Phys 344

Assignment 10. Solutions.

5-28

(a). $G_c^\circ = -1128.8\ kJ$. $\qquad G_a^\circ = -1127.8\ kJ$.

$G_c^\circ < G_a^\circ$

$\therefore$ Calcite is stable.

(b). $\left(\frac{\partial G}{\partial P}\right)_T = V$. $\qquad \frac{\Delta G}{\Delta P} = V$. $\qquad G = G^\circ + V \cdot \Delta P$.

for 1 mol. $V_c = 36.93\ cm^3 = 3.693 \times 10^{-5}\ m^3$

$V_a = 34.15\ cm^3 = 3.415 \times 10^{-5}\ m^3$.

$V_c > V_a \Rightarrow$ G_c increases faster than G_a as P increases.

when $G_c = G_a$:

$$G_c^\circ + V_c \Delta P = G_a^\circ + V_a \cdot \Delta P.$$

$$\therefore \Delta P = \frac{G_c^\circ - G_a^\circ}{V_a - V_c} = \frac{(-1128.8 + 1127.8) \times 10^3}{(3.415 - 3.693) \times 10^{-5}} = 3.6 \times 10^8\ Pa.$$

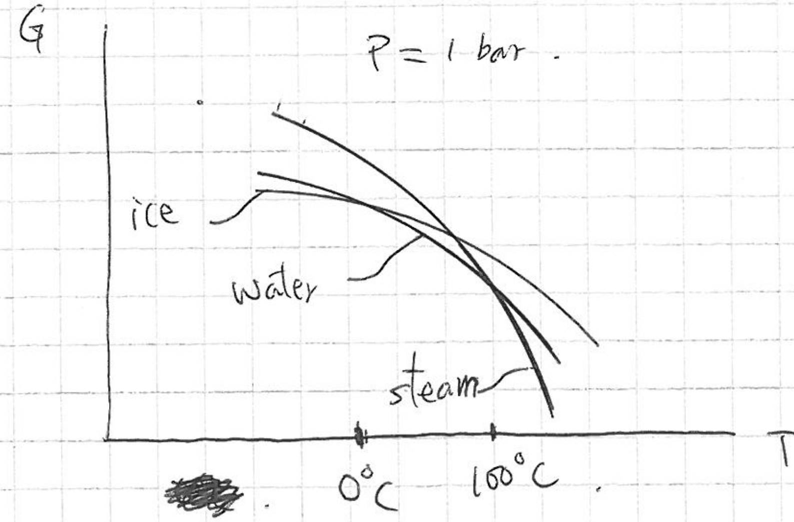
$$P = P_0 + \Delta P = 3.6 \times 10^8\ Pa.$$

5.30 . $\left(\frac{\partial G}{\partial T}\right)_p = -S$, < 0. stable phase means lower G.

$\therefore$ slope of G vs. T is negative.

and gets more negative as T increases.

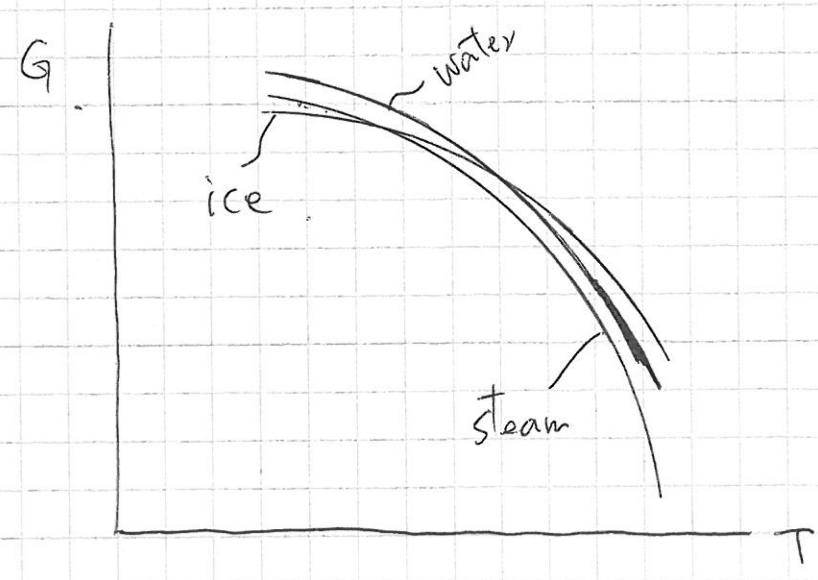
- At atmospheric pressure. (freezing point $= 0°C$. boiling point $= 100°C$)



- When $P = 0.001$ bar.

$P < P_c$. — P_c = critical pressure $= 0.006$ bar.

$\therefore$ No liquid state is stable.



5-32.

a). $$\frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V} = \frac{S_w - S_i}{V_w - V_i} = \frac{L}{T(V_w - V_i)}$$

Since. $S_w > S_i$. ($L > 0$ when melting ice).

$V_w < V_i$.

$\therefore \frac{\Delta P}{\Delta T} < 0$.

For 1 gram:

$L = 333 \ J/g$

$V_w = 10^{-6} \ m^3$

$V_i = 1.091 \times 10^{-6} \ m^3$

b) $\Delta T = -1°C = -1K$.

$$\Delta P = \frac{L \cdot \Delta T}{T(V_w - V_i)} = \frac{333 \times (-1)}{273 \times (1 - 1.091) \times 10^{-6}} = 1.34 \times 10^7 \ Pa$$

$P = P_0 + \Delta P = 1.35 \times 10^7 \ Pa$.

c). $P = \rho g h$. $h = \frac{P}{\rho g} = \frac{1.35 \times 10^7}{917 \times 9.8} = 1500 \ m$.

d). $P = \frac{mg}{A} = \frac{100 \, kg \times 9.8 \, m/s^2}{5 \times 10^{-3} \times 1 \times 10^{-1}} = \frac{9.8}{5} \times 10^6 = 2 \times 10^6 \ Pa = \Delta P$

$$\Delta T = \frac{\Delta P \cdot T \cdot (V_w - V_i)}{L} = \frac{2 \times 10^6 \times 273 \times (1 - 1.091) \times 10^{-6}}{333} = \underline{0.15K}.$$

small effect!

5.35. $\dfrac{dP}{dT} = \dfrac{L}{T\,V}$ $PV = nRT$., $V = \dfrac{nRT}{P}$

Take $n=1$. (1 mol. of material).

$$\frac{dP}{dT} = \frac{L\,P}{T\,RT} = \frac{L \cdot P}{RT^2}.$$

$$\frac{dP}{P} = \frac{L}{R}\,\frac{dT}{T^2}.$$

$$\ln P - \ln P_0 = -\frac{L}{R}\,\frac{1}{T}$$

$$P = P_0\, e^{-\frac{L}{RT}}$$

5.36. (a) $P = P_0 e^{-L/RT}$. $\left[\text{solve for } P_0: \quad P_0 = P e^{L/RT} \right]$

at $T = 50°C = 323.15K$, $P = 0.1234$ bar. $L = 42920$ J/mol.

$$P_0 = 0.1234 \times e^{42920/8.315 \times 323.15} = 1.0172 \times 10^6 \text{ bar}.$$

at $T = 100°C = 373.15K$, $P = 1.013$ bar $L = 40660$ J/mol.

$$P_0 = 1.013 \times e^{40660/8.315 \times 373.15} = 4.9755 \times 10^5 \text{ bar}.$$

Take the average of P_0, L:

$$P_0 = 7.574 \times 10^5 \text{ bar}. \quad L = 41790, \quad \frac{L}{R} = 5026.$$

Calculated end point values. $P = 7.574 \times e^{-5026/T}$

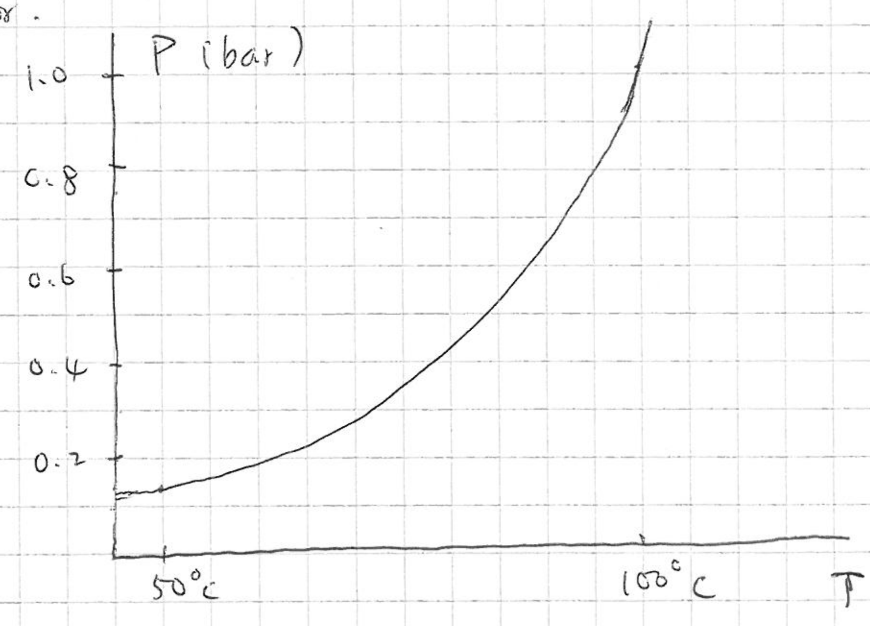
at $T = 50°C = 323.15K$

$$P = 7.574 \times 10^5 \times e^{-\frac{5026}{323.15}} = 0.133 \text{ bar}.$$

at $T = 100°C = 373.15K$.

$$P = 7.574 \times 10^5 \times e^{-\frac{5026}{373.15}} = 1.07 \text{ bar}$$

Within 10% error.



(b). Solve for T:

use $L = 40660$ J/mol.

$L/R = 4890$

$$P/P_0 = e^{-L/RT}.$$

$$\ln P/P_0 = -\frac{L}{RT}.$$

$$T = -\frac{L}{R}\frac{1}{\ln P/P_0} = -\frac{4890}{\ln\left(\frac{P}{4.976\times10^5}\right)}$$

Location	h.	P	T
Ogden	(4700 ft).	0.84 atm = 0.85 bar.	368.2 K = 95°C.
Leadville	(10500 ft)	0.69 atm = 0.70 bar.	362.9 K = 90°C
Mt. Whitney	(14500 ft)	0.59 atm = 0.60 bar	358.8 K = 86°C.
Mt. everest.	(29000 ft)	0.35 atm = 0.354 bar	345.4 K = 72°C.

(c).
$$P(z) = P(0)\,e^{-mgz/kT} = 1\,\cancel{(atm)}\cdot e^{-z/28000\,ft}$$
$$= P_1\,e^{-z/h_1}$$

$P_1 = 1$ atm $= 1.013$ bar

≈ 1 bar

$h = 28000$ ft.

$$\therefore \frac{P_1 e^{-z/h_1}}{P_0} = e^{-L/RT}.$$

$$\ln\frac{P_1}{P_0} = \ln\frac{1.013}{4.976\times10^5} = -13.1$$

$$\frac{P_1}{P_0} = e^{\left(z/h_1 - L/RT\right)}$$

$$\frac{z}{h_1} - \frac{L}{RT} = \ln\frac{P_1}{P_0}. \qquad \frac{L}{RT} = \frac{z}{h_1} - \ln\frac{P_1}{P_0}.$$

$$T = \frac{L}{R}\left(\frac{1}{z/h_1 - \ln P_1/P_0}\right) = 4890\left(\frac{1}{z/h_1 + 13.1}\right) = \frac{380}{1 + z/13.1h_1}$$

$$T \approx 380\left(1 - z\frac{1}{13.1\times h_1}\right) = 380\,(1 - 2.7\times10^{-6}z) \quad z \text{ linear.}$$

$$\Delta T/\Delta z \approx -380\times2.7\times10^{-6} = -1.04\,K/1000\,ft.$$

5.48

$$P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 : \quad \frac{-NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3} = 0 \qquad ①$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 : \quad \frac{2NkT}{(V-Nb)^3} - \frac{6aN^2}{V^4} = 0 \qquad ②$$

①/② :

$$\frac{-(V-Nb)}{2} = \frac{-V}{3}$$

Solve for V:

$$3V - 3Nb = 2V$$

$$V = 3Nb = V_c$$

subs. $V = 3Nb$ into ① :

$$\frac{-NkT}{(2Nb)^2} + \frac{2aN^2}{(3Nb)^3} = 0$$

Solve for T:

$$\frac{NkT}{4} = \frac{2aN^2}{27Nb}$$

$$T = \frac{8a}{27bk} = T_c$$

$$\therefore \quad P_c = \frac{Nk}{2Nb} \cdot \frac{8a}{27bk} - \frac{aN^2}{(3Nb)^2}$$

$$P_c = \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

$$\therefore \quad V_c = 3Nb, \quad P_c = \frac{a}{27b^2}, \quad kT_c = \frac{8a}{27b}$$

5.51. $$P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}.$$

$$\begin{cases} kT_c = \frac{8}{27}\frac{a}{b} \\ P_c = \frac{1}{27}\frac{a}{b^2}. \\ V_c = 3Nb \end{cases}$$

$$T = tT_c, \quad P = pP_c, \quad V = vV_c.$$

$$pP_c = \frac{NkT_c t}{vV_c - Nb} - \frac{aN^2}{(vV_c)^2}.$$

$$p\frac{a}{27b^2} = \frac{Nt\frac{8a}{27b}}{v\cdot 3Nb - Nb} - \frac{aN^2}{(v\cdot 3Nb)^2}$$

$$p\cdot\frac{a}{27b^2} = \frac{Nt\cdot\frac{8a}{27b}}{Nb(3v-1)} - \frac{aN^2}{9N^2b^2\cdot v^2}.$$

$$p\cdot\frac{a}{27b^2} = \frac{t}{3v-1}\cdot\frac{8a}{27b^2} - \frac{1}{v^2}\frac{a}{9b^2}$$

$$p = \frac{8t}{3v-1} - \frac{3}{v^2}$$