

Water Example:

Open water bottle  $\rightarrow$  what happens?

evaporates overnight ... but why? Water doesn't boil at room temp!

Reactions are dynamic; that is, they are always happening

- Now think about a closed water bottle

- will this evaporate? Of course not ...

but does this mean that the rxn  $H_2O(l) \rightarrow H_2O(g)$  is not happening? No  $\rightarrow$  reactions are dynamic!

- So why doesn't the water evaporate?

Simple: the reverse reaction is also happening!



The volume of the liquid does not change, nor does the pressure from the gas, But both reactions are still DEFINITELY occurring  $\Rightarrow$  But they are happening @ the same rate.

This is known as Dynamic Equilibrium. The rate of the forward reaction is equal to the rate of the reverse reaction.

Why doesn't Dynamic Eq. occur when the bottle is open? The gas is not confined, so it can float away. (Remember rates are dependent on [reactants])

Let's think about a generic example:



Dynamic  $E_q$  requires the rates to be equal!

$$\frac{\text{rate (for)}}{\text{rate (rev)}} = \frac{k_{\text{for}}[A]^a[B]^b}{k_{\text{rev}}[C]^c[D]^d}$$

group rate constants together

$$\frac{k_{\text{for}}}{k_{\text{rev}}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

this ratio is called the equilibrium constant ( $K$ )

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \Rightarrow \frac{[\text{Prod}]}{[\text{React}]}$$

So  $K$  is the ratio of products to reactants when equilibrium is established

What does it mean when  $K > 1$ ? @  $E_q$   $[\text{Prod}] > [\text{React}]$   
Products are favored

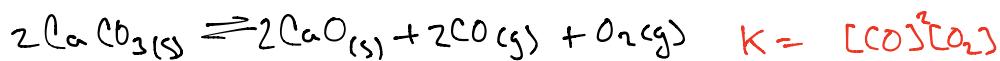
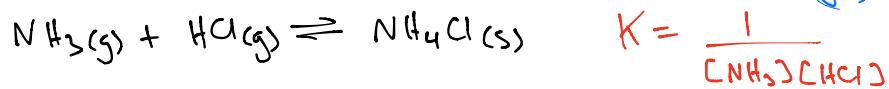
$K < 1 \rightarrow [\text{React}] > [\text{Prod}]$  @  $E_q \rightarrow$  reactants are favored

So the size of  $K$  tells us A LOT about the favorability of a reaction

Important things to note about  $K$ :

① Solids and liquids are NOT included in these expressions

Determine  $K$  for:

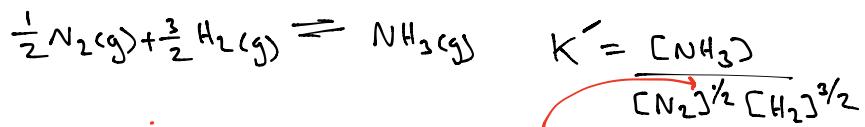
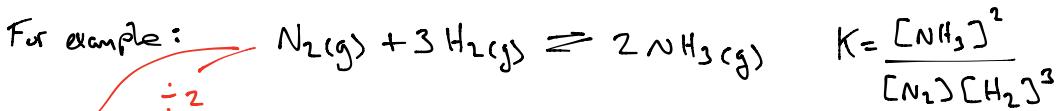




$$K = \frac{[\text{Mg}(\text{NO}_3)_2]}{[\text{MgCl}_2][\text{AgNO}_3]^2}$$

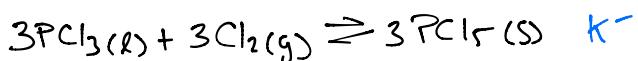
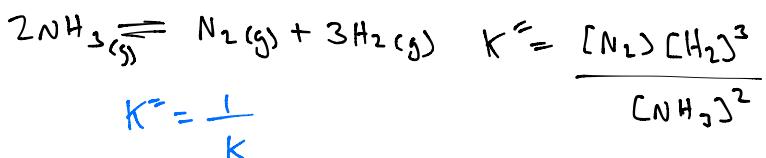
- ② Eq. Constants are temperature dependent. This should make sense because  $K$  is related to  $k$ , which are Temp sensitive (Remember Arrhenius?  $k = A e^{-E_a/RT}$ )

- ③ Equilibrium constants are reaction/stoichiometry specific



reversed  
Since All coefficients are  $\frac{1}{2}$ , all powers are  $\frac{1}{2}$

$$K' = K^{1/2}$$

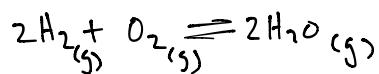


$$K' = K^3$$

④ Gases can be expressed in pressure units OR concentration

$K_p$  = Pressure units

$K_c$  = concentration



$$M = \frac{n}{V} = \frac{P}{RT} \quad P = [ ](RT)$$

$$K_p = \frac{P_{H_2O}^2}{P_{H_2}^2 P_{O_2}^2} = \frac{([H_2O]RT)^2}{([H_2]RT)^2 ([O_2]RT)} = \frac{[H_2O]^2}{[H_2]^2 [O_2]^2} \underbrace{\left(\frac{(RT)^2}{(RT)^3}\right)}_{K_c}$$

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}}$$

$$\Delta n_{\text{gas}} = \text{moles gas prod} - \text{moles gas react}$$

$$\text{in this example, } n_{\text{prod}} = 2(H_2O)$$

$$n_{\text{react}} = 3 (2H_2 + 1O_2)$$

$$K_p = K_c (RT)^{-1} \quad \Delta n_{\text{gas}} = -1$$



calculate  $K_c$

$$\Delta n_{\text{gas}} = 2 - 4 = -2$$

$$K_p = 200 = \frac{K_c}{(RT)^2} = \frac{K_c}{[0.08206(100)]^2} \quad K_c = 13468 \text{ M}^{-2}$$



① At Equilibrium:  $[\text{CH}_3\text{OH}] = 0.2\text{M}$      $[\text{CO}] = 1.8\text{M}$      $[\text{H}_2] = 0.1\text{M}$

Calculate  $K_c$

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{0.2\text{M}}{(1.8\text{M})(0.1\text{M})^2} = 11.1 \text{ M}^{-2}$$

are products or reactants favored?

② Calculate  $K_p$

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}} = 11.1 \text{ M}^{-2} (0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \cdot 100 \text{ K})^{-2}$$

$$K_p = 0.165 \text{ atm}^{-2} \quad \text{are products or reactants favored?}$$

③ Determine  $K_c$  for this reaction:  $3\text{CO(g)} + 6\text{H(g)} \rightleftharpoons 3\text{CH}_3\text{OH(g)}$

$$K_c = K_c^3 = (11.1 \text{ M}^{-2})^3 = 1368 \text{ M}^{-6}$$

④ At Equilibrium:  $[\text{CO}] = 2.00\text{M}$   
 $[\text{H}_2] = 0.50\text{M}$

Determine  $[\text{CH}_3\text{OH}]$

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2 [\text{CO}]}$$

$$11.1 \text{ M}^{-2} = \frac{x}{(0.5\text{M})^2 (2.0\text{M})}$$

$$x = 5.55 \text{ M} = [\text{CH}_3\text{OH}]$$

When a chemical system is not at Eq, it will shift to reach Eq.

So lets say we have our example reaction @ Eq.

What happens if I add more  $\text{CH}_3\text{OH}$ ?

Now we have too many products ... not ok!

The reaction will shift toward reactants (ie the rev rxn will start until eq. is reestablished)

Le Chatelier's Principle: Applying stress to a system will cause that system to adjust



$$[\text{CO}] = 1 \text{ M}$$

$$[\text{H}_2] = 1 \text{ M}$$

$$[\text{CH}_3\text{OH}] = 1 \text{ M}$$

Is this reaction @ Eq?

If not, will it shift to reactants or products?

Calculate  $Q$  exactly the same way as  $K$

reaction quotient

$$Q = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2[\text{CO}]} = \frac{1 \text{ M}}{(1 \text{ M})^2(1 \text{ M})} = 1 \text{ M}^{-2}$$

$$Q < K$$

$$\frac{[\text{Prod}]}{[\text{React}]} \quad \text{So now we have too}$$

many reactants (denominator is too big)

$$K > Q$$

follow the arrow!