1. $(Ph_3P)_3RhCl$ is a hydrogenation catalyst. Replacing all the PPh_3 ligands with PEt_3 diminishes the catalytic activity of the Rh compound. Following is the correct reason for the loss of catalytic activity.

A) Replacing PPh_3 with PEt_3 makes a 18 electron compound

B) PEt_3 is highly reactive and perform side reaction

C) Smaller cone angle of PEt_3 allows stabilization and hence dissociation of Rh-PEt_3 bond becomes difficult

D) Replacing PPh_3 with PEt_3 makes a 16 electron compound
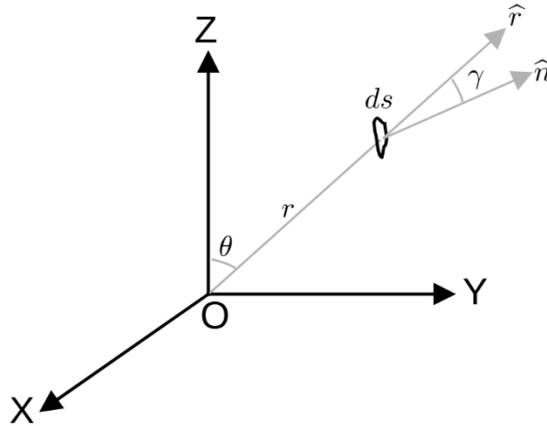
2. The point group of $Xe(O)F_4$ is

A) D_{4d}
B) D_{4h}
C) C_{4h}
D) C_{4v}

3. Consider a small area element (with area $= ds$) placed at a distance r from the origin (see diagram below). Here, $\hat{n}$ is a unit vector pointing in a direction normal to the area element ds, which is at an angle γ with the radial direction (denoted by $\hat{r}$), and θ is the angle with the z-axis. What is the correct expression of solid angle $d\Omega$ associated with this area element?
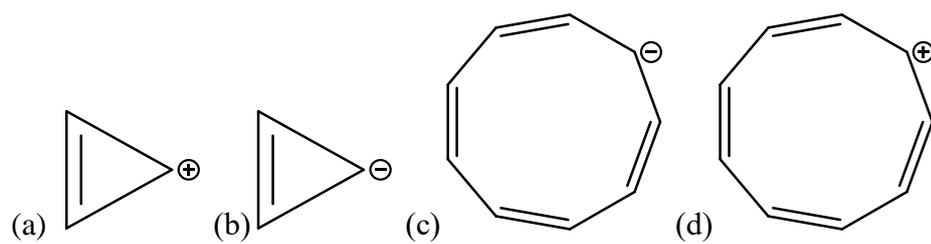

A) $d\Omega = ds \dfrac{cos(\gamma)}{r^2}$

B) $d\Omega = ds \dfrac{cos(\theta)}{r^2}$

C) $d\Omega = ds \dfrac{cos(\theta)sin(\gamma)}{r^2}$

D) $d\Omega = ds \dfrac{cos(\gamma)}{4\pi r^2}$

4. Which of the following are Hückel aromatic?

(a) (cyclopropenyl cation) ⊕   (b) (cyclopropenyl anion) ⊖   (c) (cyclooctatrienyl anion) ⊖   (d) (cyclooctatrienyl cation) ⊕

A) (a), (c)

B) (b), (c)

C) (b), (d)

D) (a), (d)

5. Consider an ensemble of atoms with two electronic energy levels involved in a laser. As a first step of the lasing process, a population inversion is done. What can one say about the formal absolute temperature of this population inverted ensemble state?

    A) temperature cannot be defined
    B) temperature is infinity
    C) temperature is negative
    D) temperature is 0

6. Consider a vector $\vec{A}$ in a X-Y coordinate system. If the coordinate system is rotated by an angle θ, $X, Y, \vec{A}$ transform to $X', Y', \vec{A}'$ (see diagram below). Which of the below expression describes the correct relation among the horizontal and vertical components of $\vec{A}$ in the new and old coordinates?
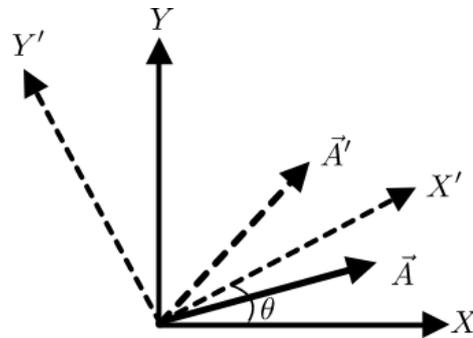
A) $\begin{bmatrix} A'_x \\ A'_y \end{bmatrix} = \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} A_x \\ A_y \end{bmatrix}$

B) $\begin{bmatrix} A'_x \\ A'_y \end{bmatrix} = \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} A_x \\ A_y \end{bmatrix}$

C) $\begin{bmatrix} A'_x \\ A'_y \end{bmatrix} = \begin{bmatrix} -\cos(\theta) & \sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} A_x \\ A_y \end{bmatrix}$

D) $\begin{bmatrix} A_x \\ A_y \end{bmatrix} = \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} A'_x \\ A'_y \end{bmatrix}$

Due to an ambiguity in the question, there is a possibility of multiple interpretations. Consequently, both (a) and (d) are acceptable answers

7. Why do gold nanoparticles show melting points much lower than bulk gold?

   A) Their density is much higher than bulk gold
   B) Surface atoms have lower coordination and weaker cohesive energy
   C) Their bandgap becomes zero
   D) They contain no free electrons

8. Determine the time required for visible light to pass vertically through a 100-µm-thick polymer film when it enters at 45° and refracts at 30°?

45°

Air medium

Polymer film

30°
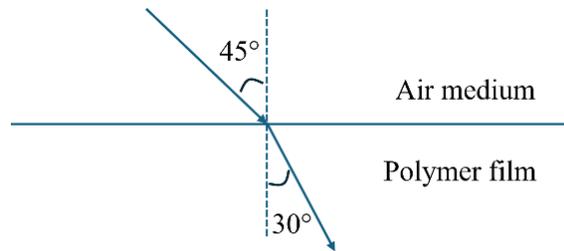
A) 471 fs

B) 544 fs

C) 333 fs

D) 500 fs

9. A species **A** decays to form **B** according to a **first-order reaction**:

$$A \xrightarrow{k} B$$
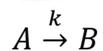
Assume the initial concentration of A is $[A]_0$ and B is absent initially. (a) The time-dependent growth of species B is proportional to what function of time? (b) How does the time-dependent ratio of concentrations B/A vary as a function of time?

A) $(a)1\text{-}e^{-kt}$; $(b)e^{kt}$

B) $(a)1\text{-}e^{-kt}$; $(b)e^{kt}\text{-}1$

C) $(a)\ e^{kt}$; $(b)e^{-kt}\text{-}1$

D) $(a)\ e^{kt}\text{-}1\ (b)e^{-kt}$

10. Raman scattering is often seen overlapping with fluorescence emanating from the sample. However fundamentally Raman process is different from fluorescence due to which of the following:

A) Raman is a two-photon process while fluorescence is not
B) Raman scattering process has a slower timescale compared to fluorescence
C) Raman process is only about vibrational states while fluorescence deals with transitions within electronic states
D) None of the above

11. Consider a quantum mechanical particle in one dimension with a potential of the following form:

$$V(x)=\infty, x<0$$
$$V(x)=+u \sin\left(\frac{\pi x}{L}\right), 0 \leq x \leq L$$
$$V(x)=\infty, x>L$$

Which of the following options correctly represents the first order correction to the ground state energy of this particle?

A) $+\dfrac{4u}{3\pi}$

B) $-\dfrac{8u}{3\pi}$

C) $+\dfrac{8u}{3\pi}$

D) $+\dfrac{u}{\pi}$

12. Metallic silver (Ag) crystal space group is $Fm\bar{3}m$. At 25 °C, lattice parameter is 4.0862 Å. Which of the following descriptions are correct for Ag crystals?

A) BCC lattice, 2 atoms per unit cell, atomic radius is 2.0431 Å

B) BCC lattice, 4 atoms per unit cell, atomic radius is 2.0431 Å

C) FCC lattice, 4 atoms per unit cell, atomic radius is 1.44 Å

D) FCC lattice, 3 atoms per unit cell, atomic radius is 0.69 Å

13. For a van der Waals gas with parameters a and b, the critical temperature T_C is given by:

A) $\dfrac{a}{27Rb}$

B) $\dfrac{8a}{27Rb}$

C) $\dfrac{a}{8Rb}$

D) $27\dfrac{a}{Rb}$

14. What is the percent composition of a mixture of (S)-(+)-2-butanol, α= +13.52°, and (R)-(-)-2-butanol, α = -13.52°, with a specific rotation α = +6.76°?

A) 75%(R) 25%(S)
B) 25%(R) 75%(S)
C) 50%(R) 50%(S)
D) 67%(R) 33%(S)

15. A ligand substitution reaction on an octahedral metal complex shows activation parameters $\Delta H^{\ddagger}$ = +60 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −140 J mol^{-1} K^{-1}. Which mechanism is most consistent and why?

A) Dissociative (D) — TS has increased disorder
B) Associative (A) — TS is highly ordered
C) Interchange dissociative (I$_d$) — TS is modestly ordered
D) Radical — unrelated to $\Delta S^{\ddagger}$

16. Consider a single-step hydrogen atom transfer reaction: $A\text{-}H+B \rightarrow A+H\text{-}B$. If the rate constant is k_H at a temperature T, then how is the rate constant, typically, going to change if the hydrogen atom is replaced by a deuterium atom? (k_D is the rate constant for the case of deuterium transfer)

A) $k_D > k_H$
B) $k_D < k_H$
C) $k_D = k_H$
D) cannot be concluded

17. If 2 fermions are placed in 6 spin-orbitals, how many unique arrangements are possible?

    A) 12
    B) 24
    C) 15
    D) 36
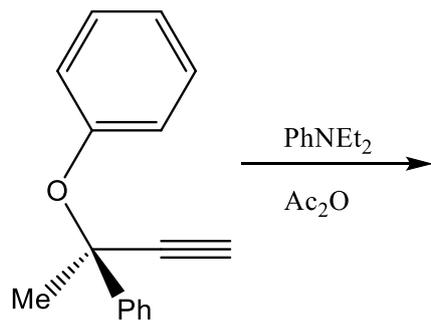
18. In the $[Ti(H_2O)_6]^{3+}$ complex

   A) All Ti-O bond distances are similar
   B) Three of the Ti-O bond distances are shorter than the other three
   C) Two of the Ti-O bond distances are longer than the other four
   D) Two of the Ti-O bond distances are shorter than the other four

19. Major product formed in the following transformation is:

i) Zn

A)

B)

C)

D) EtO₂C
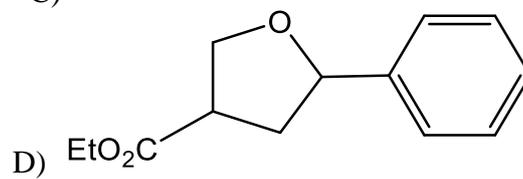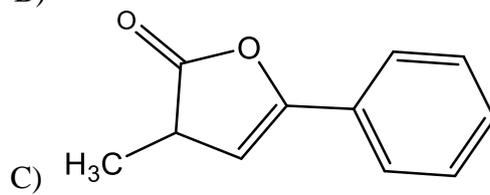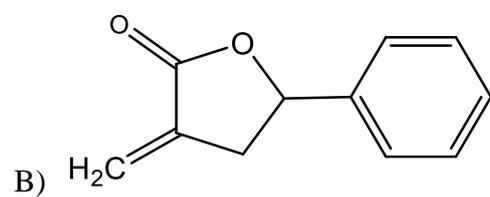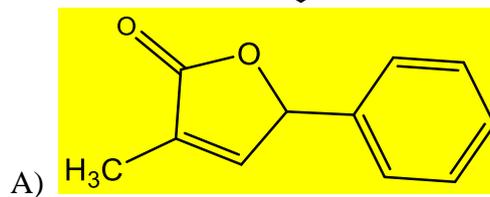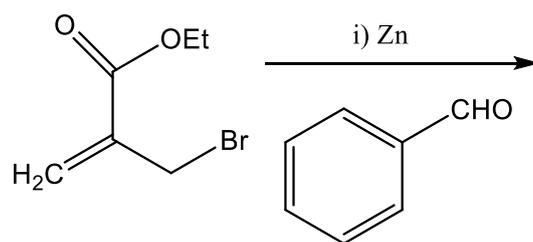
20. In the following pericyclic reaction the structure of allene formed and its configuration are

PhNEt$_2$

Ac$_2$O

Optically Pure

A) AcO, Me, C, Ph, H, R

B) AcO, Me, C, Ph, H, S

C) AcO, Ph, C, Me, H, R

D) AcO, Ph, C, Me, H, S

21. The ^{31}P NMR of phosphorus sesquisulfide, P_4S_3 reveals

   A) a singlet
   B) a singlet and a doublet
   C) a doublet and a triplet
   D) a doublet and a quartet

22. Fe(Cp)(CH$_3$P)(Et)(CO) reacts with ^{13}CO to form Fe(Cp)(CH$_3$P)(COEt)(^{13}CO). The product is symmetry inverted, because the reaction proceeds via:

A) CO insertion step
B) Ethyl migration step
C) ^{13}CO and CO exchange the position
D) None of the above

23. Consider a 1D wave-function given in the position space as $\psi(x)$. What is the result of the action of the operator $\exp\left(-\frac{ia\hat{P}}{\hbar}\right)$ on it, where $\hat{P}$ is the momentum operator?

A) $\psi(ax)$

B) $\psi(x+a)$

C) $\psi(x-a)$

D) $-a\frac{d}{dx}\psi(x)$

24. A quantum system has energy levels 0, 2ε, and 4ε. At temperature T, what is the average energy of the system?

A) $\varepsilon(1 + 2e^{\{-2\varepsilon/kT\}} + 4e^{\{-4\varepsilon/kT\}}) / (1 + e^{\{-2\varepsilon/kT\}} + e^{\{-4\varepsilon/kT\}})$

B) $2\varepsilon / (1 + e^{\{-2\varepsilon/kT\}} + e^{\{-4\varepsilon/kT\}})$

C) $\varepsilon / (1 + e^{\{-2\varepsilon/kT\}} + e^{\{-4\varepsilon/kT\}})$

D) $\varepsilon(2e^{\{-2\varepsilon/kT\}} + 4e^{\{-4\varepsilon/kT\}}) / (1 + e^{\{-2\varepsilon/kT\}} + e^{\{-4\varepsilon/kT\}})$

25. For the reaction $2NO_2(g) \rightarrow N_2O_4(g)$, ΔH = -57.2 kJ, ΔS = -175.8 J/K. At what temperature does the reaction become non-spontaneous?

A) $T > 325.37$ K
B) $T < 325.37$ K
C) $T > 175.8$ K
D) $T < 175.8$ K

26. The pKa$_1$ of carbonic acid (H$_2$CO$_3$) is 6.3 while that of bicarbonate/carbonate equilibrium (pKa$_2$) shown below is 10.3.

$$H_2CO_3 \underset{pKa_1}{\rightleftharpoons} HCO_3^- + H^+ \underset{pKa_2}{\rightleftharpoons} CO_3^{2-} + H^+$$
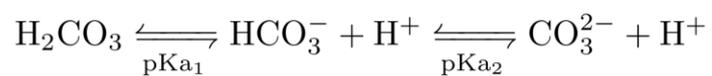
Given the above data and pK$_w$ = 14, can one predict the pH of 0.01 M sodium bicarbonate solution in water?

A) 7.5
B) 10.5
C) 8.3
D) 2.0

27. Suppose we consider the vibrational degree of freedom of a diatomic molecule to be a harmonic oscillator. Consider a pth-order spectroscopic process which couples with the vibrational dipole, what would the selection rule be? (assume the vibrational dipole to be proportional to the position of the reduced mass)

A) $\Delta n = \pm 1$
B) $\Delta n = \pm 2$
C) $\Delta n = \pm p$
D) $-p \leq \Delta n \leq p$ in steps of 2

28. Arrange the following compounds in decreasing order of acidity.
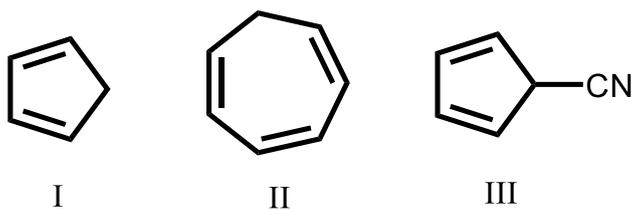
I   II   III

A) I > II > III

B) II > I > III

C) III > I > II

D) II > III > I

29. In the cluster $[Co_3(CH)(CO)_9]$ obeying 18 e⁻ rule, the number of metal-metal bonds and the bridging ligands respectively, are

    A) 3 and 1 CO
    B) 0 and 3 CO
    C) 3 and 1 CH
    D) 6 and 1 CH

30. Consider the reaction of $[Co(NH_3)_5Cl]^{2+}$ with OH^- under strongly basic conditions. Which is the most consistent pathway according to the experimental evidence?

A) Direct substitution of Cl^- by OH^- (outer-sphere mechanism)

B) Deprotonation of an amine ligand to amido ($-NH_2$) followed by intramolecular substitution

C) Radical dissociation of Cl^- to form Co(III) with 5-coordinated intermediate followed by an OH^- attack

D) Concerted associative substitution via a seven-coordinated intermediate

31. Consider two 1D oscillators, the first being harmonic and the second being anharmonic, held at an inverse temperature $\beta = \frac{1}{k_B T}$. What can be said about the average kinetic energy of these two oscillators respectively?

A) $\frac{1}{2\beta}, \frac{1}{2\beta}$

B) $\frac{1}{2\beta}, \frac{3}{2\beta}$

C) $\frac{3}{2\beta}, \frac{1}{2\beta}$

D) $\frac{3}{2\beta}, \frac{3}{2\beta}$

32. In $NiFe_2O_4$, the coordination environment around nickel and iron are

A) All the nickel ions are in tetrahedral geometry, and all iron ions are in tetrahedral geometry

B) Half the nickel ions are in octahedral geometry the other half in tetrahedral geometry while the iron ions are in octahedral geometry

C) Half the iron ions are in octahedral and the other half in tetrahedral geometry while the nickel ions are in tetrahedral geometry

D) Half the iron ions are in octahedral and the other half in tetrahedral geometry while the nickel ions are in octahedral geometry

33. Consider the following graph:
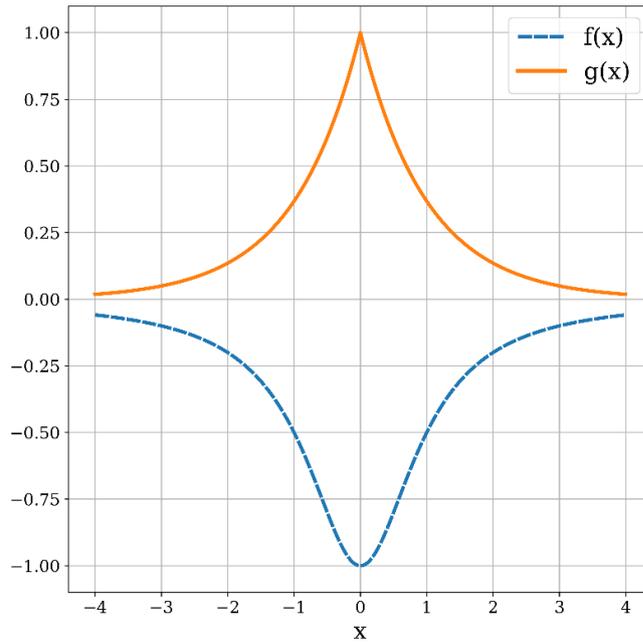
Which of the following statements is correct?

A) $f(x)=\frac{1}{1+x^2}$ and $g(x)=e^{-|x|}$

B) $f(x)=-\frac{1}{1+x^2}$ and $g(x)=e^{-|x|}$

C) $f(x)=-\frac{1}{1+x^2}$ and $g(x)=e^{|x|}$

D) $f(x)=-e^{-|x|}$ and $g(x)=\frac{-1}{1+x^2}$

34. If the partition function for a system is Z, which expression gives its average energy at temperature T?

    A) k_B T Z

B) $(\partial Z / \partial T)$

C) $-\partial(\ln Z)/\partial\beta$, where $\beta = \dfrac{1}{k_B T}$

D) $\dfrac{Z}{k_B T}$

35. Which Maxwell relation correctly links entropy (S), volume (V), temperature (T), and pressure (P)?

A) $(\partial S/\partial V)_T = (\partial P/\partial T)_V$

B) $(\partial S/\partial V)_P = (\partial T/\partial P)_S$

C) $(\partial S/\partial T)_V = (\partial V/\partial P)_S$

D) $(\partial S/\partial P)_V = -(\partial V/\partial T)_P$

36. Which of the following is true when an isolated molecule gets excited to a charge neutral excited state by visible light?

   A) Reduced ionization potential
   B) Increased ionization potential
   C) No change in ionization potential
   D) Zero ionization potential

37. In a microcanonical ensemble, which pair of quantities is held constant?

A) Pressure and Temperature
B) Volume and Temperature
C) Volume and Energy
D) Temperature and Chemical Potential

38. Consider two electrons in two different spatial orbitals whose spins are given as follows:

$$\psi_1 = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \; ; \; \psi_2 = \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}$$

where $\uparrow$ represents the up spin and $\downarrow$ represents the down spin. What can we say about the spin multiplicities of the two states?

A) Singlet; Triplet

B) Triplet; Singlet

C) Triplet; Triplet

D) Singlet; Singlet

39. In the following reaction sequence involving platinum(II) complexes:

$$[PtCl_4]^{2-} \xrightarrow[\text{Step 1}]{NH_3} [PtCl_3(NH_3)]^- \xrightarrow[\text{Step 2}]{PPh_3} [PtCl_2(NH_3)(PPh_3)]$$
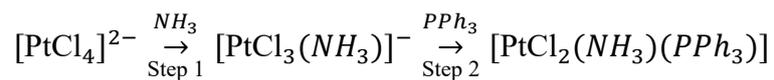
Which of the following statements correctly predicts the major isomer and the reason for its formation?

A) The trans isomer; because NH_3 has a strong trans effect and directs substitution trans to itself

B) The cis isomer; because chloride has a stronger trans effect than NH_3, promoting substitution trans to itself

C) The trans isomer; because PPh_3 replaces the ligand cis to chloride

D) The cis isomer; because both NH_3 and PPh_3 have weak trans effects.

40. In ultrafast spectroscopy, a laser pulse of shorter duration has a larger spectral bandwidth. This is because:

    A) Short pulses have higher peak intensity, which results in a broad spectrum

    B) The uncertainty principle dictates that the product of temporal and spectral widths must remain approximately constant

    C) Dispersion in optical materials compresses the pulse in time and broadens its frequency content

    D) Shorter pulses contain fewer optical cycles, reducing frequency spread