

Chemistry 553

Problem set 4

Due: 25 February 2011

From your text,

1. 11.4
2. 11.6
3. 11.11a
4. 11.12 Use $\theta_R(CO) = 2.77K$
5. 11.20
6. 12.2
7. 12.3 For the oxygen reaction, derive the T dependence for $K_\rho(T)$ and $K_P(T)$. Ignore the numbers.
8. 13.2
9. 13.3
10. 13.9

Problem set 4

1. 11.4

$$\psi_n(x) = (2/L)^{1/2} \sin(n\pi x/L)$$

$$E_n = + \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2 = \frac{n^2 \hbar^2}{8mL^2} \quad 1D$$

$$\text{in 3D} \quad E_n = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Two lowest levels, $n_x=1=n_y=n_z$, $n_x=2, n_y=n_z=1$

$$E_1 = 3\hbar^2/8mL^2 = 0.181 \times 10^{-16} \text{ J}$$

$$E_2 = 3\hbar^2/4mL^2 = 0.361 \times 10^{-16} \text{ J}$$

$$m_e = 9.109 \times 10^{-31} \text{ kg}, \quad \hbar = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$k_B = 1.380 \times 10^{-23} \text{ J/K}, \quad L = 1 \text{ \AA} = 10^{-10} \text{ m}$$

$$q = \exp(-\beta E_1) + 3 \exp(-\beta E_2)$$

$$= \exp(-\beta E_1) (1 + 3 \exp(-\beta(E_2 - E_1)))$$

$$q = \exp(-\beta E_1) (1 + 3 \exp(-\beta E_1))$$

~~q~~ $\beta E_1 = +4362$ huge ~~energy~~ energy, quantum effects dominate the sum.

2. 11.6

$$q = \frac{T}{\Theta_R}, \quad \text{if } q \sim 200 \text{ when } T = 300 \text{ K}$$

$$\text{then } q = 200 = \frac{300}{\Theta_R}, \quad \Theta_R \sim 1.5 \text{ K}$$

$$q = 10 = T/\Theta_R \Rightarrow T = 15 \text{ K}$$

3. 11.11a

$$C_V \cong \frac{3}{2} k_B \Rightarrow \frac{3}{2} R \quad \text{for Ar}$$

observed $C_V = 18.7 \text{ J/Kmol}$

$$\text{gas phase } C_V \sim (1.5) (8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}) \cong 12.5$$

Roughly 2/3 from non-interacting gas.

4. 11.12

$$S/Nk_B = \ln \left\{ \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right\} + \ln \left(\frac{T_e}{\Theta_R} \right)$$

$$P = 1 \text{ atm} \cong 1 \text{ bar} = 10^5 \text{ Pa} = k_B T \rho = k_B T (N/V)$$

$$V/N = k_B T / 10^5 \text{ Pa}$$

$$\Theta_R(\text{CO}) : \underline{k_B T} \quad \Theta_R = 2.77 \text{ K}$$

$$S/Nk_B \sim 18.1 \quad \text{translation}$$

$$S/Nk_B \sim 5.7 \quad \text{rotation}$$

5. 11.20

$$g = V/\Lambda^3$$

$$\Lambda = h / \sqrt{2\pi m k_B T} \sim 1.36 \times 10^{-8} \text{ m}$$

$$g_a(1 \text{ mm}) = (10^{-3} \text{ m})^3 / \Lambda^3 \cong 4 \times 10^{14} \text{ states}$$

$$g_b(10^{-8} \text{ m}) = 10^{-24} / \Lambda^3 \sim 0.4 \text{ states} \leftarrow$$

quantum dot.

6. 12.2

broken: $\exp(-\beta E_{\text{broken}})$, $E_{\text{broken}} = 0$

formed: $\exp(-\beta E_{\text{formed}})$, $E_{\text{formed}} = -E$

$$q = 1 + \exp(\beta E)$$

$$\text{fraction broken} = \frac{1}{1 + \exp(\beta E)}$$

$$\beta E = \left(\frac{2 \text{ kcal}}{\text{mole}} \times \frac{4.18 \text{ J}}{\text{cal}} \right) / \left(\frac{8.315 \text{ J}}{\text{K} \cdot \text{mol}} \times 300 \text{ K} \right) \approx 3.35$$

and fraction broken = 0.033.

7. 12.3

a) $P(E) = P_0 \exp(-(E - \langle E \rangle)^2 / 2 \langle \Delta E^2 \rangle)$

$$= Q^{-1} \exp(-\beta E) W(E) \quad \text{solve for } W(E)$$

$$W(E) = P(E) Q \exp(\beta E)$$

$$= \left[P_0 \exp(-(E - \langle E \rangle)^2 / 2 \langle \Delta E^2 \rangle) \right] Q \exp(\beta E)$$

$$S = k_B \ln W(E) = k_B \ln [P_0 Q \exp(\beta E)] - k_B \ln \left[\frac{(E - \langle E \rangle)^2}{2 \langle \Delta E^2 \rangle} \right]$$

$$\text{or } S = S_0 - k_B \frac{(E - \langle E \rangle)^2}{2 \langle \Delta E^2 \rangle}$$

b) E_0 corresponds to $S(E) = 0 \Rightarrow$

$$S_0 = k_B \frac{(E_0 - \langle E \rangle)^2}{2 \langle \Delta E^2 \rangle}$$

c) $ds = \frac{1}{T} dE$

$$T = \left(\frac{\partial S}{\partial E} \right)^{-1}_{E_0}$$

$$\left(\frac{\partial S}{\partial E} \right) = -k_B \frac{(E_0 - \langle E \rangle)}{\langle \Delta E^2 \rangle} = k_B \frac{[\langle E \rangle - E_0]}{\langle \Delta E^2 \rangle}$$

$$T_0 = \frac{\langle \Delta E^2 \rangle}{k_B [\langle E \rangle - E_0]}$$

8. 13.2 $K_p = \frac{p_B}{p_A} = \frac{p_B}{p_A} = \exp(-\beta \Delta \mu^\circ) = 10$

$$\Delta \mu^\circ = -k_B T \ln(10) = -0.95 \times 10^{-20} \text{ J/partikel} \\ = -5744 \text{ J/mole}$$

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = \frac{-\Delta H^\circ}{k_B} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$K_p(T_2) = K_p(T_1) \exp\left(\frac{-\Delta H^\circ}{k_B} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)\right) = 17.2$$

$$T_2 = 310, T_1 = 300, \Delta H^\circ = 10 \text{ kcal}$$

$$\Delta \mu^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta \mu^\circ) / T = \left[(10 \text{ kcal}) \left(\frac{4.18 \text{ J}}{\text{cal}} \right) + 5744 \text{ J} \right] / 300$$

$$\Delta S^\circ = 296.3 \text{ J/K}$$

$$\Delta S^\circ / R = 35.6$$

9. 13.3 $O_2 \rightleftharpoons 2O$

$$K_p = \frac{p_O^2}{p_{O_2}} = \frac{\left[T^{3/2} \exp(\beta D_0(O)) \right]^2}{T^{3/2} T \exp(\beta D_0(O_2))}$$

$$K_p \cong T^{1/2} \exp(\beta [2D_0(O) - D_0(O_2)])$$

But

$$K_p = \frac{p_O^2}{p_{O_2}} = \frac{(k_B T p_O)^2}{k_B T p_{O_2}} \\ = k_B T K_p$$

$$\therefore K_p \sim T^{3/2} \exp(\beta [2D_0(O) - D_0(O_2)])$$

10. 13.9 clusters

$$m\mu_1 = \mu_m$$

$$K_{eq} = \frac{\rho_m}{(\rho_1)^m} = \frac{(q_m/v)}{(q_1/v)^m} \sim \exp(-\beta[mD_1 - D_m])$$

chain growth is favored