Exam 1

Key for Practice Problems

1. $q(V,T) = \sum_{\text{levels},j} g_j e^{-\beta \varepsilon_j}$

$q(V,T)$: molecular partition function as a function of Volume + Temp; $q(V,T)$ is a measure of the ability of a particle to escape the ground state

g_j : the degeneracy of the system

β : $1/k_B T$ (or a parameter related to T)

ε_j : energy of the j^{th} level

2. H−C≡C−H acetylene (linear)

Total DOF = $3n = 3 \cdot 4 = 12$

Trans DOF = 3

Rot DOF = 2 (linear)

Vib DOF = 7 ($3n-5$)

3. At the Boyle temperature, a gas acts ideally.

So $\bar{V} = \bar{V}_{ideal}$ and $B_{2V} = 0$ (no deviation from ideality)

Ans : e

4. $B_{2V} = \bar{V} - \bar{V}_{ideal}$ $\quad \bar{V}_{ideal} = \frac{RT}{P}$ @ same T+P, all gases have same $\bar{V}_{ideal}$

The smallest $\bar{V}$ will result in the smallest B_{2V}. (i.e. largest deviation) This is CO_2. [Makes sense because CO_2 is largest molecule + will likely have interactions].

5. $Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}(V-Nb)^N e^{aN^2/VkT}$ $\quad b/c\ \beta = \frac{1}{k_B T}$

$\langle E\rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \qquad C_V = \frac{d\langle E\rangle}{dT}$

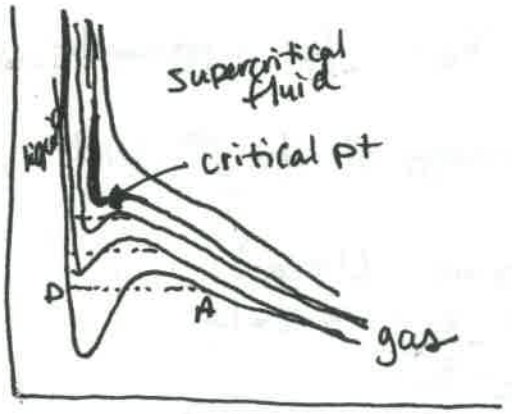
$\ln Q = -\ln N! + \frac{3N}{2}\ln\left(\frac{2\pi m k_B}{h^2}\right) + \frac{3N}{2}\ln T + N\ln(V-Nb) + \frac{aN^2}{VkT}$

$\frac{\partial \ln Q}{\partial T} = \frac{3N}{2T} - \frac{aN^2}{VkT^2}$

$\langle E\rangle = k_B T^2\left(\frac{3N}{2T} - \frac{aN^2}{VkT^2}\right) = \frac{3}{2}NkT - \frac{aN^2}{V}$

$C_V = \frac{d\langle E\rangle}{dT} = \frac{3}{2}Nk_B$

6.



- Between A + D, gases + liquids co-exist.
- van der Waals equation can't accurately describe the coexistance line. Because VDW is a cubic EOS w/ respect to $\bar{V}$, there are 3 real solutions below critical pt (1 @ critical pt; 1 real above c.p.) yielding VDW loops.

7. e Elec > Vib > rot > trans

8. b. f_2 (F) > f_2 (He) b/c it's easier to populate f_2 for F

9. Ideal gas assumptions: 1. no interactions between gases 2. no molecular size
VDW: introduces empirical parameters a + b to account for interaction + size, respectively

10. $\tilde{\nu} = \nu/c = \frac{5.3\times10^{13}\ 1/s}{2.9979\times10^{10}\ cm/s} = 1767.9\ cm^{-1}$