

Studies on the Thermodynamic Functions of the Reaction Between Lignin and Hydrogen Peroxide during Bleaching.

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SUMMARY

Kinetic studies of peroxide action on thiolignin were made. The reaction in the pH 8 to 12 range is first order in hydrogen peroxide. Kinetic dependence on thiolignin concentration and pH has been demonstrated. The reaction rate is directly dependent on the hydroxyl ion concentration and is nearly doubled with every ten degree rise of temperature. The values of first order rate constant range between $11.51 \times 10^{-4} \text{ Min.}^{-1}$ and $414.54 \times 10^{-4} \text{ Min.}^{-1}$ when the temperature is raised from 313° to 353° Kelvin under the pH levels of 9 to 12. Energy of activation varies directly with the temperature coefficient of the reaction. The values of free energy of activation are practically same showing that there is a tendency of heats and entropies to compensate each other and thus causing little change in ΔF^\ddagger . All thermodynamic functions except entropy of activation are positive. Irrespective of pH, the Boltzmann factor increases about two fold with every ten degree rise in temperature.

The statistically valid regression equations fitted to the data of temperature Vs different energy parameters under each of four pH levels have been derived. The regression equations between temperature and various energy parameters (entropy of Activation, Frequency factor, Boltzmann factor and rate constant) are of second degree. In the case of free energy of activation, the second degree equations are obtained at pH 9 and 12 while at pH 10 and 11 the first degree equations are more appropriate.

Kinetic investigations provide valuable information regarding the mechanism of the reactions. Thus from time to time, the kinetic studies of the several types of reactions involving organic substrates have been made to provide the necessary data for deciding the mechanism of a reaction. The advancements in this Branch of chemistry are associated with the advances in separation procedures, new analytical techniques, physical measuring devices and in chemical theories. The governing notion of Arrhenius¹, that the activation of some kind is essential for chemical change, is of universal validity and has dominated the subject of chemical kinetics since the days of Arrhenius:

An important aspect of kinetic study is to show how the reaction rates vary with temperature. The role of solvent in reaction kinetics has been explained by Eyring's theory of absolute reaction rates². Kinetic is regarded as the science of motion. It

will not be out of place to contrast thermodynamics with its static view point with that of chemical kinetics representing the dynamic view point. Thermodynamics is interested in the initial and final states of a system and an important fundamental postulate of thermodynamics is the state principle which leads directly to the concept of an equation of state. Because of the greater rigour of thermodynamic methods, there has been considerable effort in the last thirty-five years to approach kinetics from the thermodynamic view point, particularly combined with the methods of statistical mechanics. The important feature of this effort is to treat reaction rates as involving an equilibrium between average molecules and high energy molecules which are aligned and activated ready for

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reaction, or between molecules in the initial state and in the so called "transition state" or "activated complex". Even in such a treatment a fundamental problem remains: calculating for rate of decomposition of the activated complex. Only quantum mechanics seem to offer a complete answer^{3,5}.

Thermodynamics is a fundamental subject of great importance and it helps to lay down the criteria for predicting feasibility or spontaneity of a process, including a chemical reaction, under a given set of conditions. In other words it helps to predict whether a given process or a chemical reaction is feasible under given conditions of temperature, pressure and concentration. It also helps us to determine the extent to which a process, including a chemical reaction can proceed before attainment of equilibrium.

However, it must be clearly understood that the laws of thermodynamics apply only to matter in bulk and not to individual atoms or molecules. Thus, the laws of thermodynamics apply to the behaviour of assemblages of vast number of molecules and not to individual molecules. Thermodynamics concerns itself only with the initial and final states of the system.

In an irreversible process,

$$\Delta S_{\text{sys.}} + \Delta S'_{\text{surr.}} > 0$$

Thus, the entropy of the system and its surroundings taken together increases in a thermodynamically irreversible or spontaneous process at constant temperature, but remains unchanged in a thermodynamically reversible process.

In the present study, lignin has been selected as a substrate for the reaction with hydrogen peroxide. Lignin is a major constituent of wood and grasses and in the pulps the colouring matter is predominantly lignin. Bleaching of pulps is an important step for the preparation of paper. Hydrogen peroxide is a very promising bleaching agent which causes the bleaching of pulp without delignification and with the least oxidation potential (0.3 volt)⁶, an essential for bleaching without cellulose degradation. The peroxide-thiolignin reaction involves the action of DOH^- ions^{7,8} which cause the oxidation of chromophors and the degradation of aromatic units with free phenolic hydroxyl groups⁹.

Present work mainly deals with the utilization of kinetic data for the estimation of various thermodynamic functions for peroxide-thiolignin reaction in alkaline medium.

EXPERIMENTAL

a) Isolation of Thiolignin

The spent black liquor of sulphate process was utilized for the isolation of thiolignin¹⁰. Purification of crude thiolignin was done by Ahlm's method¹¹.

b) Preparation of Hydrogen Peroxide Solution

Standard solution of hydrogen peroxide was prepared according to the Kingzett's method¹². The solution was stored in dark polyethylene bottle in refrigerator. Solutions for the reaction were prepared from it by suitable dilutions.

a) Reaction of Thiolignin with Hydrogen Peroxide

The preliminary experiments were conducted to estimate the quantities of sodium silicate and manganese sulphate which were necessary to keep the solution of hydrogen peroxide quite stable under experimental conditions. Three necked pyrex glass round bottom flask fitted with stoppers were used for carrying out the reaction¹⁰. During the reaction, the pH was maintained constant by adding suitable quantity of N-NaOH from time to time.

RESULTS AND DISCUSSION

a) Analysis of Kinetic Data

The kinetic data was analysed by the differential method. According to this method, the rate of reaction ($-dc/dt$) is related to the concentration (C) of a reactant by the equation,

$$-\frac{dc}{dt} = kc^n \dots (1)$$

where n = Order of reaction, k = rate constant or rate coefficient or specific rate.

Taking logarithms of the above equation,

$$\log(-dc/dt) = \log k + n \log C \dots (2)$$

It is evident from equation (2) that a plot of the logarithm of the velocity against the logarithm of the concentration should give a straight line. If so, the slope represents the order of reaction with respect to the substance whose concentration is being varied and the intercept on $\log(-dc/dt)$ axis represents $\log k$.

Based on this method, the order of the reaction was found to be first ($n=1$) with respect to hydrogen peroxide concentration. The data was also analysed by following the method of integration where the reaction was found to obey the first order integrated rate equation.

b) Order of the Reaction and Variation of Rate Constant with Reaction Parameters

To determine the order of reaction, a series of kinetic experiments were conducted at different concentrations of hydrogen peroxide under otherwise constant conditions. The results of these investigations are represented graphically in Fig. 1. The kinetic data was then analysed by differential method (Fig. 2). The linearity of the $\log c$ and $\log (-dc/dt)$

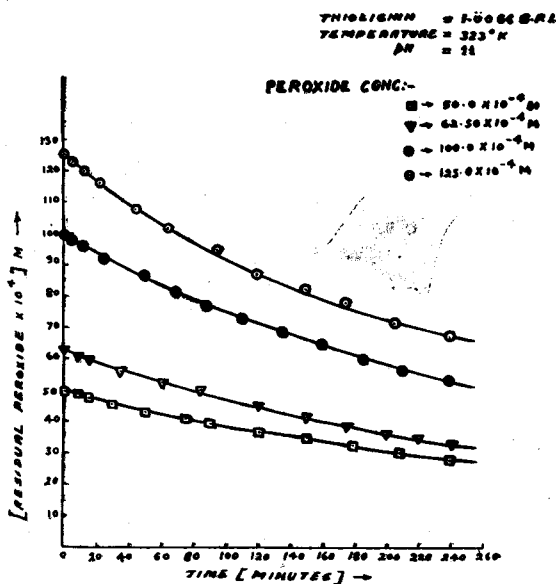


FIG. 1. CONCENTRATION-TIME CURVES FOR ANALYSING THE REACTION

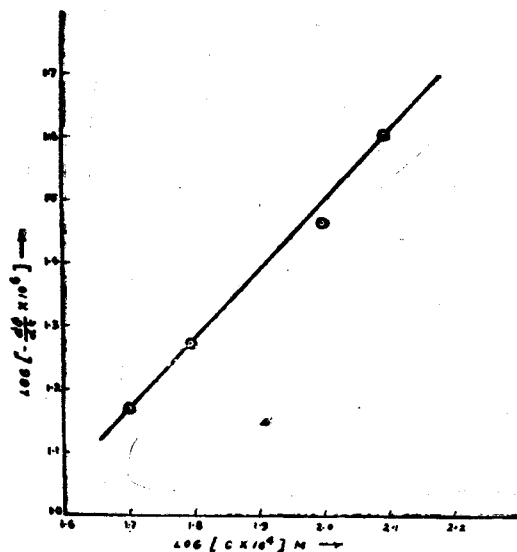


FIG. 2. ORDER OF THE REACTION WITH RESPECT TO HYDROGEN PEROXIDE.

plot from $50.0 \times 10^{-4} \text{M}$ to $125.0 \times 10^{-4} \text{M}$ validates the kinetic data in this range and from the slope it is established that the reaction is of first order in hydrogen peroxide.

Variation of first order rate constant with the increase in the initial concentration of H_2O_2 has been represented in Table-I while Table-II shows the first order rate constants as a function of thiolignin concentration. The reaction was investigated in alkaline medium in the range of pH 8 to 12. This data has been given in Table-III which shows that the reaction rate is directly proportional to the hydroxyl ion concentration. The rate constant increases nearly two times for every 10° rise of temperature, the temperature coefficient ($k_t + 10/k_t$)

being 1.99, 1.84, 1.97 and 1.94 for pH values $8.10, 11, 12$ respectively. The variation of rate constant with temperature is illustrated in Figs. 5 to 8.

Table-I. FIRST ORDER RATE CONSTANTS AS A FUNCTION OF PEROXIDE CONC.

Thiolignin = 1.0066 G.P.L.,
Temperature = 323° Kelvin

pH	(Peroxide Conc) $\times 10^4 \text{ M}$	$k \times 10^4 \text{ Min.}^{-1}$
11	50.00	24.24
11	62.50	25.58
11	100.00	27.63
11	125.00	28.78

TABLE-II FIRST ORDER RATE CONSTANTS AS A FUNCTION OF THIOLIGNIN CONC.

Peroxide Conc. = $62.50 \times 10^{-4} \text{M}$,
Temperature = 323° Kelvin

pH	Thiolignin Conc. G.P.L.	$k \times 10^4 \text{ Min.}^{-1}$
11	0.5200	21.93
11	1.0066	25.58
11	1.5133	38.38
11	2.0266	50.79

TABLE—III FIRST ORDER RATE CONSTANTS
AS A FUNCTION OF pH

Peroxide Conc. = $62.50 \times 10^{-4}M$,
Thiolignin = 1.5133 G.P.L.

Temperature °Kelvin	pH	$k \times 10^4 \text{ Min.}^{-1}$
323	8	11.51
323	9	19.73
323	10	30.30
323	11	38.38
323	12	55.44

c) Validity of Arrhenius Equation (Reaction Rates and Temperature Changes)

Log k values were plotted against reciprocal of temperature ($1/T$) which have been illustrated in Figs. 3 and 4. The linearity of $\log k - 1/T$ plot from 313°K to 353°K validates the Arrhenius equation in this range and from the slope the values of energy of activation, ΔE were calculated.

Arrhenius Equation is represented as,

$$\log_{10} k = \log_{10} A - \frac{\Delta E}{2.303 RT} \quad (3)$$

where A = Frequency factor,

E = Energy of Activation.

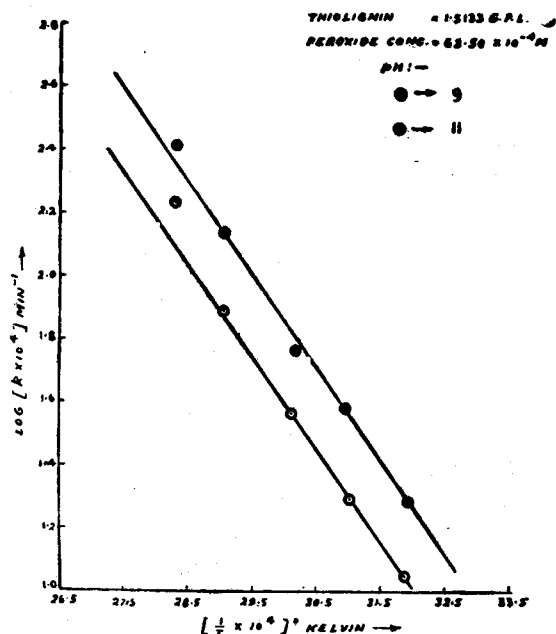


FIG. 3 PLOTS OF $\log k$ VS $1/T$
(VALIDITY OF ARRHENIUS EQUATION)

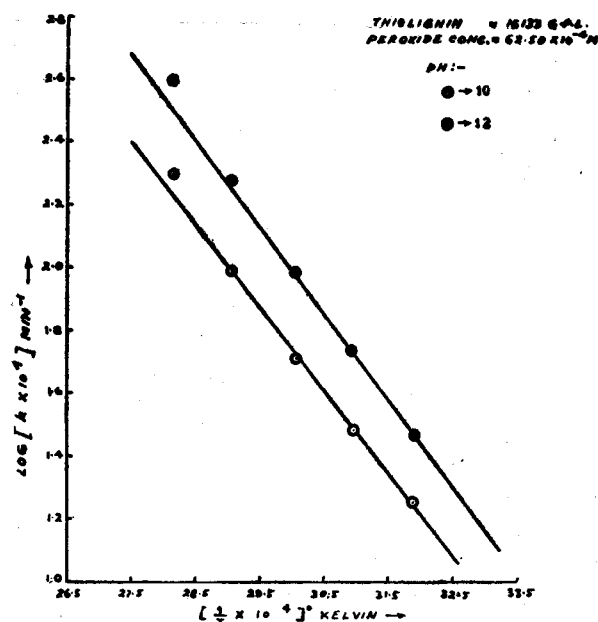


FIG. 4 PLOTS OF $\log k$ VS $1/T$
(VALIDITY OF ARRHENIUS EQUATION)

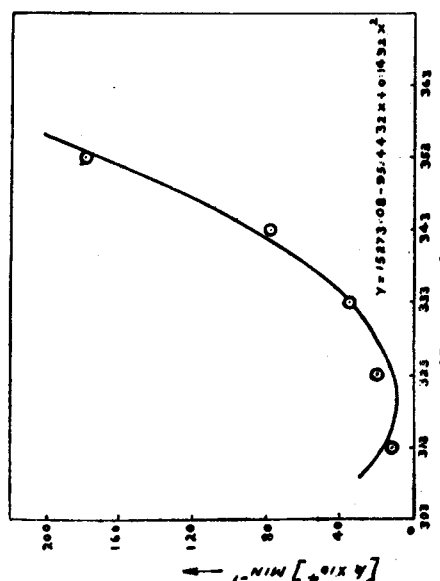


FIG. 5. TEMPERATURE DEPENDENCE OF RATE CONSTANT AT pH 9

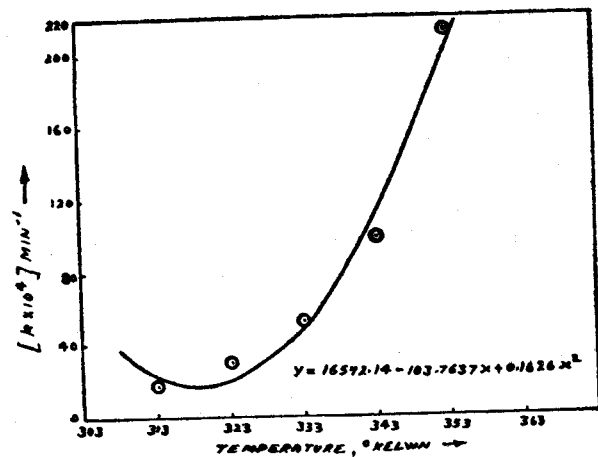


FIG. 6. TEMPERATURE DEPENDANCE OF RATE CONSTANT AT pH 10

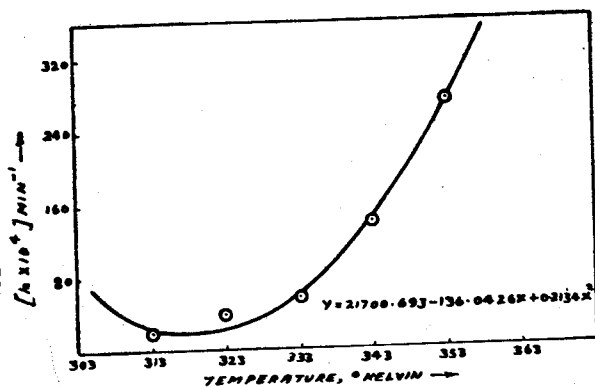


FIG. 7. TEMPERATURE DEPENDANCE OF RATE CONSTANT AT pH 11

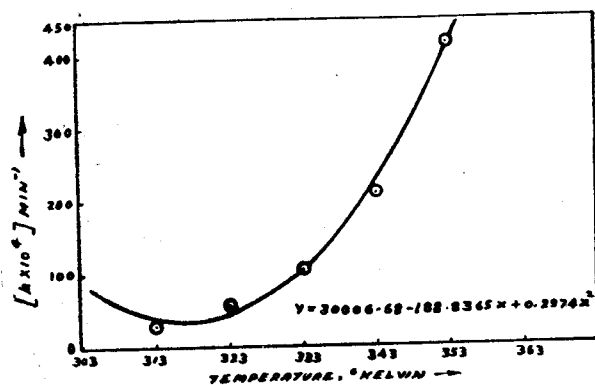


FIG. 8. TEMPERATURE DEPENDANCE OF RATE CONSTANT AT pH 12

d) Estimation of various Thermodynamic Functions

Under different pH conditions, the energy of activation was estimated from the Arrhenius plots (Figs. 3 & 4). The temperature coefficient has direct effect on the extent of ΔE which was found to be 13.72 KCal, 11.43 KCal, 13.26 KCal and 12.34 KCal at pH 9, 10, 11 and 12 respectively.

The values of other thermodynamic functions were calculated by using appropriate relationships. These functions have been summarised in Table IV. A perusal of free energy of activation shows that all the values are practically same which indicates that there is a tendency of heats and entropies to compensate each other leading to a little change in free energy of activation. Probably the formation of degradation products of lignin is responsible for the compensation of heats and entropies. Figs. 9-12 illustrate the temperature dependence of free energy of activation.

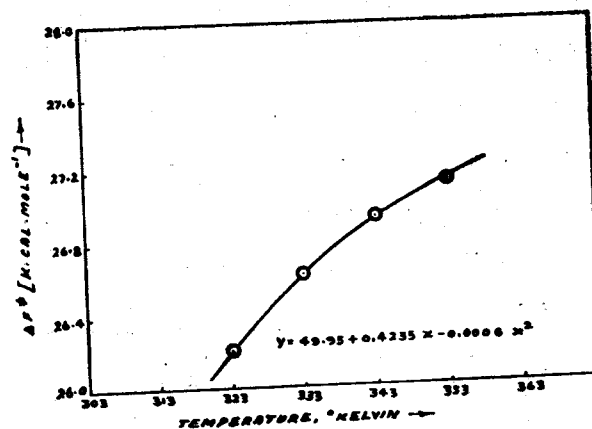


FIG. 9. PLOT OF ΔF^\ddagger VS TEMPERATURE AT pH 9

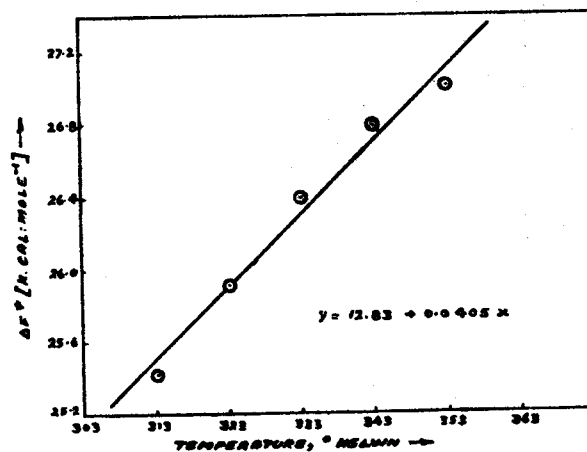
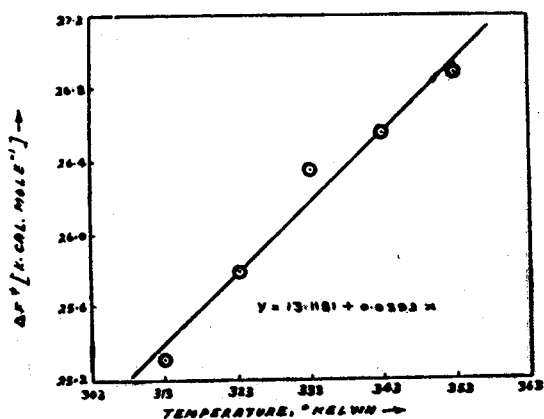
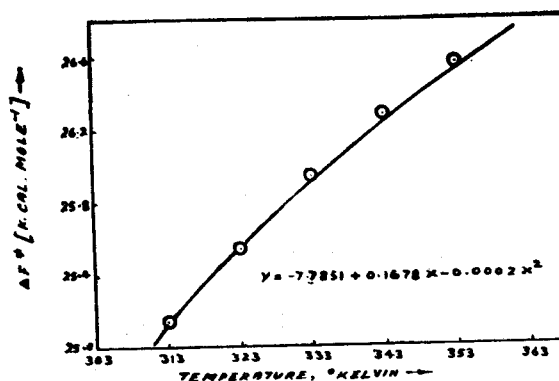


FIG. 10. PLOT OF ΔF^\ddagger VS TEMPERATURE AT pH 10

TABLE-IV THERMODYNAMIC FUNCTIONS

Hydrogen Peroxide Conc. = $62.50 \times 10^{-4} \text{M}$, Thioglignin = 1.5133 G.P.L.

Expt. No.	pH	Temp. °Kelvin	$k \times 10^4$ Min. ⁻¹	ΔE K Cal Mole ⁻¹	ΔF^\ddagger K Cal Mole ⁻¹	ΔS^\ddagger E. U.	$A \times 10^{-4}$ Mole ⁻¹ Sec. ⁻¹	Boltzmann Factor $\times 10^{10}$ Mole	Temp. Coefficient.
1.	9	313	11.51	13.72127	25.72368	-38.34635	7.32600	2.61807	
2.	9	323	19.73	13.72127	26.21957	-38.69441	6.34000	5.18611	
3.	9	333	36.84	13.72127	26.63391	-38.77674	6.27000	9.79266	1.99
4.	9	343	78.30	13.72127	26.94300	-38.54760	7.25400	17.99007	
5.	9	353	178.48	13.72127	27.13305	-37.90372	9.86500	30.15306	
6.	10	313	18.42	11.43439	25.42907	-44.71445	0.29000	103.50640	
7.	10	323	30.30	11.43439	25.94588	-44.92759	0.27590	183.63636	
8.	10	333	51.81	11.43439	26.41040	-44.97332	0.27780	311.73285	1.84
9.	10	343	97.87	11.43439	26.79065	-44.77077	0.31620	516.17088	
10.	10	353	211.10	11.43439	27.02885	-44.15692	0.44300	794.19864	
11.	11	313	19.19	13.26389	25.29940	-38.45246	5.86100	5.45640	
12.	11	323	38.38	13.26389	25.79325	-38.79105	6.04500	10.58064	
13.	11	333	55.27	13.26389	25.36584	-39.34539	4.71000	19.55626	1.97
14.	11	343	138.18	13.26389	26.55686	-38.75538	6.53100	35.26259	
15.	11	353	273.48	13.26389	26.87399	-38.55583	7.43000	61.34589	
16.	12	313	28.78	12.34912	25.15289	-40.90670	2.01700	23.77788	
17.	12	323	55.44	12.34912	25.55634	-40.88933	2.10000	44.00000	
18.	12	333	103.96	12.34912	25.94848	-40.13902	2.22400	77.90467	1.94
19.	12	343	207.27	12.34912	25.28014	-40.61537	2.56400	134.73088	
20.	12	353	414.54	12.34912	26.58135	-40.31808	3.06100	225.71055	

FIG. 11. PLOT OF ΔF^\ddagger VS TEMPERATURE AT pH 11FIG. 12. PLOT OF ΔF^\ddagger VS TEMPERATURE AT pH 12

The negative value of entropy of activation indicates that the reaction is a slow one. At constant pH, the entropy of activation was found to be nearly constant. The negative values of ΔS suggest that there will be decrease in the Entropy of system when reaction proceeds. But the entropy of the system must increase for a spontaneous change. The proper criteria for spontaneity is that the entropy of the universe (system plus surroundings) must increase for the process. Thus, it is expected that the process will be accompanied by an increase in entropy when both systems and surroundings are taken into consideration. The temperature dependence of ΔS^\ddagger is shown in Figs. 13-16, while Figs. 17-20 represent the temperature dependence of frequency factor.

FIG. 13. PLOT OF ΔS^\ddagger VS TEMPERATURE AT pH 9

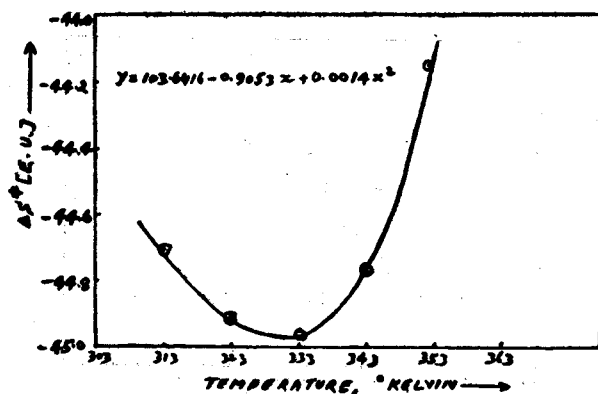
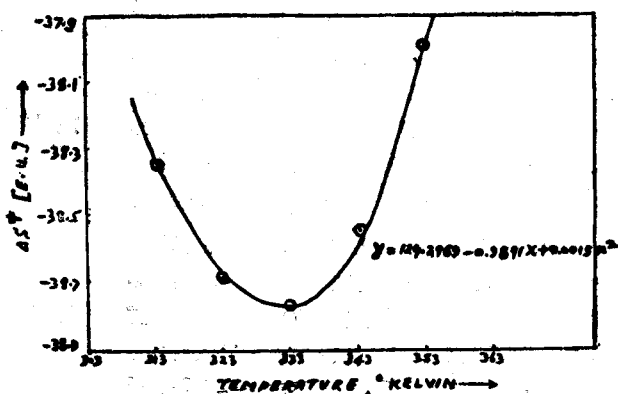


FIG. 14. PLOT OF ΔS^\ddagger VS TEMPERATURE AT pH 10

FIG. 15. PLOT OF ΔS^\ddagger VS TEMPERATURE AT pH 11

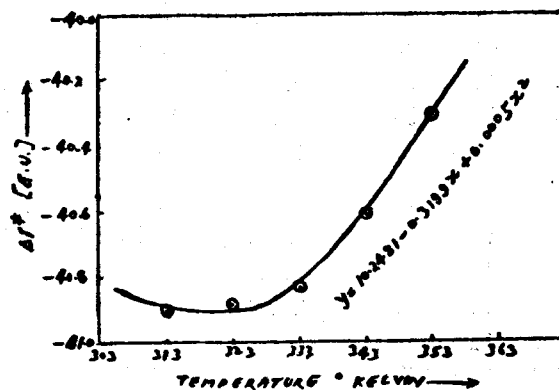
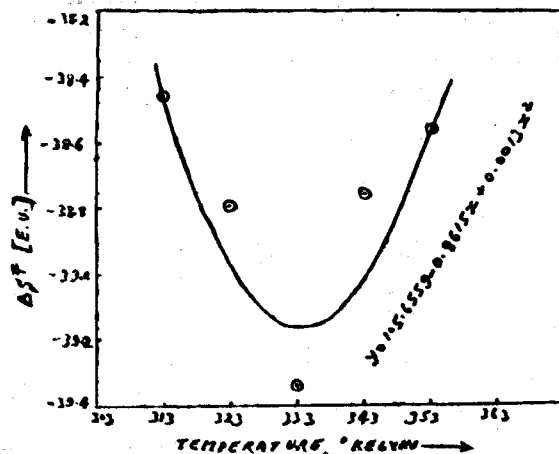


FIG. 16. PLOT OF ΔS^\ddagger VS TEMPERATURE AT pH 12

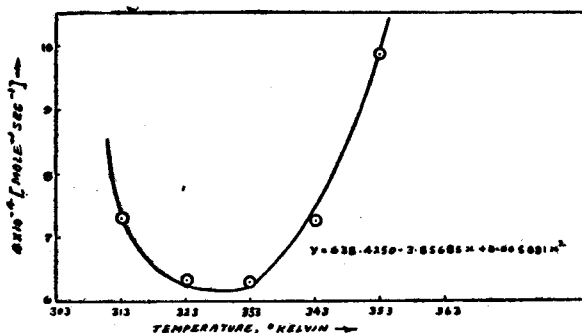


FIG. 17. PLOT OF A VS TEMPERATURE AT pH 9

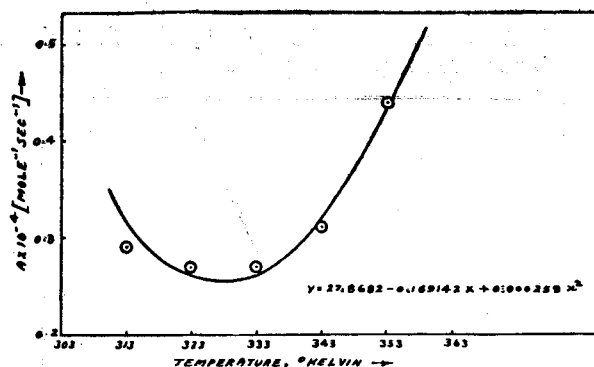


FIG. 18. PLOT OF A VS TEMPERATURE AT pH 10

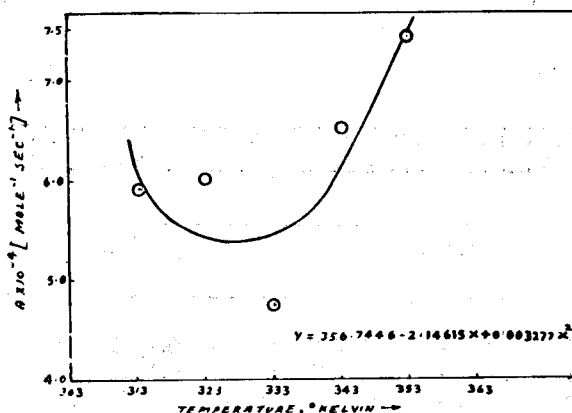


FIG. 19. PLOT OF A VS. TEMPERATURE AT pH 11

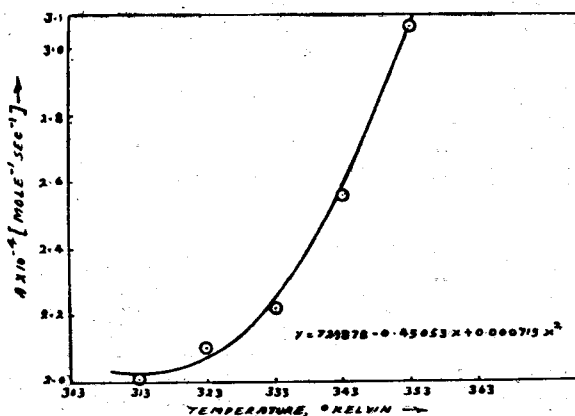


FIG. 20. PLOT OF A VS TEMPERATURE AT pH 12.

The calculation of Boltzmann Factor was also done and the values are given in Table IV, which shows that irrespective of pH the value of Boltzmann factor increases nearly two times with energy 10° rise in temperature. Figs. 21-24 illustrate the temperature dependence of Boltzmann factor under different pH levels.

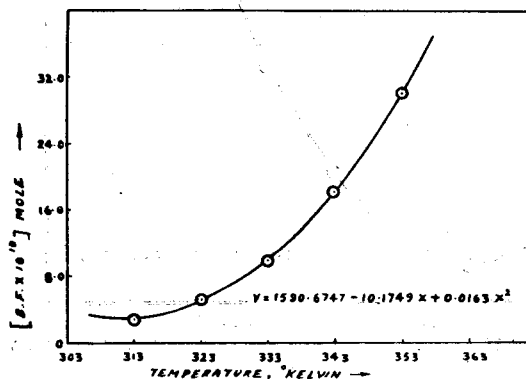


FIG. 21. PLOT OF BOLTZMANN FACTOR VS TEMPERATURE AT pH 9

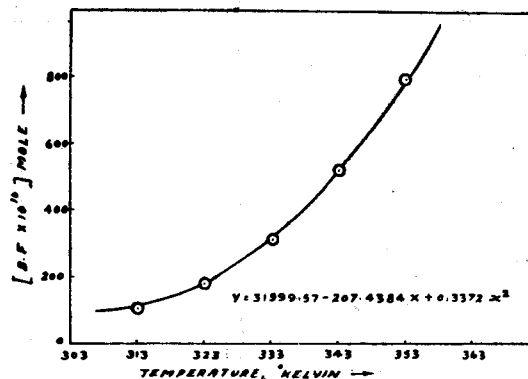
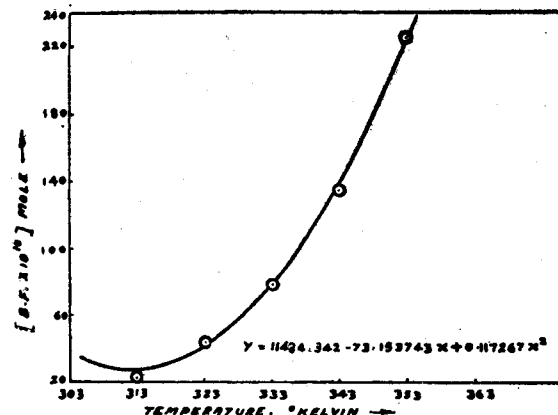
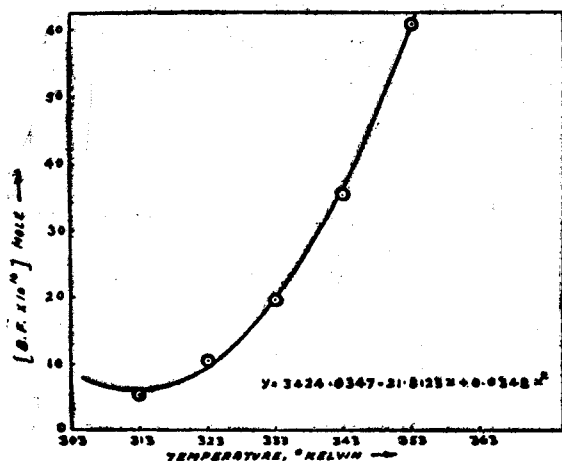


FIG. 22. PLOT OF BOLTZMANN FACTOR VS. TEMPERATURE AT pH 10

Statistically valid Regression Equations fitted to the data of temperature Vs different Energy Parameters under each of the four pH level (9,10,11 & 12) have been derived which are summarized in Table V. In Figs. 5 to 24, the regression equations calculated have been drawn along with the observed points in each case. From Table V, it is evident that the Regression Equations between rate constant (k) and temperature under each of the four pH levels are of second degree. Similarly, the equations between temperature and other energy parameters (Entropy of Activation, Frequency factor and Boltzmann factor) are also of second degree

However, in the case of Free Energy of Activation 9 and 12 while at pH 10 and 11, the first degree the second degree equations were obtained at pH equations were more appropriate.



TABLE—V STATISTICALLY VALID REGRESSION EQUATIONS BETWEEN DIFFERENT ENERGY PARAMETERS (Y) AND TEMPRATURES (X) UNDER EACH OF THE FOUR pH LEVELS.

Energy Parameters	pH	Regression	Equation
Rate Constant (k)	9	y = 15273.08 — 95.4432 x + 0.1492 x ²	
	10	y = 16572.14 — 103.7637 x + 0.1626 x ²	
	11	y = 21700.963 — 136.0426 x + 0.2134 x ²	
	12	y = 30006.68 — 188.8365 x + 0.2974 x ²	
Free Energy of Activation (ΔF^\ddagger)	9	y = — 49.95 + 0.4235 x — 0.0006 x ²	
	10	y = 12.83 + 0.0405 x	
	11	y = 13.1181 + 0.0392 x	
	12	y = — 7.7851 + 0.1678 x — 0.0002 x ²	
Entropy of Activation (ΔS^\ddagger)	9	y = 124.2969 — 0.9891 x + 0.0015 x ²	
	10	y = 103.6416 — 0.9053 x + 0.0014 x ²	
	11	y = 105.6559 — 0.8615 x + 0.0013 x ²	
	12	y = 10.2481 — 0.3199 x + 0.0005 x ²	
Frequency Factor (A)	9	y = 638.425 — 3.85685 x + 0.005881 x ²	
	10	y = 27.8682 — 0.16942 x + 0.000259 x ²	
	11	y = 356.7446 — 2.146154 x + 0.003277 x ²	
	12	y = 72.9878 — 0.45053 x + 0.000715 x ²	
Boltzmann Factor ($e^{-\Delta E/RT}$)	9	y = 1590.6747 — 10.1749 x + 0.0163 x ²	
	10	y = 31999.57 — 207.4384 x + 0.3372 x ²	
	11	y = 3424.0347 — 21.8123 x + 0.0348 x ²	
	12	y = 11434.342 — 73.153743 x + 0.117267 x ²	

CONCLUSIONS

The reaction between thiolignin and hydrogen peroxide is first order with respect to peroxide in the pH range 8 to 12. First order rate constant depends directly on pH and thiolignin concentration. Ten degree rise in temperature cause nearly two-fold increase in the rate constant and Boltzmann Factor both. Under pH levels 9 to 12, the statistically valid regression equations between temperature and different energy parameters are of second degree, but for ΔF^\ddagger , the first degree equations are valid under pH levels 10 and 11.

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