Annotated Solution
2016 USNCO National Exam Part I

Authors: Ron Shprints and William Wu
Proofreaders: Aditya Udgaonkar, Jason Zhang, and Dr. Qiang 'Steven' Chen
Editor: Dr. Qiang 'Steven' Chen

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1 Solutions

1. Suppose the formula is

$$C_xH_y + 8\,O_2 \longrightarrow x\,CO_2 + \frac{y}{2}\,H_2O$$

According to the conservation of oxygen, 8 moles of O_2 implies that

$$\frac{y}{2} + 2x = 16$$

After plugging possible options, we find that $\boxed{C_5H_{12}}$, or $\boxed{D}$ is the only possible answer. Alternatively, one can balance the equations for all of the options and see which one has 8 oxygen in the reactant side.

2. Using the molar masses of calcium and chlorine, the molar mass of $CaCl_2$ is $M(CaCl_2) = 111$ (g/mol). Thus, the moles of $CaCl_2$, and hence of Ca^{2+} ions, equal $n(CaCl_2) = n(Ca^{2+}) = \frac{7.50}{111} = 0.0676$ (mol) Remembering that $c = \frac{n}{v}$ the concentration of calcium ions can be found: $c(Ca^{2+}) = \frac{0.0676}{0.350} = \boxed{0.193\ (M)}$. Therefore, the answer is $\boxed{B}$.

3. After balancing the equation, we have

$$4\,Z + 3\,O_2 \longrightarrow 2\,Z_2O_3$$

With the given information in the question, we can set up the equation

$$\frac{0.422\ g}{M_Z} \div \frac{0.797\ g}{2 \times M_Z + 3 \times 16.0\ g/mol} = 2$$

After solving the above equation, we find that $M_Z = 27.0$ g/mol. This is the molar mass of $\boxed{Al}$ and thus the answer is $\boxed{A}$

4. According to Avogadro's principle, at constant temperature and pressure the volumes of gases are proportional to their moles. Thus, the ratio between the moles of O_2 and SO_2 is 3 : 5. Noticing that twice as much SO_2 reacts as O_2, SO_2 is the limiting reagent in this reaction. Assuming that the reaction goes to completion (100% yield), 5.0 moles of SO_2 react with 2.5 moles of SO_2 to produce 5.0 moles of SO_3, leaving 0.5 moles of O_2 that didn't react. Therefore, the final volume of the mixture is $\boxed{5.5\ (L)}$ and the answer is $\boxed{A}$.

5. Because there are only 0.040 mol of ClO^-, and $[H_2O_2] = 1.0$ M, the slope of the line n_{O_2} vs $V_{H_2O_2}$ should change to 0 after 40 mL of H_2O_2 have been added. Thus option $\boxed{D}$ is the correct answer.

6. This question tests your understanding on osmosis: the tendency of a fluid (in this case, water) to pass through the semipermeable membrane from high concentration to low concentration, the concentration here is proportional to the mole fraction of the water in the solution. When glucose ($C_6H_{12}O_6$) is dissolved in water it doesn't dissociate. However, when NaCl is dissolved, it dissociates to Na^+ and Cl^- ions. Thus, there are more particles on the right-hand side of the U-tube (considering the fact that the initial molalities and volumes of the substances are equal). Hence, the water moves from the left-hand side to the right-hand side to equalize the concentrations, causing the level on the right-hand side to increase. The correct answer is $\boxed{B}$.

7. If we know the melting point depression of the mixture, according to the formula

$$\Delta T = K_{\mathrm{f}} \times b \times i$$

When the pure solid organic compound is dissolved in an organic solvent, e.g. 1,4-dicholorobenzene here, we can determine the molality of the solution by measuring its melting point depression compared to that of the pure solvent, then we can further calculate the molar mass based on the molality, thus, B is correct. Determining the melting point of a sample is a common method to confirm the sample's purity, but can't quantify its molar mass. Heat of combustion does not work because we do not know the sample's molar change in enthalpy of combustion. Solubility in water does not necessarily correlates with molar mass. Therefore, the answer should be $\boxed{B}$

8. This question test your knowledge on qualitative analysis. When the HCl solution is added to the tested solution it reacts with the Ag^+ ions to form silver chloride:

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$

None of the other ions reacts with Cl^- to produce a precipitate.
When H_2SO_4 is added on the next step, it reacts with the Ba^{2+} ions:

$$Ba^{2+} + {SO_4}^{2-} \longrightarrow BaSO_4\downarrow$$

None of the other ions reacts with Cl^- to produce a precipitate.
The correct answer is $\boxed{B}$.

9. $Mg(OH)_2$ will not dissolve in sodium hydroxide due to common ion effect. $BaCO_3$ will not dissolve much because the concentration of carbonate ions will be much higher in basic conditions. Aluminium ions have a great tendency to form ${Al(OH)_4}^-$ in in the presence of excess OH^- as $Al(OH)_3(s)$ is amphoteric and can further reacts OH^-. Thus, $\boxed{Al_2(SO_4)_3}$ will dissolve, and the answer should be $\boxed{B}$. A question for the readers to think is under what condition will $BaCO_3$ dissolve and why. (*Hint*: consider the equilibrium between H_2CO_3, ${HCO_3}^-$, and ${CO_3}^{2-}$)

10. Let's test each claim separately, remembering that the question asks for *an error that will lead to a molar mass that is too high*:
I: The molar mass of a hydrated potassium hydrogen phthalate is larger than that of the non-hydrated form due to the presence of additional water molecules. Thus, if m grams of the hydrated form are taken for the experiment, smaller volume of NaOH reacts with the KHP, compared to m grams of the non-hydrated form. Therefore, this error leads to an overestimation (too high) concentration of the NaOH solution, and hence to an underestimated final molar mass of the acid as molar mass is reversely proportional to the moles of the analyzed compound.
II: The reaction of NaOH with CO_2 can be written as follows:

$$2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Notice that two equivalents of NaOH react with CO_2 to form Na_2CO_3 since OH^- is in excess. Thus, the actuall molarity of NaOH is get lower.
When the NaOH above is used to titrate the acid with phenolphthalein added as indicator, the Na_2CO_3 is not involved in the neutralization as phenolphthalein changes its color at $pH = 8-10$, which is close to the pH of Na_2CO_3 solution in most cases. Thus, the volume of acid needed to reach end point is smaller than it should be, and the moles of the acid is overestimated, and the molar mass of the acid is underestimated. Since neither I nor II leads to an overestimation of the molar mass, the correct answer is $\boxed{D}$.

11. A normal funnel with filter paper can indeed separate solid from liquids. However, the equipment in option C, Büchner funnel, is better at doing this job due to the porous structure of the funnel. In addition, the apparatus in C can be connected to a vacuum and thus speeding up the process and drying out the precipitate, which is crucial for filtering organic crystals. The equipment in B and D are clearly not for the separation of solid and liquid. Therefore, the answer should be $\boxed{C}$.

12. Flames tests are known to proceed according to the description of option $\boxed{C}$. Options (A) and (B) should be eliminated immediately because methanol is a flammable substance. Option (D) isn't applicable because the hot plate wouldn't cause the sample to burn (necessary to observe the flame).

13. First, larger intermolecular forces result in a higher normal boiling point. By evaluating the presence of hydrogen bonds, option C and D can be eliminated. Because propanoic acid, or CH_3CH_2COOH, has two hydrogen acceptor(two oxygens) while propanol, or $CH_3CH_2CH_2OH$, only has one hydrogen acceptor, the hydrogen bonding is more significant in $\boxed{\text{propanoic acid}}$, or option $\boxed{A}$.

14. Using the process of elimination, the correct answer can be found easily:

    (A) is incorrect because solid nitrogen is denser than liquid nitrogen. Substances that are denser in the liquid phase than in the solid phase are rare, and N_2 isn't one of them. For the interest of the reader, a few of these compounds are presented here: H_2O, Ga, Ge, Sb, Bi. You are not supposed to memorize the list as you can get the conclusion by analyzing the slope of the solid-liquid line in the phase diagram. If the slope of the line is negative, the liquid is denser as increasing pressure converts solid into liquid and hereby compresses the substance under constant temperature. If the slope is positive, solid is denser. As you can figure out that the slope of the solid-liquid line of N_2 is positive through comparing the pressure and temperature of N_2 at the triple point and normal melting point.

    (B) is incorrect because the given temperature (150 K) is higher than the temperature of the critical point (126.0 K). Above the temperature of the critical point, the gas cannot be liquefied in any pressure.

    (C) is incorrect because the coexistence of $N_2(l)$ and $N_2(s)$ under 1 atm is only possible in the normal boiling point (by definition), which exists in the temperature of 63.2 K.

    $\boxed{D}$ is the correct answer. Since the triple point exists in 0.127 atm and 63.1 K, it follows that in 60 K and 0.100 atm, N_2 is solid. Increasing the temperature under a pressure lower than that at the triple point can directly convert the solid into gas, which is commonly called sublimation.

    The best way is to sketch the phase diagram based on the information provided and analyze each option.

15. First apply the Idea Gas Law to check if there is enough solid to reach its vapor pressure.

$$n_{\text{needed}} = \frac{PV}{RT} = \frac{100.0 \text{ mmHg} \times 0.370 \text{ L}}{62.36 \text{ mmHg L/(mol K)} \times 266 \text{ K}} = 2.23 \text{ mmol}$$

$$n_{\text{actual}} = \frac{0.824 \text{ g}}{141.9 \text{ g/mol}} = 5.81 \text{ mmol}$$

There are enough solid molecules to reach its vapor pressure. Now we take a look at the Clausius-Clapeyron Equation

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

According to the equation, there is a temperature dependence on the vapor pressure, but since there is no change in T, P is constant. Alternatively, vapor pressure is an equilibrium constant, and K only changes with respect to T. Thus, the answer should be $\boxed{110.\ mmHg}$, or $\boxed{B}$

16. $HgCl_2$ is known as *corrosive sublimate*. Although it can be mistakenly interpreted as an ionic compound, $HgCl_2$ is composed of linear Cl−Hg−Cl molecules, describing its volatility.
$BaCl_2$ is an ionic compound. Due to the nature of the bonding in these compounds, answer $\boxed{A}$ is correct.
The electronegativity difference of the two elements in $HgCl_2$ is much smaller than that in $BaCl_2$ as Hg is an unreactive transition metal, this is why $HgCl_2$ has a much higher covalent character.

17. Since the bromine atoms are on the corner of the cell, each dark grey circle counts for 1/8 of a bromine atom. Hence, we have a total of $8 \cdot (1/8) = 1$ bromine atom in the unit cell. For thallium, the atom is completely in the unit cell so there is a total of 1 thallium atom in the unit cell. Recall density is mass over volume, so we now calculate the mass. Since we have 1 atom of Tl and 1 atom of Br, we have 1 molecule of TlBr. By stoichiometry, we have

$$1 \text{ formula unit TlBr} \cdot \frac{1 \text{ mol TlBr}}{6.02 \times 10^{23} \text{ formula unit TlBr}} \cdot \frac{284.3 \text{ g TlBr}}{1 \text{ mol TlBr}} = 4.72 \times 10^{-22} \text{ g TlBr}$$

Now, to calculate the volume for a cube, we cube the side lengths. Notice that the answer choice in cm^3 so we should convert 397 pm into 3.97×10^{-8} cm. Hence, the volume is $(3.97 \times 10^{-8} \text{ cm})^3 = 6.26 \times 10^{-23} \text{ cm}^3$.

$$d = \frac{m}{V} = \frac{4.72 \times 10^{-22} \text{ g}}{6.26 \times 10^{-23} \text{ cm}^3} = \boxed{7.55 \text{ g/cm}^3}, or \boxed{B}$$

18. Metals are characterized by their relatively high boiling points, which result from the strong metallic bonds. Therefore, metals are usually not volatile, and have a low vapor pressure. The correct answer is $\boxed{A}$.

19. Apply Hess's law,

$$\Delta H_{\text{xn}} = \Delta H_2 - \Delta H_1 = 702 \text{ kJ/mol} + 142 \text{ kJ/mol} = \boxed{844 \text{ kJ/mol}}, \text{or } \boxed{D}$$

20. A negative change in entropy can stem from a decrease in the number of gaseous molecules in the products compared to those in the reactants. Notice that in reaction (D), two gaseous molecules produce only one gaseous molecule. Therefore, the correct answer is $\boxed{D}$.

21. According to the second law of thermodynamics, total entropy increases for a spontaneous reaction. The heat transfer from a hot object to a cold object is definitely spontaneous. Thus, total entropy change should be larger than zero, not equal zero, so the magnitudes of entropy can't equal. Because the container is well insulated, $q_{\text{metal}} = -q_{\text{water}}$, from the first law of thermodynamics. Therefore, the answer is $\boxed{A}$.

22. For the process:

$$\text{C}_6\text{H}_6(\text{l}) \longrightarrow \text{C}_6\text{H}_6(\text{g})$$

$$\Delta G^o_{\text{vap}} = \Delta G^o_{f(\text{C}_6\text{H}_6(\text{g}))} - \Delta G^o_{f(\text{C}_6\text{H}_6(\text{l}))} \tag{1}$$

$$\Delta G^o_{\text{vap}} = \Delta H^o_{\text{vap}} - T\Delta S^o_{\text{vap}} \tag{2}$$

$$\Delta H^o_{\text{vap}} = \Delta H^o_{f(\text{C}_6\text{H}_6(\text{g}))} - \Delta H^o_{f(\text{C}_6\text{H}_6(\text{l}))} = 82.9 - 49.0 = \boxed{33.9\ (\text{kJ/mol})} \tag{3}$$

$$\Delta S^o_{\text{vap}} = S^o_{(\text{C}_6\text{H}_6(\text{g}))} - S^o_{(\text{C}_6\text{H}_6(\text{l}))} = 269.0 - 173.3 = \boxed{95.7\ (\text{J/(K mol)})} \tag{4}$$

Thus, at 298 K: $\Delta G^o_{\text{vap}} = 33.9 - 298 \times 95.7 \times 10^{-3} = \boxed{5.38\ (\text{kJ/mol})}$

From (1): $G^o_{f(\text{C}_6\text{H}_6(\text{g}))} = \Delta G^o_{\text{vap}} + G^o_{f(\text{C}_6\text{H}_6(\text{l}))} = 5.38 + 124.3 = \boxed{129.7\ (\text{kJ/mol})}$

The correct answer is $\boxed{D}$.

23. The two species are in equilibrium when $\Delta G = 0$. Thus, for reaction:

$$\text{C(s, graphite)} \longrightarrow \text{C(s, diamond)}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$0 = 2.1 \times 10^3\ \text{J/mol} - T \times (2.5 - 5.9)\ \text{J/(mol K)}$$

However, we found that there is no solution of T greater than 0 K (lowest temperature ever possible is 0 K) for the above equation. This means that graphite is always more stable than diamond as the ΔG° is always greater than 0 at any temperature. Therefore, the answer is $\boxed{D}$. A question for readers: Why do people still say "A diamond is forever" if diamond spontaneously changes into graphite at all temperature and how to convert the cheap graphite into the more precious artificial diamond?

24. This question can be solved using the Van't Hoff equation, which is given in the formula sheet as:

$$\ln K = \left(\frac{-\Delta H^o}{R}\right)\left(\frac{1}{T}\right) + \text{constant}$$

Writing the Van't Hoff equation for $K_{\text{sp1}} = 9.5 \times 10^{-11}$ at $T_1 = 287$ K and for $K_{\text{sp2}} = 7.8 \times 10^{-10}$ at $T_2 = 315$ K, and then substracting the second from the first gives:

$$\ln\left(\frac{K_{\text{sp1}}}{K_{\text{sp2}}}\right) = \frac{-\Delta H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Notice that the constant in the equation doesn't depend on the temperature.

Solving this equation gives that $\boxed{\Delta H^o = 57\ (\text{kJ/mol})}$.

The correct answer is $\boxed{C}$.

25. For first order reactions:

$$\ln\left(\frac{[\text{A}]_1}{[\text{A}]_0}\right) = -kt$$

$$\ln\left(\frac{22.0\ \text{mmHg} - 17.5\ \text{mmHg}}{22.0\ \text{mmHg}}\right) = -k \times 60\ \text{s}$$

$$k = \boxed{2.6 \times 10^{-2}\ \text{s}^{-1}}$$

Therefore, the answer is $\boxed{B}$

26. Both of the statement represent two fundamental concepts of the collision theory. The energy barrier that the collisions must surpass in order to produce products is the activation energy for the reaction. Moreover, the collisions must occur in the orientation that suits the transition state of the reaction. Therefore, the correct answer is $\boxed{C}$.

27. The fact that the graph of $[I_3^-]$ vs time is a straight line indicates that the reaction is zeroth-order in I_3^-. Acetone is first-order because doubling the concentration doubles the rate of the reaction(the slope of the line or the time to consume the same amount of I_3^-). Thus, the rate law is $\boxed{r = k[CH_3COCH_3]}$, or $\boxed{B}$.
Please be aware that the pseudo kinetic analysis is applied here as the $[CH_3COCH_3]$ is much greater than $[I_3^-]$.

28. The following designations are used in the solution:
k_1-the rate constant of the forward reaction in the first step
k_{-1} - the rate constant of the backward reaction in the first step
k_2 - the rate constant of the second reaction
k_3 - the rate constant of the third reaction
First, let's write the rate law of the reaction, which is the rate law for the formation of NO:

$$r = \frac{d[NO]}{dt} = k_2[N_2][O] + k_3[N][O]$$

However, N and O are only an intermediates. In order to write the total rate law in terms of O_2 and N_2 it is possible to use the *steady state approximation.*
For N:

$$\frac{d[N]}{dt} = 0 = k_2[N_2][O] - k_3[N][O]$$

$$k_2[N_2][O] = k_3[N][O]$$

For O:

$$\frac{d[O]}{dt} = 0 = 2k_1[O_2] - 2k_{-1}[O]^2 - k_2[N_2][O] - k_3[N][O]$$

$$\frac{d[O]}{dt} = 0 = 2k_1[O_2] - 2k_{-1}[O]^2 - 2k_2[N_2][O]$$

(The factor 2 in the first two terms stems from the fact in this step, two oxygen atoms are formed in the forward reaction, and two react in the backward reaction.)

Notice that the rate of the second reaction ($r_2 = k_2[N_2][O]$ is slower than that of the other reactions. Thus, the expression: $2k_2[N_2][O]$ can be ignored in the steady state approximation for O.
Thus, the equation rearranges to:

$$k_{-1}[O]^2 = k_1[O_2]$$

$$[O] = \sqrt{\frac{k_1}{k_{-1}}[O_2]}$$

Plugging this expression for [O] into the total rate law of the reaction:

$$r = \frac{d[NO]}{dt} = 2k_2\sqrt{\frac{k_1}{k_{-1}}}[N_2][O_2]^{\frac{1}{2}}$$

Or:

$$r = \frac{d[NO]}{dt} = k[N_2][O_2]^{\frac{1}{2}}$$

Where:

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

Therefore, the correct answer is $\boxed{C}$.

29. Apply the equation:

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

$$\ln\left(\frac{k_1}{3.2 \times 10^{-2} s^{-1}}\right) = \frac{-41.0 \times 10^3 \text{ J/mol}}{8.314 \text{ J/(mol K)}}\left(\frac{1}{410.0 \text{ K}} - \frac{1}{400.0 \text{ K}}\right)$$

After solving the equation, we have: $k_1 = \boxed{4.3 \times 10^{-2} \text{ s}^{-1}}$, or $\boxed{C}$

30. The only explanation that suits the given information is $\boxed{A}$. The reason why is that if [B] is greater than [A] then no matter how much B you put, there is not enough A for B to bind to thus the rate is constant. Since at *low concentrations of B, the rate of the reaction is found to be proportional to [B]*, rule out option (B). Furthermore, the data indicates of neither the reaction's stoichiometry nor catalysis, so you can rule out (C) and (D).

31. This is a fundamental question about the express of equilibrium constant. You should review textbook if you are not sure about the questions. Please be aware that S_8 is a solid, which is therefore not included in the expression. The answer is $\boxed{D}$.

32. According to *Le Chatelier's principle* , and exothermic reaction is shifted to the side of the products when the temperature is decreased. Thus, the correct answer is $\boxed{B}$.

33. Remember that for reaction

$$\text{A}_m\text{B}_n \longrightarrow m\text{A}^{n+} + n\text{B}^{m-}$$

The equilibrium constant, K_{sp}

$$K_{\text{sp}} = [\text{A}^{n+}]^m[\text{B}^{m-}]^n$$

If we suppose the molar solubility of A_mB_n is x, we have

$$K_{\text{sp}} = (mx)^n(nx)^m$$

Similarly, we can solve for the molar solubility (x) of all species, and we will find that $\boxed{C}$ has the largest molar solubility (Or we can estimate because we need to take the cube root of K_{sp} for C and square root for the other options).

34. $\text{HX} \longrightarrow \text{H}^+ + \text{X}^-$, $\alpha = 3.5\% = 0.035$, C=0.100 M

	HX	H^+	X^-
Initial concentration	C	0	0
Change in concentration	-αC	+αC	+αC
Equilibrium concentration	C(1-α)	αC	αC

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} = \frac{\alpha^2}{1-\alpha}C = 1.27 \times 10^{-4}$$

Using the K_a value, $[\text{H}^+]$ of the new solution is found (designated as x):

$$K_a = \frac{x^2}{0.500 - x}$$

$$x = 7.9\times10^{-3}$$
$$\text{pH} = 2.1$$

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

35. The first equivalence point represents the reaction

$$CO_3{}^{2-} + H^+ \longrightarrow HCO_3{}^-$$

The second equivalence point represents the reaction

$$HCO_3{}^- + H^+ \longrightarrow H_2CO_3$$

Note that $CO_3{}^{2-}$ transformed into $HCO_3{}^-$ and got titrated again in the experiment. Thus, according to the graph, there is 10 mL $\times$ [HCl] mol of $CO_3{}^{2-}$ and (20 mL $-$ 10 mL) $\times$ [HCl] mol of $HCO_3{}^-$. Thus, the correct answer is $\boxed{B}$.

36. This problem can be solved by rearranging the equations for the equilibrium constants(12), mass balance for CN^- ions (3), mass balance for Ni^{2+} ions (4), and charge balance (5):

$$K_a = 4.9 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} \tag{1}$$

$$K_f = 1.0 \times 10^{22} = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4]} \tag{2}$$

$$c(HCN)_i = 0.100 = [HCN] + [CN^-] + 4[Ni(CN)_4^{2-}] \tag{3}$$

$$c(Ni^{2+})_i = 0.025 = [Ni^{2+}] + [Ni(CN)_4^{2-}] \tag{4}$$

$$[H^+] + 2[Ni^{2+}] = [CN^-] + 2[Ni(CN)_4^{2-}] + [Cl^-] \tag{5}$$

There are 5 variables and 5 independent equations, so finding the values of all the variables is possible. Rearranging and solving for $[H^+]$ gives: pH = 4.05, so the answer is $\boxed{B}$.

Another way which might be easier to follow and calculate is the setup the ICE table using the overall reaction as listed below:

$$Ni^{2+} + 4\,HCN \rightleftharpoons Ni(CN)_4{}^{2-} + 4\,H^+$$

$$K_{\text{overall}} = K_a^4 \times K_f = (4.9 \times 10^{-10})^4 \times 1.0 \times 10^{22} = 5.76 \times 10^{-16}$$

	Ni^{2+}	HCN	$Ni(CN)_4{}^{2-}$	H^+
Initial concentration	0.025	0.100	0	0
Change in concentration	$-x$	$-4x$	$+x$	$+4x$
Equilibrium concentration	$0.025 - x$	$0.100 - 4x$	x	$4x$

$$K_{\text{overall}} = \frac{[Ni(CN)_4{}^{2-}][H^+]^4}{[Ni^{2+}][HCN]^4} = \frac{256x^5}{(0.025 - x)(0.100 - 4x)^4} = 5.76 \times 10^{-16}$$

As K_{overall} is very small, so x is negligible compared to 0.025 or 0.100, so we can simply the equation above into:

$$K_{\text{overall}} = \frac{256x^5}{(0.025)(0.100)^4} = 5.76 \times 10^{-16}$$

$$x = 2.2 \times 10^{-5}$$

$$[H^+] = 4x = 4 \times 2.2 \times 10^{-5} = 8.8 \times 10^{-5}$$

Thus, pH = 4.06, the answer is $\boxed{B}$.

37. Because magnesium is a metal, it tends to form cation when combined with a non-metal element. Thus, in Mg_3N_2, Magnesium is +2 while nitrogen is $\boxed{-3}$, or $\boxed{A}$

38. This question can be solved using the *Nernst equation* for the reaction: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$:

$$E = E^o - \frac{RT}{2F}\ln\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right) = 1.06$$

The answer is $\boxed{C}$.

39. Electrolysis uses a manually applied current to drive a non-spontaneous electrochemical reaction. Therefore, by definition, this is a good method of synthesizing electrochemical reactive substances. Another way to look at this is because reactive metals tend to be oxidized and form pretty stable compound, so synthesizing them via chemical reaction is harder than merely using electrolysis. Thus, the element with the smallest reductive potential, $\boxed{Al}$, or $\boxed{A}$ should be the correct choice ($Al_2O_3(l) \xrightarrow{\text{electrolysis}} 2\,Al(l) + \frac{3}{2}\,O_2(g)$). For nonreactive metals such as gold and mercury, we may directly get the elemental form of the metal in the earth (gold) or easily get the metal through mild heating ($HgO\,(s) \xrightarrow{\text{heating}} Hg\,(l) + \frac{1}{2}\,O_2(g)$). For iron, the common used way to get its elemental form is to reduce the iron oxide using $CO\,(g)$, which is the method used in industrial process. As you can see, it is not necessary to use electrolysis to get those metals.

40. We need to find E^o of the reaction:

$$Cr^{2+} + 2\,e^- \longrightarrow Cr\,(s)$$

Remembering that: $\Delta G^o = -nFE^o$, it is possible to find the ΔG^o values of the given reactions:

$$\Delta G^o(1) = -3 \times F \times (-0.73) = \boxed{211.\ (\text{kJ/mol})} \tag{1}$$

$$\Delta G^o(2) = -1 \times F \times (-0.50) = \boxed{48\ (\text{kJ/mol})} \tag{2}$$

The ΔG^o of the reaction that we investigate is:

$$\Delta G^o(3) = \Delta G^o(1) - \Delta G^o(2) = \boxed{163\ (\text{kJ/mol})} \tag{3}$$

Using the equation: $\Delta G^o = -nFE^o$, again we find that $\boxed{E^o(3) = -0.85\ \text{V}}$. The answer is $\boxed{B}$.

41. For reaction

$$Cu^{2+} + Pb \longrightarrow Cu + Pb^{2+}$$

,

$$E^\circ_{\text{rxn}} = E^\circ_{\text{cat}} - E^\circ_{\text{ano}} = 0.34\ \text{V} + 0.13\ \text{V} = 0.47\ \text{V}$$

Because E° is larger than 0, this reaction is spontaneous. Thus, the mass of lead should decrease because they are being transformed into Pb^{2+} and the color of the solution should fade because the concentration of Cu^{2+} is decreasing. Therefore, the answer is $\boxed{B}$.

42. The equation for the electrolysis of water is:

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

Notice that 2 eletrons are transferred per each oxygen atom.
The relation between the moles of transferred electrons and current is given by:

$$nF = It$$

Where:
n - moles of transferred electrons.
F - Faraday's constant.
I - the current (in A).
t - the time (in sec).
Therefore $n = \frac{It}{F} = \frac{10.0\ \text{A} \times 2.0 \times 60^2}{96500\ \text{C/mol}} = 0.75$ mol
It follows that the moles of O_2 molecules produced is exactly a quarter of this value: $m(O_2) = 0.19$ mol. The molar volume of gas at STP is 22.4 L/mol. Thus, the volume of O_2 is: $V = 0.19 \times 22.4 = 4.2$ (L). The answer is $\boxed{A}$.

43. In a graph of ψ^2, the x-intercept represents radial nodes, where the probability of finding electron is zero. For any orbital, the number of radial nodes $= n - l - 1$. Thus, for 2p, there are $2 - 1 - 1 = 0$ radial nodes. This means that $\boxed{A}$ is the correct answer.

44. The energy required to excite an electron from level n_1 to n_2 ($n_1 < n_2$) in the hydrogen atom is given by the Balmer-equation:

$$\frac{1}{\lambda} = R_{\text{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where:
λ is the wavelength of the light with the energy required for the transition. Notice that the reciprocal of the wavelength is directly proportional to the energy.
R_{H} is a constant.

First, notice that the questions asks for an *energy input*. Thus, transitions of the type $n_1 \longrightarrow n_2$ where $n_1 > n_2$ should be eliminated.
Next, the value of the expression $\frac{1}{n_1^2} - \frac{1}{n_2^2}$ should be evaluated. Since this value is the largest for transition (D), the answer is $\boxed{D}$.

45. Remember that d-block metal lose their s-orbitals electron before losing d-orbital electrons. Therefore, Mn^{2+} will have 5 d-orbital electrons. Because there are exactly 5 d-orbitals with unpaired electrons based on the Hund's rule, Mn^{2+} will have $\boxed{5}$, or $\boxed{C}$, unpaired electrons.

46. All the options represent elements which are located one below the other in the periodic table. The radii of elements from two consecutive rows in the periodic table exhibit an anomalous trend when the first d level (3d) or f level is filled due to their poorer shielding effect. These phenomenons are referred as d-block contraction and f-block (or lanthanide) contraction, respectively. The only pair that in the given options that has similar radii due to the contraction phenomenon is Zr and Hf. Therefore, the answer is $\boxed{D}$.

47. Ionization energy generally decrease down the group as the size increases but the effective nuclear charge doesn't increase much., so $\boxed{A}$ is the correct option.

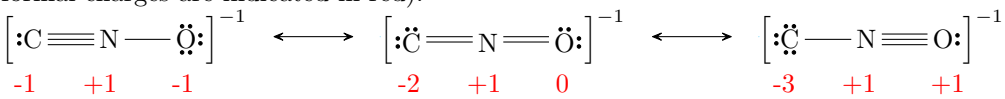
48. The ^{69}Zn isotope has an excess of neutrons. the stables product ^{69}Ga will result from the *beta* emission of this isotope as ^{69}Ga has a atomic number which is very close to the average atomic mass of Ga 69.7:

$$^{69}\text{Zn} \longrightarrow {}^{69}\text{Ga} + \beta^-$$

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

49. CO is isoelectronic to N_2 with a triple bond, thus, the bond order of CO is also 3. The answer is $\boxed{D}$.

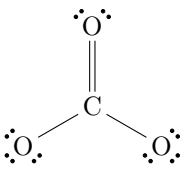
50. Drawing all the resonance structures of the fulminate ion helps solving this problem (the formal charges are indicated in red):



It is now clear that the answer is $\boxed{A}$. Notice that drawing the dominant structure (left) is also sufficient to answer this problem correctly.

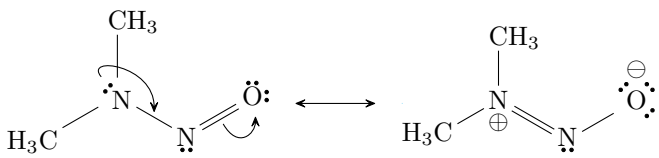
51. The geometry for SF_2 is bent. The two S−F bonds are equivalent because there is an axis of symmetry in between them. Similarly, if we analyze the geometry for SOF_2, SF_4, and SF_6, we will find that SF_4 is the only compound that have two different S−F bonds as the axial bond and equatorial bond are different in the seesaw structure.. Thus, the answer is $\boxed{C}$.

52. Draw the structure, as shown below. Remember that a double bond contains one sigma and one pi bond, and a triple bond contains one sigma bond and two pi bonds. Only $CO_3{}^{2-}$ has three sigma bonds and one pi. Thus, the answer is $\boxed{D}$.



53. Let's simplify the compound to $MA_2B_2C_2$. The easiest way is to draw all of the possible isomers by putting the ligands in different relative positions. There are $\boxed{6}$ isomers in total including a pair of enantiomers (mirror images), thus the answer is $\boxed{D}$. You may refer to the annotated solution of Q54 in the National 2020 Exam Part I for the structures of all isomers.

54. The $(CH_3)_2NNO$ molecule resonates between two structures:



It is apparent that the nitrogen atom that is bind to the oxygen atom has a bent geometry in both of the structures (in accordance with the VSEPR theory); thus, choices (A) and (C) should be immediately eliminated.
While in reality the $(CH_3)_2NNO$ molecule exists as a resonance-hybrid of these two structures, a few factors suggest that the right-hand structure has a lower energy and thus is the dominant structure:

(a) While in the right-hand structure, the bond angle between the methyl groups is 120° (trigonal planar bond angle), in the left-hand structure the bond angle must be smaller (bent geometry). Therefore, the steric-hinderence between the methyl groups is lower in the right-hand structure.

(b) The nitrogen atom is a good electron-donor. In the right-hand structure this effect puts the the negative charge on the very electronegative oxygen atom.

Indeed, *ab initio* calculations and experimental data suggest that the $(CH_3)_2NNO$ molecule exists predominantly in planar geometry, indicating of the larger contribution of the right-hand structure to the resonance-hybrid. Thus, the answer is $\boxed{B}$.
This is another example of the variance with VSEPR model due the conjugation or resonances.

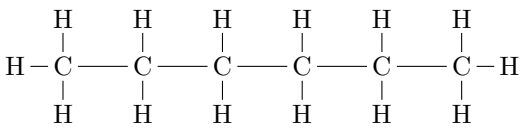
55. This reaction is known as Fischer–Speier esterification. It is not a redox reaction so (C) and (D) are incorrect. A basic catalyst will deprotonate the acid and thus impeding the reaction. Acidic catalyst can speed up the reaction by protonating carbonyl group of the acid and the leaving group. Therefore, the answer is $\boxed{A}$.

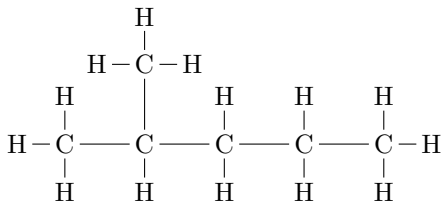
56. First, eliminate (C) and (D): the large side *tert*-butyl group sterically hinders the attack of of the hydroxy ion on the electrophilic center. Between (A) and (B), (B) will react faster due to the weaker C–I. Thus, the answer is $\boxed{B}$.

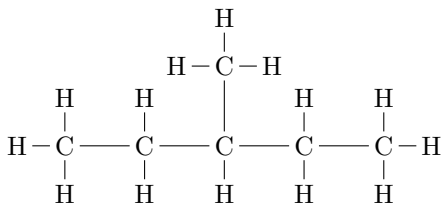
57. First calculate the degree of unsaturation of the compound:

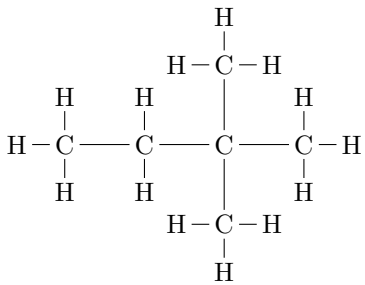
$$n = \frac{\mathrm{C} \times 2 + 2 - \mathrm{H} - \mathrm{X} + \mathrm{N}}{2}$$

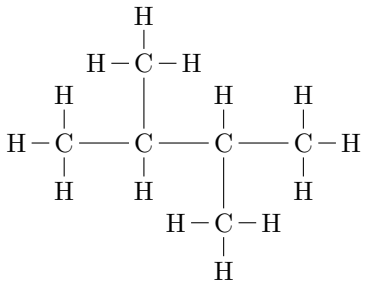
Where n is the degree of unsaturation, C is the number of carbons, X is the number of halogens, H is the number of hydrogen, and N is the number of nitrogen.
We find that for C_6H_{14}, the degree of unsaturation is zero. This suggests that the compound is a simple alkane without double bonds or ring structure. We can now draw the isomers of the compound:











Therefore, there are $\boxed{5}$ isomers, and the answer is $\boxed{C}$.

58. The reaction in the problem is a *nitration reaction* of benzene. This reaction leads to the formation of *nitrobenzene*. The correct answer is $\boxed{A}$.
Please be aware that the sulfonation ($-SO_3H$) of benzene needs fuming H_2SO_4 rather the mixture of concentrated HNO_3 and H_2SO_4.

59. (A) is incorrect because if it was true, the catalytic activity should be reduced instead of lost
(B) and (D) are incorrect because urea is not that reactive. In addition, (D) is one way that urea could denature the protein and thus change the 3-D structure of it. If (D) is correct, (C) would have to be correct as well. Therefore, the correct answer can only be $\boxed{C}$.

60. Tollens's reagent ($[Ag(NH_3)_2]^+$) is an oxidizing agent. It can only oxidize substances with aldehyde group or those can hydrolyze to obtain aldehyde group under the reaction condition, such as *reducing sugars*, which are sugars that are in equilibrium with the open-chain aldose or ketose (such as fructose, in which the hydroxyl ketone is in equilibrium with aldehyde through tautomerization). A cyclic sugar can only be in equilibrium with the open-chain form if the anomeric carbon (the only carbon that is bonded to two oxygen atoms) is bonded to a hydroxy group. This is only the case for molecule II. Sugar I is called *non-reducing sugar* because it's not in equilibrium with the open-chain form and can't be oxidized. Therefore, the correct answer is $\boxed{B}$.