A Kinetic Study of Hydrogen Peroxide Decomposition in Presence of Pyrite

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The kinetics of hydrogen peroxide decomposition in presence of pyrite has been investigated in aqueous acidic media. It was found that hydrogen peroxide decomposition is double catalyzed by iron sites found on pyrite surface (a heterogeneous reaction) and aqueous ferric iron (a homogenous reaction). The heterogeneous reaction is first order with respect to $[H_2O_2]$, and homogeneous reaction is first order with respect to $[H_2O_2]$ and $[Fe_{(aq)}]$. The rate is proportional to a fractional power of the geometric surface area (0.77) and $[H^+]$ (–0.55). The apparent activation energy of the hydrogen peroxide decomposition into oxygen and water at a temperature range of 25 to 45 °C was found to be 79.5 kJ mol^{-1}.

Key words:
Kinetics, hydrogen peroxide decomposition, pyrite, oxygen

Introduction

Pyrite is the most common and abundant mineral sulphide presents in coals and in base metals and precious metal ores.[1–5] Frequently, the gold and other mineral sulphides, such as chalcopyrite, galena and sphalerite, are very finely disseminated within a pyritic matrix. The extraction of gold from this complex assemblage is based on pyrite oxidation by an effective reagent. Of particular interest is the use of H_2O_2 as reagent for pyrite oxidation.[1–3,6] The use of H_2O_2 is preferred because apart from oxygen and water no other reaction products could be generated during its contact with mineral sulfides.[1–3,6–10] The oxidative dissolution of pyrite by H_2O_2 in acidic solutions is characterized by the following overall reaction: [1–3,6,10]

$$FeS_2 + 7.5\,H_2O_2 = Fe^{3+} + 2\,SO_4^{2-} + H^+ + 7\,H_2O \quad (1)$$
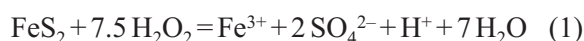
The released ferric iron acts as catalyst of H_2O_2 decomposition[1–3,8] causing a considerable loss of reagent. The H_2O_2 decomposition is due to following reaction:

$$Fe^{3+} + 0.5\,H_2O_2 = Fe^{2+} + H^+ + 0.5\,O_2 \quad (2)$$
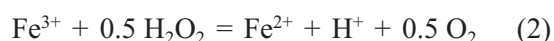
The development and optimization of the hydrometallurgical process of pyrite oxidation require knowledge of the kinetics and mechanism of the hydrogen peroxide decomposition in presence of this mineral, the main side reaction. Unfortunately, there are no detailed studies on the influence of pyrite on H_2O_2 decomposition. Hence, the purpose of this study was to investigate the kinetics and mechanism of H_2O_2 decomposition in presence of pyrite. For this purpose, the effect of variables such as hydrogen peroxide concentration, pH, geometric surface area and temperature on the decomposition rate were investigated.

Experimental

The reagents used were reagent grade hydrochloric acid and hydrogen peroxide (Merck). Solutions were prepared in double distilled water. The pyrite crystals used in these experiments were from Baia-Mare, Romania. X-ray diffraction examination showed the presence of pyrite and absence of other crystalline phases. The chemical analysis of pyrite used in this study showed the stoichiometric ratio expected for this mineral ($v_{S/Fe}$ = 1.98 ± 0.03). In addition, minor elements in the pyrite matrix were determined. The elements present with their mass fraction: w_{Co} = 0.02 %, w_{Ni} = 0.02 %, w_{Cu} = 0.01 %, w_{Zn} = 0.01 % and w_{As} = 0.13 %. The pyrite crystals were ground and classified into three size fractions by dry screening: 71–80 μm, 80–90 μm and 90–125 μm. The resulted fractions were treated for 60 s with nitric acid (c = 1 mol L^{-1}), washed repeatedly with double distilled water by rapid suspension and decanting in order to remove fine particles. Then, each fraction was rinsed with fresh acetone several times and stored under oxygen-free desiccator.

The specific surface areas of these fractions of pyrite grains are too low to be determined reliably by BET analysis. Instead, one could approximate the specific surface area assuming that it is a func-

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tion of pyrite grains diameter.[11] The specific surface area for the three fractions calculated for an assumed spherical geometry is $A = 1.12 \cdot 10^{-2}$ m^2 g^{-1}, $1.41 \cdot 10^{-2}$ m^2 g^{-1} and $1.59 \cdot 10^{-2}$ m^2 g^{-1}.

Decomposition behaviour for hydrogen peroxide in presence of pyrite was tested under reaction conditions which were as follows: initial pH from 1.00 to 2.00, temperatures from 25 to 45 °C, [H$_2$O$_2$] from 0.14 to 0.70 mol L^{-1}, pyrite specific surface area in range $1.12 \cdot 10^{-2} - 1.59 \cdot 10^{-2}$ m^2 g^{-1} and initial mass ratio $\zeta = 250 : 0.3$. The solutions pH was verified at the start of each experimental run and, if necessary, corrected by small additions of HCl ($c = 2.5$ mol L^{-1}).

The decomposition experiments were carried out in a conventional gas meter placed in water batch controlled by a thermostat.[12] When the amount of released oxygen during a decomposition experiment exceeded 100 mL (the volume of oxygen trap), the gas was deviated towards a parallel oxygen trap. The volumes of released oxygen were corrected under laboratory conditions to find the corresponding decrease c_x (mol L^{-1}) in hydrogen peroxide concentration as results of its decomposition. Here, it is worth to note that the overall decrease of hydrogen peroxide concentration (that can be evaluated by analytical determination of [H$_2$O$_{2(aq)}$]) can not directly reflect the rate of H$_2$O$_2$ decomposition. Since a fraction of hydrogen peroxide is consumed during pyrite oxidative dissolution according to eq. (1) the rate of hydrogen peroxide

decomposition into oxygen and water will be overestimated and no accurate kinetic parameters will be obtained.

Throughout the experiments, pH was measured using an Ingold InLab 400 combined pH glass electrode incorporated in the gas meter. Before use, the electrode was calibrated in Mettler pH 4.01 and 7.00 buffers.

The degree of pyrite dissolution (α/%) at the end of the experimental runs was determined by next analytical procedure: the non-reacted pyrite was filtered, washed with double distilled water, dried with acetone, and weighted in order to determine the degree of pyrite dissolution.[13]

The experimental conditions and the degree of pyrite dissolution at the end of the experimental runs are gathered in Table 1.

Results and discussion

Table 1 presents the amounts of consumed H$_2$O$_2$ by eq. (1) (n_c) and the amounts of decomposed H$_2$O$_2$ (n_d) at the end of experiments. The amounts n_c were evaluated from α values (Table 1). From Table 1 it is clear that n_d was always greater than n_c, meaning that substantial fractions of H$_2$O$_2$ were loosed by side reaction (3).

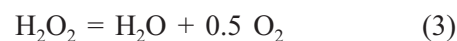$$H_2O_2 = H_2O + 0.5\ O_2 \qquad (3)$$

T a b l e 1 – *Summary of experimental conditions and results of hydrogen peroxide decomposition in presence of pyrite*

Run	$A/10^{-2}$ m^2 g^{-1}	[H$_2$O$_2$]/mol L^{-1}	pH	T/°C	α/%	$n_c/10^{-3}$ mol	$n_d/10^{-3}$ mol	$k_a/10^{-4}$ min^{-1}	$k_b/10^{-3}$ L mol^{-1} min^{-1}	R^2
D-01	1.12	0.35	1.00	25	7.6	1.4	3.0	1.52	6.82	0.999
D-02	1.41	0.35	1.00	25	8.7	1.6	3.5	1.67	7.52	0.992
D-03	1.59	0.35	1.00	25	10.1	1.9	4.2	2.04	9.16	0.999
D-04	1.12	0.14	1.00	25	4.5	0.8	1.1	1.62	7.28	0.998
D-05	1.12	0.14	1.00	25	–	–	1.4	2.04	9.18	0.989
D-06	1.12	0.53	1.00	25	11.2	2.1	5.9	1.68	7.57	0.997
D-07	1.12	0.53	1.00	25	–	–	5.5	1.65	7.41	0.996
D-08	1.12	0.70	1.00	25	14.8	2.8	6.8	1.40	6.31	0.994
D-09	1.12	0.35	1.30	25	10.3	1.9	4.2	1.92	8.62	0.986
D-10	1.12	0.35	2.00	25	15.6	2.9	17.2	5.23	23.53	0.985
D-11	1.12	0.35	1.00	35	14.2	2.7	12.8	4.69	18.75	0.972
D-12	1.12	0.35	1.00	45	22.1	4.1	53.0	12.67	50.67	0.986
D-13	1.12	0.35	1.00	45	–	–	41.9*	12.73	50.93	0.978

* registered after 150 min of reaction.

The highest values of n_d are registered at high temperature ($T = 45$ °C) and high initial pH (pH 2.00). For example, at 25 °C and $[H_2O_2] = 0.35$ mol L^{-1} n_d increases from 3 mmol (D-01) to 17.2 mmol (D-10) when pH increases from 1.00 to 2.00. At initial pH 1.00 and $[H_2O_2] = 0.35$ mol L^{-1} n_d increases from 3 mmol (D-01) to 53 mmol (D-12) when temperature increases from 25 to 45 °C.

Figure 1 shows that the decrease c_x (mol L^{-1}) in hydrogen peroxide concentration as results of its decomposition into O_2 and H_2O increases when the geometric surface area of pyrite grains, $[H_2O_2]$, pH and temperature increase. On the other hand, the variation of c_x as a function of time does not show monotonous character indicating that the rates of hydrogen peroxide decomposition increase with time. Trends of c_x as function of time suggest us that the catalytic effect of pyrite on H_2O_2 decomposition increases with reaction time. This behaviour can be explained if we accept that the hydrogen peroxide decomposition is double catalyzed by:

a) iron sites from pyrite surface

$$H_2O_2 \xrightarrow{\text{surface iron}} H_2O + 0.5\ O_2 \qquad (4)$$

and

b) released ferric iron during pyrite oxidative dissolution (aqueous iron)

$$H_2O_2 \xrightarrow{\text{aqueous iron}} H_2O + 0.5\ O_2 \qquad (5).$$
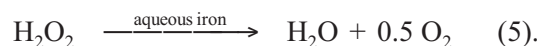
It has been argued that reactive surface area of a dissolving mineral can be considered as a constant until a very high degree of dissolution ($\alpha > 90$ %) is achieved.[14] Therefore, it is reasonable to assume that the reactive iron sites (iron sites involved into catalytic decomposition of H_2O_2) concentration at pyrite surface remains practically unchanged during the 180 min of pyrite oxidative dissolution. Instead, the aqueous ferric iron concentration, and implicitly its catalytic effect, will proportionally increase with pyrite dissolution progress.
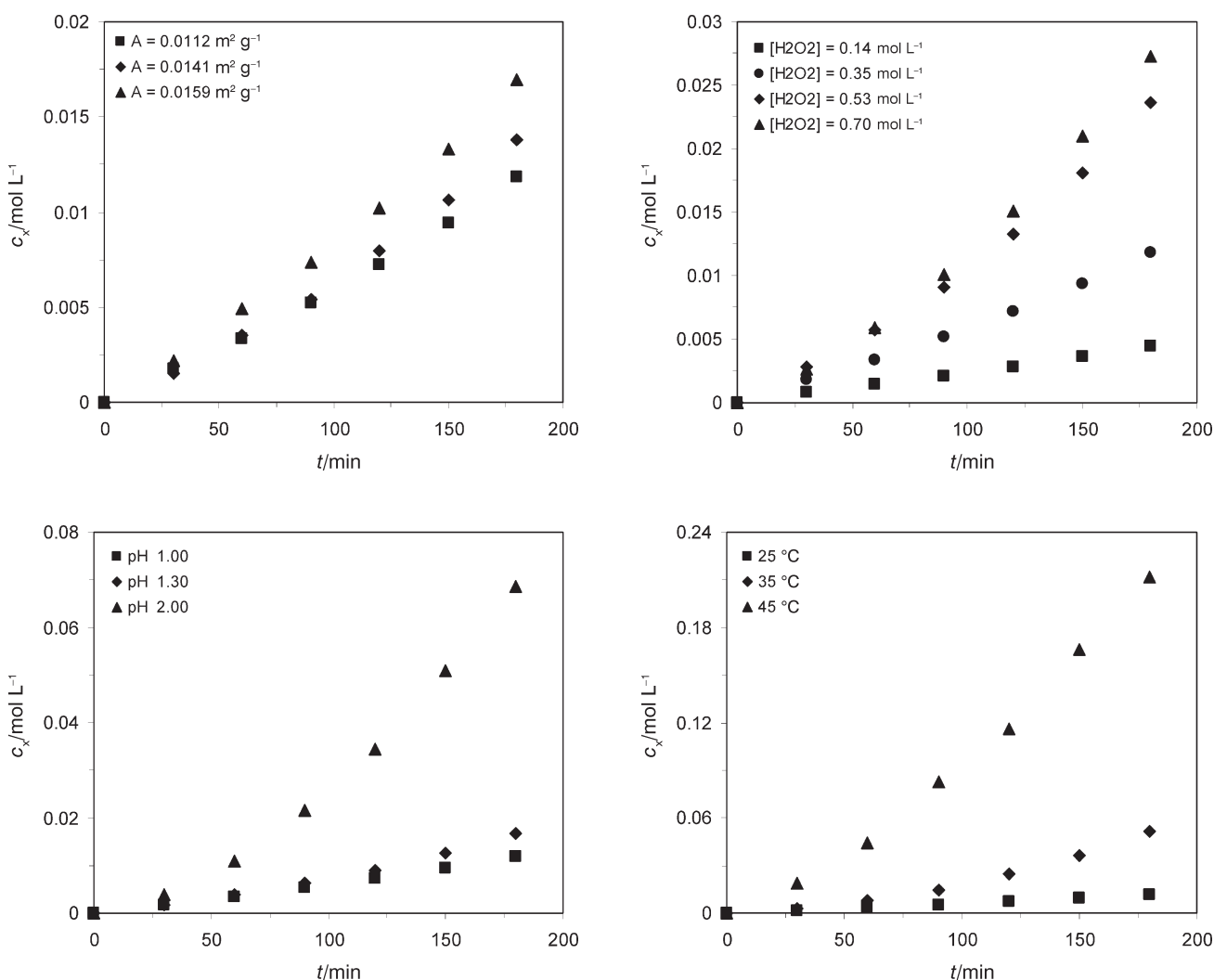

F i g . 1 – *Effect of specific surface area (a), hydrogen peroxide concentration (b), pH (c) and temperature (d) on hydrogen peroxide decomposition in presence of pyrite*

Taking into consideration the hypothesis of double catalytic effect of pyrite (by iron from its surface and by released iron) on H_2O_2 decomposition, in next section one will develop a kinetic model able to fit the experimental data. It is worth to note that the attempt to determine the kinetics parameters of H_2O_2 decomposition in presence of pyrite using the first order kinetic equation:[15,16]

$$\ln \frac{[H_2O_2]_0}{[H_2O_2]_0 - c_x} = k \cdot t \qquad (6)$$

where $[H_2O_2]_0$ is the initial hydrogen peroxide concentration, and k is the rate coefficient, gave a poor fit to majority of experimental data.

Kinetic modelling and rate coefficients estimation

According to the above-mentioned hypothesis, the rate of catalytic decomposition of H_2O_2 in presence of pyrite (r) can be expressed as the sum of the rate of H_2O_2 decomposition by iron from pyrite surface (r_a) and the rate of H_2O_2 decomposition by aqueous ferric iron (r_b):

$$r = r_a + r_b \qquad (7)$$

The first process (H_2O_2 decomposition by pyrite surface) is a heterogeneous reaction, while the second process is a homogenous reaction. If one assumes that, during each experimental run the reactive surface area of pyrite (and implicitly the concentration of reactive iron sites from pyrite surface), pH and temperature remain constant then the kinetics of the two reactions can be discussed in similar terms. The reaction (4) can be assumed first-order with respect to $[H_2O_2]$:

$$r_a = k_a \cdot [H_2O_2] \qquad (8)$$

and reaction (5) can be assumed first-order with respect to $[H_2O_2]$ and $[Fe_{(aq)}]$:

$$r_b = k'_b \cdot [H_2O_2] \cdot [Fe_{(aq)}] \qquad (9)$$

where k_a (min^{-1}) and k'_b (L mol^{-1} min^{-1}) are the rate coefficients, $[H_2O_2]$ is the hydrogen peroxide concentration, and $[Fe_{(aq)}]$ is aqueous ferric iron concentration. Summing eqs. (7), (8) and (9) one obtains:

$$r = k_a \cdot [H_2O_2] + k'_b \cdot [H_2O_2] \cdot [Fe_{(aq)}] \qquad (10)$$

Accepting that, between the concentration of released iron into solution and c_x, there is the following relation:

$$k'_b \cdot [Fe_{(aq)}] = k_b \cdot c_x \qquad (11)$$

then eq. (10) becomes:

$$r = -\frac{d[H_2O_2]}{dt} = \frac{dc_x}{dt} =$$
$$= k_a \cdot ([H_2O_2]_0 - c_x) + k_b \cdot ([H_2O_2]_0 - c_x) \cdot c_x \qquad (12)$$

where $[H_2O_2]$ is given by the difference $[H_2O_2]_0 - c_x$. If the rate is expressed in mol L^{-1} min^{-1}, $[H_2O_2]$ and c_x in mol L^{-1}, the units of rate coefficients k_a and k_b are min^{-1} and L mol^{-1} min^{-1}, respectively. Integrating eq. (12) and rearranging the terms of obtained relation we get:

$$\frac{\ln(k_a + k_b \cdot c_x) - \ln([H_2O_2]_0 - c_x)}{k_b \cdot [H_2O_2]_0 + k_a} + C = t \qquad (13)$$

where C is a constant. From initial conditions $t^0 = 0$ and $c_x = 0$ (for $t^0 = 0$) one obtains:

$$C = \frac{\ln[H_2O_2]_0 - \ln k_a}{k_b \cdot [H_2O_2]_0 + k_a} \qquad (14)$$

Inserting eq. (14) into eq. (13) and rearranging the terms one obtains:

$$\frac{\ln(k_a + k_b \cdot c_x) + \ln[H_2O_2]_0}{k_b \cdot [H_2O_2]_0 + k_a} -$$
$$- \frac{\ln([H_2O_2]_0 - c_x) + \ln k_a}{k_b \cdot [H_2O_2]_0 + k_a} = t \qquad (15)$$

The eq. (15) can be expressed as follows:

$$\ln \frac{(1 + N \cdot c_x) \cdot [H_2O_2]_0}{[H_2O_2]_0 - c_x} = k_a \cdot (1 + N \cdot [H_2O_2]_0) \cdot t \qquad (16)$$

where

$$N = \frac{k_b}{k_a} \qquad (17)$$

is a constant (L mol^{-1}).

Theoretical eq. (16) allows the estimation of k_a and k_b from slopes of $\ln \dfrac{(1 + N \cdot c_x) \cdot [H_2O_2]_0}{[H_2O_2]_0 - c_x} = \ln R$ vs. time plots. The main step in the rate coefficients estimation was the finding of the N value for that all experimental data fit eq. (16). The finding was made by linear regression analysis. Well results with enough precision and coefficients of correlation (R^2) higher than 0.97 were obtained for $N = 45$ (Fig. 2). k_a values were estimated from the slope of the regression lines, taking into consideration that slope $= k_a \cdot (1 + N \cdot [H_2O_2]_0)$. The obtained k_a values were used in order to derive k_b (according to eq. 17). All the rate coefficients (k_a and k_b) and R^2 values of experiments presented earlier are collected in Table 1.
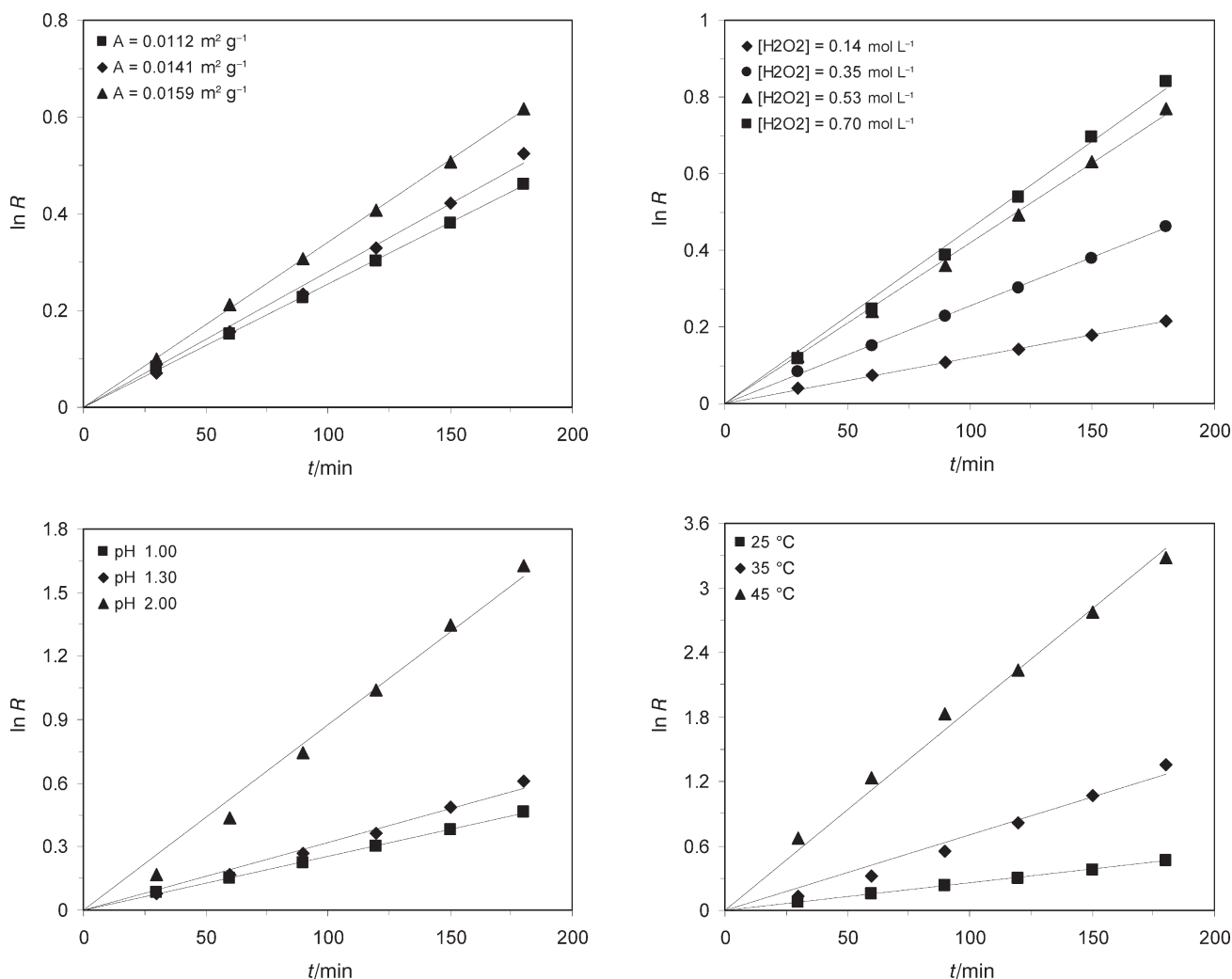
F i g . 2 – *Experimental data of hydrogen peroxide decomposition in presence of pyrite plotted according kinetic model proposed in this study. Data were obtained during experimental series designated to study the effect of specific surface area (a), hydrogen peroxide concentration (b), pH (c), and temperature (d).*

The well fitting of theoretical eq. (16) by experimental data indicates that all assumptions made in order to elaborate the kinetic model of H_2O_2 decomposition in presence of pyrite are reasonable. Furthermore, a unique N value able to fit all experimental data produces the same activation energy, geometric surface area dependence of reaction rate and reaction order with respect to $[H_2O_2]$ and $[H^+]$ for both reactions (4) and (5), indicating that the heterogeneous hydrogen peroxide decomposition and homogenous hydrogen peroxide decomposition follow similar reaction mechanisms.

Effect of [H_2O_2]

For studying the effect of H_2O_2 concentration a series of experiments (runs D-01, D-04, D-05, D-06, D-07 and D-08) were carried out in which the $[H_2O_2]$ was varied while $[H^+]$, mass of pyrite (m), solution volume (V) and temperature (T) were

held constant. In Fig. 3 the rate coefficients k_a and k_b are plotted against $[H_2O_2]$. It is clear that the ob-
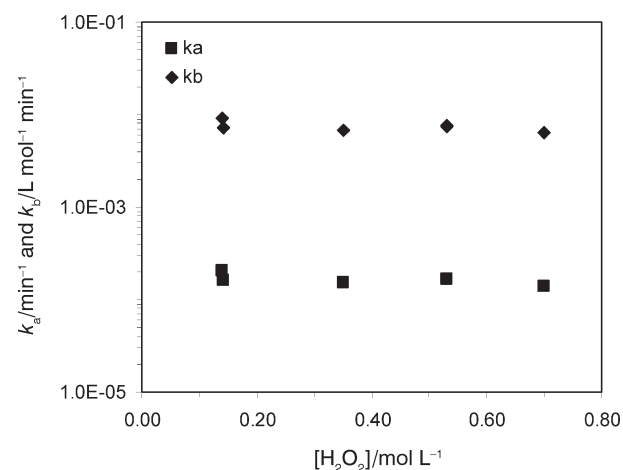

F i g . 3 – *Effect of [H_2O_2] on rate coefficients k_a and k_b for the hydrogen peroxide decomposition in presence of pyrite grains (A = 0.0121 m² g⁻¹) at pH 1.00 and 25 °C temperature*

served rate coefficients (k_a and k_b) are practically independent of [H_2O_2] in its examined range (0.14 to 0.70 mol L^{-1}). This finding confirms that the hydrogen peroxide decomposition in presence of pyrite (both reactions (4) and (5)) is first order reaction with respect to [H_2O_2]. At 25 °C and initial pH 1.00 the mean values of the rate coefficients k_a and k_b are 1.65 · 10^{-4} min^{-1} and 7.43 · 10^{-3} L mol^{-1} min^{-1}, respectively.

Effect of pH

The effect of pH on the rate constant was also examined by changing pH and keeping the value of other quantities constant (runs D-01, D-09 and D-10). The observed rate coefficients were found to increase when pH increases ([H^+] has a negative impact on reaction rate) in examined range of pH 1.00 to 2.00. The plot of –log k_a or –log k_b (not shown) vs. pH yields slopes of –0.55 ± 0.07, as shown in Fig. 4. Since the reaction order with respect to [H^+] of hydrogen peroxide decomposition in presence of dissolved ferric iron is –1,[17] the value of reaction order obtained in the present study can be view as an apparently unexpected result. To elucidate the observed fractional order of hydrogen peroxide decomposition with respect to [H^+], we have to examine the effect of time on solutions pH. The pH measurements showed that the proton concentration (10^{-pH}) increases with time during experiment conducted at 25 °C, 0.35 mol L^{-1} [H_2O_2] and initial pH 2.00 (Fig. 5). Perhaps, the main reason of pH decrease observed during experimental run conducted at initial pH 2.00 is the proton release by pyrite oxidative dissolution according to eq. (1). This pH decrease will induce an apparent decrease of hydrogen peroxide decomposition rate, causing the observed deviation of the reaction order with respect to [H^+] from –1 to –0.55.
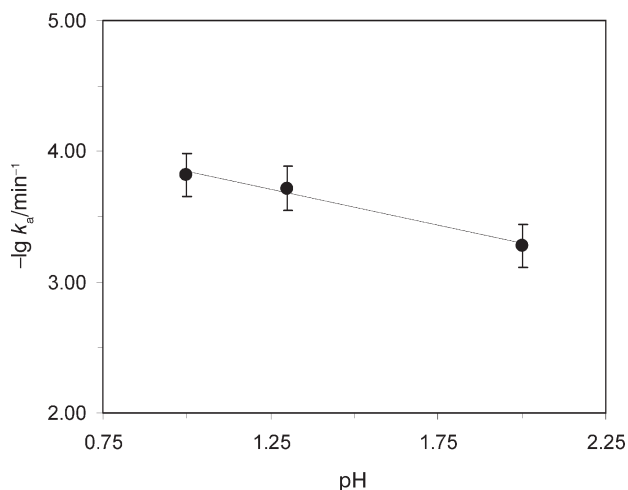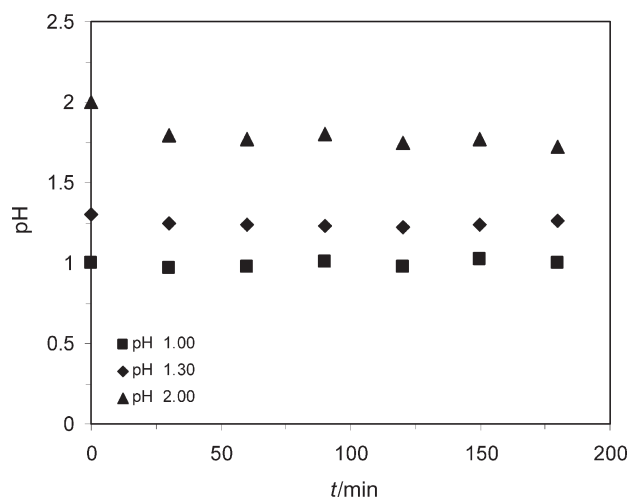
F i g . 5 – *Variation of pH with time for experimental conditions pH 1.00, 1.30, 2.00 at 25 °C and [H_2O_2] = 0.35 mol L^{-1}*

Effect of geometric surface area

A series of experimental runs (D-01, D-02 and D-03) were carried out to estimate the effect of pyrite surface area on the reaction rate coefficients. The initial hydrogen peroxide concentration (c = 0.35 mol L^{-1}), pH (1.00), mass of pyrite (m = 0.3 g), solution volume (V = 250 mL) and temperature (T = 25 °C) were held constant. The rate coefficients of hydrogen peroxide decomposition increased with increasing geometric surface area (Table 1). A straight line with the slope of 0.77 ± 0.31 was obtained (Fig. 6) when –log k_a was plotted vs. –log A (A is geometric surface area). The observed rate coefficient is dependent on a fractional power of geometric surface area. This indicates that geometric surface area and reactive area[1] of pyrite
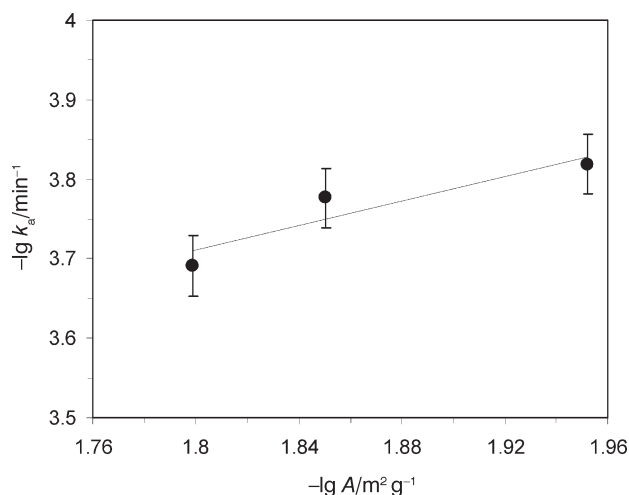
F i g . 4 – *Effect of pH on rate coefficient k_a*

F i g . 6 – *–lg k_a vs. –lg A plot for the decomposition of hydrogen peroxide in presence of pyrite at 25 °C, pH 1.00 and [H_2O_2]=0.35 mol L^{-1}*

grains are different. Most probable, the heterogeneous hydrogen peroxide decomposition occurs mainly at defective sites (sites of high excess surface energy) existing on pyrite surface. The surface concentration and reactivity of these sites can vary substantially between pyrite grains.[1] Accordingly, a nonlinear relationship between the defective sites (edges, corners, cracks and pores) concentration and pyrite geometric surface area can not be excluded. Such relationship would induce the observed deviation of geometric surface area dependence of H_2O_2 decomposition rate from unity.

Effect of temperature

The rate coefficient k_a and k_b of hydrogen peroxide decomposition in acidic solutions and in presence of pyrite are strongly affected by changes in temperature at pH 1.00 and $[H_2O_2] = 0.35$ mol L^{-1} (Table 1). The comparison of the rate coefficients observed at 25 °C (run D-01) and 45 °C (runs D-12 and D-13), respectively, shows that k_a and k_b at 45 °C increase by a factor of 8. The effect of temperature on the rate coefficient can be determined by an Arrhenius plot of –ln (rate coefficient) vs. T^{-1}. Thus, a plot of –ln k_a or –ln k_b vs. T^{-1} should yield a straight line with slope of $E_a R^{-1}$, where E_a is activation energy, and R is the gas constant. Fig. 7 shows an Arrhenius plot of –ln k_a vs. T^{-1} for the hydrogen peroxide decomposition in temperature range 25–45 °C. This yields an apparent activation energy of $E_a = 79.5 \pm 0.7$ kJ mol^{-1}. The magnitude of estimated value for apparent activation energy of the heterogeneous hydrogen peroxide decomposition suggests that the rate is controlled by a surface reaction.[18] Note that the same value for activation energy ($E_a = 79.5$ kJ mol^{-1}) is obtained when one plots –ln k_b vs. T^{-1}. This value is consistent with the
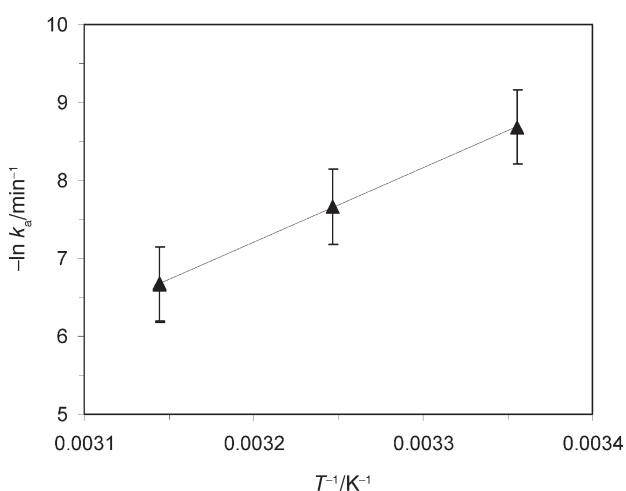
observations suggesting that the rate-controlling step of homogenous hydrogen peroxide decomposition is a chemical reaction.[19]

Taking into consideration that iron(III)-hydroperoxocomplexes ($[FeHO_2]^{2+}/[Fe(OH)(HO_2)]^+$) dissociation is the slowest step of homogenous H_2O_2 decomposition by ferric iron,[16] it can be assumed that the reactions involving pyrite surface]$FeHO_2^{2+}$/ pyrite surface]$Fe(OH)(HO_2)^+$ and $FeHO_2^{2+}{}_{(aq)}$/ $Fe(OH)(HO_2)^+{}_{(aq)}$ complexes are the rate-limiting steps of H_2O_2 decomposition in presence of pyrite:

$$\text{pyrite surface}]FeHO_2^{2+} = \\ = \text{pyrite surface}]Fe^{2+} + HO_2 \qquad (18)$$

$$\text{pyrite surface}]Fe(OH)(HO_2)^+ = \\ = \text{pyrite surface}]Fe^{2+} + HO_2 + HO^- \qquad (19)$$

$$FeHO_2^{2+}{}_{(aq)} = Fe^{2+}{}_{(aq)} + HO_2 \qquad (20)$$

$$Fe(OH)(HO_2)^+{}_{(aq)} = Fe^{2+}{}_{(aq)} + HO_2 + HO^- \qquad (21)$$

Conclusions

The kinetics of hydrogen peroxide decomposition in presence of pyrite has been studied. It was found that reaction is double catalyzed by iron sites found on pyrite surface and aqueous ferric iron. The heterogeneous reaction is first order in $[H_2O_2]$, and homogenous reaction is first order in $[H_2O_2]$ and $[Fe_{(aq)}]$. Also, hydrogen peroxide decomposition in presence of pyrite is influenced by $[H^+]$, temperature and mineral surface area. The apparent activation energy is $E_a = 79.5 \pm 0.7$ kJ mol^{-1}, and H_2O_2 decomposition rate is proportional to a fractional power of the geometric surface area (0.77 ± 0.31) and $[H^+]$ (-0.55 ± 0.07). The highest losses of H_2O_2 by decomposition into O_2 and H_2O are registered at high temperature (45 °C) and high initial pH (pH 2.00).
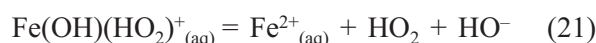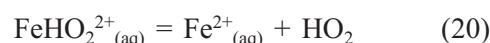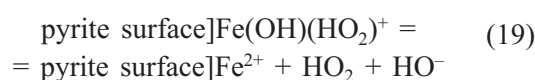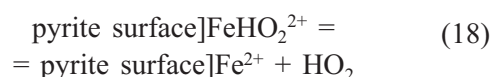
F i g . 7 – *Arrhenius plot of the hydrogen peroxide decomposition rate coefficient k_a at pH 1.00 and $[H_2O_2] = 0.35$ mol L^{-1}*

List of symbols

A – specific surface area, m^2 g^{-1}

c – concentration, mol L^{-1}

c_x – extensive quantity for all concentration, mol L^{-1}

E_a – activation enegy, kJ mol^{-1}

k_a – rate coefficient for a first order reaction, min^{-1}

k_b – rate coefficient for a second order reaction, L mol^{-1} min^{-1}

m – mass, g

n – amount of substance, mol

n_c – amount of consumed, mol

n_d – amount of decomposed, mol

R^2 – correlation coefficient

r – reaction rate, mol L^{-1} min^{-1}

T – temperature, °C

t – time, min

V – volume, L, mL

w – mass fraction, %

α – degree of dissolution, %

ζ – mass ratio

ν – stoichemetric ratio

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