LECTURE №2

Basic concepts and laws of chemical thermodynamics

07.02.2017

Chemical thermodynamics is a science of transformations of energy: *heat into other forms of energy, amount of heat gained or released from a system, a spontaneity of a reaction, Gibbs free energy function, relationship between Gibbs Free Energy and chemical equilibrium.*

The object of the study is - *thermodynamic system* – the physical body (matter) or a group of bodies (the set of substances) that are in interaction, mentally or really isolated from the environment (surroundings)
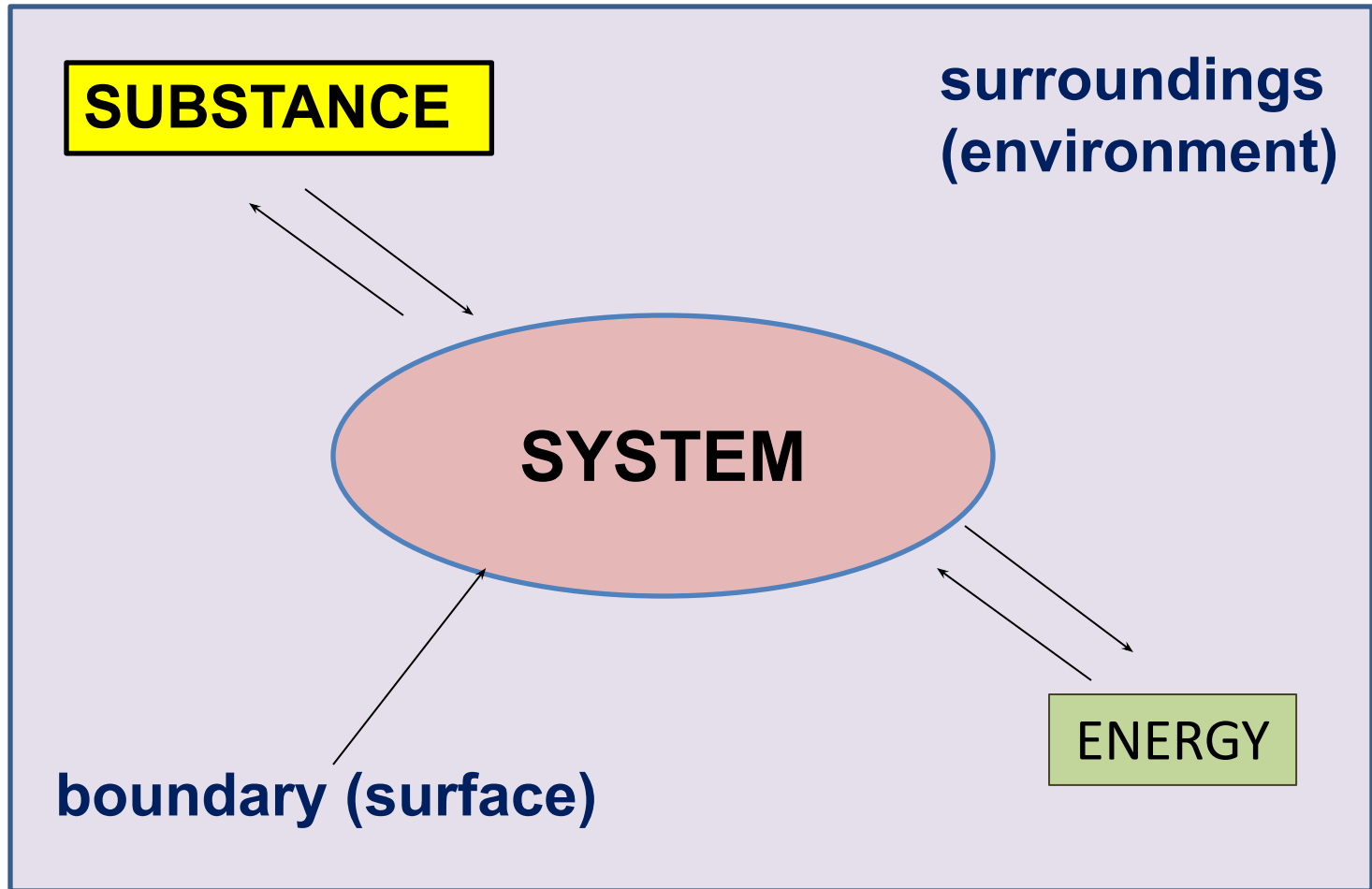
SYSTEM AND ITS SURROUNDINGS:

A system in thermodynamics refers to that part of universe in which observations or study are made and remaining universe constitutes the surroundings.

The surroundings include everything other than the system.

System and the surroundings together constitute the universe:
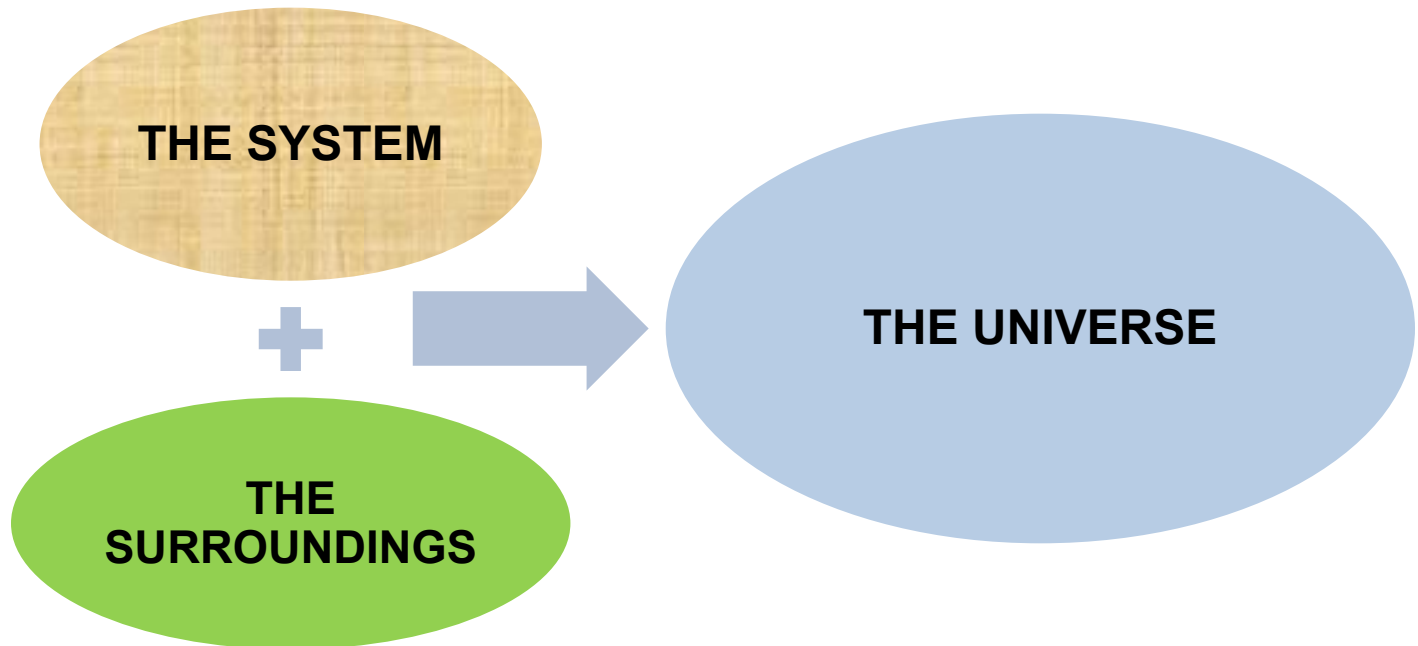
PHYSICAL STATES OF THE SYSTEM

HOMOGENEOUS SYSTEM

HETEROGENEOUS SYSTEM

Is a system without surfaces separating the different properties of the system (phase)

**Is a system, within which there is a surface separating the different properties of the system**

*   **PHASE** *is a set of homogeneous parts of a heterogeneous system, with identical physical and chemical properties, and separated from other parts through visible surfaces*

surroundings | surroundings | surroundings

energy | energy

system | system | system

matter

OPEN | CLOSED | ISOLATED
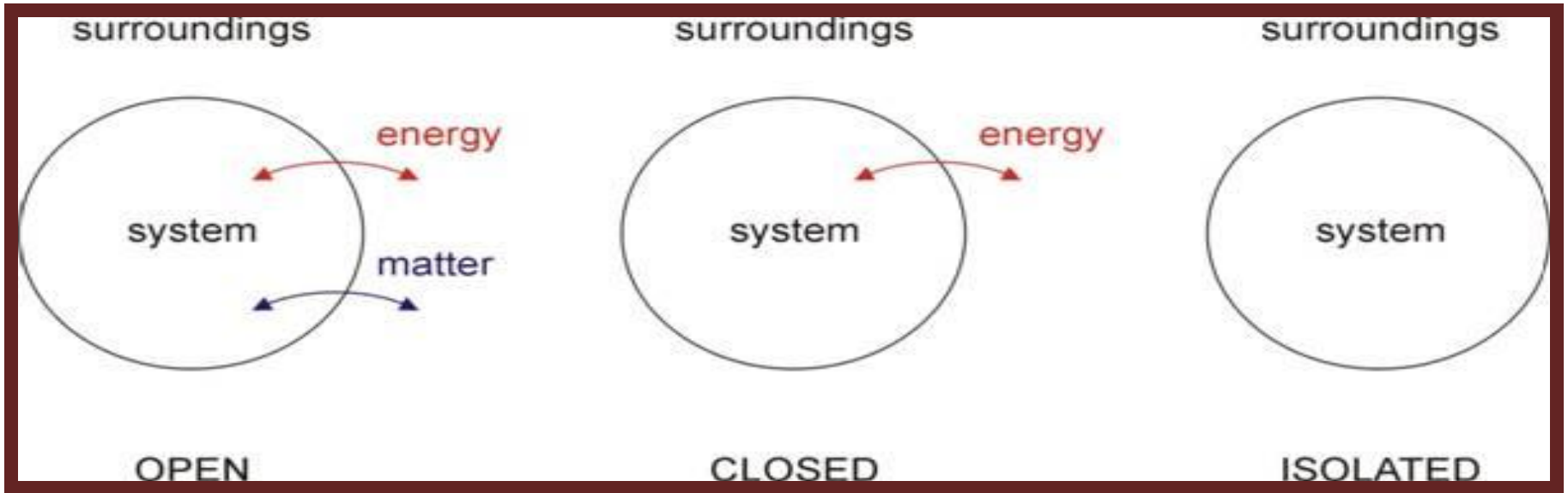
water in an open beaker is an open system as it can exchange both energy and matter with the surrounding
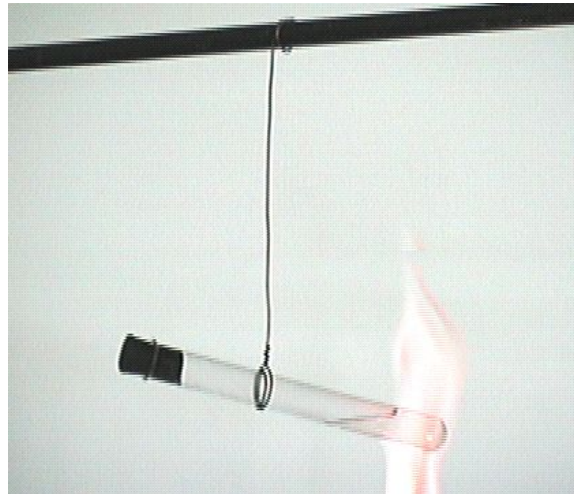
Hot water in contact with its vapour in a closed container
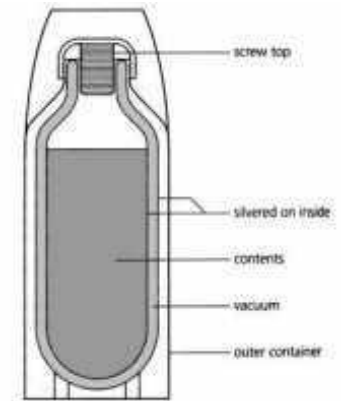
Water in contact with its vapour in a closed insulated vessel is an isolated system

By the nature of the interaction with the surroundings **thermodynamic systems are divided into 3 types:**

- **Open**: Mass and Energy can transfer between the System and the Surroundings

- **Closed**: Energy can transfer between the System and the Surroundings, but not Mass

- **Isolated**: Neither Mass nor Energy can transfer between the System and the Surroundings

The set of all physical and chemical properties of the system describes its **thermodynamic state**. <u>State of the system is described by thermodynamic parameters and functions</u>.

All quantities characterizing any macroscopic property of the system is called state parameters.

STATE PARAMETERS

The **extensive property** <u>is proportional to the system size</u> and the amount of material in the system: m, V, n, E, S,G

An **intensive property** <u>does not depend on the system size</u> or the amount of material in the system: C, P, T, ρ

INTENSIVE PROPERTIES →

- Chemical potential
- Concentration
- Density (or specific gravity)
- Ductility
- Elasticity
- Hardness
- Melting point and boiling point
- Pressure
- Specific energy
- Specific heat capacity
- Specific volume
- Spectral absorption maxima (in solution)
- Temperature
- Viscosity

EXTENSIVE PROPERTY

- Energy
- Entropy
- Gibbs energy
- Length
- Mass
- particle number
- number of moles
- Volume
- electrical charge
- Weight

Any change of parameter in the system called the thermodynamic process.

Major Types of Thermodynamic Processes:

- **Adiabatic process** - a process with no heat transfer into or out of the system.

- **Isochoric process** - a process with no change in volume, in which case the system does no work.

- **Isobaric process** - a process with no change in pressure.

- **Isothermal process** - a process with no change in temperature.

THERMODYNAMIC PROCESS

ISOTHERMAL
(T=const)

ISOBARIC
(P=const)

ISOCHORIC
(V=const)

ADIABATIC PROCESS
(Q = 0)
No heat exchange between
the system and
the surroundings

*Processes in which the system
returns to its original state
after a series of successive
transformations, called*
cyclic process
or thermodynamic cycle

Define Reversible and Irreversible Process

There are two main types of thermodynamic processes: *reversible process and the irreversible process.*

- Processes in which both the system and its surroundings can be simultaneously returned to their initial states after the process has been completed are called a **reversible process**.

- Processes in which the system and its surroundings cannot be simultaneously returned to their initial states after the process has been completed are called a **irreversible**.

The main processes in chemical thermodynamics are:
- **isobaric-isothermal (P, T = const)**
- **isochoric-isothermal (V, T = const)**

All chemical reactions take place under these conditions.

***Main objective** of thermodynamics is to be able to determine if a reaction will occur when reactants are brought together under certain conditions*.

Non-spontaneous Reaction – a reaction does not occur under specific conditions.

Spontaneous Reaction – a reaction does occur under specific conditions:
- A waterfall runs downhill
- A lump of sugar dissolves in a cup of coffee
- At 1 atm, water freezes below 0ºC and ice melts above 0ºC
- Heat flows from a hotter object to a colder object
- Iron exposed to oxygen and water forms rust

Derivative quantities, dependent on the parameters of the system state and immeasurable by direct methods are called thermodynamic functions:

THERMODYNAMIC FUNCTIONS

PROCESS FUNCTIONS:
Q – HEAT,
A – WORK

STATE FUNCTIONS:
U – Internal energy,
H – Enthalpy,
S – Entropy,
G – Gibbs free energy,

Function of the state is the total energy of the system: **E = K + P + U**

In thermodynamics, **state function is a property of a system that depends only on the current state of the system, not on the way in which the system acquired that state**. A state function describes the equilibrium state of a system.

In contrast, **process quantities** – **mechanical work and heat are not properties of the system, they characterize the process of energy exchange between the system and the surroundings, therefore they depend on the path (specific transition) of the process**.

In thermodynamics, the **internal energy (U)** **of a thermodynamic system is the total kinetic energy due to the motion of molecules (translational, rotational, vibrational) and the potential energy associated with the vibrational and electric energy of atoms within molecules and crystals.** It includes the energy in all the chemical bonds, and the energy of the free, conduction electrons in metals.

U is a state function of a system, and is a extensive quantity. The SI unit [U]=Joule.

THE 1ˢᵗ LAW OF THERMODYNAMICS

The U is essentially defined by the 1ˢᵗ **law of thermodynamics** which states that energy is conserved «*The increase in internal energy of a closed system is equal to the difference of the heat supplied to the system and the work done by it*»:

$$\Delta U = Q - A$$

where:

- **ΔU** is the change in internal energy of a system during a process;
- **Q** is heat "added to" a system (measured in joules in SI);
- **A** is the mechanical work "done on" a system (measured in joules in SI)

Thus heat Q is given the system and consumed to increase the internal energy ΔU and to perform work against external forces A:

$$Q = \Delta U + A$$

For isobar-isothermal process: p, T = const

$$\Delta U = U^2_{final} - U^1_{initial}$$

$$A_{gas} = p \cdot \Delta V \quad => \quad \Delta V = V^2_{final} - V^1_{initial}$$

$$Q = \Delta U + A \quad => \quad Q = (U^2 - U^1) + (pV^2 - pV^1)$$

$$Q = (U^2 + pV^2) - (U^1 + pV^1) \quad => \quad Q = -\Delta H$$

$$U + pV = H - Enthalpy\ function$$

The molar heat of formation of a compound (ΔH_f) is equal to its enthalpy change (ΔH) when one mole of compound is formed at 25°C and 1 atm from elements in their stable form.

Compound	ΔH_f (kJ/mol)
$H_2O(l)$	-285.8
$H_2O(g)$	-241.8
$H_2O(s)$	-291.85

Experiment on determining heat (Q) of reaction for
$MgSO_{4(s)}$ + $7H_2O$ → $MgSO_4.7H_2O$

oxygen supply
thermometer
stirrer
ignition wires
magnifying eyepiece
insulating jacket
water
air space
bucket
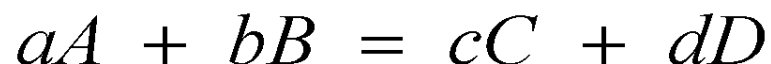heater
ignition coil
steel bomb
sample
crucible
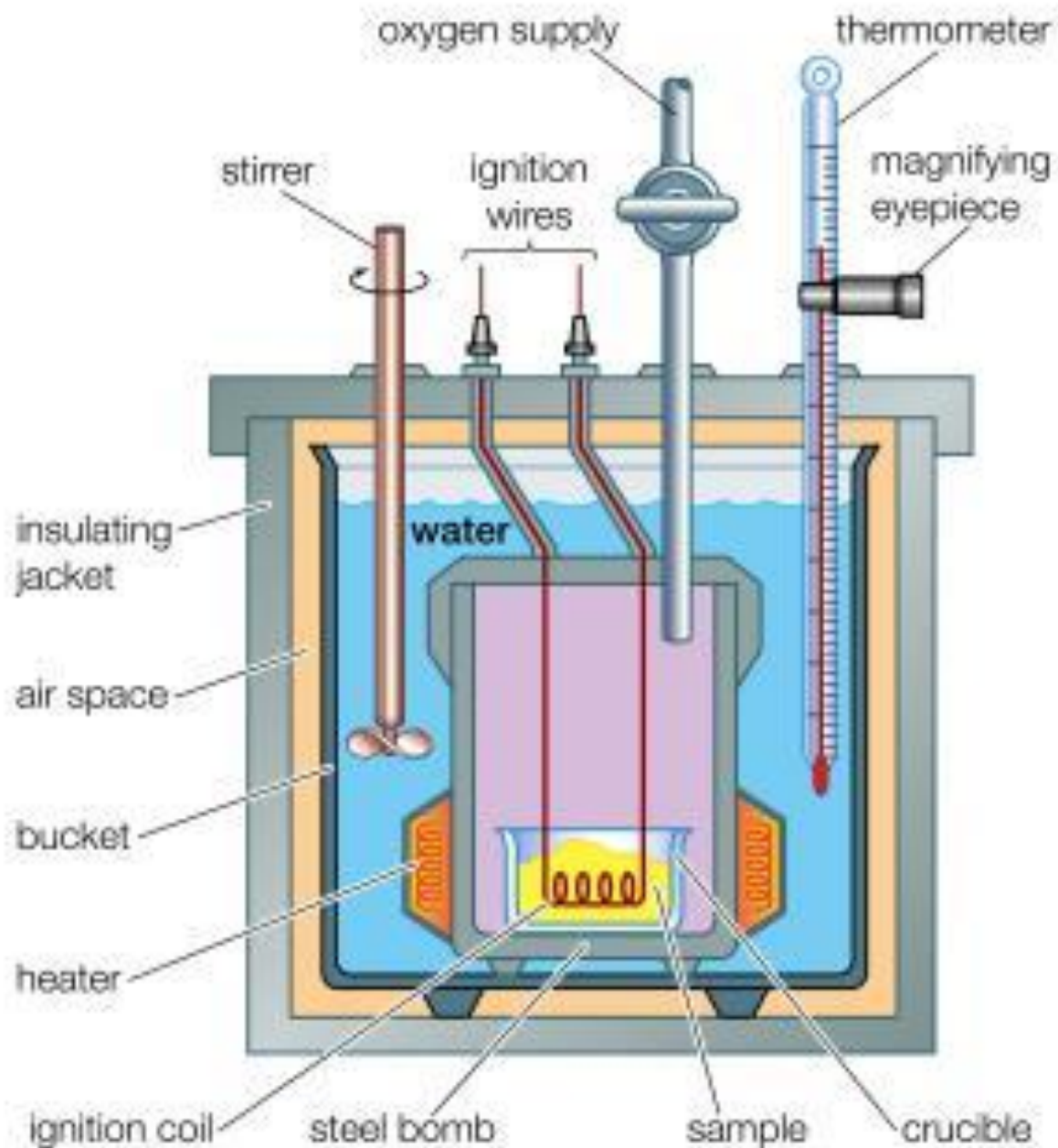
A calorimeter is a device used to measure the quantity of heat flow in a chemical reaction. Two of the most common types of calorimeters are the **coffee cup calorimeter** and the **bomb calorimeter**.

HESS'S LAW

- *overall heat change of a chemical reaction is independent of its pathway,*
- *energy change in changing A + B → C + D is the same regardless of the route (independent of route) by which the chemical changes occurs.*

$$\Delta H_{chem\ reaction} = \Sigma \Delta H^{\boxtimes}_{products} - \Sigma \Delta H^{\boxtimes}_{reac\tan ts}$$

$$aA\ +\ bB\ =\ cC\ +\ dD$$

$$\Delta H^{\boxtimes}_{A}\quad \Delta H^{\boxtimes}_{B}\quad \Delta H^{\boxtimes}_{C}\quad \Delta H^{\boxtimes}_{D}$$

$$\Delta H_{chem\ rxn} = (\Delta H^{\boxtimes}_{D} \cdot d + \Delta H^{\boxtimes}_{C} \cdot c) - (\Delta H^{\boxtimes}_{B} \cdot b + \Delta H^{\boxtimes}_{A} \cdot a)$$

Hess's Law – used to calculate ΔH for reaction which cannot be determined experimentally

Hess's Law

Hess's Law can be used to determine the heat of reaction for any reaction if you know the heats of formation (ΔH_f^0) for each of the reactants and products.

For the general reaction:

$$aA + bB \longrightarrow cC + dD$$

The heat of reaction (ΔH_{rxn}) for this reaction is calculated as follows:

$$\Delta H_{rxn} = c(\Delta H_{f,C}^0) + d(\Delta H_{f,D}^0) - a(\Delta H_{f,A}^0) - b(\Delta H_{f,B}^0)$$

$$Q = -\Delta H$$

If the reaction is generated heat (**Q>0**), enthalpy of the system is lowered (**ΔH<0**), in this case the reaction is called *exothermic*.

If the reaction is absorbed heat (**Q<0**), the system increases the enthalpy (**ΔH>0**), and it called the *endothermic* reaction.

(a) Enthalpy change during an Exothermic reaction

(b) Enthalpy change during Endothermic reaction
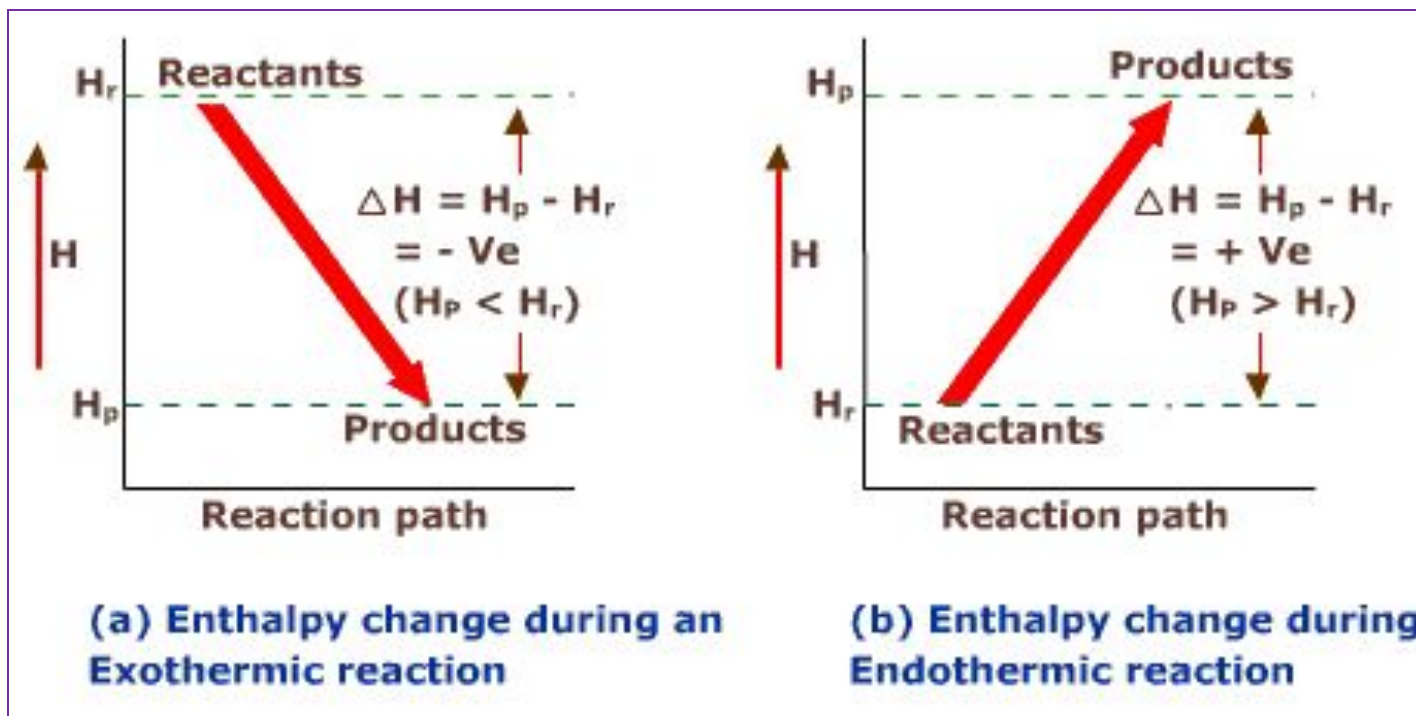
Enthalpy of reaction using combustion data
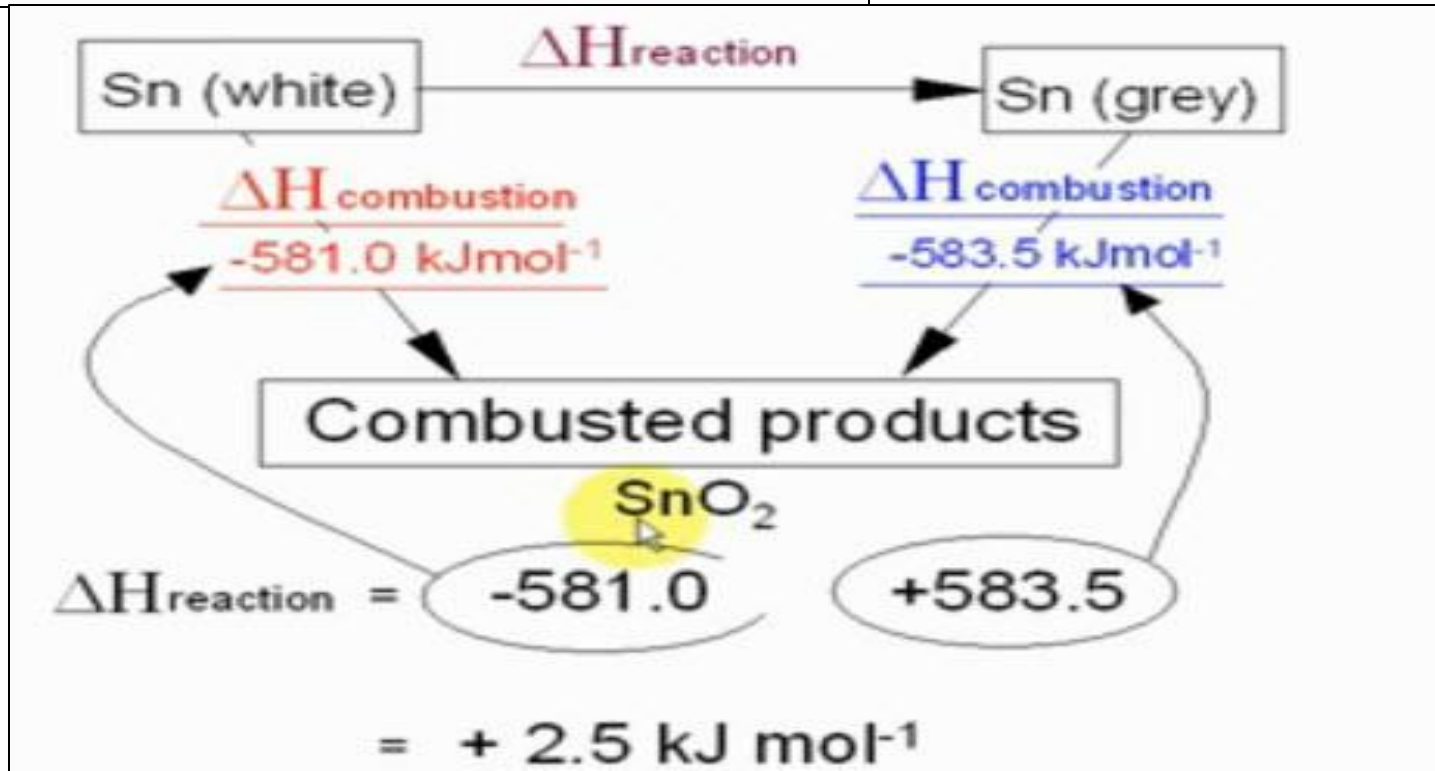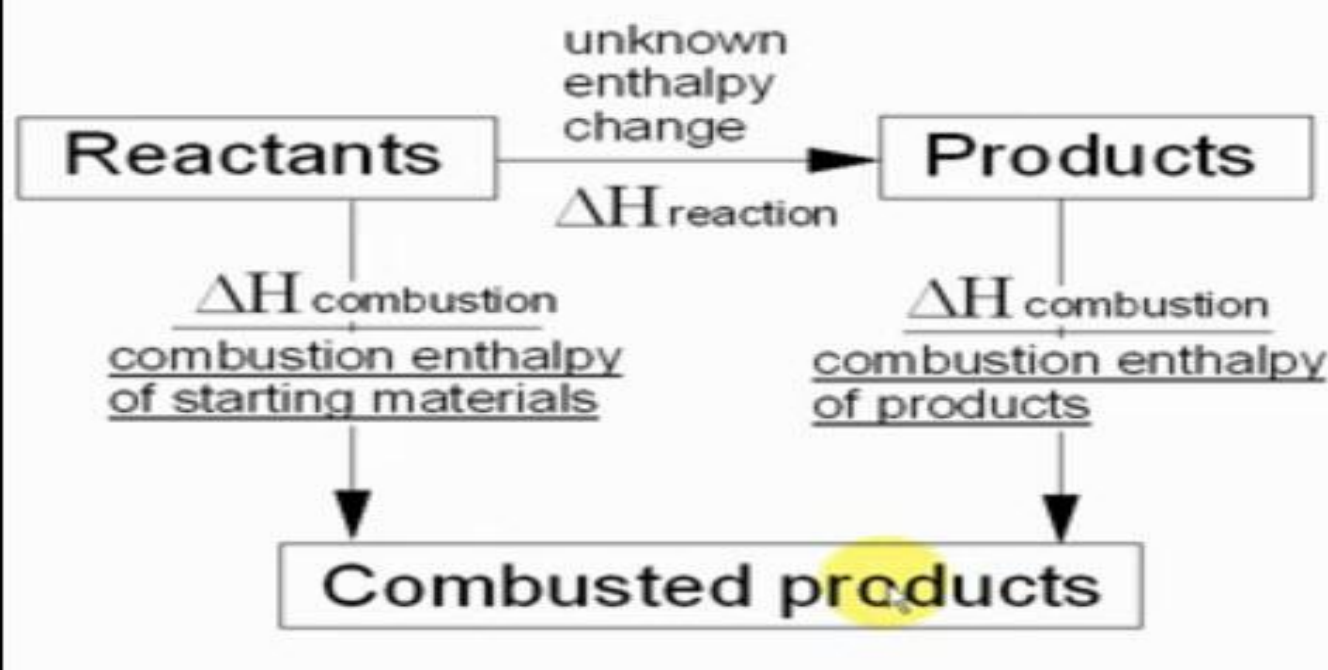
THE 2ⁿᵈ LAW OF THERMODYNAMICS

All spontaneous processes are irreversible (e.g. heat flows from hot to cold <u>spontaneously</u> and <u>irreversibly</u>)

To predict spontaneity we need:
- *Change in enthalpy.*
- *Entropy –* a measure of the randomness or disorder of a system: ↑ disorder = ↑ entropy

Entropy

1. **Entropy** is a thermodynamic property that measures the degree of randomization or disorder at the **microscopic level**. The natural state of affairs is for **entropy to be produced** by all processes.

2. A **macroscopic** feature which is associated with entropy production is a loss of ability to do useful work. Energy is degraded to a less useful form, and it is sometimes said that there is a decrease in the **availability** of energy.

3. Entropy is an extensive thermodynamic property. In other words, the entropy of a complex system is the sum of the entropies of its parts.

4. The notion that **entropy can be produced, but never destroyed**, is the **second law of thermodynamics**.

Standard Entropy

The **standard entropy of reaction** (ΔS^0) is the entropy change for a reaction carried out at 1 atm and $25^0 C$:

Standard Entropy Values (S°) for Some Substances at 25°C	
Substance	S° (J/K · mol)
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.6
C(diamond)	2.4
C(graphite)	5.69
CH_4 (methane)	186.2
C_2H_6 (ethane)	229.5
He(g)	126.1
Ne(g)	146.2

$$\Delta S_{chem\ reaction} = \Sigma S^0_{products} - \Sigma S^0_{reac\tan ts}$$

The Second Law of Thermodynamics

- *The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. (**Clausius**)*

- *"It is impossible in any way to diminish the entropy of a system of bodies without there by leaving behind changes in other bodies" (**Planck**)*

- *"In any irreversible process the total entropy of all bodies concerned is increased." (**Lewis**)*

Spontaneous process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$
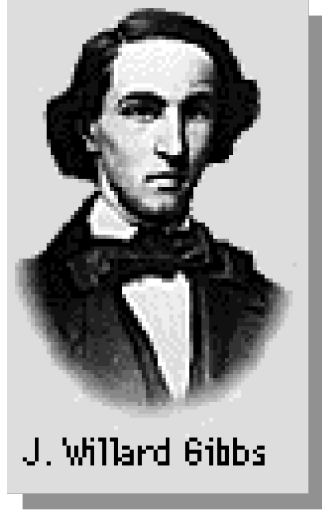
Equilibrium process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

The 3rd Law of Thermodynamics and Absolute Entropy

- **The entropy of a perfect crystalline substance is zero at the absolute zero of temperature**

Absolute zero is −273.15 °C (degrees Celsius), or −459.67 °F (degrees Fahrenheit) or 0 K (kelvin).

G – Gibbs Free Energy

- Predicts the direction of a spontaneous reaction.

- Uses properties of the system to calculate.

- For a constant pressure-temperature process: $\Delta G_T = \Delta H_{sys} - T\Delta S_{sys}$

$\Delta G < 0$ The reaction is spontaneous in the forward direction.

$\Delta G > 0$ The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$\Delta G = 0$ The reaction is at equilibrium.

J. Willard Gibbs

Standard Free-Energy Changes

The **standard free-energy of reaction (ΔG°_reac)** is the free-energy change for a reaction when it occurs under standard-state conditions.

Standard free energy of formation (**ΔG°**) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

$$\Delta G_{chem\ reaction} = \Sigma \Delta G^{\boxtimes}_{products} - \Sigma \Delta G^{\boxtimes}_{reac\tan ts}$$

Factors Affecting ΔG

TABLE 18.3

Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	ΔG	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$
+	−	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3O_2(g) \longrightarrow 2O_3(g)$
−	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

Thermodynamic Equilibrium

A system is said to be at thermodynamic equilibrium when all of its macroscopic properties are time-independent and remain so when the system is isolated from its surroundings.

Thermodynamic equilibrium, in simple words is, same temperature. At same temperature bodies do exchange heat but do not gain or lose heat.

The system is said to be in thermodynamic equilibrium if the conditions for following three equilibrium is satisfied:

1) Mechanical equilibrium
2) Chemical equilibrium
3) Thermal equilibrium

0^{eth} Law of Thermodynamics:

Two systems in thermal equilibrium with a third system are in thermal equilibrium to each other.
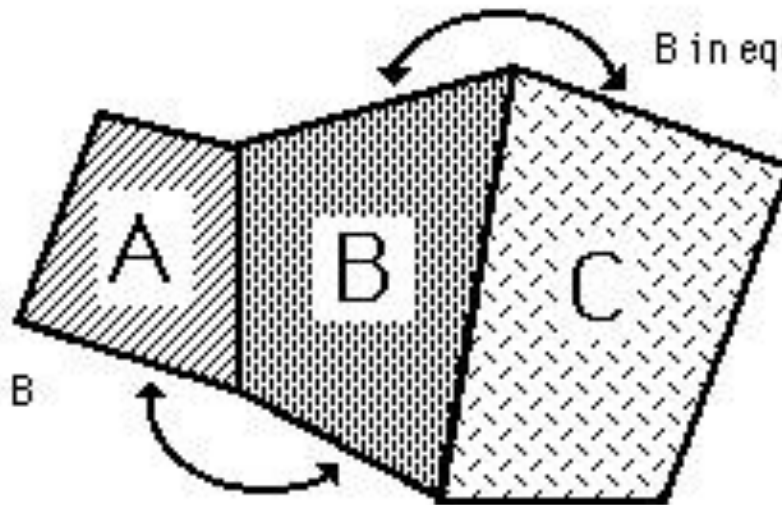
A in equilibrium with B

B in equilibrium with C

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

Free Energy and Chemical Equilibrium

$$\Delta G = \Delta G^0 + RT \ln q$$

R is the gas constant (8.314 J/K•mol)
T is the absolute temperature (K)
q is the reaction quotient
K is the equilibrium constant of reaction

At Equilibrium: $\Delta G = 0$ => q = K

$$0 = \Delta G^0 + RT \ln K$$

$$\Delta G^0 = -RT \ln K$$

Free Energy and Chemical Equilibrium

TABLE 18.4

Relation Between $\Delta G°$ and K as Predicted by the Equation $\Delta G° = -RT \ln K$

K	$\ln K$	$\Delta G°$	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

QUIZ ME

1   A pressure cooker reduces cooking time for food because …

○ heat is more evenly distributed in the cooking space

○ boiling point of water involved in cooking is increased

○ the higher pressure inside the cooker crushed the food materia

○ cooking involves chemical changes helped by a rise in temperature

NEXT

QUIZ ME

2 Which one is not a state function?

◯ **Internal energy (E)**

◯ **Enthalpy**

◯ **Heat (q)**

◯ **Volume**

NEXT

QUIZ ME

3   When no heat energy is allowed to enter or leave the system, it is called:

◯ **Irreversible process**

◯ **Reversible process**

◯ **Adiabatic process**

◯ **Isothermal process**

QUIZ ME

4   A well stoppered thermos flask contains some ice cubes. This is an example of a …

- ⭕ **Isolated system**

- ⭕ **Closed system**

- ⭕ **Open system**

- ⭕ **Non-thermodynamics system**

GLOSSARY OF LECTURE

1. Thermodynamics: Energy differences and transfers between systems.

2. Systems:

- **Isolated system:** "have walls or boundaries that are rigid, do not permit transfer of mechanical energy, perfectly insulating, and impermeable. The have a constant energy and mass content.
- **Adiabatic systems:** Perfectly insulated systems.
- **Closed systems:** have walls that allow transfer of energy in or out of the system but are impervious to matter. They contain a fixed mass and composition, but variable energy.
- **Open Systems:** have walls that allow transfer of both energy and matter to and from the system.

3. Equilibrium: "A system at equilibrium has none of its properties changing with time". A system at equilibrium will return to that state after being disturbed.

4. State Variables: Variables that define the state of a system.

- *Extensive variables are proportional* to the quantity of matter being considered (V, total Cp).
- *Intensive variables are* independent of quantity (concentration, viscosity, density, molar Cp)

5. **Work (*w*):** *"The transfer of energy from one mechanical system to another. It is* always completely convertible to the lifting of a weight". "The energy that flows across a system boundary in response to a force moving through a distance (such as happens when a system changes volume".

6. **Heat (*q*):**
- *"The transfer of energy that results from temperature differences".*
- *"The* energy that flow across a system boundary in response to a temperature gradient."
- "That part of any energy transfer that is not accounted for by mechanical work (FxD)."
- $q=\Delta U - w$

7. **Heat Capacity:** The relation between heat transferred to a body and the change in T.

8. **Enthalpy:** The increase in enthalpy of a system is equal to the heat absorbed at constant pressure, assuming the system does only PV work.

9. **Entropy:** A measure of the loss of capacity of the system to do work.

10. **Gibbs free energy** is a measure of the potential for reversible or maximum work that may be done by a system at constant temperature and pressure. It is a thermodynamic property that was defined in 1876 by Josiah Willard Gibbs to predict whether a process will occur spontaneously at constant temperature and pressure.

11. ZEROTH LAW: "Two bodies in thermal equilibrium with a third are in thermal equilibrium with each other" (Basis of the concept of temperature)

12. FIRST LAW: "The alegraic sum of all energy changes in an isolated system is zero" (Conservation of energy). Energy can be converted from one form to another but cannot be created or destroyed. $\Delta U = q + w$. *This is based only on observation*

13. SECOND LAW: "Spontaneous changes are those which, if carried out under the proper conditions, can be made to do work. If carried out reversibly they yield a maximum amount of work. In natural processes, maximum work is never obtained.

14. THIRD LAW:

- First expressed as Nernst's Heat Theorem: **"Nernst (1905): As T $\rightarrow$ 0 K , ΔS $\rightarrow$ 0 for all isothermal processes in condensed phases"**
- More general and useful formulation by M. Planck: **"Planck (1911): As T $\rightarrow$ 0 K , S $\rightarrow$ 0 for every chemically homogeneous substance in a perfect crystalline state "**
- This leads to the following interesting corollary: **"It is impossible to decrease the temperature of any system to T = 0 K in a finite number of steps "**