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SOME RELATIONS FOR VAPOR-LIQUID EQUILIBRIA
AND CRITICAL MIXTURESO. Redlich and R. W. Missen^{*}Inorganic Materials Research Division,
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September 1968

ABSTRACT

Several relations for vapor-liquid equilibria, partly well-known, are reviewed. The values of several derivatives for the critical point and the critical condensation point of a mixture are discussed. The critical condition $(\partial P / \partial V)_T = 0$ can be generalized for the critical point of a binary mixture to $(dP/dV)_{T,\text{sat}} = 0$, but the second derivative $(d^2P/dV^2)_{T,\text{sat}}$ is not zero for a critical point. It has a negative value.

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There is an essential difference between the critical point of a pure substance and that of a mixture. A pure substance splits into two phases if it is not stable with respect to a volume change. A binary mixture, however, has a second generalized coordinate, namely, the composition. The critical point of a mixture, indeed, corresponds to the failure of the stability condition with respect to the composition. If we were able to prevent the split into phases of different composition, a gaseous mixture would be stable down to a lower temperature, presumably to some temperature of the order of the "pseudocritical" temperature.

As far as we can see, the derivatives of the state variables of critical mixtures have never been exhaustively analyzed. The first question is the extension of the two critical conditions for a pure substance $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T = 0$ to mixtures. This question leads to the general examination of the derivatives.

Total Pressure and Mole Fractions

The isothermal relation between the pressure P and the mole fractions x_1 and y_1 of a binary liquid solution and its vapor has been studied by Rosanoff, Bacon and Schulze (1914). Their interesting results have been superseded by the thermodynamic relation

$$d \ln P / dy_1 = (y_1 - x_1) / y_1 y_2 \quad (1)$$

derived for the isothermal shift of equilibrium by Lewis and Murphree (1924). These authors silently assumed that the vapor is a perfect gas mixture.

If the vapor is not perfect the derivative of the pressure depends also on the fugacity coefficients ϕ_1 and ϕ_2 of the vapor, and its partial molal volumes $\bar{V}_{1G}$ and $\bar{V}_{2G}$. In addition, the molal volume V_L of the liquid

cannot be neglected beside the volume V_G of the vapor, and the partial molal volumes $\bar{V}_{1L}$ and $\bar{V}_{2L}$ have to be taken into account. We define the activity coefficients γ_1 and γ_2 as limiting values for $P = 0$ so that the pressure dependence of the free energy must be written explicitly. The advantage of this definition (Redlich 1965) is the pressure independence of the activity coefficients. Denoting the standard fugacity by f_1^0 , we express the equilibrium condition by

$$RT \ln (x_1 \gamma_1 f_1^0) + \int_0^P \bar{V}_{1L} dP = RT \ln (y_1 \phi_1 P) \quad (2)$$

and derive for the isothermal equilibrium shift

$$\begin{aligned} (\partial \ln x_1 / \partial P)_T + (\partial \ln \gamma_1 / \partial x_1)_T (dx_1 / \partial P)_T + \bar{V}_{1L} / RT \\ = (\partial \ln y_1 / \partial P)_T + (\partial \ln \phi_1 / \partial y_1)_{P,T} (dy_1 / \partial P)_T + \bar{V}_{1G} / RT. \end{aligned} \quad (3)$$

The last term comes from

$$(\partial \ln \phi_1 / \partial P)_{y,T} = \bar{V}_{1G} / RT. \quad (4)$$

Replacing the subscript 1 by 2, we obtain the analogous relation for the second component. From these two equations one can, by multiplying them with x_1 and x_2 , respectively, and adding, derive the relation (Redlich and Kister, 1962)

$$d \ln P / dy_1 = \Phi (y_1 - x_1) / y_1 y_2. \quad (5)$$

In this generalization of (1) the imperfection factor Φ is given by

$$\Phi = RT [1 + y_1 y_2 \partial \ln (\phi_1 / \phi_2) / \partial y_1] / \left(P [V_G - V_L - (y_1 - x_1) (\bar{V}_{1G} - \bar{V}_{2G})] \right). \quad (6)$$

This relation has been derived also by Ibl and Dodge (1953).

One can, however, derive also $d \ln P / dx_1$ from (3) and its analog, namely, by multiplying with y_1 and y_2 , respectively, and adding. The

result, is

$$d \ln P / dx_1 = \Gamma(y_1 - x_1) / x_1 x_2 \quad (7)$$

$$\Gamma = RT [1 + x_1 x_2 \partial \ln (\gamma_1 / \gamma_2) / \partial x_1] / \left(P [v_G - v_L - (y_1 - x_1)(\bar{v}_{1L} - \bar{v}_{2L})] \right). \quad (8)$$

Special cases of some interest are the values for $x_1 = 0$, $x_1 = 1$, for azeotropes, for the critical point and for the critical condensation point.

The results for $x_1 = 0$ and $x_1 = 1$ are conveniently presented with the aid of the relative volatility

$$\alpha = y_1 x_2 / y_2 x_1 \quad (9)$$

and the abbreviation

$$DZ = P(v_G - v_L) / RT. \quad (10)$$

The derivatives are given in Table 1. The values of α to be used are the finite limiting values of (9), α_0 for $x_1 = 0$ and α_1 for $x_1 = 1$. These results are analogous to the limiting values previously derived (Redlich and Kister, 1948) for dt/dx_1 and dt/dy_1 .

Table 1. Special Values

x_1	0	1
$d \ln P / dx_1$	$(\alpha_0 - 1) / DZ$	$(\alpha_1 - 1) / (\alpha_1 DZ)$
$d \ln P / dy_1$	$(\alpha_0 - 1) / (\alpha_0 DZ)$	$(\alpha_1 - 1) / DZ$

For an azeotrope $d \ln P / dx_1$ and $d \ln P / dy_1$ are zero, of course, but one also obtains

$$(dy_1 / dx_1)_{az} = [1 + x_1 x_2 \partial \ln (\gamma_1 / \gamma_2) / \partial x_1] / [1 + y_1 y_2 \partial \ln (\phi_1 / \phi_2) / \partial y_1]. \quad (11)$$

Critical Derivatives

For a critical point, we introduce first $V_G = V_L$ the term $y_1 - x_1$ then cancels in (5) and (6) and we obtain

$$(d \ln P / dy_1)_C = RT [1 + y_1 y_2 \partial \ln (\phi_1 / \phi_2) / \partial y_1] / [P y_1 y_2 (\bar{V}_{2G} - \bar{V}_{1G})]. \quad (12)$$

The critical condition (Redlich and Kister, 1962)

$$d \ln (\phi_1 / \phi_2) / dy_1 = -1 / y_1 y_2 \quad (13)$$

results in

$$(d \ln P / dy_1)_C = 0. \quad (14)$$

For the critical condensation point one concludes from the condition

$$(d \ln P / dy_1)_{CC} = \infty \quad (15)$$

that

$$V_G - V_L - y_1 (\bar{V}_{1G} - \bar{V}_{2G}) = x_1 (\bar{V}_{1G} - \bar{V}_{1L}) + x_2 (\bar{V}_{2G} - \bar{V}_{2L}) = 0. \quad (16)$$

This result has been illustrated before (Redlich and Kister, 1962, Fig. 14).

The figure referred to is also useful in illustrating the values of a few derivatives at the critical point of a mixture and its critical condensation point.

Table 2. Critical Mixtures

	Critical Point	Critical Condensation Point
$(dP/dy_1)_{\text{sat}}$	0	∞
$(dV/dy_1)_{\text{sat}}$	$(\partial V / \partial y_1)_P$	∞
$(dP/dV)_{\text{sat}}$	0	$(\partial P / \partial V)_y$
$V_G - V_L$	0	$(y_1 - x_1)(\bar{V}_{1G} - \bar{V}_{2G})$

For the derivation we start from Equations (14) and (15). The temperature is kept constant in all following differentiations. In the two-phase equilibrium, only one of the variables P , y , V is independent. The subscript sat will be used to indicate a shift of the two-phase equilibrium.

For the critical point, the identity

$$(dP/dy_1)_{\text{sat}} = (\partial P/\partial y_1)_V + (\partial P/\partial V)_y (dV/dy_1)_{\text{sat}} \quad (17)$$

leads to

$$(dV/dy_1)_{\text{sat}} = - (\partial P/\partial y_1)_V / (\partial P/\partial V)_y = (\partial V/\partial y_1)_P \quad (18)$$

in view of (14). Since

$$(\partial V/\partial y_1)_P = \bar{V}_1 - \bar{V}_2 \quad (19)$$

the assumption that $(\partial V/\partial y_1)_P$ is zero or assumes another prescribed value at the critical point would imply a general relation between the two partial molal volumes. But each of these is a function of the individual nature of the component. Therefore they cannot be generally related and $(\partial V/\partial y_1)_P$ is finite at the critical point.

From (18) we conclude that

$$\begin{aligned} (dP/dV)_{\text{sat},C} &= (\partial P/\partial V)_y + (\partial P/\partial y_1)_V (dy_1/dV)_{\text{sat},C} \\ &= (\partial P/\partial V)_y + (\partial P/\partial y_1)_V (\partial y_1/\partial V)_P = 0. \end{aligned} \quad (20)$$

Thus this critical condition is valid not only for pure substances but also for mixtures.

Between the critical point and the critical condensation point there is an essential difference. The singular qualities of the critical point can be established for the gas phase without any reference to a liquid.

The properties of either phase at the critical condensation point, however, are in no way singular. The singularity arises only from the coexistence of the two phases. In a similar manner as before we derive from (15)

$$(dy_1/dP)_{CC} = 0 = (\partial y_1/\partial P)_V + (\partial y_1/\partial V)_P (dV/dP)_{sat} \quad (21)$$

and

$$(dV/dP)_{sat} = (\partial V/\partial P)_y. \quad (22)$$

This derivative, as a property of the gaseous phase, is finite.

Similar to the derivation of (21), we have

$$\begin{aligned} (dy_1/dV)_{CC} &= (\partial y_1/\partial V)_P + (\partial y_1/\partial P)_V (dP/dV)_{sat} \\ &= (\partial y_1/\partial V)_P + (\partial y_1/\partial P)_V (\partial P/\partial V)_{y_1} = 0 \end{aligned} \quad (23)$$

The results are assembled in Table 2.

Second Critical Derivatives

Differentiating (17) and (20), with respect to y and V , respectively, we obtain

$$\left(\frac{d^2 P}{dy_1^2} \right)_{sat} = \frac{\partial^2 P}{\partial y_1^2} + 2 \frac{\partial^2 P}{\partial V \partial y_1} \cdot \frac{dV}{dy_1} + \frac{\partial^2 P}{\partial V^2} \cdot \left(\frac{dV}{dy_1} \right)^2 + \frac{\partial P}{\partial V} \cdot \frac{d^2 V}{dy_1^2} \quad (24)$$

and

$$\left(\frac{d^2 P}{dV^2} \right)_{sat} = \frac{\partial^2 P}{\partial V^2} + 2 \frac{\partial^2 P}{\partial V \partial y_1} \cdot \frac{dy_1}{dV} + \frac{\partial^2 P}{\partial y_1^2} \cdot \left(\frac{dy_1}{dV} \right)^2 + \frac{\partial P}{\partial y_1} \cdot \frac{d^2 y_1}{dV^2} \quad (25)$$

According to (18) we may replace $(dV/dy_1)_{sat}$ at the critical point by $(\partial V/\partial y_1)_P$.

The last two equations furnish

$$\begin{aligned}
\frac{\partial^2 P}{\partial y_1^2} + 2 \frac{\partial^2 P}{\partial V \partial y_1} \cdot \frac{dV}{dy_1} + \frac{\partial^2 P}{\partial V^2} \cdot \left(\frac{dV}{dy_1} \right)^2 \\
= \left(\frac{d^2 P}{dy_1^2} \right)_C - \frac{\partial P}{\partial V} \cdot \frac{d^2 V}{dy_1^2} \\
= \left[\left(\frac{d^2 P}{dV^2} \right)_C - \frac{\partial P}{\partial y_1} \cdot \frac{d^2 y_1}{dV^2} \right] \left(\frac{dV}{dy_1} \right)^2.
\end{aligned} \tag{26}$$

A transformation of $d^2 y_1 / dV^2$ furnishes

$$\begin{aligned}
\frac{d^2 y_1}{dV^2} &= \frac{d}{dV} \left(\frac{dy_1}{dV} \right) = \frac{dy_1}{dV} \cdot \frac{d}{dy_1} \left(\frac{1}{dV/dy_1} \right) = \\
&= - \frac{dy_1}{dV} \cdot \frac{d^2 V}{dy_1^2} / \left(\frac{dV}{dy_1} \right)^2 = - \left(\frac{dy_1}{dV} \right)^3 \cdot \frac{d^2 V}{dy_1^2}
\end{aligned} \tag{27}$$

so that

$$\frac{\partial P}{\partial y_1} \cdot \frac{d^2 y_1}{dV^2} \left(\frac{dV}{dy_1} \right)^2 = - \frac{\partial P}{\partial y_1} \cdot \frac{dy_1}{dV} \cdot \frac{d^2 V}{dy_1^2} = \frac{\partial P}{\partial V} \cdot \frac{d^2 V}{dy_1^2}. \tag{28}$$

We conclude from (26) and (28) that

$$\left(\frac{d^2 P}{dV^2} \right)_C = \left(\frac{d^2 P}{dy_1^2} \right)_C \cdot \left(\frac{dy_1}{dV} \right)^2 < 0 \tag{29}$$

since dV/dy_1 is finite and since P as a function of y_1 is at a maximum at the critical point. The second critical condition for pure substances does not apply to mixtures.

These relations may be useful in calculations for retrograde condensation, frequently occurring in deep oil wells.

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