

Thermodynamics

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Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings.

First law of thermodynamics is also called as law of conservation of energy. It states that energy can neither be created nor destroyed. It also states that the energy of an isolated system is constant.

Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w).

These quantities are related through the first law of thermodynamics via $\Delta U = q + w$. ΔU is the change in internal energy. It depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions.

We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system. We can measure the transfer of heat from one system to another which causes the change in temperature.

The magnitude of rise in temperature depends on the heat capacity (C) of a substance. Therefore, heat absorbed or evolved is $q = C\Delta T$. Work can be measured by $w = -P\Delta V$ in case of expansion of gases.

Work done in isothermal and reversible expansion of ideal gas is

$$W_{\text{rev}} = -2.303n RT \log \frac{V_f}{V_i}$$

ΔU is measured by using special calorimeter called bomb calorimeter.

We define another state function, **enthalpy**.

The enthalpy of a system may be defined as the sum of the internal energy and the product of its pressure and volume. It is denoted by the symbol H and is given by $H = U + PV$

An extensive property is a property whose value depends on the quantity or size of matter present in the system. Examples are enthalpy, mass, heat capacity, volume, internal energy, etc.

An intensive property is a property whose value does not depend on the quantity or size of matter present in the system. Examples are temperature, density, pressure, etc.

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

Relation between amount of heat, q, required to raise the temperatures of a sample, specific heat of the substance, c and change in temperatures is given as:

$$q = mc \Delta T = C \Delta T$$

Enthalpy change, $\Delta H = \Delta U + \Delta n_g RT$, can be found directly from the heat changes at constant pressure, $\Delta H = q_p$.

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive.

The enthalpy change accompanying a reaction is called the reaction enthalpy ($\Delta_r H$)
 $\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$

A balanced chemical equation together with the value of its $\Delta_r H^\ominus$ is called a **thermochemical equation**

Enthalpy of formation, combustion and other enthalpy changes can be calculated using **Hess's law**.

Hess's Law of Constant Heat Summation states: 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

Enthalpy change for chemical reactions can be determined by

$$\Delta_r H = \sum_f (a_f \Delta_f H_{products}) - \sum_t (b_t \Delta_f H_{reactions})$$

And in gaseous state by

$$\Delta_r H^\ominus = \sum \text{bond enthalpies of the reactants} - \sum \text{bond enthalpies of the products.}$$

First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems, $DU = 0$.

Born-Haber Cycle is used to determine lattice enthalpy of ionic compounds since they cannot be determined by experiment directly.

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

We define another state function, S, **entropy** for this purpose.

Second Law of thermodynamics states that the entropy of the universe is continuously increasing due to spontaneous processes taking place in it.

Entropy (S) is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated system, $DU = 0$, $DS > 0$, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured by the equation $\Delta S = \frac{q_{rev}}{T}$ for a reversible process. $\frac{q_{rev}}{T}$ is independent of path.

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 $\Delta G_{sys} < 0$ and at equilibrium, $\Delta G_{sys} = 0$.

If $\Delta G_{sys} > 0$, process is non-spontaneous.

Standard Gibbs energy change is related to equilibrium constant by

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

K can be calculated from this equation, if we know $\Delta_r G^\theta$ which can be found from $\Delta_r G^\theta = \Delta_r H^\theta - T \Delta_r S^\theta$.

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.