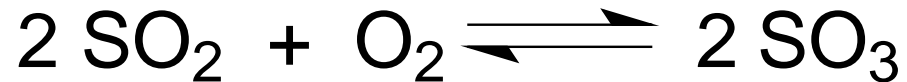


# Equilibrium

Most reactions are reversible and do not go to completion

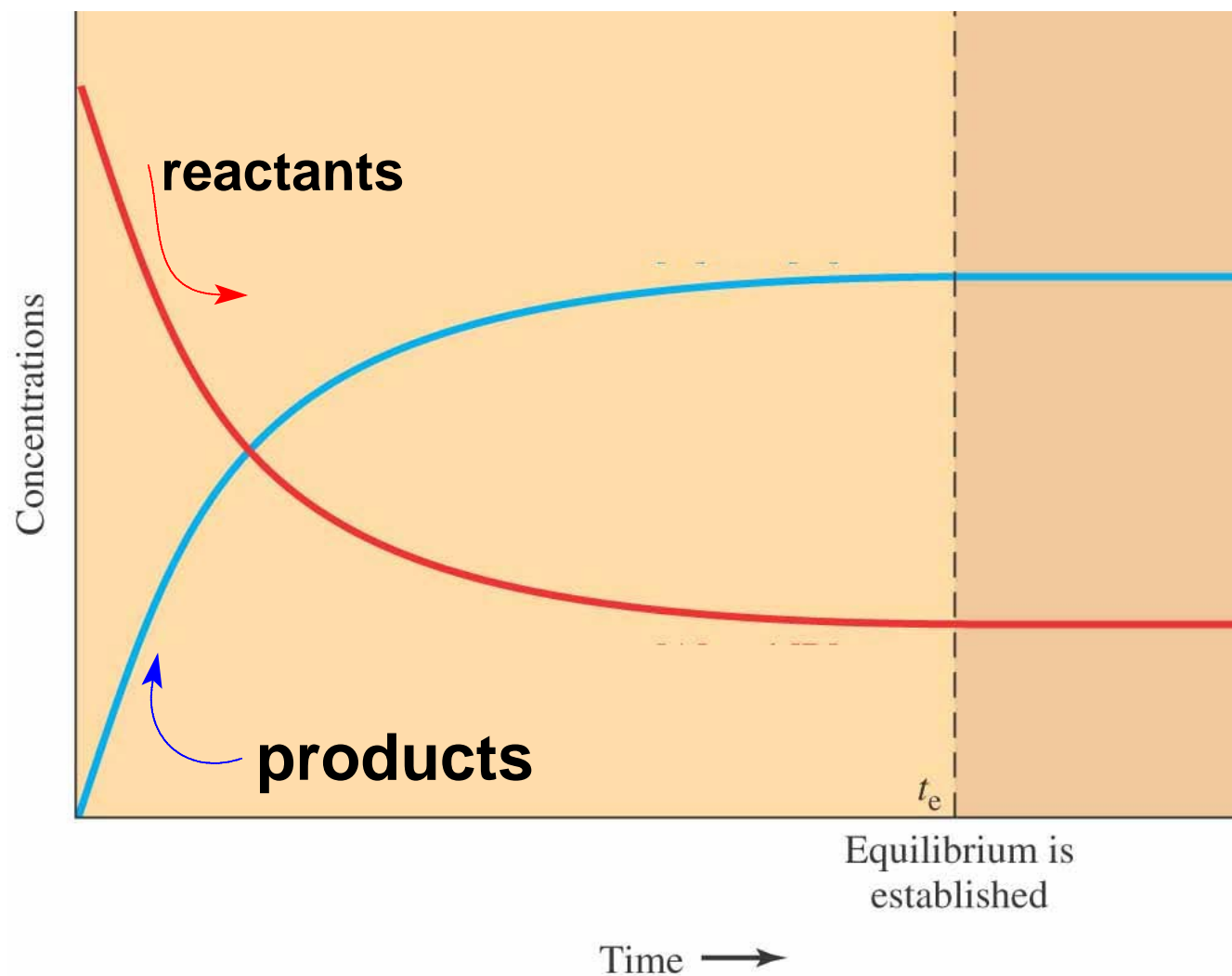


No matter how long you wait, there will always be some  $\text{SO}_2$  and  $\text{O}_2$  in the flask, along with the  $\text{SO}_3$

The reaction appears to have stopped before completely converting all of the reactants into products.

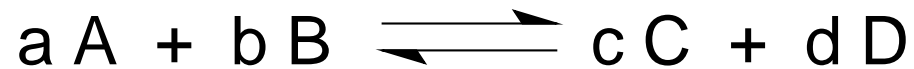
# Molecules Always in Motion!

Rather than stopping, the forward rate becomes equal to the reverse rate and concentrations no longer change.



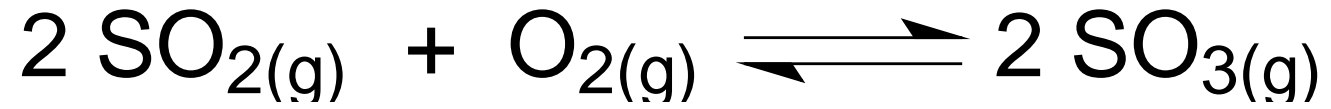
# General Expression

For any reaction:



$$K_{\text{eq}} = \frac{[\text{products}]_{\text{eq}}}{[\text{reactants}]_{\text{eq}}}$$

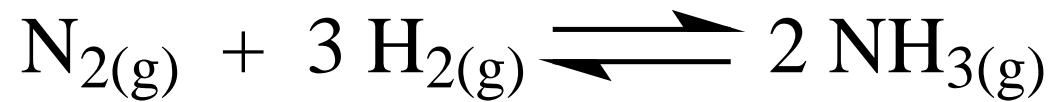
# Example



Try One

Q1

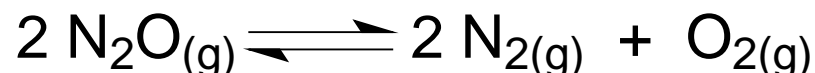
Write the equilibrium expression ( $K_c$ ) for:



# Gases and $K_p$

It is more practical to measure gas pressures than molar concentrations

for:



$$K_p = \frac{(p_{\text{N}_2})^2 (p_{\text{O}_2})}{(p_{\text{N}_2\text{O}})^2}$$

# $K_p$ and $K_c$

since  $pV = nRT$

$$p = \frac{n}{V} RT$$

$$p = M (RT)$$

molarity, **M**, is mols  
divide by liters

$$K_p = \frac{(p_{N_2})^2 (p_{O_2})}{(p_{N_2O})^2}$$

$$K_p = \frac{(M_{N_2} RT)^2 (M_{O_2} RT)}{(M_{N_2O} RT)^2}$$

# Continuing

$$K_p = \frac{(M_{N_2}RT)^2(M_{O_2}RT)}{(M_{N_2O}RT)^2}$$

$$K_p = K_c \frac{(RT)^2(RT)}{(RT)^2}$$

$$K_p = K_c(RT)^{3-2} = K_c(RT)$$

# The Relationship

$$K_p = K_c(RT)^{\Delta n}$$

Try One

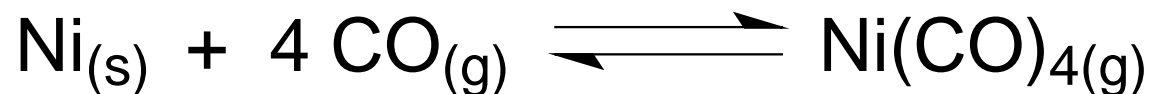
Q 1a



For this reaction,  $K_c = 2.51 \times 10^{-2}$  at  $25^\circ\text{C}$ .  
Calculate  $K_p$ .

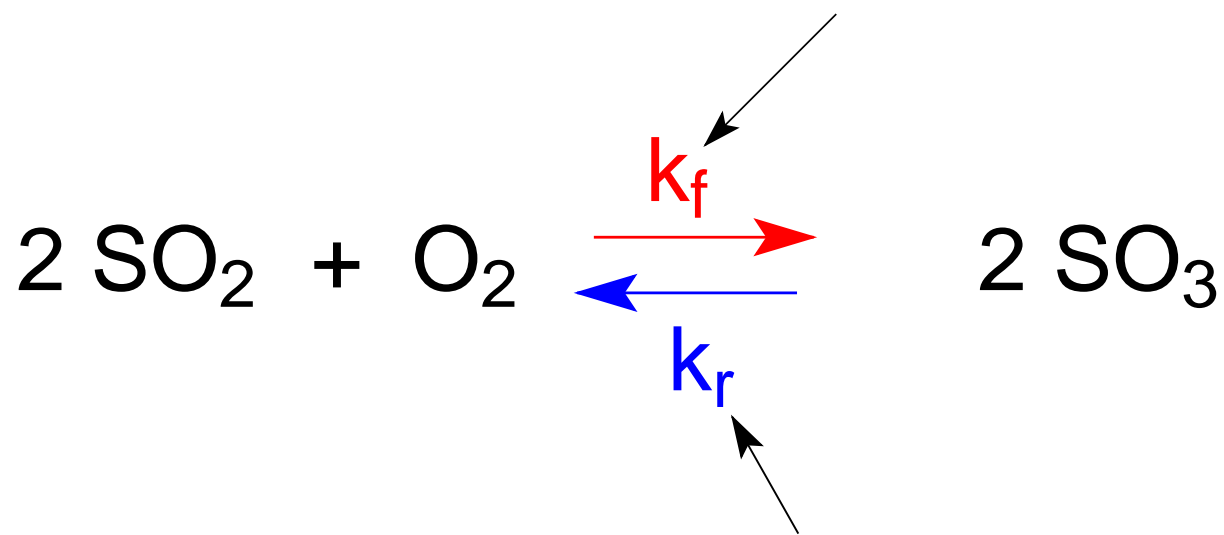
# Heterogeneous Equilibria

Not all reactants and products are included in the equilibrium expression.



$$K_{\text{eq}} = \frac{[\text{Ni}(\text{CO})_4]}{[\text{CO}]^4}$$

# A Kinetics View

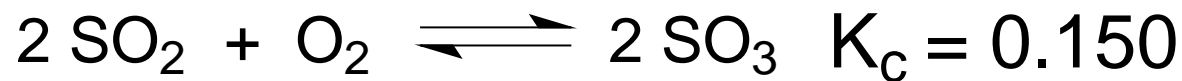


$$K_c = \frac{k_f}{k_r}$$

# More About $K_{eq}$

1. The larger the value, the more products are made  
(and the less reactants are left at equilibrium)
2.  $K$  is constant at any designated temperature  
(the equilibrium position is a function of temperature)
3. Unlike kinetics,  $K$  is independent of starting concentrations

# $K_{eq}$ Varies with Coefficients



for



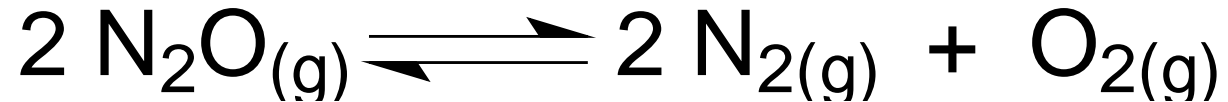
$$K'_c = \frac{[\text{SO}_3]^4}{[\text{SO}_2]^4[\text{O}_2]^2} = \left( \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \right)^2 = K_c^2$$

# One More



# Keeping Track of Everything

make (and use)  
a table!



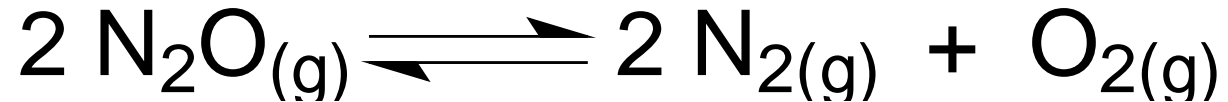
starting  
amounts

reacting

equilibrium

# A Problem to Illustrate

10.00 mols  $\text{N}_2\text{O}$  are placed into a 2.00 L flask.  
At equilibrium, 2.20 mols  $\text{N}_2\text{O}$  are left. From this  
data calculate  $K_c$  for the reaction.



starting  
amounts

reacting

equilibrium

# Calculation

$$K_c = \frac{[\text{N}_2]^2[\text{O}_2]}{[\text{N}_2\text{O}]^2}$$

$$K_c = \frac{(3.90)^2(1.95)}{(1.10)^2}$$

# Try One

## Q2

According to:



3.00 mols of  $\text{N}_2$  and 4.00 mols of  $\text{H}_2$  are placed into a 1.00 L flask. At equilibrium 2.10 mols of  $\text{N}_2$  are left. Calculate  $K_c$ .

Continuing

# Is Your System at Equilibrium?

"Q" is the reaction quotient

Substitute actual values into the K expression

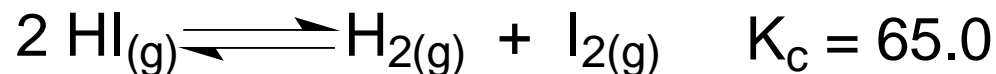
if  $Q < K$       system not at equilibrium and  
the forward reaction is favored

if  $Q > K$       system not at equilibrium and  
the reverse reaction is favored

if  $Q = K$       system is at equilibrium

# Example

for:



Is a mixture that is 0.500M in HI  
2.80M in H<sub>2</sub> and 3.40M in I<sub>2</sub>  
at equilibrium?

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

$$Q = \frac{(2.80)(3.40)}{(0.500)^2}$$

# Try One

## Q3

Is a mixture of 1.21 mols of N<sub>2</sub>, 0.344 mols of H<sub>2</sub> and 0.997 mols of NH<sub>3</sub> in a 2.00L flask at equilibrium? If not, in which direction is the reaction proceeding?

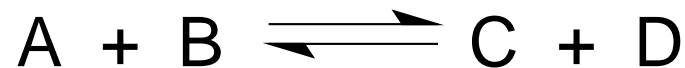


# Equilibrium Concentrations

For:



If we start with 0.200M in A  
and 0.200M in B, calculate  
the equilibrium concentrations of all species



---

starting  
amounts

0.200M 0.200M 0 0

---

reacting

---

equilibrium

---

# Solve

$$\begin{aligned}K_c &= \frac{[C][D]}{[A][B]} \\&= \frac{(x)(x)}{(0.200-x)(0.200-x)} \\&= \frac{x^2}{(0.200-x)^2} = 49.0\end{aligned}$$

a quadratic equation!

*(but we can take square root of both sides to avoid it)*

$$\frac{x}{0.200-x} = 7.00$$

$$[A] = 0.200-x = 0.025M$$

$$[B] = 0.200-x = 0.025M$$

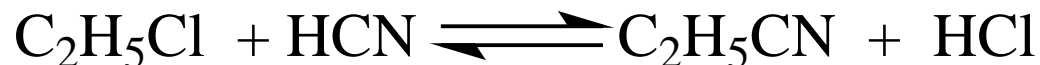
$$[C] = x = 0.175M$$

$$[D] = x = 0.175M$$

# Try One

## Q4

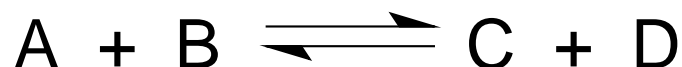
According to:



A solution 1.50M in  $\text{C}_2\text{H}_5\text{Cl}$  and 1.50M in  $\text{HCN}$  is allowed to come to equilibrium. Calculate the equilibrium concentrations of all species.  $K_c = 21.6$

# The Quadratic Solution

If we change the starting concentrations in the first example to 0.300M for A and 0.100M for B



---

starting amounts	0.300M	0.100M	0	0
------------------	--------	--------	---	---

---

reacting	x	x	x	x
----------	---	---	---	---

---

equilibrium	0.300-x	0.100-x	x	x
-------------	---------	---------	---	---

---

$$K_c = \frac{[C][D]}{[A][B]} = \frac{(x)(x)}{(0.300-x)(0.100-x)}$$

# Continuing

- $X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$ax^2 + bx + c = 0$$

$$\frac{x^2}{0.0300 - 0.0400x + x^2} = 49.0$$

$$x^2 = 1.47 - 19.6x + 49.0x^2$$

$$48x^2 - 19.6x + 1.47 = 0$$

$$a = 48$$

$$b = -19.6$$

$$c = 1.47$$

$$[A] = 0.300 - x = 0.201M$$

$$[B] = 0.100 - x = 0.001M$$

$$[C] = x = 0.099M$$

$$[D] = x = 0.099M$$

# Le Chatelier's Principle

A system at equilibrium tends to maintain the equilibrium by relieving stress placed on it

## **changes in:**

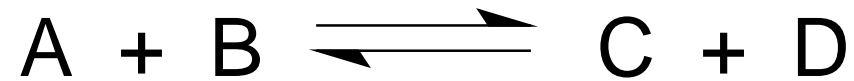
concentration of products or reactants

pressure or volume for gases

temperature (the value of  $K$  changes)

**all affect equilibrium systems**

# Concentration Changes



**add A or B**

**remove A or B**

**add C or D**

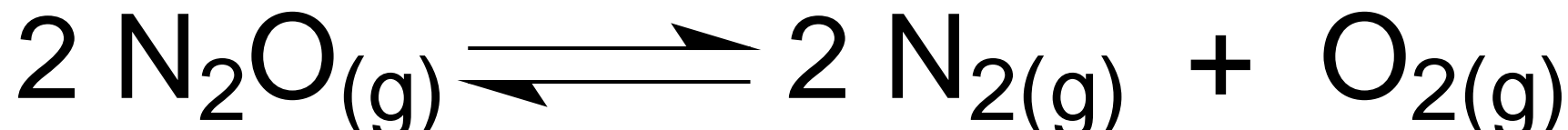
**remove C or D**

# Pressure and Volume Changes

**affects gases only!**

increasing pressure or decreasing volume favors gas molecules colliding. Therefore either will:

shift towards the **fewer number of mols of gas**



# Temperature Changes

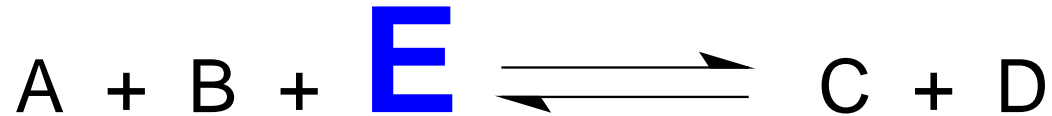
re-establish the equilibrium at a new position  
( $K_{eq}$  will change)

The direction of the shift is based on the reaction being endothermic or exothermic

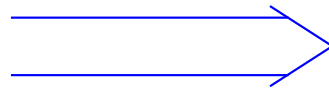
# A Point of View

for an endothermic reaction, consider energy as a reactant;  
an exothermic reaction has energy as a product

endothermic

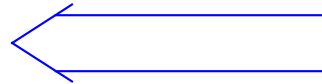


increase temperature  
("add E")



favors products  
( $K_{eq}$  increases)

decrease temperature  
("remove E")



favors reactants  
( $K_{eq}$  decreases)

# Exothermic Reactions

exothermic

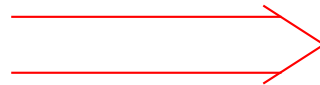


increase temperature  
("add E")



favors reactants  
( $K_{eq}$  decreases)

decrease temperature  
(remove E")

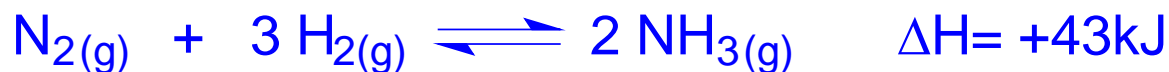


favors products  
( $K_{eq}$  increases)

# Try some

## Q5

For the following decide how the stress will affect the equilibrium (shift to the left, right, no change, changes the value of  $K_c$ ?)



add  $\text{N}_2$  \_\_\_\_\_

remove  $\text{H}_2$  \_\_\_\_\_

increase temperature \_\_\_\_\_

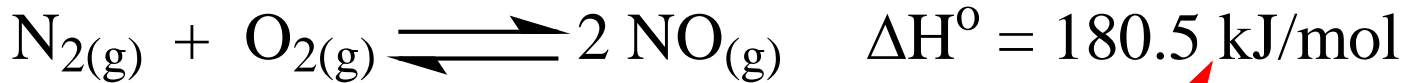
# The van't Hoff Equation

relates  $K_{eq}$  to temperature:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

# An Example

For the reaction:



If  $K_p = 4.4 \times 10^{-31}$  at 298K, calculate  $K_p$  at 2400K

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{K_2}{4.4 \times 10^{-31}} = \frac{180,500 \text{ J/mol}}{8.314 \text{ J/molK}} \left( \frac{1}{298\text{K}} - \frac{1}{2400\text{K}} \right)$$

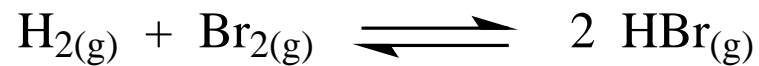
$$\ln \frac{K_2}{4.4 \times 10^{-31}} = (21710)(2.94 \times 10^{-3})$$

$$\ln \frac{K_2}{4.4 \times 10^{-31}} = 63.8$$

# Try One

## Q6

For the reaction:



$$K_c = 1.6 \times 10^5 \text{ at } 1297\text{K}$$

and

$$K_c = 3.5 \times 10^4 \text{ at } 1495\text{K}$$

**Calculate  $\Delta H$  for this reaction.**

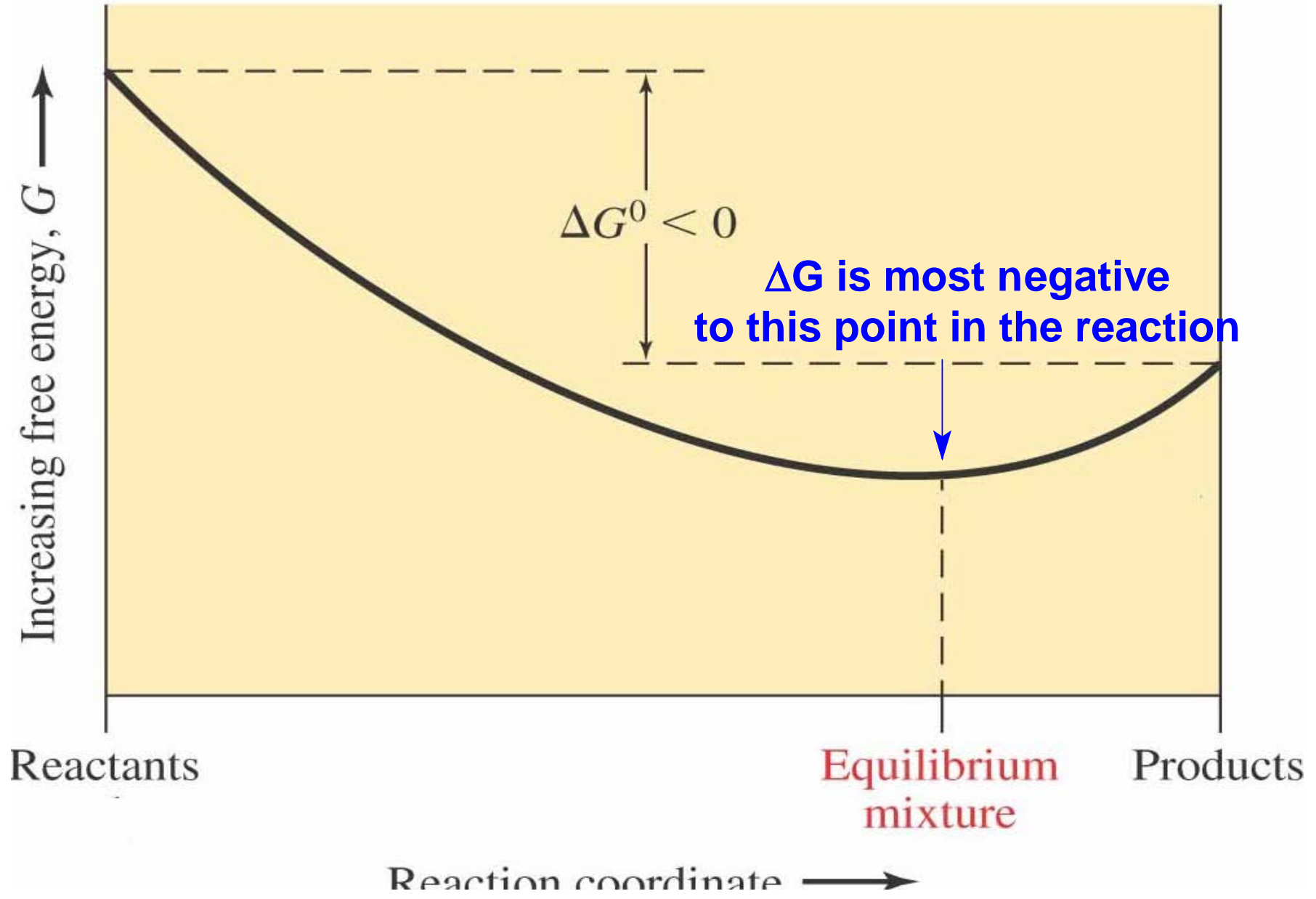
# $\Delta G$ and $K_{eq}$

Recall that  $\Delta G$  measure the "spontaneity" of a reaction and the position of the equilibrium is related to it

$$\Delta G = -RT \ln K_{eq}$$

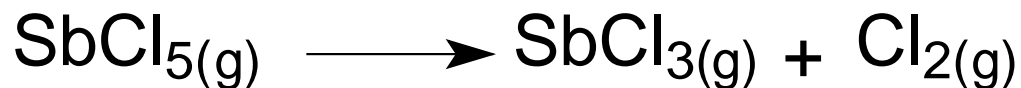
as  $\Delta G$  becomes more negative,  
 $K_{eq}$  gets larger

# A Graphical Look



# Try One

## Q7



For this reaction,  $K_c = 2.51 \times 10^{-2}$  at  $25^\circ\text{C}$ .

Calculate  $\Delta G^\circ$ .

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\Delta G^\circ = -(8.314 \text{ J/molK})(298 \text{ K}) \ln(2.51 \times 10^{-2})$$

$$\Delta G^\circ = +9130 \text{ J} = +9.13 \text{ kJ}$$