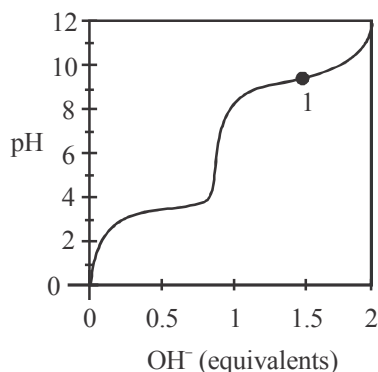


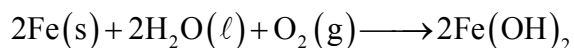
## TIFR-2011 CHEMISTRY

1. The following curve is obtained when a solution of glycine hydrochloride ( $\text{HOOC}-\text{CH}_2-\text{NH}_4^+\text{Cl}^-$ ) is titrated with a strong base. What are the predominant species present at point 1 shown on the curve?



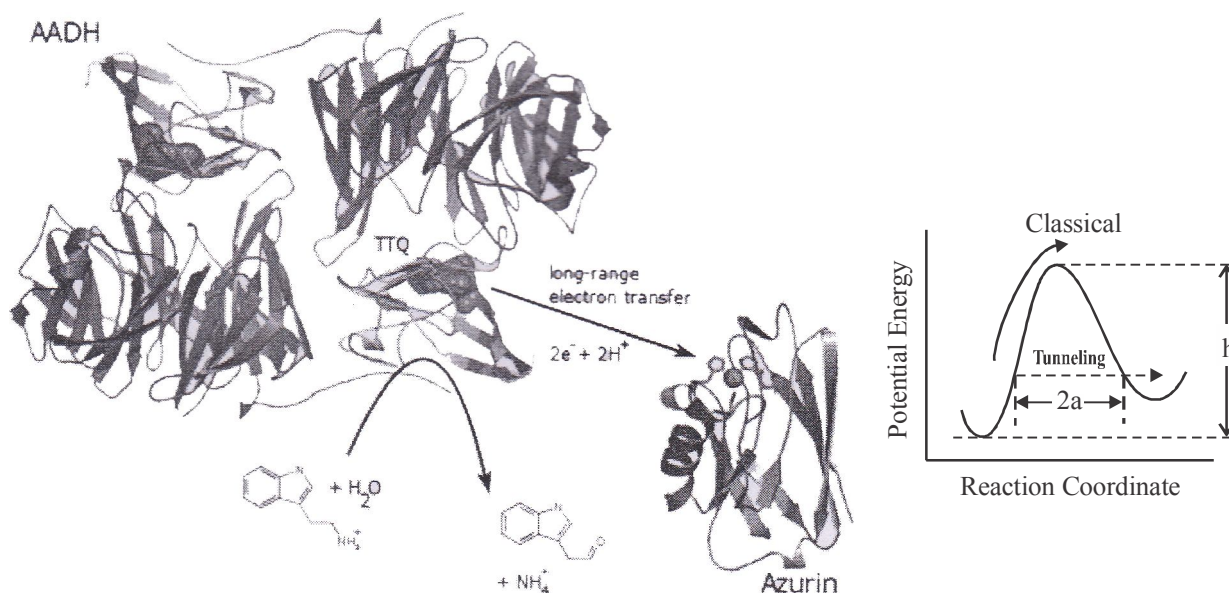
- (a)  $\text{H}_3\text{N}^+-\text{CH}_2-\text{COO}^-$  and  $\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-$   
 (b)  $\text{H}_3\text{N}^+-\text{CH}_2-\text{COO}^-$   
 (c)  $\text{H}_3\text{N}^+-\text{CH}_2-\text{COOH}$  and  $\text{H}_3\text{N}^+-\text{CH}_2-\text{COO}^-$   
 (d)  $\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-$
2. If the following probabilities were arranged in ascending order, which one would come third?  
 (a) The probability that a fair die will produce an even number  
 (b) A random digit from 1 to 9 (inclusive) is chosen, with all digits being equally probable. The probability that its square will end in 1.  
 (c) The probability that a letter chosen randomly from the English alphabet (all letters being equally probable) will be vowel.  
 (d) A random number between 1 and 20 (inclusive) is chosen. The probability that its square root will not be an integer.
3. What is the major product if HBr (in excess) is added to  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{OH}$   
 (a)  $\text{CH}_3-\text{CH}(\text{Br})-\text{CH}_2-\text{Br}$                       (b)  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{Br}$   
 (c)  $\text{CH}_3-\text{CH}(\text{Br})-\text{CH}_2-\text{OH}$                       (d)  $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$
4. Arrange the characteristic timescales of the following set of dynamical spectroscopic techniques in decreasing order of time (longest to shortest): NMR (Nuclear Magnetic Resonance), ESR (Electron Spin Resonance), Fluorescence, Raman and Absorption.  
 (a) Absorption > NMR > Fluorescence > ESR > Raman  
 (b) NMR > ESR > Fluorescence > Raman > Absorption  
 (c) Fluorescence > Absorption > ESR > NMR > Raman  
 (d) All have similar characteristic timescales.
5. A segment of a protein under physiological conditions has a tendency to bury itself in the biological cell membrane. Which of the following is this segment more likely to be?  
 (a) Valine rich              (b) Lysine rich              (c) Glutamic rich              (d) Alanine rich
6. Light of wavelength 500 nm is transmitted through a  $10^{-4}$  M dye solution which is contained in a glass cuvette of path length 1 cm. The extinction coefficient of the dye at 500 nm is  $3010 \text{ M}^{-1} \text{ cm}^{-1}$ . Due to reflection, 4% of light is reflected in the front face of the cuvette (at the air/glass interface) and 4% at the back face before exiting the cuvette (at the glass/air interface). The percentage of the intensity of light transmitted through the dye and cuvette is  
 (a) 42.6%                      (b) 27.74%                      (c) 30.1%                      (d) 46.08%

7. A 19<sup>th</sup> century iron bridge is protected from corrosion by connecting it to a block of metal (sacrificial anode), which is replaced annually. The corrosion of iron, represented by the chemical equation:



Which of the following metals is best suited as sacrificial anode?

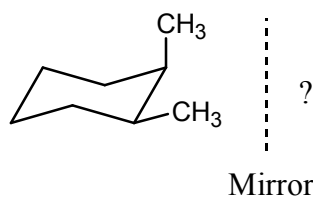
- (a) Ag:  $\text{Ag}^+ + e^- \longrightarrow \text{Ag}(s)$ ,  $E^0 = +0.80 \text{ V}$   
 (b) Cd:  $\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}(s)$ ,  $E^0 = -0.40 \text{ V}$   
 (c) Cu:  $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}(s)$ ,  $E^0 = +0.34 \text{ V}$   
 (d) Mg:  $\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}(s)$ ,  $E^0 = -2.36 \text{ V}$
8. An atom diffuses in one dimension on a x-axis. At  $t = 0$ , its position is  $x = x_0$ . After a sufficiently long time, the probability of finding the atom is maximum at:  
 (a)  $x = \text{plus infinity or minus infinity}$  (b)  $x = 0$   
 (c)  $x = x_0$  (d) Indeterminate
9. Proton tunneling process has been implicated to be important part of many enzyme reaction mechanisms like in Aromatic Amine Dehydrogenase (AADH) which does oxidative deamination of substrates to aldehydes via a protein derived Aspartate residue (shown below)

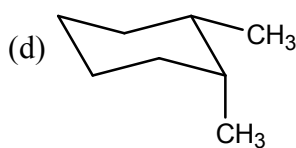
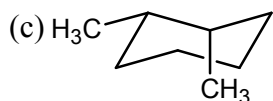
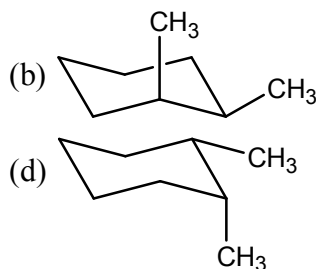
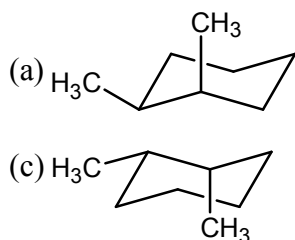


Picture reproduced from Masgrau et al. Science (2006)

Typically in such a reaction, the probability of a tunneling event should depend on:

- (a) Only the height ( $h$ ) of the barrier  
 (b) Only the width ( $2a$ ) of the barrier  
 (c) Both height ( $h$ ) and width ( $2a$ ) of the barrier  
 (d) None of the above.
10. Structure of 1, 2-dimethylcyclohexane is show below. Which of the following is an enantiomer to the given conformer?





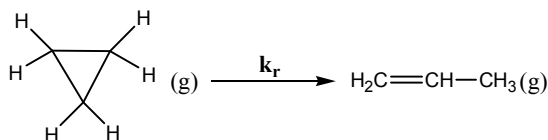
11. The pressure of a gas inside a spherical container is maintained at 2 atm. If the average velocity of the gas molecules inside the container is increased by a factor of two, keeping the pressure the same, by how much would the surface area of the container increase?  
 (a)  $2^{2/3}$  (b)  $2^{4/3}$  (c)  $2^{-1/3}$  (d) 1
12. A molecule normally absorbs in the green wavelength (ca. 500 nm). At some temperature, it is measured that for every 10 molecules in the excited state, there are about 27 molecules in the ground state. What is the approximate temperature of the molecules?  
 (a) 270K (b) 1000K (c) 500K (d) 30000K
13. The half-life for a chemical reaction:  $A \rightarrow B$  is 2.3 sec. When a single molecule of A is observed during its conversion to B, what is the predicted time for this conversion to occur?  
 (a)  $e^{-2.3}$  (b) 4.6 sec (c)  $\log 2.3$  sec (d) undefined.
14. The molar absorption coefficient of a compound in water at 532 nm is  $2200 \text{ L mol}^{-1}\text{cm}^{-1}$ . When light at that wavelength passes through an aqueous solution of this compound (kept in a 5 cm long cell), 50% of the light was absorbed. What is the concentration of the solution?  
 (a)  $2.7 \times 10^{-5} \text{ M}$  (b)  $4.5 \times 10^{-5} \text{ M}$  (c) 1.1 M (d) Insufficient data.
15. A semi-permeable membrane, that is permeable only to cations, separates two compartments A and B. A solution of a monovalent electrolyte (of the type  $X^+Y^-$ ) is contained in both the compartments. The concentrations are 0.1 M and 0.01 M in A and B respectively. When the voltage across the two compartments are measure, we find:  
 (a) No potential difference across the two solutions  
 (b) Compartment B shows + 59mV with respect to A  
 (c) Compartment A shows +10mV with respect to B  
 (d) Compartment B shows -110 mV with respect to A
16. In an NMR experiment, the relative population difference ( $\Delta N/N$ ) for  $^{13}\text{C}$  nuclei in the magnetic fields of (a) 0.5 T, (b) 2.5 T and (c) 15.0T at a temperature of 298K are in the ratio:  
 (a) 1 : 5 : 30 (b)  $e^{-1} : e^{-5} : e^{-30}$   
 (c)  $e^{-0.5/298} : e^{-2.5/298} : e^{-15/298}$  (d) 30 : 5 : 1
17. A polymer chain has 500 segments. The length of each segment is 1.2 nm. If the polymer chain is totally flexible when dissolved in water, what would be the root mean square separation of the ends of the chain?  
 (a) 600 nm (b) 417 nm (c) 27 nm (d) 300 nm
18. An electronic state of a hydrogen atom is prepared to be a superposition energy of the eigenstates of the hydrogen atom, and for which the normalized wavefunction is written as

$$\phi = \frac{1}{\sqrt{2}}|1s\rangle + \frac{1}{\sqrt{4}}|2s\rangle + C_{3s}|3s\rangle$$

here  $|1s\rangle$ ,  $|2s\rangle$  and  $|3s\rangle$  are the exact eigenstates of the hydrogen atom, and  $C_{3s}$  is a constant. What would be the average value of energy, associated with this wavefunction  $\phi$ , in a.u.?

- (a) -0.2951 a.u. (b) -0.4161 a.u. (c) -0.2269 a.u. (d) -0.3929 a.u.

19. For the reaction given below, activation energy is 271 kJ/mol. What is the value of  $k$  at 250°C? Note that  $A$  (frequency factor) =  $1 \times 10^{15} \text{ sec}^{-1}$ .

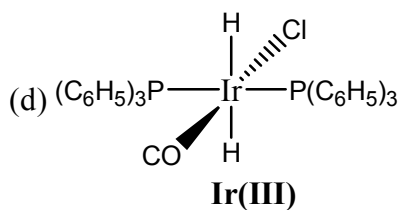
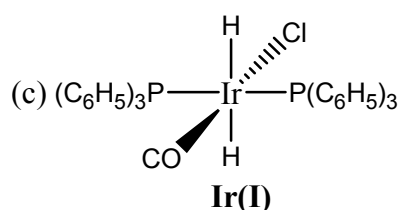
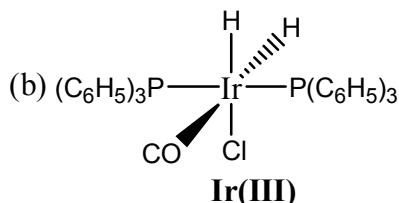
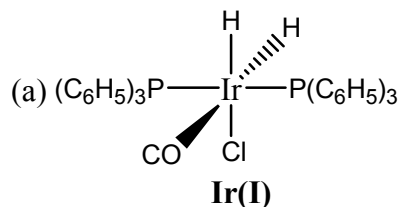


- (a)  $8.568 \times 10^{-12} \text{ s}^{-1}$                       (b)  $8.568 \times 10^{-11} \text{ s}^{-1}$   
 (c)  $5.141 \times 10^{-11} \text{ min}^{-1}$                       (d)  $5.141 \times 10^{-12} \text{ min}^{-1}$
20. In a polyatomic molecule the radiative lifetime of an allowed electronic transition is typically in the range of a few tens of nanoseconds. What will be the lifetimes of the allowed vibrationally excited states of the same molecule?  
 (a) nanoseconds      (b) picoseconds      (c) femtoseconds      (d) milliseconds
21. Vapour pressure of Cs(liq) contained in a cell of 1 litre volume is 80 Torr. IF the Cs atoms are excited to an electronically excited state with a lifetime of 192 ns, how many collisions would the excited atoms suffer before they deactivate radiatively?  
 (a) ~100                      (b) ~200                      (c)  $2.83 \times 10^{18}$                       (d)  $5.48 \times 10^8$
22. Arrange the pK<sub>a</sub>s of the hydroxy groups of methanol, trifluoroacetic acid, phenol and benzyl alcohol in ascending order:  
 (a) Trifluoroacetic acid < phenol < benzyl alcohol < methanol  
 (b) Trifluoroacetic acid < benzyl alcohol < phenol < methanol  
 (c) Phenol < trifluoroacetic acid < benzyl alcohol < methanol  
 (d) Trifluoroacetic acid < methanol < phenol < benzyl alcohol
23. Heme is a versatile molecule present in a large number of metalloproteins and enzymes. The absorption spectrum of heme is characterized by sharp band at near 400 nm and weaker bands at 520–550 nm. The origin of these absorption bands are  
 (a) MLCT transitions                      (b) LMCT transitions  
 (c) d-d transitions                      (d) pi-pi\* transitions
24. The proton NMR spectrum of a saturated hydrocarbon shows a single absorption line at 1.42 ppm with respect to TMS at room temperature. The area of the line is equivalent to 12 protons. Solely based on this observation, what are the tentative inferences you can draw about the nature of the hydrocarbon?  
 (a) It is a pure compound i.e., there are no impurities present.  
 (b) More than one conformation of the molecules may be present and they are undergoing rapid interconversion.  
 (c) The hydrocarbon is cyclohexane.  
 (d) All of the above.
25. Below is a diagram by Maurits Cornelis Escher (198-1972), A Dutch graphic artist. What elements of symmetry are present in this Escher diagram generated by tessellation of fish images?

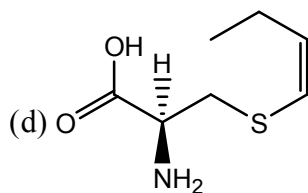
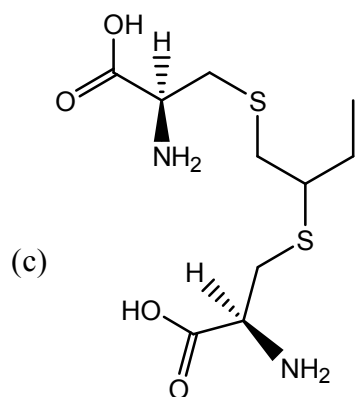
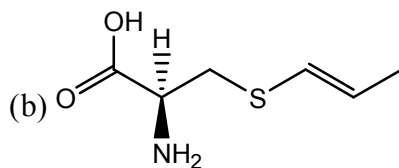
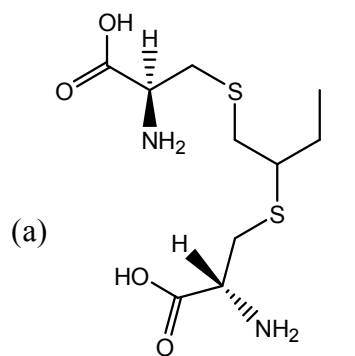
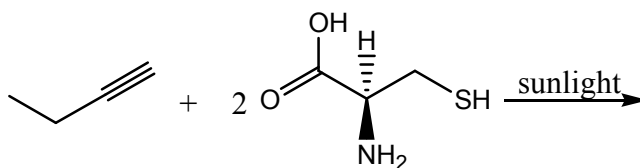


- (a) no symmetry  
 (b) 2 fold rotation axis perpendicular to plane of paper  
 (c) mirror plane and 2-fold rotation axis perpendicular to plane of paper  
 (d) mirror plane

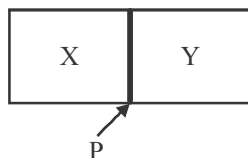
26. Imagine the world famous Koh-i-Noor diamond (mass 21.6g) is completely burnt in the presence of oxygen, the amount of which is carefully controlled. After the completion of the burning process, the mass of the gaseous product is measured. What would you expect the amount of this gas to be?
- (a) Less than 50 g  
 (b) More than 50g but less than 80g  
 (c) More than 80g  
 (d) Diamond will not decompose under the given conditions.
27.  $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$  (trans-chlorocarbonylbis(triophosphine)iridium(I)) also known as Vaska's complex can undergo oxidative addition with dihydrogen. Which of the following structures is a correct depiction of the geometry and oxidation state of the ensuing product?



28. 'Click' reactions can be used to join two molecular units with minimal side products, high chemical yield and stereospecificity. One such reaction is a thiol-yne reaction which is used in polymerization especially for dendrimer synthesis. Predict the final product of the following thiol-yne reaction between L-cysteine and 1-butyne.



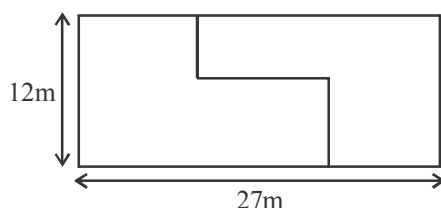
29. Two compartments X and Y are separated by an impermeable partition P. In the compartment X, the following reaction is going on:  $A_2 + B_2 \leftrightarrow 2AB$  in a solvent S, while compartment Y contains only the solvent S. Contents of both the compartments are continuously and vigorously stirred. After the reaction in the compartment X has reached equilibrium, the concentrations of  $A_2$ ,  $B_2$  and  $AB$  are measured and the equilibrium constant calculated. Then the partition is quickly removed. After waiting for a very long time, all the concentrations are measured again, and the new value of the equilibrium constant calculated. What is the most appropriate statement you can make about the result of this experiment? Assume that the chemicals are behaving ideally and the temperature is kept constant.



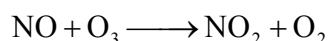
- (a) The concentrations of all the chemicals and the equilibrium constants will be less than their values before the partition was removed.  
 (b) After removing the partition, the concentrations of  $A_2$ ,  $B_2$  will increase and that of  $AB$  will decrease, leading to a lower value of the equilibrium constant.  
 (c) After removing the partition, the concentrations of  $A_2$ ,  $B_2$  will decrease and that of  $AB$  will increase, leading to a higher value of the equilibrium constant.  
 (d) After removing the partition, the concentrations of all the chemicals will decrease, but value of the equilibrium constant will not change.
30. What is the value of this continued fraction?

$$\frac{1}{2} + \frac{1}{\frac{1}{2} + \frac{1}{\frac{1}{2} + \frac{1}{\frac{1}{2} + \frac{1}{\frac{1}{2} + \dots}}}}$$

- (a)  $1/2$                       (b) 1                              (c) 2                              (d)  $\infty$
31. A rectangle with size given below is cut as shown. The two pieces are combined together to form a square. Determine the perimeter of the square.



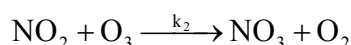
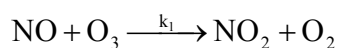
- (a) 60 m                      (b) 48 m                              (c) 72 m                              (d) 78 m
32. The reaction of nitric oxide with ozone takes place according to the following stoichiometry:

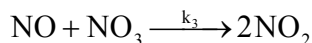


The observed rate law for the reaction is found to be

$$-\frac{d[\text{NO}]}{dt} = \alpha[\text{NO}_3] \{ [\text{NO}] + \beta[\text{NO}_2] \}$$

where  $\alpha$  and  $\beta$  are constants. To explain the above rate law, the following reaction scheme has been proposed.





Determine an expression for  $\beta$

(a) a unique expression of  $\beta$  cannot be determined from the given information.

(b)  $k_2/k_1$

(c)  $k_3/k_2$

(d)  $k_1/k_3$

33. Given  $\cos \theta = \alpha$ ,  $\pi < \theta < \frac{3\pi}{2}$ , find  $\cos(\theta/2)$

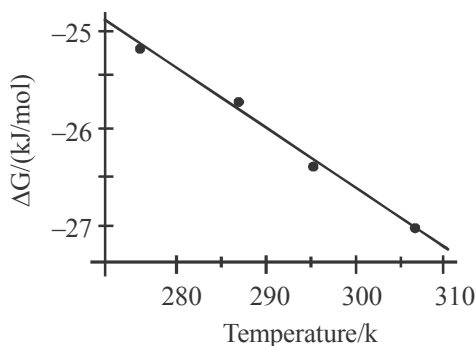
(a)  $-\sqrt{\frac{1+\alpha}{2}}$

(b)  $-\sqrt{\frac{1+2\alpha}{2}}$

(c)  $\sqrt{\frac{1+\alpha}{2}}$

(d)  $\sqrt{\frac{1+2\alpha}{2}}$

34. A student has measured the standard free energy change of a certain chemical reaction as a function of temperature. The data and a linear fit to them are shown below. From this diagram, determine approximately the standard entropy of the reaction. (Assume that the standard entropy of the reaction is independent of temperature.)



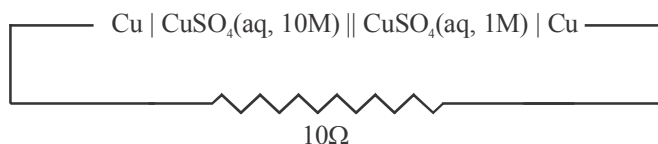
(a)  $+50 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

(b)  $+75 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

(c)  $+100 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

(d)  $-100 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

35. Consider the following electrochemical cell, from which current is drawn through an external resistor of 10 Ohms. During this process, the concentration of  $\text{CuSO}_4$  in the left and the right half-cells were measured, and the value of  $K \equiv [\text{CuSO}_4]_{\text{left}} / [\text{CuSO}_4]_{\text{right}}$  was calculated. From the initial value of  $K = 10$ , predict the value of  $K$  after a very long time when the cell stopped giving any current.



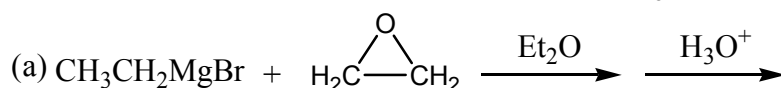
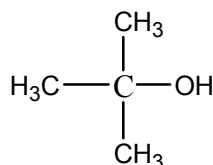
(a) An exact value cannot be predicted since  $\text{CuSO}_4$  solutions of such high concentrations, as used above, would not behave ideally.

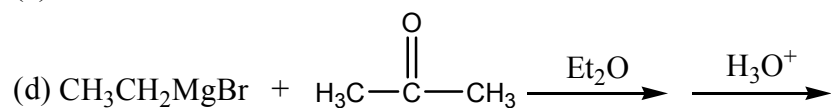
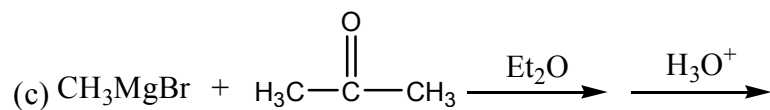
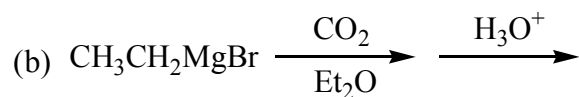
(b)  $K \approx 0.1$

(c)  $K = 1.0$

(d)  $K$  will be very small, possibly  $< 0.00001$ .

36. Which of the following reaction sequence is the correct one for synthesis of t-butyl alcohol?





37. The  $^{13}\text{C}$  NMR spectrum of a compound shows 6 peaks and the  $^1\text{H}$  NMR spectrum shows 5 peaks. Which of the following is this compound?
- (a)  $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{CH}_3$   
 (b)  $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$   
 (c)  $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{CH}_3$   
 (d)  $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}_3$
38. It is known that pKa of water is 15.7. Based on this water pKa benchmark, arrange the following solvated metal-aqua ions in order of their increasing acidity:  
 $\text{Mn}^{2+}(\text{H}_2\text{O})_6$ ,  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ ,  $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ , and  $\text{Ca}^{2+}(\text{H}_2\text{O})_8$
- (a) All have same acidities.                      (b)  $\text{Fe}^{3+} < \text{Cu}^{2+} < \text{Mn}^{2+} < \text{Ca}^{2+}$   
 (c)  $\text{Ca}^{2+} < \text{Cu}^{2+} < \text{Mn}^{2+} < \text{Fe}^{3+}$                       (d)  $\text{Ca}^{2+} < \text{Mn}^{2+} < \text{Cu}^{2+} < \text{Fe}^{3+}$
39. The  $n \times n$  matrix  $\mathbf{P}$  is idempotent if  $\mathbf{P}^2 = \mathbf{P}$  and orthogonal if  $\mathbf{P}^T\mathbf{P} = \mathbf{I}$ . Which of the following is false?
- (a) If  $\mathbf{P}$  and  $\mathbf{Q}$  are idempotent  $n \times n$  matrices and  $\mathbf{PQ} = \mathbf{QP} = \mathbf{O}$ , then  $\mathbf{P} + \mathbf{Q}$  is idempotent.  
 (c) If  $\mathbf{P}$  is idempotent, then  $-\mathbf{P}$  is idempotent.  
 (d)  $\mathbf{P} = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$  is orthogonal.
40. Which of the following statements is true for liquid crystals:
- (a) These are self-assembled structures of amphiphilic molecules, solely formed upon heating the amphiphilic solid above its melting point.  
 (b) These are solid crystals of ionic solids which have been exposed to temperatures above their melting point.  
 (c) These are a mixture of liquid and solid phase of the same compound  
 (d) These are a state of matter having properties between that of a conventional liquid and a crystalline solid.