

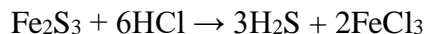
2020 National Exam Part I

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1. Sulfide is a base and reacts with acids to give the conjugate acid H_2S . Reaction is:



so we have 1.5 mol HCl (1 mol Fe_2S_3)/(6 mol HCl) = 0.25 mol, i.e. **A**.

2. 10.0 g $\text{CH}_4 \rightarrow 625$ mmol CH_4 . 15.0 g $\text{O}_2 \rightarrow 468$ mmol O_2 . We find $(468/2) = 234$ mmol of CH_4 is consumed, so 390 mmol remains, i.e., 6.25 g, i.e., **D**.

3. If you think about it a little bit, since each sample has the same mass, the answer should simply be the compound/substance whose atoms have the lowest molar mass on average. This is **B**, since it has a lot of hydrogen atoms compared to other substances.

4. The formula of nitric acid is HNO_3 , and it dissociates completely into H^+ and NO_3^- . Note that each mole of magnesium nitrate has two moles of nitrate ions.

$$c_{\text{NO}_3^-} = n_{\text{NO}_3^- \text{ total}} / V_{\text{total}}$$

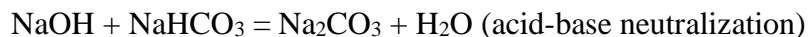
$$= [(0.2000 \text{ L})(c_{\text{HNO}_3}) + (0.3000 \text{ L})(0.200 \text{ M})(2)] / (0.2000 \text{ L} + 0.3000 \text{ L}) = 0.500 \text{ M.}$$

Solve for c_{HNO_3} , to get 0.650 M, i.e., **B**.

5. The total moles of Na^+ is $(0.50 \text{ M})(1.00 \text{ L}) = 0.50$ mol; the total moles of HCO_3^- is $(0.10 \text{ M})(1.00 \text{ L}) = 0.10$ mol.

$$n(\text{Na}^+ \text{ total}) = n(\text{NaOH}) + 3 \times n(\text{Trona}) = 0.50 \text{ mol} \quad \textcircled{1}$$

Each mole of NaOH consumes one mole of NaHCO_3 to give Na_2CO_3 , as shown below



$$n(\text{HCO}_3^- \text{ total}) = n(\text{Trona}) - n(\text{NaOH}) = 0.10 \text{ mol} \quad \textcircled{2}$$

Solving $\textcircled{1}$ and $\textcircled{2}$ gives $n(\text{Trona}) = 0.15$ mol; $n(\text{NaOH}) = 0.05$ mol, i.e., **A**.

6. NaCl adds more weight to the solution without increasing the volume much. Also, NaCl is denser than water. Increasing the concentration of nonvolatile species in a solvent decreases the freezing point. **B II only**.

7. Potassium is lilac, calcium is brick-red, strontium is also red, barium is "apple green." I once took a chemistry test that asked for which element gave an "apple green" color; copper and barium were both options! Apparently the greenish-blue flame test of copper isn't quite "apple green." **D**.

8. Color in substances is created when a substance reflects the color in question, or if it absorbs the complement of that color. Since a colorimeter measures absorbance, we pick the *complementary color* of the species in question. An easy way to remember the complement of a color is to put ROYGBIV in order on the corners of a hexagon (omit indigo); opposing colors on the hexagon will be complementary (color wheel). Thus, the complement of blue CoCl_4^{2-} is orange, which is closest to **C**.

9. Leaving a fridge open is a bad idea, because it will absorb heat from your warm room and spoil all the food. Similarly, a cold calorimeter without its lid will equilibrate with the room it's in faster. The observed temperature drop will be smaller than it should be, so the magnitude of ΔH will be too small. **C**.

10. NaN_3 reacts with acids to give the *extremely* explosive HN_3 , which really wants to form the stable N_2 and go to what has been described humorously as "entropic heaven." HN_3 is technically not a gas at room temperature and is a volatile liquid (b.p. = 35.7°C), so the question should really say vapor, but nobody is perfect. HClO_4 is *very* dangerous, but it is a strong acid, so it is difficult to protonate ClO_4^- ; it's not a gas either. SO_2 is toxic, but not explosive. CO_2 is both non-explosive and not toxic, which is a good thing! **A**.

11. Ethanol is oxidized to acetic acid, which cannot be oxidized further, so no gas is formed. Dichromate is reduced to Cr^{3+} , which causes a color change from orange to green. **A, I only**

12. The acetates of barium and copper are both soluble. Both carbonates are insoluble, but barium carbonate is colorless (generally speaking all alkali and alkaline earth salts are colorless, except if the anion is weird). CuCO_3 is responsible for the Statue of Liberty's green patina (more specifically speaking, $\text{Cu}(\text{OH})_2(\text{CO}_3)_2$). **D**.

13. This is a hard question. Highest vapor pressure means smallest intermolecular forces. CCl_4 and CBrCl_3 are very heavy and have very large dispersion forces, so they are fairly obviously not correct. But it's a tossup between CHCl_3 and CFCl_3 . F is actually not very heavy, and due to its small size, the dispersion forces are quite weak and comparable to that in CHCl_3 . Then it comes down to dipole forces. The F cancels out the pull of the 3 chlorine atoms, so it has weaker dipole forces. **B**.

14. For these kinds of questions it's often easier to just choose arbitrary numbers that work well so you don't need to think in terms of variables. We can imagine a system with 1 mol of liquid and 2 mol of vapor, and a volume of V . Then we double the volume to $2V$. *If* there was liquid remaining, the pressure would be constant (held at the vapor pressure) and the same as before (vapor pressure equals the K_p of the vaporization process, which is a constant at a certain temperature), and there would be 4 mol of vapor, but there are only 3 mol of substance total.

So, all liquid is actually vaporized, and the pressure is only $\frac{3}{4}$ of what it was before as the initial pressure is proportional to $2 \text{ mol}/V$ and the final one to be $3 \text{ mol}/2V$, i.e., a 25% decrease. **B.**

15. Hydrogen bonds are interesting in that they are actually a combination of electrostatic interactions and a *partial covalent bond*; for details read a textbook on inorganic chemistry. The bottom line is that a hydrogen bond is an interaction between *exactly* one hydrogen atom and *exactly* one lone pair as a result. NH_3 is limited in its ability to form H-bonds since it only has one lone pair; HF is also limited since it only has one hydrogen atom. Each H_2O molecule can form 2 H-bonds on average, though its H-bonds are slightly weaker than that in HF due to the smaller electronegativity difference. The answer is **A.**

16. NH_3 molecules attract each other pretty strongly, even in the gas phase, which reduces the volume of the gas compared to ideality (attractions between molecules reduce the average distance between molecules). The other gases have weak intermolecular forces since they are all nonpolar. **B.**

17. OF_2 and ClO_2 are both gases at STP since they are molecular solids with weak intermolecular forces. Then it comes down to MgF_2 and SiO_2 ; the covalent network of SiO_2 is very strong. **C.**

18. The repeating unit of the structure of solid potassium is a cube with an atom in the center of the cube, which is called body-centered cubic. **B.**

19. These problems can be solved easily with a little bit of psychology: there *must* be a solution, so you just need to track the compounds that match up and add everything up (Hess's Law actually). We want to form C_2H_2 , so we reverse reaction (1). This requires 2 mol of CO_2 , and only reaction (2) also has CO_2 , so multiply by 2. Reaction (1) also requires one mol of H_2O , so we add reaction (3) since it's the only other reaction with H_2O .

$$-\Delta H_1 + 2\Delta H_2 + \Delta H_3 = 156.7 \text{ kJ/mol.}$$

We know that acetylene is a pretty combustible gas, so we should expect a modest positive value (positive standard enthalpy of formation means the substance is thermodynamically unstable), so this checks out. Note that we don't need to go through the grunt work of guessing and checking what reactions add up, and then checking (although you should check if you have time). **C.**

20. Solids have the least entropy, followed by liquids, then gases. Choice **D** actually has very little entropy change. The correct choice is therefore **A.**

$$21. n = 2.00 \text{ g}/(184.92 \text{ g/mol}) = 10.8 \text{ mmol}$$

$$q_{\text{calorimeter}} = mc\Delta T = (100.0 \text{ g} + 2.00 \text{ g})(4.184 \text{ J/g/K})(21.56 \text{ }^\circ\text{C} - 23.00 \text{ }^\circ\text{C}) = -614 \text{ J}$$

$$\Delta H = -q_{\text{calorimeter}}/n = 56.9 \text{ kJ/mol so } \mathbf{D.}$$

22. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; for this to be a line ΔS° is a constant.
 $\Delta G^\circ/T = \Delta H^\circ(1/T) - \Delta S^\circ$; for this to be a line ΔH° is a constant.
 ΔG° versus temperature is not a constant.

By the way, someone noted that ΔH° can change linearly with temperature and it would keep linearity. The problem with this thinking is that if ΔH° is non-constant, this implies non-negligible heat capacities, and this also makes ΔS° a non-constant. Therefore, we have to assume that heat capacities are negligible. **B II only.**

23. The “tipping point” for stability, i.e., when $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ is 0, then $T = \Delta H^\circ/\Delta S^\circ = 287 \text{ K} \rightarrow 13.8 \text{ }^\circ\text{C}$ for the conversion of Sn(white) \rightarrow Sn(grey). Since ΔH° is negative and ΔS° is also negative, gray tin is stable at low temperatures ($\Delta G^\circ < 0$). The correct answer is **B**.

Interestingly, old pipe organs suffered from “tin pest,” since in the cold medieval European winters, the tin pipes would convert from the metallic, white form, to the brittle gray form, expanding in the process!

24. for $\text{Ag}_2\text{SO}_4(\text{s}) = \text{Ag}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
 $S = [\text{SO}_4^{2-}]$; $[\text{Ag}^+] = 2 \times [\text{SO}_4^{2-}] = 2S$ by charge balance.
 $K_{\text{sp}} = [\text{SO}_4^{2-}][\text{Ag}^+]^2$, and $\Delta G^\circ = -RT \ln K$
 $-\Delta G^\circ/RT = \ln K_{\text{sp}} = \ln([\text{SO}_4^{2-}][\text{Ag}^+]^2) = \ln(4S^3) = 3 \times \ln S + \ln(4) = (-\Delta H^\circ/R)(1/T) + C$
 $\ln(S) = (-\Delta H^\circ/3R)(1/T) + C'$, so the slope is $-1/3 \times \Delta H^\circ/R$; $\Delta H^\circ = (-3) \times (-689.92) \times 8.314 = 17.2 \text{ kJ/mol}$, so **D** is correct.

Whenever you see something related to $\ln(K)$ or ΔG° plotted against $1/T$, you should be suspicious; the van't Hoff equation might be useful!

25. Average rate = $-(0.3 \text{ M} - 0.6 \text{ M})/10 \text{ min} = 0.03 \text{ M min}^{-1}$, so **A**.

26. Since A has a constant half-life, we are seeing pseudo first order conditions, rate = $k[\text{A}]^1[\text{B}]^b[\text{H}^+]^h = k'[\text{A}]$ since neither [B] nor $[\text{H}^+]$ changes with time during the consumption of A, $k' = k[\text{B}]^b[\text{H}^+]^h$. Remember that half-life is inversely proportional to the rate constant, and since doubling [B] halves the half-life (double the rate constant k'), it's first order in B too, $b = 1$. A pH increases from 1 to 1.5 indicates H^+ decreasing by a factor of $10^{-1}/10^{-1.5} = 3.16$. This causes an increase in the half life by $190/60 = 3.16$ times, so H^+ is also first order, $h = 1$. **A**.

27. $20.0 \text{ min} = 1200 \text{ s}$. Based on the integrated rate law of second-order reaction:
 $1/[\text{NOCl}]_t = 1/[\text{NOCl}]_i + kt$.
 Plug in 0.043 M and 1200 s to get $[\text{NOCl}]_t = 36 \text{ mM}$, so **B** is correct.

28. Let k_a be the rate constant for alpha decay, and k_b be the rate constant for beta decay. Since both decays are first order, we can add the rate constants to get the overall rate constant.

Thus: $k_{\text{overall}} = k_a + k_b = \ln(2)/t_{1/2 \text{ overall}} = 0.693/60.6 \text{ min} = 0.0114 \text{ min}^{-1}$. Furthermore, we know that it undergoes beta decay $(64.1/35.9) = 1.79$ times more often than alpha, so $k_b = 1.79 \times k_a$.

$k_a = 0.00411 \text{ min}^{-1}$, $t_{1/2 a} = \ln(2)/k_a = 169 \text{ min}$. **D**.

29. Let the forward rate constant be k_f , and the reverse rate constant be k_r . $k_f = k_r$ since $K_{\text{eq}} = 1$.

Thus,

$$-d[A]/dt = k_f[A] - k_r[B] = k_f([A] - [B]) = k_f([A] - ([A]_0 - A)) = k_f(2[A] - [A]_0) = 2k_f([A] - 0.5[A]_0).$$

You could use calculus to prove that $\ln([A] - 0.5[A]_0)$ vs t is linear, but it should be clear without.

You can think about this intuitively by saying the rate is proportional to how much of the reaction is left to go, which kind of makes sense. **B** is correct.

30. If the first step is slow and the second step is fast, we may use steady-state approximation for the intermediate Cl, since it is formed slowly in the first step and consumed fast in the second step.

$$\text{So } d[\text{Cl}]/dt = k_1[\text{NO}_2\text{Cl}] - k_{-1}[\text{NO}_2][\text{Cl}] - k_2[\text{NO}_2\text{Cl}][\text{Cl}] = 0,$$

where k_1 , k_{-1} , k_2 are the rate constant of the forward reaction of the 1st step, backward reaction of the 1st step, and the 2nd step, respectively.

$$[\text{Cl}] = k_1[\text{NO}_2\text{Cl}]/(k_{-1}[\text{NO}_2] + k_2[\text{NO}_2\text{Cl}]) \quad \textcircled{1}$$

$$\text{Rate (overall)} = d[\text{Cl}_2]/dt = k_2[\text{NO}_2\text{Cl}][\text{Cl}] \quad \textcircled{2}$$

Substitute $\textcircled{1}$ into $\textcircled{2}$, we got

$$\text{Rate (overall)} = k_1 k_2 [\text{NO}_2\text{Cl}]^2 / (k_{-1}[\text{NO}_2] + k_2[\text{NO}_2\text{Cl}])$$

Since the first step is slow, we can assume $k_{-1}[\text{NO}_2] \ll k_2[\text{NO}_2\text{Cl}]$,

so rate (overall) = $k_1[\text{NO}_2\text{Cl}]$, I is constant.

If the first step is fast, and the second step is slow, we may assume that the first step reach equilibrium state, then

$$k_1[\text{NO}_2\text{Cl}] = k_{-1}[\text{NO}_2][\text{Cl}], [\text{Cl}] = k_1[\text{NO}_2\text{Cl}]/(k_{-1}[\text{NO}_2]) \quad \textcircled{3}$$

$$\text{Rate (overall)} = d[\text{Cl}_2]/dt = k_2[\text{NO}_2\text{Cl}][\text{Cl}] \quad \textcircled{4}$$

Substitute $\textcircled{3}$ into $\textcircled{4}$, we got

$$\text{Rate (overall)} = k_1 k_2 [\text{NO}_2\text{Cl}]^2 / (k_{-1}[\text{NO}_2]), \text{ neither I nor II is constant.}$$

So only II is inconstant regardless of the relative rates of two steps. **B**.

There might be a quick way to figure out the answer without deriving the mechanism as shown above, which is left for readers to work on.

31. ΔH is positive, so increasing T will force the reaction forward according to the Le Chatelier Principle. Since the net pressure in the piston is constant, adding Ar will increase the volume and decrease the total pressure of the substances involved in the reaction, forcing the reaction forward to produce more moles of gas molecules. Both of these processes consume SO_2Cl_2 . **C**.

32. Total concentration of formate and formic acid is $0.500/2 = 0.250$ M in the mixture. Total concentration of acetate and acetic acid is $0.100/2 = 0.0500$ M. Let [formate] = $[A^-]$, [formic acid] = [HA], [acetate] = $[B^-]$, and [acetic acid] = $[HB^-]$. Let the K_a of formic acid be called K_{a1} and that of acetic acid be K_{a2} .

Use charge balance: $[Na^+] + [H^+] = [A^-] + [B^-]$.

From mass balance: $[A^-] + [HA] = 0.250$, $[HA] = [A^-] \times ([H^+]/K_{a1})$, $[A^-](1 + [H^+]/K_{a1}) = 0.250$, so $[A^-] = 0.250(1 + [H^+]/K_{a1})^{-1}$. Likewise, $[B^-] = 0.0500(1 + [H^+]/K_{a2})^{-1}$.

$[Na^+] = 0.0500$ M. $[H^+] = 0.250(1 + [H^+]/K_{a1})^{-1} + 0.0500(1 + [H^+]/K_{a2})^{-1} - 0.0500$

This equation is very hard to solve by iteration but using a good calculator it can be done.

$[H^+] = 7.2 \times 10^{-4}$ M, pH ~ 3.14 .

A better solution:

Notice that the reaction $HA + B^- \rightarrow A^- + HB$ has $K = 10$. In other words, we can assume that the majority of the acetate will be protonated. Thus, we can guess that $[HB] = 0.0500$ M, $[B^-] = 0$ M, so $[A^-] = 0.0500$ M, and $[HA] = 0.250 - 0.0500 = 0.200$ M. pH = $pK_{a1} + \log([A^-]/[HA]) = 3.15$. At pH = 3.15, $[HB]/[B^-] = 40.7$. Thus, our assumption was reasonable, the majority of acetate ion is indeed protonated. **B** is correct.

33. $[Cd(NH_3)_6^{2+}]/([Cd^{2+}] \times [NH_3]^6) = K_f$,

$[Cd(NH_3)_6^{2+}]/[Cd^{2+}] = 2.6 \times 10^6 \times 0.12^6 = 0.776$, $0.776/(1 + 0.776) = 44\%$. **A**.

34. $[Sr^{2+}] = \frac{1}{2}[OH^-]$. $K_{sp} = [Sr^{2+}][OH^-]^2 = \frac{1}{2}[OH^-]^3 = 0.0020$, $[OH^-] = 0.16$ M, pOH = 0.80

pH = $14 - pOH$, so **D** is correct.

35. Volume is increased, but moles are the same, so everything is just a little bit more dilute. The equivalence point and pH there is of course the same. Since everything is a little bit more dilute, the pH at the beginning and end will be closer to neutral, i.e., **A**.

36. Let the forward reaction for $X \rightleftharpoons Y$ have rate constant k_f and the reverse reaction have rate constant k_r . Then $K_Y = k_f/k_r$. Looking at the graph, one thing that should clue us in is that at some time, $d[Y]/dt = 0$. In other words, $d[Y]/dt = k_f[X] - k_r[Y] = 0$. We then have $k_f[X] = k_r[Y]$.

$K_Y = k_f/k_r = [Y]/[X] \approx 3.2 \text{ atm}/0.4 \text{ atm} = 8.0$, i.e., **B**.

This is remarkable! Even though the overall system has not equilibrated, we can still determine the equilibrium constant *as long as the concentration of Y is constant at an instant*. I encourage you to think about this.

37. Here is my procedure for balancing redox equations quickly and efficiently:

a) Determine oxidation states. Mn in $Mn(OH)_2$, MnO_4^- , and MnO_4^{2-} is +2, +7, and +6 respectively.

b) Write the unbalanced half reactions: $Mn(OH)_2 \rightarrow MnO_4^{2-} + 4 e^-$; $MnO_4^- + e^- \rightarrow MnO_4^{2-}$

c) Balance the electrons: $\text{Mn}(\text{OH})_2 + 4\text{MnO}_4^- \rightarrow 5\text{MnO}_4^{2-}$

d) Balance charges with hydroxide or H^+ as necessary according to the acid-base property of the medium: $6\text{OH}^- + \text{Mn}(\text{OH})_2 + 4\text{MnO}_4^- \rightarrow 5\text{MnO}_4^{2-}$

e) Add H_2O to balance: $6\text{OH}^- + \text{Mn}(\text{OH})_2 + 4\text{MnO}_4^- \rightarrow 5\text{MnO}_4^{2-} + 4\text{H}_2\text{O}$.

So, the correct answer is 1:5, i.e., **D**. Note that we could have stopped at step c).

38. You can't just add the voltages for unbalanced half reactions!

It is better to add Gibbs free energies since it is a state function:

Since the 3rd half reaction actually = 1st one - 2nd one,

$$\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ = -F(n_1E_1^\circ - n_2E_2^\circ) = -n_3FE_3^\circ$$

$$E_3^\circ = (5(1.51 \text{ V}) + 2(-1.23 \text{ V}))/3 = +1.70 \text{ V}, \text{ so } \mathbf{D}.$$

$$39. n(e^-) = It/F = 1.2 \text{ A} \times 153 \text{ min} \times (60 \text{ s/min}) / (96500 \text{ C/mol}) = 0.114 \text{ mol } e^-$$

If the metal is a 2+ ion, there are 0.057 mol of metal; $3.92/0.057 = 68.7 \text{ g/mol}$, which doesn't match any of the options. If it's a 3+ ion, then we get a molar mass of 103.2 g/mol, which is Rh, so the answer is **C**. You should know the common oxidation states of the metals based on the group number or number of valence electrons.

40. Catalysts have no impact on the theoretical thermodynamic data. The hydrogen-oxygen fuel cell has reaction $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$, which has negative ΔS° . Thus, increasing the temperature makes ΔG° more positive, i.e., reducing the potential. **D neither I nor II**.

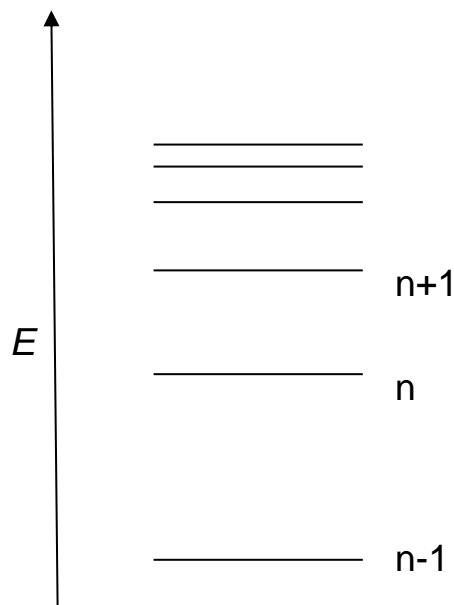
41. This mixture is called aqua regia, or royal water, although I would not recommend drinking it, even if you have royal blood. Simply using concentrated nitric acid or hydrochloric acid can't oxidize Au to Au^{3+} , because the standard reduction potential of $\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$ is too high. The chloride ion in the aqua regia can complex Au^{3+} , lowering down the reduction potential through stabilizing it as AuCl_4^- . Thus, concentrated nitric acid can oxidize Au into Au(III). **A**.

42. Note that the right half-cell is at standard state and does not affect the Nernst equation. This is a concentration cell, so E° is 0 by the way.

The overall reaction of the concentration cell here is $\text{M}^{n+}(1.00 \text{ M}, \text{cathode}) \rightarrow \text{M}^{n+}(\text{variable concentration}, \text{anode})$, $E = E^\circ - RT/nF \times \ln([\text{M}^{n+}]/1.00) = E^\circ - 0.0592/n \log([\text{M}^{n+}])$. The slope is $\approx -0.240/4.0 = -0.060$, so n is clearly 1. **A**.

Please be aware of the conversion from the natural logarithm (ln) to the logarithm with a base of 10 (log) during the calculation.

43. See the Rydberg equation. Energy is proportional to $(1/n_{\text{final}}^2 - 1/n_{\text{initial}}^2)$. Some number crunching shows that **D** has the largest effect. You can think of it this way: the energy levels look like this, getting closer and closer at higher values of n :



You can see that going from n to $n-1$ has the biggest gap.

44. **A** has a big jump from first to second ionization energy, so it forms a 1+ ion. **C** is similar. **B** and **D** have a big jump from 2nd to 3rd ionization energy, so they form 2+ ions. 2+ ions form stronger lattices than 1+ ions according to Coulomb's Law. **D** has a higher ionization energy, so it's probably a smaller atom, which also forms a stronger lattice. **D** is correct.

45. N and P both have negligible electron affinities due to their half-filled p subshells; adding another electron causes repulsion and loss of exchange energy. It turns out that S has a larger electron affinity than O, since O is quite small and there is a lot of repulsion when adding another electron. Similarly, Cl has a larger electron affinity than F though F is more electronegative than Cl. **D** is correct.

46. The oxidation number of metal elements in both TcO_4^- and ReO_4^- are +7, whereas RuO_4 and OsO_4 are +8. You might think +8 is stronger than +7, and you'd be right. It turns out that the heavier transition metals are more stable in their higher oxidation states, so RuO_4 is strongest. **B**.

47. Just draw the relevant orbitals and populate them based on the electron configuration. Be is $[\text{He}] 2s^2$, so it has 0 unpaired electrons. Al is $[\text{Ne}] 3s^2 3p^1$, so it has one unpaired p electron. Ti is $[\text{Ar}] 4s^2 3d^2$, so it has 2 unpaired d electrons. Cu is $[\text{Ar}] 4s^1 3d^{10}$, so it has one unpaired s electron. **C** is correct. You should memorize the anomalous electron configurations of certain transition metals, especially those in the 4th period.

48. See photoelectric effect. Electrons are only emitted if the incident light energy per quanta of light (i.e., a photon) is greater than some threshold called the work function (ϕ). The magnitude of

the work function is determined by the property of the metal. The energy of the electron (kinetic energy) is the energy of the photon minus the work function, so it's constant here if the laser wavelength is still 300 nm. The number of electrons emitted is proportional to the power of the incident light. So, **A** is correct.

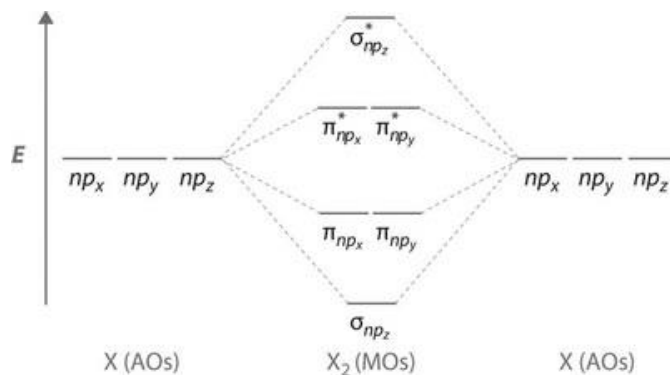
49. H–F has the shortest, and thus strongest bond. **A**.

50. NO_3^- is trigonal Planar with a bond angle of 120° , NO_2^- is bent with a bond angle of slightly smaller than 120° , FNO_2 is trigonal planar, and NF_3 is trigonal pyramidal with a bond angle of slightly smaller than 109.5° . Thus, NF_3 has the smallest bond angles, so **D**. Interestingly, due to the high electronegativity of F, the N–F bond is mostly a N p-orbital, whereas the lone pair is mostly a N s-orbital. This phenomenon is called Bent's rule. It turns out that NF_3 has a *smaller* bond angle than NH_3 , despite sterics.

51. Azide ion is linear; it's isoelectronic to CO_2 . The N atoms in $\text{N}_2\text{O}_2^{2-}$ have lone pairs (O–N=N–O), so they are bent. **A I only**.

52. The nitrogen atom is actually trigonal planar, since the nitrogen lone pair is in resonance with the carbonyl atom. If you are confused, read about the annotated solution of question #53 in local 2017 or the structure of amides. **A**.

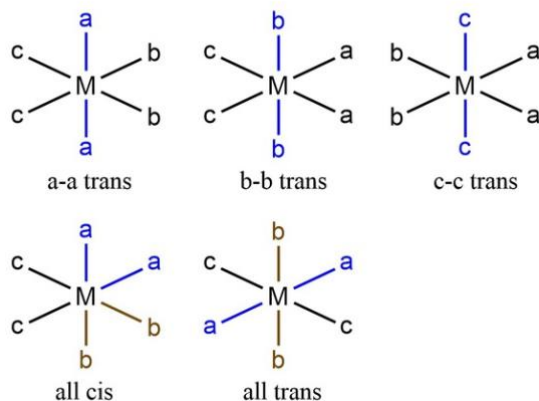
53. The answer is apparent from an MO diagram of Cl_2 , which is similar to that of O_2 with no s–p mixing but two more valence electrons, as shown below. Based on the orbital diagram ($\sigma^2\pi^4\pi^{*4}$), the lower antibonding orbital in Cl_2 is filled, and it is higher than the orbitals in atomic Cl. It turns out that Cl_2 is easy to break apart into radicals with UV light, which is an important part of its reactions, such as the free radical-based chlorination of alkanes. **C**.



54. The complex ion has six ligands; thus, it has an octahedral structure. Drawing out all of the isomers is left as an exercise for the reader :) Be warned that some of the isomers are optically

active if there is neither a mirror plane nor inversion center in the structure (all *cis* one), so you need to count their mirror images too. **C**.

5 geometrical isomers by formula $Ma_2b_2c_2$



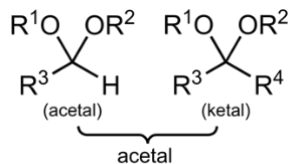
55. A molecule is chiral if it has no mirror plane or inversion center. Replacing H^I with Cl retains a vertical mirror plane. Replacing H^{II} gets rid of the mirror plane. **B II only**.

56. The bonds in the aromatic ring are roughly identical and have a bond order of about 1.5 due to resonance. Bond **C** is clearly a single bond. Bond **D** has the most double bond character, so it is the correct answer.

57. The transition state looks roughly like this: $[HO \cdots C(H_3) \cdots Br]^{-\ddagger}$. This is pentacoordinate, so trigonal bipyramidal **C**. If you are confused, read about the S_N2 reaction.

Please be aware of the difference between the transition state and intermediate, the carbocation in S_N1 reaction is the intermediate.

58. Compound **B** is an acetal $R_2C(OR')_2$, product formed through dehydration of aldehyde/ketone with 2 $-OH$ groups, as shown below), and if you look carefully, you can see that there is no way for it to react with hydroxide. Indeed, acetals are used to protect carbonyl compounds against bases. So, **B** is correct. **A** is a hemiacetal ($R^1R^2C(OH)OR$), reacts with hydroxide to expel methoxide, leaving CH_3CHO . **C** can undergo an aldol condensation in base; aldehydes are very reactive towards such reactions. Even aldehydes without alpha hydrogens will react in base via the Cannizzaro reaction. **D** is an ester and undergoes base hydrolysis to form acetate and methanol.



source: Wikipedia

59. The reaction is $\text{AcCl} + \text{Me}_2\text{NH} \rightarrow \text{AcNMe}_2 + \text{HCl}$. The HCl has to go somewhere, and it protonates another equivalent of Me_2NH to form the unreactive salt $[\text{Me}_2\text{NH}_2^+][\text{Cl}^-]$. This is why such reactions either are conducted with excess amine/base, or in a basic solvent like pyridine. **A** is correct.

60. This is not an easy question, but in general the alkylation of nitrogen relies on the nucleophilicity of the nitrogen, more specifically, the availability of the lone pair on nitrogen to attack the alkylating agents. We will use the process of elimination. The lone pair on B is involved with resonance with the amide, so is not very nucleophilic. The lone pair on A is conjugated to the aromatic ring, so it is less nucleophilic than the amidine. If you look at the resonance structures regarding nitrogen atoms C and D, you will see that they work together to make C nucleophilic. D is too sterically hindered, and besides, alkylation there would disrupt resonance. Therefore, **C** is most likely to be alkylated. Of course, in reality this mainly depends on what enzyme conducts the reaction.