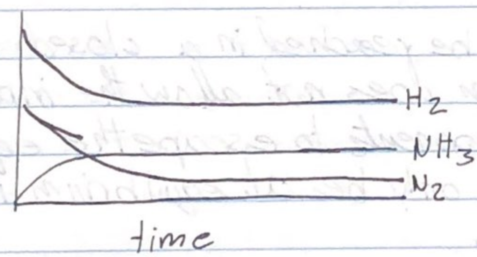
Recognizing Equilibrium

* Equilibrium occurs when opposing changes are occuring simultaneously at the same rate

Reversible Reaction:
- a reversible reaction is a chemical reaction that proceeds in both forward and reverse ~~reactions~~ directions
- in the forward ~~rea~~direction, the reactants form products
- in the reverse direction, the products decompose to re-form the reactants

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$



* at equilibrium, the concentrations of the reactants & the products are constant, and the rate of the fwd. reaction equals the rate of the rev. reaction

Two Chemical Processes That Reach Equilibrium:
1. A reaction with reactants and products in the same phase
   - Ex: gas reacts with gas to form gaseous product
   - the equilibrium they reach is called homogenous equilibrium
2. A reaction in which the reactants and products r in diff. state ~~space~~
   - Ex: aqueous solution of ions, in which ions combine to produce a slightly soluble solid that forms a precipitate
   - the equillibrium they reach is called heterogenous equilibrium

The 4 Conditions That Apply To All Equilibrium Systems:

1. Equilibrium is achieved in a reversible process when the rates of opposing changes are equal. A double arrow $\rightleftharpoons$ indicates reversible changes

$$H_2O_{(g)} \rightleftharpoons H_2O_{(l)}$$

2. The observable macroscopic properties of a system at equilibrium is constant
   - at equilibrium, there is no overall in the properties that depend on the total quantity of matter in the system
   - Ex: pH, color, concentration

3. Equilibrium can only be reached in a closed system
   - a closed system does not allow the input, energy, or any other components to escape the equilibrium
   - a system can only be at equilibrium if its at constant temp.

4. Equilibrium can be approached from either direction

Equilibrium Constant

The Equilibrium Constant:
- chemists use both thermodynamics and rate to study chemical reactions
- thermodynamics determines whether a reaction will occur at a certain temperature and when equilibrium will be reached
- the rate of a reaction determines the time it takes for a certain concentration of product to form

Reaction Dynamics:
- when a reaction starts, the reactants are consumed and products are made
  - the ~~[prod]~~ [reactant] decreases and [products] increases
    - as [reactant] decreases, the forward reaction rate decreases
- eventually, the products can react to re-form some of the reactants, assuming the products are not allowed to escape
  - as [prod] increases, the reverse reaction rate increases

Dynamic Equilibrium: the condition wherein the rates of the forward and reverse reactions are equal

Ex: $H_2 + I_2 \longrightarrow 2HI$

① $[H_2] = 8$; $[I_2] = 8$; $[HI] = 0$ — *At time 0, there are only reactants in the mixture, so only fwd. reaction can occur

② $[H_2] = 6$; $[I_2] = 6$; $[HI] = 4$ — * At time 16, there are both prod. & reactants in mixture so both fwd. & rev. reaction can occur

③ $[H_2] = 4$; $[I_2] = 4$; $[HI] = 8$ — * more products than reactants in the mixture, the fwd. reaction has slowed down as the reactants run-out, and the reverse reaction accelerated

Equilibrium ≠ Equal:
- the rates of the fwd. & rev. reaction are equal at equilibrium
- but that does not mean the concentrations of r. & P are equal
- some reactions reach equilibrium only after almost all the reactant molecules are consumed; we say the position of the equilibrium favors the products
- other reactions reach equilibrium when only a small % of the reactant molecules are consumed; we say the position of the equilibrium favors the reactants

Equilibrium Constant:

* Law of Chemical Equilibrium or Law of Mass Action:
  - In a chemical system at equilibrium, there is a constant ratio between the concentrations of the products and the concentrations of the reactants

- For the general ~~eq~~ equation of $aA + bB \rightleftarrows cC + dD$, the Law of Mass Action gives the relationship
  - lowercase letters represent coefficient of balanced chemical equation
  - always products over reactants

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

*NO UNITS

$K_{eq} \approx 1 \rightarrow$ approximately equal product and reactant formation

$K_{eq} > 1 \rightarrow$ product favored formation

$K_{eq} < 1 \rightarrow$ reactant favored formation

IV Homogenous and Heterogenous Equilibria:

Homogenous Equilibria:

- $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$
- $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 3H_{2(g)}$

Heterogenous Equilibria:

- $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
- $HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$

Ex (Homo): $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $K_{eq} = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

Ex (Hetro): $C_2H_5OH_{(l)} \rightleftharpoons C_2H_5OH_{(g)}$ $K_{eq} = [C_2H_5OH]$

Le Chatelier's Principle

Le Chatier's Principle: (LCP)
- a dynamic equilibrium tends to respond to relieve the effect of any change in the conditions that affect equilibrium
- LCP also predicts what will happen when other changes are made to an equilibrium
- if an external stress is applied to a chemical system at equilibrium, the rates of the fwd and rev reactions are temporarily unequal because stress affects reaction rates
- however, equilibrium is eventually restored

Changes in Equilibrium: (concentration)

$$aA + bB \rightleftarrows cC + dD$$

Change	Shifts Equilibrium
inc. conc. of prod.	left
dec. conc. of prod.	right
inc. conc. of rea.	right
dec. ~~react~~ conc. of react.	left

The Effect of Adding a Gas
- adding a gaseous reactant increases its partial pressure, causing the equilibrium to shift to the right
  - increasing its partial pressure increases its concentration
  - it does not increase the partial pressure of other gases in mixture
- adding an inert gas to the mixture has no effect on the position of eq.

Changes in Volume and Pressure : $\underbrace{A_{(g)} + B_{(g)}}_{2\ \text{molecule}} \rightleftarrows \underbrace{C_{(g)}}_{1\ \text{molecule}}$

change	shifts equilibrium
inc. pressure	fewest moles of gas
dec. pressure	most moles of gas
inc. volume	most moles of gas
dec. volume	fewest moles of gas

$P \propto \frac{1}{V}$

Effect of Volume Change on Equilibrium:
- decreasing volume of container increases concentration of all the gases in the container
    - increase their partial pressure
    - does not change concentration of solution
- if their partial pressure increases, then total pressure in container will inc.
- according LCP, the equilibrium should shift to remove that pressure
    - reduces the number of gas molecules in container

Effect of Temp. Change:
- writing heat as a product or reactant helps us use LCP to predict the effect of temp. change, even though heat is not matter and not written in a proper equation

exo → heat is a product

- increasing temperature is like adding heat
- according to LCP, the equilibrium will shift away from the added heat

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + heat$$

← remove heat

reaction shifts right, larger K

- adding heat will decrease conc. of products and increase [reactants]
    - will reduce value of 'K'

endo → heat is a reactant

- increasing temp. is like adding heat
- according to LCP, the equilibrium will shift away from added heat

← add heat

$$N_2O_4 + heat \rightleftharpoons 2NO_2$$

reaction shifts right, larger value of K

- adding heat will decrease [reactants] and increase [Products]
    - increase value of 'K'

The Effect of Catalyst's:

- catalysts provide an alternative, more efficient mechanism
- catalysts work for both forward and reverse reactions
- catalysts affect the rate of the forward and reverse reaction by the same factor

∴ catalysts do not affect the position of equilibrium