GS-2021 (Chemistry) X

Full Name   :

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Roll No.   :

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TATA INSTITUTE OF FUNDAMENTAL RESEARCH

Written Test in **CHEMISTRY**

March 7th, 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}

RT/F = 0.0257 V at 25°C

Faraday constant = 96500 C/mol

Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J K^{-1}

Mass of an electron = 9.109×10^{-31} kg

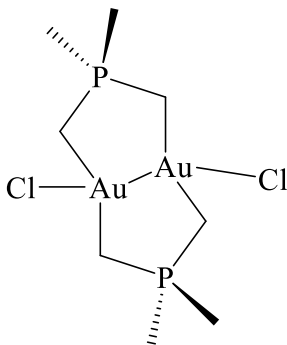$e = 1.6 \times 10^{-19}$ C
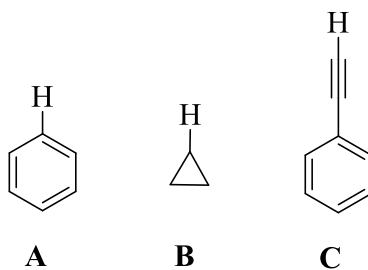
$h = 6.626 \times 10^{-34}$ J s

$c = 3 \times 10^{8}$ m s^{-1}

$R = 8.314$ J K^{-1} mol^{-1}

1. What is the oxidation state of gold in below complex?

A) 0

B) 1

C) 2

D) 3

2. What is the correct C-H bond (shown in below molecules) dissociation energy,

A) C>B>A

B) A>B>C

C) A>C>B

D) C>A>B

3. Quantum confinement results in

A) Energy gap in semiconductor is proportional to the inverse of the square root of the size

B) Energy gap in semiconductor is proportional to the inverse of the size

C) Energy gap in semiconductor is proportional to the square of size

D) Energy gap in semiconductor is proportional to the inverse of the square of size

4. A mixture of KCl and $KClO_3$ weighing 1.8 gms was heated. After the reaction, the dry oxygen gas generated occupied 140 ml at STP. What percent of original mixture was KClO3?

A) 28.4%

B) 42.9%

C) 64.3%

D) 37.5%

5. A 1 mm thick transparent crystal of a metalloprotein absorbs 75% of the incident light of wavelength 500 nm. What is the extinction coefficient? (Density of the crystal is 1.5 g/cc, Molecular weight of the protein is 100 KDa)

A) 400 $M^{-1}cm^{-1}$

B) 500 $M^{-1}cm^{-1}$

C) 920 $M^{-1}cm^{-1}$

D) None of the above

6. The lifetime (τ) of an electronic state would be the following:

If only fluorescence occurred, $\tau = 5$ ns.

If only thermal de-excitation occurred, $\tau = 10$ ns.

If only intersystem crossing occurred, $\tau = 10$ ns.

If only photobleaching occurred, $\tau = 5$ ns.

If only quenching occurred, $\tau = 5$ ns.

In reality, all of these happen together. What are the observed lifetime and the

fluorescence quantum efficiency, respectively?

A) 0.1 ns, 1

B) 1.5 ns, 0.25

C) 35 ns, 0.2

D) 1.25 ns, 0.25

7. For a particle in a 1-D box of length *2L* the normalization constant *A* for its wavefunction $\psi(x,t) = A \sin\left(\frac{n\pi x}{2L}\right)$ ($where\ n = 1,2,3 \ldots$) is given by:

A) $A = \sqrt{\frac{1}{L}}$ (Key: the length is *2L* so replace L with 2L in the standard answer C or explicit normalization.)

B) $A = \sqrt{\frac{1}{2L}}$

C) $A = \sqrt{\frac{2}{L}}$

D) $A = \sqrt{\frac{1}{4L}}$

8. The wavefunction of a particle is given by $\psi(x,t) = \sin(k\left(x - \frac{\pi}{4k}\right) + wt)$ Relative to an initial reference time of *t=0*, the probability of finding the particle at a later time $t = \frac{\pi}{4\omega}$ at the point $x = 0$

A) Increases

B) Decreases (Key: at *t=0*, the sine function has zeros at $x = \frac{n\pi}{k} + \frac{\pi}{4k}$ (where *n=0,±2, ±4....*) whereas at $t = \frac{\pi}{4\omega}$, the zeros are shifted to $x = \frac{n\pi}{k}$, thus at $x = 0$, the probability is non-zero initially and zero at the latter time point.)

C) Stays the same

D) May increase or decrease depending on *k*

9. A folded protein in solution at temperature T has two different conformations A and B with a free energy difference $\Delta G = G_B - G_A < 0$ and separated by a single transition state

(TS) barrier. A single amino acid mutation is introduced in the protein which reduces the enthalpy of both state A and B by the same amount, but increases the entropy of state B relative to state A. Additionally, the entropy of the transition state also decreases. Which of the following statements is true for the equilibrium population ratio P_A/P_B and the transition rates $k_{A \to B}$ and $k_{B \to A}$ after the mutation is introduced.

A) P_A/P_B . k_A, and k_B all increase

B) P_A/P_B decreases but k_A and k_B both increase.

C) P_A/P_B increases but k_A and k_B decrease

D) P_A/P_B . k_A, and k_B all decrease. (Key: B is entropically stabilized relative to A increasing P_B relative to A. Transition barriers should go up as both states are stabilized relative to TS lowering the rates)

10. An instrument measures the position of two independent atoms with respect to origin along a line as 20 ± 3 Å and 40 ± 4 Å. The distance between the two atoms on the line is:

   a. 20 ± 7 Å

   b. 20 ± 1 Å

   c. 20 ± 5 Å   (distance $d = x_2 - x_1$. for independent variables error in d is given by $\Delta d = \sqrt{(\Delta x_1)^2 + (\Delta x_2)^2}$

   d. 20 ± 4 Å

11. Which amongst the following metal carbonyls has paramagnetic property.

(a) $Ni(CO)_4$

(b) $Fe(CO)_4$

(c) $V(CO)_6$

(d) $Cr(CO)_6$

12. Charge polarization of C-F bond is much larger compared to C-Br bond. Which of the following statements on the dipole moments of CH_3Br and CH_3F is true?
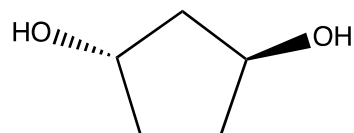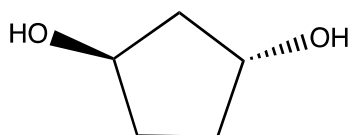
A) The dipole moment of CH_3Br is greater than CH_3F

B) The dipole moment of CH_3F is greater than CH_3Br

C) The dipole moments of CH_3F and CH_3Br are same

D) Both molecules have zero dipole moment

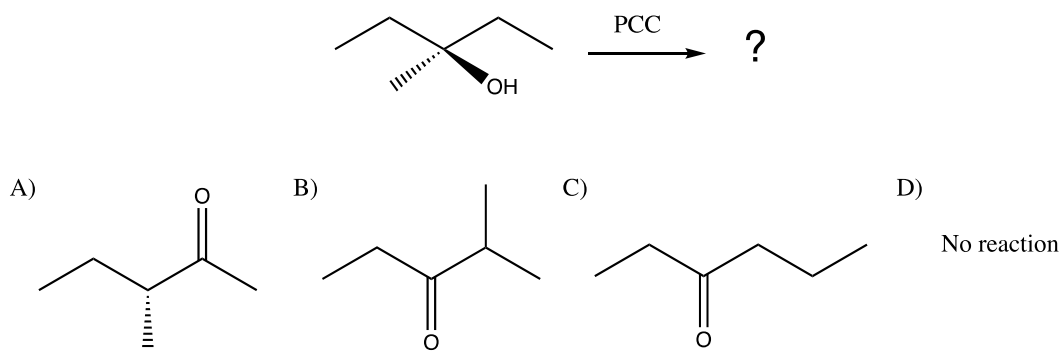13. Indicate the stereo chemical relationship between the two molecules.
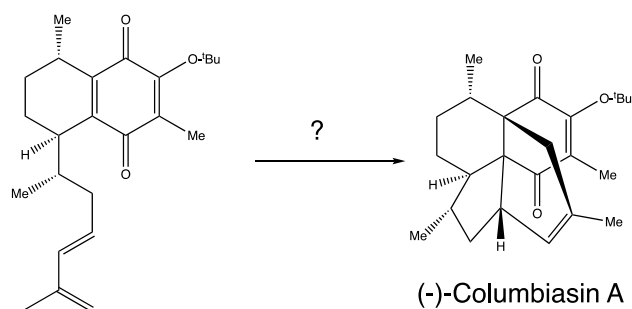

A) Enantiomers

B) Diastereomers

C) Identical and chiral

D) Identical and achiral

14. Predict the product of the following reaction [PCC = Pyridinium chlorochromate].

PCC over arrow, product "?"

A)   B)   C)   D) No reaction

15. Predict the reaction condition for the following synthetic transformation.

(-)-Columbiasin A

A) Light

B) Base

C) Heat

D) Acid

16. A magnetic moment μ placed in an external magnetic field **H** has the following energies: $E_{par} = -\mu H$ and $E_{anti} = +\mu H$, in configurations parallel and anti-parallel to the external field, respectively. Which of the following statements are true for magnitude of the average magnetic moment ($|m|$) and susceptibility $(d|m|/dH)_{H=0}$?

(A) $|m| = \mu \tanh(\mu H/k_B T)$, susceptibility decreases with increasing temperature

(B) $|m| = \mu \tanh(\mu H/k_B T)$, susceptibility increases with increasing temperature

(C) Average magnetic moment $= (1/2)\exp(-\mu H/k_B T)$, susceptibility = decreases with increasing temperature

(D) Average magnetic moment $= \exp(-\mu H/k_B T)$, susceptibility = decreases with temperature

17. Consider the following chemical reactions in gas phase:

Reaction 1: $H + D_2 \rightarrow HD + D$

Reaction 2: $D + H_2 \rightarrow HD + H$
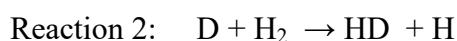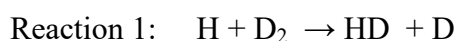
Which of the following statement is true?

(A) Reaction 1 is endothermic, Reaction 2 is endothermic

(B) Reaction 1 is endothermic, Reaction 2 is exothermic

(C) Both reactions are thermoneutral as they involve isotopes which differ by the number of neutrons, which do not play any role in chemical reactions.

(D) Reaction 1 is exothermic, Reaction 2 is exothermic

18. Consider measurement of area of a rectangle with sides 10 cm and 5 cm. If the uncertainty in the measurement in the length of the sides is 1 mm, what is the resulting uncertainty in the area? (Assume errors are uncorrelated)

(A) 2 mm^2

(B) 5 mm^2

(C) 236 mm^2

(D) 111 mm^2

19. Rank the organic amines shown below in the order of increasing pKa values.
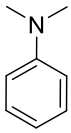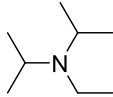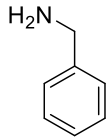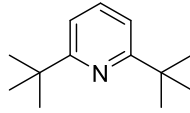
A   B   C   D

<mark>a. D < A < C < B</mark>

b. C < A < D < B

c. A < D < B < C

d. D < C < B < A

20. Viruses constitute of a protein coat encapsulating the genetic material. Methods for detecting viruses rely upon extraction of the genetic material from the viral capsid followed by polymerase chain reaction (PCR) amplification. Which of the following methods can be used to extract the genetic material from viruses?

a. heat a sample containing the virus

b. treatment with guanidinium isothiocyanate

c. treatment with detergent

<mark>d. all of the above</mark>

21. You are given an unknown organic compound X in the laboratory. The compound (molecular weight < 100 g/mol) has the following properties: 1. White crystalline volatile solid; 2. Reacts with aqueous ferric chloride to afford a violet, blue organometallic complex.

What product will be obtained if X is reacted with carbon dioxide under basic conditions under 100 atm pressure at 125 °C?

a.

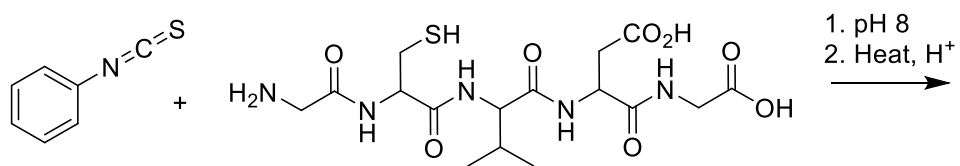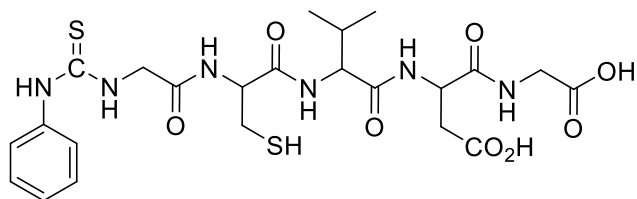CO₂H
OH

b.

CHO
CH₂OH

c.

CH₂OH
OH

d.

OH
CHO
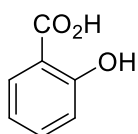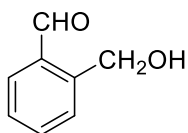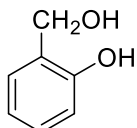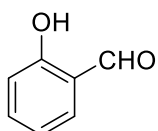
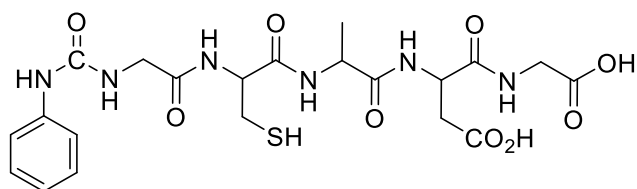22. Predict the final product/products of the following reaction.

1. pH 8
2. Heat, H⁺

a.

b.
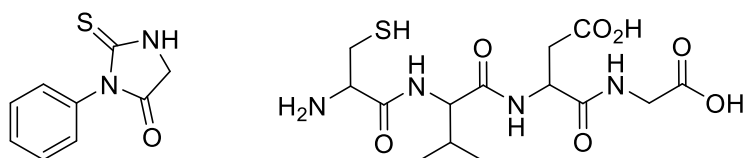
c.
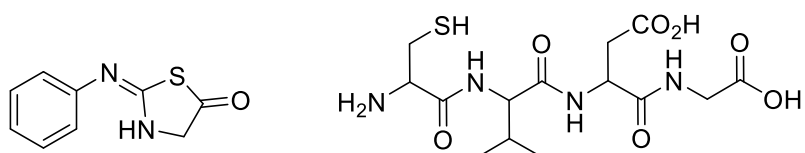
d.

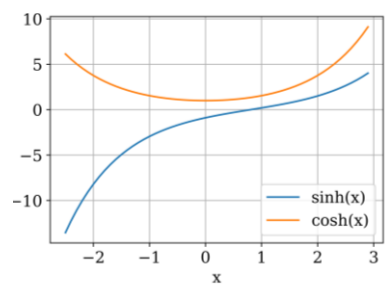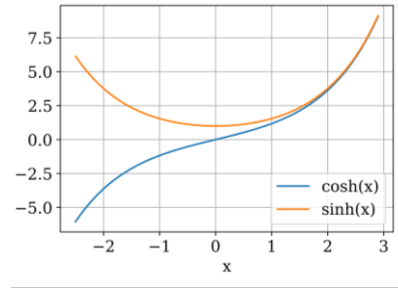23. The hyperbolic functions sinh(x) and cosh(x) are defined as follows:

$$\sinh(x) = (e^x - e^{-x})/2 \quad \text{and} \quad \cosh(x) = (e^x + e^{-x})/2$$

Which of the plots below correctly represent the above functions:
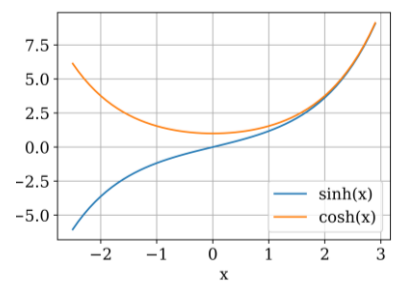
A)

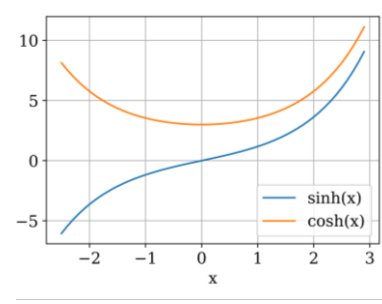B)

C)

D)

24. Evaluate $(\delta H/\delta P)_T$ for a gas whose equation of state is

Z = PV/RT = 1 + B(T)P/RT where B(T) is function of temperature
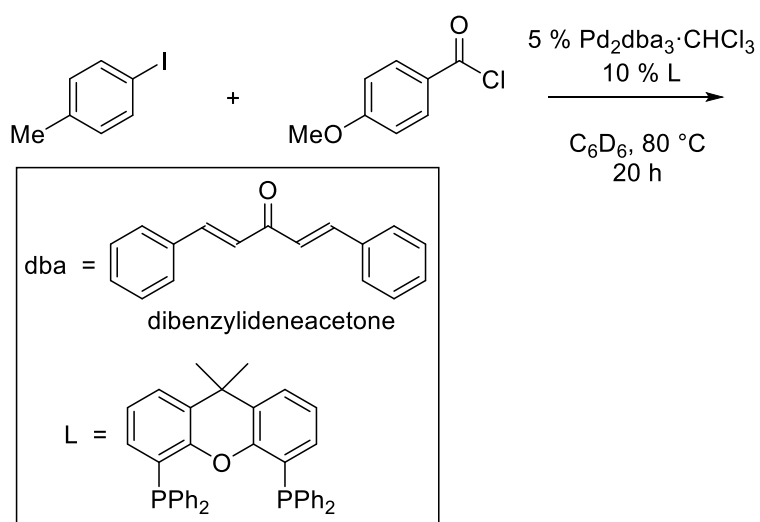
a) $(\delta H/\delta P`)_T = B(T) - T(dB/dT)$
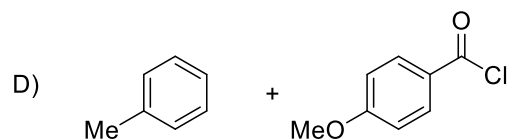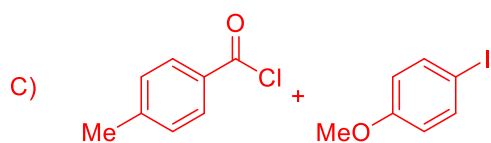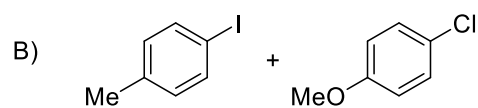
b) $(\delta H/\delta P)_T = T(dB/dT)$

c) $(\delta H/\delta P)_T = 0$

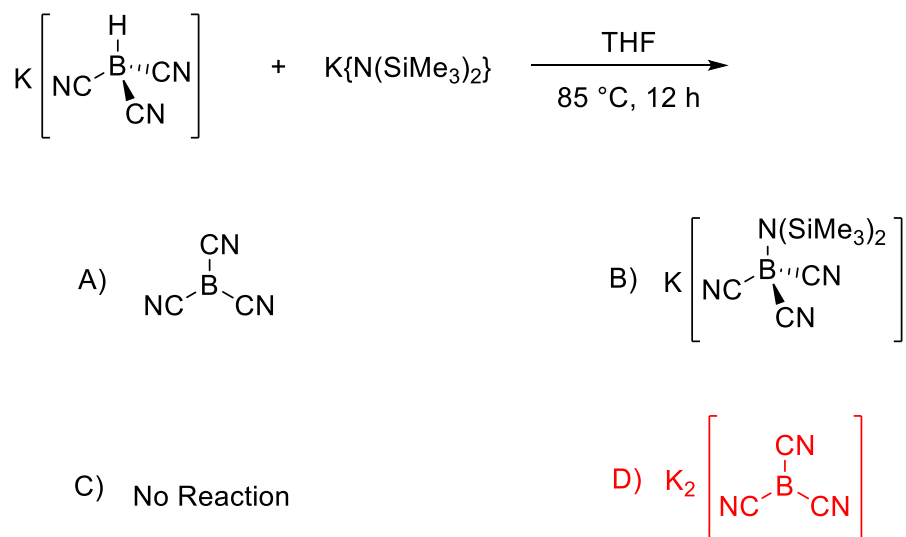d) $(\delta H/\delta P)_T = T^2(\delta^2 B/\delta T^2)$
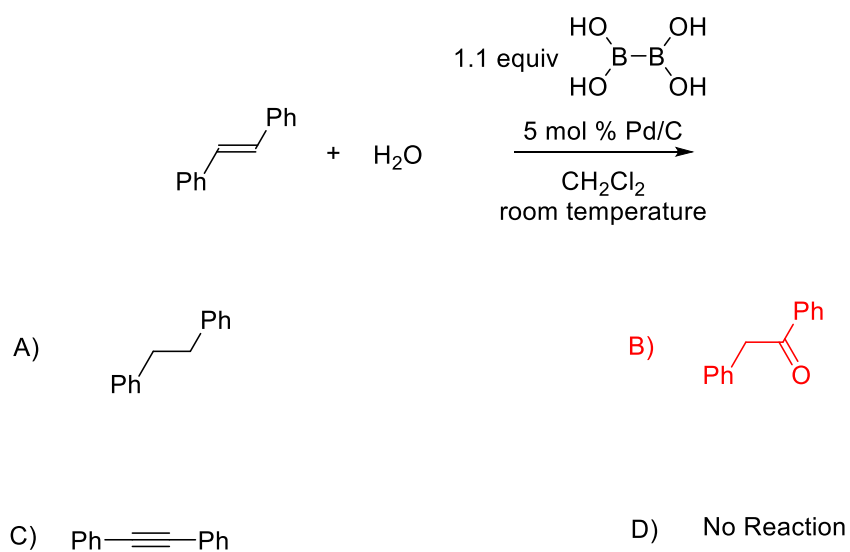
25. Predict the product of the following reaction.

A)   No Reaction

B)

C)

D)

26. Predict the product of the following reaction.

$$K\left[\ NC-\underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{B}}{}^{\cdots}CN\ \right] \quad + \quad K\{N(SiMe_3)_2\} \quad \xrightarrow[85\ °C,\ 12\ h]{THF}$$

A) $$NC-\underset{}{\overset{\overset{CN}{|}}{B}}-CN$$

B) $$K\left[\ NC-\underset{\underset{CN}{|}}{\overset{\overset{N(SiMe_3)_2}{|}}{B}}{}^{\cdots}CN\ \right]$$

C) No Reaction

D) $$K_2\left[\ NC-\underset{}{\overset{\overset{CN}{|}}{B}}{}^{\diagdown}CN\ \right]$$

27. Predict the product of the following reaction.

$$\underset{Ph}{\overset{Ph}{\diagup}}\diagup \quad + \quad H_2O \quad \xrightarrow[\substack{CH_2Cl_2 \\ room\ temperature}]{\substack{1.1\ equiv\ \ \underset{HO}{\overset{HO}{\diagdown}}B-B\underset{OH}{\overset{OH}{\diagup}} \\ 5\ mol\ \%\ Pd/C}}$$

A) $$\underset{Ph}{\diagup}\diagup\overset{Ph}{\diagdown}$$

B) $$\underset{Ph}{\diagup}\underset{O}{\overset{Ph}{\diagdown}}$$

C) Ph≡Ph

D) No Reaction

28. Predict the product of the following reaction.

A) 2 B—H + 0.5 O_2

B) + H_2

C)
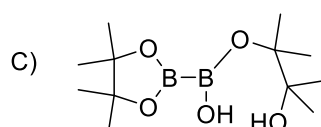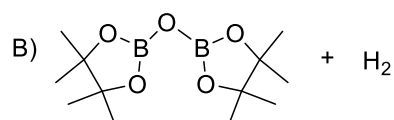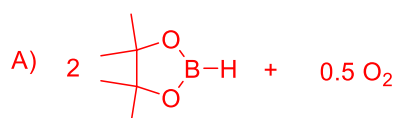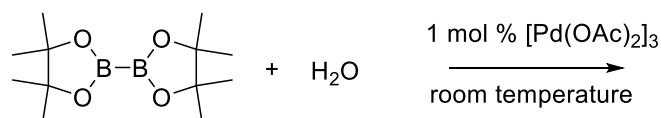
D) No Reaction

29. The change of entropy ΔS for an isothermal expansion from $V`_1$ to $V`_2$ for a gas that obeys the equation of state $P(V-b) = RT$ is given by

a) $\Delta S = R\ln(V`_2 - b/V`_1 - b)$

b) $\Delta S = R\ln(V_1/V_2)$

c) $\Delta S = 0$

d) $\Delta S = R\ln b$

30. During the electrolysis of aqueous KCl solution using inert electrodes, gaseous hydrogen is evolved at one electrode and gaseous chlorine at the other electrode. Which one of the following statements is correct?

(a) Hydrogen is forming at the anode due to water reduction ($2H_2O + 2e^- = H_2 + 2OH^-$)

(b) At the negative electrode, water oxidation is taking place ($2 H_2O = O_2 + 4H^+ + 4e^-$)

(c) The solution around the cathode becomes basic as the electrolysis proceeds

(d) At the negative electrode, electrons flow from the electrode to the external circuit

31. The addition of HCl to 1-butene and 2-butene gives the same product, the rate of 1-butene reaction is faster due to..
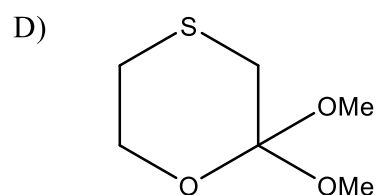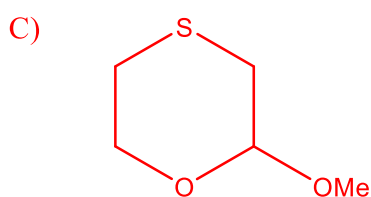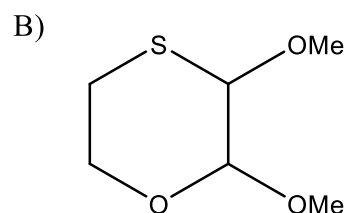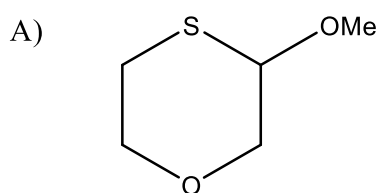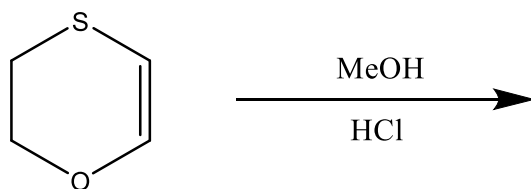
A) 2-butene is energetically higher than 1-butene

B) 1-butene is energetically higher than 2-butene

C) Nucleophilic attach of Cl⁻ is hindered

D) Formation of more stable carbocation by 1-butene

32. Predict the major product of the following reaction.

A)

B)

C)

D)

33. A molecule has two isomers A and B. When pure A is prepared at the initial time, there is an exponential decay of the isomer A and concomitant rise of the B-form. The time constant for the decay is 100 minutes. After a long time we find 50% of A-form and 50% of B-form. After the equilibrium is reached, we follow one molecule of the B-form for one whole day. Which of the following will we likely observe?

A) The molecule remains in B-form

B) The molecule has become A

C) <mark>There is equal probability to find the molecule either in the A-form or in the B-form</mark>

D) There is inadequate data given in the problem to make any prediction

34. A 100 amino acid sequence of a protein contains only Phenylalanine, Valine, Leucine, Isoleucine, Proline, Alanine and Tryptophan. Which of the following statements is do you expect to be true?
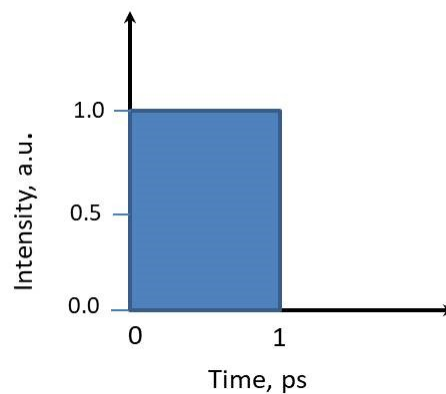
A) The protein will be very soluble in aqueous buffer and will have reasonable absorbance at 370 nm.

B) Relatively insoluble in aqueous buffer and absorb well at 370 nm

C) Very soluble in aqueous buffer and absorb well at 270 nm

D) <mark>Rather insoluble in aqueous buffer and absorb well at 270 nm</mark>

35. Suppose you want to produce the following laser pulse:

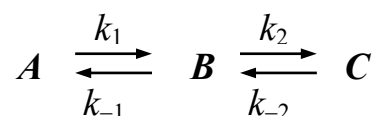What range of light frequency will you need for constructing the pulse?

A) Single frequency at 10^{12} Hz

B) A range of frequencies from 0 to 10^{12} Hz

C) A range of frequencies from 0.5 to 10^{12} Hz

D) <mark>An infinite range of frequencies</mark>

36. Formation of **C** from **A** is theoretically expected to obey the following kinetic scheme.

$$A \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; B \; \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \; C$$

An experimentalist wants to verify the above scheme, but can observe and measure the concentration of only **A** or **C**. Is it possible that under certain conditions, the measurements of [**A**] or [**C**] as function of time would lead the experimenter to conclude that the kinetic scheme is as given below, and that the species **B** is absent?

$$A \; \underset{k_{-obs}}{\overset{k_{obs}}{\rightleftharpoons}} \; C$$
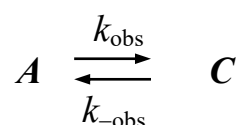
(A) No, that is not possible.

(B) Yes, if $k_{-1} \gg k_1$ and $k_{-2} \gg k_2$.

(C) Yes, if $\dfrac{k_1}{k_{-1}} = \dfrac{k_2}{k_{-2}}$.

(D) Yes, if [B] attains a steady-state concentration during the experiment.

37. Predict the order of reactivity of the organometallic compounds $MeTiCl_3$ towards the following sets of ligands NMe3, PMe3, SMe2

a) PMe3>NMe3>SMe2
b) NMe3>SMe2>PMe3
c) NMe3>PMe3>SMe2
d) NMe2=PMe3>SMe2

38. An isomer of the complex $Co(en)_2(H_2O)Cl_2Br$, on reaction with concentrated H_2SO_4 (dehydrating agent) suffers loss in weight and on reaction with $AgNO_3$ solution gives a white precipitate, which is soluble in $NH_3(aq)$. The correct formula of the complex is:

(a) $[CoCl_2Br(en)(H_2O)](en)$

(b) $[CoCl(en)_2(H_2O)]BrCl$

(c) $[CoBr(en)_2(H_2O)]Cl_2$

(d) $[CoBrCl(en)_2]Cl.H_2O$

39. Suppose 10% of the population is infected with SARS-CoV-2 virus. There are 100 hospitals that each randomly tested 5 people. What percentage of hospitals will find no cases, and wrongly conclude the virus has disappeared?
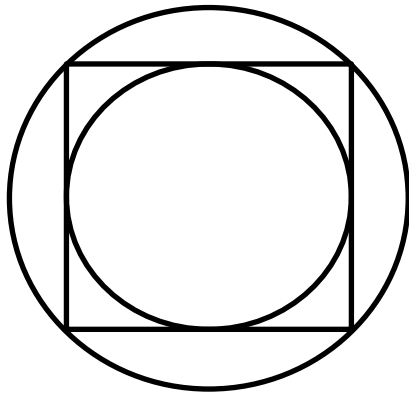
a) 10%

b) 5%

c) 60%

d) 40%

40. What is the ratio of areas of outer circle and inner circle?

a) 4

b) 2

c) sqrt(2)

d) 2*sqrt(2)