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Construction of Joule Thomson inversion curves for mixtures using equation of state

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Abstract. The Joule-Thomson effect is at the heart of Joule-Thomson cryocoolers and gas liquefaction cycles. The effective harnessing of this phenomenon necessitates the knowledge of Joule-Thomson coefficient and the inversion curve. When the working fluid is a mixture, (in mix refrigerant Joule-Thomson cryocooler, MRJT) the phase diagrams, equations of state and inversion curves of multi-component systems become important. The lowest temperature attainable by such a cryocooler depends on the inversion characteristics of the mixture used.

In this work the construction of differential Joule-Thomson inversion curves of mixtures using Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson equations of state is investigated assuming single phase. It is demonstrated that inversion curves constructed for pure fluids can be improved by choosing an appropriate value of acentric factor. Inversion curves are used to predict maximum inversion temperatures of multicomponent systems. An application where this information is critical is a two-stage J-T cryocooler using a mixture as the working fluid, especially for the second stage. The pre-cooling temperature that the first stage is required to generate depends on the maximum inversion temperature of the second stage working fluid.

1. Introduction

The adiabatic, isenthalpic flow of a fluid through a porous plug can yield a drop in temperature under certain conditions of pressure and temperature. This process, called throttling, demonstrates the Joule Thomson (JT) effect. The JT effect is an important feature of real gases and it is extensively used in JT cryocoolers and liquefaction cycles. The use of a gas mixture as the working fluid in a JT cryocooler has several advantages such as reaching cryogenic temperatures at relatively lower pressures^{[1], [2]}.

It is well known that throttling can produce cooling only when the working fluid is in a specific region of the Temperature-Pressure (TP) plane^[3]. The TP plane divides itself into two regions based on whether an isenthalpic pressure drop causes cooling or heating. The curve which separates these regions of the TP plane is the Joule Thomson inversion curve (JTIC) of the fluid^[3]. A schematic of the JTIC for a pure fluid is shown in fig. 1, where cooling occurs in the region below the JTIC^[4].

The Joule Thomson coefficient (μ_{JT}) helps quantify the cooling or heating that an isenthalpic pressure drop will cause^[4]. It is defined for pure fluids^[4] and single phase mixtures^[3] as:

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

For pure fluids, the JTIC is the locus of points on the T-P plane where $\mu_{JT} = 0$ ^[3]. Using thermodynamic relations, this condition can be recast as equation (2)^[5]. Dilay and Heidemann^[5] have used equation (2) in conjunction with p-v-T relations to obtain JTICs for pure fluids.

$$T \left(\frac{\partial p}{\partial T} \right)_v + v \left(\frac{\partial p}{\partial v} \right)_T = 0 \quad (2)$$

In the present work, JTICs are constructed for pure fluids and their mixtures using the Redlich-Kwong^[7] (RK), Soave-Redlich-Kwong^[8] (SRK) and Peng Robinson^[9] (PR) equations of state. The



working fluid is assumed to be in single phase at all temperatures and pressures. Emphasis is laid on finding T_{inv} of mixtures. R. Abbas et. al. have used advanced equations of state to predict single phase JTICs of mixtures^[17]. J. Vrabec et. al. have done the same using molecular simulations^[11].

2. JTIC for multi-phase mixtures

It may be seen in fig. 1 that the JTIC has a peak pressure. The portion of the JTIC to the right of this pressure peak is the high temperature branch of the JTIC and the portion to the left is the low temperature branch. The high temperature branch ends at the temperature axis where pressure is 0^[4]. The temperature at this point is the maximum inversion temperature (T_{inv}) of the fluid. The low temperature branch of the JTIC of a pure fluid ends at the point where it intersects the liquid-vapor saturation line^[4].

Nichita and Leibovici^[3] have investigated the construction of JTICs for two phase mixtures. Fig. 2 shows the JTIC for a mixture obtained by these authors using the Peng-Robinson EOS. As seen in fig. 2, multicomponent systems exhibit an extended multiphase region on their TP plane representation indicated by the phase envelope. The JTIC in the multiphase region is not a continuation of its single phase portion as there is a discontinuity at the phase envelope. μ_{JT} is a derivative (equation 1) and will thus be discontinuous across a phase transition line on the TP plane.

When a multiphase mixture undergoes throttling, temperature change is affected by transfer of mass between phases^[3]. Consequently, constructing the JTIC in the multiphase region is different than doing so in the single phase region. Fig. 2 indicates that the high temperature branch of the JTIC of a mixture lies outside its phase envelope. Hence, a single phase analysis is expected to predict it accurately.

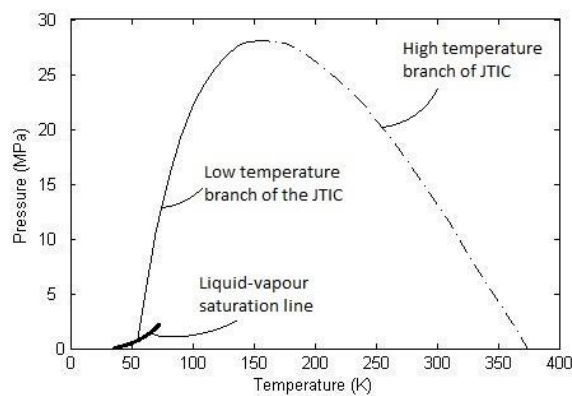


Fig. 1. Schematic of the JTIC and the vapor pressure curve of a pure fluid.

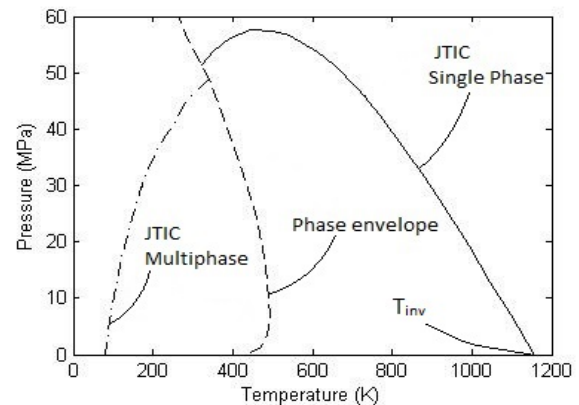


Fig. 2. JTIC and phase envelope of a North Sea gas-condensate using Peng-Robinson EOS^[3].

In JT cryocoolers, cooling effect is obtained by throttling of the working fluid. For this it is important that the state of the fluid before throttling is in the region enclosed by the JTIC. In particular, the temperature must be below T_{inv} . If a working fluid has T_{inv} below the ambient, it must first be cooled below its T_{inv} and then throttling can be done to get cooling effect.

In a two stage JT cryocooler two independent compressors and working fluids may be used. The first stage pre-cools the second stage working fluid so that its temperature reaches below its T_{inv} . Cao et. al.^[6] have used such an arrangement with N_2 ($T_{inv} = 621$ K) as working fluid for the first stage and H_2 ($T_{inv} = 205$ K) for the second stage. As pure fluids are used, operating pressures are very high (high pressure of 80.0 bar in first stage). These can be reduced if the working fluid is a mixture^[1]. In such a case, accurately estimating the T_{inv} of the working fluids is crucial for determining the first stage temperature and cooling load requirement.

2. Equation of State

The equations of state (EOS) used in this work are:

$$\text{Redlich Kwong EOS } [7] \quad p = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)} \quad (3)$$

$$\text{Soave-Redlich-Kwong EOS } [8] \quad p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (4)$$

$$\text{Peng Robinson EOS } [9] \quad p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (5)$$

The $a/T^{0.5}$ term in equation 3 and the $a(T)$ terms in equations 4 and 5 are related to attractive intermolecular forces and ‘b’ is the covolume (the term accounting for finite atomic volumes). In the mixing rules given below, $\alpha(T)$ refers to the attractive terms. x_i is the mole fraction of the i^{th} component of the mixture. The original mixing rules are simple and can be applied to all of the considered EOSs^[8]. Mixing rules involving the binary interaction parameter can also be used with suitable k_{ij} values.

$$b = \sum b_i x_i \tag{6}$$

$$\alpha(T) = \left\{ \sum x_i (\alpha_i(T))^{0.5} \right\}^2 \tag{7}$$

In equations (4) and (5), the $a(T)$ function of pure fluids depends upon the acentric factor of the fluid^{[8],[9]}. The acentric factor (ω) of a pure fluid is a measure of the deviation of its intermolecular potential from that of simple fluids^[10]. Simple fluids are fluids having spherically symmetric molecules like the heavier inert gases (Ar, Kr, Xe) and methane^[10]. Equation 8 gives the definition of ω where P_r is the reduced vapor pressure of the fluid at a reduced temperature (T_r) of 0.7.

$$\omega = -\log_{10}(P_r) - 1 \tag{8}$$

It is observed for simple fluids that $P_r = 0.1$ at $T_r = 0.7$ ^[10]. Thus, ω of simple fluids is zero. An acentricity of 0 corresponds to inert gas behavior where a very significant portion of intermolecular interactions comes from molecular collisions, and long range forces are quite weak. With polarity and large size, the importance of intermolecular attractions increases, leading to non-zero values of acentricity. In the case of hydrogen and helium, which have very small molecular sizes, quantum effects substantially influence intermolecular interactions and result in negative values of acentric factor.

In this work, JTICs are plotted for mixtures of nitrogen, methane and carbon dioxide using the above equations. These are compared to JTIC data points obtained by J. Vrabec et. al.^[11] using molecular modelling and simulations. JTICs of pure hydrogen and neon are constructed and compared with the results of Hendricks et. al.^[12], which are based on a multi-constant p-v-T relation. The work is further extended to construct JTICs for mixtures containing hydrogen, nitrogen and neon. Experimental data for inversion curves of mixtures is scarce. Therefore molecular modelling results are taken as the reference to assess the JTICs of mixtures obtained in this work.

3. Results and Discussion

To construct the JTIC for a particular mixture composition, ‘b’ is obtained from equation (6). A cubic spline interpolation is obtained for $\alpha(T)$ using equation 7. For a temperature (T), volume (v) is calculated using equation 2. Pressure is calculated at (T, v) using the EOS to get a point (T, p) on the JTIC.

3.1 JTIC of mixtures of Nitrogen, Methane and Carbon dioxide

Figs. 3 and 4 show JTICs of equimolar mixtures of N_2 and CH_4 , and N_2, CH_4 and CO_2 respectively. These are constructed according to the above procedure using RK, SRK and PR EOSs and the stated mixing rules. These are compared with simulation data as given by [11].

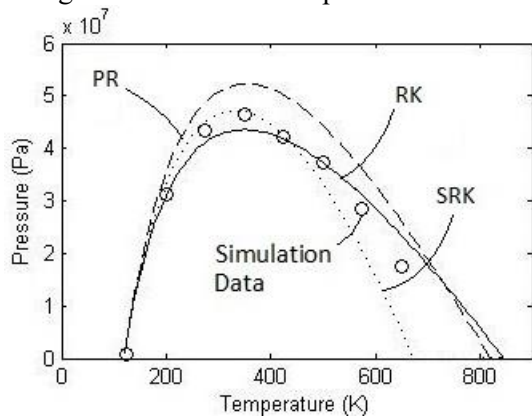


Fig. 3.

Fig. 3. JTICs for an equimolar mixture of N_2 and CH_4 .

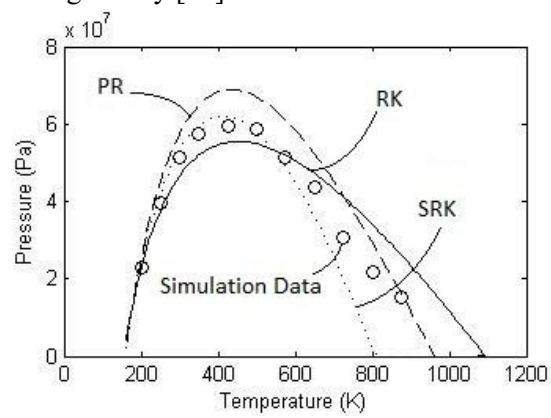


Fig. 4.

Fig. 4. JTICs for an equimolar mixture of N_2, CH_4 and CO_2 .

It may be seen from fig. 3 that the RK and PR EOSs predict the T_{inv} more accurately than the SRK EOS. This is also seen in the JTICs of the mixture components, methane and nitrogen (which are both

simple fluids), as given by [5]. With the addition of carbon dioxide, (which is a high acentricity gas, $\omega = 0.225$ [13]) the T_{inv} predictions of RK and PR EOS's differ from each other by more than 100 K, which is 10% of the predicted T_{inv} of the mixture. This is due to the inability of the RK EOS to incorporate the effect of acentric factor. [8]

As emphasized earlier, the utility of the JTICs constructed herein lies predominantly in the prediction of the high temperature branch. It has been demonstrated that cubic EOSs predict the low temperature branch of the JTIC satisfactorily but are less effective in accurately predicting the high temperature branch [5]. This problem is addressed in the subsequent section. It is thus noted that the prediction of T_{inv} is of particular interest, and the SRK EOS is unsatisfactory for this purpose. In view of this, only PR and RK EOSs are further considered.

3.2. JTIC of pure hydrogen and neon

Figs. 5 and 6 show the JTICs of pure Ne and H₂ constructed using the PR and RK EOSs. They are compared with data from a multi-constant EOS [12].

Fig. 5 shows that the PR EOS satisfactorily predicts the T_{inv} of Neon. However, as shown in fig. 6, neither PR nor RK can do so for hydrogen. Acentricity value of hydrogen is -0.22. However it may be seen that by using an acentric factor of -0.06 in the PR EOS, a good prediction of the high temperature branch is obtained. It may thus be appreciated that the actual acentricity of -0.22 gives a good prediction for the low temperature branch and -0.06 gives a good prediction for the high temperature branch.

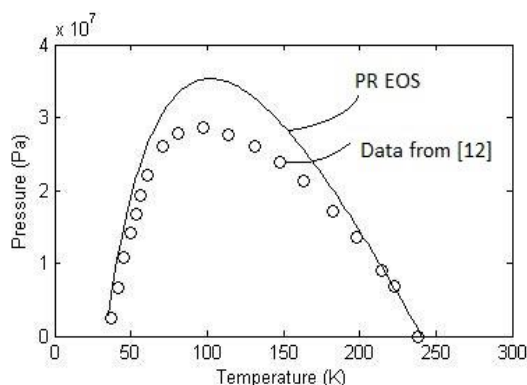


Fig. 5.

Fig. 5. JTIC of Neon.

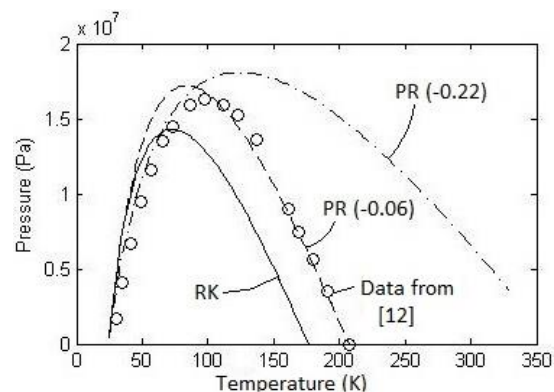


Fig. 6.

Fig. 6. JTICs of H₂.

It is possible that this phenomenon is peculiar to quantum fluids like H₂ and He. However, CO₂ is also found to exhibit such behaviour. CO₂ has an acentricity of 0.225 but it is found that $\omega = 0.15$ gives better results while constructing its JTIC using PR EOS. When the SRK EOS is used, Ghanbari and Check [15] found that $\omega = 0.05$ gives a better fit than 0.225.

As the temperature of a gas rises, average speed of its molecules increases and inertial forces felt during collisions start gaining prominence over long range intermolecular forces. Thus, the intermolecular forces a molecule will see at elevated temperatures are similar to the ones normally seen in inert gases. In consequence, the effective acentric factor at high temperatures must be closer to zero than the documented values as the latter are based on intermolecular forces in the VLE region [10]. In the JTIC of a pure fluid, the temperatures in the high temperature branch are well above twice the critical temperature [4]. Thus, to get good predictions in that region, an acentricity closer to 0 is required. This is a possible explanation for $\omega = -0.06$ giving better results than $\omega = -0.22$ for hydrogen.

Such a modification is not possible with the RK EOS which uses a two parameter principle of corresponding states [16]. In literature, the RK EOS is said to be better at predicting inversion curves [4],[14]. However, due to quantum effects involved in cryogenic fluids (like hydrogen and helium) and the flexibility of the PR EOS, we shall use the latter to estimate T_{inv} of mixtures of cryogenic fluids.

In this work, only basic cubic EOSs are considered and T_{inv} can be predicted reasonably well (figs. 5 and 6) when they are used along with an appropriate acentric factor. However, it is found that no value of acentric factor can produce a reasonable inversion curve for helium using the PR EOS. This excludes helium from the current analysis. Only neon and hydrogen are considered as mixture components.

3.3 JTIC of mixtures of nitrogen hydrogen and neon

The PR EOS is used (with $\omega = -0.06$ for H_2) to get JTICs of mixtures of N_2 , Ne and H_2 . It is desirable to have a high percentage of a gas with low critical temperature (T_c) in the working fluid of a JT cryocooler. This is to ensure that fluidity of the mixture is maintained as lower temperatures are reached. On the other hand, the available precooling should be able to cool the mixture to a temperature below its T_{inv} . In the present case, the percentage of hydrogen ($T_c = 33$ K) in the mixture is maximized while trying to achieve a T_{inv} of 300 K. This is an instance of optimizing the working mixture composition using constructed JTICs. Fig. 7 shows JTICs of binary mixtures of H_2 and N_2 while fig. 8 shows JTICs for ternary mixtures of Ne, H_2 and N_2 .

In fig. 7, a mole fraction of 0.2 for N_2 and 0.8 for H_2 gives a T_{inv} of 300K. The PR EOS is found to predict a T_{inv} of 650 K for pure N_2 , and 205 K for pure H_2 when acentricity of -0.06 is used. A weighted average hypothesis for the variation of T_{inv} with mixture composition predicts a T_{inv} of 427 K for an equimolar mixture of H_2 and N_2 , as opposed to 440 K as seen in fig. 7. The variation of T_{inv} with composition is studied for a binary mixture of nitrogen and methane. The maximum deviation from the weighted average hypothesis is found to be 17 K at equimolar composition. For the binary mixture in fig. 7 having 80% H_2 and 20% N_2 , as well as for the mixtures in fig. 8, it is found that the weighted average T_{inv} is within 10 K of the T_{inv} predicted by PR EOS. This indicates that weighted average gives a value of T_{inv} which is reasonably close to the value predicted by the PR EOS.

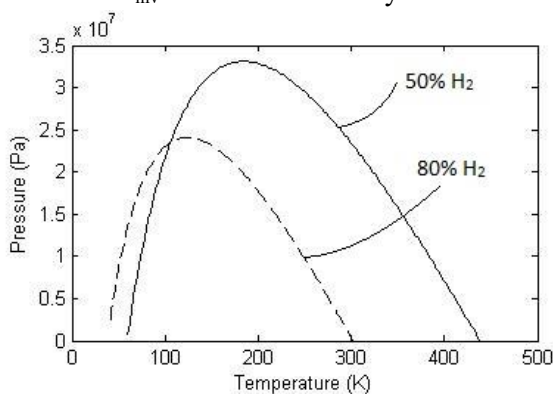


Fig. 7.

Fig. 7. JTICs for binary mixtures of N_2 and H_2

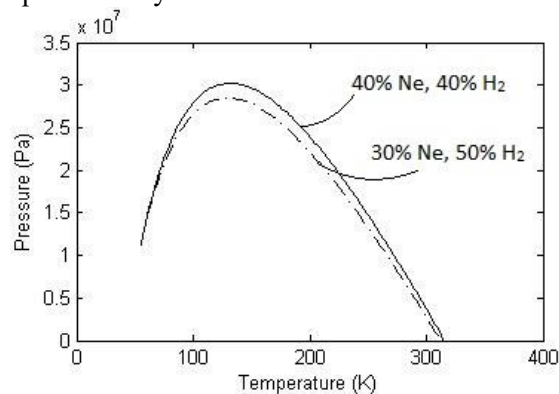


Fig. 8.

Fig. 8. JTIC for ternary mixtures of N_2 , H_2 and Ne

Fig. 8 shows the JTIC of a ternary mixture of nitrogen, hydrogen and neon. The mole fraction of nitrogen is 0.2 and that of neon and hydrogen is varied. Hydrogen has a critical temperature of 33 K and that of Neon is 44.5 K. As the higher T_c component, neon, is replaced by the lower T_c component, hydrogen, the T_{inv} of the mixture reduces slightly. In JTICs of the pure fluids, the peak pressure of neon is almost twice that of hydrogen (figs. 5 and 6). Consequently, as neon in the mixture is replaced by hydrogen, the lowering of peak pressure is substantial.

4. Conclusions

In this work, the JTIC of a mixture was obtained by first constructing JTICs of component fluids using PR EOS. For doing so, the acentric factor value was varied till the predicted T_{inv} agreed with simulation or experimental results. The shift in acentricity towards zero at elevated temperatures was attributed to differences between intermolecular interactions in the VLE and supercritical regions. Mixing rules were used along with new acentricity values to construct inversion curves of mixtures having up to three components. An extension to mixtures having many more components is possible with a minimal increase in computational cost.

The correctness of the predicted T_{inv} and high temperature branch depends on the mixing rules used. This method is limited to predicting the T_{inv} and the high temperature branch, as obtaining the full spectrum of inversion characteristics requires multiphase computations. The variation of JTIC characteristics with composition were studied and linearity in the variation of T_{inv} was investigated. Helium could not be a part of this analysis as its inversion curve was found to be beyond the scope of the cubic EOSs used here.

Advanced EOSs, which can predict inversion curves of mixtures accurately, exist only for some specific mixtures. Getting accurate inversion curves for generic mixtures needs molecular modelling and simulations. In the present work, a much simpler and faster method to get T_{inv} of cryogenic mixtures is employed, which could be used to get an optimum working fluid composition for the design of cryocoolers.

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