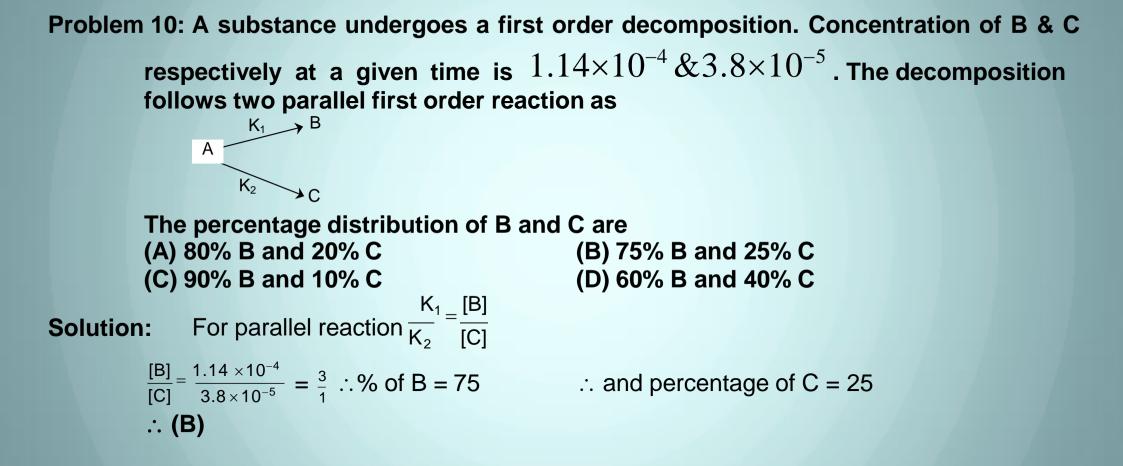
Problem 7The temperature coefficient of a reaction is 2, by what factor<br/>reaction increases when temperature is increased from 30°C to 80°C.<br/>(A) 16the rate of<br/>(B) 32the rate of<br/>(C) 64Solution: $\frac{k_{80}}{k_{30}} = 2^5 = 32$  $\therefore$  (B)

Problem 8: The rate constant, the activation energy and Arrhenius parameter of a chemical reaction at 25°C are3 × 10<sup>-4</sup> s<sup>-1</sup>, 104.4 kJ mol<sup>-1</sup> and 6 × 10<sup>14</sup> s<sup>-1</sup> respectively. The value of the rate constant atT  $\rightarrow \infty$  is (A) 2 × 10<sup>18</sup>s<sup>-1</sup> (B) 6 × 10<sup>14</sup> (C)  $\alpha$  (D) 3.6 × 10<sup>30</sup>s<sup>-1</sup>

**Solution:**  $k = Ae^{-Ea/RT}$  when  $T \longrightarrow \infty$   $\therefore$  value is  $6 \times 10^{14} s^{-1}$   $\therefore$  (B)

Problem 9:If  $t_{1/2}$  does not change with initial concentration, then order of the reaction is<br/>(A) zero(B) second(C) first(D) third11 $\therefore$  (C)



Problem 11: A tangent drawn on the curve obtained by plotting concentration of product (mole L<sup>-1</sup>) of a first order reaction vs. time (min) at the point corresponding to time 20 minute makes an angle to 30° with concentration axis. Hence the rate of formations of product after 20 minutes will be

(A) 0.580 mole L<sup>-1</sup> min<sup>-1</sup>
(B) 1.732 mole L<sup>-1</sup> min<sup>-1</sup>
(C) 0.290 mole L<sup>-1</sup> min<sup>-1</sup>
(D) 0.866 mole L<sup>-1</sup> min<sup>-1</sup>

Solution: Tangent makes an angle of 30° with concentration axis so it must make an angle of 60° with the time axis (–ve direction). The slope of the tangent will be tan60° i.e., 1.732. ∴ (B) Problem 12: For reaction  $3A \longrightarrow products$ , it is found that the rate of reaction increases 4fold when concentration of A is increased 16 times keeping the temperature constant. The order of reaction is? (A) 2 (B) 1 (C) 1 (D) 0.5 Solution: The rate data suggests the rate law as follows Rate  $\alpha \sqrt{A}$  i.e., r  $\alpha A^{1/2}$  $\therefore$  order = 0.5

∴ **(D)** 

**Problem 13:** The thermal decomposition of acetaldehyde :  $CH_3CHO \longrightarrow CH_4 + CO$ , has rate constant of 1.8  $\times$  10<sup>-3</sup> mole<sup>-1/2</sup>L<sup>1/2</sup> min<sup>-1</sup> at a given temperature. How would d[CH CHO]  $\frac{\partial y}{\partial u}$  will change if concentration of acetaldehyde is doubled keeping the temperature constant? (A) will increase by 2.828 times (B) will increase by 11.313 times (C) will not change (D) will increase by 4 times Unit of the rate constant mole  $^{-1/2}L^{1/2}$ .min<sup>1/2</sup> suggests that the reaction obeys kinetics Solution: of 1.5 order. Rate = k  $[CH_3CHO]^{3/2}$ or  $k = \frac{Rate}{[CH_3CHO]^{3/2}} = \frac{moleL^{-1}min^{-1}}{(moleL^{-1})^{3/2}} = Mole^{-1/2}, L^{1/2}.min^{-1}$ So, by doubling the concentration of acetaldehyde the rate will increase 2<sup>1.5</sup> i.e., 2.828 times. ∴ **(A)** 

**Problem 14:** The reaction ;  $2O_3 \rightarrow 3O_2$ , is assigned the following mechanism.

I)  $0_3 = 0_2 + 0$ 

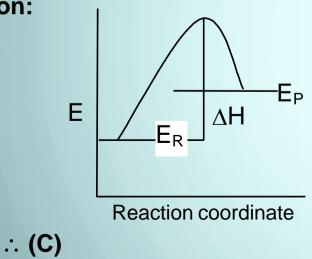
II)  $O_3 + O = 2O_2$ 

The rate law of if the reaction will, therefore be

(A)  $r \alpha [O_3]^2 [O_2]$  (B)  $r \alpha [O_3]^2 [O_2]^{-1}$  (C)  $r \alpha [O_3]$  (D)  $r \alpha [O_3] [O_2]^{-2}$ **Solution:** Step II, being r.d.s.

Rate of overall reaction = rate of Step II =  $K_{II}[O_3][O]$ Putting the value of [O] from the equilibrium of Step I,

 $K_{\parallel}K_{c}[O_{3}]^{2}$ Rate =  $[O_2]$   $\therefore$  (B) Problem 15: For an endothermic reaction where ∆H represents the enthalpy of the reaction, the minimum value for the energy of activation will be (A) Less than ∆H(B)zero (C) more than ∆H (D)equal to ∆H Solution:



## **HOME ASSIGNMENT**

#### **Rate of Reaction**

- Rate of formation of SO<sub>3</sub> in the following reaction 2SO<sub>2</sub> + O<sub>2</sub> → 2SO<sub>3</sub> is 100 kg min<sup>-1</sup>. Hence rate of disappearance of SO<sub>2</sub> will be

   (A) 100 kg min<sup>-1</sup>
   (B) 80 kg min<sup>-1</sup>
   (C) 64 kg min<sup>-1</sup>
   (D) 32 kg min<sup>-1</sup>
- 2. In a catalytic conversion of N<sub>2</sub> to NH<sub>3</sub> by Haber's process, the rate of reaction expressed as change in the concentration of ammonia per unit time is 40x10<sup>-3</sup> mol l<sup>-1</sup> s<sup>-1</sup>. If there are no side reactions, the rate of the reaction as expressed in terms of hydrogen is:
  (A) 60x10<sup>-3</sup> mol l<sup>-1</sup> s<sup>-1</sup>
  (B) 20x10<sup>-3</sup> mol l<sup>-1</sup> s<sup>-1</sup>
  (C) 10.3x10<sup>-3</sup> mol l<sup>-1</sup> s<sup>-1</sup>.

3. In the reaction of A + 2B  $\rightarrow$  C + 2 D, the initial rate, d[A]/dt at t = 0 was found to be 2.6x10<sup>-2</sup> M sec<sup>-1</sup>. What is the value of –d[B]/dt at t = 0 in Ms<sup>-1</sup>? (A) 2.6x10<sup>-2</sup> (B) 5.2x10<sup>-2</sup> (C) 1.0x10<sup>-1</sup> (D) 6.5x10<sup>-3</sup> 4. A reaction is catalysed by H<sup>+</sup> ion. In presence of HA, rate constant is 2x10<sup>-3</sup> min<sup>-1</sup> and in presence of HB rate constant is 1x10<sup>-3</sup>, HA and HB both being strong acids, we may conclude:
(A) equilibrium constant is 2
(B) HA is stronger than HB
(C) relative strength of HA to HB is 2
(D) HA is weaker than HB and relative strength is 0.5

5. 
$$xA+yB \rightarrow zC$$
 if  $-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = 1.5 \frac{d[C]}{dt}$  then, x, y and z are:  
(A) 1, 1, 1 (B) 3, 2, 3 (C) 3, 3, 2 (D) 2, 2, 3

- 6. For a gaseous reaction, the rate is often expressed in terms of  $\left(\frac{dP}{dt}\right)$  instead of  $\left(\frac{dC}{dt}\right) r \left(\frac{dn}{dt}\right)$  where C is the concentration and n is the number of mole. Hence, relation between three expression is:
  - (A)  $\frac{dC}{dt} = \frac{1}{V} \left( \frac{dn}{dt} \right) = \frac{1}{RT} \left( \frac{dP}{dt} \right)$
  - $(\mathsf{B}) \quad \frac{dC}{dt} = \left(\frac{dn}{dt}\right) \neq \left(\frac{dP}{dt}\right)$
  - (C)  $\frac{dC}{dt} = \left(\frac{dn}{dt}\right) = \frac{V(dP)}{RT} \left(\frac{dP}{dt}\right)$
  - (D) None of these

- 7. For the reaction  $2NH_3 \rightarrow N_2 + 3H_2 \frac{d[NH_3]}{dt} = k_1[NH_3], \frac{d[N_2]}{dt} = k_2[NH_3], \frac{d[H_2]}{dt} = k_3[NH_3]$ Then relation between  $k_1$ ,  $k_2$  and  $k_3$  id;p (A) 1.5  $k_1 = 3k_2 = k_3$ (B)  $2k_1 = k_2 = 3k_3$ (C)  $k_1 = k_2 = k_3$ (D)  $k_1 = 3k_2 = 2K_3$
- 8. The specific rate constant for a first order reaction is  $60 \times 10^{-4} \text{ sec}^{-1}$ . If the initial concentration of the reactant is 0.01 mol L<sup>-1</sup>, the initial rate is (A)  $60 \times 10^{-6} \text{ M sec}^{-1}$  (B)  $36 \times 10^{-4} \text{ M sec}^{-1}$ (C)  $60 \times 10^{-2} \text{ M sec}^{-1}$  (D)  $36 \times 10^{-1} \text{ M sec}^{-1}$
- 9. For a gaseous reaction 2A + B → products, the rate law is K[A]<sup>2</sup>[B]. On doubling the volume of the container the new rate will be
  (A) 4 times
  (B) 8 times
  (C) <sup>1</sup>/<sub>8</sub> times
  (D) <sup>1</sup>/<sub>1</sub>times

10. The rate constant for the reaction  $2N_2O_5 \rightarrow 4NO_2 + O_2$  is  $3.0 \times 10^{-5}$  sec<sup>-1</sup>. If the rate is 2.4  $\times 10^{-5}$  mol L<sup>-1</sup>sec<sup>-1</sup>, then conc. Of N<sub>2</sub>O<sub>5</sub> in mol L<sup>-1</sup> is (A) 1.4 (B) 1.2 (C) 0.04 (D) 0.8 11. For the reaction  $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ , given that  $\frac{-d[N_2O_5]}{dt} = K_1[N_2O_5] \quad \frac{d[NO_2]}{dt} = K_2[N_2O_5]$ and  $\frac{d[O_2]}{dt} = K_3[N_2O_5]$ The relation between K<sub>1</sub>, K<sub>2</sub> and K<sub>3</sub> is (A) 2K<sub>1</sub> = K<sub>2</sub> = 4K<sub>3</sub> (B) K<sub>2</sub> = K<sub>2</sub> = K<sub>3</sub> (C) 2K<sub>1</sub> = 4K<sub>2</sub> = K<sub>3</sub> (D) None

12.In a reaction  $2A \longrightarrow$  Products; the concentration of A decreases from 0.5 mol L<sup>-1</sup> to 0.4 mol L<sup>-1</sup> in10 min. the rate of the reaction during this interval is (A) 0.05 M min<sup>-1</sup> (B) 0.005 M min<sup>-1</sup> (C) 0.5 M min<sup>-1</sup> (D) 5 M min<sup>-1</sup>

#### **Molecularity and order of reaction**

13.In a particular reaction the time required to complete half of the reaction was found to increase 9 times when the initial concentration of the reactants was reduced to one third. What is order of the reaction?

(A) 0 (B) 1 (C) 2 (D) 3

14.The rate law for the reaction RCI + NaOH → ROH + NaCl is given by rate = k[RCI]. The rate of this reaction

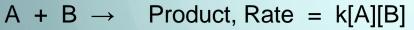
- A. is doubled by doubling the concentration of NaOH
- B. is halved by reducing the concentration of RCI by one half
- C. is increased by increasing the temperature of the reaction

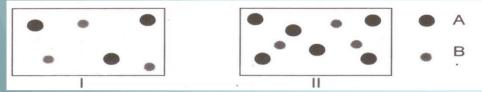
D.is unaffected by change in temperature

Which is correct?

(A) A and B (B) B and C (C) C and D (D) B and D

# 15. The following reaction is first - order in A and first - order in B:





Relative rate of this reaction in vessels I and II of equal volume is(A) 1 : 1(B) 1 : 2(C) 2 : 1(D) 1 : 4

16. Relative value of rate constants (k) in I and II of above question is :
(A) 1:1
(B) 1:2
(C) 2:1
(D) 1:3

17. 
$$A+B \rightarrow \text{Products}, \frac{dx}{dt} = k |A|^{*} |B|^{*} \text{ if } \left(\frac{dx}{dt}\right) = k$$
, the order is

(A) 4 (B) 2 (C) 1 (D) 0

18. If for the reaction  $nA \rightarrow B$ ,  $-\frac{d[A]}{dt} = 2\frac{d[B]}{dt}$  then rate law is (if the reaction is elementary) (A)  $-\frac{d[A]}{dt} = k[A]^2$ (B)  $\frac{d[B]}{dt} = k[A]$ (C)  $\frac{d[A]}{dt} = k[A]^2$ (D)  $-\frac{d[B]}{dt} = k[B]^2$ 

19. For the non-equilibrium process,  $A + B \rightarrow products$ , the rate is first – order w.r.t. A and second – order w.r.t.B.If 1.0 mol each of A and B introduced into a 1.0 L vessel, and the initial rate was 1.0 × 10<sup>-2</sup> mol L<sup>-1</sup> s<sup>-1</sup>. rate when half reactants have been turned into products is: (A)1.25 × 10<sup>-3</sup> mol L<sup>-1</sup> s<sup>-1</sup> (B)1.0 × 10<sup>-2</sup> mol L<sup>-1</sup> s<sup>-1</sup> (C)2.50 ×10<sup>-3</sup> mol L<sup>-1</sup> s<sup>-1</sup> (D)2.0 × 10<sup>-2</sup> mol L<sup>-1</sup> s<sup>-1</sup> 20.For the reaction A + B → Products, it is found that the order of A is 2 and of B is 3 in the rate expression. When concentration of both is doubled the rate will increases by
 (A) 10
 (B) 6
 (C) 32
 (D) 16

21.The rate law of the reaction A + 2B  $\longrightarrow$  Product is given by d[Product]/dt = K[A]<sup>2</sup>·[B]. If A is taken in large excess, the order of the reaction will be (A) 0 (B) 1 (C) 2 (D) 3

22.If concentration are measured in mole/lit and time in minutes, the unit for the rate constant of a 3<sup>rd</sup> order reaction are
(A) mol lit<sup>-1</sup> min<sup>-1</sup>
(B) lit<sup>2</sup> mol<sup>-2</sup>min<sup>-1</sup>
(C) lit.mol<sup>-1</sup> min<sup>-1</sup>
(D) min<sup>-1</sup>

23. The rate of reaction  $Cl_3C.CHO + NO \longrightarrow CHCl_3 + NO + CO$  is given by equation, Rate =  $k[Cl_3.CCHO][NO]$ . If concentration is expressed in moles/litre, the units of K are (A) litre<sup>2</sup>mole<sup>-2</sup>sec<sup>-1</sup> (B) mole litre<sup>-1</sup>sec<sup>-1</sup> (C) litre mole<sup>-1</sup>sec<sup>-1</sup> (D) sec<sup>-1</sup>

Integrated rate law and half life time

- 24. Rate constant of a reaction is 0.0693 min<sup>-1</sup>. Starting with 10 mol, rate of the reaction after 10 min is:
  - (A) 0.693 mol min<sup>-1</sup>
    (C) 0.0693 x 5 mol min<sup>-1</sup>

(B) 0.693 x 2 mol min<sup>-1</sup> (D) 0.693 x 5<sup>2</sup> mol min<sup>-1</sup>

25.Rate of the chemical reaction: nA → products, is doubled when the concentration of A increased four times. If the half time of the reaction at any temperature is 16 min. then time required for 75% of the reaction to complete is
(A) 24 min
(B) 27.3 min
(C) 48 min
(D) 49.4 min

26.A substance A decomposes in solution following the first order kinetics. Flask I contains 1L of 1 M solution of A and flask II contains 100 ml of 0.6 M solution. After 8 hr, the concentration of A in flask I becomes 0.25 M. What will be time for concentration of A in flask II to become 0.3 M?
(A) 0.4 hr
(B) 2.4 hr

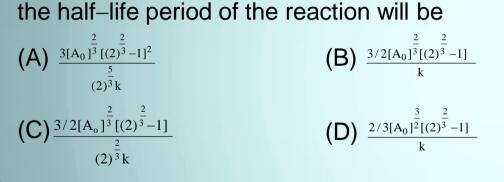
(C) 4 hr

(D) unpredictable as rate constant is not given

$$27. \quad \bigcirc \qquad \overset{N_2Cl \longrightarrow N_2Cl}{\longrightarrow} \overset{A}{\longrightarrow} \overset{N}{\longrightarrow} \overset{+Cl}{\longrightarrow}$$

Half life is independent of concentration of A. After 10 minutes volume of  $N_2$  gas is 10 L and after complete reaction 50 L. Hence rate constant is

- (A)  $\frac{2.303}{10} \log 5 \min^{-1}$  (B)  $\frac{2.303}{10} \log 1.25 \min^{-1}$ (C)  $\frac{2.303}{10} \log 2 \min^{-1}$  (D)  $\frac{2.303}{10} \log 4 \min^{-1}$
- 28. The rate of change of concentration of A for reaction A  $\longrightarrow$  product is given by  $-\frac{d[A]}{dt} = k [A]^{1/3}$



29.Select the correct statements out of I, II, III for zero order reaction.

- I: Quantity of the products formed is directly proportional to time
- II. : Larger the initial concentration of the reactant, greater the half life period..
- III.: If 50% reaction takes place in 100 minutes, 75% reaction take place in 150 minutes.
- (A)I only
- (C) II and III only

(B) I and II only (D) I, II and III 30. Rate constant of the zero order reaction can be expressed as
(A)min<sup>-1</sup> atm
(B) sec<sup>-1</sup> M
(C) hr<sup>-1</sup> lit<sup>-1</sup> mol
(D) all are correct

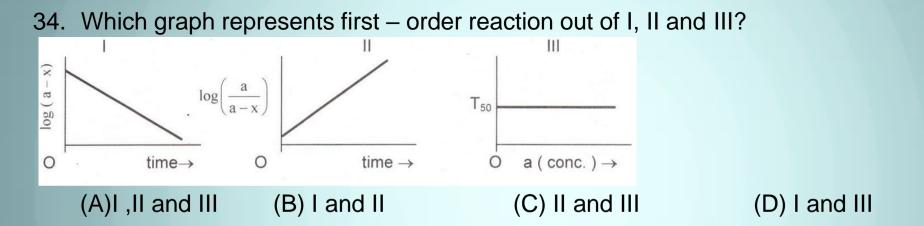
31. For the reaction A  $\rightarrow$  products,  $-\frac{d[A]}{dt} = k$  and at different time interval, [A] values are Time 5min 10min 15min 20 min [A] 20 mol 18 mol 16 mol 14 mol At 20 minute, rate will be:

(A)12 mol/min (B) 10 mol/min (C) 8 mol/min (D) 0.4 mol/min

32. If a is the initial concentration of the reactant and (a- x) is the concentration at time t for the first – order reaction (Rate constant k<sub>1</sub>). then which are correct.

I : 
$$x = a(1 - e^{k_{1}t})$$
  
II:  $(a - x) = a(\frac{1}{2})^{y}$  where  $y = \frac{t}{T_{50}}$   
III:  $K_{1} = \frac{2.303}{t} \log_{10}(\frac{a}{a - x})$   
(A)I,II (B) II,III (C) I,III (D) I,II,III

33.A reaction of first – order completed 90% in 90 minutes, hence, it is completed 50% in approximately:
(A) 50 minute
(B) 54 minute
(C) 27 minute
(D) 623 minute



 35.  $T_{50}$  (Half – life period) of first order reaction is 10 minutes . Starting with 10 mol L<sup>-1</sup> rate after 20 minute is:

 (A)0.0693 mol L<sup>-1</sup>
 (B)0.0693 × 2.5 mol L<sup>-1</sup> min<sup>-1</sup>

 (C)0.0693 × 5 mol L<sup>-2</sup> min<sup>-1</sup>
 (D)0.0693 × 10 mol L<sup>-1</sup> min<sup>-1</sup>

36. Half – lives of first – order and zero order reaction are same. Ratio of rates at the start of reaction is:

(D)  $\frac{2}{0.693}$ (A)0.693 (B) $\frac{1}{0.693}$  (C) 2 × 0.693 37. A  $\rightarrow$  products,  $\frac{dx}{dt} = k[A]^3$ . If a is the initial concentration and (a - x) is the concentration of after time t, then rate constant is given by Α (A)  $k = \frac{1}{t} \left| \frac{\Box 1}{(a-x)} - \frac{1}{a} \right|$  (B)  $k = \frac{1}{2t} \left| \frac{\Box 1}{(a-x)^2} - \frac{1}{a^2} \right|$  $(C)_{k=\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)}$  (D)  $k=\frac{x}{t}$ Half-life of a third –order reaction is 38. (A)  $T_{50} = \frac{0.696}{k}$  (B)  $T_{50} = \frac{1}{ka}$  (C)  $T_{50} = \frac{a}{2k}$  (D)  $T_{50} = \frac{1.5}{ka^2}$ 39. For a third-order reaction 2NO +  $O_{2\rightarrow}$  2NO<sub>2</sub> (A)  $+\frac{d[NO]}{dt} = k[NO]^2[O_2]$  (B)  $-\frac{d[NO]}{dt} = k[NO]^2[O_2]$ (C)  $-\frac{d[NO]}{2dt} = -\frac{d[O_2]}{dt} = +\frac{d[NO_2]}{2dt}$  (D) both (b) and (c) 40. For a reaction 2A + B  $\rightarrow$  products, rate law is,  $-\frac{d[A]}{dt} k[A]$ . At a time when t =  $\frac{1}{k}$  concentration of the reactant is: (C<sub>0</sub>=initial concentration) (A)  $\frac{C_0}{e}$  (B)  $C_0 e$  (C)  $\frac{C_0}{e^2}$  (D)  $\frac{1}{C}$ 41. Concentration of the reactant in first-order is reduced to  $\frac{1}{e^2}$  of its original value after 171

(natural life =  $\frac{1}{k}$ ) (A) one natural life-time (C) three natural life-time

(B) two natural life-time(D) four natural life-time

42. For a reaction, graph between log  $T_{50}$  (y-axis) and log a (x-axis) is a straight line parallel to x-axis. Hence, order is:

(A) 0 (B) 1 (C) 2 (D) 3 43. In a first order reaction the  $\frac{a}{a-x}$  was found to be 8 after 10 min. The rate constant is (A)  $\frac{(2.303 \times 3\log 2)}{10}$  (B)  $\frac{(2.303 \times 2\log 3)}{10}$ (C) 10 × 2.303 × 2 log 3 (D) 10 × 2.303 × 3 log 2

44.If a reaction with  $t_{1/2} = 69.3$  sec, has a rate constant  $10^{-2} \sec^{-1}$ , the order is (A) 0 (B) 1 (C) 2 (D) 3

45.The rate constant for a zero order reaction is 2×10<sup>-2</sup> molL<sup>-1</sup>sec<sup>-1</sup>. If the concentration of the reactant after 25 sec is 0.5 M, the initial concentration must have been
(A) 0.5 M
(B) 1.25 M
(C) 12.5 M
(D) 1.0 M

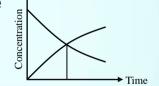
46. The rate of the first order reaction  $X \longrightarrow Products$  is  $7.5 \times 10^{-4}$  mol/L/s when the concentration of X is 0.5 mol/L. The rate constant is : (A)  $3.75 \times 10^{-4} \text{ s}^{-1}$  (B)  $2.5 \times 10^{-4} \text{ s}^{-1}$  (C)  $1.5 \times 10^{-3} \text{ s}^{-1}$  (D)  $3 \times 10^{4} \text{ s}^{-1}$ 

47. For the first order reaction the concentration of the reactants is reduced to 25% in one hour.
The half life period of the reaction is
(A) 2 hr
(B) 4 hr
(C) ½ hr
(D) ¼ hr

48.The accompanying figure depicts the species A and B for the reaction A  $\longrightarrow$  B, intersection of the twocurves represents (A) t<sub>1/2</sub>

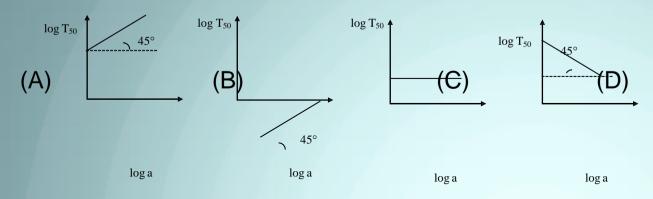
- (B) t<sub>3/4</sub>
- (C) t<sub>2/3</sub>
- (D) data insufficient to predict

### Methods to find order of reaction

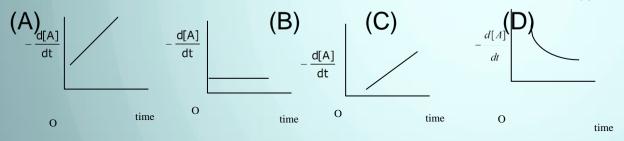


change in concentration of as a function of time the point of

49. For the reaction, of the first order, variation of log  $T_{50}$  with log a (where  $T_{50}$  is half life period and a is the initial concentration) is given by



50. Graph between concentration x of the product and time of the reaction A  $\longrightarrow$  B is straight line with +ve constant slope. Hence, graph between  $-\frac{d[A]}{dt}$  and time will be of the type



51. In the presence of acid, the initial concentration of cane sugar was reduced from 0.2 M to 0.1 M in5 hrs and 0.05 M in 10 hrs. The reaction must be of

(A) zero order (B) first order (C) second order (D) fractional order

52. In the decomposition of N<sub>2</sub>O<sub>5</sub>, the rate of reaction is  $-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$ .

For determination of the units of k,

- (A) units of time are required
- (B) units of concentration are required
- (C) units of both time and concentration are required

(D) none of these

53. For the reaction  $A + B \longrightarrow C + D$ , doubling the concentration of both the reactants increases the reaction rate by 8 time and doubling the initial concentration of only B simply doubles the reaction rate. The rate law for the reaction is

(A)  $r = k[A] [B]^2$  (B) r = k[A] [B] (C)  $r = k[A]^{1/2} [B] (D) r = k[A]^2 [B]$ 

54. Van't–Hoff's differential method is an important method to determine the order of reaction according to this equation, concentration C and rate of reaction  $\frac{dx}{dt}$  are related with order of reaction n as

(A) n= 
$$\frac{\log[(dx / dt)_2 / (dx / dt)_1]}{\log (C_1 / C_2)}$$

(B) n = 
$$\frac{\log[(dx / dt)_1 / (dx / dt)_2]}{C_1 C_2}$$

(C) 
$$n = \frac{\log[(dx/dt)_2/(dx/dt)_1]}{\log(C_2/C_1)}$$
 (D)  $n = \frac{\log[(dx/dt)_2/(dx/dt)_1]}{C_1-C_2}$ 

55. The inversion of cane sugar proceeds with half-life of 600 minute at pH = 5 for any concentration of sugar. However if pH = 6, the half life changes to 60 minute. The rate law expression for sugar inversion can be written as

(A)  $r = K[sugar]^{2}[H^{+}]^{0}$ (B)  $r = K[sugar]^{1}[H^{+}]^{1}$ (D)  $r = K[sugar]^{0}[H^{+}]^{1}$ 

56. If the reaction of aA + bB + cC → Products,
(i)if concentration of A is doubled, keeping concentration of B and C constant of the rate of reaction becomes doubled
(ii)if concentration of B is halved, concentration of A and C constant, the rate of reaction remains unaffected
(iii)if concentration of C is made 1.5 times, the rate of reaction becomes 2.25 times The order of reaction is
(A) 1
(B) 2.5
(C) 3
(D) 3.5

57.For the reaction, 2N<sub>2</sub>O<sub>5</sub>(g) → 4NO<sub>2</sub>(g) + O<sub>2</sub>(g) which of the following graph would yield a

straight line ( take first order ) (A)  $\log_{PNO} vs$  time with -ve slope
(B)  $\log_{PNO} vs$  time with +ve slope

(C) $(P_{N o})^{-}_{1}$ vs time	(D) log PNOVS time
2 5	2 5

58. Concentration of the reactant A in the reaction  $(A \rightarrow B)$  at different time are given below: Time / minutes [A]

	]	
0	0.069 M	
17	0.052 M	
34	0.035 M	
51	0.018 M	
Hence, order and rate	constant will be	
(A) zero, 0.001 M min	-1	(B) 1, 0.001 min <sup>-1</sup>
(C) 2, 0.001 M <sup>-1</sup> min <sup>-1</sup>		(D) 1, 0.01 min <sup>-1</sup>

59. For the reaction,  $A + B \rightarrow C$ 

	[A]	[B]	$-\frac{d[A]}{dt}$
1.	1.0 M	1.0 M	0.25 M min <sup>-1</sup>
2.	2.0 M	1.0 M	0.50 M min <sup>-1</sup>
3.	1.0 M	2.0 M	0.25 M min <sup>-1</sup>

Hence, rate law is:

(A) k[A][B]	(B) k[A][B] <sup>1/2</sup>	(C) k[A]	(D) k [B]
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- 60. For a first order reaction the plot of log  $[A]_t$  Vs t is linear with a
  - (A) positive slope and zero intercept
  - (B) positive slope and non zero intercept
  - (C) negative slope and zero intercept
  - (D) negative slope and non zero intercept

## **Concentration terms replaced by other terms in 1<sup>st</sup> orderkinetics**

- 61.At 373 K, a gaseous reaction A → 2B + C is found to be of first order. Starting with pure A, the total pressure at the end of 10 min was 176 mm and after a long time when A was completely dissociated, it was 270 mm. The pressure of A at the end of 10 minutes was
  (A) 94 mm
  (B) 47 mm
  (C) 43 mm
  (D) 90 mm
- 62. Acid hydrolysis of ester is first-order reaction and rate constant is given by  $K = \frac{2.303}{t} \log \frac{V_{\infty} V_0}{V_{\infty} V_t}$ where V<sub>0</sub>, V<sub>t</sub> and V<sub>∞</sub> are the volume of standard NaOH required to neutralize acid present at a given time, if ester is 50% neutralized then:

(A)  $V_{\infty} = V_t$  (B)  $(V_{\infty} = V_t - V_0)$  (C)  $V_{\infty} = 2V_t - V_o$  (D)  $V_{\infty} = 2V_t + V_0$ 

63. If no catalyst (H<sup>+</sup>) is present in acid hydrolysis of ester (in question abovequestion) then rate constant k is;

(A) 
$$\frac{2.303}{t} \log \frac{V_0}{(V_t - V_s)}$$
  
(B)  $\frac{2.303}{t} \log \frac{V_{\infty}}{(V_{\infty} - V)}$   
(C)  $\frac{2.303}{t} \log \frac{V_0}{V_t}$   
(D)  $\frac{2.303}{t} \log \frac{V_{\infty}}{(V_t - V_s)}$ 

64. Inversion of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) is first-order reaction and is studied by measuring angle of rotation at different interval of time.

 $\begin{array}{cccc} C_{12}H_{22}O_{11}+H_2O & \xrightarrow{\mu} C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{Sucrose} & \text{Glucose Fructose} \\ & d & l \\ \\ \text{If } (r_{\infty}\text{-}r_0) \equiv a \text{ and } (r_{\infty}\text{-}r_t) \equiv (a-x) \text{ (where } r_0, r_t \text{ and } r_{\infty} \text{ are the angle of rotation at the start, at the time t and at the end of the reaction respectively, then there is 50% inversion when;} \\ (A) r_0 = 2r_t \text{-} r_{\infty} & (B) r_0 = r_t \text{-} r_{\infty} & (C) r_0 = r_t \text{-} 2r_{\infty} & (D) r_0 = r_t + r_{\infty} \end{array}$ 

65. Table 1 (reactions) and table II (methods) have been matched.

Table I (Reaction)	Table II (method)
P: $A(g) \rightarrow B(g) + C(g)$	X: Titration method

Q:	RCOOR' + $H_2O \longrightarrow$	Y:	Pressure
	RCOOH + R'OH		measurement
R:			
	$N_2CI \rightarrow$	Z:	
	$Cl(l) + N_2(g)$		Volume
			measurement

Correct matching is:

	Ρ	QR			Ρ	Q	R	
(A)		Х	ΥZ		(B)	Y	Х	Ζ
(C)	Ζ	ΧY		(D)	Ζ	Y	Х	

66. For the reaction A(g)  $\rightarrow$  B(g) + C(g) rate law is  $-\frac{d(A)}{dt} = k[A]$ . At the start pressure is 100 mm and after 10 min, pressure is 120 mm, hence, rate constant (min<sup>-1</sup>) is : (A)  $\frac{2.303}{10}\log\frac{6}{5}$  (B)  $\frac{2.303}{10}\log5$  (C)  $\frac{2.303}{10}\log\frac{5}{4}$  (D)  $\frac{2.303}{10}\log\frac{5}{6}$ 

67. The reaction A(g) + 2B(g)  $\longrightarrow$  C(g) + D(g) is an elementary process. In an experiment, the initial partial pressure of A & B are P<sub>A</sub> = 0.60 and P<sub>B</sub> = 0.80 atm. When P<sub>C</sub> = 0.2 atm the rate of reaction relative to the initial rate is

(A) 1/48 (B) 1/24 (C) 9/16 (D) 1/6

68. A (g)  $\longrightarrow$  B (g) + C (g)  $-\frac{d[A]}{dt} = k[A]$ 

At the start pressure is 100 mm and after 10 min, pressure is 120 mm hence rate constant (min<sup>-1</sup>) is:

(A)  $\frac{2.303}{10} \log \frac{120}{100}$  (B)  $\frac{2.303}{10} \log \frac{100}{120}$ (C)  $\frac{2.303}{10} \log \frac{100}{80}$  (D)  $\frac{2.303}{10} \log \frac{100}{120}$ 

#### Some complex first order reaction

69. For the reaction, 
$$A + B \rightarrow C$$
  
of the products with time is  
(A) X  
(B) Y  
(C) Z  
(D) W + D. The variation of the concentration  
given by the curve

70. For the reaction A  $\xrightarrow{k} B \xrightarrow{k} C$ . If the reactions are of 1<sup>st</sup> order then d[B]/dt is equal to (A)  $-K_2[B]$  (B) + k[A]\_{k\_1} (C) K\_1[A] - K\_2[B] (D) K\_1[A] + K\_2[B] 71. For a reaction d[X]/dt is equal to  $\frac{1}{2}$ 

(A)  $K_1(a-x) - K_1(a-x)$ (B)  $K_2(a-x) - K_1(a-x)$ (C)  $K_1(a-x) + K_2(a-x)$ (D)  $-K_1(a-x) - K_2(a-x)$ 

72. A substance undergoes a first order decomposition. The decomposition follows two parallel first

order reaction's as  $k_1 = 1.26 \times 10^{-4}/\text{sec}$ A  $k_2$  C  $K_2 = 3.8 \times 10^{-4}/\text{sec}$ 

the percentage distribution of B and C are(A) 80% B, 20% C(B) 24.8 % B, 75.2% C(C) 92% B, 8% C(D) 68 % B, 32% C

73. For the complex Ag<sup>+</sup> + 2NH<sub>3</sub> $\rightleftharpoons$  [Ag (NH<sub>3</sub>)<sub>2</sub><sup>+</sup>]

 $\left(\frac{dx}{dt}\right) = 2 \times 10^7 L^2 \,mol^{-2} s^{-1} [Ag^+] [NH_3]^2 - 1 \times 10^{-2} S^{-1} [Ag(NH_3)^+]$ 

Hence, ratio of rate constants of the forward and backward reactions is: (A)2 × 10<sup>7</sup> L<sup>2</sup> mol<sup>-2</sup> (B) 2 × 10<sup>9</sup> L<sup>2</sup> mol<sup>-2</sup> (C)1 × 10<sup>-2</sup> L<sup>2</sup> mol<sup>-2</sup> (D)0.5 × 10<sup>-9</sup> L<sup>2-</sup> mol<sup>-7</sup> 74. For a reaction, net rate  $\left(\frac{dx}{dt}\right) = k[A]^{2}[B]^{2} - k'[C]$  then, select the correct statements:

- (a)  $-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt}$  is the relation among different rates.
- (b)  $2A+2B \sqcap c$  is the required reaction.
- (c) both are correct
- (d) none is correct

75. The reaction of ozone with oxygen atom in the presence of chlorine atoms can occur by the two- step process shown here with the rate constant for each step

 $O_3 + Cl \rightarrow O_2 + ClO$   $clO + O \rightarrow O_2 + Cl$   $k_1 = 5.2 \times 10^9 \text{ Lmol}^{-1} \text{s}^{-1}$  $k_2 = 2.6 \times 10^{10} \text{ Lmol}^{-1} \text{s}^{-1}$ 

Which of the values below is the closest to the rate constant of the overall net reaction, given by the equation?

 $O_3 + O \rightarrow 2O_2$ (A)5.2 × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>

(C) 3.1×10<sup>10</sup> L mol<sup>-1</sup> s<sup>-1</sup>

(B) 2.6 ×  $10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup> (D) 1.4 ×  $10^{20}$  L mol<sup>-1</sup> s<sup>-1</sup>

76. At a given temperature,  $k_1 = k_2$  for the reaction  $A + B \rightleftharpoons C + D$ . If  $\begin{bmatrix} dx \\ dt \end{bmatrix} = k_1 \begin{bmatrix} A \end{bmatrix} \begin{bmatrix} B \end{bmatrix} - k_2 \begin{bmatrix} C \end{bmatrix} \begin{bmatrix} D \end{bmatrix}$  In which set of the concentration, reaction ceases?

	[A]	[B]	[C]	[D]
(A)	0.1	0.2 M	0.3	0.4
	M		Μ	Μ
(B)	0.4	0.25	0.2M	0.5



	М	М		Μ
(C)	0.2	0.2 M	0.3	0.2
. ,	M		Μ	Μ
(D)	0.2	0.2 M	0.4M	0.2
	M			Μ

#### Effect of temperature on reaction rate

77. For an exothermic chemical process occurring in two step as

 $A + B \xrightarrow{\text{$ av } } X \xrightarrow{\text{$ ast } } AB$ 

The progress of the reaction can be best described by

(A) (B) (c) (d) all are correct A + B A +

78. Rate constant k =  $1.2x10^3 \text{ mol}^{-1} \text{ L s}^{-1}$  and  $\text{E}_a = 2.0x10^2 \text{ kJ mol}^{-1}$ . When T  $\longrightarrow \infty$ : (A) A =  $2.0x10^2 \text{ kJ mol}^{-1}$  (B) A =  $1.2x10^3 \text{ mol}^{-1} \text{ L s}^{-1}$  (C)  $A = 1.2x10^3 \text{ mol } L^{-1} \text{ s}^{-1}$  (D)  $A = 2.4x10^3 \text{ kJ mol}^{-1} \text{ s}^{-1}$ 

- 79. For a first order reaction, the plot of log k against 1/T of a straight line. The slope of the line is equal to
  - (A)  $-\frac{E_a}{R}$  (B)  $-\frac{2.303}{E_a R}$  (C)  $-\frac{E_a}{2.303}$  (D)  $-\frac{E_a}{2.303 R}$
- 80. If the reaction, rate at a given temperature becomes slower, that means
  - (A) the energy of activation is higher
  - (B) the energy of activation is lower
  - (C) the entropy changes
  - (D) the initial concentration of the reactants remains constant
- 81.The chemical reactions in which reactants require high amount of activation energy are generally
  - (A) slow (B) fast (C) instantaneous (D) spontaneous
- 82. The rate constant increases with increasing temperature.
  - (A) as it is given by Arrhenius equation
  - (B) the average energy of the products increases
  - (C) Both A and B



### (D) None

83. Which one of the following statements is incorrect?

(A)The temperature coefficient of a reaction is the ratio of the rate constant at any two temperatures.

(B)The temperature coefficient of a reaction is the ratio of the rate constant at 298 K and 308 K.

(C) The temperature coefficient of most of the reactions lies between 2 and 3.

(D) In an endothermic reaction, activation energy of reactants is more than that of the products

84. Rate constant k varies with temperature as given by equation log k (min<sup>-1</sup>) =  $5 - \frac{2000K}{T}$  Consider following about this equation, I: pre-exponential factor is  $10^5$  II: E<sub>a</sub> is 9.212 kcal III: variation of log k with 1/T is linear.

Select correct statement

(A) I, II, III (B) I, III (C) II, III (D) I, II

85. The activation energy of exothermic reaction  $A \longrightarrow B$  is 80 kJ. The heat of reaction is 200 kJ. The activation energy for the reaction  $B \longrightarrow A$  will be: (A) 60 kJ (B) 120 kJ (C) 280 kJ (D) 200 kJ 86.The activation energy for the forward reaction,  $X \longrightarrow Y$ , is 60 kJ/mol and  $\Delta H$  is -20 kJ/mol, the activation energy for the reverse reaction is :

(A) 40 kJ/mol (B) 60 kJ/mol (C) 80 kJ/mol (D) 20 kJ/mol

87.If a reaction A + B → C is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy of 70 kJ/mol, the activation energy for the reverse reaction is
(A) 30 kJ/mol
(B) 40 kJ/mol
(C) 70 kJ/mol
(D) 100 kJ/mol

88.  $A \longrightarrow B$ ,  $\Delta H = -10 \text{ kJ/mol}$ ,  $E_a = 50 \text{ kJ/mol}$  then  $E_a$  of  $B \longrightarrow A$  will be (A) 40 kJ/mol (B) 50 kJ/mol (C) -50 kJ/mol (D) 60 kJ/mol

89.An endothermic reaction, A → B has an activation energy as x kJ/mol, and enthalpy change is +y then the activation energy of the reverse reaction is :

(A) -x (B) x-y (C) x + y (D) y-x

90. Milk turns sour at 40°C three time as faster as 0°C. Hence, E<sub>a</sub>in cal of turning of milk sour is

(A) 
$$\frac{2.303 \times 2 \times 313 \times 273}{40} \log 3$$
 (B)  $\frac{2.303 \times 2 \times 313 \times 273}{40} \log \frac{1}{3}$   
(C)  $\frac{2.303 \times 2 \times 40}{273 \times 313} \log 3$  (D) None of these.

- 91. Graph between log k and 1/T (k is rate constant in s<sup>-1</sup> and T is the temperature in K) is a straight line. If OX=5 and slope of the line =  $-\frac{1}{2000 \text{K}}$  then E<sub>a</sub> is: (B)  $\frac{1}{2.303}$  cal (D) none of the<sup>T</sup>
  - (A) 2.303 × 2 cal
  - (C) 2 cal

## Mechenism of the reaction

92. The reaction of hydrogen and iodine monochloride is represented by the equation:

 $H_2(g) + 2ICI(g) \rightarrow 2HCI(g) + I_2(g)$ 

This reaction is first - order in  $H_2(g)$  and also first - order in ICI(g) Which of these proposed mechanism can be consistent with the given information about this reaction?

Mechanism I:  $H_2 + 2ICI \rightarrow 2HCI + I_2$ Mechanism II:  $H_2(g) + ICI(g) \underline{slow} HCI(G) + HI(g)$  $HI(g) + ICI(g) = Fast HCI(g) + I_2(g)$ (A) I only (B) II only (C) both I and II (D) neither I nor II

93.Consider the hypothetical reaction  $A + 2B \rightarrow AB_2$  It follows rate law, rate=k[A][B] Hence, rate determining step is:

(A)  $A + B \rightarrow AB$  (B)  $A + 2B \rightarrow AB_2$  (C)  $AB + B \rightarrow AB_2$  (D)  $AB + A \rightarrow A_2 + B$ 

94. A two step mechanism has been suggested for the reaction of nitric oxide and bromine:  $NO(g) + Br_2(g) | \square NOBr_2(g)$   $NO Br_2(g) + NO(g) \longrightarrow 2NOBr(g)$ Observed rate law is, rate = k[NO]<sup>2</sup>[Br<sub>2</sub>] Hence, rate determining step is: (A) NO(g) + Br<sub>2</sub>(g)  $\rightarrow$  NOBr<sub>2</sub>(g) (B) NO Br<sub>2</sub>(g) + NO (g)  $\rightarrow$ 2NOBr(g) (C) 2NO(g) + Br<sub>2</sub>(g)  $\rightarrow$  2NOBr(g) (D) None of these

Reaction progress  $\rightarrow$ 

otential energy

95. A reaction takes place by the fol  $A + BC \rightarrow AC + B$ 

 $AC + D \rightarrow A + CD$ 

The potential energy profile for this is shown below: Transition states are shown by:

(A) I, V (B) II, IV (C) II, III, IV (D) III only

96. Slow step (rate-determining step) involves going into a transition state (in above question). It is:

 $(A) A + BC \rightarrow AC + B \qquad (B) AC + D \rightarrow A + CD$ 

(C)  $AC + B \rightarrow BC + A$  (D)  $B + AD \rightarrow BD + A$ 

97. In the presence of catalyst, E<sub>a</sub> is lowered by 2Kcal at 27°C. Hence rate will be (A) 20 times
(B) 14 times
(C) 28 times
(D) 2 times

98.For the reaction  $2A+B \longrightarrow D + E$  the following mechanism has been proposed: A + B $\longrightarrow$ C+D(slow) A+C $\longrightarrow$ E(fast) The rate law expression for the reaction is (A) Rate = k[A]<sup>2</sup>[B] (B) Rate = k[A] [B] (C) Rate = k[A][C] (D) Rate = k[A]<sup>2</sup>[B][C]

99. The chemical reaction,  $2O_3 \rightarrow 3O_2$  proceeds as follows:  $O_3 \rightarrow O_2 + O_{\ldots}(\text{fast}) \qquad O + O_3 \rightarrow 2O_2 \dots (\text{slow})$ The rate law expression should be  $(A) r = k[O_3]^2 \qquad (B) r = k[O_3]^2[O_2]^{-1} \qquad (C) r = k[O_3][O_2] \qquad (D)$  unpredictable

100.In the sequence reaction,  $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$ ,  $k_3 > k_2 > k_1$ , then the rate determining step of the reaction is (A)  $A \longrightarrow B$  (B)  $B \longrightarrow C$  (C)  $C \longrightarrow D$  (D)  $A \longrightarrow D$ 

101. A reaction  $X_2 + Y_2 \rightarrow 2XY$  occurs by the following mechanism

 $\begin{array}{cccc} X_2 &\longrightarrow X + X \dots (slow) & X + Y_2 \longrightarrow XY + X \dots (fast) X + Y \longrightarrow XY \dots (fast) \\ \mbox{Its order would be} \\ (A) 3/2 & (B) 1 & (C) zero & (D) 2 \end{array}$ 

	17. D	35. B	53. D	71.D	89.B
1. B	18. A	36. C	54.C	72.B	90. A
1. B 2. A	19. A	37. B	55.B	73.B	91.C
2. A 3. B	20. C	38. D	56.C	74.B	92.B
з. В 4. С	21. B	39. D	57.A	75.A	93. A
4. C 5. C	22. B	40. A	58.A	76.B	94. B
6. A	23. C	41. B	59.C	77.B	95.B
7. A	24. C	42. B	60. D	78.B	96. A
8. A	25. B	43. A	61.B	79. D	97.C
9. C	26. C	44. B	62.C	80. A	98.B
10. D	27. B	45. D	63.B	81.A	99. B
11. A	28. C	46. C	64. A	82. A	100.A
12. B	29. D	47. C	65. B	83. A	101.B
13. D	30. D	48. A	66. C	84. A	
14. B	31. D	49. C	67. D	85. C	
15. B	32. D	50. B	68.C	86. C	
16. A	33. C	51. B	69.B	87. D	
	34. A	52. A	70.C	88. D	