

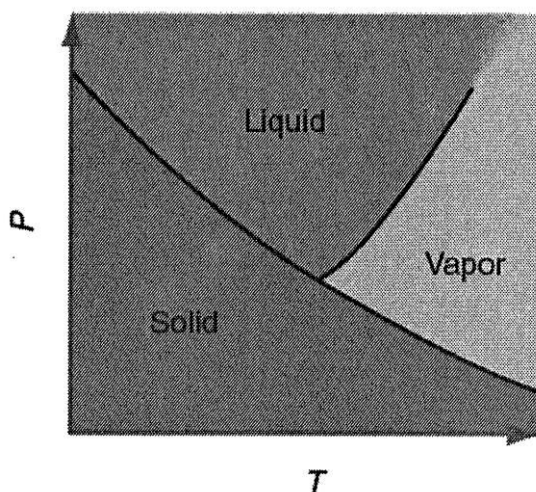
1. (5%) Why does the triple point in a  $P$ - $T$  diagram become a triple line in a  $P$ - $V$  diagram?

This is the case because a gas and a liquid are in equilibrium for the range of values of volume from that of the pure liquid to that of the pure gas at a given temperature.

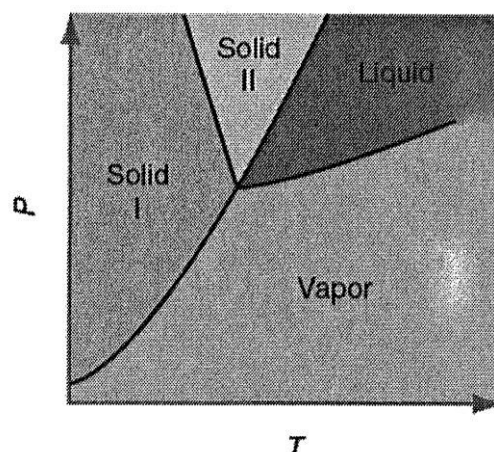
2. (5%) Is the following statement correct? Because dry ice sublimates, carbon dioxide has no liquid phase. Explain your answer.

It is not correct. Carbon dioxide has a liquid phase above the triple point, but not at 298 K.

3. (10%) Are the two  $P$ - $T$  phase diagrams below likely to be observed for a pure substance? If not, explain all features of the diagram that will not be observed.



(a)



(b)

- (a) No. The solid–vapor line must have a positive slope because the volume increases upon sublimation. The slope of the liquid–solid coexistence line can be positive or negative, but will be much larger in magnitude than the slope of the vapor–solid coexistence line.
- (b) No. Four phases of a pure substance cannot coexist according to the Gibbs phase rule.
4. (10%) The normal melting point of  $\text{H}_2\text{O}$  is 273.15K, and  $\Delta H_{\text{fusion}} = 6010 \text{ J mol}^{-1}$ . Calculate the change in the normal freezing point at 100. and 500. bar compared to that at 1 bar assuming that the densities of the liquid and solid phases remain constant at 997 and 917  $\text{kg m}^{-3}$ , respectively. Explain why your answer is positive (or negative).

Sol:

$$\begin{aligned}
 \left(\frac{dP}{dT}\right)_{\text{fusion}} &= \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}} M \left( \frac{1}{\rho_{\text{liquid}}} - \frac{1}{\rho_{\text{solid}}} \right)} \\
 &= \frac{6010 \text{ J mol}^{-1}}{273.15 \text{ K} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times \left( \frac{1}{997 \text{ kg m}^{-3}} - \frac{1}{917 \text{ kg m}^{-3}} \right)} = -1.40 \times 10^7 \text{ Pa K}^{-1} \\
 \left(\frac{dP}{dT}\right)_{\text{fusion}} &= -140. \text{ bar K}^{-1} \\
 \Delta T &= -\frac{\Delta P}{140. \text{ bar K}^{-1}} = -0.717 \text{ K at } 100. \text{ bar and } -3.58 \text{ K at } 500. \text{ bar}
 \end{aligned}$$

$\Delta T$  is negative because the liquid is more dense than the solid.

5. (10%) At 298.15 K,  $\Delta G_f^\circ$  (HCOOH, g) = -351.0 kJ mol<sup>-1</sup> and  $\Delta G_f^\circ$  (HCOOH, l) = -361.4 kJ mol<sup>-1</sup>. Calculate the vapor pressure of water at this temperature.

Sol:

$$\begin{aligned}
 \Delta G^\circ &= \Delta G_f^\circ(\text{HCOOH, g}) - \Delta G_f^\circ(\text{HCOOH, l}) = -351.0 \text{ kJ mol}^{-1} + 361.4 \text{ kJ mol}^{-1} \\
 &= 10.4 \text{ kJ mol}^{-1}
 \end{aligned}$$

$$\ln \frac{P}{P^\circ} = -\frac{\Delta G^\circ}{RT} = -\frac{10.4 \text{ kJ mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = -4.1956$$

$$P = 1.51 \times 10^{-2} \text{ bar}$$

6. (10%) Consider the transition between two forms of solid tin, Sn(s, gray) → Sn(s, white). The two phases are in equilibrium at 1 bar and 18°C. The densities for gray and white tin are 5750 and 7280 kg m<sup>-3</sup>, respectively, and the molar entropies for gray and white tin are 44.14 and 51.18 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. Calculate the temperature at which the two phases are in equilibrium at 350. bar.

Sol:

In going from 1 atm, 18°C to 200 atm,  $T$

$$\Delta G^{gray} = V_m^{gray} \Delta P - S^{gray} \Delta T$$

$$\Delta G^{white} = V_m^{white} \Delta P - S^{white} \Delta T$$

At equilibrium

$$\Delta G^{gray} - \Delta G^{white} = 0 = (V_m^{gray} - V_m^{white}) \Delta P - (S^{gray} - S^{white}) \Delta T$$

$$\begin{aligned} \Delta T &= \frac{(V_m^{gray} - V_m^{white}) \Delta P}{(S^{gray} - S^{white})} = \frac{M_{Sn} \left( \frac{1}{\rho_{gray}} - \frac{1}{\rho_{white}} \right) \Delta P}{\Delta S_{transition}} \\ &= \frac{118.71 \times 10^{-3} \text{ kg mol}^{-1} \times \left( \frac{1}{5750 \text{ kg m}^{-3}} - \frac{1}{7280 \text{ kg m}^{-3}} \right) \times 349 \times 10^5 \text{ Pa}}{-7.04 \text{ J K}^{-1} \text{ mol}^{-1}} = -21.5^\circ \text{C} \\ T_f &= -3.5^\circ \text{C} \end{aligned}$$

7. (a) (10%) Derive Clapeyron equation,  $\frac{dP}{dT} = \frac{\Delta S}{\Delta V_m}$  for two phases at equilibrium.
- (b) (10%) Derive Clausius – Clapeyron equation based on Clapeyron equation.
- What are the assumptions you have to make for the derivation?

Sol:

(a)

$$\mu_g^* = \mu_l^*$$

shift to different T,P =>

$$\mu_g' = \mu_l'$$

$$\therefore d\mu_g = d\mu_l$$

$$V_{m_g} dp - S_g dT = V_{m_l} dp - S_l dT$$

$$\Delta V dp = \Delta S dT$$

$$\frac{\Delta S}{\Delta V} = \frac{dP}{dT}$$

(b)

$$\text{take } \Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \text{ and } V_{m_g} \approx \frac{RT_b}{P} \gg V_l$$

$$\text{into } \frac{\Delta S}{\Delta V} = \frac{dP}{dT} \Rightarrow \frac{dP}{dT} = \frac{\Delta H}{RT_b} P$$

$$\Rightarrow \frac{dP}{P} = \frac{\Delta H}{RT_b} dT$$

8. (10%) The normal boiling temperature of benzene is 353.24 K, and the vapor pressure of liquid benzene is  $1.9 \times 10^4$  Pa at 293.15K. The enthalpy of fusion is  $9.95 \text{ kJ mol}^{-1}$ , and the vapor pressure of solid benzene is 137 Pa at 228.9K.

(a) calculate  $\Delta H_{\text{vaporization}}$

(b) calculate  $\Delta S_{\text{vaporization}}$

Sol:

$$\ln \frac{1.01325 \times 10^5}{1.9 \times 10^4} = -\frac{\Delta H_{\text{vap}}}{8.314} \left( \frac{1}{353.24} - \frac{1}{293.15} \right)$$

$$\Delta H_{\text{vap}} = -\frac{8.314 \times \ln \frac{1.01325 \times 10^5}{1.9 \times 10^4}}{\left( \frac{1}{353.24} - \frac{1}{293.15} \right)} = 23.97 \text{ kJ / mol}$$

$$dS = \frac{dH}{T} \quad (T, P \in \text{constant}) \Rightarrow \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b} = 67.8 \text{ J / mol} \cdot \text{K} \quad (T_b = 353.24)$$

9. For water at 298K, the vapor pressure ( $P_0$ ) is 0.0316 bar  
 $\rho = 0.9967 \text{ g/cm}^3$ , and molecular mass is 18.015 amu.

- (a) (10%) Please estimate the vapor pressure of water at 298K if 100 bar of external pressure is applied to the system.
- (b) (10%) Following (a), if bulk water at 298K is sprayed on a hydrophobic surface to form a series of water droplets with uniform spherical size (with radius  $R = 10 \text{ nm}$ ), estimate the vapor pressure of the system

$$(\gamma_{\text{H}_2\text{O}} = 7.2 \times 10^{-2} \text{ N / m})$$

Sol:

(a)

$$\mu_l^* = \mu_g^*$$

apply external force =>

$$\mu_l' = \mu_l^* + V_m(P_f - P_i) = \mu_g^* + RT \ln \frac{P}{P^*} = \mu_g'$$

$$V_m((100 - 0.0316) \text{ bar}) = RT \ln \frac{P}{0.0316}$$

$$V_m = \frac{M}{\rho} = \frac{0.018015 \text{ kg/mol}}{996.7 \text{ kg/m}^3} = 1.8 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}$$

$$P = e^{\frac{1.8 \times 99.97}{8.314 \times 298}} \times 0.0316 = 0.03398 \text{ bar}$$

(b)

Spilled water => external force is aroused from the surface tension.

$$P_{\text{surface}} = \frac{2\gamma}{r} = 144 \text{ bar}$$

using the equation form (a)

$$P_{\text{vapor}} = e^{\frac{1.8 \times (144 - 0.0316)}{8.314 \times 298}} \times 0.0316 = 0.035 \text{ bar}$$

10. (10%) The pressure on the concave side of an interface is always greater than the pressure on the convex side. The difference in pressure of the two sides is equal to  $P_s$ .

Prove that  $P_s = \frac{2\gamma}{R}$ , where  $\gamma$  is surface tension and  $R$  is radius

Sol:

\*method1:

$$\sigma = 4\pi r^2$$

$$d\sigma = 8\pi r dr$$

In order to get the information of  $\gamma$ ,

assume the bubble is expanding with an infinity small amount.

Then the amount of works can represent by  $Fdr$

$$\because \gamma d\sigma = Fdr$$

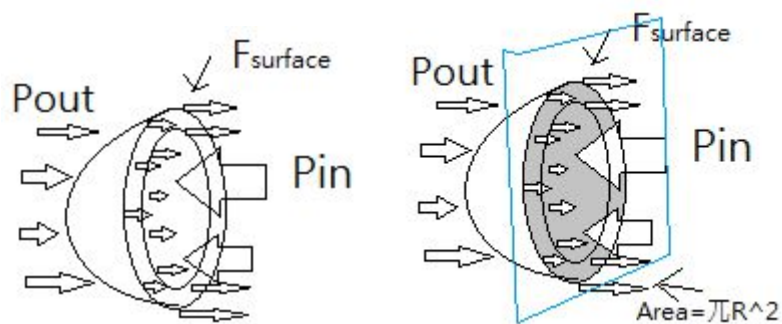
$$\therefore F_{\text{surface}} = 8\pi r \gamma$$

$$P_{\text{inside}} = P_{\text{outside}} + \frac{F_{\text{surface}}}{4\pi r^2}$$

$$P_{\text{surface}} = \frac{2\gamma}{r} \quad (\text{for droplet} \Rightarrow \text{only one layer})$$

$$P_{\text{surface}} = \frac{4\gamma}{r} \quad (\text{for bubble} \Rightarrow \text{two layers})$$

\*method 2:



(Here  $F_{\text{surface}}$  means  $F_{\text{crosssection}}$ )

\*keypoint: pressure is equal any where.

\*Force apply on any cross section are the same.

$$P_{\text{in}} = P_{\text{out}} + \frac{F_{\text{crosssection}}}{A}$$

$$F_{\text{crosssection}} = 2\pi r \gamma$$

$$A_{\text{crosssection}} = \pi r^2$$

$$P_{\text{surface}} = \frac{2\pi r}{\pi r^2} = \frac{2\gamma}{r} \quad (\text{single layer})$$

$$= \frac{4\pi r}{\pi r^2} = \frac{4\gamma}{r} \quad (\text{double layer})$$