# CHEMISTRY

# BOOKS - MODERN PUBLISHERS CHEMISTRY (HINGLISH)

# THERMODYNAMICS

## Solved Examples

**1.** Classify the following as open, closed, or isolated system.

a. A beaker containing as open, boiling water.

b. A chemical reaction taking place in an enclosed flask.

c. A cup of tea placed on a table.

d. Hot water placed in perfectly insulated closed container.

e. A thermos flask containing hot coffee.

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**2.** 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?

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**3.** Calculate the internal energy change for each of the following processes:

(i) A system absorbs 428 J of heat and does work equivalent to 286 J on its surroundings.

(ii) 62 J of work is done on the system and 128 J of heat is transferred to the surroundings.

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**4.** 2L of an ideal gas at a pressure of 10 atm expands isothermally into a

vacuum until its total volume is 10L.

(i) How much heat is absorbed and how much work is done in the

expansion?

(ii)How much heat is absorbed if this system expands againts a constant

external pressure of 1 atm?

(iii) How much heat is absorbed if the expansion is conducted reversibly

at 298 K.

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**5.** A gas absorbs $120J$ of heat and expands against the external pressure

of 1.10 atm from a volume of $0.5L$ to $2.0L$. What is the change in internal

energy? $(1Latm = 101.3J)$

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**6.** Calculate $\Delta U$, q and w when 2.0 mol of an ideal gas at $25°C$ are compressed isothermally and reversibly from 1.0 bar to 10.0 bar.

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**7.** Three moles of hydrogen gas are compressed isothermally and reversibly from 60L to 20L and 8.50 kJ of work is done on it. Assuming ideal behaviour, calculate the temperature of the gas.

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**8.** Calculate w and $\Delta U$ for the conversion of 1 mol of water at $100°C$ to steam at 1 atm pressure.Heat of vaporisation of water at $100°C$ is 40.670 kJ $mol^{-1}$.Assume ideal gas behaviour.

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**9.** A 6 litre cylinder contained 280 g of $N_2$ gas at $27°$C. Due to sudden leakage through the hole, all the gas escaped into atmosphere and the cylinder became empty.If the atmospheric pressure is 1.0 atmosphere, calculate the work done by the gas.
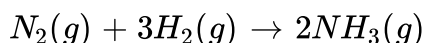
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**10.** The heat of combustion of gaseous methane $(CH_4)$ at constant volume is measured in a bomb calorimeter at $298K$ and is found to be $-885.4kJmol^{-1}$.Find the value of enthalpy change.

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**11.** The enthalpy change $(\Delta H)$ for the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

is $-92.38kJ$ at $298K$. What is $\Delta U$ at $298K$?

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**12.** Enthalpy of combustion of carbon to $CO_2$ is $-393.5 kJmol^{-1}$. Calculate the heat released upon formation of $35.2g$ of $CO_2$ from carbon and dioxygen gas.

**13.** If water vapour is assumed to be a perfect gas, molar enthalpy change for vaporisation of 1 mol of water at 1 bar and $100°C$ is 41 kJ $mol^{-1}$ .Calculate the internal energy change, when

(a) 1 mol of water is vaporised at 1 bar pressure and $100°$C.

(b) 1 mol of water is converted into ice.

**14.** The heat liberated on complete combustion of $7.8g$ of benzene at constant volume at $25°C$ has been found to be $326.39kJ$. Calculate the heat of combustion of benzene at constant pressure.

**15.** A swimming pool contains $1 \times 10^5 L$ of water. How much energy in joules is required to raise the temperature of water from $20°C$ to $25°C$? The specific heat capacity of water is $4.184 J/°Cg$.

**16.** (a) Calculate the heat that must be supplied to raise the temperature of 2 kg of water from $25°C$ to its boiling point at atmospheric pressure.The average specific heat of water in the range $25 - 100°C$ is 4.184 J $K^{-1}g^{-1}$.

(b)How long will a 2 kW heater take to supply this energy?

**17.** (a)Calculate the energy needed to raise the temperature of 10.0 g of iron from $25°C$ to $250°C$ if specific heat capacity of iron is 0.45J

$.^\circ C^{-1}g^{-1}.$

(b) What mass of copper (specific heat capacity = 0.385 J $.^\circ C^{-1}g^{-1}$) can be heated through the same temperature difference when supplied with the same amount of energy as above.

**18.** A chemist while studying the properties of gaseous $C_2Cl_2F_2$, a chlorofluoro carbon refrigerant, cooled a $1.25g$ sample at constant atmospheric pressure of $1.0atm$ from $320K$ to $290K$. During cooling, the sample volume decreased from $274$ to $248mL$. Calculate $\Delta H$ and $\Delta U$ for the chlorofluoro carbon for this process. For $C_2Cl_2F_2$, $C_P = 80.7Jmol^{-1}K^{-1}$.

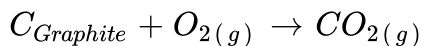**19.** Calculate the number of $KJ$ necessary to raise the temperature of $60.0g$ of aluminium from $35^\circ$ to $55^\circ C$. Molar heat capcacity of $Al$ is $24Jmol^{-1}K^{-1}$ (Answer in Joules)

**20.** $0.562g$ of graphite kept in a bomb calorimeter in excess of oxygen at $298K$ and 1 atmospheric pressure was burnt according to the equation,
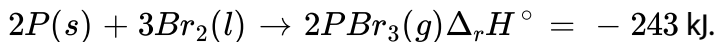
$C_{Graphite} + O_{2(g)} \rightarrow CO_{2(g)}$

durgin the reaction, temperature rises from $298K$ o $298.89K$. If the heat capacity of the calorimeter and its contents is $20.7kJ/K$, what is the enthalpy change for the above reaction at $298K$ and $1atm$?

**21.** The reaction of cyanamide, $[NH_2CN(s)]$, with dioxygen was carried out in a bomb calorimeter, and $\Delta U$ was found to be $-742.7kJmol^{-1}$ at $298K$. Calculate enthalpy change for the reaction at $298K$.

$NH_2CN(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$
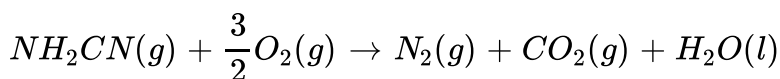
**22.** Red phosphorus reacts with liquid bromine as :

$$2P(s) + 3Br_2(l) \rightarrow 2PBr_3(g) \Delta_r H° = -243 \text{ kJ}.$$
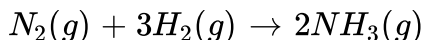
Calculate the enthalpy change when 10.32 g of phosphorus reacts with an excess of bromine.

**23.** The heat change for the reaction,

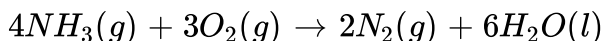$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

is $-92.2kJ$. Calculate the heat of formation of ammonia.

**24.** Calculate the heat change in the reaction,
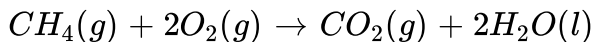
$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l)$$

at 298K given that heats of formation at 298K for $NH_3(g)$ and $H_2O(l)$ are $-46.0$ and $-286.0kJ \quad mol^{-1}$ respectively. (Write answer in magnitude and KJ form)

**25.** Calculate the enthalpy change for the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The enethalpy of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(l)$ are -74.8 kJ $mol^{-1}$, -393.5 kJ $mol^{-1}$ and $-285.8 kJmol^{-1}$ respectively.

**26.** The combusition of 1 mol of benzene $(C_6H_6)$ takes place at $298K$ and 1 bar pressure. After combustion, $CO_2(g)$ and $H_2O(l)$ are produced and $3267kJ$ of heat is liberated. Calculate the standard enthaply of formation, $\Delta_f H^\circ$ of benzene. Standard enthapies of formation of $CO_2(g)$ and $H_2O(l)$ are $-393.5 kJmol^{-1}$ and $-258.83 kJmol^{-1}$, respectively.

Strategy : Apply Eq. the mathematical form of Hesis's law, to the combustion reaction of 1 mol of benzene. Remember $\Delta_f H^\circ$ for $O_2(g)$ is zero by convention. We are give $\Delta_1 H^\circ$ and $\Delta_f H^\circ$ values for all substance except $C_6H_6(1)$. We can solve for this unknown.

**27.** 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. Calculate $\Delta_r H$ for the reaction:

$$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g).$$
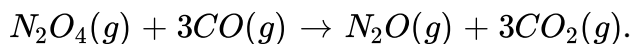
**28.** The enthalpies of combustion of $CH_4$ and $C_2H_6$ are -890.3 and -1559.7 k J $mol^{-1}$ respectively. Which of the two has greater efficiency of fuel per gram?

**29.** In a gobar gas plant, gobar gas is formed by bacterial fermentation of animal refuse. It mainly contains methane and its heat of combustion is $-809 kJmol^{-1}$ according to following equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \Delta H = -809kJ$$
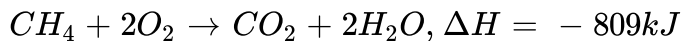
How much gobar gas would have to be produced per day for a small village of 50 families, it it is assumed that each family requires $20000kJ$ of enegry per day? The methane content in gobar gas is $80\%$ by mass.
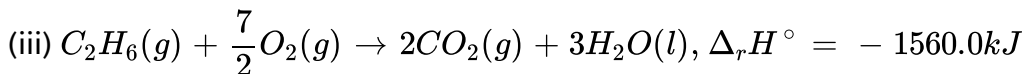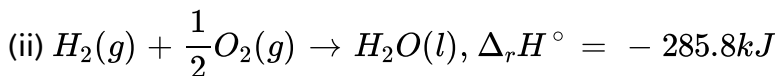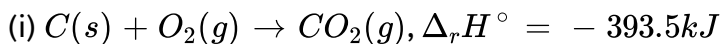
**30.** a. A cylinder of gas is assumed to contain $11.2kg$ of butane. If a normal family needs $20000kJ$ of energy per day for cooking, how long will the cylinder last? Given that the heat of combustion of butane is $2658kJmol^{-1}$.

b. If the air supply of the burner is insufficient (i.e. you have a yellow instead of a blue flame), a portion of the gas escape without combustion. Assuming that $33\%$ of the gas is wasted due to this inefficiency, how long would the cylinder last?
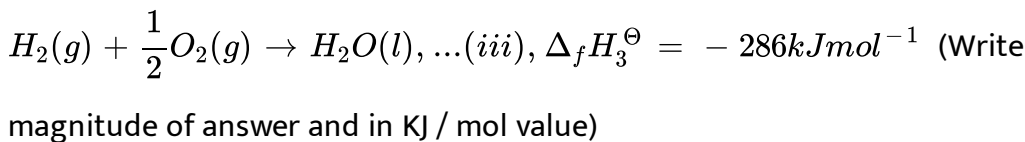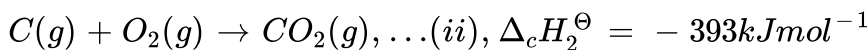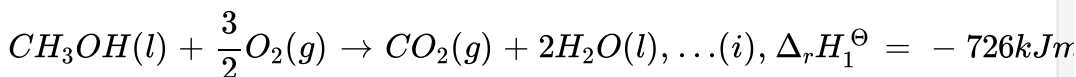
**31.** Calculate the enthalpy of formation of ethane from the following data :

(i) $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta_r H^\circ = -393.5kJ$

(ii) $H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l)$, $\Delta_r H^\circ = -285.8kJ$

(iii) $C_2H_6(g) + \dfrac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$, $\Delta_r H^\circ = -1560.0kJ$

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

$CH_3OH(l) + \dfrac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l), \ldots(i)$, $\Delta_r H_1^\ominus = -726kJm$

$C(g) + O_2(g) \rightarrow CO_2(g), \ldots(ii)$, $\Delta_c H_2^\ominus = -393kJmol^{-1}$

$H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l), \ldots(iii)$, $\Delta_f H_3^\ominus = -286kJmol^{-1}$ (Write magnitude of answer and in KJ / mol value)

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**33.** Calculate the enthalpy of formation of benzene represented by the following reaction:

$$6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$$
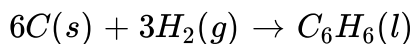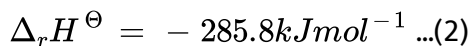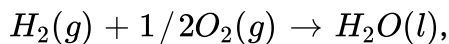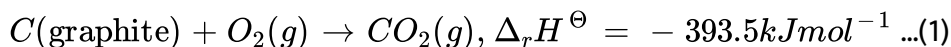
The standard enthalpy of combustion of benzene is -3266.0 kJ and standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are - 393.1 and -286.0 kJ respectively.

**34.** With the help of thermochemical equations given below, determine $\Delta_r H^{\ominus}$ at $298K$ for the following reaction:

$$C(\text{graphite}) + 2H_2(g) \rightarrow CH_4(g), \Delta_r H^{\ominus} = ?$$

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g), \Delta_r H^{\ominus} = -393.5 kJmol^{-1} \text{...(1)}$$

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l),$$

$$\Delta_r H^{\ominus} = -285.8 kJmol^{-1} \text{...(2)}$$

$$CO_2(2)(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g),$$

$$\Delta_r H^{\ominus} = +890.3 kJmol^{-1} \text{...(3)}$$
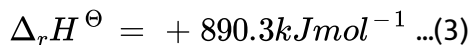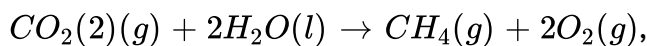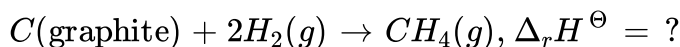
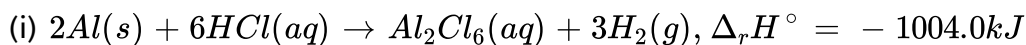**35.** The enthalpies of solution of anhydrous $CuSO_4$ and hydrated $CuSO_4.5H_2O$ are -66.5 and 11.7 kJ $mol^{-1}$ respectively.Calculate the enthalpy of hydration of $CuSO_4$ to $CuSO_4.5H_2O$.

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**36.** Calculate the enthalpy of formation of anhydrous aluminium chloride, $Al_2Cl_6$ from the following data :

(i) $2Al(s) + 6HCl(aq) \rightarrow Al_2Cl_6(aq) + 3H_2(g), \Delta_r H^\circ = -1004.0 kJ$

(ii)

$H_2(g) + Cl_2(aq) \rightarrow 2HCl(g), \Delta_r H^\circ = -183.9 kJ, \Delta_r H^\circ = -183.9 kJ$

(iii) $HCl(g) + aq \rightarrow HCl(aq), \Delta_r H^\circ = -73.2 kJ$

$Al_2Cl_6(s) + aq \rightarrow Al_2Cl_2(aq), \Delta_r H^\circ = -643.0 kJ$
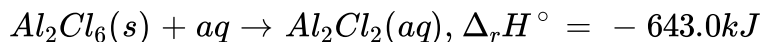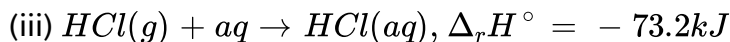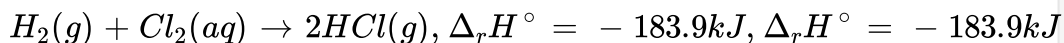
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**37.** The standard enthalpies of formation of $SO_2(g)$ and $SO_3(g)$ are - 296.6 kJ and -395.6 kJ respectively.Calculate $\Delta H^\circ$ for the reaction:

$$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g).$$

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**38.** Calculate the standard heat of formation of carbon disulphide (l). Given that the standard heats of combustion of carbon (s), sulphur (s) and carbon disulphide (l) are -393.3, -293.72 and -1108.76 kJ $mol^{-1}$ respectively.
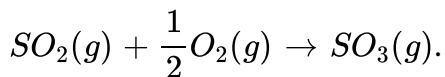
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**39.** Calculate $\Delta_f H^\circ$ for chloride ion from the following data:

$$\frac{1}{2}H_2(g) + \frac{1}{2}CI_2(g) \rightarrow HCI(g)$$

$$\Delta_f H^\circ = -92.8 kJmol^{-1}$$

$$HCI(g) + H_2O \rightarrow H_3O^+(aq) + CI^-(aq)$$
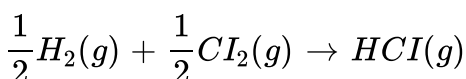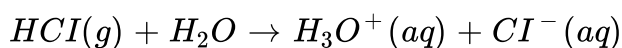
$$\Delta_{diss} H^\circ = -75.2 kJmol^{-1}.$$

**40.** Calculate $\Delta H$ for the process at $25^\circ C$ of dissolving 1.0 mol of KCl in a large excess of water..

$\Delta_f H^\circ \left[ K^+ (aq) \right] = -251.2 kJmol^{-1}$

$\Delta_f H^\circ \left[ Cl^- (aq) \right] = -167.08 kJmol^{-1}$

$\Delta_f H^\circ [KCl] = -437.6 kJmol^{-1}$.

**41.** Whenever an acid is neutralised by a base, the net reaction is :

$H^+ (aq) + OH^- (aq) \rightarrow H_2O(l) + 57.1 kJ$
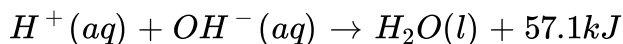
Calculate the heat evolved for the following experiments :

(i) 0.25 mol of HCl solution is neutralised by 0.25 mol of NaOH solution.

(ii) 0.60 mol of $HNO_3$ solution is mixed with 0.30 mol of KOH solution.

(iii) $100 cm^3$ of 0.2 M HCl is mixed with $200 cm^3$ of 0.3M NaOH.

$400 cm^3$ of 0.2 M $H_2SO_4$ is mixed with $600 cm^3$ of 0.1 M NaOH solution.

**42.** When $1g$ liquid naphthalene $(C_{10}H_8)$ solidifies, $149J$ of heat is evolved. Calculate the enthalpy of fusion of naphthalene. (Write answer in Joules)

**43.** Calculate the enthalpy change when 2.38 g of carbon monoxide (CO) vaporize at its normal boiling point.Enthalpy of vapourization of CO is 6.04 kJ $mol^{-1}$.

**44.** 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 vaperization at $100°C$. $\Delta_{vap}H^{\ominus}$ for water at 373 K = 40.66 kJ $mol^{-1}$

**45.** 18.0 g of water completely vaporises at $100°C$ and 1 bar pressure and the enthalpy change in the process is $40.79 kJmol^{-1}$. What will be the enthalpy change for vaporising two moles of water under the same conditions ? What is the standard enthalpy of vaporisation for water ?

**46.** Calculate $\Delta_r H°$ for the reaction:



Average bond enthalpies of C - H and C - Cl bonds are 414 kJ $mol^{-1}$ and 330 kJ $mol^{-1}$ respectively.

**47.** Calculate $\Delta_r H°$ for the reaction

The average bond enthalpies of various bonds are :

**48.** Calculate the C-C bond enthalpy from the following data :

$$2C(\text{graphite}) + 3H_2(g), \rightarrow C_2H_6(g)\Delta_rH^\circ = -84.67mkJ$$

$$C(\text{graphite}), \rightarrow C(g)\Delta_rH^\circ = 716.7kJ$$

$$H_2(g), \rightarrow 2H(g)\Delta_rH^\circ = 435.9kJ$$
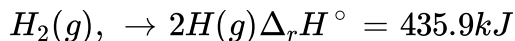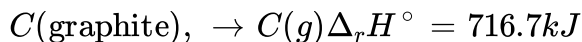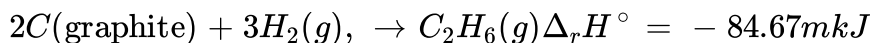
Assume 416 kJ as the C-H bond enthalpy.

**49.** Propane has the structure $H_3C - CH_2 - CH_3$ Calculate the enthalpy change, $\Delta_rH^\circ$ for the reaction :

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$ The average bond enthalpies of various bonds are

**50.** Calculate the enthalpy change for the process

$$CCl_4(g) \rightarrow C(g) + 4Cl(g)$$
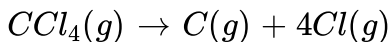
and calculate bond enthalpy of $C - Cl$ in $CCl_4(g)$.

$\Delta_{vap}H^{\ominus}(CCl_4) = 30.5kJmol^{-1}$

$\Delta_f H^{\ominus}(CCl_4) = -135.5kJmol^{-1}$

$\Delta_a H^{\ominus}(C) = 715.0kJmol^{-1}$, where $\Delta_a H^{\ominus}$ is enthalpy of atomisation

$\Delta_a H^{\ominus}(Cl_2) = 242kJmol^{-1}$

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**51.** Calculate the bond energy of $C - H$ bond, given that the heat of formation of $CH_4$, heat of sublimation of carbon and heat of dissociation of $H_2$ are $-74.8 + 719.6$ and $435kJmol^{-1}$ respectively.

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**52.** Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions, $\Delta_r H^{\ominus} = -286kJmol^{-1}$.

**53.** Predict in which of the following entropy increases/decreases :

(a) $H_2(g) \rightarrow 2H(g)$

(b) $2NaHCO_3 \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
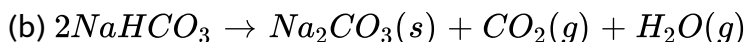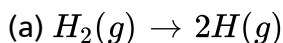
(c) A liquid crystallizes into a solid.

(d) Temperature of a crystalline solid is raised from 0 K to 115 K.

**54.** Consider the reaction for the dissolution of ammonium nitrate :

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

$\Delta H = +28.1kJmol^{-1}, \Delta S = 108.7JK^{-1}mol^{-1}$.

Calculate the change in entropy of the surroundings and predict whether the reaction is spontaneous or not at $25°C$?

**55.** The oxidation of iron occurs as:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$
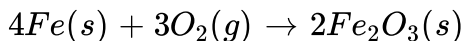
The enthalpy of formation of $Fe_2O_3 is -824.2 kJmol^{-1}$ and entropy change for the reaction is $-549 JK^{-1}mol^{-1}$ at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous at 298 K?

**56.** The standard enthalpy change for the transition of liquid water of steam is 40.8 kJ $mol^{-1}$ at 373 K. Calculate the entropy of vaporisation of water.

**57.** Calculate the enthalpy of vaporisation per mole for ethanol. Given $\Delta S = 109.8 JK^{-1}mol^{-1}$ and boiling point of ethanol is $78.5°$.

**58.** The enthalpy of vapourisation of liquid diethyl ether $(C_2H_5)_2O$ is $26.0 kJmol^{-1}$ at its boiling point $(25.0°C)$. Calculate $\Delta S°$ for the conversion of

(a) liquid to vapour and

(b) vapour to liquid at $35°C$.

**59.** For the melting of ice at $25°C$:

$$H_2O(s) \rightarrow H_2O(l)$$
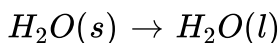
The enthalpy of fusion is $6.97 kJmol^{-1}$ and entropy of fusion is $25.4 Jmol^{-1}K^{-1}$. Calculate the free energy change and predict whether melting of ice is spontaneous or not at this temperature.

**60.** Enthalpy and entropy changes of reaction are $40.63kJmol^{-1}$ and $108.8JK^{-1}mol^{-1}$, respectively. Predict the feasibility of the reaction at $27°C$.

**61.** $\Delta H$ and $\Delta S$ for the reaction:

$$Ag_2O(s) \rightarrow 2Ag(s) + (1/2)O_2(g)$$
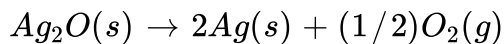
are $30.56kJmol^{-1}$ and $66.0JJK^{-1}mol^{-1}$ respectively. Calculate the temperature at which free energy change for the reaction will be zero. Predict whether the forward reaction will be favoured above or below this temperature.

**62.** Predict whether it is possible or not to reduce magnesium oxide using carbon at $298K$ according to the reaction.

$$MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$$
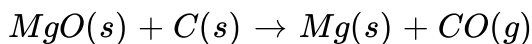
$\Delta_r H^{\ominus} = +491.18 kJmol^{-1}$ and $\Delta_r S^{\ominus} = 197.67 JK^{-1}mol^{-1}$

If not at what temperature, the reaction becomes spontaneous.

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**63.** Calculate the standard Gibbs free energy change from the free energies of formation data for the following reaction:

$$C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g)$$
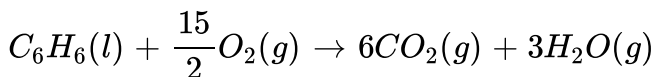
Given that $\Delta_f G^{\ominus} = [C_6H_6(l)] = 172.8 kJmol^{-1}$

$\Delta_f G^{\ominus}[CO_2(g)] = -394.4 kJmol^{-1}$

$\Delta_f G^{\ominus}[H_2O(g)] = -228.6 kJmol^{-1}$

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**64.** Consider the reaction:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l) \Delta G^\ominus = -1010.5kJ$$
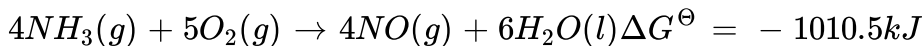
Calculate $\Delta_f G^\ominus[NO(g)]$ if $\Delta_f G^\ominus(NH_3) = -16.6 kJmol^{-1}$ and $\Delta_f G^\ominus[H_2O(l)] = -237.2 kJmol^{-1}$.

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**65.** Calculate $\Delta_r G^\ominus$ for the following reactions using $\Delta_f G^\ominus$ values and and predict which reactions are spontaneous.

a. $Ca(s) + CI_2(g) \rightarrow CaCI_2(s)$

b. $H_2O(s) \rightarrow Hg(l) + \frac{1}{2}O_2(g)$

c. $NH_3(g) + 2O_2(g) \rightarrow HNO_3(l) + H_2O(l)$
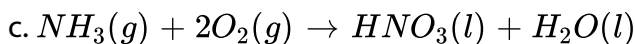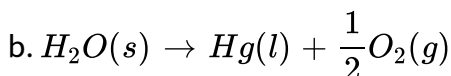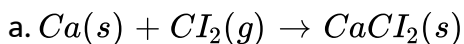
$\Delta_f G^\ominus$ value $(kJmol^{-1})$ are:

$$CaCI_2(s) = -748.1, HgO(s) = -58.84$$

$$NH_3(g) = -16.45, HNO_3(l) = -80.71,$$

$$H_2O(l) = -237.13$$

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**66.** Silane $(SiH_4)$ burns in air as:

$$SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(l)$$
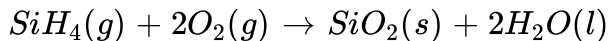
the standard Gibbs energies of formation of $SiH_4(g)$, $SiO_2(s)$, and $H_2O(l)$ are $+52.3$, $-805.0$, and $-228.6 kJmol^{-1}$, respectively. Calculate Gibbs enegry change for the reaction and predict whether the reaction in spontaneous or not.

**67.** In a fuel cell methanol is oxidised with oxygen as :

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
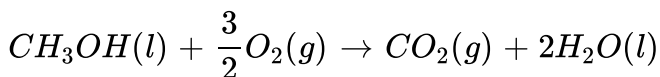
Calculate the standard Gibbs energy change for the reaction that can be converted into electrical works. If standard enthalpy of combustion for methanol is $726 kJmol^{-1}$, calculate the efficiency of conversion of Gibbs energy into useful work. The standard Gibbs energies of formation, $\Delta_f G^\circ (kJmol^{-1})$ are :

$CO_2(g) = -394.4$, $H_2O(l) = -237.2$, $CH_3OH(l) = -166.2$.
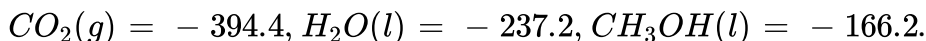
**68.** For the water gas reaction:

$$C(s) + H_2O(g) \Leftrightarrow CO(g) + H_2(g)$$

the standard Gibbs enegry for the reaction at $1000K$ is $-8.1kJmol^{-1}$.

Calculate its equilibrium constant. (Multiply your answer with 100 and

then write value)

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**69.** Calculate $\Delta G^{\ominus}$ for the conversion of oxygen to ozone,

$\left(\dfrac{3}{2}\right)O_2(g) \Leftrightarrow O_3(g) at 298K$, of $K_p$ for this conversion is $2.47 \times 10^{-29}$.
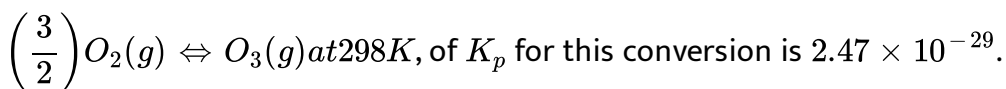
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**70.** What is the equilibrium constant $K_c$ for the following reaction at

$400K$?

$$2NOCI(g) \Leftrightarrow 2NO(g) + CI_2(g)$$
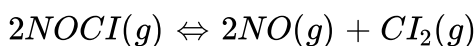
$\Delta H^{\ominus} = 77.2kJmol^{-1}$ and $\Delta S^{\ominus} = 122JK^{-1}mol^{-1} at 400K$.

**71.** The standard Gibbs energies $\left(\Delta_f G^{\ominus}\right)$ for the formation of $SO_2(g)$ and $SO_3(g)$ are $-300.0$ and $-371.0 kJmol^{-1}$ at $300K$, respectively. Calculate $\Delta G$ and equilibrium constant for the following reaction at $300K$:

$$2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$$
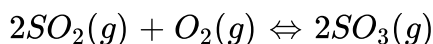
**72.** At $60°C$, dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

**73.** Find out the value of equilibrium constant for the following reaction at 298 K.

$$2NH_3(g) + CO_2(g) \Leftrightarrow NH_2CONH_2(aq) + H_2O(1)$$

Standard Gibbs energy change, $\Delta_r G^\ominus$ at the given temperature is

$-13.6 kJmol^{-1}$

**74.** It is planned to carry out the reaction:

$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$ at $1273K$ and 1bar pressure.

$\Delta_r H^\ominus = 176 kJmol^{-1}$ and $\Delta_r S^\ominus = 157.2 kJmol^{-1}$

a. Is the reaction spontaneous at this temperature and pressure ?

b. Calculate the value of

i. $K_p$ at $1273K$ for the reaction

ii. partial pressure of $CO_2$ at equilibrium

**75.** For the reaction,

$2A(g) + B(g) \rightarrow 2D(g)$

$\Delta U^\ominus = -10.5 kJ$ and $\Delta S^\ominus = -44.1 JK^{-1}$

Calculate $\Delta G^{\ominus}$ for the reaction, and predict whether the reaction may occur spontaneously. (multiply answer with 100 and answer in KJ/mol)

**76.** Using the following data, calculate the value of equilibrium constant for the following reaction at $298K$

$$3HC \equiv CH \Leftrightarrow C_6H_6(g)$$
$$\text{Acetylene} \qquad\qquad \text{Benzene}$$
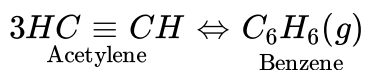
Assuming ideal behaviour

$$\Delta_f G^{\ominus}(HC \equiv CH) = 2.09 \times 10^5 \, Jmol^{-1}$$

$$\Delta_f G^{\ominus}(C_6H_6) = 1.24 \times 10^5 \, Jmol^{-1},$$

$$R = 8.314 JK^{-1}mol^{-1}$$

Can the reaction be recommended for the synthesis of benzene?

**77.** Calculate $\Delta_r S_m^{\ominus}$ for the reaction:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$
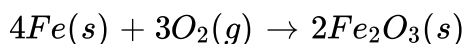
Given that $S_m^\Theta(Fe) = 27.3 JK^{-1}mol^{-1}$,

$S_m^\Theta(O_2) = 205.0 JK^{-1}mol^{-1}$ and $S_m^\Theta(Fe_2O_3) = 87.4 JK^{-1}mol^{-1}$.

**78.** Calculate the entropy changes for the following reactions :

(i) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

(ii) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
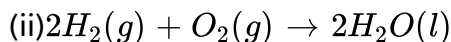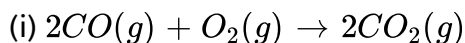
Entropies of different compounds are :

$CO(g) = 197.6 JK^{-1}mol^{-1}, O_2(g) = 205.03 JK^{-1}mol^{-1}$

$CO_2(g) = 213.6 JK^{-1}mol^{-1}, H_2(g) = 130.6 JK^{-1}mol^{-1}$

$H\_(2)O(l) = 69.96 JK^{-1}mol^{-1}$

**79.** Calculate the standard molar entropy change for the formation of gaseous propane $(C_3H_8)$ at $293K$.

$3C(\text{graphite}) + 4H_2(g) \rightarrow C_3H_8(g)$

Standard molar entropies $S_m^\ominus$ $(JK^{-1}mol^{-1})$ are:

$C(\text{graphite}) = 5.7$, $H_2(g) = 130.7$, $C_3H_5(g) = 270.2$

**80.** Calculate the free energy change at 298 K for the reaction ,

$Br_2(l) + Cl_2(g) \rightarrow 2BrCl(g)$. For the reaction $\Delta H° = 29.3kJ$ & the

entropies of $Br_2(l)$, $Cl_2(g)$ & $BrCl(g)$ at the 298 K are 152.3, 223.0, 239.7 J

$mol^{-1}K^{-1}$ respectively.

**81.** Calculate the standard Gibbs enegry change for the combustion of

$\alpha - D$ glucose at $300K$.

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$
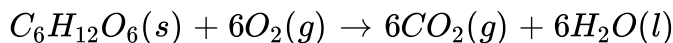
Given the standard enthalpies of formation $(kJmol^{-1})$

$C_6H_{12}O_6 = -1274.5$, $CO_2 = -393.5$, $H_2O = -285.8$.

Entropies $(JKmol^{-1})$

$C_6H_{12}O_6 = 212.1$, $O_1 = 205.0$, $CO_2 = 213$, $H_2O = 69.9$

**82.** Calculate the standard free energy change for the formation of methane at $300K$:

$$C(\text{graphite}) + 2H_2(g) \rightarrow CH_4(g)$$

The following data are given:

$\Delta_f H^{\ominus} \left( kJmol^{-1} \right) : CH_4(g) = -74.81$

$\Delta_f S^{\ominus} \left( JK^{-1}mol^{-1} \right) : C(\text{graphite}) = 5.70, H_2(g) = 130.7 CH_4(g) = 186.3$

**83.** Calculate the standard Gibbs energy change for the formation of propane at 298 K:

$$3C(\text{graphite}) + 4H_2(g) \rightarrow C_3H_8(g)$$

$\Delta_f H^{\circ}$ for propane, $C_3H_8(g) = -103.8 kJmol^{-1}$.

Given : $S_m^0[C_3H_8(g)] = 270.2 JK^{-1}mol^{-1}$

$S_m^{\circ}(\text{graphite}) = 5.70 JK^{-1}mol^{-1}$

and $S_m^0[H_2(g)] = 130.7 JK^{-1}mol^{-1}$.

**1.** Which of the following are open, close or nearly isolated systems :

(i) Human beings (ii) The Earth (iii) Can of tomato soup (iv) Ice-cube tray filled with water

(v) A satellite in a orbit (vi) Coffee in the thermos flask and (vii) Helium filled balloon.

**2.** Which of the following are state functions :

(i) Height of hill

(ii) Distance travelled in climbing the hill

(iii) Energy change in climbing the hill.

**3.** A system gives out 30 J of heat and does 75 J of work. What is the internal energy change?

**4.** During a process, a system absorbs $710J$ of heat and does work. The change in $\Delta U$ for the process is $460J$. What is the work done by the system?

**5.** Four moles of an ideal gas at 2.5 atm and $27°C$ are compressed isothermally to half of its volume by an external pressure of 3 atm. Calculate w, q and $\Delta U$.

**6.** A gas expands isothermally from $10dm^3$ to $20dm^3$ at $27°C$ and work obtained is 4.620 kJ.Calculate the number of moles of the gas.

**7.** The enthalpy changes for the following reactions at $298k$ and $1atm$ are given below:

a. $CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l), \Delta H = -874kJ$

b.

$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l), \Delta H = -1363kJ$
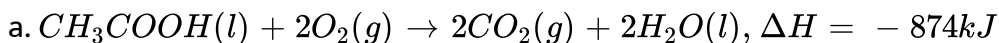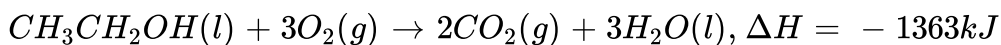
Calculate the internal enegry changes for these recaitons.

**8.** The enthalpy of combustion of benzoic acid $(C_6H_5COOH)$ at $298K$ and $1atm$ pressure is $-2546.0kJ \ mol^{-1}$. What is $\Delta U$ for the reaction?

**9.** Gaseous $N_2O$ decomposes at 298 K and forms $N_2(g)$ and $O_2(g)$.The $\Delta H$ for the reaction at 1 atm pressure and 298 K is $-163.15kJ$. What is the value of $\Delta U$ for the decomposition of 200 g of $N_2O$ under the same conditions?

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**10.** A $1.250g$ sample of octane $(C_8H_{18})$ is burned in excess of oxygen in a bomb calorimeter. The temperature of calorimeter rises from $294.05K$ to $300.78K$. If heat capacity of the calorimeter is $8.93kJK^{-1}$, find the heat transferred to calorimeter.

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**11.** $20.0g$ of ammonium nitrate $(NH_4NO_3)$ is dissolved In $125g$ of water in a coffee-cup calorimeter, the temperature falls from $296.5K$ to $286.4K$. Find the value of $q$ for the calorimeter. (Hint: heat capacity of water as the heat capacity of the calorimeter and its content)

**12.** 1g 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)$+O_2(g) \rightarrow CO_2(g)$
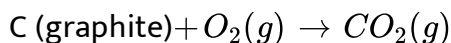
During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

**13.** The enthalpy of formation of $Fe_2O_3(s)$ is $-824.2kJmol^{-1}$.Calculate the enthalpy change for the reaction :

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$
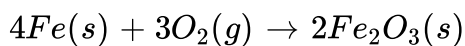
**14.** The $\Delta_r H^\circ$ for the reaction,

$$4S(s) + 6O_2(g) \rightarrow 4SO_3(g)$$
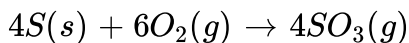
is -1583.2 kJ.Calculate $\Delta H_f^\circ$ of sulphur trioxide.

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**15.** Calculate $\Delta_f H^\circ$ for the reaction,
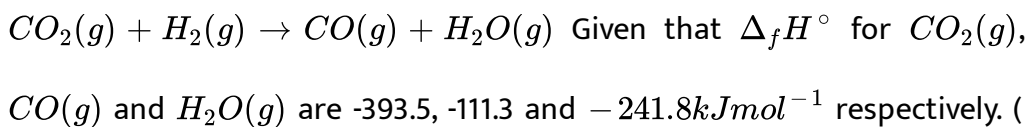
$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ Given that $\Delta_f H^\circ$ for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are -393.5, -111.3 and $-241.8 kJmol^{-1}$ respectively. ( Round of your answer in two digits and in KJ)

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**16.** The enthalpy of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are -277.0, -393.5 and -285.5 kJ/mol respectively.Calculate the enthalpy change for the reaction: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$.

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**17.** Calculate the standard enthalpy of formation of ethylene, $C_2H_4(g)$ from the following thermochemical equation :

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$
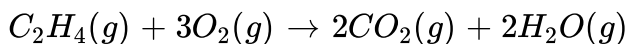
$$\Delta_r H^\circ = -1323kJ$$

Given the standard enthalpy of formation of $CO_2(g)$ and $H_2O(g)$ are -393.5 and -249 kJ $mol^{-1}$ respectively. (Answer in KJ mol"^(-1))

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**18.** The standard molar enthalpy of formation of ethane, carbon dioxide and liquid water are -21.1, -91.1 and -68.3 kcal respectively. Calculate the standard enthalpy change of the following reaction :

$$2C_2H_5(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l).$$
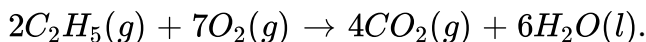
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**19.** Calculate $\Delta_r H^\circ$ for the reaction : Given $\Delta_f H^\circ$ values :

$$2H_2S(g) + 3O_2 \rightarrow 2H_2O(l) + 2SO_2(g)$$
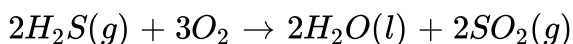
Given $\Delta_f H^\circ$ values : $H_2S(g) = -20.60$,

$H_2O(l) = -285.83$, $SO_2(g) = -296.83 kJmol^{-1}$

**20.** The enthalpy of formation of $CH_4, C_2H_6$ and $C_4H_{10}$ are -74.8, -84.7

and -126.1 kJ $mol^{-1}$ respectively. Arrange them in the order of their

efficiency as fuel per gram (enthalpy of formation of $CO_2(g)$ and $H_2O(l)$

are - 393.5 and $-285.8 kJmol^{-1}$ respectively).

**21.** Sucrose undergoes combustion as :

$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l) + 5645 kJmol^{-1}$
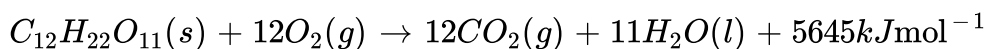
(i) How much energy will be liberated when 51.3 g of sucrose is burnt?

(ii) What is the energy required for the production of 5.472 g of sucrose?

**22.** A cylinder of indane gas contains 11.2 kg of butane.A normal family requires 25000 kJ energy per day for cooking.How long will the cylinder of gas last if the efficiency of combustion is 80%? (Heat of combustion of butane is 2658 kJ $mol^{-1}$).

**23.** An intimate mixture of ferric oxide, $(Fe_2O_3)$ and aluminium, (Al) is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows :

$\Delta H_f^0(Al_2O_3) = 399$ kcal $mol^{-1}$, $\Delta H_f^0(Fe_2O_3) = 199$ kcal $mol^{-1}$,

Density of $Fe_2O_3 = 5.2g/cc$, Density of $Al = 2.7g/cc$.

**24.** Calculate the enthalpy of formation of acetic acid $(CH_3COOH)$ if its enthalpy of combustion is $867kJmol^{-1}$.The enthalpies of fromation of $CO_2(g)$ and $H_2O(l)$ are -393.5 and -285.9 $kJmol^{-1}$ respectively.

**25.** Calculate the standard enthalpy of formation of propane $(C_3H_8)$ if its enthalpy of combustion is $-2220.2 kJmol^{-1}$. The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are -393.5 and -285.8 kJ $mol^{-1}$ respectively.

**26.** Calculate the enthalpy of formation of ethyl alcohol from the following data :

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l), \Delta_rH° = -1368.0 kJ$$

$$C(s) + O_2(g) \rightarrow CO_2(g), \Delta_rH° = -393.5 kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \Delta_rH° = -286.0 kJ$$
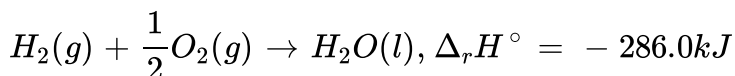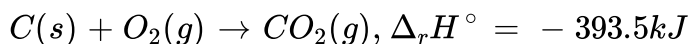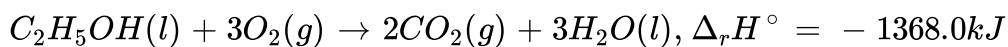
**27.** Calculate the enthalpy of formation of methane from the following

data : $C(s) + O_2(g) \rightarrow CO_2(g)\Delta_rH° = -393.5 kJ$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)\Delta_r H^\circ = -571.8kJ$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\Delta_r H^\circ = -890.3kJ$$
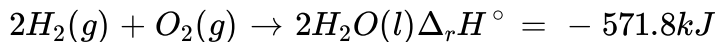
**28.** Calculate the enthalpy of allotropic transformation from monoclinic to rhombic sulphur from the following data:

$$S(\text{rhombic}) + O_2(g) \rightarrow SO_2(g)\Delta_r H^\circ = -294.1kJ$$

$$S(\text{monoclinic}) + O_2(g) \rightarrow SO_2(g)\Delta_r H^\circ = -295.4kJ$$
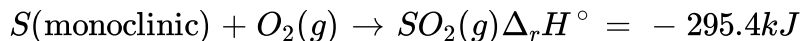
**29.** Enthalpies of solution of $BaCI_2 . 2H_2O$ and $BaCI_2$ are 8.8 and $-20.6kJmol^{-1}$ respectively.Calculate the heat of hydration of $BaCI_2 . 2H_2O$

**30.** The enthalpies of combustion of $C_2H_4(g)$, $C_2H_6(g)$ and $H_2$ are -1409.5 kJ, -1558.3 kJ and -285.6 kJ, respectively.Caalculate the enthalpy of hydrogenation of ethylene.

**31.** Calculate the enthalpy of formation of KOH(s) from the following data :

$$K(s) + H_2O(l) + (aq) \rightarrow KOH(aq) + \frac{1}{2}H_2(g)\Delta_r H^\circ = -200.8kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)\Delta_r H^\circ = -286.3kJ$$

$$KOH(s) + (aq) \rightarrow KOH(aq)\Delta_r H^\circ = -58.6kJ$$
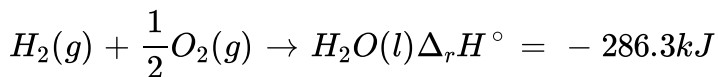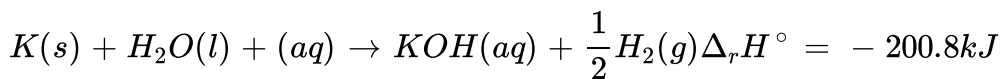
**32.** The combustion of butane $(C_4H_{10})$ is exothermic by 2878.7 kJ mol$^{-1}$ .Calculate the standard enthalpy of formation of butane given that the standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are $-393.5kJmol^{-1}$ and $-285.8kJmol^{-1}$ respectively.

**33.** Calculate the enthalpy of combustion of nitric oxide (NO) from the following data:

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g), \Delta_r H^\circ = 90.7kJ$$

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \Delta_r H^\circ = 34.0kJ$$
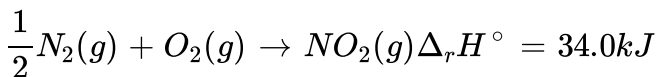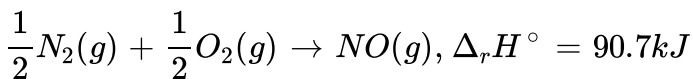
**34.** The molar enthalpies of combustion of $C_2H_2(g)$, $C(\text{graphite})$ and $H_2(g)$ are - 310.62 kcal, -94.05 kcal and -68.32 kcal respectively. Calculate the standard enthalpy of formation of $C_2H_2(g)$.

**35.** Calculate $\Delta_r H^\circ$ for the reaction,

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$
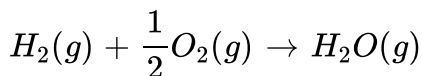
Given that bond enthalpies of H-H bond , O = O bond and O - H bond are $433$ kJ $mol^{-1}$, $492 kJmol^{-1}$ and $464 kJmol^{-1}$

**36.** Calculate the enthalpy of hydrogenation :

$$C_2H_5(g) + H_2(g) \rightarrow C_2H_6(g)$$
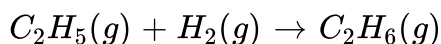
Given that the bond enthalpies of H - H , C = C, C- C and C - H bonds are $433, 615, 347$ and $413$ kJ $mol^{-1}$ respectively.

**37.** Calculate the bond enthalpy of H-CI given that the bond enthalpies of $H_2$ and $CI_2$ are $435.4$ and $242.8$ kJ $mol^{-1}$ respectively and enthalpy of formation of $HCI(g)$ is-92.2 kJ mol`

**38.** The enthalpy change for the reaction :

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)\Delta_rH^\circ = -1662kJmol^{-1}$$
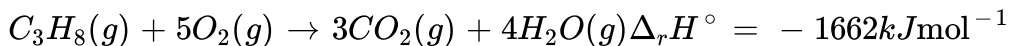
The bond enthalpies of different bonds (in kJ $mol^{-1}$) are :



Calculate bond enthalpy of O = O bond in $O_2$ molecules.

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**39.** Calculate the entropy change involved in the vaporisation of water at 373 K to vapours at the same temperature(Latent heat of vaporisation = 2.275 kJ/g).

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**40.** 30.4 kJ of heat is required to melt 1 mol of sodium chloride.The entropy change during melting of 28.4 J $mol^{-1}K^{-1}$. Calculate the melting point of sodium chloride.

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**41.** Calculate entropy changes of fusion and vaporisation for chlorine from the following data :

$$\Delta_{fus} H = 6.40 kJmol^{-1} m. \, p = -102°C$$

$$\Delta_{vap} H = 20.4 kJmol^{-1} b. \, p = -34°C$$

**42.** $\Delta_{vap}$S1 of acetone is $93.0 JK^{-1} mol^{-1}$.If boiling point of acetone is $56°C$, calculate the heat required for the vaporisation of 1 g of acetone. (Answer in Joule)

**43.** The enthalpy of vaporisation of benzene $(C_6H_6)$ is $30.8 kJmol^{-1}$ at its boiling point $(80.1°C)$. Calculate the entropy change in going from:

a. liquid to vapour and

b. vapour to liquid at $80.1°C$.

**44.** $\Delta_{vap}H°$ for water is 40.73 kJ $mol^{-1}$ and $\Delta_{vap}S°$ is 109 J $K^{-1}mol^{-1}$. Calculate the temperature at which liquid water wil be in the equilibrium with water vapour.

**45.** Calculate the entropy change of n-hexane when 1 mole of it evaporates at 341.7 K $\left(\Delta_{vap}H = 29.0kJmol^{-1}\right)$.

**46.** Calculate the Gibbs energy change on dissolving one mole of sodium chloride at $25°C$.

Lattice energy = $+777.8 kJmol^{-1}$

Hydration of $NaCI = -774.1 kJmol^{-1}$

$\Delta S at 25°C = 43 JK^{-1}mol^{-1}$.

**47.** The value of $\Delta H$ and $\Delta S$ for two reactions are given below :

Reaction A : $\Delta H = -10.5 \times 10^3 Jmol^{-1}$

$\Delta S = +31 JK^{-1}mol^{-1}$

Reaction B : $\Delta H = -11.7 \times 10^3 Jmol^{-1}$

$\Delta S = -105 JK^{-1}mol^{-1}$

Decide whether these reactions are spontaneous or not at 298 K.

**48.** At what temperature does the reduction of lead oxide to lead by carbon becomes spontaneous?

$PbO + C \rightarrow Pb(s) + CO(g)$
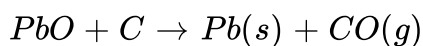
For the reacion, $\Delta H$ and $\Delta S$ at $25°C$ are $108.4 kJmol^{-1}$ and $190 JK^{-1}mol^{-1}$ respectively.

**49.** For the reaction at 298 K

$$2A + B \rightarrow C$$

$\Delta H = 40 kJmol^{-1}$ and $\Delta S = 0.2 kJK^{-1}mol^{-1}$. At what temperature will the reaction beccomes sponatneous considering $\Delta H$ and $\Delta S$ to be constant over the temperature range.

**50.** Consider the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
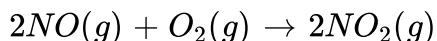
Calculated the standard Gibbs energy change at $298K$ and predict whether the reaction is spontaneous or not.

$\Delta_f G^{\ominus}(NO) = 86.69 kJmol^{-1}$, $\Delta_f G^{\ominus}(NO_2) = 51.84 kJmol^{-1}$.

**51.** Calculate the $\Delta_r G^\circ$ for the reaction:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$
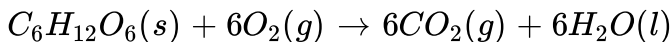
$\Delta_f G^\circ$ values (kJ $mol^{-1}$) are :

$$C_{12}H_{12}O_6(s) = -910.2, CO_2(g) = -394.4, H_2O(l) = -237.2$$

**52.** Calculate $\Delta G^\circ$ for the reaction

$NO(g) \Leftrightarrow \dfrac{1}{2}N_2(g) + \dfrac{1}{2}O_2(g)$ if $K = 1.55 \times 10^{15}$ at 298 K.
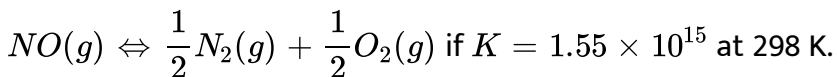
**53.** The equilibrium constant for the reaction

$CO_2(g) + H_2(g) \Leftrightarrow CO(g) + H_2O(g) at 298K$ is 73. Calculate the value

of the standard free enegry change $\left(R = 8.314JK^{-1}mol^{-1}\right)$

**54.** Calculated the equilibrium constant for the following reaction at $298K$:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$
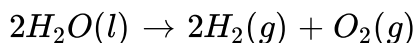
$$\Delta_f G^{\ominus}(H_2O) = -237.2kJmol^{-1}, R = 8.314Jmol^{-1}K^{-1}$$

**55.** The equilibrium constant for the reaction:

$$CH_3COOH(l) + C_2H_5OH(l) \Leftrightarrow CH_3COOC_2H_5(l) + H_2O(l) \quad \text{has}$$

been found to be equal to 4 at $25°C$. Calcuclate the free energy chnage for the reaction.

**56.** Calculate the entropy change for a reaction:

$$X \rightarrow Y$$
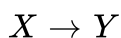
Given that $\Delta H^\ominus = 28.40 kJmol^{-1}$ and equilibrium constant is $1.8 \times 10^{-7} at 298K$.

**57.** Calculate the equilibrium constant for the following reaction at $298K$ and 1 atmospheric pressure:

$$C(s) + H_2O(l) \rightarrow CO(g) + H_2(g)$$
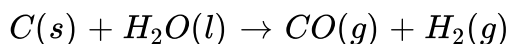
Given $\Delta_f H^\ominus at 298K$ for $H_2O(l) = -286.0 kJmol^{-1}$

for $CO(g) = -110.5 kJmol^{-1}$

$\Delta S^\ominus$ at $298K$ for the reaction $= 252.6 JK^{-1}mol^{-1}$

**58.** For the equilibrium reaction : $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$ at 298 K, $\Delta G^\circ = -474.78 kJmol^{-1}$. Calculate log K for it.

$\left( R = 8.314 JK^{-1}mol^{-1} \right)$.

**59.** Calculate the equilibrium constant for the reaction :

$$NO(g) + \frac{1}{2}O_2(g) \Leftrightarrow NO_2(g)$$
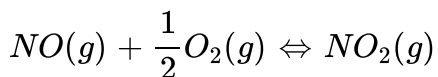
Given, $\Delta_f H°$ at $298K : NO(g) = 90.4kJmol^{-1}$, $NO_2(g) = 33.8kJmol^{-1}$

and $\Delta S°$ at $298K = -70.8JK^{-1}mol^{-1}$

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**60.** $\Delta H^\ominus$ and $\Delta S^\ominus$ for the reaction:

$$Br_2(l) + CI_2(g) \Leftrightarrow 2BrCI(g)$$
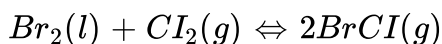
at $298K$ are $29.3kJmol^{-1}$ and $104.1JK^{-1}mol^{-1}$, respectively. Calculate the equilibrium constant for the reaction.

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**61.** Calculate the standard free energy change for the reaction :
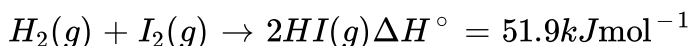
$$H_2(g) + I_2(g) \rightarrow 2HI(g) \Delta H° = 51.9kJmol^{-1} \qquad\qquad \text{Given} \qquad\qquad :$$

$$S°(H_2) = 130.6 JK^{-1}mol^{-1}$$

$$S°(I_2) = 116.7 JK^{-1}mol^{-1} \text{ and } S°(HI) = 206.3 JK^{-1}mol^{-1}.$$

**62.** Calculate $\Delta_r G°$ for the reaction :

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \Delta H° = -282.8 kJ$$
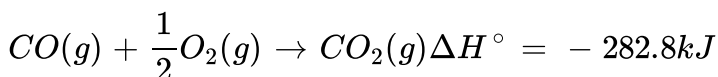
Standard entropies : $CO_2(g) = 213.6, CO(g) = 197.6$ and

$O_2(g) = 205.0$ (all in J $mol^{-1}$).Predict whether the reaction is

spontaneous or not at standard state.

**63.** Calculate the change of entropy, $\Delta_r S^{\ominus}$ at $298K$ for the reaction in

which urea is formed from $NH_3$ and $CO_2$.

$$2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)$$

The standard entropies $(JK^{-1}mol^{-1})$ are:

$$NH_2CONH_2(aq) = 174.0, H_2O(l) = 69.9$$

$$NH_3(g) = 192.3, CO_2(g) = 213.7$$

**64.** Calculate the standard molar entropy chnage for the following reactions at 298 K :

(a)$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$
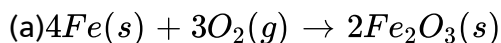
$[S^\circ(Fe_2O_3) = 87.4, S^\circ(Fe) = 27.3, S^\circ(O_2) = 205.1(allinJK^{-1}mol^{-1})$

(b) $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$
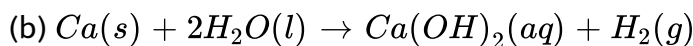
$[S^\circ Ca(OH)_2 = -74.5, S^\circ(Ca) = 41.42, S^\circ(H_2) = 130.7, S^\circ(H_2O) =$

(all in $JK^{-1}mol^{-1}$)

(c) $Na_2CO_3(s) + 2HCI(aq) \rightarrow 2NaCI(aq) + H_2O(l) + CO_2(g)$
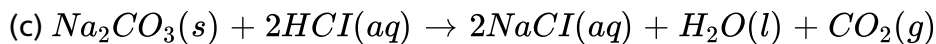
$= 115.13, S^\circ(H_2O) = 69.9, S^\circ(CO_2) = 213.74$ (all in $JK^{-1}mol^{-1}$).

**65.** Using $\Delta_f H^\circ$ and $S_m^\circ$ calculate the standard Gibbs energy of formation, $\Delta_f G^\circ$ for each following :

(a)$CS_2(l)$

(b) $N_2H_4(l)$
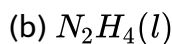
$$\Delta_f H^\circ (CS_2) = 89.70 kJmol^{-1}, \Delta_r S^\circ (CS_2) = 151.34 JK^{-1}mol^{-1}$$

$$\Delta_f H^\circ (N_2 H_4) = 50.63 kJmol^{-1}, \Delta_r S^\circ N_2 H_2 = 121.21 JK^{-1}mol^{-1}.$$

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**Advanced Level Problems**

**1.** Calcualte the enthalpy change on freezing of 1.0 mole of water at

$10.0°C$ to ice at $-10°$ C. $\Delta_{fs} H = 6.03 kJmol^{-1}$ at $0°C$.

$$C_p[H_2O(l)] = 75.3 Jmol^{-1}K^{-1}, C_P[H_2O(s)] = 36.8 Jmol^{-1}K^{-1}$$

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**2.** Consider the following reactions:

$$C(s) + O_2(g) \rightarrow CO_2(g) + x \quad kJ$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) + y \quad kJ$$
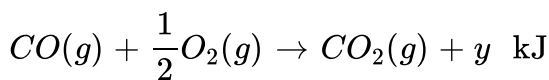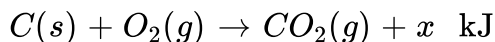
The heat formation of CO(g) is :

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**3.** The thermochemical equations for solid and liquid rocket fuels are given below :

(i) $2AI(s) \dfrac{3}{2}O_2(g) \rightarrow AI_2O_3(s), \Delta H = -1667.8kJ$

(ii) $H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l), \Delta H = -285.9kJ$
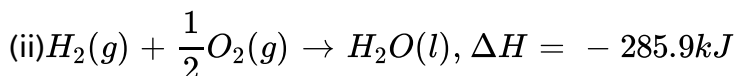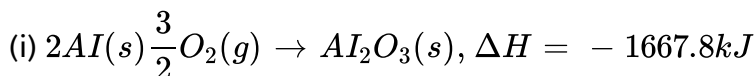
(a) If equal masses of aluminium and hydrogen are used, which is better rocket fuel?

(b) Determine $\Delta H$ for the reaction,

$AI_2O_3(s) \rightarrow 2AI(s) + \dfrac{3}{2}O_2(g).$
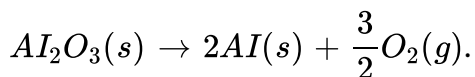
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**4.** A man takes a diet equivalent to 10000kJ per day and does work, spending his energy in all forms equivalent to 12500 kJ per day.What is change in internal energy per day? If the energy lost was stored as sucrose(1632 kJ per 100g), how many days should it takes to lose 2 kg of his weight? (Ignore water loss).

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**5.** Propane $(C_3H_8)$ is used for heating water for domestic supply. Assume that for 150 kg of how water supply per day water must be heated from $10°\,C$ to $65°\,C$. What moles and volume of propane in litres at S.T.P would have to be used for heating this amount of water?

$[\Delta H$ (combustion) $C_3H_8$ = -2050 kJ and specific heat of water = $4.184 \times 10^{-3}\,\dfrac{kJ}{g}]$.

**6.** Diborane is a potential rocket fuel which undergoes combustion according to the reaction:

$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$
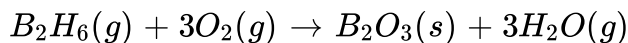
From the following data, calculate the enthalpy change for the combustion of diborane.

$2B(s) + \dfrac{3}{2}O_2(g) \rightarrow B_2O_3(s)\Delta H = -1273kJmol^{-1}$

$H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l)\Delta H = -286kJmol^{-1}$

$$H_2O(l) \rightarrow H_2O(g) \Delta H = 44kJmol^{-1}$$

$$2B(s) + 3H_2(g) \rightarrow B_2H_6(g) \Delta H = 36kJmol^{-1}.$$
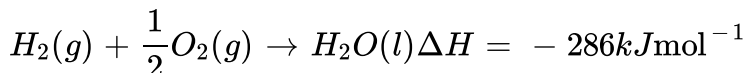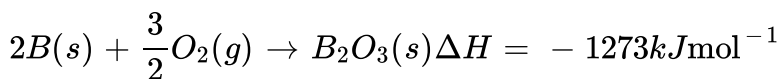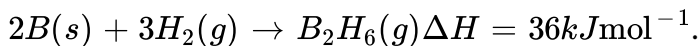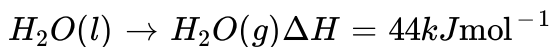
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**7.** From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propene (g) are - 393.5, -285.8 and 20.42 kJ mol$^{-1}$ respectively.The enthalpy of isomerisation of cyclopropane to propene is $-33.0kJmol^{-1}.$

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**8.** A gas expands from a volume of $3.0dm^3$ to $5.0dm^3$ against a constant external pressure of 3.0 atm. The work done during the expansion is used to heat 10.0 ml of water of temperature 290.0 K.Calculate the final temperature of water (specific heat of wate = $4.184Jg^{-1}K^{-1}$).

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**9.** Calculate the resonance energy of $N_2O$ from the following data :

$\Delta H_f^\circ$ of $N_2O = 82 kJmol^{-1}$, Bond energies of $N \equiv N$, $N = N$, $O = O$ and $N = O$ bonds are 946, 418, 498 and 607 $kJmol^{-1}$ respectively.

**10.** An athelete is given 100 g glucose of energy equivalenet to 1560 kJ. He utilizes 50% of this gained energy in an event. In order to avoid storage of energy in body, calculate the weight of water he need to perspire. Enthalpy of $H_2O$ for evaporation is 44 kJ $mole^{-1}$.

**11.** Calculate $\Delta G$ and $\Delta G^\circ$ for the reaction:

$A + B \Leftrightarrow C + D$ at $27°C$ for which $K = 10^2$.

**12.** Calculate the value of $\log K_p$ for the $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ at $25°C$. The standard enthalpy of formation of $nh_3$ is $-46kJ$ and standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191, 130 and 192 J $K^{-1}\mathrm{mol}^{-1}$ respectively.

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**13.** Sodium carbonate, $Ba_2CO_3$ can be obtained by heating sodium hydrogen carbonate $NaHCO_3$ as

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$

The essential data are :

$NaHCO_3(s) Na_2CO_3(s) + H_2O(g) + CO_2(g)\Delta_f H° - 947.7 - 1130.9 - 3$
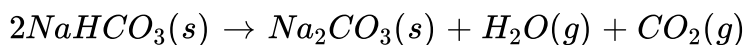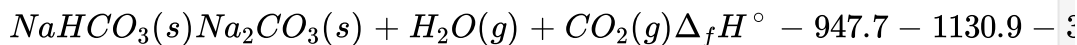
Calculate the temperature above which $NaHCO_3$ decomposes to give products at 1 bar.

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**14.** Show that the reaction :

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at 300 K is spontaneous and exothermic, when standard entropy change is $-0.094 kJmol^{-1}$.The standard Gibbs energies of formation of $CO_2$ and $CO$ are -394.4 and $-137.2 kJmol^{-1}$ respectively.

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**15.** The standard Gibbs energy change for the reaction

$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$
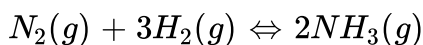
is $-33.2 kJmol^{-1}$ at 298 K.

(a) Calculate the equilibrium constant for the above reaction.

(b) What would be the equilibrium constant if the reaction is written as

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \Leftrightarrow NH_3(g)$
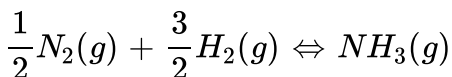
(c) What will be the equilibrium constant if the reaction is

$NH_3(g) \Leftrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g).$
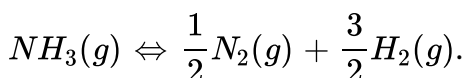
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**1.** Under what conditions is the heat of reaction equal to enthalpy change?

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**2.** Identify the kind of energy change usually associated with each of the following,(a)automobile engine (b) fluorescent lamp

(c) radio (d) friction

(e) photoelectric cell

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**3.** Show that the product of pressure and volume i.e., pV has the dimensions of energy.

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**4.** Neither q nor w is a state function but q + w is a state function.Explain why?

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**5.** What will happen to internal energy if work is done by the system?

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**6.** Is there any enthalpy change in a cyclic process?

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**7.** Why do we feel cold on touching ice?

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**8.** How many times is molar heat capacity larger than specific heat capacity of water?

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**9.** Which of the following are state functions?

(i)q (ii)heat capacity (iii) specific heat capacity (iv) $\Delta_r H^\circ$ (v) w.

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**10.** Explain why heat capacity is not a state function?

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**11.** What is the enthalpy change when 1.0 g of water is frozen at $0^\circ C$ ?

$\Delta_{fus} = H = 6.02 kJmol^{-1}$.

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**12.** Heat capacity is an extensive property but specific heat is intensive property.Comment on the statement.

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**13.** Which out of force and pressure is intensive property?

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**14.** The $C_p$ and $C_v$ of a gas are 20.834 and $12.520 JK^{-1}mol^{-1}$ respectively.What is the atomicity of the gas.

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**15.** Why heat changes reported are usually enthalpy changes and not internal energy changes?

**16.** What is the relation for work done (i) reversibly and (ii) irreversibly for the isothermal expansion of an ideal gas from volume $V_1$ to $V_2$ at temperature T?

**17.** Is $\Delta H$ always greater than $\Delta U$? Explain why or why not?

**18.** Establish a relationship between $\Delta H$ and $\Delta U$ in Haber synthesis of ammonia assuming that gaseous reactants and products are ideal.

**19.** When an ideal gas expands in vaccum, there is neither absorption nor evolution of heat. Why?

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**1.** Will the heat released be same or different in the following two reactions:

(i)$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ (ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$
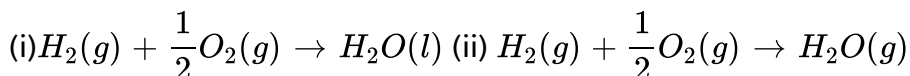
Explain.

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**2.** out of carbon (diamond)and carbon (graphite), whose enthalpy of formation is taken as zero and why?

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**3.** What is the basis of Hess's law of heat summation?

**4.** Which of the following state of bromine will have standard heat formation to be equal to zero? Liquid bromine, solid bromine, gaseous bromine molecules.

**5.** A system is changed from an initial state by a manner so that $\Delta H = q$. If the change from the initial state to the final state were made by a different path, would $\Delta H$ and q be the same as that for the first path?

**6.** Given that :

$$O(g) + e^- \rightarrow O^-(g) \Delta H = -142 kJmol^{-1}$$

$$O(g) + 2e^- \rightarrow O^{2-}(g) \Delta H = +712 kJmol^{-1}$$

what will be the $\Delta H$ for the reaction:

$$O^-(g) + e^- \rightarrow O^{2-}(g)$$
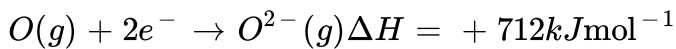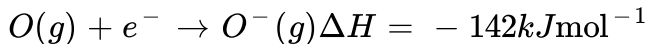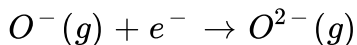
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**7.** Can enthalpy of combustion be positive?

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**8.** The heat of formation of $Fe_2O_3(s)$ is -824.0 kJ.What will be the $\Delta H$ for thereaction:

$$2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g)$$
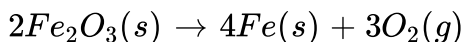
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**9.** The enthalpy of formation of gaseous iodine is $62.5 kJmol^{-1}$. What is the enthalpy of sublimation of iodine at $25°C$?

**10.** The standard enthalpy of formation of $H_2O(l)$ and $H_2O(g)$ are -285.8 and $-241.8 kJmol^{-1}$ respectively. What is the heat of vaporisation of water per gram at $25°C$ and 1 atm?

**11.** Write an expression in the form of a chemical equation of the standard enthalpy of formation of CO.

**12.** $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \Delta_r H° = -92.4kJ$

What is the standard enthalpy of formation of $NH_3$?

**13.** The enthalpy of the reaction

$H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(g)$ is $\Delta H_1$ and that of

$H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l)$ is $\Delta H_2$. Then

**14.** One kilogram of graphite is burnt in a closed vessel.The same amount of graphite is burnt in an open vessel.Will the heat evolved in two cases be same or different?

**15.** If enthalpy of fusion and enthalpy of vaporisation of sodium metal are 2.6 and $98.2 kJmol^{-1}$ respectively, what is the enthalpy of sublimation of sodium? (Keep your answer in three digits and KJ/mol)

**16.** When is bond dissociation enthalpy equal to bond enthalpy?

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**17.** At 1 atm will the $\Delta_f H^\circ$ be zero for $CI_2(g)$ and $Br_2(g)$? Explain.

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**Conceptual Questions - 3**

**1.** How does entropy change with (i) increase in temperature, (ii) decrease in pressure?

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**2.** What is entropy ? Is the entropy of the universe constant?

**3.** What is the value of change in entropy at equilibrium?

**4.** Arrange water vapour, liquid water and ice in the order of increasing entropy:

**5.** Do you expect $\Delta S$ to be $+ve,\ -ve$, or zero for the reaction

$$H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$$
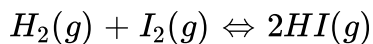
**6.** Place the following systems in order of increasing randomness :

(a)1 mol of a gas X (b) 1 mol of a solid X (c) 1 mol of a liquid X.

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**7.** Which of the following processes are accompanied by increase or entropy:

(a) Dissolution of iodine in a solvent.

(b) HCl is added to $AgNO_3$ and a precipitate of $AgCl$ is obtained.

(c) A partition is removed to allow two gases to mix.

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**8.** Predict the sign of entropy change for each of the following changes of state:

(a) $Hg(l) \rightarrow Hg(g)$

(b) `AgNO_(3) (aq) to AgNO_3(s)

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**9.** Predict the entropy change (positive / negative) in the following:

(i) $CaCO_3(s) \rightarrow CaO(s) + O_2(g)$.

(ii) $N_2(g)(1atm) \rightarrow N_2(g)(0.5atm)$.
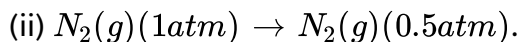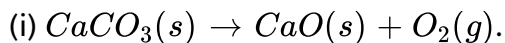
**10.** If standard free energy change for a reaction is found to be zero, what is its equilibrium constant?

**11.** What is the value of $\Delta G$ at melting point of ice?

**12.** Relate free energy with equillibrium constant. For a reaction both $\Delta H$ and $\Delta S$ are positive.Under what conditions does the reaction occur spontaneously?

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**13.** Comment on the following statements:

(a) An exothermic reaction is always thermodynamically spontaneous.

(b) Reaction with $\Delta G^\circ < 0$ always have an equilibrium constant greater than 1.

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**14.** The standard molar entropy of $H_2O(l)$ is $70 JK^{-1}mol^{-1}$.Will the standard molar entropy of $H_2O(s)$ be more or less than $70 JK^{-1}mol^{-1}$?

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**15.** Which quantity out of $\Delta_r G$ or $\Delta_r G^\circ$ will be zero at equilibrium?

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**16.** Why is entropy of substance taken as zero at absolute zero of temperature?

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**17.** Predict the signs of$\Delta H$ and $\Delta S$ for the reaction :

$2CI(g) \rightarrow CI_2(g)$.
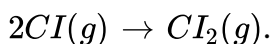
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**18.** An exothermic reaction $X \rightarrow Y$ is spontaneous in the backward direction.What is the sign of $\Delta S$ for the forward direction?

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**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

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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. $w = 0$

**3.** The enthalpies of all elements in their standard states are :

A. unity

B. zero

C. q = 0

D. different for each element

**4.** $\Delta U^\circ$ of combustion of methane is $-XkJ\text{mol}^{-1}$.The value of $\Delta H$ is

A. $= \Delta U^\circ$

B. $> \Delta U^\circ$

C. $< \Delta U^\circ$

D. $= 0$

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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 $-285$ kJ $mol^{-1}$ respectively. Enthalpy of formation of $CH_4(g)$ will be

A. $-74.8 kJmol^{-1}$

B. $-52.27 kJmol^{-1}$

C. $+74.8 kJmol^{-1}$

D. $+52.26 kJmol^{-1}$

**Answer: A**

**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: D**

**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?

**8.** 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. Calculate $\Delta_r H$ for the reaction:

$$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g).$$
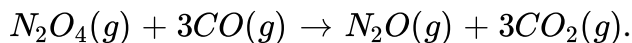
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**9.** Given:

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g), \Delta_r H^\circ = -924kJmol^{-1}$. What is the standard enthalpy of formation of $NH_3$ gas?

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

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**11.** For the reaction at $298K$

$$2A + B \rightarrow C$$
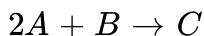
$$\Delta H = 400kJmol^{-1} \text{ and } \Delta S = 0.2kJK^{-1}mol^{-1}$$

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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**12.** For the reaction $2CI(g) \rightarrow CI_2(g)$

What are the signs of $\Delta H$ and $\Delta S$? what would be the nature of reaction

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**13.** For the reaction,
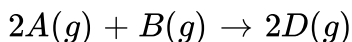
$$2A(g) + B(g) \rightarrow 2D(g)$$

$$\Delta U^{\ominus} = -10.5kJ \text{ and } \Delta S^{\ominus} = -44.1JK^{-1}$$

Calculate $\Delta G^{\ominus}$ for the reaction, and predict whether the reaction may

occur spontaneously.

**14.** The equilibrium constant for a reaction is 10. What will be the value of

$\Delta G°$?

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

**15.** Comment on the thermodynamic stability of NO(g), given,

(i) $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$

$\Delta_r H° = 90 kJmol^{-1}$

(ii)$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$
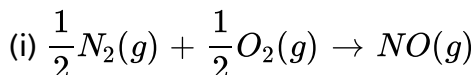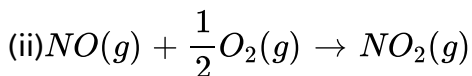
$\Delta_r H° = -74 kJmol^{-1}$.

NCERT Exemplar Problems (MCQ (Type - I))

**1.** Thermodynamics is not concerned about .............

    A. energy changes involved in a chemical reaction.

    B. the extent to which a chemical reaction proceeds.

    C. the rate at which a reaction proceeds.

    D. the feasibility of a chemical reaction.

**Answer: C**

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**2.** Which of the following statements is correct?

    A. The presence of reacting species in a covered beaker is an example

       of open system

    B. There is an exchange of enrgy as well as matter between the system

       and the surroundings in a closed system.

C. The presence of reactants in a closed vessel made up of copper is an example of a closed system.

D. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

**Answer: C**

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**3.** The state of a gas can be described by quoting the relationship between..........

A. pressure, volume, temperature

B. temperature, amount, pressure

C. amount, volume, temperature

D. pressure, volume, temperature, amount

**Answer: D**

**4.** The volume of gas is reduced to half from its original volume. The specific heat will be ...................

A. reduced to half

B. be doubled

C. remain constant

D. increased four times

**Answer: C**

**5.** During complete combustion of one mole of butane, 2658 kJ of heat is released.The termochemical reaction for above change is

A. $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l),$

$\Delta_c H = -2658.0 kJmol^{-1}$

B. $C_4H_{10}(g) + \dfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$

$\Delta_c H = -1329.0 kJmol^{-1}$

C. $C_4H_{10}(g) + \dfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

$\Delta_c H = -2658.0 kJmol^{-1}$

D. $C_4H_{10}(g) + \dfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$
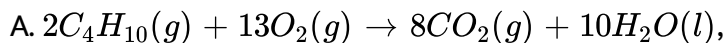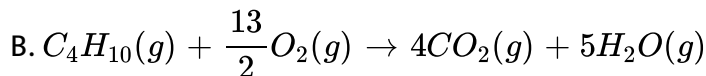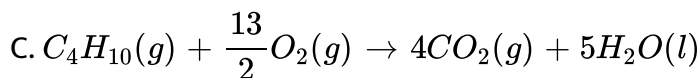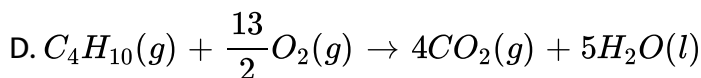
$\Delta_c H = +2658.0 kJmol^{-1}$

**Answer: C**

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**6.** $\Delta_f U^\circ$ of formation of $CII_4(g)$ at certain temperature is $-393 kJmol^{-1}$.The value of $\Delta_f H^\circ$ is

A. zero

B. $< \Delta_f U^\circ$

C. $> \Delta_f U^\circ$

D. equal to $\Delta_f U^\circ$

**Answer: B**

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7. In an adiabatic process, no transfer of heat takes place between system and surroundings.Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

A. $q = 0, \Delta T \neq 0, w = 0$

B. $q \neq 0, \Delta T = 0, w = 0$

C. $q = 0, \Delta T = 0, w = 0$

D. $q = 0, \Delta T < 0, w \neq 0$

**Answer: C**

**8.** The pressure-volume work for an ideal gas can be calculated by using the expression $w = -\int_{V_i}^{V_f} p_{ex}dV$.The work can be calculated form the $pV$- plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume $V_i$ to $V_f$, choose the correct option.

A. w (reversible) = w (irreversible)

B. w (reversible) $<$ w (irreversible)

C. w (reversible) $>$ w (irresversible)

D. w(reversible) = w(irreversible) + $p_{ex}\Delta V$

**Answer: B**

**9.** The entropy change can be calculated by using expression $\Delta S = \dfrac{q_{rev}}{T}$.

When water freezes in a glass beaker, choose the correct statement amongst the following:

A. $\Delta S$(system) decreases but $\Delta S$ (surroundings) remains the same.

B. $\Delta S$(system) increases but $\Delta S$ ("surroundings") decreases.

C. $\Delta S$ (system) decreases but $\Delta S$ (surroundings) increases.

D. $\Delta S$(system) decreases but $\Delta S$ (surroundings) also decreases.

**Answer: C**

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**10.** On the basis of thermochemical equations (a),(b) and (c), find out which of the algebric relationship given in options(i) to (iv) is correct.

(i)$C(\text{graphite }) + O_2(g) \rightarrow CO_2(g), \Delta_r H = xk\text{Jmol}^{-1}$

(ii)$C(\text{graphite}) + \dfrac{1}{2}O_2(g) \rightarrow CO(g), \Delta_r H = yKJ\text{mol}^{-1}$

(iii)$C(g) + \dfrac{1}{2}O_2(g) \rightarrow CO_2(g), \Delta_r H = zk\text{Jmol}^{-1}$
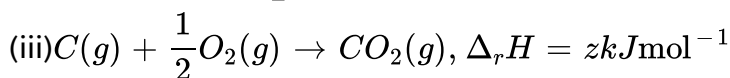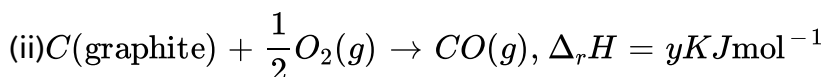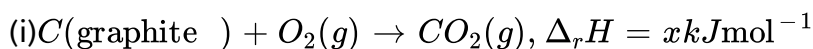
A. z = x + y

B. x = y - z

C. x = y + z

D. y = 2z - x

**Answer: C**

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**11.** Consider the reaction given below. On the basis of these reactions find out which of the algebric relations given in options (i) to (iv) is correct?

(i) $C(g) + 4H(g) \rightarrow CH_4(g), \Delta_r H = x kJmol^{-1}$

(ii) $C(\text{graphite}) + 2H_2(g) \rightarrow CH_4(g), \Delta_r H = y kJmol^{-1}$.
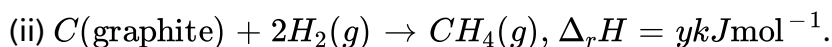
A. x = y

B. x = 2y

C. $x > y$

D. $x < y$

**Answer: C**

**12.** The enthalpies of elements in their standard states are taken as zero.The enthalpy of formation of a compound

A. is always negative

B. is always positive

C. may be positive or negative

D. is never negative

**Answer: C**

**13.** Enthalpy of sublimation of a substance is equal to

A. enthalpy of fusion + enthalpy of vaporisation

B. enthalpy of fusion

C. enthalpy of vaporisation

D. twice the enthalpy of vaporisation

**Answer: A**

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**14.** Which of the following is not correct

A. $\Delta G$ is zero for a reversible reaction

B. $\Delta G$ is positive for a spontaneous reaction

C. $\Delta G$ is negative for a spontaneous reaction

D. $\Delta G$ is positive for a non - spontaneous reaction.

**Answer: B**

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**1.** Thermodynamics mainly deals with:

A. interrelation of various forms of enrgy and their transformation from one form to another.

B. energy changes in the processes which depend only on initial and final states of the microscopic systems containing a few molecules.

C. how and at what rate these energy transformations are carried out.

D. the system in equilibrium state or moving from one equilibrium state to another equilibrium state.

**Answer: A::D**

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**2.** In an exothermic reaction, heat is evolved and system loses heat to the surrounding.For such system

    A. $q_p$ will be negative

    B. $\Delta_r H$ will be zero

    C. $q_p$ will be positive

    D. $\Delta_r H$ will be positive

**Answer: A**

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**3.** The spontaneity means, having the potential to proceed without the assistance of external agency.The processes which occur spontaneously are

    A. flow of heat from colder to warmer body

    B. gas in a container contracting into one corner

C. gas expanding to fill the available volume

D. freezing of ice

**Answer: C**

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**4.** For an ideal gas, the work of reversible expansion under isothermal condition can be calculated by using the expression $w = -nRTIn\dfrac{V_f}{V_i}$

A sample containing 1.0 mol of an ideal gas is expanded isothermally and reveribly to ten times of its original volume, in two separate experimentsThe expansion is carried out at 300 K and at 600 K respectively.Choose the correct option

A. Work done at 600K is 20 times the work done at 300 K

B. Work done at 300 K is twice the work done at 600 K

C. Work done at 600 K is twice the work done at 300 K

D. $\Delta U = 0$ in both cases

**Answer: C::D**

5. Consider the following reaction between zinc and oxygen and choose the correct options out of the options given below

$$2Zn(s) + O_2(g) \rightarrow 2ZnO_s : \Delta H = -693.8 kJmol^{-1}$$
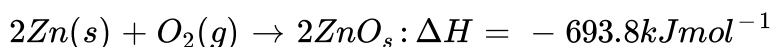
A. The enthalpy of two moles of ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

B. The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

C. $6938 kJmol^{-1}$ energy is evolved in the reaction

D. $693.8 kJmol^{-1}$ energy is absorbed in the reaction.

**Answer: A::C**

**1.** 18.0 g of water completely vapourises at $100°C$ and 1 bar pressure and the enthalpy change for the process is $40.79 kJmol^{-1}$.

(i) What will be the enthalpy change for vapourising 2 moles of water under the same conditions?

(ii) What is the standard enthalpy of vapourisation for water?

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**2.** Standard molar enthalpy of formation, $\Delta_f H°$ is just a special case of enthalpy of reaction, $\Delta_r H°$. Is the $\Delta_r H°$ for the following reaction same as $\Delta_f H°$? Give reason for your answer.

$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$,
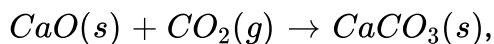
$\Delta_f H° = -178.3 kJmol^{-1}$.

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**3.** The value of $\Delta_f H^{\ominus}$ for $NH_3$ is $-91.8 kJmol^{-1}$. Calculate enthalpy change for the following reaction.

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$
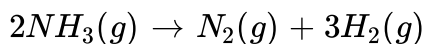
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**4.** Enthalpy is an extensive property.In general, if enthalpy of an overall reaction $A \rightarrow B$ along one route is $\Delta_r H$ and $\Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$ ... Represent enthalpies of intermediate reactions leading to product B.What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1, \Delta_r H_2$....etc, for intermediate reactions.

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**5.** The enthaply of atomisation for the reaction : $CH_4(g) \rightarrow C(g) + 4H(g)$ is $1665 kJmol^{-1}$.What is the bond enthalpy of C-H bond? (Keep your answer in KJ/mol and three digits only)

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**6.** Use the following data to calculate $\Delta_{lattice}H^{\circ}$ for NaBr. $\Delta_{sub}H^{\circ}$ for sodium metal = $108.4kJmol^{-1}$.Ionization enthalpy of sodium = 496 $kJmol^{-1}$ Electron gain enthalpy of bromine = $-325kJmol^{-1}$.Bond dissociation enthalpy of bromine = 192 kJ mol$^{-1}$. $\Delta_f H^{\circ}$ for NaBr (s) = $-360.1kJmol^{-1}$.

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**7.** Given that $\Delta H$ = 0 for mixing of two gases.Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?

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**8.** Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system.Write the

mathematical relation which relates these three parameters.

**9.** Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system.Will the temperature of system and surroundings be the same when they are in thermal equilibrium?

**10.** At 298 K, $K_p$ for the reaction : $N_2O_4(g) \Leftrightarrow 2NO_2(g)$ is 0.98. Predict whether the reaction is spontaneous or not.

**11.** A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in Fig. 1. What will be

the value of $\Delta H$ for the cycle as a whole?

**12.** The standard molar entropy of $H_2O(l)$ is $70JK^{-1}mol^{-1}$.Will the standard molar entropy of $H_2O(s)$ be more or less than $70JK^{-1}mol^{-1}$?

**13.** Identify the state functions and path functions out of the following:

enthalpy, entropy, heat, temperature, work, free energy.

**14.** The molar enthalpy of vapourisation of acetone is less than that of water.Why?

**15.** Which quantity out of $\Delta_r G$ or $\Delta_r G^\circ$ will be zero at equilibrium?

**16.** Predict the change in internal energy for an isolated system at constant volume.

**17.** Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

**18.** Expansion of a gas in vaccum is called free expansion.Calculate the work done and the change in internal energy when 1 litre of ideal gas expands isothermally into vaccum until its total volume is 5 litre?

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**19.** Heat capacity $(C_p)$ is an extensive property but specific heat (C) is an intensive property.What will be the relation between $C_p$ and C for 1 mol of water? (Keep your answer in J/K and in two digits only)

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**20.** The difference between $C_p$ and $C_v$ can be derived using the empirical relation H = U + pV. Calculate the difference between $C_p$ and $C_v$ for 10 moles of an ideal gas.

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**21.** If the combustion of 1 g of graphite produces -20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

**22.** The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules.What will be the enthalpy change for the following reaction.

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
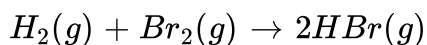
Given that bond energy of $H_2$, $Br_2$ and HBr is 435 kJ $mol^{-1}$, 192 kJ $mol^{-1}$ and $368kJmol^{-1}$ respectively. (Keep your answer in magnitude and in KJ/mol)

**23.** The enthalpy of vaporisation of $CCI_4$ is $30.5kJmol^{-1}$.Calculate the heat required for the vapourisation of 284 g of $CCI_4$ at constant

pressure. (Molar mass of $CCI_4 = 154u$). (Keep your answer in KJ and two digits only)

**24.** What will be standard enthalpy of formation of $H_2O(l)$?

**25.** What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, $p_{ext}$ in a singal step as shown in Fig.2.Explain graphically.

**26.** How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?

**27.** Represent the potential energy/enthalpy change in the following process graphically

(a) Throwing a stone from the ground to roof.

(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$ $HCl(g)\Delta_r H^\circ = -93.2 kJmol^{-1}$
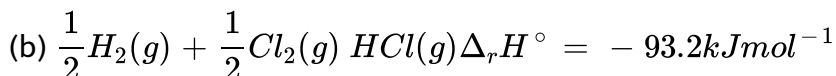
In which of the process potential energy/enthalpy change in contributing factor to the spontaneity?

**28.** Enthalpy diagram for a particular reaction is given in Fig.6.Is it possible to decide spontaneity of a reaction from given diagram.Explain.

**29.** 1.0 mol of monoatomic ideal gas is expanded from state (1) to state(2) as shown in Fig.7. Calculate the work done for the expansion of gas srom state (1) to state(2) at 298 K.



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**30.** An ideal gas is allowed to expand against a constant pressure of 2 bar from 10L too 50L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case?

(Given that 1 L bar = 100 J)

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NCERT Exemplar Problems (Matching Type Questions)

**1.** Match the following

| A | B |
|---|---|
| (I) Adiabatic process | Heat |
| II Isolated system | (b) At constant volume |
| (iii) Isothermal change | (c) First law of thermodynamics |
| Iv Path function | (d) No exchange of energy and matte |
| (v) State Function | (e) No transfer of heat |
| (iv) $\Delta U = q$ | (f) Constant temperature |
| Vii) Law of conservation of energy | (g) Internal energy |
| viii Reversible process | (h) $P_{\text{ext}} = 0$ |
| ix Free expansion | (i) At constant pressure |
| x) $\Delta H = q$ | (j) Infinitely slow process which proc |
| (xi) Intensive property | (k) Entropy |
| (xii) Extensive property | (l) Pressure |
| | (m) Specific heat |

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**2.** Match the following processes with entropy change :

Reaction

(i) A liquid vapourises

(ii) Reaction is non-spontaneous at all temperatures and $\Delta H$ is positive

(iii) Adiabetic reversible expansion of an ideal gas

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**3.** Match the following parameters with description for spontaneity

| Δ (Parameters) | | | Description |
|---|---|---|---|
| $\Delta_r H^{\ominus}$ | $\Delta_r S^{\ominus}$ | $\Delta_r G^{\ominus}$ | |
| A. + | − | + | 1. Non-spontaneous at high temperature |
| B. − | − | + at high T | 2. Spontaneous at all temperatures |
| C. − | + | − | 3. Non-spontaneous at all temperatures |

**4.** Match the following

(i) Entropy of vapourisation      (a) decreases

(ii) K for spontaneous process positive      (b) is always

iii Crystalline solid state      (c) lowest entropy

(iv) $\Delta U$ in adiabatic expansion of ideal gas      (d) $\dfrac{\Delta H_{vap}}{T_b}$

**NCERT Exemplar Problems (Assertion and Reason Type Questions)**

**1.** Assertion (A). Combustion of all organic compounds is an exothermic reaction.

Reason (R). The enthalpies of all elements in their standard state are zero

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**2.** Assertion (A) : Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason (R) : Decrease in enthalpy is a contributory factor for spontaneity.

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**3.** Assertion (A) : A liquid crystallises into a solid and is accompanied by decrease in entropy.

Reason (R) : In crystals, molecules organise in an ordered manner.

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**1.** Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.

Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

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**2.** The lattice enthalpy of an ionic compound is the enthalpy change for the dissociation of one mole of an ionic compound present into gaseous state, dissociates into its ions. Itis impossible to determine it directly by experiment.Suggest and explain an indirect method to measure lattice enthalpy of $NaCI(s)$.

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**3.** $\Delta G$ is net energy available to do useful work and is thus a measure of " free energy".Show mathematically that $\Delta G$ is a measure of free energy.Find the unit of $\Delta G$.If a reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous?

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**4.** Graphically shoe the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from $(p_i, V_i)$ to $(p_f, V_f)$. With the help of a pV plot compare the work done in the above case with that carried out against a constant pressure $p_f$.

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**Revision Exercise (Objective Question)**

**1.** I. Read the following passage and answer questions 1-5 that follows:

Spontaneity means the feasibility of a reaction.Gibbs free energy (G) is the thermodynamic quantity which helps in predicting the spontaneity of a process

$$G = H - TS$$

The change in free energy is represented by Gibbs Helmoltz equation,

$$\Delta H - \Delta H - T\Delta S$$

For spontaneity of a process, $\Delta G$ must be negative.It depends upon energy factor$(\Delta H)$ and entropy factor $(T\Delta S)$.

1. What are the signs of $\Delta H$ and $\Delta S$ for the reactions :

$2CI(g) \rightarrow CI_2(g)$ ?
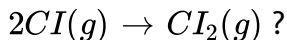
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**2.** For a reaction both $\Delta H$ and $\Delta S$ are positive.Under what conditions does the reaction occur spontaneously?

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**3.** A reaction has a value of $\Delta H = -64.5 kJ$ at $157° C$. Above $157° C$, the reaction is spontaneous and below this temperature the reaction is not spontaneous. Calculate the value of $\Delta G$ and $\Delta S$ at $157° C$.

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**4.** Which of the following reactions are accompanied by increase in entropy?

(i) $N_2(g)(1atm) \rightarrow N_2(g)(0.5atm)$

(ii) $I_2(g) \rightarrow I_2(s)$
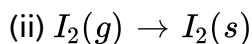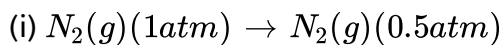
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**5.** How is $\Delta G°$ related to equilibrium constant?

▶ **Watch Video Solution**

**6.** ISOTHERMAL PROCESS

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**7.** How much heat is absorbed and how much work is done in the expansion?2L of an ideal gas at a pressure of 10 atm expansion isothermally into a vacuum until its total volume is 10L.

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**8.** How much heat is absorbed aif this system expands against a constant external pressure of 1 atm and expansion is carried out from 2.5L to final volume of 12.5L reversibly?

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**9.** How much heat is absorbed if the expansion is carried out from 2.5L to final volume of 12.5L reversibly? (Give your answer in Joule)

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**10.** q and w are not state function but q + w is state function. Why?

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## Revision Exercise (True or False)

**1.** Predict true or false.

The absolute value of internal energy of a substance can not be determined.

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**2.** Enthalpy, entropy and free energy of formation of elementary substances in the standard state are taken as zero.

**3.** The energy of the universe remains constant whereas entropy of the universe is continuously increasing. true/false

**4.** Heat and work are not state function but their sum is a state function.

**5.** Diamond is more stable than graphite at room temperature and pressure.

**6.** Entropy of perfectly crystalline solid is taken as zero at 0 K.

**7.** At the melting point of ice, $\Delta G = 0$.

**8.** For $N_{2(g)}$ at 1 atm $\rightarrow N_2(g)$ at 0.5 atm, What would be the change in entropy ?

**9.** An endothermic reaction which may be non spontaneous at low temperature because of entropy factor becomes spontaneous at high temperature.

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**10.** The unit of $\Delta G$ are same as those of energy ?

**Revision Exercise (Fill in the blanks Questions)**

**1.** During isothermal expansion of an ideal gas, the change in internal energy is ...............

**2.** Bomb calorimeter is used to determine the value of ...............

**3.** Standard state of carbon is ...........

**4.** Heat of reaction at constant pressure is equal to ............change. Write the expression between enthalpy change and internal energy

**5.** In....................process, no heat is exchanged between the system and the surroundings.

**6.** A stable compound has ............ Enthalpy of formation.

**7.** In an isothermal process, ............. Remains constant.

**8.** For the process: normal egg $\rightarrow$ hard boiled egg, the sign of $\Delta S$ is ................

**9.** If $\Delta G$ is ............the reaction does not proceed in the forward direction.

**10.** All combustion reactions are ...........

**11.** The property of a system which does not depend upon the amount of substance is called ..........property.

**12.** A system which can exchane energy with the surroundings but not matter is called.......system.

**13.** For triatomic gases such as $CO_2$ the ratio $\dfrac{C_p}{C_v}$ is equal to ...........

**14.** Molar heat capacity of iron (at mass 56) will be ........... Times its specific heat.

**15.** The allotropic form of sulphur for which standard enthalpy of formation is taken as zero is ...................

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**1.** Assertion (A): Heat of neutralisation for both $HNO_3$ and $HCI$ with $NaOH$ is $53.7 kJ per mol^{-1}$.

Reason (R ) : $NaOH$ is a strong electrolyte/base.

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**2.** Assertion: Standard enthalpy of graphite is lower than that of diamond.

Reason : Standard enthalpy of elements is taken to be zero arbitrarily.

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**3.** Assertion : Work is a state function.

Reason : Work does not depend upon the path.

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**4.** Assertion : Enthalpy of combustion is always negative

Reason : Combustion reactions proceeds with evolution of heat.

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**5.** Assertion : In a cyclic process $\Delta U = 0$.

Reason : Cyclic process represents equilibrium state.

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**6.** Assertion : Internal energy change in the heat evolved or absorbed at

constant pressure.

Reason : Internal energy is state function.

**7.** Assertion : For the combustion of methane, $\Delta E > \Delta H$.

Reason : $\Delta H$ is related to $\Delta E$ by the expression, $\Delta H = \Delta E + \Delta n_g RT$

**8.** Assertion (A): Decrease in free energy causes spontaneous reaction

Reason (R ) : Spontaneous reactions are invariably exothermic.

**9.** Assertion: Both $\Delta H$ and $\Delta U$ are state functions.

Reason : A state function depends only on the initial and final states of the system and is independent of the path.

**10.** Assetion : The temperature of a gas does not change when it undergoes on adiabatic process

Reason: During adiabatic process , heat energy is exchanged between a system and surroundings.

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**11.** Assertion : Many endothermic reactions which are non- spontaneous on increasing the temperature.

Reason : Endothermic reactions become spontaneous at high temperature if $\Delta S$ is +ve and $T\Delta S > \Delta H$.

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**12.** Statement-1: Decrease of free energy during the process under constant temperature and pressure provides a measure of its spontaneity.

Statement -2: A spontaneous change must have +ve sign of $\Delta S_{system}$.

**13.** Assertion : In a reversible process,$\Delta S_{\text{universe}}$is zero.

Reason : Entropy is an extensive property.

**14.** Assertion : At equilibrium, $\Delta G$ becomes zero.

Reason : At equilibrium, the two tendencies $\Delta H$ and $T\Delta S$ become equal and opposite.

**15.** Assertion (A): For every chemical reaction at equilibrium, standard Gibbs enegry of the reaction is zero.

Reason (R ) : At constant temperature and pressure chemical reactions are spontaneous in the direction of the decreasing Gibbs energy.

**1.** Define $\Delta H$.What will be the sign of $\Delta H$ in

(i) exothermic reaction and

(ii) endothermic reaction?

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**2.** What does the symbol $\Delta H$ denote? Define this quantity.

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**3.** What is calorific value of a fuel?

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**4.** What is the basic difference between the two notations $\Delta_r H$ and $\Delta_f H$ ?

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**5.** How is enthalpy of sublimation related to enthalpy of fusion and enthalpy of vaporisation?

> ▶ Watch Video Solution

**6.** What is enthalpy of combustion? Write chemical equation for the enthalpy of combustion of ethanol $(C_2H_5OH)$.

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**7.** The standard enthalpy of formation of sulphur dioxide $(SO_2)$ is $-296.9kJ$.Write thermochemical equation for this.What will be enthalpy

of combustion of sulphur?

**8.** Define enthalpy of fusion.

**9.** Define Hess's law of constant heat summation.

**10.** What is meant by bond dissociation enthalpy?

**11.** Ammonia is prepared as

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$
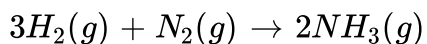
What should be the sign of $\Delta S$ for this reaction? Explain.

**12.** State first law of thermodynamics.Write it mathematical expression.

**13.** Why are we usually concerned with changes in enthalpy than changes in internal energy?

**14.** Name the two criteria which must be met for a process to be spontaneous regardless of the temperature.

**15.** Give an example of a chemical reaction for which $\Delta H^\circ > \Delta U^\circ$.

**16.** Why do we feel cold on touching a block of ice?

**17.** $\Delta_f H^\circ$ of $Fe_2O_3$ is -825 kJ. What is the enthalpy change for the reaction?

$$4Fe_2O_3 \rightarrow 8Fe + 6O_2$$
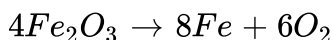
**18.** The standard enthalpies of formation of three substances A, B and C are 201.6, -52.6 and -106.4 kJ respectively.Arrange them in order of decreasing stability with respect to decomposition.

**19.** Define molar heat capacity and specific heat capacity.

**20.** What are the units of entropy and free energy?

**21.** Explain the state of a reaction when $\Delta G = 0$.

**22.** Write Gibbs Helmholtz equation giving meanings of the symbols used.

**23.** What is the sign of $\Delta S$ for

(i) evaporation of liquid water ?

(ii) freezing of liquid water to ice?

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**24.** When an ideal gas expands in vaccum, there is neither absorption nor evolution of heat. Explain.

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**25.** In a process, a system does 145 J of work on its surroundings while 85 J of heat is added to the system. What is $\Delta U$ for the system?

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**26.** How is free energy change related to equilibrium constant for the reaction?

**27.** Predict $\Delta S$ for the reaction :

$$NH_3(g) + HCI(g) \rightarrow NH_4CI(s).$$
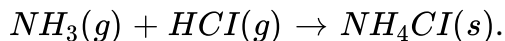
**28.** Why does the entropy of a solid increase on melting?

**29.** What is the effect of temperature on entropy?

**30.** State the second law of thermodynamics.

**31.** Write mathematical statement of first law of thermodynamics.

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**32.** Predict the sign of $\Delta S$ for the reaction :

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

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**33.** Predict whether the entropy increases or decreases during the oxidation of nitrogen:

$$N(g) + 2O_2(g) \Leftrightarrow 2NO_2(g)$$
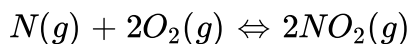
▶ Watch Video Solution

**34.** Explain how an endothermic reaction can be spontaneous.

**35.** Which of the following will have larger entropy: a mole of ice at $0°C$ or a mole of water at the same temperature?

**36.** What is entropy? Give its units.

**Revision Exercise (Short answer questions)**

**1.** Is it possible for any process to have $\Delta H = \Delta E$? If yes, state under what conditions? If no, state why not?

**2.** State Hess's law and explain its one use.

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**3.** Define the terms internal energy change and enthalpy change. How are they related?

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**4.** Explain heat and work as the modes of transference of enrgy between the system and the surroundings.

▶ Watch Video Solution

**5.** Define the terms : (i) Enthalpy of formation (ii) Enthalpy of combustion.

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**6.** What is a thermochemical equation? Explain why is it essential to mention the physical states of reactants and products in thermochemical equations.

**7.** Define heat capacity, specific heat capacity and molar heat capacity.How are they related?

**8.** Define in terms :

(i) Enthalpy of fusion (ii) Enthalpy of sublimation

(iii) Enthalpy of vaporisation.

**9.** Differentiate between

a change of state and a phase change

**10.** What is the basic difference between enthalpy of formation and enthalpy of a reaction? Illustrated with suitable examples.

**11.** What is the meant by enthalpy of formation? Write equations to express enthalpies of formation of

(i) Sulphur trioxide

(ii) Water

(iii) Enthyl alcohol

**12.** Derive relationship between $\Delta H$ and $\Delta U$.Give example when

(i) $\Delta H < \Delta U$

(ii) $\Delta H = \Delta U$

(iii) $\Delta H > \Delta U$

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**13.** Define heat of combustion of a fuel.What is its significance.

▶ Watch Video Solution

**14.** What is bond energy? How are the bond energies related to change in enthalpy of a reaction?

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**15.** How does Hess's law help in calculating the enthalpy change for the conversion of diamond to graphite?

**16.** Explain

(i) Reversible and irreversible process

(ii) Isothermal and adiabatic process.

**17.** What are extensive and intensive properties? Give two examples of each.

**18.** Explain under what conditions does the enthalpy change in a reaction become equal to change in internal energy?

**19.** Define a system. What are the types of a system?

**20.** Give the appropriate reason for the followings:

a. It is a preferable to determine a change in enthalpy than change in internal energy.

b. It is necessary to define the 'standard state.

c. It is necessary to specify the phases of the reactant and products in a thermochemical equation.

**21.** State and explain first law of thermodynamics.Give its mathematical form.

**22.** What is the difference between an open system and a closed system?

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**23.** Define enthalpy of combustion. How is it measured?

▶ **Watch Video Solution**

**24.** How is energy exchanged between the system and the surroundings in the form of

(i) heat (ii) work?

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**25.** Defien $C_p$ and $C_v$. How are these related for an ideal gas?

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**26.** Acetic acid and hydrocloric acid reacts with KOH solution. The enthalpy of neutralisation of acetic acid is $-55.8 kJmol^{-1}$ while that of hydrochloric acid is $57.1 kJmol^{-1}$.Can yoou think of how are these different?

**27.** Expalin the difference between :

Adiabatic and isothermal process

**28.** Define the following terms :

(i) System

(ii) Isothermal and adiabatic process

**29.** State whether each of the following processes will increase or decrease total energy content of the system:

(a) Heat transferred to the surroundings

(b) Work done by the system

(c) Work done on the system

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**30.** What do you mean by spontaneous process? Explain your answer with suitable examples.

▶ Watch Video Solution

**31.** Explain the terms 'entropy', 'enthalpy' and 'free energy'.

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**32.** Account for the fact that entropy of ice is less than that of water.

**33.** Why should you expect a decrease in entropy as a gas condenses into liquid? Compare it with entropy decrease when a liquid sample is converted into solid.

**34.** Correlate entropy and disorder with the help of fusion and vaporisation processes.

**35.** Expalin the state of chemical reactions when :

(i) $\Delta G = 0$ (ii) $\Delta G < 0$ and (iii) $\Delta G > 0$

**36.** What is entropy change? What is the change of entropy with change of (i) temperature and (ii) pressure? Correlate the behaviour with the randomness.

**37.** Can $\Delta H$ be used as s sole criterion for the feasibility of a chemical reaction? Explain with examples.

**38.** Fill in the blanks:

(i) The reaction which has a natural urge to procedd of its own is called ........reaction.

(ii) In the freezing of water to ice entropy...............

(iii) The decrease in ............... Is equal to the useful work done by the system.

(iv) If$\Delta G$ is ..........the reaction does not occur in the forward direction.

**39.** Define free energy and entropy of a system.

**40.** Predict whether the entropy increases or decreases for the following :

(i) 1 mol of liquid water changes to vapours.

(ii) when 1 mole of liquid water converts to ice.

**41.** Define entropy and free energy of a system.Predict the feasibility of a reaction when :

(i) Both $\Delta H$ and $\Delta S$ increase.

(ii)Both $\Delta H$ and $\Delta S$ decrease.

(iii) $\Delta H$ decreases but $\Delta S$ increases.

**42.** For a reaction both $\Delta H$ and $\Delta S$ are positive.Under what conditions does the reaction occur spontaneously?

**43.** Explain the physical significance of entropy.

**44.** Predict the sign of $\Delta S$ (positive or negative) for the following changes :

(i) $HCOOH(l) \rightarrow H_2O(l) + CO_2(g)$

(ii) $NH_3(g) + HCI(g) \rightarrow NH_4CI(s)$

(iii)$I_2(s) \rightarrow I_2(g)$

(iv) $2O_3(g) \rightarrow 3O_2(g)$

(v) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$.
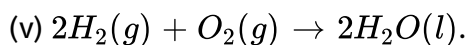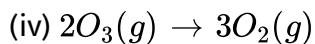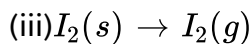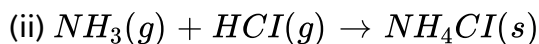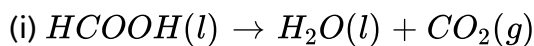
**45.** State giving reasons whether the entropy change for vaporisation of one mole of water will be more or less than entropy change per mole for fusion of ice.

**46.** What is entropy change?Predict the sign of entropy chsnge in each of the following giving reasons for your predictions :

(i) $H_2(at25°C, 1atm) \rightarrow H_2(at25°C$ and 10 atm))

(ii) $H_2O(at25°C, 1atm) \rightarrow H_2O(at50°C$ and 1 atm))

(iii) $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$
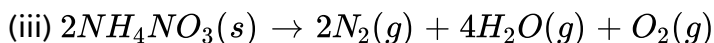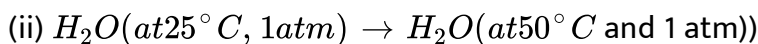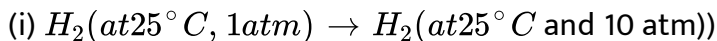
**47.** What is the value of free energy chnage for a reaction in equilibrium state?

(b) How is free energy change related to equilibrium constant of the reaction?

**48.** Comment on the statement that the energy of the universe remains constant but entropy of uniiverse is always increasing.

**49.** Which of the reaction is expectd to be spontaneous at low temperatures and non-spontaneous at high temperatures:

**50.** Wha is menat by free energy of a system? How is it related to enthalpy and entropy of the system? How is it useful for predicting the feasibility of a process?

**51.** State and explain Gibbs Helmholtz equation.

**52.** Predict or decrease of entropy :

(a) $Br_2(g) \rightarrow Br(g)$

(b) $H_2O(l) \rightarrow H_2O(s)$

(c) $Cr^{3+}(aq) + 6H_2O(l) \rightarrow [Cr(H_2O)_6]^{3+}(aq)$
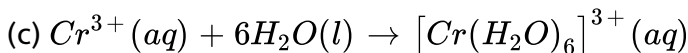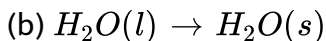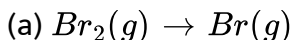
(d) Crystallisation of salt from brine solution

(e) $NaCI(s) \xrightarrow{(\text{Water})} NaCI(aq)$

(f) Sublimation of ammonium chloride.

(g) $CO_2 + H_2O \xrightarrow[\text{(Photosynthesis)}]{\text{(Light)}} Carbohydrates + O_2$
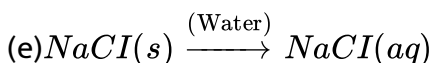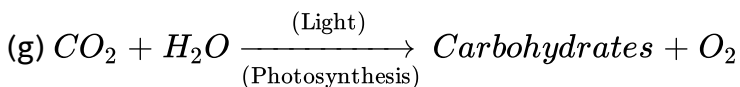
(h) Naphthalene dissoolving in benzene

(i) $CaCO_3(s) \rightarrow CaO(s) + O_2(g)$.
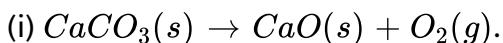
**53.** Predict the enthalpy change, free energy change and entropy change when ammonium chloride is dissolved in water and the solution becomes colder.

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**54.** Define the terms:

(i) Free energy

(ii) Thermodynamic equilibrium

(iii) Entropy

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**55.** Neither the enthalpy change nor the entropy change alone can be used to explai the spontaneity of a reaction.Explain.

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**56.** Predict the sign of $\Delta G$ for a reaction that is

(a) Exothermic and accompanied by an increase in entropy.

(b) Endothermic and accompanied by increase in entropy.

(c) Can a temperature change affect the sign of $\Delta G$ in (a) or (b)? If so, how?

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**57.** What is Gibbs free energy change? Discuss its physical significance.

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**58.** Explain the following:

(a) The entropy of a substance increases on ging from the liquid to the vapour state at any temperature.

(b) Reactions with $\Delta_r G^\circ < 0$ always have an equilibrium constant greater than 1.

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**59.** How will you distinguish between the two?

(i) Open and closed system.

(ii) Extensive and intensive properties.

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**60.** What are spontaneous and non-spontaneous process? Under what conditions will the reaction occur if:

(i) both $\Delta H$ and $\Delta S$ are positive

(ii) both $\Delta H$ and $\Delta S$ are negative?

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**61.** What is free energy? How is it related to the spontaneity of a reaction.

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**62.** Taking a specific example show that $\Delta S_{total}$ is the criterion for spontaneity of a change.

> ▶ **Watch Video Solution**

## Revision Exercise (Short Answer Questions ) (Fill in the blanks : )

**1.** $C(s)(\text{graphite}) \rightarrow C(g), \Delta H = 716.7 kJ$
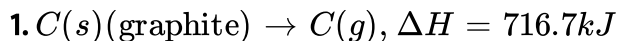
$\Delta H$ is the heat of ................of graphite.

> ▶ **Watch Video Solution**

**2.** (b) $H_2O(l) \rightarrow H_2O(s), \Delta_r H^\circ = -6.01 kJ$
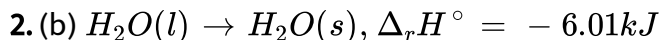
$\Delta H$ is the heat of ........of water.

> ▶ **Watch Video Solution**

**3.** (c) $H_2O(l) \rightarrow H_2O(g)$, $\Delta H = 40.7kJ$
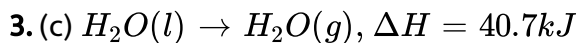
$\Delta_r H°$ is the heat of .......of water

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**4.** $C_2H_6 + \dfrac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$, $\Delta_r H° = -1560kJ$
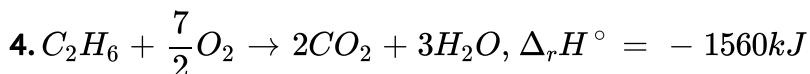
$\Delta_r H°$ is the heat of ....... of ethane

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**5.** $\dfrac{1}{2}N_2 + \dfrac{3}{2}H_2 \rightarrow NH_3$, $\Delta_r H° = -45.2kJ$
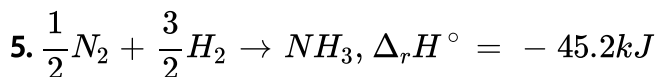
$\Delta_r H°$ is the heat of ...........of ammonia.

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Revision Exercise (Long Answer Questions)

**1.** Explain the following terms :

(i) First law of thermodynamics

(ii) Standard enthalpy of formation

**2.** State and explain Hess's law of constant heat summation.Discuss its important applications.

**3.** What are internal energy change and enthalpy change? How are these releated? Under what conditions both become equal?

**4.** Explain the following terms:

(i) Enthalpy of formation

(ii) Enthalpy of combustion

(iii) Enthalpy of phase transition.

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**5.** Write short notes on :

(i) Measurement of enthalpy of reaction

(ii) Hess's law and its applications.

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**6.** Differentiate between spontaneous and non - spontaneous processes by giving examples.

▶ **Watch Video Solution**

**7.** Explain the following terms giving examples :

(i) System

(ii) Surroundings

(iii) Entropy

▶ Watch Video Solution

**8.** Explain free energy.Discuss the effect of temperature on free energy.

▶ Watch Video Solution

**9.** How is $\Delta G$ related yo $\Delta H$ and $T\Delta S$? What is the meaning of $\Delta G = 0$?

▶ Watch Video Solution

**10.** Explain the terms entropy and free energy.Why does entropy of a solid increase on fusion?

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**11.** Graphically shoe the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from $(p_i, V_i)$ to $(p_f, V_f)$. With the help of a pV plot compare the work done in the above case with that carried out against a constant pressure $p_f$.

## Revision Exercise (Numerical Problems)

**1.** The reaction between gaseous hydrogen and chlorine is

$$H_2(g) + CI_2(g) \rightarrow 2HCI(g)$$
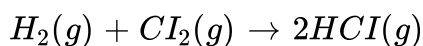
$$\Delta_r H^\circ = -184.0 kJ$$

(i) What is the enthalpy of formation of HCl?

How much heat will be liberated at 298 K and 1 atm for the formation of 365 g of HCl?

**2.** The enthalpies of combustion of $C_2H_2(g)$ and $C(2)H_6(g)$ are -1301 kJ and -1561.5 kJ respectively. The enthalpy of formation of liquid water is -286 kJ. Calculate the enthalpy change for the reaction :

$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_2(g)$ .
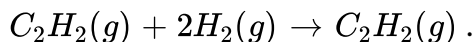
**3.** The enthapy of formation of carbon monoxide and steam are -110.5 and -243.0 kJ respectively.Calculate the heat of the reaction when steam is passed over coke as : $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ .

**4.** Calculate the enthalpy of combustion of glucose from the follwoing data :

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$

$$\Delta_r H^\circ = -395.0 kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

$$\Delta_r H^\circ = -269.4 kJ$$

$$6C(\text{graphite}) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$$
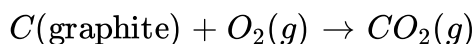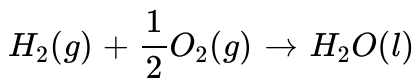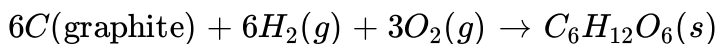
$$\Delta_r H^\circ = -1169.9 kJ$$

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5. The heat evolved in the combustion of methane is given as :

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
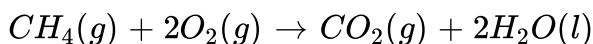
$$\Delta_r H^\circ = 890.3 kJ$$

Calculate :

(a) how many grams of methane would be required to produce 445.15 kJ of heat on combustion?

How many grams of $CO_2$ would be formed when 445.15 kJ heat is evolved?

(c) what volume of $O_2$ at S.T.P would be used in the above combustion process ?

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**6.** A gas mixture of $3.67L$ of ethylene and methane on complete combustion at $25°C$ produces $6.11L$ of $CO_2$. Find out the heat evolved on buring $1L$ of the gas mixture. The heats of combustion of ethylene and methane are $-1423$ and $-891 kJmol^{-1}$, respectively, at $25°C$.

**7.** Calculate $\Delta H°._f$ for chloride ion from the following data :

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCI(g), \Delta H°._f = \text{-92.4 kJ}$$

$$HCI(g) + nH_2O \rightarrow H^+(aq) + CI^-(aq), \Delta H° = \text{- 74.8 kJ}$$

$$\Delta H°._f\ H^+(aq) = \text{0.0 kJ}$$
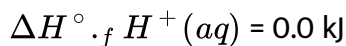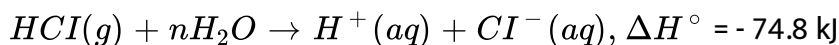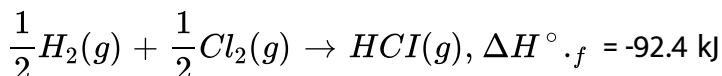
**8.** Standard vaporization enthalpy of benzene at its boiling point is $30.8 kJmol^{-1}$, for how long would a $100W$ electric heater have to

operate in order to vaporize a $100g$ sample of benzene at its boiling temperature?

**9.** When 1.3 g of butane $C_4H_{10}$ was burnt in oxygen in a flame calorimeter containing 1.8 kg of water the temperature reose from 25.3 to $33.3°C$. Calculate the enthalpy change for the combustion of 1 mol of butane?

**10.** $0.562g$ of graphite kept in a bomb calorimeter in excess of oxygen at $298K$ and 1 atmospheric pressure was burnt according to the equation,

$$C_{Graphite} + O_{2(g)} \rightarrow CO_{2(g)}$$
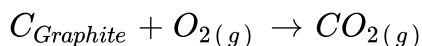
durgin the reaction, temperature rises from $298K$ o $298.89K$. If the heat capacity of the calorimeter and its contents is $20.7kJ/K$, what is the enthalpy change for the above reaction at $298K$ and $1atm$?

1. A system is changed from an initial state to by a process such that $\Delta H = q$. If the change from the initial state to the final state were made by a different path, would $\Delta H$ and q be the same as that for the first path?

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2. Air contain about 99% of $N_2$ and $O_2$ gases. Why do not they combine to form NO under the standard conditions? Standard Gibbs energy of formation of $NO(g)$ is $86.7 kJmol^{-1}$.

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3. Under what conditions will a reaction be spontaneous if

(i) both $\Delta H$ and $\Delta S$ are positive?

(ii) both $\Delta H$ and $\Delta S$ are negative?

4. Show that for an isothermal expansion of an ideal gas(i)$\Delta U = 0$ and(ii) $\Delta H = 0.$

5. While doing an experiment on bomb calorimeter, a student made the following statement :

$$\Delta H = \Delta U + p\Delta V$$

Since in the experiment $\Delta V = 0$ hence $\Delta H = \Delta U$.Is the student right or wrong? Justify.

**6.** How do the strengths of bonds in the reactants compare with those of their counterparts in the products for

(i) endothermic reaction?

(ii) exothermic reaction?

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**7.** An average healthy man needs about 10000 kJ of enrgy per day.How much carbohydrates (in mass) he will have to consume assuming that all this energy needs are met only by carbohydrates in the form of glucose? The enthalpy of combustion of glucose is $2816 kJmol^{-1}$.

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**8.** Compute the heat of formation of liquid methyl alcohol in kilo joules per mole using the following data : Heat of vaporisation of liquid methyl alcohol : 38 kJ/mol.

Heat of formation of gaseous atoms from the elements in their standard

states :

H = 218 kJ/mol,

$C = 715\dfrac{kJ}{mol} = $ and $O = 249\dfrac{kJ}{mol}.$

Average bond energies,

$C - H = 415k\dfrac{J}{m}ol, C - O = 356\dfrac{kJ}{mol}$ and $O - H = 436\dfrac{kJ}{mol}.$

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**9.** The enthalpy change involved in the oxidation of glucose is

$-2880kJmol^{-1}$ 25% of this energy is available for muscular work. If 100

kJ of muscular work is neededto walk one kilometer, what is the maximum

distance that a person will be able to walk after consuming 120 gm of

glucose?

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**10.** Determine the value of $\Delta H$ and $\Delta U$ for the reversible isothermal

evaporation of 90.0g of water at $100°C$.Assume that water vapour

behaves as an ideal gas and heat of evaporation of water is $540 calg^- R = 2.0 calmol^{-1} K^{-1}$. (Answer in calories)

**11.** The standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are $-76.2$, $-394.8$ and $-241.6 kJmol^{-1}$ respectively. Calculate the amount of heat evolved by burning $1m^3$ of methane measured at N.T.P.

**12.** The standard heat of formation values of $SF_6(g)$, $S(g)$, and $F(g)$ are $-1100$, $275$, and $80 kJmol^{-1}$, respectively. Then the average $S - F$ bond enegry in $SF_6$ (Answer in KJ/mol)

**13.** At $0°C$ ice and water are in equilibrium and $\Delta H = 6kJ \quad mol^{-1}$ for this process:

$$H_2O \Leftrightarrow H_2O(l)$$
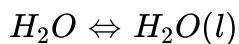
The values of $\Delta S$ and $\Delta G$ for conversion of ice into liquid water at $0°C$ are: (Answer in J/K/mol and multiply your answer with 10)

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**14.** $10g$ of argon gas is compressed isothermally and reversibly at a temperature of $27°C$ from $10L$ to $5L$. Calculate $q, w, \Delta U$, and $\Delta H$ for this process. $R = 2.0calK^{-1}mol^{-1}$, $\log_{10} 2 = 0.30$. Atomic weight of $Ar = 40$.

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**15.** Calculate the equilibrium constant for the reaction :

$$NO(g) + \frac{1}{2}O_2(g) \Leftrightarrow NO_2(g)$$
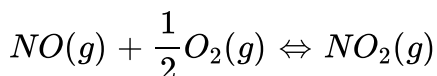
Given,

$\Delta_f H°$ at $298K: NO(g) = 90.4kJmol^{-1}$, $NO_2(g) = 33.8kJmol^{-1}$ and

$\Delta S°$ at $298K = -70.8JK^{-1}mol^{-1}$, $R = 8.31JK^{-1}mol^{-1}$.

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**16.** $100mL$ of a liquid is contained in an insulated container at a pressure of 1bar. The pressure is steeply increased to 100bar. The volume of the liquid is decreased by $1mL$ at this constant pressure. Find $\Delta H$ and $\Delta U$.

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**Competition File MCQ**

**1.** For reaction, $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ which of the following is valid?

    A. $\Delta H = \Delta U$

    B. $\Delta H > \Delta U$

C. $\Delta H < \Delta U$

D. None of the above

**Answer: C**

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**2.** Which of the following represents the first law of thermodynamics?

A. $q = \Delta U - w$

B. $\Delta H = q + w$

C. $\Delta U = \Delta H + p\Delta V$

D. $\Delta U = p\Delta V$

**Answer: A**

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**3.** The volume of gas is reduced to half from its original volume. The specific heat will be

    A. reduce to half

    B. be doubled

    C. remain constant

    D. increase four times

**Answer: C**

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**4.** In an adibatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic conditions from the following :

    A. $q = 0, \Delta T \neq 0, w = 0$

    B. $q \neq 0, \Delta T = 0, w = 0$

C. $q = 0, \Delta T = 0, w = 0$

D. $q = 0, \Delta T < 0, w \neq 0$

**Answer: C**

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**5.** For an ideal gas $C_p$ and $C_v$ are related as

A. $C_p - C_v = R$

B. $\dfrac{C_p}{C_v} = R$

C. $C_p + C_v = R$

D. $C_v - C_p = R$

**Answer: A**

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**6.** In an isothermal expansion of an ideal gas against vacuum, the work is involved is :

A. zero

B. maximum

C. minimum

D. none of these

**Answer: A**

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**7.** Which of the following statement is false?

A. work is a state function

B. temperature is a state function.

C. change in the state is completely defined when the initial and final states are specified.

D. work appears at the boundary of the system.

**Answer: A**

**8.** In a closed insulated container, a liquid is stirred with a paddle to increase the temperature. Which of the following is true?

A. $\Delta U = w \neq 0, q = 0$

B. $\Delta U = w = q \neq 0$

C. $\Delta U = 0, w = q \neq 0$

D. $w = 0, \Delta U = q \neq 0$

**Answer: A**

**9.** Five moles of gas is put through a series of changes as shown graphically in a cyclic process.The processes $A \to B, B \to C$ and $C \to A$ respectively are :



  A. isochoric, isobaric, isothermal

  B. isobaric, isochoric, isothermal

  C. isothermal, isobaric, isochoric

  D. isobaric, isothermal, isochoric

**Answer: A**

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**10.** An ideal gas expands in volume from $1 \times 10^3 m^3$ at 300 K against a constant pressure of $1 \times 10^5$ N $m^{-2}$.The work done is

  A. $-900$ J

B. $-900$ kJ

C. 270 kJ

D. 900 kJ

**Answer: A**

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**11.** The heat evolved in the combustion of benzene is given by the equation:

$$C_6H_6(g) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l), \Delta H = -3264.6 kJmol^{-1}$$
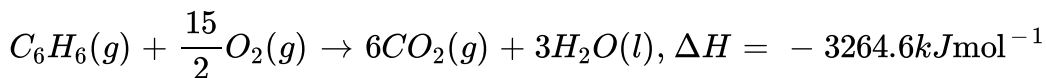
The heat energy changes when 39 g of $C_6H_6$ are burnt im an open ontainer will be:

A. $+816.15 kJmol^{-1}$

B. $+1632.3 kJmol^{-1}$

C. $-1632.3 kJmol^{-1}$

D. $-2448.45 kJmol^{-1}$

**Answer: C**

---

**12.** Write the equations represents enthalpy of formation of $H_2O$?

---

**13.** The enthalpy of neutralisation of NaOH with HCl is 57.1 kJ while with

$CH_3COOH$ it is -55 kJ

This happens because

    A. acetic acid is an organic acid

    B. acetic acid is little soluble in water

    C. acetic acid is a weak acid and requires lesser sodium acid hydroxide

       for neutralisation

    D. some heat is required to ionise acetic acid completely

**Answer: D**

**14.** The equations representing the combustion of carbon and carbon monoxide are :

$$C(s) + O_2(g) \rightarrow CO_2(g) \Delta H = -394\frac{kJ}{mol}$$

$$CO(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \Delta H = -284.5\frac{kJ}{mol}$$
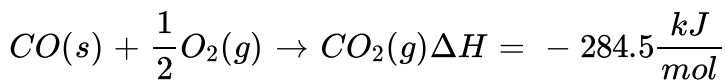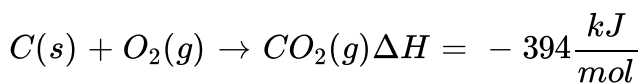
the heat of formation of 1 mol of CO(g) is :

A. $-109.5\frac{kJ}{mol}$

B. $+109.5\frac{kJ}{mol}$

C. $+180.0\frac{kJ}{mol}$

D. $+100\frac{kJ}{mol}$

**15.** $\Delta H$ for the combustion of a compound is:

A. positive

B. zero

C. negative

D. may be positive or negative

**Answer: C**

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**16.** Molar heat capacity of ethanol is $110.4JK^{-1}$. Its specific heat capacity is

A. 2.4

B. 55.2

C. 5.078

D. 110.4

**Answer: A**

**17.** Enthalpy of formation of ammonia is $-46.0kJmol^{-1}$.The enthalpy change for the reaction:

$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
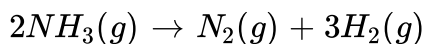
A. $46.0kJmol^{-1}$

B. $-23.0kJmol^{-1}$

C. $92.0kJmol^{-1}$

D. $-92.0kJmol^{-1}$

**Answer: C**

**18.** The $\Delta H°$ for $CO_2(g), CO(g)$ and $H_2O(g)$ are -393.5, -110.5 and $-241.8kJmol^{-1}$ respectively.The standard enthalpy change (in kJ) for the reaction :

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is
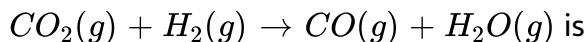
A. 524.1

B. 41.2

C. $-262.5$

D. $-41.2$

**Answer: B**

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**19.** Equal volumes of one molar HCl and $H_2SO_4$ are neutralised (separately) by dilute NaOH solution and x kcal and y kcal of heats are liberated.Which of hte following is true?

A. x = y

B. x = 0.5 y

C. $x = \dfrac{1}{2y}$

D. None

**Answer: B**

**20.** On the basis of thermochemical equations (i),(ii) and (iii), which of the algebric relationship is correct.
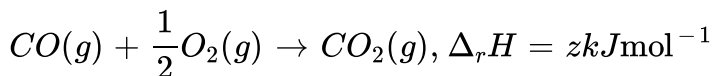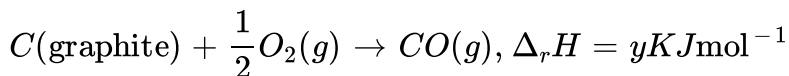
$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g), \Delta_r H = xkJ\text{mol}^{-1}$

$C(\text{graphite}) + \dfrac{1}{2}O_2(g) \rightarrow CO(g), \Delta_r H = yKJ\text{mol}^{-1}$

$CO(g) + \dfrac{1}{2}O_2(g) \rightarrow CO_2(g), \Delta_r H = zkJ\text{mol}^{-1}$

A. z = x + y

B. x = y - z

C. x = y + z

D. y = 2z - x

Answer: C

21. During complete combustion of one mole of butane, 2658 kJ of heat is

released.The termochemical reaction for above change is

A. $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$,

$\Delta_cH = -2658.0kJmol^{-1}$

B. $C_4H_{10}(g) + \dfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$

$\Delta_cH = -1329.0kJmol^{-1}$

C. $C_4H_{10}(g) + \dfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

$\Delta_cH = -2658.0kJmol^{-1}$

D. $C_4H_{10}(g) + \dfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

$\Delta_cH = +2658.0kJmol^{-1}$

**Answer: C**

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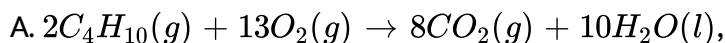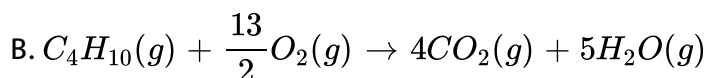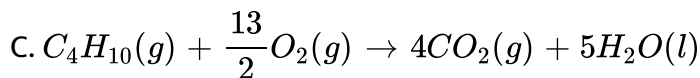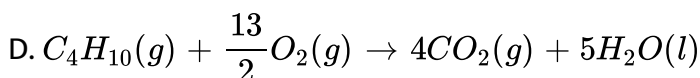
**22.** The enthalpy of vaporisation of liquid water using data

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \Delta H = -285.77kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \Delta H = -241.84kJ \text{ is}$$
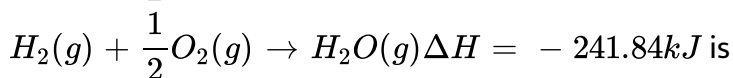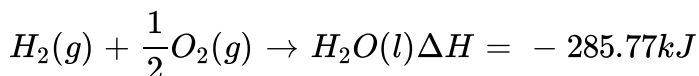
A. $+43.93kJ\text{mol}^{-1}$

B. $-43.93kJ\text{mol}^{-1}$

C. $+527.61kJ\text{mol}^{-1}$

D. $-527.61kJ\text{mol}^{-1}$

**Answer: A**

**23.** Given that

$$C + O_2 \to CO_2 \Delta H^\circ = -xkJ$$

$$2CO + O_2 \to 2CO_2 \Delta H^\circ = -ykJ$$
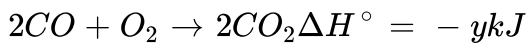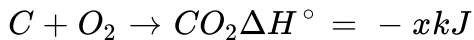
The enthalpy of formation of CO will be

A. $y - 2x$

B. $\dfrac{2x - y}{2}$

C. $\dfrac{y - 2x}{2}$

D. $2x - y$

**Answer: C**

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**24.** Given: $C + 2S \to CS_2, \Delta H = 117kJ$

$$C + O_2 \to CO_2, \Delta H = -393kJ$$

$$S + O_2 \to SO_2 \Delta H = -297kJ$$
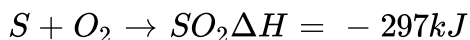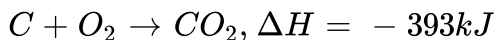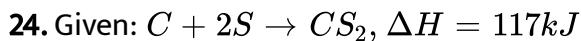
The heat of combustion of $CS_2$ to form $CO_2$ and $SO_2$ is

A. $- 1104 kJmol^{-1}$

B. $1104 kJmol^{-1}$

C. $+ 807 kJmol^{-1}$

D. $- 807 kJmol^{-1}$

**Answer: A**

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**25.** When 5 g of sulphur is burnt to $SO_2$, 46 kJ of heat is liberated. What is the enthalpy of formation of sulphur dioxide?

A. $- 147.2 kJ$

B. $+ 147.2 kJ$

C. $+ 294.4 kJ$

D. $- 294.4 kJ$

**Answer: D**

**26.** The enthalpy of formation of two compounds A and B are - 84 kJ and -156 kJ respectively. Which one of the following statements is correct?

A. A and B are endothemric compounds

B. A is more stable than B

C. A is less stable than B

D. Both are unstable

**Answer: C**

**27.** A cylinder of gas supplied by Bharat Petroleum is assumed to contain 14 kg of butane.If a normal family requires 20,000 kJ of energy per day for cooking butane gas in the cylinder last for....days($\Delta H_c$ of $C_4H_{10} = -2658$ kJ per mole)

A. 15 days

B. 20 dyas

C. 50 days

D. 40 days

**Answer: D**

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**28.** The enthalpy of hydrogenetaion of cyclohexene is $-119.5 kJmol^{-1}$.If resonance energy of benzene is $-150.4 kJmol^{-1}$, its enthalpy of hydrogeneation would be :

A. $-208.1 kJmol^{-1}$

B. $-269.9 kJmol^{-1}$

C. $-358.5 kJmol^{-1}$

D. $-508.9 kJmol^{-1}$

**Answer: A**

---

**29.** What would be the heat released when an aqueous solution containing 0.5 mol of $HNO_3$ is mixed with 0.3 mol of $OH^-$ (enthalpy of neutralisation is -57.1 kJ)?

A. $28.5kJ$

B. $17.1kJ$

C. $45.7kJ$

D. $1.7kJ$

**Answer: B**

**30.** If the bond dissociation energies of $XY$, $X_2$ and $Y_2$ ( all diatomic molecules ) are in the ratio $1:1:0.5$ and $\Delta_f H$ of $XY$ is $-200kJmol^{-1}$. The bond dissociation energy of $X_2$ will be :

A. $100kJmol^{-1}$

B. $200kJmol^{-1}$

C. $800kJmol^{-1}$

D. $400kJmol^{-1}$

**Answer: C**

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**31.** The enthaplpy changes state for the following processes are listed below:

$Cl_2(g) = 2Cl(g) : 242.3KJmol^{-1}$

$I_2(g) = 2I(g) , 151.0KJmol^{-1}$

$ICl(g) = I(g) + Cl(g) : 211.3KJmol^{-1}$
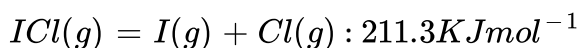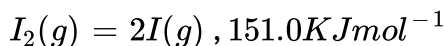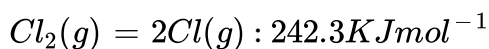
$$I_2(s) = I_2(g) , 62.76KJmol^{-1}$$

Given that the standard states for iodine chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for $ICl(g)$ is:

    A. $-16.8kJmol^{-1}$

    B. $+16.8kJmol^{-1}$

    C. $+244.8kJmol^{-1}$

    D. $-14.6kJmol^{-1}$

**Answer: B**

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**32.** The entropy change can be calculated by using expression $\Delta S = \dfrac{q_{rev}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following:

    A. $\Delta S$(syste) decreases but $\Delta S$ (surroundins) remains the same.

    B. $\Delta S$ (system) increases but $\Delta S$ (surroundings) decreases,

C. $\Delta S$ (system) decreases but $\Delta S$ (surroundings) increases.

D. $\Delta S(system) decreases$ and DeltaS` (surroundings) also decrease.

**Answer: C**

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**33.** For which of the following reactions, $\Delta S$ is not positive :

A. $I_2(s) \rightarrow I_2(g)$

B. $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$

C. $2O_3(g) \rightarrow 3O_2(g)$

D. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O_g$
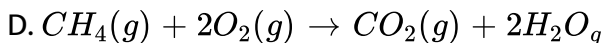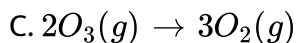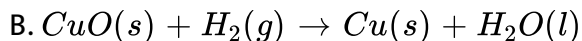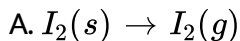
**Answer: B**

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**34.** If equilibrium constant for a reaction is K, then standard free energy change is :

A. $\Delta G^\circ = -RT \log K$

B. $\Delta G^\circ = RT In K$

C. $\dfrac{\Delta G^\circ}{RT} = -\log K$

D. $\dfrac{\Delta G^\circ}{RT} = -2.303 \log K$

**Answer: D**

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**35.** For a reversible process at equilibrium, the change in entropy may be expressed as:

A. $\Delta S = T q_{rev}$

B. $\Delta S = \dfrac{\Delta H}{T}$

C. $\Delta S = \dfrac{q_{rev}}{T}$

D. $\Delta S = T\Delta H$

**Answer: C**

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**36.** Free energy change is related to enthalpy and entropy changes as:

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

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

C. $\Delta G^\circ = \dfrac{\Delta H - \Delta S}{T}$

D. $\Delta G = \Delta H + T\Delta S$

**Answer: A**

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**37.** For a spontaneous reaction, $\Delta G$ should be :

A. positive

B. negative

C. equal to zero

D. may be positive or negative

**Answer: B**

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**38.** Which of the following conditions is not favourable for the feasibility of a reaction?

A. $\Delta H = + ve, T\Delta S + ve$ and $T\Delta S > \Delta H$

B. $\Delta H = - ve, T\Delta S = + ve$

C. $\Delta H = - ve, T\Delta S = - ve$ and $T\Delta S < \Delta H$

D. $\Delta H = + ve, T\Delta S = + ve$ and $T\Delta S < \Delta H$

**Answer: D**

**39.** The standard free energy change $\Delta G^\circ$ is related to equilibrium constant $K_p$ as

A. $K_p = \dfrac{e^{-\Delta G^\circ}}{RT}$

B. $K_P = \dfrac{-\Delta G^\circ}{RT}$

C. $K_p = RTIn\Delta G^\circ$

D. $\Delta G = \dfrac{e^{-K_p}}{RT}$

**Answer: A**

**40.** If $\Delta_f G^\circ$ for $NH_3(g)$ is $-16.4 kJmol^{-1}$, then$\Delta G^\circ$ for the reaction:

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is
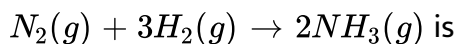
A. $32.8 kJmol^1$

B. $16.4kJmol^{-1}$

C. $-16.4kJmol^{-1}$

D. $-32.8kJmol^{-1}$

**Answer: D**

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**41.** For an ideal gas expanding adiabatically in vacuum,

A. $\Delta S(sys) = +ve, \Delta S(surr) = 0$

B. $\Delta S(sys) = 0, \Delta S(surr) = +ve$

C. $\Delta S(sys) = 0, \Delta S(surr) = 0$

D. $\Delta S(sys) = +ve, \Delta S(surr) = -ve$

**Answer: B**

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**42.** Which of the following is true for a reaction $H_2O(l) \rightarrow H_2O(g)$ at $100°C$, 1 atm. Pressure

A. $\Delta H = \Delta U$

B. $\Delta U = 0$

C. $\Delta H = 0$

D. $\Delta H = T\Delta S$

**Answer: D**

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**43.** Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

A. $\Delta S_{system} - \Delta S_{surrounding} > 0$

B. $\Delta S_{system} > 0$

C. $\Delta S_{surroundings} > 0$

D. $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

**Answer: D**

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**44.** A reaction occurs spontaneously if

A. $T\Delta S < \Delta H$ and both $\Delta H$ and $\Delta S$ are +ve

B. $T\Delta S > \Delta H$ and $\Delta H$ is +ve and $\Delta S$ are -ve

C. $T\Delta S > \Delta H$ and both $\Delta H$ and $\Delta S$ are +ve

D. $T\Delta S = \Delta H$ and both $\Delta H$ and $\Delta S$ are +ve

**Answer: C**

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**45.** The enthalpy and entropy change for the reaction:

$$Br_2(l) + CI_2(g) \rightarrow 2BrCI(g)$$
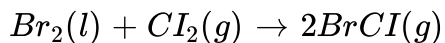
$30 kJ\text{mol}^{-1}$ and $105 JK^{-1}\text{mol}^{-1}$ respectively. The temperature at which the reaction will be in equilibrium is:

A. 273 K

B. 450 K

C. 300 K

D. 285.7 K

**Answer: D**

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**46.** For a spontaneous reaction, the $\Delta G$, equilibrium constant (K) and $E^{\circ}_{cell}$ will be respectively,

A. $-ve, \ > 1, \ + ve$

B. $+ve, \ > 1, \ -ve$

C. $-ve, \ < 1, \ -ve$

D. $-ve, \ > 1, \ -ve$

**Answer: A**

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**47.** Given that the bond energies of H - H and Cl - Cl are $430 kJmol^{-1}$ and $240 kJmol^{-1}$ respectively and $\Delta_f H$ for HCl is $-90 kJmol^{-1}$, bond enthalpy of HCl is

A. $254 kJmol^{-1}$

B. $290 kJmol^{-1}$

C. $380 kJmol^{-1}$

D. $425 kJmol^{-1}$

**Answer: D**

**48.** If 50 kJ of energy is needed for muscular work to walk a distance of 1 km, then how much glucose one has to consume to walk a distance of 5km provided only 30% energy is available for muscular work. The enthalpy of combustion of glucose in 3000 kJ $mol^{-1}$.

A. 75 g

B. 30 g

C. 180 g

D. 150 g

**Answer: D**

**49.** The average molar heat capacities of ice and water are respectively $37.8\dfrac{J}{mol}$ and $75.6\dfrac{J}{mol}$ and the enthalpy of fusion of ice is $6.012\dfrac{kJ}{mol}$

.The amount of heat required to change 10 g of ice at $-10°C$ to water at $10°C$ would be

A. 2376 J

B. 4752 J

C. 3970 J

D. 1128 J

**Answer: C**

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**50.** Entropy changes for the process

$H_2O(l) \rightarrow H_2O(g)$ at normal pressure and at 274 K are given below:

$\Delta S_{system} = -22.13, \Delta S_{surroundings} = +22.05$

The process is non - spontaneous because

A. $\Delta S_{system}$ is -ve

B. $\Delta S_{surroundings}$ is + ve

C. $\Delta_{universe}$ is -ve

D. $\Delta S_{system} \neq \Delta S_{surroundings}$

**Answer: C**

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**51.** The heat of atomisation of $PH_3(g)$ and $P_2H_4(g)$ are $954 kJmol^{-1}$ and $1485 kJmol^{-1}$ respectively. The P - P bond energy in kJ mol$^{-1}$ is

A. 213

B. 426

C. 318

D. 1272

**Answer: A**

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**52.** The values of $\Delta H$ and $\Delta S$ for the reaction,

$C(\text{graphite}) + CO_2(g) \rightarrow 2CO(g)$

are $170kJ$ and $170\dfrac{J}{K}$ respectively. This reaction will be spontaneous at

A. 910 K

B. 1110 K

C. 510 K

D. 710 K

**Answer: B**

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**53.** Standard entropies of $X_2, Y_2$ and $XY_3$ are 60,40 and 50 kJmol$^{-1}$ respectively. For the reaction:

$\dfrac{1}{2}X_2 + \dfrac{3}{2}Y_2 \Leftrightarrow XY_3, \Delta H = -30kJ$
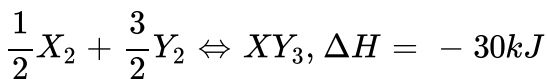
to be at equilibrium, the temperature should be

A. 500 K

B. 750 K

C. 1000 K

D. 1250 K

**Answer: B**

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**54.** Four grams of graphite is burnt in a bomb calorimeter of heat capacity of $30kJK^{-1}$ in excess of oxygen at 1 atmospheric pressure.The temperature rises from 300 to 304 K.What is the enthalpy of combustion of graphite (in $kJmol6(-1)$)?

A. 360

B. 1440

C. $-360$

D. $-1440$

**Answer: C**

55. Enthalpy change for the reaction,

$4H(g) \rightarrow 2H_2(g)$ is $-869.6kJ.$ The dissociation energy of H - H bond is

A. $434.8kJ$

B. $-869.6kJ$

C. $+434.8kJ$

D. $+217.4kJ$

**Answer: C**

56. Which of the follwoing correct option for free expansion of an ideal gas under adiabatic condition?

A. $q = 0, \Delta T \neq 0, w = 0$

B. $q \neq 0, \Delta T = 0, w = 0$

C. $q = 0, \Delta T = 0, w = 0$

D. $q = 0, \Delta T < 0, w \neq 0$

**Answer: C**

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57. In which of the following reactions, standard reaction entropy change $(\Delta S^{\circ})$ is positive and standard Gibb's energy change $(\Delta G^{\circ})$ decreases sharply with increasing temperature?

A. $C(\text{graphite}) + \dfrac{1}{2}O_2(g) \rightarrow CO(g)$

B. $CO(g) + \dfrac{1}{2}O_2(g) \rightarrow CO_2(s)$

C. $Mg_s + \dfrac{1}{2}O_2(g) \rightarrow MgO(s)$

D. $\dfrac{1}{2}C(\text{graphite}) + \dfrac{1}{2}O_2(g) \rightarrow \dfrac{1}{2}CO_2(g)$

**Answer: A**

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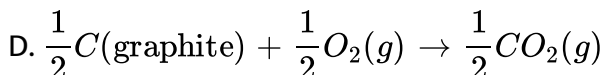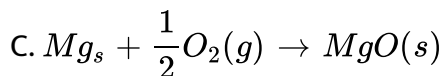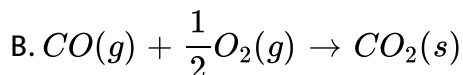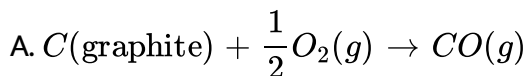
**58.** The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at $0°C$ is

A. $\dfrac{10.52cal}{molK}$

B. $\dfrac{21.04cal}{molK}$

C. $\dfrac{5.260cal}{molK}$

D. $\dfrac{0.526cal}{molK}$

**Answer: A**

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**59.** In the following reaction:

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g), \Delta H = -110kJ,$$
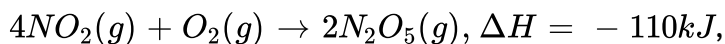
if $N_2o_5(s)$ is formed instead of $N_2O_5(g)$ in the reaction, the enthalpy change (in kJ) would be (enthalpy of sublimation of $N_2O_5(s)$ is $+53kJmol^{-1}$).

A. $-216$

B. $-162$

C. $+108$

D. $+216$

**Answer: A**

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**60.** For the reaction, $X_2O_4(l) \rightarrow 2XO_2(g)$

$\Delta U = 2.1kcal, \Delta S = 20calK^{-1}$ at 300 K hence, $\Delta G$ is

A. 2.7 kcal

B. $-2.7$ kcal

C. 9.3kcal

D. $-9.3$ kcal

**Answer: B**

**61.** The enthalpies of solution for copper sulphate pentahydrate and anhydrous copper sulphate are respectively 11.7 and $-65.5kJmol^{-1}$.The hydration enthalpy of anhydrous copper sulphate is

A. $53.8kJmol^{-1}$

B. $-9.8kJmol^{-1}$

C. $-77.2kJmol^{-1}$

D. $-53.8kJmol^{-1}$

**Answer: C**

**62.** The standard enthalpy of formation of $NH_3(g)$ is $-91.8kJmol^{-1}$.The amount of heat required to decompose 34 g of $NH_3(g)$ into its elements is

A. $183.6kJ$

B. $91.8kJ$

C. $45.9kJ$

D. $137.7kJ$

**Answer: A**

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**63.** Calculate the work done by 16g of oxygen gas (assume ideal behaviour) of molar mass 32 g $mol^{-1}$ undergoing isothermal reversible expansion at 300 K from an initial volume of 2.5 L to the final volume of 25 L in litre atm.

$(R = 8.2 \times 10^{-2} Latm \ \text{K}^{(-1)} \ mol^{-1})$

A. − 56.64

B. 28.32

C. 113.28

D. 56.64

**Answer: B**

**64.** The heat of combustion of carbon to $CO_2$ is -393.5 kJ/mol. The heat released for the formation of 35.2 g of $CO_2$ from carbon and oxygen gas is:

A. − 630 kJ

B. − 3.26 kJ

C. − 315 kJ

D. + 315 kJ

**Answer: C**

---

**65.** The correct thermodynamic conditions for the spontaneous reaction at all temperatures is

    A. $\Delta H < 0$ and $\Delta S > 0$

    B. $\Delta H < 0$ and $\Delta S < 0$

    C. $\Delta H < 0$ and $\Delta S = 0$

    D. $\Delta H > 0$ and $\Delta S < 0$

**Answer: A**

---

**66.** For a sample of perfect gas when its pressure is changed isothermally form $p_i$ to $p_p$ the entropy change is given by

A. $\Delta S = nR \in \left( \dfrac{p_f}{p_i} \right)$

B. $\Delta S = nR \in \left( \dfrac{p_i}{p_f} \right)$

C. $\Delta S = nRT \in \left( \dfrac{p_f}{p_i} \right)$

D. $\Delta S = nRT \in \left( \dfrac{p_i}{p_f} \right)$

**Answer: B**

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67.    For    a    given    reaction,    $\Delta H = 35.5 kJmol^{-1}$    and

$\Delta S = 83.6 JK^{-1}mol^{-1}$. The reaction is spontaneous at (assume that

$\Delta H$ and $\Delta S$ do not vary with temperature.

A. $T > 425K$

B. all temperatures

C. $T < 298K$

D. $T < 425K$

**Answer: A**

---

**68.** A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy $\Delta U$ of the gas in joules will be

A. $-500 J$

B. $-505 J$

C. $+505 J$

D. $1136.25 J$

**Answer: B**

**69.** The bond dissociation energies of $X_2, Y_2$ and XY are in the ratio of $1:0.5:1.$ $\Delta H$ for the formation of XY is $-200kJmol^{-1}$.The bond dissociation energy of $X_2$ will be

A. $200kJmol^{-1}$

B. $100kJmol^{-1}$

C. $800kJmol^{-1}$

D. $400kJmol^{-1}$

**Answer: C**

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**70.** Under isothermal conditions, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar.The work done by the gas is

[ Given that 1 L bar = 100 J]

A. 30 J

B. $-30J$

C. 5 kJ

D. 25 J

**Answer: B**

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**71.** In which case change in entropy is negative?

A. $2H_g \rightarrow H_2(g)$

B. Evaporation of water

C. Expansion of a gas at constant temperature

D. Sublimation of solid to gas

**Answer: A**

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**72.** Assuming the water vapour is an ideal gas, the internal energy change $(\Delta U)$ when 1 mole of water is vapourised at 1 bar pressure and $100°C$ (given molar enthalpy of vapourisation of watyer at 1 bar and 373 K = $41 kJmol^{-1}$ and R = 8.3 J$mol^{-1}K^{-1}$) will be

A. $3.7904 kJmol^{-1}$

B. $37.904 kJmol^{-1}$

C. $41.00 kJmol^{-1}$

D. $4.100 kJmol^{-1}$

**Answer: B**

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**73.** In conversion of limestone to lime,

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ the values of $\Delta H°$ and $\Delta S°$ are + 179.1 kJ $mol^{-1}$ and 160.2 J/K respectively at 298 K and 1 bar. Assuming that

$\Delta H°$ and $\Delta S°$ do not change with temperature, the temperature above which conversion of limestone to lime will be spontaneous is:

A. 1200 K

B. 845 K

C. 1118 K

D. 1008 K

**Answer: C**

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**74.** Using the following thermochemical equations

(i) $S(Rh) + \frac{3}{2}O_2(g) \rightarrow SO_3, \Delta H = -2x\frac{kJ}{mol}$

(ii)$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g), \Delta H = -y\frac{kJ}{mol}$
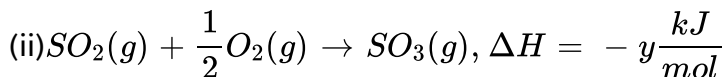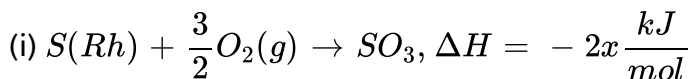
Find ut the heat of formation of $SO_2(g)$ in $\frac{kJ}{mol}$

A. $(2x + y)$

B. $(x + y)$

C. $\left(2\dfrac{x}{y}\right)$

D. $(y - 2x)$

**Answer: D**

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**75.** Oxidising power of chlorine in aqueous solution can be determined by parameters indicated below:

$\dfrac{1}{2}CI_2(g) \xrightarrow{\frac{1}{2}\Delta_{\text{diss}} H} CI(g) \xrightarrow{\Delta_{hyd} H} CI^{-aq}$ The energy involved in the conversion of $\dfrac{1}{2}CI_2(g)$ to $CI^-(aq)$ using data,

$\Delta_{\text{diss}} H_{CI2} = 240kJmol^{-1}$,

$\Delta_{eg} HCI = -349kJmol^{-1}$, $\Delta_{hyd} H_{ci} = -381kJmol^{-1}$ will be

A. $+120kJmol^{-1}$

B. $+152kJmol^{-1}$

C. $-610kJmol^{-1}$

D. $-850kJmol^{-1}$

Answer: C

76. In afuel cell, methanol is used as fuel and oxygen is used as an oxidiser.The reaction is :
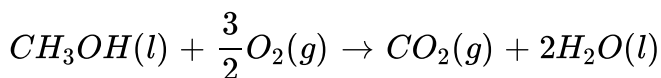
$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

At 298 K, standard Gibbs energies of formation for $CH_3OH(l), H_2O(l)$ and $CO_2(g) are - 166.2, - 237.2$ and $- 394.4k\frac{J}{m}ol$ respectively.If standard enthalpy of combustion of methanol is $- 726\frac{kJ}{mol}$ , efficiency of the fuel cell will be

A. 0.8

B. 0.87

C. 0.9

D. 0.97

Answer: D

**77.** On the basis of the following thermochemical data

$$\left(\Delta_f G^\circ H^+(aq) = 0\right)$$

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq), \Delta H = 57.32 \text{ kJ}$$

(ii) $H_2(g) + \dfrac{1}{2} \rightarrow H_\circ O(l), \Delta H = -286.2 \text{ kJ}$
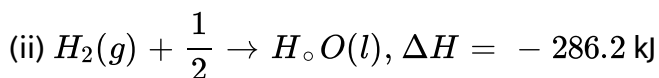
The value of enthalpy of formation of $OH^-$ at $25^\circ C$ is

A. $-22.88$ kJ

B. $-228.88$ kJ

C. $+228.88$ kJ

D. $-343.52$ Kj

**Answer: B**

**78.** For a particular reversible reaction at temperature T, $\Delta H$ and $\Delta S$ were found to be both +ve. If $T_e$ is the temperature at equilibrium, the reaction would be spontaneous when

**79.** One mole of an ideal gas expands at a constant temperature of 300 K from an initial volume of 10 litre to a final volume of 20 litre.The work done in expanding the gas is

   A. 750 Joule

   B. 1728 Joule

   C. 1500 Joule

   D. 3456 Joule

**Answer: B**

**80.** Molar heat capacity of aluminium is $25 JK^{-1} mol^{-1}$.The heat necessary to raise the temperature of 54 g of aluminium (Atomic mass 27 g $mol^{-1}$) from $30°C$ to $50°C$ is

A. 1.5 kj

B. 0.5 kJ

C. 1.0 kJ

D. 2.5 kJ

**Answer: C**

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**81.** The entropy of change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of $10 dm^3$ to a volume of $100 dm^3 at 27°C$ is

A. $38.3 Jmol^{-1}K^{-1}$

B. $35.8 J\mathrm{mol}^{-1}K^{-1}$

C. $32.3 J\mathrm{mol}^{-1}K^{-1}$

D. $42.3 J\mathrm{mol}^{-1}K^{-1}$

**Answer: A**

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**82.** The standard enthalpies of combustion of $C_6H_6(l), C(\text{graphite})$ and $H_2(g)$ are respectively $-3270 kJ\mathrm{mol}^{-1}$, $-394 kJ\mathrm{mol}^{-1}$ and $-286 kJ\mathrm{mol}^{-1}$. What is the standard enthalpy of formation of $C_6H_6(l)$ in kJ mol$^{-1}$?

A. $-48$

B. $+48$

C. $-480$

D. $+480$

**Answer: B**

---

83. The incorrect expression among the following is

    A. in isothermal process, $W_{\text{reversible}} = -nRTIn\dfrac{V_f}{V_i}$

    B. In $K = \dfrac{\Delta H° - T\Delta S°}{RT}$

    C. $K = e^{-\Delta G° RT}$

    D. $\dfrac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

**Answer: B**

---

84. For isothermal expansion of an ideal gas, the correct combination of thermodynamic parameters will be

A. $\Delta U = 0$, $q = 0$, $w \neq 0$ and $\Delta H \neq 0$

B. $\Delta U \neq 0$ $q \neq 0$, $w \neq 0$ and $\Delta H = 0$

C. $\Delta U = 0$, $q \neq 0$, $w = 0$ and $\Delta H \neq 0$

D. $\Delta U = 0$, $q \neq 0$, $w \neq 0$ and $\Delta H = 0$

**Answer: D**

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**85.** Calculate the enthalpy change for the reaction

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
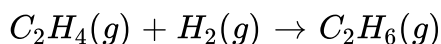
using the data given below :

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)\Delta H = -1415kJ$

$C_2H_6(g) + \dfrac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)\Delta H = -1566kJ$

$H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l)\Delta H = -286kJ$
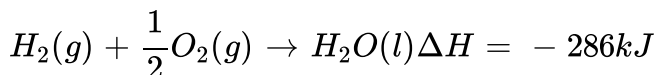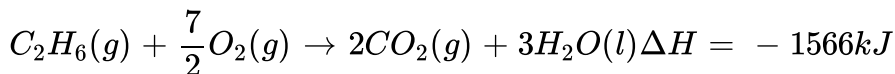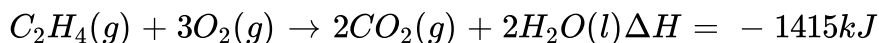
A. $-437$ kJ

B. $+35$ kJ

C. $-135\ kJ$

D. none of these

**Answer: C**

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86. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of $37.0°C$. As it does so, it absorbs 208 J of heat.The values of q and w for the process will be $\left(R = 8.314 Jmol^{-1}K^{-1}\right)$ (In 7.5 = 2.01)

A. $q = +208J, w = +208J$

B. $q = +208J, w = -208J$

C. $q = -208J, w = -208J$

D. $q = -208J, w = +208J$

**Answer: B**

**87.** The enthalpy of vaporization of a certain liquid at its boiling point of $35^\circ C$ is $24.64 kJ\mathrm{mol}^{-1}$.The value of change in entropy for the process is

A. $704 JK^{-1}\mathrm{mol}^{-1}$

B. $80 JK^{-1}\mathrm{mol}^{-1}$

C. $24.64 JK^{-1}\mathrm{mol}^{-1}$

D. $7.04 JK^{-1}\mathrm{mol}^{-1}$

**Answer: B**

**88.** The entropy of vaporization of a liquid is $58\ JK^{-1}mol^{-1}$.If 100 g of its vapour condenses at its boiling point of $123^\circ C$, the value of entropy change for the process is (molar mass of the liquid = $58 mol^{-1}$).

A. $-100 JK^{-1}$

B. $100 JK^{-1}$

C. $123 JK^{-1}$

D. $123 JK^{-1}$

**Answer: A**

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**89.** The ratio of heat liberated at 298 K from the combustion of one kg of coke and by burning, water gas obtained from 1 kg of coke is (assume coke to be 100% carbon, enthalpies of combustion of C, CO and $H_2$ as 393.5 kJ, 285 kJ, 285 kJ respectively all at 298 K).

A. $0.79 : 1$

B. $0.69 : 1$

C. $0.86 : 1$

D. $0.96 : 1$

**Answer: B**

**90.** At $25°$ C, the combustion of 1 mol of liquid benzene, the heat of reaction at constant pressure is given by

$$C_6H_6(l) + \frac{7}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$$
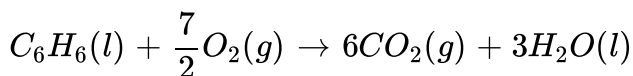
$$\Delta H = -780.980 \text{ cal}$$

Calculate the heat of reaction at constant volume.

A. 780.086 kcal

B. $-782.470$ kcal

C. $-390.043$ kcal

D. 390.043 kcal

**Answer: B**

**91.** For complete combustion of ethanol,

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ $mol^{-1}$ at $25°C$.

Assuming ideality the enthalpy of combustion, $\Delta_c H$ for the reaction will be (R = 8.314 J $mol^{-1}$)

A. $- 1350.50 kJmol^{-1}$

B. $- 1366.95 kJmol^{-1}$

C. $- 1361.95 kJmol^{-1}$

D. $- 1460.50 kJmol^{-1}$

**Answer: B**

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**92.** For the reaction $X_2Y_4(l) \rightarrow 2XY_2(g)$ at 300 K the values of $\Delta U$ and $\Delta S$ are 2.2 kcal and 20 cal $K^{-1}$ respectively.The value of $\Delta G$ for the reaction is

A. $- 3400$ cal

B. 3400 cal

C. $- 2800$ cal

D. 2000 cal

**Answer: C**

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**93.** Given R $= 8.314 JK^{-1}mol^{-1}$, the work done during combustion of 0.090 kg of ethane(molar mass = 30) at 300 K is

A. $- 18.7$ kJ

B. 18.7 kJ

C. 6.234 kJ

D. $- 6.234$ kJ

**Answer: B**

**94.** What is the amount of work done when two moles of an ideal gas is comoressed from a volume of $1m^3$ to 10 $dm^3$ at 300 K against a pressure of 100 kPa?

A. 99 kJ

B. $-99$ kJ

C. 114.9 kJ

D. $-114.9$ kJ

**Answer: A**

**95.** What is the amount of work done when 0.5 mol of methane, $CH_4(g)$ is subjected to combustion at 300K?

(given, $R = 8.314 JK^{-1}mol^{-1}$):

A. $-2494$ J

B. $-4988$ J

C. $+4988$ J

D. $+2494$ J

**Answer: D**

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**96.** The correct descending order of the heat librated (in kJ) during the neutralisation of the acids $CH_3COOH$(W), HF(X), HCOOH(Y) AND HCN(Z) under identical conditions ($K_a$ of $CH_3COOH = 1.8 \times 10^{-5}$, HCOOH = $1.8 \times 10^{-4}$, HCN = $4.9 \times 10^{-10}$ and HF = $3.2 \times 10^{-4}$) is

A. $Y > X > Z > W$

B. $X > Y > W > Z$

C. $W > X > Y > Z$

D. $Z > W > Y > X$

**Answer: B**

97. The correct statement regarding entropy is

    A. at absolute zero temperature, entropy of a perfectly crystalline

       solid is zero

    B. at absolute zero temperature, the entropy of a perfectly crystalline

       substance is + ve

    C. at absolute zero temperature, the entropy of all crystalline

       substance is zero

    D. at $0°C$ the entropy of a perfect crystalline solid is zero.

**Answer: A**

**98.** The heats of combustion of carbon and carbon monoxide are -393.5

and $-283.5 kJmol^{-1}$ respectively. The heat of formation (in kJ) of carbon

monoxide per mole is

A. 110.5

B. 676.5

C. $-676.5$

D. $-110.5$

**Answer: D**

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**99.** A reaction has both $\Delta H$ and $\Delta S$ - ve.The rate of reaction

A. cannot be predicted for change in temperature

B. increases with increase in temperature

C. increases with decrease in temperature

D. remains unaffected by change in temperature.

**Answer: C**

---

**100.** Mixing of $N_2$ and $H_2$ form an ideal gas mixture at roo, temperature in a container.For this process, which of the following statements is true?

A. $\Delta H = 0, \Delta S_{\text{surrounding}} = 0, \Delta S_{\text{system}} = 0$ and $\Delta G = -ve$

B. $\Delta H = 0, \Delta S_{\text{surrounding}} = 0, \Delta S_{\text{system}} > 0$ and $\Delta G = -ve$

C. $\Delta H > 0, \Delta S_{\text{surrounding}} = 0, \Delta S_{\text{system}} > 0$ and $\Delta G = -ve$

D. $\Delta H < 0, \Delta S_{\text{surrounding}} > 0, \Delta S_{\text{system}} < 0$ and $\Delta G = -ve$

**Answer: B**

**101.** Given

$$C_{graphite} + O_2(g) \rightarrow CO_2(g), \Delta_r H^\circ = -393.5 kJmol^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \Delta H^\circ = -285.8 kJmol^{-1}$$

$$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g), \Delta H^\circ = +890.3 kJmol^{-1}$$
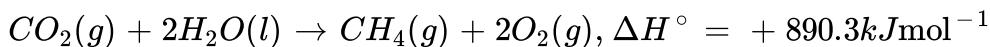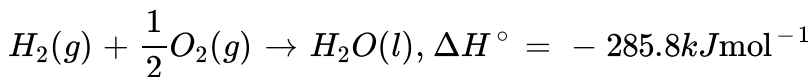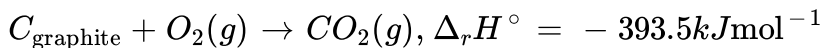
Based on the above thermochemical equations, the value of $\Delta H^\circ$ at 298

K for the reaction

$C_{graphite} + 2H_2(g) \rightarrow CH_4(g)$ will be :
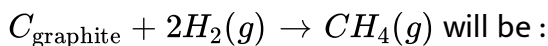
A. $+748 kJ$

B. $+144.0 kJ$

C. $-74.8 kJ$

D. $-144.0 kJ$

**Answer: C**

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**102.** $\Delta U$ is equal to

A. isochoric work

B. isobaric work

C. adiabatic work

D. isothermal work

**Answer: C**

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**103.** What will be the heat change at constant volume for the reaction whose heat change at constant pressure is -560 kcal at $27°C$? The reaction is

$$C_8H_{16} + 12O_2 \rightarrow 8CO_2 + 8H_2O$$
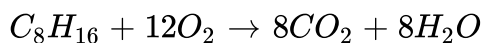
(Given R = 2 cal $mol^{-1}K^{-1}$)

A. $-557600$ calories

B. $442800$ calories

C. $-561800$ calories

D. 368240 calories

**Answer: A**

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**104.** The heat of neutralisation of a strong base and a strong acid is 13.7 kcal. The heat released when 0.6 mole HCl solution is added to 0.25 mole of NaOH is

    A. 3.425 kcal

    B. 8.22 kcal

    C. 11.645 kcal

    D. 13.7 kcal

**Answer: A**

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**105.** During reversible adiabatic process, the pressure of a gas is found to be proportional to the cube of its absolute temperature.The ratio $\dfrac{C_p}{C_v}$ for the gas is

A. $\dfrac{3}{2}$

B. $\dfrac{7}{2}$

C. $\dfrac{5}{3}$

D. $\dfrac{9}{7}$

**Answer: A**

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**106.** One mole of ethanol is produced reacting graphite, $H_2$ and $O_2$ together.The standard enthalpy of formation is $-277.7kJmol^{-1}$ .Calculate the standard enthalpy of the reaction when 4 moles of graphite is involved.

A. $-277.7$

B. $-555.4$

C. $-138.85$

D. $-69.42$

**Answer: B**

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**107.** The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$.Given that heat of combustion of benzene at constant volume is $-3263.9kJmol^{-1}$ at $25°C$, heat of combustion (in $kJmol^{-1}$) of benzene at constant pressure will be $(R = 8.314JK^{-1}mol^{-1})$.

A. 4152.6

B. $-452.46$

C. 3260

D. $-3267.6$

**Answer: D**

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**108.** Given

(i) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \Delta_r H^\circ = xkJ\text{mol}^{-1}$

(ii) $C(\text{graphite}) + \dfrac{1}{2}O_2(g) \rightarrow CO(g) \Delta_r H^\circ = ykJ\text{mol}^{-1}$

(iii) $CO(g) + \dfrac{1}{2}O_2(g) \rightarrow CO_2(g) \Delta_r H^\circ = zkJ\text{mol}^{-1}$
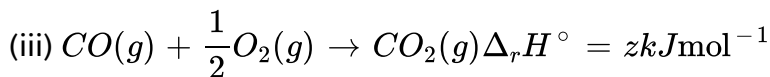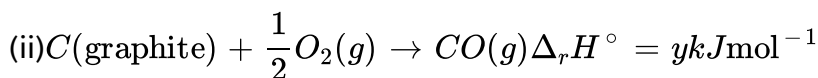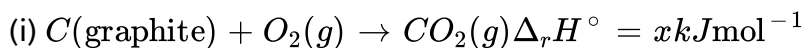
Based on the above thermochemcial equations, find out which one of the following algebraic releationship is correct?

A. z = x + y

B. x = y - z

C. x = y + z

D. y = 2z - x

**Answer: C**

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**109.** The combination of plots which does not represent isothermal expansion of an ideal gas is :

(A)

  A. (A) and (C)

  B. (A) and (D)

  C. (B) and (D)

  D. (B) and (C)

**Answer: C**

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**110.** The process with negative entropy change is

  A. Dissolution of iodine in water

  B. Synthesis of ammonia from $N_2$ and $H_2$

C. Dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$

D. Sublimation of dry ice.

**Answer: B**

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**111.** Read the following statements and choose the correct option :

A. (i) is true and (ii) is true

B. (i) is true and (ii) is false

C. (i) is false and (ii) is false

D. (i) is false and (ii) is true

**Answer: A**

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**112.** The enthalpies of formation of all the elements in their standard states are

    A. zero

    B. unity

    C. less than zero

    D. more than zero

**Answer: A**

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**113.** The heat of neutralisation will be highest in

    A. $HCI + NaOH$

    B. $NH_4OH + H_2SO_4$

    C. $CH_3COOH + NaOH$

    D. $CH_3COOH + NH_4OH$

**Answer: A**

---

114. Based on first law of thermodynamics, which one of the following is correct ?

    A. for an isochoric process, $\Delta U = -q_v$

    B. for an isothermal process, $q = +w$

    C. for an isobaric process, $q_p = \Delta U + w$

    D. for an adiabatic process, $\Delta U = -w$

**Answer: A**

---

115. Ths standard heat of formation of $CH_4$, $CO_2$ and $H_2O_l$ are -76.2, -394.8, and - 285.82 kJ $mol^{-1}$ respectively. Heat of vaporization of water is

$44 kJmol^{-1}$. Calculate the amount of heat evolved when 22.4 L to $CH_4$ kept under normal conditions is oxidized into its gaseous products.

A. 802 kJ

B. 878.4 kJ

C. 702 kJ

D. 788.4 kJ

**Answer: A**

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**116.** The reaction in which $\Delta H > \Delta U$ is .

A. $N_{2g} + O_{2g} \rightarrow 2NO_g$

B. $CaCO_3(s) \rightarrow CaO_s + CO_2$

C. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

D. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O_l$

**Answer: B**

**117.** A gas performs 0.320 kJ work on surroundings and absorbs 120 J of heat from the surroundings.Hence change in internal energy is

A. 120.32 J

B. $-200$ J

C. 400 J

D. 200 J

**Answer: B**

**118.** Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal

gas?

(Assume non-expansion work is zero)

A. Cyclic process: q = -w

B. Adiabatic process: $\Delta U = -w$

C. Ispochoric process : $\Delta U = q$

D. Isothermal process: $q = -w$

**Answer: D**

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**119.** for a diatomic ideal gas in a closed system , which of the following plots does not correctly describe the relation between various thermodynamic quantities ?

A. 

B. 

C. 

D. 

**Answer: D**

---

**120.** The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is :

(Specific heat of water liquid and water vapour are $4.2 kjK^{-1}kg^{-1}$ and $2.0kjK^{-1}kg^{-1}$ , heat of liquid fusion and vapourisation of water are $334kjkg^{-1}$ and $2491kjkg^{-1}$, respectively ). ( $\log 273 = 2.436, \log 373 = 2.572, \log 383 = 2.583$)

A. $7.90kJkg^{-1}K^{-1}$

B. $2.64kJkg^{-1}K^{-1}$

C. $8.49kJkg^{-1}K^{-1}$

D. $9.26kJkg^{-1}K^{-1}$

**Answer: D**

**121.** 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K

If $C_V = 28JK^{-1}mol^{-1}$, calculate $\Delta U$ and $\Delta pV$ for this process. (R = 8.0 $JK^{-1}mol^{-1}$]

A. $\Delta U = 14kJ, \Delta(pV) = 4kJ$

B. $\Delta U = 14kJ, \Delta(pV) = 18kJ$

C. $\Delta U = 2.8kJ, \Delta(pV) = 0.8kJ$

D. $\Delta U = 14kJ, \Delta(pV) = 0.4kJ$

**Answer: A**

**122.** The difference between $\Delta H$ and $\Delta U(\Delta H - \Delta U)$, when the combustion of one mole of heptane (l) is carried out at a temperature T,

is equal to:

A. 3RT

B. $-3RT$

C. $-4RT$

D. $4RT$

**Answer: C**

**123.** An ideal gas undergoes isothermal compression from $5m^3$ to $1m^3$ against a constant external pressure of $4Nm^{-2}$. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J $mol^{-1}K^{-1}$, the temperature of Al increases by

A. $\dfrac{3}{2}K$

B. $\dfrac{2}{3}K$

C. 1 K

D. 2 K

**Answer: B**

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**124.** A process has $\Delta H = 200 \text{ J } mol^{-1}$ and $\Delta S = 40 \text{ JK}^{-1}mol^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous :

A. 5 K

B. 4 K

C. 20 K

D. 12 K

**Answer: A**

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**125.** Among the following, the set of parameters that represents path function is :

(A) q + w (B) q

(C) w (D) H -TS

    A. (A) and (D)

    B. (B), (C) and (D)

    C. (B) and (C)

    D. (A), (B) and (C)

**Answer: C**

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**126.** An ideal gas is allowed to expand from 1L to 10 L against a constant external pressure of 1 bar. The work doen in kJ is:

    A. $-9.0$

    B. $+10.0$

C. $-0.9$

D. $-2.0$

**Answer: C**

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**127.** Two moles of an ideal gas is expanded isothermally and reversibly from 1L to 10 L at 300 K. The enthalpy change (in kJ) for the process is

A. 11.4 kJ

B. $-11.4kJ$

C. $0kJ$

D. $4.8kJ$

**Answer: B**

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**128.** The reaction A to b is not feasible but on changing entropy through a series of steps:



$$\Delta S(A \to C) = 50ev,$$

$$\Delta S(C \to D) = 30ev,$$

$$\Delta S(B \to D) = 20ev.$$

The entropy change for $A \to B$ would be

A. $100eV$

B. $60eV$

C. $-60eV$

D. $-100eV$

**Answer: B**

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**129.** For the process :

$H_2O(l)(1, 373K) \rightarrow H_2O(g)(1, 373K),$ the correct set of thermodynamic parameters is :

A. $\Delta G = 0, \Delta S = +ve$

B. $\Delta G = 0, \Delta S = -ve$

C. $\Delta G = +ve, \Delta S = 0$

D. $\Delta G = -ve, \Delta S = +ve$

**Answer: A**

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**130.** The species which by definition has zero standard molar enthalpy of formation at 298 K is

A. $Br_2(g)$

B. $CI_2(g)$

C. $H_2O(g)$

D. $CH_4(g)$
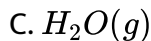
**Answer: B**

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**131.** Using the data provided, calculate the multiple bond energy (

$kJmol^{-1}$) of a $C \equiv C$ bond in $C_2H_2$.That energy is (take the bond enrgy

of a C-H bond as 350 kJ mol$^{-1}$):

$2C(s) + H_2(g) \rightarrow C_2H_2(g), \Delta H = 225kJmol^{-1}$

$2C(s) \rightarrow 2C(g), \Delta H = 1410kJmol^{-1}$

$H_2(g) \rightarrow 2H(g), \Delta H = 330kJmol^{-1}$
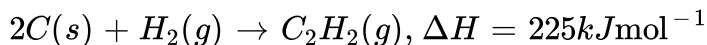
A. 1165

B. 837

C. 865

D. 815

Answer: D

**132.** The standard enthalpies fo formation of $CO_2(g)$, $H_2O(1)$, and glucose (s) at $25°C$ are $-400kJmol^{-1}$, $-300kJmol^-$, and $-1300kJmol^{-1}$, respectively. The standard enthalply of combustion per gram of glucose at $25°C$ is

A. $+2900kJ$

B. $-2900kJ$

C. $-16.11kJ$

D. $+16.11kJ$

Answer: C

**133.** For the process $H_2O(l) \rightarrow H_2O(g)$ at $T = 100°C$ and 1 atmosphere pressure, the correct choice is

A. $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$

B. $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$

C. $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$

D. $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$

**Answer: D**

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**134.** one mole of an ideal gas at 300k in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant presses of 3.0 atm. In this process. The change in entropy of surrroundings $(\Delta S)$ in $J^{-1}$ is

(1 L atm = 101.3 J)

A. 5.763

B. 1.013

C. − 1.013

D. − 5.763

**Answer: C**

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**135.** The standard state Gibbs free energies of formation of ) C(graphite

and C(diamond) at T = 298 K are

$$\Delta_f G^\circ \left[ C(\text{graphite}) \right] = 0 kJmol^{-1}$$

$$\Delta_f G^\circ \left[ C(\text{diamond}) \right] = 2.9 kJmol^{-1}$$

The standard state means that the pressure should be 1 bar, and

substance should be pure at a given temperature. The conversion of

graphite [ ) C(graphite ] to diamond [C(diamond)] reduces its volume by

$2 \times 10^{-6} m^3 mol^{-1}$. If ) C(graphite is converted to C(diamond)

isothermally at T = 298 K, the pressure at which ) C(graphite is in

equilibrium with C(diamond), is

$$\left[\text{Useful information:} 1J = 1kgm^2s^{-2}, 1Pa = 1kgm^{-1}s^{-2}, 1\text{bar} = 10^5 Pa\right]$$

A. 29001 bar

B. 58001 bar

C. 14501 bar

D. 1450 bar

**Answer: C**

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**136.** Which of the following are state functions?

A. Enthalpy

B. Heat

C. Free energy

D. work

**Answer: A::C**

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**137.** In which of the following processes, entropy increases?

A. $I_2(s) \rightarrow I_2(g)$
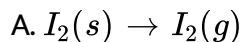
B. Crystallisation of sugar from sugar solution

C. $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

D. $H_2O(l) \Leftrightarrow H_2O(s)$

**Answer: A::C**

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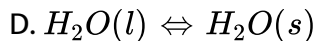
**138.** Which of the following relations is correct

A. $\Delta S = \dfrac{\Delta H - \Delta T}{T}$

B. $\Delta S = \dfrac{q_{irrev}}{T}$

C. $K = \dfrac{e^{\Delta G^\circ}}{RT}$

D. $\left(\dfrac{d(\Delta H)}{dT}\right)_p = \Delta C_p$

**Answer: A::D**

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**139.** Which of the following expression represent the criterion of spontaneity ?

A. $(dS)_{U,V} < 0$

B. $(dG)_{T,P} < 0$

C. $(dU)_{S,V} < 0$

D. $(dH)_{T,P} < 0$

**Answer: B::C**

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**140.** Which of the following are favourable conditions for spontaneous processes?

A. $\Delta H(-)$, $\Delta S(+)$ any magnitude

B. $\Delta H(-)$, $\Delta S(-)\Delta H < T\Delta S$

C. $\Delta H(+)$, $\Delta S(+)\Delta H < T\Delta S$

D. $\Delta H(+)$, $\Delta S(+)\Delta H > T\Delta S$

**Answer: A::C**

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**141.** Among the following, state function(s) is/are

A. internal energy

B. irreversible expansion work

C. reversible expansion work

D. molar enthalpy

**Answer: A::D**


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**142.** A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversibly to ten times of its original volume in two separate experiments.The expansion is carried out at 300 K and at 600 K respectively.Choose the correct option.

A. Work done at 600 K is 20 times the work done at 300 K

B. Work done at 300 K is twice the work done at 600 K

C. Work done at 600 K is twice the work done at 300 K

D. $\Delta U = 0$ in both cases

**Answer: C::D**


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**143.** For an ideal gas, consider only P-V work in going from an initial state X to the final state Z.The final state Z can be reached by either to the two paths shown in the figure.Which of the following choice(s) is (are) correct? [Take $\Delta S$ as change in entropy and W as work done]



A. $\Delta S_{X \to Z} = \Delta S_{X \to Y}$

B. $W_{X \to Z} = W_{X \to Y} + W_{Y \to Z}$

C. $W_{X \to Y \to Z} = W_{X \to Y}$

D. $\Delta S_{X \to Y \to Z} = \Delta S_{X \to Y}$

Answer: A::C

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**144.** The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure.Which of the following

statement(s) is (are) correct?



A. $T_1 = T_2$

B. $T_3 > T_1$

C. $W_{isothermal} > W_{adiabatic}$

D. $\Delta U_{isothermal} > \Delta U_{adiabatic}$

**Answer: A::C::D**

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**145.** Benzene and naphthalene form an ideal solution at room temperature. For this process,the true statement(s) is (are)

A. $\Delta G$ is positive

B. $\Delta S_{system}$ is positive

C. $\Delta S_{surroundings} = 0$

D. $\Delta H = 0$

**Answer: B::C::D**

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**146.** For a spontaneous process, the correct statement(s) is (are)

A. $\Delta G_{system} - (T, P) > 0$

B. $\left(\Delta S_{system}\right) + \left(\Delta S_{\text{surroundings}}\right) > 0$

C. $\left(\Delta G_{\text{system}}\right)_{T,P} < 0$

D. $\left(\Delta U_{\text{system}}\right)_{T,P} > 0$

**Answer: B::C**

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**147.** An ideal gas in a thermally insulated vessel at internal pressure = $P_1$, volume = $V_1$ and absolute temperature = $T_1$ expands irreversibly against zero external pressure, as shown in the diagram.The final internal pressure, volume and absolute temperature of gas are $P_2$, $V_2$ and $T_2$, respectively.For this expansion,



A. $q = 0$

B. $T_2 = T_1$

C. $P_2 V_2 = P_1 V_1$

D. $P_2 P_2^{\gamma} = P_1 V_1^{\gamma}$

**Answer: A::B::C**

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**148.** An ideal gas is expand from $(p_1, V_1, T_1)$ to $(p_2, V_2, T_2)$ under different conditions. The correct statement(s) among the following is

(are):

A. if the expansion is carried out freely, it is simultaneously both

isothermal as well as adiabatic.

B. the work done by the gas is less when it is expanded reversibly from

$V_1$ to $V_2$ under adiabatic conditions as compared to that when

expanded reversibly from $V_1$ to $V_2$ under isothermal conditions.

C. the work done on the gas is maximum when it is compressed

irreversibly from $(p_2, V_2)$ to $(p_1, V_1)$ against constant pressure $p_1$.

D. the change in internal energy of the gas is (i) zero, if it is expanded

reversibly with $T_1 = T_2$, and(ii) positive, if it is expanded reversibly

under adiabatic conditions with $T_1 \neq T_2$.

**Answer: A::B::C**

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**149.** A reversible cycle process for an ideal gas is shown below. Here P, V and T are pressure, volume and temperature, respectively.The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, repsectively.



The correct option(s) is (are)

A. $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$

B. $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

C. $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$
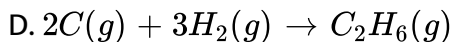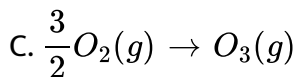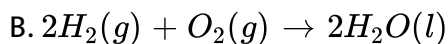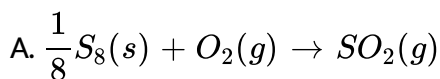
D. $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

**Answer: B::C**

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**150.** Choose the reaction, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation:

A. $\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$

B. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

C. $\frac{3}{2}O_2(g) \rightarrow O_3(g)$

D. $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

**Answer: A::C**

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**151.** Dependence of Spontaneity on Temperature:

For a process to be spontaneous , at constant temperature and pressure ,

there must be decrease in free energy of the system in the direction of

the process , i.e. $\Delta G_{P.T} < 0$. $\Delta G_{P.T} = 0$ implies the equilibrium

condition and $\Delta G_{P.T} > 0$ corresponds to non- spontaneity.

Gibbs- Helmholtz equation relates the free energy change to the enthalpy

and entropy changes of the process as :

$$\Delta G_{P.T} = \Delta H - T\Delta S \qquad\qquad ...(1)$$

The magnitude of $\Delta H$ does not change much with the change in

temperature but the entropy factor $T\Delta S$ change appreciably . Thus, spontaneity of a process depends very much on temperature.

For endothermic process, both $\Delta H$ and $\Delta S$ are positive . The energy factor, the first factor of equation, opposes the spontaneity whereas entorpy factor favours it. At low temperature the favourable factor $T\Delta S$ will be small and may be less than $\Delta H$, $\Delta G$ will have positive value indicated the nonspontaneity of the process. On raising temperature , the factor $T\Delta S$ Increases appreciably and when it exceeds $\Delta H$, $\Delta G$ would become negative and the process would be spontaneous .

For an expthermic process, both $\Delta H$ and $\Delta S$ would be negative . In this case the first factor of eq.1 favours the spontaneity whereas the second factor opposes it. At high temperature , when $T\Delta S > \Delta H$, $\Delta G$ will have positive value, showing thereby the non-spontaneity fo the process . However , on decreasing temperature , the factor $T\Delta S$ decreases rapidly and when $T\Delta S < \Delta H$, $\Delta G$ becomes negative and the process occurs spontaneously. Thus , an exothermic process may be spontaneous at low temperature and non-spontaneous at high temperature.

For the reaction at $25°$ , $X_2O_4(l) \rightarrow 2XO_2(g)$

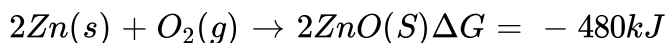$\Delta H = 2.1 Kcal$ and $\Delta S = 20 cal K^{-1}$. The reaction would be

A. $+$, $-$

B. $+$, $+$

C. $-$, $-$

D. $-$, $+$

**Answer: A**

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**152.** The $\Delta G$ values for the following reactions at $800°C$ are

$$S_2(g) + 2O_2(g) \rightarrow 2SO_2(g) \Delta G = -544kJ$$

$$2Zn(s) + S_2(g) \rightarrow 2ZnS(s)\Delta G = -293kJ$$

$$2Zn(s) + O_2(g) \rightarrow 2ZnO(S)\Delta G = -480kJ$$

The $\Delta G$ for the reaction:

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g) \text{ is}$$
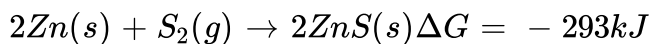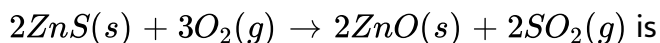
A. $-731kJ$

B. $-773kJ$

C. $-229kJ$

D. $-357kJ$

**Answer: A**

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**153.** For the equilibrium $H_2O(l) \Leftrightarrow H_2O(g)$ at 1 atm and 298 K

A. Standard free energy change is equal to zero ($\Delta G^\circ = 0$)

B. Free energy change is less than zero ($\Delta G < 0$)
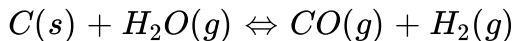
C. Standard free energy change is less than zero ($\Delta G^\circ < 0$)

D. Standard free energy change is greater than zero ($\Delta G^\circ > 0$)

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**154.** For the water gas reaction:

$$C(s) + H_2O(g) \Leftrightarrow CO(g) + H_2(g)$$

the standard Gibbs enegry for the reaction at $1000K$ is $-8.1kJmol^{-1}$.

Calculate its equilibrium constant.

  A. 0.423

  B. 4.23

  C. 264

  D. 4.63

**Answer: C**

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**155.** If $\Delta G^\circ$ is zero for a reaction, then

  A. $\Delta H^\circ = 0$

  B. $\Delta S^\circ = 0$

C. K (equilibrium constant) = 0

D. K(equilibrium constant) = 1

**Answer: D**

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**156.** Which of the following conditions is not favourable for a spontaneous reaction?

A. $\Delta H = + ve, T\Delta S = + ve$ and $T\Delta S > \Delta H$

B. $\Delta H = + ve, T\Delta S = + ve$ and $T\Delta S < \Delta H$

C. $\Delta H = - ve, T\Delta S = + ve$ and $T\Delta S > \Delta H$

D. $\Delta H = - ve, T\Delta S = - ve$ and $T\Delta S < \Delta H$

**Answer: B**

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**157.** Passage II.

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



The pair of isochoric processes among the transformation off states is

    A. K to L and L to M

    B. L to M and N to K

    C. L to M and M to N

    D. M to N and N to K

**Answer: B**

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**158.**

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.

The succeeding operations that enable this transformation of states are

A. heating, cooling, heating, cooling

B. cooling, heating, cooling,heating,

C. heating, cooling, , cooling, heating

D. cooling, heating,heating, cooling

**Answer: C**

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## Competition File (Matching Type Questions)

**1.** Match the enteries of processing given in List - I with the description given in List -II and choose the correct option (a),(b),(c) and (d) given in

code.

List-I | List-II
(P) Isobaric process | (1) process in which driving force is very differen
(Q) Isothermal process | (2) process in which no heat enters or leaves the sy
(R) Adiabatic process | (3) process in which temperature of the system rer
(S) Irreversible process | (4) A process in which pressure of the system is

A. P -4 Q -3, R -1, S-2

B. P-4, Q-3, R-2, S-1

C. P -3, Q-4, R-2, S-1

D. P-3, Q-4,R-1,S-2

**Answer: B**

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**2.** Match the sign of $\Delta H$ and $\Delta S$ given in List - I with the type of reacting

given in List - II and select the correct option.

List-I | List-II
(P) +ve and + ve | (1) Spontaneous at all temperatures.
(Q) -ve and -ve | (2) Non spontaneous at all temperatures.
(R) +ve and -ve | (3) Spontaneous only at low temperature
(S) -ve and +ve | (4) Spontaneous only at high temperature.

A. P-4, Q-2, R-3,S-1

B. P-3, Q-4,R-2, S-1

C. P -3, Q-4, R-1, S-2

D. P-4,Q-3, R-2, S-1

**Answer: D**

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**Competition File (Matrix Matching Type Questions)**

**1.** Match the term given in Column I withthe equation given in Column II

Column I

(A) Enthalpy of formation

(B) Enthalpy of combustion

(C) Enthalpy of solution

(D) Enthalpy of hydration

Column II

$(p)CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_45H_2O$

$(q)CuSO_4(s) + nH_2O(l) \rightarrow CuSO_4(aq)$

$(r)C(s) + O_2(g) \rightarrow CO_2(g)$

$(s)CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

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**2.** Match the follwoing:

Column I

(a)Entropy of vapoursation

(b) K for spontaneous process

(c)Crystalline solid state

(d)$\Delta U$in adiabatic

Column II

(p)decreases

(q)is always positive

(r)lowest entropy

(s)$\dfrac{\Delta H_{vap}}{T_b}$

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**3.** Match the term given in column I with its description in Column II

Column I

(a)Path function

(b)State function

(c)Intensive property

(d)Extensive property

Column II

(p)Heat

(q)Internal energy

(r)Entropy

(s)Specific heat

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**4.** Match the process given in Column - I with the entropy change in Column - II

| Column I | Column II |
|---|---|
| (a) Reversible adiabatic ideal gas compression. | (p) $\Delta S_{surr} = 0$ |
| (b) Reversible isothermal ideal gas expansion. | (q) $\Delta S_{system} = 0$ |
| (c) Adiabatic free expansion $(p_{ext} = 0)$ of an ideal gas | (r) $\Delta S_{surr} > 0$ |
| (d) Irreversible isothermal ideal gas compression. | (s) $\Delta S_{surr} < 0$ |

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**1.** The number of properties which are state functions among the following is :

Enthalpy, entropy, pressure, volume, heat, internal energy, temperature, molar heat capacity, work free energy.

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**2.** The number of intensive properties among the following is

Density, temperature, volume, pressure, enthalpy, entropy, viscosity, force, molar heat capacity, free energy, heat capacity.

**3.** The difference between $C_p$ and $C_v$ for a diatomic gas is nR. The value of

n is

**4.** A tank contains $10^5$ L of water. The amount of energy required to raise

the temperature of water from $15°C$ to $25°C$ is $n \times 10^6$ kJ (assume

specific heat capacity of water $4 J °C^{-1} g^{-1}$).The value of n is

**5.** The change in internal energy when 2.0 mole of an ideal gas at $25°C$

are compressed isothermally and reversibly from 1 bar to 2 bar is

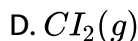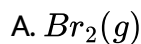**6.** All the energy realesed from the reation $X \rightarrow Y, \Delta_r G^\circ = -193kJmol^{-1}$, is used for oxidizing $M^+$ as $M^+ \rightarrow M^{3+} + 2e^-, E^\circ = -0.25V$. Under standard consistions, the number of moles of $M^+$ oxidized when on e mol of $X$ is converted to $Y$ is $\left[F = 96,500Cmol^{-1}\right]$

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Unit Practice Test

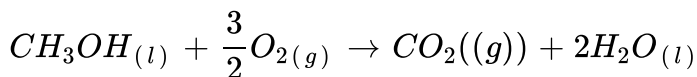**1.** The species which has zero standard molar enthalpy of formation is

A. $Br_2(g)$

B. $CH_4(g)$

C. $CO_2(g)$

D. $CI_2(g)$

**Answer: D**

**2.** In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is :

$$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \rightarrow CO_2((g)) + 2H_2O_{(l)}$$

At $298K$ standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are $-166.2$, $-237.2$ and $-394.4kJmol^{-1}$ respectively. If standard enthalpy of combustion of methanol is $-726kJmol^{-1}$, efficiency of the fuel cell will be :

A. 0.8

B. 0.97

C. 0.9

D. 0.87

**Answer: B**

**3.** The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is $-3263.9kJmol^{-1}$ at $25°C$, heat of combustion (in kJmol$^{-1}$) of benzene at constant pressure will be

(R = 8.314 JK–1 mol–1)

A. 4152.6

B. $-452.46$

C. $3260.0$

D. $-3267.6$

**Answer: A**

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**4.** Assertion: All endothermic reactions which are non-spontaneous at room temperature become spontaneous at high temperatures.

Reason : Endothermic reactions become spontaneous if $\Delta S$ is positive and $T\Delta S > \Delta H$.

A. Assertion and reason both are correct statements and reason is correct explanation for assertion.

B. Assertion and reason both are correct statements but reason is not correct explanantion for assertion.

C. Assertion is correct statement but reason is wrong statement.

D. Assertion is wrong statement but reason is correct statement.

**Answer: B**

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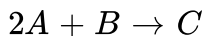**5.** Define Hess's law of constant heat summation.

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**6.** ENTHALPY OF COMBUSTION

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**7.** For the reaction at 300 K,

$2A + B \rightarrow C$

$\Delta H = 450 kJmol^{-1}$ and $\Delta S = 0.2 kJK^{-1}mol^{-1}$. At what temperature will the reaction become spontaneous considering $\Delta H$ and $\Delta S$ to be constant over the temperature range?
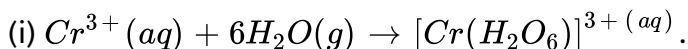
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**8.** Calculate the enthalpy of formation of ethane from the follwong enthalpy of combustion data:

C(s) : - 393.5 kJ, H_(2)(g) : - 285.8 kJ and $C_2H_6(g): - - 1560.0 kJ$

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**9.** What is meant by entropy? Predict whether the following changes involve an increases or decreases of entropy:

(i) $Cr^{3+}(aq) + 6H_2O(g) \rightarrow [Cr(H_2O_6)]^{3+(aq)}$.

(ii) Sublimation of ammonium chloride.

(iii)Crystallization of salt from brine solution.

**10.** At $60°C$, dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

**11.** 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 vaperization at $100°C$. $\Delta_{vap}H^{\ominus}$ for water at 373 K = 40.66 kJ $mol^{-1}$

**12.** Explain the effect of the following on the equilibrium constant.

(i) concentrations of the reactants are doublad (ii) The reaction is reversed

(iii) Catalyst is added to the reaction (iv) Temperature is increased.

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