

In case you care

- Exam results-usual high quality effort with two notes:
 - **learn the nomenclature**-a number of people paid a very high price. There is no “almost” in this area.
 - stoichiometry of dissolution
- Final is Tuesday, March 16 5:30-7:10-**that's two weeks from today**
 - expect approximately 1/3 exam 1, 1/3 exam 2 and 1/3 “new” kinetics and equilibrium
- Last homework assignment posted-**it's due Monday Mar 15 by 5pm.**
- The ever popular course % projector is on line and can be reached from the Chem 222 main page. It updates automatically as new data is posted.
- Page for practicing mechanisms is available Page # 124

Equilibrium Basics

- Any process which occurs in both directions necessarily has a point where the opposing rates will become equal. Why?
- From there on, there will be no further change in the macroscopic properties of the system (concentrations, etc), etc, and the system is said to be in a state of equilibrium. Again-it is a special **state of the system**.
- Microscopically, however, the forward and reverse processes continue unabated. How could you prove this?
- Both vapor pressure equilibrium and osmotic equilibrium are examples of this phenomenon. In what ways are these two processes different?

Chemical Equilibrium

- Thus far, the equilibria noted have involved physical, not chemical change.
- If a reaction is realistically chemically reversible-meaning it can occur in either direction(this is different from thermodynamic reversibility), then one can write it either way:
 - $A \Rightarrow B$ or $B \Rightarrow A$
 - the identification of products and reactants is “arbitrary” and lacks the rigidity with which one views reactions in kinetics.
 - what does “realistically chemically reversible mean”?
- $A \rightleftharpoons B$ -the “ \rightleftharpoons ” is used to denote that the reaction may be occurring in either direction. As will be seen, one of the areas of interest in chemical kinetics is the determination of the direction in which a chemical change is actually occurring.
- A system is in chemical equilibrium when the forward and reverse reactions are occurring at the same rates. Thus, despite the continual transformation of compounds into other compounds, there will be no change in the overall composition of the system.
- Again, no macroscopic changes despite constant microscopic changes
- “A reversible chemical reaction is either at equilibrium or moving toward equilibrium..”-why?

The Reaction Quotient

- In chemical equilibrium, stoichiometry and the balanced chemical equation are central. Discussion begins with the reaction quotient, Q_{rxn} or simply Q .
- $aA + bB \rightleftharpoons cC + dD$
- $Q_{\text{rxn}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- Only species with variable concentrations appear in Q_{rxn} . What species don't have variable concentrations?
- Q_{rxn} is a general function, like $y=4x^3$, and can (should) be evaluated for all states of a chemical system, not just the equilibrium state
- What are Q for the following?
- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- $2PbBr_2(g) + 3Cl_2(g) \rightleftharpoons 2PCl_3(g) + 3 Br_2(g)$
- The reaction above if Br_2 is a liquid?
- $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
- $2NH_3(g) + CO_2(g) \rightleftharpoons NH_4OCNH_2(s)$
- $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$
- $Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$
- $Fe_2O_3(s) + SO_3(g) + SO_2(g) \rightleftharpoons 2 FeSO_4(s)$

The Equilibrium Constant

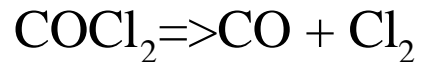
- When the system is at equilibrium, all of the concentrations become constant, so Q_{rxn} must become constant. The value Q_{rxn} at the equilibrium state is called the equilibrium constant, K
- Q s can be either molarities or pressures. If molarities $\Rightarrow K_c$, pressure $\Rightarrow K_p$
- K should have dimensions-is there value in including them?
- Values of constants normally have intrinsic merit. For example, the value of k , the rate constant, tells you about the intrinsic rate of the reaction and the activation energy.
- Does the value of K have the same usefulness? Why or why not?
- What about $K > 1$ or $K < 1$? Does this tell you whether products or reactants are favored at equilibrium?

The Basics

- As you might expect, there are two basic “introductory” calculations in this area
 - Given $[]_{\text{eq}}$ s what is the value of K ?
 - Given K , what are the $[]$ s?
- A critical issue in equilibria is learning to differentiate (and label appropriately) equilibrium and nonequilibrium $[]$ s.
- Typically, equilibrium concentrations are labeled $[]_{\text{eq}}$ and non equilibrium are either unlabeled or $[]_i$

Calculating K

- Given the balanced equation and the equilibrium concentrations shown:



Equilibrium Concentrations:

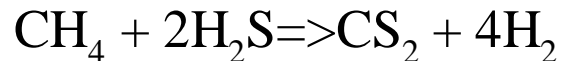
COCl_2 : 0.0699M

CO: 0.340M

Cl_2 : 0.151M

What is the value of K?

- Given the balanced equation and the equilibrium concentrations shown:



Equilibrium Concentrations:

CH_4 : 0.437M

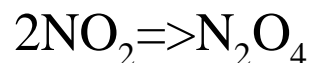
H_2S : 0.122M

CS_2 : 0.0891M

4H_2 : 0.482M

What is the value of K?

- Given the balanced equation and the equilibrium concentrations shown:



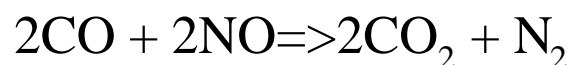
Equilibrium Concentrations:

NO_2 : 0.339M

N_2O_4 : 0.0705M

What is the value of K?

- Given the balanced equation and the equilibrium concentrations shown:



Equilibrium Concentrations:

CO: 0.482M

NO: 0.238M

CO_2 : 0.275M

N_2 : 0.448M

What is the value of K?

Calculating $[]_{eq}$

- Once a value for K is known, it can then be applied to determine the $[]_{eq}$ for other reaction systems. In this area, stoichiometry is king and very careful mathematics is critical to success
- Given the balanced equation, the K value and the partial set of equilibrium concentrations shown:
 $2\text{NOBr} \rightleftharpoons \text{NO} + 2\text{Br}_2$
 $K = 1.61 \times 10^{-1}$
Equilibrium Concentrations:
NO: 0.194M
Br₂: 0.0965M
What is the concentration of NOBr
- Given the balanced equation, the K value and the partial set of equilibrium concentrations shown:
 $2\text{CO} + 2\text{NO} \rightleftharpoons 2\text{CO}_2 + \text{N}_2$
 $K = 1.82 \times 10^1$
Equilibrium Concentrations:
CO: 0.0325M
NO: 0.247M
N₂: 0.113M
What is the concentration of CO₂?