

A TESTING OF SOME DYNAMIC KINETIC EQUATIONS

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Four equations were tested with the experimental data of catalytic decomposition of H_2O_2 in aqueous solution. It was found that Freeman and Carroll's method is the most satisfactory.

The evaluation of kinetic parameters from dynamic study seems to be initiated by Van Krevelen et al. [1]. Since then quite a few equations have been developed by various authors. Recently Sharp and Wentworth [2] have tested three equations using their own data of non-isothermal decomposition of CaCO_3 . They found that the methods of Coats and Redfern [3] and of Achar et al. [4] were of the same order of accuracy, whereas Freeman and Carroll's method [5] was less satisfactory. Their data were obtained by using a thermobalance. In this technique, although the temperature of the furnace was increased linearly, but that of the sample itself may not be so owing to the endothermic or exothermic nature of the reaction. Strictly speaking, such data are not suitable for testing these equations, all of which involve an important assumption of a linear time-temperature rise. Moreover, solid phase reactions are usually complicated and their mechanisms, not well understood. Most of them seem to be controlled by diffusion. The terms "reaction order" and "concentration" become meaningless when applied to solid phase reactions. The activation energy of a solid phase reaction derived from a certain dynamic method is also affected by many factors such as heating rate, size and the particles of the sample, pressure and the atmosphere under which the decomposition takes place, etc. [6]. On the other hand, there are many gas and liquid phase reactions whose mechanisms have been fully investigated. There is also no particle size problem in the gas and liquid phase reactions. Data obtained from these systems should, therefore, be more trustworthy for testing the validity of several dynamic equations. In the present paper, catalytic decomposition of H_2O_2 in aqueous solution was chosen for the purpose of this study. The three equations tested by Sharp and Wentworth, plus an additional equation by Horowitz and Metzger [7] were tested.

Experimental

Stock hydrogen peroxide (35%) was distilled under reduced pressure to remove the preserving agents. The concentration of hydrogen peroxide thus obtained contains approximately 6% of H_2O_2 by weight. It was diluted to 1 *N* before use. 10 ml of the 1 *N* H_2O_2 solution was pipetted into a 500 ml Erlenmeyer flask containing 260 ml of redistilled water kept in a water bath. 30 ml of the catalyst solution which had been kept in the same water bath to attain temperature equilibrium was then added into the hydrogen peroxide solution to start the reaction. The catalyst solution was 0.05 *M* in FeCl_2 , 0.005 *M* in CuCl_2 and 0.4 *M* in HCl ; this catalyst

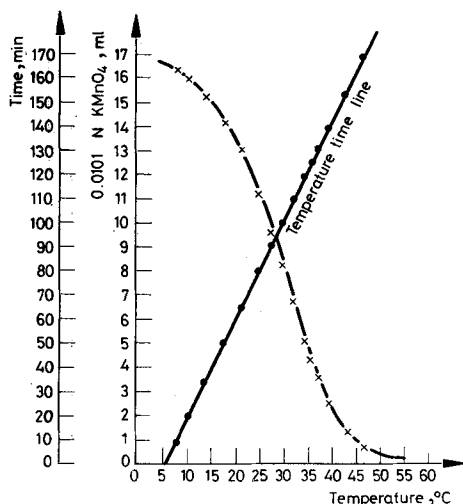


Fig. 1. Nonisothermal catalytic decomposition of H_2O_2

was investigated by Bohson and Robertson [8] in their study of catalytic decomposition of H_2O_2 . The course of reaction was followed by determination of the H_2O_2 concentration by titration with standard KMnO_4 solution. 5 ml of the sample was taken at suitable time intervals and delivered into an ice cold solution containing 10 ml 7.5 *N* H_2SO_4 and 100 ml of water to quench the decomposition reaction. It was then titrated with 0.01016 *N* KMnO_4 solution. In the dynamic method, the temperature of the water bath was increased linearly with respect to time by manual control of a rheostat. Owing to the large heat capacity of water and with some practice, the linearity of temperature rising was achieved quite satisfactorily as shown by the time-temperature line in Fig. 1.

Results and discussion

The four methods tested are briefly described as follows.

Method 1. Freeman and Carroll's treatment

The final equation derived by this method is

$$\frac{\Delta \log \left(\frac{dx}{dT} \right)}{\Delta \log (a - x)} = - \frac{\Delta E^*}{2.303R} \cdot \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log (a - x)} + n \quad (1)$$

where "a" is the initial concentration of one of the reactants. "x" is the concentration of that reactant which had reacted at the temperature T , $\frac{dx}{dT}$ is proportional to the rate of the reaction, which is measured from the slope of the tangent line of the reaction curve at the temperature T . From this equation a plot of

$$\frac{\Delta \log \left(\frac{dx}{dT} \right)}{\Delta \log (a - x)} \text{ against } \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log (a - x)}$$

results a straight line, the slope of which equals $-\frac{\Delta E^*}{2.303R}$ from which the activation energy ΔE^* can be calculated. The intercept of the line at the ordinate represents the order of reaction n .

Method 2. Coats and Redfern's treatment

The final equation derived by this method is

$$\log \frac{a^{1-n} - (a-x)^{1-n}}{(1-n)T^2} = - \frac{\Delta E^*}{2.303RT} + \log \frac{AR}{C\Delta E^*} \left[1 - \frac{2RT}{\Delta E^*} \right] \quad (2)$$

where A is the frequency factor in the Arrhenius equation, C is the heating rate. According to Coats and Redfern, the last term is essentially constant under most circumstances. Then, a plot of $\log \left[\frac{a^{1-n} - (a-x)^{1-n}}{(1-n) \cdot T^2} \right]$ vs. $\frac{1}{T}$ should result in a straight line with a slope of $-\frac{\Delta E^*}{2.303R}$ for any value of n except 1. For $n = 1$, $\log \left[- \log \left(\frac{a-x}{a} \right) / T^2 \right]$ against $\frac{1}{T}$ is plotted which should result in a straight line with the same slope.

Method 3. Achar, Brindley and Sharp's treatment

The final equation derived from this method is

$$\log \frac{\left(\frac{dx}{dT}\right)}{(a-x)^n} = -\frac{\Delta E^*}{2.303RT} + \log \frac{A}{C}. \quad (3)$$

According to this equation a plot of $\log \frac{\left(\frac{dx}{dT}\right)}{(a-x)^n}$ vs $\frac{1}{T}$ should be a straight line with a slope of $-\frac{\Delta E^*}{2.303R}$ and an intercept of $\log \frac{A}{C}$.

Method 4. Horowitz and Metzger's treatment

These authors defined a reference temperature T_s at the point of inflection of the reaction course and the variable T is thus changed to Θ by the relation, $T = T_s + \Theta$. The value of x at the inflection point, x_s , determines the order of reaction n . A plot of $\log(n)$ against x_s/a is almost linear for n equals 0.5 up to 5. If $x_s/a = 1/e$, where e is the base of the natural logarithm, then $n = 1$, and the following expression holds

$$\ln \frac{a}{a-x} = e^{(\Delta E^* \Theta)/RT_s^2}. \quad (4)$$

Thus, a plot of $\log \log \frac{a}{a-x}$ against Θ should give a straight line, with a slope of $\Delta E/2.303RT_s^2$. For $n \neq 1$, the following equation is derived

$$\frac{a^{1-n} - (a-x)^{1-n}}{1-n} = \frac{1}{n} (a-x_s)^{1-n} e^{(\Delta E^* \Theta)/RT_s^2} \quad (5)$$

and a plot of $\log \frac{a^{1-n} - (a-x)^{1-n}}{1-n}$ vs Θ should be a straight line of the same slope.

Thus, in order to test the second and the third methods, value of n must be assumed first.

The isothermal catalytic decomposition of H_2O_2 obeys first order kinetics; a plot of $\log(a-x)$ against time shows good straight line [9]. From the slopes of the lines, the rate constants were calculated to be 2.67×10^{-8} , 4.49×10^{-8} and 1.34×10^{-7} moles liter $^{-1}$ min $^{-1}$ at 10.2, 17.1 and 30.0°C respectively. The activation energy obtained by the Arrhenius plot is 13.9 kcal per mole. This value is comparable with the activation energy for the decomposition of H_2O_2 catalysed by carbon, 14.8 kcal per mole, as found by Smith, Miles and Watkins [10].

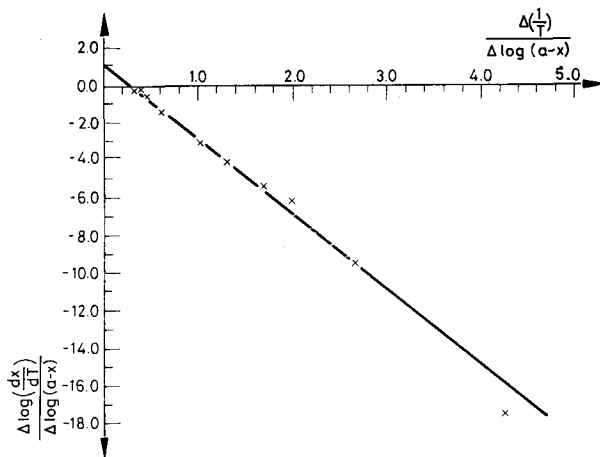


Fig. 2. Freeman and Carroll's treatment

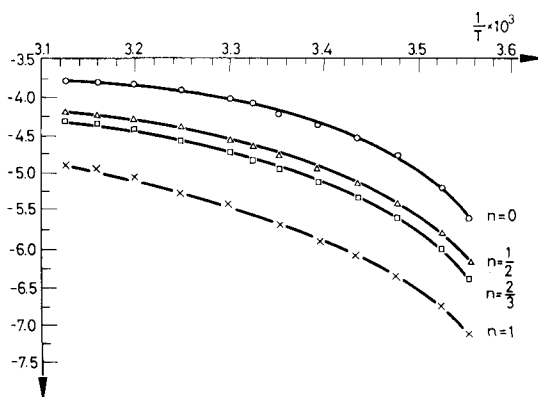


Fig. 3. Coats and Redfern's treatment

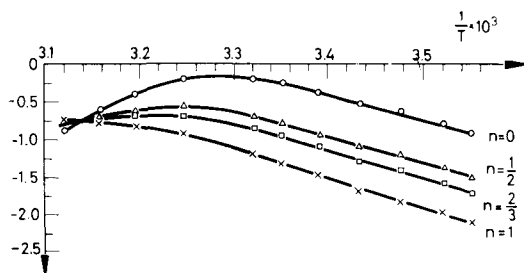


Fig. 4. Achar, Brindley and Sharp's treatment

The results of one run of dynamic kinetic study are shown in Table 1 and plotted in Fig. 1, in which the volume of the standard KMnO_4 solution required to titrate the H_2O_2 left undecomposed in the sample is plotted against the temperature of the water bath. Temperature-time line is also indicated in this figure which shows a quite good straight line. The treatment of data by Method 1 is shown in Table 2 and plotted in Fig. 2. A straight line can be drawn through all these points. From

Table 1
Nonisothermal catalytic decomposition of H_2O_2

Time, min	Temperature, °C	$a - x$, ml of 0.01 N KMnO_4 added
0.0	5.7	16.60
10.0	8.2	16.40
19.5	10.6	16.10
35.5	14.3	15.27
50.0	17.9	14.20
65.0	21.5	13.05
80.0	25.0	11.30
91.0	27.6	9.60
100.0	29.8	8.25
110.0	32.3	6.75
120.0	34.7	5.10
125.0	36.0	4.45
131.0	37.3	3.65
140.0	39.7	2.60
155.0	43.2	1.35
170.0	46.8	0.75

Table 2
Freeman and Carroll's treatment

T	$(a - x)$	$\frac{dx}{dT}$	$\frac{-\Delta \log \left(\frac{dx}{dT} \right)}{\Delta \log (a - x)}$	$\frac{\Delta \left(\frac{1}{T} \right) \cdot 10^8}{\Delta \log (a - x)}$
281.4	16.40	0.1233		
283.8	16.10	0.1700	17.50	4.25
287.5	15.30	0.2381	9.50	2.66
291.1	14.20	0.3000	6.18	1.97
294.7	13.05	0.4286	5.45	1.66
298.2	11.30	0.5629	4.08	1.27
300.8	9.60	0.6207	3.02	1.01
307.9	5.10	0.6214	1.38	0.61
312.8	2.55	0.3817	0.61	0.45
316.6	1.35	0.2358	0.26	0.37
320.0	0.75	0.1385	0.38	0.32

the slope of the straight line, an activation energy of 18.3 kcal per mole was calculated. The intercept of this line at the ordinate is unity which represents the order of the reaction.

The results obtained by Method 2 are shown in Table 3 and plotted in Fig. 3. Four different values of n (0, 1, 1/2, 2/3) were tested. It is apparent that all the lines are curved.

The treatment of data by Method 3 is shown in Table 4 and plotted in Fig. 4. Four lines are drawn through the four sets of data. The initial parts of the lines

Table 3
Coats and Redfern's treatment

T	$\frac{1}{T} \cdot 10^3$	$\log \frac{x}{T^2}$ ($n = 0$)	$\log \frac{a^{1/2} - (a-x)^{1/2}}{1/2 T^2}$ ($n = 1/2$)	$\log \frac{a^{1/3} - (a-x)^{1/3}}{1/3 T^2}$ ($n = 2/3$)	$\log \left[-\log \left(\frac{a-x}{a} \right) / T^2 \right]$ ($n = 1$)
281.4	3.554	-5.5976	-6.1997	-6.4215	-7.1798
283.8	3.524	-5.2070	-5.8126	-6.0139	-6.7802
287.5	3.478	-4.7935	-5.3936	-5.5907	-6.3680
291.1	3.435	-4.5479	-5.1413	-5.3403	-6.0967
294.7	3.393	-4.3884	-4.9731	-5.1272	-5.9197
298.2	3.353	-4.2248	-4.7949	-4.9847	-5.7263
300.8	3.324	-4.1114	-4.6662	-4.8501	-5.5802
303.0	3.300	-4.0412	-4.5822	-4.7614	-5.4806
307.9	3.248	-3.9162	-4.4169	-4.5811	-5.2591
312.8	3.197	-3.8429	-4.2955	-4.4397	-5.0801
316.6	3.159	-3.8179	-4.2357	-4.3636	-4.9638
320.0	3.125	-3.8103	-4.2030	-4.3178	-4.8814

Table 4
Achar, Brindley and Sharp's treatment

T	$\log \frac{dx}{dT}$ ($n = 0$)	$\log \frac{\left(\frac{dx}{dT} \right)}{(a-x)^{1/2}}$ ($n = 1/2$)	$\log \frac{(dx/dT)}{(a-x)^{2/3}}$ ($n = 2, 3$)	$\log \frac{\left(\frac{dx}{dT} \right)}{(a-x)}$ ($n = 1$)
281.4	-0.9091	-1.5165	-1.7190	-2.1239
283.8	-0.7696	-1.3730	-1.5742	-1.9764
287.5	-0.6232	-1.2152	-1.4124	-1.8071
291.1	-0.5229	-1.0991	-1.2911	-1.6752
294.7	-0.3680	-0.9285	-1.1117	-1.4835
298.2	-0.2496	-0.7762	-0.9517	-1.3027
300.8	-0.2071	-0.6923	-0.8620	-1.1894
307.9	-0.2066	-0.5604	-0.6784	-0.9142
312.8	-0.4182	-0.6215	-0.6892	-0.8247
316.6	-0.6275	-0.6927	-0.7144	-0.7578
320.0	-0.8585	-0.7960	-0.7752	-0.7336

are straight, while the later parts are curved. The line with $n = 1$ gives the least curvature. From the slopes of the straight portions, activation energies of 15.1, 15.6, 16.3 and 17.6 kcal per mole are calculated for $n = 0, 1/2, 2/3$ and 1 respectively.

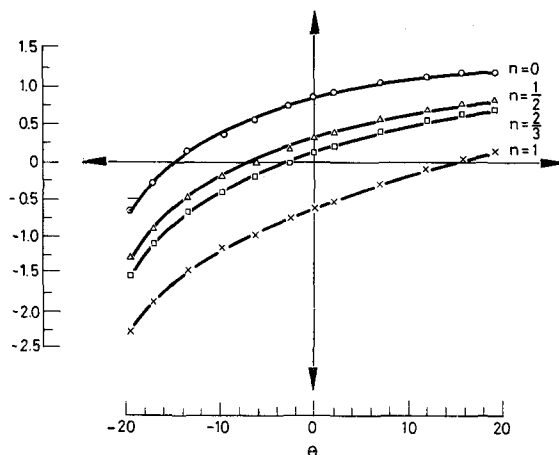


Fig. 5. Horowitz and Metzger's treatment

tively. It is interesting to note that all the lines pass through a common point of intersection corresponding to a temperature of 45.1°C, the significance of which is unknown.

To test Method 4, it is necessary to find out the point of inflection in the reaction course, from which the order of reaction may be determined. Unfortunately, the

Table 5

Horowitz and Metzger's treatment $T_s = 300.9^\circ\text{K}$

θ	$\log \log \frac{a}{a-x}$ ($n = 1$)	$\log x$ ($n = 0$)	$\log 2 [a^{1/2} - (a-x)^{1/2}]$ ($n = 1/2$)	$\log 3 [a^{2/3} - (a-x)^{2/3}]$ ($n = 2/3$)
-19.5	-2.2757	-0.6990	-1.3010	-1.5229
-17.1	-1.8761	-0.3010	-0.9066	-1.1079
-13.4	-1.4413	0.1239	-0.4789	-0.6778
-9.8	-1.1688	0.3424	-0.2132	-0.4123
-6.2	-0.9805	0.5502	-0.0343	-0.1884
-2.7	-0.7773	0.7243	0.1541	-0.0357
-0.1	-0.6238	0.8451	0.2904	0.1065
2.1	-0.5179	0.9217	0.3806	0.2014
7.0	-0.2880	1.0607	0.5599	0.3957
11.9	-0.0896	1.1476	0.6950	0.5508
15.7	0.0374	1.1832	0.7652	0.6373
19.1	0.1287	1.2001	0.8073	0.6925

inflection point can not be located from Fig. 1 very exactly. If the reaction is assumed to be of the first order, then T_s should be 300.9°K; the values of Θ are then calculated therefrom. For $n = 1$, $\log \log \frac{a}{a-x}$ is plotted against Θ . Other values of n are also tested. The data are shown in Table 5 and plotted in Fig. 5. It is seen that the lines are all curved.

From the above results, it is apparent that Method 2 and Method 4 fail completely in the present situation. The derivation of Method 2 involves several approximations. The intercept $\frac{A}{C} \frac{R}{\Delta E^*} (1 - 2RT/\Delta E^*)$ still contains the variable T . The variation of this term, in the present case, amounts to 2%. The activation energy obtained by the Freeman and Carroll's treatment agrees reasonably well with that obtained by the Achar, Brindley and Sharp's method. Mathematically, the method of Achar et al. is very sound. The reason that the line becomes curved in the later part of the reaction may be due to experimental error, because the burette readings are small. The Freeman and Carroll's method, however, has the advantage of acquiring the reaction order directly, while in the Achar, Brindley and Sharp's method, it must be obtained by trial and error, which is time consuming. That the activation energy obtained by the dynamic treatment does not agree well with that obtained by isothermal kinetics deserves further investigation.

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RÉSUMÉ — On a appliqué quatre équation aux données expérimentales de la décomposition catalytique de H_2O_2 en solution aqueuse. La méthode de Freeman et Carroll a donné les résultats les plus satisfaisants.

ZUSAMMENFASSUNG — Vier verschiedene Gleichungen wurden mit den Versuchsdaten der katalytischen Zersetzung von H_2O_2 in wässriger Lösung überprüft. Die Methode von Freeman und Carroll wurde als die befriedigendste gefunden.

Резюме — Для обработки экспериментальных данных каталитического распада H_2O_2 в водном растворе использованы 4 уравнения. Найдено, что метод Фримена и Каролла наиболее удовлетворителен.