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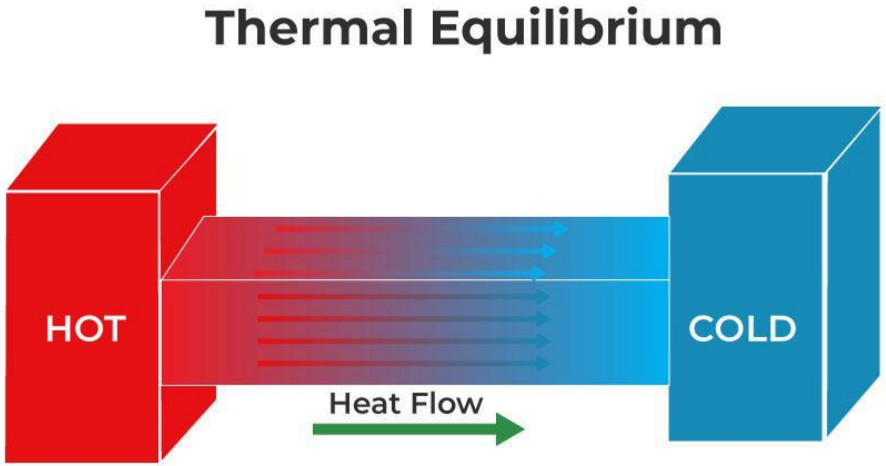
Physical Pharmacy

Thermodynamic

Thermodynamics

What is Thermodynamics

- Thermodynamics deals with the quantitative relationships of interconversion of the various forms of energy, including mechanical, chemical, electric, and radiant energy.



Thermodynamics

Terminology

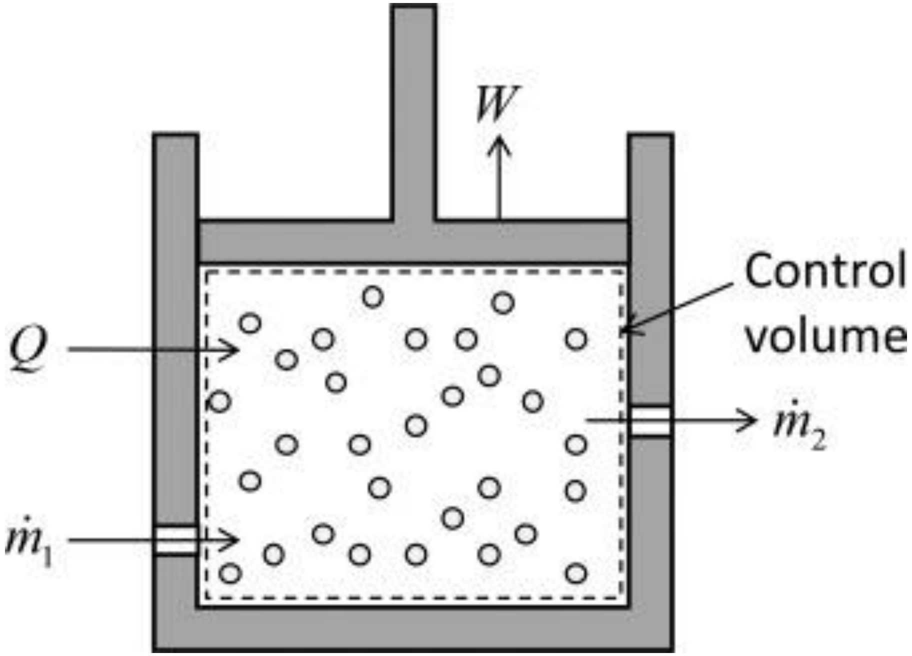
- A system in thermodynamics is a well-defined part of the universe that one is interested in studying

- The system is separated from surroundings , the rest of the universe and from which the observations are made, by physical (or virtual) barriers defined as boundaries .

- The term thermodynamic state means the condition in which the measurable properties of the system have a definite value (i.e.T&P).

Thermodynamics

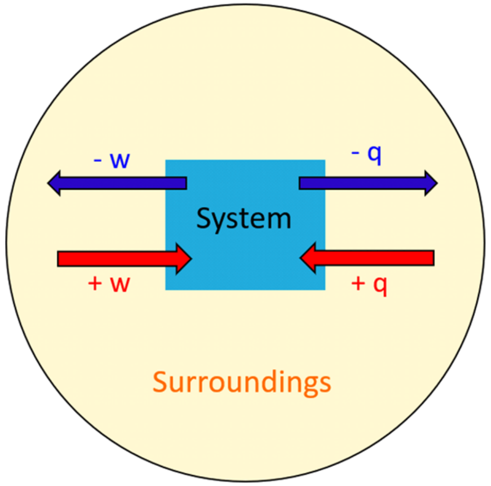
Terminology



Thermodynamics

Terminology

- Work (W) and heat (Q) also have precise thermodynamic meanings.
- Work is a transfer of energy that can be used to change the height of a weight somewhere in the surroundings,
- And heat is a transfer of energy resulting from a temperature difference between the system and the surroundings.
- It is important to consider that both work and heat appear only at the system's boundaries where the energy is being transferred.



Thermodynamics

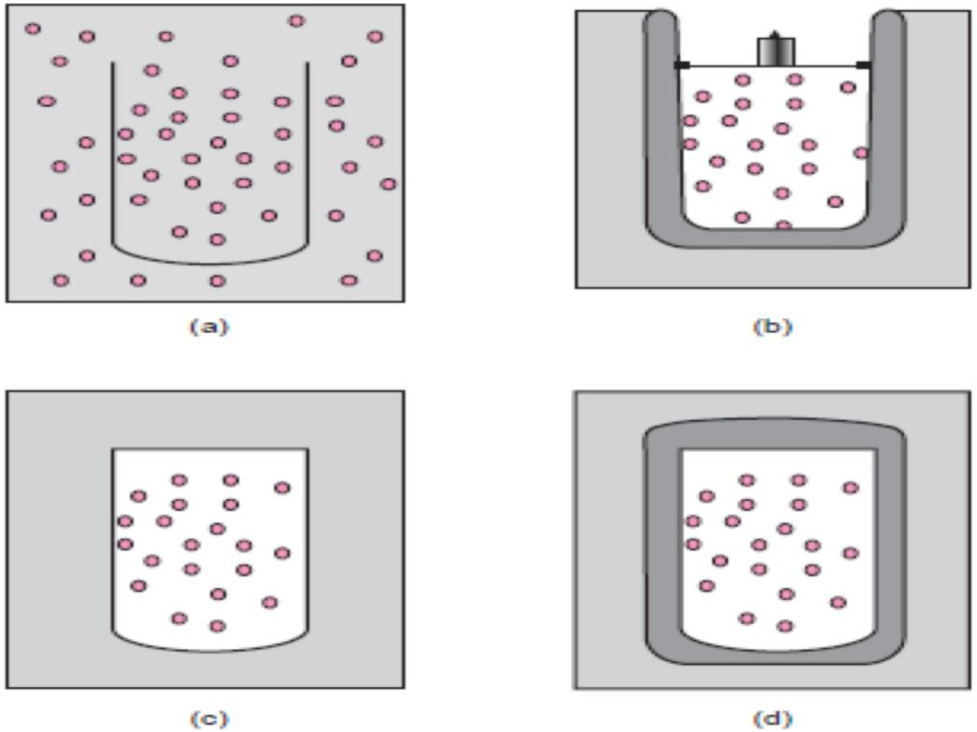
Thermodynamic system types :

- There are three types of systems that are frequently used to describe thermodynamic properties:
  - Figure 3–1a shows an open system in which energy and matter can be exchanged with the surroundings.
  - In contrast, Figure 3–1b and c are examples of closed systems , in which there is no exchange of matter with the surroundings, that is, the system’s mass is constant.
  - However, energy can be transferred by work (Fig. 3–1b) or heat (Fig. 3–1c) through the closed system’s boundaries.

Thermodynamics

Thermodynamic system types :

- The last example (Fig. 3–1d) is a system in which neither matter nor energy can be exchanged with the surroundings; this is called an isolated system .



Thermodynamics

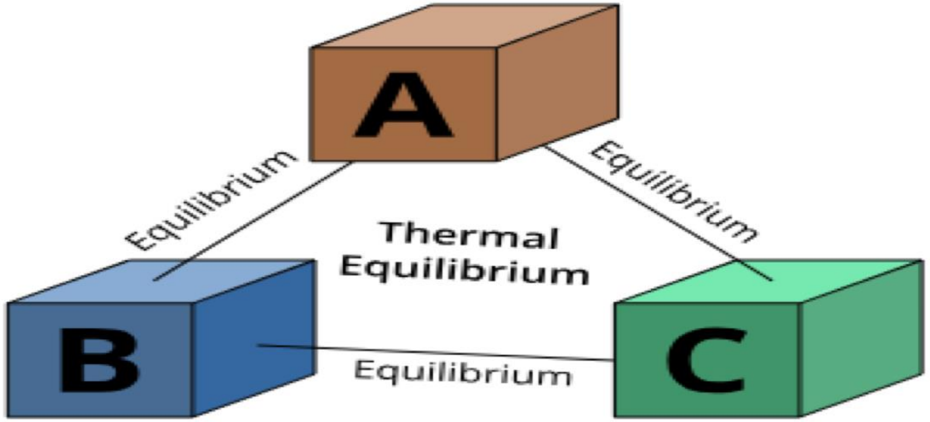
Thermodynamic processes

- Process is the change of a system from one equilibrium state to another
- Isothermal process is a process in which the temperature of the system is kept constant. e.g. placing a system in water bath.
- When heat is neither lost nor gained during a process, the reaction is said to occur adiabatically .
- Isobaric process is a process in which the pressure of the system is kept constant.
- Isochoric process is a process in which the volume of the system is kept constant

Thermodynamics

law of thermodynamics

- Zeroth law : states that “if two bodies are in thermal equilibrium with a third body, they are also in equilibrium with each other”.



Thermodynamics

THE FIRST LAW OF THERMODYNAMICS

- The first law is a statement of the conservation of energy.
- It states that, although energy can be transformed from one kind into another, it cannot be created or destroyed.
- Put in another way, the total energy of a system and its immediate surroundings remains constant during any operation.
- **Energy = (Mass change) × $(\text{Velocity of light})^2$**

Thermodynamics

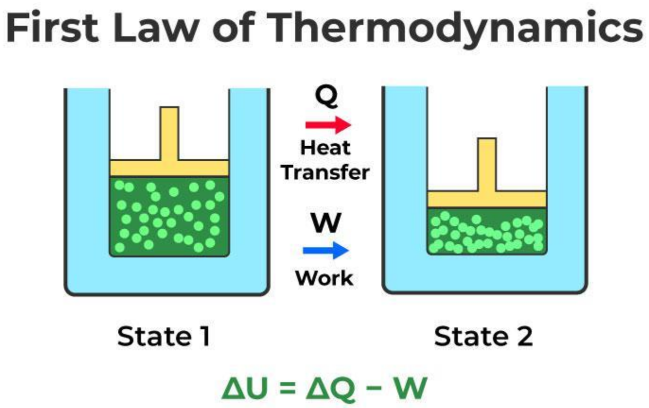
THE FIRST LAW OF THERMODYNAMICS

- Internal energy (E): is the sum of kinetic and potential energy contributions to the energy of all atoms, ions and molecules in that system

- **Kinetic energy**: is the energy which a body has as a result of its motion.

- **Potential energy:** is the energy which a body has due to its position “gravitational potential

$$Etotal = \sum Ek + \sum Ep$$



Thermodynamics

THE FIRST LAW OF THERMODYNAMICS

- According to the first law, the effects of heat(Q) and work (W)in a given system during a transformation from an initial thermodynamic state (E 1)to a final thermodynamic state (E 2)are related to an intrinsic property of the system called the internal energy, defined as :
- **$\Delta E = E - E = Q + W$**

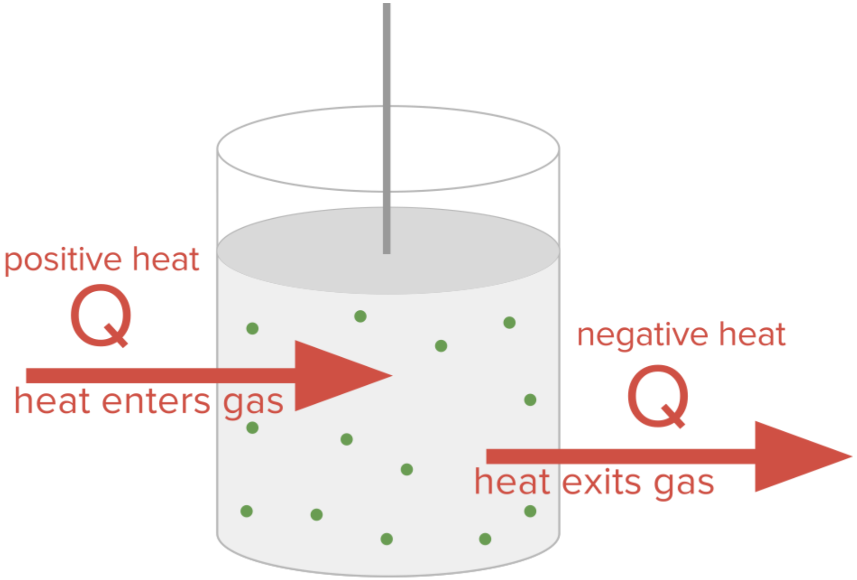
- **The change in internal energy (E)is related to Q and W transferred between the system and its surroundings.**

- Q and W are positive if the energy is gained by the system (i.e. the heat is taken up by the system or the work is done on the system).

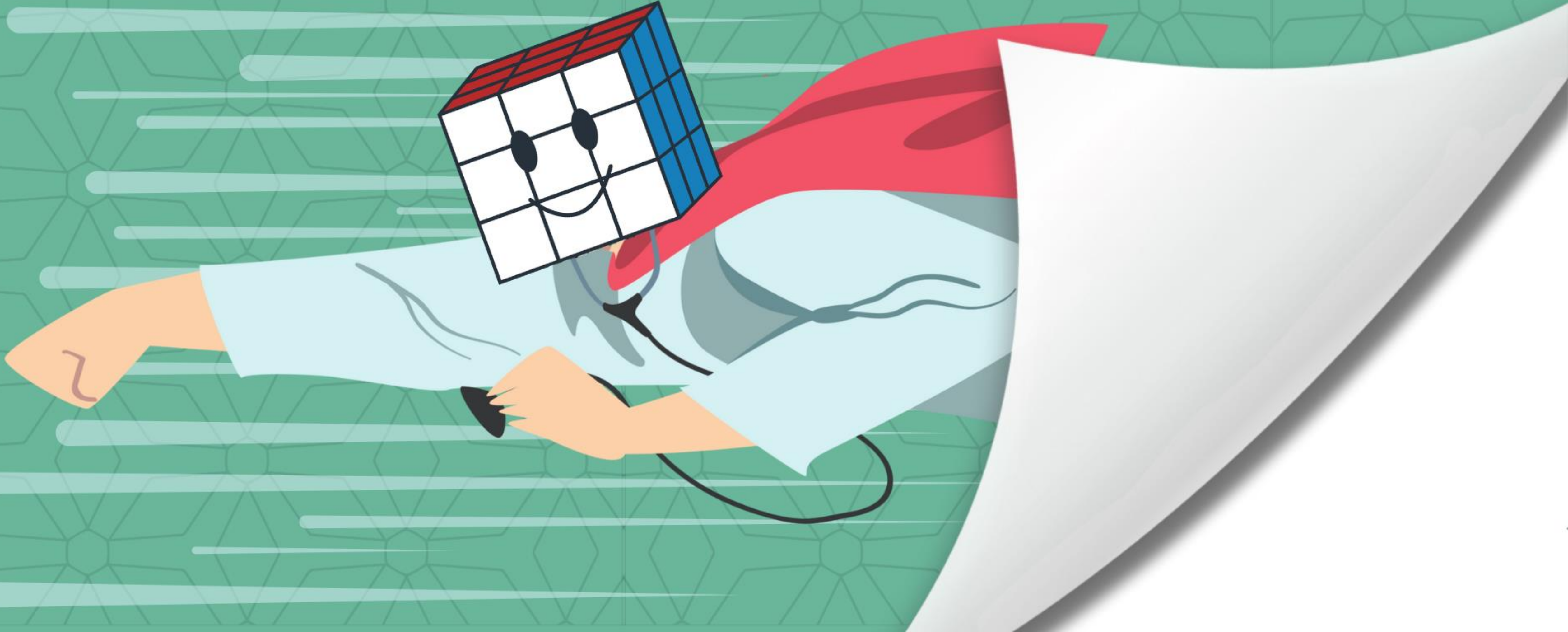
Thermodynamics

THE FIRST LAW OF THERMODYNAMICS

- Q and W are negative if the energy is lost by the system (i.e. the heat is released up by the system or the work is done by the system).
- The absolute value for the internal energy is extremely difficult to attain in practice.
- Therefore, changes in the internal energy ΔE rather than absolute energy value is the concern of thermodynamics



Conservative of energy



Thermodynamics

Conservative of energy

- If an electric motor produced 15kJ of energy each second as mechanical work and lost 2 kJ as heat to the surrounding, then the change in the internal energy each second is: **ΔE = -2kJ -15kJ = -17k**

- Suppose that, when a spring was twisted, 100J of work was done on it but 15J escaped to the surrounding as heat.

- The change in internal energy of the spring is: ΔE= -15J +100J = +85J

Thermodynamics

Work of Expansion Against a Constant Pressure

- Imagine a vapor confined in a hypothetical cylinder fitted with a weightless, frictionless piston of area **A**.

- If a constant external pressure P_{ex} is exerted on the piston, the total force is $P_{ex} \times A$.

- The vapor in the cylinder is now made to expand by increasing the temperature, and the piston moves a distance h.

- The work done against the opposing pressure in one single stage is:
- $\mathbf{W = -P_{ex} \times A \times h}$

Thermodynamics

Work of Expansion Against a Constant Pressure

- Now A × h is the increase in volume, ($\Delta V = V2 - V1$), so that, at constant pressure, **$W = -P_{ex}\Delta V = -Pex(V2 - V1)$**

Thermodynamics

Example 3-2:

A gas expands by 0.5 liter against a constant pressure of 0.5 atm at 25°C. What is the work in ergs and in joules done by the system?

Sol

$W = P\Delta V$

$1 \text{ atm} = 1.013 \times 10^{6} \text{ dynes/cm}^{2}$

$W = (0.507 \times 10^{6} \text{ dynes/cm2}) \times 500 \text{ cm}^{3}$

$= 2.53 \times 10^{8} \text{ ergs} = 25.3 \text{ joules}$

The following example demonstrates the kind of problem that can be solved by an application of the first law of thermodynamics.

Thermodynamics

Reversible Processes

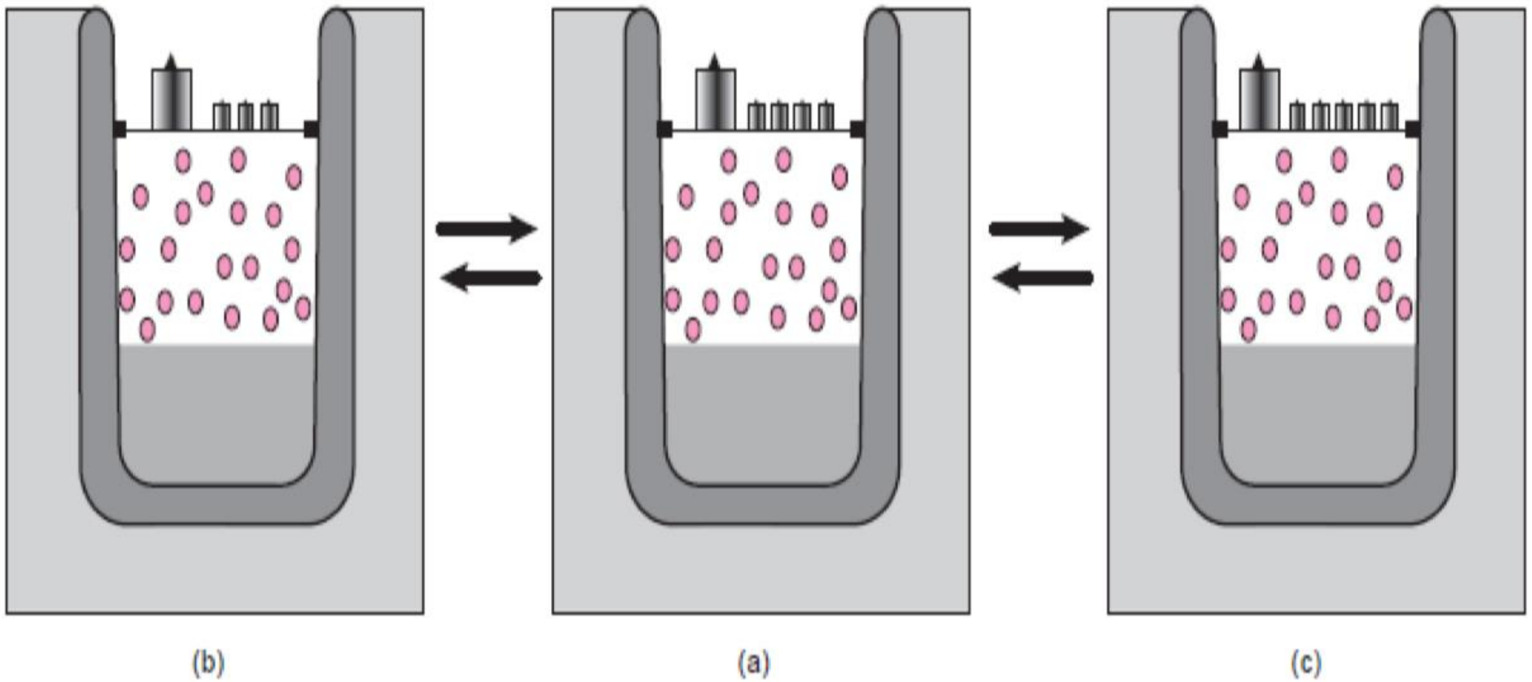
- let us imagine the hypothetical case of water at its boiling point contained in a cylinder fitted with a weightless and frictionless piston, the process is an isothermal one, that is, it is carried out at constant temperature.

- If the external pressure is decreased slightly, the volume of the system increases and the vapor pressure falls infinitesimally.

- Water then evaporates to maintain the vapor pressure constant at its original value, and heat is extracted from the bath to keep the temperature constant

Thermodynamics

Fig. 3-3. A reversible process: evaporation and condensation of water at 1 atm in a closed system. (a) System at equilibrium with P. = 1 atm; (b) expansion is infinitesimal; (c) compression is infinitesimal.



Thermodynamics

Reversible Processes

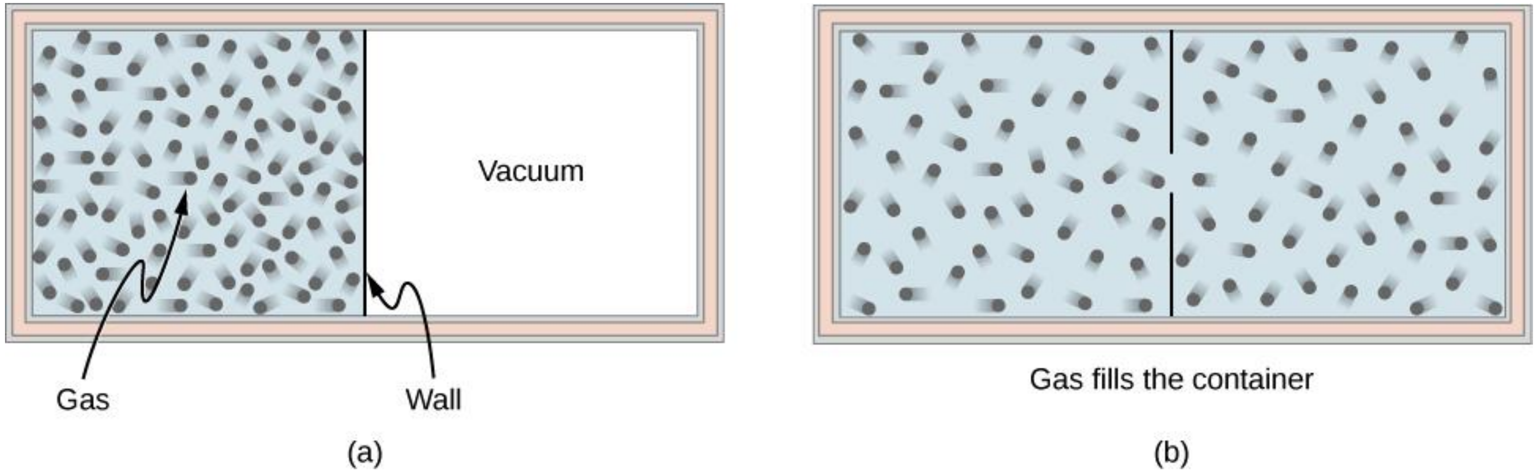
- On the other hand, if the external pressure is increased slightly by adding an infinitesimally small weight (Fig. 3–3c), the system is compressed and the vapor pressure also rises infinitesimally.

- Some of the water condenses to reestablish the equilibrium vapor pressure, because this process is always in a state of virtual thermodynamic equilibrium, being reversed by an infinitesimal change of pressure, it is said to be reversible

Thermodynamics

Reversible Processes

- If the pressure on the system is increased or decreased rapidly or if the temperature of the bath cannot adjust instantaneously to the change in the system, the system is not in the same thermodynamic state at each moment, and the process is irreversible .



Thermodynamics

Maximum Work

- The work done by a system in an expansion process is at a maximum when it is done reversibly.

- No work is accomplished if an ideal gas expands freely into a vacuum, where **$P = 0$.**

- As the P_{ex} becomes greater, more work is done by the system, and it rises to a maximum when $P_{ex} < P_{gas}$.

Thermodynamics

Maximum Work

- If the external pressure is continually increased, the gas is compressed rather than expanded, and work is done on the system rather than by the system in an isothermal reversible process.

$$W = \int_{1}^{2} dw = -\int_{V_1}^{V_2} PdV$$

- And from the ideal gas law: $P = nRT/V$, Then equation (3-8) will be:
- **W max = −nRT lnV 2 /V 1**

Thermodynamics

Maximum Work

- Note that in expansion, **V 2 > V 1 , and ln (V 2 /V 1)** is a positive quantity; therefore, the work is done by the system, so that its energy decreases (negative sign).

- When the opposite is true, **V 2 < V 1 , and ln (V 2 /V 1**) is negative due to gas compression, work is done by the system, so that its energy increases(positive sign).

- The maximum work in an isothermal reversible expansion may also be expressed in terms of pressure because, from Boyle's law, **V 2 /V 1 = P 1 /P 2** at constant temperature.

$$W_{max} = -nRT \ln \frac{P_1}{P_2} \qquad (3\text{–}11)$$

Thermodynamics

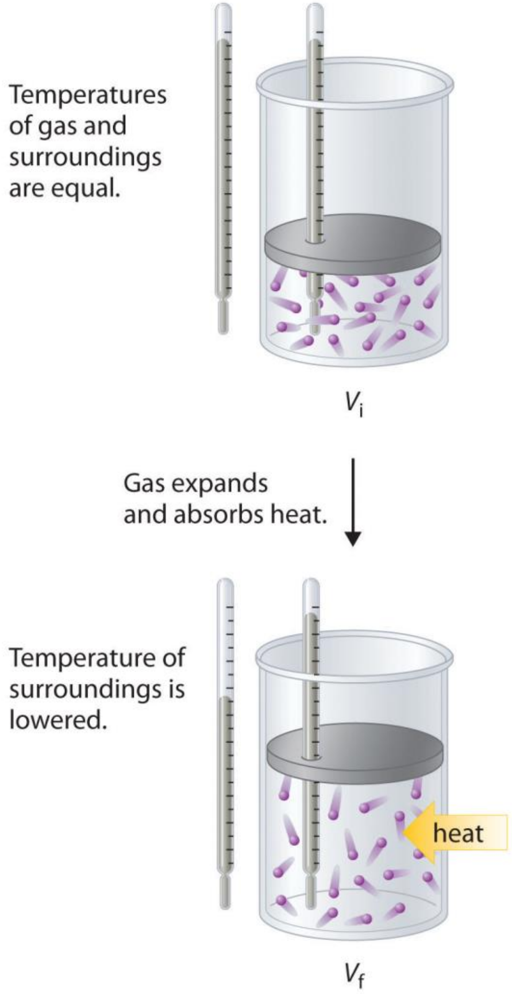
Enthalpy change (ΔH)

- Most chemical studies are conducted at constant pressure (i.e. P= 1 atm).

- Consequently the system is capable of doing work of expansion on the surrounding.
- From the first law:

- **$\Delta E = QP - W$ since $W = -P\Delta V = -P(V2 - V1)$**
- **$QP = E2 - E1 + P(V2 - V1)$**

- By defining a new state function ΔH, the enthalpy change which is equal to QP , the equation become: $\Delta H = \Delta E + P\Delta V$ ....(3–21)



Thermodynamics

Enthalpy change

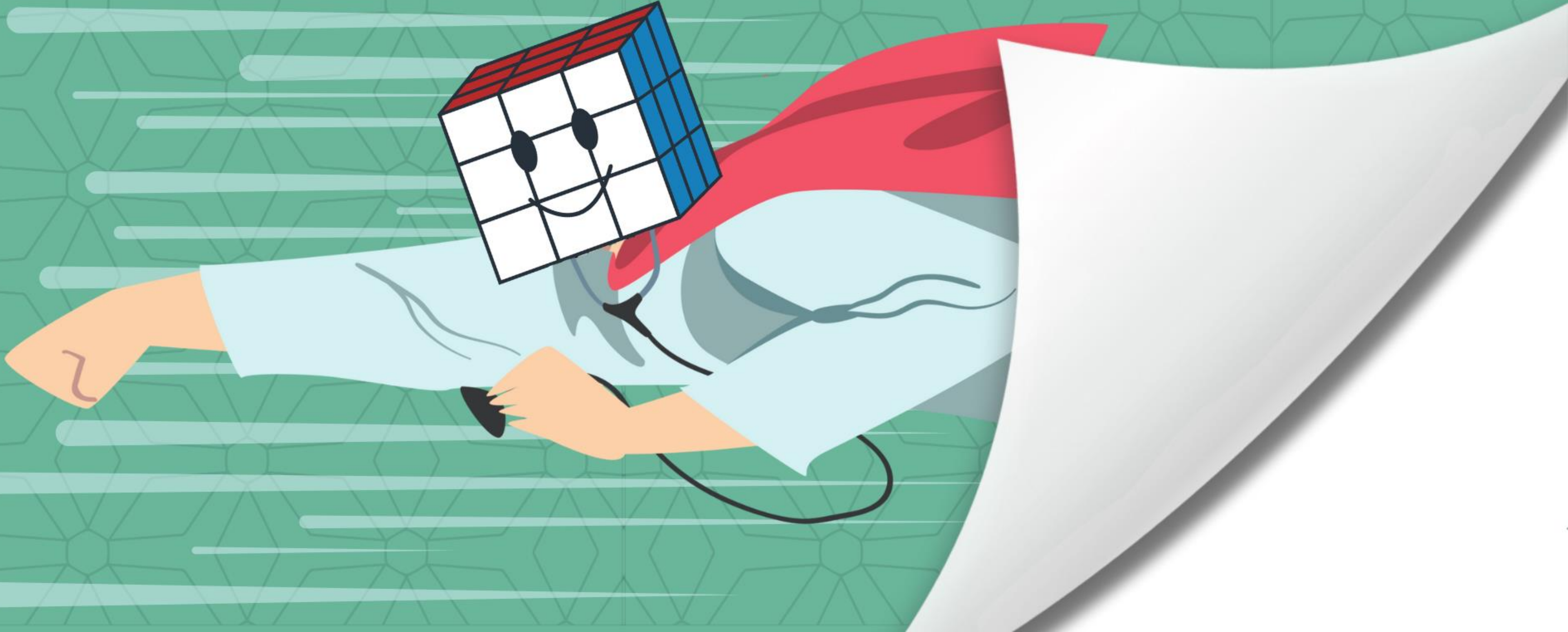
- A negative ΔH and QP means that heat is released (exothermic); a positive value of ΔH and QP means that heat is absorbed (endothermic).

- **ΔH = H products – H reactants**
- **ΔH is expressed as Cal/ mol.**

- The increase in enthalpy, ΔH, is equal to the heat absorbed at constant pressure by the system.

- It is the heat required to increase the internal energy and to perform the work of expansion.

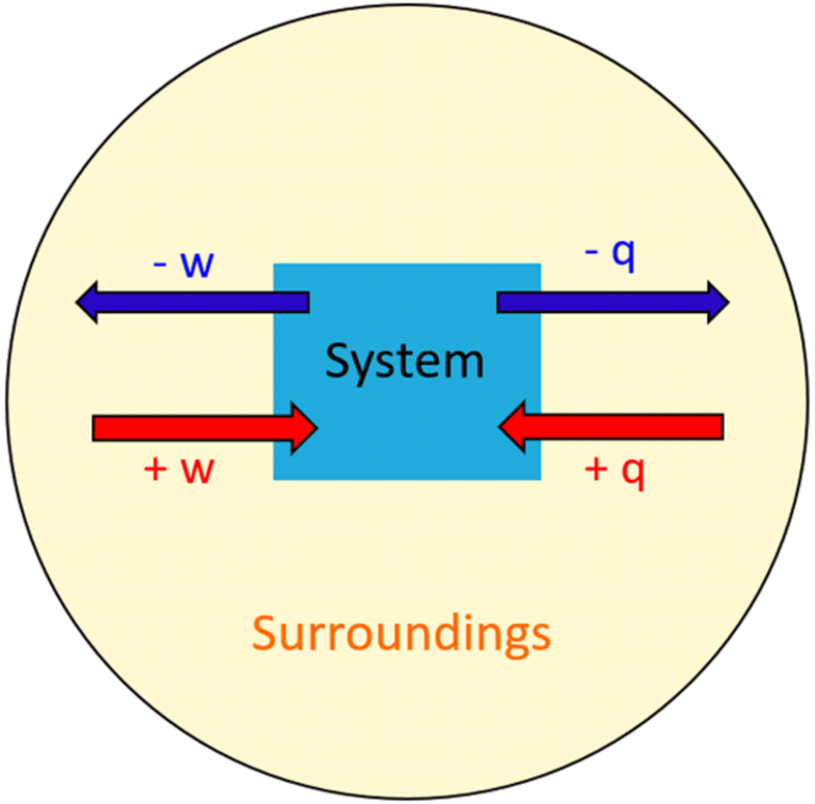
Types of Enthalpy (ΔH)



Thermodynamics

Types of Enthalpy (ΔH)

- ΔHf : the heat absorbed by solid on melting.
- ΔHr: the heat of reaction it may be positive (heat is absorbed) the process is called endothermic, or negative (heat is liberated) the process is called exothermic.
- ΔH°: the heat content at standard conditions, (25°C, 1 atm).



Thermodynamics

THERMOCHEMISTRY

- Is the study that deals with the heat changes accompanying isothermal chemical reaction at constant pressure and volume, for which values of ΔH and ΔE can be obtained.

- For any reaction represented by the chemical equation : aA + bB cC + dD’

- The enthalpy change can be written as:
- $\Delta H = \sum \Delta H product + \sum \Delta H\, reactants$

- Note: In solution reactions, the PΔV terms are not significant, so that ΔH≅ ΔE , This close approximation does not hold, however, for reactions involving gases.

Thermodynamics

Hess’s Law and Heat of Combustion

- It is not possible to directly measure the heats of formation of every known compound as in equation.

- Incomplete or side reactions often complicate such determinations.

- because ΔH depends only on the initial and final states of a system, thermochemical equations for several steps in a reaction could be added and subtracted to obtain the heat of the overall reaction.

- The principle is known as **Hess’s law of constant heat summation**

Thermodynamics

Entropy (S) and disorder

- Entropy is the measure of randomness or disorder in the universe.

- It is a quantitative measure of increasing the probability of spontaneous process.
- **$\Delta S = Q_{rev}/T$……………..(3–39)**

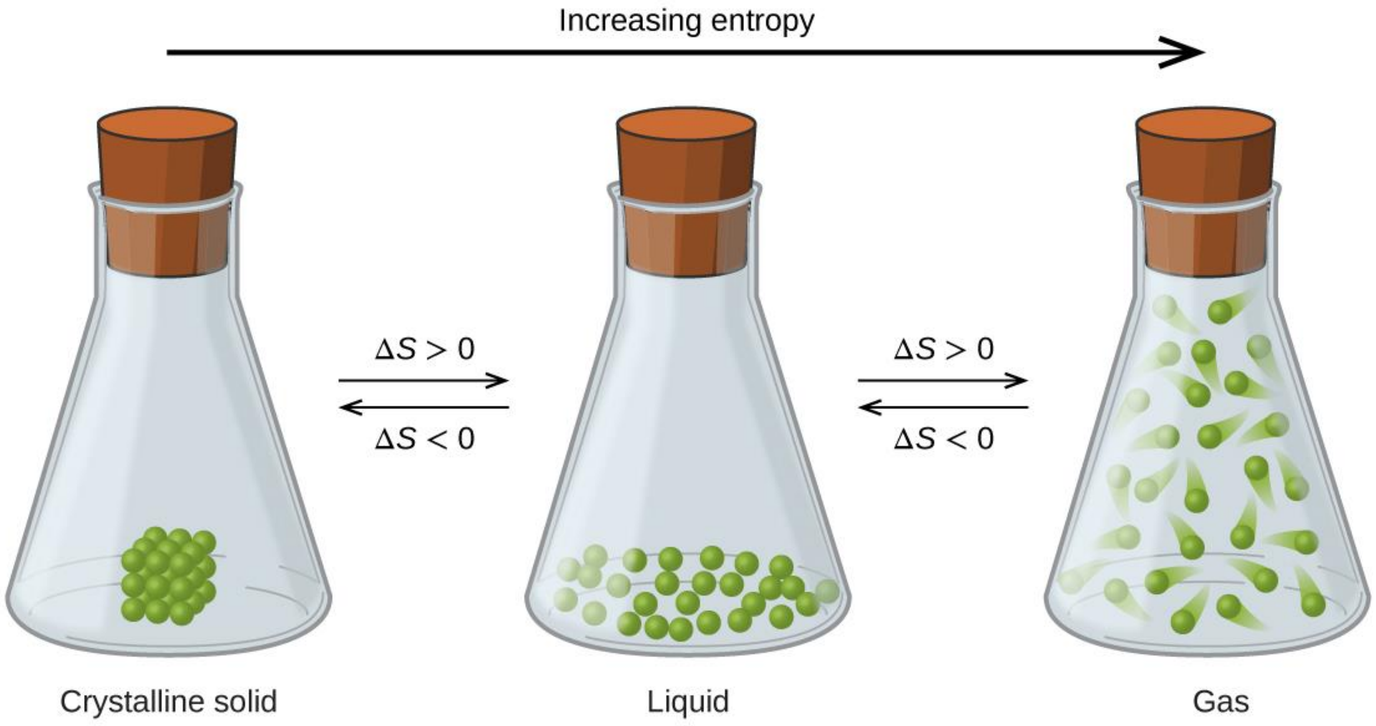
- Hence, for any system and its surroundings or universe, $\Delta S_{univ} = 0$ a system and its surrounding is at equilibrium(reversible cyclic process).

- $\Delta S_{univ} > 0$ for spontaneous process, is always positive because ΔS_{surr} is always less than ΔS_{syst} in an irreversible process.

- $\Delta S_{univ} < 0$ indicates a non-spontaneous process.

Thermodynamics

Entropy (S) and disorder



Thermodynamics

Entropy (S) and disorder : EXAMPLE 3-8

What is the entropy change accompanying the vaporization of 1 mole of water in equilibrium with its vapor at 25°C? In this reversible isothermal process, the heat of vaporization ΔHv required to convert the liquid$_2$ to the vapor state is 10,500 cal/mole.

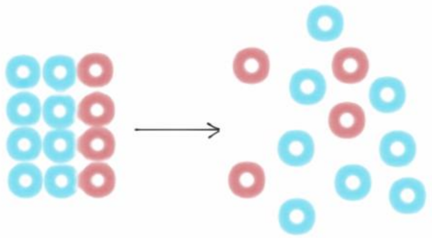
The process is carried out at a constant^3 pressure, so that Qp = ΔHv , and because it is a reversible process, the entropy change can be written as

$$\Delta S = \Delta Hv / T = 10500 / 298 = 35.2 \text{ cal / mol deg}$$

Thermodynamics

THE SECOND LAW OF THERMODYNAMICS

- Spontaneous process always proceeds in the direction of increased the entropy; when the system finally reach the equilibrium, the net entropy change undergone by the system and its surrounding is equal to zero.



- The isothermal expansion of an ideal gas increases the entropy, because of the enhanced number of configurations in a large volume compared to a smaller one (more order)

Thermodynamics

THE SECOND LAW OF THERMODYNAMICS

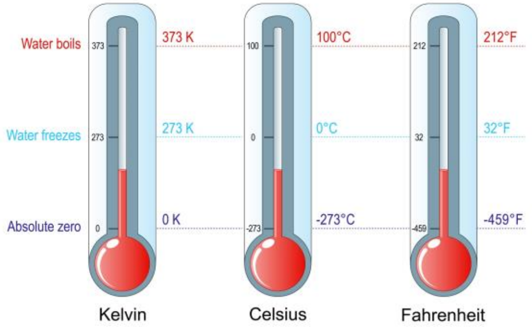
- Most natural phenomena are observed as occurring only in one direction , For instance:

1. Heat flows spontaneously only from hotter to colder bodies
2. Gases expand naturally from higher to lower pressures,
3. Solute molecules diffuse from a region of higher to one of lower concentration
4. Heat does not spontaneously flow from cold body to hot body.
5. Spontaneous processes are not thermodynamically reversible.
6. All natural processes are accompanied by a net gain in entropy of the system and its surrounding.

Thermodynamics

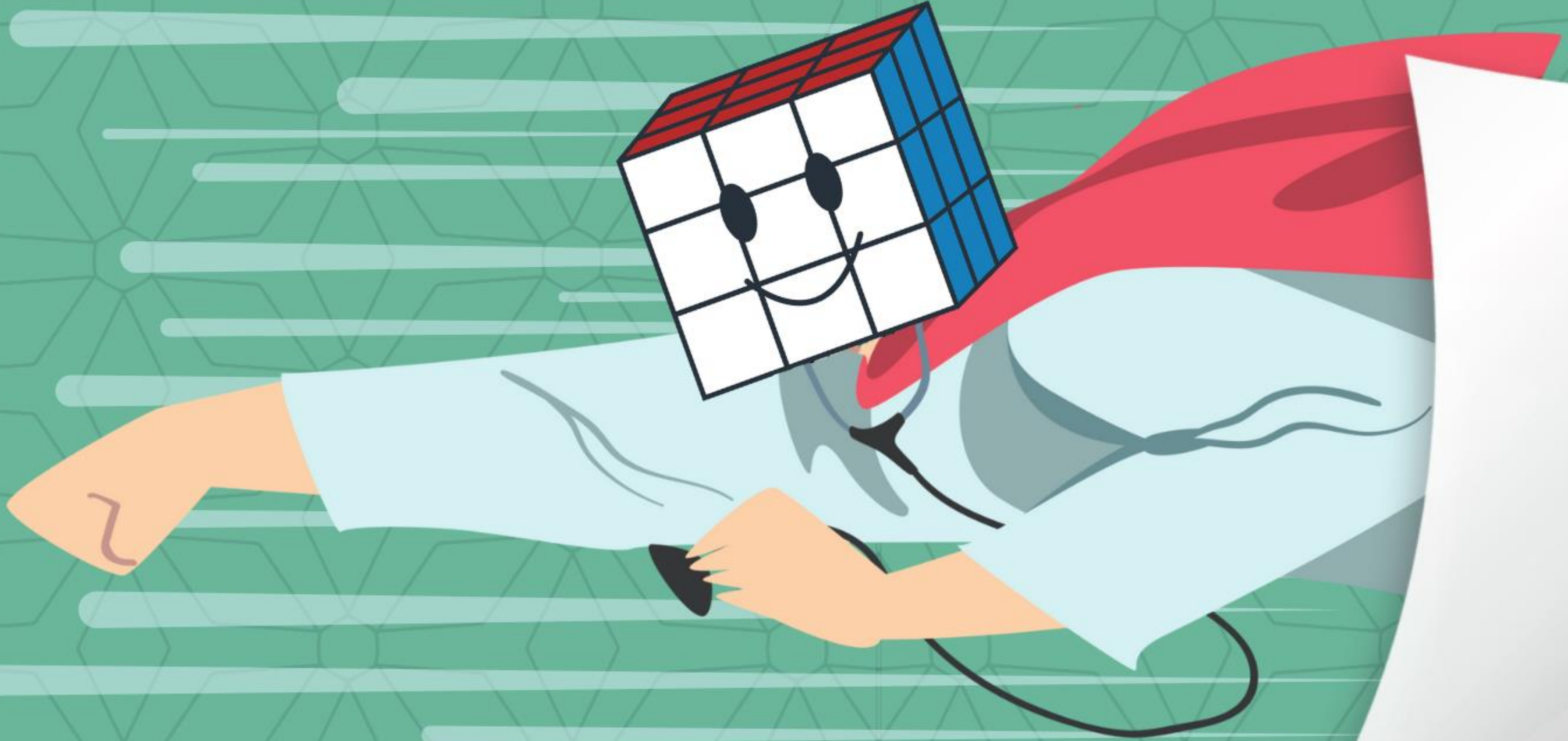
THE THIRD LAW OF THERMODYNAMICS

- The third law of thermodynamics states that the entropy of a pure crystalline substance is zero at absolute zero because the crystal arrangement must show the greatest orderliness at this temperature.



- As a consequence of the third law, the temperature of absolute zero (0 K) is not possible to reach even though sophisticated processes that use the orientation of electron spins and nuclear spins can reach very low temperatures of 2×10^3 and 10^5 K, respectively.

Gibbs free energy G



Thermodynamics

Gibbs free energy G

- There are two factors involved in determining the direction of chemical changes:

  A) the system seeks to minimize its energy (ΔH)
  B) the system seeks to maximize its entropy(ΔS)

- Gibbs free energy ΔG, is a state function that links the first and the second law of thermodynamics and determine the direction of chemical changes

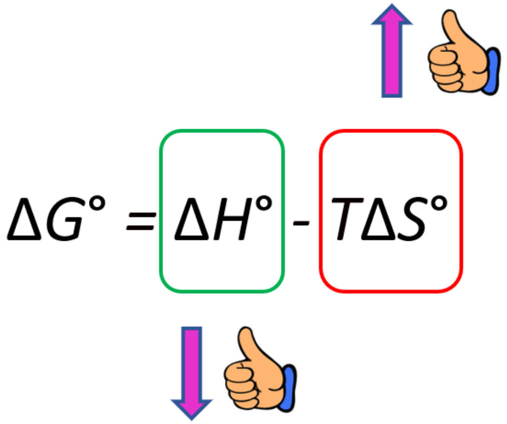
- **$\Delta G = \Delta H - T\Delta S$ ....(3–67)**

- $\Delta G = 0$ at constant (Temperature &Pressure) and the system is at equilibrium.

Thermodynamics

Gibbs free energy G

- If ΔG is negative it means that the process is spontaneous.
- If ΔG is zero, it means that the system is at equilibrium.
- If ΔG is positive it means that the process is non-spontaneous.
- A more negative ΔH and more positive ΔS favors spontaneous reaction, by making ΔG more negative.
- If TΔS < ΔH, and ΔH is negative, then ΔG will be negative (the process is spontaneous).

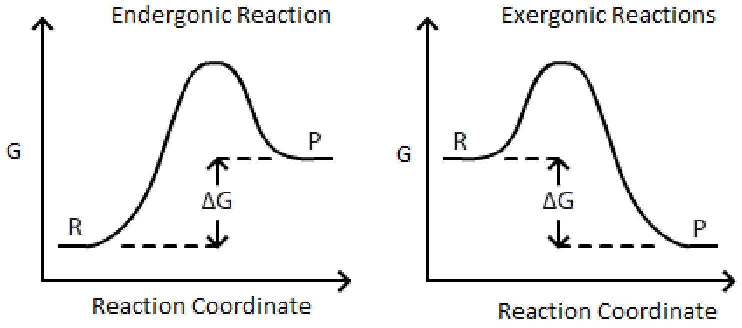


$$\Delta G^\circ = \boxed{\Delta H^\circ} - \boxed{T\Delta S^\circ}$$

Thermodynamics

Gibbs free energy G

- If TΔS < ΔH, and ΔH is positive, then ΔG will be positive(the process is non spontaneous).
- If TΔS > ΔH, then ΔG will be negative (i.e. the process is spontaneous regardless whether ΔH is negative or positive
- The entropy of all systems, as previously stated, spontaneously tends toward randomness according to the second law, so that the more disordered a system becomes, the higher is its probability and the greater its entropy. Hence, equation (3–64) can be written as



Thermodynamics

Gibbs free energy G

$$\Delta G = \begin{bmatrix} \text{Difference in bond energies or} \\ \text{attractive energies between} \\ \text{products and reactants, } \Delta H \end{bmatrix} - \begin{bmatrix} \text{Change in probability} \\ \text{during the process,} \\ T\,\Delta S \end{bmatrix} \qquad (3\text{–}69)$$

Thermodynamics

ΔG calculations

ΔH and ΔS for the transition from liquid water to ice at -10°C and at 1 atm pressure are - 1343 cal/mole and -4.91 cal/mole deg, respectively. Compute Δ for the phase change at this temperature (-10°C = 263.2 K) and indicate whether the process is spontaneous.

Write

$$\Delta G = -1343 - [263.2 \times (-4.91)] = -51 \text{ cal/mole} = -213 \text{ joules}$$

The process is spontaneous, as reflected in the negative value of ΔG.

DR CUBE

Thank You !

https://t.me/Dr_Cube