GS-2022 (Chemistry) X

Full Name :

Roll No. :

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

Written Test in **CHEMISTRY**

December 12th, 2021

Duration: Three hours (3 hours)

Please read all instructions carefully before you attempt the questions.

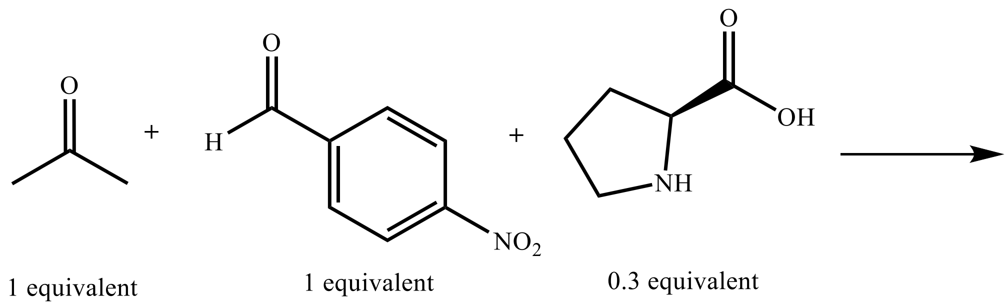
1. Write your FULL NAME and ROLL NUMBER (see hall ticket) in block letters, both on this page and on your answer sheet (at the end of this booklet).
2. This is a multiple-choice question paper with **ONE** section having a total of 40 questions. Each correct answer will get you 3 marks. Every wrong answer will get you -1 mark. Marks are not awarded or deducted when a question is not attempted. It is better not to answer a question if you are not sure.
3. Indicate your answers on the ANSWER SHEET by filling completely in the appropriate boxes. Do not mark more than one box for any question; this will be treated as an incorrect answer.
4. We advise you to first mark the correct answers in the QUESTION SHEET, and later transfer them to the ANSWER SHEET only when you are sure of your choice.
5. Rough work may be done on the back of the QUESTION SHEET. If needed, you may ask for extra rough sheets from an invigilator.
6. In answering the questions, please choose the option that best describes the solution to the problem.
7. **Use of calculators is permitted in this subject test.**

SOME USEFUL DATA

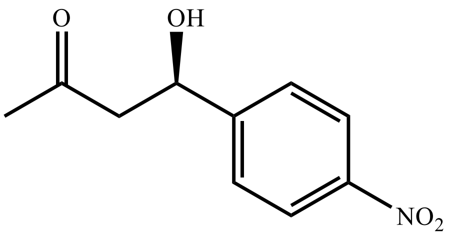
Avogadro number = 6.02×10^{23} mol^{-1}	e = 1.6×10^{-19} C
RT/F = 0.0257 V at 25°C	h = 6.626×10^{-34} J s
Faraday constant = 96500 C/mol	c = 3×10^{8} m s^{-1}
Boltzmann constant $k_B = 1.38\times10^{-23}$ J K^{-1}	R = 8.314 J K^{-1} mol^{-1}
Mass of an electron = 9.109×10^{-31} kg	

---

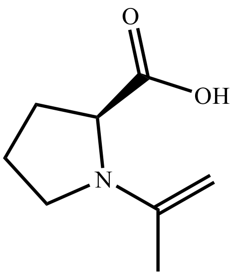
1. The 2021 Nobel Prize in Chemistry went to Benjamin List and David W.C. MacMillan 'for the development of asymmetric organocatalysis'. Predict the final product/products of the following reaction for which one of the Laureates won the prize.



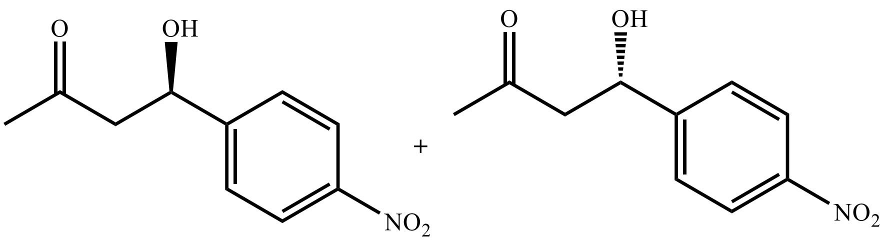
A)



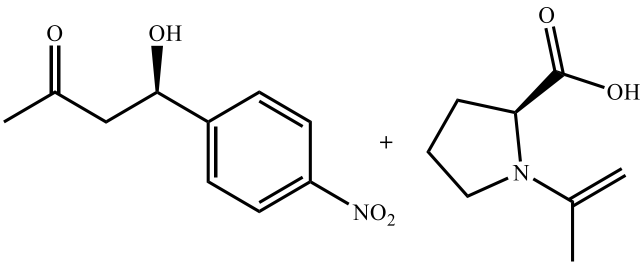
B)



C)



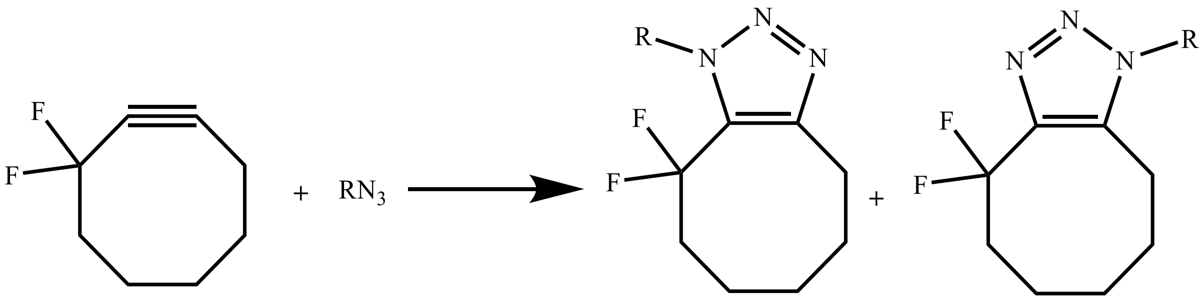
D)



Answer: C

2. Which of the following drive the reaction shown below?

   Light; Heat; Ring Strain Release; Fluorine substituents



   A) Light and Fluorine substituents

   B) Heat and Fluorine substituents

   C) Ring strain release and fluorine substituents

   D) Ring strain release

3. One of the important chemical markers for the rise in oxygen concentration on the planet earth 3500 billion years ago is the formation of Banded Iron Formation (BIF) rocks. Can you predict what form of Fe is found in these BIF structures given the ocean pH to be 8.0?

   A) $Fe(OH)_2$

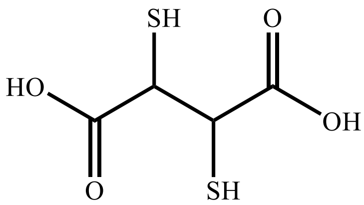
   B) $Fe(OH)$

   C) Fe_2O_3

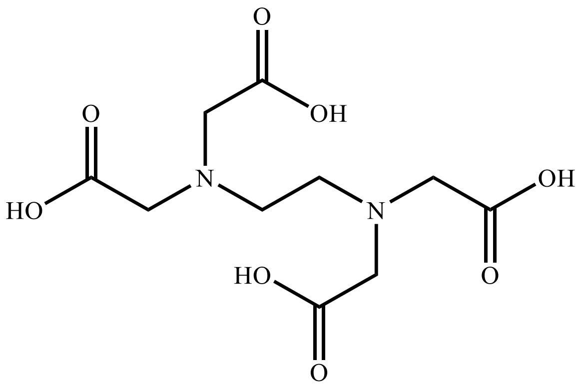
   D) FeO

4. LiCl is used as a prophylactic drug to treat bipolar disorder. It is difficult to decide the dosage that can treat patients and minor overdosage can cause severe side-effects. You are a chemist trying to design an antidote for Li(I) overdosage. Which binding scaffold would be most suitable to remove Li(I) ions from patients without removing biologically essential metal ions?

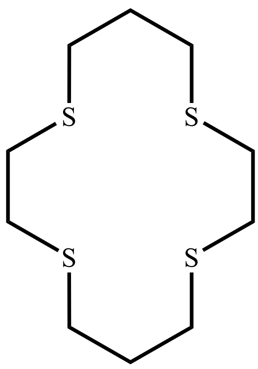
A)



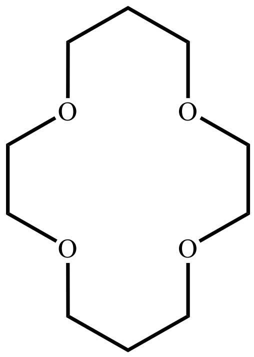
B)



C)



D)



5. Which of the following statements is true regarding amphiphillic molecules?

   A) An amphiphillic molecule consists of both a positive charge and a negative charge.

   B) Amphiphillic molecules show spontaneous aggregation behaviour in any solvent and at all concentrations.

   C) Amphiphillic molecules are insoluble in water.

   D) Amphiphillic molecules are known to form liquid crystals.

6. Metallic iron crystallizes in a cubic unit cell. The unit cell size is 287 pm. The density of iron is 7.87 g/cm^3. How many iron atoms are there within one unit cell?

   A) Not enough information is given to calculate the value.

   B) 1

   C) 2

   D) 3

7. Iron, Cobalt and Nickel are three known elements that display ferromagnetism. Which of the following statements is true about ferromagnets:

   A) In the presence of a magnetic field, the unpaired spins of a ferromagnet all align with the external field. Then in the absence of the external magnetic field, these spins then revert back immediately to their original state.

B) The origin of magnetism in a ferromagnet arises from randomly arranged paired spins in a lattice.

C) A ferromagnetic material is weaker (in its attraction to an external magnetic field) than a paramagnetic material

D) None of the above.

8. An artificial soft drink contains 11.0 gms of tartaric acid $C_4H_6O_6$, and 20 gms of its potassium salt $C_4H_5O_6K$ per liter. What is the pH of the drink? ($K_a = 1.0 \times 10^{-3}$)

A) 4.24

B) 5.21

C) 3.82

D) 3.16

9. The enthalpy of fusion of ice at 273.15 K and 1 atm is 6010 J/mol. The corresponding change in molar volume due to fusion of ice is -1.63 cm^3/mol. What is the melting point of ice at 1000 atm?

A) 282.2 K

B) 265.5 K

C) 289.2 K

D) 255.2 K

10. The vapor pressures of solid and liquid ammonia near the triple point are given by:

$$\log(P^s/P^0) = 10 - 1630/T$$

and

$$\log(P^l/P^0) = 8.46 - 1330/T.$$

Calculate the ratio of the slopes of the solid-gas curve and liquid-gas curve at the triple point. ($P^0 = 1$ torr)

A) 1.00

B) 0.23

C) 1.22

D) 2.72

11. The equilibrium constant for the reaction described by

$$2\ SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

is $K_p = 10$ at 960 K.
Which direction the reaction will proceed spontaneously for

$2\ SO_2(1.0 \text{ X } 10^{-3} \text{ bar}) + O_2\ (0.20 \text{ bar}) \rightarrow 2\ SO_3\ (1.0 \text{ X } 10^{-4} \text{ bar})$

A) The reaction will be at steady state

B) The reaction will proceed from reactant to product

C) The reaction will proceed from product to reactant

D) The reaction will not take place

12. Given that ΔH^0 has an average value of -69.8 kJ/mol over the temperature range of 500 K to 700 K for the reaction described by

$$PCl_3(g) + Cl_2\ (g) \rightarrow PCl_5(g)$$

What will be the K_p at 700 K given that $K_p = 0.0408$ at 500 K?

A) $1.6 \text{ X } 10^{-2}$

B) $2.3 \text{ X } 10^{4}$

C) $3.6 \text{ X } 10^{-4}$

D) $6.2 \text{ X } 10^{2}$

13. Mixing the $FeSO_4$ solution with $NaNO_3$, followed by a slow addition of concentrated H_2SO_4 through the side of the test tube produces a brown ring.

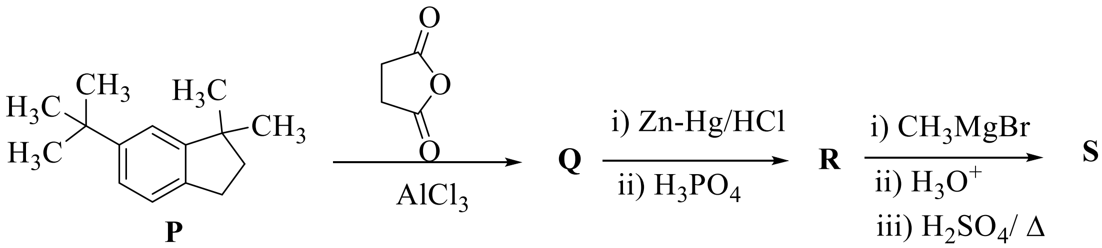
Among the following, the brown ring is due to the formation of

A) $[Fe(NO)_2(H_2O)_4]^{3+}$ B) $[Fe(NO)(H_2O)_5]^{2+}$

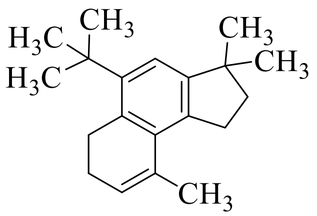
C) $[Fe(NO)_4(SO_4)_2]$ D) $[Fe(NO)_2(SO_4)_2]^{2-}$

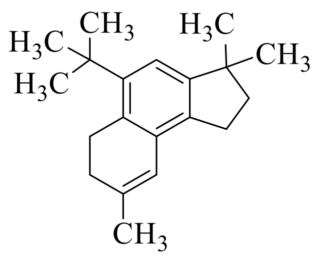
Answer: B

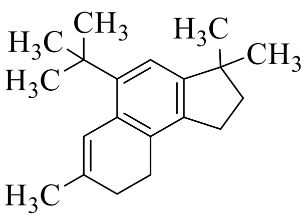
14. In the reaction scheme shown below, **Q**, **R**, and **S** are the major products.

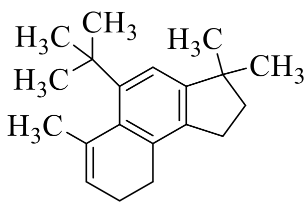


The correct structure of **S** is

A) 

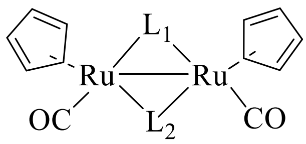
B) 

C) 

D) 

Answer: D

15. The correct combination of L_1 and L_2 among H^-, NO^-, $MeCH^{2-}$, and CO that will satisfy the 18 electron rule for both metal centres in the following neutral molecule, is (Given: atomic number of Ru is 44)



A) H^{-}, NO^{-}

B) $MeCH^{2-}$, NO^{-}

C) $MeCH^{2-}$, CO

D) H^{-}, CO

16. In a new temperature scale (°H) the melting point of hydrogen is 0 °H and the boiling point is 100 °H. PV is 28 dm^3 atm at 0 °H and 40 dm^3 atm at 100 °H. What is the value of absolute zero in this temperature scale?

A) 0 °H

B) −273.15 °H

C) −233.33 °H

D) 233.33 °H

17. Sodium nitroprusside (SNP), $Na_2[Fe(CN)_5NO]$, is used for the treatment of severe hypertension . It works by interacting with oxyhemoglobin which results in release of cyanide and nitric oxide. Which of the following is not correct about SNP.

A) It is a diamagnetic compound

B) Iron is assigned an oxidation state of +3

C) It is a low spin compound

D) It has NO^{+} as ligand

18. Jahn Teller effect is not observed in octahedral transition metal complexes with electron configuration of

A) d^4 high spin

B) d^5 low spin

C) d^5 high spin

D) d^7 low spin

19. The correct order of molar extinction coefficient for electronic transitions in $[Mn(OH_2)_6]^{2+}$, $[Ti(OH_2)_6]^{3+}$, $[MnO_4]^-$ is

A) $[Mn(OH_2)_6]^{2+} > [Ti(OH_2)_6]^{3+} > [MnO_4]^-$

B) $[Ti(OH_2)_6]^{3+} > Mn(OH_2)_6]^{2+} > [MnO_4]^-$

C) $[Ti(OH_2)_6]^{3+} > [MnO_4]^- > Mn(OH_2)_6]^{2+}$

D) $[MnO_4]^- > [Ti(OH_2)_6]^{3+} > Mn(OH_2)_6]^{2+}$

20. The value of the integral $\int_{-\pi}^{\pi} \cos(mx)\cos(nx)\,dx$ for $m = n \neq 0$ and $m \neq n$ are respectively:

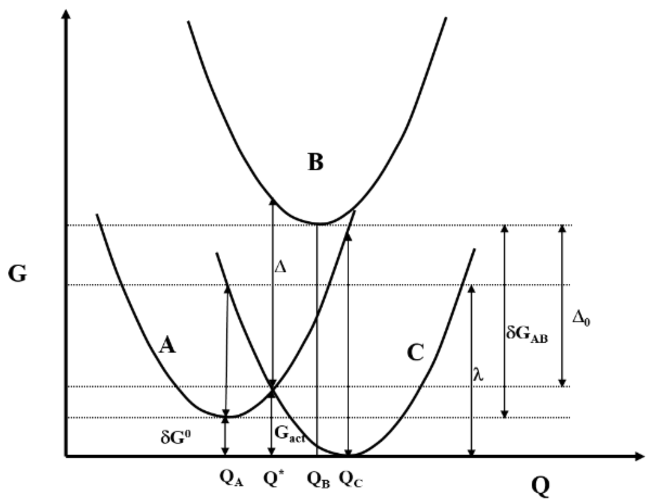
A) 0 and 2π

B) 2π and 0

C) π and 0

D) 0 and π

21. A chemical reaction involves 3 states A, B, and C (see figure below) whose dependence on a reaction coordinate Q is of the form $G_i = 0.5 * k(Q - Q_i)^2$, where i=A,B,C and all surfaces have the same curvature k.



If $|Q^* - Q_A| = |Q^* - Q_C|$, then which of the following statement on the relationship between Δ and δG_{AB} is correct

A) $\Delta < \delta G_{AB}$

B) $\Delta > \delta G_{AB}$

C) $\Delta = \delta G_{AB}$

D) Cannot be determined from the information provided

22. A gas of diatomic molecules is in thermal equilibrium at temperature T. If the potential energy of the bond *b* between atoms in each molecule can be described by a harmonic form: $0.5 * k(b - b_0)^2$, then the root mean square deviation in bond length is related to the spring constant of the bond and the temperature as:

A) $\propto \sqrt{1/kT}$

B) $\propto \sqrt{T/k}$

C) $\propto T/\sqrt{k}$

D) $\propto T/k$

23. A particle with energy E is incident on a square barrier with height H > E and width W. Which of the following statements is correct for the particle after it quantum mechanically tunnels through the barrier?

A) The particle has energy E after tunneling through the barrier

B) The energy of the particle decreases as W increases but is independent of H

C) The energy of the particle decreases as H increases but is independent of W

D) The energy of the particle decreases as H and/or W increases.

24. (i) Consider a coin with two sides (H = heads; T= tails). The probability of observing HHHHHTTTTT is equal to the probability of observing HTHTHTHTHT.
(ii) For a system at equilibrium, Gibbs free energy is maximized.

A) Statement (i) is true and Statement (ii) is false

B) Statement (i) is false and Statement (ii) is True

C) Both statements are false

D) Both statements are true

25. Given Compound I ($FeSO_4.(NH_4)_2SO_4.6H_2O$) and Compound II ($K_4[Fe(CN)_6]$), when dissolved in water the following is correct:

A) Both the compounds give positive tests for Fe^{2+}

B) Only Compound I gives positive test for Fe^{2+}

C) Only Compound II gives positive test for Fe^{2+}

D) Both do not give usual tests of Fe^{2+}

26. (i) Half-life time of a first order reaction is dependent upon the initial concentration of the reactant.
(ii) Time required for the decomposition of 99.9% of 0.1 mole reactant undergoing a first order reaction is ____________ to that of its half-life time.

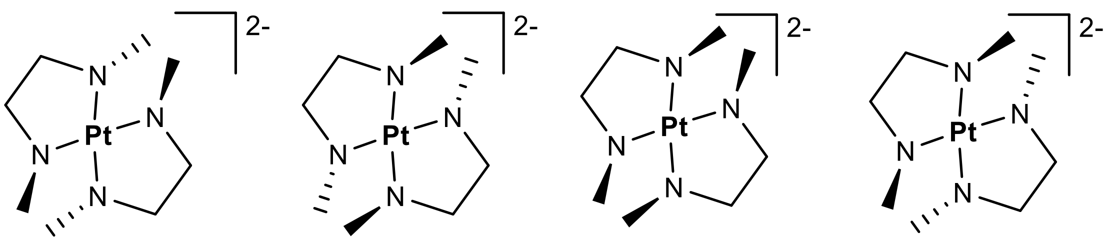
A) (i) True and (ii) Information is insufficient for the calculation

B) (ii) False and (ii) 10 times

C) (i) True and (ii) 10 times

D) (i) False and (ii) approximately 2 times

27. Following are four isomeric square planar complexes formed in a reaction between a Pt(II) salt and MeNH-CH_2-CH_2-NHMe. Identify the chiral isomers.



Pt-1 Pt-2 Pt-3 Pt-4

A) Pt-1 and Pt-2

B) Pt-1 and Pt-3

C) Pt-1 and Pt-4

D) Pt-1, Pt-3 and Pt-4

28. Predict and compare the thermochemical fuel efficiencies between the two rocket fuels N_2H_4 and $N_2H_2(CH_3)_2$.

Combustion reactions

$N_2H_4(l) + O_2(g) = N_2(g) + 2H_2O(g)$

$N_2H_2(CH_3)_2(l) + O_2(g) = N_2(g) + H_2O(g) + 2CO_2(g)$

Enthalpy of formation (kJ/mol):

$N_2H_4(l) = + 50.6$

$N_2H_2(CH_3)_2(l) = + 42$

$CO_2(g) = - 394$

$H_2O(g) = - 242$

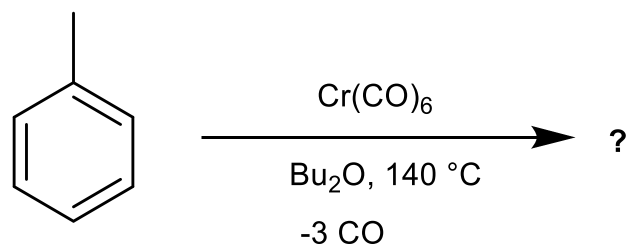
(A) $N_2H_4 = N_2H_2(CH_3)_2$

(B) $N_2H_4 > N_2H_2(CH_3)_2$

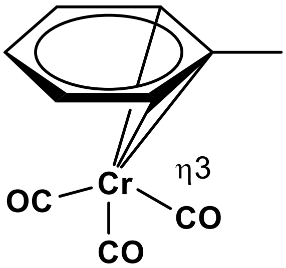
(C) $N_2H_4 < N_2H_2(CH_3)_2$

(D) Cannot be compared

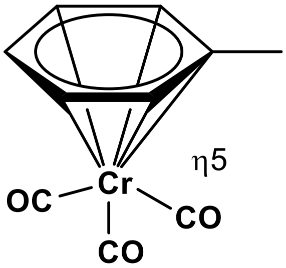
29. Predict the product of the following reaction?
The ^{1}H NMR spectral features: symmetric compound, a singlet at aliphatic region for three protons, all aromatic protons are up field shifted when compared with tolune.



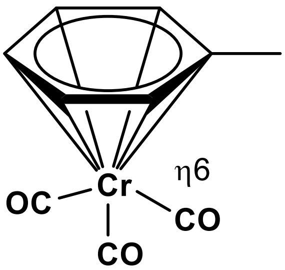
A)



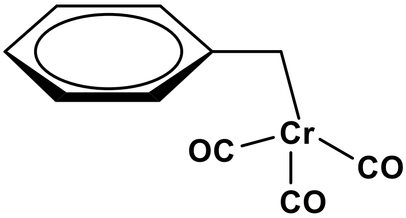
B)



C)

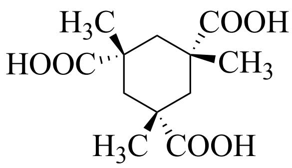


D)

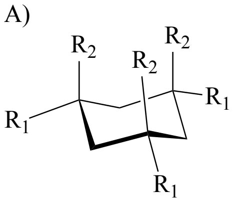


Answer: C

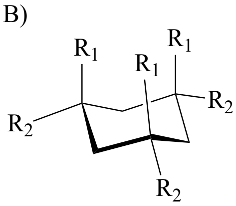
30. Predict the most stable conformation of the following molecule, called Kemp's triacid.



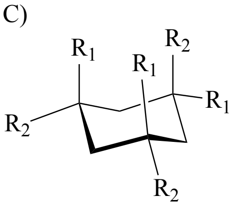
A)



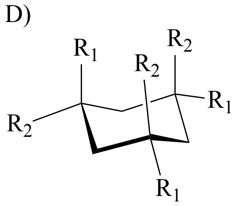
B)



C)



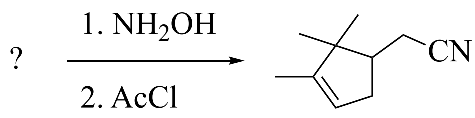
D)

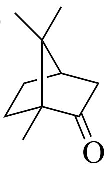
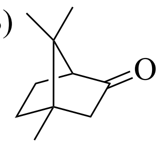
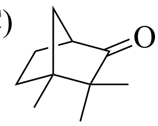
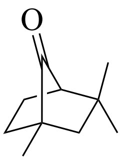


R_1 = COOH; R_2 = CH_3

Answer: B

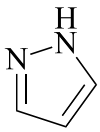
31. Predict the starting material.

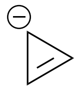


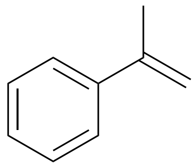
A)  B)  C)  D) 

Answer: A

32. Predict the aromaticity of the following molecules.


1


2


3

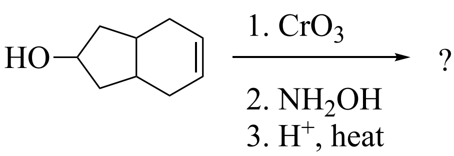
A) **1**. aromatic; **2**. antiaromatic; **3**. aromatic

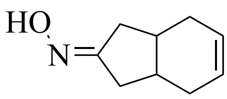
B) **1**. aromatic; **2**. nonaromatic; **3**. aromatic

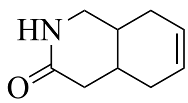
C) **1**. nonaromatic; **2**. antiaromatic; **3**. aromatic

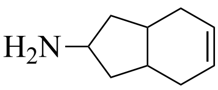
D) **1**. nonaromatic; **2**. antiaromatic; **3**. antiaromatic

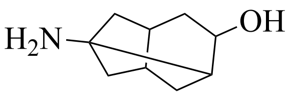
33. Predict the product.



A) 

B) 

C) 

D) 

Answer: B

34. Consider the following isotope exchange reaction being carried out in a closed container in the presence of a catalyst:

$$H_{2\,(g)} + D_{2\,(g)} \rightleftharpoons 2\ HD_{(g)}$$

Under the high temperature limit, which of the following statements is true about the value of the equilibrium constant K_{eq} for this above reaction:

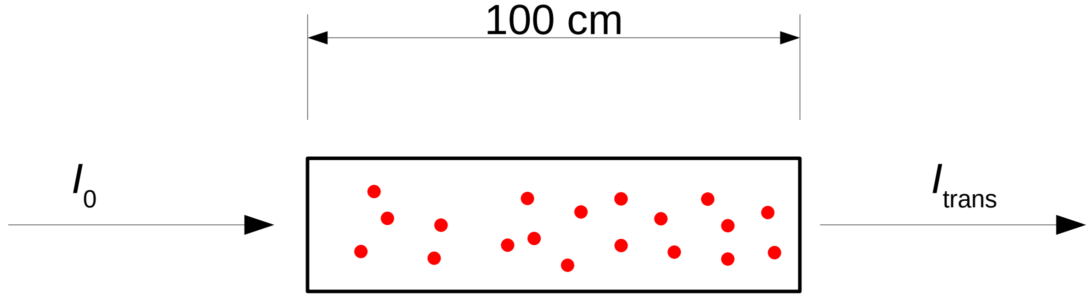
A) K_{eq} is approximately equal to 1

B) K_{eq} cannot be estimated unless the catalyst is specified

C) $K_{eq} = 2$

D) K_{eq} is approximately equal to 4

35. Consider a cylindrical tube of length 100 cm and filled with CO gas at pressure 1 bar at 298 K. Electromagnetic radiation with frequency exactly on resonance with the J = 0 to 1 rotational transition (ground vibrational state) of intensity I_0 is incident on it. The transmitted intensity is given by I_{trans}. Given that the rotational constant, B for CO = 2 cm^{-1}, which of the following statements is true?



A) $\frac{I_{trans}}{I_0}$ approximately equal to 1

B) $\frac{I_{trans}}{I_0}$ approximately equal to zero

C) $\frac{I_{trans}}{I_0} > 1$

D) Approximate estimate of $\frac{I_{trans}}{I_0}$ cannot be made in this case unless the absorption cross section or coefficient is known

36. Two students named A and B repeatedly measure the volume of a solution consumed in a titration experiment 10 times and 4 times, respectively. They report the following results:

Measurement number	Student A Volume (ml)	Student B Volume (ml)
1	20.8	19.9
2	20.3	20.9
3	19.4	19.9
4	19.8	20.5
5	21.0	x
6	20.7	x
7	20.3	x
8	20.6	x
9	20.1	x
10	20.0	x

Which option correctly represents the fractional uncertainty in the average (best estimate) values reported by students A and B?

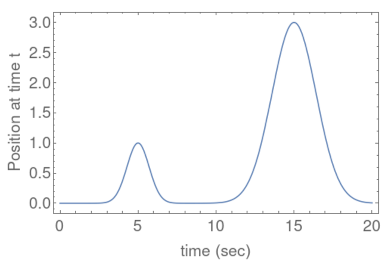
A) Fractional uncertainty for A = 0.8% and B = 0.5%

B) Fractional uncertainty for A = 0.49 % and B = 0.49 %

C) Fractional uncertainty for A = 0.8% and B = 1.2%

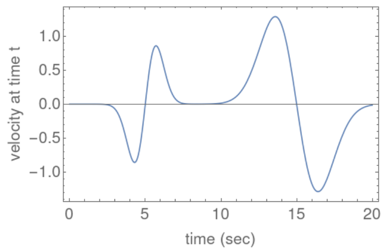
D) Fractional uncertainty for A = 5 % and B = 8 %

37. Consider a particle which is confined to move in one dimension. The following graph displays the position of this particle as a function of time:

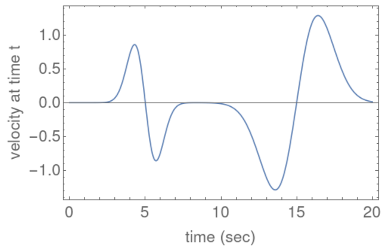


Which of the graph below correctly represents the velocity as a function of time?

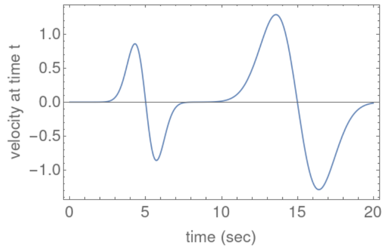
A)



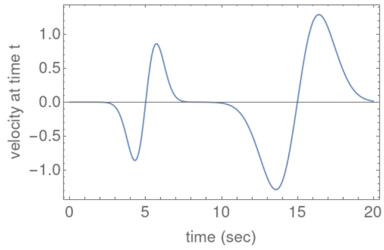
B)



C)



D)



38. Suppose you put 100 ml of water in a cup (Cup 1) at +20 °C, and 100 ml of ice in a similar cup (Cup 2) at -20 °C. Then you put both cups in the microwave and heat them for 1 min, and then measure the increase of temperature. Which of the following will most likely be true?

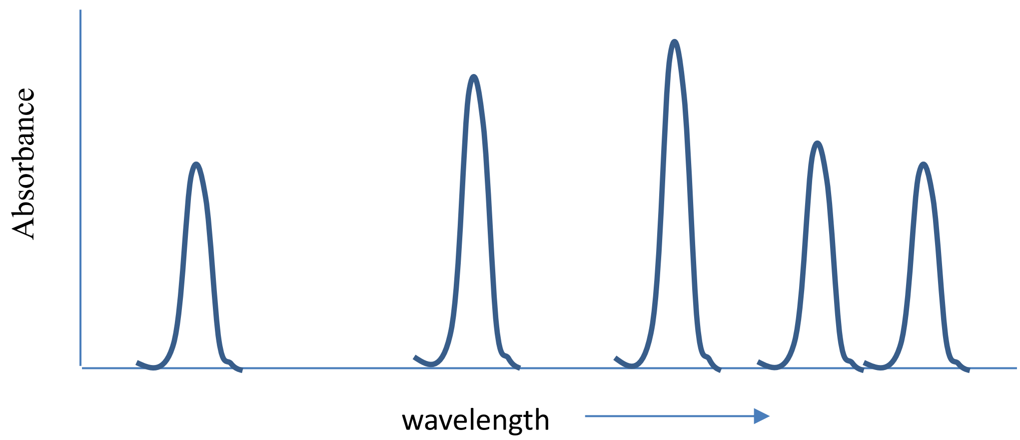
A) The temperature of both the cups would increase by equal amounts

B) The temperature of Cup 1 would increase more

C) The temperature of Cup 2 would increase more

D) The answer cannot be determined from the data given

39. You are shown the following spectrum, but the units of wavelength are missing. Which of the following answers are most likely?



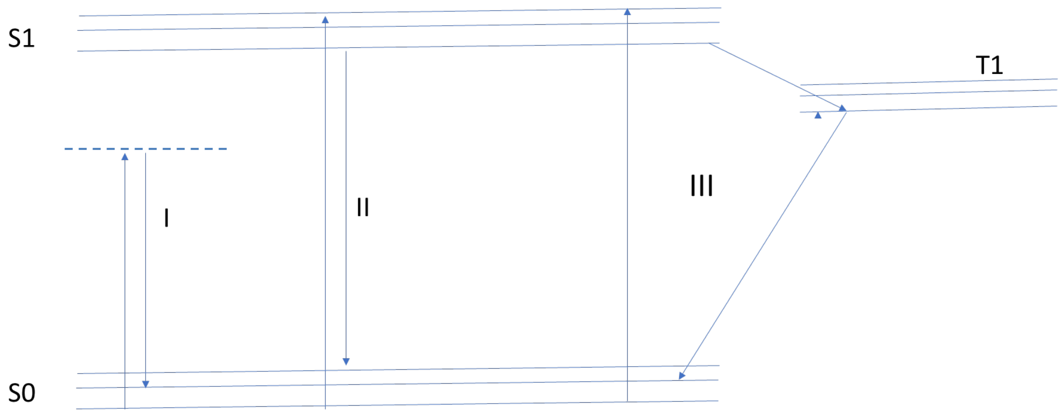
A) It is the vibrational spectrum of gaseous dioxygen

B) It is the rotational spectrum of gaseous dioxygen

C) It is the vibrational spectrum of gaseous Carbon monoxide

D) It is the rotational spectrum of gaseous Carbon monoxide

40. Following is the energy level diagram of a molecule. Each group, I, II and III, depict optical transitions which ultimately return the molecule to the ground state (note: I and II consist of two transitions, III consists of 3 transitions). Which of the following depict the right timescale of these processes?



A) II is the fastest, I is the slowest, III is intermediate

B) I is the fastest, II is the slowest, III is intermediate

C) II is the fastest, III is the slowest, I is intermediate

D) I is the fastest, III is the slowest, II is intermediate