Thermodynamics

Chemical thermodynamics is the study of the energy changes which occur during a chemical reaction.
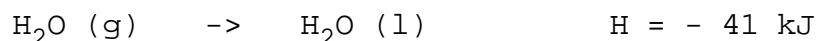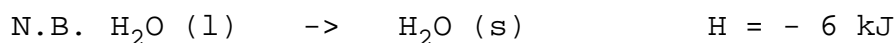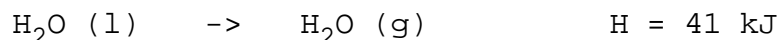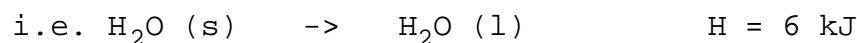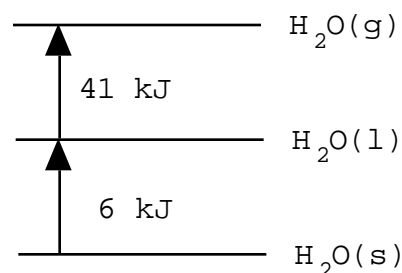
Any system of molecules has associated with it a certain amount of energy known as **Enthalpy (H).** This is the sum of the translational, rotational, vibrational and electronic energies. Actual enthalpies are not measured ; only differences in enthalpy (H) can be measured.

For a chemical reaction,

  H = enthalpy of products - enthalpy of reactants

If the reactants and products are in their standard states (solid, liquid or gas at 273 K and 1 atmosphere pressure) the enthalpy change is referred to as the 'standard enthalpy change' H^0. We will assume standard conditions throughout these notes.

Note the rise in enthalpy as solid water becomes gaseous water due to the increase in the degree of translation, rotation and vibration possible :

i.e. H_2O (s)   -> H_2O (l)   H = 6 kJ

     H_2O (l)   -> H_2O (g)   H = 41 kJ

N.B. H_2O (l)   -> H_2O (s)   H = - 6 kJ

     H_2O (g)   -> H_2O (l)   H = - 41 kJ

Since energy cannot be lost or gained during these two steps, we can deduce H for the conversion of solid water directly into gaseous water :

H_2O (s)   -> H_2O (g)   H = 47 kJ
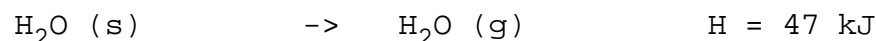
This is a consequence of the First Law of Thermodynamics.

> The **First Law of Thermodynamics** states that energy cannot be created or destroyed but may be transformed from one form into another.

Molar Enthalpy of Combustion

The molar enthalpy of combustion is the heat given out when 1 mole of a substance is burned completely in Oxygen.

e.g.the molar enthalpy of combustion of Ethanol is - 1371 kJ mol^{-1}.

Calorimetry is used to measure the enthalpy change in a chemical reaction. Heats of combustion are measured using a Bomb Calorimeter.
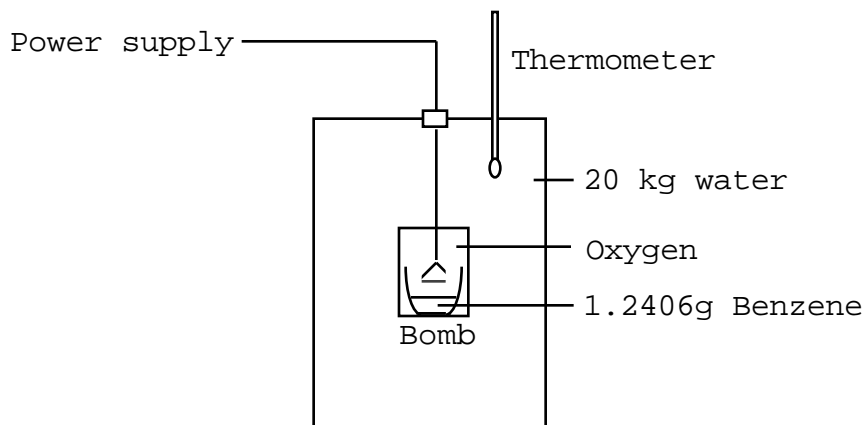
A known mass of the substance (1.2406g of Benzene in the above example) is ignited with an electrically heated wire and the heat evolved raises the temperature of a known mass of water in the surrounding jacket. Here is an example of a determination of the molar enthalpy of combustion of Benzene:

Rise in temperature =   0.6227 ^{0}C

Heat given out on burning 1.2406g of Benzene   = cm T

=>   Heat given out on burning 78g (1 mole) of Benzene   = $\dfrac{cm\ T.78}{1.2406}$

$$= \dfrac{4.18 \times 20 \times 0.6227 \times 78}{1.2406}$$

$$= \underline{3273\ kJ\ mol^{-1}}$$

Molar Enthalpy of Formation ΔH_f

The molar enthalpy of formation is the energy change when 1 mole of a substance is formed from its elements in their standard states.

The molar enthalpy of formation of Ammonium chloride is
- 315 kJ mol^{-1}. This means that H for the reaction :

$1/2\ N_2(g)\ \ +\ \ 2\ H_2(g)\ \ +\ \ 1/2\ Cl_2(g)\ \ ->\ \ NH_4^+Cl^-(s)$

is - 315 kJ.

Most values of H_f have to be found indirectly since the reactions are almost impossible to carry out.
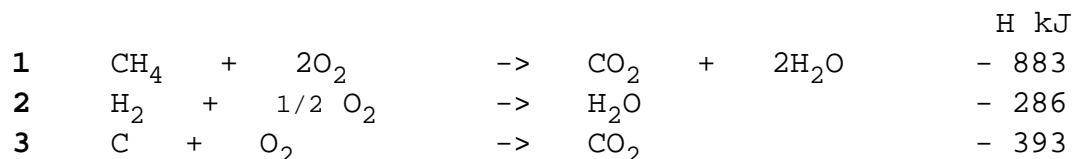
It is a consequence of the first law of thermodynamics that energy is conserved in a chemical reaction. Hess applied this law to chemical reactions to produce his own version of the first law : in a chemical reaction the energy change is always the same irrespective of the route taken.

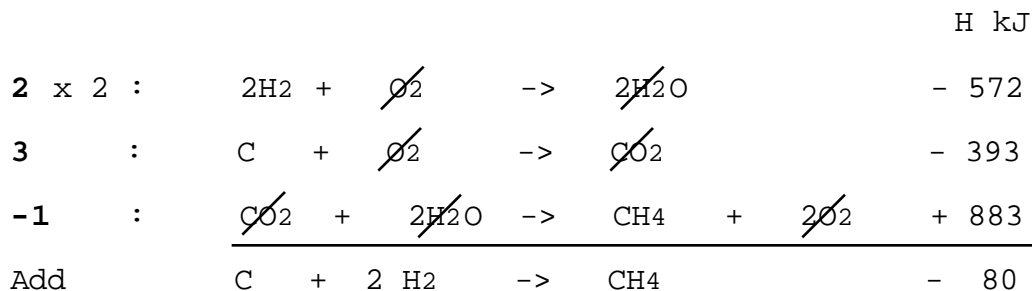We can therefore find H_f indirectly using reactions for which H *can* be measured.

e.g. the molar enthalpy of formation of CH_4

C   +   2 H_2 -> CH_4 H_f
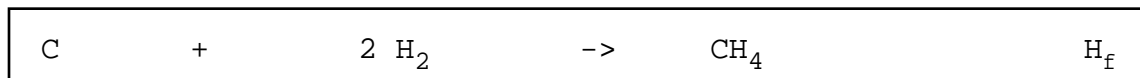
is calculated from the results of 3 separate experiments :

					H kJ
1	CH_4 + $2O_2$	->	CO_2 + $2H_2O$		– 883
2	H_2 + $1/2\ O_2$	->	H_2O		– 286
3	C + O_2	->	CO_2		– 393

Now, rewrite the above equations such that, when added together, they will give the main equation (in box) i.e. try to get C and $2H_2$ on L.H.S. and CH_4 on R.H.S :

			H kJ
2 x 2 :	2H2 + $\cancel{O2}$ -> 2$\cancel{H}$2O		– 572
3 :	C + $\cancel{O2}$ -> $\cancel{C}$O2		– 393
–1 :	$\cancel{C}$O2 + 2$\cancel{H}$2O -> CH4 + 2$\cancel{O}$2		+ 883
Add	C + 2 H2 -> CH4		– 80

Hence H_f(CH4) is <u>– 80 kJ mol^{-1}</u>

Problem : Calculate the molar enthalpy of combustion of Methane given the following heats of formation :

H_f (CH_4) =   -82 kJ mol^{-1}

H_f (CO_2) =   -394 kJ mol^{-1}

H_f (H_2O) =   -286 kJ mol^{-1}

Answer :   H kJ
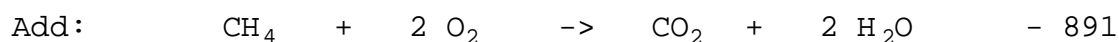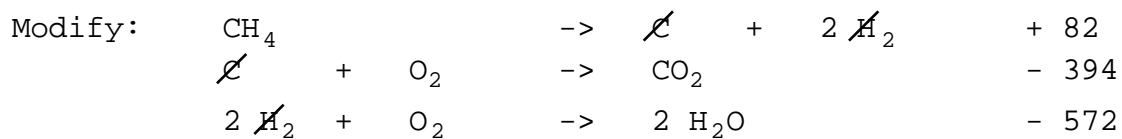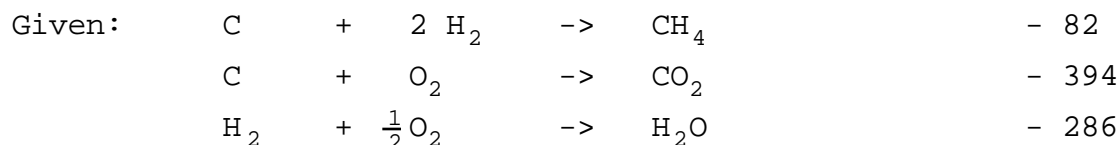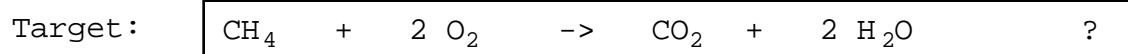
Target: | CH_4 +   2 O_2 -> CO_2 +   2 H_2O ? |

Given: C +   2 H_2 -> CH_4 − 82

           C + O_2 -> CO_2 − 394

           H_2 + $\frac{1}{2}O_2$ -> H_2O − 286

Modify: CH_4 -> $\cancel{C}$ +   2 $\cancel{H}_2$ + 82

           $\cancel{C}$ + O_2 -> CO_2 − 394

           2 $\cancel{H}_2$ + O_2 ->   2 H_2O − 572
           _____

Add: CH_4 +   2 O_2 -> CO_2 +   2 H_2O − 891
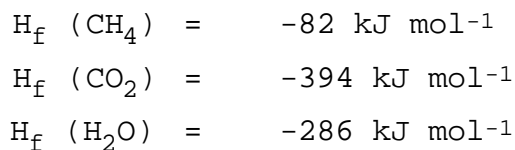
=> Molar enthalpy of combustion of CH_4 is − <u>884 kJ mol^{-1}</u>

We can shorten this method considerably. On close examination :

H   = | H_f (CO_2)   +   2 H_f (H_2O)   − H_f (CH_4) |

from which we can obtain a general equation :

        H   = H_f (products)   − H_f (reactants)

The answer to the previous question may now be written thus :

        H   = H_f P   − H_f R

            =   [−394   +   2(−286)]   −   [−82   +   2(0)]

            =   − 884 kJ mol^{-1}

[N.B. H_f (O_2)   =   0]

Molar Enthalpy of Atomisation ΔH_{at}

The molar enthalpy of atomisation is the energy taken in when 1 mole
of an element is converted into gaseous atoms e.g.

C (s)   ->   C (g) H_{at} = + 719 kJ mol^{-1}

Molar Bond Enthalpy ΔH_d

The molar bond enthalpy is the energy required to break 1 mole of
bonds e.g.

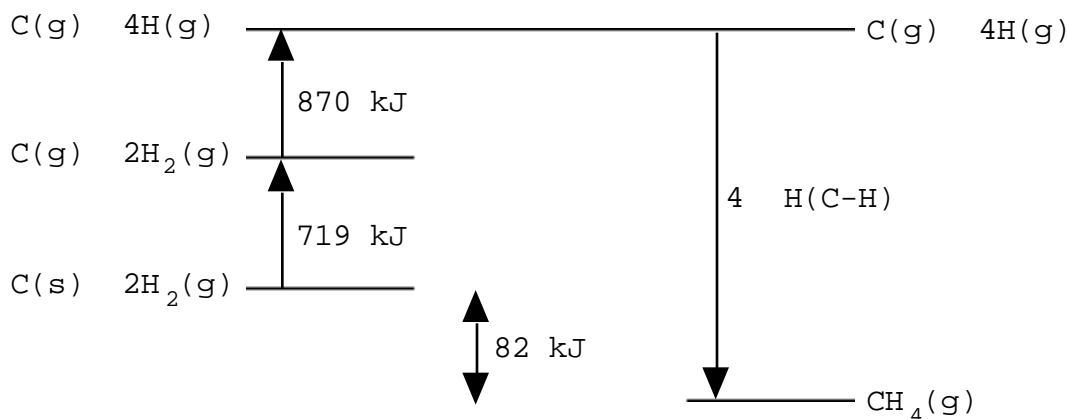C − C   ->   C   +   C H_d = + 348 kJ mol^{-1}

Mean bond enthalpies are average values e.g. the bond enthalpy of the
C-C bond varies slightly depending on the compound - Ethane, Ethanol
etc. The bond enthalpy can be calculated by considering bond
formation as one of the steps involved when a compound containing the
bond is formed from its elements.

Problem

Calculate the C-H bond enthalpy in Methane from the following information :

Molar enthalpy of atomisation of Carbon	=	+ 719 kJ mol^{-1}
H-H molar bond enthalpy	=	+ 435 kJ mol^{-1}
Molar enthalpy of formation of Methane	=	- 82 kJ mol^{-1}

Answer :

C(g) 4H(g) ——————————————————— C(g) 4H(g)

870 kJ

C(g) 2H$_2$(g) ——————

719 kJ

C(s) 2H$_2$(g) ——————

4 H(C-H)

82 kJ

CH$_4$(g)

Ignoring signs,

4 H$_d$(C-H)   = 82 + 719 + 870
                = 1671

=>   H$_d$(C-H) = $\underline{\frac{1671}{4}}$

                = $\underline{418 \text{ kJ mol}^{-1}}$

Electron affinity EA

The electron affinity is the energy change (usually given out) when 1 mole of electrons is added to 1 mole of atoms or ions in the gas state e.g.

I(g)   +   e   ->   I$^-$ (g)   H = - 314 kJ mol^{-1}
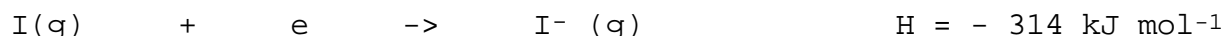
The electron affinity is greatest for small atoms close to the noble gas structure e.g. Fluorine.
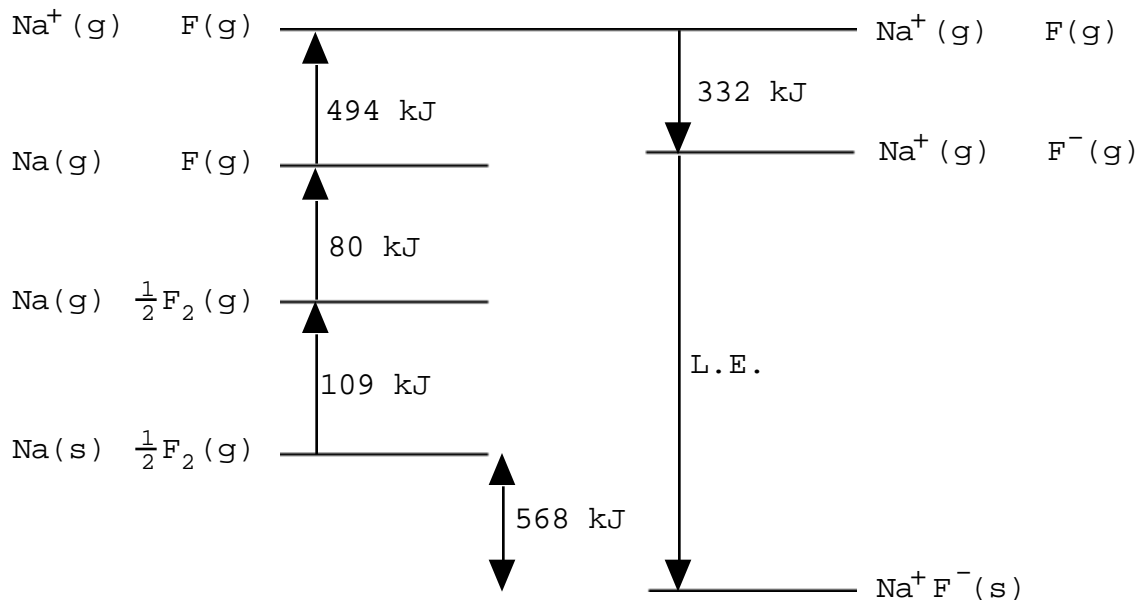
Molar Lattice Enthalpy LE

The molar lattice enthalpy is the energy given out when 1 mole of an electrovalent compound is formed from its ions in the gaseous state e.g.

K$^+$(g)   +   Cl$^-$(g)   ->   K$^+$Cl$^-$(s)   H = - 701 kJ

Lattice energy cannot be measured directly. It can be calculated by considering lattice formation as one of the steps involved when an electrovalent compound is formed from its elements.

Problem   Calculate the lattice energy of Sodium fluoride given the
             following information :

Molar enthalpy of atomisation of Sodium   =   + 109 kJ mol^{-1}
Molar bond enthalpy of F-F bond   =   + 160 kJ mol^{-1}
1st ionisation energy of Sodium   =   + 494 kJ mol^{-1}
Electron affinity of Fluorine   =   - 332 kJ mol^{-1}
Molar enthalpy of formation of Sodium fluoride = - 568 kJ mol^{-1}

$Na^+(g)$ $F(g)$ ┌─────────────────────────┐ $Na^+(g)$ $F(g)$

                    494 kJ   332 kJ

$Na(g)$ $F(g)$ $Na^+(g)$ $F^-(g)$

                    80 kJ

$Na(g)$ $\frac{1}{2}F_2(g)$

                    109 kJ   L.E.

$Na(s)$ $\frac{1}{2}F_2(g)$

                    568 kJ

                                           $Na^+F^-(s)$

Ignoring signs :

     568 + 109 + 80 + 494   =   332 + L.E.

     Hence numerical value of lattice energy is 919

=>   L.E. = – 919 kJ mol^{-1}

Molar Enthalpy of Hydration ΔH_{hyd}

The molar enthalpy of hydration is the energy given out when 1 mole
of gaseous ions is dissolved in excess water. During hydration
attractive forces are formed between the ions and the polar Water
molecules.

Example : molar enthalpy of hydration of $K^+(g)$ = - 322 kJ mol^{-1}

$K^+(g)$ -> $K^+(aq)$ H = – 322 kJ

```
    H
     \
      \
       O ——— K⁺
      /  (-)
     /
    H
```
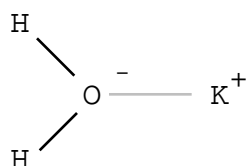
Example : molar enthalpy of hydration of $Cl^-(g)$ = $-$ 364 kJ mol^{-1}

$Cl^-(g)$ -> $Cl^-(aq)$ H = $-$ 364 kJ

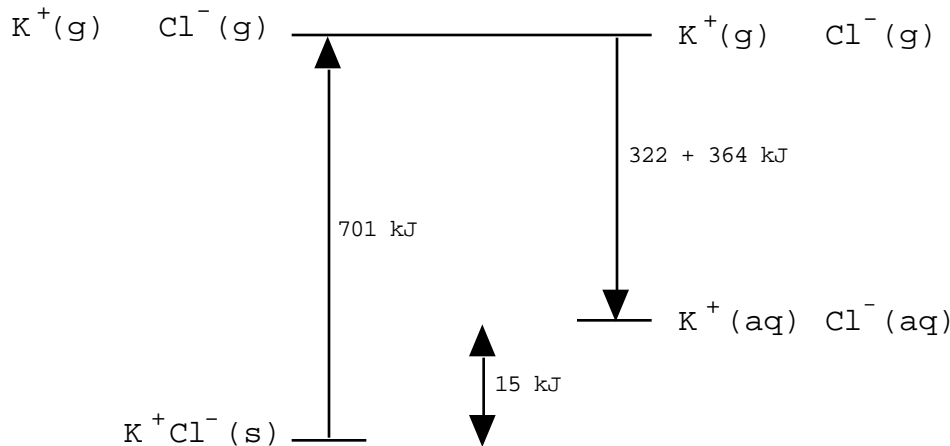$$Cl^- \quad\underline{\qquad}\quad H \overset{+}{\underline{\quad}} O \diagup^{H}$$
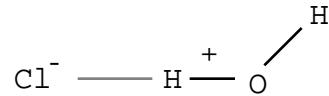
Molar Enthalpy of Solution

The molar enthalpy of solution is the energy change when 1 mole of solute is dissolved in excess water e.g.

$K^+Cl^-(s)$ -> $K^+(aq)$ + $Cl^-(aq)$ H = + 15 kJ

When an electrovalent substance dissolves in Water energy is first taken in to overcome the attractive forces between the ions (LE) then energy is given out when the Water molecules cluster round the ions (H_{hyd})

$K^+(g)$ $Cl^-(g)$ $\underline{\qquad\qquad\qquad\qquad}$ $K^+(g)$ $Cl^-(g)$

322 + 364 kJ

701 kJ

$K^+(aq)\ Cl^-(aq)$

15 kJ

$K^+Cl^-(s)$ $\underline{\quad}$

Entropy

Due to molecular randomness, not all the energy of a system of molecules is available for doing work. Imagine a system of molecules inside the following cylinder doing work against the piston pushing it out :
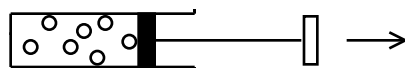
Not all the molecules will push against the piston ; some will hit the sides of the cylinder. The higher the temperature the more disordered the molecules become and the less energy is available to push against the piston

 i.e. unavailable energy(U) $\propto$ Temperature(T) or

$$\boxed{U \quad = \quad ST}$$ where S = proportionality constant
                          = unavailable energy per degree

S is a measure of the degree of disorder of a substance and is known as the **Entropy**.

Since gases are more disordered than liquids and liquids more disordered than solids, it follows that :

$S(g) > S(l) > S(s)$

> The **Third Law of Thermodynamics** states that the entropy of a perfect crystal at 0 K is 0.

All entropies are compared to the zero entropy of a perfect crystal.

Example : Water

State	S JK^{-1} mol^{-1}
gas	189
liquid	70
solid	48

The standard entropy S^0 is the entropy of the substance in its standard state. At standard conditions (273 K and 1 atmosphere pressure) Water is a solid so its standard entropy is 48 JK^{-1} mol^{-1}.

An increase in the number of gas molecules in a reaction therefore causes an increase in the entropy of the system and vice versa.

Problem : Find the change in entropy S for the reaction :

$2 H_2O(l) \rightarrow 2 H_2(g) + O_2(g)$
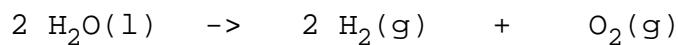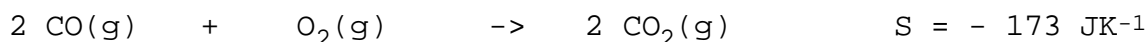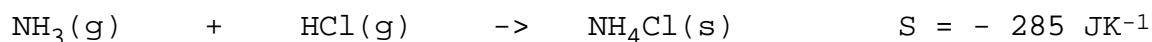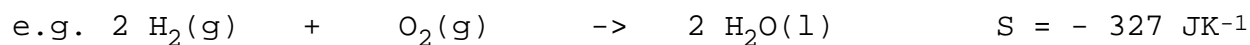
given the following data :

Substance	Entropy/$JK^{-1}mol^{-1}$
$H_2(g)$	131
$O_2(g)$	205
$H_2O(l)$	70

Answer : S = S_P - S_R

          =   [2(131) + (205)] - [2(70)]

          =   + 327 JK^{-1}

In this reaction there is an increase in entropy (S is positive) due to the increase in the number of gas molecules.

> The **Second Law of Thermodynamics** states that a reaction will proceed spontaneously (without any outside aid) only if there is an overall increase in entropy.

Many chemical reactions occur spontaneously however where the entropy *appears* to decrease!!

e.g. $2 H_2(g)$ + $O_2(g)$ -> $2 H_2O(l)$ $S = - 327$ JK^{-1}

     $NH_3(g)$ + $HCl(g)$ -> $NH_4Cl(s)$ $S = - 285$ JK^{-1}

     $2 CO(g)$ + $O_2(g)$ -> $2 CO_2(g)$ $S = - 173$ JK^{-1}

In ALL of these reactions however, H is negative - heat is given out. The surroundings heat up. The molecules of the surroundings move faster and become more disordered. The overall entropy therefore **does** increase.

Free Energy

Consider again the molecules doing work against the piston. Due to their randomness, only part of their energy is available for doing work. The energy available for doing work is called the Free Energy (G).
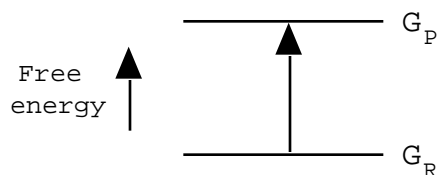
Therefore :

Free energy(G)   =   Total energy(H)   -   Unavailable energy(TS)

 or | G = H - TS |

Consider a chemical reaction in which the free energy of the products (G_P) is greater than the free of the reactants(G_R) :
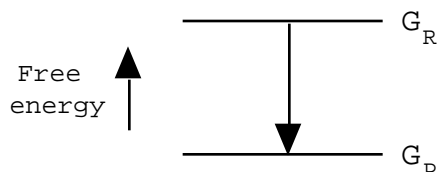

The change in free energy,

  G = G_P - G_R

is positive.

Work must be done on the reaction to get it to occur. The work required by the reaction is + G. The reaction will not occur if this energy is not supplied.

Reactions with a positive G are **non-spontaneous** - they do not proceed without outside aid.

Now consider a reaction in which the free energy of the products is less than the free energy of the reactants.

The change in free energy,

$$\Delta G = G_P - G_R$$

is negative.

We end up with less free energy than we started with, therefore free energy has been given out during the reaction ; **the reaction has done work**. The work done by the reaction is - ΔG.

Reactions with a negative ΔG are **spontaneous** - they proceed without outside aid.

The rate of change of free energy has its maximum value at the start of the reaction when reactants are changing into products most quickly.

As the reaction progresses, reactants change to products more slowly and, as a consequence, the rate of change of free energy slows down.

When equilibrium is reached and there is no further change in the quantities of reactants and products, the rate of change of free energy becomes zero. At equilibrium, therefore, $\Delta G = 0$.

Free Energy of Formation

> The **Free Energy of Formation** ΔG_f of a substance is the change in free energy when 1 mole of the substance is formed from its elements in their standard states.

e.g. the statement :

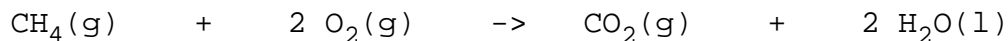'free energy of formation of $NH_4^+Cl^-$ is - 204 kJ mol^{-1} at 298 K'

means that ΔG for the reaction :

$$1/2\ N_2(g) \quad + \quad 2\ H_2(g) \quad + \quad 1/2\ Cl_2(g) \quad -> \quad NH_4^+Cl^-(s)$$

is - 204 kJ at 298 K.

As with molar enthalpies of formation, values of ΔG_f can be used to find ΔG for a reaction.

Problem : Find G for the following reaction at 298 K :

$$CH_4(g) \quad + \quad 2\ O_2(g) \quad -> \quad CO_2(g) \quad + \quad 2\ H_2O(l)$$

given the following data :

Substance	G_f /kJ mol^{-1}
$CH_4(g)$	– 50.8
$CO_2(g)$	– 395
$H_2O(l)$	– 237

N.B. G_f (O_2) = 0

Answer :   G   = G_{fP} – G_{fR}

= [– 395 + 2(– 237)] – [– 50.8 + 2(0)]

= – 818.2 kJ

This is a spontaneous reaction (G -ve) ; work done <u>by the reaction</u> is 818.2 kJ.

The Gibbs–Helmholtz Equation

Consider the changes in G, H and S during a reaction at constant temperature T.

G_R H_R
T S_R

Reactants

→

G_P H_P
T S_P

Products
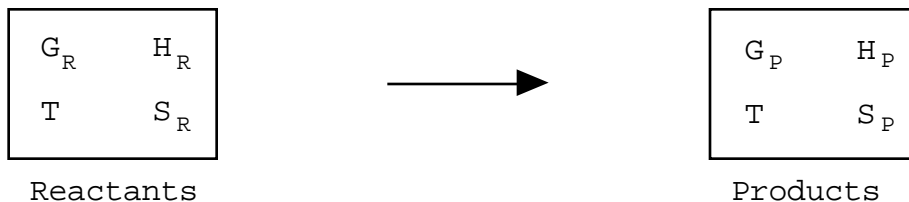
$$G_R \quad = \quad H_R \quad - \quad TS_R \qquad\qquad G_P \quad = \quad H_P \quad - \quad TS_P$$

=> $(G_P - G_R)$ = $(H_P - TS_P)$ – $(H_R - TS_R)$
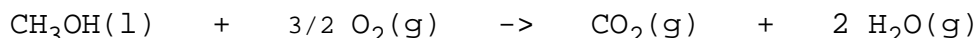
= $(H_P - H_R)$ – $T (S_P - S_R)$

=> $\boxed{\Delta G = \Delta H - T\Delta S}$

N.B.   G varies with temperature.

Four types of reaction can now be identified :

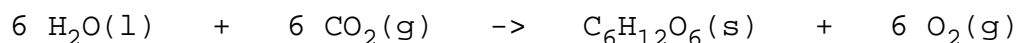| Type	H	S	G
1	- ve	+ ve	always - ve
2	+ ve	- ve	always + ve
3	- ve	- ve	- ve <=> T low
4	+ ve	+ ve	- ve <=> T high

<u>Example of Type 1</u>   H - ve   and   S + ve

$$CH_3OH(l)   +   3/2\ O_2(g)   ->   CO_2(g)   +   2\ H_2O(g)$$

This reaction is spontaneous at all temperatures.

<u>Example of Type 2</u>   H + ve   and   S - ve

$$6\ H_2O(l)   +   6\ CO_2(g)   ->   C_6H_{12}O_6(s)   +   6\ O_2(g)$$

Photosynthesis is not spontaneous at any temperature ! The reason it occurs is because the necessary work is done on the reaction by the sun's energy.

<u>Example of Type 3</u>   H - ve   and   S - ve

$$H_2(g)   +   1/2\ O_2(g)   ->   H_2O(g)$$
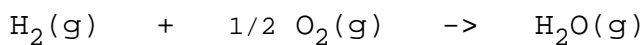
This reaction is spontaneous only at **low** temperatures.

<u>Example of Type 4</u>   H + ve   and   S + ve

$$CaCO_3(s)   ->   CaO(s)   +   CO_2(g)$$
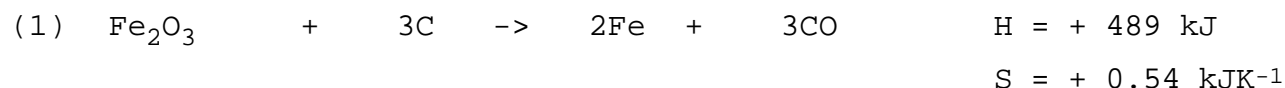
This reaction is spontaneous only at **high** temperatures.

<u>Problem</u>

The following reaction occurs in the blast furnace:

(1) Fe_2O_3 +   3C   ->   2Fe   +   3CO   H = + 489 kJ

S = + 0.54 kJK^{-1}

Calculate the temperature above which this reaction becomes spontaneous - the transitional temperature.

<u>Answer</u>
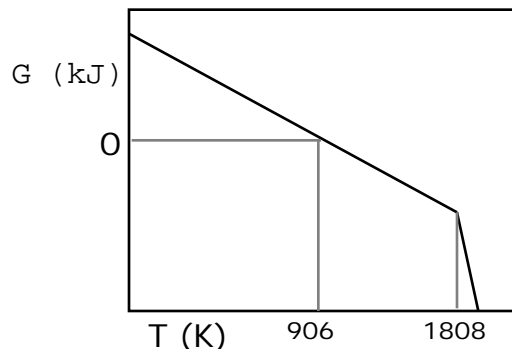
G < 0   <=>   T S > H

<=>   T > $\dfrac{H}{S}$

<=>   T > $\dfrac{489}{0.54}$

<=>   T > <u>906 K</u>

The above result can also be
obtained from a graph of G against
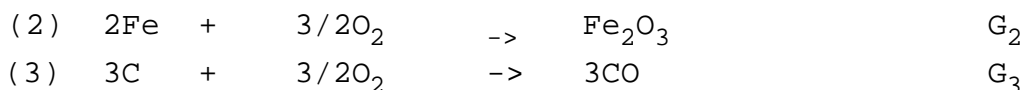Temperature, an **Ellingham diagram**

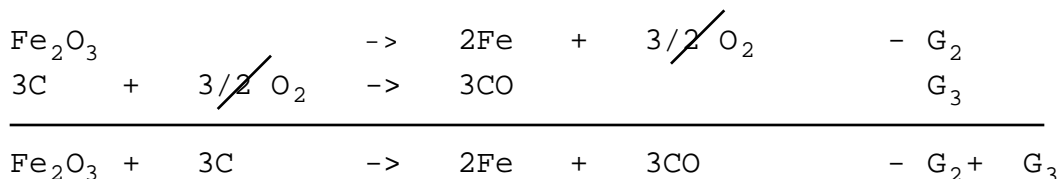Notice that the gradient of
this line is - S

i.e. $\dfrac{d(\Delta G)}{dT}$ = - S

Iron melts at 1808 K resulting in a sudden increase in entropy.

Now consider the following two reactions (2 and 3) :

(2)   2Fe   + $3/2O_2$ -> Fe_2O_3 ΔG_2
(3)   3C   + $3/2O_2$ ->   3CO ΔG_3

We can combine these two reactions as follows :

Fe_2O_3 ->   2Fe   + $3/\cancel{2} \, O_2$ - ΔG_2
3C   + $3/\cancel{2} \, O_2$ ->   3CO ΔG_3
_____

Fe_2O_3 +   3C   ->   2Fe   +   3CO   - ΔG_2 + ΔG_3

At precisely 906 K the reaction just becomes spontaneous and

- ΔG_2 + ΔG_3 = 0

or

 ΔG_2 = ΔG_3

If we therefore superimpose Ellingham graphs for reactions 2 and
3, the point of intersection of the lines will give the
temperature above which reaction (1) becomes spontaneous.
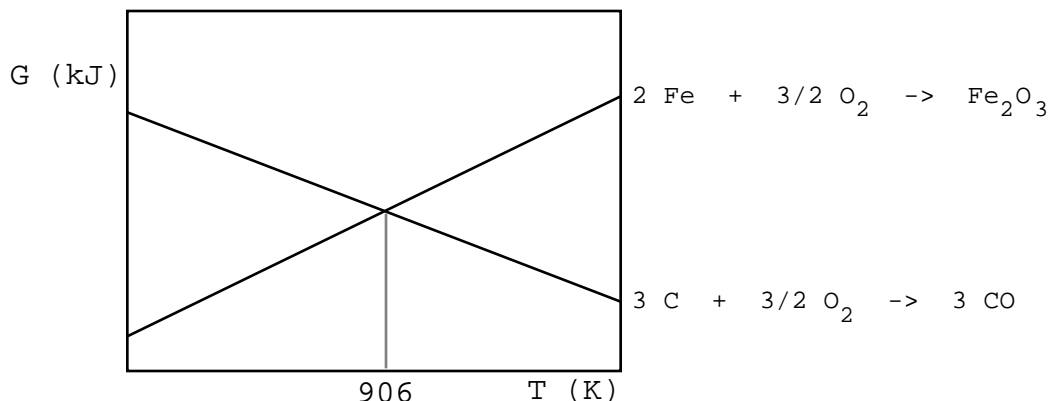
The following two problems will further illustrate the use of the Gibbs-Helmholtz equation.
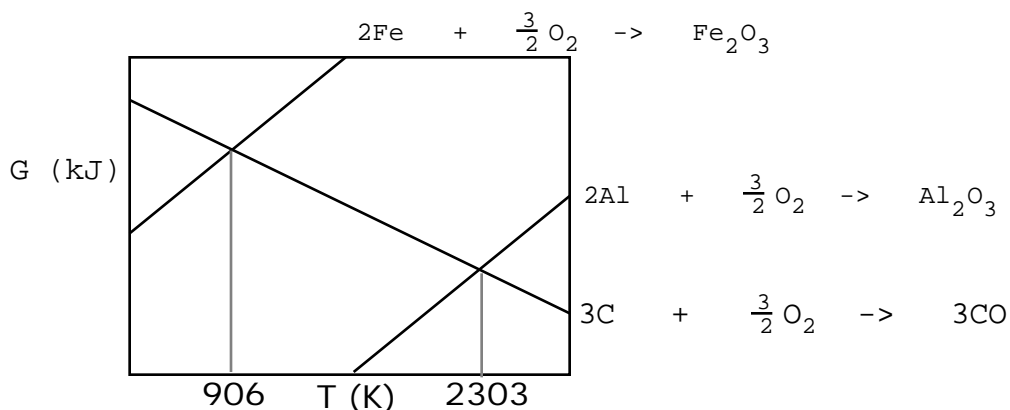
Problem

Aluminium is obtained from its ore, bauxite (impure Aluminium oxide). Unlike Iron, Aluminium cannot be obtained by reduction with Carbon because the required transitional temperature (2303 K) is too high:

Al_2O_3 +   3C   ->   2Al   +   3CO   H = + 1336 kJ
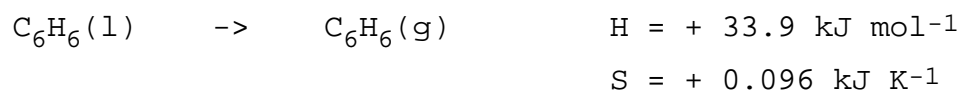
S = + 0.58 kJK^{-1}

Verify the above value of the transitional temperature.

The following Ellingham diagram confirms this temperature:

Aluminium is obtained by electrolysis of molten Al_2O_3 instead.

Problem   Calculate the boiling point of Benzene at 1 atm. pressure given the following information :

C_6H_6(l)   -> C_6H_6(g)   H = + 33.9 kJ mol^{-1}

S = + 0.096 kJ K^{-1}

Answer

A change of state, solid -> liquid or liquid -> gas, occurs when G becomes negative and the transitional temperature is known as the melting point or boiling point respectively.

Using the Gibbs-Helmholtz equation :

 G =   H -   T S

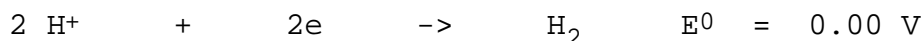 G < 0 <=>   T S   >   H

           <=>   T (+0.096) >   33.9

           <=>   T > $\dfrac{33.9}{0.096}$

                   >   353 K   (80 ^{0}C)

Electrode Potential

> The Electrode Potential E^0 is the attracting power (AP) of a half-reaction on electrons.

All values are measured in volts and are standardised, at 298 K and 1 atm. pressure, on the following half-reaction :
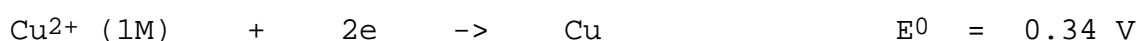
$$2 \ H^+ \quad + \quad 2e \quad -> \quad H_2 \quad E^0 \ = \ 0.00 \ V$$

Some examples from the electrochemical series :

Na^+	+	e	$\rightleftharpoons$	Na			– 2.71
Zn^{2+}	+	2e	$\rightleftharpoons$	Zn			– 0.76
$2H^+$	+	2e	$\rightleftharpoons$	H_2			0.00
SO_4^{2-}	+	$2H^+$ + 2e	$\rightleftharpoons$	SO_3^{2-}	+	H_2O	+ 0.17
Cu^{2+}	+	2e	$\rightleftharpoons$	Cu			+ 0.34
O_2	+	$2H_2O$ + 4e	$\rightleftharpoons$	$4OH^-$			+ 0.40
I_2	+	2e	$\rightleftharpoons$	$2I^-$			+ 0.54
Fe^{3+}	+	e	$\rightleftharpoons$	Fe^{2+}			+ 0.77
Br_2	+	2e	$\rightleftharpoons$	$2Br^-$			+ 1.07
Cl_2	+	2e	$\rightleftharpoons$	$2Cl^-$			+ 1.36
MnO_4^-	+	$8H^+$ + 5e	$\rightleftharpoons$	Mn^{2+}	+	$4H_2O$	+ 1.51
F_2	+	2e	$\rightleftharpoons$	$2F^-$			+ 2.87

Cu^{2+} is therefore a better oxidising agent than Na^+.

The above values are quoted for 1 mol l^{-1} (1M) solutions.

The E^0 value increases with ion concentration e.g.

$$Cu^{2+} \ (1M) \quad + \quad 2e \quad -> \quad Cu \qquad E^0 \ = \ 0.34 \ V$$

$$Cu^{2+} \ (0.01M) \ + \quad 2e \quad -> \quad Cu \qquad E^0 \ = \ 0.28 \ V$$

When these half reactions are reversed they have a pushing power (PP) on electrons equal to – E^0

e.g. for a 1 mol l^{-1} solution of Cu^{2+}

$$Cu \quad -> \quad Cu^{2+} \quad + \quad 2e \qquad\qquad – E^0 = \ – \ 0.34 \ V$$

The greater the voltage the more favourable the reaction e.g.

$$Na \quad -> \quad Na^+ \quad + \quad e \qquad\qquad – E^0 = \ + \ 2.71 \ V$$

is more favourable than

$$Zn \quad -> \quad Zn^{2+} \quad + \quad 2e \qquad\qquad – E^0 = \ + \ 0.76 \ V$$
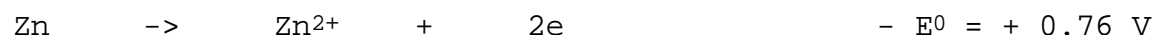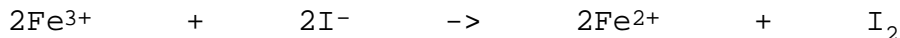
Na is therefore a better reducing agent than Zn.

Problem   Use tables of electrode potentials to predict whether
           the following reaction occurs spontaneously:

$$2Fe^{3+} \quad + \quad 2I^- \quad -> \quad 2Fe^{2+} \quad + \quad I_2$$

Answer

The net pressure(V) on the electrons transferred from the reducing
agent to the oxidising agent is equal to the pushing power (PP) of
the reducing agent + the attracting power (AP) of the oxidising
agent and must be greater than zero if the reaction is to occur.

The two half-equations are:

$2Fe^{3+}$ +	$2e$	->	$2Fe^{2+}$	AP $(+E^0)$	=	0.77 V
$2I^-$ ->	I_2 +	$2e$		PP $(-E^0)$	=	-0.54 V

$$2Fe^{3+} \quad + \quad 2I^- \quad -> \quad 2Fe^{2+} \quad + \quad I_2 \qquad V \quad = + 0.23 \text{ V}$$
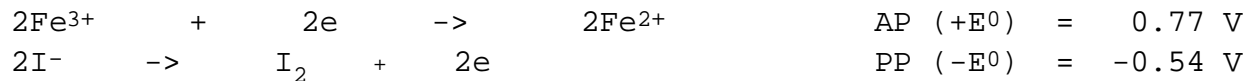
Since V is positive the reaction **will** occur.

In the previous
problem,
electrons will
flow from I^- to
Fe^{3+} under a
potential
difference of
+ 0.23 V as can
be shown with
the cell :

(a)   (b)
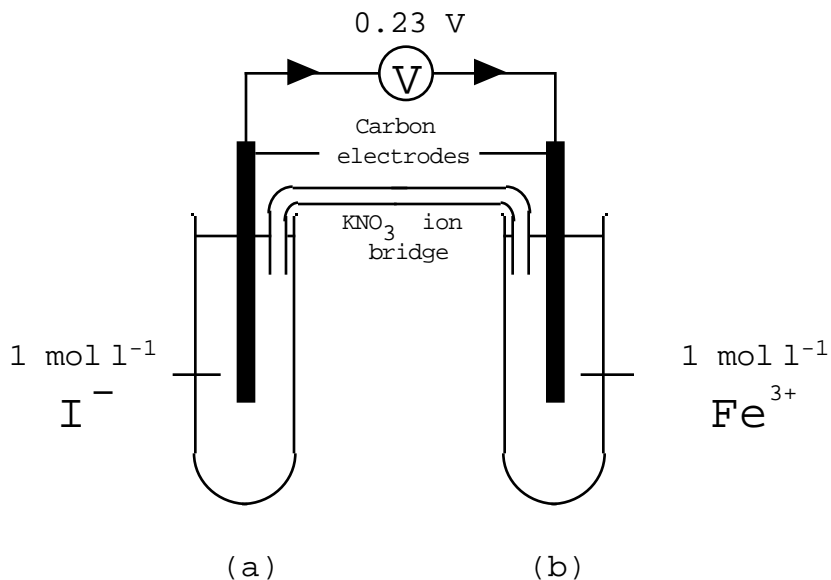
Problem : Calculate the voltage of the concentration cell shown :

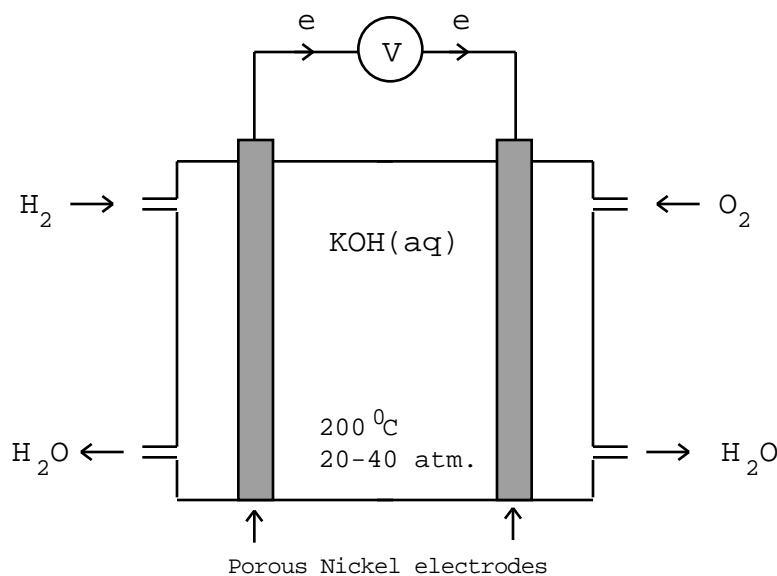|							
Answer :	**A**	Cu^{2+}	+	$2e$	->	Cu	E^0 = 0.34 V
	B	Cu	->	Cu^{2+}	+	$2e$	− E^0 = − 0.28 V
							V = 0.06 V
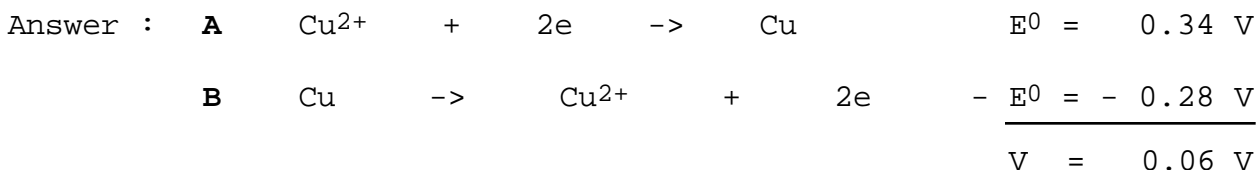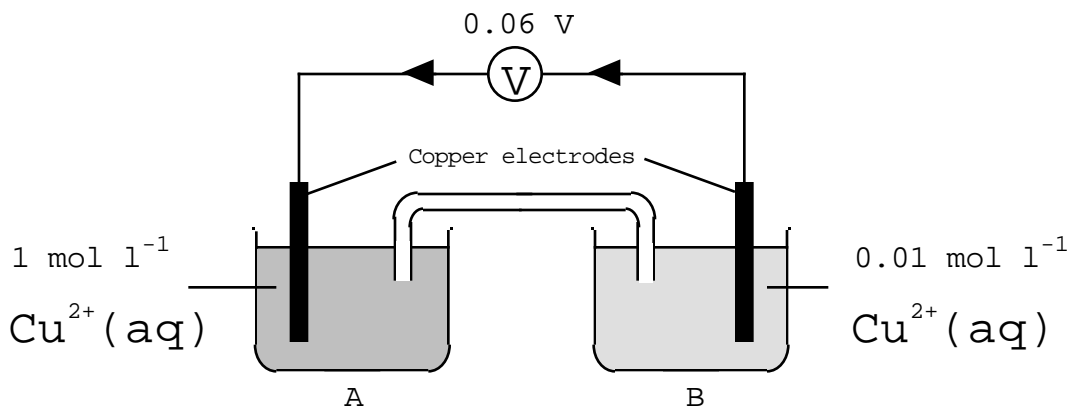
Since electrode potentials vary with concentration, the voltage of a cell is dependent on the concentrations of the reacting solutions.
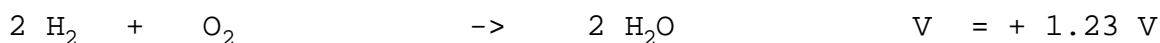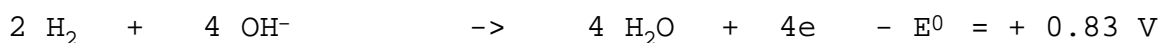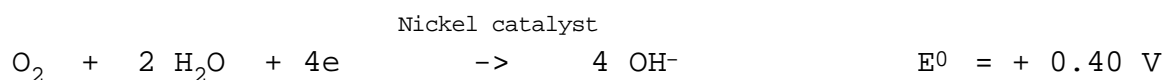
Electrode potentials also vary with temperature; cell voltage is also temperature dependent.
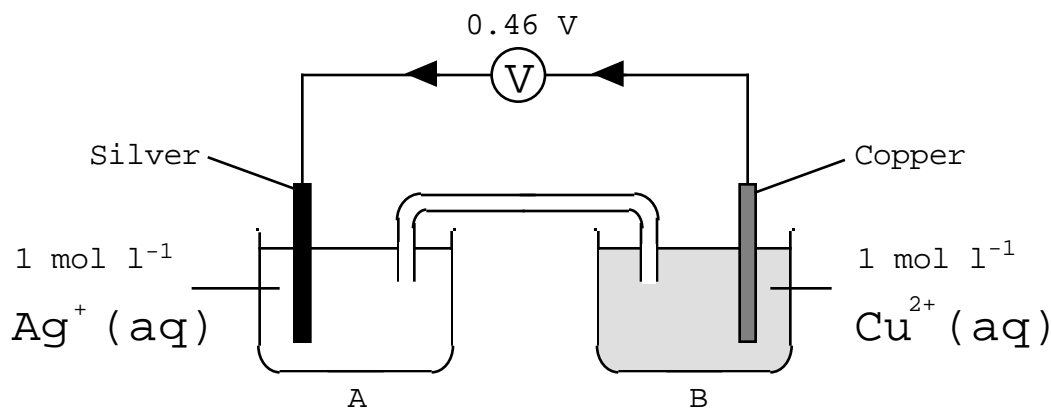
Fuel Cells

Fuel cells differ from other cells in allowing a continuous supply of reactants (or fuel) e.g. the Oxygen/Hydrogen fuel cell:

The two half-equations are:

$$\text{Nickel catalyst}$$

$$O_2 \ + \ 2\ H_2O \ + \ 4e \quad -> \quad 4\ OH^- \qquad\qquad E^0 \ = \ +\ 0.40\ V$$

$$2\ H_2 \ + \ 4\ OH^- \quad\qquad -> \quad 4\ H_2O \ + \ 4e \quad -\ E^0 \ = \ +\ 0.83\ V$$

$$2\ H_2 \ + \ O_2 \quad\qquad\qquad -> \quad 2\ H_2O \qquad\qquad V \ = \ +\ 1.23\ V$$
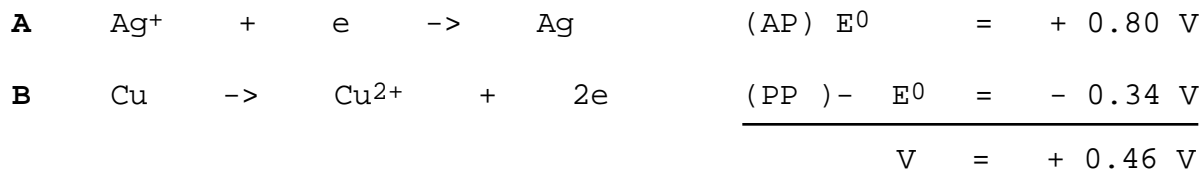
Problem : Calculate the voltage of the cell shown and deduce G
          for the cell reaction :

Answer :

Cell voltage   =   Net pressure on electrons in external circuit
                =   Attracting power (AP) of reaction in **A** +
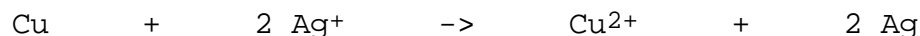   pushing power (PP) of reaction in **B**

A Ag^+ +   e   ->   Ag   (AP) E^0 =   + 0.80 V

B   Cu   -> Cu^{2+} +   2e   (PP)- E^0 =   - 0.34 V

                                                    V   =   + 0.46 V

Let F   = charge on 1 mole of electrons (Faraday)
            = 96500 coulombs

        Work done in transferring 1 coul. through a PD of 1 volt   = 1 Joule

=>   Work done in trans. 1 mole of electrons through a PD of   = F Joules
      1 volt

=>   Work done in trans. 1 mole of electrons through a PD   = FE Joules
      of E volts

=>   Work done in trans. n moles electrons through a PD   = nFE Joules
      of E volts

=>   Work done by a reaction in trans. n moles electrons   = nFE Joules
      through a PD of V volts

=> | – G = nFE |

The above cell reaction involves the transfer of 2 moles of
electrons from Cu to Ag^+ i.e.

Cu   +   2 Ag^+ -> Cu^{2+} +   2 Ag

V = 0.46 V

  – G = nFE

        = 2 x 96500 x 0.46

        = 88780 Joules

=> G = – 88.78 kJ