

**COMPLEMENTARY CHEMISTRY COURSES**  
**SEMESTER - I**  
**19U1CPCHE1: GENERAL CHEMISTRY**  
**(Common to Physical sciences and Life sciences)**

# **Thermodynamics**

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# *Contents*

- **System and Surrounding.**
- **First law of Thermodynamics**
- **Second law of Thermodynamics: free energy, Entropy and Spontaneity**
- **Statement of second law based on entropy**
- **The concept of Gibbs's free energy**
- **The third law of thermodynamics**

# Thermodynamics

Originally developed as a 19<sup>th</sup>C theory of steam engines, thermo (heat) dynamics (power or capacity) i.e. power created by heat.

Sadi Carnot (1824) *Reflections on the Motive Power of Fire*.

Scope of thermodynamics is now 'almost everything':

- heat engines, heat pumps and refrigerators (cyclic processes)
- the arrow of time
- chemistry, incl biochemistry: photosynthesis, haemoglobin, ATP
- hurricanes, plate tectonics, magnetisation & demagnetisation
- life processes e.g. ecosystems

# Four laws

Zeroth: [an afterthought]: **temperature** of a system

First: the conservation of energy - **internal energy** of a system.

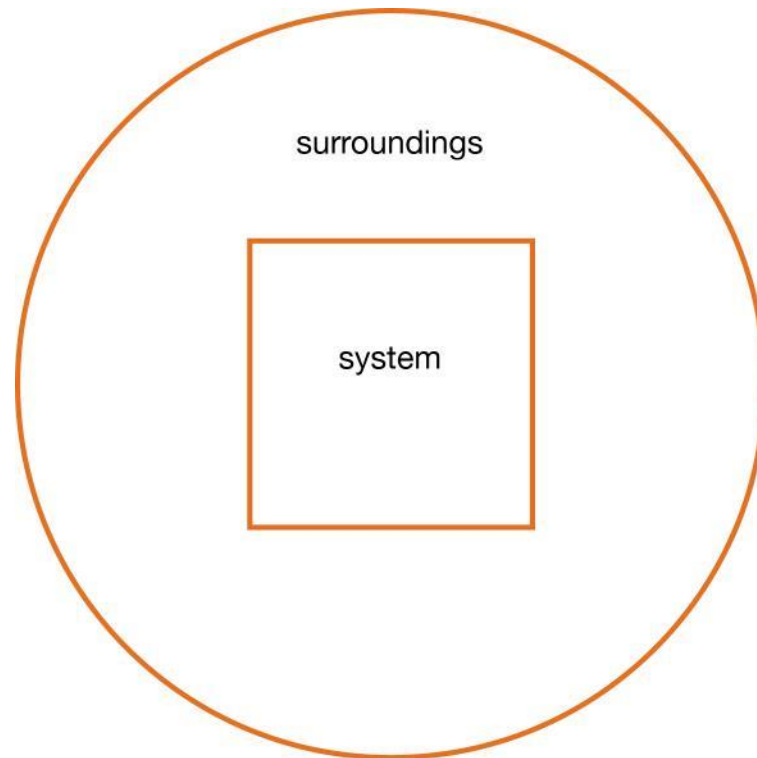
Second: why things happen as they do - **entropy** of a system

Third: Absolute Zero is unattainable, negative temperatures

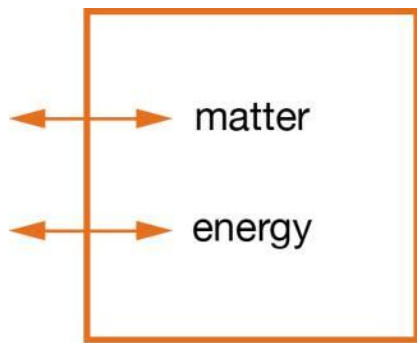
# Key terms

- **System** - part of the universe under study (open or closed)
- **Boundary** - what separates a system from its environment (surroundings) e.g. piston head in an engine
- **states & state variables**
  - fluid (pressure, volume, temperature)
  - surface (tension, area)
  - black-body radiation (energy density, radiation pressure)
  - electrical contact (potential, current)
- *equilibrium, non-equilibrium*
- *work, heat, adiabatic & isothermal changes*

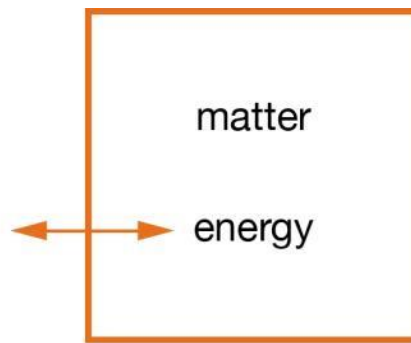
# *System and surroundings*



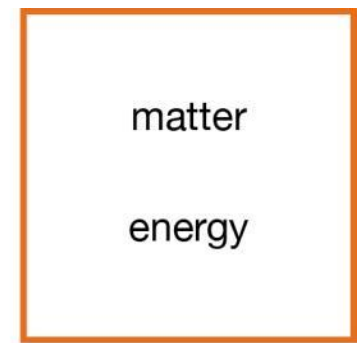
# *Different types of system*



open system

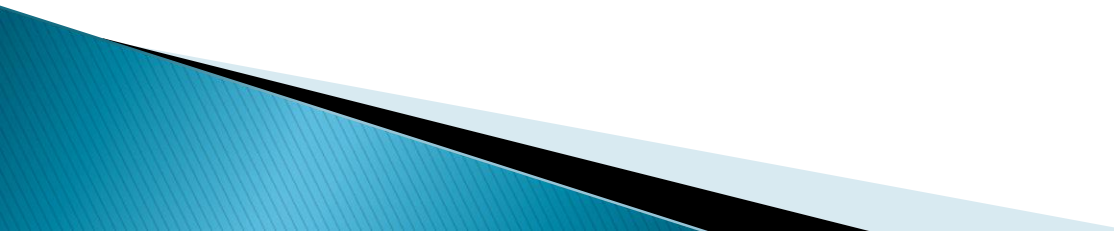


closed system



isolated system

# *Process Terminology*

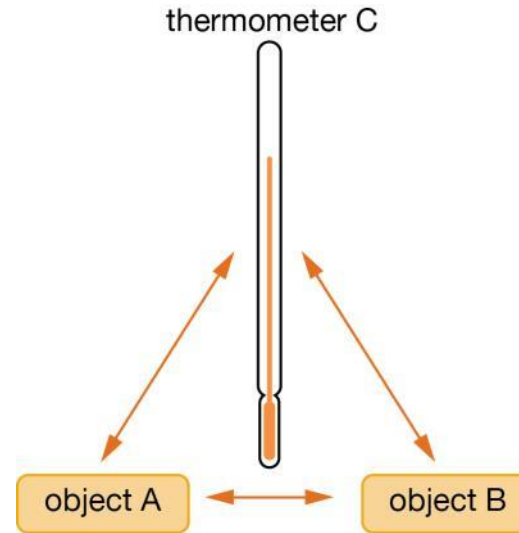
- ▶ Adiabatic – no heat transferred
  - ▶ Isothermal – constant temperature
  - ▶ Isobaric – constant pressure
  - ▶ Isochoric – constant volume
- 



# Zeroth law

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C will be in thermal equilibrium with A.

In other words, all three systems have the same 'temperature'.



Rigid walls that permit a system to change its state (by thermal transfer) are called 'diathermic'. Saucepans are diathermic vessels.

Walls that do NOT permit such changes (by thermal transfer) are called 'adiabatic'.

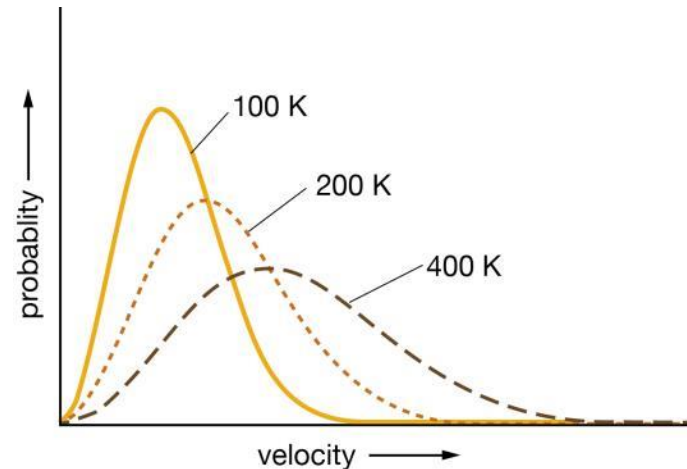
A vacuum flask is adiabatic.

**Temperature scales:** Fahrenheit, Celsius, Kelvin.

# Zeroth law - particle level

Statistical thermodynamics,  
developed by Ludwig  
Boltzmann (1844-1906),  
describes what happens at  
atomic or molecular level.

Molecules in a gas have  
quantised energy levels. In  
equilibrium, molecules are  
distributed over a range of  
allowed states.



Average  $E_k$  of a molecule

$$= \frac{3}{2} kT$$

Boltzmann constant,

$$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

smaller mass  $\Rightarrow$   $v$  larger

# First law

If the contents of the flask had been churned in a un-insulated vessel, the amount of work necessary to raise its temperature would have been greater.

The transfer of energy from a system to its surroundings, as a result of a temperature difference, is called **heat** (thermal transfer).

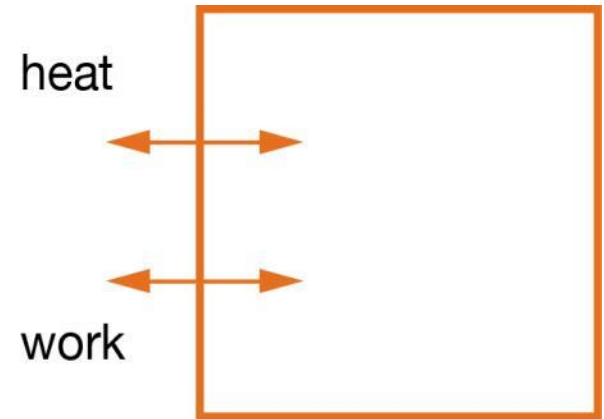
The change in internal energy,  $\Delta U$ , of a system is the sum of the work done **on** the system,  $\Delta W$ , and heat,  $\Delta Q$ , transferred **to** it.

$$\Delta U = \Delta W + \Delta Q$$

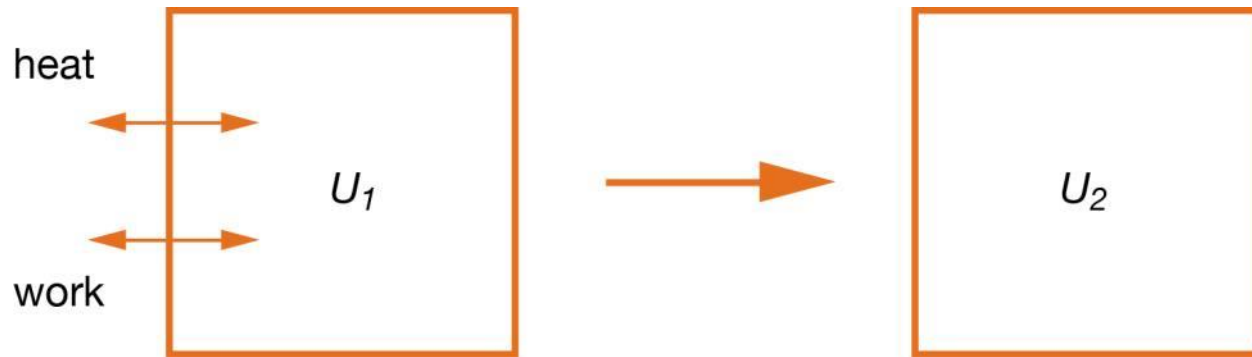
Adiabatic change:  $\Delta U = \Delta W$

# Heat and work

The two ways in which energy can be transferred into or out of a system – heat and work



# Heat and work



The total energy of a system is called its internal energy ( $U$ ) – it changes when energy is transferred into or out of the system.

# $\Delta W$ , $\Delta Q$ , $\Delta U$ at molecular level

*Work:* transfer of energy that makes use of the uniform motion of atoms in the surroundings.

*Heat:* transfer of energy that makes use of random motion of atoms in the surroundings.

*Internal energy:* kinetic energy + potential energy of the system's constituent atoms.

# Two related terms

Enthalpy,  $H$ , heat generated in combustion

$$\Delta H = \Delta U + pV$$

where  $p$  is the pressure of the system,  $V$  its volume,  $pV$  work done by the product gases.

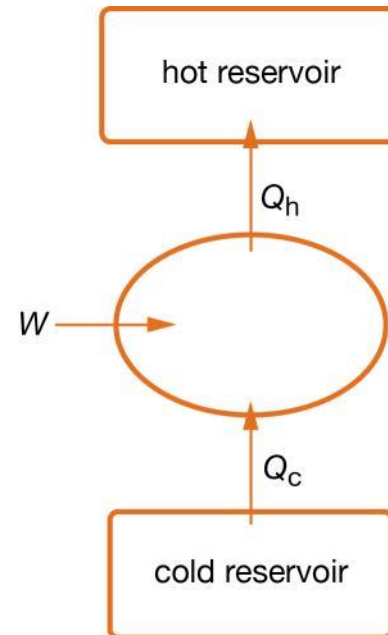
With fuel in an an open container, no work is done by the product gases,  
so  $\Delta H = \Delta U$ . **Unit**  $\text{kJ mol}^{-1}$

# Second law

Can be stated various ways:

(Kelvin): 'No cyclic process is possible in which heat is taken from a hot source and converted completely into work.' (e.g. engine)

(Clausius): 'Heat cannot pass from a body at low temperature to one at higher temperature without work being done.' (e.g. refrigerator)





# Entropy of a system, $S$

$S$  is a measure of the disorder of its matter and energy.

A gas has high entropy, crystal has low entropy.

$$\Delta S = \frac{\Delta Q}{T}$$

**Second law** (again): 'The entropy of the universe increases during any spontaneous change.'

Entropy increases in the cold sink of a heat engine (waste heat).

Time is irreversible (thermodynamic 'arrow of time').

# Free energy

in a chemical reaction can be described as

*EITHER*

$-T\Delta S$ , where  $T$  is the thermodynamic temperature and  $\Delta S$  is the total entropy change.

*OR*

the maximum amount of work that can be extracted from the reaction.

The basis of life on Earth is the free energy of captured photons from the Sun. 'Fuels' are sources of free energy, which of course can be used up.

# Predicting the Spontaneity of Reactions: Gibbs Free Energy

**The 2nd Law of Thermodynamics (Clausius, 1850):**

For all changes in a system, the total entropy of the system and its surroundings will increase.

$$\Delta S_{\text{Sys}} + \Delta S_{\text{Surr}} > 0$$

This is the criterion for reaction spontaneity



# The Third Law of Thermodynamics

The entropies of all perfect crystal approach zero as the absolute temperature approaches zero

## Gibbs free energy

Allows us to determine spontaneity considering the system alone May be thought to quantify the maximum amount of nonexpansion work the system can perform Is a state function

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \text{ (T, P = const)}$$

$\Delta G < 0$  corresponds to a spontaneous process

# Gibbs free energy of reaction and standard Gibbs free energy of formation

$$\Delta G_0 \text{ rxn} = \sum n G_0 \text{ m}(\text{products}) - \sum n G_0 \text{ m}(\text{reactants})$$

Standard Gibbs free energy of formation for a compound is the standard Gibbs free energy of a reaction to produce 1 mole of said compound from elemental compounds in their standard state. Units of J/(mol).

$$\Delta G_0 \text{ rxn} = \sum n G_0 \text{ f} (\text{products}) - \sum n G_0 \text{ f} (\text{reactants})$$

# Gibbs energy and non-expansion work

- ❖ Gibbs energy of a closed system is the measure of the energy “free” to do non-expansion work (e.g., mechanical, electrical, etc.).
- ❖ The change in free energy of a process ( $\Delta G$ ) is the maximum nonexpansion work this process can do.

J W Gibbs (late 19th Century) combined 1st and 2nd Laws to express spontaneity of reactions in terms of measurable system parameters.

$$\Delta G = \Delta H - T\Delta S.$$

$\Delta G$  : change in (Gibbs) Free Energy. Units: J/mol

- a measure of the useful work system can perform
- must be – ve for spontaneous reaction

If  $\Delta G$  is –ve; reaction exergonic; i.e. thermodynamically downhill.

If  $\Delta G$  is +ve, reaction endergonic; proceeds in reverse direction.

If  $\Delta G$  is 0: equilibrium; no change

# The Third Law of Thermodynamics

The entropies of all perfect crystal approach zero as the absolute temperature approaches zero

Statistical entropy  $S = k \ln(W)$ ,

where  $W$  is the number of different microstates for the macrostate

The statistical definition of entropy is equivalent to that derived from macroscopic observations



THANK YOU