

Lab Session 2 - Phase Transitions

FYS2160 at University of Oslo

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1 Abstract

We find out that Trouton's rule, though a good general solution to such problems, is not applicable to all types of fluids, specifically water in this case. We additionally look at different methods of finding the enthalpy of phase transitions, and find $H_m = 178898.25J$ for melting an ice cube in a 28°C water bath, and $H_v = 42883.06 \pm 831.96J$

2 Introduction

In thermodynamics, perhaps one of the most important concepts is that of phase-transitions. It is central to many concepts in our everyday life, like cooking or air-conditioning.

We'll take a closer look at the concept of phase-transitions in this report, more specifically the heat of vaporization and melting of water, respectively.

To do this, we're going to employ a few equations relating to the relationship between pressure and temperature, for example the Clausius-Clapeyron relation:

$$\frac{\delta P}{\delta T} = \frac{H}{T\Delta V} \quad (1)$$

where δP is the change in pressure, δT is the change in time, H is the enthalpy and ΔV is the change in volume.

A perhaps more intuitive way of extracting the values we wish to study (the enthalpy) would be to look at the left hand side of the equation, and realize that what we're looking at here is the slope of a $P(T)$ pressure-temperature coexistence line.

Additionally, if we examine a system in equilibrium, where we assume that the molar volumes are negligible in comparison to each other and that we're working with an ideal gas with constant enthalpy for small ΔT 's, we can rewrite Equation [1] to be:

$$\ln \frac{P_1}{P_2} = -\frac{H_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2)$$

where P_1, T_1 and P_2, T_2 are two different points on the liquid-vapour coexistence line.

Additionally, we establish two more relations which we can use to calculate the enthalpy of melting, namely:

$$m[H_m + C_v(T_2 - T_0)] = C_0(T_1 - T_2) \quad (3)$$

where m is the mass, H_m is the enthalpy of melting, C_v is the specific heat capacity of water and T_0, T_1, T_2 are temperatures at three different points along the logging of data. C_0 can be calculated as:

$$C_0 \frac{\delta T}{\delta t} = UI$$

where $\frac{\delta T}{\delta t}$ are the changes in temperature with regards to time, or more intuitively, the slope of a graph measuring these two. U and I are the voltage and current respectively. With what we've now established, we now need only to log the respectively required data (P and T for H_v and T and t for H_m), which is described below in the Method section.

3 Method

For measuring the heat of vaporization, we're going to be using an apparatus to decrease the pressure in a container to below that of the atmospheric pressure. This in turn will lower the vaporization temperature of our liquid. We repeat this for a set number of different pressures, noting the pressure and associated vaporization temperature for each one. After retrieving these values, we can do a fit on our data in order to predict the enthalpy of vaporization.

For measuring the heat of melting, we're going to first fill a calorimeter with a known volume of water. From there we will heat it to a specified, known temperature. When we've stabilized at this temperature, which we will measure using Capstone, we retrieve an ice cube of about $m = 250g$ and leave it in the calorimeter. As the ice cube melts, we continue to monitor and log the temperature change using Capstone. When all the ice is melted and the temperature has finally stabilized, we can then use the data collected in order to determine the enthalpy of melting.

4 Results

Let us first tackle the heat of vaporization. We retrieve the data-points, and plot them in regards of Equation [2]:

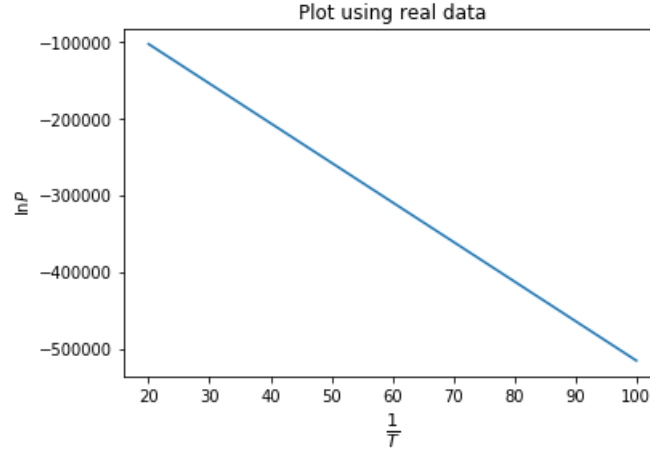


Figure 1: A least-squares fitted plot using the points logged when creating equilibrium between pressure and temperature

And we retrieve a slope as $a = -5154.40$ which is our $\frac{\Delta H}{R}$ through the points: $(T_1 = 87.1^\circ C, P_1 = 62.1 kPa)$ $(T_2 = 91.2^\circ C, P_2 = 73.0 kPa)$, such that $H = 42833.06 J$

Let us now move on to the **heat of melting**:

We retrieve a block of ice with the mass $m = 236.79 g$, which loses about $0.71 g$ worth of mass before putting it in the calorimeter. It's new mass is then $m = 236.08 g$. We note the temperature before dropping in the ice cube to be $T_1 = 28.0^\circ C$, and that the slope $a = 0.0113$, we can then find C_0 in Equation [3]

$$C_0 = \frac{90.19 V \cdot 0.7559 A}{0.0113} = 6033.15 \frac{J}{kg \cdot K}$$

We further note that the temperature at the bottom plateau (ie. where all the ice has melted), is $T_2 = 13.4^\circ C$, such that, using Equation [3]. Recall additionally that $T_0 = 0^\circ C$

$$H_m = \frac{(28^\circ C - 13.4^\circ C) \cdot 4200 J/kg \cdot K}{236.08 \times 10^{-3} kg} - (13.4^\circ C) 6033.15 J/kg \cdot K$$

$$H_m = 178898.25 J$$

5 Discussion

Regarding the sample size

One of the most glaring issues of this report is the lack of data points. This is entirely my fault, I wasn't aware of the fact that the experimental lab videos provided on the semester page [1] didn't include proper data (which they did last time), and by the time I found out it was too late. However, that being said I don't think it messes up our results too much, as I did some extra digging around and found [2] and used data from there and found much the same results, specifically:

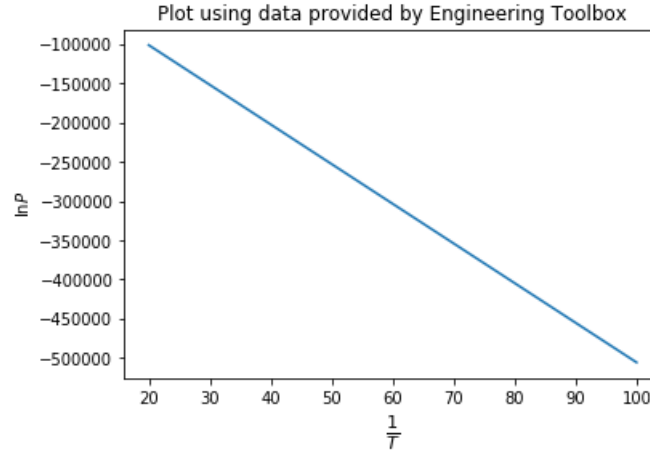


Figure 2: A least-squares fitted plot using the points extracted from Engineering Toolbox

which gives us a slope of $a = -5060.74 \pm 11.96$ which, although significantly different, indicates that our original data isn't a total disaster. Hope this isn't too much of a problem!

Accuracy of H_v

Perhaps one of the most interesting things to discuss would be to compare H to the relation:

$$\frac{H_v}{RT_b} = 11 \pm 1$$

$\frac{H_v}{R}$ is already known (it is our slope), and we can multiply this with our x-elements in the plot (these are already on the form $\frac{1}{T_b}$). We find the following values:

	Temperature [°C]	Pressure [kPa]	Constant
1:	87.07	62.07	14.31
2:	91.2	73.0	14.15

Table 1: Constants indicating whether or not our H is a realistic value.

We see that we do miss by a little bit, but not by much. Besides, the theoretical entropy of water vaporization is $H = 40650 J/mol$.

Additionally, we should remind ourselves that the system is not perfect, and that the pressure will increase again over time, instead of being constant.

All in all, I'd probably add a ± 100 to our $\frac{H_v}{R}$ meaning that $H_v = 42883.06 \pm 831.96 J$. Additionally, I'd like to say that another reason why we get such a large deviance from expected values is explained below in *Question 1*.

Accuracy of H_m

In my opinion, there aren't as many sources of error here as the other experiment. The only things I can think of are potential thermal leakage from the calorimeter, or alternatively the ice cube losing mass when being transported from the weight and into the calorimeter, although this is much less dramatic than the thermal leakage. Therefore, I decide not to include any inaccuracies to the result, as both of these factors are incredibly small in comparison to the final result. That being said, I do believe there is something wrong with my calculation here, though I can't for the life of me track down what that error may be.

In conclusion, there is an error somewhere, but otherwise we're pretty much correct, I'm assuming.

Given questions

- **1:**

My results aren't very good, but here's what I do know. The likely deviation between Trouton's rule and water is mainly (I believe) a result of physical phenomena, not inaccurate measurements. The reason I believe this is because Trouton's rule does not account for interactions between molecules, in our case the very famous hydrogen bonding, which of course causes the high boiling point of water, thus deviating from the rule's predicted values.

Do note that this is also the case for other molecules that form strong bonds like ethanol, which also hydrogen bonds

- **2:**

It will likely have a small effect on our readings, but I do believe it is ultimately negligible to the data as a whole.

- **3:**

If we turned off the cooling then the steam would travel throughout the entire system, likely causing the assumptions we made when declaring Equation [2] to fail, such as that the molar volume of water was negligible compared to the vapour.

- **4:**

Because we are interested in seeing the temperature of the vapour, not of the liquid. As the liquid is supplied energy, its temperature increases until it hits a break point where significantly more energy must be supplied until the vapour "unbonds itself" from the liquid. The reasoning for this is discussed in *Question 5* below. And as such, we might get inaccurate and/or unstable readings should we examine the liquid instead of the gas.

- **5:**

Because the energy required to transition phases from liquid to gas is significantly higher than from solid to liquid. This is the case because we need significantly more kinetic energy in order to fully separate particles, as opposed to the kinetic energy in a liquid, where the kinetic energy is "just enough so that they can move around each other".

6 Conclusion

In conclusion, we find that Trouton's rule isn't applicable to all different fluids, particularly in this case for water, H_2O because of its strong hydrogen bindings. We have also looked into different ways of extracting the enthalpy of phase-transitions, for both solid \rightarrow liquid and liquid \rightarrow vapour respectively.

We find then enthalpy of $H_m = 178898.25J$ for melting an ice cube in a 28°C water bath, and $H_v = 42883.06 \pm 831.96J$ for water boiling in a semi-vacuum.

References

- [1] URL: <https://www.uio.no/studier/emner/matnat/fys/FYS2160/h20/index.html>.
- [2] URL: https://www.engineeringtoolbox.com/water-properties-d_1573.html.
- [3] Experimental assignment. URL: https://www.uio.no/studier/emner/matnat/fys/FYS2160/h20/Labs/Lab2/lab2_experimental.pdf.
- [4] Numerical assignment. URL: https://www.uio.no/studier/emner/matnat/fys/FYS2160/h20/Labs/Lab2/lab2_numerical.pdf.

7 Appendices

Appendix A - Molecular Dynamics

We initially see that there is little to no movement at the temperature $T = 250K$. We then increase the temperature to $T = 300K$, and as the temperature of the ice approaches its melting point we see increased movement and increased degrees of freedom. The total energy of such an environment is illustrated by this plot:

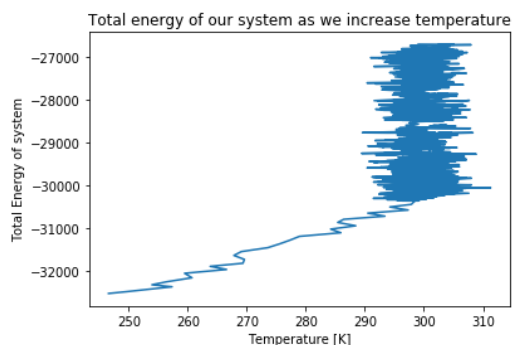


Figure 3: The total energy of H_2O as it goes from rather stationary ice and over to more free flowing water.

At first I thought something had gone wrong with this plot. I'm not too well versed with MD and I thought it was a bit weird as to why the temperature was oscillating so violently, not to mention that it was so compact. However, when you consider the fact that the entire area of the plot dedicated to liquid had a total of 20000 time-steps, and that the temperature was oscillating on the readings in the command prompt window (plus I did it twice just to be sure and got the same results), I now believe that this plot is correct.

As to commenting the results, as expected, the energy of the system increases with higher temperatures.

All in all the readings make sense, and if we increase the temperature further we get:

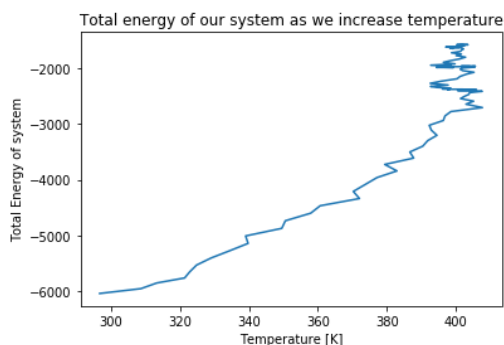


Figure 4: The total energy of H_2O as it goes from liquid into vapour

Here we see much the same behavior. In fact, we'd probably get practically the same plot as Figure [3]. The only reason I reckon this one is not the same is because I limited it to only 1000 time steps, which I felt was sufficient seeing as:

- a) The plot wasn't very interesting.
- b) The run time for 1000 time steps was already 35 minutes.

So in conclusion, we see clearly the extra energy that is supplied when the material experiences a phase shift. I imagine if we let it run for longer the, the second plot Figure [4] would probably stretch even higher.

Appendix B - the van der Waals Equation

- **The pressure**

The pressure of a van der Waals fluid is

$$P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

otherwise known as the Equation of State for a van der Waals fluid

- **Gibbs free energy**

Knowing from above P and the given F , we can express the Gibbs free energy as:

$$G = -NkT \left(\ln \left(\frac{3V}{3Nb} - 1 \right) \ln_Q(T) + 1 \right) - \frac{NaNb}{Vb} + P \frac{3NbV}{3Nb}$$

- **Entropy**

$$S = -\frac{\delta F}{\delta T}$$

$$S = NK_B \left(\ln \left(\frac{n_Q(V - Nb)}{N} \right) + 1 \right) + Nk_B T \frac{\delta}{\delta T} \ln t^{3/2}$$

$$S = NK_B \left(\ln \left(\frac{n_Q(V - Nb)}{N} \right) + \frac{5}{2} \right)$$

- **Enthalpy**

If the enthalpy is given as $H = F + TS + PV$, we know that $U = F + TS$, which gives:

$$U = N \left[\frac{3}{2} k_B T - \frac{Na}{V} \right]$$

Which means that H is given as:

$$H = N \left[\frac{3}{2} k_B T - \frac{Na}{V} \right] + P(V - Nb)$$

We can find the critical parameters using the first and second derivatives at inflection to equal zero, that is:

$$\begin{aligned}\left(\frac{\delta P}{\delta V}\right)_C &= 0 \\ \left(\frac{\delta^2 P}{\delta V^2}\right)_C &= 0\end{aligned}$$

which then gives

$$V_C = 3Nb, T_C = \frac{8a}{27bk}, P_C = \frac{a}{27b^2}$$

As such, we can use this to represent the reduced variables as:

$$V_R = \frac{V}{V_C}, T_R = \frac{T}{T_C}, P_R = \frac{P}{P_C}$$

We can now use these reduced variables to find the reduced Gibbs free energy per particle. Reader beware, this is a very ugly and messy expression (in my opinion, pretty hard to look at):

$$G = -NkT \left(\ln \left(\frac{3V}{3Nb} - 1 \right) bn_Q(T) + 1 \right) - \frac{NaNb}{Vb} + P \frac{3NbV}{3Nb}$$

Let us now insert the reduced variables, such that:

$$\frac{G}{NkT_C} = -\frac{NkT}{NkT_C} (\ln(3V_R - 1)bn_Q(T) + 1) - \frac{aN}{3bNkT_C V_R} + \frac{3bpV_R}{kT_C}$$

We see now that we can cancel out a fair bit:

$$\frac{G}{NkT_C} = -T_R \ln(3V_R - 1) + f(T_R) - \frac{aN27b}{3bNV_R a} + \frac{3bpV_R 27b}{8a}$$

We see now that we have the requested dimensionless Gibbs free energy per particle, as:

$$G_R = \frac{G}{\frac{3}{8}NkT_C} = -\frac{8}{3}T_R \ln(3V_R - 1) - \frac{3}{V_R} + P_R V_R + f(T_R)$$

The plots are as follows: We find the coexistence line to be:

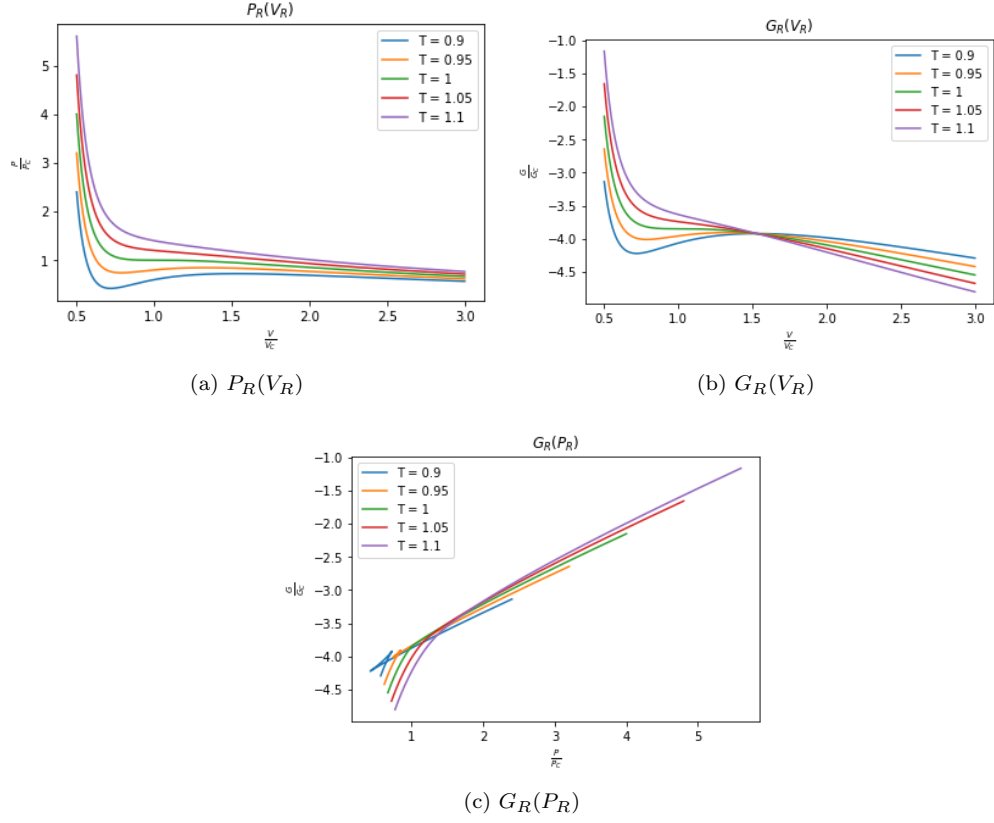


Figure 5: The different requested plots. We use the the coordinates where the function crosses itself in Figure [5c] to create a linear regressed line for the coexistence line.

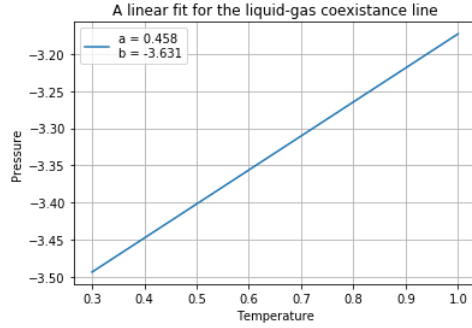


Figure 6: The coexistence line for the van der Waals fluid plotted for $0.3T_B$ to $1T_B$

This calculation should be fairly accurate, but given that I used five points to find the best-fit, we also get a deviation, and a pretty large one at that, with a standard deviation of ± 14.237 . This suggests to me that the line probably should've been a curve instead of a straight line, and as such, not very accurate (I'm assuming).

We find then that the slope is given as $a = 0.458$, giving us:

$$\frac{\Delta P}{\Delta T} = 0.458 = \frac{H}{T\Delta V}$$

I don't know what to do from here, sadly, so I cannot find H , but we can map van der Waals fluid to water as:

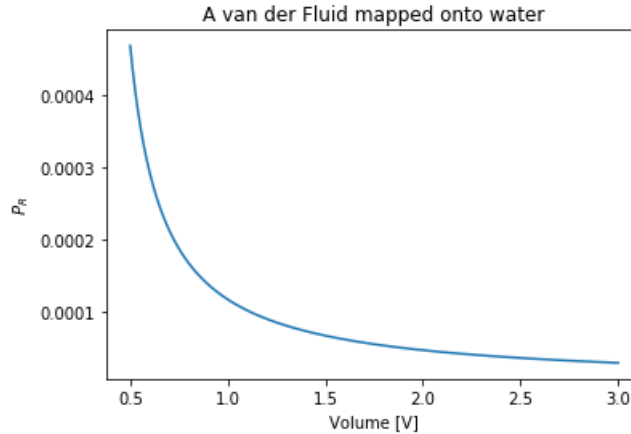


Figure 7: The van der Waals fluid mapped onto water.

- **Trouton's Rule follows corresponding states**

I'd say yes(?), but I can't argue as to why. My only reasoning is that I can't see why it wouldn't/where the two theorem/rules/ideas conflict, though that might just be my lack of understanding. I did however see some research online indicating that the two are related, citing that Trouton's rule follow the similarity of the potential function of molecular interaction, but this is beyond the bounds of my knowledge.

- **Alternative explanation for Trouton's Rule using entropy change**

Trouton's rule can be explained using Boltzmann entropy, $S = k_B \ln \Omega$, where Ω is some quantity of an ideal gas, on the relative change in free volume as a fluid goes from liquid to vapour.

Appendix C - Notes and Equipment

Notes:

I would just like to include here that I hope it's not too big a problem that I had such little data to work with, with everything that's going on (Covid, other courses etc.) I've been so busy the idea that the data wasn't included on the semester page completely crossed my mind, and although that's no excuse I'd like to apologize for that and I hope it's not too big of a deal.

For measuring H_v :

- Glass apparatus with water and pebbles
- Thermometer
- Cooling element
- Heating element
- Valve to vacuum pump
- Valve to atmosphere
- Buffer volume glass apparatus
- Pressure sensor

For measuring H_m :

- Calorimeter
- Power supply
- Amperemeter
- Voltmeter
- Thermometer compatible with Capstone
- Digital balance
- Block of ice

Appendix D - Python code

```
# -*- coding: utf-8 -*-
import numpy as np
import matplotlib.pyplot as plt
import scipy.stats as sc

"""
EXPERIMENTAL PART
Data from semester-page (not very good)
"""

plt.figure()
T = [1/(87.07+273.15), 1/(91.2+273.15)]
P = [np.log(62.07), np.log(73.0)]
lin = sc.linregress(T,P)
x = np.linspace(20,100, 1000)
def fit(x):
    return lin[0]*x + lin[1]
test = np.array(T)
cons = test*-lin[0]
plt.plot(x, fit(x))
plt.xlabel(r'$\frac{1}{T}$', size=16)
plt.ylabel(r'$\ln\{P\}$')
plt.title('Plot_using_real_data')
plt.show()

"""
Alternative data found on engineeringtoolbox
"""

plt.figure()
T = [1/(60+273.15), 1/(70+273.15), 1/(80+273.15), 1/(90+273.15), 1/(96+273.15)]
P = [np.log(19.95), np.log(31.2), np.log(47.41), np.log(70.18), np.log(87.77)]
lin = sc.linregress(T,P)
x = np.linspace(20,100, 1000)
def fit(x):
    return lin[0]*x + lin[1]
test = np.array(T)
cons2 = test*-lin[0]
plt.plot(x, fit(x))
plt.xlabel(r'$\frac{1}{T}$', size=16)
plt.ylabel(r'$\ln\{P\}$')
plt.title('Plot_using_data_provided_by_Engineering_Toolbox')
plt.show()

"""
ANALYTICAL PART

```

```

"""
V = np.linspace(0.5,3, 2000)
T = [0.9, 0.95, 1, 1.05, 1.1]
def P(V,T):
    return 8/3*T/(V-1/3)-3/(V**2)
def G(V,T):
    return -(8/3)*T*np.log(3*V-1) -3/V + P(V,T)*V
plt.figure()
lst = []
for i in T:
    lst.append(P(V,i))
j = 0
for i in lst:
    plt.plot(V, i[:], label='T=%g' % (T[j]))
    j += 1
plt.xlabel(r'$\frac{V}{V_C}$')
plt.ylabel(r'$\frac{P}{P_C}$')
plt.title(r'$P_R(V_R)$')
plt.legend()
plt.show()

plt.figure()
lst2 = []
for i in T:
    lst2.append(G(V,i))
j = 0
for i in lst2:
    plt.plot(V, i[:], label='T=%g' % (T[j]))
    j += 1
plt.xlabel(r'$\frac{V}{V_C}$')
plt.ylabel(r'$\frac{G}{G_C}$')
plt.title(r'$G_R(V_R)$')
plt.legend()
plt.show()

plt.figure()

for i in range(len(T)):
    plt.plot(lst[i], lst2[i], label='T=%g' % (T[i]))

plt.xlabel(r'$\frac{P}{P_C}$')
plt.ylabel(r'$\frac{G}{G_C}$')
plt.title(r'$G_R(P_R)$')
plt.legend()
plt.show()

```

```

plt.figure()

T2 = np.linspace(0.9,0.95,5)

for i in T2:
    plt.plot(P(V, i), G(V,i), label='T=%g' % (i))
plt.xlabel(r'$\frac{P}{P_C}$')
plt.ylabel(r'$\frac{G}{G_C}$')
plt.title('Plot used to best fit a line through the points where the plot intersects it')
plt.legend()
plt.show()

plt.figure()
Pco = [0.647, 0.686, 0.727, 0.769, 0.812]
Gco = [-4.077, -4.046, -0.417, -3.988, -3.959]

lin = sc.linregress(Pco, Gco)
def fit2(x):
    return lin[0]*x + lin[1]

x = np.linspace(0.3,1,10)
plt.plot(x, fit2(x))
plt.xlabel(r'$Temperature_{[T_B]}$')
plt.ylabel('Pressure')
plt.title('A linear fit for the liquid-gas coexistence line')
plt.legend(['a=%.3f\nb=%.3f' % (lin[0], lin[1])])
plt.grid()
plt.show()
Hv = lin[0]

V = np.linspace(0.5,3, 2000)
T = [0.9, 0.95, 1, 1.05, 1.1]
Pc = 22.064e6
Tc = 647.096
Pr = P(V,Tc)/Pc
plt.figure()
plt.plot(V, Pr)
plt.xlabel('Volume_{[V]}')
plt.ylabel(r'$P_R$')
plt.title('A van der Fluid mapped onto water')
plt.show()

```