# Chemical Equilibrium

There are two driving forces in nature that determine the direction of a chemical reaction:

(1) **Enthalpy**
- enthalpy: the heat change of a system
- a system will tend towards minimum enthalpy
- the enthalpy drive of a chemical reaction will be towards the side where the heat term is added

(2) **Entropy**
- entropy: the amount of disorder in a system
- a system will tend towards maximum entropy
- the entropy drive of a chemical reaction will be towards the side with the most molecules in the most random phase:

gases (g) >> solutions (aq) > liquids (l) >> solids (s)

- if both the enthalpy drive and the entropy drive favour the products, the reaction will be spontaneous
- if both the enthalpy drive and the entropy drive favour the reactants, the reaction will be non-spontaneous
- if the enthalpy and entropy drive are in opposite directions, the reaction will be reversible and is said to be in chemical equilibrium.

equilibrium: Both the forward reaction and the reverse reaction are occurring simultaneously with the forward rate equal to the reverse rate.

ex. For each of the following reactions, give the direction of the enthalpy drive and the entropy drive. Predict if the reaction will favour the products (spontaneous reaction), the reactants (non-spontaneous reaction), or result in equilibrium (reversible reaction).

(1) $Zn\ (s) + 2HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g) + 152\ kJ/mol$

(2) $3C\ (s) + 3H_2\ (g) + 20.4\ kJ/mol \rightarrow C_3H_6\ (g)$

(3) $2Pb(NO_3)_2\ (s) + 597\ kJ/mol \rightarrow 2PbO\ (s) + 4NO_2\ (g) + O_2\ (g)$

# Le Châtelier's Principle

There are three common stresses that can be applied to a chemical equilibrium:

(1) Temperature Change
- if temperature is increased, the equilibrium will shift away from the side where the heat term is added
- if temperature is decreased, the equilibrium will shift towards the side where the heat term is added

(2) Concentration Change
- if concentration of a chemical is increased, the equilibrium will shift away from the side with that chemical
- if concentration of a chemical is decreased, the equilibrium will shift towards the side with that chemical

(3) Pressure/Volume Change.
- If pressure is increased/volume is decreased, the equilibrium will shift towards the side with fewer molecules
- If pressure is decreased/volume is increased, the equilibrium will shift towards the side with more molecules

ex. Explain what would happen to $[NO_2]$ and to the colour for each of the following stresses.

$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g) + 58.9\ kJ/mol$
brown colourless

(1) temperature is increased

(2) temperature is decreased

(3) $[N_2O_4]$ is increased

(4) $[N_2O_4]$ is decreased

(5) volume is increased

(6) pressure is increased

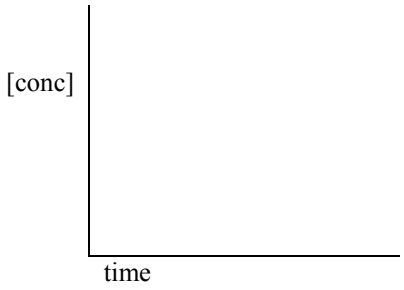
## Le Chatelier Graphs

Le Châtelier graphs show what is happening to each substance when a stress is applied to a chemical equilibrium.

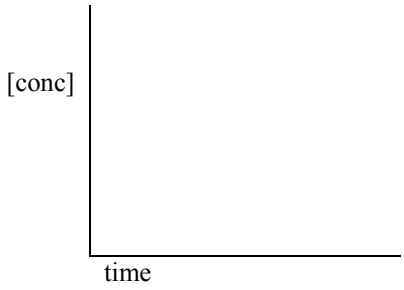
ex. Consider the following equilibrium: $2NO_2\ (g) \rightleftharpoons N_2O_4\ (g) + 58.9\ kJ/mol$
brown colourless

Draw a Le Châtelier for each of the given stresses.

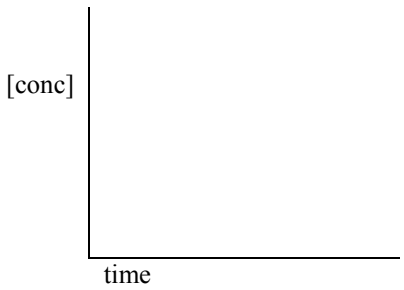
(1) temperature is increased



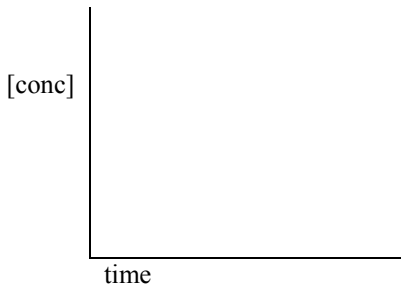

(2) $[N_2O_4]$ is increased




(3) pressure is increased




(4) volume is increased



# The Equilibrium Constant, Keq

In an equilibrium, the ratio of the reactants to the products is a constant called Keq.
Consider the general chemical equilibrium

$aW + bX \rightleftharpoons cY + dZ$

Experiments have shown that the equilibrium expression is

$$Keq = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

ex. Write an equilibrium expression for the following equilibria

(1) $N_2O_3\ (g) \rightleftharpoons NO\ (g) + NO_2\ (g)$

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

*Note: solids and liquids are NOT included in equilibrium expression.*

ex. Write an equilibrium expression for the following equilibria
(1) $NiO\ (s) + CO\ (g) \rightleftharpoons Ni\ (s) + CO_2\ (g)$

(2) $CF_4\ (g) + 2H_2O\ (l) \rightleftharpoons CO_2\ (g) + 4HF\ (aq)$

## Calculating the Equilibrium Constant

- Keq can be calculated from the concentrations of each chemical at equilibrium
- if Keq>1, the equilibrium favours the products; if Keq<1, the equilibrium favours the reactant
- Keq is unitless

ex. Write a Keq expression for each of the following equilbria. Determine the value of Keq. Does the equilibrium favour the products or the reactants?

(1) Consider the equilibrium:

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

At equilibrium, there is 0.60 M $H_2$, 0.20 M $N_2$, and 0.10 M $NH_3$. Determine Keq.

(2) Consider the equilibrium:

$2IBr\ (g) + Cl_2\ (g) \rightleftharpoons 2BrCl\ (g) + I_2\ (g)$

At equilibrium, at 10 L container has 0.50 mol IBr, 0.20 mol $Cl_2$, 1.2 mol BrCl, and 1.5 mol $I_2$. Determine Keq.