

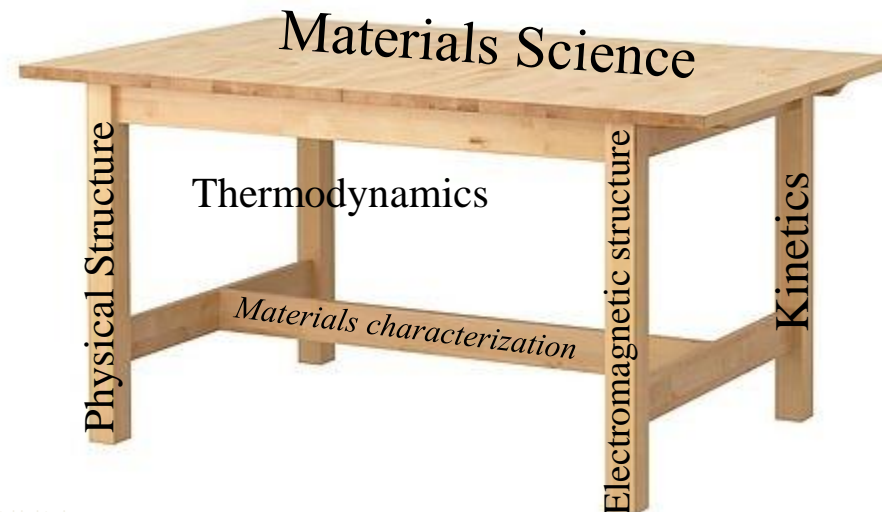
# **Equilibrium, Kinetics and Thermodynamics**

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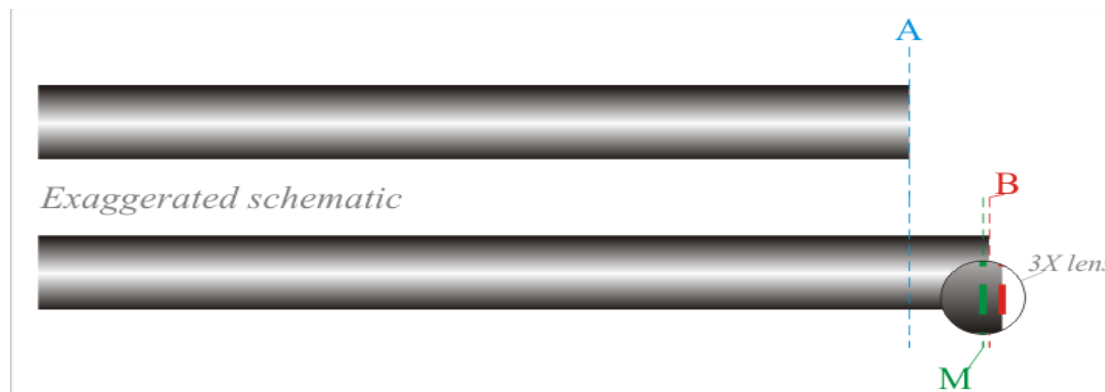
## What are the four founding pillars of materials science?

- ❑ The four pillars of Materials Science and Engineering are :
  - (i) Physical structure → Atomic structure (+ Microstructure)
  - (ii) Electromagnetic Structure → Electronic and Magnetic structure
  - (iii) Thermodynamics
  - (iv) Kinetics
- ❑ If one gains understanding of these four pillars, one can comprehend most aspects of Material behaviour and engineer materials for applications.



# Kinetics, Equilibrium and Thermodynamics

- ❑ Let us start by performing the following (thought) experiment:  
Heat a rod of Al from room temperature to  $500^{\circ}\text{C}$  → As expected the rod will expand  
( $A \rightarrow B$  in figure below).
- ❑ The expansion occurs because of **two reasons**:
  - 1 ➤ Vibration of atoms (leading to an increase in average spacing between atoms → the usual reason)  
( $A \rightarrow M$  in figure below).
  - ❑ 2 ➤ Increase in the concentration of vacancies\* (a vacancy is created when a Al atom goes to the surface and for every 4 vacancies created the volume equal to 1 unit cell is added). ( $M \rightarrow B$  in figure below).
- ❑ The 2<sup>nd</sup> reason is of subtler origin and must be surprising to many readers. Additionally, it is a smaller effect in terms of its contribution to the overall increase in length of the specimen.



Metal expands on heating due to 2 different physical reasons!

\* It costs energy for the system to put vacancies (broken bonds, distortion to the lattice)  
→ then why does the system tolerate vacancies?

**Decreased intermolecular distance:** The chains become mobile and slide past each other, decreasing the distance between atoms.

- ❑ Let us next consider the melting of a pure metal at its melting point (MP) (at constant T and P) → by supplying heat to the sample of metal (so that the metal sample is only partly molten). At the MP the liquid metal is in equilibrium with the solid metal.
  - ❑ The liquid has higher potential energy as well as higher kinetic energy (at the molecular level) than the solid.
  - ❑ Then why does the liquid co-exist with the solid?
  - ❑ The answer to this question lies in the fact that internal energy is not the measure of stability of the system.
  - ❑ We will learn in this chapter that it is the Gibbs Free Energy (G). The molten metal has higher energy (internal energy and enthalpy), but also higher Entropy. So the melting is driven by an increase in Entropy of the system. The molten metal and the crystalline solid metal have the same G → hence they co-exist in equilibrium.
- 
- ❑ Similarly we can consider the vaporization of water at 100°C and 1 atm pressure.
  - ❑ Not only that steam has higher internal energy, but also that work has to be done against atmospheric pressure to accommodate the higher volume of steam!

## Stability and Equilibrium

- ❑ **Equilibrium refers to a state** → wherein there is a *balance of 'forces'*\*.  
*Nothing happens in a system in equilibrium (as there is no 'motivation').*  
(as we shall see equilibrium points have zero slope in a energy-parameter plot).
- ❑ **Stability relates to perturbations** (usually small perturbations\*\* about an equilibrium state) (as we shall see stable relates to the curvature at the equilibrium points).

### Kinds of Equilibrium

Note: nothing happens/changes in a system under equilibrium (at least macroscopically)

- ❑ Mechanical equilibrium
  - ❑ Thermal equilibrium
  - ❑ Reaction Equilibrium
  - ❑ Phase Equilibrium
- } **Material Equilibrium**

- ❑ When conditions of reaction and phase equilibrium are satisfied, we have material equilibrium.
- ❑ The term **thermodynamic equilibrium** implies that, we have **thermal, mechanical and chemical equilibrium.**

- Under mechanical equilibrium, the P is uniform throughout the system and further equal to that of the surrounding (assuming non-rigid walls).
- Under thermal equilibrium the T is uniform throughout the system and equal that of the surrounding (assuming diathermal walls).

\* Force has been used here in a generalized sense (as an agent which can cause changes)

\*\* Perturbation is usually a small 'force/displacement' imposed in a short span of time.

*Equilibrium with respect to conversion of set of chemical species to another*

## Material equilibrium

*Number of moles of each substance (in the closed system) remains constant with time*

## Reaction equilibrium

*The fraction of reactants and products remains constant with time*

## Phase equilibrium

*The fraction of various phases remains constant with time*

*Equilibrium with respect to transport of matter between phases of a system (without conversion of one to another)*

These are dynamic equilibria

## Thermodynamic Equilibrium

### Thermal equilibrium

### Mechanical equilibrium

### Chemical equilibrium

- **Thermal equilibrium.** When the temperature of two bodies (or the system and the surroundings) is the same, then no heat transfer can take place between the bodies. The bodies are in thermal equilibrium.
- **Mechanical equilibrium.** When the forces on a body are balanced, then there is no propensity for the body to move and the body is in mechanical equilibrium.

- **Reaction equilibrium.** Let us consider the chemical reaction:  $aA + bB \rightarrow cC + dD$ . If the rate of the forward reaction is the same as the reverse reaction and the molar concentrations do not change with time (a, b, c, d are unchanged with time), then we have reaction equilibrium. i.e. the concentration of chemical species do not change with time. Under equilibrium the reaction is written as:  $aA + bB \rightleftharpoons cC + dD$ .

- **Phase equilibrium.** A simple system one can think of is a closed partly filled water bottle. Assume that the vapour phase is in equilibrium with the liquid phase. Under conditions of phase equilibrium, the concentration of the phases does not change with time. If there are two phases (say  $\beta$  and  $\alpha$ ), both containing a species 'A'. Then, under phase equilibrium conditions, the concentration of species 'A' in the  $\alpha$  and  $\beta$  phases will not change with time.

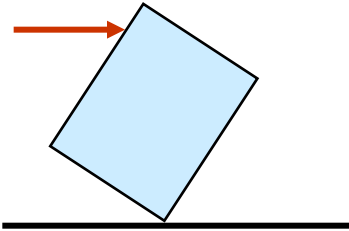


## Kinds of Stability (Equilibrium)

Four kinds of equilibrium (with respect to energy).

- ❑ (C3) Global minimum → STABLE EQUILIBRIUM (STATE).
- ❑ (C1) Local minimum → METASTABLE EQUILIBRIUM (STATE).
- ❑ (C2) Maximum → UNSTABLE EQUILIBRIUM (STATE).
- ❑ (C4) Constant energy → Neutral State/Equilibrium.

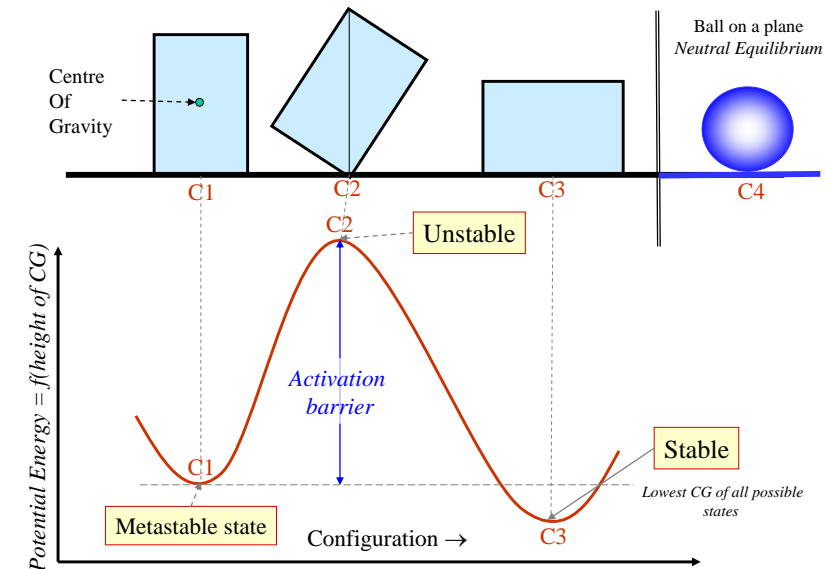
Small knock



*What is a perturbation?*

- In a mechanical system (like the block under consideration) it is a small ‘knock’ or a ‘shake’.
- In other systems, which can respond to electrical or magnetic stimuli, perturbations can be caused by such fields. (I.e. deepening on the system and the stimuli to which it can respond, other methods of ‘shake-up’ exist).

- When the block is tilted from configuration C1 to C2, the centre of gravity (CG) goes up (curve in the plot) and this raises the potential energy of the system.
- Assume now that the block is somehow in equilibrium in configuration C2, then a small tap can take it either to C1 or C3.
- In going from C1 to C3, the system has to cross an ‘activation barrier’ (the energy difference between states C2 and C1).





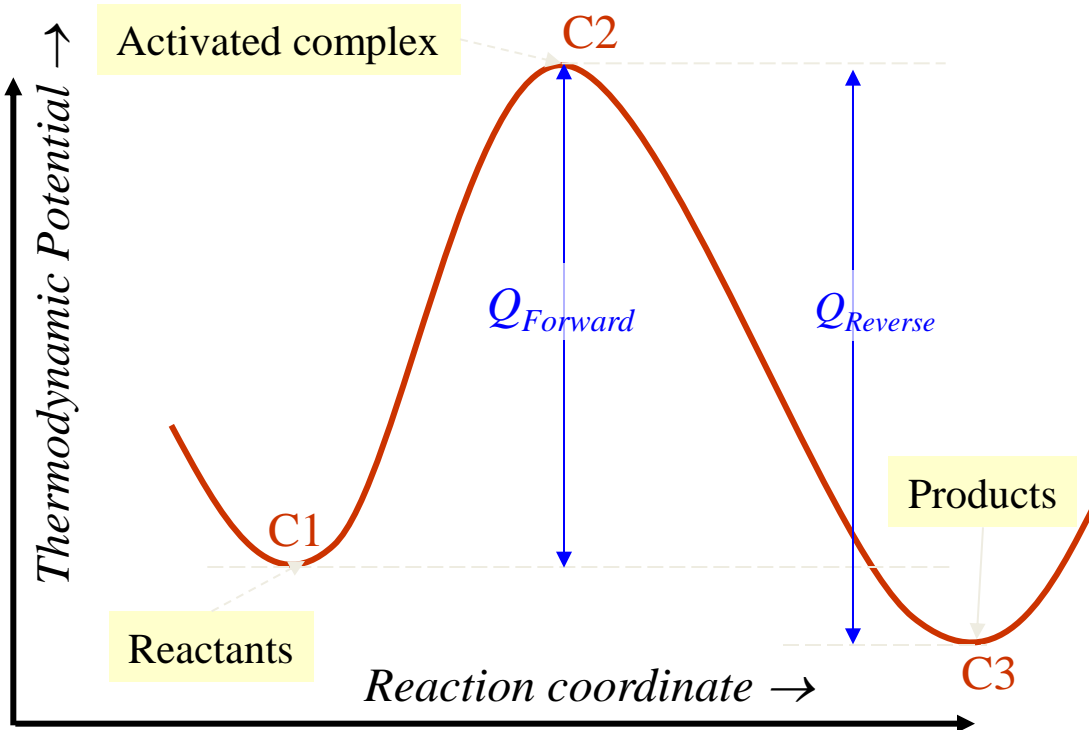
- ❑ **Kinds of equilibrium can be understood by making perturbations to the system.**
- ❑ For the mechanical system (block) perturbation corresponds to tilting the block.
- ❑ If the system changes its state after small perturbations then the system  
→ is in an **unstable state**.
- ❑ If the system returns to its original state after a small perturbation (tilt) then the system  
→ is in a **stable or metastable state** (lies in an energy minimum).
- ❑ If the system returns to its original position after small perturbations but does not do so for large perturbations then the system  
→ is in a **metastable state** (not in the global energy minimum).
- ❑ If there is no change in energy for any kind of perturbation then the system  
→ is in a state of **neutral equilibrium** (e.g. the case of the ball on a plane).
- ❑ In a **2D system** where perturbations are possible in more than one direction (i.e. the energy landscape is a surface), perturbations in one direction may be stable and in another direction it may be unstable.

- If the system tends to return to the original state after the perturbation → **Stable/Metastable** state. ▪ In *Metastable state* the system can go to a new state (of lower 'energy') if the amplitude of the perturbation is large.
- If the system goes to a different state on perturbation (the perturbation will tend to take the system to a new state 'very different' from the original state) → **Unstable** state.
- If the system goes to the 'new perturbed state' without a change in energy (the perturbation will tend to take the system to a new state 'close to' the original state, as imposed by the perturbation) → **Neutral** state.

- ❑ In Materials Science we are mainly interested with condensed matter systems (solids and liquids) (also sometimes with gases)
- ❑ The state of such a system is determined by '**Potentials**' analogous to the potential energy of the block (which is determined by the centre of gravity (CG) of the block).  
These potentials are the **Thermodynamic Potentials** (A thermodynamic potential is a Scalar Potential to represent the thermodynamic state of the system).
- ❑ The relevant potential depends on the 'parameters' which are being held constant and the parameters which are allowed to change. More technically these are the **State/Thermodynamic Variables** (A state variable is a precisely measurable physical property which characterizes the state of the system- It does not matter as to how the system reached that state). **Pressure (P)**, **Volume (V)**, **Temperature (T)**, **Entropy (S)** are examples of state variables.
- ❑ There are 4 important potentials (in some sense of equal stature).  
These are: **Internal Energy (U or E)**, **Enthalpy (H)**, **Gibbs Free Energy (G)**, **Helmholtz Free Energy (A or F)**.
  - Of these, internal energy can be conceived as a fundamental quantity, while enthalpy is a quantity that keeps track of the available heat.
  - G and A arise due to the fact that the entropy of the universe increases.

## What is the connection of the mechanical block (which we saw earlier) with reaction equilibrium?

- ❑ In the case of a chemical reaction, the x-axis is referred to as the 'reaction coordinate' and the y-axis is a 'relevant' thermodynamic potential (this is akin to the gravitational potential for mechanical systems and we will talk more about this later).
- ❑ C1 corresponds to the reactants, C2 to a 'activated complex' and C3 to the products.
- ❑ The activation barrier for the forward reaction (C1 to C3) is  $Q_{forward}$  and that for the reverse reaction (C3 to C1) is  $Q_{reverse}$ . As the activation barrier is higher for the reverse reaction, the rate of the forward reaction is higher than that for the reverse reaction.

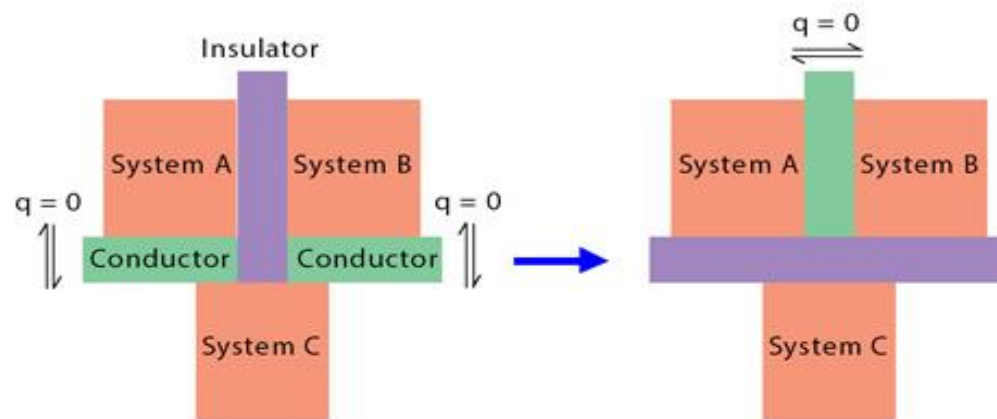


- However, there is a major difference between the mechanical system and the chemical system. The mechanical block can exist only in one of the two 'stable states' (C1 metastable or C3 stable).
- Under equilibrium conditions, the rate of the forward reaction will be equal to that of the reverse reaction and this implies that we will have a finite concentration of species corresponding to C1 and species corresponding to C3.

# Laws of Thermodynamics

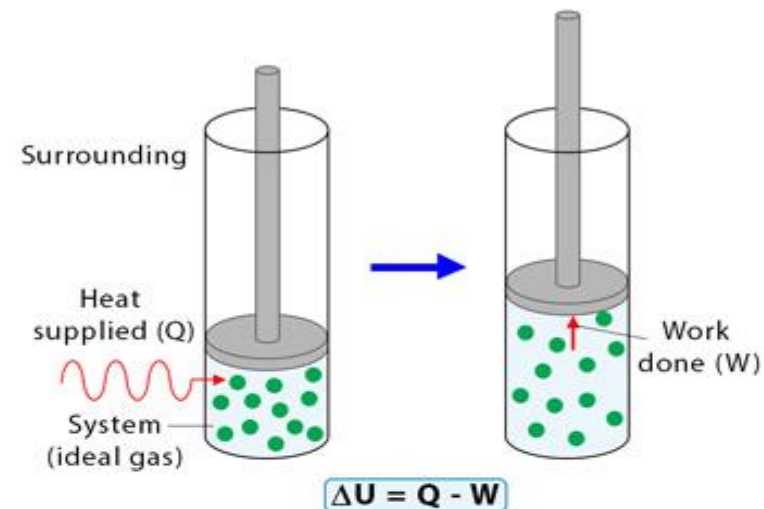
## Zeroth Law

If two thermodynamic systems are in equilibrium ( $q = 0$ ) with a third, then the two are in equilibrium with each other



## First Law

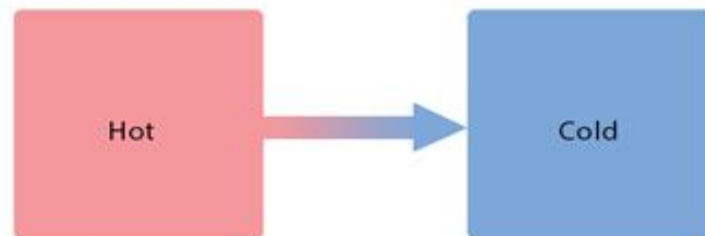
The change in internal energy ( $\Delta U$ ) of a system equals to the heat added to the system minus the work done



## Second Law

The entropy ( $S$ ) of any natural and spontaneous process either increases or remains constant

Example: Heat flow from a hot body to a cold body

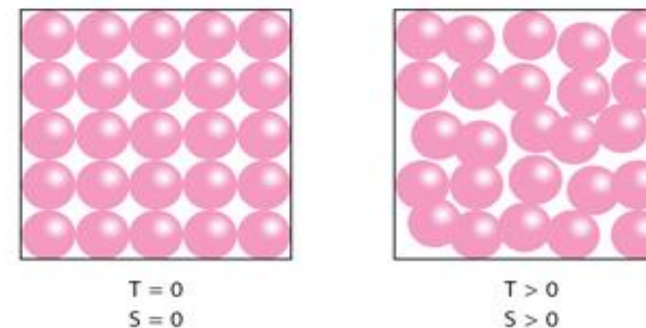


$\Delta S = 0$  For reversible process

$\Delta S > 0$  For irreversible process

## Third Law

Entropy ( $S$ ) of a pure crystal is zero as the temperature ( $T$ ) approaches absolute zero



## Internal Energy (U)

- ❑ **Internal Energy ( $U$  or  $E$ ) = Kinetic Energy ( $KE$ ) + Potential Energy ( $PE$ ).**  
(The above  $KE$  and  $PE$  are at the molecular level).
- ❑ The origin of Kinetic Energy  $\rightarrow$  Translations, Rotations, Vibrations of species\*.  
Note: the available modes (translation, rotation, vibration) depends on the degrees of freedom that a molecule possesses).
- ❑ The origin of Potential Energy  $\rightarrow$  potential energy depends on the interactions between the species in a material, which includes the bonding between atoms.
- ❑ Hence, the internal energy ( $U$ ) is the total of the energies of molecules (or atoms or ions..) and their interactions.
- ❑ The increase in internal energy ( $U$ ) on heating from  $0\text{ K}$  to  $T\text{ K}$  ( $K = \text{Kelvin}$ ) is given by the equation below; where  $C_v$  is the specific heat at constant volume and  $U_0$  is the internal energy of the system at  $0\text{ K}$ .

- From the first law we have:  $\Delta U = Q + W$ .  
For a constant volume process (wherein only P-V work is involved):  $\Delta U = Q/v$
- This implies that heat absorbed at constant volume leads to change in  $U$ .

$$U = U_0 + \int_0^T C_v dT$$

$$H = U + PV$$

- ❑ Enthalpy (H) = Internal Energy + (PV).
- ❑ Since, U, P & V are state functions, H is a state function. The combination  $U + PV$  occurs often in TD and it is useful to give it a special symbol (and status).
- ❑ Enthalpy can be thought of as the measure of the *heat content* of the system.
- ❑ Since U, V are extensive quantities, H is an extensive quantity.
- ❑ At constant pressure, the heat absorbed or evolved is given by  $\Delta H$ .

$$\Delta A = \Delta U - T \Delta S$$

- ❑ Let us now formally write down the new state function introduced: the Helmholtz free energy (A).
- ❑ Helmholtz Free Energy (*A or F*) =  $E - TS$ .
- ❑ At **constant V & T**, for a process/reaction\* to take place spontaneously the system has to reduce its Helmholtz Free Energy. For a system to go from 'state\*' 1  $\rightarrow$  2 the change in **F** would be:  

$$F_2 - F_1 = \Delta F = (U_2 - U_1) - T(S_2 - S_1) = \Delta U - T\Delta S$$

This change of 'state' would take place spontaneously if  $\Delta F$  is *Negative*.
- ❑ This implies that processes which take place at constant volume and lead to an increase in the internal energy (U) can spontaneously occur if there is an entropic benefit for the process and the temperature is sufficiently high (such that the term  $\Delta U - T \Delta S$  is negative).

\* used in the general sense



- ❑ Gibbs Free Energy ( $G = H - TS$ )
  - $S$  is the entropy of the system
- ❑ For a process/reaction\* to take place spontaneously the system has to reduce its Gibbs Free Energy (at **constant P & T**). For a system to go from 'state\*' 1  $\rightarrow$  2 the change in G would be:
 

$$G_2 - G_1 = \Delta G = (H_2 - H_1) - T(S_2 - S_1) = \Delta H - T\Delta S$$

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

This change of 'state' would take place spontaneously if  $\Delta G$  is Negative
- ❑ This implies that *even* Endothermic reactions are allowed (at a 'sufficiently high' temperature) if there is an Entropic benefit (*weighed in with T*) for the process to occur.
  - An example of the above is the presence of (an 'equilibrium concentration' of) vacancies in a crystal (more about this later).
- ❑ Many a times we are concerned with the relative stability of two phases at a given T and P. We asks questions such as  $\rightarrow$  at 1 atm. pressure & 50°C, which of the phases is stable: ice, water or steam? The answer is that the **state with a lower Gibbs free energy is stable.**

## Entropy (S)

- *“Whoever uses the term ‘entropy’ in a discussion always wins since no one knows what entropy really is, so in a debate one always has the advantage” ! John von Neumann.*
- *“Classical thermodynamics is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts”. Albert Einstein.*
- *“The energy of the Universe is constant, the entropy of the Universe tends to a maximum”. Rudolf Julius Emanuel Clausius.*

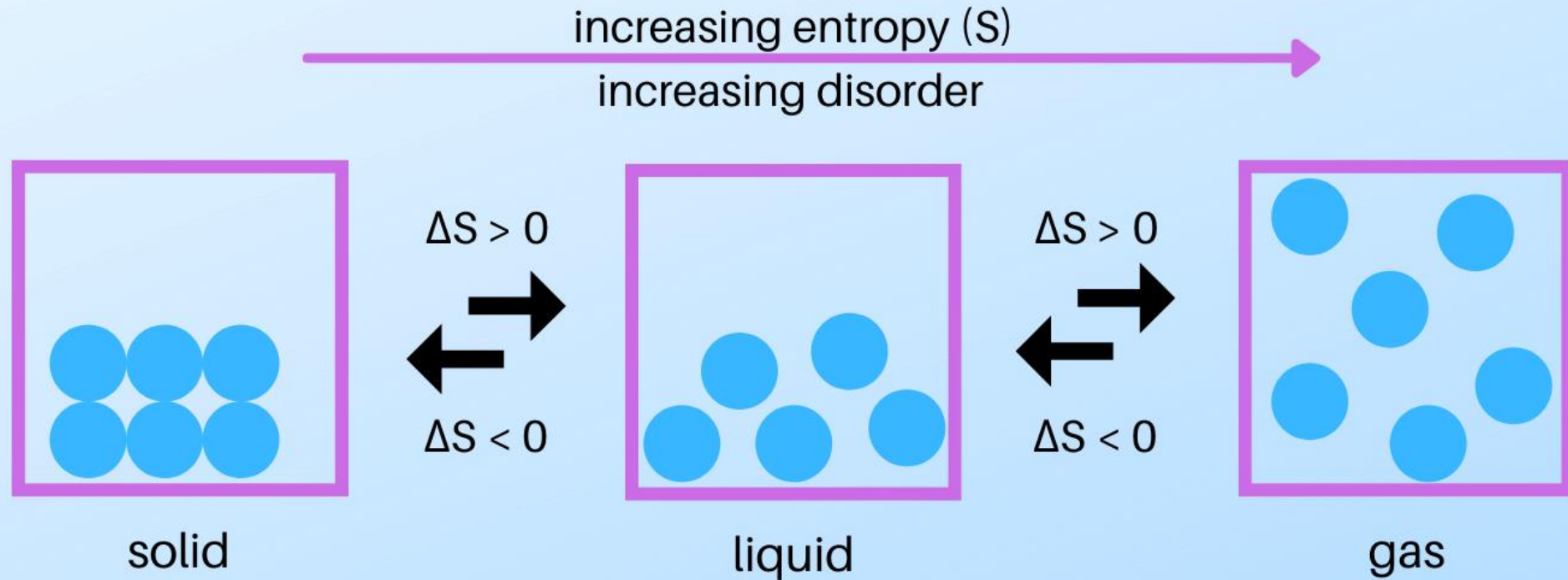
- ❑ Entropy is a scientific concept that measures a **system's disorder, randomness, or uncertainty**. It's also a measure of a **system's thermal energy per unit temperature that can't be used to do useful work**.
- ❑ Entropy can be understood looking at a **Macroscopic picture** (interpretation) or a **Microscopic picture** (interpretation) (next slide).
- ❑ Though these are different approaches to understand entropy—the result is the ‘same’ entropy.
- ❑ In the Macroscopic view we ‘work’ at the system level and worry about *observable average quantities*. In the Microscopic view we go into all the ‘*details*’ about the system.
- ❑ **The entropy of an isolated system will increase in a spontaneous process (*cannot spontaneously decrease*)** → *II law*.
- ❑ Since, the above can be applied to the entire universe (*a large isolated system!\*\**) → **the entropy of the Universe will always increase** (*here we are not using the word ‘spontaneous’ as the Universe cannot be ‘coaxed’ into doing a non-spontaneous processes!*).
- ❑ The microscopic interpretation (view) is the **Statistical Physics/Mechanics picture**, which is valid for large systems (i.e. systems with a large collections of atoms, molecules etc.).
- ❑ “Entropy is time’s arrow” → time increases in the direction of increasing entropy\*.
- ❑ For a system the Internal energy (**U**) measures the **quantity** of the energy, while Entropy (**S**) can be thought of a measure of the **quality** of that energy (*lower value of entropy will imply a better quality* → as the entropy of the universe always\* increases).

\*The universe is in a expanding phase now. If it were to stop expanding and start contracting → entropy of the universe is expected to decrease in the contracting phase.

\*\* We are ignoring ‘wormholes’, which connect our universe to other parallel universes for now (or take those universes part of ours)!!

# What Is Entropy?

Entropy is a measure of the disorder of a system or energy unavailable to do work.



## Thermodynamic Relations for a System in Equilibrium

□ A system undergoing a reversible process passes through equilibrium states (only).

The **first law** for a closed system is:  $dU = dQ + dW$  (1)

For only P-V work done reversibly  $dW = dW_{rev} = -P\Delta V$  (2) We are assuming here that work is done by the system & hence the -ve sign

Again, for a reversible process (**second law**)  $dQ = dQ_{rev} = TdS$  (3)

From (1-3) (combining the first and second laws)  $dU = TdS - P\Delta V$  (e1)

Definition of H  $H = U + PV$  (e2)

Definition of A  $A = U - TS$  (e3)

Definition of G  $G = H - TS$  (e4)

(e1) to (e6) are basic thermodynamic equations of a closed system in equilibrium

Definition of  $C_V$   $c_v = \left( \frac{\partial U}{\partial T} \right)_v$  (e5) Close system in equilibrium, P-V work only

Definition of  $C_P$   $c_p = \left( \frac{\partial H}{\partial T} \right)_p$  (e6) Close system in equilibrium, P-V work only

- We have assumed systems in equilibrium and hence concern ourselves (here) reversible processes. Reversible composition changes are included in the processes (e.g. when we heat a two phase mixture and the proportions of the two phases changes).
- The closed system condition precludes the introduction of additional species, leading to a change in the composition.
- Reaction of species, leading to a composition change is also not included in the above. This is because chemical reactions occurs spontaneously, which implies that the system is not under equilibrium.

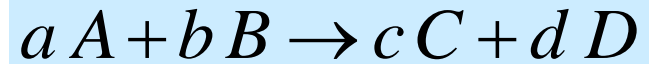
- ❑ In Equilibrium we had seen that the thermodynamic feasibility of processes is dictated by 'Thermodynamic Potentials' (e.g. **Gibbs Free Energy**, at constant T, P,  $N_i$ ).
- ❑ If (say) the Gibbs Free Energy for a process is negative then the process **CAN** take place spontaneously.
- ❑ However, IF the process WILL actually take place (and if it will take place- how long will it take to occur?) → will be determined by the '**Kinetics of the process**'.
- ❑ Deeper the 'metastable energy well', higher will be **activation energy** required to pull the system out of the 'well' and take it to the equilibrium state (or some other metastable state).
- ❑ **To give an example:** the window pane glass is in a metastable state\* → there is a tendency for it to crystallize and to lower the Gibbs Free Energy of the system. However, at room temperature the crystallization is very slow and the glass pane can remain amorphous\*\* for hundreds of years.  
➤ *Case of 'Thermodynamics warrants, Kinetics delays'*
- ❑ For a given process to occur **heat and mass transfer** may have to take place and this would take time → hence in 'kinetics' we deal with **time** and **rates** (1/t)

\* *All glasses are considered to be metastable and there exists at least one crystalline state with a lower G.*

\*\* *The terms glass and amorphous material are more often used synonymously*

- ❑ A homogenous reaction is one which involves only one phase.  
➤ E.g. a reaction involving only gaseous phase
- ❑ In a heterogeneous reaction more than one phase is present.

*Let us consider a homogenous balanced chemical reaction, occurring in a single step:*



*Rate of consumption of a reactant is proportional to the stoichiometric coefficient in a balanced reaction*

$$\frac{dn_A}{dt} \propto a \quad \frac{dn_B}{dt} \propto b \quad \Rightarrow \quad \frac{dn_A/dt}{dn_B/dt} = \frac{a}{b}$$

- $n_A \rightarrow$  number of moles of A present at time t
- $J \rightarrow$  Rate of conversion
- $r \rightarrow$  rate of reaction ( $= J/V$ )

*Rate of Conversion (J) is defined as:*

$$J = -\frac{1}{a} \frac{dn_A}{dt} = -\frac{1}{b} \frac{dn_B}{dt} = \frac{1}{c} \frac{dn_C}{dt} = \frac{1}{d} \frac{dn_D}{dt}$$

*A, B are being consumed and hence  $dn/dt$  for these species is negative and J is positive*

*J depends on system size and is an extensive quantity, the conversion rate per unit volume ( $J/V$ ) is the reaction rate is an intensive quantity*

$$r = \frac{J}{V} = \frac{1}{V} \left( -\frac{1}{a} \frac{dn_A}{dt} \right)$$

*The reaction rate (r) is a function of P, T and the concentration of species*



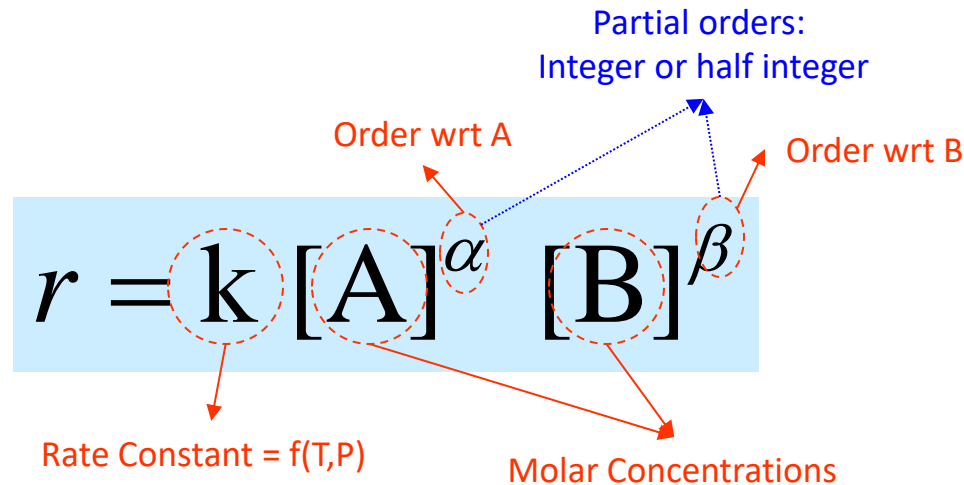
In many of the reactions the volume is constant. If the volume is constant during the reaction:

$$r = \frac{1}{V} \left( -\frac{1}{a} \frac{dn_A}{dt} \right)$$

$$r = -\frac{1}{a} \frac{d(n_A/V)}{dt} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{a} \frac{dc_A}{dt}$$

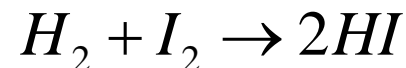
- $n_A \rightarrow$  number of moles of A present at time  $t$
- $J \rightarrow$  Rate of conversion
- $r \rightarrow$  Rate of reaction ( $= J/V$ )
- $[A] \rightarrow$  Molar concentration of A ( $= c_A$ )

For many reactions it is seen that the rate can be related to the concentration of species by a reaction of the form:



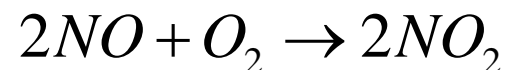
- The rate constant  $k$  is a function of  $T$  and  $P$ 
  - The pressure dependence is usually small
- The exponents:  $\alpha, \beta$  are usually integers or half integers: ( $1, \frac{1}{2}, \frac{3}{2}, \dots$ ) and are the partial orders (i.e. the reaction has got an order  $\alpha$  wrt to A and  $\beta$  wrt B)
- $\alpha + \beta = n$  is the *order of the reaction* (overall order)
- Units of  $k \rightarrow [\text{concentration}]^{1-n} [t]^{-1}$

$$r = k [A]^\alpha [B]^\beta$$



$$r = k[H_2][I_2]$$

- Gas phase reaction
- Overall Order as expected = 2



$$r = k[NO]^2[O_2]$$

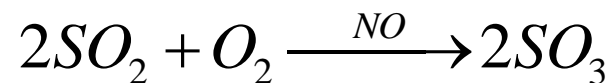
- Gas phase reaction
- Partial and Overall Order as expected
- Overall order = 3

The above are cases which are ‘intuitively’ easy to correlate with the concept of order. But, reactions may have partial order as below or even the concept of order of a reaction may not apply!



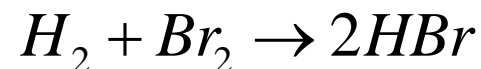
$$r = k[CH_3CHO]^{3/2}$$

- Gas phase reaction
- Partial overall order



$$r = k[NO]^2[O_2]$$

- Gas phase reaction
- Catalyst NO appears in the order while reactant SO<sub>2</sub> does not



$$r = \frac{k[H_2][Br_2]^{1/2}}{1 + j[HBr]/[Br_2]}$$

- Gas phase reaction
- Concept of order does not apply

- ☐ Looking at some of the examples in the previous slide it is clear that the exponents in the rate law can be different from the numerical coefficients in the balanced chemical reaction equation.
- ☐ Rate laws are to be determined from measurement of reaction rates and cannot be determined from reaction stoichiometry.
- ☐ Additionally, the use of concentrations in the rate equations is valid only for ideal systems.

- ❑ Rate constants depend strongly on temperature (usually increasing rapidly with increasing T).
- ❑ For many reactions in solution, a thumb rule can be used that near room temperature 'k' doubles or triples every 10°C increase in temperature.
- ❑ In 1889 Arrhenius noted that for many reactions  $k = f(T)$  fits an exponential function.

*Arrhenius equation*

$$k = A e^{\left[ -\frac{Q}{RT} \right]}$$

Frequency factor

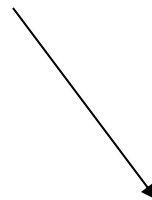
Activation Energy  
Affected by catalyst

T in Kelvin

- A → pre-exponential factor [units of k]
- Q → activation energy [J/mole]
- R → gas constant

A is a term which includes factors like the frequency of collisions and their orientation. It varies slightly with temperature, although not much. It is often taken as constant across small temperature ranges.

Reactants  $\longrightarrow$  Products



*Activated complex*

