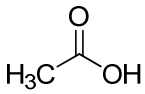
Admission Exam of the Post Graduation Program in Chemistry – Federal University of São Carlos
Academic Master Degree, 01/2012

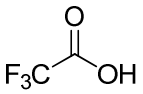
1) The acidity of some substances is associated with its structural features, energy bond, electron-delocalization phenomenon, among others. Based on the Brønsted-Lowry definition, acids are substances able to provide hydronium ion in solution. In each of items described below, what substance has a higher acidity in water? Make your response based on the aspects of the chemical structures and not only as a function of the p*Ka* values. All the p*Ka* were measured in water.

a) HNO_3 (p*Ka* = -1.3) and HNO_2 (p*Ka* = 3.3)

b)

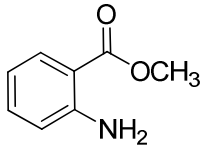


p*Ka* = 4.76



p*Ka* = 0.23

2) The esterification reactions are among the best known in chemistry, considering the applicability of its products in many sectors of the chemical industry. Methyl anthranilate, for example, simulates the *flavor of grapes* and it is used in the food industry. Write the chemical equation for the preparation of methyl anthranilate by using an esterification reaction. Considering that these reactions, in equilibrium (25 ° C), have equilibrium constants (K) with a value around 1 (K ≅ 1), which strategies could be used to promote the equilibrium displacement in direction to the products?



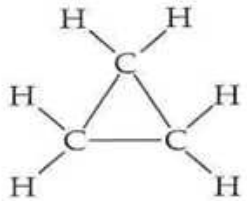
methyl anthranilate

3) Using the data given below, calculate ΔG for the following reactions:

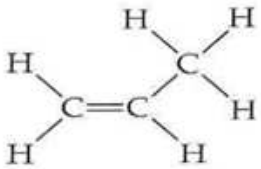
a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, for $p_{N2} = 2.6$ atm , $p_{H2} = 5.9$ atm and $p_{NH3} = 1.2$ atm ;
b) $2N_2H_4(g) + 2NO_2(g) \rightarrow 3N_2(g) + 4H_2O(g)$, for $p_{N2H4} = p_{NO2} = 5.0 \times 10^{-2}$ atm , $p_{N2} = 0.5$ atm and $p_{H2O} = 0.3$ atm;
c) $N_2H_4(g) \rightarrow N_2(g) + 2H_2(g)$, for $p_{N2H4} = 0.5$ atm, $p_{N2} = 1.5$ atm and $p_{H2} = 2.5$ atm.

$\Delta G^o[NH_3, g] = -16.66$ kJ mol^{-1}; $\Delta G^o[H_2O, g] = -228.57$ kJ mol^{-1}; $\Delta G^o[N_2H_4, g] = +159.4$ kJ mol^{-1}; $\Delta G^o[NO_2, g] = +51.84$ kJ mol^{-1}. R = 8.314 J.mol^{-1}.K^{-1}.

4) Cyclopropane and propane are C_3H_6 isomers. At 25°C, what is the molecule with higher absolute entropy? Explain your conclusion.



Cyclopropane



Propane

5) Calculate the pH and the ionized percentage of molecules in a 0.10 mol/L benzoic acid ($C_7H_6O_2$) solution. This solution was used to prepare a buffer (Benzoic acid / benzoate). In this case, answer as well:

a) Write the complete ionic equation reaction when some drops of hidrochloridric acid (HCl) solution are added to the buffer.
b) Write the complete ionic equation reaction when some drops of sodium hydroxide (NaOH) solution are added to the original buffer.

Data:
Ka = 6.3×10^{-5},
Atomic masses:
H = 1.0 g/mol,
C = 12 g/mol,
O = 16 g/mol.

6) A buffer solution was prepared mixing 5.5 mL concentrated acetic acid (CH_3COOH) and 5.0 g of sodium acetate (CH_3COONa) in water to obtain 500 mL of solution. With these data answer:
What is the pH of the buffer solution obtained?
Data:
Conjugated base Kb = 5.7×10^{-10},
Kw = 1.00×10^{-14},
Concentrated acetic acid density = 1.05 g/mL,
Concentrated acetic acid %w/w = 96%,
Atomic masses:
H = 1.0 g/mol,
C = 12 g/mol,
O = 16 g/mol,
Na = 23 g/mol

7) When 1 mol of H_2 and 1 mol of F_2 react at 298 K, 2 mol of HF form and 546 kJ of heat is released.

$H_2(g) + F_2(g) \rightarrow 2HF(g) + 546\ kJ$

Explain where these 546 kJ of heat come from.

8) Explain, in terms of molecular orbitals, which of the following species are paramagnetic. Indicate the number of unpaired electrons each of the paramagnetic species have.

a) O_2 **b)** O_2^- **c)** O_2^+