

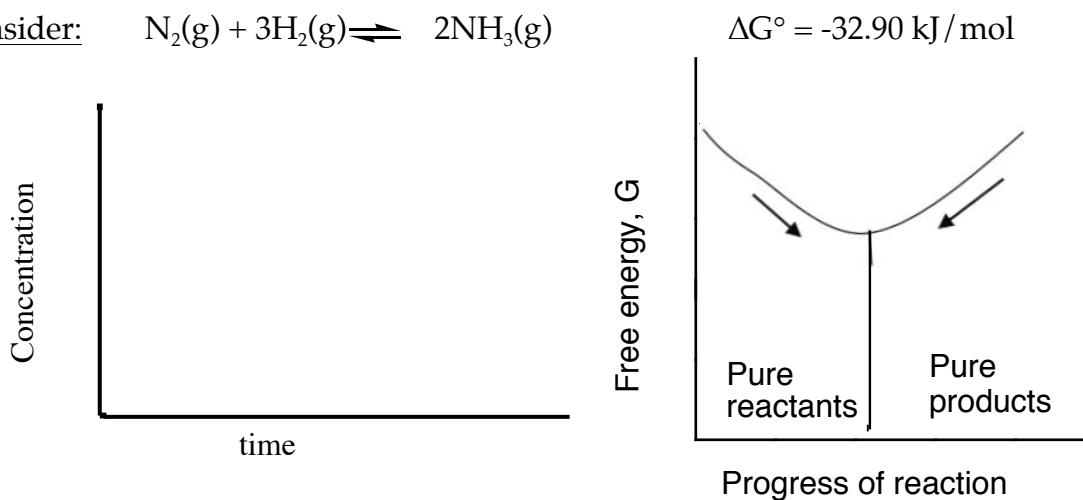
Reading for Today: Sections 10.1-10.5, 10.9 (Sections 9.1-9.4 in 4th ed.)

Reading for Lecture #19: Sections 10.9-10.13 (Section 9.4-9.5 in 4th ed.)

Topics: **Chemical Equilibrium**
 I. Nature of Chemical Equilibrium
 II. Meaning of K
 III. External Effects on K

Chemical reactions reach a state of dynamic *equilibrium* in which the rates of forward and reverse reactions are equal and there is no net change in composition.

Consider: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$



When the reaction mixture has not produced enough products to have reached equilibrium, the spontaneous direction of change is toward more products ($\Delta G_{\text{forward reaction}} < 0$).

When excess products are present (ex. pure ammonia), the reverse reaction is spontaneous ($\Delta G_{\text{forward reaction}} > 0$).

The reaction free energy (ΔG) changes as the proportion of reactants and products _____.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{Where}$$

ΔG = reaction free energy at any definite, fixed composition of the reaction mixture.

ΔG° = is the difference in free energy of the products and reactants in their standard states.

R = universal gas constant, T = Temperature, and Q = reaction quotient

For $aA + bB \rightleftharpoons cC + dD$

<p style="margin: 0;"><u>In gaseous phase</u></p> $\Delta G = \Delta G^\circ + RT \ln \underbrace{\left[\frac{(P_C/P_{\text{ref}})^c (P_D/P_{\text{ref}})^d}{(P_A/P_{\text{ref}})^a (P_B/P_{\text{ref}})^b} \right]}_Q$ <p style="margin: 0;">$P_{\text{ref}} = 1 \text{ bar}$</p> $Q = \frac{P_C^c P_D^d}{P_A^a P_B^b}$	<p style="margin: 0;"><u>in solution</u></p> $\Delta G = \Delta G^\circ + RT \ln \underbrace{\left[\frac{([C]/C_{\text{ref}})^c ([D]/C_{\text{ref}})^d}{([A]/C_{\text{ref}})^a ([B]/C_{\text{ref}})^b} \right]}_Q$ <p style="margin: 0;">$C_{\text{ref}} = 1 \text{ M and } [C] \text{ in M}$</p> $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
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At equilibrium $\Delta G = 0$ and $Q = K$ (the equilibrium constant),

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

K = is the equilibrium constant. It has the same form as _____, but only uses the amounts of products and reactants at equilibrium.

$K_p = \left\{ \frac{P_C^c P_D^d}{P_A^a P_B^b} \right\}_{\text{eq.}}$	$K_c = \left\{ \frac{[C]^c [D]^d}{[A]^a [B]^b} \right\}_{\text{eq.}}$
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We can rewrite $\Delta G = \Delta G^\circ + RT \ln Q$ as

$$\Delta G = -RT \ln K + RT \ln Q \quad \text{or}$$

$$\Delta G = RT \ln (Q/K)$$

Relationship between K and Q:

If $Q < K$, ΔG is _____ and the forward reaction will occur

If $Q > K$, ΔG is _____ and the reverse reaction will occur

Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If $K = 1.9 \times 10^{-4}$ at 400°C , and $P_{N_2} = 5.5 \text{ bar}$ $P_{H_2} = 2.2 \text{ bar}$ $P_{NH_3} = 1.1 \text{ bar}$ at 400°C , which direction will the reaction go?

$Q =$

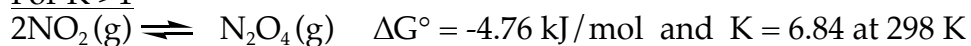
WHAT DOES K TELL US?

K tells us about the mixture of products and reactants at **equilibrium**, whether we can expect **high** or **low** concentration of products at equilibrium.

when $K > 1$, _____ products

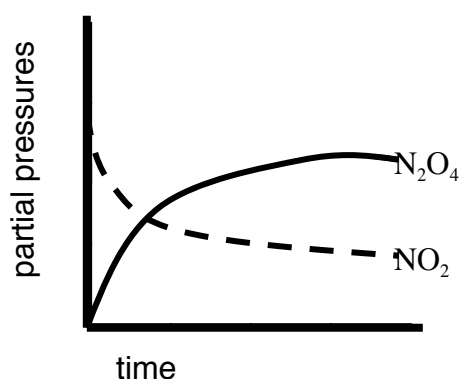
when $K < 1$, _____ products

For $K > 1$



Start with 1.000 bar of NO_2 (reactant) and no N_2O_4 (product)

so $Q < K$ and $\Delta G < 0$, and the reaction goes forward



Calculate the partial pressures of NO_2 and N_2O_4 at equilibrium using the given value of K and the given starting concentration of reactant.

	2NO_2	\rightleftharpoons	N_2O_4
initial partial pressure (bar)	1.000		0
change partial pressure			<u>+X</u>
equilibrium partial pressure			+X

$$K = 6.84 =$$

$$x = \text{_____ bar (_____)}$$

$$1.000 - 2x = 1.000 - 2(\text{_____}) = \text{_____ bar (_____)}$$

For $K > 1$, more products at equilibrium.

Relationship between ΔG° and the magnitude of K:

rewrite $\Delta G^\circ = -RT \ln K$ as

$$K = \exp [-\Delta G^\circ / RT]$$

K is large if ΔG° is ???

Consider the decomposition of baking soda at two different temperatures.



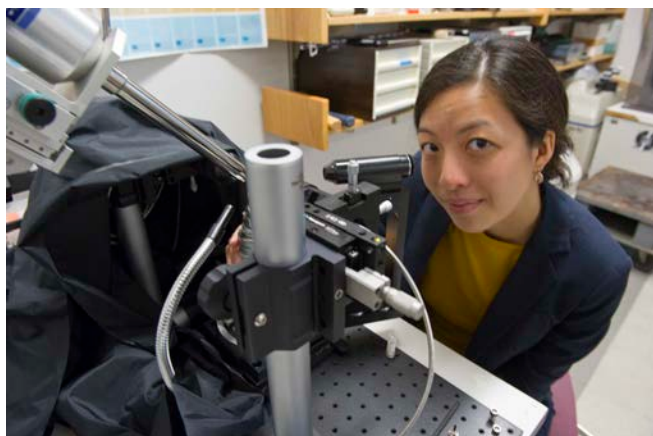
$$\Delta G^\circ = +36 \text{ kJ/mol at room temperature} \quad K = \underline{\hspace{2cm}}$$

$$\Delta G^\circ = -15 \text{ kJ/mol at } 350^\circ\text{F} \quad K = \underline{\hspace{2cm}}$$

At room temperature, very very little CO_2 is produced so bread will not rise.

Chemical equilibrium applies to large molecules (like proteins) too.

Chemical Equilibrium: In Her Own Words



Nozomi Ando discusses how chemical equilibrium relates to her research on understanding proteins that are successful chemotherapeutic targets.

Image from "Behind the Scenes at MIT". The Drennan Education Laboratory.
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Nozomi's video can be found at <http://chemvideos.mit.edu/all-videos/>

EXTERNAL EFFECTS ON K

Principle of Le Châtelier: A system in equilibrium that is subjected to stress will react in a way that tends to _____ the effect of the stress.

Le Châtelier's principle provides a way to predict qualitatively the direction of change of a system under an external perturbation.

ADDING AND REMOVING REAGENTS

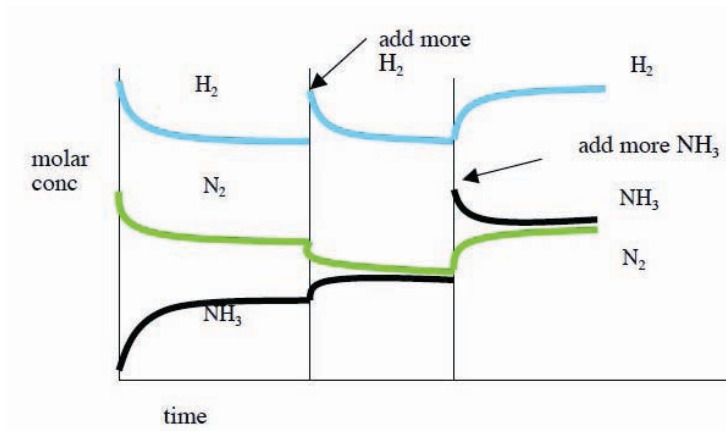
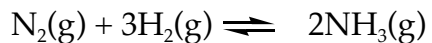


Figure by MIT OpenCourseWare.

1) ADDING MORE REACTANT

If you are at equilibrium and then add more hydrogen, according to Le Châtelier's principle, the system will tend to minimize the increase in the number of hydrogen molecules. Reaction shifts to the right toward _____.

This can be explained in terms of Q and K . When reactants are added, Q falls below K momentarily, because the reactant concentration term appears in the denominator.

$$Q = \frac{[\text{products}]}{[\text{reactants}]} \qquad K = \left\{ \frac{[\text{products}]}{[\text{reactant}]} \right\}_{\text{equilibrium}}$$

With $Q < K$, ΔG is negative, and the system responds by making more products (reaction proceeds in the forward direction).

2) ADDING MORE PRODUCT

Q rises above K . Q is larger because product term is in numerator (K is unchanged). With $Q > K$, ΔG is positive, and the reaction goes toward reactants (reaction proceeds in the reverse direction).

3) REMOVING PRODUCT

Q _____ K and ΔG is _____, so the reaction shifts to _____.

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5.111 Principles of Chemical Science
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