Chem 1011/1021 Fall semester 2013
Representative Questions for Final Exam — Solutions

1) name of $CuSO_4$: copper(II) sulfate

2a) mass% of Cu in $CuSO_4$ (anhydrous)?

$$\frac{63.55\,g\ Cu}{159.61\,g\ CuSO_4} \times 100\% = 39.8\%$$

b) mass % of Cu in $CuSO_4 \cdot 5H_2O$

$$\frac{63.55\,g\ Cu}{249.685\,g\ CuSO_4 \cdot 5H_2O} \times 100\% = 25.4\%$$

c) # O atoms in 3.47 g $CuSO_4 \cdot 5H_2O$

$$3.47\,g\ CuSO_4 \cdot 5H_2O \times \frac{1\,mol\ CuSO_4 \cdot 5H_2O}{249.685\,g\ CuSO_4 \cdot 5H_2O} \times \frac{9\,mol\ O\ atoms}{1\,mol\ CuSO_4 \cdot 5H_2O} \times \frac{6.022 \times 10^{23}\ atoms}{1\,mol\ atoms}$$

$$= 7.53 \times 10^{22}\ \text{Oxygen atoms}$$

3) mole fraction of sucrose in a soln That is ~15% sucrose by mass

assume 100g total soln

$$14.95\,g\ sucrose \times \frac{1\,mole\ sucrose}{342.296\,g\ sucrose} = 0.0436756\ mol\ sucrose$$

$$85.05\,g\ H_2O \times \frac{1\,mol\ H_2O}{18.015\,g\ H_2O} = \underline{4.7210658\ mol\ H_2O}$$

$$4.7647414\ mol\ total$$

$$\text{mole fraction sucrose} = \frac{\text{moles sucrose}}{\text{total moles}}$$

$$= \frac{0.0436756\ mol\ sucrose}{4.7647414\ mol\ total} = \quad 0.009166\%$$

4) combustion analysis 5.75g unknown compound

$$12.6\,g\ CO_2 \times \frac{1\ mol\ CO_2}{44.009\,g\ CO_2} \times \frac{1\,mol\ C}{1\,mol\ CO_2} = 0.28578\ mol\ C$$

$$2.30\,g\ H_2O \times \frac{1\,mol\ H_2O}{18.015\,g\ H_2O} \times \frac{2\,mol\ H}{1\,mol\ H_2O} = 0.25534\ mol\ H$$

$$0.28578\ mol\ C \times \frac{12.01\,g\ C}{1\,mol\ C} = 3.4322\,g\ C$$

$$0.25534\ mol\ H \times \frac{1.009\,g\ H}{1\,mol\ H} = 0.2576\,g\ H$$

$$\begin{array}{r} 5.75\,g\ total \\ -3.4322\,g\ \ C \\ -0.2576\,g\ H \\ \hline 2.0602\,g\ O \end{array}$$

$$2.0602\,g\ O \times \frac{1\ mol\ O}{16.00\,g\ O} = 0.12876\ mol\ O$$

$$\frac{0.28578\ mol\ C}{0.12876\ mol\ O} = 2.22 \approx 2\tfrac{2}{9} \quad \frac{0.25534\ mol\ H}{0.12876\ mol\ O} = 1.98 \approx 2$$

multiply thru by 4: 8.88 ≈ 9 $\boxed{C_9H_8O_4}$
to get 8 H total

5) $HA + NaOH \longrightarrow NaA + H_2O$ titration, find M_M of HA

$$0.01169\ L\ NaOH \times \frac{0.1125\ mol\ NaOH}{1\ L\ NaOH} \times \frac{1\ mol\ HA}{1\ mol\ NaOH} = 0.001315125\ mol\ HA$$

$$\frac{0.237\,g\ HA}{0.001315125\ mol\ HA} = 180.2\ g/mol$$ is the molecular mass of HA

6) $HA \rightleftharpoons H^+ + A^-$ pH = 2.72, what is K_a?

$pH = -\log_{10}[H^+]$, or $[H_3O^+] = 10^{-pH}$

if pH = 2.72, $[H^+]_{equilib} = 1.9055 \times 10^{-3}\ M = [A^-]_{equilib}$

from Q5, $[HA]_{initial} = \frac{0.0013151\ mol}{0.100\ L} = 1.3151 \times 10^{-2}\ M$

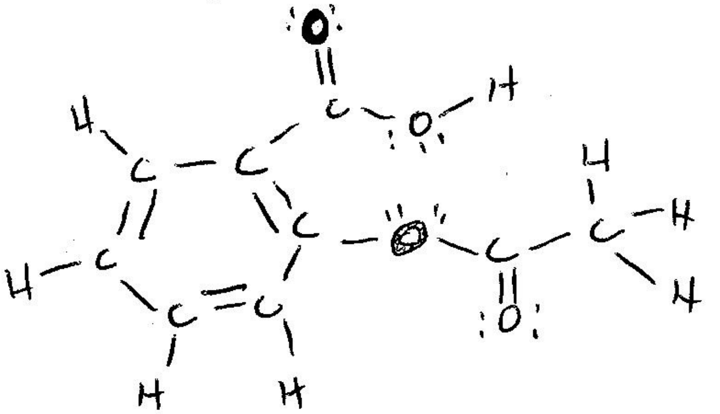
$[HA]_{equilib} = [HA]_{initial} - [H^+]_{equilib}$

$= 1.3151 \times 10^{-2} - 1.9055 \times 10^{-3} = 1.2455 \times 10^{-2}\ M$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(1.9055 \times 10^{-3})(1.9055 \times 10^{-3})}{1.12455 \times 10^{-2}} = \boxed{3.23 \times 10^{-4}}$$

(all at equilib)

7a)



b) <u>21</u> σ bonds
<u>5</u> π bonds

c) black, bolded O has <u>sp2</u> hybridization

d) ideal bond angles around grey, italicized O are <u>109.5°</u>

$\rightarrow K_a = 3.16 \times 10^{-4}$

8a) Aspirin, 180.157 g/mol, pka 3.50 determine pH

$$0.653\,\text{g HA} \times \frac{\text{mol}}{180.157\,\text{g}} \times \frac{1}{0.250\,\text{L}} = 1.4498 \times 10^{-2} \text{ is } [HA]_{\text{initial}}$$

$$\begin{array}{cccc} HA & \rightleftharpoons & H^+ + & A^- \\ 1.4498\times10^{-2} - x & & x & x \end{array} \qquad \frac{x^2}{(1.4498\times10^{-2} - x)} = 3.16\times10^{-4}$$

$$x^2 = (3.16\times10^{-4})(1.4498\times10^{-2}) - 3.16\times10^{-4}x$$

$$x^2 + 3.16\times10^{-4}x - 4.5814\times10^{-6} = 0$$

$$x = \frac{-3.16\times10^{-4} \pm \sqrt{(3.16\times10^{-4})^2 - 4(1)(-4.5814\times10^{-6})}}{2(1)}$$

$$x = 1.9882\times10^{-3} = [H^+] \swarrow$$ This is ~14% of $[HA]_{\text{initial}}$, x cannot be neglected for aspirin

$$pH = -\log_{10}[H^+] = -\log_{10}(1.9882\times10^{-3}) = \boxed{2.70}$$

b) % dissociation of HA

$$\%\text{ dissociation} = \frac{[H^+]_{\text{equilib}}}{[HA]_{\text{initial}}} \times 100\% = \frac{1.9882\times10^{-3}}{1.4498\times10^{-2}} \times 100\% = \boxed{13.7\%}$$

9a) $HA_{(aq)} + NaOH_{(aq)} \longrightarrow NaA_{(aq)} + H_2O(\ell)$ molecular eqn

$HA\ (aq) + \cancel{Na^+\ (aq)} + OH^-\ (aq) \rightarrow \cancel{Na^+\ (aq)} + A^-\ (aq) + H_2O\ (l)$

$$HA\ (aq) + OH^-\ (aq) \longrightarrow H_2O\ (l) + A^-\ (aq)$$

net ionic equ

b) $0.01812 \frac{\text{mol NaOH}}{\text{L NaOH}} \times 0.0100\ \text{L NaOH} = 0.001812$ mol NaOH were added

from Q8, $[H^+] = [A^-] = 1.9882 \times 10^{-3}\ M$

$[HA] = 1.4498 \times 10^{-2} - 1.9882 \times 10^{-3} = 0.0125098\ M$

before adding the NaOH

mol H^+ = mol $A^- = 1.9982 \times 10^{-3} \frac{\text{mol}}{\text{L}} \times 0.250\ \text{L} = 4.9955 \times 10^{-4}$ mol

mol $HA = 0.0125098 \frac{\text{mol}}{\text{L}} \times 0.250\ \text{L} = 3.12745 \times 10^{-3}$ mol

adding NaOH converts 0.001812 mol HA into A^-

after adding NaOH, mol $H^+ = 4.9955 \times 10^{-4}$ mol

mol $A^- = 4.9955 \times 10^{-4} + 0.001812 = 2.3116 \times 10^{-3}$ mol

mol $HA = 3.1274 \times 10^{-3} - 0.001812 = 1.3154 \times 10^{-3}$ mol

The new total volume of the solution is 250 + 10 = 260 mL

so $[H^+] = \frac{4.9955 \times 10^{-4}\ \text{mol}}{0.260\ \text{L}} = 1.9213 \times 10^{-3}\ M$

$[A^-] = \frac{2.3116 \times 10^{-3}\ \text{mol}}{0.260\ \text{L}} = 8.8908 \times 10^{-3}\ M$

$[HA] = \frac{1.3154 \times 10^{-3}\ \text{mol}}{0.260\ \text{L}} = 5.0592 \times 10^{-3}\ M$

now we do the ICE table (continued on next page)

9b, continued)

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

$$5.0592\times10^{-3}+x \qquad 1.9213\times10^{-3}-x \qquad 8.8908\times10^{-3}-x$$

notice that $[A^-] > [HA]$ this suggests that to reach equilibrium again, the rxn must run backwards, with A^- & H^+ recombining to regenerate HA

$$\frac{(1.9213\times10^{-3}-x)(8.8908\times10^{-3}-x)}{(5.0592\times10^{-3}+x)} = 3.16\times10^{-4}$$

$$1.7082\times10^{-5} - 1.08121\times10^{-2}x + x^2 = 1.5987\times10^{-6} + 3.16\times10^{-4}x$$

$$x^2 - 1.1128\times10^{-2}x + 1.5483\times10^{-5} = 0$$

$$x = \frac{1.1128\times10^{-2} \pm \sqrt{(1.1128\times10^{-2})^2 - 4(1)(1.5483\times10^{-5})}}{2(1)}$$

$$= 1.6302\times10^{-3} \text{ or } \cancel{9.49785\times10^{-3}}$$

This answer is bigger than $[A^-]$, so it is impossible

$$[H^+] = 1.9213\times10^{-3} - x = 1.9213\times10^{-3} - 1.6302\times10^{-3} = 2.911\times10^{-4}$$

$$pH = -\log_{10}(2.911\times10^{-04}) = 3.54$$

for comparison,

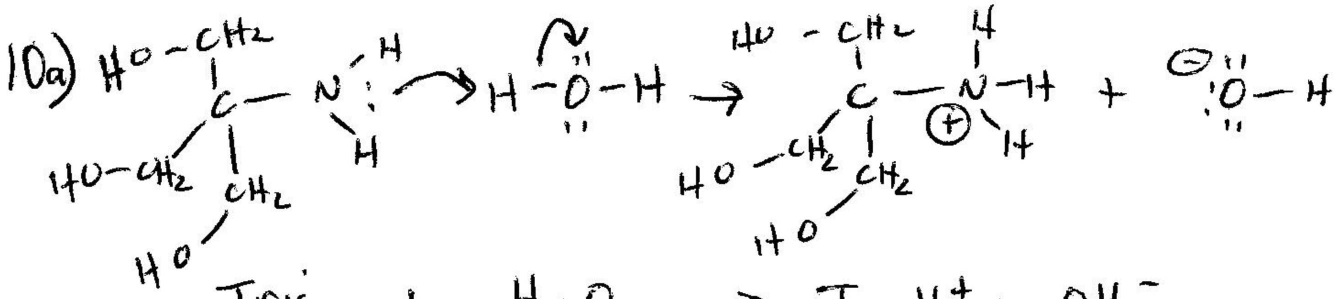
use Henderson-Hasselbach:

$$pH = pka + \log\frac{[A^-]}{[HA]} = 3.50 + \log\frac{8.8908\times10^{-3}}{5.0592\times10^{-3}}$$

$$= 3.74$$

This answer is very different because x cannot be neglected for aspirin! You will probably not see anything where x cannot be neglected on the exam itself, so if you can do this, you will be fine for the exam!

10a)



$$\text{Tris} + H_2O \longrightarrow \text{TrisH}^+ + OH^-$$

$$K_b = \frac{[\text{TrisH}^+][OH^-]}{[\text{Tris}]}$$

b) This is very similar to Example 12.4 & Exercise 12.7 in your textbook, and x can safely be ignored for Tris, allowing us to use the Henderson-Hasselbach equation

$$pH = pKa + \log\frac{[A]}{[HA^+]}$$

$$8.75 = 8.07 + \log\frac{[\text{Tris}]}{[\text{TrisH}^+]}$$

$$0.68 = \log\frac{[\text{Tris}]}{[\text{TrisH}^+]}$$

$$4.7863 = \frac{[\text{Tris}]}{[\text{TrisH}^+]}$$

$$[\text{TrisH}^+] = \frac{[\text{Tris}]}{4.7863} = \frac{0.0125}{4.7863} = 0.002612M$$

$$0.002612\frac{\text{mol Tris·HCl}}{L} \times \frac{157.60\text{g Tris·HCl}}{1\text{ mol Tris·HCl}} \times 0.250L = 0.1029\text{g}$$

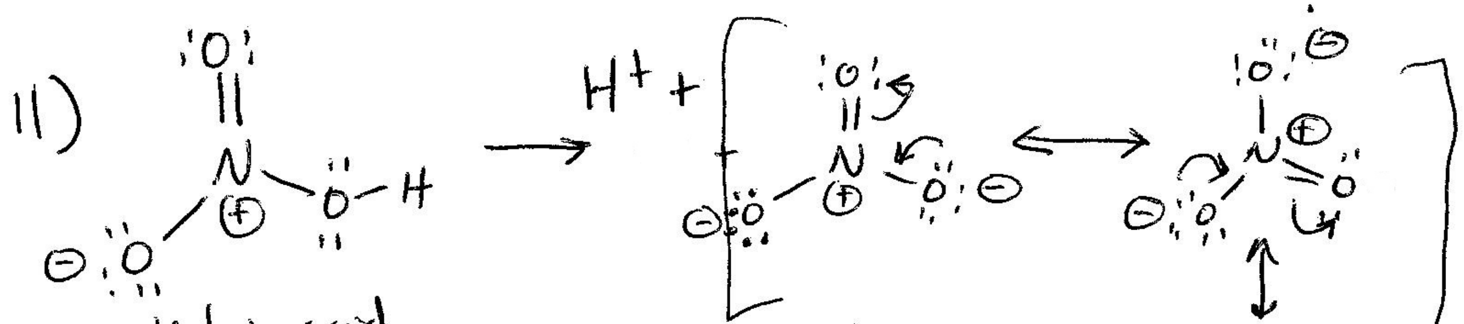
Tris·HCl are needed

c) $M_1V_1 = M_2V_2$

$$V_1 = \frac{M_2V_2}{\cancel{V}M_1} = \frac{(0.0125M)(250mL)}{(0.500M)} = 6.25\text{ mL}$$

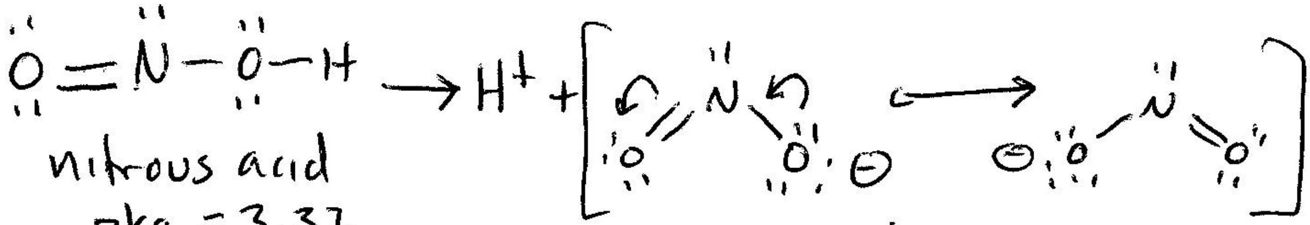
of the stock solution are required

11)



nitric acid
pka ≈ -1.4
(very strong acid)

2 ⊖ charges are shared by 3 O atoms
each O has an average charge of $-2/3$



nitrous acid
pka = 3.37
(weak acid)

1 ⊖ charge is shared by 2 O atoms
each O has an average charge of $-1/2$

greater ⊖charge delocalization & presence of ⊕ formal charge on N cause nitrate anion to be more stable than nitrite anion

12) use $M_1V_1 = M_2V_2$ to determine new [ ]s after mixing

for formic acid: $M_2 = \frac{M_1V_1}{V_2} = \frac{(0.137\,M)(25.0\,mL)}{50.0\,mL} = 0.0685\,M$

for formate: $M_2 = \frac{M_1V_1}{V_2} = \frac{(0.143\,M)(25.0\,mL)}{50.0\,mL} = 0.0715\,M$

Then use Henderson-Hasselbach!

$$pH = pka + \log\frac{[A^-]}{[HA]} = 3.75 + \log\frac{0.0715}{0.0685} = 3.77$$

13) $0.00500\text{ L HCl} \times \frac{0.250\text{ mol HCl}}{\text{L HCl}} = 0.00125\text{ mol HCl}$

H^+ + formate anion ⟶ formic acid

[formate] ↓, [formic acid] ↑

new total volume of solution is
25 + 25 + 5
= 55 mL

from Q12, we can obtain the original moles of HA ; A−:

$0.025\text{ L } HCO_2H \times \frac{0.137\text{ mol } HCO_2H}{\text{L } HCO_2H} = 0.003425\text{ mol formic acid}$

$0.025\text{ L } HCOO^- \times \frac{0.143\text{ M } HCOO^-}{\text{L } HCOO^-} = 0.003575\text{ mol formate}$

after the reaction with HCl:

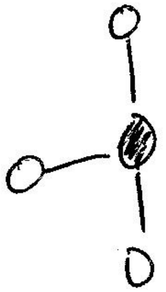
$\text{new } [HCO_2H] = \frac{0.003425 + 0.00125\text{ mol}}{0.055\text{ L}} = 0.08500\text{ M}$

$\text{new } [HCO_2^-] = \frac{0.003575 - 0.00125\text{ mol}}{0.055\text{ L}} = 0.04227\text{ M}$

now use Henderson Hasselbach:

$$pH = pKa + \log\frac{[A^-]}{[HA]} = 3.75 + \log\frac{0.04227}{0.08500} = 3.45$$

14a)



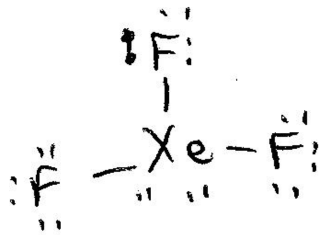
T-shaped

trigonal planar

trigonal pyramidal

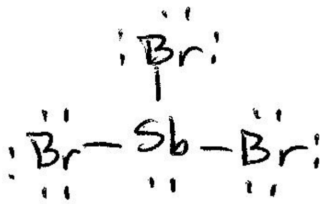
b)

XeF_3^+	$SbBr_3$	$GaCl_3$
$8+(7\times3)-1$	$5+(7\times3)$	$3+(7\times3)$
$28e^-$	$26e^-$	$24e^-$



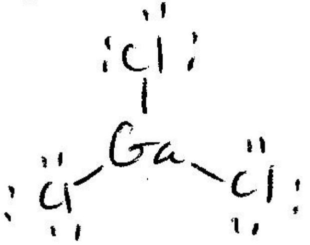
AX_3E_2

T-shaped



AX_3E

trigonal pyramidal



AX_3

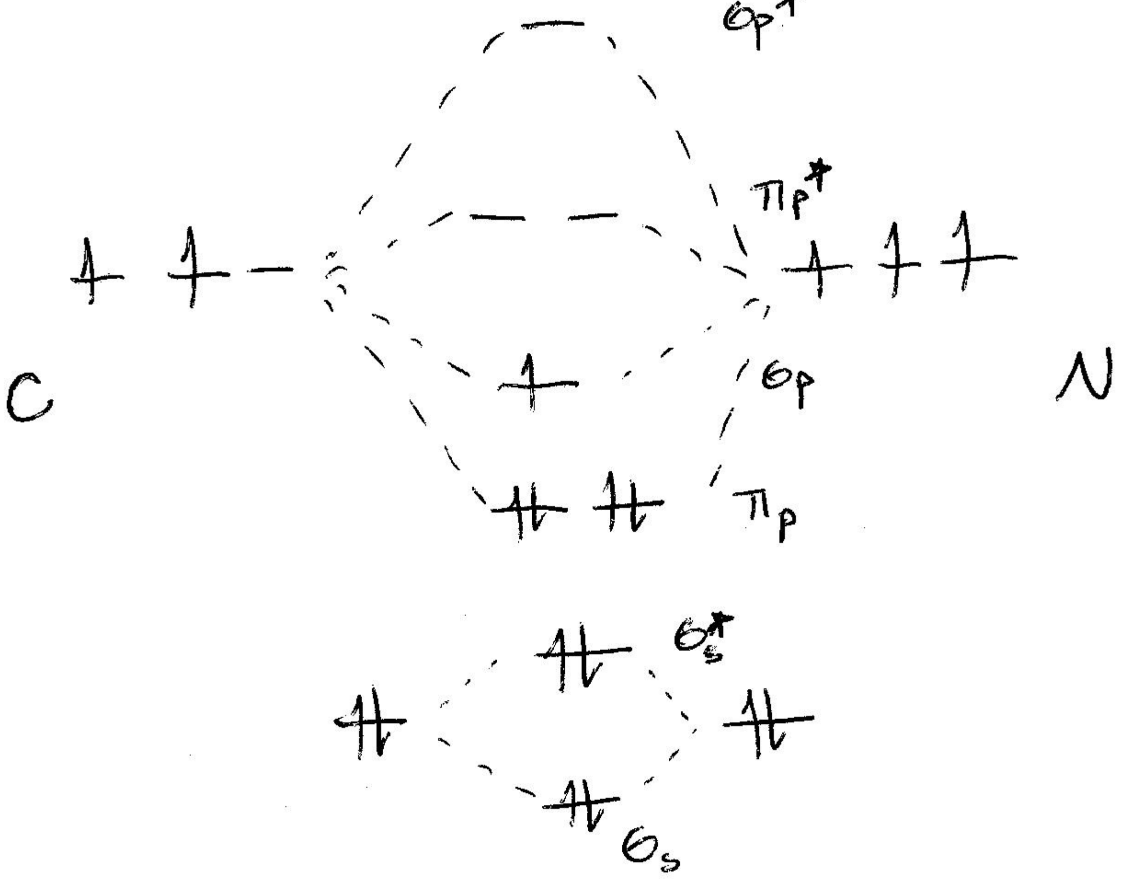
trigonal planar

c) T-shaped & trigonal pyramidal are asymmetrical ∴ polar
trigonal planar is perfectly symmetrical ∴ non-polar
$GaCl_3$/trigonal planar shape is the non-polar molecule

15a) EA generally increases to the right, so O should have a more favorable EA than N

b) IE_1 generally increases to the right/ decreases to the left, so N should have a more favorable IE_1 than O

16) a, b



c) CN is paramagnetic

d) The bond order of CN is 5/2

e) adding 1 more e⁻ to make CN⁻ fills the σp orbital, increasing the bond order to 3 and shortening the C–N bond distance

17) $\Delta E = \frac{hc}{\lambda}$ $\Delta E = E_f - E_i$

$$\Delta E = \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(2.998 \times 10^{3}\ \text{m/s})}{(93.02 \times 10^{-9}\ \text{m})}$$

$$= 2.1355 \times 10^{-18}\ \text{J}$$

$$E_f = -\frac{R_H}{n_f^2} = \frac{2.180 \times 10^{-18}\ \text{J}}{(1)^2}$$

$$= -2.180 \times 10^{-18}\ \text{J}$$

$\underline{n=1}$ for E_f because The Final state is The $\underline{\text{ground state}}$ of The atom

sign is ⊖ because photon was $\underline{\text{emitted}}$

$$-2.1355 \times 10^{-18}\ \text{J} = -2.180 \times 10^{-18}\ \text{J} - E_i$$

$$E_i = -2.180 \times 10^{-18}\ \text{J} + 2.1355 \times 10^{-18}\ \text{J}$$

$$= -4.45 \times 10^{-20}\ \text{J}$$

$$E_i = -\frac{R_H}{n_i^2}$$

$$n_i^2 = -\frac{R_H}{E_i} = \frac{-2.18 \times 10^{-18}\ \text{J}}{-4.45 \times 10^{-20}\ \text{J}} = 48.988 \approx 49$$

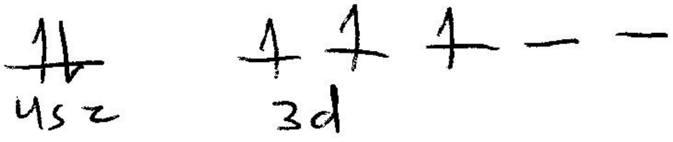
$$\boxed{n_i = 7}$$

18a) vanadium

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

condensed e⁻ config is

b) $[Ar] 4s^2 3d^3$ so valence of vanadium is



c) Vanadium is paramagnetic

d) highest energy e^-s are the $4s^2$

$n=4 \quad l=0 \quad m_l=0 \quad m_s=\pm 1/2$

e) $[V(H_2O)_6]^{2+}$: V^{2+}, d^3

$[V(H_2O)_6]^{3+}$: V^{3+}, d^2

$[VO(H_2O)_5]^{2+}$: V^{4+}, d^1

$[VO(H_2O)_5]^{3+}$: V^{5+}, d^0

molecular

19a) $2KI_{(aq)} + Pb(NO_3)_{2(aq)} \rightarrow 2KNO_{3(aq)} + PbI_{2(s)}$

$\cancel{2K^+}_{(aq)} + 2I^-_{(aq)} + Pb^{2+}_{(aq)} + \cancel{2NO_3^-}_{(aq)} \rightarrow \cancel{2K^+}_{(aq)} + \cancel{2NO_3^-}_{(aq)} + PbI_{2(s)}$

$2I^-_{(aq)} + Pb^{2+}_{(aq)} \rightarrow PbI_{2(s)}$

net ionic

b) $0.01015\ L\ KI \times \frac{0.477\ mol\ KI}{1\ L\ KI} \times \frac{1\ mol\ PbI_2}{2\ mol\ KI} \times \frac{461\ g\ PbI_2}{1\ mol\ PbI_2}$

$= \boxed{1.15\ g\ PbI_2}$

$0.00485\ L\ Pb(NO_3)_2 \times \frac{0.962\ mol\ Pb(NO_3)_2}{1\ L\ Pb(NO_3)_2} \times \frac{1\ mol\ PbI_2}{1\ mol\ Pb(NO_3)_2} \times \frac{461\ g\ PbI_2}{1\ mol\ PbI_2}$

$= 2.15\ g\ PbI_2$

$\boxed{\text{maximum yield of } PbI_2 \text{ is } 1.15g}$

c) KI is the limiting reagent

d) $\%\ yield = \frac{actual\ yield}{theoretical\ yield} \times 100\%$

$= \frac{0.697\ g\ actual}{1.15\ g\ theoretical} \times 100\% = \boxed{60.6\%}$