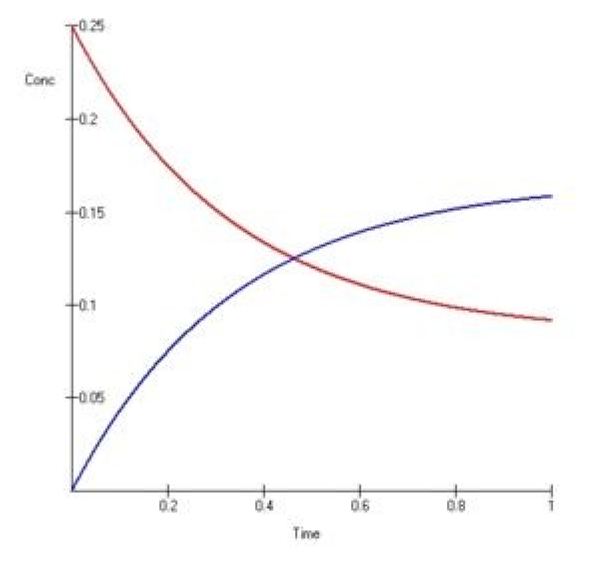
Chemical Equilibrium

Chapter 13

Chemical Equilibrium

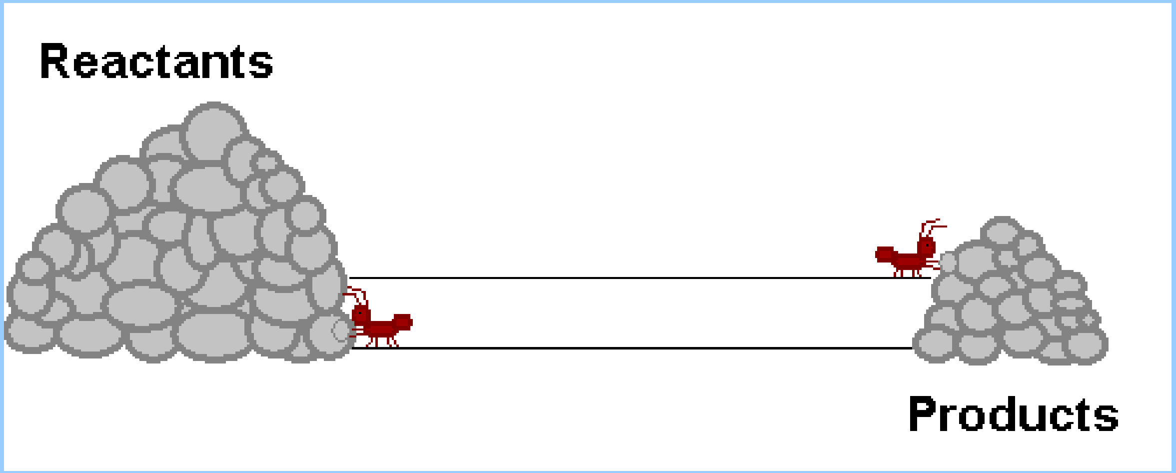
- When neither the products nor the reactant concentrations change any more with time.



Chemical Equilibrium

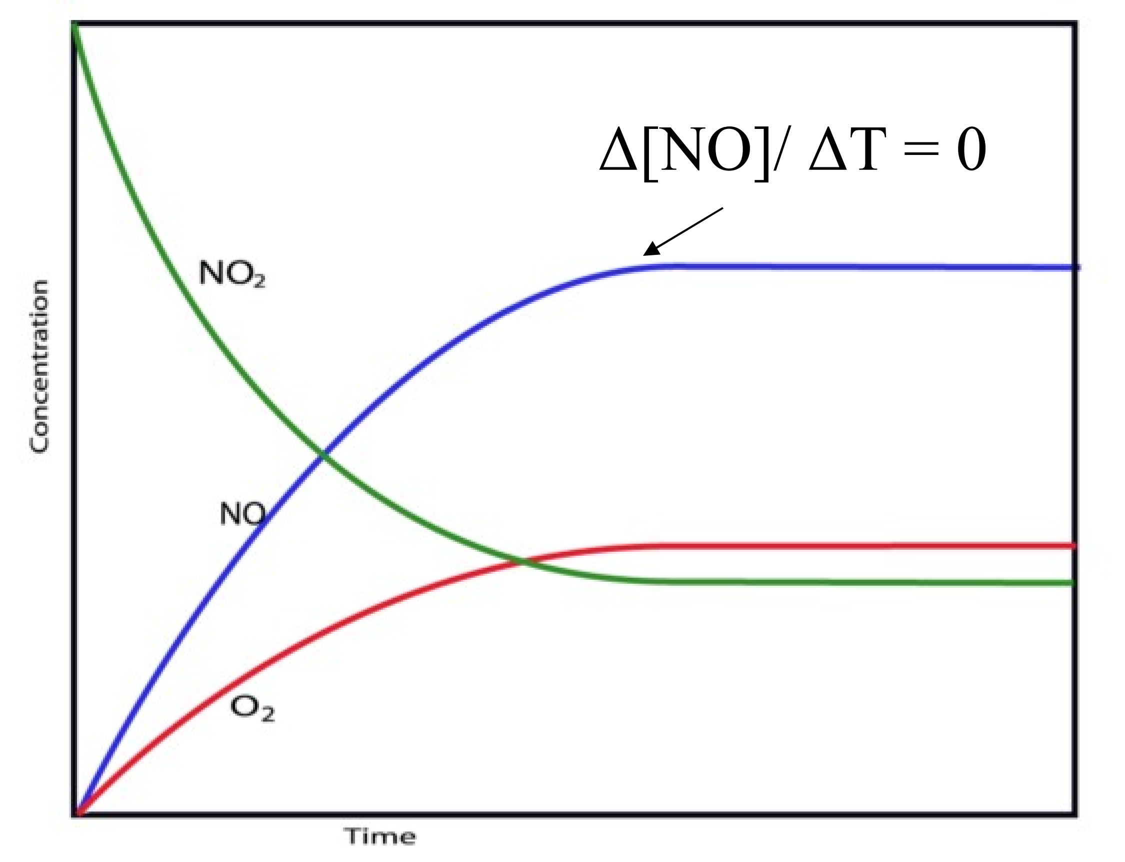
- When the forward rate of reaction is equal to the reverse rate of reaction.
- Chemical reactions at eqm are reversible.
- Open systems can never be reversed so cannot really reach eqm

Chemical Equilibrium



- Equilibrium does not mean that the reactants and products are the same.
- If each ant picks up a stone, neither pile will change in size. That’s equilibrium.

$2NO_2 \longleftrightarrow 2NO + O2$



$\Delta[NO]/ \Delta T = 0$

All chemical in a given rxn reach eqm at same point of time.

Law of mass action

- Given $xA+yB \longleftrightarrow wC + zD$
- Then $K_{eq} = \dfrac{[C]^w[D]^z}{[A]^x[B]^y}$
- This is a ratio of products over reactants
- Coefficients of the balanced chemical eqn become exponents.

Keq expression

- Ratios > 1 favor products
- Ratios < 1 favor reactants
- Keq (K) is unitless.
- Exclude pure solids and pure liquids
- ? What is their concentration anyhow?
- Limit solvent $\longrightarrow$ 0?

Writing an Eqm expression

- Start with a balanced chemical equation
- $NO_2 \longleftrightarrow NO + O_2$

Writing an Eqm expression

- Start with a balanced chemical equation
- $2NO_2 \longleftrightarrow 2NO + O_2$
- Products over reactants
- coefficients as powers
- square brackets (moles/liter)

Writing an Eqm expression

- Start with a balanced chemical equation
- $2NO_2 \longleftrightarrow 2NO + O_2$
- $$Keq = \frac{[NO]^2[O_2]}{[NO_2]^2}$$
- Always write the Keq expression w/o numbers to check to see if it makes sense

Reversing the reaction

- Products and reactants are defined as the chemical equation is written so…
- If you reverse the reaction, inverse the Keq.
- $Keq = \frac{1}{Keq'}$

Multiplying the reaction

- If you multiply a reaction by a coefficient. The new Keq is the old one raised to that power.
- Example:
- $NO_2 \longleftrightarrow NO + 1/2\ O_2$
- K’ (new) = $K^{1/2}$

Kp: Equilibrium Constant for Gases

- Recall ideal gas Law:
- $PV=nRT$ so
- If V and T are constant (one vessel one Temp) then…
- $n = P(V/RT)$ or n is directly proportional to P.
- So

Kp: Equilibrium Constant for Gases

- For a gas phase reaction like $3H_2 + N_2 \longleftrightarrow 2NH_3$ then Kp can be defined as:
- $$\frac{(P_{NH3})^2}{(P_{H2})^3\ (P_{N2})}$$
- P's are the partial pressures of each of the species at equilibrium

Kp: Equilibrium Constant for Gases

- K or Keq can be related to Kp
- $Kp = K(RT)^{\Delta n}$
- Δn is the total difference between numbers of moles of gas going from left to right in the equation as written.

Heterogeneous Equilibrium

- If more than one phase of matter is present in a reaction be aware that equilibrium does not depend on the amount of solid, or pure liquid present.
- These are excluded from the Keq expression.
- They have undefined concentrations

Heterogeneous Eqm

- Example:
- Write the balanced equation and Keq expression for the decomposition of sold phosphorous pentachloride to phosphorous trichloride liquid and chlorine gas

Heterogeneous Eqm

- Example:
- $PCl_5(s) \longleftrightarrow PCl_3(l) + Cl_2(g)$
- $Keq = \frac{[\text{products}]}{[\text{reactants}]}$
- $Keq = \frac{\cancel{[\text{PCl3}]}\ [\text{Cl2}]}{\cancel{[\text{PCl5}]}}$

Pure liquids and
solids are omitted

Heterogeneous Eqm

- Keq = $[Cl_2]$
- and Kp = P_{Cl2}

Determining Q reaction quotient

- How do you know if a system is at equilibrium.
- Calculate Q
- If Q is not = Keq then system is not at eqm yet.
- Q is a Keq expression with concentrations at some time in the reaction, but maybe not at Eqm.

Reaction Quotient Q

- For a given reaction $xA+yB \longleftrightarrow wC + zD$
- Then $Q = \dfrac{[C]^w[D]^z}{[A]^x[B]^y}$
- If Q = K (published or previously calculated) the the system is at Eqm.
- If Q > K the system will shift back to the left. [Reactants] will increase.
- If Q< K the system will continue to the right. [Products] will increase.

Solving problems: ICE method

- Water vapor will react with carbon monoxide to liberate hydrogen and produce carbon dioxide. At a certain temperature the Keq = 2.00 for this reaction. If 8 moles of H_2O and 6 moles CO_2 are placed in a one liter container, what will the final concentration of all species be?

Solving problems: ICE method

- 1: Balanced chemical equation
- $H_2O + CO \longleftrightarrow H_2 + CO_2$
- 2: Write Keq expression w/o numbers
- [H2][CO2]
- [H2O][CO]
- 3: Calculate molarity as needed (moles/L)

Solving problems: ICE method

- 4: Create ICE table

	H2O	CO	H2	CO2
Initial	8 M	6M	0	0
Change	8-x	6-x	x	x
Eqm				

Solving problems: ICE method

- 4: Create ICE table
- 5: Substitute C expressions into Keq
- 2.00 = $\dfrac{(x)(x)}{(8.00-x)(6.00-x)}$
- Solve for x
- x = 4.
- 6: Plug x into table and calc E values

Solving problems: ICE method

- 6: Complete ICE table

	H2O	CO	H2	CO2
Initial	8.00 M	6.00 M	0	0
Change	8-4	6-4	4.00	4.00
Eqm	4.00	2.00	4.00	4.00

Cheating with ICE

- If K is small, reactants are favored. Few products will be made. (n x 10^{-3})
- In this case our change expressions such as
- A_0 - x x will be small compared to A.
- So…. $A_0 - x\sim = A$
- We can avoid the quadratic. Otherwise just do it.

Cheating with ICE

- $2NOCl(g) \longleftrightarrow 2NO(g) + Cl_2(g)$ @ 35 ºC Keq = 1.6×10^{-5}
- If 1 mole of NOCl is placed in a 2 L container what is the final concentration of all species

Cheating with ICE

- $2NOCl(g) \longleftrightarrow 2NO(g) + Cl_2(g)$ @ 35 ºC
  Keq = 1.6×10^{-5}

	NOCl	NO	Cl_2
Initial	0.50 M	0	0
Change	0.5-2x	2x	x
Eqm			

Cheating with ICE

- $2NOCl(g) \longleftrightarrow 2NO(g) + Cl_2(g)$ @ 35 ºC
  $K_{eq} = 1.6 \times 10^{-5}$

- $K = \dfrac{[NO]^2[Cl]}{[NOCl]}$
- $K = \dfrac{(2x)^2(x)}{(0.50 - x)^2} = 1.6 \times 10^{-5}$
- $x = 1.0 \times 10^{-2}$ M

Cheating with ICE

- Complete the table

	NOCl	NO	Cl_2
Initial	0.50 M	0	0
Change	0.5-2x	2x	x
Eqm	0.48 M	0.002 M	0.001 M

LeChatelier's Principle

- When a system at equilibrium is placed under stress, the system will respond in such a way to relieve the stress.
- There are 4 ways to stress a system
  - Add heat
  - Change pressure
  - Add reactants
  - Add products

LeChatelier’s Principle

- Translation:
- If you do anything to mess up equilibrium, the system will respond to undo your changes and equilibrium will be re-established.

LeChatelier's Principle

- In a closed container. Ice and water are co-existing (are at equilibrium). You attempt to raise the temperature by exposing to a flame for a short time? What will happen?
- Ice + $\Delta H \rightleftharpoons$ water
- Increasing heat causes more ice to melt and consumes the heat and the temperature returns to 0C

- Think of energy as a product (exothermic reactions) or a reactant (endothermic reactions).