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Thermodynamic and Kinetic Investigations for the Decomposition of Aqueous Hydrogen Peroxide on MnO2 and PbO Surfaces at Different Temperatures

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الملخص

التفكك المحفز لفوق أكسيد الهيدروجين المائي في وجود أكاسيد المعادن غير الذائبة (MnO_2 وPbO) تُحَرّي عنه في مدى درجة حرارة (25-60ºC)، وكذلك المعاملات الثيرموديناميكية لتفاعلات التفكك في هذا المدى من درجة الحرارة. حركية هذه التفاعلات استخدمت مؤشراً على عمل المحفز. معدلات التفاعلات، ثوابت معدلات التفاعلات وأزمنة نصف العمر قدرت عند درجات حرارة مختلفة، بالإضافة إلى ذلك قُدّرتْ قيم طاقة النشاطية. وحُلِّلَتْ حركية تفاعلات التفكك من الرتبة الأولى وثوابت معدلات التفاعلات قدرت من ميول الخطوط المستقيمة لمعادلة الرتبة الأولى، ثم تم حساب أزمنة نصف العمر من قيم ثوابت معدل التفاعل، وقيمة طاقة النشاطية لتفاعلات التفكك قدرت من ميول الخطوط المستقيمة لمعادلة ارهينيوس، حيث كانت قيمتها 1.59 kJ/mol لثاني أكسيد المنجنيز و 31.60 kJ/mol لأكسيد الرصاص الثنائي. بالإضافة إلى ذلك المعاملات الثيرموديناميكية $\Delta H^{\#}$ و$\Delta S^{\#}$ قُدّرتْ من ميول وتقاطعات الخطوط المستقيمة عند رسم معادلة ايرنق. إضافة إلى ذلك قيم $\Delta G^{\#}$ حسبت من قيم $\Delta H^{\#}$ و$\Delta S^{\#}$. تأثير درجة الحرارة على حركية تفاعلات التفكك كانت ضمن خطة الدراسة.

الكلمات المفتاحية: فوق أكسيد الهيدروجين، ثاني أكسيد المنجنيز، أكسيد الرصاص الثنائي، ثابت معدل التفاعل، طاقة النشاطية، الطاقة الحرة للتنشيط.

Abstract

In this study, decomposition reactions were determined and the kinetics of these decomposition reactions were used as an indications process for catalyst. The rate, rate constants and half-lifetimes were determined at different temperatures. Additionally, the values of activation energy were also defined. The kinetics of decomposition reactions were analyzed by first-order equation and rate constants were determined from the slopes of the straight lines of the first-order equation. After that, half- lifetimes were estimated from rate constants, and the activation energy value for reactions was determined from the slopes of straight lines of the Arrhenius equation, where its value was 1.59 kJ/mol for MnO2 and 31.60 kJ/mol for PbO. Furthermore, thermodynamics parameters ΔH# and ΔS# were determined from the slopes and intercepts of linear lines when drawing the Eyring equation. In addition, the values of ΔG# were calculated from values of ΔH# and ΔS#. The temperature influence on the kinetics of the decomposition reactions was within the study plan.

Keywords: hydrogen peroxide, manganese (IV) oxide, lead (ii) oxide, rate constant, activation energy, free energy of activation.

1. INTRODUCTION

Hydrogen peroxide is environment-friendly, easy to use, efficient, and suitable for use in the remediation of contamination. However, hydrogen peroxide when used on its own is not an ideal oxidant of most substances, so the activation of hydrogen peroxide is a purpose [1]. Decomposition of hydrogen peroxide to supply oxygen for the atmosphere is a suitable method and transition metal ions, such as manganese, iron, cobalt, and lead are used for the decomposition of hydrogen peroxide [2-4].

As the production of many chemicals involves catalysis, catalysis research is a domain field in applied science and is involved in many areas of chemistry, such as material science and organometallic chemistry. Catalytic reactions are preferred in environment-friendly green chemistry due to the reduction of waste generated [5]. Reactions of H_2O_2 with metal and metal oxide surfaces have been studied to some extent, mainly due to their importance in areas ranging from catalysis to geo- and environmental chemistry and nuclear technology [6].

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This research uses MnO_2 and PbO as catalysts due to their particles having several advantages like simple and rapid preparative methods. Furthermore, there are various possibilities to modify the particle surface state and overall homogeneity[7]. As an important functional metal oxide, manganese dioxide is one of the most attractive inorganic materials because of its physical and chemical properties and wide application in catalysis, ion exchange, and molecular adsorption[8-10]. Additionally, lead is one of the pollutants of the environment, so the study of the reaction of H_2O_2 with lead oxide can lead to a better understanding of the fate of H_2O_2 and the extent of the oxidation reaction in the environment [7].

The temperature has a great effect on the reaction rate, where most experiments showed that the reaction rate increases with temperature[11].

Adding a catalyst to the reaction vessel leads to an intrinsic change in the reaction rate because of two main causes:

a) A catalyst provides an alternative reaction pathway to the reaction product. Figure (1). The rate of the reaction is increased as this alternative route has lower activation energy than the reaction route in the absence of the catalyst.

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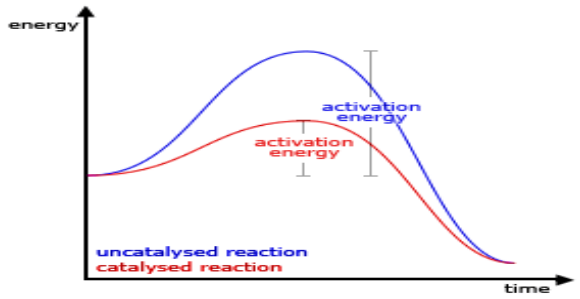


Figure 1. The activation energy of catalyzed and uncatalysed reactions

b) The catalyst increases the reaction area of the reaction particles. Figure (2) [7,12-15].

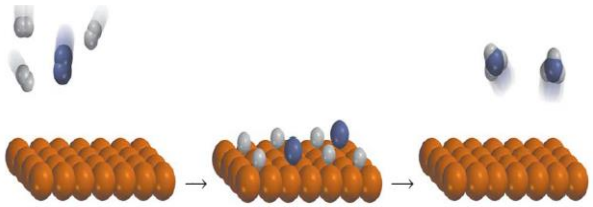


Figure 2. A catalyst acts as a surface on which the reaction can take place.

The conversion of H_2O_2 to water and oxygen is strongly affected by the catalyst [7,15].

$$2H_2O_2 \xrightarrow{catalyst} 2H_2O + O_2 \uparrow$$

The decomposition of H_2O_2 solution by MnO_2 suggested [7] the following mechanism for the H_2O_2- MnO_2 system

$$MnO_2 + H_2O_2 \rightarrow Mn^{+2} + 2HO^- + O_2$$
$$Mn^{+2} + 2HO^- \rightarrow Mn(OH)_2$$
$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$$
$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The decomposition of H_2O_2 solution by PbO suggested [7,16] the following mechanism for the H_2O_2- PbO system

$$PbO + H_2O_2 \rightarrow PbO_2 + H_2O$$
$$PbO_2 + H_2O_2 \rightarrow PbO + H_2O + O_2$$
$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The commercial importance of this research is due to the fact that hydrogen peroxide is one of the commonly cleanest, most versatile chemicals available. Additionally, hydrogen peroxide has beneficial properties; it is used in a broad variety of application areas such as chemical synthesis, electronics, environmental applications, food processing, mining, pulp & paper, recycling, textile bleaching, transportation and mouth wash [17].

2. MATERIALS AND METHODS

2.1 Materials:

The hydrogen peroxide and potassium permanganate were supplied by Farmitalia Carlo Erba Milano and distilled water was used to make a dilute solution by diluting 5ml of H_2O_2 to 100ml, and to make 0.02 M of $KMnO_4$ in one litre. The manganese dioxide and lead (II) oxide were supplied by Merck-Germany and used without purification.

2.2 Heating of Solutions:

The study used eight samples of H_2O_2, each one 100 ml. These samples were heated at different temperatures in the range between (25-60°C). Each sample was maintained at a specific temperature in this range and the temperature difference between samples was 5°C. These samples were prepared for use with the MnO_2 catalyst. Then the same heating process was repeated with eight new samples of hydrogen peroxide for use with PbO catalyst.

2.3 Concentration Measurement:

For the first eight samples, after heating to a certain temperature, we added 200 mg MnO_2 to each sample as a catalyst. Then, at five-minute intervals, 5 ml of each sample was titrated by standard 0.02M $KMnO_4$ solution in the presence of 5ml of 2M H_2SO_4 for each titration process. The same steps were repeated for the other eight samples when adding 200mg PbO as a catalyst.

Redox Reaction :

$$2(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$$
$$5(H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-)$$

Overall reaction

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

As H_2O_2 is sensitive to light, all the experiments were performed in the absence of light by wrapping black paper around the vessels to minimize error[15].

3. RESULTS AND DISCUSSION

The measured and calculated results for the decomposition of hydrogen peroxide by MnO_2 and PbO catalysts are given in figures 3, 4, 5, 6, 7 & 8, and tables (1 and 2).

3.1. Hydrogen peroxide decomposition :

The decomposition of hydrogen peroxide on the surfaces of MnO_2 and PbO is shown in figures 3,4,5, and 6. The reactions' behaviour followed a first-order rate expression with respect to H_2O_2 concentration, which is consistent with the observations of previous research [16].

Figures (3 and 4) show a linear proportional between $\ln([H_2O_2]_o/[H_2O_2])$ and reactions times due to the decomposition of H_2O_2 on the surfaces of the catalyst. From

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figure 3, we notice that the straight lines are convergent and the values of the reaction rate constants do not depend greatly on the temperature when using MnO_2 as a catalyst, while the straight line in figure 4 do not converge, and temperature has a clear effect on the values of the reaction rate constant when using PbO as a catalyst.

The relationship between $[H_2O_2]$ and reaction times for decomposition of H_2O_2 on MnO_2 and PbO surfaces is presented in figures (5 and 6), and the lines in these figures show an inverse linear relationship.

On the other hand, the rate of decrease in the concentration values after heating is more than those before heating [18,19]. This would accord with the calculated results in Table 1. These results show that the values of rate constants which are determined graphically are in agreement with the values of mean rate constants which are calculated mathematically at each temperature. Moreover, (***k***) increases with temperature, while the values of half-lifetimes ($t_{1/2}$) decrease with temperature. This could be attributed to increasing the rate of decomposition of H_2O_2 with temperature [18]. However, the results of our study showed an excellent fit to the model for this case of decomposition Table (1). With decomposition reaction, the values of rate constants obtained also show the acceptable correlation coefficient (R^2 range from 0.96 to 0.99), which suggests that the first-order reaction equation is applicable for estimation of rate constants values for decomposition H_2O_2 on MnO_2 and PbO surfaces.

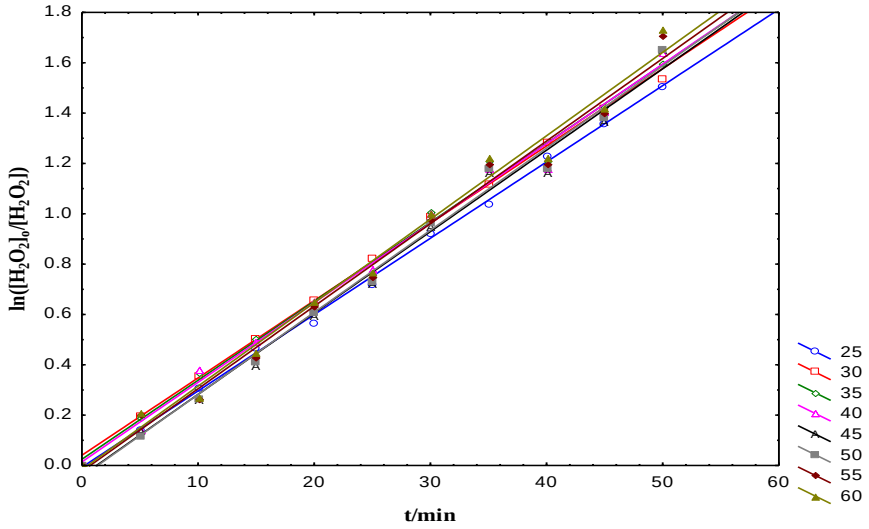


Figure 3. First-order fit of H_2O_2 decomposition on MnO_2 surface at temperature range (25-60 ^{O}C).

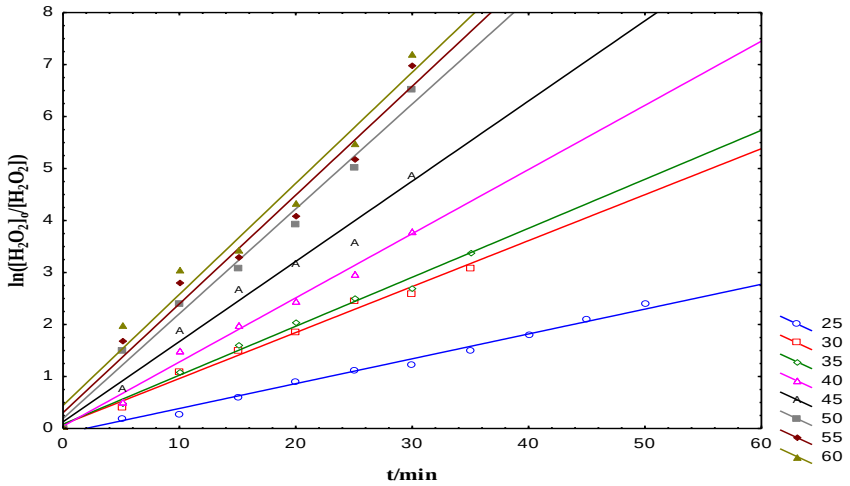


Figure 4. First-order fit of H_2O_2 decomposition on PbO surface at temperature range (25-60 ^{O}C)

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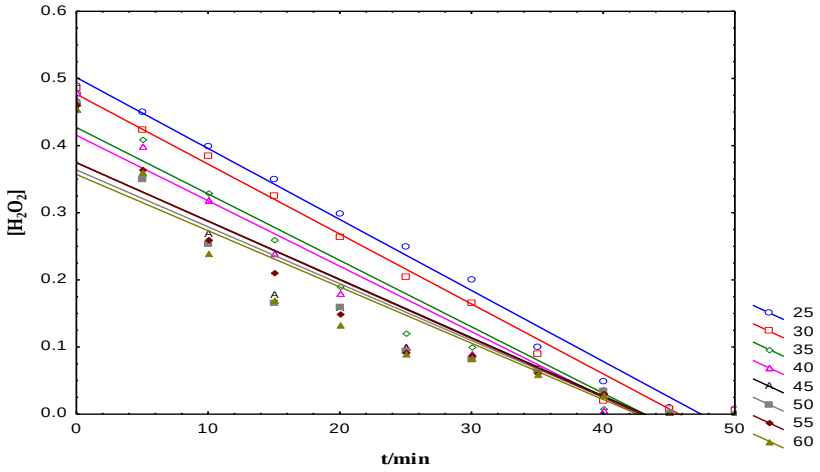


Figure 5. [H_2O_2] versus time for the decomposition of hydrogen peroxide on MnO_2 surface at temperature range (25-60 ^{O}C)

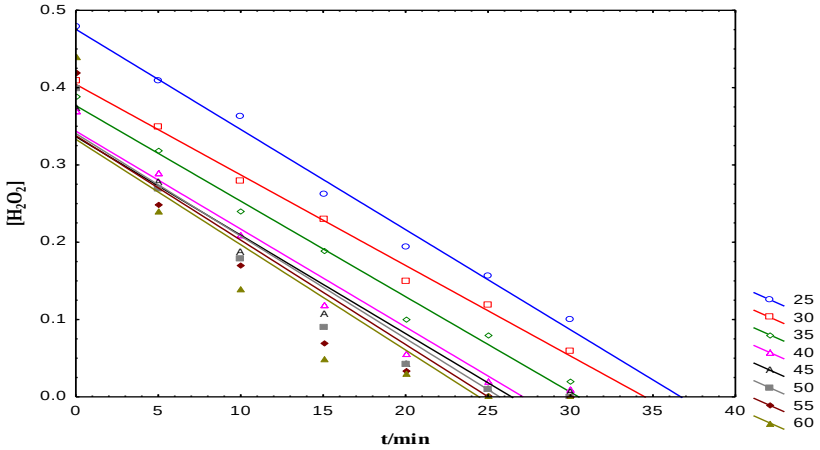


Figure 6. [H_2O_2] versus time for the decomposition of hydrogen peroxide on PbO surface at temperature range (25-60 ^{O}C).

Furthermore, a comparison of catalytic activity toward H_2O_2 decomposition for MnO_2 and PbO is shown in Table (1). From the values of the rate, rate constant, and $t_{1/2}$ we find that the catalytic activity toward H_2O_2 decomposition was the highest for MnO_2 and the lowest for PbO at the same temperature.

Furthermore, the values of rate constants in Table 1 were determined from typical linear plots of first-order reaction in Figures 3 and 4, according to the following equation [18,19]:

$$\ln \frac{[H_2O_2]_o}{[H_2O_2]} = \boldsymbol{k}t \qquad (1)$$

Also, the values of calculated rate constants (kcalculated) in the table (1)were estimated by equ. (1), where $[H_2O_2]_o$ is the initial concentration, $[H_2O_2]$ is the concentration after time t, k is the rate constant, and t is the time.

In addition, the values of the half-life times t1/2 in table 1 were estimated from the following relation [18,19]:

$$t_{1/2} = 0.693/\boldsymbol{k} \qquad (2)$$

3.2 . Activation Energy and Temperature:

Changes in the values of the reaction rate constants with temperature generally follow the Arrhenius equation [15,17]

$$\boldsymbol{k} = Ae^{-Ea/RT} \qquad (3)$$

Where Ea is the Arrhenius activation energy for the reaction; A is pre-exponential or the frequency factor; R is the gas constant; T is the absolute temperature. The respective Arrhenius plots are represented in Figure 7.

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Table 1. Rate constants, correlation coefficients, half-lifetimes, and rates for decomposition reaction of H_2O_2 on MnO_2 and PbO surfaces at temperature range (25-60°C)

T/°C	MnO_2 catalyst				
	k/min^{-1}	$k_{calcuted}$/min^{-1}	R^2	$t_{1/2}$/min	Rate/Mmin^{-1}
25	0.0317	0.0307	0.9986	21.86	0.011
30	0.0318	0.0310	0.9974	21.79	0.012
35	0.0320	0.0319	0.9958	21.65	0.013
40	0.0320	0.0328	0.9943	21.65	0.014
45	0.0325	0.0329	0.9931	21.32	0.015
50	0.0330	0.0340	0.9908	21.00	0.016
55	0.0333	0.0352	0.9885	20.81	0.017
60	0.0340	0.0361	0.9832	20.38	0.018
T/°C	PbO catalyst				
	k/min^{-1}	$k_{calcuted}$/min^{-1}	R^2	$t_{1/2}$/min	Rate/Mmin^{-1}
25	0.0088	0.0082	0.9919	78.75	0.0013
30	0.0105	0.0088	0.9885	66.00	0.0017
35	0.0123	0.0108	0.9907	56.34	0.0024
40	0.0154	0.0141	0.9895	45.00	0.0027
45	0.0201	0.0193	0.9815	34.47	0.0027
50	0.0234	0.0213	0.9865	29.62	0.0033
55	0.0268	0.0231	0.9734	25.86	0.0035
60	0.0297	0.0255	0.9685	23.33	0.0036

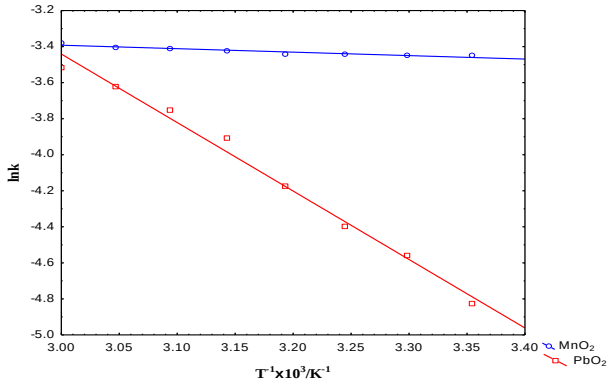


Figure 7. Arrhenius plots for the reaction of decomposition of H_2O_2 on MnO_2 (blue circle) and PbO (red square) at temperature range (25-60°C).

From Figure (7), we noted the straight line of PbO is more inclined, and therefore PbO needs higher activation energy than the activation energy needed by MnO_2, and this proves that MnO_2 is better than PbO as a catalyst for the decomposition of hydrogen peroxide, and this can be confirmed from the results.

3.3 Activation Thermodynamic Parameters:

The respective reaction enthalpies and entropies were obtained by the slopes and intercepts of linear lines of the Eyring Equation [16,20]

$$\ln\left(\frac{k}{T}\right) = \left(ln\frac{k_B}{h} + \frac{\Delta S^{\neq}}{R}\right) - \frac{\Delta H^{\neq}}{RT} \quad (4)$$

Where $\Delta H^{\neq}$ is the enthalpy of activation, k_B is the Boltzman constant, h is the Plank, s constant, and $\Delta S^{\neq}$ is the entropy of activation.

The respective Eyring plot is represented in Figure 8

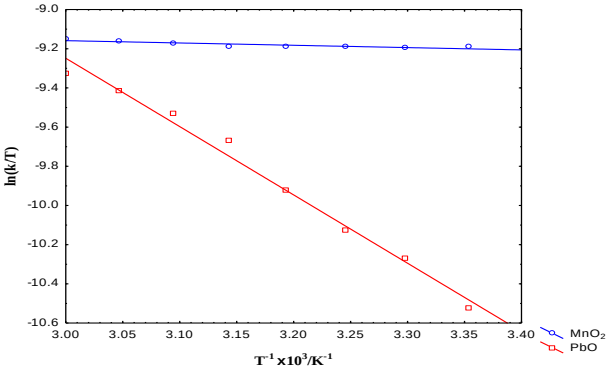


Figure. 8. Eyring plot for decomposition of H_2O_2 on MnO_2 (blue circle) and PbO (red square) at the temperature range (25-60°C).

Figure 8. shows an inversely linear relation between ln (k/T) and reciprocal of absolute temperature with a more inclined line in the case of the PbO catalyst. This behaviour can be attributed to the proportional rate constant with temperature [20]. From the upper- line which represents the decomposition of H_2O_2 on the MnO_2 surface, we note that temperature does not have a great effect on the decomposition process, while the underline which represents the decomposition of H_2O_2 on the PbO surface, gives a clear indication of the effect of temperature on the decomposition process.

Furthermore, the value of free activation energy $\Delta G^{\neq}$ is calculated from the following equation [20].

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (5)$$

The activation energy and other thermodynamic parameters of activation are listed in Table (2)

Table 2. Activation Thermodynamic Parameters of decomposition of H_2O_2 on MnO_2 and PbO surfaces in the temperature range (25-60°C).

Catalyst	Ea (kJ/mol)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (kJ/mol. K)	$\Delta G^{\neq}_{298}$ (kJ/mol)
MnO_2	1.59	0.98	-0.197	59.69
PbO	31.60	28.99	-0.195	86.11

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Aqueous hydrogen peroxide solution decomposes in a short time in the presence of the catalyst. The temperature effect has a considerable influence on the amount of hydrogen peroxide decomposed, especially in the case of PbO catalyst.

Characterization of concentration, rate, rate constant, and $t_{½}$ at different temperatures reveals the fact that MnO_2 and PbO catalysts and temperature induces decomposition of hydrogen peroxide, where the concentration of hydrogen peroxide decreases with a time of catalytic reaction, which, in turn, reduces the value of the reaction rate. However, the values of ***k*** increase with temperature, while the values of $t_{½}$decrease with temperature.

The plots of the Arrhenius equation for the decomposition of hydrogen peroxide on MnO_2 and PbO surfaces suggest that the PbO catalyst requires higher activation energy than the MnO_2 catalyst.

The plot of the Eyring equation shows that the decomposition process is endothermic in both cases (MnO_2 and PbO) with the larger value of $\Delta H^{\neq}$ for the PbO catalyst. While the values of entropies of activation are negative and close in both decomposition cases (MnO_2 and PbO).

The values of $\Delta G^{\neq}$ which measured at 298K suggest that the PbO catalyst has a higher value of free energy of activation.

Finally, from the results obtained, we conclude that MnO_2 is better than PbO as a catalyst for the decomposition of aqueous hydrogen peroxide.

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