Prediction of Vapor-Liquid Equilibria from the Corresponding States Principle

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A new ideal K value is defined which does not depend on the Lewis and Randall ideal solution rule but is derived only from composition dependent pseudo criticals and the corresponding states principle. Properties of the liquid and vapor mixtures are evaluated from either experimentally measured properties of closely related pure substances or from generalized tables of thermodynamic properties. A derivation of an improved pseudocritical expression applicable to liquids which may be approximated by simple spherical molecules is presented. The derivation illustrates the assumptions involved and points the way for a possible extension of the technique to more complex molecules.

There are some advantages to this approach. It does not require the troublesome extrapolation of liquid properties into regions where no liquid can exist, a fact which is characteristic of K value calculations from the ideal solution rule. It is especially useful for systems in which an equation of state is not available for all of the components present. It avoids the difficulties in defining combination rules for complicated equations of state. Even for systems including very complex or moderately polar molecules it provides a base for subsequent empirical modification. This base follows the correct isotherm of ln K vs. ln P up to the actual critical of the system without the difficulties associated with defining a convergence pressure or evaluating the extremely large activity coefficient corrections to the ideal solution rule in the critical region. For mixtures of simple molecules the calculated ideal K value is within about 10% of the experimental value in both the low pressure and in the critical region. The entire calculation may be expressed completely analytically for use on a digital computer and may be coupled with an equilibrium flash calculation so that the ideal K values may be determined from a given overall composition, temperature, and pressure.

This paper will show some of the possibilities of the thermodynamic corresponding states principle in developing analytical methods of predicting K values which are well suited for use with digital computers. The earliest application of the corresponding states principle to this problem was based on the Lewis and Randall ideal solution rule by defining

$$K_{\text{ideal}} = \frac{(f_1^\circ)_L}{(f_1^\circ)_V} \qquad (1)$$

If the K_{ideal} in Equation (1) is equal exactly to y_1/x_1, then the term $(f_1^\circ)_L$ is the fugacity of the pure component 1 at the temperature and pressure of the system in a state which has exactly the same molecular environment as the molecules of this component in the actual liquid phase of the system. The $(f_1^\circ)_V$ term is defined similarly for the pure component in the same environment as the vapor phase. These fugacities may be estimated from generalized thermodynamic properties by means of corresponding states, as was first pointed out by Souders, Selheimer, and Brown (*25*). Under conditions which approach the critical region of the mixture the molecular environment in the solution becomes so completely different from any conceivable pure state that K_{ideal} can differ from the true y_1/x_1 by as much as several hundred per cent. Empirical activity coefficients can be introduced so that

$$\phi_1 = \frac{(\gamma_1)_L}{(\gamma_1)_V} \text{ and}$$

$$K_1 = K_{\text{ideal}}\,(\phi_1) \qquad (2)$$

Of course there is still the difficult problem of correlating these activity coefficients, especially when they become more important than the K_{ideal} value. The value of K_{ideal} itself is awkward to define in Equation (2) because the fugacities such as $(f_1^\circ)_L$ on which these activity coefficients are based must be evaluated by some arbitrarily defined method of extrapolating liquid properties into a pressure-temperature region where the pure liquid does not exist. Smith and Watson (*27*), after defining such an extrapolation method, showed that ϕ can be roughly estimated from a very complicated graphical relationship to reduced properties. Prausnitz, Edmister, and Chao (*19*) avoided the extrapolation problem by first defining a ϕ function and then correlating the required K_{ideal} as a function of temperature and pressure. These studies have shown that it is difficult to define a ϕ function which is accurate over all composition ranges including the critical region. Furthermore if either ϕ or K_{ideal} must be read from a complicated graphical correlation, it is difficult to adapt the procedure for use with computers.

However the effectiveness of the corresponding states principle can be improved tremendously by the use of some recent theoretical developments in the application of this principle to mixtures. These methods have a great

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advantage because they are in no way based on the Lewis and Randall rule and thus avoid all the difficulties of this starting point in extremely nonideal solutions. One such method is the use of reduced virial coefficients introduced by Guggenheim and MacGlashan (*5*) and developed further by Prausnitz (*18, 20*). Prausnitz has shown that in systems consisting of liquids which can be considered to be practically pure in contact with a mixed vapor, the K value of the main constituent of the liquid can be predicted very accurately from virial coefficients for the gas phase.

This paper presents another method of the same type, but one which is valid for all vapor-liquid compositions for nonpolar substances, even in the critical region. This procedure defines a new type of ideal K value which does not depend on the Lewis and Randall rule but is based instead on composition dependent pseudocritical values for the liquid and vapor phase. Any deviations between it and the actual y/x value are due to defects in the pseudocritical concept and corresponding states principle rather than in the ideal solution rule or errors in extrapolated fugacities. It will be shown that the form used for these pseudo criticals need not be purely empirical but may be based upon firm theoretical concepts for both the liquid and vapor phase. The K values depend on differentials of these psuedo criticals so it is very important that they be defined as rigorously as possible.

PSEUDOCRITICAL VALUES FOR LIQUID MIXTURES

An earlier derivation of composition dependent pseudocritical values by Leland and Mueller (*15*) was based on gaseous mixtures. However the utility of these pseudo criticals lies in their applicability to liquids as well as to gases. This may be demonstrated theoretically by showing that these same pseudocritical expressions can also be derived from the molecular distribution function theory of the liquid state as developed by Born and Green (*1*) and by Kirkwood (*12*). Discussions of this theory are also given by Hill (*7, 8*) and by Hildebrand and Scott (*6*).

The equation of state derived from this theory is applicable to liquids in which the total intermolecular potential energy can be described as a sum of pair interactions, the potential energy between a pair depends only upon the distance between them and not on their orientations, and internal energy states of an individual molecule are independent of the density at any given temperature. With these assumptions

$$\frac{P}{kT} = \left[\rho - \frac{1}{6kT} \int_0^\infty r \left(\frac{dU(r)}{dr} \right) G(r, \rho, T)\, 4\pi r^2\, dr \right] \qquad (5)$$

where $G(r, \rho, T)$ is the probability of the existence of a pair with a separation distance between r and $r + dr$. In the limit of a high temperature and low density the molecules become distributed in a completely random manner so that

$$\lim_{\substack{\rho \to 0 \\ T \to \infty}} G(r, \rho, T) = \frac{n}{V} \left(\frac{n-1}{V} \right) \cong \rho^2 \qquad (6)$$

and in this case the function is independent of r and T. Consequently it is convenient to write

$$G(r, \rho, T) = \rho^2 g(r, \rho, T) \qquad (7)$$

where $g(r, \rho, T)$ is called the *radial distribution function*. It serves as a correction for nonrandomness due to both molecular size and intermolecular forces. In a completely random distribution such as an ideal gas its value is unity. This function is of considerable interest because, for monatomic fluids, it may be determined experimentally from X-ray scattering data. Substituting Equation (7) into Equation (5) one gets

$$\frac{P}{kT} = \left[\rho - \frac{2\pi}{3kT} \rho^2 \int_0^\infty r \left(\frac{dU(r)}{dr} \right) g(r, \rho, T)\, r^2\, dr \right] \qquad (8)$$

Kirkwood (*12*) and also Born and Green (*1*) have developed integral equations for $g(r, \rho, T)$ which can be solved numerically. The results agree well with the experimentally determined functions.

For mixtures the random distribution limit of $G(r, \rho, T)$ is $\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \rho_M^2$, where ρ_M is the total molecular density of the mixture. The summations are carried out over the total number of constituents c. A nonrandomness factor may be introduced in the same manner as for pure components, and consequently the equivalent of Equation (8) for a liquid mixture is

$$\frac{P}{kT} = \left[\rho_M - \frac{2\pi}{3kT} \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \rho_M^2 \int_0^\infty r_{ij} \left(\frac{dU(r_{ij})}{dr} \right) g_{ij}\, r^2_{ij}\, dr_{ij} \right] \qquad (9)$$

The term g_{ij} in Equation (9) represents the function $g(r_{ij}, \rho_1, \rho_2, \ldots \rho_c, T)$. In the double summation over the components it generates functions of the separation distance and number density of each component in all possible types of pairs at two positions in the fluid. In a binary system for example the summation will produce terms containing $g(r_{12}, \rho_1, \rho_2, \ldots \rho_c, T)$; $g(r_{21}, \rho_1, \rho_2, \ldots \rho_c, T)$; $g(r_{11}, \rho_1, \rho_2, \ldots \rho_c, T)$; and $g(r_{22}, \rho_1, \rho_2, \ldots \rho_c, T)$. The g_{12} and g_{21} terms are of course identical. Equation (9) is completely rigorous for any mixture conforming to the assumptions listed.

The key to the solution of Equations (8) and (9) lies in the evaluation of the radial distribution function. Unfortunately the equation of state, and consequently all thermodynamic properties, are very sensitive to the form of this function and it is difficult to get accurate numerical results by evaluating the equations directly. However in using the corresponding states principle one does not need to know an exact formulation for $g(r, \rho, T)$, since the technique of the corresponding states principle merely compares the function in one fluid with that in a similar fluid with known properties.

In order to make use of corresponding states Equations (8) and (9) must be written in reduced form. Pitzer (*21*) has shown that this can always be done for any fluid which has an intermolecular potential function in the form

$$U(r) = \epsilon\, \phi(r^*) \qquad (10)$$

where $r^* = (r/\sigma)$. Consequently

$$r \frac{dU(r)}{dr} = \left(\frac{r}{\sigma} \right) \frac{dU(r)}{d(r/\sigma)} = r^* \frac{dU(r)}{dr^*} = \epsilon\, r^* \frac{d\phi(r^*)}{dr^*} \qquad (11)$$

and the group $r^* \dfrac{d\phi(r^*)}{dr^*}$ is dimensionless. Since $g(r, \rho, T)$ is already dimensionless, it may be written in terms of reduced properties so that

$$g(r, \rho, T) = g\left(r^*, \sigma^3\rho, \frac{\epsilon}{kT} \right) \qquad (12)$$

Finally the remaining group r^2dr may be written as

$$r^2 dr = \sigma^3 (r^*)^2\, dr^* \qquad (13)$$

Substituting Equations (11), (12), and (13) into Equations (8) and (9) one gets the reduced forms

$$\left(\frac{Pv}{kT} \right) = 1 - \left[\frac{2\pi}{3} \left(\frac{\epsilon}{kT} \right) (\sigma^3\rho) \int_0^\infty r^* \frac{d\phi(r^*)}{dr^*} g\left(r^*, \sigma^3\rho, \frac{\epsilon}{kT} \right) (r^*)^2\, dr^* \right] \qquad (14)$$

and for the mixture

$$\left(\frac{Pv}{kT}\right) = 1 - \left[\frac{2\pi}{3} \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \left(\frac{\epsilon_{ij}}{kT}\right) (\sigma^3_{ij}\, \rho_M) \int_0^\infty r^*_{ij} \frac{d\phi(r^*_{ij})}{dr^*_{ij}} (g_{ij})\, (r_{ij}{}^*)^2\, dr^*_{ij} \right] \quad (15)$$

If, in Equation (14), it is assumed that $g(r^*, \sigma^3\rho, \epsilon/kT)$ may be expanded as a power series in $(\sigma^3\rho)$, then

$$g(r^*, \sigma^3\rho, \epsilon/kT) = g_o(r^*, \epsilon/kT) + g_1(r^*, \epsilon/kT)\, (\sigma^3\rho) + \ldots \quad (16)$$

With this expansion Equation (14) becomes the reduced form of the familiar virial expansion for a gas. As the gas approaches the liquid state however, this series representation becomes increasingly unsatisfactory, and for the liquid itself $g(r^*, \sigma^3\rho, \epsilon/kT)$ cannot be represented by Equation (16) at all. Nevertheless Kirkwood, Lewinson, and Alder (*14*) have shown that a satisfactory expansion for liquids can be written as follows:

$$g\left(r^*, \sigma^3\rho, \frac{\epsilon}{kT}\right) = g_o\left(r^*, \sigma^3\rho, \frac{\epsilon}{kT}\right) \left[1 + \left(\frac{\epsilon}{kT}\right)\frac{\Psi_1}{r^*} + \left(\frac{\epsilon}{kT}\right)^2 \left(\frac{\Psi_1{}^2}{2(r^*)^2} + \frac{\Psi_2}{r^*}\right) + \ldots\right] \quad (17)$$

where $g_o\left(r^*\ \sigma^3\rho, \frac{\epsilon}{kT}\right)$ is the radial distribution function for a fluid of hard spheres with no intermolecular forces. The Ψ terms are functions of r^* and a new variable λ which is a complicated dimensionless function of the reduced density. For a hard sphere liquid the value of λ becomes

$$\lambda_o = 4\pi N\, (\sigma^3\rho) \quad (18)$$

For this hard sphere fluid Kirkwood, Maun, and Alder (*13*) have shown that

$$g_o\left(r^*, \sigma^3\rho. \frac{\epsilon}{kT}\right) = \left[e^{-\frac{U_o(r^*)}{kT}}\right] \left[e^{\frac{\Psi_o}{r^*}}\right] \quad (19)$$

where Ψ_o is a function only of r^* and λ_o, $U_o(r^*) = 0$ for $r^* > 1.0$, and $U_o(r^*) \to \infty$ for $r^* \leqq 1.0$. The expansion of the radial distribution function is then

$$g\left(r^*, \sigma^3\rho, \frac{\epsilon}{kT}\right) = (e^{-U_o/kT})\,(e^{\Psi_o/r^*}) \left[1 + \left(\frac{\epsilon}{kT}\right)\left(\frac{\Psi_1}{r^*}\right) + \left(\frac{\epsilon}{kT}\right)^2 \left(\frac{\Psi_1}{2(r^*)^2} + \frac{\Psi_2}{r^*}\right) + \ldots\right] \quad (20)$$

TABLE 1. EFFECT OF REDUCED DENSITY CHANGES ON $2\pi\int_0^\infty \Phi(r^*) g\left(r^*, \rho\sigma^3, \frac{\epsilon}{kT}\right)(r^*)^2 dr^*$ FOR LIQUIDS AND COMPRESSED FLUIDS

$$\left[1.732 \frac{z}{z_c} \left(\frac{T_R}{P_R}\right)\left(\frac{\bar{E}^* - \bar{E}}{RT_c}\right)\right] \cong -2\pi\int_0^\infty \Phi(r^*) g\left(r^*, \rho\sigma^3, \frac{\epsilon}{kT}\right)(r^*)^2 dr^*$$

P_R	$T_R = 0.6$	$T_R = 0.8$	$T_R = 1.0$	$T_R = 2.0$
	$\rho_R = 2.75$ to 2.94	$\rho_R = 2.30$ to 2.73	$\rho_R = 1.00$ to 2.56	$\rho_R = 0.137$ to 1.81
0.2	0.403			
0.6	0.401	0.378		
0.8	0.401	0.374		
1.0	0.403	0.376	0.378	0.243
2.0	0.405	0.375	0.364	0.233
4.0	0.405	0.372	0.352	0.212
10.0	0.414	0.372	0.362	0.243
30.0	0.440	0.393	0.384	0.283

To derive pseudocritical properties for the mixtures described by this theory it is necessary to recognize that the pseudo criticals are by their definition the criticals of some imaginary pure substance which has the same thermodynamic properties as the mixture when each are at the same temperature and density. Consequently both this imaginary pure component and the mixture must have the same values of $\frac{3}{2\pi}\left(\frac{z-1}{\rho}\right)$ when each have the same temperature and density. Equating the group $\frac{3}{2\pi}\left(\frac{z-1}{\rho}\right)$ as given by Equations (8) and (9) one obtains

$$\frac{\bar{\epsilon}}{kT}\bar{\sigma}^3 \int_0^\infty (r^*) \frac{d\phi(r^*)}{dr^*} g\left(r^*, \frac{\bar{\epsilon}}{kT}\bar{\sigma}^3\rho_M\right)(r^*)^2 dr^* = \sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j \left(\frac{\epsilon_{ij}}{kT}\right) \sigma^3_{ij} \int_0^\infty r^*_{ij} \frac{d\phi(r^*_{ij})}{dr^*} (g_{ij})\,(r^*_{ij})^2\, dr^*_{ij} \quad (21)$$

In Equation (21) $\bar{\epsilon}$ and $\bar{\sigma}$ are the force constants in the intermolecular potential function of this imaginary pure substance, and since this component must obey the corresponding states principle, they must be proportional to its criticals. Thus

$$\bar{\epsilon} \propto T_c' \quad (22)$$

$$\bar{\sigma}^3 \propto V_c' \quad (23)$$

Although Equation (21) defines the $\bar{\epsilon}$ and $\bar{\sigma}$ required to give the same equation of state as the mixture, these parameters could equally well be defined as the force constants of the imaginary pure component which has any other thermodynamic functions the same as the mixture. For example the internal energy deviation for a fluid mixture subject to the assumptions made here is

$$\left(\frac{E - E^*}{kT}\right) = 2\pi \sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j \left(\frac{\epsilon_{ij}}{kT}\right) \sigma^3_{ij}\rho_M \int_0^\infty \phi(r^*_{ij})\, (g_{ij})\,(r^*_{ij})^2\, dr^*_{ij} \quad (24)$$

and $\bar{\epsilon}$ and $\bar{\sigma}$ are then defined equally well by

$$\left(\frac{\bar{\epsilon}}{kT}\right)\bar{\sigma}^3 \int_0^\infty \phi(r^*)\, g\left(r^*, \bar{\sigma}^3\rho_M, \frac{\bar{\epsilon}}{kT}\right) dr^* = \sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j \left(\frac{\epsilon_{ij}}{kT}\right) \sigma^3_{ij} \int_0^\infty \phi(r^*_{ij})\,(g_{ij})\,(r^*_{ij})^2\, dr^*_{ij} \quad (25)$$

Because Equations (21) and (25) can be derived from each other, any combination of $\bar{\epsilon}$ and $\bar{\sigma}$ values which satisfies one will always satisfy the other.

In applying Equations (21) or (25) to liquids it is important to note that although the radial distribution function itself is influenced considerably by variations in the reduced density, the integrals in these equations are relatively independent of the reduced density. The effect of increasing the reduced density is to increase the amplitude of the peaks corresponding to maxima in the distribution function and to decrease the ordinates of the minima in the curve. There is relatively little lateral displacement so that the area under the curves at different densities is roughly the same. This can be visualized in Figure 1, where radial distributions have been calculated from the tables given by Kirkwood, Lewinson, and Alder and plotted for two different reduced densities at the same reduced temperature. Table 1 shows numerical evidence of this, where the value of the integral in Equation (24) has been

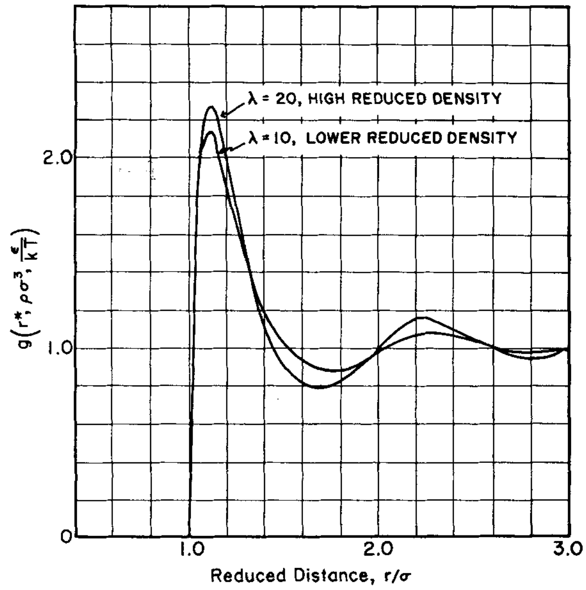

Fig. 1. Radial distribution functions at two reduced densities for $(\epsilon/kT) = 1.0$.

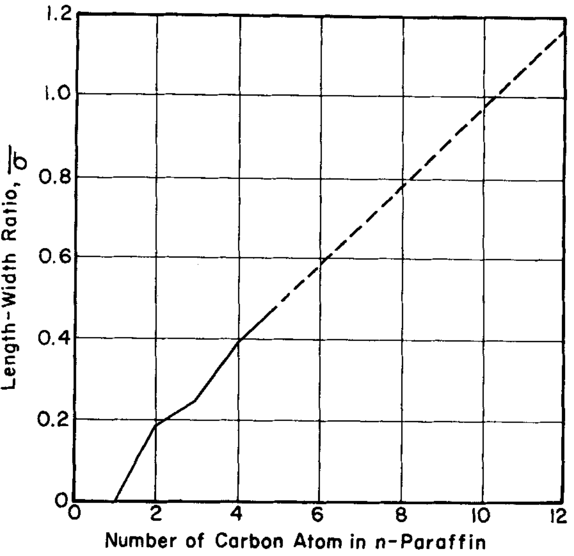

Fig. 3. Extrapolation of length-width ratios for *n*-paraffin hydrocarbons.

determined by solving the equation for the integral after replacing ϵ and σ with their related critical values. The internal energy deviation was obtained from the generalized tables of Lydersen, Greenkorn, and Hougen (*16*). The result is

$$2\pi \int_0^\infty \phi(r^*)\, g\left(r^*.\, \rho\sigma^3.\, \frac{\epsilon}{kT}\right) (r^*)^2\, dr^*$$
$$\cong 1.732\left(\frac{z}{z_c}\right)\left(\frac{T_R}{P_R}\right)\left(\frac{\bar{E}-\bar{E}^*}{R\,T_c}\right) \tag{26}$$

Table 1 shows that for liquids there is almost no effect of increasing the reduced density at constant reduced temperature, except at extremely high densities. The reduced-density effect becomes greater as one approaches the gaseous region, but for gases the radial distribution function can be treated effectively by simply expanding it in powers of density. This means that a very important simplification may be employed in evaluating the right side of Equation (21) or Equation (25) for liquid mixtures. The reduced molecular densities of the individual components which appear in the g_{ij} functions each may be replaced, with little error, by the effective pure component value $(\bar{\sigma}^3\rho_M)$ which appears on the left side of the equations. This is of course valid when only the integrals are required and not the radial distribution functions themselves.

After one makes this simplification and substitutes the expanded radial distribution function, Equation (20), into either Equation (21) or Equation (25), the result of integrating over all values of r^* can be arranged as follows:

$$\bar{\sigma}^3 f_o(\bar{\lambda}_o, T) + \bar{\sigma}^3\epsilon f_1(\bar{\lambda}, T)$$
$$+ \bar{\sigma}^3\bar{\epsilon}^2 f_2(\bar{\lambda}, T) + \ldots.$$
$$= \sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j, \sigma^3{}_{ij}\, f_o(\bar{\lambda}_o, T)$$
$$+ \sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j\, \sigma^3{}_{ij}\, \epsilon_{ij}\, f_1(\bar{\lambda}, T) + \ldots. \tag{27}$$

where $\bar{\lambda} = f(\bar{\sigma}^3\rho_M)$. Equations (21) and (25) will produce different functions of $\bar{\lambda}$ and T, but each will give a result in the form of Equation (27). The first term on each side of Equation (27) is the result for a hard sphere fluid, and the subsequent terms act as correction factors for the intermolecular forces which exist in actual fluids. Collecting terms in Equation (27) one gets

$$[\bar{\sigma}^3 - \Sigma\ \Sigma\, x_i x_j\, \sigma^3{}_{ij}] f_o(\bar{\lambda}_o, T)$$
$$+ [\bar{\sigma}^3\bar{\epsilon} - \Sigma\ \Sigma\, x_i x_j\, \sigma^3{}_{ij}\, \epsilon_{ij}] f_1(\bar{\lambda}, T)$$
$$+ \ldots. = 0 \tag{28}$$

If the pseudocritical values are to be applicable at all temperatures, then the functions $f_o(\bar{\lambda}_o, T)$; $f_1(\bar{\lambda}, T)$ . . . can take on any set of values. As a result each coefficient of $f_o(\bar{\lambda}_o, T)$; $f_1(\bar{\lambda}, T)$ . . . in Equation (28) must be equal to zero. Since this gives an infinite number of equations and only two variables, there is obviously no single set of $\bar{\sigma}$ and $\bar{\epsilon}$ values which can satisfy all of them. This means that rigorously there can be no exact pseudocritical conditions. However the series in Equation (28) may be replaced with an approximate equation containing the first, or hard sphere term, and only one of the remaining terms which account for intermolecular forces, as shown in Equation (29):

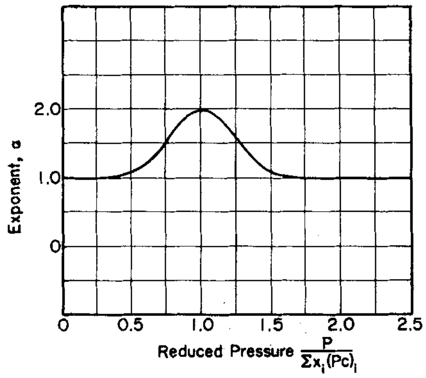

Fig. 2. Empirical evaluation of exponent in pseudocritical expressions.

$$[\bar{\sigma}^3 - \Sigma\ \Sigma\, x_i x_j\, \sigma^3{}_{ij}] f_o(\bar{\lambda}_o, T)$$
$$+ [\bar{\sigma}^3\bar{\epsilon}^\alpha - \Sigma\ \Sigma\, x_i x_j\, \sigma^3{}_{ij}\, \epsilon^\alpha{}_{ij}] \bar{f}_\alpha(\lambda, T) = 0 \tag{29}$$

The exponent α is chosen so that the difference between Equations (29) and (28) is as small as possible. The advantage of the corresponding-states method is that approximating Equation (28) with a two-term expansion is by no means as serious as it would be to attempt to limit Equation (20) to only two terms in a direct evaluation of thermodynamic properties from the radial distribution functions. If the truncation error for the mixture on the right side of Equation (27) is roughly the same as that for the pure substance on the left side, the effect on Equation (28) becomes negligible.

Approximating Equation (28) with (29) and setting the coefficients in (29) equal to zero one obtains

$$[\bar{\sigma}^3\bar{\epsilon}^\alpha - \sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j\, \sigma^3{}_{ij}\, \epsilon^\alpha{}_{ij}] = 0 \tag{30}$$

$$[\bar{\sigma}^3 - \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \, \sigma^3{}_{ij}] = 0 \quad (31)$$

Solving these for $\bar{\epsilon}$ and $\bar{\sigma}$ one obtains

$$\bar{\epsilon} = \left[\frac{\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j (\epsilon^a \sigma^3)_{ij}}{\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \, (\sigma^3)_{ij}} \right]^{1/a} \quad (32)$$

$$\bar{\sigma}^3 = \left[\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \, (\sigma^3{}_{ij}) \right] \quad (33)$$

It is interesting to note that this is the same result as derived earlier (*15*) for gases. If one sets $\bar{\epsilon}$ and $\bar{\sigma}^3$ proportional to T_c' and V_c' and uses combining rules suggested by the derivation presented by Srivastava and Madan (*28*)

$$(\epsilon^a \sigma^3)_{ij} = \sqrt{(\epsilon^a \sigma^3)_i \, (\epsilon^a \sigma^3)_j} \quad (34)$$

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (35)$$

the expressions for T_c' and P_c' in terms of the T_c and P_c values of the pure constituents may be obtained as follows:

$$T_c' = \left[\frac{\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \; a_i a_j}{\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \; (b_i + b_j)^3} \right]^{1/a} \quad (36)$$

where

$$a_i = \left(\frac{z_c \, T_c{}^{a+1}}{P_c} \right)_i^{1/2}$$

and

$$b_i = \frac{1}{2} \left(\frac{z_c \, T_c}{P_c} \right)_i^{1/3}$$

$$P_c' = \left[\frac{T_c' \sum_{i=1}^{c} x_i (z_c)_i}{\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j (b_i + b_j)^3} \right] \quad (37)$$

The value of the exponent α was determined empirically from the evaluation of both compressibility factors and *K* values in vapor-liquid systems. As would be expected from Equation (28) the values of α were found to lie between 1 and 2. It was found that these α values could be correlated empirically against $P/\sum_{i=1}^{c} x_i (P_c)_i$ as shown in Figure 2. A value of $\alpha = 1$, which means that Equation (28) can be satisfactorily approximated by the first two terms, was found to be applicable at all conditions except in the region in which $P/\sum_{i=1}^{c} x_i (P_c)_i$ approaches unity. In this region the best value of α becomes nearer to 2, indicating the increasing importance of higher terms in Equation (28). An empirical equation representing the correlation of α values in Figure 2 is $\alpha = 1.0 + \exp[-10(P/\sum x_i (P_c)_i - 1)^2]$.

K VALUES FROM PSEUDO CRITICALS

If pseudo criticals are thus applicable to both liquid and vapor phases, it is possible to develop an exact expression for the equilibrium values. Gamson and Watson (*4*) and Joffe (*10*) showed earlier that fugacities could be related to pseudocritical values and developed fugacity relationships with Kay's rule (*11*) pseudo criticals. This work extends this approach to obtain ideal *K* values from the more rigorous pseudo criticals defined here. The derivation follows from the definition of the fugacity of any homogeneous multicomponent phase at a fixed temperature and pressure:

$$n \ln f = n_1 \ln \frac{f_1}{x_1} + n_2 \ln \frac{f_2}{x_2} + \ldots\ldots \quad (38)$$

where *f* represents the fugacity of the entire phase and n_1, x_1, and f_1 represent respectively the number of moles, mole fraction, and fugacity of component 1 in the phase. Differentiating Equation (38) one gets

$$d(n \ln f) = \sum_{i=1}^{c} n_i \, d \ln f_i - \sum_{i=1}^{c} n_i \, d \ln x_i + \sum_{i=1}^{c} \left(\ln \frac{f_i}{x_i} \right) dn_i \quad (39)$$

From the Gibbs-Duhem relation

$$\left[\sum_{i=1}^{c} n_i \, d \ln f_i \right]_{T,P} = 0 \quad (40)$$

From the requirement that $\Sigma x_i = 1.0$

$$\sum_{i=1}^{c} n_i \, d \ln x_i = \sum_{i=1}^{c} n_i \frac{dx_i}{x_i} = \sum_{i=1}^{c} n \, dx_i = 0 \quad (41)$$

Upon substitution of (40) and (41) Equation (39) becomes

$$d(n \ln f) = \left(\ln \frac{f_1}{x_1} \right) dn_1 + \left(\ln \frac{f_2}{x_2} \right) dn_2 + \ldots\ldots \quad (42)$$

Equation (42) is the expression of a total differential, so that

$$\frac{\partial (n \ln f)}{\partial n_1} = \ln \frac{f_1}{x_1} \quad (43)$$

and

$$\frac{\partial (n \ln f)}{\partial n_2} = \frac{f_2}{x_2} \quad (44)$$

Expanding the left side of (43) one gets

$$\frac{\partial (n \ln f)}{\partial n_1} = \left[n \left(\frac{\partial \ln f}{\partial n_1} \right)_{T,P,n_2,n_3,\ldots} + \ln f \right] = \ln \frac{f_1}{x_1} \quad (45)$$

Applying (45) to each phase of a vapor-liquid equilibrium system one gets for the liquid phase

$$\ln \left(\frac{f_1}{x_1} \right)_L = \ln f_L + n_L \left(\frac{\partial \ln f_L}{\partial n_{1L}} \right)_{T,P,n_{2L},n_{3L},\ldots} \quad (46)$$

and for the gas phase

$$\ln \left(\frac{f_1}{y_1} \right)_G = \ln f_G + n_G \left(\frac{\partial \ln f_G}{\partial n_{1G}} \right)_{T,P,n_{2G},n_{3G},\ldots} \quad (47)$$

Equating $(f_1)_L$ to $(f_1)_G$ at equilibrium one obtains

$$\ln K_1 = \ln \frac{f_L}{f_G} + n_L \left(\frac{\partial \ln f_L}{\partial n_{1L}} \right)_{T,P,n_{2L},n_{3L}\ldots} - n_G \left(\frac{\partial \ln f_G}{\partial n_{1G}} \right)_{T,P,n_{2G},n_{3G}\ldots} \quad (48)$$

The work of Gamson and Watson (*4*) and Joffe (*10*) has shown that if $\ln f/P$ can be expressed as a function of T_R' and P_R' for each phase, then $\left(\frac{\partial \ln f_L}{\partial n_{1L}} \right)$ and $\left(\frac{\partial \ln f_G}{\partial n_{1G}} \right)$ can be expressed rigorously in terms of thermodynamic properties of the entire phase and partial derivatives of the pseudocritical properties. Using their results in Equation (48) one finds that

TABLE 2. DERIVATIVES OF VARIOUS PSEUDOCRITICAL FUNCTIONS

For n-C_4H_{10} in 100% CH_4 at 160°F., and 3,000 lb./sq. in. abs.

n-butane	Kay's function (*11*)	Joffe's function (*10*)	This work
$n\left(\frac{\partial T_R'}{\partial n_1}\right)$	—2.22	—2.71	—3.62
$n\left(\frac{\partial P_R'}{\partial n_1}\right)$	0.856	—0.195	—2.79

$$\ln(K_1)_{\text{ideal}} = \ln\frac{f_L}{f_G} + \left[\frac{1}{R(T_R')^2}\left(\frac{\bar{H}^* - \bar{H}}{T_c'}\right)\left(\frac{\partial T_R'}{\partial n_1}\right) + \left(\frac{z-1}{P_R'}\right)\left(\frac{\partial P_R'}{\partial n_1}\right)\right]_L n_L - \left[\frac{1}{R(T_R')^2}\left(\frac{\bar{H}^* - \bar{H}}{T_c'}\right)\left(\frac{\partial T_R'}{\partial n_1}\right) + \left(\frac{z-1}{P_R'}\right)\left(\frac{\partial P_R'}{\partial n_1}\right)\right]_G n_G \quad (49)$$

By noting that

$$\frac{\partial T_R'}{\partial n_1} = \frac{T}{(T_c')^2}\left(\frac{\partial T_c'}{\partial n_1}\right)$$

and also that

$$n\frac{\partial}{\partial n_1} = \frac{\partial}{\partial x_1} - \sum_{i=1}^{c} x_i \frac{\partial}{\partial x_i}$$

operating on any $f(x_1, x_2, \ldots)$. Equation (49) is equivalent to

$$\ln(K_1)_{\text{ideal}} = \ln\frac{f_L}{f_G} + [\Psi_{1L} - \Psi_{1G}] \quad (50)$$

where

$$\Psi_{1L} = -\frac{1}{RT}\left(\frac{\bar{H}^* - \bar{H}}{T_c'}\right)\left(\frac{\partial T_c'}{\partial x_1} - \sum_{i=1}^{c} x_i \frac{\partial T_c'}{\partial x_i}\right) - \left(\frac{z-1}{P_c'}\right)\left(\frac{\partial P_c'}{\partial x_1} - \sum_{i=1}^{c} x_i \frac{\partial P_c'}{\partial x_i}\right) \quad (51)$$

and Ψ_{1G} is defined similarly for the vapor phase.

Equation (49) thus defines the ideal *K* value from pseudo properties. One of the advantages of this type of equation for an ideal *K* value is that it permits a wide variety of experimental data sources to be used in its numerical evaluation. The terms $f, (\bar{H}^* - \bar{H})/T_c'$, and z may be determined for each phase from the pseudoreduced properties of the phase with generalized charts or tables or by equating these terms to the known properties of a pure reference substance evaluated at an equivalent temperature and pressure T°, and P° such that

$$T^\circ = (T_R')\,T_c^\circ \quad (52)$$

$$P^\circ = (P_R')\,P_c^\circ \quad (53)$$

T_c° and P_c° are the criticals of the reference substance chosen. These properties of the reference substance for each phase may be either expressed in the form of an equation of state or obtained directly from a tabulation of experimental data. If an equation of state is used to tabulate the properties, a different equation may be used for liquid and vapor phase, or any number may be used to represent different portions of the experimental data for the substance.

The derivatives of the pseudo criticals defined by Equations (36) and (37) are

$$\left(\frac{\partial T_c'}{\partial x_1} - \sum_{i=1}^{c} x_i \frac{\partial T_c'}{\partial x_i}\right) = \frac{2}{\alpha}\left[\frac{\sum_{i=1}^{c} x_i a_1 a_i}{\sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j a_i a_j} - \frac{\sum_{i=1}^{c} x_i (b_1 + b_i)^3}{\sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j (b_i + b_j)^3}\right](T_c') \quad (54)$$

$$\left(\frac{\partial P_c'}{\partial x_1} - \sum_{i=1}^{c} x_i \frac{\partial P_c'}{\partial x_i}\right) = \left[\left(\frac{2}{\alpha}\right)\frac{\sum_{i=1}^{c} x_i a_1 a_i}{\sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j a_i a_j} - (1+\alpha)\left(\frac{2}{\alpha}\right)\frac{\sum_{i=1}^{c} x_i (b_1 + b_i)^3}{\sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j (b_i + b_j)^3} + \left(1 + \frac{z_{c1}}{\sum_{i=1}^{c} x_i z_{ci}}\right)\right](P_c') \quad (55)$$

where

$$a_i = \sqrt{\left(\frac{z_c T_c^{\alpha+1}}{P_c}\right)_i}$$

and

$$b_i = \frac{1}{2}\left(\frac{z_c T_c}{P_c}\right)_i^{1/3}$$

Substitution in Equations (51) and (50) allows numerical evaluation of the ideal *K* value. The importance of using the proper form of the pseudocritical expressions when differentiation is required is shown in Table 2.

SELECTION OF THE REFERENCE SUBSTANCE

If the corresponding states principle were obeyed exactly by all substances, it would make no difference which substance was chosen as the source of the fugacity, enthalpy deviation, and compressibility factor needed in Equations (51) and (50). In actuality the corresponding states principle is obeyed only by those substances which have similar molecular structures, so it is very important that the reference substance chosen have as much molecular similarity as possible with the components of the solution. This can be done by defining a molecular shape factor for each component and selecting the reference substance which has the same shape factor as the average shape factor of the solution. An empirical shape factor of this type is z_c. The reference substance may be chosen as that substance which has a value of z_c nearest to the molal average z_c of the components of the mixture. This procedure has the advantage that it allows the tabulated properties of Lydersen, Greenkorn, and Hougen (*16*) to be used for the reference properties. Slightly better results can be obtained however if one defines a shape factor more clearly related to molecular dimensions. Molecular length-width ratios are examples of this type.

Molecular length-width ratios may be determined from equations of state expressed in terms of intermolecular potential functions which include orientation effects. The length-width ratios appear in the resulting equation and can be evaluated numerically from precise p-v-t data, although the calculation is a very tedious one. A number of these ratios have been determined from the orientation dependent potential function proposed by Corner (*3*). The results are tabulated in Hirschfelder, Curtiss, and Bird (*9*). In this work the Corner length-width ratios for the normal paraffin hydrocarbons through *n*-butane were plotted in Figure 3. The results for the paraffin hydrocarbons beyond *n*-butane are shown by extrapolation. The reference substance for paraffin hydrocarbon systems was then selected as the substance having the same length-width ratio as the molal average length-width ratio of the mixture. Connally and Kandalic (*2*) have shown that it is possible to define satisfactorily length-width ratios by adding the actual bond distances in the molecule. Careful choice of the reference substance is important, but it should be pointed out that choosing similar shape factors in the mixture and reference substance is only a partial correction for differences in molecular structure. A complete extension of this method to nonspherical molecules would require modification of both the intermolecular potential function in Equation (10) and the combining rules in Equations (34) and (35) to include orientation effects. It would then be necessary to determine a radial distribution function which also involves the distribution of orientations so that molecular dimensions would be incorporated into the pseudocritical expressions.

TABLE 3. RESULTS OF CORRESPONDING STATES CALCULATIONS FOR MIXTURES OF SIMILAR MOLECULES

System	Range of temp. and pres.	Avg. % error in calculated *K* ideal		No. of systems
CH_4-CO	−150°F.	CH_4	2.20	4
(*29*)	400 to 720 lb./sq. in. abs.	CO	5.91	
	(CH_4 used as reference)			
CH_4-CO	−225°F.	CH_4	16.0	4
(*29*)	110 to 300 lb./sq. in. abs.	CO	17.6	
	(CO used as reference)			
CH_4-C_3H_8	160°F.	CH_4	5.65	10
(*23*)	400 lb./sq. in. abs. to critical pressure of 1,020 lb./sq. in. abs.	C_3H_8	1.54	
	(C_3H_8 and C_2H_6 used as references.)			

Multicomponent Systems:

Borregas Field, King Ranch, 201°F., 3,827 lb./sq. in. gauge, (*17*) with *n*-pentane as liquid phase reference, *n*-butane as vapor phase reference

Component	$K = y/x$ Calc.	Expt'l.
Methane	1.992	1.757
Ethane	0.907	1.058
Propane	0.573	0.646
i-butane	0.430	0.513
n-butane	0.361	0.448
i-pentane	0.263	0.217
n-pentane	0.240	0.373
Hexanes	0.178	0.189
Heptanes	0.123	0.137
Octanes	0.0885	0.122
Nonanes	0.0626	0.0945
Decanes	0.0468	0.0705
Undecanes	0.0360	0.0502
Dodecanes	0.0282	0.0395
Tridecanes	0.0223	0.0312
Tetradecanes	0.0175	0.0212
Pentadecanes	0.0143	0.0138
Hexadecanes	0.0079	0.0148
Hepta decanes	0.0102	0.0134
Octadecanes plus	0.0005	0.0042

DISCUSSION OF RESULTS

The results of comparing the calculated ideal *K* values with experimental y/x values are shown in Tables 3 and 4. The values for the methane-carbon monoxide system are the result of coupling the ideal *K* value equation with an equilibrium flash calculation which allows one to start with a given overall composition, temperature, and pressure and determine the *K* values. An initial set of trial *K* values are assumed and used in the flash calculation to determine trial vapor and liquid compositions. From these compositions the pseudo properties are calculated and used to predict new ideal *K* values. The process is repeated with the new *K* values until there is negligible variation on successive trials. For a binary system the final *K* values are independent of the overall composition so the results are the unique ideal *K* values predicted for the given temperature and pressure. No information about the mixture is needed, and the K values are predicted solely from properties of the pure component reference substances. These reference substances for the methane-carbon monoxide system were either pure methane or pure carbon monoxide. Calculations were made on a small digital computer. For convenience the pure reference substance properties were obtained from the Benedict-Webb-Rubin Equation for pure carbon monoxide and pure methane. This is entirely an optional procedure, and the method is in no way dependent on this or any other equation of state. One of the advantages of this approach is that one need not know an equation of state. The most accurate procedure would be to obtain the reference substance properties directly from a tabulation of experimental data. In fact the representation of pure carbon monoxide by the B-W-R equation is rather poor at low temperatures, and examination of a great many points for this system showed much larger errors when carbon monoxide was used as a reference than when methane was the reference.

The values in the remainder of Table 2 are *K* values obtained by substituting experimental compositions into the pseudocritical and ideal *K* value equations, because there is generally only a small difference between these results and the final results of the iterative process starting with trial *K* values. In each case the reference substance was chosen as the normal paraffin hydrocarbon with an l/σ value nearest to the molal average l/σ of the mixture. When the molecules were not too dissimilar, very good results were obtained, even up to and including the true critical of the mixture, as shown by the methane-propane results.

This procedure is applicable to mixtures of very dissimilar molecular sizes and shapes provided there is not too great a contribution from extremely dissimilar pairs. The natural gas-heavy oil systems are an example. The gas phase consists chiefly of small molecules, while in the liquid phase the

TABLE 4. RESULTS FOR MIXTURES OF DISSIMILAR MOLECULES WITH *n*-PARAFFIN HYDROCARBONS AS REFERENCE SUBSTANCES

System	Range of temp. and pres.	Avg. % error in calculated *K* ideal		No. of systems
CH_4-$nC_{10}H_{22}$	280° to 340°F.	CH_4	28.8	3
(*23*)	2,250 to 4,000 lb./ sq. in. abs.	$nC_{10}H_{22}$	33.6	
C_3H_8-C_6H_6	160° to 400°F.	CH_4	31.9	8
(*24*)	100 to 800 lb./sq. in. abs.	C_6H_6	25.2	
C_3H_6-1-C_4H_8	100° to 220°F.	C_3H_6	13.3	6
(*24*)	100 to 600 lb./sq. in. abs.	1-C_4H_8	9.7	
C_3H_8-CO_2	70° to 160°F.	C_3H_8	7.07	5
(*24*)	250 to 550 lb./sq. in. abs.	CO_2	25.2	
CH_4-H_2S	40° to 160°F.	CH_4	33.3	10
(*24*)	300 to 1,800 lb./sq. in. abs.	H_2S	6.9	
n-C_5H_{12}-H_2S	100° to 340°F.	nC_5H_{12}	7.4	9
(*24*)	100 to 400 lb./sq. in. abs.	H_2S	23.4	

large molecules predominate. If the heavy fraction is to be combined as C_6^+ or C_7^+, its critical can be estimated by the method of Smith and Watson (*26*). These examples illustrate the advantage of this approach in cases where equations of state are not known for all the components.

In general however the ideal *K* values as developed here become inaccurate for mixtures of extremely dissimilar molecules. This is illustrated by the summary in Table 4. For the calculations presented in Table 4 the normal paraffin with an l/σ value nearest to the molal average l/σ of the mixture was chosen as the reference. Probably better results would have been obtained had the reference substance been chosen from among the constituents actually present in each system. This whole approach should not be applicable to polar molecules, but even here it is seen that the results afford a very good starting point for empirical modification and give a much better basis for activity coefficient ratios than the Lewis and Randall rule. The compressibility factors obtained in the course of the *K* value calculations for the propane-benzene and propene-1-butene systems were compared with experimental values. Discrepancies between calculation and experiment for both liquids and vapors were less than 2%.

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NOTATION

c = number of components in a phase
$E - E^*$ = difference in internal energy per molecule between a system at any given conditions and the ideal gaseous state of the system at the same temperature
$\bar{E} - \bar{E}^*$ = difference in molal internal energy between a system at given conditions and the ideal gaseous state of the system at the same temperature
f = fugacity
f = function
G = probability function for the existence of a molecular pair
g = radial distribution function
$\bar{H} - \bar{H}^*$ = difference in molal enthalpy between a system at given conditions and the ideal gaseous state of the system at the same temperature
K = equilibrium ratio, y/x
k = Boltzmann's constant
l/σ = molecular length-width ratio
N = Avogadro's number
P = pressure
R = gas constant
r = intermolecular separation distance
r^* = ratio of intermolecular separation distance to effective molecular diameter
T = temperature
$U(r)$ = intermolecular potential function
V = volume
x = mole fraction in liquid phase
y = mole fraction in gas phase
z = compressibility factor

Greek Letters

α = empirical constant in pseudo critical expressions
γ = activity coefficient
ϵ = maximum attractive intermolecular potential energy
$\bar{\epsilon}$ = value of ϵ for a hypothetical pure substance with thermodynamic properties equal to those of a mixture
λ = function of reduced density
π = 3.1416
ρ = number density, molecules per unit volume
σ = effective molecular diameter or closest approach distance without repulsion between centers of nonlinear molecules
$\bar{\sigma}$ = value of σ for a hypothetical pure substance with thermodynamic properties equal to those of a mixture
$\phi(r^*)$ = portion of intermolecular function involving only r^*, equal to $U(r)/\epsilon$ for substances obeying the corresponding states principle
Ψ = function of r^* and λ

Subscripts

c = critical property
G = gas phase
i, j = indices to indicate components in summations
L = liquid phase
M = mixture
1, 2, 3 = indices to represent components

Superscripts

$^\circ$ = reference substance property or standard state
* = ideal gas state or reduced intermolecular separation distance
= pseudocritical property

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