Chemical Equilibrium

In a *closed system* (for example a sealed container) the total mass of reactants and products remains constant.

All chemical reactions carried out in a closed system at a fixed temperature eventually reach a state of *dynamic equilibrium* in which the concentrations of all the reactants and products cease to change with time.

To the human eye it usually appears that all reactions in the system have stopped, but in reality the forward and back reactions are occurring at equal rate, so no change is visible.

In terms of collision theory, the rate of reactants successfully colliding to make products equals the rate of successful collisions of products creating reactants.

The *position* of equilibrium in a chemical system at a given temperature can be indicated by a constant, K_c, related to the concentrations of reactants and products at equilibrium.

The constant K_c has no units.

Example:

$$aA + bB \ldots \rightleftharpoons cC + dD \ldots \qquad\qquad 2H_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2H_2O_{(g)}$$

$$K_c = \frac{[C]^c[D]^d \ldots}{[A]^a[B]^b \ldots} \qquad\qquad K_c = \frac{\left[H_2O_{(g)}\right]^2}{\left[H_{2\,(g)}\right]^2\left[O_{2\,(g)}\right]}$$

Since the expression relates *concentrations*, solids and liquids are not included.

$$Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2\,(g)} \qquad K_c = \frac{\left[H_{2\,(g)}\right]}{\left[H_2O_{(g)}\right]}$$

If the equilibrium constant is <u>larger</u> then there are <u>more products</u> compared to reactants at equilibrium.
If the equilibrium constant is <u>smaller</u> then there are <u>more reactants</u> compared to products at equilibrium.

Another way of expressing this is that the <u>larger</u> the equilibrium constant, the <u>more complete</u> the reaction is at equilibrium.

Le Châtelier's principle

If a system is at equilibrium and some change is made (so that it is no longer at equilibrium) a net reaction will occur (if possible) in the direction that counteracts the change.

Note: In the following graphs the change in concentration of species (by the system reacting towards equilibrium) reflects their stoichiometric (mole) ratio.

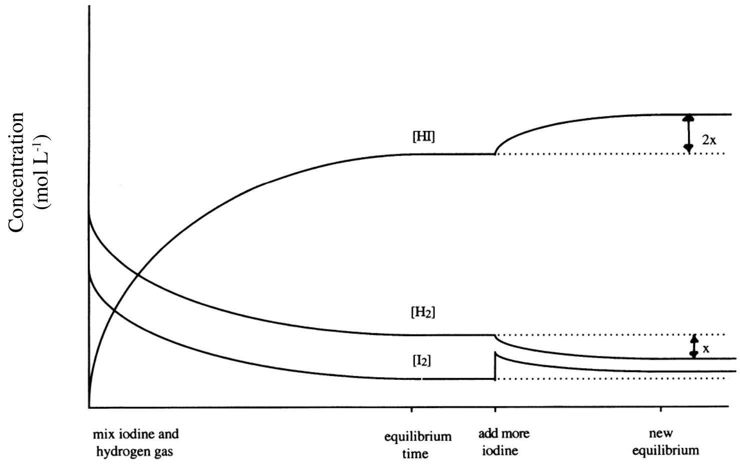
For example in $H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{(g)}$, after iodine is added:

- the reaction occurs and decreases $[I_2]$ by amount x
- since $n(I_2):n(H_2)$ is 1:1, $[H_2]$ also decreases by x
- since $n(I_2):n(HI)$ is 1:2 and they are on opposite sides of the reaction, $[HI]$ increases by 2x

Change in concentration of a reactant or product:

Since the value of K_c does not change at constant temperature, the concentration of all species will readjust to maintain the constancy of K_c.

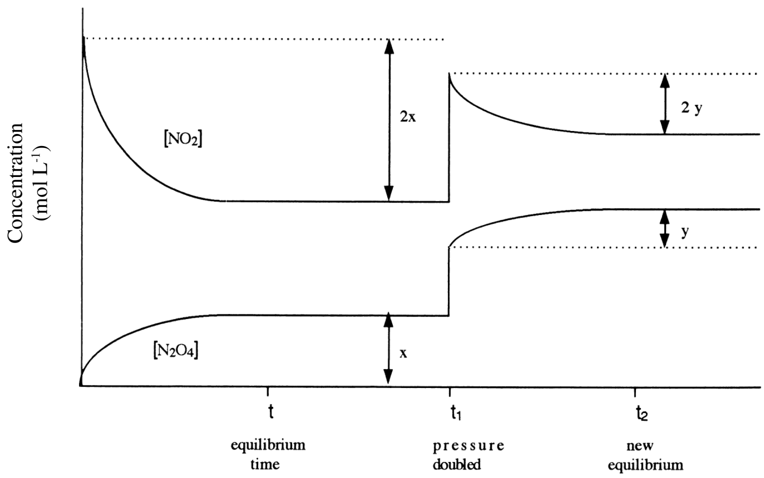
Example: $H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{(g)}$ is at equilibrium and then the concentration of I_2 is increased. The reaction acts to decrease the concentration of I_2 in response (the equilibrium position shifts to the right).



Change in overall pressure of a gaseous mixture:

Since the value of K_c does not change at constant temperature, the concentration of all species will readjust to maintain the constancy of K_c.

Example: $2NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$ is at equilibrium and then the pressure is doubled. The reaction acts to decrease the number of moles of gas in response (the equilibrium position shifts to the right).



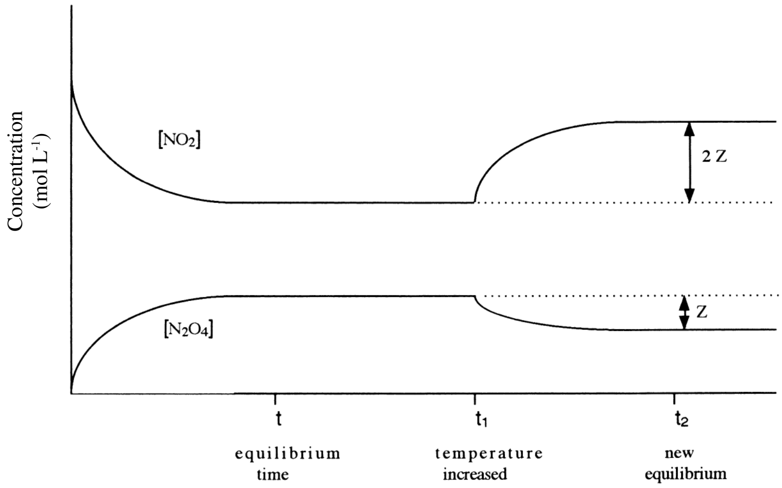
Note that in cases where there are the same number of moles of gas on both sides of the equation, pressure changes do not effect the equilibrium position.

Change in temperature of an equilibrium mixture:

Changing the temperature of a system at equilibrium will change the value of K_c, since it will increase the rate of either the forward or back reaction.

An increase in temperature will favour the reaction which tends to absorb heat, while a decrease in temperature will favour the reaction that tends to release heat.

Example: $2NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$ $\Delta H = -ve$ is at equilibrium and then the temperature is increased. The back reaction (endothermic, tends to absorb heat) is favoured, so the equilibrium shifts to the left.



Note: catalysts have no effect on the position of equilibrium or the value of K_c. All they do is increase the rates of reaction (equilibrium will be reached more quickly).

Equilibrium Problem Solving

The changes in concentrations (final minus initial) of reactants and products before reaching equilibrium are directly related by their mole ratios.

A table can be completed to find unknowns, where the columns are reactants/products and the rows are initial, final (i.e. at equilibrium) and change (in moles or moles per litre).

Example: 1 mole of hydrogen gas reacts with 1 mole of iodine gas at a certain temperature.

The equation for this reaction is $H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{(g)}$

Calculate the number of moles of the reactants at equilibrium, given there is 1 mole of HI at equilibrium.

(for the purpose of these notes, working is shown in brackets in small font in the order shown by the small number in the corner of each box)

	H_2	I_2	HI
Initial moles	1 (given) 1	1 (given) 2	0 (given) 3
Final moles	0.5 (initial + change) 8	0.5 (initial + change) 9	1 (given) 4
Change in moles	-0.5 (since in ratio 1:1 to I_2 so same amount, and on same side so same sign) 7	-0.5 (in ratio 1:2 to HI so half as much, and on opposite side so opposite sign) 6	1 (final minus initial) 5

So the answer to this question is 0.5 mol of each. Remember to convert to/from concentration if required.

Note: If two of the concentrations at equilibrium had been given and also the equilibrium constant K_c for that temperature, the third concentration could have been found using the expression for K_c.