Phys 317 assignment 7 due July 6, 2007 [P317]

Carter 8.2) For ideal gas $(Pv = RT)$

$$df = -s\,dT - P\,dv \qquad \left\{ \begin{aligned} ds &= c_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_v dv = c_v \frac{dT}{T} + \frac{R\,dv}{v} \\ s &= s_0 + c_v \ln\frac{T}{T_0} + R\ln\frac{v}{v_0} \end{aligned} \right.$$

$$= -\left(s_0 + c_v \ln\frac{T}{T_0} + R\ln\cancel{\frac{v_0}{v_0}}^{\,0}\right) dT - \frac{RT}{v}\,dv$$

(integrate from T_0, v_0 ~~to~~ T, v_0, then T, v_0 to T, v)

$$f(T,v) = f_0 - s_0(T - T_0) + c_v(T - T_0) - c_v T \ln\frac{T}{T_0} - RT\ln\frac{v}{v_0}$$

$$dg = -s\,dT + v\,dP \qquad ds = c_p\frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$g(P,T) = \int_{P_0 T_0}^{P_0 T} dT\left[-s_0 - c_p\ln\frac{T}{T_0} + R\ln\cancel{\frac{P_0}{P_0}}^{\,0}\right] \qquad s(P,T) = s_0 + c_p\ln\frac{T}{T_0} - R\ln\frac{P}{P_0}$$

$$+ RT\int_{P_0 T}^{P,T} dP\,\frac{1}{P} = g_0 - s_0(T - T_0) + c_p(T - T_0) - c_p T\ln\frac{T}{T_0} + RT\ln\frac{P}{P_0}$$

8.7) Given $g = RT\ln\left(\frac{P}{P_0}\right) - AP \qquad (A = A(T))$

(a) $v = \left(\frac{\partial g}{\partial P}\right)_T = \frac{RT}{P} - A$ so $P(v + A) = RT$

(b) $s = -\left(\frac{\partial g}{\partial T}\right)_P = -R\ln\frac{P}{P_0} + PA' \qquad \left(A' = \left(\frac{\partial A}{\partial T}\right)_P\right)$

(c) $f = g - Pv = RT\left(\ln\frac{P}{P_0} - 1\right)$

8.10) $T\,ds = c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$

(a) Constant $P \Rightarrow \quad ds_P = c_p\frac{dT_P}{T}$ or $c_p = T\left(\frac{\partial s}{\partial T}\right)_P$

$$\left(\frac{\partial c_p}{\partial P}\right)_T = \underbrace{\frac{\partial}{\partial P}\left(T\left(\frac{\partial s}{\partial T}\right)_P\right)_T = T\left[\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial P}\right)_T\right]_P}_{\text{swap order of derivatives}} = -T\left[\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_P\right]_P = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P$$

Maxwell relation $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$

(b) ideal gas $Pv = RT$ $\quad \left(\frac{\partial^2 v}{\partial T^2}\right)_P = \left[\frac{\partial}{\partial T}\left(\frac{R}{P}\right)\right]_P = 0 \Rightarrow \left(\frac{\partial c_p}{\partial P}\right)_T = 0$ and c_p depends on T but not on P

assignment 7 continued

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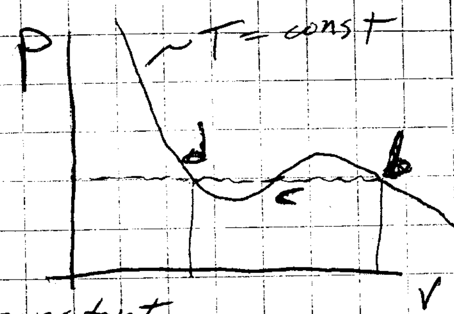

8.11) At liquid-vapor equilibrium

$g'' = g'''$ so $\Delta g = 0$

Then $f = g - Pv$ so

$\Delta f = \Delta g - P\Delta v$ (P = constant, T = constant during phase change)

$\therefore P\Delta v = 0 \Rightarrow$ areas above/below line connecting points b and d must be equal

8.14) Clausius-Clapeyron $\left(\frac{\partial P}{\partial T}\right)_{12} = \frac{l_{12}}{T(v''-v')} = \frac{3.34\cdot 10^5}{(273.15)(-9.05\cdot 10^{-5})} = -1.35\cdot 10^7 \frac{Pa}{K}$

(a)

(b) $\Delta P = \left(\frac{\partial P}{\partial T}\right)_{12}\Delta T = \left(-1.35\cdot 10^7 \frac{Pa}{K}\right)(-2K) = P_f - (1.01\cdot 10^5 Pa)$

$P_f = 2.71\cdot 10^7 Pa = 268$ atm

Additional problem) For a solid, $v = v_0[1+\beta(T-T_0) - \chi(P-P_0)]$

$ds = c_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP$ so $s = s_0 + c_p \ln\frac{T}{T_0} - v_0\beta[P-P_0]$

$dg = -s\,dT + v\,dP = -\left(s_0 + c_p \ln\frac{T}{T_0} - v_0\beta(P-P_0)\right)dT + v_0[1+\beta(T-T_0) - \chi(P-P_0)]\,dP$

Integrate

$$g = g_0 - \int_{T_0}^{T} s(P_0,T)\,dT + \int_{P_0}^{P} v(P,T)\,dP$$

$$= g_0 - s_0(T-T_0) + c_p(T-T_0) - c_p T \ln\frac{T}{T_0} + v_0\left(1+\beta(T-T_0)+\chi P_0\right)(P-P_0) - \frac{v_0\chi}{2}(P^2-P_0^2)$$