AL-Mustaqbal university college

Pharmacy department , under

graduated Study, 2rd class Study

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Physical pharmacy 1

Lecture4

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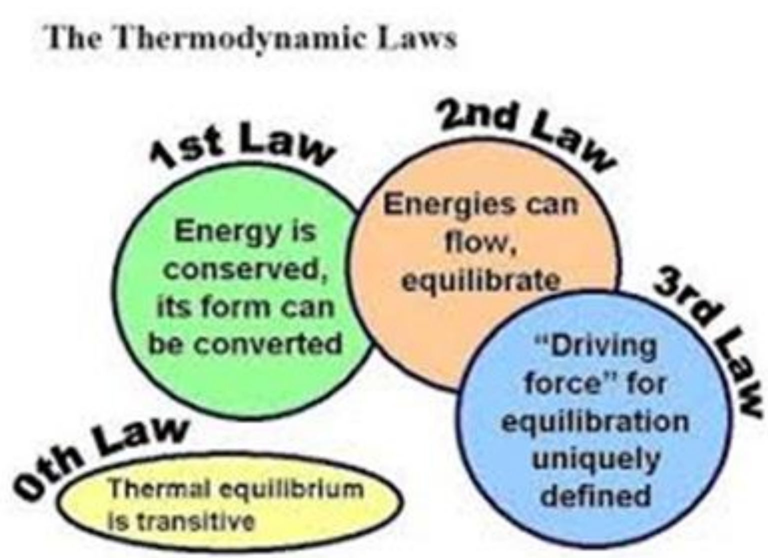
Thermodynamics

In physics, **thermodynamics** (from the Greek, **therme,** meaning "**heat** and, **dynamis**, meaning "**power**") is the study of the transformation of energy into different forms and its relation to macroscopic variables such as temperature, pressure, and volume. Its underpinnings, based upon statistical predictions of the collective motion of particles from their microscopic behavior, is the field of statistical thermodynamics, a branch of

Thermodynamics is based on **three "laws"** or facts of experience that have never been proven in a direct way, in part du [illegible] ey were derived statistical mechanics .



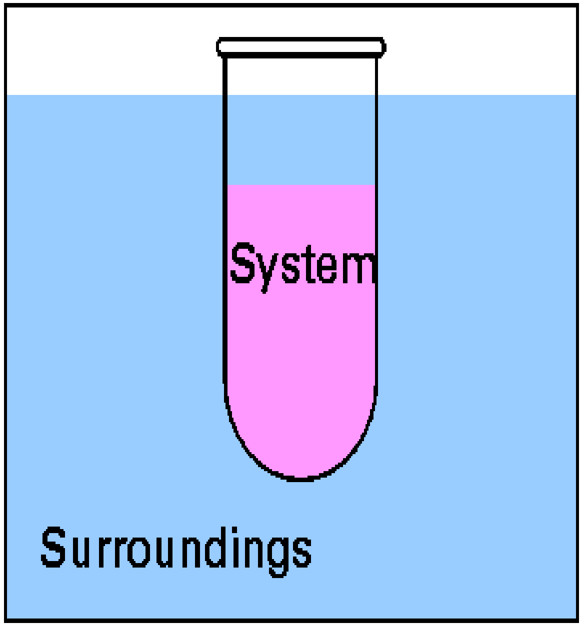
Thermodynamics:

The study of heat and its transformations. or, Thermodynamics is the study of energy transformations

Energy: **The capacity to do work or to produce heat**

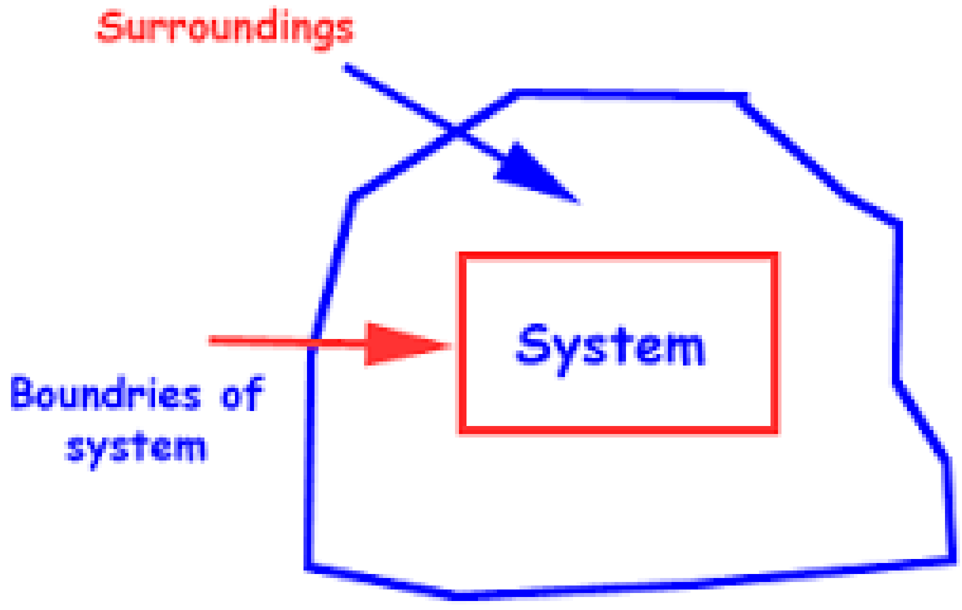
Temperature: **measure of hotness and coldness in terms of any arbitrary scales and indicating the direction which energy spontaneously flows (from a hotter body to a colder one)**

System:
The part of the universe of interest
Surroundings:
Everything else (relevant to system)
Universe:
System + surroundings



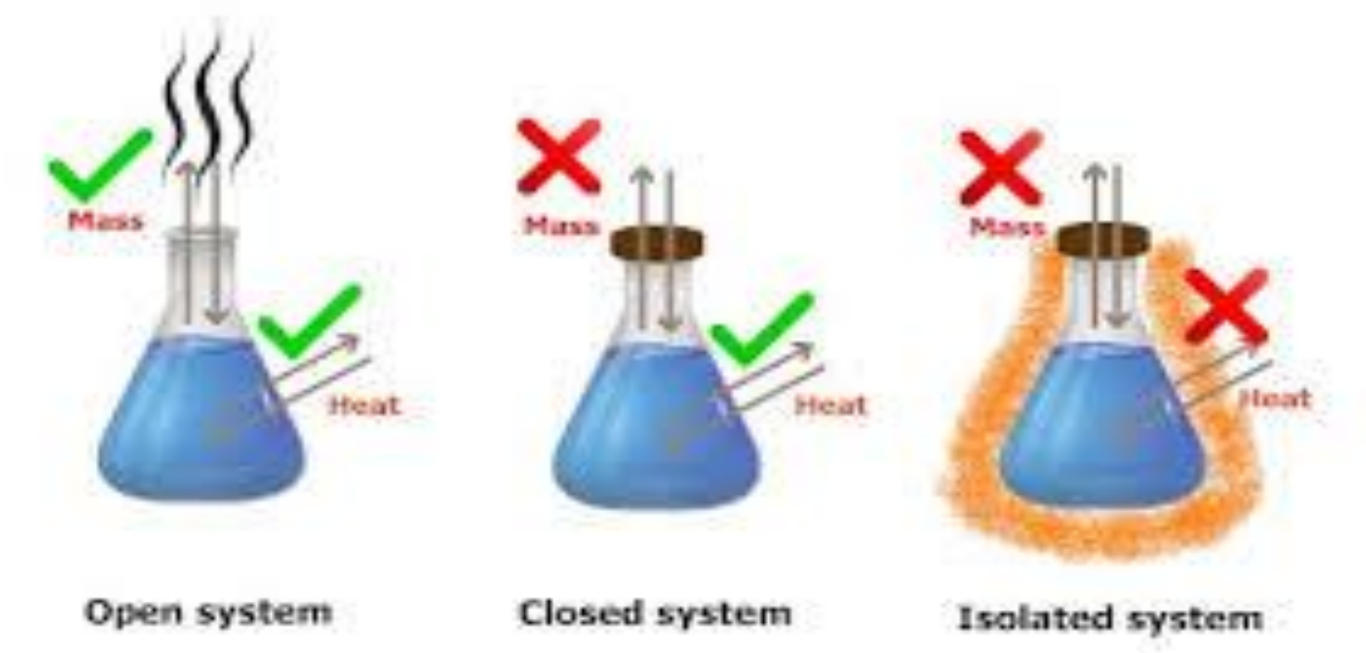
System, surroundings and boundary

- **System:** A quantity of matter or a region in space chosen for study.
- **Surroundings**: The mass or region outside the system
- **Boundary**: The real or imaginary surface that separates the system from its surroundings



The three types of systems that are frequently used to describe thermodynamic properties.

- **an <u>open system</u>** in which energy and matter can be exchanged with the surroundings.
- **<u>closed systems</u>, 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 or heat through the closed system's boundaries
- **last a system in which neither matter nor energy can be exchanged with the surroundings; this is called an <u>isolated system</u>**



Physical properties of a system-

1.Intensive properties- e.g. – temperature, pressure, viscosity, surface tension, refractive index, specific heat, density, etc.

2.Extensive properties- e.g.- mass, volume, energy, heat capacity, entropy, Gibb's free energy, ect.

Thermodynamic process

Reversible

irreversible

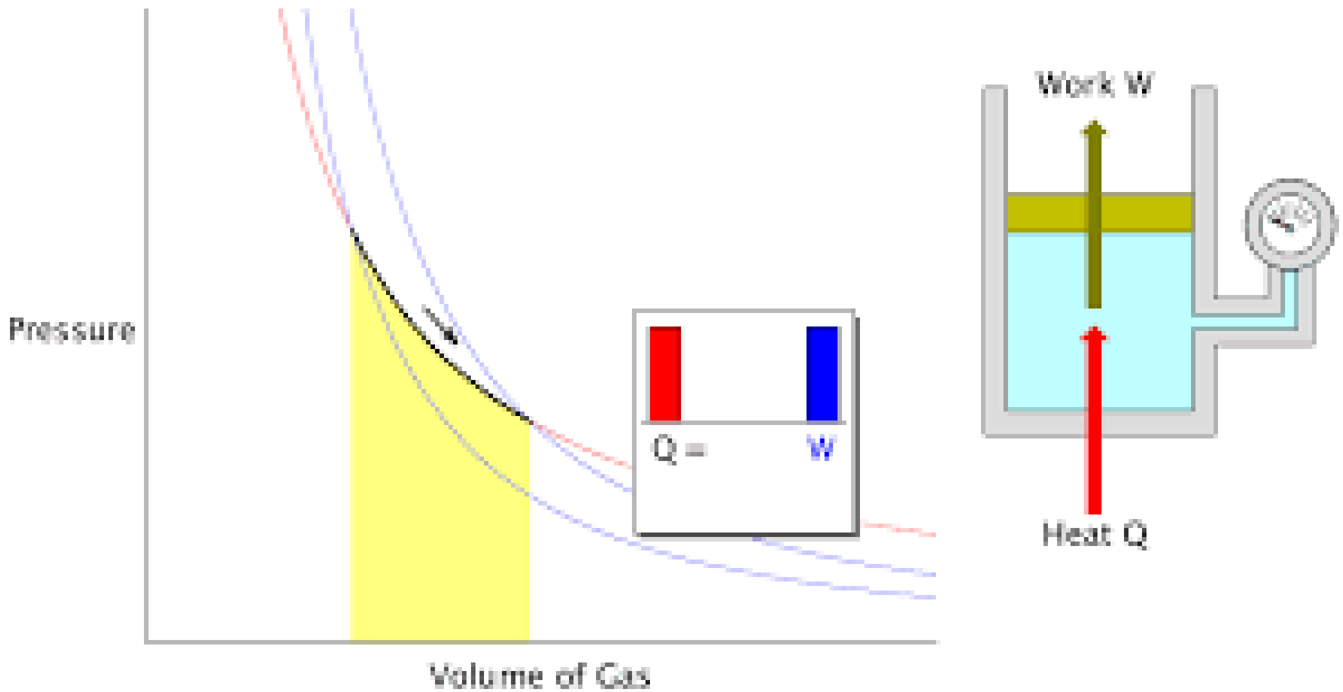
Isothermic [T]

Isobaric [p]

Isochoric [V]

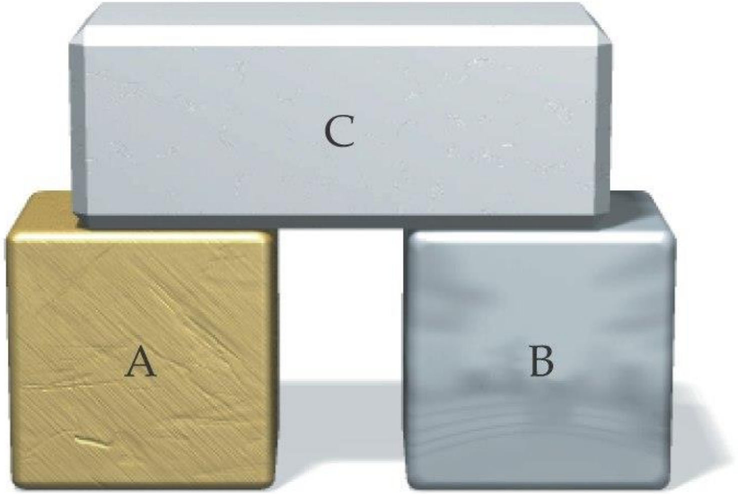
Adiabatic [Q]

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

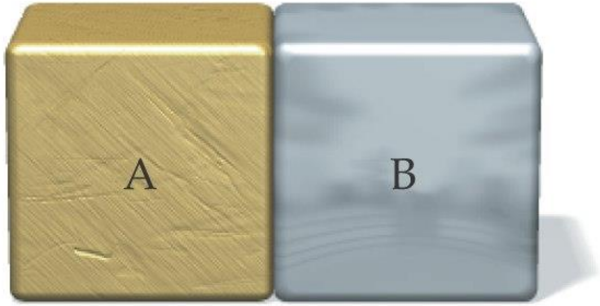


Law's of thermodynamics

Zeroth Law of thermodynamics



(a)



(b)

Thermal contact

Thermal equilibrium

If two objects are in thermal equilibrium with a third, then they are in thermal equilibrium each other
(Zeroth Law of thermodynamics)

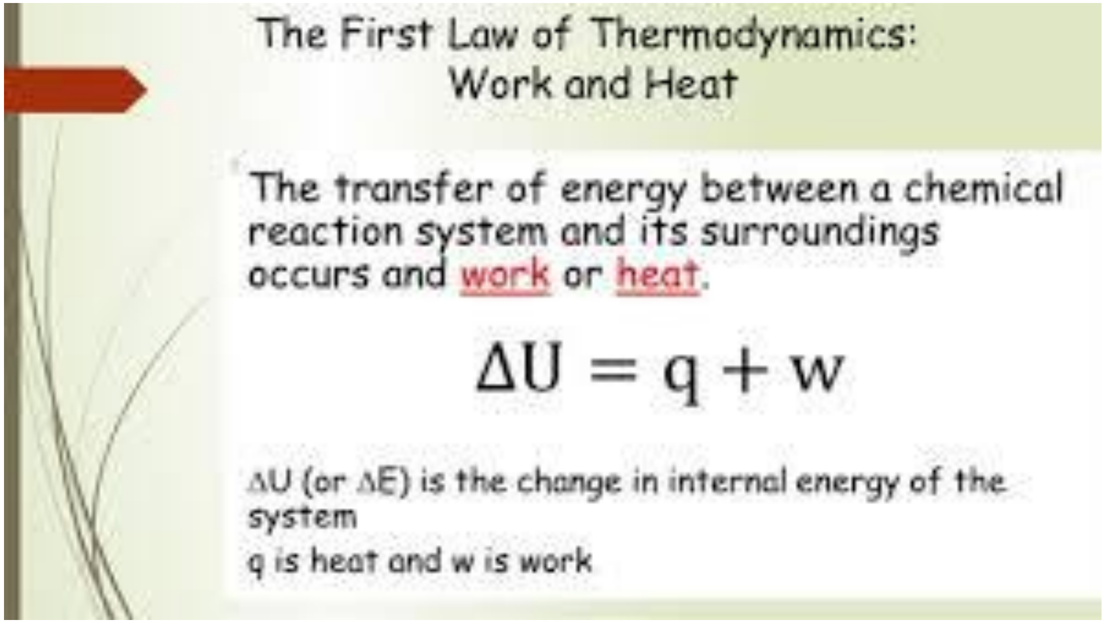
Two objects are defined to have the same temperature if they are in thermal equilibrium with each other

Law's of thermodynamics

First law of thermodynamics or law of conservation of energy-. "**Energy can neither be created nor destroyed although it can be transformed from one form to another**". **OR "The total amount of the energy of the universe is a constant.**
Or Energy can be converted from one form to another but it can neither be created not destroyed.
Such As Mechanical Energy, Heat, Light, Chemical Energy, And Electrical Energy.

- **Energy** Is the ability to bring about change Or to do work.
- **Thermodynamics** Is The Study of energy

$\Delta U = Q + W$



According to the **first law,** the effects of **Q** and **W** in a given system during a transformation from an **initia**l thermodynamic state to a **final** thermodynamic state are related to an intrinsic property of the system called the **internal energy (E, or U)**, defined as

$$\Delta E = E_2 - E_1 = Q + W$$

where **E2** is the internal energy of the system in its final state and **E1** is the internal energy of the system in its initial state ,**Q** is the heat, and **W** is the work. The change in internal energy **E** is related to **Q** and **W** transferred between the system and its surroundings.

- $\Delta U = U_f - U_i = Q + W$
  - Q is the energy transferred to the system by heat
  - W is the work done on the system
  - ΔU is the change in internal energy

Important Definitions

Reversibility

- reversible: if the process happens slow enough to be reversed.
- irreversible: if the process cannot be reversed (like most processes)

Reversible Processes

- A ***reversible process*** **is defined as a process that can be reversed without leaving any trace on either system or surroundings.**

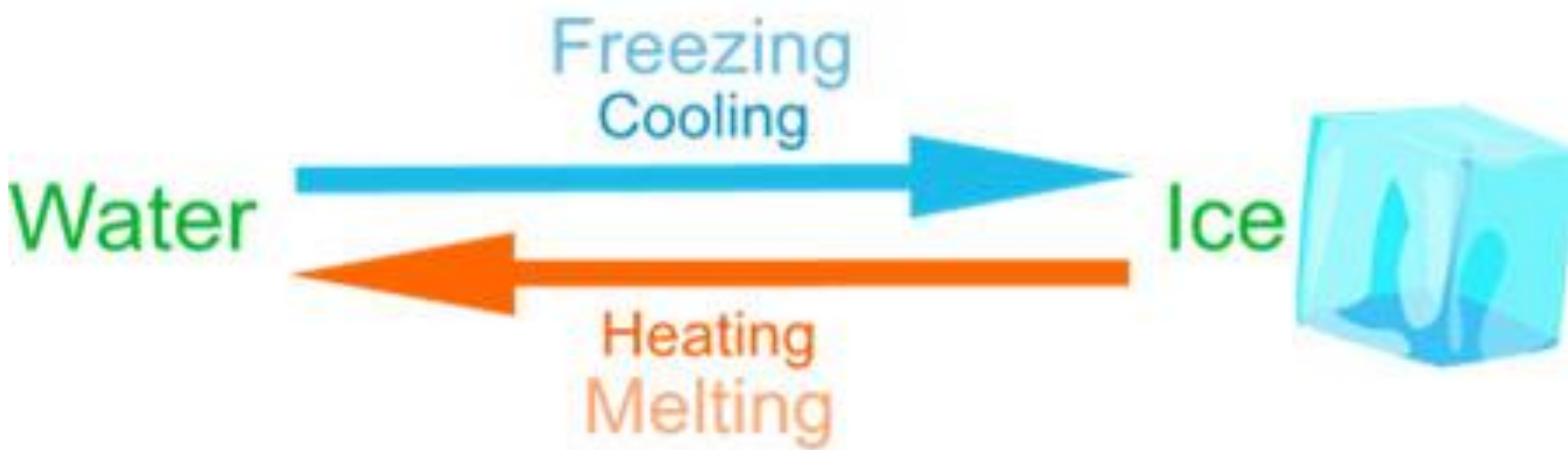
- **This is possible if the net of heat and net work exchange between the system and the surrounding is zero for the combined process (original and reverse).**

nonspontaneous

Quasi-equilibrium expansion or compression of a gas

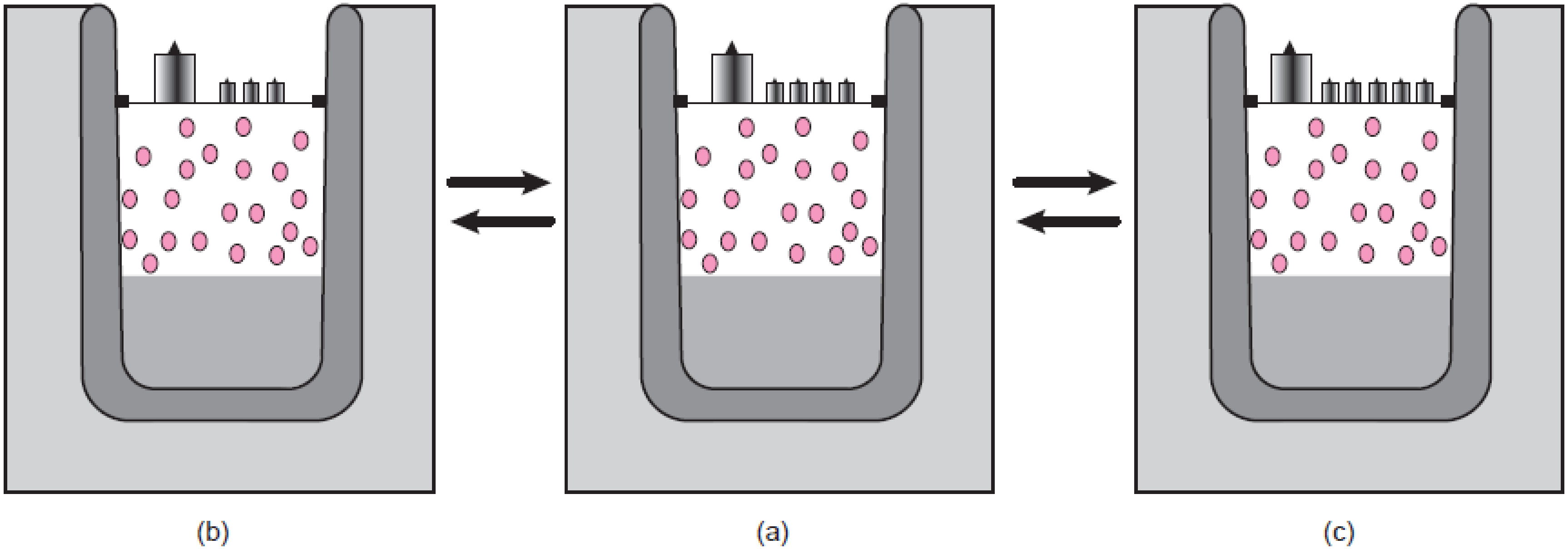
(*b*) Quasi-equilibrium expansion and compression of a gas

Reversible Changes



When we put some water in the freezer of a refrigerator it will turn into ice.

If we then warm ice it melts and changes back into water.



reversible process: evaporation and condensation of water at 1 atm in a closed system.

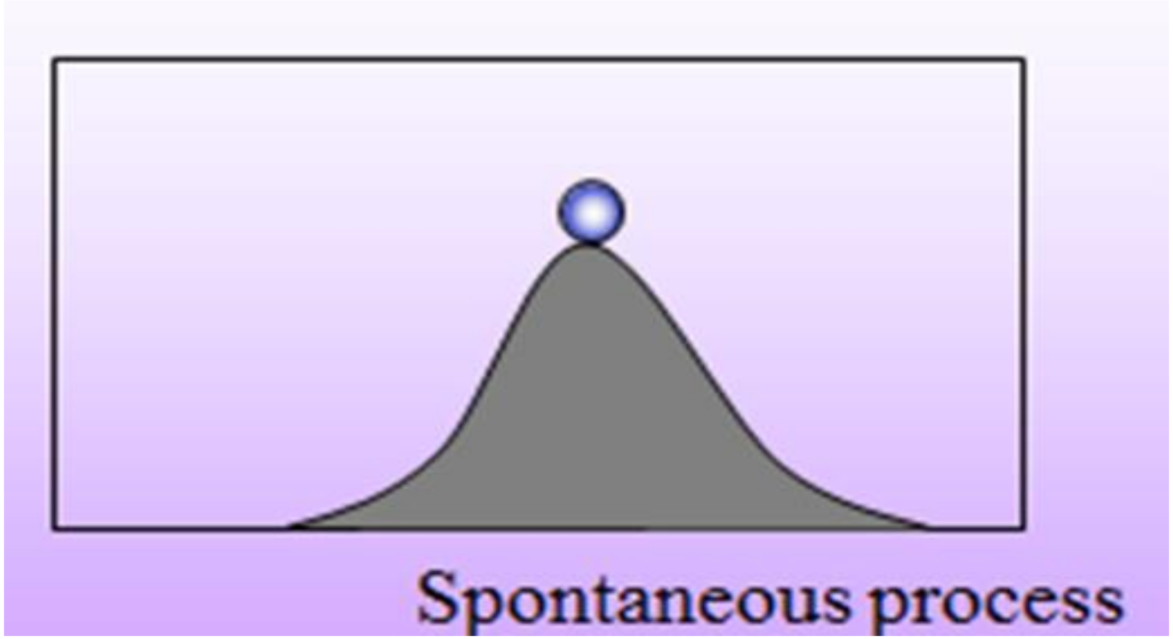
(a) System at equilibrium with P ex=1 atm;

(b) expansion is infinitesimal;

(c) compression is infinitesimal.

In thermodynamics, an irreversible process is defined as a process that cannot be reversed, process, that cannot return both the system and the surroundings to their original conditions.
During irreversible process the entropy of the system increases.

- All **Spontaneous** processes are **irreversible**.
- All **Real** processes are **irreversible**.



Isothermal process

When the temperature is kept constant during a process, thereaction is said to be conducted isothermally. An isothermal reaction may be carried out by placing the system in a large constant-temperature ($(\Delta T = 0)$)

- An isothermal process is a constant temperature process. Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium
- For ideal gases, if ΔT is zero, $\Delta U = 0$
- Therefore, $Q = (-, +)W$
  - Any energy entering the system (Q) must leave as work (W)

$$dE = đq + đw \quad \Longrightarrow \quad đw = dE$$

- An **adiabatic process** transfers no heat
  - **therefore Q = 0**
- **$\Delta U = Q - W$**
- **When a system expands adiabatically, W is positive (the system does work) so ΔU is negative.**
- **When a system compresses adiabatically, W is negative (work is done on the system) so ΔU is positive.**

the temperature significantly.
When heat is neither lost nor gained during a process, the reaction is said to occur ***adiabatically.*** A reaction carried on inside a sealed Dewar flask or "vacuum bottle" is adiabatic because the system is thermally insulated from its surroundings. In thermodynamic terms, it can be said that an adiabatic process is one in which $dq = 0$, and the first law under adiabatic conditions reduces to

Isochoric Process

- An isochoric process is a constant volume process. When the volume of a system doesn’t change, it will do no work on its surroundings. $W = 0$

$$\Delta U = Q$$

- Heating gas in a closed container is an isochoric process

Isobaric Process

- An isobaric process is a constant pressure process. ΔU, W, and Q are generally non-zero, but calculating the work done by an ideal gas is straightforward

$$W = P \cdot \Delta V$$

$$W = -P \cdot \Delta V$$

- Water boiling in a saucepan is an example of an isobar process the maximum work done in the expansion as well as the heat absorbed because

$$\boldsymbol{Q = E - W}$$

E is equal to zero for an ideal gas in an isothermal process.

The maximum work in an isothermal reversible expansion may also be expressed in terms of pressure because from **Boyle's law**, $V2/V1 = P1/P2$ at constant temperature. Therefore, equation can be

$$W_{\max} = -nRT \ln \frac{V_2}{V_1}$$

$$W_{\max} = -nRT \ln \frac{P_1}{P_2}$$

Example1

One mole of water in equilibrium with its vapor is converted into steam at 100◦C and 1 atm. The heat absorbed in the process is about 9720 cal/mole. What are the values of the three first-lawterms Q, W, and ΔE? Now, V_1 is the volume of 1 mole of liquid water at 100◦C, or about 0.018 liter

The amount of heat absorbed is the heat of vaporization, given as 9720 cal/mole. Therefore, Q = 9720 cal/mole
The work **W** performed against the constant atmospheric pressure is obtained by using equation

$$\mathbf{W = -nRT \ln(V_2/V_1).}$$

The volume V_2 of 1 mole of steam at 100◦C and 1 atm is given by the gas law, assuming that the vapor behaves ideally:

$$PV = nRT$$ **ideal gas law**

$$V_2 = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.6 \text{ liters}$$

It is now possible to obtain the work,

$$W = -(1\text{ mole})(1.9872\text{ cal/K mole})(398.15\text{ K})\ln(30.6/0.018)$$
$$W = -5883\text{ cal}$$

The internal energy change ΔE is obtained from the first-law expression,

$$\Delta E = 9720 - 5883 = 3837\text{ cal}$$

The remaining 3837 cal increases the **internal energy** of the system. This quantity of heat supplies **potential energy** to the vapor molecules, that is, it represents the work done against the non covalent forces of attraction

Example2

Calculate the work done when 1.0 mole water at 373K vaporizes against an atmospheric pressure of 1.0 atmosphere. Assume ideal gas behavior.

ANSWER

$$PV = nRT$$

$$V_2 = \frac{1.0 \times 0.0821 \times 373}{1.0} = 30.6 \text{ liter}$$

V1 is negligible w.r.t. V2

$w = -P \times \Delta V = -(1.0) \times (30.6)$ liter−atm

$= -30.6$

against an atmospheric pressure

$w = -P \times \Delta V$

$V2 >> V1$

Example3

One mole of a gas occupying $3dm^3$ expands against constant external pressure of 1atm to a volume of 13 dm^3. The work done

A- -10atm dm^3

B- -20atm dm^3

C- -39atm dm^3

D- -48atm dm^3

ANSWER

$W = -P \times \Delta V$

$= -1 \times (13-3) = -10\text{atm}\ dm^3$

Example4

-Why is alcohol used in thermometers for measuring very low temperatures, whereas mercury is used for high temperatures?

❑ The Alcohol Thermometer

This was the first to be invented and it is still in use today. The column of alcohol is quite wide, coloured (usually red) to make it easy to read. It is often used for measuring air temperatures which range between **- 20°C and +50°C. This is fine because alcohol freezes at - 80°C and boils a**t +78°C.

❑ The Mercury Thermometer

This is the most commonly used laboratory thermometer because temperatures above +78°C often need to be measured. Mercury freezes at - 39°C, so for very low temperatures it is not so useful. Mercury boils at + 357°C which is the upper limit of the thermometer

Example5

Calculate the work to vaporize 1.73 moles of water at 0.68 atm pressure and a temperature of 373K. Assume that the vapor behaves as an ideal gas.

Volume of water(V1) 0.03114L

ANSWER

$$PV = nRT$$

$$V2=\frac{1.73\times0.0821\times373}{0.68atm}=77.909 \text{ liter}$$

77.909-0.03114=77.87L

W=-P ΔV

W=-77.87X0.68=52.95liter .atm

a note to say,

thank you

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