# Annotated Solution 2018 USNCO Local Exam 

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## 1 Solutions

1. We can use Avogadro's constant, and then do some dimensional analysis.

$$
225 \mathrm{~g} \mathrm{O}_{2} \times \frac{1 \mathrm{~mol} \mathrm{O}_{2}}{32.0 \mathrm{~g} \mathrm{O}_{2}} \times \frac{2 \mathrm{~mol} \mathrm{O}}{1 \mathrm{~mol} \mathrm{O}_{2}} \times \frac{6.02 \times 10^{23} \text { atoms }}{\mathrm{mol} \mathrm{O}}=8.47 \times 10^{24} \text { atoms }
$$

Thus, the answer is $C$.
2. Because the same number of moles must remain before and after dilution, we can set up the following equation.

$$
\begin{gathered}
M_{1} V_{1}=M_{2} V_{2} \\
(1.50 \mathrm{M})\left(V_{1}\right)=(0.300 \mathrm{M})(0.500 \mathrm{~L}) \\
(1.50 \mathrm{M})\left(V_{1}\right)=0.150 \mathrm{M} \cdot \mathrm{~L} \\
V_{1}=0.100 \mathrm{~L}
\end{gathered}
$$

This is 100 mL , or $A$.
3. We first need to write the reaction in order to perform the stoichiometry. The reaction is as follows

$$
\mathrm{Cu}_{2} \mathrm{O}+\mathrm{H}_{2} \longrightarrow 2 \mathrm{Cu}+\mathrm{H}_{2} \mathrm{O}
$$

Now we can do the stoichiometry

$$
10.00 \mathrm{~g} \mathrm{Cu} \times \frac{1 \mathrm{~mol} \mathrm{Cu}}{63.55 \mathrm{~g} \mathrm{Cu}} \times \frac{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}{2 \mathrm{~mol} \mathrm{Cu}} \times \frac{18.00 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}}{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}=1.417 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}
$$

Thus, the answer is $B$.
4. Set a standard amount of enargite at an arbitrary 100.0 g . Thus, there are 48.41 g Cu , 19.02 g As, and 32.57 g S . We can divide by the molar masses of each of the compounds.

$$
\begin{gathered}
48.41 \mathrm{~g} \mathrm{Cu} \times \frac{1 \mathrm{~mol} \mathrm{Cu}}{63.55 \mathrm{~g} \mathrm{Cu}}=0.7618 \mathrm{~mol} \\
19.02 \mathrm{~g} \mathrm{As} \times \frac{1 \mathrm{~mol} \mathrm{As}}{74.92 \mathrm{~g} \mathrm{As}}=0.2539 \mathrm{~mol} \\
32.57 \mathrm{~g} \mathrm{~S} \times \frac{1 \mathrm{~mol} \mathrm{~S}}{32.06 \mathrm{~g} \mathrm{~S}}=1.016 \mathrm{~mol}
\end{gathered}
$$

Dividing by the lowest number, then there will be the ratio of $\mathrm{Cu}: \mathrm{As}: \mathrm{S}=3: 1: 4$. Thus, the formula is $\mathrm{Cu}_{3} \mathrm{AsS}_{4}$, or $C$.
5. We first need to calculate the mass ratio between the calcium nitrate and the calcium.

$$
\mathrm{Ca} \%=\frac{M_{\mathrm{Ca}}}{M_{\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}}}=\frac{40.078 \frac{\mathrm{gram}}{\mathrm{~mol}}}{164 \frac{\text { gram }}{\mathrm{mol}}}=0.244
$$

Thus, for every gram of $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$, we will have 0.244 grams of calcium. We additionally know that we have 1.0 gram of calcium, so we can determine how much calcium nitrate we have

$$
m_{\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}}=\frac{m_{\mathrm{Ca}}}{\mathrm{Ca} \%}=\frac{1.0}{0.244}=4.1
$$

Thus, for 1 gram of calcium, we have 4.1 grams of calcium nitrate to correspond. We can now determine the mass percent purity by dividing the grams of calcium nitrate by the total mass

$$
\frac{4.1}{5.0}=82 \%
$$

Thus, the answer is $D$.
6. We can use the formula for the depression in freezing point to solve this question. The formula is

$$
\Delta T=i \times K_{f} \times m
$$

where $i$ is the van 't Hoff factor, $K_{f}$ is the molal depression constant, and $m$ is the molality. $K_{f}$ will remain constant and $m$ will be approximately the same since the mass is the same and the molar masses are comparable, so the dependency of the freezing point will be on the van 't Hoff factor.

The definition of the van 't Hoff factor is the ratio between the actual concentration upon dissociation of the substance to the concentration based on mass. Thus, we must check what all of the hydrated salts dissociate into and determine the van 't Hoff factor for each.

$$
\begin{gathered}
\mathrm{CuSO}_{4} \text { disassociates into } \mathrm{Cu}^{2+} \text { and } \mathrm{SO}_{4}{ }^{2-} \\
\mathrm{NiSO}_{4} \text { disassociates into } \mathrm{Ni}^{2+} \text { and } \mathrm{SO}_{4}{ }^{2-} \\
\mathrm{MgSO}_{4} \text { disassociates into } \mathrm{Mg}^{2+} \text { and } \mathrm{SO}_{4}{ }^{2-} \\
\mathrm{Na}_{2} \mathrm{SO}_{4} \text { disassociates into } 2 \mathrm{Na}^{+} \text {and } \mathrm{SO}_{4}{ }^{2-}
\end{gathered}
$$

With this, we can now calculate the van 't Hoff factors for each of these. Labeling $i_{1}$ for $\mathrm{CuSO}_{4}$ and so on, we have

$$
\begin{aligned}
& i_{1}=1+1=2 \\
& i_{2}=1+1=2 \\
& i_{3}=1+1=2 \\
& i_{4}=2+1=3
\end{aligned}
$$

Because $\mathrm{Na}_{2} \mathrm{SO}_{4}$ has the highest van 't Hoff factor, it will have the most depression in freezing point. Thus, the hydrated salt with the lowest freezing point is $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$, or $D$.
7. In order to identify if a gas evolution reaction, we need to write out the reactions for all the answer choices.

$$
\begin{gathered}
\mathrm{A}: \mathrm{Al}+3 \mathrm{H}^{+} \longrightarrow \mathrm{Al}^{3+}+\frac{3}{2} \mathrm{H}_{2}(\mathrm{~g}) \\
\mathrm{B}: \mathrm{Zn}+2 \mathrm{H}^{+} \longrightarrow \mathrm{Zn}^{2+}+\mathrm{H}_{2}(\mathrm{~g}) \\
\mathrm{C}: 2 \mathrm{H}^{+}+\mathrm{CO}_{3}{ }^{2-} \longrightarrow+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g}) \\
\mathrm{D}: \text { no reaction, all ions are spectators }
\end{gathered}
$$

The only one of these reactions that does not cause a gas evolution reaction is $D$.
8. CaS is a precipitate in water with a relative high $K_{\mathrm{sp}}$, so it is soluble in acid with the weak electrolyte $\mathrm{H}_{2} \mathrm{~S}$ formed.

$$
\mathrm{CaS}(\mathrm{~s})+2 \mathrm{H}^{+}(\mathrm{aq}) \rightleftharpoons \mathrm{Ca}^{2+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{~S}(\mathrm{aq})
$$

MnS and ZnS are both sulfides of transition cations, which are less soluble in water but still soluble in strong acids with a similar reaction to that of $\mathrm{CaS}(\mathrm{s}) . \mathrm{CdS}$, a sulfide of the fifth period element $\mathrm{Cd}^{2+}$, has the smallest solubility in water here and even not soluble in hydrochloric acid. Thus, the correct answer is $\mathrm{Cd}^{2+}$, or $D$.

More specifically, the order of of hardness of the four cations from harder to softer are

$$
\mathrm{Ca}^{2+}>\mathrm{Mn}^{2+}>\mathrm{Zn}^{2+}>\mathrm{Cd}^{2+}
$$

according to hard-soft acid-base theory (HSAB), which states higher charged and smaller sized cations are harder Lewis acids; More electronegative, lower charged, and smaller sized anions are harder Lewis bases. $\mathrm{S}^{2-}$, relative less electronegative, larger in size, is a typical soft base, which binds strongly with soft acids and binds weakly with hard acids. So CdS, a soft acid-soft base combination, has the strongest binding affinity and the lowest solubility in water. This is why CdS is the only sulfide precipitate here which is not soluble even in strong acids.
9. The key fact to understand here are that transition metals produce colored compounds and ions. By analysis of the answer choices, $\mathrm{KMnO}_{4}$ seems to be the only answer choice with a transition metal in the compounds $\left(\mathrm{MnO}_{4}{ }^{-}\right.$is purple). Thus, the answer must be $A$.
10. AgF is soluble in water, while $\mathrm{SrF}_{2}$ is not. This means the answer is NaF , or $B$. For a more detailed explanation, refer back to the solution for the USNCO Local Exam 2019 \#9.
11. A beaker does not have accurate measurements, so D can be eliminated. A $10-\mathrm{mL}$ volumetric flask or a $10-\mathrm{mL}$ volumetric pipet is built to measure exactly 10 mL of solution, not 2.7 mL , so B and C can be eliminated. This leaves the $10-\mathrm{mL}$ graduated cylinder , or $A$, which gives the right precision.
12. To begin our analysis, phenolphthalein is pink in basic solutions getting darker as pH increases, while colorless in acidic and neutral ones. We also note that the endpoint in a colorimetric titration is when the indicator changes color.

Now, we look at the answer choices. Spilling acid indicates a use of less base, which will therefore underestimate the moles of acid. Thus, by spilling acid, we will overestimate the molar mass. In addition, the solution being a dark red indicates that the solution is overtitrated. This color also indicates that the solution is highly basic, and more base was added than needed. Thus, the endpoint is not accurate and the answer is $B$.
13. The particles in the diagram are moving quickly and in random directions, and they are colliding with the walls of the container. They are fairly evenly spaced throughout the container. This is characteristic of a gas, or $A$.
14. The strongest intermolecular forces in acetone are only dipole-dipole, while the intermolecular forces in propanol include hydrogen bonding. It is well known that hydrogen bonding is stronger than regular dipole-dipole interactions, and boiling point increases with intermolecular force strength, the answer must be $D$.
15. The formula for root mean square molecular speed is the following, where $M$ is the molar mass.

$$
v_{\mathrm{rms}}=\sqrt{\frac{3 R T}{M}}
$$

From this we see that the order of increasing average molecular speed is also of decreasing molar mass at the same temperature. The gases are ordered by decreasing molar mass in $B$.
16. Ideal gases are gases with the assumptions of no intermolecular forces among gas molecules and negligible molecular size compared to the distance among them. High temperature will increase the kinetic energy of the particles so that they will no longer be under the influence of intermolecular forces. Low pressures will cause the particles to spread farther apart which can neglect the size of gas molecules themselves. Thus, the only correct answer is $I$, or $A$.
17. Ionic compounds conduct electricity in the aqueous and molten states, but not in the solid state. This is because the ions in solids are fixed in the lattice, and cannot move freely. They also have high melting points and are often soluble in water. Thus, the only answer that fits the conditions of the question is $C$.
18. Typically, a liquid with a higher vapor pressure has relative lower normal boiling point, since normal boiling point is the temperature when the vapor pressure equals to the atmospheric pressure (1 atm)

Lower heat of vaporization tends to lead to higher vapor pressure, as molecules more easily enter the gaseous phase. We can confirm this with the equation for equilibrium constant $K_{\mathrm{P}}$ and vapor pressure of a vaporization process as follow.

$$
\begin{gathered}
\mathrm{A}(\mathrm{l}) \rightleftharpoons \mathrm{A}(\mathrm{~g}) \\
\ln K_{\mathrm{P}}=-\frac{\Delta H_{\mathrm{vap}}}{R T}+C \\
K_{\mathrm{P}}=P_{\text {vapor }}
\end{gathered}
$$

So,

$$
\ln P=-\frac{\Delta H_{\mathrm{vap}}}{R T}+C
$$

Where $C$ is a constant specific to the molecule.
If we plot $\ln P$ with $1 / T$ for a certain liquid, a linear curve is obtained with a slope of $-\frac{\Delta H_{\text {vap }}}{R}$. The only reasonable explanation for toluene having a higher vapor pressure at $25^{\circ} \mathrm{C}$ and higher normal boiling point is that toluene has a lower heat of vaporization, $\Delta H_{\text {vap }}$. With this in mind, the two lines in the figure of $\ln P$ vs $1 / T$ for toluene and water cross at a certain point with a temperature between $25^{\circ} \mathrm{C}$ and the normal boiling point of toluene. Line for toluene has a less native slope, which is under the line for water before the cross point, but above the line for water after the cross point.
19. The energy the water gained in addition to the energy the aluminum block lost must be 0 .

$$
\begin{gathered}
Q_{\text {water }}=(100.0 \mathrm{~g})\left(4.184 \frac{\mathrm{~J}}{\mathrm{~g}{ }^{\circ} \mathrm{C}}\right)\left(28.00-25.00{ }^{\circ} \mathrm{C}\right) \\
Q_{\mathrm{Al}}=(m)\left(0.900 \frac{\mathrm{~J}}{\mathrm{~g}{ }^{\circ} \mathrm{C}}\right)\left(28.00-100.0{ }^{\circ} \mathrm{C}\right) \\
Q_{1}+Q_{2}=0 \\
(100.0)(4.184)(3.00)+(m)(0.900)(-72.00)=0 \\
m=19.4 \mathrm{~g}
\end{gathered}
$$

Thus, the answer is $C$.
20. $\Delta H_{\mathrm{f}}$ is defined as the standard enthalpy change for the reaction that makes one mole of product from standard state elements. B makes 2 moles, so it can be eliminated. The standard state of elemental oxygen is $\mathrm{O}_{2}(g)$, so C and D can be eliminated. $A$ is the correct answer because $1 \mathrm{~mol} \mathrm{MgO}(s)$ is created from the elements magnesium and oxygen in their standard states at 298 K .
21. First we must write the reaction for the enthalpy of formation of $\mathrm{XeF}_{2}$.

$$
\mathrm{Xe}(\mathrm{~g})+\mathrm{F}_{2}(\mathrm{~g}) \longrightarrow \mathrm{XeF}_{2}(\mathrm{~g})
$$

The enthalpy of formation can be calculated with bond dissociation enthalpy by bonds broken minus bonds formed. We see from the reaction that one $\mathrm{F}-\mathrm{F}$ bond is broken, and two $\mathrm{Xe}-\mathrm{F}$ bonds are formed. Let $x$ be the average bond dissociation enthalpy of an $\mathrm{Xe}-\mathrm{F}$ bond. Then we have

$$
155-2 x=-108
$$

Solving for $x$ we get $132 \mathrm{~kJ} \mathrm{~mol}^{-1}$, which is $C$.
22. First we must write the reaction of formation of $\mathrm{NH}_{3}(g)$.

$$
\frac{1}{2} \mathrm{~N}_{2}(\mathrm{~g})+\frac{3}{2} \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow \mathrm{NH}_{3}(\mathrm{~g})
$$

Now we can use the equation $\Delta G^{\circ}=\Delta H^{\circ}-T \Delta S^{\circ}$.

$$
\begin{gathered}
\Delta H^{\circ}=(1)(-46)-(1 / 2)(0)-(3 / 2)(0)=-46 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
\Delta S^{\circ}=(1)(193)-(1 / 2)(192)-(3 / 2)(131)=-100 . \mathrm{J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}
\end{gathered}
$$

Remember we must use either kJ or J for everything so the units will cancel. Let's convert $\Delta S^{\circ}$ to kJ .

$$
\begin{gathered}
\Delta S^{\circ} \times \frac{1 \mathrm{~kJ}}{1000 \mathrm{~J}}=-0.100 \mathrm{~kJ} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \\
\Delta G^{\circ}=\Delta H^{\circ}-T \Delta S^{\circ}=-46-(298)(-0.100)=-16 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{gathered}
$$

Thus, the answer is $B$.
23. The first fact to establish is that vaporization is a spontaneous process. We can compare the Gibbs free energy to determine if the process is spontaneous. If $\Delta G<0$, then the process is spontaneous. Thus, the first statement is true.

The second statement is also true in that the change in internal energy of the system $\Delta U$ is equal to the enthalpy change $\Delta H$ plus the work done on the system $-P \Delta V$, where $P$ is pressure and $\Delta V$ is change in volume (which is under constant pressure and temperate). Because volume increases during the vaporization, $\Delta V>0$.

$$
\begin{gathered}
\Delta U=\Delta H-P \Delta V \\
\Delta H=\Delta U+P \Delta V>\Delta U
\end{gathered}
$$

Thus, both $I+I I$ are true, which is answer $C$.
Note: Please be aware that $E$ was also commonly used in USNCO to represent the internal energy.
24. The order of entropy for 1 mol of substance, in reference to states of matter, are

$$
\text { gas }>\text { aqueous, liquid }>\text { solid }
$$

For answer choices B, C, and D, all the reactions indicate a decrease in entropy with a decrease in mole of gases. Therefore, the only possible option is

$$
\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq}) \longrightarrow \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})
$$

The entropy change of this reaction can be further interpreted as follows. The reverse reaction actually is the neutralization of $\mathrm{NH}_{3}$ and $\mathrm{CH}_{3} \mathrm{COOH}$, which produces hydrated cations and anions. The forward reaction has an increase in entropy. Thus, the answer is $A$.
25. From the reaction, we see that for each mole of $\mathrm{CCl}_{4}$ formed, 3 moles of $\mathrm{Cl}_{2}$ are consumed.

$$
0.063 \mathrm{M} \mathrm{~min}^{-1} \times \frac{3 \mathrm{~mol} \mathrm{Cl}_{2}}{1 \mathrm{~mol} \mathrm{CCl}_{4}}=0.19 \mathrm{M} \mathrm{~min}^{-1}
$$

This is $D$.
26. We can model the mass of ${ }^{131} \mathrm{I}$ at time $t$ for a nuclear decay process based on the integrated rate law for first order reactions as follows.

$$
m(t)=5.00 \times\left(\frac{1}{2}\right)^{\frac{t}{8.02}}
$$

From this equation we see after each 8.02 d , half of the ${ }^{131} \mathrm{I}$ will decay. Plugging in 6.01 d for $t$ gives 2.97 mg , or $C$.
27. The integrated rate law for a second-order reaction is

$$
\frac{1}{[\mathrm{~A}]}=k t+\frac{1}{[\mathrm{~A}]_{0}}
$$

We see that the graph of $1 /[\mathrm{A}]$ as a function of time is linear, so the answer is $C$.
28. According to the Arrhenius equation, rate constant $k$ is related to both activation energy $E_{a}$ and a constant specific to the reaction, $C$.

$$
\ln k=-\frac{E_{a}}{R T}+C
$$

Additionally, reaction rate is also dependent on the concentrations of reactants, thus, we can eliminates both option A and B.
Another form of Arrhenius equation states that

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

Thus, observing the Arrhenius equation, an increase in $E_{a}$ will also indicate an increase in $\ln \left(\frac{k_{2}}{k_{1}}\right)$, given same increase in temperature. Thus, the reaction rate varies more with temperature, and the answer is $D$.
29. We can use a pre-equilibrium approximation (PEA) to the first step since it is a fast reversible reaction followed by a slow step.

$$
\mathrm{NO}+\mathrm{Br}_{2} \underset{\mathrm{k}_{-1}}{\stackrel{\mathrm{k}_{1}}{\rightleftharpoons}} \mathrm{NoBr}_{2} \text { (fast) }
$$

We will define $k_{-1}$ as the rate constant of the backward reaction of the first step.

$$
\mathrm{NO}+\mathrm{NOBr}_{2} \stackrel{\mathrm{k}_{2}}{\rightleftharpoons} 2 \mathrm{NOBr} \text { (slow) }
$$

According to the assumption of PEA, we can say the forward reaction rate of the first step equals to the backward reaction rate.

$$
\begin{gathered}
\text { forward rate }=k_{1}[\mathrm{NO}]\left[\mathrm{Br}_{2}\right] \\
\text { backward rate }=k_{-1}\left[\mathrm{NOBr}_{2}\right]
\end{gathered}
$$

Setting these rates equal to each other, we get

$$
k_{1}[\mathrm{NO}]\left[\mathrm{Br}_{2}\right]=k_{-1}\left[\mathrm{NOBr}_{2}\right]
$$

Solving for the intermediate $\left[\mathrm{NOBr}_{2}\right]$, we get

$$
\left[\mathrm{NOBr}_{2}\right]=\frac{k_{1}}{k_{-1}} \times[\mathrm{NO}]\left[\mathrm{Br}_{2}\right]
$$

Since the second step is the only reaction to produce the product, so the overall reaction rate can be expressed by the second step only.

$$
\text { rate }_{\text {overall }}=\text { rate }_{\text {second step }}=k_{2}[\mathrm{NO}]\left[\mathrm{NOBr}_{2}\right]
$$

Substituting $\left[\mathrm{NOBr}_{2}\right]$ into the above equation, we get

$$
\text { rate }=\frac{k_{1} k_{2}}{k_{-1}} \times[\mathrm{NO}]^{2}\left[\mathrm{Br}_{2}\right]
$$

Thus, the correct answer is $B$.
30. From the reaction, $\mathrm{NOBr}_{2}(\mathrm{~g})$ is produced and then consumed, which is an intermediate, or $A$.
31. The dissolution of AgCl can be written as follows.

$$
\mathrm{AgCl}(\mathrm{~s}) \rightleftharpoons \mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})
$$

Let $\left[\mathrm{Ag}^{+}\right]=\left[\mathrm{Cl}^{-}\right]=S$, where $S$ is the molar solubility.

$$
\begin{gathered}
S^{2}=K_{s p} \\
S=\sqrt{K_{s p}}=\sqrt{1.8 \times 10^{-10}}=1.34 \times 10^{-5} \frac{\mathrm{~mol}}{\text { liter }}
\end{gathered}
$$

Now, we can set the molarities equal to find the mass solubility $m$.

$$
\begin{gathered}
1.34 \times 10^{-5} \frac{\mathrm{~mol}}{\text { liter }}=\frac{\frac{m \mathrm{~mol}}{143.4 \mathrm{~g}}}{1 \text { liter }} \\
m=1.34 \times 143.4 \times 10^{-5}=0.00192 \mathrm{~g}=1.92 \mathrm{mg}
\end{gathered}
$$

Thus, the answer is $B$.
32. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}$is the conjugate base of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$. Therefore, we can use $K_{\mathrm{b}}=\frac{K_{\mathrm{w}}}{K_{\mathrm{a}}}$ to solve this problem.

$$
\begin{gathered}
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}+\mathrm{OH}^{-} \\
K_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right]}{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}\right]} \\
K_{\mathrm{b}}=\frac{K_{\mathrm{w}}}{K_{\mathrm{a}}}=\frac{10^{-14}}{6.5 \times 10^{-5}}=1.5 \times 10^{-10}
\end{gathered}
$$

Let $x$ be the amount of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}$that dissociates into $\mathrm{OH}^{-}$and $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$. We can make the approximation that $x$ is negligible compared to $0.20 M$, and that the initial [ $\mathrm{OH}^{-}$] produced by water is also negligible. Then we get

$$
\begin{gathered}
K_{\mathrm{b}}=\frac{x^{2}}{0.20} \longrightarrow x=5.5 \times 10^{-6} \mathrm{M}=\left[\mathrm{OH}^{-}\right] \\
\mathrm{pH}=14-\mathrm{pOH}=14+\log \left[\mathrm{OH}^{-}\right]=14+\log \left(5.5 \times 10^{-6}\right)=8.74
\end{gathered}
$$

Thus, the answer is $B$.
33. From the reaction, we use products over reactants to get

$$
\begin{gathered}
K_{\mathrm{p}}=\frac{\left(P_{\mathrm{SO}_{3}}\right)^{1}}{\left(P_{\mathrm{SO}_{2}}\right)^{1}\left(P_{\mathrm{O}_{2}}\right)^{\frac{1}{2}}} \\
K_{\mathrm{p}}=\frac{0.332}{(0.562)(0.101)^{\frac{1}{2}}}=1.86
\end{gathered}
$$

Thus, the answer is $A$.
34. The reaction requires a heat input because it is endothermic. We can think about the reaction as

$$
\text { heat }+\mathrm{PCl}_{3}+\mathrm{Cl}_{2} \rightleftharpoons \mathrm{PCl}_{5}
$$

According to Le Chatelier's Principle, if we increase the temperature (add heat), equilibrium shifts to the right, increasing the number of moles of $\mathrm{PCl}_{5}$. Thus $I$ is correct.

For volume, we see from $P V=n R T$ that if volume increases, pressure decreases. In response, the system will shift to the side with more moles of gases to reduce the pressure increase, according to Le Chatelier's Principle. This means equilibrium will shift towards $\mathrm{PCl}_{3}$ and $\mathrm{Cl}_{2}$, so $I I$ is incorrect. Thus, the answer is $A$.
35. The ionization of an acid in the general form of HA can be expressed as show below.

$$
\mathrm{HA} \rightleftharpoons \mathrm{H}^{+}+\mathrm{A}^{-}
$$

We can also determine the acidity constant $K_{a}$ from this

$$
K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

Upon ionization, both $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{A}^{-}\right]$will be $2.3 \%$ ionized, with both concentrations equal.

$$
\left[\mathrm{H}^{+}\right] \approx\left[\mathrm{A}^{-}\right]=0.12 \times 0.023=0.0028 \mathrm{M}
$$

Thus, the concentration of the remaining [HA] is $0.12-0.0028=0.117$ M. Substituting in our formula for $K_{a}$, we get

$$
K_{a}=\frac{(0.0028)^{2}}{0.117}=6.5 \times 10^{-5}
$$

Thus, the answer is $C$.
36. In order to find the relationship between solubility and pH , first, we write down the equation to show the dissolution equilibrium of $\mathrm{CaF}_{2}(\mathrm{~s})$.

$$
\mathrm{CaF}_{2}(\mathrm{~s}) \rightleftharpoons \mathrm{Ca}^{2+}(\mathrm{aq})+2 \mathrm{~F}^{-}(\mathrm{aq})
$$

According to mass balance equation, we can get the sum of $\left[\mathrm{F}^{-}\right]$and $[\mathrm{HF}]$ is always two times of $\left[\mathrm{Ca}^{2+}\right]$ no matter how much $\mathrm{F}^{-}$is converted to HF.

$$
\left[\mathrm{F}^{-}\right]+[\mathrm{HF}]=2\left[\mathrm{Ca}^{2+}\right]
$$

Assume $S$ is the molar solubility of $\mathrm{CaF}_{2}(\mathrm{~s})$, and $S=\left[\mathrm{Ca}^{2+}\right]$, then

$$
\left[\mathrm{F}^{-}\right]+[\mathrm{HF}]=2 S
$$

To find the acid dissociation constant $K_{a}$, we say that

$$
K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{F}^{-}\right]}{[\mathrm{HF}]}
$$

Solving for [HF], we get

$$
[\mathrm{HF}]=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{F}^{-}\right]}{K_{a}}
$$

Now, we can substitute this into the equation we previously got in terms of $S$, and we get

$$
\left[\mathrm{F}^{-}\right]+\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{F}^{-}\right]}{K_{a}}=2 S
$$

Solving for $\left[\mathrm{F}^{-}\right]$, we get

$$
\left[\mathrm{F}^{-}\right]=\frac{2 S}{1+\frac{\left[\mathrm{H}^{+}\right]}{K_{a}}}
$$

We also have an additional equation in terms of $K_{\mathrm{sp}}$, which is

$$
K_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}
$$

Substituting the equation we got for $\left[\mathrm{F}^{-}\right]$, we get

$$
K_{\mathrm{sp}}=S \times\left(\frac{2 S}{1+\frac{\left[\mathrm{H}^{+}\right]}{K_{a}}}\right)^{2}
$$

Our final goal is to solve for $S$, so we now get

$$
K_{\mathrm{sp}}=\frac{4 S^{3}}{\left(1+\frac{\left[\mathrm{H}^{+}\right]}{K_{a}}\right)^{2}}
$$

Thus, solving for $S$, we get

$$
S=\sqrt[3]{\frac{K_{\mathrm{sp}}\left(K_{a}+\left[\mathrm{H}^{+}\right]\right)^{2}}{4 K_{a}^{2}}}
$$

Finally, we substitute at pH 's of 3.00 and 7.00 to get

$$
\frac{s_{\mathrm{pH}=3.00}}{s_{\mathrm{pH}=7.00}}=\sqrt[3]{\left(\frac{10^{-3.17}+10^{-3.00}}{10^{-3.17}+10^{-7.00}}\right)^{2}}=1.83
$$

Thus, the correct answer is $B$.
37. We need to calculate the oxidation states of the other molecules to start. For the purpose of brevity, denote $O(n)$ as the sum of oxidation states of a group of atoms.

$$
\begin{gathered}
O\left(\left(\mathrm{Si}_{4} \mathrm{O}_{11}\right)_{2}\right)=2 \times(4 \times 4+(-2) \times 11)=-12 \\
O\left((\mathrm{OH})_{2}\right)=2(-2+1)=-2 \\
O\left(\mathrm{Na}_{2}\right)=2(1)=+2
\end{gathered}
$$

The global oxidation state must be 0 , so we can set up an equation

$$
\begin{gathered}
0=-12-2+2+O\left(\mathrm{Fe}_{5}\right) \\
O\left(\mathrm{Fe}_{5}\right)=+12
\end{gathered}
$$

Now we need to allocate the distribution of oxidation states to the ions. Because Fe usually has oxidation states that vary between +2 and +3 , we need to have an integral amount of +3 (namely $\boxed{2}$ ), and an integral amount of +2 (namely $\boxed{3}$ ) so $3 \times 2+2 \times 3=12$. Thus, the answer is $B$.
38. Because the bromine ion is a negatively charged ion, it will travel to the anode in order to be oxidized with $\mathrm{Br}_{2}$ produced (i.e lose electrons). The hydrogen gas, however, is going to be evolved in the cathode. This is because hydrogen is a positively charged ion, and will travel to the cathode to be reduced (gain electrons). Thus, the answer is $A$.
39. This is a redox reaction between $\mathrm{KMnO}_{4}$ and $\mathrm{H}_{2} \mathrm{O}_{2}$, so we need to figure out the ratio of these two reactants to solve the stoichiometry here. Under acidic condition, the +7 Mn in $\mathrm{KMnO}_{4}$ is reduced into $\mathrm{Mn}^{2+}$ with 5 electrons gained per $\mathrm{KMnO}_{4}$, and $\mathrm{H}_{2} \mathrm{O}_{2}$ is oxidized into $\mathrm{O}_{2}(\mathrm{~g})$ with 2 electrons lost per $\mathrm{H}_{2} \mathrm{O}_{2}$. So the molar ratio of $\mathrm{KMnO}_{4}$ to $\mathrm{H}_{2} \mathrm{O}_{2}$ is supposed to be $2: 5$ at the end point when the presence of extra $\mathrm{MnO}_{4}{ }^{-}$showing a pale purple color.

We can calculate the remaining mass of the hydrogen peroxide by stoichiometry and dimensional analysis.

$$
22.50 \mathrm{~mL} \times \frac{0.0200 \mathrm{~mol} \mathrm{KMnO}_{4}}{1000 \mathrm{~mL}} \times \frac{5 \mathrm{~mol} \mathrm{H} \mathrm{O}_{2}}{2 \mathrm{~mol} \mathrm{KMnO}} 44 \times \frac{34.01 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}_{2}}{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}_{2}}=0.0383 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}_{2}
$$

Finding the percent solution we do $\frac{0.0383 \mathrm{~g}}{1.00 \mathrm{~g}} \times 100 \%=3.83 \%$, or $C$.
40. From the line notation, we see that nickel is the anode and silver is the cathode.

$$
E_{\text {cell }}^{\circ}=E_{\text {cat }}^{\circ}-E_{\text {ano }}^{\circ}=+0.80-(-(0.23))=1.03 \mathrm{~V}
$$

This is $C$.
41. This is a concentration cell, which reaches equilibrium when both compartments have the same concentration of $\mathrm{Cu}^{2+}$. So the compartment with $1.0 \mathrm{M} \mathrm{Cu}^{2+}$ solution will be the cathode (reduction), and the compartment with $0.10 \mathrm{M} \mathrm{Cu}^{2+}$ solution will be the anode (oxidation).

$$
\begin{aligned}
& \text { 1.0 } \mathrm{M} \text { compartment }-\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Cu}^{2+} \\
& 0.10 \mathrm{M} \text { compartment }-\mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+}+2 \mathrm{e}^{-}
\end{aligned}
$$

Thus, the overall reaction is

$$
\mathrm{Cu}^{2+}[1.0 \mathrm{M}] \longrightarrow \mathrm{Cu}^{2+}[0.10 \mathrm{M}]
$$

Thus, the electron flow will go from the electrode in the 0.10 M solution to the electrode in 1.0 M solution.
However, we still need to determine cell potential by using Nernst's equation.

$$
E_{\text {cell }}=E_{\text {cell }}{ }^{\circ}-\frac{0.059}{n} \times \log _{10}\left(\frac{\left[\mathrm{Cu}^{2+}\right]_{\text {anode }}}{\left[\mathrm{Cu}^{2+}\right]_{\text {cathode }}}\right)
$$

We know that the number of electrons $(n)$ is 2 . We additionally know that $E_{\text {cell }}{ }^{\circ}=0$ because the given cell is a concentration cell. Substituting this additional information, we have

$$
\begin{gathered}
E_{c}=-\frac{0.059}{2} \times \log _{10}\left(\frac{0.10}{1.0}\right) \\
E_{c}=-\frac{0.059}{2} \times(-1) \\
E_{c}=0.0295 \mathrm{~V} \approx 30 \mathrm{mV}
\end{gathered}
$$

Thus, the answer is $C$.
42. We know that the charge $Q$ is equal to $n F N$, where $n$ is the number of electrons transferred per mole of analyte, $F$ is Faraday's constant which is the charge of 1 mole of electrons, and $N$ is the number of moles of analyte. We also know that $Q=I \times t_{e}$, when $I$ is the current and $t_{e}$ is the time of electrolysis. We can set these equal to each other, and solve for $N$.

$$
\begin{gathered}
(670 \mathrm{sec})(0.10 \mathrm{~A})=(1) \times\left(96500 \frac{\mathrm{C}}{\mathrm{~mol}}\right) \times(N) \\
N=6.9 \times 10^{-4} \mathrm{~mol} \mathrm{Ag}
\end{gathered}
$$

We can just multiply by the molar mass to determine the grams of Ag.

$$
6.9 \times 10^{-4} \mathrm{~mol} \mathrm{Ag} \times \frac{107.8682 \mathrm{gAg}}{1 \mathrm{~mol} \mathrm{Ag}}=0.075 \mathrm{~g} \mathrm{Ag}
$$

Then we can do the mass ratio and determine the percentage

$$
\frac{0.075 \mathrm{~g} \mathrm{Ag}}{1.00 \mathrm{~g}} \times 100 \%=7.5 \% \longrightarrow D
$$

43. The electron configuration of Al is $[\mathrm{Ne}] 3 s^{2} 3 p^{1}$. For $\mathrm{Al}^{3+}$ we must remove three electrons, leaving us with the same electron configuration as neon. The electron configuration of neon is $1 s^{2} 2 s^{2} 2 p^{6}$, or $A$.
44. Tungsten, W, has the highest melting point of all metals. Metals tend to have higher melting points as they get closer to $\mathrm{W} . \mathrm{Fe}$ is the closest to W on the periodic table, so the answer is $C$.

In general, the boiling and melting point of metals increases with increasing number of valence electrons because there is an increased force of attraction between the metal cations and the valence electrons according to the electron-sea model.
45. There is a formula relating energy and wavelength, which is below

$$
E=\frac{h c}{\lambda}
$$

where $h$ is Plank's constant, $c$ is the speed of light, and $\lambda$ is the wavelength. We can substitute our known values to solve for $E$.

$$
\begin{gathered}
E=\frac{\left(6.626 \times 10^{-34} \mathrm{~J} \times \mathrm{s}\right)}{538 \times 10^{-9} \mathrm{~m}} \times\left(2.998 \times 10^{8} \frac{\mathrm{~m}}{\mathrm{~s}}\right) \\
E=3.69 \times 10^{-19} \mathrm{~J}
\end{gathered}
$$

Thus, the answer is $A$.
46. $n=3$ and $l=1$ refers to a $3 p$ orbital. Writing the electron configuration for arsenic, we see $3 p^{6}$, meaning that all three orbitals in the $3 p$ subshell are full. Since there are 2 electrons in each full orbital, the answer is $C$.
47. From our periodic trends, ionization energy decreases down and to the left. $K$ is closest to the bottom left of the periodic table, so the answer is C.
48. Method of elimination can be used for solving this question. Option A states that electronegativity increases down the group, which is not true based on the periodic trends. Similarly, option C is also incorrect since the polarity of $\mathrm{X}-\mathrm{H}$ bond decreases down the group as the electronegativity of X decreases. The statement in option D about bond angle is obviously not related to the acid strength. Thus, only option $\sqrt[B]{\text { is reasonable, and can be used to explain }}$ the trend of acid strength. Thus, we get answer choice $B$.

The strength of acids can be analyzed through the stability of their conjugate bases. The more stable the conjugate bases, the stronger the acids. Comparing the four conjugate bases, $\mathrm{HO}^{-}, \mathrm{HS}^{-}, \mathrm{HSe}^{-}, \mathrm{HTe}^{-}$, we can see that size of the 16 -group elements increases down the group, so the polarizability of the anions is also increasing. Polarizability is defined as the tendency of an atom, an ion or a molecule's electron cloud to be distorted. The polarizability increases with the total number of electrons in the species. Thus, larger species are more polarizable than smaller ones.
49. $\mathrm{PF}_{3}$ has covalent bonds between P and F . KF is an ionic compound. $\mathrm{CH}_{3} \mathrm{COOH}$ is an organic compound with only covalent bonds. $\mathrm{MgSO}_{4}$ has an ionic bond between the $\mathrm{Mg}^{2+}$ and the $\mathrm{SO}_{4}{ }^{2-}$. There are covalent bonds between the S and the O in $\mathrm{SO}_{4}{ }^{2-}$. Thus, the answer is $D$.
50. The Lewis structure for $\mathrm{SO}_{2}$ has S in the center as the least electronegative element. There are two double bonds. Because sulfur has two bonding groups and one lone pair, the molecular geometry is bent, so the answer is $B$.
51. The major resonance of $\mathrm{ClO}_{3}{ }^{-}$is shown as follow


The single bonded oxygen carries a negative formal charge. We see from the structure that Cl has 1 lone pair, or $B$.
52. Although tetrahedral molecules such as $\mathrm{CH}_{4}$ are often drawn as squares on paper, they are not really squares. Visualizing a 3 D tetrahedral molecule such as $\mathrm{CF}_{2} \mathrm{Cl}_{2}$, we see that swapping an F with a Cl leads to the same molecule, only rotated. In contrast, visualizing a 2D square planar molecule such as $\mathrm{XeF}_{2} \mathrm{Cl}_{2}$, we see that swapping an F with a Cl leads to a different molecule that cannot be obtained by simply rotating the initial molecule, which are marked as cis and trans isomers. Therefore a pair of geometric isomers is consistent only with a square planar geometry, which is $B$.
53. $\mathrm{O}_{2}$ is a typical paramagnetic molecule with unpaired electrons, which can be explained by the molecular orbital diagram of the $\mathrm{O}_{2}$ as shown below. With 6 bonding electrons and 2 unpaired anti-bonding electrons in the valence shell, the bond order in $\mathrm{O}_{2}$ is calculated to be 2 (equivalent to a double bond) based on the equation for bond order as shown below.

$$
\text { Bond order }=\frac{1}{2}\left(\text { number of bonding } e^{-}-\text {number of antibonding } e^{-}\right)
$$

With one electron removed from $\mathrm{O}_{2}, \mathrm{O}_{2}{ }^{+}$has one less electron in the anti-bonding orbital, and therefore, the bond order in $\mathrm{O}_{2}{ }^{+}$is 2.5 . This bond is stronger than the double bond in $\mathrm{O}_{2}$ which explains the shorter bond. Because bond order increases by 0.5 for each antibonding electron that is removed, we can reason that $A$ is the correct answer. Below is the molecular orbital diagram for $\mathrm{O}_{2}$.

54. When we draw the Lewis structure of the guanidinium ion, we find the carbon makes three single bonds with each nitrogen and carries a positive formal charge. Each nitrogen makes two $\mathrm{N}-\mathrm{H}$ bonds, one $\mathrm{N}-\mathrm{C}$ single bond and a lone pair. It seemed like the nitrogen atoms need to be $s p^{3}$ hybridized with a trigonal pyramidal geometry according the VSEPR model. But if we draw all of the resonances structures, we find that there are three more resonances in which
there are one $\mathrm{C}=\mathrm{N}$ and two $\mathrm{C}-\mathrm{N}$ with the double bonded nitrogen carrying the positive formal charge and no lone pair. Then we can conclude each nitrogen needs to be $s p^{2}$ hybridized with a trigonal planer structure in order to make the delocalized system among all three nitrogens and the central carbon atom, which is $D$.
55. From the name propyne, we know the compound is an alkyne and so must have a triple bond between carbons. Drawing the molecule, we count one triple bond and no double bonds. There are $2 \pi$ bonds for each triple bond, so the answer is $C$.
56. For this problem, we must draw out all isomers.




Note that the second two "isomers" are actually identical to each other. We can obtain one by flipping the other in space. This leaves us with 3 isomers, which is $C$.
57. A molecule with a chiral carbon is called chiral, which can't be superimposed with its mirror image, similar to our left hand and right hand. And the carbon atom with four different groups connected is called a chiral carbon. Thus, when $\mathrm{H}_{\mathrm{C}}$ is replaced by Br in 1-butene, the carbon with $\mathrm{H}_{\mathrm{C}}$ originally connected changes into a chiral carbon with four different groups connected, which are $-\mathrm{H},-\mathrm{Br},-\mathrm{CH}_{3}$, and $-\mathrm{HC}=\mathrm{CH}_{2}$. So the correct answer is $C$.
58. Halogens react quickly with alkenes such as hexene, which is done by adding two bromines to each carbon in the double bond known as addition reaction. This decolorizes bromine as the bromine becomes attached to the organic compound rather than retaining its own form with a reddish brown to yellow color depending on its concentration. However, cyclohexane does not react with bromine at room temperature, since there is no double bond present to have a similar addition. Thus the answer is $A$.
59. The dehydration of alcohol under the the catalysis of acid yields different alkenes if there are different types $\beta$ hydrogens in the alcohol. In organic chemistry, the hydrogen atoms connected to the $\beta$ carbon(s) are commonly called $\beta$ hydrogens, and $\beta$ carbons are those adjacent to the $\alpha$ carbon with functional group ( -OH in alcohols and -Br in alkyl bromides) connected. Similarly, alkyl halides react with strong bases to yield different alkenes through the elimination of hydrogen halides molecules. By analyzing the types of $\beta$ hydrogens in each starting material in option $\mathrm{A}, \mathrm{B}, \mathrm{C}$, and D , we can find, both A and C yields two alkenes with different structures, D yields three different alkenes, only $B$, a tertiary alcohol with three equivalent $R$ groups, yields only one single type of alkene.
60. Photosynthesis is endothermic because it requires energy input from the sun. It forms sugars because it is the reverse reaction of cellular respiration, which breaks down sugars. Thus, the answer is $B$.

