THREE-PARAMETER CORRESPONDING STATES CORRELATIONS FOR JOULE-THOMSON INVERSION CURVES[1]

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ABSTRACT

In the present work, the Boublík-Alder-Chen-Kreglewski (BACK) equation of state was used to compute Joule-Thomson inversion curves (JTICs) of 51 fluids, including hydrocarbons and non-hydrocarbons taken from the TRC Thermodynamic Tables. Comparison with available data showed that predictions were as expected quite reliable and could be used in place of experimental values. Two sets of correlations are presented, following the TRC classification of fluids as hydrocarbons and non-hydrocarbons. The equations are valid for $T_r \leq 4.5$, giving average absolute deviations of 8.2% and 10.4% for inversion pressures and volumes, respectively. Generalized correlations were also developed therefore for JTICs generated from the Lee-Kesler equation of state (EOS). They have the same forms given above, and predict inversion pressures and volumes with respective average absolute deviations of 7.0% and 9.0% for $T_r \leq 4.0$.

KEY WORDS: correlation; corresponding states; inversion curve; Joule-Thomson.

1. INTRODUCTION

The passing of a fluid through a restriction, with its decrease in pressure is usually followed by a change in temperature. In an adiabatic process, this change can be quantified by means of the Joule-Thomson coefficient, μ_J, defined as

$$\mu_J = \left(\frac{\partial T}{\partial P}\right)_H \qquad (1)$$

where T is temperature and P is pressure. The Joule-Thomson inversion curve is the locus of thermodynamic states in which the temperature of gas is invariant with respect to isenthalpic expansion, $\mu_J = 0$.

As usually represented in pressure-temperature coordinates, the Joule-Thomson inversion curve extends from a minimum temperature corresponding to a satured state on the vapor pressure line to a maximum temperature corresponding to the ideal gas limit at zero density and pressure. The curve is parabolic in shape, with a maximum inversion pressure at an intermediate temperature. The inversion curve can also be represented in volume-temperature coordinates but is not very common. The curve has an exponential behavior and at the maximum temperature, where the volume tends to the infinite.

Direct measurement of inversion points is difficult and unreliable. At near-inversion conditions, the vanishing of the Joule-Thomson coefficient means that very large pressure changes will result in very small temperature differences. Hence, extremely accurate temperature measurements are necessary for the inversion pressures to be determined reliably. Thus, the preferred course is the use of thermodynamic relations such as

$$\mu_J = \frac{1}{C_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right] = T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T = 0 \qquad (2)$$

to compute inversion points from experimental PvT data, either by direct numerical differentiation of the raw data, or by first fitting them with a high-precision, multiconstant

equation of state (EOS). Even then, the complete inversion curves of many fluids cannot be established, as they run into regions of high temperature or pressure not accessible to experimental measurement.

Efforts have been made to derive generalized inversion curves from the known behavior of the lighter fluids. Gunn *et al.* [1] computed inversion points from volumetric data available from different references for Ar, Xe, N_2, CO, CH_4 and C_2H_6; since these failed to cover the upper temperature portion of the inversion curve, additional theoretical points were computed for argon from the third term truncated virial equation with coefficients based on the Kihara intermolecular potential. The entire set of points was then correlated by the empirical equation

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

An alternative correlation was proposed by Miller [2] on the basis of inversion data from several sources for CO_2, N_2, CO, CH_4, C_2H_6, C_3H_8, Ar and NH_3 as

$$P_r = 24.21 - \frac{18.54}{T_r} - 0.825T_r^2 \qquad (4)$$

equations (3) and (4) are two-parameter corresponding states correlations that give practically the same results, as they derive from data for the same or very similar, near-simple fluids described by Gunn *et al.* [1] as gases having small, nearly spherical molecules, whose acentric factors are close to zero and by Miller [2] that mostly gases have a critical compressibility factor of 0.29.

The computation of Joule-Thomson inversion curves has long been recognized as a very sensitive test of the predictive capabilities of an equation of state [1-5]. Comparisons of predicted and experimental Joule-Thomson inversion curves can reveal limitations and suggest improvements in the volume and temperature dependencies of an EOS. Several authors [3-5] have therefore sought to assess and rank equations of state performance by comparing predicted and empirical inversion curves [1-2], the comparison is only appropriate for simple fluids, greatly restricting the scope of the analysis. More general correlations, valid for a wider range of fluids, would clearly be a valuable tool to use in this kind of studies.

2. COMPUTATION OF INVERSION CURVES

2.1 BACK equation

One of the best equations of state based on the generalized Van der Waals model is the so-called BACK, from Boublík-Alder-Chen-Kreglewski equation. It is an augmented hard-core equation of the form

$$Z = Z^h + Z^a \qquad (5)$$

Equation (5) expresses that the compressibility factor of a real fluid is the sum of a repulsive term (Z^h) and an attractive term (Z^a). Chen and Kreglewski [6] suggested using the polynomial expansion of Alder for the attractive term and the Boublík expression for the repulsive part of the compressibility factor. This equation has 24 universal constants obtained by Alder *et al*. [7] by fitting to internal energy and PvT of liquid and gaseous argon, values of a square-well fluid, and 5 parameters characteristic of an individual compound that have to be evaluated from experimental data of pure substances.

The BACK equation appears particularly attractive for several reasons. It is highly accurate in fitting the PvT behavior of a number of substances. Only a few equation constants are required for each substance, and these are properties of the molecules about which much is already known. Additionally the range of application is very large, the equations are valid at least up to the reduced temperature $T_r = 7$ and reduced pressure $P_r = 20$. This last point is very important because most of the EOS do not reach those high values of T_r and P_r, then the inversion curves cannot be generated in that range .

2.2 LEE-KESLER equation

The Lee-Kesler [8] equation is a generalization of the Benedict-Webb-Rubin EOS within the framework of a three-parameter corresponding state theory. As described by its authors, the LK EOS accurately represents the volumetric and thermodynamic properties of nonpolar and slightly polar fluids (and their mixtures) for reduced temperatures from 0.3 to 4, and reduced pressures from 0 to 10. It has been found to give the most accurate prediction of inversion curves over the entire temperature range [4].

From Eq. (2) the inversion curve for Lee-Kesler EOS for any pure fluid is[4]:

$$X^{(0)} + \frac{\omega}{\omega^{(r)}}\left[X^{(r)} - X^{(0)}\right] = 0 \qquad (6)$$

where

$$X = -T_r\left(\frac{\partial V_R}{\partial T_r}\right)_{Pr} + V_R \qquad (7)$$

the development of the inversion curve for the simple fluid using Eqs. (6) and (7) involves the unnecessary generation of the inversion curve for the reference fluid and *viceversa.* The Eq. (6) for the simple fluid is reduced to $X^{(0)} = 0$ and for the reference fluid $X^{(r)} = 0$.

2.3 Discussion

Figure 1 compares the inversion curves computed from the LK equation, for simple fluids (ω=0), the BACK equation for oxygen (ω = 0.0218) and the correlations of Gunn *et al*. [1] and Miller [2]. This comparison includes the oxygen to generate the inversion curve from the BACK equation because it is the compound that has the acentric factor closely to zero belonging to the TRC classification [9] and by the other hand the Lee-Kesler equation provides directly the constants for simple fluids. The small differences between the predicted curves from the correlations and the inversion curves from the EOS in study can be attributed to the different kind of fluids considered.

Later, inversion curves were generated for the 51 compounds available for the BACK equation. To compute the inversion data, values of temperature, pressure, critical volume and the 5 parameters characteristic of each fluid are necessary. Correlations for P_r-T_r inversion curves as a function of the acentric factor as unique parameter of the fluid, are obtained from the developed inversion curves.

These correlations are valid from T_r = 0.9 to 4.5 for all the compounds of the TRC classification (hydrocarbons and non-hydrocarbons**),** excluding the alcohols where the correlations are valid up to T_r = 3.7. Extrapolations can be made and the behavior of the curves are the same but the deviation increases.

The following form has given better fit than several other functions:

$$P_r = \sum_{i=o}^{4}\left(a_i + b_i\omega^{n_i}\right)T_r^i \qquad (8)$$

where the corresponding correlation coefficients for Eq. (8) are given in table I.

The figure 2 shows the inversion curve in coordinates P_r-T_r for the cumene calculated from the BACK equation and it is compared with the curve obtained from the correlation. The relation between them is evident. Corresponding results were obtained for all the fluids excluding alcohols. Analogous results were obtained from the Lee-Kesler EOS.

Similarly, a correlation for the inversion curve V_R -T_r was developed

$$\frac{RT_c}{P_c}\rho = \sum_{i=o}^{4}\left(c_i + d_i\omega^{m_i}\right)T_r^{i-1} \qquad (9)$$

where ρ is the inverse of the volume and the corresponding correlation coefficients for Eq. (9) are given in table II. The curves are represented in V_R -T_r coordinates instead of V_r -T_r to avoid the errors of interpretation that may arise from the well known discrepancy between the true critical compressibility factor of a fluid, Z_c and the corresponding EOS value, ζc.

The figure 3 shows the agreement between the inversion curve in coordinates V_R -T_r predicted from the BACK equation of state and the generated correlation for n-heptane. For the rest of the fluids the behavior is alike. It is very important to point out the use of the V_R-T_r curve because V_R and T_r are independent natural variables in the calculation of thermodynamics properties using equations of state that are explicit in pressure. Similar results were achieved from the Lee-Kesler EOS.

Table III shows the average absolute deviations (AAD) obtained for each compound for both prediction reduced pressure and reduced volume from the BACK EOS. The peak of the curve and its general behavior introduce errors lower than 5%, omitting the alcohols. It was developed another correlation for them. The errors for the prediction of reduced volume is lower than 5% in all cases.

Space limitations preclude the table of the AAD for the correlations from the Lee-Kesler EOS, but the AAD for pressures and volumes are respectively 7.0% and 9.0% for $Tr \leq 4.0$.

Finally figure 4 represents the JTIC reported by Goodwin [10] for the benzene, the inversion curves predicted from the correlations for the Lee-Kesler and BACK EOS for

the same compound. It is shown that the Lee-Kesler EOS gave better predictions at the region close to the peak than the BACK EOS.

3. COMMENTS AND CONCLUSIONS

Generalized corresponding states correlations were developed for Joule-Thomson inversion curves (P_r-T_r and V_R-T_r), as functions of reduced temperature and acentric factor, generated from the BACK and Lee-Kesler equation valid for a wide range of fluids. This correlations could be used in place of experimental values for testing any equations of state, for fluids with acentric factor different to zero.

The problem of bringing predicted inversion curves from cubic equations of state into closer agreement with experimental data has been dealt with more extensively elsewhere. Colazo *et al.* [5] developed a numerical procedure to compute supercritical cohesion parameters for cubic equations of state, from available P_r-T_r inversion curves. Barré *et al*. [11] employed this procedure, together with "experimental" inversion curves generated from the LK EOS, to compute supercritical cohesion parameters for the VDW, RK and PR EOS that reproduce the inversion curves to within an arbitrarily close precision.

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CAPTIONS FIGURES

Fig. 1. Inversion curves for simple fluid from Gunn *et al*., Miller, Lee-Kesler and BACK EOS.

Fig.2. Inversion Curve (P_r-T_r) for cumene calculated from BACK EOS and compared with the predicted curve from Eq. (8).

Fig.3. Inversion Curve (V_R-T_r) for n-heptane calculated from BACK EOS and compared with the predicted curve from Eq. (9).

Fig.4. Inversion Curve (P_r-T_r) for benzene reported by Goodwin and from correlation for the Lee-Kesler and BACK EOS.

Table I. Coefficients of the inversion pressure function, Eq.(8)

Constants / y EOS	0	1	2	3	4
BACK	Hydrocarbons	n_i = 2			
a	-20.338	36.096	-12.478	1.4541	-0.0482
b	-42.815	85.759	-47.575	9.541	-0.6465
BACK	Non Hydrocabons	n_i = 1.3			
a	-16.697	28.661	-8.7013	0.7553	-0.0046
b	-40.947	83.101	-44.114	8.573	-0.5662
LEE-KESLER					
n	0.95	1.04	1.09	1.16	1.20
a	-21.938	37.431	-13.521	-1.7906	-0.08
b	-20.355	42.258	-14.355	-0.449	0.336

Table II. Coefficients of the inversion volume function, Eq.(9)

Constants / i EOS	0	1	2	3	4
BACK	Hydrocarbons				
n	-1.4	-1.1	-0.5	-0.5	-0.52
c	4.5347	1.6017	2.6438	-1.2746	0.129
d	0.0933	-0.0599	0.3496	-0.1825	0.02267
BACK	Non Hydrocabons	n_i = 1.8			
c	4.0529	1.447	2.4906	-1.1311	0.1096
d	8.0403	2.2561	5.0673	-3.8789	0.5276
LEE-KESLER					
n	1.2	1.2	1.1	1.1	1
c	1.884	5.133	0.463	-0.716	0.0824
d	12.703	-9.701	14.780	-6.482	0.587

Table III. AAD for the P_r-T_r and V_R-T_r correlations obtained from BACK EOS.

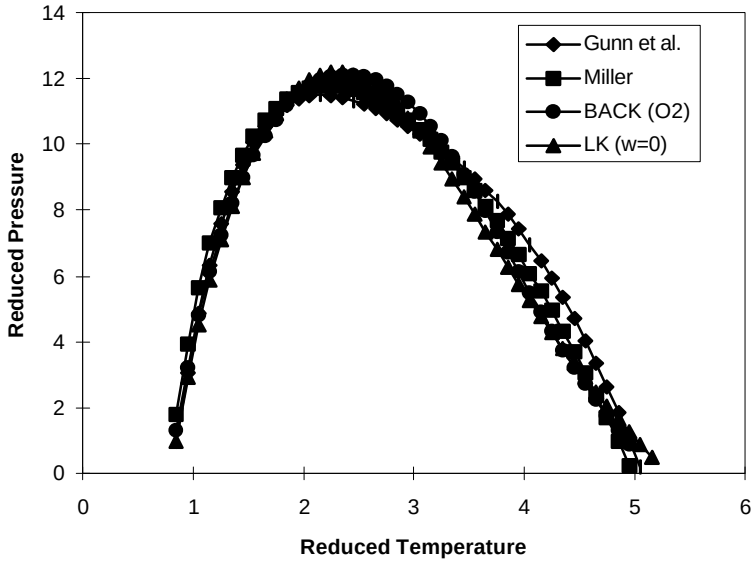
Substance	ω[12]	AAD** P_r-T_r	AAD** V_R-T_r
Oxygen	0.0218	1.39	0.76
Tetrahyrofuran	0.2264	4.86	1.54
Sulfur Dioxide	0.2451	4.38	4.00
Hydrogen Sulfide	0.0827	2.09	1.70
Methanol	0.5656	28.52	10.34
Ethanol	0.6371	30.00	21.70
1-Propanol	0.6279	35.24	24.57
2-Propanol	0.6689	18.36	25.34
2-Propanone	0.3064	18.24	11.22
Diethyl Ether	0.2846	2.09	4.34
tert-Butyl Methyl Ether	0.2674	3.59	6.67
Furan	0.1997	2.70	2.58
Trifluoromethane*	0.26	6.14	3.74
Difluroethane*	0.256	12.11	9.40
Chlorotrifluoromethane*	0.198	3.75	6.11
Dichlorodifluoromethane*	0.204	6.24	8.30
Trichlorofluromethane*	0.189	3.40	11.69
1,1-Dichloro-1,2,2,2-tetrafluoroethane*	0.2366	9.78	3.90
1,2-Dichloro-1,1,2,2-tetrafluoroethane*	0.246	8.75	10.55
1,1,2-Trichloro-1,2,2-trifluoroethane*	0.256	7.21	9.23
r-500*	0.207	1.93	3.93
Chlorodifluoromethane	0.2192	2.19	2.57
Dichlorofluoromethane	0.2069	3.37	5.04
Isoquinoline	0.2885	2.15	4.44
Methanamine	0.2813	6.79	5.51
Quinoline	0.3287	7.08	5.71

* [13]

** ABS (Σ(BACK-CORR)/BACK)*100)/N

Substance	ω[12]	AAD** T_r-P_r	AAD** T_r-V_R
n-Hexane	0.3046	10.00	1.46
n-Heptane	0.3511	6.26	9.17
n-Octane	0.3962	14.75	9.48
n-Nonane	0.4377	9.37	14.24
n-Decane	0.4842	6.95	15.82
Cyclohexane	0.2118	4.35	7.10
Methylcyclohexane	0.235	3.16	7.15
cis-Decahydronafthalene	0.2942	7.40	11.36
trans-Decahydronafthalene	0.2536	11.76	14.29
1-Butene	0.1867	2.85	7.36
Isobutene	0.1893	2.68	7.89
Propyne	0.2161	8.25	9.14
Benzene	0.2108	4.25	6.51
Toluene	0.2641	4.22	3.63
o-Xylene	0.3127	4.38	10.57
m-Xylene	0.3086	6.21	9.44
p-Xylene	0.3259	3.92	9.44
Cumene	0.3377	3.78	10.15
p-Xymene	0.3722	7.53	11.15
1,1-Biphenyl	0.3659	22.23	22.71
Naphthalene	0.3019	7.55	3.24
Tetralin	0.3278	11.08	1.95
Methanethiol	0.146	3.96	12.30
Ethanethiol	0.1921	3.34	7.62
Tetrahydrothiophene	0.1988	6.29	6.74
Thiophene	0.1928	2.33	6.51
Isooctane	0.3769	8.92	13.38

** ABS (S(BACK-CORR)/BACK)*100)/N


Gunn et al.
Miller
BACK (O2)
LK (w=0)
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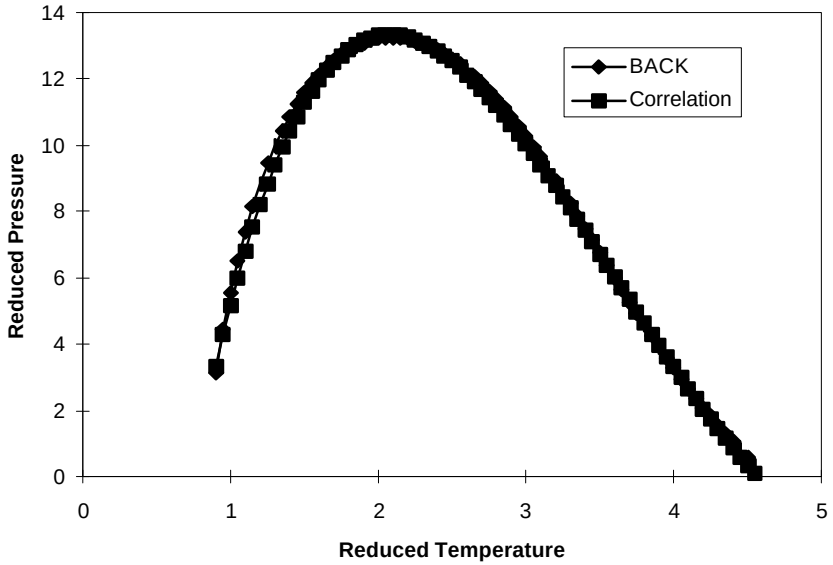
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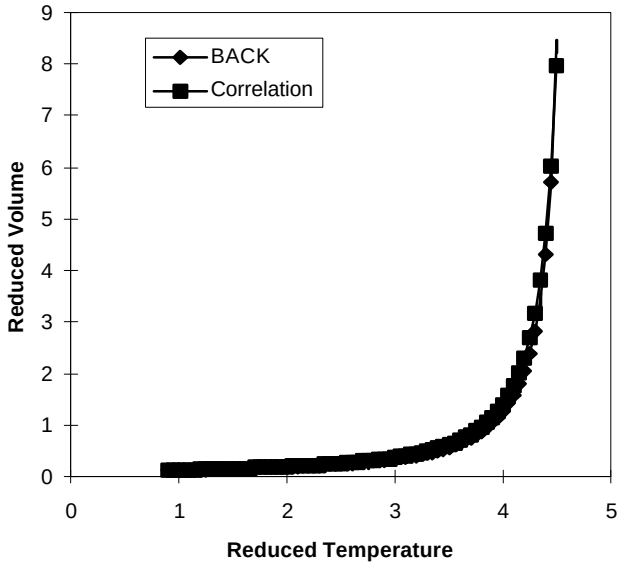
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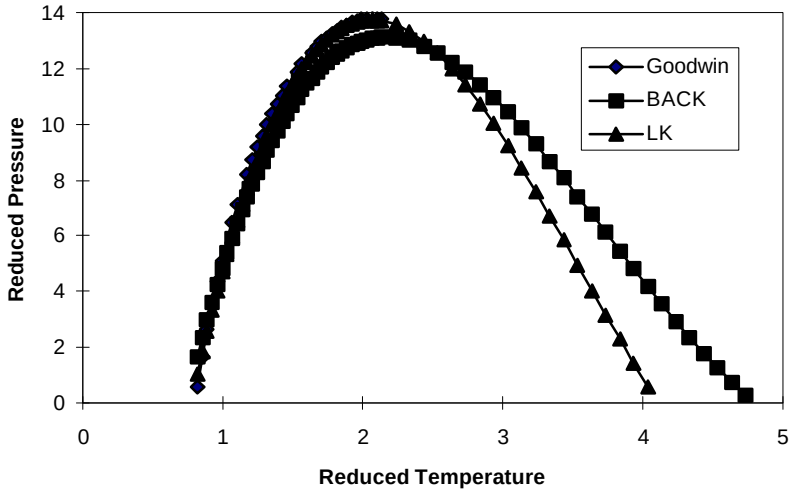
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Reduced Pressure
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