

= $-2.303 \times 2 \times 298 \times \log 50/15 = -1436$ calories.

Ex Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 to 1 atm at a constant temperature of 273 K. The gas behaves ideally will there be any change in internal energy? Also, calculate q .

Sol. We have, $W = -2.303 nRT \log P_1/P_2$

n = number of moles of hydrogen = 5 moles.

Thus $W = -2.303 \times 5 \times 273 \times \log 20/1 = -8180$ calories.

further; the change in state of the system is from a gas to a gas and therefore, at constant temperature, internal energy will not change i.e., $\Delta E = 0$.

Again, $q = \Delta E - W = 0 - (-8180) = 8180$ calories.

Ex A liquid of volume of 100 L and at the external pressure of 10 atm it is confined inside an adiabatic bath. external pressure of the liquid is suddenly increased to 100 atm and the liquid gets compressed by 1 L against this pressure then find (i) work (ii) Δu (iii) ΔH

Sol. work done = $-100 \times -1 = 100$ lit atm

$\Delta q = 0$ $\Delta w = \Delta u \Rightarrow 100 = \Delta u$

$\Delta H = \Delta u + (P_1 V_2 - P_1 V_1)$

= $100 + (100 \times 99 - 100 \times 10) = 100 + 100 \times 89 = 9000$ lit atm.

EX. For Ag, $\bar{C}_P$ ($\text{JK}^{-1} \text{mol}^{-1}$) is given by $24 + 0.006 T$. Calculate ΔH if 3 mol of silver are raised from 27°C to its melting point 927°C under 1 atm pressure.

$$\Delta H = \int_{T_1}^{T_2} C_P dT = \int_{T_1}^{T_2} (24 + 0.006T) dT$$

Sol.

$\Delta H = 24 (T_2 - T_1) + \frac{1}{2} 0.006 (T_2^2 - T_1^2) \text{ J mol}^{-1}$

For 3 mol, $\Delta H = 76950$

EX. What is the work done against the atmosphere when 25 g of water vaporizes at 373 K against a constant external pressure of 1 atm? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 42.2 kJ/mol , what is the change of internal energy in the above process?

(A) 1294.0 cal, 1247.6 cal (B) 921.4 cal, 1107.4 cal
(C) 1029.4 cal, 12470.6 cal (D) 1129.3 cal, 10207 cal

Sol. Mole of $\text{H}_2\text{O} = 1.39$

$Pv = nRT \Rightarrow 1 \times v = 1.39 \times 0.082 \times 373 \Rightarrow v = 42.80$.

$w = P_{\text{ext}} \cdot dv = 1 \times [42.80] \text{ atm} \times \text{lit.} = -42.80 \times 101.325 \text{ J} = -42.80 \times 101.325/4.2 \text{ cal} = 1024.8 \text{ cal.}$

$\Delta H = \Delta E + [P\Delta v] = 9720 \times 1.39 + 1024.8 = 12470.6 \text{ cal/s.}$

ex. There is 1 mol liquid (molar volume 100 ml) in an adiabatic container initial, pressure being 1 bar Now the pressure is steeply increased to 100 bar, and the volume decreased by 1 ml under constant pressure of 100 bar. Calculate ΔH and ΔE . [Given 1 bar = 10^5 N/m^2] [JEE 2004,2]

(A) $\Delta E = 0 \text{ J}$, $\Delta H \neq 0 \text{ J}$ (B) $\Delta H = 0 \text{ J}$, $\Delta E = 10 \text{ J}$

(C) $\Delta E = 20 \text{ J}$, $\Delta H = 890 \text{ J}$ (D) $\Delta E = 0 \text{ J}$, $\Delta H = 10 \text{ J}$

sol.B

Since the process under adiabatic condition

$q_p = 0$, $\Delta H = q_p = 0$

now $\Delta E = \Delta w$ as $q_p = 0$

= $-P_{\text{ext}} \Delta v = -100 \times -1 \text{ bar ml} = 10 \text{ J}$

SECTION (C) : RELATION BETWEEN ΔH & ΔU

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

SOL: $\Delta H = \Delta E + \Delta n gRT$

$41 \text{ kJ mol}^{-1} = \Delta E + (1) \times 8.3 \times 10^{-3} \times 373$

$\Delta E = 37.904 \text{ kJ mol}^{-1}$

SECTION (D) MOLAR HEAT CAPACITY

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

SOL: Atomic weight of Al = 27

the heat capacity required to raise the temperature of 27g Al through 1 K is 24 Joules

for 60 g Al = $60 \times 24/27 = 1.066 \text{ kJ}$

EX. When a certain amount of ethylene was burnt 6226 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of O_2 (at NTP) that entered in the reaction is

(A) 296.5 ml (B) 296.5 litre (C) 6226 x 22.4 litre (D) 22.4 litre

Sol. (B) $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$

Thus, $V_{\text{O}_2} = 6226 \times 3 \times 22.4/1411 = 296.5 \text{ litre}$

EX: Assume that for a domestic hot water supply 150 kg of water per day must be heated from 10°C to 65°C and gaseous fuel propane C_3H_8 is used for this purpose. What moles & volume of propane (in litre at STP) would have to be used for heating domestic water. ΔH for combustion of propane is $-2050 \text{ kJ mol}^{-1}$ & specific heat of water is $4.184 \times 10^{-3} \text{ kJ/g}$.

Solution: Heat taken up by water = $m \Delta T$

= $150 \times 103 \times 4.184 \times 10^{-3} \times 53 = 34518 \text{ kJ}$

2050 kJ heat is provided by 1 mole C_3H_8

34518 kJ heat is provided by = $34518/2050$

= 16.838 mole of C_3H_8

Volume of C_3H_8 at NTP = $16.838 \times 22.4 \text{ litre} = 3.77 \times 10^2 \text{ litre}$

EX. A thermally isolated vessel contains 100 g of water at 0°C .

When air above the water is pumped out, some of the water freezes and some evaporates at 0°C itself. Calculate the mass of the ice formed such that no water is left in the vessel. Latent heat of vaporization of water at 0°C = $2.10 \times 10^6 \text{ J/kg}$ and latent of fusion of ice = $3.36 \times 10^5 \text{ J/kg}$.

Sol. Total mass of the water = $M = 100 \text{ g}$

Latent heat of vaporization of water at 0°C = $L_1 = 21.0 \times 10^5 \text{ J/Kg}$

= Latent heat of fusion of ice = $L_2 = 3.36 \times 10^5 \text{ J/Kg}$

Suppose, the mass of the ice formed = m

Then the mass of water evaporated = $M - m$

Heat taken by the water in freezing = mL_2

Thus, $mL_2 = (M - m)L_1$ or $m = 86 \text{ g}$

EX. 1 mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find ΔH and ΔE if the latent heat of fusion of ice is 80 cal/g and latent heat of vaporisation of liquid water at 0°C is 596 cal/g and the volume of ice in comparison to that of water (vapour) is neglected.

Sol. No. of mole = 1, $T = 273 \text{ K}$.

$Pv = nRT \Rightarrow (4.6/760)v = 1 \times 0.82 \times 273$

$v = 3699 \text{ lit} = [3700 \text{ lit}]$

latent heat of fusion = 80 cal/gram

Latent heat of vaporisation = 596 cal/gram

$\Delta H = 80 \times 18 + 596 \times 18 = [80 + 596] \times 18 = 12168 \text{ cal}$

$\Delta H = \Delta E - P[V_2 - V_1]$

$12168 = \Delta E + (4.6/760) [3700 - 1] \times (101.325/4.2)$

$\Delta E = 12168 - 540.72 = 11627.28 \text{ cal.}$

SECTION (E) ENTHALPY OF NEUTRALIZATION

EX. Enthalpy of neutralization of HCl by NaOH is -57.1 kJ/mol and by NH_4OH is -51.1 kJ/mol . Calculate the enthalpy of dissociation of NH_4OH .

Sol. Given that

$\text{H}^+(\text{aq}) + \text{NH}_4\text{OH}(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\ell) \Delta H = -51.1 \text{ kJ/mole}$

We may consider neutralization in two steps.

(i) Ionization: $\text{NH}_4\text{OH}(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \Delta H_1 = ?$

(ii) Neutralization,

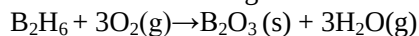
$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell) \Delta H_2 = -57.1 \text{ kJ/mole}$

Thus, $\Delta H = \Delta H_1 + \Delta H_2$

The heat of combustion of CO(g) is

(A) 68 kcal (B) -68 kcal (C) + 48 kcal (D) -48 kcal

54. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,



From the following data, calculate the enthalpy change for the combustion of diborane

i) $2\text{B}(\text{s}) + (3/2)\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s})$; $\Delta H = -1273 \text{ kJ mol}^{-1}$.

ii) $\text{H}_2(\text{g}) + (1/2)\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$; $\Delta H = -286 \text{ kJ mol}^{-1}$.

iii) $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$; $\Delta H = 44 \text{ kJ mol}^{-1}$.

iv) $2\text{B}(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{B}_2\text{H}_6(\text{g})$; $\Delta H = 36 \text{ kJ mol}^{-1}$.

55. Calculate the enthalpy of combustion of propene if bond energies of C-C, C-H, C=O, O=O & O-H bonds are 347, 414, 741, 498, & 464 kJ/mol respectively.

SECTION (J) BOND DISSOCIATION ENERGY

56. The enthalpy of combustion of $\text{H}_2(\text{g})$ at 298 K to give $\text{H}_2\text{O}(\text{g})$ is - 249 kJ mol⁻¹ and bond enthalpies of H-H and O=O are 433 kJ mol⁻¹ and 492 kJ mol⁻¹, respectively. The bond enthalpy of O-H is

(A) 464 kJ mol⁻¹ (B) - 464 kJ mol⁻¹

(C) 232 kJ mol⁻¹ (D) -232 kJ mol⁻¹

57. The bond energy enthalpies of H-H and C-Cl are 430 and 242 kJ mol⁻¹. $\Delta H_f(\text{HCl})$ is - 91 kJ mol⁻¹, the bond enthalpy of HCl would be

(A) - 214 kJ mol⁻¹ (B) -427 kJ mol⁻¹

(C) 214 kJ mol⁻¹ (D) 427 kJ mol⁻¹

58. Enthalpy of atomization of $\text{C}_2\text{H}_6(\text{g})$ and $\text{C}_3\text{H}_8(\text{g})$ are 620 and 880 kJ mol⁻¹ respectively. The

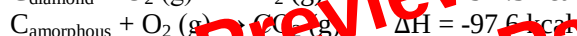
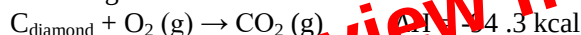
C-C and C-H bond energies are respectively

(A) 80 and 60 kJ mol⁻¹ (B) 80 and 90 kJ mol⁻¹

(C) 70 and 90 kJ mol⁻¹ (D) 100 and 80 kJ mol⁻¹

SECTION (K) ENTHALPY OF TRANSITION

59. The heat of transition for $\text{C}_{\text{Diamond}} \rightarrow \text{C}_{\text{Amorphous}}$ from the following is



(A) 3.3 kJ / mol (B) 3.3 kcal / mol

(r) - 3.3 kJ mol (D) - 3.3 kcal / mol

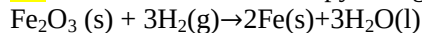
SECTION (L) ENTHALPY OF HYDROGENATION

60. From the standard enthalpies of combustion given below in (kJ mol⁻¹ and standard enthalpy of acetylene. find the standard enthalpy change when acetylene is hydrogenated to ethane.

$H^0_{\text{C}} = -394$; $H^0_{\text{H}_2} = -286$, $H^0_{\text{C}_2\text{H}_6} = -1560$, $H^0_{\text{C}_2\text{H}_2} = 227 \text{ KJmol}^{-1}$

SECTION (M) ENTROPY /ENTHALPY/ MP/BP

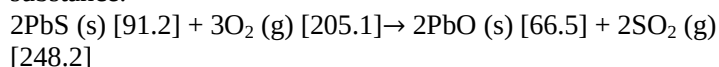
61. Calculate standard entropy change in the reaction



Given : $S^{\circ}_{\text{m}}(\text{Fe}_2\text{O}_3, \text{s}) = 87.4$, $S^{\circ}_{\text{m}}(\text{Fe}, \text{s}) = 27.3$, $S^{\circ}_{\text{m}}(\text{H}_2, \text{g}) = 130.7$, $S^{\circ}_{\text{m}}(\text{H}_2\text{O}, \text{l}) = 69.9 \text{ JK}^{-1} \text{ mol}^{-1}$.

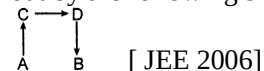
(A) -212.5 JK⁻¹ mol⁻¹ (B) -215.2 JK⁻¹ mol⁻¹ (C) -120.9 JK⁻¹ mol⁻¹ (D) None of these

62. Calculate the entropy change (J/mol K) of the given reaction. The molar entropies [J/K-mol] are given in brackets after each substance.



(A) -113.5 (B) -168.3 (C) +72.5 (D) -149.2

63. The direct conversion of A to B is difficult, hence it is carried out by the following shown path:



$\Delta S(\text{A} \rightarrow \text{C}) = 50$; $\Delta S(\text{C} \rightarrow \text{D}) = 30$; $\Delta S(\text{B} \rightarrow \text{D}) = 20$

The entropy change for the process $\text{A} \rightarrow \text{B}$ is

(A) 100 (B) - 60 (C) -100 (D) + 60

64. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure ?

(A) 80 cal (B) 540 cal (C) 620 cal (D) Zero

65. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state, is $\Delta H = - 401.7 \text{ J mol}^{-1}$ for the transition. Assume the surroundings to be an ice-water both at 0°C :

(A) - 1.09 JK⁻¹ (B) 1.47 JK⁻¹ (C) 0.38 JK⁻¹ (D) None of these

66. Calculate entropy change involved in conversion of 1 mole H_2O at 373K to vapour at same temp. Latent heat of vaporization of H_2O is 2.257 KJ/gm.

67. At 373K, the entropy change for the transition of liquid water to steam $\Delta S(\text{vap}) = 109 \text{ J mol}^{-1} \text{ K}^{-1}$. Find ΔH for this process.

68. ΔH_{vap} for water is 40.73 kJ mol⁻¹ and ΔS_{vap} is 109 JK⁻¹ mol⁻¹

The temperature at which water is in equilibrium with water vapours is

(A) 100.67 °C (B) 260.87 K (C) 128.69 K (D) 460 K

69. $\Delta H = 30 \text{ kJ/mol}$, $\Delta S = 75 \text{ J / k / mol}$. Find boiling temperature at 1 atm. [JEE 2004]

(A) 400 K (B) 300 K (C) 150 K (D) 425 K

70. Find ΔS° for a reaction for which $\Delta H^{\circ} = 28.4 \text{ KJ/mol}$ & $K_c = 1.8 \times 10^{-7}$ at 298K.

SECTION (N) GIBB'S FREE ENERGY

71. Find ΔG° and ΔH° for that the reaction $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ at 300 K respectively are, when the standard entropy change is - 0.094 kJ mol⁻¹ K⁻¹. The standard Gibbs free energies of formation for CO_2 and CO are - 394.4 and - 137.2 kJ mol⁻¹, respectively. [JEE 2000]

(A) $\Delta G^{\circ} = -257.2 \text{ kJ/mol}$, $\Delta H^{\circ} = 285.4 \text{ kJ/mol}$

(B) $\Delta G^{\circ} = 514.4 \text{ kJ/mol}$, $\Delta H^{\circ} = -570.8 \text{ kJ/mol}$

(C) $\Delta G^{\circ} = +14.0 \text{ kJ/mol}$, $\Delta H^{\circ} = 570.8 \text{ kJ/mol}$

(D) $\Delta G^{\circ} = -257.2 \text{ kJ/mol}$, $\Delta H^{\circ} = - 285.4 \text{ kJ/mol}$

72. For the reaction, $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow 2\text{D}(\text{g})$

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

Calculate ΔG° for the reaction at 300 K.

(A) 0.164 kJ (B) 0.236 kJ (C) 0.017 kJ (D) 0.0019 kJ

73. If $\Delta G = - 177 \text{ K cal}$ for (1) $2 \text{Fe}(\text{s}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s})$

and $\Delta G = -19 \text{ K cal}$ for (2) $4\text{Fe}_2\text{O}_3(\text{s}) + \text{Fe}(\text{s}) \rightarrow 3 \text{Fe}_3\text{O}_4(\text{s})$

What is the Gibbs free energy of formation of Fe_3O_4 ?

(A) + 229.6 kcal/mol (B) - 242.3 kcal/mol

(C) - 727 kcal / mol (D) - 229.6 kcal/mol

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

(A) -1.24 kJ/mol (B) -5.744 kJ/mol

(C) +1.27 kJ/mol (D) - 1.27 kJ /mol

75. For the auto-ionization of water at 25°C, $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$ is 10^{-14} . What is ΔG° for the process ?

(A) $\approx 8 \times 10^4 \text{ J}$ (B) $\approx 3.5 \times 10^4 \text{ J}$ (C) $\approx 10^4 \text{ J}$ (D) None of these

76. For a reaction $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$ at equilibrium. The partial pressure of B is found to be one fourth of the partial pressure of A. The value of ΔG° of the reaction $\text{A} \rightarrow \text{B}$ is

(A) $RT \ln 4$ (B) $- RT \ln 4$ (C) $RT \log 4$ (D) $- RT \log 4$

77. Calculate ΔG when 1 mole of NaCl is dissolved in water at 298 K. Lattice energy of NaCl = -777.8 KJ/mol, hydration energy = -774.1 KJ/mol, $\Delta S = 0.043 \text{ KJK}^{-1} \text{ mol}^{-1}$ at 298K. (Guide- $\Delta H = \text{hydration energy} - \text{lattice energy}$)

78. Standard potential for the reaction $\text{Ag}^+(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Ag}(\text{s})$ is 0.28V. Find standard free energy change for this reaction.

SECTION (O) EQUILIBRIUM CONSTANT

79. For the reaction : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$