Material for the final exam (Friday 05/07/04, 8:00 a.m.)
1/3: new material (transition metals and nuclear chemistry)
2/3: old material (see exams 1-4 for the coverage)
Total: ~12 problems. Some problems may combine concepts from different chapters.

Kinetics
Nuclear Chemistry
Equilibrium
Acids and Bases
Buffers and Solubility
Thermodynamics
Electrochemistry
Transition metals

No material from “Special research topics” and from Photochemistry
Equations will be provided except the fundamental ones
The mass ratio of $^{40}\text{Ar}$ and $^{40}\text{K}$ can be used to date geological materials. $^{40}\text{K}$ decays by two processes:

$$^{40}_{19}\text{K} + ^0_{-1}\text{e} \rightarrow ^{40}_{18}\text{Ar} \quad (10.7\%)$$

$$^{40}_{19}\text{K} \rightarrow ^{40}_{20}\text{Ca} + ^0_{-1}\text{e} \quad (89.3\%)$$

Overall half-life of $^{40}\text{K}$ is $1.27 \times 10^9$ years.

(1) What assumptions must be made in using this technique?
(2) A sedimentary rock has a $^{40}\text{Ar}/^{40}\text{K}$ ratio of 0.95. Calculate the age of the rock.
(3) How will the measured age of a rock compare with the actual age if some $^{40}\text{Ar}$ has escaped from the sample?

1. Assumptions: (i) no Ar escapes the rock; (ii) $^{40}\text{K}$ is the sole source of $^{40}\text{Ar}$.

2. Use:

$$\ln\left(\frac{N}{N_0}\right) = -kt = -\frac{\ln(2)}{t_{1/2}} t = -\frac{0.693}{t_{1/2}} t \quad t = -\ln\left(\frac{N}{N_0}\right) \cdot \frac{t_{1/2}}{0.693} = \ln\left(\frac{N_0}{N}\right) \cdot \frac{t_{1/2}}{0.693}$$

3. Determine $N_0/N$. $N$ – current amount of $^{40}\text{K}$, $N_0$ – initial amount of $^{40}\text{K}$.
   - 10.7% $N_0$ -> decomposes through channel 1, producing $^{40}\text{Ar}$ ($N_{\text{Ar}}$)
   - 100% $N_0$ -> decomposes through both channels ($N_d$)

   $$N_d = \frac{100}{10.7} \times N_{\text{Ar}} = 9.35 \times N_{\text{Ar}} : \text{total amount of }^{40}\text{K} \text{ decomposed}$$

   Balance $^{40}\text{K}$: $N_0 = N + N_d$ (initial=total=decomposed)$= N + 9.35 \times N_{\text{Ar}}$

   $$N_0/N = 1 + 9.35 \times N_{\text{Ar}} / N = 1 + 9.35 \times 0.95 = 9.878$$

4. $t = \ln(9.878) / 0.693 \times 1.27 \times 10^9 = 4.2 \times 10^9$ years

5. If some $^{40}\text{Ar}$ escaped -> the rock will be dated as a younger one.
Calculate the binding energy per nucleon for $^3_1$H. The atomic mass of $^3_1$H is 3.01605 u.

We’ll need the following constants: $m_e=9.1093819\times10^{-31}$ kg, $m_p=1.6726216\times10^{-27}$ kg, $m_n=1.6749272\times10^{-27}$ kg, $u = 1.66\times10^{-27}$ kg, $c=2.9979\times10^8$ m/s

1. Calculate mass of a $^3_1$H nucleus:
   
   $m(3_1H) = $ atomic mass-$m_e=3.01605 \times 1.66 \times 10^{-27} - 9.1093819 \times 10^{-31} = 5.00660 \times 10^{-27} – 0.00091 \times 10^{-27}=5.00569 \times 10^{-27}$ kg

2. Calculate sum of masses on elementary particles composing $^3_1$H:
   
   $sum=m_p+2m_n= 1.6726216 \times 10^{-27} + 2 \times 1.6749272 \times 10^{-27} = 5.02248 \times 10^{-27}$ kg

3. Calculate mass defect $\Delta m$:
   
   $\Delta m= m(3_1H) – sum = 5.00569 \times 10^{-27} - 5.02248 \times 10^{-27} = - 0.01679 \times 10^{-27}$ kg

   Note: mass defect is negative -> energy is released when $^3_1$H is formed from proton and two neutrons

4. Calculate total binding energy: $E= \Delta mxc^2$:
   
   $E= 0.01679 \times 10^{-27} \times (2.9979 \times 10^8)^2 = 1.509 \times 10^{-12}$ J

5. Calculate binding energy per nucleon, $E_b$:
   
   There are 3 nucleons in the tritium nucleus ->
   
   $E_b = E/3 = 1.509 \times 10^{-12} J/3 = 1.697 \times 10^{-13}$ J
Do we always need to account for electron mass?

Example: calculate energy released in the following fusion rxn:

\[ ^2_1\text{H} + ^3_1\text{H} \rightarrow ^4_2\text{He} + ^1_0\text{n} \]

We have to calculate changes in mass defect ->

\[ m_e \text{ will cancel out for this rxn:} \]

\[
\Delta\Delta m = \Delta m_{\text{products}} - \Delta m_{\text{reactants}} = \]
\[
[(m_{\text{He}} - 2m_e -2m_p -2m_n) + m_n - m_n] -
[(m_{\text{D}} - m_e - m_p - m_n) + (m_{\text{T}} - m_e - m_p - 2m_n)]
\]
\[
= m_{\text{He}} - m_D - m_T + m_n
\]

Note that a lot of masses cancelled out –

always try to simplify the expression!
Consider the following two compounds \([\text{O}_2\text{N-Co(NH}_3\text{)}_4\text{Cl}]\text{Cl} \) (I, yellow) and \([\text{ONO-Co(NH}_3\text{)}_4\text{Cl}]\text{Cl} \) (II, red).

1. What is the oxidation number of Co in these compounds?
2. Name these compounds.
3. What type of isomerism do they exhibit?
4. Suggest one structural and one stereoisomer for the compound I.
5. Based on color difference, apply crystal field theory to predict whether nitro (-NO\(_2\)) or nitrito (-ONO) group is a stronger ligand.
6. Which compound do you expect to be more stable thermodynamically? Explain.

1. Determine the oxidation number: \([\text{Co}^{x}(\text{NH}_3)_4^0\text{Cl}^{-1}(\text{NO}_2)^{-1}]\text{Cl}^{-1} \) \(\rightarrow\) \(x=+3\) \(\leftrightarrow\) Co (III)
2. tetraamminechloronitrocobalt (III) chloride and tetraamminechloronitritocobalt (III) chloride
3. I and II are structural isomers (bonds are different) – they are linkage isomers
4. I can exhibit coordinational and geometric isomerism, e.g.,
   \([\text{Co(NH}_3)_4\text{Cl}_2]\text{NO}_2\), and cis and trans arrangements of Cl and NO\(_2\) groups.
5. Color is determined by splitting of d-orbitals by ligand field.
   
   Color seen:       Color absorbed:
   II    red               blue-green
   I     yellow            violet-indigo

Thus, compound I absorbs higher energy radiation \(\rightarrow\)
NO\(_2\) is a stronger field ligand than –ONO \(\rightarrow\)
NO\(_2\) forms stronger bond \(\rightarrow\)
Compound I is more stable thermodynamically.
Consider the following rxn: \( \text{Co}^{3+} + e \rightarrow \text{Co}^{2+} \) (\( E = 1.82 \) V). Calculate the standard reduction potential for the following half-rxn: \( \text{Co(en)}_3^{3+} + e \rightarrow \text{Co(en)}_3^{2+} \). \( K_f \) for \( \text{Co(en)}_3^{2+} \) is \( 1.5 \times 10^{12} \), and \( K_f \) for \( \text{Co(en)}_3^{3+} \) is \( 2.0 \times 10^{47} \). Which is the stronger oxidizing agent, \( \text{Co}^{3+} \) or \( \text{Co(en)}_3^{3+} \)?

Use the crystal field theory to rationalize this result.

1. \( \text{Co}^{3+} + e \rightarrow \text{Co}^{2+} \) \( E_1 = 1.82 \) V
2. \( \text{Co(en)}_3^{3+} + e \rightarrow \text{Co(en)}_3^{2+} \) \( E_2 = y \)
3. \( \text{Co}^{3+} + \text{Co(en)}_3^{2+} \leftrightarrow \text{Co}^{2+} + \text{Co(en)}_3^{3+} \) \( E_{1-2} = 1.82 - y \)

Calculate equilibrium constant for the above rxn:

(a) \( \text{Co}^{3+} + 3 \text{ en} \rightarrow \text{Co(en)}_3^{3+} \) \( K_{f1} = 2.0 \times 10^{47} \)
(b) \( \text{Co}^{2+} + 3 \text{ en} \rightarrow \text{Co(en)}_3^{2+} \) \( K_{f2} = 1.5 \times 10^{12} \) (note that \( K_{f1} > K_{f2} \) – CFT)

\( (a)-(b) \) \( \text{Co}^{3+} + \text{Co(en)}_3^{2+} \leftrightarrow \text{Co}^{2+} + \text{Co(en)}_3^{3+} \) \( K = \frac{K_{f1}}{K_{f2}} = 1.3 \times 10^{35} \)

Apply Nernst equation to calculate \( E_{(a)-(b)} \) (using equilibrium conditions \( E = 0 \) & \( Q = K \)):

\[
\frac{0.0592}{n} \log(K) = E^0 = \frac{0.0592}{1} \log(1.3 \cdot 10^{35}) = 2.08V
\]

\( E = 2.08 = 1.82 - y \) \( \rightarrow y = 1.82 - 2.08 = -0.26 \) V

Thus, \( \text{Co}^{3+} \) is stronger oxidizing agent than \( \text{Co(en)}_3^{3+} \).

Crystal field theory:

\[
\text{Co}^{3+} \quad \Delta_o \quad \text{Co}^{2+}
\]

Thus, \( \text{Co}^{3+} + e \rightarrow \text{Co}^{2+} \) requires \( \Delta_o \) energy \( \rightarrow \) large \( \Delta_o \) means less favorable rxn \( \rightarrow \) weaker oxidizing agent \( \rightarrow \) better oxidant is \( \text{Co}^{3+} \) is better oxidant with weaker filed ligands \( \rightarrow \) \( \text{H}_2\text{O} \) is weaker field ligand than \( \text{en} \).
For which salt in each of the following groups will the solubility depend on pH?
(a) \( \text{AgF, AgCl, AgBr} \)
(b) \( \text{Pb(OH)}_2, \text{PbCl}_2 \)
(c) \( \text{Sr(NO}_3)_2, \text{Sr(NO}_2)_2 \)
(d) \( \text{Ni(NO}_3)_2, \text{Ni(CN)}_2 \)

Salts of weak acids (or bases): \( \text{AgF, Pb(OH)}_2, \text{Sr(NO}_2)_2, \text{Ni(CN)}_2 \rightarrow \)
Their solubility increases in an acidic media and decreases in basic

Explanation: (Le Chatelier principle):
\[
\text{AgF} \leftrightarrow \text{Ag}^+ + \text{F}^-
\]
\[
\text{F}^- + \text{H}_2\text{O} \leftrightarrow \text{HF} + \text{OH}^-
\]
\[
\text{OH}^- + \text{H}^+ \leftrightarrow \text{H}_2\text{O}
\]
A certain substance consists of two modifications A and B; $\Delta G^0$ for the transition from A to B is positive. The two modifications produce same vapor. Which has the higher vapor pressure? Which is the more soluble in a solvent common to both?

A $\leftrightarrow$ B, $\Delta G^0 = \Delta G_B - \Delta G_A > 0$ - A is more stable than B

A $\leftrightarrow$ vapor $\Delta G_1 = \Delta G(\text{vapor}) - \Delta G_A$

B $\leftrightarrow$ vapor $\Delta G_2 = \Delta G(\text{vapor}) - \Delta G_B$

Since $\Delta G_B - \Delta G_A > 0$, then $\Delta G_B > \Delta G_A$. Thus, $\Delta G_2$ is smaller, and, therefore, the equilibrium constant is larger $\Rightarrow$ 2nd equilibrium is shifted to right $\Rightarrow$ vapor pressure is higher for B.

Same reasoning applies re: solubility

\[ \Delta G \]

\[ \text{Vapor} \]

\[ \text{B} \]

\[ \text{A} \]