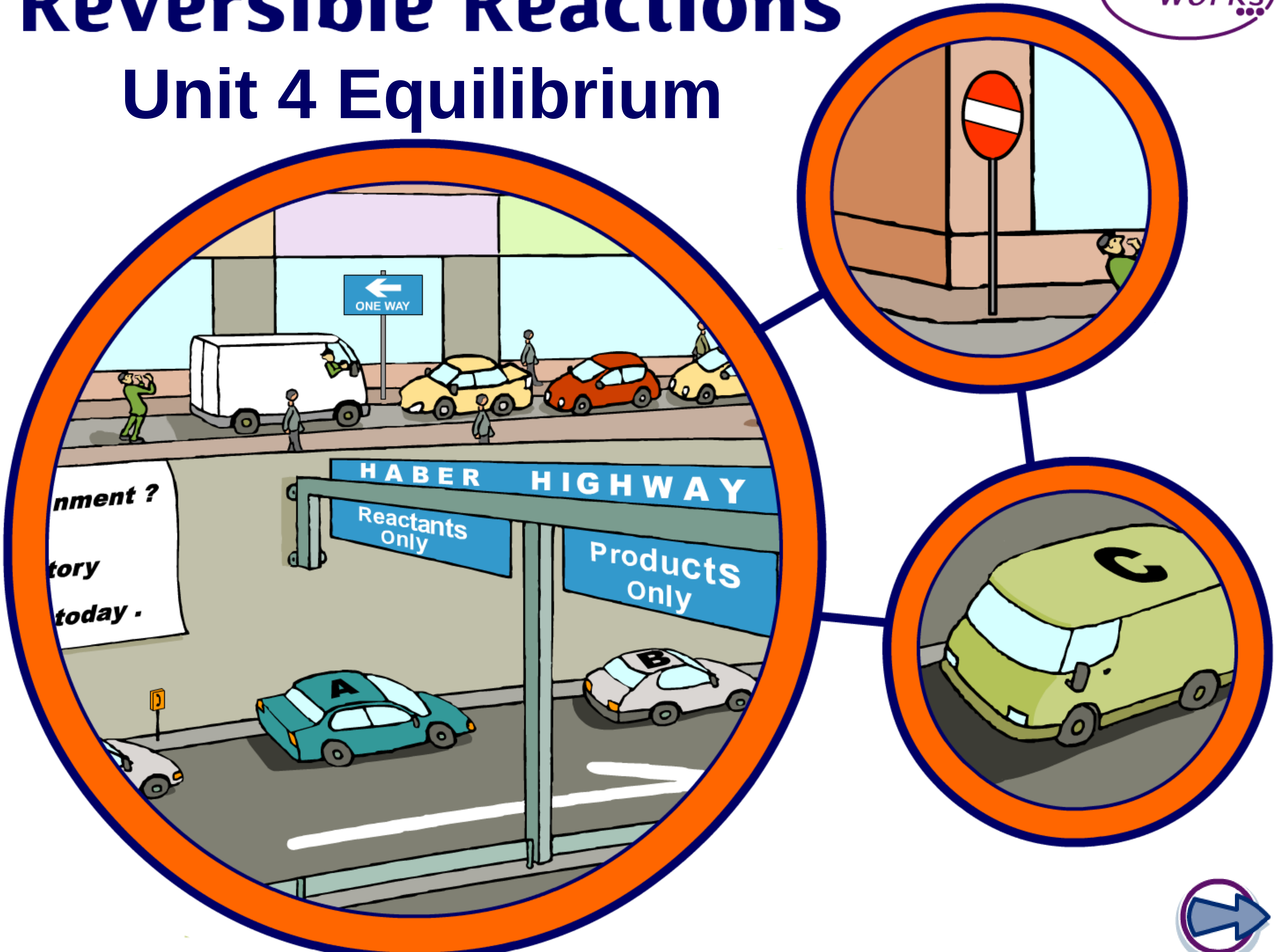
Reversible Reactions

Unit 4 Equilibrium



Irreversible reactions

Most chemical reactions are considered irreversible – the products that are made cannot readily be changed back into their reactants.

For example, when wood burns it is impossible to turn it back into unburnt wood again!

Similarly, when magnesium reacts with hydrochloric acid to form magnesium chloride and hydrogen, it is not easy to reverse the reaction and obtain the magnesium.

What are reversible reactions?

Reversible reactions occur when the backwards reaction (products → reactants) takes place relatively easily under certain conditions.

$$A + B \rightleftharpoons C + D$$

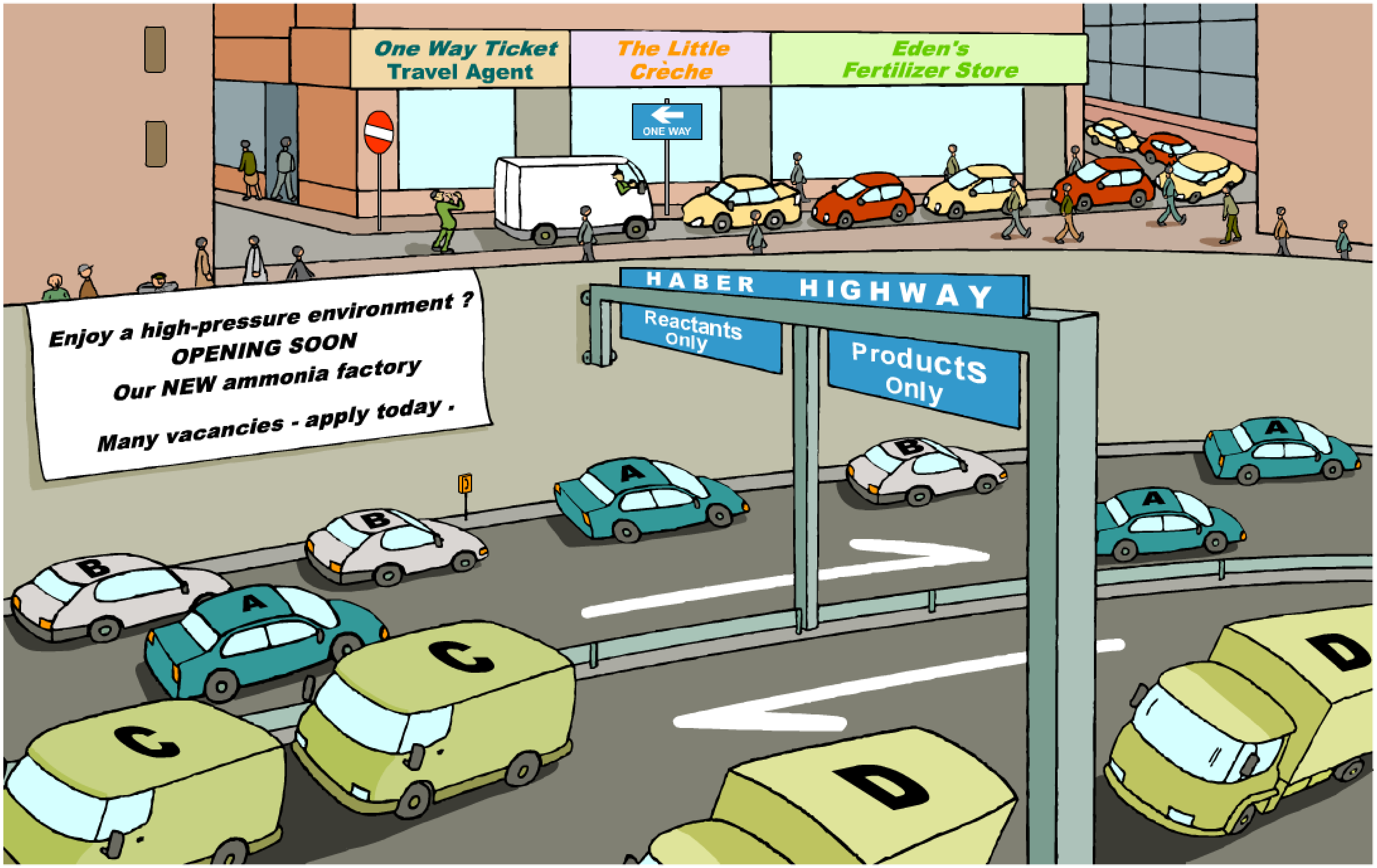
(reactants) *(products)*

For example, during a reversible reaction reactants **A** and **B** react to make products **C** and **D**.

However, products **C** and **D** can also undergo the reverse reaction, and react together to form reactants **A** and **B**.

Reversible and irreversible reactions

What kind of reactions are reversible and irreversible?



Reversible biochemical reactions

Many biochemical reactions (those that take place inside organisms) are reversible.

For example, in the lungs, oxygen binds to haemoglobin (Hb) in red blood cells to create oxyhaemoglobin.

When the red blood cells are transported to tissues, the oxyhaemoglobin dissociates back to haemoglobin and oxygen.

$$Hb + 4O_2 \rightleftharpoons Hb.4O_2$$

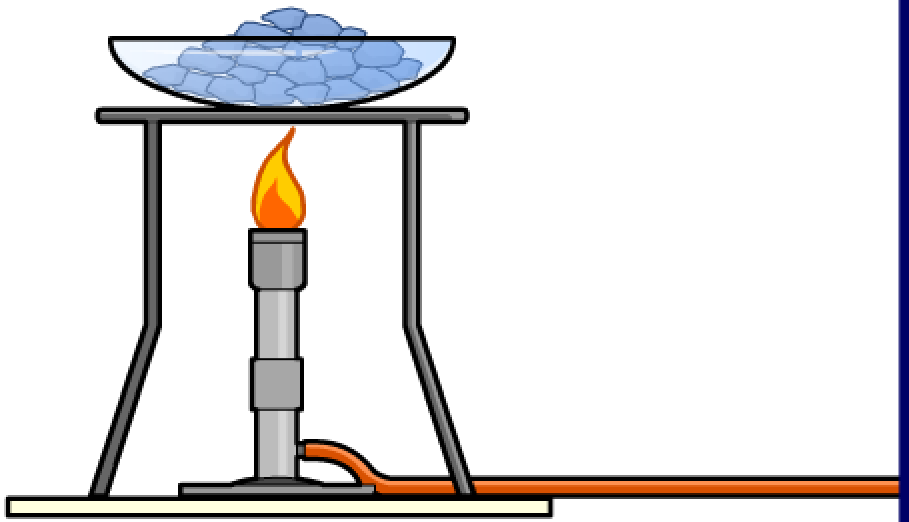
There are also some very important industrial reactions, like the Haber process, that are reversible.

Heating copper sulfate

What happens when hydrated copper sulfate is heated?

Hydrated copper (II) sulfate undergoes a reversible reaction when heated.

Click "**play**" to see what happens in this reaction.

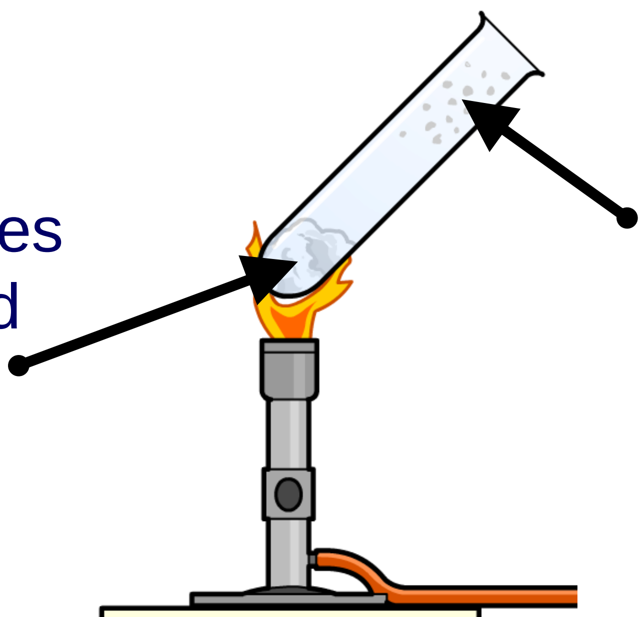


Heating ammonium chloride

An ammonium salt can be made by reacting ammonia with an acid. Some of the salt will decompose back into the reactants when heated.

ammonia	+	hydrogen chloride	$\rightleftharpoons$	ammonium chloride
NH_3 (g)	+	HCl (g)	$\rightleftharpoons$	NH_4Cl (s)

NH_4Cl decomposes back into NH_3 and HCl gases when heated



NH_4Cl reforms in the cooler part of the test tube

Example of a Reversible Reaction

- Heat + $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

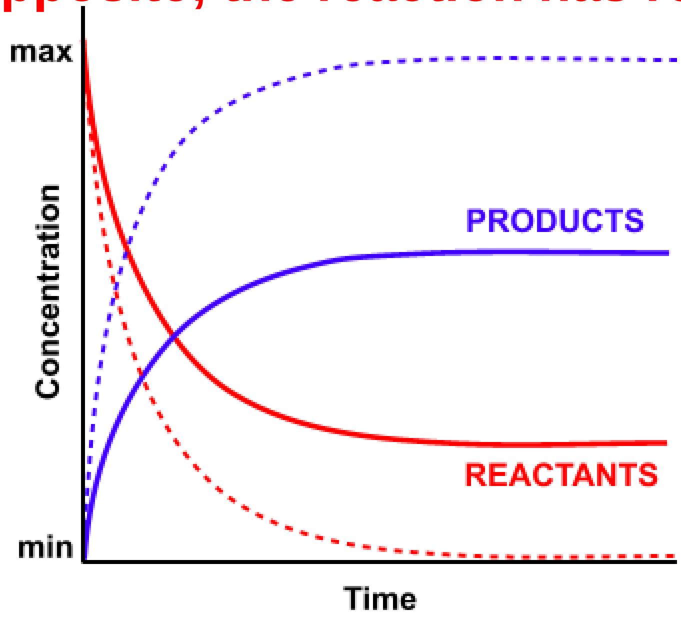
Colder temp

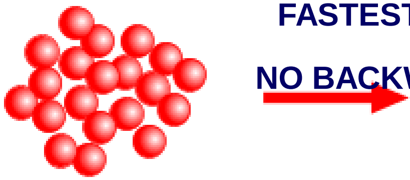
Warmer temp

http://www.youtube.com/watch?v=j1ALRRos-AA

EQUILIBRIUM REACTIONS

Initially, there is no backward reaction but, as products form, it speeds up and provided the temperature remains constant there will come a time when the backward and forward reactions are equal and opposite; the reaction has reached equilibrium.

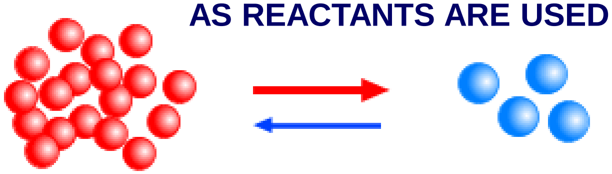




FASTEST AT THE START

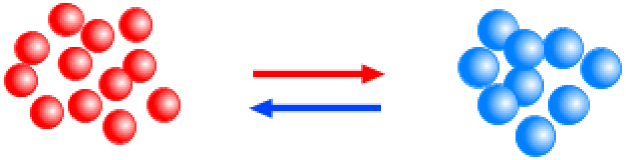
NO BACKWARD REACTION

FORWARD REACTION SLOWS DOWN AS REACTANTS ARE USED UP



BACKWARD REACTION

STARTS TO INCREASE



In an equilibrium reaction, not all the reactants end up as products; there is not a 100% conversion.

BUT IT DOESN'T MEAN THE REACTION

IS STUCK IN THE MIDDLE

AT EQUILIBRIUM THE BACKWARD AND FORWARD REACTIONS ARE EQUAL AND OPPOSITE

IMPORTANT REMINDERS

- a reversible chemical reaction is a dynamic process
- everything may appear stationary but the reactions are moving both ways
- the position of equilibrium can be varied by changing certain conditions

Trying to get up a "down" escalator gives an excellent idea of a non-chemical situation involving dynamic equilibrium.

Summary: When a chemical equilibrium is established ...

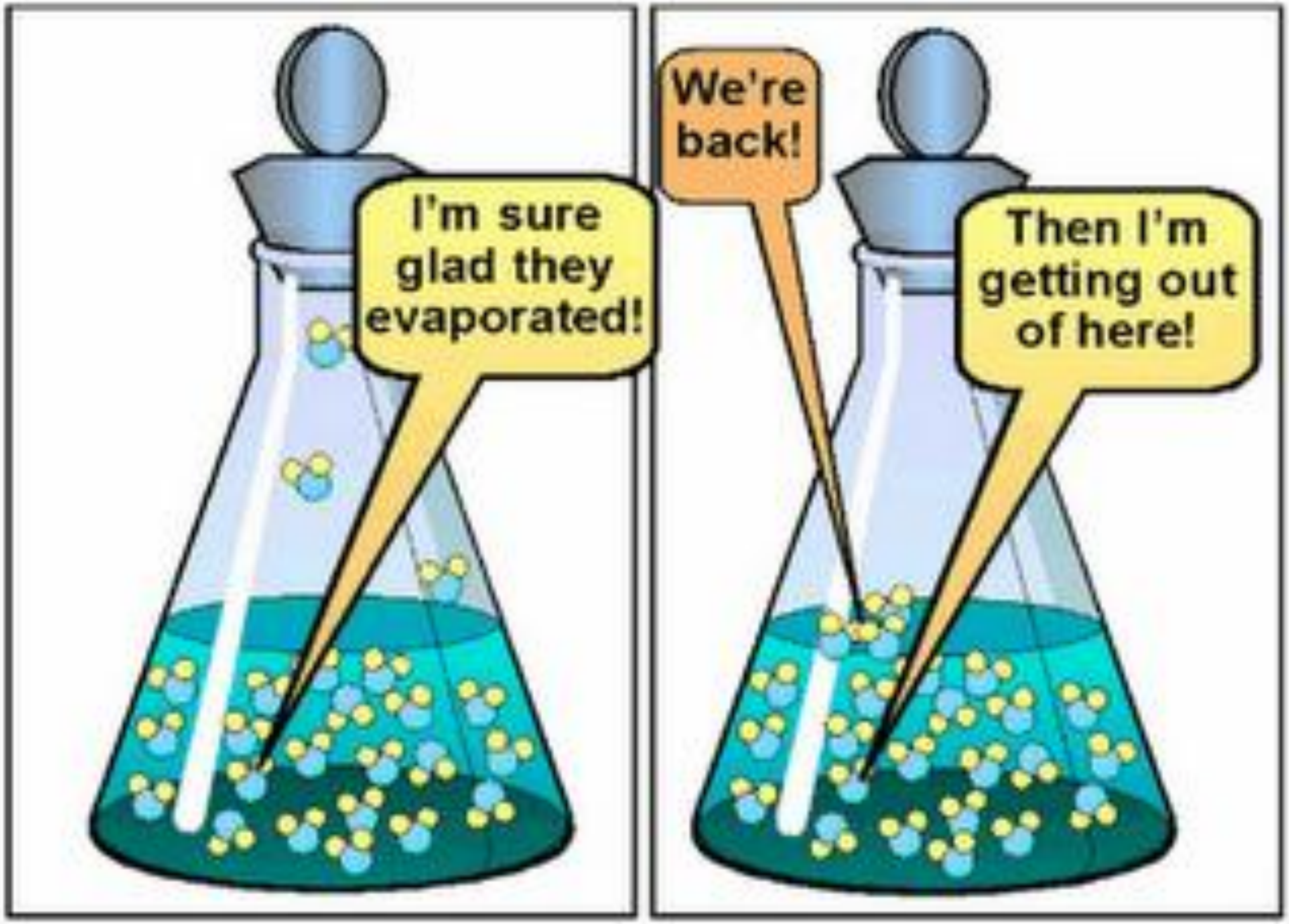
- both the reactants and the products are present at all times
- the equilibrium can be approached from either side
- the reaction is dynamic - it is moving forwards and backwards
- the concentrations of reactants and products remain constant

Analogy to Chemical Equilibrium

- Two yards with a lemon tree on the border. Older and younger person throwing lemons back and forth.

Amount on each side is constant but not equal.

Equilibrium in a Closed System



THE EQUILIBRIUM LAW

Simply states "If the concentrations of all the substances present at equilibrium are raised to the power of the number of moles they appear in the equation, the product of the concentrations of the products divided by the product of the concentrations of the reactants is a constant, provided the temperature remains constant"

See example on the next slide.

There are several forms of the constant; all vary with temperature.

K_c the equilibrium values are expressed as concentrations of mol/L

Other examples include Ksp, Ka, Kb, Kw

THE EQUILIBRIUM CONSTANT K_c

for an equilibrium reaction of the form...

$$aA + bB \rightleftharpoons cC + dD$$

then (at constant temperature), $\frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} = K_c$

where [ ] denotes the equilibrium concentration in mol/L

and K_c is a constant **known as** **the Equilibrium Constant**

Do not include solids and liquids in the expression.

Example $Fe^{3+}(aq) + NCS^{-}(aq) \rightleftharpoons FeNCS^{2+}(aq)$

$$K_c = \frac{[FeNCS^{2+}]}{[Fe^{3+}][NCS^{-}]}$$

Group Work

- Write the equilibrium constant expressions (K_c) for the following reactions:
  - ① $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
  - ② $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
  - ③ $2Na(s) + Cl_2(g) \rightleftharpoons 2NaCl(s)$

① $K_c = [CH_4][H_2O]/[CO][H_2]^3$

② $K_c = [N_2][H_2]^3/[NH_3]^2$

③ $K_c = 1/[Cl_2]$

VALUE OF K_c

AFFECTED by - a change of temperature

NOT AFFECTED by - a change in concentration of reactants or products

- a change of pressure

- adding a catalyst

The Equilibrium Constant

The Magnitude of Equilibrium Constants

- The equilibrium constant, *K*, is the ratio of products to reactants.
- Therefore, the larger *K* the more products are present at equilibrium.
- Conversely, the smaller *K* the more reactants are present at equilibrium.
- If $K >> 1$, then products dominate at equilibrium and equilibrium favours the right of the reaction.
- If $K << 1$, then reactants dominate at equilibrium and equilibrium lies to the left side of the reaction.

Manipulation of K

- $2H_2O \rightleftharpoons 2H_2 + O_2$

  $K_1 = [H_2]^2[O_2]/[H_2O]^2$

- $H_2O \rightleftharpoons H_2 + 1/2\,O_2$

  $K_2 = K_1^{1/2} = ([H_2]^2[O_2]/[H_2O]^2)^{1/2} = [H_2][O_2]^{1/2}/[H_2O]$

- $2H_2 + O_2 \rightleftharpoons 2H_2O$

  $K_3 = K_1^{-1} = ([H_2]^2[O_2]/[H_2O]^2)^{-1} = [H_2O]^2/ [H_2]^2[O_2]$

Reversible or irreversible?

Are these reactions reversible or irreversible?

reversible	irreversible

Haber process

? C solve

True or false?

Are these statements about dynamic equilibrium true or false?

1.	The position of equilibrium can be changed.	
2.	The forward and backward reactions take place at the same rate.	
3.	The equilibrium is always at a half-way point.	
4.	Only reversible reactions reach equilibrium.	
5.	Adding a catalyst changes the position of dynamic equilibrium.	
6.	Dynamic equilibrium can only take place in a closed system.	

true false

? solve

- **Once a system has reached equilibrium, are the following true or false?**
  - The reaction is finished, no more products are forming.
  - The concentrations of the reactants and the products are equal.
  - The concentrations are no longer changing.
  - The reaction is not over, but will continue forever if isolated.
  - The speed at which products are made equals the speed at which reactants form.

- **Once a system has reached equilibrium, are the following true or false?**
  - **The reaction is finished, no more products are forming. ____false________**
  - **The concentrations of the reactants and the products are equal. ____false________**
  - **The concentrations are no longer changing. ____false__**
  - **The reaction is not over, but will continue forever if isolated. ____true_____**
  - **The speed at which products are made equals the speed at which reactants form. ___true___**

More Questions

1. What is equal at equilibrium?
2. What general information can be gathered by observing the magnitude of the equilibrium constant?
3. Write the expression for K_{eq} for the reaction:

   2 NO (g) + Cl2 (g) ↔ 2 NOCl (g)
4. Write the K_{eq} for:

   2 K3PO4 (aq) + 3 Ca(NO3)2 (aq) ↔ 6 KNO3 (aq) + Ca3(PO4)2 (s)

ANSWERS

1. What is equal at equilibrium? **rate forward = rate reverse**

2. What general information can be gathered by observing the magnitude of the equilibrium constant?

- **Whether the reactants or products are favoured.**

3. Write the expression for K_{eq} for the reaction:

2 NO (g) + Cl2 (g) ↔ 2 NOCl (g)

$$K_{eq} = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$$

4. Write the K_{eq} for:

2 K3PO4 (aq) + 3 Ca(NO3)2 (aq) ↔ 6 KNO3 (aq) + Ca3(PO4)2 (s)

$$K_{eq} = \frac{[KNO_3]^6}{[K_3PO_4]^2[Ca(NO_3)_2]^3}$$

More Questions

5. Write the expression for K_{eq} for the reaction : $H_2 (g) + Br_2 (l) \leftrightarrow 2 HBr (g)$
6. Write the expression for K_{eq} for the reaction: $CO_2 (g) + CaO (s) \leftrightarrow CaCO_3 (s)$
7. For the reaction: $SiH_4 (g) + 2 O_2 (g) \leftrightarrow SiO_2 (g) + 2 H_2O (l)$

a) Write the equilibrium expression for the forward reaction.

b) Write the equilibrium expression for the reverse reaction

ANSWERS

5. Write the expression for K_{eq} for the reaction :

H2 (g) + Br2 (l) ↔ 2 HBr (g)

$$K_{eq} = \frac{[HBr]^2}{[H_2]}$$

6. Write the expression for K_{eq} for the reaction:

CO2 (g) + CaO (s) ↔ CaCO3 (s)

$$K_{eq} = \frac{1}{[CO_2]}$$

7. For the reaction: SiH4 (g) + 2 O2 (g) ↔ SiO2 (g) + 2 H2O (l)

a) Write the equilibrium expression for the forward reaction.

$$K_{eq} = \frac{[SiO_2]}{[SiH_4][O_2]^2}$$

b) Write the equilibrium expression for the reverse reaction

$$K_{eq}' = \frac{[SiH_4][O_2]^2}{[SiO_2]} = \frac{1}{K_{eq}}$$

More Questions – calculating K and Q (given concentrations)

c) What is the equilibrium constant in the forward direction if $[SiH_4]$ = 0.45M; $[O_2]$ = 0.25M; and $[SiO_2]$ = 0.15M at equilibrium?

d) What is the equilibrium constant in the reverse reaction?

e) If $[SiH_4]$ = 0.34M; $[O_2]$ = 0.22M and $[SiO_2]$ = 0.35M, what would be the reaction quotient (Q) in the forward direction and which direction will the reaction go?

ANSWERS

c) What is the equilibrium constant in the forward direction if $[SiH_4]$ = 0.45M; $[O_2]$ = 0.25M; and $[SiO_2]$ = 0.15M at equilibrium?

$$K_{eq} = \frac{[SiO_2]}{[SiH_4][O_2]^2} = \frac{0.15}{(0.45)(0.25)^2} = 5.3$$

d) What is the equilibrium constant in the reverse reaction?

$$K_{eq}' = \frac{1}{5.3} = 0.19$$

e) If $[SiH_4]$ = 0.34M; $[O_2]$ = 0.22M and $[SiO_2]$ = 0.35M, what would be the reaction quotient (Q) in the forward direction and which direction will the reaction go?

$$Q = K_{eq} = \frac{0.35}{(0.34)(0.22)^2} = 21$$

$Q = 21 > K_C = 0.053$ then the reaction will go towards the reactants

Calculating Kc (given concentrations)

Ex. Calculate the equilibrium constant for this reaction:
$2\ PO_2Br\ (aq) \leftrightarrow 2\ PO_2\ (aq) + Br_2\ (aq)$ Given:
$[PO_2Br] = 0.0255M$, $[PO_2] = 0.155M$, and $[Br_2] = 0.00351M$ at equilibrium.

$$2\,PO_2Br \leftrightarrow 2\,PO_2 + Br_2 \qquad K_{eq} = \frac{[PO_2]^2[Br_2]}{[PO_2Br]^2}$$

$$K_{eq} = \frac{(0.155)^2(0.00351)}{(0.0255)^2} = 0.130$$

Calculations using ICE tables

- ICE tables are used to organize data
  - I = initial concentration
  - C = change in concentration
  - E = equilibrium concentration

- Can use this format to SOLVE for changes
  - Coefficients from balanced equation are used to determine the CHANGE
  - Can solve equation to find equilibrium concentrations

Ex. 1 For the reaction: H_2 (g) + F_2 (g) ↔ 2 HF (g), calculate all three equilibrium concentrations when initially $[H_2] = [F_2] = 0.200$ M and Kc = 64.0.

$$H_2 \quad + \quad F_2 \quad \leftrightarrow \quad 2\,HF \qquad K_{eq} = \frac{[HF]^2}{[H_2][F_2]} = 64.0$$

	H_2	F_2	2 HF
I	0.200	0.200	0
C	- x	- x	+ 2x
E	0.200 - x	0.200 - x	+ 2x

$$K_{eq} = \frac{(2x)^2}{(0.200 - x)(0.200 - x)} = 64.0 \quad \text{perfect square}$$

$$\sqrt{\frac{(2x)^2}{(0.200 - x)(0.200 - x)}} = \sqrt{64.0}$$

$$\frac{2x}{0.200 - x} = 8.00$$

$$2x = 1.60 - 8.00x$$

$$10.00x = 1.60$$

$$x = \frac{1.60}{10.00} = 0.160$$

$$\therefore [H_2]_{eq} = [F_2]_{eq} = 0.200 - 0.160 = 0.040\text{ M and } [HF]_{eq} = 2(0.160) = 0.320\text{ M}$$

Ex. 2 For the reaction, $COCl_2(g) \leftrightarrow CO(g) + Cl_2(g)$, calculate all three equilibrium concentrations when Kc = 0.680 with initial concentrations: [CO] = 0.500 mol/L and $[Cl_2]$ = 1.00 mol/L.

	$COCl_2$	$\leftrightarrow$	CO	+	Cl_2
I	0		0.500		1.00
C	+ x		- x		- x
E	x		0.500 - x		1.00 - x

$$K_{eq} = \frac{[CO][Cl_2]}{[COCl_2]} = 0.680$$

$$K_{eq} = \frac{(0.500 - x)(1.00 - x)}{x} = 0.680$$

$$0.500 - 1.50x + x^2 = 0.680\,x$$

$$x^2 - 2.18x + 0.500 = 0$$

$$a = 1 \quad b = -2.18 \quad c = 0.500$$

$$x = \frac{-(-2.18) \pm \sqrt{4.7524 - 2}}{2}$$

$$x = \frac{2.18 \pm 1.66}{2}$$

$$x = 1.92 \quad (\text{too big}) \quad \text{or} \quad x = 0.260$$

$$\therefore [COCl_2]_{eq} = 0.260M, [CO]_{eq} = 0.500 - 0.260 = 0.240\,M$$

$$\text{and } [Cl_2]_{eq} = 1.00 - 0.260 = 0.740\,M$$

Ex. 3 We place 0.0640 mol N_2O_4 (g) in a 4.00 L flask at 200 K. After reaching equilibrium, the concentration of NO_2(g) is 0.00300 mol/L. What is Kc for the reaction $N_2O_4(g) \leftrightarrow 2\,NO_2(g)$?

$$N_2O_4 \quad \leftrightarrow \quad 2\,NO_2 \qquad K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

	N_2O_4	$2\,NO_2$
I	0.0160	0
C	- x	+ 2x
E	0.0160	+ 2x

$$\text{but } [NO_2]_{eq} = 0.00300\text{ M}$$

$$2x = 0.00300 \quad \therefore x = 0.00150$$

$$K_{eq} = \frac{(0.00300)^2}{(0.0160 - 0.00150)} = 6.21 \times 10^{-4}$$

Problems Using Approximation

To avoid using the quadratic formula, it may be possible to approximate.

First do the following check:

If the initial concentration (the smallest value if there's more than one) divided by the K_c is greater than 500, then you may approximate.

This means that you may omit any "plus or minus x values" in the equilibrium equation.

Ex. 4 Carbonyl bromide decomposes to carbon monoxide and bromine: $COBr_2(g) \leftrightarrow CO(g) + Br_2(g)$ Kc is 1.90×10^{-4} at 73°C. If an initial concentration of 0.330 mol/L $COBr_2$ is allowed to reach equilibrium, what are the equilibrium concentrations of $COBr_2$, CO, and Br_2?

$$COBr_2 \leftrightarrow CO + Br_2 \qquad K_{eq} = \frac{[CO][Br_2]}{[COBr_2]} = 1.90 \times 10^{-4}$$

	$COBr_2$	CO	Br_2
I	0.300	0	0
C	-x	+x	+x
E	0.300 - x	+x	+x

Check for approximation:

$$\frac{0.300}{1.90 \times 10^{-4}} = 1579 > 500$$

$$\therefore 0.300 - x \cong 0.300$$

$$K_{eq} = \frac{(+x)(+x)}{0.300} = 1.90 \times 10^{-4}$$

$$x^2 = 5.70 \times 10^{-5}$$

$$x = 7.55 \times 10^{-3}$$

$$\therefore [COBr_2]_{eq} = 0.300 - 0.00755 = 0.292\ M, [CO]_{eq} = [Cl_2]_{eq} = 0.00755\ M$$

Ex. 5 PCl_5 decomposes into PCl_3 and Cl_2 gas. What is the initial concentration of PCl_5 if at equilibrium the concentration of chlorine gas is 0.500mol/L? Given: Kc = 10.00 *(Hint: Use an ICE table)*

$$PCl_5 \leftrightarrow PCl_3 + Cl_2 \qquad K_{eq} = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 10.00$$

	PCl_5	PCl_3	Cl_2
I	y	0	0
C	-x	+x	+x
E	y-x	+x	+x

$$\text{and } [Cl_2]_{eq} = 0.500M = x$$

$$K_{eq} = \frac{(0.500)(0.500)}{y - 0.500} = 10.00$$

$$0.25 = 10.00y - 5.00$$

$$10.00y = 5.25$$

$$y = 0.525$$

$$[PCl_5]_i = 0.525\,M \text{ and } [PCl_5]_{eq} = 0.525 - 0.500 = 0.025\,M$$

FOLLOW-UP PROBLEM 17.8 The decomposition of HI at low temperature was studied by injecting 2.50 mol of HI into a 10.32-L vessel at 25°C. What is $[H_2]$ at equilibrium for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$; $K_c = 1.26\times10^{-3}$?

Note the moles into a 10.32 L vessel stuff ... calculate molarity.

Starting concentration of HI: 2.5 mol/10.32 L = 0.242 M

$$2\,HI \rightleftharpoons H_2 + I_2 \qquad Kc = \frac{[H_2][I_2]}{[HI]^2}$$

	2 HI	H_2	I_2
Initial:	0.242 M	0	0
Change:	-2x	+x	+x
Equil:	0.242-2x	x	x

$$Kc = \frac{[x][x]}{[0.242-2x]^2} = \frac{x^2}{[0.242-2x]^2} = 1.26x10^{-3}$$

What we are asked for here is the equilibrium concentration of H_2 … otherwise known as x. So, we need to solve this beast for x.

And yes, it's a *quadratic equation.* Doing a bit of rearranging:

$$\frac{x^2}{[0.242 - 2x]^2} = 1.26x10^{-3}$$

$$x^2 = 1.26x10^{-3}[0.242 - 2x]^2$$

$$= 1.26x10^{-3}[0.0586 - 0.968x + 4x^2]$$

$$= 7.38x10^{-5} - 1.22x10^{-3}x + 5.04x10^{-3}x^2$$

$$0.995x^2 + 1.22x10^{-3}x - 7.38x10^{-5} = 0$$

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

x = 0.00802 or –0.00925

Since we are using this to model a real, physical system, we reject the negative root.

The $[H_2]$ at equil. is 0.00802 M.

FOLLOW-UP PROBLEM 17.9 In a study of halogen bond strengths, 0.50 mol of I_2 was heated in a 2.5-L vessel, and the following reaction occurred: $I_2(g) \rightleftharpoons 2I(g)$.
(a) Calculate $[I_2]$ and [I] at equilibrium at 600 K; $K_c = 2.94\times10^{-10}$.
(b) Calculate $[I_2]$ and [I] at equilibrium at 2000 K; $K_c = 0.209$.

Initial Concentration of I_2: 0.50 mol/2.5L = 0.20 M

	$I_2 \rightleftharpoons$	2 I
Initial	0.20	0
change	-x	+2x
equil:	0.20-x	2x

$$Keq = \frac{[I]^2}{[I_2]} = 2.94x10^{-10}$$

$$= \frac{[2x]^2}{[0.20-x]} = 2.94x10^{-10}$$

Initial concentration divided by Equilibrium constant is greater than 500 so approximation will work here.

With an equilibrium constant that small, whatever x is, it's near zero, and 0.20 minus zero is 0.20 (like a million dollars minus a nickel is still a million dollars).

0.20 – x is the same as 0.20

$$\frac{[2x]^2}{0.20} = 2.94x10^{-10}$$

x = 3.83 x 10^{-6} M

FOLLOW-UP PROBLEM 17.9 In a study of halogen bond strengths, 0.50 mol of I_2 was heated in a 2.5-L vessel, and the following reaction occurred: $I_2(g) \rightleftharpoons 2I(g)$.
(a) Calculate $[I_2]$ and [I] at equilibrium at 600 K; $K_c = 2.94 \times 10^{-10}$.
(b) Calculate $[I_2]$ and [I] at equilibrium at 2000 K; $K_c = 0.209$.

Initial Concentration of I_2: 0.50 mol/2.5L = 0.20 M

	$I_2 \rightleftharpoons$	2 I
Initial	0.20	0
change	-x	+2x
equil:	0.20-x	2x

$$Keq = \frac{[I]^2}{[I_2]} = 0.209$$

$$= \frac{[2x]^2}{[0.20 - x]} = 0.209$$

Initial concentration divided by equilibrium constant is NOT greater than 500 so approximation is not possible.

Looks like this one has to proceed through the quadratic ...

"When a change is applied to a system in dynamic equilibrium, the system reacts in such a way as to oppose the effect of the change."

1. CONCENTRATION

The **equilibrium constant is not affected by a change in concentration** at constant temperature. To maintain the constant, the composition of the equilibrium mixture changes.

If you increase the concentration of a substance, the value of K_c will theoretically be affected. As **it must remain constant at a particular temperature**, the concentrations of the other species change to keep the constant the same.

CONCENTRATION

example $CH_3CH_2OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

the equilibrium constant $K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3CH_2OH]\,[CH_3COOH]} = 4$ (at 298K)

Increasing $[CH_3CH_2OH]$

- will make the bottom line larger so K_c will be smaller
- to keep it constant, some CH_3CH_2OH reacts with CH_3COOH
- this reduces the value of the bottom line and increases the top
- eventually the value of the constant will be restored

Decreasing $[H_2O]$

- will make the top line smaller
- some CH_3CH_2OH reacts with CH_3COOH to replace the H_2O
- more $CH_3COOC_2H_5$ is also produced
- this reduces the value of the bottom line and increases the top

SUMMARY of CONCENTRATION

REACTANTS $\rightleftharpoons$ PRODUCTS

THE EFFECT OF CHANGING THE CONCENTRATION ON THE POSITION OF EQUILIBRIUM	
INCREASE CONCENTRATION OF A REACTANT	EQUILIBRIUM MOVES TO THE RIGHT
DECREASE CONCENTRATION OF A REACTANT	EQUILIBRIUM MOVES TO THE LEFT
INCREASE CONCENTRATION OF A PRODUCT	EQUILIBRIUM MOVES TO THE LEFT
DECREASE CONCENTRATION OF A PRODUCT	EQUILIBRIUM MOVES TO THE RIGHT

Predict the effect of increasing the concentration of O_2 on the equilibrium position

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

EQUILIBRIUM MOVES TO RHS

Predict the effect of decreasing the concentration of SO_3 on the equilibrium position

EQUILIBRIUM MOVES TO RHS

2. PRESSURE

When studying the effect of a change in pressure, we consider the number of gaseous molecules only.

The more particles you have in a given volume, the greater the pressure they exert.

If you apply a greater pressure they will become more crowded (i.e. they are under a greater stress). However, if the system can change it will move to the side with fewer gaseous molecules - it is less crowded.

No change occurs when equal numbers of gaseous molecules appear on both sides.

THE EFFECT OF PRESSURE ON THE POSITION OF EQUILIBRIUM	
INCREASE PRESSURE	MOVES TO THE SIDE WITH FEWER GASEOUS MOLECULES
DECREASE PRESSURE	MOVES TO THE SIDE WITH MORE GASEOUS MOLECULES

Predict the effect of an increase of pressure on the equilibrium position of..

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ — MOVES TO RHS :- fewer gaseous molecules

$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ — NO CHANGE:- equal numbers on both sides

SUMMARY OF PRESSURE EFFECTS

- Pressure – changes in pressure will only affect gaseous atoms or molecules
  - Increasing the pressure will favour the direction that has ***fewer molecules***

$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

- For every two molecules of ammonia made, four molecules of reactant are used up – this equilibrium *shifts to the right* with an increase in pressure (or a decrease in volume)
- Also increasing volume is the same as decreasing pressure

3. TEMPERATURE

- temperature is the only thing that can change the value of the equilibrium constant.
- altering the temperature affects the rate of both backward and forward reactions
- it alters the rates to different extents
- the equilibrium thus moves producing a new equilibrium constant.
- the direction of movement depends on the sign of the enthalpy change (whether it is exothermic or endothermic)

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REACTION TYPE	ΔH	INCREASE TEMP	DECREASE TEMP
EXOTHERMIC	-	TO THE LEFT	TO THE RIGHT
ENDOTHERMIC	+	TO THE RIGHT	TO THE LEFT

TEMPERATURE

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EXOTHERMIC	-	TO THE LEFT	TO THE RIGHT
ENDOTHERMIC	+	TO THE RIGHT	TO THE LEFT

Predict the effect of a temperature increase on the equilibrium position of...

$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad \Delta H = +40\ kJ/mol$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -\ ive$

ANSWERS TO TEMPERATURE EXAMPLES

Predict the effect of a temperature increase on the equilibrium position of…

$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ $\Delta H = + 40 \text{ kJ mol}^{-1}$

- moves to the RHS

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -$ ive

- moves to the LHS

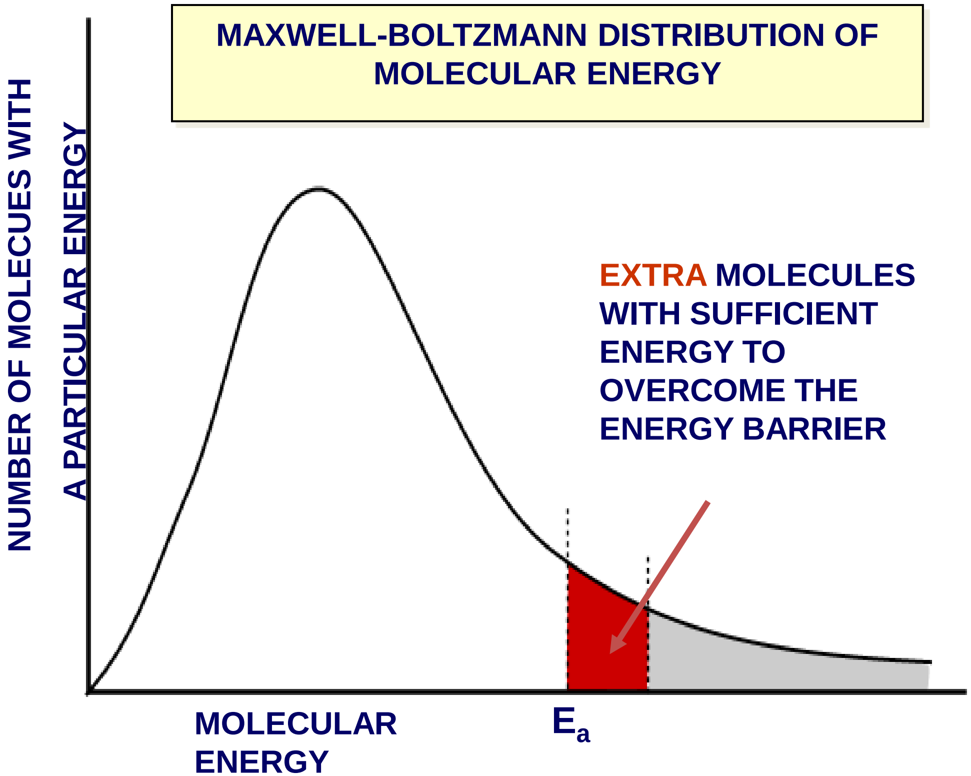
TEMPERATURE SUMMARY

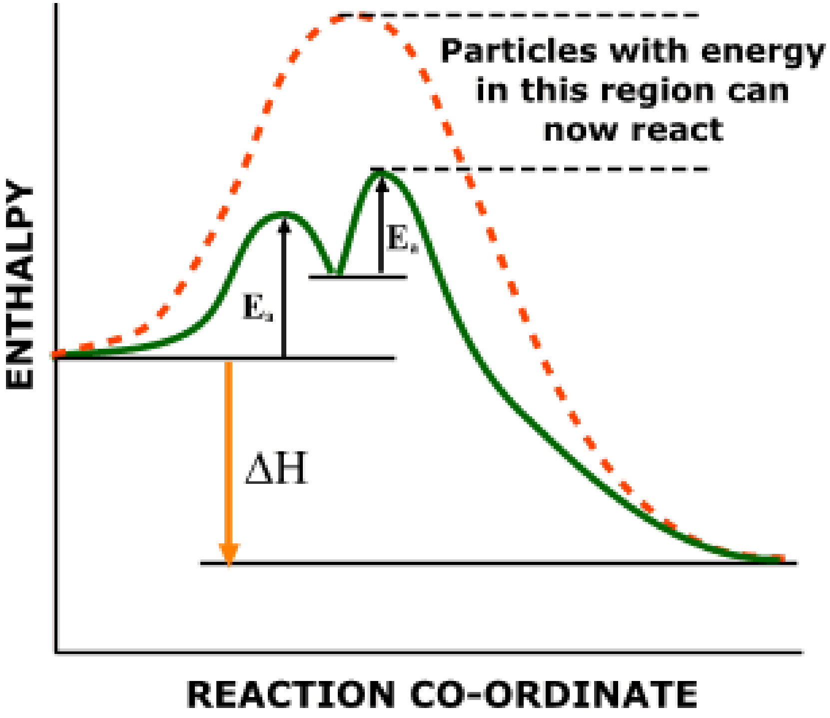
- Temperature – increasing the temperature causes the equilibrium position to shift in the direction that absorbs heat
  - If heat is one of the products (just like a chemical), it is part of the equilibrium
  - so cooling an exothermic reaction will produce more product, and heating it would shift the reaction to the reactant side of the equilibrium:

$$C + O_{2(g)} \leftrightarrow CO_{2(g)} + 393.5 \text{ kJ}$$

4. CATALYSTS

Catalysts work by providing an alternative reaction pathway involving a lower activation energy.





CATALYSTS

An increase in temperature is used to speed up chemical reactions but it can have an undesired effect when the reaction is reversible and exothermic.

In this case you get to the equilibrium position quicker but with a reduced yield because the increased temperature moves the equilibrium to the left.

In many industrial processes a compromise temperature is used (see Haber and Contact Processes). To reduce the problem one must look for a way of increasing the rate of a reaction without decreasing the yield i.e. with a catalyst.

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In many industrial processes a compromise temperature is used (see Haber and Contact Processes). To reduce the problem one must look for a way of increasing the rate of a reaction without decreasing the yield i.e. with a catalyst.

Adding a catalyst DOES NOT AFFECT THE POSITION OF EQUILIBRIUM. However, it does increase the rate of attainment of equilibrium. This is especially important in reversible, exothermic industrial reactions such as the Haber or Contact Processes where economic factors are paramount.

Opposing change

Whenever a change is made to a reversible reaction in dynamic equilibrium, the equilibrium will shift to try and oppose the change.

Condition	Effect
Temperature	Increasing the temperature shifts the equilibrium in the direction that takes in heat.
Concentration	Increasing the concentration of a substance shifts the equilibrium in the direction that produces less of that substance.
Pressure	Increasing the pressure shifts the equilibrium in the direction that produces less gas.

Exothermic and endothermic reactions

All reactions are **exothermic** (give out heat) in one direction and **endothermic** (take in heat) in the other.

If the temperature is **increased**:

- equilibrium shifts to **decrease** the temperature
- equilibrium shifts in the **endothermic** direction

If the temperature is **decreased**:

- equilibrium shifts to **increase** the temperature
- equilibrium shifts in the **exothermic** direction

Opposing changes in temperature

Nitrogen dioxide is in constant equilibrium with dinitrogen tetroxide. The forward reaction is **exothermic** and the backwards reaction is **endothermic**.

nitrogen dioxide	$\rightleftharpoons$	**dinitrogen tetroxide**
$2NO_2$ (g)	$\rightleftharpoons$	N_2O_4 (g)

What will happen if the temperature is **increased**?

- The equilibrium will shift to **decrease** the temperature, i.e. to the left (**endothermic**).
- More **NO_2** will be produced.

If the temperature is **decreased**, more **N_2O_4** will be produced.

Concentration and equilibrium

Changing the concentration of a substance affects the equilibrium of reversible reactions involving solutions.

increasing the concentration of **substance A**	**=**	equilibrium shifts to **decrease** the amount of substance A

decreasing the concentration of **substance A**	**=**	equilibrium shifts to **increase** the amount of substance A

Opposing changes in concentration (1)

Bismuth chloride reacts with water to produce a white precipitate of bismuth oxychloride and hydrochloric acid.

bismuth chloride	**+**	**water**	$\rightleftharpoons$	**bismuth oxychloride**	**+**	**hydrochloric acid**
$BiCl_3$ **(aq)**	**+**	H_2O **(l)**	$\rightleftharpoons$	**BiOCl (s)**	**+**	**2HCl (aq)**

What will happen if **more** H_2O is added?

- The equilibrium will shift to **decrease** the amount of water, i.e. to the right.
- More **BiOCl** and **HCl** will be produced.

If H_2O is **removed**, more $BiCl_3$ and H_2O will be produced.

Opposing changes in concentration (2)

Chlorine gas reacts with iodine chloride to produce iodine trichloride.

chlorine	**+**	**iodine chloride**	$\rightleftharpoons$	**iodine trichloride**
Cl_2 (g)	**+**	**ICl** (l)	$\rightleftharpoons$	ICl_3 (s)
pale green		**brown**		**yellow**

What effect will adding **more Cl_2** have on the colour of the mixture?

It will become **more yellow**.

What effect will **removing Cl_2** have on the colour of the mixture?

It will become **more brown**.

Pressure and equilibrium

Changing the pressure has an effect on the equilibrium of reversible reactions involving gases.

If the pressure is **increased:**

- equilibrium shifts to **decrease** the pressure
- equilibrium shifts in the direction of **fewest** molecules

If the pressure is **decreased:**

- equilibrium shifts to **increase** the pressure
- equilibrium shifts in the direction of **most** molecules

Opposing changes in pressure

Nitrogen dioxide is in constant equilibrium with dinitrogen tetroxide. Two molecules of nitrogen dioxide react to form one molecule of dinitrogen tetroxide.

nitrogen dioxide $\rightleftharpoons$ **dinitrogen tetroxide**

$$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

What will happen if the pressure is **increased**?

- The equilibrium will shift to **reduce** the number of molecules, i.e. to the right (only 1 molecule).
- More **N_2O_4** will be produced.

If the pressure is **decreased**, more **NO_2** will be produced.

Complete these sentences about dynamic equilibrium

1. A ______________ equilibrium will try to ______________ any change placed on it.

2. If a reaction that is exothermic from left to right is heated, ______________ product will be made.

3. If the pressure is ______________, the equilibrium will shift so there are ______________ molecules of gas.

minimizing	oppose	product	decreased
dynamic	less	more	maximizing

hide solve

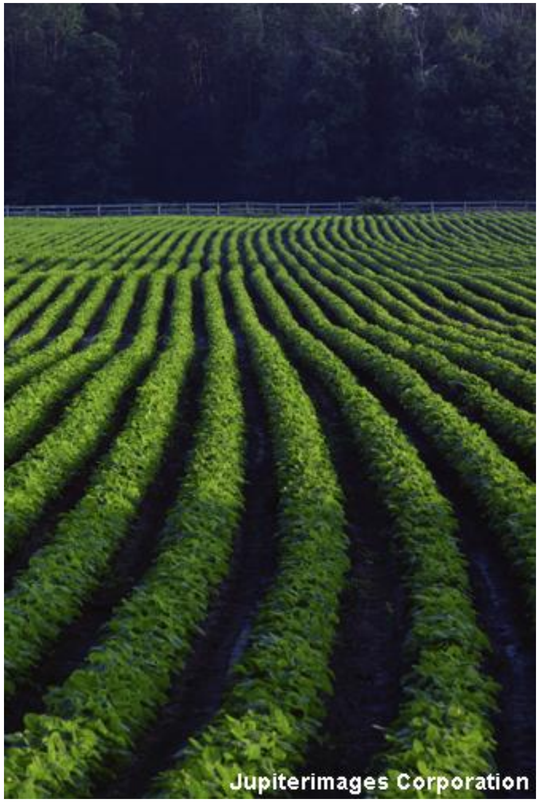
FOLLOW-UP PROBLEM 17.11 In a study of the chemistry of glass etching, an inorganic chemist examines the reaction between sand (SiO_2) and hydrogen fluoride at a temperature above the boiling point of water:

$$SiO_2(s) + 4HF(g) \rightleftharpoons SiF_4(g) + 2H_2O(g)$$

Predict the effect on $[SiF_4]$ when **(a)** $H_2O(g)$ is removed; **(b)** some liquid water is added; **(c)** HF is removed; **(d)** some sand is removed.

What is ammonia?

Ammonia is an important compound in the manufacture of fertilizer and other chemicals such as cleaning fluids and floor waxes.



It is made industrially by reacting nitrogen with hydrogen in the **Haber process**. It is a reversible reaction, so it never goes to completion.

Why is this a problem for companies making ammonia?

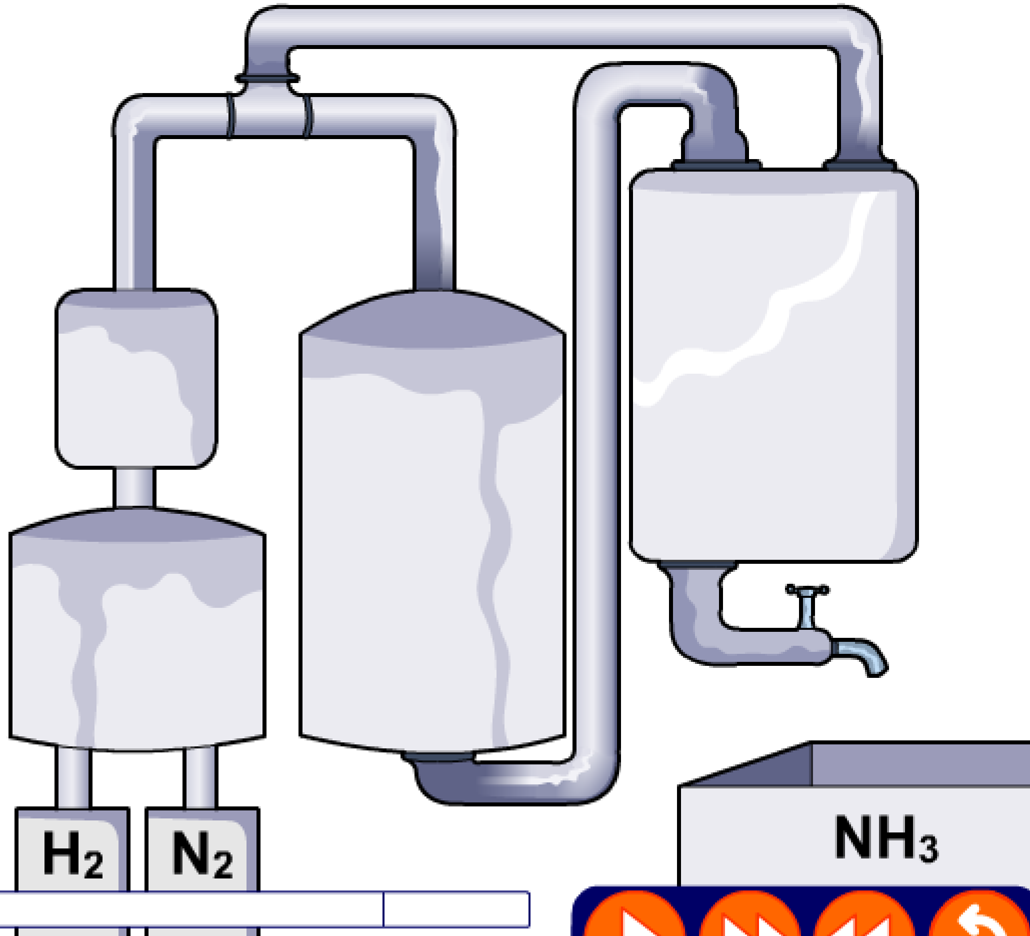
nitrogen + hydrogen ⇌ ammonia

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

How is ammonia produced in the Haber process?

The Haber process is the industrial reaction used to make **ammonia** (NH_3) from **hydrogen** (H_2) and **nitrogen** (N_2).

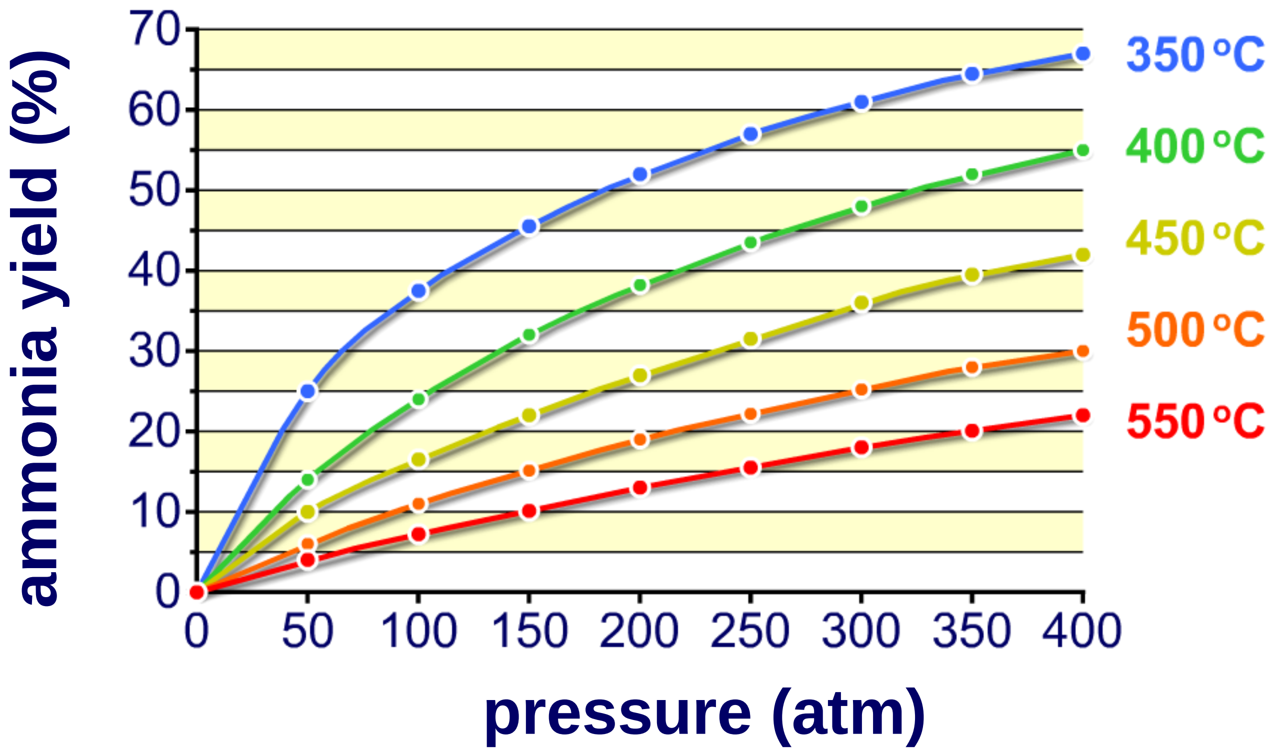
Click "**play**" to find out what happens.



What is yield?

The amount of product made in a reaction is called the **yield** and is usually expressed as a percentage.

The yield of ammonia produced by the Haber process depends on the **temperature** and **pressure** of the reaction.



What is the Haber compromise?

The highest yield of ammonia is theoretically produced by using a low temperature and a high pressure.

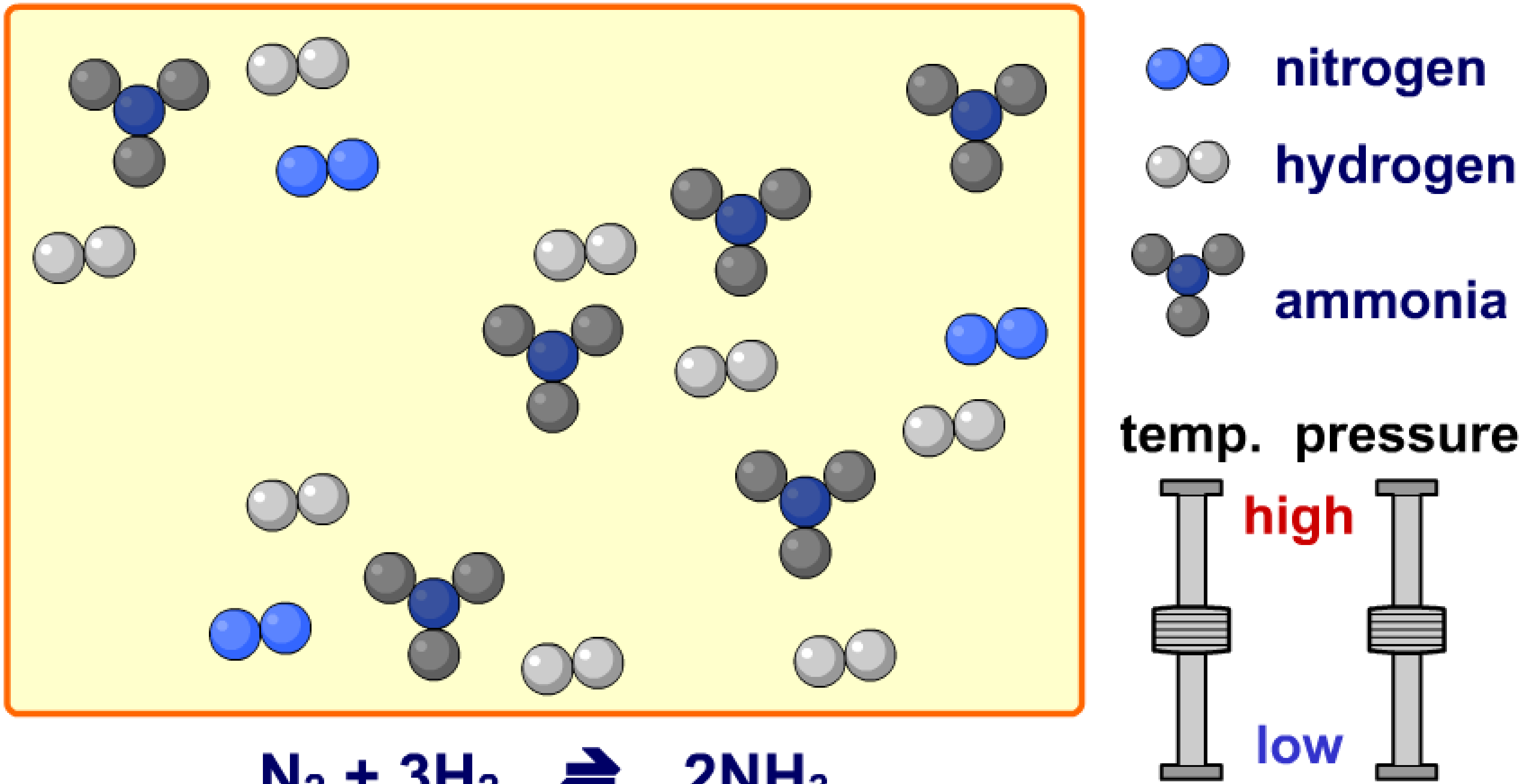
In practice, though, these conditions are not used. Why?

Lowering the temperature slows down the rate of reaction. This means it takes longer for ammonia to be produced.

Increasing the pressure means stronger, more expensive equipment is needed. This increases the cost of producing the ammonia.

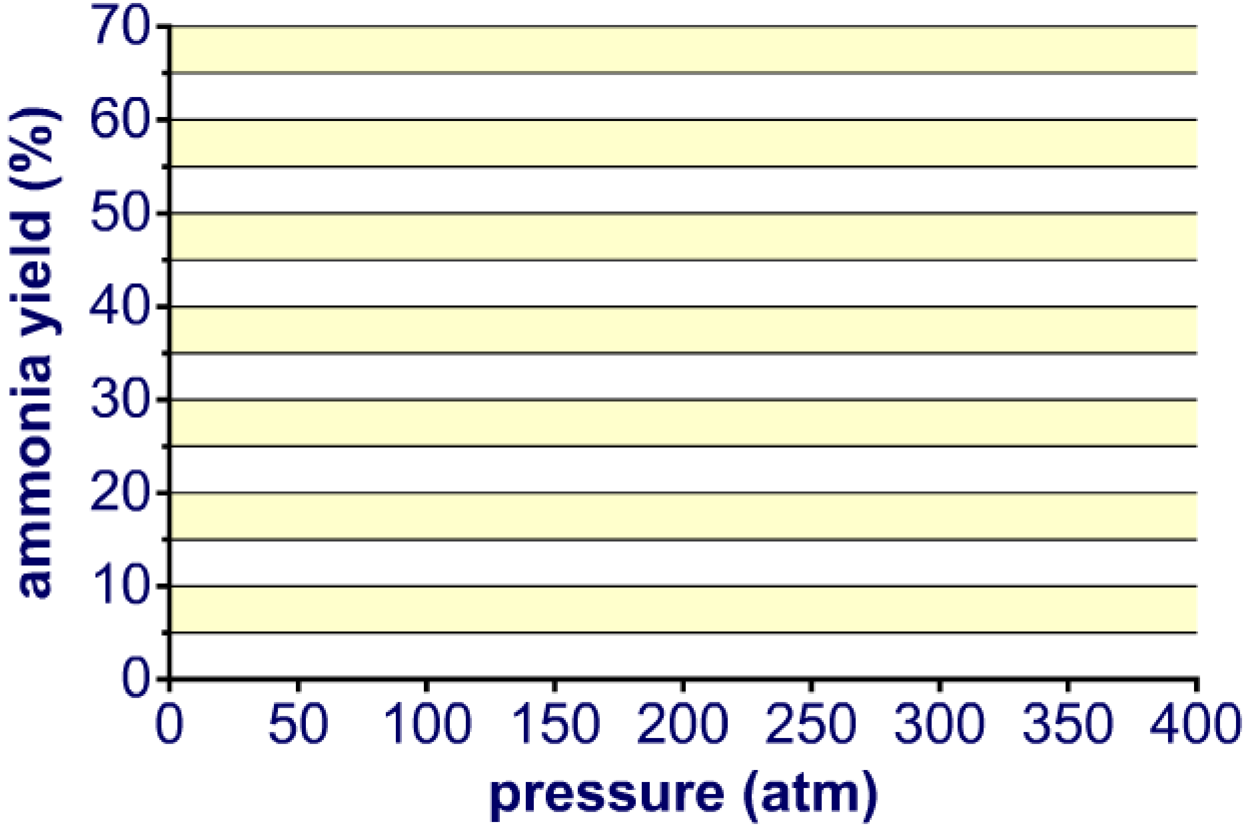
A compromise is reached to make an acceptable yield in a reasonable timeframe while keeping costs down.

How do temperature and pressure affect the Haber process?



$N_2 + 3H_2 \rightleftharpoons 2NH_3$

What conditions are used in the Haber process?



HABER PROCESS

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$: $\Delta H = -92\ kJ\ mol^{-1}$

Conditions	Pressure	20000 kPa (200 atmospheres)
	Temperature	380-450°C
	Catalyst	iron

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low temperature	**exothermic reaction - higher yield at lower temperature**
high pressure	**decrease in number of gaseous molecules**

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high temperature	**greater average energy + more frequent collisions**
high pressure	**more frequent collisions for gaseous molecules**
catalyst	**lower activation energy**

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Kinetic theory favours

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high pressure	more frequent collisions for gaseous molecules
catalyst	lower activation energy

Compromise conditions

Which is better? A low yield in a shorter time or

a high yield over a longer period.

The conditions used are a compromise with the catalyst enabling the rate to be kept up, even at a lower temperature.

IMPORTANT USES OF AMMONIA AND ITS COMPOUNDS

MAKING

FERTILISERS 80% of the ammonia produced goes to make fertilisers such as ammonium nitrate (NITRAM) and ammonium sulphate

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

MAKING

NITRIC ACID ammonia can be oxidised to nitric acid

nitric acid is used to manufacture... fertilisers (ammonium nitrate)

explosives (TNT)

The Haber compromise

To produce a high yield of ammonia, but with a fast rate of reaction and without the need for overly expensive equipment, the Haber process is carried out at **450 °C** and **200 atmospheres**.

The most important factor in deciding what conditions to use is therefore not yield, but **total cost**.

What costs are involved in the industrial production of ammonia?

- raw materials
- energy
- equipment
- wages

Maximizing productivity

What else can be done to maximise productivity in the manufacture of ammonia?

- An iron catalyst is used to increase the rate of reaction. It speeds up both the forward and backward reaction, so the position of equilibrium is not affected.

- The ammonia is cooled, liquefied and then removed as it is produced. This causes the equilibrium to shift to the right to produce more ammonia.

- Unreacted nitrogen and hydrogen are recycled and given another chance to react.

What are the missing words about the Haber process?

1a. The forward reaction in the Haber [?] produces heat.

1b. It is therefore [?]

2a. Lowering the temperature will cause the equilibrium to shift to the [?] to try and oppose the change.

2b. This will [?] the yield of ammonia.

3a. There are [?] molecules to the left of the

solve

Stages of the Haber process

What is the order of stages in the Haber process?

1. Steam is reacted with methane to make hydrogen.
2. The gases are compressed to 200 atmospheres.
3. Ammonia gas is produced, then cooled to a liquid.
4. Hydrogen is mixed with nitrogen, obtained from air.
5. Liquid ammonia is pumped off to be sold.
6. The gases are heated to 450°C.
7. Unreacted nitrogen and hydrogen are recycled.
8. The gases are passed over an iron catalyst.

?

C solve

Glossary

- **closed system –** A system in which reactants and products cannot be added or removed once the reaction has begun.
- **dynamic –** An equilibrium in which the forward and backward reactions take place at the same rate, so no overall change takes place.
- **Haber process –** The industrial-scale process for making ammonia from nitrogen and hydrogen.
- **irreversible –** A reaction that is impossible or very difficult to reverse.
- **reversible –** A reaction in which the product(s) can be turned back into the reactants.
- **yield –** The amount of product obtained from a reaction, usually expressed as a percentage.

Anagrams

How quickly can you unscramble anagrams of words about

r e v e r s i b l e

r e a c t i o n s ?

start

Multiple-choice quiz

start