Important Questions On Physical Chemistry

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1. Which of the following is true regarding HMO theory?
i) HMO is an absolute method.
ii) HMO treats pi electrons separately from sigma electrons.
iii) Pi electrons determine the properties of the conjugated molecules.
iv) HMO uses only the variation principle.
A. Only iv
B. iii and iv
C. ii and iii
D. only ii

2. The rate constant of a unimolecular reaction was 2.56×10^{-3} and 2.3×10^{-1} at T= 110K and 330K respectively. The rate constant (in s^{-1} units) at 220K would be:
A. 2.43×10^{-2}
B. 2.43×10^{-1}
C. 4.81×10^{-2}
D. 1.81×10^{-1}

3. A system is expanded Reversibly adiabatically from 1 L to 10 L. If initial temp. is 750 K, what would be the final temperature? C_P= 29.23 J/K mol.
A. 500 K
B. 200 K
C. 100 K
D. 300 K

4. Which among the following will show maximum flocculation value for $Fe(OH)_3$ Solution?
A. $(NH_4)_3PO_4$
B. Na_2S
C. NH_4Cl
D. NaCl

5. Consider the reaction
$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}$
What will be the half-cell potential at 298K where [Cu^{2+} = 5.0 M and Eº = +0.34V].
A. 4.6 mV
B. 0.466 V
C. 3.6 V
D. 0.36 V

6. The extent of dissociation of PCl_5 at a certain temperature is 20% at one atm pressure. Calculate the pressure at which this substance is half-dissociated at the same temperature.
A. 0.123
B. 0.329
C. 0.420
D. 0.789

7. Improper Axis of symmetry refers to which of the following operations?
A. Rotation
B. Reflection
C. Rotation followed by perpendicular reflection
D. None of the above

8. Calculate the maximum rotational level which can be occupied at 300K when rotational constant is $24 cm^{-1}$.
A. 1
B. 2
C. 4
D. 10

9. The ratio of HCP closed packed atoms to voids in HCP closed packing is:
A. 1:4 B. 2:3 C. 1:6 D. 1:3

10. Two miscible liquids A and B form a solution. Assume that the solution is non-ideal but the vapor above it behaves ideally. For pure A and B, the vapor pressures are 550 torr and 700 torr respectively at 35°C. If the total pressure above a solution that is 48 mole percent A, is 500 torr and the mole fraction of A in the vapor is 0.45, determine the activity coefficients of A and B in the solution.
A. 0.854, 0.756 B. 0.765, 0.324
C. 0.854, 0.765 D. 0.845, 0.765

Answer Key

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

Solutions

Solution 1. HMO calculates the energy and shape of the pi molecular orbitals of the planar conjugated molecules. The calculations are based on the variation principle along with LCAO for pi electrons. It differentiates pi electrons from sigma electrons as pi electrons take part in conjugation. This theory is approximate since it ignores electron-electron repulsions.

Solution 2. By applying Arrhenius equation:

T_1=110K and T_2=360K

$$\ln\frac{k_2}{k_1}=\frac{Ea}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\ln\frac{2.2\times10^{-1}}{2.66\times10^{-3}}=\frac{Ea}{8.314J/Kmol}\left[\frac{1}{120}-\frac{1}{360}\right]$$

$E_a=1.64\times10^{-2}$;T_1=110K and T_2=220K

$$\ln\frac{k_2}{k_1}=\frac{Ea}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]=\ln\frac{k_2}{2.66\times10^{-3}}=\frac{1.64\times10^{-2}}{R}\left[\frac{1}{110}-\frac{1}{220}\right]$$

K=2.43 x 10^{-2} s^{-1}

Solution 3. As system is reversibly adiabatically expanded, so,

PV^{γ} = Comtt

$P_1V_1^{\gamma}=P_2V_2^{\gamma}$ ...(i)

From ideal equation:

PV=nRT

P= nRT/ V

Put the volume of P in eq (i):

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ ...(ii)

Given C_P = 29.23 J/K mole

$C_P - C_V = R$

$C_V = C_P - R$

= 29.23 – 8.314

C_V = 20.9

$\gamma = \frac{C_P}{C_V} = \frac{29.2}{20.9} = 1.4$

From eq. (ii):

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$750(1)^{1.4-1} = T_2(10)^{1.4-1}$

$750 = T_2(10)^{0.4}$

T_2 = 300 K

Solution 4. Flocculation value or precipitation value is the minimum amount of an electrolyte in millimoles that must be added to one litre of colloidal sols to bring about complete coagulation or precipitation. Coagulation power is inversely proportional to coagulation value, i.e., smaller the coagulation value of an electrolyte ion, greater is the coagulating power.

Solution 5. According to Nernst equation:

$E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu} - 0.059/n \log 1/[Cu^{2+}]$

= 0.34 –0.059/2 log (1/5)

= 0.36 V

Solution 6. $K_p = \alpha^2P/ (1 - \alpha^2)$

P = 1 atm, α = 0.2

∴ $K_p = (0.2)^2$ (1 atm) / (1 – 0.04) = 0.041 atm

Let P' be the pressure at which α = 0.5, then

$K_p = \alpha^2P'/ (1 - \alpha^2)$

0.041 atm = $(0.5)^2$P'/ (1 – 0.25)

P = 0.123 atm

Solution 7. A molecule is said to have an improper Axis of rotation of order n if rotation of 2π/n about an axis followed by the reflection in a plane perpendicular to that axis.

Solution 8. Maximum rotational level that can be occupied is:

$$J_{max} = \left(\frac{kT}{2B}\right)^{1/2} - \frac{1}{2}$$

Here, B = 24 cm^{-1}, T = 300 K, k = 1.38×10^{-23} J K^{-1}

k (in cm^{-1}) = $(1.38\times10^{-23})/(6.626\times10^{-34}\times3\times10^{10})$=0.694 cm^{-1} K^{-1}

$$J_{max} = \left(\frac{0.694\times300}{(2\times24)}\right)^{1/2} - 1/2 = 1.583$$

J_{max} = 2

Solution 9. No. of Atoms present in HCP = 6
Total no. voids present in HCP = Td voids + Oh voids
= 12 + 6
= 18

Atom	:	Voids
6	:	18
1	:	3

Solution 10. $x_{A, vap} = 0.45$
Since, the vapor behaves ideally, hence,
$p_A = x_{A, vap} \times P = 0.45 \times 500$ torr = 225 torr
$p_B = P - p_A = 500$ torr – 225 torr = 275 torr
Since the solution behaves non-ideally, Raoult's law becomes:

$$p_i = a_i p_i^{\circ}$$

a_A= 225 torr/550 torr=0.41
Hence,
$\gamma_A = a_A/x_A = 0.41/0.48 =$ **0.854**
a_B= 275 torr/700 torr=0.393
$\gamma_B = a_B/x_B = 0.393/0.52 =$ **0.756**