

# Thermal & Statistical Physics

*Thermal & Statistical Physics*  
**PHYS 343**

Dr.Salwa Alsaleh

[Salwams@ksu.edu.sa](mailto:Salwams@ksu.edu.sa)

[fac.ksu.edu.sa/salwams](http://fac.ksu.edu.sa/salwams)

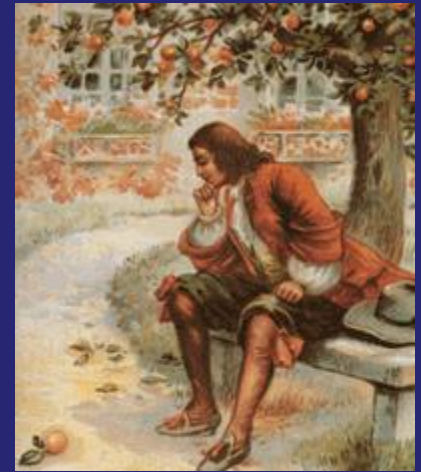
# LECTURE 11

*Thermodynamic Systems*

*Specific Heat Capacities*

*Zeroth Law*

*First Law*



# *Thermodynamic Systems*

**Thermodynamics:** Fundamental laws that heat and work obey

**System:** Collection of objects on which the attention is being paid

**Surrounding** – Everything else around

System can be separated from surrounding by:

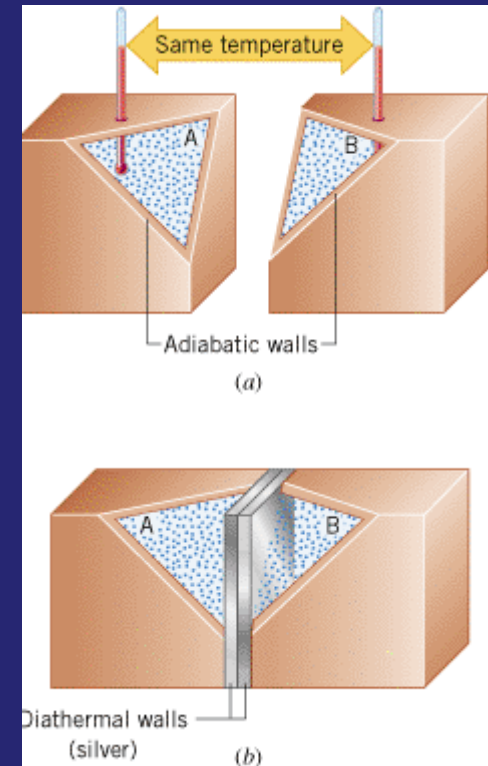
**Diathermal Walls** – Allows heat to flow through

**Adiabatic Walls** - Perfectly insulating walls that do not  
allow flow of heat

**State of a system** – the physical condition – can be defined using various parameters such as **volume, pressure, temperature etc.**

# Zeroth Law of Thermodynamics

- **Remember with Thermal equilibrium**
- Two systems are said to be in **thermal equilibrium** if there is no net flow of heat between them when they are brought into thermal contact.
- Temperature is the indicator of thermal equilibrium
- Two systems individually in thermal equilibrium with a third system are in thermal equilibrium with each other.



# *The 1<sup>st</sup> law of thermodynamics*

- **Classical thermodynamics**
- natural laws governing the behaviour of macroscopic systems

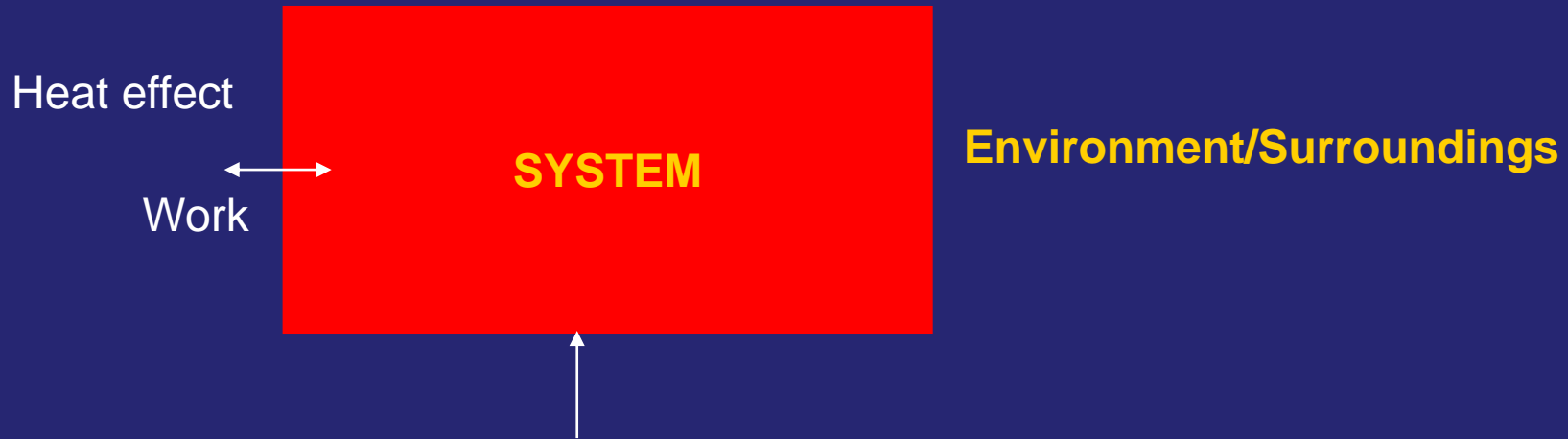
- **First Law**

$$\Delta E = Q + W$$

Internal changes =  $\Sigma$  interactions occurring at boundaries (T, P, V, ... etc)

- **Second Law**

- Reversible process
- Entropy



Boundary

- (1) adiabatic or diathermal
- (2) permeable or impermeable
- (3) rigid or movable

An isolated system: impermeable, rigid, adiabatic and independent of events in the environment

# *The 1<sup>st</sup> law of thermodynamics*

It was first a postulate. However, the overwhelming evidence accumulated over time has elevated it to the stature of a law of nature.

Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.

$$\Delta(\textit{energy of the system}) + \Delta(\textit{energy of surroundings}) = 0$$

# First Law of Thermodynamics

- When a substance involves in a process involving energy in the form of work and heat, the internal energy of the substance can change.
- **First Law:** Relationship between work, heat and change in the internal energy

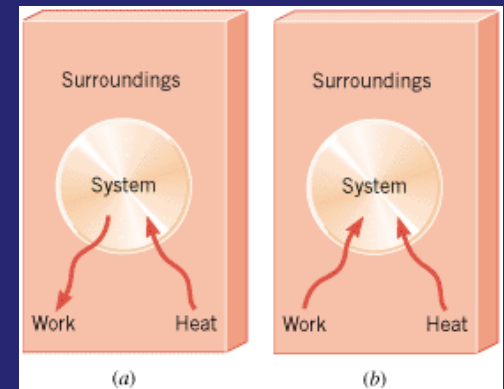
- Internal energy changes when heat is imparted:  $\Delta E = Q$

- Internal energy changes when work is done on the system or by the system:  $\Delta E = -W$

Work is +ve when it is done by the system and  
Work is -ve when it is done on the system.

- Thus system can lose or gain energy through heat or work:

$$\Delta E = E_f - E_i = Q - W$$





# Thermal Processes

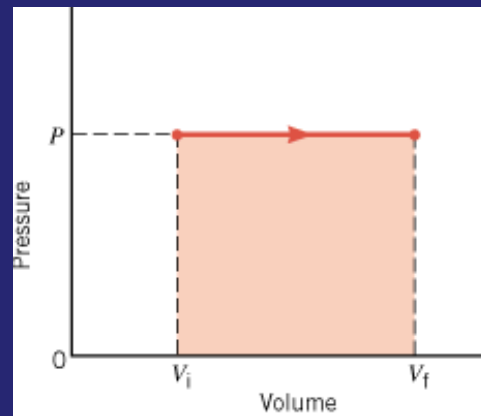
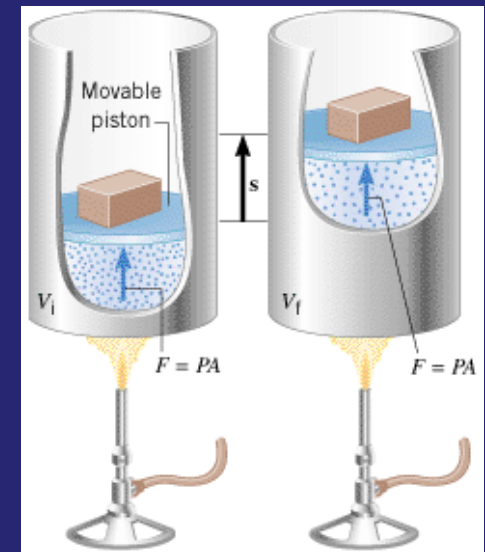
A System can interact with the surrounding in several ways – but has to obey the first law of thermodynamics.

Isobaric process – Constant pressure

*Isobaric process*  $W = P\Delta V = P(V_f - V_i)$

Work done is +ve when it expands ( $V_f > V_i$ )

Isobaric compression: work done is -ve



# Thermal Processes

*Isochoric Process*: Constant volume process

Area under the P V graph = 0  $\Rightarrow$  No work is done

So the heat given is only used to change the internal energy.

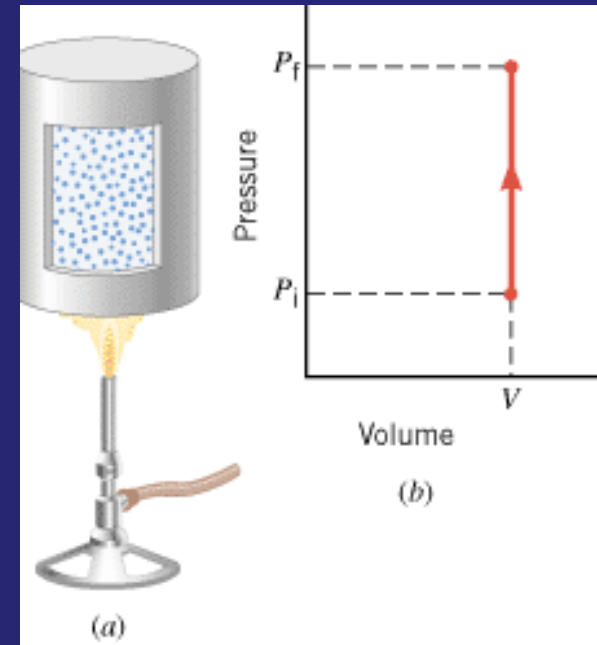
$$\Delta E = Q - W = Q$$

*Isothermal Process*: Constant temperature process.

*Adiabatic Process*: Occurs without the transfer of heat  $\Rightarrow$

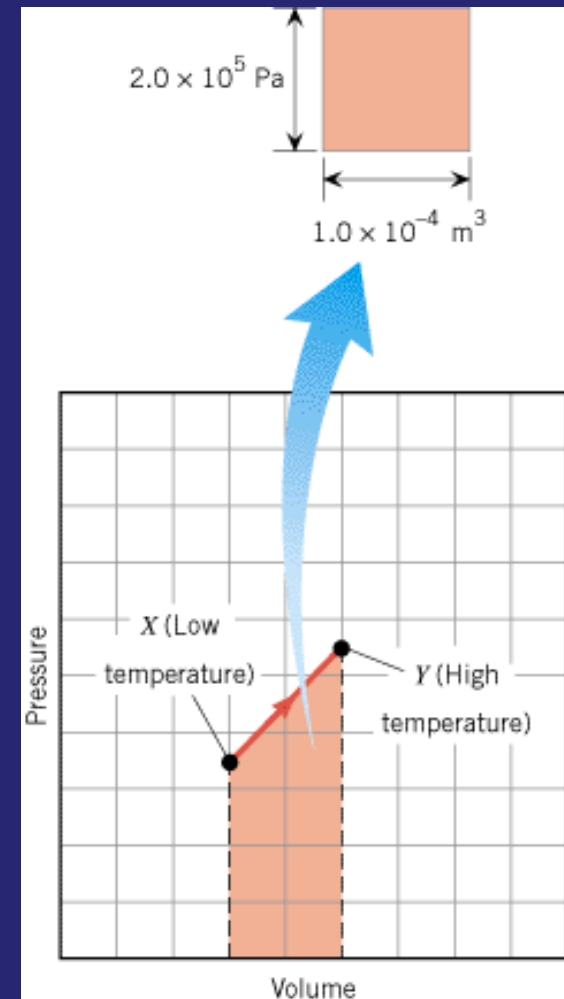
$$Q = 0 \Rightarrow \Delta E = -W$$

When work is done **by** a system adiabatically,  $W$  is **-ve** and when work is done **on** the system adiabatically,  $W$  is **+ve**



# Thermal Processes

Area under a P-V graph is the work for any kind of thermal process



# Thermal Processes using an Ideal Gas

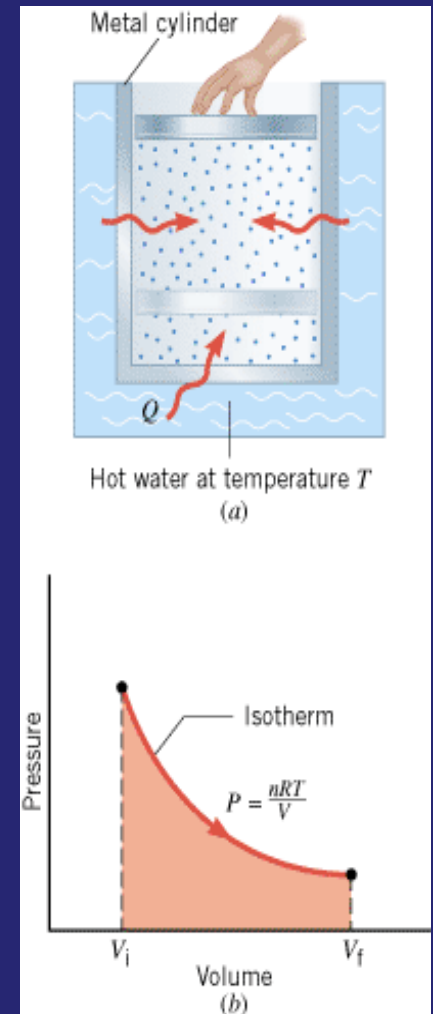
**Ideal Gas:** A gas for which the potential energy of interaction between the molecules is independent of their separation and hence is independent of the gas volume. The internal energy of such a gas depends on the temperature.

## Isothermal Compression or Expansion

When a system performs work isothermally, the temperature stays constant.

*Isothermal  
expansion or  
compression of  
an ideal gas*

$$W = nRT \ln \left( \frac{V_f}{V_i} \right)$$



# *Thermal Processes using an Ideal Gas*

What is the origin of energy for this work?

- Internal energy of an ideal gas is proportional to its Kelvin temperature,  $E = \frac{3}{2} (n RT)$

-Internal energy remains constant throughout an isothermal process and so the change in internal energy = 0

(ie)  $\Delta E = Q - W = 0 \Rightarrow Q = W$

Energy for the work originates from the heat provided.

**Expansion:** heat flows from the hot water to the gas

**Compression:** heat flows from the gas into the water

# Thermal Processes using an Ideal Gas

## Adiabatic Compression or Expansion

When a system performs work adiabatically, NO heat flows into or out of the system.

*Adiabatic  
expansion or  
compression of  
a monatomic  
ideal gas*

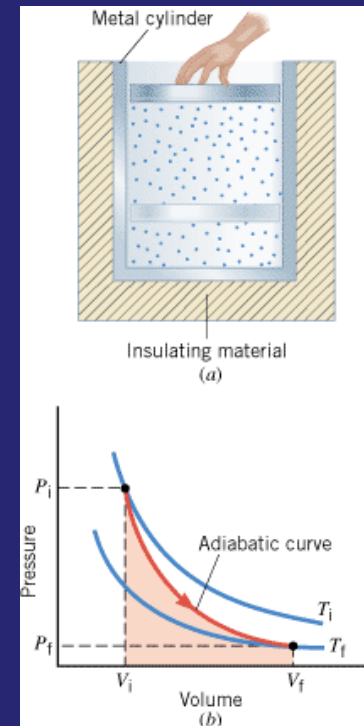
$$W = \frac{3}{2}nR(T_i - T_f)$$

Expands adiabatically  $\Rightarrow$  -ve work  $\Rightarrow T_i > T_f$   
Compress adiabatically  $\Rightarrow$  +ve work  $\Rightarrow T_i < T_f$

$$T_i = PV_i / (nR) \text{ and } T_f = PfV_f / (nR)$$

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$\gamma$  Is the ratio of specific heat capacities at constant pressure and constant vol



# Constant- $V$ and constant- $P$

- The general 1st law equation for a mechanically reversible, closed-system process:

$$dE = dQ - PdV$$

- constant total volume:

- $Q = \Delta E$

- the heat transferred is equal to the internal-energy change of the system

$$dQ = dE = d(PV)$$

$$\longrightarrow dQ = d(E = PV)$$

- constant pressure:

- $Q = \Delta H$

- the mathematical definition of **enthalpy**:  $H \equiv U + PV$
- the heat transferred is equal to the enthalpy change of the system

Calculate  $\Delta U$  and  $\Delta H$  for 1 kg of water when it is vaporized at the constant temperature of 100 °C and the constant pressure of 101.33 kPa. The specific volumes of liquid and vapor water at these conditions are 0.00104 and 1.673 m<sup>3</sup>/kg. For this change, heat in the amount of 2256.9 kJ is added to the water.

---

Imagine the fluid contained in a cylinder by a frictionless piston which exerts a constant pressure of 101.33 kPa. As heat is added, the water expands from its initial to its final volume. For the 1-kg system:

$$\Delta H = Q = 2256.9 \text{ kJ}$$

$$\begin{aligned}\Delta U &= \Delta H - P\Delta(V) \\ &= 2256.9 \text{ J} - 101.33 \text{ kPa} \times (1.673 - 0.001) \text{ m}^3 \\ &= 2256.9 \text{ kJ} - 169.4 \text{ kJ} \\ &= 2087.5 \text{ kJ}\end{aligned}$$



# *Equilibrium*

- In thermodynamics, equilibrium means not only the absence of change but the absence of any tendency toward change on a macroscopic scale.
- Different kinds of driving forces bring about different kinds of change. For example:
  - imbalance of mechanical forces tend to cause energy transfer as a work.
  - temperature differences tend to cause the flow of heat.
  - Gradients in chemical potential tend to cause substance to be transfer from one phase to another.

# Phase rule

- For any system at equilibrium, the number of independent variables that must be arbitrarily fixed to establish its *intensive* state is given by J.W. Gibbs (1875).
- The degrees of freedom of the nonreacting systems:

$$F = 2 - \pi + N$$

- where  $\pi$  is the number of phases,  $N$  is the number of chemical species
- A phase is a homogeneous region of matter. A gas or a mixture of gases, a liquid or a liquid solution, and a crystalline solid are examples of phases. Various phases can coexist, but they must be in equilibrium for the phase rule to apply.
- The minimum number of degrees of freedom for any system is zero:

$$F = 2 - \pi + N = 0$$

- $N = 1, \pi = 3$  (i.e. the triple point)

How many degrees of freedom has each of the following systems:

- (1) Liquid water in equilibrium with its vapor.
  - (2) Liquid water in equilibrium with a mixture of water vapor and nitrogen.
  - (3) A liquid solution of alcohol in water in equilibrium with its vapor.
- 

(1) 1 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 1 = 1$$

(2) 2 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 2 = 2$$

(3) 2 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 2 = 2$$

No Sir, I meant why are we here on a Saturday?

