Annotated Solution 2011 USNCO Local Exam

Authors: Ritvik Teegavarapu Proofreader and Editor: Dr. Qiang 'Steven' Chen

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1. We can eliminate A and C because they are not precise enough. The graduated cylinder has markings every 1 mL. Since the last digit is uncertain, the uncertainty is ± 0.5 mL. The 50 mL buret has markings every 0.1 mL. Since the last digit is uncertain, the uncertainty is ± 0.05 mL. Thus, the answer is B.

2. We can write possibilities of decomposition for each substance.

$$CaO(s) \longrightarrow Ca(s) + \frac{1}{2}O_2$$
$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$
$$HgO(s) \longrightarrow Hg(l) + \frac{1}{2}O_2$$
$$O_3 \longrightarrow \frac{3}{2}O_2$$

 O_3 is well known to decompose into O_2 , as we know from experience that O_2 is much more common. H_2O_2 is also known to decompose into O_2 . Comparing A and C, we see that Hg as a less reactive metal, binding with oxygen with a low affinity, that means, HgO is easier to decompose. We can expect CaO, or calcium oxide, decompose at a very high temperature. Actually, the decomposition of HgO was used by Lavoisier to produce oxygen gas in the 18th century. Thus, the answer is A.

3. In general, acids form H₂ upon reacting with metals. However, HNO₃ is known for its ability to be reduced into nitrogen oxides such as $\boxed{\text{NO}}$ upon reacting with metals. Thus, the answer is \boxed{D} . In the presence of oxygen, NO can be further oxidized into NO₂.

4. NO₂ is a reddish-brown gas known for alternating with colorless N₂O₄ in equilibrium with a strong smell. Cl₂ is a pale green gas with a known strong smell. CH₄ is colorless and odorless. Thus, two gases have color and a distinctive odor, so the answer is C.

5. Casually wrapping your arm with cloth is a terrible idea if your arm is burning with acid. Thus we can eliminate D.

A, B, and C all could neutralize the sulfuric acid, but we have to be careful. Although B and C would neutralize the sulfuric acid faster, we don't have time to do the stoichiometry to determine exactly how much is required and measure that quantity.

Bases are also skin irritants so we don't want to add too much in comparison to water, which cannot hurt you. Additionally, the neutralization of acid can release heat, which will make the hurt worse, while rinsing off the concentrated acid with a large quantity of water can absorb the heat. Thus, the answer is A.

6. First, we must determine how much $KClO_3$ is present per 100 g H₂O so we can use the graph.

$$\frac{10.0 \text{ g KClO}_3}{45.0 \text{ g H}_2\text{O}} \times \frac{\frac{100}{45}}{\frac{100}{45}} = \frac{22.2 \text{ g KClO}_3}{100 \text{ g H}_2\text{O}}$$

From the graph, we see the solubility at 20 °C is about 10 g. We have too much, so the solution is supersaturated Thus, the correct answer is D.

7. First we must determine the molarity of the original solution.

$$\frac{65.25 \text{ g} \times \frac{1 \text{ mol}}{249.7 \text{ g}}}{0.800 \text{ L}} = 0.327 \text{ M}$$

Now we can perform a standard dilution calculation.

$$(0.327 \text{ M})(V_i) = (0.100 \text{ M})(1.00 \text{ L})$$

$$V_i = 0.306 \text{ L} = 306 \text{ mL}$$

Thus, the answer is D

8. First we must write the balanced reaction.

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Now we can do dimensional analysis.

$$2.2 \text{ g } \text{C}_3\text{H}_8 \times \frac{1 \text{ mol } \text{C}_3\text{H}_8}{44.09 \text{ g } \text{C}_3\text{H}_8} \times \frac{5 \text{ mol } \text{O}_2}{\text{mol } \text{C}_3\text{H}_8} = \boxed{0.25 \text{ mol } \text{O}_2}$$

Thus, the answer is |C|.

9. Polyethylene is formed from units of C_2H_4 added together. Thus we can do dimensional analysis with Avogadro's number.

$$12.4 \text{ g} \times \frac{1 \text{ mol}}{28.05 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = 2.67 \times 10^{23} \text{ molecules}$$

This is D

10. The equivalence point is defined as the point where the moles of acid is equal to the number of moles of base. If the acid is weak, the pH will be greater than 7, so we can eliminate A. We can also eliminate B because a small amount of hydroxide will be required to neutralize the initial hydronium as the acid is weak, and then even more will be required to reach the equivalence point. We can eliminate C because they could have different concentrations. Thus, the answer is D.

11. A solution with a nonvolatile solute tend to have high boiling points than the pure solvent, which is part of the colligative properties of solutions. Thus, the answer is A.

12. Note that each $Mg(NO_3)_2$ gives two nitrate ions to the solution. We can then use the information in the question to determine the molarity. The final volume will be the sum of the volume of the two components of the solution.

$$\frac{100 \text{ mL} \times 0.200 \text{ M} + 200 \text{ mL} \times 0.100 \text{ M} \times 2}{100 \text{ mL} + 200 \text{ mL}} = \boxed{0.200 \text{ M}}$$

This is D

13. Evaporation is liquid to gas. Sublimation is solid to gas. Polymerization is not a phase change, but is the formation of a larger polymer from multiple monomer components. Thus, the answer is condensation, or A.

14. From PV = nRT, we see volume is directly proportional to temperature and inversely proportional to pressure. Thus we can set up proportions to solve this problem.

9.23 L ×
$$\frac{525 \text{ K}}{345 \text{ K}}$$
 × $\frac{1.40 \text{ atm}}{3.20 \text{ atm}}$ = $\boxed{6.14 \text{ L}}$

Thus, the answer is |B|.

15. London dispersion forces increase with the number of electrons. From the answer choices, it is clear that H_2 Te has the greatest number of electrons. Thus, the answer is D.

16. We know KCl will have a very high melting point because it is an ionic solid. Si will have the highest melting point of all because silicon forms network solids, which have extremely high melting points. CH₃OH will have a higher melting point than C₂H₆ because the -OH groups in CH₃OH will allow it to form hydrogen bonds. Thus, the ordering is as follows, and the answer is D.

$$\mathrm{C_{2}H_{6}, CH_{3}OH, KCl, Si}$$

17. Because the liquid is less dense than the solid, the solid-liquid border on the phase diagram will have a positive slope coming from the triple point. (Water is denser than ice so its phase diagram is different from normal.) Thus going straight up (higher pressure) and a little to the left (lower temperature) on the phase diagram will be in the solid only region, so the answer is A.

18. The formula for root mean square velocity is

$$v_{\rm rms} = \sqrt{\frac{3RT}{M}}$$

Where M is the molar mass. Thus to rank the mixture in order of increasing velocity, we must rank in order of decreasing molar mass. Thus, the ordering is as follows, and the answer is D.

$$\mathrm{CO}_2 < \mathrm{CH}_4 < \mathrm{He} < \mathrm{H}_2$$

19. Breaking bonds requires an energy input, while forming bonds releases energy. Thus the reaction in this problem will have a net input of energy. Therefore $\Delta H > 0$ and the reaction is endothermic. The answer is A.

20. There are three steps to this process. First we must heat the ice to 0 °C (q_1) . Then we must melt the ice to form water (q_2) . Finally, we must heat the water to 15 °C (q_3) . Each step will require a separate calculation. Also, since the quantities given to us are in moles, we must convert to moles.

$$5.0 \text{ g} \times \frac{1 \text{ mol}}{18.01 \text{ g}} = 0.278 \text{ mol}$$
$$q_1 = (0.278 \text{ mol}) \left(37.8 \frac{\text{J}}{\text{mol} \times ^\circ\text{C}} \right) (0 - (-10.0) ^\circ\text{C}) = 102 \text{ J}$$
$$q_2 = (0.278 \text{ mol}) \left(6.00 \frac{\text{kJ}}{\text{mol}} \right) \left(\frac{1000 \text{ J}}{\text{kJ}} \right) = 1620 \text{ J}$$
$$q_3 = (0.278 \text{ mol}) \left(76.0 \frac{\text{J}}{\text{mol} \times ^\circ\text{C}} \right) (15.0 - 0 ^\circ\text{C}) = 308 \text{ J}$$
$$Q = q_1 + q_2 + q_3 = \boxed{2.1 \times 10^3 \text{ J}}$$

This is |B|.

21. First we must write the combustion reaction.

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

Let the standard enthalpy of formation of C_2H_4 be x. We know the enthalpy of the combustion reaction, so we can solve for x. Since $O_2(g)$ is an element in its standard state, its enthalpy of formation is zero. Thus, the answer is B.

$$2(-394) + 2(-286) - 3(0) - x = -1411$$
$$x = 51 \text{ kJ} \cdot \text{mol}^{-1}$$

22. We can think of entropy as the number of ways the molecules can arrange themselves through movement. We know gas will have the highest entropy because it has the most freedom to move. Liquid is second most. Solid is the least because it has very little freedom to move. Thus, the ordering is as follows and the answer is A.

$$\rm S^{\circ}_{solid} < S^{\circ}_{liquid} < S^{\circ}_{gas}$$

23. Hess's law states that when you add two reactions, you also add their enthalpies. The First Law of Thermodynamics states that total energy in the universe is conserved. The Second Law of Thermodynamics states that entropy increases over time. The Third Law of Thermodynamics states that the entropy of a perfect crystal is zero at absolute zero. Thus, the answer is D.

24. From $\Delta G = \Delta H - T\Delta S$, we see that entropy becomes significant at high temperatures. At low temperatures, enthalpy is most important. Since we want the reaction to be non-spontaneous ($\Delta G > 0$) at low temperatures, where enthalpy is most important, we know $\Delta H > 0$. We want ΔG to decrease and become negative as temperature increases, so $\Delta S > 0$. Thus, the answer is A.

25. The slope of a line is "rise over run". In this case that is molarity over time, which we know is the reaction rate. Thus, the answer is A. Alternatively, from Calculus, we know that the slope of the tangent line is equal to the instantaneous rate.

26. Let's use Rate = k[A] as an example rate law. We see that the rate constant k is separate from the concentration [A], so II is incorrect. However, we also know that the rate of a reaction increases with temperature. Thus the answer is \overline{I} only, or \overline{A} .

27. We see that A has no effect on the reaction rate, so the reaction is zero order in A. The reaction rate is directly proportional to the concentration of B, so the reaction is first order in B. Thus we have A = 0, B = 1, or A.

28. An inhibitor would not appear in the balanced equation, so A is incorrect. We know that since this is a reactant, it is a part of the reaction, so B is incorrect. From the rate law we see that even at low concentrations, doubling the concentration of a reactant can potentially double of quadruple the rate, so C is incorrect. The steps after the rate-determining step do not affect the rate law. Thus the answer is D.

29. The reactants in the esterification reaction are aqueous, and the H_2SO_4 is also aqueous. Thus, we can determine that the H_2SO_4 is a homogeneous catalyst. H_2 and O_2 are gaseous, but Pt is solid. Thus Pt is a heterogeneous catalyst Therefore, the answer is B.

30. From the rate law, increasing the partial pressure of the H_2 will most likely increase the rate of the reaction (unless it is zero order in H_2 , in which case it will have no effect). Thus A is incorrect. Heating the reaction mixture or adding a catalyst will increase the rate. Adding the I_2 as one piece will decrease the surface area that is available to react. Thus, the answer is B.

31. Since the CH_3OH is liquid, it will not affect the equilibrium constant. We must have an exponent of 1 for the CO and an exponent of 2 for the H_2 because of the number of these reactants in the equation. Therefore, we have the following expression for K_c .

$$K_{c} = \frac{[CH_{3}OH]^{0}}{[H_{2}]^{2} \cdot [CO]^{1}} = \boxed{\frac{1}{[H_{2}]^{2} \cdot [CO]^{1}}}$$

Thus, the answer is D.

32. Since $\Delta H < 0$, the reaction is exothermic. By Le Chatelier's principle, if we increase the temperature, the reverse endothermic reaction will be favored to decrease the temperature again. Thus I is incorrect. If we increase the volume, pressure will decrease. By Le Chatelier's principle, the reaction will shift to increase pressure. From PV = nRT we know the side will the most moles of gases (the left) will have the highest pressure. From this, we can determine that II is also incorrect. Thus, neither I or II are correct, so the answer is D.

33. HCl is a strong acid, so we know it will have the lowest pH. HF is a weak acid, so it will have the next pH. We know the Cl⁻ ion is neutral because it is the conjugate base of the strong acid HCl. The stronger the acid, the weaker the conjugate base. Thus, KCl is neutral. We know the F⁻ ion is basic because it is the conjugate base of the weak acid HF. Thus KF is basic and will have the highest pH. Thus, the ordering is as follows and answer is \overline{C} .

$$\mathrm{HCl},\mathrm{HF},\mathrm{KCl},\mathrm{KF}$$

34. A buffer solution is made by a mixture of a weak acid and its conjugate base. For the buffer in the problem, we want both acidic HF and basic NaF. In order to partially neutralize HF (aq), the only solution that will work is one with more HF than NaOH. Thus, the answer is 15.0 mL 0.10 M NaOH and 20.0 mL 0.10 M HF, or C.

35. We know that for some $K_{\rm sp}$

$$K_{\rm sp} = [{\rm Ag}^+][{\rm BrO_3}^-]$$

 NH_3 can react with Ag^+ through the following complexation reaction, which will shift the above dissolution equilibrium to the right side and increase the solubility of $AgBrO_3$.

$$2 \operatorname{NH}_3 + \operatorname{Ag}^+ \Longrightarrow \operatorname{Ag}(\operatorname{NH}_3)_2^+$$

Thus, the solubility of $AgBrO_3$ is higher in 0.10 M NH₃ and lower in 0.10 M KBrO₃, and the answer is \overline{A} . Moreover, as HBrO₃ is a strong acid, the addition of HNO₃ has negligible effect on the solubility.

36. We can solve this question by writing the reaction for a generic weak acid HA.

$$HA \rightleftharpoons H^+ + A^-$$
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Some amount of the HA will dissociate into H^+ and A^- . Thus the amount of H^+ and A^- will be the same. We can determine this amount from the pH, as $[H^+] = -\log(pH)$.

$$K_{\rm a} = \frac{(10^{-3.52})(10^{-3.52})}{0.015 - (10^{-3.52})} = \boxed{6.2 \times 10^{-6}}$$

Thus, the answer is |B|.

37. One possible reaction for the neutralization of sodium hydroxide is

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

As the reaction proceeds from reactants to products, the oxidation state for each element stays the same (Na +1, O -2, H +1, Cl -1). Thus, the answer is C.

Option A is a combustion, which is no doubt redox. Option B is is a typical reaction to prepare oxygen gas, as shown below.

$$2 \operatorname{KClO}_3 \longrightarrow 2 \operatorname{KCl} + 3 \operatorname{O}_2(g)$$

Option D is a single displacement reaction, which is always a redox, as shown below:

$$Mg + 2 HCl \longrightarrow MgCl_2 + H_2(g)$$

38. We have to flip one of the reactions so that the electrons will cancel out. If we flip the bottom reaction, the cell potential will become negative, which is nonspontaneous. Thus we must flip the top reaction, so we can eliminate A and C. We do not change the magnitudes of the cell potentials, so D is incorrect. Flipping the top reaction gives us a standard potential of 1.69 - 0.76, or B.

39. In KMnO₄, each O has an oxidation state of -2 and the K has an oxidation state of +1. Thus, to make the molecule neutral, the Mn must have an oxidation state of +7. Then the Mn was reduced to Mn²⁺. The reducing agent must itself be oxidized, so KMnO₄ cannot be the reducing agent. CO₂ and H₃O⁺ also cannot be the reducing agent because they are not reactants. Thus the answer must be $H_2C_2O_4$, or B.

We can confirm this because C has an oxidation state of +4 in CO_2 , but C_2 has an oxidation state of +6 in $H_2C_2O_4$ so each C was oxidized from C^{3+} to C^{4+} .

40. An Ampere is a unit of current (charge per time), so this is incorrect. A Coulomb is simply a generic unit of charge. A Volt is a unit of energy per charge. A Faraday is the charge of one mole of electrons. This is the $F = 96500 \text{ C} \cdot \text{mol}^{-1}$ in the reference section at the top of the exam. Thus, the answer is C.

41. Oxidation occurs at the anode and reduction occurs at the cathode. In this case, we see that Cr will be oxidized at the anode, and Sn will be reduced at the cathode. If we dilute the Cr^{3+} , which should be located at the anode, the reaction will shift right, and the potential will increase according to $E = E^{\circ} - \frac{RT}{nF} \ln Q$. Since Q will decrease, the voltage E increases. Thus, the answer is \overline{C} .

42. We can use dimensional analysis and Faraday's constant for this problem. Also note that the oxidation state of copper is +2, so each copper ion gains two electrons.

$$2.0 \text{ g } \text{Cu}^{2+} \times \frac{1 \text{ mol } \text{Cu}^{2+}}{63.55 \text{ g } \text{Cu}^{2+}} \times \frac{2 \text{ mol } e^-}{\text{mol } \text{Cu}^{2+}} \times \frac{96500 \text{ C}}{\text{mol } e^-} \times \frac{1 \text{ s}}{4.00 \text{ C}} = \boxed{1.5 \times 10^3 \text{ s}}$$

Thus, the answer is |B|.

43. For this question, we can write the electron configuration for each element.

Ca :
$$[Ar]4s^2$$

Cr : $[Ar]4s^13d^5$
Si : $[Ne]3s^23p^2$
S : $[Ne]3s^23p^4$

We see the number of valence electrons for Si is 2 + 2 = 4. Thus, the answer is C.

44. Ag is only in the 4d block, and Ba is only in the 6s block. Thus we can eliminate A and B. Now Eu is in the 4f block, and Ir is in the 5d block. Since 4f orbitals are occupied before 5d orbitals, Eu has an empty 5d orbital. Thus the answer is D.

45. n = 3, l = 2 refers to a 3*d* subshell. Na, Mg, and P all come before the 3*d* block in the periodic table. Ti is in the 3*d* block. Thus, the answer is D.

46. From our periodic trends, we know that atomic radius will increase, and ionization energy will decrease down the group from Be to Ba. Since the atomic number is increasing, and each proton has a positive charge, we know the nuclear charge will also increase. Thus the answer is I and III, or B.

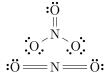
47. All the ions we are looking at are isoelectronic with Ar, except Br^- which is isoelectronic with Kr. For the ions isoelectronic with Ar, we know that the ones with the most protons will be the smallest because the protons can pull the electrons closer to the nucleus. Thus we have S^{2-} , K^+ , Ca^{2+} in order of decreasing size. Then we know Br^- is the biggest of all because it is isoelectronic with Kr, so it will have an extra electron shell. Thus, the ordering is as follows and the answer is B.

$$Br^{-}, S^{2-}, K^{+}, Ca^{2+}$$

48. We see from the left side that the sum of the mass numbers must be 252 + 11 = 263, and the sum of the atomic numbers must be 98 + 5 = 103. On the right side we already have 103 on the bottom, so we can eliminate A, B, and C as these would change the 103. Thus, the product needed to balance this equation is $5 n_0^1$, and the answer is D. We can confirm this because this will add 5 to the mass number, and 252 + 11 = 258 + 5.

49. We know the Ca will have an oxidation number of +2. Therefore, to make the molecule neutral, the $(\text{ReO}_4)_2$ must have a total oxidation number of -2. That means each ReO_4 has an oxidation number of -1. Each of the four oxygens has an oxidation number of -2, so this is -8 without the Re. To have a total oxidation number of -1 we must add +7. Thus, the answer is D.

50. Let's draw the Lewis structures of NO_3^- and NO_2^+ . For B and C we just add 1 or 2 electrons, respectively, to NO_2^+ .



From our VSEPR chart, we see that NO_3^- is trigonal planar, so it will have bond angles of 120° . NO_2^+ is linear, so it will have bond angles of 180° . Thus we can eliminate D. If we add electrons to NO_2^+ , the shape will become bent and the bond angle will decrease. Thus the species with the highest bond angle is NO_2^+ , or A.

51. Let us draw the Lewis structure of $\boxed{\operatorname{CO_3}^{2^-}}$. $\vdots \circ \vdots \circ \vdots$

From our VSEPR chart, we see that this the carbon has three bonds and no lone pairs so the molecule must be trigonal planar. Thus, the answer is A.

52. In the first reaction, four C–H bonds are broken. In the second reaction, two C–H bonds and one C=C bond is broken. Setting up a system of equations, we get that the answer is B.

$$4(C-H) = 1656$$
$$2(C-H) + (C \equiv C) = 1648$$
$$2(C-H) = \frac{1656}{2} = 828$$
$$(C \equiv C) = 1648 - 828 = \boxed{820 \text{ kJ} \cdot \text{mol}^{-1}}$$

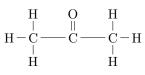
53. A carbon atom with sp^2 hybridization uses one s orbital and two of the three p orbitals for hybridization, which will make three sp^2 hybridized orbitals to form three σ bonds and one π bond through the side way overlap of the unhybridized p orbital. Thus, the carbon atom has 1π bond and 3σ bonds and the answer is C.

54. One possible Lewis structure is



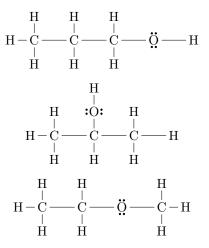
Note that we could pick any of the three oxygens to be the one with the double bond. Thus there are 3 resonance structures and the answer is C.

55. Let's draw the Lewis structure of CH₃COCH₃.



The other three molecules are similar, except they have extended carbon chains to the right. Hydrogen is not bonded to F, O, or N, so there is no hydrogen bonding and III is incorrect. There are some dipole-dipole interactions due to the polar C=O bond, but the oxygen is unchanged in the three molecules so there is no difference in the amount of dipole-dipole interactions. Thus I is incorrect. The number of electrons increases, so dispersion forces will increase. Thus the answer is Π , or B.

56. For this question we must draw out the isomers.



We cannot draw any more isomers because if we move the oxygen one more spot to the left, it will be the same as the last isomer, just flipped around. A real molecule can rotate in space so this is not a new isomer. Thus the answer is $\boxed{3}$, or \boxed{C} .

A general strategy is to to draw the alcohol isomers (with an -OH group) first, then the ether isomers (with a C-O-C group). For each category, we can draw all possible carbon chains and then add the functional group to different positions. As there are only three carbons here, there is one type of carbon chain. Reader may further practice to draw the isomers for $C_4H_{10}O$.

57. Let's draw the structure.

$$H-C = C - H$$

Each single bond and each double bond contributes 1 σ bond. Counting, we see $\boxed{6} \sigma$ bonds, or \boxed{C} .

58. Unsaturated hydrocarbons such as alkenes and alkynes react readily with halogens through addition reactions, So I and II are both correct. However, benzene, as an aromatic system, requires a catalyst to go through a *substitution* reaction, so it does not react "readily". Thus the answer is I and II, or B.

59. The name butanoic acid means there are four carbons (but-) and a -COOH group, which gives us a structure of CH₃CH₂CH₂COOH and a final formula of C₄H₈O₂. Thus, the answer is A.

60. Adenine and thymine pair with each other, while cytosine and guanine pair with each other. Thus, the answer is D.