CHEM 191
Module 2
Energetics, rates and driving forces of chemical reactions

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Brown *et al.,* 15th edition Chapter 5, 14, 19, 20, 23

Module 2, Lecture 1
Chemical Thermodynamics
Part 1

Learning Objectives:

- Understand the concepts of energy and energy change in chemical systems
- Understand the concept of enthalpy (H)
- Understand the difference between ΔH and ΔH°
- Use Hess's Law to determine ΔH°
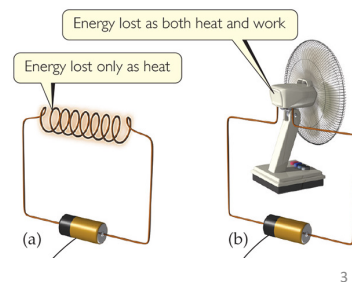
Textbook: Chapter 5

What is energy?

Energy = "The capacity to do work or transfer heat"

Work – energy used to change the position of an object

Heat – energy used to change the temperature of an object

e.g. with energy we can do work by making a fan turn

*e.g. with energy we can transfer heat and heat up a coil*

Energy lost as both heat and work

Energy lost only as heat

(a)   (b)

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What types of energy are there?

Kinetic energy – energy of motion

Potential energy – energy of position (relative to other objects/a force)
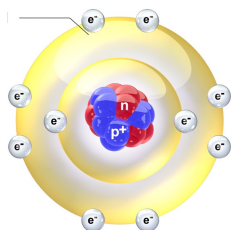
e.g. kinetic and gravitational potential energy

High potential energy, zero kinetic energy

Decreasing potential energy, increasing kinetic energy

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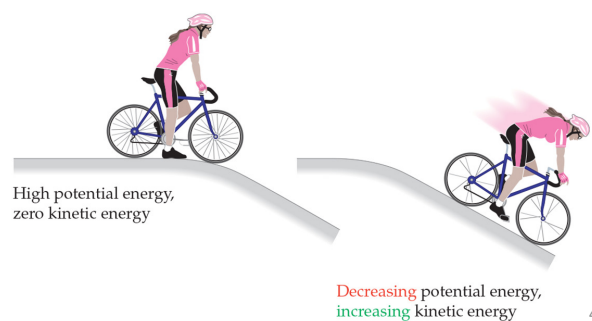
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Potential energy in chemical systems

Atoms are made up of charged particles.

Electrostatic Potential Energy

$$E_p = k \frac{q_1 q_2}{r^2}$$

If the charges q_1 and q_2 are opposite, (i.e. attractive interaction) – E_p is negative.

Chemical bonds therefore store **potential energy**.

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Units of energy

Energy is measured in units of **Joules** (J).

One J is quite a small amount, so in chemistry we normally talk about amounts of energy in kJ

🚩 **Careful!** Entropy, S, and the gas constant, R, are often in J K^{-1} and J K^{-1} mol^{-1}, respectively. Must convert units!

When reporting quantities need:

1. number
2. unit
3. **sign**

1 kJ = 1000 J

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First Law of Thermodynamics   "Energy is conserved"

BUT energy can be changed from one type to another (e.g. potential energy changes to kinetic energy when you drop something)

In chemistry we are interested in **changes** in energy
      – especially potential energy $\leftrightarrow$ heat

High potential energy,
zero kinetic energy

Decreasing potential energy,
increasing kinetic energy
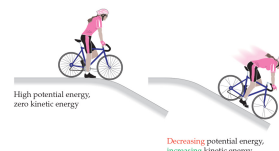
$$\Delta E = E_{final} - E_{initial}$$

 And, in a chemical reaction

$$\Delta_r E = E_{products} - E_{reactants}$$

reaction   ($\Delta_{rxn}E$, used in book)

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Thermochemistry – changes in heat energy

Heat (q) is the most readily measurable type of energy to study in chemistry.

If the products of a reaction have a lower heat content than the reactants, the reaction will release heat when it occurs.

   $\Delta_r q = q_{products} - q_{reactants}$ = **negative**.   **Exothermic Reaction**

If the products of a reaction have a higher heat content than the reactants, the reaction will absorb heat when it occurs.

   $\Delta_r q = q_{products} - q_{reactants}$ = **positive**   **Endothermic Reaction**
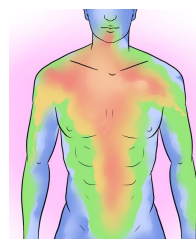
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Enthalpy – heat energy at constant pressure

Many chemical reactions, and all biochemical reactions, occur with no change in the pressures of the reactants or products (stays at atmospheric pressure) – under these conditions, we describe heat changes as **enthalpy changes (ΔH)**

$$\Delta_r q = \Delta_r H = H_{products} - H_{reactants}$$

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Enthalpy – heat energy at constant pressure

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta_r H = -483.6 \text{ kJ}$$

Using: $\qquad \Delta_r H = H_{products} - H_{reactants}$ (taking account of stoichiometry)

H(2 moles of H_2O(g)) – H(2 moles of H_2(g) plus 1 mole of O_2(g)) = -483.6 kJ

Reaction is exothermic (negative value of $\Delta_r H$) so H of the products less than H of the reactants.

What would $\Delta_r H$ for $4H_2(g) + 2O_2(g) \rightarrow 4H_2O(g)$ be?

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Hess's Law

Enthalpy is a **state function** – which means that the change in enthalpy upon the conversion of, say, A → B will be the same regardless if it occurs in one step or a number of steps.

e.g. altitude is also a state function

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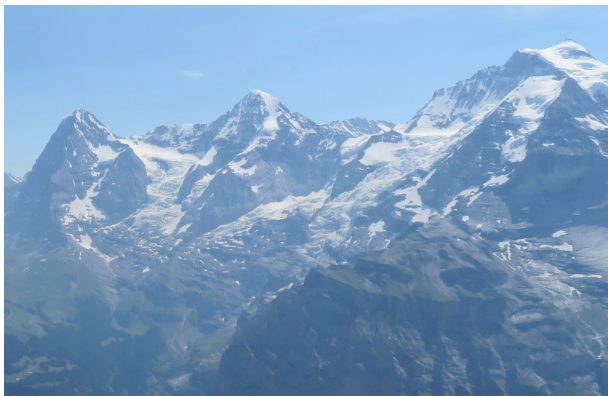
Hess's Law

Enthalpy is a **state function** – which means that the change in enthalpy upon the conversion of, say, A → B will be the same regardless if it occurs in one step or a number of steps.
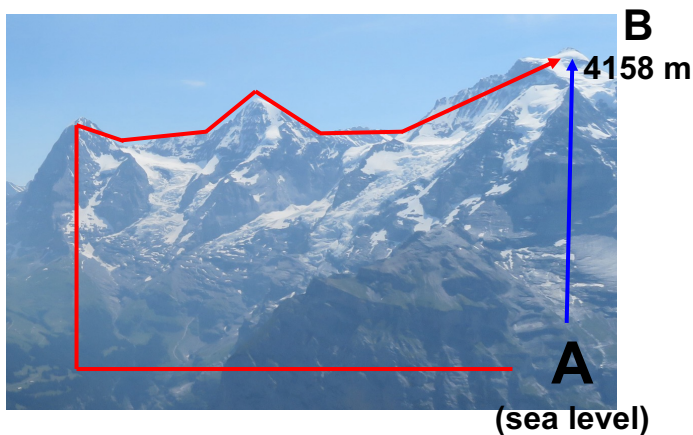
e.g. altitude is also a state function

B

4158 m

Altitude gain is 4158 m, regardless of whether red or blue path is taken.

A

(sea level)

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Hess's Law

This can provide us with a way to calculate values of Δ_rH which are difficult to measure experimentally.

Hess's Law: *If a reaction is conducted in a series of steps, Δ_rH for the overall reaction will equal the sum of the enthalpy changes for the individual steps.*

For example, the complete reaction of solid carbon with oxygen gas to make carbon monoxide is difficult as carbon dioxide is often also formed.

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta_rH = ??$$

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Hess's Law

But we can easily measure the enthalpy change for completely converting solid carbon to carbon dioxide

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_rH = -393.5 \text{ kJ}$$

And we can measure the enthalpy change for converting carbon monoxide into carbon dioxide

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta_rH = -283.0 \text{ kJ}$$
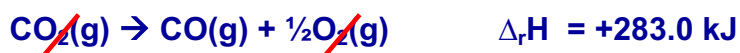
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Hess's Law

We can use the Δ_rH values from these two reactions to calculate the Δ_rH value for the conversion of $C(s)$ to $CO(g)$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_rH = -393.5 \text{ kJ}$$

(with ½ written above, O_2 and CO_2 struck through)

$$CO_2(g) \rightarrow CO(g) + \tfrac{1}{2}O_2(g) \qquad \Delta_rH = +283.0 \text{ kJ}$$

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta_rH = (-393.5) + (+283.0)$$
$$= -110.5 \text{ kJ}$$

Hess's Law says that if the equations add to give the overall equation we want, then the Δ_rH values will add to give the Δ_rH value we want.

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Hess's Law

In this example, one of the equations was **reversed** and when this was done the **sign** on the Δ_rH value was **changed**.

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta_rH = -283.0 \text{ kJ}$$
$$CO_2(g) \rightarrow CO(g) + \tfrac{1}{2}O_2(g) \qquad \Delta_rH = +283.0 \text{ kJ}$$

We can also **multiply an equation** through by some number (i.e. double everything) – when we do this we must also **multiply the Δ_rH** value by the same number.
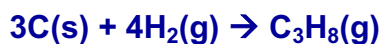
$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta_rH = -283.0 \text{ kJ}$$
$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \Delta_rH = -566.0 \text{ kJ}$$

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Hess's Law – another example

Use the following information to calculate the value of $\Delta_r H$ for the reaction

$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$$

1. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta_r H$ = -394 kJ

2. $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta_r H$ = -286 kJ

3. $C_3H_8(g) + 5O_2(g) \rightarrow 4H_2O(l) + 3CO_2(g)$ $\Delta_r H$ = -2220 kJ

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Hess's Law – solution

Equation 1 x 3
    $3C(s) + 3O_2(g) \rightarrow 3CO_2(g)$ $\Delta_r H$ = 3 x (-394) = -1182 kJ

Equation 2 x 4
    $4H_2(g) + 2O_2(g) \rightarrow 4H_2O(l)$ $\Delta_r H$ = 4 x (-286) = -1144 kJ

Equation 3 swapped around
    $4H_2O(l) + 3CO_2(g) \rightarrow C_3H_8(g) + 5O_2(g)$ $\Delta_r H$ = +2220 kJ

      $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ $\Delta_r H$ = (-1182 + -1144 +2220) kJ

                                = -106 kJ   18

Enthalpies of formation

Hess's Law allows for the calculation of enthalpy changes for various sorts of chemical reactions

$\Delta_{com}H$ for combustion reactions
$\Delta_{fus}H$ for fusion (melting) reactions
$\Delta_{vap}H$ for vaporisation (boiling) reactions

And, most importantly, Δ_fH for **formation reactions**

A formation reaction describes the formation of 1 mole of a compound from its constituent elements in their standard states

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Enthalpies of formation

Standard states – the most stable form of the element under 'normal' conditions.

State of Matter	Standard State
Gas	10^5 Pa pressure (~ 1 atmosphere)
Liquid	Pure liquid at 10^5 Pa
Solid	Pure solid at 10^5 Pa
Solution	1.00 mol L^{-1} concentration

temperature not included!

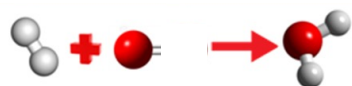We also define Δ_fH^o as the **standard enthalpy of formation**
- This refers to the formation reaction occurring under standard conditions (having all gases at standard pressure (1 bar, ~1 atm))

So Δ_fH^o (H$_2$O(l)) refers to the following equation

H$_2$(g) + ½O$_2$(g) → H$_2$O(l)

Both gases at 1 bar pressure   1 mol of H$_2$O formed

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Enthalpies of formation

Tables of $\Delta_f H^o$ values can be found in data books and online (reliable sources only!) and enable the calculation of $\Delta_r H^o$ values for almost any reaction.

$\Delta_r H^o = \sum[\Delta_f H^o \text{ (products)}] - \sum[\Delta_f H^o \text{ (reactants)}]$

(taking account of stoichiometry)

The standard enthalpy change for a reaction equals the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants.

(Just another way to think about Hess's Law)

$\sum$ means "sum of"

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Enthalpies of formation - example

Use the following data to calculate the value of $\Delta_r H^o$ for the combustion of glucose ($C_6H_{12}O_6(s)$), as described by the following equation:

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

$\Delta_f H^o$ ($C_6H_{12}O_6(s)$) = -1273 kJ mol^{-1} $\Delta_f H^o$ ($O_2(g)$) = 0 kJ mol^{-1}

$\Delta_f H^o$ ($CO_2(g)$) = -393.5 kJ mol^{-1} $\Delta_f H^o$ ($H_2O(g)$) = -241.8 kJ mol^{-1}

Note: $\Delta_f H^o$ ($O_2(g)$) = 0 kJ mol^{-1} – **any element in its standard state will have $\Delta_f H^o$ value = 0 kJ mol^{-1}**

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Enthalpies of formation - solution

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

Δ_rH^o $= \sum(\Delta_fH^o \text{ (products)}) - \sum(\Delta_fH^o \text{ (reactants)})$
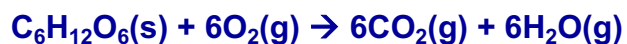
$= ((6 \times \Delta_fH^o \text{ (CO}_2\text{(g))} + (6 \times \Delta_fH^o \text{ (H}_2\text{O(g))}$
$ - (\Delta_fH^o \text{ (C}_6\text{H}_{12}\text{O}_6\text{(s))} + (6 \times \Delta_fH^o \text{ (O}_2\text{(g))}$

$= ((6 \times -393.5) + (6 \times -241.8)) - (-1273 + (6 \times 0))$

$= -2538.8 \text{ kJ}$

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✱ Homework ✱

Chemistry – the central science 15th Ed

Brown *et al.*

Problems 5.30, 5.33b, 5.34, 5.36

Answers on Blackboard

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