LITERATURE CITED

Bruni, C., et al., "A Method of Realization Based on the Moments of the Impulse Response Matrix," *IEEE Trans. Auto. Cont.*, 14, 203 (1968).

Buffham, B. A., and L. G. Gibilaro, "A Unified Time Delay Model for Dispersion in Flowing Media," *Chem. Eng. J.*, 1, 31 (1970).

Davison, E. J., "A Method for Simplifying Linear Dynamic Systems," *IEEE Trans. Auto. Cont.*, 11, 93 (1966).

———, "A New Method for Simplifying Large Linear Dynamic Systems," *ibid.*, 13, 214 (1968).

Gibilaro, L. G., and F. P. Lees, "The Reduction of Complex Transfer Function Models to Simple Models Using the Method of Moments," *Chem. Eng. Sci.*, 24, 55 (1969).

Gilbert, E. G., "Controllability and Observability in Multivariable Control Systems," *SIAM J. Cont.*, 1, 1227 (1963).

Ho, B. L., and R. E. Kalman, "Effective Construction of Linear State-Variable Models from Input/Output Functions," *Regelungstechnik*, 14, 545 (1966).

Jeffreson, C. P., "Dynamic Testing—A Unification," *Chem. Eng. Sci.*, 25, 1319 (1970).

Kallina, C., "An Approach to the Regulation Problem for Nonlinear Chemical Processes," *JACC Preprints*, 11, 329 (1970).

Kalman, R. E., "Mathematical Description of Linear Dynamical Systems," *SIAM J. Cont.*, 1, 52 (1963).

———, "On Canonical Realizations," *Proc. 2nd Allerton Conf. on Circuit and System Theory*, 32 (1964).

———, "Irreducible Realizations and the Degree of a Rational Matrix", *SIAM J.*, 13, 520 (1965).

———, "Algebraic Theory of Linear Systems," *Proc. 3rd Allerton Conf. on Circuit and System Theory*, 563 (1965).

———, "On Structural Properties of Linear Constant, Multivariable Systems," *3rd IFAC Congress*, London (1966).

———, and N. DeClaris, ed., Aspects of Network and System Theory, Holt, Rinehart, and Winston, New York (1970).

Kalman, R. E., and R. S. Engler, "Computation of A Minimal Realization," *A User Manual for ASPC, Ch. XV*, (1966).

Kropholler, H. W., "Determination of Relative Variance and Other Moments From Generalized Flow Networks or System Transfer Functions," *Ind. Eng. Chem. Fundamentals*, 9, 329 (1970).

Mayne, D. Q., "Computational Procedure for the Minimal Realization of Transfer-Function Matrices," *Proc. IEE*, 115, 1363 (1968).

Roberts, D. M., "A Computer Program for the Minimal Realization of Transfer Function Matrices," *IEEE Trans. Auto. Cont.*, 14, 412 (1969).

Rosenbrock, H. H., "Computation of Minimal Representations of a Rational Transfer-Function Matrix," *Proc. IEE*, 115, 325 (1968).

Rossen, R. H., Ph.D. thesis, Princeton University, New Jersey (1972).

Roveda, C., and R. Schmid, "An Upper Bound on the Dimension of Minimal Realizations of Linear Time-Invariant Dynamical Systems," *IEEE Auto. Cont.*, 15, 639 (1970).

Silverman, Leonard M., "Realization of Linear Dynamical Systems," *ibid.*, 16, 554 (1971).

Tether, A., "Construction of Minimum Linear State Variable Models From Finite Input/Output Data," *ibid.*, 15, 427 (1970).

Wolovich, W. A., and P. L. Falb, "On the Structure of Multivariable Systems," *SIAM J. Cont.*, 7, 437 (1969).

Wolovich, W. A., and J. Bonna, "Minimal Realization," Computer program available from W. A. Wolovich of Brown Univ., Providence, R. I. (1970).

A Study of Inversion Curves

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A comparative study has been made on the predictive capabilities of a number of the more popular equations of state in use today. The equations were compared in their ability to predict the locus of points for which the Joule-Thomson coefficient is zero, the inversion curve.

The prediction of an inversion curve is an extremely severe test of an equation of state. To date inversion curves have been calculated only for the Van der Waals, Dieterici, Lennard-Jones and Devonshire, and DeBoer-Michels equations of state. This study covers the Van der Waals and Dieterici equations as well as the Virial, Berthelot, Redlich-Kwong, Beattie-Bridgeman, Benedict-Webb-Rubin, and Martin-Hou equations of state.

The results of the investigation show, among other things, that the Redlich-Kwong equation is quite unusual in that it predicts the inversion locus with more accuracy than any of the much more complex equations of state. Its predictive capabilities extend into the liquid region.

Since the classical work of Van der Waals in 1873, numerous equations of state have appeared in the literature. Dodge (*4*) has indicated that the number may well exceed 100. Since this estimate was made more than 26 years ago, the total number now is considerably higher. Of these equations, only a handful have come to be widely known and used.

To date there have been countless numbers of articles concerning the prediction of properties of gases and liquids via the use of an equation of state. Of the many articles that compare the predictive properties of the more common equations, the most notable of recent times is the work of Shah and Thodos (*14*). For the most part, the comparisons of these equations have been made using PVT data as the basis for comparison. The use of this type of data for comparison does not, however, subject the equation of state to as severe a test as could be obtained by the prediction of derived properties, such as heat capacities and Joule-Thomson coefficients.

As has been pointed out by Gunn, Chueh, and Prausnitz (*5*), the prediction of the points at which the Joule-Thomson coefficient is zero, the inversion curve, is an extremely severe test of an equation of state. This test is

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used here to investigate the equations of state which are in common use today. To date, inversion curves for the Van der Waals, Dieterici, Lennard-Jones and Devonshire, and DeBoer-Michels equations of state have been calculated. These are presented by Corner (*3*).

As the purpose of this study was to compare the general predictive nature of the equations, the equations were transformed into reduced coordinates and the required operations then made. For the Beattie-Bridgeman (*12*) and Benedict-Webb-Rubin equations (*2*, *6*, *13*) empirically derived reduced parameter equations from the literature were used. The Martin-Hou equation had no such reduced form available, so the calculations were carried out for a number of different gases for which Martin-Hou constants were available. All calculations were made on a CDC-6400 computer.

BACKGROUND

It is easily shown that the adiabatic or isenthalpic Joule-Thomson coefficient μ is given by

$$\mu = (dT/dP)_H = \frac{T(dV/dT)_p - V}{C_p} \qquad (1)$$

or replacing $(dV/dT)_p$ by its equivalent from the cyclic identity

$$\mu = \frac{1}{C_p}\,(-T(dP/dT)_V/(dP/dV)_T - V) \qquad (2)$$

At inversion conditions $\mu = 0$ so that

$$T(dP/dT)_V + V(dP/dV)_T = 0 \qquad (3)$$

Using reduced properties defined by $T = T_rT_c$, $P = P_rP_c$, and $V = V_rV_c$, Equation (3) becomes

$$T_r(dP_r/dT_r)_{V_r} + V_r(dP_r/dV_r)_{T_r} = 0 \qquad (4)$$

Equation (3) or (4), when solved simultaneously with any given equation of state will thus provide the locus of points for which the Joule-Thomson coefficient is zero.

An equivalent expression for Equation (4) can be derived from the isothermal Joule-Thomson relation

$$\mu = \frac{RT^2}{PC_p}\,(dZ/dT)_P = 0 \qquad (5)$$

Since C_p is never zero, Equation (5) shows that the condition $(dZ/dT)_p = 0$ is sufficient to define the inversion locus. Thus, given any reliable volumetric data for a gas, it is possible to determine the inversion conditions from Equation (5) provided the range of temperature and pressure for which the data are available is sufficiently large. Gunn, Chueh, and Prausnitz (*5*) used this approach to determine an inversion curve using volumetric data for A, CH_4, C_2H_4, CO, N_2, and Xe and plotted the inversion points on reduced temperature and pressure coordinates. Equation (6) is a least-squares curve fit of 89 inversion points derived from experimental data.

$$P_r = -36.275 + 71.598\,T_r - 41.567\,T_r^2 + 11.826\,T_r^3 - 1.6721\,T_r^4 + 0.091167\,T_r^5 \qquad (6)$$

The data cover the entire range of the inversion curve. The high T_r part of the curve is, however, based only on CO data. The peak and lower portion of the inversion curve are extremely well defined. Since the components used in this correlation have acentric factors ω close to zero, the correlation is limited to simple fluids.

This fit of experimental Joule-Thomson inversion data is used as a basis for comparison of the performance of the equations of state considered here. Since only simple molecules are involved in the correlation it may be unsuitable for some of the more complex molecules involved in the data considered. Thus deviations are not reliably caused by a failure of the equations of state being tested but may reflect the limits of the Gunn-Chueh-Prausnitz correlations.

DISCUSSION

Two Constant Equations of State

The results of the simultaneous solution of Equation (4) and the various equations of state are shown in Figures 1 to 4. Figure 1 shows the results for the two-constant equations of state as given below in the original and reduced forms.

Van der Waals

$$(P + a/V^2)\ (V - b) = RT \qquad (7)$$

$$(P_r + 3/V_r^2)\ (3V_r - 1) = 8T_r \qquad (8)$$

Dieterici

$$P\,e^{a/VRT}\,(V - b) = RT \qquad (9)$$

$$P_r(2V_r - 1) = T_re^{(2-2/T_rV_r)} \qquad (10)$$

Berthelot

$$(P + a/TV^2)\ (V - b) = RT \qquad (11)$$

$$(P_r + 3/T_rV_r^2)\ (3V_r - 1) = RT \qquad (12)$$

Redlich-Kwong

$$(P + a/T^{1/2}V(V + b))\ (V - b) = RT \qquad (13)$$

$$(P_r + \beta/T_r^{1/2}V_r(V_r + \gamma))\ (V_r - \gamma) = \alpha T_r \qquad (14)$$

where $\alpha = 1/Z_c$, $\beta = 0.42748/Z_c^2$, and $\gamma = 0.08664/Z_c$. The Gunn-Chueh-Prausnitz correlation is also shown in Figure 1.

Since the range of temperatures and pressures encountered in these calculations is large, one would immediately suspect that the two-constant equations would have difficulty in adequately predicting the actual inversion locus. Such is the case for all the two-constant equations studied with the exception of the Redlich-Kwong equation. For the entire range of reduced temperature and pressure the Dieterici equation is grossly in error. The Berthelot equation, although in good agreement up to a reduced temperature of about 1.3, fails beyond that. The Van der Waals equation, like the Dieterici, is essentially inadequate for the entire range of temperature and pressure. The Redlich-Kwong equation, however, is quite remarkable. It follows the general nature of the correlation for

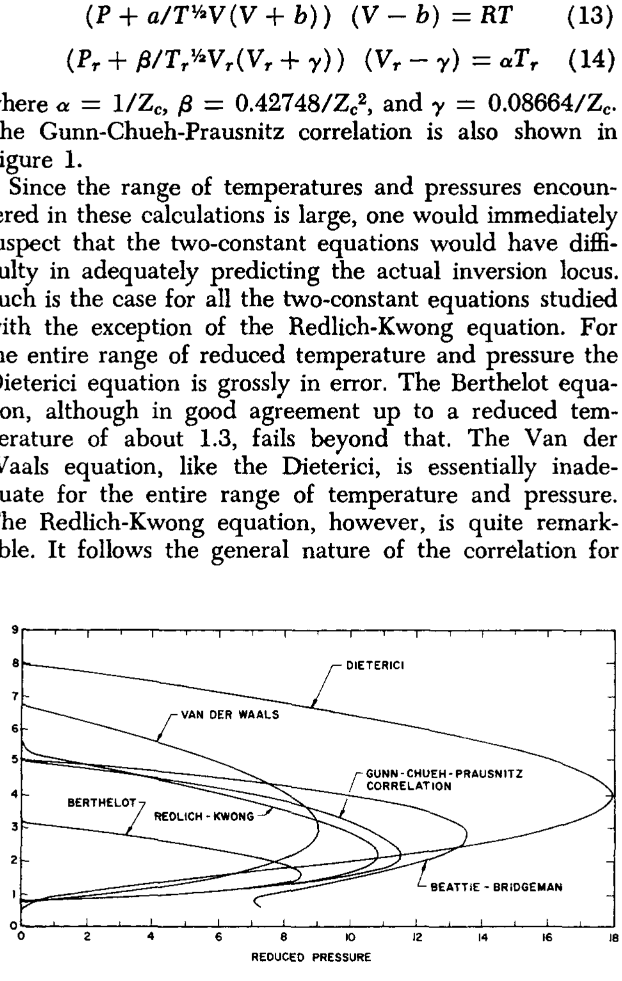

Fig. 1. Inversion curves for two-constant equations of state.

the entire range of reduced properties and predicts values of reduced pressure which are only slightly below that expected in the region of the peak. At the high temperature end of the curve a slight tailing off exists. As shown in Table 1 the Dieterici and Van der Waals equations reach their peak pressures at the critical volume. The Berthelot equation reaches this point at 2/3 the critical volume, and the Redlich-Kwong equation reaches maximum pressure at a reduced volume of 0.714.

The Truncated Virial Equation with Generalized Coefficients

Figure 2 presents results of calculations of Joule-Thomson inversion curves using the virial equation truncated after the third virial coefficient:

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} \qquad (15)$$

Unlike the two-constant equations discussed above, the constants in Equation (15) are temperature dependent. Since we are interested in the general behavior of this equation we can make use of existing generalized relationships for $B(T)$ and $C(T)$ as functions of reduced temperature. A number of such relationships have been developed for the second virial coefficient. Two of these have been considered here. McGlashan and Potter (*10*) in their work on hydrocarbon gases developed an expression for B/V_c:

$$B/V_c = 0.430 - 0.886/T_r - 0.694/T_r^2 - 0.0375(n-1)/T_r^{4.5} \qquad (16)$$

The n in the above equation indicates the number of carbon atoms in the molecule and is equal to 1 for nonhydrocarbon gases. The well-known Pitzer correlation (*11*) involves, in addition to T_r, a parameter ω, the acentric factor:

$$BZ_c/V_c = (0.1445 - 0.330/T_r - 0.1385/T_r^2 - 0.0121/T_r^3) + \omega(0.073 + 0.46/T_r - 0.50/T_r^2 - 0.097/T_r^3 - 0.0073/T_r^8) \qquad (17)$$

The correlation used for the generalized third virial coefficient was developed by Chueh and Prausnitz (*1*). It is a function of reduced temperature and a geometric shape factor d which varies from 0.0 to 4.25. The size and dipole moment strength of the molecule is a general indicator for the magnitude of d. The relationship is

$$C/V_c^2 = (0.232T_r^{-.25} + 0.468T_r^{-5})(1 - e^{(1-1.189T_r^2)}) + de^{-(2.49-2.30T_r+2.70T_r^2)} \qquad (18)$$

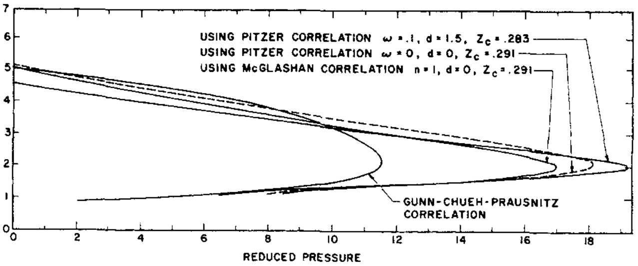

Fig. 2. Inversion curve for the virial equation truncated after the third virial coefficient. (The second virial coefficient is calculated as indicated for each curve. In all cases the correlation of Chueh and Prausnitz (Equation 18) was used for the third virial equation.)

Three distinct curves have been calculated for the purpose of illustration and are shown in Figure 2. The conditions of the parameters Z_c, ω, and d are indicated. From these graphs it can be seen that the virial equation does not predict the shape of the inversion curve accurately. Its peak occurs at values of reduced pressure at least 50% greater than that expected. The peaks, however, unlike the Dieterici, Van der Waals, and Berthelot equations, are predicted at approximately the correct value of $T_r \sim 2$. It should be noted that the best agreement obtained is with $\omega = 0$ and $d = 0$. This is as expected since the Prausnitz correlation is based on molecules with small acentric factors. As ω and d increase, the range of T_r covered by the curve decreases. For the case where $\omega = 0$ and $d = 0$, T_r ranges from 1.1 to 5.1. For the case where $\omega = .3$ and $d = 4.25$ (not shown), T_r ranges from 1.1 to 3.7. The trend is also toward the peaks appearing at higher reduced pressures. For the last set of parameters, the peak appears at a P_r greater than 21. The virial equation does not provide a solution for T_r less than 1.0.

The Beattie-Bridgeman Equation and the Benedict-Webb-Rubin Equation

A generalized form of the Beattie-Bridgeman equation has been developed by Su (*12*)

$$P_r = T_r(1/\phi^2 - C/\phi^3T_r^3)(\phi + B_0(1 - \mathrm{b}/\phi)) - A_0(1/\phi^2 - a/\phi^3) \qquad (19)$$

where ϕ represents an ideal reduced volume defined as

$$\phi = V/V_{c_{\mathrm{ideal}}} = V_r/Z_c \qquad (20)$$

TABLE 1. INVERSION TEMPERATURES, PRESSURES, AND VOLUMES FOR TWO-CONSTANT EQUATIONS OF STATE

Berthelot			Dieterici			Van der Waals			Redlich-Kwong		
T_r	P_r	V_r	T_r	P_r	V_r	T_r	P_r	V_r	T_r	P_r	V_r
0.8	0.143	0.445	0.8	0.591	0.556	0.8	0.581	0.508	0.8	1.273	0.393
1.0	4.760	0.486	1.0	1.562	0.571	1.0	2.569	0.542	1.0	4.813	0.428
1.5	8.426	0.631	1.5	5.502	0.615	1.5	5.912	0.631	1.5	9.294	0.527
2.0	7.593	0.897	2.0	9.892	0.667	2.0	7.788	0.732	2.0	10.717	0.653
2.5	4.960	1.555	2.5	13.528	0.727	2.5	8.727	0.852	2.5	10.631	0.821
3.0	1.426	5.828	3.0	16.056	0.800	3.0	9.000	1.000	3.0	9.668	1.060
			3.5	17.483	0.889	3.5	8.769	1.191	3.5	8.145	1.428
			4.0	17.927	1.000	4.0	8.138	1.448	4.0	6.242	2.069
			4.5	17.529	1.143	4.5	7.182	1.816	4.5	4.067	3.472
			5.0	16.422	1.333	5.0	5.952	2.392	5.0	1.694	9.017
			5.5	14.717	1.600	5.5	4.488	3.425			
			6.0	12.509	2.000	6.0	2.823	5.828			
			6.5	9.876	2.667	6.5	0.981	17.832			
			7.0	6.880	4.000						
			7.5	3.573	8.000						
			8.0	0.000	∞						

In the above form this equation has predicted compressibility factors for 17 gases with an overall average deviation of 1% and at densities up to the critical. The inversion curve for this equation is shown in Figure 1. It does not predict the Gunn-Chueh-Prausnitz correlation very well, and at very low values of T_r the curve exhibits an erroneous hook-type behavior.

In reduced form the Benedict-Webb-Rubin equation is

$$P_r = T_r/\phi + \frac{(B_0T_r - A_0 - C_0/T_r^2)}{\phi^2} + (bT_r - a)/\phi^3 + a\alpha/\phi^6 + \frac{(C(1+\gamma)/\phi^2)e^{-\gamma/\phi^2}}{\phi^3T_r^2} \qquad (21)$$

As in the case of the Beattie-Bridgeman equation, the parameter ϕ is the ideal reduced volume. To date several investigators have employed the Benedict-Webb-Rubin equation in reduced form. Joffe (*6*) used compressibility data for eight hydrocarbons to determine a generalized set of reduced coefficients. Su and Viswanath (*13*), using generalized compressibility charts based on experimental data for both hydrocarbons and nonhydrocarbons, were able to produce a set of constants for densities up to twice the critical density. Cooper and Goldfrank (*2*) using data for 38 compounds, determined two sets of reduced BWR constants, one for hydrocarbons and the other for nonhydrocarbons. These four sets of coefficients predicted compressibilities to within ½% of the experimental values.

The above four sets of constants have been used to determine the inversion locus for the BWR equation of state. The results are shown in Figure 3. At high temperatures (past the peak of the curve) a tailing off exists, and the equation gives no solution for $T_r < 0.9$. This equation, like most of the others, does not adequately predict the inversion locus. However, using the constants of Su and Viswanath, agreement is obtained at low T_r. The differences in shape at high T_r may result from the attempt by Su and Viswanath to include data for larger, complex molecules in their correlation. Such molecules were excluded by Gunn, Chueh, and Prausnitz.

The Martin-Hou Equation

The Martin-Hou equation (*7*) is pressure explicit as shown below in its original form.

$$P = RT/(V-b) + \sum_{i=2}^{i=5} \frac{(A_i + B_iT + C_ie^{-kT_r})}{(V-b)^i} \qquad (22)$$

In this form the equation is capable of predicting compressibility data up to 1.5 times the critical density. Modifications of the equation (*8, 9*) have included additional terms which extend the range of applicability to 2.3 times the critical density. The modified equation contains 20 constants:

$$P = RT/(V-b) + \sum_{i=2}^{i=5} \frac{(A_i + B_iT + C_ie^{-kT_r})}{(V-b)^i} + \sum_{i=6}^{i=7} \frac{(A_i + B_iT + C_ie^{-kT_r})}{e^{(i-5)aV}} \qquad (23)$$

Constants for this equation in terms of reduced properties are not yet available. Therefore, the inversion curve for this equation has been calculated for a number of different gases as shown in Figures 4a to 4c. Since the components studied, with the exception of nitrogen, are not small molecules with acentric factors close to zero, the comparison with the Gunn-Chueh-Prausnitz correlation cannot be rigorously made. Martin-Hou constants were not available for the smaller molecules such as argon, xenon, carbon monoxide, methane, and ethylene so that a better comparison with the Prausnitz correlation was not possible. For five of the components the peak appears in approximately the correct region of reduced pressure. An unusual phenomenon was observed for the components $CHClF_2$ and $CClF_3$ where it appears that two distinct and connected peaks are exhibited. This is attributed to the fact that the equation does not adequately predict

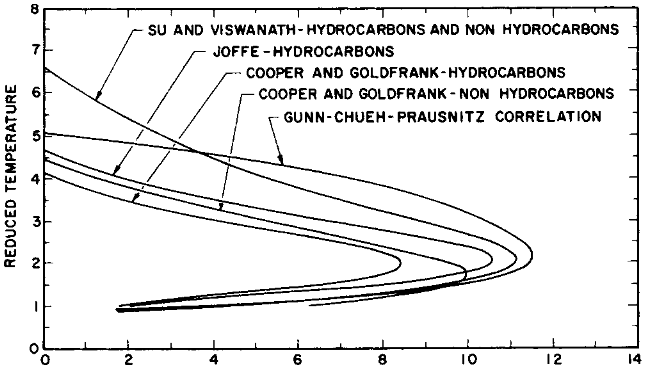

Fig. 3. Inversion curves for Benedict-Webb-Rubin equation.

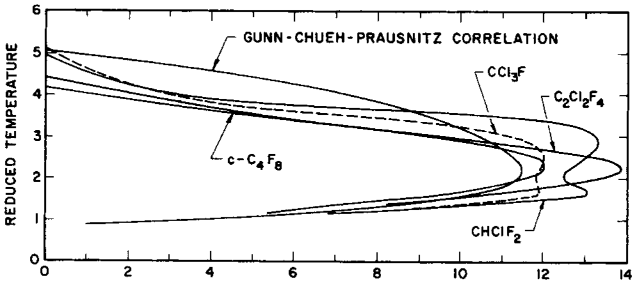

Fig. 4a. Inversion curves for Martin-Hou equation (halocarbons).

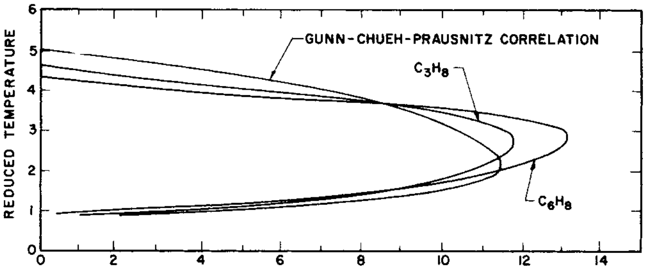

Fig. 4b. Inversion curves for Martin-Hou equation (hydrocarbons).

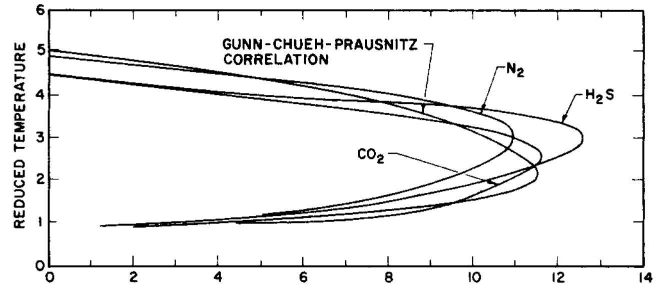

Fig. 4c. Inversion curves for Martin-Hou equation (small molecules).

Table 2. Inversion Conditions for the Beattie-Bridgeman, Virial, Benedict-Webb-Rubin, and Martin-Hou Equations of State

Beattie-Bridgeman, using $Z_c = 0.27$			BWR (16), $Z_c = 0.27$			Martin-Hou, C_3H_8			Virial $\omega = 0$ $d = 0$		
T_r	P_r	V_r	T_r	P_r	V_r	T_r	P_r	V_r	T_r	P_r	V_r
0.5	3.967	0.232	0.9	1.701	0.508	0.9	0.443	0.664	1.0	11.525	0.342
0.8	7.015	0.366	1.0	3.857	0.532	1.0	1.997	0.588	1.1	7.92	0.414
1.0	7.581	0.450	1.5	9.372	0.656	1.5	8.587	0.688	1.5	13.35	0.458
1.5	10.111	0.606	2.0	11.076	0.810	2.0	10.622	0.838	2.0	17.99	0.528
2.0	12.167	0.727	2.5	10.563	1.044	2.5	11.666	0.991	2.5	16.74	0.690
2.5	13.330	0.855	3.0	8.851	1.429	3.0	11.624	1.193	3.0	13.41	0.967
3.0	12.329	1.021	3.5	6.919	2.041	3.5	9.815	1.587	3.5	9.92	1.427
3.5	9.937	1.744	4.0	5.243	2.985	4.0	5.614	2.910	4.0	6.65	2.294
4.0	6.217	2.970	4.5	3.877	4.451	4.5	0.858	19.235	4.5	3.62	4.514
4.5	1.257	15.057	5.0	2.744	6.893				5.0	0.77	22.605
			5.5	1.772	11.635						
			6.0	0.910	24.550						

the true behavior in the very dense gas region. As with the BWR equation no solution can be found for $T_r < 0.9$.

Table 2 gives the T_r, P_r, and V_r relationships for the Beattie-Bridgeman, virial, Benedict-Webb-Rubin, and Martin-Hou equations at inversion. For the Martin-Hou equation the results for propane are given. For the Benedict-Webb-Rubin equation the values for the Su and Viswanath constants are presented and for the virial equation values as predicted by the Pitzer correlation are shown.

CONCLUSIONS

When examined for their ability to predict Joule-Thomson inversion curves, the performance of the more commonly used equations of state leads to the following conclusions:

1. As might be expected, the Van der Waals, Berthelot, and Dieterici equations of state have extremely limited capability for predicting inversion behavior.
2. The virial, Beattie-Bridgeman, and Benedict-Webb-Rubin equations predict inversion behavior poorly. The best set of BWR constants for this particular application is that of Su and Viswanath.
3. The Martin-Hou equation has been tested for several complex as well as simple molecules. For these substances it produces reasonable inversion values.
4. Despite the relative simplicity of the Redlich-Kwong equation of state, it is extraordinary in its ability to predict the inversion locus as described by the Gunn-Chueh-Prausnitz correlation. It predicts the low T_r portion of the inversion curve almost exactly up to a reduced pressure of 9.0. This is the region of maximum density. Its predictive ability even extends into the liquid region up to densities as high as 2.5 times the critical density at a reduced temperature of 0.8. These facts, coupled with the ability one has to obtain the constants of the equation without an a priori knowledge of the PVT behavior of the substance, and from critical properties alone, makes this equation extremely attractive. This reinforces the conclusions Thodos and Shaw (*19*) came to based on a PVT study.

The failure of most of these equations does not relate to their use in regions of especially high density. Although regions of high density are involved in these calculations, the predictive abilities were generally poor in the region of high reduced temperature, that is at lower densities. This is certainly true of the Berthelot, virial, and Benedict-Webb-Rubin equations. Even the Martin-Hou equation fails at reduced densities less than 2.0 in the region in which double inversion peaks are indicated.

NOTATION

A_0, A_i = constants
a = constant
B_0, B_i = constants
$B(T)$ = second virial coefficient
b = constant
C = constant
$C(T)$ = third virial coefficient
C_p = constant pressure heat capacity
d = shape factor
H = enthalpy
k = constant
P = pressure
T = temperature
V = volume
Z = compressibility factor
$_c$ = critical property
$_r$ = reduced property

Greek Letters

α = constant
β = constant
γ = constant
ϕ = ideal reduced volume
μ = Joule-Thomson coefficient

LITERATURE CITED

1. Chueh, P. L., and J. M. Prausnitz, *AIChE J.*, **13**, 896 (1967).
2. Cooper, H. W., and J. C. Goldfrank, *Hydrocarbon Process.*, **46**, 141 (1967).
3. Corner, J., *Trans. Farad. Soc.*, **35**, 784 (1939).
4. Dodge, B. F., "Thermodynamics for Chemical Engineers," McGraw-Hill, New York (1944).
5. Gunn, R. D., P. L. Chueh, and J. M. Prausnitz, *Cryogenics*, **6**, 324 (1966).
6. Joffe, J., *Chem. Eng. Progr.*, **45**, 160 (1949).
7. Martin, J. J., and Y. Hou, *AIChE J.*, **1**, 142 (1955).
8. Martin, J. J., and R. M. Kapoor, *ibid.*, **5**, 159 (1959).
9. Martin, J. J., *Am. Chem. Soc. Applied Thermodynamics Symp.*, **59**, 12 (1967).
10. McGlashan, M. L., and D. J. B. Potter, *Proc. Roy. Soc.*, **A267**, 478 (1962).
11. Pitzer, K. S., and R. F. Curl, Jr., *J. Am. Chem. Soc.*, **79**, 2369 (1957).
12. Su, G., *Ind. Eng. Chem.*, **38**, 803 (1946).
13. ———., and D. S. Viswanath, *AIChE J.*, **11**, 205 (1965).
14. Thodos, G., and K. K. Shah, *Ind. Eng. Chem.*, **57**, 3 (1965).

Manuscript received August 25, 1971; revision received March 10, 1972; paper accepted March 10, 1972.