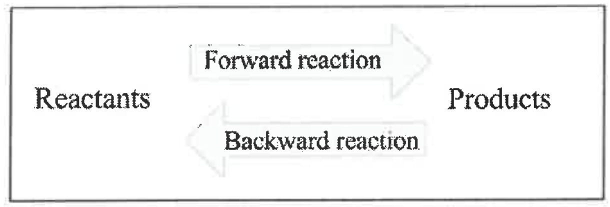
Chemical Equilibrium

Chemical Reactions

- We often assume that chemical reactions:
  - proceed in only one direction (from reactants to products)
  - have a constant rate of reaction

- But chemical reactions are not always like this!

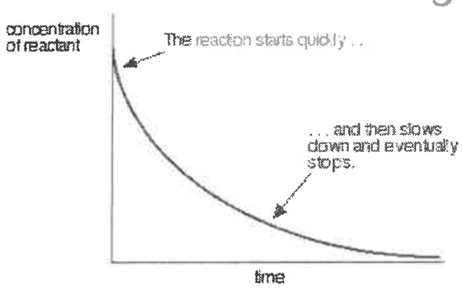
- Reactions can be reversible!
  Reactants combine to form products while the products turn back into reactants.



Example: Write the reversible reaction for hydrogen iodide gas decomposing into its elements (be sure to balance your equation and include physical states.

$$2HI_{(g)} \rightleftharpoons I_{2(g)} + H_{2(g)}$$

symbol used to show reversible reaction



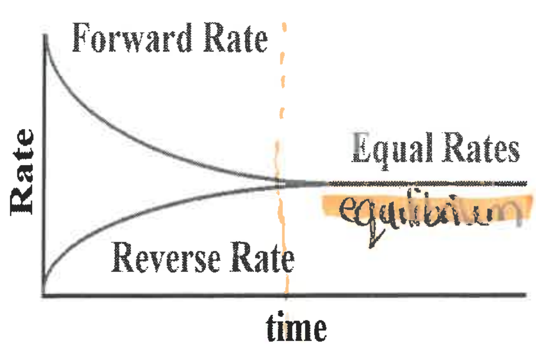
- The rate of reaction tends to decrease with time. This happens because there are less atoms left to react as the time increases.

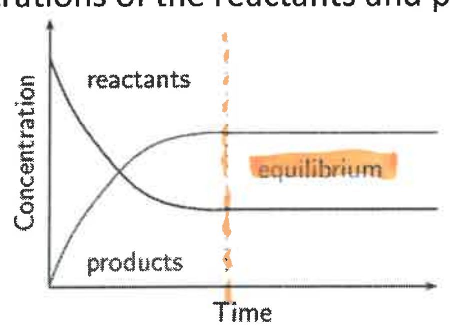
  true for both forwards and backwards reactions

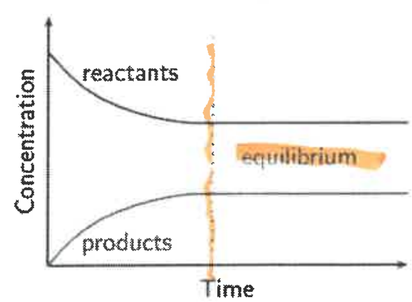
Chemical Equilibrium

- Another assumption we make is that chemical reactions always go to completion. Many do not; but instead attain chemical equilibrium.

- Chemical equilibrium: A state in which the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.







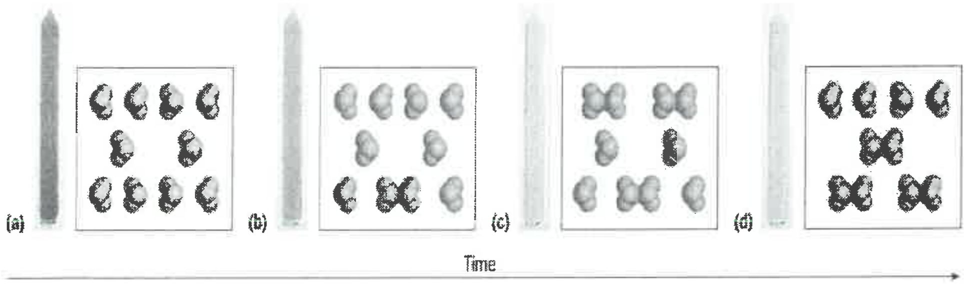
different amounts of R to P but both show concentrations that do not change

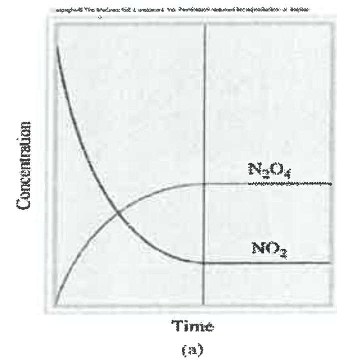
Example: Write the reversible reaction for nitrogen dioxide gas changing into dinitrogen tetroxide gas (be sure to balance your equation and include physical states).

$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$

brown colourless

When this reaction is placed into a sealed tube, the following is observed:





Notice:
- the gas never becomes colourless; indicating some NO_2 is always present
- concentrations of N_2O_4 and NO_2 are not changing (evident by constant colour and graph)
- this system has reached equilibrium

- At equilibrium, there are no observable (macroscopic) changes.
- This does not mean the reaction has stopped! Equilibrium is dynamic - both forward and reverse reactions take place but their rates are equal so there are no measurable changes in concentrations of reactants or products.
- For a closed chemical system in constant environmental conditions, the same equilibrium concentrations are reached regardless of the direction by which equilibrium was reached.

Table 1 Changes in Concentrations of $NO_2(g)$ and $N_2O_4(g)$ by the Forward or Reverse Reactions

		Initial concentrations (mol/L)		Final concentrations (mol/L)		
		$N_2O_4(g)$	$NO_2(g)$	$N_2O_4(g)$	$NO_2(g)$	
$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)}$	Experiment 1	0.750	0	0.721	0.0580	same results
$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$	Experiment 2	0	1.50	0.721	0.0580	

- In order to establish equilibrium, several conditions must be met:
  - reversible reaction
  - closed system (eg. sealed containers)
  - temperature must remain the same (otherwise the rate of rxn is changed)

The Equilibrium Constant, K_{eq}

- When equilibrium is reached, it is important to recognize that not all of the reactants will be converted into products (or products into reactants).

- There is a mathematical ratio, known as the equilibrium constant (K_{eq}), which represents the proportion of products to reactants.

For any general reaction: $aA + bB \rightleftharpoons cD + dD$

The equilibrium expression can be written as:

$K_{eq} = \frac{\text{products}}{\text{reactants}}$

$$\mathbf{K_{eq}} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

where:

- the products are placed in the numerator; reactants in the denominator
- concentrations are listed in molarity (mol/L) → expressed in square brackets [ ] and are raised to the power of the coefficients from the balanced equation.
- K_{eq} is unitless!

Example: Write the equilibrium expression for the following reaction:

$$4HCl_{(g)} + O_{2\,(g)} \rightleftharpoons 2H_2O_{(g)} + 2Cl_{2\,(g)}$$

$K_{eq} = \frac{\text{products}}{\text{reactants}} = \frac{[H_2O]^2[Cl_2]^2}{[HCl]^4\,[O_2]}$

Example: In an experiment conducted at 74°C, the equilibrium concentrations of reactants and products for the equation shown below were [CO] = 1.2×10^{-2} M, [Cl_2] = 0.054 M and [$COCl_2$] = 0.14 M.

$$CO(g) + Cl_2(g) \leftrightarrow COCl_2(g)$$

a) What is the equilibrium expression for this reaction?

$K_{eq} = \frac{\text{products}}{\text{reactants}} = \frac{[COCl_2]}{[CO][Cl_2]}$

~~watched~~

b) Calculate the value of the equilibrium constant.

$K_{eq} = \frac{[0.14]}{([1.2\times10^{-2}][0.054])} = 216$

$\boxed{K_{eq} = 220}$

Example: Write the equilibrium expression and calculate K_{eq} for the following reaction:

$$SO_{3(g)} + H_2O_{(g)} \rightleftarrows H_2SO_{4(aq)}$$

Given: At equilibrium $[SO_3] = 0.400M$ $[H_2O] = 0.480M$ $[H_2SO_4] = 0.600M$ ← ensure units are M

$$K_{eq} = \frac{\text{products}}{\text{reactants}} = \frac{[H_2SO_4]}{[SO_3][H_2O]} = \frac{[0.600]}{([0.400][0.480])} = 3.125$$

↑ watch sd

$$\boxed{K_{eq} = 3.13}$$