Chem 1B

Review for final part 3

1. a pentaaquathiocyanoiron (III) ion — orange - absorbs blue-indigo
   hexaaquairon (III) ion — yellow - absorbs indigo-violet
   higher E light ... larger splitting

b.

Both have relatively large ΔE - probably both low spin.

Fe^{3+} $[Ar]3d^5$

$Fe(H_2O)_5SCN^{2+}$: ↿⇂ ↿⇂ ↿ ___

$Fe(H_2O)_6^{3+}$: ↿⇂ ↿⇂ ↿ ___

H_2O is a stronger ligand than SCN^-

2. Experimentally determine the # of unpaired electrons in the complex. Draw both the tetrahedral and square planar splitting diagrams. See which one matches. ex:

d^7: ___ ↿ ↿ ; ↿⇂ ↿⇂ — tet, 3 unpaired

___ ↿ ; ↿⇂ ↿⇂ — 1 unpaired

d^9: ↿⇂ ↿⇂ ↿ ; ↿⇂ ↿⇂ — ↿ ; ↿⇂ ↿⇂ ↿⇂ ↿⇂

doesn't work for this one.

d^8: ↿⇂ ↿ ↿ ; ↿⇂ ↿⇂ — 2 unpaired

↿⇂ ; ↿⇂ ↿⇂ ↿⇂ — diamagnetic

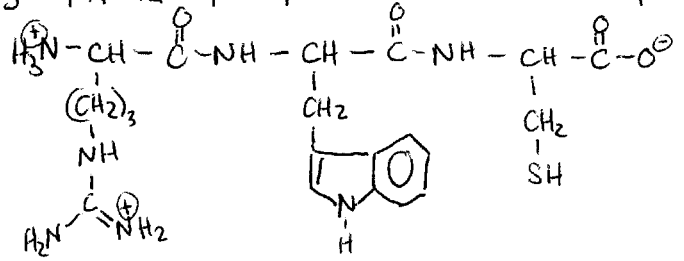
d^6: ↿ ↿ ↿ ; ↿⇂ ↿ — 4 unpaired

___ ; ___ ; ↿⇂ ; ↿⇂ ↿⇂ — diamag.

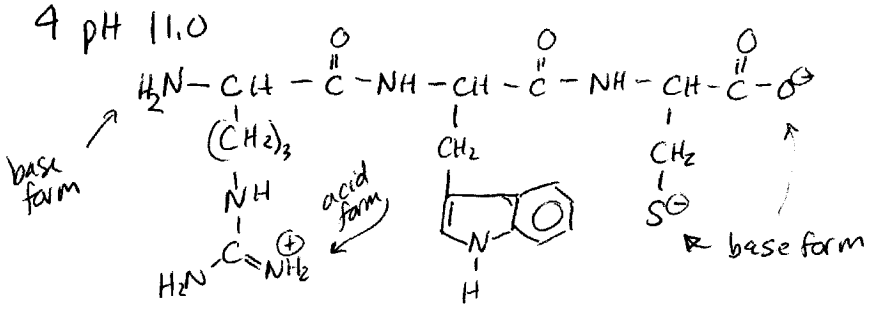
etc!

3. Not necessarily. Some ligands could be bidentate. If it has 4 ligands and 2 of them are bidentate, the coord # would be 6 (for example)

4. Terminal amino pK = 8.0 pH<pK, acid form (pH=5.0)
   Terminal carboxyl pK = 3.1 pH>pK base form
   Arg pK = 12 pH< pK acid form Trp - not acidic/basic Cys pK=8.5 pH<pK acid form



4 pH 11.0



5. Experimentally: mix together reactants, wait, measure amt of products formed
Theoretically: ① If you know value of K: $K<1$ reactant-favored
$K>1$ product favored

② If you can look up values of ΔG, ΔH, S:
calc ΔH° and ΔS°, then find ΔG° at desired temps
if ΔG° is $\ominus$, it's product-favored

③ If it's a redox rxn, look up $\mathcal{E}^\circ$ values and determine E°_{cell}.
If E°_{cell} is $\oplus$, it's product-favored

*Product-favored means mostly products at equilibrium.

6. ① Calculate Q, compare to K. If $Q>K$, then Q must decrease and rxn must go backward $R \leftarrow P$
$Q = \frac{prod}{react}$ If $Q=K$, its at eq. If $Q<K$, Q must ↗ so $R \rightarrow P$

② Calculate ΔG from $\Delta G = \Delta G^\circ + RT \ln Q$
If ΔG is $\ominus$, it will go forward to reach equilibrium. If $\Delta G = 0$, it's at eq.

③ Calculate E using Nernst equation.
If E is $\oplus$, it will go forward to reach eq. If $E=0$ it's at eq.

7. "Lies to the right" means $K>1$ (more products than reactants at eq.)
"Shifts to the right" means $Q<K$ (rxn will go forward to reach eq.)
You can have one without the other. They could also both be true at the same time. If $K>1$ and $Q<K$: Rxn is product favored, and under these (stated) conditions, it will proceed forward to get to equilibrium.
If $K>1$ and $Q>K$: Rxn is product favored. Under the stated conditions, it will proceed in the reverse direction to get to equilibrium.
Could also be the following situations: $K<1$ and $Q<K$ or $K<1$ and $Q>K$

8. CH_3OH (−2, +1, −2, +1) $Cr_2O_7^{2-}$ (+6, −2) CH_2O (0, +1, −2) Cr^{3+} (3+)

8.

$$8H^+ + 3\,CH_3OH + Cr_2O_7^{2-} \rightarrow 3\,CH_2O + 2Cr^{3+} + 7\,H_2O$$

(+12) 2(+6) (+6) (-2) (0)

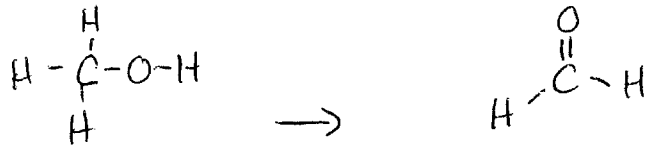
$6e^-$

$3(2e^-)$

Charge: −2 +6

O 3 + 7 = 10

b.



methanol — losing H, getting oxidized, organic definition — formaldehyde

H usually has an ox # of (+1)
O usually (−2)

If something loses H, the ox # of the remaining element gets larger
If it gains O, the ox # of remaining element gets larger.

Likewise, if it gains H and/or loses O, the remaining element (carbon)'s ox # gets smaller. oxidized

9. Normal biological solvent: water. Proteins fold so that nonpolar sidechains cluster together in the interior of the protein (away from water.)
If the normal solvent is replaced by an organic solvent, the "hydrophobic interactions" are disrupted. The protein would fold so that the polar/charged residues are on the interior and the nonpolar side chains are on the exterior of the protein. This destroys the normal folding of the protein, and it will no longer be biologically active.

10. a) * $Au^{3+} + 3e^- \rightarrow Au$ $\mathcal{E}^\circ = +1.50V$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\mathcal{E}^\circ = +0.771V$ reverse, ×3

* $3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^-$ $\mathcal{E} = -0.771$

$Au^{3+} + 3Fe^{2+} \rightarrow 3Fe^{3+} + Au$ $\mathcal{E}^\circ = 0.729$ (spontaneous direction)

If all [ ] are 1.0 M, it's at std. conditions. Voltage = +0.729 V = 0.73V

b) $\Delta G^\circ = -nF\mathcal{E}^\circ = -3(96485 C/mol\,e)(0.729V) = -211002\ J = -211\ kJ$

$\Delta G^\circ = -RT\ln K$ so $K = e^{(-\Delta G^\circ/RT)} = e^{\left(\frac{+211002}{8.314 \cdot 298}\right)} = \cancel{1.1\times10^{37}} = K$

$= e^{85.169}$ $= 9.7\times10^{36}$ (no sf) $= 10^{37} = K$

10. c. To make it <u>more</u> favorable, decrease [products] and increase [reactants] (would cause it to shift more to Rt) so: decrease $[Fe^{3+}]$, increase $[Au^{3+}]$ and $[Fe^{2+}]$

If this happens, the voltage will <u>increase</u>.

$$E = E^\circ - \frac{0.0257\,V}{n} \ln \frac{[Fe^{3+}]^3}{[Au^{3+}][Fe^{2+}]^3}$$

Q will be <u>smaller</u> so ln Q will be smaller. So a smaller # will be subtracted from E°, which means E will be <u>larger</u>.

d. Cl^- added to react w/ Au^{3+}.

This will decrease $[Au^{3+}]$ and make the rxn <u>less</u> favorable. Voltage will <u>decrease</u>.

"Assume that gold (Au^{3+}) is reduced" ... In our regular standard-state rxn, gold <u>is</u> being reduced. So we don't need to reverse the whole reaction.

$$E = E^\circ - \frac{0.0257}{n} \ln Q \quad = 0.31V = 0.729V - \frac{0.0257\,V}{3} \ln Q$$

$$\frac{(3)(0.31 - 0.729)V}{-0.0257\,V} = \ln Q = 48.91 \qquad Q = e^{48.91} = 1.744 \times 10^{21}$$ ~~(probably~~ (no sig figs)

$$Q = \frac{[Fe^{3+}]^3}{[Au^{3+}][Fe^{2+}]^3}$$

Concentrations of Fe^{3+}, Fe^{2+} not mentioned, so they must be the same as before ... 1.0 M

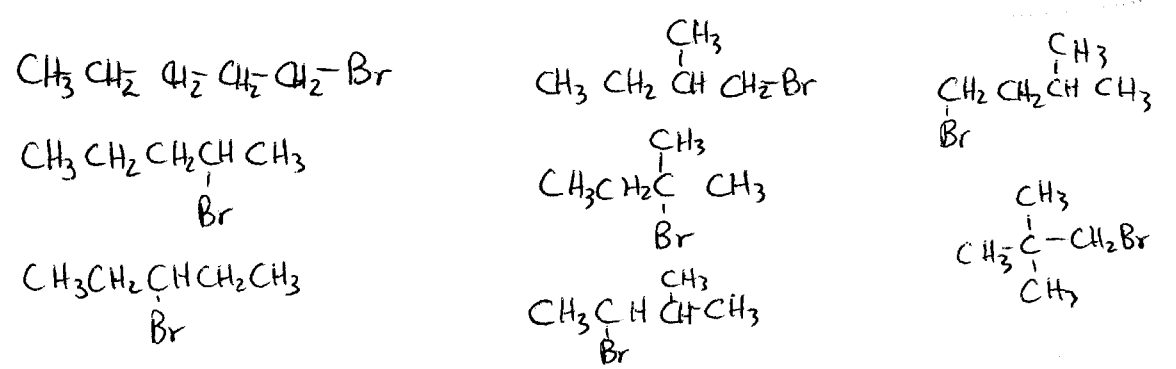
$$[Au^{3+}] = \frac{[Fe^{3+}]^3}{[Fe^{2+}]^3\,Q} = \frac{(1)^3}{(1)^3 Q} = 5.734 \times 10^{-22} = [Au^{3+}]$$

	Au^{3+}	+ $4\,Cl^-$	$\rightleftharpoons AuCl_4^-$
initial	1.0 M	lots	0
Δ	−1.0	−4	+1
eq	5.734×10^{-22} M	0.10 M	1.0 M

$$K = \frac{[AuCl_4^-]}{[Au^{3+}][Cl^-]^4} = \frac{1.0}{(5.734 \times 10^{-22})(0.10)^4}$$

$K = 1.7 \times 10^{25} = K_f$ of $AuCl_4^-$ $= 10^{25}$

11.



12. a. ΔS ⊕ gas is being produced - more disorder

b. find ΔG° @ 25°C

$CaCO_3 \rightarrow CaO + CO_2$

$-1128.79 \quad -604.03 \quad -394.359$

$\Delta G^\circ = (-604.03 - 394.359) - (-1128.79) = +130.40$ kJ NO nonspont.

c. Need to determine signs of ΔH°, ΔS°

ΔH_f	-1206.92	-635.09	-393.509
S	92.9	39.75	213.74

$\Delta H^\circ = (-635.09 - 393.509) - (-1206.92) = +178.32$ kJ

$\Delta S^\circ = (39.75 + 213.74) - (92.9) = +160.59$ J/K

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ both ΔH° and ΔS° are ⊕

will be spontaneous at higher temps ... $|T\Delta S|$ term > $|\Delta H|$ term

d. $\Delta G^\circ = 0 = \Delta H - T\Delta S^\circ$

$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{178.32 \text{ kJ}}{0.16059 \text{ kJ/K}} = 1110 \text{ K} = 837 \text{ °C}$

e. Yes. You could (if you felt like it) determine K at any temp.

At 837°C, ΔG° is 0, so K = 1

at temps higher than 837°C, K > 1

at temps lower than 837°C, K < 1 (reactant favored)

but even a reactant-favored reaction will occur to some extent. There just won't be much products at equilibrium.

13. K_{sp} $PbBr_2 = 6.3 \times 10^{-6}$ K_{sp} $AgBr = 3.3 \times 10^{-13}$

will ppt when $Q = K_{sp}$

$K_{sp} = [Pb^{2+}][Br^-]^2$

$[Br^-] = \sqrt{\frac{K_{sp}}{[Pb^{2+}]}}$

$[Br^-] = \sqrt{\frac{6.3 \times 10^{-6}}{0.010}} = 0.025$ M

$K_{sp} = [Ag^+][Br^-]$

$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{3.3 \times 10^{-13}}{0.20} = 1.65 \times 10^{-12}$ Br^-

AgBr will ppt first.
(starts to ppt at a lower $[Br^-]$)

when $PbBr_2$ starts to ppt,

$[Br^-] = 0.025$ M

so $Ag^+ = \frac{K_{sp}}{[Br^-]} = \frac{3.3 \times 10^{-13}}{0.025} = 1.3 \times 10^{-11}$ M Ag^+

14. a Present: Fe^{2+}, Cl^-, H_2O

possible ½ rxns that contain these as reactants:

$Fe^{2+} + 2e^- \rightarrow Fe$ $E^\circ = -0.447V$ RED

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ $E^\circ = -0.771V$ OX

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^\circ = -0.828V$ RED

$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$ $E^\circ = -1.229V$ OX

$2Cl^- \rightarrow Cl_2 + 2e^-$ $E^\circ = -1.358V$ OX

easiest reduction: $Fe^{2+} + 2e^- \rightarrow Fe$ $E^\circ = -0.447V$

see $Fe_{(s)}$ plating on <u>cathode</u>

easiest oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $E^\circ = -0.771V$

see Fe^{3+} being produced @ anode.

confirmatory test: add SCN^- to form orange complex

b. Present: K^+, Cl^-, H_2O

$K^+ + e^- \rightarrow K_{(s)}$ $E^\circ = -2.931V$ RED

$2Cl^- \rightarrow Cl_{2(g)} + 2e^-$ $E^\circ = -1.358V$ OX

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^\circ = -0.828V$ RED

$6H_2O \rightarrow O_2 + 4e^- + 4H_3O^+$ $E^\circ = -1.229V$ OX

easiest reduction: $2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-$ $E^\circ = -0.828V$ <u>cathode</u>

see bubbles, check pH w/ phenolpthalein - it would turn pink (basic)

easiest oxidation: $6H_2O \rightarrow O_2 + 4e^- + 4H_3O^+$

see bubbles, check pH near anode - should get <u>acidic</u>. (could use methyl red)

c. If you didn't see what you expected: Maybe the rxn with the lowest - rxn (easiest one) is <u>slower</u> than the other possible ½ rxns.

15 a) $Cu^{2+} + 4NH_3 \rightarrow Cu(NH_3)_4^{2+}$ deep blue ⇒ add NH_3, check for deep blue complex.

b) $Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$ orange ⇒ add SCN^-, check for orange complex.

16. a @ beginning: $HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$

	0.10M	lots	~0	0
	$-x$		$+x$	$+x$
	$0.10-x$		x	x

$K_a = \frac{x^2}{0.10-x} = 1.8\times10^{-5}$

$\frac{0.10}{K_a} = \frac{0.10}{1.8\times10^{-5}} = 5.6\times10^{3}$ ok to neglect x

$K_a = \frac{x^2}{0.10}$ $\quad x = \sqrt{(1.8\times10^{-5})(0.10)}$

$x = 1.34\times10^{-3}$ M H_3O^+

pH = 2.87

@ halfway point, HAc = Ac^- and pH = pKa = 4.74

@ endpoint: all HAc has reacted $(0.0250\,L)(0.10\,\frac{mol}{L}) = 0.0025$ mol

HAc +	OH^- →	Ac^- +	H_2O
0.0025	0.0025	0	lots
−0.0025	−0.0025	+0.0025	
0	0	0.0025 mol	

needs 0.0025 mol OH^- to react completely.

$(0.0025\,mol\,OH^-)/(\frac{L}{0.10\,mol}) = 0.025\,L$

need 25.0 mL NaOH to reach endpoint.

now, we have a weak base. Calc M.

$V_{total} = 50.0$ mL $\quad M\ Ac^- = \frac{0.0025\,mol}{0.050\,L} = 0.050$ M

Ac^- +	H_2O ⇌	HAc +	OH^-
0.050M	lots	0	~0
$-x$		$+x$	$+x$
$0.050-x$		x	x

$K_b = \frac{x^2}{0.050-x} = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}}$

$K_b = 5.56\times10^{-10}$ ok to neglect x because $\frac{0.050}{5.6\times10^{-10}} > 1000$.

$K_b = \frac{x^2}{0.050}$ $\quad x = \sqrt{(5.56\times10^{-10})(0.050)}$

$x = 5.27\times10^{-6}$ M OH^- $\quad$ pOH = 5.28 $\quad$ pH = 8.72