Chem 531: HW #6

(1) For CH_4 at $-50°C$, measured $\bar{V}$ values as a function of P are

$\bar{V}$ (in cm³/mol)	18224	1743	828	366
P (in atm)	1	10	20	40

$\bar{V}$ (in cm³/mol)	207	128.7	91.4	76.3
P (in atm)	60	80	100	120

Find the fugacity and fugacity coefficient of CH_4 at $-50°C$ and 120 atm (Hint: use the above data in a polynomial fit of $(Z-1)/P$). Please show all work (including plots).

Key relation: $\ln \gamma = \int_0^P \frac{Z-1}{P'} dP'$ where $f = \gamma P$

as shown on the next page, I plotted

$\frac{Z-1}{P}$ vs. P and fit this to a cubic polynomial. Integration over P gave the function needed to evaluate $\ln \gamma$

at P=120 atm ≈ 121.59 bar

$\ln \gamma = -0.61$

$\gamma = 0.55$

$f = 66.4 \text{ bar}$
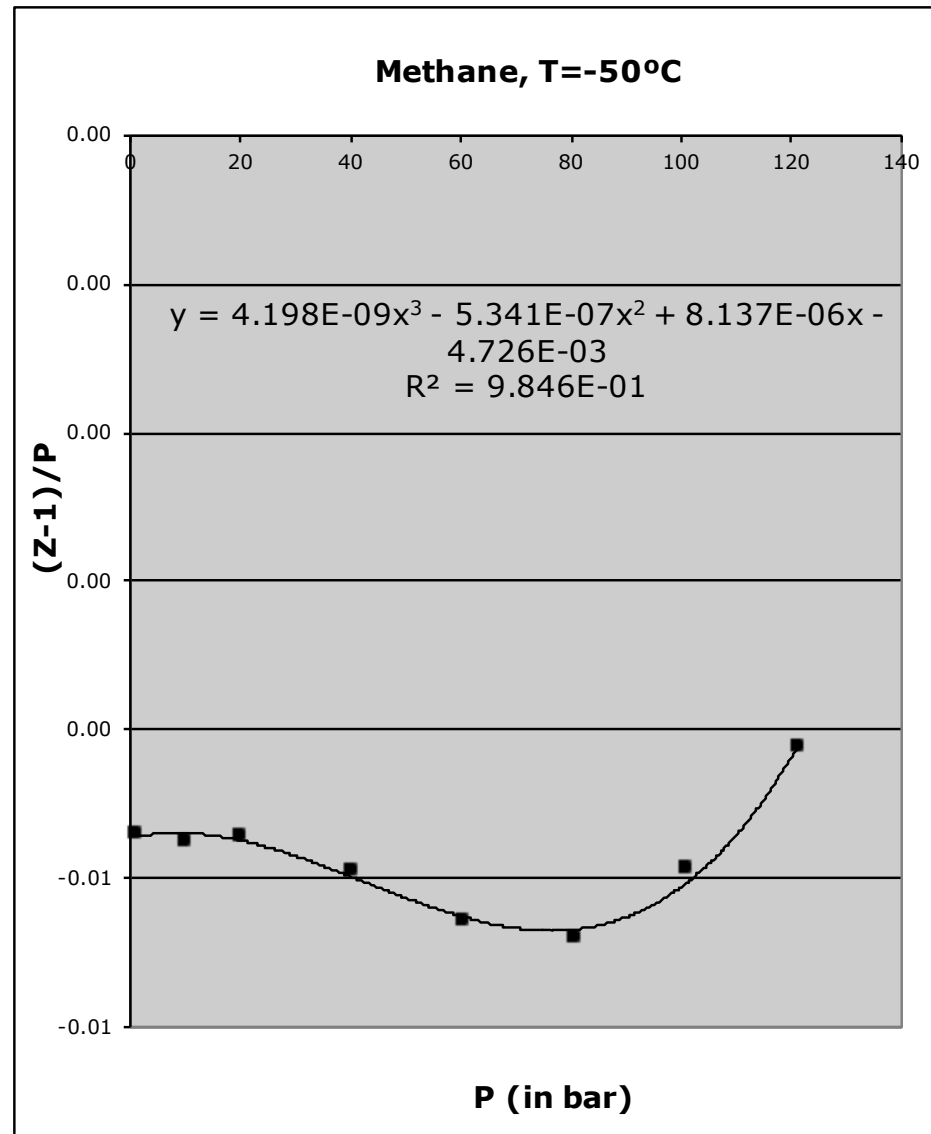
Vm (cm3/mol)	P (atm)
18224	1
1743	10
828	20
366	40
207	60
128.7	80
91.4	100
76.3	120

Vm (m3/mol)	P (bar)	Z	(Z-1)/P
1.822E-02	1.0133	0.99524	-0.00470
1.743E-03	10.1325	0.95188	-0.00475
8.280E-04	20.2650	0.90437	-0.00472
3.660E-04	40.5300	0.79951	-0.00495
2.070E-04	60.7950	0.67827	-0.00529
1.287E-04	81.0600	0.56228	-0.00540
9.140E-05	101.3250	0.49915	-0.00494
7.630E-05	121.5900	0.50002	-0.00411

at P=120 atm = 121.59 bar:

lnγ =	-0.61
γ =	0.55
f =	66.4 bar

Methane, T=-50ºC

$y = 4.198E\text{-}09x^3 - 5.341E\text{-}07x^2 + 8.137E\text{-}06x - 4.726E\text{-}03$

$R^2 = 9.846E\text{-}01$

(Z-1)/P

P (in bar)

(2) When two phases are in equilibrium, their chemical potentials are equal (for fixed T and P).
(a) Show that as the temperature is varied at constant P from the transition temperature by ΔT, the difference in chemical potentials between the two phases is equal to $-\Delta \bar{S}\,\Delta T$. Where $\Delta \bar{S}$ is the difference in molar entropies of the two phases. Assume the molar entropies are independent of T.
(b) then by what amount does the chemical potential of water exceed that of ice at $-5.00°$ C ?
(c) likewise by what amount does the chemical potential of water exceed that of steam at $105.00°$ C?

for each phase, $\quad d\mu = -\bar{S}\,dT \quad$ at const. P

(a) $\quad d\mu^{\alpha} = -\bar{S}^{\alpha}\,dT \qquad$ and $\qquad d\mu^{\beta} = -\bar{S}^{\beta}\,dT$

integrating both sides from T_1 to T_2

$$\mu^{\alpha}(T_2) - \mu^{\alpha}(T_1) = -\bar{S}^{\alpha}\Delta T \qquad \text{and} \qquad \mu^{\beta}(T_2) - \mu^{\beta}(T_1) = -\bar{S}^{\beta}\Delta T$$

if $T_1 \equiv$ transition temp, $\quad \mu^{\alpha}(T_1) = \mu^{\beta}(T_1)$

subtracting:
$$\mu^{\alpha}(T_2) - \mu^{\beta}(T_2) = -\left(\bar{S}^{\alpha} - \bar{S}^{\beta}\right)\Delta T$$
$$= -\Delta \bar{S}\,\Delta T \qquad \checkmark$$

(b) taking $\Delta\bar{S}$ of melting $= \dfrac{\Delta\bar{H}_{fus}}{T_{fus}} = \dfrac{6.008 \times 10^{3}}{273.15} = 22.0 \ J\,K^{-1}\,mol^{-1}$

$\Delta\mu = -(22.0)(-5.00) = 110 \ J/mol$

(c) likewise $\Delta\bar{S}_{vap} = \dfrac{\Delta\bar{H}_{vap}}{T_{vap}} = \dfrac{40.656 \times 10^{3}}{373.15} = 109.0 \ J\,K^{-1}\,mol^{-1}$

$\Delta\mu = -(-109.0)(5.00) = 545 \ J/mol$

(3) Carbon tetrachloride melts at 250 K. The vapor pressure of the liquid is 10,539 Pa at 290 K and 74,518 Pa at 340 K. The vapor pressure of the solid is 270 Pa at 232 K and 1092 Pa at 250 K.

(a) Calculate ΔH_{vap} and ΔH_{sub}

(b) Calculate ΔH_{fus}

(c) Calculate the <u>normal</u> boiling point and ΔS_{vap} at the boiling point

(a) Clausius-Clapeyron: $\ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$\Delta H_{vap} = \frac{-R \ln (P_2/P_1)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \frac{-(8.3145) \ln \frac{74518}{10539}}{\left(\frac{1}{340} - \frac{1}{290}\right)}$$

$$= 32,070 \text{ J/mol} = 32.07 \text{ kJ/mol}$$

likewise $\Delta H_{sub} = \dfrac{-(8.3145)\ln \frac{1092}{270}}{\left(\frac{1}{250} - \frac{1}{232}\right)} = 37,436 = 37.44 \text{ kJ/mol}$

(b) $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$

$\therefore \Delta H_{fus} = 37.44 - 32.07 = 5.37 \text{ kJ/mol}$

(c) at the <u>normal</u> boiling point $P = 1 \text{ atm} = 101,325 \text{ Pa}$

$$\ln \frac{101325}{74518} = \frac{-32070}{8.3145}\left(\frac{1}{T_b} - \frac{1}{340}\right)$$

$$T_b = 349 \text{ K}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{32,070}{349} = 91.9 \text{ J K}^{-1}\text{mol}^{-1}$$

(4) The normal melting point of H_2O is 273.15 K and $\Delta H_{fus} = 6008$ J/mol. Calculate the decrease in the normal freezing point at 500 bar assuming that the densities of the liquid and solid phases remain constant at 997 and 917 kg m^{-3}, respectively.

Clapeyron eqn: $\dfrac{dP}{dT} = \dfrac{\Delta \overline{H}_{fus}}{T \Delta \overline{V}}$ or $\Delta P = \dfrac{\Delta \overline{H}_{fus}}{\Delta \overline{V}} \ln \dfrac{T_2}{T_1}$

$\overline{V}_\ell = \dfrac{m^3}{997 \, kg} \times \dfrac{1 \, kg}{1000 \, g} \times \dfrac{18.01 \, g}{mol} = 1.8064 \times 10^{-5} \, m^3/mol$

$\overline{V}_s = \dfrac{1}{917} \times \dfrac{1}{1000} \times 18.01 = 1.9640 \times 10^{-5} \, m^3/mol$

$\Delta \overline{V} = \overline{V}_\ell - \overline{V}_s = -1.576 \times 10^{-6} \, m^3/mol$

$T_2 = T_1 \exp\left[\dfrac{\Delta P \, \Delta \overline{V}}{\Delta \overline{H}_{fus}} \right]$

$= (273.15) \exp\left[\dfrac{(500 - 1.01325)(10^5 \, Pa/bar)(-1.576 \times 10^{-6})}{6008} \right]$

$= 269.6 \, K$

$\therefore \Delta T = -3.6°$

(5) Using the integrated forms of the Clapeyron and Clausius-Clapeyron equations, construct the
(a) solid-liquid
(b) solid-gas
(c) liquid-gas
portions of the phase boundaries for pure benzene around its triple point (P_{trip}=36 torr and T_{trip}=278.5 K) by calculating the changes in pressure when the temperature is raised <u>and/or</u> lowered by 2 K around T_{trip}. For benzene, ΔH_{fus}=10.6 kJ/mol, ΔH_{vap}=30.8 kJ/mol, ΔH_{sub}=41.4 kJ/mol, $\rho(s)$=0.891 g/cm^3, and $\rho(l)$=0.879 g/cm^3.

(a) use Clapeyron eqn. with $T_2 = T_{trip} + 2 = 280.5$ K

$$\overline{V_s} = \frac{1\,cm^3}{0.891\,g} \times \frac{78.05\,g}{mol} \times \left(\frac{1m}{100\,cm}\right)^3 = 8.7598 \times 10^{-5}\,m^3/mol$$

$$\overline{V_\ell} = \frac{1}{0.879} \times 78.05 \times 1\times10^{-6} = 8.8794 \times 10^{-5}\,m^3/mol$$

$$\Delta\overline{V}_{fus} = \overline{V_\ell} - \overline{V_s} = 1.196 \times 10^{-6}\,m^3/mol$$

$$\Delta P = \frac{\Delta\overline{H}_{fus}}{\Delta\overline{V}_{fus}} \ln\frac{T_2}{T_{trip}} = \frac{10.6\times10^3}{1.196\times10^{-6}} \ln\frac{280.5}{278.5}$$

$$= 6.34 \times 10^7\,Pa = 634\,bar$$

(b) use Clausius-Clapeyron w/ $T_2 = T_{trip} - 2 = 276.5$ K

$$\ln P_2 = \ln P_{trip} - \frac{\Delta H_{sub}}{R}\left(\frac{1}{T_2} - \frac{1}{T_{trip}}\right)$$

$$= \ln(36) - \frac{41.4\times10^3}{8.3145}\left(\frac{1}{276.5} - \frac{1}{278.5}\right) = 3.454$$

$$P_2 = 31.6\,torr$$

$$\therefore \Delta P = -4.4\,torr = -5.87 \times 10^{-3}\,bar$$

ⓒ liquid-gas: use C-C again w/ $T_2 = T_{trip} + 2 = 280.5$ K

$$\ln P_2 = \ln(36) - \frac{30.8 \times 10^3}{8.3145}\left(\frac{1}{280.5} - \frac{1}{278.5}\right)$$

$$= 3.6784$$

$P_2 = 39.6$ torr $\Delta P = +3.6$ torr

$$= 4.77 \times 10^{-3} \text{ bar}$$