INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

CHEMISTRY TEST # 2 -2017 / 2018

PCC-AM-Asinsa-Eurinsa-SCAN-SHN January 8, 2018 (1h30)

No document allowed. The 2 exercises can be treated independently -
All gases may be considered as ideal. For all numerical applications, take:
R=8.314 $J.mol^{-1}.K^{-1}$; T_0 = 273 K = 0°C; 1 atm = 760 Torr = 101325 Pa = 1.013 bar.
Faraday constant F =: 96500 $C.mol^{-1}$.
All answers must be justified.

demixtion liq

I. Exercise I : Partial miscibility at liquid state (12 points)

A –Liquid / vapor equilibria

Figure 1 shows the isobaric Liquid / Vapor equilibrium phase diagram for a given binary system A-B.

1. Complete the diagram by writing in it the following information :
   - Names of the curves and specific points,
   - Number and nature of the phases stable in the different domains,
   - Variance of the system in the different domains and at the specific points.

The literal expression of the variance and the numerical values of the variables shall be given in all cases.

2. Answer the questions below Figure 1 (**do not forget to return the sheet along with your copy**).

3. What is(are) the conditions on the composition of a liquid solution made of A and B that would allow obtaining pure B by fractionated distillation?

We are considering now, at 25°C, a mixture of 1000 moles of A and B with a molar fraction of 0.10 in B.

4. Under the atmospheric pressure of 1 bar, at which temperature will this mixture start boiling? What will then be the composition of the first vapor formed?

Supposing an optimal distillation setup is used, in the best case :

5. What will be the composition of the distillate D_1 (expressed in molar fraction of B) ?

6. What will be the composition of the residue R_1 (expressed in molar fraction of B) in the boiler?

7. Calculate the number of moles of A and B (+/- 0.1 mole) which would be collected:

- In the distillate D_1
- In the residue R_1.

B – Liquid – liquid equilibria

Under a pressure of 1 bar, A and B are partly miscible at the liquid state.

8. Using the information given in Table 1 below, complete the isobaric liq / liq equilibrium phase diagram in Figure 1 by indicating the name of the curve, the number and nature of the phase(s) below the curve.

9. What is the limit of solubility of A in B at 10°C (expressed in molar fraction of B) ?

10. What is the limit of solubility of B in A at 10°C (expressed in molar fraction of B) ?

The totality of distillate D_1 (see question 7) is introduced into a separating funnel and cooled down to 10°C.

11. Determine the composition (molar fraction of B) and number of moles of A and B (+/- 0.1 mol) in each phase at equilibrium.

C – Second distillation. Conclusion

The totality of the phase having the higher content in B is collected from the separating funnel and introduced into a flask to proceed with a new distillation.

12. Give the composition (molar fraction of B) and number of moles of the phases that will be obtained.

13. Considering the 1000 moles of the initial mixture at a molar fraction of 0.10 in B, calculate:

$$100 \times \frac{n_{A\ recovered\ pure}}{n_{A\ initial}} \quad and\ 100 \times \frac{n_{B\ recovered\ pure}}{n_{B\ initial}}$$

What do you conclude?

Table I : Temperature of demixtion of A-B mixtures at various molar fraction of B (P = 1 bar)

Molar fraction in B	0,10	0,20	0,30	0,40	0,50	0,60	0,70	0,80	0,90	0,95	0,96
Temperature of démixtion (°C)	10	23	32	38	40	40	38	34	28	16	10

Exercise II : Glucose / dioxygen biological battery cells (8 points)

The capacity of many biological systems to oxidize glucose ($C_6H_{12}O_6$) in the presence of dioxygen can be used to develop battery cells according to the schematic representation shown in Figure 2 where:

- GOx refers to glucose oxidase enzyme which catalyzes the reaction of oxidation of glucose into gluconic acid ($C_6H_{12}O_7$). A catalyst allows to accelerate a reaction without taking part in the stoichiometry of the reaction.

- BOD refers to bilirubine oxidase which catalyzes the reaction of reduction of dioxygen into water.

- The enzymes are attached to the electrodes by the "mediators" noted M and M'. Neither the enzymes (GOx et BOD) nor the « mediators » (M and M') take part in the reactions.

- **The reactions take place in aqueous solution and the participation of protons is needed to balance the chemical equations.**

<u>Data and useful information</u> :

Molar mass: *$M(C_6H_{12}O_6) = 180\ g.mol^{-1}$*

Half equation relative to gluconic acid / glucose couple : *$C_6H_{12}O_7 + 2\ H_3O^+ + 2\ e^- \rightleftarrows C_6H_{12}O_6 + 3\ H_2O$*

Standard potentials at pH = 0 and 25°C :

$E°(O_2/H_2O) = 1{,}23\ V$; $E°(C_6H_{12}O_7/C_6H_{12}O_6) = 0{,}07\ V$

Nernst's law : *Considering a half-reaction expressed with the following general equation:*

$$\sum_i \nu_i A_i + n\,e^- \rightleftarrows \sum_j \nu'_j B_j$$

where $\sum_i \nu_i A_i$ refers to the reactants involved in the reaction of reduction of the oxidized species, and $\sum_j \nu'_j B_j$ the products associated to the formation of the reduced species, Nernst's law is expressed as follows:

$$E_{Ox/Red} = E°_{Ox/Red} + \frac{RT}{nF} \times \ln\left[\frac{\prod_i (a_{A_i})^{\nu_i}}{\prod_j (a_{B_j})^{\nu'_j}}\right]$$

1. Indicate which electrode in Figure 2 is the anode and which one is the cathode (justify your answer). Deduce the polarity of the considered biological battery cell.
2. Complete the schematic representation of Figure 2 by indicating with arrows:

   - the circulation of the electrons between the electrodes via the "mediators" M and M',

   - the circulation of the electric current in the résistance.

3. Give the literal expression of the potential of the cathode and the one of the anode, respectively.

4. Write the overall redox reaction taking place in the biological battery cell.

5. Calculate the thermodynamic equilibrium constant at 25°C, noted K^0_{298K}. Comment your numerical result.

In practice, the electromotive force of the biological battery cells developed today on this principle is around 0.8 V.

6. Calculate the electrical work produced by the battery cell when it consumes :

    - One mole of glucose,
    - One liter of an aqueous solution (such as blood) at a glucose concentration of 1 $g.L^{-1}$.

7. These battery cells may be used to provide electricity needed to operate heart stimulators (known as « pacemakers »). Knowing that the power supply of a pacemaker is around 10 µW, calculate the lifespan ("durée de fonctionnement") of the biological battery cell that would be implanted in the body of an individual with a glucose concentration of 1 gL^{-1}.

8. What potential advantages and disadvantages do you see in using such a system directly implanted within the organism?