Water Example:

open water bottle → what happens?

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

Reactions are dynamic; that is, they are always happen

- 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 → reactions are dynamic!

- So why doesn't the water evaporate?

  simple: the reverse reaction is also happening!

$$H_2O\,(g) \rightarrow H_2O\,(l)$$

The volume of the liquid does not change, nor does the pressure from the gas, But both reactions are still DEFINITELY occuring

↳ 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:

$$aA + bB \rightarrow cC + dD \qquad \text{rate (for)} = k_{for}[A]^a[B]^b$$
$$\text{rate (rev)} = k_{rev}[C]^c[D]^d$$

Dynamic Eq. requires the rates to be equal!

rate (for) = rate (rev)

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

group rate constants together $\boxed{\dfrac{k_{for}}{k_{rev}}} = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

this ratio is called the equilibrium constant (K)

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

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

What does it mean when $K > 1$? @ Eq [Prod] > [React]

products are favored

$K < 1 \rightarrow$ [React] > [Prod] @ Eq. $\rightarrow$ 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:

$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ $K = [H_2O]_{(gas)}$

$NH_{3(g)} + HCl_{(g)} \rightleftharpoons NH_4Cl_{(s)}$ $K = \dfrac{1}{[NH_3][HCl]}$

$2P_{(s)} + 5Cl_{2(g)} \rightleftharpoons 2PCl_{5(s)}$ $K = \dfrac{1}{[Cl_2]^5}$

$2CaCO_{3(s)} \rightleftharpoons 2CaO_{(s)} + 2CO_{(g)} + O_{2(g)}$ $K = [CO]^2[O_2]$

$$MgCl_{2(g)} + 2\,AgNO_{3(aq)} \rightleftharpoons 2\,AgCl_{(s)} + Mg(NO_3)_{(aq)}$$

$$K = \frac{[Mg(NO_3)_2]}{[MgCl_2][AgNO_3]^2}$$

② Eq. Constants are temperature dependent. this should make sense because K is related to k, which are Temp sensitive (remember Arrhenius? $k = Ae^{-Ea/RT}$)

③ Equilibrium constants are reaction/stoichiometry specific

For example: $N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$ $\quad K = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$\div 2$

$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$ $\quad K' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$

reversed

Since All coefficients are $\div 2$, all powers are $\div 2$

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

$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$ $\quad K'' = \frac{[N_2][H_2]^3}{[NH_3]^2}$

$K'' = \frac{1}{K}$

$PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$ $\quad K$

$3PCl_{3(l)} + 3Cl_{2(g)} \rightleftharpoons 3PCl_{5}(s)$ $\quad K'$

$K' = K^3$

④ Gases can be expressed in pressure units OR concentration

K_p = pressure units $\qquad$ K_c = concentration

$$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)} \qquad M = \frac{n}{V} = \frac{P}{RT} \qquad P = [\ ](RT)$$

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

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

Δn_{gas} = moles gas prod − moles gas react

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

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

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

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad K_p = 200\ atm^{-2} \ @\ 100K$$

Calculate K_c

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

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

Consider the following: $CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$

(1) At Equilibrium: $[CH_3OH] = 0.2\,M$ $[CO] = 1.8\,M$ $[H_2] = 0.1\,M$

Calculate Kc

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.2\,M}{(1.8\,M)(0.1\,M)^2} = 11.1\ M^{-2}$$

are products or reactants favored?

(2) Calculate Kp

$1 - 3 = -2$

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

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

(3) Determine Kc for this reaction: $3CO\,(g) + 6H_2\,(g) \rightleftharpoons 3CH_3OH\,(g)$

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

(4) At Equilibrium: $[CO] = 2.00\,M$

$[H_2] = 0.50\,M$

Determine $[CH_3OH]$

$$K_c = \frac{[CH_3OH]}{[H_2]^2[CO]} \qquad 11.1\,M^{-2} = \frac{x}{(0.5\,M)^2(2.0\,M)}$$

$x = 5.55\ M = [CH_3OH]$

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 CH_3OH?

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

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

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

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$

$[CO] = 1\,M$

$[H_2] = 1\,M$

$[CH_3OH] = 1\,M$

Is this reaction @ Eq?

If not, will it shift to reactants or products?

Calculate Q exactly the same way as K

reaction quotient

$$Q = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{1\,M}{(1M)^2(1M)} = 1\,M^{-2}$$

$Q < K$ $\qquad \frac{[Prod]}{[React]}$

So now we have too many reactants (denominator is too big)

$K \xrightarrow{} Q$ ($K > Q$) follow the arrow!