Thermo | HW #4 | Tanner Corrado

1\. 1. $s_{vdw}(u,v) = s_0 + R\ln(v-b) + cR\ln\left(u + \frac{a}{v}\right)$

$a(T,v) = u - Ts$

First need u. $\frac{1}{T} = \left(\frac{\partial s}{\partial u}\right)_v = \frac{cRv}{a + uv} \Rightarrow u = cRT - \frac{a}{v}$

$$a^{vdw}(T,v) = cRT - \frac{a}{v} - Ts_0 - RT\ln\left[(v-b)\left(cRT - \frac{a}{v} + \frac{a}{v}\right)^c\right]$$

$$\boxed{a^{vdw}(T,v) = cRT - \frac{a}{v} - Ts_0 - RT\ln\left[(v-b)(cRT)^c\right]}$$

2\. $\Delta a^{vdw} \doteq a_f - a_i$

$$= -RT\ln\left[\frac{(v_3-b)(v_4-b)}{(v_2-b)(v_1-b)}\right] - a\left(\frac{1}{v_3} + \frac{1}{v_4} - \frac{1}{v_1} - \frac{1}{v_2}\right)$$

$a = 365.51 \frac{J \cdot L}{mol}$ $b = 0.042816 \frac{L}{mol}$ $R = 8.314 \frac{J}{mol\,K}$ $T = 273\,K$

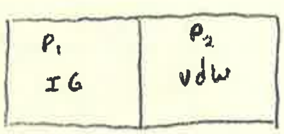
$v_1 = 1\,L$, $v_2 = 10\,L$, $v_3 = 5\,L$, $v_4 = 6\,L$

$$\boxed{\begin{aligned} \Delta a^{vdw} &= -2298.8 \frac{J}{mol} = -2.3 \frac{kJ}{mol} \\ \Delta a^{IG} &= -2.5 \frac{kJ}{mol} \quad \text{Get more work from ideal gas} \end{aligned}}$$

3\. Same as previous, but now $v_1 = 0.1$, $v_2 = 1.0$, $v_3 = 0.5$, $v_4 = 0.6$

$$\boxed{\begin{aligned} \Delta a^{vdw} &= -676.1 \frac{J}{mol} \\ \Delta a^{IG} &= -8.314 \cdot 273 \cdot \ln\left(\frac{0.5 \cdot 0.6}{0.1 \cdot 1}\right) = -2494 \frac{J}{mol} \end{aligned}}$$

Get more work from ideal gas.

4\. 

Will move to $P_1 = P_2$

$P_1 = \frac{RT}{V_1}$ $P_2 = \frac{RT}{V_2 - b} - \frac{a}{V_2^2}$

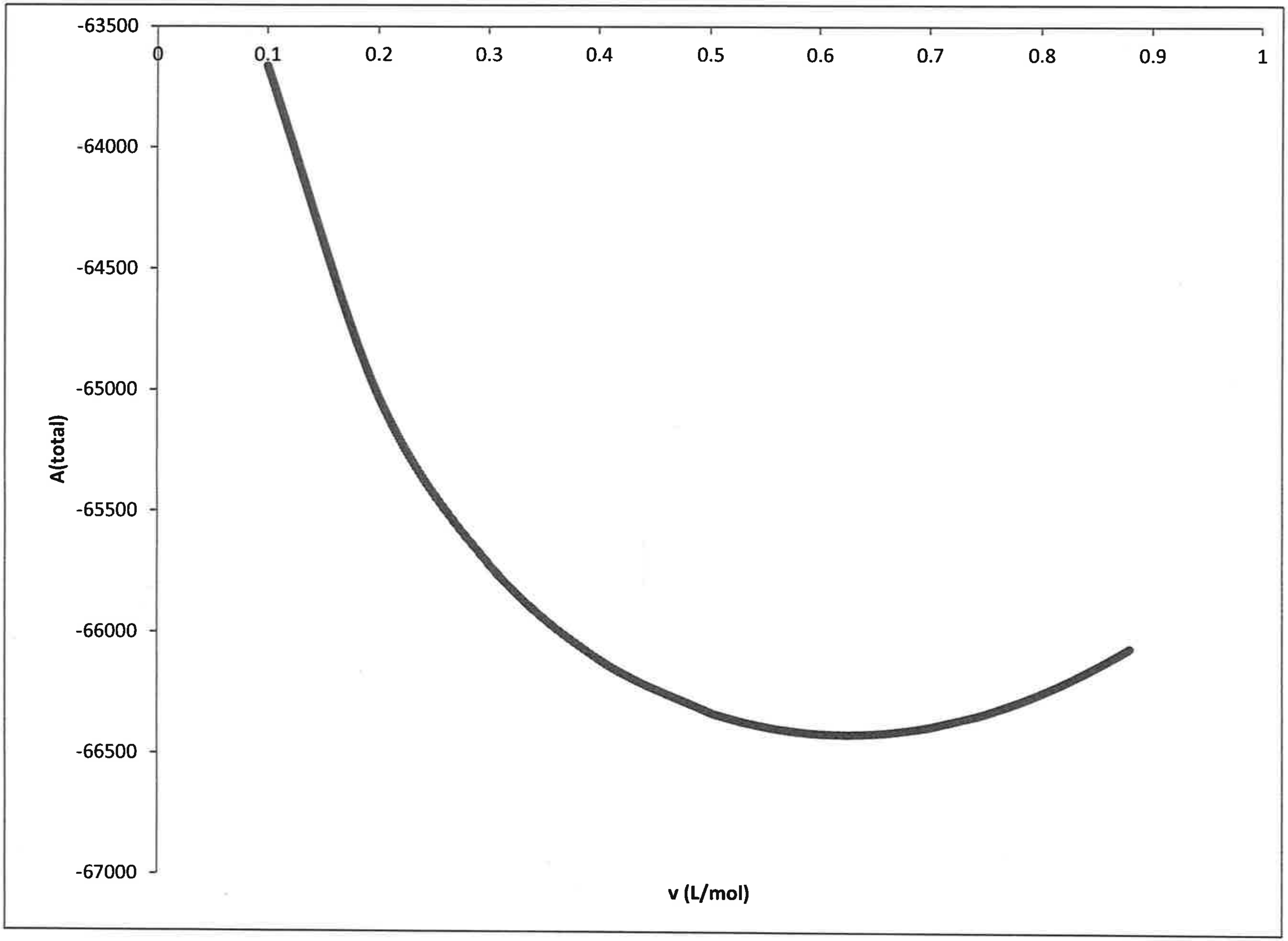
$V_1 + V_2 = 1.1\,L$

$V_2 = 1.1 - V_1$ Can substitute V_2 in ↗ and solve.

$$\boxed{V_1 = 0.625\,L \quad V_2 = 0.475}$$

Alternatively, you can plot a_{tot} vs V and find the minimum.

Tanner Corrado
Themo # 1.4



a	b	R	T	v1i	v2i	c	v1	Atot
365.51	0.042816	8.314	273	0.1	1	3.5	0.1	-63660.918
365.51	0.042816	8.314	273	0.1	1	3.5	0.2	-65024.334
365.51	0.042816	8.314	273	0.1	1	3.5	0.3	-65713.842
365.51	0.042816	8.314	273	0.1	1	3.5	0.4	-66110.581
365.51	0.042816	8.314	273	0.1	1	3.5	0.5	-66329.421
365.51	0.042816	8.314	273	0.1	1	3.5	0.51	-66343.587
365.51	0.042816	8.314	273	0.1	1	3.5	0.52	-66356.478
365.51	0.042816	8.314	273	0.1	1	3.5	0.53	-66368.118
365.51	0.042816	8.314	273	0.1	1	3.5	0.54	-66378.528
365.51	0.042816	8.314	273	0.1	1	3.5	0.55	-66387.726
365.51	0.042816	8.314	273	0.1	1	3.5	0.56	-66395.731
365.51	0.042816	8.314	273	0.1	1	3.5	0.57	-66402.559
365.51	0.042816	8.314	273	0.1	1	3.5	0.58	-66408.222
365.51	0.042816	8.314	273	0.1	1	3.5	0.59	-66412.734
365.51	0.042816	8.314	273	0.1	1	3.5	0.6	-66416.105
365.51	0.042816	8.314	273	0.1	1	3.5	0.61	-66418.344
365.51	0.042816	8.314	273	0.1	1	3.5	0.62	-66419.459
365.51	0.042816	8.314	273	0.1	1	3.5	0.625	-66419.597
365.51	0.042816	8.314	273	0.1	1	3.5	0.63	-66419.457
365.51	0.042816	8.314	273	0.1	1	3.5	0.64	-66418.343
365.51	0.042816	8.314	273	0.1	1	3.5	0.65	-66416.123
365.51	0.042816	8.314	273	0.1	1	3.5	0.66	-66412.798
365.51	0.042816	8.314	273	0.1	1	3.5	0.67	-66408.371
365.51	0.042816	8.314	273	0.1	1	3.5	0.68	-66402.845
365.51	0.042816	8.314	273	0.1	1	3.5	0.69	-66396.218
365.51	0.042816	8.314	273	0.1	1	3.5	0.7	-66388.492
365.51	0.042816	8.314	273	0.1	1	3.5	0.74	-66346.578
365.51	0.042816	8.314	273	0.1	1	3.5	0.76	-66319.003
365.51	0.042816	8.314	273	0.1	1	3.5	0.78	-66287.018
365.51	0.042816	8.314	273	0.1	1	3.5	0.8	-66250.652
365.51	0.042816	8.314	273	0.1	1	3.5	0.82	-66209.977
365.51	0.042816	8.314	273	0.1	1	3.5	0.84	-66165.143
365.51	0.042816	8.314	273	0.1	1	3.5	0.86	-66116.429
365.51	0.042816	8.314	273	0.1	1	3.5	0.88	-66064.316

Tanner Corrado
Thermo #1.4

Thermo | HW #4 | Tanner Corrado

2. 1. $\left(\frac{\partial T}{\partial v}\right)_h = -\left(\frac{\partial h}{\partial v}\right)_T\left(\frac{\partial T}{\partial h}\right)_v$ $dh = Tds + v\,dP$

$\left(\frac{\partial h}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T + v\left(\frac{\partial P}{\partial v}\right)_T$ $k_T = \frac{-1}{v}\left(\frac{\partial v}{\partial P}\right)_T$ $-k_T v = \left(\frac{\partial v}{\partial P}\right)_T$

$\left(\frac{\partial P}{\partial v}\right)_T = \frac{1}{-k_T v}$ $T\left(\frac{\partial s}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v = -T\left(\frac{\left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial P}\right)_T}\right)$

$T\left(\frac{\partial s}{\partial v}\right)_T = -T\left(\frac{\alpha v}{-v k_T}\right)$ $T\left(\frac{\partial s}{\partial v}\right)_T = \frac{T\alpha}{k_T}$ since $\left(\frac{\partial v}{\partial T}\right)_P = \alpha v$, $\left(\frac{\partial v}{\partial P}\right)_T = -v k_T$

$\left(\frac{\partial h}{\partial v}\right)_T = \frac{T\alpha}{k_T} - \frac{1}{k_T}$ $\boxed{\left(\frac{\partial h}{\partial v}\right)_T = \frac{T\alpha - 1}{k_T}}$

$\left(\frac{\partial T}{\partial h}\right)_v = \frac{1}{\left(\frac{\partial h}{\partial T}\right)_v}$ $dh = Tds + v\,dP$ $\left(\frac{\partial h}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial T}\right)_v$

$T\left(\frac{\partial s}{\partial T}\right)_v = C_v$ $\left(\frac{\partial P}{\partial T}\right)_v = \frac{-\left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial P}\right)_T} = \frac{-\alpha v}{-k_T v} = \frac{\alpha}{k_T}$

$\left(\frac{\partial h}{\partial T}\right)_v = C_v + \frac{v\alpha}{k_T} = \frac{C_v k_T}{k_T} + \frac{\alpha v}{k_T} = \frac{C_v k_T + \alpha v}{k_T}$

$\left(\frac{\partial T}{\partial h}\right)_v = \frac{k_T}{(C_v k_T + \alpha v)}$

so... $\left(\frac{\partial T}{\partial v}\right)_h = -\left(\frac{\partial h}{\partial v}\right)_T\left(\frac{\partial T}{\partial h}\right)_v$

$\left(\frac{\partial T}{\partial v}\right)_h = \left(\frac{1 - T\alpha}{k_T}\right)\left(\frac{k_T}{C_v k_T + \alpha v}\right)$ $C_v = c_P - \frac{v\alpha^2 T}{k_T}$

If we want c_P...

$\left(\frac{\partial T}{\partial v}\right)_h = \left(\frac{1 - T\alpha}{\cancel{k_T}}\right)\left(\frac{\cancel{k_T}}{k_T c_P - v\alpha^2 T + \alpha v}\right)$

$$\boxed{\left(\frac{\partial T}{\partial v}\right)_h = \frac{1 - T\alpha}{k_T c_P - v\alpha^2 T + \alpha v}}$$

2\. 2. $P(T,v) = \frac{RT}{v-b} - \frac{a}{v^2}$ (vdw)

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\left(\frac{1}{\left(\frac{\partial T}{\partial v}\right)_P}\right) = \frac{1}{v}\left(\frac{1}{\frac{2ab - av + Pv^3}{Rv^3}}\right)$$

$$\alpha = \frac{1}{v} \cdot \frac{Rv^3}{2ab - av + Pv^3}$$

$$\boxed{\alpha = \frac{Rv^2}{2ab - av + Pv^3}}$$

$$K_T = \frac{-1}{v}\left(\frac{\partial v}{\partial P}\right)_T \qquad \frac{1}{K_T} = -v\left(\frac{\partial P}{\partial v}\right)_T \qquad \left(\frac{\partial P}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3}$$

$$-v\left(\frac{\partial P}{\partial v}\right)_T = \frac{vRT}{(v-b)^2} - \frac{2a}{v^2} = \frac{1}{K_T}$$

$$\boxed{K_T = \frac{1}{\frac{vRT}{(v-b)^2} - \frac{2a}{v^2}}}$$

$$C_P = C_V + \frac{v\alpha^2 T}{K_T} \qquad C_V = T\left(\frac{\partial s}{\partial T}\right)_v = \frac{TcR}{T} = cR$$

$$\boxed{C_P = cR + \frac{v\alpha^2 T}{K_T}} \qquad \boxed{C_V = cR}$$

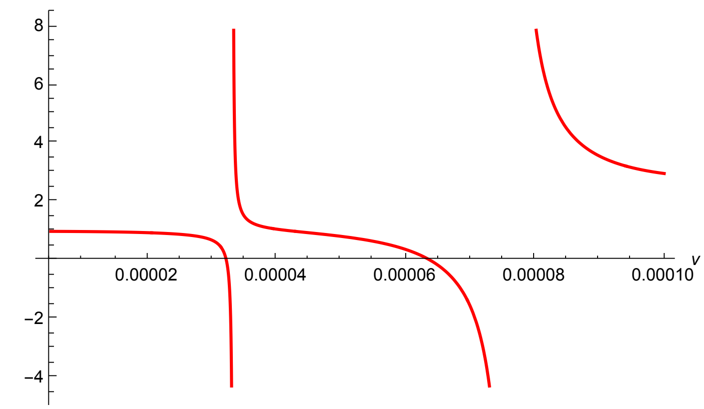
3\. See plots attached.

$T=223$ is broken into numerator and denominator to highlight sign control. Both have opposite sign up to about $v = 3.3 \times 10^{-5}$ m^3 an asymptote occurs. Another occurs around 4.3×10^{-5} m^3. Between them $\left(\frac{\partial T}{\partial v}\right)_h$ is negative, along with below $v = 3.2 \times 10^{-5}$ m^3 and above $v = 6.4 \times 10^{-5}$ m^3. Between the asymptotes and previous values $\left(\frac{\partial T}{\partial v}\right)_h$ is positive.

Similar trends occur for all temperatures.

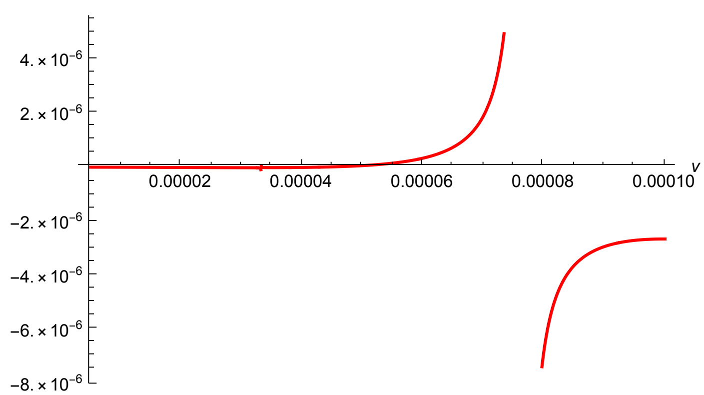
In[1894]:=
```
T = 223;
R = 8.314;
a = 0.36551;
b = 42.816 * 10^(-6);
Cv = (7 / 2) * 8.314;
Num223 =
 Plot[(1 - T * ((R * v^2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v^2))) * v^3)))),
  {v, 0.000005, 0.0001}, PlotStyle → {Red}, AxesLabel → {v, numerator}]
```

Out[1899]=



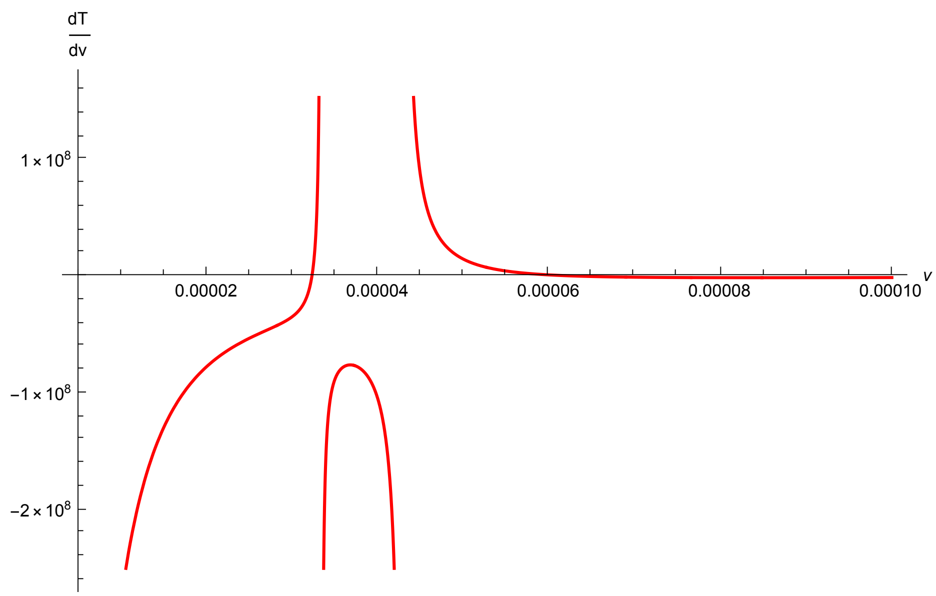
In[1900]:=
```
T = 223;
R = 8.314;
a = 0.36551;
b = 42.816 * 10^(-6);
Cv = (7 / 2) * 8.314;
Denom223 = Plot[(Cv * (1 / (((v * R * T) / ((v - b)^2)) - ((2 * a) / (v^2)))) +
     ((R * v^2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v^2))) * v^3))) * v),
  {v, 0.000005, 0.0001}, PlotStyle → {Red}, AxesLabel → {v, denominator}]
```

Out[1905]=



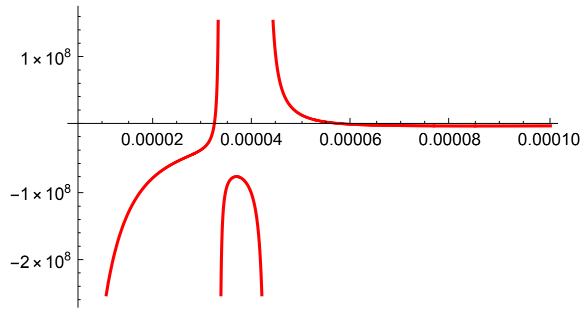
In[1906]:=
```
Plot[(1 - T * ((R * v^2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v^2))) * v^3)))) /
   (Cv * (1 / (((v * R * T) / ((v - b) ^2)) - ((2 * a) / (v^2)))) +
     ((R * v^2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v^2))) * v^3))) * v),
  {v, 0.000005, 0.0001}, PlotStyle → {Red}, AxesLabel → {v, dT / dv}]
```

Out[1906]=



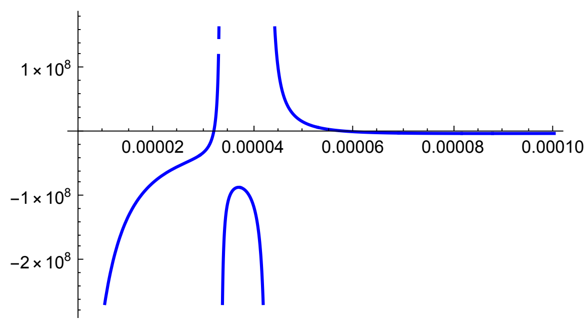
In[1843]:=
```
T = 223;
R = 8.314;
a = 0.36551;
b = 42.816 * 10 ^ (-6);
Cv = (7 / 2) * 8.314;
P223 =
 Plot[(1 - T * ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3)))) /
    (Cv * (1 / (((v * R * T) / ((v - b) ^ 2)) - ((2 * a) / (v ^ 2)))) +
      ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3))) * v),
  {v, 0.000005, 0.0001}, PlotStyle → {Red}]
```

Out[1848]=



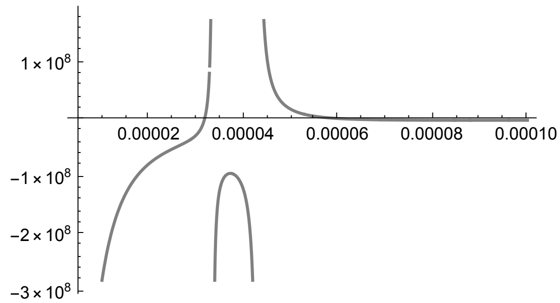
In[1849]:=
```
T = 243;
R = 8.314;
a = 0.36551;
b = 42.816 * 10 ^ (-6);
Cv = 29.099;
P243 =
 Plot[(1 - T * ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3)))) /
    (Cv * (1 / (((v * R * T) / ((v - b) ^ 2)) - ((2 * a) / (v ^ 2)))) +
      ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3))) * v),
  {v, 0.000005, 0.0001}, PlotStyle → {Blue}]
```

Out[1854]=



In[1855]:=
```
T = 263;
R = 8.314;
a = 0.36551;
b = 42.816 * 10 ^ (-6);
Cv = 29.099;
P263 =
 Plot[(1 - T * ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3)))) /
   (Cv * (1 / (((v * R * T) / ((v - b) ^ 2)) - ((2 * a) / (v ^ 2)))) +
     ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3))) * v),
  {v, 0.000005, 0.0001}, PlotStyle → {Gray}]
```

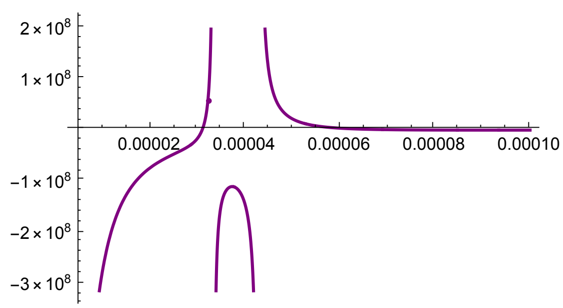
Out[1860]=



Power: Infinite expression $\frac{1}{0.}$ encountered.

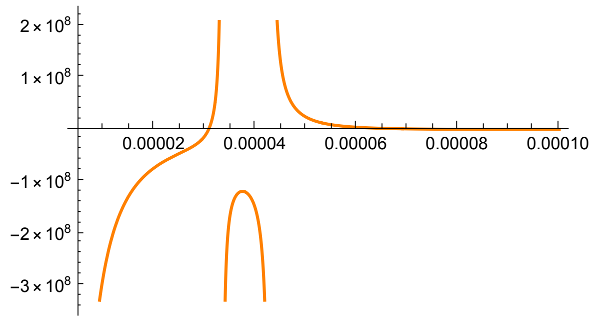
In[1867]:=
```
T = 303;
R = 8.314;
a = 0.36551;
b = 42.816 * 10 ^ (-6);
Cv = 29.099;
P303 =
 Plot[(1 - T * ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3)))) /
   (Cv * (1 / (((v * R * T) / ((v - b) ^ 2)) - ((2 * a) / (v ^ 2)))) +
     ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3))) * v),
  {v, 0.000005, 0.0001}, PlotStyle → {Purple}]
```

Out[1872]=



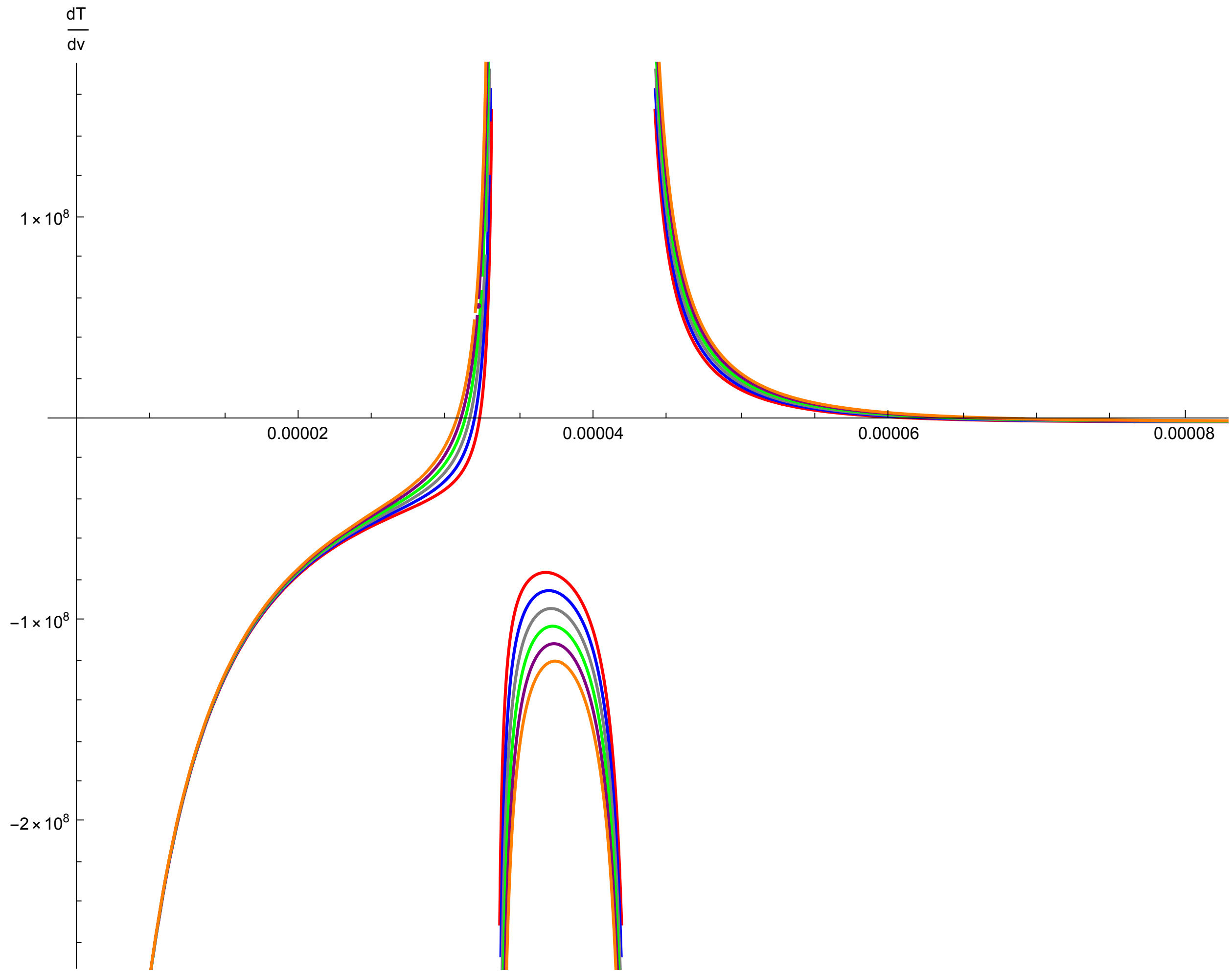
In[1873]:=
```
T = 323;
R = 8.314;
a = 0.36551;
b = 42.816 * 10 ^ (-6);
Cv = 29.099;
P323 =
 Plot[(1 - T * ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3)))) /
   (Cv * (1 / (((v * R * T) / ((v - b) ^ 2)) - ((2 * a) / (v ^ 2)))) +
     ((R * v ^ 2) / ((2 * a * b) - (a * v) + ((((R * T) / (v - b)) - (a / (v ^ 2))) * v ^ 3))) * v),
  {v, 0.000005, 0.0001}, PlotStyle → {Orange}]
```

Out[1878]=



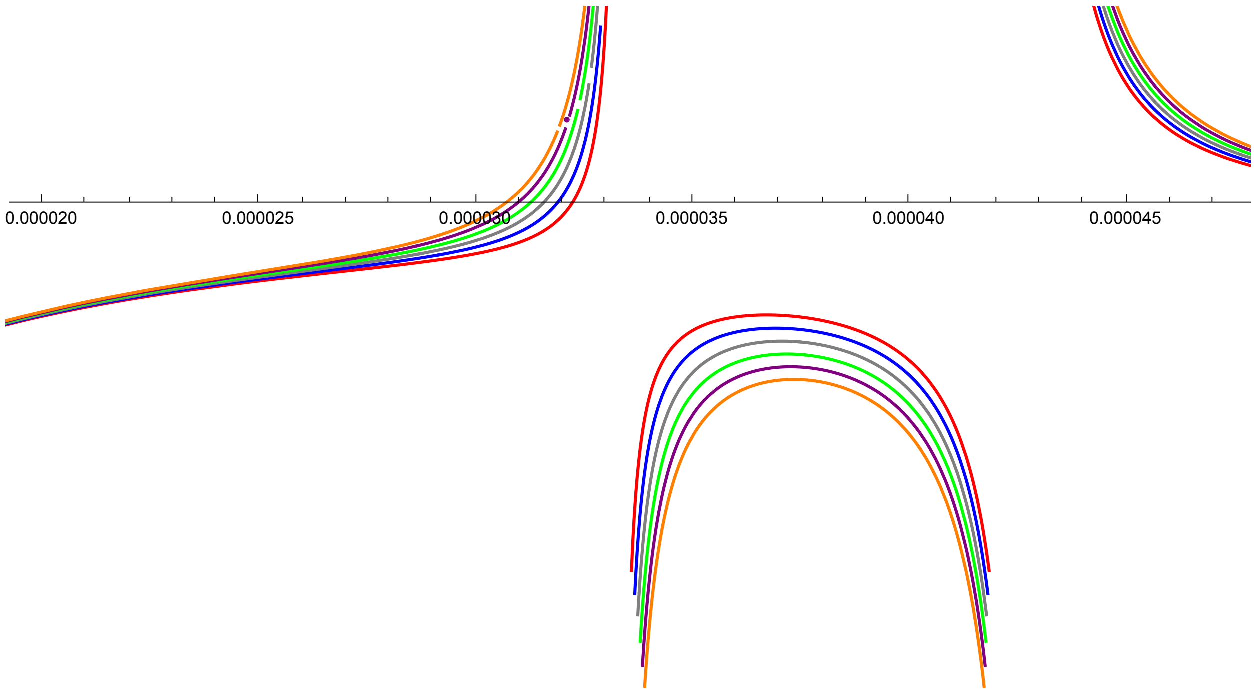
In[1879]:=
```
Show[P223, P243, P263, P283, P303, P323, AxesLabel → {v, dT / dv}]
```

Out[1879]=



In[1880]:=
```
Show[P223, P243, P263, P283, P303, P323,
 PlotRange → {{0.00002, 0.000055}, {-5 * 10 ^ 8, 10 * 10 ^ 7}}]
```

Out[1880]=



3. 1. $h^{vdw}(T, v) = u_{vdw} + P_{vdw} v$

$$= cRT - \frac{a}{v} + \left(\frac{RT}{v-b} - \frac{a}{v^2}\right) v$$

$$\boxed{h^{vdw}(T, v) = cRT + \frac{vRT}{v-b} - \frac{2a}{v}}$$

2. $\Delta h = 0$ $\quad v_1 = 0.1 \frac{L}{mol}$ $\quad v_2 = 1 \frac{L}{mol}$ $\quad T_1 = 283\ K$ $\quad c = \frac{7}{2}$

$$cRT_1 + \frac{v_1 RT_1}{v_1 - b} - \frac{2a}{v_1} = cRT_2 + \frac{v_2 R T_2}{v_2 - b} - \frac{2a}{v_2}$$

$a = 365.51 \frac{J \cdot L}{mol^2}$ $\quad b = 0.042816 \frac{L}{mol}$ $\quad R = 8.314 \frac{J}{mol\ K}$

Plug in knowns, solve for T_2

$T_2 = 152.7\ K$ $\quad \approx 130\ K$ cooling

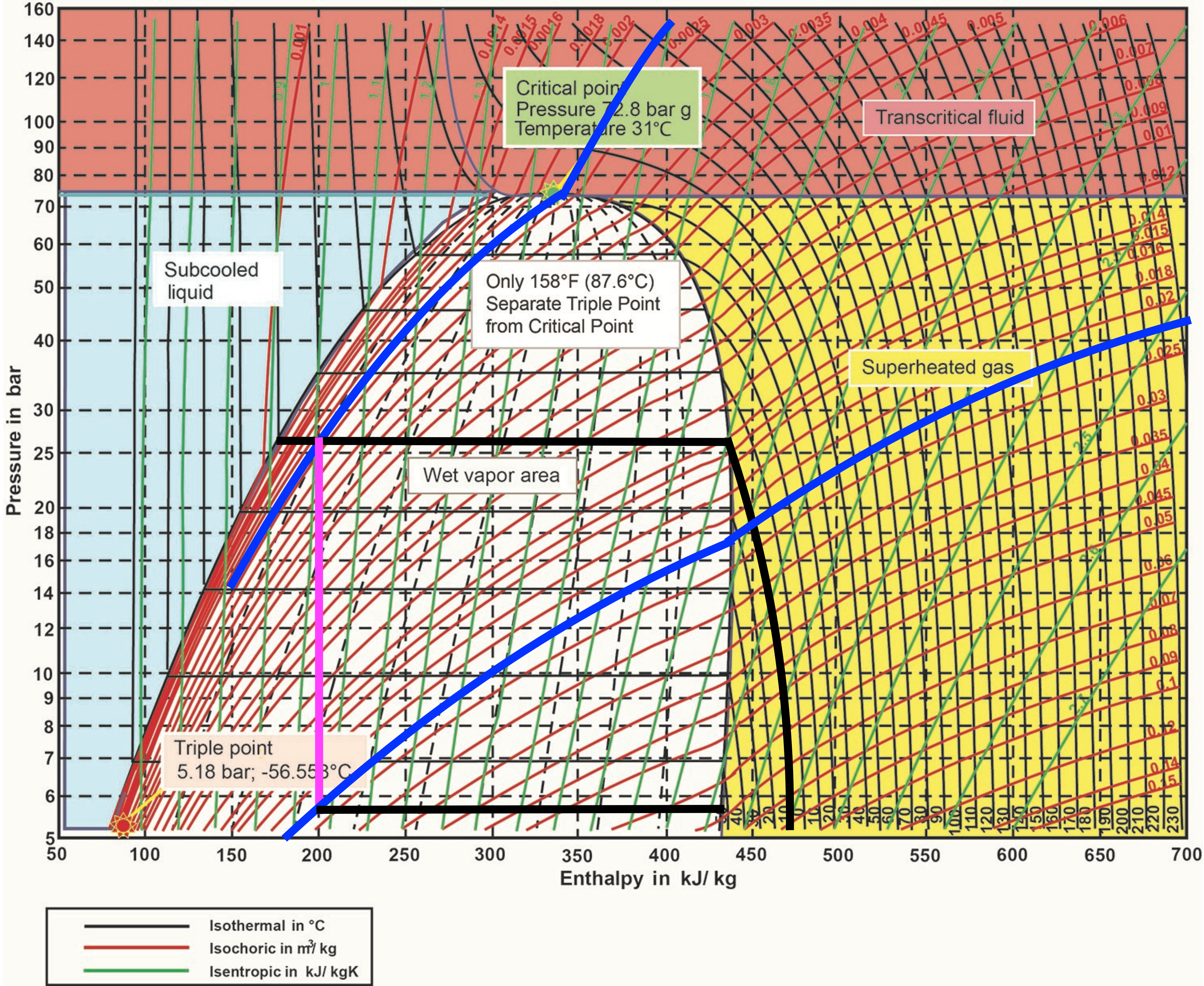
3. On diagram this corresponds to cooling from 10°C to around

$$v_1 = 0.1 \frac{L}{mol} \cdot \frac{1\ m^3}{1000\ L} \cdot \frac{1\ mol}{44.01 g} \cdot \frac{1000 g}{1\ kg} = 0.00227 \frac{m^3}{kg}$$

$$v_2 = 1 \frac{L}{mol} = 0.0227 \frac{m^3}{kg}$$

$T_1 = 283\ K = 10°C$

$T_2 \approx 220\ k = -53°C \leftarrow$ from diagram (approximate)


Pressure in bar
Enthalpy in kJ/ kg
Subcooled liquid
Only 158°F (87.6°C) Separate Triple Point from Critical Point
Critical point Pressure 72.8 bar g Temperature 31°C
Transcritical fluid
Superheated gas
Wet vapor area
Triple point 5.18 bar; -56.558°C
Isothermal in °C
Isochoric in m³/ kg
Isentropic in kJ/ kgK

Thermo HW #4 Tanner Corrado

4. 1. $\Delta s = \int_{T_1}^{T_2} \frac{C_p(T)}{T}\, dT$

(abbreviated for conciseness)

$C_p^{IG}(T) = -11.4 - 55.2\frac{T}{1000} + 5.15\left(\frac{T}{1000}\right)^2 - 0.29\left(\frac{T}{1000}\right)^3 + 6.11\left(\frac{T}{1000}\right)^{-2} + 115.93\left(\frac{T}{1000}\right)^{1/2}$

so... The given $Cp(T)$ was divided by T and then integrated from

$T_1 \rightarrow T_2$ (290 to 350 K) in wolfram to get Δs.

$\boxed{\Delta S = 7.155 \frac{J}{mol}}$

2. $\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v = \frac{-\left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial P}\right)_T} = \frac{\alpha}{K_T}$

3. $\left(\frac{\partial S}{\partial v}\right)_T^{IG} = \left(\frac{\partial P}{\partial T}\right)_v^{IG} = \frac{R}{v}$ ← also get from $\frac{\alpha}{K_T}$ for IG $\Rightarrow \frac{\frac{1}{T}}{\frac{1}{P}} = \frac{P}{T} = \frac{R}{v}$ ✓

$Pv = RT \quad P = \frac{RT}{v}$

4. $\left(\frac{\partial S}{\partial v}\right)_T^{vdw} = \left(\frac{\partial P}{\partial T}\right)_v^{vdw} = \frac{R}{v-b}$ ← also get same from $\frac{\alpha}{K_T}$ of susceptibilities in problem 3.2.

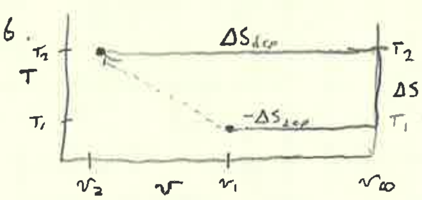
$P = \frac{RT}{v-b} - \frac{a}{v^2}$

5. $\left(\frac{\partial S}{\partial v}\right)_T^{vdw} = \frac{R}{v-b} \qquad \left(\frac{\partial S}{\partial v}\right)_T^{IG} = \frac{R}{v} \qquad (S^{vdw} - S^{IG}) = \int_\infty^v \left(\frac{\partial S}{\partial v}\right)_T^{vdw} - \left(\frac{\partial S}{\partial v}\right)_T^{IG}$ dv

$\Delta S_{dep} = \int_\infty^{v(T,P)} \frac{R}{v-b} - \frac{R}{v}\, dv = R(\ln(v-b) - \ln(v))\Big|_\infty^v$

$= R\ln\left(\frac{v-b}{v}\right)\Big|_\infty^v = \boxed{R\ln\left(\frac{v-b}{v}\right) = \Delta S_{dep}}$

6.



$\Delta S^{IG} = \int_{T_1}^{T_2} \frac{C_p}{T} dT$ ← what we did in 5.1

Nice job!!

$\Delta S = -\Delta S_{dep} + \Delta S^{IG} + \Delta S_{dep}$

$= -R\ln\left(\frac{v_1 - b}{v_1}\right) + 7.155\frac{J}{mol} + R\ln\left(\frac{v_2 - b}{v_2}\right)$

$= 0.3638\frac{J}{mol} + 7.155\frac{J}{mol} - 2.794\frac{J}{mol}$

$\boxed{\Delta S = 4.725 \frac{J}{mol}}$