Lecture Notes to

CHEM 154

Chemistry for Engineering

Winter Semester 2012

Walter Scott wscott@chem.ubc.ca

http://www2.chem.ubc.ca/personnel/faculty/scotty/index.shtml

UBC Chemistry Department

Acknowledgements

- Suzana Straus

http://www.chem.ubc.ca/our-people/profiles/suzana-straus

- Alexander Wang

http://www.chem.ubc.ca/our-people/profiles/yan-alexander-wang

- Geoffrey Herring

http://www.chem.ubc.ca/our-people/profiles/geoffrey-herring

- These lecture notes were written on an ubuntu linux system (http://www.ubuntu.com) in LaTeX using the `seminar`, `graphicx` and `animate` packages.

- Diagrams were drawn using the Xfig (http://www.xfig.org/) program.

- Images were manipulated using the GIMP (http://www.gimp.org).

- Function plots and animations were made using the **gnuplot** program (http://www.gnuplot.info/).

- Pictures of molecular systems were made using the UCSF Chimera molecular modelling system (http://www.cgl.ucsf.edu/chimera/) and Jmol (http://jmol.sourceforge.net/).

Contents

0 – Organisational Technicalities

1 – Introduction and Overview

2 – Electrons in Atoms and Periodicity

3 – Shape and Intermolecular Interactions

4 – Bulk Properties of Matter

5 – Solid State Structures

6 – Electronic Structure and Bonding

7 – Principles of Chemical Equilibrium

8 – Thermochemistry and Thermodynamics

9 – Electrochemistry

This page intentionally left blank

This page intentionally left blank

0– Organisational Technicalities

0.1 Contact Information

Office	**none**
Phone	**none**
email	**wscott@chem.ubc.ca**

0.2 Bibliography

- The **required text book** for this course is:

New Custom Edition for University of British Columbia for Chemistry 154 (ISBN 13: 9781256711445) from General Chemistry (10 ed.): Principles and Modern Applications by Petrucci, Herring, Madura and Bissonette.

$\Rightarrow$ Buy this at the UBC Book shop.

NOTE: You will be required to fulfil reading assignments from the text book.

- CHEM154 Laboratory Manual, by Nussbaum et al.,
- These course notes. . .
- Go online!

0.3 Electronic Courseware

- The course notes in pdf format can be found online:

http://elearning.ubc.ca/connect/

0.4 Laboratory Sign-Up

NOTE: In charge of CHEM154 Laboratory : Dr Sophia Nussbaum.

- Lab Check-In is Sept 10 or 12. Please come to your assigned lab section that week. Lab students will be split into three groups, A, B and C, within each section.
- On Friday Sept 7th we will post lists on the laboratory web site

`http://www2.chem.ubc.ca/courseware/154/`

informing you whether you are in Group A, B or C.

- The three groups will check into the lab at different times during the Check-In Week (Sept 10 or 12). Check-in times will be posted as well.
- Please purchase the CHEM154 lab manual at the bookstore.

BRING IT WITH YOU TO CHECK-IN.

- All students must view an on-line Lab Intro Presentation before coming to the lab for Check-In. The Lab Intro explains many confusing lab issues, and takes about 20 minutes to read. The presentation is located at:

http://www2.chem.ubc.ca/courseware/154/

- Please watch the laboratory safety video:

http://www2.chem.ubc.ca/courseware/DZEorganiclabCD1/cd1/cd1-intro1.html

- If you still have questions after watching the Lab Intro and the Safety movie, contact the lab director at `freshman154@chem.ubc.ca`.

Lab Coats

Students are required to wear lab coats.

- Students who do not wear a lab coat will be discharged for the period and will be given a total mark of zero for the missed laboratory.
- Suitable lab coats can be purchased in Chemistry D211 (at discounted prices) or in the Bookstore. The lab coats MUST be 100% cotton.
- Room D211 will be open at the following times:

Wed Sep 5 - Fri Sep 7:	9 am to 3 pm
Mon Sep 10 - Fri Sep 14:	9 am to 2 pm

- Safety glasses can also be purchased in Room D211 or in the Bookstore.
- Lab coats and glasses are not required for check-in.

0.5 Things to Do Right Now

- Get a Campus Wide Login (CWL) to access online resources.

See **`http://it.ubc.ca/service_catalogue/login-passwords/campus-wide-login`** for how to do this.

- Buy the following:

① text book

② CHEM154 lab manual

③ calculator: SHARP EL-510R

④ lab coat

⑤ safety glasses

- Read the Lab Intro Presentation
- Watch the Lab Safety Video
- Sign up for CHEM154 Lab

0.6 Scotty's Tips for Success

NOTE: There are differences between learning at the High School and University level.

High School	UBC
small classes	big classes
individual attention paid to a student	teaching to the masses
work is exactly prescribed	success depends on your motivation

NOTE: How well you adapt to the new requirements is a major factor in your success at UBC. You must learn to use your time efficiently.

NOTE: The exams are a big hurdle to overcome. Use the *whole semester* to prepare for them.

0.7 Examination Policy

- The final mark will be determined by the following table:

Grading in percent	
Mid-term exam	25
Quizzes	5
Final Exam	50
Laboratory	20

NOTE: **All exams and quizzes will be closed-book.**

NOTE: **Only non-programmable electronic calculators are allowed.**

- E.g. the SHARP EL-510R at the UBC book shop.

NOTE: Students must bring their **Student ID** to the midterm and final exams.

① Quizzes: There will be online quizzes throughout the term to reinforce the learning goals. You will be assigned reading assignments from the text book, after which you answer the quiz questions online.

- The quizzes serve two purposes:

① for you: show you where you stand.

② for me: identify problem areas that need further clarification.

② Midterm Exam.

- This will take place on **18th October 2012 at 6pm**.

(a) This exam is worth **25%** of the final mark.

(b) **There will be no make-up midterm exam**. Students who miss the mid-term exam:

- **with** appropriate medical excuse (doctor's note): the percentage of the missed exam will be added to the final exam (i.e. final exam worth 75%).
- **without** appropriate excuse: 0% recorded as midterm mark.

③ Final Exam

(a) This exam is worth **50%** of the final mark.

(b) The final exam will cover **all course material**.

(c) Submitted final exams can only be viewed if permission is obtained from the Dean of Science Office.

(d) UBC policy will be followed during writing of exams.

NOTE: Students who miss the final exam because of medical, emotional or other problem must inform the Dean of Science Office as soon as possible. Only students having a reason for their absence which is **acceptable to the Dean of Science Office** will be eligible to take a deferred exam.

④ Laboratory

(a) The laboratory section will be worth **20%** of the final mark.

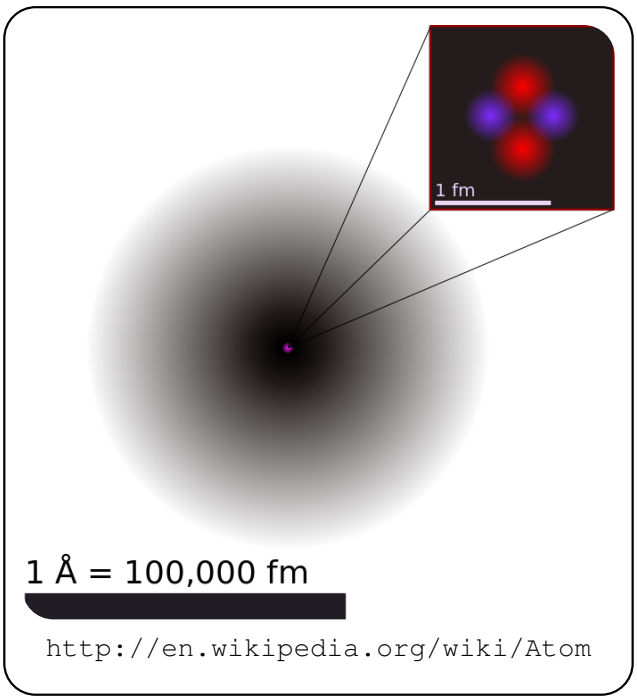
(b) However, you **must pass BOTH** the laboratory and lecture sections to obtain an overall passing grade.

1– Introduction and Overview

AIM: Provide overview of the course and introduce some key concepts.

BACKGROUND: All material is made out of atoms, which consist of protons and neutrons in a nucleus at the centre surrounded by electrons.

EXAMPLE: Helium Atom

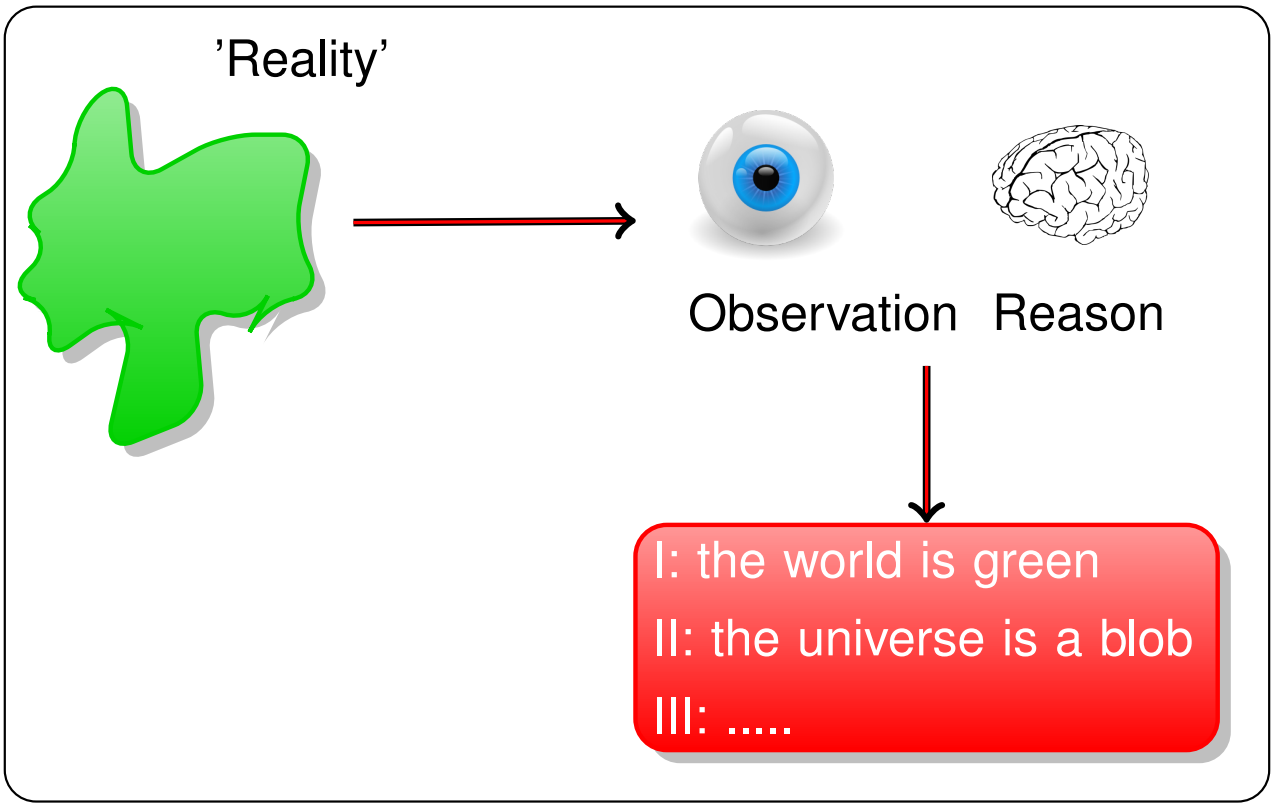


- Nuclear Physics: modification of the nucleus (not in this class).

Chemistry is the Science of pushing electrons around.

QUESTION: What is a Scientific Theory?

ANSWER: set of concepts and postulates.



- **Karl Popper: a theory is Scientific iff it is falsifiable.**
- If new observations disagree with a theory, we have to:

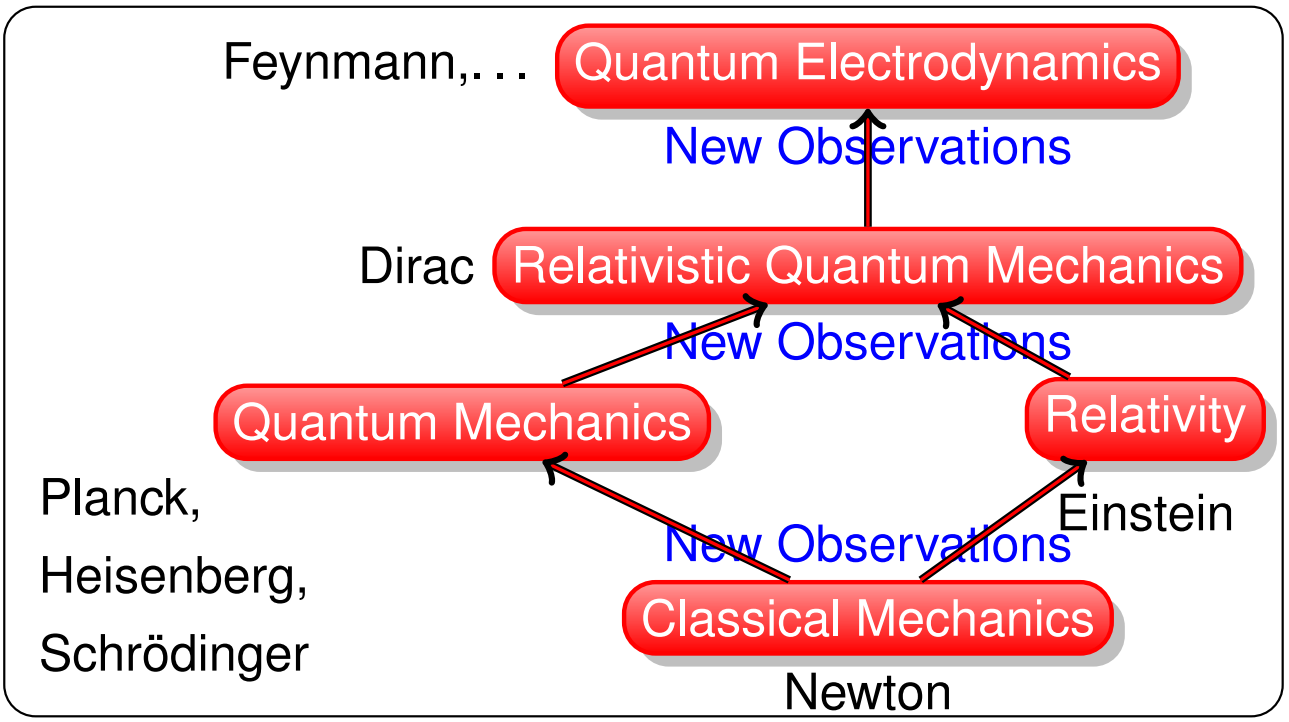
① reject it;

② modify it;

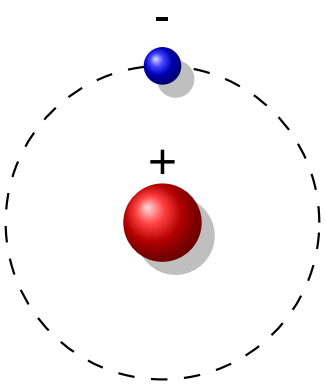
③ admit its applicability is restricted.

NOTE: In Science, there is no 'absolute truth'; we are constantly refining our Scientific theories in an iterative process. We end up with a **hierarchy of theories**.

EXAMPLE: Mechanics



NOTE: Classical Mechanics cannot explain the existence of atoms:



- There would be a 'fatal attraction' between the oppositely charged nucleus and electrons!

NOTE: In order to properly apply a theory, a Scientist or Engineer must understand the theories (especially their limits!).

EXAMPLE: We are presented with two theories:

① The Earth is flat.

② The Earth is a sphere.

QUESTION: Which theory is correct?

ANSWER: Both can be, depending on the application of the theory.

- If travelling across campus $\Rightarrow$ Earth is flat.
- If travelling across continents $\Rightarrow$ Earth is a sphere.

$\Rightarrow$ The work of a Scientist or Engineer is to know which theory to apply or which approximation is valid in a given situation.

QUESTION: How high a level of theory do we need in (Bio)Chemistry?

ANSWER:

① For behaviour of matter:

- Classical & Quantum Mechanics sufficient
- Deal with large number of particles $\Rightarrow$ theories of Statistical Mechanics & Thermodynamics

EXAMPLE: 1 mole of water weighs 18g and has $N_A \approx 6.0 \times 10^{23}$ (Avogadro's number) water molecules.

② For behaviour of light:

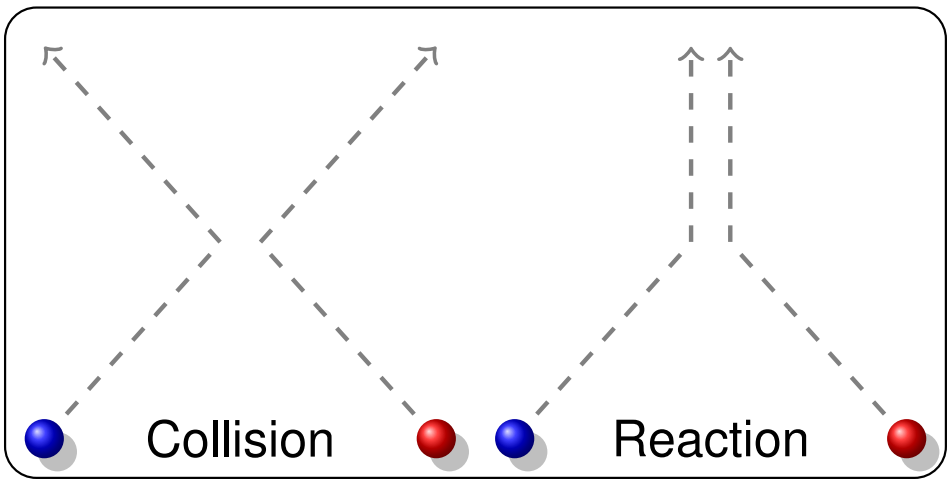
- Maxwell's Equations (not in this class)
- Classical & Quantum Mechanics

NOTE: Maxwell's Eq. not to be confused with Maxwell's Relations: 2nd year Thermodynamics.

NOTE: Quantum Mechanics (de Broglie): wave-particle duality: there is no real difference between waves and particles.

NOTE: Atoms can be combined to form molecules.

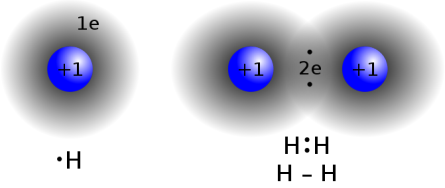
- When atoms are 'far away' from each other: they attract each other (Van der Waals forces).
- When they come close, they repel each other due to the repulsion of the electron clouds.



- If two atoms (or molecules) collide together sufficiently fast (and in the correct orientation to each other), the electron-electron repulsion can be overcome

$\Rightarrow$ we get a **chemical reaction** and the original molecules can be transformed into other ones.

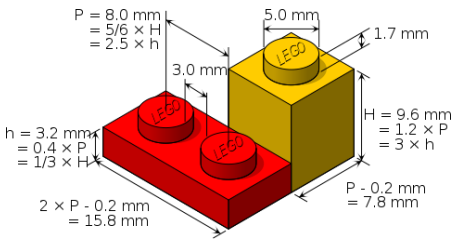
⇒ a **covalent bond** between the atoms can be formed (or broken): the electrons now can move freely between all atoms of the molecule, binding them together.



http://en.wikipedia.org/wiki/Covalent_bond

NOTE: Even with a small number of different atom types, you can create a very large number of different molecules.

ANALOGY: With many lego blocks of only a few types, you can build many different things.



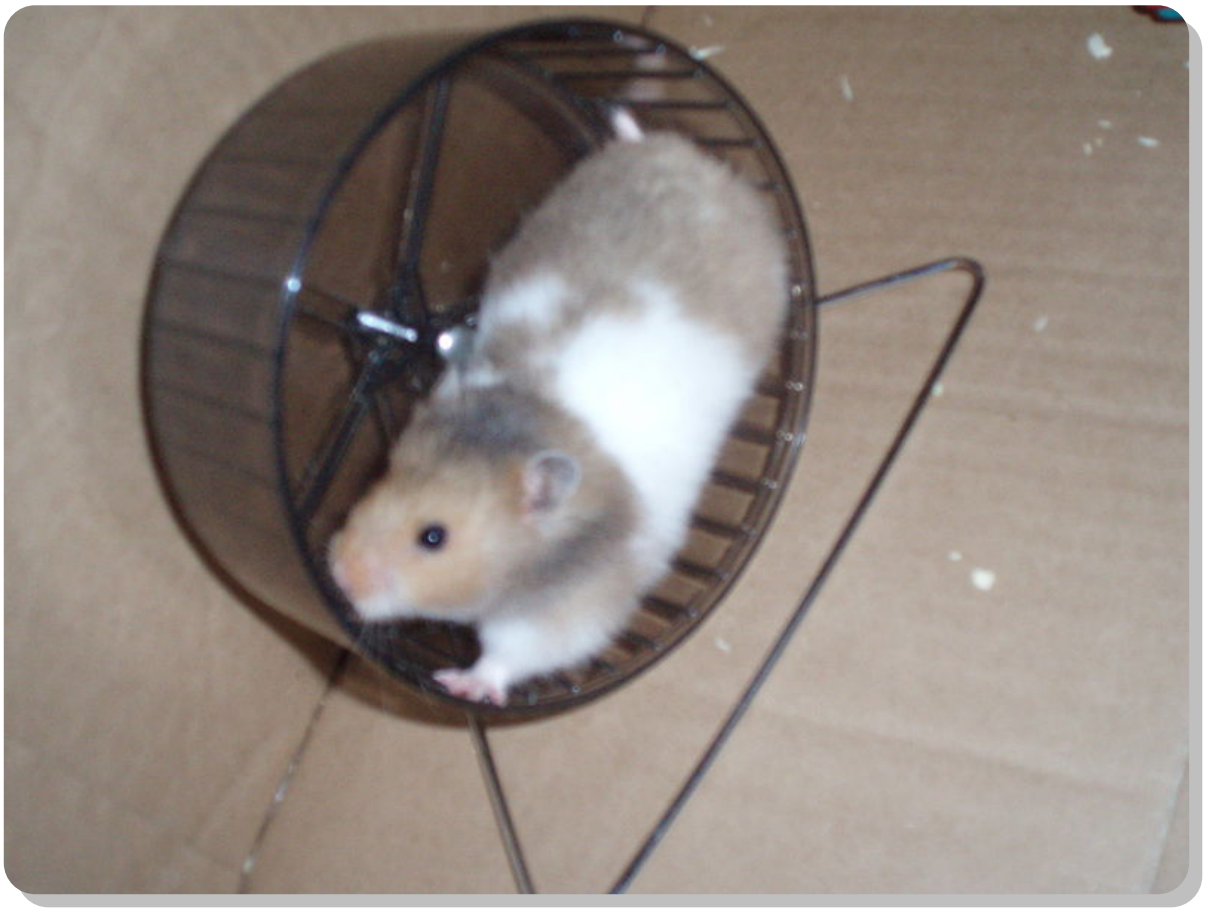
http://en.wikipedia.org/wiki/Lego

- In this class, we will spend a lot of time looking at the fundamental properties of atoms and molecules.

Thermodynamics

BACKGROUND: For centuries, Humans have devised tools and machines to help them in their work.

- For a long time, these machines were powered by converting **one form of motion into another**, e.g. by using wind- and watermills, or animals:



Melon247 http://www.wikipedia.org

NOTE: Fire was used for cooking, and to produce heat and light, but not for producing motion....mostly:

- Hero of Alexandria (10-70 AD) created a steam powered toy, the Aeolipile

Aeolipile replica made by K. Crisalli

http://en.wikipedia.org/wiki/Aeolipile

- It was not until the Industrial Revolution (early 1800's) that saw the development of heat engines, that **convert heat into motion**.
- This motivated the development of Thermodynamics (Thermos: heat, Dynamos: movement), initially as an engineering discipline.
- Later, this grew into a scientific theory that includes any form of **interconversion of energy** and transformation of states of matter.

EXAMPLE:

① Steam engines, Internal combustion engines

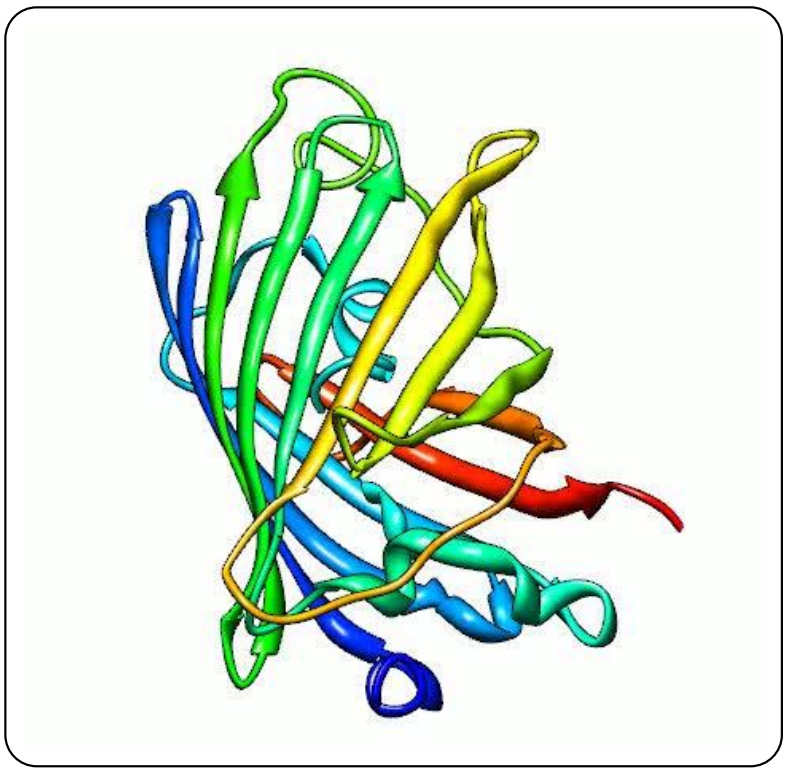
② (Steam) turbines (power plants)

③ Refrigerators

④ Chemical reactions

⑤ Biological systems (Cells, Enzymes)

EXAMPLE: The Green Fluorescent Protein (GFP) can be used as a marker in biological systems.



- All known protein structures are found in the Protein Data Bank, **http://www.pdb.org**. Have a look!

⑥ Weather systems (storm system, tornado, Chinook effect)

⑦ Nuclear decay & Radiation

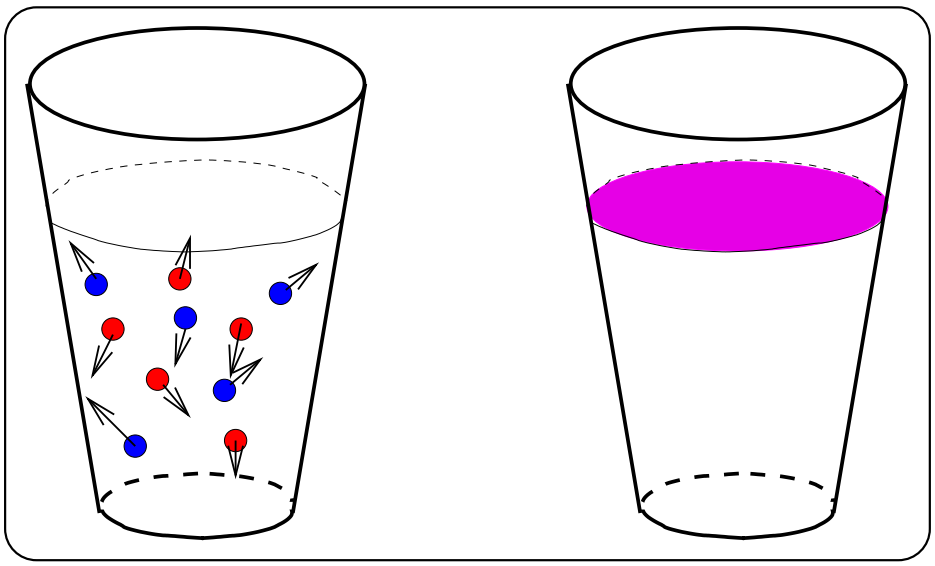
1.1 Micro- & Macroscopic Views of Matter

- In this class,

① Macroscopic means 'at the human scale'

② Microscopic means 'at the atomic or molecular scale'

EXAMPLE: A glass of water



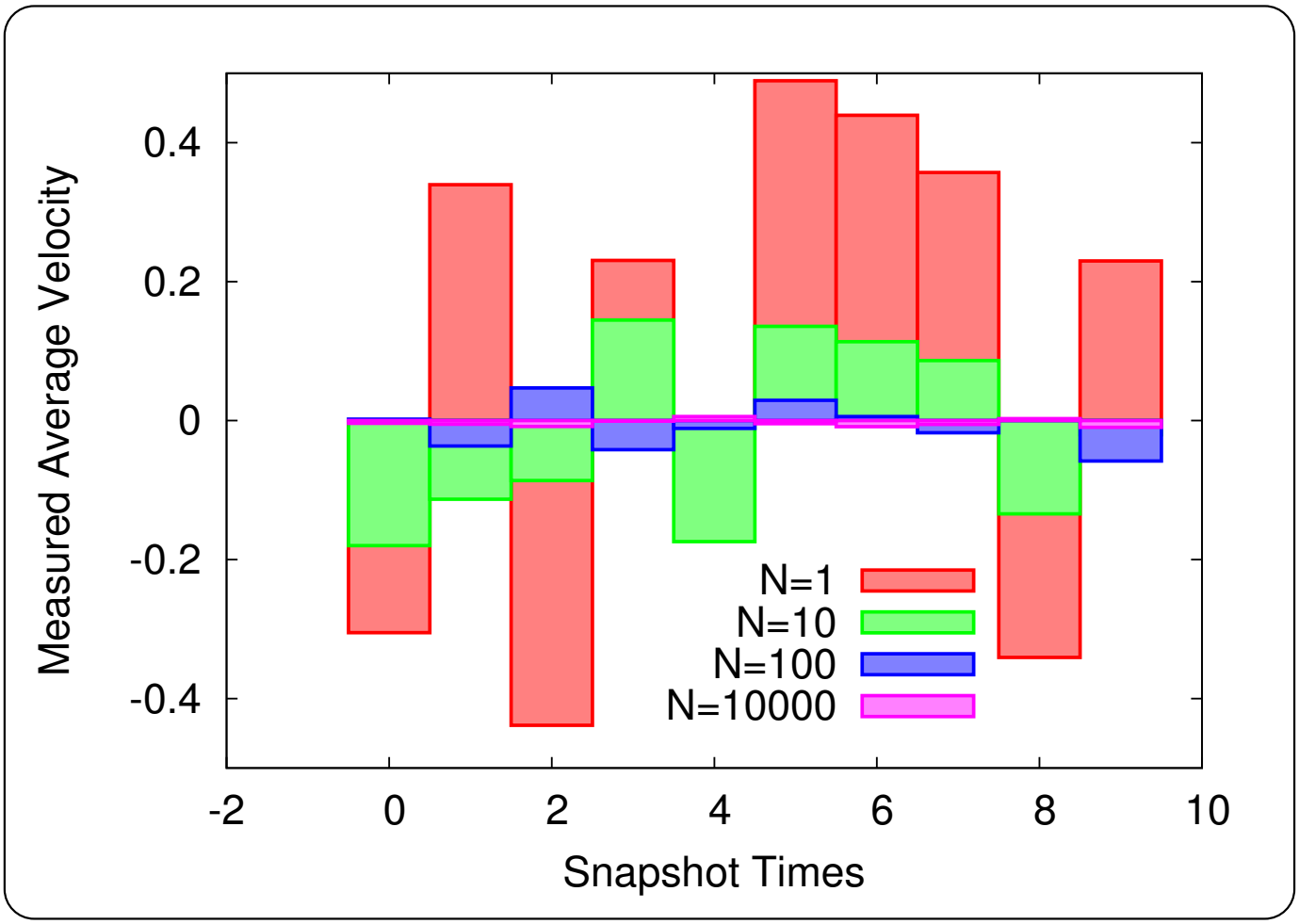
- There is a large variation in particle speeds (microscopic state) at any time, but overall (macroscopically) the fluid is at rest.

NOTE: It turns out that '**large numbers are good**' because statistics only work well for large N.

- The velocity distribution of the molecules is a Gaussian curve centred around zero. The 'width of the curve' (r.m.s. uncertainty, σ) decreases as the number of molecules increases.

EXAMPLE: Lets imagine a simple model system in one dimension. The particle velocities can fluctuate uniformly in the interval $[-0.5, 0.5]$.

- We let the system evolve freely and measure the average particle velocity at specific 'snap shots'. The deviation from zero measured will be larger for smaller system sizes:



$\Rightarrow$ There are so many molecules in a glass of water that the macroscopically observed average temperature fluctuation is too small to be observed.

$\Rightarrow$ macroscopically, we say that the water 'has a temperature of XX degrees'

1.2 Central Concepts in Thermodynamics

NOTE: There are **two central laws** in Thermodynamics:

> 'Die Energie der Welt ist konstant.
> Die Entropie der Welt strebt einem Maximum zu.'
> 'The energy of the universe is constant.
> The entropy of the universe tends to a maximum.'
> Rudolph Clausius (1865)

- We will discuss these in great detail later in this course, but for now intuitively:

① Energy E, U: easy to understand (Mechanics). Units: Joule.

② Entropy S: much less familiar in daily life. Units: $\frac{\text{Joule}}{\text{Kelvin}}$

QUESTION: How can we begin to understand Entropy?

EXAMPLE: A central question in the design of heat engines was concerned with the **maximum efficiency** possible.

- This is a difficult problem for heat engines because max. efficiency is determined by **two factors**:

Engine Type	Max. Efficiency governed by
electromechanical	energy conservation
heat engine	energy conservation 'Entropy always increases'

ANSWER:

- Engineers discovered that:

① Energy as heat is somehow 'less useful'; by spreading out energy among all atoms of a material, not all of it can be retrieved for useful work.

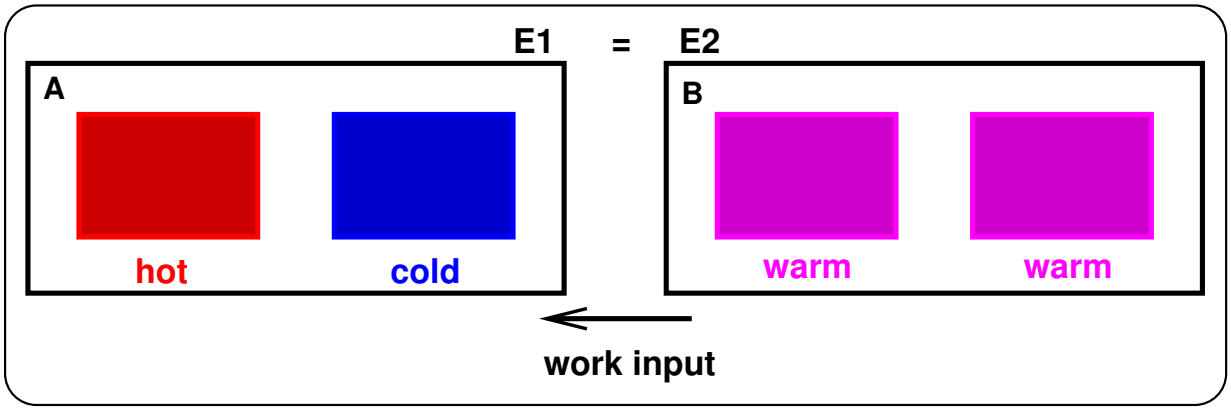
② Heat energy is more useful when there are big temperature differences.

EXAMPLE: A low temperature difference (Low Delta T, or LTD) Stirling engine. This engine will run on a temperature difference of 4° C.

American Stirling Company

http://www.stirlingengine.com/

③ Equilibration between hot and cold bodies is **irreversible**.



The system will not *spontaneously* move from state B to state A. We must input work to return to state A.

NOTE: The spontaneity of thermodynamic processes is determined by changes in both **energy** and **entropy**.

$\Rightarrow$ It is convenient to combine these into one measure called the **free energy**.

① For constant T and V:

- The Helmholtz free energy:

$$F = U - TS\,, \tag{1.1}$$

where U is the inner energy.

② For constant T and P:

- The Gibbs free energy:

$$G = H - TS \tag{1.2}$$

$$= U + PV - TS\,, \tag{1.3}$$

where H is the enthalpy (units: Joule).

NOTE: The modern convention is to leave out the expression 'free', i.e. 'Gibbs free energy' is simply called 'Gibbs energy'.

QUESTION: Why is this useful?

ANSWER:

① The free energy is a measure of the maximum amount of energy that can be extracted from the system. ('Free' meaning we can access that part of the energy).

② A thermodynamic process $A \mapsto B$ is only spontaneous iff the change in free energy is negative:

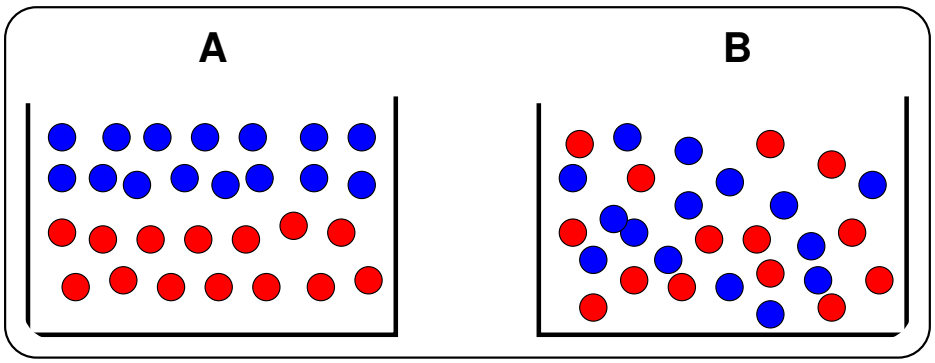
$$\begin{aligned} \Delta F_{AB} &= F_B - F_A && (1.4) \\ &= \Delta U - T\Delta S && (1.5) \\ &< 0\,. && (1.6) \end{aligned}$$

NOTE: Favourable for a process to be spontaneous is when:

① Energy (Enthalpy) **decreases**: $\Delta U < 0$

② Entropy **increases**: $\Delta S > 0$

EXAMPLE: Mixing of two fluids. State A: unmixed fluids. State B: mixed fluids.



NOTE: Entropy always wants to 'mix things up' (entropy increases, which lowers the free energy).

① milk and coffee: $\Delta U < 0$ and $\Delta S > 0$
- entropy dominates $\Rightarrow \Delta F < 0$

$\Rightarrow$ the fluids mix spontaneously

② oil and water: $\Delta U > 0$ and $\Delta S > 0$.
- unfavourable ΔU dominates $\Rightarrow \Delta F > 0$

$\Rightarrow$ the fluids do not mix spontaneously