



# Unit 6

# Kinetics

Dynamic Equilibrium, Position of Equilibrium,  
Liquid-Vapor Equilibrium, Equilibrium Law

# 7.1 Equilibrium Review

## *What is equilibrium?*

- ❖ the rate of the forward reaction is equal to the rate of the reverse reaction

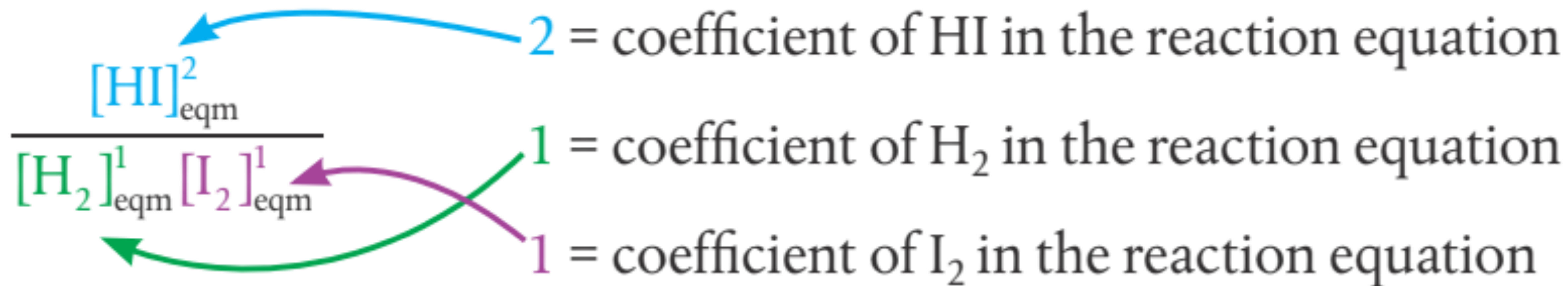
## Features of equilibrium

- ❖ It is dynamic
- ❖ It occurs in a closed system
- ❖ Concentrations of products and reactants remain **CONSTANT**
- ❖ There is no change in properties (color/density - dependent on concentration)
- ❖ Can be reached from either direction

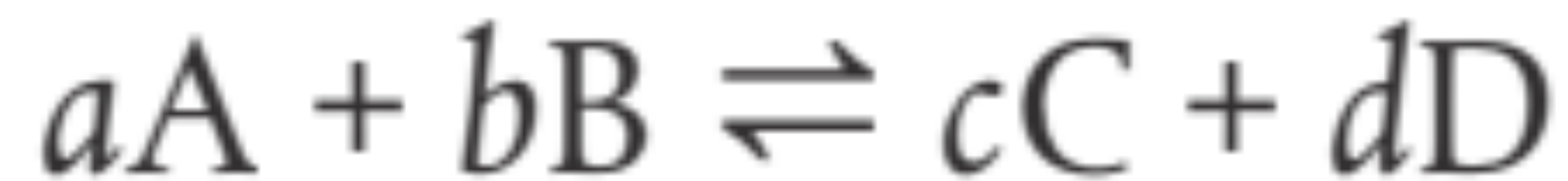


# The Position of Equilibrium

- ❖ Measured by the equilibrium constant ( $K_c$ )
- ❖ Example:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$
- ❖ When finding the  $K_c$  - the equilibrium constant is equal to the concentration of the products, divided by the concentration of the reactants



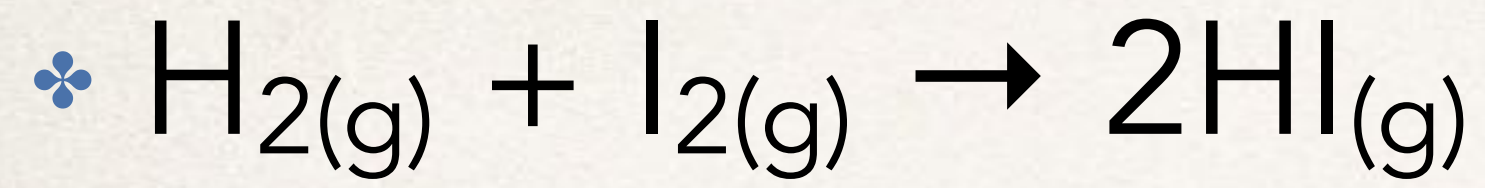
# In General



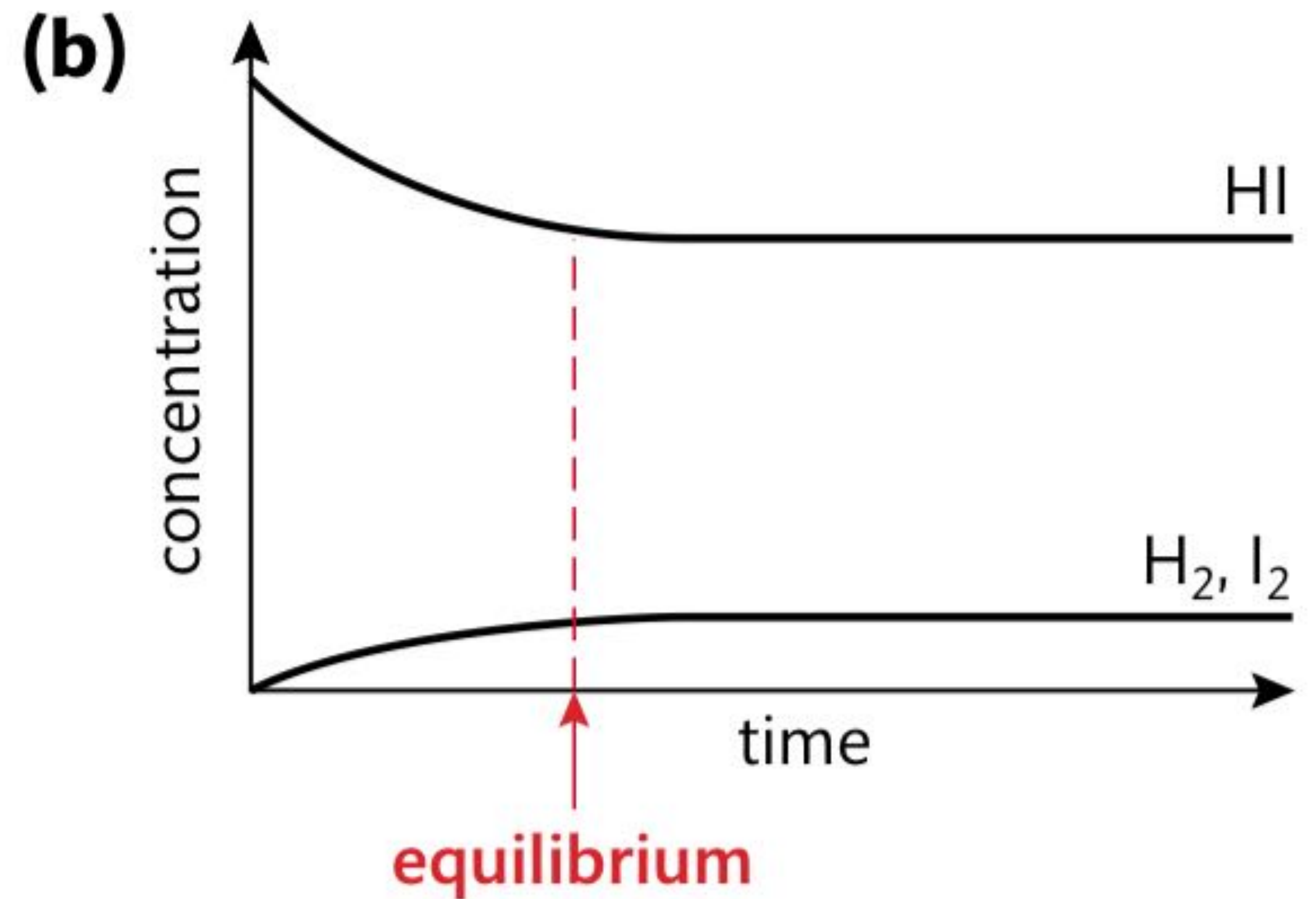
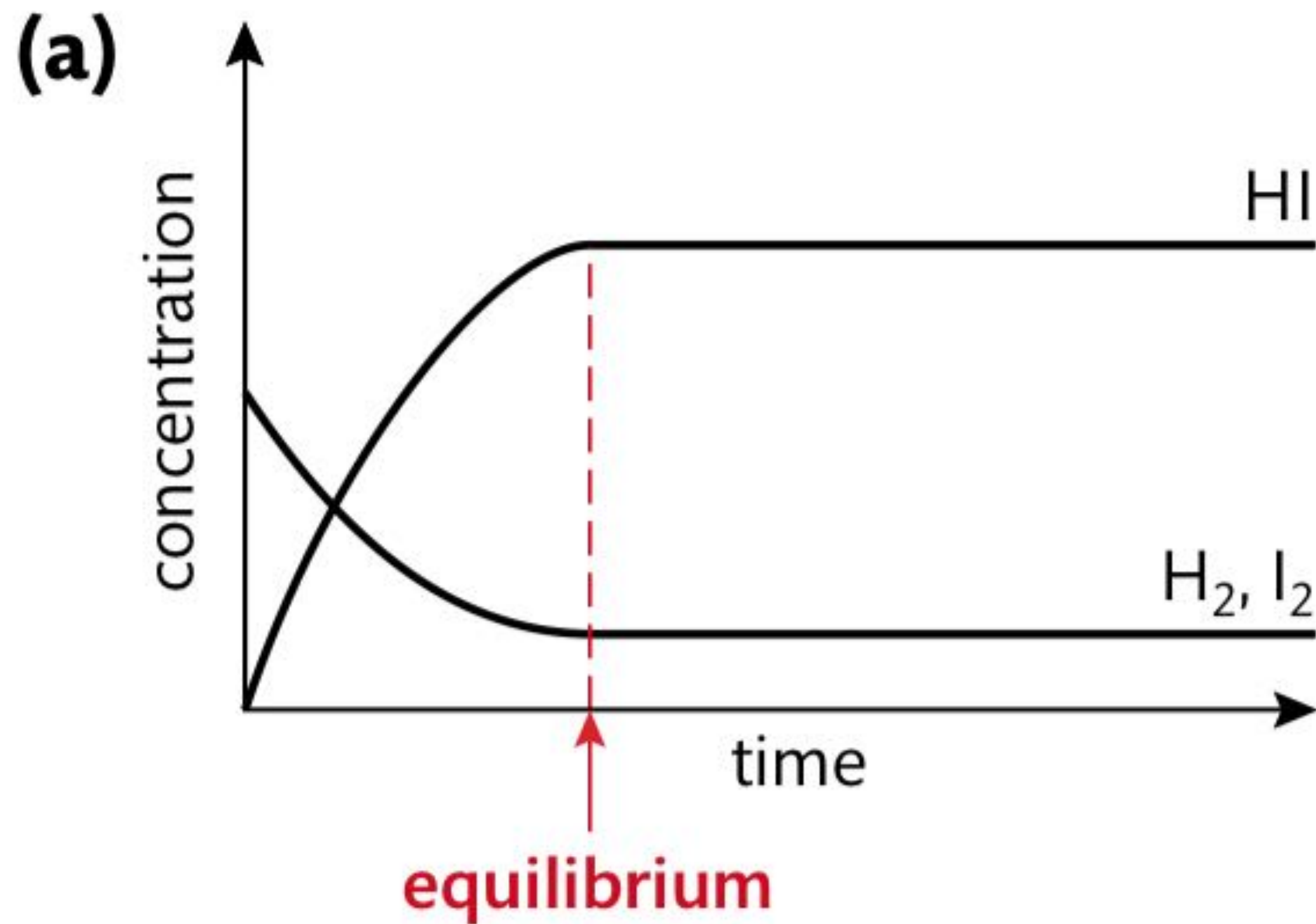
$$\frac{[C]_{\text{eqm}}^c [D]_{\text{eqm}}^d}{[A]_{\text{eqm}}^a [B]_{\text{eqm}}^b} = K_c$$

- The equilibrium constant expression has the concentrations of products in the numerator and the concentrations of reactants in the denominator.
- Each concentration is raised to the power of its coefficient in the balanced equation. (Where it is equal to one it does not have to be given.)
- Where there is more than one reactant or product the terms are multiplied together.

# Back to our Example:

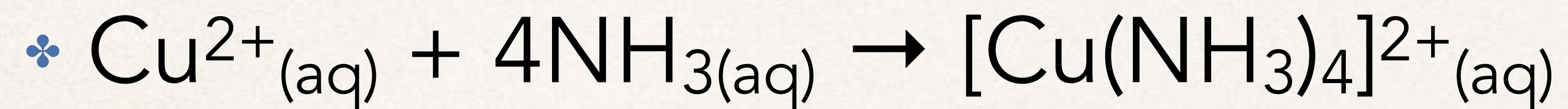


❖  $\frac{[\text{HI}]^2}{([\text{H}_2][\text{I}_2])}$



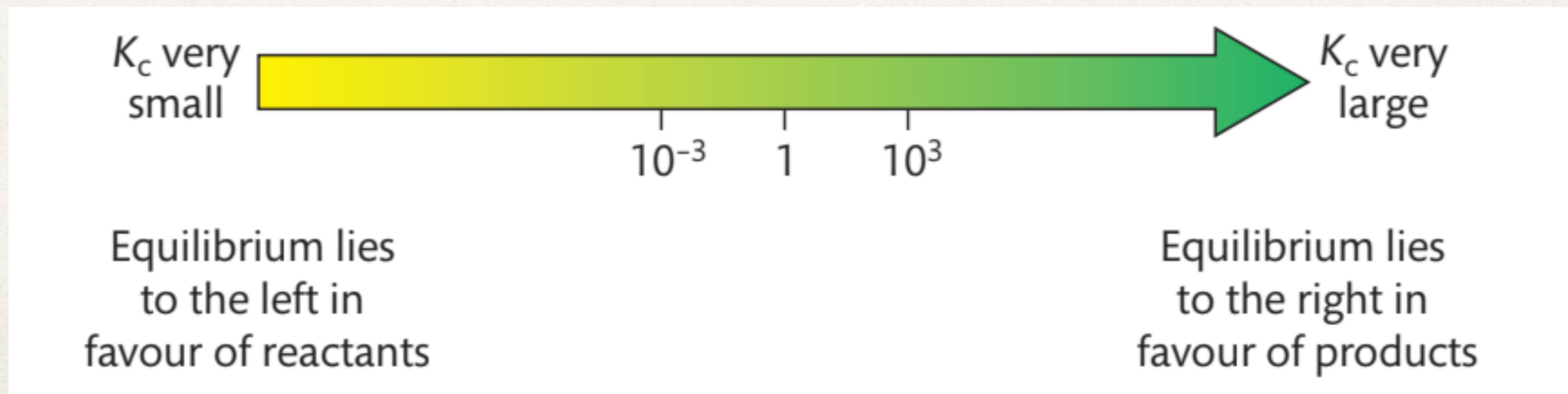
# Another Example. This Time You Try!

✦ Find the equilibrium expression for the following reaction:



# Magnitude of $K_c$

- ❖ Think basic division...
- ❖ If your reaction produces a lot of products and leaves very little reactants behind, will  $K_c$  be a high or low value?
- ❖ If your reaction does not produce much product and it stays in the reactant form, what will happen to  $K_c$ ?



# Magnitude of $K_c$

- ❖  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightarrow 2\text{HI}_{(g)}$        $K_c = 2$
- ❖  $\text{H}_{2(g)} + \text{Br}_{2(g)} \rightarrow 2\text{HBr}_{(g)}$        $K_c = 10^{10}$
- ❖  $\text{H}_{2(g)} + \text{Cl}_{2(g)} \rightarrow 2\text{HCl}_{(g)}$        $K_c = 10^{18}$
- ❖ If  $K_c \gg 1$ , the reaction is said to go to completion (very high conversion of reactants to products)
- ❖ If  $K_c \ll 1$ , the reaction hardly proceeds.
- ❖ The magnitude of  $K_c$  does NOT tell you how fast the reaction reaches equilibrium



# Reaction Quotient (Q)

- ❖ If we look at the concentrations of a reaction at a non-equilibrium point in time, we get information about the  $K_c$ .
- ❖ The value of Q changes in the direction of  $K_c$ , enabling us to predict the direction the reaction will proceed.
- ❖  $Q = K_c$  (reaction at equilibrium, no net reaction occurs)
- ❖  $Q < K_c$  (reaction proceed to the right in favor of the products)
- ❖  $Q > K_c$  (reaction proceeds to the left in favor of reactants)

# Reaction Quotient (Q)

\*  $K_c = 49.5 @ 440^\circ\text{C}$

	Experiment I: concentration at time $t$ / mol dm <sup>-3</sup>	Experiment II: concentration at time $t$ / mol dm <sup>-3</sup>
H <sub>2</sub>	0.0500	0.0250
I <sub>2</sub>	0.0500	0.0350
HI	0.100	0.300

The equilibrium constant expression =  $\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$

Experiment I, time  $t$

$$Q = \frac{(0.100)^2}{(0.0500)(0.0500)} = 4.00$$

\*  $Q < K_c$  (will shift to the right)

Experiment II, time  $t$

$$Q = \frac{(0.300)^2}{(0.0250)(0.0350)} = 103$$

\*  $Q > K_c$  (will shift to the left)

# Another Example

The equilibrium constant  $K_c = 1.7 \times 10^2$  at 500 K for the reaction



Determine whether the reaction mixture is at equilibrium when the concentrations of the components at this temperature are as follows:

$$[\text{N}_2] = 1.50$$

$$[\text{H}_2] = 1.00$$

$$[\text{NH}_3] = 8.00$$

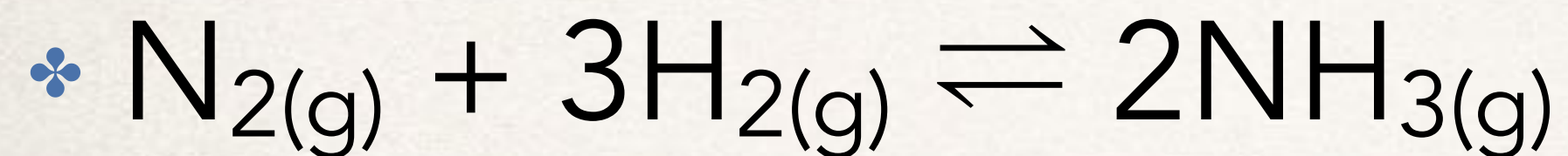
If it is not at equilibrium, state and explain in which direction the reaction will proceed.

# Disruption of Equilibrium...

- ❖ Who do we need to consider when an equilibrium shifts?
- ❖ Le Chatelier's Principle
  - ❖ *a system at equilibrium when subjected to a change will respond in such a way as to minimize the change*

# Change in Concentration

- ❖ The classical Le Chatelier's example:



- ❖ Adding a reactant will cause a shift towards the products (making more ammonia), while using up some of the other reactant

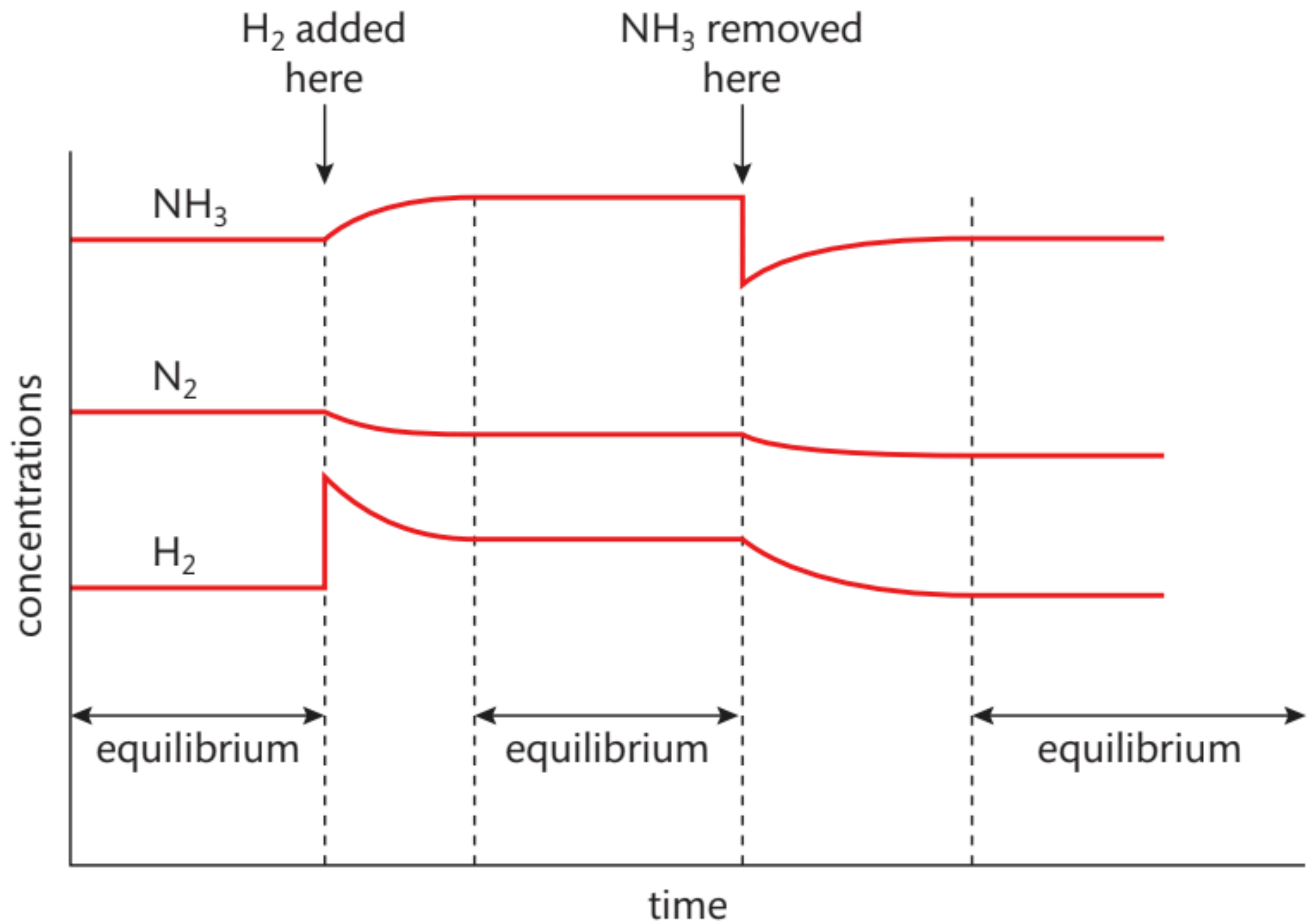
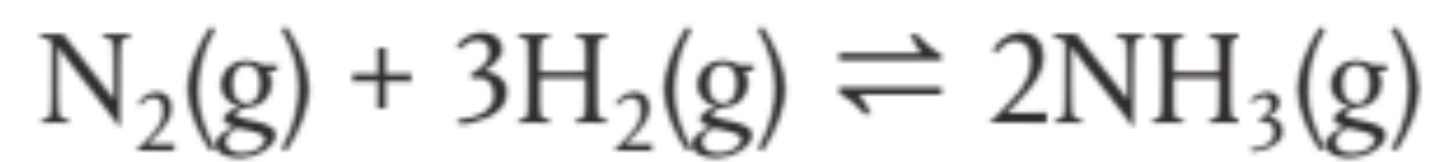
- ❖ Removing a product will cause a shift toward the products, using up reactants in the process

# Changes in Pressure

- ❖ An increase in pressure of a system, favours the side with the fewer number of gas particles
- ❖ A decrease in pressure will favour the side with more gas particles
- ❖  $\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$  - which way will it shift with an increase?

# Pressure and Concentration

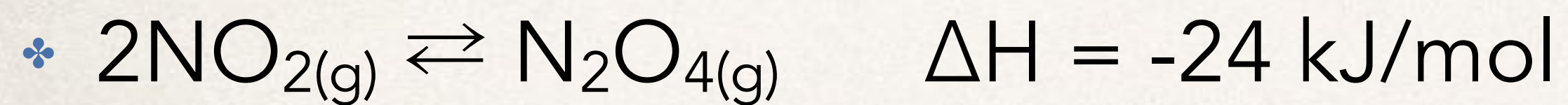
- ❖ Changes in Pressure and Concentration will cause a different position of equilibrium to be established
- ❖ BUT!...the  $K_c$  will not change



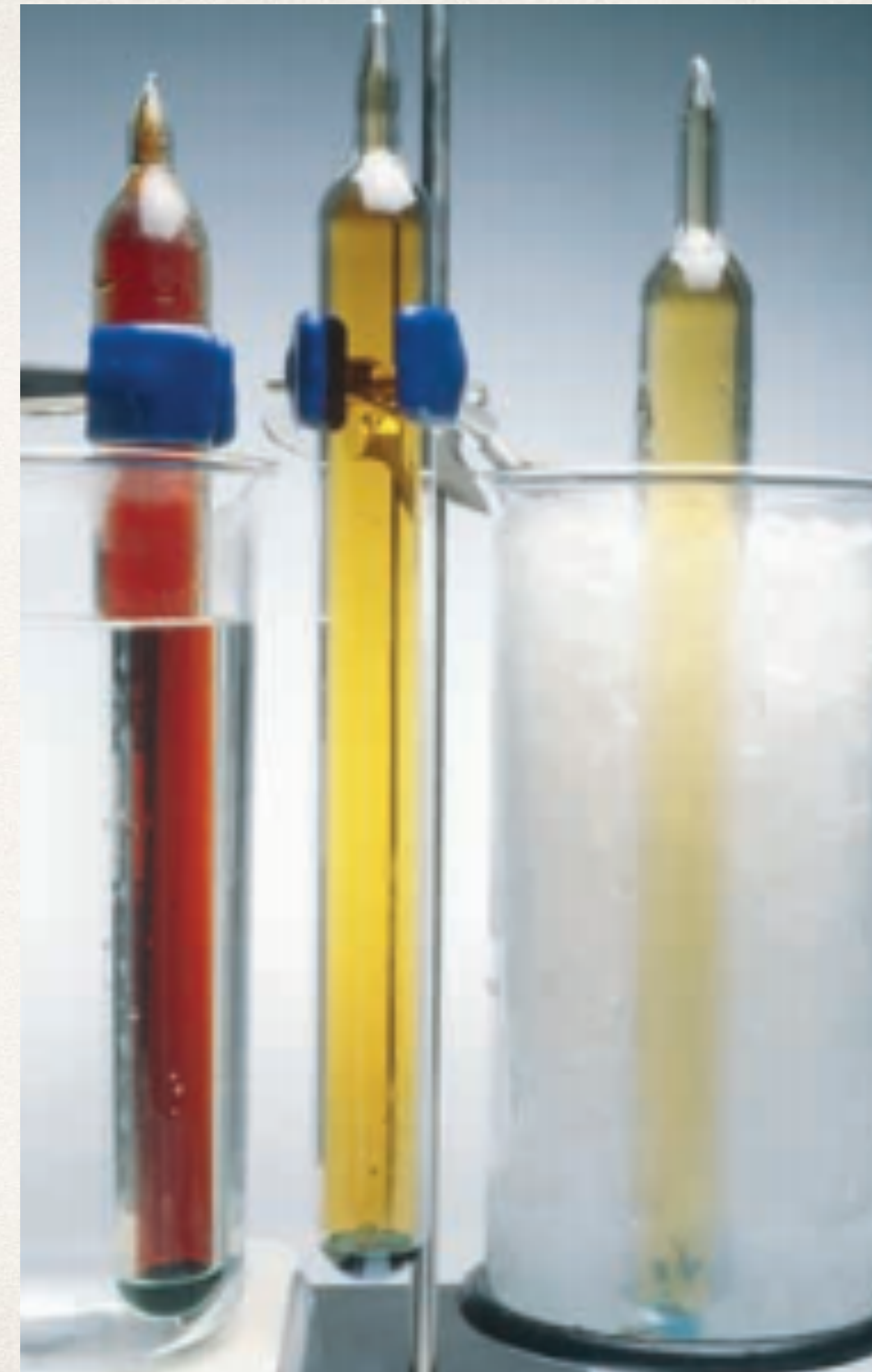


# Changes in Temperature

❖ Dependent on  $\Delta H$ : Does the reaction release or absorb energy?



brown      colorless



# Changes in Temperature

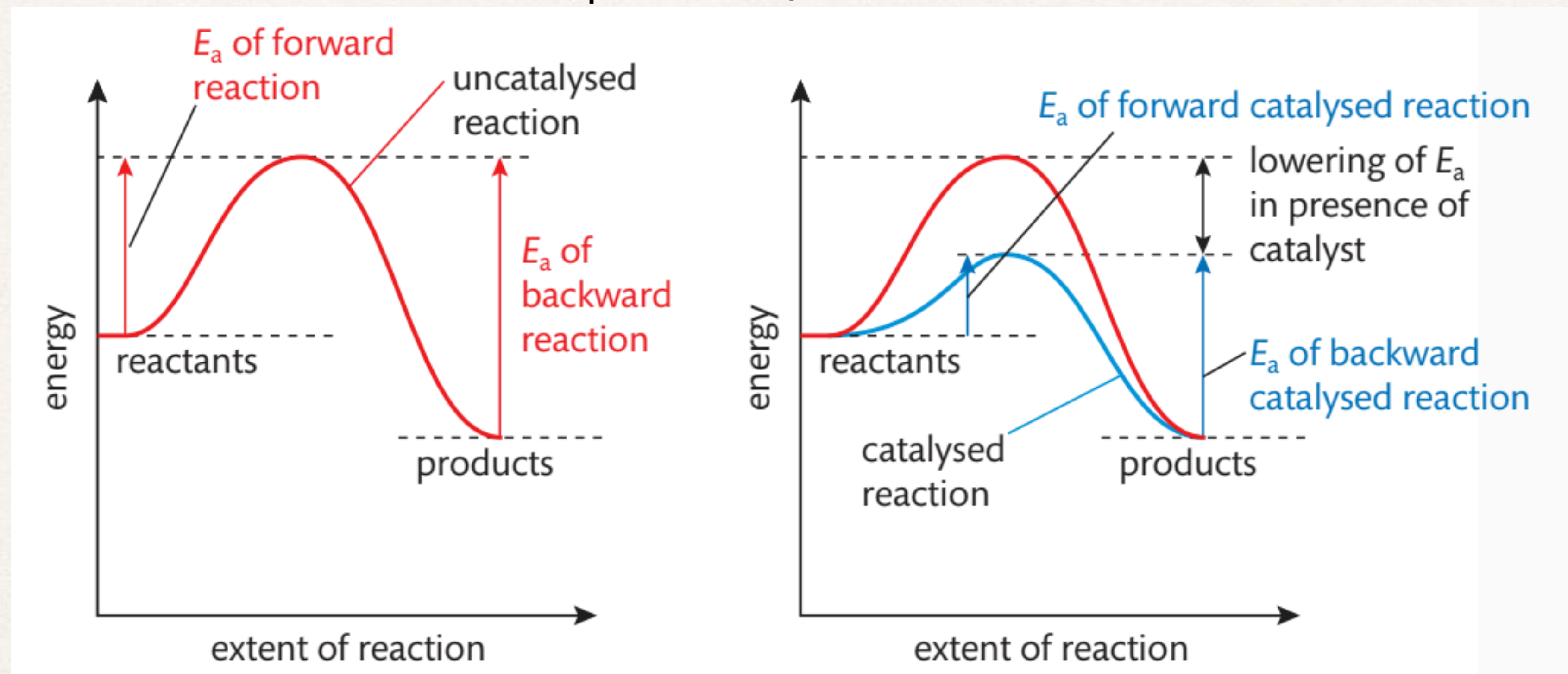


- ❖ What happens with an increase in temperature here?
- ❖ Unlike changes in pressure and concentration, if the temperature is changed in an equilibrium there will be a change in the  $K_c$  value

	$\Delta H$	T	$K_c$
exothermic	negative	increase	↓
		decrease	↑
endothermic	positive	increase	↑
		decrease	↓

# Addition of a Catalyst

- ❖ What does a catalyst do in a reaction?
- ❖ provides an alternate reaction pathway



Since the catalyst decreases the activation energy for both the forward and reverse reaction, it will have no effect on the position of equilibrium.

**Therefore,  $K_c$  will not change.**

# Summary

Effect of ...	Change in position of equilibrium	Change in value of $K_c$
1 concentration	changes	no change
2 pressure	changes if reaction involves a change in the number of gas molecules	no change
3 temperature	changes	changes
4 catalyst	no change	no change

# Industrial Applications

- ❖ What aspects are important to creating a product in the manufacturing field?
  - ❖ Yield - how much you make
  - ❖ Rate - how long it takes to complete
- ❖ It would be really nice if you were able to get a 95% yield all the time for your manufacturing process, but if it took you several years to do it...would it be worth it?

# The Haber Process

- ❖  $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)} \quad \Delta H = -93\text{kJ mol}^{-1}$
- ❖ What information can you gather from this equation?
  - ❖ All products and reactants are gases, fewer molecules on product side of the reaction
  - ❖ Forward reaction is exothermic, reverse is endothermic

# Applying Le Chatelier's to the Haber Process

**Concentration:** Increase concentration of  $\text{H}_2$  &  $\text{N}_2$  collect  $\text{NH}_3$  as it is made

**Pressure:** Increase Pressure ( $2 \times 10^7$  Pa)

**Temperature:** Favored by lower temperature, but too slow and it becomes uneconomical ( $450^\circ\text{C}$  is used)

**Catalyst:** Doesn't effect position of equilibrium, but can force the reaction to occur more quickly (finely divided iron, nowadays Ruthenium (Ru) because of decreased energy requirements).

# Testing Hint...

When discussing the Haber process, focus on the REASONS for choosing the conditions - explained using concepts of equilibrium AND kinetics



# The Contact Process - Formation of Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>)

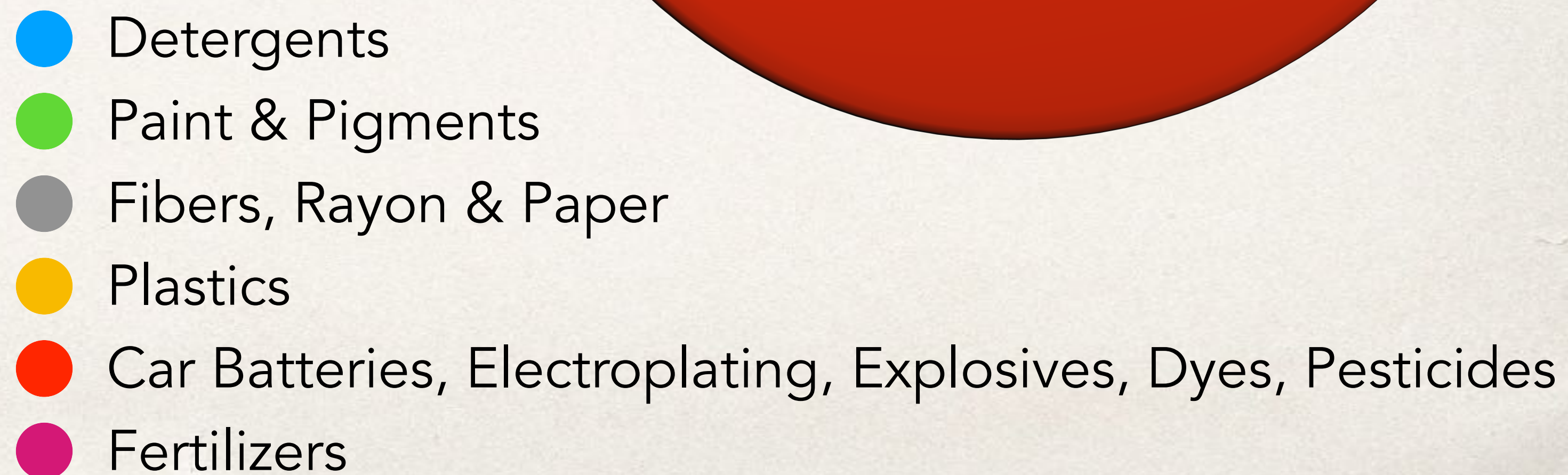
- ❖ H<sub>2</sub>SO<sub>4</sub> - 250 million tons are manufactured every year
- ❖ Contact Process (*due to 'contact' with V<sub>2</sub>O<sub>5</sub> catalyst*)
  - ❖ 3 simple reactions
    - ❖ combustion of sulfur:  $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$
    - ❖ Oxidation of sulfur dioxide:  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
    - ❖ Combination of SO<sub>3(g)</sub> with water (really violent reaction, substitute is below)
      - ❖  $SO_{3(g)} + H_2SO_{4(l)} \rightarrow H_2S_2O_7(l) + H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)}$

# Continued

- It has been determined that the second step is the rate determining step. If Le Chatelier's is applied to that step, we can maximize yield



- What can be done to increase the yield of this reaction?



# 17.1 The Equilibrium Law

- ✦ Le Chatelier's Principle
- ✦ Equilibrium Position in Relation to Entropy and Gibbs Free Energy
- ✦  $\Delta G = -RT \ln K$

# Example

- ❖ Hydrogen can be prepared by the combination of carbon monoxide and water @ 500°C. **At equilibrium**, the concentrations in the reaction mixture were found to be:
  - ❖ CO 0.150 mol dm<sup>-3</sup>
  - ❖ H<sub>2</sub>O 0.0145 mol dm<sup>-3</sup>
  - ❖ H<sub>2</sub> 0.200 mol dm<sup>-3</sup>
  - ❖ CO<sub>2</sub> 0.0200 mol dm<sup>-3</sup>
- ❖ What is a good place to start?

# Method for Solving - (R)ICE

Sometimes, you may only get data on the initial condition and some small piece of data on the equilibrium

1. (**R**eaction) Write the balanced equation.
2. Write values for each of the concentrations for initial, change and equilibrium. (Can create a table for this.)
  - \* **I**nitial - what was originally in the flask (assume [product] = 0 unless stated otherwise)
  - \* **C**hange - represents the amount that reacts to reach equilibrium (subtract reactants, add products - as same ratio in the reaction)
  - \* **E**quilibrium - can be calculated ([equilibrium] = [initial] +/- the change)
3. Write the expression for  $K_c$  from the balanced equation and substitute.

# ICE Example

- ❖ A Student placed 0.20 mol of  $\text{PCl}_{3(g)}$  and 0.10 mol of  $\text{Cl}_{2(g)}$  in a 1 dm<sup>3</sup> flask at 350°C. The reaction, which produced  $\text{PCl}_{5(g)}$ , was allowed to come to equilibrium at which time it was found that the flask contained 0.12 mol of  $\text{PCl}_{3(g)}$ . What is the value of  $K_c$  in this reaction?

# Another ICE Example

- \* The oxidation of NO to form NO<sub>2</sub> occurs during the formation of smog. When 0.60 mol of NO was reacted with 0.60 mol O<sub>2</sub> in a 2 dm<sup>3</sup> container at 500°C, the equilibrium mixture was found to contain 0.20 mol of NO<sub>2</sub>. Calculate the equilibrium constant for the reaction at this temperature.

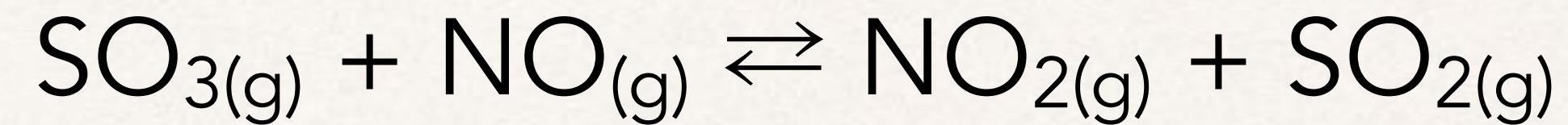
# Calculating Concentrations from the Equilibrium constant

- ❖ The reaction  $\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$  has a  $K_c = 0.500$  at 350K. If the concentrations at equilibrium are:
  - ❖  $[\text{CO}] = 0.200 \text{ mol dm}^{-3}$
  - ❖  $[\text{H}_2] = 0.155 \text{ mol dm}^{-3}$
- ❖ What is the equilibrium concentration of  $\text{CH}_3\text{OH}$ ?



# Another Example

- ❖ It gets more challenging if we need to calculate equilibrium concentrations given the  $K_c$  and initial concentrations.
- ❖ The equilibrium constant,  $K_c$ , for the reaction



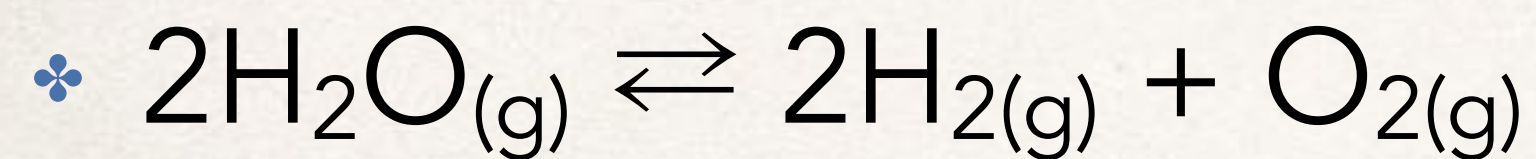
was found to be 6.78 at 400K. If the initial concentrations of NO and  $\text{SO}_3$  were both  $0.03 \text{ mol dm}^{-3}$ , what would be the equilibrium concentration of each component?

# What Happens When $K_c$ is Very Small?

- ❖ What happens to the concentrations of the reactants and products?  
(Basically, which way is the reaction favoring?)
- ❖ The change in concentration of the reactants is very small (close to zero)  
 $\therefore [\text{reactant}]_{\text{initial}} = [\text{reactant}]_{\text{equilibrium}}$

# $K_c$ is Very Small Example

- ❖ The thermal decomposition of water has a very small value of  $K_c$ . At  $1000^\circ\text{C}$ ,  $K_c = 7.3 \times 10^{-18}$  for the reaction:



Use the approximation if  $K_c < 10^{-3}$  then we ignore the *change* when calculating.

- ❖ A reaction is set up at this temperature with an initial water concentration of  $0.10 \text{ mol dm}^{-3}$ . Calculate  $[\text{H}_2]$  at equilibrium.

# Free Energy and Equilibrium

What determines whether a reaction goes to completion or not?

**$\Delta G^\ominus = \text{negative} \Rightarrow \text{reaction proceeds in the forward direction}$**

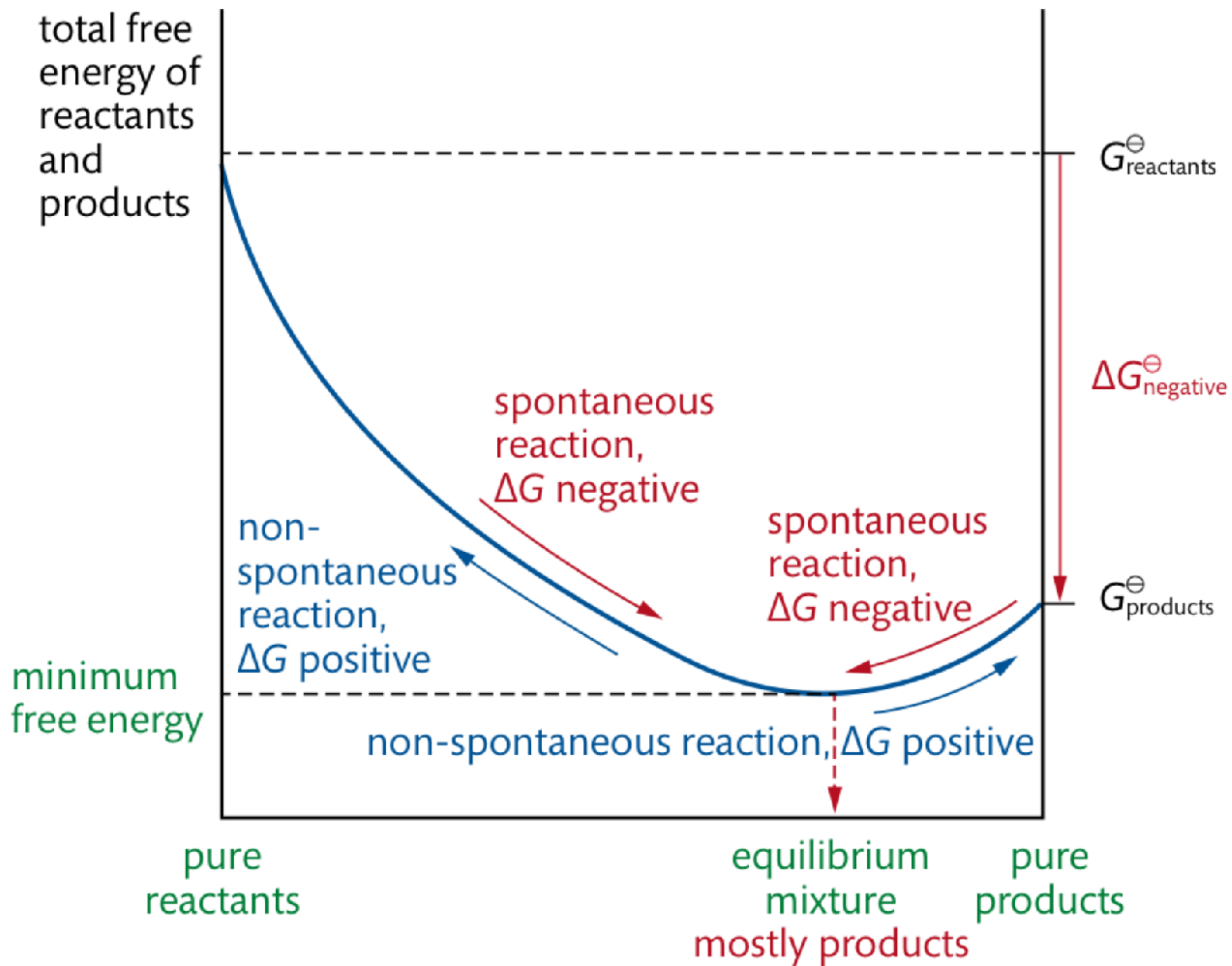
**$\Delta G^\ominus = \text{positive} \Rightarrow \text{reaction proceeds in the backward direction}$**

**$\Delta G^\ominus = 0 \Rightarrow \text{reaction is at equilibrium}$**

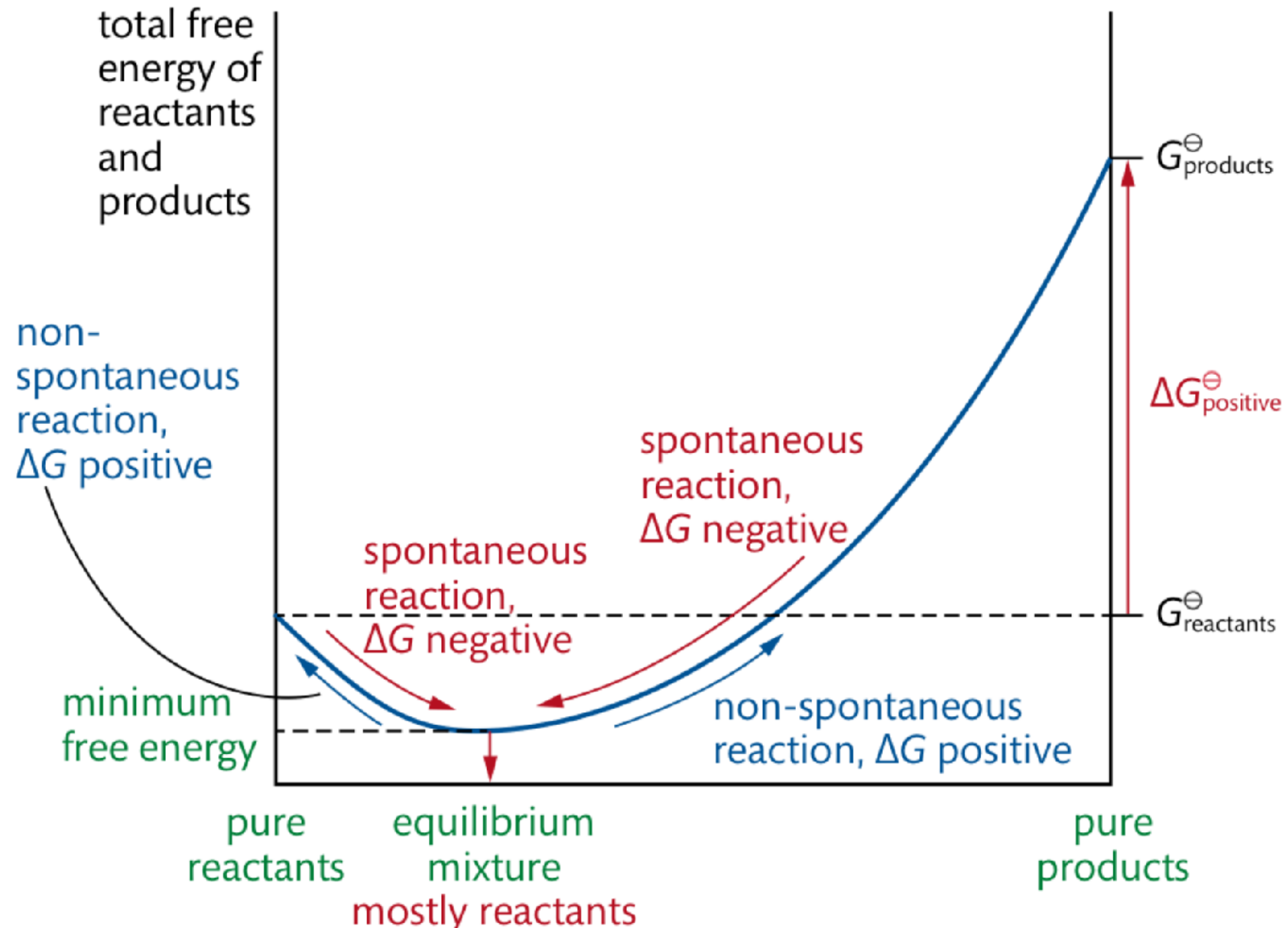
$$\Delta G^\ominus = G^\ominus_{\text{products}} - G^\ominus_{\text{reactants}}$$

$$G^\ominus_{\text{products}} = G^\ominus_{\text{reactants}} @ \text{equilibrium}$$

(a)



(b)



# $K_c$ from Thermodynamic Data

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

Given in data booklet:

$\Delta G^\ominus$  = standard free energy change of the reaction

$R$  = gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ )

$T$  = absolute temperature (Kelvin)

$\ln K$  = the natural logarithm of  $K_c$

$\Delta G^\ominus$	$\ln K$	$K$	Equilibrium mixture
$\Delta G^\ominus$ negative	$\ln K$ positive	$K > 1$	mainly products
$\Delta G^\ominus$ positive	$\ln K$ negative	$K < 1$	mainly reactants
$\Delta G^\ominus = 0$	$\ln K = 0$	$K = 1$	appreciable amounts of both reactants and products

# Example

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

The esterification reaction that produces ethyl ethanoate has a free energy change ( $\Delta G^\circ = -4.38 \text{ kJ mol}^{-1}$ ). Calculate the value of the equilibrium constant of this reaction at 298K.





# Kinetics and Equilibrium

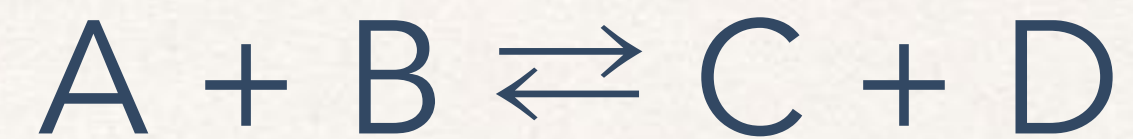


- ❖  $K_c = 10^{261}$  !!!!
- ❖ Meaning  $\Delta G$  should be large and negative.
- ❖ The reaction should go to completion.
- ❖ However, we know rusting is a SLOW process.

Magnitude of  $K_c$  gives no information on rate!

So....let's look at  $k$  for the forward and reverse reactions

# Continued



Rate of forward reaction =  $k[A][B]$

Rate of reverse reaction =  $k'[C][D]$

$$k[A][B] = k'[C][D]$$

Rearrange to give  $K_c = k/k'$

## Therefore:

If  $k \gg k' \Rightarrow K_c$  is large and the reaction progresses towards completion.

If  $k \ll k' \Rightarrow K_c$  is small and the reaction barely takes place

# Finally: Responses of Equilibrium

## Concentration:

- Increasing [reactant] increases rate of forward rxn and shifts equilibrium to the right.
- Increasing [product] increases rate of reverse rxn and shifts equilibrium to the left.
- VALUE of  $K_c$  remains constant.

## Catalyst:

- Increases values of  $k$  and  $k'$  by the same factor.  $K_c$  not affected.

## Temperature:

- Arrhenius equation; rate constant increases with increasing temp. Forward and backward reactions affected differently by temp.  $k/k'$  is temperature dependent.  
 $K_c$  increases with temp.