

Department of Chemistry, Oregon State University
Physical Chemistry Assignment 4
due: 21 November 2014

1. 4.30 from Silbey, Alberty and Bawendi
2. 4.35
3. 4.45
4. 5.5 Express K in units of mols/liter
5. In the gas phase reaction, $4A + 2B \rightleftharpoons C + D$ it was found that when 2.0 mol A, 2.00 mol B and 1.00 mol D were mixed and allowed to come to equilibrium at 25°C , the resulting mixture contained 0.25 mol C at a total pressure of 2.0 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) the equilibrium constants K_y, K_p , and (c) $\Delta G^0/R$. y is the gas phase mole fraction.
6. The equilibrium constant for a reaction was fit to

$$\ln K(T) = a + b/T + c/T^2$$

Calculate the standard reaction enthalpy, ΔH^0 and the standard reaction enthalpy, ΔS^0 in terms of a, b, c, T .

Prove the next three identities. Start on the left side and do not touch the right hand side.

7.

$$\kappa_T - \kappa_S = \frac{TV\alpha_P^2}{C_p}$$

Hint: begin with the total differential, $dV(P, S)$.

8.

$$\left(\frac{\partial E}{\partial P}\right)_T = V(\kappa_T P - \alpha_P T)$$

begin with $dE(S, V)$

9.

$$\left(\frac{\partial A}{\partial V}\right)_S = \frac{\alpha_P T S}{\kappa_T C_v} - P$$

begin with $dA(T, V)$

Problem set 4

1. 4.30

$$G(T, P) = -\frac{5}{2} T \ln T + T \ln P = -T \ln(T^{5/2}/P)$$

$$dG = -SdT + Vdp$$

$$\therefore S = -\left(\frac{\partial G}{\partial T}\right)_P = -\ln P + \frac{5}{2} \ln T + \frac{5}{2} = \ln(T^{5/2} e^{5/2}/P)$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T = \frac{T}{P} \quad \text{or} \quad PV = T \quad \text{ideal gas}$$

$$H = G + TS = -T \ln(T^{5/2}/P) + T \ln(T^{5/2} e^{5/2}/P)$$

$$H = \frac{5}{2} T = C_p T$$

$$E = H - PV = \cancel{C_p T} \Rightarrow \frac{5}{2} T - T = \frac{3}{2} T = C_v T$$

$$A = E - TS = \frac{3}{2} T - T \ln(T^{5/2} e^{5/2}/P)$$

$$A = -T \ln(T^{5/2}/Pe) = -T \ln\left(\frac{T^{5/2} \cdot V}{Te}\right)$$

$$A = -T \ln(T^{3/2} V/e)$$

2. 4.35

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

$$\uparrow$$

$$-\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha_P$$

so, at constant T,

$$\Delta S = -V\alpha_P \Delta P$$

$$\alpha_p = 3.55 \times 10^{-5} \frac{1}{K}, \quad \Delta P = (1000 - 1 = 999) \text{ bar}$$

$$\rho_{Fe} = \frac{7.86 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ mol}}{55.84 \text{ g}} \times \frac{10^6 \text{ cm}^3}{\text{m}^3} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = 0.14 \times 10^3 \frac{\text{mol}}{\text{m}^3}$$

$$\Delta \bar{S} = -\frac{1}{\rho_{Fe}} \times \alpha_p \times \Delta P \sim -25,19 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

or

$$\Delta \bar{S}/R \sim -3.03$$

3. 4.45

Ideal gas @ 300K, $P_1 = 15 \text{ bar}$

$P_2 = 1 \text{ bar}$

a) maximum work, isothermal expansion.

$$W_{by} = \int_{V_1}^{V_2} P dV = RT \ln(V_2/V_1) = RT \ln(P_1/P_2)$$

$$W_{by} = RT \ln(15) = (8.315 \frac{\text{J}}{\text{K} \cdot \text{mol}})(300) \ln 15$$

$$W_{by} = 6710 \text{ J/mol}$$

b) $\Delta E = \Delta H = 0$ isothermal expansion.

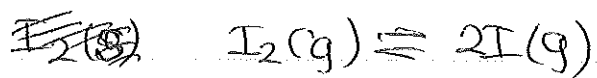
$$d) \Delta G = \Delta[H - TS] = -T\Delta S$$

$$\Delta S = R \ln V_2/V_1 = +R \ln(P_1/P_2)$$

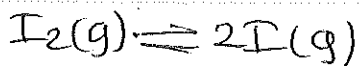
$$\Delta G = -RT \ln(P_1/P_2) = -RT \ln(15) = -W_{by}$$

$$e) \Delta S = R \ln(15) = 22,5 \text{ J/K} \cdot \text{mol}$$

4. 5.5



Initially $p(\text{I}_2) = 5.96 \times 10^{-3}$ mol/liter



$$(5.96 \times 10^{-3} - x) \rightleftharpoons 2x$$

$$\therefore \text{total density} = \frac{5.96 \times 10^{-3} \text{ moles}}{\text{l}} + x$$

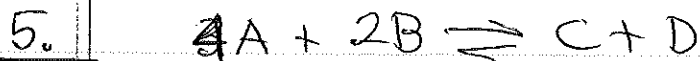
$$P_{\text{total}} = P/RT = \frac{5.96 \times 10^{-3} \text{ moles}}{\text{l}} + x = \frac{0.496 \text{ bar}}{973 \text{ K} \cdot 0.08315 \frac{\text{J}}{\text{K} \cdot \text{mol}}}$$

$$P_{\text{tot}} = \frac{6.13 \times 10^{-3} \text{ moles}}{\text{l}},$$

$$x = (6.13 - 5.96) \times 10^{-3} \text{ moles/l} = 0.17 \text{ moles/liter.}$$

$$K_p = \frac{(2x)^2}{(5.96 - x) \times 10^{-3} \text{ moles/liter}}$$

$$K_p = \frac{4x^2}{(5.96 - x) \times 10^{-3}} = 2.0 \times 10^{-5} \frac{\text{moles}}{\text{liter}}$$



$$\text{A}: 2 - 4x, \quad \text{B} = 2 - 2x; \quad \text{C} = x, \quad \text{D} = 1 + x$$

At equilibrium, $\text{C} = 0.25 \text{ mol}$

$$\therefore \text{A} = 1 \text{ mol}, \quad \text{B} = 1.5 \text{ mol}, \quad \text{C} = 0.25, \quad \text{D} = 1.25$$

$$\text{TOT} = 4 \text{ mol}$$

$$\text{mole fractions } \begin{aligned} X_A &= \frac{1}{4}, & X_B &= \frac{1.5}{4} = 0.375 \\ X_C &= \frac{0.25}{4} = 0.0625, & X_D &= 0.3125 \end{aligned}$$

$$a) \quad x_A = 0.25 \quad x_C = 0.06125 \\ x_B = 0.375 \quad x_D = 0.3125$$

$$b) \quad K_x = \frac{x_D x_C}{x_B^2 x_A^4} = 38.4$$

Total pressure = 2 bar

$$K_p = \frac{P^2}{P^4} K_x = \frac{1}{P^2} K_x = \frac{38.4}{2^2} = 2.17$$

$$c) \quad \Delta G/R = -\ln K_p = -\ln 2.17 = -0.77$$

6. $\ln K_{eq} = a + \frac{b}{T} + \frac{c}{T^2}$

$$\left(\frac{\partial(G/T)}{\partial(1/T)} \right)_P = H, \quad \Delta G = -RT \ln K_{eq}$$

$$\left(\frac{\partial \ln K_{eq}}{\partial(1/T)} \right)_P = -\frac{\Delta H}{R} = b + \frac{2c}{T}$$

Also, $dG = -SdT$

$$d(\Delta G) = -(\Delta S) dT$$

$$d(-RT \ln K_{eq}) = d\{-RTa - Rb - R^2c/T\}$$

$$+\Delta S = \frac{\partial}{\partial T} (RTa + Rb + R^2c/T)$$

$$= R\{a + c/T^2\}, \quad \frac{\Delta S}{R} = a - \frac{c}{T^2}$$

7. $K_T - K_S = TV \alpha_p^2 / C_p$

$$dV(P, S) = \left(\frac{\partial V}{\partial P} \right)_S dP + \left(\frac{\partial V}{\partial S} \right)_P dS$$

$$\left(\frac{\partial V}{\partial P} \right)_T = \left(\frac{\partial V}{\partial P} \right)_S + \left(\frac{\partial V}{\partial S} \right)_P \left(\frac{\partial S}{\partial P} \right)_T$$

$\begin{matrix} \uparrow & \uparrow & \uparrow & \leftarrow -V\alpha_p \\ -VK_T & -VK_S & \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial S} \right)_P & \end{matrix}$

$$VK_T = VK_S + \frac{V\alpha_p T}{C_p} \times V\alpha_p$$

$$\text{or } K_T = K_S + VT \alpha_p^2 / C_p$$

8. $\left(\frac{\partial E}{\partial P} \right)_T = V \{ K_T P - \alpha_p T \}$

$$dE = TdS - PdV,$$

$$\left(\frac{\partial E}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T - P \left(\frac{\partial V}{\partial P} \right)_T \leftarrow -VK_T$$

$$\begin{matrix} \uparrow \\ -V\alpha_p \end{matrix}$$

$$= PVK_T - TV\alpha_p \text{ as given above.}$$

$$9. \quad \left(\frac{\partial A}{\partial V}\right)_S = \frac{\alpha_p T S}{\kappa_T C_V} - P$$

$$dA = -SdT - PdV$$

$$\left(\frac{\partial A}{\partial V}\right)_S = -S\left(\frac{\partial T}{\partial V}\right)_S - P = +\frac{ST}{C_V}\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$\begin{aligned} & \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \end{aligned}$$

but

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\alpha_P}{\kappa_T}\right)$$

$$= \frac{1}{V\kappa_T} \quad \left(\frac{\partial V}{\partial T}\right)_P = V\alpha_P$$