INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

FIMI department - 2A

CHEMISTRY 2

Test n°2

Duration : 1h30

December 17 2018

No document allowed. Calculators are authorized.

The schedule of mark is given as an indication only.

All gases may be considered as ideal. Constants and conversion: R=8.314 J.mol^{-1}.K^{-1} and $T_{0°C}$ = 273 K

Exercise 1 : Ethanol-benzene Liquid/vapor phase diagram [10 points]

The isobaric liquid/vapor phase diagram obtained at p = 760 Torr for binary mixtures made of benzene (C_6H_6), noted B, and ethanol (C_2H_5OH), noted E is provided on page 3.

Some values for the composition of the liquid ($\mathbf{x_E}$) and the vapor ($\mathbf{y_E}$) phase in equilibrium, expressed as molar fraction in ethanol, are gathered in the following table.

$\theta_{boiling}$ (°C)	80.1	67.5	75	78.5
x_E	0	0.448	0.950	100
y_E	0	0.448	0.842	100

2-1. Complete the diagram with all the missing information (phase(s) in each domain, name of the curves, of the peculiar points, detailed expression and value of the variance for each point and domain).

2-2. Is the solution an ideal one? Justify your answer by discussing interactions between ethanol and benzene.

2-3. One ton of a solution containing 15 weight % of benzene is heated to 75°C. Give the nature of the phases at the equilibrium, their mass and the quantities (in mol) of benzene and ethanol they contain

2-4. We intend to separate the constituents of the previous mixture by fractionated distillation.

a) Recall in few words the principle of fractionated distillation.

b) Which compound can be obtained as pure by fractionated distillation? In which part of the distillation apparatus will it be collected? How much weight at best can one recover ?

2-5. Value of saturated vapor pressure p^*_E for pure ethanol is 779 Torr at 79 °C and 795.1 Torr at 79.5 °C.

Value of saturated vapor pressure p^*_B for pure benzene is 734.4 Torr at 79 °C and 745.9 Torr at 79.5° C.

If benzene and ethanol mixtures were ideal solutions, what would be the molar composition in ethanol of the liquid and of the vapor in equilibrium at these two temperatures?

Data :

Molar mass of ethanol M_E=46 g.mol^{-1} ; Molar mass of benzene M_B = 78 g.mol^{-1}.

Exercise 2 : Chromium (Cr) in aqueous solution [10 points]

Cr may be present in aqueous solutions mostly under the following chemical forms : $Cr^{3+}_{(aq)}$; $Cr(OH)_{3(s)}$; $Cr(OH)_4^-{}_{(aq)}$; $Cr_2O_7^{2-}{}_{(aq)}$. All reactions will be considered to occur at 25°C. The needed data and information are given at the end of the exercise. ***Questions 1 and 2 are independent****.*

1-1. With increasing the concentration of HO^-, Cr^{3+} ions may precipitate in the form of $Cr(OH)_{3\,(s)}$; moreover, this Chromium hydroxide may solubilize in the form of $Cr(OH)_4^-{}_{(aq)}$ at higher pH. Using the data given at the end :

a) Write down the reaction and determine the pH of precipitation of $Cr(OH)_{3\,(s)}$ (equilibrium 1) in an aqueous solution containing $Cr^{3+}{}_{(aq)}$ at a concentration of 0.1 mol.L^{-1}.

b) Express the equilibrium constant of equilibrium 2 as a function of the concentrations.

$$Cr^{3+}{}_{(aq)} + 4OH^-{}_{(aq)} \rightleftharpoons Cr(OH)_4^-{}_{(aq)} \qquad \text{(eq. 2)}$$

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c) Write the equation of dissolution of $Cr(OH)_{3\ (s)}$ in an alkaline aqueous solution (equilibrium 3). Express the equilibrium constant $K°_3$ for this equilibrium as a function of constants $K°_1$ and $K°_2$ at 25°C, then calculate $K°_3$ at the same temperature.
d) Calculate the lower value of pH at which $Cr(OH)_{3\ (s)}$ would be completely dissolved in an alkaline solution.
e) Indicate on a predominance diagram the forms of Cr that are predominant in the different pH ranges.

1.2. *We study here the reaction of dichromate ions $Cr_2O_7^{2-}{}_{(aq)}$ on ethanol $CH_3CH_2OH_{(aq)}$ at pH < 4.*

In this reaction, ethanol is oxidized into acetic acid $CH_3COOH_{(aq)}$ *according to the following half-equation:*

$$CH_3CH_2OH_{(aq)} + H_2O_{(l)} \rightleftharpoons 4\ H^+_{(aq)} + 4\ e^- + CH_3COOH_{(aq)}$$

a) Indicate on a predominance diagram the pH ranges where CH_3COOH and CH_3COO^- are respectively predominant.
b) Write the half-reaction of redox couple $Cr_2O_7^{2-}{}_{(aq)}$ / $Cr^{3+}{}_{(aq)}$
c) Write the balanced equation of the overall oxidation-reduction reaction (equilibrium 4).
d) Calculate *LnK°₄* at 25°C when pH = 0. What do you conclude ?

The reactions above are used to titrate ethanol in wine at 25°C using an aqueous solution of potassium dichromate. A volume of 20 mL of wine is pipetted into an erlenmeyer. Then, a volume of 10 mL of an aqueous solution of sulfuric acid (strong di-acid) at a concentration of $[H_2SO_4] = 10.70\ mol.L^{-1}$ is added. The titrating solution of dichromate has a concentration of $[Cr_2O_7^{2-}] = 1.15\ mol.L^{-1}$.
The result of the titration is that a volume of 23.20 mL of dichromate solution are poored at the equivalence.

e) Calculate in $mol.L^{-1}$ the concentration of ethanol in the wine analyzed here.
f) At the equivalence, calculate in the erlenmeyer (i) the overall volume of solution, (ii) the total number of moles ($n_T = n_A + n_B$) in acetic acid A (CH_3COOH) and in its conjugated base B ($CH_3CO_2^-$).
g) Calculate the pH at the equilvalence. It is required to express all the concentration terms with 4 digits.
h) Is it necessary to take into account the acid / base equilibrium CH_3COOH /CH_3COO^- to determine the pH? Justify your answer.

Data :

Constant of Faraday : F = 96500 C.

Couple	**Standard Potential at 25°C (Volt) at pH = 0**
$Cr_2O_7^{2-}{}_{(aq)}/Cr^{3+}{}_{(aq)}$	1.330
CH_3COOH/CH_3CH_2OH	0.037

Equilibrium Constants at 298 K :
Solubility product of $Cr(OH)_{3(s)}$: $K_S = 10^{-31}$
Eq. Constant of reaction $Cr^{3+} + 4OH^- \rightleftharpoons Cr(OH)_4^-$ $K°_2 = 10^{30.6}$
Acidity constant of acetic acid : $K_a\ (CH_3COOH_{(aq)}/CH_3COO^-{}_{(aq)}) = 10^{-4.75}$
Ionic product of water : $K_e^\circ = 10^{-14}$

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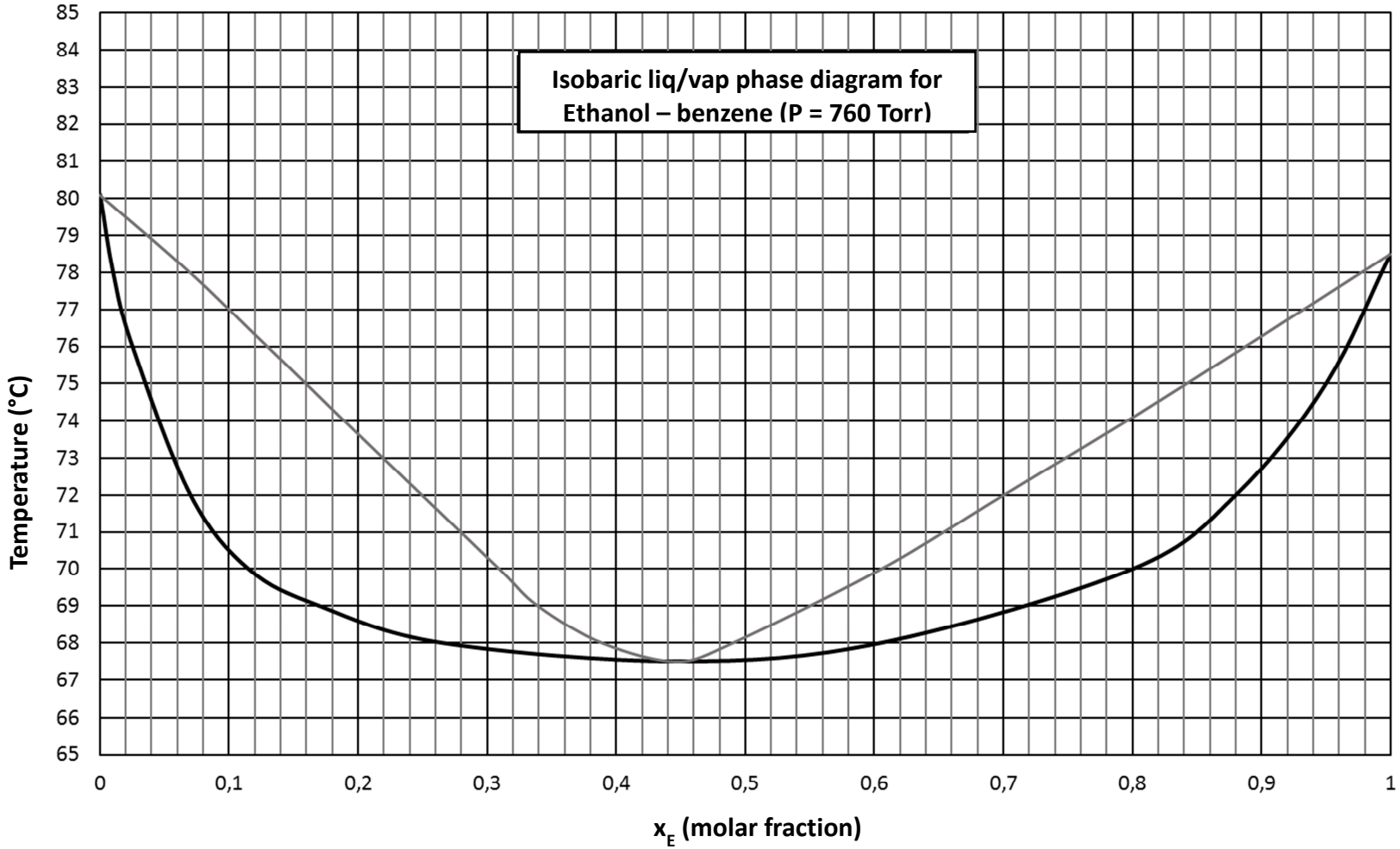
Appendix to be given back with your copy **Name :** **Surname :** **Group :**



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