

Class 11 Chemical Thermodynamics Important Questions with Answers

Short Answer Type Questions

1. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol⁻¹. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?

Answer.

Given that, the amount of water is 18.0 g, and the pressure is 1 bar.

As we all know, 18.0 g H₂O = 1 mole H₂O.

Enthalpy change for vaporising 1 mole of H₂O = 40.79 kJ mol⁻¹

∴ Enthalpy change for vaporising 2 moles of H₂O = 2 × 40.79 kJ = 81.358 kJ

Standard enthalpy of vaporisation at 100°C and 1 bar pressure,

$\Delta_{\text{vap}} \text{H}_2\text{O} = + 40.79 \text{ kJ mol}^{-1}$.

2. One mole of acetone requires less heat to vapourise than 1 mol of water. Which of the two liquids has higher enthalpy of vapourisation?

Answer.

Acetone requires less heat to vaporise due to the weak force of attraction between molecules.

As a result, water has a higher enthalpy of vaporisation.

It can be represented as:

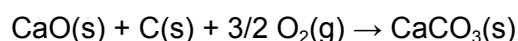
$\Delta_{\text{vap}}(\text{water}) > \Delta_{\text{vap}}(\text{acetone})$

3. Standard molar enthalpy of formation, $\Delta_f H^\ominus$ is just a special case of enthalpy of reaction, $\Delta_r H^\ominus$. Is the $\Delta_r H^\ominus$ for the following reaction same as $\Delta_f H^\ominus$? Give reason for your answer. $\text{CaO(s)} + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s})$; $\Delta_f H^\ominus = -178.3 \text{ kJ mol}^{-1}$

Answer.

No, the $\Delta_r H^\ominus$ for the given reaction is not same as $\Delta_f H^\ominus$.

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states (reference states) is called standard molar enthalpy of formation, $\Delta_f H^\ominus$.



This reaction is different from the given reaction. Hence, $\Delta_r H^\ominus \neq \Delta_f H^\ominus$.

4. The value of $\Delta_f H^\ominus$ for NH_3 is $-91.8 \text{ kJ mol}^{-1}$. Calculate enthalpy change for the following reaction:
 $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

Answer.

$\Delta_f H^\ominus$ is given for formation. For the reverse reaction, $\Delta_f H^\ominus$ changes sign because the opposite of an exothermic reaction is an endothermic reaction.

So, for one mole, $\Delta_f H^\ominus$ for decomposition is $-(-91.8) = 91.8$.

However, two moles are decomposing here.

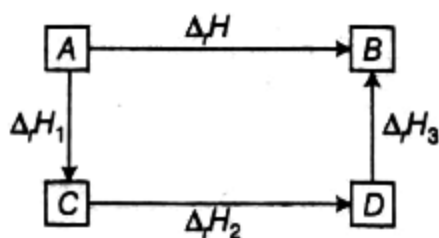
Therefore, $\Delta_r H^\ominus = 2 \times 91.8 = 183.6 \text{ kJ mol}^{-1}$.

5. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction $\text{A} \rightarrow \text{B}$ along one route is $\Delta_r H$ and $\Delta_r H_1, \Delta_r H_2, \Delta_r H_3, \dots$ represent enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1, \Delta_r H_2, \dots$ etc. for intermediate reactions.

Answer.

In general, if enthalpy of an overall reaction $\text{A} \rightarrow \text{B}$ along one route is $\Delta_r H$ and $\Delta_r H_1, \Delta_r H_2, \Delta_r H_3, \dots$ represent enthalpies of reaction leading to same product B through another route, then we have $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \dots$

For a general reaction Hess's law of constant heat summation can be represented as



6. The enthalpy of atomisation for the reaction $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$ is 1665 kJ mol^{-1} . What is the bond energy of C-H bond?

Answer.

Enthalpy of atomisation of 4 moles of C-H bonds $= 1665 \text{ kJ mol}^{-1}$

$\therefore$ C-H bond energy, per mole $= 1665 \text{ kJ mol}^{-1} / 4 = 416.2 \text{ kJ mol}^{-1}$.

7. Use the following data to calculate $\Delta_{\text{lattice}} H^\ominus$ for NaBr.

$\Delta_{\text{sub}} H^\ominus$ for sodium metal $= 108.4 \text{ kJ mol}^{-1}$

Ionization enthalpy of sodium $= 496 \text{ kJ mol}^{-1}$

Electron gain enthalpy of bromine $= -325 \text{ kJ mol}^{-1}$

Bond dissociation enthalpy of bromine $= 192 \text{ kJ mol}^{-1}$

$\Delta_f H^\ominus$ for NaBr (s) $= -360.1 \text{ kJ mol}^{-1}$

Answer.

According to Hess's Law,

$$\Delta_f H^\ominus = \Delta_{\text{sub}} H^\ominus + \Delta_{\text{IE}} H^\ominus + \Delta_{\text{diss}} H^\ominus + \Delta_{\text{tg}} H^\ominus + U$$

$$\Delta_{\text{sub}} H^\ominus \text{ for Na metal} = 108.4 \text{ kJ/mol}$$

$$\text{I.E. of Na} = 496 \text{ kJ/mol}$$

$$\Delta_{\text{tg}} H^\ominus \text{ of Br} = -325 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{diss}} H^\ominus \text{ of Br} = 192 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus \text{ for NaBr} = -360.1 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus = \Delta_{\text{sub}} H^\ominus + \text{I.E. of Na} + \Delta_{\text{diss}} H^\ominus + \Delta_{\text{tg}} H^\ominus + U$$

$$-360.1 = 108.4 + 496 + 96 + (-325) - U$$

$$U = +735.5 \text{ kJ/mol}$$

8. Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?

Answer.

It is a spontaneous process. Although the change in enthalpy is zero, the change in randomness or disorder (i.e., ΔS) increases. As a result, in the equation $\Delta G = \Delta H - T\Delta S$, the term $T\Delta S$ will be negative. As a result, ΔG will be negative.

9. Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system. Write the mathematical relation which relates these three parameters.

Answer.

Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system.

The mathematical relation which relates these three parameters is $\Delta S = q_{\text{rev}} / T$

Here, ΔS = change in entropy

q_{rev} = heat of reversible reaction

T = temperature

10. Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Will the temperature of system and surroundings be the same when they are in thermal equilibrium?

Answer.

Yes, when the system and the surroundings are in thermal equilibrium, their temperatures are same.

11. At 298 K. K_p for the reaction $\text{N}_2\text{O}_4 (\text{g}) \rightleftharpoons 2\text{NO}_2 (\text{g})$ is 0.98. Predict whether the reaction is spontaneous or not.

Answer.

For a spontaneous reaction, $\Delta_r G^\circ$ is -ve.

$$\Delta_r G^\circ = -RT \ln K_p = -RT \ln (0.98)$$

$\ln (0.98)$ is -0.02

$$\therefore \Delta_r G^\circ = -RT \times -0.02$$

$\therefore \Delta G^\circ$ will be positive.

Hence, the reaction will be non spontaneous.

12. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in Fig. 6.1. What will be the value of ΔH for the cycle as a whole?

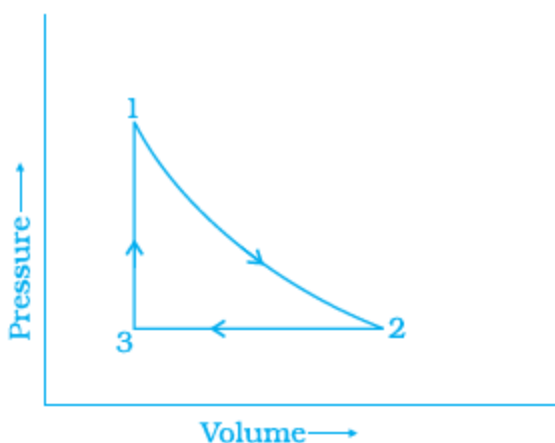


Fig. : 6.1

Answer.

The change in internal energy during a cyclic process is zero.

$$\Delta U = 0$$

As the system returns to its initial state, no work is said to have been done.

Enthalpy for a steady-state cyclic process is one single value at any given stage, but it varies at different stages.

$$\Delta H = 0$$

13. The standard molar entropy of H_2O (l) is $70 \text{ J K}^{-1} \text{ mol}^{-1}$. Will the standard molar entropy of H_2O (s) be more, or less than $70 \text{ J K}^{-1} \text{ mol}^{-1}$?

Answer.

The solid form of H_2O is ice. In ice, molecules are less random than in liquid water.

Thus, molar entropy of H_2O (s) < molar entropy of H_2O (l). The standard molar entropy of H_2O (s) is less than $70 \text{ J K}^{-1} \text{ mol}^{-1}$.

14. Identify the state functions and path functions out of the following: enthalpy, entropy, heat, temperature, work, free energy.

Answer.

State Functions: Enthalpy, Entropy, Temperature, Free energy

Path Functions: Heat, Work

15. The molar enthalpy of vaporization of acetone is less than that of water. Why?

Answer.

Acetone lacks hydrogen bond, so intermolecular forces are weaker, causing it to boil/evaporate quickly, lowering the molar enthalpy of vaporisation. Furthermore, because acetone lacks a polar O-H bond, it has a low enthalpy. Water has both a non-polar region and a strong hydrogen bond.

16. Which quantity out of $\Delta_r G$ and $\Delta_r G^\ominus$ will be zero at equilibrium?

Answer.

$\Delta_r G$ will always be zero.

$\Delta_r G^\ominus$ is zero for $K = 1$ because $\Delta_r G^\ominus = -RT \ln K$

$\Delta_r G^\ominus$ will be non zero for other values of K .

17. Predict the change in internal energy for an isolated system at constant volume.

Answer.

There is no energy transfer as heat or work in an isolated system, so $w=0$ and $q=0$.

According to the first law of thermodynamics-

$$\Delta U = q + w = 0 + 0 = 0$$

$$\Delta U = 0$$

18. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

Answer.

(i) At constant volume-

By first law of thermodynamics: $q = \Delta U + (-w)$

$$(-w) = p\Delta V$$

$$\therefore q = \Delta U + p\Delta V$$

$\Delta V = 0$, since volume is constant.

$$\therefore q_v = \Delta U + 0 \Rightarrow q_v = \Delta U = \text{change in internal energy}$$

(ii) At constant pressure

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

$$\text{But, } \Delta U + p\Delta V = \Delta H$$

$$\therefore q_p = \Delta H = \text{change in enthalpy.}$$

So, at a constant volume and at constant pressure heat change is a state function because it is equal to change in internal energy and change in enthalpy respectively which are state functions.

19. Expansion of a gas in vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of ideal gas expands isothermally into vacuum until its total volume is 5 litre?

Answer.

$$(-w) = p_{\text{ext}} (V_2 - V_1) = 0 \times (5 - 1) = 0$$

For isothermal expansion $q = 0$

By first law of thermodynamics-

$$q = \Delta U + (-w)$$

$$0 = \Delta U + 0$$

$$\text{so, } \Delta U = 0$$

20. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mol of water?

Answer.

For water, heat capacity = $18 \times$ specific heat

$$\text{or } C_p = 18 \times c$$

$$\text{Specific heat, } c = 4.18 \text{ Jg}^{-1} \text{ K}^{-1}$$

$$\text{Heat capacity, } C_p = 18 \times 4.18 \text{ JK}^{-1} = 75.3 \text{ J K}^{-1}.$$

21. The difference between C_p and C_v can be derived using the empirical relation $H = U + pV$. Calculate the difference between C_p and C_v for ten moles of an ideal gas.

Answer.

For 1 mole of gas

$$C_p - C_v = R$$

$$\text{For } n \text{ moles of gas the relation is } C_p - C_v = nR = 10 \times 4.184 \text{ J}$$

$$C_p - C_v = 41.84 \text{ J.}$$

22. If the combustion of 1g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Free the significance of sign also.

Answer.

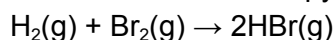
Molar enthalpy change of graphite = enthalpy change for 1g carbon × molar mass of carbon

$$\Delta H = -20.7 \text{ kJ g}^{-1} \times 12 \text{ g mol}^{-1}$$

$$\Delta H = -2.48 \times 10^2 \text{ kJ mol}^{-1}.$$

The exothermic nature of the reaction is indicated by the negative sign of ΔH .

23. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction.



Given that Bond energy of H_2 , Br_2 and HBr is 435 kJ mol^{-1} , 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.

Answer.

$$\Delta_r H^\ominus = \text{Bond energy of } \text{H}_2 + \text{Bond energy of } \text{Br}_2 - 2 \times \text{Bond energy of } \text{HBr}$$

$$\Delta_r H^\ominus = 435 + 192 - (2 \times 368) \text{ kJ mol}^{-1}$$

$$\Delta_r H^\ominus = -109 \text{ kJ mol}^{-1}.$$

24. The enthalpy of vapourisation of CCl_4 is 30.5 kJ mol^{-1} . Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of $\text{CCl}_4 = 154 \text{ g mol}^{-1}$).

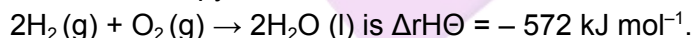
Answer.

$$q_p = \Delta H = 30.5 \text{ kJ mol}^{-1}$$

∴ Heat required for vapourisation of 284 g of CCl_4

$$= \frac{284}{154 \text{ g mol}^{-1}} \times 30.5 \text{ kJ mol}^{-1} = 56.2 \text{ kJ}$$

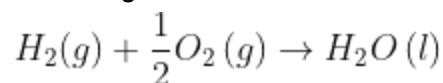
25. The enthalpy of reaction for the reaction:



What will be standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$?

Answer.

The enthalpy change for the following reaction will be the standard enthalpy of formation of H_2O , according to the definition of standard enthalpy of formation.



or the standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ will be half of the given equation's enthalpy, i.e., $\Delta_r H^\ominus$ is also halved.

$$\Delta_f H_{\text{H}_2\text{O}}^\ominus(\text{l}) = \frac{1}{2} \Delta_r H^\ominus$$

$$= \frac{-572 \text{ kJ mol}^{-1}}{2} = -286 \text{ kJ mol}^{-1}$$

26. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Fig. 6.2. Explain graphically.

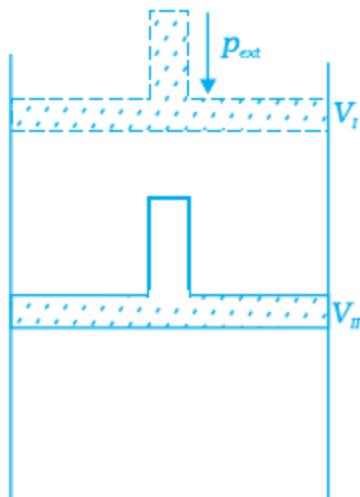


Fig. : 6.2

Answer.

Work done on an ideal gas can be calculated from p-V graph shown in Fig. 6.6. Work done is equal to the shaded area ABV_IV_{II}.

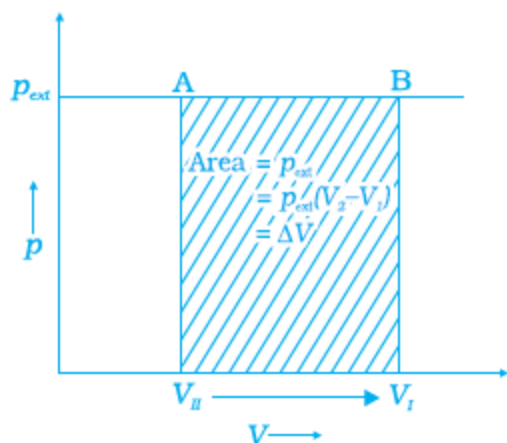


Fig. : 6.6

27. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?

Answer.

A process or change is said to be reversible if it is carried out in such a way that the process can be reversed at any time by an infinitesimal change.

When pressure is not constant and changes occur in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f , work done can be calculated using a pV-plot. The shaded area represents the work done on the gas.

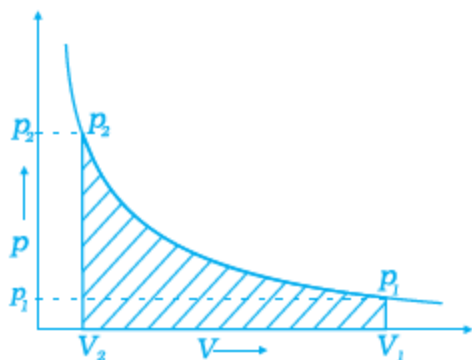


Fig. : 6.7

28. Represent the potential energy/enthalpy change in the following processes graphically.

(a) Throwing a stone from the ground to roof.

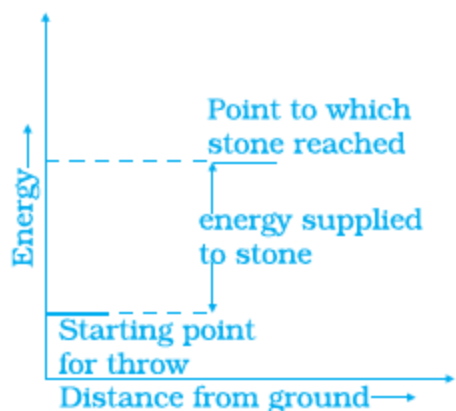
(b) $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightleftharpoons \text{HCl}(\text{g}); \Delta_r H^\ominus = -92.32 \text{ kJ mol}^{-1}$

In which of the processes potential energy/enthalpy change is contributing factor to the spontaneity?

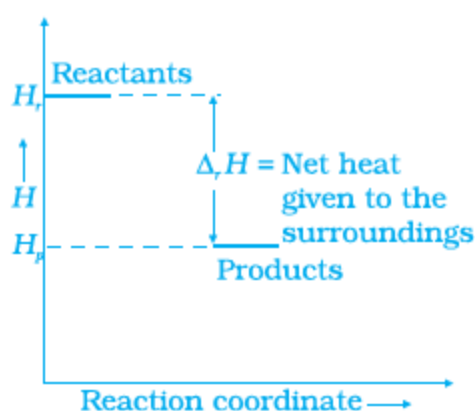
Answer.

(a) When throwing a stone from the ground to the roof, we must provide energy to the stone.

(b) When heat is produced in a reaction, it indicates that the process is followed by a decrease in energy.



(a)



(b)

Energy increases in (a) part while decreasing in (b). As a result, in process (b), the enthalpy change is a factor that contributes to the spontaneity.

29. Enthalpy diagram for a particular reaction is given in Fig. 6.3. Is it possible to decide spontaneity of a reaction from given diagram. Explain.

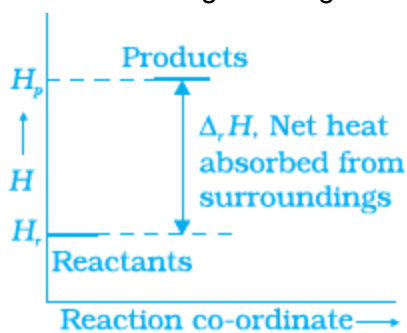


Fig. : 6.3

Answer.

No, enthalpy is not the only criterion for spontaneity; we must also consider entropy.

30. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in Fig. 6.4. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.

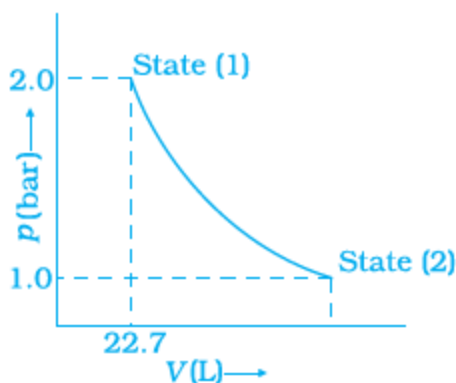


Fig. : 6.4

Answer.

Since the process is carried out in an infinite number of steps, it is clear from the diagram that it is a reversible change.

$$w = -2.303RT \log \frac{V_2}{V_1}$$

$$\frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$$

$$\therefore w = -2.303RT \log \frac{p_1}{p_2}$$

$$w = -2.303 \times 8.314 \text{ J mol}^{-1} \times 298 \text{ K}^{-1} \times \log 2$$

$$= -1717.46 \text{ J}$$

31. An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case? (Given that 1 L bar = 100 J).

Answer.

Work done in the process can be calculated as-

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

$$w = -2 \times 40 = -80 \text{ bar} = -8 \text{ kJ}$$

The negative sign indicates that the system is working on the environment. Because internal and external pressures are nearly equal at every step, the work done will be more in the reversible expansion.

Long Answer Type Questions

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

Answer.

When heated, the volume of solids and liquids does not change significantly. As a result, if the volume changes, ΔV is insignificant.

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

$$\Delta H = \Delta U + P(0)$$

$$\Delta H = \Delta U$$

When gases are involved in the reaction, the difference between the change in internal energy and the change in enthalpy becomes significant.

Consider a chemical reaction that takes place at a constant temperature, T , and pressure, P . Let's say the reactants' volume is V_A and the number of moles in the reactants is n_A . Similarly, the product volume is V_B , and the number of moles in the product is n_B .

We know from the ideal gas equation that-

$$pV = nRT$$

$$pV_A = n_A RT$$

$$pV_B = n_B RT$$

Thus,

$$pV_A - pV_B = n_A RT - n_B RT$$

$$p(V_A - V_B) = RT(n_A - n_B)$$

$$p\Delta V = \Delta n_g RT$$

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

$$\Delta H = \Delta U + \Delta n_g RT$$

2. 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.

Answer.

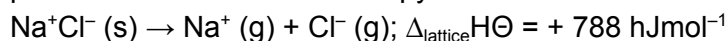
- Mass is an extensive property because it is dependent on the amount of matter.
- Internal energy is proportional to volume, making it an extensive property.
- Because pressure is independent of the amount of substance, it is an intensive property.
- Heat capacity is an extensive property, whereas molar heat capacity is an intensive property because it is the ratio of two extensive properties.
- Density is an intensive property because it is the ratio of two extensive properties.
- Since mole fraction is the ratio of two extensive properties, it is an intensive property.
- Specific heat is an intensive property because it is independent of the amount of substance.

- An intensive property is a ratio of two extensive properties therefore molarity is an intensive property.
- Temperature is also an intensive property as it is independent of the amount of substance.

3. 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).

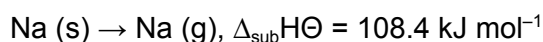
Answer.

When one mole of an ionic compound dissociates into its ions, the enthalpy change related to this process is called lattice enthalpy.

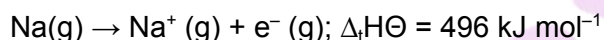


Lattice enthalpy for NaCl can be calculated as follows-

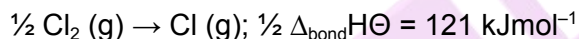
i. Sublimation of sodium metal



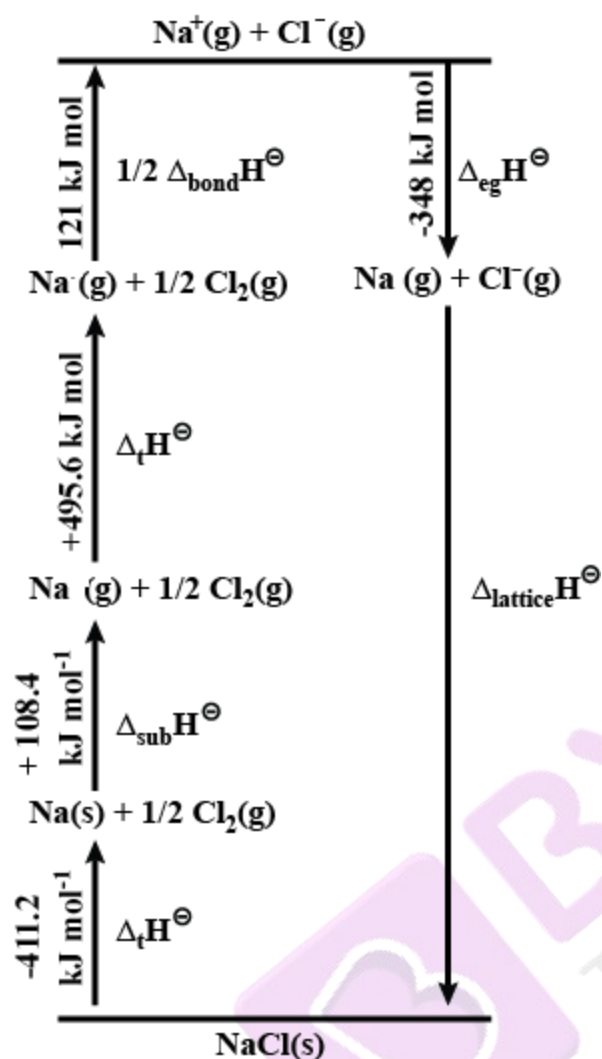
ii. Ionisation of sodium atoms



iii. Dissociation of chlorine molecule, the reaction is half the bond dissociation enthalpy.



iv. $\text{Cl}(\text{g}) + \text{e}^-(\text{g}) \rightarrow \text{Cl}^-(\text{g})$; electron gained by chlorine atoms. The electron gain enthalpy, $\Delta_{\text{eg}}\text{H}\Theta = - 348.6 \text{ kJ mol}^{-1}$.



4. 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?

Answer.

$$\Delta S_{\text{Total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

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

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

For spontaneous change, $\Delta S_{\text{Total}} > 0$

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

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

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

$$\therefore -\Delta G_{\text{sys}} > 0$$

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

ΔH_{sys} = Enthalpy change of a reaction

$T\Delta S_{\text{sys}}$ = Energy which is not available to do useful work

ΔG_{sys} = Energy available for doing useful work

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

Unit of ΔG is Joule.

The reaction will be spontaneous at high temperature.

5. 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 .

Answer.

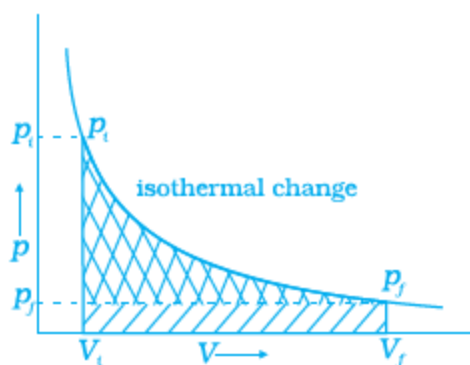


Fig. : 6.9

- (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)