

### HETEROGENEOUS EQUILIBRIUM

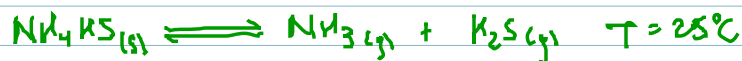


$[\text{CaCO}_3]$  think "density"  $\Rightarrow$  constant!

$$K_c = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \quad \text{same for [pure liquid]}$$



$$K_c = [\text{CO}_2] \quad K_p = P_{\text{CO}_2}$$



a) Put some solid  $\text{NH}_4\text{HS}$  in an empty container  
 Allow to come to EQ;  $P_T = 0.660 \text{ atm}$ ,  $K_p = ?$

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} \quad P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = 0.330 \text{ atm}$$

$$K_p = (0.330)(0.330) = 0.109 \text{ at } 25^\circ\text{C}$$

b) Some additional  $\text{H}_2\text{S}$  is added; once EQ is  
 re-established,  $P_{\text{H}_2\text{S}}$  is three times greater  
 than the  $P_{\text{NH}_3}$  -  $P_{\text{NH}_3} = ?$   $P_{\text{H}_2\text{S}} = ?$   $P_T = ?$  ( $T = 25^\circ\text{C}$ )

$$P_{\text{NH}_3} = x \quad P_{\text{H}_2\text{S}} = 3x$$

$$K_p = 0.109 = x \cdot 3x = 3x^2 \quad x = 0.191 \text{ atm} = P_{\text{NH}_3}$$

$$P_{\text{H}_2\text{S}} = 0.573 \text{ atm}$$

$$P_T = 0.764 \text{ atm}$$

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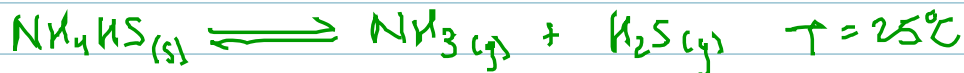
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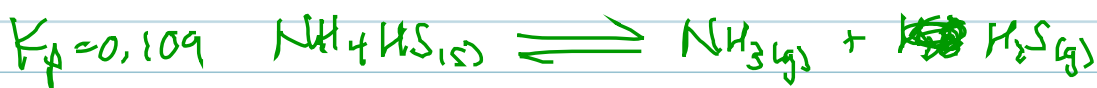
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$$P_{\text{H}_2\text{S}} = 0.573 \text{ atm}$$

$$P_T = 0.764 \text{ atm}$$

c)  $\text{NH}_3$  and  $\text{H}_2\text{S}$  are both put into an empty 1.00L container (at 25°C) so that initially  $P_{\text{NH}_3} = 0.75 \text{ atm}$  and  $P_{\text{H}_2\text{S}} = 0.50 \text{ atm}$ .

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



$$n = \frac{PV}{RT} \quad \text{NH}_3: \frac{(0.75 \text{ atm})(1.00 \text{ L})}{(0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}})(298 \text{ K})} = 0.031 \text{ mol}$$

$$\text{H}_2\text{S}: \frac{(0.50 \text{ atm})(1.00 \text{ L})}{(0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}})(298 \text{ K})} = 0.020 \text{ mol}$$

	$\text{NH}_4\text{HS}$	$\text{NH}_3$	$\text{H}_2\text{S}$
[initial]	0	0.031	0.020
$\Delta [ ]$	+x	-x	-x
[EQ]	x	0.031-x	0.020-x

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

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

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

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

$$K_c = [\text{NH}_3][\text{H}_2\text{S}]$$

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

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

$$x = 0.04, 0.0109$$

$$n_{\text{NH}_3} = 0.031 - x = 0.0201 \text{ mol}$$

$$n_{\text{H}_2\text{S}} = 0.020 - x = 0.0091 \text{ mol}$$

$$n_{\text{NH}_4\text{HS}} = x = 0.0109 \text{ mol} \xrightarrow{M_{\text{NH}_4\text{HS}}} 0.56 \text{ g NH}_4\text{HS}$$

## CONNECTION BETWEEN KINETICS & EQ

Consider a single step mechanism



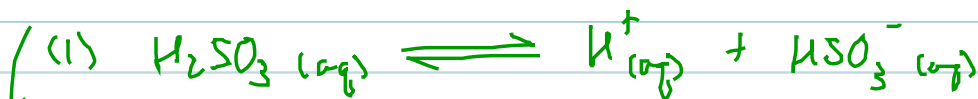
$$\text{rate}_{\text{FWD}} = k_{\text{FWD}} [A][B]^2$$

$$\text{rate}_{\text{REV}} = k_{\text{REV}} [AB_2]$$

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

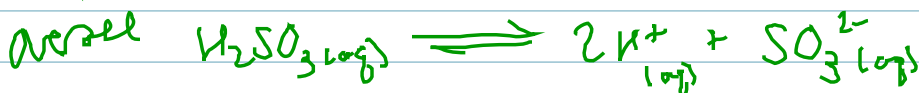
$$K_c = \frac{k_{\text{FWD}}}{k_{\text{REV}}} = \frac{[AB_2]}{[A][B]^2}$$

## MULTIPLE EQ SYSTEM



$$K_{c_1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$$

$$K_{c_2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]}$$



$$K_{c_{\text{overall}}} = \frac{[\text{H}^+]^2 [\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3]}$$

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

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