CHE 2615
Physical Chemistry

LECTURE 1: THERMODYNAMICS

UNZA
2021

Thermodynamics

References:

1. **Physical Chemistry 8th Edition** by Peter Atkins & Julio de Paula
2. **Physical chemistry by** Laidler, Meiser & Sanctury
3. **Chemistry: Atoms First** by Julia Burde & Jason Overby
4. **Any other physical chemistry book**

Content

1. The basic concepts: system and Surroundings
2. State Function & Path Function
3. Properties of System
4. First law of thermodynamics;
5. Internal energy, work and heat, pressure-volume work;
6. Enthalpy, Hess's law;
7. Heat of reaction, fusion and vaporization;

Introduction

- The term '**thermodynamics**' implies flow of heat.
- Thermodynamics deals with energy changes associated with all types of physical and chemical processes.
- It is based on three important generalizations called first, second and third laws of thermodynamics.
- All these laws are based on human experience.
- Thermodynamics helps us to ***predict whether a given process or a chemical reaction is feasible under given conditions temperature, pressure and concentration.***

Introduction

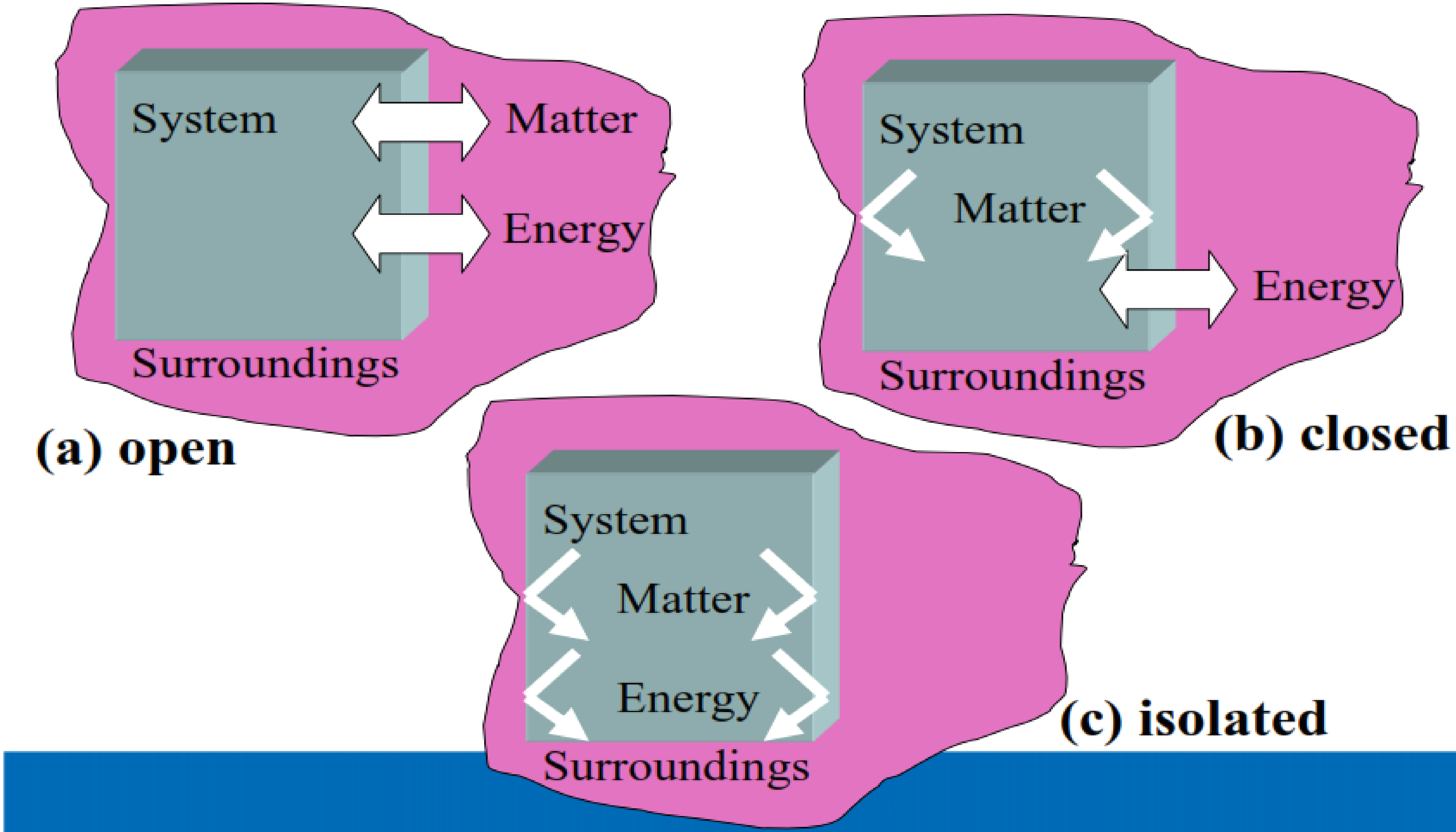
- Thermodynamics does not tell anything about the rate at which a given process may proceed.
- **It is concerned only with the initial and the final states of the system.**
- Thermodynamics is applicable to **macroscopic systems consisting of matter in bulk and** not to microscopic systems of individual atoms or molecules.
- **It ignores the internal structure of atoms and molecules.**

The basic concepts: System and Surroundings

- Physical chemists attempt to define very precisely the object of their study which is called the ***system***.
- It may be solid, liquid, gaseous or any combination of these.
- The ***system*** is a particular segment of the world (with definite boundaries) on which we focus our attention.
- Outside the system are the ***surroundings***, and the system plus the surroundings compose the ***universe.***

Types of systems

The Basic Concepts: the system



Intensive and Extensive properties

- The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes:
  a) Intensive properties
  b) Extensive properties

Intensive properties

- A property which does not depend on the quantity of matter present in the system, is known as ***Intensive Property*** (system size independent).
- Examples of intensive properties are pressure, temperature, density, and concentration.
- If the overall temperature of a glass of water (our system) is 20ºC, then any drop of water in that glass has a temperature of 20ºC.
- Similarly if the concentration of salt, NaCl, in the glass of water is 1 M, then any drop of water from the glass also has a salt concentration of 1 M.

Extensive Properties

- A property that does depend on the quantity of matter present in the system, is called an ***Extensive Property*** (system size dependent).
- Examples of extensive properties are volume, number of moles, enthalpy, entropy, and Gibbs' free energy.
- By definition, the extensive properties are additive while intensive properties are not.
- Let us consider the system 'a glass of water'. If we double the mass of water, the volume is doubled and so is the number of moles and the internal energy of the system.

Intensive and Extensive properties

Extensive Properties	Intensive Properties
Volume	Molar volume
No. of moles	Density
Mass	Refractive index
Free Energy	Surface tension
Entropy	Viscosity
Enthalpy	Free energy per mole, specific heat
Heat capacity	Pressure, Temperature, Boiling Point, Freezing Point

State of System (State Variables)

- A thermodynamic system is said to be in a certain state when all its properties are fixed.
- The quantities whose value serves to describe the system completely are called the ***thermodynamic properties of the system***.
- Once the properties of the system are completely specified, one says that the state of the system is specified.
- Thus, the defining properties are sometimes called ***state variables*** or ***state properties***.

Equation of State

- Examples of state properties are pressure, volume, temperature and composition.
- When we are considering a closed system consisting of one or more components, mass is not a state variable.
- It is not necessary to state all the properties (state variables) to define a system completely.
- For a pure gas, the composition is fixed automatically, as it is cent per cent.

Equation of State

- The remaining state variables *P*, *V*, *T* are interrelated in the form of an equation called the ***Equation of State.***
- Thus for one mole of a pure gas, the equation of state is :

$$PV = RT$$

- where *R is gas constant.*
- If of the three state variables *(P, V, T), P and T* are specified, the value of third (*V*) is fixed automatically and can be calculated from the equation of state.

Independent and Dependent state variable.

- The variables *(P and T)* which must be necessarily specified to define the state of a system, are designated as the ***Independent state variables*****.**
- The remaining state variable (V) which depends on the value of ***P and T,*** is called the ***Dependent state variable.***
- An important characteristic of a state variable (or state function) is that when the state of a system is altered, the change in the variable depends on the initial and final states of the system.

Independent and Dependent state variable.

- For example, if we heat a sample of water from 0º C to 25º C, the change in temperature is equal to difference between the initial and final temperatures.

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 25^{\circ}\text{C}$$

- The way in which the temperature change is brought about has no effect on the result.

State Function & Path Function

- A property which depends only on the initial & final state of the system but not on the path by which the initial state is converted to final state is called a ***state function***.
- Example includes pressure, volume, temperature, ΔU, ΔH, ΔS & ΔG.
- A quantity which depends on the path or route by which the system reaches from initial state to final state is called ***path function***. e.g. work & heat.

Thermodynamic equilibrium

- A system in which the macroscopic properties do not undergo any change with time is said to be in ***thermodynamic equilibrium***.
- The term Thermodynamic equilibrium implies three types of equilibriums i.e., thermal equilibrium, mechanical equilibrium and chemical equilibrium.
- A system is said to be at ***thermal equilibrium*** if there is no flow of heat from one portion of system to another.
- This is possible if temperature of system remain constant throughout in all part of system.

Thermodynamic equilibrium

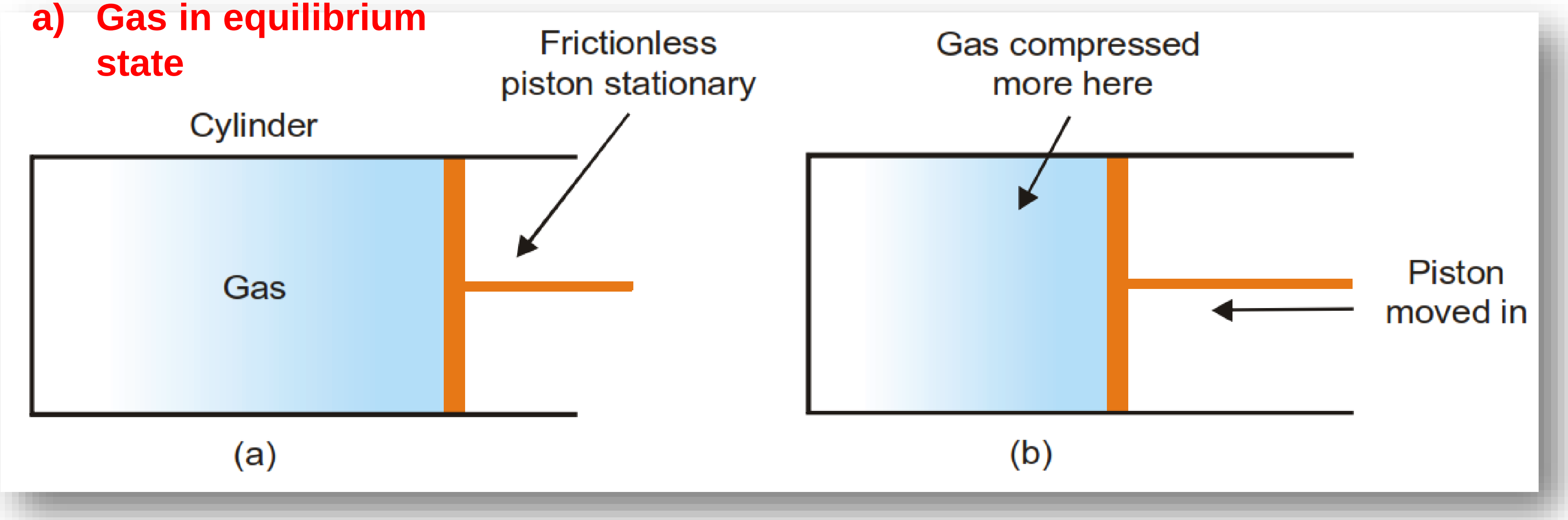
- A system is said to be under ***mechanical equilibrium*** if no mechanical work is done by one part of the system on another part.
- This is possible if pressure of the system remain constant throughout in all parts of the system.
- A system is said to be in ***chemical equilibrium*** if the composition of various phases in the system remains the same throughout.
- When all these three equilibrium established then it system is in ***thermodynamic equilibrium***, the is the **Criteria for Equilibrium.**

Thermodynamic equilibrium

- Suppose we have a gas confined in a cylinder that has a frictionless piston. If the piston is stationary, the state of the gas can be specified by giving the values of pressure and volume.
- The system is then in a ***state of equilibrium****.*
- If the gas contained in a cylinder, as stated above, is compressed very rapidly by moving down the piston, it passes through states in which pressure and temperature cannot be specified, since these properties vary throughout the gas.
- The gas near the piston is compressed and heated and that at the far end of the cylinder is not.

Thermodynamic equilibrium

- The gas then would be said to be in non-equilibrium state.



b) Rapidly compressed gas in non-equilibrium state.

a) Gas in equilibrium state

- Thermodynamics is concerned only with equilibrium states.

Thermodynamic processes

- The operation by which a system changes from one state to another state is called a process.

a) Isothermal process:

  - A process is isothermal if its temperature remains constant at all times i.e., for an isothermal process, $\Delta T = 0$ and $\Delta U = 0$

b) Adiabatic process:

  - A process is carried out under such condition that no exchange of heat takes place between the system and surroundings i.e

$$dq = 0.$$

Thermodynamic processes

c) Cyclic process:

- When a system undergoes a number of different states by different processes and finally returns to its initial state, it is said to have completed a cycle and the process is called a cyclic process. i.e. **$\Delta U = 0$** and also **$\Delta H = 0$**.

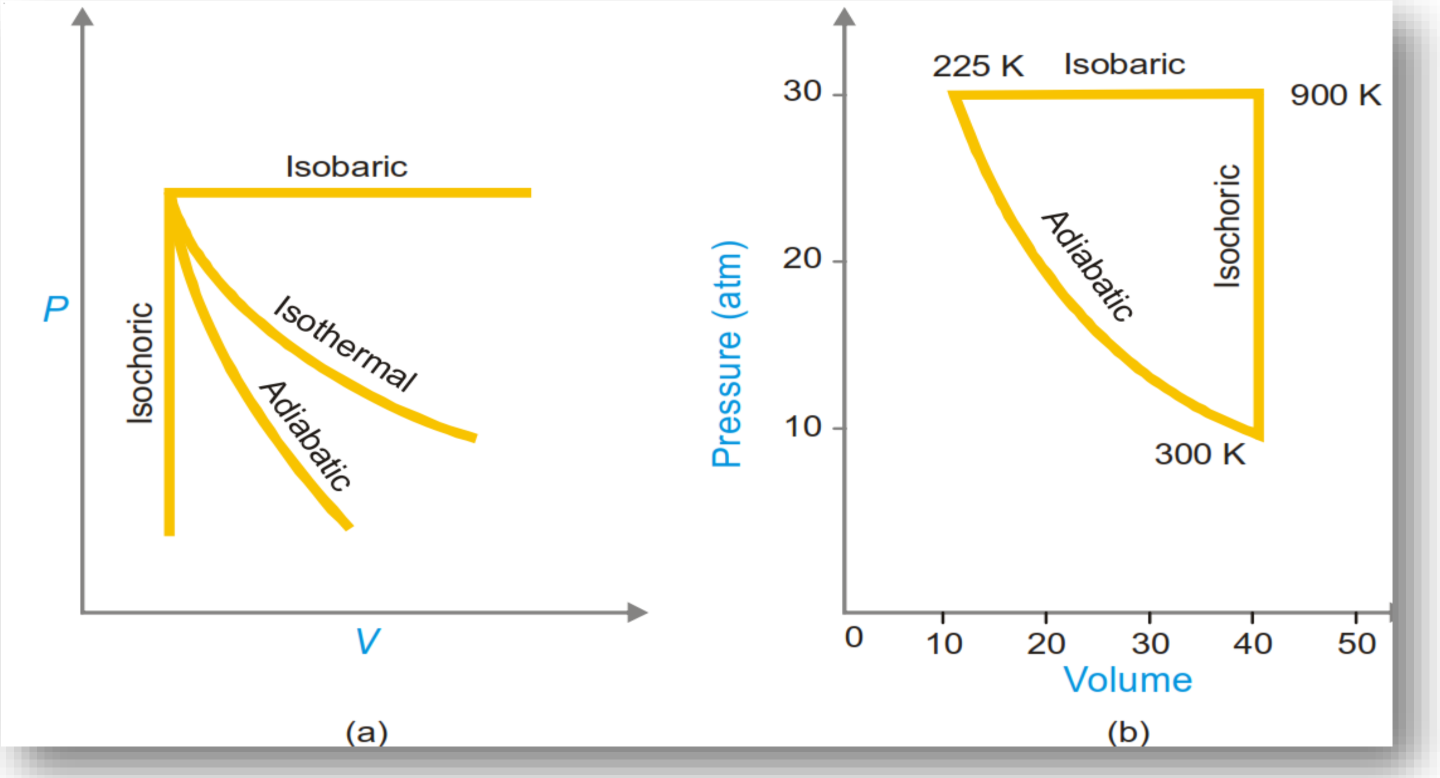
d) Isobaric process:

- The process is known as isobaric in which the pressure remains constant throughout the change i.e. **$\Delta P = 0$**

Thermodynamic processes

e) Isochoric process:

- The process is termed as isochoric in which volume remains constant through out the change i.e. ***ΔV* = 0**.



Reversible and Irreversible processes

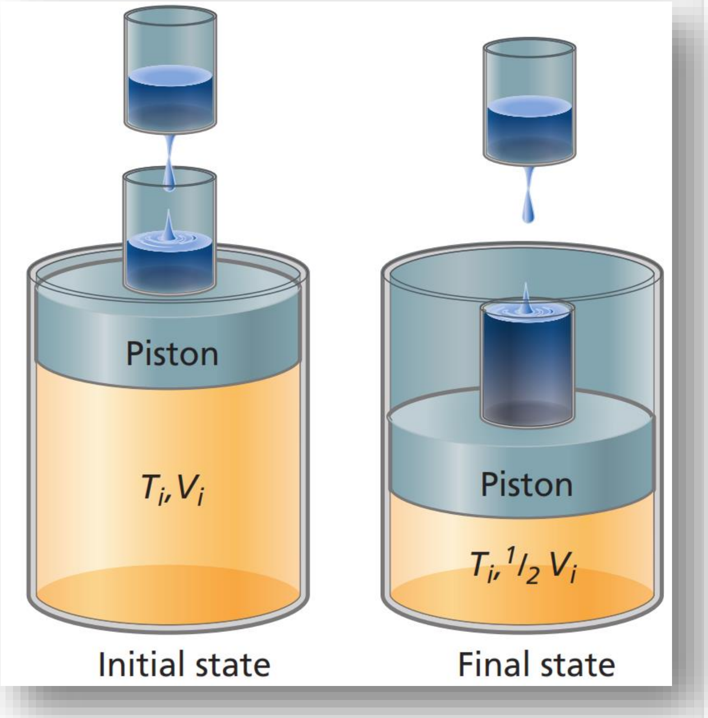
- **A thermodynamic reverse process** is a process which occurs infinitesimally slowly i.e., the opposing force is infinitesimally smaller than driving force and an infinitesimal increase in the opposing force can reverse the process.
- A reversible process is considered to proceed from the initial state to the final state through an infinite series of infinitesimally small stages.
- At the initial, final and all intermediate stages, the system is in equilibrium state.

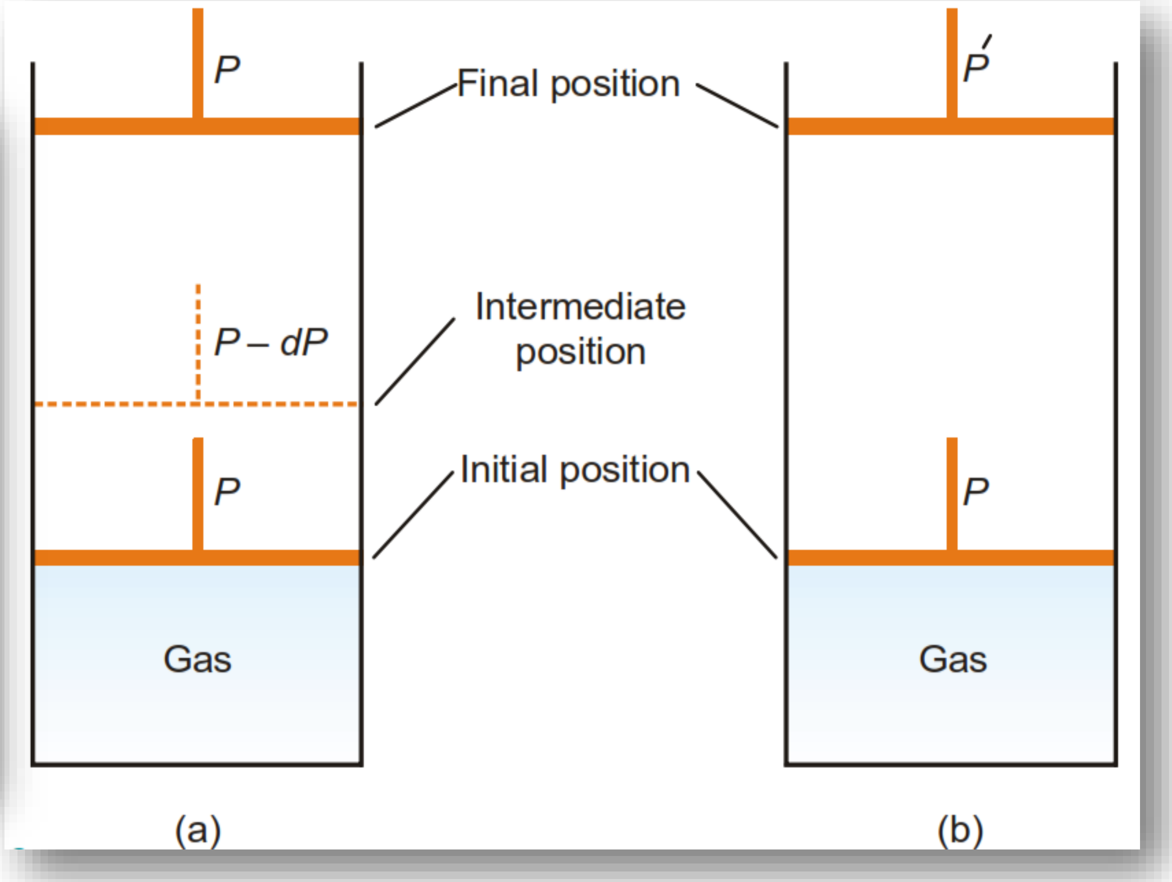
Reversible and Irreversible processes

- This is so because an infinitesimal change in the state of the system at each intermediate step is negligible.
- When a process goes from the initial to the final state in a single step and cannot be carried in the reverse order, it is said to be an **irreversible process.**
- **Here the system is in equilibrium state in** the beginning and at the end, but not at points in between.

Reversible and Irreversible processes

- Consider a certain quantity of a gas contained in a cylinder having a weightless and frictionless piston.





Reversible and Irreversible processes

- Let the pressure applied to the piston be *P* and this is equal to the internal pressure of the gas*.*
- Since the external and internal pressures are exactly counterbalanced, the piston remains stationary and there is no change in volume of the gas.
- Now suppose the pressure on the piston is decreased by an infinitesimal amount *dP* caused by the addition of one drop of wate*r.*
- Thus the external pressure on the piston being *P* – *dP,* the piston moves up and the gas will expand by an infinitesimal small amount.

Reversible and Irreversible processes

- The gas will, therefore, be expanded infinitely slowly *i.e.,* by a thermodynamically reversible process.
- At all stages in the expansion of the gas, *dP* being negligibly small the gas is maintained in a state of equilibrium throughout.
- If at any point of the process the pressure is increased by *dP,* the gas would contract reversibly.

Reversible and Irreversible processes

- On the other hand, the expansion is irreversible if the pressure on the piston is decreased suddenly.
- It moves upward rapidly in a single operation.
- The gas is in equilibrium state in the initial and final stages only or finite number of steps in finite time and cannot be reversed exactly by small changes in P, V, T etc.
- The expansion of the gas, in this case, takes place in an irreversible manner.

DIFFERENCES BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible Process	Irreversible Process
1. It takes place in infinite number of infinitesimally small steps and it would take *infinite time* to occur.	1. It takes place *infinite time*.
2. It is *imaginary* as it assumes the presence of frictionless and weightless piston.	2. It is *real* and can be performed actually.
3. It is in equilibrium state at *all stages* of the operation.	3. It is in equilibrium state only at the *initial and final stages* of the operation.
4. All changes are *reversed* when the process is carried out in reversible direction.	4. After this type of process has occurred all changes *do not return* to the initial state by themselves.
5. It is extremely slow.	5. It proceeds at *measureable speed*.
6. Work done by a reversible process is *greater* than the corresponding irreversible process.	6. Work done by a irreversible process is *smaller* than the corresponding reversible process.

Nature of Heat and Work

- When a change in the *state of a system occurs, energy is transferred to or from the surroundings.*
- This energy may be transferred as heat or mechanical work.

1) Heat (*q*)

- Heat (*q*) may be defined as the quantity of energy which flows between a system and its surroundings on account of temperature difference
- Heat always flows from high temperature to low temperature

Heat

- The unit of heat, which was used for many years, is **calorie (cal), defined as the** quantity of heat required to raise the temperature of 1 gram of water by 1º C in the vicinity of 15º C.
- Since heat and work are interrelated, **SI unit of heat is the joule (J).**
- If the heat flows from the surroundings into the system to raise the energy of the system, it is taken to be positive, +*q.*
- If heat flows from the system into the surroundings, lowering the energy of the system, it is taken to be negative, –*q.*

Work

2) Work (w)

- We shall refer the term ‘work’ for mechanical work.
- In thermodynamics, work is generally defined as the force multiplied by the distance.
- If the displacement of body under the force F is dl, the work done will be,

$$dw = Fdl$$

- The symbol dw stands for the small amount of work and also the inexactness of the function.

Work

- Several things should be noted in the definition of work:
  - ✓ Work appears only at the boundary of the system.
  - ✓ Work appears only during a change in state
  - ✓ Work is manifested by an effect in the surroundings.
- If work is done on a system by the surroundings and the energy of the system is thus increased, it is taken to be positive, $+w$.
- If work is done by the system on the surroundings and energy of the system is decreased, it is taken to be negative, $–w$.

Work

- In SI system of Units, work is expressed in Joules

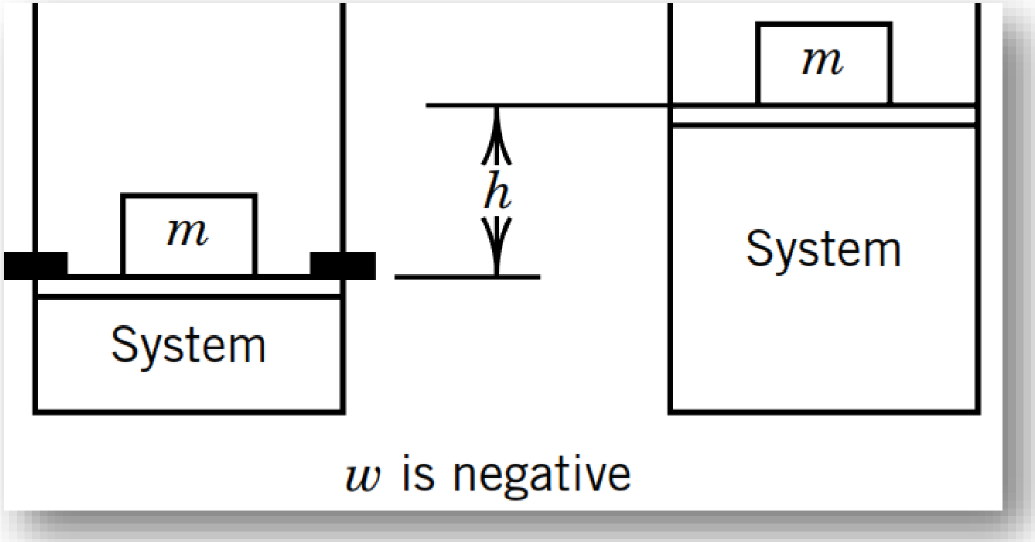
$$1\,J = 1\,Nm = \frac{kg\,m^2}{s^2}$$

Types of work

- Gravitational work
- Electrical work
- Osmotic work
- Mechanical work
- Pressure-Volume work
- E.t.c.

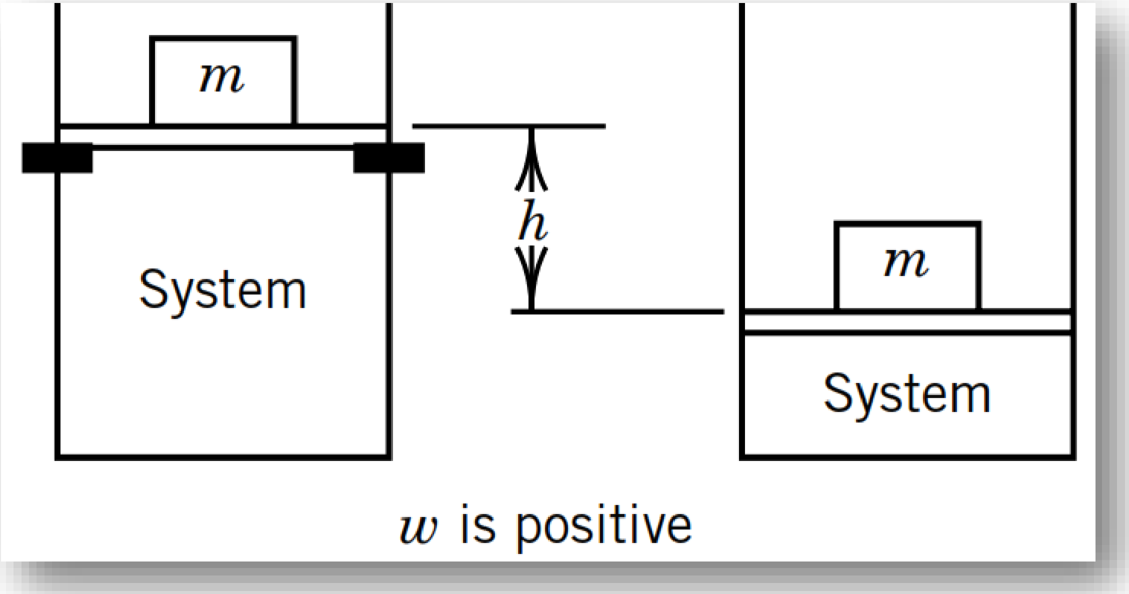
Pressure-Volume Work Processes

- Most calculations deals with the evaluation of the expansion or compression work of gases.
- If the volume of the system is increased against some pressure then work is done by the system on the surroundings (the system loses energy) and is given a -ve sign (-*w*).



Pressure-Volume Work Processes

- On the other hand, if the volume of the system is decreased, then the work is done by the surroundings on the system, the system gains energy as work and it given a positive sign (+*w*).



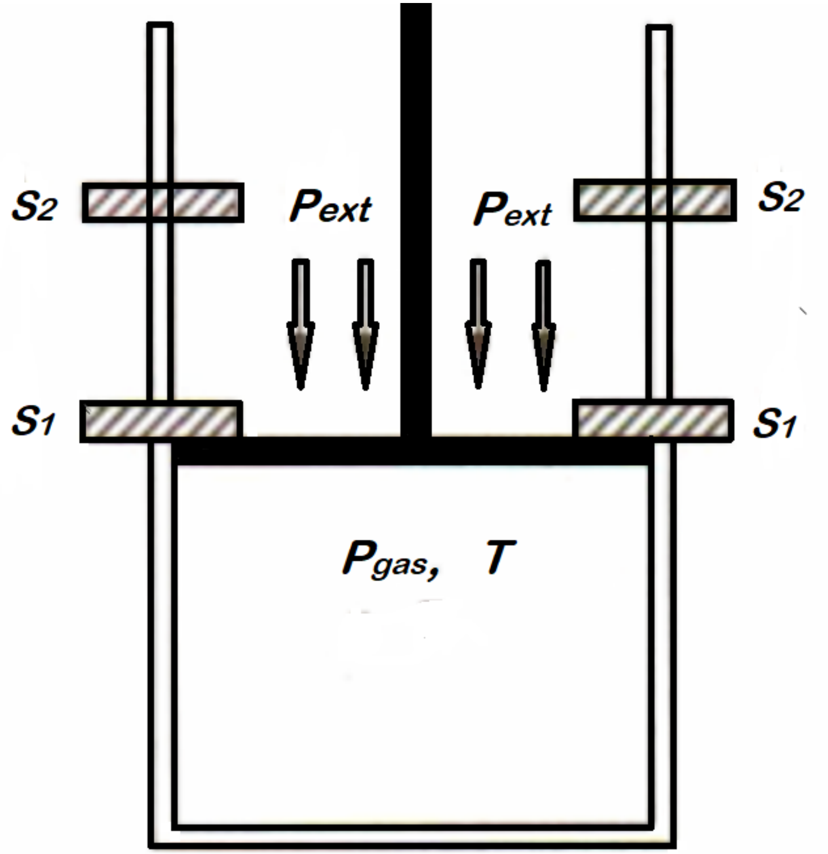
w is positive

Criterion of Expansion / Compression

- The essential criterion of expansion / compression work is that there should exist a difference between the internal pressure of the system (p_{gas}) and the external pressure (p_{ext}).
- Suppose a gas is contained in a cylinder fitted with a piston.
- Assuming that the piston has no weight and is frictionless.
- The piston can be held anywhere against a set of stops.

Criterion of Expansion / Compression

- Let the piston be initially held at stops S_1.
- If the stops S_1 are now removed, then the position of the piston will be decided by the external pressure which can be controlled by putting different masses on the piston



Criterion of Expansion / Compression

- If *m* is the mass that is put on the piston, then the force *F* acting downwards is

$$F = mg$$

- and the pressure acting downwards is

$$P_{ext} = \frac{F}{A} = \frac{mg}{A} \quad \text{or} \quad F = P_{ext}A$$

- Where A is the cross section area of the piston.

Criterion of Expansion / Compression

- If the external pressure (P_{ext}) is greater than the internal pressure (P_{gas}) of the system, the piston moves downwards i.e., **compression**.
- The volume of the system will decrease and it continues to decrease till the external pressure becomes equal to the internal pressure of the system
- If the external pressure (P_{ext}) is smaller than the internal pressure (P_{gas}), the piston moves upward resulting in expansion. i.e., **expansion**

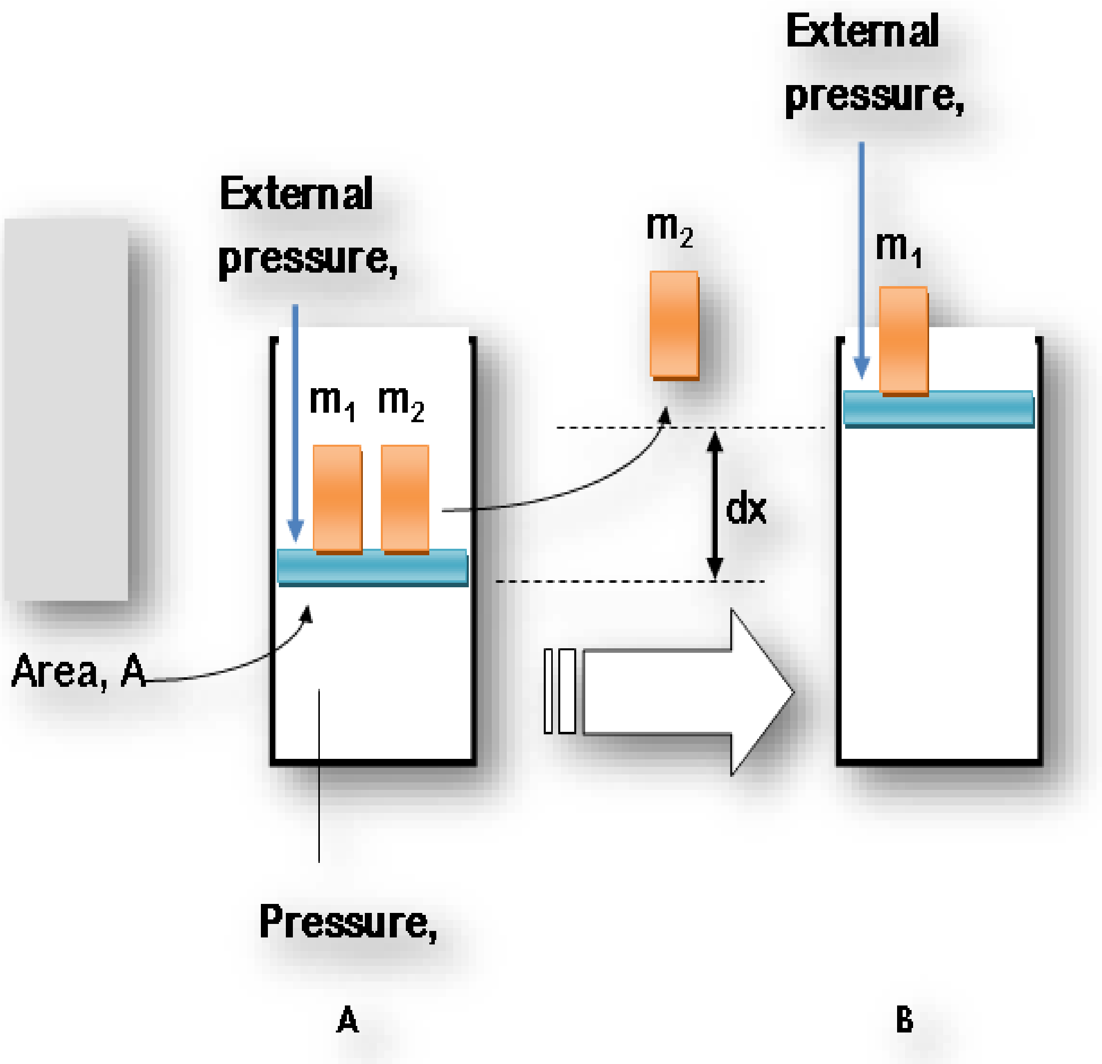
Criterion of Expansion / Compression

- Again, the volume will continue to increase till the external pressure becomes equal to the internal pressure.
- We can stop the expansion or compression in between by providing a set of stops at that stage.
- During the process of expansion or compression, we can change the external pressure.
- Thus, the process can be achieved either in one-stage or in multistage.
- In the latter, the external pressure may be different in each stage.

Mathematical Expression of Work

- Consider the diagram below in which the external pressure is viewed as weights against the gas.

- *Pressure-volume work.*
- *Expanding gas against an object of mass m through a distance h.*



Mathematical Expression of Work

- By definition, the work involved is given by:

$$w = F \times l$$

- **Since the system (gas) is doing work on the surroundings (piston), it bears negative sign.**

$$w = -F \times l$$

$$w = -P_{ext} \times A \times l$$

- **Note**: It is the external pressure, P_{ext} and not the P_{gas} which is used in evaluating work.

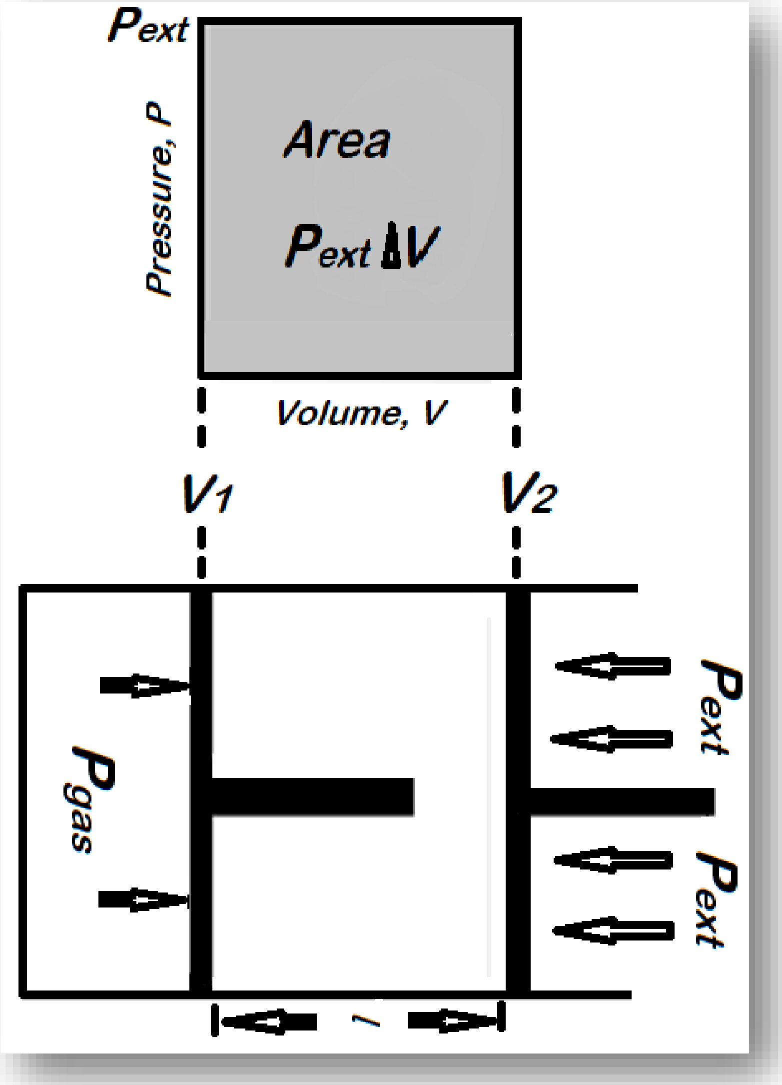
Mathematical Expression of Work

$$w = -P_{ext}\,\Delta V$$

- Where ΔV ***is the change in volume of the system*** $(A \times l)$
- If the piston moves by an infinitesimal amount, the work involved is given by:

$$dw = -P_{ext}\,dV$$

a) Expansion against constant pressure



- Consider the expansion of a gas confined in a cylinder as shown below.
- To get the work done under these condition, we integrate the equation:

$$dw = -P_{ext}\, dV$$

a) Expansion against constant pressure

- The total work done in moving from an initial state 1 to 2 will involve a change in volume from V_1 to V_2 against a constant pressure P_{ext} .

$$w = -\int_{V_1}^{V_2} P_{ex}\, dV$$

- and since P_{ext} is constant

$$w = -P_{ex} \int_{V1}^{V_2} dV$$

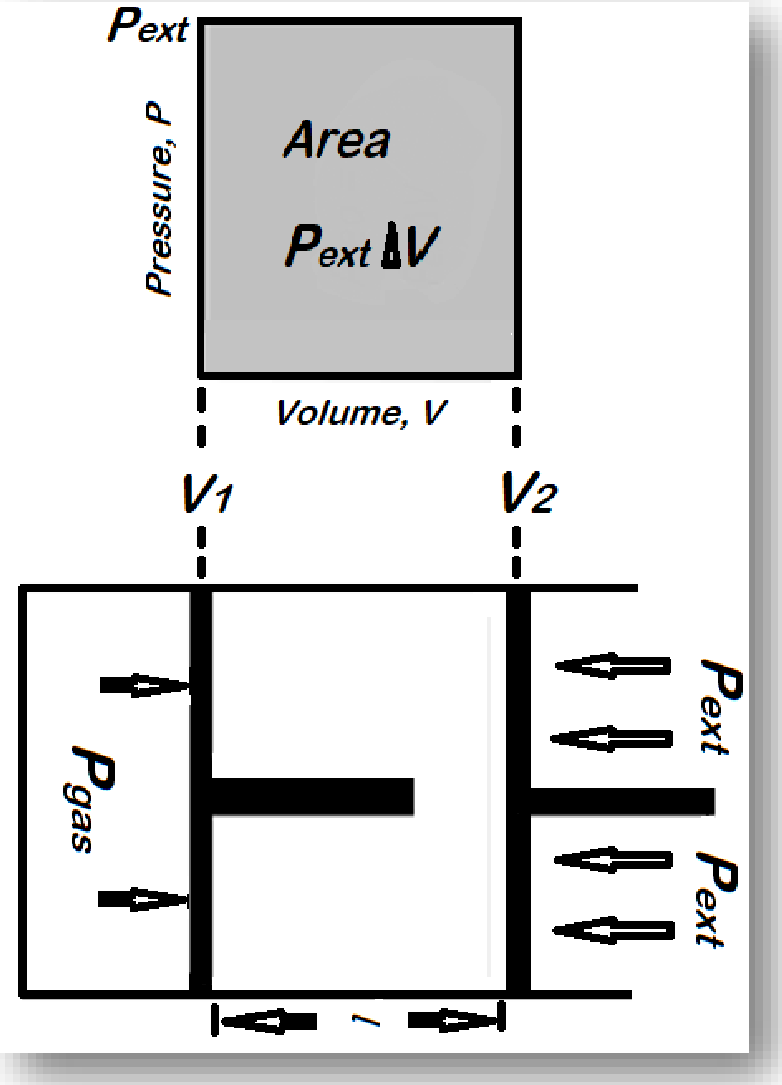
a) Expansion against constant pressure

- The expansion from the initial state (V_i) to final state (V_f)

$$w = -P_{ext}(V_f - V_i)$$

- If P_{ext} is constant

$$w = -P_{ext}\Delta V$$



a) Expansion against constant pressure

- The area under the above curve of P_{ext} represents the work done by the gas.
- A common example of this type of work is in an internal combustion engine of car where expanding gases are able to drive a piston.
- The lifting-off of rockets and space vehicles such as the space shuttle also involve expansion of gases.

b) *Isothermal Irreversible expansion of a gas*

- Suppose we have an ideal gas contained in a cylinder with a piston.
- This time the process of expansion of the gas is performed irreversibly *i.e., by instantaneously dropping the external pressure,* P_{ext}, to the final pressure P_2.
- The work done by the system is now against the pressure P_2 throughout the whole expansion and is given by the following expression:

b) Isothermal Irreversible expansion of a gas

$$w = - P_{\text{ext}} \int_{v_1}^{v_2} dV$$

$$= P_2 (V_2 - V_1)$$

$$= P_2\, dV$$

c) *Reversible expansion of an Ideal Gas*

- Suppose that the gas expands or contracts in such way that the external pressure equals the pressure of the gas.
- Such expansion/compression is said to take place in a reversible manner.
- A reversible change is one that proceeds via an infinitesimal amount and maybe changed to proceed in the opposite direction by an infinitesimal opposite action
- Thus the external pressure = internal pressure of the gas

c) Reversible expansion of an Ideal Gas

- i.e., $P_{ext} = P_{gas} = P$

$$w = -\int_{V_i}^{V_f} P_{ext}\,dV = -\int_{V_i}^{V_f} P\,dV$$

- We can evaluate the integral once we know the how the pressure of the confined gas depends on its volume
- If we know the equation of state of the gas, then we can express P in terms of V and evaluate the integral

d) Isothermal reversible expansion of an Ideal Gas

- The process described above could be done reversibly and under isothermal conditions (e.g. constant temperature water bath).
- Using the equation for an ideal gas, we can evaluate the work done during this process.

$$\boxed{w = -nRT\int_{V_i}^{V_f}\frac{dV}{V} = -\,nRT\ln\frac{V_f}{Vi}}$$

- The above expression will be positive if the initial volume, V_i, is greater than the final volume, V_f, indicating a compression process.

e) Isothermal reversible expansion of a Real Gas

- If the gas obeys the Van der Waal's equation, then the work done is given by:

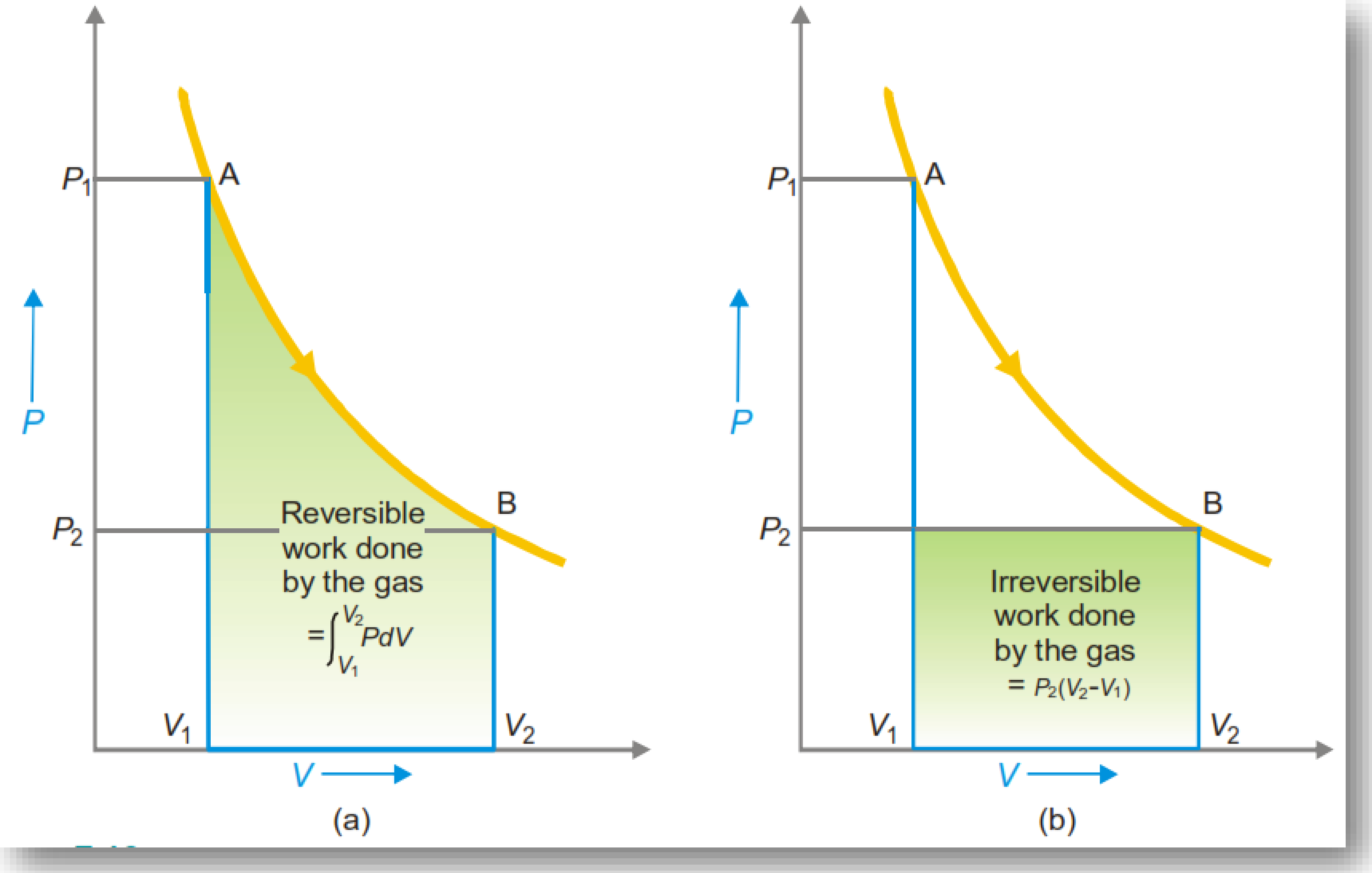
$$w = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) dV$$

$$w = -nRT \left(\frac{V_f - nb}{V_i - nb} \right) - an^2 \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$$

Maximum work done in reversible expansion

- The isothermal expansion of an ideal gas may be carried either by the *reversible process or irreversible process* as stated above.
- In both the processes, the state of the system has changed from *A to B.*
- The graphs below shows a comparison of the two modes of in which a gas can done work.
- In comparing the two areas (a and b), it is clear that more work is done during a reversible expansion against a constant external pressure than during an irreversible expansion process.

Maximum work done in reversible expansion



Maximum work done in reversible expansion

- Thus mechanical **work is not a state function** as it depends on the path by which the process is performed rather than on the initial and final states (**It is a path function).**
- It is also important to note that **the work done in the reversible expansion of a gas is the maximum work that can be done by a system (gas)** in expansion between the same initial (A) and final state (B).
- Maximum work is obtained during a reversible expansion because maximum work is ensured at every step – no wastage.

Internal energy (U)

- It is the energy associated with a system by virtue of its molecular constitution and the motion of its molecules.
- The contribution of energy due to molecular constitution is known as ***internal potential energy*** and the contribution of energy due to the motion of molecules is called ***internal kinetic energy***.
- Internal energy of a system is given by the sum of these two types of energy.

Internal energy (U)

- Every substance possesses a definite amount of energy which depends upon factors such as composition of the substance, temperature and pressure.
- This is called intrinsic or internal energy (U).

$$U = U_T + U_R + U_V + U_B + U_E$$

Where: U_T = Translational energy, U_R = Rotational energy,
U_V = Vibrational energy, U_B = Bonding energy and U_E = Electronic energy.

Internal energy (U)

- Internal energy of a system is a state function and its absolute value cannot be calculated but its change can be determined.
- When the system undergoes a change in its state, the internal energy change is given by:

$$\Delta U = U_2 - U_1$$

Where: U_1 = Internal energy in the initial state and

U_2 = Internal energy in the final state.

Internal energy (U)

- In a chemical reaction,

$$\Delta U = U_p - U_R$$

- Where: U_P = Internal energy of products and

  U_R = Internal energy of reactants.

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Free expansion work

- Free expansion involves expansion with no opposing force.
- For example if the gas were to expand into a vacuum.
- In such a case:

$$P_{ext} = 0$$

- so that the work done is equal to zero ($dw = 0$, $w = 0$) i.e. no work is done during free expansion of a gas.

First law of thermodynamics

- ***Energy may be converted from one form to another, but it is impossible to create or destroy it.***
- There are various ways of expressing the first law of thermodynamics.
- Some of the selected statements are given below:
- When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.
- Energy of an isolated system must remain constant, although it may be transformed from one form to another.

First law of thermodynamics

- Energy in one form, if it disappears will make its appearance in an exactly equivalent in another form.
- It is never possible to construct a perceptual motion machine that could produce work without consuming any energy.
- Suppose that we add heat, *q*, to a system such as a gas confined in a cylinder.
- If nothing else is done to the system, them the internal energy, *U*, increases by an amount that is exactly equal to the heat supplied.

First law of thermodynamics

$\Delta U = q$ *(with no work done)*

- This increase in internal energy is the increase in the energy of the molecules of the system.
- Suppose instead that no heat is transferred, but that by the addition of mass to the piston an amount of work, *w*, is on the system, the system then gains internal energy by the amount of work done.

$\Delta U = w$ *(with no transfer of heat)*

First law of thermodynamics

- In general, if heat, *q*, is supplied to the system and an amount of work, w, is performed on the system the increase in internal energy will be given by:

$$\Delta U = q + w$$

- This is the statement of the first law of thermodynamics.
- For an infinitesimal process, the above equation takes the form:

$$dU = dq + dw$$

The sign convention:

- According to latest S.I. convention, w is taken as ***negative if work is done by the system*** whereas it is taken as ***positive if work is done on the system***.
- When ***heat is given by the system to surrounding it is given as negative sign***.
- When ***heat is absorbed by the system from the surrounding then positive sign*** is given.

Enthalpy (H)

- In a process carried at constant volume (say in a sealed tube), the heat content of a system is the same as internal energy (*U*), as no *PV* work is done.
- But in a constant-pressure process, the system (a gas) also expends energy in doing *PV work.*
- Therefore, the total heat content of a system at constant pressure is equivalent to the internal energy *U* plus the *PV* energy.
- This is called the ***Enthalpy*** the system and is represented by the symbol ***H.***

Enthalpy (H)

- Thus enthalpy is defined by the equation:

$$H = U + PV$$

- Every substance has a definite value of enthalpy in a particular state.
- It is also a state function like internal energy and hence its value is independent of the path by which the state of the system is changed.
- The change in enthalpy accompanying a process can be determined as:

$$\Delta H = H_2 - H_1$$

Enthalpy (H)

Or

$$\Delta H = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$= \boldsymbol{\Delta U + \Delta PV}$$

- If P_{ext} is maintained constant while the gas is expanding, we can write

$$\boldsymbol{\Delta H = \Delta U + P_{ext}\Delta V}$$

.

Enthalpy (H)

- But since:

$$\Delta U = q + w \quad \textit{and} \quad P_{ext}\Delta V = w-$$

- Then:

$$\Delta H = q + w - w$$

- Thus:

$$\Delta H = q$$

- Hence the change in enthalpy of the system ΔH may be defined as the amount of heat absorbed at constant pressure.

Enthalpy (H)

- *If* ΔH *is positive* the reaction will be endothermic.
- *If* ΔH *is negative* the reaction will be exothermic.
- For a chemical reaction carried in an open vessel,

$$\Delta H = H_{products} - H_{reactants}$$

- Most chemical reactions take place at constant pressure, for example in the laboratory at atmospheric pressure.
- In such processes, volume changes do occur.

$$q_p = \Delta U + P_{ex}\Delta V \quad \text{at constant } P$$

Enthalpy (H)

- Heat evolved or absorbed at constant pressure, q_p, is known as enthalpy, symbolized by H,

$$q_p = \Delta H$$

- It follows that

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

- The enthalpy is then the change in internal energy plus the pressure-volume work.
- If it is assumed that the gases produced in a reaction behave as ideal gases, we can solve for V using the perfect gas equation to give us:

Enthalpy (H)

$$V = \frac{nRT}{P}$$

- For a change in volume:

$$\Delta V = \Delta\left(\frac{nRT}{p}\right)$$

- If the reaction is taking place at constant temperature and pressure

$$\Delta V = \Delta n\left(\frac{RT}{P}\right)$$

Enthalpy (H)

- Therefore:

$$\Delta H = \Delta E + \Delta n_{gas} RT$$

- where Δn_{gas} is given by:

$$\Delta n_{gas} = \sum n_{gas,\ products} - \sum n_{gas,\ reactants}$$

Constant pressure and constant volume process

- These are the most common processes encountered in chemical reactions.
- It is thus instructive to consider the behaviour of the first law of thermodynamics in relation to such processes.

1)Constant volume processes

- To carry out a reaction at constant volume we would need a sealed vessel to contain any gaseous products produced.

Constant pressure and constant volume process

- Typical equipment used to perform such measurements is the bomb calorimeter, frequently used to carry out combustion reactions.
- Since:

$$\Delta E = q + w$$

- If work is done by the system then

$$w = -P_{ex}\Delta V$$

- Thus,

$$\Delta E = q + (-P_{ex}\Delta V)$$

Constant pressure and constant volume process

- In this case, ΔV is zero therefore

$$\Delta E = q_v$$

- where q_v is heat involved at constant volume.
- The result is significant as it shows that the heat change at constant volume is equal to the change in internal energy of the system.
- Thus, we can experimentally determine the internal energy change for a reaction by measuring energy absorb or released in the process.

Heat capacity

- By heat capacity of a system we mean the capacity to absorb heat and store energy.
- As the system absorbs heat, it goes into the kinetic motion of the atoms and molecules contained in the system.
- This increased kinetic energy raises the temperature of the system.
- If *q* joules is the heat absorbed by mass m and the temperature rises from T_1 to T_2, the heat capacity (*c*) *is given by the expression:*

Heat capacity

$$C = \frac{dq}{dT}$$

- It is the amount of heat energy required to raise its temperature by 1 *K* (or °*C*).
- The ***specific heat capacity*** (**C_p**) of a substance is the amount of heat (*q*) required to raise the temperature of **one gram** of the substance by 1 *K* (or °*C*).

$$c = \frac{q}{m \times (T_2 - T_1)}$$

- The heat capacity of 1 mole of a substance is called its ***molar heat capacity***

Heat capacity

- The units of the molar heat capacity are calories per degree per mole (cal K^{-1} mol^{-1}), or joules per degree per mole (J K^{-1} mol^{-1}), the latter being the SI unit.
- **Heat is not a state function, neither is heat capacity.**
- It is, therefore, necessary to specify the process by which the temperature is raised by one degree.
- The two important types of molar heat capacities are those: (1) at constant volume; and (2) at constant pressure.

Molar Heat Capacity at Constant Volume

- According to the first law of thermodynamics.

$$dq = dU + PdV$$

- Dividing both sides by *dT, we have*

$$\frac{dq}{dT} = \frac{dU}{dT} + \frac{PdV}{dT}$$

Molar Heat Capacity at Constant Volume

- At constant volume *dV = 0,* the equation reduces to

$$C_V = \frac{dq_V}{dT} = \left(\frac{dU}{dT}\right)_V$$

- Thus the heat capacity at constant volume is defined as the rate of change of internal energy with temperature at constant volume.

Temperature dependence of C_v

- Not all reactions takes place at 298 K, so we must examine how the tabulated thermo-chemical data can be adapted for use under different
- Since:

$$dU = C_v dT = q_v$$

- If a substance is heated from an initial temperature T_1, to a temperature T_2, the internal energy change from $U(T_1)$ to $U(T_2)$ is according to the equation

$$U(T_2) = U(T_1) + \int_{T_1}^{T_2} C_V dT$$

Temperature dependence of C_v

$$U(T_2) - U(T_1) = \int_{T_1}^{T_2} C_V dT = q_V$$

- Hence if c_V is temperature dependent, integrating the heat capacity at constant volume gives the change in the internal energy.
- If c_V is independent of temperature, this integrates to:

$$\Delta U = C_V(T_2 - T_1) = q_V$$

Molar Heat Capacity at Constant Pressure

- According to the first law of thermodynamics.

$$dq = dU + PdV$$

- Dividing both sides by *dT, we have*

$$\frac{dH}{dT} = \frac{dU}{dT} + \frac{PdV}{dT}$$

Molar Heat Capacity at Constant Pressure

- At constant pressure:

$$\left(\frac{dH}{dT}\right)_p = \left(\frac{dE}{dT}\right)_p + P\left(\frac{dV}{dT}\right)_p$$

- Thus the heat capacity at constant pressure will be given by:

$$C_P = \frac{dq_P}{dT} = \frac{dH}{dT}$$

Temperature dependence of C_p

- Not all reactions take place at 298 K, so we must examine how the tabulated thermochemical data can be adapted for use under different conditions.
- Since;

$$\Delta H = C_P dT$$

- If a substance is heated from an initial temperature T_1 to a temperature T_2, the enthalpy change from $H(T_1)$ to $H(T_2)$ is according to the equation.

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_P dT$$

- For a chemical reaction the equation will be given as

$$\Delta H^{\circ}_{rxn}(T_2) = \Delta H^{\circ}_{rxn}(T_1) + \int_{T_1}^{T_2} \Delta_{rxn} C_P \, dT$$

- If a This equation is known as Kirchoff's law.
- If C_P is independent of temperature, this integrates to

$$\Delta E = C_P(T_2 - T_1) = q_P$$

- Since

$$dH = dE + dnRT$$

Therefore,

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(nRT)}{dT}$$

- Hence

$$C_P = C_V + nR$$

- *And*

$$C_{P,m} = C_{V,m} + R$$

- *or*

$$C_{P,m} - C_{V,m} = R$$

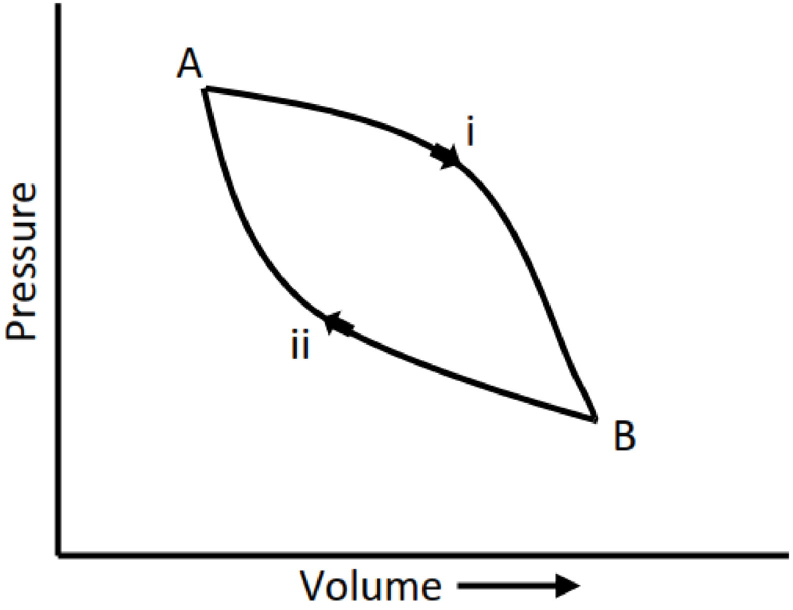
- Where $\mathrm{C_{P,m}}$ and $\mathrm{C_{V,m}}$ are the molar heat capacity at constant pressure and molar heat capacity at constant volume respectively

e) For a cyclic process,

- The change in the internal energy of the system is zero because the system is brought back to the original condition.

$$\int dE = 0$$

$$\int dq = -\int dw$$



- i.e. the total work obtained is equal to the net heat supplied.
- In an isolated system, there is no heat exchange with the surrounding i.e. dq = 0 ; $dw = dE$