Annotated Solution for USNCO National Exam 2021 – Part I

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Q1.

As $H_2(g)$ reacts with $O_2(g)$ in a mole ratio of 2:1 to form water, we can calculate that the amount of water produced in [A] is determined by 1.0 L H_2 as H_2 is the *limiting reactant*. Similarly, the amount of water obtained in [B], [C], and [D] is determined by 2.0 L H_2, 3.0 L H_2, and 1.0 L O_2 [equivalent to 2.0 L H_2], respectively. Thus, **C** will give the greatest mass of water.

Q2.

Each mole of $Sr(OH)_2$ provides two moles of hydroxide ions when reacting with KHP, so the mole ratio of $Sr(OH)_2$ and KHP is 1:2 as KHP is monoprotic. The concentration of $Sr(OH)_2$ can be calculated as follows:

$$c[Sr(OH)_2] = \frac{\frac{0.402 \text{ g}}{204 \text{ g/mol}} \times \frac{1 \text{ Sr(OH)}_2}{2 \text{ KHP}}}{28.15 \times 10^{-3} \text{ L}} = 0.0350 \text{ M}$$

Thus, the answer is **B**.

Q3.

The net ionic equation of the reaction between $Pb(NO_3)_2(aq)$ and $NaBr(aq)$ is as follow:

$$Pb^{2+}(aq) \quad + \quad 2Br^-(aq) = PbBr_2(s)$$

20.0 mL×0.15 M = 3.0 mmol   10.0 mL×0.35 M = 3.5 mmol

We can easily tell that Br^- is the *limiting reactant*, which will be completely precipitated. Thus, Br^- has the LEAST abundant ion in the supernatant, the liquid lying above a solid residue after the precipitation, **D** is the correct answer.

Q4.

Based on the conservation of oxygen atoms, half of the oxygens in CO_2 is from the lead oxide, and another half is from CO. Thus, the mass of oxygen in the lead oxide is calculated as follows:

$$m(O) = \frac{6.636 \text{ g}}{100.09 \text{ g/mol}} \times \frac{1 \text{ CO}_2}{1 \text{ CaCO}_3} \times \frac{1 \text{ O from lead oxide}}{1 \text{ CO}_2} \times 15.99 \frac{\text{g}}{\text{mol}} = 1.060 \text{ g}$$

Only D, $Pb_{12}O_{19}$ matches with the mass percentage of oxygen (1.060 g/9.736 g = 10.89%), thus, the answer is **D**.

Difficulty: Medium

Learning Objectives:

mass percent

Q5.

The mole ratio of K and S in K_2S, K_2SO_3, and K_2SO_4 is all 2:1. So if K% = 60.0%, S%= 60.0%/39.1×32.1×(1/2) = 24.6%, O% = 100% − 60.0% − 24.6% = 15.4%.

Difficulty: Hard
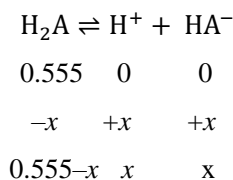
Learning Objectives:

colligative properties;

freezing point depression;

van't Hoff factor; percent

ionization of acids

Please be aware that

molality is used for

colligative properties

rather than molarity as

molality is temperature

independent. Molality is

defined as the moles of

solute divided by the mass

of solvent in kg.

Q6.

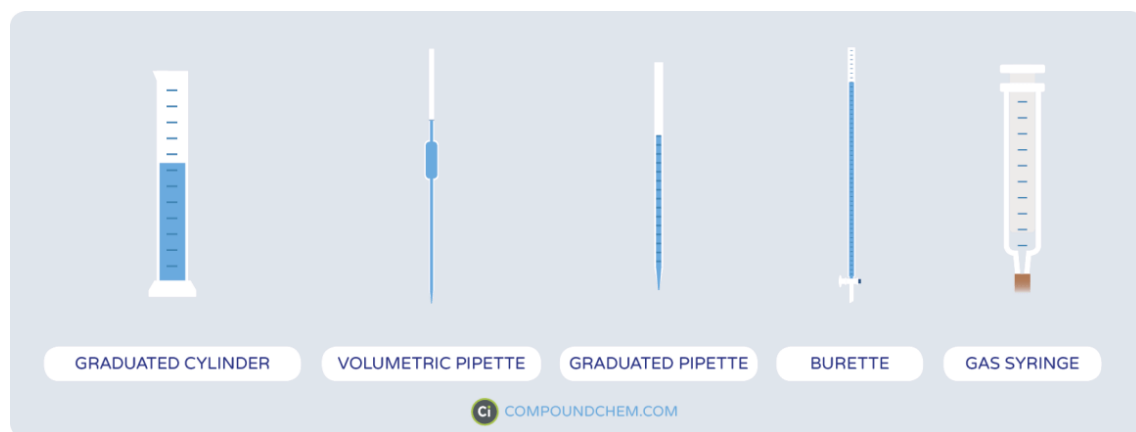According to the *freezing point depression* equation, the *molality* of all solute particles in the solution is

$$\text{molality(particles)} = \frac{\Delta T_f}{K_f} = \frac{1.31\,°C}{1.86\,°C\,m^{-1}} = 0.704\,m$$

The molality of the oxalic acid is 5.00 g/(90.04 g/mol×0.1000 kg) = 0.555 m < 0.704 m. As freezing point depression is a *colligative property*, which only depends on the number of the solute particles, but not the identity of particles. We can conclude that oxalic acid is partially dissociated as follows:

$$H_2A \rightleftharpoons H^+ + HA^-$$

	0.555	0	0
	−x	+x	+x
	0.555–x	x	x

Total molality = 0.555 − x + x + x = 0.704, x = 0.149

So, the *percent ionization* of the acid is 0.149/0.555 = 26.8%, the answer is **B**.

Difficulty: Easy

Learning Objectives:

volumetric glassware;

precision; uncertainty

The volumetric pipet is

different from the

graduated pipet. The later

one has many marks which

can measure any volume

smaller or equal to the

maximum value, but the

volumetric pipet, like the

volumetric flask, has only

one mark, which can only

be used measure a certain

volume as the mark

labeled, as shown below.

Q7.

To measure 10.00 mL of distilled water, a precise *volumetric glassware* should be used, such as a buret, a volumetric pipet, a graduated pipet, etc, which can read the volume to the second digit after the decimal point, though the last one is estimated. A 100-mL graduated cylinder is not precise enough to measure 10.00 mL water as it can only read to the first digit after the decimal point.

Test tubes, beakers, Erlenmeyer flasks, or disposable plastic/glass pipets can't be used for serious volume measurement as their marks are not precise and for reference only. Thus, the answer is **C**.

GRADUATED CYLINDER   VOLUMETRIC PIPETTE   GRADUATED PIPETTE   BURETTE   GAS SYRINGE

Ci COMPOUNDCHEM.COM

Source: Compound Interest

Q8.

Both AgCl and $PbCl_2$ are both white principates, while $PbCl_2$ is significantly more soluble in hot water. It seems like the current answer is A – only Ag^+ is present as the white precipitate formed does not appear to dissolve in hot water. But if you did a similar experiment before, you may realize that there is no obvious change even if some of the precipitate is dissolved. It is hard to notice the decrease of the precipitate amount unless the precipitate is almost or completely dissolved.

The keyword used here is "does not *appear* to dissolve in hot water", though actually it is partially dissolved. Thus, the correct answer is **C**.

This is indeed an interesting but mistake-prone question.

Difficulty: Hard

Learning Objectives: precipitation; solubility rule; hands-on laboratories

The best way to know the common precipitates and their properties is to do the hands-on experiments in the chemistry lab.

Q9.

The only yellow solution among the four options is $FeCl_3(aq)$, while $KMnO_4$, $Co(NO_3)_2$, and $CuSO_4$ solution is purple, pink, and blue, respectively. Thus, the answer is **B**.

$Fe^{3+}(aq)$ tends to hydrolyze and produce $Fe(OH)_3(s)$, which makes the solution cloudy:

$$FeCl_3(aq) + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3HCl(aq)$$

Therefore, the corresponding acid needs to be added prevent the precipitation when preparing a Fe^{3+} solution. For instance, concentrated $HCl(aq)$ is added to when dissolving $FeCl_3(aq)$ in water.
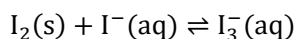
Difficulty: Easy

Learning Objectives: color of common ions

You may further calculate the highest pH to prevent the precipitation of a 0.1 M $Fe^{3+}(aq)$ using the $K_{sp}[Fe(OH)_3]$

Q10.

Ascorbic acid or vitamin C, a water-soluble vitamin found in various foods and sold as a dietary supplement, is a strong reducing agent. It can be directly titrated by iodine (I_2) as it can reduce I_2 into iodide (I^-). For such an *iodometry* titration, starch is commonly used as the indicator as starch can bind with molecular iodine to form a dark blue complex.

The iodine is not very soluble in water, and also easy to vaporize, so it is usually dissolved in a KI solution as the following spontaneous formation of triiodide, I_3^- occurs:

$$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

Thus, the correct answer to the question is **A**.

Difficulty: Easy

Learning Objectives: iodometry, iodine-starch complex; iodine-triiodide equilibrium.

Q11.

The dehydration of copper sulfate pentahydrate [$CuSO_4 \cdot 5H_2O$] is a typical experiment used for high school chemistry to demonstrate and practice the empirical formula and stoichiometry, in which the blue crystal turns to white as the hydrated water is gone with heating. So, we can eliminate [C] and [D]. Both [A] and [B] talk about the energy of light absorbed, however, heating caused expansion of the lattice as described in [B] doesn't seem reasonable as it is observed that the blue crystal turns to white powder. Thus, the correct answer to this question is **A**, heating causes water molecules bonded to copper to be replaced by sulfate, lowering the energy of the light absorbed.

Difficulty: Medium

Learning Objectives: dehydration of copper sulfate pentahydrate; d-d transition; *crystal field theory

CFT is used to explain the color many transition cations, including the colorless Zn^{2+}(aq), as there is no light absorbed due to the fulfilled d subshell and the resulted absence of d-d transition.

We can further explain the color change in a detailed way using the *crystal field theory* (CFT). The blue color of the hydrated $CuSO_4$ is caused by the *d-d transition* of the complex ion made by Cu^{2+} and water/sulfate. Originally, the water molecules are bonded to the Cu^{2+}(aq), the positions of water molecules are replaced by the sulfate anions when heated as the water is gone. You may read more information about the relative strengths of different ligands to understand the energy of the light absorbed during the d-d transition.

You don't have to know crystal field theory to solve this problem as you just need to pick up the most reasonable explanation.

Difficulty: Medium

Learning Objectives: spectroscopy; Beer's Law; calibration curve; error analysis

Q12.

UV-Vis spectroscopy is a common used method to quantitively measure the concentration of colored species in aqueous solutions. The absorbances of the standard solutions with different concentrations at λ_{max}, the wavelength of maximum absorbance, were measured to obtain a *calibration curve*. Then *Beer's law* is applied to calculate the concentration of the sample solution with an unknown concentration, as shown in the figure below.

$$Abs = \varepsilon l c$$

where *Abs* is the absorbance, ε is the molar absorptivity (the absorption of 1 M of solution with a standard light path), l is the length of light path (1 cm for a standard cuvette), c is the molarity of the solution.
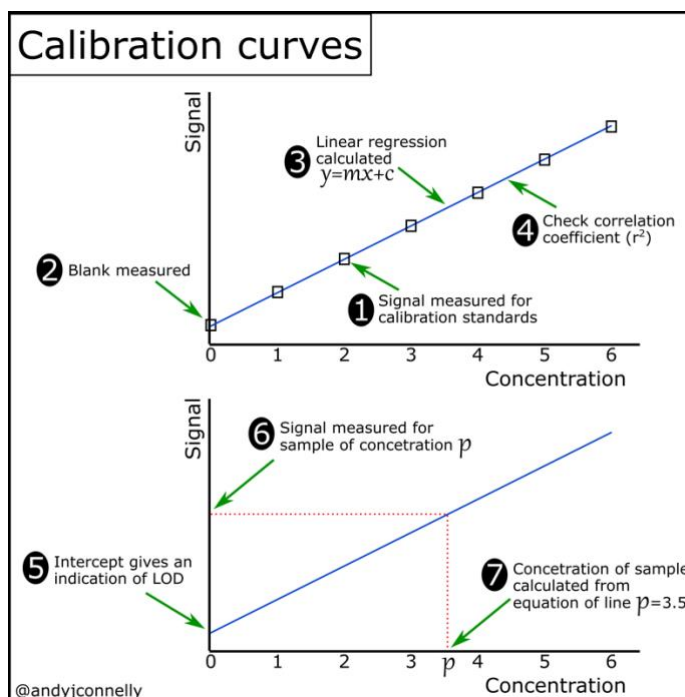
Source: Andy Connelly

For option [A], if the cuvette is not rinsed with the salt solution after being washed, the solution added to cuvette is diluted by the remained small amount of water, which will give a lower concentration; For option [B], if cuvette is not wiped off before it is inserted into the spectrophotometer, the

concentration will be measured higher as there is either some additional solution or fingerprint on the outer wall of the cuvette which can absorb or block the light. For option [C], if less than the recommended volume of solution is added to the cuvette, there will be no light absorbed by the solution as the solution is lower than the light path. For option [D], if the spectrometer is set to a wavelength different from λ_{max}, the absorbance is smaller, thus the concentration of the sample is underestimated. Thus, the correct answer to this question is **B**.

Q13.

Among the four isomers of C_3H_6O, only A is an ether, which has the lowest intermolecular forces. B is an alcohol with a hydroxyl group, which can make *hydrogen bonds* among molecules, so B has the highest boiling point; C and D are carbonyl compounds with the polar C=O bonds, which has **dipole-dipole interaction** in addition to the *London dispersion forces*, so C and D have similar boiling points but lower than that of B. A, as an ether, though having the two polar C–O bonds, but the partially positive charged carbon is embedded by the two alkyl groups, making the dipole-dipole interactions less significant.

Thus, the correct answer to this question is **A**.

Difficulty: Medium
Learning Objectives: intermolecular forces

Q14.

The equilibrium vapor pressure of dichloromethane CH_2Cl_2 at 24 °C is supposed to be a constant value of 0.53 atm in the container unless the liquid is not enough to maintain such a pressure even fully vaporized. According to the ideal gas law, the mass of CH_2Cl_2 needed to obtain an equilibrium vapor pressure of 0.53 atm can be calculated as follow:

$$m = nM = \frac{pVM}{RT} = \frac{0.53 \text{ atm} \times 5.0 \text{ L} \times 84.93 \text{ g/mol}}{0.08206 \text{ atm} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (273 + 24) \text{ K}} = 9.2 \text{ g}$$

9.2 g/13.8 g is approximately 2/3, thus, the correct answer is **B**, two-thirds of CH_2Cl_2 has evaporated.

Difficulty: Medium
Learning Objectives: vapor pressure, ideal gas law, dynamic equilibrium

Q15.

As described in the question, the $CO_2(s)$ starts to sublime first when is warmed up as the vapor pressure is low, much smaller than 5.2 atm [triple point], then the pressure in the container increases as more gas CO_2 produced, which might reach 5.2 atm at a certain point before the explosion. If the pressure is higher 5.2 atm, solid CO_2 melts into liquid first, then further vaporize into gas. Thus, **B** is the correct answer, as liquid CO_2 may be observed.

Difficulty: Medium
Learning Objectives: phase diagram; triple point sublimation

Q16.

For a primitive cubic lattice, there is only one atom located at each corner, with 1/8 of its volume inside the unit cell, so there is only one atom in total in the cubic unit cell. And the density can be calculated by using the equation below:

$$d = \frac{m}{V} = \frac{ZM}{N_A a^3}$$

Difficulty: Medium
Learning Objectives: unit cell, solid packing models, density calculation

where Z is the number of formula unit in the cell, $Z = 1$ for a primitive cubic lattice as described above, M is the molar mass of CaB_x, N_A is the Avogadro's constant, a is the edge length of the cube.

$$d = \frac{M}{6.02 \times 10^{23} \text{ mol}^{-1} \times (415 \times 10^{-10} \text{ cm})^3} = 2.45 \text{ g} \cdot \text{cm}^{-3}$$

$M = 105$ g/mol $= 40.1 + 10.8x$, $x \approx 6$, thus, the correct answer is **C**.

Difficulty: Easy

Learning Objectives: lattice energy; Coulomb's law; periodicity

Q17.

According to the *Coulomb's law*, the lattice energy of ionic compounds is proportional to the charges of ions, reversely proportional to the distance between the two adjacent cation and anion. Thus, both *I* and *II* are correct, as Mg^{2+} is smaller than Na^+ due to the higher nuclear charge of Mg^{2+}, which makes the distance between Mg^{2+} and O^{2-} smaller than that between Na^+ and O^{2-}. Both the charge and distance factor play a role in determining the lattice energy.

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

Difficulty: Hard

Learning Objectives: heating curve, ΔH_{fus} vs ΔH_{vap}

Interpretation based on diagrams is important. You may analyze the slope, the intercepts, the cross point, etc. in the diagrams to get the clues.

Q18.

This is a question about the heating curve. It is easy to realize that all four curves have two steady stages to represent the phase changes, melting and boiling, respectively. The major difference is the relative length of the two steady stages.

As the sample is heated at a constant rate, the length of the steady stage represents the heat needed for the phase change, ΔH_{fus} [melting] and ΔH_{vap} (boiling), respectively. As the boiling process needs to separate the molecules further by overcoming more intermolecular forces, ΔH_{vap} is supposed to be greater than ΔH_{fus}, thus, A is the only reasonable answer.

Difficulty: Easy

Learning Objectives: calorimetry; $q = cm\Delta T$

Q19.

The question is about calorimetry, which is based on the conservation of energy. We assume that the heat lost by the hot objects is completely absorbed by the cold object. We can further apply the equation below to solve the problem:

$$q = cm\Delta T = 100.0 \text{ g} \times 4.18 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \times (T_f - 25.0)$$
$$= 100.0 \text{ g} \times 0.385 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \times (50.0 - T_f)$$

$T_f = 27.1$ °C, thus, the correct answer is **A**.

Difficulty: Easy

Learning Objectives: entropy of different phases

Q20.

For a certain substance at the same condition, its solid state has the lowest entropy as it has the smallest disorderness. Thus, the correct answer is **A**.
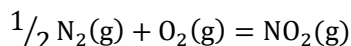
The option D is used to trick you as that $S(\text{gas}) \gg S(\text{liquid}) > S(\text{solid})$ still applies even at the triple point when all three phases coexist.

Q21.

The question is about the estimation of the enthalpy change of a reaction using the bond energies.

$$\Delta H_r = \sum BE(\text{breaking}) - \sum BE(\text{forming})$$

For the formation of $NO_2(g)$, the corresponding reaction is as follow:

$$^1/_2\, N_2(g) + O_2(g) = NO_2(g)$$

$$\Delta H_r = \Delta H_f[NO_2(g)] = {}^1/_2 \times 945.4 + 498.4 - BE(N-O) \times 2 = 33.1$$

$BE(\text{N–O}) = 469.0$ kJ/mol, thus the answer is **A**.

Please be aware there is only 1 mole of $NO_2(g)$ obtained with two moles of N–O bond formed.

Q22.

The free energy change at nonstandard conditions can be determined using $\Delta G = \Delta G^o + RT \ln Q$, where Q is the reaction quotient. Q has the same expression with K, but the concentrations or pressures used are not necessary the equilibrium values.

For a gas reaction, Q_p should be used.

$$\Delta G = -32.8 + 10^{-3} \times 8.314 \times 298 \times \ln\frac{3.00^2}{3.00 \times 3.00^3} = -38.2 \text{ kJ/mol}$$
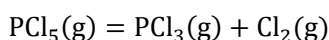
Thus, the correct answer is **D**.

Please be aware that $R = 8.314$ with a unit of $J \cdot mol^{-1} \cdot K^{-1}$ should be used here to match the unit of Gibbs free energy.

Q23.

There is a direct relationship between ΔG^o and the equilibrium constant K: $\Delta G^o = -RT \ln K$. And the ΔG^o of the reaction can be calculated by using the ΔG_f^o of the substances involved in the reaction.

$$PCl_5(g) = PCl_3(g) + Cl_2(g)$$

$$\Delta G_r^o = -286 + 0 - (-325) = 39 \text{ kJ/mol}$$

$$K_p = e^{-\Delta G_r^o/RT} = e^{-39 \times 1000/(8.314 \times 298)} = 1.5 \times 10^{-7}$$

Thus, the answer is **D**.

Please be aware that the ΔG_f^o of $Cl_2(g)$ is zero as it is the stable elemental form of chlorine.

Q24.

Based on the information provided, K_{eq} increases with temperature for the reaction. According the *van't Hoff equation* listed below, the forward reaction must be endothermic, so the $\Delta H_r^o > 0$.

$$\ln K = -\frac{\Delta H_r^o}{R} \times \frac{1}{T} + C, \text{ where } C \text{ is a constant.}$$

You may get the same conclusion using the *Le Chatelier Principle*.

By using the two K_{eq} values at different temperatures, we can calculate the ΔH_r^o:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_\mathrm{r}^o}{R} \times \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta H_\mathrm{r}^o = -\ln(0.50/0.10) \times 8.314 \times 330 \times 300/(300 - 330) = 44 \times 10^3 \text{ J/mol}$$

It is assumed that the ΔH_r^o and ΔS_r^o don't change with temperature.

Furthermore, we can use $\Delta G^o = \Delta H^o - T\Delta S^o = -RT\ln K$ to calculate the ΔS_r^o at either temperature:

$$\Delta S_\mathrm{r}^o = \frac{\Delta H_\mathrm{r}^o + RT\ln K}{T} = \frac{44 \times 10^3 + 8.314 \times 300 \times \ln(0.10)}{300} = 128 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Thus, both I and II are correct, the answer is **C**.

Difficulty: Medium

Learning Objectives: interpretation of time course of a reaction ([R] and [P] *vs t*), half-life, reaction orders

Please be aware that the reaction order with respect to R is NOT necessary to be the same as its coefficient unless the reaction is elementary.

Q25.

It is not hard to figure out that one mole of P is formed for every two moles of R that reacts, so the reaction equation is 2R → P. A good data point to confirm the stoichiometry is at $t = 20$ sec, when reactant (R) decreases from 0.08 M to 0.04 M by 0.04 M, while product (P) increases from 0.00 M to 0.02 M by 0.02 M, so *II* is incorrect.

Based on the concentration change of R with time, you may also observe that the *half-life* is around 20 sec, and it doesn't change with time. So, *I* is correct. A constant half-life is the character of first-order reaction, which can be derived based on the *integrated rate law* of the first order reaction, as shown below:

$$\ln[R] = \ln[R]_0 - kt$$

Thus, the correct answer is **A, I only**.

Difficulty: Medium

Learning Objectives: rate law measurement by initial rates; reaction order

Q26.

Let's suppose that the rate law is rate = $k[A]^m[B]^n$. By comparing the data in trial 1 and 2,

$$\frac{\text{initial rate 2}}{\text{inital rate 1}} = \frac{4.05 \times 10^{-5}}{1.80 \times 10^{-5}} = \left(\frac{0.180}{0.120}\right)^m \left(\frac{0.450}{0.300}\right)^n = 1.5^{m+n} = 2.25$$

We can get $m + n = 2$;

By comparing the data in trial 2 and 3,

$$\frac{\text{initial rate 2}}{\text{initial rate 3}} = \frac{4.05 \times 10^{-5}}{8.00 \times 10^{-6}} = \left(\frac{0.180}{0.080}\right)^m \left(\frac{0.450}{0.200}\right)^n = 2.25^{m+n} = 5.06$$

We can get $m + n = 2$;

Then we realize that we can only get the sum of m and n but NOT the specific value of m or n as the ratio of $[B]_0$ and $[A]_0$ is always 2.50 for all three trials. However, the ratio of $[B]_0$ and $[A]_0$ in trial 4 is 2.00, so its initial rate can't be determined from the information given. The correct answer is **D**.

Difficulty: Medium

Learning Objectives: Arrhenius equation; activation energy; pre-factor A

Q27.

According to *Arrhenius equation* as shown below:

$$k = Ae^{-\frac{E_\mathrm{a}}{RT}}$$

where A is the pre-factor, and E_a is the activation energy.

We can tell that k increase with A, but decreases with E_a. Intuitively, higher activation energy means slower rate.

At 370 K, all six reactions have the same rate constant, so we can conclude that as A increases, E_a should also increase to keep k the same.

Q28.

According to the *Arrhenius equation* as shown above in the annotation for **Q27**, both the forward rate constant and reverse rate constant increase with temperature. So, *I* is correct.

As the products has a lower enthalpy than reactants, the forward reaction is exothermic. According to the *Le Chatelier Principle*, we can conclude that the equilibrium shifts to the reactants side when temperature increases, which means the equilibrium constant K decreases, so, *II* is incorrect.
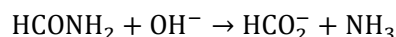
Thus, the answer is **A**.

You may get the same conclusion using the *van't Hoff equation* as described in the annotation for **Q24**.

Difficulty: Medium

Learning Objectives: energy profile of a reaction; rate dependence on temperature; equilibrium constant dependence on temperature

Q29.

By adding all four steps, we get the overall reaction of the hydrolysis of formamide in basic solution:
$$HCONH_2 + OH^- \rightarrow HCO_2^- + NH_3$$
It seems challenging to derive the rate law directly, so the method of elimination should be used here to simplify our analysis.

It is not hard to eliminate option [C] as HCO_2^- is the product rather than the intermediate. As water is only involved in the last step to convert NH_2^- into NH_3, so [D] can be eliminated as the formate ion (HCO_2^-) will not contain the deuterium if the reaction is carried out in D_2O.

Now let's focus on option [A] and [B].

As the product formate (HCO_2^-) is produced only in the third step, we can express the overall rate law using the formation rate of formate as follows:
$$rate_{overall} = \frac{d[formate]}{dt} = k_3[HCO_2(NH_2)^{2-}]$$
Let's abbreviate formamide $HCONH_2$ into FA, and $HCO(OH)(NH_2)^-$ and $HCO_2(NH_2)^{2-}$ can be abbreviated as $FA(OH)^-$ and $FA(O)^{2-}$, respectively.

As the second step is a fast equilibrium, we can apply the *pre-equilibrium approximation* to the step to figure out the expression of $[FA(O)^{2-}]$, which supposes that the consumption of $[FA(O)^{2-}]$ in the third step doesn't affect the equilibrium of the second step:
$$K_2 = \frac{[FA(O)^{2-}]}{[FA(OH)^-][OH^-]}$$
Then we can get $[FA(O)^{2-}] = K_2[FA(OH)^-][OH^-]$.

We can further assume the first step is also at equilibrium state:
$$K_1 = \frac{[FA(OH)^-]}{[FA][OH^-]}$$

Difficulty: Hard

Learning Objectives: rate law; mechanism derivation; pre-equilibrium approximation; intermediate

Picking up the formation or consumption of a certain substance to express the overall rate is critical to derive the rate law. Typically, we choose a substance appeared the least in the steps to make the derivation simple.

Similarly, $[FA(OH)^-] = K_1[FA][OH^-]$. Substituting this into the above $[FA(O)^{2-}] = K_2[FA(OH)^-][OH^-]$, we get: $[FA(O)^{2-}] = K_1K_2[FA][OH^-]^2$. Lastly, we substitute the $[FA(O)^{2-}]$ into the overall rate expression:

$$\text{rate}_{\text{overall}} = k_3[HCO_2(NH_2)^{2-}] = k_3K_1K_2[FA][OH^-]^2$$

we can conclude the overall reaction is first-order in formamide, $HCONH_2$, second order in hydroxide ion. Thus, the correct answer is **A**.

Difficulty: Hard

Learning Objectives: differential and integrated rate law; pseudo kinetic analysis; half-life

Q30.

The irreversible reaction A + B → C is first order in both A and B, we can write:

$$\text{rate} = k[A][B]$$

when $[A]_0 = 0.20$ M, $[B]_0 = 0.010$ M, as $[A]_0 > [B]_0$, we can assume the [A] doesn't change with time, then a *pseudo kinetic analysis* can be used here:

$$\text{rate} = k[A][B] = k'[B], \text{where } k' = k[A]_0$$

The reaction turns to be first order in [B] when [A] is in much excess.

As it takes 37 s for the [B] to decrease from 0.010 M to 0.0050 M, we can say the half-life the reaction $t_{1/2} = 37$ s, based on the integrated rate law of the pseudo first-order reaction:

$$k' = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{37 \text{ s}} = 0.019 \text{ s}^{-1}$$

Then, $k = k'/[A]_0 = 0.019$ s^{-1}/0.20 M = 0.095 s^{-1}·M^{-1}.

When $[A]_0 = 0.010$ M, $[B]_0 = 0.010$ M, we know that [A] is always the same with [B] during the reaction process as their initial concentrations are the same and their consumption rates are the same based on the stoichiometry, then

$$\text{rate} = k[A][B] = k[B]^2$$

Now the rate law is simplified into a second-order reaction in B. Based on the integrated rate law of the second-order reaction as shown below:

$$\frac{1}{[B]} = \frac{1}{[B]_0} + kt$$

Substituting [B] = 0.0050 M, $[B]_0 = 0.010$ M, $k = 0.095$ s^{-1}·M^{-1}, we can calculate $t = 1.1 \times 10^3$ s. Thus, the correct answer is **D**.

Difficulty: Easy

Learning Objectives: percent of ionization; pH calculation of weak acids/bases

Q31.

Percent of ionization of a weak acid is defined as follow:

$$\text{ionization\%} = \frac{\text{dissociated acid}}{\text{total acid}} \approx \frac{[H^+]}{c_{\text{acid}}}$$

The approximation in the last step is based on that the $[H^+]$ dissociated by water is negligible compared that from the acid.

According to the RICE table, the equilibrium concentration of H^+, $[H^+]$ can be calculated as below:

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

$$c_0 - x \quad x \quad\quad x$$

$$\frac{x^2}{c_0 - x} = K_a = 7.2 \times 10^{-4}$$

$$[H^+] \approx x = 8.1 \times 10^{-3} \text{ M}$$

$$\text{ionization\%} = \frac{8.1 \times 10^{-3}}{0.10} = 8.1\%$$

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

A simplified method to approximate $[H^+]$ without solving a quadratic equation is to ignore the acid dissociated and use $[H^+] \approx \sqrt{cK_a} = \sqrt{0.10 \times 7.2 \times 10^{-4}} = 8.5 \times 10^{-3}$ M, which will give you the same answer with a close ionization percent.

Q32.

The Q of the reaction as shown in the diagram can be calculated as follow:

$$Q = \frac{[AB]^2}{[A_2][B_2]} = \frac{4^2}{2 \times 2} = 4 > K_{eq} = 2.5$$

We can conclude that the reaction will shift to produce more reactants, thus, the correct answer is **C**.

Difficulty: Easy

Learning Objectives: Q vs K, shift of equilibrium

Q33.

As the forward reaction is exothermic ($\Delta H_r^\circ < 0$), increasing temperate will shift the equilibrium to the reactants side according to the *Le Chatelier Principle*, thus decreasing the equilibrium yield of the CH_3OH, *I* is incorrect. And CH_3OH is a pure liquid in the system, so removing some of it doesn't affect the equilibrium position, *II* is incorrect. Thus, the correct answer is **D**.

Difficulty: Easy

Learning Objectives: Le Chatelier Principle

Q34.

The minimum concentration of each anion to start the precipitation can be calculated as follows:

$$[SO_3^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{6.8 \times 10^{-8}}{1.00} = 6.8 \times 10^{-8}$$

$$[F^-] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]}} = \sqrt{\frac{5.3 \times 10^{-9}}{1.00}} = 7.3 \times 10^{-6}$$

$$[PO_4^{3-}] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]^3}} = \sqrt{\frac{1.0 \times 10^{-25}}{1.00^3}} = 3.2 \times 10^{-13}$$

Obviously, the anion with a lower minimum concentration will precipitate first, which is PO_4^{3-}, then SO_3^{2-} follows and F^- is the last one to precipitate.

The correct answer is **B**.

Difficulty: Medium

Learning Objective: precipitation equilibrium; K_{sp}

Difficulty: Super Hard

**Learning Objectives**:

solubility vs pH

$S = [M^{n+}]$ for B, C, and D, while $S = \frac{1}{2} [Ag^+]$ for A.

Q35.

All four precipitates are made by cation and conjugate base of a weak acid (HA). Therefore, higher pH shifts the dissociation equilibrium of HA to the side with the conjugate base, A^-.

As K_{sp} is a constant, higher $[A^-]$ decreases the cation concentration, resulting in a smaller molar solubility S, which is consistent with the graph, log S decreases with pH linearly first, and then reaches a plateau region. The plateau region is caused by the *steady* $[A^-]$ when pretty much all the acid is deprotonated at high pH. Thus, by analyzing the pH of the plateau region, we may get some sense of the pK_a of the acid. According to the Henderson-Hasselbalch equation, when pH = pK_a + 2, the conjugate base, A^- is the dominate form in the solution ($[[A^-]/[HA] = 100]$) and its concentration doesn't increase significantly with pH anymore. So based on the pH where the curve starts to level off, we may read the pK_a of each conjugate acid. So, we can eliminate [B] (AlPO$_4$) as PO$_4^{3-}$ is such a strong base that changes in solubility would be observed up to a very high pH. Similarly, we can also eliminate [C], SrSO$_4$, as SO$_4^{2-}$ has a much larger K_a (pK_a of HSO$_4^- \approx 2$, the first dissociation of H$_2$SO$_4$ is complete). The extrapolations of the descending line and the flat asymptote intersect at the pK_a, which is shown the figure below.

That leaves us with AgC$_2$O$_4$ and BaF$_2$, which have similar pK_as. The next level of discrimination is based on whether the acid is monoprotic or diprotic. This would not affect the appearance of the plateau—in all cases, there is only one leveling off point, where the fully deprotonated species becomes the dominant species in solution. What you would see with a diprotic acid such as oxalate is a "*kink*" in the linear descent region as the solubility equilibria go from involving two protons (steeper slope at lower pH) to involving only one

CaCO$_3$ solubility vs. pH

proton (shallower slope at moderate pH) before leveling off where no protons are involved in the solubility equilibria (zero slope at sufficiently high pH). The figure above is a plot of log S of CaCO$_3$ vs pH with the extrapolation lines to show you the location of pK_{a1} and pK_{a2}, as well as the "*kink*" with different slopes. It is worthy to point out that the extrapolation of two descending lines intersect at pK_{a1} = 6.37, while the extrapolations of the descending line and the flat asymptote intersect at the pK_{a2} = 10.25. Thus, we can eliminate the option [A] AgC$_2$O$_4$ with the conjugate base of a diprotic acid as we clearly see there is only one slope in the figure, which is consistent with the monoprotic acid option **D** [BaF$_2$].
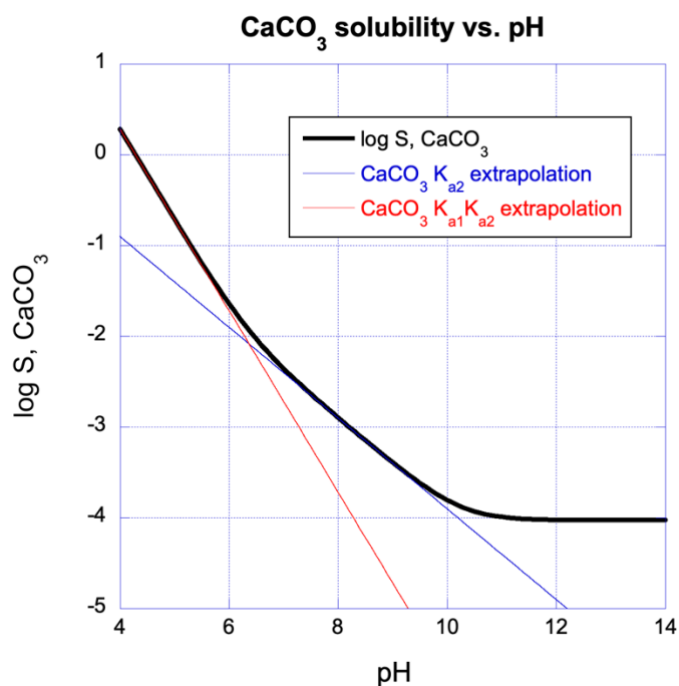
A comparison between the plot for BaF_2 and $Ag_2C_2O_4$ (for the latter, $pK_{a1} = 1.23$, $pK_{a2} = 4.19$, $K_{sp} = 5.4\times10^{-12}$ was used) is attached for your reference.

BaF_2 vs. $Ag_2C_2O_4$ Comparison
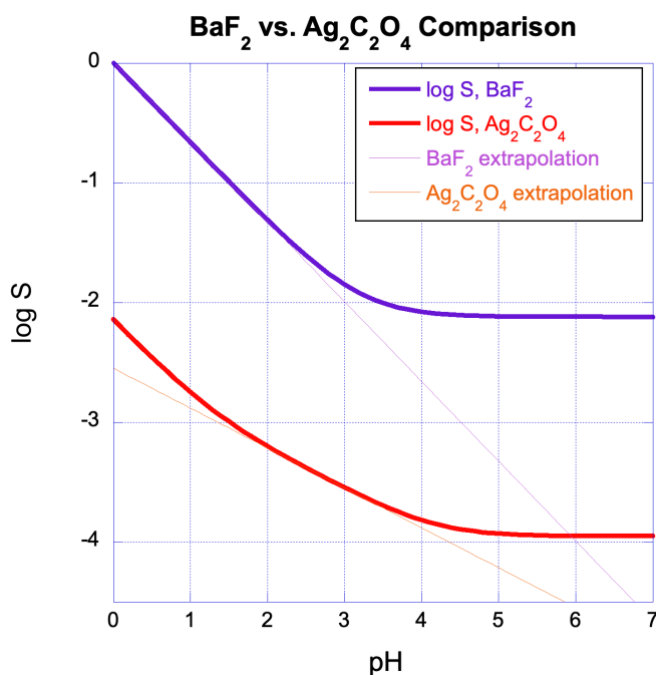
Special thanks to Dr. Seth Brown for his insightful contributions to the annotations of this question!

Difficulty: Hard

Q36.

Learning Objectives:
solubility equilibrium;
complex equilibrium;
multiple equilibrium.

When 50.0 mL of 1.00 M NaCl solution is added 100.0 mL of 1.00 M NH_3 solution, the new $[Cl^-]$ and $[NH_3]$ with the dilution considered are calculated as follow:

$$[Cl^-] = \frac{50.0 \text{ mL} \times 1.00 \text{ M}}{50.0 \text{ mL} + 100.0 \text{ mL}} = 0.333 \text{ M}; \quad [NH_3] = \frac{100.0 \text{ mL} \times 1.00 \text{ M}}{50.0 \text{ mL} + 100.0 \text{ mL}} = 0.667 \text{ M}$$

So, the minimum $[Ag^+]$ at equilibrium state to see the first sign of cloudiness is calculated based on the solubility product constant K_{sp}:

$$[Ag^+]_{eq} = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.333} = 5.4 \times 10^{-10} \text{ M}$$

Considering the dilution of all ions during the mixing is critical for getting the correct results.

Obviously, this is not a good reflection of the amount of $AgNO_3$ added, as most Ag^+ is complexed by ammonia.

So, we need to further apply the complexation equilibrium as shown below:

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_f = 1.0 \times 10^8$$

$$
\begin{array}{cccc}
c_0 & 0.667 & 0 \\
-x & -2x & +x \\
c_0 - x & 0.667 - 2x & x
\end{array}
$$

Here, we make c_0 the initial concentration of Ag^+ in the 150.0 mL solution after the mixing rather than before the NaCl solution is added. By doing this, we can ensure that all initial and equilibrium concentrations are in the same system, a 150.0 mL of mixed solution.

where c_0 is the initial concentration of Ag^+ in the 150.0 mL solution.

As K_f is very large, we can assume that the complexation goes to complete, thus, $x \approx c_0$, this is also consistent with a very small $[Ag^+]_{eq} = 5.4 \times 10^{-10} = c_0 - x$. Substitute all values in the K_f expression:

$$K_f = \frac{x}{(c_0 - x)(0.667 - 2x)^2} = \frac{c_0}{5.4 \times 10^{-10} \times (0.667 - 2c_0)^2} = 1.0 \times 10^8$$

We can calculate:

$$c_0 = 0.021 \text{ M}$$

The moles of $[Ag^+]$ equals to moles of $AgNO_3$, which is 0.021 M × 150.0 mL = 3.2×10^{-3} mole, the correct answer is **C**.

Q37.

We may either balance the disproportionation equation of Cl_2 or check the oxidation number [ON] change to get the mole ratio of Cl^- and ClO_3^-. The latter one is actually the key to balance a redox reaction, as ON change reflects the number of electrons transferred. From Cl_2 to Cl^-, the ON of Cl decreases by –1 [0 → –1], while the ON of Cl increases by +5 from Cl_2 to ClO_3^- [0 → +5]. Thus, we can conclude the mole ratio of Cl^- and ClO_3^- is 5:1, and the answer is **A**.

Q38.

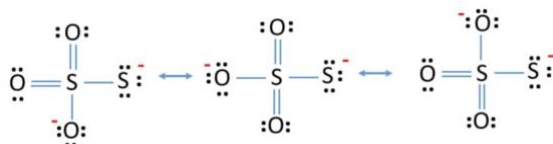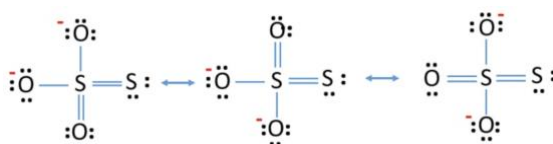To figure out the oxidation states of S atoms in thiosulfate $S_2O_3^{2-}$, we need to draw its structure:

Based on the structures above, we can see that there are five S–O bonds surrounding the central S atom, so its oxidation state of S is +5 as the more electronegative O pull bonding electrons from S. And the terminal S is supposed to –1 as the it carries a negative charge and S–S bond is nonpolar. This clearly rules out the possibility of +6, –2 oxidation states for the S atoms in thiosulfate.

The disproportionation of $S_2O_3^{2-}$ in acidic media produces sulfur element (ON = 0) and SO_2 (ON = +4). Here we assign an average ON +2 to S in $S_2O_3^{2-}$.

You may argue that the oxidation states of S atoms are +4 and 0, respectively, based on another group of resonance structures of thiosulfate. However, there is no corresponding answer in the four options. And these resonance structures with S=S bonds are unstable as the pi bond between two period ≥3 elements is week due to the poor overlap [*check Q53 of Local 2022*], thus they make minor contribution to the real structures.

Thus, the answer is **C**.

Q39.

The percent yield of H_2O_2 can be calculated using the number of electrons to reduce oxygen gas to H_2O_2 divided by the total electron number. As 2 moles of electrons are needed to reduce oxygen gas to 1 mole H_2O_2, we can calculate the percent yield as follows:

$$\text{yield\%} = \frac{2.00 \times 10^{-3} \text{ mol} \times 2e^-/\text{mol}}{\dfrac{110.0 \times 60 \text{ s} \times 0.150 \text{ A}}{96500 \text{ C/mol}}} \times 100\% = 39.0\%$$
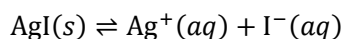
where $F = 96500$ C/mol is the Faraday's constant, meaning the charge of 1 mole of electrons.

Thus, the answer is **B**.

Difficulty: Hard

Learning Objectives: electrolysis; Faraday's law

Q40.

Put the first half reaction on the anode, and the second one on the cathode, we get an overall reaction as follows:

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.15 - 0.80 = -0.95$ V.

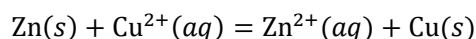Then we can apply the following equation to solve the K_{sp} of AgI.

$$\Delta G^\circ = -RT\ln K = -nFE^\circ_{\text{cell}}$$

$$K_{sp} = e^{\frac{nFE^o_{cell}}{RT}} = e^{\frac{1 \times 96500 \times (-0.95)}{8.314 \times 298}} = 8.5 \times 10^{-17}$$

Thus, the answer is **C**.

Difficulty: Medium

Learning Objectives: K_{sp} measurement using electrochemical methods

Q41.

For this typical Zn-Cu Galvanic cell, the spontaneous reaction is as follow:

$$Zn(s) + Cu^{2+}(aq) = Zn^{2+}(aq) + Cu(s)$$

As the redox reaction runs, the left cell has an elevated concentration of ions as Zn^{2+}(aq) is produced, while the right cell has a reduced concentration of ions as Cu^{2+}(aq) is consumed. The water will flow from the right cell with higher water potential to the left one with lower water potential through the half-permeable membrane, the process is called osmosis.

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

Difficulty: Medium

Learning Objectives: Galvanic cell; electrode reactions; osmosis

Q42.

According to the Nernst equation as shown below:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

When the cell is fully discharged, $E_{\text{cell}} = \Delta E = 0$ V, the cell is "dead" or at equilibrium state. As the mass of Cr(s) changes from 20.0 g to 24.50 g, the concentration of Cr^{3+}(aq) at equilibrium state can be calculated as follows:

$$Cr^{3+}(aq) = 0.10 \text{ M} - \frac{24.50 \text{ g} - 20.0 \text{ g}}{52.00 \frac{\text{g}}{\text{mol}} \times 1.00 \text{ L}} = 0.013 \text{ M}$$

Difficulty: Hard

Learning Objectives: Nernst equation; nonstandard cell

Similarly, we can calculate the concentration of $Zn^{2+}(aq)$ at equilibrium based on $[\Delta n(Zn^{2+})]:[-\Delta n(Cr^{3+})] = 3:2)$:

We can further revise the question and make it more challenging by asking for the cell potential before the switch closed. Readers may try it out to check your understanding.

[Answer = 0.028 V]

$$Zn^{2+}(aq) = 0.10 \text{ M} + \frac{24.50 \text{ g} - 20.0 \text{ g}}{52.00 \frac{\text{g}}{\text{mol}} \times 1.00 \text{ L}} \times \frac{3 \text{ Zn}^{2+}}{2 \text{ Cr}^{3+}} = 0.23 \text{ M}$$

Substitute the concentrations into Q,

$$E_{\text{cell}} = E_{\text{cell}}^{\text{o}} - \frac{RT}{nF}\ln Q = E_{\text{cell}}^{\text{o}} - \frac{8.314 \times 298}{6 \times 96500} \times \ln\frac{0.23^3}{0.013^2} = 0$$

we can get $E^{\text{o}}_{\text{cell}} = 0.018$ V.

Thus, the answer is **B**.

Difficulty: Easy

Learning Objectives:
electron configuration

Q43.

Si has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^2$. So, there are one 1s orbital, one 2s orbital, three 2p orbitals, one 3s orbital, and two 3p orbitals (Hund's rule) occupied by at least one electron.

Thus, the total number of orbitals is 8, and the answer is **D**.

Difficulty: Easy

Learning Objectives:
Bohr's model, Hydrogen's emission spectrum

Q44.

According to Bohr's model for the hydrogen atom, the energy of electron at energy level n is as follows:

$$E_n = -C \times \frac{1}{n^2}, \text{where C is a constant}$$

Then we can conclude that the energy gap between two adjacent energy levels decreases with n, in another word, the energy gap in between $n = 1$ and $n = 2$ is the largest among any adjacent energy levels, corresponding to the shortest wavelength as predicted by $E = h\nu = \frac{hc}{\lambda}$, so we can eliminate [A] and [C]. For [B] and [D], $n = 6 \rightarrow n = 2$ is releasing energy, which emits photons. Thus, the correct answer is **B**, $n = 2 \rightarrow n = 6$.

Difficulty: Easy

Learning Objectives:
electron configuration;
Hund's rule

Q45.

The electron configuration of Cr^{2+} at ground state is $3d^5$ with five unpaired electrons based on the Hund's rule. Similarly, Co^{2+} is $3d^7$ with three unpaired electrons, Ni^{2+} is $3d^8$ with two unpaired electrons, and Zn^{2+} is $3d^{10}$ with no unpaired electrons. Thus, the answer is **A**.

Difficulty: Hard

Learning Objectives:
trends in ionization energy;
diagonal relationship

Q46.

This is an interesting question; we know that ionization energy (*IE*) increases across the period and decreases down the group. However, the element in the diagonal position [top left to bottom right] of F, which is Ar, should have the closet *IE* value, as Ar has a higher *IE* than Cl, but Cl has a lower *IE* than F.

Certain pairs of diagonally adjacent elements from left to right in the second and third periods (first 20 elements) of the periodic table is called *diagonal relationship*, such as Li and Mg, Be and Al, B and Si, etc. Thus, the answer is **D**.

Q47.

In general, stable nuclei have approximately equal number of neutrons as protons, and a strong excess of one or the other will result in an unstable nucleus.[79]Se has 34 protons and 45 neutrons, is likely to have *beta* decay to convert some neutrons into protons with electrons released. The decay equation is as follow:

$$_{34}^{79}\text{Se} \rightarrow _{35}^{79}\text{Br} + _{-1}^{0}e$$
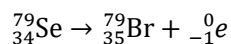
The decayed product [79]Br is a stable and common isotope of Br, as its abundance in earth is around 50%, which confirms our analysis above.

Thus, the answer is **B**.

Q48.

Methods of elimination is always a good way to explain unexpected experimental observations. We can easily eliminate [B], [C], and [D] as they don't seem reasonable in explaining the bond length similarity. The so called "lanthanide contraction", the presence of the 14 lanthanides between Pd and Pt makes Pt unexpectedly small is a reasonable explanation. Thus, the answer is **A**.

[*Quote about lanthanide contraction from Wikipedia*]

The lanthanide contraction is the greater-than-expected decrease in ionic radii of the elements in the lanthanide series from atomic number 57, lanthanum, to 71, lutetium, which results in smaller than otherwise expected ionic radii for the subsequent elements starting with 72, hafnium. The effect results from poor shielding of nuclear charge (nuclear attractive force on electrons) by 4f electrons; the 6s electrons are drawn towards the nucleus, thus resulting in a smaller atomic radius. Usually, as a particular subshell is filled in a period, the atomic radius decreases. This effect is particularly pronounced in the case of lanthanides, as the 4f subshell which is filled across these elements is not very effective at shielding the outer shell (n=5 and n=6) electrons. Thus, the shielding effect is less able to counter the decrease in radius caused by increasing nuclear charge. This leads to "lanthanide contraction". The ionic radius drops from 103 pm for lanthanum(III) to 86.1 pm for lutetium(III). The elements following the lanthanides in the periodic table are influenced by the lanthanide contraction. The radii of the period-6 transition metals are smaller than would be expected if there were no lanthanides and are in fact very similar to the radii of the period-5 transition metals since the effect of the additional electron shell is almost entirely offset by the lanthanide contraction.

Q49.

The best way to compare the bond angle is to draw the Lewis structures and apply the VSEPR model. We can easily conclude that the O–N–O bond angle is 120° in nitrate, NO_3^- as it is trigonal planar, while the bond angle in nitrite is slightly smaller than 120° as it has a bent structure with a lone pair on the central N, as shown below:
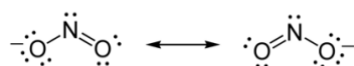
NO$_2$ has similar a Lewis structure with NO$_2^-$ but NO$_2$ is a free radical with an unpaired electron, which makes the bond angle larger 120°, as the repulsion provided by the single electron to the bonding pairs is smaller than that provided by the N–O bonding pair with an average bond order of 1.5. The actual bond angle is 134°.

N$_2$O$_4$, the dimer of two NO$_2$ molecules, has a planar structure, as shown below, so the bond angle is expected to be around 120°. More specific, it should be slightly larger than 120°, as the average bond order of N–O in N$_2$O$_4$ is 1.5, the repulsion between the two N–O bonds is greater than that between the N–O and N–N single bond. The actual bond angle is 126°.
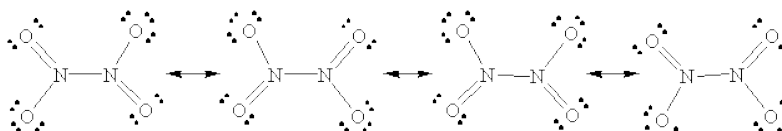
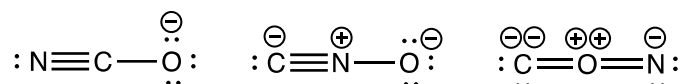Thus, the species with the largest bond angle is NO$_2$, the answer is **A**.

Q50.

Drawing the best resonance structure of each isomer and comparing their formal charges is a good way to compare the stability of different isomers.

You might be able to draw more resonances structures for each isomer.

As we can see, the first one with a central C is the most stable as it has the smallest formal charge, while the third one is the worst. All of three structures are predicted to be linear by VSPER model as there are two electron domains surrounding the central atom.

Thus, the answer is **A**.

Resonance structures are not *isomers*. Isomers have different arrangement of both atoms and electrons. Resonance forms differ only in arrangement of electrons. The real structure (the resonance hybrid) takes its character from the weighted average of all the individual resonance contributors.

Q51.

As elements in different periods can also make strong bonds such as F–H, we can conclude that [D], *whether the orbitals have the same principal quantum number* is the least important consideration in determining the strength of interaction between atomic orbitals on two atoms as they combine to form molecular orbitals. The other three options, including the distance between two atoms [A], the energy

proximity of the orbitals [B], and the relative orientation of the orbitals to overlap [C], are all important factors to determine the bond strength based on the molecular orbital theory.

Thus, the answer is **D**.

Q52.

FNNF has two isomers, *cis* and *trans*, with Lewis structures shown below:


trans   *cis*
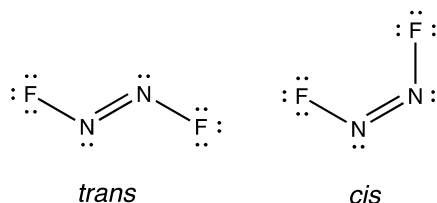
Like the *geometric isomers* of alkenes with C=C double bond, the isomer with both F atoms on the same side of the N=N is called *cis*, while another one with two F atoms on different side is called *trans*. So, [A] is a correct statement.

There are three electron domains surrounding each nitrogen, both isomers are predicted to have a trigonal planar geometry for each nitrogen, thus, [B] is also a correct statement.

Compared to N_2F_4 with a single N–N bond, the N=N bond in N_2F_2 is supposed to be shorter, so, [C] is an incorrect statement.

A reasonable Lewis structure of the *structural isomer* of N_2F_2 is shown below. As there are formal charges on both N, it is less stable than the two *geometric isomers* above without formal charge. [D] is a correct statement.
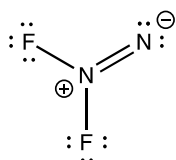

Thus, the correct answer is **C**.

Q53.

As $M(CO)_2BrCl$ can be isolated as two *geometric isomers*, the central metal must be square planar rather than tetrahedral. A tetrahedral structure doesn't form any isomers unless all four groups connected are different, which is just like the chiral carbons. Also, chiral tetrahedral complexes show *optical isomerism* rather than geometric isomers.

The two geometric isomers of $M(CO)_2BrCl$ when M is square planar are *cis* and *trans*, as shown below:

cis   *trans*
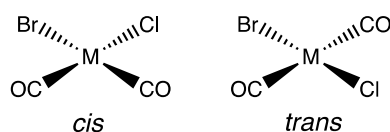
So, *I* is correct, and *II* is incorrect. The final answer is **A**, I only.

Difficulty: Medium

Learning Objectives:
Lewis structures; geometric isomers, *cis* and *trans*; structural isomers

Structural isomers have different atom arrangement, while *geometric isomers* have the same connection but different special arrangement (*cis* vs *trans*).

Difficulty: Easy

Learning Objectives:
isomerism of complexes; geometric isomers; *cis* vs *trans*

Swaping Cl and Br in both *cis* and *trans* isomers doesn't provide any new structures, as they are superimposable with the original one by flipping or rotation.

Difficulty: Medium

Learning Objectives:

conductivity of

semiconductor; *p*-type and

n-type semiconductor;

band theory

Q54.

Pure Si is a semiconductor with poor electric conductivity. The conductivity of Si can be enhanced by doping with a group V element such as As to make a negative-type (*n*-type) semiconductor as there is one extra free electron; or doping with a group III element such as B to make a positive-type (*p*-type) semiconductor as there is a hole. The more doping, the higher conductivity, regardless of the type of doping. So, the three materials in the order of increasing conductivity are pure Si < A < B, the correct answer is **A**.

Band theory is used to explain the conductivity of semiconductors.

[Quote about semiconductor and band theory from LibreText with minor revision]

The figure below shows the structures and band diagrams of n-type and p-type semiconductors (a) doping silicon with a group V element results in a new filled level between the valence and conduction bands of the host. (b) doping silicon with a group III element results in a new empty level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.
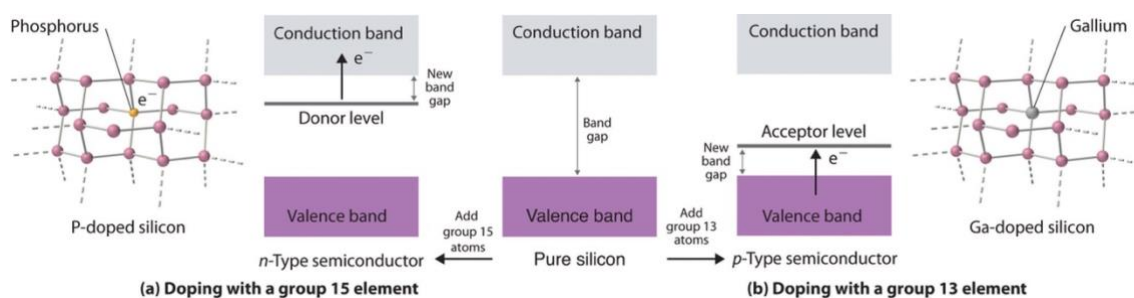
Source: LibreTexts

Difficulty: Easy

Learning Objectives:

Double Bond Equivalence;

common functional groups

Q55.

$C_6H_{12}O$ has a *Double Bond Equivalence* of 1, indicating a double bond or a ring. An acyclic ester [R–C(=O) –O–R'] looks reasonable in terms of the DBE, however, esters have at least two oxygen atoms; Please be aware that *acyclic* means no ring in the structure. A cyclic ether [R–O–R'] perfectly matched the DBE and the number of oxygens of the molecular formula. Thus, the correct answer is **B, II only**.

Difficulty: Hard

Learning Objectives:

electrophilic additions;

conjugated dienes; stability

of carbocations; allylic

Q56.

To figure out the correct answer, we firstly need to understand the mechanism of electrophilic addition reactions of alkenes. As shown below, in the first step, the electrophile X^+ is attacked by the electron-rich C=C (pi electrons) with a new C–X bond formed and a carbocation on the adjacent carbon. The second step is the nucleophile Y^- attacks the carbocation, forming the final addition product. The first step with the pi bond breaking, is slow, thus is the rate-determining step, while the second step is fast with bond formation only. So, the stability of the carbocation is key to the rate of the electrophilic additions, as well as the reactivity of alkenes. The more stable the carbocation intermediates, the faster and more reactive the alkenes towards electrophilic additions are.
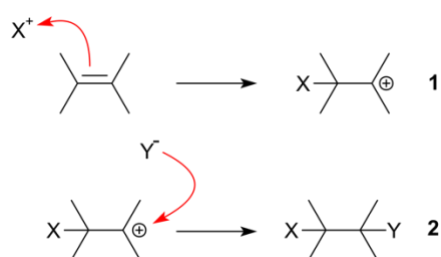
Conjugated dienes are alkenes with two adjacent C=C bonds, such as the 1,3-butadiene. They are called conjugated because the C2–C3 bond has some double bond character, which can be explained by either the resonance structure or the delocalized pi bond model, as shown in the figure below.
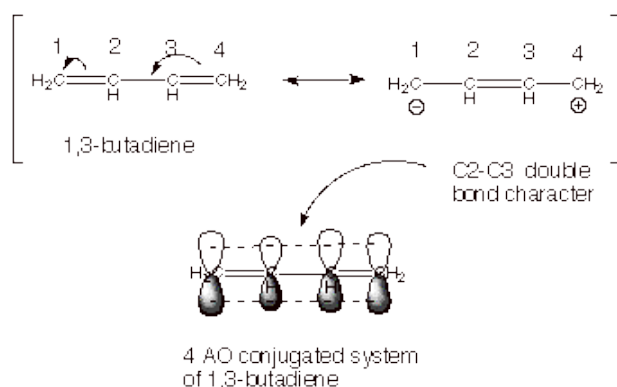

Taking the addition of HBr to 1,3-butadiene for example, when H^+ is added to one of the C=C bond, a stable *allylic* carbocation is obtained as it has two resonance structures, as shown below. Thus, **A** is the correct answer.

A site adjacent to the unsaturated carbon atom is called the allylic position or allylic site. A group attached at this site is sometimes described as *allylic*.
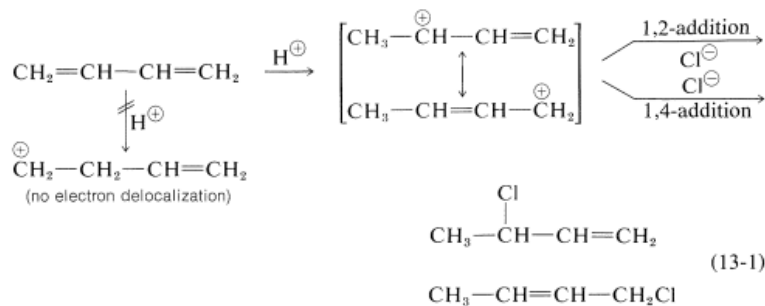
Q57.

A is the hydration product of acetone, which can be catalyzed by a base. D and C is the aldol reaction and the followed dehydration product of two molecules of acetone, respectively, as shown below. The *aldol reaction* can also be catalyzed by a base.

Only B, a 1,2-diol can't be formed directly by acetone with aqueous base.

Thus, the correct answer is **B**.
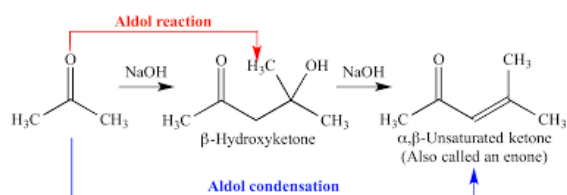
Difficulty: Hard

Learning Objectives: hydration of carbonyl; aldol reaction

Difficulty: Hard

Learning Objectives: IR spectrum.

Q58.

The stretching frequency of C=O in different carbonyl compounds is proportional to its bond strength, as chemical bonds are vibrating just like the spring, as shown by the equation below.

$$f \propto \sqrt{\frac{k}{\mu}}$$

where f is frequency of the vibration, k is bond constant, which represents the bond strength, and μ is the reduced mass.

According to the equation, stronger bonds vibrate faster and so do lighter atoms.

The unit used here is wavenumber, which is 1/wavelength. Wavenumber is commonly used in IR spectrum and is proportional to the frequency as expected by $f = hc/\lambda$.

All the four molecules are carbonyl compounds, A is an aldehyde, B, C, and D is an amide, an ester, and an acyl chloride, respectively, which are all carboxylic acid derivatives (CADs). The C=O vibration is one of the most characteristic peaks in the IR spectrum with a typical stretching frequency of 1650-1850 cm^{-1} depending on the type. As all C=O bonds involve the same atoms with the same reduced mass, the key factor of their frequencies is the strength of the bond, which can be reflected by the resonance structures. For C=O with a heteroatom X connected (X = N, O, or halogens, all having lone pair), we can draw another resonance structure with C–O$^-$ and C=X$^+$ (X = N, O, and Cl) for all three CADs, as shown below:

major   minor
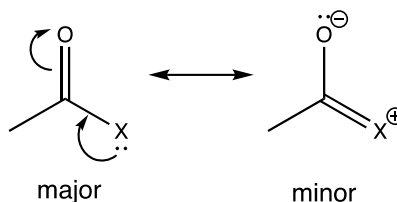
The more stable the minor resonance is, the higher contribution the minor one makes to the actual structure, in another word, the C=O has a larger character of being single, and thus lower stretching frequency.

Let's first compare the amide [B] with the ester [C], the resonance of the amide with N carrying the positive charge is the more stable than that of the ester with O carrying the positive charge, as N is less electronegative than O, then we can conclude stretching frequency is amide < ester (B < C). Then let's compare the amide [B] with the acyl chloride [D], as Cl is in the third period, the overlap between an 3p orbital on chlorine and the 2p orbital on carbon is poor, thus, the minor resonance with C=Cl is unstable, and its contribution is negligible for the acyl chloride. However, there is another competing factor to affect the frequency, the induction. Inductive effect is caused by the electronegativity, as Cl is more electron negative than C, the polar C–Cl bond will attract lone electrons from oxygen to strengthen the C=O. In other words, the electron-withdrawing induction here makes the C=O stronger with a higher stretching frequency. This also explains why acyl chloride absorbs at higher frequency than the regular carbonyl compounds, aldehydes and ketones. In summary, electron-donating resonance effect makes the C=O weaker with lower stretching frequency, while electron-withdrawing inductive effect makes it stronger with higher frequency.

Thus, the C=O with the lowest stretching frequency is in amide, **B**, while acyl chloride has the highest.

Q59.

Alkenes [C=C] and alkynes [C≡C] can react with H^+ through electrophilic addition with a carbocation formed as the intermediate, like the discussion in annotations for **Q54**. In general, C≡C is less reactive than C=C because the π electrons are "held" more tightly in C≡C bonds than in C=C bonds. The sp hybridized carbons in a C≡C is more electronegative than the sp^2 hybridized carbons in a C=C because sp hybrid has a higher percent of lower-energy s orbital. A higher percent of s orbital lowers the energy of the carbon and makes it less reactive towards electrophilic addition.

There is another way to explain why the electrophilic addition of alkynes is slower than the corresponding reaction with alkenes. The difference in rate can be attributed to the high-energy, *vinylic* carbocation intermediate that is formed when an alkyne is protonated. Similarly, a higher s-character in the vinylic carbocation can further deplete the carbon atom and make it more electron deficient that makes the carbocation highly unstable. So, we can eliminate [C] and [D].

For [A] and [B], more substituted alkene in [A] has a pi bond with higher electron density and is more reactive towards electrophilic attack by H^+ as the alkyl substitutes are electron-donating.

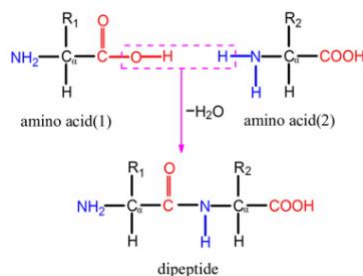Thus, the alkene in A reacts fastest with aqueous acid, the answer is **A**.

Difficulty: Hard

Learning Objectives: reactivity of alkenes and alkynes; electrophilic addition

The vinyl cation is a carbocation with the positive charge on an alkene carbon. Its general formula is $R_2C=CR^+$.
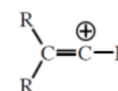
Q60.

Amino acids form peptides through the dehydration of the carboxylic acid group in one amino acid and the amine group in another amino acid, as shown below:

amino acid(1)   −H_2O amino acid(2)

dipeptide

Two different amino acids, H_2N–①–COOH and H_2N–②–COOH, can form four dipeptides, H_2N–①–①–COOH, H_2N–①–②–COOH, H_2N–②–①–COOH, H_2N–②–②–COOH, as H_2N–①–②–COOH is different from H_2N–②–①–COOH. If we follow this strategy, twenty amino acids can form 20×20 = 400 dipeptides as there are 20 choices for the #1 amino acids and 20 choices for the #2 amino acids. Thus, the correct answer is **D**.

Difficulty: Medium

Learning Objectives: formation of peptides; isomer counting