



Important Questions on Thermochemistry

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1. One mole of naphthalene was burnt in oxygen gas at constant volume and produces carbon dioxide gas and liquid water at 25°C. The heat evolved was found to be 5138.8 kJ. Calculate the enthalpy of the reaction. $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.
 - A. -5143.8 kJ
 - B. -403.21 kJ
 - C. -382.65 kJ
 - D. -636.24 kJ

2. For glucose $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, the enthalpy of combustion is $-2816 \text{ kJ mol}^{-1}$ at 25° C. Calculate ΔH_f° ($\text{C}_6\text{H}_{12}\text{O}_6$). The ΔH_f° values for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -393.5 and $-285.9 \text{ kJ mol}^{-1}$, respectively.
 - A. $-1360.2 \text{ kJ mol}^{-1}$
 - B. $-1132.4 \text{ kJ mol}^{-1}$
 - C. $-1260.4 \text{ kJ mol}^{-1}$
 - D. $-1462.3 \text{ kJ mol}^{-1}$

3. The heat evolved on dissolving $\text{CuSO}_4(\text{s})$ in water is 86.6 kJ mol^{-1} . If $\Delta H_f^\circ(\text{Cu}^{2+})$ is 64.4 kJ mol^{-1} , what is $\Delta H_f^\circ(\text{SO}_4^{2-})$? $\Delta H_f^\circ(\text{CuSO}_4(\text{s})) = -770.0 \text{ kJ mol}^{-1}$
 - A. -642.3 kJ
 - B. -543.8 kJ
 - C. -747.8 kJ
 - D. -345.9 kJ

4. In a bomb calorimeter, cyanamide was subjected to combustion at constant volume and the heat evolved was found to be 742.7 kJ at 25°C. Calculate q_p for the reaction.
 - A. -643.2 kJ
 - B. -452.8 kJ
 - C. -741.5 kJ
 - D. -327.8 kJ

5. Determine the enthalpy of formation of OH^- ions at 25°C from the following thermochemical data: $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}); \Delta H^\circ = 57.3 \text{ kJ}$
 $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H^\circ = -285.9 \text{ kJ}$
 - A. -324.8 kJ
 - B. -228.6 kJ
 - C. -278.5 kJ
 - D. -356.8 kJ

6. The enthalpy of reaction (ΔH) for the formation of ammonia according to the reaction:
 $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$ at 27°C was found to be -91.94 kJ .
 What will be the enthalpy of reaction (ΔH) at 50°C? The molar heat capacities at constant pressure and at 27°C for nitrogen, hydrogen and ammonia are 28.45, 28.32 and 37.07 joules, respectively.
 - A. -78.85 kJ
 - B. -62.70 kJ
 - C. -56.35 kJ
 - D. -92.85 kJ

7. Calculate the enthalpy change at 125° C for the reaction:
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g});$
 The molar heat capacities (in $\text{J K}^{-1} \text{ mol}^{-1}$) for the various gases involved in the reaction vary with temperature as follows:
 $C_p(\text{N}_2) = 27.26 + 5.23 \times 10^{-3} T - 4.18 \times 10^{-9} T^2$
 $C_p(\text{H}_2) = 29.02 - 8.35 \times 10^{-4} T + 20.80 \times 10^{-7} T^2$
 $C_p(\text{NH}_3) = 25.86 + 32.94 \times 10^{-2} T - 30.42 \times 10^{-7} T^2$
 - A. -83.20 kJ
 - B. -96.50 kJ
 - C. -45.60 kJ
 - D. -76.83 kJ

8. H_2 gas is mixed with air at 25°C under the pressure of one atmosphere and explodes in a closed vessel. The enthalpy of reaction $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ at constant volume, $\Delta U_{298} = -240.6 \text{ kJ}$ and C_p s for H_2O vapour and N_2 in the temperature range 298 K and 3,200 K are 39.1 J K^{-1} and 36.4 J K^{-1} , respectively. Calculate the explosion temperature under adiabatic conditions.
 - A. 3216 K
 - B. 4230 K
 - C. 2916 k
 - D. 5200 K

9. 0.50 g of benzoic acid was subjected to combustion in a bomb calorimeter when the temperature of the calorimeter system (including water) was found to rise by 0.55°C. Determine the enthalpy of combustion of benzoic acid. The ΔT calorimeter constant was found to be 23.85 kJ K⁻¹.

- A. - 3234.7 kJ mol⁻¹
- B. - 2301.9 kJ mol⁻¹
- C. - 4032.6 kJ mol⁻¹
- D. - 3201.9 kJ mol⁻¹

10. For the hypothetical reaction: $2B(g) \rightarrow B_2(g)$, ΔC_p (in joules) = $6.0 + 2.0 \times 10^{-3} T$ and $\Delta H^\circ_{298} = -20.0$ kJ mol⁻¹. Estimate the temperature at which $\Delta H^\circ = 0$ for this reaction.

- A. 2527 K
- B. 3245 K
- C. 1234 K
- D. 1200 K

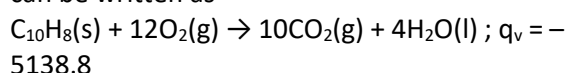
ANSWER KEY

- | | | | | | |
|------|------|------|-------|------|------|
| 1. A | 2. C | 3. C | 4. C | 5. B | 6. D |
| 7. B | 8. C | 9. D | 10. A | | |

Solutions:

Solution 1.

The thermochemical equation for the reaction can be written as



The number of moles of gaseous reactants, $n_1 = 12$.

The number of moles of gaseous products, $n_2 = 10$.

Hence,

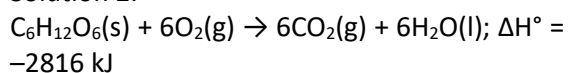
$$\Delta n_g = n_2 - n_1 = 10 - 12 = -2$$

$$q_p = q_v + \Delta n_g RT$$

Substituting the various value in above equation as:

$$q_p = -5138.8 \text{ kJ} - 2 \text{ mol} \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} = -5143.8 \text{ KJ}$$

Solution 2.



Since,

$$\Delta H = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$$

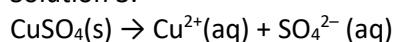
$$-2816 \text{ kJ} = 6(-393.5 \text{ kJ mol}^{-1}) + 6(-285.9 \text{ kJ mol}^{-1}) - \Delta H^\circ_f(C_6H_{12}O_6) - 6\Delta H^\circ_f(O_2)$$

$$\Delta H^\circ_f(O_2) = 0$$

On solving,

$$\Delta H^\circ_f(C_6H_{12}O_6) = -1260.4 \text{ kJ mol}^{-1}$$

Solution 3.

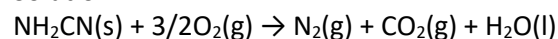


$$\Delta H = \Delta H^\circ_f(Cu^{2+}) + \Delta H^\circ_f(SO_4^{2-}) - \Delta H^\circ_f(CuSO_4(s))$$

Rearrange and substitute the given values,

$$\Delta H^\circ_f(SO_4^{2-}) = -747.8 \text{ kJ}$$

Solution 4.



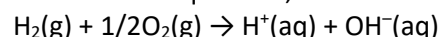
$$\Delta n_g = 1 + 1 - 3/2 = 1/2$$

$$q_p = q_v + \Delta n_g RT = -742.7 \text{ kJ} + (0.5 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})/1000 \text{ J kJ}^{-1}$$

$$= [-742.7 \text{ kJ} + 1.240 \text{ kJ}] = -741.5 \text{ kJ}$$

Solution 5.

Add the two equations,



$$\therefore \Delta H^\circ = -228.6 \text{ kJ} = 0 + \Delta H^\circ_f(OH^-(aq)) - (0 + 0),$$

since, by convention, $\Delta H^\circ_f[H^+(aq)] = 0$,

$$\therefore \Delta H^\circ_f[OH^-(aq)] = -228.6 \text{ kJ}$$

Solution 6.

According to the Kirchoff equation,

$$d(\Delta H) = \Delta C_p dT \text{ or } \Delta H_2 - \Delta H_1(T_2 - T_1) = \Delta C_p$$

In the present case,

$$\Delta H_1 = -91.94 \text{ kJ}; T_1 = 27 + 273 = 300 \text{ K and } T_2 = 50 + 273 = 323 \text{ K}$$

ΔC_p = Heat capacities of products minus heat capacities of reactants,

$$= 2 \times 37.07 \text{ J K}^{-1} - (28.45 \text{ J K}^{-1} + 3 \times 28.32 \text{ J K}^{-1})$$

$$= 39.28 \text{ J K}^{-1} = -39.28 \times 10^{-3} \text{ kJ K}^{-1}$$

If the heat capacities do not change with temperature, ΔH_2 , at 50°C, will be given as:

$$\Delta H_2 = \Delta H_1 + (T_2 - T_1) \Delta C_p$$

$$= -91.94 \text{ kJ} + (323 \text{ K} - 300 \text{ K}) (-39.28 \times 10^{-3} \text{ kJ K}^{-1}) = -92.85 \text{ kJ}$$

Solution 7.

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT$$

Let us first calculate ΔC_p .

$$\Delta C_p = -2C_p(\text{NH}_3) - [C_p(\text{N}_2) + 3C_p(\text{H}_2)]$$

Substituting the given data, the value of ΔC_p is given by:

$$\Delta C_p = -62.60 + 63.14 \times 10^{-3} T - 123.20 \times 10^{-7} T^2$$

Hence,

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} [-62.60 + 63.14 \times 10^{-3} T - 123.20 \times 10^{-7} T^2] dT$$

Or,

$$\Delta H_{398} - \Delta H_{298} = [-62.60 + 63.14 \times 10^{-3} T^2/2 - 123.20 \times 10^{-7} T^3/3]_{298}^{398}$$

Simplifying and putting $\Delta H_{298} = -92.41$ kJ,

$$\Delta H_{398} = -96.50 \text{ kJ}$$

Solution 8.

For a constant volume process under adiabatic conditions:

$$\Delta U = \Delta U_{\text{heating}} + \Delta U_{298} = 0$$

Hence,

$$\Delta U_{\text{heating}} = \Delta U_{298} = - \int_{298}^{T_f} \sum n C_v dT = -240.60 \text{ kJ}$$

Since 2 moles of unreacted N_2 are associated with 1/2 mole of O_2 ,

$$\sum n C_v = C_v(\text{H}_2\text{O}, g) + 2C_v(\text{N}_2, g) = (39.1 + 2 \times 26.4) \text{ J K}^{-1} = 91.9 \text{ J K}^{-1}$$

Hence, from Eq. (i), on integrating, we have

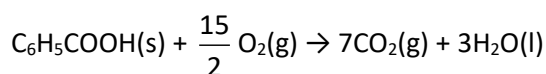
$$91.9 \text{ J K}^{-1} (T_f - 298) = 240,600 \text{ J}$$

$$T_f - 298 = 240,600 \text{ J} / 91.9 \text{ J K}^{-1} = 2618 \text{ K}$$

$$T_f = (2618 + 298) \text{ K} = 2916 \text{ K}$$

Solution 9.

$$q_v = c \times \theta \times M/m \\ = 23.85 \text{ kJ K}^{-1} \times 0.55 \text{ K} \times 122 \text{ g mol}^{-1} / 0.50 \text{ g} = 3200.7 \text{ kJ mol}^{-1} = -3200.7 \text{ kJ mol}^{-1}$$



We know that,

$$q_p = q_v + \Delta n_g RT; \Delta n = 7 - 7.5 = -0.5$$

$$q_p = -3200.7 \text{ kJ mol}^{-1} + (-0.5) (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) = -3201.9 \text{ kJ mol}^{-1}$$

Solution 10.

Using the Kirchhoff equation,

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} (\Delta C_p) dT$$

$$0 = -20,000 - \int_{298}^T (6.0 + 2.0 \times 10^{-3} T) dT$$

$$20,000 = [(6.0)(T - 298)] + [(1.0 \times 10^{-3})(T^2 - (298)^2)] = T - 1788 + 1 \times 10^{-3} T^2 - 88.8$$

$$10^{-3} T^2 + 6T - 1,876.8 = 0$$

This is a quadratic equation in T which, when solved, gives two roots – one positive and the other negative. The negative root has no physical significance. The positive root gives T = 2527 K.

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