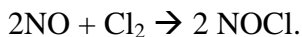


**Admission Exam of the Post Graduation Program in Chemistry**  
**Federal University of São Carlos**  
**Academic Master Degree and Doctoral Degree, 02/2014**

**Question 01**

The rate of the reaction below is 8 times faster when the concentration of both reactants is doubled. However, the rate is 2 times faster when only the concentration of  $\text{Cl}_2$  is doubled. What is the reaction order with respect to  $\text{NO}$  and  $\text{Cl}_2$ ?



**Question 02**

A cold body "A" and a hot body "B" of different compositions are placed in contact. Considering the information below, which is the equilibrium temperature after established the thermal equilibrium?

$$T_{(A)} = 10,0^\circ\text{C}$$

$$m_{(A)} = 2,50 \text{ g}$$

$$C_{p(A)} = 20,0 \text{ cal } ^\circ\text{C}^{-1} \text{ g}^{-1}$$

$$T_{(B)} = 40,0^\circ\text{C}$$

$$m_{(B)} = 4,00 \text{ g}$$

$$C_{p(B)} = 5,00 \text{ cal } ^\circ\text{C}^{-1} \text{ g}^{-1}$$

**Question 03**

Draw a molecular orbital energy-level diagram and determine the bond order expected for each of the following species: (a)  $\text{Li}_2$ ; (b)  $\text{Li}_2^+$ ; (c)  $\text{Li}_2^-$ . State in each case the number of unpaired electrons and consequently describe each molecule or ion as paramagnetic or diamagnetic.

**Question 04**

Which are the geometries that the complexes of Ni (II), of electronic configuration  $d^8$ , can display? For each case draw the diagram of crystal field splitting with the electronic distribution and then determine if the complexes are paramagnetic or diamagnetic.

**Question 05**

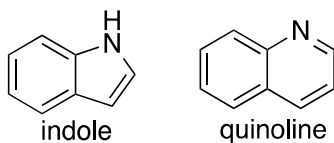
Calculate the change in pH when 10.0 mL of  $1.00 \times 10^{-1}$  mol/L NaOH is added to 100.0 mL of a solution containing  $1.00 \times 10^{-1}$  mol/L acetic acid and  $1.00 \times 10^{-1}$  mol/L sodium acetate. Take  $\text{pK}_a = 4.74$  for acetic acid. All solutions were prepared in water.

**Question 06**

The solubility of lead iodide ( $\text{PbI}_2$ ) in water at  $25^\circ\text{C}$  is 0.59 g/L. Calculate the value of  $K_s$  for lead iodide. Data: Atomic Mass Pb: 207.2 g/mol; Atomic Mass I: 126.90 g/mol.

**Question 07**

Using your knowledge of chemistry involving basicity of nitrogenated compounds, predict and explain the difference of basicity between the molecules below:

**Question 08**

Explain why benzene does not react in the presence of HBr, while propene reacts providing as the major product 2-bromo-propane. Provide the mechanism of addition of HBr to propene.