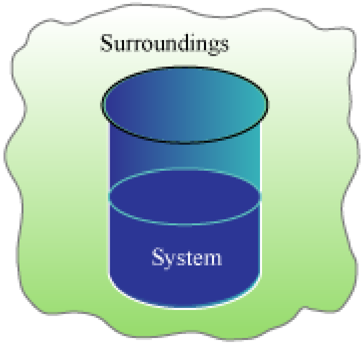
Thermodynamics

Thermodynamic Terms - System and Surroundings, Types of System

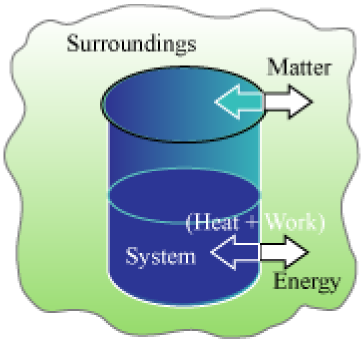
The System and the Surroundings

- System – Part of the universe in which observations are made
- Surroundings – Part of universe excluding system
- Universe = System + Surroundings



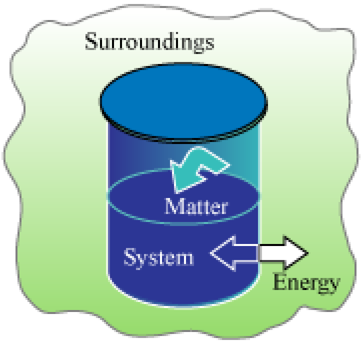
Types of the System

- Open system – There is exchange of energy and matter between system and surroundings. (shown in figure)



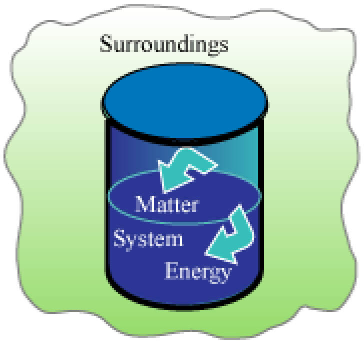
Example – Presence of reactants in an open beaker

- Closed system – There is no exchange of matter, but exchange of energy is possible between the system and the surroundings. (shown in figure)



Example – Presence of reactants in closed vessel made of conducting material

- Isolated system – There is no exchange of energy or matter between the system and the surroundings. (shown in figure)



Example – Presence of reactants in a thermos flask or any other closed insulated vessel

The State of System

- State of a thermodynamic system can be described by properties such as its pressure (p), temperature (T), volume (V), composition of the system, etc.
- Variables such as p, V, T are called state variables or state functions.
- The values of state functions or state variables depend only on the state of the system and not on how it is reached.
- To define the state of a system, it is not necessary to define all the properties of the system.

Thermodynamic equilibrium:

In an isolated system, when there is no change in the macroscopic property of the system like entropy, internal energy etc. with time, It is said to be in thermodynamic equilibrium. The state of the system which is in thermodynamic equilibrium is determined by intensive properties such as temperature, pressure, volume etc. Whenever, the system is in thermodynamic equilibrium, it tends to remain in this state infinitely and will not change spontaneously.

The operation by which a system changes from one state to another state is called a **process.**

Thermodynamic process:

A thermodynamic process is a passage of a system from an initial state to a final state of thermodynamic equilibrium. The initial and final states are the defining elements for the process. Whenever, a system changes from one state to another, it is accompanied by change in energy but in case of open systems, there may be change of matter as well.

Various types of thermodynamic processes are isothermal process, adiabatic process, isochoric process, isobaric process, reversible process and irreversible process.

1. Isothermal Process:

A process is said to be isothermal, if the temperature of the system remains constant during each stage of the process. When such a process occurs, heat transfer may take place from system to the surroundings in order to keep the temperature of the system constant. An isothermal process implies that the product of the volume and the pressure is constant for an ideal gas. i.e.

PV = Constant

For example: Isothermal processes can occur in any kind of system, including highly-structured machines and even in living cells. Various parts of the cycles of some heat engines are carried out isothermally and may be approximated by a Carnot cycle.

2. Adiabatic Process:

A process is said to be adiabatic, if no heat can flow from system to the surroundings or vice-versa. An adiabatic process is also known as isocaloric process which is a thermodynamic process, in which no heat is transferred to or from the working fluid. This system is completely insulated from the surroundings.

3. Isobaric Process:

A process is said to be isobaric, if the pressure of the system remains constant during each stage of the process. The heat transferred to the system does work but also changes the internal energy of the system.

4. Isochoric (or iso-volumetric) Process:

A process is said to be Isochoric (or iso-volumetric), if the volume of the system remains constant during each step of the process. In any Isochoric process, the work done by the system is always zero. For any two dimensional system, the heat energy transferred to that system is absorbed by it as its internal energy. The other name of this process is isometric process.

For example: When we heat up any empty container, the air inside gains internal energy which can be felt due to increase in pressure and temperature.

Difference between Reversible process and Irreversible process:

Reversible process	Irreversible process
a. The process is carried out infinitesimally slowly, i.e. all changes occuring in the direct process can be exactly reversed and the difference between driving force and the opposing force is very small.	a.The process is carried out infinitesimally rapidly, i.e. the successive steps of the direct process cannot be retraced and the difference between driving force and the opposing force is very large.
b.The system remains in the state of equilibrium with the surroundings.	b. After the completion of a process, equilibrium may exist.
c. In this process, maximum work is obtained.	c. In this process, minimum work is obtained.
d. It is an imaginary process and cannot be achieved practically.	d. These processes occur in nature.
e. Infinite time is required for the completion of a process.	e. Finite time is required for the completion of a process.

Cyclic process:

When a system returns to its original state after completing a series of changes, then it is known as cyclic process. In a cyclic process, the initial and the final state is same. As the internal energy U of the system depends only on the state of the system. So, in a cyclic process, the net change of internal energy will be equal to zero i.e. $\Delta U = 0$. Hence

From the first law:

$$\boldsymbol{\Delta U = q + w}$$

$$\boldsymbol{0 = q + w}$$

Hence, $q = -w$

Examples of a Cyclic Process:

1. Expansion at constant temperature (T_1).

2. Removal of heat at constant volume (V_2).

3. Compression at constant temperature (T_2).

4. Addition of heat at constant volume (V_1).

If the process takes place at constant temperature, then the cycle is known as isothermal cycle.

If the process takes place reversibly, then cycle is known as reversible cycle.

The process is cyclic so, work is done. There is no change in internal energy after each cycle. Therefore, the net work done in each cycle equals to the heat added to the system. Now, we analyse each of the steps in the cycle.

Step 1 - Isothermal expansion: The system does work W_1 which is equal to the heat Q_1 added to the system in the expansion, because the internal energy does not change.

Step 2 - Isochoric process: The work done is $W_2 = 0$. Heat Q_2 is removed from the system because the temperature decreases from T_1 to T_2.

Step 3 - Isothermal compression: The work W_3 done by the system is negative, but of smaller magnitude than W_1 because the area under the PV curve is less than that in step 1. The internal energy is does not change, so the heat removed is $Q_3 = W_3$.

Step 4 - Isochoric process: The reverse of step 2. $W_4 = 0$, while heat $Q_4 = - Q_2$ is added to the system.

Cycle Summary:

Because W_2 and $W_4 = 0$, the net work done is $W_{net} = W_1 + W_3$.

Because $Q_2 + Q_4 = 0$, the net heat added is $Q_{net} = Q_1 + Q_3 = W_{net}$.

Net work done:

$W_1 = nRT_1 \ln (V_2/V_1)$

$W_3 = nRT2 \ln (V_1/V_2)$

$W_{net} = nR (T_1 - T_2) \ln (V_1/V_2)$

Internal Energy as a State Function

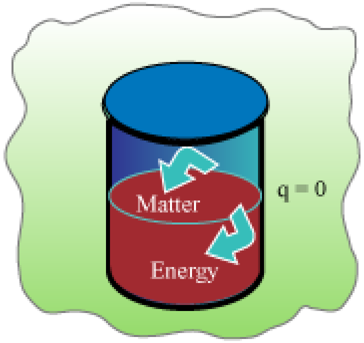
- Internal energy (U) represents the total energy of a system (i.e., the sum of chemical, electrical, mechanical or any other type of energy).

- Internal energy of a system may change when:

- Heat passes into or out of the system
- Work is done on or by the system
- Matter enters or leaves the system

Work

- For an adiabatic system which does not permit the transfer of heat through its boundary (shown in the figure), a change in its internal energy can be brought by doing some work on it.



- Initial state of the system, (1)

Temperature = T_1

Internal energy = U_1

- When some mechanical work is done, the new state (2) is obtained.

Temperature at state 2 = T_2

Internal energy at state 2 = U_2

- It is found that $T_2 > T_1$

Change in temperature, $\Delta T = T_2 - T_1$

Change in internal energy, $\Delta U = U_2 - U_1$

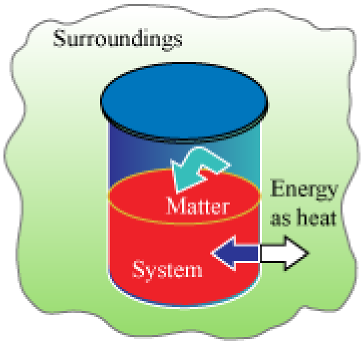
- The value of internal energy (U) is the characteristic of the state of a system.
- The adiabatic work (W_{ad}) required to bring about a change of state is equal to the change in internal energy.

  $\Delta U = U_2 - U_1 = W_{ad}$

- Thus, internal energy (U) of the system is a state function.
- When work is done on the system, W_{ad} = + ve
- When work is done by the system, W_{ad} = − ve

Heat

- Internal energy of the system can also be changed by transfer of heat from the surroundings to the system or vice versa, without doing any work.
- This exchange of energy, which is a result of temperature difference, is called heat (q).
- A system which allows heat transfer through its boundary is shown in the figure.



- At constant volume, when no work is done, the change in internal energy is, $\Delta U = q$
- When heat is transferred from the surroundings to the system, q is positive.
- When heat is transferred from the system to the surroundings, q is negative.

General Case

- When change in state is brought about both by doing work (W) and by transfer of heat (q):

  Change in internal energy, $\Delta U = q + W$

- If $W = 0$ and $q = 0$ (i.e., no transfer of energy as heat or as work), then

  $\Delta U = 0$

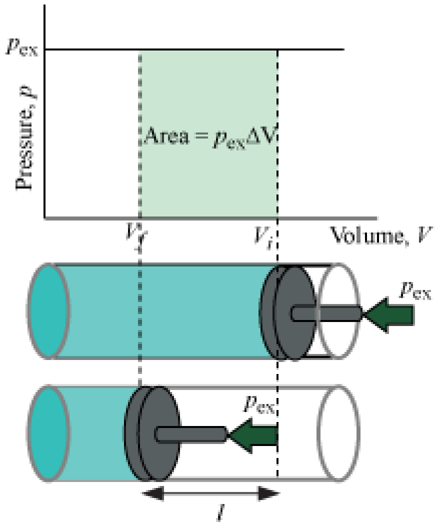
  This means that for an isolated system, $\Delta U = 0$.

- $\Delta U = q + W$, is the mathematical statement of the **first law of thermodynamics**.

- First law of thermodynamics states that "the energy of an isolated system is constant".

  Applications - Work

- Mechanical Work, i.e., Pressure-Volume Work



- Work done (W) on an ideal gas in a cylinder when it is compressed by constant pressure, p_{ex} can be derived as follows:

  Volume change = $l \times A = \Delta V = V_f - V_i$

  $$\text{Pressure } (p) = \frac{\text{Force}}{\text{Area}}$$

  $\therefore$ Force on the piston = $p_{ex} . A$

  Work (W) = Force × Distance

  $$\Rightarrow W = p_{ex} . A . l$$

  $$\Rightarrow W = p_{ex} . (-\Delta V)$$

$$\Rightarrow W = -p_{ex}\Delta V$$
$$\Rightarrow W = -p_{ex}(V_f - V_i)$$

- Negative sign indicates that work is done by the system.
- Here, $V_f - V_i$ is negative; therefore, work done will be positive.
- If the pressure is not constant at every stage of compression, but changes in a number of finite steps, then $W = -\sum p\Delta V$
- If the pressure is not constant, but changes during the process in such a way that it is always infinitesimally greater than the pressure of the gas, then the volume decreases by an infinitesimal amount, dV (at each stage of compression). In such a case

$$W = -\int_{V_i}^{V_f} p_{ex}\,dV$$

- For a reversible process:

$$W_{rev} = -\int_{V_i}^{V_f} p_{ex}\,dV = -\int_{V_i}^{V_f} (p_{in} \pm dp)\,dV$$

$dp \times dV$ is very small

$$\therefore W_{rev} = -\int_{V_i}^{V_f} p_{in}\,dV \qquad (p_{in} \rightarrow p)$$

From the ideal gas equation, we have

$$p = \frac{nRT}{V}$$

Therefore, at constant temperature (T) (i.e., for an isothermal process),

$$W_{\text{rev}} = -\int_{V_i}^{V_f} nRT \frac{dV}{V}$$

$$= -nRT \, ln \, \frac{V_f}{V_i}$$

$$\therefore W_{\text{rev}} = -2.303 \, nRT \log \frac{V_f}{V_i}$$

- Free expansion:
- Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion.
- Work done is zero during free expansion (whether the process is reversible or irreversible).
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-
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- Isothermal and free expansion of an ideal gas:
- For isothermal expansion (i.e., T = Constant) of ideal gas in vacuum,

  $w = 0$, since $p_{ex} = 0$
- Since $q = 0$, $\Delta U = 0$
- For isothermal irreversible change –

  $q = -w = p_{ex}(V_f - V_i)$
- For isothermal reversible change –

  $$q = -w = nRT \ln \frac{V_f}{V_i}$$

  $$= 2.303 \, nRT \log \frac{V_f}{V_i}$$
- For adiabatic change, $q = 0$, $\Delta U = w_{ad}$

Enthalpy as State Function, Extensive and Intensive Properties, Heat Capacity

Enthalpy

- We have $\Delta U = q + w$ (First law of thermodynamics)

  ΔU → Change in internal energy

  q → Heat absorbed by the system

  w → Work done

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- At constant volume:

  $\Delta U = q_{\mathrm{v}}$

-

- At constant pressure:

  $\Delta U = q_{\mathrm{p}} - p\Delta V$

  $(- p\Delta V)$ represents expansion work done by the system

  Or, $U_2 - U_1 = q_{\mathrm{p}} - p\ (V_2 - V_1)$

  Or. $q_{\mathrm{p}} = (U_2 + pV_2) - (U_1 + pV_1)$ …(1)

- Enthalpy (H) can be defined as

  $H = U + pV$

- Thus, from equation (1) − $q_{\mathrm{p}} = H_2 - H_1$ or, $q_{\mathrm{p}} = \Delta H$

- ΔH is independent of path, and hence, q_{p} is also independent of path.

- At constant pressure, for finite changes:

  $\Delta H = \Delta U + p\Delta V$

- At constant pressure, $\Delta H = q_{\mathrm{p}}$ (heat absorbed by the system)

- ΔH is negative for exothermic reactions (which evolve heat during the reaction)

- ΔH is positive for endothermic reactions (which absorb heat from the surroundings)

- At constant volume: $\Delta U = q_v$

  Or, $\Delta H = \Delta U = q_v$ [$\because \Delta V = 0$]

- For reactions involving gases, using ideal gas law, $p\Delta V = \Delta n_g RT$

  Δn_g = Number of moles of gaseous products − Number of moles of gaseous reactants

- Thus, $\Delta H = \Delta U + \Delta n_g RT$

Extensive and Intensive Properties

- Extensive property: Value depends on the quantity or size of matter in the system

  Examples − mass, volume, internal energy, heat capacity, etc.

- Intensive property: Value does not depend on the quantity or size of matter in the system

  Examples − temperature, density, pressure, etc.

Heat Capacity

- The increase in temperature (ΔT) is proportional to the heat transferred (q)

  q = coeff (C) × ΔT

  C → Heat capacity

- C is directly proportional to the amount of a substance.

- Molar heat capacity of a substance, $C_m = \left(\frac{C}{n}\right)$, is the heat capacity of one mole of the substance.

  Molar heat capacity is also defined as the quantity of heat required to raise the temperature of one mole of a substance by one degree Celsius (or one Kelvin).

- Specific heat capacity c (or specific heat) is the quantity of heat required to raise the temperature of a substance of one unit mass by one degree Celsius (or one Kelvin)

  $q = c \times m \times \Delta T$, Where, m = Mass of the substance

  $= C\Delta T$

- Relationship between C_p and C_v for an ideal gas

  C_p → Heat capacity at constant pressure

  C_v → Heat capacity at constant volume

  At constant volume: $q_v = C_v\Delta T = \Delta U$

  At constant pressure: $q_p = C_p\Delta T = \Delta H$

  For a mole of an ideal gas:

  $\Delta H = \Delta U + \Delta(pV)$

  $= \Delta U + \Delta(RT)$

  $= \Delta U + R\Delta T$

  $\therefore \Delta H = \Delta U + R\Delta T$

  $\Rightarrow C_p\Delta T = C_v\Delta T + R\Delta T$

  $\Rightarrow C_p = C_v + R$

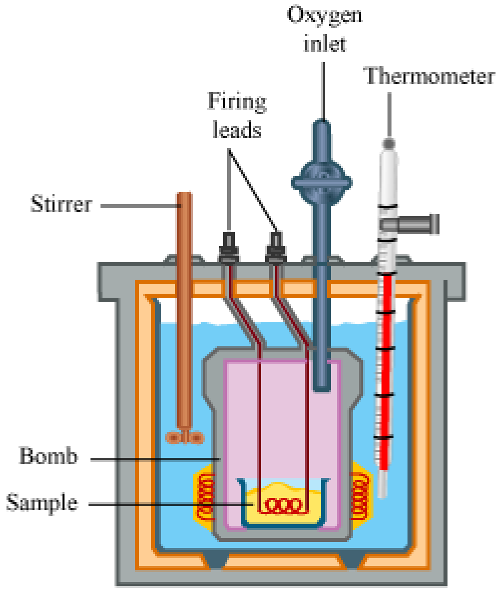
  $\Rightarrow C_p - C_v = R$

Calorimetry

- Calorimetry is the technique used for the measurement of energy changes associated with a chemical or a physical process.
- The process of calorimetry is carried out in a vessel called the calorimeter, which is immersed in a known volume of a liquid.
- To determine the heat evolved in the process, the heat capacity of the liquid in which the calorimeter is immersed and the heat capacity of the calorimeter should be known.
- Two different conditions are used for the measurements:
- At constant volume , q_v
- At constant pressure, q_p

ΔU Measurements

- Measured by using a bomb calorimeter (shown in the figure)



- A combustible substance is burnt in pure oxygen, supplied through the inlet in the bomb.
- The heat evolved during the combustion is then transferred to the water around the bomb and its temperature is monitored.
- The bomb calorimeter is sealed.

  ∴ $\Delta V = 0$

  → Work done = 0

- Energy changes associated with the reactions are measured at constant volume.
- After the completion of the reaction, temperature change (ΔT) of the calorimeter is converted into q_v by using the relation

  $q = C_v \Delta T$

  Where, C_v is the heat capacity of the bomb calorimeter

Example

0.562 g of graphite is burnt in a bomb calorimeter at 298 K and 1 atmospheric pressure. The heat capacity of the calorimeter is 20.7 kJ/K.

C (graphite) + O_2 (g) → CO_2(g)

During the reaction, the temperature rises from 298 K to 299 K. The enthalpy change for the given reaction can be calculated as

Quantity of heat absorbed by the calorimeter, $q = C_v \times \Delta T$

ΔT = (299 − 298) K

= 1 K

$\therefore q = -\ 20.7$ kJ/K × 1 K

= − 20.7 kJ

(Here, the negative sign indicates the exothermic nature of the reaction.)

Heat evolved by burning 0.562 g of graphite = −20.7 kJ

∴ Heat evolved by burning1 mol of graphite (12 g)

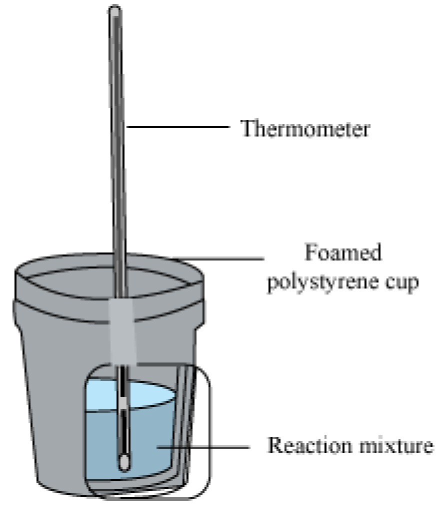
$$= \frac{-20.7 \times 12}{0.562}$$

$$= -441.99 \text{ kJ}$$

∴ Enthalpy change (ΔH) for the given reaction = −441.99 kJ

ΔH Measurements

- The calorimeter used for measuring heat change at constant pressure (generally under atmospheric pressure) is shown in the figure.



- At constant pressure, $\Delta H = q_p$

- Heat absorbed or evolved at constant pressure (q_p) is called the heat of reaction or enthalpy of reaction ($\Delta_r H$).

- For exothermic reaction: Heat is evolved and the system loses heat to the surroundings (q_p will be negative and $\Delta_r H$ will also be negative)

- For endothermic reaction: Heat is absorbed ($q_p$will be positive and $\Delta_r H$ will also be positive)

Enthalpy Changes in Various Processes

- The change in enthalpy accompanying a reaction is called the reaction enthalpy, $\Delta_r H$.

- For the reaction,

Reactants → Products

$\Delta_r H$ = (Sum of enthalpies of products) − (Sum of enthalpies of reactants)

$$\Delta_r H = \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}}$$

a_i and b_i are the stoichiometric coefficients of products and reactants respectively in the balanced chemical equation.

Standard enthalpy of reactions

- Defined as the enthalpy change for a reaction when all the participating substances are in their standard states

- Denoted by $\Delta H^{\ominus}$

Enthalpy change during phase transformations

- **Standard enthalpy of fusion (or molar enthalpy of fusion)** is the enthalpy change that accompanies melting of one mole of a solid substance in standard state.

$$H_2O(s) \longrightarrow H_2O(l);\ \Delta_{fus}H^{\ominus} = 6.00\ \text{kJ mol}^{-1}$$

- **Standard enthalpy of vaporization (or molar enthalpy of vaporization)** is the enthalpy change accompanied in the vaporization of one mole of a liquid at constant temperature and under standard pressure (1 bar).

$$H_2O(l) \longrightarrow H_2O(g);\Delta_{vap}H^{\ominus} = 40.79\ \text{kJ mol}^{-1}$$

- **Standard enthalpy of sublimation** is the enthalpy change when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1 bar).

The standard enthalpy of sublimation of solid CO_2 or 'dry ice' at 195 K is $\Delta_{sub}H^{\ominus} = 25.2\ \text{kJ mol}^{-1}$

Standard enthalpy of formation $(\Delta_f H^{\ominus})$

- Defined as the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation

- Example:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\Delta_f H^{\ominus} = -285.8\ \text{kJ mol}^{-1}$$

Thermochemical equation

- A balanced chemical equation together with the value of its $\Delta_r H$

- Example:

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);$$
$$\Delta_r H^{\ominus} = -1367\ \text{kJ mol}^{-1}$$

- Coefficients in balanced thermochemical equation represent the number of moles of reactants and products involved in the reaction.

- The numerical value of $\Delta_r H^\ominus$ refers to the number of moles of substances specified by an equation.

Example:

$$\mathrm{Fe_2O_3}(s) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{Fe}(s) + 3\mathrm{H_2O}(l)$$

$$\Delta_f H^\ominus(\mathrm{H_2O}, l) = -285.83 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus(\mathrm{Fe_2O_3}, s) = -824.2 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus(\mathrm{Fe}, s) = 0$$

$$\Delta_f H^\ominus(\mathrm{H_2}, g) = 0$$

Then,

$$\begin{aligned}\Delta_r H_1^\ominus &= 3(-285.83 \text{ kJ mol}^{-1}) - 1(-824.2 \text{ kJ mol}^{-1})\\ &= (-857.5 + 824.2) \text{ kJ mol}^{-1}\\ &= -33 \text{ kJ mol}^{-1}\end{aligned}$$

The coefficients used in these calculations are the pure numbers, which are equal to the respective stoichiometric coefficients.

If the equation is balanced differently, for example,

$$\frac{1}{2}\mathrm{Fe_2O_3}(s) + \frac{3}{2}\mathrm{H_2}(g) \longrightarrow \mathrm{Fe}(s) + \frac{3}{2}\mathrm{H_2O}(l)$$

Then,

$$\begin{aligned}\Delta_r H_2^\ominus &= \frac{3}{2}(-285.83 \text{ kJ mol}^{-1}) - \frac{1}{2}(-824.2 \text{ kJ mol}^{-1})\\ &= (-428.7 + 412.1) \text{ kJ mol}^{-1}\\ &= -16.6 \text{ kJ mol}^{-1}\\ &= \frac{1}{2}\Delta_r H_1^\ominus\end{aligned}$$

- If a chemical reaction is reversed, then the value of $\Delta_r H^\ominus$ is reversed in sign.

  For example,

  $$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g);\ \Delta_r H^\ominus = -91.8 \text{ kJ mol}^{-1}$$
  $$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g);\Delta_r H^\ominus = +91.8 \text{kJ mol}^{-1}$$

  Hess's law of constant heat summation

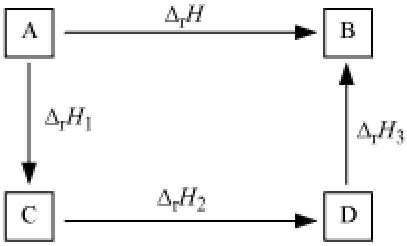
- **Statement:** When a reaction takes place in several steps, its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

- Mathematically, for the reaction A → B,

  $$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$$

  $\Delta_r H$ = Enthalpy of an overall reaction, A → B

  $\Delta_r H_1, \Delta_r H_2, \Delta_r H_3$ represent enthalpies of reactions leading to the same product (B) along another route.



  $$\therefore \Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$$

  Enthalpies for Different Types of Reactions

- **Standard Enthalpy of Combustion** $(\Delta_c H^\ominus)$

- Combustion reactions are exothermic in nature (that is, $\Delta_c H^\ominus = -\text{ve}$).

- The enthalpy change per mole of a substance when it undergoes combustion is called standard enthalpy of combustion (provided all the reactants and products should be in their standard states at the specified temperature).

- Example: 2658 kJ of heat is released by complete combustion of one mole of butane.

$$C_4H_{10}(g)+\frac{13}{2}O_2(g)\longrightarrow 4CO_2(g)+5H_2O(l);$$
$$\Delta_c H^\ominus = -2658.0\,\text{kJ mol}^{-1}$$

- **Enthalpy of Atomization** $(\Delta_a H^\ominus)$
- Enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase is called **enthalpy of atomization**.
- It is also called **bond dissociation enthalpy** (in case of diatomic molecules).
- Examples:

$$H_2(g)\longrightarrow 2H(g); \Delta_a H^\ominus = 435.0\ \text{kJ mol}^{-1}$$
$$CH_4(g)\longrightarrow C(g)+4H(g); \Delta_a H^\ominus = 1665\ \text{kJ mol}^{-1}$$

- Enthalpy of atomization is also called enthalpy of sublimation. For example: $Na(s)\longrightarrow Na(g)\ ;\ \Delta_a H^\ominus = 108.4\ \text{kJ mol}^{-1}$
- **Bond Enthalpy** $(\Delta_{bond} H^\ominus)$
- Energy is released when bond is formed and is required to break a bond.
- Two different terms are used to describe enthalpy changes associated with chemical bonds –––Bond dissociation enthalpy and Mean bond enthalpy
- **For diatomic molecules**

$$H_2(g)\longrightarrow 2H(g); \Delta_{H\text{-}H} H^\ominus = 435.0\ \text{kJ /mol}^{-1}$$

→ $\Delta_{H\text{-}H} H^\ominus$ is the bond dissociation enthalpy of H − H bond.

→ Bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

→ It is same as the atomization of dihydrogen.

- **For polyatomic molecules**

For example –

$$\mathrm{CH_4}(g) \longrightarrow \mathrm{C}(g) + 4\mathrm{H}(g); \quad \Delta_a H^{\ominus} = 1665\ \mathrm{kJ\ mol^{-1}}$$

All the four bonds are identical in length and energy.

$$\begin{aligned}
&\mathrm{CH_4}(g) \longrightarrow \mathrm{CH_3}(g) + \mathrm{H}(g); \Delta_{\mathrm{bond}} H_1^{\ominus} = +427\ \mathrm{kJ\ mol^{-1}} \\
&\mathrm{CH_3}(g) \longrightarrow \mathrm{CH_2}(g) + \mathrm{H}(g); \Delta_{\mathrm{bond}} H_2^{\ominus} = +439\ \mathrm{kJ\ mol^{-1}} \\
&\mathrm{CH_2}(g) \longrightarrow \mathrm{CH}(g) + \mathrm{H}(g); \Delta_{\mathrm{bond}} H_3^{\ominus} = +452\ \mathrm{kJ\ mol^{-1}} \\
&\mathrm{CH}(g) \longrightarrow \mathrm{C}(g) + \mathrm{H}(g); \Delta_{\mathrm{bond}} H_4^{\ominus} = +347\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

Thus, $\mathrm{CH_4}(g) \longrightarrow \mathrm{C}(g) + 4\mathrm{H}(g);$

$$\begin{aligned}
\Delta_a H^{\ominus} &= \Delta_{\mathrm{bond}} H_1^{\ominus} + \Delta_{\mathrm{bond}} H_2^{\ominus} + \Delta_{\mathrm{bond}} H_3^{\ominus} + \Delta_{\mathrm{bond}} H_4^{\ominus} \\
&= (427 + 439 + 452 + 347)\ \mathrm{kJ\ mol^{-1}} \\
\Rightarrow \Delta_a H^{\ominus} &= 1665\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

In such cases, **mean bond enthalpy** of $\mathrm{C-H}$ bond is used.

$$\begin{aligned}
\Delta_{\mathrm{C-H}} H^{\ominus} &= \frac{1}{4}(\Delta_a H^{\ominus}) \\
&= \frac{1}{4} \times (1665\ \mathrm{kJ\ mol^{-1}}) \\
&= 416\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

∴The mean bond enthalpy of C − H bond is 416 kJ mol^{-1}.

- Reaction enthalpy,

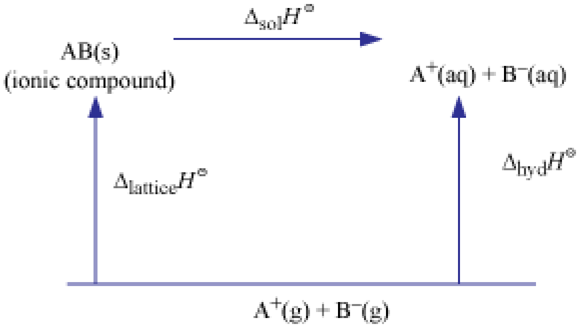
$$\begin{aligned}
\Delta_r H^{\ominus} &= \sum(\text{bond enthalpies})_{\text{reactants}} \\
&\quad - \sum(\text{bond enthalpies})_{\text{products}}
\end{aligned}$$

This relationship is applicable only when all the reactants and products in the reaction are in gaseous state.

- **Enthalpy of Solution**
-

- It is the enthalpy change when one mole of a substance dissolves in a specified amount of solvent.

- When an ionic compound is dissolved in water, the ions leave their ordered positions on the crystal lattice. Hydration or solvation of these ions also occurs at the same time.



Enthalpy of solution $(\Delta_{sol}H^\ominus)$ = Lattice enthalpy $(\Delta_{lattice}H^\ominus)$ + Enthalpy of hydration of ions $(\Delta_{hyd}H^\ominus)$

-

- For most ionic compounds, the dissociation process is endothermic i.e., $\Delta_{sol}H^\ominus = +ve$

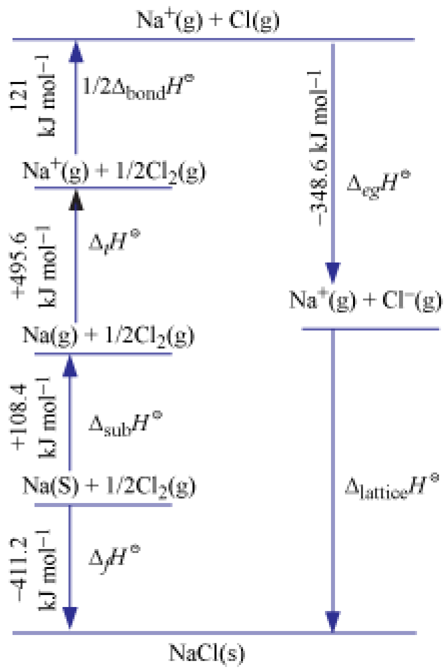
Lattice Enthalpy of an Ionic Compound

- It is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

- Example:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g);$$
$$\Delta_{lattice}\mathrm{H}^\ominus = +788 \text{ kJ mol}^{-1}$$

- Lattice enthalpy cannot be directly determined by experiment. For the determination of lattice enthalpy, an enthalpy diagram called **Born-Haber Cycle** is constructed.



-
- Sublimation of sodium metal:

$$\mathrm{Na}(s) \longrightarrow \mathrm{Na}(g)\ ;\ \Delta_{\mathrm{sol}}H^{\ominus} = 108.4\ \mathrm{kJ\ mol^{-1}}$$

-
- Ionization of sodium atoms (ionization enthalpy);

$$\mathrm{Na}(g) \longrightarrow \mathrm{Na}^{+}(g) + \mathrm{e}^{-}(g)\ ;\ \Delta_{\mathrm{i}}H^{\ominus} = 496\ \mathrm{kJ\ mol^{-1}}$$

-
- Dissociation of chlorine (reaction enthalpy is half the bond dissociation enthalpy):

$$\frac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{Cl}(g)\ ;\ \frac{1}{2}\Delta_{\mathrm{bond}}H^{\ominus} = 121\ \mathrm{kJ\ mol^{-1}}$$

-
- Electron gained by chlorine atoms (electron gain enthalpy):

$$\mathrm{Cl}(g) + \mathrm{e}^{-}(g) \longrightarrow \mathrm{Cl}(g)\ ;\ \Delta_{\mathrm{eg}}H^{\ominus} = -348.6\ \mathrm{kJ\ mol^{-1}}$$

-

- $\mathrm{Na^+}(g) + \mathrm{Cl^-}(g) \longrightarrow \mathrm{Na^+Cl^-}(s)$

  Applying Hess's Law,

  $$\Delta_{\text{lattice}} H^{\ominus} = 411.2 + 108.4 + 121 + 496 - 348.6$$
  $$\Delta_{\text{lattice}} H^{\ominus} = +788 \text{ kJ (for NaCl)}$$

-

- Internal energy is smaller by 2 RT (because $n_g = 2$) and is equal to 783 kJ mol^{-1}.

- The value of lattice enthalpy can be used to calculate the enthalpy of solution.

  Spontaneity & Entropy

  Second law of Thermodynamics can be stated as follows:

  Kelvin–Planck Statement

  It is not possible to design a heat engine which works in cyclic process and whose only result is to take heat from a body at a single temperature and convert it completely into mechanical work.

  Clausius Statement

  It is impossible for a self-acting machine, unaided by any external agency, to transfer heat from a body at lower temperature to another at higher temperature.

  Spontaneity

- A reaction is said to be spontaneous if it occurs immediately when contact is made between the reactants.

- Spontaneity means having the potential to proceed without the assistance of an external agency.

- Spontaneous processes are irreversible, and sometimes may be reversed only by an external agency.

  Enthalpy as a Criterion for Spontaneity

- With the decrease in energy (or enthalpy), the reactions become spontaneous, as in the case of an exothermic reaction.

- Examples:

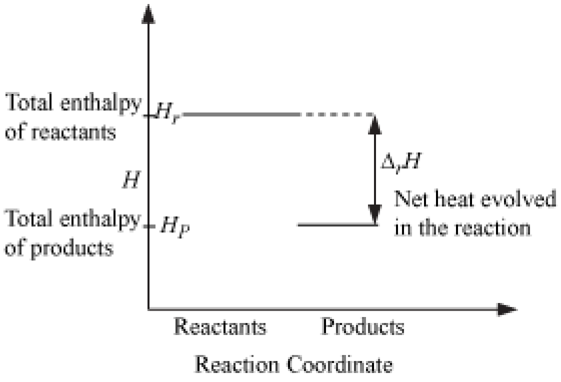
$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightarrow NH_3(g);$$

$$\Delta_r H^{\ominus}=-46.1\,\text{kJ mol}^{-1}$$

$$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\rightarrow HCl(g);$$

$$\Delta_r H^{\ominus}-92.32\,\text{kJ mol}^{-1}$$

- Decrease in energy on passing from the reactants to the products, for any exothermic reaction, is shown in the following enthalpy diagram:

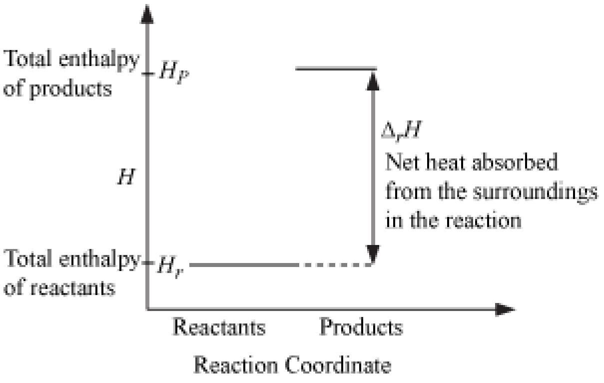


- Endothermic reactions may also be spontaneous.

- For example − C (graphite, *s*) + 2S (*l*) → CS_2 (*l*);

  $\Delta_r H^{\theta}$ = + 128.5 kJ mol^{-1}

- Increase in enthalpy from the reactants to the products, for endothermic reactions, is shown in the following enthalpy diagram:



- Though decrease in enthalpy is a contributory factor for spontaneity, it is not true for all cases.

Entropy

- It is denoted by S.
- It is a state function and ΔS is independent of path.
- Entropy is a measure of the degree of randomness or disorder in a system.
- Greater the disorder of a system, the higher is the entropy. The decrease of regularity in structure means increase in entropy.
- Crystalline solid is the state of lowest entropy (most ordered) and the gaseous state is a state of highest entropy.
- As the temperature increases, randomness increases, and thus, entropy increases.
- For a reversible reaction, entropy change (ΔS) $\propto \frac{1}{T}$
- $\Delta S = \frac{q_{\text{rev}}}{T}$ (for a reversible reaction)
- $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0$
- At equilibrium, $\Delta S = 0$
- Entropy of a spontaneous reaction increases till it reaches the maximum, and at equilibrium, $\Delta S = 0$

- Entropy is a state property. Therefore, entropy change for a reversible process is given by

$$\Delta S_{\text{sys}} = \frac{q_{\text{sys,rev}}}{T}$$

- For reversible and irreversible isothermal expansion of an ideal gas (that is under isothermal conditions), $\Delta U = 0$. But ΔS_{total} that is, $\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ is not zero for the irreversible process.

Third law of Thermodynamics

The third law of thermodynamics states that at absolute zero (0 K or -273.15 ^{o}C), the entropy of a perfectly crystalline substance is zero and it is known as absolute entropy.

Gibbs Free Energy

Gibb's free energy:

In thermodynamics, the Gibb's free energy is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and pressure. Gibb's free energy is that thermodynamic quantity of a system, it helps in the development of the criterion of spontaneity or feasibility of a process.

Gibb's energy or Gibb's function (G) can be defined as

$$G = H - TS$$

Where,
H = Heat content
T = Absolute temperature
S = Entropy of the system

G is an extensive property and a state function.

The change in Gibb's energy for the system ΔG_{sys}, is given by

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} - S_{\text{sys}}\,\Delta T$$

At constant T, $\Delta T = 0$

$$\therefore \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

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

- ΔG has the units of energy.
- ΔG is related to reaction spontaneity. It gives the criteria for spontaneity at constant pressure and temperature.
- For spontaneous process, $\Delta S_{\text{total}} > 0$

  $T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$
  $-(\Delta H_{\text{sys}} - T\Delta S_{\text{ys}}) > 0$

  $\therefore - \Delta G > 0$

  Or, $\Delta G = \Delta H - T\Delta S < 0$

- If $\Delta G < 0$ (i.e., negative), the process is spontaneous.
- If $\Delta G > 0$ (i.e., positive), the process is non-spontaneous.
- When a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous if $T\Delta S$ is large enough to outweigh ΔH.
- The following table summarises the effect of temperature on the spontaneity of reactions:

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description
−	+	− (at all T)	Reaction spontaneous at all temperatures
−	−	− (at low T)	Reaction spontaneous at low temperature
−	−	+ (at high T)	Reaction non-spontaneous at high temperature
+	+	+ (at low T)	Reaction non-spontaneous at low temperature
+	+	− (at high T)	Reaction spontaneous at high temperature
+	−	+ (at all T)	Reaction non-spontaneous at all temperatures

- The criterion for equilibrium $A + B \longleftrightarrow C + D$ is $\Delta_r G = 0$

- $\Delta_r G^\ominus$ (Gibb's energy change for a reaction in the standard state) is related to the equilibrium constant (*K*) of the reaction as follows:

  $0 = \Delta_r G^\ominus + RT \ln K$

  Or, $\Delta_r G^\ominus = -RT \ln K$

  Or, $\Delta_r G^\ominus = -2.303\ RT \log K$

  Thus $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -RT \ln K$

- The value of $\Delta_r G^\ominus$ at any temperature can be calculated if *K* is measured directly in the laboratory.

- The value of $\Delta_r G^\ominus$ can be obtained from the measurement of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$, and then *K* can be calculated at any temperature.

- For strongly endothermic reactions:

  Value of $\Delta_r H^\ominus$ = Large and positive

  Value of *K* << 1

  → The reaction is not likely to form much product

- For strongly exothermic reactions:

  The value of $\Delta_r H^\ominus$ = Large and negative

  The value of $\Delta_r G^\ominus$ = Large and negative

  ∴The value of *K* >> 1

  → Large value of *K* shows that the reaction goes to near completion.

Example

The value of equilibrium constant for a water–gas reaction, $C(s)+H_2O(g)\longleftrightarrow CO(g)+H_2(g)$ (the standard Gibbs energy for the reaction is − 8.1 kJ mol^{-1}) at 1000°C can be calculated as

$$
\begin{aligned}
\Delta G^{\ominus} &= -2.303\,RT\log K \\
\log K &= \frac{-\Delta G^{\ominus}}{2.303RT} \\
&= \frac{-\left(-\,8.1\times10^{3}\right)}{2.303\times8.314\times1273} \\
&= 0.3323 \\
\therefore K &= 2.149
\end{aligned}
$$

Helmholtz free energy:

In thermodynamics, the Helmholtz free energy is a thermodynamic potential that measures the useful work obtained from a closed thermodynamic system at a constant temperature and volume.

The Helmoholtz energy is defined as:

A = U - TS

where,

A is the Helmholtz free energy.

U is the internal energy of the system.

T is the absolute temperature.

S is the entropy of the system.

The above definition may be obtained from the internal energy function by means of one Legendre transform.

The Helmholtz free energy has (T,V) as the natural pair of variables.

Differentiating the expression for A,

$$dA = dU - TdS - SdT$$

Using the combined mathematical form of first and second laws of thermodynamics, TdS = dU + pdV,

$$\Rightarrow dA = -pdV - SdT$$

Thus, A=A(V,T)
That is why the Helmholtz free energy is known as thermodynamic potential at constant volume.
It stays constant during any isothermal-isochoric change.

For such a system, the Helmholtz free energy tends to minimize as the system tends to equilibrium.

Relationship between Gibb's free energy and Helmholtz's free energy:

According to Gibb's free energy,
G = H - TS ....(1)

We know,
H = U + PV ....(2)

Put equation (2) in equation (1)
G = U +PV - TS
But,
A = U - TS
Then,
G = A + PV
This is relationship between Gibb's free energy and Helmholtz's free energy.