Annotated Solution
2017 USNCO Local Exam

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1 Solutions

1. Set an arbitrary amount of glyoxal at 100 g. Thus, there are 41.4 g C, 3.5 g H, and 55.1 g O. We can now divide by the molar masses to determine the number of moles of each element.

$$41.4 \text{ g C} \times \frac{1 \text{ mol C}}{12.001 \text{ g C}} = 3.45 \text{ mol}$$

$$3.5 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 3.47 \text{ mol}$$

$$55.1 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.44 \text{ mol}$$

The molar ratio of the three elements is 1 : 1 : 1, which is consistent with the empirical formula of CHO, or $\boxed{A}$.

2. This is simply dimensional analysis, as well as usage of Avogadro's constant of the mole.

$$2.5 \text{ mol Mg(OH)}_2 \times \frac{2 \text{ mol OH}}{1 \text{ mol Mg(OH}_2)} \times \frac{6.02 \times 10^{23} \text{ ions OH}}{1 \text{ mol OH}} = \boxed{3.0 \times 10^{24} \text{ ions}}$$

Thus, the answer is $\boxed{D}$.

3. We first need to find the masses of the NaBr and the KI.

$$1.00 \text{ mol NaBr} \times \frac{102.894 \text{ g NaBr}}{1 \text{ mol NaBr}} = 103 \text{ g NaBr}$$

$$0.300 \text{ mol KI} \times \frac{166.0027 \text{ g KI}}{1 \text{ mol KI}} = 49.8 \text{ g KI}$$

Now that we have the total mass, we need to determine the mass of iodine in the molecule.

$$0.300 \text{ mol KI} \times \frac{1 \text{ mol I}}{1 \text{ mol KI}} \times \frac{126.9007 \text{ g I}}{1 \text{ mol I}} = 38.1 \text{ g I}$$

Now, we can find the mass percent of iodine.

$$\frac{38.1 \text{ g I}}{103 \text{ g} + 49.8 \text{ g}} \times 100\ \% = \boxed{24.9\ \%}$$

Thus, the answer is $\boxed{A}$.

4. The key fact is that the the number of moles of chloride ions in the final solution is the sum of the moles of chloride ions. Thus, we can set up an equation to solve for the concentration. Note that in $MgCl_2$, there are 2 moles of Cl^-.

$$M_i = M_f$$

$$(1.50\text{ M}) \times (0.150\text{ L}) + (0.750\text{ M}) \times (2) \times (0.250\text{ L}) = M \times (0.150\text{ L} + 0.250\text{ L})$$

$$0.600\text{ mol} = M \times (0.400\text{ L})$$

$1\text{ mol/L} = 1\text{ M}$, so $M = \boxed{1.50\text{ M}}$, or $\boxed{C}$.

5. We have the actual yield of $BaSO_4$ for this reaction. In order to determine the percent yield, we must first find the theoretical yield. First, let's find the limiting reactant.

$$10.0\text{ g Na}_2\text{SO}_4 \times \frac{1\text{ mol}}{142.1\text{ g}} = 0.0704\text{ mol}$$

$$10.0\text{ g BaCl}_2 \times \frac{1\text{ mol}}{208.2\text{ g}} = 0.0480\text{ mol} \implies \text{BaCl}_2\text{ limiting}$$

Now we can do stoichiometry to find the theoretical yield.

$$0.0480\text{ mol BaCl}_2 \times \frac{1\text{ mol BaSO}_4}{\text{mol BaCl}_2} \times \frac{233.2\text{ g}}{\text{mol}} = 11.2\text{ g BaSO}_4$$

Finally, we calculate the percent yield.

$$\frac{12.0\text{ g}}{11.2\text{ g}} \times 100\% = 107\%$$

This answer doesn't make much sense. However, if $\boxed{\text{the BaSO}_4\text{ is wet}}$, the measured mass of $BaSO_4$ would be greater than the actual mass because it would also include some mass from water. Thus, the answer must be $\boxed{D}$.

6. The increase in boiling point is proportional to the molality m. In this case all solutions are 1.0 m, so it is difficult to say which has the highest boiling point. However, $\boxed{H_2SO_4}$ is a strong acid, so it will dissociate completely in the reaction $H_2SO_4 \longrightarrow H^+ + HSO_4{}^-$. In addition, some of the $HSO_4{}^-$ dissociates further into H^+ and $SO_4{}^{2-}$. Thus the final molality will be more than 2.0 m, and the answer is $\boxed{B}$. A further analysis of the answer choices allows us to say that H_3PO_4 and CH_3COOH are both weak acids, as well as glucose being a non-electrolyte.

7. We know from experience that NaCl is soluble in water, so A can be eliminated. Additionally, there is a solubility rule stating that ionic compounds with Cl^- tend to be soluble. AgCl is an important exception to this rule, as it has very low solubility in water, so the answer is $\boxed{C}$.

8. Alkali metals fit the description given in the question. The metals are soft and react violently in water. The only option that is an alkali metal is $\boxed{\text{Na}}$, or $\boxed{A}$.

9. $NaNO_3$ and $NaClO_4$ are neutral, first of all, since they are both product of strong acids reacting with strong bases. $NaHSO_4$ is acidic since $HSO_4{}^-$ is a week acid. The reaction is depicted below

$$\text{HSO}_4{}^-(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq)$$

In addition, $\boxed{NaHCO_3}$ is well known to be basic as baking soda, which can be explained by the presence of additional OH^- ions produced by the hydrolysis of $HCO_3{}^-$ with a constant of K_w/K_{a1}.

$$\text{HCO}_3{}^-(\text{aq}) + \text{H}_2\text{O}\,(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq})$$

Thus, the answer is $\boxed{D}$.

A further analysis can be made as HCO_3^- is also a weak acid, which partially dissociates into hydronium with a constant of K_{a2}.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

By checking the constants, we can conclude that the degree of dissociation of HCO_3^- is much smaller compared to that of the hydrolysis, resulting in a basic solution. You may refer to the data in number 33 of this year's annotation below.

10. Reactive metals tend to react with acids by forming hydrogen gas. In this case, the reaction is

$$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

Thus $\boxed{I}$ is correct, as a gas evolution reaction. Looking at II, we see the reaction is

$$SO_3^{2-}(s) + 2\,H^+(aq) \longrightarrow SO_2(g) + H_2O(l)$$

SO_2 is a gas, so this is also a gas evolution reaction. Thus the answer is $\boxed{I + II}$, which is $\boxed{C}$.

11. When there is a $\boxed{\text{defecit}}$ of vinegar, there are fewer moles of acid, so less NaOH is required to reach the endpoint. However, since the student still thinks the volume of the vinegar is 25.00 mL, there will be less moles but the same volume in the calculation. This will lead to a low calculated acid concentration. Thus, the answer is $\boxed{A}$.

However, let us understand why the other answer choices are incorrect. Option B describes NaOH absorbs CO_2, which will decrease the molarity of NaOH and convert it partially into Na_2CO_3. When the impure NaOH is used to titrate the vinagar with phenophenalein as indicator, the impurity Na_2CO_3 is converted into $NaHCO_3$ at the end point, during which less acetic acid is consumed compared to that in the neutralization of pure NaOH. It means more NaOH standard solution is needed to naturalize the same amount of acetic acid. Thus, Option B will give a higher value of acetic acid content. Option C represents an overtitrated solution, shown by the end point being dark red, which will also give a higher content. Option D depicts a scenario in which the vinegar is diluted before the NaOH. This means that the titration will be not affected because mole quantities of the acid remain the same.

12. $\boxed{\text{Volumetric pipets}}$ and burets can be extremely precise with two digits after the decimal point read, but only for a specific volume. In this case, since the volumetric pipet in this question is made to deliver 25.0 mL, $\boxed{D}$ is the most accurate answer. If it was a 30-mL volumetric pipet, or if the question asked for delivery of 20.0 mL, the answer would be A.

13. From $PV = nRT$, we see that volume is directly proportional to temperature (in Kelvin). Therefore we can simply multiply the initial volume by the temperature ratio, as pressure is kept constant.

$$5.0\text{ L} \times \frac{12.5 + 273.15}{25.0 + 273.15} = \boxed{4.8\text{ L}}$$

Thus, the answer is $\boxed{B}$.

14. $\boxed{\text{London dispersion forces}}$ are a type of intermolecular force that increases with the number of electrons. Since boiling point increases with intermolecular forces, and the number of electrons increases going down the list of diatomic halogens, the answer is $\boxed{B}$. There is no hydrogen bonding or dipole-dipole forces in these molecules because there is no electronegativity difference between the two atoms of the same element.

15. SiO_2, along with carbon, is well known for its ability to form covalent network solids. These solids, such as diamond, can be very hard and difficult to melt since numerous covalent bonds need to break during the melting process. $\boxed{A}$ fits the description of a covalent network solid so it is the correct answer.

16. Visualizing a phase diagram for CO_2, we see that it is a liquid to the left of its critical point. (Make sure not to confuse critical point and triple point.) This happens at a lower temperature, so $\boxed{I}$ is correct. II is incorrect because past the critical point, liquid and gas are indistinguishable so we cannot say that CO_2 is a liquid (actually it is called super critical fluid). Therefore, the answer is $\boxed{A}$.

17. Lattice energy increases with increasing Coulomb force. From Coulomb's law, we see that the Coulomb force is proportional to the product of the charges of the ions in an ionic solid, and inversely proportional to the distance of the adjacent cation and anion squared. The explicit formula for Coulomb's law is as follows:

$$F = k\frac{q_1 q_2}{r^2}$$

Mg^{2+} and O^{2-} give a charge product of $2 \times 2 = 4$ times higher than Li^+ and F^-. This is a much more significant factor than the size of the ions, so the answer is $\boxed{C}$.

18. Solid metals form a $\boxed{\text{sea of delocalized electrons}}$ moving freely among positive nuclei. This explains the high conductivity of metals, among other things. Thus, the answer is $\boxed{A}$.

19. Using $q = mC\Delta T$, we get

$$q = (54.0)(2.48)(35.0 - 25.0) = \boxed{1340 \text{ J}}$$

This is $\boxed{C}$.

20. This is an application of Hess's law. Since P_4O_6 is a reactant, we see that we must multiply the top reaction by -1. Since just 1 P_4O_{10} is formed, we see that we keep the bottom reaction as is. Thus we get

$$P_4O_6 \longrightarrow P_4 + 3\,O_2 \quad \Delta H^\circ = +1640 \text{ kJ mol}^{-1}$$

$$P_4 + 5\,O_2 \longrightarrow P_4O_{10} \quad \Delta H^\circ = -2940 \text{ kJ mol}^{-1}$$

Adding these two reactions together, we get

$$P_4O_6 + 2\,O_2 \longrightarrow P_4O_{10} \quad \boxed{\Delta H^\circ = -1300 \text{ kJ mol}^{-1}}$$

This is equivalent to $\boxed{B}$ in scientific notation.

21. For this question we must use the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. At equilibrium when all substances are at standard pressure, $\Delta G^\circ = 0$, so solving for T we get $T = \frac{\Delta H^\circ}{\Delta S^\circ}$. Now we must find ΔH° and ΔS° using the reaction and the information from the table.

$$\Delta H^\circ = (1)(-374.9) - (1)(0) - (1)(-288.7) = -86.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = (1)(364.2) - (1)(223.1) - (1)(311.6) = -170.5 \text{ J mol}^{-1}\text{ K}^{-1}$$

We want the units to cancel out correctly, so let's convert ΔS° to kJ.

$$\Delta S^\circ \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -0.1705 \text{ kJ mol}^{-1}\text{ K}^{-1}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-86.2}{-0.1705} = \boxed{506 \text{ K}}$$

Thus, the answer is $\boxed{A}$.

22. We know the reaction for ΔH_f° of H_2O must produce 1 mole of H_2O from elements in their standard states, H_2 and O_2. Therefore, the reaction is

$$H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(l)$$

In this reaction, we break 1 H−H bond and half of an O=O bond. We then form 2 O−H bonds. Using bonds broken minus bonds formed and the information from the table, we get

$$\Delta H_\text{f}^\circ = 1(432) + \frac{1}{2}(495) - 2(467) = \boxed{-255 \text{ kJ mol}^{-1}}$$

Thus, the answer is $\boxed{D}$.

23. We know II is true because $\Delta G < 0$ for all spontaneous processes. I is a statement of the second law of thermodynamics: the total entropy of the universe (system plus surroundings) must increase. Remember that either of the two ΔS values could be less than 0, indicating a decrease, but the sum of both must be an increase. Therefore the answer is $\boxed{I + II}$, which is $\boxed{C}$.

24. The reaction we would use to find ΔG_f° of HOCl(g) must create 1 mol HOCl from the elements in their standard states $H_2(g)$, $O_2(g)$, and $Cl_2(g)$. Thus the reaction is

$$\frac{1}{2}\,\text{H}_2(g) + \frac{1}{2}\,\text{O}_2(g) + \frac{1}{2}\,\text{Cl}_2(g) \longrightarrow \text{HOCl}(g)$$

However, the reaction that is given in the question gives no information about H_2, O_2, or Cl_2. It is possible with the information given to find ΔG° for the reaction in the question. Thus we don't have enough information to answer the problem, and the answer is $\boxed{D}$.

25. From the reaction, we see 3 moles of elemental bromine (Br_2) are formed for every 5 moles of bromide ion (Br^-) consumed. We can use this for stoichiometry.

$$0.056 \text{ M s}^{-1} \times \frac{5 \text{ mol Br}^-}{3 \text{ mol Br}_2} = \boxed{0.093 \text{ M s}^{-1}}$$

This is $\boxed{D}$.

26. We can model the amount A of ^{201}Tl after t days by using the integrated rate law of first order reaction since nuclear decay is typical first order process.

$$A = A_0 \times \left(\frac{1}{2}\right)^{\frac{t}{3.05}}$$

Let's divide by A_0 on both sides. We know the final amount A is 18% of the initial amount A_0. In equations, $A = 0.18 \cdot A_0 \implies \frac{A}{A_0} = 0.18$. Therefore

$$0.18 = \left(\frac{1}{2}\right)^{\frac{t}{3.05}}$$

Now we take log base $\frac{1}{2}$ on both sides. However, because of calculator limitations on the olympiad, we must use change of base.

$$\frac{\ln 0.18}{\ln(1/2)} = \frac{t}{3.05}$$

$$t = 3.05 \times \frac{\ln 0.18}{\ln(1/2)} = \boxed{7.5 \text{ d}}$$

This is $\boxed{C}$.

27. From the first row of the table to the second, [SCN^-] is multiplied by $\frac{11}{8}$ and the reaction rate is also multipled by approximately $\frac{11}{8}$. Therefore, the reaction is first order in SCN^-. From the second row to the third, [$Cr(H_2O)_6{}^{3+}$] is multiplied by $\frac{37}{28}$ and the rate is also multiplied by about $\frac{37}{8}$. Therefore, the reaction is first order in $Cr(H_2O)_6{}^{3+}$ as well. So far we know the rate law is in the form

$$\text{Rate} = k[\text{Cr(H}_2\text{O)}_6{}^{3+}][\text{SCN}^-]$$

To determine the value of k, we can use any row of the table. Let's use the first row as an example.

$$k = \frac{\text{Rate}}{[\text{Cr(H}_2\text{O)}_6{}^{3+}][\text{SCN}^-]}$$

$$k = \frac{8.1 \times 10^{-6}}{(0.028)(0.040)} = \boxed{7.2 \times 10^{-3} \frac{1}{\text{M} \cdot \text{hr}}}$$

Now that we know k, we can look at the answer choices and see that the answer must be $\boxed{B}$.

28. Catalysts are best known for decreasing the activation energy, so we know II is correct. However, catalysts also provide an alternative path for the reaction, with different elementary steps. Because the rate law depends on the elementary steps, it is possible for a catalyst to alter the rate law. Therefore, the answer is $\boxed{I + II}$, which is $\boxed{C}$.

29. When the temperature of the system increases, equilibrium will shift to endothermic direction to reduce the temperature increase by Le Chatelier's principle. For an exothermic reaction, both forward and backward reaction rates increase with temperature, but backward reaction rate increases more than the forward one since the equilibrium needs to shift to the left side. Therefore, the answer is $\boxed{B}$.

Another way to analyze this question is to think about how temperature increase affects the rate of reactions with different activation energies. A reaction with larger activation energy is accelerated more than the reaction with a smaller one according to the Arrhenius equation. For an exothermic reaction, the backward reaction has a larger activation energy than the forward reaction according to the energy curve. With the same amount of temperature increase, both the backward and forward reactions are accelerated, but the backward reaction is accelerated more. On a more mathematical note, the Arrhenius equation explicitly allows us to relate the activation energy to the rate constants of a reaction.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Note: As temperature increases, $T_2 > T_1$, $(1/T_1 - 1/T_2)$ is positive, thus, a larger E_a results in a larger k_2/k_1.

30. First, let us write the rate for the production and consumption of the intermediate $(\text{CH}_3)_3\text{C}^+$.

$$R_{\text{production}} = k_1[(\text{CH}_3)_3\text{CBr}]$$

$$R_{\text{consumption}} = k_{-1}[(\text{CH}_3)_3\text{C}^+][\text{Br}^-] + k_2[(\text{CH}_3)_3\text{C}^+][\text{N}_3^-]$$

Because $[(\text{CH}_3)_3\text{C}^+]$ remains steady, it means the above two rates equal to each other.

$$k_{-1}[(\text{CH}_3)_3\text{C}^+][\text{Br}^-] + k_2[(\text{CH}_3)_3\text{C}^+][\text{N}_3^-] = k_1[(\text{CH}_3)_3\text{CBr}]$$

$$[(\text{CH}_3)_3\text{C}^+]\Big(k_{-1}[\text{Br}^-] + k_2[\text{N}_3^-]\Big) = k_1[(\text{CH}_3)_3\text{CBr}]$$

$$[(\text{CH}_3)_3\text{C}^+] = \frac{k_1[(\text{CH}_3)_3\text{CBr}]}{k_{-1}[\text{Br}^-] + k_2[\text{N}_3^-]}$$

We can now substitute this into the rate expression of the second step and we will get our final rate law since the second step is the one to produce the product $(\text{CH}_3)_3\text{CN}_3$.

$$R_2 = \frac{d}{dt}\Big([(\text{CH}_3)_3\text{CN}_3]\Big) = k_2[(\text{CH}_3)_3\text{C}^+][\text{N}_3^-] = \boxed{\frac{k_1 k_2[(\text{CH}_3)_3\text{CBr}][\text{N}_3^-]}{k_{-1}[\text{Br}^-] + k_2[\text{N}_3^-]}}$$

Thus, the answer is $\boxed{D}$.

31. Intuitively, we can derive the formula for percent ionization as the [concentration of deprotonated species] divided by [initial concentration of original acid multiplied by 100%. A higher K_a value (acid dissociation) means that the acid dissociates more. In turn, this leads to higher ionization. Actually, percent ionization is also dependent on the initial concentration of the acid as shown in the math work below.

$$K_\mathrm{a} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]} \approx \frac{[\mathrm{H}^+]^2}{c_\mathrm{HA}}$$

thus,

$$[\mathrm{H}^+] = \sqrt{c_\mathrm{HA} K_\mathrm{a}}$$

Substituting it into the definition of percent ionization below, we get

$$(\%\ \text{ionization}) = \frac{[\mathrm{A}^-]}{c_\mathrm{HA}} \approx \frac{[\mathrm{H}^+]}{c_\mathrm{HA}} = \sqrt{\frac{K_a}{c_\mathrm{HA}}}$$

Therefore, we need to choose the option with the smallest initial concentration and the maximum K_a. Doing a quick scan of the options, we see that $\boxed{\text{0.010 M formic acid}}$ is the solution with the greatest percent ionization. Thus, the answer is $\boxed{A}$.

32. First, we need to write the balanced equation.

$$\mathrm{CaC_2O_4}(s) \longrightarrow \mathrm{Ca^{2+}}(aq) + \mathrm{C_2O_4{}^{2-}}(aq)$$

We can then write an equation for K_sp.

$$K_\mathrm{sp} = [\mathrm{Ca^{2+}}][\mathrm{C_2O_4{}^{2-}}]$$

One key observation here is that since 1 ion of calcium is lost, and 1 ion of oxalate is lost, the concentrations for both are equal.

$$0.67\ \frac{\mathrm{mg}}{\mathrm{L}} \times \frac{1\ \mathrm{g}}{1000\ \mathrm{mg}} \times \frac{1\ \mathrm{mol\ CaC_2O_4}}{128.1\ \mathrm{g\ CaC_2O_4}} = 5.2 \times 10^{-6}\ \mathrm{M}$$

We have now solved for the concentration, and can now substitute

$$K_\mathrm{sp} = (5.2 \times 10^{-6})^2$$

$$K_\mathrm{sp} = \boxed{2.7 \times 10^{-11}}$$

Thus, the answer is $\boxed{C}$.

33. Let's first focus on the two dissociations of $\mathrm{H_2CO_3}$.

$$\mathrm{H_2CO_3} \rightleftharpoons \mathrm{HCO_3{}^-} + \mathrm{H^+} \quad K_\mathrm{a1} = 4.2 \times 10^{-7}$$

$$\mathrm{HCO_3{}^-} \rightleftharpoons \mathrm{CO_3{}^{2-}} + \mathrm{H^+} \quad K_\mathrm{a2} = 4.8 \times 10^{-11}$$

Now let's use the formula $K_\mathrm{b} = \frac{K_\mathrm{w}}{K_\mathrm{a}}$ to go backwards and figure out the behavior of the base in question, $\mathrm{CO_3{}^{2-}}$.

$$\mathrm{CO_3{}^{2-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{HCO_3{}^-} + \mathrm{OH^-} \quad K_\mathrm{b1} = \frac{K_\mathrm{w}}{K_\mathrm{a2}} = 2.08 \times 10^{-4}$$

$$\mathrm{HCO_3{}^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2CO_3} + \mathrm{OH^-} \quad K_\mathrm{b2} = \frac{K_\mathrm{w}}{K_\mathrm{a1}} = 2.38 \times 10^{-8}$$

Notice that K_b2 is negligible compared to K_b1, so we will focus on K_b1.

$$K_\mathrm{b1} = \frac{[\mathrm{HCO_3{}^-}][\mathrm{OH^-}]}{[\mathrm{CO_3{}^{2-}}]}$$

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} = 10^{\mathrm{pH}-14} = 10^{-2.1}$$

We can make the approximation that $[\mathrm{OH^-}] \approx [\mathrm{HCO_3}^-]$.

$$K_{\mathrm{b2}} = \frac{[\mathrm{OH^-}]^2}{[\mathrm{CO_3}^{2-}]}$$

$$[\mathrm{CO_3}^{2-}] = \frac{[\mathrm{OH^-}]^2}{K_{\mathrm{b2}}} = \frac{(10^{-2.1})^2}{2.08 \times 10^{-4}} = \boxed{3.0 \times 10^{-1}\ \mathrm{M}}$$

Since the $[\mathrm{HCO_3}^-]$ is negligible compared to $[\mathrm{CO_3}^{2-}]$, the answer is $\boxed{A}$.

34. The point when the pH of the solution is equal to the pK_a is the half-equivalence point. The half-equivalence point is simply halfway between the equivalence point on the axis. The equivalence point on this titration curve is reached at 60 mL, so the half-equivalence point will be reached at 30 mL. At this point, we can check the pH and determine which is the correct compound. The pH of the compound is on the lower side of 9, so by analysis of the answer choices, we get $\boxed{A}$.

35. The decrease in volume will lead to an increase in pressure. According to Le Chatelier's principle, the equilibrium is going to shift to the left side with less moles of gases as pressure increases. This is because the shift to fewer gas moles will reduce the pressure increase. First, let's find K_p using the equilibrium data.

$$K_\mathrm{p} = \frac{(P_{\mathrm{SO_2}})(P_{\mathrm{Cl_2}})}{(P_{\mathrm{SO_2Cl_2}})} = \frac{(0.10)(0.10)}{(1.00)} = 0.010$$

Now let's find Q_p. Since the volume was halved, all pressures are now doubled.

$$Q_\mathrm{p} = \frac{(P_{\mathrm{SO_2}})(P_{\mathrm{Cl_2}})}{(P_{\mathrm{SO_2Cl_2}})} = \frac{(0.20)(0.20)}{(2.00)} = 0.020$$

This confirms that the reaction must shift left. As the reaction reaches equilibrium, the pressure of $\mathrm{SO_2Cl_2}$ will increase by some amount x. We see from the reaction that $\mathrm{SO_2}$ and $\mathrm{Cl_2}$ will decrease by the same amount. Thus,

$$K_\mathrm{p} = \frac{(0.20 - x)(0.20 - x)}{(2.00 + x)}$$

We could solve this equation for x to find the final pressure of $\mathrm{SO_2Cl_2}$, but it would take time. Instead, notice that $x > 0$ because by Le Chatelier's principle, $\mathrm{SO_2Cl_2}$ must increase. Also notice that $x < 0.20$ because otherwise the partial pressures of $\mathrm{SO_2}$ and $\mathrm{Cl_2}$ would be negative. Therefore, the final $\mathrm{SO_2Cl_2}$ is between 2.00 bar and 2.20 bar, which fits the range of an $\boxed{\text{increase 1-10\%}}$. Thus, the answer is $\boxed{A}$. If we were to actually solve for x, we would get 0.06, meaning an increase of 3%.

36. Because AgCl(s) is solid, it cannot affect an equilibrium expression and so will not increase $[\mathrm{Cl^-}]$. Thus I is incorrect. On addition of $\mathrm{NH_3}(aq)$, $[\mathrm{Cl^-}]$ increases according to the reaction

$$\mathrm{AgCl(s)} + 2\,\mathrm{NH_3(aq)} \rightleftharpoons [\mathrm{Ag(NH_3)_2}]^+\mathrm{(aq)} + \mathrm{Cl^-(aq)}$$

Thus only $\boxed{II}$ is correct, and the answer is $\boxed{B}$.

37. Oxidation occurs at the anode and reduction occurs at the cathode. $\mathrm{F^-}$ is already lowest oxidation of halogens so it cannot be further reduced at the cathode. $\mathrm{Ag^+}$ can be reduced to $\boxed{\mathrm{Ag}(s)}$ at the cathode, so the answer is $\boxed{A}$. In a further analysis, the positive ions are attracted to the negative cathode. There is competition between the silver ions, $\mathrm{Ag^+(aq)}$, and the hydrogen ions, $\mathrm{H^+(aq)}$. As the silver is a very un-reactive metal, the silver ions are preferentially reduced.

38. In Cl_2, the molecule must be neutral so chlorine has an oxidation state of 0. In KClO, K must have an oxidation state of +1 and O must have an oxidation state of −2. In order for the molecule to be neutral, we know chlorine must have an oxidation state of +1. In $KClO_4$, K must have an oxidation state of +1 and each O must have an oxidation state of −2. Since there are 4 oxygens, this leaves a −7 charge without chlorine. To compensate, chlorine must have a +7 oxidation state. In $\boxed{\text{KCl}}$, K must have an oxidation state of +1, so chlorine has an oxidation state of −1 to keep the molecule neutral. Thus, $\boxed{B}$ is the lowest oxidation state.

39. Because the reaction takes place in an acidic solution, we must have the H^+ and the H_2O in the reaction, which we do. We need to check the oxidation states first.

$$\mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} + 2\,\mathrm{e}^-$$

$$\mathrm{NO_3}^- + 3\,\mathrm{e}^- \longrightarrow \mathrm{NO}$$

We can see that Cu gets oxidized, with its oxidation state going from 0 to 2. N gets reduced, and its oxidation state goes from 5 to 2. Now, we can write the half-reactions.

$$3\,\mathrm{Cu} \longrightarrow 3\,\mathrm{Cu}^{2+} + 6\,\mathrm{e}^-$$

$$2\,\mathrm{NO_3}^- + 6\,\mathrm{e}^- \longrightarrow 2\,\mathrm{NO}$$

The balanced final reaction (without addition of water and H^+) is

$$2\,\mathrm{NO_3}^-(aq) + 3\,\mathrm{Cu}(s) \longrightarrow 2\,\mathrm{NO}(g) + 3\,\mathrm{Cu}^{2+}(aq)$$

We have 6 O on the reactant's side, and 2 O on the product side. So, on the product's side we will add $4\,H_2O$. To balance on the other side, we need to add $8\,H^+$. Thus, the final reaction is

$$8\,\mathrm{H^+(aq)} + 2\,\mathrm{NO_3}^-\mathrm{(aq)} + 3\,\mathrm{Cu\,(s)} \longrightarrow 2\,\mathrm{NO\,(g)} + 3\,\mathrm{Cu}^{2+}\mathrm{(aq)} + 4\,\mathrm{H_2O\,(l)}$$

Thus, the ratio of H^+ to NO is $\frac{8}{2}$, or $\boxed{4\ :\ 1}$, which is $\boxed{D}$.

40. According to the overall reaction, the first half reaction is on the cathode being reduced, and the second half reaction is on the anode being oxidized. Thus, the answer is $-1.66 - (-0.76) = \boxed{-0.90\text{ V}}$, which is $\boxed{B}$.

41. We can do dimensional analysis with an unknown variable M using Faraday's constant F and 1 A = 1 C/s. Note that in all the answer choices, copper has an oxidation state of +2, so each copper ion gains $2e^-$.

$$1.00\text{ g} \times \frac{1\text{ mol salt}}{M\text{ g}} \times \frac{2\text{ mol }e^-}{\text{mol salt}} \times \frac{96500\text{ C}}{\text{mol }e^-} \times \frac{1\text{ s}}{0.100\text{ C}} \times \frac{1\text{ min}}{60\text{ s}} = 123\text{ min}$$

$$\frac{32167}{M} = 123$$
$$M = 262$$

This could only be $\boxed{\mathrm{Cu(ClO_4)_2}}$, or $\boxed{D}$.

42. By subtracting the first equation from the second equation, we get

$$\mathrm{Hg_2Cl_2(s)} \rightleftharpoons \mathrm{Hg_2}^{2+}\mathrm{(aq)} + 2\,\mathrm{Cl^-(aq)}$$

We also know that

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

In this case, this would be

$$E^\circ_{\text{cell}} = +0.31\text{ V} - 0.80\text{ V}$$
$$E^\circ_{\text{cell}} = -0.49\text{ V}$$

Now, that we have E_{cell}, we can use another equation in terms of E_{cell}, and solve then.

$$E^\circ_{\text{cell}} = \frac{\Delta G^\circ}{-nF} = \frac{RT\ln K}{nF}$$

Solving for K, we get

$$\frac{E^\circ_{\text{cell}} \times nF}{RT} = \ln K$$

Substituting our values of $E^\circ_{\text{cell}} = -0.49$ V, $n = 2\ e^-$, $F = 96500\ \frac{\text{C}}{\text{mol}}$, $R = 8.314\frac{\text{J}}{\text{mol}\times\text{K}}$, and $T = 298$ K, we get

$$K_{\text{sp}} = e^{-38.2} = \boxed{2.6 \times 10^{-17}}$$

Thus, the answer is $\boxed{A}$.

43. The key fact that you need to know is that there are n^2 orbitals in an energy level, and n subshells in one energy level. Thus, with $4^2 = \boxed{16}$, the answer is $\boxed{D}$. This is because the s, p, d, and f subshells have increasing odd numbers of orbitals, and the sum of the first n odd numbers is n^2. For $n = 4$, these four subshells are all present, and $1 + 3 + 5 + 7 = 16$.

44. From the electron configurations of Si and P, we see that both electrons are added to orbitals in the $3p$ subshell, so B is not correct. From our periodic trends, we see P is actually more electronegative than Si, so C is not correct. Also from periodic trends, we see P is actually smaller than Si, so D is incorrect. This leaves $\boxed{A}$ only as the correct answer.

Actually as a general trend across the period from left to right, the atoms in the 3rd period release more energy when gaining an electron. However, P has a valence electron configuration of $3s^2 3p^3$ with 3 unpaired electrons in the $3p$ subshell, which will experience a larger repulsion with the addition of one electron since the newly added electron has to be paired with another in one orbital. This elevated repulsion reduces the energy released by P. And Si with a valence electron configuration of $3s^2 3p^2$ has no issue like this. This explains why option A is correct.

45. We can solve for the energy using the equation below, with c being the speed of light, λ being the wavelength, and h being Planck's constant. Note that the speed of light is in meters per second, so we must convert the wavelength to meters.

$$E = \frac{hc}{\lambda}$$

Substituting the appropriate values, we get

$$E = 6.626 \times 10^{-34}\ \text{J}\cdot\text{s} \times \frac{3.00 \times 10^8\ \frac{\text{m}}{\text{s}}}{492 \times 10^{-9}\ \text{m}}$$

Substituting in the calculator, we get $E = \boxed{4.04 \times 10^{-19}\ \text{J}}$. Thus, the answer is $\boxed{D}$.

46. First, we need to write the electron configurations for all of the answer choices, noting that each ion has lost electrons from its neutral state.

$$\text{Cr}^{3+}\ :\ 3d^5\ 4s^1 \xrightarrow[-3e^-]{} 3d^3$$

$$\text{Co}^{3+}\ :\ 3d^7\ 4s^2 \xrightarrow[-3e^-]{} 3d^6$$

$$\text{Ni}^{2+}\ :\ 3d^8\ 4s^2 \xrightarrow[-2e^-]{} 3d^8$$

$$\text{Cu}^{2+}\ :\ 3d^{10}\ 4s^1 \xrightarrow[-2e^-]{} 3d^9$$

We also know that the d subshell has 5 orbitals, so we need to check the number of unpaired electrons for each. We can do this by drawing electron diagrams, or mathematically. For elements with more than 5 electrons in the $3d$ subshell, we can subtract 5 to find the number of full orbitals. We then subtract 5 from this to find the number of unpaired electrons. For elements with less than 5 electrons, all are unpaired. By doing this math, Cr^{3+} has 3 unpaired electrons, Co^{3+} has 4 unpaired electrons, Ni^{2+} has 2 unpaired electrons, and Cu^{2+} has 1 unpaired electron. Thus, the element with the most unpaired electrons is $\boxed{\text{Co}^{3+}}$, or $\boxed{B}$.

47. This is the application of the nuclear decay pathways. We see that from ${}^{52}_{25}\text{Mn}$ to ${}^{52}_{24}\text{Cr}$, $\Delta A = 0$ and $\Delta Z = -1$. Thus, the only pathway that works is $\boxed{\text{positron emisson}}$, which is $\boxed{C}$.

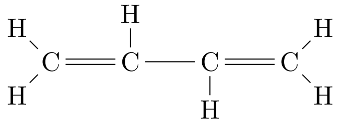
48. When the wavefunction equals 0, this counts as a node. So there are two nodes on the orbital based on the diagram. $1s$ has no node, $2s$ has one node, and $3s$ has two nodes. Thus, the answer is $\boxed{\text{3s}}$, or $\boxed{C}$.

We can further summarize the node number of ns to be $(n-1)$.

49. The oxygens in CO_2 carry a partial negative charge, while the carbon has a partial positive charge. Thus, bond dipoles are equal and opposite, and cancel out. Thus, the answer is $\boxed{\text{CO}_2}$, or $\boxed{B}$.

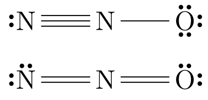
50. This is just drawing the Lewis structure and then the application of the VSEPR model. Because SF_4 has 5 electron domains including one lone pair, this fits the description for a $\boxed{\text{see-saw}}$ geometry, or $\boxed{C}$.

51. To avoid mistakes, it is helpful to not rely on the formula given in the question and to actually draw the molecule.



Each single bond will contribute 1 σ bond. Each double bond will contribute 1 σ bond and 1 π bond. We count 7 single bonds and 2 double bonds, so $\sigma = 7 + 2 = 9$ and $\pi = 2$. Thus, the answer is $\boxed{C}$.

52. There are two resonance structures of N_2O.



In both structures, there are 4 bonds around the central nitrogen and no lone pairs. Since nitrogen has 5 valence electrons, the formal charge in both cases is $5 - 4 = \boxed{+1}$. Thus, the answer is $\boxed{B}$.

53. The key word in this question is the word *a* Lewis structure. Thus, it is possible that the structure shown is one of many resonance structures. This is easily identifiable by seeing the NH_2 could be swapped, and the ion would look identical. Thus, it is safe to assume that the nitrogens should have the same electron geometry to maintain the energy configuration. This eliminates B and C.

We now need to look at the bonds to determine the type of hybridization of nitrogens. Nitrogen A with the positive formal charge has three bonding pairs, which should have a sp^2 hybridization and a trigonal planar geometry. Since B needs to be the same as A according to the analysis above, so it is also sp^2 and trigonal planar. Thus, the answer is $\boxed{A}$.

The carbon and two nitrogens in the ion are all sp^2 with one unhybridized p orbital on each atom, which is parallel to each other. These three p orbitals makes a delocalized pi system. Electrons in delocalized one can be spread in a larger system with more than two orbitals, which makes the species more stable. If any of the two nitrogens take sp^3 hybridization and trigonal pyramidal geometry, there is no delocalization any more.

54. In a neutral O_2 molecule, the two unpaired electrons are positioned in the two degenerated π anti-bonding orbitals. Upon addition of an electron in ${O_2}^-$, this new electron pairs up with one of the originally unpaired electrons, making 1 pair and $\boxed{1}$ unpaired electron. Thus, the answer is $\boxed{B}$.

55. Simply rotating either molecule 180 degrees, we see that they have exactly the same structure. Remember that the actual molecule is a physical object that can be rotated in space. Thus, the two molecules are not really distinct, and the answer is $\boxed{D}$.

56. OH^- is not a typical oxidizing agent, so it is unlikely to be reduced. It is obviously not a Lewis acid because it is a typical Lewis base. It is not a catalyst because it is consumed in the reaction and is not produced again. A $\boxed{\text{nucleophile}}$ donates electrons to form a bond. In this case, the OH^- donates electrons to bond to the partially positive-charged carbon which bonds to Br initially, with the Br^- as a leaving group. Thus, the answer is $\boxed{D}$.

57. Cr(VI) reacts readily with primary alcohols and secondary alcohols. A primary alcohol is an alcohol that contains CH_2OH, such as $\boxed{A}$. B is not an alcohol because it has no OH group. Secondary alcohols have an OH bonded to a carbon that is in turn bonded to two other carbons. The carbon in D is bonded to three other carbons which is a tertiary alcohol and can't be oxidized by Cr(VI), so it is not correct. C is a carboxylic acid which can't be further oxidized by Cr(VI).

58. In the process of polymerization, the molecule propene itself acts as the monomer. In this case, CH_3, will be attached to the central C in order to make room for a bond from the central C to the next monomer. Thus, the answer is $\boxed{B}$.

59. The primary structure is composed of an amino acid sequence. The secondary structure is composed of α-helices and β-sheets. The tertiary structure is a 3D structure, while the quaternary structure is multiple polypeptide subunits. Clearly, the one option that works is $\boxed{\text{primary}}$, or $\boxed{A}$.

60. Most macromolecules are made from single subunits, or building blocks, called monomers. The monomers combine with each other via covalent bonds to form larger molecules known as polymers. There are enzymes that do exist that break down proteins into their respective amino acids, and polysaccharides into their respective monosaccharides, by reacting with water since both proteins and polysaccharides are formed through the dehydration of their monomers. Enzymes that break down proteins are called proteases. Thus, both $\boxed{I + II}$ work, and the answer is $\boxed{C}$.