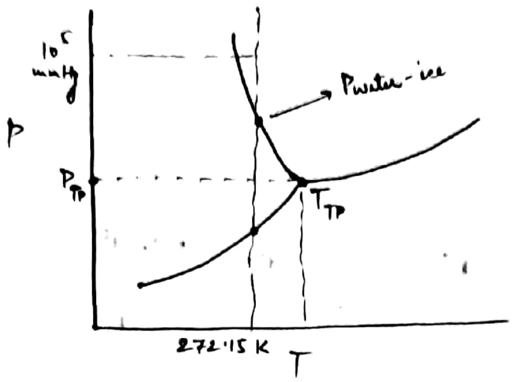
PH - 207

Tutorial - 6

1.

Q1 a)



Water at $-1°C$ = 272.15 K

P_{TP} = 4.6 mm Hg

v_{solid} = 1.12 cm^3/g

v_{liquid} = 1 cm^3/g

2.

Heat of melting = 80 Cal/g

" " vaporisation = 600 Cal/g

Water → Ice transformation

$$\frac{P - P_0}{T - T_0} = \frac{\Delta Q}{(V_{water} - V_{ice})T_0} \Rightarrow P_{water-ice} = P_0 + \frac{\Delta Q}{V_{water} - V_{ice}} \cdot \frac{T - T_0}{T_0}$$

P_0 = 4.6 mm Hg

T_0 = 273.16 K

T = 272.15 K

1 mm of Hg = 133.322 Pa

$$\Delta Q = 80 \text{ Cal/g}$$

$$P_{water-ice} = 0.775 \times 10^5 \text{ mm Hg}$$

Solid → Vapor transformation

$$V_{vapor} >> V_{ice}$$

$$V_{vapor} = \frac{k_B T}{P m}$$

$$\frac{dP}{dT} \approx \frac{L}{T V_{vapor}} = \frac{m L P}{T^2 k_B}$$

$$P_{ice-vapor} \approx P_0 \exp\left[\frac{mL}{k_B}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$m = 18$ g/mol $\qquad P_{ice-vapor} = 4.4$ mm Hg

$L = 600$ Cal/g

b) $$L = T(s_1 - s_2)$$

$$\frac{dL}{dT} = \frac{L}{T} + T\left(\frac{ds_1}{dT} - \frac{ds_2}{dT}\right)$$

$$ds_1 = \frac{C_{T_1}}{T} dT - \beta_1 V_1 dP$$

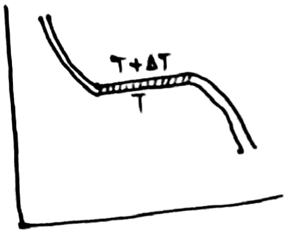
$$\beta_1 = \frac{1}{V_1}\left(\frac{\partial V_1}{\partial T}\right)_{P_1}$$

$$\frac{dL}{dT} = \frac{L}{T} + (C_{p_1} - C_{p_2}) - (\beta_1 V_1 - \beta_2 V_2) T \frac{dP}{dT}$$

$$\frac{dP}{dT} = \frac{L}{T(V_1 - V_2)}$$

$$\frac{dL}{dT} = \frac{L}{T} + (C_{p_1} - C_{p_2}) - (\beta_1 V_1 - \beta_2 V_2)\frac{L}{V_1 - V_2}$$

Q2 a)



$$\eta = \frac{W}{Q} = \frac{W}{L} = \frac{dT}{T}$$

$$W \approx dW = (P + dP)\Delta V - P\Delta V$$
$$= dP\,\Delta V$$

$$\frac{dP\,\Delta V}{L} = \frac{dT}{T} \Rightarrow \frac{dP}{dT} = \frac{L}{T\Delta V}$$

$= nk_BT$

b) $\Delta V = V_{gas} - V_{liquid} \approx V_{gas} = \frac{RT}{P}$

$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

$$\ln\frac{P_0}{P_m} = \frac{L}{R}\left(\frac{1}{T_m} - \frac{1}{T_0}\right)$$

$$\cancel{T_m = \frac{T_0}{\left(1+\frac{RT_0}{L}\right)}} \qquad T_m = \frac{T_0}{\left(1 + \frac{RT_0}{L}\ln\frac{P_0}{P_m}\right)}$$

3.

Neglect v.p. of solvent

Equilibrium : $\mu_{gas}(P,T) = \mu_{gas}^{dissolved}(P,T,x)$

$x \Rightarrow$ Molar fraction of dissolved gas in solvent

$$\mu_{gas}^{dissolved}(P,T,x) = \mu_{gas}^{dissolved}(P,T,x_0) + k_BT\ln\frac{x}{x_0}$$

$x_0 \Rightarrow$ conc^n of standard sol^n

$$\left.\frac{\partial\mu_{gas}}{\partial P}\right|_T dP = \left.\frac{\partial\mu_{gas}^{dissolved}}{\partial P}\right|_T dP = \left.\frac{\partial\mu_{gas}^{dissolved}}{\partial P}\right|_T dP + k_BT\, d\left\{\ln\frac{x}{x_0}\right\}$$

$$v_{gas}\,dP = v_{gas}^{dissolved}\,dP + k_BT\,d\left\{\ln\frac{x}{x_0}\right\}$$

$$\frac{d\left\{\ln\frac{x}{x_0}\right\}}{dP} = \frac{\left(v_{gas} - v_{gas,x_0}^{dissolved}\right)}{k_BT}$$ $\rightarrow$ vol difference in gaseous phase & in sol^n phase

$$v_{gas,x_0}^{dissolved} << v_{gas} = \frac{k_BT}{P}$$

$$\Rightarrow \ln\frac{x}{x_0} = \ln\frac{P}{P_0} \Rightarrow x = x_0\frac{P}{P_0}$$ $\rightarrow$ Law of Henry & Dalton

4. $\frac{\Delta P}{P} = x_{sub}$ $\frac{\Delta P_1}{P_{1,0}} = x_2$

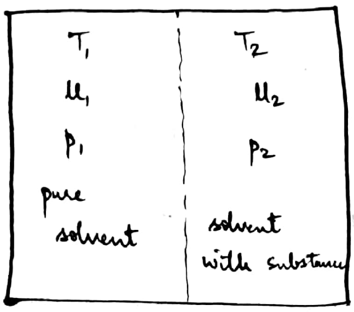
$\frac{\Delta P_2}{P_{2,0}} = x_1$

$$P_{1,0} - P_1 = x_2 P_{1,0} = (1 - x_1) P_{1,0}$$

$$P_{2,0} - P_2 = x_1 P_{2,0}$$

$$P = P_1 + P_2$$
$$= P_{2,0} + x_1 (P_{1,0} - P_{2,0})$$

5.



Equilibrium : $T_1 = T_2$

$\mu_1^{pure} = \mu_2^{soln}$

$P_1 \neq P_2$

$$\mu_1^{pure}(P_1, T) = \mu_2^{soln}(P_2, T, x_s)$$

solvent

$x_s = 1 - x_m$ → solute

$$\mu_2^{soln}(P_2, T, x_s) = \mu_2^{pure}(P_2, T) + k_B T \ln x_s$$

$$\left.\frac{\partial \mu}{\partial P}\right|_T = v \Rightarrow \mu(P_2, T) = \mu(P_1, T) + \int_{P_1}^{P_2} v(P, T)\, dP$$

$$\Rightarrow \cancel{\mu_1^{pure}(P_1, T)} = \cancel{\mu_2^{pure}(P_1, T)} + k_B T \ln x_s + \int_{P_1}^{P_2} v(P, T)\, dP$$

$$\Rightarrow 0 = k_B T \ln x_s + v(P_2 - P_1)$$

$$\pi v = -k_B T \ln(1 - x_m)$$

Osmotic pressure

$$\pi = P_2 - P_1$$

For $x_m \ll 1$,

$$\ln(1 - x_m) \approx -x_m$$

$$\pi v \approx x_m k_B T$$

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Tutorial - 7

1. $$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

a) $$\langle v \rangle = \frac{\int_0^\infty v\, f(v)\, dv}{\int_0^\infty f(v)\, dv}$$

No. of molecules / volume having velocities b/w $[v_x, v_x + dv_x]$, $[v_y, v_y + dv_y]$, $[v_z, v_z + dv_z]$

Distribution of molecular speed $\Rightarrow$ $f(v) = 4\pi v^2 f(v_x, v_y, v_z)$

$$= \frac{\int_0^\infty v^3 e^{\frac{-mv^2}{2k_B T}}\, dv}{\int_0^\infty v^2 e^{\frac{-mv^2}{2k_B T}}\, dv}$$

$$\int_0^\infty x^n e^{-ax^2}\, dx = \frac{\Gamma\left[\frac{n+1}{2}\right]}{2a^{n+1}} \qquad \Gamma[1/2] = \sqrt{\pi}$$

$$n\Gamma(n) = \Gamma(n+1)$$

$$\Gamma(0) = 0$$

$$\Gamma(1) = 1$$

$$\Rightarrow \sqrt{\frac{8k_B T}{\pi m}}$$

b) $$v_{rms} = \sqrt{\langle v^2 \rangle}$$

$$\langle v^2 \rangle = \frac{\int_0^\infty v^2 f(v)\, dv}{\int_0^\infty f(v)\, dv} = \frac{\int_0^\infty v^4 e^{-av^2}\, dv}{\int_0^\infty v^2 e^{-av^2}\, dv} = \frac{3k_B T}{m}$$

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

b)

$$\langle v_x \rangle = \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} v_x \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{\frac{-m}{2k_B T}(v_x^2+v_y^2+v_z^2)}\, dv_x\, dv_y\, dv_z}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{\frac{-m}{2k_B T}(v_x^2+v_y^2+v_z^2)}\, dv_x\, dv_y\, dv_z}$$

$$\int_{-\infty}^{\infty} v_x\, e^{\frac{-mv^2}{2k_BT}}\, dv_x = 0 = \langle v_y \rangle = \langle v_z \rangle$$

c) $$K.E. = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

2. a) Let the observation be along z-direction

$$f(v_z)\, dv_z = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{\frac{-mv_z^2}{2k_BT}}\, dv_z$$

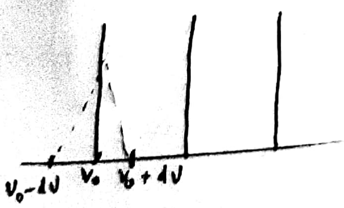
Doppler shift of frequency $\Rightarrow$ $$\nu = \nu_0 \left(\frac{c+v_z}{c}\right)$$

$$v_z = c\left(\frac{\nu-\nu_0}{\nu_0}\right)$$

Frequency distribution $\Rightarrow$

$$f(\nu) = \left(\frac{mc^2}{2\pi k_B T}\right)^{1/2} \frac{1}{\nu_0}\, e^{\frac{-mc^2}{2k_BT}\left(\frac{\nu-\nu_0}{\nu_0}\right)^2}$$

b)



$$\Delta\nu \approx \sqrt{\frac{k_B T}{mc^2}}\, \nu_0$$

$$\Delta\lambda = \sqrt{\frac{k_BT}{mc^2}}\, \lambda_0 = \sqrt{\frac{k_BT}{m}}\, \frac{\lambda_0}{c}$$

$k_B = 8.3$ J/mol-K

$T = 473$ K

$\lambda_0 = 5896$ Å

$m = 40$ gm/mol

$= 40 \times 10^{-3}$ kg/mol

$c = 3\times 10^8$ m/s

$$\Delta\lambda \approx 6 \times 10^{-3}\ \text{Å}$$

Collision broadening $\Rightarrow$ $\Delta\nu_c \approx \frac{1}{\tau}$

$$\tau = \frac{l_{mfp}}{\langle v \rangle} \qquad l_{mfp} = \frac{1}{n\pi d^2}$$

$$d \sim 10^{-10}\ m$$

$$n = \frac{N}{V} = \frac{p}{k_B T} \times N_A$$

$$\Rightarrow n \approx 2 \times 10^{23}\ m^{-3}$$

$$l_{mfp} = 0.76 \times 10^{-3}\ m$$

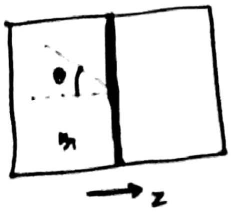
$$\langle v \rangle = \sqrt{\frac{k_B T}{m}} \approx 413\ m/s$$

$$\tau = 4 \times 10^{-7}\ sec.$$

$$\Delta\lambda = \frac{\lambda}{\nu_c}\Delta\nu_c$$

$$= \frac{\lambda^2}{c\,\tau_c} \approx 3 \times 10^{-5}\ \text{Å}$$

3. a)



Speed distribution in chamber $= \tilde{f}(v)$

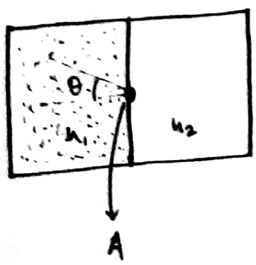
Flux of partition with speed b/w v & $v+dv$

$$= \frac{1}{4} n v \tilde{f}(v)\, dv$$

Total no. of particles hitting partition

$$= \int_0^\infty dv\, \frac{1}{4} n v \tilde{f}(v) = \frac{n}{4}\langle v \rangle$$

b)



$$n_1(0) = n_1 + n_2$$
$$n_2(0) = 0$$

$$V \frac{dn_1}{dt} = -A\frac{\langle v \rangle}{4}(n_1 - n_2)$$

$$V \frac{dn_2}{dt} = -A\frac{\langle v \rangle}{4}(n_2 - n_1)$$

$$n_1 = \frac{N}{2V}\left(1 + e^{-at}\right)$$

$$n_2 = \frac{N}{2V}\left(1 - e^{-at}\right)$$

$$a = \frac{A}{2V}\langle v \rangle$$

$$P = n k_B T$$

$$p_1 = \frac{p_0}{2}\left[1 + e^{-at}\right]$$

$$p_0 = \frac{N}{V} k_B T$$

$$p_2 = \frac{p_0}{2}\left[1 - e^{-at}\right]$$

4. a)

$$n_f = \frac{\int_{v_e}^{\infty} e^{\frac{-mv^2}{2k_BT}} v^2 \, dv}{\int_{0}^{\infty} e^{\frac{-mv^2}{2k_BT}} v^2 \, dv}$$

$$= \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} \int_{v_e}^{\infty} v^2 e^{\frac{-mv^2}{2k_BT}} \, dv$$

$$= 6 \times 10^{-5}$$

b)

$$l_{mfp} = \frac{1}{n\pi d^2}$$

$$n = 2.5 \times 10^{25} \ m^{-3}$$

$$d \sim 10^{-10} \ m$$

$$l_{mfp} = 1.3 \times 10^{-6} m$$

$$\tau = \frac{l}{v_{th}} = 5 \times 10^{-10} \ s$$

After N collisions, mean square diffusion displacement $\langle z^2 \rangle = N l_{mfp}^2$

$$\langle z^2 \rangle = d^2 \qquad N = \frac{d^2}{l_{mfp}^2}$$

$$t = N \tau_{collision}$$

$$= \frac{\tau d^2}{l_{mfp}^2} = \frac{5 \times 10^{-10} \times 10^{10}}{1.69 \times 10^{-12}} \ s$$

$$= 2.9 \times 10^{12} \ s$$