

# Thermochemistry

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The contents of this presentation is prepared to provide a brief idea about the topics, details will be discussed in the classes.  
Contents have been collected from multiple textbooks and internet.



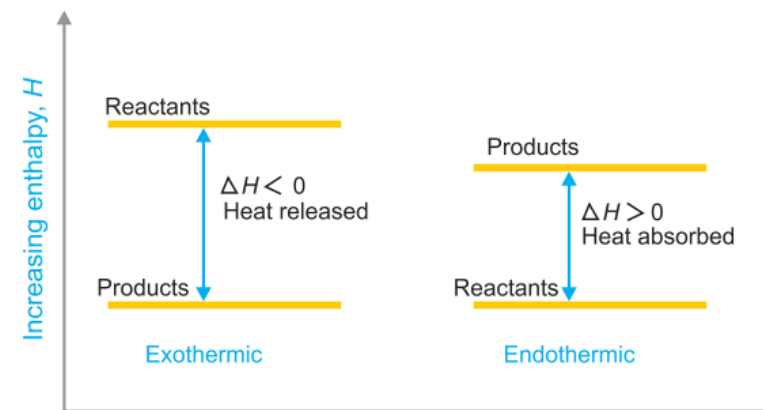
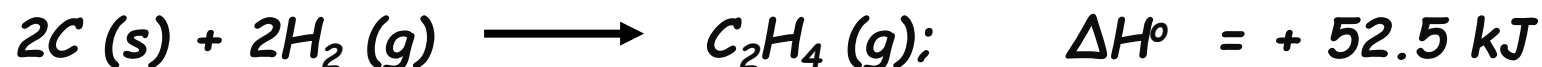
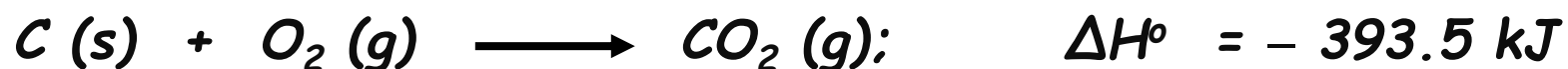
# Thermochemistry

- *'Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.'*



# Heat of Reaction or Enthalpy of Reaction

- The enthalpy of reaction is ordinarily defined as the amount of heat evolved or absorbed when the reaction has taken place at constant pressure.
- It is also defined as the difference in enthalpy or heat contents between the products and the reactants.
- If heat is evolved, the reaction is said to be exothermic; if heat is absorbed the reaction is said to be endothermic.
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$



# Heat, Energy and Work

- *Heat is an important form of energy, capable of raising the temperature of an object.*
- *Temperature gives a feeling of how hot or how cold an object is.*

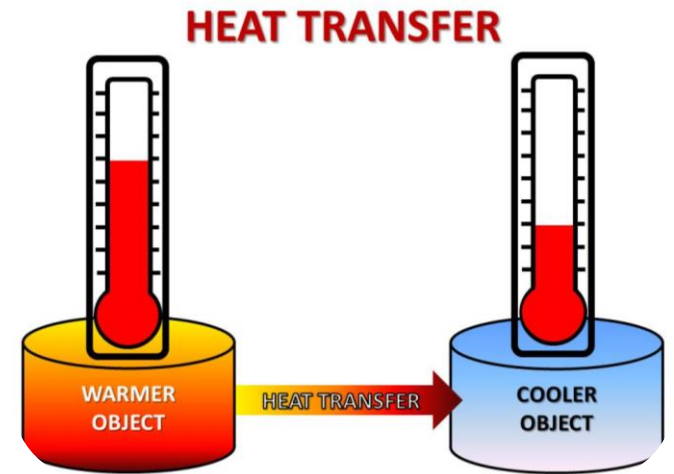
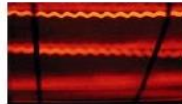


- *It also determines the tendency of an object either to lose or gain heat.*

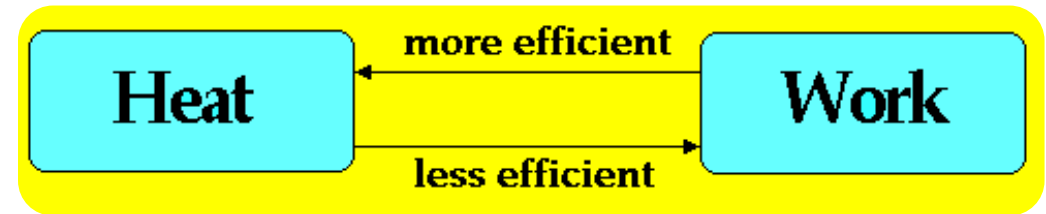


# Heat, Energy and Work

- Heat flows from a system of higher temperature to a system of lower temperature.



- Heat can be partially converted to work; other forms of energies can be completely converted to heat.





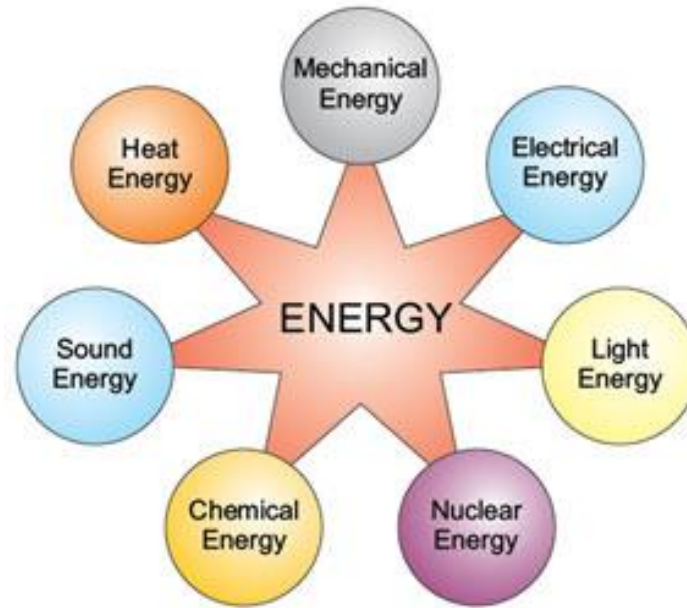
# Heat, Energy and Work

- The unit of heat is calorie (cal).
- A calorie is defined as the quantity of heat required to raise the temperature of 1.0 g of water through 1.0 °C.
- The SI unit of heat is Joule (J).
  - $1 \text{ cal} = 4.184 \text{ J}$
  - $1 \text{ J} = 0.239 \text{ cal}$
  - $1 \text{ KJ} = 1000 \text{ J}$

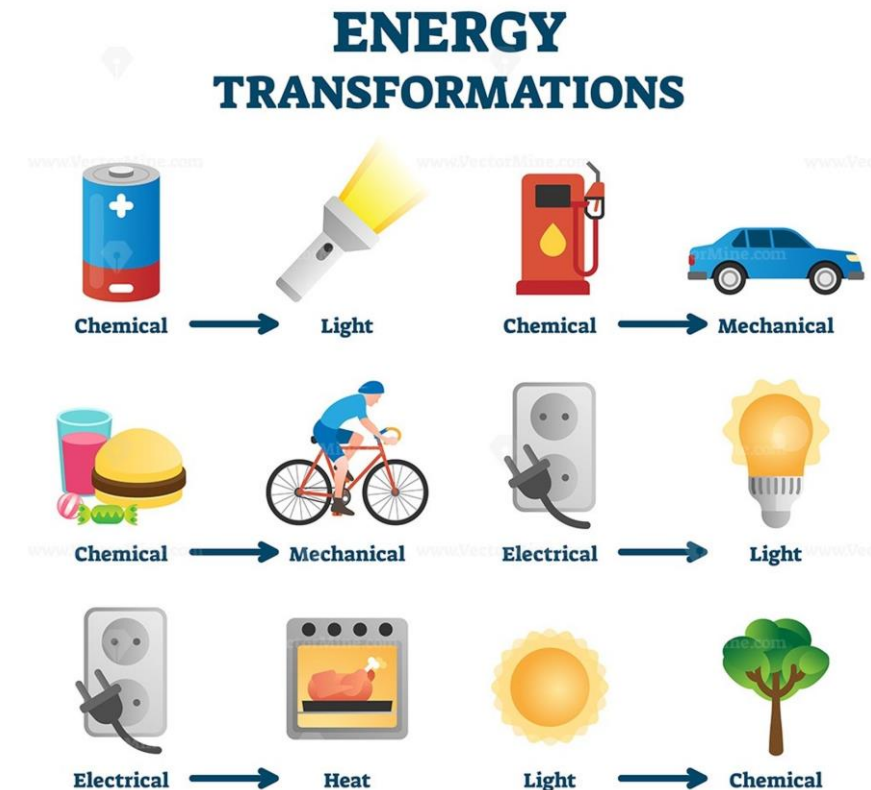


# Heat, Energy and Work

- Energy of a system is defined as 'its capacity to do work'.



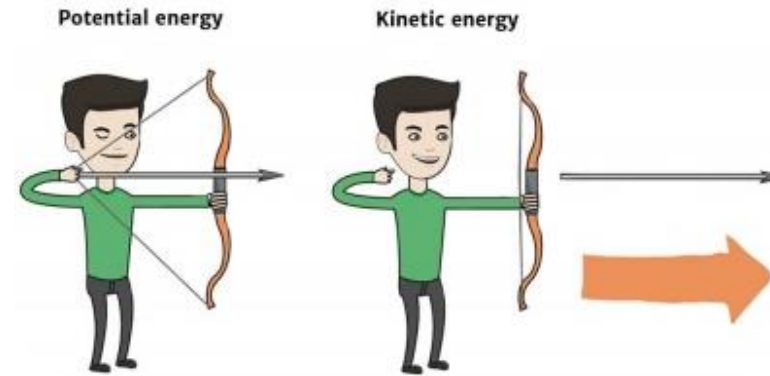
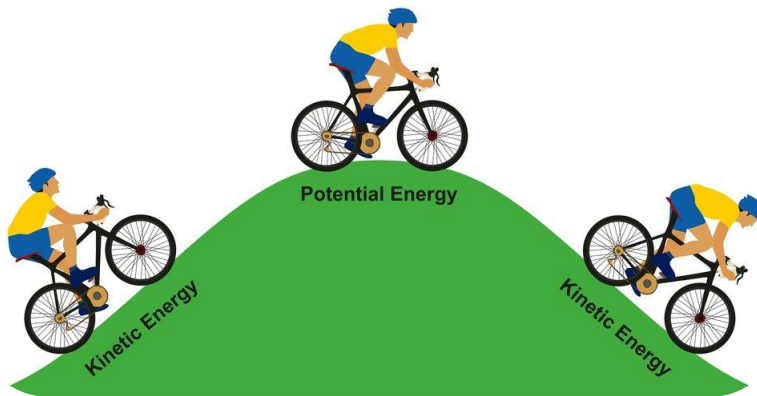
- There are various forms of energies, and conversion of one form to another is possible.



# Heat, Energy and Work

- Broadly, energy can be classified into two types -

1. **Kinetic Energy** - Energy possessed by a system by virtue of its mass and speed; its measured by the amount of work an object can do.



2. **Potential Energy** - Energy possessed by virtue of its position in a force field. An atom above the surface is under gravitational force; an atom bonded in a molecule is under the influence of binding force.





# Heat, Energy and Work

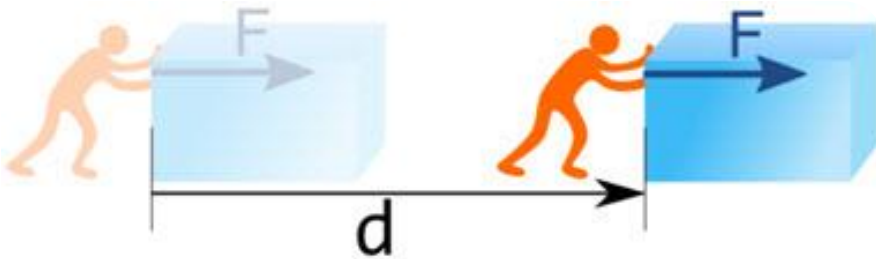
- **Internal Energy** - in thermodynamics, the total energy possessed by a system is termed as its internal energy ( $U$ ).
- It's the sum of all possible forms of energy contained in a body.
- It is impossible to determine the absolute value of the internal energy of a system. However, the change of the internal energy ( $\Delta U$ ) can be determined.
- Absorption or release of heat during a physical or chemical changes are manifestations of the change in internal energy.



# Heat, Energy and Work

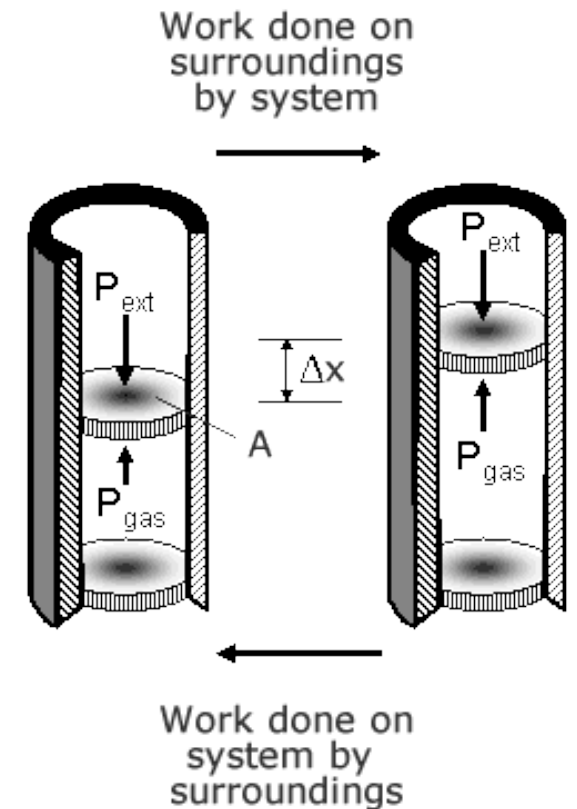
- *Work is the energy required to move an object against a force.*
- *Work,  $w$  is said to be done when an object is moved a distance  $\Delta l$  by an applied force  $F$ .*

$$w = F \times \Delta l$$



- *If the object moves by a infinitesimal distance  $dl$  by the application of force  $F$ , then the infinitesimal work  $dw$  is given by-*

$$dw = F \times dl$$



# Heat, Energy and Work

- The unit of work is *erg*; *erg* is the work done when a force of 1 dyne acts and causes a displacement of 1 cm.

$$1 \text{ erg} = 1 \text{ dyne} \times 1 \text{ cm}$$

- Since an erg of work is a small quantity, a large unit, joule is often used.

$$1 \text{ joule} = 10^7 \text{ erg.}$$



# Laws of Thermochemistry

## Hess's Law

- 'If a chemical reaction or physical change can be brought about in more than one ways, the overall enthalpy change is the same provided the initial and final states are the same.'
- For example,



Therefore, according to Hess's law,

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$



# Heat of Formation

- 'The change in enthalpy that takes place when one mole of the compound is formed from its elements is known as the **Heat of Formation**.'
- 'The change in enthalpy that takes place when one mole of a compound is formed from its elements, all substances being in their standard states (298 K and 1 atm pressure) is known as the **Standard Heat of Formation**'.



- The heats of formation data are very useful in calculating enthalpy changes of reactions which are difficult to measure directly.

$$\Delta H^\circ_{\text{reaction}} = \sum \Delta H_f^\circ)_{\text{products}} - \sum \Delta H_f^\circ)_{\text{reactants}}$$





# Heat of Reaction from Heat of Formation

- Problem: Use the heats of formation data for compounds to calculate the enthalpy of combustion of n-butane.



□ Heat of formation of the reactants,  
 $= (-124.7 + 6\frac{1}{2} \times 0) = -124.7 \text{ kJ}$

Heat of formation of the products,  
 $= 4 \times (-393.5) + 5 \times (-285.9) = -3003.5 \text{ kJ}$

Heat of combustion of n-butane,  

$$\begin{aligned} \Delta H^\circ_{\text{reaction}} &= \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ &= -3003.5 - (-124.7) \text{ kJ} \\ &= -2878.8 \text{ kJ} \end{aligned}$$

Table 6.3 Heat of formation of some compounds at 25°C in kJ mol<sup>-1</sup>

Substance	$\Delta H_f^\circ$	Substance	$\Delta H_f^\circ$
H <sub>2</sub> O(g)	-241.8	AgBr(s)	-99.5
H <sub>2</sub> O(l)	-285.9	NaCl(s)	-411.0
HF(g)	-269.9	CH <sub>4</sub> (g)	-74.9
HCl(g)	-92.3	C <sub>2</sub> H <sub>6</sub> (g)	-84.7
HBr(g)	-36.2	C <sub>3</sub> H <sub>8</sub> (g)	-104.1
HI(g)	+25.9	n-C <sub>4</sub> H <sub>10</sub> (g)	-124.7
H <sub>2</sub> S(g)	-20.2	iso-C <sub>4</sub> H <sub>10</sub> (g)	-131.6
SO <sub>2</sub> (g)	-297.5	n-C <sub>5</sub> H <sub>12</sub> (g)	-148.4
SO <sub>3</sub> (g)	-395.2	n-C <sub>6</sub> H <sub>14</sub> (g)	-167.2
C <sub>2</sub> H <sub>4</sub> (g)	+51.9	C <sub>2</sub> H <sub>2</sub> (g)	+227.0
NH <sub>3</sub> (g)	-46.2	C <sub>6</sub> H <sub>6</sub> (g)	+82.9
CO(g)	-110.5	C <sub>6</sub> H <sub>6</sub> (l)	+49.0
CO <sub>2</sub> (g)	-393.5	CH <sub>3</sub> OH(l)	-238.6
Fe <sub>2</sub> O <sub>3</sub> (s)	-824.2	C <sub>2</sub> H <sub>5</sub> OH(l)	-277.7
Al <sub>2</sub> O <sub>3</sub> (s)	-1669.8	HCOOH(l)	-409.2
AgCl(s)	-127.0	CH <sub>3</sub> COOH(l)	-487.0



# Heat of Combustion

- 'The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen is known as the Heat of Combustion ( $\Delta H_c$ ).'



- *Problem: Calculate the standard heat of formation of propane ( $\text{C}_3\text{H}_8$ ) if its heat of combustion is  $- 2220.2 \text{ kJ mol}^{-1}$ . The heats of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $- 393.5$  and  $- 285.8 \text{ kJ mol}^{-1}$  respectively.*

*Solution:*



## Heat of Solution

- The heat of solution is the change in enthalpy when one mole of a substance is dissolved in a solvent so that further dilution does not give any change in enthalpy.



## Heat of Neutralization

- The change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralised by one gram equivalent of a base or vice versa in dilute solution.



The heat of formation of an acid and a base is merely the heat of formation of water from hydrogen and hydroxyl ions.



# The First Law of Thermodynamics

Also known as the law of **conservation of energy**. May be stated in different forms -

- *Energy can neither be created nor destroyed; it can only be converted from one form into another.*
- *The total energy of an isolated system is constant.*
- *It is impossible to construct a perpetual motion machine which will create energy out of nothing.*
- *The sum of all of the energy changes for all systems participating in a process must be zero.*
- *If work is produced during a cyclic process, an equivalent amount of heat must also be consumed.*



## Second Law of Thermodynamics

- *Whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe. In other words: the entropy of the system is constantly increasing.*
- *It is impossible to construct a machine functioning in cycles which can convert heat completely into equivalent amount of work without producing changes elsewhere.*
- *Heat cannot pass from a colder to a hotter body without some other change occurring at the same time.*





# Molar Heat Capacities

- *By heat capacity of a system, we mean the capacity to absorb heat and store energy.*
- *It is a common experience that the temperature of a substance (a system) increases when heat is supplied to it.*
- *'The heat capacity of a system is defined as the amount of heat required to raise the temperature of the system by one degree.'*

$$C = q / \Delta T$$

*Where  $q$  is a amount of heat absorbed by the system, producing a difference in temperature  $\Delta T$  ( $= T_f - T_i$ ).*



# Molar Heat Capacities

Two terms related to heat capacity -

1. Specific heat capacity

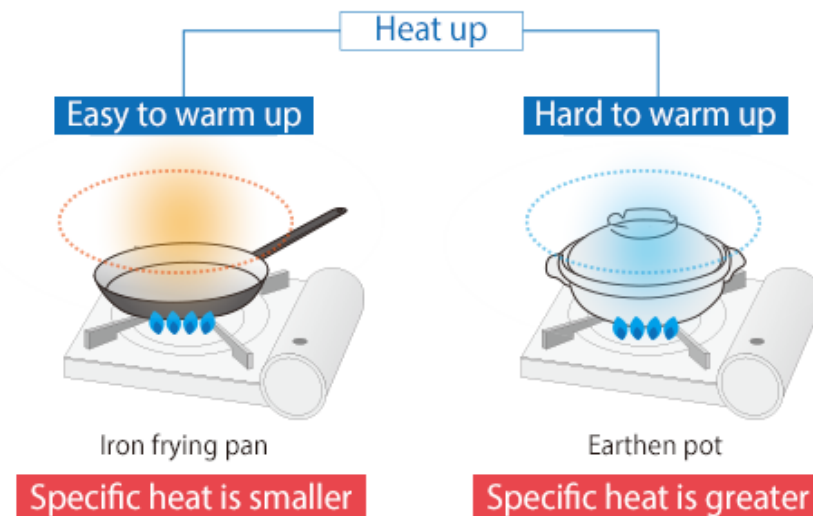
$$C_s = C/m = \text{JK}^{-1}\text{g}^{-1}$$

2. Molar heat capacity

$$C_m = C/n = \text{JK}^{-1}\text{mol}^{-1}$$

Again, heat energy can be supplied at constant volume as well as constant pressure.

The heat capacities are distinguished as  $C_v$ , heat capacity at constant volume, and  $C_p$ , heat capacity at constant pressure.



## Thermodynamic definition of $C_v$ and $C_p$

From first law of thermodynamics,

$$dU = q - PdV$$

Or  $q = dU + PdV$

Dividing both sides by  $dT$ ,

$$\frac{q}{dT} = \frac{dU + PdV}{dT} = \frac{dU}{dT} + \frac{PdV}{dT} \quad \text{--- (a)}$$

At constant volume,  $dV = 0$

Then (a) will be,  $\frac{q}{dT} = C_v = \frac{dU}{dT}$

Therefore, the heat capacity at constant volume is 'the rate of change of internal energy with temperature at constant volume.'



# Thermodynamic definition of $C_v$ and $C_p$

Equation (a) -

$$C = \frac{dU}{dT} + \frac{PdV}{dT}$$

At constant pressure,

$$C_P = \left(\frac{dU}{dT}\right)_P + P\left(\frac{dV}{dT}\right)_P \text{ ----- (b)}$$

We know,  $H = U + PV$

Differentiating this equation with respect to  $T$  at constant pressure,

$$\left(\frac{dH}{dT}\right)_P = \left(\frac{dU}{dT}\right)_P + P\left(\frac{dV}{dT}\right)_P \text{ ----- (c)}$$

Comparing (b) and (c),

$$C_P = \left(\frac{dH}{dT}\right)_P$$

Therefore, the heat capacity at constant volume is 'the rate of change of enthalpy with temperature at constant pressure.'



## Relation between of $C_v$ and $C_p$

We know,  $C_p = \frac{dH}{dT}$

And  $C_v = \frac{dU}{dT}$

Now, enthalpy,  $H = U + PV$   
 $= U + nRT$   
 $= U + RT$  (for 1 mole)

Differentiating with respect to temperature,

$$\frac{dH}{dT} = \frac{dU}{dT} + R$$

or,  $C_p = C_v + R$

or,  $C_p - C_v = R$

Thus,  $C_p$  is greater than  $C_v$  by gas constant,  $R$ .





Thank You