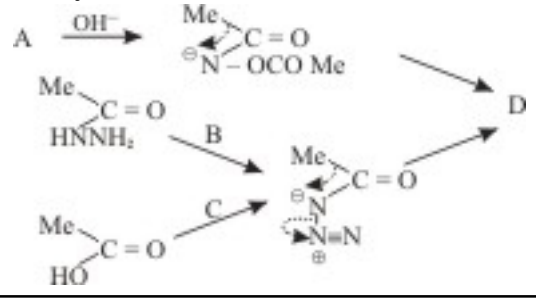
Passage (A)

A typical example of Hoffmann reaction is the conversion of an amide to an amine containing one carbon atom less, by the action of alkaline hypobromite. A salient intermediate in this reaction is the isocyanate, corresponding closely to the ketene intermediate in Wolff reaction, this too then undergoes addition of water, but the resultant carbamic acid is unstable and decarboxylates readily to yield the amine. Crossover experiments lead to no mixed products, that is, the rearrangement is strictly intramolecular, and it is further found that when R is chiral it migrates with its configuration unchanged. There is a grouop of reactions very closely related to that of Hoffmann, all of which involve the formation of an isocyante by rearrangement ofan intermediate like one on Hoffmann reaction. The Lossen reaction involves the action of base on o-acyl derivatives of hydroxamic acids and involves RCO_2^- as the leaving group. The curtius and Schimdt reactions both involve N_2 as the leaving group from the azide intermediate, and here again themigration of R occurs in a concerted process. The azide may be obtained either by nitrosation of an acid hydrazide - Curtius Reaction - or by reaction of hydrazoic acid HN_3, on a carboxylic acid - the Schimdt reaction.

1. Which reactants, intermediates, leaving group characterises a Schmidt reaction ?
   (a) acid hydrazide, isocyanate, N_2
   (b) acyl derivative of hydroxamic acid, azide, N_2
   (c) amide, isocyanate, HCO_3^-
   (d) acid, isocyanate, N_2
2. Hoffmann rearrangement is strictly
   (a) intramolecular (b) intermolecular
   (c) depends on reaction conditions
   (d) about getting mixed products with changing stereochemistry
3. When an acid hydrazide undergoes nitrosation to yield an azide which further gets hydrolysed to give an amine, the stereochemistry of the substituent group.
   (a) remains unaffected (b) gets inverted
   (c) changes if reaction is happening in an acidic medium
   (d) changes if reaction is happening in a basic medium
4. The leaving group in Lossen reaction is
   (a) N_2 (b) RCO_2^- (c) Br^- (d) none
5. Identify A, B, C, D in the reaction mechanisms below



(a) acylhydroxamic acid, sodium nitrite and hydrochloric acid, hydrazoic acid and methyl isocyanate
(b) acyl hydrazine, N_2, hydrazoic acid and methyl azide
(c) acylhydroxamic acid, sodium nitrite and hydrochloric acid, hydrazoic acid and methyl cyanate
(d) acyl hydrazide, N_2, hydrazoic acid and hydrazine

Passage (B)

When examining the temperature effects on the rates of reactions. Arrhenius concluded that they were much too large to be attributed to factors such as the temperature increases in the energy of collision of the molecules, or in the decrease in the viscosity of molecules which had the potential to react and those which actually do react.

$$k = A \exp(-Ea/RT) \quad \ldots\ldots (1)$$

where Ea is called the activation energy (which is not a term that was used by Arrhenius), and A is called the frequency factor; or together they are called the Arrhenius parameters. It is often said that the exponential term in (1) can be interpreted as the fraction of molecules with energy greater than Ea. The basis for this is that the population of energy levels is given by the Boltzmann distribution function.

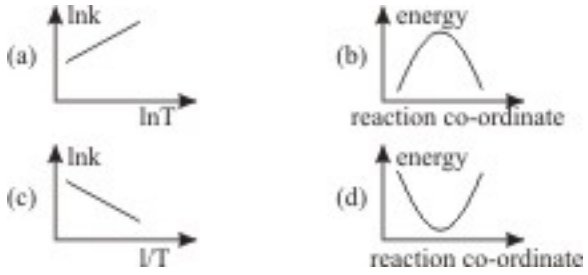
$$P(E) = N\, g(E) \exp(-E/RT) \quad \ldots\ldots (2)$$

where g (E) is a degeneracy factor for the number of states with energies E, and N is chosen so that the total population is unity. The fraction with energy greater than Ea is obtained by integrating this from Ea to infinity, and this would be equal to the Arrhenius exponential if g (E) was unity. However, this is not true even for collision energies, so this simple interpretation of the term is incorrect. A full understanding of the significance of Ea to some time to emerge. There were a number of suggestions that reactions required the formation of intermediate species, but although this is true for certain reactions, there was no evidence for its generality. Marcelin was the first to advance our understanding when he said that molecules in their average state as regards their internal energy were not capable of reacting, and they only became reactive when their internal energy rose above a critical value. Lewis later called the differences between the energy of the average state and the critical state the 'critical increment' and he identified this with Ea. Rice was following a similar line of argument.

Tolman in an important paper dealing with the statistical mechanics of chemical reactions, showed that the activation energy could be equated to the difference between the average energy of reacting molecules and the average energy of all molecules. It is worth emphasising that if a reaction is studied over a short temperature range, then the results can often be fitted by other temperature laws, a straight line relationship between lnk and lnT can, for example, almost always be achieved. The Arrhenius equation is widely accepted because its interpretation leads to the important concept of the barrier to reaction, and the theories which follow from this, rather than because of its superior fit to the data.

6. Based on theabove passage, what is/are the reason/s for increased rate of reaction with increased temperature
(i) Increased kinetic energy of molecules leading to increased collisions among reactant molecules.
(ii) Increased temperature leads to decrease in the viscosity of solutions
(iii) Increased temperature overcomes the critical difference between the average energy of reacting molecules and the average energy of all molecules
(iv) Certain reactions require formation of an intermediate species
(a) all of these (b) none of these
(c) (iii) and (iv) (d) (i) and (ii)

7. Which of the following graphs represent effect of temperature on rate of reaction



(a) (i) and (ii) (b) (ii) and (iii)
(c) (iii) and (iv) (d) none of these

8. What is the unit for frequency factor for first order reaction?
(a) second (b) $second^{-1}$
(c) $mole\ second^{-1}$ (d) none of these

9. What is the most unique contribution of Arrhenius to the study of impact of increased temperature on rate of reaction
(a) finding frequency of collisions among reactant molecules
(b) finding intermediates in reactions
(c) finding difference between the average energy of reacting molecules and theaverage energy of all molecules
(d) finding that different molecules have different amount of energy in a reaction medium

10. Besides energy higher than threshold energy, activation energy barrier can be surpassed through
(a) tunneling (b) caving
(c) can't surpass (d) none of these

Passage (C)

Reversal of the expected (inductive) order of electron donation to $CH_3 > MeCH_2 > Me_2CH > Me_3C$ could be explained on the basis of hyperconjugationn being dependent on the presence of hydrogen on the carbon atoms α- to the unsaturated system. This is clearly at a maximum with CH_3 and non-existent with Me_3C,
$H_3C-CH=CH_2 > MeCH_2-CH=CH_2 > Me_2C-CH=CH_2 > Me_3C-CH=CH_2$
Hence the increased electron donation ability of CH3 groups under these conditions. Hyperconjugation could, however, involve C – C as well as C – H bonds, and the differences in relative reactivity observed in a series of compounds may actually result from the operation of solvent, as well as hyperconjugative, effects. Hyperconjugation has also been invoked to account for the greater thermodynamic stability of alkenes in which the double bond is not terminal.

11. Which of the alkenes is most stable ?
(a) $Me_3C-CH=CH_2$ (b) $MeCH_2-CH=CH_2$
(c) $Me_2CH=CH_2$ (d) $Me_3C-CH=CH_2$

12. Which of these isomeric alkenes is most stable
(a) $Me_2C=CH-Me$ (b) $MeCH_2-CMe=CH_2$
(c) both have similar stability
(d) $CH_2=CH-CH<^{Me}_{Me}$

13. The electron release by alkyl groups due to inductive effect follows following order
(a) Me > $CH(Me)_2$ – > CMe_3 –
(b) $CH(Me)_2$ – > Me > CMe_3 –
(c) CMe_3 – > $CH(Me)_2$ – > Me
(d) none of these

14. What causes reversal of electron donating capacity of alkyl groups when attached to a C participating in a double bond
(a) hyperconjugation (b) delocalisation
(c) conjugation (d) all of these

15. $C_6H_5CH_2$ – group will be an
(a) electron donor (b) electron withdrawing group
(c) neither of 1 and 2 (d) both of 1 and 2

Passage (D)

Let us look at the processes taking place when we exert ourselves, and how the limitations of those processes restrict our exertions. We might think of the exercising person as a system, a vessel in which chemical reactions take place. Let us consider a number of processes that occur. Oxygen we take from the air during respiration reacts with carbohydrates, fats and proteins, fats and proteins in the body to produce carbon dioxide gas, urea, water and energy. The energy appears as work - the exercise itself - and as heat generated in the system. The sweat passing through the membrane of the skin contains salts from the body and deposits them on the surface of the skin. Heat buildup is controlled by evaporation of water from the surface of the skin and by the expiration of water vapour through breathing. The Everest mountaineer needs fuel and oxygen to operate. He needs to eat. He needs food as fuel, food to provide sugars, fats and proteins for conversion to energy, water, carbon dioxide and urea. The oxygen available near 5,000 meters above sea level is approximately one-half that found at sea level. The limited supply of oxygen slows the chemical reactions that produce energy. In addition, the climber's inability to eat reduces the amount of fuel available. He is losing weight quickly as he begins to convert tissue into energy and the chemical byproducts of metabolism. We will learn that teh chemical reaction rate depends upon the concentration of the reactants. And if either food or oxygen is in short supply, the processes that produce energy for work slow down. They are working hard. Their body chemistry converts the carbohydrates and fats and proteins to energy and heat and water, carbon dioxide and urea. Lots of energy, lots of heat, plenty of water.

As they breathe, the water and carbon dioxide they exhale helps to cool them. With every breath the athlete depletes the water in the body. Their exhalations contain water vapor in equilibrium with their body temperature. They exhale not just the water produced with the energy, but the normal balance of fluid in our living system. This process is called dehydration.Sweat drips from their skin. In the hot and humid environment, little of the perspiration evaporates so little cooling occurs. The athlete begins to heat up. This is called hyperthermia. The fluids in our bodies: in cells, in the vascular system and in the extracellular spaces, are solutions containing salts. Water and small molecules like salts can pass through semipermeable membranes such as the skin. Larger molecules and structures such as proteins and blood cells cannot pass through the skin. These membrane properties of the skin cause another difficulty for our football players. As they perspire, the water carries some salt away, but the water depletion far outstrips the transfer of salt through the skin. At its extreme, depletion of the body's water in the extracellular plasma causes radical changes. As the water concentration of the plasma drops, a difference in salt concentration between the extracellular fluid and the body's cells is established. By the process called osmosis, this difference in concentration causes water to flow from the cells into the fluid in an attempt to equalize the salt concentration between fluid and cells. The blood cells will shrink, the volumke of blood decreases, blood pressure drops. In extreme cases, the combination of low blood pressure and low blood volume leads to catastrophic heat stroke.

16. Heat stroke is a combination of low blood pressure and low blood volume caused due to
(i) Excessive loss of water from extracellular fluids
(ii) Fasting for long periods
(iii) Cells, eg. blood cells losing water by osmosis to maintain salt water balance in extra cellular fluids
(iv) Lack of exercise
(a) (i) and (iii) (b) (ii) and (iv)
(c) (iii) and (iv) (d) (i) and (iv)

17. After a workout in gymnasium body heats up. This condition is termed as
(a) heat stroke (b) hypothermia
(c) hyperthermia (d) dehydration

18. What remedy can you suggest for an athelete to deal with dehydration and exhaustion immediately after a race
(a) orange juice (b) a glass of sweet milk
(c) sugarcane juice
(d) plenty of water with a pinch of salt and sugar

19. At mt. Everest, a mountaineer faces following problems
(i) Hyperthermia (ii) Slow body reaction
(iii) Heat stroke (iv) Loss of body weight
(a) (i) and (iv) (b) (i) and (iii)
(c) (ii) and (iii) (d) (ii) and (iv)

20. Semipermeability means
(a) someparticles can pass through the membrane while other can not
(b) only solvent particles can pass through the membrane
(c) only solute particles can pass through the membrane
(d) none of these

Passage (E)

In general, a reduction may be represented as
Oxidation form + ne^- = reduced form ..... (1)
The corresponding Nernst equation is

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(\text{reduced form})/C^\circ}{(\text{oxidised form})/C^\circ}$$

Thus, if the activity of the oxidised form is lowered by some means keeping the activity of the reduced form unchanged, a decrease in the reduction potential will be observed. On the other hand, if the activity of the reduced form is lowered, an increase in the reduction potential will be observed. The number of electrons *n* involved in equation (1) can be determined by plotting a graph between E and In (reduced form/oxidation form). Knowing the slope and temperature T, the value of *n* can be determined. Substance which forms the soluble complex (or precipitate) with the oxidised member of the couple will decrease the effective concentration of the oxidised form. Thus, a metal which otherwise behaves as a noble metal may be converted into an active metal by lowering its reduction potential by some means. Hence whether a metal is a noble metal or an active metal, it all depends upon its environments. In an analogous way, if the activity of the reduced form of the couple is lowered, the potential of the electrode is increased. If the reduced form is a metal, the most useful method of lowering its activity is to form an alloy of the metal with another metal.

21. The graph between E and In (reduced form)/(oxidised form) will be
(a) a straight line passing through origin
(b) a straight line having slope – RT/nF
(c) a parabola with focus at E°
(d) none of these

22. If a substrate which forms soluble complex with oxidised member of the couple, then the reduction potential of the system
(a) does not change (b) is lowered
(c) is increased
(d) first it is lowered then it is increased

23. Silver in the presence I^-, S^{2-} or CN^- ions, becomes
(a) noble metal (b) active metal
(c) deactive metal (d) none of these

24. In amalgam electrodes, mercury is used to
(a) lower the activity of metal
(b) increase the activity of metal
(c) lower the reduction potential
(d) none of these

25. A cell consists of a Pt electrode immersed in the redox system $Ax^+ = A^{(x+n)} + ne^-$ is combined with a saturated calomel electrode (right side electrode). From the following data at 303 K-

Percent of reduced form	24.4	48.8	73.2	84.5
Emf/V	0.101	0.116	0.129	0.139

Find out value of *n*.
(a) 1 (b) 2 (c) 3 (d) none

Passage (F)

There are number of liquids that are considerably more acidic, by as much as $10^6 - 10^{10}$ times, than concentrated aqueous solutions of so-called very strong acids, such as nitric and sulfuric acids. These are called superacids, and in recent years a great deal of new chemistry has been found to occur in these media. Superacid systems are necessarily nonaqueous, since the acidity of any aqueous system is limited by the fact that the strongest acid that can exist in the presence of water is H_3O^+. Any stronger acid simply transfer its protons to H_2O to form H_3O^+. To measure superacidity it is necessary to define a scale that goes beyond the normal pH scale and is defined in terms of an experimental measurement. The usual one is the Hammett acidity function H_0, defined as follows.

$$H_0 = pK_{BH^+} - \log\frac{[BH^+]}{[B]}$$

where B is an indicator base, BH+ is its protonated form, and pK_{BH^+} is $-\log K$ for dissociation of BH^+. The ratio $[BH^+]/[B]$ can be measured spectrophotometrically.

26. Consider the following statements
(i) The H_0 scale becomes identical to the pH scale in dilute aqueous solutions.
(ii) Superacids can have negative values of H_0
Which of the above statements is/are correct ?
(a) only (i) (b) only (ii)
(c) (i) and (ii) (d) none of these

27. If SO_3 is added to pure very concentrated solution of H_2SO_4 ($H_0 = 12$), the value of H_0 can be
(a) -15 (b) -12 (c) -8 (d) none

28. If SbF_5 is added to hydrofluoric acid Hf having H_0 of about -11, its acidity
(a) increases (b) decreases
(c) does not change (d) cannot be determined

29. For the species I_2^+, Se_4^{2+}, S_8^{2+} and so on, superacids are
(a) good solvents (b) bad solvents
(c) alkaline solvents (d) none of these

30. $(CH_3)_3COH$ in presence of super acids will produce
(a) free radicals (b) carbon ions
(c) carbonium ions (d) none of these

Question No. 31 to 60 are multiple choice question s. Choose the correct altern ative in each:

31. The compound insoluble in acetic acid is
(a) calcium oxalate (b) calcium oxide
(c) calcium hydroxide (d) calcium carbonate

32. The reaction of $R-\overset{\overset{O}{\|}}{C}-NH_2$ with a mixture of Br_2 and KOH gives RNH_2 as a product. The intermediates involved in this reaction are

33. A mixture of 1°, 2° and 3° amines can be distinguished by using
(a) $C_6H_5SO_2Cl$ (b) $P-CH_3-C_6H_4-SO_2Cl$
(c) $\begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix}$ (d) all of these

34. Gabriel phthalmide synthesis is not used for the preparation of
(a) 1°-amine (b) aniline
(c) α-aminoacid (d) none of these

35. The product D in the following sequence of reactions is

$$CH_3-CH_2COCl \xrightarrow{NH_3} A \xrightarrow{\Delta} B \xrightarrow{P_2O_5} C \xrightarrow{Na-C_2H_5OH} D$$

(a) ester (b) amine
(c) acid (d) alcohol

36. Acetaldehyde on treating with SO_2 undergoes
(a) cyclic trimerization (b) cyclic tetramerization
(c) polymerization (d) methylsulphonic acid

37. Diethylether combines with CO under specific conditions to form
(a) ethyle thanoate (b) acetic acid
(c) ethyl propionate (d) acetone

38. When wine is put in air, it becomes sour due to
(a) oxidation of C_2H_5OH (b) reduction of C_2H_5OH
(c) formation of CH_3CH (d) dissolution of CO_2

39. On treating chloroform with antimonytrifluoride and hydrofluoric acid followed by heating around 800° C we get
(a) CHF_2Cl_2 (b) $CF_2 = CF_2$
(c) $(-CF_2-CF_2-)_n$ (d) CCl_2F_2

40. A hydrocarbon (A) having molecular formula C_8H_6 gives white ppt. with tollen's reagent. A on hydration gives a product which is also obtained on acylation of benzene in the presence of anhydrous $AlCl_3$

(a) $C_6H_5C\equiv C-H$ (b)

(c) (d) none of these

41. For the reaction $2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)$, $Kc = 1.8 \times 10^{-6}$ at 185° C, the value of Kc for the reaction. $NO\,(g) + \frac{1}{2}\,O_2 \rightleftharpoons NO$ is
(a) 0.9×10^6 (b) 7.5×10^2
(c) 1.95×10^{-3} (d) 1.95×10^3

42. The rate law for the reaction:
$RCl + NaOH\,(aq.) \longrightarrow ROH + NaCl$ is given by, Rate = k[RCl]. The rate of reaction will be
(a) unaffected by increasing temperature of the reaction
(b) doubled on doubling the concentration of NaOH
(c) halved on reducing the concentration of NaOH to one half
(d) halved on reducing the concentration of RCl to one half

43. Which of the following statements is correct for the reaction $CO\,(g) + \frac{1}{2}\,O_2\,(g) \rightleftharpoons CO_2\,(g)$ at constant temperature and pressure
(a) $\Delta H = \Delta E$ (b) $\Delta H < \Delta E$
(c) $\Delta H > \Delta E$
(d) ΔH is independent of physical state

44. The unit of cell cube length for LiCl (NaCl structure) is 5.14Å. Assuming anion-anion contact the ionic radius for chloride ion will be
(a) 18.1 Å (b) 1.81 Å
(c) 6.03 Å (d) 0.603 Å

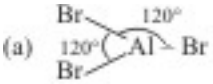
45. Molarity of water in pure water (ρ = 1 g/ml) is
(a) 55.5 M (b) 5.55 M
(c) 18 M (d) 60.60 M

46. Acetamide reacts with NaOBr in alkaline medium to form
(a) NH_3 (b) $CH_3 - CN$
(c) CH_3NH_2 (d) $CH_3 - CH_2 - NH_2$

47. A 0.01 M solution of acetic acid is 5% ionized at 25° C. Its dissociation constant is
(a) 2.63×10^{-5} (b) 1.98×10^{-4}
(c) 3.03×10^{-5} (d) 2.69×10^{-4}

48. The angular momentum of an electron in a Bohr orbit is given as
(a) $L = \frac{n\,h}{2\pi}$ (b) $L = \sqrt{l(1+1)}\ \frac{n}{2A}$
(c) $L = \frac{mh}{2\pi}$ (d) $\frac{n}{4A}$

49. Shape of $XeOF_4$ is
(a) tetrahedral (b) square pyramidal
(c) trigonal pyramidal (d) v shape

50. The structure of aluminium bromide is best represented as
(a) 
(b) $[AlBr_2]^+ [AlBr_4]^-$
(c) 
(d) 

51. The IUPAC name of $[Pt(Cl)(H)(Et_3P)_2]$
(a) platinum chlorohydrotriethyl phosphine
(b) hydrochloro triethyl phosphino platinum
(c) chloro hydrido bis triethylphosphine platinum (II)
(d) none of these

52. Which of the following have identical bond order
(1) CN^- (2) O_2^- (3) NO^+ (4) CN^+
(a) 1, 2, 4 (b) 1, 3, 4
(c) 1, 3 (d) 2, 3, 4

53. Which of the following is formed when propyne reacts with chlorine water
(a) 1-chloral and formic acid (b) 1,1-di chloro ethanal
(c) chloral and formic acid (d) 1,1-dichloro propanone

54. Benzophenone oxime on Beckmann rearrangement gives
(a) $C_6H_5NHCOC_6H_5$ (b) $C_6H_5NHCOCH_3$
(c) $C_6H_5COCH_3$ (d) none of these

55. The bond order of $(He_2)^+$ is
(a) 1 (b) 0.5 (c) 1.5 (d) 0.75

In each question (35 – 40) given below, a statement is given, which may be correct or wrong. For each statement, an explanation is given which may or may not be correct. Choose the correct answer from the codes A, B, C, D and E.

Code	***First Statement***	***Second statement***	***Explanation***
A	True	True	E is correct explanation of statement
B	True	True	E is not correct explanation of S
C	True	True	
D	False	True	
E	False	False	

56. Statement : The silver chloride goes into solution in aq. ammonia.
Explanation : The aqueous ammonia increase thesolubility product of silver chloride

57. Statement : A mixture of sodium acetate and sodium propionate forms a buffer solution
Explanation : Buffer solution reacts with added small quantities of hydrogen ions or hydroxyl ions, leaving the pH almost unchanged.

58. Statement : When a tire is pumped (assuming air to be ideal), the temperature would not rise.
Explanation : In an ideal gas, there are no intermolecular interactions.

59. Statement : The following reaction is possible to carryout
$Na_2(s) + Mg(s) = MgO(s) + 2\,Na(g)$
Explanation : E° data shown that sodium is a more powerful reducing agent than magnesium.

60. Statement : Almost all naturally occuring iron on earth exists as Fe(III) whereas that which has been found on the moon is exclusively Fe (II)
Explanation : The atmosphere of the earth is oxidising. The moon has no atmosphere.