1. The standard enthalpy of formation ($\Delta H_f°$) at 398 K for methane, $CH_{4(g)}$ is 74.8 kJ mol^{-1}. The additional information required to determine the average energy for C - H bond formation would be :
(a) The dissociation energy of H_2 and enthalpy of sublimation of carbon
(b) Latent heat of vapourisation of methane
(c) The first four ionization energies of carbon and electron gain enthalpy of hydrogen
(d) The dissociation energy of hydrogen molecule, H_2

2. For which of the following change $\Delta H \neq \Delta E$?

(a) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$

(b) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$

(c) $C(s) + O_2(g) \longrightarrow CO_2(g)$

(d) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

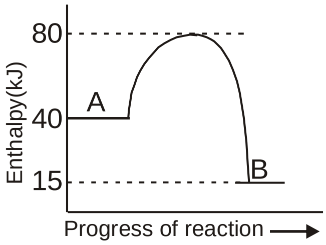
3. The heat of combustion of sucrose ($C_{12}H_{22}O_{11}$) is 1350 kcal. How much of heat will be liberated when 17.1 g of sucrose is burnt ?
(a) 67.5 kcal (b) 13.5 kcal (c) 40.5 kcal (d) 25.5 kcal

4. The following is (are) endothermic reaction(s) :
(a) Combustion of methane.
(b) Decomposition of water
(c) Dehydrogenation of ethane to ethylene.
(d) Conversion of graphite to diamond.

5. If heat of dissociation of $CHCl_2COOH$ is 0.7 kcal/mole then ΔH for the reaction :

$CHCl_2COOH + KOH \longrightarrow CHCl_2COOK + H_2O$
(a) – 13 kcal (b) + 13 kcal
(c) – 14.4 kcal (d) – 13.7 kcal

6. Look at the following diagram :



The enthalpy change for the reaction A → B will be
(a) – 25 Kj (b) – 40 kJ (c) + 25 kJ (d) – 65 kJ

7. The standard enthalpy of formation of FeO& Fe_2O_3 is -65 kcal mol^{-1} and -197kcalmol^{-1} respectively. A mixture of two oxides contains FeO& Fe_2O_3 in the mole ratio 2 : 1. If by oxidation, it is changed into a 1 : 2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture ?
(a) 13.4 kcal/mole (b) 14.6 kcal/mole
(c) 15.7 kcal/mole (d) 16.8 kcal/mole

8. Caesium chlorides is formed according to the following equation $Cs(s) + 0.5\ Cl_2(g) \rightarrow CsCl(s)$. The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs and electron affinity of chlorine are 81.2, 243.0, 375.7 and –348.3 kJ mol^{-1}. The energy change involved in the formation of CsCl is –388.6 kJ mol^{-1}. Calculate the lattice energy of CsCl.
(a) 618.7 kJ mol^{-1} (b) 1237.4 kJ mol^{-1}
(c) –1237.4 kJ mol^{-1} (d) –618.7 kJ mol^{-1}

9. The enthalpy of neutralization of 40.0 g of NaOH by 60.0 g of CH_3COOH will be :

(a) 57.1 kJ equiv^{-1}
(b) Less than 57.1 kJ equiv^{-1}
(c) More than 57.1 kJ equiv^{-1}
(d) 13.7 kJ equiv^{-1}

10. The average energy required to break a P – P bond in P_4 (s) into gaseous atoms is 53.2 kcal mol^{-1}. The bond dissociation energy of H_2(g) is 104.2 kcal mol^{-1}; ΔH_f^0 of PH_3(g) from P_4(s) is 5.5 kcal mol^{-1}. The P-H bond energy in kcal mol^{-1} is [Neglect presence of Van der Waals forces in P_4(s)]
(a) 85.2 (b) 57.6 (c) 76.9 (d) 63.3

11. 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 statements is correct ?
(a) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
(b) $(T_f)_{rev} = (T_f)_{irrev}$
(c) $T_f = T_i$ for both reversible and irreversible processes
(d) $(T_f)_{irrev} > (T_f)_{rev}$

12. In thermodynamics, a process is called reversible when –
(a) Surroundings and system change into each other
(b) There is no boundary between system and surroundings
(c) The surroundings are always in equilibrium with the system
(d) The system changes into the surroundings spontaneously

13. An electric heater of resistance 6 ohm is run for 10 minutes on a 120 volt line. The work done in this period of time is
(a) 7.2×10^3J (b) 14.4×10^5J
(c) 43.2×10^4 J (d) 28.8×10^4J

14. A piece of zinc at a temperature of 20^0C weighing 65.38 g is dropped into 180 g of boiling water (T = 100^0C). The specific heat of zinc is 0.4 J g^{-1} C^{-1} and that of water is 4.2 J g^{-1} ^{0}C^{-1}. What is the final common temperature reached by both the zinc and water ?
(a) 97.3^0C (b) 33.4^0C (c) 80.1^0C (d) 60.0^0C

15. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, Δ U and w correspond to
(a) $\Delta U < 0, w = 0$ (b) $\Delta U = 0, w < 0$
(c) $\Delta U > 0, w = 0$ (d) $\Delta U < 0, w > 0$

16. The temperature of the system decreases in an
(a) Adiabatic compression (b) Isothermal compression
(c) Isothermal expansion (d) Adiabatic expansion

17. For the isothermal expansion of an ideal gas
(a) E and H increases
(b) E increases but H decreases
(c) H increases but E decreases
(d) E and H are unaltered

18. In which one of the following sets, all the properties belong to same category (all extensive or all intensive) ?
(a) Mass, volume, pressure
(b) Temperature, pressure, volume
(c) Heat capacity, density, entropy
(d) Enthalpy, internal energy, volume.

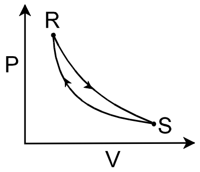
19. Match the enteries of column I with appropriate entries of column II and choose the correct option out of the four options (a), (b), (c) and (d).

Column I	Column II
(X) Isothermal	(p) DT = 0

(Y) Isobaric	(q) DV = 0
(Z) Adiabatic	(r) DP = 0
(W) Isochoric	(s) q = 0

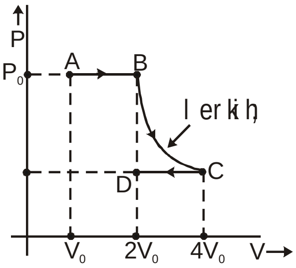
(a) X–p, Y–q, Z-r, W-x (b) X–p, Y–r, Z-s, W-q
(c) X–s, Y–p, Z-r, W-q (d) X–s, Y–p, Z-q, W-r

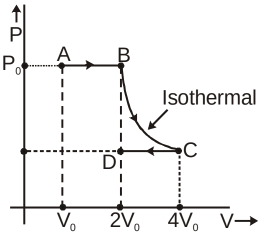
20. Consider the cyclic process R $\rightarrow$ S $\rightarrow$ R as shown in the Fig. You are told that one of the path is adiabatic and the other one isothermal. Which one of the following is(are) true?



(a) Process R $\rightarrow$ S is isothermal
(b) Process S $\rightarrow$ R is adiabatic
(c) Process R $\rightarrow$ S is adiabatic
(d) Such a graph is not possible

21. Work for the following process ABCD on a monoatomic gas is :





(a) $w = -2P_0V_0 \ln 2$, (b) $w = -2P_0V_0 \ln 2$

(c) $w = -P_0V_0(1 + \ln 2)$ (d) $w = -P_0V_0 \ln 2$,

22. 50 L of a certain liquid is confined in a piston system at the external pressure 100 atm. This pressure is suddenly released and liquid is expanded against the constant atmospheric pressure, volume of the liquid increases by 1 L and the final pressure on the liquid is 10 atm. Find the workdone.
(a) 1L.atm (b) 5 L.atm (c) 500 L.atm (d) 50 L.atm

23. In an isobaric process, the ratio of heat supplied to the system (dQ) and work done by the system (dW) for diatomic gas is
(a) 1 : 1 (b) 7 : 2 (c) 7 : 5 (d) 5 : 7

24. The increase in internal energy of 1 kg of water at 100^0C when it is converted into steam at the same temperature and at 1 atm (100 k Pa) will be [The density of water and steam are 1000 kg/m^3 & 0.6 kg/m^3 respectively. The latent heat of vapourisation of water is 2.25×10^6 J/kg.]
(a) 2.08×10^6 J (b) 4×10^7 J
(c) 3.27×10^8 J (d) 5×10^9 J

25. 1 mole of an idal gas A ($C_{v,m} = 3R$) and 2 mole of an ideal gas B are $\left(C_{v,m} = \frac{3}{2}R\right)$ taken in a container and expanded reversible and adiabatically from 1 litre to 4 litre starting from initial temperature of 320 K. ΔE or ΔU for the process is :
(a) –240 R (b) –240 R (c) 480 R (d) –960 R

26. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process ?
(a) Isothermal process : q = – w
(b) Cyclic process : q = – w
(c) Adiabatic process : $\Delta E = q$
(d) Expansion of a gas into vacuum : $\Delta E = q$

27. A gas expands adiabatically at constant pressure such that $T \propto V^{-1/2}$. The value of γ ($C_{p,m}/C_{v,m}$) of the gas will be :

(a) 1.30 (b) 1.50 (c) 1.70 (d) 2

28. 10 litres of a monoatomic ideal gas at 0^0C and 10 atm pressure is suddenly released to 1 atm pressure and the gas expands adiabatically against this constant pressure. The final temperature and volume of the gas respectively are.

(a) T = 174.9 K, V = 64 L (b) T = 153 K, V = 57 L

(c) T = 165.4 K, V = 78.8 L (d) T = 161.2 K, V = 68.3 L

29. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. I^{st} sample using reversible isothermal process and II^{nd} sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure. Then :

(a) Final volume of I^{st} sample < final volume of II^{nd} sample

(b) Final volume of II^{nd} sample < final volume of I^{st} sample

(c) Final volumes will be equal

(d) Information is insufficient

30. The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1L to 2L is ΔH_1 and for reversible adiabatic expansion for the same expansion is ΔH_2. Then

(a) $\Delta H_1 > \Delta H_2$

(b) $\Delta H_1 < \Delta H_2$

(c) $\Delta H_1 = \Delta H_2$, enthalpy being a state function ($\Delta H_1 = \Delta H_2$)

(d) $\Delta H_1 = \Delta E_1$ & $\Delta H_2 = \Delta E_2$ where ΔE_1 & ΔE_2 are magnitudes of change in internal energy of gas in these expansions respectively.

1. **(a)**

$C + 2H_2 \rightarrow CH_4; \quad \Delta H^0 = -74.8 \text{ kJ mol}^{-1}$

In order to calculate average energy for C – H bond formation we should know the followng data.

$C(\text{graphite}) \rightarrow C(g); \ \Delta H_f^o$ = enthalpy of sublimation of carbon

$H_2(g) \rightarrow 2H(g); \ \Delta H^o$ bond dissociation energy of H_2.

2. **(d)**

using $\Delta H = \Delta E + \Delta n_g RT$

3. **(a)**

Heat evolved from 1 mole of sucrose (342 g) = 1350 kcal

Heat evolved from 17.1 g of sucrose = $\frac{1350}{342} \times 17.1 = 67.5$ kcal.

4. **(c)**

Combustion reaction are exothermic, hydrogenation of alkenes are exothermic and graphite is thermodynamically more stable.

5. **(a)**

$H^+ + OH^- \longrightarrow H_2O(\ell)$

$\Delta H = -13.7$ kcal ...(i)

$CHCl_2COOH \longrightarrow CHCl_2COO^- + H^+$

$\Delta H = 0.7$ kcal ...(ii)

$CHCl_2COOH + OH^- \longrightarrow$

$CHCl_2COO^- + H_2O(\ell) \ \Delta H = ?$

Adding equation (i) and (ii) $\Delta H = -13$ kcal.

6. **(a)**

$\Delta H = H_p - H_R = 15 - 40 = -25$ kJ.

7. **(a)**

$FeO + Fe_2O_3$

2x x

$Fe + \frac{1}{2}O_2 \longrightarrow FeO \qquad \Delta H_f^0 = -65$ Kcal/mole

$2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3 \quad \Delta H_f^0 = -197$ Kcal/mole

$2FeO + \frac{1}{2}O_2 \longrightarrow Fe_2O_3$

$\Delta H = -197 + 65 \times 2 \Rightarrow \Delta H = -67$ Kcal/mole

$2FeO + \frac{1}{2}O_2 \longrightarrow Fe_2O_3$

$\frac{2}{3} \quad \frac{1}{3} \quad \frac{2}{3} \qquad\qquad -2x\,\frac{1}{3} + x$

$$\frac{\frac{2}{3}-2x}{\frac{1}{3}+x}=\frac{1}{2}$$

$$\Rightarrow x=\frac{1}{5}$$

So, energy released = $\frac{1}{5}\times 67 =$ 13.4 kcal/mole

8. (d)
Apply Born Haber's cycle

9. (b)
Since it is neutralisation of a weak acid with strong base.

10. (c)

$P_4(s) \rightarrow 4P(g) \qquad \Delta H = 53.2 \times 6$

$H_2(g) \rightarrow 2H(g) \qquad \Delta H = 104.2$

$\frac{1}{4}P_4(s) + \frac{3}{2}H_2(g) \rightarrow PH_3(g) \; \Delta H = 5.5$

$\frac{1}{4}\times 6 \times 53.2 + \frac{3}{2}\times 104.2 - 3\in_{P-H} = 5.5$

$\Rightarrow \in_{P-H} = 76.866$ i.e. 76.9 kcal mol^{-1}

11. (d)
In isolated system, the expansion of gas is carried out adiabatically. Since heat exchange between system and surrounding is not possible i.e. $q = 0$ and secondary w_{rev} is always greater than w_{irr} therefore for reversible process there must be comparatively higher decreases in internal energy i.e. ΔU for reversible process will be more negative. Hence, final temperature in reversible process will be smaller than irreversible process.

$\therefore (T_f)_{irrev} > (T_f)_{rev}$

12. (c)
In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.

13. (b)
H =

$$W = i^2Rt = \frac{V^2t}{R} = \frac{120\times 120\times(10\times 60)}{6} = 14.410^5 \text{ Joule}$$

14. (a)
Let final common temperature is T_f

Heat gained by Zinc piece = Heat lost by water

$0.4\,(T_f - 20)\times 65.38 = 4.2\,(100 - T_f)\times 180$

$\Rightarrow T_f = 97.3\,^0C$

15. (a)
Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed, so $w = 0$ and $\Delta U = q$.

$\Delta U < 0,\ w = 0$

16. (d)

When a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect.

17. (d)

In isothermal reversible process ideal gas has constant temperature and so $\Delta E = 0$ and $\Delta H = \Delta E = 0$.

18. (d)

H, E and V all are extensive.

19. (b)

In isothermal process, $\Delta T = 0$

In isobaric process, $\Delta P = 0$

In adiabatic process, $q = 0$.

In isochoric process $\Delta V = 0$

20. (d)

Because two state of a system cannot be connected by one adiabatic & one isothermal path.

21. (a)

At A and D the temperatures of the gas will be equal, so

$\Delta E = 0$,

$\Delta H = 0$

Now $w = w_{AB} + w_{BC} + w_{CD} = -P_0 V_0 - 2P_0 V_0 \ln 2 + P_0 V_0 = -2P_0 V_0 \ln 2$

22. (a)

$W = -P_{ext}(V_2 - V_1) = -1$ atm (1 L)

23. (b)

$$dE = dW + dQ; -dW = dQ - dE \quad \therefore \frac{dQ}{dW} = \frac{dQ}{dQ - dE}$$

$$= \frac{C_p}{(C_p - C_v)}$$

$$= \frac{7R}{2R} \quad (c_p = \frac{7R}{2})$$

24. (a)

Latent heat of vaporisation of water $= 2.25 \times 10^6$ J/kg

$\Delta H = 2.25 \times 10^6$ J/kg.

work done $= -P_{ext}(V_2 - V_1)$

$\Delta H = 2.25 \times 10^6$ J/kg

$\Delta H = \Delta U + P\Delta V$

(a) Now, volume of water $V = \left(\frac{m}{d}\right) = \frac{1}{1000}\ M^3 = 1L$

(b) volume of steam $= \frac{1000}{0.6} = 1666.67$ L

$2.25 \times 10^6 = \Delta U + 1\,[1666.67 - 1]\,101.325$

$\Delta U = 22.5 \times 10^5 - 1.68 \times 10^5 = 20.8 \times 10^5 = 2.08 \times 10^6$ J

25. (d)

Avg. $C_{V,\,m} = \dfrac{n_1C_{v,m}+n_2C_{v,m_2}}{n_1+n_2}$

$= \dfrac{1\times 3R + 2\times \frac{3}{2}R}{3} = 2R$

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \Rightarrow 320 \times 1^{\frac{3}{2}-1} = T_2 \times (4)^{3/2-1}$

$\Rightarrow T_2 = 160$ K

$\Delta U = (n_1 + n_2)\, C_{V,avg}\, \Delta T$

$= 3 \times 2R \times (160 - 320) = -960$ R

26. (c)

According to 1st law of thermodynamics,

$\Delta E = q + w$.

For isothermal process, $\Delta E = 0$. Hence, $q = -w$

For cyclic process, $\Delta E = 0$ Hence,

For expansion into vacuum, $w = 0$. hence $\Delta E = q$.

27. (b)

$T \propto \dfrac{1}{\sqrt{V}}$; $TV^{1/2}$ = constant

For adiabatic process, $TV^{\gamma-1}$ = constant $\therefore$

$\gamma - 1 = \dfrac{1}{2}, \gamma = \dfrac{3}{2}$

28. (a)

This is adiabatic irreversible process so, for this process

PV^{γ} = Constant, is not applicable

$W = -P_{ext}(V_2 - V_1)$

But for adiabatic process

$W = dU = \left(\dfrac{P_2V_2 - P_1V_1}{\gamma - 1}\right)$

$PV = nRT$

$\Rightarrow 10 \times 10 = n \times 0.082 \times 273$

$\Rightarrow n = 4.47$ moles $-P_{ext}(V_2 - V_1) = \left(\dfrac{P_2V_2 - P_1V_1}{\gamma - 1}\right)$

$\Rightarrow -1 \times (V_2 - 10) = \dfrac{1\times V_2 - 10\times 10}{1.67 - 1}$

$\Rightarrow (10 - V_2) = \dfrac{V_2 - 100}{0.67}$

$\Rightarrow 6.7 - 0.67\,V_2 = V_2 - 100$

$\Rightarrow 106.7 = 1.67\,V_2$

$\Rightarrow V_2 = 64$

$\therefore nR\,[T_2 - T_1] = P_2V_2 - P_1V_1$

$\Rightarrow 4.47 \times 0.082\,[T_2 - 273] = 64 - 100 = -36$

$\Rightarrow (T_2 - 273) = -98.2$

$\Rightarrow T_2 = 174.8$ K

29. **(b)**
FACT

30. **(b)**
$|W_{rev}| > |W_{Irr}|$
$T_{final(rev)} < T_{final(Irr)}$
$\Delta T_{rev} > \Delta T_{Irr}$
$\because \Delta H \propto \Delta T$
$\Delta H_{rev} > \Delta H_{Irr}$