On the Joule-Thomson coefficient for gas mixtures

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

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The possibility of synergism in the Joule-Thomson effect for gaseous mixtures has been analyzed using the Van der Waals, Redich-Kwong, Soave and Peng-Robinson equations of state, in the low pressure range where the behaviour of the mixture can be described by the virial equation of state truncated after the second term. It is shown that synergism is possible and that in this low pressure range none of the equations is capable of predicting an extreme value for the differential isenthalpic Joule-Thomson effect.

Flow of a fluid through an adiabatic porous plug test is rather severe because the derivatives of the pressure are involved.

The Joule-Thomson experiment can also be performed under isothermal conditions, the isothermal coefficient \( \phi \) is defined as

\[
\phi = \left( \frac{\partial H}{\partial P} \right)_T = v - T \left( \frac{\partial v}{\partial T} \right)_P
\]

Both coefficients are related by the simple expression \( \mu = -\phi / C_p \). The principle of corresponding states applies to the isothermal Joule-Thomson coefficient but does not apply to the isenthalpic Joule-Thomson coefficient. Miller claims that the Joule-Thomson inversion, curve can be described reasonably well by a two-parameter \((T_*, P_*)\) corresponding states correlation for all gases, but \( H_2 \) and \( He \). Several authors have studied the capability of the most common equations of state to predict the Joule-Thomson inversion curves. However, not many studies which estimate the Joule-Thomson coefficient itself have been made. Hirose et al. have developed computer programs that manipulate the equations of state to develop practical formulas for the calculation of the coefficient.

Many papers report the Joule-Thomson effect of gas mixtures but only a few have addressed the possibility of a synergistic effect: Can the isenthalpic Joule-Thomson effect of a mixture be larger than that for its constituents? Ishkin and Rogovaya measured the isothermal Joule-Thomson coefficient for mixtures of argon and nitrogen and found that it showed positive deviations from the linear additive effect at above \( 0^\circ C \) and low pres-
sures, and negative deviations for temperatures below 0°C and high pressures. Koeppen\textsuperscript{7,8} 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 \textit{et al.}\textsuperscript{9} 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 phenomena 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. The sharpness of the maximum is more pronounced at the lowest reduced temperatures where Joule-Thomson cooling is most effective and which corresponds to the region of greatest industrial importance. Sobanski and Kozak\textsuperscript{10} studied mixtures of oxygen-helium, R-114-ammonia, R-114-sulphur 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 which decreased with pressure and disappeared above 10 MPa. The specific heat of the mixture followed a similar behaviour with the maximum occurring at a higher composition than that for \(\mu\). Sobanski and Kozak\textsuperscript{10} 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\textsuperscript{11} analyzed 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 have a synergistic effect. The criteria developed by Gustafsson are based on the virial expression of Van der Waals equation of state.

It is the purpose of this work to extend the analysis of Gustafsson to modern equations of state and determine the conditions for synergism.

\textbf{Theory}

We will follow the general procedure developed by Gustafsson\textsuperscript{11}.

Assuming the enthalpy to be a function of pressure and temperature we can write

\[
dH = C_p dT + \left( \frac{\partial H}{\partial P} \right)_T dP
\]

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

\[
\int_{P_1}^{P_0} C_p(y, P_0) dT + \int_{T_1}^{T_0} \phi(y, T) dP = 0
\]

In order to calculate \(\phi\) we use the virial expansion as a pressure series

\[
\frac{P_V}{RT} = \sum_{k=1}^{\infty} B_k P^{k-1}
\]

Defining the integrated isenthalpic Joule-Thomson effect \(\Delta T_H\) as

\[
\Delta T_H = T_0 - T_1
\]

and using Eqs (5) and (6) we get

\[
\Delta T_H = \frac{RT}{C_{p_m}} \sum_{k=2}^{\infty} \frac{1}{k-1} \left( \frac{B_k}{C_{p_m}} \right) \left( P_{k-1}^m - P_0^{k-1} \right)
\]

where \(C_{p_m}\) is the heat capacity at low pressure \(P_0\).

We now define the deviation function \(\delta(P,T,y)\) as

\[
\delta(P,T,y) = \gamma_1 \Delta T_{H_1}(T,P_1) + \gamma_2 \Delta T_{H_2}(T,P_0)
\]

where \(\Delta T_{H_1}(T,P_1)\) and \(\Delta T_{H_2}(T,P_0)\) now represent the integrated isenthalpic Joule-Thomson effect for a binary mixture with composition \(y\). It is clear that \(\delta(P,T,y)\) represents the deviation from the molar weighted mean of the pure-component effects. A negative value of \(\delta\) will signal the presence of a synergistic effect.

If we limit our analysis to the pressure range where the virial equation can be truncated after the second term, and that the second virial coefficient \(B\) is related to \(B'\) by \(B = B'RT\), we can transform Eq. (9) into the following expression

\[
\delta = \left( P - P_0 \right) \frac{\gamma_1 \gamma_2 T^2}{C_{p_m}}
\]

\[
\times \frac{d}{dT} \left[ \frac{1}{T} \left( \frac{B_{11}}{C_{p_{11}}} \frac{C_{p_{11}}}{C_{p_{m1}}} + \frac{B_{22}}{C_{p_{22}}} \frac{C_{p_{22}}}{C_{p_m}} - 2B_{12} \right) \right]
\]

where \(C_{p_m}\) is the molar weighted mean of the heat capacities of the pure components at the low downstream pressure. Eq. (10) may be written
\[ \delta = K \left( P_1 - P_0 \right) \frac{y_1 y_2}{C_{P_m}} \]  

... (11)

where

\[ K = T^2 \frac{d}{dT} \left[ \frac{1}{T} \left( B_{11} \frac{C_{P_{11}}}{C_{P_m}} + B_{22} \frac{C_{P_{22}}}{C_{P_m}} - 2B_{12} \right) \right] \]  

... (12)

is a function of the temperature only.

For constant pressure and temperature \( \delta \) will have an extreme value for the following value of the composition \( (y_1^*) \):

\[ y_1^* = \frac{-C_{P_{11}} \pm \sqrt{C_{P_{11}} C_{P_{22}}}}{C_{P_{11}} - C_{P_{22}}} \frac{1}{1 + \sqrt{C_{P_{11}}}} \]  

... (13)

\( \delta \) will be maximum if \( K \) in Eq. (12) is negative and minimum if \( K \) is positive.

We will now develop a working expression for \( \mu_0 \), the Joule-Thomson coefficient at zero pressure. At sufficiently low pressures the virial equation becomes

\[ \frac{P v}{RT} = 1 + B \frac{P}{RT} = 1 + \frac{BP}{RT} \]  

... (14)

Using this expression in Eq. (2) we get

\[ \mu_0 = -\frac{1}{C_{P_m}} \left( B - T \frac{d B}{dT} \right) \frac{T^2 d(B/T)}{C_{P_m} d T} \]  

... (15)

For a binary mixture we have

\[ B = y_1^2 B_{11} + y_2^2 B_{22} + 2 y_1 y_2 B_{12} \]  

... (16)

so that Eq. (15) becomes

\[ \mu_0 = -\frac{1}{C_{P_m}} \left( y_1^2 \phi_{011} + y_2^2 \phi_{022} + 2 y_1 y_2 \phi_{012} \right) \]  

... (17)

where

\[ \phi_{0i} = B_{ij} - T \frac{d B_{ij}}{dT} = -T^2 \frac{d(B_{ij}/T)}{dT} \]  

... (18)

is the limiting value of \( \phi \) at zero pressure. \( \mu_0 \) will have an extreme value when

\[ y_1^* = \frac{\phi_{022} - \phi_{012}}{\phi_{011} + \phi_{022} - 2\phi_{022}} \]  

... (19)

Since \( 0 < y_1 < 1 \) the extreme value will be a maximum if the following conditions are met

\[ \phi_{012} < \phi_{022} \]  

... (20)

\[ \phi_{011} \]

Results

Eqs (10) and (17) will be used to calculate the deviation function and the isenthalpic Joule-Thomson effect at zero pressure, using the Van der Waals, Redlich-Kwong, Soave and Peng-Robinson equations of state. All these equations have the following general structure

\[ P = \frac{RT}{v - b} - \frac{a}{v^2 + cv + d} \]  

... (21)

and can be expressed in virial coefficients

\[ B = b - \frac{a}{RT} \]

\[ C = b^2 + \frac{ac}{RT} \]  

... (22)

\[ D = b^3 + \frac{a(d - c^2)}{RT} \]

Most methods for treating thermodynamic properties of gas mixtures make the basic assumption that the equation of state for mixtures has the same form as the equations that describe the component species. Constants for mixture relations are obtained by a combination of the constants of the components.

Van der Waals

The Van der Waals equation can be written in the following virial form

\[ \frac{P v}{RT} = 1 + \left( b - \frac{a}{RT} \right) \frac{1}{v} + \frac{b^2}{v^2} + \frac{b^2}{v^3} + ... \]  

... (23)

It is clear that the second virial coefficient is

\[ B_{vw} = b - \frac{a}{RT} \]  

... (24)

Assuming that Eq (24) describes \( B_{ii} \) and \( B_{ij} \) and the following mixing rules

\[ a_{12} = \sqrt{a_{11} a_{22}} \]  

... (25)

\[ b_{12} = 0.5(b_{11} + b_{22}) \]  

... (26)

Eq. (10) becomes
\[ \delta_{vw} = (P_1 - P_0) \frac{y_1 y_2}{C_{pm}} \left( (C_{Pm} - C_{Pn}) \left( \frac{b_{22} - b_{11}}{C_{Pm}} - \frac{b_{11}}{C_{Pn}} \right) \right) \]
\[ + \frac{2}{RT} \left[ \left( a_{11} \frac{C_{Pn}}{C_{Pm}} \right)^{0.5} - \left( a_{22} \frac{C_{Pn}}{C_{Pm}} \right)^{0.5} \right]^2 \] ... (27)
\[ \delta_{RK} = (P_1 - P_0) \frac{y_1 y_2}{C_{pm}} \left( (C_{Pm} - C_{Pn}) \left( \frac{b_{22} - b_{11}}{C_{Pm}} \right) \right) \]
\[ + \frac{2.5}{RT^{1.5}} \left[ \left( a_{11} \frac{C_{Pn}}{C_{Pm}} \right)^{0.5} - \left( a_{22} \frac{C_{Pn}}{C_{Pm}} \right)^{0.5} \right]^2 \] ... (34)

\[ \delta_{vw} = K_{vw}(P_1 - P_0) \frac{y_1 y_2}{C_{pm}} \] ... (28)

where

\[ K_{vw} = \left( (C_{Pm} - C_{Pn}) \left( \frac{b_{22} - b_{11}}{C_{Pm}} \right) \right) \]
\[ + \frac{2}{RT} \left[ \left( a_{11} \frac{C_{Pn}}{C_{Pm}} \right)^{0.5} - \left( a_{22} \frac{C_{Pn}}{C_{Pm}} \right)^{0.5} \right]^2 \] ... (29)

Using Eqs (17) and (18) we obtain for \( \mu_0 \), the zero-pressure Joule-Thomson coefficient

\[ \langle \mu_0 \rangle_{vw} = -\frac{1}{C_{Pm}} \left[ y_1 b_{11} + y_2 b_{22} \right] \]
\[ - \frac{2}{RT} \left( y_1 \sqrt{a_{11}} + y_2 \sqrt{a_{22}} \right)^2 \] ... (30)

\( \langle \mu_0 \rangle_{vw} \) will have an extreme value for [Eq. (19)]

\[ y_1^* = \frac{\frac{RT}{4} \left( b_{11} - b_{22} \right) - \sqrt{a_{22} (\sqrt{a_{11}} - \sqrt{a_{22}})}}{(\sqrt{a_{11}} - \sqrt{a_{22}})^2} \] ... (31)

subject to the restriction \( 0 < y_1^* < 0 \).

**Redlich-Kwong**

The Redlich-Kwong equation of state is

\[ P = \frac{RT}{v - b} - \frac{a}{T^{0.5}} \left( \frac{1}{v + b} \right) \] ... (32)

so that according to Eq. (20)

\[ B_{RK} = b - \frac{a}{RT^{0.5}} \] ... (33)

Assuming the same mixing rules as for the Van der Waals equation [Eqs (25) and (26)] and substituting in Eq. (10) we get

\[ \langle \mu_0 \rangle_{RK} = -\frac{1}{C_{Pm}} \left[ y_1 b_{11} + y_2 b_{22} \right] \]
\[ - \frac{2.5}{RT^{1.5}} \left( y_1 \sqrt{a_{11}} + y_2 \sqrt{a_{22}} \right)^2 \] ... (37)

\( \langle \mu_0 \rangle_{RK} \) will have an extreme value for [Eq. (19)]

\[ y_1^* = \frac{\frac{RT^{1.5}}{5} \left( b_{11} - b_{22} \right) - \sqrt{a_{22} (\sqrt{a_{11}} - \sqrt{a_{22}})}}{(\sqrt{a_{11}} - \sqrt{a_{22}})^2} \] ... (38)

subject to the restriction \( 0 < y_1^* < 0 \).

**Soave**

The Soave equation of state is

\[ P = \frac{RT}{v - b} - \frac{a a}{v (v + b)} \] ... (39)

where \( a \) is the following function of the acentric factor \( \omega \) and the reduced temperature \( T_r \):

\[ a = [1 + (0.48508 + 1.55171 \omega - 0.15613 \omega^2) \times (1 - T_r^{0.5})^2] \] ... (40)

\[ a = [1 + \beta (1 - T_r^{0.5})^2] \] ... (41)
The mixing rules are
\[ a = \Sigma y_i y_j (a a)_{ij} \]  \[ b = \Sigma y_i b_i \]  
... (42)  
\[ b = \frac{a a}{RT} \]  
... (43)  

The second virial coefficient is
\[ B_s = b - \frac{a a}{RT} \]  
... (44)  

Replacing in Eq. (10) we get
\[ \delta = (P_1 - P_0) \frac{y_1 y_2}{C_{p_m}} \left[ (C_{p_0} - C_{p_0}) \left( \frac{b_{22}}{C_{p_{02}}} - \frac{b_{21}}{C_{p_{01}}} \right) \right. \]
\[ + \frac{2}{RT} \left( \sqrt{a_{11} a_{11}} \frac{C_{p_{01}}}{C_{p_{11}}} - \sqrt{a_{22} a_{22}} \frac{C_{p_{02}}}{C_{p_{22}}} \right)^2 \]
\[ + \frac{1}{RT^{0.5}} \left( \sqrt{a_{11} a_{11}} \frac{C_{p_{01}}}{C_{p_{11}}} - \sqrt{a_{22} a_{22}} \frac{C_{p_{02}}}{C_{p_{22}}} \right)^{0.5} \]
\[ \times \left( \frac{\beta_{11}}{T_{c_1}} - \frac{\beta_{22}}{T_{c_2}} \right) \left( \sqrt{a_{11} a_{11}} \frac{C_{p_{01}}}{C_{p_{11}}} - \sqrt{a_{22} a_{22}} \frac{C_{p_{02}}}{C_{p_{22}}} \right) \]  
... (45)  

\[ \delta_s = K_s (P_1 - P_0) \frac{y_1 y_2}{C_{p_m}} \]  
... (46)  

The Peng-Robinson equation of state is
\[ P = \frac{RT}{v - b} - \frac{a a}{v^2 + b v - b^2} \]  
... (48)  

where \( \alpha \) is the following function of the acentric factor \( \omega \) and the reduced temperature \( T_r \)
\[ \alpha = [1 + (0.37464 + 1.54226 \omega - 0.26992 \omega^2) \times (1 - T_r^{0.5})^2] \]  
... (49)  

\[ \alpha = [1 + \beta (1 - T_r^{0.5})^2] \]  
... (50)  

with the same mixing rules as the Soave equation [Eqs (42) and (43)]  

The second virial coefficient is
\[ B_{PR} = b - \frac{a a}{RT} \]  
... (51)  

Since \( B_{PR} \) has the same structure as \( B_s \), the equation for \( \delta_{PR} \) will be the same as for that \( \delta_s \), except that the expression for \( \beta \) will be different
\[ \beta_{11} = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \]  
... (52)  

and
\[ \delta_{PR} = K_{PR} (P_1 - P_0) \frac{y_1 y_2}{C_{p_m}} \]  
... (53)  

Inspection of the \( \delta \) expressions for the four equations of state indicates that they have the same basic structure
\[ \delta = \frac{K (P_1 - P_0) y_1 y_2}{C_{p_m}} \]  
... (40)  

and thus they all predict the same composition at which at extreme value of \( \delta \) may occur. The nature of the extreme value (maximum/minimum) will be a function of the intensity of \( K \), and, hence, of the nature of the equation of state.
Table 1—Predicted values of the maximum integral isenthalpic Joule-Thomson effect, assuming $P_1 - P_0 = 10$ bar

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$T, K$</th>
<th>$y_1^* [\text{Eq. (13)}]$</th>
<th>$\text{VW}$</th>
<th>$\text{RK}$</th>
<th>$\text{S}$</th>
<th>$\text{PR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen-methane</td>
<td>300</td>
<td>0.542</td>
<td>-0.0167</td>
<td>-0.0150</td>
<td>-0.0188</td>
<td>-0.0175</td>
</tr>
<tr>
<td>Nitrogen-water</td>
<td>300</td>
<td>0.520</td>
<td>0.497</td>
<td>2.06</td>
<td>2.737</td>
<td>2.50</td>
</tr>
<tr>
<td>Nitrogen-argon</td>
<td>300</td>
<td>0.458</td>
<td>0.106</td>
<td>0.125</td>
<td>0.144</td>
<td>0.151</td>
</tr>
<tr>
<td>Oxygen-argon</td>
<td>300</td>
<td>0.457</td>
<td>0.0876</td>
<td>0.0833</td>
<td>0.0891</td>
<td>0.104</td>
</tr>
<tr>
<td>Carbon dioxide-ethane</td>
<td>300</td>
<td>0.558</td>
<td>0.105</td>
<td>0.136</td>
<td>0.193</td>
<td>0.198</td>
</tr>
<tr>
<td>Nitrous oxide-ethylene</td>
<td>273</td>
<td>0.510</td>
<td>0.0055</td>
<td>0.0040</td>
<td>0.0067</td>
<td>0.0057</td>
</tr>
<tr>
<td>R-114-ammonia</td>
<td>423</td>
<td>0.345</td>
<td>0.531</td>
<td>0.642</td>
<td>0.727</td>
<td>0.749</td>
</tr>
</tbody>
</table>

$\text{VW} = \text{Van der Waals}, \text{RK} = \text{Redlich-Kwong}, \text{S} = \text{Soave}, \text{PR} = \text{Peng-Robinson}$

Defining $F(y)$ as

$$F(y) = \frac{y_1 y_2}{y_1 C_{P_1} + y_2 C_{P_2}}$$  \hspace{1cm} \text{(54)}

we get that the value of the function at the extreme point is

$$F(y)^* = \frac{1}{(\sqrt{C_{P_1}} + \sqrt{C_{P_2}})^2}$$  \hspace{1cm} \text{(55)}

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

We have proceeded to calculate the values of $y_1^*$, $\delta$, and $\mu_0$ predicted by the four equations of state for some typical binary mixtures. The results are given in Table 1, physical properties were taken from Reid et al\textsuperscript{12} and the critical constants were calculated applying the condition for the critical point. It is seen that within the pressure range considered, all four equations 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.

Nomenclature

$a, b = \text{constants in equation of state}$

$B = \text{second virial coefficient, volume series}$

$B' = \text{second virial coefficient, pressure series}$

$C_p = \text{specific heat at constant pressure}$

$F = \text{function of composition, Eq. (52)}$

$H = \text{enthalpy}$

$P = \text{pressure}$

$R = \text{universal gas constant}$

$T = \text{absolute temperature}$

$T_c = \text{critical temperature}$

$T_r = \text{reduced temperature, } T/T_c$

$\Delta T_0 = \text{integrated isenthalpic Joule-Thomson coefficient, Eq. (7)}$

$\nu = \text{volume}$

$\gamma = \text{composition}$

$\gamma^* = \text{composition at maximum value}$

Greek letters

$\alpha = \text{function in the Soave and Peng-Robinson equations}$

$\beta = \text{function defined by Eqs (41) and (49)}$

$\delta = \text{deviation function, Eq. (9)}$

$\mu = \text{isenthalpic Joule-Thomson coefficient, Eq. (2)}$

$\phi = \text{isothermal Joule-Thomson coefficient, Eq. (3)}$

$\omega = \text{acentric factor}$

References