Phys 114 2018
Seminar 3
Problem Solutions

1: G&T problem 2.65

We are asked to show H is right free energy if S & N are fixed.

$$H = E + PV$$

Since $A = E + P_{bath}V - T_{bath}S$

S fixed $\Rightarrow \Delta A = \Delta E + P_{bath}\Delta V$

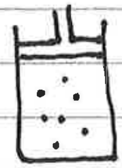
Need $\Delta A \leq 0$

If $H = E + PV = E + P_{bath}V$

$\Delta H = \Delta E + P_{bath}\Delta V = \Delta A$ we want.

Another way to view it... natural variables of H are $H(S, P, N)$ ... but this is why.

2:



$n = 10^{-2}$ mole

$P_i = 1\text{ atm} = 10^5\ N/m^2$ (really $1.01\times10^5\ N/m^2$ but...)

$T_i = 72°F = (72-32)\ 5/9 = 22.2°C$
$= 295.2\ K$

$V_i = \dfrac{nRT_i}{P_i} = 0.000245\ m^3$

$(= 245\ cm^3)$

Now $dG = VdP - SdT$ (see warmup problem!)

Thus at const. P, $dG = -SdT$ $\quad S = n S_{permole}$

from Table... $= -10^{-2}\cdot(154.8\ \frac{J}{K})(10\ K)$

$dT = 18°F$
$10°C$
$= T_f - T_i$

$= -15.5\ J$

* see next page... letting $S(T,V)$ vary is not too impt.

To raise G by changing pressure (need to raise it, as it has dropped by adding heat)

we need $\int V dP = +15.5\ J$

If this were a solid or liquid, would take $V = V_i = $ const. But have to be a little careful. When increase pressure, V decreases. So write $V = \dfrac{nRT_f}{P}$

$$\Rightarrow \quad \Delta G = nRT_f \int_{P_i}^{P_f} \frac{dP}{P} = nRT_f \ln \frac{P_f}{P_i}$$

Since $nRT_f = (10^{-2} mol)(8.3\ \frac{J}{mol\ K})(305.2\ K) = 25.3\ J$

$15.5\ J = 25.3\ J \ \ln\left(\frac{P_f}{P_i}\right) \Rightarrow P_f = 1.8\ P_i = \underline{1.8\text{ atm}}$

Here is calculation where we assume S changes ... we write S(T,V) = S(Ti,Vi) + ΔS with the latter as given for an ideal gas, on p. 78 of G&T. Doesn't make much difference to do this, rather than to just take S(Ti,Vi).

```
In[43]:= Vi = .000245

Out[43]= 0.000245

In[44]:= Vf = Vi * (315 / 295)

Out[44]= 0.00026161

In[45]:= Ti = 295

Out[45]= 295

In[57]:= Tf = 315

Out[57]= 315

In[58]:= NIntegrate[Log[x / Ti], {x, Ti + .001, Tf}]

Out[58]= 0.663144

In[61]:= .01 * 154.8 * 10 + 3 / 2 * .01 * 8.3 * NIntegrate[Log[x / Ti], {x, Ti + .001, Tf}]
          + .01 * 8.3 * NIntegrate[Log[x / Vi], {x, Vi + .001, Vf}]

Out[61]= 15.5626
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3: G&T 2.32

Finding Legendre Transforms

(a) Suppose $f(x) = x^3$ restrict domain to $x > 0$; $m > 0$

Then $m = f'(x) = 3x^2$

$\Rightarrow \quad x = +\sqrt{m/3}$

Legendre transform is $g = f - xm$

$= x^3 - 3x^3$

$= -2x^3$

$= -2\left(\frac{m}{3}\right)^{3/2}$

$= -\sqrt{\frac{4}{27}}\, m^{3/2}$

Note further $\frac{\partial g}{\partial m} = \ldots = \ldots$

$= \sqrt{m/3} = x$

$\Rightarrow f(x) = g(m) + mx = -2x^3 + 3x^3 = x^3$

(b) Now consider $f(x) = x$

Then $m = f'(x) = 1$ so

$g = f - xm = x - x = 0$. This seems* weird but it works. However, it cannot* be inverted: $f(x) \neq g(m) + \frac{dg}{dm} m$ ... m

Need $f''(x)$ monotonic. Here $f''(x) = 0$! Also... all m are same; $m = 1$ so $x = -\frac{\partial g}{\partial m}$

Now consider $f(x) = \sin x$

Then $m = f'(x) = \cos x$

and $x = \cos^{-1} m$. Then

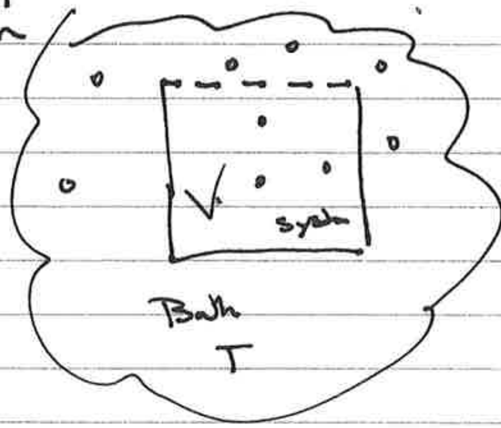
$g = f - xm = \sin(\cos^{-1} m) - m\cos^{-1} m$

But $\sin x$ is not monotonic $\Leftrightarrow$ $\cos^{-1} m$ is not unique. This is not a well-defined transform.

* of course could do $f(x) = g(m) + mx$ so can invert perhaps so &

4: The Landau Pot'l G+T 2.66

To find: Ω where
T is fixed by heat bath, V fixed,
but particles can move btwn system
+ bath



$$A = E + P_{bath}V - T_{bath}S - \mu_{bath}N$$

V fixed $\Rightarrow$ $\Delta A = \Delta E - T_{bath}\Delta S - \mu_{bath}\Delta N$

as equilib is established and $\Delta A \leq 0$

If $\Omega = E - TS - \mu N$

Then $\Delta\Omega \leq 0$

p. 83 of G+T argues (1st law)

$$d\Omega = dF - \mu dN - N d\mu$$
$$= -SdT - PdV - Nd\mu$$

$$\Omega = U - TS - \mu N = G - PV - \mu N = \boxed{-PV}$$ since $G = \mu N$

$$G = H - TS = U + PV - TS$$

5

5: Helmholtz free energy of hydrogen (Schroeder problem 5.20)
The first excited energy level of a hydrogen atom has an energy of *10.2 eV*, if we take the ground state energy to be zero. However, the first excited state is really four independent states all with the same energy. We can assign it (as we'll see very soon in seminar) as having entropy $S = kln4$. For what temperatures is the Helmholtz free energy of a hydrogen atom in the first excited state positive, and for what temperatures is it negative? (Why is this useful? When F is negative, the atom will spontaneously go from the ground state, where $F \equiv 0$, into that level ... since the natural direction toward equilibrium is that F tends toward its m minimum value. Of course, for a system this small - only five states- , random fluctuations could be significant.)

The Helmholtz free energy of the first excited level is

$$F = U - TS = (10.2 \text{ eV}) - T(k \ln 4).$$

At low temperatures this is positive, so the atom would rather be in the ground state (which has $F = 0$); at high temperatures, however, F for the excited level becomes negative, so this level becomes preferred over the ground state. The transition temperature is where $F = 0$, i.e., when $kT \ln 4 = 10.2$ eV or $kT = 7.36$ eV or

$$T = \frac{7.36 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} = 8.5 \times 10^4 \text{ K}.$$

This is more than ten times hotter than the surface of the sun.

6: G&T prob 2.68

(a) Want to derive $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$ First ID

NOTE: this is kind of DONE in Ex. 16.4 of B+B ☺ $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ Second ID

First ID: To do this, we use maxwell rel'n we've already used to eg. do warmup prob: (involves mixed partials of G)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (1)$$

Now $C_P = T\left(\frac{\partial S}{\partial T}\right)_P \Rightarrow \left(\frac{\partial C_P}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(T\left(\frac{\partial S}{\partial T}\right)_P\right)\Big|_T$

$$= T\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\Big|$$

Thus $\left(\frac{\partial C_P}{\partial P}\right)_T \underset{\text{order of partials Not impt}}{=} T\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\Big|_P$

$$\underset{\text{from (1)}}{=} -T\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\Big|_P$$

So $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$ QED

Second ID: Start with F instead of G,

and maxwell rel'n $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (2)$

Now, $C_V = T\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = T\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\Big|_T$

change order as above $\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = T\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T \underset{\text{from (2)}}{=} T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ QED

(b) To show: $$\frac{K_T}{K_S} = \frac{C_P}{C_V}$$

where $K_X = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_X$ is the compressibility at const X

Once we have shown this, we should be able to use it and G+T Eq (2.205).

$$C_P - C_V = V\frac{T}{K_T}\alpha^2$$

to get $$K_T - K_S = \frac{TV}{C_P}\alpha^2$$

Solution:

Note: This is kind of one in Ex. 16.7 of B+B

$$\frac{K_T}{K_S} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}{\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S}$$

from antisymm identity

$$= \frac{-\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V}{-\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_V}$$

from $\frac{\partial y}{\partial x} = \frac{1}{\frac{\partial x}{\partial y}}$

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

cancel ∂V from num + ∂P from denom

$$= \frac{T\left(\frac{\partial S}{\partial T}\right)_P}{T\left(\frac{\partial S}{\partial T}\right)_V} = \frac{C_P}{C_V}$$:)

Now last thing

from G&T Eq. (2.205)

$$C_p - C_v = \frac{VT}{K_T}\alpha^2$$

NB book doesn't say it but it's isothermal compressibility

$$= C_p\left(1 - \frac{C_v}{C_p}\right) = C_p\left(1 - \frac{K_S}{K_T}\right)$$ just shown

$\therefore$ ~~α~~

$$K_T C_p\left(1 - \frac{K_S}{K_T}\right) = VT\alpha^2$$

$$\Rightarrow (K_T - K_S) = \frac{VT\alpha^2}{C_p}$$ QED

7: B & B Problem 16.2

(a) To derive:

(i) $\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]$

(ii) $\left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{C_V} T\left(\frac{\partial p}{\partial T}\right)_V$

(iii) $\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$

and want to say what kind of expansion the LHS is appropriate for ....

For (i) again use antisymm id so $\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V\left(\frac{\partial U}{\partial V}\right)_T$

Thus $= -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T \underset{\text{1st law}}{=} -\frac{1}{C_V}\left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right]$

$\underset{\text{Maxwell rln}}{=} -\frac{1}{C_V}\left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)$

This is an <u>energy-conserving process</u>. Example is <u>Joule expansion</u>.

(ii) $\left(\frac{\partial T}{\partial V}\right)_S \underset{\text{antisymm id}}{=} -\left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T$

<u>Adiabatic expansion</u>

$= -\left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial p}{\partial T}\right)_V$

$= -\frac{T}{C_V}\left(\frac{\partial p}{\partial T}\right)_V$

(iii) $\left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p\left(\frac{\partial H}{\partial p}\right)_T = \frac{1}{C_p}\left(T\left(\frac{\partial S}{\partial p}\right)_T + V\right)$

Use $dH = TdS + Vdp$

<u>Joule-Kelvin Expansion</u> $= \frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_p - V\right)$

(b) Want to verify using relns of (a) that for ideal gas $\left(\frac{\partial T}{\partial V}\right)_U = 0$

$$\left(\frac{\partial T}{\partial P}\right)_H = 0$$

and $\left(\frac{\partial T}{\partial V}\right)_S \Rightarrow pV^{\gamma} = \text{const}$

So if $pV = nRT$ then

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[\frac{TnR}{V} - p\right] \checkmark$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[T\left(\frac{nR}{p}\right) - V\right] \checkmark$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{C_V} T \frac{nR}{V}$$

$$\Rightarrow \frac{\partial T}{T} = \frac{\partial V}{V}\frac{nR}{C_V} = \frac{\partial V}{V}\frac{C_p - C_V}{C_V}$$

$$= \frac{\partial V}{V}\cdot(\gamma - 1)$$

$$\Rightarrow TV^{\gamma-1} = \text{const}$$

$$\Rightarrow pV^{\gamma} = \text{const} \; \ddot\smile$$

11

8) **Helmholtz and Gibbs:**

a) The Helmholtz F and Gibbs G free energies are two important thermodynamic potentials. Each of these is minimized by a system under certain

b) Each of F and G represent "available work", so which one is preferable to use for

i) calculating the energy needed to materialize a rabbit on a table ?

ii) finding the chemical potential μ ?

iii) determining if the following chemical reaction will go at a temperature of $500K$?

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2$$

c) Please say which potential is best to use, and then use it to solve this problem: A cylinder contains an internal piston on each side of which is one mole of a monatomic ideal gas. The cylinder walls are diathermal, and the system is immersed in a heat reservoir at temperature $0°C$. The initial volumes of the two gaseous subsystems (on either side of the piston) are 10 L and 1 L, respectively. The piston is now moved reversibly, so that the final volumes are 6 L and 5 L, respectively. How much work is delivered?

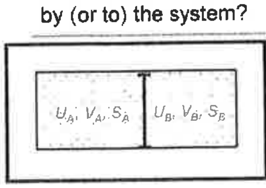
Processes at T = const

In general, if we consider processes with "other" work: $\boxed{dF = -SdT - PdV + \delta W_{other}}$

For the processes at T = const (in thermal equilibrium with a large reservoir): $(dF)_T = (-PdV + \delta W_{other})_T$

The **total** work performed on a system at T = **const** in a **reversible** process is equal to the change in the Helmholtz free energy of the system. In other words, for the T = **const** processes the Helmholtz free energy gives all the reversible work.

Problem: Consider a cylinder separated into two parts by an adiabatic piston. Compartments ***a*** and ***b*** each contains one mole of a monatomic ideal gas, and their initial volumes are V_{ai}=10*l* and V_{bi}=1*l*, respectively. The cylinder, whose walls allow heat transfer only, is immersed in a large bath at 0°C. The piston is now moving reversibly so that the final volumes are V_{af}=6*l* and V_{bi}=5*l*. How much work is delivered by (or to) the system?



The process is isothermal: $(dF)_T = (-PdV)_T$

The work delivered by the system: $\delta W = \delta W_a + \delta W_b = \int_{V_{ai}}^{V_{af}} dF_a + \int_{V_{bi}}^{V_{bf}} dF_b$

For one mole of monatomic ideal gas:

$$F = U - TS = \frac{3}{2}RT - \left(\frac{3}{2}RT\ln\frac{T}{T_0} - RT\ln\frac{V}{V_0} + Tf(N,m)\right)$$

$$\delta W = RT\ln\frac{V_{af}}{V_{ai}} + RT\ln\frac{V_{bf}}{V_{bi}} = 2.6\cdot 10^3\ \mathrm{J}$$

Answers with thx to
Chrissy M, P114 2016

Applications: Gas Compression

Q: Use either Gibbs or Helmholtz in the following problem: A cylinder contains an internal piston on each side of which is one mole of a monatomic ideal gas. The cylinder walls are diathermal, and the system is immersed in a heat reservoir at temperature 0C. The initial volumes of the two gaseous subsystems (on either side of the piston) are 10 L and 1 L, respectively. The piston is now moved reversibly, so that the final volumes are 6 L and 5 L, respectively. How much work is delivered?

A: F because total volume does not change

Helmholtz Free Energy

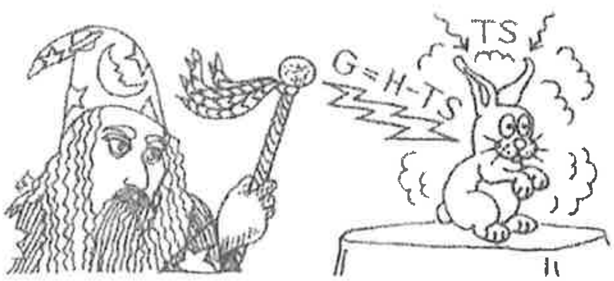
- Helmholtz function defined to be F =U-TS
- Differential is given by dF = - S dT + p dV
- For a system at constant temperature and volume:
  - dV=dT=0
  - This reduces the definition of dA to dF
  - Require that A is less than or equal to 0 for a process to occur spontaneously
  - Minimum F for equilibrium

Gibbs Free Energy

- Gibbs function defined to be G =H-TS
- Differential is given by dG = - S dT + V dp
- For a system at constant temperature and pressure:
  - dp=dT=0
  - This reduces the definition of dA to dG
  - Require that A is less than or equal to 0 for a process to occur spontaneously
  - Minimum G for equilibrium

Gibbs vs. Helmholtz

For **constant temperature and pressure**, minimizing the **Gibbs** free energy function, G, gives the equillibrium state



For constant temperature and volume, minimizing the **Helmholtz** free energy function gives the equillibrium state

Applications: Materializing Rabbit

Q: Should we use Gibbs or Helmholtz to calculate the energy needed to materialize a rabbit on a table?

A: Either, but G is more likely because pressure is easier to keep constant. F could be done if we had a box filled with a certain amount of air in a container and the rabbit replaced the air in the box.

Applications: Chemical potential

Q: Which should we use to find the chemical potential?

A: G=mu*N, easier to use because labs generally at constant pressure rather than volume, could also use F

Applications: Decomposing water

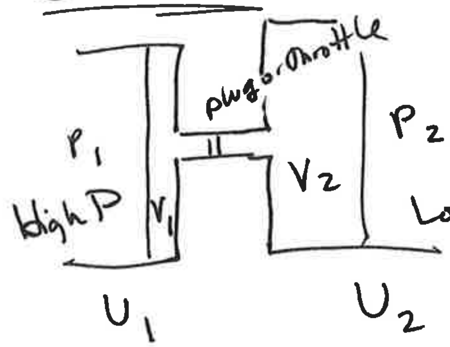
Q: Using Gibbs or Helmholtz, determine if the decomposition of water will go at 500 K.

A: G again because this reaction is more likely to go at a constant pressure rather than volume

Problem 9: Liquifying gasses B+B 27.2

To Explain, why H is conserved.

Answer: As shown in Fig 27.2



Cons. of energy

$$\Downarrow$$

$$U_2 - U_1 = \underbrace{W_{\text{on gas in 1}}}_{\text{To move that fixed volume of gas thru space, Pressure } P_1 \text{ does this work}} - \underbrace{W_{\text{on gas in 2}}}_{\text{This is work done by gas against pressure } P_2}$$

Thus

$$U_2 - U_1 = P_1 V_1 - P_2 V_2$$

$$\Rightarrow U_2 + P_2 V_2 = U_1 + P_1 V_1$$

But $H \equiv U + PV$ is def of enthalpy

Thus Enthalpy is conserved! (proof: Rabbit! I get it!!)

Thus now need to deduce

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

(which is μ_{JK} ...) when positive gas is cooled!

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{-(\partial T/\partial H)_P}{(\partial P/\partial H)_T} = \frac{-(\partial H/\partial P)_T}{(\partial H/\partial T)_P}$$

$$= -\frac{1}{C_P}\left[\left.\frac{\partial H}{\partial P}\right|_T\right]$$

Since $dH(S,P) = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP = T\,dS + VdP$

we have

$$\left.\frac{\partial H}{\partial P}\right|_T = T\underbrace{\left(\frac{\partial S}{\partial P}\right)_T}_{\text{maxwell rel'n}} + V$$

$$= T\left(\frac{\partial V}{\partial T}\right)_p + V$$

So finally $\left(\frac{\partial T}{\partial P}\right)_H \equiv \mu_{JK} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$

QED :)

Estimate for Helium ...

Use hint that we can write equation of state as $P = \ldots$ + use $\left(\frac{\partial V}{\partial T}\right)_p = -\frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T}$

Also can assume

one mole I guess!

(i) $\frac{PV}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} + \ldots$ ("virial series")

(ii) "Boyle temp" is $\frac{a}{bR} = 19\,K \equiv T_{Boyle}$

this is where $b - \frac{a}{RT}$ vanishes ...

Sol'n: $P = \frac{RT}{V} + \frac{bRT}{V^2} - \frac{a}{V^2}$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} + \frac{bR}{V^2}$$

and $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} - \frac{2bRT}{V^3} + \frac{2a}{V^3}$

Thus $\left(\frac{\partial V}{\partial T}\right)_p = -\frac{+R/V + bR/V^2}{-RT/V^2 - 2bRT/V^3 + 2a/V^3}$

$$= -\frac{(RV + bR)}{-RTV - 2bRT + 2a} \cdot V$$

Prob 11 (cont)

Thus

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = 0 \quad \text{becomes}$$

$$V\left[\frac{-T(V+b)}{-TV-2bT+\frac{2a}{R}} - 1\right] = 0$$

common denom

$$\Rightarrow \quad -TV - bT + TV + 2bT - \frac{2a}{R} = 0$$

$$bT - \frac{2a}{R} = 0 \quad \text{at } T = T_{inv}$$

$$\Rightarrow T_{inv} = \frac{2a}{bR} = 2T_{Boyle} = 38\,K$$

Wow! Pretty close to expt.

Also cool that T_{inv} relates to T_{Boyle}.

T_{Boyle} is temp at which non-ideal gas "acts ideal" to 1st order in density at least :)