P317 assignment 8 due July 17, 2007 P317

Carter problems

9.2) For an ideal gas (shown many times already)

(a) $S(T,V) = S_0 + nc_v \ln\frac{T}{T_0} + nR\ln\frac{V}{V_0}$

then $dG = -SdT + VdP \rightarrow G = G_0 - S_0(T-T_0) - nc_v T\ln\frac{T}{T_0} + nc_v(T-T_0)$
$+ nRT\ln\frac{V}{V_0}$

$\therefore \mu = \frac{G}{n} = c_v T - c_v T\ln T - RT\ln V - s_0 T + \underline{\text{constant}}$

not c_p as in Carter

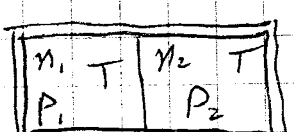
$\frac{G_0}{n} + s_0 T_0 + c_v \ln T_0 + c_v T_0 - RT\ln V_0$

(b) Same procedure but start with
$S(T,P) = S_0 + nc_p\ln\frac{T}{T_0} - nR\ln\frac{P}{P_0}$

$\rightarrow \mu(T,P) = c_p T - c_p T\ln\frac{T}{T_0} + RT\ln\frac{P}{P_0} - s_0 T + \text{constant}$

so if $T = \text{constant} \rightarrow \mu = \mu_0 + RT\ln\frac{P}{P_0}$

9.6) $\pi = 2$ (solid, gas)
$k = 4$ (S, O_2, SO_2, SO_3)
$r = 2$
} variance $f = k - \pi - r + 2 = 2$

9.8) 

$n_1 = 1$ kilomole $T = 300K$ $n_2 = \frac{P_2 V}{RT} = \frac{P_2}{RT}\frac{n_1 RT}{P_1} = \frac{1}{4}$ kilomole
$P_1 = 4$ atm $P_2 = 1$ atm

(a) $Q = 0,\ W = 0 \rightarrow U = \text{constant} \xrightarrow[\text{ideal gas}]{} T = \text{constant}$

$T_f = T = 300\,K$ $P_f = \frac{(n_1+n_2)RT}{2V} = P_1\frac{n_1+n_2}{2n_1} = \frac{5}{2}$ atm

(b) $G_i = n_1(RT\ln P_1 + \phi_1(T)) + n_2(RT\ln P_2 + \phi_2(T))$
$G_f = n_1(RT\ln p_{1f} + \phi_1(T)) + n_2(RT\ln p_{2f} + \phi_2(T))$

$p_{1f} = \frac{n_1 RT}{2V} = \frac{P_1}{2}$
$p_{2f} = P_2/2$

$\Delta G = (n_1+n_2)RT\ln\frac{1}{2} = -2.16\cdot 10^6\,J$

(c) $\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P = 7.20\cdot 10^3\,\frac{J}{K}$ (Carter solution is wrong)

P317 assignment 8 continued

P317

9-10) 1st order phase transition $\rightarrow \Delta S \neq 0$, $\Delta V \neq 0$

(a) At phase eq^m, $S = n_1 s_1 + n_2 s_2$ where the subscripts refer to the two phases in eq^m

$$= n(x_1 s_1 + (1-x_1) s_2)$$

and $V = n(x_1 v_1 + (1-x_1) v_2) \rightarrow x_1 = \left(\frac{V}{n} - v_2\right) / (v_1 - v_2)$

$\boxed{\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \text{const at } T = \text{const also works}}$

and $S = -n \frac{v_2}{v_1 - v_2} s_1 + n \frac{v_1}{v_1 - v_2} s_2 + V \frac{s_1 - s_2}{v_1 - v_2}$ $\therefore$ linear f^n of V QED

(b) $T dS = dU + P dV$. At fixed T, P,

$\Delta U = T \Delta S - P \Delta V = L - P \Delta V$

Clausius-Clapeyron eq^n $\rightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V} \rightarrow \Delta V = \Delta S \frac{dT}{dP} = \frac{L}{T} \frac{dT}{dP}$

$\rightarrow \Delta U = L\left(1 - \frac{P}{T} \frac{dT}{dP}\right) = L\left(1 - \frac{d \ln T}{d \ln P}\right)$

-11) Gibbs-Duhem: $S dT - V dP + \sum_i n_i d\mu_i = 0$

(a) so dividing by $\sum_i n_i$ and setting T, P constant

$\rightarrow \sum_i x_i d\mu_i = 0$

(b) Two components $\rightarrow x_2 = 1 - x_1$ and $dx_2 = -dx_1$.

Then $x_1 d\mu_1 = -x_2 d\mu_2 = \frac{dx_1}{dx_2} x_2 d\mu_2$ or $x_1 \frac{d\mu_1}{dx_1} = \frac{x_2 d\mu_2}{dx_2}$

$\therefore \left(\frac{d\mu_1}{d \ln x_1}\right)_{T,P} = \left(\frac{d\mu_2}{d \ln x_2}\right)_{T,P}$

(c) Ideal gas $\rightarrow \mu(T, P) = \mu_0 + f(T) + RT(\ln P + \ln x)$

Equilibrium $\rightarrow \mu_1^{gas}$ μ_1^{liquid}, same for μ_2

$\therefore d\mu_1 = RT(d\ln P_1 + d\ln x_1)$; $\left(\frac{d \ln P_1}{d \ln x_1}\right)_{T,P} = \left(\frac{d \ln P_2}{d \ln x_2}\right)_{T,P}$

Additional: $L = L_0\left(1 + \frac{F}{YA} + a(T - T_0)\right)$ and $\delta W = -F dL$ $(P \leftrightarrow -F, V \leftrightarrow L)$

1st $T dS$ eq^n $T dS = nc_L dT - T\left(\frac{\partial F}{\partial T}\right)_L dL$

$dT = 0$, $\left(\frac{\partial F}{\partial T}\right)_L = -aYA$ so $\Delta S = \int_{L_0}^{L_1} aYA \, dL = aYA(L_1 - L_0)$