

# **“THERMODYNAMICS”**

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# SYNOPSIS

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- ☐ Interoduction
  - ☐ Defination
  - ☐ Terms used in chemical thermodynamics
  - ☐ Internal energy
  - ☐ Law's of thermodynamics
  - ☐ Difference between 1<sup>st</sup> and 2<sup>nd</sup> low of thermodynamics
  - ☐ FREE ENERGY OR GIBB'S FREE ENERGY(G)
  - ☐ Energy crises in nature
  - ☐ Conclusion
  - ☐ Refrence
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# INTRODUCTION

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- The word 'thermodynamics' means study of flow of heat.

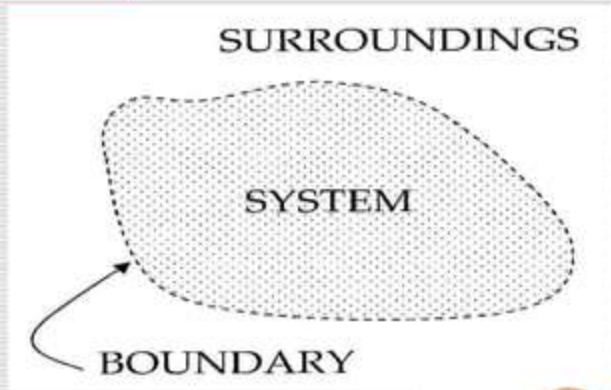
## □ DEFINATION

The branch of physical chemistry which deals with the energy changes accompanying a chemical reaction.

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# TERMS USED IN CHEMICAL THERMODYNAMICS

- ❑ System-
- ❑ Surroundings.
- ❑ Types of system-
  - Open system
  - Closed system
  - Isolated system



# Physical properties of a system-

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- ❑ 1.Intensive properties-  
eg. – temperature, pressure, viscosity, surface tension, refractive index, specific heat, density, etc.
- ❑ 2.Extensive properties-  
❑ eg.- mass, volume, energy, heat capacity, entropy, Gibb's free energy, ect.
- ❑ Thermodynamic process-
  - Isothermal process
  - Adiabotic process
  - Isobaric process
  - Isochoric process
  - Reversible process
  - irreversible process



# INTERNAL ENERGY

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- Every substance possesses a definite amount of energy which depends upon its chemical nature, temperature, pressure and volume. This is called internal energy (E).

$$E_{\text{total}} = E_t + E_r + E_v + E_e + E_n + E_i$$

$$\Delta E = E_2 - E_1$$

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# LAW'S OF THERMODYNAMICS

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- First law of thermodynamics or law of conservation of energy-  
-First stated by Meyer and Helmholtz in 1840.  
“Energy can neither be created nor destroyed although it can be transformed from one form to another”.

OR

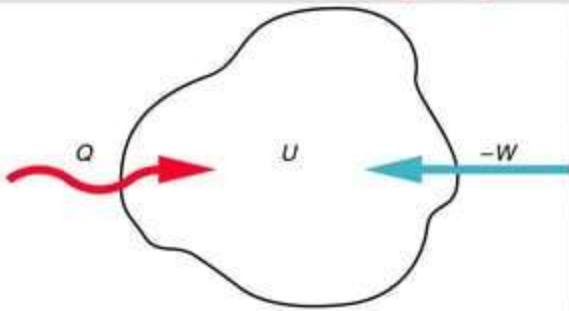
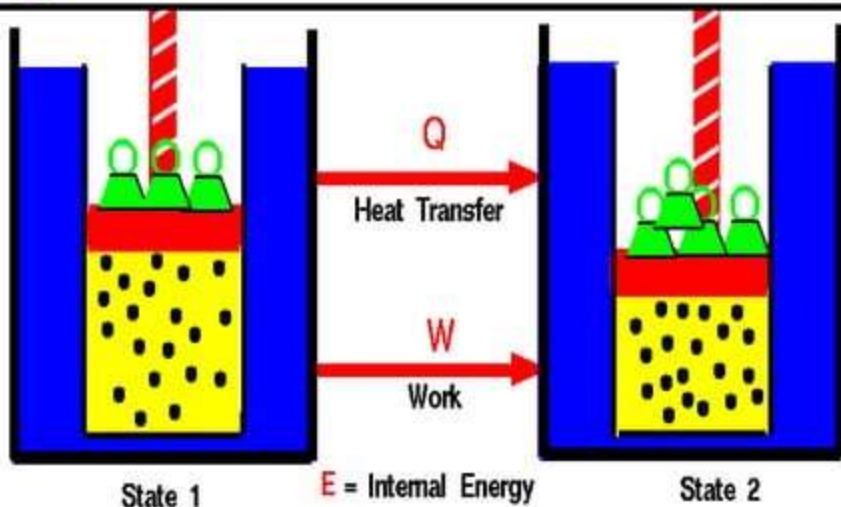
“The total amount of the energy of the universe is a constant”.

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# First Law of Thermodynamics

Glenn  
Research  
Center



$$E_2 = E_1 + q + w \quad \text{.....(1)}$$

$$E_2 - E_1 = q + w \quad \text{.....(2)}$$

$$E = q + w$$



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$$E_2 = E_1 + q + w \quad \dots\dots\dots(1)$$

$$E_2 - E_1 = q + w \quad \dots\dots\dots(2)$$

$$\Delta E = q + w$$

- ☐ If work is done by the system, then

$$\Delta E = q - w$$

- ☐ +q= heat absorbed by the system.
  - ☐ -q= heat liberate by the system.
  - ☐ +w= work done on the system.
  - ☐ -w= work done by the system.
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## ENTHALPY(H) AND ENTHALPY CHANGE( $\Delta H$ )

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- Enthalpy is the amount of heat stored in the system under particular condition and is termed as heat content of the system.

$$H=E+PV \quad \text{.....(1)}$$

- Enthalpy change,  $\Delta H= H_2-H_1$

- On constant P,

$$H_p, E_p, \text{ and } V_p. \quad \text{.....(A).}$$

- Heat absorbed by the system on constant P, then

$$H_R, E_R, \text{ and } V_R. \quad \text{.....(B).}$$

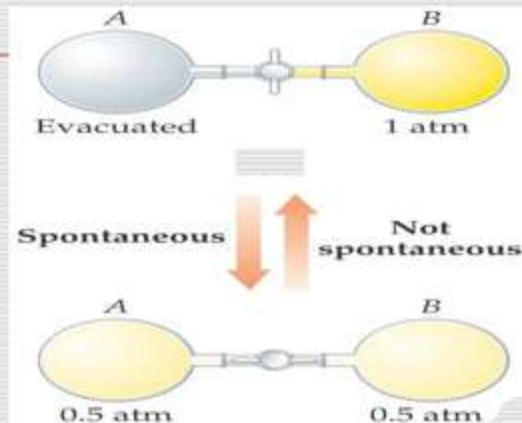
- Eq. ( B)- Eq. ( A ),

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

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# SPONTANEOUS PROCESS

- Spontaneous processes are those that can proceed without any outside intervention.
- Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.



# ENTROPY(S)

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- Entropy can be thought of as a measure of the randomness of a system.

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$



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

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

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

## SECOND LAW OF THERMODYNAMICS

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

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

- Where,

$\Delta S_{total} > 0$  (Irreversible (real, spontaneous):

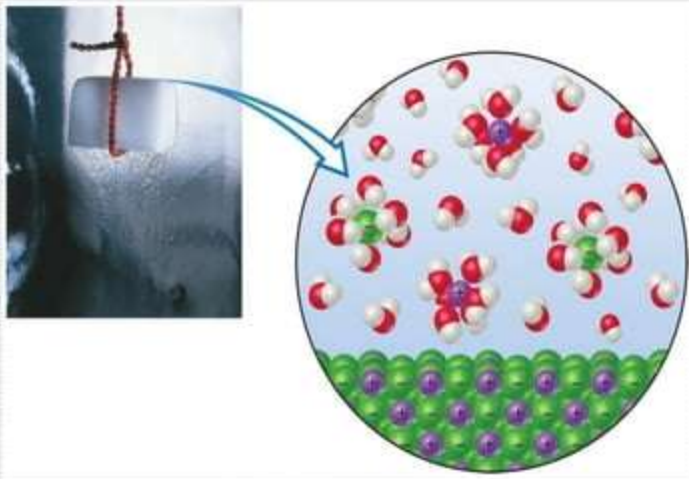
$\Delta S_{total} = 0$  (equilibrium) Reversible (ideal):

$\Delta S_{total} < 0$  non spontaneous

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# SECOND LAW OF THERMODYNAMICS

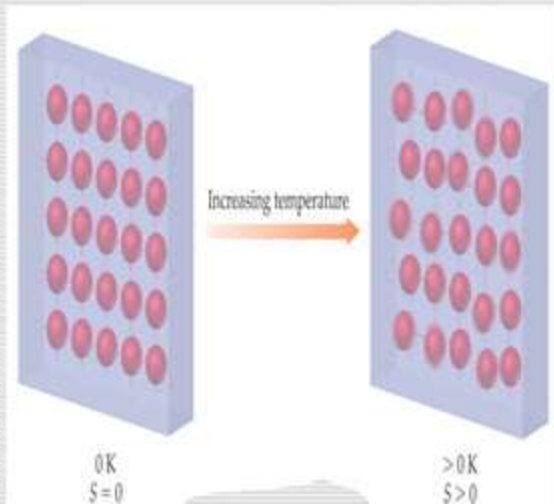
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# THIRD LAW OF THERMODYNAMICS

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- Nernst(1906)
- The entropy of a pure crystalline substance at absolute zero is 0.



## DIFFERENCE B/N 1<sup>st</sup> and 2<sup>nd</sup> law

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- ❑ 1<sup>st</sup> law is concerned with the accounting of the various kinds of energy involved in a given process.
- ❑ 2<sup>nd</sup> law is concerned with the availability of the energy of a given system for doing useful work.
- ❑ Combining the 1<sup>st</sup> and 2<sup>nd</sup> law of thermodynamics (Gibb's in 1878)

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

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## FREE ENERGY OR GIBB'S FREE ENERGY(G)

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- In 1878 J.V. Gibb's created the free energy function by combining the 1<sup>st</sup> and 2<sup>nd</sup> law of thermodynamics.

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

- Free energy change ( $\Delta G$ )

$G_1, H_1$  and  $S_1$

$G_2, H_2$  and  $S_2$

- A/C to Gibb's

$G_1, H_1$  and  $S_1$  .....(a)

$G_2, H_2$  and  $S_2$  .....(b) where T is constant.

- Eq. (b)- Eq. (a),

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

# FREE ENERGY CHANGES AND SPONTANEITY OF A PROCESS

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- For spontaneous process-

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

or 
$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + (-q/T)_{\text{system}}$$
  
( $q_{\text{p, surroundings}} = -q_{\text{p, system}}$ )

or 
$$\Delta S_{\text{total}} = \Delta S - \Delta H/T \quad (q_{\text{p}} = \Delta H)$$

- Multiply of  $-T$  on both side,

$$-T\Delta S_{\text{total}} = -T\Delta S + \Delta H$$

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

- For Gibb's Free energy,

$$\Delta G = \Delta H - T(\Delta S) \quad (\text{For spontaneous process-})$$

## Predicting Sign of $\Delta G$ in Relation to Enthalpy and Entropy

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$\Delta H$	$\Delta S$	$\Delta G$
-	+	Always negative (spontaneous)
+	-	Always positive (nonspontaneous)
-	-	Neg. (spontaneous) at low temp Pos. (nonspontaneous) at high temp.
+	+	Pos. (nonspontaneous) at low temp Neg. (spontaneous) at high temp.

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# CONCLUSION

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- ☐ The direction of a reaction whether from left to right or vice versa.
  - ☐ The accomplishment of work whether useful or not.
  - ☐ Whether the energy for driving a reaction must be delivered from an external source.
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# REFERENCE

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- ☐ A text book from:-
  - ☐ - Fundamental of biochemistry- Dr. A C Deb.
  - ☐ - Fundamental of biochemistry (Multicolored Edition) by J.L. Jain.
  - ☐ Principle of biochemistry by Nelson, Cox and Lehninger.
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*THANKYOU*

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