

## Topic 7: Thermochemistry

Thermochemistry is the branch of chemistry concerned with the *quantities of heat evolved or absorbed* during a chemical reaction.

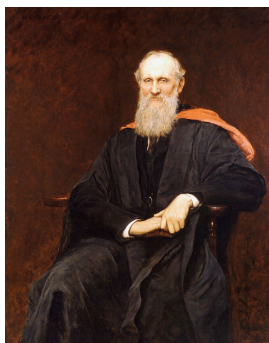
*What is the difference between heat and temperature?*

Heat is a **transfer of energy** between a system and its surroundings because of a difference in temperature. Energy that is transferred as heat moves from an area or system of higher temperature to one that is cooler (lower temperature). When two systems are at the same temperature they exist in **thermal equilibrium**.

*The Kelvin Scale*

When measuring temperatures in chemistry we don't generally use the Celsius scale ( $^{\circ}\text{C}$ ), instead temperature is measured in kelvin (K). The kelvin scale is an absolute scale with its minima at absolute zero,  $-273.15^{\circ}\text{C}$  (more on this later!) Conversion of temperature in degrees Celsius to thermodynamic or absolute temperatures is done by adding 273.15. Therefore, a temperature difference in kelvin is the same as the temperature difference in degrees Celsius. Change in Temperature can also be written as  $\Delta T$ , where  $\Delta$  means change:

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$



Lord Kelvin,  
(born William  
Thomson)  
1824–1907

A Belfast born physicist and engineer who worked at the University of Glasgow. Absolute temperatures are reported in the units of kelvin to honour his determination of absolute zero as  $-273.15^{\circ}\text{C}$ .

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### Example

On average the coldest Sydney month is July, where mean maximum temperature is  $16.3^{\circ}\text{C}$  and mean minimum temperature is  $8.1^{\circ}\text{C}$ .\* Assuming that these temperatures represent averages for day and night, calculate  $\Delta T$  from day to night. Convert both temperatures to kelvin and work out  $\Delta T$  in both kelvin and degrees Celsius.

\*Stats from: [http://www.bom.gov.au/climate/averages/tables/cw\\_066062.shtml](http://www.bom.gov.au/climate/averages/tables/cw_066062.shtml)

*Types of Energy*

The word energy is derived from the Ancient Greek word 'energeia', which means 'work within' and energy is indeed the capacity to do work. All energy exists in one of two

states, **kinetic** and **potential** energy. Kinetic is another Greek word, which means motion, and hence kinetic energy is the energy of a moving object. When a moving object collides with another object then work is done as the energy is transferred to the second object, for example when one snooker ball hits another. One way of viewing potential energy is motion about to happen, examples would be an apple in a tree or a parachutist waiting to leap out of a plane. When the apple falls from the tree or the parachutist is brave enough to jump, the potential energy is transferred into a form of kinetic energy. Energy cannot be created or destroyed but is transformed from one form into another, therefore total energy is equal to the sum of both kinetic energy and potential energy:

$$\text{Total Energy} = \text{Kinetic Energy} + \text{Potential Energy}, E_{\text{tot}} = E_k + E_p$$

Energy is measured in the SI unit of joules (J), which is a derived unit that can also be expressed in terms of SI base units:

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

Energy can be transferred as heat or as work and both are also measured using in Joules.

#### *Heat Capacity*

Heat transfer causes a change in temperature and we can measure the amount of energy (in the form of heat) required to afford a specific change in temperature. We can't measure heat directly so instead we calculate it from the resultant change in temperature ( $\Delta T$ ) when heat ( $q$ ) is transferred between systems. There is a linear relationship between heat and temperature given by:

$$q = \text{constant} \times \Delta T$$

The constant is dependent on the amount of substance (mass or moles) and is different for different substances. The constant used depends on whether we are considering *molar heat capacity*, **C** or *specific heat capacity*, **c**. Molar heat capacity of a substance is defined as: **the amount of heat required to raise the temperature of 1 M of the substance by 1 °C**. The specific heat capacity of a substance is defined as: **the amount of heat required to raise the temperature of 1 g of the substance by 1 °C**.

Hence,

$$q = mc\Delta T \text{ or } q = nC\Delta T$$

where **q** = heat (J), **m** = mass of substance (g), **c** = specific heat capacity ( $\text{J g}^{-1}\text{K}^{-1}$ ) and **C** = molar heat capacity ( $\text{J mol}^{-1}\text{K}^{-1}$ )

***A note on Calories vs. calorie***

1 calorie = 4.184 J  
= energy to heat 1 g of water by 1 °C  
1 "Calorie" = 1 kilocalorie = 1000 calories

**Question:**

How much energy (heat) does it take to heat an aluminium saucepan (0.2 Kg) containing 1L of water from room temperature (20 °C) to boiling? Assume thermal equilibrium between the pan and water at all times.

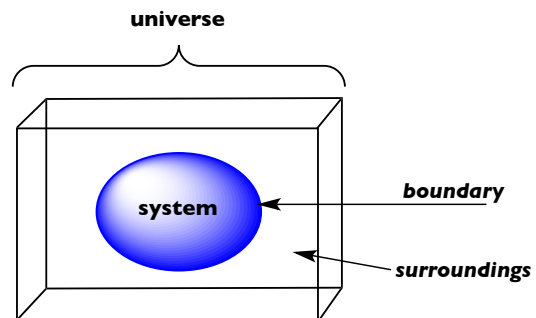
**Critical thinking**

Why might it radiator antifreeze (ethylene glycol) be a bad idea in summer?

*Some Key Concepts*

The words **system**, **surrounding** and **universe** will be referred to frequently during this part of the course. Together a system and the surroundings make up the universe.

These terms are helpful when describing the thermodynamics of a system and allow us to describe the heat flow between system and surroundings, or vice versa.

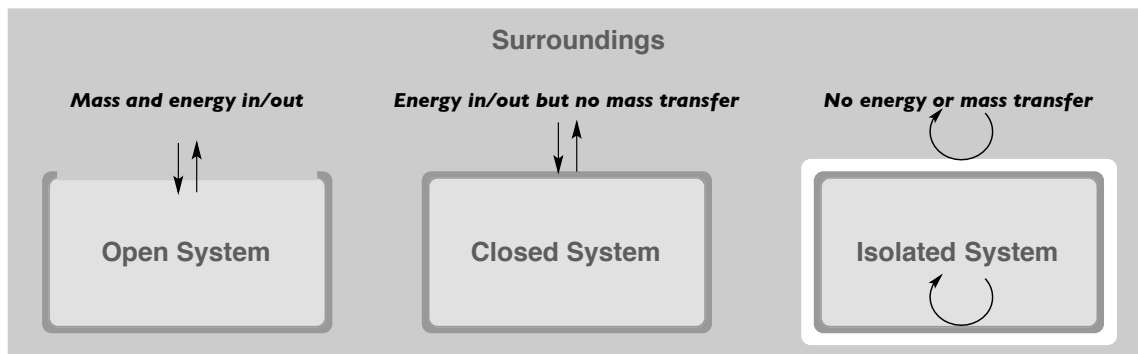


There are three different types of system, defined by whether or not mass and/or energy can cross the boundary:

**Open System** can gain or lose mass and energy across the boundary  
e.g.

**Closed System** can gain or lose energy, but not mass across the boundary  
e.g.

**Isolated System** cannot exchange energy or mass with the surroundings, also known as an adiabatic system  
e.g.



#### *The First Law Of Thermodynamics*

When heat is absorbed by or emitted from a system or when work is done on or by a system then the energy of the system and its surroundings change. Within a chemical system the sum of all kinetic and potential energy, or total energy is called the **internal energy**,  $E_{\text{int}}$  or  $U$ . A system contains only internal energy and not heat and work, which are the means for energy transfer between a system and its surroundings. The relationship between heat ( $q$ ), work ( $w$ ) and internal energy ( $U$ ) is expressed as:

$$\Delta U = q + w$$

This equation represents the **first law of thermodynamics**, which means that energy can be transferred between a system and its surroundings as either heat or work *but* it can't be created or destroyed. In an isolated system heat and energy cannot be exchanged with the surroundings and therefore **the energy of an isolated system is constant**. We can also write this mathematically as:

$$\Delta U_{\text{isolated}} = 0 = q + w$$

#### *Chemical Reactions and Energy*

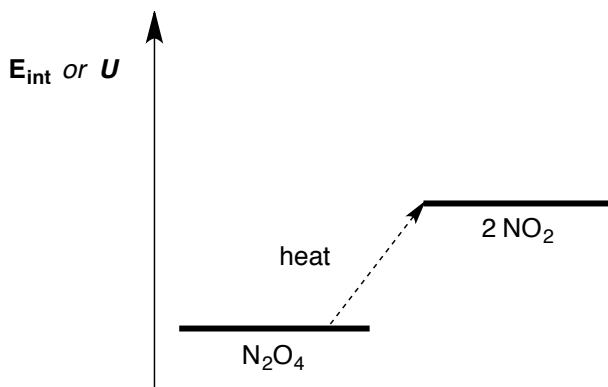
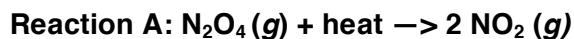
In a chemical reaction the change in internal energy ( $\Delta U$ ) can be described as:

$$\begin{aligned}\Delta U &= U_{\text{final}} - U_{\text{Initial}} \\ &\text{or} \\ \Delta U &= U_{\text{products}} - U_{\text{reactants}}\end{aligned}$$

Within a chemical system there are a number of contributions to the internal energy, both in the form of kinetic and potential energy, can you think of some examples?

A chemical system, or a substance in any state contains *only* internal energy in the form of potential and kinetic energy. Heat and work only exist when changes are made to a system, for example in a chemical reaction.

e.g. The dissociation reaction of dinitrogen tetroxide:

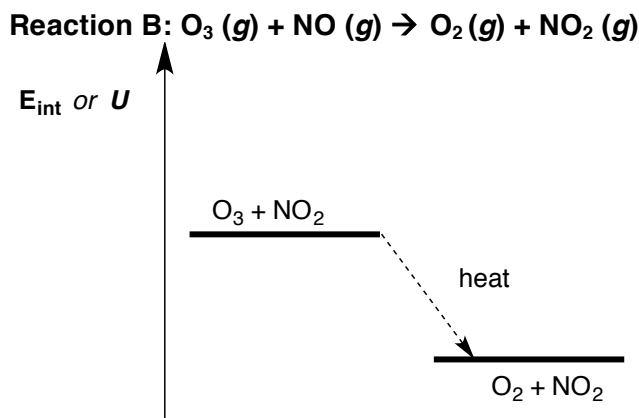


It is not possible to measure *absolute* internal energy ( $U$ ) but only the *change* in internal energy ( $\Delta U$ ). Lets consider the type of  $U$  that we have changed:

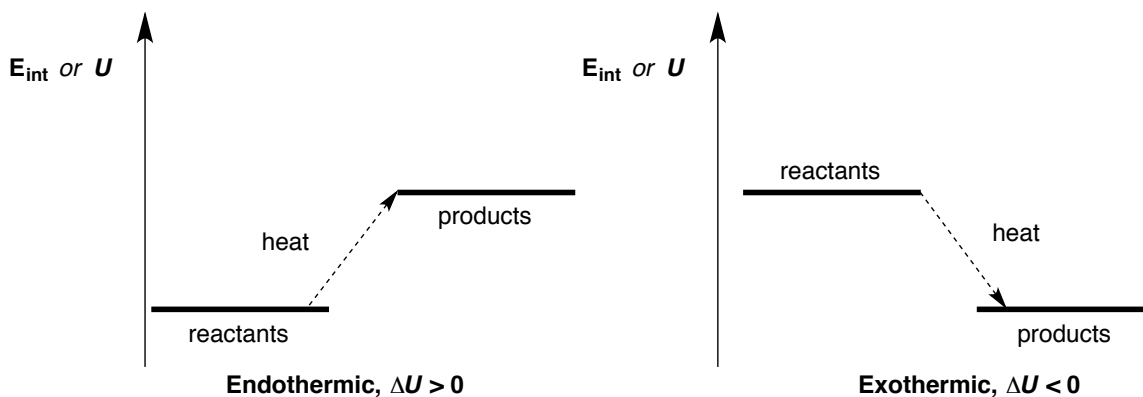
- Nuclear?
- Atomic?
- Vibration?
- Bond?

**The major change in potential energy in a chemical reaction is associated with bond energy**

Let's consider a slightly more complex reaction, the transfer reaction between ozone and nitric oxide:



In Reaction A, heat was absorbed by the starting material meaning that  $\Delta U$  has a positive value as the reactants are of a lower energy than the products. When  $\Delta U$  for a reaction is positive ( $\Delta U > 0$ ) the reaction is **endothermic**. Conversely, Reaction B is an example of an **exothermic** reaction as it emits heat. The reactants possess a higher internal energy than the products and so  $\Delta U$  has a negative value, ( $\Delta U < 0$ ).



*What about other types of energy and work?*

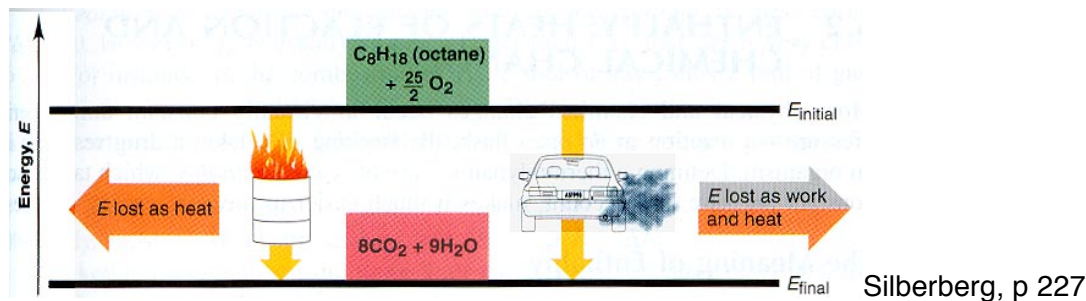
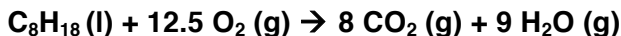
So far, we have only considered the heat and the general concept of work. The reactions above reference only heat ( $q$ ) as method of energy transfer. There are of course other types of energy changes in a chemical reaction, all of which are types of work:

Type	example	field	equation
electrical		electrochemistry	$E = VIt$
light		photochemistry	$E = h\nu$
piston		thermochemistry	$E = -p\Delta V$
spring		mechanics	$E = \frac{1}{2}kx^2$

Exercise: Energy is always measured in the unit of joules (J). Look up any unknown

symbols and their units and convince yourself that each type of the above has the units of energy (J). [Reminder:  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ ]

Let's consider the energy changes involved in the combustion of oxygen in car engine:



### Question

Consider a fully charged battery, what kind of energy is produced in each case?

1. Discharge through incandescent light bulb
2. Discharge through motor to drive piston
3. Discharge through wire

Remembering the first law of dynamics:

$$\Delta U = q + w$$

We know that a change in internal energy ( $\Delta U$ ) of a system is the result of an exchange of heat ( $q$ ) and/or work ( $w$ ) between the system and surroundings. For the moment we will only consider one form of work during this topic of thermochemistry (NB We will cover electrochemistry later in this module and photochemistry is taught in 2<sup>nd</sup> and 3<sup>rd</sup> year chem). The work done by or on a system can be expressed as:

$$w = -p\Delta V$$

Or alternatively that work can be quantified in terms of the change in volume ( $\Delta V$ ) against an opposing pressure.

We can now rewrite the first law of thermodynamics as:

$$\Delta U = q + -p\Delta V$$

When the potential energy changes in a reaction it produces or uses heat and/or the pressure/volume of the reactants is altered.

### *Enthalpy*

Enthalpy ( $H$ ) is a term used to express the changes of energy in a system. It can be determined through measurement of the temperature change during a chemical reaction or a physical change at constant pressure.

$$\Delta U = q + -p\Delta V$$

can be rearranged to:

$$\Delta U + p\Delta V = q = \Delta H$$

Reactions that evolve or consume gases commonly involve large changes in volume, in this case the difference between  $\Delta H$  and  $\Delta U$  can be huge. If a chemical reaction occurs without a change in volume (no expansion or contraction) then the change in internal energy is equal to heat absorbed or emitted in the reaction, and so:

$$\Delta U = q$$

Hence, under conditions of constant volume:

$$\Delta H = \Delta U$$

This relationship is very useful as most chemical reactions are performed under conditions of constant pressure rather than constant volume.

Can you think of some examples?

Change in enthalpy ( $\Delta H$ ) is also referred to as 'heat of reaction' and is the **experimentally** observed heat change for a chemical reaction under constant pressure, hence when the heat change of a reaction is **measured** this value is  $\Delta H$ , not  $\Delta U$ .

### *Calorimetry*

In order to measure  $\Delta H$  of a reaction, it is necessary to perform the reaction in a system that has been designed to minimise heat transfer to or from the surroundings. A specially designed apparatus called a **calorimeter** can be used either at constant pressure or volume.

The 'bomb' calorimeter operates at constant volume. As  $p\Delta V = 0$ ,  $q = \Delta U$ .

The calorific quantities of the food we eat are measured using the bomb calorimeter by burning them in excess oxygen under constant volume. The heat generated in the

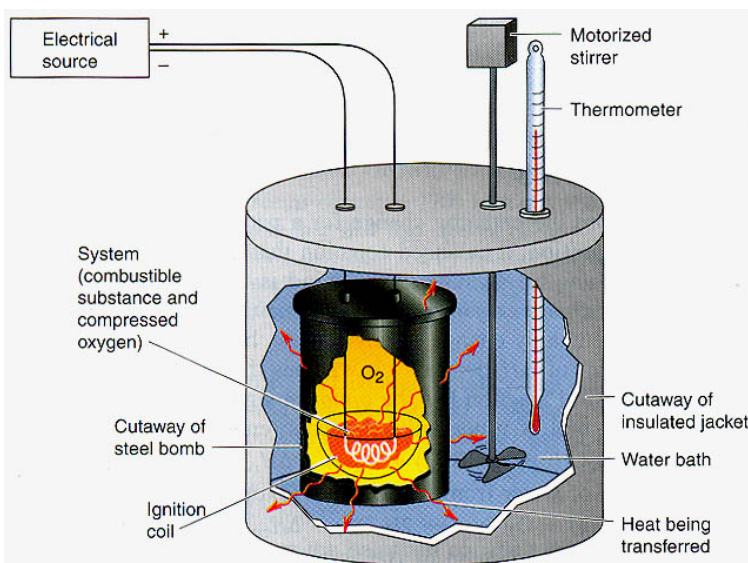


reaction is absorbed by the calorimeter and the surrounding water. The observed  $\Delta T$  can be used to measure the amount of heat generated in the reaction. The heat emitted in the reaction ( $q_{\text{reaction}}$ ) is numerically equal to the heat gained in the calorimeter ( $q_{\text{calorimeter}}$ ) but the sign is opposite:

$$q_{\text{calorimeter}} = -q_{\text{reaction}}$$

This relationship holds whether the reaction is exo- or endothermic.

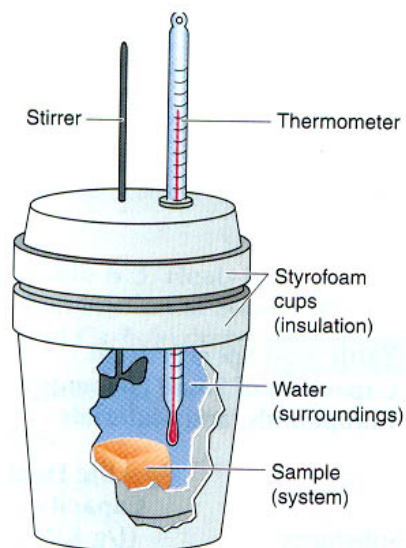
### The Bomb Calorimeter



- thermally insulating
- usually used for combustion reactions
- must know heat capacity of the calorimeter

A much simpler constant pressure 'coffee-cup' calorimeter' and can be used to measure the heat of reaction,  $\Delta H$ .

### The Coffee-Cup Calorimeter



- thermally insulating
- usually used for liquids
- especially good for
  - heat of dissolution
  - heat capacity of solids
  - aqueous reactions

### Some Key Types of Reaction Enthalpy

- Enthalpy of combustion:  
e.g. BBQ fuel (butane)  
 $\text{C}_4\text{H}_{10}(\text{g}) + 6.5 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2(\text{g}) + 5 \text{H}_2\text{O}(\text{g}) \quad \Delta H_{\text{comb}} = -2877 \text{ kJ mol}^{-1}$
- Enthalpy of vaporisation:  
e.g.  $\text{H}_2\text{O}$  at  $100^\circ\text{C}$   
 $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H_{\text{vap}} = +40.7 \text{ kJ mol}^{-1}$
- Enthalpy of atomisation:  
e.g. butane  
 $\text{C}_4\text{H}_{10}(\text{g}) \rightarrow 4 \text{C}(\text{g}) + 10 \text{H}(\text{g}) \quad \Delta H_{\text{atom}} = +5544 \text{ kJ mol}^{-1}$

### Bond Enthalpy

Bond enthalpy or bond dissociation enthalpy is the energy required to break one mole of a specific chemical bond to give separated atoms in the gas phase at a specified temperature, T.

### Bond Enthalpy Table

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**Table 9.2** Average Bond Energies (kJ/mol)

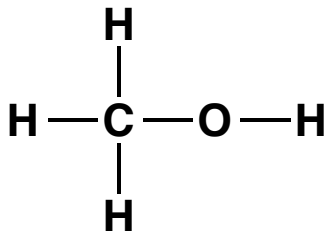
Bond	Energy	Bond	Energy	Bond	Energy	Bond	Energy
<b>Single Bonds</b>							
H—H	432	N—H	391	Si—H	323	S—H	347
H—F	565	N—N	160	Si—Si	226	S—S	266
H—Cl	427	N—P	209	Si—O	368	S—F	327
H—Br	363	N—O	201	Si—S	226	S—Cl	271
H—I	295	N—F	272	Si—F	565	S—Br	218
		N—Cl	200	Si—Cl	381	S—I	~170
C—H	413	N—Br	243	Si—Br	310		
C—C	347	N—I	159	Si—I	234	F—F	159
C—Si	301					F—Cl	193
C—N	305	O—H	467	P—H	320	F—Br	212
C—O	358	O—P	351	P—Si	213	F—I	263
C—P	264	O—O	204	P—P	200	Cl—Cl	243
C—S	259	O—S	265	P—F	490	Cl—Br	215
C—F	453	O—F	190	P—Cl	331	Cl—I	208
C—Cl	339	O—Cl	203	P—Br	272	Br—Br	193
C—Br	276	O—Br	234	P—I	184	Br—I	175
C—I	216	O—I	234			I—I	151
<b>Multiple Bonds</b>							
C=C	614	N=N	418	C≡C	839	N≡N	945
C=N	615	N=O	607	C≡N	891		
C=O	745	O <sub>2</sub>	498	C≡O	1070		
	(799 in CO <sub>2</sub> )						

Silberberg Table 9.2

*Atomisation Energy,  $\Delta H_{\text{atom}}$*

The atomisation energy is the sum of the individual bond enthalpies.

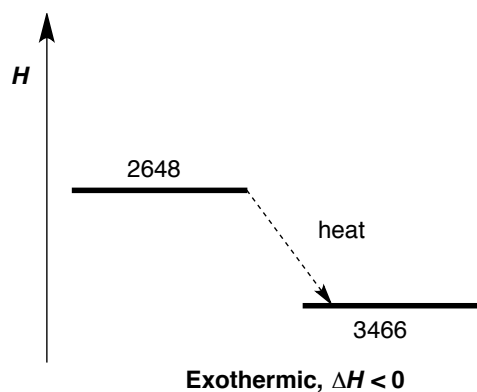
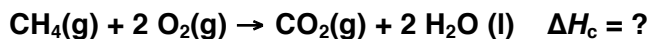
**Question:** Calculate  $\Delta H_{\text{atom}}$  for Methanol.



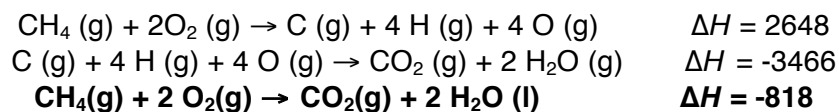
$\Delta H_{\text{atom}}$  is useful as it enables the estimation of thermodynamic quantities for reactions that we haven't measured. We can do this using **Hess's Law**, which reemphasises the first law of thermodynamics and the principal of conservation of energy. Hess's Law States:

**The change of enthalpy in a chemical reaction (e.g. heat generated at constant pressure) is independent of the route taken**

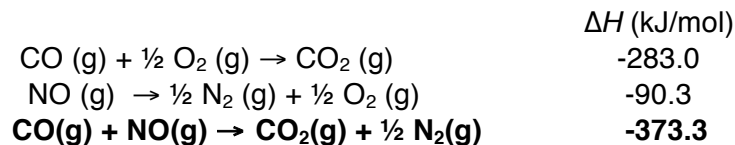
This means that we add up values for individual bond enthalpies to obtain a value for the overall enthalpy of a reaction, for example:



<i>Enthalpy of Reactants</i>		<i>Enthalpy of Products</i>	
4 x C-H:	1652	2 x C=O:	1598
2 x O=O:	996	4 x O-H:	1868
Total:	2648	Total:	3466



Hess's law can also be used in reactions that aren't atomization:

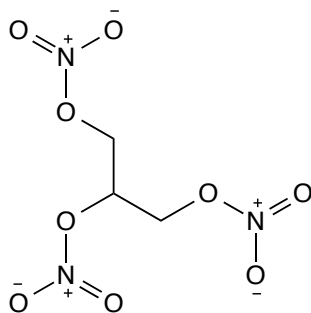


**Question:**

A manufacturer claims that their dessert has 'fewer than 50 kJ per serving'. The Consumer Affairs Department commissioned you to test the claim.

One serving of the dessert is placed into a bomb calorimeter ( $c = 8.15 \text{ kJ/K}$ ) and burnt to completion in excess  $\text{O}_2$ . The temperature increased by  $4.94 \text{ }^\circ\text{C}$ , is the claim justified?

**Question:** Nitroglycerine is an explosive. How much energy is released when 10 g of nitroglycerine is exploded? Nitroglycerine is  $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$  (*l*) and is converted to gaseous  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$  and  $\text{O}_2$ .

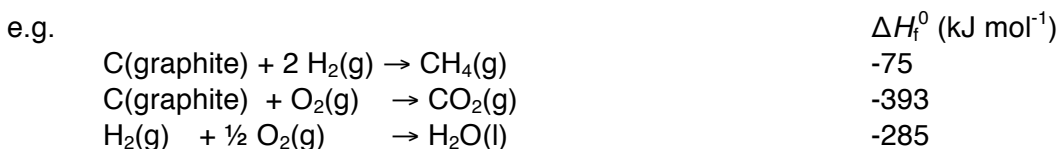


### Enthalpies of Formation, $\Delta H_f$

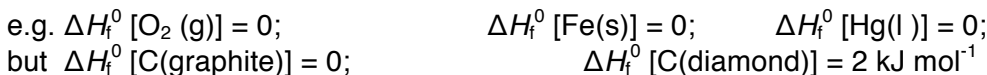
Despite the utility of Hess's Law, there are some problems with using bond enthalpy to predict thermodynamic quantities.

- Bond enthalpies depend on the molecule and tabulated data represents approximate averages and doesn't include ionic or metallic bonds.
- Atoms are hard to isolate and hence generating bond enthalpies for all common compounds represent a difficult experimental challenge.

To get around this problem we no longer use atoms in the isolated gaseous state but instead refer to the state in which the atom is most commonly found in, this is called the **standard state**. Rather than breaking bonds to form atoms we can look at the formation of compounds and refer to this thermodynamic value as the **enthalpy of formation** or **heat of formation**.



**Heat of formation of an element in its standard state is by definition zero**



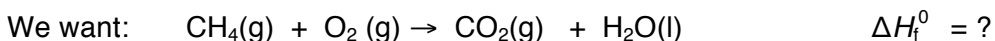
### Standard States

When defining an element at 'standard state' we have to define the standard conditions we are referring to:

- Gas: 1 atm (and behaving 'ideally')
- Temperature: 298 K
- Solution: 1 mol L<sup>-1</sup> (1 M)
- Elements: usual form (most stable) at standard conditions
- Compounds: usual form (most stable) at standard conditions

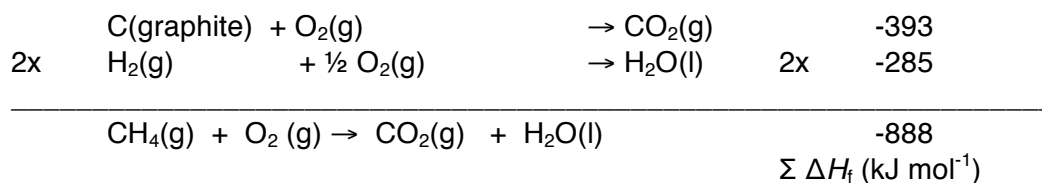
**Question:** Calculate the Heat of combustion of methane (CH<sub>4</sub>) using (i) Hess's Law and (ii) standard enthalpies of formation.

Add up formation reactions in the right way to make the overall reaction you want.



(i) We can get this using Hess's Law by adding the equations in the correct way:





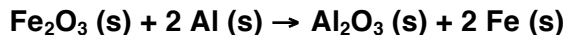
(ii) A short-cut also based on Hess's Law using enthalpies of formation is as follows:

$$\Delta H_r = \Sigma \Delta H_f(\text{prod}) - \Sigma \Delta H_f(\text{react.})$$

$$= \{2x \cdot -285 + -398\} - \{-75 + 0\} = -888 \text{ kJ mol}^{-1}$$

$\Delta H_f$  (kJ mol<sup>-1</sup>)       $\text{CO}_2(\text{g})$     -393       $\text{CH}_4(\text{g})$  -75,     $\text{H}_2\text{O}(\text{l})$       -285  
 (enthalpies of formation are widely available for many compounds)

**Question:** Predict (using the heat of formation tables – text book), whether the following reaction is exothermic or endothermic.

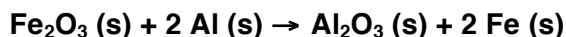


$$\Delta H_r = \Delta H_f(\text{prod.}) - \Delta H_f(\text{react.}) = -1669.8 - (-822.2) = -847.6 \text{ kJ mol}^{-1}$$

which is highly exothermic

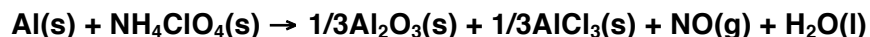
Which is the better fuel based on the kJ g<sup>-1</sup> basis?

Thermite reaction:



$$\Delta H_r^0 = -848 \text{ kJ mol}^{-1} = \underline{4.0 \text{ kJ g}^{-1} \text{ reactants}}$$

Or space shuttle solid fuel:



$$\Delta H_r^0 = -978 \text{ kJ mol}^{-1} = \underline{6.8 \text{ kJ g}^{-1} \text{ reactants}}$$

**Question:**

6.0 g of urea, (NH<sub>2</sub>)<sub>2</sub>CO, was burnt in O<sub>2</sub> to yield H<sub>2</sub>O (l), N<sub>2</sub> (g) and CO<sub>2</sub> (g). The reaction was performed at constant pressure 63.4 kJ being produced.

- Write a balanced equation for the reaction.
- What is  $\Delta H_c$  for urea?
- What is the standard heat of formation of urea?

### *The Second Law of Thermodynamics*

The first law of thermodynamics deals with the conservation of energy. Another process of interest in chemical systems is spontaneity; **the tendency for a system to undergo change without external influence**. Any reaction, which is not at equilibrium will have a preferred direction of change, it is *spontaneous (irreversible)* in a particular direction. The direction is specified by the Second Law.

#### **Question:**

Can you think of some examples of spontaneous processes?

Most exothermic reactions ( $\Delta H < 0$ ) are spontaneous as are some endothermic reactions ( $\Delta H > 0$ ). Therefore, to predict spontaneity we need to consider the role of the state function called *Entropy (S)*.

#### **A note on state functions**

We have now been introduced to several state functions:  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$  and soon  $\Delta G$ .

A state function is special as its value only depends on the current state of the system and not how it got there.

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

A state function depends **only on the initial and final states of the system and not on the path**

### *Thermodynamic States and Processes*

Entropy depends on the number of states a system has. Such states can be positional or thermal, the latter being associated with translational, vibrational and rotational energies, the greater the number of states in a system, the greater the entropy. Typically, highly specific (ordered states) result in low entropy since they are less numerous while random states are more numerous and result in high entropy. The latter are therefore more likely.

#### **Question:**

Which of the following systems has the higher entropy?

- (i) 1 or 2 L of  $\text{H}_2$  (g) under the same conditions
- (ii) 0.1 mole  $\text{H}_2$  at  $20^\circ\text{C}$  or at  $20^\circ\text{C}$  in a fixed volume
- (iii) 1 mol  $\text{H}_2$  or 1 mol  $\text{CH}_4$  under the same conditions
- (iv) 0.1 mole ice or 0.1 mole water at the triple point of water
- (v) 0.1 mole steam or 0.1 mole water at the normal boiling point of water.

### A reminder about thermodynamic systems

- *The system* - the portion of the universe being studied (usually the chemical reaction)
- *The surroundings* - everything that is outside the system (usually the immediate surroundings to the chemical reaction)
- *The universe* - the system + the surroundings

### Thermodynamic processes

- *isothermal* - carried out at constant temperature
- *isobaric* – carried out at constant pressure
- *adiabatic* – carried out without heat exchange with the surroundings
- *reversible/irreversible* – carried out under equilibrium or non-equilibrium conditions

In words the second law of thermodynamics is:

**In a spontaneous process the entropy of the universe must increase**

or

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 = \Delta S_{\text{universe}}$$

If, as stated above,  $\Delta S_{\text{universe}} = > 0$ , then the process is spontaneous in the direction described. In order to determine whether a process is spontaneous or not we need to calculate the entropy change of **both** the system and surroundings.

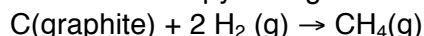
So, whereas the **energy** of the universe is **conserved** according to 1<sup>st</sup> Law of Thermodynamics, entropy is every **increasing**.

Entropy is a measure of randomness or disorder: the natural progression of things is from an ordered to a disordered state.

### Calculating Entropy Changes

Determining entropy changes for chemical reactions is not difficult under standard conditions, since standard entropies  $S^\circ$  are available for many elements and compounds. Note that the values, unlike standard enthalpies of formation are not zero for elements.

**Example:** Calculate the entropy change for the following reaction:



$S^\circ$  values (Aylward and Findlay): C(s) = 6; H<sub>2</sub>(g) = 131; CH<sub>4</sub>(g) = 186 JK<sup>-1</sup>mol<sup>-1</sup>

$$\begin{aligned} \Delta &= \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants}) \\ &= (186 - (6 + (2 \times 131))) \\ &= -82 \text{ JK}^{-1}\text{mol}^{-1} \end{aligned} \quad \text{why negative?}$$

**Question:** Is this the entropy change for (i) the system, (ii) the surroundings or (iii) the universe?



**Example:**

Calculate the standard entropy change for the fusion (melting) of ice at its normal melting point (i.e. at 1 atm).  $\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$ ,  $\Delta H^\circ_{\text{fus}} = 6.03 \text{ kJ mol}^{-1}$  at 273 K.

$$\begin{aligned}\Delta S_{\text{fus}} = \Delta H_{\text{fus}} / T_{\text{fus}} &= 6030 \text{ J mol}^{-1} / 273 \text{ K} \\ &= 22.1 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

**Example:**

Calculate the normal boiling point of water (i.e. at 1 atm).

$\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)}$ ,  $\Delta H^\circ_{\text{vap}} = 40.7 \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ_{\text{vap}} = 109 \text{ J mol}^{-1} \text{ K}^{-1}$

$$\begin{aligned}T_{\text{(bp)}} &= \Delta H_{\text{vap}} / \Delta S_{\text{l-g}} = 40700 \text{ J mol}^{-1} / 109 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 373 \text{ K}\end{aligned}$$

**Question:**

$\Delta S^\circ = 1.09 \text{ J mol}^{-1} \text{ K}^{-1}$  for the transition of solid rhombic sulfur to solid monoclinic sulfur at 95.5 °C. What is the enthalpy change,  $\Delta H^\circ$ , for this transition?

**The Effect of Temperature on Spontaneity**

Let's consider the process:



1 mol of  $\text{H}_2\text{O (l)}$  = 18 g = 18 mL (volume)

1 mol of  $\text{H}_2\text{O (g)}$  at 1 atm and 100 °C

**V = 31000 (31 L)!**

**Many** more positions available to molecules so  $\Delta S_{\text{sys}} > 0$

*In the case of the vaporisation of water, T is important:*

T > 100 °C **vaporisation is spontaneous**

T < 100 °C **condensation is spontaneous**

**Heat Flow, change in enthalpy ( $\Delta H$  at constant pressure)**

$\Delta S_{\text{surr}}$  is governed mainly by **energy** flowing into and out of the system as **heat**.

The temperature of the surroundings affects heat flow. If the surroundings are already hot then heat flowing into the surroundings will have less effect on the motion of the already hot particles. So, for example if 50 J of energy is transferred to the surroundings, the impact of this transfer on the surroundings depends greatly on **T**.

$\Delta S_{\text{surr}}$  can be expressed in terms of a change of enthalpy ( $\Delta H$ ) for a process at constant pressure:

$$\Delta S_{\text{surr}} = -\Delta H/T$$

+ value for  $\Delta H$  indicates endothermic (heat into system)

- value  $\Delta H$  indicates exothermic (heat out of system)

**Question:**

Antimony, the pure metal is recovered by *via* different reactions:

a) *Reduction by iron of the antimony in sulfide ores*



b) *Reduction by carbon of the antimony in oxide ores*



Calculate  $\Delta S_{\text{surr}}$  for each process at 25 ° C and 1 atm:

a)

b)

- In an **exothermic** process heat flows from system to surroundings,  $\Delta S_{\text{surr}} > 0$
- In an **endothermic** process heat flows from surroundings to system,  $\Delta S_{\text{surr}} < 0$

The spontaneity of the process is determined by the **entropy change** it produces in the universe:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

The magnitude of  $\Delta S_{\text{system}}$  and  $\Delta S_{\text{surroundings}}$  is therefore important in determining the sign of  $\Delta S_{\text{universe}}$ :

$\Delta S_{\text{system}}$	$\Delta S_{\text{surroundings}}$	$\Delta S_{\text{universe}}$	Spontaneous?
+	+	+	Yes
-	-	-	No (opp. direction)
+	-	?	Yes, if $\Delta S_{\text{sys}}$ greater
-	+	?	Yes, if $\Delta S_{\text{surr}}$ greater

### Gibbs Free Energy

We have seen that the spontaneity of a reaction can be predicted by making two measurements,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{sys}}$ . A useful State Function for predicting the spontaneity of a chemical reaction at constant pressure is the Gibbs Free Energy,  $G$  defined as follows:

$$G = H - TS$$

At constant temperature this gives:

$$\Delta G = \Delta H - T\Delta S$$

For a spontaneous process  $\Delta G < 0$

The Gibbs Free Energy is a function that combines a system's entropy and enthalpy, where  $\Delta H$  is the enthalpy change and  $T\Delta S$  is the entropic energy change. It takes account of the fact that:

- Chemical reactions and physical systems almost always absorb and release energy as heat ( $H$  relates to heat absorbed or released)
- Energy may be distributed throughout a chemical system in a large number of ways – some with a higher probability than others ( $S$  measure of number of ways energy is distributed)

$$\Delta G_{\text{reaction}} = \sum \Delta G^{\circ}_{\text{f}} (\text{products}) - \sum \Delta G^{\circ}_{\text{f}} (\text{reactants})$$

The usefulness of this function is that calculations need only be made for the chemical system **not** the system and the surroundings.  $\Delta G$  is essentially the maximum amount of energy that can be 'freed' from the system to perform useful work. For reactions we are usually most interested in the standard free energy,  $\Delta G^{\circ}$  (that is the free energy when substances are in their standard states at 1 atm pressure). Knowing the value of  $\Delta G^{\circ}$  enables comparison of the relative tendencies of reactions to occur. The more negative the value of  $\Delta G^{\circ}$ , the further the reaction will go towards completion. It is important to define standard free energy for these comparisons as free energy changes with pressure or concentration.

**Example:** Calculate  $\Delta G^{\circ}$  (298 K) for the reaction  $\text{CO (g)} + \frac{1}{2} \text{O}_2 \text{(g)} \rightarrow \text{CO}_2 \text{(g)}$   
 ( $\Delta G^{\circ}_{\text{f}} (\text{CO}) = -137.2 \text{ kJ mol}^{-1}$ ,  $\Delta G^{\circ}_{\text{f}} (\text{CO}_2) = -394.4 \text{ kJ mol}^{-1}$  and, by definition,  $\Delta G^{\circ}_{\text{f}} (\text{element}) = 0$ .)

$$\begin{aligned} \Delta G (298 \text{ K}) &= -394.4 - \{(-137.2) - \frac{1}{2}(0)\} \\ &= -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

The reaction is spontaneous at this temperature. **NB** This in no way indicates the *rate* at which the reaction will occur. A spontaneous process is one that increases the entropy of the universe. Since  $\Delta G_{\text{sys}} = -T\Delta S_{\text{universe}}$ , and  $T$  is always positive, the sign of  $\Delta G$  predicts whether a reaction will be spontaneous or not.

$\Delta G > 0$	Reaction is not spontaneous
$\Delta G = 0$	System is at equilibrium
$\Delta G < 0$	Reaction is spontaneous

**Example:**

At what temperature is the following process spontaneous at 1 atm?



What is the normal boiling point of  $\text{Br}_2$ ?

The vaporisation process will be spontaneous at all temperatures where  $\Delta G$  is negative.

$\Delta S^\circ$  favours *vaporisation* - increase in positional entropy

$\Delta H^\circ$  favours *condensation* (opposite process): exothermic

At the Boiling Point, liquid and gaseous  $\text{Br}_2$  are in equilibrium (both are in their standard states) hence  $\Delta G^\circ = 0$  (rather than  $\Delta G = 0$ ) when a system is undergoing a phase change.

Can only measure change in **free energy**  $\Delta G$ .

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad \text{we can set } \Delta G^\circ = 0 \quad T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{3.10 \times 10^4 \text{ J/mol}}{93.0 \text{ J/K mol}} = 333 \text{ K}$$

Thus  $\Delta H^\circ = T \Delta S^\circ$

If  $T > 333\text{K}$  then  $\Delta G^\circ < 0$  ( $T = 333\text{K} = 59^\circ\text{C}$ )

$T > 333\text{K}$   $\Delta S^\circ$  controls.  $\text{Br}_2$  will be vaporised

$T < 333\text{K}$   $\Delta H^\circ$  controls spontaneous in the direction which is exothermic

$T = 333\text{K}$   $\Delta G^\circ = 0$  liquid and gas coexist - boiling point

**Question:** Complete the following table

Reaction at 298 K	$\Delta H^\circ$ kJ mol <sup>-1</sup>	$T\Delta S^\circ$ kJ mol <sup>-1</sup>	$\Delta G^\circ$ kJ mol <sup>-1</sup>	Spontaneous ?
$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	+178	+48		
$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g})$	+181	+8		
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-285	-49		
$\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$	+13	+61		

## Entropy changes in chemical reactions

At constant T and P:

Entropy changes in the *surroundings* are determined by the *heat flow* that occurs as the reaction takes place

Entropy changes in the system are determined by *positional probability*

Consider:  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

If no. of gas<sub>reactant</sub> > no. of gas<sub>product</sub> molecules, then positional entropy has decreased and  $\Delta S$  will be negative for the reaction

## The Third Law of Thermodynamics

At absolute zero there is only one arrangement of the system and that is its lowest energy state. A solid at 0 K – molecular motion virtually ceases

### Entropy of a perfect crystal at 0 K is zero

As the temperature of the crystal is **increased**, disorder within the crystal increases—disorder increases, thus entropy increases with T

**Entropy** of a substance **increases** as a substance goes from: *solid* → *liquid* → *gas*  
NB. standard entropy values are listed in SI data books - units are always in  $\text{JK}^{-1}\text{mol}^{-1}$

### Question:

Do you remember the temperature of absolute zero in degrees Celsius?

For any substance  
 $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$

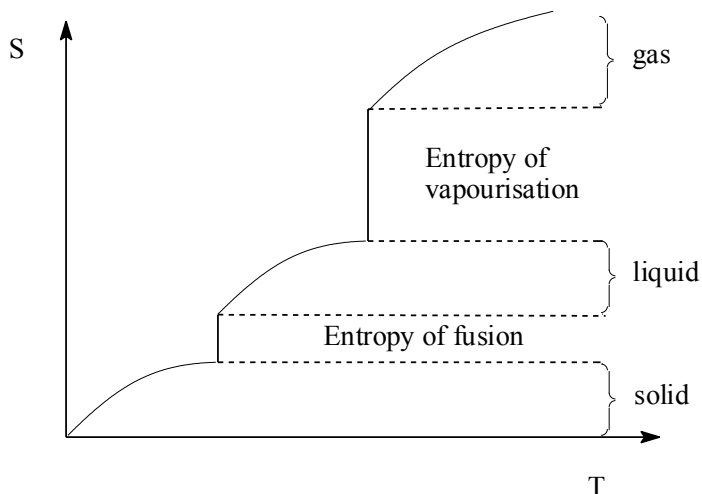
In general,  $\Delta S = q_{\text{rev}} / T$

for example:

$$\Delta S_{\text{s-l}} = \Delta H_{\text{fusion}} / T_{\text{fusion}}$$

and

$$\Delta S_{\text{l-g}} = \Delta H_{\text{vap}} / T_{\text{vap}} (\text{bp})$$



$$\Delta S^{\circ}_{\text{reaction}} = \sum mS^{\circ}_{\text{products}} - \sum nS^{\circ}_{\text{reactants}}$$

NB. The number of moles of the substance must be taken into consideration

**Question:**

The entropy of diamond is extremely low  $2 \text{ JK}^{-1} \text{ mol}^{-1}$  and graphite is slightly higher at  $6 \text{ JK}^{-1} \text{ mol}^{-1}$  why is this?

**Example:**

Calculate  $\Delta S^\circ$  at  $25^\circ\text{C}$  for the reaction



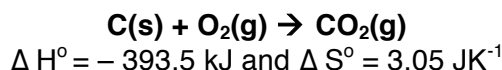
Substance	$S^\circ(\text{JK}^{-1} \text{ mol}^{-1})$
$\text{SO}_2(g)$	248
$\text{NiO}(s)$	38
$\text{O}_2(g)$	205
$\text{NiS}(s)$	53

$$\begin{aligned} \Delta S^\circ &= 2S^\circ(\text{SO}_2(g)) + 2S^\circ(\text{NiO}(s)) - 2S^\circ(\text{NiS}(s)) - 3S^\circ(\text{O}_2(s)) \\ &= 2(248) + 2(38) - 2(53) - 3(205) \text{ JK}^{-1} \\ &= -149 \text{ JK}^{-1} \end{aligned}$$

We would expect  $\Delta S^\circ < 0$  since the number of gaseous molecules **decreases** in this reaction.

**Free Energy and Chemical Reactions**

In chemical reactions we are mainly interested in the **standard** free energy  $\Delta G^\circ$  that is the free energy when substances are in their standard states. We **cannot** measure free energy directly from experiments, but **can** calculate it from other measured quantities.  $\Delta G^\circ$  values for reactions determines the **relative tendencies** of reactions to occur. The more **negative** the value of  $\Delta G^\circ$  the further the reaction will go towards completion.

**Example:**

Calculate  $\Delta G^\circ$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -3.935 \times 10^5 \text{ J} - (298 \text{ K})(3.05 \text{ JK}^{-1}) \\ &= -3.944 \times 10^5 \text{ J} \\ &= -394.4 \text{ kJ (per mole of CO}_2) \end{aligned}$$

**Standard Free Energy of Formation,  $\Delta_f G^\circ$** 

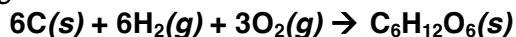
$\Delta_f G^\circ$  = The free energy change that occurs when one mole of a compound is made from its elements with all components in their standard states

$$\Delta G^\circ_{\text{reaction}} = \sum m \Delta G^\circ_{\text{products}} - \sum n \Delta G^\circ_{\text{reactants}}$$

$\Delta_f G^\circ$  values have properties similar to  $\Delta H_f^\circ$  values

- $\Delta_f G^\circ$  of an element is zero
- an equation coefficient multiplies  $\Delta_f G^\circ$  by that number
- reversing an equation changes the sign of  $\Delta_f G^\circ$
- tables of  $\Delta_f G^\circ$  are available

**Example: Formation of glucose**



Remember the standard free energy of formation of an element in its standard state is zero. Thus:  $\Delta G^\circ_{\text{reactants}} = 0$  since all are elements.

$$\Delta_f G^\circ_{\text{(glucose)}} = \sum \Delta G^\circ_{\text{products}} = -911 \text{ kJ mol}^{-1}$$

The standard free energy associated with this process is called the free energy of formation of glucose

### Gibbs Free Energy and Pressure

For Ideal gases, enthalpy is not pressure-dependent. Entropy is pressure-dependent because of its dependence on volume

Consider 1 mole of ideal gas at a given temperature: If  $V = 10.0 \text{ L}$ , the gas has many more positions available for the molecules to occupy than if  $V = 1.0 \text{ L}$ .

$$\begin{aligned} S_{\text{large volume}} &> S_{\text{small volume}} \\ \text{or because } P \text{ and } V \text{ are inversely related} \\ S_{\text{low pressure}} &> S_{\text{high pressure}} \end{aligned}$$

**The entropy and therefore the free energy of an ideal gas depends on pressure.**

### Gibbs Free Energy and Temperature

$\Delta G$  depends on temperature and some reactions, which are not spontaneous at one temperature, may become so at a different temperature

$$\Delta G = \Delta H - T\Delta S$$

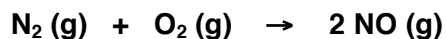
The table below shows some possible reaction possible outcomes:

		$\Delta H$	
		+	-
$\Delta S$	+	spontaneous at high temperatures nonspontaneous at low temperatures	spontaneous at all temperatures
	-	nonspontaneous at all temperatures	nonspontaneous at high temperatures spontaneous at low temperatures

Blackman Figure 8.20



**Question:** At what temperature will the following reaction become spontaneous?



Data supplied:	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{N}_2(\text{g})$	191.4	0
$\text{O}_2(\text{g})$	204.9	0
$\text{NO}(\text{g})$	210.5	90.4

### Free Energy and Work

We need to be able to find whether or not a reaction will occur spontaneously as well as whether we are wasting our time trying to make a reaction occur. We need to see also how much work (be it chemical) a reaction can do for us.

**The maximum possible useful work obtainable from a given process at constant temperature and pressure is equal to the change in free energy**

*Or*

$W_{max} = \Delta G$  This is why we call it **free energy**

After any real cyclic process the surroundings have gained thermal energy and the entropy of the universe has increased. This is another way of stating the second law of thermodynamics. When energy is used to do work it becomes less organised and less concentrated and thus less useful.

## Topic 8: Chemical Equilibrium

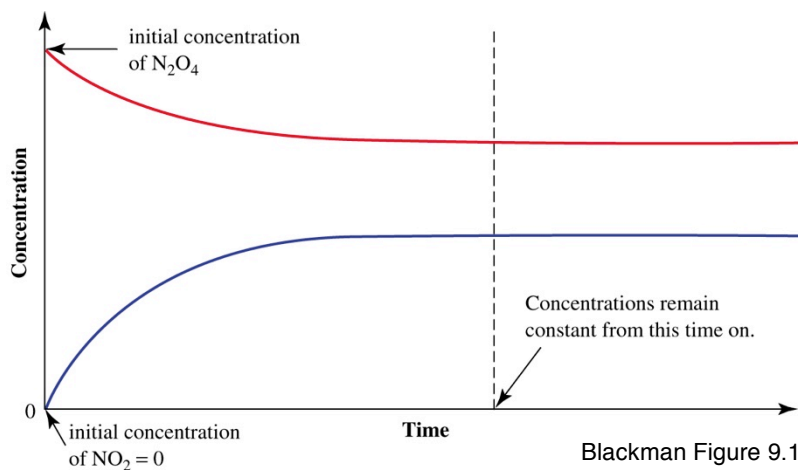
Chemical equilibrium is concerned with the reversibility of chemical reactions. Up until now we have assumed that all reactions reach completion - that all reactants are transformed into products. This is not always the case, many reactions do not go to completion and instead both reactants and products exist in equilibrium. Equilibrium is a dynamic process and can proceed from  $L \rightarrow R$  and  $R \rightarrow L$  as shown in the following examples:

- A.  $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$
- B.  $2 \text{NO} + \text{Cl}_2 \rightleftharpoons 2 \text{NOCl}$
- C.  $\text{Cl} + \text{O}_2 \rightleftharpoons \text{ClO}_2$

Note that equilibrium processes are represented by a double-headed arrow ( $\rightleftharpoons$ ).

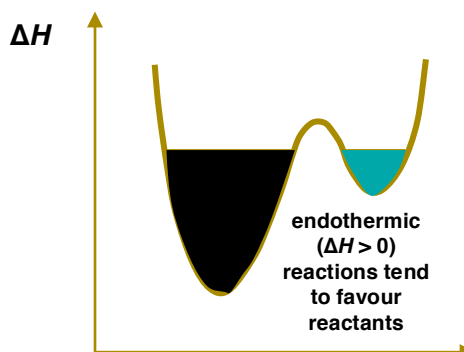
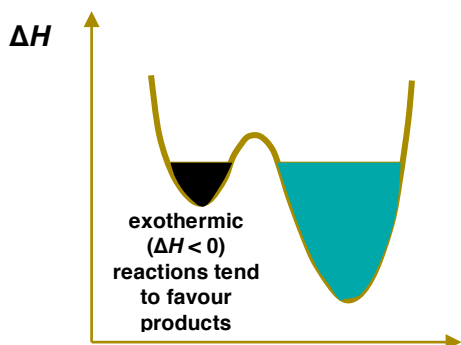
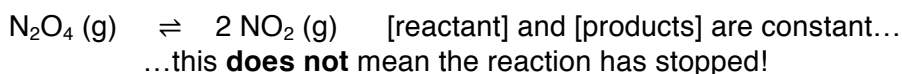
Equilibrium is attained when no net change in the concentration of reactants and products occurs,  $\Delta G = 0$ . Two Norwegian chemists, Guldberg and Waage, were the first to state the fundamental observation of chemical equilibrium in 1864:

**“At a given temperature, a chemical system reaches a state in which a particular ratio of reactant and product concentrations has a constant value”**



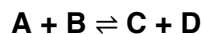
### Dynamic Equilibrium

Equilibrium concentrations do not change with time so that for the reaction:



For a simple reaction the reaction and equilibrium expression can be expressed as follows:

**Reaction:**

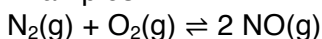


**Expression:**

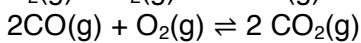
$$K_{eq} = \frac{[C] \times [D]}{[A] \times [B]}$$

In general,  $aA + bB \rightleftharpoons cC + dD$ ;  $K_{eq} = \frac{[D]^d \times [C]^c}{[A]^a \times [B]^b}$   $K_{eq} = \frac{\pi [\text{products}]}{\pi [\text{reactants}]}$

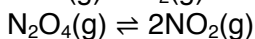
Examples:



$$K_{eq} = 1 \times 10^{-30}$$



$$K_{eq} = 2.2 \times 10^{22} \text{ L mol}^{-1}$$



$$K_{eq} = 0.211 \text{ mol L}^{-1}$$

**Question:**

For the above systems which compounds are favoured at equilibrium?

*Hint: remember that  $K = P[\text{prod.}] / P[\text{react.}]$*

Small  $K_{eq}$ : Equilibrium favours \_\_\_\_\_

Large  $K_{eq}$ : Equilibrium favours \_\_\_\_\_

Medium  $K_{eq}$ : \_\_\_\_\_ are present at equilibrium

### **The Reaction Quotient, Q**

This is important when we consider systems that may not be at equilibrium. The reaction quotient,  $Q$ , is calculated in exactly the same way as  $K$ , except using current concentrations rather than equilibrium concentrations.

**Question:**

When conducting the reaction:  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

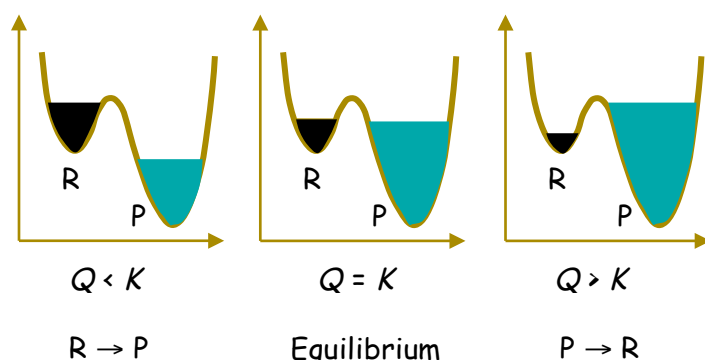
$$K_{eq} = 4.34 \text{ L mol}^{-1}$$

I put the following concentrations into a flask:

Compound	Concentration (M)	
	Expt 1	Expt 2
SO <sub>2</sub>	2.00	0.500
O <sub>2</sub>	1.50	0.100
SO <sub>3</sub>	3.00	0.350

Is the reaction at equilibrium? If not, which way will it move to achieve equilibrium?

The reaction quotient,  $Q$ , is calculated in exactly the same way as  $K$ , except using current concentrations rather than equilibrium concentrations.

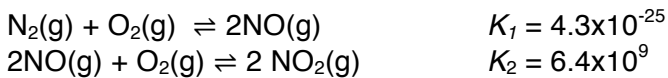


### Stoichiometry and Units

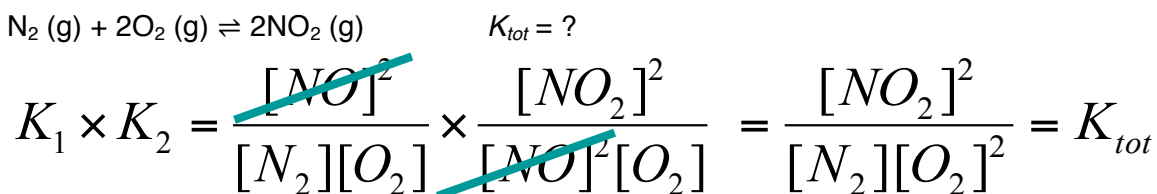
The equilibrium constant must be associated with a specific stoichiometric chemical equilibrium.

- If you multiply the stoichiometry by  $n$ , you change  $K$  by a **power of  $n$**
- If you reverse the chemical equation, you take the **inverse of  $K$**
- **Notice that the UNITS change**
- In equilibrium problems the units of  $K$  are often omitted – we'll see why in the tutorial.

Equilibria for coupled reactions



We can add up these chemical reactions to provide an overall reaction:



**i.e. when you ADD chemical equations, you MULTIPLY the  $K$ 's**

***Different kinds of equilibrium constant***

So far we have used the symbol  $K_{eq}$  or just  $K$  to represent the equilibrium constant. Sometimes we want to associate the equilibrium constant with a particular type of reaction, or particular units. We then use a different subscript on the  $K$  but really there is no difference to the way we treat the problem.

e.g.	$K_a$	=	acid dissociation equilibrium constant;
	$K_b$	=	base dissociation equilibrium constant;
	$K_w$	=	water dissociation equilibrium constant;
	$K_p$	=	equilibrium constant in units of pressure;
	$K_c$	=	equilibrium constant specifically in concentration units;
	$K_{stab}$	=	equilibrium constant for stability of a complex;
	$K_{sp}$	=	solubility product constant.

***Relation between  $K_p$  and  $K_c$***

In reactions involving gaseous reactants and/or products, equilibrium constants  $K_p$  or  $K_c$  can be written based on either partial pressures or molar concentrations for each component. These equilibrium constants are related since partial pressures and molar concentrations are related through the ideal gas equation:  $PV = nRT = (n/V)RT = (C)RT$ .

**Question:** Show that for the reaction:  $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  this relation is:

$$K_p = K_c (RT)^{-1}$$

**Question:** Show that for the general equation:  $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$  it is:

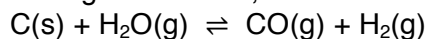
$$K_p = K_c (RT)^{(c+d)-(a+b)} = K_p = K_c (RT)^{\Delta n}$$

$$\text{Where } \Delta n = (c+d) - (a+b)$$

Note: P is in atm and C in mol L<sup>-1</sup> so R must have the units of [0.082] L atm K<sup>-1</sup> mol<sup>-1</sup>

### **Equilibria involving (l) and (s)**

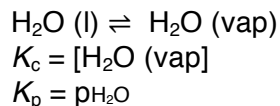
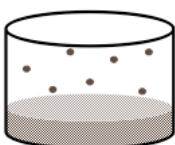
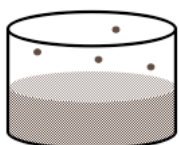
- Consider the “water gas” reaction, used to make combustible gases from coal:



The equilibrium constant can be written as:

$$K = \frac{[CO][H_2]}{[H_2O][C]}$$

In general, equilibrium constant expressions **do not** contain concentration factors for pure solids or liquids. Consider two identical closed flasks containing different amounts of water at the same temperature:



Vapour pressure does not depend on how much liquid is present.

*Decomposition of calcium carbonate:*



The equilibrium doesn't depend on the amount of solid, only on the amount of gas.

**Question:**

What is  $K_p$  for this reaction?

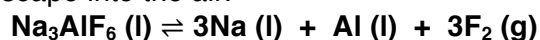
What is  $K_c$  for this reaction?

### Practising Equilibrium Calculations

It is important that you are comfortable with different types of equilibrium calculations. Working through the following examples will aid your understanding.

#### Example 1: Aluminium production by electrolysis:

Molten cryolite,  $\text{Na}_3\text{AlF}_6$ , is used as a solvent for aluminium ore *bauxite* ( $\text{Al}_2\text{O}_3$ ). Cryolite undergoes slight decomposition with heat to produce small amounts of  $\text{F}_2$ , a toxic gas which may escape into the air.



$$K_c = 2 \times 10^{-104} \text{ mol}^3 \text{ L}^{-3} \text{ at } 1300 \text{ K}$$

What is the concentration of  $\text{F}_2$  at this temperature?

$$K_c = [\text{F}_2]^3; \quad \text{so } [\text{F}_2] = (2 \times 10^{-104})^{1/3} = 3 \times 10^{-35} \text{ mol L}^{-1}$$

#### Example 2:

We have already investigated the equilibrium between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  so that we know that  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  exist in equilibrium.

A 0.0240 mol sample of  $\text{N}_2\text{O}_4(\text{g})$  is allowed to come into equilibrium with  $\text{NO}_2 (\text{g})$  in a 0.372 L flask at  $25^\circ\text{C}$ . Calculate the amount, in moles, of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is present at equilibrium.



Approach:

1. Work out concentration of  $\text{N}_2\text{O}_4$  initially
2. Let  $x$  = change in concentration
3. Write down equilibrium equation in terms of  $x$
4. Solve for  $x$
5. Substitute  $x$  to work out final concentrations or amounts

$$\begin{aligned} \text{Initial concentration of } \text{N}_2\text{O}_4 \\ &= 0.0240 / 0.372 \text{ mol L}^{-1} \\ &= 0.0645 \text{ mol L}^{-1} \end{aligned}$$

Initially:	$\text{N}_2\text{O}_4 (\text{g})$	$\rightleftharpoons$	$2 \text{NO}_2 (\text{g})$		
	0.0645		0	mol L <sup>-1</sup>	<b>Let <math>x</math> = amount of <math>\text{N}_2\text{O}_4</math></b>
Change:	-x		+2x	mol L <sup>-1</sup>	
Equilibrium	0.0645-x		2x	mol L <sup>-1</sup>	

$$K = 4.61 \times 10^{-3} = [\text{NO}_2]^2 / [\text{N}_2\text{O}_4] = (2x)^2 / (0.0645-x)$$

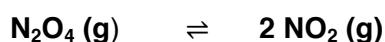
$$4.61 \times 10^{-3} = 4x^2/(0.0645-x)$$

$$2.973 \times 10^{-4} - 4.61 \times 10^{-3} x = 4x^2$$

$$4x^2 + 4.61 \times 10^{-3} x - 2.973 \times 10^{-4} = 0 \quad \text{solve the quadratic equation:}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 8.065 \times 10^{-3} \quad \text{or} \quad -9.217 \times 10^{-3}$$



Equilibrium	0.0645-x	⇌	2x	mol L <sup>-1</sup>
-------------	----------	---	----	---------------------

$$[\text{N}_2\text{O}_4] = 0.0645 - x = 0.0564 \text{ mol L}^{-1}$$

$$[\text{NO}_2] = 2x = 0.0161 \text{ mol L}^{-1}$$

Question asked for moles, therefore

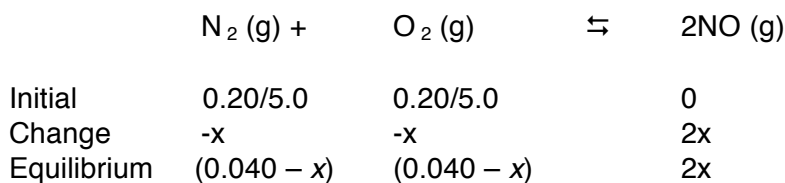
$$n (\text{N}_2\text{O}_4) = 0.0564 \text{ mol L}^{-1} \times 0.372 \text{ L} = 0.0210 \text{ mol}$$

$$n (\text{NO}_2) = 0.0161 \text{ mol L}^{-1} \times 0.372 \text{ L} = 0.0060 \text{ mol}$$

### Example 3:

Find the equilibrium concentrations of N<sub>2</sub>, O<sub>2</sub> & NO at 2400 K if we start with 0.20 mol N<sub>2</sub> and 0.20 mol O<sub>2</sub> in a 5.0 L vessel.

$$K_c = 2.5 \times 10^{-3} \text{ at } 2400 \text{ K}$$



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(0.040 - x)(0.040 - x)} = 2.5 \times 10^{-3}$$

$$4x^2 = 2.5 \times 10^{-3} \times (0.040 - x)(0.040 - x)$$



Could solve as quadratic, but suspect that  $x$  is small,

$$4x^2 = 2.5 \times 10^{-3} \times (0.040) \times (0.040), \quad \text{gives } x = 1.0 \times 10^{-3} \text{ M}$$

Check approximation:

$$x \text{ indeed small: } 0.040 - x = 0.039 \approx 0.040$$

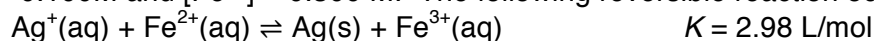
(solving quadratic:  $x = 0.98 \times 10^{-3} \text{ M}$ , so approx. is good)

$$\Rightarrow 2x = 2.0 \times 10^{-3} \text{ M} = [\text{NO}]$$

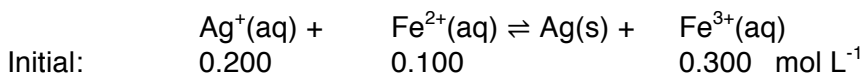
$$\Rightarrow [\text{N}_2] \text{ \& \ } [\text{O}_2] = 0.040 - 1.0 \times 10^{-3} = 0.039 \text{ M}$$

#### Example 4:

Solid silver is added to a solution with these initial concentrations:  $[\text{Ag}^+] = 0.200\text{M}$ ,  $[\text{Fe}^{2+}] = 0.100\text{M}$  and  $[\text{Fe}^{3+}] = 0.300 \text{ M}$ . The following reversible reaction occurs:

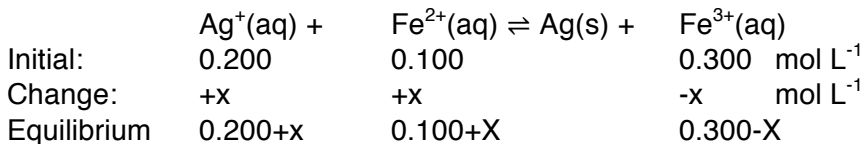


What are the ion concentrations when equilibrium is established?



Which way does the equilibrium shift?

$$Q = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^+]} = \frac{0.300}{(0.100) \times (0.200)} = 15.00$$



$$K = 2.98 = \frac{0.300 - x}{(0.100 + x) \times (0.200 + x)}$$

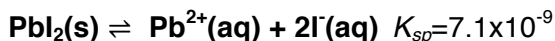
The allowable solution of this quadratic equation is  $x = 0.11$ . (You should check this.)

Therefore,  $[\text{Ag}^+] = 0.200 + x = 0.31 \text{ M}$ ;  
 $[\text{Fe}^{2+}] = 0.100 + x = 0.21 \text{ M}$ ;  
 $[\text{Fe}^{3+}] = 0.300 - x = 0.19 \text{ M}$ .

**Example 5:**

Lead iodide is an almost insoluble salt with a dense golden yellow colour. (It is used in ornamental work requiring a gold-like colour). The solubility product equilibrium constant is  $7.1 \times 10^{-9} \text{ mol}^3 \text{ L}^{-3}$ . Calculate the solubility of  $\text{PbI}_2$  (assume excess solid).

The balanced equation is:



Initial:	0	0	$\text{mol L}^{-1}$
Change:	+x	+2x	$\text{mol L}^{-1}$
Equilibrium	x	2x	$\text{mol L}^{-1}$

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = (x)(2x)^2 = 7.1 \times 10^{-9} \text{ mol}^3 \text{ L}^{-3}$$

**Question:** Solve for x and work out how many  $\text{mol L}^{-1}$  of  $\text{PbI}_2$  will dissolve.

$\text{NOCl}$  is an important transient molecule in the ozone cycle of the stratosphere. It exists in equilibrium with  $\text{NO}$  and  $\text{Cl}_2$ . At  $35^\circ\text{C}$  the equilibrium constant,  $K = 1.6 \times 10^{-5} \text{ mol L}^{-1}$ . In a laboratory experiment where the decomposition of  $\text{NOCl}$  was being studied, 1.0 mole of  $\text{NOCl}$  was placed into a 2.0 L flask. What are the equilibrium concentrations of  $\text{NOCl}$ ,  $\text{NO}$  and  $\text{Cl}_2$ ?

The balanced equation is:

	$2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$	$K = 1.6 \times 10^{-5}$
Initial:	0.50      0      0	$\text{mol L}^{-1}$
Change:	-2x      +2x      +x	$\text{mol L}^{-1}$
Equilibrium	0.50-x      2x      x	$\text{mol L}^{-1}$

$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2x)^2(x)}{(0.50-x)^2} = 1.6 \times 10^{-5}$$

This is a difficult cubic equation to solve!

However, note that  $K$  is small, therefore the reaction will not proceed to products to any large extent. Consequently, x is likely to be small, compared with the original 0.50M.

$$\frac{(2x)^2(x)}{(0.50)^2} = 1.6 \times 10^{-5} \quad \Rightarrow \quad 4x^3 = 0.25 \times 1.6 \times 10^{-5} \quad x^3 = 1.0 \times 10^{-6}$$

$$x = 1.0 \times 10^{-2}$$

## Le Chatelier's Principle

**“If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.”**

To understand Le Chatelier properly let's look at some specific changes:

### 1. Change in concentration



$$\text{At equilibrium: } Q = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = 24.0$$

Q. What happens if more  $\text{Cl}_2(\text{g})$  is injected?

A. Q gets smaller, so the equilibrium shifts to produce more product

If **concentration increases**, the system acts to **consume** some of it

If **concentration decreases**, the system acts to **produce** some of it

### 2. Change in pressure

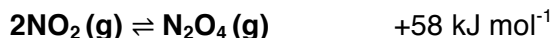
The pressure of a system can be changed in three ways:

- Add or remove a gaseous reactant or product (*same as changing concentration*)
- Add an inert gas (*one not involved in the reaction*)  
This changes **total pressure** but **not partial pressure** – this means that if an inert gas is added at constant volume then it has no effect on the equilibrium position.
- Change the volume of the container

### 3. Change the volume (*related to above*)

When volume **decreases**, the partial pressures of everything **increases**. According to Le Chatelier's principle, the system moves to the side with the least moles of gas in order to oppose the change.

What would be the outcome of compressing a syringe containing an equilibrium mixture of the following reaction:



### 4. Change the temperature

The exo- or endothermic nature of a reaction determines the way in which, the system changes with temperature. Is the above reaction exo- or endothermic? Which way will the reaction move if the temperature is raised?

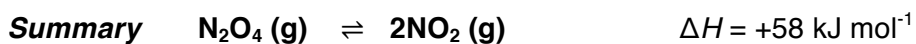
The best way to think about this is to consider temperature as one of the reactants in an endothermic reaction or as one of the products in an exothermic reaction:

An endothermic takes in heat, so:



So, if temperature is raised the system will react to oppose the change and move to the right.

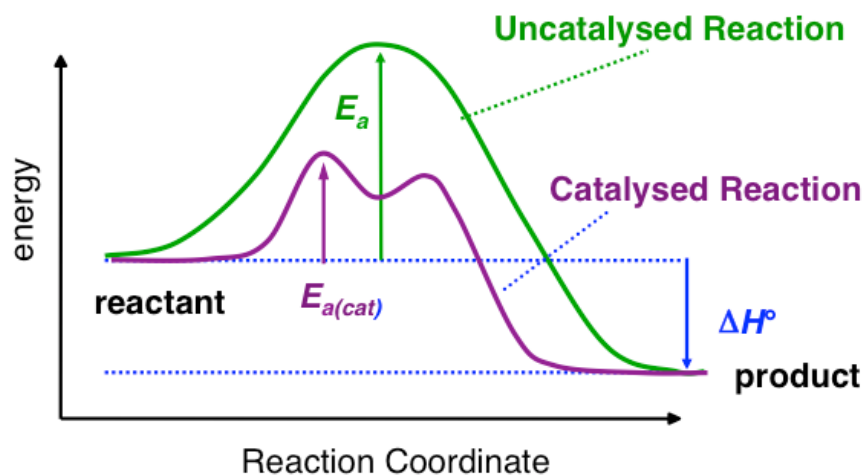
**NB. A change in temperature results in a change to the equilibrium that results in a change to the equilibrium constant  $K$ .** As long as temperature remains constant, changes in pressure, volume or concentration don't change the value of  $K$ .



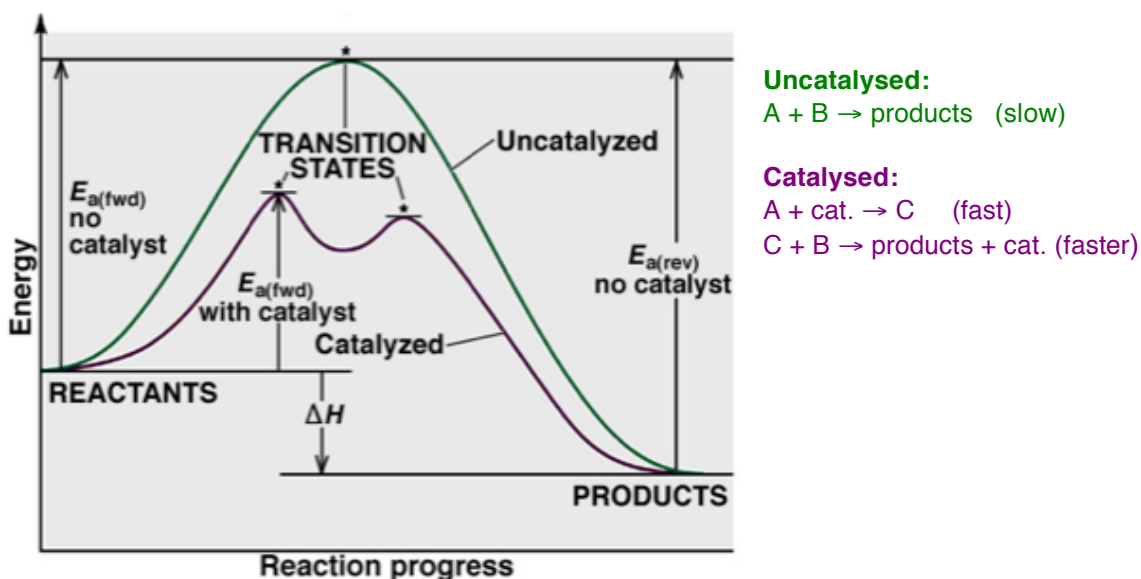
<b>Change</b>	<b>Shift</b>
<i>Addition of <math>\text{N}_2\text{O}_4 (\text{g})</math></i>	Right
<i>Addition of <math>\text{NO}_2 (\text{g})</math></i>	Left
<i>Removal of <math>\text{N}_2\text{O}_4 (\text{g})</math></i>	Left
<i>Removal of <math>\text{NO}_2 (\text{g})</math></i>	Right
<i>Addition of <math>\text{He}(\text{g})</math> at const. <math>V</math></i>	None
<i>Decrease container volume</i>	Left
<i>Increase container volume</i>	Right
<i>Increase temperature</i>	Right
<i>Decrease temperature</i>	Left

## Catalysis

The addition of a catalyst to a reaction increases the rate by providing an alternative reaction pathway or mechanism. As the catalyst is **not consumed** in the reaction they are not considered in the overall rate equation and therefore do not effect the equilibrium of the reaction but only the rate. (NB You will learn more about the rate of the reaction when you study kinetics).

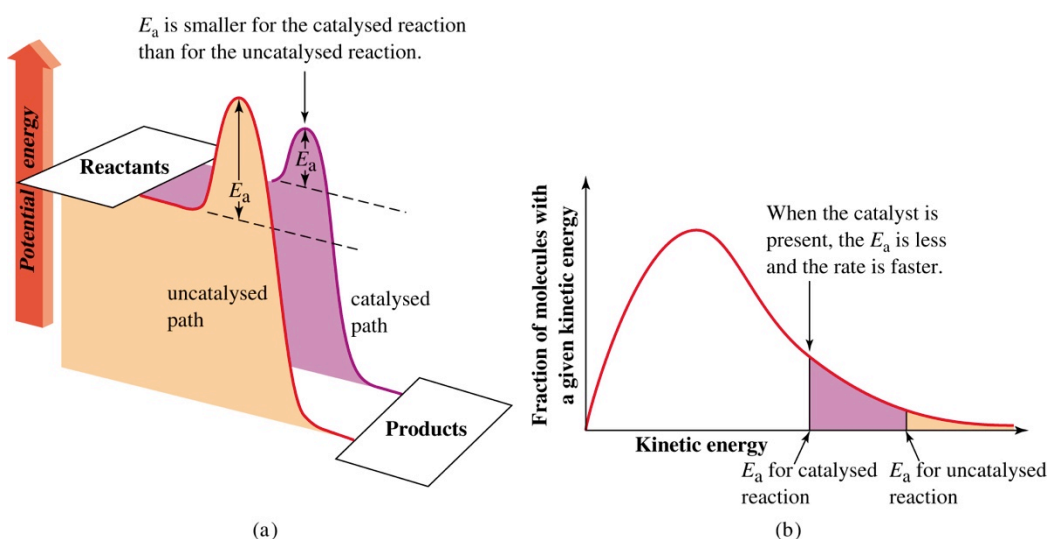


A catalyst lowers the **activation energy**,  $E_a$  for both forward and reverse reactions. The term 'activation energy' was first introduced in 1880 by a Swedish scientist, Svante Arrhenius, to describe the minimum amount of energy input required potential reactants to start a chemical reaction. As both forwards and backwards reactions pass through the same **transition state(s)**, a catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount and hence both the rates of forwards and backwards reaction increases by the same factor.



Catalysts are of extreme practical importance – in the research labs upstairs, industry and in the human body. In industry they help to improve the efficiency of chemical processes by shortening reaction time, reducing temperature etc. Often only very small amounts of catalyst are required and they can also often be recycled since they are not used up in the chemical process.

- Examples:
- nitrogenous fertilizers ( $N_2 + 3H_2 \rightarrow 2NH_3$ ) – **Pt** catalyst
  - removal of NO in vehicle exhaust – **Pd** oxide catalyst
  - hydrogenating natural oils for margarine
  - cracking petroleum → petrol, nylon, etc. – zeolite catalyst
  - enzymes in saliva breaking down food



Blackman Figure 14.14

### Free Energy and the Effect of Temperature on K

There is an important link between thermodynamics and equilibrium given by the expression for free energy for a reaction. This is:

$$\Delta G = \Delta G^{\circ} + RT \ln Q \quad \text{where } Q \text{ is the reaction quotient.}$$

**Case 1:**  $\Delta G^{\circ} = 0$  Free energy of the reactants and products are equal (standard states)  $P=1\text{atm}$  for all and  $K=1$

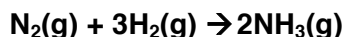
**Case 2:**  $\Delta G^{\circ} < 0$  system not at equilibrium,  $\Delta G^{\circ}_{\text{products}} < \Delta G^{\circ}_{\text{reactants}}$  system will adjust to the right to reach equilibrium  $K > 1$

**Case 3:**  $\Delta G^{\circ} > 0$  system not at equilibrium,  $\Delta G^{\circ}_{\text{products}} > \Delta G^{\circ}_{\text{reactants}}$  system will adjust to the left to reach equilibrium  $K < 1$

$$\begin{array}{ll} \Delta G^\circ = 0 & K=1 \\ \Delta G^\circ < 0 & K>1 \\ \Delta G^\circ > 0 & K<1 \end{array}$$

If  $\Delta G = 0$  the system is at equilibrium and  $Q = K$ , so:  $\Delta G^\circ = -RT \ln K$

**Example:** Predict the direction in which the system will shift to reach equilibrium



$\Delta G^\circ = -33.3 \text{ kJ}$  per mole of  $\text{N}_2$  consumed at  $25^\circ\text{C}$   
for

a)  $P(\text{NH}_3) = 1.00 \text{ atm}$ ,  $P(\text{N}_2) = 1.47 \text{ atm}$ ,  $P(\text{H}_2) = 1.00 \times 10^{-2} \text{ atm}$

b)  $P(\text{NH}_3) = 1.00 \text{ atm}$ ,  $P(\text{N}_2) = 1.00 \text{ atm}$ ,  $P(\text{H}_2) = 1.00 \text{ atm}$

a) First calculate the value of  $\Delta G$  using:

$$\Delta G = \Delta G^\circ + RT \ln(Q), \text{ where } Q = \left( \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3} \right)$$

$Q = 6.8 \times 10^5$ ,  $T = 298 \text{ K}$ , and  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta G^\circ = -33.3 \text{ kJ mol}^{-1} = -33.3 \times 10^4 \text{ J mol}^{-1}$

**Thus  $\Delta G = 0$ , and the system is already at equilibrium**

b) The system is in its standard state since all pressures are  $1 \text{ atm}$   $\rightarrow Q = 1$

And  $\Delta G = \Delta G^\circ + RT \ln 1.00$

giving  $\Delta G = \Delta G^\circ = -33.3 \text{ kJ mol}^{-1}$

The negative value means that in their standard states, the products have a lower free energy than the reactants so the system will move to the right.

### Summary

For Le Chatelier: "If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change."

#### **Q $\rightarrow$ K**

Increase reactant concentrations: *more products produced*

Increase pressure / decrease volume: *less gas produced*

#### **K changes, then Q $\rightarrow$ K**

Increase temperature: *endothermic reaction favoured*

#### **Q = K**

Add catalysts: *no change*

<b>Disturbance</b>	<b>Net Direction of Reaction</b>	<b>Effect on value of <math>K</math></b>
Increase [reactant]	More product formed	None
Decrease [reactant]	Towards the reactant(s)	None
Increase pressure at constant volume	Towards the side with the fewer gas molecules	None
Decrease pressure at constant volume	Towards the side with the greater number of gas molecules	None
Increase temperature	Exothermic reactions more to reactant side; endothermic reactions more to product side	Decreases Increases
Decrease temperature	Exothermic reactions more to product side; endothermic reactions more to reactant side	Increases Decreases
Add a catalyst	No change in position of equilibrium; rate at which equilibrium is reached is increased	None