

1. Why is the standard freezing point of water (0.00 °C)

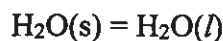


[1]

nearly identical to the triple point temperature of water (0.01 °C)?



2. a) Calculate $\Delta S_{\text{fus,m}}^\circ$ and $\Delta G_{\text{fus,m}}^\circ$ for melting one mole of ice at 0.00 °C and 1.00 bar.



[7]

Data: The standard enthalpy of fusion of ice is 6010 J mol⁻¹ at 0.00 °C.

- b) Use the equation $dG = -SdT + Vdp$ for the Gibbs energy to show

$$\frac{d\Delta G_{\text{fus,m}}^\circ}{dT} = -\Delta S_{\text{fus,m}}^\circ$$

- c) Use the results from a and b to prove that freezing liquid water at 1.00 bar is spontaneous at temperatures below 0.00 °C.

- d) Why is it correct in c to use the ordinary d/dT derivative instead of the partial $\partial/\partial T$ derivative at constant pressure?

3. The following information describes the phase diagram of ammonia:

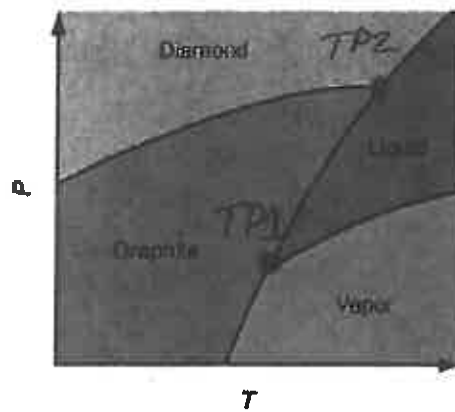
The normal melting and boiling temperatures are 195.2 K and 239.82 K, respectively (at one atmosphere). The triple point pressure and temperature are 6077 Pa and 195.41 K. The critical point pressure and temperature are 112.8×10^5 Pa and 405.5 K.

[7]

Sketch the p - T phase diagram for ammonia (not necessarily to scale) and state which phases are present at equilibrium at:

- 195.41 K and 9506 Pa
- 195.41 K and 6077 Pa
- 245.45 K and 101,325 Pa
- 415 K and 105×10^5 Pa
- 185.5 K and 6077 Pa

4. This question refers to the p - T phase diagram for carbon:



[5]

- Does graphite float in liquid carbon (like ice floats in liquid water)? Justify your answer.
- How many triple points are indicated? Identify the phases present at each triple point.
- According to the diagram, diamond, liquid carbon and carbon vapor can never be in equilibrium. Why?

(Q1) a) $\text{H}_2\text{O}(s) = \text{H}_2\text{O}(l)$ at equilibrium at
 0.00°C and 1.00 bar
 (standard melting point)

$\text{H}_2\text{O}(s) = \text{H}_2\text{O}(l) = \text{H}_2\text{O}(g)$ at equilibrium (all 3 phases)
 at 0.01°C and 0.000612 bar
 (triple point)

$$\frac{dT}{dp} \approx \frac{0.00 - 0.01^\circ\text{C}}{1.00 - 0.000612 \text{ bar}} = -0.01 \frac{\text{K}}{\text{bar}}$$

(Small!)

Why is the standard melting point only 0.01°C lower than the triple point temperature?

The melting point ($s = l$, $\Delta n_{\text{gas}} = 0$) has a very small volume change: $\Delta V_m = V_m(l) - V_m(s) \approx 0$

This makes the solid/liquid equilibrium

$$\mu_{\text{liq}}(T, P) = \mu_{\text{solid}}(T, P) \quad (\text{or } G_{m, \text{liq}}(T, P) = G_{m, \text{solid}}(T, P))$$

this equilibrium is insensitive to changes in pressure.

$$dG = -SdT + Vdp \Rightarrow dG_T = Vdp$$

$$\left(\frac{\partial G_{m, \text{liq}}}{\partial P}\right)_T = V_{m, \text{liq}}$$

$$\left(\frac{\partial G_{m, \text{solid}}}{\partial P}\right)_T = V_{m, \text{solid}}$$

$$\left(\frac{\partial G_{m, \text{fus}}}{\partial P}\right)_T = \Delta V_{m, \text{fus}} = V_{m, \text{liq}} - V_{m, \text{solid}}$$

even smaller

the molar volume of ice is about 10% larger than the molar volume of liquid water ($V_m = 18.0 \text{ cm}^3 \text{ mol}^{-1}$)

along the solid-liquid equilibrium line $\frac{dp}{dT} = \frac{\Delta H_{\text{fus}, m}}{T \Delta V_{\text{fus}, m}}$

$$\frac{dT}{dp} = \frac{T \Delta V_{\text{fus}, m}}{\Delta H_{\text{fus}, m}} \approx \frac{(273 \text{ K})(-1.8 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{6010 \text{ J mol}^{-1}} = -8.1 \times 10^{-8} \frac{\text{K}}{\text{Pa}}$$

$$\frac{dT}{dp} = -0.0082 \frac{\text{K}}{\text{bar}}$$

(Small!)

(273.15 K)
 (Q2) a) $H_2O(s) = H_2O(l)$ at $0.00^\circ C$ and 1.00 bar
 (standard melting point)

$\Delta G_{\text{fus}}^\circ(273.15 \text{ K}) = 0 \iff \left\{ \begin{array}{l} \text{solid and liquid water} \\ \text{are in equilibrium} \end{array} \right\}$
 ($\Delta G = 0$)

$$\Delta G_{\text{fus},m}^\circ = \Delta H_{\text{fus},m}^\circ - T \Delta S_{\text{fus},m}^\circ = 0$$

$$\Delta S_{\text{fus},m}^\circ = \frac{\Delta H_{\text{fus},m}^\circ}{T} \left(= \frac{q_{\text{rev}}}{T} \right)$$

$$\Delta S_{\text{fus},m}^\circ = \frac{6010 \text{ J mol}^{-1}}{273.15 \text{ K}} = 22.00 \frac{\text{J}}{\text{K mol}}$$

WHY?
 because ΔH at
 fixed pressure (1 bar)
 = q and the process
 is reversible at
 equilibrium,
 so $q = q_{\text{rev}}$

b) $dG = -SdT + Vdp \implies dG_P = -SdT_P$

$$\frac{dG_P}{dT_P} = -S \implies \left(\frac{\partial G}{\partial T} \right)_P = -S$$

$$\left(\frac{\partial \Delta G_{\text{fus},m}^\circ}{\partial T} \right)_P = \frac{\partial}{\partial T} [G_m^\circ(\text{liquid}) - G_m^\circ(\text{solid})]$$

$$= \left(\frac{\partial G_m^\circ(\text{liquid})}{\partial T} \right)_P - \left(\frac{\partial G_m^\circ(\text{solid})}{\partial T} \right)_P = -S_m^\circ(\text{liquid}) - (-S_m^\circ(\text{solid}))$$

$$= -(S_m^\circ(\text{liquid}) - S_m^\circ(\text{solid}))$$

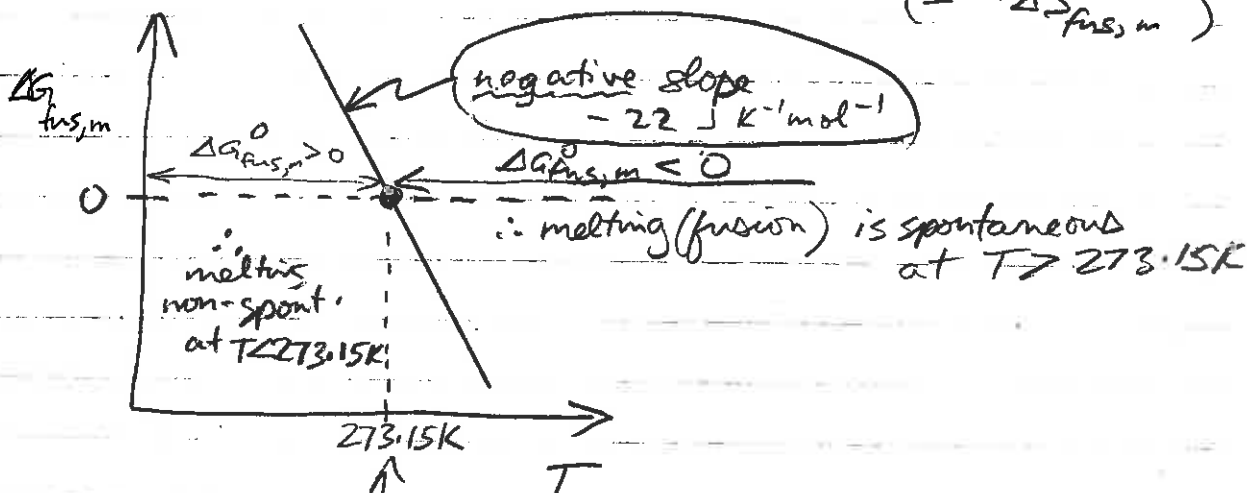
$$\left(\frac{\partial \Delta G_{\text{fus},m}^\circ}{\partial T} \right)_P = -\Delta S_{\text{fus},m}^\circ$$

\implies a plot of $\Delta G_{\text{fus},m}^\circ$
 against temperature T
 has slope $-\Delta S_{\text{fus},m}^\circ$
 Slope = $-22.00 \text{ J K}^{-1} \text{ mol}^{-1}$

(Q2, cont.)

c) at 1.00 bar pressure, the Gibbs energy of fusion of water is zero at 273.15 K (0.00 °C)

and the slope of $\Delta G_{\text{fus,m}}^{\circ}$ against T is $-22.00 \text{ J K}^{-1} \text{ mol}^{-1}$
($= -\Delta S_{\text{fus,m}}^{\circ}$)



\rightleftharpoons equilibrium ($\Delta G_{\text{fus,m}}^{\circ} = 0$) at 273.15 K

this means :

$$\underline{T = 273.15 \text{ K} \quad (0.00 \text{ }^{\circ}\text{C})}$$

$$\Delta G_{\text{fus,m}}^{\circ} = 0$$

$\text{H}_2\text{O(s)}$ and $\text{H}_2\text{O(l)}$
are in equilibrium

$$\underline{T < 273.15 \text{ K}}$$

notice $\Delta G_{\text{fus,m}}^{\circ} > 0$ (non-spontaneous)

$\therefore \Delta G_{\text{m}}^{\circ} < 0$ for freezing (the opposite of freezing)
ice is stable

$$\underline{T > 273.15 \text{ K}}$$

notice $\Delta G_{\text{fus,m}}^{\circ} < 0$ (spontaneous) liquid water is stable

(Q2 cont.)

$H_2O(s) \rightleftharpoons H_2O(l)$ $P = 2$ phases
Phase Rule: $F = 3 - P = 3 - 2 = 1$
1 degree of freedom (one independent variable)

d) Why can $\frac{d\Delta G_{fus,m}^{\circ}}{dT}$ instead of $\left(\frac{\partial \Delta G_{fus,m}^{\circ}}{\partial T}\right)_P$?

$\Delta G_{fus,m}^{\circ}$ means $\Delta G_{fus,m}$ at standard pressure
($p^{\circ} = 1 \text{ bar}$)

specifying standard pressure fixes the pressure

only T can vary \Rightarrow one independent variable

as a result, the ordinary derivative $\frac{d}{dT}$
can be used for $\Delta G_{fus,m}^{\circ}(T)$ that depends only on T

Q3 Phase diagram sketch for ammonia (not to scale!)

data:

normal melting temperature 195.2 K at 1 atm (1.01325 bar)
($\log_{10}(P/\text{bar}) = 0.0427$)

normal boiling temperature 239.82 K at 1 atm (1.01325 bar)

triple point at 195.41 K and 6077 Pa (0.06077 bar)
($\log_{10}(P/\text{bar}) = -1.216$)

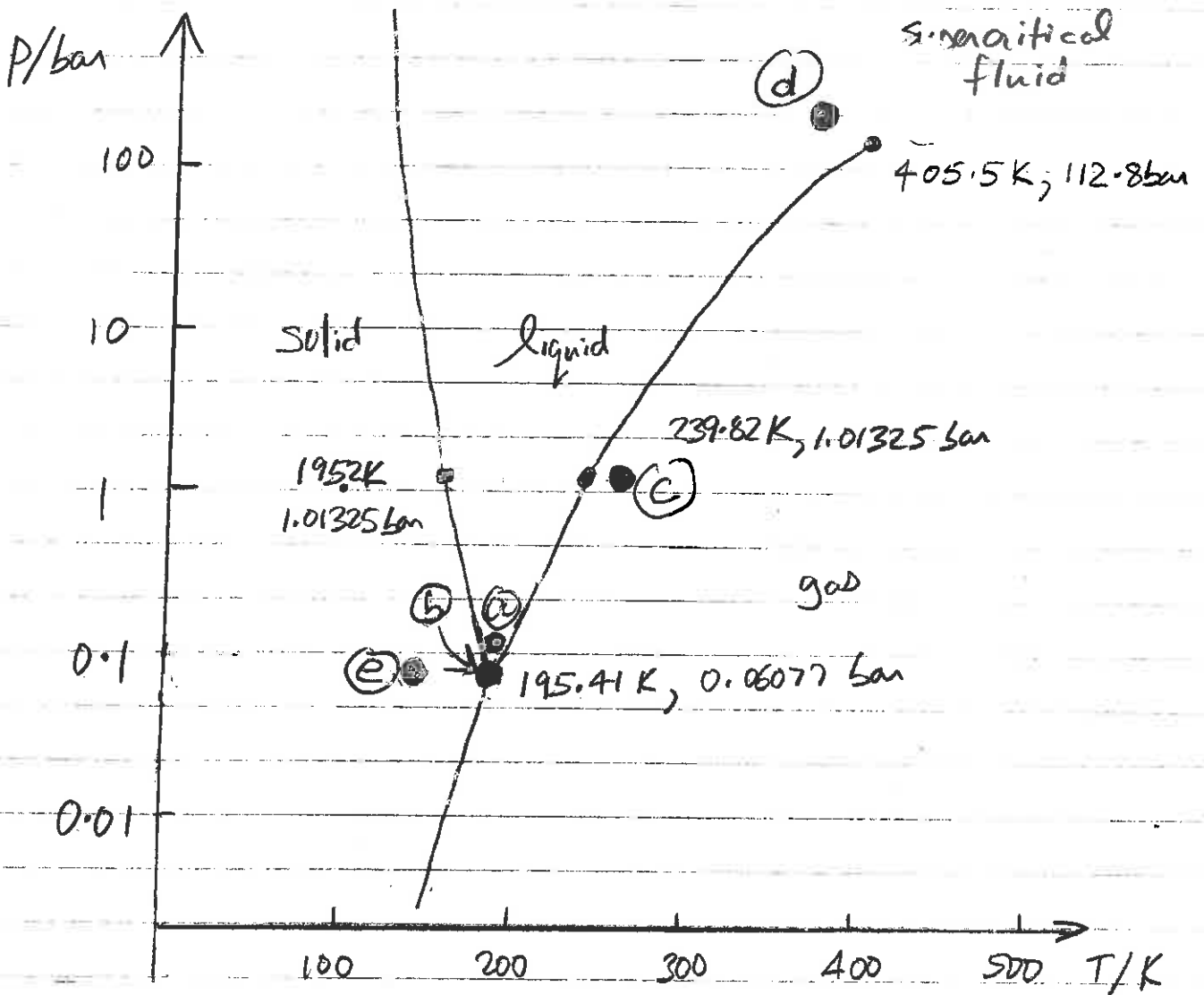
critical point at 405.5 K and $112.8 \times 10^5 \text{ Pa}$ (112.8 bar)
 $\log_{10}(P/\text{bar}) = 2.052$

\Rightarrow 4 points on the p - T phase diagram

notice: melting temperature decreases with pressure
(195.41 K @ 6077 Pa ; 195.2 K @ 1.01325 Pa)

(Q3 cont.)

rough sketch of the ammonia phase diagram based on the (limited) information provided:



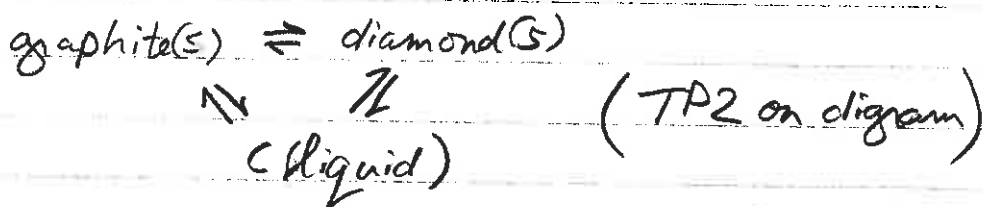
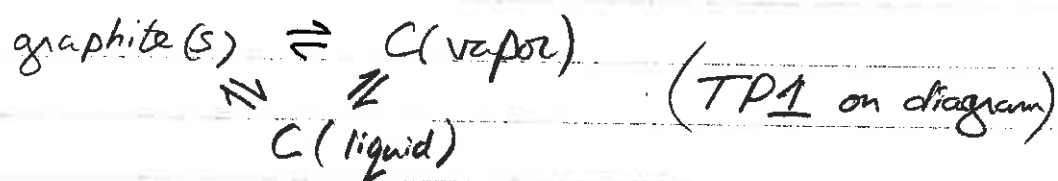
see diagram

- a) $195.41 \text{ K}, 0.09506 \text{ bar} \Rightarrow$ just above triple point \Rightarrow all liquid NH_3 (higher pressure)
- b) $195.41 \text{ K}, 0.06077 \text{ bar} \Rightarrow$ triple point $\Rightarrow \text{NH}_3(\text{l}), \text{NH}_3(\text{s}), \text{NH}_3(\text{g})$
- c) $245.45 \text{ K}, 1.01325 \text{ bar}$ $\text{NH}_3(\text{l})$
- d) $415 \text{ K}, 105 \text{ bar}$ supercritical NH_3 (dense fluid)
- e) $185.5 \text{ K}, 0.06077 \text{ bar}$ at triple point pressure, but lower T all $\text{NH}_3(\text{s})$

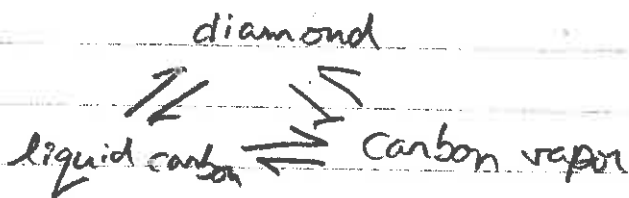
(Q4) a) the solid carbon = liquid carbon
equilibrium line has positive slope $\frac{dp}{dT} > 0$

increasing the pressure can freeze liquid graphite,
favouring the denser solid phase, so solid graphite
will sink in liquid carbon
(water shows the opposite behaviour: $dp/dT < 0$, ice floats)

b) two triple points:



c) Impossible to have the triple point:



with diamond, C (liquid), C (vapor)
in equilibrium

no such triple point exists on the phase diagram