Chemistry 12: Equilibrium
Lesson 3 – Predicting if a reaction is spontaneous or not

Enthalpy

In an exothermic *Reaction (ΔH is* negative*), the* enthalpy *is* **decreasing.**
The heat term is on the products side.

In an endothermic *Reaction (ΔH is* positive*), the* enthalpy *is* **increasing.**
The heat term is on the reactant side.

Look at the following examples:

1. A + B ⇄ C + D ΔH = -24 kJ is exo so enthalpy is decreasing
2. X + Y ⇄ Z ΔH = 87 kJ is endo so enthalpy is increasing
3. E + D ⇄ F + 45 kJ is exo so enthalpy is decreasing
4. G + J + 36 kJ ⇄ L + M is endo so enthalpy is increasing

In an exothermic reaction. The Products ***will be favoured*** because the products have ***minimum*** enthalpy. In other words, there is a natural tendency here for reactants to spontaneously form products.

See if you can predict what would happen in an ***endothermic reaction***.

In an ***endothermic reaction***, the reactants have minimum enthalpy, so the reactants will be favoured. In other words, if the reactants are mixed they will (tend to remain as reactants / spontaneously form products)

1. Tell whether each of the following is *endothermic* or *exothermic* and state which has ***minimum enthalpy***, the *reactants* or the *products*:

a. $PCl_{5(g)} \rightleftarrows Cl_{2(g)} + PCl_{3(g)}$ $\Delta H = 92.5$ kJ

endo thermic and the reactants have *minimum enthalpy*.

b. $2NH_{3(g)} + 92.4 \text{ kJ} \rightleftarrows N_{2(g)} + 3H_{2(g)}$

endo thermic and the reactants have *minimum enthalpy*.

c. $CO_{(g)} + 3H_{2(g)} \rightleftarrows CH_{4(g)} + H_2O_{(g)} + 49.3 \text{ kJ}$

exo thermic and the products have *minimum enthalpy*.

d. $Cl_{2(g)} \rightleftarrows Cl_{2(aq)}$ $\Delta H = -25$ kJ

exo thermic and the products have *minimum enthalpy*.

2. When no other factors are considered, a reaction will move in such a way (left or right) in order to achieve a state of minimum enthalpy.

3. Given the equation: $2NH_{3(g)} + 92.4 \text{ kJ} \rightleftarrows N_{2(g)} + 3H_{2(g)}$

If only the *enthalpy* is considered, the (reactant / products) ~~products~~ reactants will be favoured at equilibrium.

4. Given the equation: $Cl_{2(g)} \rightleftarrows Cl_{2(aq)}$ $\Delta H = -25$ kJ

If only the *enthalpy* is considered, the (reactant / products) products will be favoured at equilibrium.

5. If the reaction : $CO_{(g)} + 3H_{2(g)} \rightleftarrows CH_{4(g)} + H_2O_{(g)} + 49.3 \text{ kJ}$

was proceeding to the *right*, the enthalpy would be decreasing ing. Is this a *favourable* change? yes.

6. If the reaction: $PCl_{5(g)} \rightleftarrows Cl_{2(g)} + PCl_{3(g)}$ $\Delta H = 92.5$ kJ

was proceeding to the *right*, the enthalpy would be increasing ing. Is this a *favourable* change? no.

7. If the reaction: $Cl_{2(g)} \rightleftarrows Cl_{2(aq)}$ $\Delta H = -25$ kJ

was proceeding to the *right*, the enthalpy would be decreas ing. Is this a *favourable* change? yes.

8. If the reaction: $2NH_{3(g)} + 92.4\ kJ \rightleftarrows N_{2(g)} + 3H_{2(g)}$

was proceeding to the *right*, the enthalpy would be increasing ing. Is this a *favourable* change? no .

As you can see by looking at the exercises above, there are two ways of looking at what happens to the *enthalpy*:

If the reaction is exothermic ***, the*** products ***have minimum enthalpy and the formation of products (move toward the right) is favourable.***

If the reaction is endo ***, the*** ~~products~~ reactants ***have minimum enthalpy and the formation of products (move toward the right) is unfavourable. In this case the formation of reactants (move toward the left) is favourable.***

Entropy

***Entropy** simply means **disorder**, or lack of order.*

→ randomness

Entropy of a Solid < Entropy of a Liquid < Entropy of aqueous < Entropy of a Gas

Chemists and successful Chemistry Students (THAT'S YOU!) can look at a chemical equation with subscripts showing the phases and tell which has ***maximum entropy***, the *reactants* or the *products*.

In other words, they can look at an equation and tell whether ***entropy*** is ***increasing*** or ***decreasing*** as the reaction *proceeds to the right*.

In the following examples, the ***entropy is increasing*** (or the ***products*** have ***greater entropy***):

1. There is a *gas* (or gases) on the *right*, when there are *no gases* on the *left* of the equation:

$$CaCO_{3(s)} + 2\ HCl_{(aq)} \rightleftarrows CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

2. When there are *gases on both sides*, the ***products*** have ***greater entropy*** when there

are ***more moles of gas on the right*** (add up coefficients of gases on left and right.):

$$4NH_{3(g)} + 5O_{2(g)} \rightleftarrows 4NO_{(g)} + 6H_2O_{(g)}$$

There are (4 + 5) = 9 moles of gas on the left

There are (4 + 6) = 10 moles of gas on the right.

Another way to look at the last example is to say that:

" The side with the greater number of moles of gas has the greatest entropy. "

3. When a ***solid*** *dissolves in water*, the ***products*** (the aqueous solution of ions) have ***greater entropy***. This makes sense because:

SOLID = lots of order = low enthropy
AQUEOUS = solid dissolves = less order incease in entropy

Here are few exercises for you:

9. For each of the following, decide whether the ***reactants*** or the ***products*** have ***greater entropy***:

a) $I_{2(s)} \rightleftarrows I_{2(aq)}$ The products have greater entropy.

b) $2NH_{3(g)} \rightleftarrows N_{2(g)} + 3H_{2(g)}$ The Products have greater entropy.

c) $NH_{3(g)} \rightleftarrows NH_{3(aq)}$ The reactants have greater entropy.

d) $CO_{(g)} + Cl_{2(g)} \rightleftarrows COCl_{2(g)}$ The reactants have greater entropy.

e) $MgCO_{3(s)} + 2HCl_{(aq)} \rightleftarrows MgCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

The products have greater entropy.

There is a natural tendency in nature toward *maximum disorder* or ***maximum entropy***!

Chemical systems will tend toward a state of <u>maximum entropy</u> if no other factors are considered.

To summarize both trends:

In nature, there is a tendency toward ***<u>minimum enthalpy</u>*** *and* ***<u>maximum entropy</u>***.

We say that:

When the two tendencies oppose eachother (one favours reactants, the other favours products), the reaction will ***reach a state of*** equilibrium

That is, there will be some reactants and some products present. The relative amounts of each depends on conditions like temperature, pressure, concentration etc.

Processes in which both the tendency toward ***minimum enthalpy*** and toward ***maximum entropy*** favour the ~~products~~ reactants, will ***not*** ~~completion~~ react at all

(ie. None of the reactants will be converted into products. There will be no products formed!)

Processes in which both the tendency toward ***minimum enthalpy*** and toward ***maximum entropy*** favour the products, will ***go to*** completion

(ie. All reactants will be converted into products. There will be no reactants left once the process is finished!)

<u>Here's something for you to do</u>:

10. For each of the following reactions decide which has ***minimum enthalpy*** (reactants or products), which has ***maximum entropy*** (reactants or products), and if the reactants are mixed, what will happen? (go to completion/ reach a state of equilibrium/not occur at all).

a) $PCl_{3(g)} + Cl_{2(g)} \rightleftarrows PCl_{5(g)}$; $\Delta H = -92.5$ kJ exo

The products has/have minimum enthalpy. ΔH

The reactants has/have maximum entropy.

If PCl_3 and Cl_2 are put together, what should happen?(go to completion/ reach a state of equilibrium/not occur at all) eq.

b) $2NO_{2(g)} \rightleftarrows N_2O_{4(g)}$ + energy

The ~~reactant~~ products has/have minimum enthalpy.

The reactants has/have maximum entropy.

If NO_2 was put in a flask, what should happen?(go to completion/ reach a state of equilibrium/not occur at all) eq.

c) $P_{4(s)}$ + $2H_{2(g)}$ + 37 kJ $\rightleftarrows$ $4PH_{3(g)}$

The reactants has/have minimum enthalpy.

The products has/have maximum entropy.

If $P_{4(s)}$ and $6H_{2(g)}$ was put in a flask, what should happen?(go to completion/ reach a state of equilibrium/not occur at all) eq.

d) $Na_2CO_{3(s)} + 2HCl_{(aq)} \rightleftarrows 2NaCl_{(aq)} + CO_{2(g)} + H_2O_{(l)} + 27.7$ kJ

enthalpy: Prod.
entro. : Prod.
rxn will go to completion

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