FC - AMERINSA - ASINSA - EURINSA - SCAN -SHN

Friday February 7, 2024

IEFS CHEMISTRY 2 (3 hours)

- *No documents allowed. Any type of calculator allowed.*
- *Your answers and approach must be justified. Literal formulas must be clearly shown before numerical applications.*
- *The Ellingham approximation can be applied to the various equilibria.*
- *We can directly equate the activities of solutes in solution with their concentrations, and the activity of gases with their partial pressures.*
- $R = 8.314\ J \cdot K^{-1} \cdot mol^{-1};\ 0\ °C = 273\ K;\ 1\ atm = 101\ 325\ Pa = 1.01325\ bar = 760\ Torr$
- *Faraday constant:* $96\ 500\ C \cdot mol^{-1}$

Exercise 1: Physical and chemical equilibria in wine

Wine production involves understanding and controlling numerous physical and chemical equilibria to obtain optimal taste qualities.

The **INSA Oenology Club** wants to study some of these balances to better understand their role. To do this, it is looking at a bottle of white wine at $pH = 2.50$ with an alcohol content of $10.0\ \%_{volume}$

Notes:

- *The three parts of this exercise can be treated independently;*
- *For the rest of the exercise, tartaric acid, malic acid and lactic acid are noted as H_2Tar, H_2Mal and $HLac$, respectively, in order to simplify and improve the clarity of the writing;*
- *It will be assumed that the volumes of water and ethanol are additive in the mixtures.*

Part A: Study of malolactic fermentation

During wine fermentation, malic acid is converted into lactic acid according to the following equilibrium:

$$H_2Mal_{(aq)} \rightleftharpoons HLac_{(aq)} + CO_{2\ (g)}$$

This fermentation reaction is essential, as it improves the wine's taste by adding new aromas. The wine studied (whose final compositions of different acids are given in **Table2**) had a malic acid concentration of $3.10\ g.L^{-1}$ before fermentation.

A.1) From the statement and the data in the exercise, considering that fermentation takes place under atmosphere at a pressure of $P_{ext} = 1\ bar$ and at $20\ °C$, in an open environment (P_{CO_2} will be constant), determine:

a) The dissociation coefficient of malic acid; defined as $\alpha = \frac{number\ of\ moles\ of\ acid\ dissociated}{initial\ number\ of\ moles\ of\ acid}$

b) The expression and value of the reaction constant.

A winemaker decided to carry out this fermentation in a closed environment (a bottle of $1\ \mathrm{L}$ filled with $750\ \mathrm{mL}$ wine) at $20\ °\mathrm{C}$ initially containing $3.10\ \mathrm{g \cdot L^{-1}}$ malic acid.

A.2) Show that the amount of lactic acid present before the fermentation step can be neglected.

A.3) Determine the dissociation coefficient of malic acid under these conditions. What is the final pressure in the bottle? For this question, neglect the dissolution of $CO_{2\,(g)}$ in the wine.

A.4) In fact, the dissociation coefficient of malic acid under these conditions is higher than the value obtained in the previous question.

a) Explain the influence of dissolving $CO_{2\,(g)}$ in the wine on the progress of the fermentation reaction.

b) What physical phenomenon can you observe in the wine when the bottle is suddenly opened?

c) The real dissociation coefficient is $20\ \%$. Calculate the concentrations at equilibrium in $\mathrm{mol \cdot L^{-1}}$ of malic acid and lactic acid, as well as the concentration of dissolved $CO_{2\,(aq)}$.

d) Express and calculate the Henry's law constant of $CO_{2\,(g)}$ at $20\ °\mathrm{C}$ (in Pa) in wine, considering it as a water-ethanol mixture at $10\ \%_{\mathrm{volume}}$

Part B: Precipitation of potassium bitartrate (KHTar)

In wine, the presence of the potassium ion can lead to the precipitation of a solid, potassium bitartrate $KC_4H_5O_6$ (noted as KHTar), under certain conditions of pH and temperature. This solid is part of the deposit that can be found at the bottom of wine bottles.

First, we look at the solubility of KHTar in a **water-ethanol mixture at 10** $\%_{\mathbf{volume}}$. The**Table3** gives its constant as a function of temperature.

B.1 a) Write the chemical equation for the dissolution of potassium bitartrate and the literal expression of the associated equilibrium constant.

b) Calculate the variation of standard Gibbs free energy of this reaction in a water-ethanol mixture at 5 and $20\ °\mathrm{C}$.

c) Deduce the variation of standard enthalpy and entropy of dissolution of the precipitate in this water-ethanol mixture. Comment on their values.

We are now interested in the formation of this precipitate in the studied wine ($\mathrm{pH} = 2.5$), which has a total K^+ concentration of $1.20\ \mathrm{g \cdot L^{-1}}$

B.2 a) Plot the predominance diagram of tartaric acid as a function of pH and explain qualitatively the influence of wine's pH on the precipitation of potassium bitartrate.

b) Express and calculate the variation of Gibbs free energy of the dissolution reaction at $20\ °\mathrm{C}$ for pH of $1, 3$ and 5 for which the concentration of the bitartrate ion ($\mathrm{HTar^-}$) is $0.135\ \mathrm{mmol \cdot L^{-1}}$, $6.97\ \mathrm{mmol \cdot L^{-1}}$ and $2.68\ \mathrm{mmol \cdot L^{-1}}$, respectively.
Conclude on the presence of the precipitate or not for these different values of pH.

B.3) In order to limit the risk of precipitation, one process consists in cooling the wine before bottling, then filtering it to remove the solid in a controlled manner. Based on the variation of Gibbs free energy, calculate the temperature below which potassium bitartrate spontaneously precipitates in the studied wine ($\mathrm{pH} = 2.5$).

Part C: Armagnac production by wine distillation

From wine, it is possible to obtain armagnac by continuous fractional distillation in order to increase the alcohol content and develop new aromas. The Oenology Club proposes to look at the distillation of wine into armagnac, modeling it on a binary water-ethanol mixture with an ethanol content of $10.0\ \%$.

C.1) Assuming that the water-ethanol system behaves as an ideal mixture, establish the literal expression for the molar ethanol composition of the liquid and vapor phases.

C.2) Draw and annotate the liquid-vapour diagram of the mixture as a function of the ethanol mass fraction from the data **(Table4**). What can you conclude about the ideal character of the mixture? Specify the type of deviation from Raoult's law, if any.

We are now interested in the distillation of $100\ \mathrm{L}$ of this wine into armagnac. A fractional distillation column is used, with a bottom temperature of $100\ °\mathrm{C}$ and a top temperature of $78\ °\mathrm{C}$.

C.3) At what column height, i.e. at what temperature, must the vapors be collected to obtain a distillate with an ethanol mass composition of $46{,}1\ \%$?

C.4) Then determine the ethanol mass composition of the distillation residue and the distillate, assuming a perfect distillation process. Calculate the mass of the distillate and the residue, as well as the mass of water and ethanol contained in each. Present your results in tabular form.

C.5) What is the final volume and alcohol content by volume of the armagnac obtained at the end of the distillation column?

C.6) Explain why it is difficult to obtain absolute ethanol (pure ethanol) by distillation under atmospheric pressure.

Bonus question: Suggest a method for obtaining absolute ethanol.

Exercise 2: Designing a reversible redox flow battery (RFB)

During peaks in the production of intermittent renewable energy, storage of the surplus enables it to be restored during periods of low production or when electricity is more expensive. Redox flow batteries (RFB) are suitable for stationary applications, with modularity ranging from a few $\mathrm{kW/kWh}$ to $175\ \mathrm{MW/700\ MWh}$ (China) for the largest unit currently available.

In this exercise, we will study the compromise of an all-liquid organic / inorganic hybrid battery using as electrolyte the Ox/Red couples ($\mathrm{A^{2-}/H_2A^{2-}}$ and $\mathrm{VO^{+}_{2(aq)}/VO^{2+}_{(aq)}}$) in an acidified aqueous medium.

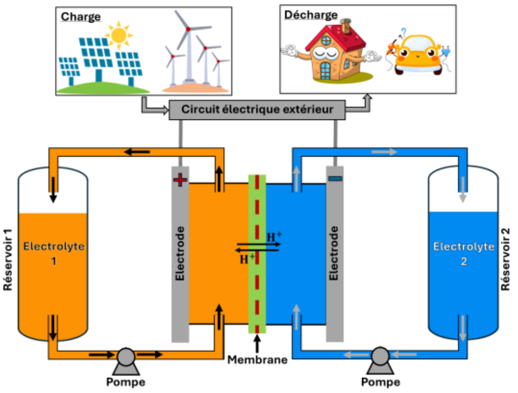


Figure1 : Schema of a redox flow battery

As illustrated in Figure1, redox flow batteries consist of:

- **Two storage tanks** equipped with 2 pumps to circulate electrolytes.
- **An electrochemical cell** that behaves like a rechargeable battery, i.e. it can perform charge and discharge cycles.
- **A semi-permeable** proton ($\mathrm{H^+}$) **exchange membrane** separates the 2 electrochemical half-cells.

The redox flow battery thus consists of two half-cells A and B :

Half-cell A: $\mathbf{A^{2-}_{(aq)}/H_2A^{2-}_{(aq)}}$ **couple**

In solution: $[H_2A^{2-}] = 0.10\ mol \cdot L^{-1};\ [A^{2-}] = 0.40\ mol \cdot L^{-1}$ at $pH = 2.$

Half-cell B: $\mathbf{VO^{+}_{2(aq)}/VO^{2+}_{(aq)}}$ **couple**

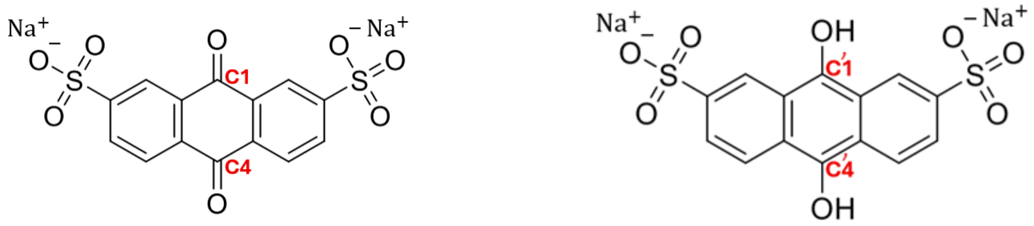
In solution: $[VO^{2+}] = 0.80\ mol \cdot L^{-1};\ [VO_2^{+}] = 0.20\ mol \cdot L^{-1};\ [H_2SO_4] = 2\ mol \cdot L^{-1}$

1) Course questions:

a) Draw a complete schema of a Daniell battery under standard conditions (*i.e.* Zinc-Copper battery with salt separator), specifying the reactions involved and their directions.

b) What are the differences between this salt battery and our redox flow battery? To do this, compare the type of used electrode, the type of separator, the relationship between cell size and capacity, and rechargeability in the given table in the appendix.

2) Justify the oxidation numbers of carbons C1, C'1, C4 and C'4 in the A^{2-}/H_2A^{2-} couple and of vanadium atoms in the $VO^{+}_{2(aq)}/VO^{2+}_{(aq)}$ couple.



$2\ Na^{+}A^{2-}\ (2\ Na^{+}, C_{14}H_6O_8S_2^{2-})$ $2\ Na^{+}, H_2A^{2-}\ (2\ Na^{+}, C_{14}H_8O_8S_2^{2-})$

Figure2 : LEWIS representation of the a) disodium anthraquinone-2,7-disulfonate and b) disodium 1,4-dihydroanthraquinone-2,7-disulfonate salts.

3) **a)** Write down the redox half-equations.

b) Express and calculate the Nernst potential for each half-cell. Deduce the overall chemical equation when the battery is functioning.

c) Check that the electromotive force of the battery is $+0{,}926\ V$ at $25\ °C$.

4) At constant P and T, can the reaction be considered total?

5) We are now interested in the battery consisting of the SHE and the $VO^{+}_{2(aq)}/VO^{2+}_{(aq)}$ couple half-cell. The temperature coefficient of the standard potential of this couple with respect to SHE is equal to:

$$\frac{d\left(E^{\circ}\left(VO^{+}_{2(aq)}/VO^{2+}_{(aq)}\right)\right)}{d\,T} = -0.22\ mV \cdot K^{-1}$$

Deduce the value of $\Delta_r S^{\circ}_{(298\ K)}$ then $\Delta_r H^{\circ}_{(298\ K)}$ from the half-equation of redox couple.

6) In view of electrochemical equilibria, why is it not recommended to exceed a recharge voltage of $1.23\ V$?

Bonus question: In order to increase the voltage and therefore the power of the battery without increasing its size, we are looking to replace the VO_2^{+}/VO^{2+} couple by the Al^{3+}/Al^{0} couple. What parasitic reactions are likely to occur **in aqueous media** when the battery is operating at $pH = 0$ and $pH = 8$? Use the apparent standard potentials of these species as a guide.

Data

Densities: • $\rho_{eau}(20\ °C) = 1.000\ g \cdot cm^{-3}$ • $\rho_{ethanol}(20\ °C) = 0.789\ g \cdot cm^{-3}$

Molar composition of air:

N_2	O_2	Ar	CO_2	Other gases
78.1 %	20.9 %	0.93 %	0.04 %	0.03 %

Table1 : Molar mass ($g \cdot mol^{-1}$) of various atoms and chemical compounds.

H	C	N	O	Na	K	S	V	Fe	Ethanol	KHTar	VO^{2+}, SO_4^{2-}	A^{2-}
1.0	12.0	14.0	16.0	23.0	39.1	32.1	50.9	55.8	46.1	188.2	163.0	366.3

Table2 : Data on various organic acids contained in the wine studied.

	Chemical formula	Molar mass ($g \cdot mol^{-1}$)	$pK_{a,1}$	$pK_{a,2}$	Mass concentration ($g \cdot L^{-1}$)
Tartaric acid	$C_4H_6O_6$	150.1	3.04	4.34	2.24
Malic acid	$C_4H_6O_5$	134.1	3.46	5.14	0.05
Lactic acid	$C_3H_6O_3$	90.0	3.90		2.05

*Table3 : Solubility constants of **potassium bitartrate** in a **water-ethanol mixture at** $10\ \%_{volume}$ as a function of temperature.*

Temperature (°C)			
5	10	15	20
$48.7 \cdot 10^{-6}$	$79.7 \cdot 10^{-6}$	$117 \cdot 10^{-6}$	$185 \cdot 10^{-6}$

Table4 : Mass composition (%) of ethanol in the liquid and vapor phases as a function of temperature in a binary water-ethanol mixture at atmospheric pressure.

	Temperature (°C)										
	100	97.0	93.0	89.0	84.0	82.0	80.0	78.5	78.0	78.1	78.3
Liquid	0	2.6	7.3	14.5	32.8	47.8	68.8	85.6	94.5	97.6	100
Steam	0	25.8	46.1	60.0	72.5	76.9	82.1	88.7	94.5	97.4	100

Table5 : Standard potential $E^{\circ}_{(Ox/Red)/SHE}$ *for various Ox/Red couples.*

$\mathbf{Al^{3+}_{(aq)}/Al^{0}_{(s)}}$	$\mathbf{Zn^{2+}_{(aq)}/Zn^{0}_{(s)}}$	$\mathbf{H_2O_{(\ell)}/H_{2(g)}}$	$\mathbf{A^{2-}_{(aq)}/H_2A^{2-}_{(aq)}}$	$\mathbf{Cu^{2+}_{(aq)}/Cu^{0}_{(s)}}$
−1.67 V	−0.76 V	0.00 V	+0.21 V	+0.34 V
$\mathbf{Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}}$	$\mathbf{Hg^{2+}_{2(aq)}/Hg^{0}_{(\ell)}}$	$\mathbf{VO^{+}_{2(aq)}/VO^{2+}_{(aq)}}$	$\mathbf{O_{2(g)}/H_2O_{(\ell)}}$	-
+0.77 V	+0.79 V	+1.00 V	+1.23 V	-

Table6 : Equilibrium constants for various species.

$\mathbf{pK_s(Al(OH)_3)}$	$\mathbf{pK_f(Al(OH)_4^-)}$
32	−1.0

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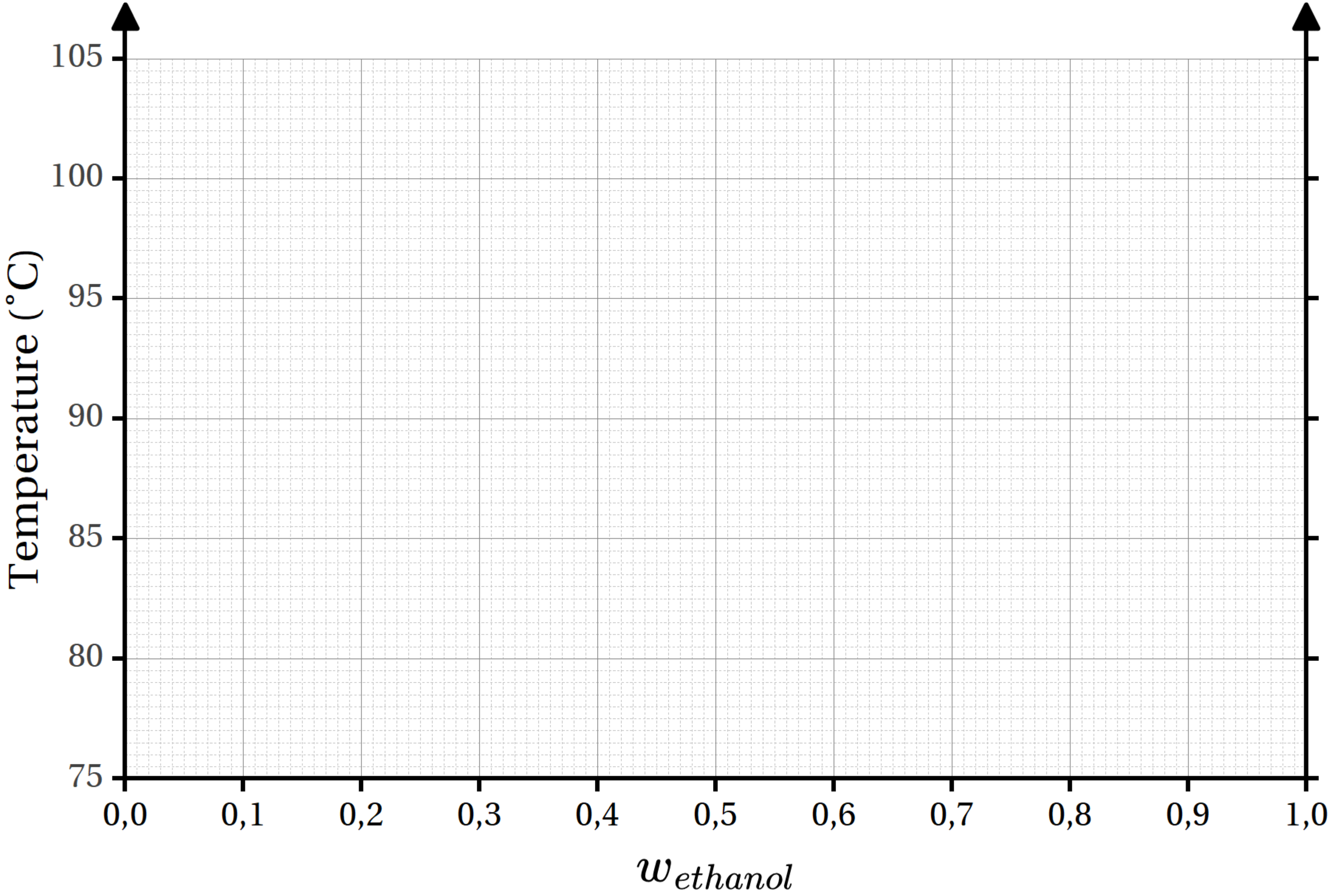

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	Redox flow battery	**Salt battery**
Electrode		
Separator		
Size/capacity		
Rechargeability		