**PHYSICAL CHEMISTRY**

**DPP**

**DAILY PRACTICE PROBLEMS**

# DPP No. 53

**Total Marks : 30**

**Max. Time : 33 min.**

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**Topic : Thermodynamics & Thermochemistry**

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| **Type of Questions** | | **M.M., Min.** |
|---|---|---|
| Single choice Objective ('–1' negative marking) Q.1 | (3 marks, 3 min.) | [3, 3] |
| Subjective Questions ('–1' negative marking) Q.2 to Q.4 | (4 marks, 5 min.) | [12, 15] |
| Comprehension ('–1' negative marking) Q.5 to Q.9 | (3 marks, 3 min.) | [15, 15] |

**1.** For a gas having molar mass M, specific heat at constant pressure can be given as :

(A) $\frac{\gamma R}{M(\gamma-1)}$ (B) $\frac{\gamma}{RM}$ (C) $\frac{M}{R(\gamma-1)}$ (D) $\frac{\gamma RM}{\gamma+1}$

**2.** 1 mole of ice at 0ºC and 4.6 mm Hg pressure is converted to water vapour at constant temperature and pressure. Find $\Delta H$ and $\Delta E$ if the latent heat of fusion of ice is 80 Cal/g and latent heat of vaporisation of liquid water at 0ºC is 596 Cal/g and the volume of ice in comparison to that of water vapour is neglected.

**3.** Calculate q, W and $\Delta E$ when 100 g of calcite form of $CaCO_3$ is converted into its aragonite form at 100 bar pressure. Given density of calcite = 2 g/cc, density of aragonite = 2.5 g/cc and

$CaCO_3 \rightleftharpoons CaCO_3$ $\Delta H = 2$ kJ/mole
Calcite Aragonite

**4.** A person inhales 640 g of $O_2$ per day. If all the $O_2$ is used for converting sugar into $CO_2$ and $H_2O$, how much sucrose ($C_{12}H_{22}O_{11}$) is consumed in the body in one day and what is the heat evolved ? $\Delta H$ (combustion of sucrose) = – 5472 kJ/mol.

**Comprehension # (Q.5 to Q.9)**

Enthalpy of sublimation may be determined experimentally, but instead of that let us explore an easier route for its calculation. Figure-1 shows the three phases of water on an enthalpy scale. Since enthalpy is a state function, enthalpy changes depend only on the initial and the final states and not on the path. Therefore, we must find the same value for enthalpy change whether the system goes directly from solid to gas or through the intermediate state of liquid. Therefore, $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$ ....(1)

There is a small oversight in the way we obtained $\Delta H_{sub}$ . Equation (1) is true only if enthalpies are independent of temperature or if their values are measured or deduced at the same temperature. Suppose we have enthalpy data at different temperatures as is usually the case. How do we proceed then?

We will illustrate the procedure with an estimate of $\Delta H_{sub}$ at 0°C from $\Delta H_{vap}$ at 100°C and $\Delta H_{fus}$ at 0°C. In order to calculate $\Delta H_{sub}$ at 0°C, figure-2 shows that the heat absorbed in the process

$$\text{Solid (0°C)} \longrightarrow \text{Gas (0° C)}$$

is equal to the heat absorbed in the process

$$\text{Solid (0°C)} \longrightarrow \text{Liquid (0°C)} \longrightarrow \text{Liquid (100°C)} \longrightarrow \text{Gas (100 °C)} \longrightarrow \text{Gas (0°C)}$$

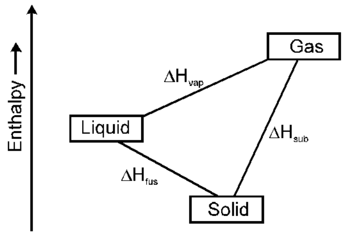

**Figure-1**

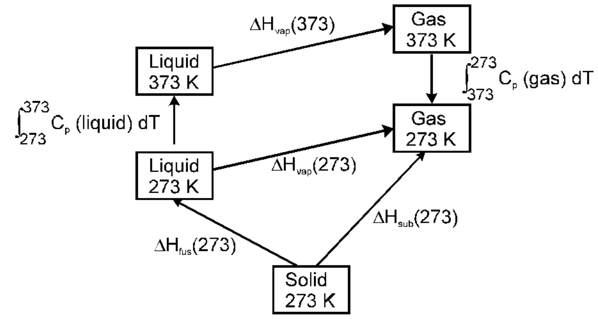

**Figure-2**

The enthalpy of sublimation at 0°C is therefore given by :

$$\Delta H_{sub}\,(0°C) = \Delta H_{fus}\,(0°\ C) + \int_{273}^{373} C_p(\text{liquid})\,dT + \Delta H_{vap}\,(100°C) + \int_{373}^{273} C_p(\text{gas})\,dT$$

During chemical reactions also, we may not obtain the products at the temperature at which reactant were present initially. Then too, we can calculate the enthalpy change during the reaction at temperature of reactants. The basis of Kirchoff's equations in thermodynamics is also the same. The Kirchoff's equations are :

At constant pressure : $$\Delta H_2^o = \Delta H_1^o + \int_{T_1}^{T_2} \Delta C_P\,dT$$

Where $\Delta H_1^o$ is enthalpy change of reaction at temperature $T_1$,
and $\Delta H_2^o$ is enthalpy change of reaction at temperature $T_2$.
$\Delta C_P$ is difference in molar heat capacities at constant pressure of products and reactants.
Similarly

At constant volume : $$\Delta E_2^o = \Delta E_1^o + \int_{T_1}^{T_2} \Delta C_V\,dT$$

**USE THE FOLLOWING DATA :**

Molar heat capacity of

$H_2O$ (solid) = 40 J $K^{-1}$ $mol^{-1}$
$H_2O$ (liquid) = 75 J $K^{-1}$ $mol^{-1}$
$H_2O$(vapour) = 30 J $K^{-1}$ $mol^{-1}$
Latent heat of vaporisation = 40 kJ $mol^{-1}$
Latent heat of fusion of $H_2O$ = 6 kJ $mol^{-1}$

**5.** Molar enthalpy of vaporisation of $H_2O$ at 0°C is :
(A) 44 kJ $mole^{-1}$
(B) 44.5 kJ $mole^{-1}$
(C) 50.5 kJ $mole^{-1}$
(D) – 44.5 kJ $mole^{-1}$

**6.** Molar enthalpy of sublimation of $H_2O$ at 223 K is :
(A) 48 kJ $mole^{-1}$
(B) 40 kJ $mole^{-1}$
(C) 51 kJ $mole^{-1}$
(D) 53 kJ $mole^{-1}$

**7.** If enthalpy change of reaction :

$H_2O(\ell) \longrightarrow H_2O$ (g) at 300 K is 43285 J $mole^{-1}$, then enthalpy change at 400 K will be :

(A) 34285 J $mole^{-1}$
(B) 43285 J $mole^{-1}$
(C) 47785 J $mole^{-1}$
(D) 38785 J $mole^{-1}$

**8.** For a chemical reaction, $\Delta C_P$ is negative ($\Delta C_P < 0$).
The heat required to increase temperature of reactants of this reaction by a certain amount = $q_1$ and heat required to increase temperature of products of the same reaction by same amount = $q_2$. Then :
(A) $q_1 > q_2$
(B) $q_1 < q_2$
(C) $q_1 = q_2$
(D) $q_1$ may or may not be equal to $q_2$ and it will depend on nature of reactants and products.

**9.** If for reaction :

$N_2\,(g) + 3H_2\,(g) \longrightarrow 2NH_3\,(g), \Delta H_1^o = -30$ kJ/mole at temperature 300 K and if specific heat capacities of different species are $s_{P,\,N_2} = 1$ J/g°C, $s_{P,\,H_2} = 10$ J/g°C and $s_{P,\,NH_3} = 2$ J/g °C, then $\Delta H_2^o$ at 400 K for the same reaction will be : (assume heat capacities to be constant in given temperature range)
(A) – 32 kJ/mole
(B) – 28 kJ/mole
(C) – 32.7 kJ/mole
(D) – 27.3 kJ/mole

# Answer Key

## DPP No. # 53

**1.** (A) **2.** DH = 12.168 Kcal ; DE = 11.622 Kcal.

**3.** W = 0.1 KJ, q = 2KJ, DE = 2.1 KJ. **4.** 570 g of sucrose ; 9120 kJ. **5.** (B)

**6.** (C) **7.** (D) **8.** (A) **9.** (A)

# Hints & Solutions

## DPP No. # 53

**2.** Latent heat of fusion of ice per mole = 80 × 18 = 1440 cal.

Latent heat of vpourisation of liquid water per mole = 596 × 18 = 10728 cal.

$\therefore$ Total q = (1440 + 10728) cal = 12168 cal.

$\therefore$ $q_p = \Delta H = 12168$ cal Ans.

$\Delta E = \Delta H - P\Delta V = q_p - P\Delta V$

$V_2$ = volume of 1 mole of $H_2O$ (g) and $V_1 \approx 0$.

$\therefore$ $P\Delta V = 546$ Cal

$\therefore$ $\Delta E = (12168 - 546)$ cal = 11622 Cal.

**3.** W = 0.1 KJ, q = 2KJ, DE = 2.1 KJ.

**4.** $n_{O_2}$ (inhaled) = $\frac{640}{32} = 20$

12 mole $O_2$ consumes 1 mole = 342 g sucrose.

$\therefore$ Mass of sucrose consumed = $\frac{342}{12} \times 20$ g = 570 g.

and heat liberated = $\frac{5472}{342} \times 570$ kJ. = 9120 kJ.

**5.** $\Delta H_{vap}(0^\circ C) = \int_{273}^{373} C_p\,(\text{liquid})\,dT + \Delta H_{vap}(100^\circ C) + \int_{373}^{273} C_p\,(\text{gas})\,dT$

$= 75 \times 100 + 40{,}000 - 30 \times 100$

$= 44{,}500 \text{ J mole}^{-1} = 44.5 \text{ kJ mole}^{-1}$

**6.** $\Delta H_{sub}(223K) = \int_{223}^{273} C_p \text{ (solid) } dT + \Delta H_{fus} (0^\circ C) + \int_{273}^{373} C_p \text{ (liquid) } dT + \Delta H_{vap} (100^\circ C) + \int_{373}^{223} C_p \text{ (gas) } dT$

$= 50 \times 40 + 6000 + 100 \times 75 + 40000 - 150 \times 30$

$= 51$ kJ/mole.

**7.** $\Delta H_2^o = \Delta H_1^o + \Delta C_p (T_2 - T_1) = 43.285 + (-45 \times 100)$

$= 38785 \text{ J mole}^{-1}$.

**8.** $\Delta C_p = -ve$

$C_{p\text{ (products)}} < C_{p\text{ (Reactants)}}$ so $q_2 < q_1$

**9.** $\Delta H_0^2 = [-30 \text{ kJ/mole}] + [\{2 \times 2 \times 17 - 28 - 3 \times 2 \times 10\} (100) \text{ J/mole}]$

$= (-30 \text{ kJ/mole}) + (-2000 \text{ J/mole}) = -32$ kJ/mole.