

Thermodynamics

- A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.
- The wall that separates the system from the surroundings is called boundary. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.
- Types of the System

- Open System

In an open system, there is exchange of energy and matter between system and surroundings. The presence of reactants in an open beaker is an example of an open system.

- Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.

- Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

- The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. Variables like p , V , T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.
- Internal energy, U of the 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.
- $\Delta U = q + w$ is mathematical statement of the first law of thermodynamics, which states that “The energy of an isolated system is constant.”
- A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as irreversible processes.

- Isothermal and free expansion of an ideal gas

For isothermal ($T = \text{constant}$) expansion of an ideal gas into vacuum ; $w = 0$ since $p_{\text{ex}} = 0$. Also, Joule determined experimentally that $q = 0$; therefore, $\Delta U = 0$

$\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:

- For isothermal irreversible change

$$q = -w = p_{\text{ex}} (V_f - V_i)$$

For isothermal reversible change

$$q = -w = nRT \ln (V_f/V_i)$$

- = 2.303 nRT log (V_f/V_i)

- 3. For adiabatic change, $q = 0$,

$$\Delta U = w_{\text{ad}}$$

- $\Delta H = \Delta U + \Delta n_g RT$
- ΔH is negative for exothermic reactions which evolve heat during the reaction and ΔH is positive for endothermic reactions which absorb heat from the surroundings.
- An extensive property is a property whose value depends on the quantity or size of matter present in the system .
For example, mass.
- Those properties which do not depend on the quantity or size of matter present are known as intensive properties.
For example, temperature.
- For finding out the heat, q , required to raise the temperatures of a sample, we multiply the specific heat of the substance, c , by the mass m , and temperatures change, ΔT as
$$q = c \times m \times \Delta T$$
- $C_p - C_v = R$

- The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$.
- $\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$
- The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.
- The standard state of a substance at a specified temperature is its pure form at 1 bar.
- The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{\text{fus}} H^0$.
- Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{\text{vap}} H^0$.
- Standard enthalpy of sublimation, $\Delta_{\text{sub}} H^0$ is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1 bar).

- The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^0$.
- It would be necessary to remember the following conventions regarding thermochemical equations.
 - The coefficients in a balanced thermochemical equation refer to the number of moles (never molecules) of reactants and products involved in the reaction.
 - The numerical value of $\Delta_r H^0$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^0$ will have units as kJ mol^{-1} .
- Hess's Law : If a reaction takes place in several steps then 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 .

- ΔS is related with q and T for a reversible reaction as :

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

- The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

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

- When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$. We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

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

- Gibb's function $G = H - TS$
- Chemical reactions are generally carried at constant pressure, so we define another state function Gibbs energy, G , which is related to entropy and enthalpy changes of the system by the equation:

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

- For a spontaneous change, $\Delta G_{\text{sys}} < 0$ and at equilibrium, $\Delta G_{\text{sys}} = 0$.
- Standard Gibbs energy change is related to equilibrium constant by

$$\Delta_r G^0 = -RT \ln K.$$

- K can be calculated from this equation, if we know $\Delta_r G^0$ which can be found from $\Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction.

Sample Examples

- Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

Solution

We have $q = -w = p_{\text{ex}}(10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

- Consider the same expansion, but this time against a constant external pressure of 1 atm.

Solution

We have $q = -w = p_{\text{ex}}(8) = 8 \text{ litre-atm}$

- Consider the same expansion, to a final volume of 10 litres conducted reversibly.

Solution

We have $q = -w = 2.303 \times 10 \log(10/2)$

= 16.1 litre-atm

- If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol⁻¹. Calculate the internal energy change, when
 - (i) 1 mol of water is vaporised at 1 bar pressure and 100°C.
 - (ii) 1 mol of water is converted into ice.

Solution

(i) The change $\text{H}_2\text{O} \rightarrow \text{H}_2$

$$\Delta H = \Delta U + \Delta n$$

or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get

$$\Delta U = 41.00 \text{ kJ} - 8.3 \text{ J} * 373 \text{ K} * 1$$

$$= 37.904 \text{ kJmol}^{-1}$$

(ii) The change $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

There is negligible change in volume,

So, we can put $p\Delta V = n_g RT$ in this case,

$$\Delta H \cong \Delta U$$

so, $\Delta U = 41$.