# 2021 U.S. NATIONAL <br> CHEMISTRY OLYMPIAD <br> NATIONAL EXAM PART I 

Prepared by the American Chemical Society Chemistry Olympiad Examinations Task Force

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The 2021 National Examination was modified so it could be conducted digitally. The following describes this exam as given this year. Part III was removed from the examination, and time limits remained the same for Part 1 and Part II. This file was published for record keeping purposes after the examination was complete.

The periodic table and other useful information, as shown on page 2 of this document, were included for student reference on both Part I and Part II.

National Exam Nominee agreement forms, which required students to certify that they are either U.S. citizens or permanent residents, were collected prior to the administration of Part I.
For Part I and Part II, students were permitted to use only non-programmable calculators. The use of a programmable calculator, or accessing information outside of the standard reference document, was grounds for disqualification.

Part I of this test was administered through the ACS Learning Center and consisted of 60 multiple-choice questions. Answers were entered using this system and only submitted answers were considered (i.e. no scratch paper was accepted). This test was held for the majority of students on Saturday, April 17, 2021. The time limit was one hour and thirty minutes.
Part II was administered solely to the top 200 performing students on Part I. A similar document, describing the variations in exam administration and formatted similarly to previous years, will be published separately. The time limit for this part of the exam, which included 8 questions, remained at one hour and forty-five minutes.

Invitation to take Part II did NOT signify that a student earned the honors or high honors recognitions. As always, these consider performance on the full examination.

| ABBREVIATIONS AND SYMBOLS |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| amount of substance | $n$ | Faraday constant $F$ | molar mass | M |
| ampere | A | free energy $G$ | mole | mol |
| atmosphere | atm | frequency $v$ | Planck's constant | $h$ |
| atomic mass unit | u | gas constant $\quad R$ | pressure | $P$ |
| Avogadro constant | $N_{\text {A }}$ | gram g | rate constant | $k$ |
| Celsius temperature | ${ }^{\circ} \mathrm{C}$ | hour h | reaction quotient | Q |
| centi- prefix | c | joule J | second | s |
| coulomb | C | kelvin K | speed of light | c |
| density | d | kilo- prefix k | temperature, K | $T$ |
| electromotive force | E | liter L | time | $t$ |
| energy of activation | $E_{\text {a }}$ | measure of pressure mm Hg | vapor pressure | VP |
| enthalpy | H | milli- prefix m | volt | V |
| entropy | S | molal m | volume | V |
| equilibrium constant | K | molar M | year | y |

$$
\begin{array}{||c|}
\hline \hline \text { CONSTANTS } \\
\hline R=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \\
R=0.08314 \mathrm{~L} \mathrm{bar} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \\
F=96,500 \mathrm{C} \mathrm{~mol}^{-1} \\
F=96,500 \mathrm{~J} \mathrm{~V}^{-1} \mathrm{~mol}^{-1} \\
N_{\mathrm{A}}=6.022 \times 10^{23} \mathrm{~mol}^{-1} \\
h=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}^{2} \\
c=2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1} \\
0^{\circ} \mathrm{C}=273.15 \mathrm{~K}
\end{array}
$$

$1 \mathrm{~atm}=1.013 \mathrm{bar}=760 \mathrm{~mm} \mathrm{Hg}$ Specific heat capacity of $\mathrm{H}_{2} \mathrm{O}=$ $4.184 \mathrm{~J} \mathrm{~g}^{-1} \mathrm{~K}^{-1}$

## EQUATIONS

$$
E=E^{\mathrm{o}}-\frac{R T}{n F} \ln Q \quad \ln K=\left(\frac{-\Delta H^{\circ}}{R}\right)\left(\frac{1}{T}\right)+\text { constant }
$$

$\ln \left(\frac{k_{2}}{k_{1}}\right)=\frac{E_{a}}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)$

1 PERIODIC TABEE OF THE EEEMENTS


| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | $\mathbf{Y b}$ | Lu |
| 140.1 | 140.9 | 144.2 | (145) | 150.4 | 152.0 | 157.3 | 158.9 | 162.5 | 164.9 | 167.3 | 168.9 | 173.0 | 175.0 |
| 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
| $\underset{232.0}{\text { Th }}$ | $\underset{231.0}{\mathbf{P a}_{2}}$ | $\underset{238.0}{\mathbf{U}}$ | Np <br> (237) | Pu <br> (244) | Am <br> (243) | $\underset{(247)}{\mathbf{C m}}$ | $\underset{(247)}{\mathbf{B K}}$ | $\underset{(251)}{\text { Cf }}$ | $\underset{(252)}{\text { Es }}$ | Fm <br> (257) | Md <br> (258) | $\underset{(259)}{\text { No }}$ | $\underset{(262)}{\mathbf{L r}}$ |

## DIRECTIONS

- When you have selected your answer to each question, blacken the corresponding space on the answer sheet using a soft, \#2 pencil. Make a heavy, full mark, but no stray marks. If you decide to change an answer, erase the unwanted mark very carefully.
- There is only one correct answer to each question. Any questions for which more than one response has been blackened will not be counted.
- Your score is based solely on the number of questions you answer correctly. It is to your advantage to answer every question.

1. Hydrogen and oxygen gas are combined in a reaction vessel and reacted completely to form water. What volumes of gases (at STP) will give the greatest mass of water?
(A) $1.0 \mathrm{~L} \mathrm{H}_{2}$ and $4.0 \mathrm{~L} \mathrm{O}_{2}$
(B) $2.0 \mathrm{~L} \mathrm{H}_{2}$ and $3.0 \mathrm{~L} \mathrm{O}_{2}$
(C) $3.0 \mathrm{~L} \mathrm{H}_{2}$ and $2.0 \mathrm{~L} \mathrm{O}_{2}$
(D) $4.0 \mathrm{~L} \mathrm{H}_{2}$ and $1.0 \mathrm{~L} \mathrm{O}_{2}$
2. Potassium hydrogen phthalate (KHP, $M=204$ ) is a monoprotic acid used as a primary standard in acid-base titrations. It takes 28.15 mL of a solution of $\mathrm{Sr}(\mathrm{OH})_{2}$ to neutralize 0.402 g KHP. What is the concentration of the $\mathrm{Sr}(\mathrm{OH})_{2}$ solution?
(A) 0.00197 M
(B) 0.0350 M
(C) 0.0700 M
(D) 0.100 M
3. 20.0 mL of 0.15 M aqueous $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ and 10.0 mL of 0.35 M aqueous NaBr are mixed, giving a white precipitate. Which ion is LEAST abundant in the supernatant?
(A) $\mathrm{Pb}^{2+}$
(B) $\mathrm{Na}^{+}$
(C) $\mathrm{NO}_{3}^{-}$
(D) $\mathrm{Br}^{-}$
4. A sample of 9.736 g of a lead oxide is reduced completely with excess carbon monoxide to give metallic lead. The resulting gas is bubbled into saturated lime water, resulting in the precipitation of 6.636 g calcium carbonate ( $M=100.09$ ) after drying. What is the formula of this lead oxide?
(A) PbO
(B) $\mathrm{Pb}_{2} \mathrm{O}_{3}$
(C) $\mathrm{Pb}_{3} \mathrm{O}_{4}$
(D) $\mathrm{Pb}_{12} \mathrm{O}_{19}$
5. A mixture of $\mathrm{K}_{2} \mathrm{~S}, \mathrm{~K}_{2} \mathrm{SO}_{3}$, and $\mathrm{K}_{2} \mathrm{SO}_{4}$ is found to contain $60.0 \% \mathrm{~K}$ by mass. What is the mass percent of oxygen in the mixture?
(A) $15.4 \%$
(B) $22.3 \%$
(C) $30.3 \%$
(D) $36.7 \%$
6. A solution of 5.00 g oxalic acid $\left(\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}, M=90.04\right)$ in $100.0 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}$ has a freezing point of $-1.31^{\circ} \mathrm{C}$. What is the percent ionization of oxalic acid in this solution? The freezing point depression constant of water is $K_{\mathrm{f}}=1.86{ }^{\circ} \mathrm{C} \mathrm{m}^{-1}$.
(A) $13.5 \%$
(B) $26.8 \%$
(C) 70.4\%
(D) $100 \%$
7. Which glassware would be most appropriate for measuring 10.00 mL of distilled water?
(A) A $10-\mathrm{mL}$ test tube
(B) A 25-mL beaker
(C) A 50-mL buret
(D) A 100-mL graduated cylinder
8. A solution that may contain either $0.1 \mathrm{M} \mathrm{Ag}^{+}(a q), 0.1 \mathrm{M}$ $\mathrm{Pb}^{2+}(a q)$, or both, is treated with 1 M aqueous HCl . A white precipitate forms which does not appear to dissolve in hot water. Which conclusion about the cations present may be drawn?
(A) Only $\mathrm{Ag}^{+}$is present.
(B) Only $\mathrm{Pb}^{2+}$ is present.
(C) $\mathrm{Ag}^{+}$is present, and $\mathrm{Pb}^{2+}$ may be present.
(D) $\mathrm{Pb}^{2+}$ is present, and $\mathrm{Ag}^{+}$may be present.
9. Addition of 10 mL of distilled water to 0.1 g of which salt produces a yellow, slightly cloudy solution?
(A) $\mathrm{KMnO}_{4}$
(B) $\mathrm{FeCl}_{3}$
(C) $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2}$
(D) $\mathrm{CuSO}_{4}$
10. The amount of ascorbic acid in a vitamin $C$ tablet is determined by titration with a solution of iodine in aqueous potassium iodide. A small amount of starch is added to the vitamin $C$ solution before the titration. What is the function of the starch?
(A) It forms an intensely colored complex with triiodide ion.
(B) It increases the viscosity of the analyte solution.
(C) It catalyzes the dissociation of triiodide into iodine and iodide.
(D) It binds to the inert ingredients of the vitamin C tablet.
11. When blue solid $\mathrm{CuSO}_{4} \bullet 5 \mathrm{H}_{2} \mathrm{O}$ is heated, it turns white. Which is the best explanation for this observation?
(A) Heating causes water molecules bonded to copper to be replaced by sulfate, lowering the energy of the light absorbed.
(B) Heating causes an expansion of the lattice, leading to a decrease in the coordination number of copper and raising the energy of the light absorbed.
(C) Heating causes reduction of copper(II) to copper(I).
(D) Heating causes reduction of sulfate to sulfite.
12. A student performs an experiment to determine the concentration of a colored salt solution by measuring the absorbance of the solution at the wavelength of maximum absorbance of the salt ( $\lambda_{\max }$ ) and using Beer's Law to calculate the concentration. Which of the following could cause the measured concentration to be higher than the actual concentration?
(A) The cuvette is not rinsed with the salt solution after being washed.
(B) The cuvette is not wiped off before it is inserted into the spectrophotometer.
(C) Less than the recommended volume of salt solution is added to the cuvette.
(D) The spectrometer is set to a wavelength different from $\lambda_{\text {max }}$.
13. Which $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}$ isomer has the lowest normal boiling point?
(A)

(B)

(C)

(D)

14. Dichloromethane $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, M=84.93\right)$ is a volatile liquid with a vapor pressure of 0.53 atm at $24^{\circ} \mathrm{C} .13 .8 \mathrm{~g}$ of dichloromethane is introduced into a $5.0-\mathrm{L}$ evacuated container maintained at $24^{\circ} \mathrm{C}$. Which is the best description of the system at equilibrium?
(A) One-third of the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ has evaporated.
(B) Two-thirds of the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ has evaporated.
(C) All of the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ has evaporated to give a pressure of 0.53 atm .
(D) All of the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ has evaporated to give a pressure of 0.79 atm .
15. A piece of solid $\mathrm{CO}_{2}$ initially at $-78^{\circ} \mathrm{C}$ is placed in a small plastic container, which is then sealed and allowed to warm up in a room whose temperature is $22^{\circ} \mathrm{C}$. Ultimately the plastic container explodes, ending any further observations. Which statement best describes the possibility of observing liquid $\mathrm{CO}_{2}$ before the container explodes? (The phase diagram of $\mathrm{CO}_{2}$ is shown below.)

(A) Liquid $\mathrm{CO}_{2}$ must be observable, since the explosion is driven by hydrostatic pressure of liquid $\mathrm{CO}_{2}$.
(B) Liquid $\mathrm{CO}_{2}$ may be observed, since the triple point may be reached during this experiment.
(C) Liquid $\mathrm{CO}_{2}$ may not be observed, since only sublimation of solid $\mathrm{CO}_{2}$ is possible under the conditions of the experiment.
(D) Liquid $\mathrm{CO}_{2}$ may not be observed, but supercritical $\mathrm{CO}_{2}$ may be observed.
16. A solid calcium boride $\mathrm{CaB}_{x}$ has a density of $2.45 \mathrm{~g} \mathrm{~cm}^{-3}$. It has a primitive cubic lattice with an edge length $a=$ 415 pm and with one calcium atom per unit cell. What is the value of $x$ ?
(A) 2
(B) 4
(C) 6
(D) 8
17. The lattice enthalpy of $\mathrm{Na}_{2} \mathrm{O}$ is $-2600 \mathrm{~kJ} \mathrm{~mol}^{-1}$ while the lattice enthalpy of MgO is $-3900 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Which factors contribute to the larger magnitude of the lattice enthalpy of MgO ?
I. $\mathrm{Mg}^{2+}$ has a larger charge than $\mathrm{Na}^{+}$.
II. $\mathrm{Mg}^{2+}$ is smaller than $\mathrm{Na}^{+}$.
(A) I only
(B) II only
(C) Both I and II
(D) Neither I nor II
18. A sample of benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)$ is heated at a constant rate. Which graph most accurately represents how the temperature changes with time?

(B)

(C)

(D)

19. An insulated container holds 100.0 g of water at $25.0^{\circ} \mathrm{C}$. A 100.0 g piece of copper at $50.0^{\circ} \mathrm{C}$ is added to the container. What is the final temperature of the mixture in the container at equilibrium? The specific heat capacity of copper is $0.385 \mathrm{~J} \mathrm{~g}^{-1} \mathrm{~K}^{-1}$.
(A) $27.1^{\circ} \mathrm{C}$
(B) $27.5^{\circ} \mathrm{C}$
(C) $34.9^{\circ} \mathrm{C}$
(D) $37.5^{\circ} \mathrm{C}$
20. At the triple point of water $\left(0.01^{\circ} \mathrm{C}, 0.006 \mathrm{~atm}\right)$, in which phase would 1.0 mol of water have the lowest entropy?
(A) Solid
(B) Liquid
(C) Gas
(D) It would have the same entropy in all three phases.
21. The standard enthalpy of formation of $\mathrm{NO}_{2}(g)$ is 33.1 $\mathrm{kJ} \mathrm{mol}^{-1}$. What is the average bond dissociation enthalpy of a nitrogen-oxygen bond in $\mathrm{NO}_{2}(\mathrm{~g})$ ?

| Bond | Bond dissociation enthalpy, $\mathrm{kJ} \mathrm{mol}^{-1}$ |
| :---: | :---: |
| $\mathrm{~N} \equiv \mathrm{~N}$ | 945.4 |
| $\mathrm{O}=\mathrm{O}$ | 498.4 |

(A) $469.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(B) $502.1 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(C) $705.4 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(D) $738.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$
22. The formation of ammonia from nitrogen and hydrogen has a standard free energy change of $-32.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ at 298 K.

$$
\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \rightarrow 2 \mathrm{NH}_{3}(g) \quad \Delta G^{\circ}=-32.8 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

What is $\Delta G$ at 298 K if the partial pressures of all three gases are 3.00 bar?
(A) $-30.1 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(B) $-32.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(C) $-35.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(D) $-38.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$
23. What is $K_{p}$ for the dissociation of $\mathrm{PCl}_{5}(g)$ at 298 K ?

$$
\operatorname{PCl}_{5}(g) \rightarrow \mathrm{PCl}_{3}(g)+\mathrm{Cl}_{2}(g) \quad K_{p}=\text { ??? }
$$

| Substance | $\Delta G^{\circ}, \mathrm{kJ} \mathrm{mol}^{-1}$ |
| :---: | :---: |
| $\mathrm{PCl}_{5}(\mathrm{~g})$ | -325 |
| $\mathrm{PCl}_{3}(\mathrm{~g})$ | -286 |

(A) $1.8 \times 10^{-16}$
(B) $5.9 \times 10^{-11}$
(C) $6.0 \times 10^{-9}$
(D) $1.5 \times 10^{-7}$
24. A reaction has $K_{\text {eq }}=0.10$ at 300 K and $K_{\text {eq }}=0.50$ at 330 K. Which statements about this reaction in this temperature range must be correct?
I. $\Delta H^{\circ}{ }_{\mathrm{rxn}}>0$
II. $\Delta S^{\circ}{ }_{\mathrm{rxn}}>0$
(A) I only
(B) II only
(C) Both I and II
(D) Neither I nor II
25. The time course of a reaction in which a reactant $R$ is converted to a product P is shown below. Which statements about the reaction are correct?
I. The reaction is first order in $R$.
II. Two moles of P are formed for every mole of R that reacts.

(A) I only
(B) II only
(C) Both I and II
(D) Neither I nor II
26. In a reaction $\mathrm{A}+2 \mathrm{~B} \rightarrow \mathrm{C}+\mathrm{D}$, initial rates were measured as shown in the table. What is the initial rate of the reaction with $[\mathrm{A}]_{0}=0.200 \mathrm{M}$ and $[\mathrm{B}]_{0}=0.400 \mathrm{M}$ ?

| $[\mathrm{A}]_{0}, \mathrm{M}$ | $[\mathrm{B}]_{0}, \mathrm{M}$ | Initial rate, $\mathrm{M} \mathrm{s}^{-1}$ |
| :---: | :---: | :---: |
| 0.120 | 0.300 | $1.80 \times 10^{-5}$ |
| 0.180 | 0.450 | $4.05 \times 10^{-5}$ |
| 0.080 | 0.200 | $8.00 \times 10^{-6}$ |
| 0.200 | 0.400 | $? ? ?$ |

(A) $3.20 \times 10^{-5} \mathrm{M} \mathrm{s}^{-1}$
(B) $4.00 \times 10^{-5} \mathrm{M} \mathrm{s}^{-1}$
(C) $5.00 \times 10^{-5} \mathrm{M} \mathrm{s}^{-1}$
(D) It cannot be determined from the information given.
27. The temperature-dependence of the rate constants of a series of six related reactions are studied, and the reactions are all found to have the same rate constant at 370 K (their isokinetic temperature). Which statement best describes the relationship between the reactions' Arrhenius pre-factors $A$ and their activation energies $E_{a}$ ?
(A) The reactions share a common pre-factor $A$ but differ in their activation energies $E_{\mathrm{a}}$.
(B) The reactions share a common activation energy $E_{\mathrm{a}}$ but differ in their pre-factors $A$.
(C) As the reactions' pre-factors $A$ increase, their activation energies $E_{\mathrm{a}}$ increase.
(D) As the reactions' pre-factors $A$ increase, their activation energies $E_{\mathrm{a}}$ decrease.
28. Which properties of the reaction whose reaction coordinate is shown below increase with increasing temperature?

I. The forward rate constant of the reaction, $k_{f}$
II. The equilibrium constant of the reaction, $K_{e q}$
(A) I only
(B) II only
(C) Both I and II
(D) Neither I nor II
29. The hydrolysis of formamide to formate ion in basic aqueous solution is proposed to proceed by the following steps:

$$
\begin{array}{cr}
\mathrm{HCONH}_{2}+\mathrm{OH}^{-} \leftrightarrows \mathrm{HCO}(\mathrm{OH})\left(\mathrm{NH}_{2}\right)^{-} & \text {unfavorable } \\
\mathrm{HCO}(\mathrm{OH})\left(\mathrm{NH}_{2}\right)^{-}+\mathrm{OH}^{-} \leftrightarrows & \text { fast, } \\
\mathrm{HCO}_{2}\left(\mathrm{NH}_{2}\right)^{2-}+\mathrm{H}_{2} \mathrm{O} & \text { unfavorable } \\
\mathrm{HCO}_{2}\left(\mathrm{NH}_{2}\right)^{2-} \rightarrow \mathrm{HCO}_{2}^{-}+\mathrm{NH}_{2}^{-} & \text {irreversible } \\
\mathrm{NH}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{NH}_{3}+\mathrm{OH}^{-} & \text {fast, } \\
\text { favorable }
\end{array}
$$

Which of the following statements is necessarily true, given this mechanism?
(A) The reaction is first-order in $\mathrm{HCONH}_{2}$.
(B) The reaction is first-order in hydroxide ion.
(C) $\mathrm{HCO}_{2}^{-}$is an intermediate in this reaction.
(D) If the reaction is carried out in deuterium oxide, the formate ion will contain deuterium.
30. An irreversible reaction $A+B \rightarrow C$ is first-order in both $A$ and $B$. In a solution with $[A]_{0}=0.20 \mathrm{M}$, it takes 37 s for the concentration of B to decrease from its initial value of 0.010 M to 0.0050 M . How long will it take the concentration of B to decrease from an initial value of 0.010 M to 0.0050 M if the initial concentration of A is 0.010 M ?
(A) 37 s
(B) 110 s
(C) 740 s
(D) 1100 s
31. What is the percent ionization of a 0.10 M solution of nitrous acid $\left(\mathrm{HNO}_{2}, K_{\mathrm{a}}=7.2 \times 10^{-4}\right)$ ?
(A) $1.1 \%$
(B) $3.6 \%$
(C) $8.1 \%$
(D) $14 \%$
32. The reaction mixture below represents the reaction $\mathrm{A}_{2}(g)+\mathrm{B}_{2}(g) \leftrightarrows 2 \mathrm{AB}(g)$ with $K_{\text {eq }}=2.5$. Which statement correctly describes the situation?

(A) The reaction is at equilibrium.
(B) The reaction will shift to produce more products.
(C) The reaction will shift to produce more reactants.
(D) Not enough information is given to make a prediction.
33. The hydrogenation of carbon monoxide represented below is exothermic.

$$
\mathrm{CO}(g)+2 \mathrm{H}_{2}(g) \leftrightarrows \mathrm{CH}_{3} \mathrm{OH}(l) \quad \Delta H_{\mathrm{rxn}}^{\circ}<0
$$

Which changes will increase the equilibrium yield of $\mathrm{CH}_{3} \mathrm{OH}$ ?
I. Increasing the temperature of the system
II. Removing some of the $\mathrm{CH}_{3} \mathrm{OH}(\mathrm{l})$
(A) I only
(B) II only
(C) Both I and II
(D) Neither I nor II
34. To a solution that is 0.010 M each in fluoride, sulfite, and phosphate ions is added dropwise a 1.00 M solution of $\mathrm{CaCl}_{2}$. In what order will the solids precipitate?

| Solid | $K_{\text {sp }}$ |
| :---: | :---: |
| $\mathrm{CaSO}_{3}$ | $6.8 \times 10^{-8}$ |
| $\mathrm{CaF}_{2}$ | $5.3 \times 10^{-9}$ |
| $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$ | $1.0 \times 10^{-25}$ |

(A) First $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$, then $\mathrm{CaF}_{2}$, last $\mathrm{CaSO}_{3}$
(B) First $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$, then $\mathrm{CaSO}_{3}$, last $\mathrm{CaF}_{2}$
(C) First $\mathrm{CaSO}_{3}$, then $\mathrm{CaF}_{2}$, last $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$
(D) First $\mathrm{CaF}_{2}$, then $\mathrm{CaSO}_{3}$, last $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$
35. The graph shows the logarithm of the molar solubility $S$ of an ionic solid as a function of pH . Which solid is it?

(A) $\mathrm{Ag}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$
(B) $\mathrm{AlPO}_{4}$
(C) $\mathrm{SrSO}_{4}$
(D) $\mathrm{BaF}_{2}$
36. Some solid silver nitrate is dissolved in 100.0 mL of 1.00 $\mathrm{M} \mathrm{HH}_{3}$ solution. To this solution, 50.0 mL of 1.00 M NaCl solution must be added to see the first sign of cloudiness. How much $\mathrm{AgNO}_{3}$ was present? The $K_{\text {sp }}$ of AgCl is $1.8 \times 10^{-10}$ and the $K_{\mathrm{f}}$ of $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}$is $1.0 \times 10^{8}$.
(A) $8.1 \times 10^{-11} \mathrm{~mol}$
(B) $2.1 \times 10^{-3} \mathrm{~mol}$
(C) $3.2 \times 10^{-3} \mathrm{~mol}$
(D) $4.9 \times 10^{-3} \mathrm{~mol}$
37. In basic solution, $\mathrm{Cl}_{2}(g)$ disproportionates to form $\mathrm{Cl}^{-}(a q)$ and $\mathrm{ClO}_{3}-(a q)$. What is the mole ratio of $\mathrm{Cl}^{-}(a q)$ to $\mathrm{ClO}_{3}^{-}$ $(a q)$ produced in this reaction?
(A) $5: 1$
(B) $4: 1$
(C) $3: 1$
(D) $3: 2$
38. What are the oxidation states of the sulfur atoms in the thiosulfate ion, $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ ?
(A) Both sulfur atoms have an oxidation state of +2 .
(B) Both sulfur atoms have an oxidation state of +3 .
(C) One sulfur atom has an oxidation state of +5 and one has an oxidation state of -1 .
(D) One sulfur atom has an oxidation state of +6 and one has an oxidation state of -2 .
39. A new electrode material is being tested for its ability to selectively reduce oxygen gas to hydrogen peroxide. After running an electrolytic cell using this electrode for 110.0 minutes at a current of 0.150 A , the solution in the cathode compartment is analyzed and is found to contain $2.00 \times 10^{-3} \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}_{2}$. What is the percent yield of $\mathrm{H}_{2} \mathrm{O}_{2}$ based on the current passed through the cell (the faradaic yield)?
(A) 19.5\%
(B) $39.0 \%$
(C) 78.0\%
(D) $100 \%$
40. What is the $K_{\text {sp }}$ of AgI at 298 K ?

| Half-reaction | $E^{\circ}, \mathrm{V}$ |
| :---: | :---: |
| $\mathrm{Ag}^{+}(a q)+e^{-} \rightarrow \mathrm{Ag}(s)$ | +0.80 |
| $\mathrm{AgI}(s)+e^{-} \rightarrow \mathrm{Ag}(s)+\mathrm{I}^{-}(a q)$ | -0.15 |

(A) $4.8 \times 10^{-26}$
(B) $1.0 \times 10^{-22}$
(C) $8.5 \times 10^{-17}$
(D) $1.0 \times 10^{-11}$
41. In the diagram below, an electrochemical cell's anode and cathode are linked by a semi-permeable membrane that allows only water to pass. The concentrations of $\mathrm{Zn}\left(\mathrm{NO}_{3}\right)_{2}(a q)$ and $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}(a q)$ are initially each 0.10 M . Which of the following diagrams best shows the water levels in each cell at equilibrium?

(A)

(B)

(C)

(D)

42. Consider the voltaic cell below at $25^{\circ} \mathrm{C}$ with 1.00 L of solution in each half-cell. When the switch is closed, the mass of the $\mathrm{Cr}(s)$ electrode increases until the cell is fully discharged (i.e., $\Delta E=0 \mathrm{~V}$ ). If the final mass of $\operatorname{Cr}(s)$ is 24.50 g , what is $\Delta E^{\circ}$ at $25^{\circ} \mathrm{C}$ for the reaction shown below?

$$
\begin{gathered}
2 \mathrm{Cr}^{3+}(a q)+3 \mathrm{Zn}(s) \rightarrow 2 \mathrm{Cr}(s)+3 \mathrm{Zn}^{2+}(a q) \\
\Delta E^{\circ}=? ? ?
\end{gathered}
$$


(A) 0.012 V
(B) 0.018 V
(C) 0.024 V
(D) 0.054 V
43. How many orbitals are occupied by at least one electron in the ground state of a gas-phase Si atom?
(A) 3
(B) 5
(C) 7
(D) 8
44. Which transition of a hydrogen atom would involve absorbing a photon with the longest wavelength?
(A) $n=1 \rightarrow n=3$
(B) $n=2 \rightarrow n=6$
(C) $n=3 \rightarrow n=1$
(D) $n=6 \rightarrow n=2$
45. Which gas-phase ion has the greatest number of unpaired electrons in its ground state?
(A) $\mathrm{Cr}^{2+}$
(B) $\mathrm{Co}^{2+}$
(C) $\mathrm{Ni}^{2+}$
(D) $\mathrm{Zn}^{2+}$
46. The ionization energy of which element is closest to that of fluorine (F)?
(A) O
(B) Ne
(C) Cl
(D) Ar
47. By what mode does the isotope ${ }^{79}$ Se undergo radioactive decay?
(A) Alpha decay
(B) Beta decay
(C) Gamma decay
(D) Electron capture
48. Despite the fact that atomic radius generally increases with period, the palladium-chlorine distance in $\mathrm{PdCl}_{4}{ }^{2-}$ is essentially identical to the platinum-chlorine distance in $\mathrm{PtCl}_{4}{ }^{2-}(2.30 \AA)$. Which is the best explanation of why the two bond lengths are the same?
(A) The presence of the 14 lanthanides between Pd and Pt makes Pt unexpectedly small.
(B) $\mathrm{PdCl}_{4}{ }^{2-}$ is tetrahedral, while $\mathrm{PtCl}_{4}{ }^{2-}$ is square planar and so has shorter bonds than expected.
(C) The metal-chlorine bonds are highly covalent and so are insensitive to the trend in atomic radius.
(D) The large negative charge on the complex ions makes the chloride-chloride repulsions, not the metal-chloride attractions, the dominant factor in determining the bond distance.
49. Which species has the largest $\mathrm{O}-\mathrm{N}-\mathrm{O}$ bond angle?
(A) $\mathrm{NO}_{2}$
(B) $\mathrm{N}_{2} \mathrm{O}_{4}$
(C) $\mathrm{NO}_{2}^{-}$
(D) $\mathrm{NO}_{3}^{-}$
50. Which best describes the isomer of the ion with the formula $[\mathrm{CNO}]^{-}$that is the most stable?
(A) Linear, with a central C
(B) Linear, with a central N
(C) Linear, with a central O
(D) Cyclic
51. Which is the least important consideration in determining the strength of interaction between atomic orbitals on two atoms as they combine to form molecular orbitals?
(A) How close the atoms are to one another
(B) How close in energy the orbitals are
(C) What the orbitals' relative orientation is
(D) Whether the orbitals have the same principal quantum number
52. Which statement about FNNF is NOT correct?
(A) It exists as two distinct geometric isomers.
(B) It is planar.
(C) Its nitrogen-nitrogen bond is longer than that in $\mathrm{N}_{2} \mathrm{~F}_{4}$.
(D) It is more stable than its structural isomer with both fluorine atoms bonded to the same nitrogen.
53. A four-coordinate transition metal complex $\mathrm{M}(\mathrm{CO})_{2}(\mathrm{Br})(\mathrm{Cl})$ can be isolated as two geometric isomers. With which geometries at the metal center is this observation consistent?
I. Square planar
II. Tetrahedral
(A) I only
(B) II only
(C) Either I or II
(D) Neither I nor II
54. A sample of pure Si is doped with 1.0 part per million of As to form material A. Material $\mathbf{A}$ is then doped with 0.5 ppm of B to form material $\mathbf{B}$. What is the correct order when the three materials are arranged in order of increasing electrical conductivity?
(A) Pure $\mathrm{Si}<$ A $<$ B
(B) B $<$ A $<$ Pure Si
(C) $\mathbf{B}<$ Pure $\mathrm{Si}<\mathbf{A}$
(D) Pure $\mathrm{Si}<\mathbf{B}<\mathbf{A}$
55. Which of these could have the formula $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}$ ?
I. An acyclic ester
II. A cyclic ether
(A) I only
(B) II only
(C) Either I or II
(D) Neither I nor II
56. Which is the best explanation for the higher reactivity of conjugated dienes relative to non-conjugated alkenes in electrophilic addition reactions?
(A) Conjugated dienes can form allylic cations on reaction with electrophiles while non-conjugated alkenes cannot.
(B) Conjugated dienes have more potentially reactive sites than do non-conjugated alkenes.
(C) The $\pi$ bonding in conjugated dienes is weaker than the $\pi$ bonding in non-conjugated alkenes.
(D) Conjugated dienes are nonplanar while nonconjugated alkenes are planar.
57. Which compound will NOT form in the reaction of acetone (propanone) with aqueous base?
(A)

(B)

(C)

(D)

58. Which compound would have the lowest $\mathrm{C}=\mathrm{O}$ stretching frequency in its infrared spectrum?
(A)

(B)

(C)

(D)

59. Which compound reacts fastest with aqueous acid?
(A)

(B)

(C)

(D)

60. How many possible dipeptides can be formed using the twenty commonly occurring amino acids?
(A) 40
(B) 200
(C) 210
(D) 400

## END OF TEST

## Olympiad 2021 USNCO National Exam, Part 1 KEY

| Number | Answer | Number | Answer |
| :---: | :---: | :---: | :---: |
| 1. | C | 31. | C |
| 2. | B | 32. | C |
| 3. | D | 33. | D |
| 4. | D | 34. | B |
| 5. | A | 35. | D |
| 6. | B | 36. | C |
| 7. | C | 37. | A |
| 8. | C | 38. | C |
| 9. | B | 39. | B |
| 10. | A | 40. | C |
| 11. | A | 41. | C |
| 12. | B | 42. | B |
| 13. | A | 43. | D |
| 14. | B | 44. | B |
| 15. | B | 45. | A |
| 16. | C | 46. | D |
| 17. | C | 47. | B |
| 18. | A | 48. | A |
| 19. | A | 49. | A |
| 20. | A | 50. | A |
| 21. | A | 51. | D |
| 22. | D | 52. | C |
| 23. | D | 53. | A |
| 24. | C | 54. | D |
| 25. | A | 55. | B |
| 26. | D | 56. | A |
| 27. | C | 57. | B |
| 28. | A | 58. | B |
| 29. | A | 59. | A |
| 30. | D | 60. | D |

