di-isopropyl ether (19)	7.12	7.84	4.8	-	+	water + dioxane (11)	10.99	10.86	0.59	na	na

^a T1 is the point-to-point test and T2 is the area test. ^b Data sources for vapor-liquid equilibrium data: (1) Bachman, K. C.; Simons, E. L. *Ind. Eng. Chem.* 1952, 44, 202. (2) Ballard, L. H.; Van Winkle, M. *Ind. Eng. Chem.* 1953, 45, 1803. (3) Burke, D. E.; Williams, G. C.; Plank, V. C. A. *J. Chem. Eng. Data* 1964, 9, 212. (4) Dalager, P. J. *Chem. Eng. Data* 1969, 14, 298. (5) Gurukul, K. A.; Raju, B. N. *J. Chem. Eng. Data* 1966, 11, 501. (6) Hanson, D. O.; Van Winkle, M. J. *Chem. Eng. Data* 1967, 12, 319. (7) Hellwig, L. R.; Van Winkle, M. *Ind. Eng. Chem.* 1953, 45, 624. (8) Hill, W. D.; Van Winkle, M. *Ind. Eng. Chem.* 1952, 44, 203. (9) Hill, W. D.; Van Winkle, M. *Ind. Eng. Chem.* 1952, 44, 208. (10) Krishna, S.; Tripathi, R. P.; Rawat, S. J. *Chem. Eng. Data* 1980, 25, 11. (11) Kato, M.; Konishi, H.; Hirata, M. *J. Chem. Eng. Data* 1970, 15, 501. (12) Landwehr, J. C.; Yerazunis, S.; Steinhäuser, H. H. *Chem. Eng. Data Ser.* 1968, 3, 231. (13) Lo, T. C.; Bieber, H. H.; Karr, A. E. *J. Chem. Eng. Data* 1962, 7, 327. (14) Lu, C. B.-Y. *Can. J. Technol.* 1957, 34, 468. (15) Mann, R. S.; Shemilt, L. W.; Waldichuck, M. J. *Chem. Eng. Data* 1963, 8, 502. (16) Nagata, I. *Kanazawa Daigaku Kogakuku Kiyō* 1963, 3, 1. (17) Nagata, I. *J. Chem. Eng. Data* 1962, 7, 367. (18) Nagata, I. *J. Chem. Eng. Data* 1965, 10, 106. (19) Nakanishi, K.; Nakasato, K.; Toba, R.; Shirai, H. *J. Chem. Eng. Data* 1967, 12, 440. (20) Nakanishi, K.; Shirai, H.; Nakasato, K. *J. Chem. Eng. Data* 1968, 13, 188. (21) Nakanishi, K.; Toba, R.; Shirai, H. *J. Chem. Eng. Jpn.* 1969, 2, 4. (22) Prabhu, P. S.; Van Winkle, M. J. *Chem. Eng. Data* 1963, 8, 210. (23) Puri, P. S.; Raju, K. S. N. *J. Chem. Eng. Data* 1970, 15, 480. (24) Richards, A. R.; Hargreaves, E. *Ind. Eng. Chem.* 1944, 36, 805. (25) Venkateswara Rao, K.; Raviprasad, A.; Chiranjivi, C. J. *Chem. Eng. Data* 1977, 22, 44. (26) Treybal, R. E.; Weber, L. D.; Daley, J. F. *Ind. Eng. Chem.* 1946, 38, 812. (27) Vriens, G. N.; Metcalf, E. C. *Ind. Eng. Chem.* 1953, 45, 1098. (28) Willock, J. M.; Van Winkle, M. J. *Chem. Eng. Data* 1970, 15, 281. (29) Yuan, K. S.; Ho, J. C. K.; Keshpande, A. K.; Lu, B. C.-Y. *J. Chem. Eng. Data* 1963, 8, 549.

bubble point of the mixture:

$$T = \sum T_k^\circ x_k \Delta s_k^\circ / \Delta s - G^E / \Delta s + RTw / \Delta s \quad (13)$$

Malesinski (1965) has shown that w is always negative and that its maximum value is zero at the azeotropic point.

Equation 13 has been modified by Wisniak and Tamir (1976) by assuming a Redlich-Kister type expansion for G^E and incorporating the factors $\Delta s_k^\circ / \Delta s$ and Δs into the empiricism of G^E . For a binary mixture eq 13 becomes

$$T = \sum T_k^\circ x_k + w + x_1 x_2 \sum C_k (x_1 - x_2)^k \quad (14)$$

Extensive use of this equation has shown that the contribution of w can be safely neglected and, more importantly, data that are normally well fit by eq 14, as indicated by the root mean square deviation statistic, are usually thermodynamically consistent.

We can transform eq 14 into a thermodynamic consistency test by rearranging eq 13 as follows:

$$L_i = \sum T_k^\circ x_k \Delta s_k^\circ / \Delta s - T = G^E / \Delta s - RTw / \Delta s = W_i \quad (15)$$

The left-hand side, L_i , of eq 15 will always be positive, except for the case where an azeotrope is present. The sign of G^E (calculated using eq 7) will be positive or negative depending on whether the system presents positive or

negative deviations from ideality. The value of $RTw / \Delta s$ will usually not be negligible, as assumed when using eq 14. The value of w is obtained from eq 12. The sign of the right-hand side, W_i , of the equation will be consistent with that of L_i .

Multiplying both sides of eq 15 by dx_1 and integrating for the full concentration range yields

$$L = \int_0^1 L_i dx_1 = \int_0^1 W_i dx_1 = W \quad (16)$$

In other words, if the data are thermodynamically consistent, the values of the integrals L and W should be identical. For real data this requirement is not exactly fulfilled because of experimental error and also because of assumptions made in calculations (ideal instead of real vapor phase) and in the derivation of eq 15 (particularly in the use of the Clausius-Clapeyron equation). Since we do not know which of the values L and W is more accurate, we define a deviation D :

$$D = 100 \frac{|L - W|}{L + W} \quad (17)$$

which should not be exceeded. The limit for this deviation is arbitrary and will depend on the needs for which the data are required. The errors involved in the experimental

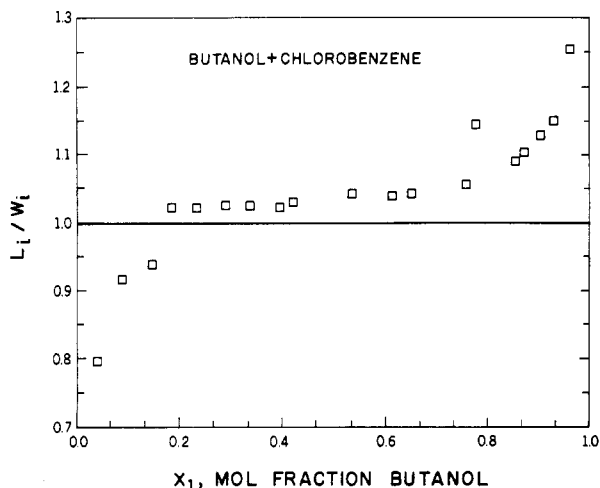


Figure 1. Point-to-point test and use of eq 15 to detect experimental errors. Data of Venkateswara Rao et al. (1977).

data required to evaluate L and W are similar to those present in the area and Herington tests for consistency; hence it is estimated that values of D less than 3–5 will indicate thermodynamic consistency. The higher limit is proposed for the case where the heats of vaporization are not available and must be estimated. We have proceeded to calculate the values of L and W for 57 systems selected from the compilation of Gmehling and Onken (1977) in which the point tests T1 of Fredenslund et al. (1977) and Van Ness et al. (1973) are combined with the area tests T2 of Herington (1951) and Redlich–Kister (1948) to qualify the data as consistent (+) or not consistent (–). The pertinent results are summarized in Table I.

Equation 15 must be fulfilled for every experimental point; hence it may be considered as an alternative point-to-point consistency test that does not imply measurement of the slope of the plots of $\ln \gamma_k$ vs x_k , as required by the Gibbs–Duhem equation. Plot of the corresponding values of L_i and W_i will allow an easy identification of outliers, that is, experimental data that are in serious error. As an example, consider Figure 1, a plot of eq 15 using the vapor-liquid equilibria data for the system butanol + chlorobenzene at 760 mmHg (Venkateswara Rao et al., 1977). As shown in Table I, the data are consistent by the DECHEMA criteria and also by the new L – W integral test proposed here. Nevertheless, the point-to-point analysis indicates that data in the range $0.1 > x_1, x_1 > 0.9$ are not consistent.

The proposed test is somewhat more elaborate than that proposed by Herington, but is theoretically more sound. It is also more useful than the new test proposed by Kojima because it does not require information on heats of mixing as a function of pressure and composition. Instead, it requires knowledge of the heats of vaporization of the pure components at the operating pressure. These can be either obtained from the literature or estimated rather accurately using the Pitzer acentric-factor correlation or the Watson equation (Reid et al., 1987). A very important advantage of the proposed method is that the point-to-point test and the area test are conducted simultaneously. Hence any problem of error cancellation present in the area test will be detected immediately.

An objection that can be raised against the use of eq 15 is that inclusion of the term w is equivalent to using the information provided by three variables (T, x, y) instead of the two required by the phase rule. Nevertheless, T, x, y information must be used if we must consider the possible nonideality of the vapor phase.

The point-to-point test given by eq 15 can be easily extended to multicomponent mixtures by proper use of

eqs 7, 11, and 12. For a ternary system we will have

$$\Delta s = x_1 \Delta s_1^\circ + x_2 \Delta s_2^\circ + x_3 \Delta s_3^\circ \quad (11a)$$

$$w = x_1 \ln(y_1/x_1) + x_2 \ln(y_2/x_2) + x_3 \ln(y_3/x_3) \quad (12a)$$

Since many equilibrium compositions are possible for a given value of the boiling temperature T , we can expect that for these data points the difference ($L_i - W_i$) will vary significantly, even if the data are arranged in an increasing T manner, as required by the McDermott–Ellis test (1965), which is normally used for testing the thermodynamic consistency of ternary systems.

Nomenclature

C_k = constant, eq 14

D = deviation function defined by eq 17

G^E = Gibbs excess function

ΔH = molar enthalpy of mixing

Δh_k° = molar enthalpy of vaporization of component k

k = component

L = function defined by eq 16

P = pressure

P_k° = vapor pressure of pure component k

R = universal gas constant

Δs_k° = molar entropy of vaporization of component k

Δs = function defined by eq 11

T = temperature

T_k° = boiling point of pure component k

ΔV = molar volume of mixing

x_k = mole fraction of component k in liquid

y_k = mole fraction of component k in vapor

w = function defined by eq 12

W = function defined by eq 16

Greek Letters

γ_k = activity coefficient

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