

OCTOBER 2012

P/ID 40123/PCHC

Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

All questions carry equal marks.

1. What is ideal solution?
2. Define the standard state of liquid.
3. Calculate the activation energy of a reaction whose rate constant is tripled by a 10°C rise in temperature in the vicinity of 27°C.
4. What is meant by partition function?
5. Predict the effect of increase in ionic strength on the rate constant for each of the following
 - (a) $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{Hg}^{2+} \rightarrow$
 - (b) $\text{Fe}^{2+} + [\text{Co}(\text{SO}_4)_3]^{2-} \rightarrow$
6. What is general acid catalysis?

7. Assign the point group of the following molecules
 - (a) Trans dichloro ethylene
 - (b) BF_3 .
8. Define the following terms
 - (a) Abelian and non-abelian group
 - (b) Class.
9. What is collision number?
10. What is kinetic isotope effect?

PART B — ($4 \times 20 = 80$ marks)

Answer ALL questions.

All questions carry equal marks.

11. (a) (i) Write a note on excess functions for non-ideal solutions. How are excess functions determined experimentally?
 - (ii) Discuss the solubility method for the determination of activity and activity coefficients.

Or

- (b) (i) Discuss the variation of chemical potential with temperature and pressure.
 - (ii) Explain the determination of fugacity by using equation of state.

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12. (a) (i) For the hydrolysis of sulphamic acid, the rate constant is $1.16 \times 10^{-3} \text{ mol}^{-3} \text{ dm}^3 \text{ sec}^{-1}$ at 363 K while $E_a = 127490 \text{ J/mol}$. From these data find ΔG^\ddagger , ΔS^\ddagger , ΔH^\ddagger of the reaction at 363 K.
- (ii) Explain the significance of entropy of activation and enthalpy of activation.

Or

- (b) (i) Derive Eyring's equation? In what way ARRT is superior to the collision theory.
- (ii) Discuss the potential energy surface of a reaction.
13. (a) (i) Discuss the linear free energy relationship with an example.
- (ii) Discuss the Bronsted catalysis law.

Or

- (b) (i) Explain the mechanism of acid-base catalysis.
- (ii) Discuss the primary salt effect and explain its significance.

14. (a) (i) Explain the electronic spectra of ethylene.

(ii) Obtain the hybrid orbitals for SF_6 .

Or

(b) (i) Obtain the symmetries of vibrational modes of BF_3 .

(ii) Construct the character table for C_{3v} point group.
