Application of the Corresponding States Principle to Mixtures of Low Molecular Weight Gases at Low Temperatures and High Pressures

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This paper presents an extension of the corresponding states principle to mixtures of low molecular weight, nonpolar gases at low temperatures. It corrects the corresponding states principle for quantum mechanical effects but neglects any deviation from Maxwell-Boltzmann statistics. A comparison is made between compressibility factors obtained from reduced second-virial coefficients and those obtained from pseudo-critical values. The use of reduced virial coefficients is limited by the fact that there are not enough experimental data to permit extensive correlations of third-virial coefficients. The pseudo-critical expressions derived for higher temperatures are accurate at cryogenic temperatures provided the reference substance chosen has a molecular weight close to that of the mixture as well as a similar molecular shape.

There are two main avenues of approach in applying the corresponding states principle to multicomponent systems. One is through the use of reduced virial coefficients introduced by Guggenheim (*4*), Guggenheim and McGlashan (*5*), and further developed by Prausnitz and Gunn (*34*). The other is through the use of composition dependent pseudo-critical properties proposed originally by Kay (*13*) with later improvements by Joffe (*11*), Stewart, et al. (*38*), and Leland and Mueller (*19*). The method of reduced virials is more rigorous theoretically, but the thermodynamic properties evaluated from it are usually limited at present to conditions under which the gas behavior can be described by equations involving only the second virial. The method of pseudo-criticals, while more empirical in nature, does not completely neglect the effect of higher virials. It is the purpose of this paper to study the possibilities of extending each method to low-temperature systems and to compare the results as to their present utility and future potentialities.

REDUCED VIRIAL COEFFICIENTS

Guggenheim and McGlashan (*5*) showed that

$$\frac{B_{ij}}{\sigma_{ij}^{3}} = f\left(\frac{T}{\epsilon_{ij}}\right) \tag{1}$$

Plots of Equation (1) have been prepared (*5*) for molecules which are similar to each other and free from quantum effects. The total second virial for a mixture is then (*15*)

$$B_M = \sum_i \sum_j x_i\, x_j\, B_{ij} \tag{2}$$

In evaluating σ_{ij} and ϵ_{ij} for unlike pairs the usual practice is to use

$$\sigma_{ij} = \frac{1}{2}\,(\sigma_{ii} + \sigma_{jj}) \tag{3}$$

which should be valid for rigid spherical molecules and

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\ \epsilon_{jj}} \tag{4}$$

which is based on London's theory of dispersion forces (*20, 21*). Equation (4) is valid only for similar nonpolar molecules and is completely inadequate for many systems of interest. Prausnitz and Gunn (*34*) have correlated correction factors for Equation (4) for systems at room temperature and above. An empirical correction factor which is applicable at low temperatures is proposed here.

In applying Equation (1) to systems of light molecules at cryogenic temperatures it is necessary to use force constants evaluated from a virial expansion which considers quantum effects. Uhlenbeck and Beth (*39*) and Kirkwood (*16*) have shown that the second-virial coefficient may be written as

$$B = B_{cl} + B^{(1)} + B^{(2)} + \ldots \tag{5}$$

At still lower temperatures, below approximately 20°K., it is necessary to include an additional term in Equation (5) which accounts for the deviation from Maxwell-Boltzmann statistics. The

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systems studied here were all at temperatures where this statistical correction term is negligible.

In Equation (5) B_{c1} is the classical second-virial coefficient given by

$$B_{c1} = 2\pi N \int_0^\infty (1 - e^{-U(r)/kT})\, r^2\, dr \tag{6}$$

and $B^{(1)}$ and $B^{(2)}$ are quantum corrections. The first is given by

$$B^{(1)} = \frac{2\pi N \hbar}{12\, m\, k^3\, T^3} \int_0^\infty e^{-U(r)/kT} \left[\frac{d\,U(r)}{dr}\right]^2 r^2\, dr \tag{7}$$

In order for the corresponding states principle to apply, Pitzer (33) showed that the intermolecular potential function must have the form

$$U(r) = \epsilon \left[f\left(\frac{\sigma}{r}\right) \right] \tag{8}$$

For gases with large molecular weights at high temperatures Equation (6) alone applies. Under these conditions when one substitutes a potential function in the form of Equation (8) into Equation (6) and uses the critical criteria $\left(\frac{\partial P}{\partial V}\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$ the result is

$$\sigma^3 = a\ V_c \tag{9}$$

$$\epsilon = b\, T_c \tag{10}$$

where a and b have the same values for all substances conforming to Equation (8).

However if one substitutes Equation (8) into Equation (5) when the $B^{(1)}$, $B^{(2)}$, ... terms are considered, which is necessary for cryogenic temperatures, the result is

$$\sigma^3 = \phi\, (a\, V_c) \tag{11}$$

$$\epsilon = \theta\, (b\, T_c) \tag{12}$$

where ϕ and θ are no longer universal constants but are functions of the dimensionless group $h/\sigma\sqrt{m\epsilon}$. Furthermore, as was first shown by Lunbeck (22) and de Boer (2), Equation (1) now applies only to substances which have the same value of this parameter $h/\sigma\sqrt{m\epsilon}$. A table of σ and ϵ values obtained from Equation (5) by using the Lennard-Jones potential for Equation (8) is presented by Hirschfelder, Curtiss, and Bird (7). These values may be used in Equation (1) for systems described adequately by this potential. For gases having any potential in the form of Equation (8) in which the contributions of $B^{(1)}$, $B^{(2)}$, ..., are significant, substituting Equation (11) and Equation (12) into Equation (1) one gets

$$\frac{B_{11}}{\phi_1 (V_c)_1} = f\left(\frac{T}{\theta_1 (T_c)_1}\right) \tag{13}$$

When one uses the combining rules in Equations (3) and (4) the interaction virials become

$$\frac{B_{12}}{\left[\frac{1}{2}(\phi_1 V_{c_1})^{1/3} + \frac{1}{2}(\theta_2 V_{c_2})^{1/3}\right]^3} = f\left(\frac{T}{\sqrt{\theta_1 T_{c_1}\, \theta_2 T_{c_2}}}\right) \tag{14}$$

This procedure avoids the necessity of a tedious solution for the force constants in cases not already evaluated in the literature and no longer requires the system to have a potential described by the Lennard-Jones relation. However the force constants evaluated from the Lennard-Jones potential can be used to evaluate θ and ϕ, since

$$\phi = \left(\frac{\sigma_q}{\sigma_{c_1}}\right)^3 \tag{15}$$

and

$$\theta = \left(\frac{\epsilon_q}{\epsilon_{c_1}}\right) \tag{16}$$

The ratios will cancel some of the inadequacies of the Lennard-Jones potential. The values of ϕ and θ used here were correlated by plotting the ratios of the Lennard-Jones potential force constants given in Hirschfelder, Curtiss, and Bird (7) against $1/V_c^{1/3}\sqrt{m\,T_c}$. The results are shown in Table 1 and Figure 1.

Because of the restriction that Equations (13) and (14) can apply only to substances which have a potential function described by Equation (8) and the same value of $h/\sigma\sqrt{m\epsilon}$, it is convenient to have a means of evaluating $h/\sigma\sqrt{m\epsilon}$ directly from critical constants. This is done by defining a parameter Q as

$$Q = \frac{59.0}{(\phi\, V_c)^{1/3}\, \sqrt{m\,\theta\, T_c}} \tag{17}$$

where the numerical constant results from combining other constants and has units of (cc./g. mole)$^{1/3}$ (°K)$^{1/2}$. The parameter Q is very closely equal to $h/\sigma\sqrt{m\epsilon}$.

For the prediction of virial coefficients at low temperatures a plot of Equation (13) with experimental virial coefficient data for He, H_2, D_2, CH_4, and Ne was prepared, with Q as a parameter. The plot is sketched in Figure 2, and smoothed values from the plot are presented in Table 2. A discussion of the experimental data selected has been presented in greater detail (*28, 29*). At high molecular weights θ and ϕ become unity and Q approaches zero. In this case the plot and table become independent of Q and reduce to the same type of correlation as presented by Guggenheim and McGlashan (5).

For many systems it is necessary to account for the shortcomings of Equation (4) by introducing a correction factor. Equation (14) then becomes

$$\frac{B_{12}}{\left[\frac{1}{2}(\phi_1 V_{c_1})^{1/3} + \frac{1}{2}(\phi_2 V_{c_2})^{1/3}\right]^3} = f\left(\frac{T}{\xi\sqrt{\theta_1 T_{c_1}\, \theta_2 T_{c_2}}}\right) \tag{18}$$

where ξ is evaluated empirically. For low-temperature systems it is difficult to evaluate this correction factor, and it can be quite important. There is considerable disagreement among many of the experimental data on interaction virials at low temperatures. Any theoretical evaluation of ϵ_{12} requires analysis of the electronic structures of the individual molecules themselves and is difficult to generalize. However examination of London's dispersion-force theory furnishes some qualitative guides as to the factors to be considered in correlating an empirical correction term. The important factors are enumerated below.

1. The London dispersion force arises from fluctuations in the molecular electron configurations, and Equation (4) considers that these fluctuations may be described by simple harmonic oscillators with the same frequency in each molecule. This should be valid only for very similar molecules which have like sizes and electron configurations. For a given difference in molecular size the difference in character of the oscillators should be greater when the oscillations involve only a small number of electrons than when the number is large. As a rough measure of the effect of electronic configuration differences an empirical factor was defined as the absolute value of the difference in the effective molecular volume, a number proportional to ϕV_c, divided by the total atomic number of the two molecules. It thus represents a volume difference per electron in the oscillating pair.

2. The presence of permanent dipoles and nonspherical electronic configurations is not considered in the derivation of Equation (4). These effects require an angular dependence or orientation effect in the potential function. This angular dependence may be eliminated by considering that all molecules which interact always possess an average orientation. The procedure for averaging however introduces a temperature dependence into the potential, since the various orientations are, in the classical case,

weighted by the Boltzmann factor $e^{-U_{12}(r)/kT}$ to give:

$$\overline{U_{12}(r)} = \frac{\iint U_{12}(\mathrm{r}, \omega_1, \omega_2)\, e^{-U_{12}(r,\omega_1,\omega_2)/kT}\, d\omega_1 d\omega_2}{\iint e^{-U_{12}(r,\omega_1,\omega_2)/kT}\, d\omega_1 d\omega_2} \tag{19}$$

The ω_1 and ω_2 terms are angular orientation variables for each molecule. This temperature effect should become more pronounced at low temperatures owing to the increasing magnitude of the exponent. For like pair interactions this temperature dependence is taken into account by plotting Equation (13) from experimental data and restricting the plot to substances with similar shapes; however when B_{12} is evaluated by means of Equation (14) from plots drawn from pure component data, this temperature effect must appear in ξ when there is a difference in structure in the pair.

These two effects are combined in Figure 3 by plotting values of ξ required to predict experimental data against the ratio

$$\frac{|\Delta(\phi V_c)|}{(\Sigma\, \nu_i A_i)\, T}\ (10^8)$$

Figure 3 was determined with mixture data from the references in Table 3. The ν_i term represents the number of atoms of the ith kind with atomic number A_i. The $\Sigma \nu_i A_i$ term is the total number of electrons in the pair. Figure 3 must be regarded as a rough approximation, although for molecules containing relatively few atoms it gives some improvement over Equation (4) at temperatures between about 60°K. and room temperature. The correlation becomes unreliable for values of the abscissa greater than 40, and for values less than 10, ξ was found to be always unity. The value of ξ depends so much on individual molecular properties that very probably no completely satisfactory general correlation is possible. There is a great need for more experimental data and further study on interaction virials and combining rules for ϵ and σ.

In using the reduced virial method of predicting compressibility factors or other thermodynamic properties the pure component virials are found by interpolation among the values of Table 1 or Figure 2 which represent Equation (13) at different Q values. The necessary values of θ and ϕ are read from Figure 1. Interaction virials are also obtained from Table 2, but the virials and temperature are reduced as in Equation (18). The ξ correction term is read from Figure 3. In order to interpolate between values in Table 2 it is necessary to define a Q_{12} value for an unlike pair virial. This is done by calculating $\theta_{12} = \sqrt{\theta_1 \theta_2}$ and reading $\left(\frac{1}{V_c^{1/3}\sqrt{m\,T_c}}\right)_{12}$ at this θ_{12} value for the pair in Figure 1. The corresponding ϕ_{12} term is then read at this $\left(\frac{1}{V_c^{1/3}\sqrt{m\,T_c}}\right)_{12}$ value on the other curve in Figure 1. The value of Q_{12} for the unlike pair is then

$$Q_{12} = \left(\frac{59.0}{V_c^{1/3}\sqrt{m\,T_c}}\right)_{12} \left(\frac{1}{\theta_1\,\theta_2}\right)^{1/4} \left(\frac{1}{\phi_{12}}\right)^{1/3} \tag{20}$$

Since $\sqrt{\theta_1\,\theta_2} = \frac{\sqrt{(\epsilon_1)_q\,(\epsilon_2)_q}}{\sqrt{(\epsilon_1)_{cl}(\epsilon_2)_{cl}}}$, it is assumed that any ξ correction term for errors in this combination procedure will cancel in numerator and denominator

The virial for the mixture B_m is then calculated from Equation (2), and an equation of state at this temperature can be written as

$$z = 1 + \left(\frac{B_m}{RT}\right) P \tag{21}$$

Obviously this procedure for calculating the compressibility factor is applicable only in the regions where the compressibility factor isotherms are nearly linear.

PSEUDO-CRITICAL VALUES

The derivation of pseudo-critical values for multicomponent mixtures at moderate and high temperatures has been discussed in an earlier article (*19*). This same technique can be extended to apply to light gases at low temperatures when quantum effects are important (*28, 29*). The form of the pseudo-critical equations under these conditions can be deduced from the type of equations which result when potential functions conforming to Equation (8) are substituted into Equations (6) and (7). A typical potential function conforming to Equation (8) for which virials have been calculated is the Lennard-Jones potential:

$$U(r) = 4\,\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{22}$$

This potential function serves only as an example to show the form of the equations which are obtained. The final results are in no way dependent on the validity of the Lennard-Jones potential and can be applied to systems for which the Lennard-Jones potential is a poor representation.

Using Equation (22) as a potential function in Equations (6) and (7) produces results in the following form:

$$B_{cl} = \sum_{\nu=0}^{\infty} f_\nu(T)\, \sigma^3\, \epsilon^{\frac{4}{1+2\nu}} \tag{23}$$

$$B^{(1)} = \sum_{\gamma=0}^{\infty} g_\gamma(T)\, \frac{\sigma}{m}\, \epsilon^{\frac{1+6\gamma}{12}} \tag{24}$$

In accordance with Equation (5) the second-virial coefficient for a pure component contains the sum of these equations. For a mixture the result, by Equation (2), is

$$B_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i\, x_j \sum_{\nu=0}^{\infty} f_\nu(T)\, \sigma_{ij}^{\ 3}\, \epsilon_{ij}^{\frac{1+2\nu}{4}} + \sum_{i=1}^{n}\sum_{j=1}^{n} x_i\, x_j \sum_{\gamma=0}^{\infty} g_\gamma(T)\, \frac{\sigma_{ij}}{m_{ij}}\, \epsilon_{ij}^{\frac{1+6\gamma}{12}} \tag{25}$$

If the pseudo-critical concept is valid, then for each constant composition of the mixture there must exist a hypothetical pure substance with criticals P_c', V_c', and T_c' which obeys the corresponding states principle and which has thermodynamic properties identical with those of the mixture when each are at the same P, V, and T conditions. The only way this can occur is for each to have identical virial expansions. To obey the corresponding states principle this pure substance must have a potential function in the form of Equation (8), and when quantum effects are important, it must also obey both Equations (23)

TABLE 1. QUANTUM MECHANICAL EFFECTS ON FORCE CONSTANTS OF VARIOUS GASES (7)

	$\frac{1}{V_c^{1/3}(mT_c)^{1/2}}$, (cc./g. mole)$^{-1/3}$ °K.$^{-1/2}$	$\theta = \frac{\epsilon_q}{\epsilon_{cl}}$	$\phi = \left(\frac{\sigma_q}{\sigma_{cl}}\right)^3$	Q
He	0.0562	2.56	0.488	2.63
H_2	0.0305	1.45	0.633	1.739
D_2	0.0206	1.18	0.718	1.250
Ne	0.00970	1.04	0.841	0.594
CH_4	0.00392	1.01	0.945	0.234

TABLE 2. REDUCED SECOND-VIRIAL COEFFICIENT $B/\phi V_c$ AS A FUNCTION OF REDUCED TEMPERATURE $T/\theta T_c$ AT VARIOUS Q

$T/\theta T_c$	$Q = 2.63$	$Q = 1.74$	$Q = 1.25$	$Q = 0.234$
0.25	−3.475			
0.30	−2.860			
0.40	−2.090			
0.45	−1.750	−3.170		
0.50	−1.525	−2.735	−3.390	
0.60	−1.170	−2.100	−2.480	
0.70	−0.915	−1.590	−1.875	−2.665
0.80	−0.720	−1.220	−1.435	−2.040
0.90	−0.585	−1.000	−1.150	−1.610
1.00	−0.480	−0.835	−0.965	−1.275
1.25	−0.268	−0.530	−0.630	−0.800
1.50	−0.105	−0.330	−0.410	−0.520
1.75	0.000	−0.188	−0.270	−0.338
2.00	+0.095	−0.080	−0.160	−0.210
2.25	0.160	0.000	−0.070	−0.108
2.50	0.206	+0.060	0.000	−0.030
3.00	0.262	0.148	+0.093	+0.080
4.00	0.312	0.252	0.208	0.202
5.00	0.338	0.309	0.269	0.264
7.00	0.378	0.357	0.331	0.327
8.45	0.400	0.378	0.354	0.354
10.00	0.414	0.396	0.368	0.368
15.0	0.424	0.420	0.414	0.414
20.0	0.419	0.419	0.419	0.419
30.0	0.402	0.402	0.402	0.402
Based on	He	H_2	D_2	CH_4 and heavier
References	*(14, 31)* *(36, 37)*	*(8, 10)* *(25, 26)*	*(27, 37)*	*(9, 10, 12)* *(28, 35)*

and (24). If $\bar{\sigma}$ and $\bar{\epsilon}$ are the parameters of this hypothetical pure substance, then Equations (23) and (24) in terms of these parameters must equal Equation (25) for the mixture, as shown in Equation (26):

$$\left\{ \begin{aligned} &\sum_{\nu=0}^{\infty} f_\nu(T)\, \bar{\sigma}^3 \bar{\epsilon}^{\frac{1+2\nu}{4}} + \sum_{\gamma=0}^{\infty} g_\gamma(T)\, \frac{\bar{\sigma}}{\bar{m}}\, \bar{\epsilon}^{\frac{1+6\gamma}{12}} = \\ &\sum_{i=1}^{n} \sum_{j=1}^{n} x_i\, x_j \sum_{\nu=0}^{\infty} f_\nu(T) \sigma_{ij}{}^3\, \epsilon_{ij}{}^{\frac{1+2\nu}{4}} + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i\, x_j \sum_{\gamma=0}^{\infty} g_\gamma(T)\, \frac{\sigma_{ij}}{m_{ij}}\, \epsilon_{ij}{}^{\frac{1+6\gamma}{12}} \end{aligned} \right. \qquad (26)$$

Similar equalities must hold for third and higher virials. Collecting terms in Equation (26) one gets

$$\begin{aligned} &f_0(T) \left[\bar{\sigma}^3\, \bar{\epsilon}^{1/4} - \sum_{i=1}^{n} \sum_{j=1}^{n} \sigma_{ij}{}^3\, \epsilon_{ij}{}^{1/4} \right] \\ &+ f_1(T) \left[\bar{\sigma}^3\, \bar{\epsilon}^{3/4} - \sum_{i=1}^{n} \sum_{j=1}^{n} x_i\, x_j\, \sigma_{ij}{}^3\, \epsilon_{ij}{}^{3/4} \right] + \ldots \qquad (27) \\ &+ g_0(T) \left[\frac{\bar{\sigma}\, \bar{\epsilon}^{1/2}}{\bar{m}} - \sum_{i=1}^{n} \sum_{j=1}^{n} x_i\, x_j\, \frac{\sigma_{ij}}{m_{ii}}\, \epsilon_{ij}{}^{1/2} \right] + \ldots = 0 \end{aligned}$$

Similar groups are produced by collecting terms from higher virials. The functions $f_\nu(T)$ and $g_\gamma(T)$ are not homogeneous in temperature, so that if Equation (27) is to be valid for a fixed-gas composition over a range of temperatures, all terms in brackets must equal zero. The form of Equation (27) does not depend on the particular intermolecular potential used in its derivation as long as it satisfies the general expression given in Equation (8). Different potential functions will affect only the temperature-dependent coefficients and the values of the exponents of ϵ.

As this hypothetical substance has only three arbitrary parameters $\bar{\epsilon}$, $\bar{\sigma}$, and $\bar{m}$, the values assigned them can make only three of the coefficients in Equation (27) equal to zero. The $\bar{m}$ term appears only in the coefficients of the $g_\gamma(T)$ terms, so that $\bar{\epsilon}$ and $\bar{\sigma}$ may be determined by setting any two coefficients of the $f_\nu(T)$ terms equal to zero and $\bar{m}$ by equating any one of the $g_\gamma(T)$ coefficients to zero.

Suppose that the three most important coefficients are equated to zero and used to solve for the parameters after substitution of the best possible two parameter potential function. All of the remaining coefficients will be unequal to zero. The equations selected may be represented by

$$\bar{\sigma}^3\, \bar{\epsilon}^{\alpha} - \sum_{i=1}^{n} \sum_{j=1}^{n} x_i\, x_j\, \sigma_{ij}{}^3\, \epsilon_{ij}{}^{\alpha} = 0 \qquad (28)$$

$$\bar{\sigma}^3\, \bar{\epsilon}^{\beta} - \sum_{i=1}^{n} \sum_{j=1}^{n} x_i\, x_j\, \sigma_{ij}{}^3\, \epsilon_{ij}{}^{\beta} = 0 \qquad (29)$$

$$\frac{\bar{\sigma}\, \bar{\epsilon}^{\mu}}{m} - \sum_{i=1}^{n} \sum_{j=1}^{n} x_i\, x_j\, \frac{\sigma_{ij}}{m_{ij}}\, \epsilon_{ij}{}^{\mu} = 0 \qquad (30)$$

Ideally, these three coefficients chosen to equal zero exactly are selected so that all other coefficients in (27) and also those in third and higher virials will be made as small as possible. The exponents in the equations thus selected to equal zero are represented by α, β, and μ. In this manner the effect of higher virials is not entirely neglected. Instead of omitting the higher virial coefficients entirely only the differences between them and the corresponding higher virials of a closely similar pure substance are assumed negligible.

For determining pseudo criticals from Equations (28), (29), and (30) the following relations may be used:

$$\epsilon \propto \theta T_c \text{ and } \bar{\epsilon} \propto T_c' \qquad (31)$$

$$\sigma^3 \propto \phi\, V_c \text{ and } \bar{\sigma}^3 \propto V_c' \qquad (32)$$

This procedure would define a pseudo-critical volume and temperature. However it is more convenient to change the pseudo-critical volume variable to a pseudo-critical pressure by defining an empirical pseudo-critical compressibility factor for the mixture

$$z_c' = \sum_{i=1}^{n} x_i (z_c)_i \qquad (33)$$

The term V_c in Equation (34) is then replaced by $z_c\, T_c/P_c$, so that

$$\sigma^3 \propto \phi V_c \propto \phi \left(\frac{z_c\, T_c}{P_c} \right) \qquad (34)$$

The terms in the summations in Equations (28), (29), and (30) when $i \neq j$ are based on the corrected form of Equation (4) for ϵ_{ij}:

$$\epsilon_{ij} = \xi \sqrt{\epsilon_{ii}\, \epsilon_{jj}} \qquad (35)$$

and from Equation (3) for σ_{ij} when $i \neq j$.

The m_{ij} term is defined empirically as

$$m_{ij} = \frac{1}{2} m_i + \frac{1}{2} m_j \qquad (36)$$

These ϵ_{ij}, σ_{ij}, and m_{ij} terms were substituted in Equations (28), (29), and (30) and the resulting set of equations solved for T_c', P_c', and $\overline{m}$. For algebraic simplification the term

$$(\sqrt{\epsilon_{ii}\,\epsilon_{jj}})\left[\frac{1}{2}(\sigma_{ii})+\frac{1}{2}(\sigma_{jj})\right]^3$$

which arises in Equation (30) was replaced by $\sqrt{(\epsilon_{ii}\,\sigma_{ii}^3)(\epsilon_{jj}\,\sigma_{jj}^3)}$, since the two expressions are numerically almost equal. Leland and Mueller (*19*) showed that the exponent β is very nearly zero. The resulting equations when $\beta = 0$ are

$$T_c' = \left\{\frac{\displaystyle\sum_{i=1}^{n}\sum_{j=1}^{n} x_i\,x_j\left(\theta^a\,\phi\,\frac{z_c\,T_c^{a+1}}{P_c}\right)_i^{1/2}\left(\theta^a\,\phi\,\frac{z_c\,T_c^{a+1}}{P_c}\right)_j^{1/2}\xi_{ij}}{\displaystyle\sum_{i=1}^{n}\sum_{j=1}^{n} x_i\,x_j\left[\frac{1}{2}\left(\phi\,\frac{z_c\,T_c}{P_c}\right)_i^{1/3}+\frac{1}{2}\left(\phi\,\frac{z_c\,T_c}{P_c}\right)_j^{1/3}\right]^3}\right\} \qquad (37)$$

$$P_c' = \frac{\displaystyle T_c'\sum_{i=1}^{n} x_i\,(z_c)_i}{\displaystyle\sum_{i=1}^{n}\sum_{j=1}^{n} x_i\,x_j\left[\frac{1}{2}\left(\phi\,\frac{z_c\,T_c}{P_c}\right)_i^{1/3}+\frac{1}{2}\left(\phi\,\frac{z_c\,T_c}{P_c}\right)_j^{1/3}\right]^3} \qquad (38)$$

$$\overline{m} = \frac{\displaystyle (T_c')^{\mu}\left(\frac{z_c'\,T_c'}{P_c'}\right)^{1/3}}{\displaystyle\sum_{i=1}^{n}\sum_{j=1}^{n} x_i\,x_j\left[\frac{1}{2}\left(\phi\,\frac{z_c\,T_c}{P_c}\right)_i^{1/3}+\frac{1}{2}\left(\phi\,\frac{z_c\,T_c}{P_c}\right)_j^{1/3}\right]\frac{2\left[(\theta T_c)_i\,(\theta T_c)_j\right]^{\mu/2}}{m_i+m_j}} \qquad (39)$$

The value of ξ_{ij} in Equation (37) is unity except when $i \neq j$, in which case it is given by Figure 3. Pseudo-reduced temperature and pressure are defined by

$$T_R' = \frac{T}{T_c'} \qquad (40)$$

$$P_R' = \frac{P}{P_c'} \qquad (41)$$

Thus any pure substance, similar in molecular shape to the molecules in the mixture, should have similar thermodynamic properties when its reduced properties equal T_R' and P_R' and if it has a mass equal to the $\overline{m}$ value calculated for the mixture.

In selecting this pure substance an additional parameter accounting for the shape of the molecules should be used. The average critical compressibility factor z_c' as defined by Equation (33) is often used as an empirical shape factor parameter. However when the molecular weights of the gases become small or at low temperatures the pseudo-mass as calculated in Equation (39) becomes important in addition to shape factors. If a reference substance with known properties is selected in this manner, it is convenient to define an equivalent temperature and pressure $T°$ and $P°$ as

$$T° = T_R'\,T_c° \qquad (42)$$

$$P° = P_R'\,P_c° \qquad (43)$$

where $T_c°$ and $P_c°$ are the critical constants of the reference substance. Any thermodynamic property of the mixture may be found by equating it to this property of the reference at $T°$ and $P°$.

Changing the values of the exponents α and μ in the pseudo-critical equations is equivalent to changing the intermolecular potential function while keeping it in the same form as Equation (8). Setting the exponent β *in Equation (29) equal to zero*, as was done here, is equivalent to choosing a potential such that when $U(r)$ is plotted against r a vertical line represents the intermolecular repulsion. The α value determines the shape of that portion of the function which accounts for attraction. The value of α must be obtained by comparison with experimental data on similar systems. The numerical value of the μ exponent can be estimated roughly from Equation (24) which was obtained with the Lennard-Jones potential. The exponents of ϵ in the expansion of the the equation are 1/12, 7/12, 13/12, 19/12, ... If third and higher virials are small, the value of μ would be the exponent which makes the value of a single term in the series most nearly equal to the value of the entire series. It was found that values between 0.5 and 1.0 gave $\overline{m}$ values very nearly the same as the molal average value. Smaller values of μ cause $\overline{m}$ to be considerably less than the molal average. The exact value of μ is not critical, especially when there are only a few reference substances available, as is the case with many low-temperature systems. With the limited number of reference substances available for the methane-hydrogen system,

TABLE 3. COMPARISON OF PREDICTED INTERACTION VIRIAL COEFFICIENTS WITH EXPERIMENTAL VALUES

Reference	System	Temperature, °K.	Experimental B_{12}, cc./g. mole	Predicted B_{12} with $\epsilon_{12} = \xi\sqrt{\epsilon_1\epsilon_2}$, cc./g. mole	Predicted B_{12} with $\epsilon_{12} = \sqrt{\epsilon_1\epsilon_2}$, cc./g. mole
(*1*)	CO_2-He	333	21.6	16.7	16.7
(*41*)	CH_4-$Si(CH_3)_4$	323	—145.0	—214.0	—218.0
(*18*)	He-N_2	303	21.8	18.5	18.9
(*6*)	He-CO_2	303	22.4	15.5	15.5
(*3*)	N_2CO_2	303	—40.6	—42.4	—42.4
(*3*)	CO_2-O_2	303	—41.5	—50.6	—50.6
(*3*)	N_2-O_2	303	—9.7	—10.1	—10.1
(*41*)	CH_4-$C(CH_3)_4$	303	—165.0	—208.0	—230.0
(*3*)	CO_2-O_2	298	—58.3	—55.1	—55.1
(*23*)	CO_2-CH_3F	293	—149.0	—144.0	—144.0
(*23*)	H_2-CO_2	293	—1.1	—1.19	—1.19
(*23*)	N_2-CO_2	293	—42.6	—46.4	—46.4
(*23*)	N_2-CH_3F	293	—36.0	—53.4	—53.4
(*28, 30*)	CH_4-H_2	283	7.50	7.54	5.61
(*28, 30*)	CH_4-H_2	255	4.91	5.10	2.30
(*28, 30*)	CH_4-H_2	228	2.75	2.87	—2.07
(*28, 30*)	CH_4-H_2	200	—0.48	—0.22	—7.73
(*28, 30*)	CH_4-H_2	172	—4.55	—4.02	—14.35
(*28, 30*)	CH_4-H_2	144	—9.71	—7.55	—25.8
(*17*)	He-H_2	90	12.8	11.7	9.05
(*17*)	Ne-N_2	90	—31.0	—22.4	—39.2
(*17*)	He-A	90	6.6	4.17	—3.2
(*17*)	He-N_2	90	12.4	12.5	0.8
(*17*)	He-O_2	90	—4.4	2.8	—2.0
(*17*)	Ne-A	90	—35.2	—49.0	—53.5
(*17*)	He-Ne	90	7.4	7.26	7.26
(*32*)	H_2-N_2	60	—92.0	—94.0	—94.0
(*32*)	H_2-CO_2	60	—108.0	—97.0	—209.0

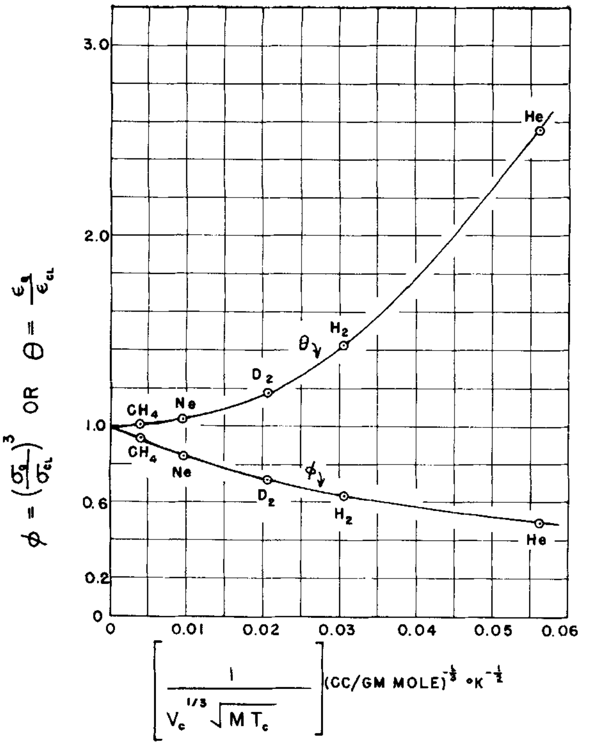

Fig. 1. Quantum effects on the force constants of gases.

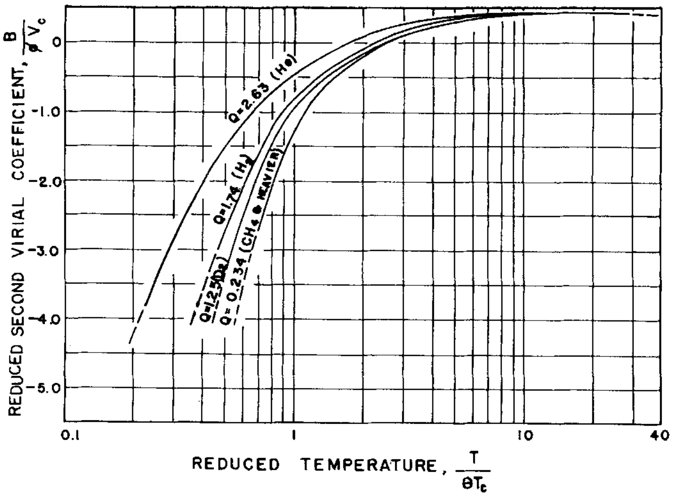

Fig. 2. Reduced virial coeffficients for low molecular weight gases.

values of μ between 0.1 and 1.0 made very little change in predicted values of compressibility factors for this mixture.

The values of θ, ϕ and ξ in the pseudo-critical equations for mixtures with quantum effects have relatively small effect on the calculated values of compressibility factors. In calculating compressibility factors of methane and hydrogen mixtures at temperatures down to —200°F. good results were obtained setting θ, ϕ, and ξ equal to 1. Other properties, for example fugacities, are much more sensitive to the pseudo-critical values, and in these cases the corrections should be much more important. They will probably be important even for compressibility-factor calculations at temperatures below the —200°F. system investigated here. With ϕ, θ, and ξ equal unity the equations for the pseudo-critical values become identical with those developed earlier (*28, 29*). All quantum effects are accounted for in this case only by requiring the reference substance to have a mass equal to the $\overline{m}$ predicted by Equation (39), which is very nearly the molal average mass of the pure component molecules.

The pseudo-critical values were tested, with ϕ, θ, and ξ set equal to unity, by comparison of predicted compressibility factors with the experimentally determined values for hydrogen and methane mixtures. The value of α was taken from the following correlation developed earlier for high temperature systems (*19*):

$$\alpha = -0.75\left(\frac{P\,\Sigma\,x_i\,(T_c)_i}{T\,\Sigma\,x_i\,(P_c)_i}\right) + 2.44 \tag{44}$$

For values of $P\,\Sigma\,x_i\,(T_c)_i/T\,\Sigma\,x_i\,(P_c)_i \geqq 2.0$, α is set $=$ 1.0, and for values $\leqq 0.4$, α is set at 2.2.

The only pure reference substances available with known compressibility factors were methane, hydrogen, and deuterium. The P-V-T properties of these substances were plotted and values were selected by interpolation. Hydrogen data came from Michels et al. (*25*) and from Woolley et al. (*40*). Deuterium data came from Michels (*25*) and Schäfer (*37*). Methane data came from the author's experimental work (*28, 30*) and from Schamp et al. (*35*).

Calculations were carried out on a medium speed digital computer in the following sequence:

1. Calculation of $P\sum_i^n x_i(T_c)_i/T\sum_i^n x_i(P_c)_i$ from the given composition.
2. Selection of α from Equation (44).
3. Calculation of T_c', P_c' and $\overline{m}$ from Equations (37), (38), and (39).
4. Calculation of reduced temperature and pressure from Equations (40) and (41).

A pure reference substance was then selected from the group hydrogen, deuterium, methane having a value of m nearest $\overline{m}$. The equivalent temperature and pressure $T°$ and $P°$ were calculated from Equations (43) and (44). The compressibility factor was then found by interpolation at $T°$ and $P°$. The average over-all absolute per cent error for 257 data points in the methane-hydrogen system is 1.61% with a maximum error of 6.7% for μ = 1.0. Using μ = 0.1 reduced the average over-all per cent error to 1.56% with a maximum error of 8.0%. In general the largest errors were found at pressures above 1,000 lb./sq. in. abs., and all systems at pressures above this value were included in computing this average error. Less than 25% of the data included were below this pressure. Pressures ranged from 100 to 7,000 lb./sq. in. abs. and temperatures ranged from —200° to +50°F.

The method proposed here was compared with the use of Kay's rules for finding pseudo-critical conditions. These rules are given by the following equations:

$$P_c' = \sum_{i=1}^{n} x_i\,(P_c)_i \tag{45}$$

$$T_c' = \sum_{i=1}^{n} x_i\,(T_c)_i \tag{46}$$

The pseudo-reduced conditions resulting from the use of these equations were used with the same reference substance selected by the method proposed here for μ = 0.1. A comparison was made on sixty-two representative systems. The average error was 2.31% with a maximum error of 9.9%. When one used the generalized charts of Lyderson (*24*) with Kay's method for these sixty-two systems, the average error was 3.78% with a maximum error of 17.2%.

The $\overline{m}$ calculated from Equation (40) decreases with increasing pressure. This effect would result in the choice of a lighter reference substance at high pressure and a heavier reference at low pressure. Hydrogen gives better results at high pressures, and deuterium gives better results at low

TABLE 4. COMPARISON OF COMPRESSIBILITY FACTORS OBTAINED FROM VARIOUS CORRESPONDING STATES METHODS FOR THE HYDROGEN-METHANE SYSTEM

Temperature, °F.	Pressure, lb./sq. in. abs.	CH_4, mole %	Experimental, z	This pseudo-critical method, z	Kay's rule, z	Reduced second virial, z
+50	1,090.16	64.9	0.9642	0.965	0.962	0.948
+50	253.55	22.0	1.0067	1.005	1.010	1.006
0	1,178.72	64.9	0.9321	0.937	0.930	0.872
0	325.75	22.0	1.0081	1.006	1.012	1.007
−50	1,077.06	43.5	0.9713	0.972	0.974	0.959
−50	1,148.90	79.8	0.7936	0.816	0.808	0.738
−100	337.28	22.0	1.0013	0.996	0.995	1.002
−100	290.14	64.9	0.9462	0.948	0.940	0.922
−150	1,072.48	43.5	0.9056	0.897	0.941	0.856
−150	476.01	79.8	0.7365	0.734	0.725	0.677
−200	128.09	79.8	0.8886	0.883	0.896	0.896

pressures. This shows that $\overline{m}$ introduces corrections in the right direction.

COMPARISON OF THE TWO METHODS

A comparison of compressibility factors obtained by each method is presented in Table 4. For the methane-hydrogen system the reduced virial method is applicable only up to pressures around 1,000 lb./sq. in. abs., since only second-virial coefficients were evaluated. The accuracy could be improved by extending this method to higher virials, but unfortunately there are not enough reliable experimental data at present to allow the construction of a complete set of curves such as Figure 1 for third virials. A fairly good estimate might be made by constructing curves with theoretically calculated third virials in addition to the limited data which are presently available. The chief drawback to the reduced virial method is the uncertainty about the interaction virials for unlike molecules. The empirical parameter proposed here in Figure 3 indicates pairs for which the Lorentz-Berthelot combinations [Equations (3) and (4)] can be used with confidence when $|\Delta(\phi V_c)|/(\Sigma \nu_i A_i)T < 10$ and likewise indicates pairs for which there is no reliable way to estimate the deviation from Equations (3) and (4), when $|\Delta(\phi V_c)|/(\Sigma \nu_i A_i)\ T > 40$. The actual correction factors predicted by the correlation however are only rough approximations.

The calculated values of a number of B_{12} virials are shown in Table 3. As would be expected Table 3 shows that even at high temperatures, when there is a large size or shape difference between the molecules, the agreement is generally poorer. The methane-tetramethylsilane and carbon dioxide-helium pairs are examples. In these cases there is probably no inter molecular potential function in the form of Equation (8) which applies accurately, and molecular shape factors should be considered.

Low-temperature data on unlike pair virials is meager and often uncertain. The helium-oxygen system at 90°K. is an example of this difficulty. The experimental value reported used Keesom's (*14*) average value for the virial of pure helium in its determination. This point falls in a reduced-temperature range (between 1.8 and 4.0) where there is considerable disagreement between Keesom's recommended helium virials and those measured by Schäfer (*37*). The values used here in Table 2 and Figure 2 were those of Schäfer. These seemed to agree best with the data of Holburn and Otto (*8, 9, 31*) and the extrapolation of the more recent data of Schneider (*36*). Furthermore using these data in a crossplot against the Q values at constant temperature seems much more reasonable than Keesom's values. Had the curve for pure helium in *Figure* 2 used Keeson's values, the agreement would have been much better for this particular system. Outside this reduced-temperature range there is good agreement between all the values for helium.

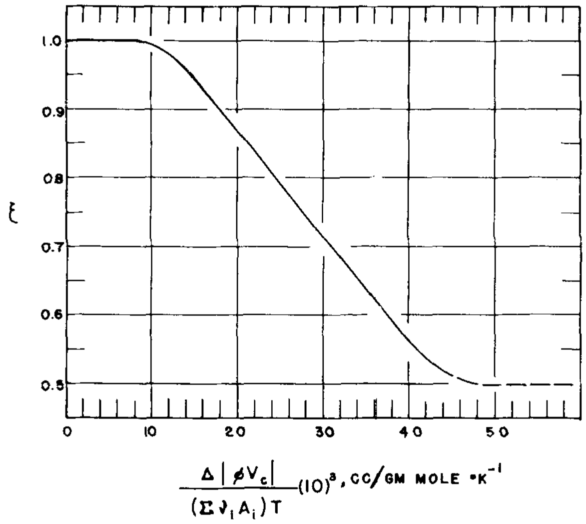

Fig. 3. Empirical correlation for correction factor ξ in $\epsilon_{12} = \xi\sqrt{\epsilon_{11}\epsilon_{22}}$.

Agreement with the data of Varekamp and Beennakker (*40*) at 20°K. for helium-hydrogen and helium-deuterium was found to be poor. However the value of the correlating parameter $|\Delta(\phi V_c)|/(\Sigma \nu_i A_i)T$ in Figure 3 was much greater than 40. The experimental value of B_{12} for helium-hydrogen was reported as −17 cc./g. mole. The calculated value with $\xi = 0.5$ was − 6.2, and with $\xi = 1.0$ the result is − 35. At temperatures this low it is necessary to have a very precise evaluation of $T/\theta T_c$, since the virials change very rapidly with temperature in this region.

Although the accuracy of the reduced-virial approach in its present state seems poorer than that of the pseudo-critical method, it nevertheless has considerable promise. The reason for this is that as more basic information about higher virial coefficients and molecular interactions becomes known, the way is clearly indicated in which this knowledge can be used directly to improve and extend the reduced virial method.

The pseudo-critical method gives more accurate results at present, although the manner in which new theoretical knowledge could be used to improve the method is not as clear. Certainly one improvement would be to include quantum corrections ϕ and θ in the pseudo criticals and re-evaluate the α parameter. The results should be better at lower temperatures and higher pressures.

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NOTATION

a, b = proportionality constants
A = atomic number
B = second-virial coefficient
B_{ij} = pair interaction second-virial coefficient
B_M = second virial-coefficient for mixture
B_{cl} = classical second-virial coefficient
$B^{(1)}$ = first quantum correction
$B^{(2)}$ = second quantum correction
h = $h/2\pi$
$\bar{h}$ = Planck's constant
k = Boltzmann's constant
m = mass per molecule or molecular weight
N = Avogadro's number
P = pressure
Q = parameter in reduced second virial correlation, Equation (17)
r = intermolecular separation
R = ideal gas law constant
T = absolute temperature
$U(r)$ = intermolecular potential function
V = volume
x = mole fraction
z = compressibility factor

Greek Letters

α, β, γ = experimentally determined parameters in pseudo-critical expressions
σ, ϵ = force constants in intermolecular potential function
$\sigma_{c1}, \epsilon_{c1}$ = force constants evaluated from the classical virial expression
$\sigma_{ij}, \epsilon_{ij}$ = force constants in a two parameter potential function between a pair of molecules
σ_q, ϵ_q = force constants evaluated from the quantum mechanically corrected virial expansion
ϕ = quantum correction factor to critical volume
θ = quantum correction factor to critical temperature
ξ = correction factor for deviation from root mean square combining rule to obtain
ω = angular orientation variable
$\Sigma \nu_i A_i$ = summation of atomic numbers of a pair

Subscripts

c = critical property
R = reduced property

Superscripts

(′) = pseudo critical property
(-) = hypothetical pure substance parameters
(°) = pure reference substance

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APPENDIX

Procedure for Calculation of Second Virial Coefficient of a Mixture

For Pure Component Virials

1. From critical properties calculate $1/V_c^{1/3}\sqrt{mT_c}$.
2. From Figure 2 read θ and ϕ.
3. From Equation (17) calculate Q
4. At desired temperature calculate reduced temperature $T/\theta T_c$.
5. From Figure 1 (Table 1) read reduced second-virial coefficient $B/\phi V_c$.
6. Calculate B for each pure component obtaining B_{11} and B_{22}.

For Interaction Virial

7. Using θ's from Step (2) calculate $\theta_{12} = \sqrt{\theta_1\theta_2}$.
8. From Figure 2 read $1/V_c^{1/3}\sqrt{MT_c}$ and ϕ_{12}.
9. Calculate $\dfrac{|\Delta\phi V_c|}{(\Sigma\nu_i A_i)T}\ 10^3$ at desired temperature
   where

$$|\Delta\phi V_c| = |\phi_1 V_{c1} - \phi_2 V_{c2}|$$

$\Sigma\nu_i A_i$ = sum of atomic numbers of every atom in the pair.

10. From Figure 3 read ξ.
11. Calculate Q_{12} using data from Steps (7) and (8), from Equation (20).
12. At desired temperature calculate reduced temperature

$$\frac{T}{\xi\sqrt{\theta_1 T_{c1}\ \theta_2 T_{c2}}}$$

13. From Figure 1 (Table 1) read reduced second-virial coefficient at Q_{12} and T_R from Step (12).
14. Using

$$(\phi V_c)_{12} = \left[\frac{1}{2}(\phi_1 V_{c1})^{1/3} + \frac{1}{2}(\phi_2 V_{c2})^{1/3}\right]^3$$

calculate B_{12}.

For Mixture Virial

15. At desired composition calculate

$$B_M = x_1^2 B_{11} + 2\,x_1 x_2 B_{12} + x_2^2 B_{22}$$