Thermodynamics Chemistry Questions with Solutions

Q1. Under what conditions the heat evolved or absorbed is equal to the internal energy change?

Answer. The heat evolved or absorbed is equal to the internal energy change at constant volume.

Q2. Why enthalpy of neutralization of HF is greater than 57.1 kJ mol^{-1}?

Answer. This is due to the high hydration energy of fluoride ions.

Q3. Define a cyclic process.

Answer. A cyclic process is one in which the initial and final states are the same. It is a series of processes that end with the system in the same state in which it began.
The initial and final internal energies of a system are equal when it goes through a cyclic process. As a result, in any cyclic process, the internal energy change is zero.

Q4. Name two intensive and extensive properties of a system.

Answer. The intensive and extensive properties are as follows:
Intensive properties: Viscosity, refractive index.
Extensive properties: Mass, volume, heat capacity, etc.

Q5. Which of the following statements is correct?

a) The presence of reacting species in a covered beaker is an example of an open system.
b) There is an exchange of energy as well as a matter between the system and the surroundings in a closed system.
c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

Correct Answer: (c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.

Explanation: There is no exchange of matter in a closed system (for example, the presence of reactants in a closed vessel made of conducting material, such as copper), but there is an exchange of energy between the system and its surroundings.

Q6. What are the applications of Hess's Law of constant heat summation?

Answer. Hess's law is used-

- To calculate the heat of formation, combustion, neutralisation, ionisation, and other processes.
- Determine the enthalpies of the reactants and products.
- Calculate the bond enthalpies.
- Calculate the lattice energies of crystalline solids.

Q7. What are heat capacities at constant volume and constant pressure? What is the relationship between them?

Answer. Heat capacity at constant volume (Cv): The amount of heat supplied to a system to raise its temperature by one degree Celsius while keeping the volume of the system constant is referred to as its heat capacity at constant volume (Cv).
Heat capacity at constant pressure (Cp): The amount of heat supplied to a system to raise its temperature by one degree Celsius while keeping the external pressure constant is referred to as its heat capacity at constant pressure (Cp).
Cp – Cv = R is the relationship between Cp and Cv.

Q8. (i) For a reaction both ΔH and ΔS are negative. Under what conditions does the reaction occur spontaneously?
(ii) For a reaction both ΔH and ΔS are positive. Under what conditions does the reaction occur spontaneously?

Answer. $\Delta G = \Delta H - T\Delta S$
For a reaction to be spontaneous ΔG should be negative.

(i) Both ΔH and ΔS are negative, ΔG can be negative only if $T\Delta S < \Delta H$ in magnitude.
$\Delta G = \Delta H - T\Delta S$
$\Delta G = (-) - T(-)$
This is possible only if either ΔH has a large negative value or T is so low that $T\Delta S < \Delta H$.

(ii) Both ΔH and ΔS are positive so ΔG will be negative only if $T\Delta S > \Delta H$ in magnitude.
$\Delta G = \Delta H - T\Delta S$
$\Delta G = (+) - T(+)$
Thus either ΔS should be very large so that even if T is low, TΔS is greater than ΔH, or if ΔS is small, T should be high so that $T\Delta S > \Delta H$.

Q9. How will you get to the relationship $q_p = q_v + \Delta n_g RT$?

Answer: The relationship can be derived as follows-
Enthalpy change $\Delta H = q_p$, where q_p is the heat change at constant pressure,
Internal energy change $\Delta U = q_v$, where q_v is the heat change at constant volume.

Now $\Delta H = \Delta U + P\Delta V$
For ideal gases $PV = nRT$
$\therefore \Delta H = \Delta U + (PV_2 - PV_1)$
$= \Delta U + P(V_2 - V_1) = \Delta U + (n_2RT - n_1RT)$
$= \Delta U + RT(n_2 - n_1) = \Delta U + \Delta n_gRT$
or
$q_p = q_v + \Delta n_gRT$

Q10. Calculate the maximum work obtained when 0.75 mol of an ideal gas expands isothermally and reversible at 27°C from a volume of 15 L to 25 L.

Answer.
For an isothermal reversible expansion of an ideal gas
$w = -nRT \log V_2/V_1 = -2.303\, nRT \log V_2/V_1$
Putting n = 0.75 mol; V1 = 15 L; V2 = 25 L, T = 27 + 273 = 300 K R = 8.314 JK-1 mol-1.
$w = -2.303 \times 0.75 \times 8.314 \times 300 \log 25/15$
w = -955.5J.

Q11. Calculate the enthalpy of formation of carbon disulfide given that the enthalpy of combustion of it is 110.2 kJ mol^{-1} and those of sulfur and carbon are 297.4 kJ and 394.5 kJ/g atoms respectively.

Answer.
$C(s) + 2S(s) \rightarrow CS_2(l); \Delta H = ?$
Given
(i) $CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g); \Delta H = -110.2$ kJ mol^{-1}
(ii) $S(s) + O_2(g) \rightarrow SO_2(g); \Delta H = -297.4$ kJ mol^{-1}
(iii) $C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = -394.5$ kJ mol^{-1}

On adding eq. (iii) + 2(ii) and subtracting (i), it gives, on rearranging
$C(s) + 2S(s) \rightarrow CS_2(l);$
$\Delta H = (-394.5) + -2(-297.4) - (-110.2)$
$= -879.1$ kJ mol^{-1}.
Thus the enthalpy of formation of $CS_2 = -879.1$ kJ mol^{-1}.

Q12. Calculate the work done when 2 moles of an ideal gas expand reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.

Answer.
n = 2 moles
V_i = 500ml = 0.5lit
V_f = 2lit
T = 25°C = 298K

$w = −2.303\ nRT \log (V_f / V_i)$

$w = −2.303 × 2 × 8.314 × 298 × \log(2/0.5)$

$w = −2.303 × 2 × 8.314 × 298 × \log(4)$

$w = − 2.303 × 2 × 8.314 × 298 × 0.6021$

$w = − 6871J$

$w = − 6.871kJ.$

Q13. For the reaction $Ag_2O(s) \rightarrow 2Ag(s) + ½ O_2(g)$: $ΔH = 30.56\ kJ\ mol^{-1}$ and $ΔS = 6.66JK^{-1}\ mol^{-1}$ (at 1 atm). Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

Answer.

Given:

$ΔH = 30.56\ kJmol^{-1} = 30560Jmol^{-1}$

$ΔS = 6.66 ×10−3kJ\ K^{-1}mol^{-1}$

T = ? at which ΔG = 0

$ΔG = ΔH − TΔS$

$0 = ΔH − TΔS$

$T = ΔH / ΔS$

$T = (30.56\ kJmol^{-1}) / (6.66×10−3\ kJ\ K^{-1}mol^{-1})$

$T = 4589K$

(i) At 4589K ; ΔG = 0 the reaction is in equilibrium.

(ii) At temperature below 4589k, ΔH > TΔSΔG = ΔH −TΔS > 0, the reaction in the forward direction, is non spontaneous. In other words, the reaction occurs in the backward direction.

Q14. Define-

(i) Standard enthalpy of formation.

(ii) Standard enthalpy of combustion

(iii) Enthalpy of atomization

(iv) Enthalpy of solution

(v) Lattice enthalpy

Answer.

(i) Standard enthalpy of formation.

The change in enthalpy when one mole of a compound is formed from its elements in their standard states under standard conditions, i.e. at 298K and 101.3kPa pressure, is referred to as the standard enthalpy of formation.

(ii) Standard enthalpy of combustion

The enthalpy change when one mole of a compound is completely burned in oxygen with all reactants and products in their standard state under standard conditions is defined as standard enthalpy of combustion (298K and 1 bar pressure).

(iii) Enthalpy of atomization
This is the enthalpy change that occurs when one mole of a substance is completely broken down into its atoms in the gas phase.

(iv) Enthalpy of solution
The heat change that occurs when one mole of a substance dissolves in a specified amount of a solvent is defined as the enthalpy of solution. The enthalpy of solution at infinite dilution is the enthalpy change observed when dissolving two moles of a substance in an infinite amount of solvent.

(v) Lattice enthalpy
The enthalpy change that occurs when one mole of an ionic compound dissociates into its ions in a gaseous state is referred to as the lattice enthalpy of an ionic compound.

Q15. 1 g or graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atm pressure according to the reaction
$C(graphite) + O_2(g) \rightarrow CO_2(g)$.
During the reaction, the temperature rises from 298 K to 299 K. If the heat, the capacity of the bomb calorimeter is 20.7 kJ K^{-1} what is the enthalpy change for the above reaction at 298 K and 1 atm?

Answer.
q = Heat change = Cv × ΔT, where q is the heat absorbed by the calorimeter.
The quantity of heat from the reaction will have the same magnitude, but the opposite sign, because heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.
$\therefore$ q = – Cv × ΔT = – 20.7 kJ K-1 × (299 – 298) K
= –20.7kJ.
Here, the negative sign indicates the exothermic nature of the reaction.
Thus, ΔU for the combustion of 1 g of graphite = – 20.7 kJ K^{-1}
For combustion of 1 mol of graphite
= – [12.0×(−20.7)]/1 = – 2.48 × 102 kJ mol^{-1}

Since $\Delta n_g = 0$
$\therefore$ ΔH = ΔU = – 2.48 × 102 kJ mol^{-1}.

Practise Questions on Thermodynamics

Q1. When heating a solution, a scientist detects a temperature increase in the solution during a period of time. Which of the following statements accurately characterizes the solution during this period?

a) The solution's temperature increase is proportional to its $\Delta H_{vaporization}$
b) The solution is at boiling point.
c) The solution is undergoing a phase change.
d) The velocity of molecules in the solution is increasing.

Correct Answer. (d) The velocity of molecules in the solution is increasing.

Q2. A hot object is placed next to a cold object so that they are touching. Which of the following statements is true?

I. Heat will transfer from the hot object to the cold object because the hot object has a higher temperature.
II. The two objects are in thermal equilibrium
III. Internal energy will transfer from the hot object to the cold object because the hot object has greater internal energy.

a) I
b) II
c) I & III
d) III

Correct Answer. (a) I. Heat will transfer from the hot object to the cold object because the hot object has a higher temperature

Q3. One mole of CO_2 at 300 K and 1 atm pressure is heated in a closed vessel so that the temperature is 500 K and the pressure is 5 atm. Then it is cooled so that the temperature is 300 K and the pressure is 1 atm. What is the change in the internal energy of the gas?

Answer. Internal energy is a state function, and the system has returned to its original state, so there has been no change.

Q4. Enthalpy and entropy changes of a reaction are 40.63 kJ mol-1 and 108.8 JK^{-1} mol–1 respectively. Predict the feasibility of the reaction at 27°C.

Answer.
$\Delta H = 40.63\ kJ\ mol^{-1} = 40630\ Jmol^{-1}$
$\Delta S = 108.8\ JK^{-1}\ mol^{-1}$
$T = 27°C = 27 + 273 = 300\ K$
Now $\Delta G = \Delta H - T\Delta S$

$= 40630 – 3 \times 108.8 = 7990 \text{ Jmol}^{-1}$

Since ΔG is positive (i.e., ΔG > 0), the reaction is not feasible at 27°C in the forward direction.

Q5. Derive the relationship Cp – Cv = R.

Answer. The derivation of the relationship is as follows:
If q is the amount of heat involved in a system. Then, at constant volume,
$q = q_v = C_v\Delta T = \Delta U$ (eq. 1)

At constant pressure,
$q = q_p = C_p\Delta T = \Delta H$ (eq. 2)

For one mole of an ideal gas (n=1)
Therefore, the change in enthalpy will be
$\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(pT)$
$\Delta H = \Delta U + R\Delta T$ (eq. 3)

Substituting the values of ΔH and ΔU in eq.3 from eq. 1 and eq. 2.
$C_p\Delta T = C_v\Delta T + R\Delta T$
OR
$C_p = C_v + R$
Hence, $C_p - C_v = R$