

Important Questions on Physical Chemistry- Part III



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1. $A \xrightleftharpoons[k_2]{k_1} B$

Having a rate constant $k_1 = 10^{-1} \text{ s}^{-1}$
 $k_2 = 10^{-2} \text{ s}^{-1}$
 If the initial concentration is 10 M. Calculate the concentration of A after 0.1 second.

A. 9.9
 B. 3.0
 C. 4.6
 D. 8.9
2. Calculate the entropy change that is accompanied by the freezing of one mole of water at 25°C to ice at -10°C ; given that the heat of fusion of ice at its fusion point (0°C) is 6.00 kJ mol^{-1} , the heat capacity of ice is $36.82 \text{ J K}^{-1} \text{ mol}^{-1}$ and heat capacity of liquid water is $75.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

A. -25.23 J/K mol
 B. -32.30 J/K mol
 C. -20.45 J/K mol
 D. -29.96 J/K mol
3. The mass x of a solute adsorbed per gram of a solid adsorbed is given by the Freundlich adsorption isotherm as $x = kc^n$, here k and n are 0.160 and 0.431, respectively. Calculate the amount of acetic acid ($M_m = 60.05 \text{ g mol}^{-1}$) that 1 kg of charcoal would adsorb from a 0.837 M vinegar solution.

A. 4.32 mol
 B. 2.47 mol
 C. 1.57 mol
 D. 3.26 mol
4. Determine the mean activity coefficient of NaCl at a molality of 0.01 in aqueous solution at 25°C .

A. 0.789
 B. 0.889
 C. 0.650
 D. 0.899
5. Which statement is correct according to Le-Chatelier principle for the following reaction $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ when mixing of inert gas takes place at constant volume?

A. Equilibrium shift towards the high molecular side.
 B. Equilibrium shift towards the lower molecular side.
 C. Equilibrium shifts towards the high molecular side, and pressure increases into the reaction container.
 D. Pressure increases in the reaction container, but equilibrium is unchanged.
6. Point group of optically active allene is:

A. C_2
 B. C_s
 C. C_{2v}
 D. C_{2h}
7. Which of the following radiation is responsible for Rotational Raman Spectroscopy?

A. UV –Visible radiation
 B. Infrared radiation
 C. X- rays
 D. Microwave radiations

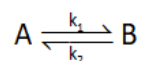
8. Suppose the wave function of a one-dimensional system is $\Psi = \sin(kx) \exp(3ikx)$. In an experiment measuring the momentum of the system, one of the expected outcomes is?
- A. 0
B. $\hbar k$
C. $2\hbar k$
D. $3\hbar k$
9. Sodium has a bcc structure with nearest neighbour distance 365.9 pm. Calculate its density (Atomic mass of sodium = 23).
- A. 0.95 g cm^{-3}
B. 0.12 g cm^{-3}
C. 0.01 g cm^{-3}
D. 1.51 g cm^{-3}
10. At constant temperature and volume what will be the highest translational Molar Entropy?
- A. Cl_2
B. Br_2
C. F_2
D. I_2

Answer Key

- | | | | | | | |
|------|------|-------|------|------|------|------|
| 1. A | 2. D | 3. B | 4. B | 5. D | 6. A | 7. B |
| 8. B | 9. D | 10. D | | | | |

Solutions

Solution 1.



$$t = 0 \quad A_0 \quad 0$$

$$t = t \quad A_0 - x \quad x$$

$$t = t_{eq} \quad A_0 - x_e \quad x_e$$

$$[A]_t = A_0 \left(\frac{k_1}{k_1 + k_2} \right) \left[\frac{k_2}{k_1} + e^{-(k_1 + k_2)t} \right]$$

$$k_1 = 10^{-1} \quad ; \quad k_2 = 10^{-2}$$

$$k_1 + k_2 = 10 \times 10^{-2} + 10^{-2}$$

$$= 11 \times 10^{-2}$$

$$A_0 = 10M$$

$$[A_t] = 10 \left[\frac{10 \times 10^{-2}}{11 \times 10^{-2}} \right] \left[\frac{10^{-2}}{10^{-1}} + e^{-(11 \times 10^{-2}) \times 0.1} \right]$$

$$= \frac{100}{11} [1.089]$$

$$= 9.9 M$$

Solution 2.

The irreversible freezing of water at -10°C can be split into the following three reversible processes:

$$(i) \text{H}_2\text{O}(l) \text{ at } 25^{\circ}\text{C} \rightarrow \text{H}_2\text{O}(l) \text{ at } 0^{\circ}\text{C}; \Delta S = \int_{298}^{273} C_{P(l)} \frac{dT}{T}$$

$$(ii) \text{H}_2\text{O}(l) \text{ at } 0^{\circ}\text{C} \rightarrow \text{H}_2\text{O}(s) \text{ at } 0^{\circ}\text{C}; \Delta S = -\frac{\Delta H_{\text{fus}}}{T}$$

$$(iii) \text{H}_2\text{O}(s) \text{ at } 0^{\circ}\text{C} \rightarrow \text{H}_2\text{O}(s) \text{ at } -10^{\circ}\text{C}; \Delta S = \int_{273}^{263} C_{P(s)} \frac{dT}{T}$$

The total entropy change is the sum of the entropies involved in the three steps indicated above. Thus,

$$\begin{aligned} \Delta S_{\text{total}} &= \int_{298}^{273} (75.31 \text{ J K}^{-1} \text{ mol}^{-1}) \frac{dT}{T} - \frac{6000 \text{ J mol}^{-1}}{273 \text{ K}} + \int_{273}^{263} 36.82 \text{ J K}^{-1} \text{ mol}^{-1} \frac{dT}{T} \\ &= (75.31 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{T_2}{T_1} - \frac{6000 \text{ J mol}^{-1}}{273 \text{ K}} + (36.82 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{T_2}{T_1} \\ &= (75.31 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{273 \text{ K}}{298 \text{ K}} - 21.98 \text{ J K}^{-1} \text{ mol}^{-1} + (36.82 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{263 \text{ K}}{273 \text{ K}} \\ &= -29.96 \text{ J K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

Solution 3.

$$\begin{aligned} x &= k c^n = (0.160) (0.837)^{0.431} \text{ per gram of charcoal} \\ &= (0.148 \text{ g acetic acid}) (\text{g charcoal})^{-1} = (148 \text{ g acetic acid}) (\text{kg charcoal})^{-1} \\ &= \frac{(148 \text{ g acetic acid})(\text{kg charcoal})^{-1}}{60.05 \text{ mol}^{-1}} = 2.47 \text{ mol acetic acid (kg charcoal)}^{-1} \end{aligned}$$

Solution 4.

For 0.01 m solution of NaCl, the ionic strength (I) is given by:

$$I = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2) = \frac{1}{2} (0.01 \times 1^2 + 0.01 \times 1^2) = 0.01$$

(For a uni-univalent electrolyte, the ionic strength is, evidently, equal to its molality).

The mean activity coefficient (γ_{\pm}) is given by the equation:

$$\log \gamma_{\pm} = -A z_+ z_- \sqrt{I}$$

For water at 25°C , the constant $A = 0.509$.

Therefore,

$$\log \gamma_{\pm} = -0.509 \times 1 \times 1 \times \sqrt{0.01} = -0.509$$

$$\gamma_{\pm} = 0.889$$

Solution 5.

When mixing of inert gas takes place at constant volume, then the total pressure of the container is increased, but individual active mass or number of a mole per unit volume remains unchanged. So, the equilibrium condition will be unchanged.

Solution 6.

Molecules with no improper axis of rotation are optically active. Note that $S_1 = \sigma$ and $S_2 = i$. Point groups have no mirror planes, centres of inversion or other improper rotations are C_1 , C_n , and D_n . Therefore, optically active allene has C_2 point group.

Solution 7.

In rotational Raman spectroscopy, we use Infrared radiations. The selection rule for this is:

$$\Delta J = 0, +2, -2$$

For a molecule to be Rotational Raman active, it should be anisotropically polarisable, i.e its polarizability ellipsoid should change its radius on rotating the molecule.

Solution 8.

$$\Psi = \sin x = \frac{e^{ikx} - e^{-ikx}}{2i} \quad (\text{For expected value})$$

$$\text{Momentum} = \hat{p} = -i\hbar \frac{d}{dx}$$

$$[\Psi \hat{p}] \text{ Expected outcomes} = -i\hbar \frac{d\Psi}{dx}$$

$$\hat{p}\Psi = -i\hbar \frac{d}{dx} \left(\frac{e^{ikx} - e^{-ikx}}{2i} \right) e^{3ikx}$$

$$= -\frac{i\hbar}{2i} \frac{d}{dx} [e^{4ikx} - e^{2ikx}]$$

$$= -\frac{\hbar}{2} [(4ike^{4ikx} - 2ike^{2ikx})] \left[\because \frac{de^{ax}}{dx} = ae^{ax} \right]$$

$$= -\frac{\hbar}{2} [2ik(2e^{4ikx} - e^{2ikx})]$$

$$= -\frac{\hbar}{2} [2ik(-2e^{4ikx} + e^{2ikx})]$$

$$= \hbar k [-2e^{4ikx} + e^{2ikx}]$$

$$= \hbar k [-i2e^{4ikx} + ie^{2ikx}]$$

$$(\Psi \hat{p}) = \hbar k \text{ (expected value)}$$

Solution 9.

$$\text{For BCC, neighbor nearest distance} = (d) = \frac{\sqrt{3}}{2} a$$

$$a = \frac{2}{\sqrt{3}} d$$

$$a = \frac{2}{\sqrt{3}} \times 365.9$$

$$= 422.5 \text{ pm}$$

$$\text{For BCC, } Z = 2$$

$$M = 23$$

$$d = \frac{Z \times M}{a^3 \times N_A}$$

$$= \frac{2 \times 23 \text{ g mol}^{-1}}{(422.5 \times 10^{-10} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= 1.51 \text{ g/cm}^3$$

Solution 10.

For molar translational entropy,

$$[S_m^T] = R \left[\ln \frac{V e^{5/2}}{N_A \lambda^3} \right] \dots (1)$$

$$[S_m^T] \propto \ln \frac{1}{\lambda^3}$$

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Put in Equation (1) as:

$$S_m^T = R \left[\ln V + \ln e^{5/2} - \ln N_A - 3 \ln h + \ln (2\pi m k T)^{3/2} \right]$$

$$S_m^T = R \left[\ln V + \frac{5}{2} - \ln N_A - 3 \ln h + \ln (2\pi k)^{3/2} + \ln m^{3/2} + \ln T^{3/2} \right]$$

Therefore,

$$S_m^T \propto \ln m^{3/2}$$

Molar mass of I_2 is the highest hence, having the highest molar entropy.

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