

Premier Cycle - 2A

Application of thermodynamics to the treatment of domestic wastewaters

Duration: 3 hours. No documents allowed. Any calculator allowed.

The scale of points is indicative. Data are gathered in the appendix.

The 4 exercises are independent.

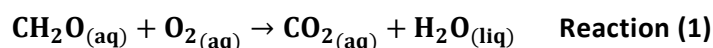
Domestic wastewaters are produced from toilets, kitchens and bathrooms. They must be treated before being returned to the environment so as not to pollute natural environments. The treated water can be re-used or useful nutrients can be recovered. In addition, the treatment of industrial wastewater can allow the recovery of some compounds of interest. This subject addresses some aspects of these treatments.

Exercise A: Treatment of organic compounds by microbial oxidation (4.75 points / 20)

Organic compounds are substances whose main element is carbon. Domestic wastewater contains complex organic compounds made of carbon, hydrogen and oxygen. All of these organic molecules are called the **"organic load" of the wastewater and described here for simplification by the global formula CH_2O .**

At the top of the basins in the treatment plants, wastewater is in direct contact with the air which allows dioxygen to dissolve into water. It will be admitted that a partition equilibrium is established which can be described by Henry's law.

- 1) Using the data gathered in the appendix and considering water and dioxygen as the only constituents of the system, show that at 25°C under an atmospheric pressure of 1 bar, the concentration of dissolved dioxygen in water is equal to $0.25 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. This concentration represents the saturation value of dioxygen in water under atmospheric pressure at 25°C.
- 2) Microorganisms in wastewater use dissolved dioxygen to oxidize organic compounds according to the redox reaction (1):



- a) Knowing that reaction (1) occurs in the forward direction, which of the redox couples $\text{CO}_2/\text{CH}_2\text{O}$ or $\text{O}_2/\text{H}_2\text{O}$ shows the higher potential (cathode)?
- b) Write the balanced half-reactions of oxidation of CH_2O into CO_2 and reduction of O_2 into H_2O . Protons in solution may be denoted H^+ or H_3O^+ .
- 3) The following notations are used:

E_A : potential of couple $\text{O}_2/\text{H}_2\text{O}$

E_B : potential of couple $\text{CO}_2/\text{CH}_2\text{O}$

ε_1 : difference between potentials E_A and E_B ($\varepsilon_1 > 0$)

ε_1^0 : difference between standard potentials E_A^0 and E_B^0 ($\varepsilon_1^0 > 0$)

- a) Give the literal forms of Nernst equations expressing respectively E_A and E_B as a function of the standard potentials E_A^0 and E_B^0 and the concentrations of the involved chemical species.

- b) Let us consider a wastewater at pH = 7, saturated with dissolved dioxygen and whose composition leads to a value of -0.47 V for the potential E_B of couple $\text{CO}_2/\text{CH}_2\text{O}$. Calculate under these conditions the numerical value of $\Delta_{r1}G_{298}$ of reaction (1) expressed in $\text{kJ}\cdot\text{mol}^{-1}$ of CH_2O .
- c) Comment the sign of $\Delta_{r1}G_{298}$.
- 4) This question deals with the evolution of the potentials during wastewater treatment.
- a) Assuming that the pH of the wastewater remains constant at 7 and that the aeration system keeps $[\text{O}_{2(\text{aq})}]$ constant at the saturation value given in question 1, explain, without doing any calculation, how E_B and ε_1 are supposed to evolve during the treatment of this wastewater.
- b) The treatment is considered finished when the final concentration of the organic load $[\text{CH}_2\text{O}]_{\text{end}}$ is 1% of the initial concentration $[\text{CH}_2\text{O}]_{\text{ini}}$. Using the assumptions of 4a and also considering to simplify that $[\text{CO}_{2(\text{aq})}]$ does not vary significantly, calculate $E_{B\text{end}}$ et $\varepsilon_{1\text{end}}$ at the end of the treatment.

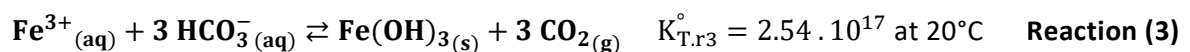
Exercise B: Phosphates precipitation by FeCl_3 (6.25 points / 20)

In wastewater treatment plants, phosphate ions PO_4^{3-} can be removed from wastewater by adding ferric chloride FeCl_3 which dissolves into the solution releasing ferric ions Fe^{3+} . Ferric ions then react with phosphate ions to form a precipitate of ferric phosphate $\text{FePO}_4(\text{s})$ according to reaction (2):



- The solubility of ferric chloride FeCl_3 in pure water at 20°C is $920 \text{ g}\cdot\text{L}^{-1}$. Calculate its solubility product K_s at 20°C .
- We consider here a wastewater whose phosphate concentration $[\text{PO}_4^{3-}]$ is $31.0 \text{ mg}\cdot\text{L}^{-1}$. To authorize the release of treated water to the natural environment, environmental regulation requires that its phosphate concentration be $0.1 \text{ mg}\cdot\text{L}^{-1}$ or less.
 - Calculate the number of moles of phosphate ions which have to be precipitate from 100 liters of wastewater to comply with this regulation.
 - Since the treatment is carried out by precipitation of phosphates according to reaction (2) above, what is the minimal mass of FeCl_3 to be added to the 100 L of wastewater to achieve this goal?

In reality, when ferric chloride FeCl_3 is dissolved into wastewater, the released ferric ions Fe^{3+} also react with hydrogeno-carbonate ions HCO_3^- present in the wastewater according to reaction (3):



- Give the literal expression of the constant $K_{T,r3}^\circ$ of this heterogeneous equilibrium, displaying any relevant standard reference magnitudes (C° , P°).
- How would the equilibrium evolve under the effect of an addition of HCO_3^- in the solution? Same question under the effect of an increase in the pressure of CO_2 . Answer without doing any calculations.

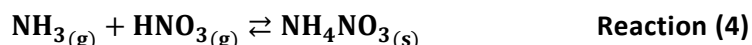
- 5) Considering that equilibria 2 and 3 occur simultaneously, what can be said about the mass of FeCl_3 calculated in question 2?
- 6) In addition to the $31.0 \text{ mg}\cdot\text{L}^{-1}$ of phosphates, the wastewater contains $112 \text{ mg}\cdot\text{L}^{-1}$ of HCO_3^- . Furthermore, the water is in contact with the air at a pressure of CO_2 taken as constant and equal to $P_{\text{CO}_2} = 4 \cdot 10^{-4} \text{ bar}$.

Calculate the mass of ferric chloride necessary to treat 100 L of wastewater, considering the simultaneous equilibria 2 and 3. For this calculation, it is recommended to follow the successive steps below:

- a) Write a table of advancement for both equilibria.
- b) Using this table, express the respective equilibrium constants of equilibria 2 and 3.
- c) Knowing that 6.20 g of $\text{Fe}(\text{OH})_3(\text{s})$ are produced from the treatment of 100 L of wastewater, calculate the mass of ferric chloride FeCl_3 needed for this treatment.
- d) Calculate the percentage of precipitation of Fe. Could you have predicted this result?

Exercise C: Nitrogen recovery and production of fertilizers (4 points / 20)

With few exceptions, plants cannot fix nitrogen from the air. Ammonium nitrate is a chemical fertilizer used in conventional agriculture to provide nitrogen to the plants, both as nitrate ions NO_3^- for rapid assimilation and ammonium ions NH_4^+ for slow assimilation. It is synthesized from nitric acid HNO_3 and ammonia NH_3 according to the forward direction of reaction (4):



- 1) Calculate the mass percentage of nitrogen contained in ammonium nitrate.
- 2) Calculate the enthalpy change $\Delta_{\text{r}4}\text{H}_{298}^0$ and the entropy change $\Delta_{\text{r}4}\text{S}_{298}^0$ of reaction (4) under standard conditions. Comment the sign of $\Delta_{\text{r}4}\text{S}_{298}^0$.
- 3) The synthesis is performed using a stoichiometric gaseous mixture of ammonia and nitric acid under a total pressure of 3 bar. Knowing that each reactant must be brought to the gaseous state in the reactor, show that it is necessary to operate at the minimum temperature T_{min} of 96°C .
- 4) Calculate at $T_{\text{min}} = 96^\circ\text{C}$ the standard variation of Gibbs $\Delta_{\text{r}4}\text{G}_{298}^0$ and the value of the equilibrium constant $K_{T_{\text{min}},\text{r}4}^0$. Deduce the minimum pressures of ammonia and nitric acid required for the formation of ammonium nitrate to occur at temperature T_{min} . Is your result compatible with the pressure conditions given?

Exercise D: Acetone recovery from an industrial effluent (5 points / 20)

Acetone ($\text{C}_3\text{H}_6\text{O}$) is an organic solvent commonly used in chemistry laboratories (cf. your chemistry lab classes). Water (compound A) and acetone (compound B) are miscible in all proportions at the liquid state.

- 1) Specifying the necessary simplification(s) and/or assumption(s), integrate Clapeyron's equation $\frac{dP}{dT} = \frac{\Delta_{\text{vap}}\bar{H}}{T(\bar{V}_{\text{g}} - \bar{V}_{\text{l}})}$ relative to the liquid/vapor equilibrium in the form $\ln P_{\text{B}}^* = -\frac{\alpha}{T} + \beta$. Taking P_{B}^* in bar, calculate to a relative accuracy of 10^{-4} the coefficients α and β for acetone.

- 2) The respective temperatures of ebullition of two solutions of water and acetone are measured under a given atmospheric pressure and the same temperature is obtained for both solutions. Assuming that the liquid mixtures of water and acetone are ideal solutions, can we conclude that the two solutions have the same composition? Justify your answer.
- 3) Still assuming that water and acetone form ideal liquid solutions, establish the literal relationship between the mole fraction of acetone in the liquid phase at ebullition (denoted x_B), the total pressure P and the saturating vapor pressures P_A^* and P_B^* .
- 4) Calculate the theoretical value of x_B (molar fraction of acetone in the liquid phase in equilibrium with gas phase) and y_B (molar fraction of acetone in the gas phase in equilibrium with the liquid) at 70 and 90°C under a pressure of 1 bar.
- 5) Using the data thus calculated and those relative to each of the pure substances, draw on the attached graph paper the isobaric L/V equilibrium diagram of the binary system water/acetone under a pressure of 1 bar. Indicate the nature of the phases in each area and the names of the curves.
- 6) We wish to separate the 2 compounds by distillation of a liquid mixture made of 20 L of water and 20 L of acetone. Make a schematic representation of the distillation system and indicate on it the mass (X_B) and molar (x_B) fractions of acetone in the feed solution, the distillation residue and the distillate, respectively.
- 7) The temperature of ebullition measured experimentally for the mixture described in question 6 is $91 \pm 1^\circ\text{C}$ under a pressure of 1 bar. Is this result in agreement with the assumption of ideal solution behavior?

----- End of the subject

APPENDIX (Data sheet)

Gases shall be considered ideal

$R = 8,314 \text{ J.mol}^{-1}.\text{K}^{-1}$; $760 \text{ Torr} = 1 \text{ atm} = 1,013 \text{ bar} = 101325 \text{ Pa}$, $T_0 = 273 \text{ K} = 0 \text{ }^{\circ}\text{C}$.

	H	C	N	O	P	Cl	Ca	Fe	acetone	H ₂ O
Molar masses (g.mol ⁻¹)	1.0	12.0	14.0	16.0	31.0	35.5	40.1	55.8	58	18

	NH ₄ NO ₃ (s)	acetone (liq)	water (liq)
Volumetric masses (g.cm ⁻³)	1.73	0.786	1.000

Specific data for exercise A

The molar fraction of O_{2(g)} in air will be considered equal to 0.20.

Henry's law : $P_{O_2} = K_{H(O_2)} \cdot x_{O_2}$ with $K_{H(O_2)} = 4.44 \cdot 10^4 \text{ bar}$ (Henry's constant at 25°C)
and x_{O_2} = molar fraction of O_{2(aq)} in water.

Standard potential of couple O₂/H₂O at 25°C : $E_A^0 = 1.23 \text{ V}$

Nernst's law: For a reaction $\sum_i \nu_i A_i + n e^- \rightleftharpoons \sum_j \nu_j B_j$ the expression is:

$$E_{\text{Ox/Red}} = E_{\text{Ox/Red}}^0 + \frac{RT}{nF} \ln \left[\frac{\prod_i (a_{A_i})^{\nu_i}}{\prod_j (a_{B_j})^{\nu_j}} \right] \quad \text{with } F \text{ (Faraday)} = 96500 \text{ C}$$

Approximation of Nernst's law at 25 °C : $E_{\text{Ox/Red}} \approx E_{\text{Ox/Red}}^0 + \frac{0.06}{n} \log \left[\frac{\prod_i (a_{A_i})^{\nu_i}}{\prod_j (a_{B_j})^{\nu_j}} \right]$

For any positive number X, $\log X = \frac{\ln X}{\ln 10}$

By convention $pX = -\log X$

Specific data for exercise C

Compound	NH ₃ (g)	HNO ₃ (g)	NH ₄ NO ₃ (s)
Physical state	gas	gas	solid
$\Delta_f H_{298}^0 \text{ kJ.mol}^{-1}$	-46.2	-134.2	-364.8
$\bar{S}_{298}^0 \text{ J.mol}^{-1}.\text{K}^{-1}$	192.5	264.8	130.0

The influence of the heat capacities will be neglected

$$\ln P_{NH_3}^* = -\frac{3093}{T} + 13.0 \quad \text{and} \quad \ln P_{HNO_3}^* = -\frac{4573}{T} + 12.8$$

P^* : saturated vapor pressure (here in bar) and T in K.

Specific data for exercise D

$P_{B20^\circ C}^* = 0.245 \text{ bar}$ and $P_{B50^\circ C}^* = 0.805 \text{ bar}$ with P_B^* saturated vapor pressure

$\ln P_A^* = -\frac{5072}{T} + 13.61$ with P_A^* saturated vapor pressure in bar and T in K

This sheet is to be completed and returned with your copy

FAMILY NAME:

Given name:

Group number:

