Pseudocritical Constants

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Pseudocritical rules provide a means to determine reduced properties for mixtures so that pure component corresponding states correlations may be used to estimate mixture properties. The most common pseudocritical rules are examined and shown to stem from a common base. Points of divergence as well as similarity are pointed out in tracing out the development of the rules. Reduction of all rules to simpler forms is made and criteria attached to allow one to determine when such simplifications are justifiable. All rules reduce to Kay's rule in certain limiting cases.

The so-called *law of corresponding states* expressed in terms of reduced properties has proved a very valuable tool in correlating equilibrium and transport properties of pure materials of a nonpolar nature. The natural course of action has been to extend this law to mixtures. However, to accomplish this task, some technique must be chosen to determine the correct mixture critical properties so that the pure component reduced state correlations will be valid. The use of true mixture critical properties does not, in general, lead to satisfactory mixture correlations. Consequently, considerable use has been made of the pseudocritical concept, based on the supposition that a single pure fluid may exist and possess the same properties as a mixture if each are at the same temperature and pressure. The critical properties of this pure fluid are then the proper pseudocritical properties of the mixture. Only nonpolar, simple molecule systems have been successfully characterized in such a manner.

Various rules have been published in the literature suggesting how such pseudocritical mixture constants may be calculated. The simplest and most widely used is Kay's rule (*11*), where the pseudocritical temperature and pressure are simply mole fraction averages of pure component criticals:

$$T_{c_m} = \sum_i x_i T_{c_i} \tag{1}$$

$$P_{c_m} = \sum_i x_i P_{c_i} \tag{2}$$

It is sometimes stated that Equation (1) is often satisfactory but that use of Equation (2) may lead to considerable error. Many other pseudocritical constant rules have been suggested, and those of Joffe (*10*), Leland and Mueller (*14*), Prausnitz and Gunn (*22*), and Stewart, Burkhardt, and Voo (*25*) are the most well known. All are considerably more complex than Kay's rule and in some cases do not yield significantly different results. The derivations of all these complex rules appear, at first reading, to be very different and involve different simplifying assumptions.

It is the purpose of this paper to show that all the rules can be obtained from a common base and to show the points of divergence as well as those of similarity. Finally, the reduction of all rules to simpler forms will be made and criteria attached to allow one to determine when such simplifications are justifiable. All rules reduce to Kay's rule in certain limiting cases. The accuracy of the various pseudocritical rules to predict physical properties is not considered. All rules are sufficiently accurate that they are widely used in engineering work. Specific comparison with experimental data is found in the references given above.

GENERAL DERIVATION OF PSEUDOCRITICAL RULES

In deriving pseudocritical rules for mixtures one must begin with assumptions made originally by Pitzer (*20*) in deriving the corresponding states principle for pure components. These assumptions include the basic requirement that the properties of the fluid can be derived from any pair interaction potential which has the form

$$U(r) = \epsilon_0 f\left(\frac{r}{\sigma}\right) \tag{3}$$

This leads to a two-parameter corresponding states theorem for pure components. Equation (3) is not applicable to complex molecules, but the corresponding states principle can still be obtained if the pair potential can be factored similarly to Equation (3) into the product of an energy term and a function of dimensionless groups involving separation distance, orientations, and the principal molecular dimensions. The reduced equation of state derived from this type of potential function will contain additional dimensionless groups of molecular dimensions such as length-width ratios.

Since the corresponding states principle does not require any particular analytical form of the function in Equation (3), the two-parameter theory will still apply to complex molecules provided they all have similar values of whatever additional dimensionless ratios are added to the equation of state. The most common method of assuring that all such additional ratios will be reasonably constant is to define a third parameter which is sensitive to molecular shape. If fluids are then grouped into classes according to the third parameter, the two-parameter theory will apply within each class. For molecules which have similar third parameters this will produce a dimensionless equation of state for pure components in the form

$$f\left(\frac{\epsilon_0}{kT}, \frac{P\sigma^3}{\epsilon_0}, \frac{V}{N_0\sigma^3}\right) = 0 \tag{4}$$

Since engineering applications of the corresponding states principle are based on variables reduced with critical constants rather than force constants, it is necessary to show the relation between the parameters σ and ϵ_0 and critical properties. This relation is established by applying Equation (4) to the critical point, where

$$f\left(\frac{\epsilon_o}{kT_c}, \frac{P_c\sigma^3}{\epsilon_o}, \frac{V_c}{N_o\sigma^3}\right) = 0 \qquad (5)$$

$$(\partial P/\partial V)_{T=T_c} = 0 \qquad (6)$$

$$(\partial^2 P/\partial V^2)_{T=T_c} = 0 \qquad (7)$$

Simultaneous solution of these three equations yields three unique values for the dimensionless groups:

$$\epsilon_o/kT_c = a \qquad (8)$$

$$P_c\sigma^3/\epsilon_o = b \qquad (9)$$

$$V_c/N_o\sigma^3 = c \qquad (10)$$

The values a, b, c are constants for all fluids with the same third parameters provided that they have an intermolecular potential function which can be factored like Equation (3). For these fluids then

$$\sigma^3 \propto V_c \qquad (11)$$

$$\epsilon_o \propto T_c \qquad (12)$$

All of these assumptions in the theory for pure components carry over in the extension to mixtures, and some additional assumptions need to be made as well. The most general basis for pseudocritical equations can be developed by applying Equation (3) to generate an equation of state for multicomponent dense fluids through the use of radial distribution functions. The resulting general equation of state is

$$Z = 1 - \frac{1}{6kT}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \rho_m \int_o^\infty r_{ij}\frac{dU(r_{ij})}{dr} g(r_{ij}, \rho_1, \ldots \rho_n, T)\, 4\pi r_{ij}^2\, dr_{ij} \qquad (13)$$

A discussion of the derivation of Equation (13) is given by Hill (7). It can be put in reduced form wherever $U(r_{ij})$ has the form of Equation (3). To develop the pseudocritical concept it is necessary to find a pure component with force parameters $\overline{\sigma}^3$ and $\overline{\epsilon}_o$ which has the same Z value as the mixture when each are at the same T, P, and ρ. The equation for this pure component in reduced form is

$$Z = 1 - \frac{1}{6}\left(\frac{\overline{\epsilon}_o}{kT}\right)(\rho_m\overline{\sigma}^3)\int_o^\infty\left(\frac{r}{\overline{\sigma}}\right)\frac{df(r/\overline{\sigma})}{d(r/\overline{\sigma})} g\left(\frac{r}{\overline{\sigma}}, \rho_m\overline{\sigma}^3, \frac{\overline{\epsilon}_o}{kT}\right)4\pi\left(\frac{r}{\overline{\sigma}}\right)^2 d\left(\frac{r}{\overline{\sigma}}\right) \qquad (14)$$

Equating the right sides of Equations (13) and (14) one gets an equation which defines $\overline{\epsilon}_o$ and $\overline{\sigma}^3$ for this pure component. Relating these to critical properties by means of Equations (11) and (12) one defines pseudocriticals for the mixture. In order that $\overline{\sigma}^3$ and $\overline{\epsilon}_o$ can be found by this procedure, some additional assumptions must be made because almost nothing is known about radial distribution functions for dense fluid mixtures. Depending on the particular assumptions made, equations can be developed which lead to either the Leland and Mueller (LM) Stewart, Burkhardt, and Voo (SBV) or Prausnitz and Gunn (PG) rules.

The pair radial distribution function $g(r_{ii}, \rho_1, \rho_2, \ldots \rho_n, T)$ depends on the separation distance, the molecular number densities of each component, and the temperature. The LM and PG pseudocritical rules follow if it is assumed that this complex function can be replaced in the summations in Equation (13) by

$$g(r_{11}, \rho_1, \rho_2, \rho_3, \ldots \rho_n, T) = g\left(\frac{r_{11}}{\sigma_{11}}, \rho_m\overline{\sigma}^3 \frac{\epsilon_{o_{11}}}{kT}\right) \qquad (15)$$

$$g(r_{12}, \rho_1, \rho_2, \rho_3, \ldots \rho_n, T) = g\left(\frac{r_{12}}{\sigma_{12}}, \rho_m\overline{\sigma}^3, \frac{\epsilon_{o_{12}}}{kT}\right) \qquad (16)$$

The term on the right of Equation (15) represents the distribution function of pure component 1 at the pseudoreduced density of the mixture. The right side of Equation (16) is the distribution function for an imaginary pure fluid with force constants equal to $\epsilon_{o_{12}}$ and σ_{12} at the pseudoreduced density. There is no theoretical justification for this assumption except that the pure component which has the parameter $\overline{\sigma}^3$ is chosen to be as nearly as possible an effective replacement for the mixture. It can be justified empirically for van der Waals fluid mixtures whenever the a and b terms for the mixture are given by the empirical $\Sigma\,\Sigma\, x_i x_j a_{ij}$ and $\Sigma\,\Sigma\, x_i x_j b_{ij}$. In this case van der Waals equation can be rearranged as follows in the form of Equation (13) after the distribution functions have been approximated by (15) and (16):

$$Z = 1 - \frac{1}{kT}\sum_i\sum_j x_i x_j \rho_m \left\{a_{ij} - \left[\frac{kT}{1 - b_m\rho_m}\right]b_{ij}\right\} \qquad (17)$$

Since the van der Waals b term is proportional to V_c and to σ^3, the term $(b_m\rho_m)$ is proportional to $(\overline{\sigma}^3\rho_m)$ and the pseudoreduced density of the mixture.

This assumption in Equations (15) and (16) considerably modifies the dependence of the radial distribution function on composition. It assumes that in addition to r and T the distribution function is dependent only on the force parameters of the molecules in the pair and the average reduced density of the mixture around the pair.

If the terms on the right side of Equations (15) and (16) are now expanded about a hard sphere distribution function in powers of (ϵ_o/kT) as developed for pure components by Kirkwood, Lewinson, and Alder (*12*), the result after performing the integrals in Equations (13) and (14) is

$$\overline{\sigma}^3 f_o(\rho_m\overline{\sigma}^3, T) + \overline{\sigma}^3\overline{\epsilon}_o f_1(\rho_m\overline{\sigma}^3, T) + \ldots = \sum_i\sum_j x_i x_j \sigma^3_{ij} f_o(\rho_m\overline{\sigma}^3, T) + \sum_i\sum_j x_i x_j \sigma^3_{ij}\epsilon_{o_{ij}} f_1(\rho_m\overline{\sigma}^3, T) + \ldots \qquad (18)$$

The details of the expansion in terms of (ϵ_o/kT) in order to derive pseudocriticals have been shown by Leland, Chappelear, and Gamson (*15*). Since this equation must hold for all temperatures and densities of the mixture, the coefficients of the functions f_o, f_1, f_2 ..... on each side of the equation must be equal. The result is

$$\left[\overline{\sigma}^3 - \sum_i\sum_j x_i x_j \sigma^3_{ij}\right] = 0 \qquad (a)$$

$$\left[\overline{\sigma}^3\overline{\epsilon}_o - \sum_i\sum_j x_i x_j \sigma_{ij}\epsilon_{o_{ij}}\right] = 0 \qquad (b)$$

$$\left[\overline{\sigma}^3\overline{\epsilon}_o^2 - \sum_i\sum_j x_i x_j \sigma_{ij}\epsilon^2_{o_{ij}}\right] = 0 \qquad (c) \quad (19)$$

– – – – etc. – – – –

Setting $\overline{\sigma}^3 \propto V_{c_m}$ and $\overline{\epsilon}_o \propto T_{c_m}$ and $\epsilon_{o_{ij}} \propto T_{c_{ij}}$ and $\sigma^3_{ij} \propto V_{c_{ij}}$ provides the starting point for PG and LM.

The SBV rule is developed by making a different assumption in Equations (15) and (16). To produce the form leading to the SBV equation the radial distribution functions on the right sides of Equations (13) and (14) are replaced with pure component forms and are likewise expanded in powers of (ϵ_o/kT) to produce a series of integrals. To obtain the source of the SBV equations each integral produced from the expansion of Equation (14) is then replaced by an arbitrary function $\psi(T_c, P_c, Z_c)_m$. Each integral arising from the expansion of Equation (13) is replaced by the same function $\psi(T_c, P_c, Z_c)_m$ in terms of the individual critical constants. This produces the set

$$[\psi_o(T_c, P_c, Z_c)_m - \sum_i \sum_j x_i x_j \, \psi_o(T_c, P_c, Z_c)_{ij}] = 0 \; (a)$$

$$[\psi_1(T_c, P_c, Z_c)_m - \sum_i \sum_j x_i x_j \, \psi_1(T_c, P_c, Z_c)_{ij}] = 0 \; (b) \qquad (20)$$

-------- etc. ---------

In the principle the SBV approach is more general in that the arbitrary functions could be evaluated empirically for several density ranges and for different composition ranges as characterized by an average third parameter such as $\sum_i x_i Z_{c_i}$. SBV proposed functions consistent with the low-pressure asymptotes of the Van der Waals and Dieterici equations and tested several possible forms.

The same basic equations (*19*) and (*20*) are also obtained for the special case in which Equations (13) and (14) are applied to gases at moderate pressures. In this situation the assumptions of Equations (15) and (16) in regard to the composition dependence of the radial distribution function need not be made, and the radial distribution function may be expanded in a Taylor's series about the ideal gas state of zero molecular density for each component. This develops a power series in the number molecular density of each component and leads directly to the mixture virial expansion:

$$Z = 1 + (\sum_i \sum_j x_i x_j \, B_{ij})\rho_m + (\sum_i \sum_j \sum_k x_i x_j x_k \, C_{ijk})\rho_m^2 + \ldots \qquad (21)$$

The virial coefficients B_{ij}, C_{ijk}, etc. depend only on temperature. This expansion however does not converge at high densities. Equating to the virial expansion for a pure component and expanding the virials in powers of ϵ_o/kT one obtains

$$\bar{\sigma}^3 f_o(T) + \bar{\sigma}^3 \bar{\epsilon}_o f_1(T) + \bar{\sigma}^3 \bar{\epsilon}_o^2 f_2(T) + \ldots$$

$$= \sum_i \sum_j x_i x_j \, \sigma^3_{ij} f_o(T) + \sum_i \sum_j x_i x_j \, \sigma^3_{ij} \epsilon_{o_{ij}} f_1(T) + \ldots \qquad (22)$$

which is analogous to Equation (18). This leads also to Equations (19) and (20). In fact all three authors PG, SBV, LM used the virial expansion in their original developments. The treatment developed here explains the success of all of the pseudocritical rules for liquids and dense gases where the virial expansion does not apply and shows that they may all be obtained from a common source. From this common source further divergence between the various rules takes place depending on subsequent assumptions made.

In the series of equations in (*19*) or (*20*) each term must equal zero. Relationships between the mixture parameters and the pure or interaction parameters are then obtained. However, too many equations result. Only two are necessary to yield correlations for the two-mixture parameters, whereas an infinite set are available. All methods differ somewhat in the method of dealing with this dilemma.

The Random Mixture Solution

For certain types of mixtures Equation (18) or (22) may be solved exactly and the difficulty of overdetermination of the parameters $\bar{\epsilon}_o$ and $\bar{\sigma}^3$ will not arise. In mixtures of this type, molecules have enough similarity so that the radial distribution functions in Equation (15) and (16) are equal for all pairs regardless of the molecular species involved, and molecular sizes are similar enough so that $\sigma_{11} = \sigma_{22} = \sigma_{12} \ldots\ldots$ for all of the pairs. In this case Equation (18) has the exact solution:

$$\bar{\epsilon}_o f\left(\frac{r}{\bar{\sigma}}\right) = \sum_i \sum_j x_i x_j \, \epsilon_{ij} f\left(\frac{r}{\sigma_{ij}}\right) \qquad (19d)$$

This solution then replaces all those shown in (19*a*), (19*b*), and (19*c*). If the potential function $\bar{\epsilon}_o f(r/\bar{\sigma})$ is then assumed to have one Lennard-Jones form, the repulsive portion of the potential on each side of (19*d*) must be equal and similarly for the attractive portion. This produces two equations which may be solved exactly for $\bar{\epsilon}_o$ and $\bar{\sigma}$.

The development of pseudo criticals with this approximation has been worked out by many different authors and is summarized in detail by Rowlinson (*23*). For the Lennard-Jones 12-6 potential the result is

$$\bar{\epsilon}_o = \frac{[\sum \sum x_i x_j \, \epsilon_{ij} \, \sigma^6_{ij}]^2}{[\sum \sum x_i x_j \, \epsilon_{ij} \, \sigma_{ij}^{12}]}$$

$$\bar{\sigma}^3 = \left[\frac{\sum \sum x_i x_j \, \epsilon_{ij} \, \sigma_{ij}^{12}}{\sum \sum x_i x_j \, \epsilon_{ij} \, \sigma_{ij}^{6}}\right]^{1/2} \qquad (19e)$$

Equations (11) and (12) can be used to express the result in terms of criticals. Although this is an exact solution, the molecular requirements for it are seldom met by the mixtures of interest in engineering. All of the pseudo critical rules discussed here are approximate solutions to the set of equations in (19*a*), (19*b*), and (19*c*).

LM Method

The first term is chosen along with one general term involving ϵ_o^{a}, where the best value of α is to be chosen from experimental data:

$$\sigma_m^3 - \sum_i \sum_j x_i x_j \, \sigma_{ij}^3 = 0 \qquad (23)$$

$$\sigma_m^3 \epsilon^{a}_{o_m} - \sum_i \sum_j x_i x_j \, \sigma_{ij}^3 \, \epsilon^{a}_{o_{ij}} \qquad (24)$$

All other terms will not be equal to zero:

$$\sigma_m^3 \, \epsilon^{\gamma}_{o_m} - \sum_i \sum_j x_i x_j \, \sigma_{ij}^3 \, \epsilon^{\gamma}_{o_{ij}} \neq 0, \gamma \neq 1, \alpha \qquad (25)$$

Ideally, the best choice of the exponent α should make all the remaining terms, as represented by (25), as small as possible. A value of $\alpha = 1$ is always a good approximation.

SBV Method

Again, only the first two terms of the equation set (20) are chosen in the expansion. These are the ψ_o and ψ_1 terms. All other ψ expressions are assumed $\neq 0$.

PG Method

Equation set (19*a*, *b*, *c*) is used with Equations (11) and (12). The first term is then

$$V_{c_m} - \sum_i \sum_j x_i x_j \, V_{c_{ij}} = 0 \qquad (26)$$

but the second and third terms are added to give

$$V_{c_m}[K_1(T/T_{c_n})^{-1} + K_2(T/T_{c_m})^{-2}] = \frac{K_1}{T} \sum_i \sum_j x_i x_j \, V_{c_{ij}} \, T_{c_{ij}}$$

$$+ \frac{K_2}{T^2} \sum_i \sum_j x_i x_j \, V_{c_{ij}} \, T_{c_{ij}}^2 \qquad (27)$$

Higher terms are not considered.

EFFECTS OF MOLECULAR DISSIMILARITY

The assumption of a two-parameter intermolecular potential as in Equation (3) actually leads to the requirement that all the components in the mixture must obey a two-constant equation of state. Furthermore, since it is necessary to the development of pseudocriticals that the same intermolecular potential function apply to all components, it follows that the functional form of this two-constant equation of state is the same for all substances. This means that any pseudocritical rules based on a two-parameter intermolecular potential function cannot rigorously correct for deviations from the simple similar molecular corresponding states theory, and in this case Z_c is rigorously required to be a universal constant, as is true for any generalized two-constant equation of state.

A rigorous extension of the pseudocritical concept to mixtures of highly dissimilar molecules based on theoretical considerations is very complicated and in practice requires simplifying approximations to produce useful pseudocritical rules. It will aid the understanding of the various pseudocritical definitions to examine briefly the essential characteristics of the theoretical extension to nonpolar dissimilar molecules and to identify the simplifying approximations made by the different rules.

The first principle to be noted is that if Z_c is a variable, the analysis must include at least one variable characteristic of the molecular species other than Z_c in addition to the variables needed for the simple corresponding states theory. This can be shown both by examining the nature of the intermolecular potential for complex molecules and also by dimensional analysis. In the simple corresponding states theory for similar molecules derived from a two-parameter intermolecular potential, dimensional analysis shows that there are

Dimensioned quantities = $P, V, T, P_c, V_c, T_c, R$ = 7
Dimensions = mass, length, time, temperature = 4

Variable dimensionless groups = 3

The law of dimensional analysis requires that the number of variable dimensionless groups be equal to the number of dimensional quantities less the rank of the exponent coefficient matrix less the number of independent equations among the exponents resulting from any relations applying among subgroups of the dimensioned quantities. In this case the rank of the exponent coefficient matrix is 3 (Figure 5), and there is one equation resulting from the fact that the definition of R requires that $R = \lim_{p \to 0} (PV/T)$. This relationship means that the exponent on R must always be restricted to equal the exponent on T. The number of variable dimensionless groups is then (7-3-1) = 3. These three groups may be chosen so that $f(PV/RT\ P/P_c, T/T_c) = 0$. Then solving for the value of Z at the critical shows that Z_c must be a universal constant for all components. Now in order to predict properties of dissimilar molecules, suppose Z_c is included as an additional variable, instead of as a constant for all fluids. In this case the number of variable dimensionless groups is now 4. The number of dimensions, the rank of the matrix, and the restriction on the exponent of R remain the same so that there must now be 8 dimensioned quantities instead of 7. Consequently, in any pseudocritical rule with pure component properties defined only by the 7 dimensioned quantities P, V, T, P_c, V_c, T_c, and R, the term Z_c cannot completely account for the deviations from simple corresponding states theory caused by molecular dissimilarity. Some new dimensioned variable is needed. Suppose this new variable is designated by L, defined as the length of some principle molecular axis. Then grouping these 8 dimensioned quantities into the 4 dimensionless groups by the conventional method will always include L in some of them.

The introduction of this additional variable stems from molecular interactions which require a more elaborate potential function in Equation (3). In order for a corresponding states principle to apply, this new potential must still be factorable into an ϵ_0 term and a dimensionless function f, but the f function must now contain at least one dimensionless group such as r/L in addition to the r/σ variable shown in Equation (3). In order to describe the interaction accurately, other variables may be needed also. An example might be r/W, where W is another molecular parameter representing a molecular width. For complex nonpolar molecules which can be represented by rigid ellipsoids, spherocylinders, rods, or disks a good discussion of the molecular dimensions required for the potential function and the resulting dimensionless groups introduced into the virial coefficients is presented by Hirschfelder, Curtiss, and Bird (8). There are many different ways of defining dimensions analogous to L and W and the resulting dimensionless groups introduced into the equation of state for various molecular shapes.

The equation of state analogous to Equation (4) obtained from this new potential will now contain additional dimensionless groups such as V/L^3 and V/W^3. Equations (8), (9), and (10) will no longer have universal constants on their right-hand sides. Instead, the a, b, and c terms would be functions of V_c/L^3 and V_c/W^3. Since the ratio ab/c is seen from Equations (8), (9), and (10) to be equal to Z_c, this means that Z_c is no longer a universal constant but is now a function of the new groups V_c/L^3 and V_c/W^3 which involve the molecular structure.

The same methods as used before can derive an equation analogous to (18). Equating the coefficients on the right and left side of the new Equation (18) will likewise produce a set of equations as in (19). This time, however, there are four variables and four sets of equated coefficients to be solved simultaneously.

If it is desired to find the correct $(Z_c)_m$, the critical compressibility of this pure reference component, one could use the fact that Equations (8) through (10) show that $(Z_c)_m$ for this component is defined by $(V_c)_m/\overline{L}^3$ as discussed above. A plot or table of Z_c vs. V_c/L^3 and V_c/W^3 for various substances could be made to establish this relationship so that $(Z_c)_m$ could then be obtained rigorously from $\overline{L}$ and $\overline{W}$ for the reference component.

This inclusion of more equations to be solved simultaneously in (19), although necessary for dissimilar molecules, makes the solution almost prohibitively complicated. The different rules thus make various empirical approximations at this point. None of the rules have derivations which solve more than two simultaneous equations. Consequently it is necessary to define the variables $\overline{L}$ and $\overline{W}$ arbitrarily so that the reference fluid is selected empirically as the fluid whose molecular properties are some reasonable average of those in the mixture.

The SBV and LM procedures solve two equations based on a two-parameter potential function with no additional molecular variables such as L and W included in the two equations. Deviations due to molecular dissimilarities are accounted for empirically by replacing Z_c wherever it appears with the actual Z_c of the component, instead of the universal constant Z_c as rigorously required by the derivation. The value of $(Z_c)_m$ is defined empirically as $(Z_c)_m = \sum_i x_i Z_{ci}$, and, in place of solving more than two equations, the reference fluid is selected as the one with a Z_c value nearest to $\sum_i x_i Z_{ci}$.

The PG procedure also solves only two equations, but they do include additional molecular parameters. The equations whose solution gives $(T_c)_m$ contains new variables r and s which are related to the average of Pitzer's acentric factor $\sum_i x_i\omega_i$ by means of a separate empirical correlation. Since only two equations are solved, the reference fluid is chosen arbitrarily as the one with an acentric factor nearest to $\sum_i x_i\omega_i$.

INTERACTION CONSIDERATIONS

At this point, each method has generated a pair of equations. The first member [Equations (19*a*), (20*a*), and (26)] will be used to determine a pseudocritical volume and the second member [Equations (19*b*), (20*b*), and (27)] a pseudocritical term involving the product of volume and energy. Algebraic manipulation and an equation of state will eventually lead to explicit expressions for the pseudocritical temperature and pressure. At this point, however, some consideration must be given to the question of relating the interaction terms $V_{c_{ij}}$, σ_{ij}, $\epsilon_{o_{ij}}$, etc. to properties of the pure components.

The only theoretical basis for predicting interaction parameters for unlike nonpolar molecules is London's description of the attractive interaction between nonpolar symmetrical molecules. The London Equation (*16*) is

$$-U(r_{ij}) = \frac{3h}{2}\left(\frac{\nu_i\,\nu_j}{\nu_i+\nu_j}\right)\frac{\alpha_i\,\alpha_j}{r_{ij}^6} \tag{28}$$

A discussion of the physical origin of this attraction is presented by Margenau (*18*). Equation (28) involves one dimensional vibrational frequencies of the separated molecules ν_i and ν_j and their polarizabilities α_i and α_j. Equation (28) describes only the attractive portion of the potential function and does not express the repulsion at very short distances and, as written, does not apply to molecules with permanent dipole moments.

For a pure component, Equation (28) becomes

$$-U(r_{ii}) = \frac{3}{4}\,(h\,\nu_i)\;\alpha_i^2/r_{ii}^6 \tag{29}$$

The energy $h\nu_i$ can be determined from the experimental measurement of the variation of the index of refraction with the frequency of the incident light. From these results it is found that the energy $h\nu$ is approximately equal to the ionization potential I, or energy required to remove one of the outermost electrons from the molecule. If one uses this approximation and then compares Equation (29) with the attractive portion of the Lennard-Jones potential, the result is

$$4\epsilon_{o_i}\,\sigma_i^6 = \frac{3}{4}\,(h\nu_i)\;\alpha_i^2 = \frac{3}{4}\,I_i\,\alpha_i^2 \tag{30}$$

For an unlike pair the corresponding relation is

$$4\epsilon_{o_{ij}}\,\sigma_{ij}^6 = \frac{3}{2}\left[\frac{I_i\,\alpha_i\,I_j\,\alpha_j}{I_i+I_j}\right] \tag{31}$$

From Equation (30) it is seen that

$$\left[\frac{2\sqrt{I_iI_j}}{I_i+I_j}\right]\sqrt{\frac{3}{4}\,I_i\alpha_i^2}\;\sqrt{\frac{3}{4}\,I_j\alpha_j^2} = \frac{3}{2}\left[\frac{I_i\,\alpha_i\,I_j\,\alpha_j}{I_i+I_j}\right] \tag{32}$$

Substituting Equations (30) and (31) into (32) and rearranging one gets

$$\epsilon_{o_{ij}}\,\sigma_{ij}^6 = \left[\frac{2\sqrt{I_iI_j}}{I_i+I_j}\right](\sigma_i^3\sigma_j^3)\;\sqrt{\epsilon_{o_i}\epsilon_{o_j}} \tag{33}$$

Equation (33) thus relates the unlike interaction parameters to those for pure components.

For many substances the ionization potential is unknown. It can be predicted from the fact that it is approximately a linear function of $(1/\sigma^3)$. When one uses a linear relation between I and $(1/\sigma^3)$, Equation (33) becomes

$$\epsilon_{o_{ij}} = \left[\frac{2\sqrt{\left(\dfrac{m}{\sigma_i^3}+A\right)\left(\dfrac{m}{\sigma_j^3}+A\right)}}{\left(\dfrac{m}{\sigma_i^3}+A\right)+\left(\dfrac{m}{\sigma_j^3}+A\right)}\left(\frac{\sigma_i^3\sigma_j^3}{\sigma_{ij}^6}\right)\right]\sqrt{\epsilon_{o_i}\epsilon_{o_j}} \tag{34}$$

where m and A are the slope and intercept of I plotted vs. $(1/\sigma^3)$.

Equation (34) is as far as one can go in predicting theoretically the unlike pair parameters from those for like pairs alone. It is still necessary to have an additional equation to define σ_{ij}. Nothing theoretically can be done better than to use the result for hard spheres:

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

From Equation (33) and a correlation between I and σ^3 it is seen that whenever $\sigma_i \sim \sigma_j$, and Equation (34) applies, Equation (33) reduces to the familiar Berthelot relation:

$$\epsilon_{o_{ij}} = \sqrt{\epsilon_{o_i}\epsilon_{o_j}} \tag{36}$$

The use of Equation (33) if the ionization potential is known and various approximations like Equation (34) if it is unknown has been examined by various authors (*1*, 3, 9, *24*). Although it is an improvement over Equation (36), its numerical value is not sufficiently different from $\sqrt{\epsilon_{o_i}\epsilon_{o_j}}$ to account for the occasionally large deviations encountered experimentally for some dissimilar molecular pairs. This is not surprising considering the crudity of the model from which it is derived. Consequently, various authors simplify the equation or modify it empirically. Equation (36) usually gives values of $\epsilon_{o_{ij}}$ which are too high. The helium-xenon pair, for example, after allowances are made for the quantum mechanical behavior of the helium, still requires an $\epsilon_{o_{ij}}$ value about 0.6 times that given in Equation (36). No reasonable definition of σ_{ij} will ever produce coefficients of $\sqrt{\epsilon_{o_i}\epsilon_{o_j}}$ in Equation (34) which are this small. Some sort of empirical modification is necessary.

Prausnitz and Gunn (*22*) assume that since σ^3 is roughly proportional to V_c, Equation (34) could be written as

$$\epsilon_{o_{ij}} = \sqrt{\epsilon_{o_i}\,\epsilon_{o_j}} - f(V_{c_i}/V_{c_j}) \tag{37}$$

Assuming a proportionality between ϵ_o and T_c one defines $T_{c_{12}}$ from Equation (37). The function f is correlated empirically for various binary systems.

An obvious simplification of Equation (33) is to note that even for quite dissimilar pairs the ratio $2\sqrt{I_i\,I_j}/(I_i + I_j)$ is always very nearly unity. For example, the pair Ne-C_2H_4 (neon-ethylene), which has I values of 21.5 and 12.2 ev, respectively, gives a value of 0.962 for this ratio. With this simplification

$$\epsilon_{o_{ij}}\,\sigma_{ij}^6 = \sigma_i^3\,\sigma_j^3\,\sqrt{\epsilon_{o_i}\,\epsilon_{o_j}} \tag{38}$$

In using corresponding states, the usual practice is to use criticals instead of force constants by assuming

$$\begin{gathered}\epsilon_o \propto T_c\\ \sigma^3 \propto V_c\end{gathered} \tag{39}$$

For complex molecules this simple proportionality is not valid. The effects of deviation from Equation (39) and the effects of omitting the ionization potential term can be considered to cause the following empirical modification of Equation (38):

$$\epsilon_{o_{ij}}\,\sigma_{ij}^{3} = \sqrt{\sigma_i^{3}\epsilon_{o_i}\,\sigma_j^{3}\epsilon_{o_j}} \tag{40}$$

or, perhaps, more generally

$$\epsilon_{o_{ij}}^{a}\,\sigma_{ij}^{3} = \sqrt{\sigma_i^{3}\epsilon_{o_i}^{a}\,\sigma_j^{3}\epsilon_{o_j}^{a}} \tag{40a}$$

In introducing criticals $V_{c_{ij}}$ is defined as

$$V_{c_{ij}} = \left[\frac{V_{c_i}^{1/3} + V_{c_j}^{1/3}}{2}\right]^{3} \tag{41}$$

and the combining rule, for the case of $\alpha = 1$, becomes

$$T_{c_{ij}}V_{c_{ij}} = \sqrt{V_{c_i}T_{c_i}\;V_{c_j}T_{c_j}} \tag{42}$$

As shown later, Equation (42) is the combining rule used by LM rather than Equation (38). This has been found empirically to be an improvement over Equation (38) and (36) for dissimilar molecules. An example of the improvement is the very dissimilar pair methane-neopentane. The value of B_{12} was determined experimentally at 303°K. by Hamann (*6*) as −165 cc./g. mole. Equation (38) with Equations (35) and (39) predicted this virial within about 8% from the reduced virial curve for methane (*17*). Equations (42) and (35), when used with Equation (39) and the methane virial curve, predicted the result within about 3%. Combining rules based on Equations (36) and (35) predicted the result within 14.5%. Comparable results are obtained for the data of Fox and Lambert (*4*) on *n*-hexane-diethyl ether using the reduced virial curve for diethyl ether obtained from Danon and Pitzer's (*2*) correlation as a reference. For dissimilar molecules best results have been obtained to date with Equations (40) and (41) with force constants proportional to criticals as in Equation (39). The best reference is the reduced virial equation for the component in the pair which has the smallest acentric factor ω as defined by Pitzer (*21*). Data on dissimilar nonpolar molecules, however, are limited, and the results of all the combining rules are often within the experimental error of the determination of B_{12}. For more similar pairs, the results of using either Equation (38) or (40) or (36) become almost identical.

In summary, among the combining rules which do not involve empirical constants there are only slight differences, but there is definitely a small improvement over the simple geometric mean. The greatest improvement comes from including empirical constants, but no equation has been developed to date which correlates all of the available experimental data of comparable accuracy.

FINAL VOLUME TERMS

LM

Equation (23) with Equations (35) and (39) yields

$$V_{c_m} = \frac{1}{8}\sum_i\sum_j x_i x_j\,[V_{c_i}^{1/3} + V_{c_j}^{1/3}]^{3} \tag{43}$$

SBV

To illustrate this technique, a value of ψ_o must be assumed. SBV choose many different forms for ψ_o, but the final recommended form was

$$\psi_o = C_o\,(T_c/P_c) \tag{44}$$

To use Equation (44) in Equation (20*a*) some combination rule must be devised to obtain $(T_c/P_c)_{ij}$. Since (T_c/P_c) is approximately proportional to a critical volume reasoning from Equation (35)

$$(T_c/P_c)_{ij}^{1/3} = [(T_c/P_c)_i^{1/3} + (T_c/P_c)_j^{1/3}]/2 \tag{45}$$

Then, from Equations (20*a*), and (45)

$$(T_c/P_c)_m = \frac{1}{8}\sum_i\sum_j x_i x_j\,[(T_c/P_c)_i^{1/3} + (T_c/P_c)_j^{1/3}]^{3} \tag{46}$$

PG

Equations (26) and (35) combined yield the same volume equation as LM, Equation (43).

SIMPLIFICATION OF VOLUME TERMS

First it may be noted that all methods yield very similar results, Equation (46) reducing to Equation (43) if the critical compressibilities of all components are equal. Next, SBV suggested a convenient mathematical simplification in that

$$(1/8)\,(V_{c_i}^{1/3} + V_{c_j}^{1/3})^{3} \cong (1/3)\left[\left(\frac{V_{c_i} + V_{c_j}}{2}\right) + 2\sqrt{V_{c_i}V_{c_j}}\right] \tag{47}$$

This approximation is within 0.3% for $0.125 < V_{c_j}/V_{c_i} < 8.0$. In fact Equation (47) may often be simplified further by approximating the right-hand side by $(V_{c_i} + V_{c_j})/2$. The fractional error introduced is about equal to

$$(2/3)\,(V_{c_i}^{1/2} - V_{c_j}^{1/2})^{2}/(V_{c_i} + V_{c_j})$$

For example, in a binary system suppose $V_{c_1} = 27$ and $V_{c_2} = 64$ cc./mole. This is an extreme case for most binary systems. Then the left hand side of Equation (47) is 43.0 cc./g. mole the right hand side 42.9 cc./g. mole, and the simple arithmetical average 45.5 cc./g. mole. The error introduced by the first approximation is 0.2% and by the second 5.8%. For systems with more comparable critical volumes, the latter error is much less and the arithmetical approximation probably justified in view of the assumptions involved in deriving Equations (43) or (46). PG have selected this simple form and express the critical mixture volume as

$$V_{c_m} = \sum_i\sum_j x_i x_j\left(\frac{V_{c_i} + V_{c_j}}{2}\right) = \sum x_i V_{c_i} \tag{48}$$

FINAL VOLUME-ENERGY TERMS

LM

When one expresses the interaction terms in Equation (24) by (39) and makes use of (40*a*), Equation (24) becomes

$$\begin{aligned} T_{c_m}^{a} &= \frac{1}{V_{c_m}}\sum_i\sum_j x_i x_j\,[(V_cT_c^{a})_i(V_cT_c^{a})_j]^{1/2} \\ &= \frac{1}{V_{c_m}}\left(\sum_i x_i V_{c_i}^{1/2}T_{c_i}^{a/2}\right)^{2} \end{aligned} \tag{49}$$

where V_{c_m} is given by Equation (43).

SBV

In Equation (20*b*), ψ_1 may be chosen in any manner consistent with the dimensions of (energy) (volume). As ψ_o was taken as T_c/P_c, a logical choice of ψ_1 would be $C_1(T_c^2/P_c)$. Using the geometric mean analogue of Equation (42) one obtains

$$(T_c^2/P_c)_{ij} = [(T_c^2/P_c)_i (T_c^2/P_c)_j]^{1/2} \tag{50}$$

Equation (20*b*) then becomes

$$(T_c^2/P_c)_m = \sum_i \sum_j x_i x_j \, [(T_c^2/P_c)_i \, (T_c^2/P_c)_j]^{1/2}$$

$$= \Bigl[\sum_i x_i \, (T_{c_i}^2/P_{c_i})^{1/2} \Bigr]^2 \tag{51}$$

PG

Equation (27) may be reduced to a quadratic form by replacing T by $T_{r_m} T_{c_m}$ and defining β^1, γ^1, l_1, and l_2 as shown in the nomenclature; then

$$T_{c_m} = \frac{l_1 \beta^1}{V_{c_m}} + \frac{l_2 \gamma^1}{V_{c_m} T_{c_m}} = \frac{\beta^1 + \sqrt{(\beta^1)^2 + r V_{c_m} \gamma^1}}{2s V_{c_m}} \tag{52}$$

where $r = 4l_2/l_1$ and $s = 1/l_1$. PG found that r and s were functions of T_{r_m} and the Pitzer acentric factor (*21*) and are given in convenient plots in their article (*22*). V_{c_m} is given by Equation (48). Solution of Equation (52) is trial and error since T_{c_m} must be known to obtain T_{r_m} to get r and s; however, as a first guess it was suggested that T_{c_m} be approximated as β^1/V_{c_m}. This approximation results from the fact that in many cases the ratio $(V_{c_m}\gamma^1/\beta^{1^2})$ is about unity, and the parameters r and s are closely approximated as $r = 4\,s\,(s - 1)$. Insertion of these results into Equation (52) yields

$$T_{c_m} \cong \beta^1/V_{c_m} \tag{53}$$

Equation (53) is identical to LM Equation (54) if α is taken as unity and the geometric mean rule [Equation (42)] is used to obtain the interaction product $(V_{c_{ij}} T_{c_{ij}})$.

PG did not recommend that Equation (42) be applied to obtain $(V_{c_{ij}} T_{c_{ij}})$; rather they combined Equations (37) and (39) to obtain $T_{c_{ij}}$ and approximated $V_{c_{ij}}$ as $(V_{c_i} + V_{c_j})/2$ + a small correction term to account for asymmetry. The simplifications to reduce LM and PG rules to a common form illustrate some of the major difference in the two recommended equations.

SIMPLIFICATION OF ENERGY-VOLUME TERMS

The three methods discussed lead to similar results. LM's rule is given by Equation (49), SBV's rule by Equation (51), and PG's rule by Equation (52) or, approximately, Equation (53) if the critical compressibilities of all components are assumed equal. LM correlated the value of α with the ratio of $P_r(K)/T_r(K) = \theta^*$, where the reduced conditions are determined from Kay's rule, Equations (1) and (2). α may be expressed rather conveniently as

$$\begin{aligned} &= 2.43 - 0.74\,\theta,\ 1.9 > \theta > 0.5 \\ &= 2.2,\ \theta < 0.5 \\ &= 1.0,\ \theta > 1.9 \end{aligned} \tag{54}$$

It can be seen that α may differ somewhat from unity except at low values of $T_r(K)$ and/or high values of $P_r(K)$.

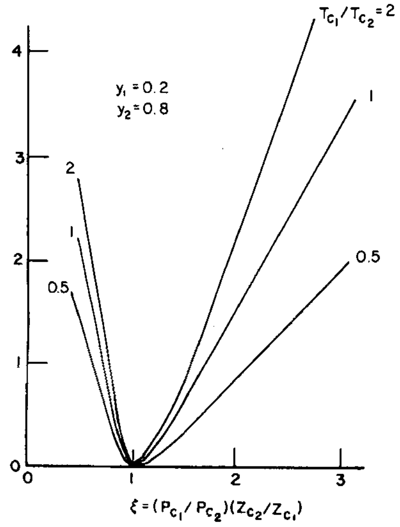

Fig. 1. Deviation of Kay's pseudocritical temperature rule from theoretical rules.

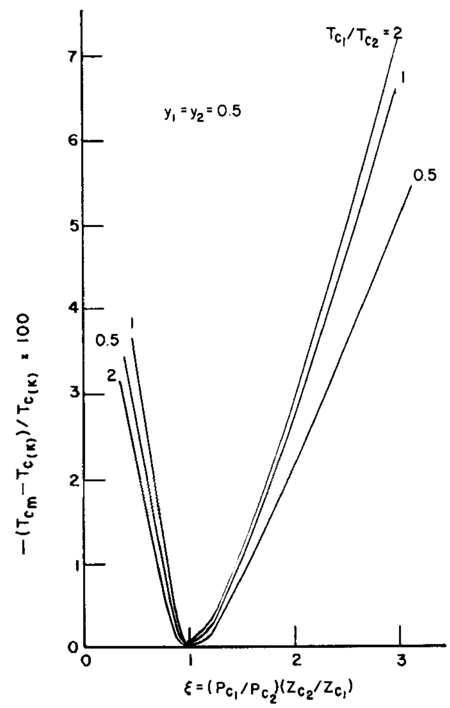

Fig. 2. Deviation of Kay's pseudocritical temperature rule from theoretical rules.

Joffe's Rule

Joffe's rule was originally derived from Van der Waal's equation by making certain assumptions relating the interaction constants a_{ij} and b_{ij} to pure component constants (*10*). b_{ij} was considered a volume term, and Equation (35) was used. The constant a_{ij} was assumed a geometric mean of a_j and a_i [as in Equation (42)]. Equation (21) was used to relate mixture parameters to interaction or pure component parameters. Joffe's resulting expressions for T_{c_m} and P_{c_m} are identical to Equations (46) and (51) developed by SBV with their particular choices of ψ_o and ψ_1.

REDUCTION OF ALL METHODS TO KAY'S RULE

Pseudocritical Temperature

The first task is to reduce all the methods to a general form. For LM's rule, Equation (49), α is assumed about unity and V_{c_m} approximately by Equation (48). For PG's, the simplified form, Equation (53), is chosen with product $(V_{c_{ij}} T_{c_{ij}})$ given by the geometric mean of the pure component values. As before, V_{c_m} is approximated by Equation (48). For SBV's rule, Equation (51), one may ex-

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* Note in the original article the definition of θ was mistakenly inverted.

press $P_c = Z_c\, RT_c/V_c$ for all components in the mixture, and in addition

$$V_{c_m}/Z_{c_m} \cong \sum_i x_i\, V_{c_i}/Z_{c_i} \qquad (55)^*$$

Then all the methods reduce to

$$T_{c_m} = \left(\sum_i T_{c_i}^{1/2} X_i^{1/2} \right)^2 \Bigg/ \sum_i x_i X_i \qquad (56)$$

where

$$\begin{aligned} X_i &= V_{c_i} \text{ (LM or PG)} \\ &= V_{c_i}/Z_{c_i} \text{ (SBV)} \end{aligned}$$

Comparison with Kay's rule may be made by calculating $[T_{c_m} - T_c(K)]/T_c(K)$, the fractional deviation of the pseudocritical temperature as given by Equation (56) from that predicted by Kay's rule, Equation (1). To illustrate the magnitude of the deviation, it may be shown for a binary system of 1 and 2

$$\frac{T_{c_m} - T_c(K)}{T_c(K)} = \frac{-(\xi^{1/2} - 1)^2 x_1 x_2}{\dfrac{T_{c_1}}{T_{c_2}} x_1^2 + (\xi + 1) x_1 x_2 + \left[\xi \Big/ \left(\dfrac{T_{c_1}}{T_{c_2}} \right) \right] x_2^2} \qquad (57)$$

where

$$\begin{aligned} \xi &= (T_{c_1}/T_{c_2})(X_2/X_1) \\ &= (T_{c_1}/T_{c_2})(V_{c_2}/V_{c_1}) = (P_{c_1}/P_{c_2})(Z_{c_2}/Z_{c_1}) \text{ LM or PG} \\ &= (T_{c_1}/T_{c_2})(V_{c_2}/V_{c_1})(Z_{c_1}/Z_{c_2}) = (P_{c_1}/P_{c_2}) \text{ SBV} \end{aligned}$$

In Equation (57), since the ratio Z_{c_i}/Z_{c_j} is usually quite near unity, the deviation appears to depend primarily on the ratio of the critical pressures, becoming zero if $P_{c_1} = P_{c_2}$ independent of composition or the critical temperature ratio of the pure components. Equation (57) is shown plotted in Figures 1 and 2 for $x_1 = 0.2$ and $x_1 = 0.5$ and for T_{c_1}/T_{c_2} ratios of 0.5, 1, and 2. The most striking point about these figures is the small deviation from Kay's rule shown even for systems widely divergent in pure critical properties; the deviation is always negative and rarely exceeds 1 or 2% except for vastly dissimilar systems. For components present in small concentrations, Kay's rule will always yield pseudocritical temperatures closer to the other rules if the minor component has a smaller critical temperature. The curve for $x_1 = 0.8$ was not drawn, as it may be inferred from the $x_1 = 0.2$ plot by interchanging all subscripts. Also on Figure 2 for an equal-molar mixture the expected symmetry can be noted; that is for $T_{c_1}/T_{c_2} = 1$, the deviations are identical for any ξ and $1/\xi$, or, similarly, for example, the deviation for $T_{c_1}/T_{c_2} = 2$, $\xi = 0.5$ is the same as $T_{c_1}/T_{c_2} = 0.5$, $\xi = 2$ since one may arbitrarily choose which component is designated 1 or 2.

Pseudocritical Pressure

It is more difficult to obtain a direct comparison between pseudocritical pressures calculated by the theoretical rules and Kay's rule since the former are not expressed explicitly for P_{c_m} but rather all rules yield a mixture volume. However, an approximation may be made as follows: Kay's rule is chosen as a suitable rule for T_{c_m} based on the small errors illustrated by Figures 1 and 2, and

$$P_{c_m} = Z_{c_m}\, RT_{c_m}/V_{c_m} \qquad (58)$$

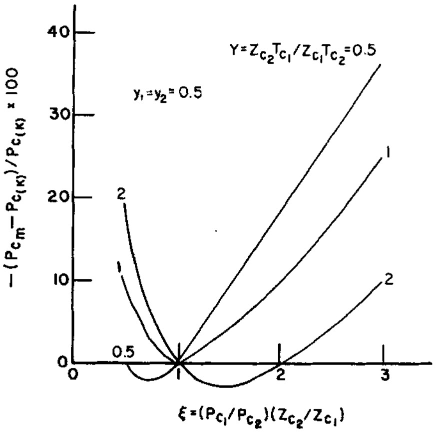

Fig. 3. Deviation of Kay's pseudocritical pressure rule from theoretical rules.

where V_{c_m} is given by Equation (48); that is

$$V_{c_m} = \sum_j x_j\, V_{c_j} = R \sum x_j\, Z_{c_j}\; T_{c_j}/P_{c_j}$$

and Z_{c_m} is assumed a linear mole fraction average. Combining, one obtains

$$P_{c_m} = \left(\sum_j x_j Z_{c_i} \right) \left(\sum_j x_j T_{c_j} \right) \Bigg/ \sum_j x_j Z_{c_j} T_{c_j}/P_{c_j} \qquad (59)$$

The deviation from Kay's rule can then be shown to be, for a binary system

$$\frac{P_{c_m} - P_c(K)}{P_c(K)} = \frac{-x_1 x_2 [\xi^2 - (1 + Y)\,\xi + Y]}{Q\,\xi\,Y\,x_1^2 + x_1 x_2\,(\xi^2 + Y) + \xi\, x^2/Q} \qquad (60)$$

where ξ is defined as in Equation (57):

$$\begin{aligned} Y &= (T_{c_1}/T_{c_2})(Z_{c_2}/Z_{c_1}) \\ Q &= Z_{c_1}/Z_{c_2} \end{aligned}$$

Thus the deviation depends upon composition, ξ, Y, and Q. To illustrate the magnitude of the deviations, neglect the effect of Z in the denominator, i.e., let $Q \sim 1$. Values of Z differ only slightly from unity, and, in any case, the result is not appreciably affected if Q is allowed to take on values other than unity. Figures 3 and 4 have been drawn to show the deviations from Kay's rule for $x_1 = 0.2$ and $x_1 = x_2 = 0.5$, respectively.

The deviations of Kay's rule [Equation (2)] from P_{c_m} given by Equation (59) may be relatively large. However, if either $\xi = 1.0$ or $Y = \xi$, then interestingly enough the deviation is zero. The criteria $\xi = 1.0$ indicates that the pure component critical pressures are equal (actually $P_{c_2}/Z_{c_2} = P_{c_1}/Z_{c_1}$), and the criteria $Y = \xi$ indicates that $V_{c_2} = V_{c_1}$. If either of these conditions are met, then ap-

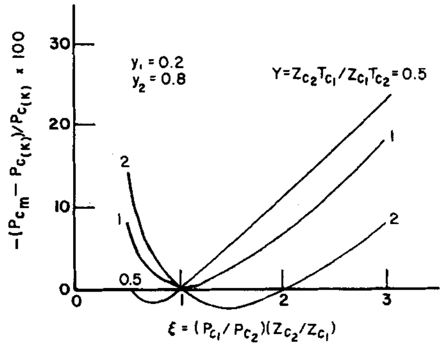

Fig. 4. Deviation of Kay's pseudocritical pressure rule from theoretical rules.

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[*] This approximation assumes that, for a binary system

$$x_1 x_2 \{[(V_{c_1}/Z_{c_1}) - (V_{c_2}/Z_{c_2})]\,[Z_{c_2} - Z_{c_1}]\}$$

is small compared with

$$\sum_i x_i V_{c_i} / \sum_i x_i Z_{c_i} \text{ or } V_{c_m}/Z_{c_m}$$

$$\begin{array}{l|ccccccc|}
 & P & V & R & T & P_c & V_c & T_c \\
\text{Mass} & 1 & 0 & 1 & 0 & 1 & 0 & 0 \\
\text{Length} & -1 & 3 & 2 & 0 & -1 & 3 & 0 \\
\text{Time} & -2 & 0 & -2 & 0 & -2 & 0 & 0 \\
\text{Temperature} & 0 & 0 & -1 & 1 & 0 & 0 & 1
\end{array}$$

Rank = 3

Fig. 5. Exponent coefficient matrix for simple molecule reduced equation of state.

parently Kay's rule is as satisfactory as any other method for estimating the pseudocritical pressure. For other cases, the deviation may be large and Kay's rule a poor approximation.

It may also be noted that the deviations from Kay's rule of both T_{c_m} and P_{c_m} usually increase with ξ values greater or less than unity. This would indicate that in calculating a compressibility factor, Z_m from T_{r_m} and P_{r_m}, that increases in T_{r_m} will be associated with corresponding increases in P_{r_m}. Such a behavior will tend to negate changes in the estimation of Z_m in the T_r, P_r range, where Z vs. P_r has a negative slope but not in the compressed fluid region where both P_r and $T_r > 1$. In addition, Z is often more sensitive to changes in T_r than P_r, so that errors in the estimation of P_{r_m} may not be as significant as those for T_{r_m}. This might indicate that for these regions Kay's rule for P_{c_m} would still be suitable for most engineering work. This conclusion may not, however, be valid at low values of T_r or near the critical point.

The discussion given above relating T_{c_m} and P_{c_m} to Kay's values is, of course, based on the several simplifying assumptions to reduce the various theoretical rules to common form. However, Figures 1 through 4 do indicate in an approximate manner the percentage deviations which may be expected if expediency requires one to use Kay's rules rather than those founded on a more theoretical basis. If one were to establish criteria for deciding when to use Kay's rules, perhaps the following would be useful as a guide for binary mixtures.

1. For T_{c_m}, Kay's rules will differ by less than 2% from other rules if $0.5 < T_{c_1}/T_{c_2} < 2$ and $0.5 < P_{c_1}/P_{c_2} < 2$. For other values of T_{c_1}/T_{c_2} and P_{c_1}/P_{c_2} outside this range, Equation (57) should be used to estimate the errors.

2. For P_{c_m}, Kay's rule appears to yield values of P_{c_m} close to other rules if either $P_{c_1} = P_{c_2}$ or $V_{c_1} = V_{c_2}$. For other cases, differences are usually less than 10% for $0.5 < P_{c_1}/P_{c_2} < 2$ and T_{c_1}/T_{c_2} near unity. For other ranges, Figures 3 or 4 or Equation (60) should be used to obtain an estimate of the deviation.

NOTATION

a = van der Waal's constant; or dimensionless group in Equation (8)
A = constant in Equation (34)
b = van der Waal's constant; or dimensionless group in Equation (9)
B = second virial coefficient
c = dimensionless group in Equation (10)
C = third virial coefficient; proportionality constant between ψ and some function of T_c and P_c as in Equation (44)
h = Planck's constant
I = ionization potential
g = radial distribution function
k = Boltzmann's constant
K = constant
(K) = Kay's rule
l_1 = $(K_1/T_{r_m})/(K_1T_{r_m}^{-1} + K_2T_{r_m}^{-2})$
l_2 = $(K_2/T_{r_m})/(K_1T_{r_m}^{-1} + K_2T_{r_m}^{-2})$
m = constant in Equation (34)
N_o = Avogadro's number
P = pressure
Q = parameter in Equation (60)
r = distance of separation in molecules or $4l_2/l_1^2$
R = gas constant
s = $1/l_1$
T = temperature
U = potential energy of attraction
V = molar volume
x = mole fraction
X = parameter defined in Equation (56)
Y = parameter defined in Equation (60)
Z = compressibility factor

Greek Letters

α = exponent in Equation (24) or polarizability
β' = $\sum_i \sum_j x_i x_j V_{c_{ij}} T_{c_{ij}}$
γ = exponent in discarded terms in Equation (25)
γ' = $\sum_i \sum_j x_i x_j V_{c_{ij}} T_{c_{ij}}^2$
ϵ = interaction energy
θ = $P_r(K)/T_r(K)$
ν = frequency of vibration
ξ = parameter defined in Equation (57)
σ = distance of separation between molecules at $\epsilon = 0$ or empirical factor
ψ = function in Equation (20)
ρ = density

Subscripts

c = critical
i = component i
j = component j
ij = interaction term between components i and j
m = mixture
o = condition at minimum energy of interaction or an interaction energy parameter
1 = component 1
2 = component 2

Bar over a symbol represents a force parameter for a pure component which has same compressibility factor as mixture at same T, P, and ρ.

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Feedback Control of an Overdetermined Storage System

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Although it is already known how to apply feedforward control to an overdetermined system (*2*), feedback control is more difficult because overdeterminancy involves more measured variables than controllers. Feedback control is possible for a system of production units separated by storage tanks holding intermediate products and perturbed by random external upsets (*1*). Two types of feedback control are studied: local control in which each manipulated variable is controlled by the levels in the two tanks immediately adjacent, and central control in which all the levels simultaneously affect each manipulated variable. The behavior of these systems for three-action linear controllers is described. Proportional local control is shown to have a structure similar to those of the unrefluxed countercurrent separation processes of the chemical industry. Such systems are therefore inherently stable. Central control, although requiring a more complicated equipment arrangement, actually has a simpler dynamic behavior because it cancels out interactions between controllers.

An overdetermined control system is one in which the number of variables to be controlled, that is held within predetermined limits, exceeds the number of variables manipulated by the controllers (2). Past work on overdetermined systems has been confined to feedforward schemes in which the manipulated variables are adjusted as functions of the uncontrollable disturbances upsetting the system (*1*, *2*, *3*). This article shows how to control an overdetermined system by feedback, that is by making the manipulated variables depend on the variables to be regulated. Since in an overdetermined system there are more measurements of controlled variables than there are controllers, how to apply feedback control is not obvious.

The particular overdetermined system considered is a set of production units in series separated from each other by storage tanks holding intermediate product (*1*). Any or all of the levels in these tanks are subjected to random disturbances from outside the system. The control problem is to regulate the production rates to counteract the disturbances and prevent any tank from becoming completely full or empty. This problem, quite common in the chemical industry, is usually handled now on an ad hoc basis by planning and coordinating groups.

After a brief review of previous work, definition of terms, and mathematical statement of the control problem, two feedback schemes are analyzed. The first, local control, makes each production rate depend only on the levels in the tanks holding feed and product for that particular production unit. The second is called *central control* because each production rate is influenced by the levels of all the tanks in the system. Local control is simpler to implement but more difficult to analyze. Despite the complicated interactions between the manipulated flow rates resulting from local control, it is possible to show that local control is inherently stable if linear controllers are used. On the other hand, the more intricate physical layout required by central control is offset by the surprising simplicity of its dynamic behavior, for the extra information channels actually cancel out all controller interactions. Thus while local control has the slowness of a high-order system, central control behaves more like a set of independent (and inherently stable) first-order systems. Incidentally, local proportional control gives a system with a structure, that is signal flow diagram, resembling that of unreflexed countercurrent multistage separation processes, for which the dynamic behavior is already known in some detail (*7*, *8*).

Full proofs are outlined only for the major results involving the asymptotic behavior of local control and the absence of controller interaction in centrally controlled systems. Consequences that would be fairly obvious to engineers experienced in linear control theory are merely