Annotated Solution
1999 USNCO National Exam Part I

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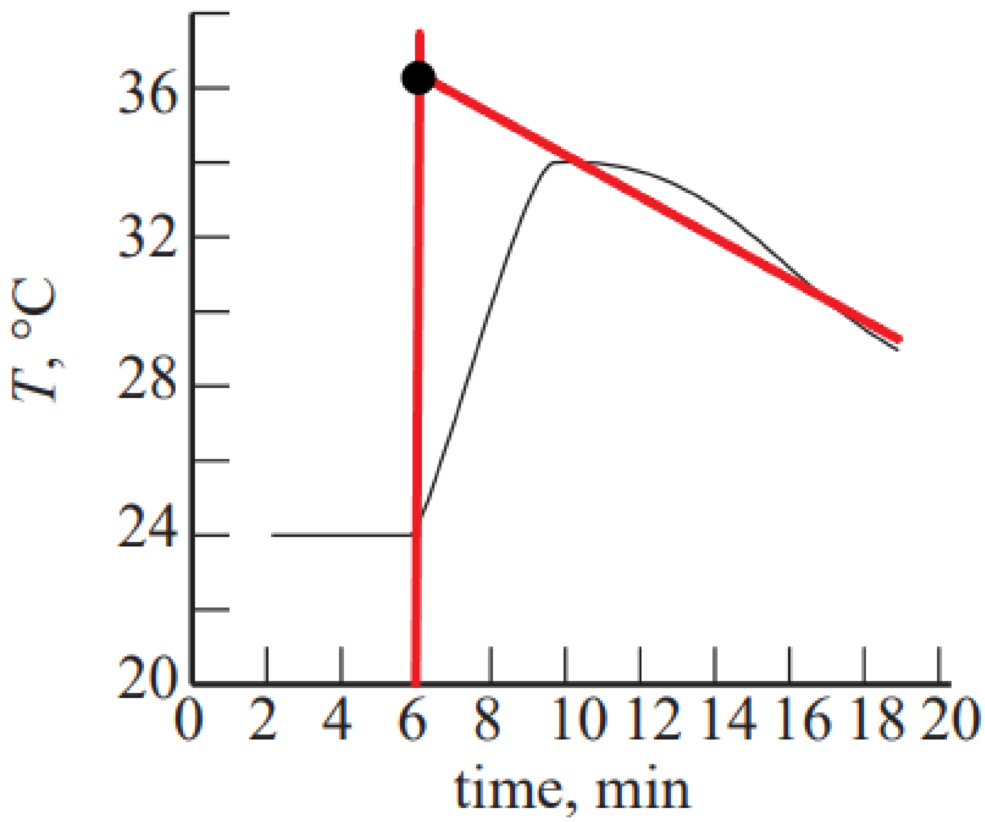
Created on July 1st, 2021
Revised on July 15th, 2022

1 Solutions

1. Glucose is a polar molecule due to its many alcohol groups and lithium chloride is a polar ionic compound, so both will not be soluble in nonpolar solvents. Although graphite is also nonpolar, it is composed of sheets of network covalent bonds. The energy required to break network covalent bonds is too large for graphite to dissolve. Elemental sulfur is in the form $\boxed{S_8}$ molecules, which will dissolve in nonpolar solvents, so the answer is $\boxed{D}$

2. $\boxed{KMnO_4}$ is one of the most well known self indicators, since during the titration, it will be reduced to a pale pink Mn^{2+} ion. However, once the endpoint is reached, the excess permagnate will turn the solution dark purple. I_2 is a solid which are not suitable for being titrants. NaOCl has a pale yellow color that is not suitable for indicating the end of a titration. $K_2Cr_2O_7$ which is a orange color will be reduced to Cr^{3+} which is a green color. Since both of these colors are very visible, the transition at the endpoint will not be clear. Therefore, the answer is $\boxed{D}$.

3.



To account for the heat that was lost while the reaction was occurring, we must extrapolate the temperature to the beginning of the reaction to determine the actual change in temperature. The extrapolation as shown above gives an answer of around $36 - 24 = \boxed{12}$ which is $\boxed{\text{D}}$.

4. In order to find the equilibrium constant of a reaction, it suffices to find the concentration of each substance. Since the $FeSCN^{2+}$ ion is a blood red color, its concentration can be determined through $\boxed{\text{D. spectrophotometry}}$

5. Zn will react with H^+ in an oxidization-reduction reaction resulting in Zn^{2+} and H_2. However, H_2 is less dense than air. $Pb(NO_3)_2$ will only react with HCl to form a $PbCl_2$ precipitate with no gas evolution. HCl will have no reaction with NaBr. H^+ will react with $\boxed{HCO_3^-}$ to form H_2CO_3 which decomposes to H_2O and CO_2. CO_2 is more dense than air since it has a molar mass of 44 and air is mostly composed of nitrogen and oxygen which have molar masses of 28 and 32 respectively. The answer is $\boxed{\text{D}}$.
Note: Densities of gases can be compared through their molar masses, since the density of a gas is proportional to its molar mass under a certain temperature and pressure. Reader can try to derive the equation using the ideal gas law.

6. The titration uses the following reaction:

$$Ba(OH)_2 + 2\,HCl \rightarrow BaCl_2 + 2\,H_2O$$

There are

$$27.15\,\text{mL} \cdot 0.245\,\text{M HCl} = 6.65\,\text{mmol HCl}$$

consumed in the reaction. From the reaction coefficients, we know that there must have been

$$6.65\ \text{mmol HCl}\ \frac{1\ \text{mmol Ba(OH)}_2}{2\ \text{mmol HCl}} = 3.33\ \text{mmol Ba(OH)}_2$$

in the solution. Therefore, we can solve for the concentration by using

$$3.33\ \text{mmol Ba(OH)}_2 = 20.00\ \text{mL} \cdot x\,\text{M Ba(OH)}_2$$

which gives $x = \boxed{1.66}$ M $Ba(OH)_2$ so the answer is $\boxed{\text{A}}$.

7. Ionic hydrides such as LiH will undergo an oxidization-reduction reaction with water with the reaction:

$$LiH + H_2O \rightarrow Li^+ + OH^- + H_2$$

which produces $\boxed{\text{hydrogen gas and a hydroxide ion which is highly basic}}$. Therefore the answer is $\boxed{\text{C}}$.

8. We can set up the following equation:

$$\frac{0.250\ \text{g M}}{0.547 - 0.250\ \text{g F}} = \frac{x\ \text{g/mol M}}{6 \cdot 19.0\ \text{g/mol F}_6}$$

Which gives M a molar mass of x=96.0 g/mol which matches the element $\boxed{\text{Mo}}$. Therefore the answer is $\boxed{\text{B}}$.

9. There are $20\,\text{mL} \cdot 0.40\,\text{M}\ Na_3PO_4 = 8\,\text{mmol}\ Na_3PO_4$ in the solution. However, each mol of Na_3PO_4 dissociates into three mols of Na^+ so the answer is $3 \cdot 8\,\text{mmol}\ Na_3PO_4 = \boxed{24\ \text{mmol}}\ Na_3PO_4$ which gives $\boxed{\text{B}}$.

10. There are a total of $4 \cdot 3 + 18 = 30$ atoms of O in each molecule, which account for the $30 \cdot 16.0\ \text{g/mol O} = 480\ \text{g/mol}$ of the molecule. The percentage is $480/666.43 = \boxed{72.0\%}$ which is $\boxed{\text{D}}$.

11. In this oxidization-reduction reaction, the Mn goes from Mn^{2+} to ${MnO_4}^-$ which is a change in oxidization number of +5. Similarly, the Bi goes from ${BiO_3}^-$ to Bi^{3+} which is a change in oxidization number of −2. Therefore, the ratio of coefficients of the Mn compounds to Bi compounds is 2 : 5 in order to balance the electrons. We now have the reaction

$$2\,\mathrm{Mn^{2+}} + 5\,\mathrm{BiO_3}^- + \_\,\mathrm{H^+} \longrightarrow 5\,\mathrm{Bi^{3+}} + 2\,\mathrm{MnO_4}^- + \_\,\mathrm{H_2O}$$

Note that there are currently $5 \cdot 3$ atoms of O on the reactants side and $2 \cdot 4$ atoms of O on the products side. To balance this out, we must have 7 molecules of H_2O on the products side to balance the O atoms. Now, we need 14 H^+ atoms on the reactant side to balance out the H atoms. The final balanced reaction is

$$2\,\mathrm{Mn^{2+}} + 5\,\mathrm{BiO_3}^- + \boxed{14}\,\mathrm{H^+} \longrightarrow 5\,\mathrm{Bi^{3+}} + 2\,\mathrm{MnO_4}^- + 7\,\mathrm{H_2O}$$

and as a double check we can verify that the total charge on both sides are equal. Therefore the answer is $\boxed{\text{D}}$.

12. This is just simply conversion between grams, moles, and atoms.

$$2.5\,\mathrm{g\,O_2}\,\frac{1\,\mathrm{mol\,O_2}}{32\,\mathrm{g\,O_2}}\,\frac{6.02 \cdot 10^{23}\,\mathrm{molecules\,O_2}}{1\,\mathrm{mol\,O_2}} = \boxed{4.7\times10^{22}}\,\mathrm{molecules\,O_2}$$

so the answer is $\boxed{\text{C}}$.

13. A substance is in a supercritical condition if the pressure and temperature is higher than a specific point, leading to it having both liquid and gas like properties. This is displayed at the point $\boxed{\text{B}}$.

14. The vapor pressure of a liquid depends only on temperature and not quantity or surface area. This is due to the fact that the vapor pressure is determined by an equilibrium constant, which does not fluctuate based on concentrations or volumes, only $\boxed{\text{temperature}}$. Therefore the answer is $\boxed{\text{A}}$.

15. Gibbs phase rule states that $N = C - F + 2$ where N is the number of phases, C is the number of components, and F is the number of degrees of freedom. Since we are referring to a point in a single component system, we have $C = 1$ and $F = 0$, which gives N to be a maximum of $\boxed{3}$. This is observed in the triple point of many substances so the answer is $\boxed{\text{C}}$.

16. Using the idea gas law, we get that for each liter, we have

$$1\,\mathrm{L} \cdot 740\,\mathrm{mmHg}\,\frac{1\,\mathrm{atm}}{760\,\mathrm{mmHg}} = 0.0821\,\frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}} \cdot n\,\mathrm{mol} \cdot 298\,\mathrm{K}$$

n=.0398 mol of gas. Therefore, the molar mass is

$$\frac{5.8\,\mathrm{g}}{1\,\mathrm{L}}\,\frac{1\,\mathrm{L}}{.0398\,\mathrm{mol}} = \boxed{150}\,\mathrm{g/mol}$$

which gives $\boxed{\text{C}}$.

17. The greatest surface tension means the greatest intermolecular forces. Molecule A does not have any hydrogen bonding so we can eliminate that one. Although B, C, and D all have hydrogen bonding, $\boxed{\text{D}}$ is the only molecule with two H atoms capable of hydrogen bonding, which results in a higher surface tension.

18. By writing the ΔH change as products − reactants, we just need to solve the equation

$$-879.6 = 3\,(-241.8) - 2\,(-45.9) - 3\,(x)$$

which gives $x = \boxed{82\ \mathrm{kJ/mol}}$ so the answer is $\boxed{\text{B}}$.

19. From the first law of thermodynamics, we have $\Delta E = q + w = -65 + -38 = \boxed{-103}$. q is negative since the reaction releases heat and w is negative since the the reaction does work. Therefore, the answer is $\boxed{\text{A}}$.

20. The sign of ΔH is negative since this is a combustion reaction and combustion reactions are highly exothermic. The sign of ΔS is positive since the number of mole of gas increases, which decreases order. Therefore the answer is $\boxed{\text{B}}$.

21. The rate of disappearance and appearance for each species is proportional to its coefficient. Therefore the answer is

$$2.0 \cdot 10^{-7}\,\text{M/s}\,\frac{3\,\text{mol}\,O_2}{2\,\text{mol}\,O_3} = \boxed{3.0\times10^{-7} M/\text{s}}$$

which is choice $\boxed{\text{C}}$.

22.
1. The standard entropy for all elements are positive since each element has some amount of disorder.
2. The standard entropy for aqueous ions can be negative since the charge that they hold when dissolved in water can induce order in the solution.
3. A reaction is spontaneous when the free energy is negative. This does not necessarily imply a positive entropy change. For example, an exothermic reaction with a positive entropy change can still be spontaneous.
Since $\boxed{\text{only 1}}$ is true, the answer is $\boxed{\text{A}}$.

23. Just applying the formula $\Delta G = -RT\ln K$ with $R = 8.314, T = 298, K = 1.7 \times 10^7$ gives $\Delta G = \boxed{-41.2 \text{ kJ/mol}}$ which is $\boxed{\text{A}}$.

24. The ΔH of a reaction can be calculated using the sum of the BDE of the reactants minus the products. We start by breaking each molecule into the bonds that make it up. C_2H_4 is composed of one C=C double bond and four C−H single bonds. H_2 is composed of one H−H single bond. C_2H_6 is composed of one C−C single bond and six C−H single bonds. If we subtract the bonds of the products from the reactants, we will get one C=C double bond and one H−H single bond subtracted by one C−C single bond and two C−H single bonds. This gives the answer of $\boxed{\text{A}}$.

25. A positive voltage signifies a spontaneous reaction. This means that $\boxed{\Delta G < 0 \text{ and } K > 1}$, which is answer choice $\boxed{\text{A}}$.

26. The total order is 3, so doubling each reactant will increase the rate by $2^3 = \boxed{8}$ times which is $\boxed{\text{D}}$.

27. Applying the formula for half life $\frac{\ln 2}{k} = t$ gives $t = 1260$ sec $= \boxed{21 \text{ min}}$ which is $\boxed{\text{C}}$.

28. Looking at the equation, we want to make $-\frac{E_a}{RT}$ as small (negative) as possible. This is when $\boxed{E_a \text{ is large and } T \text{ is low}}$ which matches choice $\boxed{\text{C}}$.

29. Since the second step is the rate determining step, we can write the rate of the reaction as proportional to [Cl][$CHCl_3$]. This means the first reaction is at equilibrium, so $k = \frac{[Cl]^2}{[Cl_2]}$ can be written as $[Cl] = k[Cl_2]^{\frac{1}{2}}$ Substituting this into the rate determining step gives the overall rate to be $\boxed{k[Cl_2]^{\frac{1}{2}}[CHCl_3]}$ which is $\boxed{\text{D}}$.

30. Apply the formula

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

with $E_a = 87000, R = 8.314, T_1 = 288, T_2 = 310$. This gives $\frac{k_2}{k_1} = \boxed{13}$ which is $\boxed{\text{C}}$.

31. The equilibrium constant expression is the product of the pressures of each gaseous product raised to the power of their coefficient divided the product of each gaseous reactant raised to the power of their coeffecient. Therefore, the answer is $\frac{P^4_{\text{PCl}_3}}{P^6_{\text{Cl}_2}}$ which corresponds to $\boxed{\text{D}}$.

32. Notice that the second reaction is one half of the first reaction reversed. Therefore, the equilibrium constant for the second reaction is the square root of the reciprocal of the first. Deriving this simply requires writing out the two expressions. The K value for the second reaction is

$$\frac{1}{\sqrt{6.10 \times 10^{-3}}} = \boxed{12.8}$$

which gives $\boxed{\text{C}}$.

33. Since this is a sample of pure water, we have $[H^+]$=$[OH^-]$ and $[H^+][OH^-]$=$4.0 \cdot 10^{-14}$ which gives $[H^+]$=$2.0 \cdot 10^{-7}$. Therefore, pH=$-\log(2.0 \cdot 10^{-7})$=$\boxed{6.7}$ which gives $\boxed{\text{A}}$. One can also note that the pH must be smaller than 7 since the equilibrium constant increased, so it must be A.

34. Since all the equilibrium in this question are favorable, that must mean the acid on the reactants side is stronger than the acid on the products side since it readily gets deprotonated. Using this information, the first equation tells us $N_2H_5{}^+ > NH_4{}^+$, the second one tells us HBr $> NH_4{}^+$, and the third tells us HBr $> N_2H_5{}^+$. Combining these three inequalities gives us $\boxed{\text{HBr} > N_2H_5{}^+ > NH_4{}^+}$, which is choice $\boxed{\text{A}}$. Note that we can completely skip all the equations since HBr is the only strong acid so it has to be A.

35. Since the K_b of NH_3 is much larger than the K_a of HCN, we can say that NH_3 is a stronger base than HCN is acid. Therefore, the solution will be $\boxed{\text{weakly basic}}$ which gives $\boxed{\text{D}}$.

36. Let x be the amount of dissociation. Since x is insignificant compared to [HCN], we can assume [HCN] remains constant. This gives the equation

$$K_a = 6.2 \cdot 10^{-10} = \frac{x^2}{.010}$$

and solving gives $x = 2.5 \times 10^{-6}$. To find the percent dissociation, we divide x by [HCN]=.010 and multiply by 100% which gives $\boxed{.025\%}$ so the answer is $\boxed{\text{B}}$.

37. Let x be the number of moles of HCOONa added. Then we have the equation

$$K_a = 2 \cdot 10^{-4} = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{10^{-3.4}x}{.10}$$

Solving gives $x = \boxed{.05}$ mol so the answer is $\boxed{\text{B}}$.

38. Since the pH is on the basic end of the indicator, the color will be $\boxed{\text{yellow}}$ which is $\boxed{\text{D}}$. Note that in order for the color to display as a mixture of red and yellow, the pH usually has to be within 1 unit of the pK_a. This is due to the fact that most human eyes cannot perceive the color when it is less than 10% concentration.

39. For each compound, we can write the equilibrium expression and calculate the $[Ag^+]$ where a precipitate will form.

- AgBr: $K_{sp} = 5.0 \times 10^{-13} = [Ag^+][Br^-] = [Ag^+](.1) \implies [Ag^+] = 5.0 \cdot 10^{-12}$ M
- AgCl: $K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-] = [Ag^+](.1) \implies [Ag^+] = 1.8 \cdot 10^{-9}$ M
- Ag_2CO_3: $K_{sp} = 8.1 \times 10^{-12} = [Ag^+]^2[CO_3{}^{2-}] = [Ag^+]^2(.1) \implies [Ag^+] = 9.0 \cdot 10^{-6}$ M

- Ag_3AsO_4: $K_{sp} = 1.0 \times 10^{-22} = [Ag^+]^3[AsO_4{}^{3-}] = [Ag^+]^3(.1) \implies [Ag^+]=1.0 \cdot 10^{-7}$ M

This shows that $\boxed{\text{AgBr}}$ will precipitate first so the answer is $\boxed{\text{A}}$.

40. Since $\boxed{\text{Cd}}$ has a negative reduction potential, it will be oxidized at the anode of the reaction. The total voltage is simply the sum of the two half reactions, which is $\boxed{1.20\text{V}}$.

41. C and D cannot react spontaneously since solid Calcium and Magnesium are alkaline earth metals which are super reactive with water. B cannot occur since reactions between halogens will result in the larger, less reactive halogen forming the diatomic molecule. Therefore, the answer is $\boxed{\text{A}}$ since $\boxed{Ag^+}$ has a very high reduction potential.

42. Each mole of Al produced requires three moles of electrons while each mole of O_2 produced requires four. Therefore, the ratio they are formed in is $\boxed{4:3}$, so the answer is $\boxed{\text{D}}$.

43. This is just an application of the formula $\Delta G^o = -nE^oF$. In this case, $n = 6$, $E^o = 0.43$, and $F = 96500$. However, since this product is in joules, we have to divide by 1000 to get kilojoules. Therefore, the answer is $\boxed{\frac{-6\times 96500\times 0.43}{1000}}$ which is $\boxed{\text{C}}$.

44. This is just an application of the Nernst equation, $E = E^o - \frac{RT}{nF}\ln Q$. In this case, $E^o = 0.43$, $R = 8.314$, $T = 298$, $n = 6$, $F = 96500$, and $Q = \frac{[Cr^{3+}]^2}{[Cu^{2+}]^3} = 10^{-4}$. Plugging this all in gives $E = \boxed{0.47\text{ V}}$ which is $\boxed{\text{C}}$.

45. Choice $\boxed{\text{B}}$ breaks the rule $n > l$.

46. Cr is most well know for its oxidization-reduction reactions between 3+ states and 6+ states. Pb can either lose its p subshell electrons for 2+ or both s and p for 4+. Sr has a s^2 electron configuration so it can only exhibit 2+ states. Therefore the answer is $\boxed{\text{B. 1 and 2 only}}$.

47. Note that these three species are isoelectronic. Therefore, the atom with the highest nuclear charge is the smallest and vise versa. Therefore, the size goes in order of nuclear charge/nuclear number $\boxed{Ca^{2+} < K^+ < Cl^-}$ which is $\boxed{\text{D}}$.

48. $\boxed{\text{Be}}$ has properties least similar to other group two elements due to its tiny size so the answer is $\boxed{\text{A}}$.

49. The general trend for ionization energy is that it increases going up and right on the periodic table. Therefore, the answer is $\boxed{\text{C. Mg}}$.

50. The number of valence electrons of a species can be determined by the sum of the valence electrons of the atoms and the charge of the molecule. For example, $NO_3{}^-$ has $5 + 3 \times 6 + 1 = 24$ valence electrons. Repeating this process with each molecules reveals that $\boxed{NF_3}$ has $5 + 3 \times 7 = 26$ valence electrons, which is not isoelectronic to $NO_3{}^-$ so the answer is $\boxed{\text{C}}$.

51. CO_2, Cl_2, and CCl_4 are all molecular compounds. Therefore, the answer is $\boxed{\text{B}}$. Just to check, we can eliminate A, C, and D with the ionic compounds NH_4Cl, AlF_3, and CaO respectively.

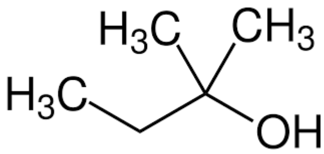
52. Remember that N_2 has a triple bond, O_2 has a double bond, and F_2 has a single bond. Triple bonds are stronger than double bonds which are stronger than single bonds so the order goes $\boxed{F_2, O_2, N_2}$ which gives $\boxed{\text{B}}$.

53. Using the VSPER model, the central P atom has no lone pairs and 4 bonds. Therefore, it is $\boxed{\text{A. Tetrahedral}}$. Note this is isoelectronic to CCl_4 which is much more common.

54. Using the VSPER model, NCl_3 is trigonal pyramidal so it has dipole moment. SO_3 is trigonal planar so it has no dipole moment. PCl_5 is trigonal bipyramidal so it also does not have dipole moment. Therefore, the nonpolar molecules are $\boxed{\text{D. 2 and 3 only}}$.

55. The key insight is to count the hydrogen molecules and realize the structure is actually $CH_3-CH=CH_2$. The first carbon is attached to all sigma bonds so it is sp^3 while the second carbon as one pi bond so it is sp^2. This corresponds to choice $\boxed{\text{B}}$.

56.



We can count $\boxed{\text{C. 4}}$ carbon-carbon bonds.

57. *Cis-trans* stereoisomers occur when there is a double bond such that both substituents on each carbon is different. The molecule that satisfies this is $\boxed{\text{A. CHF=CHF}}$.

58. Since I^- is a weak base but strong nucleophile, the reaction is going to be a substitution instead of elimination. The substitution reaction products are $\boxed{\text{A}}$.

59. Rule of thumb: Polymers that end with -amide or -ester are usually condensation since amide signifies $-COOH$ and $-NH_2$ group condensation and ester signifies $-COOH$ and $-OH$ group condensation. Polymers that end in -ene or -yne are usually addition since the split of the pi bonds to form sigma bonds is the basis of addition polymers. Applying this, the answer is $\boxed{\text{B. 2 only}}$.

60. $\boxed{\text{A. Hexene}}$ is not aromatic since it is not cyclic nor planar. All other choices are cyclic, planar molecules with delocalized pi bonds and satisfy the $4n + 2$ rule.