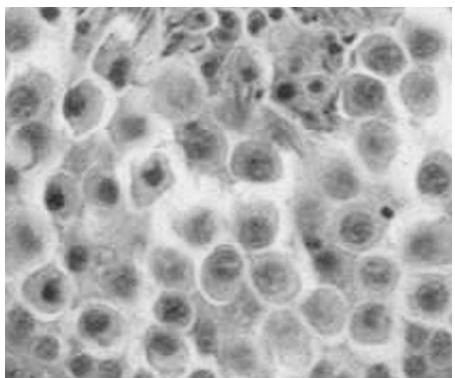




# ENGINEERING



**ENGINEERING SCIENCE/CHEMICAL & MATERIALS**  
**ENGGEN 140**

Part 2 Notes Semester 1 2018

# ENGGEN 140

## Biology and Chemistry for Engineers

Part 2

# Engineering Biology and Chemistry

Last updated—April 5, 2018

## Contents

<b>1</b>	<b>Introduction to Energy</b>	<b>1</b>
1.1	Conservation and constitutive equations . . . . .	1
1.2	Dimensions and units . . . . .	5
1.2.1	Notation . . . . .	6
1.2.2	SI units . . . . .	7
1.2.3	Conversion of units . . . . .	9
1.2.4	Base and derived SI quantities and units . . . . .	11
1.3	Some key quantities involved in the physics of energy . . . . .	14
1.4	Forms of energy and energy conversions . . . . .	17
1.4.1	What is energy? . . . . .	17
1.4.2	Kinetic or potential energy? . . . . .	20
1.4.3	Work and energy . . . . .	20
1.4.4	Forms of energy . . . . .	21
1.5	Planetary energy balance . . . . .	27
1.5.1	The radiant energy of the sun . . . . .	28
1.5.2	How much reaches earth? . . . . .	29
1.5.3	How much of the energy is absorbed by the Earth? . . . . .	31
1.5.4	What happens to the energy that is absorbed by the Earth? . .	32

1.6	Human energy consumption and supply patterns: global and NZ . . . . .	34
1.6.1	Global consumption patterns . . . . .	34
1.6.2	Energy consumption and supply sources . . . . .	40
1.6.3	Energy consumption and supply sources: NZ in particular . . . . .	43
1.7	Case study: Life at low Reynolds number . . . . .	49
<b>2</b>	<b>Thermodynamics</b>	<b>53</b>
2.1	Overview and basic concepts of thermodynamics . . . . .	53
2.1.1	The scope of thermodynamics . . . . .	53
2.1.2	The laws of thermodynamics: a preview . . . . .	56
2.1.3	Thermodynamic systems . . . . .	56
2.1.4	Properties . . . . .	58
2.1.5	Interactions . . . . .	59
2.2	Equilibrium and the zeroth law . . . . .	61
2.2.1	Equilibrium, steady state and quasi-steady-state . . . . .	62
2.2.2	State? . . . . .	63
2.3	Processes, paths and cycles . . . . .	64
2.4	Internal energy, work and heat . . . . .	66
2.4.1	Internal energy . . . . .	66
2.4.2	The first law of thermodynamics . . . . .	68
2.5	Heat transfer . . . . .	71
2.5.1	Heat capacity . . . . .	71
2.5.2	Latent heat and phase transitions . . . . .	74

2.6 Work: pistons and heat engines . . . . .	75
2.6.1 Pistons . . . . .	76
2.6.2 Processes and PV diagrams . . . . .	79
2.6.3 Heat engines, efficiency limits and the second law . . . . .	83
2.7 Spontaneous processes: entropy and energy . . . . .	85
2.7.1 The second law of thermodynamics . . . . .	85
2.7.2 Spontaneous processes - isolated systems . . . . .	87
2.7.3 Energy functions for spontaneous processes in non-isolated systems . . . . .	88
2.8 Calorimetry and the enthalpy of combustion . . . . .	95
2.9 Case study: Combustion engines and Otto cycles . . . . .	100
<b>3 Biological Energetics</b>	<b>106</b>
3.1 Sources and transformations of energy in biological systems . . . . .	106
3.1.1 Thermodynamics in biology . . . . .	106
3.1.2 Composition . . . . .	107
3.1.3 The carbon cycle and photosynthesis . . . . .	107
3.2 Cells, membranes and organelles . . . . .	109
3.2.1 The structure of cells . . . . .	110
3.2.2 The cell membrane . . . . .	112
3.2.3 The nucleus . . . . .	113
3.2.4 Mitochondria . . . . .	114
3.3 Animal energy consumption and measurement . . . . .	116
3.3.1 Measuring energy . . . . .	116

3.4	Gibbs free energy applied to biological systems . . . . .	120
3.4.1	Gibbs free energy and coupling . . . . .	121
3.5	ATP: the energy currency of the cell . . . . .	125
3.5.1	Hydrolysis of ATP . . . . .	127
3.5.2	The ATP cycle . . . . .	129
3.6	Chemical kinetics . . . . .	130
3.6.1	Rate of reaction . . . . .	132
3.6.2	Catalysts and enzymes . . . . .	134
3.7	Cellular respiration . . . . .	137
3.7.1	Glycolysis . . . . .	139
3.7.2	Krebs Cycle . . . . .	141
3.7.3	Electron Transport . . . . .	142
3.7.4	Cellular efficiency . . . . .	143
3.7.5	Just glucose? . . . . .	144
3.8	Fermentation . . . . .	144

# 1 Introduction to Energy

## Learning Objectives

- Understand the concepts of conservation laws and constitutive equations and how these can help organise scientific and engineering knowledge.
- Understand the difference between base SI units and derived SI units. Derive correct SI units for force, energy, power and pressure and carry out basic calculations involving these quantities.
- Be aware of some of the various forms that energy comes in and how these can be interconverted. Carry out basic energy conversion calculations including accounting for efficiency limits.
- Understand the planetary energy balance and carry out basic calculations involved in this.
- Be aware of global and NZ energy consumption patterns, read basic graphs and carry out simple energy estimates and conversions.
- Apply your knowledge of energy balances and constitutive equations to simple case studies.

## 1.1 Conservation and constitutive equations

One of the most important and generally applicable concepts in science and engineering is the idea of a **conservation law** or **balance equation**. The idea is roughly to ask yourself: *when things change, what stays the same?* Fundamental examples of quantities that are *conserved* during physical processes include: mass, energy and momentum. We focus primarily on the first two in this course, but the third is the basis of much of your courses in engineering mechanics. In even more fundamental physics, these ideas can be seen as different sides of the same coin: e.g. conservation of mass-energy. In ‘messier’ scenarios it can still be helpful to look for other approximate conserved quantities or approximate *invariants*.

In a given situation these define what processes are *possible*: violating conservation of mass, energy and/or momentum is a serious offence!

---

—Newton's second law: momentum and energy

---

An issue arises, however: in considering the bending of a beam made of wood vs one made of steel, both satisfy the same high-level conservation principles and yet they exhibit different behaviour (e.g. different yield strengths when subject to mechanical testing). What distinguishes these if not conservation principles? While at the level of fundamental physics these are perhaps governed by the same laws of particle physics (or string theory or whatever...), at the *macroscopic* level of observation and experiment we need to introduce additional, *approximate* ‘laws’ or equations which describe *particular details* of the materials, substances, forces or interactions that we are dealing with.

These *force laws*, *transport laws* and/or *material property* equations ‘fill in the details’ of our particular application, telling us about the substances we’re dealing with. Here we call these **constitutive equations**. These tell us about how *particular* substances interact and what processes *actually* occur.

---

—Conservation and constitutive equations: some examples

---

---

An interesting case is *entropy*: as you probably already know, entropy *stays the same or increases* in an isolated system. It is *non-decreasing*. This is not quite a conservation equation in the usual sense, but it is also more general than just an ordinary constitutive equation. The non-decrease of entropy can be thought of as a **one-sided conservation law or directional principle**. This is essentially a statistical principle and tells us about what processes *probably* or *almost certainly* occur.

---

—A broken glass: energy and entropy

---

Upshot: it is *possible* for a broken glass to spontaneously reform (this process satisfies conservation of energy), but it *overwhelmingly unlikely* to occur (is very improbable). In more advanced courses, directional principles such as the second law of thermodynamics are often used to place constraints on constitutive equations: e.g. to ensure that diffusion occurs *down* a concentration gradient, one deduces that the diffusion coefficient in Fick's law must be positive<sup>1</sup>. Macroscopic diffusion is a *bulk* or *averaged* phenomenon, and can be thought of as driven by the *net entropic force* generated by imbalanced macroscopic concentrations. We will return to entropy and thermodynamics later in this course.

### Example Problems 1: Conservation and constitutive equations

1. (2018 SS Exam Q) Is Hooke's law an example of a conservation equation or a constitutive equation? If the latter, to what sort of material does it apply?
2. Use appropriate conservation and constitutive equations to derive a *closed* model of the motion of a mass on a spring subject to the force of gravity.
3. What assumption have you made about entropy in the above? What effect could you include that would change this assumption? What effect would you expect this to have on the long-term dynamics of the system.

---

### —Answers

---

<sup>1</sup>Entropy can also be connected to ideas of *stability* and/or *typicality*: entropy increase ‘picks out’ the long-term, stable/typical - and hence *observable* - phenomena.

## 1.2 Dimensions and units

You have already looked at **dimensions** and **units** in the first half of this course, but these are important enough to revisit here. We will also consider some key players in energy calculations and their associated units: *force*, *power*, *pressure* and, of course, *energy*!

The idea of a system of units for measuring different types of quantity is surprisingly

subtle. We need to

- Decide what ‘kinds of thing’ there are.
- For each ‘kind of thing’, choose a ‘standard’ reference object of that type.

The ‘kind of thing’ is called the **dimension** or **type** of a quantity, while a ‘standard reference’ for a thing of a given type is called a **unit**.

---

### —Measuring length—

---

#### 1.2.1 Notation

We will use the notation:

$[X]$  means ‘Units of X’ or ‘Dimensions of X’

While we could introduce a different symbol for each meaning (units and dimensions, respectively), we prefer to let the context make it clear which is meant.

---

—Units and dimensions of X

---

### 1.2.2 SI units

The International System of Units - Système international d'unités, abbreviated as SI - is the modern form of the metric system, built upon *seven base quantities and units*. The system also establishes *prefixes* to be used when specifying multiples and fractions of units, e.g. *milli*, *centi* etc. See below.

The metric system was originally conceived and introduced in 1799 as a system of measurement *based on natural phenomena*. Technical limitations at the time required the use of human artefacts to describe the metre and kilogram. However, the metre was redefined in 1960 in terms of wavelength of light and the kilogram looks set to be officially changed on 16 November 2018, to be defined relative to the equivalent energy of a photon via the Planck constant.

Table 1 summarises the base SI quantities, units of measurement and their proposed definitions. The difference between base and derived SI units is discussed further below.

Table 2 summarises some common SI prefixes.

Quantity	Dimension	SI Unit	SI Unit Symbol	SI Unit Definition
Time	T	Second	s	Defined by taking the fixed numerical value of the caesium frequency $\Delta\nu_{cs}$ , the unperturbed ground-state hyperfine transition frequency of the caesium 133 atom, to be 9192631770 when expressed in the unit Hz, which is equal to $s^{-1}$ .
Length	L	Metre	m	Defined by taking the fixed numerical value of the speed of light in vacuum $c$ to be 299792458 when expressed in the unit $m \cdot s^{-1}$ , where the second is defined in terms of the caesium frequency $\Delta\nu_{cs}$ .
Mass	M	Kilogram	kg	Defined by taking the fixed numerical value of the Planck constant $h$ to be $6.62607015 \times 10^{-34}$ when expressed in the unit J·s, which is equal to $kg \cdot m^2 \cdot s^{-1}$ , where the metre and the second are defined in terms of $c$ and $\Delta\nu_{cs}$ .
Current	I	Ampere	A	Defined by taking the fixed numerical value of the elementary charge $e$ to be $1.602176634 \times 10^{-19}$ when expressed in the unit C, which is equal to A·s, where the second is defined in terms of $\Delta\nu_{cs}$ .
Temperature	$\Theta$	Kelvin	K	Defined by taking the fixed numerical value of the Boltzmann constant $k$ to be $1.380649 \times 10^{-23}$ when expressed in the unit $J \cdot K^{-1}$ , which is equal to $kg \cdot m^2 \cdot s^{-2} \cdot K^{-1}$ , where the kilogram, metre and second are defined in terms of $h$ , $c$ and $\Delta\nu_{cs}$ .
Amount	N	Mole	mol	One mole contains exactly $6.02214076 \times 10^{23}$ elementary entities. This number is the fixed numerical value of the Avogadro constant, $N_A$ , when expressed in the unit $mol^{-1}$ and is called the Avogadro number. The amount of substance, symbol $n$ , of a system is a measure of the number of specified elementary entities.
Luminous Intensity	J	Candela	cd	Defined by taking the fixed numerical value of the luminous efficacy of monochromatic radiation of frequency $540 \times 10^{12}$ Hz, $K_{cd}$ , to be 683 when expressed in the unit $lm \cdot W^{-1}$ , which is equal to $cd \cdot sr \cdot W^{-1}$ , or $cd \cdot sr \cdot kg^{-1} \cdot m^{-2} \cdot s^3$ , where the kilogram, metre and second are defined in terms of $h$ , $c$ and $\Delta\nu_{cs}$ . The symbol sr stands for the dimensionless unit steradian or square radian, which is defined geometrically.

Table 1: Base SI Units and new proposed definitions. Based on [https://en.wikipedia.org/wiki/Proposed\\_redefinition\\_of\\_SI\\_base\\_units](https://en.wikipedia.org/wiki/Proposed_redefinition_of_SI_base_units).

	Prefix name		deca	hecto	kilo	mega	giga	tera	peta	exa
Multiples	Prefix symbol		da	h	k	M	G	T	P	E
	Factor	$10^0$	$10^1$	$10^2$	$10^3$	$10^6$	$10^9$	$10^{12}$	$10^{15}$	$10^{18}$
<hr/>										
Fractions	Prefix name		deci	centi	milli	micro	nano	pico	femto	atto
	Prefix symbol		d	c	m	$\mu$	n	p	f	a
	Factor	$10^0$	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-6}$	$10^{-9}$	$10^{-12}$	$10^{-15}$	$10^{-18}$

Table 2: SI prefixes. (From notes by Thor Besier, based on [https://en.wikipedia.org/wiki/International\\_System\\_of\\_Units](https://en.wikipedia.org/wiki/International_System_of_Units)).

### 1.2.3 Conversion of units

While the dimensions of a quantity cannot be changed, *the units that we measure a quantity in are arbitrary and we can thus change between different units.*

A simple idea for changing units is to ‘multiply by one’, where the numerator and denominator represent the ‘same thing’ in the different units. This process is perhaps best illustrated via examples, as follows.

—Converting between different units

---

#### 1.2.4 Base and derived SI quantities and units

As mentioned above, the SI system is based on the idea that we can usefully classify and measure all scientific quantities according to **seven basic types of quantity**<sup>2</sup>. For each of these types we define a **base SI unit** for measuring that quantity, and other **derived** units can be derived based on these.

Table 3 summarises some common derived SI units.

---

<sup>2</sup>other systems are possible, e.g. in fundamental physics Lorentz–Heaviside units, Gaussian units and/or Planck units are also commonly used.

Name	Symbol	Quantity	Expressed in terms of other SI units	Expressed in terms of SI base units
hertz	Hz	frequency	1/s	s <sup>-1</sup>
radian	rad	angle	m/m	dimensionless
newton	N	force, weight		kg·m·s <sup>-2</sup>
pascal	Pa	pressure, stress	N/m <sup>2</sup>	kg·m <sup>-1</sup> ·s <sup>-2</sup>
joule	J	energy, work, heat	N·m	kg·m <sup>2</sup> ·s <sup>-2</sup>
watt	W	power, radiant flux	J/s	kg·m <sup>2</sup> ·s <sup>-3</sup>
coulomb	C	electric charge or quantity of electricity	F·V	s·A
volt	V	Voltage, electrical potential difference, electromotive force	W/A J/C	kg·m <sup>2</sup> ·s <sup>-3</sup> ·A <sup>-1</sup>
farad	F	electrical capacitance	C/V s <sup>-1</sup> ·Ω	kg <sup>-1</sup> ·m <sup>-2</sup> ·s <sup>4</sup> ·A <sup>2</sup>
ohm	Ω	electrical resistance, impedance, reactance	V/A	kg·m <sup>2</sup> ·s <sup>-3</sup> ·A <sup>-2</sup>
degree Celcius	°C	Temperature relative to 273.15 K		K
sievert	Sv	equivalent dose of ionizing radiation	J/kg	m <sup>2</sup> ·s <sup>-2</sup>

Table 3: Common derived SI units. (From notes by Thor Besier, based on [https://en.wikipedia.org/wiki/International\\_System\\_of\\_Units](https://en.wikipedia.org/wiki/International_System_of_Units)).

---

### —Examples of derived SI units

---

**Example Problems 2: Dimensions and Units**

1. What is the unit of energy expressed in base SI units?
2. Show that kinetic energy and gravitational potential energy have dimensionally consistent base SI units.
3. What are the base SI units of force?
4. (2017 Exam Q) Using base SI units, show that the units for work are dimensionally consistent with the units of gravitational potential energy.

**Answers**

---

### 1.3 Some key quantities involved in the physics of energy

Let's take a look at some key quantities that you might encounter in the physics of energy: *force, power, pressure* and...*energy*.

We can derive the SI dimensions/units of these by considering some simple examples. In addition, some numerical examples can help give us a feel for the typical 'human' orders of magnitude of these quantities when expressed in SI units.

---

—Units of force from Newton's second law

---

---

—Typical gravitational force on a person

---

—Units of energy from translational kinetic energy

---

—Typical kinetic energy of a person walking

---

—Units of power from rate of change of energy—

---

—Typical power of a person climbing stairs—

---

—Units of pressure from force per unit area

---

—Typical pressure on the soles of a person's feet

---

## 1.4 Forms of energy and energy conversions

### 1.4.1 What is energy?

Let's ask a seemingly basic question - what is energy? To motivate our answer consider the following example.

---

—A bishop on a chess board

---

---

How is this related to our question of ‘what is energy?’ Let’s see how this example ‘pops up’ in the following answer to our question, given by the physicist Richard Feynman (1918-1988) in his famous *The Feynman Lectures on Physics*:

From Section 4-1 What is Energy? in *The Feynman Lectures on Physics* (1964, revised and expanded 2005):

*There is a fact, or if you wish, a law, governing all natural phenomena that are known to date. There is no known exception to this law - it is exact so far as we know. The law is called the conservation of energy. It states that there is a certain quantity, which we call energy, that does not change in the manifold changes which nature undergoes. That is a most abstract idea, because it is a mathematical principle; it says that there is a numerical quantity which does not change when something happens. It is not a description of a mechanism, or anything concrete; it is just a strange fact that we can calculate some number and when we finish watching nature go through her tricks and calculate the number again, it is the same...Something like the bishop on a red square, and after a number of moves - details unknown - it is still on some red square. It is a law of this nature...*

*...when we are calculating the energy, sometimes some of it leaves the system and goes away, or sometimes some comes in. In order to verify the conservation of energy, we must be careful that we have not put any in or taken any out....energy has a large number of different forms, and there is a formula for each one. These are: gravitational energy, kinetic energy, heat energy, elastic energy, electrical energy, chemical energy, radiant energy, nuclear energy, mass energy. If we total up the formulas for each of these contributions, it will not change except for the energy going in and out...*

*...It is important to realize that in physics today, we have no knowledge of what energy is. We do not have a picture that energy comes in little blobs of a definite amount. It is not that way. However, there are formulas for calculating some numerical quantity, and when we add it all together it gives "28" - always the same number. It is an abstract thing in that it does not tell us the mechanism of the reasons for the various formulas.*

OK! So maybe our question is not so straightforward, though clearly it has something to do with the advice we saw earlier - *when things change, ask yourself: what stays the same?*

Here is Feynman's summary, captured in a picture taken during his original lectures (1961-1963):



Figure 1: Summary of Feynman's lectures on energy. From [http://www.feynmanlectures.caltech.edu/I\\_04.html](http://www.feynmanlectures.caltech.edu/I_04.html)

#### 1.4.2 Kinetic or potential energy?

Energy is sometimes classified into *kinetic* or *potential* energy categories. This isn't always so unambiguous: e.g. kinetic energy can be thought of as 'stored' in the form of translational or rotational motion energy.

#### 1.4.3 Work and energy

A perspective on energy that is particularly helpful for an engineer is: *energy represents a capacity to do work, stored in a particular form.*

Similarly, we can say *work represents a transfer or change of energy from one form to another.*

Most importantly, it is *differences* in energy that represent either the potential to do work or the result of doing work: *energy is only defined up to an arbitrary reference value.* We will look more carefully at work and the transfer/conversion of energy in the next section when we discuss thermodynamics, where we will also discuss heat and entropy in more detail.

#### 1.4.4 Forms of energy

With that out of the way, let's consider some basic 'forms' of (or 'ways of accounting for') energy, including how these are 'stored' and/or how they might be used to 'do work' or be converted to different forms.

---

—**Gravitational potential energy**—

---

—**Electrical potential energy**—

---

—Chemical potential energy

---

—Elastic potential energy

---

—Nuclear energy

---

---

—Radiant energy—

---

—Kinetic energy—

---

—Thermal energy

---

—Sound energy

---

**Example Problems 3: Forms of energy and work**

1. Consider a cylinder of mass  $m$ , radius  $R$  and moment of inertia  $I = \frac{1}{2}mR^2$  perched just at rest at the top of a flat incline, raised a distance  $h$  above the level ground. Suppose it receives a tiny nudge, just enough to cause it to begin to roll down the inclined plane. Calculate the linear speed of the cylinder when it reaches the level ground.
2. Why don't we need to consider nuclear energy in a typical mechanics problem such as the previous one?
3. Verify that the following all have units of energy:
  - (a) Kinetic energy
  - (b) Mechanical work (force times distance)
  - (c) Pressure work
  - (d) Thermal energy of an ideal gas
  - (e) Energy of a light quantum (photon)
  - (f) Rest mass energy
4. (2017 Exam Q) Auckland's Sky Tower is 328m high. Determine whether the energy content of a 'Whopper' burger (from you-know-where) would be sufficient to fuel a person weighing 72kg to climb the Sky Tower. The nutrition information shows that on average a Whopper contains 2649kJ. Assume 20% efficiency in converting nutritional energy to mechanical energy.
5. What happens to the other 80% of the energy content? Does it just 'disappear'?

---

—Answers

---



## 1.5 Planetary energy balance

Energy is crucial for life on Earth. Human society uses various forms of energy to - hopefully - improve quality of living. We will look at patterns of human energy consumption soon; first, we ask the more basic question: *where does the energy we use come from in the first place?*

The simple answer is: **the Sun!** It *radiates* energy generated from nuclear fusion reactions. Only a small part of this reaches us, however!

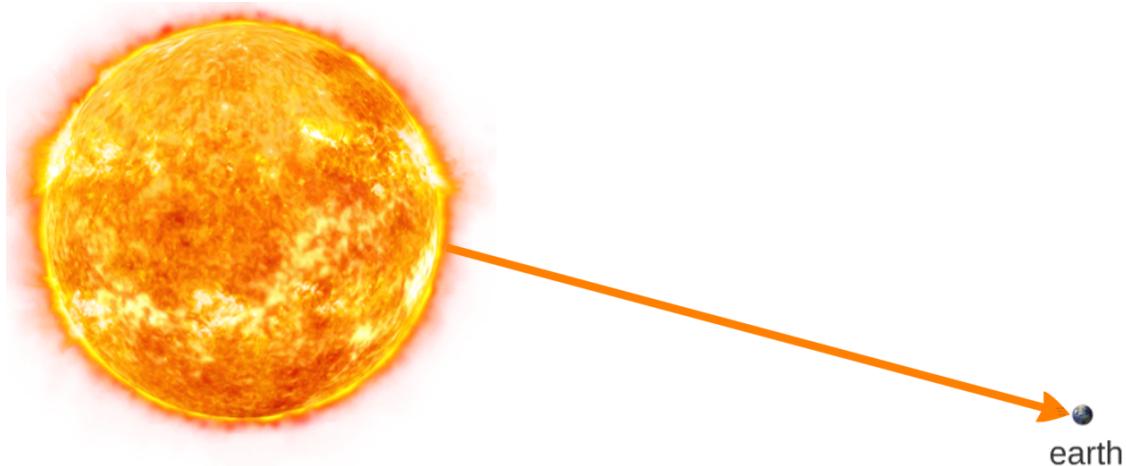


Figure 2: The Sun!

Let's do some calculations to look at this in more detail.

Consider the following questions:

1. What is the total radiant energy of the Sun?
2. How much reaches Earth?
3. How much of the energy is absorbed by the Earth?
4. What happens to the energy that is absorbed by the Earth?

We'll primarily focus on calculating the answers to the last three questions, taking the first for granted. We *may* look at a calculation of the answer to the first question in a tutorial lecture slot.

### 1.5.1 The radiant energy of the sun

Here we'll just state the facts.

### 1.5.2 How much reaches earth?

Consider Figure 3. Some key features to note: the Earth is very far from the Sun, and the Earth is much smaller than the Sun! These account for the fact that only a small amount of the total energy of the Sun actually reaches us.

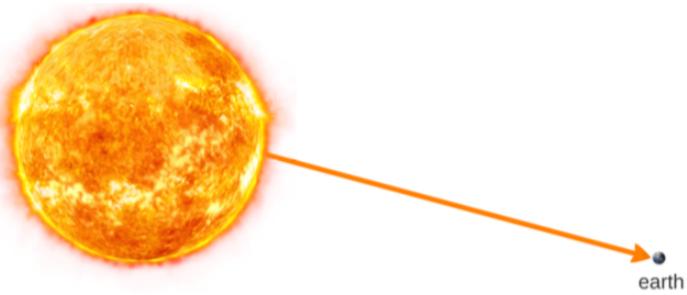


Figure 3: The Sun! Again...

### 1.5.3 How much of the energy is absorbed by the Earth?

Even given that only a small fraction of the total energy output of the Sun reaches the Earth, *we also need to account for what happens to the energy that reaches the outer atmosphere*. In particular, **not all of this energy is absorbed on earth**. This is illustrated in Figure 4.

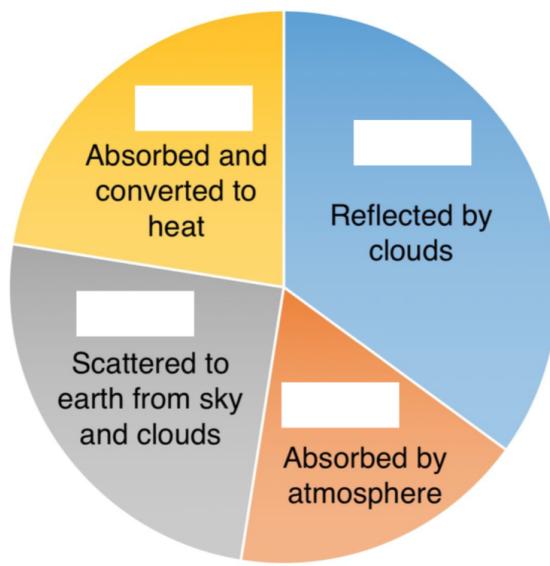


Figure 4: The relative distribution of the energy that reaches the Earth.

### 1.5.4 What happens to the energy that is absorbed by the Earth?

Continuing to follow the energy, we now consider what happens to that absorbed by the Earth. This is illustrated in Figure 5.

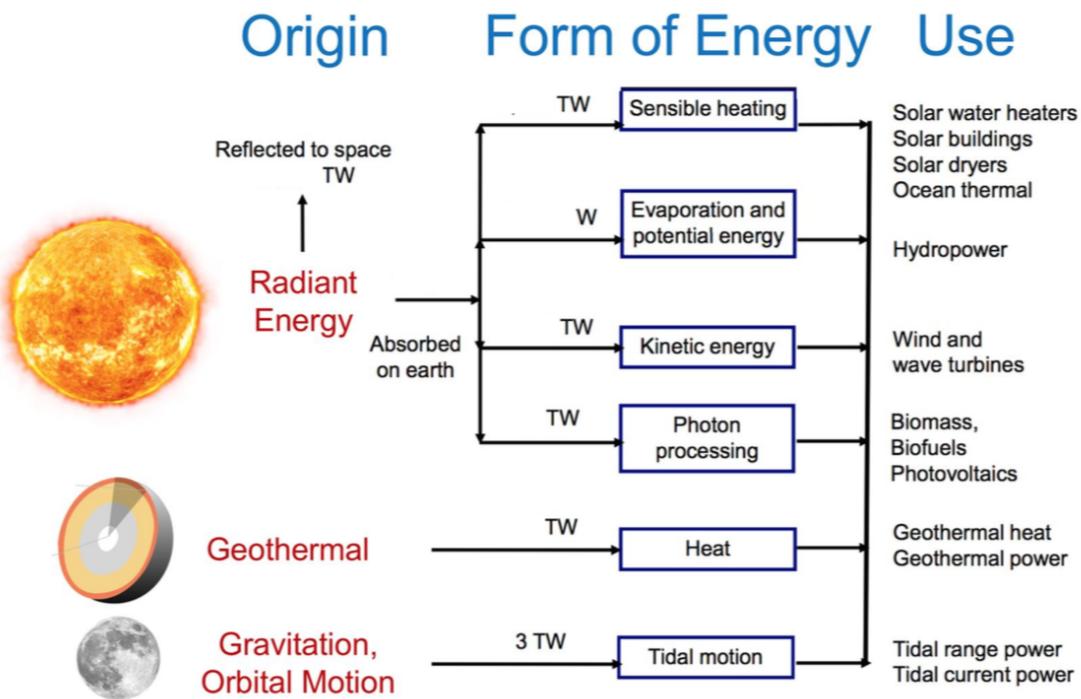


Figure 5: Planetary energy balance.

Note that radiant energy provides orders of magnitude more energy than geothermal or gravitational energy.

**Example Problems 4: Planetary energy balance**

1. By what factor is the radiant energy provided by the Sun greater than that provided by geothermal and gravitational (tidal) energy combined?
2. In the next section we will estimate the human worldwide energy use per year as about 17 TW. Hence comment on the potential to use tidal motion (gravitational energy) as a renewable energy source.
3. Why could geothermal energy ultimately be considered a form of nuclear energy?
4. Geothermal energy appears useful for use in heat pumps. What does this have to do with refrigerators?

---

—**Answers**—

---

## 1.6 Human energy consumption and supply patterns: global and NZ

As engineers we are particularly interested in patterns of *human energy consumption*, both worldwide and NZ. Here we consider some general facts and figures and do some basic calculations to help interpret the data.

### 1.6.1 Global consumption patterns

Consider the Figures 6-8, obtained from <https://yearbook.enerdata.net/total-energy/world-consumption-statistics.html>.

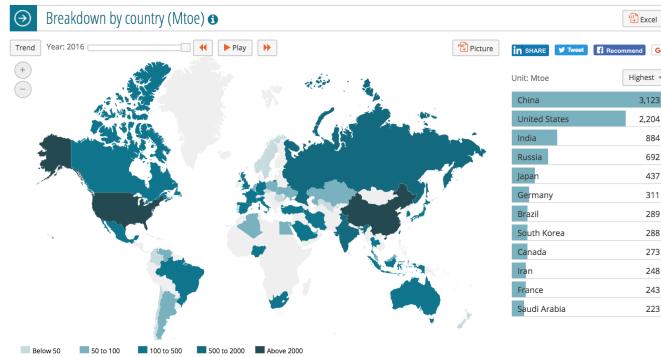


Figure 6: Global energy consumption (2016 data).

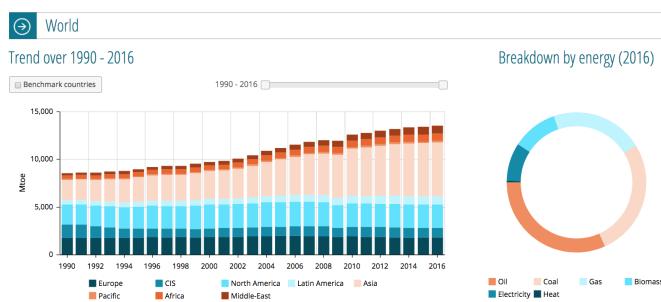


Figure 7: Global energy consumption trends 1990-2016.



Figure 8: Global energy consumption: key drivers.

Let's look at the who, what, where, why etc! To help us, we'll also include some data on population growth - see Figure 9.

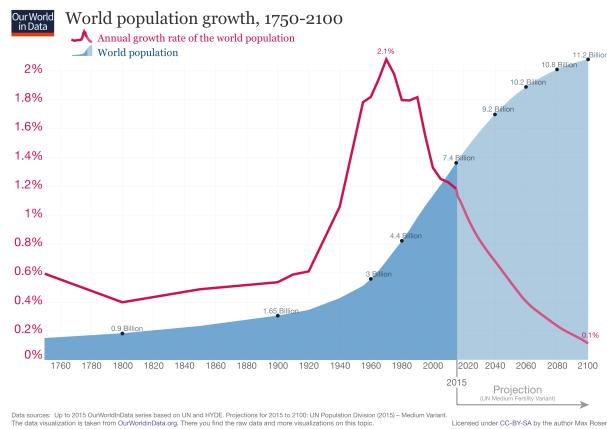


Figure 9: Worldwide population growth.

Consider the following questions:

#### Example Problems 5: Global energy

1. Who is using the most energy?
2. What trends do you notice in energy consumption?
3. Given the growth in our population over the last 16 years, why are we not seeing this growth in energy consumption?

—Answers

---

---

**Example Problems 6: More on global energy**

1. What does Mtoe stand for? Convert Mtoe to J.
2. Convert worldwide energy consumption in 2016 to TW (tera =  $10^{12}$ ). What type of quantity is this?
3. Convert China's energy consumption in 2016 to TW.

---

—**Answers**



### 1.6.2 Energy consumption and supply sources

Here we are interested in questions like: where does the energy we consume come from? What forms of energy do we consume the most of? How is our electricity produced? Note: electricity is not the same as total energy!

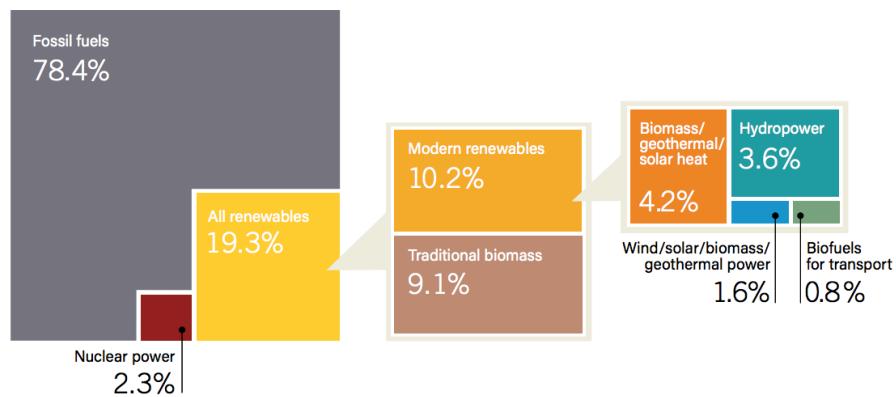
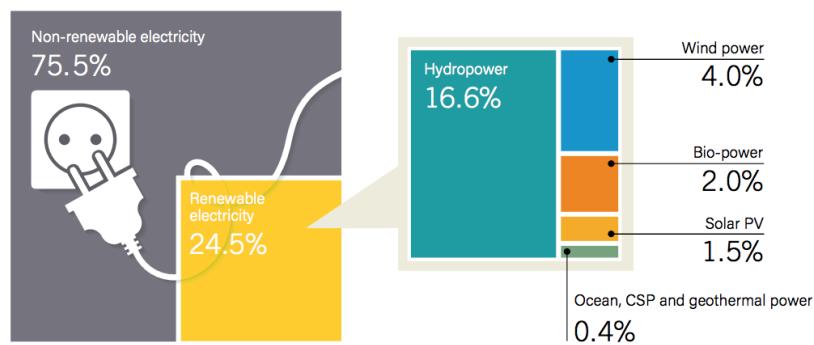
**Estimated Renewable Energy Share of Total Final Energy Consumption, 2015****Estimated Renewable Energy Share of Global Electricity Production, End-2016**

Figure 10: Global renewable energy consumption and electricity production.

Note: what is a fossil fuel? (via Wikipedia!):

*A fossil fuel is a fuel formed by natural processes, such as anaerobic decomposition of buried dead organisms, containing energy originating in ancient photosynthesis.*

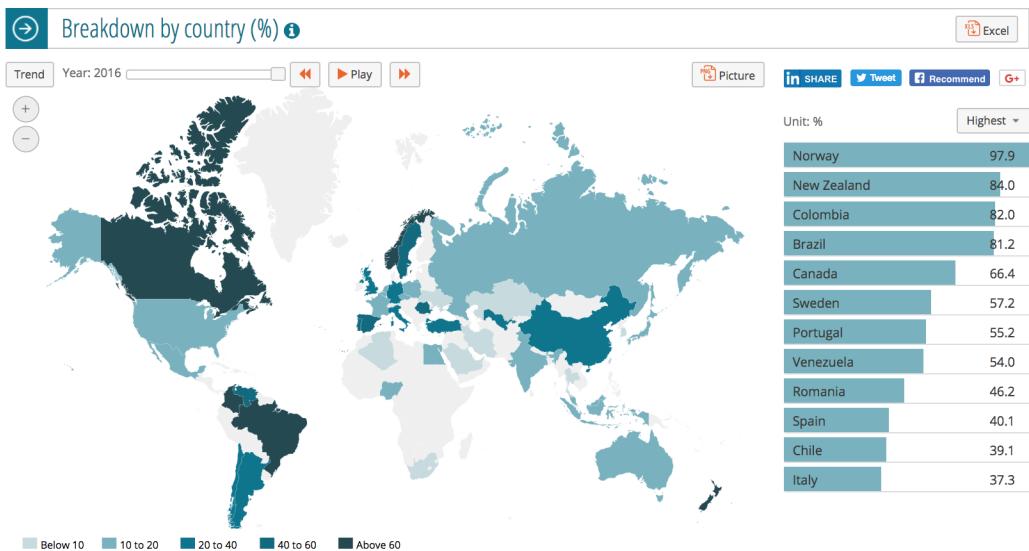


Figure 11: Global electricity production: percentage from renewable sources.

### Example Problems 7: Worldwide energy consumption sources

1. Approximately what percentage of worldwide energy supply is met by fossil fuels?
2. Approximately what percentage of worldwide *electricity* production is from renewable sources?
3. Which countries produce the highest percentage of electricity from renewable sources?
4. Is electricity the main form of energy consumed worldwide?

### —Answers

### **1.6.3 Energy consumption and supply sources: NZ in particular**

Let's focus some more on NZ energy consumption and supply. Some key facts and figures are shown in Figures 12-15.

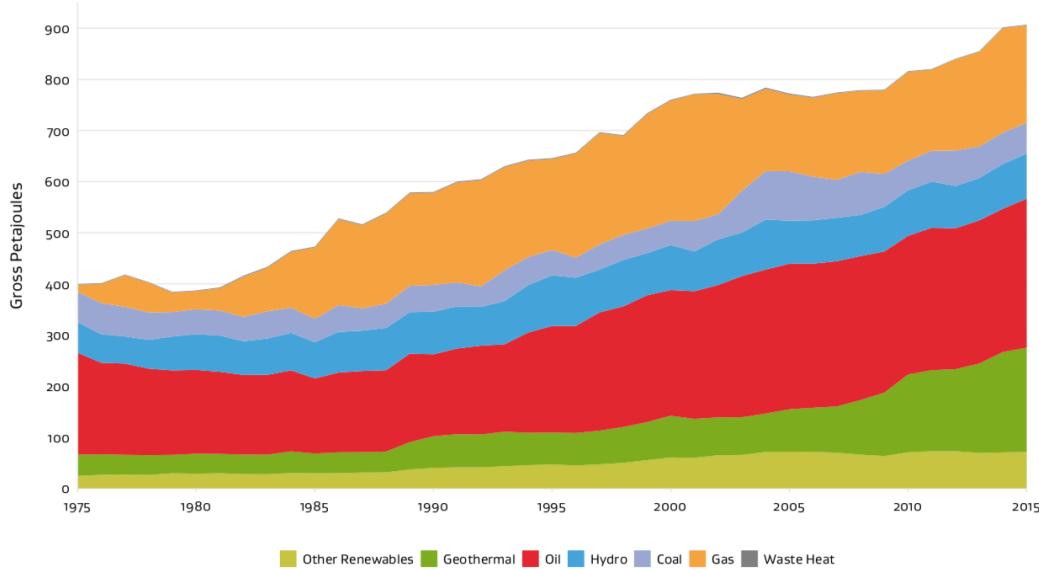


Figure 12: NZ total primary energy supply by fuel (2016 MBIE report).

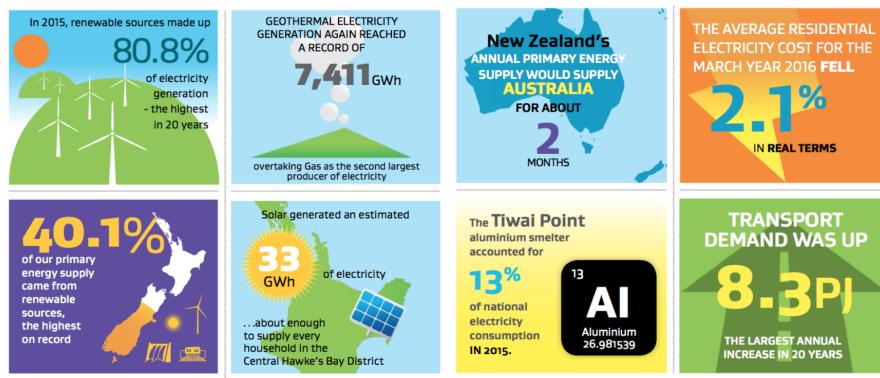


Figure 13: NZ energy: various facts (2016 MBIE report).

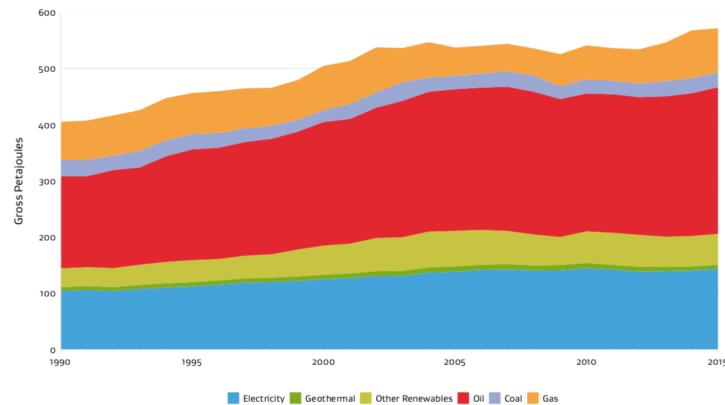


Figure 14: NZ consumer energy demand by fuel (2016 MBIE report).

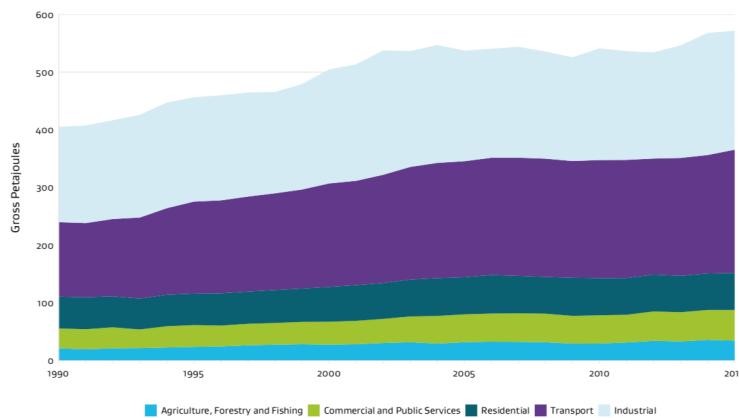


Figure 15: NZ consumer energy demand by sector (2016 MBIE report).

**Example Problems 8: NZ energy consumption and supply**

1. What was NZ's total primary energy supply in 2015?
2. What percentage of NZ's total primary energy supply in 2015 is from renewable sources?
3. Which energy source has experienced the most growth in the last 10 years in NZ?
4. What energy source continues to dominate NZ's primary energy supply?
5. What is the main source of the rise in NZ consumer demand of energy?
6. What sector is causing this growth?
7. What could consumers do to alter these figures in the coming decades?

---

**—Answers—**

---

**Example Problems 9: More on NZ energy consumption**

1. Estimate NZ's energy consumption per capita.
2. Look up data on some other countries and compare NZ's per capita consumption to them.

---

—**Answers**



## 1.7 Case study: Life at low Reynolds number

### Problem formulation

## Calculations

## Calculations

## Conclusions

## 2 Thermodynamics

### Learning Objectives

- Understand the scope and limitations of thermodynamics. State and apply the zeroth, first and second laws of thermodynamics.
- Understand the concept and types of thermodynamic ‘system’. Identify state properties and distinguish them from process variables. Understand the concepts of equilibrium, process, path and cycle.
- Understand the concepts of heat, thermal energy and internal energy. Understand and do basic calculations involving heat capacity and latent heat.
- Recognise various types of thermodynamic process, including isothermal, adiabatic and isobaric. Calculate work done/heat transferred during different process types and sketch associated process diagrams.
- Understand heat engines and do basic efficiency calculations. Understand the connection between the second law, limits on work extraction and the definition of ‘reversible’ processes.
- Understand the concept of a spontaneous process, identify which processes are spontaneous in different types of system and know which energy function - internal energy, Helmholtz free energy, Gibbs free energy or enthalpy - governs spontaneous processes in which type of system. Calculate changes in Gibbs free energy and/or enthalpy.
- Carry out basic calorimetry (energy measurement) calculations, e.g. know how to determine the heat capacity of an unknown substance.

### 2.1 Overview and basic concepts of thermodynamics

#### 2.1.1 The scope of thermodynamics

Thermodynamics is a *general science of macroscopic ‘systems’ and energy transfer between systems*. A key characteristic of it is that it doesn’t require detailed knowledge of the internal structure of the system, nor the specific process carried out.

This may remind you of our discussion of energy conservation and its independence from specific, detailed mechanisms - if so, you are on the right track! For example, Pierre Duhem (1861–1916), a prominent French physicist and philosopher of science in the nineteenth and early twentieth centuries, promoted ‘energetics’, essentially thermodynamics, as the foundation of all physical theory including mechanics, chemistry, physics etc<sup>3</sup>. Towards the end of the nineteenth century, before the existence of atoms was definitively established, Duhem famously argued against atomism; more precisely, he argued that the chemistry of the time was *independent of*, and consequently offered no support for, atomism! In a sense he wasn’t wrong - much of thermodynamics and its associated application *is* independent of the particular constitution of matter.

This generality continues to be a key feature of modern thermodynamics: it applies to all systems, regardless of their details. This is just like conservation of energy - actually, conservation of energy is the first law of thermodynamics! The generality of thermodynamics can clearly be considered both a strength and a weakness: while it can often tell us a lot about what’s possible/impossible, it often isn’t enough to tell us precisely what actually happens, nor the rate at which it happens. As we discussed previously, conservation of energy is not sufficient to (macroscopically) explain e.g. the differences in the material properties of wood and metal. To answer these sorts of more detailed questions we need to supplement thermodynamics with constitutive equations and/or kinetic/statistical theories. It helps to know, after all, that atoms really do exist!

---

<sup>3</sup>He is also well-known in philosophy of science for his contributions to what is now called the Quine-Duhem thesis: in essence the idea that any given body of empirical data is equally consistent with multiple theories.

—Thermodynamics, mechanics and partial descriptions—

---

### 2.1.2 The laws of thermodynamics: a preview

Here we give a brief overview of the content of the laws of thermodynamics. In the next few subsections we will get a feel for what these ‘really’ mean by using them!

1. **Zeroth Law:** Establishes the concept of thermal equilibrium and the existence of empirical temperature.
2. **First Law:** Energy is conserved.
3. **Second Law:** Entropy in an isolated system is non-decreasing (stays the same or increases).

One of the key themes of thermodynamics is the *interplay between the first and second laws*. We will see that the upshot of this interplay is:

1. Energy is conserved and can be transferred to macroscopic systems via both ‘work’ and ‘heat’.
2. There are limitations on how efficiently energy can be transferred between macroscopic systems, and this is intimately related to entropy increase.

Now we develop the key thermodynamic concepts in more detail.

### 2.1.3 Thermodynamic systems

A thermodynamic **system** is a *macroscopic* object, collection of objects or region that an analysis is performed on. ‘Macroscopic’ means that our region or object has

1. A boundary
2. A volume
3. A surroundings

---

—A system

---

The distinction between macroscopic/macroscale and microscopic/microscale is not precise and is often relative.

In practice, one can imagine ‘macroscopic’ to mean the scale at which we treat a collection of entities as ‘a whole’, while microscopic as the scale at which we consider the individual entities making up that whole. For example one might consider a planet to be a ‘microscopic’ - or more appropriately a microscale - entity when considered as part of a galaxy<sup>4</sup>!

Choosing a system also requires us to define what *interactions* are possible between the system and its surroundings. In particular, this leads us to distinguish between the following types of system:

1. **Open:** both matter and energy can cross the boundary
2. **Closed:** energy can cross the boundary, but matter cannot
3. **Isolated:** neither matter nor energy can cross the boundary

---

<sup>4</sup>There is no reason, however, why we can’t consider a ‘continuum’ of scales from the smallest particle (or perhaps string!) to the largest collection of entities. In practice it is also common to explicitly introduce a ‘mesoscopic’, intermediate scale, lying in-between our smallest and largest scales.

## —Open, closed and isolated systems

---

The key is to ask yourself what types of interactions or *transfers* are possible: mass and/or energy.

### Example Problems 1: Classification of systems

Classify the following systems as open, closed or isolated:

1. A river.
2. The interior of a closed can of L&P.
3. The interior of a closed freezer that is turned off.
4. Interior of a closed freezer that is turned on.
5. A cat.

#### 2.1.4 Properties

A **thermodynamic property** is any measurable characteristic of a macroscopic system ‘at equilibrium’, e.g. volume, pressure, temperature etc. The concept of *equilibrium* is discussed further below, but is roughly ‘nothing is happening’ on the

macroscopic measurement scale of interest. In order to apply our ideas to the real world, however - which is never fully at equilibrium - we really need to be able to measure and define quantities ‘outside of equilibrium’. This is a somewhat controversial topic; we discuss it a little later on.

Note: atoms are continually ‘jiggling’ at the *microscopic* level, even at thermodynamic - i.e. macroscopic - equilibrium!

Properties can be classified as either

1. **Intensive:** independent of the size (mass, volume etc) of the system.
2. **Extensive:** depends on the size (mass, volume etc) of the system.

We can *convert* extensive properties to intensive properties by dividing by the size of the system (e.g. mass, volume etc), or by taking the *ratio* of two extensive quantities.

---

#### —Examples of extensive and intensive properties

---

##### 2.1.5 Interactions

What do we mean by ‘interactions’ and what types are possible? Roughly, an interaction is an exchange of mass or energy<sup>5</sup>.

---

<sup>5</sup>In fact, mass can be considered as a special type of energy transfer, that of mass-energy.

We assume here that the basic ideas of **mechanics** are known and given, e.g. we take *mechanical work* and *mechanical energy* as known concepts. For example, we assume that the idea of mechanical work as given by *force times distance* (or integrated over a series of displacements) is familiar. Furthermore, we usually classify e.g. electrical current etc interactions as ‘mechanical’ processes here. The increments in work of these processes can also be expressed in the form ‘force times displacement’.

Thermodynamics introduces the idea of a *new type of macroscopic interaction*, not given by ‘ordinary’ (conservative/reversible) macroscopic mechanics: **thermal interactions**. A thermal interaction is roughly defined as a type of interaction that is...‘*not macroscopic mechanical work nor mass transfer*’!

This arises because we *know from experience* that we can place two closed (no mass transfer) systems into ‘contact’ and have them *exchange energy without either doing macroscopic mechanical work on the other*.

This form of ‘thermal energy transfer’ or ‘thermal interaction’ will be called **heat** and is discussed in detail later.

---

### —Thermal interactions: macroscopic and microscopic pictures

---

It is important to remember that **interactions are not properties of the system**, they are *exchanges* of quantities between systems. Think: *bank transfer* (interaction between systems) vs *bank balance* (property of a system).

## 2.2 Equilibrium and the zeroth law

As mentioned above, **macroscopic equilibrium** is essentially the idea that *nothing is happening* on the macroscopic scale of interest.

This includes **both the system and the environment**: *neither* is changing (in time or space) at equilibrium. No macroscopic ‘interactions’ or processes are occurring at equilibrium (though microscopic interactions continue in general).

**Thermal equilibrium** is a special type of equilibrium: two systems are in thermal equilibrium when they are placed in thermal contact and no thermal interaction (i.e. heat flow) takes place between them. This leads to the idea of the zeroth law, which allows us to define a *property*, called **temperature** to *compare systems thermally*. In particular, we can now say that *systems at the same temperature do not thermally interact (exchange heat)*.

---

### —Zeroth law and temperature

---

That *heat flows from higher to lower temperatures* is an empirical fact that, when generalised, becomes a form of *the second law of thermodynamics*, which is discussed later.

### 2.2.1 Equilibrium, steady state and quasi-steady-state

At **steady state** the *system properties* are not changing in time but *the environment properties may be*. Interactions may be occurring as long as the *system* properties are unchanging. Hence *a steady-state is a non-equilibrium condition*.

In order for this definition to make sense we must suppose that we can *measure* system properties at steady state in essentially the same manner as we do at equilibrium. One way of doing this is to introduce the idea of a *measurement device* and use the idea of *equilibrium between the system and the measurement device*, rather than between the system and the environment, to define system properties. Thus we imagine that *a system can be in equilibrium with a measuring device while out of equilibrium with its environment*.

This appears to violate the zeroth law, however! To avoid this we can suppose that the ‘inside’ of the system is in one state, the environment in another, and that there is a *boundary or transition region* separating the two. The measuring device is imagined to have ‘access’ to the internal state of the system, while the environment can only interact via the outside of the boundary. Hence the inside of the system and the environment can have two well-defined, but different, temperatures without violating the zeroth law.

---

#### —Equilibrium vs steady state

---

### 2.2.2 State?

The term **state** refers (roughly) to a *list of properties sufficient to describe our macroscopic system*. This is also relative to our analysis goals: e.g. we do not need to characterise the nuclear state of our system if we are not interested in nuclear processes.

For example a  $(P, V)$  system is a system sufficiently described by its pressure and volume.

---

—State of a lung

---

## 2.3 Processes, paths and cycles

How can we apply thermodynamics under time-varying conditions - everything so far refers essentially to *static* conditions<sup>6</sup>?

To make these ideas more precise will give some definitions. These are perhaps best understood via pictures, however, so we draw these afterwards.

1. A **thermodynamic process** is a *change or series of changes from one equilibrium (or steady) state of the system to another*. We don't necessarily specify the path between, but always give the start and end states. We may or may not specify how the environment changes.
2. A **process path** is a continuous sequence of equilibrium (or steady) states between two start and end states of the system.
3. A **cycle** is any process path that returns to its initial state, i.e. where the starting state and end state are the same.
4. A **quasi-equilibrium process** is when a system follows a well-defined process path of equilibrium states during a process. Similarly, a **quasi-steady-state process** is when a system follows a well-defined process path of steady-states.
5. A **non-equilibrium process** is when the system doesn't have a well-defined process path of *equilibrium* states during the process. We will assume in general that it does however, start and end in a well-defined equilibrium state. Note: *a quasi-steady-state process is in general a non-equilibrium process*.
6. A **process diagram** is when we plot a process in state space, i.e. on a diagram with the state variables as the axes.

---

—Illustration of our process definitions—

---

<sup>6</sup>In fact, some argue that thermodynamics would be better named *thermostatics*!

---

—Example: a beating heart

---

**Example Problems 2: Basic concepts of thermodynamics**

1. Which of the following statements is **false**, regarding properties of a thermodynamic system:
  - A. Extensive properties can be converted to intensive properties by dividing by moles.
  - B. Intensive properties are independent of the quantity of matter.
  - C. Volume is an extensive property.
  - D. Heat is a property of the system.
  - E. Temperature is a property of the system.

---

**Answers**

---

## 2.4 Internal energy, work and heat

### 2.4.1 Internal energy

Given a thermodynamic system, we define the **internal energy** as the ‘total’ energy stored (or ‘allocated’) *inside* the system. Some key points:

1. By ‘inside’, we mean we exclude the *bulk* translational and rotational kinetic energy of the system as a whole, relative to the environment or other external frame of reference.
2. We do, however, include the translational, rotational and vibrational energy of the *microscopic* constituents of the system (as measured relative to the bulk system motion).
3. This ‘microscopic’ kinetic energy is called the **thermal energy**.

4. We also include in the internal energy (but not in the thermal energy) the chemical energy in bonds, long range interactions between molecules, nuclear energy etc.
5. Since internal energy, like all energies, is *only defined up to a reference value/reference state* we don't actually need to track all energy sources, *just those that will change or those that affect our problem.*

---

**—Internal energy of an ideal gas**

---

### 2.4.2 The first law of thermodynamics

The **first law of thermodynamics** is ‘simply’: **energy is conserved**. Hidden in this, however, is that *energy can be transferred between systems via both (macroscopic) mechanical work and heat*. Another more explicit statement is: **the change in internal energy of a system equals the sum of energy transferred, where energy can be transferred via both mechanical work and heat**.

Recognition of the existence - and essential equivalence between - heat and work, in terms of both being energy transfers, was a crucial point in the development of thermodynamics. Originally heat and work were measured in different units - James Prescott Joule carried out the original experiments relating heat and work, starting around 1840, and established the conversion between the old unit of heat, the calorie, and the measurement of work. The conversion factor  $1 \text{ cal} = 4.2 \text{ joule}$  is called *the mechanical equivalent of heat*.

---

#### —Key equation and sign conventions

---

As discussed previously, **work** can be usefully thought of as a type of energetic interaction or exchange of energy. Similarly, **heat** can be considered as a form of ‘thermal work’: a new form of macroscopic ‘work’ not fitting under our usual definition of macroscopic mechanical work.

Like mechanical work, heat is an energetic interaction. Ultimately, heat can be thought of as arising from microscopic mechanical work *that we do not directly observe*. Instead we macroscopically observe the differences in microscopic kinetic energy as ‘temperature’ differences, and observe the resulting macroscopic energy exchange, due to the net microscopic differences and microscopic work, as ‘heat flow’.

In mechanics of course, we express work in terms of a force times a displacement (or integrated over a series of displacements). In the reversible case we will see that ‘thermal work’, i.e. heat flow, can also be imagined as a sort of ‘force times displacement’, where temperature is the force and entropy is the ‘displacement’.

Things are not completely symmetric, however: we will return to how work and heat differ in the *irreversible* case when we discuss the second law and *entropy*. This asymmetry prevents thermodynamics from being completely reduced to macroscopic mechanics<sup>7</sup>; instead, *thermodynamics can be considered as an extension of macroscopic mechanics to deal with irreversible processes*.

---

### —Work from internal energy

---

<sup>7</sup>We assume it *is* potentially reducible to microscopic mechanics; however, doing this fully rigorously is still an incomplete task to date.

---

**—Converting heat to work—**

---

**Example Problems 3: Internal energy and the first law**

1. Briefly define internal energy  $U$ .
2. What is the relationship between internal energy, heat and work (i.e. the first law of thermodynamics)?
3. For an ideal gas, what does the internal energy represent?

---

**—Answers—**

---

## 2.5 Heat transfer

Key mechanisms/types of heat transfer include

1. **Conduction**
2. **Convection**
3. **Radiation**

Each of these has different types of constitutive equation governing the interactions between the system and its surroundings.

We won't look at these in too much detail here; we will, however, consider some constitutive (material specific) properties of substances that measure their 'capacity for receiving heat', regardless of the source or mechanism of transfer.

### 2.5.1 Heat capacity

The **heat capacity** of a substance measures the 'amount of heat', i.e. amount of energy transfer, required to change a given substance's *temperature* by a given amount.

It comes in two flavours:

1. An *extensive* version  $C$ , just called *heat capacity*.
2. An *intensive* version  $c$ , called *specific heat capacity*.

In both cases however, you need to specify whether the heat capacity is measured at constant pressure or constant volume: otherwise it is *path dependent* and hence not a true 'state property' of the system. The symbols  $C_p$  or  $c_p$  are used for measuring heat capacity at constant pressure, while  $C_v$  or  $c_v$  are used when measuring it at constant

volume. Their ratio, denoted  $\gamma = C_p/C_v = c_p/c_v$ , is called the *heat capacity ratio* or the *ratio of specific heats*. Usually  $\geq 1$ , e.g. for air  $\gamma = 1.4$ .

Heat capacities can be measured using a **calorimeter**; we will return to more detailed examples of this later after we have covered a few more concepts.

---

### —Units and key equations for heat capacity

---

---

#### Example Problems 4: Heat capacity calculations

---

- Given the specific heat capacity of water is  $4.186 \text{ J.g}^{-1} \cdot \text{degC}^{-1}$ , how much

- heat is required to raise the temperature of 200 g of water from 20 to 50 °C?
2. A 5.10 g sample of iron is heated from 36.0 °C to 75.0 °C. The amount of energy required is 89.5 J. What is the specific heat capacity of iron?
  3. A 350.0 g sample of metal is heated to 100.0 °C, then dropped into 400.0 g of water at 21.4 °C. The temperature of the water rises to 28.9 °C. Assuming there is no heat lost to the surrounds, what is the heat capacity of the metal?

---

**—Answers—**

### 2.5.2 Latent heat and phase transitions

Similarly to heat capacities, we can define various types of **latent heat** as *the amount of heat/energy transfer required to completely carry out a change in phase for a given substance*. These can also be measured in extensive or intensive versions.

A change in phase is e.g. a change between solid, liquid, gas (or plasma!). For example the **latent heat of fusion** is the heat energy required to carry out melting, while the **latent heat of vaporisation** is the energy required to carry out boiling.

Some latent heat data is given in Table 1 of this section. We can use this to answer the following questions.

Substance	Specific Latent Heat of Fusion (kJ.kg <sup>-1</sup> )	Melting Point (°C)	Specific Latent Heat of Vaporisation (kJ.kg <sup>-1</sup> )	Boiling Point (°C)
Water	334	0	2264.76	100
Alcohol, ethyl	108	-114	855	78.3
Oxygen	13.9	-219	213	-183
Hydrogen	48	-259	455	-253
Carbon dioxide	184	-78	574	-57
Lead	23	327.5	871	1750

Table 1: Examples of specific latent heat of fusion and specific latent heat of vaporisation. (From notes by Thor Besier.)

#### Example Problems 5: Latent calculations

- What is the energy (heat) required to convert 250 g of ice to liquid water?

2. What is the energy required to evaporate 28 g of sweat?
3. Given the specific heat capacity of water is  $4.18 \text{ J.g}^{-1.\circ\text{C}^{-1}}$ , what is the effective cooling effect of this evaporation for a 70 kg person?

---

**—Answers**

---

---

## 2.6 Work: pistons and heat engines

As engineers we are very often interested in *extracting work from* systems, as well as in *doing work on* systems (e.g. to change their shape during manufacturing).

Here we'll look at two simple examples of getting work into and out of systems, and the interplay of this with heat transfer: *pistons containing an ideal gas*, and *heat engines and their efficiency limits*.

### 2.6.1 Pistons

The canonical engineering example of a thermodynamic system is a **piston containing an ideal gas**.

This is sketched out below.

—Piston containing an ideal gas—————

A subtle point is the difference between the **external work**,  $W_{ext}$ , and the **system work**, here  $P\Delta V$ : they are only equal for ideal, i.e. *reversible/quasi-equilibrium* processes (no entropy production - see below as well as later). This is essentially the same point as came up when discussing how to measure properties outside of equilibrium.

---

—External vs system work—

---

**Example Problems 6: Pistons**

1. How much work is done by a gas expanding against a piston from 46 L to 65 L at a constant external pressure of 101,325 Pa (1 atmosphere)?
2. Consider a gas in a cylinder at room temperature ( $T = 293$  K) with a volume of  $0.065\ m^3$ . The gas is confined by a piston with a weight of 100 N and an area of  $0.65\ m^2$ . The pressure above the piston is atmospheric pressure. What is the pressure of the gas?
3. The gas is heated, expanding it and moving the piston up. If the volume occupied by the gas doubles, how much work has the gas done?

---

—Answers

---

## 2.6.2 Processes and PV diagrams

In general to calculate the work we need to *integrate the force times displacement along the full path*. This will also depend on the particular material or substance we are studying.

For an ideal gas in a piston, however, we can save some effort by identifying some special cases. These are

1. **Isobaric** processes: constant *pressure*
2. **Isochoric** processes: constant *volume*
3. **Isothermal** processes: constant *temperature*
4. **Adiabatic** processes: *no heat transfer*

Let's derive formulae for the work done during these process (note: in general you don't need to re-derive these - you can just use the results).

---

### —Isobaric work

---

—Isochoric work

---

—Isothermal work

---

—Adiabatic work

---

**Warning:** These formulae and derivations are only valid for ideal gases in pistons undergoing reversible processes.

### Example Problems 7: Work and different process types

1. How much work is done by 1.88 mols of a gas expanding isothermally at 298 K against a piston from 46 L, at  $1.013 \times 10^5$  Pa, to 65 L?
2. How much work is done by 1.88 mols of a gas expanding adiabatically at 298 K against a piston from 46 L, at  $1.013 \times 10^5$  Pa, to 65 L and  $6.24 \times 10^4$  Pa?
3. One mole of an ideal gas, initially at  $T_1 = 25^\circ\text{C}$ ,  $P_1 = 101.3$  kPa and  $V_1 = 24.5 \times 10^{-3}$  m<sup>3</sup>, undergoes the following mechanically reversible processes in a closed system:
  - (a) **Process I:** Adiabatic compression to  $T_2 = 473^\circ\text{C}$ ,  $P_2 = 505$  kPa and  $V_2 = 7.65 \times 10^{-3}$  m<sup>3</sup>.
  - (b) **Process II:** Isobaric cooling to  $T_3 = 25^\circ\text{C}$  and  $V_3 = 4.89 \times 10^{-3}$  m<sup>3</sup>

Draw these two processes on a pressure-volume graph, label the axes and identify each state, process and path.

---

### Solutions



### 2.6.3 Heat engines, efficiency limits and the second law

The second law of thermodynamics arose out of the practical question in the nineteenth century: *how much useful work can we get from steam engines?* This is the topic of **heat engines**. Here ‘useful’ means, in essence ‘macroscopic’, ‘bulk’ or ‘organised’ work, i.e. usually not including e.g. microscopic ‘random jiggling’ of atoms.

Heat engines:

1. Convert thermal energy and/or heat input into useful work
2. Usually carry out a **cycle** or series of cycles.
3. Have **limits** on their efficiency.

The discovery of the *existence of efficiency limits* on heat engines was in fact the **first discovery of the second law of thermodynamics**. By now we know, however, that the idea applies more generally than just the practical topic of ‘steam engines’!

The more basic idea is that *macroscopic mechanical work can be completely converted to heat transfer/thermal energy, but not vice-versa*. Intuitively, when trying to convert thermal energy or heat input, i.e. microscopic mechanical energy, to macroscopic mechanical work, some of that energy is always ‘lost’ to, or retained as, microscopic mechanical energy, i.e. thermal energy.

---

—Carnot efficiency of heat engines

---

**Upshot:** Once macroscopic mechanical energy is ‘lost’ from the ‘macroscopic’ mechanical world to the ‘microscopic mechanical world’ (e.g. the jiggling of atoms) it can never be fully recovered as macroscopic mechanical energy. Of course conservation of total energy - including thermal and mechanical energies - still holds! The second law is a statement about **efficiency** of the conversion of one type of energy to another.

### Example Problems 8: Heat engines

1. A reversible heat engine operates between a hot reservoir at 900 K and a cold reservoir at 500 K.
  - (a) Calculate the maximum efficiency of the engine.
  - (b) The temperature of one of the heat reservoirs can be changed by 100 K up or down. What is the highest efficiency that can be achieved by making this temperature change?
2. A startup company claims to have designed a new heat engine that has 42% efficiency, using a heat source at 500 K and a cold sink at 300 K. Is this reasonable?

## 2.7 Spontaneous processes: entropy and energy

As mentioned, the second law extends far beyond just steam engines. Here we look at the ideas in more generality. Later in the course we will see how to apply them to help us understand biological processes!

**Warning:** You may find some of the following material difficult - most do, including me! - the key takeaways are simple, however: **know what sorts of processes are natural in which types of system** and **know how to calculate free energy or enthalpy changes in given processes**.

### 2.7.1 The second law of thermodynamics

While the ‘interpretation’ of the second law of thermodynamics is subtle and relates to order/disorder, probability, the arrow of time etc, it’s relatively simple to state verbally:

**The second law of thermodynamics:** *The entropy of an isolated system is non-decreasing.* That is, the change in entropy in any process is  $\geq 0$ .

It’s also *relatively* simple to state mathematically:

$$\delta Q \leq TdS$$

where  $\delta Q$  is a ‘small amount’ of heat added,  $T$  is the *absolute* temperature and  $dS$  is a small change in *entropy*. This equation applies to any system, isolated or not: note that when  $\delta Q = 0$  (isolated system) it becomes  $dS \geq 0$  ( $T \geq 0$  since it is the absolute temperature).

Entropy is a state variable which is why we use a normal ‘ $d$ ’ to represent a differential (small difference) *in state space* while  $\delta$  just represents a small change of any quantity, not necessarily a state quantity.

For *reversible* processes we have

$$\delta Q \stackrel{\text{rev}}{=} TdS$$

Note the analogy to e.g.  $PdV$  work. This equality condition can actually be taken as the **definition of a reversible process**. Another way of making this clear is to introduce the **entropy production**  $\delta^i S$  via:

$$TdS = T(\delta^r S + \delta^i S) = T\delta^r S + T\delta^i S$$

where

$$\delta Q = T\delta^r S, \text{ & } \delta^i S \geq 0$$

Reversibility corresponds to

$$T\delta^i S \stackrel{rev}{=} 0$$

i.e. **a reversible process is one in which there is no entropy production.** Entropy production can be thought of as ‘extra internal disorder’ created during a process, over and above that introduced by external heat addition. **Real processes are irreversible processes and have positive entropy production.**

To ‘integrate’ or ‘add up’ a  $\delta$  during an arbitrary, finite process we need to follow a *specific path*, while to determine a  $d$  change we just need to know the difference in start and end states: state variable differences are *path independent*. For finite heat transfers  $Q$  we can write

$$Q \leq \int_{S_1}^{S_2} TdS$$

This is usually written in the form of the *Clausius inequality*:

$$\Delta S = S_2 - S_1 \geq \int_C \frac{\delta Q}{T}$$

where the integral is a *path/line integral* that requires a specific path of integration to be given (and is denoted here by  $C$ ). Note that we use  $\Delta$  for the changes in a state variable but not for process variables like  $Q$  or  $W$ .

You will likely cover the details of these ideas in future courses. *For now we will only need the basics!*

### 2.7.2 Spontaneous processes - isolated systems

As mentioned above, all ‘real’ macroscopic processes are associated with a positive entropy production. A **spontaneous process** is one for which  $\delta^i S \geq 0$ . This applies whether the system is isolated or not because we account for the contribution of (reversible) heat transport.

#### Isolated systems

It’s helpful to think about spontaneous processes in the context of isolated systems (indeed as we have seen the second law is usually stated for isolated systems). Here **spontaneous processes are ‘natural’ or ‘probable’ processes that are likely to occur in isolated systems**, i.e. without needing any mass or energy input. In the case of isolated systems the second law corresponds to  $\Delta S \geq 0$  since  $\delta Q = 0$  by definition.

You can thus imagine, when considering isolated systems, that these processes are ‘driven’ by entropy differences (in a similar way to how energy differences provide driving potentials for mechanical processes). Importantly, an isolated system will continue to undergo spontaneous processes that increase the entropy until the system maximises its entropy: thus **thermodynamic equilibrium in an isolated system occurs at maximum entropy**.

---

#### —Free expansion of a gas

---

### 2.7.3 Energy functions for spontaneous processes in non-isolated systems

What about non-isolated systems? Again we could consider entropy *production*; however, just as it is helpful to think of entropy (not just entropy production) as providing the ‘potential’ or ‘natural direction’ for spontaneous processes in isolated systems, **we can define ‘natural potentials’ for spontaneous process in different types of system.**

These can be specified either in terms of ‘entropy-like’ functions or in terms of ‘energy-like’ functions. Energy-type functions are most common, however. With this in mind we first translate the tendency of isolated systems to move towards the state of *maximum entropy* into an **equivalent minimum energy principle**.

---

—Maximum entropy, minimum energy

---

---

### Other systems

For other types of system it can be shown that **other ‘energy-like’ functions are minimised at equilibrium**. We won’t discuss the details here but deriving these make use of the important mathematical concept of a **Legendre transformation**. These show up in many mechanics and thermodynamics applications.

In particular we find that the **Helmholtz free energy**, the **enthalpy** and the **Gibbs free energy** are each natural potentials for different types of system. We discuss these, and the types of system for which they are natural, below. In this course the enthalpy and the Gibbs free energy will be the most useful to us.

---

#### —Helmholtz free energy

---

---

#### —Enthalpy

---

---

**Gibbs free energy**

---

---

**Terminology**

For Gibbs free energy and enthalpy, respectively, we introduce the following terminology.

---

**Gibbs free energy: exergonic or endergonic?**

---

---

**—Heat/enthalpy: exothermic or endothermic?**

---

Importantly, we can also apply these energy functions to cases involving multiple processes/steps.

**—Free energy in multiple processes or steps**

---

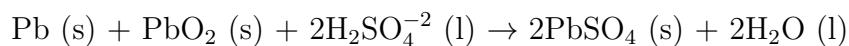
The Tables 2-3 will be helpful for our examples.

Substance	Phase	Chemical Formula	$\Delta G_f^\circ$ (kJ.mol <sup>-1</sup> )
Water	liquid	H <sub>2</sub> O	-237.14
Water	gas	H <sub>2</sub> O	-228.61
Oxygen	gas	O <sub>2</sub>	0
Hydrogen	gas	H <sub>2</sub>	0
Carbon dioxide	gas	CO <sub>2</sub>	-394.39
Lead	solid	Pb	0
Lead sulfate	solid	PbSO <sub>4</sub>	-813.2
Lead oxide	solid	PbO <sub>2</sub>	-215.48
Sulfuric acid	liquid	H <sub>2</sub> SO <sub>4</sub>	-744.63

Table 2: Examples of standard Gibbs free energy of formation, which is the Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard state. Given at 298 K and 1 atm. (From notes by Thor Besier.)

### Example Problems 9: Gibbs free energy

- Calculate the energy released if you oxidised the entire glucose content of a 65g chocolate bar. Assume the glucose content of the bar is 70g per 100g. Gibbs free energy of glucose is -2870 kJ/mol. The molecular weight of glucose is 180.16 g/mol.
- A typical lead acid battery undergoes the following chemical reaction to produce energy:



Given the values for Gibbs free energy of formation in the table above, determine

Substance	Phase	Chemical Formula	$\Delta H_f^o$ (kJ.mol <sup>-1</sup> )
Water	liquid	H <sub>2</sub> O	-285.83
Water	gas	H <sub>2</sub> O	-241.8
Oxygen	gas	O <sub>2</sub>	0
Hydrogen	gas	H <sub>2</sub>	0
Carbon dioxide	gas	CO <sub>2</sub>	-393.5
Lead	solid	Pb	0
Lead sulfate	solid	PbSO <sub>4</sub>	-919.94
Lead oxide	solid	PbO <sub>2</sub>	-274.47
Sulfuric acid	liquid	H <sub>2</sub> SO <sub>4</sub>	-909.27

Table 3: Examples of enthalpy of formation values. Given at 298 K and 1 atm. (From notes by Thor Besier.)

the electrochemical work produced at 298 K.

---

—Answers—

---

---

**Example Problems 10: Enthalpy**

1. Calculate the heat of reaction (enthalpy of reaction)  $\Delta H_f$  for the chemical reaction of the lead acid battery in the problem above.
2. Describe whether this reaction is endothermic or exothermic.
3. Compare the Gibbs free energy value with the heat of reaction. What does this mean in terms of heat to/from the environment?
4. Calculate  $\Delta H$  if a piece of metal with a specific heat of 0.98 kJ/(kg.K) and a mass of 2 kg is heated from 22 °C to 28°C.

---

—Answers—

## 2.8 Calorimetry and the enthalpy of combustion

Calorimetry is the science of measuring heat transfer during physical or chemical processes such as chemical reactions. As briefly mentioned previously, it can also be used to measure heat capacities.

It is often used to measure the **enthalpy of combustion**, also called the **heat of combustion**. This is the heat energy available by ‘burning’ or ‘exploding’ a substance - i.e. when it reacts rapidly and completely with oxygen in a high-temperature, exothermic redox reaction. This clearly involves **the conversion of chemical energy to heat** (which, typically in engineering applications, is then used to produce work). A related term is **energy density**, which is the enthalpy of combustion per unit mass.

Calorimetry could hence be used to determine the energy available from a new potential fuel source. The basic example for doing this is a so-called **bomb calorimeter**. We discuss how this is used below.

---

—Bomb calorimeter

---

---

**Example Problems 11: Calorimetry**

1. A 1 g sample of octane is burned in a bomb calorimeter containing 1200 g of water at an initial temperature of 25 °C. After the reaction the final temperature of the water is 33°C. The heat capacity of the calorimeter (the calorimeter constant) is 837 J/°C. The specific heat of water is 4.184 J/(g.°C). Calculate the heat of combustion of octane in kJ/mol.

---

—Answers

---

---

Table 4 gives some typical **standard enthalpies of combustion**,  $\Delta H_c^0$ , which is defined as the enthalpy change when 1 mole of a compound is completely burnt in oxygen gas at 298 K and 1 atm.

Substance	Phase	Chemical Formula	$\Delta H_c^o$ (kJ.mol <sup>-1</sup> )
Octane	liquid	C <sub>8</sub> H <sub>18</sub>	-5471
Benzene	liquid	C <sub>6</sub> H <sub>6</sub>	-3268
Glucose	liquid	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	-2808
Propane	gas	C <sub>3</sub> H <sub>8</sub>	-2220
Ethanol	liquid	C <sub>2</sub> H <sub>5</sub> OH	-1368
Acetylene	gas	C <sub>2</sub> H <sub>2</sub>	-1300
Methane	gas	CH <sub>4</sub>	-890
Carbon	solid	C	-394
Hydrogen	gas	H <sub>2</sub>	-286

Table 4: Examples of standard enthalpy of combustion values at 298 K and 1 atm.  
(From notes by Thor Besier.)

### Example Problems 12: Enthalpy of combustion

1. How much heat is released when 4.5 g of methane gas is burned at constant pressure? Molar mass of methane is 16.04 g/mol.
2. For fuels used in transportation the enthalpy/weight ratio is important

because the car/plane has to carry the fuel. Compare the energy densities in MJ/kg of the following fuels to petrol (approx. 46 MJ/kg):

- (a) Methane: molar mass 16 g/mol
- (b) Ethanol: molar mass 46 g/mol
- (c) Propane: 44 g/mol

---

### —Answers

---

## 2.9 Case study: Combustion engines and Otto cycles

### Problem background

In this case study we consider the basic ideas behind **combustion engines** i.e. the process of transforming: chemical energy → heat → work → kinetic energy.

A key part of this case study is learning about the **Otto cycle** which is the basis of the simple four stroke **Otto engine**, named after its inventor Nikolaus Otto.

**Fuel combustion and work extraction**

We will assume our car runs on...kerosene! Let's calculate the enthalpy of combustion, the energy density etc, and then consider some different hypothetical methods of burning kerosene and extracting work.

### Some questions

Consider the following questions:

1. What is the energy source for the heat released in a chemical reaction?
2. What is the term used to describe the ‘amount of heat’ of the reaction?
3. Where does the energy go when heat is absorbed in a chemical process (i.e. in endothermic reactions)?
4. If energy is released as heat and work, what happens to the internal energy  $U$ .
5. True or False: internal energy does not depend on  $P, T$  and  $V$ ?
6. True or False: internal energy cannot be measured directly, however  $\Delta U$  can be?
7. What are the units of energy density in terms of SI base units?

## The Otto cycle and Otto engine

To understand in more detail how the heat released by combustion is converted into ‘PV work’, we look here at one of the simplest combustion engine types: the **Otto engine**. This operates according to...a (four stroke) **Otto cycle**. We assume this contains an *ideal gas*.

A super glossy illustration of the Otto cycle is shown below.

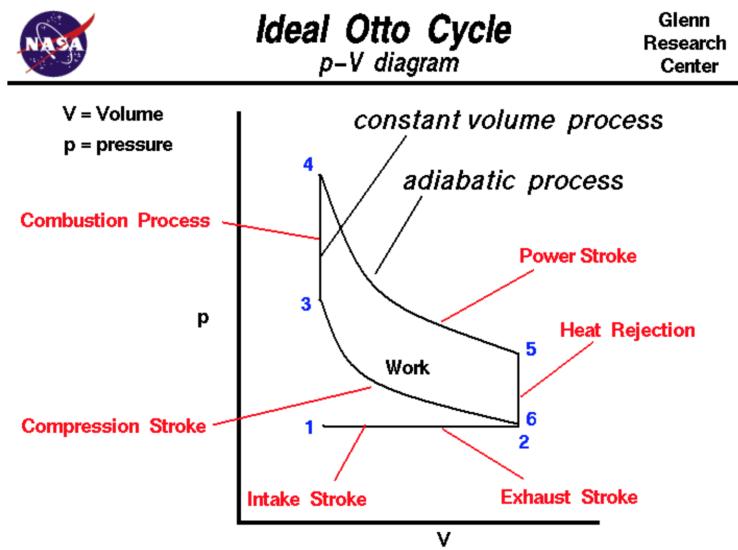


Figure 16: The ideal Otto cycle (From <https://www.grc.nasa.gov/www/k-12/airplane/otto.html.>)

Recall the expression for the *work done during adiabatic processes*:

## Final calculations and conclusions

Suppose our engine operates according to an Otto cycle under the conditions given in Table 5 below.

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
<b>Temperature, K</b>	323	742	1173	511
<b>Pressure, Pa</b>	$1.1 \times 10^5$	$2.02 \times 10^6$	$3.19 \times 10^6$	$1.74 \times 10^5$
<b>Volume, m<sup>3</sup></b>	$8.0 \times 10^{-4}$			
Compression ratio = 8    Cylinder volume = 0.8L $c_v = 20.78 \text{ Jmol}^{-1}\text{K}^{-1}$ n=0.0327				

Note: check for consistent units and calculate any missing P, T, V, and n using Ideal Gas Law;  $PV = nRT$

Table 5: Hypothetical Otto cycle data. (From notes by Thor Besier.)

We can calculate the work of compression, the work of expansion and the net work done. We can also calculate the heat transferred to and lost by the gas, and hence calculate the thermal efficiency of the engine.



## 3 Biological Energetics

### Learning Objectives

- Understand the general sources and transformations of energy in biological systems.
- Understand and describe the basic functions, structure and scales of the cell, cell membrane, nucleus and mitochondria.
- Calculate the energy content of food and conversion into activities. Understand the concept of ‘indirect calorimetry’ and carry out basic calculations.
- Understand the key role of Gibbs free energy in biological problems and known how to apply it/ calculate with it. Understand the role and use of ATP as an energy source driving cellular processes.
- Calculate reaction rates and interpret chemical kinetics figures. Understand the role of and factors affecting catalysts/enzymes.
- Understand the three stages of cellular respiration - glycolysis, Krebs cycle and electron transport - and their inputs/outputs. Calculate cellular efficiency.
- Understand the process of fermentation, when it occurs and its inputs/outputs.

### 3.1 Sources and transformations of energy in biological systems

#### 3.1.1 Thermodynamics in biology

From a thermodynamics point of view, biological systems are **open systems**: they constantly exchange energy and matter with their environments. They are also ‘non-equilibrium’ systems, e.g. operating near ‘non-equilibrium steady states’ (or just non-equilibrium states in general!). Since equilibrium means ‘no energy/mass exchanges or other processes occurring’, for a biological system **equilibrium = death!**

While the ‘far from equilibrium’ conditions can make applications of thermodynamics to biology more difficult, we nevertheless find that **thermodynamic concepts are typically still very useful** in understanding biological processes. After all, **the same laws of physics and chemistry apply to biology as to the rest of the universe!**

We will see in particular that the **Gibbs free energy** is a key driver of spontaneous processes in biological systems: we can often approximate biological systems as **open systems at constant pressure and temperature**.

In contrast to some of the more ‘human-scale’ applications common in traditional engineering, the energy in biological systems tends to be stored mainly at the **molecular and cellular levels**.

### 3.1.2 Composition

What are biological systems made of? They are usually distinguished from ‘non-organic matter’ by being based heavily on **carbon compounds**. For example, humans are about 60% carbon.

Fundamentally, **life is made of ‘star stuff’**: hydrogen, carbon, nitrogen, oxygen and phosphorus.

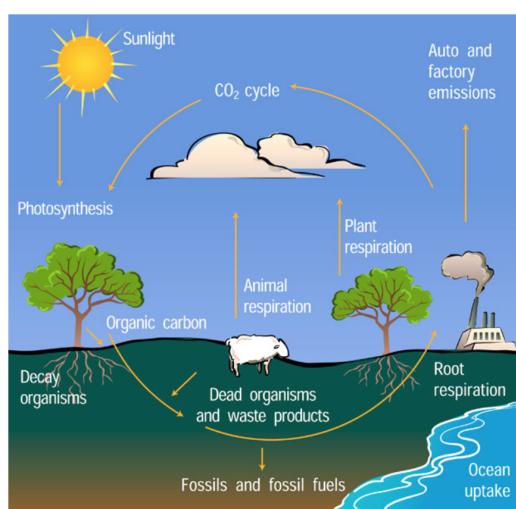
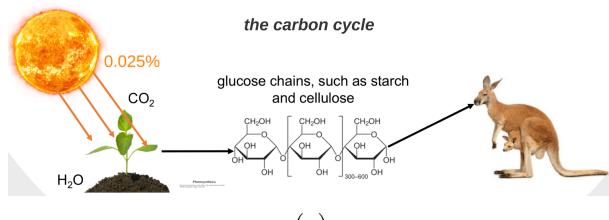
### 3.1.3 The carbon cycle and photosynthesis

This leads to the important idea of the **carbon cycle**, pictured below.

A key process involved in this is **photosynthesis**, carried out by plant life. This is the process of *using the radiant energy of the Sun to convert water and carbon dioxide into glucose, oxygen and heat*.

Glucose monomers are joined together to form polymers of various types, including **cellulose**, which is the most abundant organic compound on earth.

Photosynthesis is performed in plants by **chlorophylls**, which are ‘molecular antennas’ that absorb photons over a limited energy spectrum. The efficiency of this process is quite low - only about 1%!



This fairly basic carbon cycle diagram shows how carbon atoms 'flow' between various 'reservoirs' in the Earth system. This depiction of the carbon cycle focusses on the terrestrial (land-based) part of the cycle; there are also exchanges with the ocean which are only hinted at here. Note that carbon atoms are incorporated into various molecules as they flow around the cycle; for example, photosynthesis in plants captures carbon atoms in sugar molecules and atmospheric carbon is contained in molecules such as carbon dioxide and methane. Credit: UCAR

(b)

Figure 17: Illustrations of the carbon cycle.

The resulting energy is **stored** in, for example,

1. The **covalent and non-covalent bonds** of macromolecules
2. **Unequal concentrations** of ions across semi-permeable membranes (cell membranes).

Note: an unequal concentration gradient is just like an energy potential - in fact it *is* a form of potential energy, available to do work (e.g. osmotic work etc). The energy in chemical bonds is also a type of potential energy that can be 'released' and used

to do useful work.

### Example Problems 1: Sources and transformations of energy

1. The radiant energy of from the Sun that reaches the Earth is  $1.74 \times 10^{17}$  W. Approximately 52% of these photons are either reflected back to space or absorbed by the atmosphere. We know that 0.025% of the energy that reaches the land is absorbed by photosynthetic organisms. Calculate the radiant energy that is converted by photosynthetic organisms over one year.

### —Answers

---

## 3.2 Cells, membranes and organelles

**Cells are the fundamental functional units** of all living things. Humans are made up of *trillions* of cells, each performing different functions, while some organisms, such as bacteria, function as *one cell*.

Again, we emphasise that the key energy transfers and functions of biological systems ultimately occur at the molecular and cellular level. Cells:

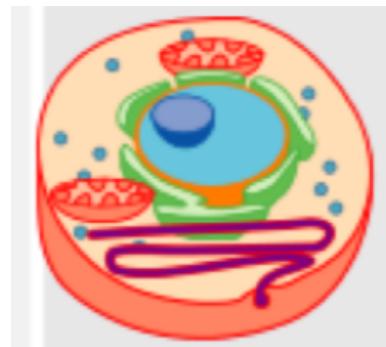
1. Take in radiant or chemical energy and use this energy to do mechanical work or create molecules (most energy is ‘discarded’ as waste heat).

2. Make their own internal structure, mostly in terms of proteins.
3. Reproduce or duplicate.
4. Maintain their internal composition and their volume despite the changing exterior conditions ('homeostasis')
5. Can often move about by 'crawling', 'swimming' or even 'rolling'.
6. Sense and respond to environmental conditions.
7. Sense their own internal conditions and use this in feedback loops.

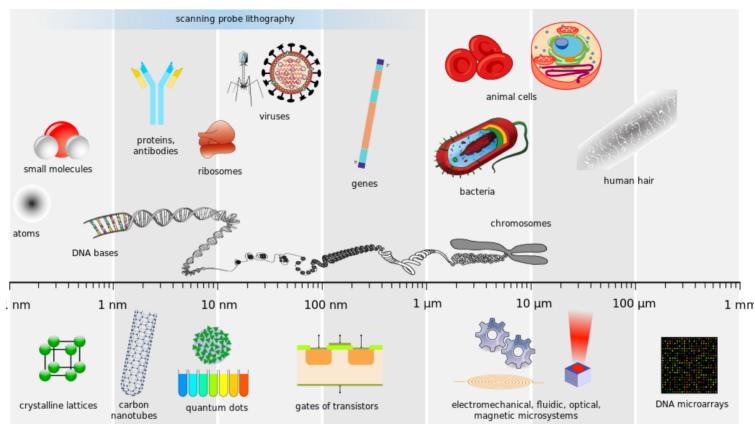
The first cell was described by Robert Hooke in 1665. **Cell theory** - the idea that all living things are made from cells - was proposed much later, in the 1800s. The invention of **electron microscopes** in the 1950s allowed us to see the *inner structure and workings of the cell*. This leads to...

### 3.2.1 The structure of cells

An overview of cell structure and relevant reference scales is shown below.



(a)



[<https://commons.wikimedia.org/w/index.php?curid=4326462>]

(b)

Figure 18: (a) A typical animal cell and (b) Logarithmic scale illustrating the size of biological structures and comparing them to several man-made technologies.

Key features include the **cell membrane, the nucleus and the mitochondria**, which we look at in more detail next.

### 3.2.2 The cell membrane

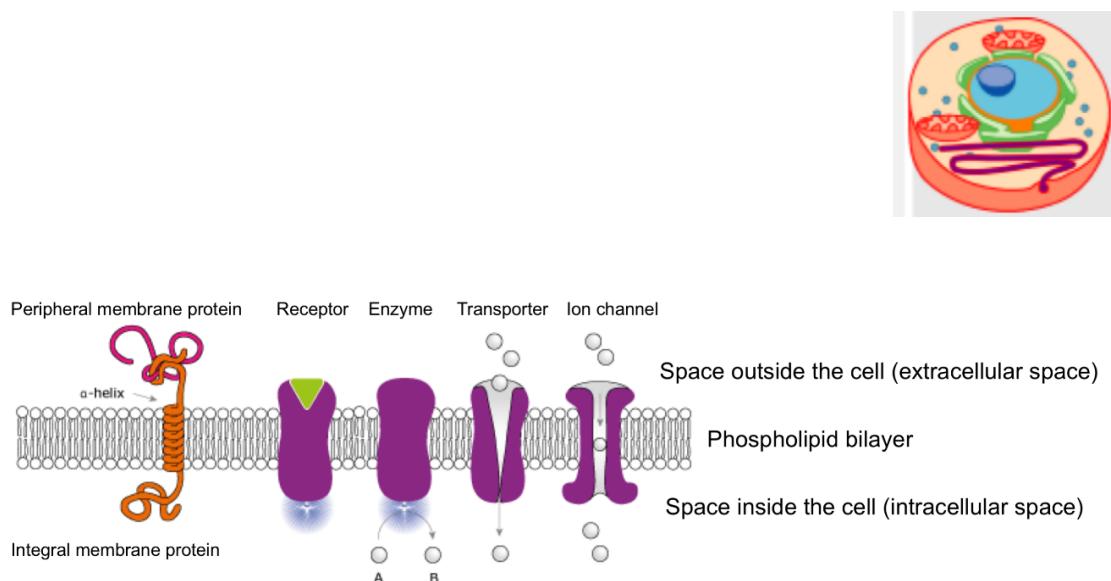


Figure 19: The cell membrane and membrane proteins within the phospholipid bilayer of a cell. Membrane proteins control the regulation of substances in and out of the cell and also communicate to other cells and sense the external environment. Oxygen can pass freely into the cell and carbon dioxide can pass freely out of the cell through the membrane. Glucose can only be transported into the cell using a transport protein. From <https://www.proteinatlas.org/humanproteome/secretome>.

### 3.2.3 The nucleus

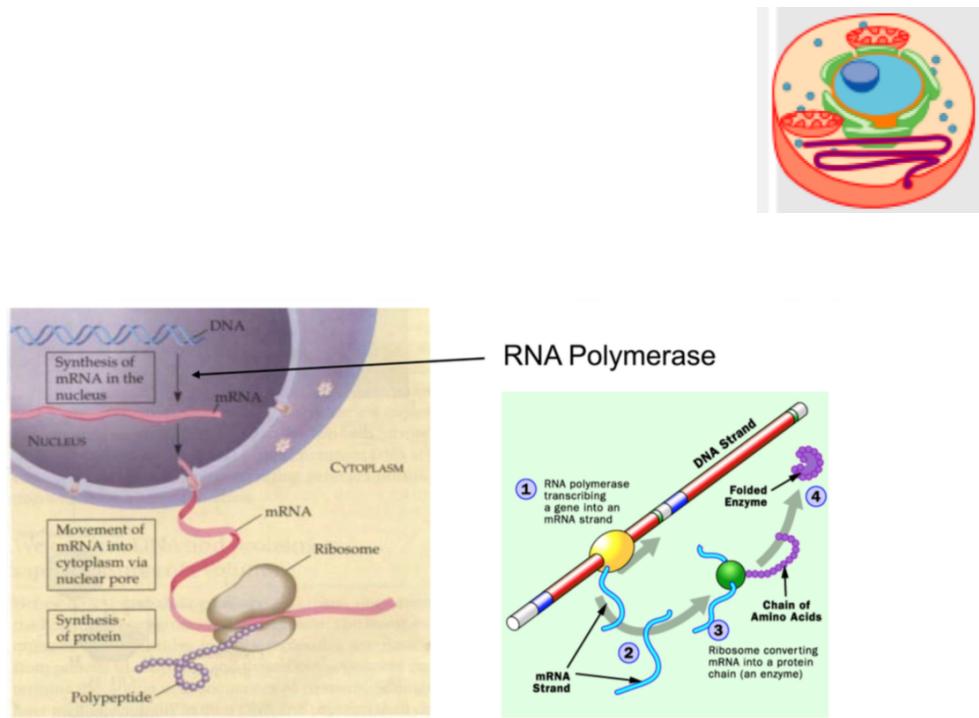


Figure 20: The nucleus and “the central dogma of molecular biology”, i.e. DNA (code/genotype)  $\rightarrow$  mRNA  $\rightarrow$  Protein (function/phenotype). From *Molecular Biology of the Cell* (4ed) via [www.ncbi.nlm.nih.gov/books/NBK26887/](http://www.ncbi.nlm.nih.gov/books/NBK26887/).

### 3.2.4 Mitochondria



Figure 21: The structure of a mitochondrion (this is the singular term for mitochondria). From *Molecular Biology of the Cell* (4ed) via [www.ncbi.nlm.nih.gov/books/NBK26887/](http://www.ncbi.nlm.nih.gov/books/NBK26887/).

**Example Problems 2: Structure and function of cells**

1. There are over 200 different cell types in the human body. Different cells have different proportions of organelles to suit their function. Which organelle would a human cardiac (heart) cell have in significantly greater number than a human skin cell? Why?
2. List two key functions required of the cell membrane and briefly explain the features that enable it to meet these requirements.
3. Mitochondria pump  $10^{21}$  protons ( $H^+$ ) per second during cellular respiration. This generates a voltage gradient of 180 mV across the 6 nm mitochondrial membrane. Calculate the voltage gradient across the mitochondrial membrane in terms of volts/m.

---

—**Answers**—

### 3.3 Animal energy consumption and measurement

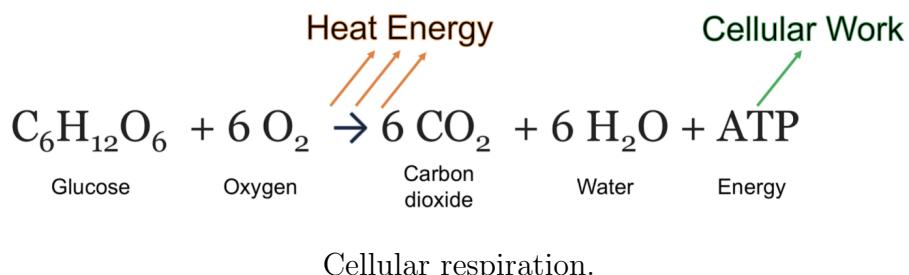
Or...food, energy and life!

**Food content:** food is primarily composed of the macromolecules:

1. Carbohydrate
2. Protein
3. Fat

(Macromolecules are ‘very large’ molecules,  $\sim$  1000s of atoms).

About 40% of the energy of food is converted to **cellular work**, and the rest to body heat, via **cellular respiration**. This is discussed in detail later, but illustrated below.



#### 3.3.1 Measuring energy

How can we measure how much energy is required for various animal (e.g. human) activity? In particular, **we can't burn or explode people** (well, we probably shouldn't...).

Instead, we can calculate this energy *indirectly*, via so-called **indirect calorimetry**. This takes into account:

1. The *consumption* of oxygen
2. The *production* of waste (carbon dioxide and nitrogen).

For example the **Weir equation** is

$$\text{Energy Expenditure} = 1.44[3.94V_{\text{O}_2} + 1.106V_{\text{CO}_2}]$$

where  $V_{\text{O}_2}$  is the volume of oxygen consumption and  $V_{\text{CO}_2}$  is the volume of carbon dioxide consumption. This can be measured using a setup like that shown in Figure 22.



Figure 22: Indirect calorimetry. (From <https://peakzonefitness.com/product/vo2-max-test/>.)

The upshot for use is that we can measure **energy input** (food) and **energy output** (activity).

The table below gives some useful data on food inputs and activity outputs.

### Example Problems 3: Energy and activity

1. A calorie is a unit of energy that is often found in older texts and is still common in food science. One calorie = 4.184 J, which is the energy required to increase the temperature of 1 g of H<sub>2</sub>O from 14.5 °C to 15.5 °C. Using

Substance	Energy yield		Form of Activity	Total energy expenditure (kcal.h <sup>-1</sup> )
	kJ.mol <sup>-1</sup>	kJ.g <sup>-1</sup>		
Glucose	2,817	15.6	Lying still, awake Sitting at rest Walking, level ground Sexual intercourse Biking, level ground Walking, uphill Jogging Rowing	77
Lactate	1,364	15.2		100
Palmitic acid	10,040	39.2		200
Carbohydrate	-	16		280
Fat	-	37		305
Protein	-	23		360
Ethyl alcohol	-	29		570
Coal	-	28		830
Oil	-	48		1440
			Maximal activity (untrained)	

Table 1: Heat released upon oxidation to CO<sub>2</sub> and H<sub>2</sub>O and total energy expenditure during some example activities, as measured using *indirect calorimetry*. (From notes by Thor Besier.)

the tables given, calculate the total energy expenditure (in J) following 20 mins of jogging, and compare this to 2 h of walking on level ground.

- Estimate how high a ladder could a 70kg person climb, fueled by a chocolate bar with the following nutritional content: 10g fat, 45g sugar, and 3g protein. Assume muscle is 24% efficient and obtain energy yield from the given tables.
- The average power output from a human labourer is 100 W. What does this equate to in terms of total energy per day (let's assume you can work for 24 hrs straight)?
- The energy density of fat is 37 kJ/g. A 70kg human might have  $\sim$  10kg of fat. What is the total amount of energy in our bodies that can be derived from fat?
- The energy density of a lithium-ion battery is 0.4 MJ/kg. What is the total energy that can be derived from a 10kg li-ion battery and compare this to

the equivalent energy derived from fat.

6. A 2017 model S Tesla can be purchased with a top-range 100 kWh battery. What is the total energy equivalent of this battery and how does this compare to the potential energy derived from fat from a human?

---

—Answers—

### 3.4 Gibbs free energy applied to biological systems

Recall that a spontaneous process can be thought of as, loosely, a change from a ‘less natural’ state to a ‘more natural’ state. E.g. for an *isolated* system is it ‘natural’ to move from ‘order’ to ‘disorder’, i.e. for **entropy to increase towards a maximum**.

For **open systems** the more natural principle is for the **Gibbs free energy to decrease towards a minimum**.

We recap some key facts below.

---

—Gibbs free energy—

---

---

### 3.4.1 Gibbs free energy and coupling

In a given process we need the **overall** process to be favourable. But individual steps/components can be unfavourable (when in isolation) as long as they are appropriately **coupled**. This is particularly true of *biochemical* reactions which are often highly coupled.

A chemical reaction is called **exergonic**, i.e. gives off energy, if it has  $\Delta G < 0$ . These are **spontaneous**.

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  $\Delta G$  refers to the **overall** change in free energy, not to the intermediate steps.

These ideas are illustrated below.

---

—**Coupled processes**—

---

---

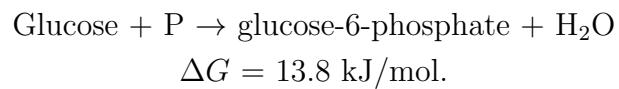
—Exergonic and endergonic reactions

---

---

**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



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—**

---

### 3.5 ATP: the energy currency of the cell

The big picture of this section is:

Food/Light  $\xrightarrow{\text{'bank'}/\text{store energy}}$  ATP  $\xrightarrow{\text{'spend'}/\text{use energy}}$  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—

---

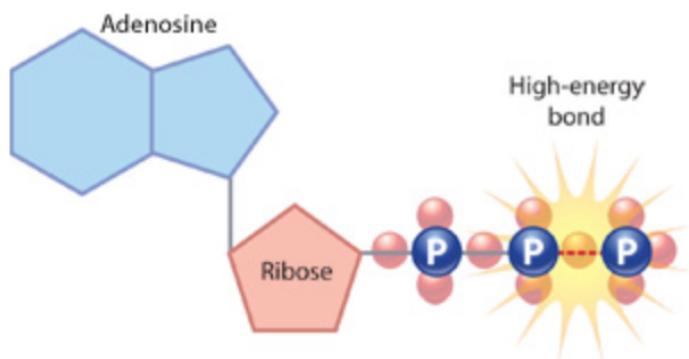
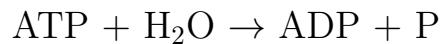


Figure 23: ATP molecule emphasising the high energy bond. (From <https://www.nature.com/scitable/topicpage/cell-energy-and-cell-functions-14024533>).

### 3.5.1 Hydrolysis of ATP

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



where ‘TP’ means *triphosphate* (three phosphate) and ‘DP’ means *diphosphate* (two phosphate).

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

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—

---

### 3.5.2 The ATP cycle

Cells are *constantly using ATP*. For example, a working muscle cell uses around  $10 \times 10^6$  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—

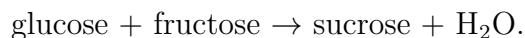
---

---

Making new ATP (from ADP etc) requires energy input, of course. This comes from the process Food  $\rightarrow$  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 are combined to form the disaccharide sucrose. This reaction is given by:



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

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

---

**—Answers—**

---

---

### 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—

---

### 3.6.1 Rate of reaction

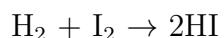
The **rate of reaction** is defined as the rate at which **product** is formed, unless otherwise specified.

#### —Rate of reactions—

---

#### Example Problems 6: Reaction rates

1. What is the rate of *consumption* of hydrogen gas in the following reaction when its concentration decreases by 0.2 mol/L in 10 s?



2. Is the rate the same if expressed in terms of HI? What is this latter quantity called?
3. The average rate of combustion of a candle made of paraffin is  $8.33 \times 10^{-4}$ . The molar mass of paraffin is 352.6 g/mol. You want the candle to burn for 4h. The candle is only sold in four sizes: 25, 50, 75 or 100 g. Which one is the smallest that you could use?

---

—Answers

---

---

**Biological reactions**, as opposed to combustion etc, tend to be

1. Slow (naturally)
2. Efficient
3. Highly controlled

How can we speed up reactions? One idea is motivated by the (kinetic) **collision theory**: a reaction requires high energy collisions to break bonds. So, for example,

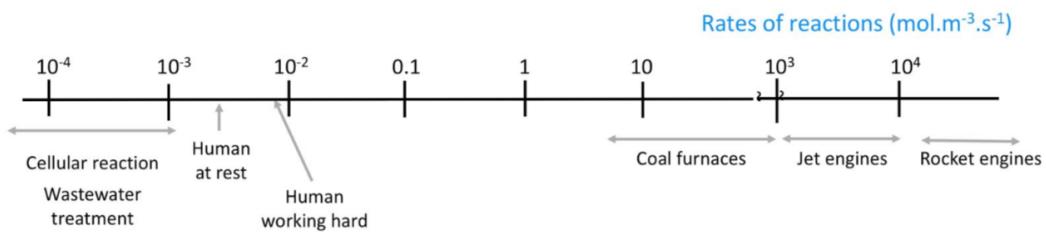


Figure 24: Typical rates of reactions. (From notes by Thor Besier.)

we might suppose that higher temperature  $\rightarrow$  more high energy collisions  $\rightarrow$  faster reaction.

While this is in fact true, we have an issue: **body temperature is stable** at around  $37^\circ\text{C}$ . We can't boil cells!

Instead, we turn to enzymes, a kind of biological catalyst.

### 3.6.2 Catalysts and enzymes

A **catalyst** is a molecule that **speeds up a reaction, without being consumed itself**. It functions to **lower the activation energy** of the reaction.

Nearly all cellular reactions are catalysed by enzymes. These enable increased speed, control and efficiency. Details are given below.

#### —Enzymes

---

---

**Enzymes are affected by**

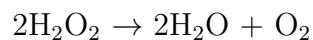
1. Temperature (best at body temperature)
2. pH (usually best at 7.4 but can vary)
3. Substrate concentration ( $\uparrow$ )
4. Enzyme concentration ( $\uparrow$ )
5. Enzyme inhibition ( $\downarrow$ )
  - (a) Competitive inhibition is when two or more molecules attempt to simultaneously bind to the active site.
  - (b) Non-competitive inhibition is when a molecule binds to another, non-active, site leading to a modification of the substrate's ability to bind to the active site.

---

**—Enzyme activity—**

**Example Problems 7: Enzymes**

Enzymes are biological catalysts. The enzyme ‘catalase’ catalyses the following reaction of H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide) in cells:



1. Draw a diagram showing free energy vs reaction progress for the above reaction. Include both uncatalysed and catalysed reactions, activation energies, reactants and products.
2. Various factors affect the activity of enzymes. Explain how surrounding temperatures of 20°C, 37°C and 50°C would affect the activity of catalyse.

---

**Answers**

---

### 3.7 Cellular respiration

Here we return to

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

In particular, we focus on the **first step of Food  $\rightarrow$  ATP via a particular metabolic pathway** known as **cellular respiration**. This ‘pathway’ consists of a *series of enzyme catalysed reactions*. Cellular respiration is one of the most important ways of extracting energy from food, but not the only way.

The more general term **metabolism** is used to refer to *all reactions involved in maintaining the living state* of an organism. Within this, **catabolism** refers to the *breakdown* of molecules for energy while **anabolism** refers to the *synthesis* of useful molecules.

While cellular respiration can make use of e.g. fats and proteins, here we focus on the key process of **conversion of glucose to ATP**.

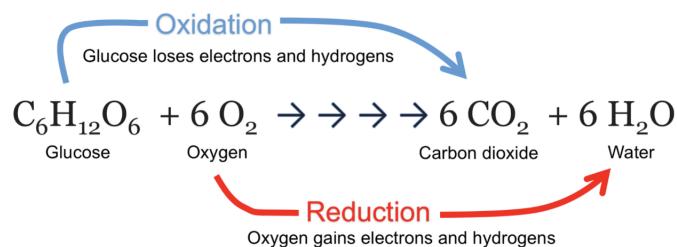
This reaction takes the form:



Some terminology: a **redox reaction** (reduction-oxidation) concerns reactions involving the **transfer of electrons**. A key mnemonic is OIL-RIG: Oxidation Is Losing Elections, Reduction is Gaining Electrons.

During cellular respiration:

1. Glucose is **oxidised** (loses electrons and hydrogen).
2. Oxygen is **reduced** (accepts electrons and hydrogen).



Cellular respiration as a redox reaction.

There are **three key stages of cellular respiration**:

1. **Glycolysis**: breakdown of glucose started.
2. **Krebs Cycle**: breakdown of glucose completed and carbon dioxide formed.
3. **Electron Transport**: energy from breakdown of glucose converted to ATP.

An overview is shown below; we will consider each of these in detail.

---

—NAD and FAD?

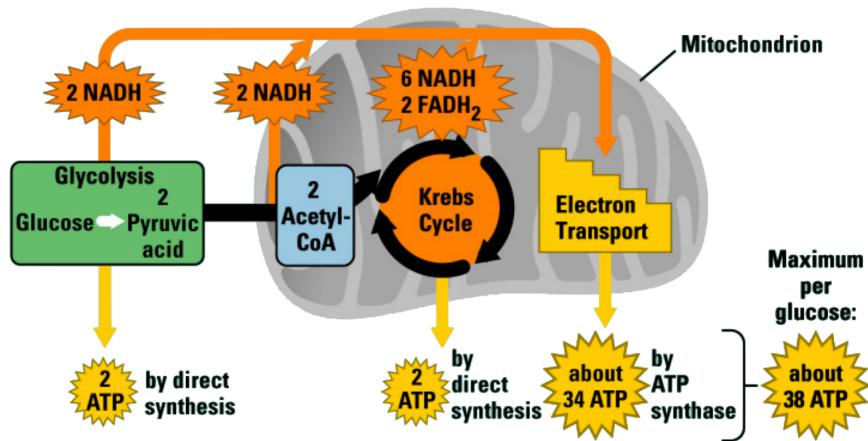


Figure 25: Stages of cellular respiration. During cellular respiration, 1 molecule of glucose creates  $\sim 38$  molecules of ATP. One cell can have 1000-2000 mitochondria producing many energy-rich ATP molecules.

### 3.7.1 Glycolysis

Glycolysis is a series of nine reactions in the cytosol of the cell that **begins the breakdown of glucose**. It took about 100 years to discover and elaborate the full pathway!

The **inputs and outputs** are illustrated below.

Initial 'splitting' of glucose, involving a series of 9 reactions

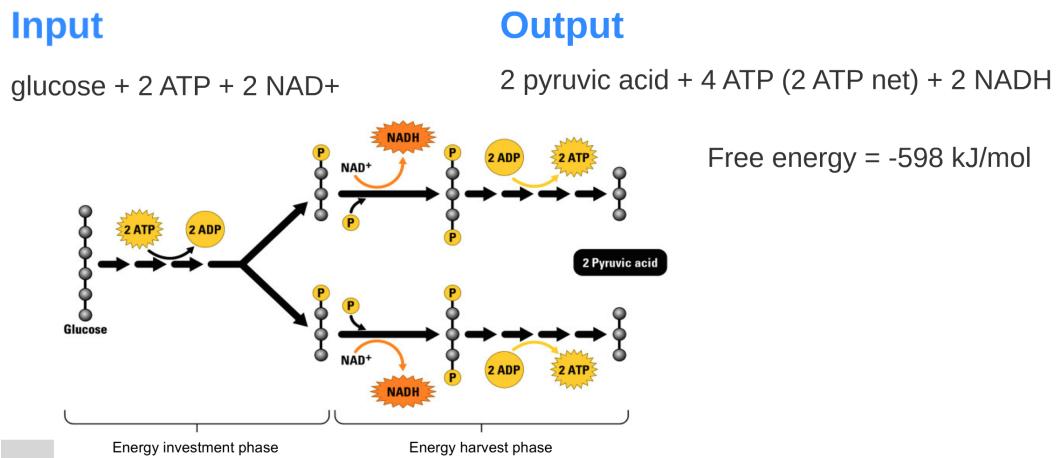


Figure 26: Glycolysis mechanism.

### 3.7.2 Krebs Cycle

Also known as the 'citric acid cycle' occurs in the mitochondria and completes the energy extraction from glucose

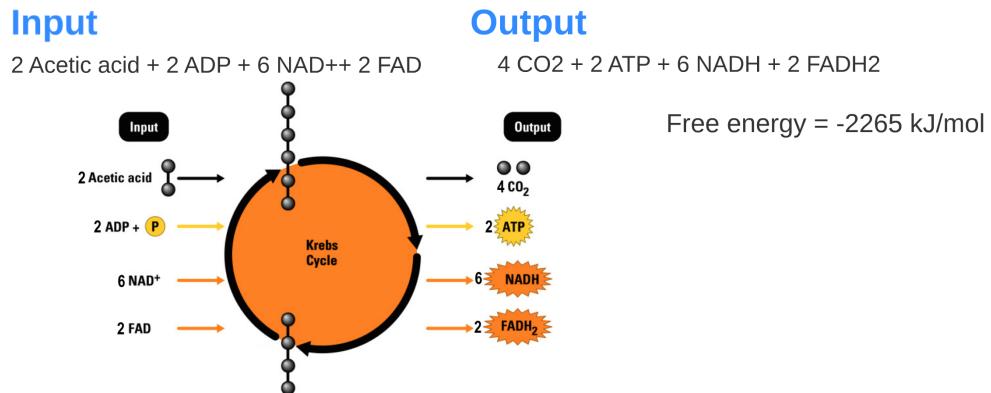
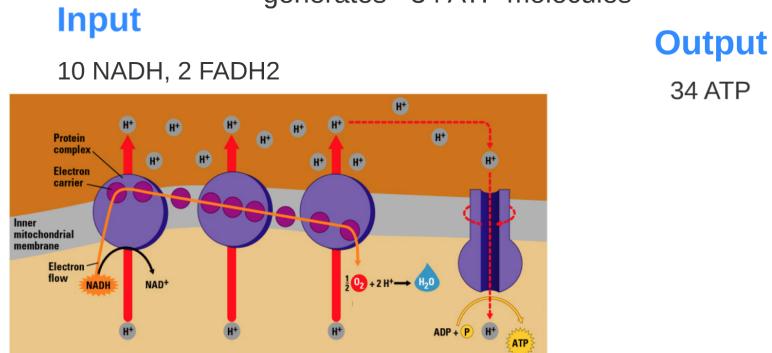


Figure 27: Krebs cycle stages.

### 3.7.3 Electron Transport

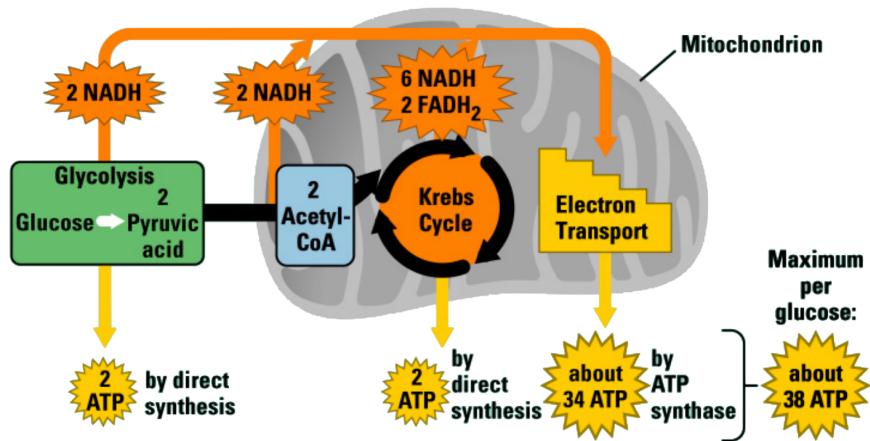
Most of the energy is now in the electrons within the carriers NAD<sup>+</sup> and FAD. The **electron transport chain** completes the process of cellular respiration and generates ~34 ATP molecules



Electron transport stages.

### 3.7.4 Cellular efficiency

Consider again the overall picture from before.



Stages of cellular respiration.

We can calculate the **efficiency** of the conversion of food to ATP energy.

—Cellular efficiency—

### 3.7.5 Just glucose?

No! Cellular respiration can use many different food molecules to generate ATP.

## Cellular respiration can use many different food molecules to generate ATP

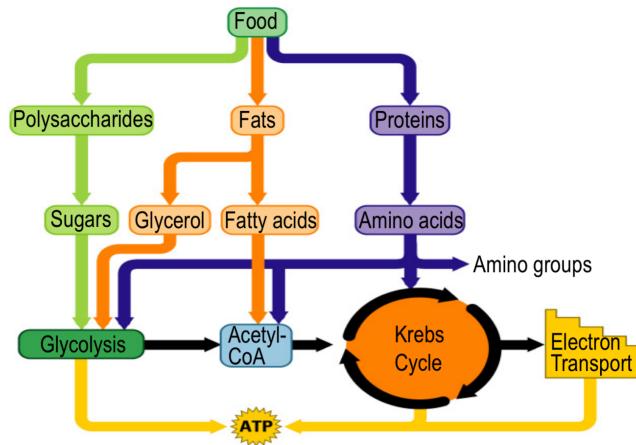


Figure 28: Alternative pathways for cellular respiration.

## 3.8 Fermentation

How about just cellular respiration? No again! For example the process of **fermentation** is an *alternative* way to generate ATP. In particular, while parts of cellular respiration require oxygen - i.e. are aerobic - fermentation does not.

While stage one of cellular respiration, glycolysis, **doesn't require oxygen**, it only produces 2 ATP (c.f. 38 ATP)!

**Fermentation allows glycolysis to continue** and can generate ATP without oxygen present, i.e. under **anaerobic conditions**.

---

### —Fermentation

---

For example, during intense exercise, **human muscle cells** may not receive enough O<sub>2</sub>. Fermentation then proceeds, and leads to the production of *lactic acid*. Note: lactic acid is not the cause of the burning sensation you might feel during intense exercise (actually, lactic acid tends to *counteract* this).

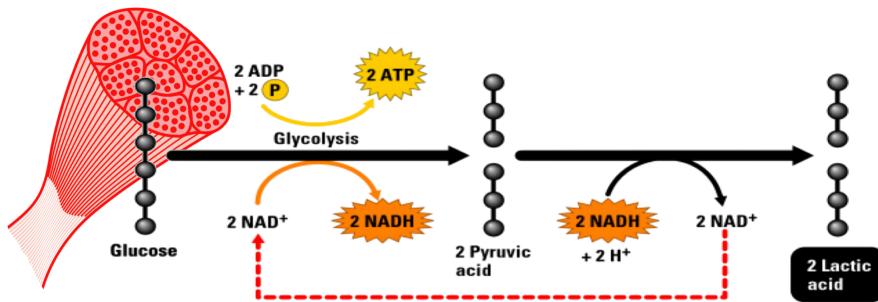


Figure 29: Human muscle cells. Oxygen is supplied to your muscles via the blood stream for aerobic cellular respiration to take place and make ATP. However, during exercise, the supply of oxygen can be insufficient and ATP must be made anaerobically, leading to lactic acid as a by-product.

**Micro-organisms/bacteria** (e.g. yeast) can perform *both* respiration and fermentation.

The ‘waste’ product of such processes are often the *desired* product: e.g. alcohol, biofuels etc.

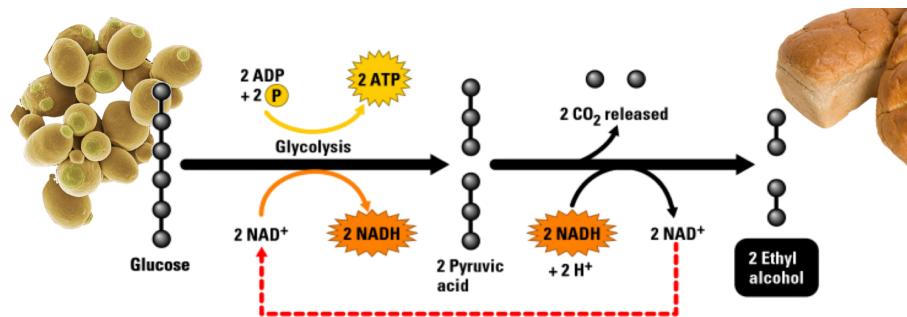


Figure 30: Fermentation processes in micro-organisms.

### Example Problems 8: Respiration and Fermentation

1. Which of the following TWO statements about respiration are TRUE?
  - A. Oxygen gas is reduced during cellular respiration.
  - B. Fermenting yeast cells produce lactic acid during bread making.
  - C. The Krebs Cycle produces citric acid.
  - D. Glycolysis requires an initial input of energy to split glucose.
  
2. Which of the following statements is FALSE with regard to the electron transport chain?
  - A. The electron transport chain occurs along the inner wall of the mitochondria.
  - B. ATP Synthase uses the energy of the hydrogen ion gradient to generate ADP from ATP.
  - C. Electrons are accepted by oxygen at the end of the transport chain.
  - D. Potential energy stored in the hydrogen ion gradient is released when the hydrogen ions re-enter the mitochondria.
  - E. The high energy electrons carried in NADH and FADH<sub>2</sub> are passed from molecule to molecule in the electron transport chain in a series of redox reactions.
  - F. ATP can also be generated in the absence of oxygen (i.e. anaerobic conditions), which involves the process of fermentation. Comment on the number of ATP molecules you would produce from just glycolysis alone, compared to aerobic respiration.

—Answers

---