Physical Chemistry Assignment

Q 1) Write the general expression to find the average value of any physical property of a quantum mechanical system. Show that the mean position of a free particle in a 1-D box of length 'a' is a/2.

Ans: The expression for average value of any physical property of a quantum mechanical system is as follows –

$$\langle a \rangle = \int_{\text{all space}} \psi^* A \, d\tau$$

$$\langle x \rangle = \int_0^a \psi^* x \psi \, dx$$

$$\langle x \rangle = \frac{2}{a} \int_0^a x \sin^2\left(\frac{n\pi}{a}\right) x \, dx$$

$$\langle x \rangle = \frac{2}{a} \int_0^a x \left[\frac{1 - \cos\left(\frac{2n\pi}{a}\right) x}{2}\right] dx$$

$$\langle x \rangle = \frac{1}{a} \int_0^a \left[x - x\cos\left(\frac{2n\pi}{a}\right) x\right] dx$$

$$\langle x \rangle = \frac{1}{a}\left[\left(\frac{x^2}{2}\right)_0^a - \left\{x - \frac{a}{2n\pi} \sin\left(\frac{2n\pi}{a}\right) x + \frac{a}{2n\pi} \cos\left(\frac{2n\pi}{a}\right) x \right\}_0^a\right]$$

where n = 1 .....

$$\langle x \rangle = \frac{1}{a}\left[\frac{a^2}{2}\right]$$

$$\langle x \rangle = \frac{a}{2}.$$

Therefore, the mean position of a free particle in a 1-D box of length 'a' is $a/2$.

Q 2) The chemical shift of the CH_3 protons in diethylether is $\delta = 1.16$ and that of the CH_2 protons is 3.36. What is the difference in local magnetic field between the two regions of the molecule when the applied field is

(i) 1.9 T (ii) 16.5 T

Ans: $B_{loc} = (1 - \sigma) B_0$

$|\Delta B_{loc}| = |(\Delta \sigma)| B_0$

Constant σ is proportional to chemical shift

$\Delta \sigma = \Delta \delta$

$|\Delta B_{loc}| = |(\Delta \delta)| B_0$

$\because |\Delta B_{loc}| \approx |(\Delta \delta)| B_0$

$\approx |1.16 - 3.36| \times 10^{-6} B_0$

$= 2.2 \times 10^{-6} B_0$

(i) Ans: $B_0 = 1.9 T$

$|\Delta B_{loc}| = 2.2 \times 10^{-6} \times 1.9 T$

$= 4.18 \times 10^{-6} T$

(ii) $B_0 = 16.5\,T$

$|\Delta B_{loc}| = 2.2 \times 10^{-6} \times 16.5\,T$

$= 3.63 \times 10^{-5}\,T$

Q 3) Write the Sackur - Tetrode equation and Calculate the molar entropy of argon (39.95 amu) at 1 bar (10^5 Kg / m s^{-2}) and 298 K.

Ans: $\bar{S}_T = R \ln \left[\frac{(2\pi m k_B T)^{3/2}}{h^2} \frac{k_B T}{P} e^{5/2} \right]$

This above equation is known as Sackur Tetrode equation.

$S(T) = nR \ln \left(\frac{e^{5/2} V}{n N_A \Lambda^3} \right)$ where $\Lambda = \frac{h}{(2\pi m k T)^{1/2}}$

$\Lambda = \frac{6.6 \times 10^{-34} \text{ Js}}{(2 \times 3.14 \times 39.95 \times 1.6 \times 10^{-27} \times 1.38 \times 10^{-23} \times 298)^{1/2}}$

$\Lambda = \frac{6.6 \times 10^{-34}}{(165078.97 \times 10^{-50})^{1/2}}$

$$= \frac{6.6 \times 10^{-34+25}}{406.29}$$

$$= 0.0160 \times 10^{-9}\ m$$

$$= 1.60 \times 10^{-11}\ m$$

$$\Lambda = 1.60 \times 10^{-11}\ m$$

As we know that

$$1\ bar = 10^{5}\ N\ m^{-2}$$

By using the formula,

$$S_m^{\circ} = R \ln \left\{ \frac{e^{5/2} \times (1.38 \times 10^{-23}\ J/K \times 298K)}{10^{5}\ Nm^{-2} \times (1.60 \times 10^{-11}\ m)^{3}} \right\}$$

$$= R \ln \left\{ \frac{e^{5/2} \times 4.12 \times 10^{-21}\ J}{10^{5}\ N m^{-2} \times (1.60 \times 10^{-11} m)^{3}} \right\}$$

$$= R \ln \left\{ \frac{e^{5/2} \times 4.12 \times 10^{-21}\ J}{10^{5} \times 4.096 \times 10^{-33}\ N\ m} \right\}$$

$$= 18.6\ R$$

$$= 18.6 \times 8.314$$

$$= 154.6\ J\ K^{-1}\ mol^{-1}$$

$$\simeq 155\ J\ K^{-1}\ mol^{-1}$$

The entropy of argon gas at 1 bar and 298 K

$$= 155\ J\ K^{-1}\ mol^{-1}$$