

# Annotated Solution

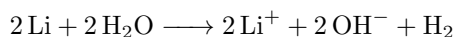
## 2017 USNCO National Exam Part I

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### Solutions

1. The reaction described in the question is



From the equation, we can see that

$$n_{\text{Li}} = n_{\text{LiOH}}$$

or

$$\frac{m}{6.9} = \frac{12}{6.9 + 1.0 + 16}$$

After solving the equation, we find that  $m = \boxed{3.5 \text{ g}}$ . The answer is thus  $\boxed{B}$ .

2. The mass of carbon in 3.38 g  $\text{CO}_2$  is

$$m(\text{C}) = 3.38 \text{ g} \times \frac{12.0}{12.0 + 2 \times 16.0} = 0.922 \text{ g}$$

Based on the mass conservation, the mass of carbon in the hydrocarbon is the same as that in the  $\text{CO}_2$ , so

$$m(\text{H}) = 1.00 \text{ g} - 0.922 \text{ g} = 0.078 \text{ g}$$

We may further use the atomic mass of carbon and hydrogen to calculate the mole ratio of the two elements in the hydrocarbon and get the empirical formula:

$$\frac{n(\text{C})}{n(\text{H})} = \frac{0.922/12.0}{0.078/1.01} = \frac{1}{1}$$

Thus, the answer should be  $\boxed{\text{CH}}$ , or  $\boxed{A}$ .

3. We can easily see that the binary metal chloride contains 62.07% metal and 37.93%. We then can solve this problem by calculating the percentage composition for all of the four possible answers.

(A) Cu % in  $\text{CuCl}_2 = 27.26\%$

(B) Cd % in  $\text{CdCl}_2 = 61.32\%$

(C) Ce % in  $\text{CeCl}_4 = 49.70\%$

(D) Th % in  $\text{ThCl}_4 = 62.07\%$

Therefore, the answer is  $\boxed{\text{Th}}$ , or option  $\boxed{D}$ .

4. When nitrogen gas is the only nitrogen-containing product, its mass can be calculated by calculating the percentage mass of nitrogen presented in the initial nitrogen compound. Even without calculation, we can see that  $\boxed{\text{NH}_3}$ , or option  $\boxed{D}$ , has the highest percentage mass of nitrogen as oxygen atoms are far heavier than hydrogen atoms.

5. From the chemical equation, we can have

$$\frac{1}{2} \times 0.150 \text{ M} \times 35.0 \times 10^{-3} \text{ L} = \frac{1}{5} \times [\text{H}_2\text{O}_2] \times 50.0 \times 10^{-3} \text{ L}$$

After solving the equation above, we have  $[\text{H}_2\text{O}_2] = \boxed{0.263 \text{ M}}$ , or  $\boxed{C}$ .

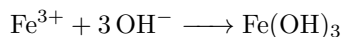
6. The equation for freezing point depression is:

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

$\Delta T$  is the change in freezing point temperature.  $K_f$  is the cryoscopic constant.  $b$  is molality.  $i$  is the van't Hoff factor.

From the equation, we can see that the higher the amount of the solute is (or larger  $b$  and  $i$ ), the larger the freezing point depression. Thus, we need to find the compound that can dissociate into most ions. B and D can not be the correct answers because we are given equal mass of all substances and they have higher molar mass. Although  $\text{MgSO}_4$  has a smaller molar mass,  $\text{Na}_2\text{S}_2\text{O}_3$  can dissociate into two  $\text{Na}^+$  and one  $\text{S}_2\text{O}_3^{2-}$  while  $\text{MgSO}_4$  can only dissociate into one  $\text{Mg}^{2+}$  and one  $\text{SO}_4^{2-}$ . After all,  $\boxed{\text{Na}_2\text{S}_2\text{O}_3}$  can dissociate into more ions, thus the answer is  $\boxed{C}$ .

- 7.

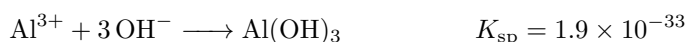


$\text{Fe}(\text{OH})_3$  is a reddish-brown precipitate in answer choice  $\boxed{A}$ . Note that  $\text{BaCl}_2$  is not a precipitate.

8. In the condition given by the question,  $\text{F}_2$  and  $\text{Cl}_2$  are gas,  $\text{I}_2$  is a solid, and  $\boxed{\text{Br}_2}$  or  $\boxed{C}$  is a liquid. Fun fact, the only two element that are liquid in room temperature and atmospheric pressure are  $\text{Br}_2$  and  $\text{Hg}$ .

9. A spectrophotometer measures the concentration of the analyte by recording the absorption of light and using the Beer-Lambert Law. The reason why some solutions have color is that some wavelength of visible light is absorbed by the solution. Thus, spectrophotometer can be efficiently used to detect colored solution. Option C and D are both colorless. Although  $\text{Mn}^{2+}$  has a very light pink color (almost colorless),  $\text{Co}^{2+}$  has a much darker pink color (you'll know this if you have done some classic AP Chem experiment), which means larger absorption. Thus,  $\boxed{B}$  is the correct answer.

10. We can first eliminate option B because it's not acidic at all.  $\text{NaHCO}_2$  is the conjugate base of  $\text{H}_2\text{CO}_2$ , which is also known as formic acid. Formic acid is a monoprotic weak acid, so  $\text{NaHCO}_2$  is basic in water. High-charged or transition metal cations are actually pretty acidic in water solutions because they form complexes with water molecules, for example  $\text{Al}(\text{OH}_2)_6^{3+}$ . Oxygen in water will donate some of its electrons to the metal cation in order to stabilize the complex. This makes complexed water molecules more acidic because compared with normal water molecules, oxygens in the complex are relatively electron deficient, and the conjugate base is also more stable. We can do a simple calculation to estimate the pH of 0.1 M of  $\text{Al}^{3+}$ :



Given that  $[\text{Al}^{3+}] = 0.1 \text{ M}$ :

$$[\text{OH}^-] = \sqrt[3]{\frac{1.9 \times 10^{-33}}{0.1}} = 5.7 \times 10^{-8}$$

$$\text{pH} = 14 + \log([\text{OH}^-]) = 3.4$$

Thus, the pH of a solution of 0.1 M of  $\text{Al}^{3+}$  must be lower than 3.4, which is even more acidic than a solution of 0.1 M of  $\text{H}_2\text{CO}_3$ . Therefore, the answer is  $\boxed{\text{Al}^{3+}}$  or  $\boxed{\text{A}}$ .

11. Because the height of the mercury has reached equilibrium, the pressure on the two ends must be the same (If they are not the same, the height will adjust until they are the same). Thus, because one end is open to the atmosphere, we have

$$\text{pressure} = 65 \text{ mmHg} + 615 \text{ mmHg} = \boxed{680 \text{ mmHg}}$$

or  $\boxed{\text{C}}$ .

12. When reading numbers on volumetric glassware, we always read the number on the bottom of the meniscus. In this case, the result would be  $\boxed{30.30 \text{ mL}}$  or  $\boxed{\text{C}}$ .

13. (A) is incorrect because the process of boiling is an endothermic process and the gas is continuously leaving the system, not to mention that the beaker is not well insulated. Thus, you would need to continuously inputting heat in order to keep the solution boiling.

$\boxed{\text{B}}$  is correct because boiling separates the molecules to greater distance, which disrupts the hydrogen bonds between the molecules. This is also why water has such a high boiling point.

(C) is incorrect because there is no ion dipole interaction in the solution. (No ions)

(D) is incorrect because the reaction is unfounded.

14. The diffusion rate of a gas is inversely proportional to the square root of its molar mass. Thus, because HCl is heavier, it effuses at slower rate, the solid will be formed closer to the end with  $\boxed{\text{HCl}}$  or  $\boxed{\text{B}}$ .

15. When a liquid is at its boiling point, its vapor pressure is equal to the ambient atmospheric pressure. If we alter the volume of the vapor above the liquid, the amount of vapor will change accordingly, and the vapor pressure still equals to the ambient pressure. For example, if we keep the liquid at its boiling point, but increase the volume above liquid, or the volume of the vapor, the equilibrium will shift towards the vapor side and more vapor will be formed. Similarly, because temperature did not change in the question, the pressure of the vapor is still  $\boxed{1.0 \text{ atm}}$  or  $\boxed{\text{B}}$ .

16. We know that water has a high boiling point due to hydrogen bonding. If hexane were to be miscible with water, the strong hydrogen bonding must be broken due to the separation of water molecules. Thus,  $\boxed{\text{B}}$  is correct.

(A) There is no strong intermolecular forces between hexane molecules as there are only London dispersion forces existed.

(C) Molar mass does not necessarily correlate with miscibility. For example, Triethylene glycol,  $\text{C}_6\text{H}_{12}\text{O}_4$ , is miscible with water.

(D) Water is a polar solvent, so the larger the difference in electronegativity, the more soluble hexane is.

17.  (A) is correct because stronger bonds require more energy to break. And Si–O is indeed stronger than Si–Si as O is smaller in size than Si.  
 (B) is incorrect because silicon is not a metal and silicon dioxide is not an ionic solid.  
 (C) is incorrect because silicon dioxide is not polar. (dipole moments are canceled out in the tetrahedral structure)  
 (D) is incorrect because both silicon dioxide and silicon form network covalent compounds.

18. Atoms on the corner of the cube is shared by 8 cubes. Thus each is counted as 1/8. Similarly, atoms on the face of the cube is counted as 1/2 and inside the cube is counted as 1. After counting, we found that  (C) is correct.  
 Alternatively, by looking at the empirical formula, we know that the number of Zn in the cube must equal to that of S. The cube clearly has more than one Zn and S. Thus, the correct answer is  (C).

19. Apply Hess's Law, the standard enthalpy change of the reaction equals to that the sum of the standard enthalpy of formation of all products subtracts the sum of the standard enthalpy of formation of all reactants.

$$\Delta H = 2 \times (-296.4 \text{ kJ/mol}) + 2 \times (-285.8 \text{ kJ/mol}) - 2 \times (-20.15 \text{ kJ/mol}) = \boxed{-1124 \text{ kJ/mol}}$$

Thus, the answer is  (D). Please be aware that the standard enthalpy of O<sub>2</sub>(g) is 0 as it is the stable elemental form of oxygen.

20. Note that the question asks for the change in Gibbs free energy, not the standard change in Gibbs free energy,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Reaction quotient is influenced by the concentration of species. Thus, the answer is  (C).

21. Let's do some derivation:

$$\Delta G = \Delta H - T\Delta S = -RT \ln K$$

Because the reaction is vaporization, the equilibrium constant equals the vapor pressure of the liquid. Thus,

$$\ln P = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Therefore, the slope of the graph in the question equals  $-\frac{\Delta H}{R}$ . After calculation, we can find that  $\Delta H = -4544 \times (-8.314) \text{ J/mol} = \boxed{37.8 \text{ kJ/mol}}$ . Thus, the answer is  (C).

22. Generally, gas has a larger entropy than liquid, which has a larger entropy than solid if all are 1 mol. More gas molecules would make the system more chaotic and thus higher entropy. D has 0.5 mol more gas than C. Thus,  (D) is the correct answer.

23. Consider the reaction  $\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ . Using the table, we can find

$$\Delta H^\circ = -74.8 \frac{\text{kJ}}{\text{mol}} + 2(-241.8 \frac{\text{kJ}}{\text{mol}}) - (-393.5 \frac{\text{kJ}}{\text{mol}}) = -164.9 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S^\circ = 186.3 \frac{\text{J}}{\text{mol K}} + 2(188.8 \frac{\text{J}}{\text{mol K}}) - 4(130.7 \frac{\text{J}}{\text{mol K}}) - 213.7 \frac{\text{J}}{\text{mol K}} = -172.6 \frac{\text{J}}{\text{mol K}}$$

Combining these together, we get

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -164.9 \frac{\text{kJ}}{\text{mol}} - 298 \text{ K}(-172.6 \frac{\text{J}}{\text{mol K}}) = -113.5 \frac{\text{kJ}}{\text{mol}}$$

Furthermore, we have

$$\Delta G^\circ = \Delta G_f^\circ(\text{CH}_4) + 2\Delta G_f^\circ(\text{H}_2\text{O}) - 4\Delta G_f^\circ(\text{H}_2) - \Delta G_f^\circ(\text{CO}_2)$$

Plugging in values, we get

$$\Delta G_f^\circ(\text{CH}_4) = -113.5 \frac{\text{kJ}}{\text{mol}} - 2 \times (-228.6 \frac{\text{kJ}}{\text{mol}}) - 394.4 \frac{\text{kJ}}{\text{mol}} = \boxed{-50.7 \frac{\text{kJ}}{\text{mol}}}$$

Thus the answer is  $\boxed{A}$

Please be aware the challenge of this problem is the setup of the reaction to include all species in the table.

24. Because the mass of water is larger, the increase in temperature should be lower ( $q = mc\Delta T$ ) with the same amount of heat. In addition, because there are equal amount of reactant, the point where NaOH gets consumed should be the same. Therefore, the answer should be  $\boxed{B}$ .

25. We can first eliminate option A and B simply by comparing each option. Because [A] is second-ordered in the rate law, the change in rate made by option C is going to be  $2^2 \times 2 = 8$  fold, while that of D is 4 fold. Therefore, the correct answer is  $\boxed{C}$ .

26. We know that,

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{65 \text{ kJ/mol}}{R} \left(\frac{1}{22 + 273} - \frac{1}{37 + 273}\right)$$

The ratio between  $k_2$  and  $k_1$  is thus

$$\frac{k_2}{k_1} = e^{-1.28} = 0.277$$

Because  $k_2$  is now 27.7% of  $k_1$ , the rate constant has decrease  $1 - 0.277 = \boxed{72\%}$  Thus the answer is  $\boxed{D}$ .

27. For a first order reaction:

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

Therefore, a plot of  $\ln[A]$  over time should be linear with slope equal to the negative rate constant. Thus, the answer should be  $\boxed{C}$ . Note that if there are multiple species in the rate law with one specie's concentration much larger than the other, or pseudo first order reaction, the slope will equal to the observed rate constant,  $k'$ , which has the relationship:  $k' = k \times [B]^b$ .

28. Let  $M = [^{99}\text{Mo}]$  and  $T = [^{99\text{m}}\text{Tc}]$ . Then, according to the reactions given, we have  $\frac{dM}{dt} = -k_1M$ , where  $k_1 = \frac{\ln 2}{65}$  and  $\frac{dT}{dt} = k_1M - k_2T$ , where  $k_2 = \frac{\ln 2}{6}$ .

Now let's consider the ratio of activities

$$r = \frac{k_2T}{k_1M}$$

Using the quotient rule, we have

$$\frac{dr}{dt} = \frac{k_2 \frac{dT}{dt} M - \frac{dM}{dt} T}{M^2}$$

Plugging in our above equations, we get

$$\frac{dr}{dt} = \frac{k_2}{k_1} \left( \frac{(k_1M - k_2T)M + k_1MT}{M^2} \right) = \frac{k_2}{k_1} \frac{k_1M + k_1T - k_2T}{M} = k_2 + (k_1 - k_2) \frac{k_2}{k_1} \frac{T}{M} = k_2 + (k_1 - k_2)r$$

Thus we hypothesize that  $r$  is of the form  $Ae^{(k_1-k_2)t} + B$ . Since  $T = 0$  at  $t = 0$ ,  $r = \frac{k_2 T}{k_1 M} = 0$  as well and we have  $A + B = 0$ . Plugging our hypothesis into the differential equation, we get

$$A(k_1 - k_2)e^{(k_1-k_2)t} = k_2 + (k_1 - k_2)(Ae^{(k_1-k_2)t} - A) \implies 0 = k_2 - A(k_1 - k_2) \implies A = \frac{k_2}{k_1 - k_2}$$

Plugging our result in, we get

$$r = \frac{T}{M} = \frac{k_2}{k_1 - k_2}(e^{(k_1-k_2)t} - 1)$$

Since  $k_1 < k_2$  ( $^{99}\text{Mo}$  decays slower than  $^{99\text{m}}\text{Tc}$ ),

$$t \rightarrow \infty \implies e^{(k_1-k_2)t} \rightarrow 0 \implies r \rightarrow \frac{-k_2}{k_1 - k_2} = \frac{\frac{\ln 2}{65\text{h}}}{\frac{\ln 2}{65\text{h}} - \frac{\ln 2}{6\text{h}}} = \frac{65}{59} = 1.10$$

Since the activities of  $^{99}\text{Mo}$  and  $^{99}\text{Tc}$  become roughly equal as time goes on, we can eliminate A) and B). Furthermore, when  $t = 20$ , we have

$$r = \frac{65}{6 - 65}(e^{(k_1-k_2)t} - 1) = \frac{65}{-59}(e^{(\frac{\ln 2}{65\text{h}} - \frac{\ln 2}{6\text{h}}) \times 20\text{h}} - 1) = \frac{65}{-59}(-0.88) = 0.97 \approx 1$$

Thus the activities become approximately equal after 20 hours, and the answer is C

Of course, in a test scenario, chemical reasoning/intuition would show that the activities become approximately equal as time goes on and that 20 hours seems like a more reasonable time frame than 120 hours (two entire  $^{99}\text{Mo}$  half-lives) for this to happen. Since Tc decays faster than Mo, it will build up until a steady state equilibrium is reached so it will not exceed the activity of Mo, we can also eliminate A and B.

29. A is correct because  $\text{IO}^-$  is being formed at a rate that is much faster than it is being consumed. (B) is incorrect because  $\text{IO}^-$  is in the rate determining step, and the formation rate of  $\text{IO}^-$  is positively correlated with the concentration of  $\text{I}^-$ . (C) is incorrect because the concentration of peroxide clearly influences the rate of the reaction. (D) is incorrect because  $\text{O}_2$  is not in the rate law as it is a product of a irreversible step.

30. From the energy profile, we can write the following elementary reactions:



We can use the steady state approximation to derive a rate law.

$$\begin{aligned} [\text{C}] &= \frac{k_1[\text{B}]}{k_{-1} + k_2[\text{A}]} \\ r &= \frac{k_1 k_2 [\text{A}][\text{B}]}{k_{-1} + k_2[\text{A}]} \end{aligned}$$

There is only one intermediate, C, in the reaction. The reaction is not second-ordered. Therefore, the correct answer is D.

Please be aware that A is added to B as the reactant of the first step to fairly compare with the energy of A + C though A is not involved in the first step.

31. Use an ICE table:

	$\text{CN}^-$	$\text{HCN}$	$\text{OH}^-$
I	0.25	0	0
C	$-x$	$+x$	$+x$
E	$0.25 - x$	$x$	$x$

Using the relation  $pK_a + pK_b = 14$ , we get that the  $pK_b$  of  $\text{CN}^-$  is 4.79. Using the equilibrium constant expression, we can write

$$1.62 \times 10^{-5} = 10^{-4.79} = K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{x^2}{0.25 - x}$$

Since  $\text{CN}^-$  is a weak acid, we assume for the moment that  $x \ll 0.25$ , so that  $0.25 - x \approx x$ . Now our equation becomes

$$1.62 \times 10^{-5} = \frac{x^2}{0.25} \implies x = \sqrt{0.25 \times 1.62 \times 10^{-5}} = 2.0 \times 10^{-3}$$

Since  $\frac{x}{0.25M} = 0.008 < 5\%$ , we can now justify our previous assumption on numerical evidence. Thus  $[\text{OH}^-] = x = 2.0 \times 10^{-3}$  and  $\text{pH} = 14 - \text{pOH} = 14 - (-\log([\text{OH}^-])) = \boxed{11.3}$

The answer is  $\boxed{C}$

32. From the equation

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

we can see that exothermic reactions ( $\Delta H^\circ < 0$ ) are less favorable at high temperatures and endothermic reactions ( $\Delta H^\circ > 0$ ) are more favorable. Since  $K_w$  for water is larger at  $60^\circ$  than at  $25^\circ$ , we can conclude that the auto-ionization of water is endothermic. Thus I is incorrect.

Water at  $60^\circ$  is just as acidic as water at room temperature! Another way of thinking about this would be to compare the amounts of  $\text{H}^+$  and  $\text{OH}^-$  in solution. Raising the temperature increases  $[\text{H}^+]$  and  $[\text{OH}^-]$ , but they still maintain a 1:1 ratio, and the solution is neutral. Thus II is incorrect.

The answer is  $\boxed{D}$

33. Let's examine the equilibrium constant expression for this reaction. We omit solids and liquids, since their "concentrations" are essentially constant and can be absorbed into the equilibrium constant  $K$ . Thus we simply have  $K_p = [\text{CO}_2]$ . Since neither the amount of  $\text{BaCO}_3(\text{s})$  nor the container volume can change  $K_p$ , which is dependent solely on temperature, I and II are both incorrect.

The answer is  $\boxed{D}$

34. Using an ICE table, we can compute  $[\text{Ca}^{2+}]$  before the addition of  $\text{NaOH}$ .

	$\text{Ca}^{2+}$	$\text{OH}^-$
I	0	0
C	$+x$	$+2x$
E	$x$	$2x$

Now solving  $8.0 \times 10^{-6} = K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = x(2x)^2 = 4x^3$ , we get  $[\text{Ca}^{2+}] = x = 0.013 \text{ M}$ .

We again use an ICE table to compute  $[\text{Ca}^{2+}]$  after the addition of  $\text{NaOH}$ . Since we added 0.10 mol  $\text{NaOH}$  to a 1.00 L solution, the initial concentration of  $\text{OH}^-$  is 0.10 M.

	$\text{Ca}^{2+}$	$\text{OH}^-$
I	0	0.10
C	$+x$	$+2x$
E	$x$	$0.10 + 2x$

Since we are only looking for approximate answers here, we can go ahead and simplify  $0.10 + 2x \approx 0.10$ . Thus  $8.0 \times 10^{-6} = K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = x(0.10)^2 \implies [\text{Ca}^{2+}] = x = 8.0 \times 10^{-4} \text{ M}$ .

Since  $\frac{8.0 \times 10^{-4} \text{ M}}{0.013 \text{ M}} = 0.061 \approx 5\%$ , we can conclude that  $100\% - 5\% = \boxed{95\%}$  of the  $\text{Ca}^{2+}$  in solution has precipitated out.

The answer is  $\boxed{C}$

35. When choosing titration indicators, we would like one that changes color right around the equivalence point. For this titration, the equivalence point occurs when all of the formic acid has been deprotonated to form formate. At this point, our solution is *basic* because formate is the conjugate base of a weak acid. Thus we would like an indicator that changes color in slightly basic solutions, so we choose II.

The answer is B

36. Diluting the solution from 1.00 L to 2.00 L would approximately halve the concentrations of all species in solution. Granted, the equilibrium will shift somewhat to the right because of the greater amount of aqueous species on the right hand side (RHS), but it won't be sufficient to overcome a  $2x$  dilution. Thus I is incorrect. For those not convinced, a more rigorous argument follows:

Assume for contradiction that  $[H^+]$  actually did increase upon dilution. Since one molecule of  $NH_3$  is produced by the reaction for every molecule of  $H_3O^+$ ,  $[NH_3(aq)]$  also *has* to increase. But because of the dilution and the (assumed) rightward shift of equilibrium,  $[NH_4^+]$  *has* to decrease. Because of these changes, the fraction  $\frac{[H_3O^+][NH_3]}{[NH_4^+]}$  now *has* to have increased. But we know that  $\frac{[H_3O^+][NH_3]}{[NH_4^+]}$  is *always* equal to the equilibrium constant. Contradiction, so I is incorrect.

Since  $\Delta H^\circ > 0$ , the equation  $\ln K = \left(\frac{-\Delta H^\circ}{R}\right)\frac{1}{T} + \text{constant}$  shows that  $K$  will increase with temperature for this reaction. An increase in  $K$  means that more products will be present at equilibrium, so II is correct. You may get the same conclusion through applying the Le Chatelier Principle here as the reaction shifts to the product side for an endothermic reaction when temperature increases.

The answer is B

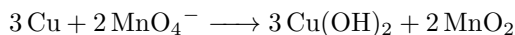
37. Using the cell notation conventions, we can see that the overall reaction is  $Cu(s) + 2 Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2 Ag(s)$ . Since the Nernst Equation gives  $E = E^\circ - \frac{RT}{nF} \ln Q$ , increasing  $Q$  will decrease  $E$ , while decreasing  $Q$  will increase  $E$ . We have, by definition,  $Q = \frac{[Cu^{2+}]}{[Ag^+]^2}$ .

Increasing  $[Cu^{2+}]$  will increase  $Q$  and decrease  $E$ , so I is incorrect.

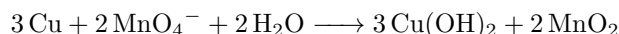
Adding  $Cl^-$  to the  $Ag^+/Ag(s)$  cell precipitates some of the  $Ag^+$  as  $AgCl$ , decreasing  $[Ag^+]$ . This increases  $Q$  and decreases  $E$ , so II is incorrect.

The answer is D

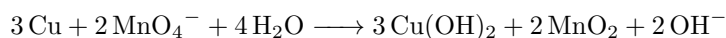
38. The general practice for balancing aqueous redox reactions is to first balance the electrons transferred, and then to add  $H^+$ ,  $H_2O$ , and  $OH^-$  as needed to balance the atoms. This reaction turns  $Cu(0)$  into  $Cu(II)$  and  $Mn(VII)$  into  $Mn(IV)$ . In other words,  $Cu$  loses two electrons and  $MnO_4^-$  gains three electrons. Thus we need a  $3 : 2$  ratio of  $Cu$  to  $MnO_4^-$ , and our tentative balanced reaction becomes



Now for phase 2. There are 6 hydrogens and 10 oxygens on the right, and 8 oxygens on the left. We add  $H_2O$  until the oxygens are balanced, getting



Now we balance the hydrogens. The left side still needs 2 more hydrogens, but we cannot add  $H^+$ , which doesn't exist in significant concentrations in a basic solution. So instead, we add  $2H_2O$  to the left and  $2OH^-$  to the right. Our final balanced equation is



The answer is B



39. Remember that both oxidation states and formal charges are calculated by subtracting the number of electrons an atom "has" from the number it "should have," i.e. its valence number. For oxidation states, all of the electrons in a bond are assigned to the most electronegative atom. If their electronegativities are equal (i.e. they're the same element) the electrons are evenly split. Since assigning electrons to the most electronegative atom and counting valence electrons both end up counting all of the electrons in a compound once, the sum of oxidation states simply equals the total charge. Some simplifications for quick computation follows.

Since O, F, Cl, Br, and I are so electronegative, they're usually in their maximal oxidation state, which is  $-2$  for O and  $-1$  for the halogens. H is not very electronegative and only has one valence electron in the first place, so it's usually  $+1$ . Now for some calculations:

- A) Using the oxidation state rules and simplifications, we assign  $-2$  to oxygen. But charge balance means that Os has to have an oxidation state of  $+8$  to balance out the four  $-2$  oxygens.  
 B) This is a little more tricky. From the formula, we can see that the compound is composed of Mn atoms and CO molecules. As CO is a neutral molecule, so the oxidation state for Mn is simply 0.  
 C) This is also tricky. Due to some structural technicalities, individual atoms can be assigned fractional oxidation states that add up to  $+1$ . So the average oxidation state of each nitrogen is  $+1/5$   
 D) Using the oxidation state rules and simplifications, we assign  $-1$  to F. To achieve an overall charge of  $-2$ , we need to assign a  $+6$  charge to Xe.

The answer is A.

40. We need to add the two given half-reactions to get the desired half-reaction  $2\text{Hg}^{2+}(\text{aq}) + 4\text{e}^{-} \longrightarrow 2\text{Hg}(\text{l})$ . Remember that when we add reactions, we can add their  $\Delta G^{\circ}$ s to get  $\Delta G^{\circ}$  for their sum. Since  $\Delta G^{\circ} = -nFE^{\circ}$ , we can see that  $E^{\circ}$  for the sum of reactions (1) and (2) is  $\frac{n_1FE_1^{\circ} + n_2FE_2^{\circ}}{(n_1+n_2)F} = \frac{n_1E_1^{\circ} + n_2E_2^{\circ}}{n_1+n_2}$ , simply the weighted average of the individual reaction potentials. Applying the formula to our problem, we get  $E^{\circ} = \frac{2(+0.90\text{ V}) + 2(+0.80\text{ V})}{2+2} = \boxed{+0.85\text{ V}}$

The answer is B

41. As the cell is discharged, both reactions proceed forwards (this is just convention). Since we see that  $\text{H}^{+}$  is consumed in the first reaction,  $[\text{H}^{+}]$  decreases as the reaction progresses. Thus I is correct.

Since  $\text{Pb}^{2+}$  does not appear anywhere in the equation (it's constantly precipitated out by  $\text{SO}_4^{2-}$ ) the reaction doesn't affect  $[\text{Pb}^{2+}]$  and II is incorrect.

The answer is A

42. Recall the Nernst Equation:  $E = E^{\circ} - \frac{RT}{nF} \ln Q$ . Thus as  $Q = \frac{1}{p(\text{O}_2)[\text{H}^{+}]^4} = \frac{1}{[\text{H}^{+}]^4}$  increases, the potential decreases. Remember that *increasing* pH actually *decreases*  $[\text{H}^{+}]$ . Thus  $Q$  would increase and  $E$  would decrease as the pH increases.

The answer is A

You may further figure out the slope of the  $E - \text{pH}$  diagram by yourself.

43. Using the rules of quantum numbers, we see that this corresponds to electrons in a specific 3p orbital ( $x$ ,  $y$ , or  $z$  - it doesn't matter). Looking at the position of P in the periodic table, we see that its electron configuration is  $[\text{Ne}]3s^23p^3$ . By Hund's rule, all 3p orbitals thus have exactly one electron in them to achieve maximum multiplicity.

The answer is B

44. From ionization energy trends, we can see that 1)  $\text{Si} < \text{P}$ , 2)  $\text{Ge} < \text{As}$ , 3)  $\text{Ge} < \text{Si}$ , and 4)  $\text{As} < \text{P}$ . Thus P has the largest ionization energy and Ge the least. To assign the positions of Si and As, we

have to realize that the decrease in ionization energy going down a group is significantly less than the increase upon going right in a period. This makes intuitive sense, since we'd expect elements in the same group to have similar behavior and similar ionization energies than elements in the same period. Thus  $\text{Si} < \text{As}$  and the final order is  $\text{Ge} < \text{Si} < \text{As} < \text{P}$

The answer is  $\boxed{C}$ .

45. Since there are 4s electrons, we know that the atom cannot be an ion (transition metal ions have all of their electrons in the d orbital). Now the electron configuration of  $[\text{Ar}]4s^23d^7$  means that we have the 9<sup>th</sup> element in period 4, or Co.

The answer is  $\boxed{B}$ .

46. Recall that the energy levels of a hydrogenic atom are proportional to  $-\frac{1}{n^2}$ . Thus larger energy levels are closer together than smaller energy levels. Furthermore, larger  $n$  corresponds to less negative, and thus higher energy levels, so emission requires a jump *down* in principle quantum number. Using these two principles, we see that the transition  $5 \rightarrow 2$  has the lowest energy (and thus longest wavelength) emission. Please be aware that the transition in option C ( $n=1 \rightarrow n=5$ ) has a larger energy difference but it absorbs light as the energy level increases.

The answer is  $\boxed{B}$ .

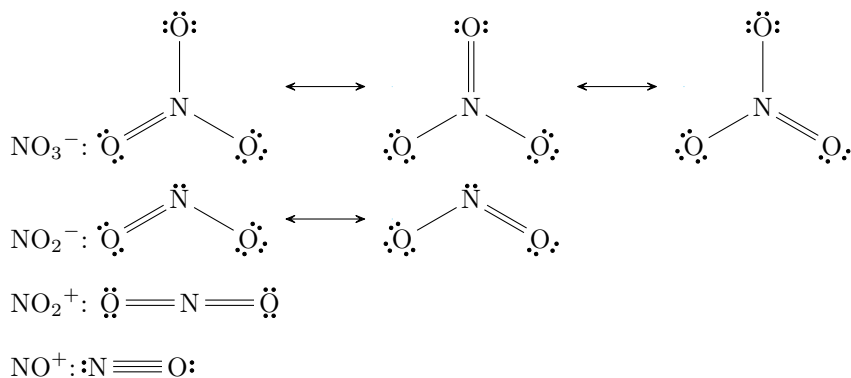
47. A key term here is "diagonal relationship". From electronegativity trends, we can see that electronegativity  $\chi$  increases across a period and decreases down a group. Thus it's somewhat intuitive that the increase in  $\chi$  going from  $\text{B} \rightarrow \text{C}$  is somewhat canceled out by the decrease going from  $\text{C} \rightarrow \text{Si}$ , leading to similar electronegativities between B and Si.

The answer is  $\boxed{C}$

48. The key here is to realize *where* the color comes from. Both  $\text{MnO}_4^-$  and  $\text{TcO}_4^-$  are  $d^0$  compounds - i.e. they have oxidation state equal to their valence: +7. Since there are no  $d$  electrons, the color doesn't come from d-d transitions, which cause the color in most transition metal complexes. In fact, the permanganate ion having tetrahedral geometry is intensely purple due to strong absorption involving charge transfer from MO derived primarily from filled oxygen p orbitals to empty MO derived from manganese(VII), which is called ligand to metal charge transfer (LMCT). These transitions are typically high in energy, but the stronger oxidizing power of Mn(VII) decreases this energy gap (it "wants" to take electrons more than Tc does), bringing the photon absorbed into the visible range.

The answer is  $\boxed{A}$

49. Let's draw Lewis structures for the compounds:

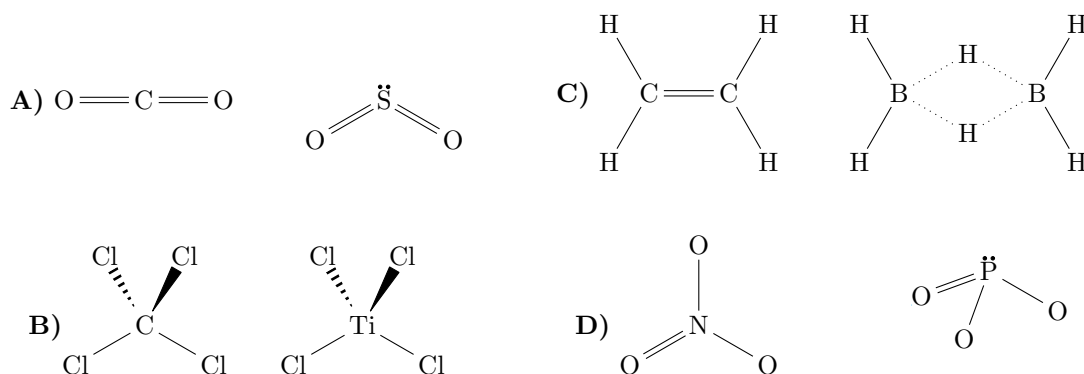


Looking at these resonance structures, we can see that the N – O bond order is  $1\frac{1}{3}$  in  $\text{NO}_3^-$ ,  $1\frac{1}{2}$  in  $\text{NO}_2^-$ , 2 in  $\text{NO}_2^+$ , and 3 in  $\text{NO}^+$ . A larger bond order corresponds to a stronger and shorter

bond, so  $\text{NO}_3^-$  has the longest bond.

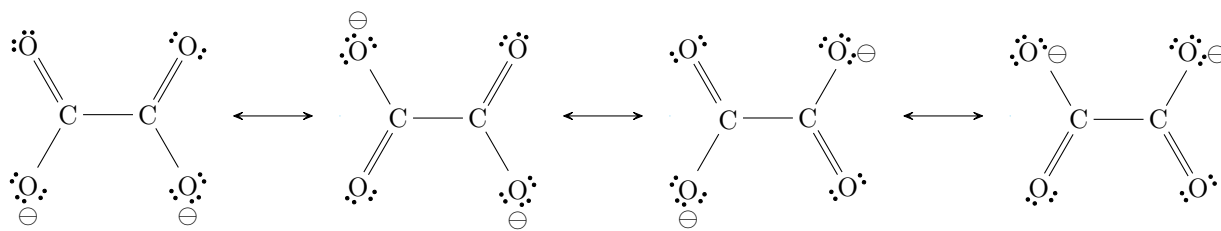
The answer is **A**.

50. Let's draw Lewis structures for all of these compounds:



The answer is **B**.

51. Each carboxylate group has two identical C–O bonds by resonance, and the carboxylates are identical by symmetry, so there's only one bond length. The full resonance structure is given below:



The answer is **A**.

52. Molecular orbitals form an "orthogonal basis" meaning that the net overlap of any two molecular orbitals must be zero. Thus *A* is correct. Explanations for the other answers follows:

B) Consider  $\text{N}_2$ . Its valence layer has a bonding-antibonding pair of sigma molecular orbitals, two degenerate bonding-antibonding pairs of pi orbitals. Each antibonding pi orbital has 2 nodal planes: one in the plane of the molecule and one bisecting the molecule. Thus, B is incorrect.

C) This is never true. The number of molecular orbitals is *always* equal to the number of constituent atomic orbitals. This is a consequence of the specific mathematical way in which molecular orbitals are constructed.

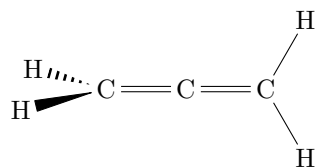
D) The opposite is true: bonding character equals low energy and antibonding character equals high energy in a molecular orbital pair.

The answer is **A**.

53. Recall that  $sp^3$  orbitals are  $109^\circ$  apart, while  $sp^2$  orbitals are  $120^\circ$  apart and  $sp$  orbitals are  $180^\circ$  apart. Thus greater *s* character explains the greater bond angle in  $\text{NF}_3$ . Other factors, like the greater electronegativity of N compared to P, provide auxiliary explanations that help us understand *why* the participation of *s* orbitals is different, but do not directly explain the bond angles.

The answer is **A**.

54. Recall that the two  $p$  orbitals of an  $sp$ -hybridized carbon are orthogonal (perpendicular to each other). Furthermore, the  $p$  orbital of an  $sp^2$ -hybridized carbon is perpendicular to the plane of the molecule. Since the two  $p$  orbitals of the central carbon are perpendicular, the planes formed by the end carbons must be perpendicular. Since the central carbon is  $sp$ -hybridized, it's linear. The structure of allene is drawn below:



The answer is  B .

55. For a molecule to be chiral, it must not have any improper rotation axes. However, we usually only need to check for the absence of reflection planes and inversion centers.

A), C), and D) there's a plane of symmetry perpendicular to the molecule running through the Cl atom and bisecting the bottom C-C bond.

B) There is no plane of symmetry. If you're confused about these kind of stereochemical problems, it's best to build a molecular model and see for yourself that the official answer is correct.

The answer is  B .

56. All four examples involve an acid-base extraction. To effectively separate the molecules, we need to completely deprotonate one without significantly deprotonating the other. The deprotonated molecule will then pass into the polar aqueous layer, while the relatively nonpolar neutral molecule will remain in the organic (diethyl ether) layer.

A) Water is not sufficiently basic to completely deprotonate benzoic acid, which has a  $pK_a$  of around 4.

B) Bicarbonate will completely deprotonate benzoic acid, as the  $pK_{a1}$  of  $H_2CO_3$  is  $\approx 7$ . However, it will not significantly deprotonate the other molecule, which is a phenol with an electron-withdrawing group, and so has a  $pK_a$  of approximately 7. This leads to good separation and yields and B is correct.

C) The very basic hydroxide ion will deprotonate both molecules, leading to very poor separation.

D) While the selective protonation of one compound does work in many cases, HCl is not sufficiently acidic to quantitatively protonate either molecule. For reference, the  $pK_a$  of HCl is approximately  $-7$ , while the  $pK_a$ s of protonated carbonyl groups and phenols are also around  $-7$ .

The answer is  B .

57. A) They are not structural isomers because their connectivity is the same. Each atom is connected (or not connected) to each other atom with the same numbers and kinds of bonds.

B) Each molecule has a mirror plane in the plane of the molecule. Thus they are achiral and cannot be mirror images of each other, so they are not enantiomers.

C) Because these molecules are stereoisomers (they differ in the spatial arrangement of atoms) but are not enantiomers, they are diastereomers, though they are typically specified as geometrical

isomers. C is correct.

D) There is no way to rotate one molecule so that it can be superimposed on the other molecule. The methyl groups in the (*Z*)-alkene will always be on opposite sides of the double bond, while the (*E*)-alkene will always have them on the same side. They are not identical molecules.

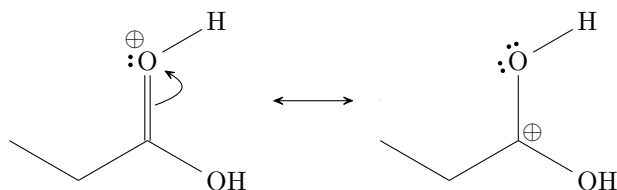
The answer is  C

58. A) Because the catalyst doesn't appear in the overall reaction, it cannot shift the position of equilibrium. Catalysts only help the reaction reach equilibrium more quickly.

B) There is no base produced in this reaction - only water. *If* the acid did serve that purpose, it *would* have appeared on the reactants side.

C) In general, electrophiles are (partially or completely) positively charged, while nucleophiles are (partially or completely) negatively charged. Thus protonation will not make a molecule more nucleophilic

D) This is correct. The acid catalyst protonates the ester on the carbonyl group, making it a better electrophile. The reactive electrophile is shown below:



The answer is  D .

59. The isoelectric point of a protein is mainly determined by its amine and carboxylic acid functionalities. Since the  $pK_a$  of an  $-\text{NH}_3^+$  group is around 9 while the  $pK_a$  of a carboxylic acid is around 4, the isoelectric point is somewhere in between 4 and 9, where the number of  $-\text{NH}_3^+$  groups equals the number of  $-\text{CO}_2^-$  groups. At this pH range, alkyl groups are neither significantly protonated nor deprotonated, so C) and D) would not have any effect on the isoelectric point.

Comparing the other two answers, we see that A) involves a transition from the neutral  $-\text{OH}$  group to the basic  $-\text{NH}_2$  group, while B) involves a transition from the basic  $-\text{NH}_2$  group to a neutral  $-\text{SCH}_3$  group. Thus A would have the greatest change on the isoelectric point of a protein.

The answer is  A

If this didn't make sense, try reading more information about the isoelectric point (pI) on your own, and then come back.

60. To solve this problem, we need to compare the positions (up or down) of the hydroxyl and hydroxymethyl groups on the two monosaccharides in each sugar carbon-by-carbon, except for the "anomeric carbon" (the one with *two* oxygens attached) which can have either configuration.

A) Starting at the anomeric carbon and working through the rest of the carbon skeleton, we see that the monosaccharide on the left has the configurations (going clockwise) "up-down-up-up-up," whereas the other sugar has the configuration (going counterclockwise) "down-up-down-up-down." Since we went in a different directions this time, we need to flip each configuration when we compare the two sugars to get "up-down-up-down-up." The two sugars do not have the same configurations, and A) is incorrect.

B) We will omit the detailed explanations for the rest of the answers and simply give the configurations. The left sugar is (going cw) "down-down-up-up-up," while the right sugar is (going cw) "up-down-up-down-up." They are not the same sugar, and B is incorrect.

C) The left sugar is (going ccw) "down-up-up-down-up" and the right sugar is (going cw) "up-down-up-down-up." They are not the same, and C is incorrect.

D) The left sugar is (going cw) "up-down-up-down-up" and the right sugar is (going ccw) "up-up-down-up-down." Flipping the (ccw) sugar's configurations gives "down-down-up-down-up." Even though the sugars differ on the carbon, its configuration doesn't actually matter since it's the anomeric carbon. Indeed, a solution of a pure monosaccharide will actually have both configurations at the anomeric carbon in a fixed ratio due to an equilibrium between the cyclic hemiacetal and linear ketone/aldehyde forms.

The answer is  D