

Chapter 9

P10

Solutions

9.1 (a)

$$dG = -\sigma d\tau + V dp + \mu dN$$

$$-\sigma = \left(\frac{\partial G}{\partial \tau}\right)_{P,N} \quad V = \left(\frac{\partial G}{\partial P}\right)_{\tau,N}$$

$$\therefore \left(\frac{\partial V}{\partial \tau}\right)_P = \frac{\partial^2 G}{\partial \tau \partial P} = -\left(\frac{\partial \sigma}{\partial P}\right)_\tau$$

$$\text{also } \mu = \left(\frac{\partial G}{\partial N}\right)_{\tau,P} \quad V = \left(\frac{\partial G}{\partial P}\right)_{\tau,N}$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial P}\right)_N = \left(\frac{\partial V}{\partial N}\right)_P$$

and

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{\tau,P} \quad -\sigma = \left(\frac{\partial G}{\partial \tau}\right)_{P,N}$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial \tau}\right)_P = -\left(\frac{\partial \sigma}{\partial N}\right)_\tau$$

(b) $\sigma \rightarrow \text{const.}$ as $\tau \downarrow 0 \Rightarrow \left(\frac{\partial \sigma}{\partial P}\right)_\tau \rightarrow 0$ as $\tau \downarrow 0$, hence

$$\sqrt{\left(\frac{\partial V}{\partial \tau}\right)_P} \rightarrow 0 \text{ as } \tau \downarrow 0, \text{ by } \left(\frac{\partial V}{\partial \tau}\right)_P = -\left(\frac{\partial \sigma}{\partial P}\right)_\tau$$

9.2 (a) Law of mass action for $e + H^+ \rightleftharpoons H$ is

$$\frac{n(e) n(H^+)}{n(H)} = \frac{n_q(e) n_q(H^+)}{n_q(H)} \left[e^{F_{int}(e) - F_{int}(H^+) + F_{int}(H)} \right] / \tau$$

$$F_{int}(H) - F_{int}(H^+) - F_{int}(e) \approx U(H) - U(H^+) - U(e) = \text{bonding energy of H atom} = -I$$

$$n_q(H^+) \approx n_q(H) \quad (\text{mass of H} \approx \text{mass of } H^+)$$

so

$$\frac{[e][H^+]}{[H]} \approx n_q(e) e^{-I/\tau} \quad (n(e) \equiv [e], n(H^+) \equiv [H^+], n(H) \equiv [H])$$

$$\text{If } [e] = [H^+] \text{ then } [e] = ([H] n_q e^{-I/\tau})^{1/2}$$

$$(b) [H^{(exc)}] \approx [H] e^{-3/4 I/\tau} = 10^{23} e^{-23.664} = 10^{23 - 23.664/\log 10} \approx 10^{12.7} \approx 10^{13} \text{ cm}^{-3}$$

$$T = 5000 \text{ K} \Rightarrow \tau = \frac{5}{1.16} \times 10^1 \text{ eV} \quad I \approx 13.6 \text{ eV} \quad \frac{3/4 I/\tau}{20} = \frac{3.48}{20} \cdot 136 = 3.48 \cdot 6.8 = 23.664$$

$$[e] = \sqrt{10^{23} n_a} e^{-\frac{2}{3}(23.664)}$$

$$n_a = \left(\frac{\pi}{2\pi\hbar^2/m} \right)^{3/2} = \left[\frac{5/1.16 \cdot 10^{-1} \text{ eV}}{\frac{4.136 \times 10^{-15} \text{ eV-sec}}{9.11 \times 10^{-28} \text{ g}} \cdot \frac{1.05 \times 10^{-27} \text{ erg-sec}}{10^{-15} \text{ cm}^{-3}}} \right]^{3/2} = \left(\frac{45.55 \times 10^{13}}{5.04} \right)^{3/2}$$

$$= 8.6 \times 10^{20}$$

$$\therefore [e] \approx 10^{22 - 15.776/20.6} \approx 10^{15} \text{ cm}^{-3}$$

[e] conc. is about 2 orders of magnitude higher.

$$[9.3] E_d \approx +\frac{13.6}{\epsilon^2} \frac{m^*}{m} \quad (\text{ground state en. of H atom is } \propto e^4 m)$$

$$= +\frac{13.6}{(11.7)^2} 0.301 = +0.03 \text{ eV}$$

$$n_d = 10^{17} \text{ cm}^{-3} \quad \tau = \frac{1}{1.16} \times 10^{-2} \text{ eV} = 8.62 \times 10^{-3} \quad -E_d/\tau = -3.48$$

$$e^{-E_d/\tau} = 0.031$$

$$n_d^+ = 3 \times 10^{15} \text{ cm}^{-3} \quad \xrightarrow{\uparrow} \text{fraction of ionized donors}$$

$$[10.1] \quad (a) \text{ For VdW} \quad F = -N\tau \left\{ \log \left[n_a (V-Nb)/N \right] + 1 \right\} - \frac{N^2 a}{V}$$

$$-\sigma = \frac{\partial F}{\partial \tau} = -N \left\{ \log \left[n_a \frac{(V-Nb)}{N} \right] + 1 \right\} - N\tau \cdot \frac{3}{2} \frac{1}{\tau}$$

$$\sigma = N \left[\log \left(n_a \frac{V-Nb}{N} \right) + \frac{5}{2} \right]$$

$$(b) \quad U = F + \tau\sigma = \frac{3}{2} N\tau - \frac{N^2 a}{V}$$

$$(c) \quad H = U + pV = \frac{3}{2} N\tau - \frac{N^2 a}{V} + \left[\frac{N\tau}{V-Nb} - \frac{N^2 a}{V^2} \right] V$$

$$= \frac{3}{2} N\tau - \frac{2N^2 a}{V} + \frac{N\tau V}{V-Nb} \approx \frac{5}{2} N\tau - \frac{2N^2 a}{V} + \frac{N^2 b}{V}$$

$$P \approx \frac{N\tau}{V} \left(1 + \frac{N}{V} b \right) - \frac{N^2 a}{V^2} = \frac{N\tau}{V} + \frac{N^2 (b\tau - a)}{V^2}$$

$$v^2 p = v\tau + (b\tau - a) \Rightarrow v = \frac{\tau + \sqrt{\tau^2 + 4(b\tau - a)p}}{2p} \approx \frac{2\tau + \frac{2(b\tau - a)}{\tau}}{2p}$$

i.e. $v = \frac{\tau + (b - a/\tau)p}{p} = \frac{V}{N}$

$$\therefore H = \frac{3}{2} N\tau - \frac{N^2 a}{V} + p \cdot N \frac{\tau + (b - a/\tau)p}{p} = \frac{5}{2} N\tau + Nb p - \frac{Nap}{\tau} - \frac{Nap}{\tau}$$

10.2

$$\frac{dp}{dT} \approx \frac{L}{T^2} P$$

$L = 2260 \text{ J/g}$ at $T = 373 \text{ K}$

$$T = 1.4(373) \cdot 10^{-23} \text{ J}$$

$$\frac{dT}{dp} = \frac{T^2}{LP}$$

$$P = 1 \text{ atm}$$

$$L = \text{latent heat per molecule} = \frac{L_0}{N_A} \quad L_0 = \text{latent heat per mole.}$$

$$\text{one mole } H_2O \approx 18 \text{ g} \quad L_0 = 18 \cdot 2260 \text{ J/mole}$$

$$L = \frac{L_0}{N_A} = \frac{18}{6} \cdot 2260 \times 10^{23} \text{ J/atom} = 6.780 \times 10^{20} \text{ J/atom}$$

$$\frac{dT}{dp} = \frac{27.3 \times 10^{-46} \text{ J}^2}{6.78 \times 10^{20} \text{ J-atm}} = 4.02 \times 10^{-26} \text{ J/atm}$$

$$\frac{dT}{dp} = \frac{4.02 \times 10^{-26} \text{ J/atm}}{1.4 \times 10^{-23} \text{ J/K}} = 2.87 \times 10^{-3} \text{ K/atm}$$

10.3

$$P = 3.88 \text{ mm at } T = 271 \text{ K}$$

$$P = 4.58 \text{ mm at } T = 273 \text{ K}$$

$$P(T) = P_0 e^{-(L_0/RT)} \Rightarrow \frac{P(273)}{P(271)} = e^{(L_0/R)(\frac{1}{271} - \frac{1}{273})} = \frac{4.58}{3.88}$$

$$L_0 = \frac{\log(4.58/3.88)}{\frac{1}{8.31} \frac{2}{271+273}} = \frac{8.31 \cdot (271) \cdot (273)}{2} \log\left(\frac{4.58}{3.88}\right) \text{ J/mol}$$

$$= 50,986 \text{ J/mol}$$

assuming L_0 between 0 and -2°C is equal to its value at -1°C