

Admission Exam of the Post Graduation Program in Chemistry
Federal University of São Carlos
Academic Master Degree and Doctoral Degree, 01/2013

Question 01

BF_3 reacts with F^- to give BF_4^- , but AlF_3 reacts with F^- to give AlF_6^{3-} . Explain.

Question 02

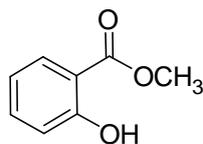
At ordinary temperatures sulfur exists as S_8 , but oxygen exists as O_2 . Explain.

Question 03

Two isomeric substances (A and B) were found in some laboratory with their labels erased. In these labels were identified only the molecular formula ($\text{C}_2\text{H}_6\text{O}$ for both) and the boiling points -19°C and $+74^\circ\text{C}$, respectively. Give the structures of compounds A and B and justify briefly your conclusions based on the provided physical proprieties and in your knowledge about intermolecular forces.

Question 04

Methyl salicylate is an ester with medicinal proprieties and is present in some topic medicines. Write the chemical equation for the preparation of methyl salicylate by using an esterification reaction. Considering that these reactions, in equilibrium (25°C), have equilibrium constants (K) around 1 ($K \cong 1$), which strategies could be used to promote the equilibrium displacement in direction to the products?



methyl salicylate

Question 05

Demonstrate with calculations how the titration of 1.00×10^{-1} mol/L HCl ($V_{\text{solution}} = 25.00$ mL) with 1.00×10^{-1} mol/L NaOH differ from titration of 1.00×10^{-1} mol/L CH_3COOH ($V_{\text{solution}} = 25.00$ mL) with this same alkaline solution concerning to the following points:

- (a) pH at the beginning of the titration (i.e. $V_{\text{titrant}} = 0$).
- (b) pH at the equivalence point.

Data: $K_{\text{CH}_3\text{COOH}} = 1.75 \times 10^{-5}$ (25°C) and $K_w = 1.00 \times 10^{-14}$ (25°C)

Question 06

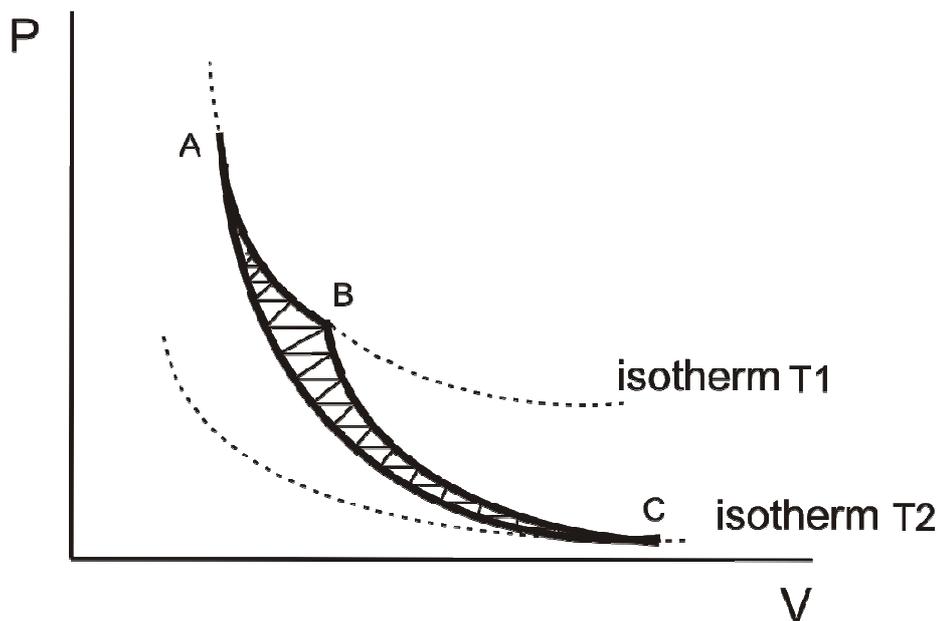
The K_{sp} for AgI is 8.3×10^{-17} and the K_f for $[\text{Ag}(\text{CN})_2]^-$ is 1.0×10^{21} (both at 25°C).

- (a) Calculate the AgI solubility in a saturated solution of this salt.
- (b) Calculate the AgI solubility after addition of 1.0×10^{-2} mol of I⁻ in 1 L of the solution mentioned in (a).
- (c) Calculate the equilibrium constant for the following equation:



Question 07

The figure below shows a reversible thermodynamic cycle for an ideal gas between two isotherms T_1 and T_2 , being $T_1 > T_2$. Explain if this cycle can occur or if there is some thermodynamic impediment.



Question 08

The rate constant for the decomposition of a certain substance is $k_1 = 2.80 \times 10^{-3} \text{ L / mol s}$ at 30°C and $k_2 = 1.38 \times 10^{-2} \text{ L / mol s}$ at 50°C .

- Show that this reaction is of second order.
- Evaluate the Arrhenius parameters of this reaction?