

**CHEM 121**  
**Spring 2006**  
**Quiz 5**

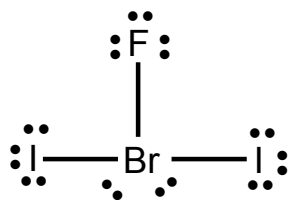
Name: \_\_\_\_\_

1a. (10 Points) There are two different structures possible for the compound  $\text{BrFI}_2$  that have the same central atom, but with a different arrangement of the other atoms about the central atom. Draw these structures (both structures will obey all VSEPR rules). Note that you will need to draw the Lewis dot structures first.

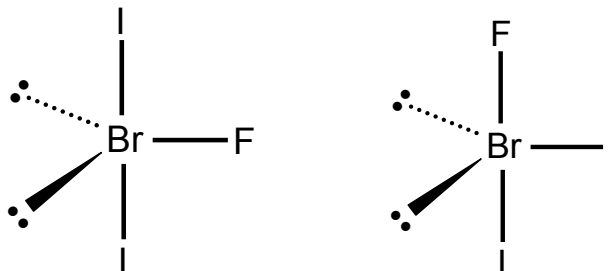
*Electron count*

<b>Br</b>		<b>7</b>
<b>F</b>		<b>7</b>
<b>2 I</b>	<b>2 x 7 = 14</b>	
<b>Total</b>		<b>28</b>

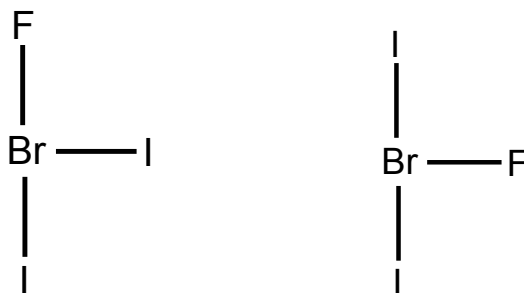
*Lewis dot structure*



*Electron Pair Geometries (both are trigonal bipyramidal in accordance with VSEPR)*



*Structures*



b. (1 Point) If these two different structures exist, they would belong to the family of stereoisomers known as **diastereomers**.

c. (3 Points) In principle, the structures that you drew in part a could exist in equilibrium with each other. However, most compounds with this particular electron pair geometry interconvert between different structures so quickly that none can be isolated. What does this imply about  $E_a$  for the process that converts the two structures? FYI this is called an isomerization reaction.

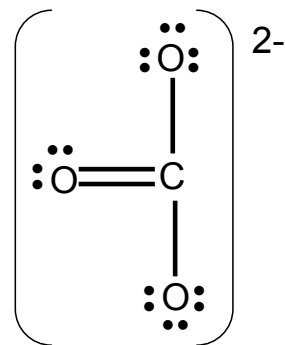
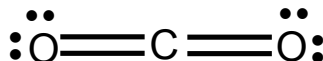
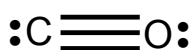
**According to the Arrhenius equation the rate constant,  $k$ , for a reaction has the following dependence on the activation energy,  $E_a$ ,  $k = Ae^{-E_a/RT}$ . Fast reactions have small rate constants, and therefore have small activation energies. If this reaction is very fast, then it has a very low activation energy.**

d. (3 Points) Why must the process described in part c be an equilibrium and not resonance?

**The positions of the atoms are changed between the two structures. This is not allowed in resonance where the atoms must remain in the same place and only the electrons are placed in different positions. Therefore, this process is an equilibrium, not resonance.**

2a. (10 Points) Calculate the formal charges and oxidation numbers on each atom for the following chemical species CO, CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>.

CO	CO <sub>2</sub>	CO <sub>3</sub> <sup>2-</sup>
C            4	C            4	C            4
O            6	2 O        12 = 2 x 6	3 O        18 = 6 x 3
Total 10	Total 16	Total 24



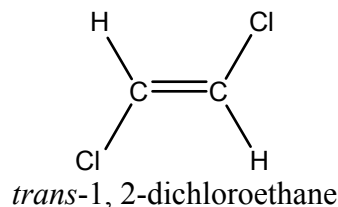
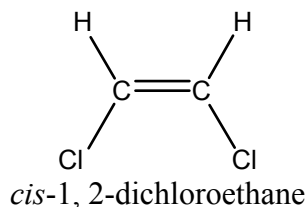
only one resonance structure shown

**Formal charge on  $C\equiv$  =  $4 - 2 - \frac{1}{2}(6) = -1$**   
**Formal charge on  $O\equiv$  =  $6 - 2 - \frac{1}{2}(6) = +1$**   
**Formal charge on  $C=$  =  $4 - 0 - \frac{1}{2}(8) = 0$**   
**Formal charge on  $O=$  =  $6 - 4 - \frac{1}{2}(4) = 0$**   
**Formal charge on  $O^-$  =  $6 - 6 - \frac{1}{2}(2) = -1$**   
**Oxidation number on C in CO =  $4 - 2 = +2$**   
**Oxidation number on C in CO<sub>2</sub> =  $4 - 0 = +4$**   
**Oxidation number on C in CO<sub>3</sub><sup>2-</sup> =  $4 - 0 = +4$**   
**Oxidation number on O in all species =  $6 - 8 = -2$**

b. (1 Point) The transformation of CO to CO<sub>2</sub> or to CO<sub>3</sub><sup>2-</sup> is what kind of reaction?

**The reaction of CO to CO<sub>2</sub> or to CO<sub>3</sub><sup>2-</sup> is an oxidation.**

3. (4 Points) We have discussed the isomers *cis*-1, 2-dichloroethane and *trans*-1, 2-dichloroethane, whose structures are shown below. One of these compounds has a much higher dipole moment than the other. Which one is it and why?



**Both compounds have polar C–Cl bonds (the C–H bonds are only slightly polar because C and H have almost identical electronegativities). In the *cis* isomer both chlorines are on one side of the molecular and both hydrogens are on the other. This means the molecular is asymmetric and the charges caused by the electronegativity difference will be asymmetrically distributed (the Cl side is negative and the H side is positive). In the *trans* isomer the chlorines and the hydrogens are diametrically opposed to each other and the main charge asymmetry is cancelled out (note that the *trans* isomer has inversion symmetry and the *cis* isomer does not). So, the *cis* isomer is expected to be more polar than the *trans* (which it is).**

4. (10 Points) Please attach problem 15-74 to this sheet.

a. To determine  $k$  for this reaction we must know the rate law and to determine the rate law we need to have  $[SO_2Cl_2]$ , or the partial pressure of  $SO_2Cl_2$  (since they are proportional to each other). We are given the total pressure, and so we need to convert this into the partial pressure of  $SO_2Cl_2$ .

The partial pressure of any gas is proportional to the number of moles of the gas present. So, we can work in pressure and are not required to convert to moles or concentration. **Let  $x$  equal the partial pressure of  $SO_2$  (and  $Cl_2$ ) formed.** We can then write the following table.

	$SO_2Cl_2$ (g)	$\rightarrow$	$SO_2$ (g)	$+ Cl_2$ (g)
initially (atm)	4.93		0	0
change (atm)	-x		+x	+x
at any time (atm)	$4.93 - x$		x	x

At any time  $p_{SO_2Cl_2} = 4.93 - x$ ,  $p_{SO_2} = x$  and  $p_{Cl_2} = x$  (all in units of atm). The total pressure,  $p_{total}$ , is given by Dalton's Law of Partial Pressures as

$$P_{total} = p_{SO_2Cl_2} + p_{SO_2} + p_{Cl_2}$$

Substituting in the expressions from the table gives that the total pressure, in units of atm, is

$$p_{total} = 4.93 - x + x + x = 4.93 + x$$

Solving this expression for  $x$  and substituting back into the expression for  $p_{SO_2Cl_2}$  in the table gives

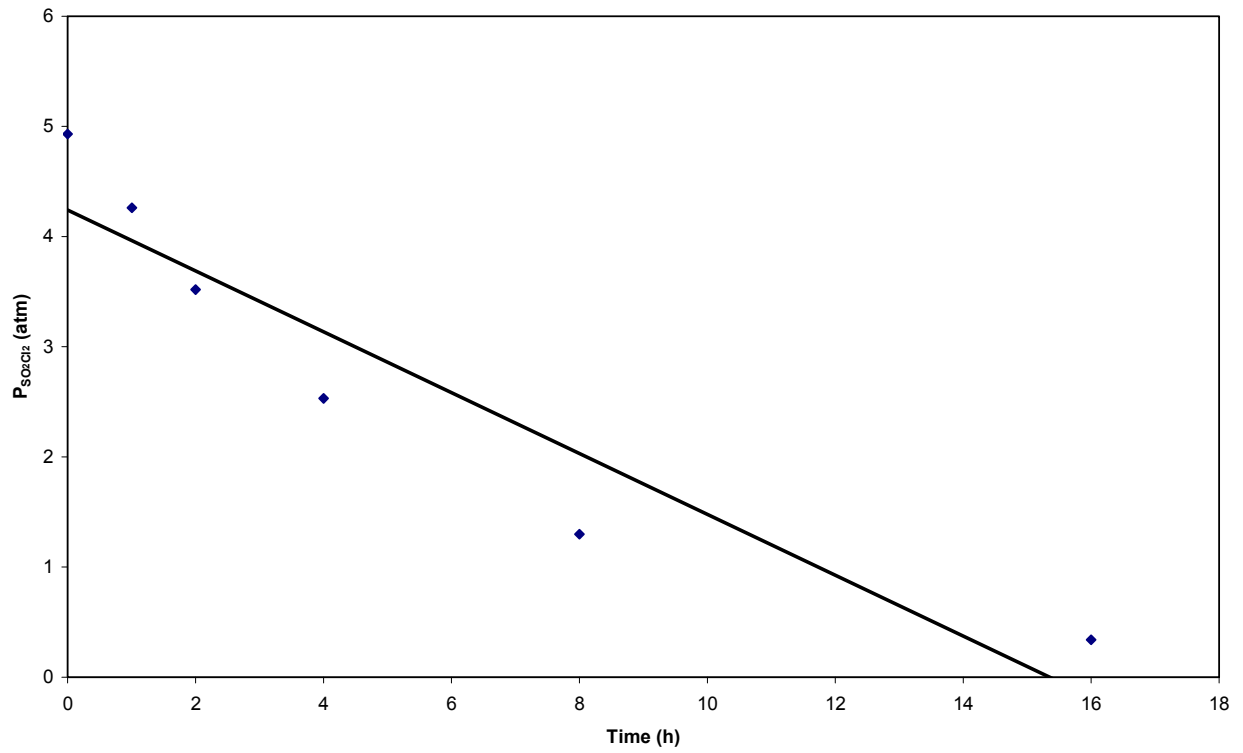
$$p_{SO_2Cl_2} = 9.86 - p_{total}$$

Using Excel to do the calculation for us gives the following results (rounded to the correct number of significant figures).

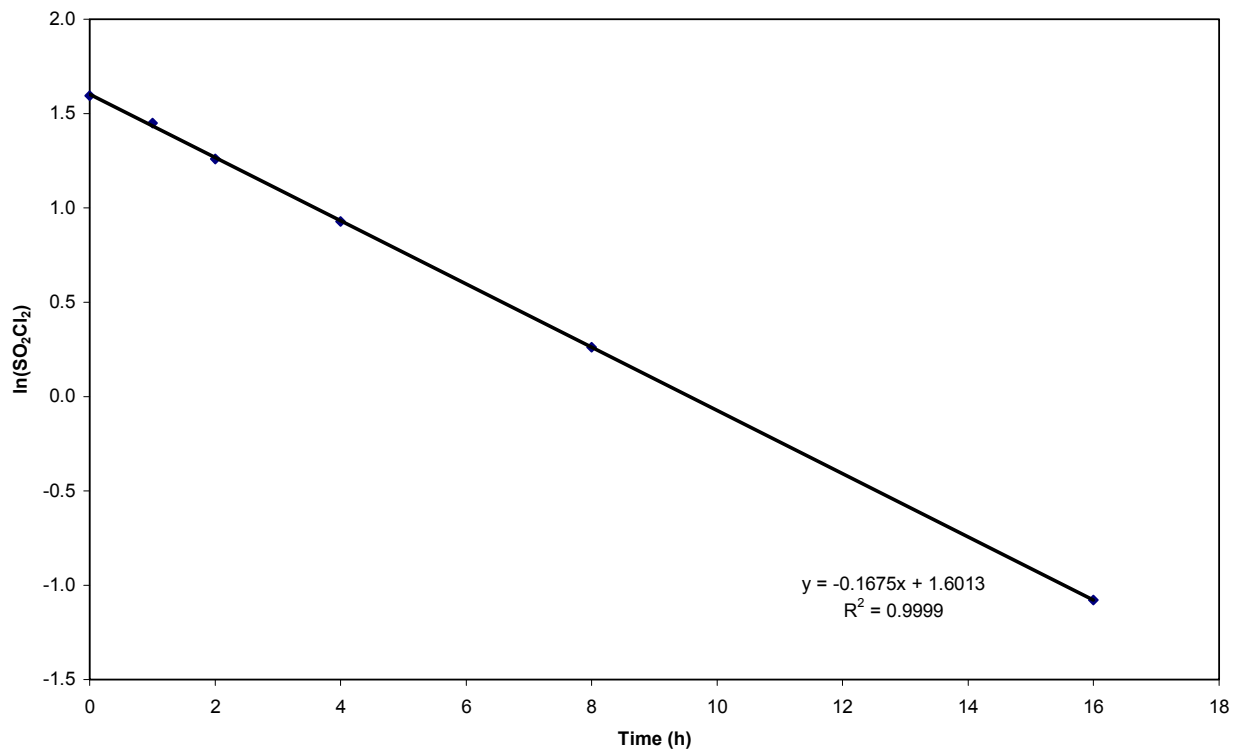
Time (h)	$p_{total}$ (atm)	$p_{SO_2Cl_2}$ (atm)	$\ln(p_{SO_2Cl_2})$	$1/p_{SO_2Cl_2}$ ( $atm^{-1}$ )
0.00	4.93	4.93	1.595	0.203
1.00	5.60	4.26	1.449	0.235
2.00	6.34	3.52	1.258	0.284
4.00	7.33	2.53	0.928	0.395
8.00	8.56	1.30	0.262	0.769
16.00	9.52	0.34	-1.079	2.94

The following graphs are prepared for the each of the integrated rate laws and it is clear that the first order graph is linear.

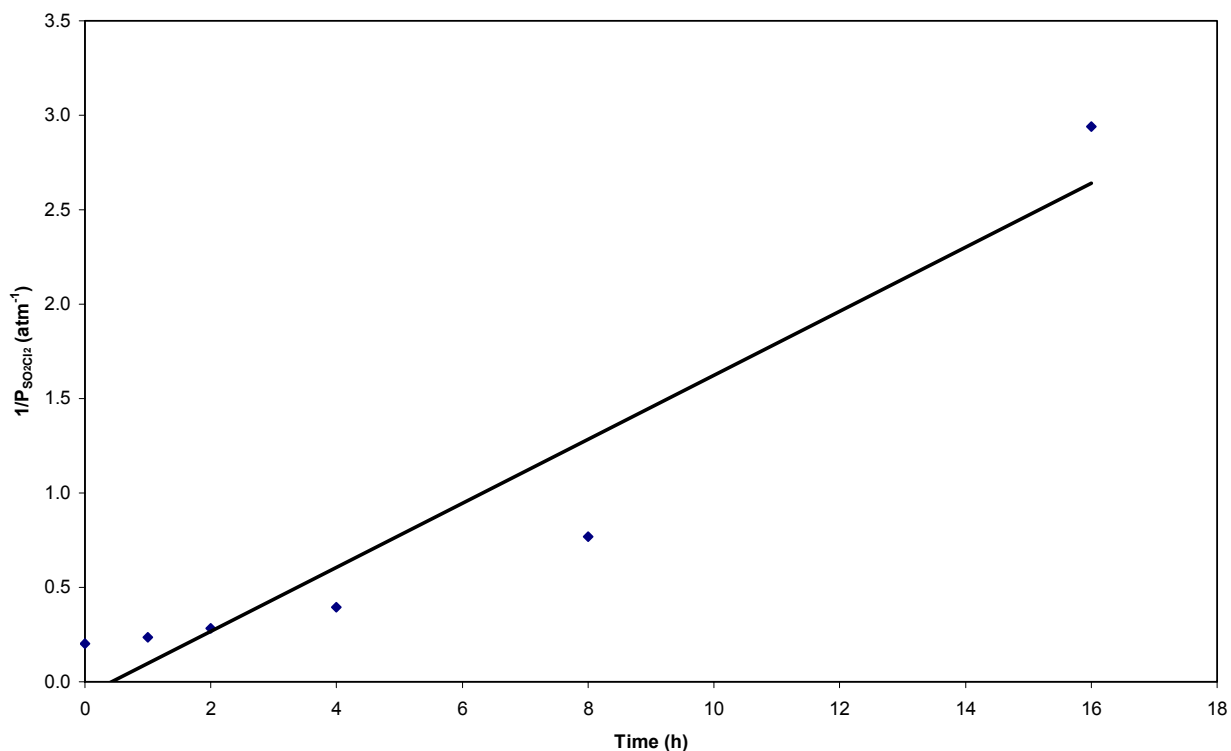
Graph for Zeroth-Order Rate Law for the Reaction of  $\text{SO}_2\text{Cl}_2$



Graph for First-Order Rate Law for the Reaction of  $\text{SO}_2\text{Cl}_2$



Graph for Second-Order Rate Law for the Reaction of  $\text{SO}_2\text{Cl}_2$



From the slope of the first-order integrated rate graph, we can obtain the rate constant for this reaction as  $0.168 \text{ h}^{-1}$ . Because it is first order there will be no dependence on concentration (or pressure) and the rate constant will be the same whether we use pressure or concentration.

b. The half-life for a first order reaction is given by the following expression; substituting in the rate constant determined above gives  $t_{1/2}$ .

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.168 \text{ h}^{-1}} = 4.14 \text{ h}$$

**The half-life of this reaction is 4.14 h.**

c. The pressure in the vessel at any time can be found by first finding the  $\ln(p_{\text{SO}_2\text{Cl}_2})$  by substituting the given times into the integrated rate law. Once we have  $p_{\text{SO}_2\text{Cl}_2}$  we can find  $p_{\text{SO}_2}$  and  $p_{\text{Cl}_2}$  as described in part a. These results are summarized below (again Excel is really useful here).

Time (h)	$\ln(p_{\text{SO}_2\text{Cl}_2})$	$p_{\text{SO}_2\text{Cl}_2}$ (atm)	$p_{\text{SO}_2}$ (atm)	$p_{\text{Cl}_2}$ (atm)	$p_{\text{total}}$ (atm)
0.500	1.518	4.56	0.37	0.37	5.30
12.0	-0.409	0.66	4.27	4.27	9.20

The total pressure after 0.500 h is 5.30 atm and after 12.0 h the total pressure is 9.20 atm.

d. Again we go back to the integrated rate law, substitute in  $t = 20.0$  h and solve for  $\ln(p_{\text{SO}_2\text{Cl}_2})$ . From this we can find  $p_{\text{SO}_2\text{Cl}_2}$  at this time.

$$\ln(p_{\text{SO}_2\text{Cl}_2})_t = -kt + \ln(p_{\text{SO}_2\text{Cl}_2})_0 = -(0.168 \text{ h}^{-1})t + 1.60$$

$$\ln(p_{\text{SO}_2\text{Cl}_2})_t = -(0.168 \text{ h}^{-1})(20.0 \text{ h}) + 1.60 = -1.75$$

$$p_{\text{SO}_2\text{Cl}_2} = 0.17 \text{ atm}$$

The fraction remaining (as a percent) is

$$\frac{(p_{\text{SO}_2\text{Cl}_2})_{20}}{(p_{\text{SO}_2\text{Cl}_2})_0} = \frac{0.17 \text{ atm}}{4.93 \text{ atm}} \times 100 = 3.5\%$$

At 20.0 h 3.5% of the  $\text{SO}_2\text{Cl}_2$  remains.