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On the Joule–Thomson effect inversion curve

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Abstract

A new procedure has been developed to investigate the capability of an equation of state to predict in a mathematical way an experimental inversion curve. Application of the proposed method to the four cubic equations of state van der Waals, Redlich–Kwong, Soave and Peng–Robinson in their ability to predict the experimental inversion curve of nitrogen has indicated that the Redlich–Kwong equation of state gives the best results. The proposed procedure was also used to find the best of three well known mixing rules, using the Redlich–Kwong equation of state and the experimental inversion curve of air.

Keywords: Equations of state; Inversion curve; Joule–Thomson effect; Mixing rules

List of symbols

a	parameter in equation of state
b	parameter in equation of state
C_p	specific heat at constant pressure
D	variable in Eqs. (7) and (8)
H	enthalpy
P	pressure
R	universal gas constant
T	absolute temperature
T_c	critical temperature
V	volume
V_c	critical volume

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- y composition
 z_c real fluid critical compressibility equal to $P_c V_c / RT_c$

Greek letters

- α function in the Soave and PR equations
 ζ_c critical compressibility factor
 μ adiabatic Joule–Thomson coefficient
 ϕ isothermal Joule–Thomson coefficient

Subscripts

- c critical state
 mix mixture
 1 component 1
 2 component 2

1. Introduction

The Joule–Thomson effect has been much investigated because of its importance for theoretical and practical purposes. According to the method of operation we distinguish between two types of effect: the differential adiabatic effect μ , defined as

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H \quad (1)$$

and the isothermal Joule–Thomson effect, ϕ , defined as

$$\phi = \left(\frac{\partial H}{\partial p} \right) = -\mu C_p = V - T \left(\frac{\partial V}{\partial T} \right)_p \quad (2)$$

The locus of points for which $\mu = 0$ (or $\phi = 0$) is called the inversion curve. As shown in Fig. 1 the inversion curve divides the p – T plane into two zones [1]. In the zone inside the inversion curve the adiabatic Joule–Thomson effect is positive, so that decreasing the pressure leads to a decrease in temperature. Outside the inversion curve the adiabatic Joule–Thomson effect is negative and a decrease in pressure leads to an increase in temperature. It can be shown that an expansion that begins from the inversion pressure leads to the highest cooling effect.

Francis and Luckhurst [2] investigated the Joule–Thomson coefficient and claimed that the law of “corresponding states” fits the isothermal Joule–Thomson coefficient but not the adiabatic Joule–Thomson coefficient because of the specific heat. They also claimed that the law of corresponding states conforms not only to pure gases but also to their mixtures. The ideas of Francis and Luckhurst have been used by some workers to correlate the generalized inversion curve using reduced coordinates.

Gunn et al. [3] developed a generalized inversion curve to fit the experimental data of real gases that have a small acentric factor. They concluded that, in general, the

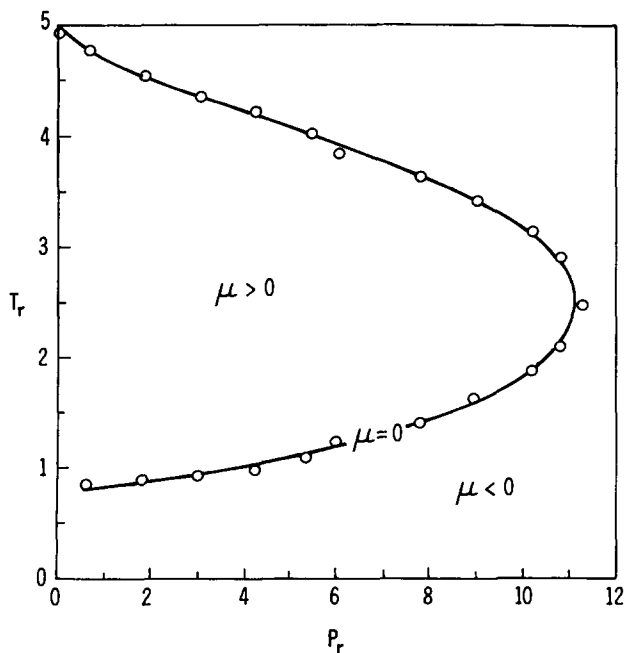


Fig. 1. Typical inversion curve—data for nitrogen (Roebuck and Osterberg [1]).

inversion curve could be described by the theorem of corresponding states, but the use of the two-parameter corresponding states theorem was not accurate enough and that a third parameter, like the acentric factor, was needed to improve the fit. Miller [4] correlated the experimental data of a number of real gases with a generalized inversion curve and concluded that the inversion curve could be described reasonably well by the two-parameter corresponding states theory for all gases but H_2 , He and Ne. Of all the equations of state that Miller investigated (Dieterici, van der Waals, Redlich–Kwong and Martin) the Redlich–Kwong (RK) equation of state proved to be best. Juris and Wenzel [5] used the generalized experimental inversion curve correlated by Gunn et al. [3] to investigate the capability of a number of the most popular equations of state to predict the inversion curve. They concluded that the RK equation of state predicted the inversion locus with the best accuracy, even better than some of the more complex equations of state. Dilay and Heidemann [6] investigated some more recent equations of state in their ability to predict the inversion curve and concluded that the Lee–Kesler (LK) equation of state gave the best overall results. The predicted inversion curves were inferior to the inversion curve found from the RK equation of state. The peak of the inversion curve and its high-temperature branch showed large variations with acentricity when using the Peng–Robinson (PR) equation of state. Feroiu and Geana [7,8] investigated the general cubic equation of state and concluded that this equation of state is very adjustable and can give very good results for predicting vapor–liquid equilibria and the Joule–Thomson inversion curve. When compared to other equations of state in their ability to predict the general inversion curve, the general equation of

state, corrected by a function of the type $\exp [m(1 - T_r)]$ in the attraction factor, gave the best results. Colazo et al. [9] investigated the ability of seven equations of state to predict the inversion curve and concluded that the maximum of the inversion curve depends upon the critical compressibility factor ζ_c (different from the real fluid value z_c). They found a way to express the supercritical cohesion parameter $\alpha(T_r)$ for all equations of state. The seven equations of state, including the new cohesion parameters, predicted the inversion curve better than the old ones.

Few of the experimental reports give information about the inversion curve for more than one gas and for the complete curve. Most reports describe the inversion curves for refrigerant gases or other low-molecular weight gases. Hendricks et al. [10] measured the Joule–Thomson coefficient and related coefficients for the nine pure gases CH_4 , N_2 , O_2 , Ar, CO_2 , Ne, CO, H_2 and ^4He and reported their complete inversion curves. Perry and Green [11] reported the complete inversion curves for the gases air, Ar, CO_2 , D_2 , and H_2 , and partial inversion curves for the gases CH_4 , C_2H_6 and C_3H_8 . Najjar et al. [12] reported the inversion curve of air and calculated the van der Waals (vW) equation of state parameters that allow a better prediction of the experimental inversion curve. Karnatsevich et al. [13] reported the inversion curve of ^3He in p – T coordinates and the entropy–temperature diagram using p – V – T data for ^3He from the literature. Roebuck and Osterberg [14] reported the partial inversion curves at the high-temperature branch for the mixture He + N_2 for four different mole fractions of He: 75.5%, 51.0%, 33.2% and 16.6%. Roebuck and Osterberg [15] reported the partial inversion curves at the high-temperature branch for the mixture He + Ar at three different mole fractions of He: 75.8%, 50.6% and 33.5%. Trappeniers et al. [16] measured the thermodynamic properties of Kr between the temperatures 273 and 423 K and densities up to 620 amagat, including the Joule–Thomson effect. Their results may be used to obtain the low-temperature branch of the inversion curve. Goodwin [17] reported the thermodynamic properties of benzene including the partial inversion curve at the low-temperature part.

There are other reports which describe the Joule–Thomson coefficient of different gases but do not contain information on the complete inversion curve.

2. Theory

For the inversion curve $\mu = 0$, hence Eq. (2) yields

$$V = T \left(\frac{\partial V}{\partial T} \right)_p \quad (3)$$

or

$$\left(\frac{\partial \ln V}{\partial \ln T} \right)_p = 1 \quad (4)$$

Outside the inversion curve $\mu < 0$ or

$$\left(\frac{\partial \ln V}{\partial \ln T} \right)_p < 1 \quad (5)$$

In order to calculate the inversion curve for any gas in a theoretical way we must use both an equation of state and the conditions given by Eqs. (3) or (4).

The general cubic equation of state is

$$p = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + ubV + Wb^2} \quad (6)$$

where u and W are adjustable parameters of the equation of state.

Using Eq. (6) the derivative in Eq. (4) becomes

$$\frac{\frac{RT}{V-b} - \frac{a}{D} T \frac{\partial \alpha}{\partial T}}{\frac{VRT}{(V-b)^2} - \frac{a\alpha}{D^2}(2V^2 + ubV)} = 1 \quad (7)$$

where

$$D = V^2 + ubV + Wb^2 \quad (8)$$

A comparison between cubic equations of state can be made by applying the condition given by Eq. (4) to the specific equation of state and using an experimental inversion curve. The experimental inversion curve is used to find the connection between p , T and the equation of state is used to give the volume that corresponds to those p and T values. The left handside of Eq. (7) can be calculated using the p - V - T properties and should yield the value 1 if the equation of state correctly describes the phenomena. In practice the calculated value will differ from unity because of experimental errors and the limitations of the equation of state. The most appropriate equations of state will produce the overall smallest deviations from the value 1.

We have used the experimental inversion curve reported by Hendricks et al. [10] for N_2 gas to find each pair of values (p_r , T_r) on the inversion curve. The pertinent results are given in Table 1. Using the p_r , T_r data the volume can be found for each particular equation of state and then the derivative in Eq. (7) can be calculated. The corresponding results are reported in Table 1.

As shown in Table 1, the Redlich–Kwong (RK) equation of state gives the best results, with a deviation from the value 1 not exceeding $\pm 15\%$. The RK equation of state gave results smaller than 1 (negative deviation) for most points on the inversion curve. As indicated by Eq. (5) a negative deviation means that the predicted inversion curve will intersect with the experimental inversion curve. This is in agreement with the results of Miller [4] where it can be seen that the inversion curve predicted by the RK equation of state is inside the generalized inversion curve over most of the temperatures.

The new suggested method for comparison of the equations of state using Joule–Thomson effect data has particular advantage when comparing the calculated adiabatic Joule–Thomson coefficients with the experimental ones. The latter are usually calculated from Eq. (2) which requires accurate knowledge of the ideal specific heat, a fact that may increase the overall calculation error. Every comparison between

Table 1

The derivative $[\partial(\ln V)/\partial(\ln T)]_p$ for the four different equations of state for the experimental inversion curve of nitrogen (Hendricks et al. [10])

T_i	vW		RK		Soave		PR	
	V	$\left(\frac{\partial \ln V}{\partial \ln T}\right)_p$	V	$\left(\frac{\partial \ln V}{\partial \ln T}\right)_p$	V	$\left(\frac{\partial \ln V}{\partial \ln T}\right)_p$	V	$\left(\frac{\partial \ln V}{\partial \ln T}\right)_p$
1.00	57.8	0.660	45.6	1.151	45.6	1.181	41.0	1.249
1.13	58.0	0.601	47.3	1.061	47.6	1.119	43.0	1.192
1.25	58.8	0.589	49.1	1.013	49.6	1.087	45.1	1.158
1.50	61.5	0.610	53.4	0.970	54.5	1.053	50.0	1.118
1.75	65.3	0.660	58.6	0.961	60.4	1.036	55.9	1.095
2.70	92.2	0.900	90.0	0.985	94.4	0.991	89.4	1.041
3.11	114.3	0.975	113.6	0.994	119.0	0.979	113.8	1.026
3.63	163.2	1.026	163.9	1.002	170.5	0.972	165.0	1.013
3.92	214.1	1.035	215.5	1.005	222.7	0.973	217.1	1.009
4.30	340.8	1.031	342.7	1.005	350.6	0.978	344.9	1.004

^a V : volume ($\text{m}^3 \text{mol}^{-1} \cdot 10^6$).

experimental and calculated inversion curves, reported in the literature were done qualitatively and not using statistical criteria.

The fact that the new method proposed here points to the RK equation of state as the one giving the best results is in agreement with a similar conclusion reported in the literature [4,5] where the analytical inversion curve was developed using Eq. (2).

The utility of an equation of state is greatly increased when it can be made applicable to a mixture. Often this can be accomplished by expressing the parameters of the mixture in terms of the composition and the parameters of the pure components (Reid et al. [18]). The procedure described in this publication can also be used to compare between different mixing rules. In this report a comparison will be made only between three mixing rules.

The simplest mixing rule is that of Kay where the pseudocritical properties of a mixture are calculated as the mole-averages of the properties of the pure components. Another common rule is to mole-average the parameters of the equation of state (Sandler [19]), this procedure will be referred in short as "Equation Par". According to this method

$$b_{\text{mix}} = \sum y_i b_i \quad (9)$$

$$a\alpha_{\text{mix}} = \sum \sum y_i y_j (a\alpha)_{ij} \quad (10)$$

A third rule, suggested by Gunn et al. [3], uses the critical temperatures and volumes of the pure constituents as follows:

$$T_{c,\text{mix}} = \sum y_i T_{ci} \quad (11)$$

$$V_{c,\text{mix}} = \sum y_i V_{ci} \quad (12)$$

Table 2

The derivative $[\partial(\ln V)/\partial(\ln T)]_p$ calculated using the RK equation of state for the experimental inversion curve of air (Perry and Green [11])

T_r	p_r	Eq. par [19] ^a	Kay [19]	Gunn [3]
1.04	4.68	1.112	1.116	1.104
1.18	6.68	1.029	1.038	1.027
1.39	8.69	0.986	0.998	0.987
1.60	10.02	0.967	0.979	0.969
2.00	11.36	0.955	0.965	0.958
2.61	11.36	0.964	0.972	0.967
3.15	10.02	0.979	0.984	0.981
3.56	8.69	0.986	0.989	0.987
3.98	6.68	0.994	0.996	0.996
4.30	4.68	1.000	1.002	1.001
% Mean value absolute deviation from 1		3.10	2.73	2.87
% Standard deviation		3.75	3.67	3.48

^a Eq. par = equation of state parameters.

and the critical pressure of the mixture is given by:

$$p_{c,\text{mix}} = \frac{RT_{c,\text{mix}}}{V_{c,\text{mix}}} \sum y_i z_i \quad (13)$$

The complete inversion curve of a mixture of gases is known only for air. Using the inversion curve reported by Perry and Green [11] for air, the relationship between pressure and temperature can be found in the same manner as for a pure gas. The pertinent results appear in Table 2. In this particular case the RK equation of state was used to calculate the derivative in Eq. (7) using every time one of the three mixing rules described above. The pertinent results are also given in Table 2. The relative merits of the three mixing rules were determined on the basis of two statistics; (a) the mean absolute deviation from 1 and (b) the standard deviation from 1.

From Table 2 it is evident that there are no large differences between the three mixing rules. The largest mean absolute deviation from the value 1 was found for the mixing rule which makes use of the equation of state parameters. Kay's rule has a standard deviation larger than the rule proposed by Gunn et al. [3], but this is caused by the deviation of the first point. Kay's rule described the inversion curve better over most of the points in comparison to the other mixing rules.

3. Conclusions

(1) The RK equation of state gave the best overall results in predicting the experimental inversion curve of nitrogen gas in comparison to the three cubic equations of state: vW, Soave and PR.

(2) Based on Redlich–Kwong's equation of state and the experimental inversion curve of air, the best mixing rule is that of Gunn if judgement is on the basis of the smallest standard deviation, and Kay's rule if judgement is on the basis of smallest mean absolute deviation.

(3) The procedure suggested here provides a very easy mathematical method for comparison of different equations of state using an experimental inversion curve.

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