Engineering Chemistry

Module:1

Chemical thermodynamics and kinetics

- Laws of thermodynamics - Entropy change (selected processes)
- Spontaneity of a chemical reaction and Gibbs free energy - heat transfer
- Kinetics - (selected processes) – spontaneity of a chemical reaction and Gibbs free energy- Carnot cycle;
- Kinetics – Order of reactions (excluding the derivations and half-life calculations)- Concept of activation energy and energy barrier
- Arrhenius equation- effect of catalysts (homo and heterogeneous)
- Enzyme catalysis (Michaelis-Menten Mechanism)

1. Basic concepts of Thermodynamics

- The branch of science that explains the inter-relations between different forms of energy and heat is called thermodynamics.
- It consists of four laws which state the ways of inter-conversion of these different forms of energy.

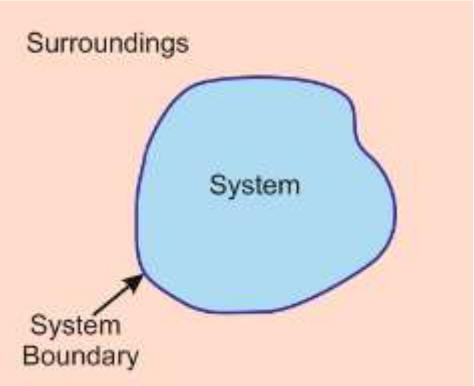
System and Surroundings

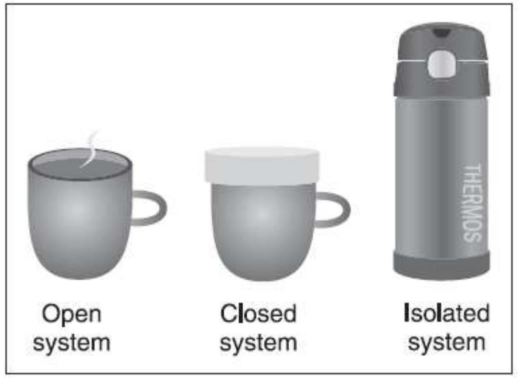
- One of the basic assumptions of thermodynamics is that the **universe is divided into two parts—system and surroundings.**

(a) System: *A system in thermodynamics is defined as the quantity of matter or a region in space over which the investigation is done.* Here, the quantity of matter may be gas, solid or liquid.

A system can be of three types:

- **Open system:** The system which can exchange both mass and energy with the surroundings is known as open system. *Example*: a cup of hot tea.
- **Closed system:** The system which can exchange energy but not mass with the surroundings is known as a closed system. *Example*: a cup of hot tea closed with lid.
- **Isolated system:** The system which can neither exchange energy nor mass with the surroundings is known as isolated system. *Example*: hot tea in thermos flask.





(b) Surroundings: *Everything other than the system is called the surroundings or environment.*

(c) Boundary or wall: The system generally is separated from the surroundings by a boundary or wall or partition. This wall can be of two types:

i) Diathermal wall: The wall or boundary which allows heat but not matter to pass across it.

ii) Adiabatic wall: The wall or boundary which allows neither heat nor matter to pass across it.

***System and surroundings together constitute the universe.

***Size of the universe depends on the size of the system and surroundings.

1.1 Thermodynamic Properties

These properties are generally associated with the bulk of matter and are hence called macroscopic properties. They contain large number of atoms, ions or molecules and can be categorized into:

(a) Extensive properties

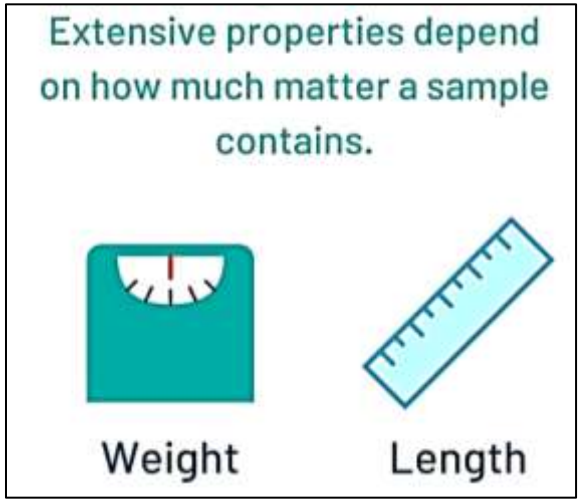
The properties of a system that depends on the system size or the amount of material present in the system.

Ex: volume, internal energy are extensive properties.

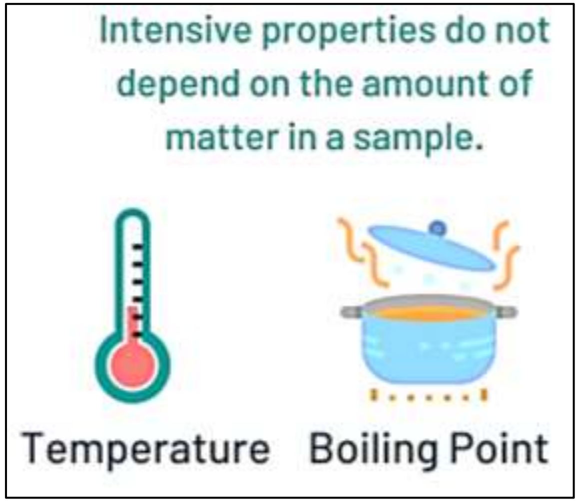
(b) Intensive properties

The properties of a system that does not depend on the size of the system or the amount of material present in the system.

Ex: density, pressure, temperature, etc.



Extensive properties depend on how much matter a sample contains.



Intensive properties do not depend on the amount of matter in a sample.

1.2 Thermodynamic functions and variables

The variables that are required to specify the state of a thermodynamic system are temperature (*T*), pressure (*P*), volume (*V*) and composition or amount (*n*).

There are two types of thermodynamic functions:

(a) State function

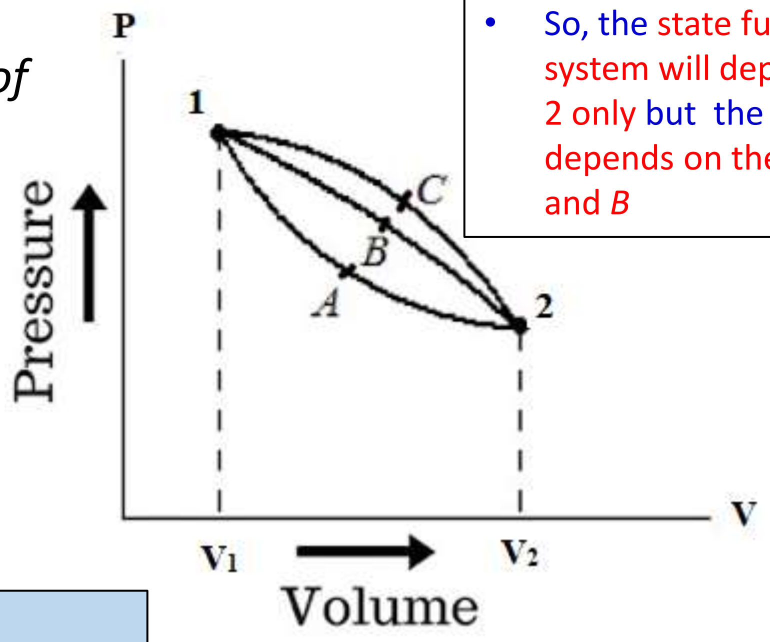
The thermodynamic system that depends only on initial and final states of a system at equilibrium (a gas, a liquid, a solid, etc.) and not on the path using which the system had attained the present state is known as state function.

Ex: temperature (*T*), pressure (*P*), volume (*V*).

(b) Path function

The function which depends on the path using which a system changes from initial state to the final state is known as path function.

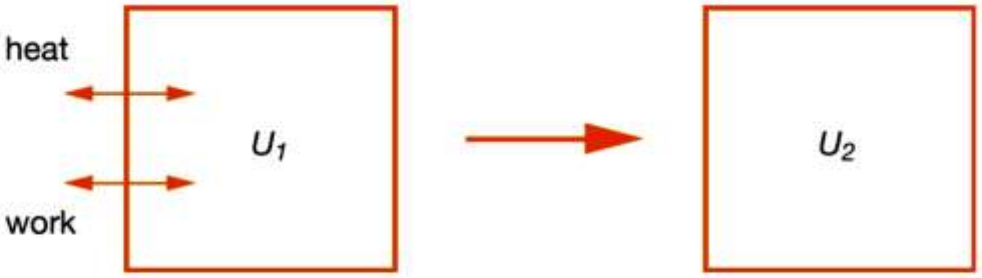
Ex: heat and work.



- Here, 1 and 2 represent the initial and final states.
- So, the state function of the system will depend on 1 and 2 only but the path function depends on the path, i.e., *A* and *B*

Internal energy (U) = Kinetic energy + Potential energy

- It's a **state function** & an **extensive property** of the system.
- Internal energy of a system changes when **energy is transferred** into or outside the system in the form ***heat or work***

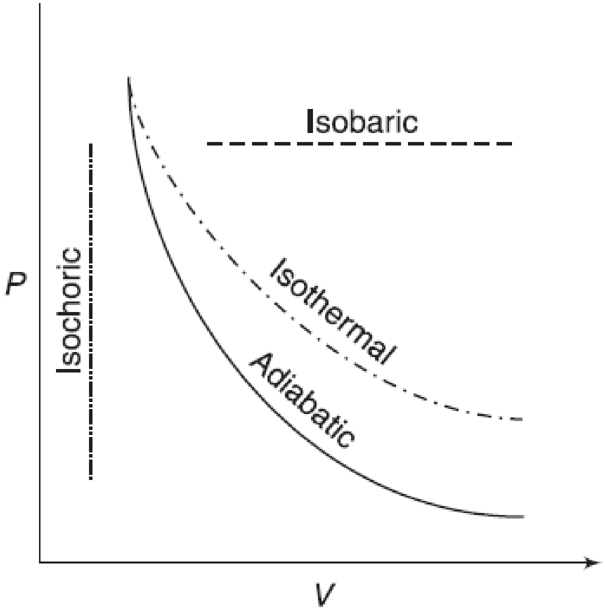


➢ $\Delta Usystem = Ufinal_{state} - Uinitial_{state}$

1.3 Thermodynamic Process

A thermodynamic process occurs when the system goes from one equilibrium state to the other.

This results in a **change in variable properties of the system** such as **T, P** etc.



(a) Isothermal process

- For an isothermal process **$dT = 0$ and $dU = 0$**.
- An isothermal process is achieved by using thermostatic control.
- In an isothermal process, heat can be exchanged between system and surroundings.

(b) Isochoric process

- It occurs at a constant volume, i.e., **$dV = 0$**. If a chemical reaction is occurring in a closed the process will be isochoric.

(c) Isobaric process

- It occurs at a constant pressure, i.e., **$dP = 0$**. This process occurs with pressure being unchanged at every step of the process. Ex. water changes to vapour at a constant pressure of 1 atm.

(d) Adiabatic process

- For an adiabatic process **$q = 0$**. In this process there is no transfer of matter or heat since the system is separated from its surroundings by a thermally insulating wall.

(e) Isoenthalpic process

Isoenthalpic process is the one that proceeds without any change in enthalpy, **$dH = 0$**.

(f) Cyclic process

The process in which the system returns to its original state after a series of cyclic changes.
A cyclic process occurs with constant internal energy, i.e., **$dU = 0$ and $dH = 0$.**

(g) Reversible process

A reversible process is generally carried out infinitesimally slowly and can be reversed without leaving any evidence of that change on the surroundings. It means both system and surroundings are restored to their initial states at the end of the reverse process. **Maximum work is obtained in this process.**

(h) Irreversible process

This process occurs rapidly and simultaneously and there is no establishment of equilibrium. Work obtained in irreversible process is generally less than that in reversible process [**$W_{rev} > W_{irr}$ (Expansion)**].

1.4 Heat and Work

(a) Heat (*q*):

- If **two systems** are considered such that they have **temperature difference** between them, exchange of energy will take place between them. This **exchange of energy** takes place as **heat.**
- **Energy will flow from** the system having **higher temperature to** that having **lower temperature**.
- *The* ***amount of energy exchanged*** *between the* ***system and the surroundings*** *due to temperature difference between them is called* ***heat****.*
- In accordance with the first law, the **net effect of *q* is to change *U* of the system and the surroundings**.

According to sign convention in thermodynamics,

- **heat absorbed by a system is positive [$q > 0$]**;
- but **heat released by a system is negative [$q < 0$].**
- (v) The SI unit of heat is joule.
- Relation between calorie and joule: **1 cal = 4.184 J**

(b) Work

- Work is a **kind of energy**, like heat.
- It **interacts between a system and its surroundings** and is **associated with a process**.
- In thermodynamic sign convention,
- the **work done by the system** on the surrounding (energy leaves the system) is **negative.**
- When **work done on the system** by its surrounding, is **positive.**
- Units of work are the same as the units of heat.

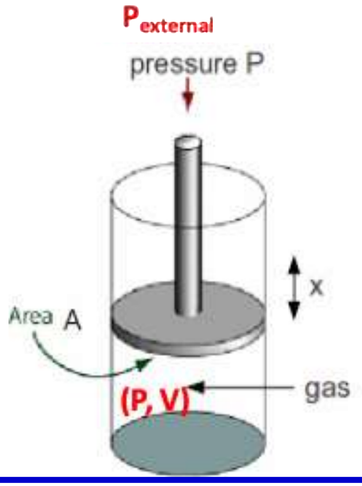
⇒ If one mole of an ideal gas is enclosed in a cylinder fitted with a weightless and frictionless piston, initially, the volume of the gas will be V_i and internal pressure of the gas be p.

Gas is heated ⇒ 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}:

$$\mathbf{d}w = -P_{ex}\mathbf{d}V$$

- Total work done by the system to expand from volume V_i to V_f: $W = -\int_{v_i}^{v_f} P_{ex}\,dv$
- This is an example of the **system doing the work on the surrounding**



❑ ***A thermodynamic 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.

Ex 1: **Thermal equilibrium of two systems with the same temperature**

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

Ex 2: **Reversible expansion**: Suppose a gas is confined by a piston…

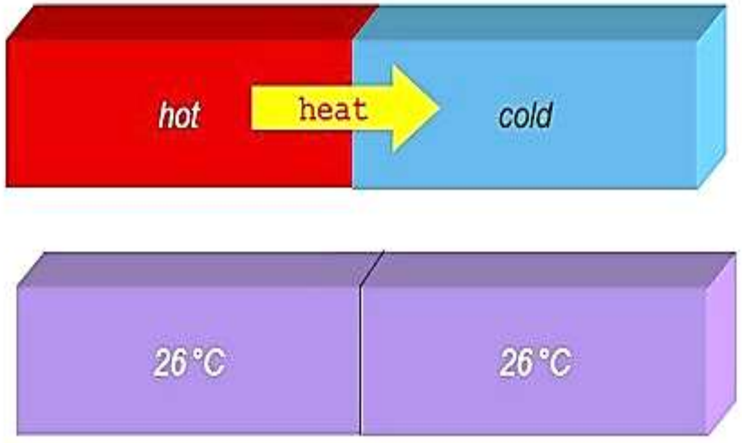
External pressure (P_{ex}) = Pressure (P) of the confined gas.

- *Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in the opposite directions.*

$$dw = -P_{ex}dV = -pdV$$

$$W = -\int_{v_i}^{v_f} p\,dv$$

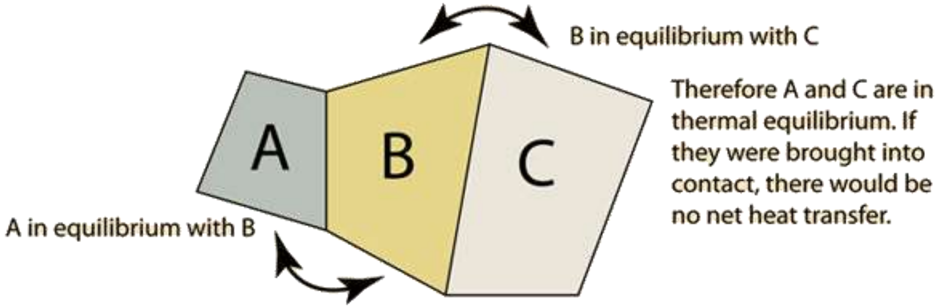
0th Law of Thermodynamics

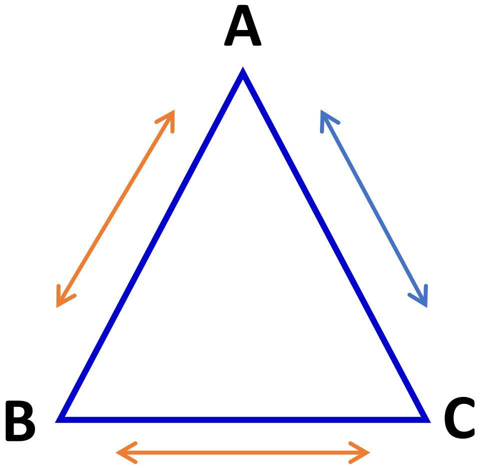


- ❑ **Two physical systems are in thermal equilibrium if there is no net flow of heat (thermal energy) between them when they are connected by a path permeable to heat.**

➢ 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.





- **A** is in equilibrium with **B**
- **B** is in equilibrium with **C**

∴ **A and C are in thermal equilibrium. If they brought in to contact, there would be no net heat transfer.**

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

1st Law of Thermodynamics

- It's the law of conservation of energy

☐ *Energy can be converted from one form to another, but it is neither created nor destroyed*. This observation, one of the most important in all of science, is known as the **first law of thermodynamics**.

- **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 mathematical form of first law is $\boxed{\boldsymbol{\Delta U = q + w}}$
- For a system, if *w* = work done on a system,

  q = energy transferred as heat to a system &

  Δ*U* = resulting change in internal energy

The sign of ***w*** :

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

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

Therefore,

change in internal energy (ΔU) of a system = heat lost by the system (q) – **the work done *by* the system (w)**

$$\boxed{\boldsymbol{\Delta U = q - w}}$$

Enthalpy & Heat Capacity

- 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,

$$w = -P\,(V_f - V_i\,)$$

$$\Delta U = q + w$$

$$\therefore\ \Delta U = q - P\,(V_f - V_i)$$

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

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

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

$$\Rightarrow\ H_f - H_i = q$$

$$\boldsymbol{\Delta U = \Delta H - P\Delta V}$$

or, $\boxed{\boldsymbol{\Delta H = \Delta U + P\Delta V}}$

- ☐ Heat capacity (**C**) of a system between any two temperatures – the quantity of heat (q) required to raise the temperature of the system from the lower temperature (T_1) to the higher temperature (T_2) divided by the temperature difference.

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

- ❖ 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 varies with temperature $\boxed{C = \frac{dq}{dT}}$

- ☐ **Molar heat capacity at constant volume**

at constant volume, w = 0

$$\Delta U = q + 0 = q$$

$$\boldsymbol{\Delta U = q}$$

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

Heat Capacity

❑ Molar heat capacity at constant pressure (C_p)

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

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

ΔU = q + w

ΔU = q – P ($V_f - V_i$)

or, **q = ΔU + pΔV**

q = ΔH

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

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

❑ Relationship between C_p & C_v

For a system, ***ΔH = ΔU + Δ(PV)***

On both sides diffen. w.r.t ‘T’

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

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

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

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

$C_p = C_v + \frac{R\Delta(T)}{\Delta T}$

$C_p = C_v + R$

$$\boxed{C_p - C_v = R}$$

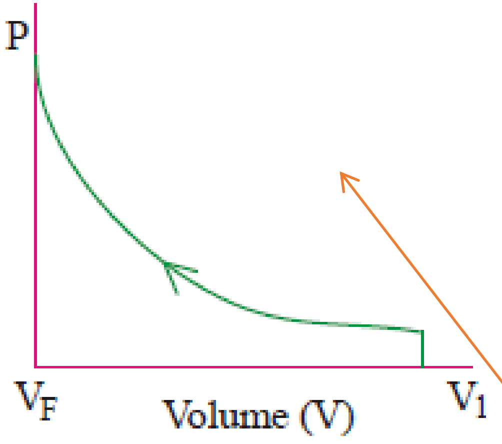
C_V = 3/2 R (For monoatomic ideal gas)

C_p = 5/2 R (For monoatomic ideal gas)

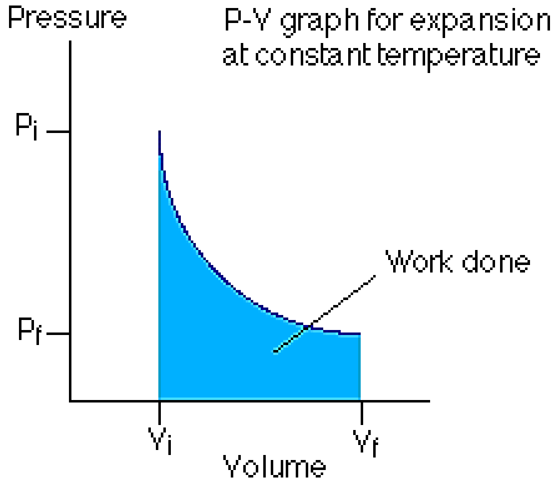
Heat capacity ratio, $\gamma = \frac{C_p}{C_v}$ **= 5/3 for a monoatomic ideal gas**

Application of 1st Law to the Expansion Work

➢ Isothermal Process (constant temperature)

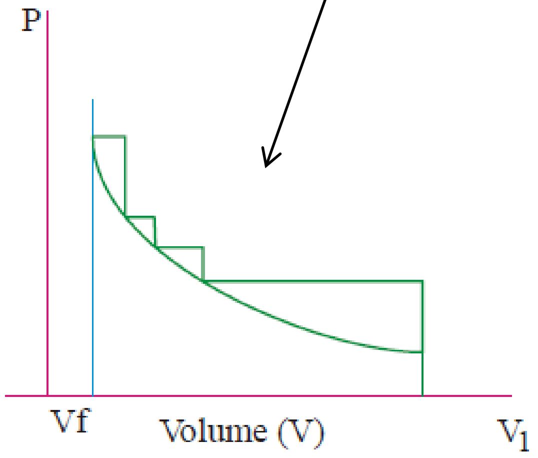


- In an isothermal process, the temperature stays constant, so **the pressure and volume** are **inversely proportional** to one another



$\Rightarrow$ **For an ideal gas,**

\# **Magnitude of *w*** depends on whether the expansion is **reversible** or **irreversible**.



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

if **T = fixed, $\Delta U = 0$** (according to 1st law, which deals with ΔU)

As, $\Delta U = q - w = 0$

$\Rightarrow$ ***q = w***

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

Application of 1st Law to the Expansion Work

➢ Reversible isothermal expansion:

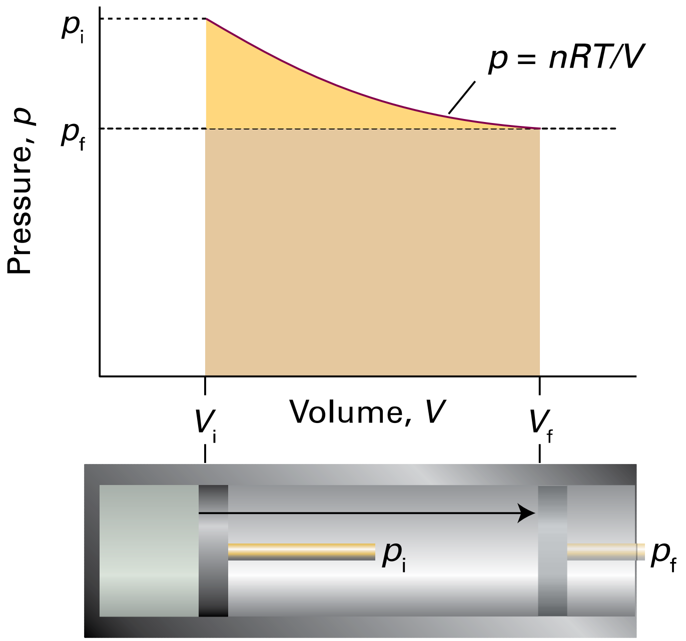
$$w = \int_{v_i}^{v_f} P\,dv = \int_{v_i}^{v_f} \frac{nRT}{V}\,dv \qquad \boxed{(\text{as } PV = nRT)}$$

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

- Work done by the *n* moles of gas can be 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) ($P_{ext} = 0$)

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

b) Volume of the gas expands against a constant pressure.

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

➢ 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.**

Application of 1st Law to the Expansion Work

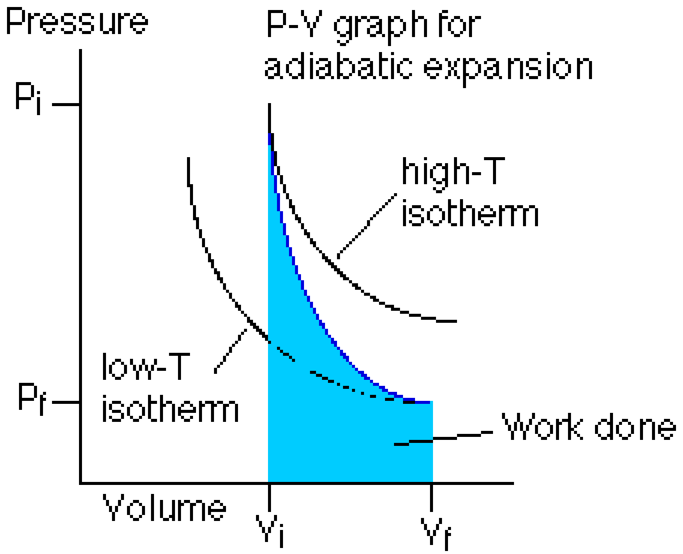
➢ **Adiabatic process (constant heat)**

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

- no heat is added/removed from a system.
- 1st law of thermodynamics: **$\Delta U = w$**

✓ *Ex: 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, ΔU = — 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 for ideal gas

Q = 0

$\Rightarrow dU = dw$

$\Rightarrow C_v \, dT = - P d_v$

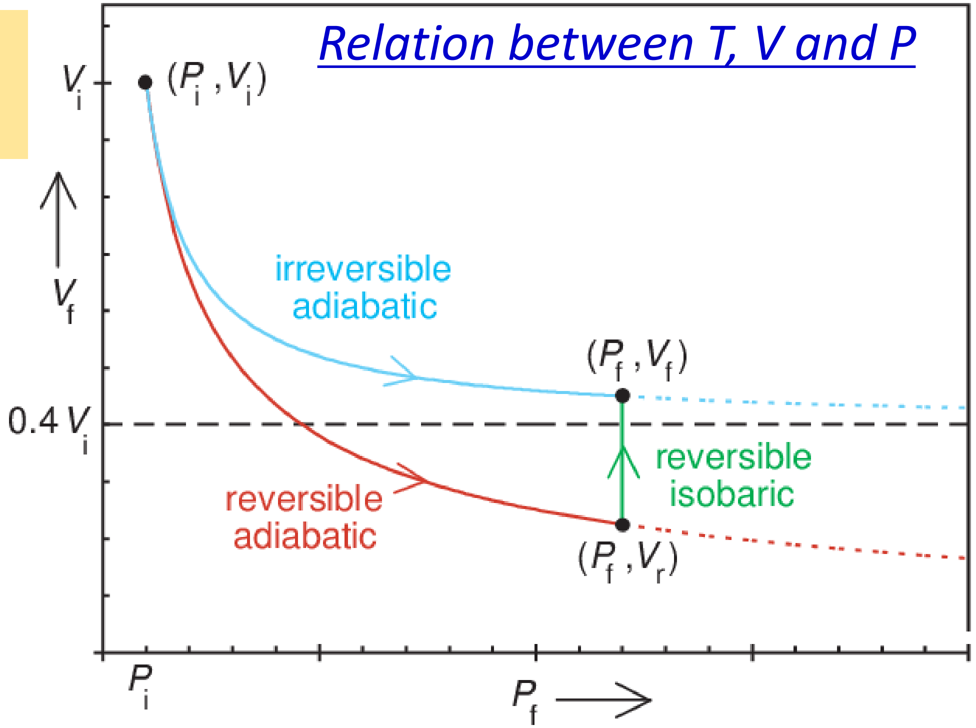
$\Rightarrow C_v \, dT = - \frac{RTd_v}{V}$

$\Rightarrow \int_{T_i}^{T_f} C_v \frac{dT}{T} = - \int_{v_i}^{v_f} \frac{Rd_v}{V}$

C_v = constant

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

Relation between T, V and P



➢ Irreversible adiabatic expansion (expansion in vacuum)

- **Free expansion (P_{ex} = 0):**

$$\Delta T = 0, W = 0, \Delta H = 0$$

- **Irreversible adiabatic expansion** against a constant pressure:

$$w = - \int_{v_i}^{v_f} P_{ex} \, . \, d_v = - P_{ex} (V_f - V_i)$$

$$= - P_{ex} \left(\frac{RT_f}{P_f} - \frac{RT_i}{P_i} \right) = - P_{ex} \left(\frac{T_f}{P_f} - \frac{T_i}{P_i} \right) \text{ x } R$$

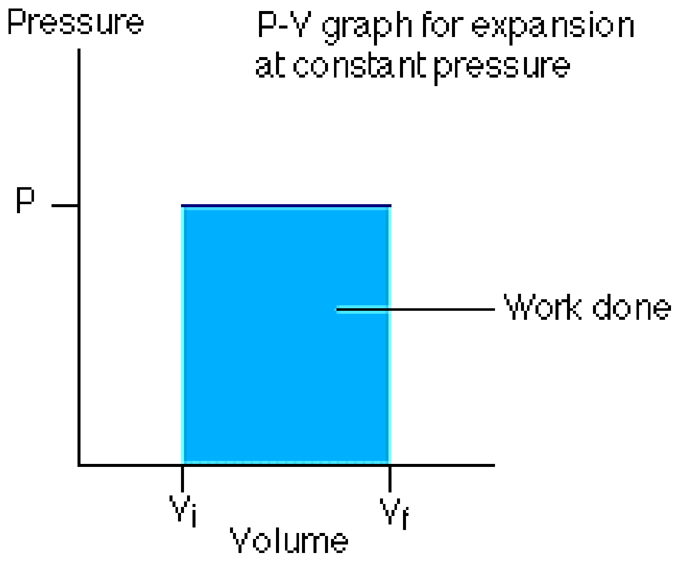
$$\boxed{C_v \left(T_f - T_i\right) = - R \, P_{ex} \left(\frac{T_f P_i - T_i P_f}{P_i P_f} \right)}$$

Application of 1st Law to the Expansion Work

➢ 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

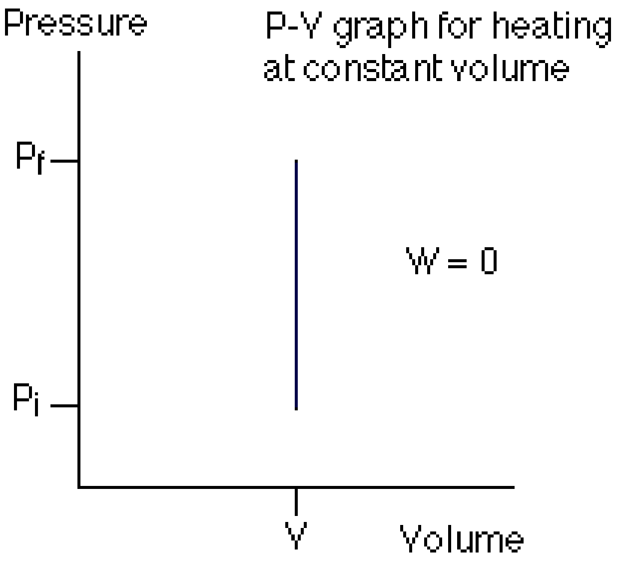
✓ Ex : ***A gas, being slowly heated or cooled, confined by a piston in a cylinder.***



➢ Isochoric process (constant volume)

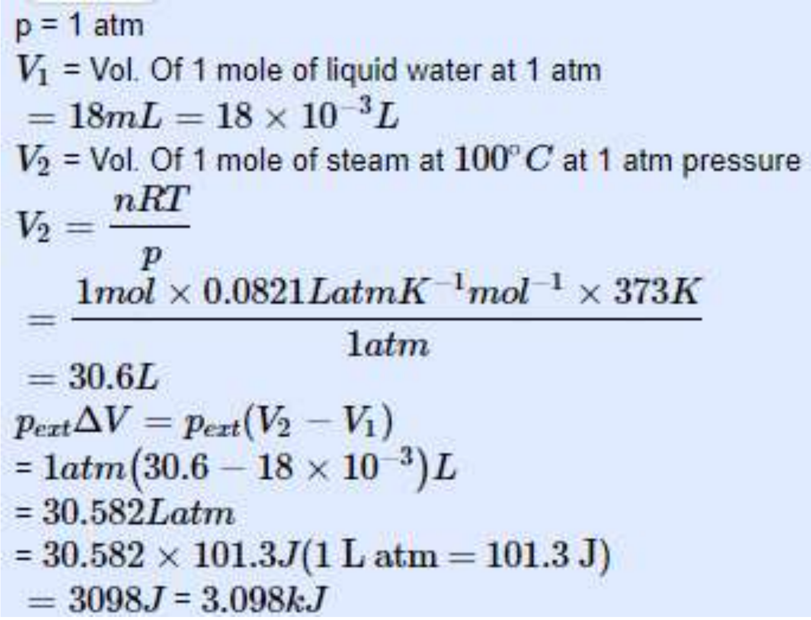
- **the volume is kept constant**
- The **work done is zero** in an isochoric process

✓ Ex: ***A gas in a box with fixed walls***



Numerical from of 1st Law

- **Ex1:** **Calculate w and ΔU for the conversion of 1 mole of water at 100 ℃ to steam at 1 atm pressure. Heat of vaporisation of water at 100 ℃ is 40670 $Jmol^{-1}$**



p = 1 atm

V_1 = Vol. Of 1 mole of liquid water at 1 atm

$= 18mL = 18 \times 10^{-3}L$

V_2 = Vol. Of 1 mole of steam at $100^\circ C$ at 1 atm pressure

$$V_2 = \frac{nRT}{p}$$

$$= \frac{1mol \times 0.0821 LatmK^{-1}mol^{-1} \times 373K}{1atm}$$

$= 30.6L$

$p_{ext}\Delta V = p_{ext}(V_2 - V_1)$

= $1atm(30.6 - 18 \times 10^{-3})L$

= $30.582Latm$

= $30.582 \times 101.3J(1 \text{ L atm} = 101.3 \text{ J})$

$= 3098J$ = $3.098kJ$

Since, conversion of water to steam is accompanied by increase in volume, work is done by the system on the surroundings.

Hence, $\boldsymbol{w} = \mathbf{-\ 3.098\ kJmol^{-1}}$

$$\boldsymbol{\Delta U = q - w} = \mathbf{40.670 - 3.098 = 37.572\ kJmol^{-1}}$$

- **Ex 2:** **1 mole of an ideal gas expands against a constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 30 dm^3. Calculate the work done by the gas in Joules.**

Solution: $\boldsymbol{w = -Pex\,\Delta V}$

$$= -(1\ atm)(30\ dm^3 - 10\ dm^3)$$

$$= -20\ dm^3\ atm$$

R = 8.314 $Jmol^{-1}K^{-1}$ = 0.08206 dm^3 atm K^{-1} mol^{-1}

$$1\text{ atm} = \frac{8.314\ J\ mol^{-1}K^{-1}}{0.08206\ dm^3\ mol^{-1}K^{-1}}$$

Therefore,

$$w = -20\ dm^3\ atm$$

$$= -20\ dm^3 \times \frac{8.314\ J\ mol^{-1}K^{-1}}{0.08206\ dm^3\ mol^{-1}K^{-1}} = \mathbf{-\ 2026\ J}$$

Numerical from of 1st Law

- **Example 3**: 1 mole of an ideal monoatomic gas at 27 °C expands reversibly and adiabatically from a volume of 10 dm^3 to a volume of 20 dm^3. Calculate q, ΔU, W and ΔH. Given $\frac{C_v}{R} = \frac{3}{2}$

Solution:

Since the process is adiabatic, ***q = 0***

$$C_v \ln\frac{T_f}{T_i} = R\ \ln\frac{V_i}{V_f}$$

$$\Rightarrow\ \frac{3}{2}\ln\frac{T_f}{300} = \ln\left(\frac{10\ dm^3}{20\ dm^3}\right) \qquad \Rightarrow\ T_f = 189K$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \Rightarrow dU = C_v\, dT$$

For a finite change in n moles,

$$\Delta U = nC_v\Delta T$$

$$= (1\ mol)\left(\frac{3}{2} \times 8.314\ J\ mol^{-1}K^{-1}\right)(189 - 300)K$$

$$= \boldsymbol{-1384\ J}$$

Since for an adiabatic process, q =0,

hence ΔU = w = – 1384 J

ΔH = ΔU + ΔPV = ΔU + ΔnRT

= ΔU + nR(T_f- T_i)

$$\rightarrow nR(T_f - T_i)$$

$$\rightarrow = (1\ mol)(8.314\ J\ mol^{-1}K^{-1})(189 - 300)$$

$$= -923\ J$$

ΔH = *– 1384 J – 923 J* = – **2307 J**

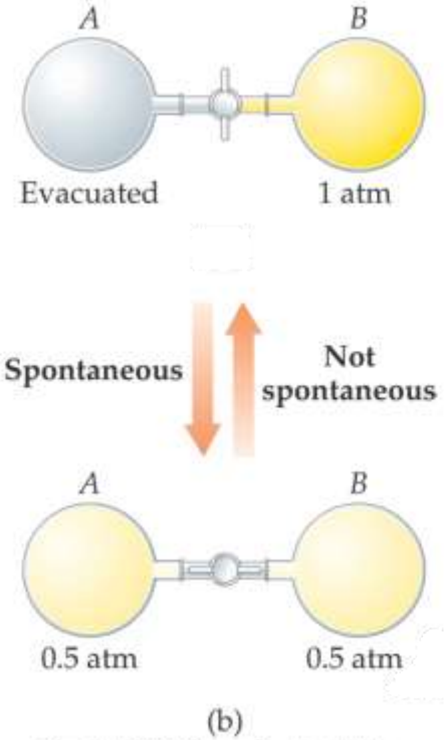
 # Note: ΔH can also be calculated by using the relation $dH = C_p\, dT$

- **Example 4**: 10 moles of an ideal gas expands reversibly and isothermally from a pressure of 10 atm to 2 atm at 300 K. Calculate the work done.

Solution: w $= -nRT\ln\frac{P_i}{P_f} = -(10\ mol)(8.314\ J\ mol^{-1}K^{-1})(300\ K)\ \ln\frac{10\ atm}{2\ atm} = -\mathbf{40.15 \times 10^3 J}$

Spontaneous Processes

- Spontaneous processes are those that can proceed without any outside intervention.
- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it will *not* effuse spontaneously.
- Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.
- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.
- All **Spontaneous** processes are **irreversible**.
- All **Real** processes are **irreversible**.



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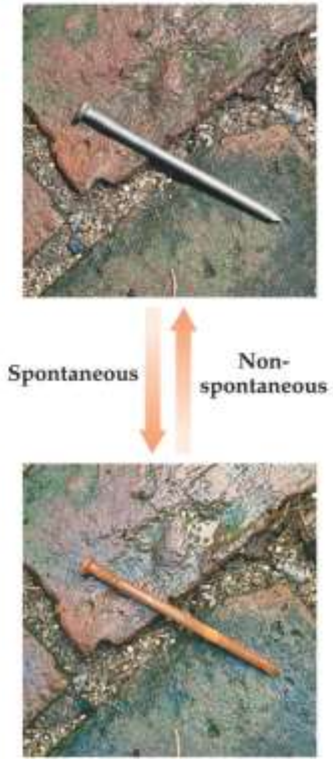
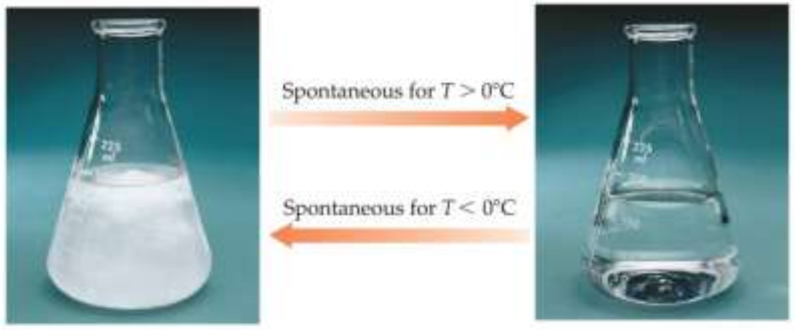




2nd Law of Thermodynamics

- **Why we need for the 2nd law of thermodynamics?**

→ The 1st law of thermodynamics does not tell us anything about **the direction of change**.

→ The direction of spontaneous change of a process is defined by the 2nd law of thermodynamics

❑ 2nd law of thermodynamics

- The entropy (**S**) of an isolated system increases in the course of a spontaneous change.

$$\Delta S_{tot} > 0$$

Where, $S_{tot} = S_{sys} + S_{sur}$

S_{sys} = the entropy of the system of interest, &

S_{sur} = the entropy of the surroundings

\# ***Note:*** *when considering applications of the 2nd law – it is a statement about the* ***total entropy*** *of the overall isolated system (****the 'universe'****), not just about the entropy of the system of interest.*

- the **1st law** uses the **internal energy** to identify ***permissible* changes**
- the **2nd law** uses the **entropy** to identify which of these **permissible changes are *spontaneous***.

→ A **spontaneous process** points towards the **direction** in which the ***total entropy increases***.

- Entropy (**S**) is a **state function**

➢ Thermodynamic definition of entropy

→ *The thermodynamic definition of entropy concentrates on the change in entropy (**dS**) that occurs as the result of a physical or chemical process.*

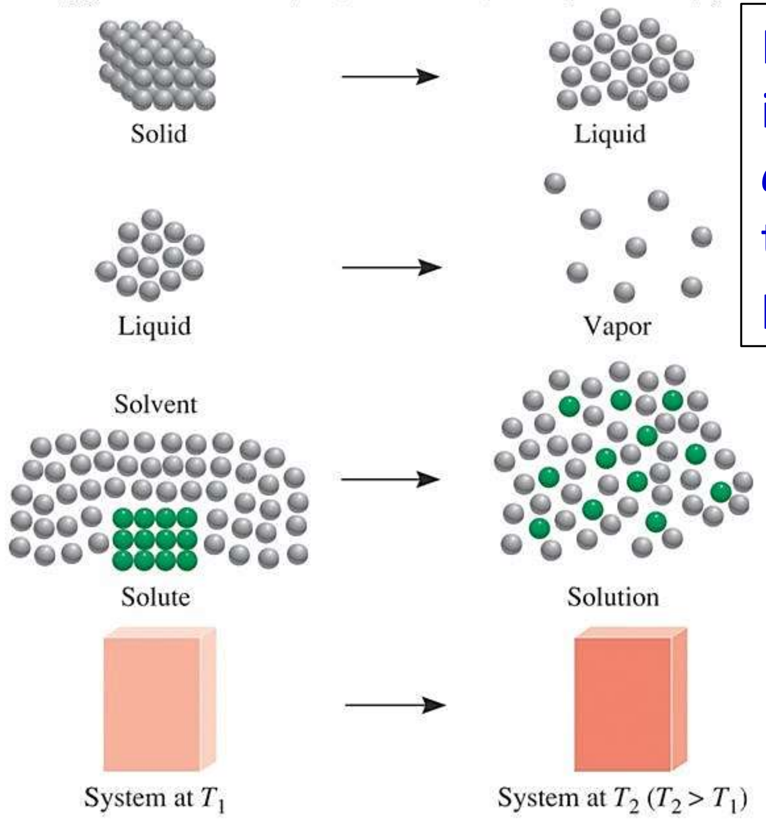
→ **dq_{rev} is the energy transferred as heat reversibly to the system at the absolute temperature *T*.**

$$\boxed{dS = {}^{dq_{rev}}\!/_{T}, \qquad \Delta S = \int_i^f \frac{dq_{rev}}{T}}$$

Entropy

- *Entropy* (*S*) is a term coined by Rudolph Clausius in the 19th century.
- Clausius was convinced of the significance of the ratio of heat delivered and the temperature at which it is delivered, **q/T.**
- **Entropy can be thought of as a measure of the randomness of a system.**

Processes that lead to an increase in entropy ($\Delta S > 0$)



Notice the increasing ***disorder*** in these processes

Like total energy, *E*, and enthalpy, *H*, entropy is a state function.
Therefore,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

- **Entropy change for the *system* of an isothermal expansion of a perfect gas**

$\Delta U = 0$, $q = -w$ $\quad \Rightarrow q_{rev} = -w_{rev}$

as, $w_{rev} = -\, nRT \ln(V_f / Vi)$

[from the expression of work done in a reversible isothermal expression]

$$\therefore q_{rev} = nRT\, ln(V_f / Vi)$$

$$\text{as } dS = {dq_{rev}}/{T}$$

$$\Rightarrow \boxed{\Delta S = nR\, ln(Vf/Vi)}$$

$$\boxed{\Delta S_{sys} = nR\, ln(Vf/Vi)}$$

Entropy

➢ Total Entropy change in irreversible (spontaneous) process of a perfect gas

✓ Ex: ***Isothermal*** expansion of an ideal gas at constant temperature into **vacuum**

As, w = 0, $\Delta U = 0 \Rightarrow q = 0$ [from 1st law]

$\Rightarrow$ no heat is absorbed by or removed from the surrounding,

Hence, $\Delta S_{surrounding} = 0$

$$\Delta S_{Sys} = R\ ln(Vf/Vi)$$

As, $S_{total} = S_{system} + S_{surrounding}$

$$\therefore \boldsymbol{\Delta S_{total}} = \Delta S_{system} + \Delta S_{surrounding}$$

$$= R\ ln(Vf/Vi) + 0 = \boldsymbol{R\ ln(V_f/Vi)}$$

→ As $\boldsymbol{V_f > Vi}$, this spontaneous (irreversible) isothermal expansion of a gas is accompanied by the increase in entropy.

⇒ ***The entropy of the universe does not change for reversible processes and increases for spontaneous processes.***

➢ Isothermal *Reversible* expansion

$W_{rev} = -p\Delta V$ & $q_{rev} = p\Delta V$ (i.e. $q_{rev} = -w_{rev}$)

$$\therefore \Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

$$= \left(\frac{q_{rev}}{T}\right) + \left(-\frac{q_{rev}}{T}\right)$$

$$= 0$$

➢ Clausius inequality

$$\boxed{dS \geq \frac{dq}{T}}$$

- In an isolated system, there is no heat transfer and $dq = 0$, thus $dS \geq 0$

⇒ ***all natural processes are spontaneous & irreversible***.

- **Reversible process:**

$$\boldsymbol{dS_{total} = dS_{system} + ds_{surrounding} = 0}$$

⇒ **Spontaneous in neither direction and is at equilibrium**

- **Irreversible process**

$$\boldsymbol{dS_{total} > dS_{system} + ds_{surrounding} > 0}$$

⇒ ***all spontaneous process occurring in Nature is irreversible, entropy of the universe is increasing continuously***

Entropy

- The 1st law & the 2nd law of thermodynamics were summed up by German Physicist Rudolf Clausius as below:

The energy of the universe remains constant; the entropy of the universe tends towards a maximum

➢ Entropy change during different processes

- For an ideal gas (1 mole) with **variable T & V**

$$\Delta S = C_v \ln\frac{T_f}{T_i} + R\ln\frac{V_f}{V_i}$$

- For an ideal gas with **variable P & T**

$$\Delta S = C_p \ln\frac{T_f}{T_i} - R\ln\frac{P_f}{P_i}$$

- For an ideal gas in **an isothermal process**

$$\Delta S_T = R\ln\frac{V_f}{V_i} = - R\ln\frac{P_f}{P_i}$$

- For an ideal gas in **an isobaric process**

$$\Delta S_P = C_p \ln\frac{T_f}{T_i}$$

- For an ideal gas in **an isochoric process**

$$\Delta S_v = C_v \ln\frac{T_f}{T_i}$$

➢ Heat engine

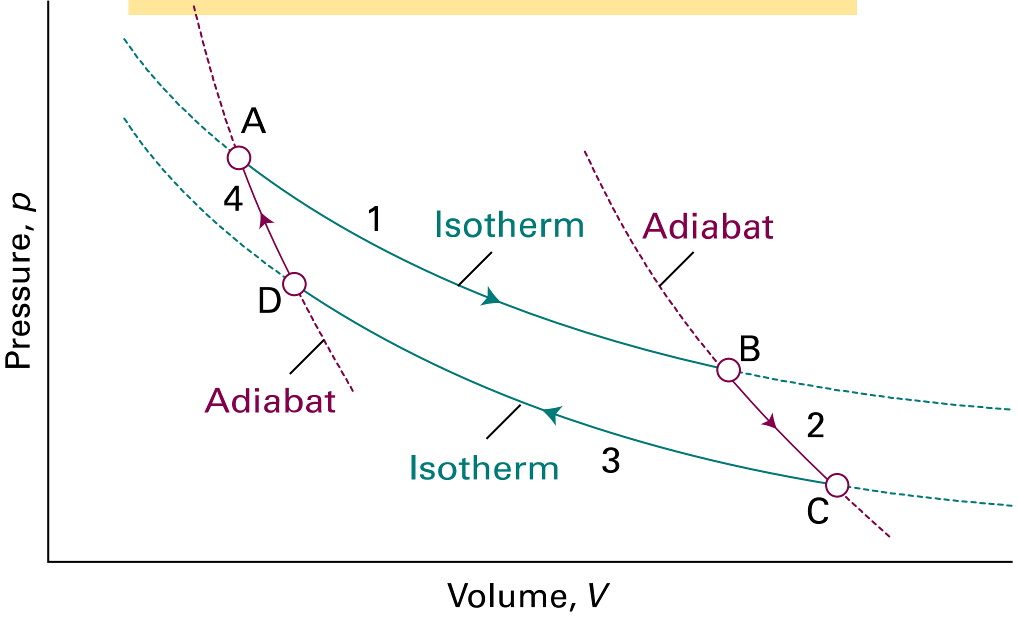
- Its a device which transforms heat into work
- This happens in a cyclic process
- Heat engines require a hot reservoir to supply energy (**Q_H**) and a cold reservoir to take in the excess energy (**Q_C**)
  - **Q_H** is defined as **positive**, **Q_C** is defined as **negative**

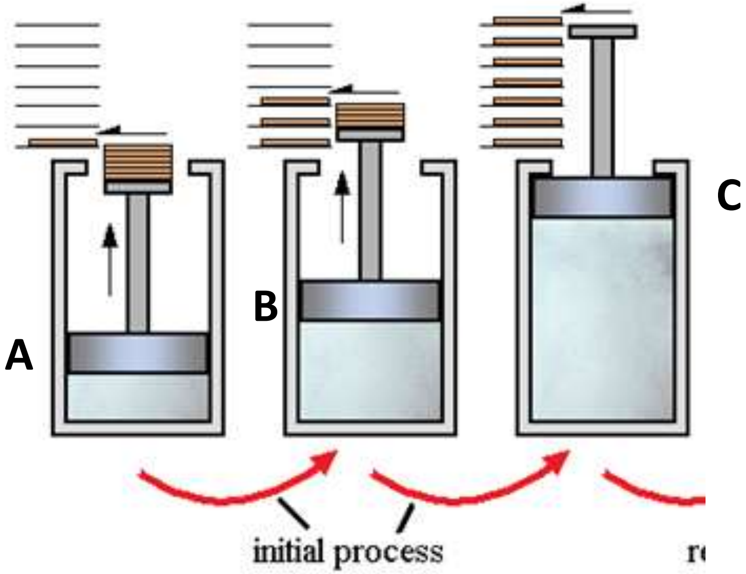
➢ Carnot Cycle

- A ***Carnot cycle*** (named after the French engineer Sadi Carnot) consists of **four reversible stages** in which a *gas (the working substance) is either* ***expanded/compressed*** *in various ways*
- To demonstrate the maximum convertibility of heat into work…
- The system consists of **1 mole of an ideal gas** which is subjected to **four strokes**

Carnot Cycle

- **Four stages of Carnot Cycle:**





A. 1st stroke: Curve AB: A→B: **Isothermal expansion** at T_h
Work done *by* the gas

⇒ The gas is placed in thermal contact with $\boldsymbol{q_H}$ (at $\boldsymbol{T_h}$) and undergoes reversible isothermal expansion from A to B.

⇒ The entropy change is $\boldsymbol{q_h/T_h}$ (q_h = the energy supplied to the system as heat from the hot source)

$$q_h = -w_1 = RT_h \ln\frac{V_B}{V_A}$$

B. 2nd stroke: Curve BC (B → C): **Adiabatic expansion,**
Work done *by* the gas

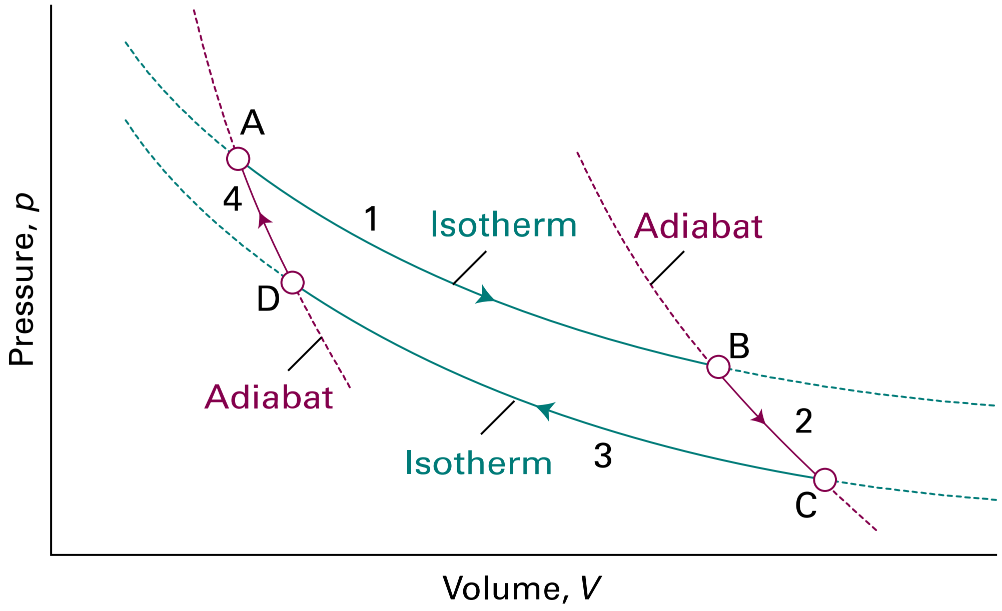
⇒ Contact with $\boldsymbol{q_H}$ is broken & the gas undergoes reversible adiabatic expansion from B to C.

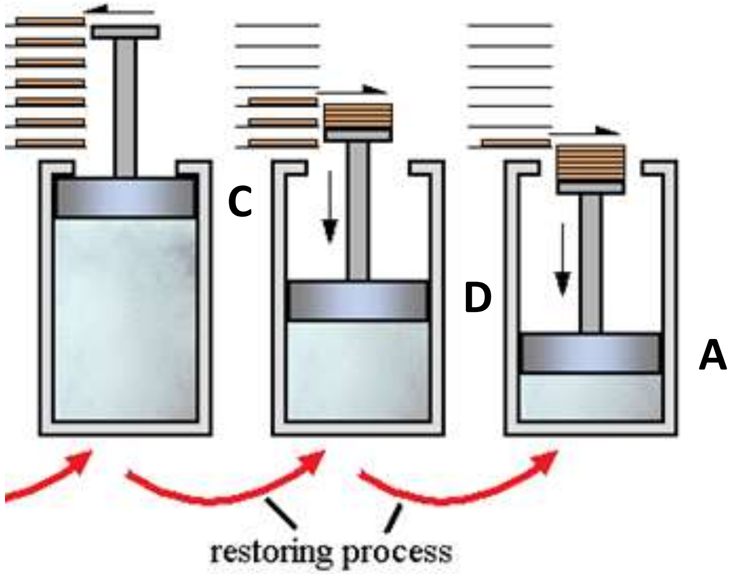
⇒ No energy leaves the system as heat, **$\Delta S = 0$**

⇒ The expansion is carried on until the temperature of the gas falls from **T_h to T_c** (the temperature of $\boldsymbol{q_c}$)

$$-w_2 = -C_v\,(T_h - T_c)$$

Carnot Cycle





C. 3rd stroke: Curve CD (C → D): **Isothermal compression** at T_C, Work done *on* the gas.

- The gas is placed in contact with the cold sink ($\boldsymbol{q_c}$) and undergoes a reversible isothermal compression from C to D at $\boldsymbol{T_c}$.
- Energy is released as heat to the cold sink; the entropy change of the system = $\boldsymbol{q_c/T_c}$, where $\boldsymbol{q_c}$ **is negative**.

$$-q_c = w_3 = RT_c \ln\frac{V_D}{V_C}$$

D. 4th stroke: Curve DA (D → A): **Adiabatic compression** Work done *on* the gas

- Contact with $\boldsymbol{q_c}$ is broken and the gas undergoes reversible adiabatic compression from D to A such that the final temperature is $\boldsymbol{T_h}$.
- No energy enters the system as heat, so the change in entropy is zero. **ΔS = 0**

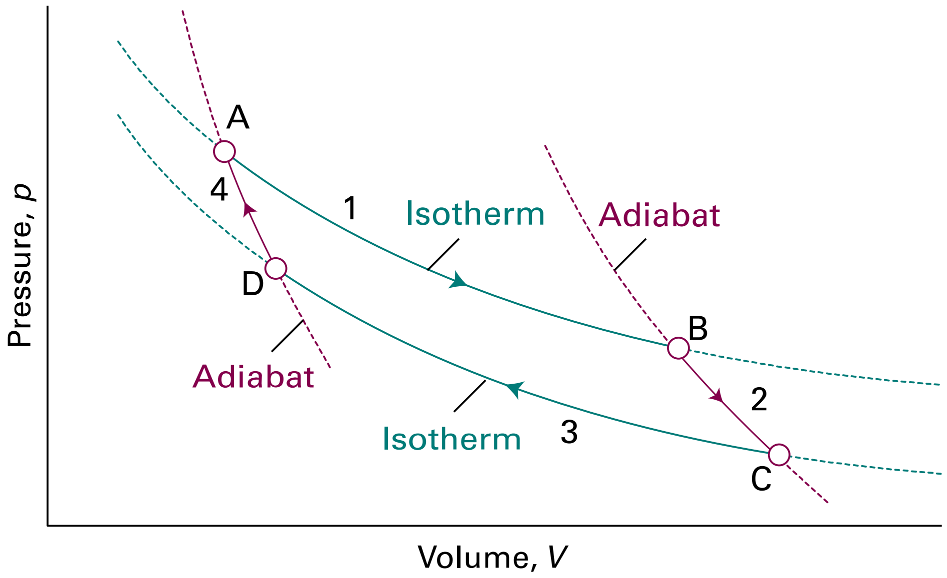
$$w_4 = C_v\,(T_h - T_c)$$

Carnot Cycle

- **The area enclosed by the four curves represents the net work done by the engine in one cycle**
- **The total change in entropy around the cycle is the sum of the changes in each of these four steps:**

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

❖ **For an ideal gas,** $\oint dS = 0$ and $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$



Efficiency of a heat engine

- The thermal efficiency of a heat engine is

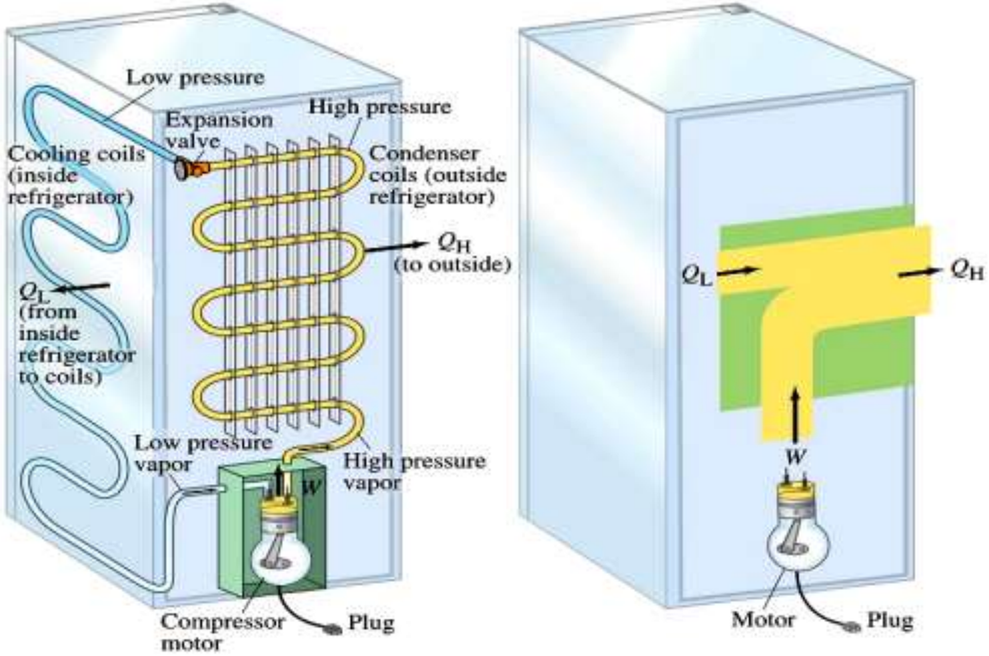
$$\eta = \frac{work\ performed}{heat\ abosrbed\ from\ the\ hot\ source} = \frac{W}{q_H} = 1 - q_C/q_H = 1 - T_C/T_H$$

- The **"engine"** statement of the 2nd Law:
  - it is impossible for any system to have an efficiency of 100% (η = 1) **[Kelvin's statement]**

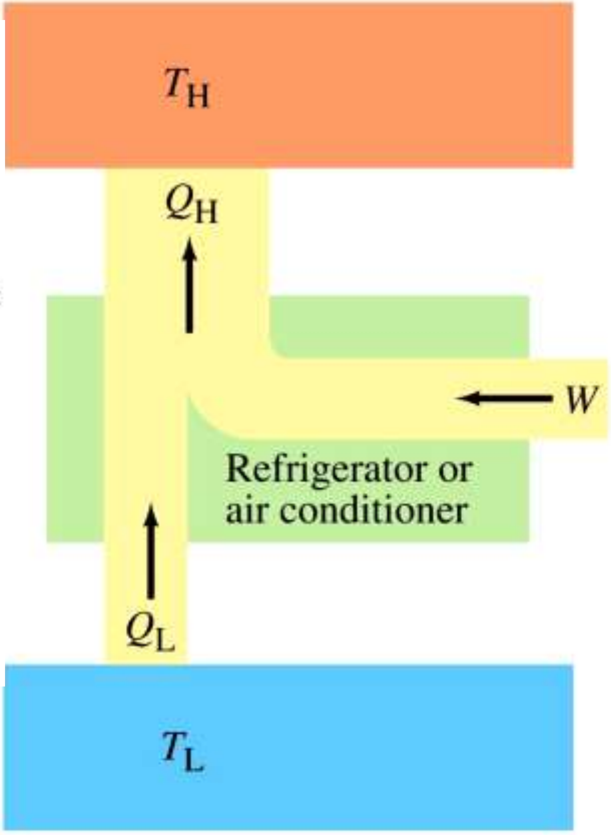
- Another statement of the 2nd Law:
  - It is impossible for any process to have as its sole result the transfer of heat from a cooler object to a warmer object **[Clausius's statement]**

Application of the Carnot Cycle

- **Energy efficiency** of the Carnot cycle is **independent** of its **working substance**.
- Any cyclic process that **absorbs heat** at one temperature and **rejects heat** at another temperature and is **reversible** has the **energy efficiency** of a Carnot cycle (directions of heat and work interactions are reversed in Carnot heat-engine cycle).



Carnot heat pump and refrigeration cycle



→ Thermal devices or thermal machines are one of the applications of this cycle.

✓ The heat pumps to produce heating,

✓ the refrigerators to produce cooling,

✓ the steam turbines used in the ships,

✓ the combustion engines of the combustion vehicles

✓ the reaction turbines of the aircraft

→ **Refrigeration, Air conditioners & Heat pumps**

- These appliances are heat engines operating in reverse.
- **By doing work, heat is extracted from the cold reservoir & exhausted to the hot reservoir**

Temperature & Free Energy

➢ Free energy and the spontaneity

- As, $\boldsymbol{\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}}$

and ΔS_{total} is a criterion for the spontaneity/feasibility of a process.

$$\Delta S_{sur} = -\Delta H^{o}{}_{sys}/\mathrm{T}$$

$$\Delta S_{universe} = \Delta S_{system} + (-\Delta H^{o}{}_{syst}/\mathrm{T})$$

$$\Delta S_{universe}\, T = T\Delta S_{system} + (-\Delta H^{o}{}_{syst})$$

– Gibbs Free Energy

Rearranging this as…

$$-\mathrm{T}\Delta S_{universe} = \Delta H^{o}{}_{sys} - T\Delta S_{system}$$

Gibbs Free Energy

$$\boldsymbol{\Delta G^{o} = \Delta H^{o}{}_{sys} - T\Delta S^{o}{}_{system}}$$

There are two parts to the free energy equation:

- $\Delta H°$— the enthalpy term
- $T\Delta S°$ — the entropy term

The temperature dependence of free energy comes from the entropy term.

$-\mathrm{T}\Delta S_{universe}$ is defined as the Gibbs free energy, ΔG.

For spontaneous processes: $\Delta S_{universe} > 0$

And therefore: $\Delta G < 0$

Gibbs Free Energy

- **Free energy** *is energy that is available to do work*.
- The free energy change of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^o = \Delta H^o_{sys} - T\Delta S^o_{system}$$

- **The** Changes in Enthalpy (ΔH), Entropy (ΔS), and Free Energy (ΔG) **of a reaction are the driving forces behind all chemical reactions.**

Conditions for Spontaneity of a Chemical Reaction:

- A spontaneous reaction is one that releases free **energy**, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible combinations as shown in the table below.

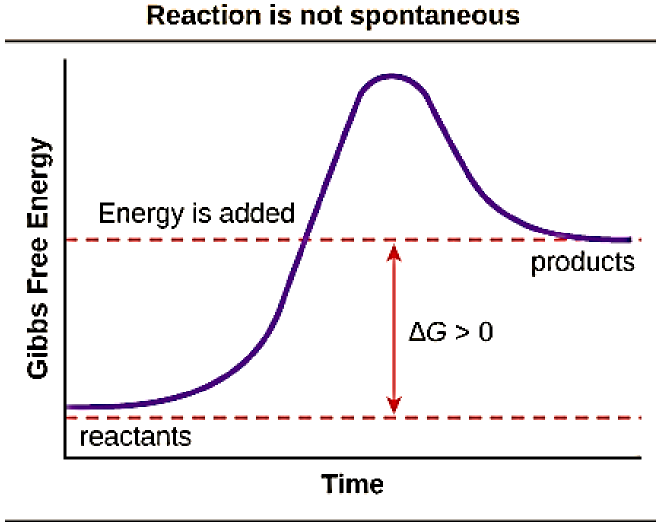
ΔH°	ΔS°	ΔG°
Negative	**Positive**	**Always negative**
Positive	**Positive**	**Negative at higher temperatures,** **Positive at lower temperatures**
Negative	**Negative**	**Negative at lower temperatures,** **Positive at higher temperatures**
Positive	**Negative**	**Always positive**

ΔH	ΔS	T	ΔG	Comments	Examples
-	+	high or low	-	spontaneous at all temperature	$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$
+	+	high	-	spontaneous at high temperature	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
-	-	low	-	spontaneous at low temperature	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
+	-	high or low	+	nonspontaneous at all temperature	$2H_2O(l) + O_2(g) \rightarrow 2H_2O_2(l)$

Free Energy

- ***In an endothermic reaction:***

- **d*H* > 0**
- but if such a reaction is to be spontaneous at constant temperature and pressure, Gibbs Free Energy (*G*) must decrease.



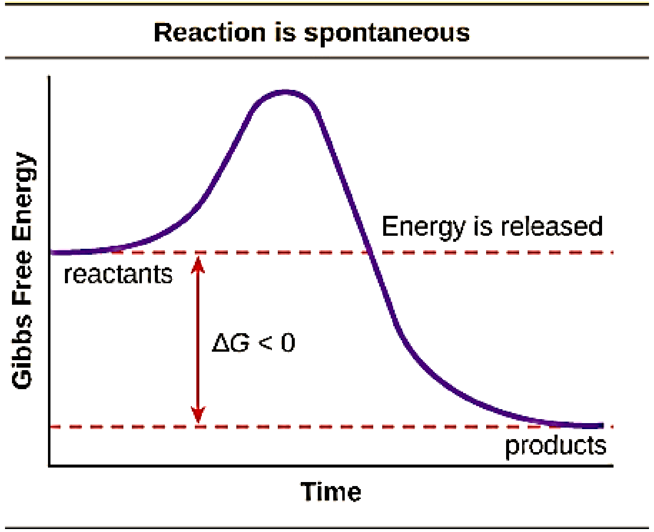
as d*G* = d*H* – *TdS*,
it is possible for d*G* to be negative provided that the entropy of the system increases so much that *TdS* outweighs d*H*.

- **Endothermic reactions** are therefore driven by the ***increase of entropy*** of the **system**

- **At chemical equilibrium,**

- ***dG = 0***

- **In an exothermic reactions**



- **d*H* < 0**

commonly spontaneous because d*H* < 0
& then d*G* < 0
provided *TdS* is not so negative that it outweighs the decrease in enthalpy.

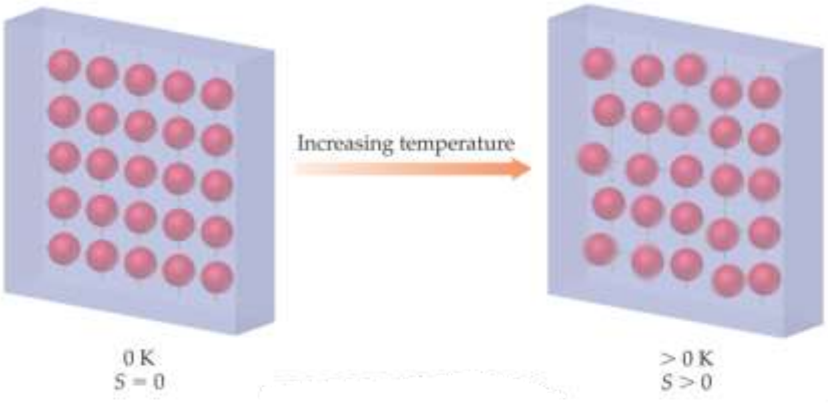
3rd Law of Thermodynamics

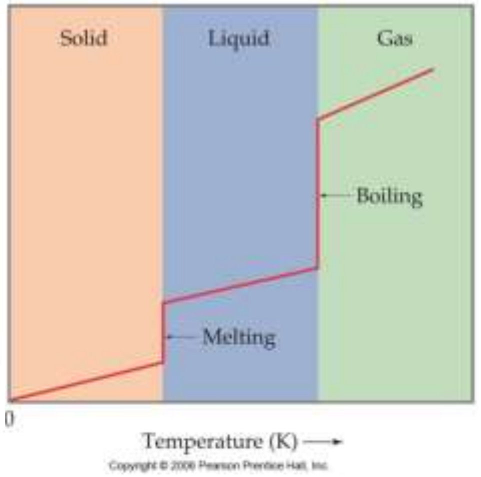
- At $T = 0$ K, all energy of **thermal motion has been quenched and in a perfect crystal** all the **atoms/ions are in a regular, uniform array**.
- The localization of matter and the absence of thermal motion suggest that such materials also have **zero entropy.**
- Statistical or microscopic definition of entropy:

$$\boxed{S = k \ln W}$$

where, **S** = the entropy,
k = Boltzmann constant,
W = the number of microstates *or* the total number of ways a molecular state can be distributed over the energy states for a specific value of total energy.

The entropy of a substance increases with temperature.





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$\rightarrow$ When $T = 0$, $W = 1$
$\therefore S = k \ln W$
$= 0$

A phase change is isothermal (no change in T).

$\Rightarrow$ if the value zero is ascribed to the entropies of elements in their perfect crystalline form at $T = 0$, then all perfect crystalline compounds also have zero entropy at $T = 0$

➢ **Third law of thermodynamics:** **The entropy of all perfect crystalline substances is absolute zero at $T = 0$.**

Is absolute zero temperature achievable?

Numerical from 2nd Law of Thermodynamics

- **Example 1:** Calculate the efficiency of a certain power station operates with superheated steam at 300 °C (T_h = 573 K) and discharges the waste heat into the environment at 20 °C (T = 293 K).

Solution:

$$T_c = (1 - \eta)T_h$$
$$\Rightarrow \eta = 1 - (T_c / T_h)$$

Theoretical efficiency (η) = 1 – (293K/573K)

= 0.489

= **48.9 %**

\# In practice, there are other losses due to mechanical friction and the fact that turbines do not operate reversibly.

- **Example 3:** Heat supplied to a Carnot engine is 1897.8 kJ. How much useful work can be done by the engine which works between 0 °C and 100 °C.

Solution:

T_c = 0 + 273 = 273 K, T_h = 100 + 273 = 373 K

q_h = 1897.8 kJ

$$\therefore w = q_h \times \left(1 - \frac{T_c}{T_h}\right)$$
$$= 1897.8 \text{ kJ} \times \left(1 - \frac{273\ K}{373\ K}\right)$$
$$= 508.7 \text{ kJ}$$

∴ Work done by the engine is **508.7 kJ**

- **Example 2:** Calculate the maximum efficiency of a heat engine operating between 100 °C and 25 °C

Solution:

For engines, we have

T_c = 25 + 273 = 298K

T_h = 100 + 273 = 373 K

$$T_c = (1 - \eta)T_h$$
$$\Rightarrow \eta = 1 - (T_c / T_h)$$

η = 1 – (298 K/373 K)

= 0.201

= **20.1 %**

Numerical from 2nd Law of Thermodynamics

- **Example 4:** 5 mole of an ideal gas expands reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27 °C. Calculate the change in entropy.

Solution:

$$\Delta S = nRln(V_f/V_i)$$

Given that n = 5, V_f = 80 dm^3, V_i = 8dm^3

ΔS = (5 mol) (8.314 J K^{-1}mol^{-1}) ln(80 dm^3/8 dm^3)

= **95.73 JK^{-1}**

- **Example 5:** Calculate the change in entropy accompanying the heating of 1 mole of Helium gas (assumed ideal) from a temperature of 298 K to a temperature of 1000 K at constant pressure. Assume C_v =3/2 R

Solution:

As $C_p - C_v = R$

$\Rightarrow$ Cp =$C_v + R = 2.5\, R$

$$\Delta S_P = C_p \ln\frac{T_f}{T_i} = (2.5 \times 8.314\, Jmol^{-1}K^{-1}) \ln\left(\frac{1000K}{298K}\right)$$

$$= 25.17\, Jmol^{-1}K^{-1}$$

- **Example 6:** 1 mol of an ideal gas expands reversibly from a volume of 10 dm^3 at 298 K to a volume of 20 dm^3 at temperature 250 K. Assuming C_v =3/2 R, calculate the entropy change for the process.

Solution:

$$\Delta S = C_v \ln\frac{T_f}{T_i} + R\ln\frac{V_f}{V_i}$$

$$= 1.5\,(8.314\, Jmol^{-1}K^{-1}) \ln\left(\frac{250\ K}{298K}\right) + (8.314\, Jmol^{-1}K^{-1}) \ln(20\ dm^3/10\ dm^3)$$

= 3.57 JK^{-1}mol^{-1}

7. Calculate the entropy in the surroundings when 1 mol H_2O (l) is formed from its elements under standard conditions at 298 K.

H_2 (g) + ½ O_2 (g) → H_2O (l) [ΔH^o for 1 mol H_2O = -285.8 kJ].

$\Delta S_{\text{surr}} = -\Delta H/T_{\text{surr}}$

$\Delta S_{\text{surr}} = -(-285.8 \text{ X } 10^3 \text{ J})/298\text{K}$

$\mathbf{\Delta S_{\text{surr}} = +\ 958.6\ JK^{-1}}$

8. Calculate the std. reaction entropy of

H_2 (g) + ½ O_2 (g) → H_2O (l) at STP.

[ΔS^o of H_2O = 69.9 $JK^{-1}mol^{-1}$,

ΔS^o of H_2 = 130.7 $JK^{-1}mol^{-1}$, ΔS^o of O_2 = 205.1 $JK^{-1}mol^{-1}$].

ΔS for reaction = ΔS [H_2O (l)] – ΔS [H_2 (g) + ½ O_2 (g)]

ΔS for reaction = 69.9 – 130.7 – ½ (205.1) $JK^{-1}mol^{-1}$

ΔS for reaction = –163.4 $JK^{-1}mol^{-1}$

9. Calculate the change in Gibbs function when 1 mol N_2O_4 (g) forms 1 mol NO_2 (g) at STP. The $\Delta S = +4.8\ JK^{-1}$ for this reaction.

N_2O_4 (g) → $2NO_2$ (g),

[ΔH^o for N_2O_4 (g) = +9.2 kJ, ΔH^o for NO_2 (g) = +33.2 kJ].

Std. reaction enthalpy is

$\Delta H = 2\ (33.2) - (9.2)\text{kJ/mol}$

$= +\ 57.2\ \text{kJmol}^{-1}$

$\Delta G = \Delta H - T\Delta S$

$= +57.2\ \text{kJ} - (298\ \text{K})\ (+4.8\ \text{JK}^{-1})$

ΔG = +55.8 kJ

Solved problem-1

10. How can you say that the following reaction is spontaneous or not? Justify the answer using the standard entropy values given in the table.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Standard Entropy Values at 25°C

Substance	S° (J/K. mol)
H_2 (g)	131.0
O_2 (g)	205.0
H_2O (l)	69.9

Ans: From the absolute entropies of substances, we can calculate the entropy change by

$$\Delta S^o = S^o \text{ of Products} - S^o \text{ of Reactants}$$

$$\Delta S^o = 2\,(69.9) - [2(131) + 1\,(205)]$$

$$\Delta S^o = -327 \text{ J/K. mol}$$

- **The entropy change for this reaction is highly negative because three gaseous molecules are being converted into two liquid molecules.**
- **According to the drive towards higher entropy, the formation of water from hydrogen and oxygen is an unfavourable reaction.**
- **In this case, the reaction is highly exothermic and the drive towards a decrease in energy allows the reaction to occur.**

Solved problem-2

11. What is ΔG for the melting of ice at -10°C, if the H = 6.01 kJ/mol and S = 0.022 kJ $K^{-1}mol^{-1}$?

T = −10°C + 273 = 263 K

$$\Delta G = \Delta H - T\,\Delta S$$

$$= 6.01\ \text{kJ/mol} - 263\text{K} \times 0.022\ \text{kJK}^{-1}\ \text{mol}^{-1}$$

$$= 6.01\ \text{kJ/mol} - 5.79\ \text{kJ/mol}$$

$$\Delta G = 0.22\ \text{kJ/mol}$$

Thus, we see that at −10°C, the Gibbs free energy change ΔG is positive for the melting of water.
Therefore, we would predict that the reaction is *not* spontaneous at −10°C.