CH10090 Thermodynamics (part 2)

Let's remember what we did in CH10089

Enthalpy changes during reactions

$$\Delta H^\circ_{298}\ (\text{reaction}) = \sum \nu_i\ \Delta H^\circ_{f,298}(\text{products}) - \sum \nu_i\ \Delta H^\circ_{f,298}(\text{reactants})$$

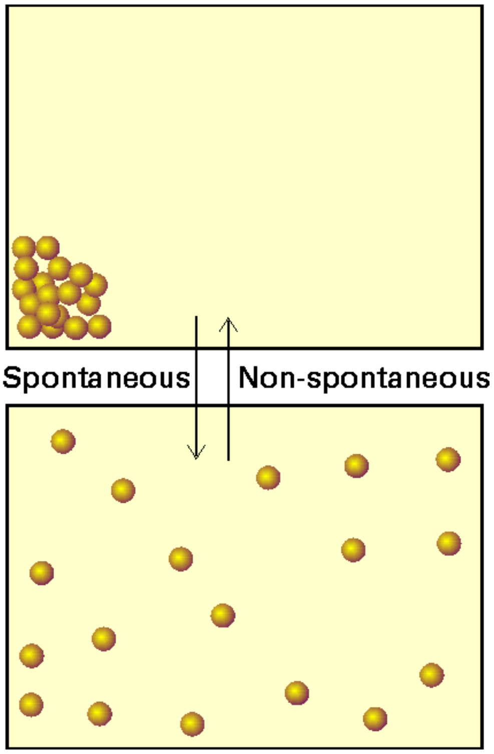
ν_i represents the stoichiometric coefficient.

This method can be used to calculate ΔH for any reaction where we have $\Delta H^\circ_{f,298}$ data for the components.

AT 25 °C !

The Second Law of Thermodynamics

Spontaneous processes are those which increase the entropy of the Universe



Entropy ⇒ related to order ∴ spontaneous processes are those which lead to an increase in disorder.

$$\Delta S = S_{final} - S_{initial}$$

$$\Delta S = \frac{q_{rev}}{T}$$

The Third Law of Thermodynamics

The entropy of a perfect crystal at zero Kelvin is zero

The standard entropy, S^{o}_{298} of a compound is the molar entropy at 298.15 K and 1 bar pressure

Entropy changes in chemical reactions

the standard entropy of reaction as the difference in standard entropy of the products from that of the reactants

$$\Delta S^\circ_{298}\ (\text{reaction}) = \Sigma\, \nu_i\, S^\circ_{298}\ (\text{products}) - \Sigma\, \nu_i\, S^\circ_{298}\ (\text{reactants})$$

AT 25 °C !

Now we need to be able to work at other temperatures

The Gibbs function or Gibbs free energy, G.

$G = H - TS$ or $\Delta G = \Delta H - T\,\Delta S$

For a spontaneous process at constant T, p there must be a lowering of the Gibbs free energy or

$$(\Delta G)_{p,\,T} < 0$$

Entropy as a predictor of chemical reactivity

$$\mathbf{2\,H_{2\,(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(l)}}$$

$$\Delta S^\circ_{298} = [2 \times S^\circ_{298}(H_2O)] - [2 \times S^\circ_{298}(H_2) + S^\circ_{298}(O_2)]$$

$$= [2 \times 70] - [2 \times 131 + 205] \ \mathbf{= -327\ J\ K^{-1}\ mol^{-1}}$$

There is a large loss of entropy on forming water. WHY?

This is for the H_2 / O_2 / H_2O *system*. The 2nd Law refers to the entropy of *the Universe* increasing as a requirement for spontaneity.

$$\Delta S(\text{Universe}) = \Delta S(\text{system}) + \Delta S(\text{surroundings})$$

ΔS(surround) = ΔH°(surround) / T = - ΔH°(system) / T

ΔH°_{298} for the above reaction (the system) is -571.6 kJ.

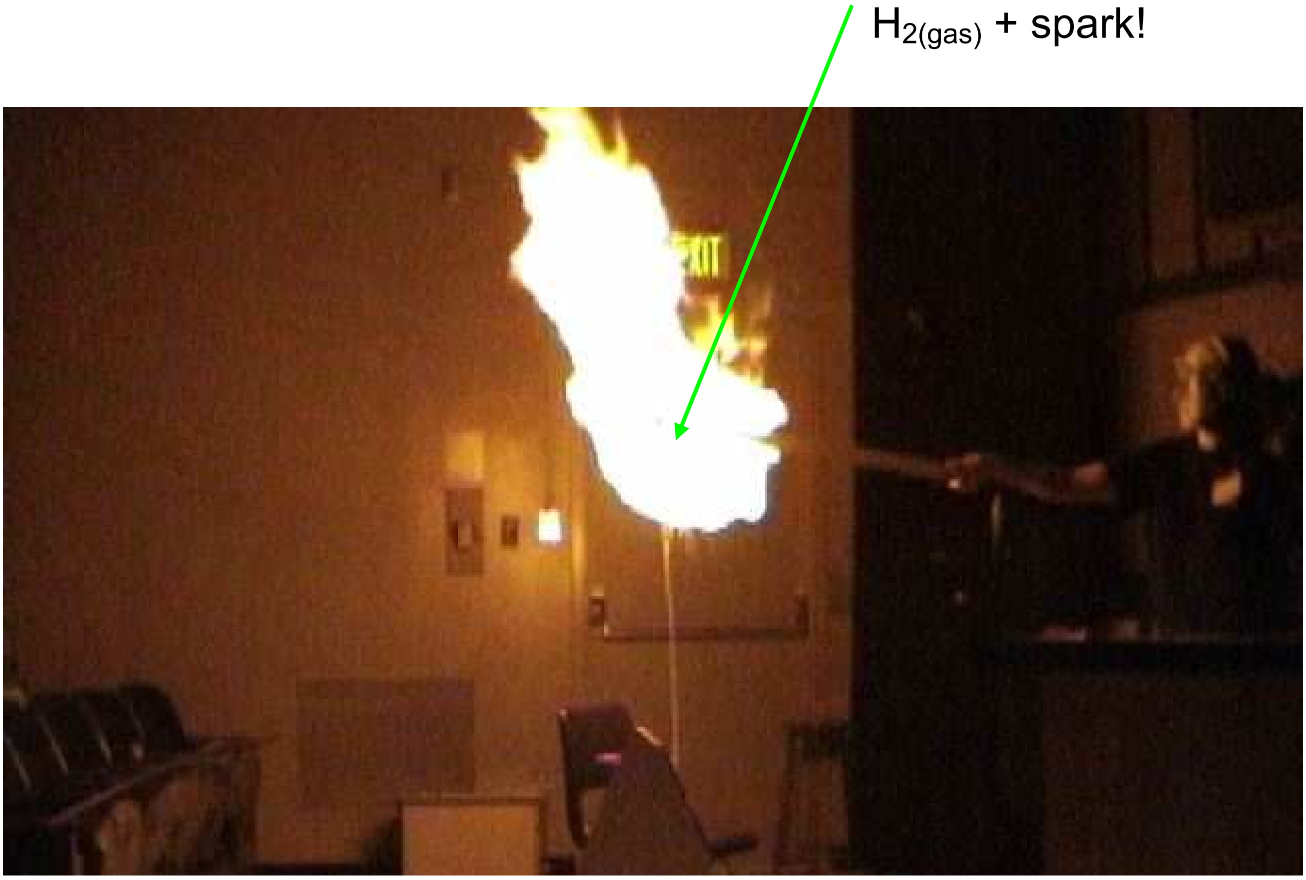
So ΔS(surround) = + 571.6 x 10^3 J / 298 K = + 1920 J K^{-1}

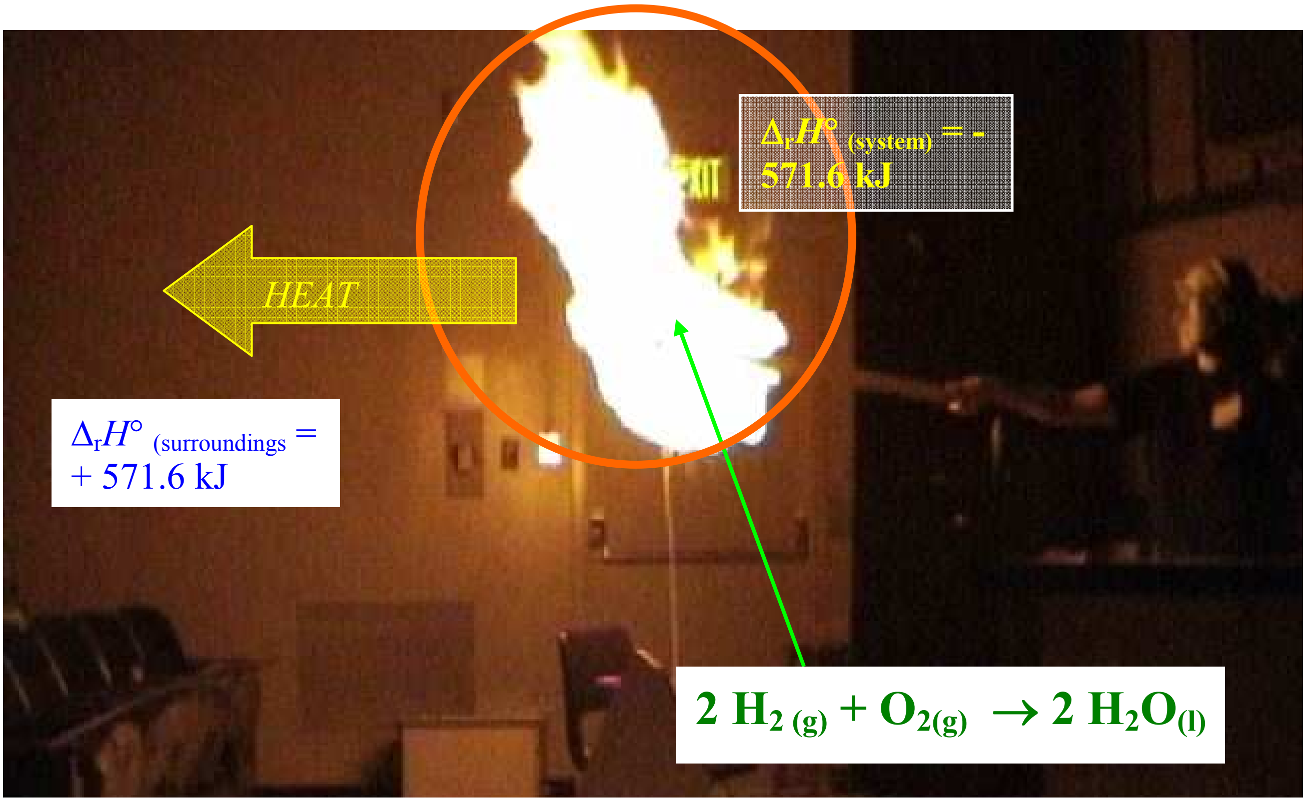
$$\Delta S(\text{Universe}) = \Delta S(\text{system}) + \Delta S(\text{surroundings})$$

$$= -327 + 1920 \ \mathbf{= +1593\ J\ K^{-1}}$$

Hence, there is an overall *increase* in the total entropy of the Universe, in accord with the second law.

Balloon containing $H_{2(gas)}$ + spark!





$\Delta_r H°$ (system) = - 571.6 kJ

$\Delta_r H°$ (surroundings = + 571.6 kJ

$$2\ H_{2\ (g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)}$$

The Gibbs function or Gibbs free energy, G.

From 2nd Law, for a spontaneous process at constant T, p :

$$\Delta S(\text{Universe}) = \Delta S(\text{Sys.}) + \Delta S(\text{Surr.}) > 0$$

or

$$\Delta S(\text{Universe}) = \Delta S(\text{Sys.}) + \{\Delta H(\text{Surr.}) / T\} > 0$$

We don't want to focus on the Universe every time: Since,

$\Delta H(\text{Surr.}) = -\Delta H(\text{Sys.})$.

$$\Delta S(\text{Sys.}) + (-\Delta H(\text{Sys.}) / T) > 0$$

So we can write

$$\boxed{\Delta H - T\Delta S < 0}$$

The value of $\Delta H - T\Delta S$ is the *Gibbs function or Gibbs free energy, G.*

$$G = H - TS \quad \text{or} \quad \mathbf{\Delta G = \Delta H - T\Delta S}$$

For a spontaneous process at constant T, p there must be a lowering of the Gibbs free energy or

$$\boxed{(\Delta G)_{p,T} < 0}$$

In general, we can conclude that *if a process or reaction results in a lowering of the free energy, it will be spontaneous i.e.* that it will be favourable and CAN happen. It does not mean that it WILL happen.

e.g. at 1 bar and 25 °C

$2\ H_{2(g)} + O_{2\ (g)} \rightarrow 2\ H_2O_{\ (l)} \quad \Delta G^\circ = -\ 273.2\ kJ\ mol^{-1}$

However, a mixture of hydrogen and oxygen gases in a container will not react until started by a catalyst or source of ignition.

The reaction is *thermodynamically* very favourable but occurs extremely slowly. It is *kinetically* unfavourable as it has a high activation energy.

Key points so far:

- The Second Law of Thermodynamics: Spontaneous processes increase the entropy of the Universe
- the Third Law of Thermodynamics : The entropy of a perfect crystal at zero Kelvin is zero
- ΔS°_{298} (reaction) $= \Sigma \nu_i S^\circ_{298}$ (prod.) - $\Sigma \nu_i S^\circ_{298}$ (react.)
- Gibbs function or Gibbs free energy, G. An exact definition of G is: $G = H - TS$ or $\Delta G = \Delta H - T \Delta S$
- For a spontaneous process at constant T, p $(\Delta G)_{p,\,T} < 0$

Derivation of equations is NOT important. You do need to perform calculations using the equations and interpret the results in terms of the chemistry

Calculate the Gibbs free energy change at 298 K and estimate the temperature at which the reaction just becomes spontaneous.

$$2\ \mathrm{Fe_2O_{3(s)}} + 3\ \mathrm{C_{(s)}} \rightarrow 4\ \mathrm{Fe_{(s)}} + 3\ \mathrm{CO_{2(g)}}$$

	$\mathrm{Fe_2O_{3\ (s)}}$	$\mathrm{C_{(s)}}$	$\mathrm{Fe_{(s)}}$	$\mathrm{CO_{2(g)}}$
$\Delta_f H^\circ_{298}$ / kJ $\mathrm{mol^{-1}}$:	-824.2	0	0	-393.5
S°_{298} / J $\mathrm{K^{-1}\ mol^{-1}}$:	87.4	5.7	27.3	213.7

Solution

- calculate $\Delta_r H^\circ_{298}$ and $\Delta_r S^\circ_{298}$

$$\Delta_r H^\circ_{298} = \sum \nu_\mathrm{i}\ \Delta_f H^\circ_{298}(products) - \sum \nu_\mathrm{i}\ \Delta_f H^\circ_{298}(\mathrm{reactants})$$

$\Delta_r H^\circ_{298}$ = [0 + 3 × (-393.5)] - [2 × (-824.2) + (0)] = + 467.9 kJ $\mathrm{mol^{-1}}$.

$$\Delta_r S^\circ_{298} = \sum \nu_\mathrm{i}\ \mathrm{S}^\circ_{298}(products) - \sum \nu_\mathrm{i}\ S^\circ_{298}(\mathrm{reactants})$$

$\Delta_r S^\circ_{298}$= [4 × (32.7)+3 ×(213.7)] - [2 × 87.4 + 3 × 5.7] = + 558.4 J $\mathrm{mol^{-1}\ K^{-1}}$.

- calculate $\Delta_r G^\circ_{298}$

$$\begin{aligned}\Delta_r G^\circ_{298} &= \Delta_r H^\circ_{298} - T\Delta_r S^\circ_{298} \\ &= +\ 467.9\ -\ (298.15) \times (558.4 \times 10^{-3})\ \mathrm{kJ\ mol^{-1}}. \\ &= +\ 301.4\ \mathrm{kJ\ mol^{-1}}.\end{aligned}$$

The Gibbs free energy change is positive and so the reaction is non-spontaneous at 298 K. It becomes spontaneous when $\Delta_r G = \Delta_r H - T\,\Delta_r S = 0$.

- Substitute the values of $\Delta_r H^\circ_{298}$ and $\Delta_r S^\circ_{298}$ to find T when $\Delta_r G$ = 0

$$\Delta_r G = 0$$

$$\Delta_r H - T\,\Delta_r S = 0$$

$$+\,467.9\ \text{kJ mol}^{-1} - (T / \text{K}) \times (558.4 \times 10^{-3})\ \text{kJ mol}^{-1}\ \text{K}^{-1} = 0$$

- Rearrange to find T

$$+\,467.9\ \text{kJ mol}^{-1} = (T / \text{K}) \times (558.4 \times 10^{-3})\ \text{kJ mol}^{-1}\ \text{K}^{-1}$$

$$\frac{+\,467.9 kJmol^{-1}}{558.4 \times 10^{-3} kJmol^{-1} K^{-1}} = (T / \text{K})$$

$$T = 838\ \text{K}$$

Variation of enthalpy with temperature

What do we already know?

- Enthalpy ≡ 'Heat energy' (at constant pressure)
- We have data at 25 °C
- Heat capacities describe changes in energy with temperature

We define a *constant pressure heat capacity, Cp,* -

" the amount of heat energy needed to raise the temperature of 1 mole of substance by 1 K at constant pressure"

$$C_p = \left(\frac{dq_p}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p \quad \text{or} \quad dH = C_p\, dT$$

So, H must increase by ($C_p\,dT$) if heated by dT.

$$\int dH = \int_{T_1}^{T_2} C_p\, dT$$

the *Kirchoff Equation*

Approximation: treat c_p as independent of T for small temp. ranges and use the average value over the range of T

If a compound has an enthalpy H_1 at temperature T_1 etc.

$$H_{T_2} - H_{T_1} = C_p(T_2 - T_1)$$

Particularly useful: standard enthalpies of formation are defined at 25 °C. Hence,

$$\boxed{\Delta H^\circ_{f,\,T} = \Delta H^\circ_{f,\,298} + C_p\,(\,T - 298.15\,)}$$

How can we use this?

C$_p$ for liquid mercury at 25 °C is 27.98 J mol^{-1} K^{-1}. Calculate the enthalpy of formation at 50 °C.

$$\Delta H^\circ_{f,\,T} = \Delta H^\circ_{f,\,298} + C_p\,(\,T - 298.15\,)$$

$\Delta H^\circ_{f,}$ at 25 °C is 0 (by definition).

$$\Delta H^\circ_{f,\,323} = 0 + (27.98\text{ J mol}^{-1}\text{ K}^{-1})\,(\,323.15 - 298.15\,)\text{ K}$$

$$= 699\text{ J mol}^{-1}$$

Enthalpies of Reaction

A model reaction: $\mathbf{R} \rightarrow \mathbf{P}$

The enthalpy of R at 25 °C is $\Delta H^\circ_{f,\,298}\,(R)$.

The enthalpy at some other temperature T is
$[\Delta H^\circ_{f,\,298}\,(R) + C_p\,(R)\,(T - 298.15)]$.

$$\Delta H^\circ_T\,(\text{reaction}) = [\Delta H^\circ_{f,\,T}\,(P)\,] - [\Delta H^\circ_{f,\,T}\,(R)]$$

$$= [\Delta H^\circ_{f,\,298}\,(P) + C_p(P)\,(T - 298.15)\,] - [\Delta H^\circ_{f,\,298}\,(R) + C_p(R)\,(T - 298.15)]$$

$$= [\Delta H^\circ_{f,\,298}(P) - \Delta H^\circ_{f,\,298}(R)\} + \{[\,C_p(P) - C_p(R)]\,(T - 298.15)\}$$

or

$$\boxed{\Delta H^\circ_T\,(\text{reaction}) = \Delta H^\circ_{298}\,(\text{reaction}) + \Delta\, C_p\,(T - 298.15)}$$

where

$$\Delta C_p = \sum \nu_i\, \mathrm{C_p}\,(\text{products}) - \sum \nu_i\, \mathrm{C_p}\,(\text{reactants})$$

so, we can now calculate the enthalpy of reaction *at any temperature.*

The complete combustion of ethane releases 1558.8 kJ mol^{-1} at 25 °C. Calculate ΔH°(combustion) at 100 °C.

c_p / J K^{-1} mol^{-1}: $C_2H_{6(g)}$ 52.6; $O_{2(g)}$ 29.4; $CO_{2(g)}$ 37.1; $H_2O_{(l)}$ 75.3

$C_2H_{6(g)} + 3\frac{1}{2}\ O_{2(g)} \rightarrow 2\ CO_{2(g)} + 3\ H_2O_{(l)} \quad \Delta H^\circ_{298} = -1558.8\ \text{kJ mol}^{-1}$

$$\begin{aligned}\Delta C_p &= [2\ C_p(CO_2) + 3\ C_p(H_2O)] - [C_p(C_2H_6) + 3\tfrac{1}{2}\ C_p(O_2)] \\ &= [2(37.1) + 3(75.3)] - [52.6 + 3\tfrac{1}{2}(29.4)] \\ &= 144.6\ \text{J K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{373} &= \Delta H^\circ_{298} + \Delta C_p\,\Delta T \\ &= -1558.8 \times 10^3\ (\text{J mol}^{-1}) + (144.6\ \text{J K}^{-1}\ \text{mol}^{-1})(75\ \text{K}) \\ &= -1547.9\ \text{kJ mol}^{-1}\end{aligned}$$

(See CH10089 notes for this problem at 25 °C)

A gas mixture consisting of 25% N_2 and 75% H_2 (by volume) was passed over a catalyst at a rate of 112 dm^3 min^{-1} (Gas volumes corrected to 0 °C and 1 atm pressure). The reaction took place at 450 °C and 1 bar pressure and complete conversion to ammonia was achieved. Calculate the rate of heat evolution or absorption.

$\Delta H^\circ_{f,\,298}(NH_3)$ - 46.0 kJ mol^{-1}

Mean Cp / J K^{-1} mol^{-1}: N_2 29.7; H_2 29.3; NH_3 39.7.

$$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$$

$$\Delta H^\circ_{298} = [\ 2 \times \Delta H^\circ_{f,\ 298}\ (NH_3)]\ - [\Delta H^\circ_{f,\ 298}\ (N_2) + 3\ \Delta H^\circ_{f,\ 298}\ (H_2)]$$
$$= [\ -92.0\ ]\ - [\ 0\ ]\quad kJ\ mol^{-1}$$

$$\mathbf{\Delta H^\circ_{298} = -92.0\ kJ\ mol^{-1}}$$

Changing to 450 °C using the Kirchoff Eqn.

$$\Delta H^\circ_T\ (reaction) = \Delta H^\circ_{298}\ (reaction) + \Delta \bar{c}_p\ (T - 298.15)$$

$$\Delta Cp = [2 \times \bar{c}_p\ (NH_3)] - [\bar{c}_p (N_2) + 3 \times \bar{c}_p (H_2)\}$$
$$= [2 \times 39.7] - [\ 29.7 + (3 \times 29.3)]$$
$$= -38.2\ \ J\ K^{-1}\ mol^{-1}$$

$$\Delta H^\circ_{723} = -92000\ Jmol^{-1} + (-38.2\ \ J\ K^{-1}\ mol^{-1}\ )\ (723.15 - 298.15)K$$
$$= -92000\ Jmol^{-1} + (\ -16235\ Jmol^{-1}\ )$$

$$\mathbf{\Delta H^\circ_{723} = -108.24\ kJ\ mol^{-1}}$$

Hence, at 450 °C, 108.24 kJ is evolved for each mole of the equation i.e 108.24 kJ is evolved per mole of nitrogen which reacts.

Since, for a gas, volume $\propto$ number of moles, the 1:3 mixture is in the stoichiometric amount. At 0 °C and 1 atm pressure, 1 mole occupies 22.4 dm^3. Thus, the total amount of gas passing over the catalyst amounted to 5 moles per minute, of which 1.25 moles were N_2.

$$\text{Rate of heat evolution} = (\text{mol of } N_2\ \text{min}^{-1}\ )\ (\text{heat per mole } N_2)$$
$$= (\ 1.25\ \text{mol min}^{-1}\ )\ (-\ 108.24\ kJ\ (\text{mol } N_2^{-1}\ )$$
$$\mathbf{= -135.3\ kJ\ min^{-1}}$$

The negative sign indicates an exothermic reaction so that heat is evolved.

Effect of temperature on entropy

From before, we know that:

q_{rev} = Cp dT at constant pressure.

and

$$\Delta S = \frac{q_{rev}}{T}$$

The entropy at T_f is related to entropy T_i by

$$\Delta S = S_{T_f} - S_{T_i} = \frac{dq_{rev}}{T} = \int_{T_i}^{T_f} \frac{c_p}{T} dT$$

If we approximate c_p is constant over the temperature range involved, then providing no change of phase occurs:

$$S_{T_f} = S_{T_i} + \bar{c}_p \int_{T_i}^{T_f} \frac{1}{T} dT = S_{T_i} + \bar{c}_p \, ln\left(\frac{T_f}{T_i}\right)$$

Given the heat capacities of ice and water at 0 °C are 2.2 and 4.18 J K^{-1} g^{-1} and the enthalpy of fusion is 332 J g^{-1}, calculate the entropy change for the freezing of 1 mole of supercooled water at -10 °C.

Clearly, $H_2O_{(l)}$, -10 °C → $H_2O_{(s)}$, -10 °C cannot be carried out in a reversible manner.

Thus, in order to calculate ΔS, we must separate the process into a series of reversible changes and sum ΔS for each. This procedure is valid since entropy is a state function.

$$\text{water, -10 °C} \xrightarrow{\Delta S_1} \text{water, 0 °C} \xrightarrow{\Delta S_2} \text{ice, 0 °C} \xrightarrow{\Delta S_3} \text{ice, -10 °C}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 4.18 \ln\left(\frac{273}{263}\right) + \frac{-332}{273} + 2.2 \ln\left(\frac{263}{273}\right) \quad \text{J K}^{-1}\text{g}^{-1}$$

$\Delta S = 0.156 + (-1.216) + (-0.082) = -1.142$ J K^{-1} g^{-1}

Hence,

$\Delta S = (18 \text{ g mol}^{-1})(-1.142 \text{ J K}^{-1} \text{ g}^{-1}) = -20.556 \text{ J K}^{-1} \text{ mol}^{-1}$

Note: We have a negative entropy change arising from a liquid forming a more ordered solid.

Standard or Absolute Entropies

For convenience, entropies are listed under standard conditions.

The standard entropy, S°_{298} of a compound is the molar entropy at 298.15 K and 1 bar pressure

e,g. Consider a gas at room temperature. How can we find the *standard entropy,* S°_{298} ?

1. Heating from 0K to T_m.

$$\Delta S^{\circ}_{1} = \int_{0}^{T_m} \frac{\bar{c}_p\,(\text{solid})}{T}\,dT$$

2. Melting at Tm

$$\Delta S^{\circ}_{2} = \frac{\Delta H^{\text{fus.}}}{T_m}$$

3. Heating from T_m to T_b

$$\Delta S^{\circ}_{3} = \int_{T_{im}}^{T_b} \frac{\bar{c}_p\,(\text{liquid})}{T}\,dT$$

4. Vaporization at T_b

$$\Delta S^{\circ}_{4} = \frac{\Delta H^{\text{vap.}}}{T_b}$$

5. Heating from T_b to 298 K

$$\Delta S^{\circ}_{5} = \int_{T_b}^{298} \frac{\bar{c}_p\,(\text{vapour})}{T}\,dT$$

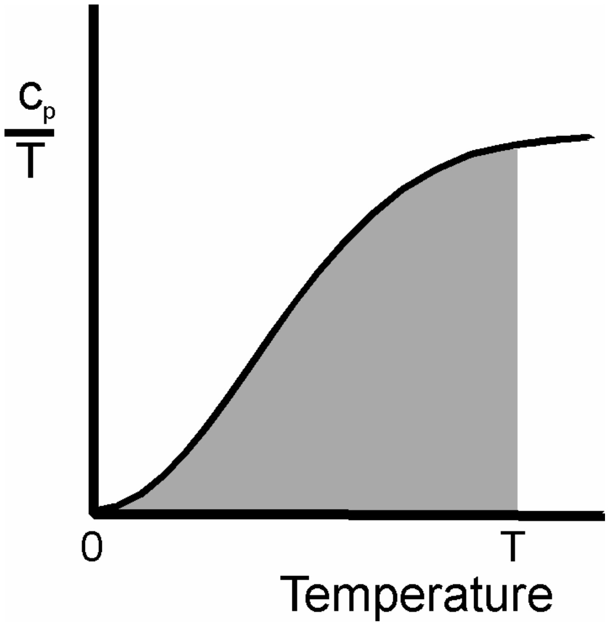
$$S^{\circ}_{298} = \Delta S^{\circ}_{1} + \Delta S^{\circ}_{2} + \Delta S^{\circ}_{3} + \Delta S^{\circ}_{4} + \Delta S^{\circ}_{5}$$

For liquids at 298 K and 1 bar, omit steps 4 and 5 and replace T_b with 298 in step 3

Where there is more than one phase in the solid, the additional ΔS entropy for the phase changes must also be taken into account.

ΔS°_1 can't be calculated in this form – it must be evaluated graphically or numerically.

The shaded area is equivalent to the standard entropy at temperature T



Entropy changes in chemical reactions

$$\Delta S^\circ_{298}\,(\text{reaction}) = \Sigma\, \nu_i\, S^\circ_{298}\,(\text{products}) - \Sigma\, \nu_i\, S^\circ_{298}\,(\text{reactants})$$

The entropy change at other temperatures can be calculated by

$$\Delta S_{T_2} = \Delta S_{T_1} + \int_{T_1}^{T_2} \frac{\Delta c_p}{T}\, dT$$

Using mean heat capacities,

$$\Delta S_{T_2} = \Delta S_{T_1} + \Delta c_p \int_{T_1}^{T_2} \frac{1}{T} dT = \Delta S_{T_1} + \Delta c_p \; ln\left(\frac{T_2}{T_1}\right)$$

This allows us to calculate entropy changes during reactions at any temperature.

Using these values, at any temperature, T

$$\boxed{\Delta G_T = \Delta H_T - T\,\Delta S_T}$$

Key points so far:

- Calculation of ΔH for reactions at any temperature
- Calculation of ΔS for reactions at any temperature
  - Definition and measurement of absolute entropies
  - Calculation of ΔG for reactions at any temperature

Variation of Gibbs free energy with conditions

We begin with a single component. From the definition of free energy:

$$G = H - TS = (U + PV) - TS$$

To find the change in Gibbs free energy, dG, caused by small changes in any of the other conditions, we take the *total differential*

$$dG = dU + PdV + VdP - TdS - SdT$$

From earlier lectures,

$$dU = dq + dw = dq - PdV$$

and

$$dS = dq / T \quad \text{or} \quad dq = TdS \qquad dU = TdS - PdV$$

Substituting this:

$$dG = (TdS - PdV) + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

$$\boxed{dG = VdP - SdT}$$

the master equation or the fundamental equation - allows us to calculate the effect on G of changing conditions.

Note: Strictly, this is for a single component. We will look at mixtures with varying composition later.

How can we use the Master equation?

Variation of G with temperature

$$dG = VdP - SdT$$

at constant pressure: $dP = 0$

$$dG = -S\,dT \quad \text{or} \quad \left(\frac{dG}{dT}\right)_P = -S$$

If we know the entropy of a substance, we can find out how G varies with temperature.

- an alternative interpretation of entropy - the T dependence of G

For chemical reactions, $\left(\frac{d\,\Delta G}{dT}\right)_P = -\Delta S$

However, it is usually easier to calculate ΔH_T and ΔS_T from data and then use $\Delta G_T = \Delta H_T - T\,\Delta S_T$

Given the pure component data below, calculate the standard free energy change for the following reaction at 25 °C and 1025 °C.

$$MgO_{(s)} + CO_{(g)} \rightarrow Mg_{(s)} + CO_{2(g)}$$

	$MgO_{(s)}$	$CO_{(g)}$	$Mg_{(s)}$	$CO_{2(g)}$
ΔH° / kJ mol^{-1} :	-601.7	-110.5	0	-393.5
S° / J K^{-1} mol^{-1} :	26.9	197.7	32.7	213.7
Cp / J K^{-1} mol^{-1} :	37.2	29.1	24.9	37.1

$$\Delta H^\circ_{298} = [\,0 + (-393.5)] - [\,(-601.7) + (-110.5)] = +\,318.7\ \text{kJ mol}^{-1}.$$
$$\Delta S^\circ_{298} = [\,32.7 + 213.7] - [\,26.9 + 197.7] = 21.8\ \text{J mol}^{-1}\ \text{K}^{-1}.$$

$$\Delta G^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298} = 318.7 - (298.15)(\,21.8 \times 10^{-3})\ \text{kJ mol}^{-1}.$$
$$= +\,312.2\ \text{kJ mol}^{-1}.$$

To convert ΔH°_{298} and ΔS°_{298} to the higher temperature, we need ΔCp.

$$\Delta Cp = [\,24.9 + 37.1] - [\,37.2 + 29.1] = -4.3\ \text{J mol}^{-1}\ \text{K}^{-1}.$$

$$\Delta H^\circ_{1298} = \Delta H^\circ_{298} + \Delta Cp\,(1298 - 298) = 318.7 + (-4.3 \times 10^{-3})(1000)$$
$$= 314.4\ \text{kJ mol}^{-1}.$$

$$\Delta S^\circ_{1298} = \Delta S^\circ_{298} + \Delta Cp\,\ln\,(1298 / 298) = 21.8 + (-4.3)(1.471)$$
$$= 15.47\ \text{J mol}^{-1}\ \text{K}^{-1}.$$

$$\Delta G^\circ_{1298} = \Delta H^\circ_{1298} - T\Delta S^\circ_{1298} = 314.4 - (1298.15)(15.47 \times 10^{-3})\ \text{kJmol}^{-1}$$
$$= +\,294.3\ \text{kJ mol}^{-1}.$$

Reduction of a metal oxide with CO is sometimes used to recover the metal from an ore.

In this case, is this approach feasible ?

Variation of G with pressure

$$dG = VdP - SdT$$

At fixed temperature, $dT = 0$.

$dG = VdP$ or $\left(\frac{dG}{dp}\right)_T = V$

Molar volumes of solids and liquids, and their changes during reactions, are small so G or ΔG changes little with pressure.

For an ideal gas. $\left(\frac{dG}{dp}\right)_T = V = \frac{nRT}{p}$

If the free energy changes from G_1 to G_2 when the pressure changes from p_1 to p_2,

$$\int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} \frac{nRT}{p}\, dp = nRT \int_{p_1}^{p_2} \frac{1}{p}\, dp$$

which leads to $\boxed{G_2 - G_1 = nRT\, ln\left(\frac{p_2}{p_1}\right)}$

G° is the value at the standard pressure of $p^\circ = 1$ bar.

$$G = G^\circ + nRT\, \mathit{ln}\,(p / p^\circ) = G^\circ + nRT\, \mathit{ln}\,(p / 1\ \text{bar})$$

This is often written as "$G = G^\circ + nRT\, \mathit{ln}\,(p)$" - OK as long as the pressure is measured in units of bar

For gases, pressure $\propto$ concentration so this gives a measure of how the free energy depends on concentration for a gas or gaseous reaction.

The thermodynamic activity

To get a consistent representation of the composition dependence of G in all systems, we define the *activity* or "effective concentration" of the component.

We can use the general equation

$$\boxed{G = G^\circ + nRT\, \mathit{ln}\, a}$$

with the activity, a, and standard states defined.

$$\boxed{\text{Ideal gases:} \quad a = p / p^\circ \qquad p^\circ = 1\ \text{bar}}$$

The effect of pressure on solids and liquids is negligible:
$G = G^\circ$ for a pure liquid or solid so the activity must be one.

$$\boxed{a_{(\text{pure solid})} = a_{(\text{pure liquid})} = 1}$$

we can deal with non-ideal gases (but not here…….!!)

Variation of G with concentration

We use the same form for solutions by using *molar concentrations* so that we adopt as our standard state a concentration of 1 mol dm^{-3}.

$$G_i = G_i^\circ + nRT\,ln\,(\,[i]\;/\;1\text{ mol dm}^{-3}\,) = G_i^\circ + nRT\,ln\,[i]$$

Note: The use of molar concentrations is a sort of "ideal" approximation which is valid at low concentrations.

We can now take data (available in tables) and calculate the enthalpy, entropy and free energy of reactions under a wide range of conditions.

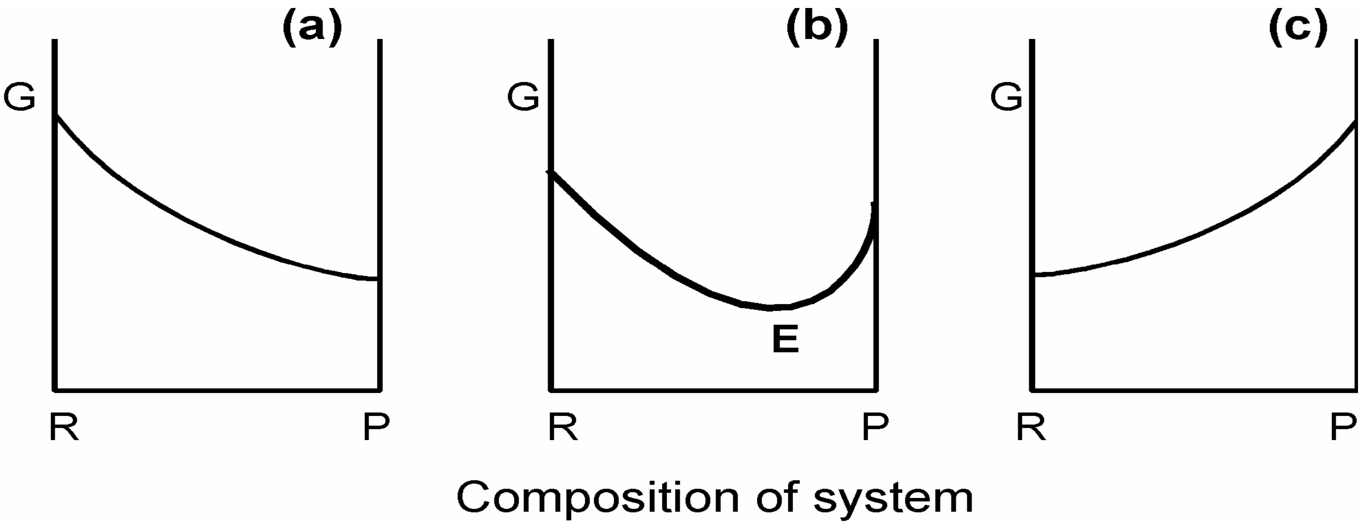
But, can we do more than predict spontaneity ??

Free energy and equilibrium

The free energy of the system will change throughout a reaction depending on the amounts of reactants and products.

It will reach a minimum at some composition (100% reactant – no reaction – or 100% product – complete reaction – or any value in between)

At the minimum, the reaction will have no tendency to go anywhere and so will stop. It has reached equilibrium.

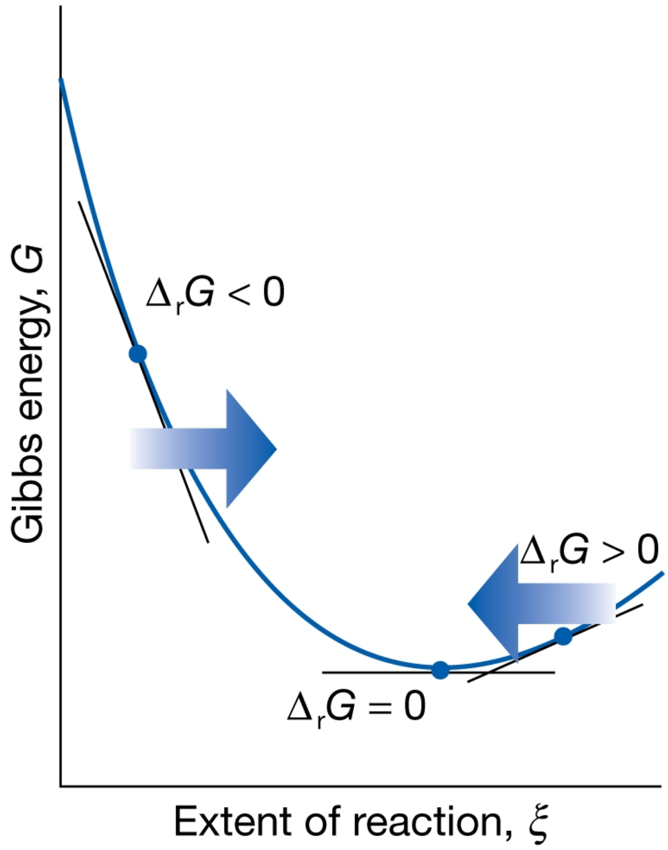


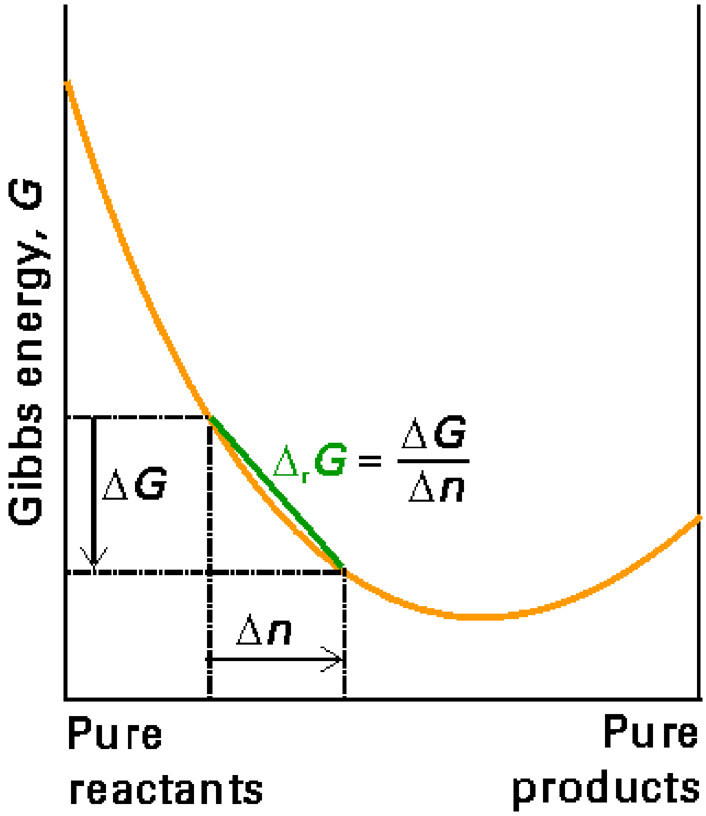
R = reactants P = products E = equilibrium

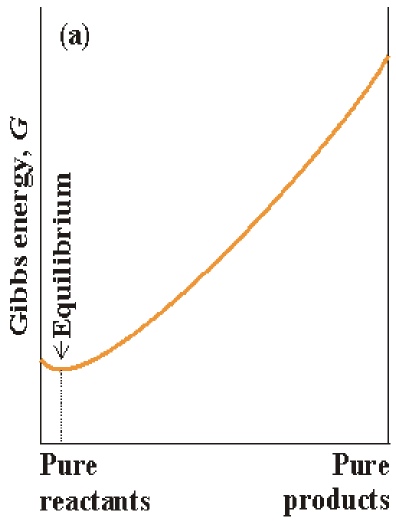
In (a), G(products) < G(reactants). ΔG is negative so the reaction goes forward. The opposite is true for (c).

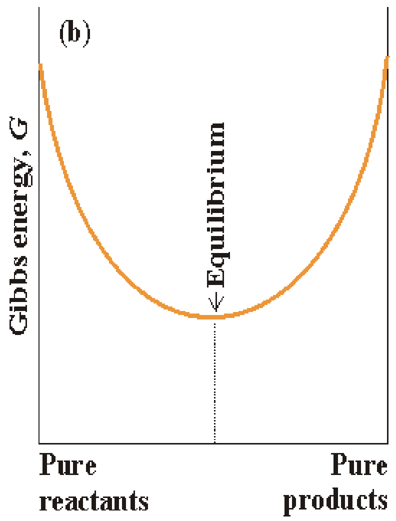
For (b), ΔG would be negative if the system started at either end so the reaction would proceed until point E. If the composition changes, G would increase.

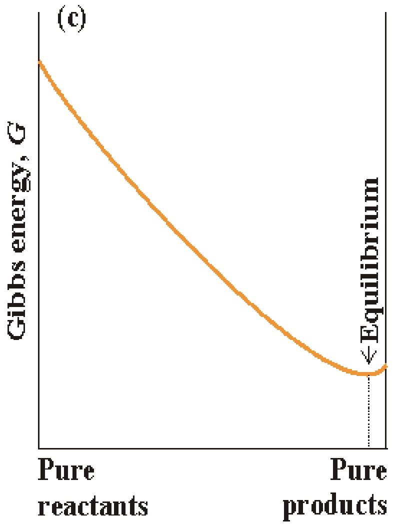
Thus, the reaction cannot change from this composition - ***it has come to equilibrium***.


Gibbs energy, G
$\Delta_r G < 0$
$\Delta_r G > 0$
$\Delta_r G = 0$
Extent of reaction, ξ


Gibbs energy, G
ΔG
$\Delta_r G = \dfrac{\Delta G}{\Delta n}$
Δn
Pure reactants
Pure products


(a)
Gibbs energy, G
Equilibrium
Pure reactants
Pure products


(b)
Gibbs energy, G
Equilibrium
Pure reactants
Pure products


(c)
Gibbs energy, G
Equilibrium
Pure reactants
Pure products

This schematic approach allows us to define one of the fundamental statements of chemistry

A system will come to equilibrium when it has reached its minimum free energy.

We need a quantitative measure of the composition of a reaction mixture. The easiest uses the *Law of Mass Action* to define the Reaction Quotient, Q

For our general reaction, $\alpha\,A + \beta\,B \rightarrow \gamma\,C + \delta\,D$

$$Q = \frac{(a_C)^{\gamma}(a_D)^{\delta}}{(a_A)^{\alpha}(a_B)^{\beta}}$$

When the system reaches equilibrium,

$$Q_{eqm} = \frac{(a_C)^{\gamma}_{eqm}(a_D)^{\delta}_{eqm}}{(a_A)^{\alpha}_{eqm}(a_B)^{\beta}_{eqm}} = K_{eqm}$$

K_{eqm} is therefore the *equilibrium constant*

$$Q = \frac{\prod (a_{(products)})^{\nu}}{\prod (a_{(reac\tan ts)})^{\nu}}$$

ν is the stoichiometric coefficient.

The symbol Π is shorthand for "the product of"

$$\prod_1^5 (a_i) = a_1 \times a_2 \times a_3 \times a_4 \times a_5$$

Different types of equilibrium constant can be defined:

If K_{eqm} is calculated from gas pressures - K_p.

If calculated from concentrations - K_c.

Examples.

$N_{2(g)} + 3\,H_{2(g)} \leftrightarrow 2\,NH_{3(g)}$

$$K_p = \frac{(p_{NH_3})^2_{eqm}}{(p_{H_2})^3_{eqm}(p_{N_2})_{eqm}}$$

$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)}$

$$K_p = \frac{(a_{CaCO_3})}{(p_{CO_2})_{eqm}(a_{CaO})} = \frac{1}{(p_{CO_2})_{eqm}(1)} = \frac{1}{(p_{CO_2})_{eqm}}$$

$HCOOH_{(aq)} + C_2H_5OH_{(aq)} \leftrightarrow HCOOC_2H_{5(aq)} + H_2O_{(l)}$

$$K_c = \frac{[HCOOC_2H_5]_{eqm}[H_2O]_{eqm}}{[HCOOH]_{eqm}[C_2H_5OH]_{eqm}}$$

$CH_3COOH_{(aq)} \leftrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$

$$K_c = \frac{[CH_3COO^-]_{(eqm)}[H^+]_{(eqm)}}{[CH_3COOH]_{(eqm)}}$$

Although we write press. or conc. in the expressions, they are in fact ratios *e.g.* p / 1 bar, c / mol dm^{-3} *etc*. so K_{eqm} is dimensionless and has no units.

The definitions of Q and K_{eq} allow us to predict the direction of a chemical reaction. We can say that:

If $\Delta G < 0$ or	$Q < K_{eqm}$	the forward reaction proceeds
If $\Delta G > 0$ or	$Q > K_{eqm}$	the reverse reaction proceeds
If $\Delta G = 0$ or	$Q = K_{eqm}$	the system is at equilibrium

But there's more ………..

Relation between ΔG and K_{eqm}

Consider the reaction ($\nu_I = 1$) $\quad A + B \rightarrow C + D$

$$\Delta G(\text{react.}) = G\,(\text{prod}) - G\,(\text{react}) = (G_C + G_D) - (G_A + G_B)$$

Let's start by assuming: $\quad G_A = G^\circ + RT\, \mathit{ln}\, a_A$ etc

$$\Delta G(\text{react.}) = \{(G^\circ_C + RT\, \mathit{ln}\, a_C) + (G^\circ_D + RT\, \mathit{ln}\, a_D)\} - \{(G^\circ_A + RT\, \mathit{ln}\, a_A) + (G^\circ_B + RT\, \mathit{ln}\, a_D)\}$$

$$=\{(G^\circ_C+G^\circ_D)-(G^\circ_A+G^\circ_B)\} + RT\{(\mathit{ln}\, a_C + \mathit{ln}\, a_D) - (\mathit{ln}\, a_A+\mathit{ln}\, a_D)\}$$

$$= \{(G°_C + G°_D) - (G°_A + G°_B)\} + RT\ ln\left(\frac{a_C a_D}{a_A a_B}\right)$$

or, $$\boxed{\mathbf{\Delta G(reaction) = \Delta G°(reaction) + RT}\ \boldsymbol{ln}\ \mathbf{Q}}$$

At equilibrium, G is a minimum, ΔG(reaction) = 0 and Q = $K_{eq.}$

$$0 = \Delta G°(reaction) + RT\ ln\ K_{eqm}$$

$$\boxed{K_{eqm} = exp\left(\frac{-\Delta G°}{RT}\right)}$$

At equilibrium, ΔG for the reaction under the equilibrium conditions will be zero;

ΔG° which is defined under standard conditions will not in general equal zero

Any stoichiometry or reaction leads to the above expression.

NB: The above definition is not quite strictly true - but it is close enough (for now……..)

Gibbs Free Energy and Reactivity

We know that if $\Delta G^\circ < 0$, $K_{eqm} > 1$ so the forward reaction takes place. The products will be present in larger concentration than the reactants at equilibrium. Can we quantify this?

Define a complete reaction as a yield of 99.99% products.

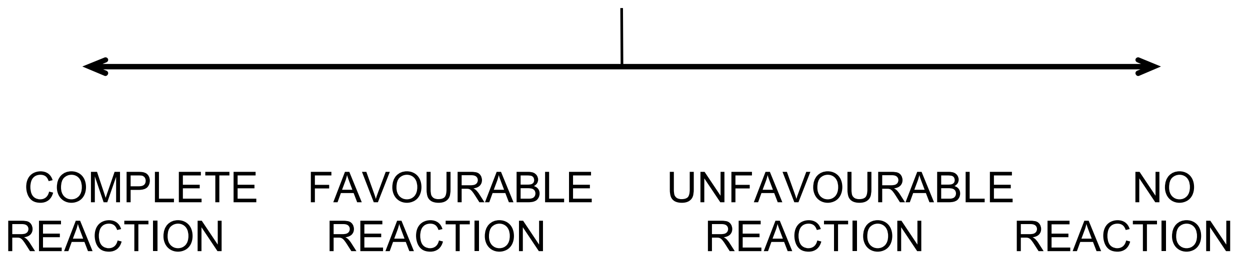
$$K_{eqm} = \frac{\text{Amount of products}}{\text{Amount of reactants}} = \frac{99.99}{0.01} = 9999 \approx 10^4$$

For $K_{eqm} = 10^4$ at 298 K, ΔG° must be -22.8 kJ mol^{-1} so any reaction with a more negative value will go to completion.

If $\Delta G^\circ > +22.8$ kJ mol^{-1} the reaction will not occur.

Between these "limits", a variety of behaviour results.

K_{eqm}	10^4	1	10^{-4}
ΔG°/ kJ mol^{-1}	-23	0	+ 23



These "limits" are temperature dependent because of the $-T\Delta S^\circ$ contribution to the Gibbs free energy.

Pause for breath – where are we ?

Let us recap. We can take data in terms of $S°_{298,}$ $\Delta H°_{f,298}$ and Cp for the components in a reaction, calculate $\Delta H°$ and $\Delta S°$ at any temp., calculate $\Delta G°$ and hence the K_{eqm}.

We can predict the course of the reaction and the position of equilibrium. This gives us the maximum possible yield of products.

Worked Example: $Ag_2CO_{3(s)}$

The next step is to quantify the yields of products and reactants at equilibrium.

Silver carbonate decomposes on heating. Calculate the equilibrium constant at 110 °C for the reaction.

$$Ag_2CO_{3(s)} \rightarrow Ag_2O_{(s)} + CO_{2(g)}$$

	$AgCO_{3(s)}$	$Ag_2O_{(s)}$	$CO_{2(g)}$
ΔH° / kJ mol^{-1} :	-501.4	-29.07	-393.5
ΔS° / J K^{-1} mol^{-1} :	167.3	121.7	213.7
Cp / J K^{-1} mol^{-1} :	109.6	68.6	37.1

ΔH°_{298} = [(-29.07) + (-393.5)] - [(-501.4)] = + 79.03 kJ mol^{-1}.

ΔS°_{298} = [121.7+ 213.7] - [167.3] = 168.0 J mol^{-1} K^{-1}.

ΔCp = [68.6 + 37.1] - [109.6] = -3.9 J mol^{-1} K^{-1}.

ΔH°_{383} = 79.03 + (-3.9×10^{-3})(383.15 - 298.15) = 78.70 kJ mol^{-1}

ΔS°_{383} = 168.0 + (-3.9) ln (383.15/298.15) = 167.0 J mol^{-1} K^{-1}.

ΔG°_{383} = 78.7 - (383.15)(167.0×10^{-3}) = 14.71 kJ mol^{-1}.

$$K_p = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = e\text{xp}\left(\frac{-14.71 \text{ x } 10^3}{(8.314)(383.15)}\right) = 9.87 \text{ x } 10^{-3}$$

Say a sample of $Ag_2CO_{3(s)}$ is to be dried in an oven.

Q for this reaction is simply p(CO_2).

If the conditions in the oven are such that the partial pressure of CO_2 is > 9.9×10^{-3} (or ~ 1% by volume) then the silver carbonate will not decompose.

Relating the Equilibrium Constant to Experiment

Take an example:- gas phase reaction:

$$N_2O_{4(g)} \leftrightarrow 2\ NO_{2(g)}$$

Introduce 1 mol of N_2O_4 into a container and allow to reach eqm at a total pressure of P_{tot}

At the start of the reaction: 1 mole N_2O_4, 0 moles NO_2

If α moles of N_2O_4 have reacted when the reaction comes to equilibrium,

$(1 - \alpha)$ mol of N_2O_4 remain, 2α mol of NO_2 have been formed.

The total number of moles of gas present at equilibrium is $(1 - \alpha) + 2\alpha = (1 + \alpha)$ mol.

α is better defined as the fraction of moles of reactant which react and is often termed *the degree of dissociation.*

We now know the number of moles of each component and the total pressure so we can work out an expression for the equilibrium constant!

For gases acting ideally, the partial pressure, p, is given by Dalton's Law: p = mole fraction × total pressure = $x\ P_{tot}$. x is given by:

$$x = \frac{\text{No of moles of component}}{\text{Total No. of moles present}}$$

From now on, we need some algebra.

For: $N_2O_{4(g)} \leftrightarrow 2\ NO_{2(g)}$

$$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})} = \frac{(x_{NO_2} P_{tot})^2}{(x_{N_2O_4} P_{tot})} = \frac{\left(\frac{2\alpha}{1+\alpha} P_{tot}\right)^2}{\left(\frac{1-\alpha}{1+\alpha} P_{tot}\right)}$$

$$K_p = \frac{4\alpha^2 P_{tot}{}^2 (1+\alpha)}{(1-\alpha)(1+\alpha)^2 P_{tot}} = \frac{4\alpha^2 P_{tot}}{(1-\alpha)(1+\alpha)}$$

or $$\boxed{K_p = \frac{4\alpha^2 P_{tot}}{(1-\alpha^2)}}$$

Hence, if we calculate K_p we can calculate α at any temp. and pressure. From this, the maximum amount of product can be readily found.

BUT: each different reaction stoichiometry leads to a different expression for K_p (or K_c as appropriate)so each must be worked out separately – no standard formulae to learn!!.

Many stoichiometries give rise to quadratic or cubic equations.

Numerical solution of the equations is easy.

To get an idea, we often assume that the degree of reaction is small so that $\alpha << 1$ so that $(1 - \alpha) \approx 1$.

e.g. for the reaction above,

$$K_p \approx 4\alpha^2 P_{tot} \quad \text{and so} \quad \alpha \approx \sqrt{K_p / 4 P_{tot}}.$$

This gives a useful first estimate.

Worked Example: Formulate expressions … α …

Formulate expressions in terms of the degree of dissociation for the equilibrium constants for the following reactions.

(a) $Ni(CO)_{4(g)} \leftrightarrow Ni_{(s)} + 4\ CO_{(g)}$

(b) $2\ HgO_{(s)} \leftrightarrow 2\ Hg_{(l)} + O_{2(g)}$

(c) $CH_3COOH_{(aq)} \leftrightarrow CH_3COO^-_{(aq)} + H^+_{(aq)}$

(a) If we start with 1 mole $Ni(CO)_{4(g)}$ and α react, then at eqm., $1-\alpha$ moles remain. α moles of $Ni_{(s)}$ together with 4α moles of CO form. When considering K_p, only gases contribute to the partial pressures. The total number of gas moles = $(1-\alpha) + 4\alpha = (1+3\alpha)$

$$K_p = \frac{(1)\ (p_{CO})^4}{p_{Ni(CO)_4}} = \frac{(1)\left(\frac{4\alpha}{1+3\alpha}\right)^4 P_{tot}^4}{\left(\frac{1-\alpha}{1+3\alpha}\right)P_{tot}} = \frac{(4\alpha)^4(1+3\alpha)P_{tot}^3}{(1-\alpha)(1+3\alpha)^4} = \frac{256\ \alpha^4 P_{tot}^3}{(1-\alpha)(1+3\alpha)^3}$$

(b) The only gas involved is O_2. Thus, since the activity of solids is 1 and the only gas present is oxygen,

$$K_p = \frac{(a_{Hg})^2\ (p_{O_2})}{(a_{HgO})^2} = \frac{(1)^2\ (p_{O_2})}{(1)^2} = P_{tot}$$

(c) If the initial concentration is c mol dm^{-3} and α is the fraction which reacts, at equilibrium there will be (αc) mol dm^{-3} of H^+, (αc) mol dm^{-3} of CH_3COO^- and (1-α)c mol dm^{-3} of CH_3COOH. Thus

$$K_c = \frac{[H^+]\ [CH_3COO^-]}{[CH_3COOH]} = \frac{(\alpha\ c)\ (\alpha\ c)}{(1-\alpha)\ c} = \frac{\alpha^2\ c}{1-\alpha}$$

Effect of conditions on reaction yields and K_{eqm}

Effect of pressure

K_{eqm} depends on ΔG° which is only valid at 1 bar pressure and hence K_{eqm} *is a thermodynamic constant which does not vary at constant temperature.*

Just for emphasis:

K_{eqm} does not vary with Pressure / Concentration at constant temperature

This does *not* mean that pressure has no effect on the *position* of equilibrium. e.g. for $N_2O_4 \leftrightarrow 2\ NO_2$

$$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})} \quad K_p = \frac{4\alpha^2 P_{tot}}{(1-\alpha^2)}$$

If K_p is constant, if P_{tot} changes α changes to compensate.

Effect of temperature

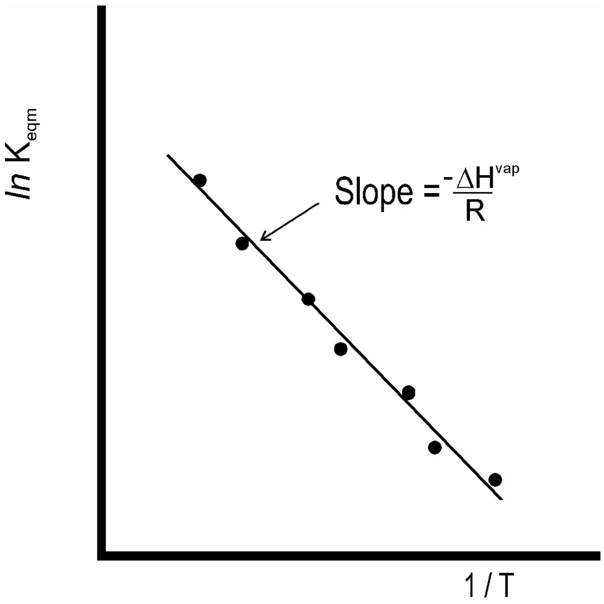
Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad = \quad - RT\ ln\ K_{eqm},$

$$ln\ K_{eqm} = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{T\Delta S^\circ}{RT}$$

or

$$\boxed{ln\ K_{eqm} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}}$$

This is a variation of *the Van't Hoff* equation.



If ΔH° and ΔS° are independent of temperature then

$$ln\ K_{eqm} = (\text{cons} \tan \text{t})\ - \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right)$$

so there is a linear relation between *ln* K_{eqm} and (1/T).

Alternatively, if K_{eqm} is known at two temperatures T_1 and T_2,

$$ln\left(\frac{K_{eqm}(T_2)}{K_{eqm}(T_1)}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

If we have an exothermic reaction, ΔH is negative, then K_{eqm} will decrease as T increases. The opposite is true for an endothermic reaction.

Le Chatelier's principle

The above provides the explanation of a principle suggested by Le Chatelier on the basis of empirical observations.

If a system is subjected to a constraint, it will react so as to minimise the effect of the constraint.

e.g. increased p reduced the yield of NO_2 from N_2O_4.

If we increase the pressure of a reactant, the reaction moves toward the side of the equation with the lowest number of moles of gas *i.e.* if the pressure is raised, the system reacts by minimising the pressure of gas produced.

If T is increased in an exothermic reaction, the system will react so as to absorb the extra energy and so change to minimise the production of energy by the reaction. The reaction therefore proceeds to a lesser extent so that the yield is lowered.

Worked Example: Acetic acid dimerizations

The only way to become comfortable with this material and the methods which have been described is to attempt LOTS of problems (after working through the text.

In the vapour, acetic acid partially associates into dimers. At a total pressure of 0.2 bar, acetic acid is 92% associated at 25 °C and 82% associated at 45 °C. Calculate the enthalpy and entropy changes for the association reaction. What will be the effect on the dissociation of changing the total pressure?

The reaction can be represented as $2HOAc \leftrightarrow (HOAc)_2$

If we begin with 100 mol and 92% dimerises, 8 mol remain at eqm.

The 92 mol which react give rise to 46 mol of dimer. The total number of moles present is therefore 54.

Hence, at 25 °C, K_p is given by

$$K_p = \frac{p_{(HOAc)_2}}{(p_{HOAc})^2} = \frac{x_{(HOAc)_2}\, p_{tot}}{(x_{HOAc}\, p_{tot})^2} = \frac{(46\,/\,54)\ 0.2}{\{(8\,/\,54)\ 0.2\}^2} = 194.1$$

Using the data at 45 °C gives $K_p = 37.33$.

$\Delta G^\circ = -13.06$ kJ mol^{-1} at 25 °C and -9.576 kJ mol^{-1} at 45 °C.

$$ln\left(\frac{K_{eq}(T_2)}{K_{eq}(T_1)}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right); ln\left(\frac{37.33}{194.1}\right) = \frac{\Delta H^\circ}{8.314}\left(\frac{1}{298.15} - \frac{1}{318.15}\right)$$

Hence, $\Delta H^\circ = -65.0$ kJ mol^{-1}.

Using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ gives $\Delta S^\circ = -174.2$ J K^{-1} mol$^{-1.}$

As expected, it is an endothermic reaction since the extent of dimerisation decreases as the temperature rises.

The dimerisation must lead to an increase in order, hence the negative entropy change.

Applying Le Chatelier’s principle, an increase of pressure should favour the side of the reaction with the lower number of gas moles *i.e.* favour the dimerisation.

$$K_p = \frac{p_{(HOAc)_2}}{(p_{HOAc})^2} = \frac{x_{(HOAc)_2}\, p_{tot}}{(x_{HOAc}\ \ p_{tot})^2} = \frac{x_{(HOAc)_2}}{(x_{HOAc})^2\, p_{tot}}$$

i.e. if P_{tot} increases, $x_{(HOAc)2}$ must also go up to compensate and keep K_p constant

An alternative approach to calculating the values would be to write the two equations:

$$\Delta G^\circ(25^\circ C) = -13.06 \text{ kJ mol}^{-1} = \Delta H^\circ - (298.15)\,\Delta S^\circ$$
$$\Delta G^\circ(45^\circ C) = -\,9.58 \text{ kJ mol}^{-1} = \Delta H^\circ - (318.15)\,\Delta S^\circ$$

and solve simultaneously assuming that ΔH° and ΔS° do not vary with temperature**.**

Chemical potential

Earlier, we made the assumption that $G_A = G^\circ + RT\, ln\, a_A$ in a mixture

- suggests the free energy of the component is independent of all the other components in the mixture. OK for ideal gases but not for other systems.

e.g. think about 1 mole of water. Will the free energy change will be the same if it is added to a large amount of water, or benzene, or ethanol or sulphuric acid?

We need the free energy change when a component is added to the system with all other conditions and amounts of other components kept equal.

This is given by the *partial differential* of G with respect to that component.

$$\boxed{\overline{G}_A = \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B}}$$

$\overline{G}_A$ is the *partial molar free energy* of component A and represents the free energy change when 1 mole of A is added to a system at constant conditions.

the *chemical potential,* given the symbol μ.

For a pure substance, μ_A corresponds to the molar Gibbs free energy.

If we have a large amount of a substance, B, and we add an amount dn_A moles of A, then the free energy change at constant T, p, dG, is

$$dG = \mu_A \, dn_A$$

For a multicomponent system, this can be generalised to

$$(dG)_{p,T} = \sum_i \mu_i \, dn_i$$

We can now write the fundamental equation of thermodynamics as

$$\boxed{dG = V\,dP - S\,dT + \sum_i \mu_i \, dn_i}$$

Why is μ important ?

$$G = G^\circ + nRT \ln (p / p^\circ).$$

If we consider solely component A in the mixture, then

$$\left(\frac{\partial G}{\partial n_A}\right) = \left(\frac{\partial G^\circ}{\partial n_A}\right) + RT \ln \left(\frac{p_A}{p_A{}^\circ}\right)$$

$$\mu_A = \mu_A{}^\circ + RT \ln (p_A / p_A{}^\circ)$$

$\mu_A{}^\circ$ is the standard chemical potential at the standard partial pressure of $p_A{}^\circ$ = 1 bar. This is identical with the free energy of 1 mole of pure A

Also, since dG = 0 at equilibrium.

$$\left(dG\right)_{p,T} = \sum_i \mu_i \, dn_i$$

$$0 = (\mu_A\,(-dn)) + \mu_B\,dn$$

or

$$\mu_A\,dn = \mu_B\,dn \quad \text{or} \quad \boldsymbol{\mu_A = \mu_B}$$

this is an example of *a general requirement for chemical equilibrium.*

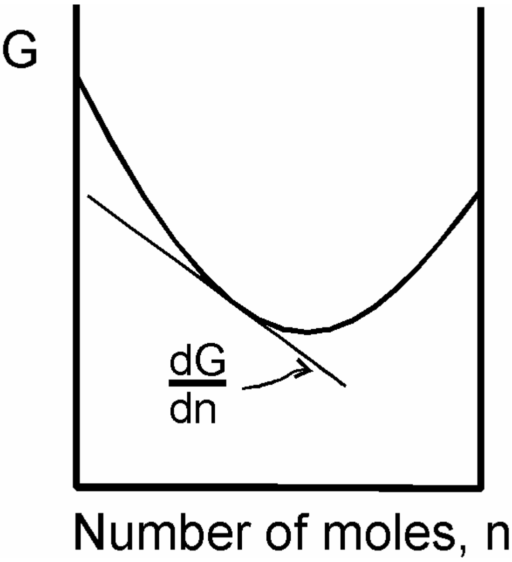
A reaction comes to equilibrium at constant temperature and pressure under conditions where the chemical potential of the reactants equals that of the products.

"Why the name - chemical potential ?".

At a higher altitude – a body has a greater "driving force" to fall to earth - we say it has a higher *gravitational potential.* The body will spontaneously move from high gravitational potential to one low.

In an electric circuit a high voltage - or *electric potential* - provides a greater driving force for the electrons to move from high potential to low.

The chemical potential can be thought of as the “driving force” for a chemical process. μ is equivalent to the slope of the Gibbs free energy *versus* composition curve.



The steeper the curve - hence higher μ - the greater the tendency for the system to move toward equilibrium where μ is zero.

Investigation of many chemical systems involves calculating the free energy / chemical potential and seeing how this varies with the conditions - more later……….

Kinetics and Thermodynamics of Equilibrium

We are concentrating on thermodynamic aspects of equilibrium. Perhaps easier is the kinetic approach.

This also emphasises the *dynamic* nature of chemical equilibrium. The reaction does not stop when equilibrium is reached but the overall proportion of reactants and products does not change.

If we have the general reaction $A + B \rightarrow C$

- the rate of the forward reaction is given by $k_f\,[A]\,[B]$
- the rate of the reverse reaction is $k_b\,[C]$.

At equilibrium, these rates are equal so that:

$$k_f[A]_{eqm}[B]_{eqm} = k_b[C]_{eqm} \quad \text{or} \quad \frac{k_f}{k_b} = \frac{[C]_{eqm}}{[A]_{eqm}[B]_{eqm}} = K_c$$

Thus, the ratio of the forward and reverse rate constants also gives the equilibrium constant.

An analogous argument using partial pressures holds for K_p.

We must also consider the kinetics in determining the optimum conditions for a particular reaction.

e.g. with an exothermic reaction, Le Chatelier's principle shows the yield would be maximised by reducing the temperature. However, this will slow down the reaction. A balance must be worked out between these factors.

The standard enthalpy of formation of water is -241.8 kJ mol^{-1}. Use mean heat capacities and standard entropies to estimate the percentage dissociation of water vapour at 2000 °C and 0.01 bar pressure.

The reaction of interest is the *dissociation* of water

$$H_2O_{(g)} \rightarrow H_{2(g)} + ½O_{2(g)}$$

25°C, $\Delta H°_{298} = – \Delta H°_{f,298} = +241.8$ kJ mol^{-1}

$\Delta S°_{298} = [130.7 + ½(205.1)] - [188.3] = 44.95$ J mol^{-1} K^{-1}.

To convert $\Delta H°_{298}$ and $\Delta S°_{298}$ to the higher temperature, we need ΔCp.

$\Delta Cp = [28.8 + ½(29.4)] - [33.6] = 9.9$ J mol^{-1} K^{-1}.

At 2000 °C, 2273 K.

$\Delta H°_{2273} = \Delta H°_{298} + \Delta Cp\,(2273 - 298) = 241.8 + (9.9 \times 10^{-3})(1975)$
$= 261.35$ kJ mol^{-1}.

$\Delta S°_{2273} = \Delta S°_{298} + \Delta Cp\, ln\, (2273 / 298) = 44.4 + (9.9)\, ln(7.628)$
$= 65.06$ J mol^{-1} K^{-1}.

$\Delta G°_{2273} = \Delta H°_{2273} - T\Delta S°_{2273} = 261.35 - (2273)(65.06 \times 10^{-3})$ kJ mol^{-1}.
$= + 113.46$ kJ mol^{-1}.

$K_p = exp\,(-\Delta G°/RT) = exp\,(-113.46 \times 10^3 / 2273\,R) = 2.47 \times 10^{-3}$ bar

If we start with 1 mol of water and the degree of dissociation is α, at equilibrium there will be α mol of H_2, $½\alpha$ mol of O_2 and $(1-\alpha)$ mol of H_2O.

$$K_p = \frac{(p_{H_2})(p_{O_2})^{1/2}}{(p_{H_2O})} = \frac{(x_{H_2} p_{tot})(x_{O_2} p_{tot})^{1/2}}{(x_{H_2O}\ p_{tot})}$$

$$= \left(\frac{(\alpha)}{(1 + 0.5\alpha)}\right)\left(\frac{(0.5\ \alpha)^{1/2}}{(1 + 0.5\alpha)^{1/2}}\right)\left(\frac{(1 + 0.5\alpha)}{(1 - \alpha)}\right)\frac{p^{3/2}}{p} = \frac{\sqrt{0.5}\ \alpha^{3/2}\ p^{1/2}}{(1 - \alpha)\ (1 + 0.5\alpha)^{1/2}}$$

If we now make the assumption that α is small, then $\alpha <<1$, $(1-\alpha) \approx (1 + 0.5\ \alpha) = 1$ so that

$$K_p = \frac{\sqrt{0.5}\ \alpha^{3/2}\ p^{1/2}}{1} = 0.7071\ (0.1)\ \alpha^{3/2} = 2.47 \text{ x } 10^3$$

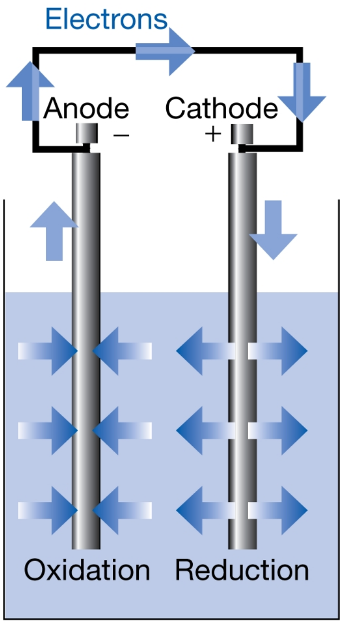
Hence $\alpha \approx 0.00653$ or 0.65%.

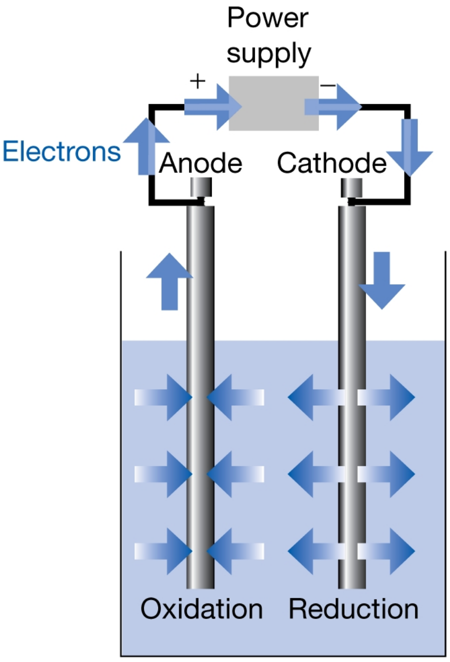
Note: As well as the mathematical approximation in the final step, the result is an approximation in that the mean heat capacities used are unlikely to give an accurate result over such a large temperature range.

Electrochemical cells

An important class of reaction not so far discussed is that of electron transfer or ***redox*** reactions.

Essentially the chemistry of electron transfer reactions





If pure Zn metal is placed in a solution of $CuSO_{4\,(aq)}$, the zinc rapidly coats with a brown deposit of Cu metal. The chemical reaction taking place is

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

This can be split into two *half-reactions*

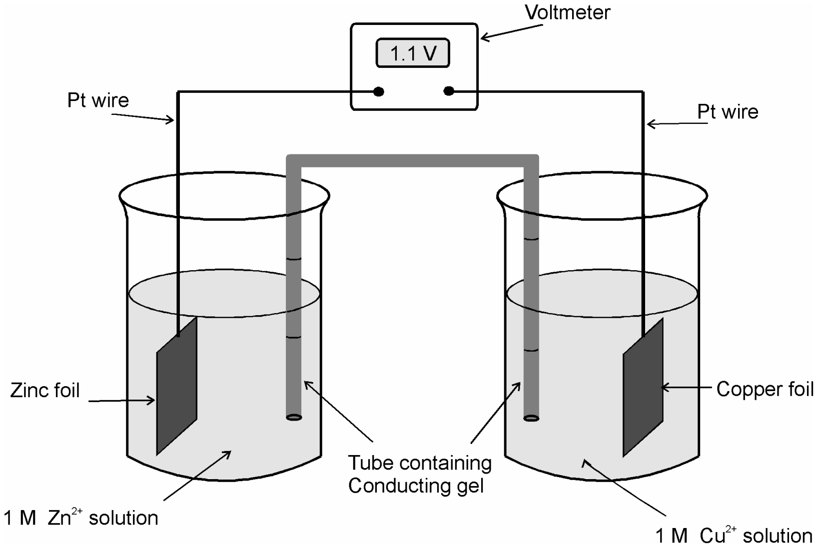
$$Zn_{(s)} - 2\,e \rightarrow Zn^{2+}_{(aq)} \qquad \textit{Oxidation}$$

$$Cu^{2+}_{(aq)} + 2\,e \rightarrow Cu_{(s)} \qquad \textit{Reduction}$$

Reactions involving electron gain - **reductions**
Reactions involving electron loss - **oxidations**.

There must be a net balance of electrons and so both must take place concurrently, hence the name *redox* reaction.

If we keep the two half reactions separate (but linked together) electrons can be made to flow around an external circuit.



The *potential difference* between the electrodes provides the “driving force” for the electron flow.

If we use a voltmeter with a very high resistance, no electrons can flow so we just measure the e.m.f. (*or* potential *or* voltage) of the cell. Under these conditions, the cell acts reversibly.

There are many types of half-cell and electrochemical reaction – we will only consider a short introduction to the topic from a thermodynamic point of view.

Read…..

Standard electrode potentials

The voltage generated clearly depends on the nature of the two half cells. Again, we need to fix *a standard*.

We set to zero, the potential for a half-cell involving the reaction

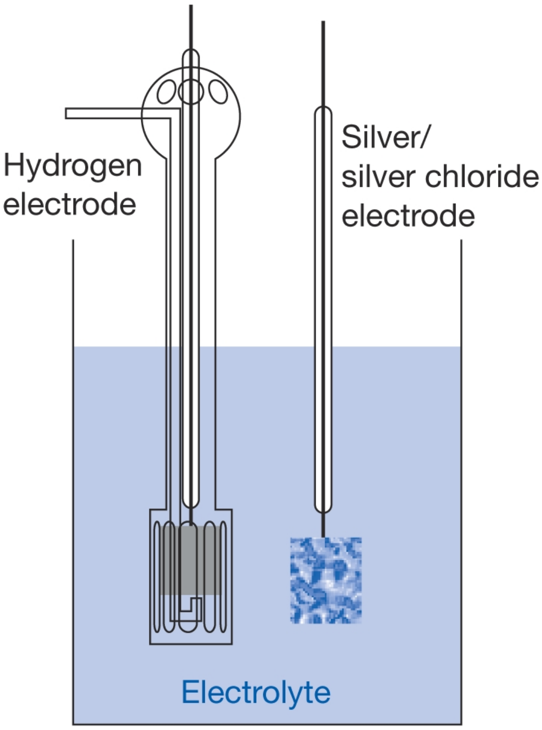
$$H^+_{(aq)} + e \rightarrow \tfrac{1}{2}H_{2(g)}$$

at 298 K, 1 bar of hydrogen pressure and 1 mol dm^{-3} concentration of H$^+$.

> Note: Again the definition of 1 mol dm^{-3} as the standard concentration is an approximation and it should be defined as *unit activity*.

Construction of a cell in which one half consists of this *Standard Hydrogen Electrode, S.H.E.* allows the potential for any other half-cell to be determined. Extensive lists of these values have been published.

(For example, see your Inorganic textbook and Atkins)

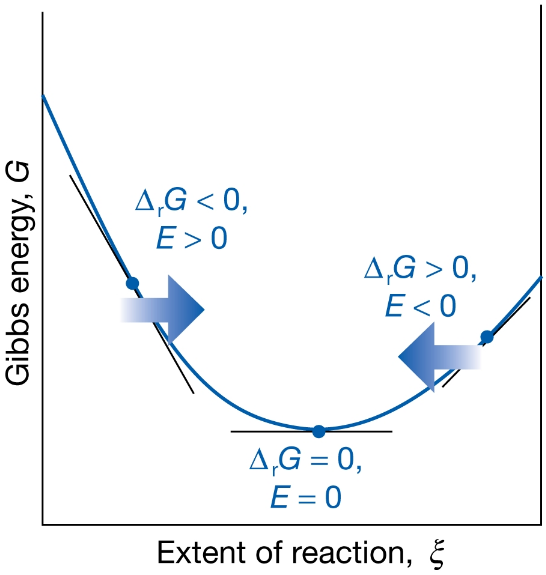


Electrode potentials measured under these standard conditions are given the symbol E° while E represents the voltage generated when the cell operates under conditions other than those specified above.

The e.m.f. of the cell, E, tells us about the tendency for electrons to flow around the circuit - the same as the tendency for the redox reaction to occur - so it must be related to the reaction free energy

e.g. higher E = more tendency to happen

Higher E will oxidise lower E (or lower E will reduce higher)



For the two *half-reactions*

$Zn_{(s)} - 2\,e \rightarrow Zn^{2+}_{(aq)}$ $\quad E^o = +0.76\ V$

$Cu^{2+}_{(aq)} + 2\,e \rightarrow Cu_{(s)}$ $\quad E^o = +0.34V$

For the overall reaction, we add these together

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$ $\quad E^o = (+0.76 + 0.34) = 1.11\ V$

Note: In texts, the E^o values are always listed as standard **reduction** potentials so that you will see $Zn^{2+}_{(aq)} + 2\,e \rightarrow Zn_{(aq)}$ $E^o = -0.76\ V$. For the opposite reaction, we switch the sign of the potential.

The same principles hold if conditions other than standard are used.

Electrode Potentials and free energy changes

The tendency for a reaction to happen is correlated by ΔG so there must then be a direct connection between E and ΔG.

If n electrons are transferred in a reaction, then the total charge per mole, Q, is $n\Im$. $\Im$ is the **Faraday constant** which is the total charge on 1 mole of electrons - 96485 C mol^{-1}.

When a charge Q moves through a potential difference E, the work done is given by

$$w_{\mathrm{elec}} = \int_{Q_{\mathrm{initial}}}^{Q_{\mathrm{final}}} -E\,dQ$$

If the potential difference, or voltage, is constant, the work done in transferring a charge $n\Im$ is simply $w_{\mathrm{elec}} = -n\,\Im\,E$

At constant T, p, this work is done as a result of the lowering of the system free energy Thus, we can write

$$\Delta G = -n\,\Im\,E$$

In the particular case of standard conditions and all components in their standard states, then

$$\boxed{\Delta G^\circ = -n\,\Im\,E^\circ}$$

Since E and ΔG, have opposite sign, if a cell has a positive cell potential the reaction taking place will be spontaneous.

Thermodynamic measurements by electrochemistry

Electrochemistry allows us to make thermodynamic measurements on systems which would be difficult to perform calorimetry e.g. biochemical systems.

We already know that $\left(\frac{dG}{dT}\right)_P = -S \text{ or } \Delta S^\circ = -\left(\frac{d\Delta G^\circ}{dT}\right)_p$

$$\Delta S^\circ = n\Im\left(\frac{dE^\circ}{dT}\right)_p$$

so that, as long as we are operating at constant p, the temperature variation of the cell voltage allows us to measure the entropy change for the reaction.

Once ΔG° (= $-n\,\Im\,E^\circ$) and ΔS° are known, ΔH° can be calculated.

An electrochemical cell with the following reaction generates a standard electrode potential of 1.055 V at 25 °C and 1.015 V at 0°C. Calculate the standard enthalpy, entropy and free energy changes for the reaction at 25 °C.

$$\mathrm{Zn_{(s)} + 2\ AgCl_{(s)} \rightarrow ZnCl_{2(aq)} + 2\ Ag_{(s)}}$$

The standard free energy change at 298 K follows directly from

$\Delta G^\circ = -\,n\Im E^\circ = -(2)\ (96485)\ (1.055) = -203.58\ \mathrm{kJ\ mol^{-1}}$

We will make the approximation that the voltage is a linear function of temperature. The standard entropy arises from the temperature dependence

$$\Delta S^\circ = n\Im \left(\frac{dE^\circ}{dT}\right)_p = (2)\ (96485) \left(\frac{1.055 - 1.015}{298.15 - 273.15}\right) = 308.75\ \mathrm{J\ K^{-1} mol^{-1}}$$

ΔH° can then be found

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = (-203.58 \times 10^3) + (298.15)(308.75)$$
$$= -\ 111.53\ \mathrm{kJ\ mol^{-1}}$$

Concentration dependence of electrode potentials

We saw earlier that the free energy change for reactions in solution can be described by

$$\Delta G = \Delta G^\circ + RT\,\mathit{ln}\,Q$$

Substituting for the free energy in terms of electrode potentials,

$$n\,\Im\,E = -n\,\Im\,E^\circ + RT\,\mathit{ln}\,Q \quad \text{or} \quad E = E^\circ - \frac{RT}{n\Im}\ln Q$$

This is known as the ***Nernst*** equation.

For example, what is the potential of a cell for the following reaction with a copper sulphate concentration of 0.05 mol dm^{-3} and zinc sulphate of 0.1 mol dm^{-3} ?

We know from above that E° = 1.1 V for the reaction

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}{}_{(aq)}$$

Applying the Nernst equation, remembering that the activity of a solid is 1,

$$E = E^\circ - \frac{RT}{n\Im}\ln Q = E^\circ - \frac{RT}{n\Im}\ln\left(\frac{a_{Cu}a_{Zn^{2+}}}{a_{Cu^{2+}}a_{Zn}}\right)$$

$$E = 1.1 - \frac{(8.314\mathrm{JK^{-1}mol^{-1}})(298\mathrm{K})}{(2)(96485\mathrm{Cmol^{-1}})}\ln\left(\frac{(1)(0.1)}{(0.005)(1)}\right)$$

Hence, E = 1.061 V

When the cell reaction reaches equilibrium, Q = K_{eqm} and electron flow stops and E = 0. Thus, it follows that

$$E^{\circ} = \frac{RT}{n\Im} \ln K_{eq}$$

This provides a very convenient method for estimating the equilibrium constants and standard free energy changes since E° values are available for a very wide range of reactions.

Applications of electrochemical cells

Many and various:
Batteries, energy storage, thermodynamic measurements, study of reactions such as corrosion, **analytical chemistry**

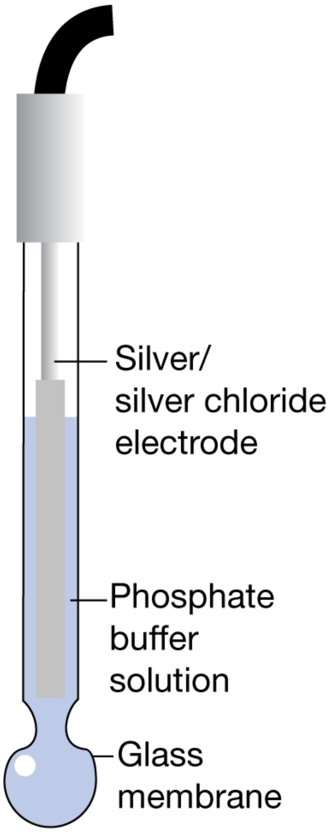
If we can arrange an electrochemical cell such that we constant activity of all components *except* H^+ then we can write

E_{cell} = (const.) – (const.) *ln* (const.) $[H^+]$

In other words, the potential depends only on the log of $[H^+]$. This forms the basis of a pH meter (see Atkins for details).

pH = - $\log_{10} [H^+]$

Similar *ion selective electrodes* are available for a wide range of cations and anions.



Where *could* we go from here

We have discussed a small number of applications of equilibrium constants and electrode potentials. The aim was to introduce the basic principles. There are many other areas of chemistry where related principles can be applied and you should be aware of these from reading textbooks. These include: acid-base equilibria, solubility of salts and other compounds.

Atkins (Elements III) Chapter 9

Exercises: 10, 21, 24, 32, 29, 30