Annotated Solution
2003 USNCO National Exam Part I

Authors: Charley Cheng
Proofreader and Editor: Dr. Qiang 'Steven' Chen

Created on July 1$^{\text{st}}$, 2021
Revised on July 15$^{\text{th}}$, 2022

1 Solutions

1. When water is vaporized from the sample, the mass will decrease. When successive weighings give the same mass, there is no more water in the sample. Therefore the answer is $\boxed{\text{D.}}$

2. When a liquid is cooled, it will remain a liquid even when cooled below its freezing point. This is called a supercooled state, indicated by L on the graph. Then, the liquid will rise back to its freezing point, indicated by $\boxed{\text{B. M}}$ on the graph and proceed to freeze.

3. When finished using chemicals, one should dispose of it in a waste container. The answer is $\boxed{\text{B.}}$

4. $\boxed{\text{C. OCl}^-}$ can undergo oxidization and reduction. In the anion, the chlorine has a oxidization number of +1. It can be reduced to Cl_2 with a formal charge of 0 or oxidized to ${ClO_2}^-$ with a formal charge of +3 or even higher.
Typically, the highest oxidation number of a main group element equals to its group number (IA-VIA), while its lowest oxidation number equals to the group number−8. Take S in option D for example, as S is in VIA group, so −2 is its lowest oxidation, thus S^{2-} can't be further reduced.

5. $57.48/12.01 = 4.786$, $4.22/1.008 = 4.22$, $38.29/16.00 = 2.393$ forms a $8 : 7 : 4$ ratio so the empirical formula is $\boxed{\text{D. C}_8\text{H}_7\text{O}_4}$

6. From the graph, the solubility decreases from 60 grams to 25 grams, meaning that $60 - 25 = 35$ grams of solute will precipitate out per 100 mL of solution. However, we are only working with a fifth of that amount, so only $35/5 = \boxed{\text{A. 7.0}}$ grams will recrystallize.

7. The largest change in water level will be created by the object with largest volume, which can be calculated by mass divided by density. Doing this, we get that we have the largest volume of oak. However, oak **floats in water**, decreasing the displacement significantly. Therefore, the highest volume for an object more dense than water is $\boxed{\text{B. Al}}$

8. Since the reaction only produces 70% of the theoretical yield, the theoretical yield must produce $0.200 \times \frac{100}{70} = 0.286$ mol of B_2H_6. Using mol ratios, $0.286 \times \frac{3}{2} = \boxed{\text{D. 0.429 mol}}$ of $NaBH_4$ is needed.

9. Let x be the volume needed. Balancing the mols, we have $6.0x + 1.0 \times 10. = 3.0 \times 20.$ which gives $x = \boxed{\text{C. 8.3 L}}$

10.
$$\frac{1330 \text{ g} \times 30.0 \text{ \%NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol}}{40.00 \text{ g}} = \boxed{\text{B. 9.98 M}}$$

11. Increasing the temperature excites the molecules and makes then favor the gas state. Decreasing the pressure also favors the gas state. Thus, the answer is $\boxed{\text{D. Neither 1 nor 2}}$

12. The molality of this solution is $\frac{0.0500}{.125} = 0.400$ m. However, since the solute dimerizes, that halves the number of particles dissolved in the water, so the effective molality is only 0.200 m. Therefore, the new freezing point is $5.50 - 5.10 \times 0.200 = \boxed{\text{B. } 4.48\ ^\circ\text{C}}$

13. The ideal gas law states there are $\frac{1 \times 720}{760 \times .0821 \times 328} = 0.0352$ mol of gas in a liter. Therefore, the molar mass is $\frac{2.53\text{ g}}{0.0352\text{ mol}} = 71.9$ g/mol. This matches with $\boxed{\text{C. } C_5H_{12}}$

14. Using the formula

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$\ln\left(\frac{760}{40}\right) = \frac{\Delta H}{8.314}\left(\frac{1}{292.2} - \frac{1}{351.5}\right)$$
$$\Delta H = \boxed{\text{A. } 42.4\text{ kJ/mol}}$$

15. Graham's Law states that the ratio of the effusion is equal to the square root of the reciprocal of the molar masses (derived from a constant $KE = \frac{1}{2}mv^2$), so the answer is $\sqrt{\frac{254}{146}} = \boxed{\text{A. } 1.32/1}$

16. Since the volume of gasses are ignored with the ideal gas law, the $\boxed{\text{D. volumes of molecules in real gases}}$ often lead to a larger volume than expected.

17. $\boxed{\text{D. Semiconductors}}$ are known for their conductivity greatly increasing with temperature.

18. The slope of both boiling point and melting point lines is positive. Therefore, as the pressure increases, so do the boiling and melting points. Thus, the answer is $\boxed{\text{B.}}$

19. Entropy is the measure of disorder in a system. A gas will have much more disorder since the molecules are moving rapidly while a solid will have a lot less disorder. Therefore, the ranking goes $\boxed{\text{A. } CO_2(s) < CO_2(aq) < CO_2(g)}$

20. Based on $q = cm\Delta T$, the heat released was $(50. + 50.) \times 1.0 \times 3.0 \times 4.2 = 1.26$ kJ from $0.050 \times 0.10 = .0050$ mol of HCl. Therefore, $\Delta H = \frac{-1.26}{.0050} = \boxed{\text{C. } -2.5 \times 10^2\text{ kJ}}$ (negative since it's exothermic)

21. The combustion reaction is $CS_2 + 3\,O_2 \longrightarrow CO_2 + 2\,SO_2$ $\Delta H = \frac{-215}{0.200} = -1075$ kJ/mol. Based on Hess's Law, the equation $-1075 = -393.5 + 2(-296.8) - \Delta H_f$ gives $\Delta H_f = \boxed{\text{B. } 87.9}$

22. Since the number of moles of gas is decreasing, the entropy is most likely negative. Since ΔH and ΔS are both negative, $\Delta G = \Delta H - T\Delta S$ will be negative only at low temperatures. Thus, the answer is $\boxed{\text{A.}}$

23. If we use $\Delta G = -RT\ln K$, we can see that when ΔG is very negative, K will be a large positive number. When ΔG is very positive, K will be a small positive number. This gives the answer of $\boxed{\text{B.}}$

24. The first law of thermodynamics states $\Delta E = q + w$ (E stands for the internal energy of the system). At constant volume, $w = 0$, so $\Delta E = q_v$ (q_v is the heat at constant volume), at constant pressure, $\Delta E = q + w = q_p - p\Delta V$ (q_p is the heat at constant pressure), $\Delta E + p\Delta V = q_p = \Delta H$ (enthalpy H is defined as $E + pV$). Since ΔV is positive in this case

(moles of gas increases) we have $\boxed{\text{A. } \Delta E < \Delta H}$.
As shown above, $w = -p\Delta V$, as the volume of the system increases, the system does work to the environment, thus, the internal energy of the system decreases, this is why there is a negative sign in expressing the work, w.

25. The only reactions whose half life is constant is first order. Therefore, the answer is $\boxed{\text{D.}}$

26. The half life formula states $t = \frac{\ln 2}{k} = \frac{\ln 2}{0.0541 \text{ s}^{-1}} = \boxed{\text{B. 12.8 s}}$

27. Since the total order is 3, tripling each reactant will increase the rate $3^3 = \boxed{\text{D. 27-fold}}$

28. The left side has units $\text{mol} \cdot \text{L}^{-1} \cdot \text{sec}^{-1}$ and the right side has units $k \cdot (\text{mol/L})^3$. If we set these equal, we get that k has units $\boxed{\text{C. } \text{L}^2 \cdot \text{mol}^{-2} \cdot \text{sec}^{-1}}$

29. $\boxed{\text{D.}}$ is the only mechanism that both satisfies the rate law and sums to the given equation. It has a rate law of Rate=[B][C]=k[A][B]^2 if pre-equilibrium approximation is applied to express the concentration of the intermediate, [C], as shown below. As the first step of option D is a fast equilibrium, $k_1[\text{A}][\text{B}] = k_{-1}[\text{C}]$.

30. The formula

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

states that $\boxed{\text{D. ln (rate constant) vs } \text{T}^{-1}}$ will give a straight line with a slope of $-E_a/R$ that gives the activation energy.

31. Half of the reverse of a reaction is equivalent to taking the square root of the reciprocal of the equilibrium constant. The new equilibrium constant is $\sqrt{\frac{1}{1.8 \times 10^{-5}}} = \boxed{\text{C. } 2.4 \times 10^2}$

32. The equilibrium constant is equal to the forward rate constant divided by the reverse rate constant. This can be derived by setting the forward and backwards rates equal to each other, which is the character of the equilibrium state. Therefore, we can solve $1.5 \times 10^{-39} = \frac{1.4 \times 10^{-28}}{k_b} \implies k_b = \boxed{\text{C. } 9.3 \times 10^{10}}$

33. Let $x = [\text{OH}^-]$. $K_b = 4.4 \times 10^{-4} = \frac{x^2}{0.25 - x} \implies x = 0.011$ and $[\text{H}^+] = \frac{10^{-14}}{0.011} = \boxed{\text{D. } 9.5 \times 10^{-13}}$

34. $0.010 \times 0.40\% = 4.0 \times 10^{-5}$ M has been ionized, so the equilibrium constant is $\frac{(4.0 \times 10^{-5})^2}{0.010} = \boxed{\text{B. } 1.6 \times 10^{-7}}$

35. The .005 mol of $[\text{OH}^-]$ will convert $1.0 \times 0.10 = 0.10$ mole H_2CO_3 to HCO_3^-, resulting in .095 M H_2CO_3 and .105 M HCO_3^-. Therefore, we have $K_a = 4.2 \times 10^{-7} = \frac{.105[\text{H}^+]}{.095} \implies [\text{H}^+] = \boxed{\text{C. } 3.8 \times 10^{-7}}$

36. We wish to find the answer choice that will precipitate with the lowest $[\text{Pb}^{2+}]$. For choice D. we can find the amount by using $K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] \implies [\text{Pb}^{2+}] = 1.8 \times 10^{-5}$. Repeating this calculation for each choice reveals $\boxed{\text{D.}}$ to be the smallest.

37. Since the chloride has a oxidation number of -1 in Cl^- and $+5$ in ClO_3^-, their coefficients need to be $5:1$ in order to match the oxidation number change. Now, with conservation of charge, there is a charge of -6 on the left, so there needs to be $\boxed{\text{D. 6}}$ hydroxide ions to balance that out. The final equation is $3\,Cl_2 + 6\,OH^- \longrightarrow 5\,Cl^- + ClO_3^- + 3\,H_2O$

38. We add the inverse of the first half reaction with the second half reaction which gives $0.141 + 0.800 = \boxed{\text{B. 0.941 V}}$

39. The discharging of a lead battery use the reaction $Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O$. No hydrogen gas is produced. $PbSO_4$ is produced from PbO_2. The density of the electrolyte solution decreases since ${SO_4}^{2-}$ ions are being precipitated out. Thus, the answer is $\boxed{\text{D. 2 and 3 only}}$

40. Using the formula $\Delta G = -nEF = -6 \times 2.02 \times 96500 = \boxed{\text{A. } -1170 \text{ kJ}}$

41. The overall reaction of the cell is Fe + Cu^{2+}(aq) = Cu + Fe^{2+}(aq). Using the Nernst equation, we get

$$0.807 = E^\circ - \frac{8.314 \times 298}{2 \times 96500} \ln\left(\frac{0.0010}{0.10}\right) \implies E^\circ = \boxed{\text{C. } 0.748 \text{ V}}$$

42. Based on Faraday's Law of electrolysis, the number of mols of Ni precipitating is $\frac{2.0 \times 3.0 \times 3600}{96500 \times 2} =$ .112 mol. This results in a $\boxed{\text{C. } \frac{0.500 \times 1.0 - 0.112}{0.500} = 0.78 \text{ M}}$ solution supposing the volume of the solution doesn't change.

43. $\boxed{\text{C. Ultraviolet}}$ light has the shortest wavelength and highest energy based on $E = h\nu = \frac{hc}{\lambda}$.

44. $\boxed{\text{B. } Cu^{2+}}$ has a d^9 configuration since Cu loses both of its $4s^1$ electron and one of the $3d^{10}$ electrons, so it does not have a full d orbital.

45. Based on the Aufbau Principle, we see that $\boxed{\text{A. } 6s}$ comes right before $4f$.

46. $\boxed{\text{A.}}$ is the only one that follows the rules $n > l \geq |m_l|$ and $m_s = \pm 1/2$

47. The general trend states that ionization energy increases when moving right in the periodic table. However, Be has full s orbital, so it requires more energy to remove than a lone p electron in B. Thus, the correct order is $\boxed{\text{A. Li, B, Be}}$

48. The periodic trend for alkalinity is that it increases going down and left in the periodic table. This is due to the fact that those elements are less electronegative, so they adopt a positive charge much easier such as in $Al(OH)_3 \longrightarrow {Al(OH)_2}^+ + OH^-$. Using that trend, we see that $\boxed{\text{A. } Al_2O_3}$ is the most basic anhydride. All other three oxides produce acidic solutions when added to water.

49. There 6 valence electrons on each S and O atom, for a total of 60. The molecule also has a -2 charge, which adds 2 more valence electrons for a total of $\boxed{\text{C. 62}}$

50. The bonds are equal in length due to the two equivalent resonances of each species, so the answer is $\boxed{\text{C. both 1 and 2}}$

51. From Coulomb's law, the attraction is proportional to the charge of the ions and inversely proportional to the distance between the adjacent cation and anion, which equals to the sum of the radius of the cation and anion. $\boxed{\text{C. MgO}}$ both maximizes the charge of the ions while minimizing the radius.

52. $\boxed{\text{A. Trigonal planar}}$ structures are unlikely to come from a trigonal bipyrimidal electron geometry since electron pairs prefer to occupy equatorial positions over axial positions.

53. From molecular orbital theory (or noting NO^+ is isoelectronic to N_2) we see that $\boxed{\text{B. } NO^+}$ has a bond order of 3, which is the strongest bond.

54. After a combustion reaction, carbon goes from CH_4 to CO_2. Based on the number of electron domains around the central carbon, CH_4 is sp^3 hybridized and CO_2 is sp hybridized.

That means the answer is $\boxed{\text{A. } sp^3 \text{ to } sp}$

55. There are 10 hydrogen atoms in the figure, 6 of them are shown in the methyl groups and 4 are not shown but connected to the benzene ring. Therefore the answer is $\boxed{\text{A. } C_8H_{10}}$

56. Tertiary carbons are most likely to react with the S_N1 mechanism since the carbocation forme as the intermediate is stabilized with hypercongugation effects. The only substance with a tertiary carbon is $\boxed{\text{C. } (CH_3)_3CCl}$

57. The substance that will react with Br_2 the quickest is a substance with a C=C pi bond through an addition reaction. $\boxed{\text{D. propene}}$ is the only structure with a C=C pi bond. (Benzene does not count since it is aromatic with all of its pi bonds delocalized.)

58. $\boxed{\text{B. Butyne}}$ has a triple bond which results in *sp* hybridized carbons.

59. $\boxed{\text{B. } CH_3CH_2CH_2OCH_3}$ has the highest vapor pressure since it does not have hydrogen bonding.

60. $\boxed{\text{B.}}$ since it is the only structure such that the carbon is connected to 4 different things.