First Exercise(7pts)

Acid – base Reactions

Given:

Conjugate acid/base pair	$CH_3NH_3^+$ / CH_3NH_2	NH_4^+/ Nh_3	HF/F	$HCOOH/HCOO^-$
PK_a	10.7	9.2	3.2	3.8

- The ionic product of water : K_w=$1.0x10^{-14}$
- Sodium methanoate HCOONa and ammonium chloride NH_4Cl are ionic compounds highly soluble in water.

Four beakers contain each an aqueous solution of one the chemical compounds given in the table below. The solution have all the same molar concentration C_o

Number of the beaker	Chemical compound	PH
1	Sodium methanoate	PH_1
2	Ammonium chloride	PH_2
3	Methylamine CH_3NH_2	PH_3
4	Hydrogen fluoride HF	PH_4

1- PH of the Aqueous Solution:

1-1 Classify the PH of these four solutions by ascending order.

1-2 The PH of the solution in beaker N^o 4 has the value of 2.65.

1-2-1 Write the equation of the reaction between HF and water.

1-2-2 Show that the molar concentration C_o is equal to 1.0 x 10^{-2} mol $.1^{-1}$

1-3 Distilled water is added to a volume V_o= 10 mL of the solution of beaker N^o3 until we obtain a solution S of volume V= 100mL. the PH of the solution of beaker N^o3 and that of solution S are measured. The results are given in the following table:

Solution	Beaker N^o3	S
C (mol.L^{-1})	$1.0x10^{-2}$	1.0 x 10^{-3}
PH	11.3	10.7
α	0.2	

Where α is the coefficient of conversion of methylamine during its reaction with water

1.3.1- Write the equation of the reaction between methylamine and water

1.3.2- Name the glassware used to measure with precision the two volumes V_o and V used in the preparation of solution S.

1.3.3- Determine the value of α in solution S missing in the above table. Conclude?

2- Preparation of a Buffer solution

To prepare a buffer solution of PH=9.0 a volume $V_1$of sodium hydroxide solution of concentration C=$1.0x10^{-2}$ mol.L^{-1} is added to a volume V_2= 40 mL of the solution of beaker N^o2 (ammonium chloride solution).

2.1- Write the equation of the reaction which takes place in this mixture

2.2- Show that this reaction is complete.

2.3- Determine V_1.

Second Exercise(7pts)

Kinetic Study of the Decomposition Reaction of Dinitrogen Oxide.

To ensure suitable atmosphere in the space capsules, the decomposition of N_2O gas is carried out according to a complete reaction of the following equation:

$2N_2O_{(g)} \rightarrow 2N_{2(g)} + O_{2\,(g)}$

1- Study of the reacting System

Introduce in to an evacuated flask, maintained at Θ=600°C,n_0 mol of N_2O.

1-1- represents the number of moles of oxygen gas formed at instant t . copy the following table on the answer sheet . and complete it in terms of n_0 and x

Time	N_2O(mol)	N_2(mol)	O_2(mol)
0	n_0	0	0
t			
End of reaction			

1-2 Determine the pressure P in the flask at the end of the reaction knowing that the initial pressure is $P_0=1.0\times10^5$ Pa

2- kinetic Study of this Reaction

In order to study the Kinetic of this slow reaction, the pressure P inside the flask is measured at different instants. The concentration of oxygen gas, $[O_2]$, is determined based on the measurement of P at each instant t . The results are given in the following table:

t (min)	0	12	25	45	70	100	130	160
$[O_2]$ (mol.m^{-3})	0	0.88	1.68	2.68	3.72	4.56	5.12	5.40

2-1. Show that the concentration of O_2 at instant t,$[O_2]_t$, is given by the relation $[O_2]_t=1.38 \times 10^{-4}(P-P_0)$
Take: R=8.3Pa.m^3.mol^{-1}.K^{-1}

2-2. plot on a graph paper, the curve $[O_2]$=f(t). take the following scale:

Abscissa :1cm for 10 min and ordinate :1cm for 0.4 mol.m^{-3}.

2-3. Describe how to determine, graphically at instant t, the rate of this reaction

2-4. Deduce the kinetic factor responsible for the change of this rate with time.

2-5. Determine graphically the half-life of this reaction

2-6. the same study, in the same flask is done, at a temperature $\Theta_1 > \Theta$

Specify the effect of the elevation of temperature on:

2-6-1. the rate of the reaction

2-6-2. the concentration of O_{2gas},$[O_2]_\infty$, at the end of the reaction

Third Exercise(6pts)

Decomposition of javel Water

Javel water is an aqueous solution containing the following ions: hypochlorite ClO^-, chloride Cl^- and sodium Na^+. it is very often used as a disinfectant due to the oxidizing character of the hypochlorite ions.

Javel water decomposes very slowly according to the reaction of the following equation:

$2ClO^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + O_{2(g)}$

This reaction could be accelerated by light or by using a catalyst of a cobalt compound such as cobalt (II) chloride ($CoCl_2$)

Given:

- Take molar volume of gas :V_m= 24 $L.mol^{-1}$

1- Decomposition of javel water

In order to study the kinetic of the decomposition reaction of javel water,, at the instant when the cobalt ions Co^{2+} are introduced into a volume V=110ml of javel water solution called (S), the volume of the obtained oxygen gas is measured. The concentration of the remaining ions (ClO^-) in the solution (S) at each instant is then deduced the results are given in the following table:

t(s)	0	30	60	90	120	150	180	210	240	300
$[ClO^-]$ $mol.L^{-1}$	0.24	0.20	0.17	0.14	0.12	0.10	0.080	0.060	0.046	0.026

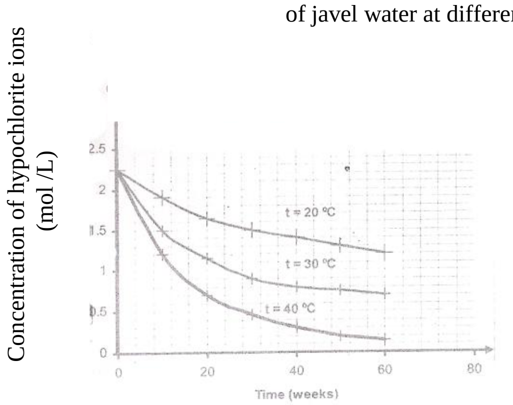
1- plot, on a graph paper, the curve representing the variation of (CLO^-) versus time . take the following scales: abscissa: 1cm for 30s , ordinate: 1cm for 0.02mol/l
2- Determine the rate of disappearance of ClO^- at instant t=210s
3- Knowing that the rate of disappearance of CLO^-, at instant t=0, is $1.6x10^3 mol.L^{-1}.s^{-1}$
4- Determine, graphically, the half – life of the reaction $t_{1/2}$
5-
   a) Show that the concentration of hypochlorite ions $[ClO^-]_t$, in $mol.L^{-1}$, and the volume of oxygen gas $V(O_2)_t$, in mL, at instant t, are related by the following relation $[ClO^-]_t=0.24 -7.57x10^{-4}xV(O_2)_t$.
   b) Identify the chemical speices which are present in the solution (S) when the volume $V(O_2)$=317mL

2- Stability and Precautions of use

Among the recommendations on the label of a bottle of javel water it is written : "store in cold place without exposure to sun and light".

The graph below shows the progress of the decomposition reaction of javel water at different temperatures.

Graph representing the kinetic of the decomposition of javel water at different temperature



Referring to the above graph, justify the recommendation " stored in cold place without exposure to sun …"

Bareme

Answer

First Exercise

1.1	Starting with the same initial concentration, the smallest value of PK_a corresponds to the most strong acid and consequently the lowest value of PH: $PK_a(HF/F^-) < pK_a(NH_4^+/NH_3)$ thus $pH_4<pH_2<7$. Starting with the same initial concentration, the smallest value f pK_a corresponds to the most weak base and consequently the lowest value of pH: $pK_a(HCOOH/HCOO^-) < pK_a(CH_3NH_3^+/CH_3NH_2)$ thus $7<pH_1<pH_3$. The order of increasing pH is then : pH_4, pH_2, pH_1, pH_3.
1.2.1	The equation of this reaction is : $HF+H_2O = F^- + H_3O^+$
1.2.2	According to the equation of this reaction, we can write: $[F^-]=[H_3O^+]=10^{-PH}=10^{-2.65}=2.23 \text{ x } 10^{-3}$ mol.L$^-$and $[HF]=C_0-[F]$. In addition , $K_a(HF/F^-)=\frac{[H3O^+]\times[F^-]}{[HF]}$ and $C_0=\frac{(2.23 \times10^{-3})^2}{6.31 \times10^{-4}}+2.23\times10^{-3}=1.01\times10^{-2}\ m0l.L^-$
1.3.1	The equation of this reaction is : $CH_3NH_2+H_2O = OH^-+CH_3NH_3^+$
1.3.2	To take V_0, we use a volumetric pipette of 10 mL and to have volume V, we use a volumetric flask of 100 mL.
1.3.3	In solution S: $a=\frac{n(CH3NH2)transformed}{n\ (CH3NH2)initial}=\frac{n(OH^-)formed}{n(CH3NH2)initial}=\cdots=\frac{[OH^-]}{C}=\frac{10^{PH-14}}{10^{-3}}=0.5.$ The dilution of the solution of ethylamine favors its reaction with water.
2.1	The equation of this reaction is : $OH^-+NH_4^+=NH_3+H_2O$
2.2	Te constant K_r of this reaction is : $K_r=10^{14-9.2}=6.4\text{x}10^4>10^4$; thus this reaction is complete.

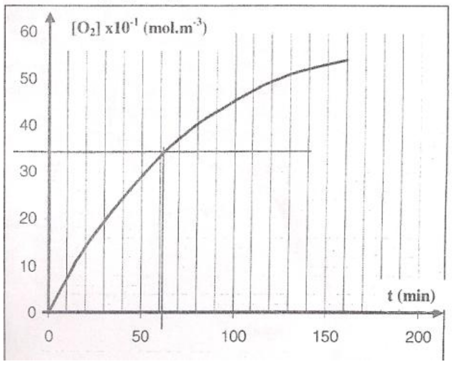
2.3	Calculation of V_1, knowing that $C=C_0$: Since the solutions buffer, NH_4^+ and NH_3 coexist , HO^- is the limiting reactant. $OH^- \quad + \quad NH_4^+ \rightarrow \quad NH_3 \quad + H_2O$ Initial state $\quad CxV_1 \quad C_0xV_2 \quad 0 \quad$ Solvant Obtained solution $\quad 0 \quad C(V_2-V_1) \quad CxV_1 \quad$ solvant pH (solution)= pK_a (NH_4^+/NH_3)+ log $\frac{[NH3]}{[NH4^+]}$; so $\log\frac{V1}{V2-V1} = 9 - 9.2 = 0.2$ and $V2 = 40mL$, hence $V1 = 15.5mL$.

Second Exercise

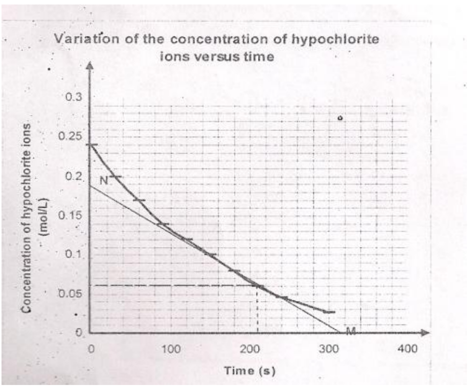
1.1 The table

Time	$2N_2O$	$2N_2$	O_2
0	n_0	0	0
T	n_0-2x	2x	x
End of reaction	0	n_0	$\frac{n0}{2}$

1.2	At the end of the reaction, the number of moles is :n=$\frac{3n0}{2}$. However the ratio n moles is equal to the pressures, because the volume and the temperature remain the same. We have: $P=\frac{n}{n_0}p_0 = \frac{3\times1.00\times10^5}{2}$=1.50x 10^5 Pa.
2.1	According to equation of state of ideal gases, we have: $P(O_2)xV=n(O_2)xRxT;[O_2]_t=\frac{n(O_2)}{V} = \frac{P(O_2)}{R\times T}$. Or : at any moment, we have : $P(N_2)=2P(O_2)$; $P(N_2O)=P_0-P(O_2)$; $P=P(N_2O)+P(N_2)+P(O_2)=P_0+P(O_2)$. Where : $P(O_2)=P-P_0$ and $$[O_2]_t = \frac{p\_p_0}{8.3(600+273)} = 1.38\times10^{-4}(P-P_0)mol.m^{-3}$$

2.2	The curve : $[O_2]= f(t)$: 
2.3	The rate of this reaction at instant is equal to the rate of formation of O_2 So: To determine the rate of the reaction at an instant t: - Trace the tangent to the curve $[O_2]= f(t)$, at the point of abscissa t - Calculate the slope of this tangent The rate of the reaction is equal to the value of this slope.
2.4	The observation of the curve shows that this value decreases when the time passes. This decrease in the rate is due to the decrease in the concentration of the reactant (N_2O).
2.5	the half-life of the reaction is the time when the concentration of O_2 will be equal to half of its concentration at the end of the reaction. $[O_2]_{t1/2}=\frac{[O_2]_{t\infty}}{2} = \frac{1.38\times10\ (1.50\times10^5-1.00\times10^5)}{2} = 3.45 mol.m^{-3}$ According to the graph, this concentration corresponds to: $T_{1/2}$ =62min
2.6.1	The increase in the temperature increases the reaction rate
2.6.2	$[O_2]=\frac{n(O_2)}{V}$.knowing that $n[O_2]_{t\infty}$ and V are constants whatever is the temperature so the final concentration of O_2 does not vary with the temperature.

third Exercise

I	**Decomposition of javel water**
1-	The curve representing the variation of $[CLO^-]$ versus time: 

2-	The rate of disappearance of CLO^- r=$\frac{d[CLO^-]}{dt}$; is equal to the negative slope of the tangent to the curve at instant t=210s Calculation of the rate :M&N are two points on the tangent of coordinates M(320-0) and N(0-0.19) So r= $\frac{0-0.19}{320-10} = 5.9 \times 10^{-4}\ mol.L^{-1}.S^{-1}$
3-	Rate at t=$_0$> rate t=$_{210}$, the rate decrease with time. The factor that is responsible for this decrease is the concentration of hypochlorite ions that lead to reduce the rate .
4	The half-life of the reaction is the time needed for half the concentration of $[CLO^-]_0$ to disappear. It becomes 0.12 $mol.L^{-1}$ at time $t_{1/2}$=138s.
5-	a- $[ClO^-]_t = \frac{n(CLO^-)_t}{v\ (solution\ )_1} = \frac{n_0 - n_{reacting}}{V} = [CLO^-]_0 - \frac{2n(O_2)_{formed}}{V}$ $[CLO^-]_t$=0.24-$\frac{2xV(O_2)_t}{24\times10^3\times110\times10^{-3}}$=0.24-7.57xV$(O_2)_t$. b- for a volume $V(O_2)_t$= 317mL we have : $[CLO^-]_t$=0 . this means that the hypochlorite ions reacted completely and the species that are present in the solution other than water are the ions: chloride and cobalt.
II	The graph shows that the increase in temperature accelerates the rate of the decomposition of hypochlorite ions. This leads to a decrease in the concentration of hypochlorite ions that reduces its disinfecting power . thus it should be stored away from heat sources.