

The Joule–Thomson Coefficient for Pure Gases and Their Mixtures

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Abstract: The properties of the Joule–Thomson coefficient are discussed in general for pure gases, and the possibility of a nonlinear effect in binary mixtures is analyzed using the First Law of Thermodynamics and some common cubic equations of state. It is shown that although theoretically a binary mixture of gases may exhibit a Joule–Thomson effect different from the molar-weighted mean of the pure-component effects, the possibility of observing a positive difference is very low.

Introduction

Consider the steady-state flow of a fluid down a heavily insulated duct that contains a restriction to the flow (Figure 1). This restriction might be some type of porous plug, a slightly opened valve, an orifice, or a long and narrow capillary tube. In general, a process in which a gas is made to suffer a loss of pressure on passing a constriction is referred to as *throttling*.

The work interaction and the changes in kinetic and potential energies within the control surfaces 1 and 0 may be considered negligible. It is easy to see that the material moving along a flow line going directly through the hole will take the shortest time to cross the obstruction; all other flow lines will collide with the vertical plate and change their direction several times until they are able to cross the restriction. In addition, because the mass flow is constant, the stream velocity will increase when going through the hole, and then at a certain distance after the obstruction it will decrease to the same value it had upstream of the hole. The changes in direction of the flow lines and of the stream velocity will be reflected in turbulent wakes on both sides of the obstruction. The presence of turbulence will result in a decrease in the available energy for doing work, making the process of flow through a restriction *internally irreversible*. It should also be noted that it is impossible to increase the pressure by means of adiabatic throttling, and that P_0 will always be smaller than P_1 for all substances. The first law for a steady state process is

$$\dot{Q} - \dot{W} = \Delta \dot{H} + \Delta \dot{KE} + \Delta \dot{PE} \quad (1)$$

in units of energy time⁻¹ and

$$\dot{q} - \dot{w} = \Delta \dot{h} + \Delta \dot{ke} + \Delta \dot{pe} \quad (2)$$

in units of energy mass⁻¹ time⁻¹. In equation 1, ΔKE and ΔPE are the changes in kinetic and potential energy, respectively, and Q is considered positive for heat entering the system. If the control surfaces are located far enough upstream and downstream of the restriction, then the flow lines are parallel to each other. Application of equation 2 to control volume 1-0 under these conditions yields

$$h_0 = h_1 \quad (3)$$

Equation 3 should be interpreted properly: it indicates that the enthalpy in state 1 is equal to the enthalpy in state 0, but it *does not* indicate that the process is *isenthalpic*. Because of irreversibility the process is actually *not* isenthalpic.

We will now proceed to analyze in detail the characteristics of the phenomenon and determine what makes it important, not only theoretically, but also industrially. To do so let us assume that we perform the following two series of experiments. First, we keep the upstream conditions constant while varying the degree of opening of the restriction. Although each equilibrium state 0 will have a different pressure, P_0 , all the possible states will have the *same enthalpy* as indicated by equation 3. During such experiments it will be observed that, depending on the nature of the fluid and the upstream conditions, the downstream temperature, T_0 , will be sometimes lower and sometimes higher than the upstream temperature, T_1 . If the variations of the degree of opening are made sufficiently small, the points will be close enough to draw a continuous curve, which can be assumed to be isenthalpic. In the second series of experiments we use a given opening but change the upstream conditions. The results appear in Figure 2 where it is seen that the behavior of the curve will vary substantially depending on the value of the initial upstream enthalpy. Above a certain value, h_{\max} , of the enthalpy, the isenthalpic curves all ascend monotonically in the direction of decreasing pressure. For values of $h < h_{\max}$, the curves now exhibit a characteristic maximum, all maxima forming a locus, shown in the figure and known as the *inversion curve*. Again, below a certain value, h_{\min} , of the enthalpy, the maximum will disappear and the curves will show the same general behavior as that for which $h > h_{\max}$. As will be shown below, the inversion curve can be described by an empirical function, $\varphi(T_i, P_i) = 0$, between the inversion temperature and the inversion pressure.

The Adiabatic Joule-Thomson Effect. The change in temperature, $\Delta T_H = T_0 - T_1$, associated with throttling is referred to as the *Joule–Thomson effect*. When the pressure drop ($P_0 - P_1$) is large it is customary to speak of the *integral* Joule–Thomson effect, whereas the *differential* Joule–Thomson effect is said to occur when this difference is extrapolated to zero. In the latter case the magnitude and direction of the effect is described by the *adiabatic Joule–Thomson coefficient*, μ .

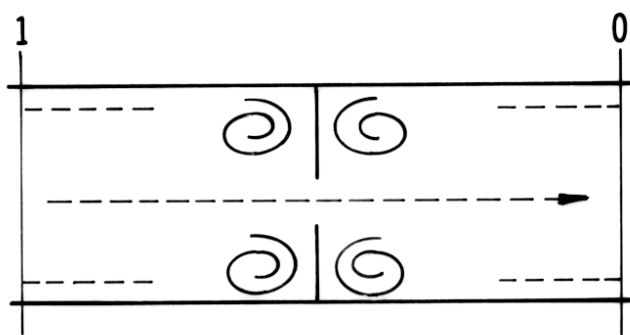


Figure 1. Throttling process.

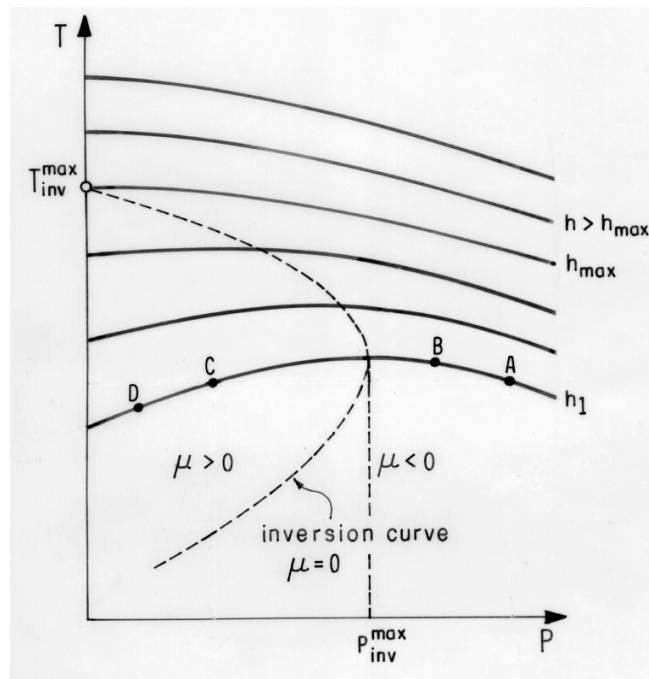


Figure 2. Throttling experiments conducted under different upstream conditions and restriction intensities.

$$\mu \equiv \left(\frac{\delta T}{\delta P} \right)_H \quad (4)$$

The difference between the differential and integral Joule–Thomson effects can be visualized with the help of Figure 2. Consider a throttling process that begins from point A. The differential Joule–Thomson effect corresponds to the *local slope* of the curve at point A and will vary from the original slope to the slope at the final pressure. The integral Joule–Thomson effect represents the *total* temperature change during a finite pressure drop. As seen from Figure 2, the value of μ may be positive or negative. Levine [1] indicates that typical values of μ for pure gases range from +3 to –0.1 K, depending on the gas and on its initial temperature and pressure. From its definition ($\mu = 0$) it follows that the inversion curve separates those states for which $\mu < 0$ (outside) from those for which $\mu > 0$ (inside). Thus, there exists a *maximum inversion temperature*, $T_{\text{inv}}^{\text{max}}$, at $P = 0$, which is obtained by extrapolation to zero pressure. The inversion curve, on the

Table 1. Maximum Inversion Temperature, K, for Various Gases

Gas	$T_{\text{inv}}^{\text{max}}$
Helium - 3	40
Hydrogen	205
Neon	270
Air	603
Nitrogen	625
Argon	723
Oxygen	750
Krypton	1050
Xenon	1290

other hand, passes through a *maximum pressure*, $P_{\text{inv}}^{\text{max}}$, for a temperature that depends on the nature of the gas. At pressures greater than $P_{\text{inv}}^{\text{max}}$, μ is always negative. Consider now a throttling process represented by point A on curve h_1 ; depending on the downstream pressure, the temperature of the gas may increase (point B), may remain the same (point C), or it may decrease (point D); remember that all the points are located in the *same* isenthalph. In other words, if we want to cool the gas it is necessary to expand it to a pressure below that of point D. Values of the maximum inversion temperature, $T_{\text{inv}}^{\text{max}}$, for several gases are given in Table 1. It is seen that for most gases the maximum inversion temperature is higher than room temperature and that it is lower only in the case of hydrogen and helium. This characteristic is particularly important for hydrogen supply lines, owing to the explosive nature of hydrogen and atmospheric oxygen. When a leak occurs in a supply line, the gas is subject to a throttling effect, and, in the case of hydrogen, this leads to a discharge of heated gas into the atmosphere creating favorable conditions for an explosion.

From the industrial viewpoint, the integral Joule–Thomson effect is the most interesting because it has units of temperature and expresses the *overall* cooling (or heating) that takes place when a fluid passes through a restriction. Most of the interest in the Joule–Thomson effect is due to its practical application in the liquefaction of gases, cryogenic coolers, and refrigeration equipment. If the upstream fluid is in a saturated liquid state, the drop in pressure through the restriction will result in evaporation of part of the liquid with the corresponding large heating (cooling) effect.

The Joule–Thomson experiment also provides information that can be used to examine the nature of intermolecular forces operative between pure gases or their mixtures. The Joule–Thomson inversion curve has often been used to test equations of state at temperatures and pressures above the critical values. The test is rather severe because, as shown by equation 7 below, the derivatives of the volume are involved.

We can use the chain rule to derive a working expression for the Joule–Thomson coefficient:

$$\mu \equiv \left(\frac{\delta T}{\delta P} \right)_H = - \left(\frac{\delta T}{\delta H} \right)_P \left(\frac{\delta H}{\delta P} \right)_P \quad (5)$$

but, by definition

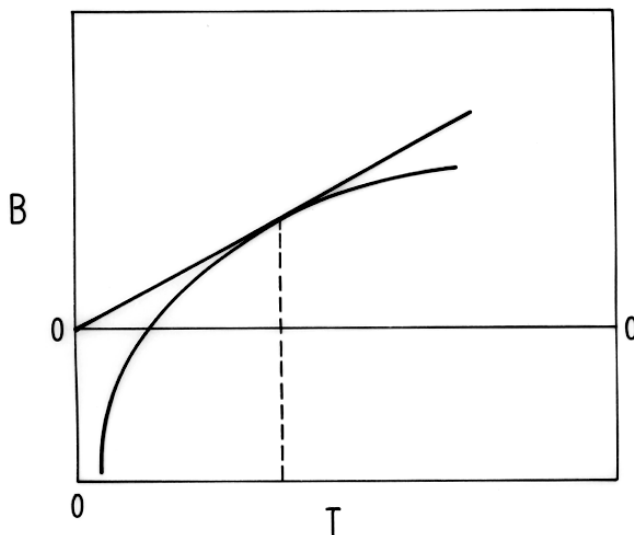
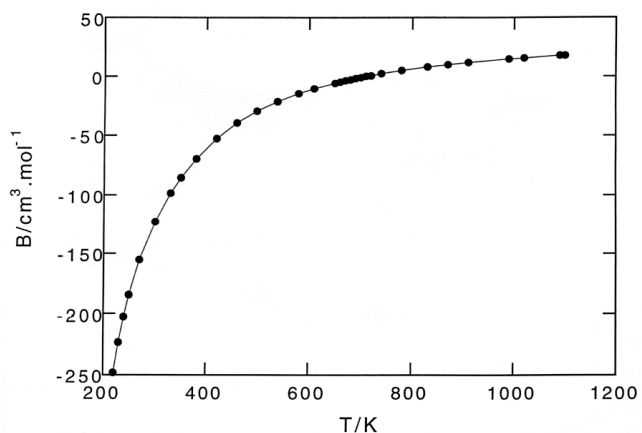


Figure 3. (a) Variation of the second virial coefficient, B , of CO_2 with temperature; (b) the solution to equation 15 for CO_2 .

$$C_p = \left(\frac{\delta H}{\delta T} \right)_p$$

and from the Maxwell relations [1].

$$\left(\frac{\delta H}{\delta P} \right)_T = V - T \left(\frac{\delta V}{\delta T} \right)_p \quad (6)$$

so that

$$\mu = \frac{1}{C_p} \left[T \left(\frac{\delta v}{\delta T} \right)_p - v \right] \quad (7)$$

Thus, the Joule–Thomson coefficient may be calculated from a knowledge of the PVT relationship of the fluid (equation of state) and the specific heat at constant pressure. If equation 7 is applied to an ideal gas we get $\mu^{\text{ideal}} = 0$, hence an ideal gas undergoes *no change in temperature* upon throttling. This is not surprising because it is known that the enthalpy of an ideal gas is solely a function of the temperature. Let us now use equation 3 to investigate the effect of throttling on an incompressible fluid. Equation 3 may be written

$$u_1 + P_1 v_1 = u_0 + P_0 v_0 \quad (8)$$

Rearranging and taking into account that the fluid is incompressible ($v_1 \approx v_0 = v$)

$$u_0 - u_1 = v(P_1 - P_0) \quad (9)$$

and because $P_1 - P_0 > 0$ we get

$$u_0 > u_1 \quad (10)$$

In other words, throttling of an incompressible fluid will result in an *increase* in the temperature.

Calculation of the Maximum Inversion Temperature

It is of interest so see how the maximum inversion temperature, $T_{\text{inv}}^{\text{max}}$, can be calculated from an equation of state. Because by definition it is fixed by the intersection of the inversion curve with the T axis, we need first the equation of the inversion curve. The equation of the inversion curve is $\mu = 0$, hence from equation 7

$$v = T \left(\frac{\delta v}{\delta T} \right)_p \quad (11)$$

Assuming that the behavior of the gas can be described by the pressure expansion of the virial equation of state [1],

$$z = 1 + \tilde{B}P + \tilde{C}P^2 + \tilde{D}P^3 + \dots \quad (12)$$

where z is the compressibility factor ($= Pv/RT$) and \tilde{B} , \tilde{C} , \tilde{D} , ... are coefficients that are functions of the temperature alone, we have

$$\left(\frac{\delta v}{\delta T} \right)_p = \frac{R}{P} + \frac{d\tilde{B}RT}{dT} + P \frac{d\tilde{C}RT}{dT} + \dots \quad (13)$$

Substituting equation 13 into equation 11 and passing to the limit $P = 0$, we find that $T_{\text{inv}}^{\text{max}}$ occurs when

$$\frac{\tilde{B}RT}{T} = \frac{d\tilde{B}RT}{dT} \quad (14)$$

Equation 14 can be written in a more compact form recalling that the coefficient \tilde{B} is related to the second virial coefficient B by the simple relation $B = \tilde{B}RT$ [1], so that

$$\frac{B}{T} = \frac{dB}{dT} \quad (15)$$

In other words, the maximum inversion temperature can be found by drawing the tangent from the origin to the curve that describes the variation of the second virial coefficient with temperature (Figure 3b). Miller [2] claims that the Joule–Thomson inversion curve can be described reasonably well by

a two-parameter (T_T , P_T) corresponding states correlation for all gases but H_2 and He. Several authors [3, 4] have studied the capability of the most common equations of state to predict the Joule–Thomson inversion curves; however, not many studies that estimate the Joule–Thomson coefficient itself have been made. Hirose et al. [5] have developed computer programs that manipulate the equations of state to develop practical formulas for the calculation of the coefficient. The calculation of the Joule–Thomson effect at very low pressures has been discussed by Rasiel and Freeman [6], who have shown that the coefficient of a real gas is generally nonzero in the limit of zero pressure.

The Isothermal Joule–Thomson Coefficient

The Joule–Thomson experiment can also be performed under isothermal conditions. In this case the *isothermal Joule–Thomson coefficient*, ϕ , is defined as

$$\phi = \left(\frac{\partial h}{\partial P} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_P \quad (16)$$

Both Joule–Thomson coefficients are related by the simple expression, $\mu = -\phi/C_p$. According to Francis and Luckhurst [7] the principle of corresponding states applies to the isothermal Joule–Thomson coefficient but does not apply to the isenthalpic Joule–Thomson coefficient.

The Joule–Thomson Coefficient for Gas Mixtures

All the relations we have developed thus far are general; they apply both to a pure gas *and* to a mixture of gases. Many papers report the Joule–Thomson effect of gas mixtures, but only a few have addressed the question of whether the effect for a mixture of gases is equal to or different from the molar-weighted mean of the effect for the pure components under the same conditions of pressure and temperature. Can the effect be larger (synergism) or smaller (depression) than this linear combination? For example, Ishkin and Rogovaya [8] measured the isothermal Joule–Thomson coefficient for mixtures of argon and nitrogen and found that it showed positive deviations from the linear additive effect above 0 °C and at low pressures and negative deviations for temperatures below 0 °C and high pressures. Koeppe [9, 10] measured the integral and differential Joule–Thomson effect for $N_2 + Ar$, $N_2 + O_2$, $O_2 + Ar$, $He + N_2$, $He + Ar$, and $N_2 + H_2$ mixtures at various temperatures and pressures and found that the integrated effect was larger or equal to the molar-weighted mean of the integrated effects of the constituents. Gunn et al. [11] determined the inversion curves for mixtures of methane and hydrogen and found that the inversion pressure at 214 K plotted against the mole fraction exhibited a maximum. They claimed that this phenomenon should be common to those binary mixtures whose pure-component critical temperatures are such that the pure-component reduced temperatures lie on different sides of the maximum of the generalized curve (expressed in terms of reduced variables). Sobanski and Kozak [12] studied the throttling behavior of mixtures of oxygen + helium, R-114 + ammonia, R-114 + sulfur dioxide, and R-170 + nitrogen, as a function of pressure and composition and detected the presence of extreme values of

the differential Joule–Thomson coefficient. For example, for a mixture of R-114 and NH_3 at 423 K, the differential Joule–Thomson coefficient showed a sharp maximum value at 4 MPa that decreased with pressure and disappeared above 10 MPa. The specific heat of the mixture followed a similar behavior with the maximum occurring at a higher composition than that for μ . Sobanski and Kozak [12] concluded that the specific heat of the mixture was the essential parameter that determined whether or not there would be an extreme value in the coefficient, and that the phenomena was characteristic of components with considerable difference in their critical parameters. Gustafsson [13] used the virial expression of the van der Waals equation of state to analyze the theoretical aspects of the problem and concluded that synergism is possible. He also discussed the criteria that must be satisfied by the constituent gases in order that the mixture has a synergistic effect. Wisniak and Abraham [14] analyzed the adiabatic Joule–Thomson effect in the low-pressure range where only the second virial coefficient is considered, and they concluded that none of the equations of state was capable of predicting an extremum.

Synergism in the Joule–Thomson Effect for Binary Gas Mixtures

In order to explore the possibility of a nonlinear effect we define a *deviation function*, δ , as follows [13].

$$\delta(P, T, y) = y_1 \Delta T_{H1}(T, P) + y_2 \Delta T_{H2}(T, P) - \Delta T_{H, \text{mix}}(T, P, y) \quad (17)$$

where ΔT_{H1} , ΔT_{H2} represent the integral Joule–Thomson effect for components 1 and 2, respectively, and $\Delta T_{H, \text{mix}}$ that of a mixture of mole fraction y_1 . From its definition it is seen that δ represents the deviation from the molar-weighted mean of the pure-component effects. For most pure gases the integral Joule–Thomson effect, $\Delta T_{H,i}$ is negative, hence a positive value of δ will indicate the presence of a synergistic effect.

The possibility of synergism will be analyzed by developing an expression for the deviation function, δ . Assuming the enthalpy to be a function of pressure and temperature, we can write

$$dh = c_p dT + \left(\frac{\partial h}{\partial P} \right)_T dP \quad (18)$$

Integrating from the upstream state (P_1 , T_1) to the downstream state (P_0 , T_0) and applying the condition, $\partial h = 0$, we get

$$\int_{T_1}^{T_0} c_p(y, P_0) dT + \int_{P_1}^{P_0} \phi(y, T) dP = 0 \quad (19)$$

In order to calculate the isothermal Joule–Thomson coefficient, ϕ , we will use the virial expansion as a pressure series

$$\frac{P_V}{RT} = \sum_{k=1}^{\infty} \tilde{B}_k P^{k-1} \quad (20)$$

Using equations 19 and 20 we get

$$\Delta T_H = -\frac{RT_1^2}{c_{P_0}} \sum_{k=2}^{\infty} \left(\frac{d\tilde{B}_k}{dT} \right) \frac{1}{k-1} (P_1^{k-1} - P_0^{k-1}) \quad (21)$$

where c_{P_0} is the heat capacity at the low pressure P_0 (assumed to be constant).

If we limit our analysis to the pressure range where the virial equation can be truncated after the second term and remember that $B = \tilde{B}RT$, we can transform equation 21 into the following expression.

$$\delta = (P_1 - P_0) \frac{y_1 y_2 T^2}{c_{P_{0m}}} \frac{d}{dt} \left[\frac{1}{T} \left(B_{11} \frac{c_{P_{02}}}{c_{P_{01}}} + B_{22} \frac{c_{P_{01}}}{c_{P_{02}}} - 2B_{12} \right) \right] \quad (22)$$

where $c_{P_{0m}}$ is the molar-weighted mean of the heat capacities of the pure components at the low downstream pressure. Equation 22 may be written in the more compact form

$$\delta = K (P_1 - P_0) \frac{y_1 y_2}{c_{P_{0m}}} \quad (23)$$

where

$$K = T^2 \frac{d}{dt} \left[\frac{1}{T} \left(B_{11} \frac{c_{P_{02}}}{c_{P_{01}}} + B_{22} \frac{c_{P_{01}}}{c_{P_{02}}} - 2B_{12} \right) \right] \quad (24)$$

is a function of the temperature only. For constant pressure and temperature, δ will have an extreme value for the following value of the composition, y_1^* :

$$y_1^* = \frac{-c_{P_{02}} \pm \sqrt{c_{P_{01}} c_{P_{02}}}}{c_{P_{01}} - c_{P_{02}}} = \frac{1}{1 + \sqrt{\frac{c_{P_{01}}}{c_{P_{02}}}}} y_1^* \quad (25)$$

δ will be a maximum if K in equation 24 is negative and a minimum if K is positive.

We will now develop a working expression for μ_0 , the Joule–Thomson coefficient at zero pressure. At sufficiently low pressures the virial equation becomes

$$\frac{P_V}{RT} = 1 + \tilde{B}P = 1 + \frac{BP}{RT} \quad (26)$$

Using this expression in equation 7 we get

$$\mu_0 = -\frac{1}{c_{P_0}} \left(B - T \frac{dB}{dT} \right) = \frac{T^2}{c_{P_0}} \frac{d(B/T)}{dT} \quad (27)$$

The second virial coefficient of a binary mixture is [15]

$$B = y_1^2 B_{11} + y_2^2 B_{22} + 2y_1 y_2 B_{12} \quad (28)$$

where B_{12} is the mixed coefficient. Equation 27 then becomes

$$\mu_0 = -\frac{1}{c_{P_{0m}}} (y_1^2 \phi_{0,11} + y_2^2 \phi_{0,22} + 2y_1 y_2 \phi_{0,12}) \quad (29)$$

where

$$\phi_{0,ij} = B_{ij} - T \frac{dB_{ij}}{dT} = -T^2 \frac{d(B_{ij}/T)}{dT} \quad (30)$$

is the limiting value of ϕ at zero pressure. μ_0 will have an extreme value when

$$y_1^* = \frac{\phi_{0,22} - \phi_{0,12}}{\phi_{0,11} + \phi_{0,22} - \phi_{0,12}} \quad (31)$$

Because $0 < y_1 < 1$, the extreme value will be a maximum if the following conditions (equations 32) are met.

$$\phi_{0,12} < \phi_{0,11} \text{ and } \phi_{0,12} < \phi_{0,22} \quad (32)$$

Equations 22 and 29 can easily be used to calculate the deviation function and the isenthalpic Joule–Thomson effect at zero pressure with common equations of state like those of van der Waals, Redlich–Kwong, Soave, and Peng–Robinson [16]. All these are cubic equations that have the following general structure

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + cv + d} \quad (33)$$

and can be expressed in virial form using the following relations for the second, third, and fourth virial coefficients [15].

$$B = b - \frac{a}{RT} \quad (34)$$

$$C = b^2 + \frac{ac}{RT} \quad (35)$$

$$D = b^3 + \frac{a(d-c^2)}{RT} \quad (36)$$

Most methods for treating thermodynamic properties of gas mixtures make the basic assumption that equations of state for mixtures have the same form as the equations that describe the component species. In this case the parameters of the equation are obtained by a combination of the constants of the components (mixing rule). The parameters are a function of the critical constants and the proper functionality is well reported in the literature [1, 15].

We will illustrate the calculation procedure in detail for the van der Waals equation [16]. The van der Waals equation can be written in the following virial form [15].

$$\frac{P_V}{RT} = 1 + \left(b - \frac{a}{RT} \right) \frac{1}{v} + \frac{b^2}{v^2} + \frac{b^3}{v^3} + \dots \quad (37)$$

Thus, the second virial coefficient is

$$B_{vW} = b - \frac{a}{RT} \quad (38)$$

Assuming that equation 38 describes B_{ii} and B_{ij} using the mixing rules suggested by van der Waals

$$a_{12} = \sqrt{a_{11}a_{22}} \quad (39)$$

equation 22 becomes

$$\delta_{vW} = (P_1 - P_0) \frac{y_1 y_2}{c_{P_{0m}}} \left\{ (c_{P_{02}} - c_{P_{01}}) \left(\frac{b_{22}}{c_{P_{02}}} - \frac{b_{11}}{c_{P_{01}}} \right) + \frac{2}{RT} \left[\left(a_{11} \frac{c_{P_{02}}}{c_{P_{01}}} \right)^{0.5} - \left(a_{22} \frac{c_{P_{01}}}{c_{P_{02}}} \right)^{0.5} \right]^2 \right\} \quad (40)$$

Equation 40 may be written in the same compact form as equation 22

$$\delta_{vW} = K_{vW} (P_1 - P_0) \frac{y_1 y_2}{c_{P_{0m}}} \quad (41)$$

where

$$K_{vW} = \left\{ (c_{P_{02}} - c_{P_{01}}) \left(\frac{b_{22}}{c_{P_{02}}} - \frac{b_{11}}{c_{P_{01}}} \right) + \frac{2}{RT} \left[\left(a_{11} \frac{c_{P_{02}}}{c_{P_{01}}} \right)^{0.5} - \left(a_{22} \frac{c_{P_{01}}}{c_{P_{02}}} \right)^{0.5} \right]^2 \right\} \quad (42)$$

Finally, using equations 29 and 30, we obtain the following expression for μ_0 , the zero-pressure Joule–Thomson coefficient.

$$\mu_{0,vW} = -\frac{1}{c_{P_{0m}}} \left[y_1 b_{11} + y_2 b_{22} - \frac{2}{RT} (y_1 \sqrt{a_{11}} + y_2 \sqrt{a_{22}})^2 \right] \quad (43)$$

$\mu_{0,vW}$ will have an extreme value for (equation 31)

$$y_{1,vW}^* = \frac{\frac{RT}{4} (b_{11} - b_{22}) - \sqrt{a_{22}} (\sqrt{a_{11}} - \sqrt{a_{22}})^2}{(\sqrt{a_{11}} - \sqrt{a_{22}})^2} \quad (44)$$

subject to the restriction $0 < y_1 < 1$.

Application of the above procedure to other cubic equations of state yields the interesting result that all expressions for δ have the compact form given by equations 22 and 41. The particular equation of state is identified by the pertinent expression for K as follows:

Redlich–Kwong.

$$K_{RK} = (c_{P_{02}} - c_{P_{01}}) \left(\frac{b_{22}}{c_{P_{02}}} - \frac{b_{11}}{c_{P_{01}}} \right) + \frac{2.5}{RT^{1.5}} \left[\left(a_{11} \frac{c_{P_{02}}}{c_{P_{01}}} \right)^{0.5} - \left(a_{22} \frac{c_{P_{01}}}{c_{P_{02}}} \right)^{0.5} \right]^2 \quad (45)$$

$$\mu_{0,RK} = -\frac{1}{c_{P_{0m}}} \left[y_1 b_{11} + y_2 b_{22} - \frac{2.5}{RT^{1.5}} (y_1 \sqrt{a_{11}} + y_2 \sqrt{a_{22}})^2 \right] \quad (46)$$

$$y_{1,RK}^* = \frac{\frac{RT^{1.5}}{5} (b_{11} - b_{22}) - \sqrt{a_{22}} (\sqrt{a_{11}} - \sqrt{a_{22}})}{(\sqrt{a_{11}} - \sqrt{a_{22}})^2} \quad (47)$$

Soave.

$$K_S = (c_{P_{02}} - c_{P_{01}}) \left(\frac{b_{22}}{c_{P_{02}}} - \frac{b_{11}}{c_{P_{01}}} \right) + \frac{2}{RT} \left(\sqrt{a_{11} \alpha_{11} \frac{c_{P_{02}}}{c_{P_{01}}}} - \sqrt{a_{22} \alpha_{22} \frac{c_{P_{01}}}{c_{P_{02}}}} \right)^2$$

$$\frac{1}{RT^{0.5}} \left(\sqrt{a_{11} \alpha_{11} \frac{c_{P_{02}}}{c_{P_{01}}}} - \sqrt{a_{22} \alpha_{22} \frac{c_{P_{01}}}{c_{P_{02}}}} \right)$$

$$\left(\frac{\beta_{11}}{\sqrt{T_{c1}}} \sqrt{a_{11} \alpha_{11} \frac{c_{P_{02}}}{c_{P_{01}}}} - \frac{\beta_{22}}{\sqrt{T_{c2}}} \sqrt{a_{22} \alpha_{22} \frac{c_{P_{01}}}{c_{P_{02}}}} \right) \quad (48)$$

where

$$\beta_S = 0.48508 + 1.55171 ar - 0.15613 ar^2 \quad (49)$$

$$(\mu_0)_S = -\frac{1}{c_{P_{0m}}} \left[(y_1 b_{11} + y_2 b_{22}) - \frac{2}{RT} (y_1 \sqrt{a_{11} \alpha_{11}} + y_2 \sqrt{a_{22} \alpha_{22}})^2 \right]$$

$$- \frac{1}{R \sqrt{T}} (y_1 \sqrt{a_{11} \alpha_{11}} + y_2 \sqrt{a_{22} \alpha_{22}}) \left(y_1 \beta_{11} \sqrt{\frac{a_{11}}{T_{c1}}} + y_2 \beta_{22} \sqrt{\frac{a_{22}}{T_{c2}}} \right) \quad (50)$$

Peng–Robinson. The second virial coefficient of the Peng–Robinson equation has the same structure as that of Soave

Table 2. Predicted Values of the Deviation Function, δ , at 300 K for a Pressure Drop of 0.202 MPa

Mixture	van der Waals	Redlich–Kwong	Soave	Peng–Robinson
nitrogen/oxygen	7.9×10^{-4}	-5.1×10^{-3}	-8.6×10^{-3}	-4.6×10^{-3}
argon/oxygen	-0.169	-0.158	-0.169	-0.210
nitrogen/carbon monoxide	-1.6×10^{-3}	-2.6×10^{-3}	-2.9×10^{-3}	-3.1×10^{-3}
carbon dioxide/ethylene	-0.106	-0.092	-0.042	-0.148
nitrogen/helium	-0.996	-1.034	-0.097	-0.402
methane/ethane	-0.273	-0.550	-0.609	-1.416
krypton/hydrogen	-0.941	-1.142	-1.139	-1.378

equation, except that the expression for β (see equation 49) is as follows.

$$\beta_{PR} = 0.37464 + 1.54226 ar - 0.26992 ar^2 \quad (51)$$

As previously stated, the δ expression for all four equations of state has the structure given by equation 41; thus, all of the equations predict the same composition at which an extreme value of δ may occur. The nature of the extreme value (maximum or minimum) will be a function of the intensity of K and hence of the nature of the equation of state. Defining $F(y)$ as

$$F(y) = \frac{y_1 y_2}{y_1 c_{R_1} + y_2 c_{R_2}} \quad (52)$$

we obtain the value for the function at the extreme point

$$F(y)^* = \frac{1}{\sqrt{c_{R_1}} + \sqrt{c_{R_2}}} \quad (53)$$

the function $F(y)$ will be nil at $y = 0$ and $y = 1$.

The values of δ_{\max} predicted by the four equations of state have been calculated for some typical binary mixtures and the results given in Table 2. It can be seen that, within the pressure range considered, all four equations of state predict that synergism will be present in mixtures of nitrogen and methane, although the effect is very small. None of the equations of state is capable of predicting an extreme value for the zero-pressure differential Joule–Thomson coefficient; in every case the calculated value of y_1^* falls outside the range 0–1.

Conclusion

When a gas flows through a restriction (throttling process), its pressure will always decrease but its temperature may increase or decrease. This phenomenon, called the Joule–Thomson effect, has important industrial applications in the areas of refrigeration, gas liquefaction, and cryogenics. The properties of the Joule–Thomson coefficient were discussed in general for pure gases, and the possibility of a nonlinear effect in binary mixtures was analyzed using the First Law of Thermodynamics and some common cubic equations of state. It was shown that, although theoretically a binary mixture of gases may exhibit a Joule–Thomson effect different from the molar-weighted mean of the pure-component effects, the possibility of observing a positive difference is very low.

Nomenclature

a	constant in an equation of state
b	constant in an equation of state
B	second virial coefficient, volume series
\tilde{B}	second virial coefficient, pressure series
c_p	specific heat at constant pressure
F	function of composition, equation 52
H	enthalpy
h	specific enthalpy
P	pressure
R	universal gas constant
T	absolute temperature
T_C	critical temperature
T_r	reduced temperature, T/T_C
ΔT_H	integrated isenthalpic Joule–Thomson coefficient, equation 17
V	volume
v	specific volume
y	molar composition of gas
y_1^*	molar composition of gas at maximum value
α	function in the Soave and Peng–Robinson equations
β	function defined by equations 49 and 51
δ	deviation function, equation 17
μ	isenthalpic Joule–Thomson coefficient, equation 4
ϕ	isothermal Joule–Thomson coefficient, equation 16
ω	acentric factor

References and Notes

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