Chemistry 1220
Solutions for Ch 20, 21 and 23 Problems for New Material

1)

Calculate the voltage generated by a **concentration cell** at 25°C. This is a cell which uses the same two standard electrodes but the solutions have different conc. For such a cell the dilute solution winds up being the anode and the concentrated solution winds up as the cathode for a spontaneous reaction (voltaic cell). This means we could have a nonstandard cell overall and have to use the Nernst Eqn.

$$E = E^\circ - \frac{0.059159\ \text{V}}{n} \log(Q) \qquad \text{Nernst Eqn.}$$

In this problem you have Cr^{3+} at conc. of 0.040 M and 1.0 M. The std electrode potential is given, although you will see you don't need it.

$$Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr(s) \qquad E^\circ = -0.74\ \text{V}$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = (-0.74\ \text{V}) - (-0.74\ \text{V}) = 0.00\ \text{V}$$

The E°_{cell} will always be 0 V for a concentration cell.

Need to determine the reaction quotient Q. The dilute soln will wind up as the anode.

Anode: $Cr(s) \longrightarrow Cr^{3+}(aq,\ 0.040\ M) + 3\,e^-$

Cathode: $Cr^{3+}(aq,\ 1.0\ M) + 3\,e^- \longrightarrow Cr(s)$

$Cr(s) + Cr^{3+}(aq,\ 1.0\ M) \longrightarrow Cr^{3+}(aq,\ 0.040\ M) + Cr(s)$

The reaction is spontaneous and goes in the direction from concentrated to dilute so during the operation of the voltaic cell the conc. of the ion in the anode 1/2-cell (dilute soln) is increasing while the conc. of the ion in the cathode 1/2-cell (conc. soln) is decreasing. The cell is "moving" spontaneously from conc. toward dilute to try to equalize the conc.

$$Q = \frac{[Cr^{3+}]_{dilute}}{[Cr^{3+}]_{conc}}$$

So we wind up with the following expression:

$$E = -\frac{0.059159\ \text{V}}{n} \log\left(\frac{[\text{dilute}]}{[\text{conc.}]}\right)$$

$$E = -\frac{0.059159\ \text{V}}{n} \log\left(\frac{[Cr^{3+}]_{dilute}}{[Cr^{3+}]_{conc}}\right)$$

n = 3 e^- transferred

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1) (cont.)

n = 3 e transferred

$$E = -\frac{0.059159\ \text{V}}{3} \log \left(\frac{(0.040\ \text{M})}{(1.0\ \text{M})}\right)$$

$$E = +0.02\underline{7}566\ \text{V}$$

$$E = +0.028\ \text{V}$$

A little more spontaneous than it would be if both were under standard state conditions of 1.0 M. Makes sense since Cr^{3+} in the dilute solution is the product and when you remove product you would expect the reaction to proceed toward what was removed and go more toward the products, in the forward direction, spontaneously.

B

2)

Given the following balanced reaction equation and standard electrode potentials, what is the concentration (M) of Ag^+ if the emf of the cell is 0.350 V when the concentration of Cu^{2+} is 3.50 M?

$$Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$$

Anode (ox) **Cathode (red)**

$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$ E° = +0.337 V

$Ag^+(aq) + e^- \longrightarrow Ag(s)$ E° = +0.799 V

Nonstandard state conditions meaning the Nernst Eqn. It is best to write out this eqn (even though it's given on the info page) because it helps you to see what you need.

$$E = E^\circ - \frac{0.059159\ \text{V}}{n} \log Q$$

Q = thermodynamic reaction quotient
n = # of electrons transferred

Based on the standard cell notation given above (anode on left||cathode on right), the copper electrode will be the anode and the silver electrode will be the cathode. We need to write the 1/2-cell rxns in the correct way, balance the number of electrons (to get "n") and then add the equations to get the overall cell rxn using the state symbols (to get the correct expression for Q). We also need to get E°.

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2) (cont.)

$$\begin{array}{ll} \text{Anode:} & Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^{-} \\ \text{Cathode:} & 2\,(Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)\,) \\ \hline & Cu(s) + 2\,Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + Ag(s) \qquad n = 2\,e^{-}\ \text{transfer} \end{array}$$

$$Q = \frac{[Cu^{2+}]}{[Ag^{+}]^{2}} \qquad E^{\circ} = E^{\circ}_{cathode} - E^{\circ}_{anode} = (+\,0.799\ V) - (+\,0.337\ V) = 0.462\ V$$

$$E = E^{\circ} - \frac{0.059159}{n} \log Q$$

$$0.350\ V = 0.462\ V - \frac{0.059159\ V}{2} \log Q$$ Solve this eqn first for Q and then the $[Cr^{3+}]$

Solve this eqn for Q

$\log Q = 3.78\underline{\mathbf{6}}4 \qquad Q = 10^{3.78\mathbf{64}} = 61\underline{\mathbf{1}}5.136$

$$Q = \frac{[Cu^{2+}]}{[Ag^{+}]^{2}} = 61\underline{\mathbf{1}}5.136$$

$[Ag^{+}]^{2} = [Cu^{2+}]/Q = (3.50\ M)/(61\underline{\mathbf{1}}5.136) = 5.7\underline{\mathbf{2}}350 \times 10^{-4}$

$[Ag^{+}] = 0.023\underline{\mathbf{9}}23\ M = 0.0239\ M$

E

3)

Consider an electrochemical cell in which the following reaction occurs and predict which changes will increase the cell voltage.

$$2\,Cr^{2+}(aq) + HClO(aq) + H^{+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + Cl^{-}(aq) + H_2O(l)$$

Can approach this problem in two ways: Using Le Chatelier's Principle (LCP) or using the Nernst Equation.

$$E = E^\circ - \frac{0.0592\ V}{n}\log(Q) \qquad \text{Nernst Eqn.}$$

Need Q (thermodynamic reaction quotient):

$$Q = \frac{[Cr^{3+}]^2\,[Cl^-]}{[Cr^{2+}]^2\,[HClO]\,[H^+]}$$

Remember:

$E > 0$ (+) E Spontaneous

$E < 0$ (−) E Nonspontaneous

I) Inc. in [HClO]: Inc. conc. of a reactant.

Using LCP if the conc. of a reactant inc. the rxn. should shift to the right (i.e. proceed more to the right). This means it would be more spont. going in the forward direction. If it's more spont. in the forward direction the E would have to inc. (be larger than it was before adding HClO).

Using the Nernst Eqn. if the conc. of a reactant inc. the value of Q will decrease (since reactants are in the denominator). If Q dec. then log(Q) dec. and we are subtracting a smaller number from E°. This will increase E.

II) Inc. size of inert electrodes: This has no effect. If it did when you did the VOL exp we would have told you to make sure your electrodes were a certain size. It really doesn't make a difference if they weren't inert electrodes but electrodes which participate in the reactions.

III) Dec. pH: Inc. in $[H^+]$: Inc. conc. of a reactant.

Same reasoning as in (I).

E (I & III)

4)

Calculate the standard voltage that can be obtained from an ethane-oxygen ($C_2H_6(g)$-$O_2(g)$) fuel cell at 25°C.

$$C_2H_6(g) + 7/2\ O_2(g) \rightleftarrows 2\ CO_2(g) + 3\ H_2O(\ell) \qquad \Delta G^\circ = -1467\ \text{kJ}$$

Use the eqn:

$$\Delta G^\circ = -\,n\,F\,E^\circ$$

Need "n", the number of electrons transferred. Use the change in oxidation numbers to determine this. Since the C atom appears in only one reactant and one product it is the easiest one to consider.

$$\overset{(-3)}{C_2H_6(g)} + 7/2\ O_2(g) \rightleftarrows \overset{(+4)}{2\ CO_2(g)} + 3\ H_2O(\ell)$$

Since the C atom changes from an oxidation state of -3 to +4 that's a change of +7, meaning each C atom loses 7 e^-. Since there are 2 C atoms this gives a total e^- transfer of 14 e^-.

$$n = 14\ e^-\ \text{transferred}$$

$$E^\circ = \frac{\Delta G^\circ}{-\,n\,F} = \frac{-\,1467 \times 10^3\ \text{J}}{-\,(14\ e^-)\,(96485.3\ \text{C/mol}\ e^-)} = 1.085\ \text{J/C} = 1.09\ \text{V}$$

(1 J = 1 C•V)

A

5)

Remember:

Voltaic Cell	**Electrolytic Cell**
Spontaneous ($E>0$)	**Non**spontaneous ($E<0$)
Anode: oxidation Cathode: reduction	Anode: oxidation Cathode: reduction
Anode: may lose mass Cathode: may gain mass	Anode: may lose mass Cathode: may gain mass
Anode: (−) sign **Cathode**: (+) sign	**Anode**: (+) sign **Cathode**: (−) sign
e− flow spont. from anode to cathode	battery pumps e− onto cathode and pulls e− from the anode

The **anode** in an **electrolytic cell** appears to **attract negative ions** since the **anode** has a **positive** charge (anions can move toward the anode to be oxidized). Even in a voltaic cell anions move toward the anode. Cations move toward the cathode.

D

6)

Using standard electrode potentials, calculate the ΔG (kJ) for the following electrochemical cell.

Anode (**ox**): $Hf^{4+}(aq) + 4\,e^- \longrightarrow Hf(s)$ E° = −1.7000 V

Cathode (**red**): $V^{3+}(aq) + 3\,e^- \longrightarrow V(s)$ E° = −1.7980 V

Need to get E° and the number of electrons being transferred.

Multiply reactions by factors to balance electrons

Anode: $3\,(Hf(s) \longrightarrow Hf^{4+}(aq) + 4\,e^-)$

Cathode: $4\,(V^{3+}(aq) + 3\,e^- \longrightarrow V(s)\,)$

Anode: $3\,Hf(s) \longrightarrow 3\,Hf^{4+}(aq) + 12\,e^-$

Cathode: $4\,V^{3+}(aq) + 12\,e^- \longrightarrow 4\,V(s)$

$4\,V^{3+}(aq) + 3\,Hf(s) \longrightarrow 4\,V(s) + 3\,Hf^{4+}(aq)$ n = 12 e^- transfer

$E^\circ = E^\circ_{cathode} - E^\circ_{anode} = (-1.7980\text{ V}) - (-1.7000\text{ V}) = -0.0980\text{ V}$

$$\Delta G^\circ = -\,n\,F\,E^\circ$$

$\Delta G^\circ = -(12\text{ mole e-})(96485\text{ C/mol }e^-)(-0.0980\text{ V})$

$= +1.1\underline{\mathbf{3}}466 \times 10^5\text{ J} = +11\underline{\mathbf{3}}.466\text{ kJ} = +113\text{ kJ}$

B

7)

Calculate the mass (**kg**) of Li formed by electrolysis of molten LiCl by a current of 6.6×10^4 A flowing for a period of 12 h. Assume the cell is 85 percent efficient. (atomic weight: Li = 6.941)

Remember 1 C = 1 A • s $\qquad$ $6.60 \times 10^4 \text{ A} = 6.60 \times 10^4 \text{ C/s}$

Also, $\text{Li}^+ (\ell) + 1\ \text{e}^-) \longrightarrow \text{Li(s)}$

Do the stoichiometry type problem assuming 100% efficiency, 1 mol of Li produced per mole of e^-.

$$? \text{ g Li} = 12.0 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}} \times \frac{6.60 \times 10^4 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol Li}}{1 \text{ mol e}^-} \times \frac{6.941 \text{ g Li}}{1 \text{ mol Li}} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$= 20\underline{\mathbf{5}}.11 \text{ kg}$$

Multiply this by 0.85 (85% efficiency):

$0.85 * 20\underline{\mathbf{5}}.11 \text{ kg} = 17\underline{\mathbf{4}}.3 \text{ kg} = 174 \text{ kg}$

C

8) By what process does thorium-230 decay to radium-226?

A. gamma emission
B.* alpha emission
C. beta emission
D. electron capture
E. positron emission

${}^{4}_{2}\text{He}$ is an alpha particle (technically has a 2+ chg since it's just a helium nucleus but the charge is generally not shown) - α often used instead of ${}^{4}_{2}\text{He}$ for alpha part.

$${}^{230}_{90}\text{Th} \rightarrow {}^{226}_{88}\text{Ra} + {}^{4}_{2}\text{X}$$

${}^{4}_{2}\text{X}$ is an alpha particle, ${}^{4}_{2}\text{He}$

Remember, the number of nucleons is conserved. This means the mass numbers and atomic numbers bust be balanced in all nuclear equations.

9) What is the missing product from the following reaction?

$$ {}^{32}_{15}\mathrm{P} \rightarrow {}^{32}_{16}\mathrm{S} + \underline{\qquad} $$

A. ${}^{4}_{2}\mathrm{He}$	alpha particle, often symbolized by α
B.* ${}^{0}_{-1}\mathrm{e}$	beta particle, often symbolized by β or β^-
C. ${}^{0}_{0}\gamma$	gamma ray (high-energy photon)
D. ${}^{0}_{+1}\mathrm{e}$	positron (same mass as an electron but opposite charge, β^+)
E. ${}^{0}_{1}\mathrm{p}$	

Remember, the number of nucleons is conserved. This means the mass numbers and atomic numbers bust be balanced in all nuclear equations.

10) Radium undergoes alpha decay. The product of this reaction also undergoes alpha decay. What is the product of this second decay reaction?

A.* Po
B. Rn
C. U
D. Th
E. Hg

$$ {}^{A}_{88}\mathrm{Ra} \rightarrow {}^{A-4}_{86}\mathrm{Rn} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{A-4-4}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{He} $$

11) In the nuclear transmutation represented by, ${}^{27}_{13}\mathrm{Al}$ (n, ?) ${}^{24}_{11}\mathrm{Na}$, what is the emitted particle?

A.* an alpha particle
B. a beta particle
C. a gamma photon
D. a proton
E. a neutron

${}^{27}_{13}\mathrm{Al}$ (n, ?) ${}^{24}_{11}\mathrm{Na}$	This is the condensed notation which represents a nuclear transmutation. It starts with the target nucleus, the bombarding particle, the ejected particle and product nucleus.

$$ {}^{27}_{13}\mathrm{Al} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{24}_{11}\mathrm{Na} + {}^{4}_{2}\mathrm{He} $$

Thus, the ejected particle is an alpha particle.

12) Bombardment of ^{238}U with a deuteron ($^{2}_{1}$H) generates ^{237}Np and _______ neutrons.

A. 1
B. 2
C.* 3
D. 4
E. 5

$$^{238}_{92}\text{U} + {}^{2}_{1}\text{H} \rightarrow {}^{237}_{93}\text{Np} + 3\,{}^{1}_{0}\text{n}$$

13) A freshly prepared sample of curium-243 undergoes 3312 disintegrations per second. After 6.00 yr, the activity of the sample declines to 2755 disintegrations per second. What is the half-life (in yr) of curium-243?

A. 4.99 yr
B. 32.6 yr
C. 7.2 yr
D. 0.765 yr
E.* 22.6 yr

Radioactive decay is a first-order process so we need 1st-order rate law, 1st-order integrated rate eqn and the 1st-order half-life eqn., where N is the number of disintegrations per second.

$$\text{rate} = k \bullet N \qquad \ln(N_t/N_0) = -\,k \bullet t \qquad t_{1/2} = 0.693/k$$

For this problem, since it's asking for the half-life (in years). To do this we need to use the half-life eqn.,

$$t_{1/2} = 0.693/k$$

Need to use the integrated rate eqn. and solve for **k** given the following disintegrations and time:

N_t = 2755 disintegrations/s N_0 = 3312 disintegrations/s

t = 6.00 yr

$$\ln\left(\frac{2755}{3312}\right) = -\,k * 6.00\text{ yr}$$

$$k = 3.0689 \times 10^{-2}\text{ yr}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.0689 \times 10^{-2}\text{ yr}^{-1}} = 22.58\text{ yr} = 22.6\text{ yr}$$

14) ^{210}Pb has a half-life of 22.3 years and decays to produce ^{206}Hg. If you start with a 7.50 g of ^{210}Pb, how many grams of ^{206}Hg will you have after 17.5 years?

A. 4.35 g
B. 3.15 g
C.* 3.09 g
D. 0.0600 g
E. 1.71 g

$^{210}_{82}\text{Pb} \rightarrow {}^{206}_{80}\text{Hg}$

$t_{1/2} = 0.693/k$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{22.3\text{ yr}} = 0.0311\text{ yr}^{-1}$$

$\ln (N_t/N_0) = - k \bullet t$

Starting with 7.50 g of Pb determine how much Pb is left after 17.5 years and convert to Hg.

$$N_t = N_0\, e^{-k \bullet t} = (7.50\text{ g Pb})\ e^{-(0.0311\text{ 1/yr}) \bullet (17.5\text{ yr})}$$

$$N_t = 4.353\text{ g Pb remaining}$$

How many grams of Pb have been converted to Hg?

? g Pb converted = 7.50 - 4.353 = 3.1**4**6 g Pb converted to Hg

$$?\text{ g Hg} = 3.1\underline{\mathbf{4}}6\text{ g Pb} \times \frac{206\text{ g Hg}}{210\text{ g Pb}} = 3.0\underline{\mathbf{8}}6\text{ g Hg} = 3.09\text{ g Hg}$$

The ratio used is the ratio of the mass numbers, which are technically in amu, but the ratio will be the same in grams.

15. In which of the following complexes does the transition metal have a d^5 configuration?

A. $PtCl_4^{2-}$
B. $Cu(H_2O)_6^{2+}$
C. $Ni(CO)_4$
D. $Zn(NH_3)_4^{2+}$
E.* $Fe(CN)_6^{3-}$

A. $PtCl_4^{2-}$ $X_{Pt} + 4(-1)_{Cl-} = -2$ $X_{Pt} = +2$

Pt: [Xe] $4f^{14}$ $5d^9$ $6s^1$ Pt^{2+}: [Xe] $4f^{14}$ $5d^8$ 8 e^- in d orbitals

B. $Cu(H_2O)_6^{2+}$ $X_{Cu} + 4(0)_{H2O} = +2$ $X_{Cu} = +2$

Cu: [Ar] $3d^{10}$ $4s^1$ Cu^{2+}: [Ar] $3d^9$ 9 e^- in d orbitals

C. $Ni(CO)_4$ $X_{Ni} + 4(0)_{CO} = 0$ $X_{Ni} = 0$

Ni: [Ar] $3d^8$ $4s^2$ 8 e^- in d orbitals

D. $Zn(NH_3)_4^{2+}$ $X_{Zn} + 4(0)_{NH3} = 0$ $X_{Zn} = +2$

Zn: [Ar] $3d^{10}$ $4s^2$ Zn^{2+}: [Ar] $3d^{10}$ 10 e^- in d orbitals

E. $Fe(CN)_6^{3-}$ $X_{Fe} + 6(-1)_{CN-} = -3$ $X_{Fe} = +3$

Fe: [Ar] $3d^6$ $4s^2$ Fe^{3+}: [Ar] $3d^5$ 5 e^- in d orbitals

16. Which of the following coordination compounds will form a precipitate when treated with an aqueous solution of $AgNO_3$?

A. $[Cr(NH_3)_3Cl_3]$
B.* $[Cr(NH_3)_6]Cl_3$
C. $[Cr(NH_3)Cl](NO_3)_2$
D. $Na_3[Cr(CN)_6]$
E. $Na_3[CrCl_6]$

This is related to what Werner did in developing his theory about coordination compounds and the coordination sphere of a complex. The ligands in the coordination sphere are bound so tightly to the metal they do not dissociate when the complex is dissolved in water. These ligands don't react easily. The counter ions outside the coordination sphere (outside the square brackets in the formula) can react.

$[Cr(NH_3)_6]Cl_3$ + H2O —> $[Cr(NH_3)_6]^{3+}$ + 3 Cl^-

These 3 Cl^- ions can react with 3 moles of Ag+, 3 Ag^+ (aq) + 3 Cl^- (aq) —> 3 AgCl (s)

17. From the following pairs of coordination compounds which pair are linkage isomers?

A. $K_2[NiBr_2Cl_2]$ and $Na_2[NiBr_2Cl_2]$
B. $K_4[Pt(Cl)_2(NCS)_4]$ and $Na_4[Pt(Cl)_4(NCS)_2]$
C. $[Ni(NH_3)_3(H_2O)]Br_2$ and $[Ni(NH_3)_2(H_2O)_2]Cl_2$
D.* $K_4[Pt(Cl)_2(SCN)_4]$ and $K_4[Pt(Cl)_2(NCS)_4]$
E. $[Ni(NH_3)_3Br]Cl$ and $[Ni(NH_3)_3Cl]Br$

Linkage isomers can occur when the same ligand is capable of coordinating to a metal in two ways. There are two common linkage isomers given in the textbook,

SCN^-	can bind through a lone-pair on the S or the N. It's a weak-field ligand when bound through the S and a strong-field ligand when bound through the N.
NO_2^-	can bind through a lone-pair on the O or the N. It's a weak-field ligand when bound through the O and a strong-field ligand when bound through the N.

18. From the following pairs of coordination compounds which pair are coordination-sphere isomers?

A. $K_2[NiBr_2Cl_2]$ and $Na_2[NiBr_2Cl_2]$ - not isomers (just different cation counter ion)
B. $K_4[Pt(Cl)_2(NCS)_4]$ and $Na_4[Pt(Cl)_4(NCS)_2]$ - not isomers (just different cation counter ion)
C. $[Ni(NH_3)_3(H_2O)]Br_2$ and $[Ni(NH_3)_2(H_2O)_2]Cl_2$ - not isomers (just different anion counter ion)
D. $K_4[Pt(Cl)_2(SCN)_4]$ and $K_4[Pt(Cl)_2(NCS)_4]$ - linkage isomers
E.* $[Ni(NH_3)_3Br]Cl$ and $[Ni(NH_3)_3Cl]Br$

Coordination-sphere isomers are isomers that differ in which species in the complex act as ligands, and which are outside the coordination sphere (counter ions).

$[Ni(NH_3)_3Br]Cl$	has a Br^- in the coord. sphere and a Cl^- as a counter ion
$[Ni(NH_3)_3Cl]Br$	has a Cl^- in the coord. sphere and a Br^- as a counter ion

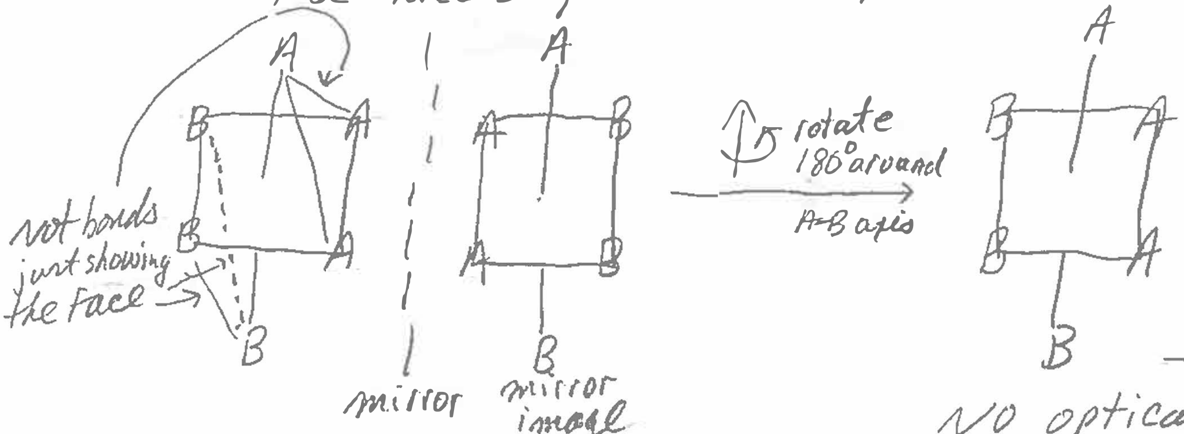
19. How many geometric isomers are possible for the complex ion $[Co(NH_3)_3(H_2O)_3]^{3+}$?

MA_3B_3

A. 4
B. 1
C. 0
D.* 2
E. 3

This is an MA_3B_3 octahedral complex. There's two geometric isomers (fac and mer) but no optical isomerism for either fac or mer.

fac - all three A ligands on one face of the octahedron & the three B ligands on an opposite face.

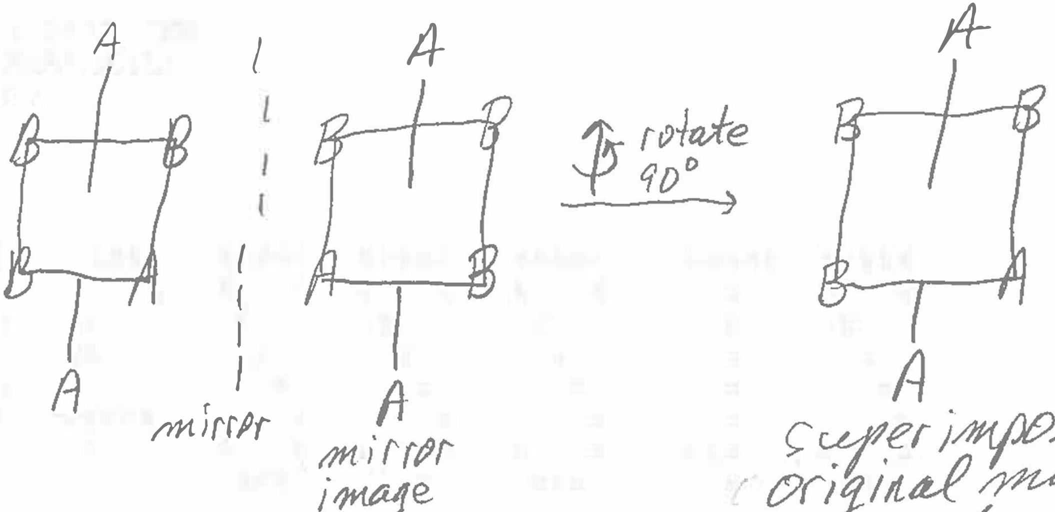


this is superimposable on the original molecule
- NOT chiral

NO optical isomers

this mirror image is superimposable so it's simply the same molecule

mer - two A's are trans to each other & cis to the third A
- same for B's



superimposable on the original molecule
thus the mirror image & original molecule are simply the same molecule

NOT chiral - NO optical isomers

20. Which of the following transition metal complexes can exhibit the phenomenon of optical isomerism?

A. $[Co(NH_3)_4Cl_2]$ - two isomers, Cl atoms cis and trans to each other - no optical isomerism

B. $[CoCl_6]^{4-}$ - no isomers, all the same ligands

C. $[Fe(H_2O)_6]^{3+}$ - no isomers, all the same ligands

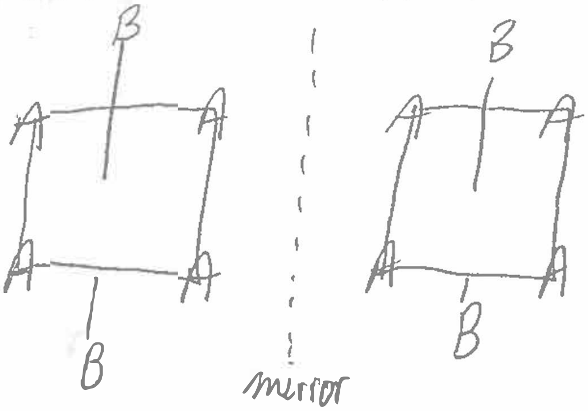
D. $[Ni(SCN)_3Br_3]^{4-}$ - this is an MA_3B_3 complex, two isomers, fac and mer, no optical isomers, as in problem 19.

E.* $[Mn(C_2O_4)_2Br_2]^{4-}$ - two isomers, Cl atoms cis and trans to each other - oxalate is a bidentate ligand (like "en", ethylenediame) - possible optical isomers

A. $[Co(NH_3)_4Cl_2]$ - This is an MA_4B_2 complex.

The two B atoms can be trans or cis to each other so there's two geometric isomers.

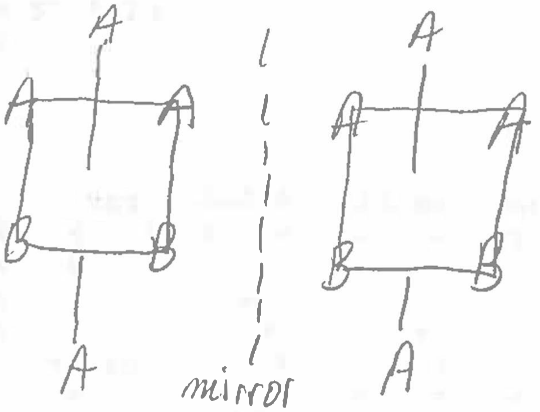
B's trans to each other



mirror image is superimposable on original. NOT chiral. same molecule

No opt. isomers

B's cis to each other - easiest to see when put B's in the plane.



mirror image is superimposable on original. NOT chiral. same molecule

No opt isomers

Thus, MA_4B_2 has cis & trans isomers but no optical isomers

20. (Cont.)

E.* $[Mn(C_2O_4)_2Br_2]^{4-}$

$C_2O_4^{2-}$ This is the oxalate, ox, ligand, a bidentate ligand - generally drawn as two O atoms with a "ribbon" between them (similar to ethylenediamine, en)

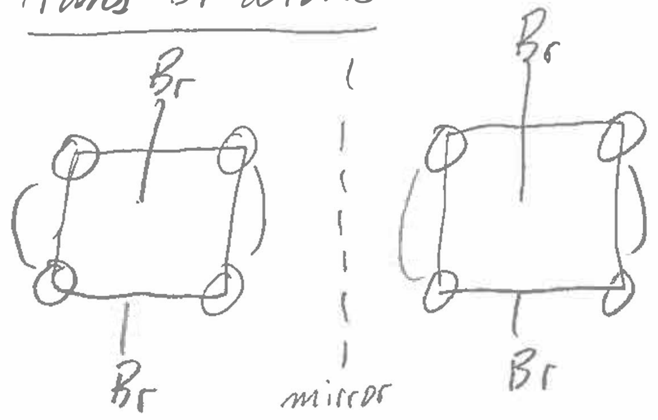
$[Mn(ox)_2Br_2]^{4-}$

The two Br^- can be trans or cis to each other.

Optical isomers are possible in this case, unlike the $[Co(NH_3)_4Cl_2]$ in answer A because of the bidentate ligand.

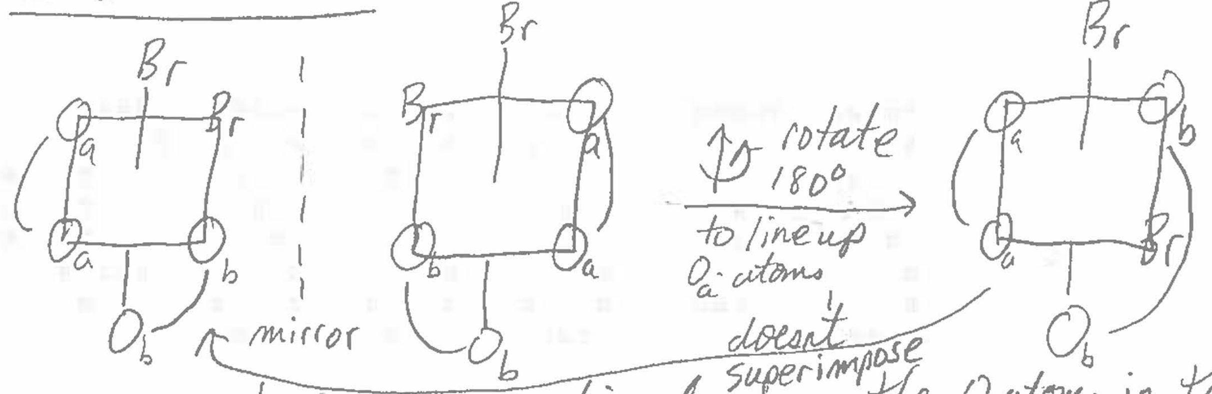
When dealing w. bidentate ligands is easiest to label the binding atoms when drawing the mirror image + rotating it to see if not only the atoms match the original molecule but so do the "ribbons"

trans Br atoms



this is superimposable on the orig. molecule. NOT chiral. Same molecule
NO opt. isomers

cis Br atoms



Opt. isomers - chiral (enantiomers)
one rotates plane-polarized light in one direction by some angle + the other rotates by same amt. in opp. dir

The O atoms in the plane line up w. O atoms in original drawing. However, Br atoms do not match + neither to the O_b atoms + ribbon - Non superimposable

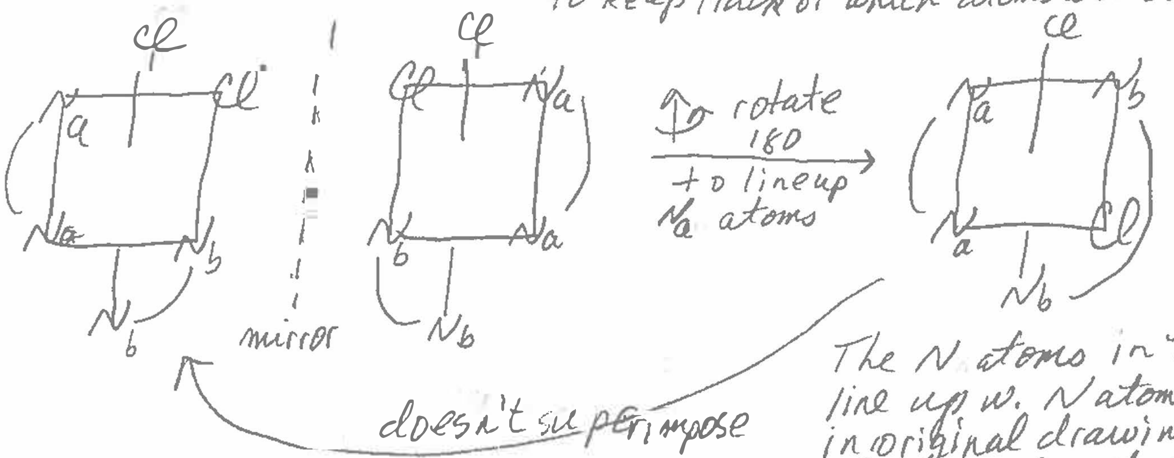
21. Which of the following complexes are chiral?

1) $[Cr(en)_2Cl_2]^+$ cis Cl
2) $[Cr(en)_2(NH_3)_2]^{3+}$ trans-NH_3
3) $[Cr(en)_3]^{3+}$
4) $[Cr(en)Cl_2(NH_3)_2]^+$ cis Cl cis NH_3

A. 1, 2, 3
B.* 1, 3, 4
C. 2, 3, 4
D. 1, 3
E. 2, 4

* 1) $[Cr(en)_2Cl_2]^+$ cis Cl

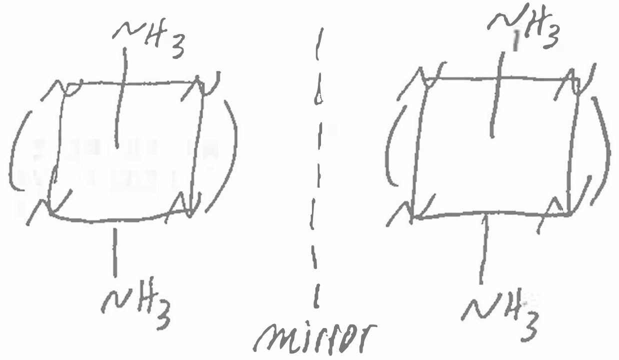
when dealing w. bidentate ligands label binding atoms to keep track of which atoms are connected.



doesn't superimpose
opt. isomers (enantiomers)
chiral

The N atoms in the plane line up w. N atoms in the plane in original drawing. However, the Cl atoms do not match & neither do the N_b atoms.

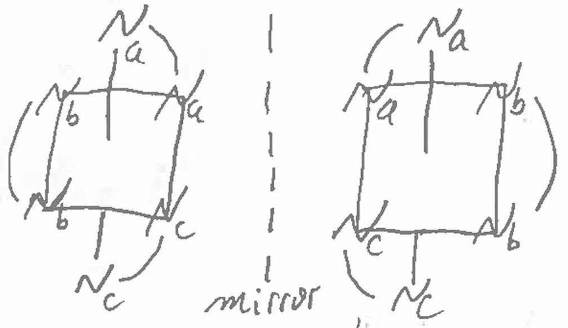
2) $[Cr(en)_2(NH_3)_2]^{3+}$ trans NH_3



this is superimposable on the orig. molecule. NOT chiral.
same molecule.
No opt. isomers

21. (Cont.)

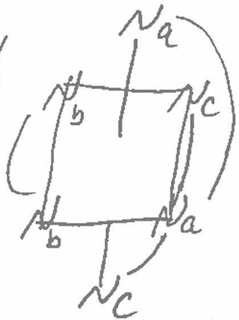
✱3) $[Cr(en)_3]^{3+}$ Very impt to label binding atoms which are part of the same en molecules when there are 3 bidentate ligands in order to keep track of them as you draw the mirror image and then rotate it. N atoms in en have to be in cis positions



doesn't match orig

rotate 180°

so N_b atoms match orig.

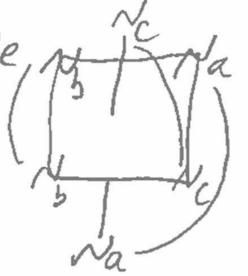


enantiomers (opt. isomers -chiral)

Non-superimposable

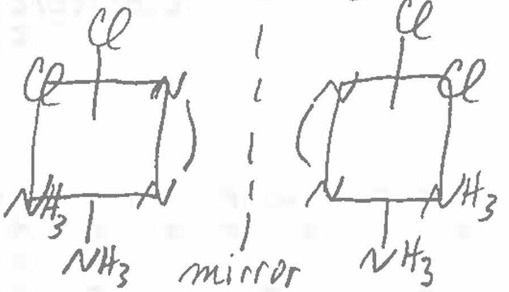
flip over 180° (rotate 180° around axis coming out toward you)

while the N_b atoms line up w. orig. molecule the attached N atoms in plane (N_b atoms) the other en molecules (the ones w. attached N's) don't match.



doesn't match up. w. orig. drawing

✱4) $[Cr(en)Cl_2NH_3]^+$ cis Cl cis NH_3



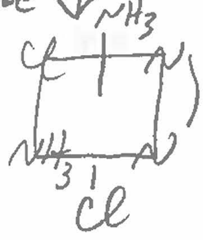
rotate 180°

to match up N atoms in en

the N atoms of the en match w. orig. molecule but Cl atoms don't match & the NH_3 molecules don't match

flip over

Non-superimposable chiral opt isomers (enantiomers)



the N atoms of the en match orig. the Cl & NH_3 in plane match orig. However, the Cl is now below the plane & NH_3 is above the plane so they don't match the orig.