

Examination 1—Spring 1998

Sulfur-containing compounds are extremely important in our environment and in biochemistry. This exam explores some important aspects of sulfur chemistry.

MOLECULAR BONDING AND STRUCTURE

1. (22 points) Draw the Lewis structure for each molecule or ion below.

(a) Draw the electron dot structure for the sulfite ion, SO_3^{2-} .

The electron pair geometry of the ion is _____ and the O–S–O angle is _____. The S atom hybridization is _____. The formal charge on the S atom is _____ and that on the O atom is _____. The order of the S–O bond is _____.

(b) Draw the electron dot structure of the SF_5^- ion. The electron pair geometry of the molecule is _____ and the hybridization of the S atom is _____.

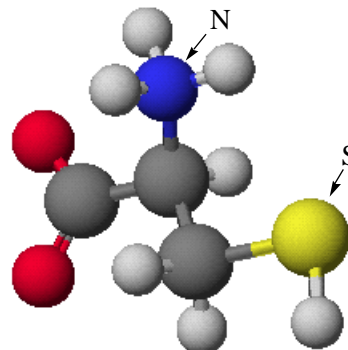
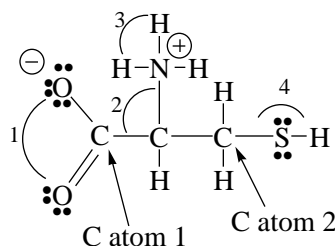
(c) Cysteine, a sulfur containing compound, is an essential amino acid. As the correct pH, the compound has the structure shown below.

What is the C–O bond order? _____

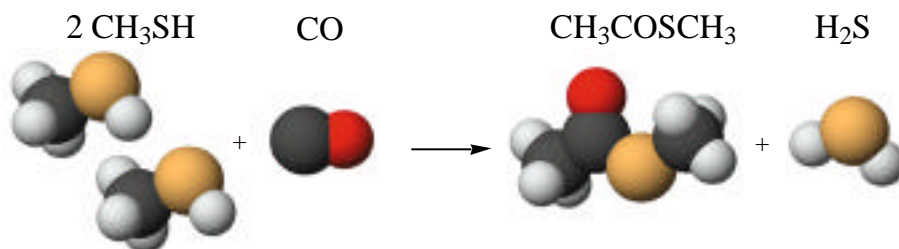
What are the values of the following bond angles: 1 = _____, 2 = _____, 3 = _____, 4 = _____

The hybridization of the N atom is _____. The hybridization of the C atom 1 is _____ whereas that of C atom 2 is _____.

Note that the molecule has a formal charge of -1 on one O atom and a formal charge of +1 on the N atom.



2. (6 points) Scientists recently published experiments showing that metal sulfides, such as iron pyrite, which exists in smokers or volcanoes and is ubiquitous on earth, can act as a catalyst to promote the formation of a compound with a C—C bond from molecules present in the gases from smokers. [C. Huber and G. Wächtershäuser, *Science*, Vol. 276, April 11, 1997, p. 245.] This is important for several reasons. First, simple molecules with carbon-carbon bonds have been prepared under conditions similar to a black smoker. Second, the product of the reaction reacts with water to form biochemically important acetic acid. Third, the reaction is much like that known to occur in primitive organisms called archaeobacteria. The reaction depicted here is one that they reported.

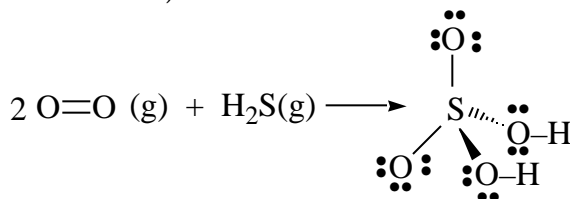


- (i) Is the molecule CH_3SH polar or nonpolar? _____
 (ii) Draw an electron dot structure for CO .

The hybridization of C in CO is _____ whereas it is _____ in the CO carbon atom of $\text{CH}_3\text{COSCH}_3$.

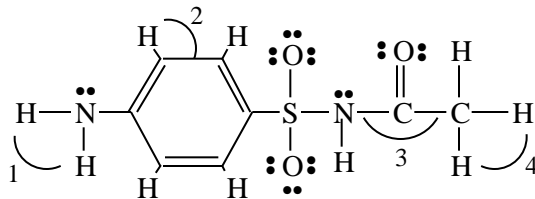
3. (3 points) Dr. Palmer, of OSC's Earth Science Department, recently described an expedition to a cave in Mexico and the discovery of "snotites." In addition, the cave ceiling is the source of droplets containing a high concentration of sulfuric acid, H_2SO_4 .

- (a) Suppose the sulfuric acid comes from the reaction of O_2 and H_2S , calculate the energy involved in this reaction using bond energies. (In addition to the bond energies in your text book, you need to know that $D(\text{S-O}) = 522 \text{ kJ/mol}$.)

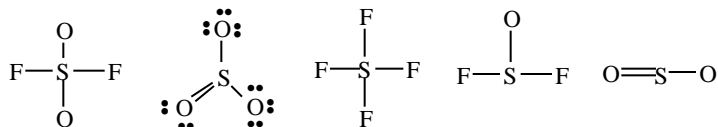


- (i) -1342 kJ
 (ii) +1342 kJ
 (iii) -1490 kJ
 (iv) +1490
 (iv) -2062 kJ
 (v) None of the above

4. (12 points) The molecule pictured here is sulfacetamide, $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{SO}_2-\text{NH}-\text{COCH}_3$, one of a large class of compounds referred to as sulfa drugs.



- (a) The hybridization used by the N atoms is _____
- (b) There are _____ (pi) bonds and _____ (sigma) bonds in the molecule.
- (c) The most polar bond or bonds in the molecule are _____
- (d) Circle the *longest* carbon-carbon bond in the molecule.
- (e) Bond angles: 1 = _____, 2 = _____, 3 = _____, 4 = _____, and N-S-O = _____
- (f) What is the hybridization of the S atom? _____ What is its formal charge? _____
5. (10 points) Polarity and hybridization. (*NOTE: Lone pairs of electrons are not always shown in the sketches below. Also, the drawings are not generally meant to indicate the actual geometry of the molecule.*)



Polar molecule? _____

S atom hybridization _____

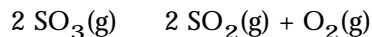
5. (3 points) You have isolated an unknown sulfur-containing compound. To find its molar mass, you release 0.25 g of the gas into a flask with a volume of 186 mL volume at 21 °C. The gas pressure in the flask is 242 mm Hg. What is the formula of the gas?
- (a) 260 g/mol
(b) 9.8 g/mol
(c) 102 g/mol
(d) 32 g/mol
6. (7 points) You are given a solid mixture of NaNO_2 and NaCl and are asked to analyze it for the amount of NaNO_2 present. To do so you allow it to react with sulfamic acid, HSO_3NH_2 , in water according to the equation



What is the weight percentage of NaNO_2 ($M = 69$ g/mol) in 1.232 g of the solid mixture if reaction with sulfamic acid produces 295 mL of N_2 gas with a pressure of 715 mm Hg at 21 °C?

GENERAL EQUILIBRIUM

1. (9 points) You place 1.00 mol of SO_3 gas in a 1.00 L flask at 1000 K. The compound decomposes according to the equation

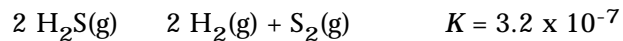


When equilibrium has been attained, 0.925 mol of SO_3 remains.

	$\text{SO}_3(\text{g})$	$\text{SO}_2(\text{g})$	$\text{O}_2(\text{g})$
Initial concentration (M)	1.00	0	0
Change in concentration			
Equilibrium concentration (M)			

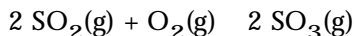
- (a) Complete the table above.
(b) Calculate K_c .

2. (4 points) The equilibrium constant for the decomposition of H_2S has been measured at a high temperature in the gas phase.



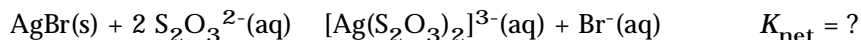
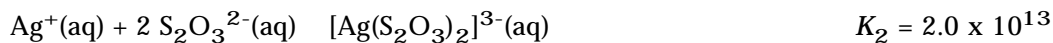
- (a) Is this reaction product-favored or reactant-favored? _____
- (b) If the reaction is written as $\text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + 1/2 \text{S}_2(\text{g})$, the value of K is now
- (i) 3.2×10^{-7}
 - (ii) 5.6×10^{-4}
 - (iii) 1.0×10^{-13}
 - (iv) 1.6×10^{-7}

3. (3 points) A mixture of SO_2 , O_2 , and SO_3 at 1000 K contains the gases at the following concentrations: $[\text{SO}_2] = 5.0 \times 10^{-3} \text{ mol/L}$, $[\text{O}_2] = 1.9 \times 10^{-3} \text{ mol/L}$, and $[\text{SO}_3] = 6.9 \times 10^{-3} \text{ mol/L}$. Assuming the reaction is not at equilibrium, which way will the reaction proceed to reach equilibrium?



Assume K_c for the reaction is 279.

- (a) SO_2 and O_2 will be consumed to produce SO_3
- (b) SO_3 will be consumed to produce more SO_2 and O_2
- (c) The concentration of SO_2 and SO_3 will both increase and that of O_2 will decline.
4. (3 points) The thiosulfate ion forms water-soluble complexes with silver(I) ions. The process can be thought of as occurring by two chemical equilibria.



What is the value of K_{net} ?

- (a) $K_{\text{net}} = K_1 \cdot K_2 =$
- (b) $K_{\text{net}} = K_1/K_2 =$
- (c) $K_{\text{net}} = K_2/K_1 =$
- (d) $K_{\text{net}} = K_1^2/K_2 =$
5. (6 points) The value of K_c for the decomposition of ammonium hydrogen sulfide is 1.8×10^{-4} at 25 °C.



When the pure salt decomposes in a flask, what are the equilibrium concentrations of NH_3 and H_2S ?

- (a) 0.00018 M
- (b) 0.00036 M
- (c) 0.013 M
- (d) 0.026 M

What is the total pressure in a 1.50 L flask at 25 °C when the decomposition has reached equilibrium?

- (a) 0.21 atm
- (b) 0.33 atm
- (c) 0.65 atm
- (d) 1.28 atm
- (e) none of the above (I hope!)

