= -2.303 x 2 x 2 x 298 x log 50/15 = -1436 calories.

Ex Calculate the maximum work done when pressure on 10 g of hydrogen is reduced form 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 = -2.303x5x2 x 273 x 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 adibatic 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 x -1 = 100 lit atm

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

$\Delta H = \Delta u + (P_1V_2 - P_1V_1)$

= 100 + (100 X 99 - 100 X 10) =100+100X89 = 9000 lit atm.

EX. For Ag, $\overline{C}_P$ ($JK^{-1}\ mol^{-1}$) 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.

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

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

For 3 mol, ΔH = 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 9721 cal/mole, what is the change of internal energy in the above process ?

(A) 1294.0 cals, 12470 cals (B) 921.4 cals, 11074 cals

(C) 1029.4 cals, 12470.6 cals (D) 1129.3 cals, 10207 cals

Sol. Mole of H_2O = 1.39

Pv = nRT ⇒ 1 x v= 1.39 x 0.082 x 373 ⇒ v = 42.80.

w = Pext. dv = 1 x [42.80] atm x lit. = - 42.80 x 101.325 J = - 42.80 x 101.325/ 4.2cal = 1024.8 cal.

$\Delta H = \Delta E + [P\Delta v]$. = 9720 X 1.39+ 1024.8= 12470.6 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) $\Delta E = 0\ J, \Delta H \neq 0\ J$ (B) $\Delta H = 0\ J, \Delta E = 10\ J$

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

sol.B

Since the process under adiabatic condition

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

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

$= -P_{ext}\ \Delta v = -100x\ -1\ bar\ ml = 10j$

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 charge, when 1 mol of water is vapourised at 1 bar pressure and 100°C

SOL: $\Delta H = \Delta E + \Delta ngRT$

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

$\Delta E = 37.904k.Jmol^{-1}$

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 J $mol^{-1}\ K^{-1}$.

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 x 24/27 =1.066kJ

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) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

Thus, V_0used= 6226 x 3 x 22.4/1411= 296.5 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 kJ mol^{-1} & specific heat of water is.4.184 x 10^{-3} kJ/g.

Solution: Heat taken up by water = m SΔT

= 150 x 103 x 4.184 x 10^{-3} ×53=34518 kJ

2050 kJ heat is provided by 1 mole C_3H_8

34158 kJ heat is provided by = 34518/2050

=16.838 mole of C_3H_8

Volume of C_3H_8 at NTP = 16.838 x 22.4 litre =3.77X 102 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 x 10^6 J/kg and latent of fusion of ice = 3.36 x 10^5 J/kg.

Sol. Total mass of the water = M = 100 g

Latent heat of vaporization of water at 0°C = L_1 = 21.0 x 10^5 J/Kg

= Latent heat of fusion of ice = L_2 = 3.36 x 10^5 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 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 K.

Pv = nRT ⇒ (4.6/760)v = 1× 0.82 × 273

v = 3699 lit= [3700 lit]

latent heat of fusion = 80 cal/gram

Latent heat of vaporisation = 596 cal/gram

ΔH = 80 × 18 + 596 × 18 = [80 + 596] × 18 = 12168 cal

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

12168 = ΔE + (4.6/760) [3700 –1] × (101.325/4.2)

ΔE = 12168 – 540.72 = 11627.28 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

$H^+(aq) + NH_4OH(aq) \rightarrow NH_4^+(aq) + H_2O(\ell)\ \Delta H$ = -51.1 kJ/mole

We may consider neutralization in two steps.

(i) Ionization: $NH_4OH(aq) \rightarrow NH_4^+(aq) + OH^-(aq)\ \Delta H_1$ = ?

(ii) Neutralization,

$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)\ \Delta H_2$ = - 57.1 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,
$B_2H_6 + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$
From the following data, calculate the enthalpy change for the combustion of diborane
i) $2B(s) + (3/2)\ O_2(g) \rightarrow B_2O_3(s)$: $\Delta H = -1273$ kJ mol^{-1}.
ii) $H_2(g) + (1/2)\ O_2(g) \rightarrow H_2O(l)$; $\Delta H = -286$ kJ mol^{-1}.
iii) $H_2O(l) \rightarrow H_2O(g)$; $\Delta H = 44$ kJ mol^{-1}.
iv) $2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$; $\Delta H = 36$ 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 $H_2(g)$ at 298 K to give $H_2O(g)$ 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 C1- Cl are 430 and 242 kJ mol^{-1}. ΔH_f(HCl) is - 91 kJ mol^{-1}, the bond enthalpy of HC1 would be
(A) - 214 kJ mol^{-1} (B) -427 kJ mol^{-1}
(C) 214 KJ mol^{-1} (D) 427 kJ mol^{-1}

58. Enthapy of atomization of $C_2H_6(g)$ and C_3H_8 (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 $C_{Diamond} \rightarrow c_{Amorphous}$ from the following is
$C_{diamond} + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -94.3$ kcal
$C_{amorphous} + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -97.6$ kcal
(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.
$H^0_C = -394$; $H^0_{H2} = -286$, $H^0_{C2H6} = -1560$, $H^0_{C2H2} = 227$ KJmol^{-1}

SECTION (M) ENTROPY /ENTHALPY/ MP/BP

61. Calculate standard entropy change in the reaction
$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$
Given : S°m (Fe_2O_3, S) = 87.4, S°$_m$ (Fe, S) = 27.3, S°m (H_2, g) = 130.7, S°m (H_2O, l) - 69.9 JK^{-1} 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.
$2PbS(s)$ [91.2] + $3O_2(g)$ [205.1] → $2PbO(s)$ [66.5] + $2SO_2(g)$ [248.2]
(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:

[JEE 2006]
$\Delta S(A \rightarrow C) = 50$; $\Delta S(C \rightarrow D) = 30$; $\Delta S(B \rightarrow D) = 20$
The entropy change for the process A →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 $\Delta H = -401.7$ J mol^{-1} for the transition. Assume the surroundings to be an ice-water both at 0°C :
(A) - 1.09 JK^{-1} (6)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 $\Delta S(vap) = 109$J mol^{-1} 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 temperautre at which water is in equilibrium with water vapours is
(A) 100.67 ^{0}C (B) 260.87 K (C) 128.69 K (D) 460 K

69. $\Delta H = 30$ kj/ mol , $\Delta S = 75$ 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^o for a reaction for which $\Delta H^o = 28.4$KJ/mol & Kc = 1.8×10^{-7} at 298K.

SECTION (N) GIBB'S FREE ENERGY

71. Find ΔG^o and $\Delta H°$ for that the reaction $CO(g) + ½\ O_2(g) \rightarrow CO_2(g)$ 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) $\Delta G^o = 257.2$ kJ/mol, $\Delta H° = 285.4$ kJ/mol
(B) $\Delta G^o = 514.4$ kJ/mol, $\Delta H° = -570.8$ kJ/mol
(C) $\Delta G^o = +514.4$ kJ/mol, $\Delta H° = 570.8$ kJ/mol
(D) $\Delta G^o = -257.2$ kJ/mol, $\Delta H° = -285.4$ kJ/mol

72. For the reaction, $2A(g) + B(g) \rightarrow 2D(g)$
$\Delta U^O = -10.5$kj and $\Delta S^0 = -44.1$JK^{-1}
Calculate ΔG^O for the reaction at 300 K.
(A) 0.164 kJ (B)0.236kj (C) 0.017 kj (D) 0.0019kJ

73. If $\Delta G = -177$ K cal for (1) $2\ Fe(s) + 3/2 O_2(g) \rightarrow Fe_2O_3(S)$ and $\Delta G = -19$ K cal for (2) $4Fe_2O_3(s) + Fe(s) \rightarrow 3\ Fe_3O_4(S)$
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^O ? (R = 8.314 JK^{-1} mol^{-1}, T = 300 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, $H_2O(l) \rightleftharpoons H^+(aq) + OH^{-1}(aq)$ is 10^{-14}. What is ΔG^0 for the process ?
(A) $\approx 8 \times 10^4$ J (B) $\approx 3.5 \times 10^4$ J (C) $\approx 10^4$ J (D) None of these

76. For a reaction A (g) ⇌ B(g) at equilibrium. The partial pressure of B is found to be one fourth of the partial pressure of A. The value of ΔG^O of the reaction A → 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 = -774.1KJ/mol, $\Delta S = 0.043$KJK^{-1}mol^{-1} at 298K. (Guide- ΔH = hydration energy – lattice energy)

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

SECTION (O) EQUILIBRIUM CONSTANT

79. For the reaction : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$