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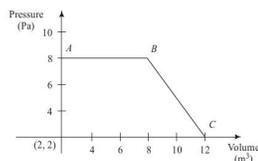
## Thermodynamics



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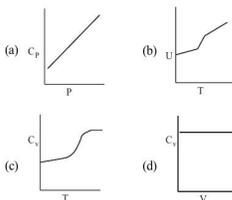
### TOPIC 1 First Law and Basic Fundamentals of Thermodynamics

- Five moles of an ideal gas at 1 bar and 298 K is expanded into vacuum to double the volume. The work done is : [Sep. 04, 2020 (II)]
  - $C_v(T_2 - T_1)$
  - $-RT(V_2 - V_1)$
  - $-RT \ln V_2/V_1$
  - zero
- The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is [NV, Jan. 08, 2020 (I)]



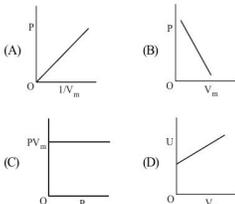
- At constant volume, 4 mol of an ideal gas when heated from 300 K to 500 K changes its internal energy by 5000 J. The molar heat capacity at constant volume is [NV, Jan. 08, 2020 (II)]
- An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is : [April 12, 2019 (I)]
  - 9.0
  - +10.0
  - 0.9
  - 2.0
- Among the following, the set of parameters that represents path functions, is: [April 9, 2019 (I)]
  - $q + w$
  - $q$
  - $w$
  - $H - TS$
  - (B) and (C)
  - (B), (C) and (D)
  - (A) and (D)
  - (A), (B) and (C)

- During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy, "U (in kJ) is: [April 9, 2019 (II)]
  - 12
  - 8
  - 8
  - 12
- Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas ? (Assume non-expansion work is zero) [April 8, 2019 (I)]
  - Cyclic process :  $q = -w$
  - Adiabatic process :  $\Delta U = -w$
  - Isochoric process :  $\Delta U = q$
  - Isothermal process :  $q = -w$
- 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If  $C_v = 28 \text{ J K}^{-1} \text{ mol}^{-1}$ , calculate  $\Delta U$  and  $\Delta pV$  for this process. ( $R = 8.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ) [April 8, 2019 (II)]
  - $\Delta U = 14 \text{ kJ}$ ;  $\Delta(pV) = 18 \text{ kJ}$
  - $\Delta U = 14 \text{ kJ}$ ;  $\Delta(pV) = 0.8 \text{ kJ}$
  - $\Delta U = 14 \text{ kJ}$ ;  $\Delta(pV) = 4 \text{ kJ}$
  - $\Delta U = 14 \text{ kJ}$ ;  $\Delta(pV) = 8.0 \text{ kJ}$
- For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities? [Jan. 12, 2019 (I)]



10. The combination of plots which does not represent isothermal expansion of an ideal gas is:

[Jan. 12, 2019 (II)]



- (a) (B) and (D) (b) (A) and (C)  
(c) (B) and (C) (d) (A) and (D)

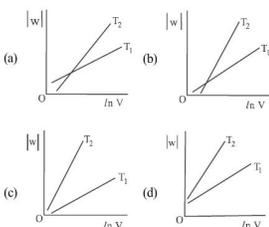
11. An ideal gas undergoes isothermal compression from  $5 \text{ m}^3$  to  $1 \text{ m}^3$  against a constant external pressure of  $4 \text{ Nm}^{-2}$ . Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ , the temperature of Al increases by:

[Jan. 10, 2019 (II)]

- (a)  $\frac{3}{2} \text{ K}$  (b)  $2 \text{ K}$  (c)  $\frac{2}{3} \text{ K}$  (d)  $1 \text{ K}$

12. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures,  $T_1$  and  $T_2$  ( $T_1 < T_2$ ). The correct graphical depiction of the dependence of work done ( $w$ ) on the final volume ( $V$ ) is:

[Jan. 9, 2019 (I)]



13. An ideal gas undergoes a cyclic process as shown in Figure.



$\Delta U_{BC} = -5 \text{ kJ mol}^{-1}$ ,  $q_{AB} = 2 \text{ kJ mol}^{-1}$   
 $W_{AB} = -5 \text{ kJ mol}^{-1}$ ,  $W_{CA} = 3 \text{ kJ mol}^{-1}$

Heat absorbed by the system during process CA is:

[Online April 15, 2018 (I)]

- (a)  $-5 \text{ kJ mol}^{-1}$  (b)  $+5 \text{ kJ mol}^{-1}$   
(c)  $18 \text{ kJ mol}^{-1}$  (d)  $-18 \text{ kJ mol}^{-1}$

14.  $\Delta U$  is equal to [2017]

- (a) Isochoric work (b) Isobaric work  
(c) Adiabatic work (d) Isothermal work

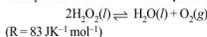
15. A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A:

[Online April 9, 2017]

- (a) 10 J of the work will be done by the gas.  
(b) 6 J of the work will be done by the gas.  
(c) 10 J of the work will be done by the surrounding on gas.  
(d) 6 J of the work will be done by the surrounding on gas.

16. If 100 mole of  $\text{H}_2\text{O}_2$  decomposes at 1 bar and 300 K, the work done (kJ) by one mole of  $\text{O}_2(g)$  as it expands against 1 bar pressure is:

[Online April 10, 2016]



- (a) 124.50 (b) 249.00  
(c) 498.00 (d) 62.25

17. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of  $37.0^\circ \text{C}$ . As it does so, it absorbs 208 J of heat. The values of  $q$  and  $w$  for the process will be:

[2013]

( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\ln 7.5 = 2.01$ )

- (a)  $q = +208 \text{ J}$ ,  $w = -208 \text{ J}$   
(b)  $q = -208 \text{ J}$ ,  $w = -208 \text{ J}$   
(c)  $q = -208 \text{ J}$ ,  $w = +208 \text{ J}$   
(d)  $q = +208 \text{ J}$ ,  $w = +208 \text{ J}$

18. Which of the following statements/relationships is not correct in thermodynamic changes? [Online April 23, 2013]

(a)  $\Delta U = 0$  (isothermal reversible expansion of a gas)

(b)  $w = -nRT \ln \frac{V_2}{V_1}$  (isothermal reversible expansion of an ideal gas)

(c)  $w = nRT \ln \frac{V_2}{V_1}$  (isothermal reversible expansion of an ideal gas)

(d) For a system of constant volume heat involved directly changes to internal energy.

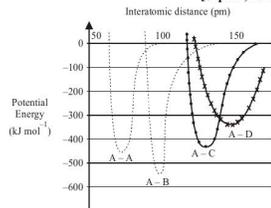
19. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If  $T_i$  is the initial temperature and  $T_f$  is the final temperature, which of the following statements is correct? [2006]

- (a)  $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$   
(b)  $T_f = T_i$  for both reversible and irreversible processes  
(c)  $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$   
(d)  $T_f > T_i$  for reversible process but  $T_f = T_i$  for irreversible process

20. An ideal gas expands in volume from  $1 \times 10^{-3}$  to  $1 \times 10^{-2}$  m<sup>3</sup> at 300 K against a constant pressure of  $1 \times 10^5$  Nm<sup>-2</sup>. The work done is [2004]  
 (a) 270 kJ (b) -900 kJ  
 (c) -900 J (d) 900 kJ
21. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy? [2003]  
 (a) >40 kJ (b) <40 kJ  
 (c) Zero (d) 40 kJ
22. A heat engine absorbs heat  $Q_1$  at temperature  $T_1$  and heat  $Q_2$  at temperature  $T_2$ . Work done by the engine is  $J(Q_1 + Q_2)$ . This data [2002]  
 (a) violates 1<sup>st</sup> law of thermodynamics  
 (b) violates 1<sup>st</sup> law of thermodynamics if  $Q_2$  is -ve  
 (c) violates 1<sup>st</sup> law of thermodynamics of  $Q_2$  is -ve  
 (d) does not violate 1<sup>st</sup> law of thermodynamics.
23. The heat required to raise the temperature of body by 1 K is called [2002]  
 (a) specific heat (b) thermal capacity  
 (c) water equivalent (d) none of these.

### TOPIC 2 Laws of Thermochemistry

24. Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol<sup>-1</sup> and 4 kJ mol<sup>-1</sup>, respectively. The hydration enthalpy of NaCl is: [Sep. 05, 2020 (II)]  
 (a) -780 kJ mol<sup>-1</sup> (b) 780 kJ mol<sup>-1</sup>  
 (c) -784 kJ mol<sup>-1</sup> (d) 784 kJ mol<sup>-1</sup>
25. For one mole of an ideal gas, which of these statements must be true? [Sep. 04, 2020 (I)]  
 (1) U and H each depends only on temperature  
 (2) Compressibility factor  $z$  is not equal to 1  
 (3)  $C_{p,m} - C_{v,m} = R$   
 (4)  $dU = C_v dT$  for any process  
 (a) (1) and (3) (b) (2), (3) and (4)  
 (c) (3) and (4) (d) (1), (3) and (4)
26. The intermolecular potential energy for the molecules A, B, C and D given below suggests that: [Sep. 04, 2020 (I)]



- (a) A-D has the shortest bond length  
 (b) A-A has the largest bond enthalpy  
 (c) D is more electronegative than other atoms  
 (d) A-B has the stiffest bond
27. The internal energy change (in J) when 90 g of water undergoes complete evaporation at 100°C is \_\_\_\_\_. (Given:  $\Delta H_{\text{vap}}$  for water at 373 K = 41 kJ/mol,  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ) [NV, Sep. 02, 2020 (I)]
28. The heat of combustion of ethanol into carbon dioxide and water is -327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is ( $R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ ) \_\_\_\_\_. [NV, Sep. 02, 2020 (II)]
29. If enthalpy of atomisation for  $\text{Br}_2(l)$  is  $x$  kJ/mol and bond enthalpy for  $\text{Br}_2$  is  $y$  kJ/mol, the relation between them: [Jan. 09, 2020 (I)]  
 (a) is  $x = y$  (b) does not exist  
 (c) is  $x > y$  (d) is  $x < y$
30. For the reaction;  $\text{A}(l) \rightarrow 2\text{B}(g)$   
 $\Delta U = 2.1 \text{ kcal}$ ,  $\Delta S = 20 \text{ cal K}^{-1}$  at 300 K.  
 Hence  $\Delta G$  in kcal is. [NV, Jan. 07, 2020 (I)]
31. The standard heat of formation ( $\Delta_f H_{298}^\circ$ ) of ethane (in kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are -1560, -393.5 and -286 kJ/mol, respectively is \_\_\_\_\_. [NV, Jan. 07, 2020 (II)]
32. Enthalpy of sublimation of iodine is 24 cal g<sup>-1</sup> at 200°C. If specific heat of  $\text{I}_2(s)$  and  $\text{I}_2(\text{vap})$  are 0.055 and 0.031 cal g<sup>-1</sup> K<sup>-1</sup> respectively, then enthalpy of sublimation of iodine at 250°C in cal g<sup>-1</sup> is: [April 12, 2019 (II)]  
 (a) 2.85 (b) 5.7  
 (c) 22.8 (d) 11.4
33. The difference between  $\Delta H$  and  $\Delta U$  ( $\Delta H - \Delta U$ ), when the combustion of one mole of heptane (l) is carried out at a temperature  $T$ , is equal to: [April 10, 2019 (II)]  
 (a)  $-4RT$  (b)  $-3RT$   
 (c)  $4RT$  (d)  $3RT$
34. For silver,  $C_p(\text{JK}^{-1} \text{ mol}^{-1}) = 23 + 0.01T$ . If the temperature ( $T$ ) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of  $\Delta H$  will be close to: [April 8, 2019 (I)]  
 (a) 62 kJ (b) 16 kJ (c) 21 kJ (d) 13 kJ
35. (i)  $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_r H^\circ = x \text{ kJ mol}^{-1}$   
 (ii)  $\text{C}(\text{graphite}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}); \Delta_r H^\circ = y \text{ kJ mol}^{-1}$   
 (iii)  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_r H^\circ = z \text{ kJ mol}^{-1}$

- Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct? **[Jan. 12, 2019 (II)]**
- (a)  $x = y + z$  (b)  $z = x + y$   
 (c)  $y = 2z - x$  (d)  $x = y - z$
36. The combustion of benzene (l) gives  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ . Given that heat of combustion of benzene at constant volume is  $-3263.9 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ ; heat of combustion (in  $\text{kJ mol}^{-1}$ ) of benzene at constant pressure will be : **[2018]**  
 (R =  $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )  
 (a) 4152.6 (b) -452.46  
 (c) 3260 (d) -3267.6
37. For which of the following reactions,  $\Delta H$  is equal to  $\Delta U$ ? **[Online April 15, 2018 (I)]**
- (a)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$   
 (b)  $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$   
 (c)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$   
 (d)  $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$
38. Given  
 $\text{C}_{(\text{graphite})} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta H^\circ = -393.5 \text{ kJ mol}^{-1}$   
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H^\circ = -285.8 \text{ kJ mol}^{-1}$   
 $\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}); \Delta H^\circ = +890.3 \text{ kJ mol}^{-1}$
- Based on the above thermochemical equations, the value of  $\Delta H^\circ$  at  $298 \text{ K}$  for the reaction  
 $\text{C}_{(\text{graphite})} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$  will be : **[2017]**  
 (a)  $+74.8 \text{ kJ mol}^{-1}$  (b)  $+144.0 \text{ kJ mol}^{-1}$   
 (c)  $-74.8 \text{ kJ mol}^{-1}$  (d)  $-144.0 \text{ kJ mol}^{-1}$
39. For a reaction,  $\text{A}(\text{g}) \rightarrow \text{A}(\text{l}); \Delta H = -3\text{RT}$ . The correct statement for the reaction is : **[Online April 8, 2017]**  
 (a)  $\Delta H = \Delta U \neq 0$  (b)  $\Delta H = \Delta U = 0$   
 (c)  $|\Delta H| < |\Delta U|$  (d)  $|\Delta H| > |\Delta U|$
40. The enthalpy change on freezing of 1 mol of water at  $5^\circ\text{C}$  to ice at  $-5^\circ\text{C}$  is : **[Online April 8, 2017]**  
 (Given  $\Delta_{\text{m}}H = 6 \text{ kJ mol}^{-1}$  at  $0^\circ\text{C}$ ,  
 $C_p(\text{H}_2\text{O}, \text{l}) = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  
 $C_p(\text{H}_2\text{O}, \text{s}) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$ )  
 (a)  $5.44 \text{ kJ mol}^{-1}$  (b)  $5.81 \text{ kJ mol}^{-1}$   
 (c)  $6.56 \text{ kJ mol}^{-1}$  (d)  $6.00 \text{ kJ mol}^{-1}$
41. The heats of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283.5 \text{ kJ mol}^{-1}$ , respectively. The heat of formation (in kJ) of carbon monoxide per mole is : **[2016]**  
 (a)  $-676.5$  (b)  $-110.5$   
 (c)  $110.5$  (d)  $676.5$
42. The heat of atomization of methane and ethane are  $360 \text{ kJ/mol}$  and  $620 \text{ kJ/mol}$ , respectively. The longest wavelength of light capable of breaking the C-C bond is (Avogadro number =  $6.02 \times 10^{23}$ ,  $h = 6.62 \times 10^{-34} \text{ J s}$ ): **[Online April 10, 2015]**  
 (a)  $2.48 \times 10^4 \text{ nm}$  (b)  $1.49 \times 10^3 \text{ nm}$   
 (c)  $2.48 \times 10^3 \text{ nm}$  (d)  $1.49 \times 10^4 \text{ nm}$
43. For complete combustion of ethanol,  
 $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ ,  
 the amount of heat produced as measured in bomb calorimeter, is  $1364.47 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . Assuming ideality the enthalpy of combustion,  $\Delta_c H$ , for the reaction will be: (R =  $8.314 \text{ kJ mol}^{-1}$ ) **[2014]**  
 (a)  $-1366.95 \text{ kJ mol}^{-1}$  (b)  $-1361.95 \text{ kJ mol}^{-1}$   
 (c)  $-1460.95 \text{ kJ mol}^{-1}$  (d)  $-1350.50 \text{ kJ mol}^{-1}$
44. The standard enthalpy of formation of  $\text{NH}_3$  is  $-46.0 \text{ kJ/mol}$ . If the enthalpy of formation of  $\text{H}_2$  from its atoms is  $-436 \text{ kJ/mol}$  and that of  $\text{N}_2$  is  $-712 \text{ kJ/mol}$ , the average bond enthalpy of N-H bond in  $\text{NH}_3$  is : **[Online April 9, 2014]**  
 (a)  $-1102 \text{ kJ/mol}$  (b)  $-964 \text{ kJ/mol}$   
 (c)  $+352 \text{ kJ/mol}$  (d)  $+1056 \text{ kJ/mol}$
45. The standard enthalpy of formation ( $\Delta_f H^\circ_{298}$ ) for methane,  $\text{CH}_4$  is  $-74.9 \text{ kJ mol}^{-1}$ . In order to calculate the average energy given out in the formation of a C-H bond from this it is necessary to know which one of the following? **[Online April 12, 2014]**  
 (a) The dissociation energy of the hydrogen molecule,  $\text{H}_2$   
 (b) The first four ionisation energies of carbon.  
 (c) The dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon (graphite).  
 (d) The first four ionisation energies of carbon and electron affinity of hydrogen.
46. Given :  
 (I)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H^\circ_{298\text{K}} = -285.9 \text{ kJ mol}^{-1}$   
 (II)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta H^\circ_{298\text{K}} = -241.8 \text{ kJ mol}^{-1}$
- The molar enthalpy of vapourisation of water will be : **[Online April 9, 2013]**  
 (a)  $241.8 \text{ kJ mol}^{-1}$  (b)  $22.0 \text{ kJ mol}^{-1}$   
 (c)  $44.1 \text{ kJ mol}^{-1}$  (d)  $527.7 \text{ kJ mol}^{-1}$
47. Given
- | Reaction   | Energy Change (in kJ)    |
|--|--------------------------|
| $\text{Li}(\text{s}) \rightarrow \text{Li}(\text{g})$                                    | 161                      |
| $\text{Li}(\text{g}) \rightarrow \text{Li}^+(\text{g})$                                  | 520                      |
| $\frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{F}(\text{g})$                         | 77                       |
| $\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$                       | (Electron gain enthalpy) |
| $\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{LiF}(\text{s})$          | -1047                    |
| $\text{Li}(\text{s}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{LiF}(\text{s})$ | -617                     |
- Based on data provided, the value of electron gain enthalpy of fluorine would be : **[Online April 22, 2013]**  
 (a)  $-300 \text{ kJ mol}^{-1}$  (b)  $-350 \text{ kJ mol}^{-1}$   
 (c)  $-328 \text{ kJ mol}^{-1}$  (d)  $-228 \text{ kJ mol}^{-1}$

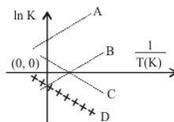
48. In which of the following exothermic reactions, the heat liberated per mole is the highest? [Online April 25, 2013]
- $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$
  - $\text{SrO} + \text{H}_2\text{O} \rightarrow \text{Sr}(\text{OH})_2$
  - $\text{BaO} + \text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2$
  - $\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$
49. Given that: [Online April 25, 2013]
- $\Delta_f H^\circ$  of  $\text{N}_2\text{O}$  is  $82 \text{ kJ mol}^{-1}$
  - Bond energies of  $\text{N}=\text{N}$ ,  $\text{N}=\text{O}$ ,  $\text{O}=\text{O}$  and  $\text{N}=\text{O}$  are 946, 418, 498 and  $607 \text{ kJ mol}^{-1}$  respectively. The resonance energy of  $\text{N}_2\text{O}$  is :
    - 88 kJ
    - 66 kJ
    - 62 kJ
    - 44 kJ
50. The difference between the reaction enthalpy change ( $\Delta_r H$ ) and reaction internal energy change ( $\Delta_r U$ ) for the reaction:
- $$2\text{C}_2\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$$
- at 300 K is ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) [Online May 12, 2012]
- $0 \text{ J mol}^{-1}$
  - $2490 \text{ J mol}^{-1}$
  - $-2490 \text{ J mol}^{-1}$
  - $-7482 \text{ J mol}^{-1}$
51. The enthalpy of neutralisation of  $\text{NH}_4\text{OH}$  with  $\text{HCl}$  is  $-51.46 \text{ kJ mol}^{-1}$  and the enthalpy of neutralisation of  $\text{NaOH}$  with  $\text{HCl}$  is  $-55.90 \text{ kJ mol}^{-1}$ . The enthalpy of ionisation of  $\text{NH}_4\text{OH}$  is [Online May 19, 2012]
- $-107.36 \text{ kJ mol}^{-1}$
  - $-4.44 \text{ kJ mol}^{-1}$
  - $+107.36 \text{ kJ mol}^{-1}$
  - $+4.44 \text{ kJ mol}^{-1}$
52. The value of enthalpy change ( $\Delta H$ ) for the reaction
- $$\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$$
- at  $27^\circ\text{C}$  is  $-1366.5 \text{ kJ mol}^{-1}$ . The value of internal energy change for the above reaction at this temperature will be :
- $-1369.0 \text{ kJ}$
  - $-1364.0 \text{ kJ}$  [2011RS]
  - $-1361.5 \text{ kJ}$
  - $-1371.5 \text{ kJ}$
53. Consider the reaction :
- $$4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g})$$
- $\Delta H = -111 \text{ kJ}$ .  
If  $\text{N}_2\text{O}_5(\text{s})$  is formed instead of  $\text{N}_2\text{O}_5(\text{g})$  in the above reaction, the  $\Delta H$  value will be :  
(given,  $\Delta H$  of sublimation for  $\text{N}_2\text{O}_5$  is  $54 \text{ kJ mol}^{-1}$ )
- $+54 \text{ kJ}$
  - $+219 \text{ kJ}$  [2011RS]
  - $-219 \text{ kJ}$
  - $-165 \text{ kJ}$
54. The standard enthalpy of formation of  $\text{NH}_3$  is  $-46.0 \text{ kJ mol}^{-1}$ . If the enthalpy of formation of  $\text{H}_2$  from its atoms is  $-436 \text{ kJ mol}^{-1}$  and that of  $\text{N}_2$  is  $-712 \text{ kJ mol}^{-1}$ , the average bond enthalpy of  $\text{N}-\text{H}$  bond in  $\text{NH}_3$  is [2010]
- $-964 \text{ kJ mol}^{-1}$
  - $+352 \text{ kJ mol}^{-1}$
  - $+1056 \text{ kJ mol}^{-1}$
  - $-1102 \text{ kJ mol}^{-1}$
55. On the basis of the following thermochemical data :
- $$(\Delta_f G^\circ \text{H}^+_{(\text{aq})} = 0)$$
- [2009]
- $$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}); \Delta H = 57.32 \text{ kJ}$$
- $$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}); \Delta H = -286.20 \text{ kJ}$$
- The value of enthalpy of formation of  $\text{OH}^-$  ion at  $25^\circ\text{C}$  is:
- $-228.88 \text{ kJ}$
  - $+228.88 \text{ kJ}$
  - $-343.52 \text{ kJ}$
  - $-22.88 \text{ kJ}$
56. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:
- $$\frac{1}{2}\text{Cl}_2(\text{g}) \xrightarrow{\frac{1}{2}\Delta_{\text{diss}}H^\circ} \text{Cl}(\text{g}) \xrightarrow{\Delta_{\text{aq}}H^\circ} \text{Cl}^-(\text{g})$$
- $$\xrightarrow{\Delta_{\text{hyd}}H^\circ} \text{Cl}^-(\text{aq})$$
- The energy evolved in the conversion of
- $$\frac{1}{2}\text{Cl}_2(\text{g}) \text{ to } \text{Cl}^-(\text{aq})$$
- (using the data,
- $$\Delta_{\text{diss}}H^\circ_{\text{Cl}_2} = 240 \text{ kJ mol}^{-1}, \quad \Delta_{\text{aq}}H^\circ_{\text{Cl}^-} = -349 \text{ kJ mol}^{-1},$$
- $$\Delta_{\text{hyd}}H^\circ_{\text{Cl}^-} = -381 \text{ kJ mol}^{-1}),$$
- will be [2008]
- $+152 \text{ kJ mol}^{-1}$
  - $-610 \text{ kJ mol}^{-1}$
  - $-850 \text{ kJ mol}^{-1}$
  - $+120 \text{ kJ mol}^{-1}$
57. Assuming that water vapour is an ideal gas, the internal energy change ( $\Delta U$ ) when 1 mol of water is vapourised at 1 bar pressure and  $100^\circ\text{C}$ , (given : molar enthalpy of vapourisation of water at 1 bar and  $373 \text{ K} = 41 \text{ kJ mol}^{-1}$  and  $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ) will be [2007]
- $41.00 \text{ kJ mol}^{-1}$
  - $4.100 \text{ kJ mol}^{-1}$
  - $3.7904 \text{ kJ mol}^{-1}$
  - $37.904 \text{ kJ mol}^{-1}$
58. The standard enthalpy of formation ( $\Delta_f H^\circ$ ) at  $298 \text{ K}$  for methane,  $\text{CH}_4(\text{g})$  is  $-74.8 \text{ kJ mol}^{-1}$ . The additional information required to determine the average energy for  $\text{C}-\text{H}$  bond formation would be [2006]
- the first four ionization energies of carbon and electron gain enthalpy of hydrogen
  - the dissociation energy of hydrogen molecule,  $\text{H}_2$
  - the dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon
  - latent heat of vapourization of methane
59. The enthalpy changes for the following processes are listed below: [2006]
- |  |                             |
|--|-----------------------------|
| $\text{Cl}_2(\text{g}) = 2\text{Cl}(\text{g}),$                    | $242.3 \text{ kJ mol}^{-1}$ |
| $\text{I}_2(\text{g}) = 2\text{I}(\text{g}),$                      | $151.0 \text{ kJ mol}^{-1}$ |
| $\text{ICl}(\text{g}) = \text{I}(\text{g}) + \text{Cl}(\text{g}),$ | $211.3 \text{ kJ mol}^{-1}$ |
| $\text{I}_2(\text{s}) = \text{I}_2(\text{g}),$                     | $62.76 \text{ kJ mol}^{-1}$ |
- Given that the standard states for iodine and chlorine are  $\text{I}_2(\text{s})$  and  $\text{Cl}_2(\text{g})$ , the standard enthalpy of formation for  $\text{ICl}(\text{g})$  is: [2006]
- $+16.8 \text{ kJ mol}^{-1}$
  - $+244.8 \text{ kJ mol}^{-1}$
  - $-14.6 \text{ kJ mol}^{-1}$
  - $-16.8 \text{ kJ mol}^{-1}$
60. ( $\Delta H - \Delta U$ ) for the formation of carbon monoxide ( $\text{CO}$ ) from its elements at  $298 \text{ K}$  is [2006]
- $$(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$
- $-2477.57 \text{ J mol}^{-1}$
  - $2477.57 \text{ J mol}^{-1}$
  - $-1238.78 \text{ J mol}^{-1}$
  - $1238.78 \text{ J mol}^{-1}$
61. Consider the reaction :  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$  carried out at constant temperature and pressure. If  $\Delta H$  and  $\Delta U$  are the enthalpy and internal energy changes for the reaction, which of the following expressions is true? [2005]
- $\Delta H > \Delta U$
  - $\Delta H < \Delta U$
  - $\Delta H = \Delta U$
  - $\Delta H = 0$

62. If the bond dissociation energies of  $XY$ ,  $X_2$  and  $Y_2$  (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and  $\Delta H_f$  for the formation of  $XY$  is  $-200 \text{ kJ mol}^{-1}$ . The bond dissociation energy of  $X_2$  will be [2005]  
 (a)  $400 \text{ kJ mol}^{-1}$  (b)  $300 \text{ kJ mol}^{-1}$   
 (c)  $200 \text{ kJ mol}^{-1}$  (d)  $100 \text{ kJ mol}^{-1}$
63. The enthalpies of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283 \text{ kJ mol}^{-1}$  respectively. The enthalpy of formation of carbon monoxide per mole is [2004]  
 (a)  $-676.5 \text{ kJ}$  (b)  $676.5 \text{ kJ}$   
 (c)  $110.5 \text{ kJ}$  (d)  $-110.5 \text{ kJ}$
64. If at  $298 \text{ K}$  the bond energies of  $C-H$ ,  $C-C$ ,  $C=C$  and  $H-H$  bonds are respectively  $414$ ,  $347$ ,  $615$  and  $435 \text{ kJ mol}^{-1}$ , the value of enthalpy change for the reaction  
 $H_2C=CH_2(g) + H_2(g) \rightarrow H_3C-CH_3(g)$  at  $298 \text{ K}$  will be [2003]  
 (a)  $-250 \text{ kJ}$  (b)  $+125 \text{ kJ}$   
 (c)  $-125 \text{ kJ}$  (d)  $+250 \text{ kJ}$
65. The enthalpy change for a reaction does **not** depend upon [2003]  
 (a) use of different reactants for the same product  
 (b) the nature of intermediate reaction steps  
 (c) the differences in initial or final temperatures of involved substances  
 (d) the physical states of reactants and products
- TOPIC 3 Entropy and Second Law of Thermodynamics**
66. The true statement amongst the following is: [Jan. 09, 2020 (II)]  
 (a) Both  $\Delta S$  and  $S$  are functions of temperature.  
 (b) Both  $S$  and  $\Delta S$  are not functions of temperature.  
 (c)  $S$  is not a function of temperature but  $\Delta S$  is a function of temperature.  
 (d)  $S$  is a function of temperature but  $\Delta S$  is not a function of temperature.
67. Two blocks of the same metal having same mass and at temperature  $T_1$  and  $T_2$ , respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy,  $\Delta S$ , for this process is: [Jan. 11, 2019 (I)]  
 (a)  $C_p \ln \left[ \frac{(T_1 + T_2)^2}{4T_1 T_2} \right]$  (b)  $2C_p \ln \left[ \frac{(T_1 + T_2)^2}{T_1 T_2} \right]$   
 (c)  $2C_p \ln \left[ \frac{T_1 + T_2}{4T_1 T_2} \right]$  (d)  $2C_p \ln \left[ \frac{T_1 + T_2}{2T_1 T_2} \right]$
68. The process with negative entropy change is: [Jan. 10, 2019 (II)]  
 (a) Dissociation of  $CaSO_4(s)$  to  $CaO(s)$  and  $SO_3(g)$   
 (b) Sublimation of dry ice  
 (c) Dissolution of iodine in water  
 (d) Synthesis of ammonia from  $N_2$  and  $H_2$
69. The entropy change associated with the conversion of  $1 \text{ kg}$  of ice at  $273 \text{ K}$  to water vapours at  $383 \text{ K}$  is: (Specific heat of water liquid and water vapour are  $4.2 \text{ kJ K}^{-1} \text{ kg}^{-1}$  and  $2.0 \text{ kJ K}^{-1} \text{ kg}^{-1}$ ; heat of liquid fusion and vapourisation of water are  $334 \text{ kJ kg}^{-1}$  and  $2491 \text{ kJ kg}^{-1}$ , respectively). [Jan. 9, 2019 (II)]  
 $(\log 273 = 2.436, \log 373 = 2.572, \log 383 = 2.583)$   
 (a)  $7.90 \text{ kJ kg}^{-1} \text{ K}^{-1}$  (b)  $2.64 \text{ kJ kg}^{-1} \text{ K}^{-1}$   
 (c)  $8.49 \text{ kJ kg}^{-1} \text{ K}^{-1}$  (d)  $9.26 \text{ kJ kg}^{-1} \text{ K}^{-1}$
70. For which of the following processes,  $\Delta S$  is negative? [Online April 16, 2018]  
 (a)  $C(\text{diamond}) \rightarrow C(\text{graphite})$   
 (b)  $N_2(g, \text{latm}) \rightarrow N_2(g, \text{5atm})$   
 (c)  $N_2(g, 273\text{K}) \rightarrow N_2(g, 300\text{K})$   
 (d)  $H_2(g) \rightarrow 2H(g)$
71. The molar heat capacity ( $C_p$ ) of  $CD_2O$  is  $10 \text{ cal}$  at  $1000 \text{ K}$ . The change in entropy associated with cooling of  $32 \text{ g}$  of  $CD_2O$  vapour from  $1000 \text{ K}$  to  $100 \text{ K}$  at constant pressure will be: ( $D = \text{deuterium, atomic mass} = 2$ ) [Online April 11, 2014]  
 (a)  $23.03 \text{ cal deg}^{-1}$  (b)  $-23.03 \text{ cal deg}^{-1}$   
 (c)  $2.303 \text{ cal deg}^{-1}$  (d)  $-2.303 \text{ cal deg}^{-1}$
72. The  $(S^\circ)$  of the following substances are:  
 $CH_4(g)$   $186.2 \text{ JK}^{-1} \text{ mol}^{-1}$   
 $O_2(g)$   $205.2 \text{ JK}^{-1} \text{ mol}^{-1}$   
 $CO_2(g)$   $213.6 \text{ JK}^{-1} \text{ mol}^{-1}$   
 $H_2O(l)$   $69.9 \text{ JK}^{-1} \text{ mol}^{-1}$   
 The entropy change ( $\Delta S^\circ$ ) for the reaction  
 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$  is: [Online April 12, 2014]  
 (a)  $-312.5 \text{ JK}^{-1} \text{ mol}^{-1}$  (b)  $-242.8 \text{ JK}^{-1} \text{ mol}^{-1}$   
 (c)  $-108.1 \text{ JK}^{-1} \text{ mol}^{-1}$  (d)  $-37.6 \text{ JK}^{-1} \text{ mol}^{-1}$
73. The entropy of a sample of a certain substance increases by  $0.836 \text{ J K}^{-1}$  on adding reversibly  $0.3344 \text{ J}$  of heat at constant temperature. The temperature of the sample is: [Online May 7, 2012]  
 (a)  $2.5 \text{ K}$  (b)  $0.3 \text{ K}$   
 (c)  $0.016 \text{ K}$  (d)  $0.4 \text{ K}$
74. One mole of an ideal gas is expanded isothermally and reversibly to half of its initial pressure.  $\Delta S$  for the process in  $\text{J K}^{-1} \text{ mol}^{-1}$  is  $[\ln 2 = 0.693 \text{ and } R = 8.314, \text{ J/(mol K)}]$  [Online May 26, 2012]  
 (a)  $6.76$  (b)  $5.76$   
 (c)  $10.76$  (d)  $8.03$
75. Standard entropy of  $X_2$ ,  $Y_2$  and  $XY_2$  are  $60$ ,  $40$  and  $50 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. For the reaction,  
 $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3$ ,  $\Delta H = -30 \text{ kJ}$ , to be at equilibrium, the temperature will be [2008]  
 (a)  $1250 \text{ K}$  (b)  $500 \text{ K}$   
 (c)  $750 \text{ K}$  (d)  $1000 \text{ K}$

76. In conversion of lime-stone to lime,  
 $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are  $+179.1 \text{ kJ mol}^{-1}$  and  $160.2 \text{ J/K}$  respectively at 298 K and 1 bar. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is [2007]
- (a) 1118 K (b) 1008 K  
 (c) 1200 K (d) 845 K.

**TOPIC 4 Spontaneity and Gibbs Free Energy**

77. For a dimerization reaction,  $2\text{A}(\text{g}) \rightarrow \text{A}_2(\text{g})$ ,  
 at 298 K,  $\Delta U^\ominus = -20 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ominus = -30 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  
 then the  $\Delta G^\ominus$  will be \_\_\_\_\_ J.  
 [NV, Sep. 05, 2020 (II)]
78. A process will be spontaneous at all temperatures if:  
 [April 10, 2019 (I)]
- (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  $\Delta S > 0$
79. For the chemical reaction  $\text{X} \rightleftharpoons \text{Y}$ , the standard reaction Gibbs energy depends on temperature T (in K) as  $\Delta_r G^\ominus$  (in  $\text{kJ mol}^{-1}$ ) =  $120 - \frac{3}{8} T$   
 The major component of the reaction mixture at T is:  
 [Jan. 11, 2019 (I)]
- (a) Y if T=300 K (b) Y if T=280 K  
 (c) X if T=350 K (d) X if T=315 K
80. The reaction  
 $\text{MgO}(\text{s}) + \text{C}(\text{s}) \rightarrow \text{Mg}(\text{s}) + \text{CO}(\text{g})$ , for which  
 $\Delta H^\ominus = +491.1 \text{ kJ mol}^{-1}$  and  $\Delta S^\ominus = 198.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  
 is not feasible at 298 K. Temperature above which reaction will be feasible is [Jan. 11, 2019 (II)]
- (a) 2040.5 K (b) 1890.0 K  
 (c) 2480.3 K (d) 2380.5 K
81. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by  $\Delta_r G^\ominus = A - BT$  where A and B are non-zero constants. Which of the following is true about this reaction? [Jan. 11, 2019 (II)]
- (a) Exothermic if  $B < 0$   
 (b) Endothermic if  $A > 0$   
 (c) Endothermic if  $A < 0$  and  $B > 0$   
 (d) Exothermic if  $A > 0$  and  $B < 0$
82. A process has  $\Delta H = 200 \text{ J mol}^{-1}$  and  $\Delta S = 40 \text{ J K}^{-1} \text{ mol}^{-1}$ . Out of the values given below, choose the minimum temperature above which the process will be spontaneous: [Jan. 10, 2019 (I)]
- (a) 20 K (b) 12 K (c) 5 K (d) 4 K
83. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction? [2018]



- (a) A and B (b) B and C  
 (c) C and D (d) A and D
84. At 320 K, a gas  $\text{A}_2$  is 20% dissociated to  $\text{A}(\text{g})$ . The standard free energy change at 320 K and 1 atm in  $\text{J mol}^{-1}$  is approximately: [Online April 16, 2018]  
 ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $\ln 2 = 0.693$ ;  $\ln 3 = 1.098$ )
- (a) 1844 (b) 2068 (c) 4281 (d) 4763
85.  $\Delta_r G^\ominus$  at 500 K for substance 'S' in liquid state and gaseous state are  $+100.7 \text{ kcal mol}^{-1}$  and  $+103 \text{ kcal mol}^{-1}$ , respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to: ( $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$ ). [Online April 15, 2018 (II)]
- (a) 100 atm (b) 1 atm  
 (c) 10 atm (d) 0.1 atm
86. Given [Online April 15, 2018 (II)]
- (i)  $2\text{Fe}_2\text{O}_3(\text{s}) \rightarrow 4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g})$ ;  
 $\Delta_r G^\ominus = +1487.0 \text{ kJ mol}^{-1}$
- (ii)  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$ ;  
 $\Delta_r G^\ominus = -514.4 \text{ kJ mol}^{-1}$
- Free energy change,  $\Delta_r G^\ominus$  for the reaction  
 $2\text{Fe}_2\text{O}_3(\text{s}) + 6\text{CO}(\text{g}) \rightarrow 4\text{Fe}(\text{s}) + 6\text{CO}_2(\text{g})$  will be:
- (a)  $-112.4 \text{ kJ mol}^{-1}$  (b)  $-56.2 \text{ kJ mol}^{-1}$   
 (c)  $-208.0 \text{ kJ mol}^{-1}$  (d)  $-168.2 \text{ kJ mol}^{-1}$
87. An ideal gas undergoes isothermal expansion at constant pressure. During the process: [Online April 9, 2017]
- (a) enthalpy increases but entropy decreases.  
 (b) enthalpy remains constant but entropy increases.  
 (c) enthalpy decreases but entropy increases.  
 (d) Both enthalpy and entropy remain constant.
88. A reaction at 1 bar is non-spontaneous at low temperature but becomes spontaneous at high temperature. Identify the correct statement about the reaction among the following: [Online April 9, 2016]
- (a)  $\Delta H$  is negative while  $\Delta S$  is positive  
 (b) Both  $\Delta H$  and  $\Delta S$  are negative  
 (c)  $\Delta H$  is positive while  $\Delta S$  is negative  
 (d) Both  $\Delta H$  and  $\Delta S$  are positive.

89. The incorrect expression among the following is: [2012]
- (a)  $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$
- (b) In isothermal process,  
 $w_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$
- (c)  $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$
- (d)  $K = e^{-\Delta G^\circ/RT}$
90. For a particular reversible reaction at temperature T,  $\Delta H$  and  $\Delta S$  were found to be both +ve. If  $T_e$  is the temperature at equilibrium, the reaction would be spontaneous when
- (a)  $T_e > T$  (b)  $T > T_e$  [2010]
- (c)  $T_e$  is 5 times T (d)  $T = T_e$
91. Identify the correct statement regarding a spontaneous process: [2007]
- (a) Lowering of energy in the process is the only criterion for spontaneity.
- (b) For a spontaneous process in an isolated system, the change in entropy is positive.
- (c) Endothermic processes are never spontaneous.
- (d) Exothermic processes are always spontaneous.
92. 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 change in entropy ( $dS$ ), satisfy the criteria [2003]
- (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)  $(dS)_{V,E} < 0, (dG)_{T,P} < 0$
93. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant  $K_c$  is
- (a)  $-\Delta G = RT \ln K_c$  (b)  $\Delta G^\circ = RT \ln K_c$  [2003]
- (c)  $-\Delta G^\circ = RT \ln K_c$  (d)  $\Delta G = RT \ln K_c$
94. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then [2002]
- (a)  $\Delta H$  is -ve,  $\Delta S$  is +ve
- (b)  $\Delta H$  and  $\Delta S$  both are +ve
- (c)  $\Delta H$  and  $\Delta S$  both are -ve
- (d)  $\Delta H$  is +ve,  $\Delta S$  is -ve
95. For the reactions, [2002]
- $2C + O_2 \rightarrow 2CO_2; \Delta H = -393 \text{ J}$
- $2Zn + O_2 \rightarrow 2ZnO; \Delta H = -412 \text{ J}$
- (a) carbon can oxidise Zn
- (b) oxidation of carbon is not feasible
- (c) oxidation of Zn is not feasible
- (d) Zn can oxidise carbon.



## Hints & Solutions



1. (d) In expansion against vacuum

$$P_{\text{ext}} = 0$$

$$W = -P_{\text{ext}} \Delta V = 0$$

$$W = 0$$

2. (48.00)

Work done is given by the area under the trapezium.

$$\therefore |w| = \frac{1}{2} (6 + 10) \times 6 = 48 \text{ J}$$

3. (6.25)  $\Delta U = nC_v \Delta T$   
 $5000 = 4 \times C_v (500 - 300)$   
 $C_v = 6.25 \text{ JK}^{-1} \text{ mol}^{-1}$

4. (c)  $w = -P \Delta V$   
 $= -(1 \text{ bar}) \times (9 \text{ L})$   
 $= -(10^5 \text{ Pa}) \times (9 \times 10^{-3}) \text{ m}^3$   
 $= -9 \times 10^2 \text{ N.m}$  [ $\because 1 \text{ Pa} = 1 \text{ N/m}^2$ ]  
 $= -900 \text{ J} = -0.9 \text{ kJ}$

5. (a) We know that heat and work are not state functions but  $q + w = \Delta U$  is a state function.  $H - TS$  (i.e.  $G$ ) is also a state function.

6. (c)  $w = 10 \text{ kJ}$   
 $q = -2 \text{ kJ}$   
 $\Delta U = q + w = -2 + 10 = 8 \text{ kJ}$

7. (b) From first law of thermodynamics,  $\Delta U = q + w$   
 For adiabatic process,  $q = 0$   
 $\therefore \Delta U = w$

For isothermal process,  $\Delta U = 0 \Rightarrow q = -w$

For cyclic process,  $\Delta U = 0 \Rightarrow q = -w$

For isochoric process,  $w = 0 \Rightarrow \Delta U = q$

8. (c)  $\Delta U = n C_v \Delta T = 5 \times 28 \times 100 = 14 \text{ kJ}$   
 $\Delta(PV) = nR(T_2 - T_1) = 5 \times 8 \times 100 = 4 \text{ kJ}$

9. (a) For ideal gas,  $C_p$  and  $C_v$  are dependent on temperature only.

$$C_p = \frac{7}{2} R \text{ (Independent of } P)$$

$$C_v = \frac{5}{2} R \text{ (Independent of } P)$$

Thus,  $C_p$  will not change with pressure.

10. (a) Isothermal expansion

$$PV_m = K \text{ (graph - C)}$$

$$P = \frac{K}{V_m} \text{ (graph - A)}$$



Therefore (B) and (D) are not correct representation.

11. (c) We know that,

$$w = -P_{\text{ext}}(V_f - V_i)$$

$$w = -4 \text{ Nm}^{-2}(1 - 5) \text{ m}^3$$

$$w = 16 \text{ Nm} \Rightarrow 16 \text{ J}$$

For isothermal compression,

$$\Delta U = q + w$$

$$\Rightarrow q = -w = -16 \text{ J} (\because \Delta U = 0 \text{ for isothermal process})$$

From calorimetry,

Heat given  $= n C \Delta T$

$$\text{So, } 16 = \frac{1 \times 24 \text{ J} \times \Delta T}{\text{mol K}}$$

$$\therefore \text{Change in temperature, } \Delta T = \frac{2}{3} \text{ K}$$

12. (b) For reversible isothermal expansion,

$$w = -nRT \ln \frac{V_2}{V_1}$$

$$\Rightarrow |w| = nRT \ln \frac{V_2}{V_1}$$

$$|w| = nRT (\ln V_2 - \ln V_1)$$

$$|w| = nRT \ln V_2 - nRT \ln V_1$$

$$y = mx + c$$

So, slope of curve 2 is more than curve 1 and intercept of curve 2 is more negative than curve 1.

13. (b)  $\Delta U_{AB} = q_{AB} + W_{AB} = 2 + (-5) = -3 \text{ kJ/mol}$

$$\Delta U_{BC} = -5 \text{ kJ/mol}$$

For cyclic process,  $\Delta U = 0$

$$\Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA} = 0$$

$$\Delta U_{CA} = -\Delta U_{AB} - \Delta U_{BC}$$

$$\Delta U_{CA} = -(-3) - (-5) = 8 \text{ kJ/mol}$$

$$\Delta U_{CA} = q_{CA} + W_{CA}$$

$$8 = q_{CA} + 3$$

$$q_{CA} = +5 \text{ kJ/mol}$$

Heat absorbed has positive sign.

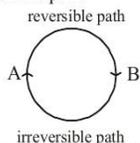
14. (c) From 1<sup>st</sup> law of thermodynamics

$$\Delta U = q + w$$

For adiabatic process :  $q = 0$

$$\therefore \Delta U = w$$

15. (d)  $A \xrightarrow{q=+5, w=8J} B$   
 $\Delta U_{AB} = q + w = +5 + (-8) = -3$   
 $q = -3, \Delta U_{BA} = +3$   
 $\Delta U_{BA} = q + w$   
 $\Rightarrow 3 = -3 + w \Rightarrow w = +6$  (work done on the system).
16. (a)  $2H_2O_2(l) \rightleftharpoons 2H_2O(l) + O_2(g)$   
 $w = -P_{ext}(\Delta V) = -n_{O_2}RT$   
 $\therefore 100 \text{ mole } H_2O_2 \text{ on decomposition give } 50 \text{ mole } O_2.$   
 $\therefore w = -(50)(8.3)(300) = -124500 \text{ J} = -124.5 \text{ kJ}.$
17. (a) Process is isothermal reversible expansion, hence  $\Delta U = 0$ , therefore  $q = -w$ .  
 Since  $q = +208 \text{ J}, w = -208 \text{ J}$
18. (c) For isothermal reversible expansion.  
 $w = -nRT \ln \frac{V_2}{V_1}$
19. (e) According to first law of thermodynamics  
 $\Delta Q = \Delta U + \Delta W$   
 An isolated system is adiabatic. This means  $\Delta Q = 0$ . The first law in this case yields  
 $0 = \Delta U + \Delta W \Rightarrow \Delta W = -\Delta U$  ..... (i)  
 For expansion,  $\Delta W$  is positive and hence  $\Delta U$  is negative. This means  $T_f$  is less than  $T_i$  in both the cases.  
 For the same expansion of volume, the work done in irreversible process is greater than that in reversible one because the system has to work against friction etc. Thus  
 $\Delta W_{irreversible} > \Delta W_{reversible}$   
 $\Rightarrow -\Delta U_{irreversible} > -\Delta U_{reversible}$   
 [from equation (i)]  
 $\Rightarrow \Delta U_{irreversible} < \Delta U_{reversible}$   
 $\Rightarrow \Delta T_{irreversible} < \Delta T_{reversible}$   
 $\Rightarrow T_{f \text{ irreversible}} > T_{f \text{ reversible}}$
20. (e)  $w = -P\Delta V = -10^5 [(1 \times 10^{-2}) - (1 \times 10^{-3})]$   
 $= -900 \text{ J}$
21. (e) For a cyclic process, the net change in the internal energy is zero because the change in internal energy does not depend on the path.



22. (a) According to first law of thermodynamics energy can neither be created nor destroyed although it can be converted from one form to another.  
**Note:** Carnot cycle is based upon this principle but during the conversion of heat into work some mechanical energy is always converted to other form of energy hence this data violates 1st law of thermodynamics.

23. (b) The heat required to raise the temperature of body by 1K is called thermal capacity or heat capacity.
24. (c)  $\Delta_{sol.}H^\circ = \Delta_{lattice}H^\circ + \Delta_{hyd.}H^\circ$   
 $4 = 788 + \Delta_{hyd.}H^\circ$   
 $\Delta_{hyd.}H^\circ = -784 \text{ kJmol}^{-1}$

25. (d)  
 (1) For ideal gas U and H are function of temperature.  
 (2) Compressibility factor for an ideal gas is 1.  
 (3)  $C_p - C_v = R$   
 (4)  $\Delta U = C_v dT$  for all processes.
26. (d) A-B bond has highest intermolecular potential energy among the given molecules. Hence, it is strongest bond and has maximum bond enthalpy.

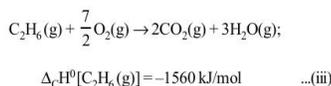
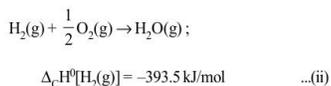
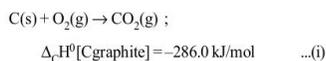
27. (189494)  
 $\Delta H = \Delta U + \Delta n_g RT$   
 $n = \frac{90}{18} = 5 \text{ mol}$   
 $H_2O(l) \rightleftharpoons H_2O(g)$   
 $\Delta n = 1$   
 $41000 = \Delta U + 1 \times 8.314 \times 373$   
 $\Rightarrow \Delta U = 37898.875 \text{ J}$   
 For 5 moles,  $\Delta U = 37898.87 \times 5 = 189494 \text{ J}$

28. (-326400)  
 $C_2H_5OH(l) + O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);$   
 $\Delta H_c = -327 \text{ Kcal}$   
 $\Delta H = \Delta U + \Delta n_g RT$   
 $\Rightarrow -327 \times 10^3 = \Delta U + (-1) \times 2 \times 300$   
 $\Rightarrow \Delta U = -327 \times 10^3 + 600$   
 $\therefore \Delta U = -326400 \text{ cal}$

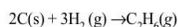
29. (e)  $\Delta H_{atomisation} = \Delta H_{vap} + \text{Bond energy}$   
 Hence  $x > y$

30. (-2.70)  
 $\Delta U = 2.1 \text{ kcal} = 2.1 \times 10^3 \text{ cal}$   
 $\Delta n_g = 2$   
 $\Delta H = \Delta U + \Delta n_g RT$   
 $= 2.1 \times 10^3 + 2 \times 2 \times 300$   
 $= 2100 + 1200$   
 $= 3300 \text{ cal}$   
 $\Delta G = \Delta H - T\Delta S$   
 $= 3300 - 300 \times 20$   
 $= 3300 - 6000$   
 $= -2700 \text{ cal}$   
 $= -2.7 \text{ kcal}$

## 31. (-192.5)



The reaction of formation of ethane is



$$\therefore \Delta_f H^\circ \text{ of } \text{C}_2\text{H}_6(\text{g}) =$$

$$2 \times \Delta_c H^\circ[\text{C}_{\text{graphite}}] + 3 \times \Delta_c H^\circ[\text{H}_2(\text{g})] - \Delta_c H^\circ[\text{C}_2\text{H}_6(\text{g})]$$

$$= 2 \times (-286.0) + 3(-393.5) - (-1560)$$

$$= -192.5 \text{ kJ/mol}$$

32. (c)  $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$ 

Heat of reaction depend upon temperature i.e., it varies with temperature, as given by Kirchoff's equation,

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT$$

where  $\Delta C_p = C_p$  of product -  $C_p$  of reactant

$$\therefore \Delta C_p = 0.031 - 0.055 = -0.024 \text{ cal/g}$$

$$\text{Now, } \Delta H_{T_2} - \Delta H_{T_1} = \Delta C_p (T_2 - T_1)$$

$$\Delta H_{(250)} - \Delta H_{(200)} = -0.024 (523 - 473)$$

$$\Delta H_{(250)} = 24 - 50 \times 0.024 = 22.8 \text{ cal/g}$$

33. (a)  $\text{C}_7\text{H}_{16}(\text{l}) + 11\text{O}_2(\text{g}) \xrightarrow{\Delta} 7\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})$ 

$$\Delta H - \Delta U = \Delta n_g RT$$

$\Delta n_g =$  no. of moles of product in gaseous state - no. of moles of reactant in gaseous state.

$$\therefore \Delta n_g = -4$$

$$\therefore \Delta H - \Delta U = -4RT$$

34. (a) Given:  $n = 3$ 

$$T_1 = 300; T_2 = 1000$$

$$C_p = 23 + 0.01T$$

The relation between  $\Delta H$  and  $C_p$  is

$$\Delta H = \int_{T_1}^{T_2} n C_p dT \quad \dots(\text{i})$$

After putting all variable values in eq. (i), we get

$$\Delta H = n \int_{300}^{1000} (23 + 0.01T) dT$$

$$= 3 \left[ 23T + \frac{0.01T^2}{2} \right]_{300}^{1000}$$

$$= 3 \left[ 23(1000 - 300) + \frac{0.01}{2} (1000^2 - 300^2) \right]$$

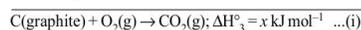
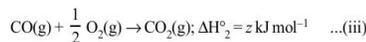
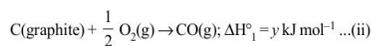
$$= 3[16100 + 4550]$$

$$= 3 \times 20650 = 61950 \text{ J}$$

$$= 61.95 \text{ kJ}$$

$$\approx 62 \text{ kJ}$$

## 35. (a) Equation (i) can be obtained by adding equations (ii) and equation (iii)



$$\therefore \Delta H_3 = \Delta H_1 + \Delta H_2$$

$$x = y + z$$

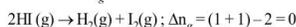
36. (d)  $\text{C}_6\text{H}_6(\text{l}) + \frac{15}{2} \text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ 

$$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2}$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$= -3263.9 + \left(-\frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

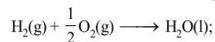
$$= -3263.9 + (-3.71) = -3267.6 \text{ kJ mol}^{-1}$$

37. (b)  $\Delta H = \Delta U + \Delta n_g RT$ 

$$\therefore \Delta H = \Delta U + 0$$

38. (c)  $\text{C}_{\text{(graphite)}} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g});$ 

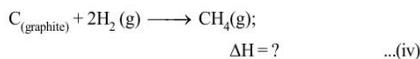
$$\Delta_f H^\circ = -393.5 \text{ kJ/mol}^{-1} \dots(\text{i})$$



$$\Delta_f H^\circ = -285.8 \text{ kJ/mol}^{-1} \dots(\text{ii})$$



$$\Delta_f H^\circ = +890.3 \text{ kJ/mol}^{-1} \dots(\text{iii})$$



$$[\text{Eq. (i)} + \text{Eq. (iii)}] + [2 \times \text{Eq. (ii)}] = \text{Eq. (iv)}$$

$$\therefore [\Delta H_1 + \Delta H_3] + [2 \times \Delta H_2] = \Delta H_4$$

$$[(-393.5) + (890.3)] + [2(-285.8)]$$

$$= -74.8 \text{ kJ/mol}$$

39. (d)  $\text{A}(\text{g}) \longrightarrow \text{A}(\text{l})$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\text{Given, } \Delta H = -3RT$$

Here

$$\Delta n_g = n_p - n_r = 0 - 1 = -1$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Rightarrow -3RT = \Delta U - RT$$

$$\Rightarrow -3RT + RT = \Delta U$$

$$\Rightarrow -2RT = \Delta U$$

$$|\Delta H| > |\Delta U|$$

40. (e) In order to calculate the enthalpy change for  $\text{H}_2\text{O}$  at  $5^\circ\text{C}$  to ice at  $-5^\circ\text{C}$ , we need to calculate the enthalpy change of all the transformation involved in the process.

- (a) Energy change of 1 mol,  $\text{H}_2\text{O}(\text{l})$ , at  $5^\circ\text{C}$

$$\rightarrow 1 \text{ mol, } \text{H}_2\text{O}(\text{l}), 0^\circ\text{C}$$

- (b) Energy change of 1 mol,  $\text{H}_2\text{O}(\text{l})$ , at  $0^\circ\text{C}$

$$\rightarrow 1 \text{ mol, } \text{H}_2\text{O}(\text{s}) (\text{ice}), 0^\circ\text{C}$$

- (c) Energy change of 1 mol, ice (s), at  $0^\circ\text{C}$

$$\rightarrow 1 \text{ mol, ice (s)}, -5^\circ\text{C}$$

Total  $\Delta H$

$$= C_p [\text{H}_2\text{O}(\text{l})] \Delta T + \Delta H_{\text{freezing}} + C_p [\text{H}_2\text{O}(\text{s})] \Delta T$$

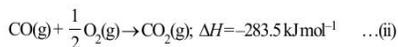
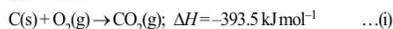
$$= (75.3 \text{ J mol}^{-1} \text{ K}^{-1})(0-5)\text{K} + (-6 \times 10^3 \text{ J mol}^{-1})$$

$$+ (36.8 \text{ J mol}^{-1} \text{ K}^{-1})(-5-0)\text{K}$$

$$\Delta H = -6.56 \text{ kJ mol}^{-1} \text{ (exothermic process)}$$

$$\text{So, } \Delta H = 6.56 \text{ kJ mol}^{-1}.$$

41. (b) Given



$$\therefore \text{Heat of formation of CO} = \text{eq}^{\text{a}}(\text{i}) - \text{eq}^{\text{b}}(\text{ii})$$

$$= -393.5 - (-283.5)$$

$$= -110 \text{ kJ}$$

42. (b) In  $\text{CH}_4$ ,  $4 \times \text{BE}_{(\text{C-H})} = 360 \text{ kJ/mol}$

$$\therefore \text{BE}_{(\text{C-H})} = 90 \text{ kJ/mol}$$

$$\text{In } \text{C}_2\text{H}_6, \text{BE}_{(\text{C-C})} + 6 \times \text{BE}_{(\text{C-H})} = 620 \text{ kJ/mol}$$

$$\therefore \text{BE}_{(\text{C-C})} = 80 \text{ kJ/mol}$$

$$\therefore \text{BE}_{(\text{C-C})} = \frac{80 \times 10^3}{6.023 \times 10^{23}} \text{ J/mol}$$

$$\text{Now, } E = \frac{hc}{\lambda}$$

$$\therefore \lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{80 \times 10^3}$$

$$\lambda = 1.49 \times 10^{-6} \text{ m} \quad (\because 1 \text{ nm} = 10^{-9} \text{ m})$$

$$\therefore \lambda = 1.49 \times 10^3 \text{ nm}$$

43. (a)  $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

Bomb calorimeter gives  $\Delta U$  of the reaction

$$\text{Given, } \Delta U = -1364.47 \text{ kJ mol}^{-1}$$

$$\Delta n_g = -1$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$= -1364.47 - \frac{1 \times 8.314 \times 298}{1000}$$

$$= -1366.95 \text{ kJ mol}^{-1}$$

44. (c) Given  $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftharpoons \text{NH}_3$ ;

$$\Delta_f H = -46.0 \text{ kJ/mol}$$

$$\text{H} + \text{H} \rightleftharpoons \text{H}_2; \Delta_f H = -436 \text{ kJ/mol}$$

$$\text{N} + \text{N} \rightleftharpoons \text{N}_2; \Delta_f H = -712 \text{ kJ/mol}$$

$$\Delta_f H(\text{NH}_3) = \frac{1}{2}\Delta H_{\text{N-N}} + \frac{3}{2}\Delta H_{\text{H-H}} - 3\Delta H_{\text{N-H}}$$

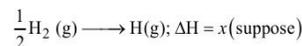
$$-46 = \frac{1}{2}(712) + \frac{3}{2}(436) - 3\Delta H_{\text{N-H}}$$

$$-3\Delta H_{\text{N-H}} = -1056$$

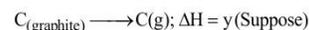
$$\Delta H_{\text{N-H}} = 352 \text{ kJ/mol}$$

45. (c) To calculate average enthalpy of C-H bond in methane following informations are needed

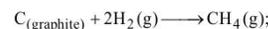
- (i) dissociation energy of  $\text{H}_2$  i.e.



- (ii) Sublimation energy of  $\text{C}(\text{graphite})$  to  $\text{C}(\text{g})$

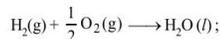


Given

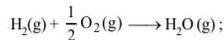


$$\Delta H_g = -74.9 \text{ kJ mol}^{-1}$$

46. (c) Given



$$\Delta H^\circ = -285.9 \text{ kJ mol}^{-1} \quad \dots \text{(i)}$$

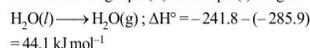


$$\Delta H^\circ = -241.8 \text{ kJ mol}^{-1} \quad \dots \text{(ii)}$$

We have to calculate



On subtracting eqn. (ii) from eqn. (i) we get



47. (c) Applying Hess's Law

$$\Delta_f H^\circ = \Delta_{\text{sub}} H + \frac{1}{2} \Delta_{\text{diss}} H + \text{I.E.} + \text{E.A.} + \Delta_{\text{lattice}} H$$

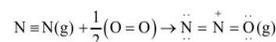
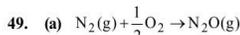
$$-617 = 161 + 520 + 77 + \text{E.A.} + (-1047)$$

$$\text{E.A.} = -617 + 289 = -328 \text{ kJ mol}^{-1}$$

∴ electron affinity of fluorine

$$= -328 \text{ kJ mol}^{-1}$$

48. (a)



$$\Delta_f H^\circ = [\text{Energy required for breaking of bonds}] - [\text{Energy released for forming of bonds}]$$

$$= (\Delta H_{\text{N}=\text{N}} + \frac{1}{2} \Delta H_{\text{O}=\text{O}} - (\Delta H_{\text{N}=\text{N}} + \Delta H_{\text{N}=\text{O}}))$$

$$= (946 + \frac{1}{2} \times 498) - (418 + 607) = 170 \text{ kJ mol}^{-1}$$

Resonance energy = observed  $\Delta_f H^\circ$  - calculated  $\Delta_f H^\circ$ 

$$82 - 170 = -88 \text{ kJ mol}^{-1}$$

50. (d)  $\Delta H = \Delta U + \Delta n_g RT$ For the reaction  $\Delta n_g = 12 - 15 = -3$ 

$$\Delta H - \Delta U = -3 \times 8.314 \times 300$$

$$= -7482.6 \text{ J mol}^{-1}$$

51. (d)  $\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^- \quad \dots \text{(i)}$ 

Strong acid (Complete ionisation)

Weak base  $\Delta H = x \text{ kJ mol}^{-1}$ 

$$\Delta H = -55.90 \text{ kJ mol}^{-1}$$

(from neutralisation of strong acid and strong base)

From equation (i), (ii) and (iii)



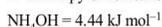
$$\Delta H = -51.46 \text{ kJ mol}^{-1}$$

$$\therefore x + (-55.90) = -51.46$$

$$x = -51.46 + 55.90$$

$$= 4.44 \text{ kJ mol}^{-1}$$

∴ Enthalpy of ionisation of

52. (b)  $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ 

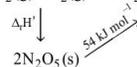
$$\Delta n_g = 2 - 3 = -1$$

$$\Delta U = \Delta H - \Delta n_g RT$$

$$= -1366.5 - [(-1) \times 8.314 \times 300]$$

$$= -1366.5 + \left[ (1) \times \frac{8.314}{10^3} \times 300 \right]$$

$$= -1366.5 + 0.8314 \times 3 = -1364 \text{ kJ}$$

53. (d)  $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g}), \Delta_r H = -111 \text{ kJ}$ 

$$\Delta_f H^\circ = \Delta_f H - 54$$

$$= -111 - 54$$

$$= -165 \text{ kJ}$$

54. (b)  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3 \quad \Delta H = 2 \times -46.0 \text{ kJ mol}^{-1}$ Let  $x$  be the bond enthalpy of N - H bond then

[Note : Enthalpy of formation or bond formation enthalpy is given which is negative but the given reaction involves bond breaking hence values should be taken as positive.]

$$\Delta H = \Sigma \text{Bond energies of reactants}$$

$$- \Sigma \text{Bond energies of products}$$

$$2 \times -46 = 712 + 3 \times (436) - 6x - 92 = 2020 - 6x$$

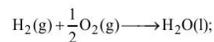
$$6x = 2020 + 92$$

$$6x = 2112$$

$$x = +352 \text{ kJ/mol}$$

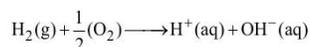
55. (a)  $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}^+(\text{aq.}) + \text{OH}^-(\text{aq.});$ 

$$\Delta H = 57.32 \text{ kJ} \quad \dots \text{(i)}$$



$$\Delta H = -286.20 \text{ kJ} \quad \dots \text{(ii)}$$

By adding equation (i) &amp; (ii) we get,

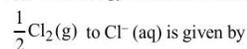


$$\Delta H = 57.32 - 286.2 = -228.88 \text{ kJ}$$

Here  $\Delta_f H^\circ$  of  $\text{H}^+(\text{aq}) = 0$

$$\therefore \Delta_f H^\circ \text{ of } \text{OH}^- = -228.88 \text{ kJ}$$

56. (b) The energy involved in the conversion of



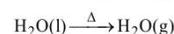
$$\Delta H = \frac{1}{2}\Delta_{\text{diss}}H^\circ_{\text{Cl}_2} + \Delta_{\text{eg}}H^\circ_{\text{Cl}} + \Delta_{\text{hyd}}H^\circ_{\text{Cl}}$$

Substituting various values from given data, we get

$$\begin{aligned} \Delta H &= \left(\frac{1}{2} \times 240\right) + (-349) + (-381) \\ &= (120 - 349 - 381) = -610 \text{ kJ mol}^{-1} \end{aligned}$$

57. (d) Given  $\Delta H = 41 \text{ kJ mol}^{-1} = 41000 \text{ J mol}^{-1}$

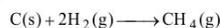
$$T = 100^\circ\text{C} = 273 + 100 = 373 \text{ K}$$



$$\Delta n_g = 1 - 0 = 1$$

$$\begin{aligned} \Delta U &= \Delta H - \Delta n_g RT = 41000 - (1 \times 8.314 \times 373) \\ &= 37898.88 \text{ J mol}^{-1} \approx 37.9 \text{ kJ mol}^{-1} \end{aligned}$$

58. (c) The standard enthalpy of formation of  $\text{CH}_4$  is given by the equation :



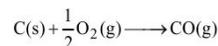
Hence, dissociation energy of hydrogen and enthalpy of sublimation of carbon is required.

59. (a)  $\text{I}_2(\text{s}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{ICl}(\text{g})$

$$\begin{aligned} \Delta H &= [\Delta H_{\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})} + \Delta H_{\text{I}-\text{I}} + \Delta H_{\text{Cl}-\text{Cl}}] - 2[\Delta H_{\text{I}-\text{Cl}}] \\ &= 62.76 + 151.0 + 242.3 - 2 \times 211.3 = 33.46 \end{aligned}$$

$$\Delta H_f^\circ(\text{ICl}) = \frac{33.46}{2} = 16.73 \text{ kJ/mol}$$

60. (d) For the reaction,



$$\Delta H = \Delta U + \Delta n_g RT \text{ or } \Delta H - \Delta U = \Delta n_g RT$$

$$\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2};$$

$$\begin{aligned} \Delta H - \Delta U &= \frac{1}{2} \times 8.314 \times 298 \\ &= 1238.78 \text{ J mol}^{-1} \end{aligned}$$

61. (b)  $\Delta H = \Delta U + \Delta n_g RT$  for



$$\Delta n_g = 2 - 4 = -2$$

$$\therefore \Delta H > \Delta U - 2RT$$

$$\text{or } \Delta U = \Delta H + 2RT \quad \therefore \Delta U > \Delta H$$

62. (N)  $\frac{1}{2}\text{X}_2 + \frac{1}{2}\text{Y}_2 \longrightarrow \text{XY}, \Delta H = (-200) \text{ J}$

Let  $x$  be the bond dissociation energy of  $\text{X}_2$ . Then

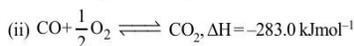
$$\Delta H_f = -200 = \frac{1}{2}\Delta H_{\text{X-X}} + \frac{1}{2}\Delta H_{\text{Y-Y}} - \Delta H_{\text{X-Y}}$$

$$-400 = x + 0.5x - 2x = -0.5x$$

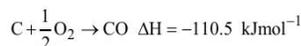
$$\text{or } x = \frac{400}{0.5} = 800 \text{ kJ mol}^{-1}$$

(In the question paper, this option was not mentioned. So the answer has been marked 'N')

63. (d) (i)  $\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2, \Delta H = -393.5 \text{ kJ mol}^{-1}$



Operating (i) - (ii), we have



64. (c)  $\text{CH}_2 = \text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_3 - \text{CH}_3$

Enthalpy change = Bond energy of reactants - Bond energy of products.

$$\Delta H = 1(\text{C}=\text{C}) + 4(\text{C}-\text{H}) + 1(\text{H}-\text{H}) - 1(\text{C}-\text{C}) - 6(\text{C}-\text{H})$$

$$= 1(\text{C}=\text{C}) + 1(\text{H}-\text{H}) - 1(\text{C}-\text{C}) - 2(\text{C}-\text{H})$$

$$= 615 + 435 - 347 - 2 \times 414 = 1050 - 1175$$

$$= -125 \text{ kJ.}$$

65. (b) Enthalpy change for a reaction does not depend upon the nature of intermediate reaction steps.

66. (a) A system at higher temperature has greater entropy (randomness).  $S$  and  $\Delta S$  are related with  $T$  as:

$$S_T = \int_0^T \frac{nC \cdot dT}{T} \quad \Delta S = \int \frac{dq}{T}$$

Thus both  $S$  and  $\Delta S$  are function of temperature.

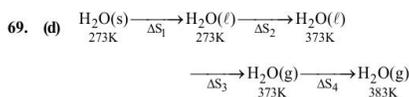
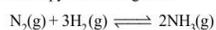
67. (a) Final temperature =  $\frac{T_1 + T_2}{2}$ , let  $T_2 > T_1$

$$\therefore dS = \frac{dq}{T} = \frac{C_p dT}{T}$$

$$\therefore \Delta S = C_p \ln \left( \frac{T_f}{T_i} \right)$$

$$\begin{aligned} \therefore \Delta S_{\text{Total}} &= C_p \ln \left( \frac{T_1 + T_2}{2T_1} \right) + C_p \ln \left( \frac{T_1 + T_2}{2T_2} \right) \\ &= C_p \ln \left[ \frac{(T_1 + T_2)^2}{4T_1 T_2} \right] \end{aligned}$$

68. (d) In the process of synthesis of ammonia from  $N_2$  and  $H_2$ , number of moles decreases which implies that the change in entropy will be negative.



$$\begin{aligned} \Delta S_1 &= \frac{\Delta H_{\text{fus}}}{273} \\ &= \frac{334}{273} = 1.22 \end{aligned}$$

$$\begin{aligned} \Delta S_2 &= m C \ln \left( \frac{T_2}{T_1} \right) \\ &= 4.2 \times \ln \left( \frac{373}{273} \right) \\ &= 4.2 \times 2.303 \times \log 373 - \log 273 \\ &= 4.2 \times 2.303 \times 2.572 - 2.436 \\ &= 1.31 \end{aligned}$$

$$\Delta S_3 = \frac{\Delta H_{\text{vap}}}{373} = \frac{2491}{373} = 6.68$$

$$\begin{aligned} \Delta S_4 &= m C \ln \left( \frac{T_2}{T_1} \right) \\ &= 2 \times \ln \left( \frac{383}{373} \right) \\ &= 2 \times 2.303 \times \log 383 - \log 373 \\ &= 2 \times 2.303 \times 2.583 - 2.572 \\ &= 0.05 \end{aligned}$$

$$\begin{aligned} \therefore \text{Total entropy change} \\ \Delta S &= 1.28 + 6.68 + 1.31 + 0.05 \\ &= 9.26 \text{ kJ kg}^{-1} \text{ K}^{-1} \end{aligned}$$

70. (b)

(a) When diamond is converted into graphite (it is heated to  $1500^\circ\text{C}$ ) entropy is increased,  $\Delta S > 0$

(b) When pressure increases then molecules of gas will come closer and intermolecular distance decreases, so entropy will also decrease,  $\Delta S < 0$

(c) When we increase the temperature of a gas then randomness is increased as the kinetic energy gained by molecules. So,  $\Delta S > 0$

(d)  $H_2$  molecule is converted into atoms, the no. of particles increases. Thus entropy will increase,  $\Delta S > 0$

71. (b) Given,  $C_p = 10$  cal at 1000 K

$$T_1 = 1000 \text{ K}, T_2 = 100 \text{ K}$$

$$m = 32 \text{ g}$$

$$\Delta S = ?$$

at constant pressure

$$\begin{aligned} \Delta S &= C_p \ln \frac{T_2}{T_1} \\ &= 2.303 \times C_p \log \frac{T_2}{T_1} \\ &= 2.303 \times 10 \log \frac{100}{1000} \\ &= -23.03 \text{ cal deg}^{-1} \end{aligned}$$

72. (b)  $\Delta S^\circ = S^\circ_{\text{CO}_2} + 2 \times S^\circ_{\text{H}_2\text{O}} - \left( S^\circ_{\text{CH}_4} + 2 \times S^\circ_{\text{O}_2} \right)$   
 $= (213.6 + 2 \times 69.9) - (186.2 + 2 \times 205.2)$   
 $= -242.8 \text{ J K}^{-1} \text{ mol}^{-1}$

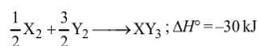
73. (d)  $\Delta S = \frac{\Delta H}{T}$ ;  $T = \frac{\Delta H}{\Delta S} = \frac{0.3344}{0.836} = 0.4 \text{ K}$

74. (b) For isothermal process ( $\Delta T = 0$ )

$$\begin{aligned} \Delta S &= R \ln \frac{P_1}{P_2} = 8.314 \ln 2 \\ &= 8.314 \times 0.693 = 5.76 \end{aligned}$$

75. (c) For a reaction to be at equilibrium  $\Delta G^\circ = 0$ . Since  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  so at equilibrium  $\Delta H^\circ - T\Delta S^\circ = 0$  or  $\Delta H^\circ = T\Delta S^\circ$

For the reaction



Calculating  $\Delta S^\circ$  for the above reaction, we get

$$\begin{aligned} \Delta S^\circ &= 50 - \left[ \frac{1}{2} \times 60 + \frac{3}{2} \times 40 \right] \\ &= 50 - (30 + 60) = -40 \text{ J K}^{-1} \end{aligned}$$

At equilibrium,  $T\Delta S^\circ = \Delta H^\circ$  [ $\because \Delta G^\circ = 0$ ]

$$\therefore T \times (-40 \text{ JK}^{-1}) = -30 \times 1000 \text{ J} \quad [\because 1 \text{ kJ} = 1000 \text{ J}]$$

$$\text{or } T = \frac{-30 \times 1000}{-40} = 750 \text{ K}$$

76. (a)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

For a spontaneous reaction  $\Delta G^\circ < 0$

$$\text{or } \Delta H^\circ - T\Delta S^\circ < 0 \Rightarrow T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$\Rightarrow T > \frac{179.3 \times 10^3}{160.2}$$

$$> 1117.9 \text{ K} \approx 1118 \text{ K}$$

77. (-13538)

$$\text{From } \Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$

$$\Delta H^\circ = -20 \times 1000 - 1 \times 8.314 \text{ J/mol.K} \times 298 \text{ K}$$

$$= -22477.57 \text{ J}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -22477.57 - (298 \times -30)$$

$$= -13538 \text{ J}$$

78. (c) A reaction is spontaneous if  $\Delta G_{\text{sys}}$  is negative.

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

A reaction will be spontaneous at all temperatures if

$\Delta H_{\text{sys}}$  is negative and  $\Delta S_{\text{sys}}$  is positive.

79. (d) At 315 K;  $\Delta G^\circ = 120 - \frac{3}{8} T$

$$\Delta G^\circ = 120 - 118.125 = \text{positive}$$

Since  $\Delta G^\circ$  is positive then  $K_{\text{eq}} < 1$ .

$$\text{So } \frac{[Y]}{[X]} < 1.$$

$$\therefore [X] > [Y]$$

80. (c)  $\text{MgO (s)} + \text{C (s)} \rightarrow \text{Mg (s)} + \text{CO (g)}$

For a reaction to be spontaneous

$$\Delta G < 0$$

$$\Delta H^\circ - T\Delta S^\circ < 0$$

$$\Rightarrow T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T > \frac{491.1 \times 1000}{198}$$

$$T > 2480.3 \text{ K}$$

81. (b)  $\Delta G^\circ = A - BT$

A and B are non-zero constants

$$\therefore \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = A - BT$$

$\therefore$  Reaction will be endothermic if  $\Delta G^\circ > 0$ .

Hence,  $A > 0$  and  $B < 0$ .

82. (c)  $\Delta H = 200 \text{ J mol}^{-1}$

$$\Delta S = 40 \text{ JK}^{-1} \text{ mol}^{-1}$$

For spontaneous reaction,

$$\Delta G < 0$$

$$\Delta H - T\Delta S < 0; \Delta H < T\Delta S$$

$$\frac{\Delta H}{\Delta S} < T; \frac{200}{40} < T$$

$$5 < T$$

So, minimum temperature is 5 K

83. (a) From thermodynamics relation.

$$\Delta G^\circ = -RT \ln K$$

$$\Delta H^\circ - T\Delta S^\circ = RT \ln K$$

$$-\frac{\Delta H^\circ}{RT} + \frac{T\Delta S^\circ}{RT} = \ln K$$

$$\text{or } \ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

For exothermic reaction,  $\Delta H^\circ = -ve$

$$\text{slope} = -\frac{\Delta H^\circ}{R} = +ve$$

So from graph, lines should be A & B.

84. (d)  $\Delta G_{\text{rxn}}^\circ = \Delta_f G^\circ(\text{vapour}) - \Delta_f G^\circ(\text{liquid})$

$$\Delta G_{\text{rxn}}^\circ = 103 - 100.7 = 2.3 \text{ kcal/mol} = 2300 \text{ cal/mol}$$

$$\Delta G_{\text{rxn}}^\circ = -RT \ln K_p (K_p = P_{\text{vap}})$$

$$2300 \text{ cal/mol} = -2 \text{ cal/mol.K} \times 500 \text{ K} \times \ln K_p$$

$$\ln K_p = -2.3$$

$$\log_{10} K_p = -1$$

$$K_p = \text{Antilog } -1 = 0.1 \text{ atm}$$

$\therefore$  Vapour pressure of liquid 'S' at 500 K is approximately equal to 0.1 atm.

85. (b) (i)  $2\text{Fe}_2\text{O}_3(\text{s}) \rightarrow 4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g});$

$$\Delta_f G^\circ = +1487.0 \text{ kJ mol}^{-1}$$

(ii)  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g});$

$$\Delta_f G^\circ = -514.4 \text{ kJ mol}^{-1}$$

Multiple reaction (ii) with 3, we get

(iii)  $6\text{CO}(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g});$

$$\Delta_f G^\circ = 3 \times -514.4 = -1543.2 \text{ kJ mol}^{-1}$$

When we add reaction (i) and reaction (iii),

we get reaction (iv)

(iv)  $2\text{Fe}_2\text{O}_3(\text{s}) + 6\text{CO}(\text{g}) \rightarrow 4\text{Fe}(\text{s}) + 6\text{CO}_2(\text{g})$

Free energy change,  $\Delta_r G^\circ$  for the reaction will be

$$1487.0 - 1543.2 = -56.2 \text{ kJ mol}^{-1}$$

86. (c) In the reaction  $A_2 \rightleftharpoons 2A$   
Initially, let  $[A_2] = 1 \text{ M}$  and  $[A] = 0 \text{ M}$   
After 20% dissociation, 80% of  $A_2$  remains.  
 $[A_2] = 1 \times \frac{80}{100} = 0.8 \text{ M}$   
  
20% of 1 M is  $1 \times \frac{20}{100} = 0.2$ .  $[A] = 2 \times 0.2 = 0.4 \text{ M}$   
The equilibrium constant,  
 $K = \frac{[A]^2}{[A_2]}$ ;  $K = \frac{[0.4]^2}{[0.8]} = 0.2$   
  
 $\Delta G^\circ = -RT \ln K = -8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 320 \text{ K} \times \ln 0.2$   
 $= 4281 \text{ J/mol}$
87. (b)  $\Delta H = nC_p \Delta T = 0$  means  $\Delta H$  constant.  
 $\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) \geq 0$   $\Delta S$  increases.
88. (d)  $\Delta G = \Delta H - T\Delta S$   
For a spontaneous reaction  $\Delta G = -ve$   
which is possible when both  $\Delta H$  and  $\Delta S$  are positive at high temperature and hence the reaction becomes spontaneous.
89. (c)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$   
 $-RT \ln K = \Delta H^\circ - T\Delta S^\circ$   
 $\ln K = -\frac{\Delta H^\circ - T\Delta S^\circ}{RT}$
90. (b) At equilibrium  $\Delta G = 0$   
Hence,  $\Delta G = \Delta H - T_e \Delta S = 0$   
 $\therefore \Delta H = T_e \Delta S$  or  $T_e = \frac{\Delta H}{\Delta S}$   
For a spontaneous reaction  
 $\Delta G$  must be negative which is possible only if  $\Delta H < T\Delta S$   
or  $T > \frac{\Delta H}{\Delta S}$ ;  $T_e < T$
91. (b) Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.
92. (a) For spontaneous reaction,  $dS > 0$  and  $dG$  should be negative i.e.  $< 0$ .
93. (c)  $\Delta G^\circ = -RT \ln K_c$  or  $-\Delta G^\circ = RT \ln K_c$
94. (b)  $\Delta G = \Delta H - T\Delta S$   
For an endothermic reaction,  
 $\Delta H = +ve$  and at low temperature  $\Delta S = +ve$   
Hence  $\Delta G = (+)\Delta H - T(+)\Delta S$   
and if  $T\Delta S < \Delta H$  (at low temp)  
 $\Delta G = +ve$  (non spontaneous)  
But at high temperature, reaction becomes spontaneous i.e.  $\Delta G = -ve$   
because at higher temperature  $T\Delta S > \Delta H$
95. (d)  $\Delta H$  negative shows that the reaction is spontaneous. Higher negative value for Zn shows that the reaction is more feasible.