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JOULE-THOMSON COEFFICIENT PREDICTION BY USING CUBIC PLUS ASSOCIATION (CPA) EQUATION OF STATE

Erich T. Tiuman

Matheus V. Rocha Pereira

Moisés A. Marcelino Neto

Dalton Bertoldi

Rigoberto E. M. Morales

Multiphase Flow Research Center (NUEM), Postgraduate Program in Mechanical and Materials Engineering (PPGEM), Federal University of Technology – Paraná (UTFPR) – Av. Sete de Setembro, 3165 - Rebouças CEP 80230-901 - Curitiba - PR – Brasil
erich_tiuman@hotmail.com; matheusv_rp@hotmail.com; mneto@utfpr.edu.br; daltonbertoldi@utfpr.edu.br; rmorales@utfpr.edu.br

Abstract. *The Joule Thomson effect happens when a fluid pass through any kind of restriction such as a nozzle or an expansion valve with enough speed so the process of expansion may occur without significant change of enthalpy. When it occurs the temperature will either fall or rise with the pressure drop. The proportion between the pressure drop and the change of temperature is given by the coefficient of Joule-Thomson, this coefficient depends on physical factors as initial temperature, initial pressure and fluid phase and also depends on chemical factors for example the composition of the fluid. Due its dependence on many factors the prediction of the coefficient of Joule-Thomson represents a challenge from the point of view of thermodynamics, but because of the wide application of this effect in chemical and petrochemical industries some methodologies have been developed in order to predict this coefficient. This work aims to evaluate the use of a cubic equation of state plus association factor (CPA) in a procedure to calculate the Joule-Thomson coefficient for simple associative and not associative substances (propane, water, hydrogen sulfide and carbon dioxide.). The results acquired were compared with both experimental and correlated data. It was found the CPA is able to deliver satisfactory results for practical applications in the industry.*

Keywords: *Joule-Thomson coefficient, equation of state, associative substance*

1. INTRODUCTION

If there is a drop of pressure during a constant enthalpy process when a fluid is passing through a throttling process the temperature will also change, this effect is known as the Joule-Thomson effect (Maric, 2005). The property that establishes the proportion between the pressure drop and the temperature change is the Joule-Thomson coefficient (Moran, 2013). There are some cases when a drop in the pressure can even produce a rise in the temperature of the fluid, in this case the Joule Thomson coefficient is negative (Adamson, 1973). The Joule Thomson coefficient is defined as

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_h \quad (1)$$

That is the variation of temperature due a change in the pressure keeping enthalpy constant. The Joule-Thomson coefficient is represented by μ_{JT} , and the thermodynamic variables of temperature and pressure are represented by T and p respectively. Due the fact this coefficient only depends on thermodynamic proprieties, beyond the fluid composition, it can be considered a thermodynamic propriety (Moran, 2013).

The throttling process could be caused by many pipe fittings such as an orifice (Maric, 2005), nozzles, throttling valves (Wang, 2017) and even porous bodies (Moran, 2013).

This propriety is very important for many industries like the cryogenic industry (Wisniak, 1993). It is very important also in the oil and gas industry since many oil proprieties are closely related to the temperature, so that the Joule-Thomson phenomenon could cause several collateral effects in the production equipment's compromising even its security (Regueira, 2017).

Because of its importance, many methodologies have been developed along the years in order to predict the Joule-Thomson coefficient. Most of them use an equation of state (EoS) to determinate the inversion curve (Rocha, 2016), that

is the curve that unites the points (defined by temperature and pressure) where the Joule-Thomson coefficient is zero. This curve divides the region where a drop of pressure causes a temperature increase or decrease (Nichita, 2006).

One of the main issues about prediction of Joule-Thomson coefficient is the strong sensibility it has related to the initial proprieties of temperature, pressure and chemical composition. This sensibility is so strong that the calculation of this coefficient is sometimes used to evaluate some equations of state (Randeiman, 1988). It also makes harder to use experimental measurements in order to supply the industry demand, particularly because many of the extreme conditions in the oil wells (Wang, 2017).

Rocha *et al.* (2016) described a procedure based on the Soave-Redlich-Kwong equation of state (SRK). The results presented were satisfactory for pure gases and mixtures of not associative components. For associative components and their mixtures is necessary the use of a more complex EoS such as the CPA (Cubic Plus Association). The possibility of predict mixtures of associative and not associative substances allows the study of systems more similar to the ones found in the oil and gas industry.

The purpose of this work is to present a methodology of calculation for the Joule-Thomson coefficient that uses the Cubic Plus Association EoS in order to complement the work developed by Rocha *et al.* (2016). This work also intends to compare the results for SRK and CPA EoS for not associative gases. The presented method will be applied for simple associative and not associative substances (propane, water, etc.).

2. METHODOLOGY

The following procedure was used in order to predict the Joule-Thomson coefficient with an algorithm implemented in a Matlab code. This code uses the CPA EoS to calculate most of the intermediary proprieties required. The first section will present the model for Joule-Thomson coefficient as well as its derivation. The second section will describe the EoS used.

2.1 Thermodynamic relations

As explained by Maric (2005), Eq. (1) can be rewrite in order to create a better expression to calculate the coefficient. Starting with the fundamental relation

$$dh = Tds + vdp \quad (2)$$

where h express specific enthalpy, s specific entropy and v specific molar volume. Dividing this equation by and differential of pressure keeping the temperature constant the expression become

$$\left(\frac{\partial h}{\partial p}\right)_T = -T \left(\frac{\partial s}{\partial p}\right)_T + v \quad (3)$$

Using the Maxwell relations:

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad (4)$$

Appling Eq. (4) in Eq. (3):

$$\left(\frac{\partial h}{\partial p}\right)_T = -T \left(\frac{\partial v}{\partial T}\right)_p + v \quad (5)$$

Expressing the total diffential enthalpy

$$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp \quad (6)$$

By definition $\left(\frac{\partial h}{\partial T}\right)_p$ is the heat capacity at constant pressure, therefor c_p . Appling Eq. (5) in Eq. (6)

$$dh = c_p dT + \left[-T \left(\frac{\partial v}{\partial T}\right)_p + v\right] dp \quad (7)$$

Assuming an isenthalpic process, that is $dh = 0$, and dividing the equation by an differential of pressure, Eq. (7) can be rewrite as:

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_h = \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] \quad (8)$$

With Eq. (8) is possible to calculate the Joule-Thomson coefficient for a given temperature, pressure and fluid composition. The other values are taken from the EoS or from a commercial software.

2.2 Cubic Plus Association EoS

The CPA EoS uses a cubic equation of state similar to the Soave-Redlich-Kwong plus an associative term similar to the association term of the Statistical Associating Fluid Theory (SAFT). The following equations were taken from Kontogeorgis and Folas (2010).

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} - \frac{1}{2} \frac{RT}{v} \left(1 + \frac{-v^2}{g} \frac{\partial g}{\partial v} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (9)$$

Equation (9) is the main form of CPA EoS, where R is the universal constant of gases, x_i is the molar fraction of the component i and b , $a(T)$, g and X_{A_i} are CPA constants presented below. The molecular volume is obtained applying the Newton method.

The following equations refer to the constants of CPA:

$$b = \sum_{i=1}^n x_i b_i \quad (10)$$

where b_i is a constant taken from Kontogeorgis and Folas (2010) or correlated papers.

$$a(T) = \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - k_{ij}) \sqrt{(a_{0i} \alpha_i)(a_{0j} \alpha_j)} \quad \alpha_i = [1 + c_{1i}(1 - \sqrt{T_{r,i}})]^2 \quad (11)$$

where k_{ij} is the interaction constant, $T_{r,i}$ is the reduced temperature of the component and a_{0i} and c_{1i} are constants also taken from Kontogeorgis and Folas (2010) or correlated papers.

$$g = \frac{1}{1-1.9\eta} \quad \eta = \frac{b}{4v} \quad (12)$$

The variable X_{A_i} refers to the associating sites of the substances involved, as a result for any substance or mixture a deep analyses of the associating sites is necessary. The sub index A represents the association site whereas i represent the substance it belongs. As a general rule X_{A_i} is given by:

$$X_{A_i} = \frac{1}{1 + \frac{1}{v} \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad \Delta^{A_i B_j} = g \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad b_{ij} = \frac{1}{2}(b_i + b_j) \quad (13)$$

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are constants also taken from Kontogeorgis and Folas (2010) or correlated papers. When this equation is applied for each of the association sites in the substance or mixture it creates a nonlinear equation system that needs to be solved separately before applying in the main CPA equation.

The derivate of molecular volume in relation to the temperature at constant pressure is obtained by a second order approximation as follows:

$$\frac{\partial v}{\partial T} = \frac{v(T+\Delta T) - v(T-\Delta T)}{2\Delta T} \quad (14)$$

The heat capacities were calculated using FORTRAN subroutines of the commercial software REFPROP (NIST, 2002) for each component. Table (1) shows the CPA constants used.

Table 1. CPA constants

	a_0 [Pa m ⁶ mol ⁻²]	b [m ³ mol ⁻¹]	c_1	$\varepsilon^{A_i B_j}$ [Pa m ³ mol ⁻¹]	$\beta^{A_i B_j}$
Water ⁽¹⁾	0.12277	1.45 x 10 ⁻⁵	0.67359	16655.0	0.0692
Propane ⁽¹⁾	0.91187	5.78 x 10 ⁻⁵	0.63070	0	0
Hydrogen sulfide ⁽²⁾	0.44505	2.72 x 10 ⁻⁵	0.60265	8327.5	0.0655
Carbon dioxide ⁽³⁾	0.37050	2.99 x 10 ⁻⁵	0.82470	0	0

⁽¹⁾ Kontogeorgis and Folas (2010)

⁽²⁾ Nezhad (2013)

⁽³⁾ Classic parameters for CO₂ described below

As previously explained, the CPA EoS have part of its terms similar to the SRK EoS therefore the constants for some substances, which the constants are not mentioned in Kontogeorgis and Folas (2010), were calculated using the classical parameters for SRK, as follows:

$$a_{0i} = 0.42747 \frac{(RT_{c,i})^2}{P_{c,i}} \quad (15)$$

where $T_{c,i}$ and $P_{c,i}$ are respectively the critical temperature and critical pressure of the component i .

$$b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \quad (16)$$

And:

$$c_{1i} = 0.48 + 1.547\omega_i - 0.17\omega_i^2 \quad (17)$$

where ω_i is the acentric factor.

3. RESULTS AND DISCUSSIONS

CPA is a great EoS for prediction of phase equilibria and other thermodynamic properties in a lot of applications related to gas and oil industry.

The Joule-Thomson coefficient for pure components, i.e. H₂S, H₂O, CO₂ and C₃H₈ were calculated using the Cubic Plus Association EoS and it was compared with commercial software data. The average absolute deviation (AAD) was used to evaluate this comparison:

$$AAD = \frac{1}{n} \sum_{i=1}^n \left| \frac{\mu_{JT,i,cal} - \mu_{JT,i,sof}}{\mu_{JT,i,sof}} \right| \quad (18)$$

where n is the number of points used and the subscripts *cal* and *sof* refer to calculated points or commercial software points, respectively.

Figure (1) shows the comparison between predicted Joule-Thomson and commercial software data for C₃H₈. It can be seen that there is a good agreement between these two data by the AAD obtained of 7.9183%. The points of greater error occur in the liquid phase, where other bounding forces have stronger influence on the fluid.

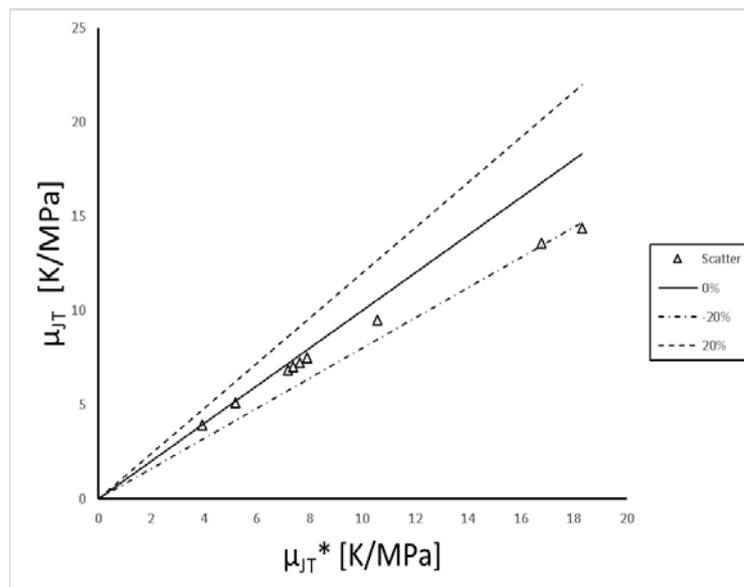


Figure1 - Comparison between obtained data from CPA and commercial software data REFPROP for C₃H₈.

In Figure (2) there is a comparison between commercial software data and the Joule-Thomson coefficient for H₂O. It also shows a good agreement by the AAD obtained of 8.7016%. Water is an associative fluid which could not be calculated by a simple cubic EoS. The CPA was capable of predict with good precision the value for the Joule-Thomson coefficient for this fluid, supporting the advantages of applying this EoS for prediction of this coefficient. The model for the association sites of the water used in this paper is the 4C model.

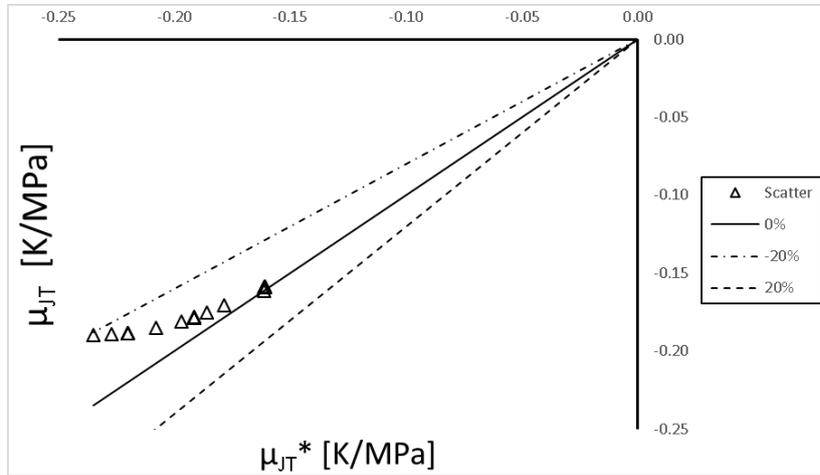


Figure 2 - Comparison between obtained data from CPA and commercial software data REFPROP for H₂O.

Figure (3) shows the predicted Joule-Thomson coefficient together with experimental data for H₂S at different pressures and temperatures. The AAD calculated for it was 17.6886%, exhibiting a satisfactory agreement between the predictions and experimental data over a significant range of pressure and temperature. It should be noted that the Joule-Thomson coefficient for H₂S liquid is very near the inversion point, that is, its value is close to zero, what makes the perceptual error grater once the absolute precision of the program is the same for the higher values of the coefficient. Another model for the association sites of the H₂S different from the 4C used could have better results.

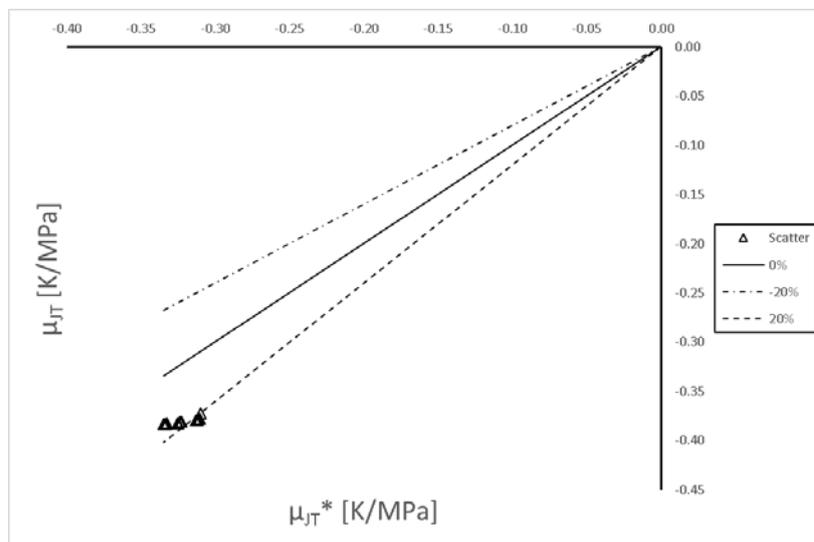


Figure 3 - Comparison between obtained data from CPA and commercial software data REFPROP for H₂S.

Figures (4) shows the predicted Joule-Thomson coefficient together with data from REFPROP (NIST (2002)) for CO₂ at different pressures and temperatures. It was also observed a good agreement between predicted and experimental/commercial software data AAD obtained of 4.1062%.

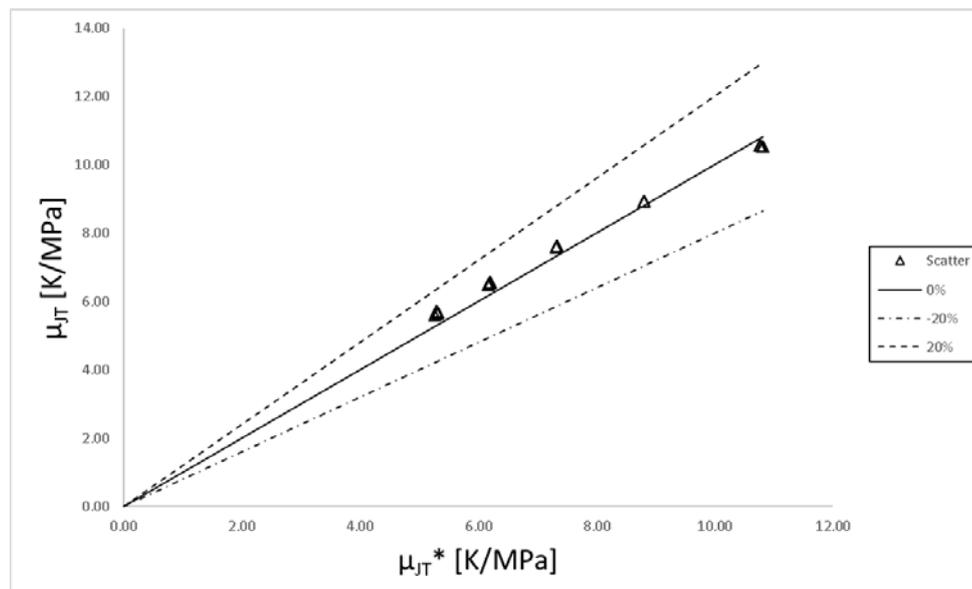


Figure 4 - Comparison between obtained data from CPA and commercial software data REFPROP for CO₂.

4. CONCLUSIONS

In this article, it was presented a thermodynamic approach to calculate the Joule-Thomson coefficient using the Cubic Plus Association EoS and a subroutine provided by REFPROP to calculate the heat capacities. There was a good agreement between the Joule-Thomson coefficient and the data provided by a commercial software for pure compounds in the whole temperature and pressure range. It was evidenced by those AAD found that were under 20%. It also evidenced that the Joule-Thomson coefficient for associative fluids could be calculated with a CPA EoS presenting satisfactory results, especially for liquid water which AAD was below 10%.

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