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## CHEMISTRY

## NCERT - NCERT CHEMISTRY(HINGLISH)

## THERMODYNAMICS

## Solved Example

1. Express the change in internal energy of a system when
(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have?
ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?
(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?
2. Two litres of an ideal gas at a pressure of 10 atm expands isothermally at $25^{\circ} \mathrm{C}$ into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

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3. Consider the same expansion, but this time against a constant external pressure of 1 atm.

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4. Consider the expansion given in problem 6.2 , for 1 mol of an ideal gas conducted reversibly

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5. If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and $100^{\circ} \mathrm{C}$ is $41 \mathrm{~kJ} \mathrm{~mol}{ }^{-1}$. Calculate the internal energy change, when 1 mol of water is vapourised at 1 bar pressure and $100^{\circ} \mathrm{C}$.

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6. 1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation

C (graphite) $+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})$
During the reaction, temperature rises from 298 K to 299 K . If the heat capacity of the bomb calorimeter is $20.7 \mathrm{~kJ} / \mathrm{K}$, what is the enthalpy change for the above reaction at 298 K and 1 atm ?

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7. A swimmer coming out from a pool is covered with a film of water weighing about 18 g . How much heat must be supplied to evaporate this
water at 298 K ? Calculate the internal energy of vaporisation at 298 K .
$\Delta_{\text {vap }} H^{\ominus}$ for water
at $298 \mathrm{~K}=44.01 \mathrm{~kJ} \mathrm{~mol}^{-1}$

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8. Assuming the water vapour to be a perfect gas, calculate the internal energy change when 1 mol of water at $100^{\circ} \mathrm{C}$ and 1 bar pressure is converted to ice at $0^{\circ} \mathrm{C}$. Given the enthalpy of fusion of ice is 6.00 kJ $\mathrm{mol}^{-1}$ heat capacity of water is $4.2 \mathrm{~J} / \mathrm{g}^{\circ} \mathrm{C}$

The change take place as follows:

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9. The combustion of 1 mol of benzene takes place at 298 K and 1 atm .

After combustion, $\mathrm{CO}_{2}(\mathrm{~g})$ and $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ are produced and 3267.0 kJ of heat is librated. Calculate the standard entalpy of formation, $\Delta_{f} H^{\Theta}$ of benzene

Given: $\Delta_{f} H^{\Theta} \mathrm{CO}_{2}(g)=-393.5 \mathrm{kJmol}^{-1}$
$\Delta_{f} H^{\Theta} H_{2} O(l)=-285.83 k^{J m o l^{-1}}$.

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10. Predict in which of the following entropy of the system increases / decreases:
(P) A liquid crystalizes into a solid
(Q) Temperature of a crystalline solid is raised
(R) $2 \mathrm{NaHCO}_{3}(s) \rightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}(s)+\mathrm{H}_{2} \mathrm{O}(g)+\mathrm{CO}_{2}(g)$
(S) $\mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}(\mathrm{g})$

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11. For oxidation of iron.
$4 \mathrm{Fe}(\mathrm{s})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})$
entropy change is $-549.4 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ at 298 K . Inspite of negative entropy change of this reaction, why is the reaction spontaneous?
$\left(\Delta_{r} H^{\ominus}\right.$ for this reaction is $\left.-1648 \times 10^{3} \mathrm{Jmol}^{-1}\right)$

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12. Calculate $\Delta G^{\Theta}$ for the conversion of oxygen to ozone, $\left(\frac{3}{2}\right) O_{2}(g) \Leftrightarrow O_{3}(g)$ at $298 K$, of $K_{p}$ for this conversion is $2.47 \times 10^{-29}$.

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13. Find out the value of equilibrium constant for the following reaction at 298 K .
$2 \mathrm{NH}_{3}(g)+\mathrm{CO}_{2}(g) \Leftrightarrow \mathrm{NH}_{2} \mathrm{CONH}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(1)$
Standard Gibbs energy change, $\Delta_{r} G^{\ominus}$ at the given temperature is $-13.6 \mathrm{kJmol}^{-1}$

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14. At $60^{\circ} \mathrm{C}$, dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

## Exercise

1. Choose the correct answer. A thermodynamic state function is a quantity
A. used to determine heat changes
B. whose value is independent of path
C. used to determine pressure volume work
D. whose value depends on temperature only.

## Answer:

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2. For the process to occur under adiabatic conditions, the correct condition is
A. $\Delta T=0$
B. $\Delta p=0$
C. $q=0$
D. $w=0$

## Answer:

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3. The enthalpies of the elements in their standard states are arbitrarily assumed to be
A. unity
B. zero
C. $<0$
D. different for each element

## Answer:

4. $\Delta U^{\Theta}$ of combustion of methane is $-X k \mathrm{Kmol}^{-1}$. The value of $\Delta H^{\Theta}$ is
A. $=\Delta U^{\ominus}$
B. $>\Delta U^{\ominus}$
C. $<\Delta U^{\ominus}$
D. $=0$

## Answer:

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5. The enthalpy of combustion of methane, graphite and dihydrogen at $298 \mathrm{~K}^{\text {are, }}-890.3 \mathrm{kJmol}^{-1}-393.5 \mathrm{kJmol}^{-1}$, and $-285.8 \mathrm{kJmol}^{-1}$ respectively. Enthapy of formation of $\mathrm{CH}_{4}(\mathrm{~g})$ will be
A. $-74.8 \mathrm{kJmol}^{-1}$
B. $-52.27 \mathrm{kJmol}^{-1}$
C. $+74.8 \mathrm{kJmol}^{-1}$
D. $+52.26 \mathrm{kJmol}^{-1}$

## Answer:

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6. A reaction $A+B \rightarrow C+D+q$ is found to have a positive entropy change, the reaction will be:
A. possible at high temperature
B. possible only at low temperature
C. not possible at any temperature
D. possible at any temperature

## Answer:

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?

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8. The reaction of cyanamide, $\mathrm{NH}_{2} \mathrm{CN}(\mathrm{s})$, with dioxygen was carried out in a bomb calorimeter, and $\Delta U$ was found to be $-742.7 \mathrm{kJmol}^{-1}$ at 298 K . Calculate enthalpy change for the reaction at 298 K .
$\mathrm{NH}_{2} \mathrm{CN}(\mathrm{g})+\frac{3}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$

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9. Calculate the number of $k J$ of heat necessary to raise the temperature of 60.0 g of aluminium from $35^{\circ} \mathrm{C}$ to $55^{\circ} \mathrm{C}$. Molar heat capacity of Al is $24 \mathrm{Jgm}^{-1}$.

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10. Calculate the enthalpy change of freezing of 1.0 mol of water at $10^{\circ} \mathrm{C}$ to ice at $-10^{\circ} \mathrm{C}, \Delta_{\text {fus }} H=6.03 \mathrm{kJmol}^{-1}$ at $0^{\circ} \mathrm{C}$.
$\mathrm{C}_{\mathrm{P}}\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\right]=75.3 \mathrm{Jmol}^{-1} \mathrm{~K}^{-1}$
$\mathrm{C}_{\mathrm{P}}\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{s})\right]=36.8 \mathrm{Jmol}^{-1} \mathrm{~K}^{-1}$

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11. Enthalpy of combustion of carbon to $\mathrm{CO}_{2}$ is $-393.5 \mathrm{kJmol}^{-1}$. Calculate the heat released upon formation of $35.2 g$ of $\mathrm{CO}_{2}$ from carbon and dioxygen gas.

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12. Find the value of $\Delta_{f} H^{\circ}$ for the reaction
$\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})+3 \mathrm{CO}(\mathrm{g}) \rightarrow \mathrm{N}_{2} \mathrm{O}(\mathrm{g})+3 \mathrm{CO}_{2}(\mathrm{~g})$
Standard enthalpies of formation of $\mathrm{CO}(\mathrm{g}), \mathrm{CO}_{2}(\mathrm{~g}), \mathrm{N}_{2} \mathrm{O}(\mathrm{g})$, and
$\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ are $-110,-393,81$, and $9.7 \mathrm{kJmol}^{-1}$, respectively.
Strategy : The standard enthalpy change of a reaction is equal to the sum of the standard molar enthalpie of formation of the products each multiplied by its stiochiometric coefficient in the balanced equation, minus the corresponding sum of the standard molar enthalpies of formation of the reactants

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13. Given
$\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NH}_{3}(\mathrm{~g}), \Delta_{r} H^{\ominus}=-92.4 \mathrm{kJmol}^{-1}$
What is the standard enthalpy of formation of $\mathrm{NH}_{3}$ gas?

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14. Calculate the standard enthalpy of formation of $\mathrm{CH}_{3} \mathrm{OH}(l)$ from the following data:
$\mathrm{CH}_{3} \mathrm{OH}(l)+\frac{3}{2} \mathrm{O}_{2}(g) \rightarrow \mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}), \ldots(i), \Delta_{r} \mathrm{H}_{1}^{\Theta}=-726 \mathrm{kJr}$

$$
C(g)+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}), \ldots(i \mathrm{i}), \Delta_{c} H_{2}^{\Theta}=-393 \mathrm{kmol}^{-1}
$$

$$
H_{2}(g)+\frac{1}{2} O_{2}(g) \rightarrow H_{2} O(l), \ldots(i i i), \Delta_{f} H_{3}^{\Theta}=-286 \mathrm{kJmol}^{-1}
$$

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15. Calculate the enthalpy change for the process

$$
C C l_{4}(g) \rightarrow C(g)+4 C l(g)
$$

and calculate bond enthalpy of $C-C l$ in $C C l_{4}(g)$.
$\Delta_{\text {vap }} H^{\Theta}\left(C C l_{4}\right)=30.5 \mathrm{kJmol}^{-1}$
$\Delta_{f} H^{\Theta}\left(C C l_{4}\right)=-135.5 \mathrm{kJmol}^{-1}$
$\Delta_{a} H^{\Theta}(C)=715.0 \mathrm{kJmol}^{-1}$, where $\Delta_{a} H^{\Theta}$ is enthalpy of atomisation
$\Delta_{a} H^{\Theta}\left(C l_{2}\right)=242 \mathrm{kJmol}^{-1}$

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16. For an isolated system, $\Delta U=0$, what will be $\Delta S$ ?

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17. For the reaction at $298 K$
$2 A+B \rightarrow C$
$\Delta H=400 \mathrm{kJmol}^{-1}$ and $\Delta S=0.2 \mathrm{kJK}^{-1} \mathrm{~mol}^{-1}$
At what temperature will the reaction becomes spontaneous considering
$\Delta H$ and $\Delta S$ to be contant over the temperature range.

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18. For the reaction
$2 C l(g) \rightarrow C l_{2}(g)$, what are the signs of $\Delta H$ and $\Delta S ?$

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19. For the reaction,
$2 A(g)+B(g) \rightarrow 2 D(g)$
$\Delta U^{\Theta}=-10.5 k J$ and $\Delta S^{\Theta}=-44.1 J K^{-1}$
Calculate $\Delta G^{\Theta}$ for the reaction, and predict whether the reaction may occur spontaneously.
20. The equilibrium constant for a reaction is 10 . What will be the value of $\Delta G^{\Theta} ? R=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}, T=300 \mathrm{~K}$.

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21. Comment on the thermodynamic stability of $N O(g)$, given
$\frac{1}{2} \mathrm{~N}_{2}(g)+\frac{1}{2} \mathrm{O}_{2}(g) \rightarrow N O(g), \Delta_{r} H^{\Theta}=90 \mathrm{kJmol}^{-1}$
$\mathrm{NO}(g)+\frac{1}{2} \mathrm{O}_{2}(g) \rightarrow \mathrm{NO}_{2}(g), \Delta_{r} H^{\Theta}=-74 \mathrm{kJmol}^{-1}$

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22. Calculate the entropy change in surroundings when 1.00 mol of $\mathrm{H}_{2} \mathrm{O}(l)$ is formed under standard conditions, $\Delta_{r} H^{\Theta}=-286 \mathrm{kJmol}^{-1}$.

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