

CHEMISTRY 2 - IEFS (3 hours)

- No documents but any type of calculator allowed.
- Your answers and approach must be justified. Literal formulas must be clearly shown before numerical calculations.
- $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $F = 96500 \text{ C} \cdot \text{mol}^{-1}$, $0^\circ\text{C} = 273 \text{ K}$,
 $1 \text{ atm} = 101\,325 \text{ Pa} = 1.01325 \text{ bar} = 760 \text{ Torr}$

Exercise 1: Copper-iron galvanic cell (~ 8 pts)

The two half-cells that make up a galvanic cell are described below:

- **Half-cell A:** a copper metal electrode is immersed in 100 mL of a $0.500 \text{ mol} \cdot \text{L}^{-1}$ cupric ion (Cu^{2+}) solution.
- **Half-cell B:** a platinum metal wire is immersed in 100 mL of a solution of ferric ion (Fe^{3+}) and ferrous ion (Fe^{2+}) at concentrations of $0.200 \text{ mol} \cdot \text{L}^{-1}$ and $0.100 \text{ mol} \cdot \text{L}^{-1}$, respectively.

The temperature is assumed to be 298 K.

Part 1: Study of the copper-iron cell

1. For each half-cell, write down the half-reaction associated to the relevant redox couple, then formulate and calculate the electrode potential.
2. Write down the overall reaction representing the operation of this cell made up of these two half-cells.
3. Determine the cell electromotive force (emf).
4. Draw a complete electrochemical cell scheme.
5. Show that the reaction can be considered quantitative.

Part 2: Influence of pH

6. To obtain metal cation concentrations given for each half-cell, it was necessary to acidify the solutions. Determine the value below which the pH of the solution of half-cell B should be.
7. If the quantity of acid added to prepare half-cell B was insufficient, what effect would this have on the electromotive force of the cell?
8. Assuming that the pH of the solution is in fact 4, calculate the new cell potential value
9. What conclusions can be drawn?

Part 3: Influence of a complexing agent

Here we consider the two half-cells initially described.

10. Do you see any benefit in adding a complexing agent to half-cell A? (Justify.)

Starting from a solution of Cu^{2+} ions at pH 1, ammonia (NH_3) is added until the initial concentration of Cu^{2+} ions (0.500 M) is divided by 500, under the assumption that there is no change in volume.

11. Calculate the ammonia concentration at equilibrium.

12. Calculate the initial ammonia concentration.

Data:

Standard potentials: $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.345 \text{ V}$; $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = 0.770 \text{ V}$

Solubility products: $\text{Fe}(\text{OH})_2$: $\text{p}K_{\text{s},1} = 15.1$; $\text{Fe}(\text{OH})_3$: $\text{p}K_{\text{s},2} = 38$

Stability constants of complexes:

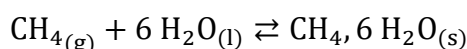
$K_{\text{f}}(\text{Cu}(\text{NH}_3)_4^{2+}) = 4,0 \cdot 10^{12}$, $K_{\text{f}}(\text{Fe}(\text{CN})_6^{4-}) = 1,5 \cdot 10^{35}$, $K_{\text{f}}(\text{Fe}(\text{CN})_6^{3-}) = 2,0 \cdot 10^{43}$

$\text{p}K_{\text{a}}(\text{NH}_4^+/\text{NH}_3) = 9.2$

$\text{p}K_{\text{w}} = 14$

Exercise 2: Methane hydrate: fire under the ice (~ 6 pts)

Methane hydrate is a solid, ice-like compound. It is formed from methane (gas) and water (liquid) according to the following equilibrium reaction:



Under certain temperature and pressure conditions, the methane formed during the decomposition of organic matters is found in the form of methane hydrate. Methane hydrate is naturally present in considerable quantities in deep marine sediments: the quantity of methane trapped in this form would correspond to twice the current reserves of conventional fossil fuels (oil, gas and coal all together!). The stability conditions of this methane hydrate are the subject of this exercise.

1. Express the equilibrium constant as a function of the constituents and deduce the effect of pressure on this equilibrium.
2. Give the expression (literal, then numerical) of the standard Gibbs free energy change $\Delta_{\text{r}}G^0(\text{T})$ of the reaction as a function of temperature.
3. Here, we're looking for the conditions for the stability of methane hydrates within the ocean floor.
 - a. From the expression of $\Delta_{\text{r}}G_{\text{T},\text{P}}$, express in literal equation the pressure above which methane hydrate is stable (it will be assumed that the gas phase consists only of methane).
 - b. From which depth (in m) can methane hydrate be found in the Mediterranean (deep-water temperature: 13 °C)?
 - c. Same question for the North Atlantic (deep-water temperature: 4 °C)?

4. Here, we investigate the conditions under which methane hydrates can be stored for energy exploitation.
- What happens when methane hydrate is released to the surface without any precautions being taken?
 - Calculate the temperature at which methane hydrate must be stored so that the methane pressure does not exceed 1 bar.
 - What volume of methane gas (measured at 1 atm and 273 K) is obtained by dissociating 1 kg of methane hydrate? Do you find it beneficial (or not) to transport methane in the form of methane hydrate rather than in free gas form?
 - 810 kg of methane hydrate are placed in a hermetic 1 m³ container maintained at -25 °C, initially in the presence of nitrogen at atmospheric pressure (1 atm). Describe the evolution of the system up to equilibrium (number of moles of methane gas, total pressure). The volume of each phase will be considered constant.
5. What consequences will global warming have on the methane currently trapped in the form of methane hydrates?

Data:

Volumetric mass of methane hydrate: 900 kg·m⁻³

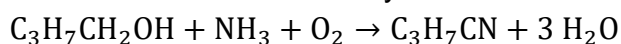
Molar mass in g·mol⁻¹: C = 12.0 ; O = 16.0 ; H = 1.0 ; N = 14.0

	State	$\Delta_f H^\circ_{298}$ (kJ · mol ⁻¹)	S°_{298} (J · mol ⁻¹ · K ⁻¹)
CH ₄	Gas	-74.9	186.30
H ₂ O	Liquid	-285.8	69.95
H ₂ O	Gas	-241.8	188.70
CH ₄ , 6 H ₂ O	Solid	-1860.0	325.00
N ₂	Gas		191.60

In water, pressure increases by 1 bar for every 10 meters of depth.

Exercise 3: Water–butyronitrile binary system (~ 6 pts)

Butyronitrile C₃H₇CN is an organic compound widely used in the manufacture of pharmaceuticals (drugs) and materials (plasticizers and vulcanizing agents). During its synthesis, carried out by the oxidation reaction of butanol in the presence of ammonia, 3 moles of water are produced for 1 mole of butyronitrile:



Water (A) and butyronitrile (B) are poorly soluble in each other in the liquid state. In this exercise, we'll study the behavior of the A-B binary mixture.

Part 1: Study of the water-butyronitrile system (assumed to be totally immiscible)

In this part, we assume that water and butyronitrile are totally immiscible in the liquid state.

1. Demonstrate that for a given pressure, liquid mixtures of the two pure compounds boil at a fixed temperature noted T_{eb} .
2. Determine T_{eb} with an accuracy of $0.1\text{ }^{\circ}\text{C}$ under pressure $P = 760\text{ Torr}$ (clearly state the used resolution method, given that T_{eb} is between 80 and $100\text{ }^{\circ}\text{C}$).
3. Calculate the mass percentage of B in the vapor phase in equilibrium with the liquids.

Part 2: Real system study (partial miscibility in the liquid state)

In reality, water and butyronitrile are partially miscible in the liquid state. The binary diagram for this system is given in the appendix. It is plotted as a function of the mass fraction of B, noted w_B .

Note that at $20\text{ }^{\circ}\text{C}$, B is soluble in water up to its mass fraction of 3.5% (i.e., 3.5 g of B per 100 g of solution); likewise, water is soluble in B to its mass fraction of 2.5% .

4. Complete Figure 1 in the appendix, clearly indicating the name of the curves, the characteristic points, as well as the phases present in the 6 areas bordered by the curves.
5. What volume (in mL) of B needs to be added to 1.000 L of water to cause a cloudy appearance at $20\text{ }^{\circ}\text{C}$?

Butyronitrile is synthesized at high temperatures ($> 200\text{ }^{\circ}\text{C}$).

We consider here 1.000 kg of the mixture M resulting from this synthesis, consisting of 3 moles of water for 1 mole of B.

6. Calculate the composition of mixture M in mass fraction ($w_{B,M}$).
7. Using the diagram, describe in detail the phenomena that occur during the cooling of mixture M from $120\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$ (notable temperatures, appearance or disappearance of phases, nature and composition of the phases).
8. After calculating the mass of the phases present at $20\text{ }^{\circ}\text{C}$, indicate the proportion of butyronitrile (relative to the mixture M) recovered in the richest fraction.

Data:

Molar masses in $\text{g}\cdot\text{mol}^{-1}$: Water (A) = 18.0 ; Butyronitrile (B) = 69.0

Saturation vapor pressure of water (range of temp.: $50\text{ }^{\circ}\text{C} - 110\text{ }^{\circ}\text{C}$):

$$\ln P_A^* (\text{Torr}) = -\frac{4989.5}{T} + 20.010$$

Saturation vapor pressure of butyronitrile (range of temp.: $50\text{ }^{\circ}\text{C} - 140\text{ }^{\circ}\text{C}$):

$$\ln P_B^* (\text{Torr}) = -\frac{4506.5}{T} + 18.173$$

Volumetric mass of water is $1.00\text{ g}\cdot\text{cm}^{-3}$ and that of B is $0.79\text{ g}\cdot\text{cm}^{-3}$.

End of the subject

Surname:

First name:

Group:

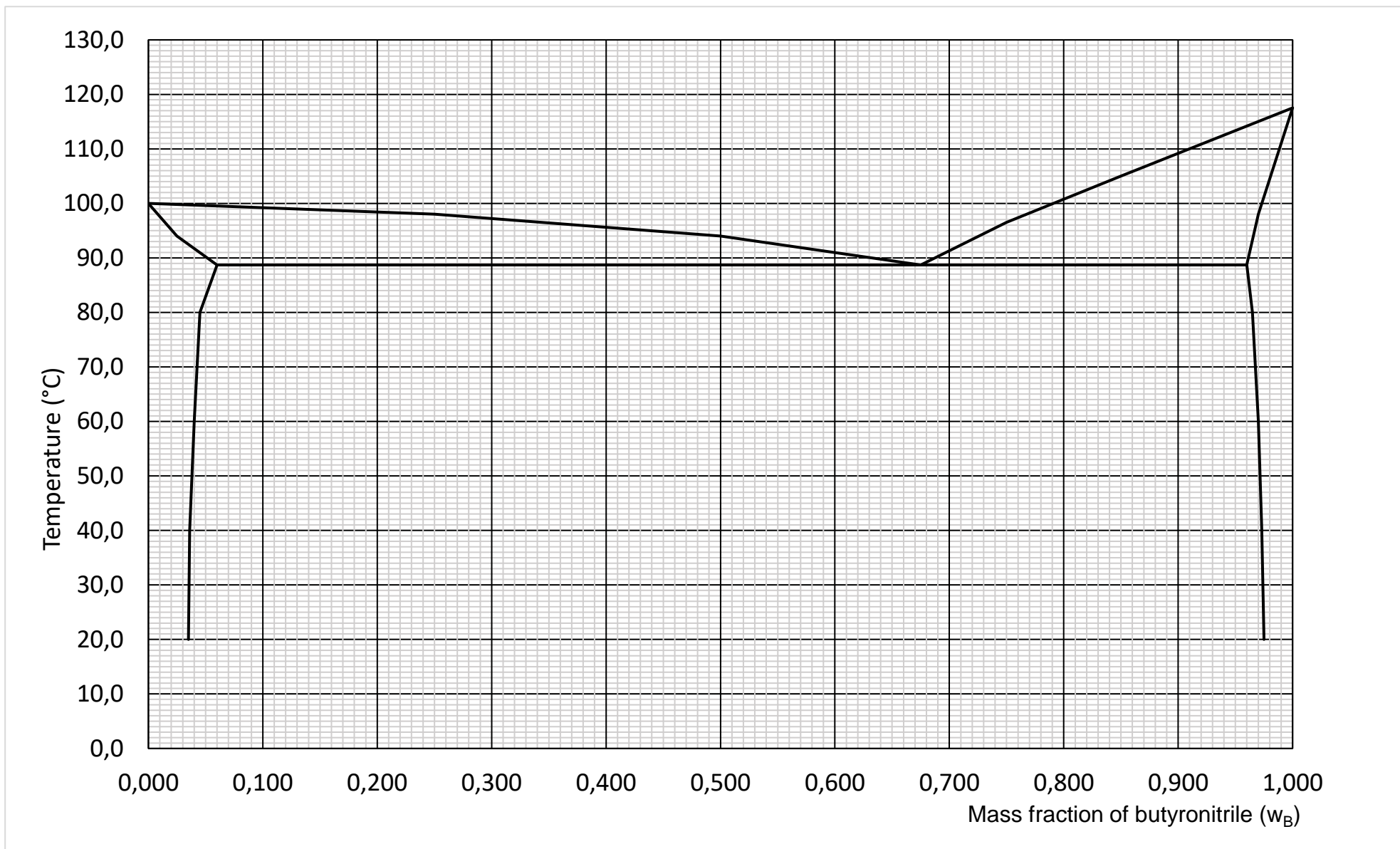


Figure 1: Liquid-vapor phase diagram of the water-butyronitrile system at 760 Torr