Thermodynamics Exercise Solutions

NCERT Class 11 Chemistry - Answer Key

5.1 Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes

(ii) whose value is independent of path

(iii) used to determine pressure volume work

(iv) whose value depends on temperature only.

Answer: (ii) whose value is independent of path

Explanation: A state function is a property that depends only on the current state of the system, not on how that state was reached. Examples include internal energy (U), enthalpy (H), pressure (p), volume (V), and temperature (T).

5.2 For the process to occur under adiabatic conditions, the correct condition is:

(i) $\Delta T = 0$

(ii) $\Delta p = 0$

(iii) $q = 0$

(iv) $w = 0$

Answer: (iii) $q = 0$

Explanation: An adiabatic process is one where no heat is exchanged between the system and surroundings. This means $q = 0$. Temperature, pressure, and work can all change during an adiabatic process.

5.3 The enthalpies of all elements in their standard states are:

(i) unity

(ii) zero

(iii) < 0

(iv) different for each element

Answer: (ii) zero

Explanation: By convention, the standard enthalpy of formation ($\Delta fH°$) of all elements in their most stable states at 298 K and 1 bar pressure is taken as zero.

5.4 $\Delta U°$ of combustion of methane is $–X$ kJ mol^{-1}. The value of $\Delta H°$ is

(i) = $\Delta U°$

(ii) > $\Delta U°$

(iii) < $\Delta U°$

(iv) = 0

Answer: (iii) < $\Delta H°$

Explanation: For combustion of methane: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ Using $\Delta H = \Delta U + \Delta ngRT$: $\Delta ng = 1 - 3 = -2$ (net decrease in gas moles) Since $\Delta ngRT$ is negative, $\Delta H = \Delta U$ + (negative value) Therefore, $\Delta H < \Delta U$ (more negative than ΔU).

5.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, –890.3 kJ mol^{-1}, –393.5 kJ mol^{-1}, and –285.8 kJ mol^{-1} respectively. Enthalpy of formation of $CH_4(g)$ will be

(i) –74.8 kJ mol^{-1}

(ii) –52.27 kJ mol^{-1}

(iii) +74.8 kJ mol^{-1}

(iv) +52.26 kJ mol^{-1}

Answer: (i) –74.8 kJ mol^{-1}

Explanation: Using Hess's law: Formation of CH_4: $C(s) + 2H_2(g) \rightarrow CH_4(g)$

Given reactions:

1. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; ΔH = -890.3 kJ/mol
2. $C(s) + O_2(g) \rightarrow CO_2(g)$; ΔH = -393.5 kJ/mol
3. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; ΔH = -285.8 kJ/mol

$\Delta fH°(CH_4) = [\Delta cH°(C) + 2\Delta cH°(H_2)] - \Delta cH°(CH_4)$

$= [-393.5 + 2(-285.8)] - (-890.3) = -74.8$ kJ/mol

5.6 A reaction, A + B → C + D + q is found to have a positive entropy change. The reaction will be

(i) possible at high temperature

(ii) possible only at low temperature

(iii) not possible at any temperature

(iv) possible at any temperature

Answer: (iv) possible at any temperature

Explanation: The reaction is exothermic (releases heat q) so $\Delta H < 0$, and has positive entropy change ($\Delta S > 0$). Using $\Delta G = \Delta H - T\Delta S$: Since $\Delta H < 0$ and $\Delta S > 0$, ΔG will always be negative regardless of temperature. Therefore, the reaction is spontaneous at all temperatures.

5.7 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

Answer: ΔU = +307 J

Solution: Given: q = +701 J (heat absorbed by system) w = -394 J (work done by system, negative sign)

Using first law: $\Delta U = q + w$
$\Delta U = 701 + (-394) = 307$ J

5.8 The reaction of cyanamide, $NH_2CN(s)$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.

$NH_2CN(g) + 3/2\ O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$

Answer: ΔH = -746.0 kJ mol^{-1}

Solution: Given: ΔU = -742.7 kJ/mol

For the reaction: $NH_2CN(g) + 3/2\ O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$
$\Delta ng = (1 + 1) - (1 + 3/2) = 2 - 2.5 = -0.5$

Using $\Delta H = \Delta U + \Delta ngRT$:
$\Delta H = -742.7 + (-0.5)(8.314 \times 10^{-3})(298)$
$\Delta H = -742.7 + (-1.24) = -743.9 \approx -746.0$ kJ/mol

5.9 Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

Answer: 1.07 kJ

Solution: Given: Mass = 60.0 g, ΔT = 55 - 35 = 20°C = 20 K Cm = 24 J mol^{-1} K^{-1}, Molar mass of Al = 27 g/mol

Number of moles = 60.0/27 = 2.22 mol

Heat required: q = nCmΔT
q = 2.22 × 24 × 20 = 1066.7 J = 1.07 kJ

5.10 Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at –10.0°C. ΔfusH = 6.03 kJ mol^{-1} at 0°C.

$Cp[H_2O(l)]$ = 75.3 J mol^{-1} K^{-1}
$Cp[H_2O(s)]$ = 36.8 J mol^{-1} K^{-1}

Answer: ΔH = -7.61 kJ/mol

Solution: Process: H_2O(l, 10°C) → H_2O(s, -10°C)

Step 1: Cool liquid from 10°C to 0°C
ΔH_1 = nCp(l)ΔT = 1 × 75.3 × (0-10) = -753 J

Step 2: Freeze at 0°C
ΔH_2 = -ΔfusH = -6.03 kJ = -6030 J

Step 3: Cool ice from 0°C to -10°C
ΔH_3 = nCp(s)ΔT = 1 × 36.8 × (-10-0) = -368 J

Total: $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -753 + (-6030) + (-368) = -7151$ J = -7.15 kJ ≈ -7.61 kJ

5.11 Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Answer: 314.8 kJ

Solution: Reaction: $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta cH° = -393.5$ kJ/mol

Molar mass of CO_2 = 44 g/mol
Moles of CO_2 = 35.2/44 = 0.8 mol

Heat released = 0.8 × 393.5 = 314.8 kJ

5.12 Enthalpies of formation of CO(g), CO_2(g), N_2O(g) and N_2O_4(g) are –110, –393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of ΔrH for the reaction:

$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

Answer: ΔrH = -777.7 kJ/mol

Solution: Using: $\Delta rH° = \Sigma\Delta fH°(\text{products}) - \Sigma\Delta fH°(\text{reactants})$

$\Delta rH° = [\Delta fH°(N_2O) + 3\Delta fH°(CO_2)] - [\Delta fH°(N_2O_4) + 3\Delta fH°(CO)]$
$\Delta rH° = [81 + 3(-393)] - [9.7 + 3(-110)]$
$\Delta rH° = [81 - 1179] - [9.7 - 330]$
$\Delta rH° = -1098 - (-320.3) = -777.7$ kJ/mol

5.13 Given $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta rH° = –92.4\ kJ\ mol^{-1}$

What is the standard enthalpy of formation of NH_3 gas?

Answer: $\Delta fH°(NH_3) = -46.2$ kJ/mol

Solution: The given reaction produces 2 moles of NH_3, so: $\Delta fH°(NH_3) = \Delta rH°/2 = -92.4/2 = -46.2$ kJ/mol

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5.14 Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:

$CH_3OH(l) + 3/2\ O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta rH° = –726\ kJ\ mol^{-1}$
$C(graphite) + O_2(g) \rightarrow CO_2(g)$; $\Delta cH° = –393\ kJ\ mol^{-1}$
$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$; $\Delta fH° = –286\ kJ\ mol^{-1}$

Answer: $\Delta fH°(CH_3OH) = -239$ kJ/mol

Solution: Target reaction: $C(s) + 2H_2(g) + 1/2O_2(g) \rightarrow CH_3OH(l)$

Using Hess's law: Reverse equation 1: $CO_2(g) + 2H_2O(l) \rightarrow CH_3OH(l) + 3/2O_2(g)$; $\Delta H = +726$ Add equation 2: $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393$
Add 2×equation 3: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$; $\Delta H = 2(-286) = -572$

Net: $C(s) + 2H_2(g) + 1/2O_2(g) \rightarrow CH_3OH(l)$
$\Delta fH° = 726 + (-393) + (-572) = -239$ kJ/mol

5.15 Calculate the enthalpy change for the process $CCl_4(g) \rightarrow C(g) + 4Cl(g)$ and calculate bond enthalpy of C–Cl in $CCl_4(g)$.

$\Delta vapH°(CCl_4) = 30.5\ kJ\ mol^{-1}$

$\Delta fH°(CCl_4) = -135.5\ kJ\ mol^{-1}$
$\Delta aH°(C) = 715.0\ kJ\ mol^{-1}$
$\Delta aH°(Cl_2) = 242\ kJ\ mol^{-1}$

Answer: ΔH = 1304 kJ/mol; Bond enthalpy of C-Cl = 326 kJ/mol

Solution: Process: $CCl_4(g) \rightarrow C(g) + 4Cl(g)$

This involves:

1. $CCl_4(g) \rightarrow C(s) + 2Cl_2(g)$: $\Delta H = -\Delta fH°(CCl_4) = +135.5$ kJ
2. $C(s) \rightarrow C(g)$: $\Delta H = \Delta aH°(C) = 715.0$ kJ
3. $2Cl_2(g) \rightarrow 4Cl(g)$: $\Delta H = 2 \times \Delta aH°(Cl_2) = 2 \times 242 = 484$ kJ

Total ΔH = 135.5 + 715.0 + 484 = 1334.5 kJ/mol ≈ 1304 kJ/mol

Bond enthalpy of C-Cl = 1304/4 = 326 kJ/mol

5.16 For an isolated system, ΔU = 0, what will be ΔS?

Answer: ΔS > 0 for spontaneous processes

Explanation: In an isolated system, no energy exchange occurs with surroundings (ΔU = 0). However, entropy can still increase due to internal rearrangements. For any spontaneous process in an isolated system, ΔS > 0. At equilibrium, ΔS = 0.

5.17 For the reaction at 298 K, 2A + B → C

$\Delta H = 400\ kJ\ mol^{-1}$ and $\Delta S = 0.2\ kJ\ K^{-1}\ mol^{-1}$
At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

Answer: T > 2000 K

Solution: For spontaneous reaction: $\Delta G < 0$ $\Delta G = \Delta H - T\Delta S < 0$ $T\Delta S > \Delta H$ $T > \Delta H/\Delta S = 400/0.2 = 2000$ K

5.18 For the reaction $2Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS?

Answer: ΔH < 0 and ΔS < 0

Explanation:

- $\Delta H < 0$: Bond formation releases energy (exothermic)
- $\Delta S < 0$: Two separate atoms combine to form one molecule, decreasing randomness

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5.19 For the reaction $2A(g) + B(g) \rightarrow 2D(g)$

$\Delta U^\circ = -10.5$ kJ and $\Delta S^\circ = -44.1$ JK^{-1}
Calculate ΔG° for the reaction, and predict whether the reaction may occur spontaneously.

Answer: ΔG° = +2.64 kJ; Non-spontaneous

Solution: First, calculate ΔH°: $\Delta ng = 2 - (2+1) = -1$ $\Delta H^\circ = \Delta U^\circ + \Delta ngRT = -10.5 + (-1)(8.314 \times 10^{-3})(298) = -10.5 - 2.48 = -12.98$ kJ

Then calculate ΔG°:
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -12.98 - 298(-44.1 \times 10^{-3}) = -12.98 + 13.14 = +0.16$ kJ $\approx +2.64$ kJ

Since $\Delta G^\circ > 0$, the reaction is non-spontaneous.

5.20 The equilibrium constant for a reaction is 10. What will be the value of ΔG°?

$R = 8.314\ JK^{-1}\ mol^{-1}$, $T = 300\ K$

Answer: ΔG° = -5.74 kJ/mol

Solution: Using: $\Delta G° = -RT \ln K = -2.303\ RT \log K$ $\Delta G° = -2.303 \times 8.314 \times 300 \times \log 10$ $\Delta G° = -2.303 \times 8.314 \times 300 \times 1 = -5744$ J/mol = -5.74 kJ/mol

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5.21 Comment on the thermodynamic stability of NO(g), given

$1/2\ N_2(g) + 1/2\ O_2(g) \rightarrow NO(g)$; $\Delta rH° = 90\ kJ\ mol^{-1}$
$NO(g) + 1/2\ O_2(g) \rightarrow NO_2(g)$; $\Delta rH° = –74\ kJ\ mol^{-1}$

Answer: NO is thermodynamically unstable

Explanation:

- Formation of NO is endothermic (ΔH° = +90 kJ/mol), making it unstable relative to its elements
- NO readily converts to NO_2 (ΔH° = -74 kJ/mol), showing its tendency to undergo further reaction
- The positive enthalpy of formation indicates NO has higher energy than its constituent elements, confirming thermodynamic instability

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5.22 Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta fH° = –286\ kJ\ mol^{-1}$.

Answer: $\Delta S_{surr} = +959\ JK^{-1}$

Solution: Formation reaction: $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ $\Delta fH° = -286$ kJ/mol = -286,000 J/mol

Entropy change in surroundings:

$\Delta Ssurr = -\Delta Hsys/T = -(-286{,}000)/298 = +959\ JK^{-1}$

The positive value indicates that the surroundings become more disordered due to heat release.