

### Clarifying rate vs. rate constant

\*Entire rate law – must figure out  $k$  as well as exponents

### You can compare graphs to determine the correct form of the rate law

if  $[\text{H}_2\text{O}_2]$  vs.  $t$  is a straight line = zero order

if  $\ln([\text{H}_2\text{O}_2])$  vs.  $t$  is a straight line = first order

if  $1/[\text{H}_2\text{O}_2]$  vs.  $t$  is a straight line = second order

(only one of these can be a straight line, or maybe none of them if it's none of these orders)

\*Rate is first order in  $[\text{H}_2\text{O}_2]$  because the  $\ln([\text{H}_2\text{O}_2])$  vs.  $t$  graph is linear

\*Slope of linear graph =  $k$

### Key points so far on Equilibrium

\* $Q$  and  $K$  have common form (equation) and no units

\*At this point in learning chemistry we can think about the reaction progress ( $x$ -axis) as time

\*Lowest entropy = whichever state is most ordered

\*Highest entropy = whichever state is most disordered

\*Reaction will take place in most disordered state

\* $K$  depends on temperature, but is independent of time

Most ordered  $\longrightarrow$  Most disordered  
Solid                      Liquid                      Aqueous                      Gas

### Which chemicals are part of the expression of $Q$ ?

\*Reaction only takes place in highest entropy phase

\*Not all chemicals in highest entropy phase will react (for example, spectator ions don't react)

#3 – All (aq) chemicals will react because aqueous is the most disordered (has highest entropy).  
Spectator ions do not participate.

\*\*You should be able to write expression for  $K$

### Concentration (moles per unit volume) of a pure solid or liquid has a constant value

\*How much  $[\text{H}_2\text{O}]$  changes is negligible compared to  $[\text{H}^+]$  and  $[\text{OH}^-]$

### Converting between $K_c$ and $K_p$

\*Can relate to  $K_c$  and  $K_p$  to  $RT^x$

### $K_c$ or $K_p$ : Different equilibrium constants?

\*Figure out if it's being given to you in concentration or partial pressure

\*You can figure out concentration and convert to partial pressure

\*Inert (non-reactive) gas = does not affect partial pressures or concentrations of chemicals involved in the equilibrium, because:

- partial pressure is related to how many particles of a given chemical are crashing into the sides of the container, and if there is an inert gas present the total pressure will go up but the partial pressure of the other chemicals will stay the same
- concentration is moles of a chemical divided by total volume, so if there's an inert gas present in a container of a fixed volume, neither the moles of the chemical of interest nor the size of the container changes, so the concentration of the chemical doesn't change either

### Values of $K_{eq}$ have been measured for many reactions

\*If K is big, it means Numerator weighs a lot and Denominator is small

\*If K is small, it means Numerator is small and Denominator is big

$$K_a = \frac{[H_3O^+][H_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

This equilibrium constant is small. It means  $CH_3COOH$  (acetic acid) does not dissociate very much, and mostly remains as complete molecules in a vinegar solution.

$$K_{sp} = [Pb^{2+}][Br^-]^2 = 6.6 \times 10^{-6}$$

Don't get much  $Pb^{2+}$  or  $Br^-$  but these things are relative, and this is actually a pretty large value for a  $K_{sp}$

### ICE tables make it easy to keep track of the stoichiometry

\*Will show partial pressures or concentration change when equilibrium is reached

### A simple example of using ICE

#### Vocabulary

- \*Vessel = container
- \*Charged = started off initially
- \*Sealed = nothing escapes and nothing enters
- \*Decomposing = breaking apart

\*In equilibrium equation you cannot assume that initially only reactants are present, you have to look at what the problem says is the starting condition

\*Initial reactant in this example is only  $SO_3$

- "Initially, the vessel is charged at 1000 K with  $SO_3$  at a partial pressure of .500 atm."

\*All 3 chemicals are in gas phase, so all three will be in equilibrium constant

\*atm indicates that we are working with partial pressure

$$P_{SO_2} = 2x = 0.300 \text{ atm}$$

$$P_{O_2} = x = 0.150 \text{ atm}$$

$$K_p = \frac{(P_{SO_2})^2 (P_{O_2})}{(P_{SO_3})^2} = \frac{(.300)^2 (.150)}{.200^2} = .338$$

\*\*  $K_p$  has no units

**If you now use the value of  $K_c$  and the initial conditions you can figure out the final concentrations – Use an ICE table**

\*Sign of change on reactant side must be opposite the signs on product side

\*All chemicals are in gas phase so all chemicals will appear in the expression of equilibrium

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 33$$

$$33 = \frac{(2x)^2}{(.006 - x)(.006 - x)}$$

$$33 = \frac{(2x)^2}{(.006 - x)^2}$$

$$\sqrt{33} = \frac{\sqrt{(2x)^2}}{\sqrt{(.006 - x)^2}}$$

$$5.745 = \frac{2x}{.006 - x}$$

$$0.00445 = x$$

At Equilibrium

$$[\text{HI}] = 2x = .0089 \text{ M}$$

$$[\text{H}_2] = .00600 - x = .00155 \text{ M}$$

$$[\text{I}_2] = .00600 - x = .00155 \text{ M}$$

\*Keep more sig figs than you think you need, and reduce to correct sig figs when you get to the end of the problem. That way you won't lose sig figs while in the middle of the calculations.