Subject : Chemistry

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and

Marking Scheme:

- (i) Each question is allotted 4 (four) marks for each correct response.
- (ii) <sup>1</sup>/<sub>4</sub> (one fourth) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- Q.1 For the first order reaction,  $A(g) \rightarrow B(g) + C(g) + D(s)$ taking place at constant pressure temperature condition. Initially volume of the container containing only A was found to be  $V_0$ and after time 't' it was Vt. Rate constant for

the reaction is –  
(A) 
$$\frac{1}{t} \ln \frac{V_0}{2V_0 - V_t}$$
 (B)  $\frac{1}{t} \ln \frac{V_0}{V_0 - V_t}$   
(C)  $\frac{1}{t} \ln \frac{2V_0}{2V_0 - V_t}$  (D)  $\frac{1}{t} \ln \frac{2V_t}{2V_0 - V_t}$ 

The rate law for the dimerisation of  $NO_2$  is Q.2

 $\frac{-d[NO_2]}{d} = k [NO_2]^2$ . Which of the following

changes will change the value of the specific rate constant, k :

- (A) Doubling the total pressure on the system
- (B) doubling the temperature
- (C) both

(D) none

Q.3 According to the Arrhenius equation a straight line is to be obtained by plotting the logarithm of the rate constant of a chemical reaction (log k) against –

(A) T	(B) log T
(C) 1/T	(D) $\log(1/T)$
The mechanism of the	e reaction :

**Q.4**  $Nu^- + R - X \rightarrow R - Nu + X^-$  is:

 $Nu^- + R - X \rightarrow$  [Transition state] (slow)

[Transition state]  $\rightarrow$  Nu – R + X<sup>-</sup> (fast)

- The rate of reaction can be increased by:
- (A) Increasing the conc. of Nu<sup>-</sup> only.
- (B) Increasing the conc. of R X only.
- (C) Increasing the conc. of both  $Nu^-$  and R X
- (D) Decreasing the conc. of both Nu<sup>-</sup> and R-X

- 0.5 The rate of a reaction increases 4-fold when concentration of reactant is increased 16 times. If the rate of reaction is  $4 \times 10^{-6}$  mole L<sup>-1</sup> S<sup>-1</sup> mole L<sup>-1</sup> when concentration of the reactant is  $4 \times 10^{-4}$ , the rate constant of the reaction will be
  - (A)  $2 \times 10^{-4}$  mole<sup>1/2</sup> L<sup>-1/2</sup> S<sup>-1</sup>
  - (B)  $1 \times 10^{-2} \text{ S}^{-1}$

(C) 
$$2 \times 10^{-4}$$
 mole<sup>-1/2</sup>, L<sup>1/2</sup> S<sup>-1</sup>

(D)  $25 \text{ mole}^{-1} \text{ Lmin}^{-1}$ 

**Q.6** The rate of the simple reaction  $2NO + O_2 \rightarrow 2NO_2$ ,

> when the volume of the reaction vessel is doubled-

(A) will grow eight times of its initial rate (B) rate reduce to one-eights of its initial rate (C) will grow four times of its initial rate (D) reduce to one-fourth of its initial rate

**O.7** For any reaction,

 $C_6H_5N_2Cl \xrightarrow{\Delta} C_6H_5Cl + N_2$ 

the half life is independent of concentration. The volume of  $N_2$  produced after 5 minutes is 15 litres and after completion of reaction it is 45 litres. Which of the following statements is incorrect -

(A) It is a first order reaction.

(B) Rate constant k =  $\frac{2.303}{5} \log 1.5 \min^{-1}$  for this reaction

(C) Rate constant  $k = \frac{2.303}{5} \log 3 \min^{-1}$  for this

reaction

(D) Half life  $(t_{1/2})$  of this reaction = 0.693/K

For the reaction,  $H_2(g + Br_2(g) = 2HBr(g))$ , the Q.8 reaction rate =  $K[H_2][Br_2]^{1/2}$ . Which statement is true about this reaction (A) The reaction is of second order (B) Molecularity of the reaction is 3/2

(C) The unit of K is  $sec^{-1}$ 

(D) Molecularity of the reaction is 2.

Q.9 The first order rate constant for the decomposition of dimethyl ether is  $3.2 \times 10^{-4} \text{s}^{-1}$ at 450°C.

 $(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$ 

The reaction is carried out in a constant volume flask. Initially only dimethyl ether is present and the pressure is 0.350 atm. What is the pressure of the system after 8 minutes ? (Assume ideal behaviour).

[Antilog 0.0667 = 1.166]

(A) 0.35 atm (B) 0.40 atm (C) 0.45 atm (D) 0.50 atm

- **Q.10** In which of the following case,  $E_a$  of the backward reaction is greater than that of the forward reaction?
  - (A) A + 10 kcal  $\rightarrow$  B, E<sub>a</sub> = 50 kcal
  - (B)  $A + 20 \text{ kcal} \rightarrow B, E_a = 40 \text{ kcal}$
  - (C) A + 40 kcal  $\rightarrow$  B, E<sub>a</sub> = 10 kcal
  - (D)  $A 40 \text{ kcal} \rightarrow B$ ,  $E_a = 20 \text{ kcal}$
- **Q.11** The chemical reaction,  $2O_3 \longrightarrow 3O_2$  proceeds as follows:

 $O_3 \square O_2 + O$  ..... (fast)

 $O + O_3 \rightarrow 2O_2$  ..... (slow)

The rate law expression should be:

(A) 
$$r = K [O_3]^2$$
 (B)  $r = K[O_3]^2 [O_2]^{-1}$ 

(C)  $r = K [O_3][O_2]$  (D) Unpredictable

**Q.12** Time required to decompose half of the substance for nth order reaction is inversely proportional to : (A)  $a^{n+1}$  (B)  $a^{n-1}$ 

(A)  $a^{(B)} a^{(B)} a^{(C)}$  (B)  $a^{(D)} a^{(D)} a^{(D)}$ 

Q.13 In which rate law is the overall reaction order equal to 3?

(A) rate = 
$$k [A]^2 [B]^0$$
 (B) rate =  $k [A]^2 [B]^{-1}$ 

(C) rate = k [A]<sup>1</sup>[B]<sup>3</sup> (D) rate = k [A]<sup>3</sup>[B]<sup>0</sup>

Q.14 For the elementary step,

 $(CH_3)_3.CBr (aq) \rightarrow (CH_3)_3 C^+(aq) + Br^- (aq)$ the molecularity is:

(A) Zero (B) 1

(D) cannot ascertained

- **Q.15** For a reaction for which the activation energies of the forward and reverse directions are equal in value:
  - (A) the stoichiometry is the mechanism
  - (B)  $\Delta H = 0$

(C) 2

- $(\mathbf{C})\,\Delta\mathbf{S}=\mathbf{0}$
- (D) the order is zero.

Q.16 Which statement is not true for the reaction

 $C + D \rightarrow F + G$  if the rate law is rate

 $= k[C]^{2}[D]^{1/2}?$ 

- (A) If the concentration of D is increased by a factor of 4, then the reaction rate will double.
- (B) If the concentration of C is doubled and the concentration of D is tripled, then the reaction rate will increase by a factor of 6.9.
- (C) If the concentration of C is increased by a factor of 3 and the concentration of D is decreased by a factor of 4, then the reaction rate will increase by a factor of 4.5.
- (D) If the concentrations of C and D are doubled, then the reaction rate will double.
- Q.17 The rate of reaction triples when temperature change from 20°C to 50°C. Calculate energy of activation for the reaction.
  - $[\ln 3 = 1.098]$

(A)  $28.81 \text{ kJ mol}^{-1}$  (B)  $38.51 \text{ kJ mol}^{-1}$ 

- (C) 18.81 kJ mol<sup>-1</sup> (D) 8.31 kJ mol<sup>-1</sup>
- **Q.18** Which statement is true regarding the experimental determination of a rate law?
  - (A) In order to determine the value of an exponent for a reactant in the rate law, the concentration of that reactant and one other reactant must be changed.
  - (B) The instantaneous rate at the midway point of the reaction is used to determine the exponents and rate law for that equation.
  - (C) The average rate of reaction at the midway point of the reaction is used to determine the exponents and rate law for that equation.
  - (D) Initial rates of reaction are used to determine the exponents and rate law for that equation.
- **Q.19** The reaction  $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$  is first order with respect to CO, and 3/2 order with respect to Cl<sub>2</sub>. If the units for rate are M/min, what are the units of the rate constant in this reaction?

(A) min . $M^{3/2}$	(B) $1 / (\min M^{3/2})$
(C) 1/ (min.M <sup>5/2</sup> )	(D) 1 / (min.M <sup>7/2</sup> )

- **Q.20** Which situation is not characteristic of the collision theory model of the reaction  $A + BC \rightarrow AB + C?$ 
  - (A) The electron density around A, B, and C must change.
  - (B) The orientation of the two species must be correct.
  - (C) As A approaches BC, a strong attraction between any filled shells of electrons will develop between the two species.
  - (D) The kinetic energy of the molecules may be the only source of energy for attaining the activation energy. The collisions of A and BC that result in a reaction are a very small fraction of the total number of collisions.

## For Q.21-Q.25 :

The answer to each question is a NUMERICAL VALUE.

- Q.21 The elementary step of the reaction,  $2Na + Cl_2 \rightarrow 2NaCl$  is found to follow III order kinetics, its molecularity is :
- Q.22 If for any reaction, the rate constant is equal to the rate of the reaction at all concentration. The order is :

- **Q.23** If a reaction  $A + B \rightarrow C$  is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy 70 kJ/mol, the activation energy (in kJ/mol) for the reverse reaction is
- **Q.24** The rate of the reaction :  $A + B + C \rightarrow$  Product is given by rate  $=d[A]/dt = k[A]^{1/2} [B]^{1/4} [C]^0$ . The order of reaction is (X/4). Find value of X.
- **Q.25** If the rate expression for the reaction  $5Br^{-} + BrO_{3}^{-} + 6H^{+} \rightarrow 3Br_{2} + 3H_{2}O$ ; is  $K[Br^{-}][BrO_{3}^{-}][H^{+}]^{2}$ ; the order of reaction is

