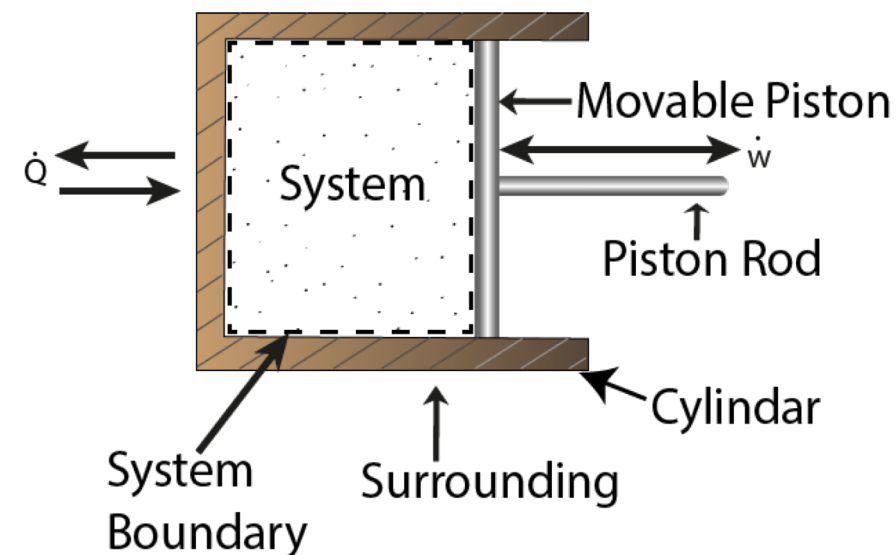
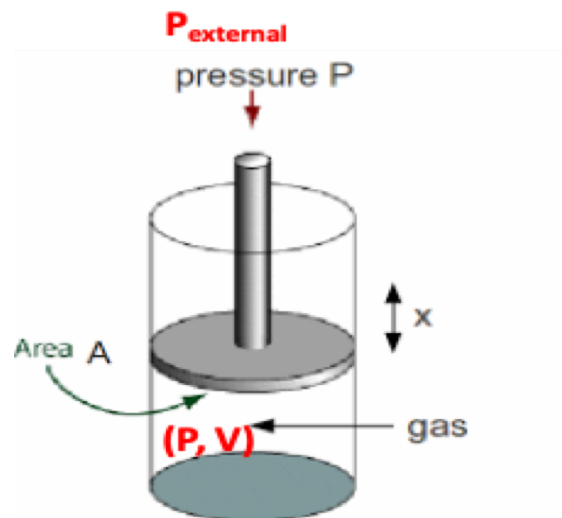


Work done on/by the system

W (Work) = F (force) \times w (distance moved in the direction of force)



➤ **Gas is heated** \Rightarrow it will expand and push the piston, thereby doing work on the piston.

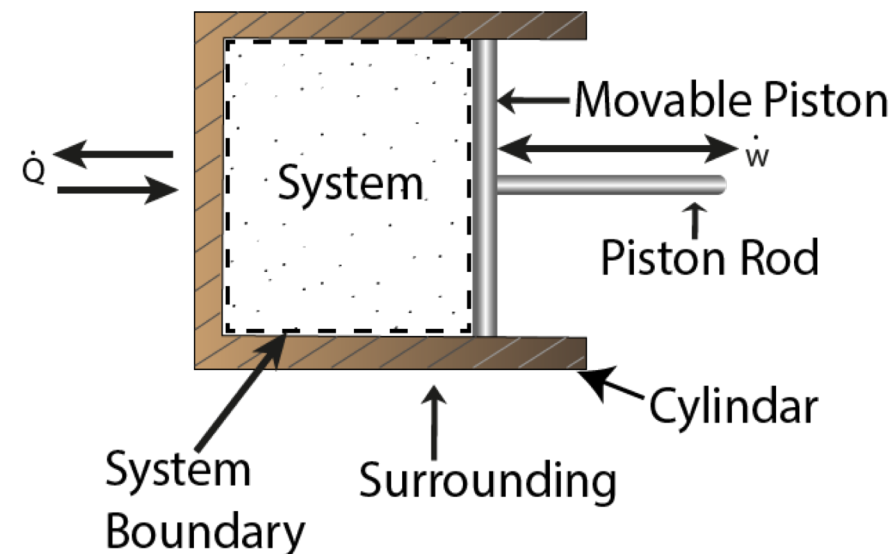
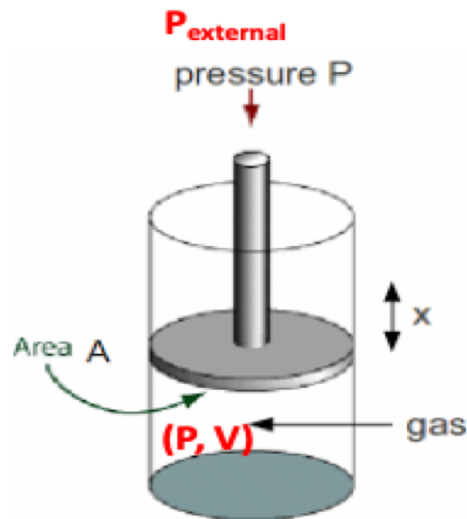
The work done (dW) when the system expands by dV against a pressure P_{ex} : $dW = -P_{\text{ex}}dV$

Total work done by the system to expand from volume V_i to V_f : $W = -\int_{V_i}^{V_f} P_{\text{ex}}dV$

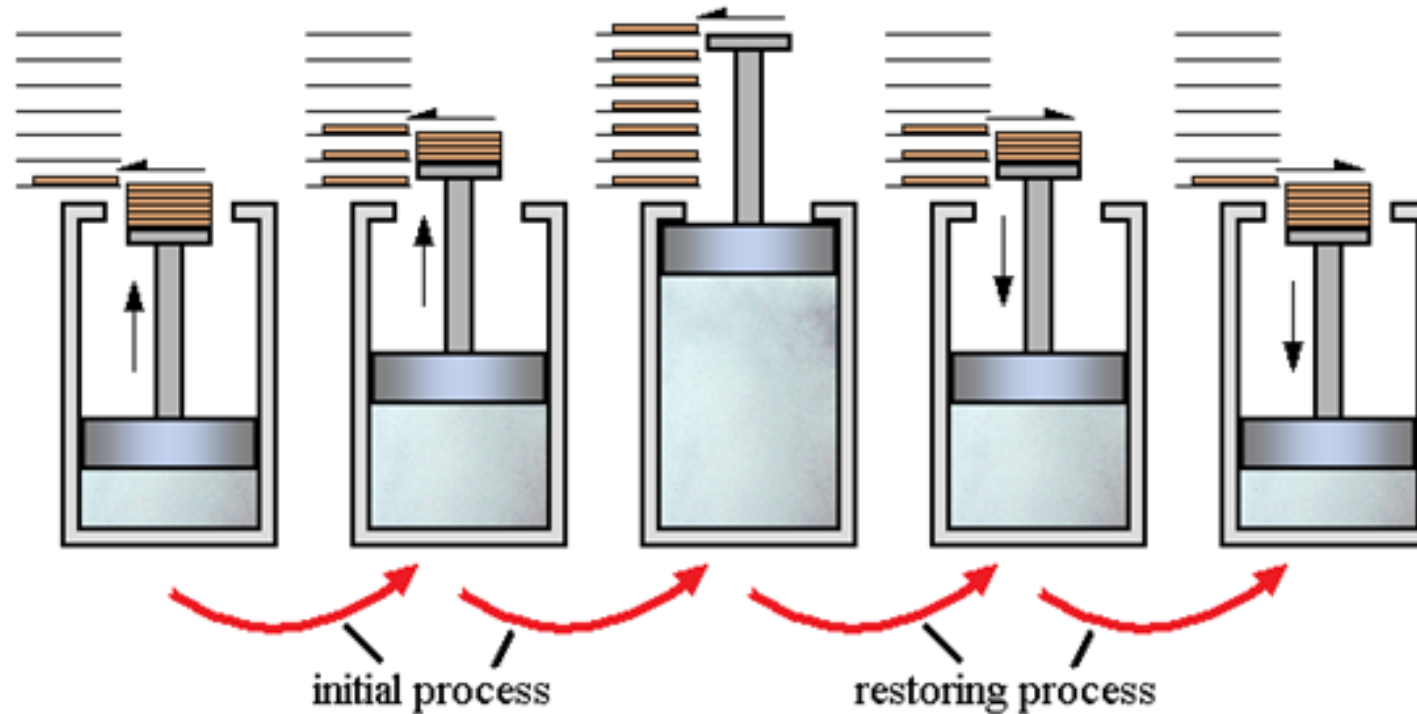
☑ This is an example of the **system doing the work on the surrounding**

Work done on/by the system

W (Work) = F (force) \times w (distance moved in the direction of force)



- If the *piston is pushed down*, on the other hand, the *piston does work on the gas*. This is an example of the surrounding doing work on the system.
- If the volume doesn't change, no work is done.
- If the external pressure is constant throughout the expansion, $W = -P_{\text{ex}}\Delta V$



- ❑ Ideally, a thermodynamics process is reversible if the process can be turned back such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe.

- ❑ A thermodynamics process is reversible if the process can be turned back such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe.

- In reality, no such processes as reversible processes can exist. Thus, a more appropriate definition is a reversible change in thermodynamics is

A change that can be reversed by an infinitesimal modification of a variable.

Example 1:

Thermal equilibrium of two systems with the same temperature

- If the temperature of either system is lowered infinitesimally, then energy flows into the system with the lower temperature.
- If the temperature of either system at thermal equilibrium is raised infinitesimally, then energy flows out of the hotter system

Example 2:

Reversible expansion:

Suppose a gas is confined by a piston.

external pressure (P_{ex}) = pressure (P) of the confined gas.

- Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in P_{ex} in either direction causes changes in volume in the opposite directions.

If P_{ex} becomes infinitesimally smaller than P , then the gas will undergo *infinitesimal expansion*

If P_{ex} becomes infinitesimally larger than P , then the gas will undergo *infinitesimal contraction*

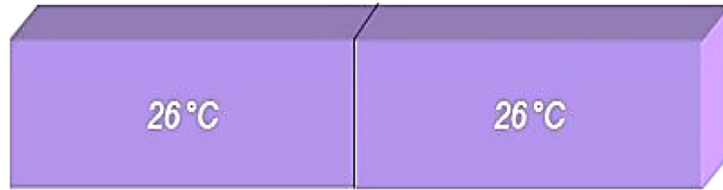
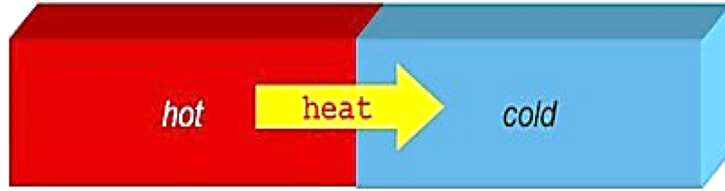
If $P_{\text{ext}} \gg P$, an infinitesimally decrease in P_{ext} will not make it smaller than P and thus the direction of the process will not be changed. Here, the system is not in mechanical equilibrium with the surrounding.

To achieve reversible expansion P_{ex} is set equal to P at each stage of the expansion.

$$dW = -P_{\text{ex}}dV$$
$$W = - \int_{v_i}^{v_f} p dv$$

Examples of Reversible Process

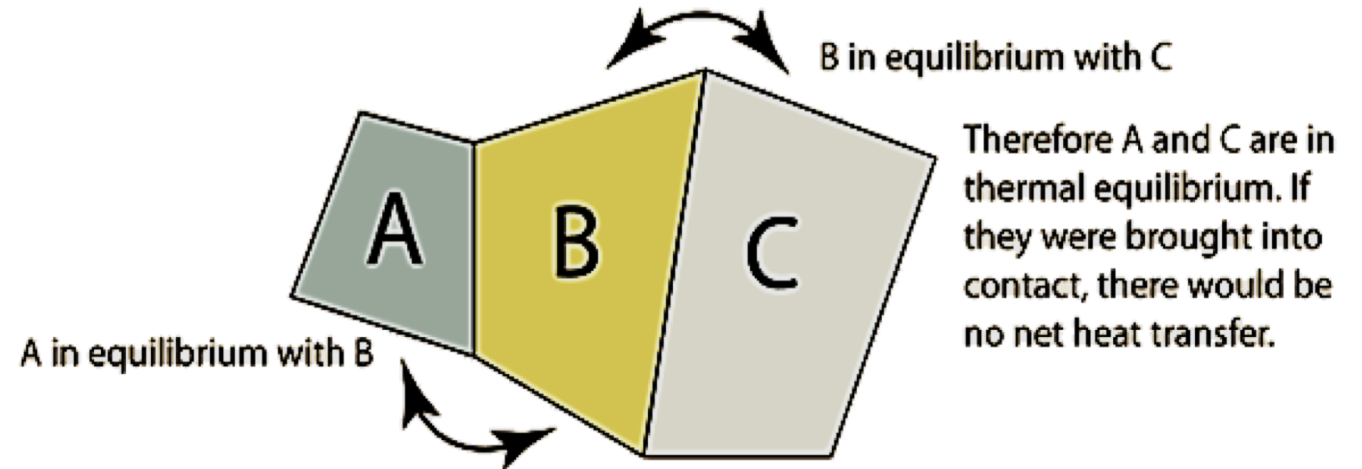
- extension of springs
- **slow adiabatic compression or expansion of gases**
- electrolysis (with no resistance in the electrolyte)
- the frictionless motion of solids
- slow isothermal compression or expansion of gases



- ❑ Two physical systems are in **thermal equilibrium** if there is no net flow of heat (thermal energy) between them when they are connected by a path permeable to heat.

➤ According to 0th law:

If **two systems** are in **thermal equilibrium** with a **third system**, then those two systems are in thermal equilibrium with each other.



- The 0th law of thermodynamics defines thermal equilibrium and forms a basis for the definition of temperature.

- It's the law of conservation of energy

□ **The energy of an isolated system remains constant. Whenever a quantity of energy (some form) disappears, an exactly equivalent quantity of energy (some other form) must make an appearance.**

➤ **Heat (q) and work (w)** are equivalent ways of changing the internal energy of a system

→ Example:

- If a weight has been raised/lowered in the surroundings, transfer of energy happens by doing the work.
- If ice has melted in the surroundings, it indicated transfer of energy as heat.

The sign of w and q:

✓ **+ve** if **energy is transferred to the system** as work/heat

✓ **-ve** if **energy is lost** from the system.

➤ For a system, if w = **work done on a system**, q = energy transferred as heat to a system & ΔU = resulting change in internal energy, then,

$$\Delta U = q + w$$

If w = work is done by the system,

change in internal energy (ΔU) of a system = heat added to the system (q) - the work done **by** the system (**w**)

$$\Delta U = q - w$$

➤ Isothermal Process (constant temperature)

- In an isothermal process, the temperature stays constant, so **the pressure and volume are inversely proportional** to one another

⇒ **For an ideal gas,**

The internal energy (U) \propto Temperature (T)

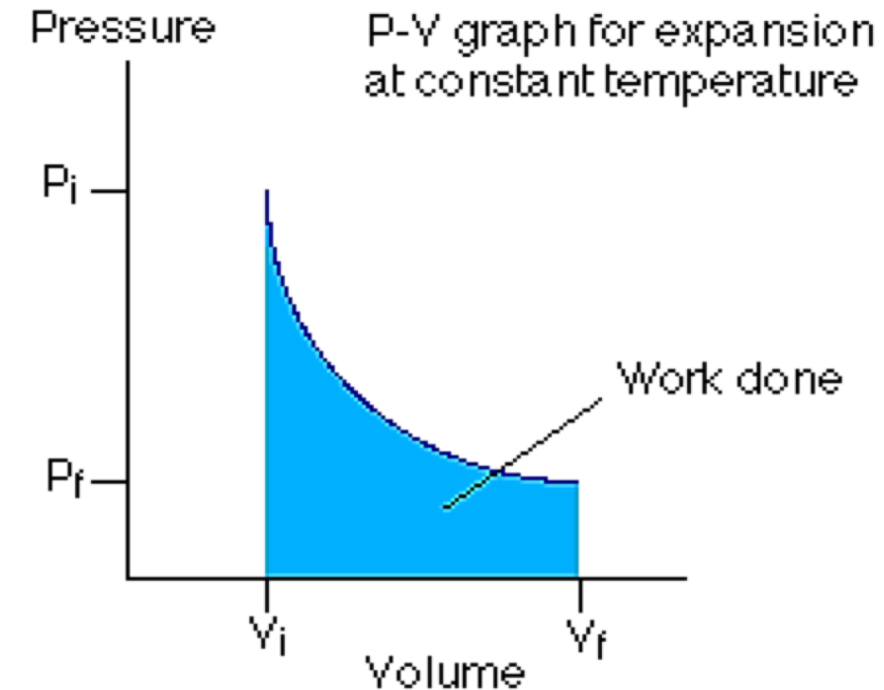
if $T = \text{fixed}$, $\Delta U = 0$

$$\text{As, } \Delta U = q + w = 0$$

$$\Rightarrow q = -w$$

- If the **system does work**, the energy comes from **heat flowing into the system from the surrounding**
- if **work is done on the system**, heat flows **out of the system to the surrounding**.

The work done w depends on whether the expansion is reversible or irreversible.



What would be q and w for an isolated system?

- If the change of a system is brought about at **constant pressure**, there will be change in volume.

V_i = volume of initial state, V_f = volume of final state.

Work done by the system, $w = -P (V_f - V_i)$

$$\therefore \Delta U = q + w$$

$$\text{or, } \Delta U = q - P (V_f - V_i)$$

$$\Rightarrow U_f - U_i = q - P (V_f - V_i)$$

$$\Rightarrow (U_f + PV_f) - (U_i + PV_i) = q$$

- The quantity **(U + PV)** is called the **enthalpy (H)** of the system

$$\Rightarrow H_f - H_i = q$$

$$\Delta U = \Delta H - P\Delta V$$

or,

$$\Delta H = \Delta U + P\Delta V$$

Heat capacity of a system between any two temperatures is defined as the quantity of heat (q) required to raise the temperature of the system from the lower temperature to the higher temperature divided by the temperature difference.

$$C = \frac{q}{T_2 - T_1}$$

- ☺ If mass of the system is 1 g,
the heat capacity is called the **specific heat of the system**
- ☺ For 1 mol of substance,
the heat capacity is termed as '**molar heat capacity**'

□ **Molar heat capacity at constant volume**

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

$\Delta U = q + w$ @ constant volume $w = 0$ & $\Delta U = q$

❑ Molar heat capacity at constant pressure (C_p)

$$\Delta U = q + w$$

@ constant pressure,
there is change in volume
& some work is done

$$\Delta U = q - P (V_f - V_i)$$
$$\text{or, } q = \Delta U + p\Delta V$$



As quantity (U+PV) is the
enthalpy (H) of the system

\Rightarrow

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

❑ Relationship between C_p & C_v

For a system, $\Delta H = \Delta U + \Delta(PV)$

$$\text{or, } \frac{\Delta H}{\Delta T} = \frac{\Delta U}{\Delta T} + \frac{\Delta(PV)}{\Delta T}$$

$$\text{or, } C_p = C_v + \frac{\Delta(PV)}{\Delta T}$$

- For ideal gas, $PV = RT$ (for 1 mole)

$$\Delta(PV) = R \Delta T$$

$$C_p = C_v + \frac{R\Delta(T)}{\Delta T} \quad \text{or, } C_p = C_v + R$$

$$\text{or, } C_p - C_v = R$$

$$C_v = 3/2 R \text{ (For monoatomic ideal gas)}$$

$$C_p = 5/2 R \text{ (For monoatomic ideal gas)}$$

$$\text{Heat capacity ratio, } \gamma = \frac{C_p}{C_v} = 5/3 \text{ for a monoatomic ideal gas}$$

➤ Reversible isothermal expansion:

$$w = \int_{v_i}^{v_f} P dv = \int_{v_i}^{v_f} \frac{nRT}{V} dv \quad (\text{as } PV = nRT)$$

(throughout the expansion, $P_{\text{ex}} = P$ as the expansion is reversible)

- Work done **by** the n moles of gas is evaluated as:

$$w = -nRT \ln \frac{V_f}{V_i} = -nRT \ln \frac{P_i}{P_f}$$

(since $\frac{V_f}{V_i} = \frac{P_i}{P_f}$ in an isothermal expansion of a perfect gas)

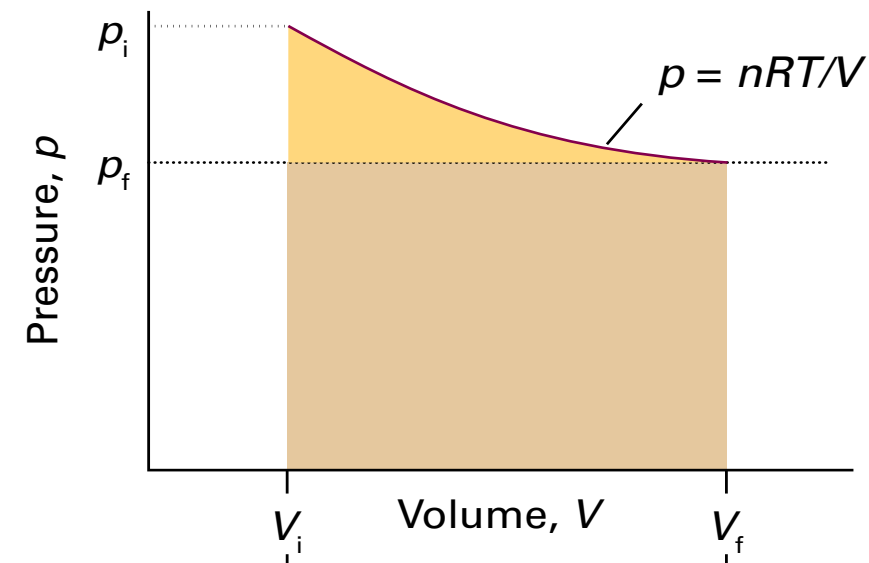
➤ Relations for Irreversible Isothermal expansion

- a) Free expansion (expansion in vacuum)

$$w = -\int_{v_i}^{v_f} P_{\text{ex}} dv = 0$$

- a) Volume of the gas expands **against a constant pressure**.

$$w = -\int_{v_i}^{v_f} P_{\text{ex}} dv = -P_{\text{ex}} (V_f - V_i)$$



- The work done by a perfect gas when it expands **reversibly and isothermally** is equal to the area under the isotherm $p = nRT/V$.
- The work done during the **irreversible expansion** against the same final pressure is equal to the rectangular area shown slightly darker. **Note that the reversible work done is greater than the irreversible work done.**

➤ Adiabatic process (constant heat)

- no heat is added/ removed from a system.
- 1st law of thermodynamics:

$$\Delta U = w$$

(as no heat is allowed to enter/leave the system, $q = 0$)

✓ Example: A gas expanding so quickly that no heat can be transferred. Due to the expansion work, temperature drops. **This is exactly what happens with a carbon dioxide fire extinguisher, with the gas coming out at high pressure and cooling** as it expands at atmos. pressure

→ **Expansion:** $w = -ve$, $\Delta U = -ve$;

So, **T** of the system falls

⇒ Work is done by the system at the expense of its internal energy

- $w = \Delta U = C_v \Delta T$ (for 1 mole of gas)
- $\Delta H = C_p \Delta T$ (for 1 mole of gas)

➤ Reversible adiabatic expansion

- Relation between T, V and P

$$\left(\frac{T_i}{T_f}\right) = \left(\frac{V_f}{V_i}\right)^{\gamma-1} \Rightarrow \ln\left(\frac{T_i}{T_f}\right) = (\gamma - 1) \ln\left(\frac{V_f}{V_i}\right)$$

$$\Rightarrow \ln\left(\frac{T_i}{T_f}\right) = \left(\frac{C_p}{C_v} - 1\right) \ln\left(\frac{V_f}{V_i}\right) \quad [as, \gamma = \frac{C_p}{C_v}]$$

$$\Rightarrow \ln\left(\frac{T_i}{T_f}\right) = \left(\frac{R}{C_v}\right) \ln\left(\frac{V_f}{V_i}\right) \quad [as, C_p - C_v = R]$$

$$\Rightarrow \boxed{C_v \ln\left(\frac{T_i}{T_f}\right) = R \ln\left(\frac{V_f}{V_i}\right)}$$

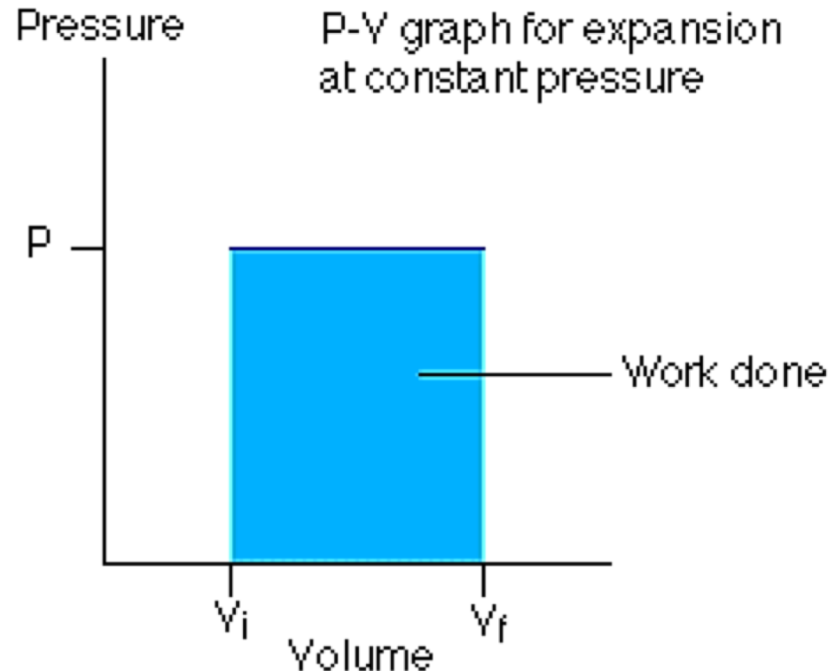
➤ Irreversible adiabatic expansion

- Free expansion ($P_{ex} = 0$) : $\Delta T = 0, W = 0, \Delta H = 0$
- Expansion against a constant pressure:

$$C_v (T_f - T_i) = R P_{ex} \left(\frac{T_i P_f - T_f P_i}{P_i P_f} \right)$$

➤ Isobaric process (constant pressure)

- the pressure is kept constant.
- The work done by the system in an isobaric process is simply the pressure multiplied by the change in volume
- ✓ Example of an isobaric system: A gas, being slowly heated or cooled, confined by a piston in a cylinder.



➤ Isochoric process (constant volume)

- the volume is kept constant
- The work done is zero in an isochoric process
- ✓ . Example of an isochoric system: A gas in a box with fixed walls

