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# APPLICATION OF THE VAN DER WAALS EQUATION OF STATE TO THE PROCESS OF ENHANCED OIL RECOVERY

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*ENCH 610: CHEMICAL ENGINEERING THERMODYNAMICS  
RESEARCH PROJECT*

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## ABSTRACT

This project deals with the application of the Van der Waals Equation of State to study the various thermodynamic properties of Carbon Dioxide. The thermodynamic properties are studied and compared with the data observed for the real gas and deviations from ideality are noted. The properties are also used to study the compression of carbon dioxide to suitable pressures for its use as a solvent in Enhanced Oil Recovery which involves injection of CO<sub>2</sub> under high pressures in the oil wells.

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# 1. INTRODUCTION

The ideal gas equation is the simplest and the basic form of equation relating the Pressure (P), Temperature (T) and Volume (V) of a system. It assumes particles to be point particles (molecules do not occupy space) and does not take into consideration that the molecules within a system interact with each other. It is given by a simple relation:

$$PV = nRT \quad (1)$$

Where,

$n \rightarrow$  number of moles

$R \rightarrow$  Universal Gas Constant

## 1.1. VAN DER WAALS EQUATION OF STATE

Van der Waals Equation of State was the first equation to be used for real gases that took into consideration various aspects relating temperature, pressure and volume. The equation gave possible reasons as to why real gases do not follow the ideal gas law. Van der Waals equation accounts for the fact that molecules interact with each other in a system and that they occupy space. This equation adds correction factors as constants 'a' and 'b' that would relate the real gas properties.

Van der Waals Equation of State:

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

The term  $\frac{a}{V^2}$  takes into account the reduction in pressure of the walls of the container due to the intermolecular attractions between the molecules. Similarly, the constant  $b$  accounts for the fact that molecules occupy a finite amount of space within the container.

## 1.2. STABILITY CRITERIA

At the critical point ( $T_C$ ,  $P_C$ , and  $V_C$ ) we have a point where the vapor volume and liquid volume are at the same point and is the starting point for the supercritical fluid hence our first derivative is set equal to zero:

$$\left(\frac{\partial P}{\partial V}\right)_{T, \text{critical}} = 0 \quad (3)$$

Our point of inflection also coincides at the critical point, which can be found by setting the second derivative to zero:

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T, \text{critical}} = 0 \quad (4)$$

Differentiating the Van der Waals equation of state from (2):

$$\frac{\partial P}{\partial V} = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \quad (5)$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{2RT}{(V-b)^3} + \frac{6a}{V^4} = 0 \quad (6)$$

Substituting (5) in (6):

$$V_C = 3b \quad (7)$$

Substituting (7) in Equation (4):

$$T_C = \frac{8a}{27Rb} \quad (8)$$

Substituting the critical volume,  $V_C$  from (7) and critical temperature,  $T_C$  from (8) in the Van der Waals Equation of State (2):

$$P_C = \frac{a}{27b^2} \quad (9)$$

We can determine the constants in terms of the critical values for a given system:

Dividing Equation (8) by (9):

$$\frac{T_C}{P_C} = \frac{8b}{R} \quad (10)$$

Therefore:

$$b = \frac{RT_C}{8P_C} \frac{m^3}{mol} \quad (11)$$

Substituting (11) in (8)

$$a = \frac{27(RT_C)^2}{64P_C} Pa \frac{m^6}{mol} \quad (12)$$

### 1.2.1. THERMAL STABILITY

The thermal stability criteria is defined as:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_V \geq 0 \quad (13)$$

### 1.2.2. MECHANICAL STABILITY

The mechanical stability criteria is defined as:

$$-\left( \frac{\partial P}{\partial V} \right)_T = \left( \frac{\partial P}{\partial \rho} \right)_T \geq 0 \quad (14)$$

## 1.3. REDUCED PROPERTIES FOR VAN DER WAALS EQUATION OF STATE

Reduced properties are state variables that are normalized at the fluid's state properties at its Critical Point.

Hence,

$$P_r = \frac{P}{P_C} \rightarrow P = P_r P_C \quad (15)$$

$$T_r = \frac{T}{T_C} \rightarrow T = T_r T_C \quad (16)$$

$$V_r = \frac{V}{V_C} \rightarrow V = V_r V_C \quad (17)$$

Where  $V_r$  is the reduced molar volume,  $P_r$  is the reduced Pressure,  $T_r$  is the reduced Temperature.

Substituting in (7), (8), (9), (15), (16), (17) in (2):

$$P_r P_C = \frac{RT_r T_C}{V_r V_C - b} - \frac{a}{(V_r V_C)^2} \quad (18)$$

$$P_r \left( \frac{a}{27b^2} \right) = \frac{RT_r \left( \frac{8a}{27Rb} \right)}{V_r(3b) - b} - \frac{a}{(V_r(3b))^2} \quad (19)$$

Van der Waals Equation of State in terms of Reduced Variables:

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \quad (20)$$

## 1.4. CARBON DIOXIDE (CO<sub>2</sub>)

Carbon dioxide is one of the most abundant gases present in the atmosphere. It is essentially a colorless gas and has various applications in industries. A few of its applications include use in carbonated drinks, fire extinguishers, agricultural fertilizers, etc. One of the major applications is its use in enhanced oil recovery where it is injected into oil wells under supercritical conditions. Under these conditions, CO<sub>2</sub> is miscible in oil where it acts both as a pressurizing agent as well as an agent for reducing the viscosity significantly.

For the purpose of studies, we must first evaluate the several properties relating the primary factors of Pressure, Volume and Temperature for CO<sub>2</sub> as a gas.

To evaluate the Van der Waals constants, we use the Critical Pressure and Temperature as a reference since both the quantities can be measured with high precision and accuracy in comparison to the Critical Volume.

From Table B1 of the Smith, et al. textbook for Chemical Engineering Thermodynamics:

$$T_c = 304.2K$$

$$P_c = 73.83 \text{ bar}$$

Substituting the obtained values in (11) and (12):

$$a = 0.3656 \text{ Pa} \frac{\text{m}^6}{\text{mol}} \quad (21)$$

$$b = 4.284 * 10^{-5} \frac{\text{m}^3}{\text{mol}} \quad (22)$$

The critical molar volume is obtained using the constants:

$$V_c = 128.46 \text{ cm}^3$$

We see that this value obtained deviates to a great extent from the actual measured value obtained from the NIST data webbook:

$$V_c(\text{actual}) = 91.9 \text{ cm}^3$$

This might be due to the lack of accuracy in the calculation of the molar volume and hence the quantity obtained from the Van der Waals equation of state would be an inaccurate measurement. Also, Van der Waals equation of state does not take into account the molecular interactions to a great extent causing the equation to be slightly inaccurate. The measured values must be used for all practical purposes of calculations.

## 2. THERMODYNAMIC PROPERTIES

Herein we have calculated the various essential thermodynamic properties using the Van der Waals Equation of State as functions of molar volume and temperature.

## 2.1. INTERNAL ENERGY

Internal Energy is an extensive thermodynamic property that defines the energy contained within the system. Changes in internal energy are caused due to the absorbance or loss of energy caused by changes in the internal state of the system. It does not take into account the kinetic energy or the potential energy of the system.

To evaluate this property, we assume Internal Energy,  $U$ , to be a function of the molar volume and temperature.

$$U = f(V, T) \quad (23)$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad (24)$$

The partial differential of internal energy with temperature at constant volume is the specific heat capacity of the fluid for an isochoric process.

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad (25)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \quad (26)$$

From Maxwell's Equations:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (27)$$

Hence,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (28)$$

Substituting (25) and (28) in (24):

$$dU = C_V dT + \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad (29)$$

Differentiating the Van der Waals Equation of State with respect to Temperature at constant volume:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b} \quad (30)$$



Therefore,

$$T \left( \frac{\partial P}{\partial T} \right)_V - P = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2} \quad (31)$$

Hence,

$$dU = C_V dT + \frac{a}{V^2} dV \quad (32)$$

Integrating from standard state  $U^0$  to the current state of the system  $U$ :

$$U - U^0 = \int C_V dT - \frac{a}{V} \quad (33)$$

$C_V$  is a function of temperature and its dependence on temperature must be taken into consideration when integrating the formula.

Internal Energy as a function of density ( $\rho$ ):

$$U = \int C_V dT - a\rho \quad (34)$$

We assume that the standard state of internal energy is zero.

## 2.2. ENTROPY

Entropy of a system is an extensive thermodynamic property that represents the unavailability of the system's thermal energy for conversion to mechanical work. It is often seen as a property defining the degree of disorder of the system. The second law of thermodynamics states that the entropy of an isolated system always increases, it is zero for an ideal reversible system only.

Assuming Entropy,  $S$ , to be a function of the molar volume and temperature.

$$S = f(V, T) \quad (35)$$

Differential form of entropy can be written as:

$$dS = \left( \frac{\partial S}{\partial V} \right)_T dV + \left( \frac{\partial S}{\partial T} \right)_V dT \quad (36)$$

Similar to (25):

$$\left( \frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \quad (37)$$

Substituting (27) and (37) in the differential form for entropy (36):

$$dS = \frac{C_V}{T} dT + \left( \frac{\partial P}{\partial T} \right)_V dV \quad (38)$$

Using (30) and substituting in (38):

$$dS = \frac{C_V}{T} dT + \frac{R}{V-b} dV \quad (39)$$

Integrating from standard state  $S^0$  to the current state of the system  $S$ :

$$S - S^0 = \int \frac{C_V}{T} dT + R \ln(V - b) \quad (40)$$

Assuming that the standard state of the system is zero:

$$S = \int \frac{C_V}{T} dT + R \ln(V - b) \quad (41)$$

$C_V$  is a function of temperature and its dependence on temperature must be taken into consideration when integrating the formula.

Entropy as a function of density ( $\rho$ ):

$$S = \int \frac{C_V}{T} dT + R \ln\left(\frac{1}{\rho} - b\right) \quad (42)$$

Similarly, For an Ideal Gas:

$$S^{ig} = \int \frac{C_V}{T} dT + R \ln(V) \quad (43)$$

As a function of density:

$$S^{ig} = \int \frac{C_V}{T} dT + R \ln\left(\frac{1}{\rho}\right) \quad (44)$$

Normalized Density of Entropy using (42) and (44):

$$\rho S_{norm} = \rho S - \rho S^{ig} \quad (45)$$

$$\rho S_{norm} = \rho R \ln(1 - \rho b) \quad (46)$$

### 2.3. ENTHALPY

Enthalpy is a thermodynamic quantity that defines the total heat content of a system. It is defined as the sum of internal energy and the product of pressure and volume of the system.

$$H = U + PV \quad (47)$$

Differentiating (31):

$$dH = dU + VdP + PdV \quad (48)$$

Differentiating the Van der Waals Equation of State (2):

$$dP = \frac{R}{V-b}dT - \frac{RT}{(V-b)^2}dV + \frac{2a}{V^3}dV \quad (49)$$

Substituting (2), (32) and (49):

$$dH = C_V dT + \frac{a}{V^2}dV + \frac{RV}{V-b}dT - \frac{RTV}{(V-b)^2}dV + \frac{2a}{V^2}dV + \left[ \frac{RT}{V-b} - \frac{a}{V^2} \right]dV \quad (50)$$

Solving the above equation:

$$dH = \left[ C_V + \frac{RV}{V-b} \right]dT + \left[ \frac{2a}{V^2} - \frac{RTb}{(V-b)^2} \right]dV \quad (51)$$

Integrating from standard state  $H^0$  to the current state of the system  $H$ :

$$H - H^0 = \int C_V dT + RT \left[ \frac{V}{(V-b)} \right] - \frac{2a}{V} \quad (52)$$

In terms of  $C_P$ ,

$$H - H^0 = \int (C_P - R)dT + RT \left[ \frac{V}{(V-b)} \right] - \frac{2a}{V} \quad (53)$$

For an isotherm, Temperature of the system remains constant and hence,  $dT = 0$ :

$$dH = \left[ \frac{2a}{V^2} - \frac{RTb}{(V-b)^2} \right]dV \quad (54)$$

Integrating and solving (37) for an isotherm:

$$H - H^0 = \frac{VRT}{V-b} - \frac{2a}{V} \quad (55)$$

Assuming that the standard state of the system is zero.

$$H = \frac{RTV}{V-b} - \frac{2a}{V} \quad (56)$$

Enthalpy can also be written as a function of density as:

$$H = \frac{RT}{1 - b\rho} - 2a\rho \quad (57)$$

## 2.4. CHEMICAL POTENTIAL

Chemical potential is defined as the change of the Gibbs free energy of a system corresponding to the change in the number of molecules added or removed from the system and is defined as:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j}$$

Gibbs free energy gives us the total amount of reversible work that can be performed by the system under isothermal and isobaric conditions. It is equal to the enthalpy of the system minus the product of entropy and the temperature of the system.

Chemical Potential for a system consisting of only one species is equal to the change in Gibbs free energy of the System. So to find the chemical potential, we calculate the Gibbs free energy:

$$\mu = G = H - TS \quad (58)$$

Substituting (40) and (55) in (58):

$$G = \int C_V dT + RT \left[ \frac{V}{V-b} \right] - \frac{2a}{V} + H^o - T \left[ \int \frac{C_V}{T} dT + R \ln(V-b) + S^o \right] \quad (59)$$

$$G - G^o = RT \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{V} + \int C_V dT - T \int \frac{C_V}{T} dT \quad (60)$$

In terms of  $C_P$ ,

$$G - G^o = RT \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{V} + \int (C_P - R) dT - T \int \frac{(C_P - R)}{T} dT \quad (61)$$

The standard state of Gibbs free energy can be calculated as:

$$G^o = H^o - TS^o \quad (62)$$

For Isotherms,  $dT = 0$ :

$$G - G^o = \frac{VRT}{V-b} - RT \ln(V-b) - \frac{2a}{V} \quad (63)$$

Assuming the standard states to be zero:

$$G = \frac{VRT}{V-b} - RT \ln(V-b) - \frac{2a}{V} \quad (64)$$

**Chemical Potential:**

$$\mu - \mu^o = RT \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{V} + \int C_V dT - T \int \frac{C_V}{T} dT \quad (65)$$

In terms of  $C_P$ ,

$$\mu - \mu^o = RT \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{V} + \int (C_P - R) dT - T \int \frac{(C_P - R)}{T} dT \quad (66)$$

Where,

$$\mu^o = H^o - TS^o \quad (67)$$

For an isotherm:

$$\mu = \frac{RTV}{V-b} - RT \ln(V-b) - \frac{2a}{V} \quad (68)$$

Chemical Potential can also be written as a function of molar density ( $\rho$ ):

$$\mu = \frac{RT}{1-b\rho} - RT \ln\left(\frac{1}{\rho} - b\right) - 2a\rho \quad (69)$$

**2.5. HELMHOLTZ ENERGY**

Helmholtz free energy is the thermodynamic work that measures the total useful work of a system under isothermal and isochoric process.

Helmholtz Energy is given as a function of internal energy,  $U$  and the entropy,  $S$ :

$$A = U - TS \quad (70)$$

Substituting (24) and (30):

$$A = \int C_V dT - \frac{a}{V} + U^o - T \left[ \int \frac{C_V}{T} dT + R \ln(V-b) + S^o \right] \quad (71)$$

$$A - A^o = -\frac{a}{V} - RT \ln(V-b) + \int C_V dT - T \int \frac{C_V}{T} dT \quad (72)$$

In terms of  $C_P$ ,

$$A - A^o = -\frac{a}{V} - RT \ln(V-b) + \int (C_P - R) dT - T \int \frac{(C_P - R)}{T} dT \quad (73)$$

The standard state of Helmholtz Energy can be calculated as:

$$A^o = U^o - TS^o \quad (74)$$

For an isotherm,  $dT = 0$ :

$$A = -\frac{a}{V} - RT \ln(V - b) \quad (75)$$

## 2.6. FUGACITY

Fugacity is analogous to pressure for real gas systems and is used for accurate measurements in chemical equilibrium calculations. At lower pressures, fugacity is equal to the mechanical pressure of the system.

Fugacity is used to calculate the actual Gibbs free energy of a gas given by the equation:

$$dG = RT \ln(f) \quad (76)$$

Integrating between the standard state and the current state:

$$G - G^o = RT \ln(f) \quad (77)$$

Substituting the equation for Gibbs Energy from (61):

$$RT \ln(f) = RT \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{V} + \int C_v dT - T \int \frac{C_v}{T} dT \quad (78)$$

Solving for Fugacity,

$$f = \exp \left[ \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{VRT} + \frac{1}{RT} \int C_v dT - \frac{1}{R} \int \frac{C_v}{T} dT \right] \quad (79)$$

In terms of  $C_p$ ,

$$f = \exp \left[ \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{VRT} + \frac{1}{RT} \int (C_p - R) dT - \frac{1}{R} \int \frac{(C_p - R)}{T} dT \right] \quad (80)$$

For an isotherm:

$$f = \exp \left[ \frac{V}{V-b} - \ln(V-b) - \frac{2a}{VRT} \right] \quad (81)$$

## 2.7. FUGACITY COEFFICIENT

Fugacity coefficient is defined as the ratio of fugacity to the mechanical pressure of the system and can be written as:

$$\phi = \frac{f}{P} \quad (82)$$

At lower pressures, the fugacity coefficient is equal to 1.

Equations (79) and (2) give us fugacity and the pressure for a Van der Waals Fluid:

$$\phi = \frac{\exp \left[ \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{VRT} + \frac{1}{RT} \int C_V dT - \frac{1}{R} \int \frac{C_V}{T} dT \right]}{\frac{RT}{V-b} - \frac{a}{V^2}} \quad (83)$$

In terms of  $C_P$ ,

$$\phi = \frac{\exp \left[ \left[ \frac{V}{V-b} - \ln(V-b) \right] - \frac{2a}{VRT} + \frac{1}{RT} \int (C_P - R) dT - \frac{1}{R} \int \frac{(C_P - R)}{T} dT \right]}{\frac{RT}{V-b} - \frac{a}{V^2}} \quad (84)$$

For an Isotherm:

$$\phi = \frac{\exp \left[ \frac{V}{V-b} - \ln(V-b) - \frac{2a}{VRT} \right]}{\frac{RT}{V-b} - \frac{a}{V^2}} \quad (85)$$

## 2.8. DENSITY OF HELMHOLTZ ENERGY

Density of Helmholtz energy is given as a function of chemical potential and pressure which is derived from the grand potential of the system:

$$\rho A = \rho \mu - P \quad (86)$$

Substituting the equation for pressure and chemical potential from (2) and (59) respectively:

$$\rho A = \rho \left[ RT \left[ \frac{V}{(V-b)} - \ln(V-b) \right] - \frac{2a}{V} + \int C_V dT - T \int \frac{C_V}{T} dT + \mu^o \right] - \frac{RT}{V-b} - \frac{a}{V^2} \quad (87)$$

The density of a fluid can be defined as the reciprocal of Volume:

$$\rho = \frac{1 \text{ mol}}{V \text{ m}^3} \quad (88)$$

Solving equation (87):

$$\rho A = \rho \int C_V dT - \rho T \int \frac{C_V}{T} dT - RT\rho \ln\left(\frac{1}{\rho} - b\right) - a\rho^2 + \rho\mu^o \quad (89)$$

For an Isotherm:

$$\rho A = \rho \left[ -RT \ln\left(\frac{1}{\rho} - b\right) - a\rho + \mu^o \right] \quad (90)$$

Solving the above equations and simplifying, we get the Density of Helmholtz Energy as:

$$\rho A - \rho A^0 = \left[ -RT \ln\left(\frac{1}{\rho} - b\right) - a\rho \right] \quad (91)$$

To obtain the density of Helmholtz energy from (73):

Dividing the equation by molar volume to obtain the density of Helmholtz Energy:

$$\rho A = -a\rho^2 - RT\rho \ln\left(\frac{1}{\rho} - b\right) + \rho \int C_V dT - \rho T \int \frac{C_V}{T} dT + \rho A^0 \quad (92)$$

We assume the standard state to be at absolute zero and hence our pressure can be considered to be zero. Comparing the equations (82) and (85) we can see that the density of standard Helmholtz energy can be assumed to be:

$$\rho A^0 = \rho \mu^o = \rho(U^0 - TS^0) \quad (93)$$

### 3. THERMODYNAMIC PLOTS

#### 3.1. PRESSURE – VOLUME

We use the Van der Waals equation to plot the various isotherms at the given temperatures approximately in the range of 10% from the critical point.

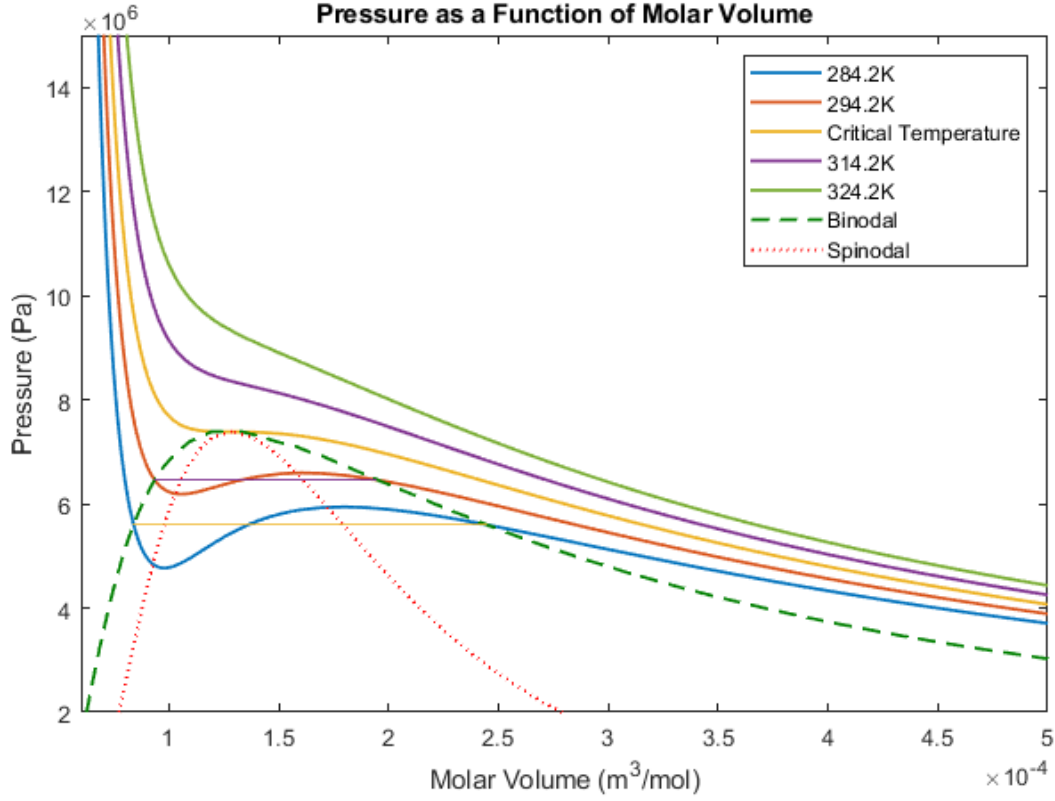
While plotting the vapor-liquid saturation curve (binodal), we ensure that the equilibrium criteria for the two phases are ensures. The equilibrium criteria states that the temperature, pressure and the chemical potential of the two phases are equal.

The plots obtained are as expected and clearly show the vapor liquid saturation curve. They also show the metastable region between the binodal and the spinodal.



The region encompassed by the spinodal is the unstable region and gives is the region where the mechanical stability criteria is not satisfied. In this region:

$$-\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial \rho}\right)_T \leq 0$$

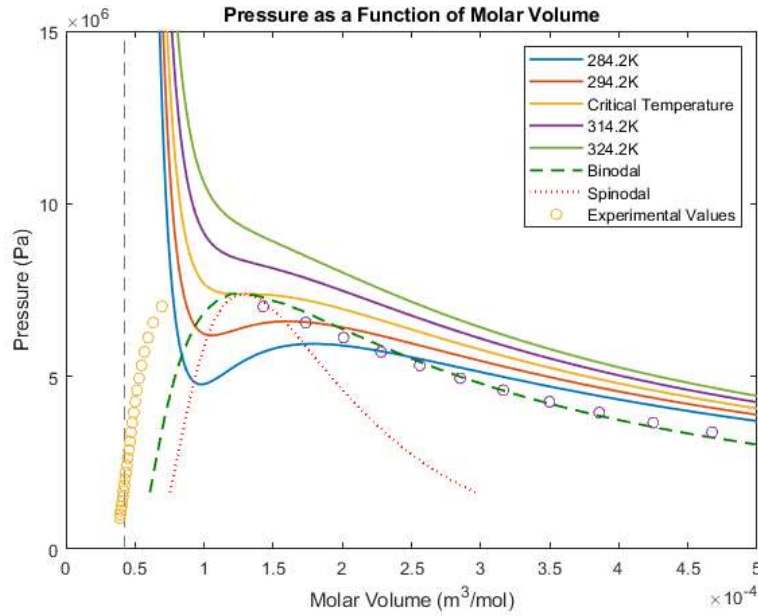


**Figure 1:** Pressure as a function of Volume

From the Pressure – Volume Saturation Curve we obtain the following vapor and liquid volumes for the corresponding isotherms:

TEMPERATURE (K)	LIQUID SATURATION VOLUME (m <sup>3</sup> /mol) (*10 <sup>-5</sup> )	VAPOR SATURATION VOLUME (m <sup>3</sup> /mol) (*10 <sup>-4</sup> )
274.2	7.7792	2.9901
279.2	8.0585	2.7045
284.2	8.3951	2.4465
289.2	8.8107	2.1978
294.2	9.354	1.9505

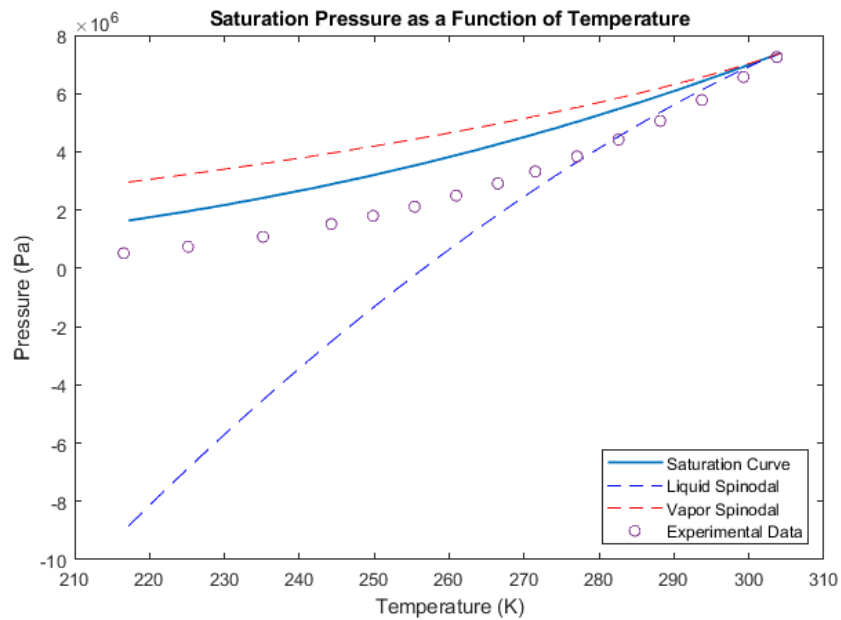
**Table 1:** Vapor and Liquid Points for the Saturation curve for carbon dioxide.



**Figure 2:** Comparison of Pressure as a Function of Volume with Experimental Data.

The above plot shows the deviations of the real gas from ideality. The experimental values are similar to the theoretically obtained volumes for the gas phase whereas they show very high deviations for the liquid phase region. This may be due to the fact that the gas behaves ideal at very high volumes and lower pressures.

### 3.2. PRESSURE – TEMPERATURE



**Figure 3:** Saturation Pressure as a function of Temperature.

The above depicts the large deviations in the temperature – pressure data obtained using the Van der Waals equation of state from the actual measured saturation pressure data.

The temperature dependence of the pressure along the vapor-liquid saturation curve is also given by several equations:

**a. Antoine Equation:**

$$\ln P_r^{sat} = A - \frac{B}{T + C} \quad (94)$$

Where, A, B and C are experimentally determined constants. This equation is only applicable in a particular range of temperature and shows large deviations from experimental data outside the range.

For CO<sub>2</sub>:

*Temperature Range* = 154.26K to 195.89K

$A = 6.81228$

$B = 1301.679$

$C = -3.494$

**b. Wagner Equation:**

$$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1 - \tau} \quad (95)$$

Where,  $\tau = 1 - T_r$

This equation gives a very accurate representation of the vapor pressure data over a wider temperature range. It expresses reduced vapor pressure as a function of reduced temperature.

For CO<sub>2</sub>:

*Temperature Range* = 217K to 304.10K

$A = -6.956260$

$B = 1.196950$

$C = -3.126240$

$D = 4.859390$

**c. Lee and Kesler Equation:**

$$\ln P_r^{sat}(T_r) = \ln P_r^0(T_r) + \omega \ln P_r^1(T_r) \quad (96)$$

Where,

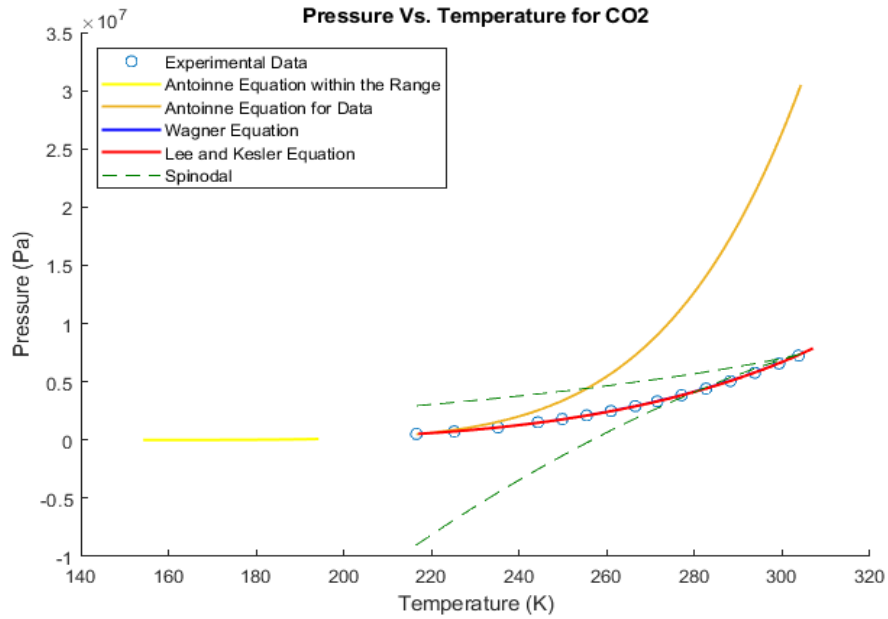
$$\ln P_r^0(T_r) = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln(T_r) + 0.169347 T_r^6 \quad (97)$$

$$\ln P_r^1(T_r) = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.43577 T_r^6 \quad (98)$$

$$\omega = \frac{\ln(P_{rn}^{sat}) - \ln Pr^0(T_{rn})}{\ln P_r^1(T_{rn})} = 0.224 \quad (99)$$

$T_{rn}$  is the reduced normal boiling point and  $P_{rn}^{sat}$  is the reduced vapor pressure corresponding to 1 standard atmosphere.

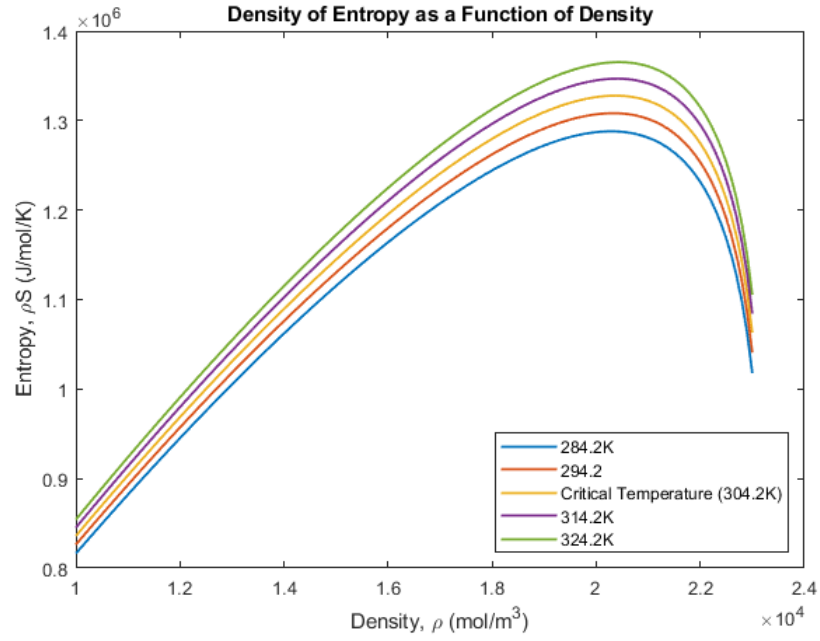
This equation is similar to the Wagner Equation and expresses the reduced vapor pressure as a function of reduced temperature. It is used for Vapor Pressure of non-polar, non-associating fluids.



**Figure 4:** Pressure as a Function of Temperature along the Vapor – Liquid Saturation Curve for various equations.

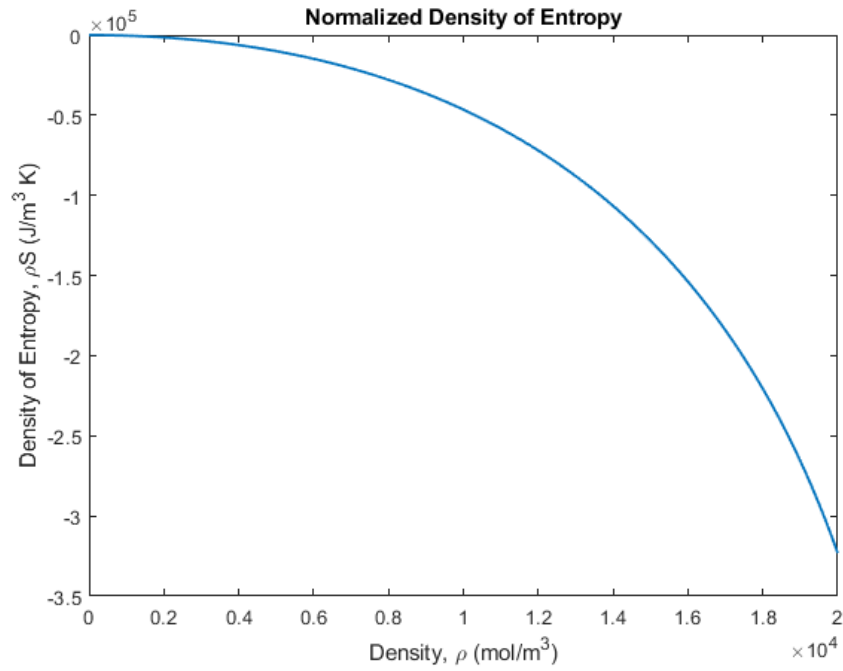
The above plots show that the Wagner Equation and the Lee and Kesler Equation give highly accurate prediction of the saturation pressure data and coincide exactly with the measured data. Both the equations give the similar pressures as functions of temperatures and overlap each other.

### 3.3. ENTROPY



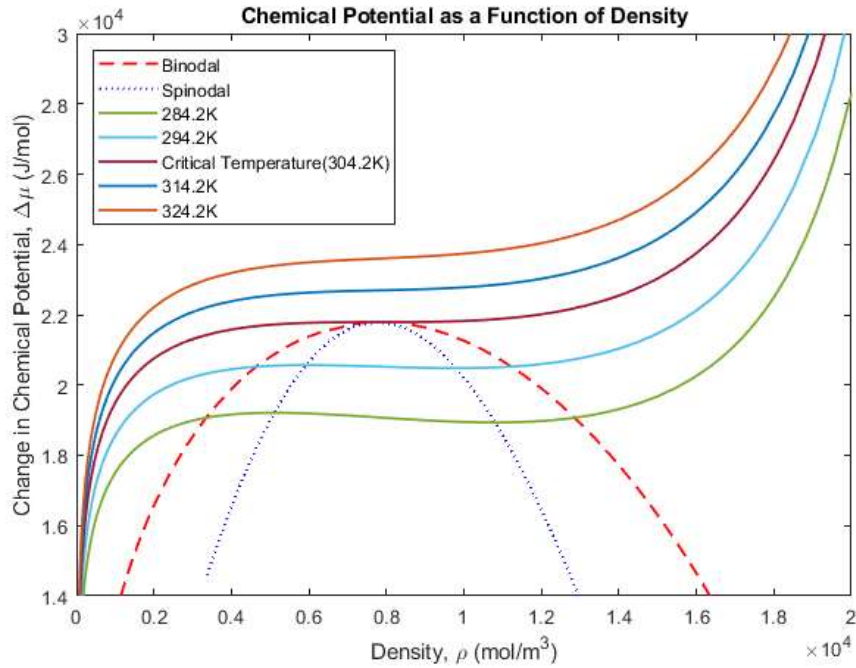
**Figure 5:** Density of Helmholtz Energy as a Function of Density.

The normalized density of entropy can be evaluated as a function of density using equation (46).

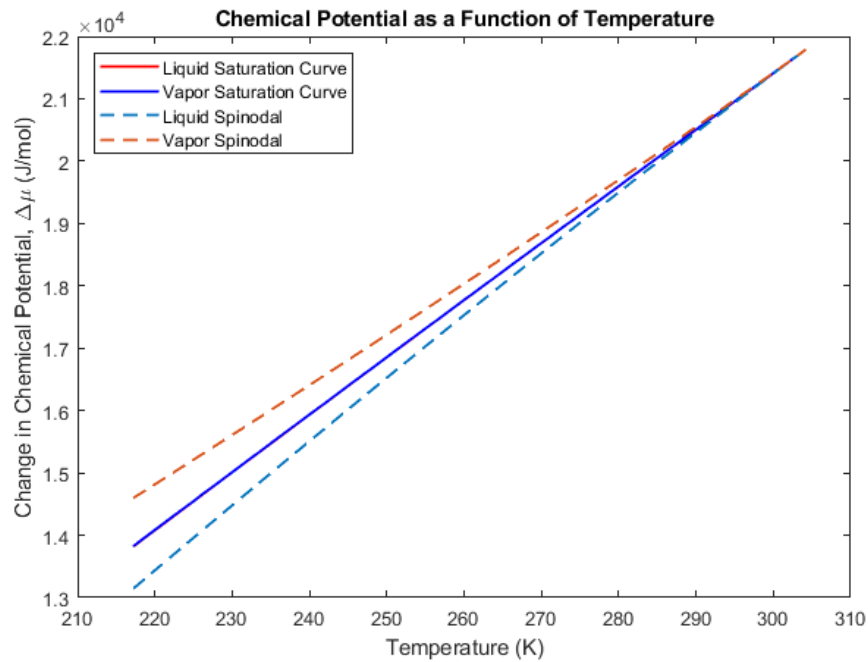


**Figure 6:** Normalized Density of Entropy as a Function of Density.

### 3.4. CHEMICAL POTENTIAL



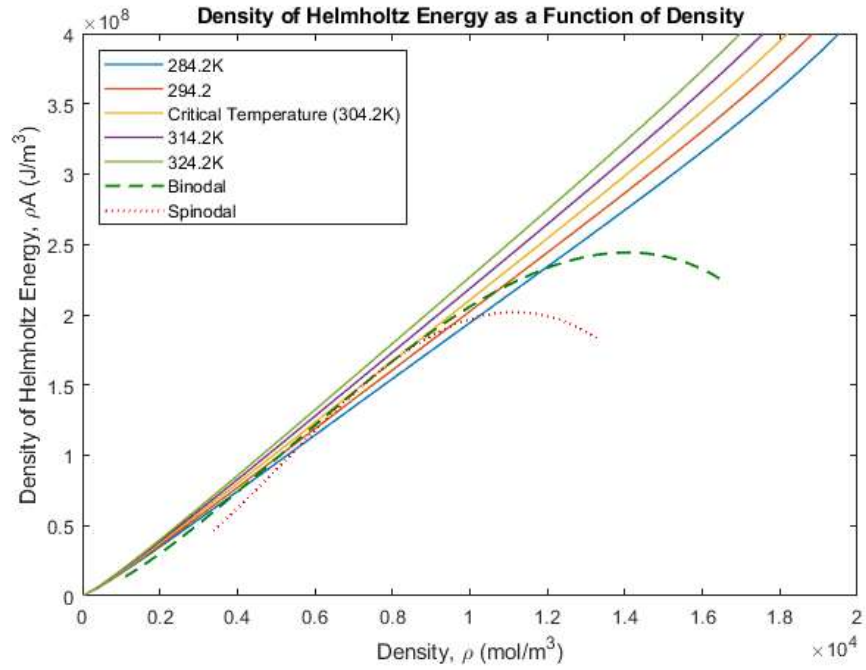
**Figure 7:** Chemical Potential as a Function of Density



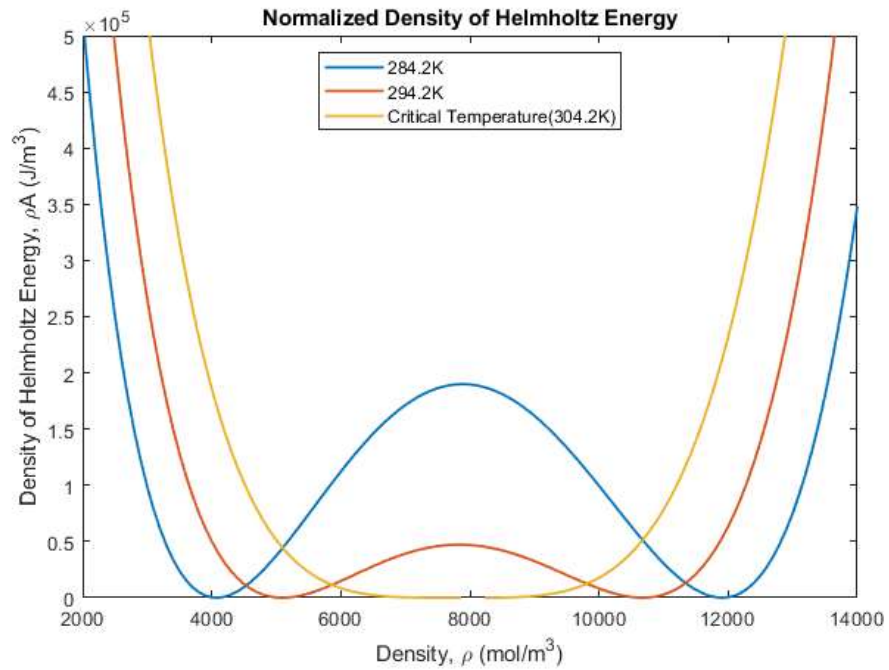
**Figure 8:** Chemical Potential as a Function of Temperature

From the figure above we notice that the vapor saturation curve coincides with the liquid saturation curve which agrees with the stability criteria that the chemical potential of the two phases are equal.

### 3.5. DENSITY OF HELMHOLTZ FREE ENERGY



**Figure 9:** Helmholtz Energy Density as a Function of Density



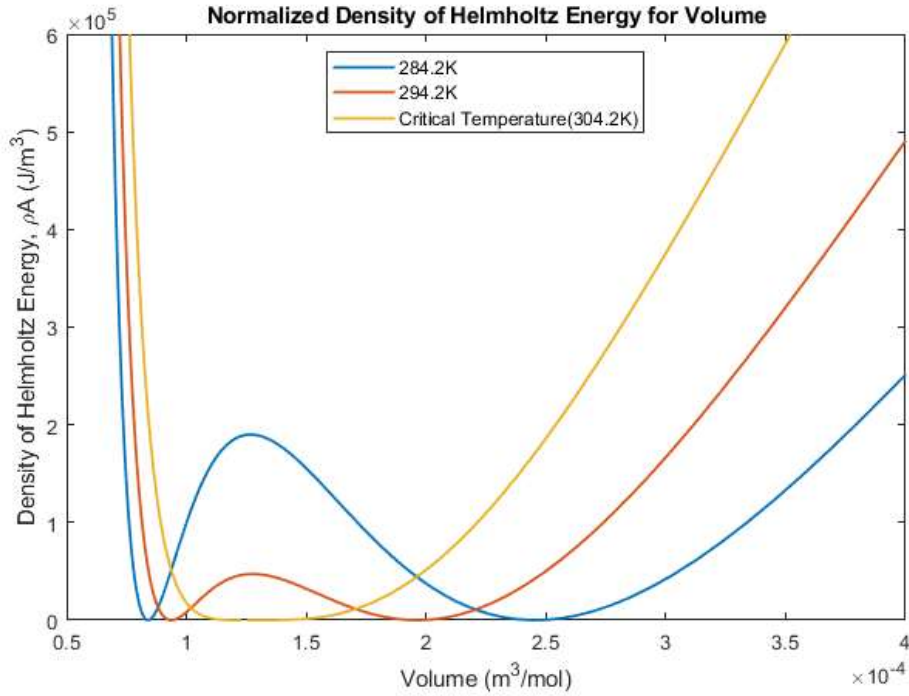
**Figure 10:** Normalized density of Helmholtz Free Energy as a function of Density.

The Helmholtz energy density curve shown in Figure 9 shows very small deviations and is almost a straight line which is not suitable to find the liquid and vapor densities along the saturation curve. This plot is normalized as shown in Figure 10 by subtracting the equation of the line joining the two points:

$$\rho A_{norm} = \rho A - (m\rho + c) \quad (100)$$

Where,  $m \rightarrow \text{slope}$  and  $c \rightarrow \text{intercept}$  corresponding to the isotherm.

The plot for the normalized density of Helmholtz energy shows very distinct curves and gives the vapor and liquid densities for the saturation curve. Similarly, a plot for the normalized density of Helmholtz energy as a function of volume is plotted which also has very distinct curves giving the accurate vapor and liquid volumes for the saturation curve for the isotherm.



**Figure 11:** Normalized Density of Helmholtz Free Energy as a function of Volume.



## 4. PART B

### 4.1. OIL RECOVERY PROCESS

Carbon dioxide is used in enhanced oil recovery operations by flooding the reservoir with CO<sub>2</sub> gas under very high pressures. Enhanced oil recovery using carbon dioxide involves injecting the gas under high pressure allowing the gas to flow through fractures permeating the structure and occupies the pore spaces. The gas thus pushes out the oil through the fractures into the production wells. The gas is then separated, recycled and re-injected into the well to repeat the process. This results in extraction of about 30 to 60 percent of the oil to be recovered compared to the 20 to 40 percent of the oil recovery using the conventional techniques.

Under supercritical conditions, the compound's liquid-vapor boundary ceases to exist and the fluid properties can be manipulated by implementing changes in pressure and temperature. A supercritical fluid has liquid – like density, but exhibits gas – like diffusivity, viscosity and surface tension properties. The gas – like properties allow high mass transfer and high miscibility.

Carbon dioxide is a preferred solvent under supercritical conditions for oil recovery over water as it is an organic solvent and would show very high miscibility in oil as compared to supercritical water which is a polar inorganic solvent. Carbon dioxide also has relatively low critical point values in comparison to water as can be seen in the table below. This allows easier designs and maintenance for equipment being used.

Carbon dioxide is desirable over other organic solvents due to its relatively inert nature and is inflammable, making it ideal for oil recovery. CO<sub>2</sub> also leaves lower amounts of residue in the products and it is available in relatively pure form in large quantities.

To compress the gas to high pressures, the gas is first compressed under adiabatic conditions resulting in high pressures and temperatures. The gas is then cooled at constant pressure releasing heat, thus obtaining gas at room temperature and high pressures. The system is considered to be an open system and is a steady state process.

### 4.2. PROCESS PARAMETERS:

<b>Flow Rate</b>	1000 kg/hr
<b>Compressor Efficiency</b>	80%
<b>State 1</b>	Pressure: 0.138 MPa Temperature: 25°C = 298K Volume = 0.0178 m <sup>3</sup> /mol Volumetric Flow Rate = 404.545 m <sup>3</sup> /hr
<b>State 2</b>	Pressure = 6.89 MPa
<b>State 3</b>	Pressure = 6.89 MPa Temperature = 298K Volume = 9.6977*10 <sup>-5</sup> m <sup>3</sup> /mol Volumetric Flow Rate = 2.204 m <sup>3</sup> /hr

**Table:** Process Parameters for the Oil Recovery Process

The volume of various states of the process are evaluated using the Van der Waals Equation of State.

### 4.3. WORK AND HEAT REQUIREMENTS

The process path is evaluated using the Van der Waals Equation of State to find the intermediate and final conditions of the gas. The work requirements for the compressor can be estimated using the second law of thermodynamics which states that the change in entropy for a reversible process is zero.

$$\Delta S = 0 \quad (101)$$

Entropy change is defined using equation (41).

Solving the above equation along with the Van der Waals equation of state, (2) to find the temperature and volume of the final conditions at the end of the adiabatic compression. The result obtained gives the conditions for the reversible process.

$$T_{2rev} = 635.76 \text{ K}$$

$$V_{2rev} = 7.4268 * 10^{-4} \frac{m^3}{mol}$$

Flow rate at the end of the reversible adiabatic compression:

$$V'_{2rev} = 16.879 \frac{m^3}{hr}$$

To find the work for the actual system (irreversible process), the efficiency of the compressor must be taken into account. The work for the irreversible process is calculated using the enthalpy change of the system using the overall energy balance for an open system for a steady state process is given by:

$$\Delta \left[ H + \frac{1}{2} u^2 + zg \right] = Q + W \quad (102)$$

Since there is no change in the flow rate,  $\Delta u = 0$ .

Also there is no potential energy change as the level of the gases entering the system and leaving the system are the same, giving us,  $(\Delta z)g = 0$ .

For an adiabatic process,  $Q = 0$ .

Therefore, the reversible work is given as:

$$W = \Delta H = [H_f - H_i] \quad (103)$$

The specific heat capacity at constant pressure is a function of temperature:

$$C_p = R[5.457 + 1.045 * 10^{-3}T - 1.157 * 10^{-5}T^{-2}] \quad (104)$$

For the reversible process, using (53), work done for the adiabatic process,

$$W_{rev} = 1.4353 * 10^4 \frac{J}{mol}$$

The work done for the irreversible process,

$$W_{irr} = \frac{W_{rev}}{\eta} \quad (105)$$

For the actual work requirements for the adiabatic compression,

$$W_{irr} = 1.7942 * 10^4 \frac{J}{mol}$$

Using the work done for the irreversible process and equating it to the enthalpy change as in (53), the actual temperature and pressure is evaluated.

$$T_2 = 708.34 \text{ K}$$

$$V_2 = 8.3745 * 10^{-4} \frac{m^3}{mol}$$

Volumetric Flow rate at the end of the irreversible adiabatic compression:

$$V_2' = 19.033 \frac{m^3}{hr}$$

From equation (102), the energy balance for isobaric cooling is:

$$\Delta H = W + Q \quad (106)$$

Work done for a constant pressure process, the work done is stated as:

$$W = -P\Delta V \quad (107)$$

Work required for the isobaric cooling,

$$W = 5.1018 * 10^3 \frac{J}{mol}$$

The heat for the process can hence be evaluated as:

$$Q = \Delta H + P\Delta V \quad (108)$$

Heat released from the system,

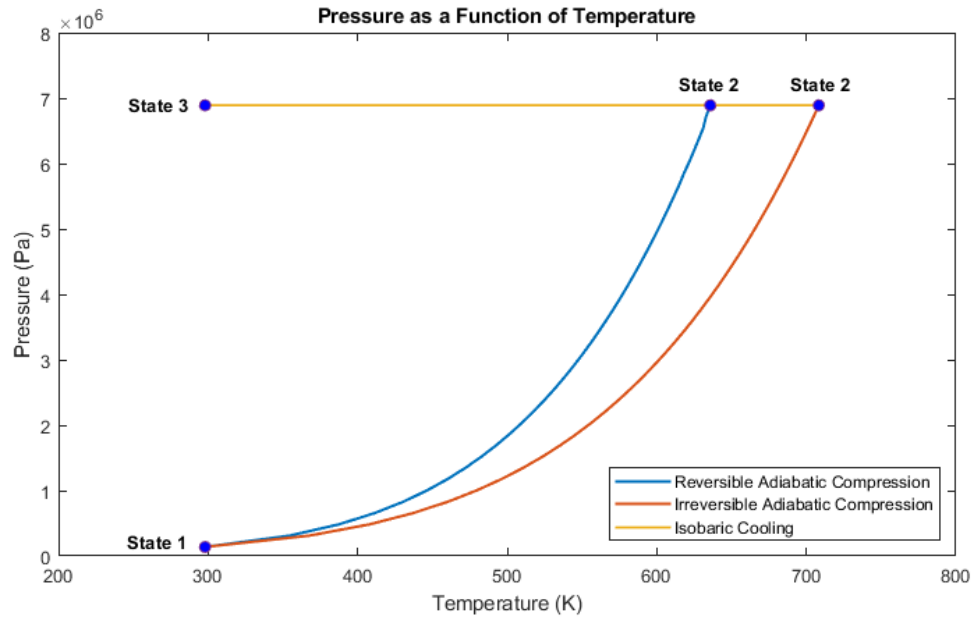
$$Q = -2.8666 * 10^4 \frac{J}{mol}$$

PROCESS	ENERGY (kJ/hr.)	ENERGY (kJ/sec)
Reversible Adiabatic Compression	326,204.5455	90.6123
Irreversible Adiabatic Compression	407,772.7273	113.2702
Isobaric Cooling (Work)	115,950	32.2083
Isobaric Cooling (Heat)	-651,500	180.972

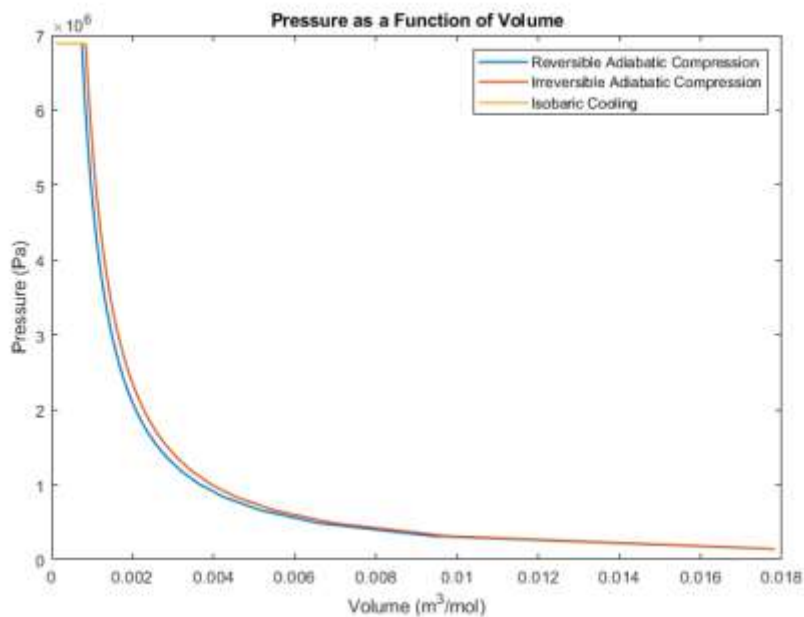
**Table:** Work and Heat Requirements

#### 4.4. PROCESS PATHS

The process paths for the two processes give us important details regarding the heat and work requirements and the effectiveness of the processes.



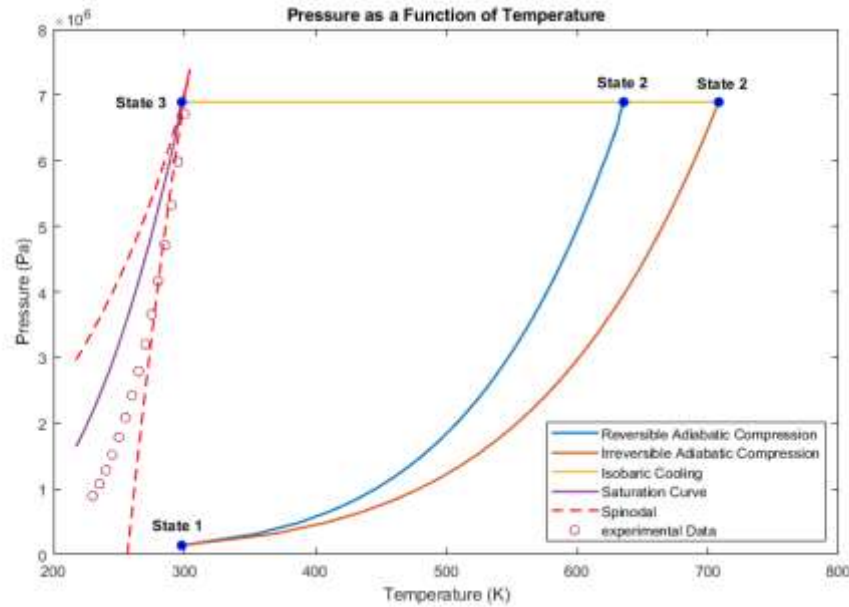
**Figure 12:** Pressure as a function of Temperature for the Oil Recovery Process.



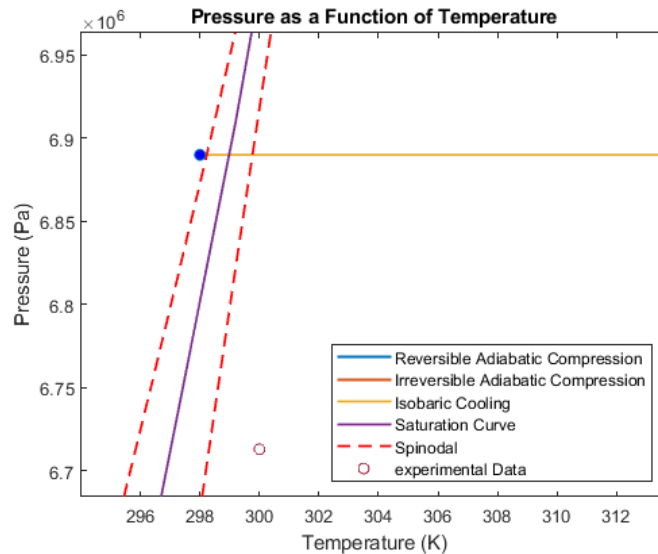
**Figure 13:** Pressure as a function of Temperature for the Oil Recovery Process.

The pressure – volume graph shows that there is a very small change in the volume for the isobaric cooling process as compared to the temperature for the same process. Whereas, the adiabatic compression leads to a large change in the volume of the gas resulting in effective compression to high pressures as required for the oil recovery.

The comparison of the process paths with the data plots obtained in the introductory part for the pressure, temperature and volume data for the liquid – vapor saturation curve (binodal) shows us that the final state is in the liquid phase as seen in figure 13 and figure 14. This ensures that the gas can be pumped efficiently through the pumps without any hindrance to the extraction process.

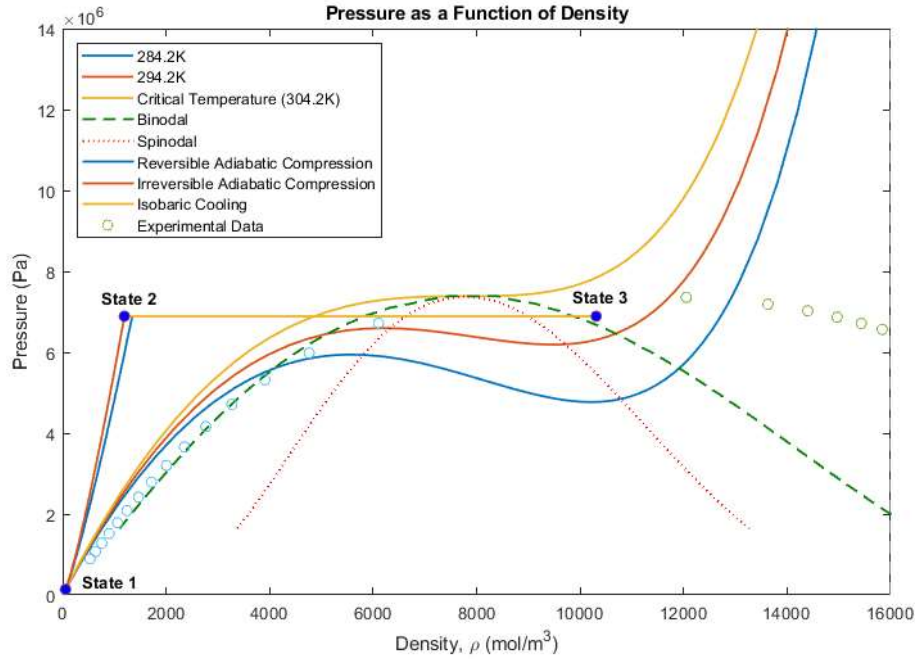


**Figure 14:** Pressure as a function of Temperature for the Oil Recovery Process.



**Figure 14.1:** Pressure as a function of Temperature for the Final State.

The process path in figure 14.1 when compared to the experimental saturation data for show that the final state (State 3) is in the liquid phase region. However, comparison of the process path with the experimental liquid – vapor saturation data in Figure 15, points out that the final state is in the two phase region. This result is not suitable for the operation of pumping the gas into the oil reservoir. This would cause extensive damage to the pumps being used resulting in very poor efficiency of extraction.



**Figure 15:** Pressure as a function of Density for the Oil Recovery Process.

## 5. CONCLUSION

Enhanced Oil Recovery using Carbon dioxide was studied assuming the Van der Waals equation of state is applicable to carbon dioxide. Several thermodynamic plots were studied and conclusions were drawn. The thermodynamic properties derived using the Van der Waals Equation of State provided satisfactory data and results. However, comparison with the experimental data for real gas showed large deviations. Hence, Van der Waals equation is not the most suitable equation of state for the studies of real gases. Several other alternative equations of state exist which account for the various deviations from ideality to a great extent and take into the acentric factor. Most of these equations are used to find the Vapor – Liquid saturation data.

The generalized cubic equation of state for the vapor and vapor like roots are:

$$V = \frac{RT}{P} + b - \frac{a(T)}{P} \left( \frac{V - b}{(V + \epsilon b)(V + \sigma b)} \right)$$

Similarly, the generalized cubic equation of state for the liquid and liquid like roots:

$$V = b + (V + \epsilon b)(V + \sigma b) \left[ \frac{RT + bP - VP}{a(T)} \right]$$

The numerical assignment for parameters are given as:

Equation of State	A(Tr)	$\sigma$	$\epsilon$	$\Omega$	$\Psi$	$Z_c$
Van der Waals	1	0	0	1/8	27/64	3/8
Redlich/Kwong	$Tr^{-1/2}$	1	0	0.08664	0.42748	1/3
Peng/Robinson	$\alpha(Tr, \omega)$	$1 + \sqrt{2}$	$1 - \sqrt{2}$	0.07780	0.45724	0.30740

**Table:** Parameter Assignments for Equations of State

$$\alpha(Tr, \omega) = \left[ 1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) \left( 1 - Tr^{\frac{1}{2}} \right) \right]^2$$

The most accurate of the equations of state is the Peng/Robinson equation due to the consideration of the eccentric factor.

## 6. REFERENCES

1. Smith, J.M., Van Ness, H.C., Abbott, M.M. (1959). *Introduction to Chemical Engineering Thermodynamics, Seventh Edition*. New York: McGraw-Hill.
2. Mikhail, A. (2018). *ENCH 610 Chemical Engineering Thermodynamics Lecture Notes*.
3. Cox, J.D., Wagman, D.D., Medvedev, V.A., *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corp., New York, 1984, 1.
4. Chase, M.W., Jr., *NIST-JANAF Thermochemical Tables, Fourth Edition*, J. Phys. Chem. Ref. Data, Monograph 9, 1998, 1-1951.
5. Span, R.; Wagner, W., *A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa*, J. Phys. Chem. Ref. Data, 1996, 25, 6, 1509-1596.
6. Newman, Nicholas, *How to recycle CO<sub>2</sub>*, Article on the Eniday website.