

# Good comments from the discussion

I think when the temperature achieves the absolute zero, which is 0K, the reaction might stop because the molecule cannot move anymore.

All human activities which will lead to global warming, can increase the rate of reaction. As the temperature is increasing, molecules are likely to have more successful collisions.

- if reactants only collide for a small number of times, will the reaction achieve equilibrium?
- The whole universe should be at a equilibrium. So the helium released back to the atmosphere can be considered a type of equilibrium.
- The universe is now still expanding in size, it's not easy to believe universe is at equilibrium. There is no difference between recent expanding and the big bang.
- the helium particles will be spread throughout the air, and the process will never stop, thus there is no equilibrium.

## Questions you did not answer: (well enough)

If a salt is considered insoluble in water, can it react with another salt that is soluble?

Does concentration of the reactants tell you when the reaction will stop?

What is the  $\Delta G$  of boiling liquid water at 100 C? Will this reaction go forward or backward?

Does the number of steps that it takes for a reaction to occur in the forward direction always equal the number of steps that it takes for a reaction to occur in the reverse direction?

Does the number of steps that it takes for a reaction to occur in the forward direction always equal the number of steps that it takes for a reaction to occur in the reverse direction?

An onion scented candle is burning in Mr. Lawlor's office. You see the fire and know that a chemical reaction is happening, but you don't observe any change in the flame after 30 seconds of observation. Why is this?

The famous writer Dante wrote about the nine circle. . .

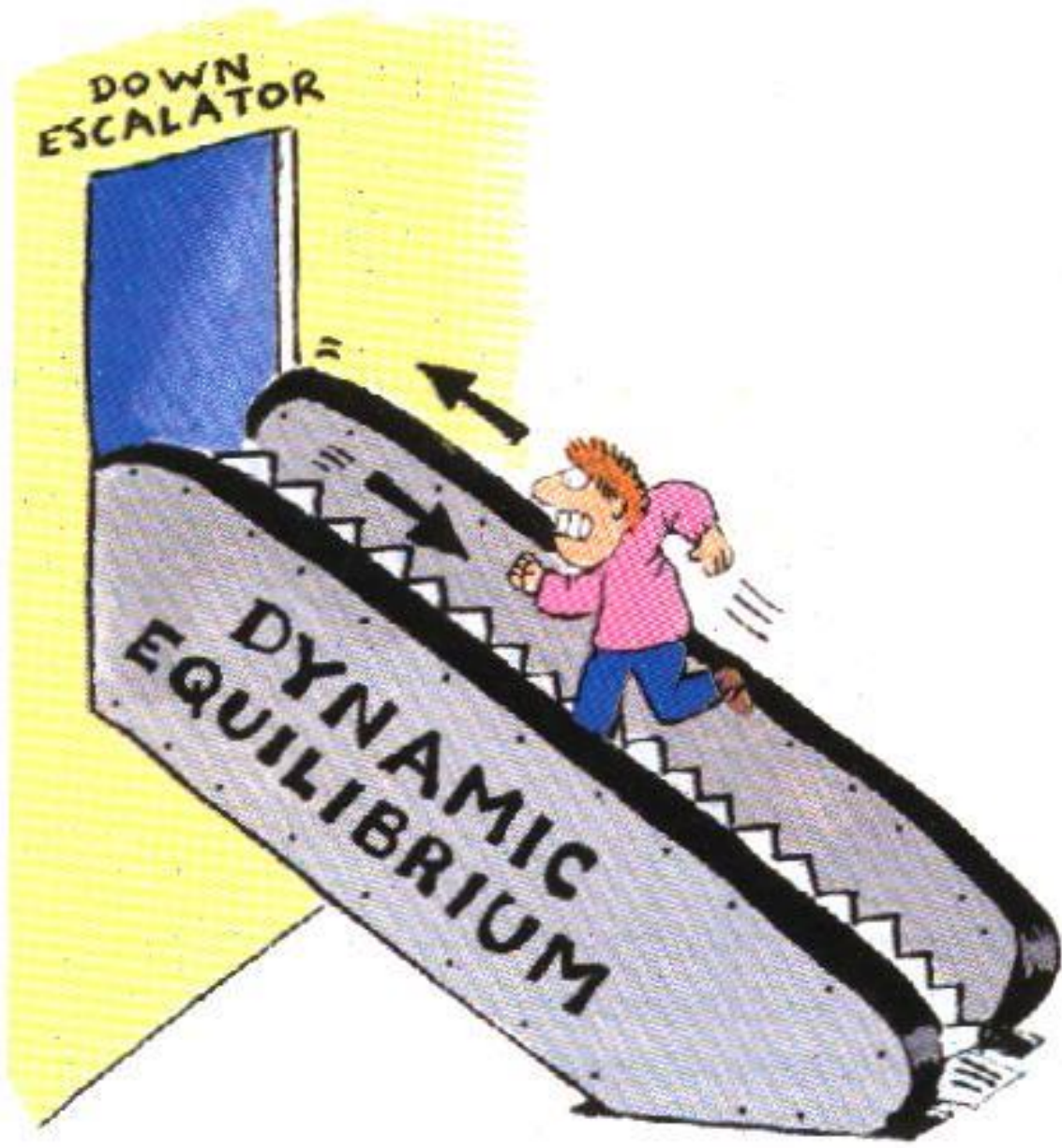
Study these before the midterm

# Equilibrium

- The reactions considered until now have had reactants react completely to form products. These reactions “went” only in one direction. **“Steady state”**
- Some reactions can react in either direction. They are “reversible”. When this occurs some amount of reactant(s) will always remain in the final reaction mixture.

- A chemical system where the concentrations of reactants and products remain **constant** over time.
- On the **molecular level**, the system is **dynamic**: The rate of change is the same in either the forward or reverse directions.

# **DYNAMIC EQUILIBRIA**





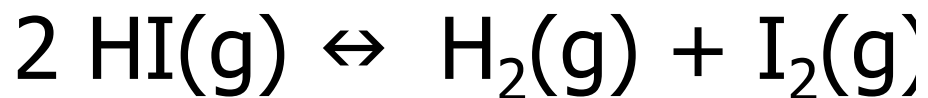
# DYNAMIC EQUILIBRIUM

## DYNAMIC

- The forward and reverse reactions are both taking place.

## EQUILIBRIUM

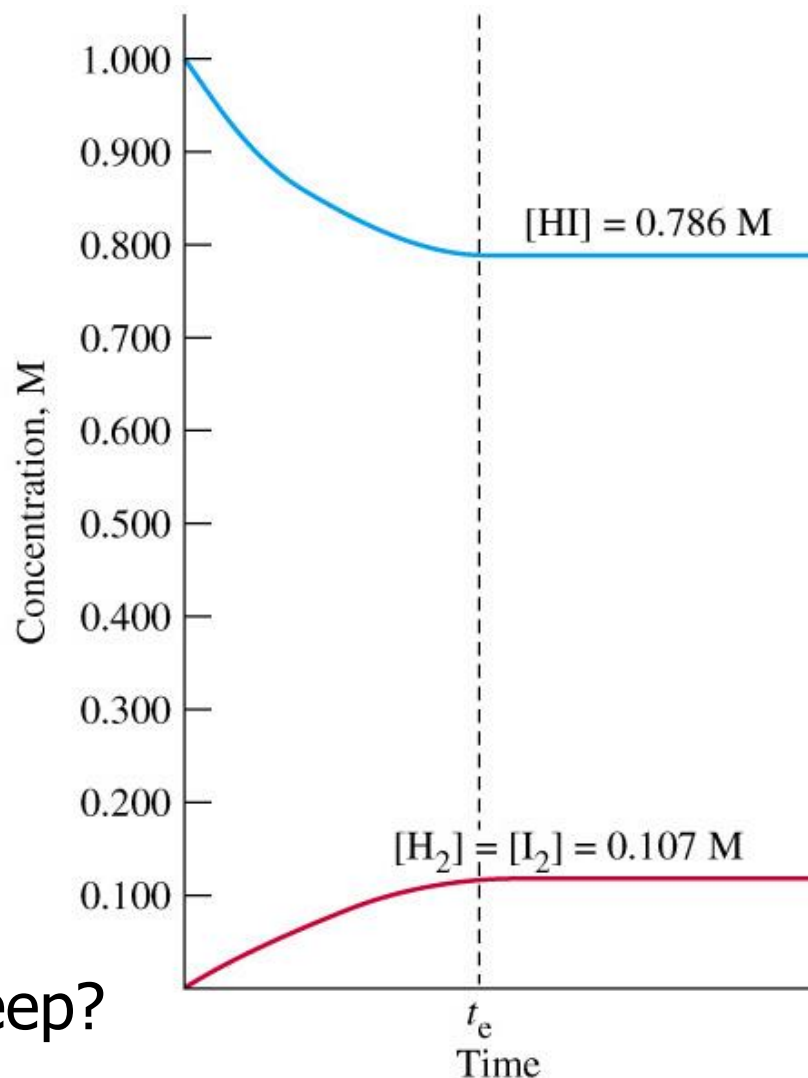
- The reactions take place at the same speed.
- All reactants and products are present.
- The concentration of all reactants and products remain constant.

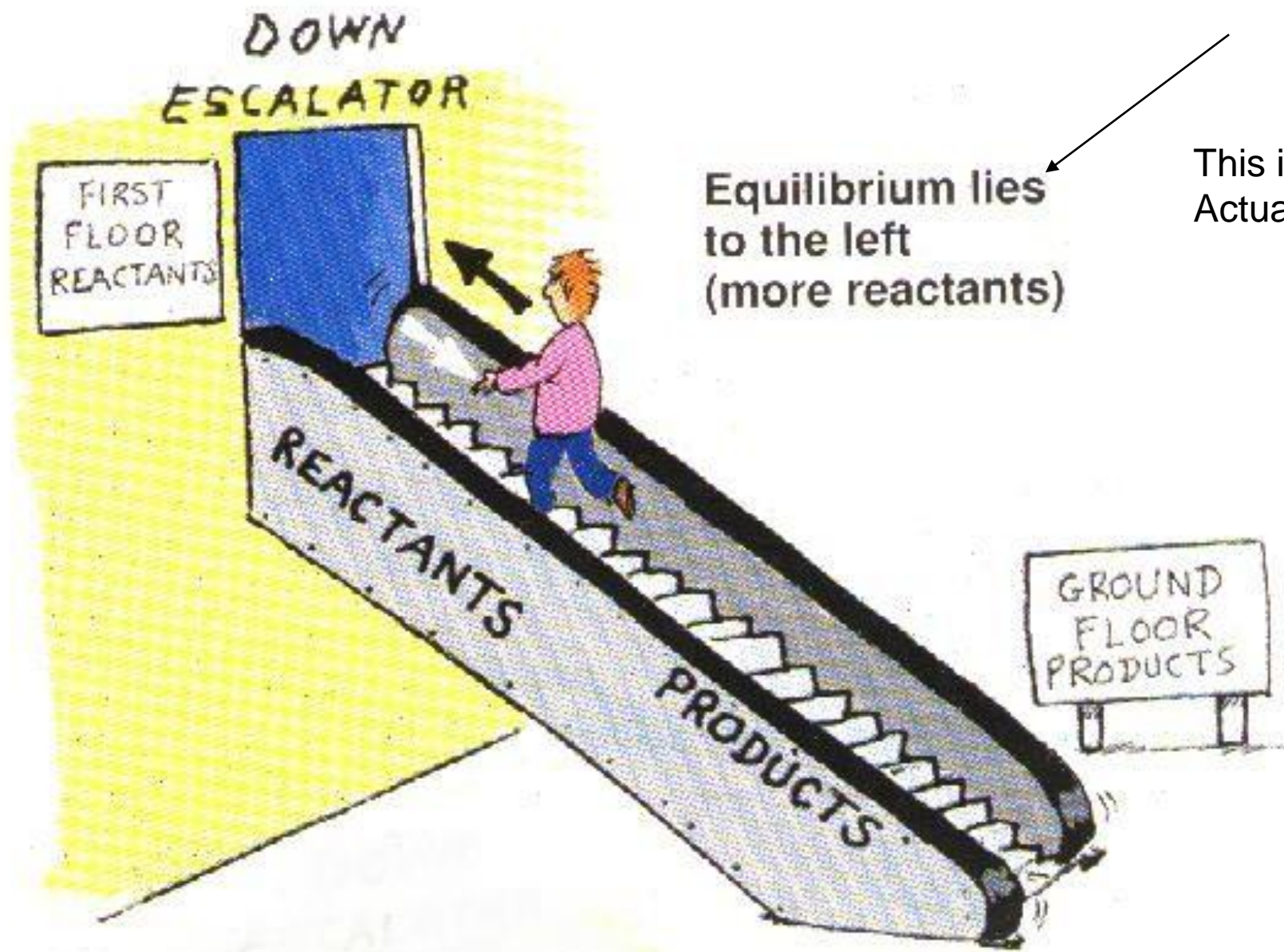


Imagine you start with 0.100 M HI. It breaks down to form  $\text{H}_2$  and  $\text{I}_2$ . However,  $\text{H}_2$  and  $\text{I}_2$  react to form HI.

After a time, equilibrium is reached with the rate at which HI decomposes equals the rate at which it is formed.

Why is the blue line twice as steep?





DOWN  
ESCALATOR

FIRST  
FLOOR  
REACTANTS

REACTANTS

PRODUCTS

GROUND  
FLOOR  
PRODUCTS

Equilibrium lies  
to the left  
(more reactants)

This is an  
Actual phrase



when equilibrium lies to the left:

there are more reactants than products  
(i.e. more  $\text{H}_2$  and  $\text{N}_2$  than  $\text{NH}_3$ )

DOWN  
ESCALATOR

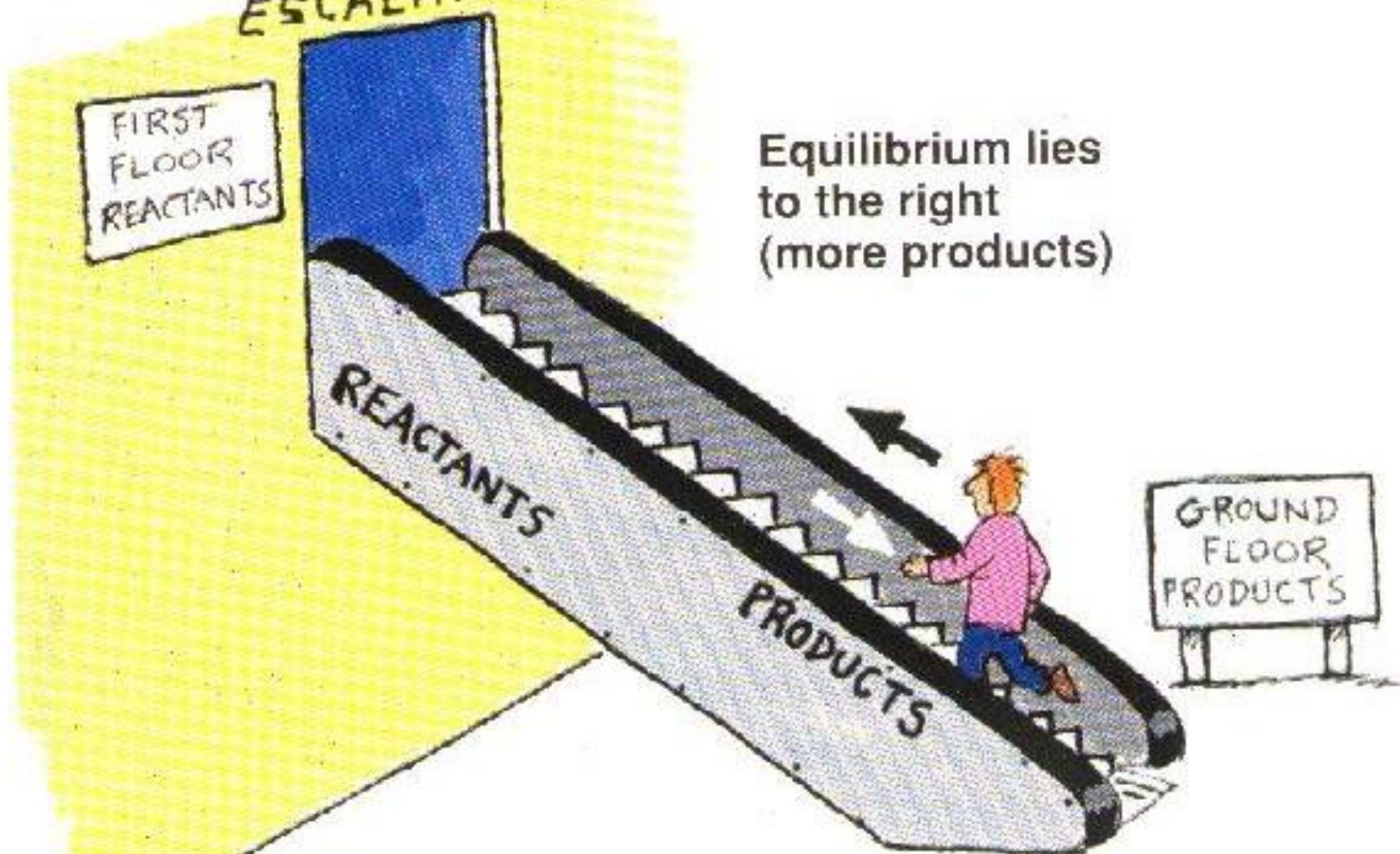
FIRST  
FLOOR  
REACTANTS

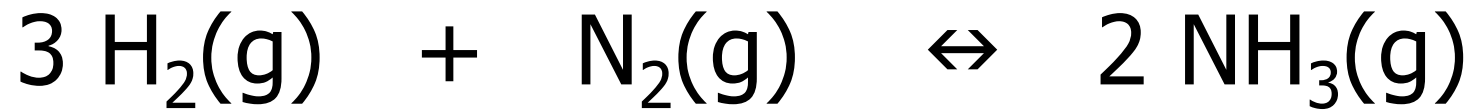
Equilibrium lies  
to the right  
(more products)

REACTANTS

PRODUCTS

GROUND  
FLOOR  
PRODUCTS





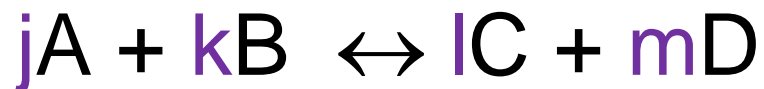
when equilibrium lies to the right:

there are more products than reactants  
(i.e. more  $\text{NH}_3$  than  $\text{H}_2$  and  $\text{N}_2$ )

## Law of Mass Action

# (Equilibrium Expression)

- For a reaction:



- The law of mass action is represented by the Equilibrium Expression: where K is the Equilibrium Constant.

$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

This is not the same as the rate law!!!

# QUESTION

One of the environmentally important reactions involved in acid rain production has the following equilibrium expression. From the expression, what would be the balanced chemical reaction?

Note: all components are in the gas phase.

$$K = [\text{SO}_3]/([\text{SO}_2][\text{O}_2]^{1/2})$$

- A.  $\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + 2\text{O}_2(\text{g})$
- B.  $\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$
- C.  $\text{SO}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$
- D.  $\text{SO}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$



# Answer

D) properly shows the product  $\text{SO}_3$  on the right and incorporates the previous exponents from the equilibrium expression as coefficients in the chemical equation.

# Properties of K

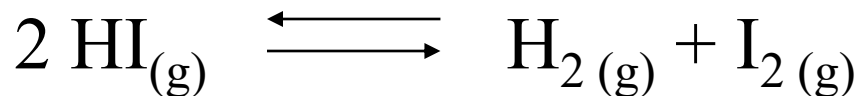
- ☐ 1) If a reaction is re-written where the reactants become products and products-reactants, the new Equilibrium Expression is the reciprocal of the old.

$$K_{\text{new}} = 1 / K_{\text{original}}$$

- ☐ 2) When the entire equation for a reaction is multiplied by n,

$$K_{\text{new}} = (K_{\text{original}})^n$$

# Calculating $K_c$ from Concentration Data



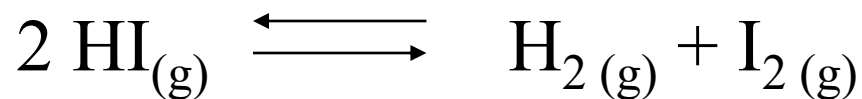
4.00 mol HI was placed in a 5.00 L vessel at 458°C, the equilibrium mixture was found to contain 0.442 mol I<sub>2</sub>. What is the value of  $K_c$ ? Calculate the molar concentrations, and put them into the equilibrium expression to find it's value.

$$\text{Starting conc. of HI} = \frac{4.00 \text{ mol}}{5.00 \text{ L}} = 0.800 \text{ M}$$

$$\text{Equilibrium conc. of I}_2 = \frac{0.442 \text{ mol}}{5.00 \text{ L}} = 0.0884 \text{ M}$$

Conc. (M)	$2\text{HI}_{(g)}$	$\rightleftharpoons$	$\text{H}_{2(g)}$	$\text{I}_{2(g)}$
Initial	0.800		0	0
Change	- 2x		x	x
Equilibrium	0.800 - 2x		x	x = 0.0884

# Calculating $K_c$ from Concentration Data (continued)



$$[\text{HI}] = M = (0.800 - 2 \times 0.0884) M = 0.623 M$$

$$[\text{H}_2] = x = 0.0884 M = [\text{I}_2]$$

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.0884)(0.0884)}{(0.623)^2} = 0.0201$$

*What does the value 0.0201 mean? Does the decomposition proceed very far under these temperature conditions?*

**Note:** *The initial concentrations, and one at equilibrium were provided. The others that were needed to calculate the equilibrium constant were deduced algebraically.*

# *homework*

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- Questions 9-11 on page 73

# LE CHATELIER'S PRINCIPLE

- If the conditions of an equilibrium are changed, the position of the equilibrium moves to oppose the change.

**Make it hotter** – equilibrium moves to cool it.

**Make it colder** – equilibrium moves to heat it.

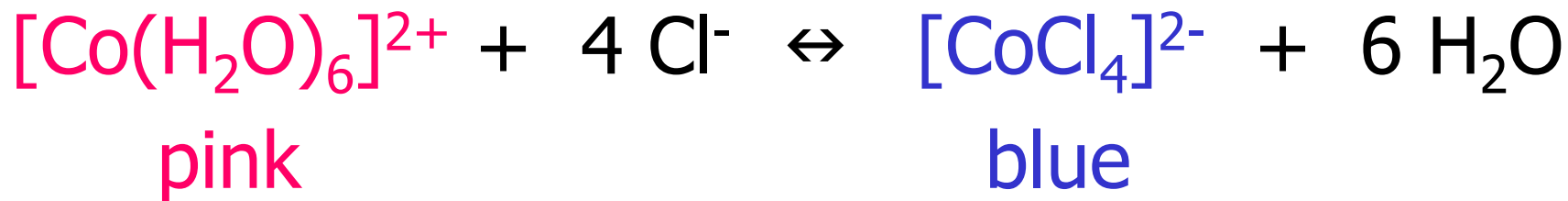
**Raise the pressure** – equilibrium moves to lower it.

**Lower the pressure** – equilibrium moves to raise it.

**Add a chemical** – equilibrium moves to get rid of it.

**Remove a chemical** – equilibrium moves to make more.

# THE EFFECT OF CONCENTRATION

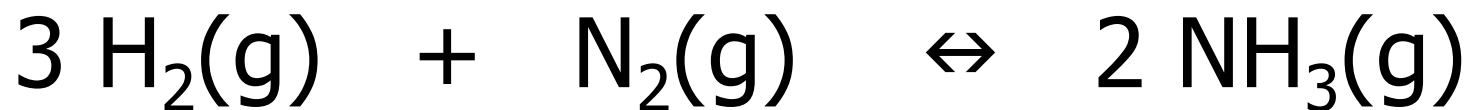


add  $\text{Cl}^-$

add  $\text{H}_2\text{O}$

add  $\text{Cl}^-$

# THE EFFECT OF TEMPERATURE



forward reaction is exothermic:  $-76 \text{ kJ mol}^{-1}$

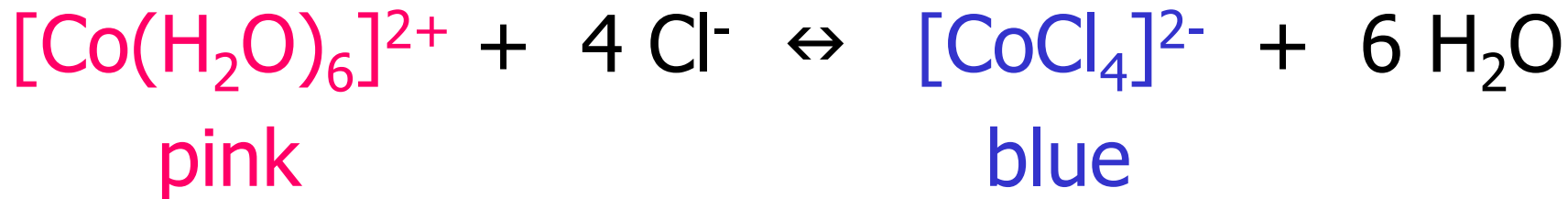
reverse reaction is endothermic :  $+76 \text{ kJ mol}^{-1}$

If the temperature is raised – the equilibrium moves to cool down by moving in the endothermic direction.

If the temperature is lowered – the equilibrium moves to heat up by moving in the exothermic direction.



# THE EFFECT OF TEMPERATURE



forward reaction is endothermic

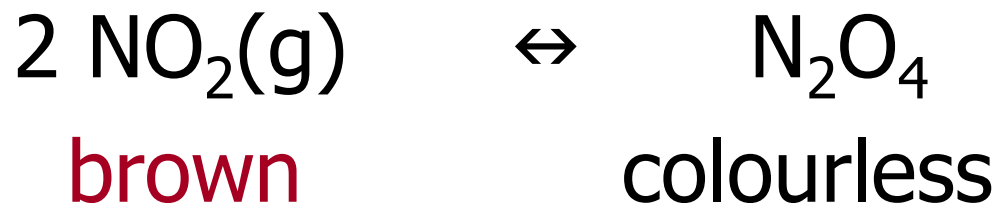
reverse reaction is exothermic

heat up the equilibrium mixture:

cool down the equilibrium mixture:



# THE EFFECT OF TEMPERATURE



forward reaction is exothermic  
reverse reaction is endothermic

heat up the equilibrium mixture:

cool down the equilibrium mixture:



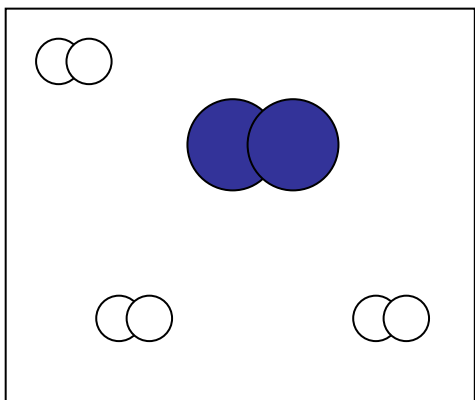
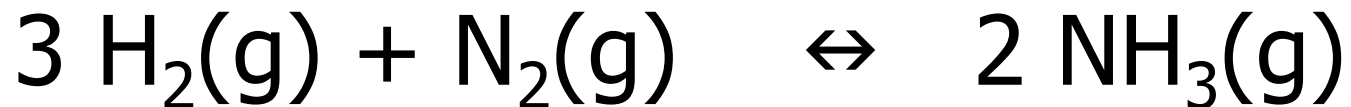
high  
temperature

low  
temperature

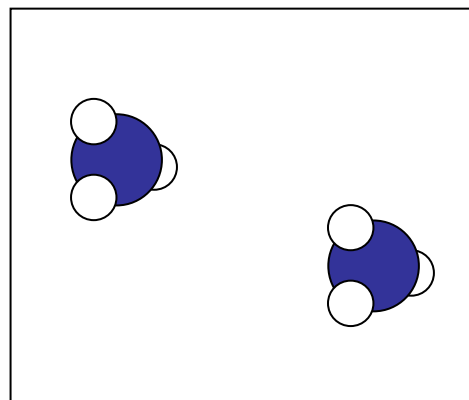




# THE EFFECT OF PRESSURE



4 molecules  
More pressure



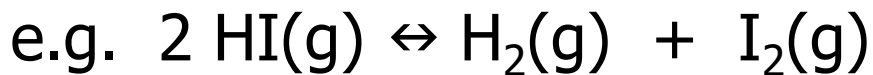
2 molecules  
Less pressure

# THE EFFECT OF PRESSURE

If the pressure is raised – the equilibrium moves to reduce the pressure by moving to the side with fewest gas molecules.

If the pressure is lowered – the equilibrium moves to increase the pressure by moving to the side with most gas molecules.

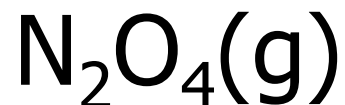
If there are the same number of gas molecules on both sides of the equation, then the equilibrium cannot move to oppose the change.



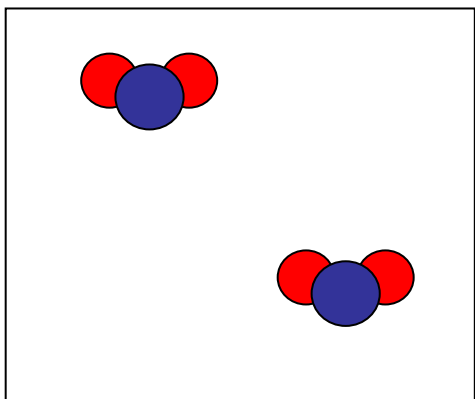
# THE EFFECT OF PRESSURE



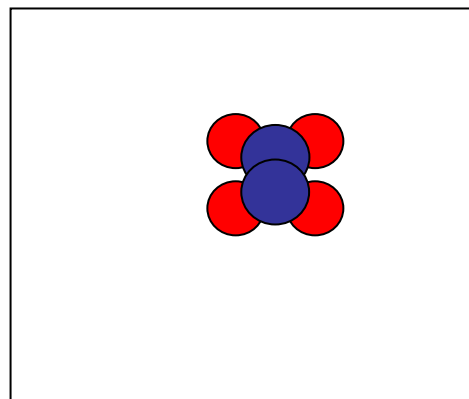
brown



colourless



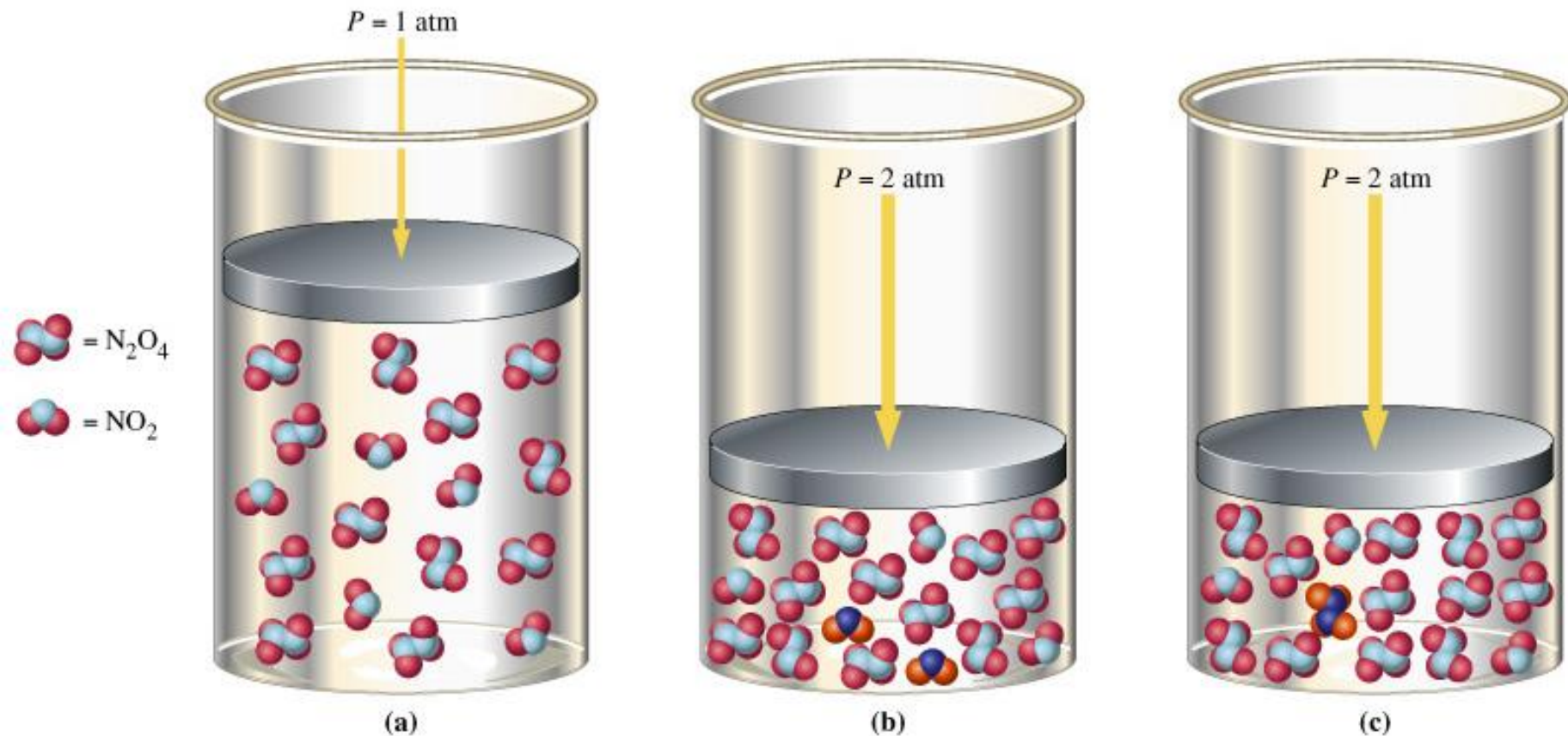
2 molecules  
More pressure



1 molecule  
Less pressure







- (a) Equilibrium is established at a total pressure of 1 atm. For every 17 molecules, 5 are  $\text{NO}_2$  and 12 are  $\text{N}_2\text{O}_4$ .
- (b) The total pressure is increased to 2 atm. Momentarily, the same 17 molecules are present.
- (c) The system accommodates to the reduced volume. Two  $\text{NO}_2$  molecules combine to form one  $\text{N}_2\text{O}_4$  molecule. The new equilibrium has 16 molecules in place of the original 17. Of these, 3 are  $\text{NO}_2$  and 13 are  $\text{N}_2\text{O}_4$ .

[Notice that in every case the same total number of atoms is present: 29 N atoms and 58 O atoms.]



# Homework

- Page 2.2
- 1,3,4,5,6,8,
- On your book