31.(ACD) In adiabatic expansion temperature always decreases. In case of expansion

$W_{\text{isothermal}} > W_{\text{adiabatic}}$

32.(C) L $\rightarrow$ M At constant V —isochoric, N $\rightarrow$ K

33.(B) Plan By Boyle's law at constant temperature, $P \propto \dfrac{1}{V}$

By Charles' law at constant pressure, $V \propto T$

Process taking place at

Constant temperature – isothermal, Constant pressure – isobaric

Constant volume-isochoric, Constant heat – adiabatic

K $\rightarrow$ L	At constant p, volume increases	Thus, heating
L $\rightarrow$ M	At constant V, pressure decreases	Thus, cooling
M $\rightarrow$ N	At constant p, volume decreases	Thus, cooling
N $\rightarrow$ K	At constant V, pressure increase	Thus, heating

34.(ABC) Adiabatic expansion against zero external pressure is isothermal process.

35.(B) For reversible process $\Delta S_{\text{system}} + \Delta S_{\text{surroun}} = 0$

36.(B)

$$X_2(g) \rightleftharpoons 2X(g)$$

$$\begin{array}{lll} t = 0 & 1 & - \\ t = t_{eq} & 1 - \dfrac{\beta_{eq}}{2} & \beta_{eq} \end{array}$$

$$p_{x_2} = 2\left(\frac{1 - \dfrac{\beta_{eq}}{2}}{1 + \dfrac{\beta_{eq}}{2}}\right) \qquad p_x = 2\left(\frac{\beta_{eq}}{1 + \dfrac{\beta_{eq}}{2}}\right)$$

$$K_p = \frac{\left(\dfrac{2\beta_{eq}}{1 + \dfrac{\beta_{eq}}{2}}\right)^2}{2\left(\dfrac{1 - \dfrac{\beta_{eq}}{2}}{1 + \dfrac{\beta_{eq}}{2}}\right)} = \frac{2\beta_{eq}^2}{1 - \dfrac{\beta_{eq}^2}{4}} = \left(\frac{8\beta_{eq}^2}{4 - \beta_{eq}^2}\right)$$

37.(C) **(A)** It is true statement $X_2(g) \rightleftharpoons 2X(g)$

If P is decreased then reaction will move in forward direction according to Le-Chatelier's principle.

(B) It is true statement

At start of reaction Q = 0

$\therefore \quad \Delta G = \Delta G^0 + RT \ln Q$

If $Q = 0$

Then $\Delta G = -\text{ve}$, $\quad \therefore$ Reaction is spontaneous

29. **[A $\rightarrow$ r, t] [B $\rightarrow$ p, q, s] [C $\rightarrow$ p, q, s] [D $\rightarrow$ p, q, s, t]**

In freezing of water entropy decreases and due to equilibrium condition $\Delta G = 0$.

Adiabatic expansion against vaccum is isothermal q = 0, w = 0, $\Delta U = 0$.

In case of isolated condition $q = 0 \;\; w = 0 \;\; \Delta U = 0$

In case of D, path (reversible heating and reversible cooling) & state (300 K, 1 atm) both are same therefore change in state function or path function would be zero.

30.(AC) Entropy is a state function, it does not depend on path.

16.(9.8) $\Delta H - \Delta U = \Delta(PV) = (P_2V_2 - P_1V_1) = \left(100 \times \frac{99}{1000} - 1 \times \frac{100}{1000}\right) = \frac{100}{1000} \times 98 = 9.8$ L-bar

17.(D) For an irreversible, adiabatic process; $0 = C_v(T_2 - T_1) + p_e(V_2 - V_1)$

Substituting the values $C_V(T - T_2) = 1(2-1)\text{atm L}$

$$\Rightarrow \quad T - T_2 = \frac{1}{C_V} - \frac{2}{3R} \Rightarrow T_2 = T - \frac{2}{3 \times 0.082}$$

18.(A) $C_m = C_v + \frac{R}{1-x}$; $\quad C_m = \frac{5R}{10} + \frac{R}{1-(-1)}$; $\quad$ Since $\frac{p}{V} = 1 \quad \Rightarrow \quad pV^{-1} = 1$

19.(A) Entropy is a state function $\Delta S_{A\to C} + \Delta S_{C\to D} + \Delta S_{D\to B} = \Delta S_{A\to B}$

20.(B) Catalyst does not alter the equilibrium established in lesser time in the presence of catalyst.

21.(B) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; $\quad \Delta G^\circ = 2.303RT\log_{10} k$

22.(A) At equilibrium $\Delta G = 0$

Liquid $\to$ Gas $\Delta S = +\text{ve}$

23.(D) At equilibrium $\Delta G = 0$ $\Delta G^\circ \neq 0$

As ΔG decreases reaction becomes more spontaneous.

24.(B) II law of thermodynamics

25.(AD) Reversible or irreversible both expansion work are path function.

26.(2) Work done along dashed path $|-W| = \Sigma p\Delta V = 4 \times 1.5 + 1 \times 1 + \frac{2}{3} \times 2.5 = 8.65\,\text{L atm}$

Work done along solid path

$$-W = nRT\ln\frac{V_2}{V_1} = p_1V_1\ln\frac{V_2}{V_1} = 2 \times 2.3\log\frac{5.5}{0.5} = 2 \times 2.3\log 11 = 4.79$$

$$\Rightarrow \quad \frac{W_d}{W_s} = \frac{8.65}{4.79} = 1.80 \approx 2$$

27.(7) $V = \frac{nRT}{p} = \frac{0.1 \times 0.08 \times 273}{(1 - 0.68)} = 7$

28. **[A $\rightarrow$ p, r, s] [B $\rightarrow$ r, s] [C $\rightarrow$ t] [D $\rightarrow$ p, q, t]**

(A) $CO_2(s) \to CO_2(g)$

It is just a phase transition (sublimation) as no chemical change has occurred. Sublimation is always endothermic. Product is gas, more disordered, hence ΔS is positive.

(B) $CaCO_3(s) \to CaO(s) + Co_2(g)$

It is a chemical decomposition, not a phase change. Thermal decomposition occur at the expense of energy, hence endothermic. Product contain a gaseous species, hence, $\Delta S > 0$.

(C) $2H \to H_2(g)$

A new H–H covalent bond is being formed, hence, $\Delta H < 0$. Also, product is less disordered than reactant, $\Delta S < 0$.

(D) Allotropes are considered as different phase, hence $P_{(\text{white, solid})} \to P_{(\text{red, solid}}$ is a phase transition as well as allotropic change.

Also, red phosphorus is more ordered than white phosphorus, $S < 0$.

Daily Tutorial Sheet-1	JEE Advanced (Archive)

1.(T) I law does not predict about spontaneity of a process

2.(R) $C_p - C_v = R$ for ideal gas

3.(900) Total energy $= 3 \times \frac{1}{2} nRT = 3 \times \frac{1}{2} \times 1 \times 2 \times 300 = 900\,\text{Cal}$

4.(T) C_v for diatomic gas $= \frac{5R}{2}$

C_v for monoatomic $= \frac{3R}{2}$

5. Isolated system $\longrightarrow$ No exchange of mass and energy

6. Enthalpy is mass dependent.

7.(0) $Fe(s) + 2HCl(aq) \longrightarrow FeCl_2 + H_2(g)$

$w = 0$ (as $\Delta V = 0$)

8. -116.4 J

$\Delta H = nC_p\Delta T$

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \quad \Rightarrow \quad \gamma = \frac{C_p}{C_v}$

$C_p = \frac{5R}{2}$; $\quad C_V = \frac{3R}{2}$ for He Ar

9.(B) Free isothermal expansion, $w = 0, \Delta U = 0 \quad \Rightarrow \quad q = 0$

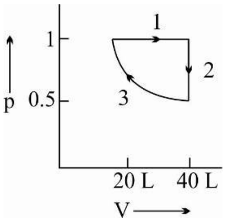
Volume occupied by molecular of an ideal gas is zero

10. $\Delta_r G^\circ = -257.2 \text{ kJ} < 0$; $\Delta H^\circ = -285.4 \text{ kJ} < 0$

11. $\Delta G_1^\circ = 16 \text{ kJ}$; $\Delta G_2^\circ = 12.3 \text{ kJ}$

12.(C) $\Delta H = \Delta U + \Delta(pv)$, $\Delta H = \Delta U + (p_2v_2 - p_1v_1)$

13. **(i)**



(ii) $W = -6.14$ L atm $\quad Q = 6.14$ L atm

(iii) All the state functions, $\Delta U, \Delta H$ and ΔS are zero for cyclic process.

14. He is monatomic, so it has only three degree of freedom (translational only) at all temperature hence, C_V value is always $\frac{3}{2}R$.

Hydrogen molecule is diatomic, has three translational, two rotational and one vibrational degree of freedom. The energy spacing between adjacent levels are in the order of:

Translational < rotational < vibrational

At lower temperature only translational degree of freedom contribute to heat capacity while at higher temperature rotational and vibrational degree of freedom starts contributing to heat capacity.

15.(B) $\Delta S = \frac{\Delta H}{T_b}$

$\Delta_r S = +198.0\,J\,K^{-1}\,mol^{-1}$

$\Delta G = 0$ at equilibrium

$$T = \frac{\Delta H}{\Delta S} = \frac{491.1\times10^3}{198.0} = 2480.3\,K$$

22.(A) For spontaneous process

$\Delta G = (\Delta H - T\Delta S)$ should be negative

$\therefore \quad \Delta G < 0$

23.(C) q & w are path functions.

Option (C) is correct

24.(D) Maltose is a disaccharide made up two D-glucose units. On treatment with dil. HCl is undergoes hydrolysis to give two D-glucose units. (Monosaccharide)

25.(D) $\Delta H = \int nC_P dT = 3\int_{300}^{1000}(23+0.01T)\,dT = 3\left[23T + \frac{0.01T^2}{2}\right]_{300}^{1000}$

$$= 3\left[23000 + \frac{0.01}{2}(1000)^2 - 23(300) - \frac{0.01(300)^2}{2}\right]$$

$$= 3[23000 + 5000 - 6900 - 450] = 61950\,J \simeq 62\,kJ$$

26.(B) According to first law of thermodynamics : $\Delta U = q + w$

For adiabatic process, $q = 0$

Hence, $\Delta U = w$

27.(A) $\Delta U = q + W$

$\Delta U = (-2) + 10 = 8\,kJ$

28.(A) $\Delta U = nC_v\Delta T = \frac{5\times28\times100}{1000} = 14\,kJ$

$\Delta(pV) = nR\Delta T = \frac{5\times8\times100}{1000} = 4\,kJ$

29.(6.25) $\Delta U = nC_v\Delta T$

$500 = 4\times C_v\times(500-300)$

$C_v = \frac{5000}{4\times200} = 6.25JK^{-1}mol^{-1}$

30.(D) $\Delta S = \int\frac{dq}{T}$; $S = \int_0^T \frac{nCdT}{T}$

31.(48.00) Work done = Area under the curve $= \frac{1}{2}(6+10)\times6 = 48\,J$

32.(–2.70) $A(\ell) \longrightarrow 2B(g)$

$\Delta U = 2.1\,kcal,\ \Delta S = 20\,cal/k,\ T = 300K$

$\Delta G = \Delta H - T\Delta S$

$\Delta H = \Delta U + \Delta ng\,RT \qquad \Delta ng = 2$

$\Delta G = 3300 - (300)(20) = 3300 - 6000 = -2700\,cal = -2.7\,kcal$

16.(A) **(A)** $N_2 + 3H_2 \longrightarrow 2NH_3$

Since number of gaseous moles are decreasing hence entropy change $\Delta S = S_{products} - S_{reactants}$ is negative

(B) $\underset{(s)}{CaSO_4} \longrightarrow \underset{(s)}{CaO} + \underset{(g)}{SO_3}$

$\Delta S:$ positive, as number of gas moles increases

(C) $CO_2(s) \longrightarrow CO_2(g)$

$\Delta S:$ positive, as number of gaseous moles are increasing

(D) $I_2(s) \longrightarrow I_2(aq)$

$\Delta S:$ positive, as randomness of the system has increased

17.(D) Heat released by one block at T_2 = Heat absorbed by block at T_1

$-ms(T - T_2) = ms(T - T_1)$(where $T_2 > T_1$) ; T is equilibrium temperature

$$(T_2 - T) = (T - T_1), T = \frac{T_1 + T_2}{2}$$

$$\Delta S = C_p \ln\frac{T}{T_1} + C_p \ln\frac{T}{T_2} = C_p \ln\left(\frac{T}{T_1} \times \frac{T}{T_2}\right) \quad \Rightarrow \quad \Delta S = C_p \ln\frac{T^2}{T_1T_2}$$

$$\Delta S = C_p \ln\frac{(T_1 + T_2)^2}{4T_1T_2}$$

18.(C) $C_v = \frac{f}{2}R$

$C_P = \left(\frac{f}{2} + 1\right)R$ Where f = degree of freedom at normal temperature.

At normal temperature f = 5 for diatomic gas.

At higher temperature vibrational degree of freedom also becomes active, so the value of f in both C_v and C_P will shot up after a particular temperature. Hence graph (C) is incorrect.

19.(A) For the process to be spontaneous $\Delta G: -$ ve

$\Delta G = \Delta H - \Delta(TS)$

At a particular Temperature $\Delta G = \Delta H - T\Delta S$

For spontaneity $\Delta G < 0$

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

$T\Delta S > \Delta H$

T(40) > 200 T = 5K ⇒ T > 5

20.(D) $\Delta G^0 = \Delta H^0 - T\Delta S^0$

$A = \Delta H^0$

$B = \Delta S^0$

For endothermic Reaction $\Delta H > 0$

21.(A) The reaction

$MgO(s) + C(s) \longrightarrow Mg(s) + CO(g)$

$\Delta_r H = +4941.1 kJ/mol$

$\Delta S_b = 4.2 \ln\left(\frac{373}{273}\right) = 1.31$

$\Delta S_c = \frac{\Delta H_{\text{vapourisation}}}{373} = \frac{2491}{373} = 6.67$

$\Delta S_a = 2 \ln\left(\frac{383}{373}\right) = 0.05$

$\Delta S_{\text{Total}} = \Delta S_a + \Delta S_b + \Delta S_c + \Delta S_d = 1.22 + 1.31 + 6.67 + 0.05 \simeq 9.26\,\text{kJ kg}^{-1}\,\text{K}^{-1}$

15.(D) $V_i = 5\text{m}^3$; $V_f = 1\text{m}^3$

$P_{\text{ext}} = 4\,\text{N/m}^2$

Isothermal $\xrightarrow{\quad} \Delta U = 0$

$q + W = 0$

$q = -W = -\left[-\int P_{\text{ext}} dV\right] = \int P_{\text{ext}} dV = P_{\text{ext}} \int dV = P_{\text{ext}} \Delta V = 4[1-5] = 4 \times (-4) = -16\,\text{J}$

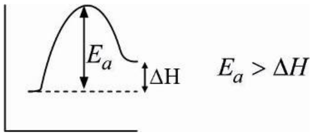
Heat lost by the system = 16J

$16 = nC\Delta T$

$16 = (1)(24)\Delta T \quad \Rightarrow \quad \Delta T = \frac{16}{24} = \frac{2}{3}$

Daily Tutorial Sheet-1	JEE Main (Archive)

1.(C)



2.(BD) Refractive index depend only on nature of substance

3.(BCD) In B, C, D, energy is required

4.(C) A reversible process is that in which system and surroundings are always in equilibrium.

5.(A) Work and heat are path function **6.(C)** $\Delta H = nC_p\Delta T$

7.(A) Work and heat are path function.

8.(AB) Molar conductivity and emf. are intensive properties

9.(A) $w = -2.303nRT\log\frac{v_f}{v_i}$

10.(D) $\Delta G_r^o = -RT\ln K_p$

11.(D) For adiabatic process : q = 0

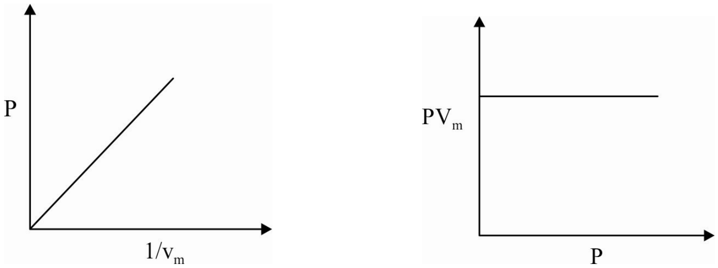
So from Ist law $\Delta U = q + w$

We can write $\Delta U = w$

12.(A) Isothermal T = constant

PV_m = constant PV_m will remain constant with increase of pressure

$P = k\times\frac{1}{V_m}$ Pressure will increase linearly with increase in 1/Vm



13.(D) For reversible isothermal expansion of an ideal gas :

$w = -nRT\ln\frac{V_2}{V_1}$ $\begin{pmatrix} V_2 \to \text{Final volume} \\ V_1 \to \text{Initial volume}\end{pmatrix}$

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

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

So in a graph of $|w|$ versus $\ln V_2$, the intercept cannot be positive.

14.(A) Overall process

$$\underset{273K}{H_2O(ice)} \xrightarrow{a} \underset{273K}{H_2O(\ell)} \xrightarrow{b} \underset{373K}{H_2O(\ell)} \xrightarrow{c} \underset{373K}{H_2O(g)} \xrightarrow{d} \underset{383K}{H_2O(g)}$$

$\Delta S_a = \frac{\Delta H_{fusion}}{273} = \frac{334}{273} = 1.22$

140.(114.51)

$\Delta H = n \times C_p \times \Delta T$ and $C_p = C_v + R = 12.48 + 8.314 = 20.794\,JK^{-1}\,mol^{-1}$

For a given sample of argon gas, mole (n)

$$n = \frac{PV}{RT} = \frac{1 \times 1.25}{0.0821 \times 300} = 0.05\,\text{mole}$$

Also, for reversible adiabatic change $TV^{\gamma-1}$ = constant

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

or $$T_2 = T_1 \times \left(\frac{V_1}{V_2}\right)^{\gamma-1} = 300 \times \left(\frac{1.25}{2.50}\right)^{1.66-1} = 300 \times \left(\frac{1}{2}\right)^{0.66}$$

$$T_2 = 189.86\,K$$

$\Delta T = T_2 - T_1 = 189.86 - 300 = -110.14\,K$

$\Delta H = 0.05 \times 20.794 \times (-110.14) = -114.51\,J$

131.(172.28)

$$w = P(V_g - V_e) = PV_g = nRT = \frac{10^3}{18} \times 8.314 \times 373 = 172284.56\,J = 172.28\,kJ$$

132.(50) $Q_p = C_p \cdot \Delta T \quad \therefore \quad C_p = \frac{70}{5} = 14\,cal^\circ C^{-1}$

$C_p - C_v = nR$

$C_v = 14 - 2 \times 2 = 10\,cal\,K^{-1}$

$Q_v = C_v \Delta T = 10 \times 5 = 50\,cal$

133.(0) For isothermal process $\Delta U = 0$

134.(9.2) $\Delta S = 2.303 nR \log \frac{V_2}{V_1} = 2.303 \times 2 \times 2 \log \frac{20}{2} = 9.2\,cal\,K^{-1}\,mol^{-1}$

135.(2.4) $q = n \cdot C_P \Delta T$

$1000 = \frac{100}{18} \times 75 \times \Delta T$

$\Delta T = 2.4K$

136. $\Delta S_{surr} = \frac{q_{surr}}{T} = -\frac{q_{sys}}{T} = \frac{W_{sys}}{T}$

$\Delta S_{surr} = \frac{-P_{ext}(V_f - V_i)}{T} = \frac{-3(2-1)}{300} L\,atm\,K^{-1}$

$= -0.01\,L\,atm\,K^{-1} = -0.01 \times 101.3\,JK^{-1} = -1.013\,JK^{-1}$

137.(32) $\frac{u_{rmsT_1}}{u_{rmsT_2}} = \sqrt{\frac{T_1}{T_2}}$

$\frac{2 \times u}{u} = \sqrt{\frac{T_1}{T_2}}$

$\frac{T_1}{T_2} = 4$

$T_2 = \frac{T_1}{4}$

From $TV^{\gamma-1}$ = constant for adiabatic expansion

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$\left[\frac{V_1}{V_2}\right]^{\gamma-1} = \frac{T_2}{T_1} = \frac{1}{4}$

$\left[\frac{V_1}{V_2}\right]^{1.4-1} = \frac{1}{4} \quad \Rightarrow \quad \frac{V_2}{V_1} = 32$

138.(2.7) $\Delta H = \Delta U + \Delta nRT = 2100 + 2 \times 2 \times 300 = 3300\,cal/mol$

$\Delta G = \Delta H - T\Delta S = 3300 - 300 \times 20 = 2700\,cal$

139.(6.3) $\Delta H = \Delta U + P\Delta V$

$P = \frac{\Delta H - \Delta U}{\Delta V} = \frac{50 - 113}{-10} = 6.3\,k\,Nm^{-2}$

Daily Tutorial Sheet-11	Numerical Value Type

126.(223.53)

$$C_p = C_v + R = (3/2)R + R = \frac{5}{2}R$$

At constant pressure

Heat given to 1 mole gas $= C_p.\Delta T$

Or $\Delta H = q_p = 1 \times (5/2)R \times (373 - 298)$

Or $\Delta H = q_p = 1 \times (5/2) \times 1.987 \times 75$

$\Delta H = q_p = 372.56\,\text{cal}$

Also, work done in process (irreversible)

$\Delta U = q + w = 372.56 - 149.03 = 223.53\,\text{cal}$

$= -nR(T_2 - T_1) = -1 \times 1.987 \times (373 - 298) = -149.03\,\text{cal}$

127.(32) $w = -8J;\ q = 40J$

From I law $\Delta U = q + w = 40 - 8 = 32$ joule

128.(290.81K)

Work is done against external pressure and thus process is irreversible

$w = -P\Delta V$

$\Delta V = (5 - 3) = 2\text{dm}^3 = 2 \times 10^{-3}\text{m}^3$

$P = 3\,\text{atm} = 3 \times 1.013 \times 10^5\,\text{N m}^{-2}$

$w = -3 \times 1.013 \times 10^5 \times 2 \times 10^{-3} = -607.8\text{J}$

Since, the work is used in heating water and thus

$-w = q = n \times C \times \Delta T$

Or $607.8 = 10 \times 4.184 \times 18 \times \Delta T$

$\Delta T = 0.81$

Final temperature $= 290 + 0.81 = 290.81\text{K}$

129.(190.7)

$dU = -P_{\text{ext.}} \cdot dV$

$$nC_v(T_2 - T_1) = -P_{\text{ext.}}[V_2 - V_1] = -P_2\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]$$

$$C_v(T_2 - T_1) = -P_2 \times R\left[\frac{T_2}{P_2} - \frac{T_1}{P_1}\right]$$

$$1.5 \times (T_2 - 298) = -1.013 \times 10^5 \times R\left[\frac{T_2}{1.013 \times 10^5} - \frac{298}{1.013 \times 10^6}\right]$$

$T_2 = 190.7\text{K}$

130.(2.98)

Entropy change of fusion, $\Delta S_f = \Delta H_f / T$

$\Delta H_f = 6 \times 10^3\text{J};\ T = 273\text{K}$

$$\Delta S_f = \frac{(6 \times 10^3)}{273} = 21.98\,\text{JK}^{-1}\,\text{mol}^{-1}$$

125.(B) $Cu_2O(s) + \frac{1}{2}O_2(g) \rightleftharpoons 2CuO(s)$

$\Delta G^{\circ}_{\text{reaction}} = [2 \times (-30.4)] - (-34.98) = -25.82 \text{ kcal}$

and $-25.82 \times 10^3 = -2.303 \times 2 \times 298 \log K$

$\therefore$ $K \approx 10^{19}$, a very high value, hence reaction will be almost complete with a trace of Cu_2O.

Daily Tutorial Sheet-10	Level-2

116.(B) For a reaction to be spontaneous ΔG must be negative. According to relationship of ΔG,

$$\Delta G = \Delta H - T \cdot \Delta S$$

If ΔH and ΔS both are positive, then term T. ΔS will be greater than ΔH at high temperature and consequently ΔG will be negative at high temperature. (Boiling point of water) and reaction becomes feasible.

117.(B) Entropy of vapour is higher than liquid higher than solid.

118.(C) $\Delta G = \Delta H - T\,\Delta S$

If $\Delta G = -\text{ve}$ $\Rightarrow$ reaction is spontaneous $\Delta H > 0$ and $\Delta S > 0$

It implies that entropy term can make ΔG negative which is possible at higher temperature.

119.(A) $\Delta G = \Delta H° - T\Delta S° = \left(179.1 - \dfrac{298 \times 160.2}{1000}\right) \text{kJ / mol} = 179.1 - 47.74 = 131.36\,\text{kJ} = +\text{ve}$

$\Rightarrow$ non-spontaneous at 298K.

Let at T, reaction is spontaneous.

$$\Delta G \le 0 \quad \Rightarrow \quad \Delta H - T\Delta S \le 0$$

$$T \ge \frac{\Delta H}{\Delta S} = \frac{179.1 \times 1000}{160.2}\text{K}$$

$$T \ge 1118\,\text{K}$$

120.(D) $\dfrac{1}{2}X_2 + \dfrac{3}{2}Y_2 \rightleftharpoons XY_3$

$$\Delta S = 50 - \left(\frac{1}{2} \times 60 + \frac{3}{2} \times 40\right) = 50 - 90 = -40\,\text{kJ / mol}$$

$$\Delta G = 0 = -30 \times 10^3 - T \times (-40)$$

$$40T = 30 \times 10^3 \quad \Rightarrow \quad T = 750\ \text{K}$$

121.(C) $\Delta G = \Delta G° + RT\,\ell nQ$

At equilibrium $\Delta G = 0$ and $\Delta G° = \Delta H - T\,\Delta S°$ and $Q = K$

$$\ell nK = -\frac{\Delta H° - T\,\Delta S°}{RT}$$

122.(D) $\Delta S = -\text{ve}$

$\Delta H = -\text{ve}$

$\Delta G = \Delta H - T\Delta S$

For a reaction to be spontaneous ; $\Delta G = -\text{ve}$ which can be below a certain temperature only

123.(B) $\Delta G = \Delta H - T\Delta S = -2808 - 310 \times 182.4 \times 10^{-3} = -2864.5\ \text{kJ}$

124.(A) Since, expansion occurred at constant temperature,

$$\Delta S = nR\ \ln\frac{V_2}{V_1} = \frac{1}{32} \times 8.314\ \ln\frac{3.0}{0.75} = 0.36\ \text{JK}^{-1}$$

Since, this is case of free expansion, $P_{ext} = 0$ $\Rightarrow$ $-W = P_{ext}\Delta V = 0,\ q = 0$

Also, since, $\Delta T = 0 \Rightarrow \Delta H = \Delta E = 0.$

Daily Tutorial Sheet-9	Level-2

106.(ACD) Absolute value of heat content, internal energy and Gibbs energy of the system can not be calculated. Absolute value of entropy can be calculated.

107.(ACD) $H_2O(s) \longrightarrow H_2O(\ell)$ [spontaneous process because $\Delta G < O$; $\Delta S < O$]

108.(A) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta_r H^\circ_{298\,K} = -241\,kJ/mol^{-1}$

$$\Delta_r H^\circ_{373\,K} = \Delta_r H^\circ_{298\,K} + \Delta C_P(T_2 - T_1) = -241.8 + \left[(C_P)_{H_2O} - (C_P)_{H_2} - \frac{1}{2}(C_P)_{O_2}\right](373-298)$$

$$= -241.8 + [33.6 - 28.8 - \frac{1}{2} \times 29.4] \times (373-298) \times 10^{-3} = -242.6\,kJ/mol$$

109.(D) Larger the molecule, more is the entropy. Also, Entropy of a molecule is larger in gaseous state them in solid state.

$\Rightarrow \quad S_{C_2H_2} < S_{C_2H_6}$; $S_{CO_2} > S_{CO}$; $S_{I_2(s)} < S_{I_2(g)}$

110.(A) $Protein_A(S) \rightleftharpoons Protein_A(\ell)\ \Delta_r H_A = 2.73\,kcal/mol$

$Protein_B(S) \rightleftharpoons Protein_B(\ell)\ \Delta_r H_B = 3.0\,kcal/mol$

$\Delta S_A = \frac{\Delta_r H_A}{T_A} = \frac{2.73}{273} \times 10^3 = 10\,Jmol^{-1}K^{-1}$ and $\Delta S_A = \frac{\Delta_r H_B}{T_B} = \frac{3.03}{303} \times 10^3 = 10\,Jmol^{-1}K^{-1}$

111.(A) Using : $-\Delta_r G^\circ = RT\,\ell n\,K_{eq} \quad \Rightarrow \quad -\Delta_r G^\circ = 8.314 \times 298 \ln 10^{-14} = 7.99 \times 10^4\,J$

112.(B) $\Delta G = \Delta H - T\Delta S$ At equilibrium, $\Delta G = 0$

For a reaction to be spontaneous ΔG should be negative, so T should be greater than T_e.

113.(B) Standard Gibb's energy of formation (ΔG°_f) of a substance is defined as the Gibb's energy change when mole of the substance is formed from its elements in their standard states. The following reaction define ΔG°_f, $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g)$

114.(B)

$$\begin{tikzcd} C \arrow[r] \arrow[d] & D \arrow[d] \\ A & B \end{tikzcd}$$

Given, $\Delta S_{(A\to C)} = 50\,eu$

$\Delta S_{(C\to D)} = 30\,eu$; $\Delta S_{(B\to D)} = 20$ eu

Where, eu is entropy unit

Therefore, $\Delta S_{(A\to B)} = \Delta S_{(A\to C)} + \Delta S_{(C\to D)} + \Delta S_{(D\to B)}$

$$= \Delta S_{(A\to C)} + \Delta S_{(C\to D)} - \Delta S_{(B\to D)} = 50 + 30 - 20 = 60\,eu$$

115.(D) Variation of K_{eq} with temperature t is given by van't Hoff equation $\ln K_{eq} = -\underset{A}{\underline{\frac{\Delta H^\circ}{R}}} \cdot \frac{1}{T} + \underset{R}{\underline{\frac{\Delta S^\circ}{R}}}$

Slope of the given line is positive indicating that term A is positive thus ΔH° is negative. Thus, reaction is exothermic.

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96.(B) $\Delta_{vap}H^{o} = 29.4\,\text{kJ mol}^{-1}$ and $T_{boiling} = 334.7\,\text{K}$

$\Delta_{vap}H° = 29.4\,\text{kJ mol}^{-1}$ and $T_{boiling} = 334.7\,\text{K}$

$$\Rightarrow \quad \Delta_{vap}S° = \frac{\Delta_{vap}H°}{T_{boiling}} = 87.84\,\text{J mol}^{-1}\text{K}^{-1} = 10.6\,R$$

97.(D) Sucrose (molecular weight) $= 342$

From $\Delta G = \Delta H - T\Delta S = -6000\times10^{3} - 300\times180 = -6054\times10^{3}\,\text{kJ/mol}$

For $34.2\,\text{gm}$ energy available $= \dfrac{6054}{342}\,\text{kJ}\times34.2 = 605.4\,\text{kJ}$

98.(D) $H_2O(\ell) \rightleftharpoons H_2O(s);\qquad \Delta_rH < 0$ and $\Delta_rS < 0$

99.(C) $-\Delta_rG° = RT\ell n\,K_{eq} < 0 \qquad [\because K_{eq} < 1]$

$\Rightarrow \quad \Delta_rG° > 0$ and $\Delta_rG° = \Delta_rH° - T\Delta_rS°$

Clearly, $\Delta_rS° > 0 \quad \Rightarrow \quad \Delta_rG° < \Delta_rH°$

100.(CD) $\Delta S \propto \dfrac{1}{T}$ and $\Delta_rG = \Delta_rH - T\Delta_rS$

101.(A) $\Delta_rH° = \Delta_fH^{\circ}_{CH_4} = -74.9\,\text{kJ/mol}$

and $\Delta_rS° = S^{\circ}_{CH_4} - 2S^{\circ}_{H_2} - S^{\circ}_{C} = 186.3 - 2\times130.7 - 5.6 = -80.7\,\text{J/mol}$

$$\Delta_rG° = \Delta_rH° - T\Delta_rS° = -74.9 - 298\times(-80.7)\times10^{-3} = -50.85\,\text{kJ/mol}$$

$\Rightarrow$ Reaction is spontaneous due to highly negative enthalpy change.

102.(B) $CCl_4(\ell) \rightleftharpoons CCl_4(g)$

$\Delta_fH°$	-135.4	-103.0	$\Delta_rH° = -103 - (-135.4) = 32.4\,\text{kJ/mol}$
S°_{m}	215.4	308.7	$\Delta_rS° = 308.7 - 215.4 = 93.3\,\text{J/K/mol}$

$$T_{boiling} = \frac{\Delta_rH°}{\Delta_rS°} = \frac{32.4\times10^{3}}{93.3} = 347.3\,\text{K} = 74.3°\text{C}$$

103.(C) For an isothermal process : $dG = VdP \quad \Rightarrow \quad \Delta G = \int VdP = \int \dfrac{nRT}{P}\cdot dP$

$$\Rightarrow \quad \Delta G = nRT\,\ell n\frac{P_2}{P_1} = 1\times8.314\times293\,\ell n\frac{2}{1} = +1.7\,\text{kJ/mol}$$

104.(A) $\Delta_rS^{\circ}_{Total} = 56 = \Delta_rS^{\circ}_{system} + \Delta_rS^{\circ}_{surrounding}$

$$\Delta S_{surr} = \frac{-\Delta_rH^{\circ}_{system}}{373} = \frac{4.1\times10^{4}}{373} = 109.9\,\text{J/K}$$

$\Delta S_{sys} = 56 - 110 = -54\,\text{J/K}$

105.(D) $\Delta S_{surrounding} = \dfrac{q_{surrounding}}{T_{surrounding}} = \dfrac{64\times10^{3}}{300} = 213.3\,\text{J/K}$

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86.(B) $(\Delta S)_{sys} = nC_{V,m}\ell n\frac{T_2}{T_1} + nR\,\ell n\frac{V_2}{V_1} = nR\,\ell n\frac{V_2}{V_1}(T_2 = T_1) = 2\times 8.314\times \ell n\frac{10}{1} = 38.29\,J\,K^{-1}mol^{-1}$

87.(B) Expansion from state A to state B occurs at constant pressure (isobaric expansion) = 2P

88.(C) Expansion from state D state A occurs at constant volume (isochoric process) = V

89.(A) Work done in cyclic process = area of PV curve

$|w| = PV$

Work = –PV (clockwise)

90.(D) In conversion from B to C, volume does not change or $\Delta V = 0$, therefore w = 0.

91.(D) $q = -w \quad \therefore \quad q = PV$

92.(A) $T = \frac{PV}{nR}$

93.(D) In cyclic process, $\Delta H = 0$

94.(B) In expansion from state 1 to state 2.

$P = 1$ atm

$V_1 = 22.44L$

$V_2 = 44.88L$

$C_V = \frac{3}{2}R$

$\Delta T = T_2 - T_1 = 546 - 273 = 273K$

$\therefore \qquad \Delta U = nC_v\Delta T = 1\times\frac{3}{2}\times 8.314\times 273 = 3.40\times 10^3 J$

95.(C) In conversion from state 2 to state 3

$\Delta T = T_2 - T_1 = 273 - 546 = -273K$

$C_V = \frac{3}{2}R$

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76.(BCD) **(A)** Expansion of an ideal gas against vaccum is an irreversible process.

(B) Spontaneous process is always irreversible.

(C) As per definition of reversible process.

(D) If expansion is carried out reversibly, system will do work and hence, it will absorb more heat from the surroundings.

77. **[A : 1, 2] ; [B : 3] ; [C : 1, 2, 3] ; [D : 4]**

(A) For isothermal process : $\Delta U = \Delta H = 0$

(B) For reversible adiabatic process : $\Delta S = 0$

(C) For cyclic process : $\Delta U = \Delta H = \Delta S = 0$

(D) For isochoric process : $w = 0$

78.(C) $W_{irr} = -P_{ext}(V_2 - V_1)$

$$W = -1(20-10) = -10\,dm^3\,atm = -10\,dm^3 \times \frac{8.314\ JK^{-1}\,mol^{-1}}{0.0821\ dm^3\,K^{-1}\ mol^{-1}} = -1013\,J$$

From, 1st w of thermodynamics $\Delta U = q + W = 800\,J + (-1013\,J) = -213\,J$

79.(D) In neutralization reaction, when acid and base both are weak, a large amount of heat is utilized to ionise them. Thus, for such reactions, enthalpy of the reaction is least.

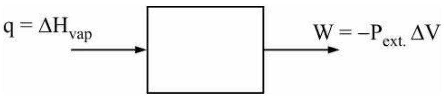
Hence, enthalpy is least for $HCN + NH_4OH \longrightarrow NH_4CN + H_2O$

80.(B) $\Delta S = 16\,J\,mol^{-1}\,K^{-1},\ \Delta H_v = 6\,kJ\ mol^{-1}$

$$T_{bp} = \frac{\Delta H_{vapour}}{\Delta S_{vapour}} = \frac{6 \times 1000}{16} = 375\,K$$

81.(A) In bomb calorimeter, volume is constant, so, w = 0 and $\Delta U = q$.
Since q is calculated by the change in temperature of calorimeter, we have to notice the sign of ΔU. For exothermic ΔU is negative and for endothermic ΔU is $+$ve.

82.(D)



$$\Delta U = q + W = 41000 - 1 \times 10^5 \times \left(\frac{1 \times 8.314 \times 373}{1 \times 10^5} - 0\right) = (41000 - 3101.122)\,J = 37.9\ kJ$$

83.(B) $W = -P_{ext}(V_2 - V_1) = -3 \times 2 = -6\,lt\text{-}atm = -6 \times 101.3 = -607.8\,J$

$\therefore \quad 607.8 = ms\Delta T$

$\Rightarrow \quad 607.8 = 10 \times 18 \times 4.18 \times \Delta T$

$\Delta T = 0.8 \quad \Rightarrow \quad T_2 = 290.8\,K$

84.(BCD) $\frac{P}{Q}, PQ, \frac{dP}{dQ}$ are intensive properties

85.(AB) For isothermal and cyclic process, $\Delta E = 0$

71.(D) $\Delta H = -\text{ve}$ (combustion reaction)

$\Delta S = +\text{ve}$ (spontaneous at all temperature)

$\Delta G = -\text{ve}$ (because reaction is spontaneous)

72.(A) For spontaneous process, system and surrounding entropy should be positive

$\Rightarrow \quad \Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} > 0$

73.(A) $A(\ell) \rightleftharpoons A(g)$ at boiling point

$\Delta H = -100 - (-130) = 30 \text{ kJ / mol}$; $\Delta S = 200 - 100 = 100 \text{ kJ / mol}$

For equilibrium $\Delta G = 0 \quad \Rightarrow \quad T_b = \dfrac{\Delta H}{\Delta S} = 300\,\text{K}$

74.(A) For equilibrium $\Delta G = 0$

75.(A) $H_2O(1\,\text{bar}, 373\,\text{K}) \longrightarrow H_2O(g)(1\,\text{bar}, 373\,\text{K})$

$\Rightarrow$ equilibrium $\Rightarrow$ $\Delta G = 0$

Since liquid $\longrightarrow$ gaseous phase $\Delta S > 0$