CHEMISTRY TEST n°1 (1h30)

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° = 1 bar
All gases may be considered as ideal

Gaseous carbon dioxide CO_2 released by human activities is the main cause of the increase in the greenhouse effect. To meet the environmental regulations that aim to reduce the emission of CO_2 in the atmosphere and limit its concentration, technical solutions are studied.

The 2 exercises can be treated independently - **All answers must be justified.**
No documents allowed.

Exercise I – Mineral sequestration of gaseous carbon dioxide CO_2 (8 points)

Mineral carbonation is one of the possible alternatives for storing CO_2. The objective of this study is to determine whether solid iron oxide (FeO) could be used to capture CO_2, according to reaction (1):

$$FeO\ (s) + CO_2\ (g) \leftrightarrows FeCO_3\ (s) \quad (1).$$

Note that the two solids FeO and $FeCO_3$ are not miscible at all.

1- Give the literal expressions then calculate the standard molar enthalpy change $\Delta_{R1}H^0_{298}$ and standard molar entropy change $\Delta_{R1}S^0_{298}$ of reaction of carbonation of FeO(s) at 298K.
2- Give the literal expression then calculate the standard molar free enthalpy change $\Delta_{R1}G^0_{298}$ of reaction of carbonation of FeO(s) at 298K.
3- Give the literal expression then calculate the thermodynamic equilibrium constant K^0_{298K} at 298K.
4- Taking into account the composition of air (see data section), calculate the partial pressure of CO_2 (in bar) when the pressure of air is 1 bar.
5- Can the reaction of carbonation of FeO occur spontaneously at 25°C with a total pressure of air is 1 bar?
6- If not, at which temperature would this reaction become spontaneous under the air pressure of 1 bar? Can this temperature be easily reached in industrial conditions?
7- What other experimental condition (s) could you suggest to facilitate the reaction?

Data :

Compound	$\overline{\Delta_f H^0_{298}}$ (kJ.mol^{-1})	$\overline{S^0_{298}}$ (J.mol^{-1}.K^{-1})
FeO (s)	-272.0	61.0
$FeCO_3$ (s)	-737.0	91.0
CO_2 (s) g	-393.5	214

The influence of the thermal capacities will be neglected.
Composition of air expressed in volume percentage:

N_2 = 78.08 O_2 = 20.95 Ar = 0.93 CO_2 = 0.035 others= 0.005.

Exercise II – Quantification of residual CO_2 after absorption (12 points)

The carbon dioxide contained in a gaseous effluent can be separated from the rest of the gases by absorption (gas-liquid transfer). The amount of residual CO_2 after treatment can be determined by various methods, including gravimetric and acid-base titrations which are discussed below.

A- Gravimetric titration

In this case, the gas recovered after absorption is bubbled in a basic solution of divalent cation (here based on strontium Sr^{2+}): this makes it possible both to trap CO_2 in the form of carbonate ions (CO_3^{2-}) and to precipitate these carbonate ions as $SrCO_3$; we can then quantify them by weighing the formed solid.

To do this, 5 L of a solution of strontium hydroxide ($Sr(OH)_2$) at 0.16 mol.L^{-1} are used. In this solution, $Sr(OH)_2$ is completely dissociated into Sr^{2+} and OH^- ions.

In part A, it will be assumed that CO_2 is only in the form of CO_3^{2-}.

1- Calculate the solubility of strontium carbonate (in mol.L^{-1}) at 25°C.

2- Calculate the concentration of carbonate ions at the beginning of the precipitation of strontium carbonate.

3- Calculate the concentration of carbonate ions present in solution when 0.54 mole of CO_2 have reacted. Comment on your result: is this gravimetric titration relevant?

Data :

$K_s(SrCO_3) = 1.6 \times 10^{-9}$ at 25°C :

Molar mass (g.mol^{-1}) : Sr : 121.6 O : 16.0 H : 1.0 C : 12.0 S : 32.1

B- Acid-base titration

In this case, the gas recovered after absorption is bubbled at 25 ° C in 3 L of a sodium hydroxide solution (which initial concentration is [NaOH] = 0.5 mol.L^{-1}) which traps the CO_2. The resulting solution is referred as the "bubbled solution" in the following.

To quantify the entrapped CO_2, a sample of this bubbled solution is taken and titrated with a hydrochloric acid (HCl) solution, a strong acid.

1- Caption the distribution diagram of the carbonate species present in aqueous solution as a function of pH (figure given in appendix: do not forget to give it back with your copy !!). Among other information, specify on the diagrams the remarkable values.

2- Calculate the initial pH of the sodium hydroxide solution contained in the flask (note that sodium hydroxide is a strong base).

3- **a)** At this pH, calculate the following ratios : $[CO_3^{2-}]/[HCO_3^-]$ and $[HCO_3^-]/[H_2CO_3]$.

b) Which is the predominant carbonate form in the bubbled solution?

c) Was this predictable without calculation?

4- During the titration of the bubbled solution with hydrochloric acid, the three following reactions occur :

$$HCO_3^- + H_3O^+ \leftrightharpoons H_2CO_3 + H_2O \quad (2)$$

$$OH^- + H_3O^+ \leftrightharpoons 2H_2O \quad (3)$$

$$CO_3^{2-} + H_3O^+ \leftrightharpoons HCO_3^- + H_2O \quad (4)$$

a) Calculate the equilibrium constant at 25°C for each reaction (K_2, K_3, K_4).

b) Deduce the order in which reactions occur as hydrochloric acid is added.

Data (25°C):

Couple H_2CO_3/HCO_3^- : $pK_{A1} = 6.3$

Couple HCO_3^-/CO_3^{2-} : $pK_{A2} = 10.3$

$pK_e = 14$