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The Role of Vapor Phase Composition in Data Reduction of Vapor-Liquid Equilibria

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For vapor-liquid equilibrium (VLE) data which are characterized by insufficient consistency, there is only one poor agreement between the excess Gibbs function $G^E_{(P,y)}$ derived from P - x - y data and $G^E_{(P)}$ calculated by an integration procedure without using y data. As pointed out in earlier publications, in these cases the $G^E_{(P)}$ values should be preferred (Kehlen, 1969; Kehlen and Peil, 1972; Van Ness et al., 1973; Kuschel et al., 1974; Prausnitz, 1975; Van Ness, 1975). Therefore, efforts in experimental work should be directed to achieve more accurate P - x values and not to determine P - x - y simultaneously. To support this conclusion, this note discusses some selected examples and presents calculations with model systems.

TREATMENT OF DATA

Calculation of the molar excess Gibbs function G^E from isothermal P - x - y data is performed by the conventional procedure. Because of the Gibbs-Duhem equation, there exists also the possibility of calculating G^E only from P - x data. For this purpose we used the procedure developed by Barker (1953).

To test the consistency of data measured at n different mole fractions x_i , the consistency parameter K is calculated. K is defined by

$$K = \frac{\sum_{i=1}^n |G^E_{(P,y)}(x_i) - G^E_{(P)}(x_i)|}{n} \quad (1)$$

If the measurements (and the data reduction) are carried out without errors, then $G^E_{(P,y)}$ and $G^E_{(P)}$ must be identical ($K = 0$). But in real systems, no total agreement occurs, indicating that there is no perfect consistency; hence $K > 0$. For good consistency, the requirement is $K \leq 15$ J/mole (Kehlen et al., 1969).

In principle, one can achieve sufficient agreement by improving the accuracy of the measurements. But this is often very difficult, especially in systems with high rela-

tive volatility. Thus, in the case of inconsistency, the question arises whether $G^E_{(P)}$ or $G^E_{(P,y)}$ possesses the higher reliability.

DISCUSSION OF SELECTED EXAMPLES

For the system carbon disulfide (1) + acetone (2), the following data exist:

- (a) v.Zawidski (1900):
 35.17°C; P - x - y data; $K = 15.5$ J/mole
- (b) Hirshberg (1932):
 29.2°C; P - x - y data; $K = 56.2$ J/mole
- (c) Schmidt (1926):
 35°C; P - x data

Figure 1 shows the result of data reduction for the cases (a) and (b). Good agreement is obtained between $G^E_{(P)}$ (a), $G^E_{(P,y)}$ (a), and $G^E_{(P)}$ (b). There is also good agreement with the $G^E_{(P)}$ data based on the measurements of Schmidt (1926). Only the $G^E_{(P,y)}$ values, calculated from the measurements of Hirshberg (1932), indicate bad consistency and do not agree with the other results.

Brown (1952) has reported P - x - y measurements for the system cyclohexane + nitrobenzene at 80°C. From his results we obtained $G^E_{(P,y)} \approx 1640$ J/mole; $G^E_{(P)} \approx 1150$ J/mole ($x = 0.5$). Brown (1952) explained the poor consistency of his results ($K = 430$ J/mole) by experimental difficulties (relative volatility $\alpha = 105$). Mecke and Zirker (1964) studied the liquid-liquid and the liquid-solid equilibrium of this system as well as the heat of mixing. Their measurements yield at $x = 0.5$; $G^E \approx 1250$ J/mole (at -2.5°C) and $H^E \approx 1680$ J/mole (at 20°C). These data permit the calculation of G^E at 80°C: $G^E \approx 1105$ J/mole ($x = 0.5$). This value shows good agreement with $G^E_{(P)}$ of Brown (1952) but very bad agreement with $G^E_{(P,y)}$.

Udovenko and Frid (1948) reported sets of P - x - y data for the five binary systems methanol + 2-methyl-propan-1-ol, methanol + 3-methyl-butan-1-ol, ethanol + propan-1-ol, ethanol + 2-methyl-propan-1-ol, and ethanol + 3-methyl-butan-1-ol at 50°, 60°, and 70°C. For most of the measurements, the thermodynamic consistency is insufficient ($K > 15$ J/mole). Table 1 summarizes $G^E_{(P,y)}$ and $G^E_{(P)}$ as well as the excess enthalpies determined by Hirobe (1925) at 25°C.

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TABLE 1. G^E AND H^E FOR EQUIMOLAR MIXTURES OF ALCOHOLS, J/MOLE

System	$G^E_{(P,y)}$ 50°C	$G^E_{(P)}$	$G^E_{(P,y)}$ 60°C	$G^E_{(P)}$	$G^E_{(P,y)}$ 70°C	$G^E_{(P)}$	H^E 25°C
CH ₃ OH + C ₄ H ₉ OH	178	231	183	243	176	253	172
+ C ₅ H ₁₁ OH	421	255	475	267	211	277	188
C ₂ H ₅ OH + C ₃ H ₇ OH	159	157	153	160	162	166	25
+ C ₄ H ₉ OH	139	166	151	172	138	178	71
+ C ₅ H ₁₁ OH	172	183	152	194	164	201	75

TABLE 2. REDLICH-KISTER PARAMETERS AND P_i^{sat} VALUES FOR MODEL CALCULATIONS (70°C)

System	a	b	c	d	e	f
A	0.160	0.160	0.160	0.080*	0.160†	0.700**
B	-0.010	-0.010	-0.010	0.010*	-0.010†	-0.080**
C	-0.006	-0.006	-0.006	-0.010*	-0.006†	0.040**
P_1^{sat} , mm Hg	617.43*	88.72†	10.65**	88.72	88.72	88.72
P_2^{sat} , mm Hg	544.89*	544.89†	544.89**	544.89	544.89	544.89

* Corresponding approximately to the carbon tetrachloride + cyclohexane system (Kuschel et al., 1974).

† Corresponding approximately to the titanium tetrachloride + cyclohexane system (Kuschel et al., 1974).

** Corresponding approximately to the aniline + cyclohexane system (Hosseini and Schneider, 1963).

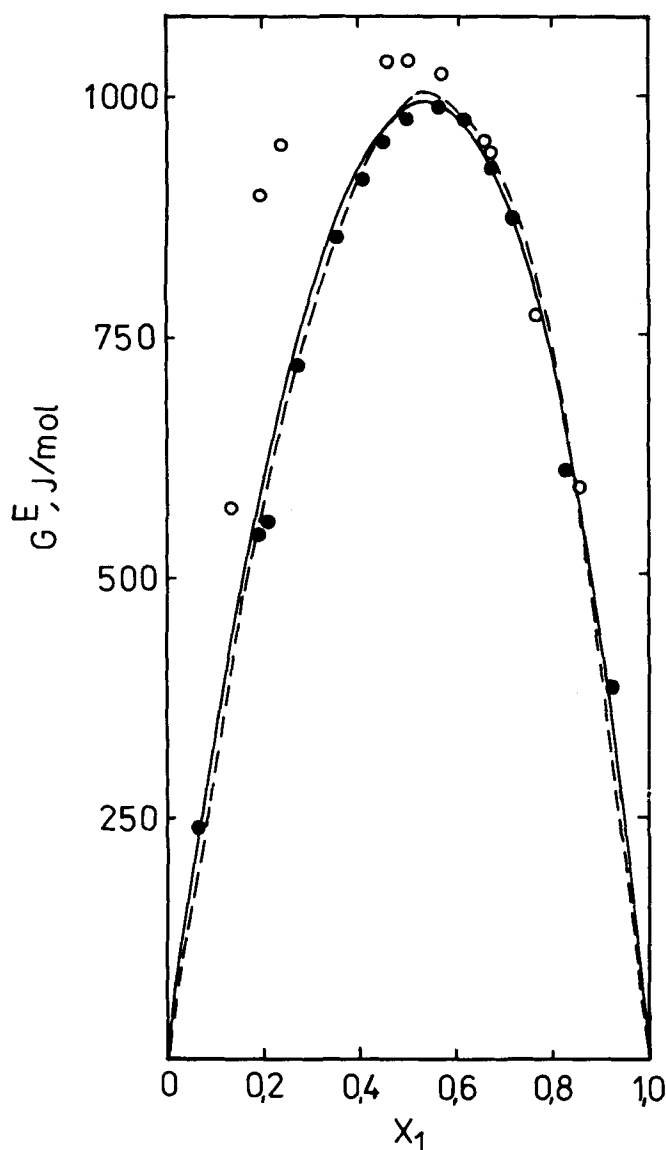


Fig. 1. G^E vs. x_1 for Carbon disulfide (1) + Acetone (2).
○ $G^E_{(P,y)}$, --- $G^E_{(P)}$: from 29.2°C data of Hirshberg (1932).
● $G^E_{(P,y)}$, — $G^E_{(P)}$: from 35.17°C data of Zawidzki (1900).

TABLE 3. CALCULATIONS FOR MODEL SYSTEMS

System	a	b	c	d	e	f
α	1.13	6.14	51.2	6.14	6.14	6.14
k for case (I)	1.01	1.14	1.48	1.17	1.14	1.30
k for case (II)	0.99	1.88	11.55	1.88	1.88	1.93
k for case (III)	1.00	1.73	9.63	1.67	1.73	1.87

Table 1 shows that in all cases the relation $G^E > H^E$ holds corresponding to $\partial G^E / \partial T > 0$. Table 1 also indicates that only the $G^E_{(P)}$ values show this temperature dependence.

A further statement on the G^E values follows from experience concerning the mixing behavior of members of homologous series. According to Bronsted and Koefoed's principle of congruence (1946), mixing effects in homologous series are increasing with increasing structural difference in the components. Table 1 shows that for a given component one $G^E_{(P)}$ increases with an increase in C atoms in the second component. This consistency with the principle of congruence is not always obeyed by $G^E_{(P,y)}$.

CALCULATIONS WITH MODEL SYSTEMS

To study the influence of errors on $G^E_{(P)}$ and $G^E_{(P,y)}$, some calculations with model systems were carried out (Kuschel, 1969). Consistent P - x - y data were perturbed by systematic errors, and the resulting variations of $G^E_{(P)}$ and $G^E_{(P,y)}$ were considered.

Six model systems a, b, \dots, f have been studied as shown in Table 2. These differ with respect to the degree of nonideality expressed by the parameters A, B, C of the Redlich-Kister equation

$$\frac{G^E}{RT} = x_1(1 - x_1) [A + B(2x_1 - 1) + C(2x_1 - 1)^2] \quad (2)$$

and with respect to the ratio of the P_i^{sat} values of the pure components. The vapor phase is treated as an ideal gas.

Cases *a, b, c* show an increasing ratio of P_i^{sat} and a constant degree of nonideality. Cases *d, e, f* show increasing nonideality and constant relative volatility.

From the data of Table 2, the correct values P_c , $y_{1,c}$, and G_c^E were calculated at $x_1 = 0.1; 0.2; \dots; 0.9$. Then, the following systematic errors were introduced:

Case (I): addition of 0.5 mm Hg to P_c

Case (II): subtraction of 0.002 from $x_{1,c}$ and $y_{1,c}$

Case (III): for $\partial P/\partial x_1 > 0$: increase of P according to (I), reduction of x_1 and y_1 according to (II)

For $\partial P/\partial x_1 < 0$: subtraction of 0.5 mm Hg from P_c , reduction of x_1 and y_1 according to (II).

From the changed P - x - y data, $G_{(P,y)}^E$ and $G_{(P)}^E$ were calculated, and these values were compared with G_c^E . For this purpose the quotient

$$k = \frac{\sum_i |G_{(P,y)}^E(x_i) - G_c^E(x_i)|}{\sum_i |G_{(P)}^E(x_i) - G_c^E(x_i)|} \quad (3)$$

was defined; $k > 1$ indicates that the influence of the introduced errors on $G_{(P)}^E$ is on the average smaller than on $G_{(P,y)}^E$, while $k < 1$ indicates the opposite. The results of the calculations are shown in Table 3 which shows that the systematic errors have a smaller influence on $G_{(P)}^E$ than on $G_{(P,y)}^E$. The quotient k depends to a large extent on α . The degree of nonideality has only a small influence on k . The y values calculated from $G_{(P)}^E$ agree with those reported by Mackay and Salvador (1971). The model calculations are in some respects similar to those performed by Van Ness (1975).

CONCLUSION

The examples considered here, as well as the calculations with model systems, demonstrate again that in the case of inconsistency, the $G_{(P)}^E$ values should be preferred. The superiority of the $G_{(P)}^E$ values is most striking in systems having large α values. In these systems, the inclusion of y values into the data reduction process produces considerable deterioration of the calculated G^E values. The results obtained here support the recommendation, in performing VLE measurements at low pressures, to aim at an improvement of P - x measurements and not at simultaneous determination of P - x - y data.

NOTATION

A, B, C = parameters of Redlich-Kister Equation (2)
 G^E = excess Gibbs function, liquid phase
 $G_{(P)}^E$ = excess Gibbs function, calculated by Barker's method from P - x data
 $G_{(P,y)}^E$ = excess Gibbs function, calculated from P - x - y data
 H^E = excess enthalpy, liquid phase
 k = error quotient defined by Equation (3)

K = consistency parameter defined by Equation (1)
 P_i^{sat} = vapor pressure of pure i
 T = absolute temperature
 x_i = mole fraction of i , liquid phase
 y_i = mole fraction of i , vapor phase
 α = relative volatility

Subscripts

1, 2 = two components of a binary system
 c = the correct values of x_i , y_i , P , and G^E

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