

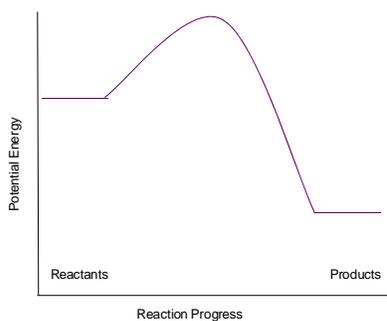
Chemical Equilibrium

Simplifications/assumptions we've been working under:

1. Reactions go to completion ("→")
2. Only the forward reaction is involved
3. Reactions stop when completed

None of these things are strictly true!

What have we learned from kinetics?

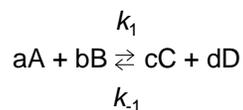


Chemical Equilibrium

Reasonable to write ALL reactions as reversible.

– Requirements?

Generic Equilibrium:



At equilibrium rate forward = rate reverse

$$k_1(\mathcal{A}_A)^a(\mathcal{A}_B)^b = k_{-1}(\mathcal{A}_C)^c(\mathcal{A}_D)^d$$

\mathcal{A}_A = "activity" of compound (or element) A

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Chemical Equilibrium

Moving all the constants to one side

Activity is a measure of effective reactivity... "opportunity to get involved" in the process of interest.

$$A_A = \gamma_A[A] \text{ (for solutions) or } A_A = \gamma_A p_A \text{ (for gases)}$$

In equilibrium considerations, we typically relate (ratio) all conditions to a "reference state", c° (1 M for solutions, 1 atm for gases)

$$K = \frac{\left(\frac{\gamma_C[C]}{c^\circ}\right)^c \left(\frac{\gamma_D[D]}{c^\circ}\right)^d}{\left(\frac{\gamma_A[A]}{c^\circ}\right)^a \left(\frac{\gamma_B[B]}{c^\circ}\right)^b}$$

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Equilibrium Constant Expression

Generic Equilibrium Constant Expressions ("kind of" ... A):

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{[\text{products}]^x}{[\text{reactants}]^y} \quad K_p = \frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b} = \frac{p_{\text{products}}^x}{p_{\text{reactants}}^y}$$

NOTE: K is dimensionless!

IMPORTANT! CRITICAL! ESSENTIAL! CRUCIAL!

1. In order for a system (reaction) to be at equilibrium, the K_{eq} expression MUST be satisfied!!!
2. If the K_{eq} expression is satisfied, the system is in equilibrium!

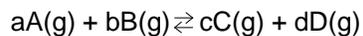
We can use this to predict the extent of a reaction and/or the direction a reaction is likely to proceed.

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Equilibrium Constant Expression

Expressing K_{eq} in various concentrations:

- Gases
Describe K in terms of partial pressures
WHY?



$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

- Solutions
Describe K in terms of molar concentrations (M)
Often noted as K_c

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Linking Kinetics and Thermodynamics

- Relationship between tendencies and activation parameters
 - Thermodynamics and kinetics must cooperate for a reaction to proceed toward products

K	$k_1 ? k_{-1}$	Diagram	ΔG_{rxn}	Tendency
>1				

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Linking Kinetics and Thermodynamics

K	$k_1 ? k_{-1}$	Diagram	ΔG_{rxn}	Tendency
< 1				
$= 1$				

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Golden Rules of Equilibria

- K_{eq} is dimensionless and constant at a given temperature.
- When writing equilibrium constant expressions, omit solids, pure liquids, and solvents.
 - WHY?
- Always use smallest integer coefficients when balancing equations and writing K_{eq} .

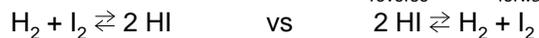


@ Eq.: $[\text{HI}] = 1.58 \text{ M}$, $[\text{H}_2] = 0.212 \text{ M}$, $[\text{I}_2] = 0.212 \text{ M}$, calculate K_c .

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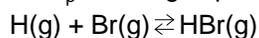
Golden Rules of Equilibria

4. When a balanced reaction is reversed, $K_{\text{reverse}} = 1/K_{\text{forward}}$



5. When adding reactions, K_{eq} for the net reaction is the *product* of the K_{eq} 's for the individual reactions.

Example: Calculate the K_p for the gas phase reaction:



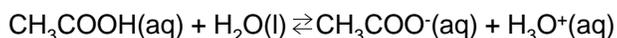
$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g})$	$K_1 = 7.9 \times 10^{11}$
$\text{Br}_2(\text{g}) \rightleftharpoons 2 \text{Br}(\text{g})$	$K_2 = 4.8 \times 10^{-41}$
$\text{H}_2(\text{g}) \rightleftharpoons 2 \text{H}(\text{g})$	$K_3 = 2.2 \times 10^{-15}$

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Golden Rules of Equilibria

6. At equilibrium, the concentrations of reactants and products **MUST** satisfy the equilibrium constant expression!!

Example: Acetic acid is a weak acid that dissociates via the equilibrium shown below. We dissolve 1.00 mole of acetic acid in 1.00 L of water. After allowing the solution to come to equilibrium, the $[\text{H}_3\text{O}^+]$ is measured to be 0.00423 M. If the equilibrium constant for this process is 1.8×10^{-5} , what is the ratio of dissociated to undissociated acid?



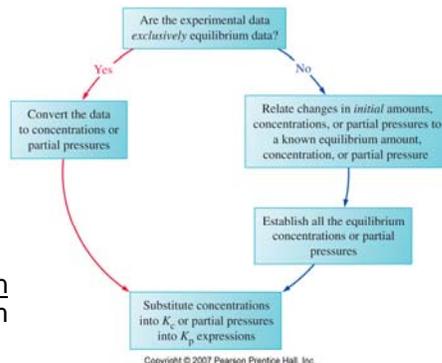
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Using K_{eq} to Predict "Direction" of Reaction

When given a set of conditions (concentrations) ask:

1. Is the system already at equilibrium?
2. If yes, you're done! If no, what does the system need to do to reach equilibrium?

Accomplish (1) by calculating Reaction Quotient (Q): K with nonequilibrium values. Compare Q with K_{eq}



$Q = K_{eq}$	System is in equilibrium
$Q > K_{eq}$	System too product "heavy"
$Q < K_{eq}$	System too reactant "heavy"

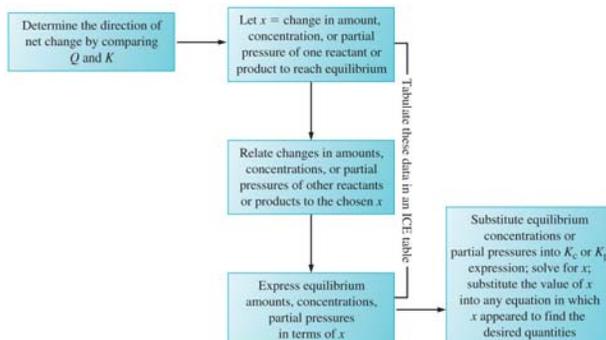
Accomplish (2) by "mapping" the reaction and doing a little math.

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Using K_{eq} to Predict "Direction" of Reaction

Example: $N_2 + O_2 \rightleftharpoons 2 NO$

At 2000K the K_c for the formation of NO is 4.0×10^{-4} . You have a container in which, at 2000 K, the concentration of N_2 is 0.50 M, O_2 is 0.25 M, and NO is 4.2×10^{-3} M. Is the system at equilibrium? If not, which direction must the reaction proceed to approach equilibrium? Calculate the equilibrium concentrations of N_2 , O_2 , and NO.



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Le Chatelier's Principle and Bullying Reactions

Le Chatelier's Principle

Start with system in equilibrium, what happens if we perturb things?

1. Change Concentrations:
2. Change Pressure:
3. Change Temperature: