NCERT SOLUTIONS

CLASS - 11th



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Class : 11th
Subject : Chemistry
Chapter : 6
Chapter Name : Thermodynamics

Q6.1 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. A thermodynamic state function is a quantity Whose value is independent of a path. Functions like p, V, T etc. depend only on the state of a system and not on the path.
Hence, alternative (ii) is correct.

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Q6.2 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. A system is said to be under adiabatic conditions if there is no exchange Of heat between the system and its surroundings. Hence, under adiabatic conditions, $q = 0$.
Therefore, alternative (iii) is correct,

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Q6.3 The enthalpies of all elements in their standard states are:
(i) unity
(ii) zero
(iii) < 0
(iv) different for each element

Answer. The enthalpy of all elements in their standard state is zero. Therefore, alternative (ii) is correct

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Q6.4 $\Delta U^{\ominus}$ of combustion of methane is $-\mathrm{X\ kJ\ mol^{-1}}$. The value of $\Delta H^{\ominus}$ is
(i) $= \Delta U^{\ominus}$
(ii) > $\Delta U^{\ominus}$
(iii) < $= \Delta U^{\ominus}$
(iv) = 0

Answer. Since $\Delta H^{\theta}=\Delta U^{\theta}+\Delta n_{g} RT$ and $\Delta U^{\theta}=-X \mathrm{k3mol}^{-1}$
$\Delta H^{\theta}=(-X)+\Delta n_{g} RT$
$\Rightarrow \triangle H^{\theta}<\Delta U^{\theta}$
Therefore, alternative (iii) is correct.

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Q6.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, –890.3 $\mathrm{kJmol}^{-1}-393.5 \mathrm{kJmol}^{-1}, \text{ and } -285.8 \mathrm{kJmol}^{-1}$ respectively. Enthalpy of formation of CH4 will be
(i) $-74.8 \mathrm{kJmol}^{-1}$
(ii) $-52.27 \mathrm{kJmol}^{-1}$
(iii) $+74.8 \mathrm{kJmol}^{-1}$
(iv) $+52.26 \mathrm{kJmol}^{-1}$

Answer. According to the question,
(i) $\mathrm{CH}_{4(\mathrm{g})}+2 \mathrm{O}_{2(\mathrm{g})} \longrightarrow \mathrm{CO}_{2(\mathrm{z})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}$
$\Delta H=-890.3 \mathrm{kJmol}^{-1}$
(ii) $\mathrm{C}_{(x)}+\mathrm{O}_{2(y)} \longrightarrow \mathrm{CO}_{2(g)}$
$\Delta H=-393.5 \mathrm{kJmol}^{-1}$
(iii) $2 \mathrm{H}_{2(g)}+\mathrm{O}_{2(z)} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(g)}$
$\Delta H=-285.8 \mathrm{kJmol}^{-1}$
Thus, the desired equation is the one that represents the formation of CH4(g) i.e..,

$$\mathrm{C}_{(s)}+2 \mathrm{H}_{2(g)} \longrightarrow \mathrm{CH}_{4(g)}$$

$$\Delta_{f} H_{\mathrm{CH}_{4}}=\Delta_{c} H_{\mathrm{c}}+2 \Delta_{c} H_{\mathrm{H}_{2}}-\Delta_{c} H_{\mathrm{CO}_{2}}$$

$$=\left[-393.5+2(-285.8)-(-890.3)\right] \mathrm{kJ\ mol}^{-1}$$

$$=-74.8 \mathrm{\ kJ\ mol}^{-1}$$

$\therefore$ Enthalpy of formation of $\mathrm{CH}_{4(\mathrm{g})}=-74.8 \mathrm{kJmol}^{-1}$
Hence, alternative (i) is correct.

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Q6.6 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. For a reaction to be spontaneous, ΔG should be negative.

$\Delta G = \Delta H - T\Delta S$

According to the question, for the given reaction,

$\Delta S =$ positive

$\Delta H =$ negative (since heat Is evolved)

$\Rightarrow \Delta G =$ negative

Therefore, the reaction is spontaneous at any temperature.

Hence, alternative (iv) is correct.

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Q6.7 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. According to the first of thermodynamics,

Where,

ΔU = change in internal energy for a process

g = heat

W = work

Given,

q = + 701 J (Since heat is absorbed)

W = - 394 J (Since work is done by the system)

Substituting the values in expression (i), we get

$\Delta U = 701\text{J} + (-394\text{J})$

$\Delta U = 307\text{J}$

Hence, the charge in Internal energy for the given process is 307 J.

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Q6.8 The reaction of cyanamide,$\text{NH}_2\text{CN(s)}$ with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJmol^{-1}at 298 K. Calculate enthalpy change for the reaction at 298 K.

$\text{NH}_2\text{CN(g)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$

Answer. Enthalpy change for a reaction (ΔH) is given by the expression,

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

Where,

$\Delta U =$ change in internal energy

$\Delta \eta_g =$ change in number of moles

For the given reaction,

$\Delta n_g = \sum n_g(\text{ products }) - \Sigma n_g(\text{ reactants })$

$= (2 - 2.5) \text{ moles}$

$\Delta n_e = -0.5 \text{ moles}$

And,

$\Delta U = -742.7\text{kJmol}^{-1}$

$T = 298\text{K}$

$\text{R} = 8.314 \times 10^{-3}\text{kJmol}^{-1}\text{K}^{-1}$

Substituting the values in the expression of ΔH:

$$\Delta H = \left(-742.7\text{kJmol}^{-1}\right) + (-0.5\text{mol})(298\text{K})\left(8.314 \times 10^{-3}\text{kJmol}^{-1}\text{K}^{-1}\right)$$
$$= -742.7 - 1.2$$
$$\text{WH} = -743.9\text{kJmol}^{-1}$$

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Q6.9 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 $\text{mol}^{-1}\text{K}^{-1}$.

Answer. $\text{From the expression of heat (q)}$
$q = m \cdot \text{ c. } \Delta T$
Where,
$\text{c} = \text{ molar heat capacity}$
$m = \text{ mass of substance}$
$\Delta T = \text{ change in temperature}$
$\text{Substituting the values in the expression of } q \text{ :}$

$$q = \left(\frac{60}{27}\text{mol}\right)\left(24\mathbf{J}\text{mol}^{-1}\text{K}^{-1}\right)(20\text{K})$$
$$q = 1066.7\text{J}$$
$$q = 1.07\text{k}$$

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Q6.10 Calculate the enthalpy change on freezing of 1.0 mol of water at10.0°C to ice at –10.0°C.
$\Delta_{fus}H = 6.03\text{kJmol}^{-1}$ at 0°C
$C_p\left[\text{H}_2\text{O(I)}\right] = 75.3\text{Jmol}^{-1}\text{K}^{-1}$
$C_\rho\left[\text{H}_2\text{O(s)}\right] = 36.8\text{Jmol}^{-1}\text{K}^{-1}$

Answer. Total enthalpy change involved in the transformation is the of the following changes:
(a) Energy change involved in the transformation of 1 mol of water at $10_{\circ}$C to 1 mol of water at 0 C.
(b) Energy change involved in the transformation of 1 mol of water at 0° to 1 mol of ice at 0°C_
(c) Energy change involved in the transformation of 1 mol of ice at 0°C to 1 mol of ice at -10°C.
$\Delta\text{H} = C_p\left[\text{H}_2\text{OCl}\right]\Delta T + \Delta H_{\text{fivering }} + C_\rho\left[\text{H}_2\text{O}_{(s)}\right]\Delta T$
$= (75.3]\text{mol}^{-1}\text{K}^{-1})(0-10)\text{K} + \left(-6.03 \times 10^3\text{Jmol}^{-1}\right) + (36.8]\text{mol}^{-1}\text{K}^{-1})(-10-0)\text{K}$
$= -7533\text{mol}^{-1} - 6030\text{Jmol}^{-1} - 368\text{Jmol}^{-1}$
$= -7151\text{Jmol}^{-1}$
$= -7.151\text{kJmol}^{-1}$
Hence, the enthalpy change involved in the transformation is -7.151kJmol^{-1}.

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Q6.11 Enthalpy of combustion of carbon to CO2 is –393.5 -7.151kJmol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Answer. Formation of CO_2 from carbon and dioxygen gas can be represented as:
$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$
$\Delta_f H = -393.5 \mathrm{kJmol}^{-1}$
$(1 \text{ mole } = 44 \mathrm{g})$
$\text{Heat released on formation of } 44 \mathrm{g} CO_2 = -393.5 \mathrm{kJmol}^{-1}$
$\therefore \text{ Heat released on formation of } 35.2 \mathrm{g} CO_2$
$= -314.8 \mathrm{kJmol}^{-1}$

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Q6.12 Enthalpies of formation of $CO(g), CO_2(g), N_2O(g)$ and $N_2O_4(g)$ are $-110, -393, 81$ and 9.7 kJmol^{-1} respectively. Find the value of ΔH for the reaction:
$N_2O_4(g) + 3CO(g) \rightarrow N_2O \,(g + 3CO_2(g]$

Answer. $\Delta_r H$ for a reaction is defined as the difference between ΔH value of products and ΔH value of reactants.
$\Delta, H = \sum \Delta, H(\text{ products }) - \sum \Delta_f H(\text{ reactants })$
For the given reaction,
$N_2O_{4(g)} + 3CO_{(g)} \longrightarrow N_2O_{(g)} + 3CO_{2(g)}$
$\Delta_r H = \left[\left\{\Delta_f H\left(N_2O\right) + 3\Delta_J H\left(CO_2\right)\right\} - \left\{\Delta_f H\left(N_2O_4\right) + 3\Delta_j H(CO)\right\}\right]$
Substituting the values of ΔH for N_2O, CO_2, N_2O_4 , and CO
From the question, we get:
$\Delta_r H = \left[\left\{81 \mathrm{kJmol}^{-1} + 3(-393) \mathrm{kJmol}^{-1}\right\} - \left\{9.7 \mathrm{kJmol}^{-1} + 3(-110) \mathrm{kJmol}^{-1}\right\}\right]$
$\Delta_r H = -7777 \mathrm{kJmol}^{-1}$
Hence, the value of $\Delta_r H$ for the reaction is $-777.7 \mathrm{kJmol}^{-1}$.

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Q6.13 Given
$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(y)}; \Delta_r H^\theta = -92.4 \mathrm{kJmol}^{-1}$
What is the standard enthalpy of formation of NH_3 gas?

Answer. Standard of formation of a compound is the charge in enthalpy that takes place during the formation of 1 mole Of a substance in its standard form from its constituent elements in their standard state.
Re-writing the given equation for 1 mole of $NH_{3(g)}$.
$\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \longrightarrow NH_{3(g)}$
$\therefore \text{ Standard enthalpy of formation of } NH_{3(g)}$
$= 1/2 \Delta_r H^\theta$
$= 1/2 \left(-92.4 \mathrm{kJmol}^{-1}\right)$
$= -46.2 \mathrm{kJmol}^{-1}$

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Q6.14 Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:

$\mathrm{CH_3OH(l)} + \frac{3}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + 2\mathrm{H_2O(l)} : \Delta, H^{\circ} = -726\mathrm{kJmol^{-1}}$
$C(graphite) + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} : \Delta_{\mathrm{e}} H = -393\mathrm{kJmol^{-1}}$
$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{H_2O}(1); \Delta, H = -286\mathrm{kJmol^{-1}}$

Answer. The reaction that takes place during the formation of $\mathrm{CH_3OH_{(l)}}$ can be written as:
$\mathrm{C}_{(s)} + 2\mathrm{H_2O}_{(g)} + \frac{1}{2}\mathrm{O}_{2(\mathrm{G})}, \longrightarrow \mathrm{CH_3OH}_{(\eta)}(1)$
The reaction (I) can be obtained from the given reactions by following the algebraic calculations as:

Equation (ii) + 2 × equation (iii) − equation (i)

$\Delta_f H^{\theta}\ [CH_3OH_{(l)}] = \Delta_c H^{\theta} + 2\Delta_f H^{\theta}\ [H_2O_{(l)}] - \Delta_r H^{\theta}$

$= (-393\ kJ\ mol^{-1}) + 2(-286\ kJ\ mol^{-1}) - (-726\ kJ\ mol^{-1})$

$= (-393 - 572 + 726)\ kJ\ mol^{-1}$

$\therefore \Delta_f H^{\theta}\ [CH_3OH_{(l)}] = -239\ kJ\ mol^{-1}$

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Q6.15 Calculate the enthalpy change for the process
$\mathrm{CCl}_{4(g)} \rightarrow \mathrm{C}_{(g)} + 4\mathrm{Cl}_{(g)}$
and calculated bond enthalpy of $\mathrm{C} - \mathrm{Cl}$ in $\mathrm{CCl}_{4(g)}$
$\Delta_{vap} H^{\theta}\left(CC|_4\right) = 30.5\mathrm{kJmol^{-1}}$
$\Delta_f H^{\theta}\left(\mathrm{CCl_4}\right) = -135.5\mathrm{kJmol^{-1}}$
$\Delta_a H^{\theta}(\mathrm{C}) = 715.0\mathrm{kJmol^{-1}},$ where $\Delta_{\mathrm{a}} H^{\theta}$ is enthalpy of atomisation
$\Delta_2 H^{\theta}\left(\mathrm{Cl_2}\right) = 242\mathrm{kJmol^{-1}}$

Answer. The chemical equations imply to the given values of enthalpies are:

(i) $CCl_{4(l)} \longrightarrow CCl_{4(g)}$ $\Delta_{vap}H^{\theta} = 30.5\ kJ\ mol^{-1}$

(ii) $C_{(s)} \longrightarrow C_{(g)}$ $\Delta_{a}H^{\theta} = 715.0\ kJ\ mol^{-1}$

(iii) $Cl_{2(g)} \longrightarrow 2Cl_{(g)}$ $\Delta_{a}H^{\theta} = 242\ kJ\ mol^{-1}$

(iv) $C_{(g)} + 4Cl_{(g)} \longrightarrow CCl_{4(g)}$ $\Delta_{f}H = -135.5\ kJ\ mol^{-1}$

Enthalpy change for the given process $CCl_{4(g)} \longrightarrow C_{(g)} + 4Cl_{(g)}$, can be calculated using the following algebraic calculations as:

Equation (ii) + 2 × Equation (iii) − Equation (i) − Equation (iv)

$\Delta H = \Delta_{a}H^{\theta}(C) + 2\Delta_{a}H^{\theta}(Cl_2) - \Delta_{vap}H^{\theta} - \Delta_{f}H$

$= (715.0\ kJ\ mol^{-1}) + 2(242\ kJ\ mol^{-1}) - (30.5\ kJ\ mol^{-1}) - (-135.5\ kJ\ mol^{-1})$

$\therefore \Delta H = 1304\ kJ\ mol^{-1}$

Bond enthalpy of C−Cl bond in $CCl_{4\,(g)}$

$= \frac{1304}{4}\ kJ\ mol^{-1}$

$= 326\ kJ\ mol^{-1}$

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Q6.16 For an isolated system, ΔU = 0, what will be ΔS ?

Answer. ΔS will be positive i.e., greater than zero
Since ΔU = 0, ΔS will be positive and the reaction will be spontaneous.

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Q6.17 For the reaction at 298 K,
2A + B → C
ΔH = 400 $kJmol^{-1}$ and ΔS = 0.2 $kJmol^{-1}$
At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

Answer. From the expression
$\Delta G = \Delta H - T\Delta S$
Assuming the reaction at equilibrium, δ T for the reaction would be:
$T = (\Delta H - \Delta G)\frac{1}{\Delta S}$
$= \frac{\Delta H}{\Delta S}(\Delta G = 0 \text{ at equilibrium})$
$= \frac{400 kJmol^{-1}}{0.2 kJK^{-1}mol^{-1}}$
$T = 2000K$
For the reaction to be spontaneous, ΔG must be negative. Hence, for the given reaction to be

spontaneous, T should be greater than 2000 K.

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Q6.18 For the reaction, $2\mathrm{Cl}_{(g)} \rightarrow \mathrm{Cl}_{2(g)}$, what are the signs of ΔH and ΔS ?

Answer. ΔH and ΔS are negative
The given reaction represents the formation of chlorine molecule from chlorine atoms. Here, bond formation is taking place. Therefore, energy Is being released. Hence ΔH is negative.
Also, two moles of atoms have more randomness than one mole of a molecule. Since spontaneity is decreased, ΔS is negative for the given reaction.

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Q6.19 For the reaction
$2\mathrm{A(g)} + \mathrm{B(g)} \rightarrow 2\mathrm{D(g)}$
$\Delta U^{\mathrm{e}} = -10.5\mathrm{kJ}$ and $\Delta \mathrm{S}^{\circ} = -44.1\mathrm{JK}^{-1}$
Calculate $\Delta G^{\ominus}$ for the reaction, and predict whether the reaction may occur spontaneously

Answer. For the given reaction,
$2\mathrm{A}_{(g)} + \mathrm{B}_{(g)} \rightarrow 2\mathrm{D}_{(g)}$
$\Delta \eta_g = 2 - (3)$
$= -1 \text{ mole}$
Substituting the value of ΔU^{θ} in the expression of ΔH:
$\Delta H^{\theta} = \Delta U^{\theta} + \Delta n_g RT$
$= (-10.5\mathrm{k}J) - (-1)\left(8.314 \times 10^{-3}\mathrm{kJK}^{-1}\mathrm{mol}^{-1}\right)(298\mathrm{K})$
$= -10.5\mathrm{kJ} - 2.48\mathrm{kJ}$
$\Delta H^{\ominus} = -12.98\mathrm{k}J$
Substituting the values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ in the expression of $\Delta G^{\ominus}$
$\Delta G^{\theta} = \triangle H^{\theta} - T\Delta S^{\theta}$
$= -12.98\mathrm{kJ} - (298\mathrm{K})\left(-44.1\mathrm{JK}^{-1}\right)$
$= -12.98\mathrm{kJ} + 13.14\mathrm{kJ}$
$\Delta G^{\ominus} = +0.16\mathrm{kJ}$
Since ΔG^{θ} for the reaction is positive, the reaction will not occur spontaneously.

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Q6.20 The equilibrium constant for a reaction is 10. What will be the value of $\Delta G^{\ominus}$? R = 8.314 $\mathrm{JK}^{-1}\mathrm{mol}^{-1}$ T = 300 K.

Answer. From the expression,
$\Delta G^{\theta} = -2.303 \mathrm{~RT} \log k_{\mathrm{eq}}$

ΔG^{θ} for the reaction,

$= (2.303)\left(8.314 \mathrm{JK}^{-1} \mathrm{mol}^{-1}\right)(300 \mathrm{K}) \log 10$

$= -5744.14 \mathrm{Jmol}^{-1}$

$= -5.744 \mathrm{kkmol}^{-1}$

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Q6.21 Comment on the thermodynamic stability of $\mathrm{NO}_{(}g)$, given

$\frac{1}{2} \mathrm{N}_2(\mathrm{g}) + \frac{1}{2} \mathrm{O}_2(\mathrm{g}) \rightarrow \mathrm{NO}(\mathrm{g}) \quad ; \quad \Delta_r H^{\ominus} = 90 \mathrm{kJmol}^{-1}$

$\mathrm{NO}(g) + \frac{1}{2} \mathrm{O}_2(\mathrm{g}) \rightarrow \mathrm{NO}_2(\mathrm{g}) \quad : \quad \Delta_r H^{\mathrm{e}} = -74 \mathrm{kJmol}^{-1}$

Answer. The positive value of $\Delta_r H$indicates that heat is absorbed during the formation of NO(g), j. This means that NO(g) has higher than the reactants $\left(\mathrm{N}_2 \text{ and } \mathrm{O}_2\right)$.
Hence, NO(g) is unstable.
The negative value of $\Delta_r H$H indicates that heat is evolved during the formation of $\mathrm{NO}_{2(g)}$ from $\mathrm{NO}_{(g)}$ and $\mathrm{O}_{2(g)}$. The product, $\mathrm{NO}_{2(\mathrm{g})}$ is stabilized with minimum energy.
Hence, unstable $\mathrm{NO}_{(g)}$ changes to unstable $\mathrm{NO}_{2(g)}$.

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Q6.22 Calculate the entropy change in surroundings when 1.00 mol of $\mathrm{H}_2\mathrm{O}_{(l)}$ is formed under standard conditions. $\Delta H^{\theta} = -286 \mathrm{kJmol}^{-1}$

Answer. It is given that 286 kJ mol^{-1} of heat is evolved the formation of 1 mol of $\mathrm{H}_2\mathrm{O}_{(\mathrm{l})}$. Thus, an equal amount of heat will be absorbed by the surroundings.
$q_{surr} = +286 \mathrm{kJmol}^{-1}$
Entropy change $\left(\Delta S_{\text{surr}}\right)$ for the surroundings = $\frac{q_{\text{surr}}}{7}$

$= \frac{286 \mathrm{kJmol}^{-1}}{298 \mathrm{k}}$

$\therefore \Delta S_{surt} = 959.73 \mathrm{Jmol}^{-1} \mathrm{K}^{-1}$

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