CHEMISTRY

BOOKS - PRADEEP CHEMISTRY (HINGLISH)

THERMODYNAMICS

33390

1. Calculate $\Delta_r S_m^{\Theta}$ 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 $S_m^{\Theta}(Fe_2O_3) = 87.4 JK^{-1} mol^{-1}$.

Problem 1

1. Express the change in internal energy of a system when

(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?

ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?

(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

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2. The combustion of 1 mole of benzene takes place at 298K and 1 atm. After combustion, $CO_{2(g)}$ and $H_2O_{(l)}$ are produced and 3267.0 KJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^0$ of benene. Standard enthalpies of formation of $CO_{2(g)}$ and $H_2O_{(l)}$ are -393.5 KJ mol^{-1} and - 285.83 KJ mol^{-1} respectively

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3. Calculate the entropy change involved in conversion of one mole (18g) of solid ice at 273K to liquid water at the same temperature (latent heat of fusion $= 6025 J mol^{-1}$)

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4. Enthalpy and entropy changes of reaction are $40.63 kJ mol^{-1}$ and $108.8 JK^{-1} mol^{-1}$, respectively. Predict the feasibility of the reaction at $27^{\circ} C$.

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Problem 2

1. Calculate the internal energy change in each of the following cases :

(i) A system absorbs 5 kJ of heat and does 1 kJ of work.

(ii) 5 kJ of work is done on the system and 1 kJ of heat is given out by the system.

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2. Calculate the enthalpy of formation of methane given that the enthalpies of combustion of methane, graphite and hydrogen are 890.2 KJ, 393.4 KJ and 285.7 KJ mol^{-1} respectively

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3. Entropy change involve in conversation of 1mole of liquid water at $373K$to vapour at the same temperature (latent heat of vaporisation of water=$2.257kJg^{-1}$)

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4. At $0^{\circ}C$ 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 ΔS and ΔG for conversion of ice into liquid water at $0^\circ C$ are:

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Problem 3

1. Calculate the amount of work done in each of the following cases : $-$

(i) One mole of an ideal gas contained in a bulbof 10 litre capacity at 1 bar is allowed to enter into an evacuated bulb of 100 litre capacity.

(ii) One mole of a gas is allowed to expand from a volumeof 1 litre to a volume of 5 litres against the constant external pressure of 1 bar (1 litre bar = 100 J)

Calculate the internal energy change (ΔU) in each case if the process were carrid out adiabatically.

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2. Calculate the heat of formation of KCl from the following data :

$(i) \quad KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l), \quad \Delta H = -57.3kJ$

$(ii) \quad H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \quad \Delta H = -286.2k$

$(iii) \quad \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) + aq \rightarrow HCl(aq), \quad \Delta H = -164.4k$

$(iv) \quad K(s) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) + aq \rightarrow KOH(aq), \quad \Delta H = -487.4k$

$(v) \quad KCl(s) + aq \rightarrow KCl(aq), \quad \Delta H = +18.4kJ$

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3. A heated copper block at $130^\circ C$ loses 340 J of heat to the surroundings which are at room temperature of $32^\circ C$. Calculate

(i) the entropy change of the system (copper block) (ii) the entropy change in the surrounding

(iii) the total entropy change in the universe due to this process

Assume that the temperature of the block and the surroundings remains constant.

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4.

$A + B \rightarrow C + D, \Delta H = -10,000 J mol^{-1}, \Delta S = -33.3 J mol^{-1} K^{-1}$

(i) At what temperature the reaction will occur spontaneously from left to right ?

(ii) At what temperature , the reaction will reverse?

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Problem 4

1. Calculate w, q and ΔU when 0.75 mol of anideal gas expands isothermally and revensibly at $27^{\circ} C$ from a volume of 15L to 25L

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2. $C_2H_4 + CI_2 \rightarrow C_2H_4CI_2$

$\Delta H = -270.6 kJ mol^{-1} K^{-1}, \Delta S = -139 J$

a. Is the reaction favoured by entropy, enthalpy both or none?

b. Find ΔG if $T = 300K$.

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Problem 5

1. Carbon monoxiole is allowed to expand isothermally and reversibly from $10m^3$ to $20m^3$ at 300K and work obtained is 4.754KJ. Calculate the number of moles of carbon monoxide

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Problem 6

1. A $5L$ cylinder contained 10 moles of oxygen gas at $27^\circ C$. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmospheric pressure is $1.0 atm$, calculate the work done by the gas.

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Problem 7

1. Two moles of an ideal gas initially at $27^\circ C$ and one atmospheric pressure are compressed isothermally and reversibly till the final pressure of the gas is 10 atm calculate q, w and Δw for the process

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Problem 8

1. Two litres of an ideal gas at a pressure of 10 atm expands Isothermally into vacuum until its total volume is 10 litres. How muach heat is absorbed and howmuch work is done in the expansion ? What would be the heat absorbed andwork done

(i) if the same expansion takes place against a constant external pressure of 1 atm ?

(ii) if the same expansion takes place to a final volume of 10 litres conducted reversibly?

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Problem 9

1. The heat of combusion of benzene in a bomb calorimeter (i.e constant volume) was found to be $3263.9kJmo1^{-1}$ at $25^{\circ}C$ Calculate the heat of combustion of benzene at constan pressure .

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Problem 10

1. If water vapour is assumed to be a perfect gas, molar enthalpy change for vaporisation of 1 mol of water at 1 bar and $100^{\circ}C$ 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.

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Problem 11

1. 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 $100^{\circ}C$.

$\Delta_{vap}H^{\Theta}$ for water at 373 K = 40.66 kJ mol^{-1}

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Problem 12

1. Find out the internal energy change for the reaction $A(l) \rightarrow A(g)$ at 373 K . Heat of vaporisation is 40.66 kJ $/$ mol and $R = 8.3 Jmol^{-1}K^{-1}$

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Sample Problem 1

1. (a)Calculate the energy needed to raise the temperature of 10.0 g of iron from 25°C to $250^{\circ}C$ 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.

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2. 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?

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3. Calculate enthalpy of formation of methane (CH_4) from the following data :

(i) $C(s) + O_2(g) \rightarrow CO_2(g), \Delta_r H^\circ = -393.5 KJmol^{-1}$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), D\eta_r H^\circ = -285.5 kJmol^{-1}$

(iii)

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l), \Delta_r H^\circ = -890.3 kJmol^{-1}$.

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4. Calculate the ethalpy of combustion of ethylene (g) to form CO_2 (gas) and H_2O (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of CO_2, H_2O and C_2H_4 are $-393.7, \ -241.8 + 52.3$ kJ per mole respectively.

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5. Given the following thermochemical equations :

(i) S(rhombic) $+O_2(g) \rightarrow SO_2(g), \Delta H = \ -297.5kJmol^{-1}$

(ii) S (monoclinic) $+O_2 \rightarrow SO_2(g), \Delta H = \ -300.0kJmol^{-1}$

Calculate ΔH for the transformation of one gram atomof rhombic sulphur into monochlinic sulphur.

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6. Predict in which of the following entropy of the system increases / decreases:

(P) A liquid crystalizes into a solid

(Q) Temperature of a crystalline solid is raised

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

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

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Sample Problem 2

1. $5.6dm^3$ of an unknown gas at $S.T.P$ requires 52.25J of heat to raise its temperature by $10^\circ C$ at constant volume. Calculate C_V, C_P and atomicity of the gas

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2. Calculate the amount of heat evolved when

(i) $500cm^3$ of 0.1 M hydrochloric acid is mixed with $200cm^3$ of 0.2 M sodium hydroxide solution

(ii) $200cm^3$ of0.2 M sulphuric acid is mixed with $400cm^3$ of 0.5 M potassium hydroxide solution.

Assuming that the specific heat of water is $4.18JK^{-1}g^{-1}$ and ignoring the heat absorbed by the container, thermometer, stirrer etc, what would be the rise in temperature in each of the above cases ?

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3. Calculate the enthalpy of formation of carbon monoxide (CO) from the following data

(i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}, \Delta_r H^0 = -393.5 KJ \text{ mole}^{-1}$

(ii) $CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}, \Delta_r H^0 = -283.5 KJ \text{ mole}^{-1}$

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4. Enthalpies of solution of $BaCI_2. 2H_2O$ and $BaCI_2$ are 8.8 and $-20.6 kJmol^{-1}$ respectively.Calculate the heat of hydration of $BaCI_2. 2H_2O$

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5. Predict the sign of entropy change in each of the following :

(i) $H_2($ at 298 K, 1 atm $) \rightarrow H_2$ at 298 K, 10 atm)

(ii) $H_2O($ at 298K, 1 atm $) \rightarrow H_2O$ (at 330K, 1atm)

(iii) $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$

(iv) Crystallization of copper sulphate from its saturated solution.

(v) $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$

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Sample Problem 3

1. Calculate the enthalpy change accompanying the transformation of C(graphite) to C(diamond). Given that the enthalpies of combustion of graphite and diamond are 393.5 and 395.4 KJ respectively

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Sample Problem 4

1. Calculate the enthalpy of hydration of anhydrous copper sulphate $(CuSO_4)$ into hydrated copper sulphate $(CuSO_4 \cdot 5H_2O)$. Given that the enthalpies of solution of anhydrous copper sulphate and hydrated copper sulphate are -66.5 and $+11.7kJmol^{-1}$ respectively.

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Problem

1. Calculate the enthalpy of hydrogenation of ethylene, given that the enthalpy of combustion of ethylene, hydrogen and ethane are -1410.0,-286.2 and -1560.6 kJ mol^{-1} respectively at 298 K

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2. The thermite reaction used ofr welding of metals involves the reaction

$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$

What is ΔH° at $25^\circ C$ for this reaction ? Given that the standard heats of formation of Al_2O_3 and Fe_2O_3 are - 1675.7 kJ and - 828.4 kJ mol^{-1} respectively.

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3. The heat evolved in the combustion of methane is given by the equation :

$CH_4(s) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l), \Delta H = -890.3 kJ mol^{-1}$

(a) How manygrams of methane would be required to produce 445.15 kJ of heat of combustion ?

(b) How many grams of carbon dioxide would beformed when 445.15 kJ of heat is evolved ?

(c) What volume of oxygen at STP would be used in the combustion process (a) or (b) ?

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4. The heat evolved in the combustion of glucose is shown in the equation :

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g), \Delta_c H = -2840 kJ mol^{-1}$

What is the energy requirement for production of 0.36g of glucose by the reverse reaction ?

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5. The heat evolved in the combustion of benzene is given by the equation:

$$C_6H_6(g)+\frac{15}{2}O_2(g)\rightarrow 6CO_2(g)+3H_2O(l), \Delta H=-3264.6kJ\text{mol}^{-1}$$

The heat energy changes when 39 g of C_6H_6 are burnt im an open ontainer will be:

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6. The thermochemical equation for solid and liquid rocket fuel are given below:

$$2AI(s)+1\frac{1}{2}O_2(g)\rightarrow AI_2O_3(s), \Delta H=-1667.8kJ$$

$$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l), \Delta H=-285.9kJ$$

a. If equal masses of aluminium and hydrogen are used, which is a better rocket fuel?

b. Determine ΔH for the reaction

$$AI_2O_3(s) \rightarrow 2AI(s) + 1\frac{1}{2}O_2(g)$$

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7. When $1g$ liquid naphthalene $(C_{10}H_8)$ solidifies, $149J$ of heat is evolved. Calculate the enthalpy of fusion of naphthalene.

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8. If a man takes a diet which giveshim energy equal to 9500 kJ per day and he expends energy in all forms to a total of 12000 kJ per day, what is the change in internal energy per day ? If the energy lost was stored as sucrose (1632kJ per 100 g) , how many days should it take to lose 1 kg ? Ignore the water loss.

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9. Standard vaporisation enthalpy of benzene at its boiling point is 230.8 kJ mol^{-1}. For how long would a 100 W electric heater have to operate to vaporize a 100 g sample of benezene at its boiling temperature ? (power $=$ energy / time , 1 W $= 1Js^{-1}$)

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10. Calculate the bond enthalpy of HCl. Given that the bond enthalpies of H_2 and Cl_2 are $430KJmol^{-1}$ and $242KJmol^{-1}$ respectively and $\Delta_f H^0 HCl$ is $-91KJmol^{-1}$)

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11. 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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12. Calculate the enthalpy change for the reaction $H_2(g) + Br_2 \rightarrow 2HBr(g)$ Give that the bond enthalpies ofH-H,Br-Br and H-Br are435, 192 and 364kJ mol^{-1} respectively.

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13. Propane has the structure $H_3C - CH_2 - CH_3$. Calculate the change in enthalpy for the reaction :

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

Given that average bond enthalpies are :

$C-C$	$C-H$	$C=0$	$O=O$	$O-H$
347	414	714	498	$464kJmol^{-1}$

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14. Calculate the energy of C-Cl bond from the following data :

$CH_4(g) + Cl_2(g) \rightarrow CH_3(g) + HCl(g) + HCl(g), \Delta H = -100.3kJ$

The bond energy of C-H, Cl- Cl and H-Cl bonds are 413, 243 and 431 kJ mol^{-1} respectively.

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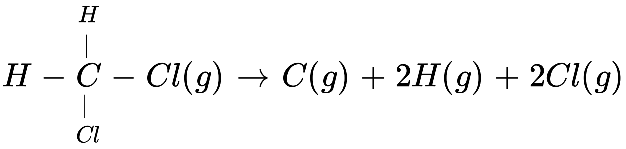
15. Calculate ΔH of the reaction



$$H-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-Cl(g) \rightarrow C(g)+2H(g)+2Cl(g)$$

The average bond energies of C-H bond and C-Cl bond are 416kJ and 325 kJ mol^{-1} respectively.

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16. Calculate the standard free energy change for the reaction,

$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(l)}$. Given that the standard free energies of formation $(\Delta_f G^0)$ for $NH_{3(g)}, NO_{(g)}$ and $H_2O_{(l)}$ are - 16.8, + 86.7 and - 237.2 KJ mol^{-1} respectively. Predict the feasiblity of the above reaction at the standard state.

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17. Calculate ΔG^{Θ} for the conversion of oxygen to ozone, $\left(\frac{3}{2}\right)O_2(g) \Leftrightarrow O_3(g)at298K$, of K_p for this conversion is 2.47×10^{-29}.

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18. Hydrolysis of sucrose gives

$\text{Sucrose}+H_2O \Leftrightarrow \text{Glucose} + \text{Fructose}$

Equilibrium constant K_c for the reaction is 2×10^{13} at $300K$. Calculate $\Delta G^{\ominus}$ at $300K$.

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19. Calculate the equilibrium constant, K for the following reaction at 400K?

$2NOCl_{(g)} \Leftrightarrow 2NO_{(g)} + Cl_{2(g)}$

Given that $\Delta_r H^0 = 80.0KJmol^{-1}$ and $\Delta_r S^0 = 120JK^{-1}mol^{-1}$ at 400 K.

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

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PROBLEMS FOR PRACTICE

1. 500 joule of heat was supplied to a system at constant volume. It resulted in the increase of temperature of the system from $20^\circ C$ to $25^\circ C$. What is the change in internal energy of the system ?

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2. What would be the work done on $/$ by the system if the internal energy of the system falls by the 100 joules even when 200 joules of heat is supplied to it ?

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3. Calculate the work done when 1.0 mol of water at $373K$ vaporises against an atmosheric pressure of $1.0 atm$. Assume ideal gas behaviour.

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4. Two moles of an ideal gas at $2 atm$ and $27^{\circ} C$ is compressed isothermally to one-half of its volume by an external pressure of $4 atm$. Calculate q, w, and ΔU.

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5. The heat of combustion of $CH_4(g)$ at constant volume is measured in a bomb calorimeter at 298.2 K and found to be -885389 J/mol . Find the value of enthalpy change.

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6. The enthalpy change (ΔH) for the reaction

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

is $-92.38kJ$ at $298K$. What is ΔU at $298K$?

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7. The internal energy change (ΔU) for the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ is - 885kJ mol^{-1} at 298 K . What is ΔH at298 K ?

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8. When $NH_4NO_2(s)$ decomposes at373K , it forms $N_2(g)$ and $H_2O(g)$. The ΔH . For the reaction at one atmospheric pressure and 373 K is -223.6 kJ $mol^{-1}$of $NH_4NO_2(s)$ decomposed. What is the value of ΔU for the reaction under the same conditions ? (Given $R = 8.31JK^{-1}mol^{-1}$)

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9. When 0.532g of benzene (C_6H_6), boiling point 353 K, is burnt with excess of oxygen in a constant volume system 22.3 kJ of heat is given out. Calculate ΔH for the combustion process $\left(R = 8.31JK^{-1}mol^{-1}\right)$.

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10. The heat of combustion of naphthalene $(C_{10}H_8(s))$ at constant volume was found to be - 5133 k J mol^{-1} . Calculate the value of enthalpy change.

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11. The molar heat of formation of $NH_4NO_3(s)$ is $-367.5kJ$ and those of $N_2O(g)$ and $H_2O(l)$ are $+81.46kJ$ and $-285.78kJ$ respectively at $25^\circ C$ and 1 atmospheric pressure. Calculate the ΔH and ΔU for the reaction,

$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$

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12. Determine the value of ΔH and ΔU for the reversible isothermal evaporation of 90.0g of water at $100^{\circ} C$.Assume that water vapour behaves as an ideal gas and heat of evaporation of water is $540 cal g^{-} R = 2.0 cal mol^{-1} K^{-1}$.

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13. It is required to raise the temperature of water of a swimming pool from $20^{\circ} C$ to $25^{\circ} C$. The pool holds $10^5 L$ of water . How much energ in joules will be required ? Given that the specific heat of water is 4.184 $JK^{-1} g^{-1}$

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14. Specific heat of an elementary gas is found to be 0.313 J at constant volume. If the molar mass of the gas is 40 g mol^{-1} , what is the atomicity of the gas ?

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PROBLEM FOR PRACTICE

1. A 1.250 g sample of octane (C_8H_{18}) is burned in excess of oxygen in a bomb calorimeter. The temperatre of the calorimeter rises from 294.05 K to 300.78K. If heat capacity of the calorimeter is 8.93kJ/K, find the heat transferred to the calorimeter. Also calculate the enthalpy combustion of the sample of octane.

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2. $20.0g$ 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)

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3. 0.16 g of methane was subjected to combustion at 27° C in a bomb calorimeter. The temperature of calorimeter system (including water) was found to rise by 0.5° C. Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of the calorimeter system is $17.7kJK^{-1}$.

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4. Ethylene on combustion gives carbon dioxide and water. Its heat of combustion is $1410.0kJmol^{-1}$. If the heat of formation of CO_2 and H_2O are $393.3kJ$ and $286.2kJ$, respectively. Calculate the heat of formation of ethylene.

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5. 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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6. Calculate the enthalpy of formation of sucrose $(C_{12}H_{22}O_{11})$ from the following data :

(i) $C_{12}H_{22}O_{11}+12O_2\rightarrow 12CO_2+11H_2O, \Delta H=-5200.7kJmol^{-1}$

(ii) $C+O_2\rightarrow CO_2, \Delta H=-395.5kJmol^{-1}$ (iii)

$H_2+\frac{1}{2}O_2\rightarrow h_2O, \Delta H=-285.8kJmol^{-1}$

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7. Calculate the standard enthalpy of formation of SO_3 at 298 K using the following reactions and enthalpies.

$S_8(s)+8O_2(g)\rightarrow 8SO_2(g), \Delta H^\circ=-2775kJmol^{-1}$

$2SO_2(g)+O_2(g)\rightarrow 2SO_3(g), \Delta H^\circ=-198kJmol^{-1}.$

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8. Calculate the enthalpy of formation of anhydrous aluminium chloride, Al_2Cl_6 from the following data :

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

(ii)

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

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

$Al_2Cl_6(s) + aq \rightarrow Al_2Cl_2(aq), \Delta_r H^\circ = -643.0kJ$

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9. From the following thermochemical equations, calculate the standard enthalpy of formation of HCl(g) .

(A) $H_2(g) \rightarrow 2H(g), \Delta H^0 = +436.0kJmol^{-1}$

$(B)Cl_2(g) \rightarrow 2Cl(g), \Delta H^0 = +242.7kJmol^{-1}$

(C) $HCl(g) \rightarrow H(g) + Cl(g), \Delta H^0 = +431.8kJmol^{-1}$

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10. 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.

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11. The enthalpy of combustion of ethyl alcohol (C_2H_5OH) is 1380.7 kJ mol^{-1}. If the enthalpies of formation of CO_2 and H_2O are 394.5 and 286.6kJ mol^{-1} respectively, calculate the enthalpy of formation of ethyl alcohol.

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12. Calculate the heat of combustion of benzene form the following data:

a. $6C(s)+3H_2(g)\rightarrow C_6H_6(l), \Delta H=49.0kJ$

b. $H_2(g)+1/2O_2(g)\rightarrow H_2O(l), \Delta H=-285.8kJ$

c. $C(s)+O_2(g)\rightarrow CO_2(g), \Delta H=-389.3kJ$

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13. The enthalpies of formation of methane,carbon dioxide and water (liquid) are - 74.8, -393.5 and-286.2 kJ respectively . Calculate the enthalpy of combustion of methane at ordinary temperature.

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14. Calculate the enthalpy of reaction for$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

Given $C(s) + O_2(g) \rightarrow CO_2(g), \Delta H = -393.5 kJ mol^{-1}$

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \Delta H = -110.5 kJ mol^{-1}$

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15. Find the enthalpy of combustion of carbon (graphite) to produce carbon monoxide(g)on the basis of data given below: C (graphite) $+O_2(g) \rightarrow CO_2(g) + 393.4 kJ mol^{-1}$

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) + 283.0 kJ mol^{-1}$

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16. 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:

(i) $2B(s) + \left(\frac{3}{2}\right)O_2(g) \rightarrow B_2O_3(s), \Delta H = 01273kJ/mol$

(ii) $H_2(g) + \left(\frac{1}{2}\right)O_2(g) \rightarrow H_2O(l), \Delta H = -286kJ/mol$

(iii) $H_2O(l) \rightarrow H_2O(g)\Delta H = 44kJ/mol$

(iv) $2B(s) + 3H_2(G) \rightarrow B_2H_6(g), \Delta H = 36kJ/mol$

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17. The enthalpies of combustion of graphite and diamond are 393.5 kJ and 395.4 kJ respectively. Calculate the enthalp change accompanying the transformation of 1 mole of graphite into diamond.

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18. There are two crystalline forms of PbO , one is yellow and the other isred. The standard enthalpies of formation of these twoforms are - 217.3 and -219.0 kJ per mole respectively. Calculate the enthalpy change for the solid - solid phase transition.

PbO(yellow) $\rightarrow$ PbO (red)

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19. 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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20. 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 : $C(s) + H_2O(g) \to CO(g) + H_2(g)$.

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21. Chloroform is passed from methane according to the reaction :

$CH_4(g) + 3Cl_2(g) \to CHCl_3(l) + 3HCl(g)$

Calculate ΔH for the reaction given that enthalpies of formation of HCl(g), $CH_4(g)$ and $CHCl_3(g)$ are - 92.0 ,-74.9 and -134.3kJ per mole respectively.

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22. Calculate the enthalpy of reaction $(\Delta H^\circ)$when ammonia is oxidized :

$4NH_3(g) + 5O_2(g) \to 6H_2O(g) + 4NO(g)$

Standard enthalpies of formation $(\Delta_f H^\circ)$ at $25^\circ C$for$NH_3(g), H_2O(g)$ and $NO(g)$ are - 46.2, -241.8 and $+90.4kJ /$ mole respectively.

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23. The enthalpy of formation of $Fe_2O_3(s)$ is $-824.2kJ\text{mol}^{-1}$.Calculate the enthalpy change for the reaction :

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

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24. The standard ethelpy of combustion at $25^\circ C$ of hydrogen, cyclohexene (C_6H_{10}), and cyclohexane (C_6H_{12}) are $-241, \ -3800$, and $-3920kJmol^{-1}$ repectively. Calculate the heat of hydrogenation of cyclohexane.

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25. Calculate ΔH for the reaction : $2Li(s) + 2H_2O(l) \rightarrow 2Li^+(aq) + 2OH^-(aq) + H_2(g)$

Given that the standard enthalpies of formation of $Li^+(aq), OH^-(aq)$

and $H_2O(l)$ are - 278.5, - 228.9 and - 285.8 kJ mol^{-} respectively (all at 298 K)

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26. The molar heat of formation of $NH_4NO_3(s)$ is $-367.5kJ$ and those of $N_2O(g)$ and $H_2O(l)$ are $+81.46kJ$ and $-285.78kJ$ respectively at $25^\circ C$ and 1 atmospheric pressure. Calculate the ΔH and ΔU for the reaction,

$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$

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27. Which is a good fuel CH_4 orC_2H_6 ?

The standard enthalpy of formation of CH_4, C_2H_6, CO_2 and H_2O are $-74.8, -84.6, -393.5$ and $-286kJmol^{-1}$ respectively.

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28. Given that:

i. $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g), \Delta H = -393.7kJ$

ii. $C(\text{diamond}) \rightarrow C(\text{graphite}), \Delta H = -2.1kJ$

a. Calculate ΔH for burning of diamond of CO_2.

b. Calculate the quantity of graphite that must be burnt to evolve $5000kJ$ of heat.

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29. Compare quantity of heat produced by the combustion of 1.0 g glucose $(C_6H_{12}O_6)$ with that produced by 1.0g sucrose $(C_{12}H_{22}O_{11})$. Given that the standard heats of formation of CO_2, H_2O glucose and sucrose are $-393.5, -285.9, -1260$ and $-2221kJmol^{-1}$ respectively.

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30. Calculate the enthalpy change for the reaction between CO_2 and H_2O to produce one mole of glucose $(C_6H_{12}O_6)$. What would be enthalpy change for the production of 18 g of glucose ? The enthalpy of combustion of glucose is $2840 kJ mol^{-1}$.

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31. a. A cylinder of gas is assumed to contain $11.2 kg$ of butane. If a normal family needs $20000 kJ$ of energy per day for cooking, how long will the cylinder last? Given that the heat of combustion of butane is $2658 kJ mol^{-1}$.

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?

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32. An average personneeds about 10,000 kJ per day. How much carbohydrates (in mass) will he haveto consume, assuming that all his energy needs are met only by carbohydrates in the form glucose ? Given that the heat of combustion of glucose is 2900 kJ mol^{-1}

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33. Red phosphorus reacts with liquid bromine in an exothermic reaction

$2P(s) + 3Br_2(l) \rightarrow PBr_3(g), \Delta_r H^\circ = -243kJ$

Calculated the enthalpy change when $2.63g$ of phosphorus reacts with an excess of bromine in this way.

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34. Calculate the enthalpy change when $2.38g$ of carbon monoxide (CO) vaporise at its normal boiling point.

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35. Which is a good fuel CH_4 orC_2H_6 ?

The standard enthalpy of formation of CH_4, C_2H_6, CO_2 and H_2O are $-74.8, \ -84.6, \ -393.5$ and $-286kJmol^{-1}$ respectively.

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36. Standard heat of formation of CH_4, CO_2 and $H_2O_{(g)}$ are $-76.2, \ -394.8$ and $-241.6kJmol^{-1}$ respectively. Calculate the amount of heat evolved by burning $1m^3$ of CH_4 measured under normal conditions.

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37. A gas fired power plant burns methane, $CH_4(g)$ for which standard enthalpy of combustion is -890 kJ mol^{-1}. How many moles of CO_2 gas are produced for every 1.0 MJ (mega joule) of energy produced by it ?

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38. Find the enthalpy of formation of hydrogen flouride on the basis of following data:

Bond energy of $H - H$ bond $= 434 kJ mol^{-1}$

Bond energy of $F - F$ bond $= 158 kJ mol^{-1}$

Bond enegry of $H - F$ bond $= 565 kJ mol^{-1}$

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39. Calculate the enthalpy change for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$

Given that the bond energies of H-H,I-I and H-I are433, 151 and 299 $kJ mol^{-1}$ respectively.

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40. Calculate the enthalpy of formation of water, given that the bond energies of $H - H, O = O$ and $O - H$ bond are $433 kJ mol^{-1}$, $492 kJ mol^{-1}$, and $464 kJ mol^{-1}$, respectively.

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41. From the following data at $25^{\circ} C$, calculate the bond energy of O – H bond:

(i) $H_2(g) \rightarrow 2H(g), \Delta H_1 = 104.2 kcal$

(ii) $O_2(g) \rightarrow 2O(g), \Delta H_2 = 118.4 kcal$

(iii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g), \Delta H_3 = -57.8 kcal$

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42. Calculate the enthalpy of hydrogenation of $C_2H_2(g)$ to $C_2H_4(g)$.

(Given bond energies: $C - H = 414.0 kJ mol^{-1}$,

$C \equiv C = 827.6 kJ mol^{-1}$,

$C = C = 606.0 kJ mol^{-1}$,

$H - H = 430.5 kJ mol^{-1})$

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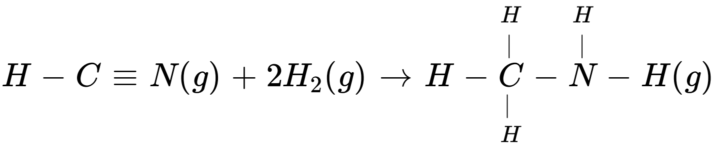
43. ΔH for the reaction



$$H-C\equiv N(g)+2H_2(g)\rightarrow H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{N}-H(g)$$

is $-150kJ$. Calculate the bond energy of $C\equiv N$ bond.

[Given bond energies of $C-H=414kJmol^{-1}$, $H-H=435kJmol^{-1}$, $C-N=293kJmol^{-1}$, $N-H=396kJmol^{-1}$]

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44. 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.

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45. Calculate ΔH° for the reaction

$CH_2 = CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

Given that the average bond energies of the different bonds are :

Bond	$C-H$	$O=O$	$C=O$	$O-H$	$C=C$
Bond energy $(kJmol^{-1})$	414	499	724	460	619

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46. Calculate enthalpy change of the following reaction :

$H_2C = CH_{2(g)} + H_{2(g)} \rightarrow H_3C - CH_{3(g)}$

The bond energy of $C-H, C-C, C=C, H-H$ are $414, 347, 615$ and $435kJmol^{-1}$ respectively.

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

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48. Calculate the temperature in centrigrade when vaporisation of water in equilibrium at one atmospheric pressure (Enthalpy of vaporisation $= 40.63 \times 10^3 Jmol^{-1}, \Delta_{vap}S = 108.8JK^{-1}mol^{-1})$

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49. Enthalpy change $(\Delta_{vap}H)$ for the transition of liquid water to steam at $100^\circ C$ is$40.8kJmol^{-1}$. Calculate the entropy change for the process.

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50. Ethanol boils at $78.4^\circ C$ and the enthalpy of vaporisation of ethanol is $42.4kJmol^{-1}$. Calculate the entropy of vaporisation of ethanol.

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51. What is entropy change for the conversion of one gram of ice to water at 273 K and one atmospheric pressure?

$(\Delta H_{\text{fusion}} = 6.025 kJ \quad mol^{-1})$

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52. The entropy change for the vaporisation of water is 109 $JK^{-1}mol^{-1}$. Calculate the enthalpy change for the vaporisation of water at 373K.

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53. Calculate the entropy change for the conversion of2 moles of liquid water at 373K to vapours , if Δ_{vap} H is $37.3 kJmol^{-1}$.

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54. The enthalpy of vaporisation of benzene (C_6H_6) is $30.8 kJ mol^{-1}$ at its boiling point $(80.1^\circ C)$. Calculate the entropy change in going from:

a. liquid to vapour and

b. vapour to liquid at $80.1^\circ C$.

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55. 10 kg of cold water at $2^\circ C$ absorbs 50J of heat from the surrounding which were at a temperature of$37^\circ C$. What is the entropy change of (i) the system (ii) the surroundings (iii) the universe ? Assume the change in temperature of the water and the surroundings to be negligible.

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56. The enthalpy and entropy changes for the reaction C(s) diamond $+O_2 \rightarrow CO_2(g)$ at $25^\circ C$ and 1 atm. Are -393.4 kJ mol^{-1} and 0.006 $kJ mol^{-1} K^{-1}$ respectively . Is the conversion of diamond to CO_2 at room temperature a spontaneous process ?

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57. ΔH and ΔS for the reaction:

$Ag_2O(s) \rightarrow 2Ag(s) + (1/2)O_2(g)$

are $30.56 kJ mol^{-1}$ and $66.0 JJK^{-1} mol^{-1}$ 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.

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58. ΔH and ΔS for the system $H_2O(l) \Leftrightarrow H_2O(g)$ at $1 atm$ are $40.63 kJ mol^{-1}$and $108.8 JK^{-1} mol^{-1}$, respectively. Calculate the temperature at which the rates of forward and backward reactions will be the same. Predict the sign of free enegy for this transformation above this temperature.

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59. In the reaction $A^{+} + B \to A + B^{+}$, there is no entropy change. Enthalpy change, ΔH equals 22 kJ mol^{-1} of A^{+}. Calculate the ΔG for the reaction . Under what condition free energy change will have negative value ?

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60. Calculate the free energy change in dissolving one mole of sodium chloride at $25^{\circ}C$. Lattic energy $= +777.8kJmol^{-1}$. Hydration energy of $NaCl = -774.1kJmol^{-1}$ and ΔS at $25^{\circ}C = 0.043kJK^{-1}mol^{-1}$

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61. The following data is known about the melting of KCl:

$\Delta H = 7.25kJ \quad mol^{1}$ and $\Delta S = +0.007JK^{-1} \quad mol^{-1}$ Calcualte its melting point.

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62. The free enegry changes for the two reactions given below are

a. $SO_2(g) + CI_2(g) \rightarrow SO_2CI_2(g), \Delta G = -2270 cal$

b. $S(Rhom) + O_2(g) + CI_2(g) \rightarrow SO_2CI_2(g), \Delta G = -74060 cal$

Find ΔG for the reaction $S(Rhom) + O_2(g) \rightarrow SO_2(g)$

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63. 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, ΔH and ΔS at $25^\circ C$ are $108.4 kJ mol^{-1}$ and $190 JK^{-1} mol^{-1}$ respectively.

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64. For the reaction $: 2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, the enthalpy and entropy changes are - 113.0 kJ mol^{-1} and $-145 JK^{-1} mol^{-1}$ respectively. Find the temperature below which this reaction is spontaneous.

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65. For a hypothetical reaction , $X \rightarrow Y$, the enthalpy and entropy changes are 46.3 $kJmol^{-1}$ and $108.80JK^{-1}mol^{-1}$ respectively. Find the temperature. Find the temperature above which this reaction is spontaneous

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66. The standard free energy change for a reaction is -212.3 kJ mol^{-1}. If the enthalpy change of the reaction is $-216kJmol^{-1}$, calculate the entropy change for the reaction.

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67. For the reaction $N_2(g)+3H_2(g) \rightarrow 2NH_2(g), \Delta H = -95.4Kj$ and $\Delta S = -198.300JK^{-1}$. Calculate the temperature in centrigrade at which it attains equilibrium.

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68. A chemist claims that the following reaction is feasible at 298 K

$SF_6(g) + 8HI(g) \rightarrow H_2S(g) + 6HF(g) + 4I_2(g)$

Verify his claim . Given that ΔG_f° for $SF_6(g)$, $HI(g)$, $H_2S(g)$ and $HF(g)$ are - 991.61, 1.30, -33.01 and -270.73kJ mol^{-1} respectively.

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69. Calculate the standard free energy change for the reaction : $Fe_2O_3(s) + 4H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$ Given that the standard free energies of formation ofFe_2O_3 and H_2O are - 741.0 and -237.2kJ mol^{-1} respectively.

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70. A chemist claims that the following reaction is feasible at 298 K

$SF_6(g) + 8HI(g) \rightarrow H_2S(g) + 6HF(g) + 4I_2(g)$

Verify his claim . Given that ΔG_f° for $SF_6(g), HI(g), H_2S(g)$ and $HF(g)$ are - 991.61, 1.30, -33.01 and -270.73kJ mol^{-1} respectively.

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71. The value of K_p for the water gas reaction, $CO + H_2O \Leftrightarrow CO_2 + H_2$ is 1.06×10^5 at $25^\circ C$. Calculate the standard free energy change for the reaction at $25^\circ C$.

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72. Calculate the equilibrium constant for the reaction : $NO(g) + \frac{1}{2}O_2(g) \Leftrightarrow NO_2(g)$

Given,

$\Delta_f H^\circ at298K : NO(g) = 90.4kJ\text{mol}^{-1}, NO_2(g) = 33.8kJ\text{mol}^{-1}$ and ΔS° at $298K = -70.8JK^{-1}\text{mol}^{-1}, R = 8.31JK^{-1}\text{mol}^{-1}$.

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73. Calculate the standard entropy change for a reaction $X \leftrightarrow Y$, If the value of $\Delta H^\circ = 28.40 kJ$ and equilibrium constant is 1.8×10^{-7} at 298 K.

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

$$\underset{\text{Acetylene}}{3HC \equiv CH} \Leftrightarrow \underset{\text{Benzene}}{C_6H_6(g)}$$

Assuming ideal behaviour

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

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

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

Can the reaction be recommended for the synthesis of benzene?

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75. 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 $-13.6 kJ \text{mol}^{-1}$

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76. Calculate the standard free energy change for the reaction :

$H_2(g) + I_2(g) \rightarrow 2HI(g) \Delta H^\circ = 51.9 kJ \text{mol}^{-1}$ Given :

$S^\circ(H_2) = 130.6 JK^{-1} \text{mol}^{-1}$

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

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77. Calculate the standard entropy change for the following reaction :

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ at 298 K

Given $S^{\circ}_{H_2} = 131 JK^{\circ} mol^{-1}, S^{\circ}_{Cl_2} = 223 JK^{-1} mol^{-1}$ and $S^{\circ}_{HCl} = 187 JK^{-1} mol^{-1}$

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78. 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 : $S^0_m[C_3H_8(g)] = 270.2 JK^{-1}\text{mol}^{-1}$

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

and $S^0_m[H_2(g)] = 130.7 JK^{-1}\text{mol}^{-1}$.

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79. For oxidation of iron.

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

entropy change is $-549.4 JK^{-1} mol^{-1}$ at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous?

$\left(\Delta_r H^{\ominus}\right.$ for this reaction is $-1648 \times 10^3 J \text{mol}^{-1})$

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CURIOSITY QUESTIONS

1. Can we convert graphite into diamond ? Which one is more stable and why ?

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2. Which reaction is a source of energy in our body ?

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3. NaCl crystals require energy (called lattice energy) to break into ions. Then why NaCl is soluble in water ?

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4. If we mix H_2 and O_2, they do not combine to form H_2O, is the reaction spontaneous or non-spontaneous ? Give reason.

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ADVANCED PROBLEMS (FOR COMPETITIONS)

1. In a gobar gas plant, gobar gas in obtained by bacterial fermentation of animal refuse. The main combustible gas present in the gobar is found to be methane $(80\%$ by weight) whose heat of combustion is 809 $kJmol^{-1})$. How much gobar gas would have to produced per day for a village of 100 families, if the average consumption of a family is 20,000kJ per day to meet all its energy requirements .

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2. In an ovan , due to insufficient supply of oxygen, 60% of the carbon is converted to carbon dioxide wehreas the remaining 40% is converted into carbon monoxide. If the heat of combustion of carbon to $CO_2$is $394kJmol^{-1}$ while that of its oxidation to CO is 111 kJ mol^{-1}, calculate the total heat produced in the oven by burning 10 kg of coal containing 80% carbon by weight .Also calculate the efficiency of the oven.

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3. (a) A 1000 watt hour is kept on in a room whose dimensions are $5m \times 5m \times 3m$. Howmuch temperature of the room will rise after half an hour? Given the following data :

Heat capacity ofair at room temperature and 1 atm $= 0.71Jg^{-1}K^{-1}$

Density ofair $= 1.22 \times 10^{-3}gmL^{-1}$

(b) How much temperature of the room willrise if 25% heat is lost by radiation ?

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4. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value per cm^3 of the mixture. Heats of formation and densities are as follows:

$H_{f(Al_2O_3)} = -399kcal \quad mol^{-1}, H_{f(Fe_2O_3)} = -199kcal \quad mol^{-1}$

ltbr. Density of $Fe_2O_3 = 5.2g/cm^3, \quad \text{Density of} \quad Al = 2.7g/cm^3$

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5. A gas mixture of $3.67L$ of ethylene and methane on complete combustion at $25^{\circ}C$ 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 $-891kJmol^{-1}$, respectively, at $25^{\circ}C$.

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6. In order to get maximum calorific output a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as required theoretically for complete combustion of fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane C_4H_{10}. In order to get some calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion etc., are the same for both fuels and that gases behave ideally. Heals of combustion, $CH_4 = -809kJ/\text{mol}, C_4H_{10} = -2878$ kJ/mol.

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7. A sample of argon gas at $1atm$ pressure and $27^\circ C$ expands reversibly and adiabatically from $1.25dm^3$ to $2.50dm^3$. Calculate the enthalpy change in this process. C_{vm} for orgon is $12.48JK^{-1}mol^{-1}$.

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8. $1mol$ of an ideal gas undergoes reversible isothermal expansion form an initial volume V_1 to a final volume $10V_1$ and does $10kJ$ of work. The initial pressure was $1 \times 10^7 Pa$.

a. Calculate V_2.

b. If there were $2mol$ of gas, what must its temperature have been?

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9. There is $1mol$ liquid (molar volume $100ml$) in an adiabatic container initial, pressure being 1 bar Now the pressure is steeply increased to 100 bar, and the volume decreased by $1ml$ under constant pressure of 100 bar. Calculate ΔH and ΔE. [Given $1\text{bar} = 10^5 N/m^2$]

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10. For the reaction: $N_2O_4(g) \Leftrightarrow 2NO_2(g)$

(i) In a mixture of $5molNO_2$ and 5 mol N_2O_4 and pressure of 20 bar. Calculate the value of ΔG for the reaction. Given $\Delta G_f^\circ(NO_2) = 50$ KJ/mol, $\Delta G_f^\circ((N_2O_4) = 100$ KJ/mol and T=298 K. (ii) Predict the direction in which the reaction will shift, in order to attain equilibrium

[Given at $T = 298K, 2.303\text{RT} = 5.7$KJ/mol.]

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11. Calcualte the work done when 11.2 g of iron dissolves in hydrochloric acid in (i) a closed vessel (ii) an open beaker at $25^{\circ} C$ (Atomic meass of $Fe = 56u)$

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12. It is planned to carry the reaction

$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$

at 1273K and 1 bar

(a) Is this reaction spontaneous at this temperature and pressure ?

(b) Calculate the value of

(i) K_p at 1273 K for the reaction and

(ii) partial pressure of CO_2 at equilibrium

Given $\Delta_f H^{\circ}$ values $(kJmol^{-1})$:

$CaCO_3(s) = -1206.9, CaO(s) = -635.1, CO_2(g) = -393.5$

S° value $(JK^{-1}mol^{-1})$

$CaCO_3(s) = 92.9, CaO(s) = 39.8, CO_2(g) = 213.7.$

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13. A chemist while studying the properties of gaseous CCl_2F_2, a chlorofluorocarbon refrigerant, cooled a 1.25 g sample at constant atmospheric prssure of 1.0 atm from 320 K to 293 K . During cooling the sample volume decreased from 274 to 248 mL. Calculate ΔH and ΔU for the chlorofluorocaron for this process. For $CCl_2F_2, C_p = 80.7J/(molK)$.

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14. When 10 g of anhydrous $CaCl_3$ is dissolved in 200 g of water, the temperature of the solution rises by $7.7^{\circ}C$. Calculate the heat of hydration of $CaCl_2$ to $CaCl_2.\ 6H_2O$. Given that the heat of dissolution of $CaCl_2.\ 6H_2O$ is $19.08kJmol^{-1}$. Assume specific heat of the solution to be same as that of water, i.e., $4.184Jg^{-1}K^{-1}$

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15. Calculate the entropy change when $1kg$ of water is heated from $27^\circ C$ to $200^\circ C$ forming supper heated steam under constant pressure. Given specific heat of water $= 4180 JKg^{-1}K^{-1}$and specific heat of steam $= 1670 + 0.49 T Jkg^{-1}K^{-1}$ and latent heat of vaporisation $= 23 \times 10^5 Jkg^{-1}$.

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16. The lattice energy of NaCl is 180 kcal / mol . The dissociation of the solid in water in the form of ioins is endothermicto the extent of 1 kcal / mol.If the solvation energies ofNa^+ and Cl^- ions are in theratesof$6 : 5$, calculate the enthalpy of hydration of Na^+ ions.

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17. An ideal gas has a molar heat capacity at constant pressure of $Cp = 2.5R$. The gas is kept in a closed vessel of volume $0.0083m^3$, at a temperature of $300K$ and a pressure of $1.6 \times 10^6 Nm^{-2}$. An amount

$2.49 \times 10^4 J$ of heat energy is supplied to the gas. Calculate the final temperature and pressure of the gas.

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18. A room of $10m \times 15m \times 4m$ dimenstion having perfectly insulated walls, ceiling and floor has 60 students seated inside. The air inside the room is at $25^\circ C$ and 1 atm pressure. If each student loses 200 joules of heat in one second, calculate the rise in temperature noticedin 20 minutes (Neglect loss of air to the outside as temperature is raised and C_p for air $= \frac{7}{2}R \Big)$.

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19. In a measurement of quantum efficiency of photosynthesis in gree plants , it was found that 8 quanta of red light of 6850 Å were needed to evolve 1 moleculeof CO_2. The average energy storage in the photosynthesis process is 112 kcal $/$ mol O_2 evolved. Calculatethe percent efficiency of energy conversion in this experiment.

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20. 1.2g of Mg atoms in vapour phase absorb $50.0kJ$ of energy to convert Mg atoms into Mg ions. The energy absorbed is needed for the following changes :

$Mg(g) \rightarrow Mg^{+}(g) + e^{-}, \Delta H = 750kJmol^{-1}$

$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}, \Delta H = 1450kJmol^{-1}$

Calculate the percentage of Mg^{+} and Mg^{2+} ions in the final mixture.

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TEST YOUR GRIP(MULTIPLE CHOICE QUESTIONS)

1. Which one of the following pairs does not represent example for intensive property ?

A. Temperature and density

B. Pressure and molar volume

C. Molar heat capacity and density

D. Heat capacity and enthalpy

Answer: D

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2. One mole of an ideal gas at $300K$ is expanded isothermally from an inital volume of 1 litre to 10 litres. The ΔE for this process is $\left(R = 2calmol^{-1}K^{-1}\right)$

A. 16.3cal

B. zero

C. 138.1 cal

D. 9 lit atm.

Answer: b

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3. Which of the following are not state functions?

(I) $q + w$

(II)q

(III) w

(IV) $H - TS$

A. (I) and (IV)

B. (II), (III) and (IV)

C. (I),(II) and (III)

D. (II) and (III)

Answer: d

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4. 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 $30^{\circ} C$ to $50^{\circ} C$ is

A. 1.51kJ

B. 0.5 kJ

C. 1.0 kJ

D. 2.05 Kj

Answer: A::C::D

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5. Which of the following reactions is defines $\Delta_f H^{\Theta}$?

A. $C_{\text{diamond}} + O_2(g) \rightarrow CO_2(g)$

B. $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \rightarrow HF(g)$

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

D. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

Answer: B

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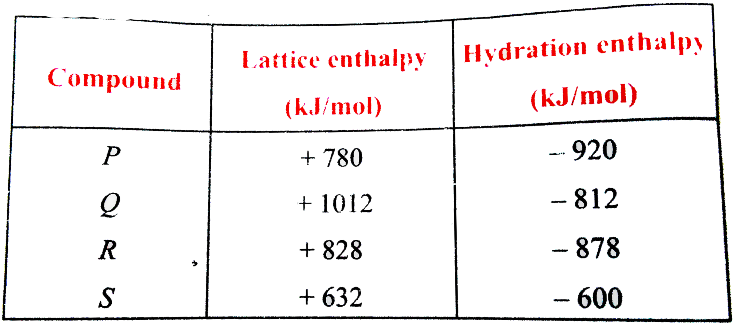
6. The lattice enthalpy and hydration enthalpy of four compounds are given below:



Compound	Lattice enthalpy (kJ/mol)	Hydration enthalpy (kJ/mol)
P	+ 780	− 920
Q	+ 1012	− 812
R	+ 828	− 878
S	+ 632	− 600

the pair of compounds which is soluble in water is:

A. P and Q

B. Q and R

C. R and S

D. P and R

Answer: d

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7. The standard enthalpies of formation of $A(NH_3), B(CO_2), C(HI)$ and $D(SO_2)$ are respectively -46.19,-393.4, +24.94 and -296.9 kJ mol^{-1}. The increasing order of their stability is

A. $B < D < A < C$

B. $C < A < D < B$

C. $D < B < C < A$

D. $A < C < D < B$

Answer: b

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8. The species which by definition has zero standard molar enthalpy of formation at 298 K is

A. $Br_2(g)$

B. $Cl_2(g)$

C. $H_2O(g)$

D. $CH_4(g)$

Answer: b

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9. Thermodynamically the most stable form of carbon is

A. diamond

B. graphite

C. fullerences

D. coal

Answer: b

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10. The sublimation energy of I_2 (solid) is 57.3 KJ/mole and enthalpy of fusion is 15.5 KJ/mole. The enthalpy of vapourisation of I_2 is

A. 41.8 kJ $/$ mol

B. $-41.8kJ/$ mol

C. 72.8 kJ$/$ mol

D. $-72.8kJ/$mol

Answer: a

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11. Given that $C+O_2 \rightarrow CO_2,\ \Delta H^\circ = -xkJ$

$2CO+O_2 \rightarrow 2CO_2, \Delta H^\circ = -ykJ$

What is heat of formation of CO?

A. $y-2x$

B. $\dfrac{2x-y}{2}$

C. $\dfrac{y-2x}{2}$

D. $2x-y$

Answer: c

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12. The bond energies of $H--H$, $Br--Br$ and $H--Br$ are $433,\ ,192$ and $364KJmol^{-1}$ respectively. The ΔH° for the reaction $H_2(g)+Br_2(g)\rightarrow 2HBr(g)$ is

A. $-261kJ$

B. $+103kJ$

C. $+261kJ$

D. $-103kJ$

Answer: d

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13. Predict the sign of ΔS° for the following reaction :

$2H_2S(g)+3O_2(g)\rightarrow 2H_2O(g)+2SO_2(g)$

A. $+ve$

B. $-ve$

C. zero

D. cannot be predicted

Answer: b

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14. Which one of the following demonstrates a decrease in entropy ?

A. Dissolving a solid into solution

B. An expanding universe

C. Burning a log in a fire place

D. Raking up leaves into a trash bag

Answer: D

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15. If the enthalpy change for the transition of liquid water to steam is $30kJmol^{-1}$ at $27^{\circ}C$, the entropy change for the process would be

A. $100Jmol^{-1}K^{-1}$

B. $10Jmol^{-1}K^{-1}$

C. $1.0Jmol^{-1}K^{-1}$

D. $0.1Jmol^{-1}K^{-1}$

Answer: a

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16. A catalyst

A. increase the free energy change of the reaction

B. decreases the free energy change of the reaction

C. neither increases nor decreases the free energy of the reaction

D. may increases or decrease depending upon the nature of the catalyst

Answer: c

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17. A process is taking place at constant temperature and pressure. Then

A. $\Delta H = \Delta E$

B. $\Delta H = T \Delta S$

C. $\Delta H = 0$

D. $\Delta S = 0$

Answer: b

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18. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and the change in entropy (dS) satisfy the criteria

A. $(dS)_{V,E} > 0, (dG)_{T,P} < 0$

B. $(dS)_{V,E} = 0, (dG)_{T,P} = 0$

C. $(dS)_{V,E} = 0, (dG)_{T,P} > 0$

D. $(dS)_{V,E} < 0, (dG)_{T,P} < 0$

Answer: a

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19. A reaction occurs spontaneously if

A. $T\Delta S > \Delta H$ and ΔH is$+ve$ andΔS is -ve

B. $T\Delta S = \Delta H$ and both ΔH and ΔS are $+ve$

C. $T\Delta S < \Delta H$ and both ΔH and ΔS are $+ve$

D. $T\Delta S > \Delta H$ and both ΔH and ΔS are $+ve$

Answer: d

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20. Ths standard free energy change ΔG° is related to K (equilibrium constant) as`

A. $K_p = -RT \ln \Delta G^\circ$

B. $K = \left(\frac{e}{RT}\right)^{\Delta G^\circ}$

C. $K_p = \frac{\Delta G^\circ}{RT}$

D. $K_p = e^{-\Delta G^\circ / RT}$

Answer: d

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21. If $K < 1.0$, what will be the value of ΔG° out of the following ?

A. 1.0

B. Zero

C. Negative

D. Positive

Answer: d

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FILL IN THE BLANKS

1. A system which can exchange energy with the surroundings but no matter is called

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

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3. Force is . . .. property whereas pressure is . . .. property in thermodynamics .

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4. A process in which heat can flow from system to surroundings or vice-versa is called $\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ process.

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

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6. For the isothermal reversible expansion of an ideal gas from volume V_1 to volume V_2, the work done is given by $w_{rev} = \ldots\ldots\ldots\ldots\ldots\ldots$ whereas for the irreversible expansion , it is given by $w_{\text{irrev}} = \ldots\ldots\ldots\ldots$

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7. If a system absorbs heat and expands through a volume ΔV against external pressure, P accompanied by increas in internal energy, ΔU, then

$q = \ldots\ldots\ldots\ldots\ldots\ldots$

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8. If a gas expands through a volume of 100mL against atmospheric pressure, the work done by the gas $= \ldots\ldots\ldots\ldots\ldots\ldots$ joule .

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9. Internal energy change of a system is the heat absorbed or evolved at constant $\ldots\ldots\ldots\ldots\ldots$ whereas enthalpy change is that at constant $\ldots\ldots\ldots\ldots\ldots\ldots$

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10. If in a reaction at constant temperature, n_1 moles of the gaseous reactants change inton_2 moles of gaseous products , the difference in the enthalpy change and internal energy change of the reaction will be equal to ....

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11. Molar heat capacity of aluminium will be .... times its specific heat.

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12. For n moles of a gas, the difference between the molar heat capacity at constant pressure and that at constant volume is equal to ....

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

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14. Bomb calorimeter is used to determine the value of ....

Watch Video Solution

15. For exothermic reactions, the enthalpy of products is. . ... than enthalpy of reactants.

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16. The enthalpy of combustionof 1 mole of H_2 to form $H_2O(l)$ is . . .. kJ whereas to form $H_2O(g)$, it is . . .. kJ.

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17. The heat produced from the complete combustion of 1 g of fuel or food is called its. . ...

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

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19. The enthalpy of solution of sodium chloride is $4kJmol^{-1}$ and its enthalpy of hydration of ion is $-784kJmol^{-1}$. Then the lattice enthalpy of $NaCl$ (in $kJmol^{-1}$) is

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20. 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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21. The bond energy of H_2 is found to be 435 kJ mol^{-1}. Therefore, the enthalpy of formation of hydrogen atom will be . . ..

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22. Enthalpy of dissociation of H_2O molecules into H^+ and OH^- ions is . . ..$kJmol^{-1}$

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23. For an endothermic process to be spontaneous, the factor $T\Delta S$ should be . . ..ΔHin magnitude (equal to or less than or greater than) .

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24. Why is the enthalpy of sublimation equal to the sum of enthalpy of fusion and enthalpy of vaporisation ?

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25. The expression for the entropy change when a gas expands from volume V_1 to volume V_2 at constant temperature T is $\Delta S_T = \ldots\ldots\ldots\ldots\ldots\ldots\ldots$

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26. Gibbs-Helmholtz equation is.............. .

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27. In terms of work, the decrease in free energy during a process is equal to $\ldots\ldots\ldots\ldots\ldots\ldots$

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28. Free energy change (ΔG) is related to the total entropy change $(\Delta S_{\text{total}}$viz$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}})$ as ....

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29. A reaction is nono-spontaneous at high temperature but became spontaneousat low temperature . The reaction is . . ..

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30. Standard free energy change(ΔG°) of a reaction is related to its equilibrium constant as : $K = 10^x$ where $x =$ . . ..

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

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CONCEPTUAL QUESTIONS(I. General Introduction andsome basic terms and concepts)

1. To what type of system the following belong ?

(i) Tree (ii) Pond(iii) Animals (iv) Tea placed in a kettle (v) Tea placed in thermos flask(vi) Tea placed in a cup.

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2. Separate out the following into extensive and intensive.

Volume, Temperature, Pressure, Boiling point, Free energy.

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3. One mole of CO_2 at 300 K and1 atm pressure is heated in a closed vessel so that temperature is 500 K is pressure is 5 atm. Then it is cooled so that temperature is 300 K and pressure is 1 atm. What is the change in internal energy of the gas ?

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4. One litre-atmosphere is approximately equal to

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CONCEPTUAL QUESTIONS(II. First law of thermodynamics)

1. Water decomposes by absorbing 286.2 kJ of electrical energy per mole. When H_2 and O_2 combine to form one mole of $H_2O, 286.2kJ$ of heat is produced. Which law is proved ? What statement of the law followsfrom it?

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CONCEPTUAL QUESTIONS(III.Enthalpy change and its relation with internal energy change)

1. Under what condition ΔH becomes equal to ΔU ?

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2. C_v value of He isalways 3 $R/2$ but C_v value of H_2 is $3R/2$ at low temperature and$5R/2$ at moderate temperature and more than $5R/2$ at higher temperature . Explain in two or threelines.

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3. In a bomb calorimeter , volume is constant . Do you think that $\Delta H = \Delta U$? Why or why not ?

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4. Why standard heat of formation of diamond is not zero though it is an element ?

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5. The enthalpy of formation of gaseous iodine is $62.5 kJ \text{mol}^{-1}$. What is the enthalpy of sublimation of iodine at $25^{\circ} C$?

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6. Given that :

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

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

what will be the ΔH for the reaction:

$O^{-}(g) + e^{-} \rightarrow O^{2-}(g)$

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7. Is the bond energy of all the four $C-H$ bonds in CH_4 molecule equal? If not then why? How is the bond energy then reported?

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8. Water can be lifted into the water tank at the top of the house with the help of a pump . Then why is not considered to be spontaneous ?

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9. We are consuming a lot of electrical energy, solar energy etc. Do you, therefore, conclude that energy of the universe is continuously decreasing ? Explain which other thermodynamic quantity is continuously increasing or decreasing ?

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10. Under what condition, the heat evolved or absorbed in a reaction is equal to its free change ?

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11. The standard free energy of a reaction is found to be zero. What is its equilibrium constant ?

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12. Calculate ΔG and ΔG° for the reaction : $A+B \Leftrightarrow C+D$ at $27^{\circ}C$ .Equilibrium constnat(K) for this reaction $=10^{2}$

Watch Video Solution

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

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NCERT QUESTIONS AND EXERCISES WITH ANSWERS

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

(i) used to determine the heat changes

(ii) whose value is independent of path

(iii) used to determine pressure - volume work

(iv)whose the value depends on temperature only.

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2. For the process to occur under adiabatic conditions, the correct condition is

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

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4. ΔU° of combustion of methane is $-XkJmol^{-1}$. The value of ΔH° is :

(i) $= \Delta U^{\circ}$ (ii) $> \Delta U^{\circ}$ (iii) $< \Delta U^{\circ}$ (iv) $= 0$

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5. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are $-890.3kJmol^{-1}$, $-393.5kJmol^{-1}$ and $-28.5kJmol^{-1}$ respectively. Enthalpy of formation of $CH_4(g)$ will be :

(i) $-74.8kJmol^{-1}$ (ii) $-52.27kJmol^{-1}$ (iii) $+74.8kJmol^{-1}$ (iv) $+52.26kJmol^{-1}$

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

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

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

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

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6. A reaction, $A + B \rightarrow C + D + q$ is found to havea positive entropy change. The reaction will be

(i) possible at high temperature (ii) possible only at low temperature

(iii) not possible at any temperature (iv) possible at any temperature

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

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

$$NH_2CN(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$$

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9. Calculate the number of KJ necessary to raise the temperature of $60.0g$ of aluminium from 35° to $55^\circ C$. Molar heat capcacity of Al is $24Jmol^{-1}K^{-1}$

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10. Calcualte the enthalpy change on freezing of 1.0 mole of water at $10.0^\circ C$ to ice at -10°C. $\Delta_{fs}H = 6.03kJmol^{-1}$ at $0^\circ C$.

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

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

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12. Enthalpies of formation of $CO(g)$, $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are -110, -393, 81 and 9.7 kJ mol^{-1} respectively. Calculate $\Delta_r H$ for the reaction:

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

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13. Given

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g), \Delta_r H^{\ominus} = -92.4kJmol^{-1}$

What is the standard enthalpy of formation of NH_3 gas?

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

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

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

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \ldots(iii), \Delta_f H_3^{\ominus} = -286kJmol^{-1}$$

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15. Calculate the enthalpy change for the process

$$CCl_4(g) \rightarrow C(g) + 4Cl(g)$$

and calculate bond enthalpy of $C - Cl$ in $CCl_4(g)$.

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

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

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

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

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

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17. For the reaction at $298K$

$2A + B \rightarrow C$

$\Delta H = 400kJmol^{-1}$ and $\Delta S = 0.2kJK^{-1}mol^{-1}$

At what temperature will the reaction becomes spontaneous considering

ΔH and ΔS to be contant over the temperature range.

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18. For the reaction

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

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19. For the reaction,

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

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

Calculate ΔG^{Θ} for the reaction, and predict whether the reaction may occur spontaneously.

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20. The equilibrium constant for a reaction is 10. What will be the value of ΔG^{Θ}? $R = 8.314JK^{-1}mol^{-1}, T = 300K$.

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21. Comment on the thermodynamic stability of $NO(g)$, given

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g), \Delta_r H^{\Theta} = 90kJmol^{-1}$

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

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

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NCERT SUPPLEMENTARY EXERCISE

1. State second law of thermodynamics.

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2. Write the conditions in terms of ΔH and ΔS when a reaction would be always spontaneous.

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3. When $\Delta H > 0$ and$\Delta S < 0$, reaction is never spontaneous. Explain .

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4. Comment on the spontaneity of a reaction at constant temperature and pressure in the following cases. (i)$\Delta H < 0$ and $\Delta S > 0$ (ii) $\Delta H > 0$ and $\Delta S < 0$ (iii) $\Delta H < 0$ and $\Delta S < 0$ (iv)$\Delta H > 0$ and$\Delta S > 0$

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5. State the third law of thermodynamics.

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6. Explain the term residual entropy.

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTIONS(MULTIPLE CHOICE QUESTIONS-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 statement is correct ?

A. The presence of reaction speciesin a covered beaker is an example of open system.

B. There is an exchange of energy 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 insolated vessel isan example of a closed system.

Answer: c

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3. The state of 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

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4. 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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5. During complete combustion of one mole of butane ,2658Kj of heat is released. The thermochemical reaction for above change is

A.

$$2C_4H_{10}(g)+13O_2(g)\to 8CO_2(g)+10H_2O(l)\Delta_cH=-2658.0kJm$$

B.

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)\Delta_cH = -1329.0kJm$$

C.

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)\Delta_cH = -2658.0kJm$$

D.

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)\Delta_cH = +2658.0kJm$$

Answer: c

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6. $\delta_f U^{\ominus}$ of formation of $CH_4(g)$ at a certain temperature is $-393 Jmol^{-1}$. The value of $\delta H^{\ominus} is:$

A. zero

B. $< \Delta_f U^{c-}$

C. $> \Delta_f U^{c-}$

D. equalto $\Delta_f U^{c-}$

Answer: b

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7. 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. $q = 0, \Delta T \ne 0, w = 0$

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

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

D. $q = 0, \Delta T = 0, w \ne 0$

Answer: c

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8. The pressure volume work for an ideal gas can be calculated by using the expression $w = -\int_{V_i}^{v_f} PexdV$. The work can also be calculated from 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 (irreversible)

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

Answer: b

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9. The entropy change can be calculated by using the expression $\Delta S - \frac{q_{rev}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following:

A. ΔS(system) decreases butΔS(surroundings) remainsthe same.

B. ΔS (system) increases but ΔS (surroundings) decreases

C. ΔS (system) decreases but ΔS (surroundings) increases.

D. ΔS (system) decreases andΔS (surroundings) also decreases.

Answer: c

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10. On the basic of thermochemical equations (I),(II)and (III), Find out which of the algebraic relationships given in options (a)to (d) is correct ?

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

$\Delta_r H = XKJmol^{-1}$

(II)$C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g),$

$\Delta_r H = yKJmol^{-1}$

$(III)CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g), \Delta_r H = zKJmol^{-1}$

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 reactions given below .On the basis of these reactions ,Find out which of the algebraic relations given in options (a) to(d) is correct?

$(p)C(g) + 4H(g) \rightarrow CH_4(g), \Delta_r H = xKJmol^{-1}$

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

$\Delta_r H = yKJmol^{-1}$

A. $x = y$

B. $x = 2y$

C. $x > y$

D. $x < y$

Answer: c

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12. The enthalpy of elements in their standard atates 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

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

A. enthalpy of fusion $+$ enthalpy of vaporisation

B. enthalpy of fustion

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. ΔG is zero for a reversible reaction

B. ΔG is positive for a spontaneous reaction

C. ΔG is negative for a spontaneous reaction

D. ΔG is positive for a non- spontaneous reaction

Answer: B

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTIONS(MULTIPLE CHOICE QUESTIONS-II)

1. Thermodynamics mainly deals with:

A. interrelation of various forms of energy and their transformation from one formto another.

B. energy changes in the processes which depend only on initial and final statesof the microscopic system 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 negative

C. $_ \ (p)$will be positive

D. $\Delta_r H$ will be positive

Answer: a,b

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

A. 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. burning carbon in oxygen to give carbon dioxide.

Answer: c,d

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4. For an ideal gas, the work of reversible expansion under isothermal condition can be calculated by using expression $= -nRT\ln.\frac{V_f}{V_i}$. A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversible 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 at the work done at 300K

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

$2Zn(s) + O_2(g) \rightarrow 2ZnO_s : \Delta H = -693.8 kJ mol^{-1}$

A. The enthalpy of two molesof ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8kJ

B. The enthalpy of two 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. 693.8 kJ mol^{-1} energy is evolved in the reaction

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

Answer: a,c

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NCERT EXEMPLAR PROBLEMS WITH ANSWERS, HINTS AND SOLUTIONS(SHORT ANSWER QUESTIONS)

1. 18.0 g of water completely vaporises at $100^\circ C$ and 1 bar pressure and the enthalpy change in the process is $40.79 kJ mol^{-1}$. 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 ?

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2. One mole of acetone requires less heat to vaporise than 1 mole of water. Which of the two liquids has higher enthalpy of vaporisation ?

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3. Standard molar enthalpy of formation, $\Delta_f H^\Theta$ is just a special case of enthalpy of reaction, $\Delta_r H^\Theta$. Is the $\Delta_r H^\Theta$ for the following reaction same as $\Delta_f H^\Theta$? Given reason for your answer.

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

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

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

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5. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction $A \to B$ 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 $\Delta_r H$ overall reaction and $\Delta_r H_1, \Delta_r H_2$ ... etc for intermediate reaction.

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6. The enthaply of atomisation for the reaction : $CH_4(g) \rightarrow C(g) + 4H(g)$ is $1665 kJ \text{mol}^{-1}$.What is the bond enthalpy of C-H bond?

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

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8. 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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9. 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.

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10. 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?

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11. 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.

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12. A sample of 1.0 mole of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in figure. What will be the value of ΔH for the cycle as a whole ?

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

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14. Identify the state functions and path functions out of the following: enthalpy, entropy, heat, temperature, work, free energy.

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

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

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

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18. 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.

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19. 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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20. 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?

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21. 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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22. 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.

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23. 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 $368 kJ mol^{-1}$ respectively.

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24. The enthalpy of vaporisation of CCI_4 is $30.5kJ\text{mol}^{-1}$.Calculate the heat required for the vapourisation of 284 g of CCI_4 at constant pressure. (Molar mass of $CCI_4 = 154u$).

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25. The enthalpy of reaction for thr equation

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ is $\Delta H^\circ = -572k\frac{j}{m}ol$

what will be the standard enthalpy for the formation of H_2O(l)?

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26. 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 single step as shown in Figure. Explain graphically.

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

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

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

(b) $\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\ HCl(g)\Delta_r H^\circ = -93.2kJmol^{-1}$

In which of the process potential energy/enthalpy change in contributing factor to the spontaneity?

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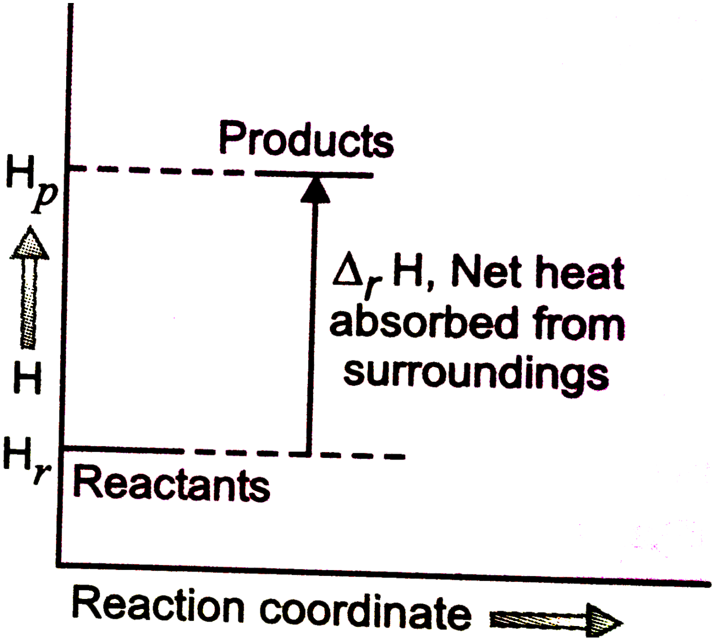
29. Enthalpy diagram for a particular reaction is given in the figure, below. Is it possible to decide spontaneity of a reaction from given diagram ?

Explain .



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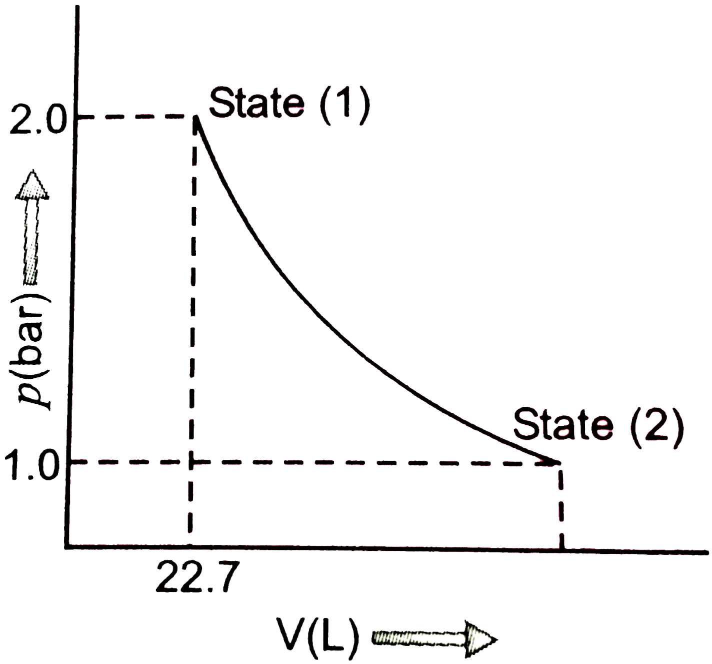
30. 1.0 mol of a monoatomic ideal gas isexpanded from state (1) to state (2) as shown in the adjoining figure. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K



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31. An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. The amount of work done by the gas is x. if the same expansion were carried out reversible, what is the relation of work done with the earlier case?

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MATCHING TYPE QUESTIONS

1. In the following questions morethan one correlation is possible between options of both columns.

Match the following :

	A		B
(i)	Adiabatic process	(i)	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 ma
(v)	State function	(e)	No transfer of heat
(vi)	$\Delta U = q$	(f)	Constant temperature
(vii)	Law of conservation of energy	(g)	Internal energy
(viii)	Reversible process	(h)	$p_{ext} = 0$
(ix)	Free expansion	(i)	At constant pressure
(x)	$\Delta H = q$	(j)	Infinitely slow process which
(ξ)	Intensive property	(k)	Entropy
(ξ)	Extensive property	(l)	Pressure
		(m)	Specific

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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. In the following questions morethan one correlation is possible between options of both columns.

Match the following :

Δ(Parameters) Description

	$\Delta_r H^{c-}$	$\Delta_r S^{c-}$	$\Delta_r G^{c-}$		
(i)	$+$	$-$	$+$	(a)	None-spontaneous at high temp
(ii)	$-$	$-$	$+$at high T	(b)	Spontaneous at all temperatur
(iii)	$-$	$+$	$-$	(c)	Non-spontaneous at all tempera

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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) ΔU in adiabatic expansion of ideal gas	(d) $\frac{\Delta H_{\text{vap}}}{T_b}$

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5.

	Column I		Column II
(A)	Isothermal process	(p)	$q = \Delta U$
(B)	Adiabatic process	(p)	$w = -pP\Delta V$
(C)	Isobaric process	(r)	$w = \Delta U$
(D)	Isochoric process	(s)	$w = nRT\ln(V_2/V_1)$

(a) $A - s, B - q, C - r, D - p$ (b) $A - s, B - r, C - q, D - p$ (c) $A - p, B - r, C - q, D - s$ (d) $A - r, B - p, C - s, D - q$

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6.

	Column I(Solutions mixed)		Colu
(A)	$500 mL of 0.1$M HCl acid $+ 200 mL of 0.2 M NaOH$solution	(p)	4568
(B)	$200 mL of 0.2 M H_2SO_4 + 400 mL of 0.5 M KOH$solution	(q)	2284
(C)	$500 mL of 0.1 M HCl + 500 mL of 0.1 M NH_4OH$	(r)	2760
(D)	$500 mL of 0.1 M$acetic acid $+ 500 mL of 0.1 M NaOH$	(s)	2575

(a) $A-r, B-p, C-s, D-q$ (b) $A-p, B-r, C-q, D-s$ (c)

$A-q, B-p, C-s, D-r$ (d) $A-, B-s, C-p, D-r$

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7.

	Column I (Gas)		Column II(Ratio $\gamma = C_p/C_v$)
(A)	Ammonia	(p)	1.20
(B)	Carbon dioxide	(q)	1.30
(C)	Carbon monoxide	(r)	1.40
(D)	Helium	(s)	1.66

(a) $A-s, B-r, C-q, D-p$ (b) $A-p, B-q, C-r, D-s$ (c)

$A-s, B-q, C-r, D-p$ (d) $A-r, B-s, C-q, D-p$

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8. Match List -I (Equations) with List -II (Type of processes) and select the correct option.

	List -I		List -II
	Equation		Type of processes
(a)	$K_p > Q$	(i)	Non spontaneous
(b)	$\Delta G^\circ < RT \ln Q$	(ii)	Equilibrium
(c)	$Kp = Q$	(iii)	Spontaneous and endothermic
(d)	$T > \frac{\Delta H}{\Delta S}$	(iv)	Spontaneous

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ASSERTION AND REACTION TYPES 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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LONG ANSWER QUESTIONS

1. Derive the relationship between $\Delta H \text{ and } \Delta U$ for an ideal gas. Explain each term involved in the equation.

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2. 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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3. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compoud present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain in indirect method to measure lattice enthalpy of NaCl(s).

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

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5. 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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6. Define 'thermodynamics' . Briefly describe the importance and limitations of thermodynamics.

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7. Define the following terms : (i) System (ii) State variables (iii) State function (iv) Extensive and intensive properties (v)Isothermal process (vi) Adiabatic process (vii) Reversible process (viii) Internal energy .

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8. Briefly explain the terms 'internal energy ' and 'internal energy change'.

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9. State the first law of thermodynamics.

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10. Explain the term enthalpy. How is it related to the internal energy of the system?

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11. Briefly explain the following :

(i) Heat of combustion (ii) Bond energy .

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12. Explain the difference between bond energy and dissociation energy with the help of one example of each type.

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13. What do you understandby a spontaneous process ?Explain with suitable examples. Explain why neither the energy facor nor the randomness factor alone can explain the spontaneity of a process.

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14. Define entropy. Why is it a state function? Explain the effect of increased temperature on the entropy of a substance.

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15. State and explain second law of thermodynamics. What is its significance?

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16. What are the limitations of the first law of thermodynamics?State second law of thermodynamics in as many ways as you can.

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17. Explain the terms 'entropy', 'enthalpy' and 'free energy'.

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18. Explain what is meant by Gibb's free energy change. "The sign of the free energy is very important .' Justify the statement.

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19. Briefly explain the effectof temperature on the spontaneity of

(a) an endothermic reaction

(b) an exothermic reaction.

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20. Define ' standard free energy of formation '. Taking a suitable example , explain the spontaneity of a reversible reaction.

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21. State and explain the 'third law of thermodynamics'.

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ADDITIONAL QUESTIONS(VERY SHORT ANSWER QUESTIONS)

1. Which of the thermodynamic properties out of E,S,T,P,V,H and G are intensive propertiesand why ?

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2. Why internal energy is a state function but work is not ?

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3. Intensive property.

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4. Extensive property.

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5. In an adiabatic process

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6. In thermodynamics, a process is called reversible when-

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7. What are diathermic and adiabatic containers?

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8. Write mathematical statement of first law of thermodynamics.

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9. What is the relationship betweenq_p and q_v ?

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10. Write the relationship between enthalpy change, $\Delta H$and internal energy change, ΔU , for a process occuring at constant pressure and constant temperature.

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11. What is the value of ΔH in the following reaction at 300 K ?

$CH_4(g)2O_2(g) \rightarrow CO_2(g) + 2H_2O(l), \Delta U = 885389J/mol.$

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

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13. Define molar heat capacity and specific heat capacity.

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14. Why is 'bomb calorimeter ' called so ?

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15. Two reactions are given below :

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

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

Which one will have greater value of ΔH and why ?

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

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

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

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19. Comment on the bond energies of four C-H bonds present in CH_4.

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20. What is the limitation of the first law of thermodynamics?

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21. Write a general expression for the entropy change during a phase transformation, or Give a relation between entropy change and heat absorbed or evolved for a reversible reaction occuring at temperature T.

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22. What is entropy? Give its units.

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23. Predict the sign of entropy change in the following reaction :

(i) $O_2(g) + 2SO_2(g) \rightarrow 2SO_3(g)$

(ii) $CaC_2O_4(s) \rightarrow CaCO_3(s) + CO(g)$

(iii) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

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24. What is the effect of temperature on entropy?

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25. Entropy of diamond is less than that of graphite.What conclusion do you draw from this ?

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

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27. What do you meanby Entropy of vaporisation or Entropy of fusion or Entropy of sublimation .

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28. Give a statement which includes the main ideas of the first law and second law of the thermodynamics.

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29. State the second law of thermodynamics.

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30. What is the Gibbs Helmhotz equation ?

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

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32. How are internal energy change(at constant pressure) , free energy change and entropy change related to one another?

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33. How are the following related ? (Give mathematical relation)

(i) Free energy change and electrical work .

(ii) Free energy change, enthalpy change and entropy change.

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34. A reversible reaction has ΔG° negative for forward reaction ? What will be sign of ΔG° for backwork reaction ?

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35. What is the criteria for spontaneity in terms of free energy change ?

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36. Why for predicting the spontaneity of a reaction , free energy criteria is better than the entropy criteria ?

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37. State the thermodynamic condition of spontaneous occurance of a process?

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38. Why a non- spontaneous reaction becomes spontaneous when coupled with a suitable spontaneous reaction ?

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39. Write down the expression for standard free energy change in terms of equilibrium constant. State meaning of the symbols used.

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40. State the third law of thermodynamics.

▶ Watch Video Solution

41. When is the entropy of a perfectly crystalline solid zero?

▶ Watch Video Solution

42. State the law governing entropy and temperature.

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43. Which out of the following can be determined ?

Absolute internal energy, absolute enthalpy, absolute entropy.

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SHORT ANSWER QUESTIONS

1. What do you understand by open, closed and isolated system ?

Illustrate with suitable examples.

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

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3. Classify, giving reason, the following into intensive and extensive properties.

(i)Entropy (ii) Viscosity (iii) Heat capacity (iv) Surface tension (v) Vapour pressure (vi) Refractive index

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4. Explain, giving reasons, which of the quantities out of internal energy, heat and work are state functions and which is not .

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5. Derive an expression for the work of expansion of a gas $(w = -P\delta V)$.

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6. How will you distinguish between the two?

(i) Open and closed system.

(ii) Extensive and intensive properties.

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7. State the law of conservation of energy. Give some examples in which this law is obeyed.

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

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9. Discuss the significance of the mathematical expression in which the heat absorbed by a system is related to internal energy and work done by the system.

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10. State first law of thermodynamics.Write it mathematical expression.

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11. Briefly explain the term 'enthalpy' . How does if differ from internal energy ?

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12. Starting with the thermodynamic relationships, $\Delta U = q - P\Delta V$ and $H = V + PV$,derive the relationship $\Delta H = q_p$.

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13. Starting with the thermodynamic relationships$H = U + PV$ derive the following relationship :

$\Delta H = \Delta U + (\Delta n)RT$

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14. Derive the relationship between heat of reaction at constant pressure q_p and heat of reaction at constant volume q_v.

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15. What do you understand by K_c and K_p ? Derive a relationship between them.

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16. Explain the calculations involved in the determination of heat of combustion by bomb calorimeter?

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17. Define ΔH.What will be the sign of ΔH in

(i) exothermic reaction and

(ii) endothermic reaction?

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18. Briefly explain the term 'standard heat of formation' . What is standard state of an element and what is its value for the standard heat of formation ?

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19. What is the basic difference between enthalpy of formation and enthalpy of reaction? Illustrate with suitable examples.

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20. Define Hess's law of constant heat summation.

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21. Define the term 'bond enthalpy'.Why an average value is taken in the polyatomic molecules ?

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22. What is meant by average bond energy? In what way is it different from bond energy of a diatomic molecule ? Give suitable examples.

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23. Explain spontaneous and non-spontaneous processes.

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24. What is meant by enthalpy ? Can a decrease in enthalpy be the criterion for the sponatneity of all reactions? If not, why?

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

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26. What is entropy ? State the effect of increased temperature on the entropy of a substance.

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27. Explain the entropy concept and discuss the nature of change in entropy (increase or decrease) for :

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

(ii) $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

(iii) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

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

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29. What is Entropy ? What are the units of Entropy ? What is its significance of Entropy change ?

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30. Giving suitable reasons, predict the sign of entropy change $(\Delta S)$for the following :

(i) sublimation of ammonium chloride

(ii) $NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$

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31. Will entropy increase or decrease in the following changes and give reasons for your answer ?

(i) Sugar dissolves in water (ii) Water freezes to form ice.

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32. Predict whether entropy change in the following processes would be positive or negative.

(i) $N_2O_3(g) \rightarrow N_2O(g) + O_2(g)$ (ii) Freezing of water

(iii) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

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

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34. State whether the entropy of the system increases,decreases or remains unchanged in the following processes :

(a)one gram of water evaporates into steam at the same pressure and temperature.

(b) one gram of water freezes into ice at the same pressure and temperature.

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35. How does $T\Delta S$ determine the spontaneity of process?

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36. Derive the criteria for predicting the spontaneity of a process in terms of entropy change $(\Delta S_{\text{total}})$

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37. Give two statements for the second law of thermodynamics.

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

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39. What do symbols$\Delta H, \Delta S$andΔG signify ? How are they inter-related?

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40. State Gibbs-Helmholtz equation and explain its use in predicting the spontaneity of a reaction.

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41. Explain the terms entropy and free energy.Entropy of a solid substance increases on melting. Explain.

Watch Video Solution

42. What is meant by free energy of a subtance ? Entropy of a solid substance increases on melting . Explain.

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43. Explain why is ΔG, the free energy change, called free energy. Define efficiency of a process.

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44. What is the energy and free energy change?Show that change is free energy is equal to the useful work done.

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45. Starting with the thermodynamics relationship $\Delta U = q + w$,derive the following relationship :

$-\Delta G = w_{\text{non- expansion}}$

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46. Explain : (i) Spontaneity (ii) Free energy (iii) Reversibility (iv) Internal energy

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47. What atre the conditions for the spontaneity of a reaction in terms of enthalpy and entropy changes ?

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48. How is spontaneity of a change related to change in entropy and free energy ?

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49. For a reaction both ΔH and ΔS are positive.Under what conditions does the reaction occur spontaneously?

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50. Predict the feasibility of a reaction when (i) both ΔH andΔS increase (ii) both ΔH and ΔS decrease (iii) ΔH decrease but ΔS increases (iv) ΔH increases and ΔS decreases.

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51. Expalin the state of chemical reactions when :

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

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52. How Gibbs free energy is related to enthalpy , entropy and temperature of a system? How itthis used in determining the spontaneity of a process ?

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53. What is meant by free energy of a system? Derive Gibbs- Helmholtz equation . What is the value of free energy when the system is in equilibrium?

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54. What are spontaneous processes? Mention the condition for a reaction to be spontaneous at a constant temperature and pressure.

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55. (a) An endothermicreaction $A \rightarrow B$ proceeds to completion . Predict the sign of ΔS.

(b) What will be the sign of ΔS for the reaction $: N_2(g) + O_2(g) \rightarrow 2NO(g)$?

Given reasons in support of your answer.

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56. 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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57. For a hypothetical process, $A \rightarrow B$, predict whether the process is spontaneous or not when.

(a) ΔH is $+ve$, $T\Delta S$ is$+ve$ and $T\Delta S$ is greater than Δ

(b) ΔH is $+ve$,$T\Delta S$ is $-ve$ and $T\Delta S$ is equal to ΔH

(c) ΔH is $-ve$, $T\Delta S$ is $-ve$ and $T\Delta S$ is greater than ΔH

(d) ΔH is $-ve$, $T\Delta S$ is $-ve$ andΔH is greater than $T\Delta S$.

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58. Starting with the thermodynamic relationship , $G = H - TS$,derive the following relationship :

$\Delta G = \ -T\Delta S_{\text{total}}$

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59. Write Gibb's Helmhotz equation which relates the enthalpy change and the energy change of a process at constant temperature and pressure. Explain the effect of temperature on feasiblity for

(a) Endothermic process

(b) Exothermic process in terms of Gibb['s Helmholtz equation.

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60. Define the terms 'standard free energy change' and'standard free energy of formation '. How is the former related to the equilibrim constant of a reaction ?

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61. How is that a reversible reaction is spontaneous in the forward as well as backward reaction?

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62. Define " Third law of thermodynamics".Give its molecular interpretation.What is the most important application of this law ?

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63. Enthalpy of formation of an elements in its standard stat (298 K, 1 atm) is zero but entropy of formation is not zero under the same condition . Explain.

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64. State third law of thermodynamics. Discuss its one application or How is this law useful for calculating the absolute value of the entropy?

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65. Define the following :

(i) Second law of thermodynamics (ii) Third law of thermodynamics (iii) Entropy of a system. (iv) Enthalpy of a system (v) Free energy of a system.

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ANALYTICAL QUESTIONS AND PROBLEMS WITH ANSWERS / SOLUTIONS

1. Can the absolute value of internal energy be determined ? Why or why not ?

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2. For the same increase in volume,why work done is more if the gas is allowed to expand reversibly at higher temperature?

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3. 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?

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4. Same mass of diamond and graphite (both being carbon) are burnt in oxygen. Will the heat produced be same or different? Why?

Give reasons for the following:

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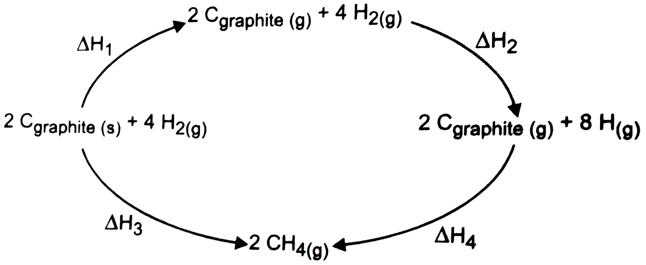
5.



Find out : (i) Heat of formation of CH_4 in terms of $\Delta H_1, \Delta H_2$ etc.

(ii) Heat of sublimation of C_{graphite} in terms of $\Delta H_1, \Delta H_2$ etc.

(iii) Heat of dissociation of H_2 in terms of $\Delta H_1, \Delta H_2)$ etc.

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6. Rank the following in the order of increasing entropy :

(a) 1 mole of $H_2O(l)$ at $25^\circ C$ and 1 atm. Pressure.

(b) 2 moleof $H_2O(s)$ at $0^\circ C$ and 1 atm. Pressure.

(c) 1 moleof $H_2O(v)$ at $100^\circ C$ and 1 atm. Pressure.

(d) 1 mole of $H_2O(l)$ at $0^\circ C$ and 1 atm. pressure.

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7. An exothermic reaction $A \rightarrow B$ is spontaneous in the backward direction. What will be the sign of ΔS for the forward reaction ?

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8. Predict whether following reaction will be exothermic or endothermic . Give reaction for your answer

$H - H(g) + Cl - Cl(g) \rightarrow 2H - Cl(g)$

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9. At a certain temperature 'T',the endothermic reaction $A \rightarrow B$ proceeds virtually to the end. Determine.

(i) Signof ΔS for this reaction

(ii) sign of ΔS for the reaction $B \rightarrow A$ at the temperature T, and

(iii) the possibility of reaction $B \rightarrow A$ proceeding at a low temperature.

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10. Why endothermic reactions are favoured at high temperature?

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11. Comment on the validity of the following statements, giving reasons :

(i) Thermodynamically, an exothermic reaction is sometimes not spontaneous.

(ii) The entropy of steam is more than that of water at its boiling point.

(iii)The equilibrium constant fora reaction isone or more if $\Delta_r G^\circ$ for it is less than zero.

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12. Give reasons : (a) Neither q nor w is a state function but $q + w$ is a state function.

(b) The dissociation of ammonium chloride in water is endothermic still it dissolved in water.

(c) A real crystal has more entropy than an ideal crystal.

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13. Show that in an isothermal expansion of an ideal gas, a $\Delta U = 0$ and b. $\Delta H = 0$.

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14. 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 $86.7 kJ mol^{-1}$.

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15. What is meant by entropy driven reaction? How can the reaction with positive change of enthalpy and entropy driven?

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

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17. Justify the following statement :

(a) An exothermic reaction is always thermodynamically spontaneous.

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

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18. Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?

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19. Justify the following statements :

(a)Reactions with $\Delta G^{\circ} < 0$always have an equilibrium constant greater than 1.

(b)Many thermodynamically enthalpy feasible reactions do not occur under ordinary conditions.

(c) At low temperature , enthalpy change dominates the ΔG expression and at high temperatures, it is entropy whch dominatest the value of ΔG .

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20. A system containing an idealgas was subjected to a number of changes as shown in the P.V.diagram. Temperature at different points are indicated in the diagram.

(i) Name the type of presence at each step.

(ii) What will be the value of $\Delta U$for the complete process?

(iii) At which point, the number of moles of the gas will be maxmimum ?

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21. Write expression for the work done by 1 mole of the gas in each of the following cases :

(i) For irreversible expansion of the gas from volume V_1 to V_2.

(ii) For reversible isothermal expansion of the gas from volume V_1 toV_2.

(iii)For expansion of the gas into an evaluated vessel.

(iv) For reversible isothermal compression of the gas from pressure P_1 to P_2

(v)For adiabatic expansion resulting into change of temperature from T_1 to T_2.

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22. Calculate the work of expansion when 100g of water is electrolysed at a constant pressureof1 atm and temperature of $25^\circ C$.

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23. An athelete is given $100g$ of glucose $(C_6H_{12}O_6)$ of energy equivalent to $1560kJ$. He utilises 50% of this gained enegry in the event. In order to avoid storage of enegry in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is $441kJ/mol$.

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24. Using the data (all values are in kilocalorie per mole at $25^{\circ}C$) given below, calculate the bond enegry of $C-C$ and $C-H$ bonds.

$\Delta H^{\ominus}$ combustion of ethane $= -372.0$

$\Delta H^{\ominus}$ combustion of propane $= -530.0$

$\Delta H^{\ominus}$ for $C($ garphite$) \rightarrow C(g) = +172.0$

Bond enegry of $H-H$ bond $= +104.0$

$\Delta_f H^{\ominus} of H_2O(l) = -68.0$

$\Delta_f H^{\ominus} of CO_2(g) = -94.0$

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25. Calculate the resonance energy of N_2O from the following data :

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

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26. The enthalpy change involved in the oxidation of glucose is $-2880 kJ \text{mol}^{-1}$. Twenty five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose?

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27. The polymerisation of ethylene to linear polyethylene is represented by the reaction

$nCH_2 = CH_2 \rightarrow (- CH_2 - CH_2 -)_n$

When n has a large integral value. Given theat the average enthalpies of bond dissociation for $C = C$ and $C - C$ at $298K$are $+590$ and $+331 kJmol^{-1}$ respectively, calculate the enthalpy of polymerisation per mole of ethylene at $298K$.

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28. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at $25^{\circ}C$ are -156 and $+49 kJmol^{-1}$, respectively. The standard enthaly of hydrogenation of cyclohenxene (l) at $25^{\circ}C$ is $-119 kJmol^{-1}$ Use this data to estimate the magnitude of the resonance enegry of benzene.

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29. Compute the heat of formation of liquie methyl alcohol is kilojoule per mol using the following data. Heat of vaporisation of liquid methyl alcohol $= 38kJ/mol$. Heat of formation of gaseous atoms from the elements in their standard states $: H = 218kJ/mol, C = 715kJ/mol, O = 249kJ/mol.$

Average bond energies :

$C - H415kJ/mol, C - O356kJ/mol, O - H463kJ/mol.$

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30. $10g$ of argon gas is compressed isothermally and reversibly at a temperature of $27^{\circ}C$ from $10L$ to $5L$. Calculate q, w, ΔU, and ΔH for this process. $R = 2.0calK^{-1}\text{mol}^{-1}, \log_{10}2 = 0.30$. Atomic weight of $Ar = 40$.

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31. From the following data, calculate the enthalpy change for the combustion of cyclopropane at $298K$. The enthalpy of formation of $CO_{2(g)}, H_2O_{(l)}$ and $Propene_{(g)}$ are $-393, -285.8$ and $20.42kJmol^{-1}$ respectively. The enthalpy of isomerisation of cyclopropane to propene is $-33.0kJmol^{-1}$

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32. Estimate the average $S-F$ bond enthalpy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, $S(g)$ and $F(g)$ are :-1100, 274 and $80kJmol^{-1}$ respectively.

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33. Two moles of a perfect gas undergo the following processes:

a. A reversible isobaric expansion from $(1.0 atm, 20.0 L)$ to $(1.0 atm, 40.0 L)$.

b. A reversible isochroic change of state from $(1.0 atm, 40.0 L)$ to $(0.5 atm, 40.0 L)$

c. A reversible isothermal expansion from $(0.5 atm, 40.0 L) \rightarrow (1.0 atm, 20.0 L)$.

i. Sketch with lables each of the processes on the same $P-V$ diagram.

ii. Calculate the total work (w) and the total heat change (q) involved in the above process.

iii. What will be the values of ΔH for the overall process?

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34. For the reaction, $2CO + O_2 \rightarrow 2CO_2, \Delta H = -560 kJ$. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K.

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35. The internal energy change in the conversion of 1.0 mole of the calcite form of $CaCO_3$ to the aragonite form is $+0.21KJ$. Calculate the enthalpy change when the pressure is 1.0bar, given the densities of the solids are $2.71gcm^{-3}$ and $2.93gcm^{-3}$ respectively.

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36. CalculateΔU andΔH in calories if one mole ofa monoatomic ideal gas is heated at constant pressure of 1 atom from $25^\circ C$ to $50^\circ C$

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37. 5 moles of an ideal gas expand isothermally and reversible from a pressure of 10 atm to 2 atom at 300K. What is the largest mass which can be lifted through a height of 1 metre in this expansion?

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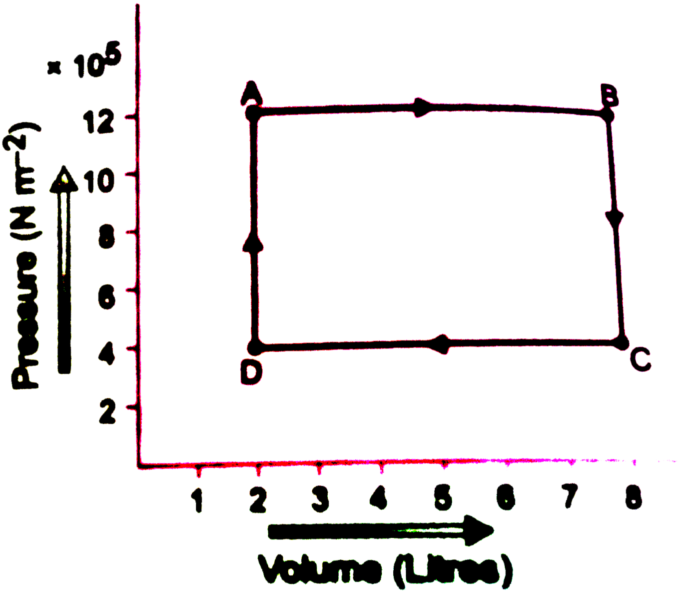
38. The figure given below represents P -V diagram of different stages of a thermodynamic process. Calculate thework done in each stage and also the net work done in the complete cyclic process.



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39. The enthalpy change for the reaction , $Zn(s)+2H^{+}(aq)\rightarrow Zn^{2+}(aq)+H_2(g)$, is $-154.0kJmol^{-1}$. The formation of 2g of hydrogen expands the system by 22.4litresat1 atm pressure. What is the internal energy of the reaction ?

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40. Sodium carbonate $(Na_2CO_30$can be obtained by heating sodium hydrogen carbonate,$NaHCO_3$

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

Calculate the temperature above which $NaHCO_3$ decomposes to form products at 1 bar .

Given

$\Delta_f H^\circ\left(kJmol^{-1}\right):NaHCO_3(s)==-947.7, Na_2CO_3(s)=-1130.9$

,

$H_2O(g)=-241.8, CO_2(g)=-393.5$

$S^{\circ}\left(JK^{-1}mol^{-1}\right): NaHCO_3(s) = 102.1, Na_2CO_3(s) = 136.0,$

$H_2O(g) = 188.8, CO_2(g)213.7$

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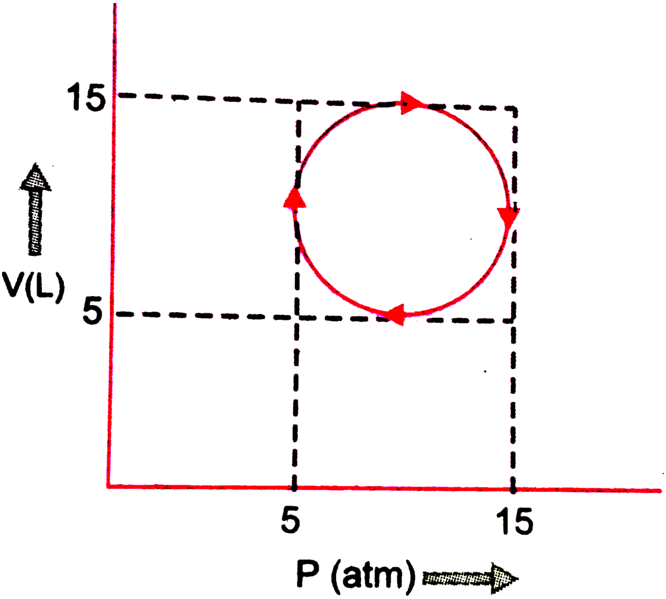
41. Calculate the amount of heat absorbed in the cyclic process shown below :



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42. Work done in expansion of an ideal gas from 4 dm^3 to $6dm^3$against a constant external pressure of 2.5 atm was usedup to heat1 mole of water at $20^\circ C$. Calculate the final temperature of water (Given : specific heat of water $= 4.184 J g^{-1} K^{-1}$).

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43. Consider the following reaction : $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ When 10.0mLof 1.0 M$AgNO_3$ solution is added to 10 mL of 1.0 mL NaCl solution at $25^\circ C$ in a calorimeter , a white ppt. of AgCl is formed and the temperature of the aqueous mixture mixture risesto $32.6^\circ C$. Assuming that the specific heatof the aqueous mixture is $4.18 J/g/^\circ C$, that the density of the mixture is $1.0 gmL^{-1}$ and that the calorimeter itself absorbs a negligible amountofheat, calculate the value of enthalpy change accompanying the processin kJ mol^{-1} ofAgCl.

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44. Calculate $q, W, \Delta U$ and ΔH for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of $273K$.

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45. Calculate the value of $\log K_p$ for the reaction, $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$ at $25^\circ C$. The standard enthalpy of formation of $NH_{3(g)}$ is $-46kJ$ and standard entropies of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ are 191, 130, 192 $JK^{-1}mol^{-1}$. respectively. ($R = 8.3JK^{-1}mol^{-1}$)

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COMPETITION FOCUS (JEE (main andAdvanced) /Medical Entrance Special)

1. Which one of the following sets of units represents the smallest and the largest amout of energy, respectively?

A. J and erg

B. erg and cal

C. cal and eV

D. eV and lit atm

Answer: d

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2. A gas expands from a volume of $1m^3$ to a volume of $2m^3$ against an external pressure of $10^5 Nm^{-2}$. The work done of the gas will be

A. $10^5 kJ$

B. $10^2 kJ$

C. $10^2 J$

D. $10^3 J$

Answer: b

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3. Calculate the work done (in joules) when 0.2 mole of an ideal gas at $300K$ expands isothermally and reversible from an initial volume of 2.5 litres to the final volume of 25 litres.

A. 996

B. 1148

C. 11.48

D. 897

Answer: b

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4. Calculate the work done when 1 mol of an ideal gas is compressed reversibly from 1 bar to 4 bar at a constant temperature of 300 K

A. $3.46kJ$

B. $-8.20kJ$

C. $18.02kJ$

D. $-14.01kJ$

Answer: A

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5. The different in the work done when one mole of $Al_4C_3(s)$ reacts with water in a closed vesselat $27^\circ C$ against atmospheric pressure and that in an open vessel under the same conditions is

A. greater in the open vessel by 600 cal

B. greater in the closed vessel by 600 cal

C. greater in the open vessel by 1800 cal

D. greater in the closed vessel by 1800cal

Answer: C

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6. If W is the amount of work done by the system and q is the amount of heat supplied to the system, identify the type of the system

A. isolated system

B. closed system

C. open system

D. system with thermally conducting walls

Answer: b

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7. Changes in a system from a initial state to the final state were made by a different manner that ΔH remains same but q changes because

A. ΔH is a path function and q is astate function

B. ΔH is a state function and q is a path function

C. Both ΔH andq are state function

D. Both ΔH and q are path function

Answer: b

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8. A piston filled with 0.04 mol of an ideal gas expands reversibly from $50.0mL$ to $375mL$ at a constant temperature of $37.0^{\circ} C$. As it does so, it absorbs $208J$ of heat. The value of q and w for the process will be: $(R = 8.314J/molK)(\ln 7.5 = 2.01)$

A. $q = +208J, w = +208J$

B. $q = +208J, w = -208J$

C. $q = -208J, w = -208J$

D. $q = -208J, w = +208J$

Answer: b

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9. Which of the following is correct option for the free expansion of an ideal gas under adiabatic condition ?

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

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

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

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

Answer: D

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10. When 1 mol of gas is heated at constant volume temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct ?

A. $q = W = 500J, \Delta U = 0$

B. $q = \Delta U = 500J, W = 0$

C. $q = W = 500J, \Delta U = W = 0$

D. $\Delta U = 0, q = W = \; - 500J$

Answer: B

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11. Which one of the following equations does not correctly respresents the first law of thermodynamics for the given process?

A. isothermal process : $q = \; - w$

B. cyclic process : $q = \; - w$

C. isochoric process : $\Delta E = q$

D. adiabatic process : $\Delta E = \; - w$

Answer: d

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12. ΔE is always positive when

A. system absorbs heat and work id done on it.

B. system emits heat and work is done on it.

C. system emits heat and nowork is done on it

D. system absorbs heat and work is done by it

Answer: a

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13. Based on first law of thermodynamics, which one of the following is correct ?

A. For an isochoric proces, $\Delta U = -q$

B. For an adiabatic process, $\Delta U = -w$

C. For an isothermal process, $q = +w$

D. For a cyclic process,$q = -w$

Answer: D

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14. δU is equal to

A. adiabatic work

B. isothermal work

C. isochoric work

D. isobaric work

Answer: a

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15. A gas is allowed to expand in a well insulated container against a constant external pressure of $2.5atm$ from an initial volume of $2.50L$ to a final volume of $4.50L$. The change in internal energy ΔU of the gas in joules will be:

A. 1136.25J`

B. $-500J$

C. $-505J$

D. $+505J$

Answer: c

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16. Standard enthalpy of vaporisation$\Delta V_{vap}. H^{\Theta}$ for water at $100^{\circ} C$is $40.66kJmol^{-1}$.The internal energy of Vaporization of water at $100^{\circ} C\left(\text{in kJ mol}^{-1}\right)$is

A. $+37.56$

B. -43.76

C. $+43.76$

D. $+40.66$

Answer: A

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17. The value of enthalpy change (ΔH) for the reaction

$C_2H_5OH(l)+3O_2(g)\rightarrow 2CO_2(g)+3H_2O(l)$

at $27^{\circ}C$ is $-1366.5kJmol^{-1}$.

The value of internal energy change for the above reactio at this temperature will be

A. $-1371.5kJ$

B. $-1369.0kJ$

C. $-1364.0kJ$

D. $-1361.5kJ$

Answer: c

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18. One mole of non - ideal gas undergoes a change of state (2.0 atm , 3 .0 L , 95 K $\rightarrow$ (4.0 atm , 5.0 L , 245 K) with a change in internal energy , $\Delta U = 30.0L$ atm . The change in enthalpy (ΔH) of the process in L atm is

A. 40.0

B. 42.3

C. 44.0

D. non defined , because process is no constant

Answer: C

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19. Two moles of an ideal gas is expanded isothermally and reversibly from 1 liter to 10 liter at $300K$. The enthalpy change (in kJ) for the process

A. 11.4 kJ

B. $-11.4kJ$

C. $0kJ$

D. $4.8kJ$

Answer: c

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20. The temperature of 2 moles of an ideal gas is raised from $27^\circ C$to $77^\circ C$. What is the value for$\Delta H - \Delta U$ for the process ? $(R = 8.3JK^{-1}mol^{-1})$

A. 415 J

B. 830 J

C. 1660 J

D. None of these

Answer: b

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21. The reaction $A \to B$, $\Delta H = +24kJ/\text{mole.}$ For the reaction $B \to C, \Delta H = -18kJ/\text{mole.}$ The decreasing order of enthalpy of A, B , C follow the order

A. A,B,C

B. B,C,A

C. C,B,A

D. C,A,B

Answer: B

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22. For the complete combustion of ethanol, $C_2H_5OH(l) + 3O_2(g) \to 2CO_2(g) + 3H_2O(l)$ the amount of heat produced as measured in bomb calorimeter is $1364.47 KJmol^{-1}$ at $25^\circ C$. Assuming ideality, the enthalpy of combustion, ΔH_C, for the reaction will be

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

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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23. 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 $25^\circ C$, 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

D. -3267.6

Answer: D

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24. Molar heat capacity of water in equilibrium with ice at constant pressure is

A. zero

B. infinity

C. $40.50 kJK^{-1} mol^{-1}$

D. $75.48 JK^{-1} mol^{-1}$

Answer: B

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25. One mole of an ideal monoatomic gas is mixed with 1 mole of an ideal diatomic gas The molar specific heat of the mixture at constant volume is .

A. 4 cal

B. 6 cal

C. 8 cal

D. 3 cal

Answer: A

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26. The temperature of 1 mole helium gas is increased by $1^\circ C$. Find the increase in internal energy.

A. 2 cal

B. 3 cal

C. 4 cal

D. 5 cal

Answer: B

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27. When 0.1 mol of a gas absorbs $41.75J$ of heat at constant volume, the rise in temperature occurs equal to $20^\circ C$. The gas must be

A. triatomic

B. diatomic

C. polyatomic

D. monoatomic

Answer: B

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28. How many calories are required to heat $40g$ of argon from $40^\circ C$ to $100^\circ C$ at constant volume? $\left(R = 2calmol^{-1}K^{-1}\right)$

A. 120

B. 2400

C. 1200

D. 180

Answer: D

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29. $4.48L$ of an ideal gas at STP requires 12 cal to raise its temperature by $15^{\circ}C$ at constant volume. The C_P of the gas is

A. 3 cal

B. 4 cal

C. 7 cal

D. 6 cal

Answer: D

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30. A $1.0g$ sample of substance A at $100^{\circ}C$ is added to $100mL$ of H_2O at $25^{\circ}C$. Using separate $100mL$ portions of H_2O, the procedure is repeated with substance B and then with substance C. How will the final temperatures of the water compare ?

Substance	Specific heat
A	$0.60Jg^{-1}$^(@)C^(-1)),(B,0.40 J g^(-1) $^{\circ}C^{-1}$
C	$0.20Jg^{-1\circ}C^{-1}$

A. $T_C > T_B > T_A$

B. $T_B > T_A > T_C$

C. $T_A > T_B > T_C$

D. $T_A = T_B = T_C$

Answer: C

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31. Which one of the following is correct when an ideal gas is expanded adaibatically and reversibly ?

A. $q = 0, W = nC_v dT, \Delta U = nC_v dT$

B. $q = 0, W = 0, \Delta U = nC_v dT$

C. $q = 0, W = nC_v d, \Delta U = 0$

D. None of the above

Answer: A

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32. Under which of the following conditions is the relation, $\Delta H = \Delta E + P\Delta V$ valid for a system :-

A. constant pressure

B. constant temperature

C. constant temperature and pressure

D. constant temperature, pressure and composition

Answer: A

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33. The heat liberated when $1.89g$ of benzoic acid is burnt in a bomb calorimeter at $25^\circ C$ increases the temperture of $18.94kg$ of water by $0.632^\circ C$. If the specific heat of water at $25^\circ C$ is $0.998cal/g\deg$, the value of the heat of combustion of benzoic acid is

A. $88.11kcal$

B. $771.4kcal$

C. $981.1kcal$

D. $871.2kcal$

Answer: B

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34. An endothermic reaction is allowed to take place very rapidly in the air. The temperature of the surrounding air

A. increase

B. decreases

C. remain unaffected

D. may increases or decrease

Answer: B

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35. The enthalpy of the reaction $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(g)$ is ΔH_1 and that of $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l)$ is ΔH_2. Then

A. $\Delta H_1 > \Delta H_2$

B. $\Delta H_1 < \Delta H_2$

C. $\Delta H_1 = \Delta H_2$

D. None of these is correct

Answer: b

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36. In the reaction $: S + \frac{3}{2}O_2 \to SO_3 + 2xkJ$ and $SO_2 + \frac{1}{2}O_2 \to SO_3 + ykJ$ heat of formation of SO_2 is

A. $x - y$

B. $2x + y$

C. $x + y$

D. $y - 2x$

Answer: d

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37. Calorific value of hydrogen gas is $-143kJg^{-1}$. The standard enthalpy of formation of H_2O will be

A. $-143kJmol^{-1}$

B. $+143 kJmol^{-1}$

C. $-286 kJmol^{-1}$

D. $+286 kJmol^{-1}$

Answer: C

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38. Find out the heat evolved in combustion if 112 litre (at 1 atm, 273 K) of water gas (mixture of equal volume of $H_2(g)$ and CO(g)) is combusted with excess oxygen.

$$H_2(g)+\frac{1}{2}O_2(g)\to H_2O(g), \Delta = -241.8kJ$$

$$CO(g)+\frac{1}{2}O_2(g)\to CO_2(g), \Delta = -283kJ$$

A. $-1414.\ 0kJ$

B. $-1209.0kJ$

C. $-1312.0kJ$

D. $-524.8kJ$

Answer: c

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39. Heat of dissociation of acetic acidis 0.30 kcalmol^{-1} . Hence,enthalpy change when 1 mol of$Ca(OH)_2$ is completely neutralized by acetic acid would be

A. $-13.4kcal$

B. $-27.1kcal$

C. $-26.8kcal$

D. $-27.4kcal$

Answer: c

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40. The enthalpy change when 1 L of 1 M H_2SO_4 is completely neutralized by 1L of1 M $Ca(OH)_2$ will be

A. $-13.7kcal$

B. $-27.4kcal$

C. $-1.37kcal$

D. $-2.74kcal$

Answer: b

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41. 0.06 mole of KNO_3 is added to $100cm^3$ of water at $298K$. The enthalpy of $KNO_3(aq)$ solution is $35.8kJmol^{-1}$. After the solute is dissolved, the temerature of the solution will be

A. 293K

B. 298K

C. 301K

D. 304 K

Answer: a

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42. The bond energies of $C=C$ and $C-C$ at $298K$ are 590 and $331kJmol^{-1}$, respectively. The enthalpy of polymerisation per mole of ethaylene is

A. $+259kJmol^{-1}$

B. $+72kJmol^{-1}$

C. $-259kJmol^{-1}$

D. $-72kJmol^{-1}$

Answer: D

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43. If $150kJ$ of energy is needed for muscular work to walk a distance of one km, than how much of gulcose one has to consume to walk a distance of five km, provided only 30% energy is available for muscular work.The enthalpy of combustion of glucose is $3000kJmol^{-1}$

A. 75g

B. 30g

C. 180g

D. 150g

Answer: d

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44. The bond dissociation energies for Cl_2, I_2 and ICl are 242.3, 151.0 and $211.3kJ/\text{mole}$ respectively. The enthalpy of sublimation of iodine is

$62.8kJ/\text{mole}$. What is the standard enthalpy of formation of $ICI(g)$ nearly equal to

A. $-211.3kJ/\text{mole}$

B. $-14.6kJ/\text{mole}$

C. 16.8 kJ / mole

D. $33.5kJ/$ mole

Answer: C

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45. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below

$$\frac{1}{2}CL_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^{\ominus}} Cl(g) \xrightarrow{\Delta H^{\ominus}_{Eg}}$$

$$Cl^-(g) \xrightarrow{\Delta_{hyd}H^{\ominus}} Cl^-(aq)$$

The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^-(aq)$

(Using the data $\Delta_{diss}H^{\ominus}_{Cl_2} = 240KJmol^{-1}$)

$\Delta_{Eg}H^{\Theta}_{Cl} = -349KJmol^{-1}$,

$\Delta_{Eg}H^{\Theta}_{Cl} = -381KJmol^{-1}$) will be

A. $-850kJmol^{-1}$

B. $+120kJmol^{-1}$

C. $+152kJmol^{-1}$

D. $-610kJmol^{-1}$

Answer: D

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46. Which of the ions in the table below would have the largest value of enthalpy of hydration?

Ionic radius in nm Charge of ion

A.

Ionic radius in nm	Charge of ion
0.0065	+2

B.

Ionic radius in nm	Charge of ion
0.095	+1

C.

Ionic radius in nm	Charge of ion
0.135	+2

	Ionic radius in nm	Charge of ion
D.	0.169	$+1$

Answer: A

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47. The enthalpies of solution for copper sulphate pentahydrate and anhydrous copper sulphate are respectively 11.7 and $-65.5 kJmol^{-1}$.The hydration enthalpy of anhydrous copper sulphate is

A. $53.8 kJmol^{-1}$

B. $-9.8 kJmol^{-1}$

C. $-77.2 kJmol^{-1}$

D. $-53.8 kJmol^{-1}$

Answer: c

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48. On the basis of the following thermochemical data : $\left(\Delta_f G^\circ H^+_{(aq.)} = 0\right)$

$H_2O_{(l)} \rightarrow H^+_{(aq.)} + OH^-_{(aq.)}, \Delta H = 57.32 kJ$

$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}, \Delta H = -286.20 kJ$

The value of enthalpy of formation of OH^- ion at $25^\circ C$ is :

A. $-22.88 kJ$

B. $228.88 kJ$

C. $+228.88 kJ$

D. $-343.52 kJ$

Answer: b

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49. The enthalpy of neutralization of oxalic acid by strong acid is $-25.4 kcal mol^{-1}$. The enthalpy of neutralization of strong acid and strong base is $-13.7 kcal equil^{-1}$. The enthalpy of dissociation of $H_2C_2O_4 \Leftrightarrow 2H^+ + C_2O_4^{2-}$ is

A. $1.0 kcal mol^{-1}$

B. $2.0 kcal mol^{-1}$

C. $18.55 kcal mol^{-1}$

D. $11.7 kcal mol^{-1}$

Answer: B

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50. When 400 ml of 2.0 N solution of a weak acid is neutralized by a dilute aqueous solution of sodium hydroxide under standard conditions, 4.4 kJ amount of heat is liberated. Therefore, the standard enthalpy of neutralization of this weak acid in kJ eq^{-1} is

A. -11

B. -44

C. -55

D. -22

Answer: C

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51. Which of the following will produce the highest risein temperature?

A. 67 mL of 1M NaOH $+$ 33 mL of 0.5M H_2SO_4

B. 33 mL of 1 M NaOH $+$ 67 mL of 0.5 M H_2SO_4

C. 40 mL of 1 M NaOH $+$ 60 mL of 0.5 M H_2SO_4

D. 50 mL of 1 M NaOH $+$ 50 mLof 0.5M H_2SO_4

Answer: D

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52. The following two reactionas are known

$FeO_3(s) + 3CO(g) \rightarrow 2Fe(s) + CO_2(g):$

$\Delta H = -26.8KJ$

$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g) : \Delta H = -16.5KJ$

The value of ΔH for the following reaction

$Fe_2O_3(s) + CO(g) \rightarrow 2FeO_2(s) + CO_2(g)$ is

A. $+10.3kJ$

B. $-43.3kJ$

C. $-10.3kJ$

D. $+6.2kJ$

Answer: D

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53. The standard enthalpies of combustion of $C_6H_6(l)$,C (graphite) and $H_2(g)$ are respectively $-3270kJmol^{-1}, -394kJmol^{-1}$ and $-286kJmol^{-1}$. What is the standard enthalpy of formation of $C_6H_6(l)$ in $kJmol^{-1}$?

A. -48

B. $+48$

C. -480

D. $+480$

Answer: b

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54. The heat of combustion of carbon to CO_2 is -393.5 kJ/mol. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is

A. $+315kJ$

B. $-630kJ$

C. $-3.15kJ$

D. $-315kJ$

Answer: D

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55. The amount of heat evolved when $500cm^3 0.1 MHCl$ is mixed with $200cm^3$ of $0.2 MNaOH$ is

A. 2.292 Kj

B. 1.292 kJ

C. $0.292kJ$

D. $3.\ 292kJ$

Answer: A

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56. $NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(g) + 3HCl(g), \qquad \Delta H_1$

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

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g), \qquad \Delta H_3$

The heat of formation of NCl3(g) in the terms of $\Delta H_1, \Delta H_2$ and ΔH_3 is

:

A. $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

B. $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

C. $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

D. None of the above

Answer: A

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57. The change of energy on freezing $1.00 kg$ of liquid water at $0^\circ C$ and1 atmis

A. $236.7 kJ kg^{-1}$

B. $333.4 kJ kg^{-1}$

C. $-333.4 kJ kg^{-1}$

D. $-236.7 kJ kg^{-1}$

Answer: C

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58. A boy after swimming comes out from a pool covered with a film of water weighing 80 g .How much heat must be supplied to evaporate this water ? $\left(\Delta_v H^\circ = 40.79 kJmol^{-1}\right)$

A. $1.61 \times 10^2 kJ$

B. $1.71 \times 10^2 kJ$

C. $1.81 \times 10^2 kJ$

D. $1.91 \times 10^2 kJ$

Answer: C

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59. The enthalpy of solution of sodium chloride is $4 kJmol^{-1}$ and its enthalpy of hydration of ion is $-784 kJmol^{-1}$. Then the lattice enthalpy of $NaCl$ (in $kJmol^{-1}$) is

A. $+788$

B. $+4$

C. $+398$

D. $+780$

Answer: A

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60. Enthalpy of $CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH$ is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively, then which relation is correct?

A. $x > y$

B. $x < y$

C. $x = y$

D. $x \geq y$

Answer: B

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61. The standard heats of formation of $NO_2(g)$ and $N_2O_4(g)$ are 8.0 and 2.0 Kcal mol^{-1} respectively the heat of dimerization of NO_2 in Kcal is

A. 10.0

B. -6.0

C. $+14.0$

D. -14.0

Answer: D

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62. Consider the reaction,

$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g), \Delta_r H = -111kJ.$ If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be

(Given, ΔH of sublimation for N_2O_5 is $54 kJ mol^{-1}$)

A. $-165 kJ$

B. $+54 kJ$

C. $+219 kJ$

D. $-219 kJ$

Answer: A

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63. Consider the following processes :-

$$\begin{array}{ll} & \Delta H(kJ/mol) \\ \frac{1}{2}A \rightarrow B & +150 \\ 3B \rightarrow 2C + D & -125 \\ E + A \rightarrow 2D & +350 \\ \text{For } \ B + D \rightarrow E + 2C, & \Delta H \ \text{ will be} \end{array}$$

A. $525 kJ/mol$

B. $-175 kJ/mol$

C. $-325kJ/mol$

D. $325kJ/mol$

Answer: B

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64. The standard enthalpies fo formation of $CO_2(g), H_2O(1)$, and glucose (s) at $25^\circ C$ are $-400kJmol^{-1}, -300kJmol^{-}$, and $-1300kJmol^{-1}$, respectively. The standard enthalpy of combustion per gram of glucose at $25^\circ C$ is

A. $+2900kJ$

B. $-2900kJ$

C. $-16.11kJ$

D. $+16.11kJ$

Answer: C

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65. The heats of combustion of carbon and carbon monoxide are -393.5 and $-283.5 kJ mol^{-1}$ respectively. The heat of formation (in kJ) of carbon monoxide per mole is:

A. 676.5

B. -676.5

C. -110.5

D. 110.5

Answer: C

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66. Given $C_{(\text{graphite})} + O_2(g) \rightarrow CO_2(g)$,

$\Delta_r H^0 = -393.5 kJ \quad mol^{-1}$

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

$\Delta_r H^0 = -285.8 \text{ kJ } mol^{-1}$

$CO_2(g) + 2H_2O(1) \rightarrow CH_4(g) + 2O_2(g)$,

$\Delta_r H^0 = +890.3 kJ \quad mol^{-1}$

Based on the above thermochemical equations, the value of $\Delta_r H^0$ at at 298 K for the reaction

$C_{(\text{graphite})} + 2H_2(g) \rightarrow CH_4(g)$ will be:

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

B. $-144.0 kJmol^{-1}$

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

D. $+144.0 kJmol^{-1}$

Answer: A

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67. The bond energy of an $O - H$ bond is 109 K. cal mole^{-1}. When a mole of water is formed

A. 109 kcal is released

B. 218 kcal is released

C. 109 kcal is absorbed

D. 218 kcal is absorbed

Answer: B

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68. 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 $-200 kJmol^{-1}$. The bond dissociation energy of X_2 will be :

A. $100 kJmol^{-1}$

B. $200 kJmol^{-1}$

C. $400 kJmol^{-1}$

D. $800 kJmol^{-1}$

Answer: D

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69. For the reaction:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g), \Delta H = -571kJ$

bond enegry of $(H - H) = 435kJ$ and of $(O = O) = 498kJ$. Then, calculate the average bond enegry of $(O - H)$ bond using the above data.

A. 484

B. -484

C. 271

D. -271

Answer: A

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70. Formation of ozone takes place as $O_2(g) + O(g) \rightarrow O_3(g), \Delta H^\circ = -107.2 kJ$. Assuming $O = O$ bond energy as $498.8 kJmol^{-1}$, the average bond energy of ozone is

A. $391.6 kJmol^{-1}$

B. $606.0 kJmol^{-1}$

C. $107.2 kJmol^{-1}$

D. $302.6 kJmol^{-1}$

Answer: D

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71. Calculate the standard enthalpy change (in kJ mol^{-1}) for the reaction $H_2(g) + O_2(g) \rightarrow H_2O_2(g)$, given that bond enthalpy of H-H, O=O,O-H and O-O (in kJ mol^{-1}) are respectively 438, 498, 464 and 138.

A. -130

B. 65

C. $+130$

D. -334

Answer: A

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72. Enthalpy change for the reaction, $4H_{(g)} \rightarrow 2H_{2(g)}$ is -869.6 kJ

The dissociation energy of H-H bond is :

A. $+217.4kJ$

B. $-434.8kJ$

C. $-869.6kJ$

D. $+434.8kJ$

Answer: D

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73. Using the data provided, calculate the multiple bond energy ($kJ\text{mol}^{-1}$) 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}):

$2C(s)+H_2(g)\rightarrow C_2H_2(g), \Delta H=225kJ\text{mol}^{-1}$

$2C(s)\rightarrow 2C(g), \Delta H=1410kJ\text{mol}^{-1}$

$H_2(g)\rightarrow 2H(g), \Delta H=330kJ\text{mol}^{-1}$

A. 1165

B. 837

C. 875

D. 815

Answer: D

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74. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of $1:0.5:1$. ΔH 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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75. For the reaction $2H(g) \rightarrow H_2(g)$, the sign of ΔH and ΔS respectively are :

A. $+, \ -$

B. $+, \ +$

C. $-, \ -$

D. $-, \ +$

Answer: C

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76. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of $10dm^3$ to a volume of $100dm^3$ at $27^\circ C$ is

A. $35.8Jmol^{-1}K^{-1}$

B. $32.3Jmol^{-1}K^{-1}$

C. $42.3Jmol^{-1}K^{-1}$

D. $38.3Jmol^{-1}K^{-1}$

Answer: C

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77. If water kept in an insultated vessel at $-10^\circ C$ suddenly freezes, the entropy change of the system

A. decreases

B. increases

C. is zero

D. equals to that of the surroundings.

Answer: C

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78. The direct conversion of A to B is difficult. Hence it is carried out by the following shown path:

$\Delta S(A \rightarrow C) = 50e.\,u.$, $\Delta S(C \rightarrow D) = 30e.\,u,$

$\Delta S(B \rightarrow D) = 20e.\,u$ where e.u is entropy unit.

Then $\Delta S(A \rightarrow B)$,

A. $+100e.u.$

B. +60 e.u. `

C. $-100e.u.$

D. $-60e.u.$

Answer: B

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79. Given an idealgas is expanded adiabatically and irreversibley form volume V_1 to $V_2)$, then which one of the following is correct ?

A. ΔS (system) $= 0 \& \Delta S$ (surroundings) $= +ve$

B. ΔS (system) $= +ve \& \Delta S$ (surroundings) $= 0$

C. ΔS (system) $= 0 \& \Delta S$ (surroundings) $= 0$

D. ΔS (system) $= +ve \& \Delta S$ (surroundings) $= -ve$

Answer: a

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80. When you freeze water in your freezer to make ice cubes,the amount of order in the molecules ofwater increases. However , second law of thermodynamics says that the amount of order in the isolated system can only stay constant or decrease with time. How can thus making of ice violate second law ?

A. because water expands during ice formation

B. because ice formation takes place at $0^\circ C$

C. because ice issolid

D. because ice cubes do not constitute isolated system.

Answer: d

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81. For the process $H_2O(l) \rightarrow H_2O(g)$ at $T = 100^\circ C$ 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: B

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82. 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 (ΔS) in J^{-1} is

(1 L atm = 101.3 J)

A. 5.763

B. 1.013

C. -1.013

D. -5763

Answer: c

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83. The correct thermodynamic conditions for the spontaneous reaction at all temperature 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,c

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84. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f , the entropy change is given by

A. $\Delta S = nR\ln\left(\frac{p_f}{p_i}\right)$

B. $\Delta S = nR\ln\left(\frac{p_i}{p_f}\right)$

C. $\Delta S = nRT\ln\left(\frac{p_f}{p_i}\right)$

D. $\Delta S = nRT\ln\left(\frac{p_i}{p_f}\right)$

Answer: b

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85. Solutions A and B are both clear and colourles. When solution A is mixed with solution B, the temperature of the mixture increases and a yellow precipitate is observed. What can be concluded from these observations?

A. The reaction is thermodynamically favoured (spontaneous) at all temperatures

B. The reaction is thermodynamically favoured (spontaneous) only athigh temperature

C. The reaction is thermodynamically favoured (spontaneous) only at low temperature

D. The reaction is not thermodynamically favoured (spontaneous) at any temperature.

Answer: C

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86. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as :

$S_2(s) + 2O_2(g) \rightarrow 2SO_2(g), \Delta G = -544kJ$

$2Zn(s) + S_2(s) \rightarrow 2ZnS(s), \Delta G = -293$ kJ

$2Zn(s) + O_2(g) \rightarrow 2ZnO(s), \Delta G = -480$ kJ

Calculate the ΔG for the reaction:

$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$

A. $-731kJ$

B. $-787kJ$

C. $-534kJ$

D. $-554kJ$

Answer: a

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87. The incorrect expression among the following is

A. $K = e^{-\Delta G^\circ / RT}$

B. $\dfrac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

C. In isothermal process,

$$W_{\text{reversible}} = -nRT\ln.\left(\frac{V_f}{V_i}\right)$$

D. $\ln K = \dfrac{\Delta H^\circ - T\Delta S^\circ}{RT}$

Answer: D

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88. In which of the following reactions,standard reaction entropy change $(\Delta S^\circ)$is positive and standard Gibb,s energy change(ΔG°)decreases sharply with increasing temperature?

A. C(graphite) $+\frac{1}{2}O_2(g) \rightarrow CO(g0$

B. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

C. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

D. $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

Answer: A

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89. The following reaction is performed at 298 K ?

$2NO(g) + O_2(g) \Leftrightarrow 2NO_2(g)$

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K.

What is the standard free energy of formation of $NO_2(g)$ at 298 K ?

$\left(K_p = 1.6 \times 10^{12}\right)$

A. $R(298)\ln\left(6 \times 10^{12}\right) - 86600$

B. $86600 + R(298K)\ln\left(1.6 \times 10^{12}\right)$

C. $86600 - \dfrac{\ln\left(1.6 \times 10^{12}\right)}{R(298)}$

D. $0.5\left[2 \times 86,600 - R(298)\ln\left(1.6 \times 10^{12}\right)\right]$

Answer: d

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90. Which of the following thermodynamic relation is correct?

A. $dG = Vdp - SdT$

B. $dE = PdV + TdS$

C. $dH = \ -VdP + TdS$

D. $Dg = vDp + SdT$

Answer: a

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91. The densities of graphite and diamond at $298K$ are 2.25 and $3.31gcm^{-3}$, respectively. If the standard free energy difference (ΔG^0) is equal to $1895Jmol^{-1}$, the pressure at which graphite will be transformed into diamond at $298K$ is

A. $9.92 \times 10^8 Pa$

B. $9.92 \times 10^7 Pa$

C. $9.92 \times 10^6 Pa$

D. none of these

Answer: D

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92. In view of the signs of $\Delta_r G^0$ for the following reactions

$PbO_2 + Pb \to 2PbO, \Delta_r G^0 < 0$

$SnO_2 + Sn \to 2SnO, \Delta_r G^0 > 0$

Which oxidation state are more characteristic for lead and tin?

A. For lead $+4$, for tin $+2$

B. For lead $+2$, for tin $+2$

C. For lead $+4$ for tin $+4$

D. For lead $+2$, for tin$+4$

Answer: d

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93. The values of ΔH and ΔS for the reaction,

$C_{\text{graphite}} + CO_2(g) \rightarrow 2CO(g)$

are $170KJ$ and $170JJK^{-}$ respectively. This reaction will be spontaneous at

A. 910 K

B. 1110K

C. 510K

D. 710 K

Answer: B

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94. For a given reaction, $\Delta H = 35.5kJmol^{-1}$ and $\Delta S = 83.6JK^{-1}mol(-1)$. The reaction is spontaneous at : (Assume that ΔH and ΔS do not vary with temperature)

A. $T < 425K$

B. $T > 425K$

C. All temperatures

D. $T > 298K$

Answer: B

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95. As O_2 (l) is cooled at 1 atm pressure , it freezes to form solid I at 54.5 K. At a lower temperature , solid rearrange to solid II, which has a different crystal that for the phase transition solid to slid II , $\Delta H = -743.1 J mol^{-1}$ and $\Delta S = -17.0 J K^{-1} mol^{-1}$. At what temperature are solids I and II in equilibrium ?

A. 2.06K

B. 31.5K

C. 43.7 K

D. 53.4 K

Answer: C

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96. At the sublimation temperature, for the process $CO_2(S) \rightarrow CO_2(g)$

A. ΔH, ΔS andΔG are all positive

B. $\Delta H > 0$, $\Delta S > 0$ and $\Delta G < 0$

C. $\Delta H < 0$, $\Delta S > 0$ and $\Delta G < 0$

D. $\Delta H > 0$, $\Delta S > 0$ and$\Delta G = 0$

Answer: D

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97. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when

A. T_e is 5 times T

B. $T = T_e$

C. $T_e > T$

D. $T > T_e$

Answer: D

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98. A chemical reaction is spontancous at $298K$ but non spontaneous at $350K$. Which one of the following is true for the reaction ?

A. $\begin{array}{ccc} \Delta G & \Delta H & \Delta S \\ - & - & + \end{array}$

B. $\begin{array}{ccc} \Delta G & \Delta H & \Delta S \\ + & + & + \end{array}$

C. $\begin{array}{ccc} \Delta G & \Delta H & \Delta S \\ - & + & - \end{array}$

D. $\begin{array}{ccc} \Delta G & \Delta H & \Delta S \\ - & - & - \end{array}$

Answer: D

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99. The value of $1og_{10}$ K for a reaction $A \Leftrightarrow B$ is:

(Given,

$\Delta_r H^\circ_{298K} = -54.07kJ \quad mol^{-1}, \Delta_r S^\circ_{298K} = 10JK^{-1} \quad mol^{-1}$ and $R =$

)

A. 5

B. 10

C. 95

D. 100

Answer: b

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100. ΔG° for a reaction is $46.06 kcal mol^{-}$. K_P for the reaction at $300K$ is

A. 10^{-8}

B. $10^{22.22}$

C. $10^{-33.33}$

D. none of these

Answer: C

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101. Reaction that have standard free energy changes less than zero always have equilibrium constant equal to

A. unity

B. greater than unity

C. less than unity

D. zero

Answer: B

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102. Standard entropies of X_2, Y_2 and XY_3 are 60, 30 are $50JK^{-1}mol^{-1}$ respectively. For the reaction $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \Leftrightarrow XY_3, \Delta H = -30kJ$ to be at equilibrium, the temperature should be :

A. 500K

B. 750 K

C. 1000K

D. 1250 K

Answer: b

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103. For the reaction:

$X_2O_4(l) \rightarrow 2XO_2(g)$

$\Delta U = 2.1 cal, \Delta S = 20 \text{cal} K^{-1} \text{at} 300K$

Hence ΔG is

A. 2.7 kcal

B. $-2.7 kcal$

C. 9.3 kcal

D. $-9.3 kcal$

Answer: b

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104. Some subtances posses some residual entropy even at absolute zero.

This is because

A. they contain some impurities

B. they attain different orientations of moleculeseven at absolute zero

C. it is difficult to attain absolute zero of temperature

D. all the above factors are responsible

Answer: B

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105. When one mole of a monoatomic ideal gas at initial temperature T K expands adiabatically from 1 litre to 2litres , the final temperature in Kelvin would be

A. T

B. $\dfrac{T}{2^{2/3}}$

C. $T-\dfrac{2}{3\times 0.0821}$

D. $T+\dfrac{2}{3\times 0.0821}$

Answer: b

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106. When 1 mol of $CO_2(g)$ occupying a volumeof 10 L at 27° isallowed to expand under adiabatic conditions, temperature fallsto $-123^\circ C$. Hence, final volume of the gas will be :

A. 20L

B. 40L

C. 60L

D. 80L

Answer: d

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107. 1 mol of NH_3 gas$(\gamma = 1.33)$ at $27^\circ C$is allowed to expand adiabatically so that the final volume becomes 8 times. Work done will be

A. 450 cal

B. 1800 cal

C. 900 cal

D. 300 cal

Answer: C

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108. Temperature of1 mole of a gas is increased by 1° at constant pressure. Work done is

A. 2 cal

B. 3 cal

C. 4 cal

D. 5 cal

Answer: a

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109. For the reaction , $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2(l), \Delta C_p=32JK^{-1}, \Delta H$ at $27^\circ C=-285.8kJmol^{-1}. W\widehat{w}illbethevalueof$Delta H at 127@degreeC` ?

A. $-289.0kJmol^{-1}$

B. $-282.6kJmol^{-1}$

C. $-317.0kJmol^{-1}$

D. $-253.8kJmol^{-1}$

Answer: b

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110. Two separate experiments were carried out involving adiabatic reversible expansion, taking monoatomic gas in one case and a diatomic gas in the second case.In each case, the initialtemperature wasT_i and expansion was from volume $V_1$to volume V_2. The final temperatures attained were T_M formonoatomic gas and $T_9D)$ for diatomic gas. Then

A. $T_M = T_D < T_i$

B. $T_M < T_D < T_i$

C. $T_D > T_M > T_i$

D. $T_D < T_M < T_i$

Answer: b

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111. Efficiency of Carnot engine is $100\ \%$ if

A. sing is at$0^\circ C$

B. sink is at 0K

C. source is at $273^{\circ} C$

D. source is at $100^{\circ} C$

Answer: b

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112. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statement is correct ?

A. $(T_f)_{rev} = (T_f)_{irrev}$

B. $T_f = T_i$ for both reversible and irreversible processes

C. $(T_f)_{irrev} > (T_f)_{rev}$

D. $T_f > T_i$ for revrsible process but $T_f = T_i$ for irreversible processes.

Answer: b

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113. The enthalpy of hydrogenation of cyclohexene is $-119.5KJ$. If resonance energy of benzene is $-150.4KJMol^{-1}$, its enthalpy of hydrogenation of benzene would be

A. $-269.9kJmol^{-1}$

B. $-358.5kJmol^{-1}$

C. $-508.9kJmol^{-1}$

D. $-208.1kJmol^{-1}$

Answer: d

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114. Water is supercooled to $-4^{\circ}C$. The enthalpy (H) is

A. same as ice at $-4^{\circ}C$

B. more than ice at $-4^{\circ} C$

C. same as ice at $0^{\circ} C$

D. less than ice at $-4^{\circ} C$

Answer: d

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115. Enthalpy is equal to

A. $T^{2}\left[\frac{\partial(G/T)}{\partial T}\right]_{P}$

B. $-T^{2}\left[\frac{\partial(G/T)}{\partial T}\right]_{P}$

C. $T^{2}\left[\frac{\partial(G/T)}{\partial T}\right]_{V}$

D. $-T^{2}\left[\frac{\partial(G/T)}{\partial T}\right]_{V}$

Answer: b

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116. Consider the following liquid-vapour equilibrium.

$\text{Liquid} \Leftrightarrow \text{Vapour}$

Which of the following relations is correct?

A. $\frac{d\ln P}{dT^2} = -\frac{\Delta H_v}{T^2}$

B. $\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT^2}$

C. $\frac{d\ln S}{dT^2} = \frac{\Delta H_v}{RT^2}$

D. $\frac{d\ln S}{dT} = -\frac{\Delta H_v}{RT}$

Answer: b

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117. The standard state Gibbs free energies of formation of) C(graphite and C(diamond) at T = 298 K are

$\Delta_f G^\circ[\text{C(graphite)}] = 0kJmol^{-1}$

$\Delta_f G^\circ[\text{C(diamond)}] = 2.9kJmol^{-1}$

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. 58001 bar

B. 1450 bar

C. 14501 bar

D. 29001 bar

Answer: c

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118. For the adiabatic expansion of an ideal gas:

A. $PV^{\gamma} =$ constant

B. $TV^{\gamma-1} =$ constant

C. $TP^{1-\gamma} =$ const.

D. $TP^{1/\gamma} =$ constant

Answer: a,b

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119. In which of the following entropy increases?

A. Rusting of iron

B. Melting of ice

C. Crystallization of sugar from solution

D. Vaporisation of camphor

Answer: a,b,d

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120. The criteria for spontaneity of a process is/are

A. $(dG)_{T,P} < 0$

B. $(dE)_{S,V} < 0$

C. $(dH)_{S,P} < 0$

D. $(dS)_{E,V} < 0$

Answer: a,b,c,d

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121. Which of the following statement are not correct ?

A. The standard value of absolute entropy of elementary substances is taken as zero.

B. Work done in isothermal expansion is greater than that in the adiabatic expansion for same increase in volume.

C. During adiabatic expansion of a real gas,there is no change in the enthalpy of the system.

D. Expansion against vaccum is very large and hence work done is also very large

Answer: a,d

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122. Which of the following relationship are correct?

A. $\frac{\Delta H - \Delta E}{\Delta n \times T} =$ Constant

B. $\Delta G = \ - T\Delta S_{\text{Total}}$

C. $K = e^{- \Delta G^{\circ} / RT}$

D. $\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_p$

Answer: a,b,c,d

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123. Which of the following reactions is an endothermic reaction?

A. Combustion of methane

B. Decomposition of water

C. Dehydrogenation of ethaneto ethene

D. Conversion of graphite to diamond

Answer: b,c,d

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124. Among the following , the state funcation (s) is (are)

A. Internal energy

B. Irreversible expansion work

C. Reversible expansion work

D. Molar enthalpy

Answer: a,d

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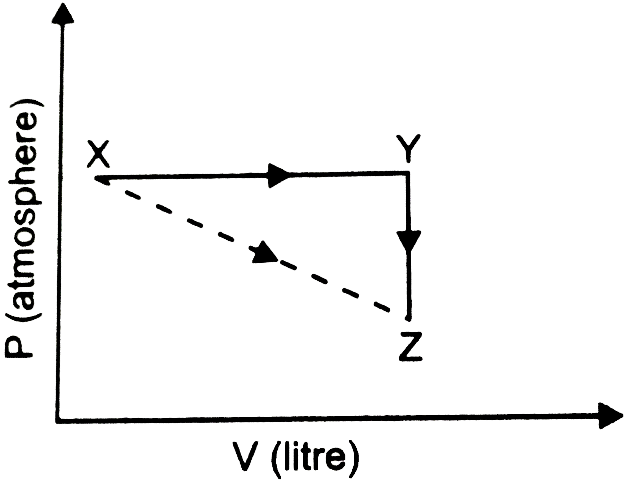
125. For an ideal gas,consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure.Which of the following choice (s) is (are)correct? [take ΔS as change in entropy andw as work done.]



A. $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$

B. $w_{x \rightarrow z} = w_{x \rightarrow y} + w_{y \rightarrow z}$

C. $w_{x \rightarrow y \rightarrow z} = w_{x \rightarrow y}$

D. $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

Answer: A::C

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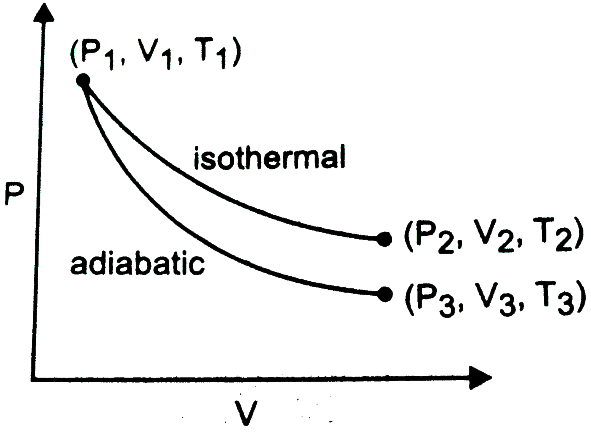
126. The reversible expansion of an ideal gas under adiabatic and isothermal consition is shown in the figure.Which of the folloiwng statement(s) is (are) correct ?



A. $T_1 = T_2$

B. $T_3 > T_1$

C. $w_{\text{isothermal}} > w_{\text{adiabatic}}$

D. $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

Answer: a,c,d

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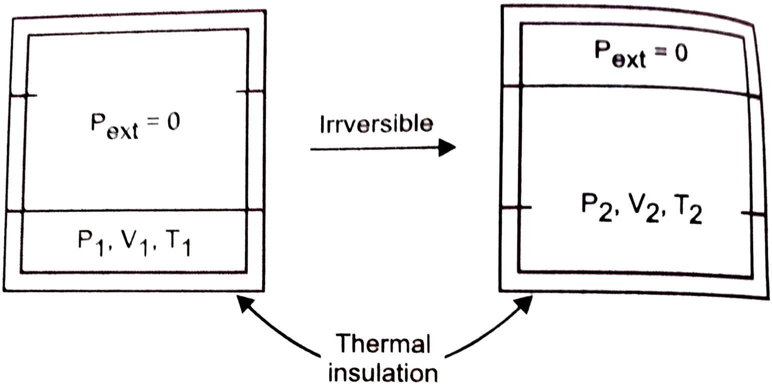
127. An ideal gas in a thermally insulated vesselat internal pressure $= P_1$, volume $= V_1$and absolute temperature $= T_1$ expands irreversibly against zero external pressure, as shoen in the diagram . The final internal pressure, volume and absolute temperature ofgas are P_2, V_2 and T_2 respectively. For this expansion.



A. $q = 0$

B. $T_2 = T_1$

C. $P_2V_2 = P_1V_1$

D. $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

Answer: A::B::C

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128. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant Kin terms of change in entropy is described by

A. With increase in temperature, the value of K for endothermic reaction increase because unfavourable change in entropy of the surroundings decreases

B. With increase temperature , the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases.

C. With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is positive.

D. With increase in temperature , the value of K for exothermic reaction decreasesbecause the entropy change of the system is positive.

Answer: a,b

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129. 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. The work done by the gas is less when it is expanded reversibly from V_1 to V_2under adiabatic conditions as compared to that when expanded reversibley from $V_1$to V_2 under isothermal conditions.

B. The change in internal energy of the gas is (i) zero, if it isexpanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adaibatic conditions with $T_1 \neq T_2$

C. If the expansion is carried out freely , it is simulataneously both isothermal as well as adiabatic

D. The work done on the gas is maximum irreveribly from (p_2, V_2) to (p_1, V_1) against constant pressurep_1.

Answer: a,c,d

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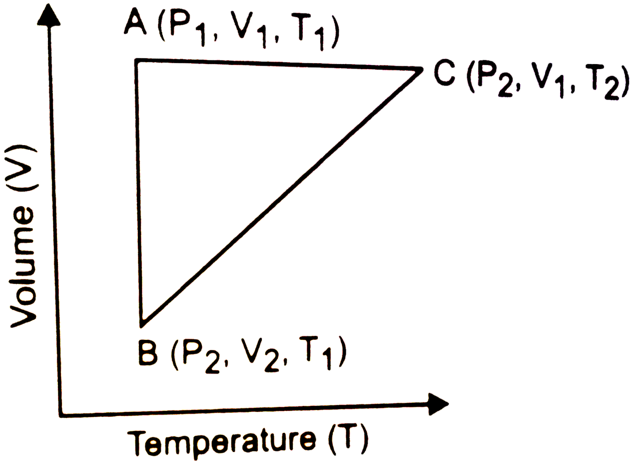
130. A reversible cyclic process for an ideal gas is shown below. Here P,V and T are pressure, volume and temperature respectively. The thermodynamic parameters of q,w,H and U are heat, work , enthalpy and internal energy respectively.



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 $q_{AC} = \Delta H_{AC}$

D. $q_{BC} = \Delta U_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

Answer: b,c,d

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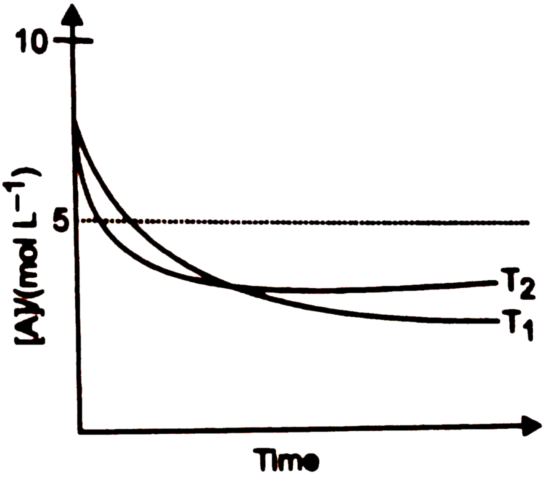
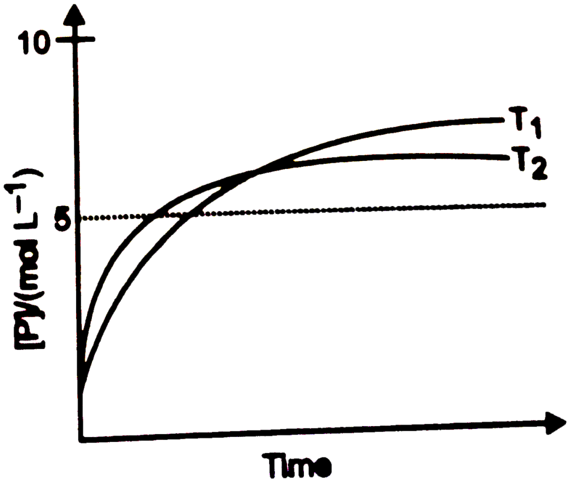
131. For a reaction $A \Leftrightarrow P$,the plots of[A] and[P] with time at temperature T_1 and T_2 are given below :





If$T_2 > T_1$, the correct statement (s) is (are) (Assume ΔH° and ΔS° are independent of temperature andratio ofln K at T_1 to lnK T_2 is greater than T_2/T_1 . Here, H,S,G andK are enthalpy , entropy, Gibbs energy and equilibrium constant respectively)

A. $\Delta H^{\circ} < 0, \Delta S^{\circ} < 0$

B. $\Delta G^{\circ} < 0, \Delta H^{\circ} > 0$

C. $\Delta G^{\circ} < 0, \Delta S^{\circ} < 0$

D. $\Delta G^{\circ} < 0, \Delta S^{\circ} > 0$

Answer: a,c

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Comprehension 1

1. In a fuel celll, methanol is used as a fuel and O_2 is used as oxidizer. The standard enthalpy of combustion of methanol is -726 kJ mol^{-1}. The standard free energies of formation of $CH_3OH(I), CO_2(g)$ and $H_2O(I)$ are -166.3, -394.4 and -237.1 kJ mol^{-1} respectively.

The standard free energy change of the reaction will be

A. $-597.8kJmol^{-1}$

B. $-298kJmol^{-1}$

C. $-465.2kJmol^{-1}$

D. $-702.3kJmol^{-1}$

Answer: d

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Comprehension 2

1. In a fuel cell (device used for producing electricity directly from a chemical reaction)methanol is used as a fuel and oxygen gas is used asan oxidizer. The standard enthalpy of combustion of methanol is $-721kJmol^{-1}$. The standard free energiesof formation of $CH_3OH(l, CO_2(g)$ and $H_2O(l)$ are- 166.3 , -394.4 and $-237.1kJmol^{-1}$ respectively.

The efficiency of the fuel cell will be

A. $96.7\,\%$

B. $66.2\,\%$

C. $41.3\,\%$

D. $85.1\,\%$

Answer: a

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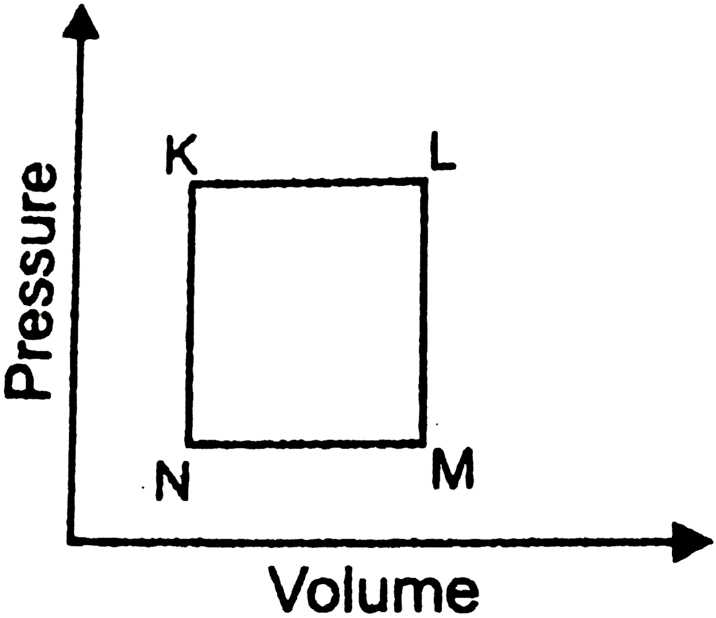
2. A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



The succedding operations that enable the transformation of state are

A. Heating, cooling,heating , cooling

B. Cooling, heating, cooling, heating

C. Heating, cooling, cooling, heating

D.

Answer: c

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Comprehension 3

1. In a fuel cell (device used for producing electricity directly from a chemical reaction)methanol is used as a fuel and oxygen gas is used asan oxidizer. The standard enthalpy of combustion of methanol is $-721kJmol^{-1}$. The standard free energiesof formation of $CH_3OH(l, CO_2(g)$ and $H_2O(l)$ are- 166.3 , -394.4 and $-237.1kJmol^{-1}$ respectively.

The standard internal energy change of the cell reaction will be

A. $-727.24kJmol^{-1}$

B. $-724.76kJmol^{-1}$

C. $-728.48kJmol^{-1}$

D. $-723.\ 42kJmol^{-1}$

Answer: b

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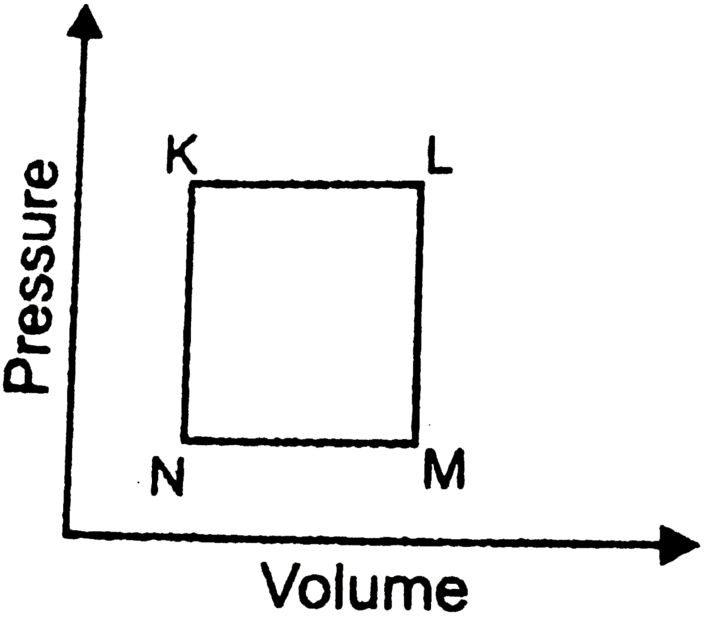
2. A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



The pair of isochoric processes among the transformation of 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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Comprehension 4

1. In a fuel cell (device used for producing electricity directly from a chemical reaction)methanol is used as a fuel and oxygen gas is used asan oxidizer. The standard enthalpy of combustion of methanol is $-721kJmol^{-1}$. The standard free energiesof formation of $CH_3OH(l, CO_2(g)$ and $H_2O(l)$ are- 166.3 , -394.4 and $-237.1kJmol^{-1}$ respectively.

The standard entropy change accopanying the cell reaction willbe

A. $+24.11JK^{-1}$

B. $-24.1JK^{-1}mol^{-1}$

C. $+19.1JK^{-1}mol^{-10}$

D. $-19.1JK^{-1}mol^{-1}$

Answer: d

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INTEGER TYPE QUESTIONS

1. The number of intensive properties among the following is Temperature, Pressure, Volume , Heat capacity ,Density ,pH of a solution , EMF of a cell,Entropy, Free energy,Enthalpy , Surface tension, Viscosity , Boiling point

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2. The number of properties which are state function among the following is Pressure, Volume , Temperature,Heat, Work , Entropy, Enthalpy , Free energy, Internal energy,C_p andC_v.

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3. A gas expands against a constant external pressure so that the work done is $607.8J$. The work done in litre atmosphere is

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4. The number of moles of an ideal gas that should be taken in a closed vessel of 30L capacity at a temperature of $27^{\circ}C$ so that the pressure exerted by the gas on the walls of the container is 4.1 atmosphere is

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5. If for a particular reaction, the difference in the heat evolved when the reaction is carried out at constant pressure and that at constant volume at $27^{\circ}C$ is nearly $5kJmol^{-1}$, then the difference in the number of moles of gaseous eactants and products is

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6. The ratio ofC_p value of a triatomic gas to the C_v value of a monoatomic gas is

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7. The enthalpy of neutralisation of 0.4 M H_2SO_4 will be how many times the enthalpy of neutralisation of 0.1 M HCl ?

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8. In a constant volume calorimeter, $3.5g$ of a gas with molecular weight 28 was burnt in excess oxygen at $298.0K$. The temperature of the calorimeter was found to increase from $298.0K \rightarrow 298.45K$ due to the combustion process. Given that the heat capacity of the calorimeter is $2.5kJK^{-1}$, find the numerical value for the enthalpy of combustion of the gas in $kJmol^{-1}$

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NUMBERICAL VALUE TYPE QUESTIONS (in Decimal Notation)

1. For the following question, enter the correct numerical value, (in decimal - notation , truncated /rounded - off to the second decimal place, e.g., 6.50, 7.00, - 0.33, 30.27, - 127.30) using the mouse and the onscreen virtual numeric keypad in the place designated to enter the answer.

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ASSERTION - REASON TYPE QUESTIONS (TYPE 1)

1. Statement -1 . Entropy of all elements is zero at 0K.

Statement -2. Standard entropy of all elements is greater than zero.

A. Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation of Statement-1

B. Statement-1 is True Statement-2 is True, Statement-2 is NOT a correct explanation for Statement -1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is False

Answer: D

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2. Statement-1. Entropy is not a state function because its value depends upon the conditions of temperature and pressure.

Statement -2. A state function depends only on the initial and the final states of the system and is independent of the path.

A. Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation of Statement-1

B. Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement -1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True

Answer: d

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3. Statement-1.During isothermal expansion of an ideal gas, there is no change in the internal energy.

Statement -2.During isothermal expansion of an ideal gas , as temperature remains constant, no heat enters or leaves the system.

A. Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation of Statement-1

B. Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement -1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True

Answer: c

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4. Statement -1. If free energy change of the system is negative, the process is spontaneous even if the total free energy change of the system and the surroundings is positive.

Statement -2. The spontaneity of a process depends only on the free enegy change of the system.

A. Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation of Statement-1

B. Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement -1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True

Answer: a

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5. Statement -1. A compound is formed from its elements only if free energy of formation of the compound is positive .

Statement -2. Many photochemical reactions have positive value for the free energy change.

A. Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation of Statement-1

B. Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement -1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True

Answer: d

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6. Statement-1. Enthalpy change at constant pressure is always greater than enthalpy change at constant volume for any reaction.

Statement -2. Work is done by the system at constant pressure for a given change in volume but no work is done by the system at constant volume.

A. Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation of Statement-1

B. Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement -1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True

Answer: d

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7. Statement -1: For every chmical reaction at equilibrium , standard Gidds energy of reaction is zero

Statement-2: At constant temperature and pressure , chemical reactions are spontaneious in the direction of decreasing gibbs energy.

A. Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation of Statement-1

B. Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement -1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True

Answer: d

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8. Statement-1: There is a natural asymmetry between work to heat and converting heat to work .

Statement-2: No process is possible in which the sole result is the absorption of heat from a reservoir and its complaete conversion into work .

A. Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation of Statement-1

B. Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement -1.

C. Statement-1 is True, Statement-2 is False.

D. Statement-1 is False, Statement-2 is True

Answer: a

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ASSERTION - REASON TYPE QUESTIONS (TYPE 2)

1. Assertion. Heat energy is completely transformed into work during the isothermal expansion of an ideal gas.

Reason . During an isothermal process, the change in internal energy of a gas due to decrease in pressure is nullified by the change due to increase in volume.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: A

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2. Assertion. The temperature of a gas does not change when it undergoes an adiabatic expansion.

Reason . During an adiabatic expansion of a real gas, the internal energy of the gas remains constant.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: d

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3. Assertion: The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

Reason: The volume occupied by the molecules of an ideal gas is zero.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: c

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4. Assertion. When a real gas expands adiabatically , the decrease in internal energy is equalto the adiabatic work done by the system.

Reason. During adiabatic expansion,no heat entersor leaves the system.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: a

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5. (A) For reaction $2NH_3(g) \rightarrow N_2(g) + 3H_2(g), \qquad \Delta H > \Delta E$

(R) Enthalpy change is always greater than internal energy change.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: c

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6. Assertion. ForCO_2 , the ratio of the molar heat capacities (C_p/C_v) is 1.40.

Reason . For $CO_2, C_v = \frac{5}{2}R$ and $C_p = \frac{7}{2}R$

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: d

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7. Assertion. The heat of combustion found by using bomb calorimeter gives the value of internal energy change ΔU and not enthalpy change ΔH.

Reason.In a closed vessl,$\Delta U = \Delta H$ only if pressure inside the calorimeter remains constant.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: a

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8. Statement - The water pouch of instant cold pack for treating athletic injuries breakes when squeezed and NH_4NO_3 dissolves lowering the temperature.

Explanation - Addition of non-volatile solute into solvent results into depression of freezing point of solvent.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: b

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9. Assertion: The enthalpy of formation of gaseous oxygen molecules at $298K$ and under1 atm is zero.

Reason: The entropy of formation of gaseous oxygen molecules under the same condition is zero.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: C

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

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

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: B

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11. Assertion.The bond enthalpy of C-H bondin CH_4 is nearly 416 k J mol^{-1}

Reason . First , second, third and fourth C-H bonds in CH_4 have same bond enthalpy.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: c

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

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

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: a

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13. Assertion (A): Enthalpy of graphite is lower than that of diamond.

Reason (R) : Entropy of graphite is lower than that of diamond.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: b

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14. Assertion :- Water in liquid state is more stable than ice at room temperature.

Reason :- Water in liquid from has higher entropy than ice.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: a

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15. Assertion. Chlorine when solidifies doe not have zero entropy even at absolute zero.

Reason. Chlorine is a pungent smelling gas and it is difficult to solidify it.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: b

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16. Assertion: Molar entropy of vaporization of water is different from ethanol.

Reason: Water is more polar than ethanol.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: C

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17. Assertion : A process for which ΔS_{syst} as well as $\Delta H > 0$, passes from non spontaneous to spontaneous state as temperature is increased.

Reason : At higher temperature, $T\delta S$ exceeds ΔH

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: a

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

Reason (R) : Spontaneous reactions are invariably exothermic.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: C

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19. Assertion. At 298 K and 1 atm pressure, solids do not have any entropy but liquids and gases have definite values of entropy.

Reason . At 298 K and 1 atm pressure, particle in a solid are fixed and do not have translatory, rotatory or vibraory motion whereas in liquids and gases, molecules have all the three types of motion.

A. If both A and R are true,andR is the true explanation of A.

B. If both A and R are true,but R is not the true explanation of A.

C. If A is true, but R is false

D. If both A and R are false.

Answer: d

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MULTIPLE CHOICE QUESTION (BASED ON PRACTICAL CHEMISTRY)

1. 50mL of 0.10 B $Ba(OH)_2$ is added to 50 mLof $0.10 M H_2SO_4$. The rise in temperature isΔT_1 . If experiment is replaced by taking 100 mL of each solution, the rise in temperature is$\Delta T_{92})$. Then

A. $\Delta T_1 = 2\Delta T_1$

B. $\Delta T_2 = 2\Delta T_1$

C. $\Delta T_2 = \Delta T_1$

D. $\Delta T_2 = 4\Delta T_1$

Answer: C

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2. Enthalpies of formation of $K^{+}(aq), Cl^{-}(aq)$ and $KCl(s)$ are $-60.0, \ -40.0$ and -104.0 kcalmol^{-1}. If one mole of KCl(s) is dissolved in large excess of water at $25^{\circ}C$, the enthalpy of solution will be

A. $-4.0kcalmol^{-1}$

B. $+4.0kcalmol^{-1}$

C. $-20.0kcalmol^{-1}$

D. $-20.0kcalmol^{-1}$

Answer: b

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3. 500 mL of0.1 MH_2SO_4 was added into 1 L of 0.1 M NaOH solution. The heat evolved was x calories. If further 500 mL of H_2SO_4 is added into the solution, now heat evolved will be

A. $x cal$

B. 2 x cal

C. zero

D. $x / 2cal$

Answer: c

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