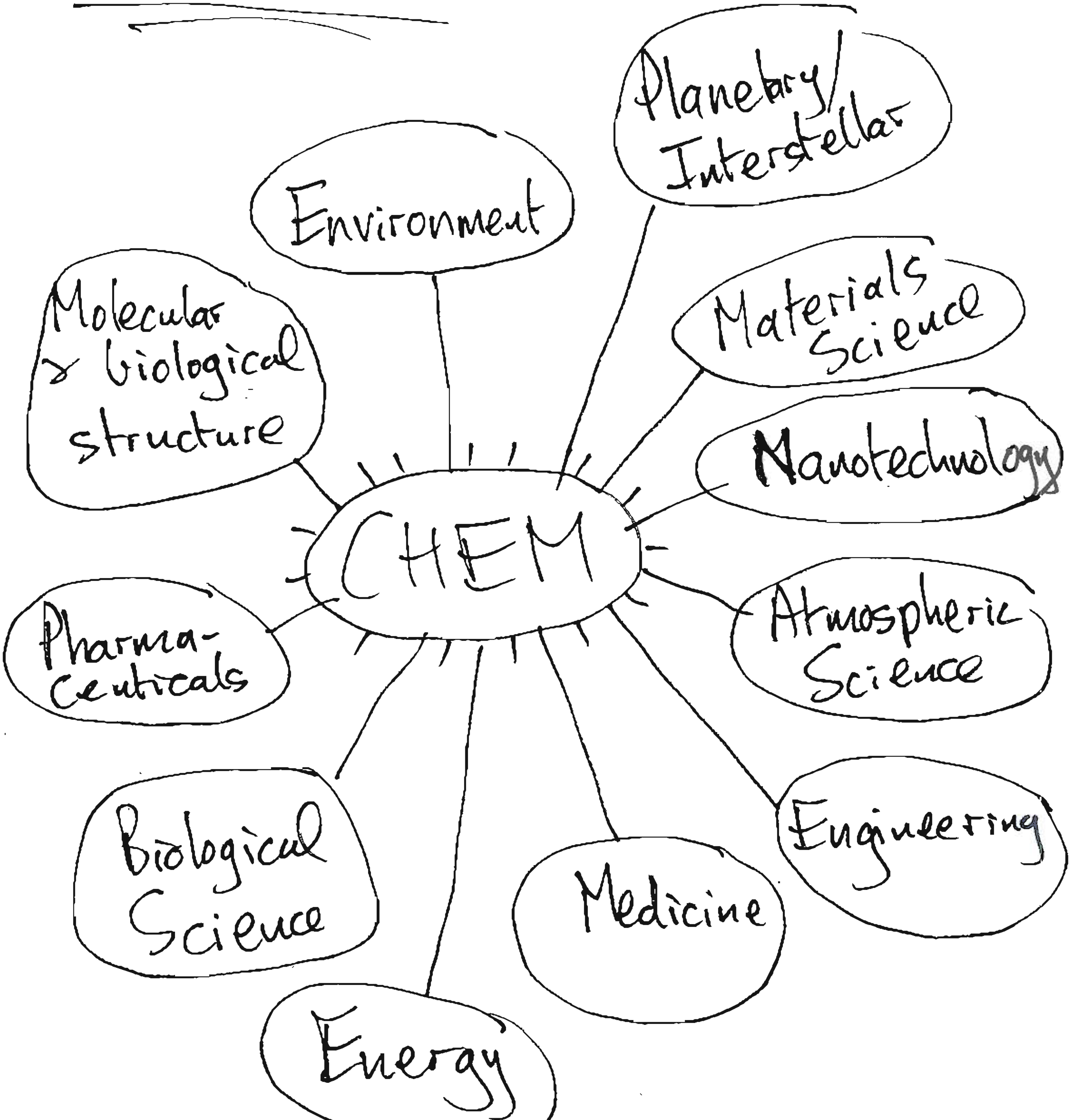
CHEM * 1050


CHEM
Environment
Planetary/ Interstellar
Materials Science
Nanotechnology
Atmospheric Science
Engineering
Medicine
Energy
Biological Science
Pharma-ceuticals
Molecular & biological structure

CHEM *1050

MICROSCOPIC WORLD

Atoms, molecules
Bonding, Structure
Spectroscopy
Quantum mechanics

Differential equations
Matrix algebra

⇕

Statistical methods

MACROSCOPIC WORLD

Bulk Properties
Solution Equilibria
Thermodynamics
Electrochemistry
Kinetics

Calculus

THERMODYNAMICS

- the science of the interconversion of different forms of energy

  e.g heat, mechanical work, electrical work, chemical energy. etc.

- an essential foundation for understanding physical and biological sciences
- at the centre of any physical description of living matter

Key questions

1. Interconversion of energy – how, why, what, etc.
2. Is a particular rxn. possible?
3. How much useful work can be obtained from a rxn.?

(2) 4. Can we understand chemical equilibria?

THERMOCHEMISTRY (Chapt. 6)
(a subset of thermodynamics) and 19.1 — 8 Ed; 18.1 — 9 Ed

Chemical reactions involve a transfer of energy between the system and the surroundings

A few definitions

(1) The "SYSTEM"

- the thing under observation, e.g. an engine, an electrical cell, a rx. in a flask ...

The "system" can be:

Open – both mass and energy may leave and enter.

⇒ Closed – energy can be exchanged
– no mass can enter or leave

Isolated – neither mass or energy may enter or leave.

(2) The SURROUNDINGS are the rest of the Universe

(3) The STATE of a system is characterised by a set of variables, e.g. P, V, T, n etc. – these are STATE VARIABLES or STATE FUNCTIONS

These can be classified as either:

Intensive	or	Extensive
Independent of size of system.		Proportional to size of system
e.g. P, T, ...		e.g. mass, V, n, ...
		U
		H
		S
		G

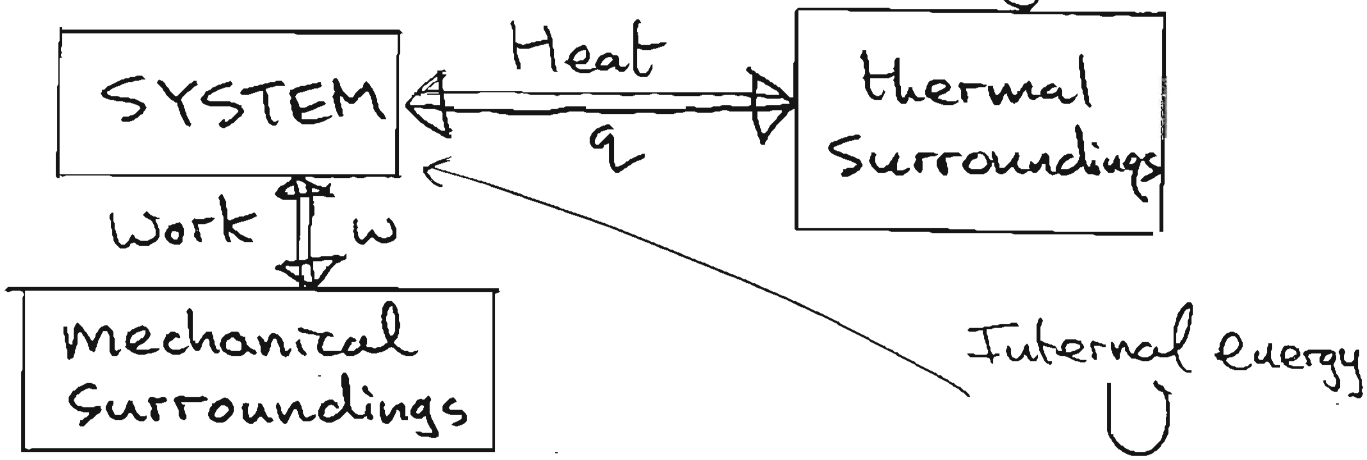
(4)

ENERGY TRANSFER

We can transfer energy in and out of a system, with the result that the internal energy of the system, U (sum of KEs and PEs) may be changed.

Two ways - either as HEAT (q) or as WORK (w).

[Another way is by adding or removing MASS
Not encountered in "closed" systems]



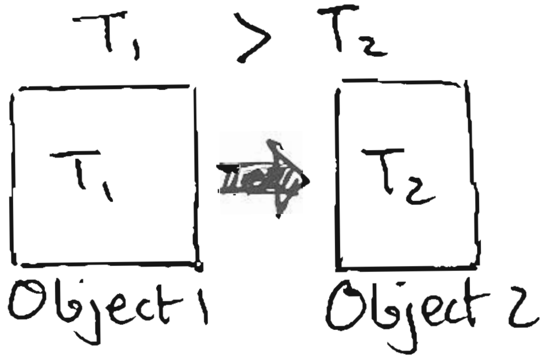
We can change the internal energy, U, by any combination of q and w

$\therefore U_{final} - U_{initial} = \boxed{\Delta U = q + w}$

- a statement of the conservation of energy. 1st law of Thermodynamics.

Heat energy ... heat transfer ... temperature

$\Delta U = q + w$ tells us that we cannot create or destroy energy, but it can be transferred in and out of the system.



- temperature – an indication of heat content.
- Objects at same T do not exchange heat energy.
- If T's are different, energy (heat) flows from high T object to low T object, until thermal equilib. is reached.

Energy flow determined by molecular motions.

e.g. chemical reactions may release heat to the surroundings

$$CH_4(g) + 2O_2(g) \Rightarrow CO_2(g) + 2H_2O(\ell)$$

- a combustion reaction
- heat is released ∴ EXOTHERMIC Rx.

(arises because of differences in bonding energy of reactants and products)

For other rxs. heat may be absorbed
- ENDOTHERMIC

(we will return to this when looking in detail at chemical reactions)

Note:

The amount of heat depends on the size of a system.

i.e. an EXTENSIVE property, like, e.g. mass, V, n

Sign convention for Work & Heat Processes

Process	Sign
A. Work done by the system on the surroundings	–
B. Work done on the system by the surroundings	+
C. Heat absorbed by the system from the surroundings (endothermic)	+
D) Heat absorbed by the surroundings from the system (exothermic)	–

w and q are +ve when they tend to increase U of the system, or work done by the system is a reduction in U, hence –ve

WORK

Examples

Mechanical $w = F\Delta x$ (force x distance)

Units: (mass)(accel)(x) $= kg\,m^2s^{-2}$

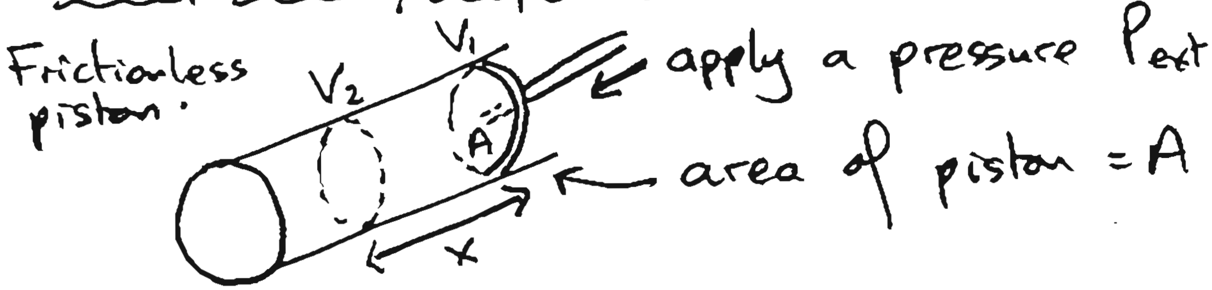
kg ms^{-2} m $= Nm = J$

Electrical $w = E\Delta Q$ (potential x charge)

Units: (Volts)(Coulombs) $= J$

V C

Compression/expansion



Work done, w = force x distance $= F.x$

(compression) $w = \frac{F}{A}.A.x = -P_{ext}\Delta V$

↳ work done **on** the system. Negative sign to account for sign convention (since $\Delta V = V_2 - V_1 < 0$)

↳ compression work +ve

Expansion work would be −ve

9

Units for energy are Joules (J)

$$1\,J = 1\,kg\,m^2 s^{-2}$$ SI definition.

i.e. mass × velocity^2

or .. in the case of PΔV work (prev. page)

$$w = -P_{ext}\Delta V \quad (Pa.m^3 \text{ or } atm.L)$$

Now, $Pa = Nm^{-2} = kg\,m^{-1}s^{-2}$

↑ force (mass × accel.)

So, $Pa.m^3 = (kg\,m^{-1}s^{-2}).m^3 = kg\,m^2 s^{-2}$

$= J$

An older unit - still used is the calorie

$$1\,cal = 4.184\,J \quad (\text{by definition})$$

(non S-I unit)

A couple of Q's.

Q1. A gas sample is heated in a cylinder using 550 kJ of heat. A piston compresses the gas, doing 700 kJ of work. What is the change in internal energy of the system?

$$\Delta U = q + w = +550\text{ kJ} + 700\text{ kJ} = \underline{1250\text{ kJ}}$$

Q2. Calculate the work done when 6300 L of an ideal gas (initially at 1.00 atm) is compressed (at constant T) by a constant pressure of 1.40 atm. to a final volume of 45 L.

$$\boxed{w = -P\Delta V} = -1.40\text{ atm}\,(\overset{V_f}{45} - \overset{V_i}{6300})\text{ L}$$
$$= \underline{+8757\text{ L.atm}}$$ ← work done on system, +ve

Convert to J

1 L. atm = ?

$$= 10^{-3}\text{ m}^3 \times 1.013 \times 10^5\text{ Pa}$$
$$= 101.325\text{ Pa.m}^3 \leftarrow \text{J.}$$

Hence $w = \underline{+887.3\text{ kJ}}$.

[Note: the gas constant R is given by,
$R = 8.314\text{ J K}^{-1}\text{mol}^{-1}$
$R = 0.0821\text{ L.atm K}^{-1}\text{mol}^{-1}$]