INSA Lyon 24-11-2025

Written Test « CHEMISTRY 2 »

(Duration 2 h 00)

No document allowed. Any type of calculator allowed.

Your answers and your approach must be concisely justified. Literal formulas must clearly appear, then put into numerical form before giving the result of your calculations.

The appendix should be given back with your copy.

Gases are assumed to behave as ideal gases.

For the calculations, use:

$R = 8.314\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$; $0\ °\mathrm{C} = 273\ \mathrm{K}$

$1\ \mathrm{atm} = 760\ \mathrm{mm\ Hg} = 760\ \mathrm{Torr} = 101\,325\ \mathrm{Pa} = 1.013\ \mathrm{bar}$,

Exercise I: Liquid-Vapor isobaric diagram for Ethanol (C_2H_5OH) – Benzene (C_6H_6) (~ 12 pts)

Ethanol (E) and benzene (B) are totally miscible in the liquid state.

1) By specifying the necessary hypotheses for the integration of Clapeyron's equation, show that the variation of the saturation vapour pressure of ethanol as a function of temperature can be put in the form $LnP_E^* = -\frac{a}{T} + b$. Determine the values of a and b to calculate P_E^* in atm (the same precision will be used on these coefficients as that used for the benzene coefficients shown in the data table at the end of the problem).
2) In this question, it is assumed that ethanol and benzene can form an ideal solution.

2a) Express, at the liquid-vapor equilibrium under a total pressure P, the compositions (expressed in molar fraction of ethanol) x_E of the liquid phase and y_E of the vapor phase as a function of P and the saturation vapour pressures of ethanol P_E^* and benzene P_B^*.

2b) Numerical application: to within 3 significant digits, calculate x_E and y_E for a total pressure $P = 1.00\ atm$ and a temperature of 79.0°C.

3) Experimentally, the study of the liquid-vapor equilibrium of the ethanol-benzene mixture under $P = 1.00\ atm$ lead to the diagram provided in the appendix.

3a) Can we consider this mixture as ideal (a concise but well-argued answer is expected)?

3b) Complete the diagram by mentioning all the essential information (particular points, name of curves and axes, phases present in the different domains).

4) A mass of 1000 g of a mixture denoted M containing 85.0 % in weight of ethanol is heated up to 75.0 °C. At this temperature, what are the phases present, their weight and the number of moles of ethanol and benzene they contain?

5) We want to separate the mixture M by fractionated distillation.

5a) Recall the principle of fractional distillation (in a few words).

5b) What pure compound will be possible to obtain, and where in the distillation device?

5c) Calculate the weight of pure product recovered, at best.

Data:

	Ethanol (E)	**Benzene (B)**
Molar mass ($g.mol^{-1}$)	46.0	78.0
Boiling temperature °C ($P = 1.00\ atm$)	78.5	80.1
Enthalpy of vaporisation $\Delta_{vap}H^0$ ($kJ.mol^{-1}$)	38.6	30.7
Saturation vapor pressure (in atm)		$LnP_B^* = -\frac{3692.6}{T} + 10.458$

Clapeyron's equation for a Liquid-Vapor equilibrium of a pure compound: $\frac{dP}{dT} = \frac{\Delta_{vap}H^0}{T(\overline{V_{gas}} - \overline{V_{liq}})}$

Exercise II: Chemical equilibrium in gaseous phase (~ 8 pts)

Phosphorus pentachloride PCl_5 is a compound used as a reagent in organic chemistry to add chlorine atoms to a carbon chain.
When placed in gaseous state, it decomposes spontaneously into phosphorus trichloride PCl_3 and dichlorine Cl_2, giving rise to an equilibrium in the gas phase, according to the following chemical equation:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad (1)$$

In this whole exercise, the PCl_5 compound is considered to be the only reactant present in the initial state.

1) Define the dissociation coefficient of PCl_5, noted α.
2) After establishing a detailed table of advancement, express literally the equilibrium constant of the reaction as a function of the dissociation coefficient of PCl_5 and the total pressure.

We want to evaluate the impact of the conditions under which the experiment is carried out on the value of the dissociation coefficient.

Part 1:

After vacuuming a reactor of variable volume, 1.00 mole of PCl_5 is introduced and then brought to 250°C under a constant pressure of 1.00 bar.

3) Calculate the dissociation coefficient of PCl_5.
4) What is the volume occupied by the gas mixture at equilibrium?

Part 2:

After vacuuming a reactor with a fixed volume V = 30.0L, 1.00 mole of PCl_5 is introduced and then brought to 250°C.

5) From your answer to question 2), and using the law of ideal gases, express literally the equilibrium constant of the reaction as a function of the dissociation coefficient of PCl_5, the volume of the reactor and the temperature, among other parameters.
6) Show then that the dissociation coefficient of PCl_5 satisfies the following equation:

$$\alpha^2 + 1.23\alpha - 1.23 = 0$$

7) Calculate the dissociation coefficient of PCl_5.
8) What is the total pressure exerted by the gas mixture at equilibrium?

Part 3:

After vacuuming a reactor of variable volume, 1.00 mole of PCl_5 is introduced then brought to 350°C under a constant pressure of 1.00 bar.

9) Calculate the dissociation coefficient of PCl_5.

Conclusion:

10) Discuss your results with respect to the Le Chatelier's principle when the chemical system undergoes:
    a) An increase of pressure,
    b) An increase of temperature.

Data:

The equilibrium constant at θ = 250°C (T = 523K) is $\boldsymbol{K^{\circ}_{523K} = 1.78}$
Molar enthalpy of reaction (1) ascribed to the decomposition of PCl_5 at 298K, assumed to be independent on temperature, is $\boldsymbol{\Delta_r H^0_{298K} = +120.4\ kJ/mol}$.