CHEMISTRY TEST #2 (1h30)

All type of calculators allowed

The three exercises are independent. Each answer must be justified.

For calculations, please consider: R = 8.314 $J.mol^{-1}.K^{-1}$; T (K) = $\Theta(°C) + 273$ K ;

1 atm = 760 Torr = 101325 Pa = 1.013 bar. P° = 1 bar

All gases are supposed ideal.

Exercise A. pH and solubility equilibria (11.0 points).

Magnesium hydroxide $Mg(OH)_2$ is a base having a low solubility in pure water :

$s_{Mg(OH)2} = 2.10^{-4}$ $mol.L^{-1}$ at room temperature (T = 298°K).

1) Write the dissolution equilibrium of magnesium hydroxide.
2) Calculate the dissolution equilibrium constant (solubility product) K_s of magnesium hydroxide at room temperature.
3) Calculate the pH of a saturated solution of magnesium hydroxide.

Solubility of magnesium hydroxide increases in the presence of ammonium chloride (NH_4^+, Cl^-). Ammonium ion (NH_4^+) is a weak acid.

4) Write the equilibria which establish in an aqueous solution of ammonium chloride saturated with magnesium hydroxide.
5) Deduce the global reaction which takes place between magnesium hydroxide and ammonium ion (NH_4^+).
6) Considering that ammonium ion (NH_4^+) is a weak acid, justify why magnesium hydroxide solubility is increased when placed in an ammonium chloride solution

In an aqueous solution of ammonium chloride at an initial concentration of 1 $mol.L^{-1}$, magnesium hydroxide solubility is 1000 times higher than the one in pure water : $s'_{Mg(OH)2} = 2.10^{-1}$ $mol.L^{-1}$.

7) Calculate the concentrations in NH_4^+ and NH_3 once magnesium hydroxide has been fully dissolved. It is assumed that $Mg(OH)_2$ quantity is close to 0.
8) Calculate the pH of this solution.
9) Show that the pK_a of NH_4^+/NH_3 acid/base couple is close to 9.

Exercise B. Hydrogen and redox: electrolysis (6.0 points).

Dihydrogen is a source of energy which is expected to play a key-role in the efforts towards a carbon-free energy supply. The so-called Green dihydrogen is produced from water electrolysis using renewable electricity.

In this exercise, temperature is supposed constant (25°C / 298K).

Water electrolysis is performed by applying a voltage difference at the two terminals of an electrolyzer made of two electrodes. Thus, the following reactions occur:

At electrode 1: $H_2O \rightarrow {}^1/_2\, O_{2(g)} + 2H^+_{(aq)} + 2e^-$

At electrode 2: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

1) Which electrode is the cathode? Same question for the anode? To which terminal of the electrolyzer must the positive pole of the power generator be connected so that electrolysis takes place?

2) Express the electrical potential of each electrode. Deduce the literal expression of the minimal voltage which has to be applied at electrolyzer terminals to enable electrolysis.

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3) Under standard conditions, calculate the minimal quantity of electrical energy which has to be provided to produce 1 mol of dihydrogen.

4) It is assumed that both compartments are at the same pressure (electrode 1: pure dioxygen and electrode 2: pure dihydrogen). If the pressure was increased, what would be the consequence on the minimal voltage that is required to enable electrolysis?

A very common water electrolysis route is based on water hydrolysis in basic medium (so-called alkaline hydrolysis) The involved redox couples are O_2/OH^- (electrode 1) and H_2O/H_2 (electrode 2). Thus, the following reactions occur:

Electrode 1 : $2OH^-_{(aq)} \rightarrow \frac{1}{2}O_{2(g)} + H_2O + 2e^-$

Electrode 2 : $2H_2O + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)}$

5) Express the electrical potential of each electrode. Then, calculate the value of standard electrical potential of each involved couple.

6) Under standard conditions, calculate the minimal voltage which has to be applied at electrolyzer terminals to enable electrolysis.

Exercise C. Liquid ideal mixture (3.0 points).

A round bottom flask which has been first emptied of any gas, is filled with a gaseous mixture of two pure compounds, denoted as A and B, respectively. The mixture molar composition is 0.4 in A. This gas mixture is then compressed in isothermal conditions. At the chosen temperature, the saturated vapor pressures of A and B are $P_A^* = 0.4$ atm and $P_B^* = 1.2$ atm, respectively.

1) Give the definition of an ideal solution.

2) Calculate the molar composition of the first drop of liquid which appears and the total pressure which allow liquefaction to begin. Your methodology has to be detailed.

Data :

Nernst equation: $E_{ox/red} = E°_{ox/red} + \frac{RT}{nF} Ln \frac{\prod a_{ox}^{\nu_j}}{\prod a_{red}^{\nu_i}}$

Standard electrical potentials: $E°_{H^+/H_2} = 0.00\ V;\ E°_{O_2/H_2O} = 1.23\ V$

A (ampere) = $C.s^{-1}$

F = 96 500 C per mol of electrons

Molar volume of ideal gas in NCTP: 22.4 L.

At 25°C : $\frac{RT}{F} Lnx = 0.059 logx$

Molar masses :

Mg : 24.2 $g.mol^{-1}$

Cl : 35.5 $g.mol^{-1}$

O : 16.0 $g.mol^{-1}$

Water self-dissociation equilibrium constant: $K_e = 10^{-14}$;