Annotated Solution for USNCO National Exam 2022 Part I

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Question 1:

The first step to any stoichiometry problem is to write the balanced chemical equation. In this case, $Sr(s) + 2NH_3(l) = Sr(NH_2)_2(s) + H_2(g)$. We are given that Sr is the limiting reagent, and we can calculate that $0.125 \text{ g} / 87.62 \text{ g·mol}^{-1} = 0.00143$ mol Sr reacts. By the balanced chemical equation (1 mole Sr reacts to form 1 mol H_2) we get that 0.00143 moles of H_2 are produced. **B** is the answer.

If you are not sure about what is strontium amide, you may still figure out the stochiometric ratio of Sr and H_2 by knowing that each Sr loses two electrons during the reaction. Moreover, the amide here is the conjugate base (NH_2^-) of ammonia, which is different from the amide (-C(=O)–NH-) in organic chemistry.

Difficulty: Medium
Learning Objectives: stoichiometry

Question 2:

One strategy for this question is to go through each answer choice and verify the % arsenic by mass.

A) %As = $(1\times74.92) / (12.01 + 3 + 74.92 + 14.01) \times 100\% = 72.1\%$.

B) %As = $(1\times74.92) / (12.01\times2 + 6 + 74.92) = 71.4\%$.

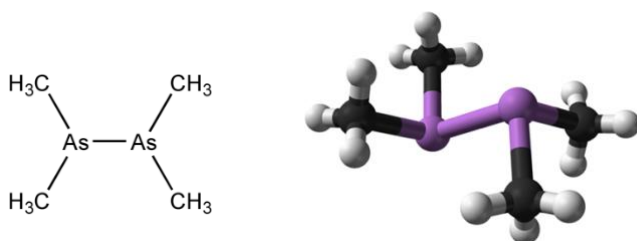C) %As = $(2\times74.92) / (12.01\times2 + 6 + 74.92\times2 + 14.01\times2) = 72.1\%$

D) %As = $(2\times74.92) / (12.01\times4 + 12 + 74.92\times2) = 71.4\%$

We are between B and D for the correct answer, and it comes down to whether each compound is para or diamagnetic. Typically, MO theory is preferred for issues of magnetism, but since each of these compounds is relatively complex, we will use Lewis structures instead. Drawing the Lewis structure of each molecule, we notice that 3 unbonded electrons are found on the central As in the Lewis structure for C_2H_6As. This means that one unpaired electron exists in compound B and B is paramagnetic. No radical electrons exist on compound D. **D** is thus our answer since it has the right %As and is also diamagnetic. You may interpret $C_4H_{12}As_2$ as the dimer of C_2H_6As, which pair the single electron on As through the dimerization.

The compound $C_4H_{12}As_2$ is actually called cacodyl, or tetramethyldiarsine with the structure and geometry shown below.

Difficulty: Hard
Learning Objectives: mass percent and empirical formula; paramagnetic vs diamagnetic; prediction of unpaired electron(s)

Source: Wikipedia

Difficulty: Medium

Learning Objectives: stoichiometry; limiting reactant; graph reading

Question 3:

Let us go through each answer choice.

A) A seems reasonable. When only 1.00 g of Fe was added, the graph is still upward sloping meaning adding more Fe would increase product yield. This implies that Br_2 is still present in the system and Fe is limiting.

B) From the graph, we can easily see that 10.6 g product is obtained when 2.00 g of Fe is added. If $FeBr_2$ is the product, let's check the stoichiometry, $2.00 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g}} \times \frac{1 \text{ mol FeBr}_2}{1 \text{ mol Fe}} \times \frac{(55.85+77.90\times2) \text{ g}}{1 \text{ mol FeBr}_2} = 7.72$ g. This is not 10.6 g, thus answer choice B is incorrect. The product is actually $FeBr_3$, which is reasonable as Br_2 is a strong oxidant and oxidizes Fe(s) to a higher oxidation state.

C) Looking at the graph, when 2.50 g of Fe are added, this is already well into the flat region of the graph (the vertex exists when 2.00 g of Fe are added). The flat region means that adding additional Fe here will not produce any more product because no more bromine is left to react (Br_2 is the limiting reagent). Adding any more Fe past 2.00 g will be in excess, thus an excess 0.50 g Fe exists when 2.50 g Fe is added. C is incorrect.

D) Once again looking at the graph, 3.50 g added Fe also is in the flat region where Br_2 is the limiting reagent. D is clearly incorrect.

A is thus our answer.

Note: The chemical equation is Fe(s) + 3/2 Br_2(l) = $FeBr_3$(s).

Difficulty: Medium

Learning Objectives: stoichiometry; mixture analysis

Question 4:

We know the masses of Cu_2S and CuS in the ore must add to 89.0 g. We also know that there must be in total 67.5 g / 63.55 g·mol^{-1} = 1.06 moles of copper total between Cu_2S and CuS. Calling the moles of Cu_2S x and the moles of CuS y, we can set up the following system of equations.

$$2x + y = 1.06 \text{ (balancing the number of moles of copper)}$$
$$(63.55\times2 + 32.07)x + (63.55 + 32.07)y = 89.0 \text{ (balancing mass)}$$

Solving the system gives us $y = 0.290$ mol of CuS, multiplying that by the molar mass of (63.55+32.0) g·mol^{-1} gives us 27.7 g of CuS, approximately **B.**

You may set up the mass of each compound and use the Cu% in each to obtain a similar system of equations.

Difficulty: Medium

Learning Objectives: solution stoichiometry

Question 5:

This is a simple stoichiometry problem, although it may look complicated. We know that there are 0.02123 L × 0.0235 M = 4.98×10^{-4} mol $S_2O_3^{2-}$ added. Since I_3^- and $S_2O_3^{2-}$ react in a 1:2 ratio (by the 2nd equation), we know that there must be 4.98×10^{-4} /2 = 2.49 × 10^{-4} mol I_3^-. Now looking at the first equation, 1 mol of I_3^- forms when 1 mol OCl$^-$ reacts. Thus, the 2.49×10^{-4} mol OCl$^-$ react and are present in the bleach sample. To find the concentration of hypochlorite, we divide 2.49×10^{-4} by the volume of 0.0750 to get a concentration of 0.00332 M, or **C.**

Question 6:

This question tests your understanding of colligative properties. The boiling point elevation is directly proportional to the number of particles in solution. We can rank the boiling points of each aqueous solution by taking the product of the salt concentration and the number of ions formed per formula unit of salt dissolving.

A. 0.10×4 ions ($3\ Na^+$ and $1\ PO_4^{3-}$) $= 0.40$

B. 0.30×3 ions ($2\ Na^+$ and $1\ HPO_4^{2-}$) $= 0.90$

C. 0.50×2 ions ($1\ Na^+$ and $1\ H_2PO_4^-$) $= 1.00$

D. $0.70 \times$ appx. 1 "particle" (H_3PO_4 does not fully ionize) $= 0.70$

Though H_3PO_4 is triprotic, even the first dissociation is very limited as indicated by a small K_{a1} value, similarly, the dissociation of HPO_4^{2-} and $H_2PO_4^-$ is more negligible.

C forms the greatest number of particles and thus **C** has the highest boiling point.

(For those wanting the mathematical explanation, $\Delta T = imK_b$. i represents the number of ions formed per formula unit of salt, m is the molality of the salt, and K_b is a constant that depends on the solvent identity. K_b is constant for all the answer choices since the solvent is water for all trials. We can approximate molality using molarity for a dilute aqueous solution since 1 L of solution typically uses very close to 1 kg of solvent.)

Question 7:

Flame test colors for IA and IIA metals should be memorized. Al does not have a clear flame test, B is green typically, Na is bright yellow, and Sr is red. **D** is our answer.

Question 8:

A) Chlorine is more reactive than Bromine and thus the Br_2 cannot reduce and displace Cl^-. Looking at a reduction potential table, indeed Cl_2 has a more positive reduction potential than Br_2. No reaction and thus no color change occurs.

B) The chemical reaction that occurs is $CO_3^{2-}(aq) + 2H^+(aq) = H_2O(l) + CO_2(g)$. None of the reactants or products are colored, thus no color change occurs.

C) A complexation reaction occurs $3C_2O_4^{2-}(aq) + Fe^{3+}(aq) = [Fe(C_2O_4)_3]^{3-}(aq)$. Complex ion reactions often involve color changes. Even if you didn't know that trioxalatoferrate(III) is green (compared to the yellow Fe^{3+} ion in the reactants and colorless oxalate ion), you could guess **C** is the correct answer.

D) No reaction occurs for this answer choice and no color change occurs. Note that Co^{2+} is a pink ion in solution.

Question 9:

Three elements are known to form protective oxide coatings: Al, Si, and Cr. **A** is aluminum and the correct answer. We can eliminate the other answer choices since B) and D) are alkaline earth metals and oxidize to form oxides in air, which further reacts with water and CO_2 from the air, and C) is iron which is known to rust by oxidizing in air (in the presence of water).

Difficulty: Medium

Learning Objectives: colligative properties of solutions; dissociation of strong and weak electrolytes

Question 10:

Determining the number of components in a mixture is best done by chromatography. Boiling point determination does not tell us the number of compounds in a mixture if the boiling points of the components are relative close. Combustion analysis is typically used to identify the empirical formula of a sample, this will not tell us the number of compounds in a mixture. In this case, nail polish remover consists of many volatile organic compounds, such as acetone. Since they vaporize at low temperatures, gas chromatography is preferred to paper chromatography (works best for non–volatile and colored species such as dyes). **A** is the answer.

Difficulty: Hard

Learning Objectives: solubility rules; HSAB theory

Question 11:

Knowing solubility rules, we can eliminate A and D since alkaline earth metal sulfides tend to be soluble. If you are familiar with the cation qualitative separation scheme, you know that CdS precipitates out in acidic conditions while MnS only precipitates out once base is added. **C**

You may use **hard-soft acid-base (HSAB)** theory to get a more detailed understanding of this problem. Here the annotation to a similar problem in Local 2018 (Q8) is quoted with minor revision for your reference:

According to hard-soft acid-base theory (HSAB), hard acids bind strongly with hard bases, soft acids bind strongly with soft bases. The order of the hardness of the four cations from hard to soft is $Ba^{2+} > Ca^{2+} > Mn^{2+} > Cd^{2+}$, as higher charged and smaller sized cations are harder Lewis acids; more electronegative, lower charged, and smaller sized anions are harder Lewis bases. S^{2-}, less electronegative, larger in size, is a typical soft base, which binds strongly with soft acids and binds weakly with hard acids. So CdS, a soft acid-soft base combination, has the strongest binding affinity and the lowest solubility in water. Therefore, CdS is the only sulfide precipitate here which is not soluble even in strong acids.

In general, metal sulfide precipitates tend to be more soluble in acid as the formation of the weak electrolyte H_2S, indicated by $MS(s) + 2H^+(aq) \rightarrow M^{2+}(aq) + H_2S(aq)$. So, if the precipitate has a smaller K_{sp} (less soluble), it is harder to dissolve in both water and in acid.

Difficulty: Hard

Learning Objectives: laboratory and error analysis; ideal gas law; partial pressure of water vapor

Question 12:

Let us write a skeleton equation for the reaction: $M(s) + H_2SO_4(aq) = MSO_4(aq) + H_2(g)$. The collection of gas over water is an essential laboratory technique. A reaction occurs in a water through such that the gasses produced are collected in a flask or graduated cylinder. Their volume is determined and, by using the ideal gas law, the number of moles of gas produced can be calculated. $P(H_2)$ for the ideal gas law is calculated by subtracting the vapor pressure of water from the atmospheric pressure. Checking each answer choice:

A) This will cause no effect. Firstly, if you accurately take into account the new concentration of sulfuric acid your calculations still should be accurate. Secondly, the reaction likely will occur with sulfuric acid in excess, so the number of moles of sulfuric acid truly does not matter for the calculation.

B) Since M is oxidized in the reaction, replacing some M with its already oxidized form will effectively reduce the number of moles of M in the reaction. Less moles of gas will be produced with less M reactant, making the calculated number of moles of M also decrease. Since the mass of "M" (including the oxide) is weighed to be the same, the molar mass will be too high. **B** is the answer.

C) This makes the pressure in the ideal gas law artificially high; since pressure is directly proportional to moles, the number of moles of H_2 calculated will also be artificially high. By the balanced equation, this also makes the calculated number of moles of M too high while keeping the measured mass of M the same. This makes the calculated molar mass of M too low.

D) The vapor pressure must be subtracted from the atmospheric pressure to find $P(H_2)$ used in the ideal gas law; not subtracting the vapor pressure will make $P(H_2)$ artificially high. Just like in answer choice C, this results in a too high calculated number of moles of M, making the calculated molar mass too low.

Question 13:

A) Using the Ideal Gas Law, we can find the initial moles of Ar as 1.0 L × 1.00 atm ÷ (0.08206 L atm / mol K × 298 K) = 0.0409 mol and the initial moles of Kr as 2.0 L × 0.5 atm ÷ (0.08206 L atm / mol K × 298 K) = 0.0409 mol. We know the total volume of the system with the open stopcock is 1.0 + 2.0 = 3.0 L, and that the total number of moles is 0.0409 × 2 = 0.0818 mol. Using the ideal gas law, we can find the final pressure as $P = nRT/V$ = 0.0818 × 0.08206 × 298 / 3.00 = 0.666 atm. This is not 1.00 atm, thus A is incorrect.

B) We calculated that the total number of moles of each gas is equal, thus B seems correct. However, we must be careful with this answer. We know the moles of Ar and Kr in the whole system are equal, but we cannot know how these moles are distributed (in the 2.0 L container or the connected 1.0 L container). B is a trick answer. The number of moles of Ar in the 2.0-L container is supposed to be 2/3 of the total moles of Ar, while the number of moles of Kr in the 1.0-L container is 1/3 of the total moles of Kr.

C) The average speed is dependent on temperature and molar mass. $u_{rms} = 3RT/M$. Both gasses are at the same T but have different molar masses, thus their average speed (represented by the root mean squared velocity, u_{rms}) cannot be equal.

D) From our last calculation, we know this is correct. Since $P = nRT/V$, equal number of moles of each gas indicate that each gas has the same partial pressure. **D** is the answer.

Question 14:

Carbon and Bromine have an electronegativity difference, yet it isn't very much. By Pauling's electronegativity scale, Carbon and Bromine differ in electronegativity only by 0.3. Both CH_2Br_2 and $CHBr_3$ are polar molecules, but since the electronegativity difference is slim the charge separation is also slim. Thus, both molecules do not have strong dipole–dipole interactions. Clearly, hydrogen bonding does not occur since there is no O–H, F–H, or N–H very polar bond. Additionally, we know both molecules do not have long range covalent bonds (they are molecular compounds held together

by intermolecular forces); thus, D does not make sense as an answer. The only valid option is London Dispersion Force differences, or **A**. Bromine is a very polarizable atom, and replacing H by Br adds 34 electrons. The electron cloud of $CHBr_3$ is much larger and more polarizable than CH_2Br_2, thus London Dispersion Force differences would significantly increase the boiling point of $CHBr_3$ compared to CH_2Br_2.

Difficulty: Hard

Learning Objectives: states of matter; phase diagram

Question 15:

There are two possibilities for this phase diagram. The slope of the solid–liquid boundary can be either positive or negative.

A) This is accurate. In either scenario if the pressure is below the Triple Point Pressure, the solid–liquid line does not extend to this pressure. The only boundary is between solid and gas, thus increasing the temperature will sublime the solid to a gas. **A** is the answer.

B) The relative densities of the solid and liquid state depend on the slope of the solid–liquid boundary line. Whichever state is favored at the higher pressure will be denser. Since we do not know the slope of the solid–liquid boundary, we cannot identify which state is denser.

C) At 193 K (slightly higher than the triple point temperature), in the bottom figure with a negative solid–liquid boundary slope, solid is not thermodynamically stable at 193 K. ×However, if the solid–liquid slope is positive (top diagram), the solid state is thermodynamically stable at high pressure. Once again, this statement depends on the sign of the slope, which we are not given.

D) This is clearly incorrect. The pressure can be any number and so can the temperature.

Difficulty: Hard

Learning Objectives: ideal gas law; the deviation of real gases

Question 16:

Intuitive Solution: What affects the volume of a real gas that makes it deviate from ideal nature? Intermolecular forces and molecular size. Molecular size stays constant; thus, we consider changes in intermolecular force strength when evaluating the answer choices below.

I. When you heat a gas, the gas molecules move more rapidly and escape the attractive intermolecular forces that tie them closer with other molecules. As a result of the lower intermolecular forces at higher temperature, the volume of the real gas should more than double when doubling the temperature at constant pressure. Thus, statement I is correct.

II. When gasses are at high pressure, they collide often with the walls of the container and with each other. The molecules are packed close together, thus, they experience significant intermolecular forces with their neighbors. When the gas pressure decreases and the volume expands, once again the gas molecules are no longer close to each other, and their intermolecular forces decrease. This further decreases the attraction between the molecules and increases the volume the molecules occupy – making the volume more than double when pressure is halved. Thus, statement II is correct.

C is thus our answer.

Technical Solution: This question relies on the idea of the compressibility factor for a real gas, Z. The compressibility factor quantifies a gas's deviation from ideal nature (ideal gas has $Z = 1$) and is defined as $Z = PV/nRT$. As the graphs below show, Z typically decreases with increasing pressure when P is

less than ~100 atm and increases with higher temperature. Statement I has an increase in temperature, meaning Z will decrease during this process. If the gas were ideal, V would double, but since Z increases, V will increase by more than a factor of 2. Statement I is correct. Statement II has a decrease in pressure with a very small P (far left of the top graph), thus this will increase Z. In this case V will increase by more than a factor of two. Statement II is also correct; thus, **C** is the correct answer.
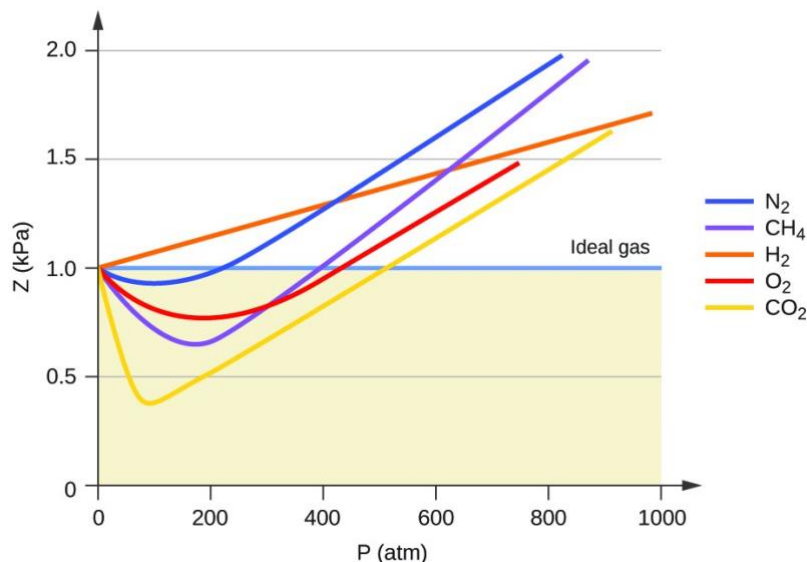
[Source: Lumen Learning]
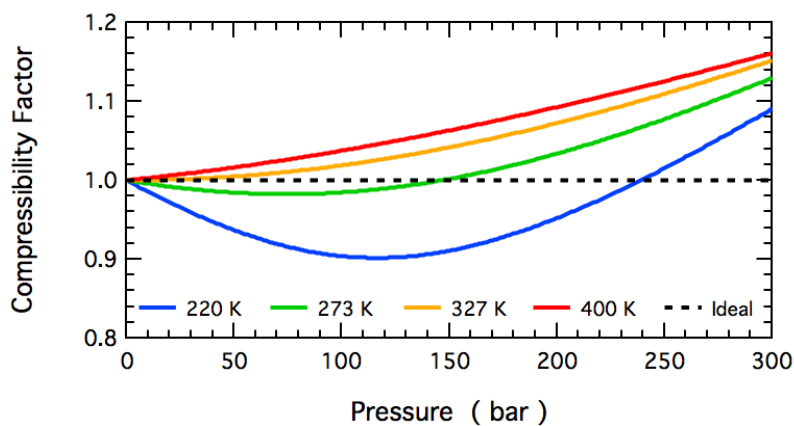

Source: Chemistry Stack Exchange

Question 17:

This problem is typical and challenging in the recent years of USNCO, which is about the best explanation of an unexpected experimental result. An equimolar mixture of C_6H_6 and C_6F_6 melts **sharply** at 23.7 °C, which is higher than the melting points of both. Choice A and C can be easily eliminated, the two reasonable explanations are (B) C_6H_6 and C_6F_6 form a crystal containing equal amounts of the two substances, and (D) The enthalpy of mixing of C_6H_6 and C_6F_6 is negative. If the mixing is exothermic, which means the interaction between C_6H_6 and C_6F_6 is stronger than that among C_6H_6 molecules and that among C_6F_6 molecules, the mixture is expected to melt at a higher temperature. However, this explanation can't explain the keyword "sharply", as it is a mixture which

Difficulty: **Hard**

Learning Objectives:

melting point of mixtures

typically has a melting range rather than a sharp melting point, thus, D is not the best explanation. Let's check out B, if C_6H_6 and C_6F_6 form a crystal, which is a new compound with a stronger interaction, the melting point is expected to be higher and sharp. If we go further to think about why and how the two compounds can form a crystal, we may realize that benzene is electron–rich with the delocalized pi system, while C_6F_6 is electron–deficient as the six more electronegative fluorines attract the electrons from the benzene ring, making it positive. So, it is reasonable to predict the two ring structures can stack together to form an adduct through the electrostatic interaction in a 1:1 molar ratio. Thus, the correct answer is **B**.

The above analysis is also confirmed by the reference: Williams, J. H.; Cockcroft, J. K.; Fitch, A. N. *Angew. Chem., Int. Ed.* **1992**, 31, 1655. A diagram is shown below for the readers to get a better understanding.
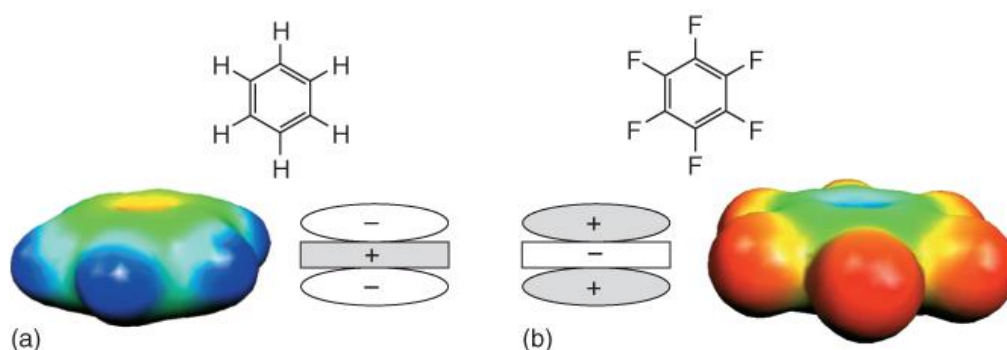
Source: Peer Kirsch, Modern Fluoroorganic Chemistry – Synthesis, Reactivity, Applications Second, Completely Revised and Enlarged Edition

Difficulty: Easy

Learning Objectives: solid models; coordination number

Question 18:

A nearest neighbor in a crystal structure is simply the atoms most closely surrounding another atom. In the case of atoms of type C (edge center), they are most closely surrounded by 2 atoms of B in a linear fashion (the B atoms are directly adjacent to C on either side of it). Other A and C atoms are further away. As a result, **A** is the answer.

Difficulty: Medium

Learning Objectives: heat and work; entropy and temperature

Question 19:

I) Work is defined as – external pressure times change in volume. $w = -P\Delta V$. By definition, if the volume of the balloon changes by deflation, work is done by the surroundings (nitrogen) on the system (balloon). This is the case because ΔV is negative, making work positive (positive work is work done on the system). Statement I is correct.

II) Entropy for a gas increases as temperature increases because the molecules of the gas are more disordered (thermal entropy). When the balloon is immersed in very cold liquid nitrogen, heat will flow away from the balloon and into the nitrogen surroundings. The nitrogen will heat up as a result, making nitrogen's entropy increase. Statement II is correct.

Thus, **C** is the correct answer.

Question 20:

Assume we have 1 L = 1000 g of water. For the heat of the water to increase by 1.0 degree Celsius (from 25. 0 to 26.0 °C), $q = mc\Delta T$ = 1000 g × 4.18 J / g °C × 1.0 °C = 4180 J. (We assume the mass of the solution does not change since its density and volume remain constant). The dissolution of KOH provides this heat. Each mole of KOH dissolving releases 57600 J, thus we need 4180/57600 = 0.0726 moles of KOH. The concentration of OH^- at the final state is 0.0726 mol / 1 L = 0.0726 M. pOH = –log[OH^-] = 1.14. pH = 14 – pOH = 12.9. **D**

Question 21:

Write the reaction of the formation of ClF_3 (g): $3/2F_2(g) + 1/2Cl_2(g) = ClF_3(g)$

$$\Delta H^o{}_f = -158.9 \text{ kJ/mol}$$

$$\Delta S^o{}_f = S^o{}_m[ClF_3(g)] - 1/2\ S^o{}_m[Cl_2(g)] - 3/2\ S^o{}_m[F_2(g)]$$

$$= 281.6 - 1/2 \times 223.1 - 3/2 \times 202.8$$

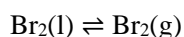$$= -134.15 \text{ J/molK}$$

$$\Delta G^o{}_f = \Delta H^o{}_f - T\Delta S^o{}_f = -158.9 \times 1000 \text{ J} - 298 \text{ K} \times (-134.15) \text{ J / mol K}$$

$$= -118900 \text{ J/mol} = -118.9 \text{ kJ/mol}$$

C

Question 22:

At the triple point, the liquid and vapor phases are in equilibrium.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

$$\Delta G^o{}_{vap} = -RT\ln K = -RT\ln P[Br_2(g)] = -8.314 \times 265.9 \times \ln(0.058) = 6300 \text{ J/mol}$$

$$\Delta G^o{}_{vap} = 6300 \text{ J/mol} = \Delta H^o{}_{vap} - T\Delta S^o{}_{vap} = \Delta H^o{}_{vap} - 265.9 \times 89.0$$

$$\Delta H^o{}_{vap} = 30.0 \text{ kJ/mol}$$

D

Note: A common misconception for this problem is to interpret the $\Delta G^o{}_{vap} = 0$ at 265.9 K and 0.058 bar as the liquid and vapor phases are in equilibrium, then a wrong value of $\Delta H^o{}_{vap} = T\Delta S^o{}_{vap} = 265.9 \times 89.0 = 23.7$ kJ/mol, is obtained. Please be aware the difference between ΔG^o and ΔG. At equilibrium state, $\Delta G = 0$, however, ΔG^o is not necessary to be 0 unless the equilibrium constant $K = 1$. Back to this problem, 0.058 bar is not standard pressure, in another word, the equilibrium temperature of the liquid and vapor phases at standard state (1 bar) is NOT 265.9 K. So, another way to solve this problem is to combine Clausius-Clapeyron equation with the normal boiling point T_b and $\Delta G^o = \Delta H^o - T\Delta S^o = 0$ at standard state, as shown below.

$$\ln \frac{1 \text{ bar}}{0.058 \text{ bar}} = -\frac{\Delta H^o_{vap}}{8.314} \times \left(\frac{1}{T_b} - \frac{1}{265.9}\right)$$

$$\Delta H^o_{vap} - T_b\Delta S^o_{vap} = \Delta H^o_{vap} - T_b \times 89.0 = \Delta G^o_{vap} = 0$$

Solving the system of equations gives us the same results of $\Delta H^o{}_{vap} = 30.0$ kJ/mol, as well as $T_b = 337.1$ K.

Difficulty: Hard

Learning Objectives:
intermolecular forces;
hydrogen bonding; entropy
change of vaporization

Question 23:

This question is fundamentally one about intermolecular forces. Straight chain alkanes only are held together by London forces, while primary alcohols are held together by London forces as well as dipole interactions and hydrogen–bonding. In general, permanent dipole and hydrogen–bonding interactions are stronger than London forces – breaking these strong, stabilizing interactions during the vaporization process heavily increases the system disorder, thus the standard entropy of vaporization of alcohols is expected to be consistently higher than those of alkanes of the same molar mass. Furthermore, the alcohol is still expected to have an upward (positive) slope, since its London forces will increase when the molar mass increases, similar to the alkane – thus causing more "stability" to be lost when vaporizing. **A** is the graph best fitting these deductions.

Extension: Another interesting fact to point out is that the gap between the two trend lines is getting larger as the molar mass increases. How to explain that?

For short chain alcohols, each individual molecule can align in many different orientations since the overall interactions in the liquid are dominated by hydrogen bonding. However, in longer chain alcohols, in the liquid form the molecules tend to arrange all in the same direction with the hydrophobic hydrocarbon region on one side and the hydrogen bonding alcohol groups on the other side. This additional order that is removed when the liquid vaporizes will increase the ΔS_{vap} of the longer chain alcohols in comparison to simply the alkanes. This explains why the gap between the two lines increases as molar mass increases.

[Note: A common mistake on this problem is a misapplication of Trouton's Rule, which states that the standard molar entropy of vaporization of liquids is always around 88 J/mol K. However, this does not apply to hydrogen bonding liquids – a heavy limitation that prevents its application for alcohols].

Difficulty: Hard

Learning Objectives:
van't Hoff equation; K_{sp} vs
molar solubility;
interpretation of graphs

Question 24:

The graph is based on the concept of van't Hoff equation, which states that $\ln(K_2/K_1) = -(\Delta H^o_{rxn}/R) \times (1/T_2 - 1/T_1)$. This can be rewritten as

$$\ln(K) = -\frac{\Delta H^o_{rxn}}{R} \times \left(\frac{1}{T}\right) + C \quad (1)$$

with C being a constant. The x–axis of the graph does show $1/T$, however the y axis shows ln(molar solubility) instead of $\ln(K)$. In $NaIO_3$, there are two ions formed. The K_{sp} expression would thus be $K_{sp} = [Na^+][IO_3^-]$ or S^2 by mass balance. Thus, K is the square of the molar solubility. Taking the ln of both sides, we get that $\ln(K_{sp}) = \ln(S^2) = 2\ln(S)$ by exponent rules. We can thus rewrite expression (1) as
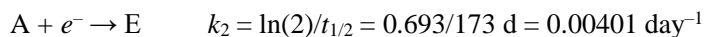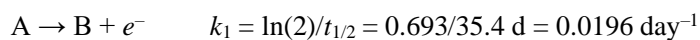
$$2\ln(S) = -\frac{\Delta H^o_{rxn}}{R} \times \left(\frac{1}{T}\right) + C$$

$$\ln(S) = -\frac{\Delta H^o_{rxn}}{2R} \times \left(\frac{1}{T}\right) + C' \quad (2)$$

We now know that the slope between $\ln(S)$ and $1/T$ is $-(\Delta H^o_{rxn}/2R)$. Since the slope given to us is -2088, we multiply this by $-2R = -2(8.314)$ to get ΔH^o_{rxn} to be equal to 34720 J/mol, or **D.**

Question 25:

This question requires logical thinking. Let us call the actinium isotope A, the *beta* decay product B, and the electron capture product E. Note that nuclear decays are first ordered processes.

$$A \rightarrow B + e^- \qquad k_1 = \ln(2)/t_{1/2} = 0.693/35.4 \text{ d} = 0.0196 \text{ day}^{-1}$$
$$A + e^- \rightarrow E \qquad k_2 = \ln(2)/t_{1/2} = 0.693/173 \text{ d} = 0.00401 \text{ day}^{-1}$$

The rate constants sum for the overall rate of A's decomposition. This is intuitive but is also supported with proof. As a result, the overall rate constant k_{total} for A's decomposition is $0.0196 + 0.00401$ day^{-1} = 0.0236 day^{-1}. The overall half-life is $t_{1/2} = \ln(2)/k_{total} = 0.693/0.236$ day^{-1} = 29.4 d. **A.** *Intuitively this makes sense. The half-life of the overall decomposition of A must be smaller than the half-lives of each individual nuclear reaction.*

Question 26:

This is a classic differential rate law question. Between trials 1 and 2, [NO$_2$] is kept constant while [CO] doubles. However, the initial rate does not change implying 0th order rate dependence on [CO]. Between trials 2 and 3, [CO] is kept constant while [NO$_2$] triples (pay attention to the exponents). The initial rate increases by a factor of 9, or 3^2, implying 2nd order dependence on [NO$_2$]. The overall rate law must be Rate = k[NO$_2$]^2. **B.**

Question 27:

This is a fundamental conceptual question. The activation energy is the energy required in a molecular collision for a reaction to occur and progress to the transition state.

A. This is the opposite. Catalysts decrease the activation energy by providing a different mechanism. The decrease in activation energy allows catalysts to speed up reaction rates.

B. Activation energy does not depend on temperature. Temperature changes increase or decrease the probability a collision exceeds the activation energy barrier but will not change the barrier itself.

C. **This is the correct answer.** However, if you did not know this fact previously, the process of elimination is the best way to decide the correct answer. The overall activation energy of a process is determined based on the energy difference from the highest transition state and the reactants. Intermediates, almost always higher in energy than the reactants will never be higher in energy than the highest transition state (remember intermediates are local minima on a reaction coordinate while transition states are local maxima). Thus, the reactant is closer in energy to the intermediate than the highest transition state, making the energy change for the formation of an intermediate less than the activation energy of the process.

D. Clearly this does not make sense. Very few reactions have negative activation energies, but many exothermic reactions exist (with positive activation energies).
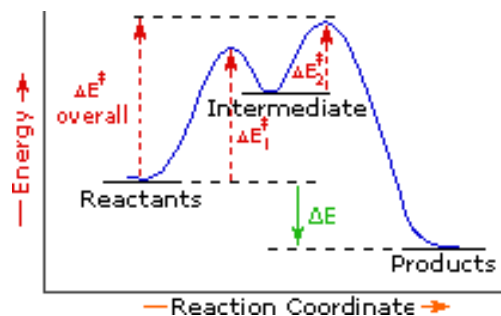
Source: LibreTexts

Question 28:

The fading of crystal violet experiment is a common AP chemistry lab. This question relies on the knowledge that crystal violet is colored (violet, as you would expect) and sodium hydroxide is colorless.

I. This is correct. As the crystal violet reacts the violet color should disappear. A linear slope between ln(*absorbance*) and time implies first order dependence on crystal violet, the colored species in solution. The presence of excess NaOH ensures the concentration of NaOH doesn't change with time, which is crucial for pseudo kinetic analysis.

II. This is incorrect. The experiment never varied the concentration of hydroxide and measured how the hydroxide concentration affected the rate law.

A is the correct answer.

Question 29:

The wording of the question is confusing, but essentially it asks, "which reaction diagram has the reaction reach equilibrium the fastest." We can immediately eliminate C and D. These two mechanisms have high activation energies and thus their reactions would go slowly. Deciding between A and B is trickier. In mechanism A, the equilibrium heavily favors P due to the strongly exergonic ΔG^o. The concentration of P at equilibrium state would be very high. On the contrary, mechanism B does not have very high concentrations of products as ΔG^o is barely negative. This, paired with the important fact that both reactions, regardless of equilibrium position, proceed at the same rate since their activation energies are the same, indicates **B** as the mechanism that would reach equilibrium first. Another way to interpret this is the similar activation energies of forward and backward reaction in choice B, which implies a faster rate to reach equilibrium.

This concept is similar to that of kinetic vs thermodynamic control of reactions. Only thermodynamics (ΔG^o) governs where equilibrium lies, and only kinetics (activation energy) governs the reaction rate. I encourage you to research more on this.

Question 30:

By inspection of the graph, we identify that increasing [B] increases the initial rate significantly when [B] is low, but barely any when [B] is high. This should remind you of enzyme kinetics (Michaelis–Menten), the rate increases with the concentration of the substrate when the substrate is low in concentration, while it levels off when the concentration gets higher as all binding sites of the enzyme are occupied by the excess substrate. We expect that the rate law of this mechanism will not be linear, but instead be in a form similar to Rate = k[B]/C+[B], C is a constant here. (This equation has linear dependence of Rate and [B] when [B] is low but no dependence on [B] when [B] is high). We then proceed through the answer choices and write rate laws consistent with each proposed mechanism.

A) First, let us write out the balanced equations.

$$A \rightleftharpoons I \quad (k_1, k_{-1})$$

$$I + B \rightarrow P \quad (k_2)$$
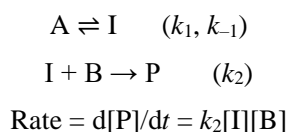
$$\text{Rate} = d[P]/dt = k_2[I][B]$$

Using steady state approximation for intermediate I,

$$d[I]/dt = k_1[A] - k_{-1}[I] - k_2[I][B]$$

$$[I] = \frac{k_1[A]}{k_{-1} + k_2[B]}$$

$$\text{Rate} = d[P]/dt = \frac{k_1 k_2[A][B]}{k_{-1} + k_2[B]}$$

Since [A] is a constant, we notice that this mechanism DOES follow the skeleton rate law we proposed above. Changes in [B] only affect the rate at low concentrations of [B]. **A is the correct answer.**
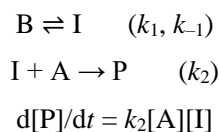
B)

$$A \rightleftharpoons I \quad (k_1, k_{-1})$$

$$I + 2B \rightarrow P \quad (k_2)$$

$$d[P]/dt = k_2[B]^2[I]$$
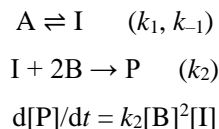
Using steady state approximation for intermediate I,

$$d[I]/dt = k_1[A] - k_{-1}[I] - k_2[I][B]^2$$

$$[I] = \frac{k_1[A]}{k_{-1} + k_2[B]^2}$$

$$\text{Rate} = d[P]/dt = \frac{k_1 k_2[A][B]^2}{k_{-1} + k_2[B]^2}$$

Unlike answer choice A, this rate law would not produce the desired graph. This graph would have a region of concave up (quadratic) dependence of rate on [B] when [B] is low; the graph shown in the problem appears linear and not quadratic at low [B] concentrations.

C)

$$B \rightleftharpoons I \quad (k_1, k_{-1})$$

$$I + A \rightarrow P \quad (k_2)$$

$$d[P]/dt = k_2[A][I]$$

Using steady state approximation for intermediate I,

$$d[I]/dt = k_1[B] - k_{-1}[I] - k_2[I][A] = 0$$

$$[I] = k_1[B]/k_{-1} + k_2[A]$$

$$[I] = \frac{k_1[B]}{k_{-1} + k_2[A]}$$

$$Rate = d[P]/dt = \frac{k_1 k_2 [A][B]}{k_{-1} + k_2 [A]}$$

This has the proto Michaelis–Menten relationship for [A], whereas the graph shows such a relationship for [B].

D) D has the same problem as C)

Intuitively, without deriving the rate law for each choice, we can see that the function of B in choice A is more similar to that of the substrate in the enzyme kinetics, in another words, rate increases with [B] when [B] is small but will be limited by [I] when [B] is getting high.

Difficulty: Medium

Learning Objectives: K calculation with the RICE table method

Question 31:

Firstly, by Dalton's law we know that if the mixture is equimolar there exists 1.00 bar of both CO and H_2. Addition of the catalyst is irrelevant to the equilibrium position. We then set up an RICE table.

R	CO	+	2 H$_2$	⇌	CH$_3$OH
I	1.00 bar		1.00 bar		0
C	$-x$		$-2x$		$+x$
E	1.00$-x$		1.00$-2x$		x

Total pressure = 1.29 bar = $1.00 - x + 1.00 - 2x + x = 2.00 - 2x \rightarrow x = 0.355$ bar

$K_p = x(1.00-2x)^2/(1.00-x) = 0.355 \times 0.2902 / 0.645 = 6.54$. **B**

Difficulty: Medium

Learning Objectives: acid ionization equilibrium; K_a of acids, percent ionization

Question 32:

The first step is to use the data given to calculate K_a.

$K_a = [H^+][A^-]/[HA] = (0.038 \times 0.10)^2 / (0.10 - 0.038 \times 0.10) = 1.5 \times 10^{-4}$.

We then use this K_a for the new concentration of acid.

$K_a = 1.5 \times 10^{-4} = [H^+][A^-]/[HA] = x^2 / (0.50-x) \approx x^2 / 0.50 \rightarrow x = 0.0087$ (<5% of 0.50, assumption valid)

$\%I = 0.0087/0.50 \times 100\% = 1.7\%$ **A**

Moreover, the calculation result is consistent with the Le Chatelier prediction, diluting the solution of a weak acid shifts the ionization equilibrium to the right side. In another words, the more diluted the weak acid is, the higher the degree of ionization is.

Question 33:

The key point of this problem is that adding a significant volume of sodium chromate will dilute both itself and the barium solution.

Let V be the added chromate volume.

$$K_{sp} = 1.2 \times 10^{-10} = [Ba^{2+}][CrO_4^{2-}] = [1.5 \times 10^{-5}\ M \times 1.0\ L/(1.0 + V)]^2$$
$$(1.5 \times 10^{-5}\ M \times 1.0\ L)\ /\ (1.0 + V) = 1.10 \times 10^{-5}$$
$$1.0 + V = 0.73$$

A negative V does not make sense. This implies that regardless of the volume of chromate you add, the concentrations of chromate and barium are never enough to induce precipitation. The issue is the concentration of the chromate solution added is too dilute. **D**

Difficulty: Medium
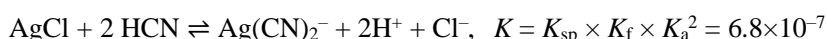**Learning Objectives**: K_{sp} and solubility

Question 34:

I. We know by Le Chatelier's principle that if K_{eq} increases with increasing temperature, the reaction must be endothermic. Statement I is incorrect.

II. This statement requires math to verify. Since $\Delta G^o = -RT\ln(K)$, $\Delta G^o = -8.314 \times 300 \times \ln(0.020) =$ 9800 J. ΔG^o is positive meaning the reaction is nonspontaneous. We know that ΔH^o is also positive contributing to the positive ΔG^o. We cannot say the sign of ΔS^o without knowing specifically the magnitude of ΔH^o. ΔH^o could be slightly positive and require a strong negative entropy term to make the reaction have its respective ΔG^o or be very positive and ΔS may end up being positive and counter the magnitude of ΔH^o. Statement II is incorrect.

D is the correct answer.

Difficulty: Medium
Learning Objectives: sign analysis of ΔG^o, ΔH^o and ΔS^o

Question 35:

Let us write the net equation:

$$AgCl + 2\ HCN \rightleftharpoons Ag(CN)_2^- + 2H^+ + Cl^-, \quad K = K_{sp} \times K_f \times K_a^2 = 6.8 \times 10^{-7}$$

Then apply the RICE table method to set up the equation:

R	AgCl	+	2 HCN	⇌	Ag(CN)₂⁻	+	2 H⁺	+	Cl⁻
I	*0.010 mol*		n mol		0		0		0
C			−0.020		+ 0.010		+ 0.020		+ 0.010
E			n–0.020		0.010 M		0.020 M		0.010 M

Note: the volume of the final solution of the system above is 1.00 L.

$$6.8 \times 10^{-7} = 0.010 \times (0.020)^2 \times (0.010)\ /\ (n-0.020)^2$$
$$\rightarrow n = 0.26\ mol.$$

C

Difficulty: Hard
Learning Objectives: multiple equilibria; calculation with the RICE table method

Difficulty: Hard

Learning Objectives:
LCP; shift of equilibrium at constant pressure

Question 36:

For this problem, assume each molecular structure represents 1 mol of gas and the initial volume is 1.0 L.

Firstly, in order for the total pressure to be kept constant while additional moles of gas are added, the volume of the container must increase. We eliminate A and B as their volumes remain constant. Secondly, we must recognize that the equilibrium mixture still must have ratios of NO_2 and N_2O_4 that follow K. In this case, let us use K_c. Our initial mixture contains 4 moles of NO_2 and 4 moles of N_2O_4. In the 1 L container, each gas has a molarity of 4 M. Because the balanced equation for the dimerization is $2NO_2 \rightleftharpoons N_2O_4$, $K = (4)/(4^2) = 0.25$. The correct answer must have a ratio of $[N_2O_4]/[NO_2]^2$ consistent with this. In C, 4 moles of each gas are present, however the volume doubles and the concentration of each gas is 2.0 M. $K = (2)/(2^2) = 0.5$. This is incorrect. In D, 6 moles of NO_2 are present and 3 moles of N_2O_4. The concentrations are thus 3 M NO_2 and 1.5 M N_2O_4. $K = (1.5)/(3^2) = 0.25$. **D** is the correct answer.

We may apply the Le Chatelier Principle to get the answer without quantitative analysis. As some noble gas is added to a constant pressure system, the "net" pressure of the reactants and products actually decreases as the total pressure including the partial pressure of the noble gas keeps constant. According to LCP, the equilibrium will shifts to the decomposition side to produce more gas molecules (more NO_2(g)), which can reduce the pressure decrease. The only correct choice with more NO_2 (less N_2O_4) is D.

Difficulty: Easy
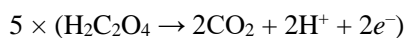
Learning Objectives:
oxidation states

Question 37:

In A), P is in the +5 oxidation state. In B), Mn is in the +6 oxidation state. In C), S is in the +4 oxidation state. In D), N is in the +5 oxidation state. **B** is the answer.

Difficulty: Easy

Learning Objectives:
balance redox equations using half-reaction method

Question 38:

Write and balance the half reactions.

$$5 \times (H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-)$$
$$2 \times (5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O)$$

The coefficient of H2O is 8. D

Difficulty: Medium

Learning Objectives:
electrolysis and Faraday's law

Question 39:

$$\text{mol } e^- = 0.153 \text{ A} \times 16400 \text{ s} / (96500 \text{ C/mol } e^-) = 0.0260 \text{ mol}$$

2 moles of electrons are required to deposit 1 mol of Cu and 3 moles of electrons for 1 mol of Rh. We write two equations, 1 to balance the moles of electrons and 1 to balance mass. Let x be the moles of Cu and y be the moles of Rh.

$$2x + 3y = 0.0260$$
$$63.55x + 102.91y = 0.826$$

Solving the system of equations, we get $x = 0.0130$, $y = 0$. Thus, we know the metal is only copper. **A**

Question 40:

Firstly, calculate ΔH^o and ΔS^o.

$$\Delta H^o = -153.89 - 2\times55.19 + 2\times61.84 = -140.59 \text{ kJ/mol}$$

$$\Delta S^o = -112.1 + 42.6 + 2\times111.3 - 2\times115.5 - 41.6 = -119.5 \text{ J/mol}\times\text{K}$$

Calculate ΔG^o from the above values

$$\Delta G^o = \Delta H^o - T\Delta S^o = -140.5 + 119.5\times298/1000 = -105 \text{ kJ/mol}$$

I. $E^o = -\Delta G^o/nF = 105000/(2\times96500) = 0.544 \text{ V} = 0.54 \text{ V}$. Correct

II. Since ΔS^o is negative, increasing the temperature will make ΔG^o more positive due to the expression $\Delta G^o = \Delta H^o - T\Delta S^o$. ΔG^o becoming more positive will make the cell potential more negative, since $= -\Delta G^o/nF$ (n and F are kept constant). Incorrect.

The answer is thus **A.**

However, the equation provided in the problem is actually not balanced, there is a coefficient of 2 missed for Ag in the product side. This issue won't affect the calculation of ΔH^o as the standard enthalpy of formation of Ag(s) is 0, but it will affect the ΔS^o value, thus further affect ΔG^o and E^o. Thus, statement I actually is incorrect, and correct answer is D if the equation is balanced.

Note: both A and D are accepted. You may further realize how important it is to balance the equation for any equilibrium or stoichiometry problem.

Question 41:

Let us write the balanced equations:

$$\text{Ni} + 2\text{Ag}^+ \rightarrow 2\text{Ag} + \text{Ni}^{2+} \quad (x)$$
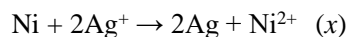
For this expression, $\Delta G^o = -nFE^o = -2\times96500\times1.05 = -203000 \text{ J/mol} = -RT\ln K_x = -8.314\times298\times\ln(K_x)$ $K_x = 3.33\times10^{35}$

$$\text{Ni}^{2+} + 4 \text{ CN}^- \rightarrow \text{Ni(CN)}_4^{2-} \quad (y)$$

$$\text{Ag}^+ + 2 \text{ CN}^- \rightarrow \text{Ag(CN)}_2^- \quad (z)$$

$$(x + y - 2\times z) \quad \text{Ni} + 2\text{Ag(CN)}_2^- \rightarrow 2\text{Ag} + \text{Ni(CN)}_4^{2-} \qquad K = K_x \times K_y / K_z^2$$
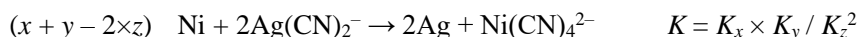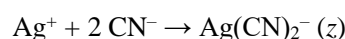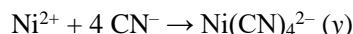
$$K = 3.33\times10^{35} \times 2.0\times10^{31} / (9.8\times10^{21})^2 = 6.94 \times 10^{22}$$

$$E^o = RT\ln(K)/nF = 8.314\times298\ln(6.94\times10^{22})/(2\times96500) = 0.68 \text{ V}.$$

A

Question 42:

The key principle in this question is that reduction potentials are intensive properties, which are not summable (not a state function). Note: Calculating the cell potential using the reduction potential of the cathode to subtract that of the anode doesn't mean potentials are summable, as cell potential actually is the potential difference between the cathode and the anode. So, in order to relate the desired half reaction with the provided half reactions, we need to convert to ΔG^o first.

$$\Delta G^o{}_1 = -nFE^o{}_1 = -4\times96500\times0.74 = -286000 \text{ J/mol}$$

$$\Delta G^o{}_2 = -nFE^o{}_2 = -2\times96500\times1.15 = -221950 \text{ J/mol}$$

The desired equation is a sum of the first and second equations; ΔG° is a state function and thus its values can be summed.

$$\Delta G^{\circ}{}_3 = \Delta G^{\circ}{}_1 + \Delta G^{\circ}{}_2 = -507950 = -nFE^{\circ} = -6 \times 96500 \times E^{\circ}{}_3$$

$$E^{\circ}{}_3 = 0.88 \text{ V}$$

A

Difficulty: Easy

Learning Objectives: electron configuration of atoms/ions at ground state

Question 43:

Using the Aufbau principle, the electron configuration for Ni is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$. The 4s electrons are lost first when ionizing, thus Ni^{2+} has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$. **D**

Question 44 was omitted from the exam.

Difficulty: Medium

Learning Objectives: trends of bond strength down a group; uniqueness of the 2nd period elements

Question 45:

B is the answer. It can be interpreted in the following manner: Br_2 and I_2 have atoms with very large covalent radii. Their bonds will be very long and as a result will be very weak. Their bond dissociation enthalpies will be very low. Using this logic, you may deduce F–F would have the highest bond enthalpy. However, all these halogen molecules have 3 lone pairs on each of the two atoms. In F–F, these three lone pairs surround very small F atoms and exist very close to each other due to the short F–F bond. There is significant repulsion as a result; this repulsion destabilizes and weakens the F–F bond. Cl is large enough to not experience very high repulsion due to lone pairs yet is not large enough to make the covalent bond ridiculously long either.

Generally, for main group elements, the bonds get weaker down the group, however, the second period elements are typical exceptional due to their much smaller sizes. So, this is a typical example of the uniqueness of the second period elements.
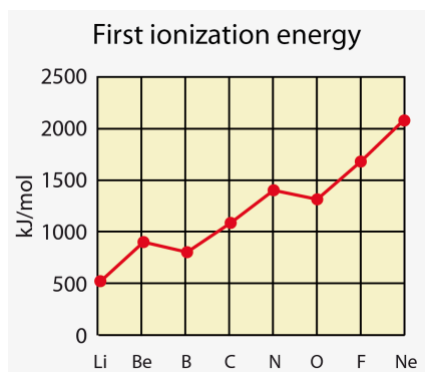
Difficulty: Medium

Learning Objectives: periodic trends and exceptions; electron affinity

Question 46:

When looking at the orbital structures, adding an electron to a group 1 element will add to the valence s orbital and pair with the existing s electron. Adding an electron to a group 2 element must add to a higher energy p orbital. As a result, adding an electron to a group 2 element will release less energy due to the orbital it adds in. **B**

Another choice which also looks correct is C, more energy is released by the group 2 elements because they have more protons in the nucleus. Recall the first ionization energies ($IE1$) of elements across a period, taking the second period as an example, the general trend is increasing, however, there are two elements which are lower in $IE1$ than the previous element, B (group 3) and O (group 6). Taking the $2p^1$ electron from B needs less energy ($IE1$ of B), which means adding one electron to the 2p orbital of Be releases less energy (electron affinity of Be). Similar trends also occur in other periods. Thus, we can eliminate C. In summary, though the trends in electron affinity is not as regular as the $IE1$, we can expect group 2 and group 5 elements to have lower electron affinity (releasing less energy or even absorbing energy).

First ionization energy
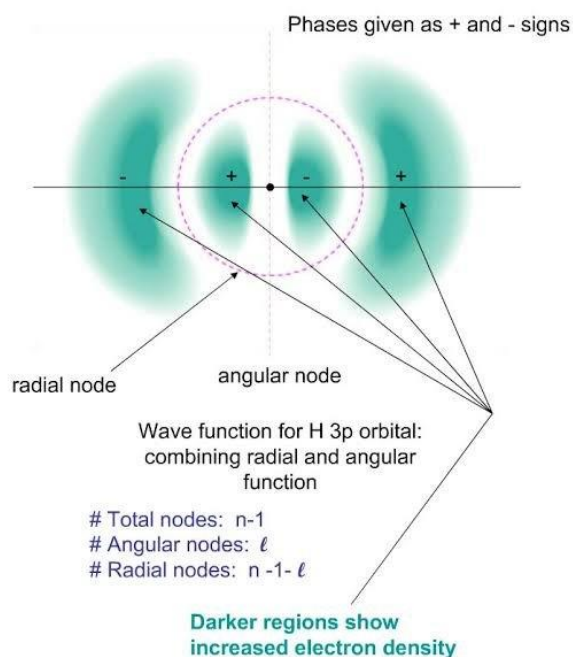
Electron Affinities (kJ/mol)

Source: Wikipedia (left) and Pearson (right)

Question 47:

If two orbitals have the same shape and orientation, by definition they must have the same values of l and m_l, since l governs the orbital shape (s, p, d, f) and m_l the orientation. The different number of nodes must be radial nodes (cannot be angular nodes, since l is the same), which depends on the number of principal shells there are (specifically, the *n*.) *n* thus will vary. **A** is the correct answer.

(Alternative solution: the total number of nodes is defined as n – 1, thus if the number of nodes differ n must differ)

Here we provide a good website to help you visualize the shape and nodes of each orbital. A node of the orbital is generally the place with an electron probability of 0. Taking the 3p orbital for example, as shown below, there is one radial node (a spherical surface) and one angular node (a nodal plane here). As indicated by the name, radial nodes are related to the radius, the distance to the nucleus, while angular nodes are related to the angular part of the orbital (wavefunction), which are typically planes.

Phases given as + and - signs

radial node

angular node

Wave function for H 3p orbital: combining radial and angular function

\# Total nodes: n-1
\# Angular nodes: ℓ
\# Radial nodes: n -1- ℓ

Darker regions show increased electron density

Source: Quara

You may need to review the meaning and value of each quantum number by doing some homework, either check the local exam annotation or do some googling.

Question 48:

We are familiar that the Balmer series containing all electron transitions to the $n = 2$ energy level ($n = k \rightarrow n = 2, k > 2$) corresponds to visible light emission and that the Lyman series containing all electron transitions to the $n = 1$ energy level ($n = k \rightarrow n = 1$) corresponds to UV light emission. Similarly, in order to absorb visible light, the electron will be initially present in the $n = 2$ energy level and then get excited to a higher state. In order for the atom to emit a UV photon, the electron must subsequently fall to the $n = 1$ energy level. **B** is the answer that follows these principles.

You may mathematically confirm the above series using the Rydberg's formula for hydrogen atoms, as shown below:

$$\Delta E \propto \frac{1}{\lambda} = -R_H \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where the n_f and n_i represents the final and initial energy level, and $R_H = 1.10 \times 10^7 \text{ m}^{-1}$ is the Rydberg's constant.

Question 49:

Drawing Lewis structures is the key to solve this problem.

A) HCNO has one resonance structure with a triple bond between C and N and another with double bonds between C=N and N=O. The triple bond resonance structure is more favorable since the – formal charge is on oxygen, the most electronegative element.

B) HNCO has one resonance structure with a triple bond between N and C but a much more stable resonance form with 0 formal charge when there is a double bond between N=C and also C=O (lone pair on N).
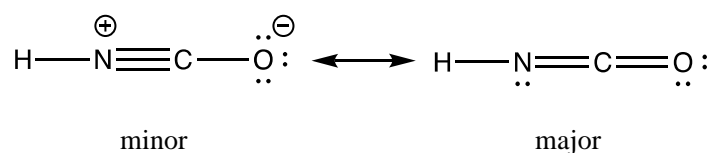
C) H_3CNO is most stable with a lone pair on nitrogen and a double bond between N=O. There may only be a single bond between C and N since C already has three bonds to hydrogen and can only form 1 more bond without expanding its octet.

D) Similar to above, C can only form a single bond with N since C cannot exceed 4 bonds.

HCNO

major   minor

HNCO

minor   major
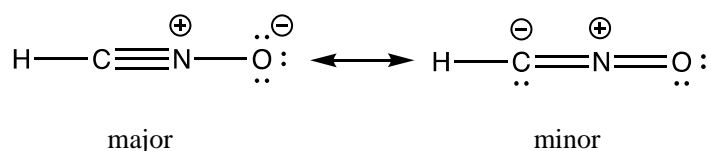
When comparing these molecules, we can eliminate C and D which have C–N single bonds. A and B both have two resonance forms: one with a CN double bond and one with a triple bond. However, in structure A the triple bond resonance is more stable by formal charge and thus contributes more to the overall molecular structure. As a result of A having more triple bond character between C and N, it is expected that **A** will have the shortest C–N bond length.

Question 50: Bonding, Medium

Draw the Lewis structure to begin.
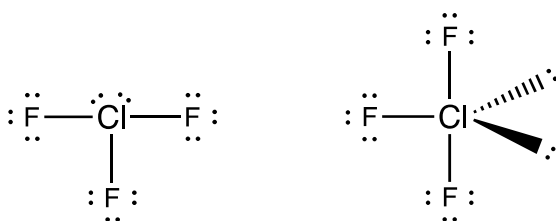
The electron cloud geometry of this molecule (5 electron domains) is trigonal bipyramidal, as shown above in the right. One F is located in the equatorial plane with the 2 lone pairs and the other two Fs are located above and below the plane in axial positions. *(the more repulsive lone pairs both preferentially occupy equatorial positions to avoid destabilizing 90 degree interactions with axial pairs)*

I. This statement is incorrect. Looking at the Lewis structure above, two of the F–Cl–F bond angles are 90 degrees, however the bond angle between the two axial Fs is 180 degrees.

II. In trigonal bipyramidal electron pair geometry, the axial and equatorial bond lengths are not equal. The 3c–4e type bonding of axial bonds makes the axial bonds longer. As a result, the Cl–F bond lengths are not all equal. **D is the correct answer.**

Question 51:

This question is very easy to tackle if you are familiar with MO theory. Isoelectronic to O_2, the NF MO diagram is very similar to that of O_2, except that the atomic orbitals of F is lower in energy than N as F is more electronegative. (This fact does not affect the correct answer, however). Seeing the attached MO diagram, there are two electrons in the π^*_{2p} molecular orbitals, which by Hund's law will each occupy separate orbitals. There are 2 unpaired electrons, making **C** the correct answer.

Source: Student Solutions Manual for Whitten/Davis/Peck/Stanley's Chemistry, 9th edition
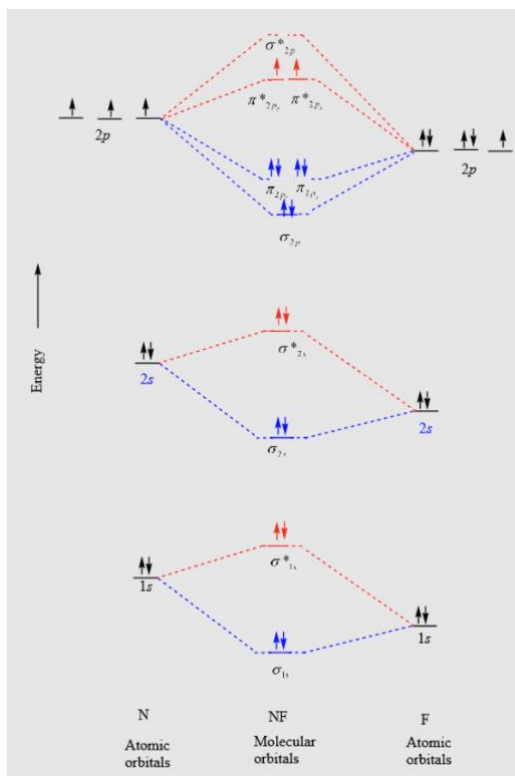
Difficulty: Medium
Learning Objectives:
Lewis structures;
molecular geometry;
VSEPR model

Difficulty: Medium
Learning Objectives:
concepts of isoelectronics;
molecular orbital diagram

Question 52:

This question again relies on molecular orbital theory. When drawing out the MO diagram of NF, the HOMO (Highest Occupied Molecular Orbitals) containing the highest energy electrons (π^*_{2p}) is an antibonding orbital. By definition, antibonding orbitals are higher in energy than both atoms that form it (N and F). Ionizing an electron from a higher energy orbital would require LESS added energy as the energy is already at a more excited state and needs less energy to overcome the nuclear attraction. As a result, the correct answer for the ionization energy of NF must be less than the ionization energy of N and also F. In this case, **A** is the only answer that fits this criterion.

Moreover, as predicted by the molecular orbital diagram above, the *IE* of NF is closer to that of N.

Question 53:

To approach this question, first draw out the Lewis structure for guanidinium. We have $4 + (5+1+1)\times3 - 1 = 24$ electrons. Subtracting 9×2 for 9 single bonds, we get 6 electrons left. In order for every atom to have an octet, we draw two N atoms with lone pairs and the third N atom with a double bond to the central C. This is only one resonance structure, however. Any of the nitrogens can be the one with the double bond, leading to two more resonance structures. What is important to realize is that the existence of a partial π bond involving each of the N atoms means that each N atom must have a 2p orbital available for π bonding. As a result, each N atom cannot fully sp^3 hybridize, as then it would lose the ability to π bond. Since each N atom is now sp^2 hybridized, they each must be trigonal planar in geometry as sp^2 hybridization dictates. **A** is the correct answer.
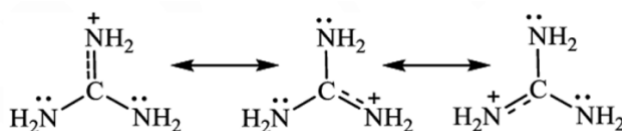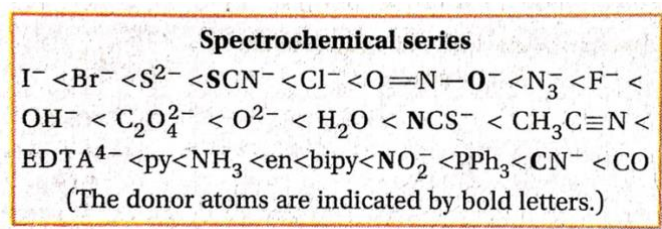

Source: Semantic Scholar

One more resonance can be drawn with each nitrogen single bonded to the central carbon, which carries a positive formal charge. This is a minor resonance as the central carbon disobeys the octet rule, which is much worse than the three resonances above, and it won't affect our analysis.

In summary, when there are delocalized involved (indicated by multiple resonances), the geometry and hybridization may be different from the results predicted by the VSEPR mode.

Question 54:

This question relies on crystal field theory. Firstly, it is important to understand that the absorption of visible light of transition metal complexes typically occurs by d–d transition, or the energy required to promote one d electron from a lower d orbital energy level to a higher energy level. This energy, called splitting energy, is determined based on three factors 1) coordination geometry, 2) metal charge, 3) ligand strength. What you can notice is that each molecule listed has cobalt in the same oxidation state of +3. Additionally, all of the complexes have 6 bonding pairs and are in the octahedral geometry. Thus, the splitting energy is dependent only on ligand strength. Since we are looking for the complex

ion that absorbs the longest wavelength and we know that energy of light is inversely proportional to its wavelength, we are looking for the ligand that will induce the smallest splitting energy. By the spectrochemical series, we know that halogens such as F⁻ are some of the weakest field ligands and thus would induce a very low splitting energy. All of the other ligands are strong field ligands and would induce a high splitting energy and absorb short wavelengths for d–d transition. Thus, the fluoro complex **C** is our answer.

Spectrochemical series

$I^- < Br^- < S^{2-} < \textbf{S}CN^- < Cl^- < O{=}N{-}\textbf{O}^- < \textbf{N}_3^- < F^- <$

$OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < CH_3C{\equiv}N <$

$EDTA^{4-} < py < NH_3 < en < bipy < NO_2^- < PPh_3 < CN^- < CO$

(The donor atoms are indicated by bold letters.)

Source: Stack Exchange

You may not need to memorize the whole spectrochemical series, but you'd better know some general trends, such as, halides are weak ligands with small splitting energy, while CN⁻ and CO with carbon as the donor are strong ligands with large splitting energy and nitrogen containing ligands are something in between.

Question 55:

For drawing isomer questions, the strategy is four fold: 1) determine the degree of hydrogen unsaturation (also commonly called double bond equivalence) to determine the possible functional groups (functional isomers), 2) draw all possible carbon skeletons (chain isomers), 3) add functional groups to different positions (positional isomers), 4) look for stereoisomers, especially enantiomers.

1. Unsaturation degree $= 2(\#C) + 2 - \#H - \#Cl = 2(3) + 2 - 6 - 2 = 0$. This means that all carbons are saturated, and no rings or double bonds are present. So the molecule is a chloroalkane.

2. For a 3 carbon backbone with no rings, only one skeleton exists. A "linear" 3 carbon chain (propane) without branches.

3. Functional groups (Cl atoms) can be added in the following manners. Make sure to count all locations, especially when two Cls attach to the same carbon atom.

1,1-dichloropropane

1,2-dichloropropane

1,3-dichloropropane

2,2-dichloropropane
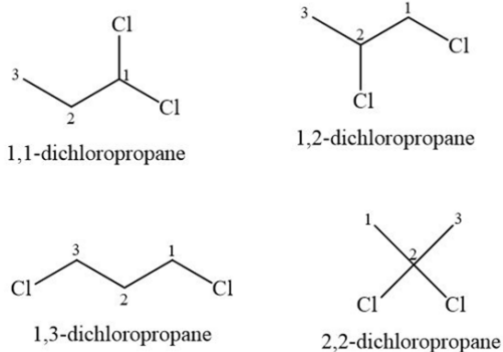
4. Going through each constitutional isomer, we realize that since there are no double bonds or rings, no *cis–trans* isomerism will exist. We then search for enantiomers. 1,1–dichloropropane,

1,3–dichloropropane, and 2,2–dichloropropane are achiral. Carbon 2 of 1,2–dichloropropane is chiral as C2 connects to four different groups or the structure lacks a mirror plane. As a result, 1,2–dichloropropane exists as two enantiomers. This makes a total of 5 structures; **B** is our answer.

Difficulty: Hard
Learning Objectives: S_N2 reactions

Question 56:

A nitrile is a compound in the form R–CN. Sodium cyanide is a good nucleophile and the DMSO solvent (polar aprotic) signals to us that this reaction likely is S_N2 (bimolecular nucleophilic substitution). We know S_N2 requires an electrophile with a good leaving group attached to a saturated carbon. Going through the answer choices.

A) No leaving groups (or really any functional groups) at all are present here. This is a very unreactive compound.

B) The alcohol group is reactive but will not undergo S_N2 unless it is made into a better leaving group in the first place. This will not produce a nitrile.

C) The double bond (a weak nucleophile) indicates electrophilic addition, but as the cyanide anion itself is a nucleophile, no reaction will occur here. We are looking for S_N2.

D) This is the best answer. We have a bromine (good leaving group) attached to a saturated, primary carbon. S_N2 will occur rapidly here with the cyanide attacking the carbon and displacing bromine to form a nitrile. **D** is the correct answer.

Difficulty: Hard
Learning Objectives: molecular orbital diagram of conjugated dienes

Question 57:

The molecular orbital diagram for the pi bonds of a conjugated diene can be made by drawing p orbitals on each carbon atom with different orientations. The lowest energy MO is made when the diagram has no nodes (all p orbitals have the same orientation), the second lowest when there is 1 node (there is one plane at which the two p orbitals directly adjacent to it have opposite orientations), etc. For 1,3–butadiene, there are 4 carbon atoms and thus 4 p–orbitals drawn in each MO. 4 MO configurations exist: one with 0 nodes, one with 1 node, one with 2 nodes, and one with 3 nodes (be aware that for four p–orbitals, there can only be 3 "transitions" between p–orbital orientation for adjacent orbitals, thus 3 nodal planes). Each MO, like an atomic orbital, can fit 2 pi bonding electrons. Since there are 2 pi bonds and thus 4 pi bonding electrons, the two MOs with the least amount of energy (0 nodes and 1 node) are occupied (2 and 3 node MOs are empty). Looking at the answer choices, I has 2 nodes and II has 1 node. Thus, only MO II is filled, making **B** the correct answer.

Readers may draw the other two anti-bonding MOs for practice.

Question 58:

The reaction hinted here is acetal hydrolysis. Acetals consist of two ether groups attached to the same carbon atom, which is the product of the dehydration of aldehyde/ketone with two molecules of alcohols (or a diol). An acetal can be hydrolyzed and yield back the aldehyde/ketone ONLY under acidic conditions. Thus, an acetal is a protecting group used to protect a carbonyl group from reacting under neutral or basic conditions, which can be further deprotected under acidic condition.

Difficulty: Hard

Learning Objectives: hydrolysis of acetals; comparison of acetals and hemiacetals

Acid-Catalyzed Hydrolysis of Acetals
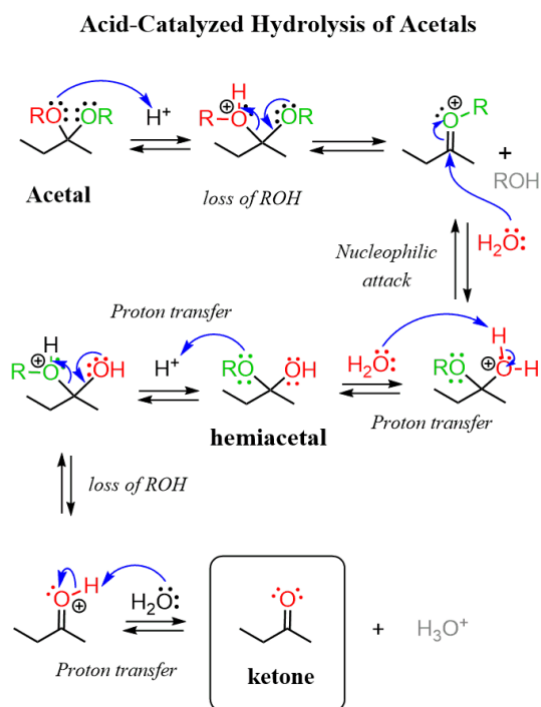
Source: Chemistry Steps

Under basic conditions, the alkoxide is a bad leaving group and will not leave from the acetal to reform a carbonyl, thus acetals can't react with water to hydrolyze under basic condition. Now we are looking for an acetal in the answer choices. **B is the correct answer here.** It is easy to see the methoxide as an ether, yet the other functional group attached to the top carbon is also an ether, albeit intramolecular. Reacting B with acid and water will yield an aldehyde. None of the others react exclusively with water under acidic conditions. Hemiacetals (D) can decompose to the carbonyl under both acidic and basic conditions – under basic conditions the hydroxyl group can get deprotonated by the base, then the lone pair on the negative charged oxygen goes down, forms a double bond to reform the carbonyl and force the alkoxide to leave.

Choice A is an ether, which is much more stable than the acetals and hemiacetals. Note: ethers can hydrolyze under acidic condition but less readily.

Readers may try to draw the product (aldehyde) of the hydrolysis of B under acidic conditions as a practice.

Difficulty: Medium

Learning Objectives: IR spectrum; IR absorption of common functional groups

Question 59:

The simplest way to get this question right is through memorization. A sharp IR signal around 1700 cm^{-1} is characteristic of a carbonyl group. This matches answer choice **C.** It is more difficult to derive this answer from the formula for wavenumber relating force constant and reduced mass. Ethers (A, B) have signals in the fingerprint region (<1500 cm^{-1}), alkenes (A, B) have weak signals around 2200 cm^{-1}, and alcohols (D) have strong and broad signals above 3000 cm^{-1} induced by the hydrogen bonded O–H bonds.

Difficulty: Hard

Learning Objectives: reduction of disulfide bonds

Question 60:

Any changes to the chemical structure of a protein can change its function, thus any of the options could satisfy the criteria of deactivating insulin. The true question is which of the following organic processes requires the use of a mild reducing agent? In organic reactions, reduction typically involves addition of hydrogen/hydride.

A) Cleaving a disulfide bridge into two thiol (R–SH) groups clearly requires a reducing agent. Two hydrogen atoms are added to cleave the bond.

B) Cleaving peptide bonds into a carboxylic acid and an amine is a hydrolysis reaction, not a reduction. Water instead of hydrogen is added.

C) Any substitution occurring at an alcohol group would not be a reduction. The only way to reduce an alcohol group would be to remove the functional group completely, a synthesis that would require more than a "mild" reducing agent.

D) Reducing agents may decrease overall charge, yet they are typically balanced with proton transfers that nullify net charge changes. Overall, this is a weak answer as the main reason proteins change in functionality is a change in functional groups and thus structure.

A is the correct answer.