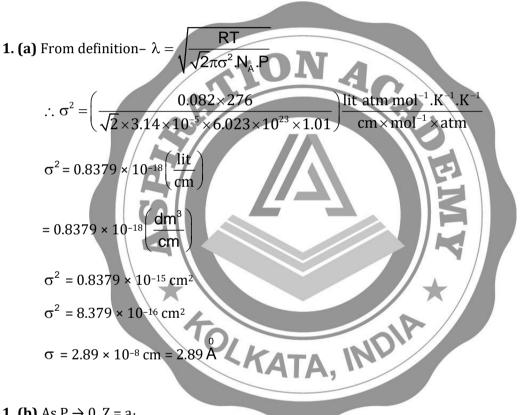


## Solution of Full Syllabus xamination

## **SET-4**



**1. (b)** As  $P \rightarrow 0$ ,  $Z = a_1$ 

again when  $P \rightarrow 0$ , Z = 1 (for ideal behaviour)

Thus,  $Z = 1 + a_2P + a_3P^3$ 

Pressure  $P_0$  can not be (–) ve, So  $a_2$  and  $a_3$  should have opposite sign. Now, at  $P_0$ , Z < 1 (shows minima)

and  $Z = 1 + a_2 P_0 + a_3 P_0^2$ 





$$= 1 - a_2 \cdot \frac{a_2}{3a_3} - a_3 \cdot \frac{a_2^2}{4a_3^2} = 1 - \frac{a_2^2}{2a_3} - \frac{a_3 \cdot a_2^2}{4a_3^2}$$
$$= 1 - \frac{a_2^2}{4a_3}$$

 $a_2^2$  is always is always (+) ve. Thus  $a_3$  should (-) ve so that Z < 1 at temperature T<sub>1</sub> and P<sub>0</sub>. So  $a_3$  is (-) ve.

## 3. (a) Lennard-Jones Potential:-

It is a mathematical approximation that illustrates the energy of interactions between two non-bounding atoms or molecules based on their distance of separation.

The equation takes into account the difference between attractive forces (dipole-dipole, dipole – induced dipole, and London interactions) and repulsive forces. The Lennard – Jones potential is given the following equation.

Where,

V = intermolecular potential between two atoms or molecules

- $\sigma$  = van der Waal's radius
- r = Distance separating between two molecules.
- **3. (b)** If degrees of freedom for a free molecular system be 'f' excepting the vibrational degree of freedom, at ordinary temperature then

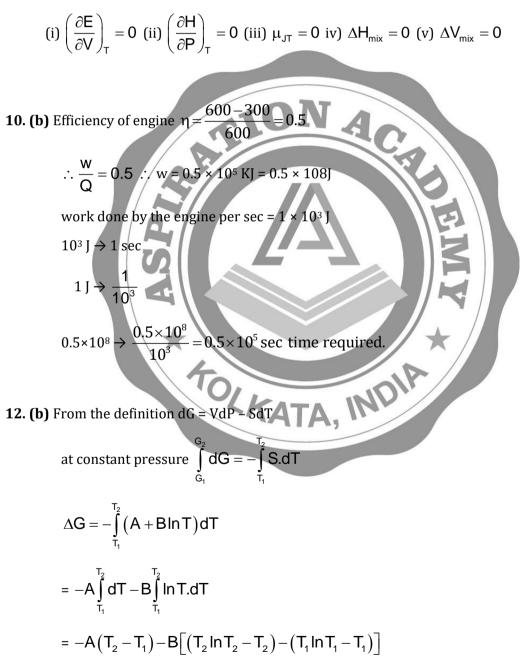
Energy per mole (E) = 
$$\frac{1}{2} f RT$$
  
 $C_{V} = \left(\frac{\partial E}{\partial T}\right)_{V} = \frac{1}{2} f R$   
 $C_{P} = C_{V} + R = \frac{1}{2} f R + R$ 

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: 
$$\gamma = \frac{C_{p}}{C_{v}} = \frac{\frac{f+2}{2}}{\frac{f}{2}} = \frac{f+2}{f} = 1 + \frac{2}{f}$$

8. (b) Thermodynamic criteria of a gas to be ideal-



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$$= -A(T_2 - T_1) - BT_2 \ln T_2 + BT_2 + BT_1 \ln T_1 - BT_1$$
  
$$= -A(T_2 - T_1) + B(T_2 - T_1) - B[T_2 \ln T_2 - T_1 \ln T_1]$$
  
$$= (T_2 - T_1)(B - A) - B[T_2 \ln T_2 - T_1 \ln T_1]$$
  
$$= (400 - 300)(30 - 25) - 30[400 \ln 400 - 300 \ln 300]$$

 $\Delta G = 500 - 30 \times 685.45$ 

 $\Delta G = -20063.5J$ 

**13.** Let the temperature of hot reservoir be T.

$$\therefore \frac{T-298}{T} = 0.4 \therefore T = \frac{298}{0.6} = 496.67K$$

To have 50% efficiency let the temperature of the reservoir be T'

$$\therefore \frac{T'-298}{T'} = 0.5 \text{ or } T' = 596K$$

So, the temperature of the hot reservoir is to be increased by (596 – 496.67)K = 99.33K.

**15. (a)** Let us consider a reversible reaction,  $A \xleftarrow{K_1}{K_1} B$ . Where  $K_1$  and  $K_{-1}$  are the specific rates for forward and backward reaction respectively.

Equilibrium constant 
$$K = \frac{K_1}{K_1}$$
  $\therefore K = \frac{A_1 \cdot e}{A_2 \cdot e}$ 

: 
$$K = \frac{A_1}{A_2} \cdot e^{-(E_1 - E_2)/RT}$$

AC

A constant catalyst reduces the activation energy by x, so that the activation energy now is  $(E_1 - x)$ . Similarly, activation energy for backward rxn is  $(E_2 - x)$ . There is no reason for the change in frequency factor (A).

 $\therefore$  Equilibrium constant of the catalyzed reaction



$$K_{\circ} = \frac{A_{1}^{c}}{A_{2}^{c}} \cdot e^{-\left[\frac{(E_{1}-x)-(E_{2}-x)}{RT}\right]} = \frac{A_{1}}{A_{2}} \cdot e^{-\frac{(E_{1}-E_{2})}{RT}} = K$$

 $\therefore$  K<sub>c</sub> = K; the equilibrium position is not changed.



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