Problem 1:

(a)

E-o-S: $\left(P + \frac{a}{kTv^2}\right)(v - v_0) = kT$

demand: $U \to \frac{5}{2} NkT$ ⊛

We are looking for: A.

Need to demand ⊛.

Strategy: Use $P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$ to get A

Use $U = A - T\left(\frac{\partial A}{\partial T}\right)_{V,N}$ to get U

Use U to enforce condition ⊛.

Use whatever constraint found to rewrite A.

From E-o-S: $P = \frac{NkT}{V - V_0} - \frac{a}{kT}\frac{N^2}{V^2}$

$$\Rightarrow +\left(\frac{\partial A}{\partial V}\right)_{T,N} = -\frac{NkT}{V - V_0} + \frac{a}{kT}\frac{N^2}{V^2}$$

Integrate both sides:

$$A = -\frac{a}{kT}\frac{N^2}{V} - NkT\log(V-V_0) + \underbrace{N f(N,T)}_{\text{Some fct. that may depend on } N \text{ and } T \text{ (cannot depend on } V)}$$

Now: Calculate $U = A - T\left(\frac{\partial A}{\partial T}\right)_{V,N}$

$$\Rightarrow U = -\frac{a}{kT}\frac{N^2}{V} - \underline{NkT\log(V-V_0)} + Nf(N,T)$$

$$- T\frac{a}{kT^2}\frac{N^2}{V} + \underline{TNk\log(V-V_0)} - NT\left(\frac{\partial f(N,T)}{\partial T}\right)_{V,N}$$

$$= Nf(N,T) - NT\left(\frac{\partial f(N,T)}{\partial T}\right)_{V,N} - 2N\frac{a}{kT}\left(\frac{N}{V}\right) \longrightarrow 0$$

(per assignment)

cannot have V dependence here

$$\stackrel{!}{=} \frac{5}{2}NkT$$

enforce

So: $f(N,T) - T\left(\frac{\partial f(N,T)}{\partial T}\right)_N = \frac{5}{2}kT$

$$\Rightarrow \left(\frac{\partial f(N,T)}{\partial T}\right)_N = \frac{1}{T} f(N,T) - \frac{5}{2} k$$

$$\Rightarrow f(N,T) = -\frac{5}{2} kT \log T + cT$$

we need this here to get the units right!

$$\Rightarrow \boxed{A = -\frac{a}{kT}\frac{N^2}{V} - NkT\log(V-V_0) - \frac{5}{2} NkT \log T + cTN}$$

(b) Want $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

But: $$U = N\left[f(N,T) - T\left(\frac{\partial f}{\partial T}\right)_{V,N} - \frac{2a}{kT}\frac{N}{V}\right]$$

$$T\frac{\partial f}{\partial T} = T\left(-\frac{5}{2} k \log T - \frac{5}{2} k + c\right)$$

$$\Rightarrow U = N\left[-\frac{5}{2} kT\log T + cT + \frac{5}{2} kT \log T + \frac{5}{2} kT - cT - \frac{2a}{kT}\frac{N}{V}\right]$$

$$= N\left[\frac{5}{2} kT - \frac{2a}{kT}\frac{N}{V}\right]$$

$$\Rightarrow C_V = \left(\frac{\partial u}{\partial T}\right)_V = N\left(\frac{5}{2}k + \frac{2a}{kT^2}\,\frac{N}{V}\right)$$

$$= N\,\frac{5}{2}k\left(1 + \underbrace{\frac{4a}{5k^2T^2}\,\frac{N}{V}}\right)$$

goes to zero in
high T and in $n = \frac{N}{V} \to 0$
limits

Homework 5, Problem 2:

(a)

From Problem 1:

$$p = \frac{kT}{v - v_0} - \frac{a}{kT\, v^2}$$

and

$$\varepsilon = \frac{U}{N} = -\frac{2a}{v\,(kT)} + \frac{5}{2} kT$$

What are the units of a and v_0?

v_0 : same units as $v \rightarrow L^3$

a : We know $\left[\frac{a}{kT\, v^2}\right] = [P]$

units of

$$[kT] = E$$

$$[v^2] = L^6$$

$$[P] = \frac{E}{L^3}$$

$\Rightarrow$ units of a : $E^2 L^3$

It is clear: to make v dimensionless, we have to divide by v_0

to make kT dimensionless, we have to divide by $\sqrt{a/v_0}$

to make ε dimensionless, we have to divide by $\sqrt{a/v_0}$

to make P dimensionless, we have to divide by $\sqrt{a/v_0^3}$

let's see if we can rewrite P and ε in terms of these dimensionless quantities

$$P = \frac{kT}{v-v_0} - \frac{a}{kT v^2}$$

$$\Rightarrow \frac{P}{\sqrt{a/v_0^3}} = \underbrace{\frac{kT}{v-v_0}\sqrt{\frac{v_0^3}{a}}}_{\frac{\frac{kT}{\sqrt{a/v_0}}}{\frac{v}{v_0}-1}} - \underbrace{\frac{a}{kT v^2}\sqrt{\frac{v_0^3}{a}}\sqrt{\frac{v_0}{v_0}}}_{\frac{1}{\frac{kT}{\sqrt{a/v_0}}\frac{v^2}{v_0^2}}}$$

divide l.h.s. and r.h.s. by $\sqrt{a/v_0^3}$

and hence
$$\boxed{\tilde{P} = \frac{\tilde{\tau}}{\tilde{v} - 1} - \frac{1}{\tilde{\tau}\,\tilde{v}^2}}$$

where
$$\boxed{\tilde{P} = \frac{P}{\sqrt{a/v_0^3}}}$$

$$\boxed{\tilde{\tau} = \frac{kT}{\sqrt{a/v_0}}}$$

$$\boxed{\tilde{v} = \frac{v}{v_0}}$$

Next:
$$\varepsilon = -\frac{2a}{v(kT)} + \frac{5}{2} kT$$

$$\Rightarrow \frac{\varepsilon}{\sqrt{\frac{a}{v_0}}} = -\underbrace{\frac{2a}{v(kT)\sqrt{\frac{a}{v_0}}}}_{\frac{2}{\frac{kT}{\sqrt{\frac{a}{v_0}}}\frac{v}{v_0}}} + \frac{5}{2}\underbrace{\frac{kT}{\sqrt{\frac{a}{v_0}}}}_{\tilde{\tau}}$$

Thus:
$$\boxed{\tilde{\varepsilon} = -\frac{2}{\tilde{\tau}\,\tilde{v}} + \frac{5}{2}\tilde{\tau}}$$

where
$$\boxed{\tilde{\varepsilon} = \frac{\varepsilon}{\sqrt{\frac{a}{v_0}}}}$$

What do we have?

We can plot $\tilde{p}$ as a fct. of $\tilde{v}$ for fixed $\tilde{\tau}$

↳ these are isotherms

The resulting plot is applicable to any gas, provided a and v_0 are known and provided pressure, $k \cdot$ temperature, and volume are scaled by constants that are determined by a and v_0

(b) Let us calculate the critical temperature:

$$\frac{\partial \tilde{p}}{\partial \tilde{v}} \stackrel{!}{=} 0 \quad \text{and} \quad \frac{\partial^2 \tilde{p}}{\partial \tilde{v}^2} \stackrel{!}{=} 0$$

equations define $\tilde{\tau}_c$ and $\tilde{v}_c$

$$\frac{\partial \tilde{p}}{\partial \tilde{v}} = - \frac{\tilde{\tau}}{(\tilde{v}-1)^2} + \frac{2}{\tilde{\tau}\,\tilde{v}^3}\Bigg|_{\substack{\tilde{\tau}=\tilde{\tau}_c \\ \tilde{v}=\tilde{v}_c}} = 0$$

$$\frac{\partial^2 \tilde{p}}{\partial \tilde{v}^2} = + \frac{2\tilde{\tau}}{(\tilde{v}-1)^3} - \frac{6}{\tilde{\tau}\,\tilde{v}^4}\Bigg|_{\substack{\tilde{\tau}=\tilde{\tau}_c \\ \tilde{v}=\tilde{v}_c}} = 0$$

Rearrange: $$\frac{\tilde{\tau}_c}{(\tilde{v}_c - 1)^2} = \frac{2}{\tilde{\tau}_c \tilde{v}_c^3} \quad A$$

$$\frac{\tilde{\tau}_c}{(\tilde{v}_c - 1)^3} = \frac{3}{\tilde{\tau}_c \tilde{v}_c^4} \quad B$$

A/B : $(\tilde{v}_c - 1) = \frac{2}{3}\tilde{v}_c$ or $\frac{1}{3}\tilde{v}_c = 1 \Rightarrow \tilde{v}_c = 3$

$\tilde{v}_c = 3$ into A : $\tilde{\tau}_c^2 = \frac{2}{27} \cdot 2^2 = \frac{8}{27}$

$$\Rightarrow \tilde{\tau}_c \approx 0.544$$

Physically: $$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$ isothermal compressibility

For $\left(\frac{\partial P}{\partial V}\right)_T \to 0$, we have $\kappa_T \to \infty$

What does $\left(\frac{\partial P}{\partial V}\right)_T < 0$ imply?

The pressure decreases if we expand a substance at fixed temperature.

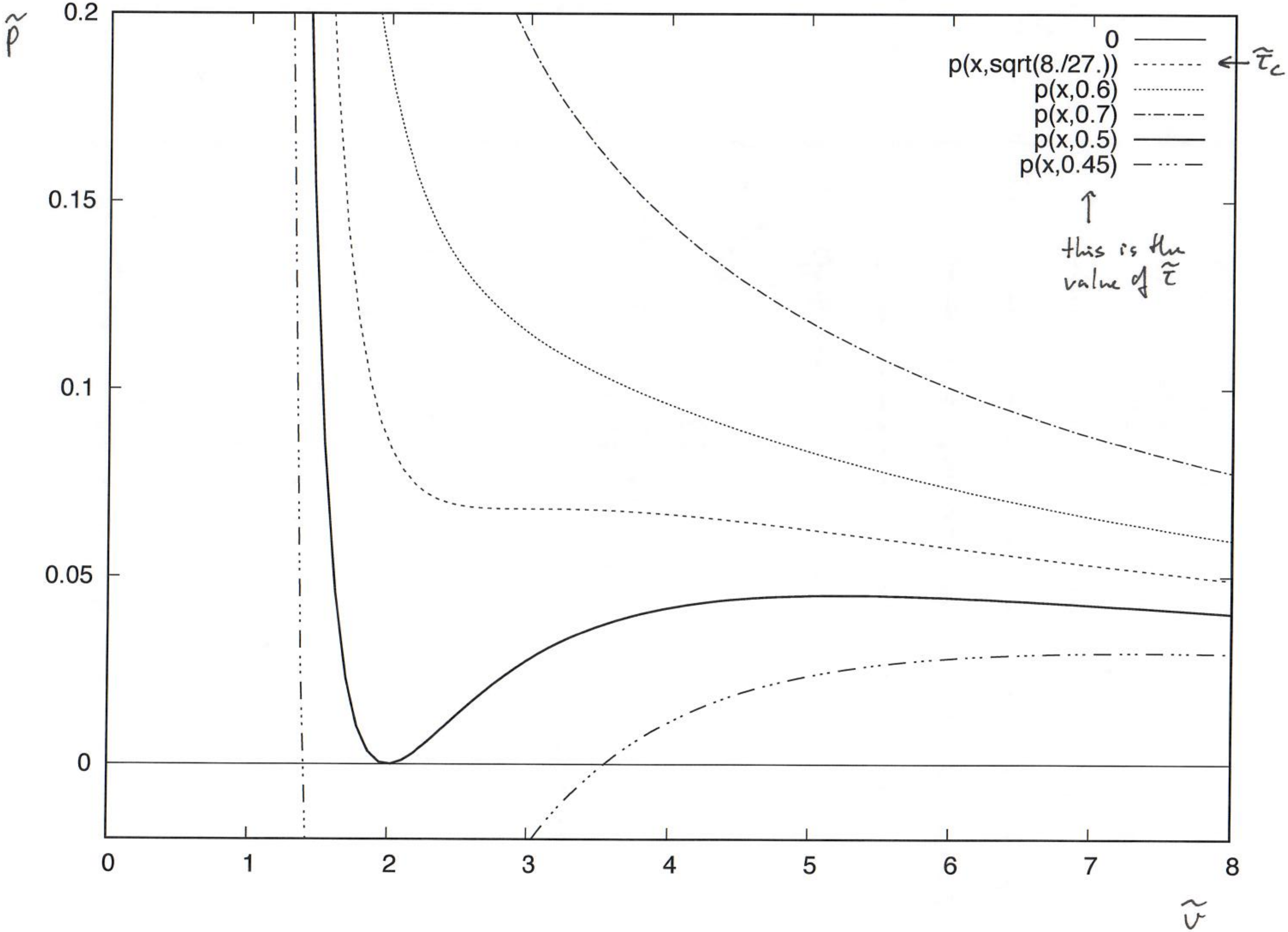
This makes intuitive sense.

When $\left(\frac{\partial p}{\partial V}\right)_T > 0$, we enter an "unphysical regime" of the E-o-S.

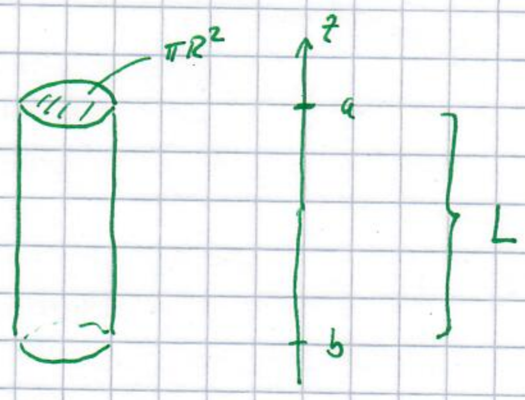
corresponds to negative compressibility

This means that the Berthelot eq. does not provide a valid description of a uniform phase in certain regions.

(c)


$\tilde{p}$
0.2
0.15
0.1
0.05
0
0
1
2
3
4
5
6
7
8
$\tilde{v}$
0
p(x,sqrt(8./27.))
p(x,0.6)
p(x,0.7)
p(x,0.5)
p(x,0.45)
$\leftarrow \tilde{\tau}_c$
this is the value of $\tilde{\tau}$

Problem 3:



(a) Consider a single particle:

$$Q_1 = \frac{1}{h^3} \int e^{-\beta \mathcal{H}} \, d^3\vec{q} \; d^3\vec{p}$$

working in the canonical ensemble

$$= \frac{1}{h^3} \underbrace{\int e^{-\beta K z} \, d^3\vec{q}}_{\underbrace{\pi R^2}_{} \int_b^a e^{-\beta K z} \, dz} \quad \underbrace{\int e^{-\beta \frac{\vec{p}^2}{2m}} \, d^3\vec{p}}_{\left(\frac{\pi \, 2m}{\beta}\right)^{3/2}}$$

from the integration over $\rho \, d\rho \, d\varphi$ cylindrical coordinates

$$= \pi R^2 \frac{1}{-\beta K} \, e^{-\beta K z} \Big|_b^a$$

So: $Q_1 = \frac{1}{h^3} \pi R^2 \frac{1}{\beta K} \left(e^{-\beta K b} - e^{-\beta K a}\right) \left(\frac{\pi 2m}{\beta}\right)^{3/2}$

$$Q_N = \frac{1}{N!} Q_1^N$$

(b) Let's think about this a bit first.

Usually: $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$

where $A = -kT \log Q_N$

$Q_N = e^{-\beta A}$

A: Helmholtz free energy

In our case: Pressure on the wall at $z=a$ and $z=b$

So: Volume $\hat{=}$ $\pi R^2 \cdot$ length

$$P_a = -\frac{\partial A}{\pi R^2 \partial a}$$

$$P_b = -\frac{\partial A}{\pi R^2 \partial(-b)} = \frac{\partial A}{\pi R^2 \partial b}$$

P_a
gas pushing in up direction

P_b
gas pushing in down direction

$$\Rightarrow P_a = -\frac{1}{\pi R^2} \frac{\partial}{\partial a} \left(-N \log\left(e^{-\beta K b} - e^{-\beta K a}\right)\right)$$

$$= + \frac{1}{\pi R^2} N \frac{+\beta K e^{-\beta K a}}{e^{-\beta K b} - e^{-\beta K a}}$$

$$= + \frac{N\beta K}{\pi R^2} \frac{-1}{\left(-e^{\beta K L} + 1\right)}$$

$L = a - b$

Similarly: $P_b = \frac{N\beta K}{\pi R^2} \frac{+e^{-\beta K b}}{e^{-\beta K b} - e^{-\beta K a}}$

$$= \frac{N\beta K}{\pi R^2} \frac{+1}{1 - e^{-\beta K L}}$$

(d) Let $KL >> kT$: $\Rightarrow e^{-\beta K L} \to 0$

$$P_b = + \frac{N\beta K}{\pi R^2}$$

$$-\left(-e^{\beta K L} + 1\right)^{-1} \to + e^{-\beta K L}$$

huge

$$P_a = + \frac{N\beta K}{\pi R^2} e^{-\beta K L}$$

$P_a < P_b$

higher potential
lower density

Homework 5, Problem 4:

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

$$v = \frac{V}{N}$$

Rearrange: $$\frac{P}{kT} = -\frac{a}{kTv^2} + \frac{1}{v-b}$$

$$\frac{Pv}{kT} = -\frac{a}{kTv} + \underbrace{\frac{1}{1-\frac{b}{v}}}_{\frac{1}{1-bn} \approx 1 + bn}$$

$$\Rightarrow \frac{Pv}{kT} \approx 1 + \underbrace{\left(b - \frac{a}{kT}\right)}_{\text{correction due to interactions}} n + \dots$$

So, in the ultra dilute limit, we are recovering the ideal gas law.

(b) For neon: $\left(b - \frac{a}{kT}\right) \xrightarrow{T \to \infty} 1.3 \cdot 10^{-5} \frac{m^3}{mol}$

$$\xrightarrow{T = 125K} 0$$

From this: $b = 1.3 \cdot 10^{-5} \frac{m^3}{mol}$

$$a = b\,k \cdot 125\,K \quad (***)$$

$$= b \cdot 1.381 \cdot 10^{-23} \frac{J}{K} \cdot 125\,K$$

$$= \frac{1.3 \cdot 1.381 \cdot 125 \cdot 6.022 \cdot 10^{-5}}{6.022 \cdot 10^{23}} \frac{J\,m^3}{mol}$$

$$= 0.0135\ J\,m^3/mol^2$$

(c) At critical T and critical v, we have:

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \quad (*)$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 \quad (**)$$

(*) $\frac{1}{kT}\left(\frac{\partial p}{\partial v}\right)_T = \frac{2a}{kTv^3} - \frac{1}{(v-b)^2} \stackrel{!}{=} 0$

$\Rightarrow kT_c = \frac{2a}{v_c^3}(v_c - b)^2$ (*')

(**) $\frac{1}{kT}\left(\frac{\partial^2 p}{\partial v^2}\right)_T = -\frac{6a}{kTv^4} + \frac{2}{(v-b)^3} \stackrel{!}{=} 0$

$\Rightarrow kT_c = \frac{6a}{v_c^4}\frac{1}{2}(v_c-b)^3$

$kT_c = \frac{3a}{v_c^4}(v_c - b)^3$ (**')

Set (*') and (**') equal:

$2 = \frac{3}{v_c}(v_c - b) \Rightarrow 2 = 3 - 3\frac{b}{v_c} \Rightarrow 1 = \frac{b}{v_c}3$

$\Rightarrow \boxed{v_c = 3b}$

Plug $v_c = 3b$ into (*'): $kT_c = \frac{2a}{27b^3}(3b-b)^2$

$\boxed{kT_c = \frac{8}{27}\frac{a}{b}}$

So: $kT_c = \frac{8}{27} k \cdot 125\,K = k \cdot 37\,K$

using (***)

So: $\boxed{T_c = 37\ K}$

Plugging T_c and v_c into e-o-s

Critical pressure: $$\frac{P_c}{k T_c} = -\frac{a}{k T_c v_c^2} + \frac{1}{(v_c - b)}$$

$$= -\frac{27}{8}\frac{b}{9b^2} + \frac{1}{2b}$$

$$\frac{a}{k T_c} = \frac{27 b}{8}$$

$$v_c = 3b$$

$$= \left(-\frac{3}{8} + \frac{4}{8}\right)\frac{1}{b}$$

$$= \frac{1}{8}\frac{1}{b}$$

$$P_c = \frac{k \cdot 37\ K}{8 \cdot 1.3 \cdot 10^{-5}\ \frac{m^3}{mol}}$$

$$= \frac{1.381 \cdot 10^{-23}\ J/K \cdot 37\ K}{8 \cdot 1.3 \cdot 10^{-5} \cdot (6.022 \cdot 10^{23})^{-1}\ m^3}$$

$$= 2.96 \cdot 10^{6}\ \frac{N}{m^2} = 29.2\ atm \qquad \boxed{P_c = 29.2\ atm}$$

$$1\ Pa = 1\ \frac{N}{m^2} = 9.87 \cdot 10^{-6}\ atm$$

The agreement w/ the experimentally determined values is not so bad:

Our treatment: $T_c = 37\,K$

$P_c = 29.2\,atm$

Experiment: $T_c = 44.5\,K$

$P_c = 26.9\,atm$

Given the simplicity of the e-o-s, the agreement appears quite reasonable.

↳ or disagreement