

Annotated Solution

2015 USNCO Local Exam

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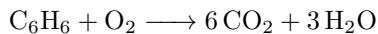
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1. Start by writing and balancing the combustion reaction.



There are 6 H on the reactants side, and only 2 on the products side. Additionally, we have 6 C on the reactants side and 1 on the products side. Thus, we can add a coefficient of 6 to the CO₂ and 3 to the H₂O. The new reaction becomes



The only thing left to balance is the oxygens. Counting the number of oxygens on the products side, we have 15 O. Thus, the coefficient on the O₂ must be $\frac{15}{2}$. The balanced reaction is

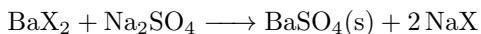


With the balanced reaction, use stoichiometry to solve for the moles of O₂.

$$1 \text{ mol C}_6\text{H}_6 \times \frac{7.5 \text{ mol O}_2}{1 \text{ mol C}_6\text{H}_6} = \boxed{7.5 \text{ mol O}_2}$$

Thus, the correct answer is **[B]**.

2. Let us first write a balanced reaction.



BaX₂ is used here based on the form of the salt in the four options. Na₂SO₄ is in excess, so BaX₂ is the limiting reagent. The number of moles of BaX₂ must equal the number of moles of BaSO₄, due to their identical coefficients. Find the number of moles of BaSO₄.

$$11.21 \text{ g Ba}_2\text{SO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.4 \text{ g BaSO}_4} = 0.04803 \text{ mol BaSO}_4$$

Knowing that there are 10.00 grams of BaX₂:

$$0.04803 \text{ mol} = \frac{10.00 \text{ g}}{M_W}$$

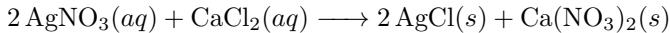
Solving for M_W, we get M_W = 208.2 $\frac{\text{g}}{\text{mol}}$, matching with **[BaCl₂]**, or **[A]**.

3. Molarity (M) measures concentration and is in units mol solute/L solution. Converting the mass to moles and dividing by volume of solution, we get the following. Thus, the correct answer is **[D]**.

$$32.0 \text{ g Mg(NO}_3)_2 \times \frac{1 \text{ mol Mg(NO}_3)_2}{148.3 \text{ g Mg(NO}_3)_2} \times \frac{2 \text{ mol NO}_3^-}{\text{mol Mg(NO}_3)_2} \times \frac{1}{0.425 \text{ L}} = \boxed{1.02 \text{ M}}$$

4. PO_4^{3-} has a charge of 3-. From TbPO_4 , we surmise that Tb (like most lanthanides) forms the Tb^{3+} ion. Sulfate is SO_4^{2-} . The compound must have an overall charge of 0. To balance the ion charges, we get $\boxed{\text{Tb}_2(\text{SO}_4)_3}$, or \boxed{C} .

5. Start by writing a balanced reaction:



Using stoichiometry, calculate the moles of AgNO_3 and CaCl_2 .

$$\frac{0.15 \text{ mol AgNO}_3}{1 \text{ L}} \times 0.0250 \text{ L} = 0.00375 \text{ mol AgNO}_3$$

$$3.58 \text{ g CaCl}_2 \times \frac{1 \text{ mol CaCl}_2}{111.0 \text{ g CaCl}_2} = 0.0323 \text{ mol CaCl}_2$$

$$0.00375 \text{ mol AgNO}_3 \times \frac{1 \text{ mol CaCl}_2}{2 \text{ mol AgNO}_3} = 0.00188 \text{ mol CaCl}_2 \text{ needed}$$

$\boxed{\text{CaCl}_2 \text{ is in excess}}$ of the amount needed, so $\boxed{\text{AgNO}_3 \text{ must be the limiting reagent}}$. The answer that fits this description is \boxed{B} .

6. Freezing point depression is determined by the following equation:

$$\Delta T = K_f \times i \times m$$

Where K_f is the molal freezing point depression constant, i the van't Hoff factor (i.e., how many ions a salt dissociates into), and m molality. K_f remains constant for a given solvent, so find the salt with the largest $i \times m$ product.

$$\text{KBr} : 2 \times 1.0 \text{ m} = 2 \text{ m}$$

$$\text{C}_6\text{H}_{12}\text{O}_6 \text{ (not ionic)} : 1 \times 0.75 \text{ m} = 0.75 \text{ m}$$

$$\text{MgCl}_2 : 3 \times 0.5 \text{ m} = 1.5 \text{ m}$$

$$\text{Ga}_2(\text{SO}_4)_3 : 5 \times 0.25 \text{ m} = 1.25 \text{ m}$$

Thus is $\boxed{\text{KBr}}$, or \boxed{A} .

7. A salt must react with HCl, if it is more soluble in HCl than H_2O . Look for basic ions that can neutralize HCl. In A, CO_3^{2-} is weakly basic; in B, OH^- is strongly basic; in D, PO_4^{3-} is weakly basic. In C, SO_4^{2-} has virtually no basic activity, because it is a conjugate for a much stronger acid, HSO_4^- . Thus, $\boxed{\text{gypsum}}$, or \boxed{C} , is unlikely to be more soluble in HCl than water.

8. Group 2 (alkaline earth metals), while still reactive, are less reactive than Group 1 (alkali) metals. Eliminate Ca (D). Larger alkali metals are more reactive, since their valence electrons are more shielded from the nucleus and less tightly bound. Since atomic radii increases down a column, $\boxed{\text{K}}$, or \boxed{C} , is the most reactive.

9. Many transition metal ions are colored due to the presence of incompletely filled d subshells. Zn exclusively forms Zn^{2+} , which has a completely filled d subshell and is consequently colorless. $\boxed{\text{Zn}(\text{NO}_3)_2}$, or \boxed{D} is also colorless.

10. Different glassware have different purposes. The $\boxed{\text{graduated cylinder}}$, or \boxed{A} , has lines for every 1.0 mL and is used to accurately measure volumes of liquids. The volumetric pipet (B) can only measure specific volumes: 50 mL, in this case. Beakers (C) are not precise and are used for storage and mixing. Erlenmeyer flasks (D) are also imprecise and mainly used for mixing.

11. Both AgCl and PbCl_2 are insoluble white precipitates, so color is not a differentiating factor. The difference is that PbCl_2 is soluble in hot water, whereas AgCl is less soluble and remains insoluble even upon heating. Thus, the answer is $\boxed{0.1 \text{ M Pb}^{2+}}$, or \boxed{B} .

12. Boiling point increases with intermolecular force strength. All the given species contain polar covalent bonds and have dipole-dipole interactions in addition to London Dispersion Forces. HF, however, participates in hydrogen

bonding; fluorine is one of three most electronegative elements (N, O, F) that engage in hydrogen bonding. The rest have comparable dipole-dipole interactions, but significantly different masses. LDF increases with mass, giving us this ranking:



HCl, or **[B]**, has the lowest boiling point.

13. Vapor pressure refers to the pressure exerted by a vapor in equilibrium with its condensed state (i.e., liquid or solid). Vapor pressure increases with temperature, as heat excites particles and makes it easier for them to break into the gaseous phase. However, adding a nonvolatile solute would decrease vapor pressure (see Raoult's law). The correct answer is **I only**, or **[A]**.

14. Distillation separates components of a mixture by selective boiling and condensation. **A** contains the unpurified mixture, which will be at whatever temperature the student is heating it to. At point **B**, any vapor that forms will condense and then travel through the tunnel to condense at **C** and eventually get collected in **D**. The temperatures at points **C** and **D** only have to be between the melting point (to prevent clogging) and the boiling point, and do not have to be exactly 61 °C. CHCl₃ will vaporize first due to its lower boiling point and be the first distillate. At point **B**, it will be at its boiling point, 61°, just on the verge of condensing. Thus, the correct answer is **[B]**.

15. Turning a solid to a liquid excites molecules, allowing them to flow over each other, but they are still close enough to feel intermolecular attraction. Turning a liquid to a gas requires the complete breakage of any intermolecular forces. Thus, the enthalpy of vaporization (liquid to gas) is **greater** than the enthalpy of fusion (solid to liquid).

The answer is **[A]**.

16. Since volume is constant, we can use Gay-Lussac's law:

$$\frac{T_1}{P_1} = \frac{T_2}{P_2}$$

Always convert temperatures to Kelvin:

$$\frac{(25 + 273) \text{ K}}{1.0 \text{ atm}} = \frac{(125 + 273) \text{ K}}{P_2}$$

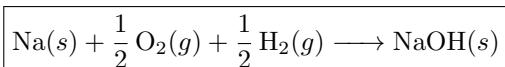
Solving, we get $P_2 = 1.3 \text{ atm}$, or **[C]**.

17. Diamond is made up of a large network of tetrahedral carbon atoms connected by covalent bonds. Long-range order based on covalent bonds is endemic to a **network covalent** structure, or **[D]**. Other such compounds include crystalline silicon, silica (SiO₂), and silicon carbide (SiC).

18. The first law of thermodynamics is the conservation of energy: the total amount of energy in the universe remains constant, merely changing from one form to another. A is the ideal gas law, reshuffled. The equation **$\Delta E = q + w$** , or **[B]**, states that changes in internal energy are equal to the sum of heat added to the system from the surroundings (q) and work done on the system by the surroundings (w). C defines ΔH , or enthalpy change. D defines ΔG , or Gibbs' free energy change, in terms of ΔH and ΔS , or entropy, and is used to determine when/if a reaction is spontaneous.

19. Atoms on edges, faces, and vertices of unit cells are shared with other unit cells and should be counted partially. A is in the center, so it will contribute 1 atom. B is at the corners, with each corner atom contributing $\frac{1}{8}$ of an atom: $\frac{1}{8} \times 8 = 1$ atom of B. C is on the edges, contributing $\frac{1}{4} \times 12 = 3$ atoms. The empirical formula is **[ABC₃]**, or **[B]**.

20. In order for the enthalpy change of the reaction to be equal to ΔH_f° of NaOH, all of the reactants must be in their elemental state, and one mole of NaOH must be produced. Fractions are allowed for diatomic elements. The reaction that fits this is



Thus, the correct answer is **[B]**.

21. The energy gained by the water must be equal to the energy lost by the gold block. We can write expressions for these energies using $q = mC\Delta T$. (Note that the difference in temperature ΔT is the same for Kelvin and Celsius; we simply add a constant to both temperatures, which cancels upon subtraction.)

$$q_{\text{Au lost}} = \left(0.129 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) \times (37.5 \text{ g}) \times (83.0^\circ\text{C} - T_f)$$

$$q_{\text{H}_2\text{O gained}} = \left(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) \times (100.0 \text{ g}) \times (T_f - 22.0^\circ\text{C})$$

Setting these two equal, we get

$$\left(0.129 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) \times (37.5 \text{ g}) \times (83.0^\circ\text{C} - T_f) = \left(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) \times (100.0 \text{ g}) \times (T_f - 22.0^\circ\text{C})$$

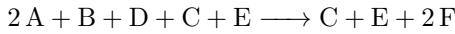
Solving for T , we get $T_f = 22.7^\circ\text{C}$, or \boxed{A} .

22. Entropy increases when the moles of gas increases, or when a solid melts. A indicates a decrease in entropy as the state of matter goes from liquid to solid. Both B and C indicate a decrease in entropy as the state of matter goes from gas to aqueous or solid in D, and gas to aqueous in C while the number of moles also decreases. The reaction shown below, however, is correct.



In this reaction, the products contain one more mole of gas than the reactants, which indicates an increase in entropy. Thus, the correct answer is \boxed{D} .

23. Manipulate the given reactions to get the final reaction. By reversing the third equation, we will have 2F on the product's side. Adding all the reactions, we now have



Cancelling C + E, we get our desired reaction. To find its ΔH , we get the expression below. Notice that we must reverse the ΔH for the third reaction.

$$\Delta H = -35 + 20 - (+15) = \boxed{-30 \frac{\text{kJ}}{\text{mol}}}$$

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

24. We can use the van 't Hoff equation to solve for the $K_{\text{a}2}$.

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substituting $\Delta H^\circ = -14.2 \frac{\text{kJ}}{\text{mol}}$, $T_1 = 25+273 = 298 \text{ K}$, $T_2 = 60+273 = 333 \text{ K}$, $R = 8.314 \frac{\text{J}}{\text{mol}\times\text{K}}$, and $K_{\text{a}1} = 7.6 \times 10^{-3}$, we get

$$\ln \left(\frac{K_{\text{a}2}}{7.6 \times 10^{-3}} \right) = \frac{14200}{8.314} \left(\frac{1}{333} - \frac{1}{298} \right)$$

$$\ln \left(\frac{K_{\text{a}2}}{7.6 \times 10^{-3}} \right) = -0.598$$

$$K_{\text{a}2} = e^{-0.598} \times 7.6 \times 10^{-3}$$

$$K_{\text{a}2} = \boxed{4.2 \times 10^{-3}}$$

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

25. We can use stoichiometry to determine the rate of H_2O . Thus, the correct answer is \boxed{C} .

$$0.50 \frac{\text{M NH}_3}{\text{s}} \times \frac{6 \text{ mol H}_2\text{O}}{4 \text{ mol NH}_3} = \boxed{0.75 \frac{\text{M H}_2\text{O}}{\text{s}}}$$

26. Because the reaction is first order, we can say that

$$\text{Rate} = k[\text{H}_2\text{O}_2]$$

Solving for k , we get

$$k = \frac{\text{Rate}}{[\text{H}_2\text{O}_2]} = \frac{4.83 \times 10^{-6} \frac{\text{M}}{\text{s}}}{0.150 \text{ M}} = [3.22 \times 10^{-5} \text{ s}^{-1}]$$

Thus, the correct answer is **[B]**.

27. Integrated rate laws for 0th, 1st, and 2nd order reactions yield linear plots. Commit these to memory.

$$\text{0th order: } [\text{A}] = -kt + [\text{A}]_0$$

$$\text{1st order: } \ln [\text{A}] = -kt + \ln [\text{A}]_0$$

$$\text{2nd order: } 1/[\text{A}] = kt + 1/[\text{A}]_0$$

A linear $1/[\text{A}]$ vs t plot is characteristic of a **second order** reaction, or **[C]**.

28. Use the first order rate law:

$$A = A_0 e^{-kt}$$

First, use the half-life to solve for k .

$$k = \frac{\ln(2)}{t_{1/2}} = \frac{0.693}{8.02 \text{ day}} = 0.0864 \text{ day}^{-1}$$

With k , we can now solve for t . $A = 0.20\text{A}_0$, since 80.% has decayed.

$$0.20 = e^{-0.0864t}$$

$$t = -\ln(0.20)/0.0864 \text{ day}^{-1} = 18.6 \text{ days}$$

This rounds up to **[19 days]**, or **[C]**.

29. First, figure out what changes are occurring over the course of this reaction.



There is no pH change, as no acids or bases are produced or consumed. A pH meter would be useless. There is a color change, though. Cl_2 is a light green gas, whereas Br_2 is a strong reddish-brown color. **Spectrophotometers** measure the intensity of light absorbed or emitted by a solution and thus picks up on color changes. Thus, the answer is **[B]**.

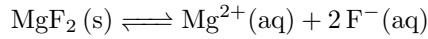
30. K_{eq} is the ratio of products to reactants and consequently a thermodynamic measure. From Le Chatelier's principle, we know that increases in temperature shift the equilibrium state of exothermic reactions towards the reactants, as the reaction attempts to consume heat from the temperature increase. k_f and k_r (forward and reverse rates) are kinetic measures and both increase with temperature. Increases in temperature excite the molecules and increase the chances of favorable collisions. The correct answer is thus **K_{eq} decreases and k_f increases**, or **[D]**.

31. Both barium acetate and sodium acetate contain the acetate ion, which is the conjugate base of acetic acid (weak acid). The conjugate base of weak acid is basic in aqueous solution due to its hydrolysis. However, barium has 2 acetate ions, while sodium has 1. The ammonium acetate has 1 ammonium ion in addition to 1 acetate ion. Ammonium ions, conjugate acid of weak base ammonia, act as weak acids, making $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ less basic than the others. Thus, the correct ordering is

$$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 < \text{NaC}_2\text{H}_3\text{O}_2 < \text{Ba}(\text{CH}_3\text{O}_2)_2$$

Thus, the correct answer is **[A]**.

32. First, write the reaction that corresponds to K_{sp} .



Let $[\text{Mg}^{2+}] = x$, and $[\text{F}^-] = 2x$. Then solve for x with the below equation.

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^-]^2$$

$$K_{\text{sp}} = x(2x)^2$$

$$6.8 \times 10^{-9} = 4x^3$$

$$x = \boxed{1.2 \times 10^{-3} \text{ M}}$$

Thus, the correct answer is **D**.

33. K_c and K_p can be inter-converted using the equation below, where Δn denotes the difference in moles of gas from reactants to products.

$$K_p = K_c(RT)^{\Delta n}$$

$$\frac{K_c}{K_p} = (RT)^{-\Delta n}$$

We see that there are 3 moles of gas on the products side, and 4 moles of gas on the reactants side. This makes $\Delta n = -1$. Thus, we have

$$\frac{K_c}{K_p} = (RT)^{-(-1)} = [(0.0821) \times (723 + 273)] = \boxed{81.8}$$

Thus, the correct answer is **D**.

Note: Please pay attention to the value and unit of R used here. With different combination of units for pressure and volume, R has different values and units. There are two common used value/unit combination for R used.

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1} = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

$$R = 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

When R is used together with ΔH or ΔG , such as Nernst equation and Clapeyron-Clausius equation, the R with a unit of $\text{J mol}^{-1} \text{ K}^{-1}$ should be used to cancel out the unit of J mol^{-1} in ΔH or ΔG . However, the case in this question is different, atm (actually should be bar, which is the unit of pressure in standard state) is used as unit when expressing the K_p , so 0.08206 is used here.

34. We can use the Henderson-Hasselbalch equation for bases.

$$\text{pOH} = \text{p}K_b + \log_{10} \left(\frac{[\text{BH}^+]}{[\text{B}]} \right)$$

where $K_b = 1.8 \times 10^{-5}$, $[\text{B}] = [\text{NH}_3] = 3.00 \text{ M}$, and $[\text{BH}^+] = [\text{NH}_4^+]$.

$$1.00 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.5 \text{ g NH}_4\text{Cl}} \times \frac{1 \text{ mol NH}_4^+}{\text{mol NH}_4\text{Cl}} \times \frac{1}{0.0300 \text{ L}} = 0.623 \text{ M NH}_4^+$$

Substituting our values, we get

$$\text{pOH} = -\log_{10}(1.8 \times 10^{-5}) + \log_{10} \left(\frac{0.623}{3.00} \right) = 4.05$$

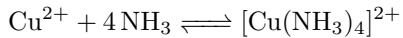
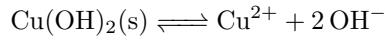
To find $[\text{H}_3\text{O}^+]$, we need to find pH. Thus, the correct answer is **C**.

$$\text{pOH} + \text{pH} = 14$$

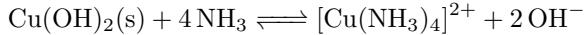
$$\text{pH} = 9.95$$

$$[\text{H}_3\text{O}^+] = 10^{-9.95} = \boxed{1.2 \times 10^{-10} \text{ M}}$$

35. We can start by writing reactions for solubility (K_{sp}) and formation (K_f).



The first reaction has an equilibrium constant of the given K_{sp} value, while the second reaction has an equilibrium constant of K_f . Adding both of these reactions will give us the desired reaction with equilibrium constant K_{eq} :



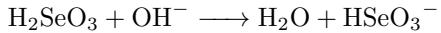
In adding the reactions, we actually multiply our equilibrium constants. Thus, we have the equation below,

$$K_{\text{eq}} = K_f \times K_{\text{sp}}$$

We can solve for K_f using the equation below to get \boxed{C} .

$$K_f = \frac{K_{\text{eq}}}{K_{\text{sp}}} = \frac{4.0 \times 10^{-7}}{2.2 \times 10^{-20}} = \boxed{1.8 \times 10^{13}}$$

36. From the titration curve, we see two equivalence points. Thus, we know the H_2SeO_3 is a diprotic acid. The marked point is the first equivalence point, where enough NaOH has been added to neutralize the H_2SeO_3 in the equation



We have not yet reached the second equivalence point, where the NaOH will neutralize the HSeO_3^- in the equation



Therefore, while the H_2SeO_3 has been completely used up, no SeO_3^{2-} has been produced yet at the first equivalence point. The only species representing more than 10% of the total selenium is $\boxed{\text{HSeO}_3^-}$, which is \boxed{C} .

37. Formaldehyde, a neutral molecule, must have an overall charge of 0. We can balance oxidation states of the atoms involved. In organic molecules, hydrogen has an oxidation state of +1, and oxygen has an oxidation state of -2:

$$\text{O(C)} + 2(+1) + 1(-2) = 0$$

$$\text{O(C)} = \boxed{0}$$

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

38. Galvanic cells are electrochemical cells hosting spontaneous reactions with positive voltages. As with any cell, reduction happens at the cathode. ("Cat-" is often associated with positive ions, and "cathodes" are named as such because cations flow towards them.) In this reaction, $\boxed{\text{Ce}^{4+}}$ gains an electron to form Ce^{3+} . Thus, the answer is \boxed{B} .

39. We can use the equation below to help us solve this.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

In order to maximize the voltage of the cell, the standard reduction potential in the cathode must be as positive as possible, and the standard reduction potential in the anode must be as negative as possible. Options $\boxed{\text{III} + \text{IV}}$ are the most positive and negative, respectively. Thus, the answer is \boxed{D} .

40. Faraday's law of electrolysis states that amount of substance produced at each electrode is directly proportional to the quantity of charge flowing through the cell and manifests as such:

$$m = \frac{M_W}{n} \times \frac{It}{F}$$

where m is the mass deposited, M_W the molecular weight of the metal, n the number of electrons required to reduce each metal cation into metal atom, I the intensity of the current, t how long the current is run, and F Faraday's constant (96500 Coulombs per mole).

The mass of metal deposited depends on the molecular weight and the moles of electrons needed to reduce the metal ions; other variables such as time and current intensity are kept constant.

$$m \propto \frac{M_W}{n}$$

We can calculate M_W and n for each of the answer choices, and calculate the greatest m , which is what the question is asking for.

$$\text{TlNO}_3 : M_W = 204.38, n = 1, \frac{M_W}{n} = 204.38$$

$$\text{Pb(NO}_3)_2 : M_W = 207.2, n = 2, \frac{M_W}{n} = 103.6$$

$$\text{ZnCl}_2 : M_W = 63.58, n = 2, \frac{M_W}{n} = 31.79$$

$$\text{In(NO}_3)_3 : M_W = 114.81, n = 3, \frac{M_W}{n} = 38.27$$

Thus, $\boxed{\text{TlNO}_3}$, or \boxed{A} , will have the greatest mass deposited.

41. Increasing pH leads to a decrease in H^+ . The exact magnitude can be determined via the Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$\Delta E = E - E^\circ = -\frac{RT}{nF} \ln Q = -\frac{(8.314 \frac{\text{J}}{\text{mol K}})(298 \text{ K})}{(4)(96500 \frac{\text{C}}{\text{mol}})} \ln \left(\frac{1}{[\text{H}^+]^4 P_{\text{O}_2}} \right)$$

Standard reduction potentials use concentrations of 1 M. If the pH of the solution has been increased by one unit, then the new $[\text{H}^+] = 0.1 \text{ M}$. Note: the pressure of O_2 is still 1 bar since all other species are in standard states except $[\text{H}^+]$.

$$\Delta E = -\frac{(8.314 \frac{\text{J}}{\text{mol K}})(298 \text{ K})}{(4)(96500 \frac{\text{C}}{\text{mol}})} \ln \left(\frac{1}{[0.1]^4} \right) = -0.059 \text{ V}$$

This is equivalent to a $\boxed{\text{decrease by } 59 \text{ mV}}$, or \boxed{A} .

42. First, find E° . We can then find ΔG and then solve for K_{sp} . If we flip the bottom reaction, and then add the two reactions, we get



From this, we see $n = 2e^-$. Now calculate E° :

$$E^\circ = 0.446 - 0.799 = -0.353 \text{ V}$$

ΔG can be solved for using:

$$\Delta G^\circ = -nFE^\circ = -(2 \text{ mol}) \left(96450 \frac{\text{J}}{\text{mol V}} \right) (-0.353 \text{ V}) = 6.81 \times 10^2 \text{ J/mol}$$

Then find K_{sp} using:

$$\Delta G^\circ = -RT \ln(K_{\text{sp}})$$

$$6.82 \times 10^2 \text{ J/mol} = -\left(8.314 \frac{\text{J}}{\text{mol K}} \right) (298 \text{ K}) \ln(K_{\text{sp}})$$

$$K_{\text{sp}} = \boxed{1.16 \times 10^{-12}}$$

Thus, the correct answer is \boxed{C} . Alternatively, we can note that at equilibrium, $E = \Delta G = 0$.

$$0 = E^\circ - \frac{RT}{nF} \ln K_{\text{sp}}$$

$$\ln K_{\text{sp}} = \frac{E^\circ nF}{RT} = \frac{(-0.353)(2)(96500)}{(8.314)(298.15)} = -27.48$$

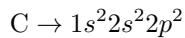
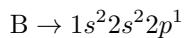
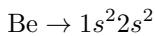
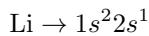
$$K_{\text{sp}} = e^{-27.48} = 1.16 \times 10^{-12}$$

43. For any p -subshell, $[l = 1]$. Thus, the answer is \boxed{A} .

44. Elements within the same column (or group, or family) have the same number of valence electrons and tend to have similar chemical properties. Of the choices, N and As are in the same column (Group 15) as P. Generally, third and forth row (or period) congeners are more alike than second and third period congeners due to the 3d contraction. In this case, As and P both have medium electronegativities (both are around 2.2), whereas N is much more electronegative (around 3.0). As such, $\boxed{\text{As}}$, or \boxed{D} , is most chemically similar.

45. For Group 1 metals, melting points decrease as you traverse down the group. The atoms in a metal are held together by the attraction of the nuclei to the delocalized electrons. In larger atoms, the nuclei are further from the electrons, and the attractive forces are weaker. $\boxed{\text{Rb}}$, or \boxed{D} , will have the lowest melting point.

46. By writing out the electron configurations for all of the elements, we can determine which one has no unpaired electrons.



Upon analysis of the electron configurations, by Hund's rule, only $\boxed{\text{Be}}$, or \boxed{B} , has no unpaired electrons.

47. Electron affinity is the change in energy (in kJ/mole) of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative gaseous ion. Fluorine may seem to have the greatest electron affinity, because it is most electronegative. However, fluorine is small, and the addition of an electron causes significant electron-electron repulsion. $\boxed{\text{chlorine}}$, or \boxed{B} , has larger $3p$ orbitals and does not experience such a big repulsion.

48. An important equation for this problem is the equation for the energy of an electromagnetic wave, $E = \nu h$. ν is the frequency and h is Planck's constant. We also know $c = \nu\lambda$, where c is the speed of light and λ is the wavelength. Thus we can say $E = \frac{hc}{\lambda}$. There is another important equation for this question. The energy emitted by an electron transmission from $n = i$ to $n = f$ in a hydrogen atom is

$$E = 2.18 \times 10^{-18} \text{ J} \times \left(\frac{1}{f^2} - \frac{1}{i^2} \right)$$

Now we can solve for the wavelength.

$$\frac{hc}{\lambda} = 2.18 \times 10^{-18} \text{ J} \times \left(\frac{1}{f^2} - \frac{1}{i^2} \right)$$

$$\lambda = \frac{hc}{2.18 \times 10^{-18} \text{ J} \times \left(\frac{1}{f^2} - \frac{1}{i^2} \right)}$$

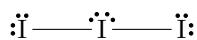
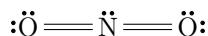
Note we can eliminate B and C because the electron is transitioning to a higher energy level. Thus, energy will be absorbed, not emitted. We can now determine the wavelengths for A and D using the constants h and c provided at the top of the exam.

$$i = 5, f = 2 : \lambda = 4.34 \times 10^{-7} \text{ m} = 434 \text{ nm}$$

$$i = 3, f = 1 : \lambda = 1.03 \times 10^{-7} \text{ m} = 103 \text{ nm}$$

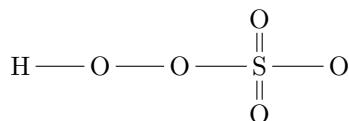
Visible light ranges from about 380 nm to 700 nm. Thus, the electronic transition that corresponds to the emission of visible light is $\boxed{n = 5 \rightarrow n = 2}$, or \boxed{A} .

49. Let's draw Lewis structures for both NO_2^+ and I_3^- .



According to the Lewis structures, NO_2^+ is no doubt to linear with two electron domains around the central N atom. I_3^- has five electron domains around the central I atom with three lone pairs on the equatorial positions according to VSEPR model, which also gives a linear geometry with the two remaining bonding pairs on the axial positions. Thus, the answer is I + II, or C.

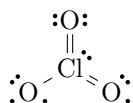
50. According to the name, "peroxymonosulfate anion", we can draw the structure for HSO_5^- to determine the correct answer.



As you can see, there is a S(+6), consistent with the monosulfate, and a O–O bond, consistent with the peroxy prefix. By looking at the Lewis dot structure, we have 4 S–O bonds and 1 O–O bond. Thus, the answer is B.

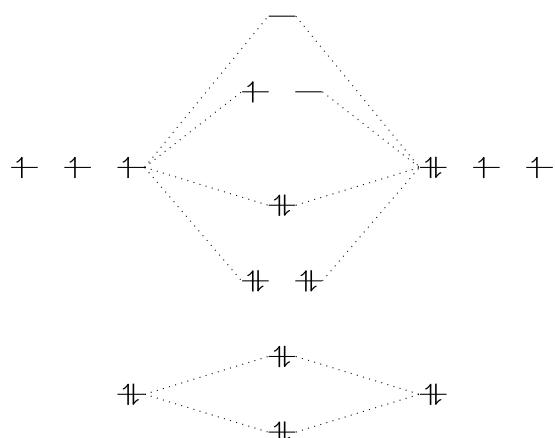
51. Single covalent bonds consist of a σ bond, where orbitals directly overlap. Double bonds consist of one σ bond and one π bond, and triple bonds consist of one σ bond and two π bonds; from this, C can be eliminated. π bonds are formed through sideways overlap of p orbitals, so D is out. σ bonds are stronger than π bonds, because they involve direct orbital overlap, so B is out. (Note: double bonds are stronger than single bonds in general, because they consist of a σ bond *and* a π bond, but they are not twice as strong, and π bonds by themselves are weaker.) This leaves us with A. Indeed, sigma bonds are cylindrically symmetric around the bonding axis.

52. First, draw the Lewis structure for ClO_3^- .



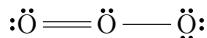
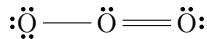
There are four electron domains around the central chlorine atom, giving it a tetrahedral shape for electron geometry. One of those domains is a lone pair; if you take that away, you get a trigonal pyramidal geometry, or B.

53. Let's go through the steps of drawing a molecular orbital diagram for NO. First, we see there are $5 + 6 = 11$ valence electrons, from the valence electrons of nitrogen and oxygen. Nitrogen (left) is $[\text{He}]2s^22p^3$, and oxygen (right) is $[\text{He}]2s^22p^4$. We then fill in the 11 valence electrons in between.



There are 4 pairs of bonding electrons, or 8 bonding electrons. There is 1 pair of antibonding electrons, plus one more antibonding electron for a total of 3 antibonding electrons. To find the bond order, we subtract the of antibonding electrons from the of bonding electrons and divide by 2. Thus, our final answer is $\frac{8-3}{2} = [2.5]$, or D.

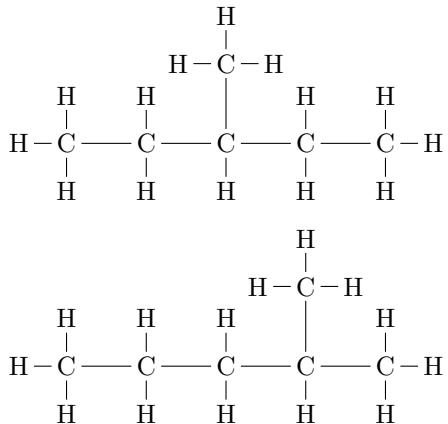
54. Ozone has two possible resonance structures.



In both of these, we see that the formal charge of the central oxygen is $6 - 2 - 3 = \boxed{+1}$, or \boxed{D} because oxygen has six valence electrons and we can subtract one for each bond and electron dot.

55. Hydrogenation refers to adding H_2 across a double bond. This is not to be confused with *hydration*, or adding water. Alkenes have carbon-carbon double bonds, and adding H_2 turns them into single bonds. The result is an $\boxed{\text{alkane}}$, or \boxed{A} .

56. Draw structures for the two compounds.



They are clearly not identical (A), since the methyl groups are on different carbons. Stereoisomers (B) are isomers where atoms are connected in the same ways, but oriented differently in space. Geometric isomers (C) refer to *cis/trans* alkenes, and there are no alkenes here. $\boxed{\text{Structural isomers}}$, \boxed{D} have the same molecular formula but different bond connections, and most aptly describes the given pair.

57. Alcohols have hydroxyl groups, or $-\text{OH}$. Amides have amide groups, or $-\text{C}(=\text{O})\text{NH}-$. $\boxed{\text{Amines}}$, or \boxed{C} have amino groups, or $-\text{NH}_2$ (or $-\text{NHR}$ or $-\text{NRR}'$), and are the only class with no oxygen. (Think ammonia, NH_3 .) Ketones have carbonyl groups, or $\text{C}=\text{O}$, in the middle of a carbon chain.

58. Ionic bonding is much stronger than intermolecular forces among hydrocarbons, thus ionic compounds will have much higher melting points than hydrocarbons (801 – 801 °C for NaCl , versus 174 °C for decane). Water, a polar solvent capable of hydrogen bonding, interacts more favorably with charged ions than it does with nonpolar hydrocarbons. Thus, the answer is $\boxed{\text{neither}}$, or \boxed{D} .

59. The degree of unsaturation (or IHD, index of hydrogen deficiency) for a molecule is a calculation that determines the number of pi bonds and rings. Each ring and pi bond is one degree of unsaturation, and so an alkyne with one triple bond has two degrees of unsaturation. The following equation can be used to calculate IHD:

$$\text{IHD} = \frac{2C + 2 + N - H - X}{2}$$

where C is the number of carbon atoms, N the number of nitrogen atoms, H the number of hydrogen atoms, and X the number of halogen atoms. From this equation, we can see that an alkane (formula $\text{C}_n\text{H}_{2n+2}$) has an IHD of 0. An alkene, with one pi bond, has formula C_nH_{2n} . An alkyne, with two pi bonds, has formula $\text{C}_n\text{H}_{2n-2}$. Of the given choices, only $\boxed{\text{C}_6\text{H}_{10}}$, or \boxed{C} has an appropriate formula for a molecule containing one triple bond. Please be aware that IHD is independent of the number of oxygen atoms.

60. A biopolymer is a natural polymer produced by the cells of living organisms. Collagen (A) is a protein, a polymer of amino acids. $\boxed{\text{Glucose}}$, or \boxed{B} , is not composed of many smaller units, but rather, it is a monosaccharide and monomer. Cellulose (C) and chitin (D) are both polysaccharides, made of monosaccharide monomers.