

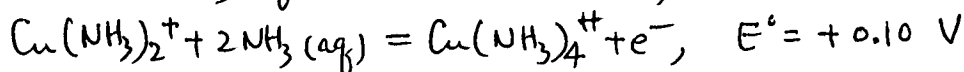
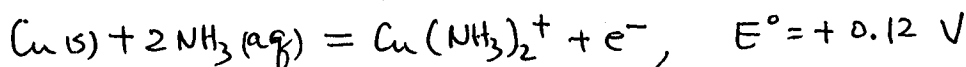
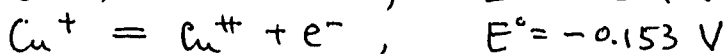
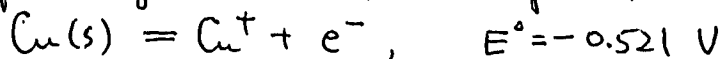
- Define or explain of the following: (12%)
  - Frank-Condon principle
  - Zero-point energy
  - Charge-transfer absorption
  - Negative deviations from Raoult's law
- Explain why the dielectric constant of acetone at 25°C, 20.7, is less than that of methanol, 32.6, even though the dipole moment of acetone, 2.80 D, is greater than that of methanol, 1.70 D. (6%)
- List the symmetry elements of the  $\text{CCl}_4$  molecule. (5%)
  - List the operators associated with the  $S_3$  element and their equivalents, if any. How many distinct operations are produced? (5%)
- What is the sufficient condition for optical isomer to occur? (5%)
- The spacing of a series of lines in the microwave spectrum of  $\text{AlH}$  is constant at  $12.604 \text{ cm}^{-1}$ .
  - Calculate the moment of inertia. (4%)
  - Calculate the internuclear distance of the molecule. (4%)
  - What would be the effect upon the microwave spectrum of the expansion of the dimension of the molecule by a factor of 100? Assume that the mass and electrical properties remain the same. (4%)

(atomic weight of  $\text{Al} = 27.0 \text{ g/mole}$ ,  $c = 3.0 \times 10^{10} \text{ cm/sec}$ )
- Acetylene,  $\text{C}_2\text{H}_2$ , has seven normal modes of vibration, two of which are doubly degenerate. These normal modes may be represented as follows:
 
$$\begin{array}{cccccc} \leftarrow \text{H}-\overset{\rightarrow}{\text{C}} \equiv \overset{\leftarrow}{\text{C}}-\text{H} \rightarrow, & \text{H} \rightarrow \overset{\leftarrow}{\text{C}} \equiv \overset{\leftarrow}{\text{C}}-\text{H}, & \text{H} \rightarrow \leftarrow \text{C} \equiv \overset{\leftarrow}{\text{C}}-\text{H} \rightarrow, & \text{H} \uparrow \overset{\uparrow}{\text{C}} \equiv \overset{\uparrow}{\text{C}}-\text{H} \downarrow, & \text{H} \uparrow \downarrow \overset{\uparrow}{\text{C}} \equiv \overset{\uparrow}{\text{C}}-\text{H} \downarrow \\ \nu_1 & \nu_2 & \nu_3 & \nu_4 & \nu_5 \end{array}$$
  - Which are the doubly degenerate vibrations? (b) Which vibrations are infrared active? (c) Which vibrations are Raman active? Explain your answers. (12%).
- Why do we say that one of the factors that influences reaction rate is the nature of the reactants? (5%)

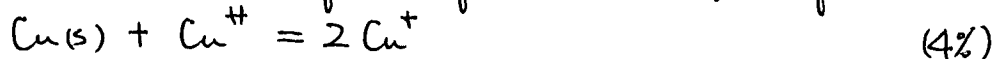
8. The decomposition of  $\text{C}_2\text{H}_5\text{Cl}$  is a first order reaction having  $k = 3.2 \times 10^{-2} \text{ sec}^{-1}$  at  $550^\circ\text{C}$  and  $k = 9.3 \times 10^{-2} \text{ sec}^{-1}$  at  $575^\circ\text{C}$ . What is the activation energy, in kilocalories per mole, for this reaction? ( $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$ ) (8%)

9. Calculate the root-mean-square speed of oxygen molecules having a kinetic energy of  $10 \text{ KJ mol}^{-1}$ . At what temperature would this be the root-mean-square speed? ( $R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$ , atomic weight of  $\text{O} = 16.0 \text{ g/mole}$ ) (8%)

10. The following standard oxidation potentials are given:



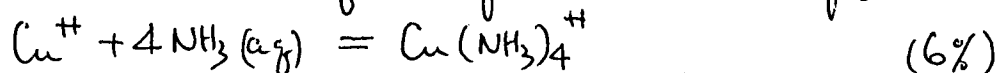
(a) Calculate the value of the equilibrium constant for the reaction:



(b) Calculate the value of  $E^\circ$  for the half-reaction:



(c) Calculate the value of the equilibrium constant for the reaction:



( $R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$ ,  $F = 96500 \text{ C mole}^{-1}$ )

11. In the photobromination of cinnamic acid to dibromocinnamic acid, using blue light of  $435.8 \text{ nm}$  at  $30.6^\circ\text{C}$ , a light intensity of  $1.4 \times 10^{-3} \text{ J sec}^{-1}$  produced a decrease of  $0.075$  millimole of  $\text{Br}_2$  during an exposure of  $1105 \text{ sec}$ . The solution absorbed  $80.1\%$  of the light passing through it. What is the quantum yield? ( $h = 6.62 \times 10^{-34} \text{ J.s}$ ) (8%)