INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

PCC – AM – ASINSA- EURINSA - SCAN - SHN

January 6th 2020

CHEMISTRY TEST n°2 (1h30)

All types of calculators are allowed.

The two exercises are independent. All answers must be justified.

For all numerical applications, take : R = 8.314 J.mol^{-1}.K^{-1} ; T (K) = Θ(°C) + 273 K ;

1 atm = 760 Torr = 101325 Pa = 1.013 bar. P^0 = 1 bar

All gases may be considered as ideal.

The schedule of mark is for indication only.

Exercise A. Liquid-vapor equilibrium of dioxygen-dinitrogen binary mixture (12 pts).

1. From the integration of the Clapeyron equation, express the saturated vapor pressure of dinitrogen ($P^*_{N_2}$) in bar as a function of temperature. Give the hypotheses used for the integration of this relationship.

2. Fill in table 1 (appendix A) to be given back with your copy.

3. In figure 1 (appendix A), indicate which is/are the phase(s) present in each domain, denominate each equilibrium curves and notable points.

4. What are the conditions to be respected for a solution to be ideal?

5. Prove by calculation that dioxygen-dinitrogen binary mixture is ideal. Justify your methodology and fill in table 2 (appendix A). (Molar fraction will be given to within 0.01)

6. Complete figure 2 (appendix A). Give the coordinates of points located on this figure. Indicate the phase(s) present in each domain and denominate the equilibrium curves.

7. From graphic readings and considering the gas mixture of air, with a molar composition of 80% of dinitrogen and 20% of dioxygen :
   a. Determine the pressure at which this gas mixture starts liquefying at T = 86 K,
   b. Determine the molar composition of the first drop of liquid when the air pressure decreases,
   c. At what pressure is air completely liquid? What is the molar composition of the last bubble of gas?

8. One ton of a liquid mixture constituted of 60 % of dinitrogen and 40 % of dioxygen (molar percentage) is prepared under a constant pressure of 1 bar. This mixture is introduced into a distillation column, on a plateau which is at 82K. What are the respective masses of liquid and gas which are found on this plateau? At which temperature of the column, a liquid at 75 mol. % of N_2 can be found? Is it located above or below the plateau at which the mixture has been initially introduced?

Data :

Molar masses: $\bar{M}_{O_2} = 32$ g.mol^{-1} ; $\bar{M}_{N_2} = 28$ g.mol^{-1}

$$\ln P^*_{O_2} = -\frac{887.4}{T} + 9.86$$ with P in bar.

At $T = 77.0$ K, $P^*_{N_2} = 1$ bar ; at $T = 62.9$ K, $P^*_{N_2} = 0.125$ bar

At T=86.0 K under P = 2 bar, one liquid and one vapor of respective compositions, $x_{N_2} = 0.68$ et $y_{N_2} = 0.90$ are in equilibrium.

Exercise B. Na-CO_2 electrochemical cell (8 pts).

A new hybrid electrochemical cell $Na_{(s)}$-CO_2 has been designed to produce both electrical energy and dihydrogen (H
through an efficient conversion of CO_2 which is dissolved in ocean (see scheme 1 in appendix B)

1. Write the half-reactions of the two involved couples.
2. When the cell produces electricity,

a. Locate on scheme 1 (appendix B) the anode and the cathode. Justify your answer.

b. Indicate with arrows the direction of electrons on scheme 1 (appendix B).

c. Write the equation of the involved redox reaction.

3. Calculate the e.m.f. of the cell, E_{cell} (25°C) in sea water (see data below) when one mole of dihydrogen is produced.
4. The electrode $Na_{(s)}$ is plunged into an organic solution (electrolyte) which is separated from the aqueous solution by an ionically conductive Na membrane (NASICON). Based on the cells you already built during the dedicated lab session, elucidate the role of this membrane.
5. This cell is rechargeable? Give the half-reaction which takes place on the platinum electrode?

While producing electricity, this cell promotes the dissolution of CO_2 into the aqueous electrolyte through the first dissociation of carbonic acid (see equation below).

$$H_2CO_{3\,(aq)} \rightarrow HCO_{3\,(aq)}^- + H_{(aq)}^+$$

While H^+ is involved in the cell inner workings, HCO_3^- reacts with Na^+ to form sodium bicarbonate ($NaHCO_3$) in the aqueous solution. Thus CO_2 which is contained in air is caught and converted into sodium bicarbonate.

6. This cell can produce an electrical current of 100 mA during 500 h in seawater. During this operation:

a. Calculate the electrical charge.

b. Calculate the theoretical volume of CO_2 (gas) (measured in NCTP conditions) which is initially contained in air and which can be caught in the aqueous electrolyte within this timeframe.

7. What are the positive environmental impacts of this cell?

Data:

- Concentrations of each dissolved species in seewater (salted water) under P_{atm}
  $[H^+(aq)] = 2.29*10^{-6}$ mol.L^{-1}
  $[Na^+(aq)] = 0.486$ mol.L^{-1}
- Nernst equation at 25°C : $E = E^0 + \frac{RT}{nF} \ln\left(\frac{a_{ox}^{\nu_{ox}}}{a_{red}^{\nu_{red}}}\right)$
- Activity of H_2 : $a_{H_2} = 1$
- Standard potentials :
  $E^\circ_{Na^+/Na} = -2.71\,V\,;\,E^\circ_{H^+/H_2} = 0.00\,V\,;\,E^\circ_{H_2O/O_2} = 1.23\,V$
- A (ampere) = C.s^{-1}
- F = 96 500 C per mole of e^-
- Molar volume of ideal gas in NCTP: 22.4 L.

APPENDIX A

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Table 1. Saturated vapor pressures at different temperatures.

T (K)	77	82	86	90
$P^*_{O_2}$ (bar)	0.19	~~0,43~~	0.63	1.00
$P^*_{N_2}$ (bar)	1.00	1,72	2.63	3,65

0,5

Table 2. Respective compositions of liquid and vapor phases in equilibrium at different temperatures.

T (K)	77	82	86	90
Molar fraction in the liquid phase x_{N_2}	1 ~~0~~	0,44	0,185	0
Molar fraction in the gas phase y_{N_2}	1 ~~0~~	~~0,189~~	~~0,117~~	0

0,5

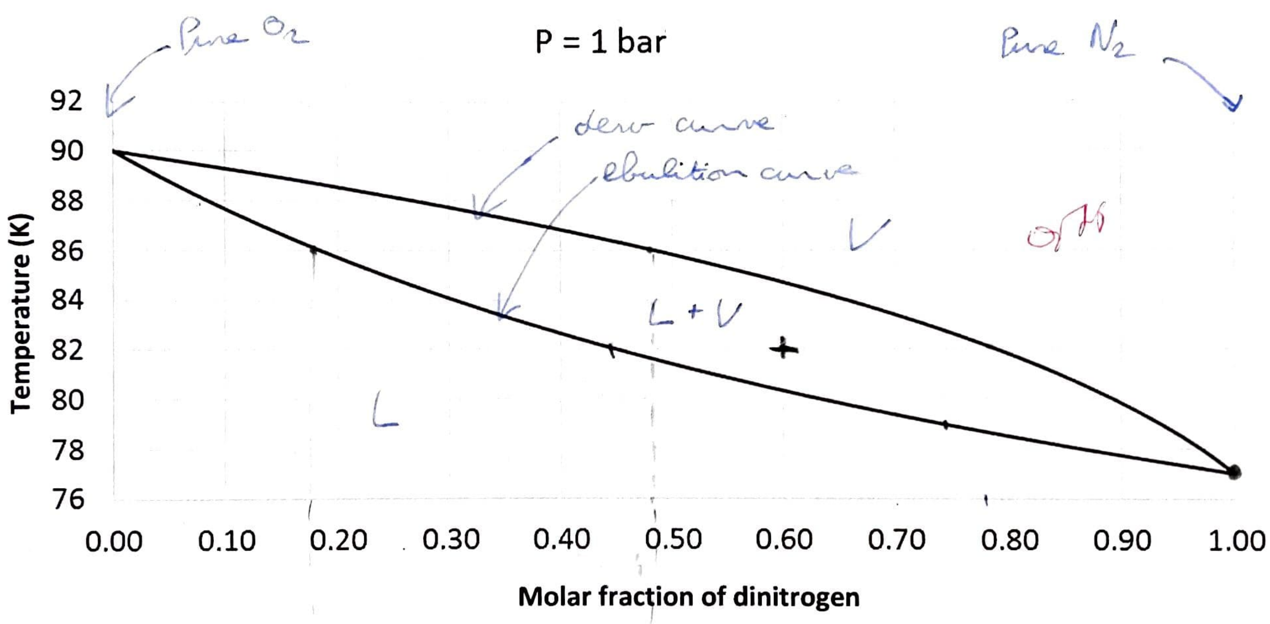


Figure 1. Isobaric liquid-vapor phase diagram of nitrogen – oxygen binary mixture (p=1 bar)

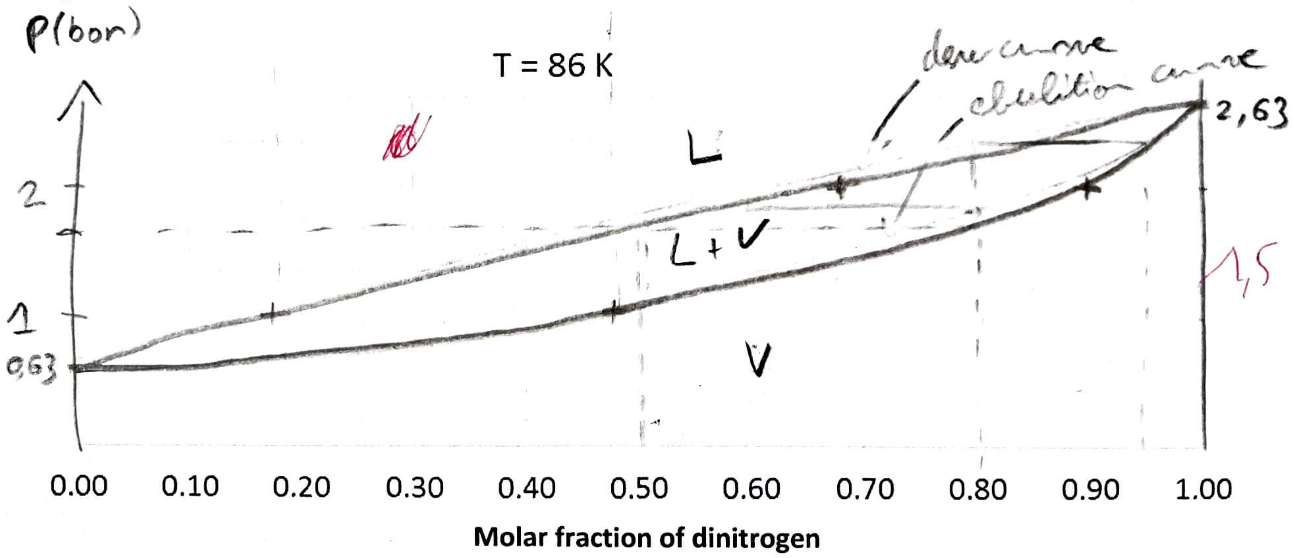
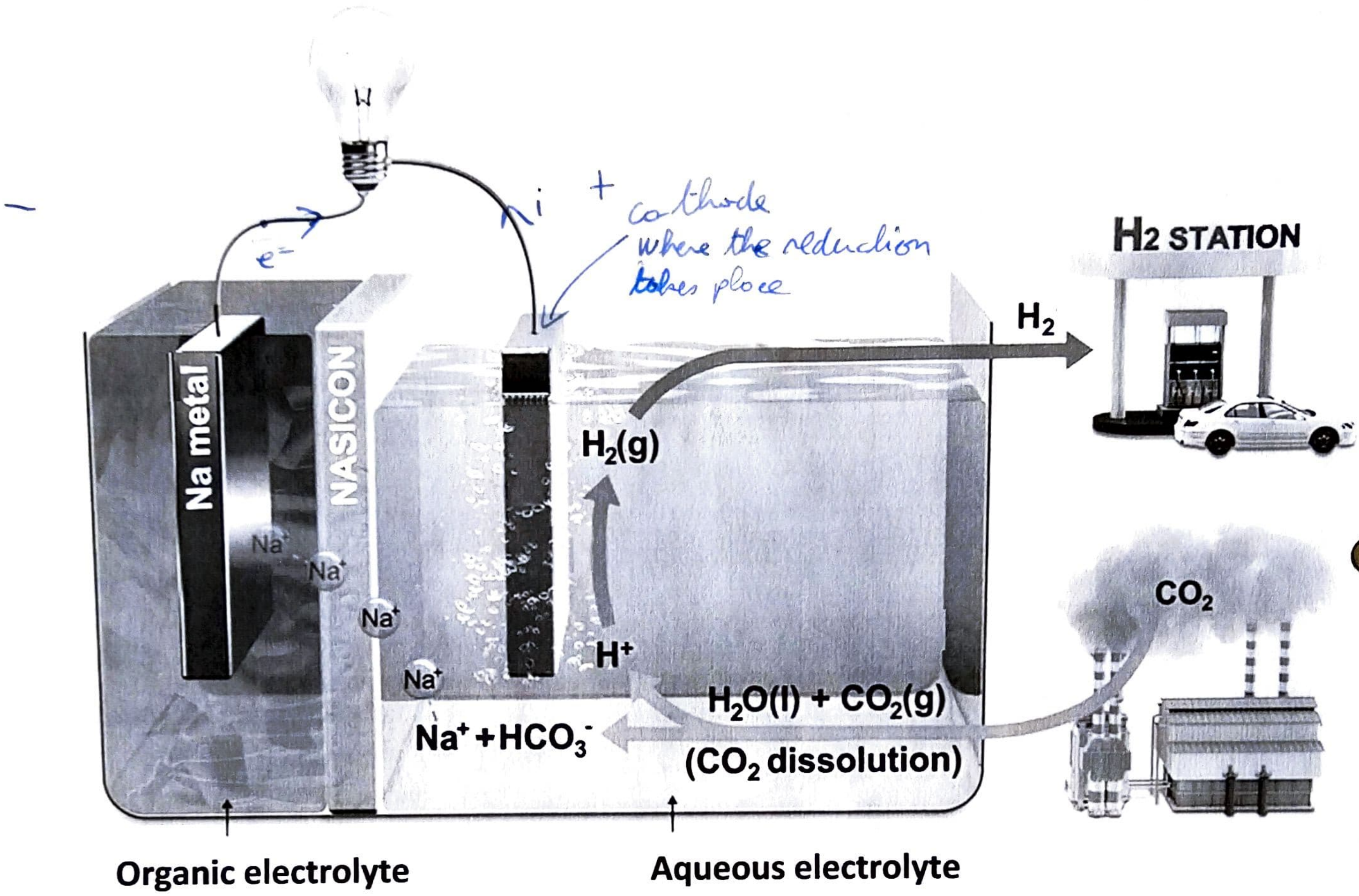


Figure 2. Isothermal liquid-vapor phase diagram of dinitrogen – dioxygen binary mixture (T=86K)

APPENDIX B



Scheme 1 : $Na_{(s)}$-CO_2 electrochemical cell