HETEROGENEOUS EQUILIBRIUM

$$CaCO_{3(s)} \overset{H_2O}{\rightleftharpoons} Ca^{2+}_{(aq)} + CO_{3(aq)}^{2-}$$

$[CaCO_3]$ think "density" ⇒ constant!

$K_c = [Ca^{2+}][CO_3^{2-}]$ same for [pure liquid]

$$CaCO_{3(s)} \overset{\Delta}{\rightleftharpoons} CO_{2(g)} + CaO_{(s)}$$

$K_c = [CO_2]$ $K_p = P_{CO_2}$

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)} \quad T = 25°C$$

a) Put some solid NH_4HS in an empty container. Allow to come to EQ; $P_T = 0.660$ atm, $K_p = ?$

$K_p = P_{NH_3} \cdot P_{H_2S}$ $P_{NH_3} = P_{H_2S} = 0.330$ atm

$K_p = (0.330)(0.330) = 0.109$ at 25°C

b) Some additional H_2S is added; once EQ is re-established, P_{H_2S} is three times greater than the P_{NH_3}. $P_{NH_3} = ?$ $P_{H_2S} = ?$ $P_T = ?$ $(T = 25°C)$

$P_{NH_3} = x$

$P_{H_2S} = 3x$

$K_p = 0.109 = x \cdot 3x = 3x^2$ $x = 0.191$ atm $= P_{NH_3}$

$P_{H_2S} = 0.573$ atm

$P_T = 0.764$ atm

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$$CaCO_{3(s)} \underset{}{\overset{H_2O}{\rightleftharpoons}} Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

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$K_c = [Ca^{2+}][CO_3^{2-}]$ same for [pure liquid]

$$CaCO_{3(s)} \overset{\Delta}{\rightleftharpoons} CO_{2(g)} + CaO_{(s)}$$

$K_c = [CO_2]$ $K_p = P_{CO_2}$

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)} \quad T = 25°C$$

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$P_{H_2S} = 0.573$ atm

$P_T = 0.764$ atm

c) NH_3 and H_2S are both put into an empty 1.00L container (at 25°C) so that initially $P_{NH_3} = 0.75$ atm and $P_{H_2S} = 0.50$ atm.

moles @ EQ? $K_c = ?$ mass of solid @ EQ?

$K_p = 0.109$ $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

$n = \frac{PV}{RT}$

NH_3 : $\frac{(0.75\,atm)(1.00L)}{(0.0821\,\frac{atm \cdot L}{mol \cdot K})(298K)} = 0.031$ mol

H_2S : $\frac{(0.50\,atm)(1.00L)}{(0.0821\,\frac{atm \cdot L}{mol \cdot K})(298K)} = 0.020$ mol

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

$K_c = \frac{K_p}{RT^{\Delta n}}$

$= \frac{0.109}{(0.0821 \cdot 298)^2}$

$K_c = 1.82 \times 10^{-4}$

	NH_4HS	NH_3	H_2S
[initial]	0	0.031	0.020
Δ [ ]	+x	−x	−x
[EQ]	x	0.031 − x	0.020 − x

$K_c = [NH_3][H_2S]$

$1.82 \times 10^{-4} = (0.031 - x)(0.020 - x)$

$1.82 \times 10^{-4} = 0.00062 - 0.051x + x^2$

$x = \sout{0.04}, 0.0109$

$n_{NH_3} = 0.031 - x = 0.0201$ mol

$n_{H_2S} = 0.020 - x = 0.0091$ mol

$n_{NH_4HS} = x = 0.0109$ mol $\xrightarrow{M_m}$ 0.56g NH_4HS

CONNECTION BETWEEN KINETICS & EQ

consider a single step mechanism

$$A + 2B \rightleftharpoons AB_2$$

$$rate_{FWD} = k_{FWD}[A][B]^2$$

$$rate_{REV} = k_{REV}[AB_2]$$

$$k_{FWD}[A][B]^2 = k_{REV}[AB_2]$$

$$K_c = \frac{k_{FWD}}{k_{REV}} = \frac{[AB_2]}{[A][B]^2}$$

MULTIPLE EQ SYSTEM

(1) $H_2SO_{3\,(aq)} \rightleftharpoons H^+_{(aq)} + HSO_3^-{}_{(aq)}$

(2) $HSO_3^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + SO_3^{2-}{}_{(aq)}$

$$K_{c_1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} \qquad K_{c_2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$$

overall $H_2SO_{3\,(aq)} \rightleftharpoons 2H^+_{(aq)} + SO_3^{2-}{}_{(aq)}$

$$K_{c_{overall}} = \frac{[H^+]^2[SO_3^{2-}]}{[H_2SO_3]}$$

$$K_c = K_{c_1} \cdot K_{c_2}$$

* If I double the [ ]'s in a step $\Rightarrow K_{new} = K_{OLD}^2$
triple $K_{new} = K_{OLD}^3$