

Torrey Chemistry Tournament

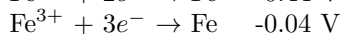
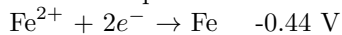
April 2015

1 Equilibria

- a) Consider an elementary gas-phase reaction in equilibrium with $\Delta H < 0$ and no net formation or removal of gas molecules ($\Delta V = 0$). Prove that, as the temperature is increased, Q will exceed K_p until equilibrium is re-established. Your response should be in the form of a proof, and no concepts outside of AP Chemistry are required to solve this problem. (*Hint: Consider the relationship between kinetics and equilibrium, how Q and K_p change immediately after the temperature increase, and what a "shift in the reaction" means at a fundamental level.*)
- b) Consider an equilibrated elementary reaction $AB(g) \rightarrow A(g) + B(g)$ taking place in a thermally controlled container. Prove that, upon an isothermal compression of the container, Q will exceed K_p until equilibrium is re-established. Your response should be in the form of a proof. (*Hint: Read up on Collision Theory and try solving 1a first.*)
- c) Explain why increasing the pressure in the container by adding inert gas would NOT have the same effect as above. What effect would it have? A proof is not necessary here - an explanation will suffice.
- d) Provide a mathematical explanation of Le Chatelier's Principle - that is to say, show that a reaction not in equilibrium will shift in the direction that will take it towards equilibrium. You may assume that the reaction is elementary and that all reactants are gases.

2 Spinel

The reduction potentials for Fe^{2+} and Fe^{3+} are as follows:



- a) What is the potential for the reduction $Fe^{3+} + e^- \rightarrow Fe^{2+}$? Give your answer to two significant figures and indicate proper sign. Show your work.

- b) Magnetite is a mineral that takes the formula Fe_3O_4 ; it includes both Fe^{2+} and Fe^{3+} ions. Knowing that magnetite adopts a spinel crystal structure, would it be expected to be a normal spinel or an inverse spinel? Support your answer with calculations using octahedral and tetrahedral splitting energies. Assume that $\Delta_{\text{tet}} = \frac{4}{9}\Delta_{\text{oct}}$, and that Fe^{2+} and Fe^{3+} are both high spin.
- c) Propose at least one mineral of the form $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{O}_4$ with a normal spinel crystal structure. Provide calculations that show that your mineral is expected to have a normal spinel crystal.

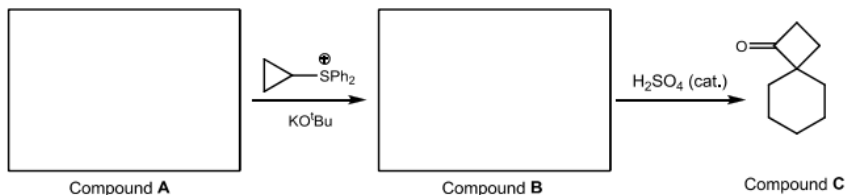
3 Latimer

Latimer diagrams are useful for connecting various oxidation states of an element to their reduction potentials.

- a) Using the corresponding Latimer diagram, construct a Frost diagram involving chlorine-containing species with the y-axis being the value nE° and the x-axis being the oxidation state of the compound or ion. Let Cl_2 have an nE° value equal to zero. You should attach either a link or the picture of the Latimer diagram that you used.
- b) Write the equation for the half reaction involving the reduction of ClO_2^- to OCl^- in basic solution.
- c) Chlorine water exists as an equilibrium between the following four species: H_2O , Cl_2 , HOCl , and HCl . Write an equation for this equilibrium. Then, suggest concentrations for any relevant species such that the formation of neither side (products or reactants) is favored over another.

4 Sulfonium

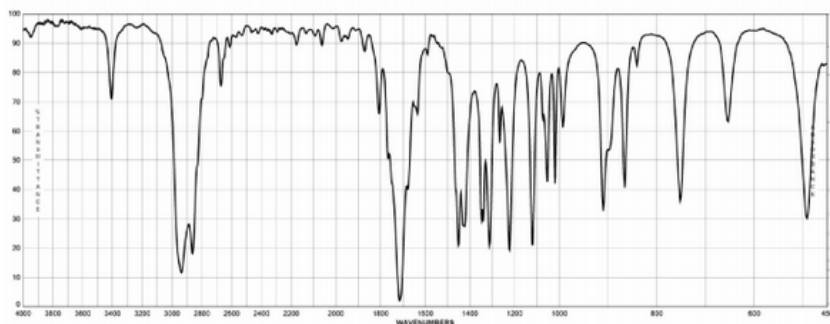
When compound **A** is treated with the illustrated sulfonium salt under basic conditions, compound **B** is formed. Under acidic conditions, compound **B** rearranges to give product **C** which is shown.



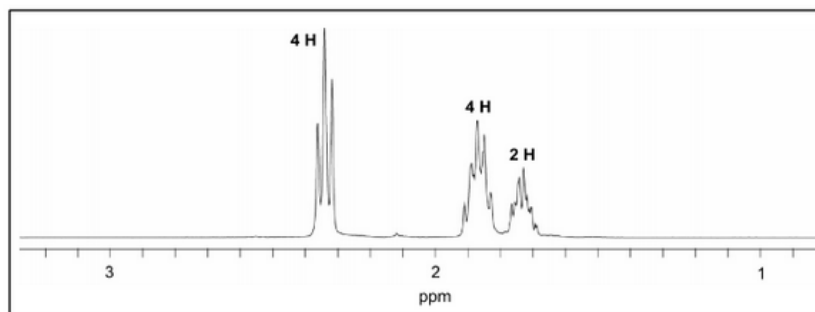
- a) IR and NMR spectra for compound **A** are provided below. Using this data, as well as your knowledge of the reactivity of sulfonium salts, deduce the

structures of **both** compounds **A** and **B**. Place your structures in the boxes above.

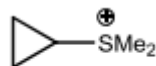
• The infrared spectrum of compound **A** is:



• The ^1H NMR spectrum of compound **A** is:



- Provide a complete curved-arrow mechanism for all steps in the transformation from compound **A** to compound **C**.
- Explain why replacing the sulfonium salt in this transformation with the related sulfonium salt shown below might result in a lower yield of product **C**.



5 Copper

Copper crystallizes in a FCC structure. Given that the atomic radius of Cu is 128 pm,

- What is the coordination number of the lattice and number of atoms in the lattice? Provide a diagram and show how you arrived at your answers.

- b) What is the length of one side of the unit cell? Show calculations and diagram as necessary.
- c) Copper is known to be very ductile. Explain this phenomenon - why is copper so ductile?
- d) The five-cent nickel in American currency is an alloy of copper and nickel.
 - iv) Given that the composition of a five-cent nickel is 75% Cu and 25% Ni by mass, calculate the relative number of atoms of nickel and copper respectively in this alloy.
 - iv) Based on general knowledge of the transition metals, would you predict this cupronickel to be an interstitial or substitutional alloy? Explain.
 - iv) Predict some properties of this binary alloy that differs from the properties of either Cu or Ni alone.