Development of a Three Dimensional Pressure-Volume-Temperature Model for use in Teaching Environments

by

Camilo Aladro

Submitted to the Department of
Mechanical Engineering in Partial
Fulfillment of the Requirements for the
Degree of

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ABSTRACT

Three phase equilibrium can be a difficult concept to comprehend, since it has geometric relationships in three dimensions. A teaching aid was developed to aid in explaining phase diagrams to student. The curve was made from transparent sheets of acrylic so the saturation curve could be projected onto the wall from the model. Virial Equations of State, Van der Waals Equation, Benedict-Webb-Rubin Equation, and Redlich-Kwong Equation were evaluated to find the best formula to design the model with. A three dimensional curve for water and carbon dioxide was built using Redlich-Kwong. The major issues with the hardware were scaling inconsistencies between the two plots and incorrect trends on the solid/liquid transition line. These issues can be repaired by adjusting the scale on the matlab file where the curves were generated and consulting experimental data where the Redlich-Kwong approximation fails.

Thesis Supervisor: Gareth H. McKinley
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1 Introduction

Three phase equilibrium can be a difficult concept to thoroughly describe to students, especially using two dimensional media. In essence, a substance's state can be described based on the pressure, temperature, and density of the substance. In many cases, the inverse of density, specific volume, is used as a parameter instead of the density. Specific volume is the volume per unit mass but can also be described in volume per unit mole of molecules. Pressure, volume, and temperature data is needed for many thermodynamic calculations. The heat transfer coefficient (h), entropy (s), and internal energy (u) of a substance can all be determined from the P-V-T data. Three dimensions are needed to understand the parameters which determine whether a substance is a solid, liquid, gas, or plasma.

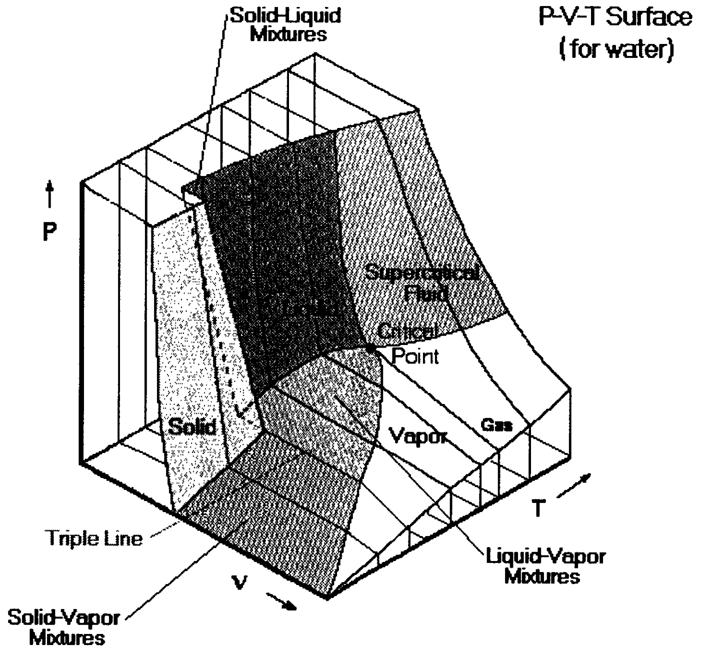


Figure1: P-V-T Surface for Water [1]

Figure 1 is a three dimensional rendering of the states of water. This figure is based on temperature, specific volume, and pressure. One can clearly see the range of a state for all three parameters. If one of three descriptive factors is held constant, a two dimensional "slice" of the system can be plotted. This is a very specific condition that may not be applicable to many situations. This thesis will focus on making a three dimensional set of slices that will allow students to have a better understanding of phase equilibrium as a whole.

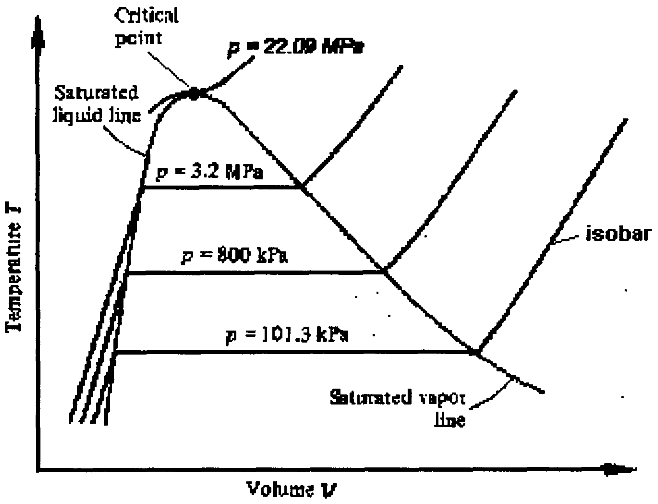


Figure 2: Saturated Substance curve [1]

Figure 2 is a component of phase equilibrium that can be explained via a 3 dimensional model. In figure 1 there is a shaded region marked Liquid-Vapor Mixtures; that region is projected onto a two dimensional plot in figure 2. The curve represents the parameters where a solution is a saturated liquid or saturated gas. The region under the curve denotes the circumstances where vapor and liquid coexist. The chart is very useful in determining the efficiency of a thermodynamic cycle. Saturation of substances does not occur at a constant pressure, volume, or temperature. With a transparent P-V-T model, a professor could color in the mixture region, place the model on an overhead projector, and project the two dimensional curve directly from the three dimensional model. This thesis will focus on making a three dimensional set of slices that will allow students to have a better understanding of phase equilibrium as a whole. Water and carbon dioxide will be modeled to demonstrate how the two substances behave differently when they freeze into their solid state.

2 Three Dimensional Plots

One of the most famous plots was made by the Head of the Cavendish Laboratory at Cambridge University, James Clerk Maxwell, who sent a plaster cast of an energy-entropy-volume (U-S-V) surface to Willard Gibbs in 1874. Gibbs, a physicist at Yale, published a series of papers describing his graphical method for modeling thermodynamic properties of fluids. A surface plot was described mathematically using few diagrams because Gibbs could visualize this plot in his head. The papers did not generate much interest because readers had difficulty envisioning the plot. Maxwell, who was interested in the geometric approach to thermodynamics, built a solid U-S-V model for water. Two plaster casts were made of the model. The model is shown below:

Figure 3: Photograph of Maxwell's cast U-S-V model [3]

Maxwell's cast not only made Gibbs famous, but it made the scientific community aware of the geometric relationships which occur in thermodynamics. Because it was made by hand, the model is just an approximation of the mathematical curve. The U-S-V model described the complex equations in Gibbs' papers. Energy and Entropy are not properties of a substance that are not very tangible. Physical properties like specific volume and pressure are better suited for a student being introduced to thermodynamics. A combination of three-dimensional plots will ultimately make the relationship of thermodynamic properties of a substance more clear.

3 Equations of State

Before any physical model of a pressure-volume-temperature plot can be made, equations describing the physical properties of solutions must be derived. These equations have been calculated and need to be adjusted to the desired parameters. The development of the equations should be understood in order to work with them.

3.1 Ideal Gas Law

The most well know aspect of phase equilibrium is the ideal gas law which was developed by Benoit Paul Emile Clapeyron when he combined Boyle's Law and Charles'law. The ideal gas law is commonly written:

$$P = \rho \, R T \qquad (1)$$

Where P is the pressure of the substance described, ρ is the density, T is the temperature and R is a constant known as the ideal gas constant. The equation provides a model for certain gases which behave "ideally." Furthermore, this model only describes these ideal gasses when in the gaseous phase.

3.2 Virial Equation of State

The ideal gas law was developed from the virial equation of state. A pressure-volume-temperature correlation was developed from a relationship to the substances compressibility factor. One form of the function is:

$$Z = 1 + B(T)/v + C(T)/v^2 + D(T)/v^3 + \ldots \qquad (2)$$

Z is the compressibility factor of the substance and v is the specific volume. B, C, and D are called the viral coefficients which are usually calculated from a model describing the molecular interactions of the molecules of the gas. The first few coefficients can also be determined by matching the plot to empirical data. In the case of ideal gasses, where the molecules interactions are insignificant, the viral coefficients become negligible. The compressibility factor is defined as:

$$Z = P\ v / (R\ T) \tag{3}$$

So for ideal gasses Z = 1; when the terms are rearranged equation 1 is yielded. The formula is very limited in range due to its simplicity.

3.3 Van der Waals Equation

An improvement was made on the virial equation of state by Johannes Diderik van der Waals in 1873. He took into account the volume of the molecules, the inter-particle forces, and the forces the molecules had with the container which lowered the pressure. The van der Waals equation is:

$$P = (R\ T / (v - b)) - (a / v^2) \tag{4}$$

The volume of the molecules is characterized by the constant b which is determined from the molecular diameter known as the van der Waals diameter. a / v^2 adjusts the equation to the less than ideal pressure caused by the molecular forces. Van der Waals' equation did a decent job determining the phase transition line between liquid and gas. The equation does not model the region where liquids and gasses coexist.

3.4 B-W-R Equation

The Benedict-Webb-Rubin (BWR) equation was proposed in 1940 as an improvement on the van der Walls model. Eight constants were used in the BWR equation. The complexity of the function makes it difficult to manipulate. The formula reads:

$$\begin{aligned} P = (R\ T / v) + (R\ T\ B - A - (C/T^2) / v^2) + (R\ T\ b\text{-}a)/v^3 \\ + a\ \alpha/v^6 + c / (v^3\ T^2)\ (1+ \gamma/v^2)\ \exp(-\gamma/v^2) \end{aligned} \tag{5}$$

This complicated needs all eight constants derived for the substance being modeled. Each of these constants is empirically derived by matching a plot of the BWR equation to data collected from a solution which is at the vapor-liquid equilibrium. BWR constants are commonly determined from a specific volume in terms of m^3/kmol. However, having the specific volume in m^3/kg is more applicable in thermodynamic applications. Only select solutions have had their constants determined because of the rigorous process required to find their values.

Table 1: B-W-R Constants [4]

Constant	Units	Butane (C_4H_{10})	Carbon Dioxide (CO_2)	Methane (CH_4)	Nitrogen (N_2)	Carbon Monoxide (CO)
Molar mass m_o	(g / mol)	58.44	44.11	16.11	28.02	28.11
R	(N * m) / (g * K)	0.14226	0.1884833	0.5160769	0.29671	0.2957666
From Moran and Shapiro						
A_o	(bar * $(m^3$ / kmol$)^2$	10.218	2.7737	1.8796	1.0676	1.359
B_o	$(m^3$/ kmol)	0.12436	0.04991	0.0426	0.04074	0.05454
C_o	(bar * K^2 * $(m^3$ / kmol$)^2$	1006000	140400	22870	8166	8676
a_o	(atm * $(m^3$ / kmol$)^3$	1.9073	0.1386	0.0501	0.0254	0.0371
b_o	$(m^3$ / kmol$)^2$	0.039998	0.00721	0.00338	0.002328	0.002632
c_o	(bar * K^2 * $(m^3$ / kmol$)^3$	320600	15120	2579	738.1	1054
α_o	$(m^3$ / kmol$)^3$	0.001101	0.0000847	0.0001244	0.0001272	0.000135
γ_o	$(m^3$ / kmol$)^2$	0.034	0.00539	0.006	0.0053	0.006
For Model						
A	((N / m^2) * $(m^3$ / kg$)^2$)	299.189	142.5559573	724.22640	135.97914	171.98784
B	$(m^3$ / kg)	0.0021279	0.0011314	0.0026443	0.00145	0.0019402
C	((N / m^2) * K^2 * $(m^3$ / kg$)^2$)	29456257.	7215941.3	8812012.0	1040095.2	1097988.6
a	((N / m^2) * $(m^3$ / kg$)^3$)	0.9556269	0.1614923	1.1982601	0.11545	0.1670288
b	$(m^3$ / kg$)^2$	1.17116E-05	3.70562E-06	1.30234E-05	2.96515E-06	3.33092E-06
c	((N / m^2) * K^2 * $(m^3$ / kg$)^3$)	160632.3068	17617.35143	61682.89107	3355.141281	4745.238814
α	$(m^3$ / kg$)^3$	5.51641E-09	9.86898E-10	2.97532E-08	5.78206E-09	6.07787E-09
γ	$(m^3$ / kg$)^2$	9.9554E-06	2.77022E-06	2.31185E-05	6.75056E-06	7.59328E-06

The first set of constants is straight out of a table in terms of bar, m^3/kmol, and K. However, the model is going to be made in terms of N/m^2, m^2/kg, and K. The second set of constants is used in the model and was determined from the first set of constants using the molar mass of the substance. The table only had five substances and did not have water listed. This lack of substances makes the equation less appealing for the model's development. After rigorously checking to make sure that the units on all the constants balanced the equation B-W-R was plotted. All plots are done in a log-log scale.

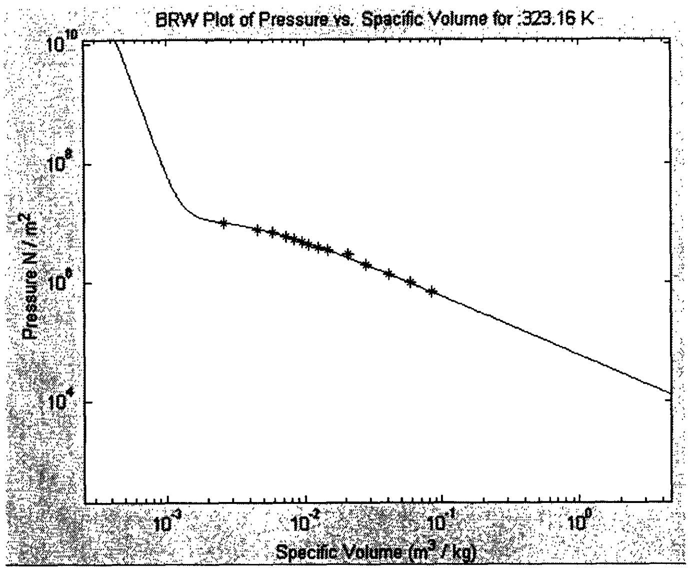


Figure 4: B-R-W plot of CO_2 vs. data at 50°C

B-W-R does an excellent job of modeling the behavior of CO_2 as can be seen in figure 4. However, at lower temperatures, where multiple phases can simultaneously exist, the model is less reliable.

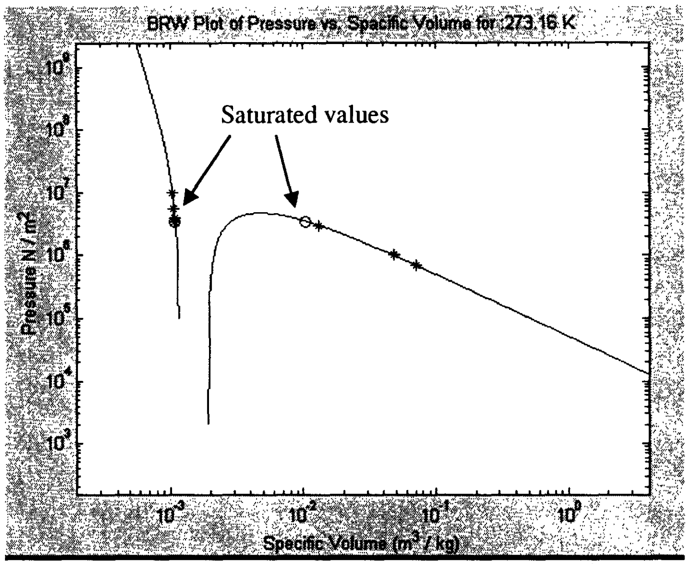


Figure 5: B-R-W plot of CO_2 vs. data at 0°C

The model behaves as a cubic function in the region of coexistence. That is difficult to see here, because B-W-R has been plotted on a loglog scale. This problem is remedied by using measured data. All pressures between the two saturated values have the same pressure. To model substances, B-W-R is plotted till the first saturated value (saturated liquid), then a horizontal line connects the two saturated values, and B-W-R is used again from the second saturated value on.

3.5 Redlich-Kwong Equation

In 1949 Redlich and Kwong proposed a modification to van der Waals formula. The formula was developed with basically empirical methods so the constants were not developed from molecular relations. The Redlich-Kwong equation is:

$$P = (R * T) / (v - b) - (a / (v\ (v + b))\ T^{1/2})) \qquad (6)$$

The constants a and b are not the same as the constants of the van dar Waals equation. Unique to each substance, the values can be determined from the critical pressure and temperature of the solution. The constants are defined as:

$$a = 0.42748\ R^2\ T_c^{5/2} / P_c \qquad (7)$$

and

$$b = 0.08664\ R\ T_c / P_c \qquad (8)$$

These constants were also determined empirically. "The Redlich-Kwong equation [is] considered by many to be the best of the two-constant equations of state." [4] Many constants were also readily available.

Table 2: Redlich-Kwong constants [4]

		From Moran and Shapiro		For Model		
Substance	Molar mass m_o	a_t	b_t	a	b	R
	g/mol	bar * $(m^3 / kmol)^2$ * $K^{1/2}$	m^3 / kmol	N * m^4 * $K^{1/2}$ / kg^2	m^3 /kg	J / (g *K)
Air	28.90	15.989	0.02541	1914.36884	0.000879239	287.6817
Butane (C_4H_{10})	58.44	289.55	0.08060	8478.19018	0.001379192	142.2656
Carbon Dioxide (CO_2)	44.11	64.43	0.02963	3311.41808	0.00067173	188.4833
Carbon Monoxide (CO)	28.11	17.22	0.02737	2179.27208	0.000973675	295.7666
Methane (CH_4)	16.11	32.11	0.02965	12372.2653	0.001840472	516.077
Nitrogen N_2)	28.02	15.53	0.02677	1978.04056	0.000955389	296.7166
Oxygen (O_2)	32.00	17.22	0.02197	1681.64062	0.000686563	259.8125
Propane (C_3H_8)	44.33	182.23	0.06242	9273.08867	0.001408076	187.5479
Refrigerant 12	120.91	208.59	0.06731	1426.81951	0.000556695	68.76189
Sulfur Dioxide (SO_2)	64.07	144.8	0.03945	3527.43576	0.000615733	129.7643
Water (H_2O)	18.00	142.59	0.02111	44009.2592	0.000148047	461.8889

$a_t * (10^5 / m_o^2) = a$

$b_t / (m_o * 10^3) = b$

The equations at the bottom of the table were used to convert the constants into units that were relevant to the plot. Similar to B-W-R, the molar mass was used to make the adjustments. The improvement over van der Waals can especially be seen at higher temperatures. The Redlich-Kwong model, with only two constants, is comparable to B-W-R.

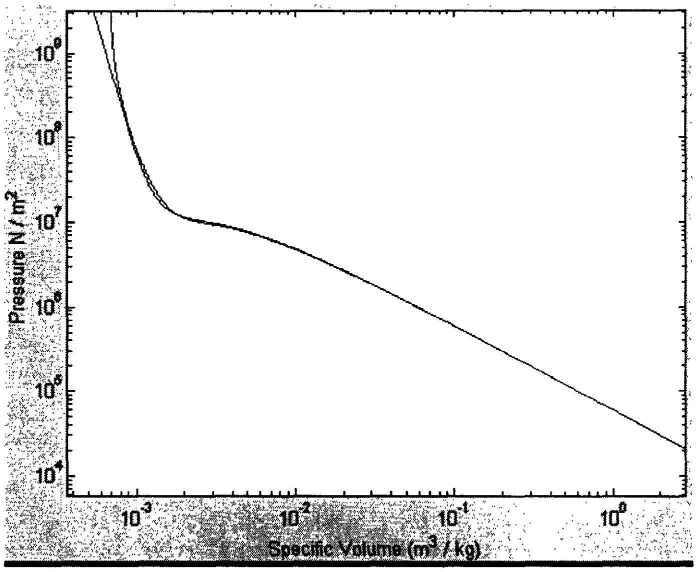


Figure 6: Plot of Redlich-Kwong and B-W-R for CO_2 at 50°C

The two plots are almost identical until the figure moves into higher temperatures. Since the model will not display pressures higher than 10^9 N/m^2 this inconsistency is not a problem. Redlich-Kwong has the same problem plotting the region of coexistence as B-W-R. The correction was done using measured data as well.

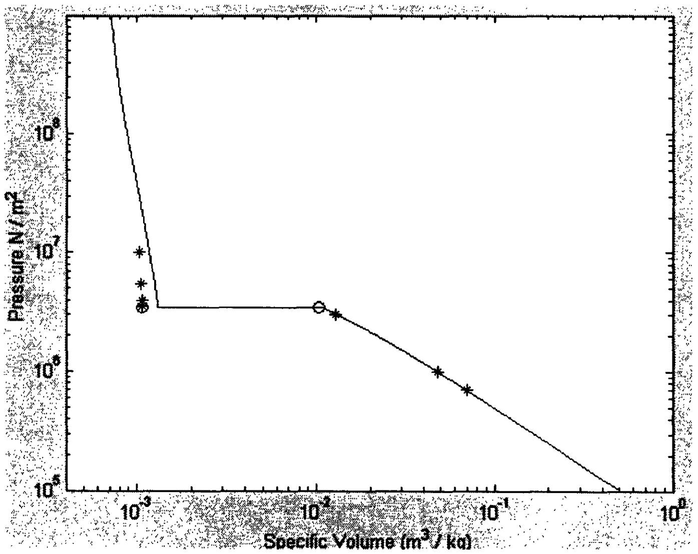
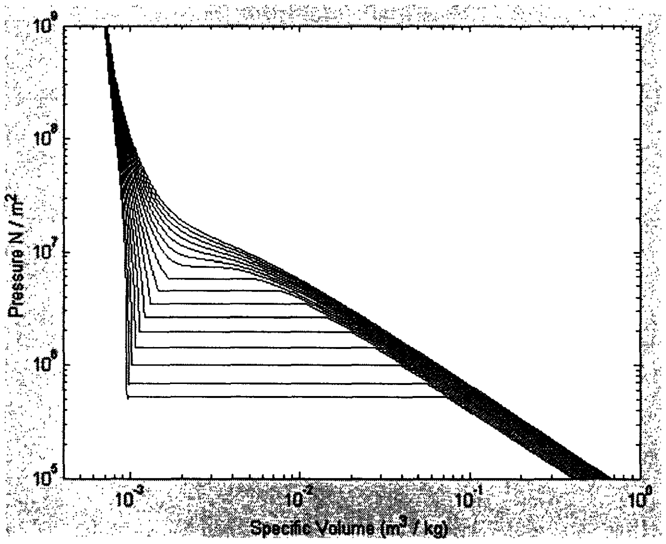
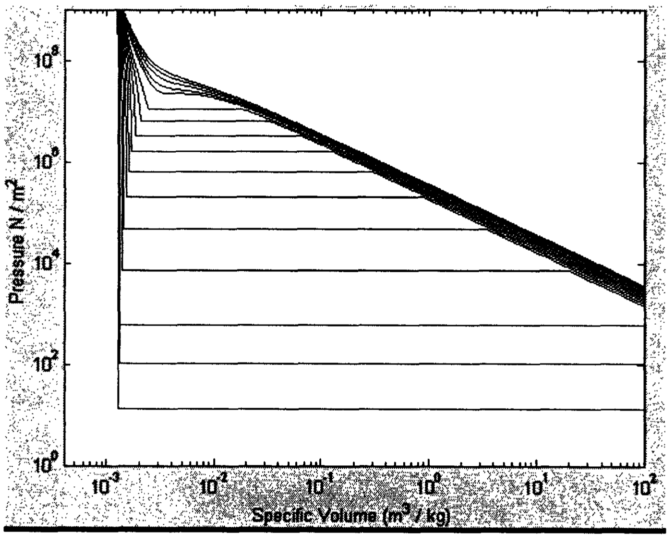


Figure 7: Corrected Redlich-Kwong plot of CO_2 at 0°C

The model does not match the data for pressures above the saturated line. The correct trend is represented by the model. While B-W-R matches the data better, the constants for water were not found. Redlich-Kwong had many solutions and while not as accurate as B-W-R still represented the behavior of substances over all regions. The Redlich-Kwong model was used to sculpt the hardware. The different temperatures were plotted against each other to demonstrate what the models shape will be.



Carbon Dioxide



Water

Figure 8: Redlich-Kwong plots of all temperatures

The figures are plotted on the scales that they were built. The pressure scales on the two plots are not the same because the carbon dioxide slices were cut before the water design was made. The P scale was focused in on the saturation curve of CO_2 which was between 10^5 and 10^9 N/m^2. Specific volume ranged from 10^{-3} to 10^2 m^3/kg, which contained all the points from the pressure range already determined. When the water data was plotted the region of coexistence covered a larger area than the CO_2 plot. The two plots have the same maximum pressure for the plots, but water requires a scale where the pressure is as low as 1 N/m^2 and a specific volume as high as $100 m^3/kg$. The three scales can be seen below:

Table 3: Range of variables for Redlich-Kwong plots

	Specific volume range (m^3/kg)	Pressure Range (N/m^2)	Temperature values plotted (°C)
CO_2	4e-4 to 1	1e5 to 1e9	-56, -50,-40,-30,-20,-10,0,10,20,31, 40,50,60,70,80,90
H_2O	4e-4 to 100	1 to 1e9	-40,-20,0,40,80,120,160,200,240,280,320,373.95,400,440,480,520

If CO_2 were to be plotted on the same scale as water it would look like:

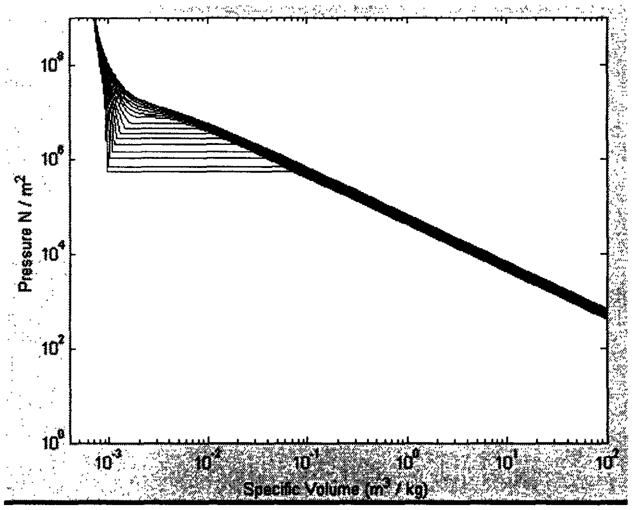


Figure 9: Redlich-Kwong plot of CO_2 on same scale as H_2O

This plot allows the student to get an idea of the relationships between the two solutions. However, the shape of the curve is compressed to a tighter region. The plots in figure 8 were exported to be cut for the model.

4 Model Development

The Redlich-Kwong data needs to be transferred to sheets of plastic and a base needs to be designed to hold all these sheets.

4.1 Material

To satisfy the design parameters, the entire model must be clear. One rigid transparent material is Poly(methyl methacylate) (PMMA) which is commonly know as acrylic or Plexiglas. PMMA is a shatterproof clear plastic which is used in large aquariums and ice rink barriers. The model is made out of Acrylite which is a type of clear cast acrylic that is lightweight, can be machined, and can handle reasonably high loads. Unlike glass, acrylic can be up to thirteen inches thick and still be clear. Since it can be cut on the laser cutter, acrylic is an ideal material to use for the assembly of the model. A hairline beam is run through the plastic vaporizing a minimal piece of the material leaving the cut surface clean and polished. Complex shapes could be programmed into the laser cutter which could be cut out from the .25" thick acrylite. The base, which was one inch thick, was made from the same material as the sheets. 92% of light will transmit through the base. Clear acrylic will make for a firm model which can still be used for projecting overhead lectures.

4.2 Design

The base was designed in solid works and machined using a CNC Milling Machine. While the slides were derived from Matlab and imported to a graphics program called Correl Draw which could communicate with the laser cutter easily.

4.2.1 Base

The 1" acrylic base was originally designed to have fins for each slice in a large slot for all the different temperatures as shown in figure 10.

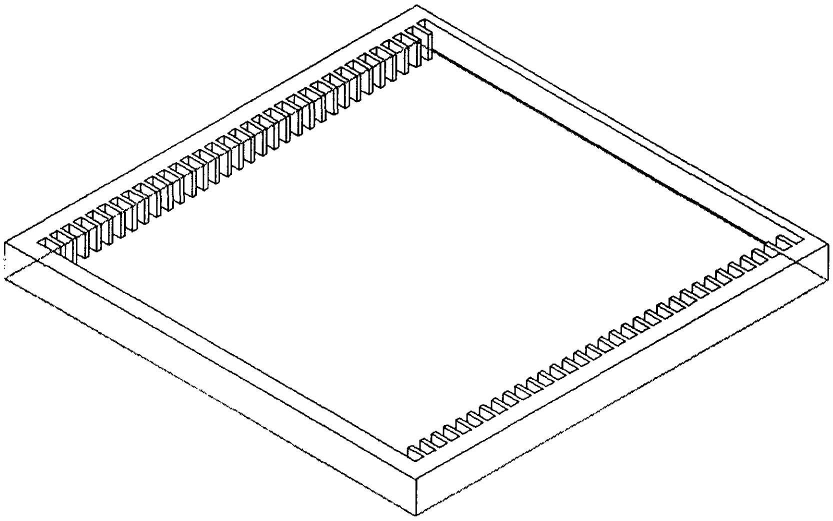


Figure 10: Original Base design

This base was a simple method for organizing the sheets which required minimal material. However, this model has a few problems. To keep optimum transmittance of light through the base, one piece of material should be used rather than assembling many pieces. Glue or mechanical fixtures would cast an unwanted shadow on the projection. To machine figure 5 from one piece would be take a long time and waste most of the material. Any stress placed on the slides when in the base will be concentrated on the length of the short fins. The base was redesigned to:

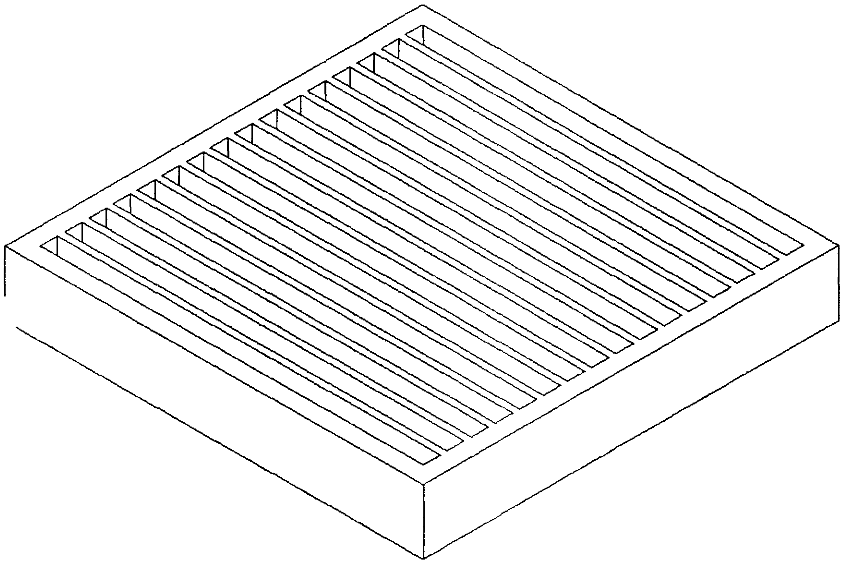
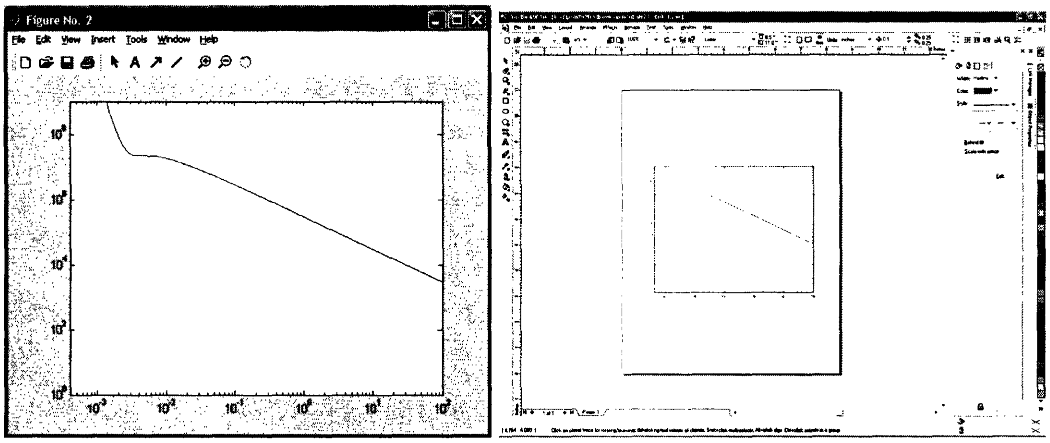


Figure 11: Final Base design

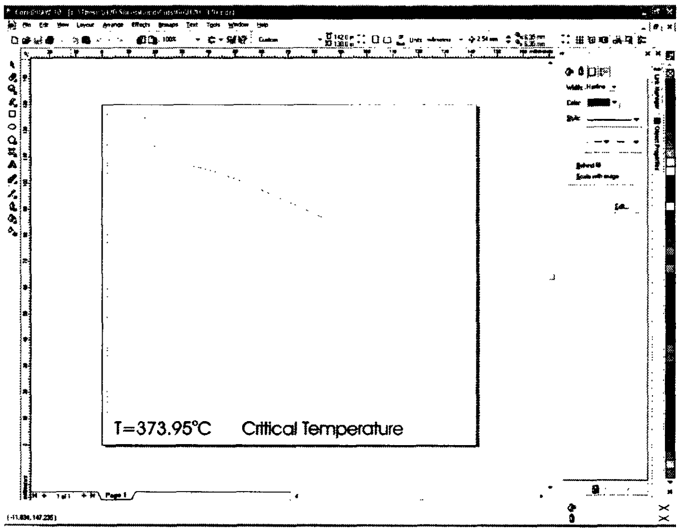
In the final design each slice has an individual slot. The load on the base is distributed over 5.64" rather than the .5" originally designed. There are fewer slides in the final design. .25" sheets were the thinnest pieces of acrylite that could handle the stresses expected. The base was designed to be six square inches. Looking at the plots derived, sixteen plots demonstrated the behavior of the curve and fit nicely inside the six inch boundary. The slots were milled out of a 1" x 6" x 6" clear acrylic block. Some of the transparency was lost when the slots were machined but light can still shine through the base. Because of the nature of milling out openings, the slots have rounded corners which required some redesign.

4.2.2 Slides

A sample m-file which plotted the Redlich-Kwong plot is shown in appendix A. Once the Redlich-Kwong curve was plotted using Matlab, the file would be exported as an encapsulated postscript file (EPS). This format maintained the versatility of the data so that the curve could be manipulated in Corel Draw to the shape of the slide. As an EPS, the plot was cut into many line segments and the unwanted aspects of the Matlab plot could easily be removed. The cut was made from the Corel Draw file.



Matlab file EPS file



Corel Draw file ready to cut

Figure 12: Slide Development

Figure 12 shows screen shots from the three major phases of development of the critical temperature slide of water.

To fit the rectangular slices into the curved slots, adjustments needed to be made. Rounding the sides of the slices would allow the parts to mate; this was done by belt-sanding the side of the slice. Sanding the clear sides made the parts less astatically pleasing and reduced the transparency. Instead of rounding the ends of the slides the slots in the base were extended to fit the slices.

5 The Model

The model satisfied most of the design requirements and was visually pleasing.

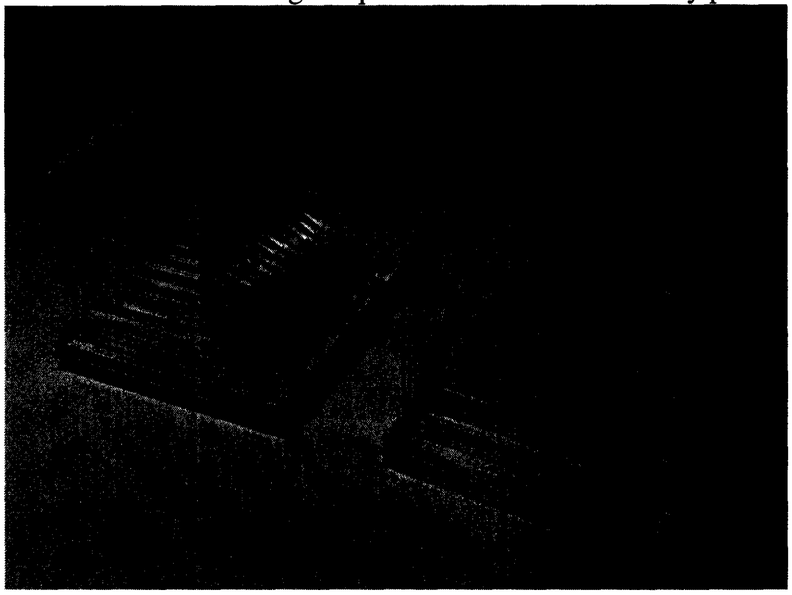


Figure 13: Photograph of models (CO_2 on the left and H_2O on the right)

The saturation curves can be clearly seen and the shape is consistent with the data of the substances.

5.1 Problems

The laser cutter made clean cuts into the .25” sheets but the curves look rough because the laser cutter was very sensitive to all the line segments of the plot.

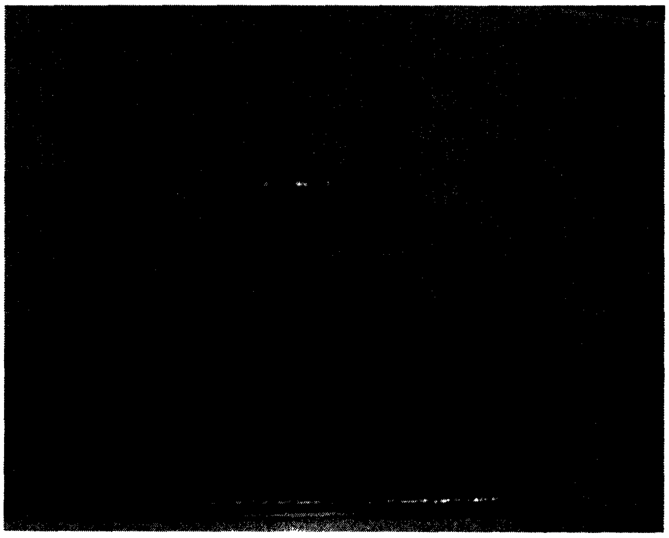


Figure 14: Edge of slice

The roughness, which is shown in figure 14, can be corrected by reducing the number of points plotted by Matlab. However, if the number of points is reduced too much the accuracy of the plot will be lost. There were also singe marks on the edge of some of the slices. A honeycomb surface holds the material being cut by the laser cutter; small pieces of debris fall into the gaps of the honeycomb. If the laser's power is too high, the laser will quickly cut through the piece and start to burn the scrap down in the honeycomb. This small fire leaves a burn mark in the shape of the honeycomb on the edge of the piece being cut. The problem was remedied after a few cuts, but because of limited resources some of the singed pieces needed to be used for the model.

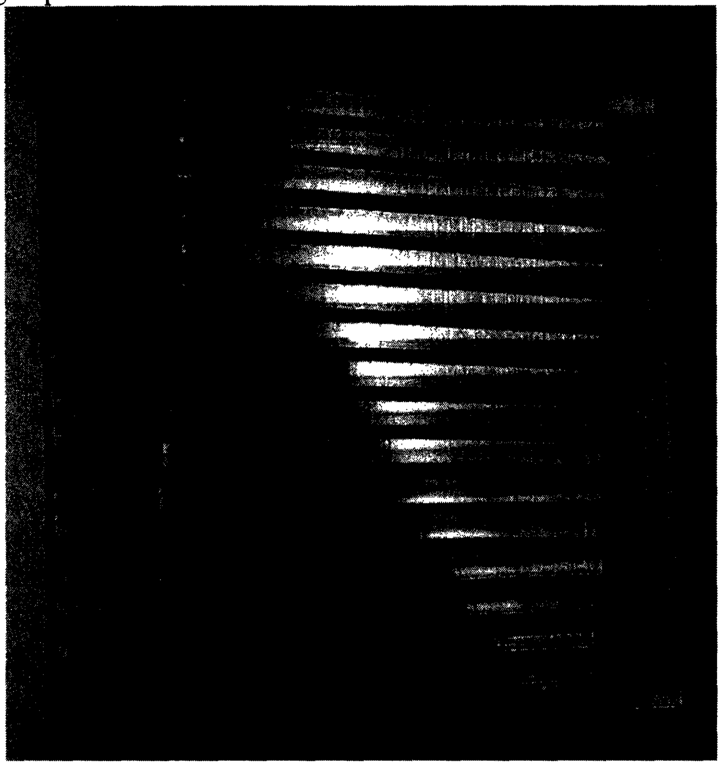


Figure 15: Top View of Model

Figure 15 shows the rectangular shape of all the slices. Ideally the slices would have the top surface at an angle, to have smoother transition from one slice to the next.

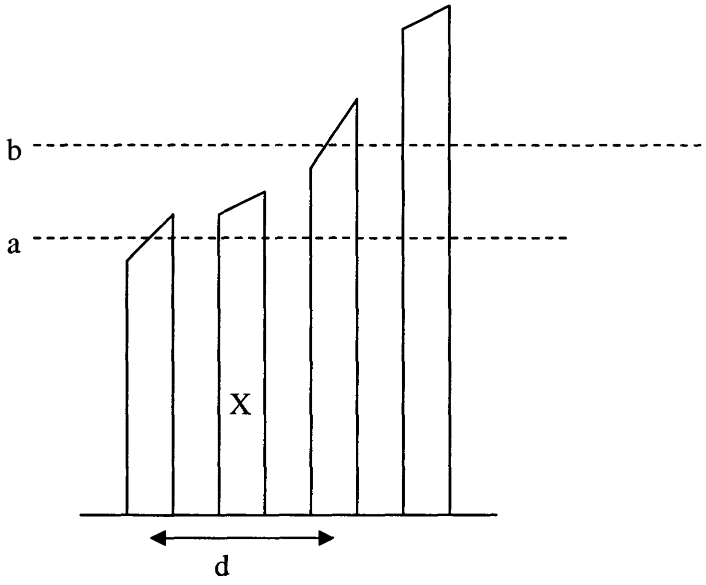


Figure 16: Determination of slope of top of sheets

The slope at which the top of slice X needs to be cut is equal to (b-a)/d. This is a difficult value to calculate because (b-a) has a different value for every point on the curve. Finding the average difference over the entire curve would be a reasonable approximation of that curvature. Machining this angle was another problem. To maintain the smooth top surface the acrylic needs to be cut with the laser cutter, which can not cut the draft angle. Using a band saw, mill, or belt sander will make the top surface rough and the model will loose some of its transparency. The top of the pieces remained flat.

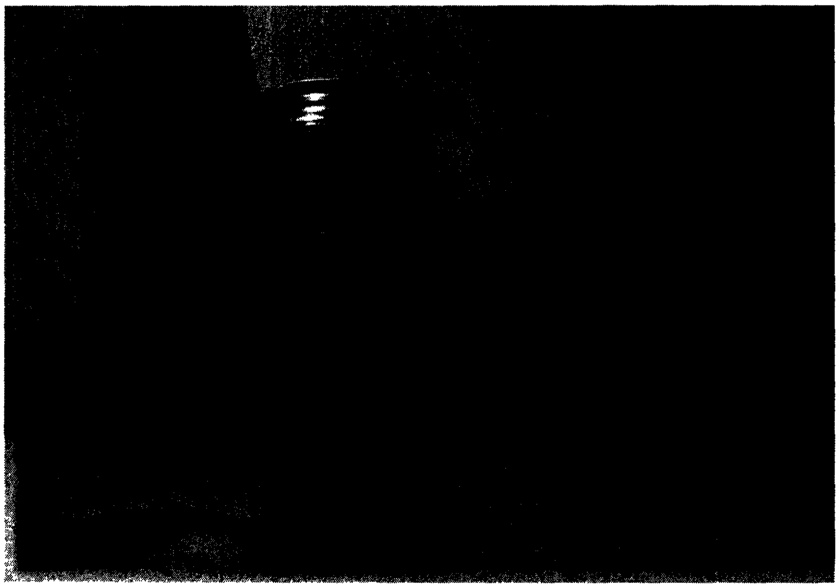


Figure 17: Transparency of model

Figure 17 shows how object remain quite visible through the sixteen slices that comprise the model. Marks can be made on the model and be seen though the piece.

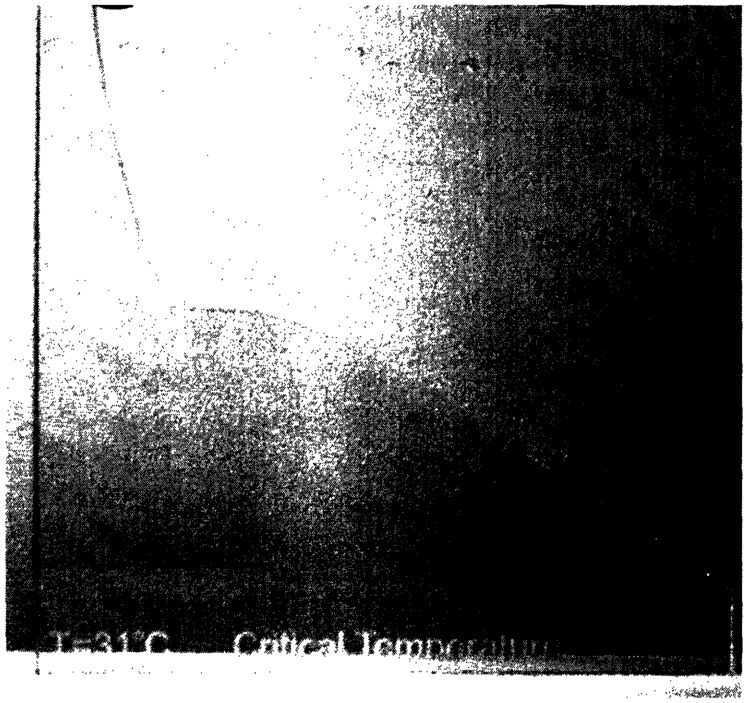


Figure 18: Photograph of CO_2 slice

Figure 18 shows the slice for the critical temperature of carbon dioxide. The temperature and "critical temperature" are both engraved on the piece in the region where the slice slides into the base.

One of the major flaws of the models is the liquid/solid phase line. Figure 1 demonstrates the solid state of water having a higher specific volume than the liquid phase.

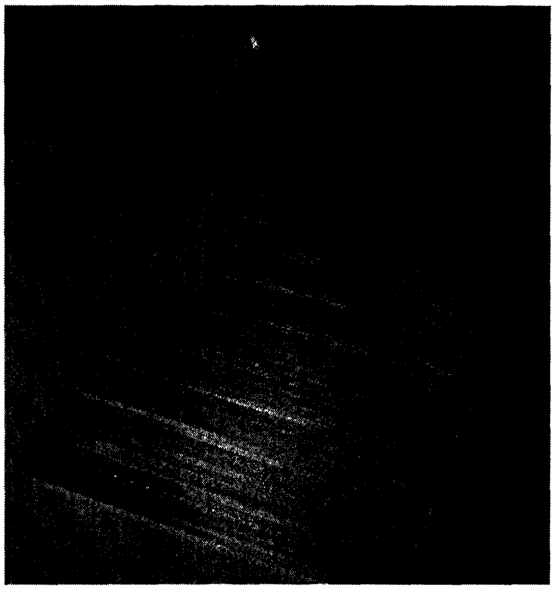


Figure19: Photograph of H_2O plot

The solid phase of the model actually has a lower specific volume than the liquid phase. This problem can be corrected by using more data than Redlich-Kwong equation to develop all slides which have a lower temperature than the triple line. The carbon dioxide plot does not have this problem because no temperatures below the triple line were plotted.

Carbon Dioxide's slices all had different widths because the Redlich-Kwong plots intercepted the x axis under the set domain and range. If the carbon dioxide plot were set to the same range as water, all the carbon dioxide slides would have the same width and the model would be neater like the water model.

5.2 Future Work

If someone were to pick up the project there are three major problems that should be focused on. First, the position of the solid phase with respect to liquid should be corrected. Next, the scale of carbon dioxide should be set to that of the water model so the slides are all the same size and the two models are more comparable. Finally, the top of the slices need to be machined to make the curve look smoother without compromising the transparency of the slides.

5.3 Conclusion

This model sets out to perform the same task that Maxwell's model performed over one hundred years ago; to be used as an aid to explain the geometry of thermodynamics. If the plot demonstrates the behavior of a substance, which a student can clearly see, then the student will have a better understanding of the two dimensional graphs that are required for problem solving.

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Appendix A

Below is the m-file used to plot the Redlich-Kwong plot for carbon dioxide. The sample is for a graph at 10°C. To plot a different curve the same m-file was used, but the new temperature and saturated pressure were keyed in.

```
eqs1=’ P = 188.5262 * (273.16+10) / (v - .00067173) - 3311.418081 / (v * (v +
.00067173) * (273.16+10)^(1/2)), P =4.497e6’;
```

The line above calculated the intersection of the Redlich-Kwong plot and the horizontal line at the saturated pressure.

```
[P1,v1]=solve(eqs1);
l= eval(log(v1(1))/log(10));


RA = 8.314;                  % % J / (mol * K) --> General gas constant

% %Constants specific to substance modeled

a = 3311.418081;             % % N * m^4 * K^(1/2) / kg^2
b = .00067173;               % % m^3 / kg
mo = 44.11/1000;             % % kg/mol --> molar mass of substance
R = RA / mo;                 % % J / (g *K) -->Gas constant for substance
T = 273.16+10;              % % K -->Tempreture
v= logspace(-5, 1, 10000);     % % m^3 / kg -->Specific volume

P = R * T ./ (v - b) - a ./ (v .* (v + b) .* T^(1/2)); % % Redlich-Kwong Equation
```

The plot was made in piece wise fashion. The intersections calculated above were used as endpoints for the segments.

```
loglog(v,P);


hold on

l2= eval(log(v1(3))/log(10));

v2 = logspace(l, l2, 100);
p2= v2./v2 * 4.497e6;

loglog(v2,p2);
v3 = logspace(l2, 3, 10000);
P3 = R * T ./ (v3 - b) - a ./ (v3 .* (v3 + b) .* T^(1/2));
loglog(v3,P3);

axis([4e-4 1 1e5 1e9]);
```