Entrance Exam 2009-2010 **Chemistry** **Time: 1 hour**
July 12, 2009

First exercise (10 points)
Kinetic Study by Following the Pressure

The aim of this exercise is to determine the half-life, t½, of the reaction between hydrochloric acid and magnesium. The equation of this reaction is:

$$Mg_{(s)} + 2\ H_3O^+_{(aq)} \rightarrow H_{2(g)} + Mg^{2+}_{(aq)} + 2\ H_2O_{(l)}.$$

The transformation is supposed to be complete.

<u>Procedure</u>:
A volume V = 10 mL of a concentrated solution of hydrochloric acid ($H_3O^+ + Cl^-$) of concentration C = 8 mol.$L^{-1}$is introduced into a flask. At the initial instant a magnesium ribbon of length *l* = 5.1 cm is plunged (without any noticeable variation in the volume of the solution). The flask is quickly closed with a pierced stopper and a tube connected to a pressure gauge is immediately introduced in the flask by means of the stopper's hole.
The value of the pressure indicated on the pressure gauge is regularly recorded.
<u>Given</u>:

- One meter of the magnesium ribbon weighs 1g.
- Molar mass of magnesium: 24.3 g.mol^{-1}.
- Volume of the empty flask: V_0 = 100 mL.
- Ideal gas equation: PV = nRT
- Atmospheric pressure: $P_{atm} = 1.1\times10^5$ Pa.
- Temperature: T= 293 K.
- Constant of ideal gas: R= 8.31 I.S.

1- Preliminary <u>Study of the Reaction</u>

1.1- Determine the number of moles of each of the two reactants at the initial state.

1.2- Determine at the end of the reaction

1.2.1- The number of moles of hydrogen gas

1.2.2- The concentration of each of the chemical species, other than water, present in the solution.

1.3- At the initial instant, the pressure in the flask is equal to the atmospheric pressure. The pressure will increase progressively with the production of the gas. Its general expression is
$P = P_{atm} + P(H_2)$ where $P(H_2)$ is the pressure of hydrogen gas occupying all available volume in the flask at each instant.
Establish the relation which links the quantity of matter of hydrogen gas produced9in moles) at each instant t and the pressure P (expressed in Pascal).

2- Follow-up of the Kinetic of the Reaction

The results obtained are given in the following table:

t(s)	0	10	20	30	40	50	60	70	80
$n(H_2)$ 10^{-3} mol	0	0.11	0.52	0.89	1.15	1.41	1.68	1.85	2.03

2.1- Plot the curve that represents the variation of the number of moles of hydrogen gas versus time : $n(H_2) = f(t)$. Take the following scale: 1 cm (2 squares) for 10 s in abscissa and 1 cm (2 squares) for 0.2×10^{-3} mol in ordinate.

2.2- Determine graphically the half-reaction the half-life of the reaction t½.

2.3- At t = 80 s can we say that the reaction is finished? Justify.

3- Influence of Some Parameters

Justify if the value of the half- life of the reaction it would have been greater or smaller than in the preceding experiment:

3.1- If the same mass of magnesium (as previously) was used but in the form of filings (fine powder).

3.2- If the flask was placed in a crystallizer containing icy water.

Second Exercise (8 points)
Identification of Some Organic Compounds

Four bottles not labeled and numbered I, II, III, IV are available in a laboratory, each containing a different liquid organic compound. In order to identify the content of each bottle, different tests on samples or aqueous solutions of the content of each bottle are carried out. The results of these tests are given in the following table

Bottle/compound	I/A	II/B	III/C	IV/D
BTB	Yellow	Green	Green	Green
DNPH	Negative	Positive	Negative	Negative
Fehling's solution	Negative	Positive	Negative	Negative
Acidified permanganate	Negative	Positive	Positive	Negative

- The bromothymol blue (BTB) is an acid-base indicator of pH range:
  yellow] 6.0 (green) 7.6 [blue.
- Molar mass in $g.mol^{-1}$: H = 1; C = 12; O = 16.
- The purple color acidified solution of potassium permanganate is an oxidizing solution for some organic functions.

1- Organic Functions

Some experiments carried out show that:

- The content of the bottle I (compound A) can be obtained either starting with bottle II (compound B) or from bottle III (compound C).
- The dehydrogenation of the content of bottle III gives the content of the bottle II.
- The content of the bottle IV (compound D) can be obtained by a reaction between the content of the bottles I and III.

1.1- Specify, with justifying, the nature of the organic functions of the involved compounds.
1.2- Indicate the observation for each positive test.

2- Identification of the Contents of the Bottle I (compound A)

The density of liquid I (compound A) is $d = 1{,}05\ g.mL^{-1}$. A solution is prepared by dissolving 6 mL of A in water to obtain 1 L of an aqueous solution S_A. The titration of 40 mL of solution S_A with a $(Na^+ + OH^-)$ solution of molar concentration $C_b = 0.2\ mol.L^{-1}$ requires a volume $V_b = 21$ mL.

2.1- Show that the molar mass of compound A is: $M_A = 60\ g.mol^{-1}$.
2.2- Write the condensed structural formula and give the name of each of compound A, B, C and D.

Third Exercise (2 points)
Cracking of Methane

The equation of the thermal cracking reaction of methane is:

$$CH_{4(g)} \rightleftharpoons C_{(s)} + 2\,H_{2(g)}$$

Starting with CH_4 only, at 500 ºC and under the pressure P = 1 atm the gas mixture contains at equilibrium 53.4% of CH_4 and 46.6% of H_2 (in volume).

1- Calculate the equilibrium constant Kp at this temperature.
2- Knowing that the yield of this cracking at 500 ºC is 30.4% and that it reaches 99% at 1300 ºC, specify whether the cracking reaction of methane is exothermic or endothermic.

Entrance Exam 2009-2010 **Solution of Chemistry** **Time: 1 hour**
July 12, 2009

First Exercice (10 points)
Kinetic Study by Following the Pressure

1- Preliminary Study of the Reaction

1.1- Initial number of moles:

Mg : $n_1 = \dfrac{\text{mass}}{\text{Molar mass}} = \dfrac{5.1\times10^{-2}}{24.3} = 2.1\times10^{-3}$ mol.

Hydronium ions: $n_2 = C\times V = 8\times10\times10^{-3} = 80.0\times10^{-3}$ mol. **(1 pt)**

1.2.1- According to stœchiometric coefficients, we have:

$r_1 = \dfrac{2.1\times10^{-3}}{1} < r_2 = \dfrac{80.0\times10^{-3}}{2} = 40.0\times10^{-3}$. Magnesium is than the limiting reactant. The number of moles of hydrogen gas at the end of the reaction is then: $n(H_2)_{max} = 2.1\times10^{-3}$ mol.

(1 pt)

1.2.2- $[Mg^{2+}] = \dfrac{2.1\times10^{-3}}{10\times10^{-3}} = 0.21$ mol.L^{-1}; $[Cl^-] = 8.0$ mol.L^{-1}(spectator ions) ;

$[H_3O^+] = \dfrac{80.0\times10^{-3} - 2\times2.1\times10^{-3}}{10\times10^{-3}} = 7.58$ mol.L^{-1}. **(1.5 pt)**

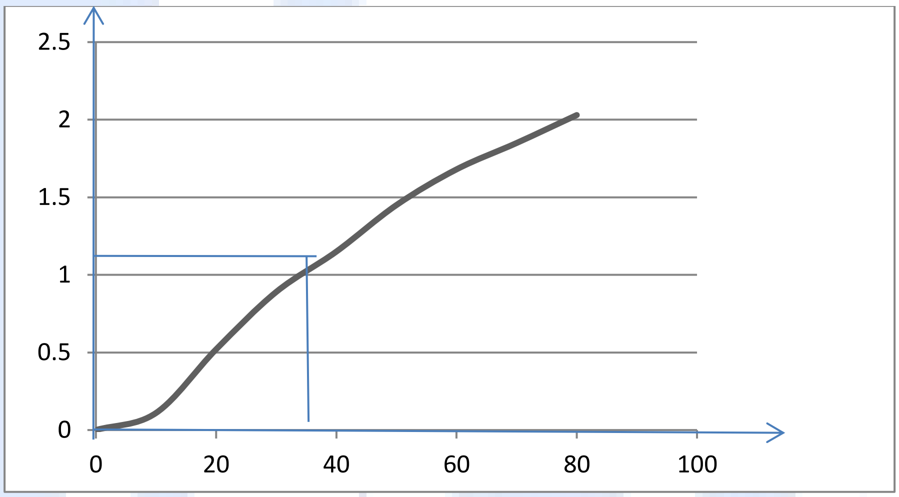
1.3- The number of moles of hydrogen gas could be given by the equation of ideal gas:

$n(H_2) = \dfrac{P(H_2)\times V(H_2)}{RT} = \dfrac{P - P_{atm}(V_0 - V)}{RT} = \dfrac{10^5(P-1.1)(100-10)10^{-6}}{8.31\times293} =$

$(P - 1,1)\times3.70\times10^{-3}$ mol. **(1.5 pt)**

2- Follow-up of the Kinetic of the Reaction

2.1- The curve is the following: **(1 pt)**



2.2- The half-life of the reaction is the time during it the number of moles of hydrogen formed is equal to the half of its number of moles at the end of the reaction which is equal to the number of moles of the limiting reactant (the magnesium): $n(H_2)_{1/2} = \dfrac{2.1\times10^{-3}}{2} = 1.05\times10^{-3}$ mol that corresponds, according to the graph, to $t_{1/2} = 35$ s. **(1.5 pt)**

2.3- The number of moles of hydrogen gas at t = 80 s (2.03×10^{-3} mol) is less than the number of moles at the end of the reaction (2.1×10^{-3} mol). This is not the end of the reaction. **(0.5 pt)**

3- <u>Influence of Some Parameters</u>

3.1- When magnesium is used in the form of filings the surface of contact with H_3O^+ ions becomes taller, the reaction rate increases and the half life time of the reaction becomes smaller. **(1 pt)**

3.2- When the flask is placed in a crystallizer containing of ice-cold water, the reaction rate decreases and the of half-life time of the reaction becomes larger. **(1 pt)**

Second Exercise
Identification of Some Organic Compounds

1- Organic Functions

1.1- Compound A is an acid that gives a yellow color with the BTB
Compound B is an aldehyde because it reacts with DNPH and with Fehling agent.
Compound C reacts with potassium permanganate and gives by dehydrogenation an aldehyde. C is than a primary alcohol.
Compound D is an ester because that derives from the reaction of an acid with an alcohol. **(2 pts)**

1.2- With DNPH a yellow precipitate is observed.
With Fehling agent a red-brick precipitate is observed.
With the permanganate a pink color is observed which becomes colorless. **(1.5 pt)**

2- Identification of the Contents of the Bottle I (compound A)

2.1- At equivalence the reactants react completely: n acid = n base

$\frac{6\times 10.5}{M}\times 40 = 0.2\times 21$. We have: $M = \frac{6\times 1.05\times 40}{0.2\times 21} = 60\ g.mol^{-1}$. **(1 pt)**

2.2- The formula of the acid is $C_nH_{2n}O_2$, we obtain n = 2 than the condensed structural formula of A is CH_3—C OOH (ethanoic acid); B : CH_3—CHO (ethanal) ; C : CH_3—CH_2OH (ethanol) ;
D : CH_3—C OO—CH_2—CH_3 (ethyl ethanoate). **(1.5 pt)**

Third Exercise
Cracking of Methane

1- The constant of the equilibrium Kp is given with the relation : Kp = $\frac{P(H_2)^2}{P(CH_4)}$

$P_{H2} = X_{H2}P_{total} = 0.466 \times 1 = 0.466$ atm
$P_{CH4} = 0.534$ atm
We obtain: Kp = $\frac{(0.466)^2}{0.534} = 0.41$ **(1 pt)**

2- Starting with CH_4 the yield is by definition R = $\frac{\text{n reacting}}{\text{ninitial}}$

	CH_4	**C**	**H_2**	**n total**
t = 0	n	0	0	n
t	n-x	x	2x	n+x
X_i	$\frac{n-x}{n+x}$		$\frac{2x}{n+x}$	

x = $\frac{1-\frac{x}{n}}{1+x/n} = \frac{1-R}{1+R}$ (1+R) X = 1-R ; R = $\frac{1-X}{1+X}$ = 0.304. **(1.5 pt)**

The yield increased when the temperature increases. The forward reaction is then endothermic because the rise in the temperature supports the reaction in the endothermic direction. **(1 pt)**