Hwk #6 Key

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26-1

a)
$$\begin{array}{llll} & SO_2Cl_2\,(g) \rightleftharpoons & SO_2\,(g) \; + & Cl_2\,(g) \quad @\ eq. \\ (1) & n_0 - \xi & \xi & \xi \\ (2) & n_0 - \xi & n_1 + \xi & \xi \end{array}$$

b)
$$\begin{array}{llll} & 2\,SO_3\,(g) \rightleftharpoons & 2SO_2\,(g) \; + & O_2\,(g) \\ (1) & n_0 - 2\xi & 2\xi & \xi \\ (2) & n_0 - 2\xi & 2\xi & n_1 + \xi \end{array}$$

c)
$$\begin{array}{lll} N_2\,(g) \; + & 2O_2\,(g) \rightleftharpoons & N_2O_4\,(g) \\ n_0 - \xi & 2n_0 - 2\xi & \xi \\ n_0 - \xi & n_0 - 2\xi & \xi \end{array}$$

26-3

$$\begin{array}{lll} & N_2O_4\,(g) \rightleftharpoons & 2NO_2\,(g) \\ I & n_0 & 0 \\ E & n_0 - \xi & 2\xi \end{array}$$

total # mol : $n_0 - \xi + 2\xi = n_0 + \xi$

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

$$P_{NO_2} = X_{NO_2} P_{tot} = \frac{2\xi}{n_0+\xi} P_{tot}$$

$$P_{N_2O_4} = X_{N_2O_4} P_{tot} = \frac{n_0-\xi}{n_0+\xi} P_{tot}$$

$$= \frac{4\xi^2 P_{tot}^{\cancel{2}}}{(n_0+\xi)^{\cancel{2}}} \cdot \frac{\cancel{(n_0+\xi)}}{n_0-\xi\,\cancel{P_{tot}}}$$

$$= \frac{4\xi^2}{n_0^2-\xi^2} P_{tot}$$

divide by n_0^2 ... $K_p = \dfrac{4\,(\xi/n_0)^2}{1-(\xi/n_0)^2} P_{tot}$

<u>solve for ξ_{eq}/n_0</u>

$$K_p - K_p(\xi/n_0)^{2} = 4(\xi/n_0)^2 P_{tot}$$

$$K_p = K_p + 4P_{tot}(\xi/n_0)^2$$

$$\xi/n_0 = \left(\frac{K_p}{K_p+4P}\right)^{1/2}$$

@ 100°C ... $K_p = 6.1$

- See attached graph/data from Excel
- This follows Le Châtelier's principle b/c there is more mol gas on product side + increasing P should cause rxn to go from R to L.

26-9

$$\xcancel{k_p(\text{bar}) = \frac{P_Y^{\nu_Y}/(\text{bar})\ P_Z^{\nu_Z}/(\text{bar})}{P_A^{\nu_A}/(\text{bar})\ P_B^{\nu_B}/(\text{bar})}}$$

Skipped

26-10 Find $\Delta_r G^\circ(T)$ and $k_p(T)$ @ 25°C

(a) $N_2O_4(g) \rightleftarrows 2\,NO_2(g)$

$$\Delta_r G^\circ = 2\,\Delta G_f^\circ(NO_2) - \Delta G_f^\circ(N_2O_4)$$
$$= 2(51.258) - 97.787$$
$$= 4.729 \text{ kJ/mol}$$

$k_p = e^{-\Delta_r G^\circ/RT}$ $T = 25 + 273 = 298\text{ K}$

$= 0.148$ ★ remember to use similiar units for $\Delta_r G^\circ$ + R... ★

(b) $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$

$$\Delta_r G^\circ = 2\Delta G_f^\circ(HI) - \Delta G_f^\circ(I_2) - \Delta G_f^\circ(H_2)$$
$$= 2(1.560) - 19.325 - 0$$
$$= -16.205 \text{ kJ/mol}$$

$k_p = e^{-\Delta_r G^\circ/RT}$

$= 692$

(c) $3H_2(g) + N_2(g) \rightleftarrows 2NH_3(g)$

$$\Delta G_r^\circ = 2(-16.367) - 0 - 0 = -32.734 \text{ kJ/mol}$$

$K_p = 5.5 \times 10^5$

26-13 $I_{2\,(g)} \rightleftharpoons 2I_{(g)}$

P_{tot} = total pressure = 36.0 torr
P_{I_2} = partial pressure of I_2 = 28.1 torr } @ 1400°C (1698 K

Find k_p (1 bar std state) + k_c (1 M std state)

$P_{tot} = 0.04799$ bar

$P_{I_2} = 0.03746$ bar

$P_I = P_{tot} - P_{I_2} = 0.01053$ bar

$$k_p = \frac{P_I^2}{P_{I_2}} = 2.96 \times 10^{-3}$$

$$\begin{aligned} k_c &= k_p \left(\frac{P^\circ}{c^\circ RT}\right)^{\nu_Y + \nu_Z - \nu_A - \nu_B} \\ &= k_p \left(\frac{1\text{ bar}}{1\text{ M}\cdot RT}\right)^{2-1} \\ &= 2.10 \times 10^{-5} \end{aligned}$$

R = 0.08~~206~~314 L bar / K mol
T = 1698 K

26-22 $2H_{2\,(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$

$$Q = \frac{P_{CH_3OH}}{P_{CO}\,P_{H_2}^2} = \frac{10.0\text{ bar}/1\text{ bar}}{\left(\frac{0.0050\text{ bar}}{1\text{ bar}}\right)\left(0.10\text{ bar}/1\text{ bar}\right)^2} = 2 \times 10^5$$

$Q > k_p$ Rxn will proceed to left

(Also... $\Delta_r G = RT \ln Q/k_p$. $\Delta_r G > 0$ here)

26-25 $\Delta_r H^\circ = -12.93$ kJ/mol

$k_p(700\text{ K}) = ?$
$k_p(1000\text{ K}) = 29.1$

van't Hoff Eq
$$\ln \frac{k_p(T_2)}{k_p(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{29.1}{k_p(700)} = -\frac{(-12.93 \times 1000\text{ J/mol})}{8.314\text{ J/mol}}\left(\frac{1}{1000} - \frac{1}{700}\right.$$

$$\ln \frac{29.1}{K_p(700)} = -0.666$$

$$\frac{29.1}{K_p(700)} = e^{-0.666}$$

$$\frac{29.1}{e^{-0.666}} = K_p(700)$$

$$K_p = 56.6$$

Note: back of book (+ soln manual) is wrong. Kp (1000) must be less than kp (700) b/c this is an exothermic rxn.

26-29

$$2\,C_3H_6\,(g) \rightleftarrows C_2H_4\,(g) + C_4H_8\,(g)$$

$$\ln K_p(T) = -2.395 - \frac{2505}{T} + \frac{3.477\times10^6}{T^2} \qquad 300 < T < 600\ K$$

Eq 26.11 Find $\Delta_r G^\circ$, $\Delta_r H^\circ$ + $\Delta_r S^\circ$ @ 525 K.

$$\Delta_r G^\circ = -RT\ln K_p(T) = -RT\left(-2.395 - \frac{2505}{T} + \frac{3.477\times10^6}{T^2}\right)$$

T = 525 K

$$= -23.78\ \text{kJ/mol}$$

Eq 26.29 $\Delta_r H^\circ = RT^2 \dfrac{d\ln K_p(T)}{dT}$

$$= RT^2\left(\frac{2505}{T^2} - \frac{2(3.477\times10^6)}{T^3}\right) \quad @\ 525\ K$$

$$= -89.30\ \text{kJ/mol}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

$$\Delta_r S^\circ = -\frac{(\Delta_r G^\circ - \Delta_r H^\circ)}{T} = -124.8\ \text{J/mol·K}$$

26-38 Find K_c + K_p @ 700 K for $3H_2(g) + N_2(g) \rightleftarrows 2NH_3(g)$
(using stat mech + ch. 18)

$$K_c = \frac{(q_{NH_3}/V)^2}{(q_{N_2}/V)(q_{H_2}/V)^3}$$

From Eq 18.39

$$\frac{q_{N_2}}{V} = \left(\frac{2\pi \overset{\text{in kg}}{M} k_B T}{h^2}\right)^{3/2} \frac{T}{\sigma \Theta_{rot}} \frac{e^{-\Theta_{vib}/2T}}{1-e^{-\Theta_{vib}/T}} g_{el} e^{D_e/k_BT}$$

$\sigma = 2$

$M = 28.02 \text{ g/mol} \cdot \frac{1.66\times10^{-27}\text{kg}}{1 \text{ g/mol}} = 4.65\times10^{-26}$ kg

$\Theta_{rot}^{N_2} = 2.88$ K

$\Theta_{vib}^{N_2} = 3374$ K $\qquad k_B = 1.38\times10^{-23}$ J/K

$D_e = 953.0$ kJ/mol $= 1.58\times10^{-21}$ kJ/molecule

$\uparrow$ needed to get units to cancel in e^{D_e/k_BT}

$g_{el} = 1$

$$= \left(\frac{2\pi(4.65\times10^{-26}\text{kg})\cdot1.38\times10^{-23}\text{J/K}\cdot700\text{K}}{(6.626\times10^{-34}\text{ J}\cdot\text{s})^2}\right)^{3/2} \frac{700}{2(2.88)} \frac{e^{-3374/2\cdot700}}{1-e^{-3374/700}} \cdot 1\, e^{\frac{1.58\times10^{-18}}{1.38\times10^{-23}\cdot700}}$$

$$= 5.15\times10^{32}\cdot121.5\cdot0.0905\cdot1\cdot1.08\times10^{71}$$

$$= 6.12\times10^{104}\text{ m}^{-3}$$

$$\frac{q_{H_2}}{V} = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{T}{\sigma \Theta_{rot}} \frac{e^{-\Theta_{vib}/2T}}{1-e^{-\Theta_{vib}/T}} g_{el} e^{D_e/k_BT}$$

$\sigma = 2$

$M = 3.36\times10^{-27}$ kg

$\Theta_{rot}^{H_2} = 85.3$

$\Theta_{vib}^{H_2} = 6332$

$D_e = 457.6$ kJ/mol $= 7.6\times10^{-19}$ J/molecule

$$= 1.00\times10^{31}\cdot4.103\cdot0.01086\cdot1\cdot1.473\times10^{34}$$

$$= 6.56\times10^{63}\text{ m}^{-3}$$

From Eq 18.60

$$\frac{q^{NH_3}}{V} = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{rot A}\Theta_{rot B}\Theta_{rot C}}\right)^{1/2} \prod_{j=1}^{\overset{6}{3n-6}} \frac{e^{-\Theta_{vib,j}/2T}}{1-e^{-\Theta_{vib,j}/T}}\, g_{e1}\, \underset{\underset{\text{cancels w/ } e^{-\Theta_{vib}/2T}}{\uparrow}}{\underset{e^{D_0/k_BT}\, e^{h\nu/2k_BT}}{\uparrow}}{e^{D_e/k_BT}}$$

$\sigma = 3$ (see Ex 18-7, pg 752) or table 18.4 p 750

$\Theta_{rot B} = \Theta_{rot A} = 13.6\,K$

$\Theta_{rot C} = 8.92$

$\Theta_{vib_1} = 4800\,K$ $\Theta_{vib2} = 1360\,K$ $\Theta_{vib3} = = \Theta_{vib4} = 4880\,K$

$\Theta_{vib5} = \Theta_{vib6} = 2330\,K$

$D_0 = 1158$ kJ/mol → 1.92×10^{-18} J/molecule

~~$D_e = D_0 + h\nu/2 \approx D_0$~~

$M = 2.83\times10^{-26}$ kg

$$= \left(\frac{2\pi\,(2.83\times10^{-26})\,1.38\times10^{-23}\cdot700}{(6.626\times10^{-34}\,J.s)^2}\right)^{3/2} \frac{\pi^{1/2}}{3}\left(\frac{700^3}{(13.6)(8.92)(13.6)}\right)^{1/2}\cdot1\cdot e^{+\frac{1.92\times10^{-18}}{1.38\times10^{-23}\cdot700}}\cdot$$

$$\left(\frac{\overset{1}{\cancel{e^{-4800/2\cdot700}}}}{1-e^{-4800/700}}\right)\left(\frac{\overset{1}{\cancel{e^{-1360/2\cdot700}}}}{1-e^{-1360/700}}\right)\left(\frac{\overset{1}{\cancel{e^{-4880/2\cdot700}}}}{1-e^{-4880/700}}\right)^2\left(\frac{\overset{1}{\cancel{e^{-2330/2\cdot700}}}}{1-e^{-2330/700}}\right)^2$$

$$= 2.45\times10^{32}\cdot0.591\cdot\overset{455.96}{\cancel{2.08\times10^{5}}}\cdot2.09\times10^{86}\cdot\overset{1.001}{\cancel{0.0335}}\cdot\overset{1.167}{\cancel{0.4419}}\cdot\overset{1.003}{\cancel{9.4\times10^{-4}}}\cdot\overset{1.076}{\cancel{0.03856}}$$

$$= \overset{1.74\times10^{121}}{\cancel{7.18\times10^{114}}}\ m^{-3}$$

$$K_c = \frac{(q_{NH_3}/V)^2}{(q_{H_2}/V)^3(q_{N_2}/V)} = \frac{\left(\overset{1.74\times10^{121}}{\cancel{7.18\times10^{114}}}\right)^2}{(6.56\times10^{63})^3(6.12\times10^{104})} = \overset{1.75\times10^{-54}}{\cancel{2.99\times10^{-63}}}$$

$$K_p = K_c\left(\frac{c^\circ RT}{P^\circ}\right)^{\nu_{NH_3}-\nu_{N_2}-\nu_{H_2}}$$

$$= K_c\left(\frac{c^\circ RT}{N_A P^\circ}\right)^{-2}$$

$c^\circ = 1$ molecule/m^3

$P^\circ = 1$ bar $= 10^5$ Pa

$$\left(\frac{c^\circ RT}{N_A P^\circ}\right)^{-2} = \cancel{9.34\times10^{-51}}\ 1.07\times10^{50}$$

$$K_p = \overset{1.87}{\cancel{1.23}}\times10^{-4} \text{ or } \overset{18.7}{\cancel{12.3}}\times10^{-5}$$

← larger than experimental b/c of approx.

26-58 Calculate activity as function of P from 1 bar to 100 bar @ 20.0°C. $\rho = 0.9982$ g/mL + liquid is incompressible

Eq 26.69 $\ln a = \frac{\bar{V}}{RT}(P-1)$ $\bar{V} = \frac{1}{\rho}$ if ρ is mol/L

$0.9982\ \text{g/mL} \times \frac{1\ \text{mol}}{18.0152\ \text{g}} \times \frac{1000\ \text{mL}}{1\ \text{L}}$

$\rho = 55.4\ \text{mol/L}$

$\bar{V} = 0.018\ \text{L/mol}$

$$\ln a = \frac{0.018\ \text{L/mol}}{0.08314\ \frac{\text{L bar}}{\text{mol K}} \cdot 293\ \text{K}}(P-1)$$

$$= 7.39 \times 10^{-4}(P-1)$$

P/bar	ln a	a
1 bar	0	1.00
10 bar	0.0067	1.007
30 bar	0.0214	1.022
50 bar	0.0362	1.037
70 bar	0.05099	1.052
90 bar	0.0658	1.068
100 bar	0.0732	1.076

26-61 $CaCO_3$ (calcite) $\rightleftharpoons$ $CaCO_3$ (aragonite) $\Delta_r G° = 1.04$ kJ/mol (298 K)

see Ex 26-13

$\rho_{calcite} = 2.710\ \text{g/cm}^3$ $\rho_{aragonite} = 2.930\ \text{g/cm}^3$

$$\bar{V}_{cal} = \left(2.710\ \text{g/mL} \cdot \frac{1\ \text{mol}}{\cancel{100g}\ 100.09} \cdot \frac{1000\ \text{mL}}{\text{L}}\right)^{-1}$$

$= \cancel{[illegible]}\ 0.0369$ L/mol

$$\bar{V}_{ara} = \left(2.930\ \text{g/mL} \cdot \frac{1\ \text{mol}}{100.09\ \text{g}} \cdot \frac{1000\ \text{mL}}{\text{L}}\right)^{-1}$$

$= 0.0342$ L/mol

$$\Delta G° = -\cancel{RT}\left[\frac{\Delta\bar{V}}{\cancel{RT}}(P-1)\right]$$

Note: $\frac{-\Delta_r G°}{\Delta\bar{V}}$ must be in bar!

$$P = \frac{-\Delta_r G°}{\Delta\bar{V}} + 1$$

$$= \frac{-1040\ \text{J}/\cancel{\text{mol}}}{0.0342 - 0.0369\ \text{L}/\cancel{\text{mol}}} \cdot \frac{0.08314\ \text{L bar}/\cancel{\text{mol K}}}{8.3145\ \text{J}/\cancel{\text{mol K}}} + 1$$

$= 3853$ bar

26-64

See Ex 26-14

Calculate the solubility of $CaF_{2(s)}$ in a solution that is 0.0150 M in $MgSO_{4}(aq)$. $K_{sp} = 3.9 \times 10^{-11}$ for CaF_2.

$$CaF_{2(s)} \rightleftarrows Ca^{2+}_{(aq)} + 2F^{-}_{(aq)}$$

$$K_{sp} = a_{Ca^{2+}} a^{2}_{F^-} = C_{Ca^{2+}} C^{2}_{F^-} \gamma_{\pm}^{3} = 3.9 \times 10^{-11}$$

$$C_{Ca^{2+}} C^{2}_{F^-} = \frac{3.9 \times 10^{-11}}{\gamma_{\pm}^{3}}$$

Step 1: Let $\gamma_{\pm} = 1$ and $\overset{\text{solubility}}{s} = C_{Ca^{2+}}$

$2s = C_{F^-}$

$$s(2s)^2 = 3.9 \times 10^{-11}/1$$

$$4s^3 = 3.9 \times 10^{-11}$$

$$s = 2.136 \times 10^{-4}\ M$$

Step 2: Ionic strength...

$$I_c = \frac{1}{2}\left(2^2 \cdot s + (-1)^2 \cdot 2s + 2^2 \cdot 0.015 + (-2)^2 \cdot 0.015\right)$$

$$= 0.0606\ M$$

$C_{Ca^{2+}} = s$ $z = 2$

$C_{F^-} = 2s$ $z = -1$

$C_{Mg} = 0.015$ $z = 2$

$C_{SO_4} = 0.015$ $z = -2$

Step 3: use Extended Debye Huckel for $\ln \gamma_{\pm}$ + $\gamma_{\pm}$

$$\ln \gamma_{\pm} = \frac{-1.173 |z_+ z_-| I_c^{1/2}}{1 + I_c^{1/2}}$$

$z_+ = 2$

$z_- = -1$

$$= -0.463$$

$$\gamma_{\pm} = 0.629$$

Step 4: Repeat Step 1 w/ new $\gamma_{\pm} = 0.629$

$$4s^3 = 3.9 \times 10^{-11} / (0.629)^3$$

$$s = 3.396 \times 10^{-4}\ M$$

Step 5: repeat Step 2 w/ new $S = 3.396 \times 10^{-4}$ M
$I_c = 0.0610$ M

Step 6: repeat Step 3 w/ new I_c ...

$$\ln \gamma_{\pm} = \frac{-1.173\,|2 \cdot -1|\,(0.0610^{1/2})}{1 + (0.0610)^{1/2}} = -0.4647$$

$$\gamma_{\pm} = 0.628$$

Repeat cycle...

Step 7: $S = 3.402 \times 10^{-4}$ M

Step 8: $I_c = 0.0610$ M

Step 9: $\ln \gamma_{\pm} = -0.4647$ $\gamma_{\pm} = 0.628$

Step 10: $S = 3.402 \times 10^{-4}$ M

$\boxed{\text{To two sig figs (to match Kp)} \quad S = 3.4 \times 10^{-4}\ M}$

#2... Based on Le Chatelier's principle

$$2NO_2 \rightleftarrows N_2O_4 \qquad \Delta_r \bar{H}^\circ = -58.04\ \text{kJ/mol}$$

a) B/c rxn is exothermic, ~~add~~ raising temp causes equilibrium to shift from right to left. (Kp decreases)

b) B/c ~~peae~~ mol reactant > mol product, increasing P causes equilibrium from left to right. (No change in Kp)

c) If volume expands, gases are "diluted". Equilibrium shifts from right to left. (Kp is unchanged)

d) ~~pressure with increase~~ A catalyst effects only rate not equilibrium position or K