

PREDICTION OF DIFFERENTIAL JOULE-THOMSON INVERSION CURVES FOR CRYOGENS USING EQUATIONS OF STATE

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In many cryogenic applications, Joule–Thomson (J–T) effect is used to produce low temperatures. The isenthalpic expansion of gas results in lowering of temperature only if the initial temperature of the working fluid is below its characteristic temperature, called the inversion temperature. Inversion curves are helpful in studying the inversion temperatures. The prediction of inversion curves solely depends on the equation of state (EOS) for the working fluid. In the present work, various EOS are explored in order to predict the Joule–Thomson differential inversion curve for various commonly used cryogenics viz. nitrogen, argon, carbon dioxide, helium, hydrogen and neon. The widely accepted EOS such as Van der Waals, Redlich–Kwong and Peng–Robinson EOS are used for this purpose.

Key words: Inversion curve, Joule Thomson Effect, Van der Waal, Redlich Kwong, Peng Robinson

INTRODUCTION

The Joule-Thomson (J-T) effect has been widely investigated because of its importance for theoretical and practical purposes. It has many cryogenic applications and is widely used in gas liquefaction. The effect describes the temperature change of a gas or liquid when it is forced through a valve or porous plug under adiabatic conditions.

The rate of change of temperature with respect to pressure in a J-T process (that is, at constant enthalpy) is called the differential

Joule–Thomson coefficient, μ_{JT} and is given as,

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

The locus of points for which $\mu_{JT} = 0$ is called the differential inversion curve. The inversion curve divides the p-T plane into two zones as shown in Figure 1. The J–T coefficient is positive inside the inversion curve, while it is negative outside the curve.

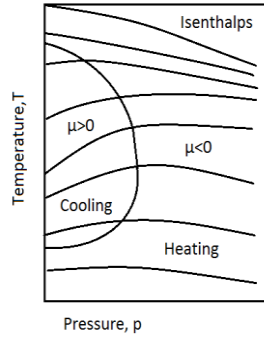


Figure 1: J-T inversion curve dividing the p-T plane into two zones.

The prediction of inversion curves depends solely on the equation of state (EOS) that is used for a given working fluid, which operates in a particular p - T region. This prediction has been studied by various researchers [1-2]. Miller [3] suggested that it would be desirable for constructors of new EOS to include a comparison of the predicted inversion curve with an experimental one. Prior to 1970, J-T inversion curves were plotted only for a few EOS namely, Van der Waals, Dieterici, Lennard-Jones-Devonshire, and DeBoer-Michels EOS [4]. Miller calculated inversion curves for the Redlich-Kwong (RK) and Martin EOS, while Juris and Wenzel calculated inversion curves for the virial, Berthelot, Beattie-Bridgeman, Benedict-Webb-Rubin, Redlich-Kwong, and Martin-Hou EOS.

Dilay and Heldermaun [5] used four recently published EOS to calculate the J-T inversion curves; namely, Soave Redlich Kwong, Peng Robinson (PR), Perturbed hard chain and Lee Kesler EOS. They concluded that none of the EOS were able to predict the entire inversion curve accurately; however the Lee Kesler EOS gave the best overall prediction. The obtained inversion curves were then compared with the inversion curve developed by Gunn Chueh, and Prausnitz [2] from the data available for simple fluids. Maytal and Shavit [6] developed the integral inversion curve concept, involving the locus of all points with a vanishing integral Joule Thomson effect, ΔT_h and isothermal enthalpy change, ΔH_T . Wisniack and

Avraham [7], developed a new procedure to investigate the capability of an EOS to predict an experimental inversion curve in a mathematical way.

There are many EOS available in the literature which are claimed to be accurate for specific fluids and for a range of operating conditions only. Therefore, selection of suitable EOS to predict accurate inversion curve for the given cryogen is an important step in the simulation or design studies of the cryogenic equipment involving J-T expansion.

The present work focuses on the applicability of various EOS for predicting the J-T differential inversion curve for various commonly used cryogenes, Nitrogen (N_2), viz. Argon (Ar), Carbon dioxide (CO_2), Helium (He), Neon (Ne) and Hydrogen (H_2). The paper presents the calculations of differential inversion curves and their comparison with the experimental data available in the literature.

THEORY AND ANALYSIS

The differential inversion curve is defined as the locus of all points where the Joule-Thomson coefficient μ_{JT} vanishes. It has a maximum inversion temperature, i.e., the maximum temperature when the pressure is zero. For cooling, it is necessary for the gas to be below this temperature and inside the inversion curve.

In the present work, three equations of state, i.e, Van der Waals, RK, PR have been analysed to understand their applicability to predict the inversion curves. Eqn. (2) gives the condition for differential inversion curve.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T \left(\frac{\partial V}{\partial T} \right)_P - V}{C_p} = 0 \quad (2)$$

$$\text{Thus, } T \left(\frac{\partial V}{\partial T} \right)_P - V = 0 \quad (3)$$

Which can also be written as,

$$\mu_{JT} = T \left(\frac{\partial P}{\partial T} \right)_V + V \left(\frac{\partial P}{\partial V} \right)_T = 0 \quad (4)$$

The condition so derived in Eqn. (4) is applied to the above mentioned EOS based on which the inversion curves are developed for various gases. The following section gives these details.

Van der Waals equation of state

The Van der Waals EOS is expressed in Eqn. (5):

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (5)$$

The Van der Waals constant 'a' is a measure of strength of the Van der Waals force between the molecules of the gas, while the Van der Waals constant 'b' represents effective volume of the gas molecules.

The equation can be written in its reduced form, as given in Eqn. (6), using pressure, temperature and volume at the critical point. The reduced pressure (P_r), temperature (T_r) and volume (V_r) are given as P/P_c , V/V_c and T/T_c respectively.

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8T_r}{3} \quad (6)$$

By applying the equation for differential condition, P_r can be written as,

$$P_r = 24\sqrt{3T_r} - 12T_r - 27 \quad [7]$$

Redlich Kwong Equation of State

The RK EOS [5] is given as:

$$P = \frac{RT}{V-b} - \frac{a}{\sqrt{T}V(V+b)} \quad (8)$$

Where parameters 'a' and 'b' have the same physical significance as in Van der Waals EOS. However, their values are different which are given as below:

$$a = \frac{0.4275R^2T_c^{5/2}}{P_c}$$

$$b = \frac{0.08664RT_c}{P_c}$$

In the reduced form it is:

$$P_r = \frac{T_r}{\Omega_b(x-1)} - \frac{\Omega_a}{\Omega_b^2\sqrt{T_r}x(x+1)} \quad (9)$$

Where x is the reduced volume and Ω_a and Ω_b are constants with values as given,

$$\Omega_a = 0.4275$$

$$\Omega_b = 0.08664$$

By applying the equation for differential condition, T_r can be written as,

$$T_r^{3/2} = \frac{\Omega_a(5x+3)(x-1)^2}{\Omega_b 2x(x+1)^2} \quad (10)$$

Peng Robinson equation of state

The PR EOS is as given in Eqn. (11)

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2+2bV-b^2} \quad (11)$$

Where parameters a, b and α are given by:

$$a = \frac{0.457235R^2T_c^2}{p_c}$$

$$b = \frac{0.077796RT_c}{p_c}$$

$$\alpha = \left(1 + k(1 - \sqrt{T_r})\right)^2$$

Where k is:

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

Where ω is the acentric factor, which is a conceptual number useful in the description of matter. It is a measure of the non sphericity of molecules.

In the present work, ω has been assumed to be zero, which leads to the value of $k=0.37464$.

In the reduced form, the PR EOS is:

$$P_r = \frac{T_r}{\Omega_b(x-1)} - \frac{\Omega_a[1+k(1-\sqrt{T_r})]^2}{\Omega_b^2(x^2+2x-1)} \quad (12)$$

Where x is the reduced volume

$$\Omega_a=0.457235$$

$$\Omega_b=0.077796$$

When the equation for differential condition is applied, T_r can be written as,

$$T_r[\Omega_a(x-1)^2(x^2+1)k^2 - \Omega_b(x^2+2x-1)^2] + \sqrt{T_r}[-\Omega_a(x-1)^2k(k+1)(3x^2+2x+1)] + 2\Omega_ax(x+1)(x-1)^2(1+k)^2 = 0 \quad (13)$$

The above derived expressions in terms of reduced pressure, temperature and volume are solved to obtain various values of Pr for different values of Tr to get various inversion curves. These reduced forms of the equations are solved in MATLAB®. For the RK and PR EOS, for different values of reduced volume x, the corresponding values of reduced temperature T_r are computed using equations (10) and (13) respectively. These combinations of x and T_r are substituted in the equation of state to get the value of Pr.

RESULT AND DISCUSSION

The results are plotted in terms of Tr-Pr curves for various gases using different EOS. These curves are compared with the experimentally obtained curve available in the literature. Based on these curves, T-P curves are plotted for each cryogen (gas) for each EOS. Its intersection with the T axis gives the maximum inversion temperature for any cryogen. The maximum inversion temperatures so obtained for various cryogens using different EOS are compared with the experimental values in the literature.

Figure 2 shows the comparison of differential inversion curves obtained from various EOS in terms of their reduced properties. Van der Waals, PR and RK EOS

are used and results are compared with the experimental data [5] for the inversion curve.

As is evident from the figure, the inversion curves appear to be qualitatively similar to each other. But when studied closely, they give varied data of the inversion temperatures. The curves are divided into two temperature zones - a high temperature branch and a low temperature branch. The low temperature branch of these curves closely match with the experimental curve. However, at higher temperatures, the curves deviate significantly from the experimental data. It is seen in Figure 2, that Van der Waals EOS gives good prediction of the low temperature branch of the inversion curve below 2 bar, whereas RK and PR EOS give good prediction of the same upto 8 bar. The peak pressure also varies for each EOS, being less than the experimental data for Van der Waals EOS, and more than that for RK and PR EOS. It is 9 bar for Van der Waals, 10.8 bar for RK, 13 for PR and 11.5 bar for the experimental inversion curve. Thus, the high temperature branch and the peak pressure of the inversion curve prove to be sensitive to the EOS that is used. The RK equation of state gives the best prediction of the inversion curve closest to the experimental curve.

The cryogenic gases may be classified into two groups. Group 1, which consists of N_2 , Ar and CO_2 , has its inversion temperature above the room temperature. They can be expanded at room temperature to obtain cooling effect. Group 2 consists of the quantum gases, H_2 , He, Ne, which have inversion temperatures below the room temperature. These gases need to be precooled below their inversion temperature before being expanded, in order to obtain cooling effect.

In the present study, the inversion curves are developed for cryogens of both the groups. Figures 3-6 show the inversion curves for gases from group 1 i.e. N_2 , Ar, CO_2 respectively, and the Table 1 shows the comparison of the experimental inversion temperatures and those obtained from the developed inversion curves.

It may be seen that the Van der Waals EOS performs very poorly for these cryogenics of group 1. The maximum inversion temperature is highly above the experimental value, while the maximum pressure is considerably less than the experimental values. For N₂ and Ar, the deviation in maximum inversion temperature is around 220K, while for CO₂, it is more than 500K.

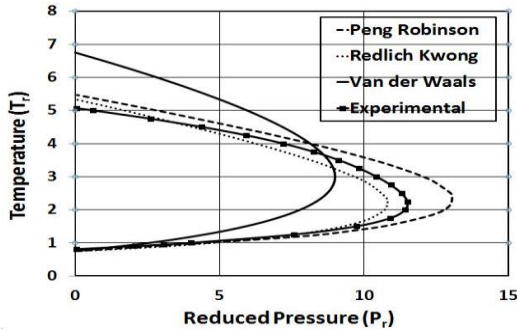


Figure 2: Differential Inversion curves

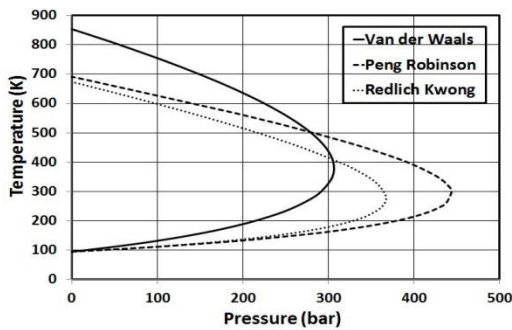


Figure 3: Differential inversion curves for N₂

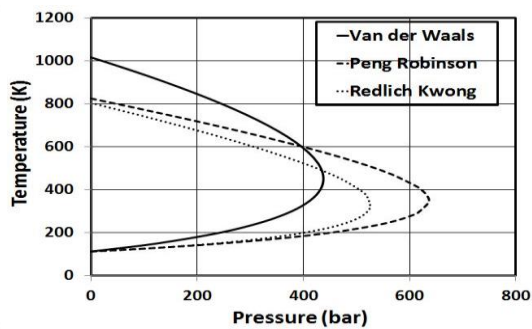


Figure 4: Differential inversion curves for Ar

PR EOS does fairly well and is an improvement over Van der Waals EOS. As compared to Van der Waals EOS, the maximum inversion temperature predicted by PR EOS is closer to the experimental

value. As seen from Table 1, the difference in the predicted and the experimental value is about 90K for N₂, 30K for Ar and 165K for CO₂.

The most accurate inversion curve is predicted by using the RK EOS. It predicts the maximum inversion temperature quite close to the experimental value. The deviation is minimal, i.e, 50K for N₂, 10K for Ar and 123K for CO₂ as seen from Table 1.

Figures 5-7 show inversion curves of gases from group 2 namely H₂, He, Ne respectively.

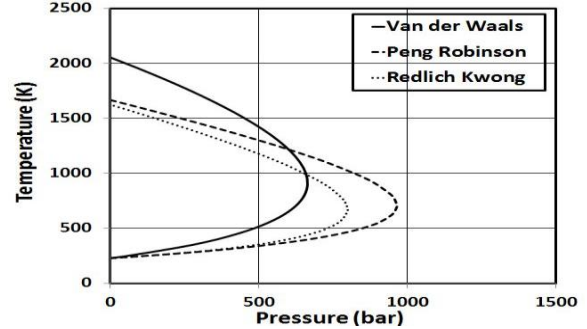


Figure 5: Differential inversion curves for CO₂

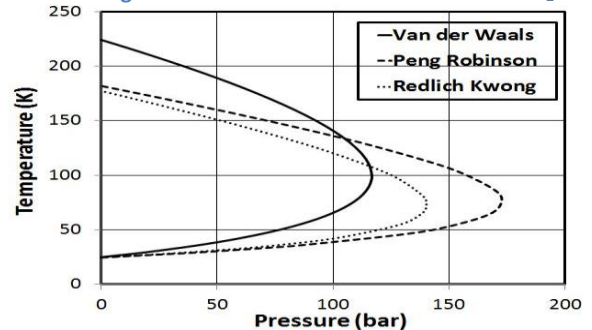


Figure 6: Differential inversion curves for H₂

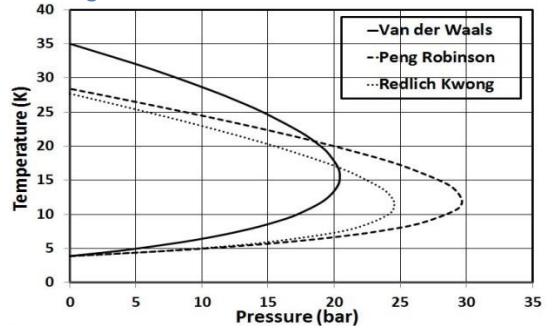


Figure 7: Differential inversion curves for He

These quantum gases do not follow the principle of corresponding states. It is due to their quantum effects at low temperatures and high pressures. This means, when compared at the same reduced temperature

and pressure, they do not have the same compressibility factor. Thus, the quantum gases do not exhibit ideal gas behaviour.

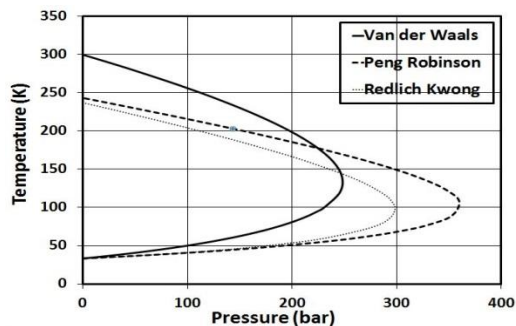


Figure 8: Differential inversion curves for Ne

Table 1: Comparison of maximum inversion temperatures

Sr. No	Gas	Maximum Inversion Temp (K)			
		VDW	PR	RK	Actual
1.	Nitrogen	854	691	674	621
2.	Argon	1017	825	804	794
3.	Carbon Dioxide	2053	1666	1623	1500
4.	Hydrogen	224	182	177	205
5.	Helium	35	28	27	45
6.	Neon	300	243	237	250

This is the reason for the variations observed in maximum inversion temperature for the quantum gases. It may be seen that for H_2 and He, Van der Waals EOS predicts the best inversion curve, whereas for Ne it is PR EOS. It is known that Van der Waals EOS is the most inaccurate EOS among the three EOS studied. Thus, the fact that Van der Waals EOS predicts the best inversion curve is contradictory. So, it can be concluded that there is an anomaly in the calculated inversion curves because of the quantum effects.

Other higher equations of state need to be used for these gases, which take quantum effects of gases into consideration.

CONCLUSION

Differential inversion curves from three equations of state are successfully

developed and compared with the experimental values available in literature. It may be seen that RK EOS gives the overall best prediction of the inversion curve. The Van der Waals equation is most inaccurate, while PR EOS results are closer to that of RK.

All three equations, namely Van der Waals, PR and RK EOS give good prediction of the lower temperature branch of the inversion curve. Hence, the higher temperature branch and the peak of the inversion curve decide which EOS predicts the best inversion curve.

The quantum gases, H_2 , He and Ne, need to be evaluated separately using EOS that considers the quantum effects.

NOMENCLATURE

P- Pressure

T- Temperature

V- Volume

V_m - Molar Volume

Pr- Reduced pressure

Tr- Reduced temperature

V_r/x - Reduced volume

μ_{JT} – Joule Thomson coefficient

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