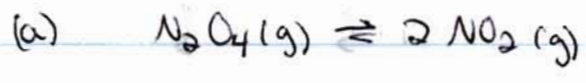


26-9

~~$$K_p(\text{bar}) = \frac{P_V^{v_V}(\text{bar}) P_Z^{v_Z}(\text{bar})}{P_A^{v_A}(\text{bar}) P_B^{v_B}(\text{bar})}$$~~ Skipped

26-10

Find $\Delta_r G^\circ(T)$ and $K_p(T)$ @ 25°C

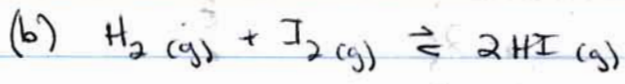


$$\begin{aligned} \Delta_r G^\circ &= 2 \Delta_f G^\circ(\text{NO}_2) - \Delta_f G^\circ(\text{N}_2\text{O}_4) \\ &= 2(51.258) - 97.787 \\ &= 4.729 \text{ kJ/mol} \end{aligned}$$

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

$$= 0.148$$

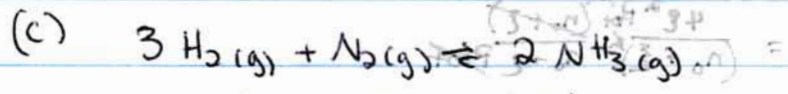
* remember to use similar units for $\Delta_r G^\circ + R \dots$



$$\begin{aligned} \Delta_r G^\circ &= 2 \Delta_f G^\circ(\text{HI}) - \Delta_f G^\circ(\text{I}_2) - \Delta_f G^\circ(\text{H}_2) \\ &= 2(1.560) - 0 - 0 \\ &= 3.120 \text{ kJ/mol} \end{aligned}$$

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

$$= 692$$



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

$$K_p = 5.5 \times 10^5$$

$$K_p = K_c (RT)^{\Delta n}$$

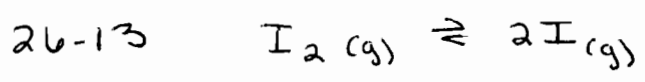
$$K_p = K_c (RT)^{-2}$$

$$K_c = \frac{K_p}{(RT)^{-2}}$$

$$K_c = 1.0 \text{ at } 100^\circ\text{C}$$

- see attached graph/data from Excel

- This follows Le Chatelier's principle as there is more mol gas on the side + increase in strength (more rxn) to go from R to L.



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)

$P_{tot} = 0.04799 \text{ bar}$

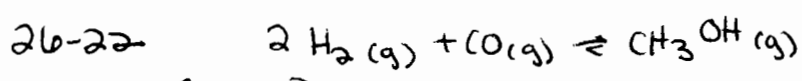
$k_p = \frac{P_I^2}{P_{I_2}} = 2.96 \times 10^{-3}$

$P_{I_2} = 0.03746 \text{ bar}$

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

$k_c = k_p \left(\frac{P^0}{c^0 RT} \right)^{\nu_y + \nu_z - \nu_x - \nu_b}$
 $= k_p \left(\frac{1 \text{ bar}}{1 \text{ M} \cdot RT} \right)^{2-1}$
 $= 2.10 \times 10^{-5}$

$R = 0.08314 \text{ L bar / K mol}$
 $T = 1698 \text{ K}$



$Q = \frac{P_{CH_3OH}}{P_{CO} P_{H_2}^2} = \frac{10.0 \text{ bar / bar}}{(0.0050 \frac{\text{bar}}{\text{bar}})(6.10 \text{ bar / bar})^2} = 2 \times 10^5$

$Q > K_p$ Rxn will proceed to left
 (Also... $\Delta_r G = RT \ln Q/K_p$. $\Delta_r G > 0$ here)

26-25 $\Delta_r H^0 = -12.93 \text{ kJ/mol}$

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

van't Hoff Eq $\ln \frac{k_p(T_2)}{k_p(T_1)} = -\frac{\Delta_r H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

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

$$\ln \frac{29.1}{K_p(700)} = -0.6666$$

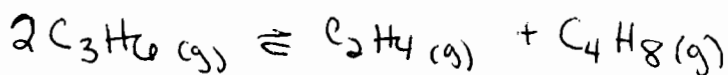
$$\frac{29.1}{K_p(700)} = e^{-0.6666}$$

$$\frac{29.1}{e^{-0.6666}} = K_p(700)$$

$$K_p = 56.6$$

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

26-29



$$\ln K_p(T) = -2.395 - \frac{2505}{T} + \frac{3.477 \times 10^6}{T^2} \quad 300 < T < 600 \text{ K}$$

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

$$\begin{aligned} \Delta_r G^\circ &= -RT \ln K_p(T) = -RT \left(-2.395 - \frac{2505}{T} + \frac{3.477 \times 10^6}{T^2} \right) \\ & \quad T = 525 \text{ K} \\ &= -23.78 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \text{Eq 26.29 } \Delta_r H^\circ &= RT^2 \frac{d \ln K_p(T)}{dT} \\ &= RT^2 \left(\frac{2505}{T^2} - \frac{2(3.477 \times 10^6)}{T^3} \right) \quad @ 525 \text{ K} \\ &= -89.30 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ \\ \Delta_r S^\circ &= -\frac{(\Delta_r G^\circ - \Delta_r H^\circ)}{T} = -124.8 \text{ J/mol}\cdot\text{K} \end{aligned}$$

26-38 Find K_p^{+Kp} @ 700 K for $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$
 (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

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

$\sigma = 2$

$M = 28.02 \text{ g/mol} \cdot \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ g/mol}} = 4.65 \times 10^{-26} \text{ kg}$

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

$\Theta_{vib}^{N_2} = 3374 \text{ K}$

$k_B = 1.38 \times 10^{-23} \text{ J/K}$

$D_e = 953.0 \text{ kJ/mol} = 1.58 \times 10^{-21} \text{ kJ/molecule}$

$g_{el} = 1$

needed to get units to cancel in $e^{D_e/k_B T}$

$$= \left(\frac{2\pi (4.65 \times 10^{-26} \text{ kg}) \cdot 1.38 \times 10^{-23} \text{ J/K} \cdot 700 \text{ K}}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2} \right)^{3/2} \frac{700}{2(2.88)} \frac{e^{-3374/700}}{1 - e^{-3374/700}} \cdot 1 \cdot e^{\frac{1.58 \times 10^{-21}}{1.38 \times 10^{-23} \cdot 700}}$$

$= 5.15 \times 10^{32} \cdot 121.5 \cdot 0.0905 \cdot 1 \cdot 1.08 \times 10^7$
 $= 6.12 \times 10^{40} \text{ m}^{-3}$

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

$\sigma = 2$

$M = 3.36 \times 10^{-27} \text{ kg}$

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

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

$D_e = 457.6 \text{ kJ/mol} = 7.6 \times 10^{-19} \text{ J/molecule}$

$= 1.00 \times 10^{31} \cdot 4.103 \cdot 0.01086 \cdot 1 \cdot 1.473 \times 10^{34}$

$= 6.56 \times 10^{63} \text{ m}^{-3}$

From Eq 18.60

$$\frac{q_{NH_3}}{V} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{rotA} \Theta_{rotB} \Theta_{rotC}} \right)^{1/2} \prod_{j=1}^{3n-6} \frac{e^{-\Theta_{vib,j}/2T}}{1 - e^{-\Theta_{vib,j}/T}}$$

De/k_BT
 \uparrow
 $e^{De/k_B T}$
 \uparrow
 $e^{h\nu/k_B T}$
 \uparrow
 cancels w/ $e^{-\Theta_{vib,j}/T}$

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

$\Theta_{rotB} = \Theta_{rotA} = 13.6 \text{ K}$

$\Theta_{rotC} = 8.92$

$\Theta_{vib1} = 4800 \text{ K} \quad \Theta_{vib2} = 1360 \text{ K} \quad \Theta_{vib3} = \Theta_{vib4} = 4880 \text{ K}$

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

$D_0 = 1158 \text{ kJ/mol} \rightarrow 1.92 \times 10^{-18} \text{ J/molecule}$

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

$M = 2.83 \times 10^{-26} \text{ kg}$

$$= \left(\frac{2\pi (2.83 \times 10^{-26}) (1.38 \times 10^{-23} \cdot 700)}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2} \right)^{3/2} \frac{\pi^{1/2}}{3} \left(\frac{700^3}{(13.6)(8.92)(13.6)} \right)^{1/2} \cdot 1 \cdot e^{+ \frac{1.92 \times 10^{-18}}{1.38 \times 10^{-23} \cdot 700}}$$

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

$$= 2.45 \times 10^{32} \cdot 0.591 \cdot \frac{455.96}{2.08 \times 10^5} \cdot 2.09 \times 10^{86} \cdot 1.001 \cdot 1.167 \cdot 1.007 \cdot \frac{1.076}{0.03856}$$

$$= \frac{1.74 \times 10^{121}}{7.18 \times 10^{114}} \text{ m}^{-3}$$

$$K_c = \frac{(q_{NH_3}/V)^2}{(q_{N_2}/V)^3 (q_{H_2}/V)} = \frac{(1.74 \times 10^{121})^2}{(6.56 \times 10^{63})^3 (6.12 \times 10^{104})} = \frac{1.75 \times 10^{-54}}{2.99 \times 10^{-63}}$$

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

$$= K_c \left(\frac{c^{\circ} R T}{N_A p^{\circ}} \right)^2$$

$c^{\circ} = 1 \text{ molecule/m}^3$
 $p^{\circ} = 1 \text{ bar} = 10^5 \text{ Pa}$

$$\left(\frac{c^{\circ} R T}{N_A p^{\circ}} \right)^2 = \frac{9.34 \times 10^{-51}}{1.07 \times 10^{50}}$$

$K_p = \frac{1.87}{2.23} \times 10^{-4}$ or $\frac{18.7}{2.23} \times 10^5$

\leftarrow larger than experimental b/c of approx.

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

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

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

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

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

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

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

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	0.0509	1.052
90 bar	0.0658	1.068
100 bar	0.0732	1.076

26-61 CaCO_3 (calcite) \rightleftharpoons CaCO_3 (aragonite) $\Delta_r G^\circ = 1.04 \text{ kJ/mol}$
 (298 K)

see Ex 26-13

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

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

$$= 0.369 \text{ L/mol}$$

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

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

$$= 0.342 \text{ L/mol}$$

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

Note: $-\frac{\Delta_r G^\circ}{\Delta T}$ must be in bar!

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

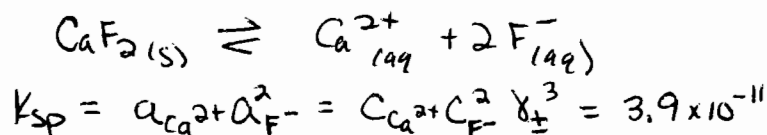
$$= \frac{-1040 \text{ J/mol}}{0.0342 - 0.0369 \text{ L/mol}} \cdot \frac{0.08314 \text{ L bar/mol K}}{8.3145 \text{ J/mol K}} + 1$$

$$= 3853 \text{ bar}$$

26-64

Calculate the solubility of $\text{CaF}_2(s)$ in a solution that is 0.0150 M in $\text{MgSO}_4(aq)$. $K_{sp} = 3.9 \times 10^{-11}$ for CaF_2 .

See Ex 26-14



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

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

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

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

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

Step 2: Ionic strength...

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

$$= 0.0606 \text{ M}$$

$C_{\text{Ca}^{2+}} = s$	$z = 2$
$C_{\text{F}^{-}} = 2s$	$z = -1$
$C_{\text{Mg}} = 0.015$	$z = 2$
$C_{\text{SO}_4} = 0.015$	$z = -2$

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

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

$$= -0.463$$

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

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

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

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

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

Step 6: repeat Step 3 w/ new $I_c \dots$

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

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

Repeat cycle...

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

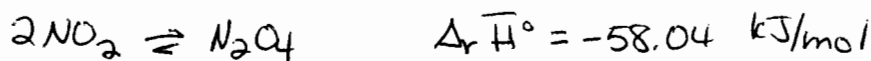
Step 8: $I_c = 0.0610 \text{ M}$

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

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

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

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



- a) B/c rxn is exothermic, ~~add~~ raising δ temp causes equilibrium to shift from right to left. (K_p decreases)
- b) B/c ~~more~~ ^{mol reactant} > mol product, increasing P causes equilibrium from left to right. (No change in K_p)
- c) If volume expands, gases are "diluted". Equilibrium shifts from right to left. (K_p is unchanged)
- d) A catalyst ^{effects} only rate not equilibrium position or ~~pressure~~ ^{with increase}