
CBSE Class 11 Chemistry
NCERT Exemplar Solutions
Chapter 6
Thermodynamics

Long Answer Type

58. Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

Ans. We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_V$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure $\Delta U = q_p - p\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2.

We can rewrite the above equation as

$$U_2 - U_1 = p(V_2 - V_1)$$

On rearranging, we get

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \dots (1)$$

Now, we can define another thermodynamic function, the enthalpy H [Greek word enthalpien, to warm or heat content] as:

$$H = U + pV \dots (2)$$

So, equation (1) becomes

$$q_p = H_2 - H_1 = \Delta H$$

Although, q is a path dependent function, H is a state function because it depends on U , p and V , all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path.

For finite changes at constant pressure, we can write equation (2) as

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

Since p is constant, we can write:

$$\Delta H = \Delta U + p\Delta V \dots (3)$$

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

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.

At constant volume ($\Delta V = 0$), $\Delta U = q_v$, therefore, equation (3) becomes
 $\Delta H = \Delta U = q_v$

Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$pV_A = n_A RT$$

$$\text{and } pV_B = n_B RT$$

$$\text{Thus, } pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A) RT$$

$$\text{or } p(V_B - V_A) = (n_B - n_A) RT$$

$$\text{or } p\Delta V = \Delta n_g RT \dots (4)$$

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ from equation (4) in equation (3), we get

$$\Delta H = \Delta U + \Delta n_g RT \dots (5)$$

59. Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.

Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole

fraction, specific heat, temperature and molarity.

Ans. In thermodynamics, a distinction is made between extensive properties and intensive properties. An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, the following are extensive properties: mass, volume, internal energy, enthalpy, heat capacity.

Those properties which do not depend on the quantity or size of matter present, are known as intensive properties. For example, the following are intensive properties: temperature, density, pressure. A molar property, χ_m , is the value of an extensive property χ of the

$$\chi_m = \frac{\chi}{n}$$

system for 1 mol of the substance. If n is the amount of matter, χ_m is independent of the amount of matter. The ratio of two extensive properties is always an intensive property.

$$\frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$$

e.g.,
$$\text{Mole fraction} = \frac{\text{Moles}}{\text{Total number of moles}} = \frac{(\text{Extensive})}{(\text{Extensive})}$$

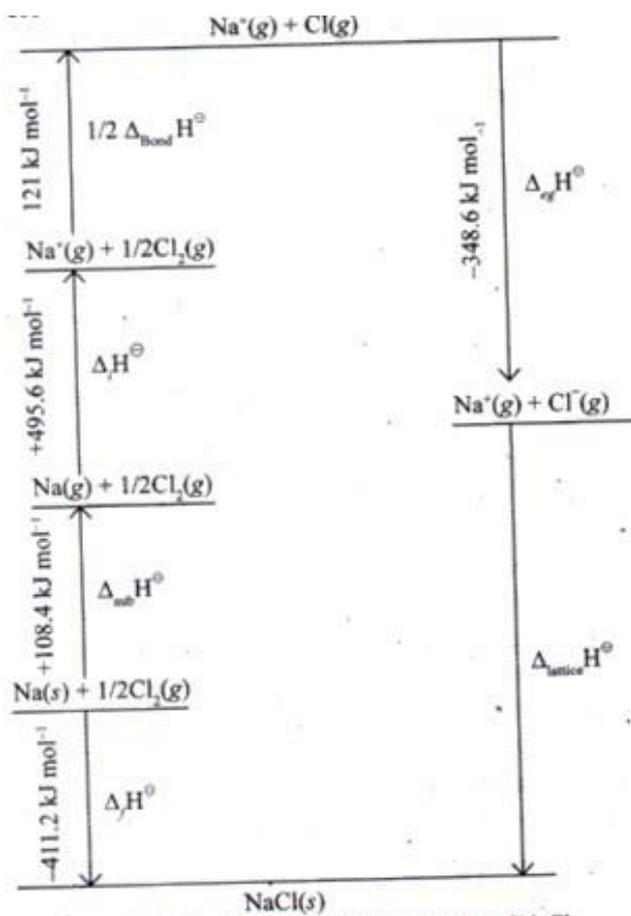
60. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of NaCl(s).

Ans. 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.



$$\Delta_{\text{lattice}} H^\ominus \rightarrow +788 \text{ kJ mol}^{-1}$$

Let us now calculate the lattice enthalpy of $\text{Na}^+ \text{Cl}^- (s)$ by following steps given below:



Enthalpy diagram for lattice enthalpy of NaCl

1. $Na(s) \rightarrow Na(g)$, sublimation of sodium metal, $\Delta_{sub}H^\ominus = 108.4 \text{ kJ mol}^{-1}$.
2. $Na(g) \rightarrow Na^+(g) + e^-(g)$ the ionization of sodium atoms, ionization enthalpy. $\Delta_iH^\ominus = 496 \text{ kJ mol}^{-1}$
3. $\frac{1}{2}Cl_2(g) \rightarrow Cl^-(g)$, the dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy. $\frac{1}{2}\Delta_{bond}H^\ominus = 121 \text{ kJ mol}^{-1}$.
4. $Cl(g) + e^-(g) \rightarrow Cl(g)$ electron gained by chlorine atoms. The electron gain enthalpy, $\Delta_{eg}H^\ominus = -348.6 \text{ kJ mol}^{-1}$
5. $Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s)$

61. ΔG is net energy available to do useful work and is thus a measure of “free energy”. Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG . If a

reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous?

Ans. We know,

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surv}}$$

If the system is in thermal equilibrium with the surroundings, then the temperature of the surroundings is same as that of the system. Also, increase in enthalpy of the surroundings is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{\text{surv}} = \frac{\Delta H_{\text{surv}}}{T} = -\frac{\Delta H_{\text{sys}}}{T}$$
$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} = \left(-\frac{\Delta H_{\text{sys}}}{T} \right)$$

Rearranging the above equation:

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

For spontaneous process,

$$\Delta S_{\text{total}} > 0, \text{ so}$$

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

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

The above equation can be written as

$$-\Delta G > 0$$

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

ΔH_{sys} is the enthalpy change of a reaction, $T \Delta S_{\text{sys}}$ is the energy which is not available to do useful work. So, ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

ΔG gives a criteria for spontaneity at constant pressure and temperature,

(i) If ΔG is negative (<0), the process is spontaneous.

(ii) If ΔG is positive (>0), the process is non-spontaneous.

• Unit of ΔG is Joule.

• The reaction will be spontaneous at high temperature.

62. Graphically show the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_f, V_f) . With the help of a pV plot compare the work done in the above case with that carried out against a constant external pressure p_f .

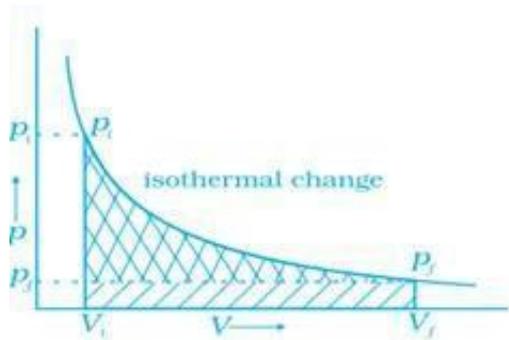


Fig. : 6.9

Ans.(i) Reversible work is represented by the combined areas  and .

(ii) Work against constant pressure, p_f is represented by the area  Work (i) > Work (ii).