Lecture 15 : Energy at molecular / biochemical level.

- **Gibbs** cont'd.
  - ↳ " max available chemical work* " } 1st & 2nd laws

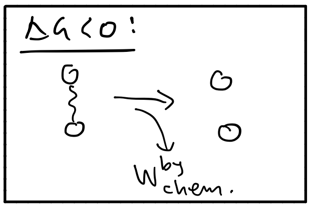
(* actually $-\Delta G$ is the max chemical work)

eg $\Delta G = -30\,kJ$

$\Rightarrow \underbrace{W^{by}_{chem} \leq +30\,kJ}$

ie available work from reaction

↳ use $-\Delta G$ to do work:



↳ coupling reactions together.

↳ vs. rates.

- **ATP**: Energy currency of the cell
  - ↳ storing & transferring energy.
    - ↳ bank free energy in ATP
    - ↳ pay with free energy released from ATP.

Example questions

2017 Exam.

39) The phosphorylation of glucose is the initial step in the catabolism of glucose in the cell.

Glucose + P $\rightarrow$ glucose-6-phosphate + H_2O
$\Delta G = 13.8$ kJ/mol

a. Explain why this reaction does not take place spontaneously. **(1 mark)**

Answer:

b. In the cell, the reaction is coupled to the hydrolysis of ATP. Explain how coupling the reaction to ATP hydrolysis enables the phosphorylation of glucose to take place in the cell. **(1 mark)**

Answer:

2018 SS

34) The phosphorylation of glucose is the initial step in the catabolism of glucose in the cell.

Glucose + P $\rightarrow$ glucose-6-phosphate + H_2O
$\Delta G = 13.8$ kJ/mol

a. In the cell, the above reaction is coupled to the hydrolysis of ATP. Explain how coupling the reaction to ATP hydrolysis enables the phosphorylation of glucose to take place in the cell.

(2 marks)

Answer:

b. Write down the coupled reaction and calculate the free energy change for the coupled reaction under standard conditions. The free energy of hydrolysis of ATP is -29 kJ/mol under standard conditions.

(2 marks)

Answer:

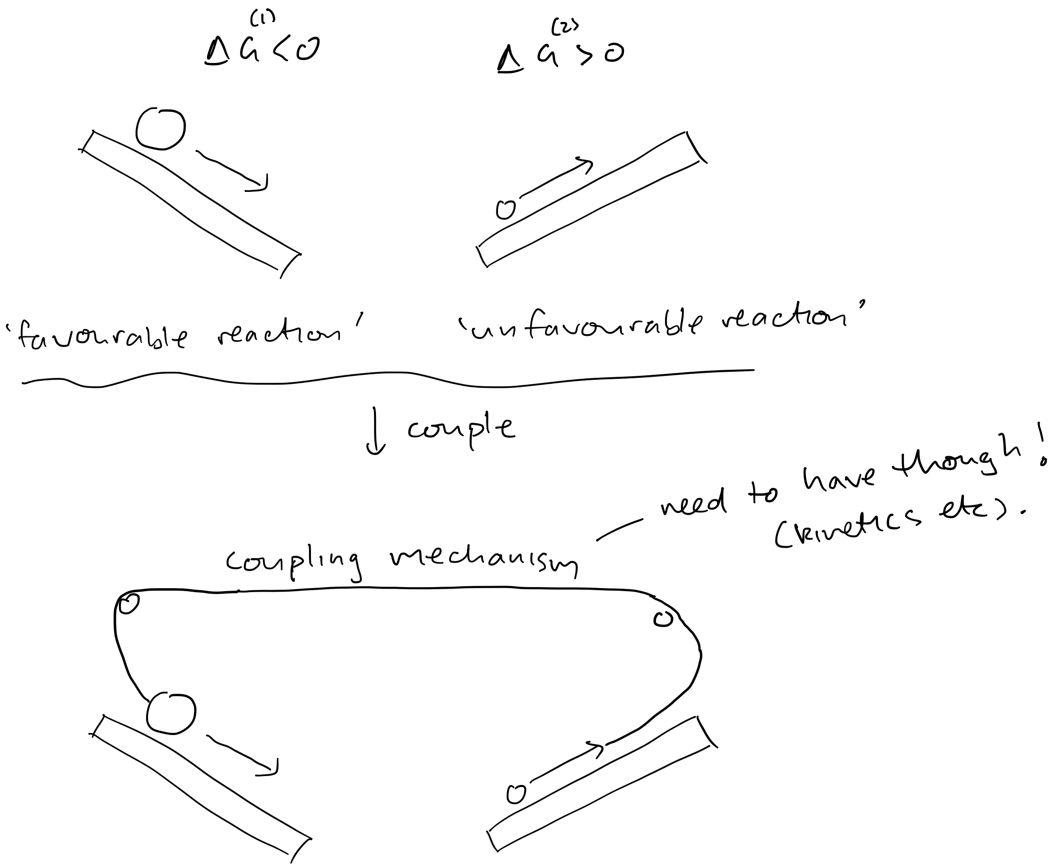
35) The free energy available from glucose is $\Delta G = -2862$ kJ/mol under standard conditions. In respiration, 38 ATP molecules are synthesised for each glucose molecule. Under standard conditions, each ATP can contribute $\Delta G = -29$ kJ/mol to drive reactions in the cell. What is the efficiency of the cell?

(2 mark)

Conversely, a chemical reaction is called **endergonic**, i.e. requires energy input, if it has $\Delta G > 0$. These are **not spontaneous**, and must be 'driven' by, or coupled to, other favourable processes. Note that ΔG refers to the **overall** change in free energy, not to the intermediate steps.

These ideas are illustrated below.

Coupled processes



overall is favourable. $\Delta G^{overall} = \Delta G^{(1)} + \Delta G^{(2)} < 0$

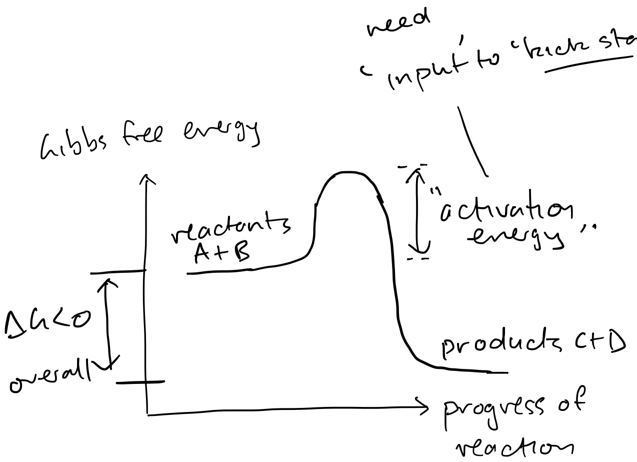
(thermodynamically)

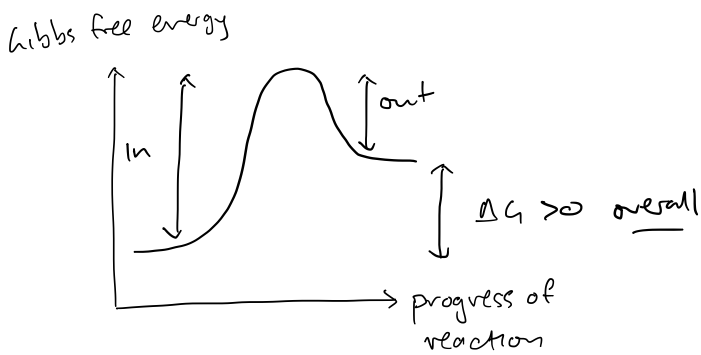
↳ 'possible', but thermo. doesn't say how or how fast

↳ need chemical kinetics (constit. eqns etc.

Exergonic and endergonic reactions

$$\boxed{A + B \rightarrow C + D}$$





Exergonic
(favourable
overall)

$\Delta G < 0$

Endergonic
(unfavourable
overall)

$\Delta G > 0$

Example Problems 4: Gibbs free energy

The phosphorylation of glucose is the initial step in the catabolism of glucose in the cell. It occurs according to

$$\text{Glucose} + \text{P} \rightarrow \text{glucose-6-phosphate} + H_2O$$
$$\Delta G = 13.8 \text{ kJ/mol.}$$

1. Explain why this reaction does not take place spontaneously.
2. In the cell, the above reaction is coupled to the hydrolysis of ATP. The free energy of hydrolysis of ATP is -29 kJ/mol under standard conditions. Explain how coupling this reaction to ATP hydrolysis enables the phosphorylation of glucose to take place in the cell.
3. What is the free energy change of the coupled reaction?

Answers

1. $\Delta G > 0$ ($\Delta G < 0$ for spontaneous)

2. $\Delta G^{overall} = \Delta G^{(1)} + \Delta G^{(2)}$

$= 13.8 + (-29)$ kJ/mol

$= -15.2$ kJ/mol < 0

$\Rightarrow$ overall favourable (in principle).

3. See above! $\Delta G^{coupled} = -15.2$ kJ/mol

3.5 ATP: the energy currency of the cell

The big picture of this section is:

$$\text{Food/Light} \xrightarrow{\text{`bank'/store energy}} \text{ATP} \xrightarrow{\text{`spend'/use energy}} \text{Useful Processes.}$$

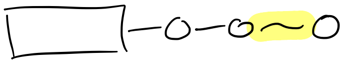
What is this **ATP**? Adenosine triphosphate, or ATP, is like a **molecular battery**. It is the most abundant *energy carrier molecule* in cells and is made of a nitrogen base (adenine), a ribose sugar, and three phosphate groups. The word adenosine means adenine plus a ribose sugar.

Importantly, **the bond between the second and third phosphate groups is a high-energy bond**. Forming this bond 'stores' energy - charges the battery - while breaking this bond 'releases' energy - discharges or uses the battery. See below.

ATP

Tri (3)

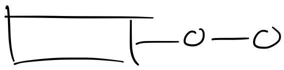
ATP



break bond ⟹ release energy

Di (2)

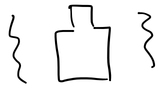
ADP



+

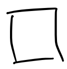
P_i ~O

High energy



charged battery

Low energy



used battery

+

O → charge/current

(attaches and 'charges' something else – like 'current' flowing)

A : adenosine

TP : triphosphate (3 phosphate)

DP : diphosphate (2 phosphate)

ie, a "Molecular battery":

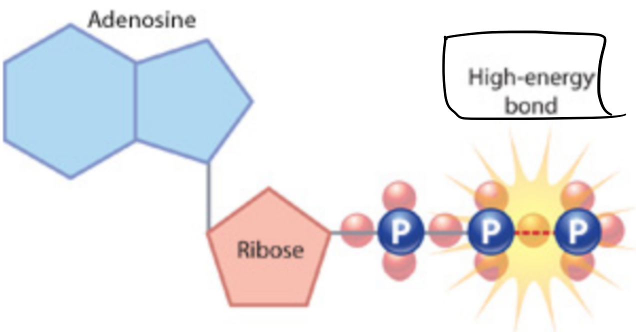


Figure 23: ATP molecule emphasising the high energy bond. (From `https://www.nature.com/scitable/topicpage/cell-energy-and-cell-functions-14024533`).

3.5.1 Hydrolysis of ATP

water splitting

The key reaction for 'breaking' the high energy bond, and hence releasing the stored energy, is called **hydrolysis**. Note that hydro ∼ water, lysis ∼ splitting: it is the splitting of ATP using water!

This reaction is given by

KNOW THIS. →

$$\boxed{ATP + H_2O \rightarrow ADP + P}$$

(technically + some other hydrogen stuff)

where 'TP' means *tri*phosphate (three phosphate) and 'DP' means *di*phosphate (two phosphate).

provides available work.

The **hydrolysis of ATP is spontaneous** with $\Delta G = -29kJ/mol$ under standard conditions. Hence it can be used to drive other reactions.

"passing along current"

Adding a phosphate group is called **phosphorylation** and is a key method of 'transferring' energy between molecules. When a phosphate group is added to a molecule, the molecule becomes 'energised', i.e. moves to a higher energy state. This can then be used to drive a range of **cellular work processes**, e.g. mechanical, chemical and/or transport work processes.

ATP coupling

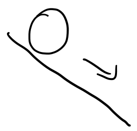
ATP Hydrolysis ($\Delta G < 0$):

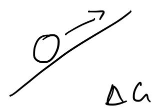
$\boxed{ATP + H_2O \rightarrow ADP + P}$

Something else! ($\Delta G > 0$)

eg 'phosphorylation of glucose':

$\boxed{\text{glucose} + P \rightarrow \underbrace{\text{glucose-6-phosphate}}_{\text{extra } P} + H_2O}$

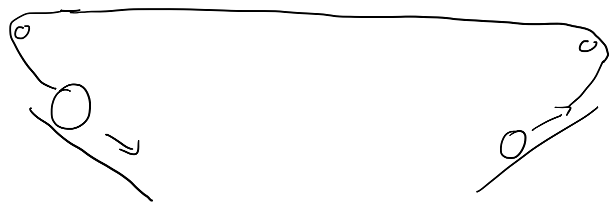




$\Delta G = +13.8 kJ/mol$.

$\Delta G = -29 kJ/mol$

couple : transfer of P (directly or to helper molecule.)



$$\underbrace{ATP + \cancel{H_2O} + \text{glucose} + \cancel{P}}_{\text{all reactants}} \longrightarrow \underbrace{ADP + \cancel{P} + \text{glucose-6-phosphate} + \cancel{H_2O}}_{\text{all products}}$$

Simplify : $\boxed{ATP + \text{glucose} \rightarrow ADP + \text{glucose-6-phosphate}}$

$$\Delta G = \Delta G^{(1)} + \Delta G^{(2)} = -29 + 13.8 < 0$$

(spontaneous)

3.5.2 The ATP cycle

Cells are *constantly using ATP*. For example, a working muscle cell uses around 10×10^6 ATP molecules per second!

The majority of ATP is *not made from scratch*. Instead, it is generated from ADP by **recycling** - i.e. re-phosphorylating or 're-charging' - it.

ATP cycle

Making new ATP (from ADP etc) requires energy input, of course. This comes from the process Food → ATP, i.e. **cellular respiration** (next section).

Example Problems 5: ATP coupling

1. Write down the reaction for ATP hydrolysis coupled to the phosphorylation of glucose. ✓

2. The total quantity of ATP in the human body is about 0.1 mole. The average human recycles 100-150 moles of ATP daily. What does this tell us about the number of times each ATP molecule is recycled during a single day?

3. In the sugar cane plant, the overall reaction in which two monosaccharides (one) are combined to form the disaccharide sucrose. This reaction is given by:
two

$$\text{glucose} + \text{fructose} \rightarrow \text{sucrose} + H_2O.$$

This is an endergonic reaction with $\Delta G = +23\text{kJ/mol}$.

requires energy input.

Calculate the change in free energy if the reaction is coupled with the hydrolysis of 2 ATP molecules.

Answers

2. 1 cycle = 0.1 mol used (all)

$\Rightarrow$

$\sim$ 100 to 150 ~~moles~~/day $\times$ $\frac{1 \text{ cycle}}{0.1 \text{ ~~mol~~}}$

$\sim$ 1000 to 1500 cycles/day.

3. $g + f \rightarrow s + H_2O \quad \} \; \Delta G = +23 \text{ kJ/mol}$

$2ATP + 2H_2O \rightarrow 2ADP + 2P \quad \} \; \Delta G = 2 \times -29 \text{ kJ/mol}$

Overall reaction:

$\underbrace{g + f + 2ATP} + \cancel{2}H_2O \rightarrow \underbrace{s + 2ADP + 2P} + \cancel{H_2O}$

(H_2O terms not so important to include explicitly)

$\Delta G = \Delta G^{(1)} + \Delta G^{(2)}$

$= 23 \text{ kJ/mol} + 2 \times (-29 \text{ kJ/mol})$

$= -35 \text{ kJ/mol}$

3.6 Chemical kinetics

While thermodynamics concerns what processes are *possible*, it does not tell us exactly *how* or *how fast* processes occur. Typically we focus on *path independent* properties.

As introduced in the first lecture, we need **constitutive models of specific mechanisms and rates** for processes.

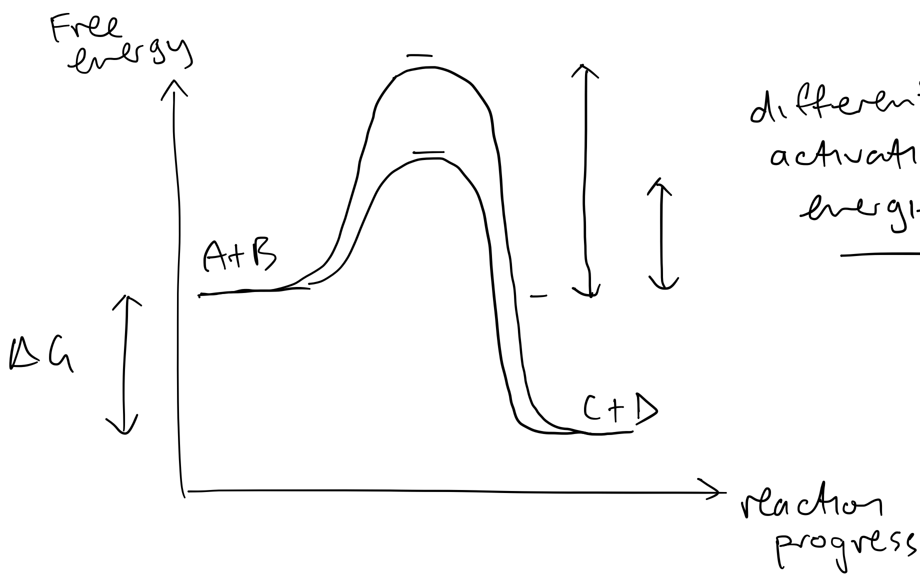
The subject of **chemical kinetics** concerns the *how* and *how fast* processes occur. It gives us a *specific pathway* or *mechanism* for a given process. It also connects with the concept of intermediate energy barriers, i.e. **activation energies**, that can be present even though the overall reaction is favourable.

These ideas are illustrated below.

Free energy, reaction progress and activation energy

same as before : - ΔG overall same
- different path, activation energy, rate

$A + B \rightarrow C + D$



different activation energies } different 'barriers' to starting/continuing.

End L15.