Thermodynamics

Is a branch of science that deals with heat, work, and temperature, and their **relation to energy, entropy**

- It tells us about the initial & final states of the system, it does not talk about the rate of chemical reaction
- It is applied to the **macroscopic systems**

The difference between thermodynamics and kinetics

- Thermodynamics is the science that describes the overall properties, behavior, composition of a system. and equilibrium
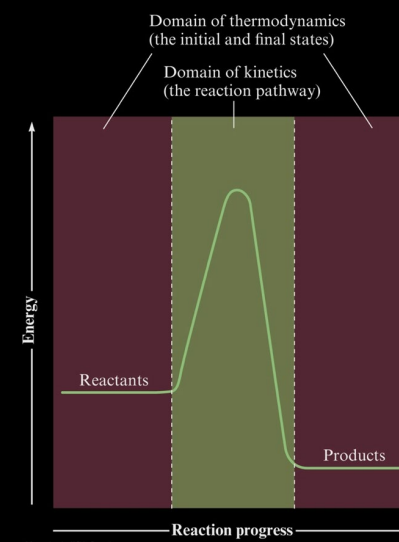
- Kinetics is the determine the chemical reaction, the science that study rates and describe the conditions which can change the reaction rates

Thermodynamics

Thermodynamics: is the science that deals with the transfer of energy from one system to another, and from one form to another

Thermochemistry

Thermochemistry: is the science that deals with the heat changes during the chemical reactions and the physical changes

In a chemical reaction

Domain of thermodynamics
(the initial and final states)

Domain of kinetics
(the reaction pathway)

Energy

Reactants

Products

Reaction progress

© Cengage Learning. All Rights Reserved.

Domain of kinetics -> the rate of a reaction itself
Domain of thermodynamics -> whether the reaction is spontaneous or not

System
Is the part we are studying in the universe, and it has three types

Open system	**Closed System**	**Isolated system**
A system whose boundaries allow the transfer of energy / matter	A system whose boundaries do not allow the transfer of matter, but allows the transfer of energy.	A system whose boundaries do not allow the transfer of energy / matter

The chemical reaction as a system

Is divided to

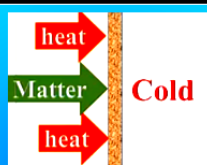| The system	The system boundary	The surrounding
Expresses	Expresses	Expresses
The reactants and products (The reaction medium)	The wall of container (a flask or a test tube) at which the reaction occurs	The medium surrounding the reaction container (The laboratory)

heat
Matter → Cold
heat

Matter → Cold
heat
heat

1-The adiabatic boundary it is the boundary that doesn't allow the heat transfer between system and surrounding, and do not allow the transfer of matter across it.
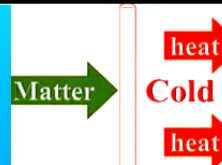
2-The diathermic boundary it is the boundary that allows heat transfer between system and surrounding, but do not allow the transfer of matter across it.

Internal Energy (U or E)
The total energy contained in a thermodynamic system

It includes **kinetic** and **potential** energy
It represents
- Chemical nature of a substance
- Pressure
- Volume
- Change in state of matter
    - For example
    - The change in internal energy when heating one mole of water from **1C to 100C** is **1.8 Kcal**

$$\Delta U = U_F - U_i$$

The SI Unit of internal energy is **joules** but we can also express it as **calories** where

$1 \text{ cal} = 4.184 \text{ j}$

Heat (H)
Is the energy transferred because of a temperature difference between two systems
$$Q = C \times \Delta T$$

WHERE
- The amount of heat transferred (Q)
    - When the system absorbs heat, then Q is positive
    - When the system gives out heat, then Q is negative
- The change in temperature (ΔT)
- The heat capacity (C)
    - It is the quantity of heat required to raise the temperature of the body by $1C^o$
    - 1 cal is the amount of heat required to raise the temperature of 1 gram of water from 1C to 15C

Work (W)
It is the displacement of the system against some force originating from the sorroundings

When work is
- Done by system -> its energy decreases
- Done on system -> its energy increases

Pressure/volume work
Is the work generated by the compression/expansion of a system
in liquids and solids, this type of work has a small effect
But in gasses, the change in volume is substansial
so, the work done by gas in the system is equal to the change in volume against pressure
$$W = P \times \Delta V$$

WHERE
- W -> pressure volume work
- P -> pressure
- ΔV -> change in volume

Work & Heat are **pathway-dependent** reactions, meaning that not just the beginning and end states of a reaction are important, but the effects along the journey aswell

Change in type of energy are **pathway-independent** reactions, meaning that the initial and final states are the only two important things

work	Heat
Work is defined as a force causing the movement of an object. IT IS THE ENERGY TRANSFERRED TO THE MOTION OF **OBJECTS**	The degree of the hotness or the coldness of a body or environment . IT IS THE ENERGY TRANSFERRED TO THE MOTION OF **ATOMS AND MOLECULES**
W = + When energy done by the system expansion	Q = - In exothermic
W = - When the work done on the system compression	Q = + In endothermic
Its symbol is capital W	Its symbol is capital Q

TYPES OF WORK

EXPANSION WORK	NON-EXPANSION WORK
It's where the volume of a system changes like **pressure-volume work**	It's where work is done without changes to the volume, like **electrical work** where electrons move across

The First Law of Thermodynamics

The energy of the universe it is constant, it is just in various forms that are interchanged in physical and chemical reactions, and in different positions

For example when methane and oxygen react, their potential energy will be lost and converted into heat after the reaction

CH4 + 2O2   2H2O + CO2 + Heat
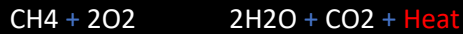
So the internal energy in a system might decreases, but in others it increase
as we said before, this is the result of when
a system **gets heat**, it **does work**
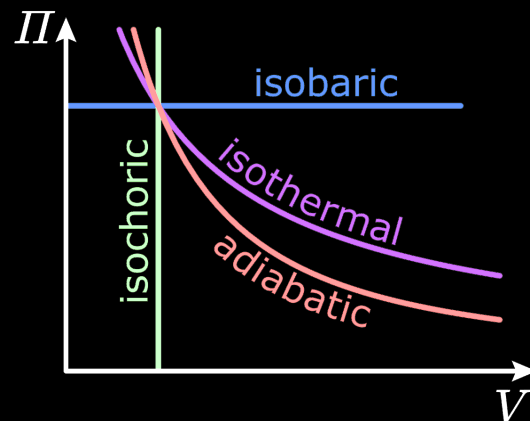
$$\Delta E = Q - W$$

Where
- Change of internal energy
- Amount of heat supplied to the system
- Amount of work done by the system

When the change is equal to 0, this means that the system uses all the energy supplied to it

- In **cyclic processes**
  - The values of the initial and final values are the same, so Q is equal to W
- **Isochoric process (a process where the volume is constat)**
  - The system is under **constant volume**, so pressure-volume work is 0, so the change in energy equals the change in temperature (Heat)
- **Adiabatic process (a process where no heat is applied)**
  - Because there is No change in temperature (heat) involved, the change in energy = -W
- **Isobaric process (a process where no change in pressure)**
  - Because pressure is constant, P in W = P x ΔV is constant, and the work in a PV diagram is just a rectangle , so the change in temperature can be expressed as Q − P x ΔV
- **Isothermal process**
  - When the temperature is constant, this leads to change in energy being 0
  - The work here can be calculated with this complex equation
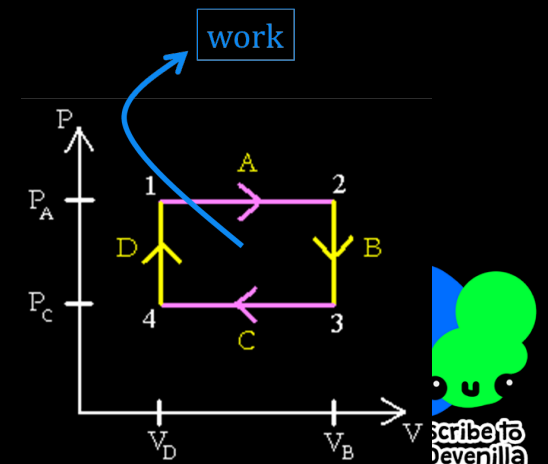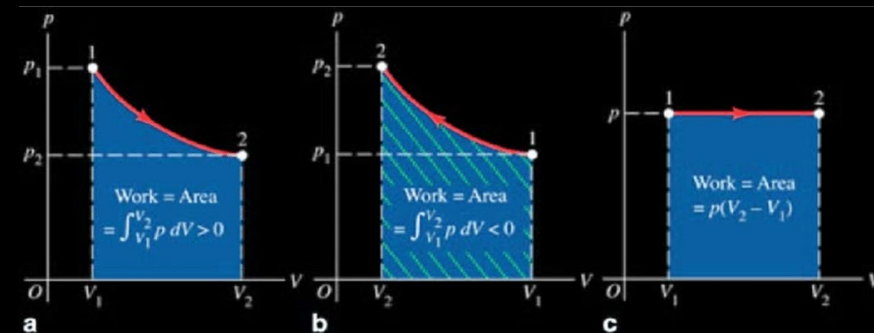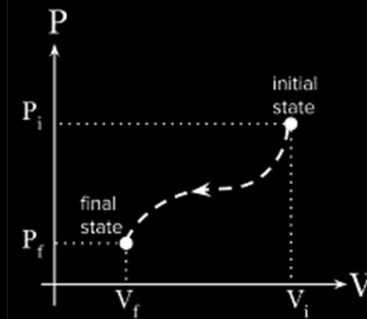 - $W = nRT \cdot ln(\frac{V_i}{V_f})$

Pressure Volume diagrams
It is used to calculate the amount of work
done by a gas during expansion
or compression

CYCLIC PROCESS
VERSUS
REVERSIBLE PROCESS

A cyclic process is a chemical process that comes back to the initial state after progression	A reversible process is a process that can be reversed in order to obtain the initial state of a system
Can be reversible or irreversible	Essentially reversible
Have an enclosed PV curve	Not an enclosed PV curve

In cyclic reactions, there is no internal energy chain because the change in temperature is countered by te change in work
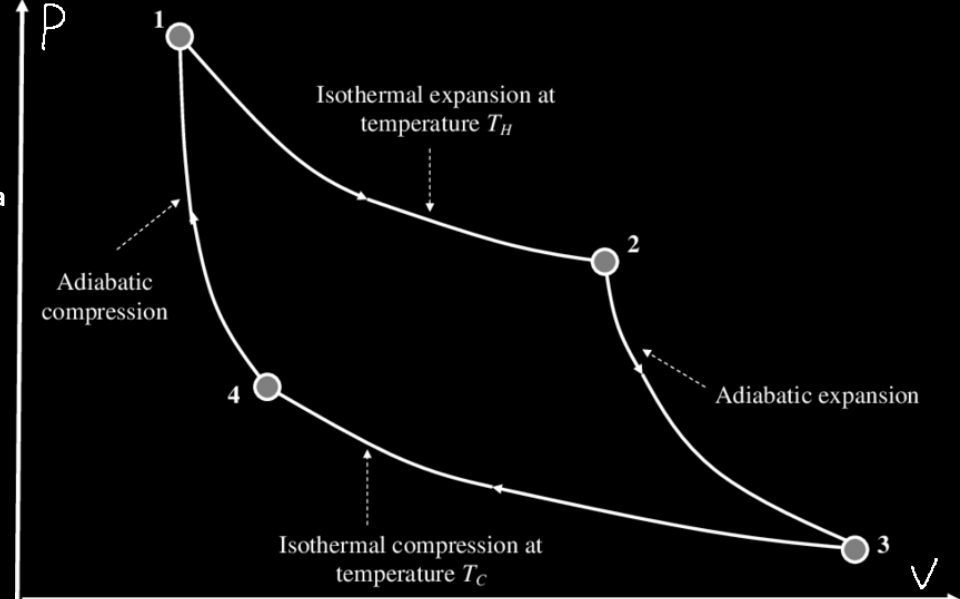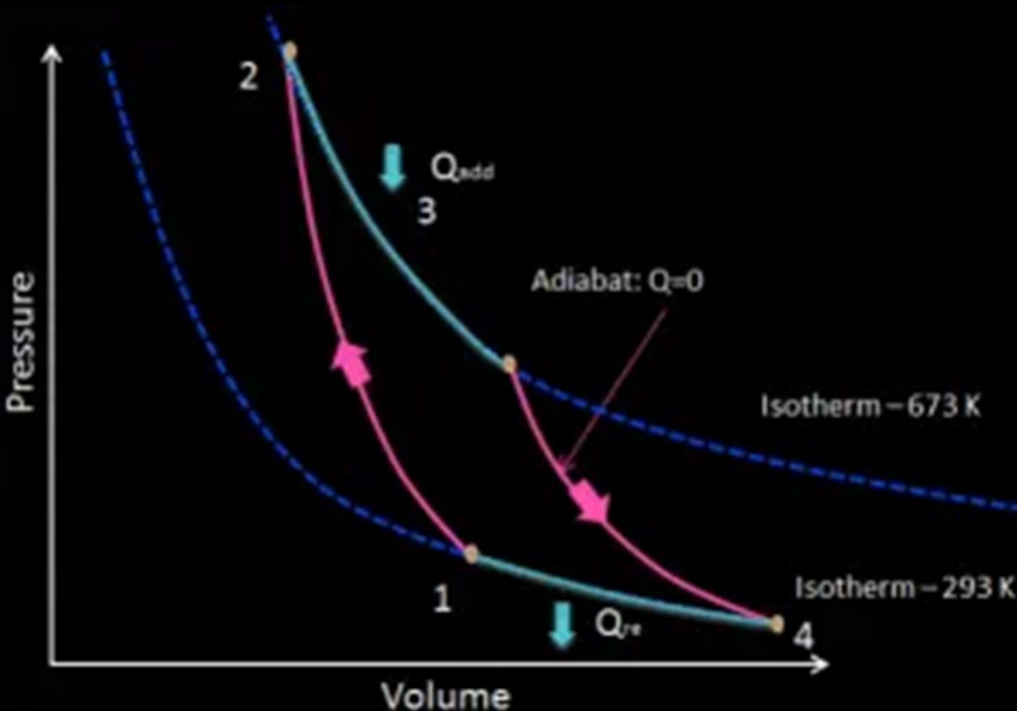
Famous (Carnot Cycle)
The idea reversible closed thermodynamic cycle proposed by French physicist
Sadi Carnot in 1824
It is like two isotherms switching
NOTE -> isotherms are guidelines that indicate the function of Pressure and volume at a certain temperature

Calculate the change in internal energy
(a) the system absorbs 300 J of heat and <u>perform</u>s 500 J of work.

$$\Delta E = 300 - 500 = -200 J$$

(b) the system absorbs 720 J of heat energy and the <u>surrounding performs</u> 300 J on the system

$$\Delta E = 720 + 300 = 1020 J$$

(c) 400 J of work and the system losses 225 J of heat energy.

$$-225 = H - 400 = 175 J$$

How much work is done to compress a <u>monoatomic</u> ideal gas at a pressure of $2.5 * 10^5$ pa from n initial volume of $0.015 m^3$ to a final volume of $0.010 m^3$ what is the change in internal energy of the system if the system releases $\underline{350}$ J in the process.
                                                                    H

$$W = P \times \Delta V = 2.5 \times 10^5 \times (0.010 - 0.015) = -1250 J$$

$$\Delta E = H - W = -350 - (-1250) = 900 J$$

Enthalpy changes

Is the heat change accompanying a chemical reaction at constant volume or pressure, it tells us how much heat was absorbed/evolved during a reaction and it is denoted as ΔH

$$\Delta H = E + PV$$

Where E is the internal energy
P is the pressure
V is the volume

When a system loses heat -> enthalpy is negative
when a system gains heat -> enthalpy is positive

ΔH = heat of products – heat of reactants

Hess's law of constant heat

It says that the heat absorbed or liberated in a given chemical equation, is always constant and is the same whether the process occurs in a single or multiple steps

$$\Delta H^o{}_{reaction} = \sum H_{f}^{o}{}_{products} - \sum H_{f}^{o}{}_{reactants}$$

Here
- AH^0 represents the standard enthalpy for the **overall reaction**
- $\sum n_\rho \Delta H_f^0$ (products) represents the sum of all standard enthalpies for every product
- $\sum n_\rho \Delta H_f^0$ (reactants) represents the sum of all standard enthalpies for every reactant

INTERNAL ENERGY IN CHEMICAL SUBSTANCES

It splits into
- Stored energy in the atom 'between nucleus and electrons"
- Stored energy in molecules "bonds between atoms"
- Stored energy between molecules "intermolecular forces"

The heat content exchange = heat content of the products – heat content of the reactants

Endothermic change	Exothermic change
• Absorbs heat from surroundings • Temperature decreases as reaction progresses • Requires input of energy to proceed	• Releases heat to surroundings • Temperature of **surroundings** increases as the reaction progresses • Does not need a continuous energy input

In chemical reactions, bonds are broken and rearranged
breaking them needs energy so it is an **endothermic change**
Forming bonds releases energy so it is an **exothermic change**

Spontaneous reaction	Nonspontaneous reaction
• A reaction that favors the formation of products at the given set of conditions • "thermodynamically favored" • Does not need outside intervention to happen • Example -> heat flows from hotter body	• A reaction that does not favor the formation of products • "thermodynamically unfavored" • Needs outside intervention to happen • Example -> boiling of water at 100c

Spontaneous reactions can be
- Endothermic -> like how the melting of ice H_2O (s) -> H_2O (l)
- Exothermic -> like how the combustion of methane $CH_4 + 2O_2$ $CO_2 + 2H_2O$ + Heat

Rust

The rusting of steel when exposed to humid air (spontaneous)
Iron oxide turning back into iron and oxygen (nonspontaneous)

Entropy (randomness)
Measures how much disorder there is in a system
the tendency of a system to take its most probable form

The driving force for a spontaneous reaction is an increase in entropy

Gas entropy > liquid entropy > solid entropy
Entropy increases when a substance is broken up into multiple parts and decreases if otherwise

Entropy increase as temperature increase because the particles kinetic energy increase and the particles disorder increase

low entropy means the energy is concentrate and The energy tends to spread out

THE SECOND LAW OF THERMODYNAMICS
The entropy of the universe is increasing, so the entropy change of the whole universe is **positive**
$$\Delta s_{universe} = \Delta s_{system} + \Delta s_{surrounding}$$

NOTE
According to the first law of thermodynamics, the **total energy** of the universe is constant, but according to the second law of thermodynamics the **entropy** of the universe is increasing

Case	Result
ΔS positive, ΔH negative	Spontaneous at all temperatures
ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at *any* temperature (reverse process is spontaneous at *all* temperatures)

The Gibbs free energy
a combination of $\Delta H, \Delta S, and\ T$ to determine if the change is spontaneous at given temperature "negative means spontaneous"
The maximum amount of non-expansion work that can be extracted from a closed system

The Gibbs free energy change
At constant pressure and temperature, the system free-energy change ΔG is the difference between the enthalpy change ΔH and the product of the **kelvin** temperature and the entropy change TΔS

$$\Delta G = \Delta H - T \Delta S \text{ (at constant T and P)}$$

Activation energy (Ea)
The minimum amount of extra energy needed by a reactant to convert to a product, its SI Unit is **Joules** or **Kilojoules/mole (kJ/mol)** or **Kilocalories/mole (Kcal/mol)**
It depends on two factors
- **Nature of reactants**
  - Ionic reactants give low activation energy
  - Covalent reactants give higher activation energy
- **Effect of Catalyst**
  - Positive catalysts give low activation energy
  - Negative catalysts give high activation energy

Catalyst

They are substances which alter the rate of reaction by changing the path of reaction, normally it is here to speed up reactions, but here they help break/rebuild chemical bonds

Features of a catalyst
- Doesn't initiate the reaction
- Isn't consumed in the reaction
- tend to react with reactants to form intermediates and at the same time facilitate the production of the final reaction product. After the whole process, a catalyst can regenerate.

Types of catalysts

Positive catalyst	Negative catalyst
They increase the rate of the reaction by lowering the activation energy barriers	They decrease the rate of the reaction by increasing the activation energy barriers

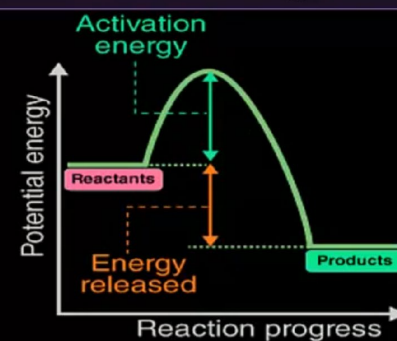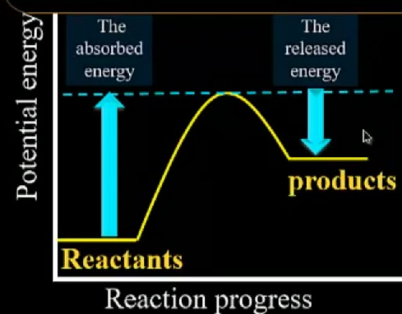| Promotor / accelerators	Poisons / inhibitors
increases the catalyst activity	decrease the catalyst activity

| The Endothermic Reaction	The Exothermic Reaction

The potential energy diagram It is the diagram that shows the change in potential energy occurs during the chemical reaction of a system when reactants are converted into products. It includes the activation energy.
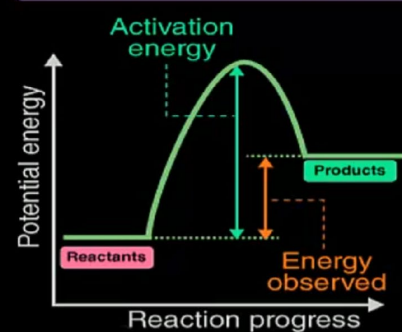
The released heat energy in forming the products bonds is less than that absorbed when breaking the reactants bonds.	The released heat energy in forming the products bonds is more than that absorbed when breaking the reactants bonds.
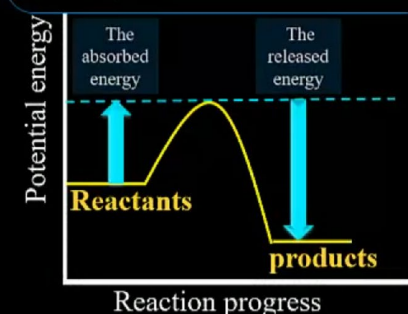
NOTE ....
The heat content change = heat content of the products - heat content of the reactants. $\Delta H^o = \Sigma H_{products} - \Sigma H_{reactants}$

The sum of heat contents of the products is higher than the sum of the heat contents of the reactants. $\Sigma H_{products} > \Sigma H_{reactants}$	The sum of heat contents of the products is less than the sum of heat contents of the reactants. $\Sigma H_{products} < \Sigma H_{reactants}$

The heat content or enthalpy change (ΔH^o) has positive sign. $\Delta H^o > 0$	The heat content or enthalpy change (ΔH^o) has negative sign. $\Delta H^o < 0$

Example:- ▪ Melting solid salts. ▪ Sublimation of dry ice into carbon dioxide gas. ▪ Evaporating liquid water. ▪ Making an anhydrous salt from a hydrate.	Example:- ▪ a neutralization reaction. ▪ rusting of iron ▪ reaction between water and calcium chloride. ▪ reaction between potassium permanganate and glycerol.