

# Annotated Solution

## 2019 USNCO National Exam Part I

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### Solutions

1.  $n = m/M_w$ , where  $n$  is number of moles,  $m$  is the mass, and  $M_w$  is the molecular weight. Applying this calculation to all the options gives us choice  $\boxed{B}$ .
2. The stoichiometric ratio is one mole of oxygen for two moles of hydrogen, or 16 g : 2 g to form 18 g (0.50 mol) of product. Option **A** fits this, and **B** and **C** have a limiting reagent. Option **D** has more of *both* reactants than the amounts needed to make 18 g, so it's  $\boxed{D}$ .
3. One mole of troegerite has  $2 \times 3 + 4 \times 2 + 12 = 26$  moles of oxygen.  
( $N_A$  is Avogadro's number)

$$N_A \times \left( \frac{1.00 \text{ g}}{M_w} \right) \times \left( \frac{26 \text{ mol O}}{1 \text{ mol troegerite}} \right) = 6.022 \times 10^{23} \text{ mol}^{-1} \times \left( \frac{1.00 \text{ g}}{1304.0 \text{ g/mol}} \right) \times \left( \frac{26 \text{ mol O}}{1 \text{ mol troegerite}} \right) = 1.20 \times 10^{22}$$

i.e.  $\boxed{C}$ .

4. Since we are told Hünig's base is *monobasic*, it is not a daring assumption to say it probably only has one nitrogen atom (organic bases are amines, in which one, two or three hydrogens in  $\text{NH}_3$  are replaced by alkyl groups, R). If we assume there are 100.0 g of base, we get 14.82 g of H and 10.84 g of N, i.e. 14.82 mol of H and 0.7737 mol of N, so a mole ratio of 19:1. A quick calculation of the moles of carbon confirms that this is a real molecule. Hence, it's  $\boxed{D}$ .
5. Let  $x$  be the number of moles of  $\text{MgO}$ , and  $y$  be the number of moles of  $\text{Mg}_3\text{N}_2$ . Thus, since each mole of the nitride has 3 moles of magnesium, the total number of moles of magnesium in the sample is  $x + 3y$ . We started off with 1.000 g of Mg, i.e. 41.14 mmol of Mg, so we have the following equations:

$$x + 3y = 0.04114 \text{ mol}$$

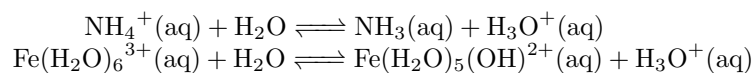
$$40.31x + 100.95y = 1.584 \text{ g (the sum of the masses of the nitride and the oxide is the mass of the final sample).}$$

Solving gives  $x = 0.02998$  mol and  $y = 0.003721$  mol, so  $3y = 0.01116$  mol of Mg is in the nitride form. Hence,  $0.01116/0.04114 = 27.13\%$  is in the nitride form;  $\boxed{C}$ .

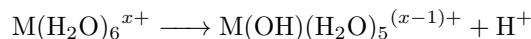
6. This is a very acidic solution, so the dissociation of  $\text{CH}_3\text{COOH}$  is basically zilch. We really only need to look at the number of moles of  $\text{HNO}_3$  and  $\text{HCl}$ ; each mole of acid contributes one mole of  $\text{H}^+$  since both acids are strong.  $n(\text{H}^+) = (45.0 \text{ mL})(0.10 \text{ M}) + (50.0 \text{ mL})(0.20 \text{ M}) = 0.0145$  mol. The total volume is  $45.0 \text{ mL} + 50.0 \text{ mL} + 55.0 \text{ mL} = 0.145 \text{ L}$ . So, the overall concentration of  $\text{H}^+$  is about 0.10 M,  $\text{pH} = 1.00$ , so  $\boxed{C}$ .
7. Hydrated  $\text{Cu}^{2+}(\text{aq})$  is well-known to be blue. So, it's  $\boxed{C}$ .

**Note:**  $\text{Na}_2\text{S}_2\text{O}_4$  is a colorless solution,  $\text{K}_2\text{CrO}_4$  is yellow, and  $\text{Zn}(\text{OH})_2$  is a white precipitate.

8.  $\text{KNO}_3$  and  $\text{Ba}(\text{NO}_3)_2$  are both neutral as they are made by a strong acid and a strong base.  $\text{NH}_4^+$  is an acid, and so is  $\text{Fe}^{3+}$ , as shown by the following equations:



Strongly charged metal ions like  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  or  $\text{Cr}^{3+}$  are often acidic, because their aquo complexes readily lose  $\text{H}^+$ :

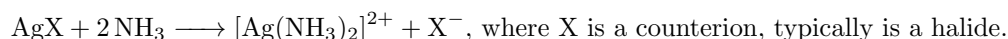


It is helpful to know the approximate  $\text{p}K_a$ s of various acids. Ammonia, and similar amines, are decently strong bases, so their conjugate acids are quite weak, with  $\text{p}K_a$ s of between 9 and 10. The aquo complexes of strongly charged metal ions can be quite acidic, with  $\text{p}K_a$ s between 3 and 7. Of course, the higher the charge density the stronger the acid. Thus, it's D.

9. The purpose of a reflux is to allow a reaction to take place at a high temperature in a certain solvent, i.e. the boiling point, without the solvent simply boiling away. To achieve this, a condenser is used to cool the solvent vapors so that they turn back into a liquid, so that the solvent doesn't boil away. If the solvent were to boil away, it would be a waste of solvent, the solvent would need to be replenished, and if the solvent boils to dryness the temperature will spike and lead to bad things as the temperature exceeds the boiling point.
- In setup **A**, there is a hole meant for attaching a vacuum line, obviously having a hole for solvent vapor to escape defeats the point (there needs to be an opening at the top of the condenser, but ideally vapor cannot escape the condenser as it is cooling down and condenses).
  - **C** has a similar issue as **A**.
  - **D** is an improper use of a volumetric flask, which usually aren't meant to withstand the high heat. Besides, the surface area of the liquid is miniscule compared to the volume, which means the boiling liquid will be confined, potentially causing an explosion. Certainly, it will be very violent.
  - Setup **B** is the proper one, with the Erlenmeyer flask providing a safe vessel to contain boiling solvent and vapors.

Hence, it's B.

10. The relevant reaction is:



This reaction will proceed if the  $K_{\text{eq}}$  of the dissolution reaction above is greater than one. It is not too hard to imagine that if  $\text{AgX}$  has a smaller  $K_{\text{sp}}$ , the  $K_{\text{eq}}$  of the dissolution will be smaller (note that the  $K_{\text{eq}}$  of dissolution is equal to  $K_{\text{f}} \times K_{\text{sp}}$ , where  $K_{\text{f}}$  is the formation constant for  $[\text{Ag}(\text{NH}_3)_2]^+$ .) Thus, it is sensible to choose the salt  $\text{AgX}$  with the lowest  $K_{\text{sp}}$ , so that it does not dissolve in ammonia.  $\text{Ag}^+$  is very *soft* (lower in charge, larger in size, and less electronegative), so we should pick a very *soft* counterion, i.e. iodide, so the answer is C.

$\text{AgI}$  is also pretty yellowish. Note that  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  has a much larger  $K_{\text{f}}$  than  $[\text{Ag}(\text{NH}_3)_2]^+$  since S in  $\text{S}_2\text{O}_3^{2-}$  is *softer* than N, so  $\text{AgI}$  is still soluble in thiosulfate. Also,  $\text{AgF}$  and  $\text{Ag}(\text{CH}_3\text{COO})$  are water soluble, so you only need to pick between  $\text{AgI}$  and  $\text{AgCl}$ .

If you are confused by the "hard and soft acid/base" here, you may refer to the annotated solution of Q8 in local 2018. Actually even if you are not sure about the solubility difference of  $\text{AgX}$  in ammonia and thiosulfate, you may also eliminate  $\text{AgCl}$  using its color.

11. Titration is useless if the molar mass is unknown, and besides, the impurities might also react with  $\text{NaOH}$ . Combustion only gives elemental analysis, and is useless to assess the purity of *unknown* impure compounds. UV-vis is similarly unhelpful, since we have no idea what functional groups should be present in the compound that might absorb UV-vis light. Melting point is useful, since it *does not require the melting point to be known*. A pure substance will usually display a clear melting point, melting uniformly at a single temperature. An impure substance will exhibit a lower, more broad melting point. Hence, A.

- 12.
- Error **A** with some  $\text{Na}_2\text{CO}_3$  used in the standardization spilled will result in less  $\text{Na}_2\text{CO}_3$  being used in the standardization, so less HCl solution will be used. This will mean the concentration of HCl will appear to be higher because of the reduced volume. Since the concentration of HCl will appear to be higher than it actually is, the concentration of ammonia will also appear higher, so **A** is correct.
  - If error **B** is committed,  $\text{NH}_3$  is being removed from the titration flask with the paper towel, so less HCl will be used, and the amount of ammonia will appear lower (it's better to just swirl the flask, or use magnetic stirring, and further use deionized water to rinse the buret tip and inner wall of the flask to make sure that all titrant added is reacted with the analyte).
  - If error **C** is committed,  $\text{NH}_3$  will be partially neutralized by  $\text{CO}_2$  in the air, thus its concentration is lower than the actual one.
  - Error **D** should not change the results, since shifting the pH curve up and down does not change where the sharp change occurs.

The answer is  **A**.

13. Metals don't dissolve in  $\text{CCl}_4$  (a nonpolar solvent), and they don't dissolve in water (some metals do react with water, but this is arguably not dissolution, rather a chemical process). Metals are also conductive at pretty much all temperatures. Thus, the answer should be  **A**. Don't be off put by the low melting point; some metals have quite low melting points such as alkali metals with few valence electrons. By the way, **D** describes a semiconductor like silicon.
14.  $\text{I}_2$  is quite nonpolar, and would preferentially dissolve in the dense, nonpolar  $\text{CCl}_4$ .  $\text{CCl}_4$  does not mix with polar water. So, we see a deep violet layer containing  $\text{I}_2$  beneath a colorless aqueous layer (I don't think it would be perfectly colorless; dissolved iodine in water is usually pale yellow). Thus, it's  **C**.
15.  $\text{CH}_2=\text{CH}_2$  has weak IMFs and can be immediately eliminated. As the rest of the choices have similar molar masses, it is as simple as considering which compound is capable of forming the most hydrogen bonds. Hydrazine ( $\text{H}_2\text{NNH}_2$ ), with 2 lone pairs on nitrogens (hydrogen bond acceptors) and 4 N-H bonds (H as the hydrogen bond donors) that are able to engage in hydrogen bonding, is the clear winner.  **B**.
16. As the container expands, liquid pentane will enter the vapor phase, and the pressure will be maintained at the saturated vapor pressure until all the pentane becomes a gas, at which point the pressure will drop as there is no more liquid pentane to vaporize to fill the expanding container. This is the behavior seen in chart **C**. A quick calculation confirms that there is not enough pentane to fill an 8.0 L container at the vapor pressure, so **D** is incorrect. Answer is  **C**.

$$pV = nRT = \frac{mRT}{M}$$

In order to fit the 8.0 L container with a saturated vapor pressure of 620 mmHg,

$$m(\text{minimum}) = \frac{pVM}{RT} = \frac{620 \times 8.0 \times 72.15}{62.36 \times (273 + 30)} = 18.9 \text{ g} > 10.0 \text{ g}$$

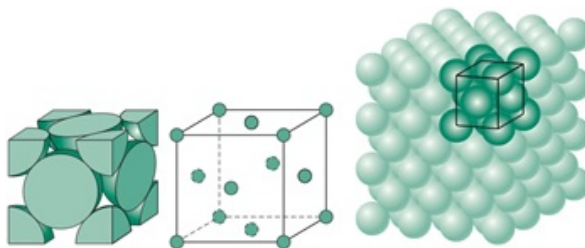
17. HBr reacts with  $\text{CH}_3\text{NH}_2$  when the vapors meet in the middle of the tube to form a salt, which is observed as a white ring of  $[\text{CH}_3\text{NH}_3^+]\text{Br}^-$ . Since HBr has a high molecular weight, it diffuses slowly, so the methylamine diffuses further, and the white ring appears closer to the HBr side. It's  **A**.

You may read Graham's effusion law for further quantitative analysis.

18.

$$\rho = \frac{m}{V} = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

In the fcc lattice, each unit cell has 4 metal atoms (8 atoms in the corner  $\times 1/8$  + 6 atoms in the face centers  $\times 1/2 = 4$ ), as shown below:



source: Callister & Rethwisch 5e

Thus,

$$\rho = \frac{4 \times M_w(\text{metal})}{N_A a^3}, \text{ where } a \text{ is the edge length of the unit cell (cube).}$$

It is convenient to convert  $a$  to cm (1 pm =  $10^{-10}$  cm) as density of solids is commonly expressed as  $\text{g}/\text{cm}^3$ . We obtain

$$M_w(\text{metal}) = \frac{\rho a^3 N_A}{4} = \frac{12.45 \times (380.3 \times 10^{-10})^3 \times 6.02 \times 10^{23}}{4} = 103 \text{ g/mol}$$

i.e. Rh,  $\boxed{C}$ .

By the way, you could probably guess the answer to this.  $12 \text{ g}/\text{cm}^3$  is pretty dense, much denser than light potassium (which floats on water). The first row transition metals like vanadium usually have moderate densities, about  $5 \text{ g}/\text{cm}^3$ . Only the second and third row transition metals are really dense (especially third row).

Please be aware that the  $Z$  in the parenthesis is the atomic number, not the relative atomic mass.

19. The freezing of water forms more structured hydrogen bonds between the water molecules. The formation of stronger IMFs in the solid phase means this process is exothermic. Or you may easily get the similar conclusion through thinking that the melting of ice absorbs heat. At low temperatures (below the freezing point), the freezing of water is favorable, so it's also spontaneous.  $\boxed{A}$ .

20. Only reaction (3) has glucose, so start from there. This reaction produces  $\text{CO}_2$ ; the only other reaction that produces  $\text{CO}_2$  is reaction (2), so reverse reaction (2) and multiply by 2, so that overall the reaction will produce 2 moles of  $\text{CO}_2$ . This produces 2 moles of acetic acid, which we deal with by reversing reaction (1) and multiplying it by 2. Note that we can also come to these conclusions by noting that 2 moles of ethanol will be needed, so we should reverse reaction (1) and double it. Thus, we have:

$$\Delta H_3 + (-2)\Delta H_2 + (-2)\Delta H_1 = -2805.0 + (-2) \times (-874.2) + (-2) \times (492.6) = -71.4 \text{ kJ/mol } \boxed{A}$$

Actually this is how you apply Hess's Law to solve problems like this.

21. Note that the dissolution of  $\text{Li}_2\text{CO}_3$  is unfavorable, as  $K_{\text{sp}} = 0.175^2 < 1$  ( $\Delta G^\circ = -RT \ln K > 0$ ). Furthermore, increasing temperature decreases the solubility. In accordance with Le Chatelier's principle, we expect an *exothermic* reaction to shift towards reactants as temperature increases, i.e. decreasing  $K_{\text{sp}}$ . This can also be easily seen from the van't Hoff equation. Therefore, the dissolution of  $\text{Li}_2\text{CO}_3$  has  $\Delta H^\circ < 0$ . But since the reaction is unfavorable at 298 K,  $\Delta S^\circ$  must also be less than 0 as  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . So the answer is  $\boxed{D}$ .

By the way, although the dissolution of a salt might appear to be an increase in disorder, the solvation of ions requires forming tight knit solvation shells, so often  $\Delta S^\circ$  for dissolution is close to 0 or negative.

22. A rigid, well insulated container is an isolated system, which can't exchange either matter or energy with the environment. According to the second law of thermodynamics, the entropy of any isolated system must increase in a spontaneous process, so the answer is  $\boxed{C}$ .

*Why is it not Gibbs free energy?* The short answer is that Gibbs free energy is used for constant pressure systems, not constant volume systems.

23. (1) Use the equation  $\Delta G = \Delta G^\circ + RT \ln Q$ ;  $T = 298$  K.  
 (2) First compute

$$\begin{aligned}\Delta G^\circ &= \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants}) \\ &= [(-394 \text{ kJ/mol}) + (-604 \text{ kJ/mol})] - [(-1129 \text{ kJ/mol})] \\ &= 131 \text{ kJ/mol}\end{aligned}$$

(3)

$$Q = \frac{a(\text{CO}_2) \times a(\text{CaO})}{a(\text{CaCO}_3)}$$

The activity of any pure liquid or solid  $a$  is simply 1. The activity of a gas is simply its pressure. If you don't know what activity is, you may just use  $Q_p = P(\text{CO}_2)$ .

$$Q_p = \frac{(0.4 \text{ mbar})(1)}{(1)} = 0.0004 \text{ bar. You need to convert to bars, since the standard pressure is 1 bar.}$$

You may see other problems in USNCO use 1 atm as standard pressure, since they are quite close in value (1 atm = 1.013 bar), but the actual standard pressure is 1 bar according to the latest IUPAC definition.

$$\therefore \Delta G = \Delta G^\circ + RT \ln Q = 131 \text{ kJ/mol} + 8.314 \times 298 \times \ln(0.0004) = 112 \text{ kJ/mol, so it's } \boxed{B}.$$

24. (1) Note that  $q_{\text{rxn}} = -q_{\text{calorimeter}}$ .  
 (2)  $q_{\text{calorimeter}} = C \times \Delta T$ ; where  $C$  is the heat capacity.  
 (3) To find the heat capacity, multiply the mass by the specific heat capacity, and don't forget the mass of salt:

$$\begin{aligned}C &= [10.0 \text{ g} + 100.0 \text{ g}] \times 4.184 \text{ J/g/K} = 460.2 \text{ J/K} \\ q_{\text{calorimeter}} &= C \times \Delta T = 460.2 \text{ J/K} \times [17.11^\circ\text{C} - 24.00^\circ\text{C}] = -3.17 \text{ kJ, so } q_{\text{rxn}} = 3.17 \text{ kJ.}\end{aligned}$$

- (4) We need the *molar* change in enthalpy, i.e the change in enthalpy per mole. There are 10.0/80.05 = 0.125 mol of  $\text{NH}_4\text{NO}_3$ .

$$\therefore \Delta H^\circ = q_{\text{rxn}}/n = 3.17/0.125 = 25.4 \text{ kJ/mol, i.e. } \boxed{D}.$$

25. The rate is simply the rate of the slow step.

$$\text{Rate}_{\text{slow step}} = k[\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+]$$

Since the first step is fast and reversible, we can assume it is in equilibrium state, and we can use that to solve for the concentration of the intermediate.

$$K_{\text{eq}} = \frac{[\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+]}{[\text{CH}_3\text{COCH}_3][\text{H}^+]}, \text{ so } [\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+] = K_{\text{eq}}[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

$$\text{Rate}_{\text{slow step}} = k[\text{CH}_3\text{C}(\text{OH})\text{CH}_3^+] = kK_{\text{eq}}[\text{CH}_3\text{COCH}_3][\text{H}^+] = k_{\text{eff}}[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

i.e.  $\boxed{A}$ .

26. Use the Arrhenius equation:

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

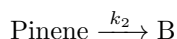
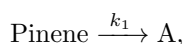
$$T_1 = 25.0 + 273.15 = 298.2 \text{ K}, T_2 = 35.0 + 273.15 = 308.2 \text{ K}$$

We know the rate doubles when temperature increases, so  $\frac{k_2}{k_1} = 2$

Plug and chug:  $E_a = 52.9 \text{ kJ/mol}$ , so  $\boxed{A}$ .

Please be aware the  $R$  used here must be  $8.314 \text{ J/mol/K}$  to cancel the unit.

27. (1) Imagine two reactions happening simultaneously:



(2) Rate of consumption of pinene in the first reaction is  $k_1[\text{Pinene}]$

Rate of consumption of pinene in the second reaction is  $k_2[\text{Pinene}]$

(3)  $k_1[\text{Pinene}] + k_2[\text{Pinene}] = (k_1 + k_2)[\text{Pinene}]$ , the overall rate constant is  $k_1 + k_2$ . In the example of the problem, the answer would be  $0.22 + 0.13 = 0.35$ .

So,  $\boxed{D}$ .

28.  $\text{Cl}_2(\text{g}) + 3\text{F}_2(\text{g}) \longrightarrow 2\text{ClF}_3(\text{g})$ , for every 3 mol of  $\text{F}_2$  consumed, 2 mol of  $\text{ClF}_3$  is produced. Thus, you also need to flip a sign.

Therefore,  $\Delta[\text{ClF}_3]/\Delta t = -(2/3)\Delta[\text{F}_2]/\Delta t$ , so  $\boxed{C}$ .

29. A catalyst needs to reduce the activation energy of reaction through altering the reaction path. **A** and **B** don't reduce the activation energy, so they can't possibly be the answer. **D** has an "intermediate" which is *more stable* than the product, so the product can't even form! The correct answer is therefore  $\boxed{C}$ .

30.
  - **A is wrong**, since the rate clearly depends on the concentration of azide according to the rate law. In this case, the concentration of azide is a constant, so the effective rate constant is  $k_{\text{eff}} = k[\text{N}_3^-]$ ;  $[\text{N}_3^-]$  has a strong impact on the effective rate constant.
  - **C is wrong** because the reaction is irreversible, so the product  $\text{I}^-$  has essentially no effect on the reaction.
  - **D is wrong**, since the second order kinetics is compatible with a single elementary step of  $\text{CH}_3\text{I} + \text{N}_3^- \longrightarrow \text{CH}_3\text{N}_3 + \text{I}^-$ .

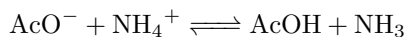
Therefore,  $\boxed{B}$  is correct.

If the initial concentrations of  $\text{CH}_3\text{I}$  and azide are equal, rate =  $k[\text{CH}_3\text{I}][\text{N}_3^-] = k[\text{CH}_3\text{I}]^2$ , so the rate law changes into second order since  $[\text{CH}_3\text{I}] = [\text{N}_3^-]$  all the time during the reaction. According to the integrated rate law for second order reaction,  $1/[\text{CH}_3\text{I}] = 1/[\text{CH}_3\text{I}]_0 + kt$ , the half-life  $t_{1/2} = 1/(k[\text{CH}_3\text{I}]_0)$ , which means the half-life is reversely proportional to the initial concentration of  $[\text{CH}_3\text{I}]$ , then it takes half as long for  $[\text{CH}_3\text{I}]$  to decrease to 0.005 M as it does for it to decrease from 0.005 M to 0.0025 M.

31.  $K_{\text{sp}} = [\text{Pb}^{2+}][\text{F}^-]^2$ . The concentration of  $\text{Pb}^{2+}$  is simply equal to the solubility. Since one mole of  $\text{PbF}_2$  has 2 moles of fluoride, the concentration of  $\text{F}^-$  is double the solubility. Plug and chug, you get  $K_{\text{sp}} = 4 \times (2.1 \times 10^{-3})^2 = 3.7 \times 10^{-8}$ , so  $\boxed{C}$ .

32. This is an example of an amphoteric salt, where one ion is a weak base and the other is a weak acid. We don't know the concentration of  $\text{NH}_3$  or  $\text{CH}_3\text{COOH}$ , so it's impossible to use the Henderson-Hasselbalch equation. It turns out that in this kind of situation, where the salt is composed of a weak acid with  $K_{a1}$  and a weak base whose conjugate acid has  $K_{a2}$ , the  $\text{pH} = (\text{p}K_{a1} + \text{p}K_{a2})/2 = 7$ , so **C**. The same equation can be applied to calculate the  $\text{pH}$  of  $\text{NaHCO}_3(\text{aq})$ , which is amphoteric.

But we should derive this equation. Note that strongest base present is acetate ( $\text{AcO}^-$ ), and the strongest acid present is  $\text{NH}_4^+$ , so the dominant reaction is the reaction of these two species:



To find  $\text{H}^+$ , we should use the two  $K_a$  expressions:

$$\frac{[\text{H}^+][\text{AcO}^-]}{[\text{AcOH}]} = K_a(\text{acetic acid})$$

$$\frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = K_a(\text{ammonium})$$

$$K_a(\text{acetic acid}) \times K_a(\text{ammonium}) = \frac{[\text{H}^+][\text{AcO}^-]}{[\text{AcOH}]} \times \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = [\text{H}^+]^2 \left( \frac{[\text{NH}_3]}{[\text{AcOH}]} \right) \times \left( \frac{[\text{AcO}^-]}{[\text{NH}_4^+]} \right)$$

Note that because of our original reaction equation,  $[\text{AcOH}] \approx [\text{NH}_3]$ , and of course,  $[\text{AcO}^-] \approx [\text{NH}_4^+]$  since they are in 1:1 ratio in the salt.

$$[\text{H}^+]^2(1)(1) = K_{a1} \times K_{a2}$$

Taking the log of both sides gives the equation we had earlier.

33. Use RICE diagram:

Reaction	$P(\text{PCl}_5)$	$P(\text{PCl}_3)$	$P(\text{Cl}_2)$
Initial	2.7 bar	2.7 bar	0
Change	$-x$	$+x$	$+x$
Equilibrium	$2.7 - x$	$2.7 + x$	$+x$

$$K_{\text{eq}} = \frac{x(2.7 + x)}{2.7 - x} = 0.015$$

$$x = 0.015 \text{ bar}$$

Note that since  $K_{\text{eq}}$  is small, the reaction won't go forward much, so  $P(\text{PCl}_5)$  and  $P(\text{PCl}_3)$  approximately cancel out. Thus, it's **A**.

34. **A is incorrect**, because increasing the volume will force the reaction to the side with more particles by Le Chatlier's principle, i.e. to the right.
- B is incorrect** because increasing the total pressure by adding an inert gas has no effect on the partial pressures of the relevant species.
- C is incorrect** because adding more  $\text{PCl}_5$  will also shift the reaction to the right.
- D is correct** because this reaction is endothermic, so reducing the temperature shifts the reaction to the left.

The reaction must be endothermic, since although  $\Delta G^\circ = -RT \ln K_p$ , is positive ( $K_p < 1$ ),  $\Delta S^\circ$  is also positive, so  $\Delta H^\circ$  must also be positive. The answer is **D**.

35. Let's assume the salt has the formula  $M[SO_4]_n$ , where  $n$  is some number.

Then, we have

$$K_{sp} = [M^{2n+}][SO_4^{2-}]^n$$

Taking the log of both sides, we have

$$\log K_{sp} = \log[M^{2n+}][SO_4^{2-}]^n$$

Using our log rules, we have

$$\log[M^{2n+}] + n \log[SO_4^{2-}] = \log K_{sp}, \text{ or } \log[M^{2n+}] = \log K_{sp} - n \log[SO_4^{2-}]$$

Hence, the slope is  $-n$ . Looking at the graph, we see the slope is  $-1.5/3.0 = -1/2$ , so we have  $M(SO_4)_{1/2}$ , which is the same as  $M_2SO_4$ , so **A** is correct.

36.
  - In this back titration, some weak base is reacted with a bunch of HCl. The *excess* HCl is then neutralized with the strong base. We have  $1.00/285.34 = 3.50$  mmol of morphine if the pill was pure, and  $50.0 \times 0.1000 = 5.00$  mmol of HCl. Since morphine is monobasic, it reacts 1:1 with HCl, so we have 1.5 mmol of extra HCl. This requires 15.0 mL 0.1000 M NaOH to be back titrated, so **I is wrong**.
  - At the end point, only the *excess* HCl was titrated, so the species to determine the acidity is mainly protonated morphine,  $BH^+$  at the end point. This makes the endpoint slightly acidic, so methyl red with a pH transition range of  $4.4 \sim 6.2$  is a good choice. Hence, **II is correct**. You can calculate the pH at the endpoint to confirm that it is in the correct pH range. The transition range of the indicator needs to be within the pH windows, the significant change of the pH the titrant added. Generally, it's *ok* if the pH at the endpoint is within one pH unit of the color change range of the indicator, so 3.4 to 7.2 would be the acceptable pH range for the endpoint.

**B** is correct.

Let's further calculate the pH at the end point, in which  $BH^+$  is the major species with a molarity of  $\frac{3.50 \text{ mmol}}{(50.0 \text{ mL} + 15.0 \text{ mL})} = 0.0538 \text{ M}$



$[H^+] = \sqrt{0.0538 \times 10^{-8.21}} = 1.82 \times 10^{-5}$ , pH = 4.74, perfectly matches the transition range of the methyl red.

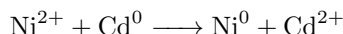
37. We have  $(0.5 \text{ A})(250 \text{ s}) = 125 \text{ C}$  of charge, or  $125/F = 125/96500 = 1.3$  mmol of electrons to work with. Ag has a more positive reduction potential than Cu since Ag is less reactive, so Ag will deposit first (if there was any Cu deposited while  $Ag^+$  was still in solution, the Cu would react with  $Ag^+$  to form Ag and  $Cu^{2+}$  ion). Since there are only 1 mmol of  $Ag^+$  ions, which consumes only 1 mmol of electrons, 1 mmol of Ag will deposit, and the rest of the electrons will be used to deposit copper. So, **C**.

You may ask how do we know that Ag is less reactive than Cu. We may get it from life experience since statues made by Cu are relatively easier to rust with a layer of green copper(II) carbonate hydroxide,  $Cu_2CO_3(OH)_2$  while Ag products are more resistant. We may also analyze the trends of metal reactivity down the group in IIB, copper, silver, and gold, no doubt, gold is the most unreactive thus the most stable here, similarly, we can conclude copper is more reactive than silver.

38. Na is +1, O is -2.  $2(+1) + 4(-2) + 2x = 0$ ,  $x = +3$ . Drawing the structure of the dithionite ion and then electron counting gives the same result which is **B**.



39. We see that  $\text{Ni}^{2+}$  has a more positive reduction potential than  $\text{Cd}^{2+}$ , meaning  $\text{Ni}^{2+}$  is a stronger oxidizing agent than  $\text{Cd}^{2+}$ . Thus, the reaction that proceeds is:



More rigorously, we should use the Nernst equation to determine the spontaneity, but we are at standard state so we can just look at standard potentials.

- Reduction occurs at nickel, so nickel is the cathode, **A is incorrect**.
- Cell potential is an entirely thermodynamic quantity, and does not depend on the size of the electrodes involved, thus **C is incorrect**.
- Adding  $\text{Ni}^{2+}$  to the cathode forces the reaction further to the right by Le Chatelier's principle (see the rxn above) so it would increase the potential. You may get the same conclusion by applying the Nernst equation, **D is incorrect**.
- **B is correct**. When  $\text{Ni}^{2+}$  is consumed and reduced to  $\text{Ni}^0$ ,  $\text{K}^+$  needs to be added to balance charges from the salt bridge.

Thus, the answer is  $\boxed{B}$ .

40. You can't just add the voltages for unbalanced half reactions since reduction potential is NOT a state function!

It is better to add Gibbs free energies as the target half reaction is the sum of the two half reactions listed in the table:

( $F$  = Faraday's constant)

$$\begin{aligned}\Delta G_{\text{total}}^{\circ} &= \Delta G_1^{\circ} + \Delta G_2^{\circ} \\ -n_{\text{total}}FE_{\text{total}}^{\circ} &= -F(n_1E_1^{\circ} + n_2E_2^{\circ}) \\ E_{\text{total}}^{\circ} &= \frac{2(-1.13 \text{ V}) + 1(-0.26 \text{ V})}{3} \\ &= -0.84 \text{ V}\end{aligned}$$

So,  $\boxed{B}$ .

41. This is, in effect, a concentration cell. In the anode, there is a very low concentration of  $\text{Ag}^+$  due to the presence of ammonia to convert most  $\text{Ag}^+$  into complex  $\text{Ag}(\text{NH}_3)_2^+$ :

$$\begin{aligned}\frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} &= K_f \\ \frac{0.010}{[\text{Ag}^+] \times 0.40^2} &= 1.6 \times 10^7 \\ [\text{Ag}^+] &= 3.9 \times 10^{-9} \text{ M}\end{aligned}$$

The cathode has  $[\text{Ag}^+] = 0.010 \text{ M}$ .

The reaction that happens is  $\text{Ag}^+_{\text{cathode}}(0.010 \text{ M}) + \text{Ag}_{\text{anode}} \longrightarrow \text{Ag}_{\text{cathode}} + \text{Ag}^+_{\text{anode}}$  (very little). This makes sense based on Le Chatelier's principle: the anode has very little  $\text{Ag}^+$  so it would prefer to oxidize Ag to make more; the cathode has a lot of  $\text{Ag}^+$  so it prefers to reduce  $\text{Ag}^+$ .



$$\begin{aligned}K_f &= \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+]_{\text{anode}}[\text{NH}_3]^2} \implies [\text{Ag}^+]_{\text{anode}} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{K_f[\text{NH}_3]^2} \\ [\text{Ag}^+]_{\text{anode}} &= \frac{0.010}{1.6 \times 10^7 \times 0.40^2} \\ &= 3.9 \times 10^{-9}, \text{ consistent with the discussion above.}\end{aligned}$$

The standard cell potential  $E^{\circ}$  of the above reaction is 0 (nothing is really happening), and we can use the Nernst equation.

$$E = E^{\circ} - \frac{RT}{nF} \ln \left( \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}} \right) = 0 - \frac{0.0592}{1} \log \frac{3.9 \times 10^{-9}}{0.010} = 0.38 \text{ V}$$

Hence, it's  $\boxed{B}$ .

42. First, we calculate the  $E^\circ$ :

$$E^\circ = 1.36 \text{ V} - 1.33 \text{ V} = 0.03 \text{ V}$$

Next, the formula for  $K_{\text{eq}}$  is:

$$K_{\text{eq}} = e^{(-\Delta G/RT)} = e^{(nFE^\circ/RT)}$$

From the equation in the question, we deduce that there are 6 electrons being transferred per reaction, so  $n = 6$ . Plugging in the values into the formula and upon solving,  $K_{\text{eq}} = 1.1 \times 10^3$  that is  $\boxed{B}$ .

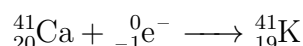
43. You may need to have a clear sense of the four distinct lines in the Hydrogen's emission spectrum (Balmer series) and be aware that the wavelength of light is inversely proportional to its energy ( $E = h\nu = hc/\lambda$ ). You may recognize 656 nm as the red end of the visible spectrum (400 – 700 nm), i.e. the red end of the Balmer series of transitions. It corresponds to the  $n = 3 \rightarrow 2$  transition. Recalling the Rydberg equation, we know that energies are proportional to  $1/n^2$  in a hydrogen atom. Your intuition should tell you that  $n = 3 \rightarrow 1$  should have a much shorter wavelength. Thus, the  $n = 4 \rightarrow 3$  transition is less energetic than the  $3 \rightarrow 2$  transition, and the  $4 \rightarrow 2$  transition is more energetic. So the electron in the  $n = 4$  shell can clearly emit light with a longer or shorter wavelength than 656 nm, but mathematically, there is no transition from  $n = 4 \rightarrow x$ ,  $x < 4$  that has the same energy release as the  $3 \rightarrow 2$  transition. So the answer is  $\boxed{D}$ .

44.  $2+$  ions are generally smaller than  $1+$  ions unless  $2+$  ions have many layers of electrons, and ionic radius increases as you go down the group. This immediately singles out  $\text{Rb}^+$  as the largest ion and  $\text{Ca}^{2+}$  as the smallest.  $\text{Sr}^{2+}$  is smaller than the diagonal  $\text{K}^+$ , one way to rationalize this is to see that Sr has a bunch of extra protons because of the presence of the d-block, and the d electrons don't shield as much as s and p electrons. This phenomenon is known as the d-block contraction, similar to the 4f contraction in lanthanide (lanthanide contraction). Thus, it's  $\boxed{C}$ .

45. O and N are actually pretty electronegative because of their small size. However, O is more electronegative due to the one extra proton in the nucleus. Hence, the correct answer is  $\boxed{B}$ .

46. The electron configuration of Ti is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ . Counting the orbitals we have:  $1s + 1s + 3p + 1s + 3p + 1s + 2d = 12$  orbitals. There are two partially filled d orbitals in accordance with Hund's rule and the answer is  $\boxed{B}$ .

47. Write out the nuclear equation:



- Note that electron capture converts a proton into a neutron, the numbers on the bottom sum the same for the products and reactants ( $20 + (-1) = 19$ ) for the charge and the same holds for the numbers on the top for the mass number. Potassium is not scandium, so **I** is **wrong**.
- All nuclear reactions that are favorable must be energetically favorable, so by  $E = mc^2$ , the mass *must* decrease. The mass that "disappears" gets turned into nuclear binding energy. This question confused some people in 2019 because free neutrons are slightly heavier than free protons; this mass difference is of course negligible compared to the nuclear binding energy. So is the mass of an electron by the way, thus, **II** is also **wrong**.

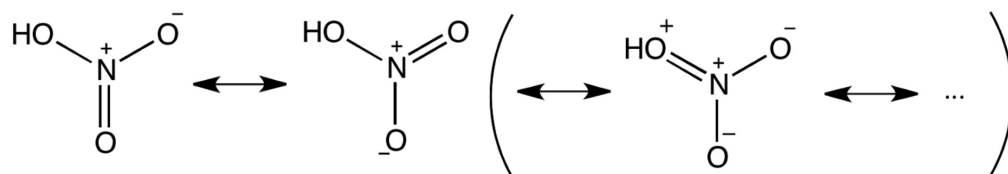
So,  $\boxed{D}$ .

48. The extra electron in Al ( $3s^2 3p^1$ ) when compared to Mg ( $3s^2$ ) goes into a 3p orbital. This 3p orbital experiences partial shielding from the previously filled 3s orbital, which is most consistent with  $\boxed{C}$ , since 3s electrons penetrate into the nucleus and 3p electrons don't. Interestingly, the maximum peak in the radial distribution function of 3s is further away from the nucleus compared to that in the 3p one.

49. Draw Lewis structures of all these molecules and you'll see that in  $\text{SO}_3$ , all the bond dipoles cancel since it is trigonal planar according to the VSEPR model. Thus, it's  $\boxed{D}$ .

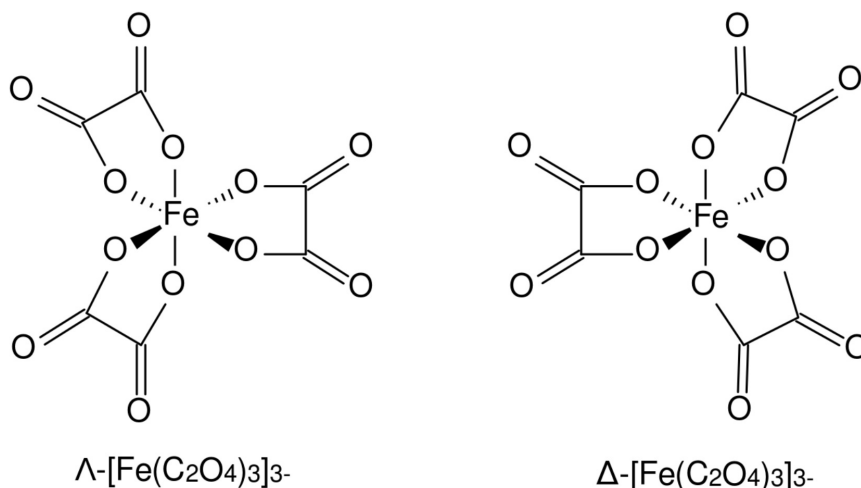
50. CO has a triple bond, which is stronger than the double bond in  $\text{CO}_2$ . So,  $\boxed{A}$  is correct.

51. By drawing the Lewis structure of triiodide ion, the central iodine atom in  $\text{I}_3^-$  has 3 lone pairs and is bonded to two terminal iodine atoms. This is consistent with a trigonal bipyramidal electron domain geometry. The 3 lone pairs all go in equatorial positions, so the molecule is linear, **A**. You may further figure out which atom carries the negative charge.
52. The more oxygens there are, the stronger the electron-withdrawing inductive effect, which can stabilize the negative charge on the oxygen in the conjugate base of the acid. Additionally, due to resonance, the negative charge of the ion can be spread over more oxygen atoms. Thus,  $\text{HBrO}_4$  is the most acidic, so **D**.
53. **D** has the wrong atom connectivity since H on N is not acidic in aqueous solution, and **C** has the wrong H-O-N bond angle since it is supposed to be bent due to the existence of two lone pairs on oxygen. Thus, we have to choose between **A** and **B**. The lone pair on the oxygen atom is in resonance with the other oxygen atoms:



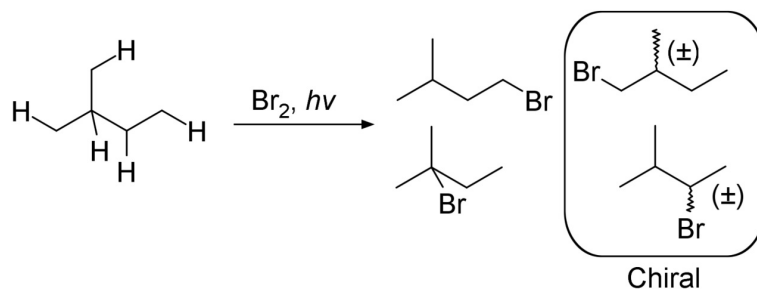
In fact, we can think of all the oxygen atoms being  $sp^2$  hybridized. Thus, the molecule is completely planar. **B** is the correct answer.

54.  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  is chiral since there is no mirror plane and inversion center in the structure, see  $\Lambda$  and  $\Delta$  isomers, which are mirror image of each other (enantiomers). Looking at the structure, we can see all iron-oxygen bond lengths are equivalent. Furthermore, there are indeed 6 oxygen iron bonds (this fits with an octahedral geometry). But we can see that some C-O bonds are closer to single bonds (those with O bonded to Fe), and some are closer to double bonds. Thus, **C** is the correct choice.

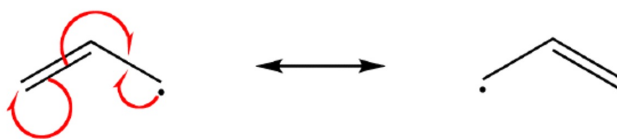


55.  $\text{CN}^-$  is a good nucleophile, but it is a fairly weak base, so it is more likely to be substitution rather than elimination. Acetone, being polar aprotic, also helps with  $\text{S}_{\text{N}}2$  reactions, Thus, **D** is correct.

56. There are 4 distinct hydrogen chemical environments that can be replaced with chlorines; two primary, one secondary, and one tertiary. Please be aware that the two  $-\text{CH}_3$  groups connected to the same carbon have the same chemical environments, which means they give the same chlorinated compound. However, some of the chlorinated compounds are chiral, and exist as pairs of enantiomers. Thus, there are 6 possible compounds including two stereoisomers since two of them have a chiral carbon in the structure, as shown below, so  $\boxed{C}$ .

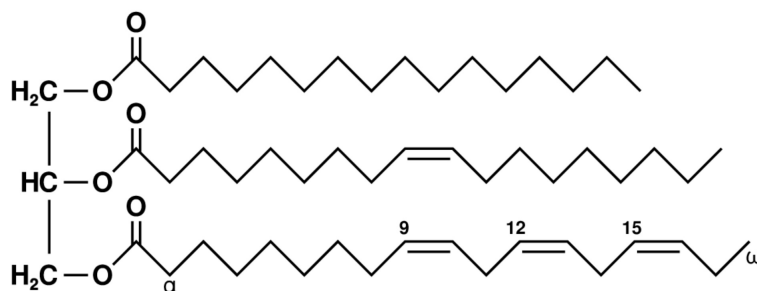


57. This compound has an HDI (hydrogen deficiency index) of  $[5 \times 2 + 2 - 8]/2 = 2$ . Since there is one double bond, there must be one ring (for details, read about hydrogen deficiency index, which is also called double bond equivalence or degree of unsaturation). So, it's  $\boxed{B}$ .
58. When a C–H bond is broken, a radical is formed (bond strengths usually refer to the homolytic bond dissociation energy, which is generally much less than the heterolytic bond dissociation energy for nonpolar bonds). Thus, we want to see which C–H bond should be broken to produce the most stable radical. *Allylic* radicals are quite stable due to resonance as shown below, which corresponds to  $\boxed{B}$ .



Note: In a molecule, the position next to an alkene is called allylic.

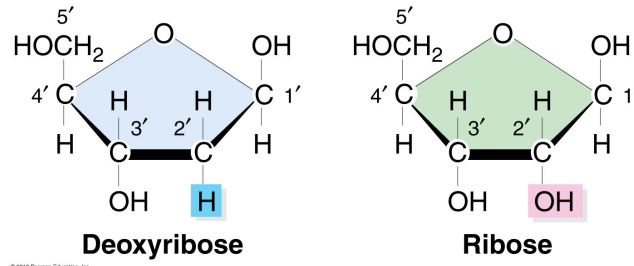
59. A typical fat (triglyceride) has the following structure:



Note the presence of the three esters. Hydrolysis of these esters in base gives one equivalent of glycerol (a triol), and three equivalents of fatty acid, but since this is in base, the fatty acids are deprotonated to give the corresponding salts. (Note that these salts are the main components of old fashioned soaps, this is why the process is called saponification). Thus, the correct answer is  $\boxed{C}$ .

60. Just memorize this (or not, I don't tell you how to live your life).

On a more serious note, it is possible to guess the answer to this one. The cyclic phosphate ester is much more stable than the phosphate esters of ATP or ADP, so it's not likely to be used as an energy source, you may eliminate **B**, though you might easily connect AMP with ADP/ATP. You should know that DNA is based on a backbone of the sugar deoxyribose, which lacks an oxygen at the 2 position, so you may eliminate **C** and **D**.



cAMP has an oxygen at the 2 position, so it's likely to not have much to do with DNA. (In reality, deoxyribose is derived from ribose, but in a more contrived way).

By process of elimination, **A** is correct. (Interestingly, 48% of test takers got this right, which is better than average. This implies people know more biology than chemistry).