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The chemical effect of ultrasound on cyanide solutions

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THE CHEMICAL EFFECT OF ULTRASOUND ON CYANIDE SOLUTIONS

BY

NABIL R. ZAKI

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEW JERSEY INSTITUTE OF TECHNOLOGY

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Newark, New Jersey

1975

Abstract

An experimental study was undertaken to investigate the chemical effects of high intensity ultrasonic radiation on cyanide solutions. The effects of aeration, concentration of cyanide and temperatures on the reaction rate are investigated. The experiment was performed in a 30 mm pyrex tube immersed at a fixed height in a constant volume water bath. Ultrasonic energy was applied through the use of a transducer epoxied at the bottom of the water bath. The power inputs to the transducer were 40W (27KHz) and 100W (21KHz).

At a power of 40W, ultrasound had no chemical effect on cyanide solutions. At 100W, hydrogen peroxide formed during the process and reacted with the cyanide. The mechanism of reaction is assumed to include both oxidation and hydrolysis of the cyanide in solution. However, the catalytic effect of hydrogen peroxide under these conditions increased leading to substantial hydrolysis of cyanide.

As a result, the overall reaction yield increased by 200 - 300% over the yield normally obtained from equal amounts of hydrogen peroxide in conventional cyanide - peroxide reactions.

APPROVAL OF THESIS

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ON CYANIDE SOLUTIONS

BY

NABIL R. ZAKI

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

FACULTY COMMITTEE

APPROVED: _____

NEWARK, NEW JERSEY

SEPTEMBER, 1975

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INTRODUCTION

Cyanide solutions react with oxidizing agents such as chlorine, ozone, hydrogen peroxide to yield reaction products ranging from cyanate to carbon dioxide and nitrogen.

Ultrasonic radiation under certain conditions was found to produce unusual chemical phenomena.

The oxidation effect of Ultrasound on aqueous solutions and the formation of hydrogen peroxide has been verified and studied for a number of years.

When a cyanide solution was exposed to a high intensity ultrasonic radiation an oxidation process started and the cyanide concentration in solution gradually decreased. Since the formation of hydrogen peroxide is a function of the available dissolved oxygen in solution, continuous aeration replenished the oxygen consumed in the reaction and maintained the oxidation process.

THEORY

I. SONOCHEMISTRY

Practically all of the observed chemical effects of Ultrasonics in liquid systems occur only in the presence of ultrasonic intensities sufficient in magnitude to produce cavitation and in conditions that will support cavitation within the liquid.⁽⁴⁾

The cavitation process includes the generation of bubbles in an acoustic field, the motion of these bubbles and the physical effects brought about by this motion. Impurities such as microdust particles or gas bubbles act as nuclei in initiating cavitation.

In the case of water saturated with air, when the acoustic pressure is above the cavitation threshold pressure, some of the air at the nucleation sites come out of the solution in the form of minute bubbles. These bubbles grow during the rarefaction or negative phase of the sound wave. During the other half of the sound wave cycle the acoustic pressure increases and the bubble begins to collapse. During this phase of the wave, the contents of the bubble are compressed adiabatically to very high local pressures of several thousand atmospheres and local temperatures may be as high as 10,000°K.⁽¹³⁾ Electrical charges also occur as the result of the electrical potential built between opposite walls of the cavity. It is not precisely known which of these aspects of cavitation is of fundamental importance in producing chemical reactions.

Some investigators suggest that water is mechanically separated to H and OH ions, while many believe that electrical discharge, through the intermediation of luminescence results in the photochemical decomposition of water into reactive H and OH radicals.⁽¹⁰⁾

A. Effect of Experimental Variables on Sonochemical Phenomena:

1 Dissolved Gas - The dissolved gas in a liquid influences the cavitation action; if water is carefully degassed and freed from suspended particles its apparent cohesive strength is much greater than usual. Chemical reactions are not observed in thoroughly degassed liquids with the usual ultrasonic input powers. When the dissolved gas is air, argon, neon, xenon, oxygen, nitrogen or helium it is possible to liberate chlorine readily by ultrasonic means from mixtures of carbon tetrachloride and water. If the gas is carbon dioxide, nitrous oxide, or dichlorodifluoromethane, disruption of the CCl_4 molecule does not take place. It is difficult to explain this on the basis of the ratio of the specific heats of the gas, because carbon dioxide will permit ultrasonic depolymerization in toluene solutions.⁽¹⁵⁾ It has been suggested that if the electrical discharge accompanying cavitation is the cause of the reaction, this anomaly can be explained by the electrical conduction of a carbon dioxide in an aqueous solution. A high potential could not exist, while the opposite would apply for a toluene solution.⁽¹⁶⁾

2 Frequency - The resonant absorption of energy by molecules does not occur as in the optical case. The normal ultrasonic frequencies are far too low; the highest frequencies so far generated are in the region

of 1000 Mc/s but these are still 10 times smaller than infra-red frequencies. It follows that frequency of the sound wave has little or no effect on the chemical reaction rate. Considerable evidence exists to support this generalization and it appears to be true over a wide band of frequencies from as low as 1 kc/s up to several megacycles per second. Various reactions have been studied in which the applied ultrasonic frequency has been a variable. The rate of rearrangement of benzazide in aniline solution does not vary with frequency from 16-478 kc/s.⁽¹⁾ G. Schmid and W. Poppe have shown that the rate of depolymerization of polymethyl methacrylate in benzene is nearly independent of frequency in the range 10-284 kc/s.⁽¹¹⁾ For the emulsion polymerization of styrene, essentially the same results were obtained at 15 kc/s and at 500 kc/s, while the hydrolysis of dimethyl sulphate is not influenced by frequency.⁽⁹⁾

3 Intensity - At very low intensities which are below the threshold for cavitation,⁽⁴⁾ no chemical change is observed. Above this threshold the reaction rate increases more or less linearly with ultrasonic intensity, as found for the formation of water-kerosene emulsions; the rearrangement of benzazide, with power inputs ranging from 100 to 250 watts; and the reduction of curd tension in milk up to a power input of 2000 watts.

However, several investigators have noted that there is an optimum intensity which coincides with the maximum formation of cavitation bubbles, and above which further increases cause a decrease in yield. For the production of hydrogen peroxide from water, the value found for this optimum ultrasonic power is 0.10 watt per gram of solution;⁽²⁾ for the closely related liberation of iodine from KI solution, the optimum energy density is 215 ergs/cm,⁽¹⁰⁾ which corresponds to a pressure amplitude of 3.0 atmospheres.

4 Treatment Time - When all reactants are present in excess, the yield shows an approximately linear increase with time of irradiation. For example, this has been observed in the liberation of iodine from KI solutions both in the presence and absence of carbon tetrachloride.

The amount of hydrogen peroxide generated by ultrasonic irradiation of water containing dissolved air increases linearly with time up to 5 hours.⁽¹⁰⁾ However, the quantity of nitrous acid first increases and then decreases while the nitric acid formed concurrently increases somewhat more than linearly with time. The relative amounts of nitrate and nitrite synthesized depend on the pH of the solution.

5 Pressure - Changes of static pressure have a profound effect on the cavitation process, and therefore on the yield of the sonochemical reaction. For example, Polotskii found that the amount of hydrogen⁽¹⁰⁾

peroxide, nitrite, and nitrate produced by ultrasonic irradiation of water is zero at air pressures (above the liquid) less than 100 mm, above which it increases to a maximum at 1520 mm, finally decreasing to zero at 4180 mm.

6 Temperature - It is difficult to achieve precise temperature control in a liquid undergoing irradiation, because the absorption of ultrasonic energy may be very high if high intensities are being used, and represents a heat source of considerable magnitude. In addition to the overall heating, dispersed particles if present in the liquid are raised to a temperature several degrees above the average temperature of the suspension. If direct irradiation into the liquid is employed the electrical losses in the transducer will also raise its temperature and this heat will be transferred to the liquid surrounding the body of the transducer.

Below 50° C. the ambient temperature does not appear to be a critical factor in many sonochemical effects. Ultrasonic disintegration of starch paste is hardly affected by temperatures over the range 15-60° C, and the liberation of iodine from potassium iodide-carbon tetrachloride aqueous solution shows only a slight decrease with temperature from 2-60° C. Above 60° C, however, there is a sharp decrease in the rate of ultrasonic depolymerization of

solutions of polystyrene and nitrocellulose.

In view of the frequent attributing of sonochemical reactions to the local heating effect, it is surprising that higher temperatures result in smaller yields. Alternatively, as the vapour pressure is higher in a hot solution the collapse of the cavitation bubbles will be less violent.

The rate of formation of hydrogen peroxide and nitric acid by irradiation of air-containing water decreases with increasing temperature from 10-50° C. ⁽¹⁴⁾ and the oxidation of dilute ferrous sulphate solution is suppressed at temperatures above 50° C.

B. Mechanism of Sonochemical Reactions

(5)
V. Griffing carried out a number of experiments under controlled conditions, to study the role of ultrasonics on chemical reactions. He was able to classify the reactions observed in three stages.

(1) Reactions due to cavitation.

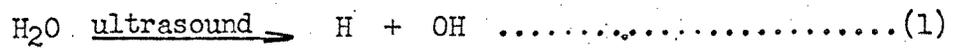
- (a) Gas must be present in the form of minute bubbles, either suspended in the liquid or formed during irradiation, if the reaction is to take place.
- (b) All primary actions due to ultrasonic waves take place inside the bubbles. Thus, no reactant is affected directly unless it has an appreciable vapour pressure.
- (c) The reactions taking place in the gas phase are primarily thermal, due to the heat developed during adiabatic compression. This is considered to be demonstrated by the observed dependence of the rate of hydrolysis of carbon tetrachloride on the thermal properties of the dissolved gas and by the inhibition of these reactions when small quantities of ether or other liquids of high vapour pressure are added.

(2) Many reactions in the liquid phase thought to be due to ultrasonics now appear to be secondary reactions. Oxidizing agents such as hydrogen peroxide which have formed in the bubbles when oxygen is present, may dissolve in the liquid and cause a further reaction. As examples, the decomposition of potassium iodide and the oxidation of sodium sulphite to sodium sulphate can be quoted. The change in solution pH brought about by reactions in the gas bubbles is responsible for other reactions attributed directly to cavitation. In this category

the increase in the rate of inversion of sucrose is an example.

(3) Some reactions are due to local increases in temperature caused by absorption of ultrasonic energy, if the intensity is high and the beam path length short. The denaturation of proteins is considered to be caused mainly by the temperature effect.

An analogy has been proposed between radiochemical and cavitation effects in a number of stimulated reactions. O. Lindstrom and O. Lamm⁽⁶⁾ have assumed that the primary reaction in water is

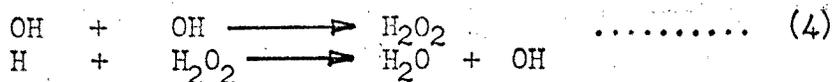
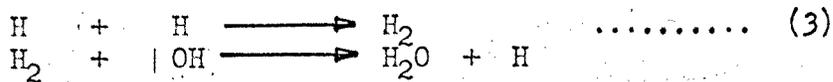
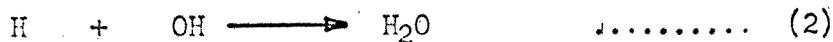


It is then possible to explain the effects of oxidation and reduction in water solutions subjected to ultrasonic cavitation. It is also believed that the increase in oxidation in the presence of dissolved oxygen does not depend so much on a direct activation of oxygen as on the effect exerted by molecular oxygen on the secondary reactions, in which the radicals H and OH take part. Even if oxygen is absent there is still a noticeable oxidation, although to a lesser degree.

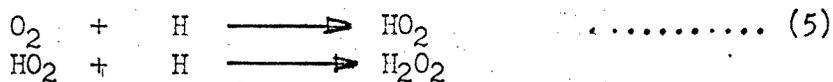
The above reaction is regarded as the fundamental and typical reaction produced by electrical discharges in water vapour and by ionizing radiations in water. The subsequent reaction involving these primarily produced radicals is of a complicated and not fully understood nature. Experimental results have shown a production of oxygen, hydrogen and hydrogen peroxide.

The action of the free radicals after primary dissociation of water depends on many factors influencing chain reactions when the chain carriers

are free radicals. However, the predominant reactions are the back reactions: ⁽³⁾

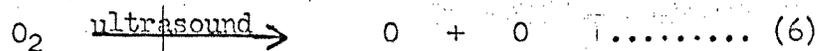


When chemically pure water is treated the net results will therefore be zero, since the equilibrium concentration of hydrogen peroxide and hydrogen may be too small to be detected. The presence of dissolved substances in the water will increase the possibility of other reaction series, particularly compounds with a high vapour pressure, which may occur in a higher concentration in the cavitation voids. In the case of dissolved oxygen the reaction is probably



Hydrogen atoms are withdrawn to some extent from the back reactions (2), (3) and (4). Simultaneously, the corresponding amount of hydroxyl radicals will react with other oxidizable substances. This is in agreement with the experimental conclusion that dissolved oxygen greatly increases the oxidation effects produced by irradiation and that the amount of hydrogen peroxide produced by irradiation is too small to explain the oxidation.

These circumstances are generally considered to be caused by a direct activation of oxygen as



Such a reaction is obviously possible and will occur simultaneously with reaction (1). The concentration of oxygen is small compared with that of water, even within the cavities, and for that reason the influence of dissolved oxygen is best represented by equation (5), whereas equation (6) is of secondary importance.

In this way it is possible to explain most of the chemical reactions produced by ultrasonic treatment of water-based solutions, for example, the oxidation of potassium iodide, hydrogen sulphide, organic dyestuffs and hydrocarbon halides such as chloroform. Similarly, the reduction of potassium permanganate and mercuric chloride, and the production of ammonia, ammonium hydroxide, NO_2 and NO_3 in the presence of dissolved nitrogen can be elucidated.

C. Mechanism of Sonochemical Oxidation and Formation of Peroxide

Oxidations promoted by ultrasonic radiations were observed and several reactions involving the liberation of iodine from iodide have been studied. The formation of hydrogen peroxide from water and oxygen under radiation naturally suggests itself, and Schmitt, Johnson and Olson⁽¹²⁾ obtained positive tests for hydrogen peroxide with titanium sulfate in the majority of trials. However, the depth of color produced by a three-minute period of radiation of potassium iodide solution was of the same order of magnitude as that produced by one part in a million of hydrogen peroxide. A mixture of equal volumes of a 3% solution of hydrogen peroxide and of the aqueous solution of hydrogen sulfide produced opalescence at a much slower rate than that observed under the influence of ultrasonic radiation. In a study of the effect of radiation on indicators it was observed that addition of 1 cc. of 2% hydrogen peroxide to 15 cc. of a dilute indicator solution did not produce any observable effect while ultrasonic radiation destroyed the color of the indicator permanently. It was clear from these observations that the production of hydrogen peroxide required confirmation and that it plays, if at all, only an insignificant part in ultrasonic oxidation.

Another possibility is the formation of ozone. Schmitt, Johnson and Olson failed to detect this substance with manganous sulfate, although they did not consider their result conclusive. A third possibility is the direct activation of oxygen by radiation.

(7)
S. C. Liu and A. Wu (1934) exposed different solutions to an ultrasonic radiation under controlled conditions in attempt to explain the mechanism of oxidation and made the following observations:

1. Necessity of Oxygen and Cavitation.

A carbon tetrachloride-water-potassium iodide-starch mixture was boiled in a long tube to free it from air. The tube was then sealed and radiated. Neither cavitation nor liberation of iodine occurred. The tube was then opened, shaken with air and again radiated. Cavitation and blue color appeared immediately.

To show the necessity of cavitation, silicic acid sol and gel (saturated with air before setting) containing potassium iodide and starch were radiated. The sol showed cavitation and slight coloration, while in the gel neither cavitation nor coloration occurred. To show that cavitation alone cannot cause ultrasonic oxidation, a carbon tetrachloride-water-potassium iodide-starch mixture, made gas free by boiling, was saturated with hydrogen or carbon dioxide after cooling. With carbon dioxide neither cavitation nor liberation of iodine occurred; while with hydrogen, potassium iodide was not oxidized even though vigorous cavitation took place.

The necessity of oxygen is shown further by the following experiment. Seven cc. of water, 1 cc. of 1% starch and 1 cc. of 1% potassium iodide were mixed in the small test-tube and radiated for different lengths of time. After exposure the amount of iodine liberated was determined by titration. The content of the tube was transferred to a 50-cc. flask and rinsed with 10 cc. of water; 1 cc. of 1 N thiosulfate. The amount of

iodine was found to increase with the time of radiation very rapidly during the first six minutes and became practically constant after eight minutes. This is probably due to the fact that most of the dissolved oxygen was either consumed or expelled during the first seven or eight minutes of radiation. To prove the correctness of this explanation, potassium iodide-starch mixture was radiated for seven minutes, when cavitation almost ceased. A fine stream of oxygen was bubbled slowly through the mixture, while the radiation was continued. The amount of iodine liberated under these conditions was found to increase steadily.

2. Formation of Peroxide

They exposed a dilute solution of potassium permanganate (about 0.002 N) to radiation. The permanganate was decolorized. Addition of potassium permanganate to water which has been radiated showed the same result. Since hydrogen peroxide is the only substance which can be formed from oxygen and water and is capable of decolorizing potassium permanganate; they regarded the observation as a conclusive proof of the production of hydrogen peroxide under the influence of radiation.

The amount of hydrogen peroxide formed in 8 cc. of water after seven minutes radiation was found by titration with 0.002 N potassium permanganate to be about 0.006 mg. Taking the amount of oxygen dissolved in water from air to be 6 cc. per liter, 0.15 mg. of hydrogen peroxide should be produced if all the oxygen dissolved in 8 cc. of water is converted into hydrogen peroxide by radiation. Hence only about 4% of the oxygen is converted into hydrogen peroxide under the conditions of the experiment.

3. Reaction with Chloroform and Carbon Tetrachloride.

Schmitt, Johnson and Olson⁽¹²⁾ found that when carbon tetrachloride was added to potassium iodide and starch solution, an intense blue color developed immediately upon radiation. Chloroform is just as effective. To test whether the formation of hydrogen peroxide can account for such a reaction, a solution of 3% hydrogen peroxide was added to chloroform-potassium iodide-starch mixture without exposing to radiation. No immediate development of color was observed, even when a large amount of hydrogen peroxide was added. This proves that peroxide formation cannot account for this reaction.

Addition of potassium iodide-starch to a mixture of chloroform or carbon tetrachloride and water after radiation also gives the iodine reaction immediately. Addition of silver nitrate gives a positive test for chloride, while a mixture of 3% hydrogen peroxide and carbon tetrachloride or chloroform without radiation gives a negative test. It is clear from these observations that chloroform or carbon tetrachloride does not act catalytically in the oxidation of potassium iodide, but is itself decomposed, giving rise to some free chlorine.

4. Absence of Ozone.

Potassium iodide reacts with ozone and hydrogen peroxide while potassium permanganate reacts with hydrogen peroxide but not with ozone. If there is any ozone present, iodine titration should indicate more oxidizing power than potassium permanganate titration. They compared iodine titration with potassium permanganate titration. Several portions of radiated water were mixed and divided into two portions. One

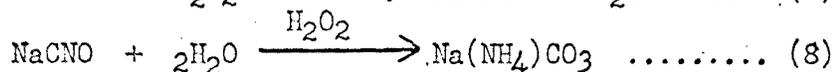
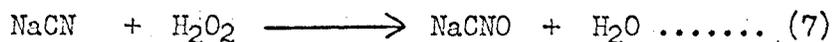
was titrated immediately with potassium permanganate and to the other potassium iodide was added. After standing for one hour, the iodine liberated was titrated with 0.002 N thiosulfate. The amounts of oxidizing power calculated from the two titration values were identical within the limit of experimental error (about 5%). If there is any ozone produced by radiation; the amount cannot be more than one part in 20 million. Such a small amount of ozone certainly cannot account for any of the oxidation observed.

As a conclusion to these observations the mechanism of oxidizing can be explained as follows:

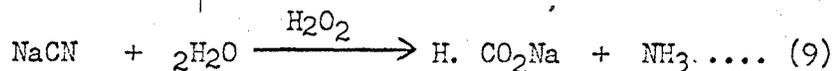
Oxygen is necessary for ultrasonic oxidation. The amount of hydrogen peroxide, the only oxidizing agent formed during radiation, cannot account for all the reaction observed. It is therefore concluded, that oxygen is directly activated under the influence of ultrasonic radiation. Cavitation being essential, it is clear that only the oxygen molecules on the surface of the bubbles are active during radiation. As soon as radiation ceases, the activity of the oxygen disappears. The active oxygen can liberate iodine from iodide or react with water to form hydrogen peroxide. When carbon tetrachloride or chloroform is present, it reacts with the active oxygen to give free chlorine.

II- Reaction of Sodium Cyanide with Hydrogen Peroxide

According to Masson,⁽⁸⁾ the main products of the action between sodium cyanide and hydrogen peroxide are sodium cyanate and sodium ammonium carbonates. Of these, the former seems to be the primary product while hydrogen peroxide acts as a catalyst.



Taken together, the cyanate and carbonate were found to account for approximately 80% of the original cyanide and an equimolecular quantity of peroxide. The balance of the cyanide (20%) is never oxidized, even though a large excess of peroxide be employed, but is converted by hydrolysis into sodium formate and ammonia. In this action also the peroxide plays the part of a catalytic agent.



Experimental

I Scope of investigation

This study investigated the chemical effect of ultrasound on sodium cyanide solutions. The operating parameters considered were power input to the system, concentration of cyanide, aeration and temperature.

II Description of Apparatus

The apparatus used in this study can be described as follows:

(see Figure 11)

- 1- Air regulating valve
- 2- Low pressure air pump
- 3- Air regulating valve
- 4- U-tube with calcium chloride
- 5- Reaction tube
- 6- Aeration tube, with sealed fine porosity fritted disc
- 7- Constant volume water bath
- 8- Constant temperature water jacket
- 9- Air pump
- 10- Regulating valve
- 11- Air cooling nozzle
- 12- Fibra-Sonics 21KHz, 100W lead-zirconate-titanate sandwich type transducer
- 13- Fibra-Sonics G-100 MK I Ultrasonic Oscillator
- 14- Fibra-Sonics G-100 MK I Ultrasonic Amplifier
- 15- Glass Plate

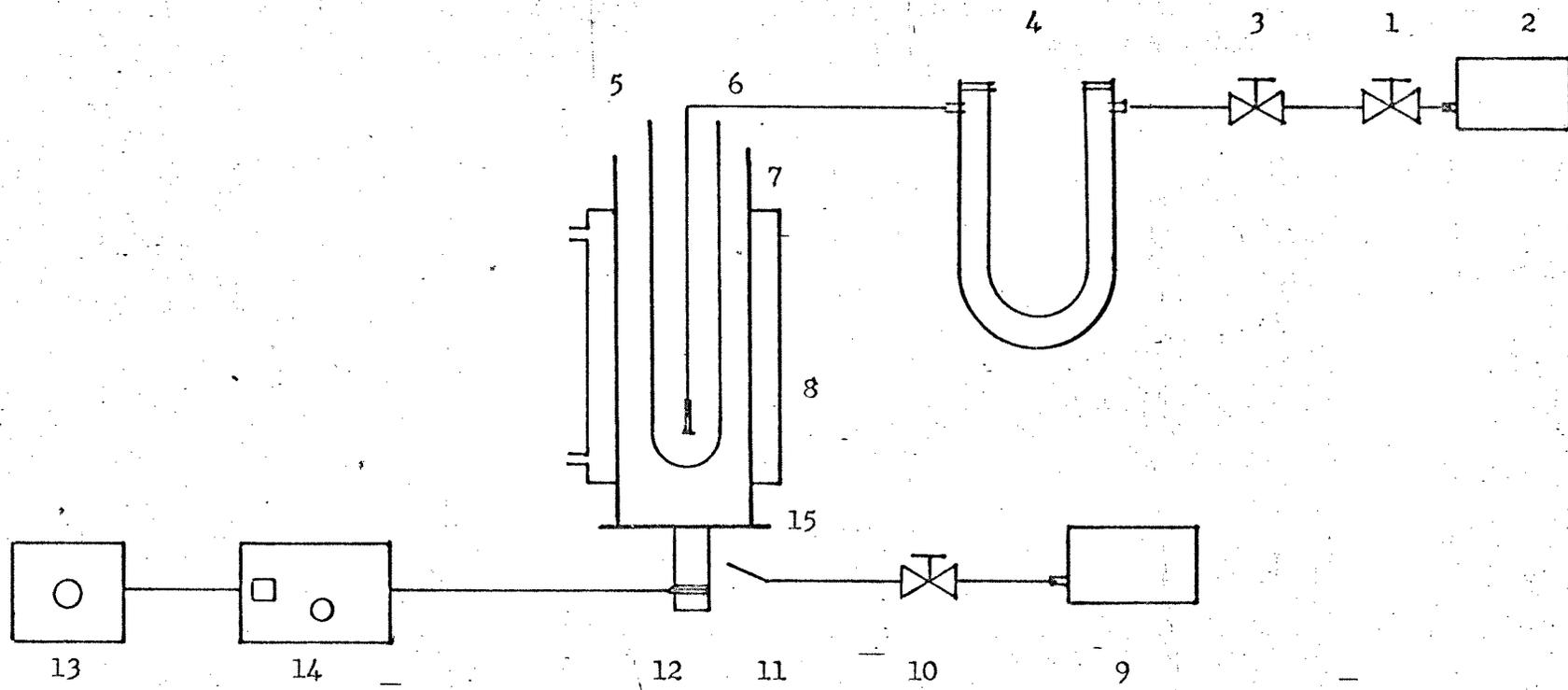


Figure 11 - Experimental Apparatus

III Experimental Procedure

A known volume, 30 or 40 mls of the solution to be investigated was introduced in the inner reaction tube and the experimental variables were applied as required to the system. These included:

- Aeration by bubbling air at the bottom of the solution at a constant rate which was maintained in all experiments.
- Temperature control of solutions using the water jacket.
- Ultrasonic radiation supplied by a transducer fixed at the bottom of the water bath.

All solutions were analyzed for initial cyanide concentration before each run. At given time intervals, 5 mls samples of the reacting solution were taken from the reaction tube with a 5 mls pipette. The sample was cooled rapidly and analyzed for free residual cyanide with 0.1 N silver nitrate and potassium iodide indicator. (see Appendix A for analytical procedure)

The reacted cyanide was then calculated and plotted as a function of time. A 250 mls constant volume water bath surrounding the reaction tube eliminated the effect of changing volume of reacting solution on the cavitation intensity in the reaction tube. Temperature of the solution was constantly monitored and recorded as a function of time. Runs which required ultrasonic radiation were investigated at 40W - 27KHz and 100W - 21KHz. The power was determined by a power meter located on the ultrasonic amplifier. Changes in

power during radiation due to heating of transducer and solution were recorded as a function of time. The transducers were air cooled during the test to minimize the heat effect.

Reagent grade sodium cyanide and 3% hydrogen peroxide solution were used for the study of reaction rates without ultrasound. De-ionized water which has been aerated for one hour was used in the make up of the cyanide solutions for all runs. The solutions investigated ranged in initial cyanide concentration from 1.0 to 20.0 g/l.

DATA AND RESULTS

Reaction data of NaCN with Hydrogen Peroxide*Solution

Table I

Effect of concentration and ratio of reactants:

<u>NaCN initial concentration</u>	<u>Molar Ratio H₂O₂: NaCN</u>	<u>Time (min)</u>	<u>NaCN destroyed (ppm)</u>	<u>Temp. (°C)</u>	<u>Power (watt)</u>
1- 1.0 g/l	1.00				
(a) Without air					
(b) With air (same results)					
		0	0	18	0
		10	69	18	0
		20	118	19	0
		25	167	20	0
		40	216	21	0
		85	314	24	0
		95	363	29	0
		100	363	28	0
2- 6.13 g/l	1.016				
		0	0	20	0
		7.5	490	20	0
		15	1029	20	0
		30	1715	20	0
		45	2205	20	0
		60	2695	20	0
		90	3430	20	0
3- 11.76 g/l	1.00				
		0	0	20	0
		7	1862	20	0
		15	3318	20	0
		30	4900	20	0
		60	7840	20	0
		90	9163	20	0

* A 3% Hydrogen Peroxide solution was used in all experiments.

4- 12.15 g/l

0.60

0	0	20
7.5	1029	20
15	2156	20
30	3528	20
45	4557	20
60	5292	20
90	6321	20

Table II

Effect of ultrasonic radiation with free temperature rise, at 40W - 27KHz.

<u>NaCN initial concentration</u>	<u>Molar Ratio H₂O₂: NaCN</u>	<u>Time (min)</u>	<u>NaCN destroyed (ppm)</u>	<u>Temp. (°C)</u>	<u>Power (watt)</u>
1.0 g/l	1.00				
(A) <u>Without Air</u>		0	0	18	38
		10	50	19	38
		15	98	20	37
		20	98	23	37
		30	245	25	36
		35	245	26	35
(B) <u>With Air</u>		0	0	18	38
		10	50	19	38
		15	98	20	37
		20	147	23	37
		25	196	24	36
		35	245	26	35
		60	392	30	34
		80	441	36	32

Table III

Effect of controlled temperature on reaction rate.

(A)- With Ultrasonic Radiation; at 40W - 27KHz

<u>NaCN initial concentration</u>	<u>Molar Ratio H₂O₂: NaCN</u>	<u>Time (min)</u>	<u>NaCN destroyed (ppm)</u>	<u>Temp. (°C)</u>	<u>Power (watt)</u>
1.0 g/l	1.00				
<u>With Air</u>		0	0	20	38
		10	147	22	37
		20	147	23	37
		30	245	23	36
		40	245	23	36
		50	294	22	36
		60	343	22.5	36
		70	343	23	35
		80	392	22.5	35
		89	421	23	34
		96	421	23	34
		101	441	23	34

(B)- Without Ultrasonic Radiation:

<u>With Air</u>	0	0	20	0
	10	147	22	0
	20	147	23	0
	30	245	23	0
	40	245	23	0
	50	294	22	0
	60	343	23	0
	70	362	23	0
	80	392	22	0
	89	421	23	0
	96	421	23	0
	101	441	23	0

Reaction by Ultrasonic Radiation

Table IV

Effect of NaCN concentration and aeration on reaction rate.

(A) Transducer data:

Power = 40 watt
 Frequency = 27 KHz

<u>NaCN initial concentration</u>	<u>Time (min)</u>	<u>NaCN destroyed (ppm)</u>	<u>Temp. (°C)</u>	<u>Power (watt)</u>
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1- 1.0 g/l (1000 ppm) Starting Volume = 30 mls

(a) Without Air

0	0	21	38
10	0	23	38
15	0	25	37
20	0	26	37
25	0	27	36
35	0	30	35

(b) With Air

0	0	21	38
10	0	23	38
15	0	25	37
20	0	26	37
25	0	27	36
35	0	30	35

2- 5.0 g/l (5000 ppm) Starting Volume = 30 mls

(a) Without Air

0	0	21	38
10	0	23	38
15	0	25	37
20	0	26	37
25	0	27	36
30	0	29	35

(b) With Air

0	0	21	38
10	0	23	38
15	0	25	37
20	0	26	37
25	0	27	36
30	0	29	35

(B) Transducer data:

Power = 100 watt
Frequency = 21 KHz

<u>NaCN initial concentration</u>	<u>Time (min)</u>	<u>NaCN destroyed (ppm)</u>	<u>Temp. (°C)</u>	<u>Power (watt)</u>
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1- 2.5 g/l (2500 ppm) Starting Volume = 30 mls

(a) Without Air

0	0	23	85
10	0	35	80
25	20	46	75
41	60	59	70
60	60	64	68

(b) With Air

0	0	23	85
10	-	35	80
25	50	46	75
41	147	59	70
60	294	64	68

2- 5 g/l (5000 ppm) Starting Volume = 30 mls

(a) Without Air

0	0	23	90
10	trace	36	87
25	55	50	72
41	75	58	65
60	98	64	61

(b) With Air

0	0	23	90
10	60	37	87
25	160	51	72
41	260	57	65
60	392	64	60

3- 10 g/l (10,000 ppm) Starting Volume = 30 mls

(a) Without Air

0	0	22	90
10	trace	35	87
25	100	51	71
41	150	60	67
60	150	64	61

(b) With Air

0	0	23	90
10	100	37	87
25	250	51	71
41	380	60	67
60	380	64	61

4- 20 g/l (20,000 ppm) Starting Volume = 30 mls

With Air

0	0	23	95
13	160	40	80
25	350	50	70
41	350	61	65
60	350	66	60

Table V

Effect of temperature and aeration* on rate of reaction.

<u>NaCN initial concentration</u>	<u>Time (min)</u>	<u>NaCN destroyed (ppm)</u>	<u>Temp. (°C)</u>	<u>Power (watt)</u>
1- 5 g/l (5000 ppm) Starting Volume = 40 mls				
<u>Cycle I</u>	-30	0	21	0
	0	0	21	95
	10	(60)**	36	85
	66	(392)**	61	59
	83	392	63.5	59
--- Power off, solution cooled to room temperature, with continuous air bubbling for 1 hr.				
<u>Cycle II</u>	143+ 0	392	25	95
	143+11	392+ 88	38	80
	143+60	392+265	63	60
	143+66	392+330	65.5	60
	143+93	392+330	66	59
2- 5 g/l (5000 ppm) Starting Volume = 40 mls				
<u>Cycle I</u>	-30	0	22	0
	0	0	22	95
	10	(60)**	36	85
	60	(392)**	61	59
	83	392	64	59
--- Power off and cooling to room temperature without aeration for 1 hr. Aeration resumed simultaneously with ultrasonic radiation after 1 hr.				
<u>Cycle II</u>	143+ 0	392	25	95
	143+10	392	38	80
	143+60	392	64	60

* Air bubbled in solutions at constant rate 30 min before application of ultrasound and throughout the test.

** Taken from Table IV - B2

3- 20 g/l (20,000 ppm)

<u>Cycle I</u>	-30	0	21	0
	0	0	21	95
	4	-	24	90
	13	(160)*	31	80
	25	350	43	70
	41	(350)*	55	65
	60	350	66	60

---Power off and cooling to room temperature without aeration for 1 hr. Aeration resumed simultaneously with ultrasonic radiation after 1 hr.

<u>Cycle II</u>	120+ 0	350	23	95
	120+11	350	42	80
	120+25		52	70
	120+60	350	67	60

* Values from Table IV -4

Figure 1 - Reaction of Sodium Cyanide with Hydrogen Peroxide at 20°C

H₂O₂: NaCN = 1.0

Without Ultrasound

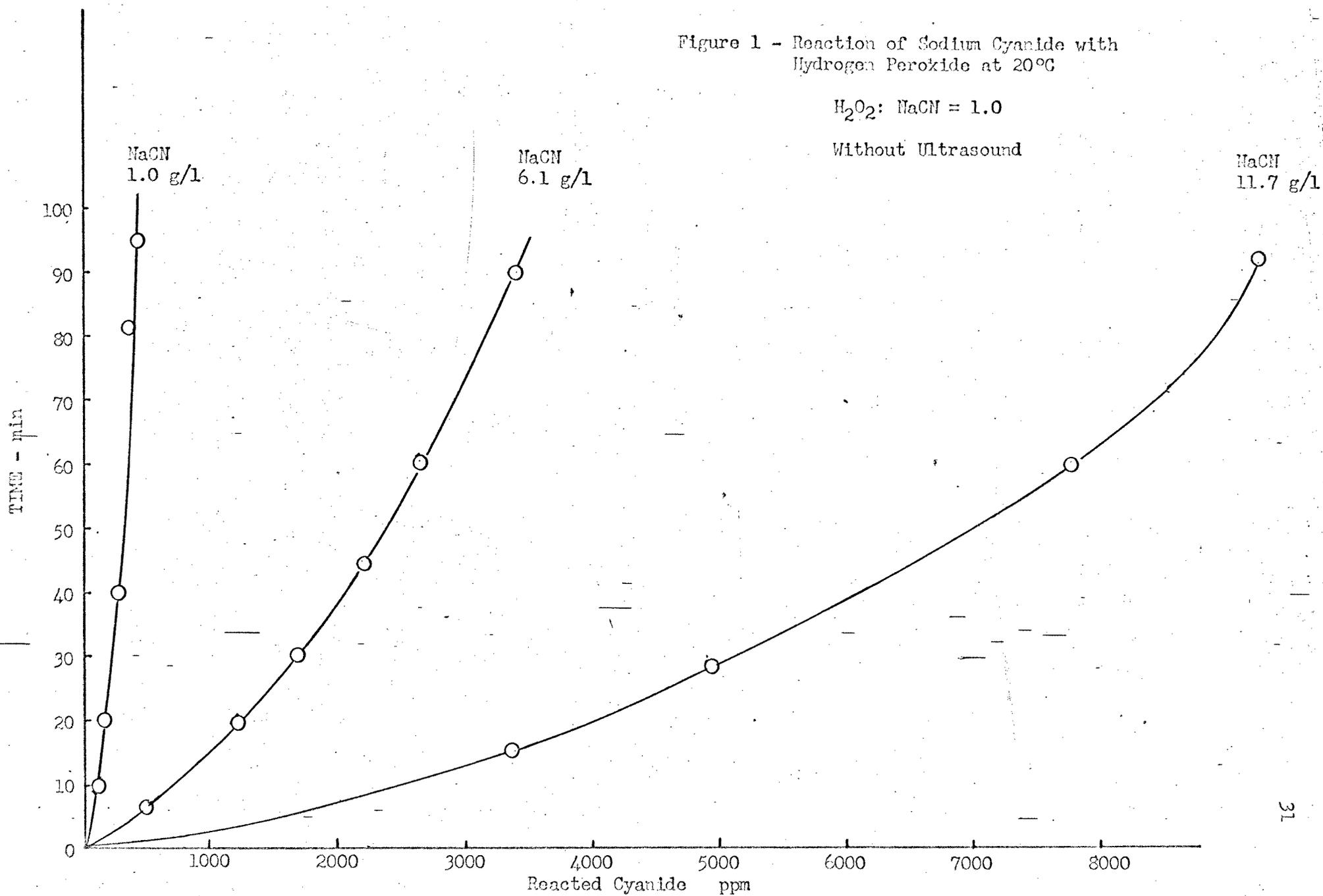


Figure 2 - Reaction of Sodium Cyanide with Hydrogen Peroxide at 20°C - Without Ultrasound

○ H₂O₂: NaCN = 1.0

△ H₂O₂: NaCN = 0.6

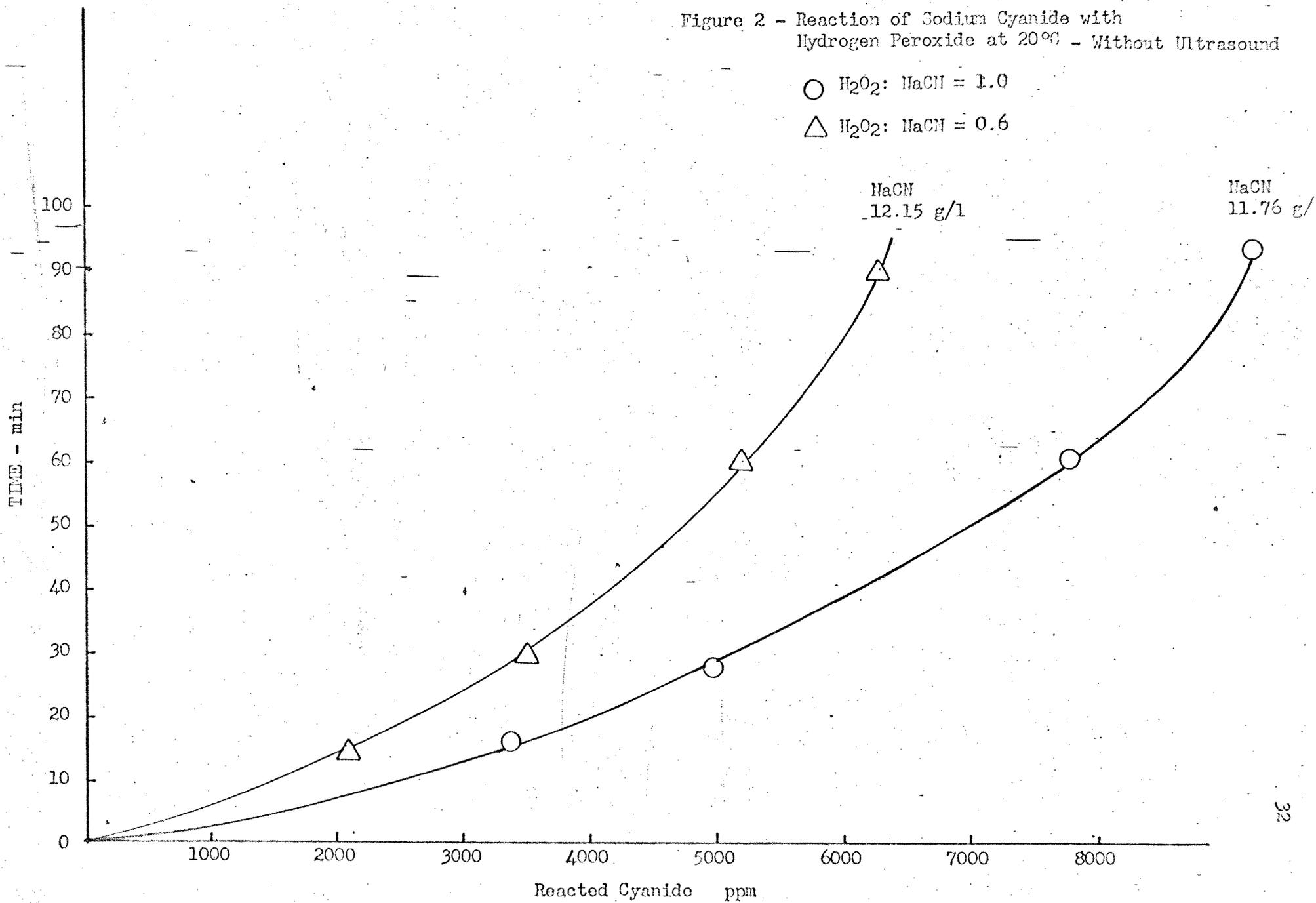


Figure 3 - Effect of ultrasound at 40W - 27KHz on cyanide solutions with aeration

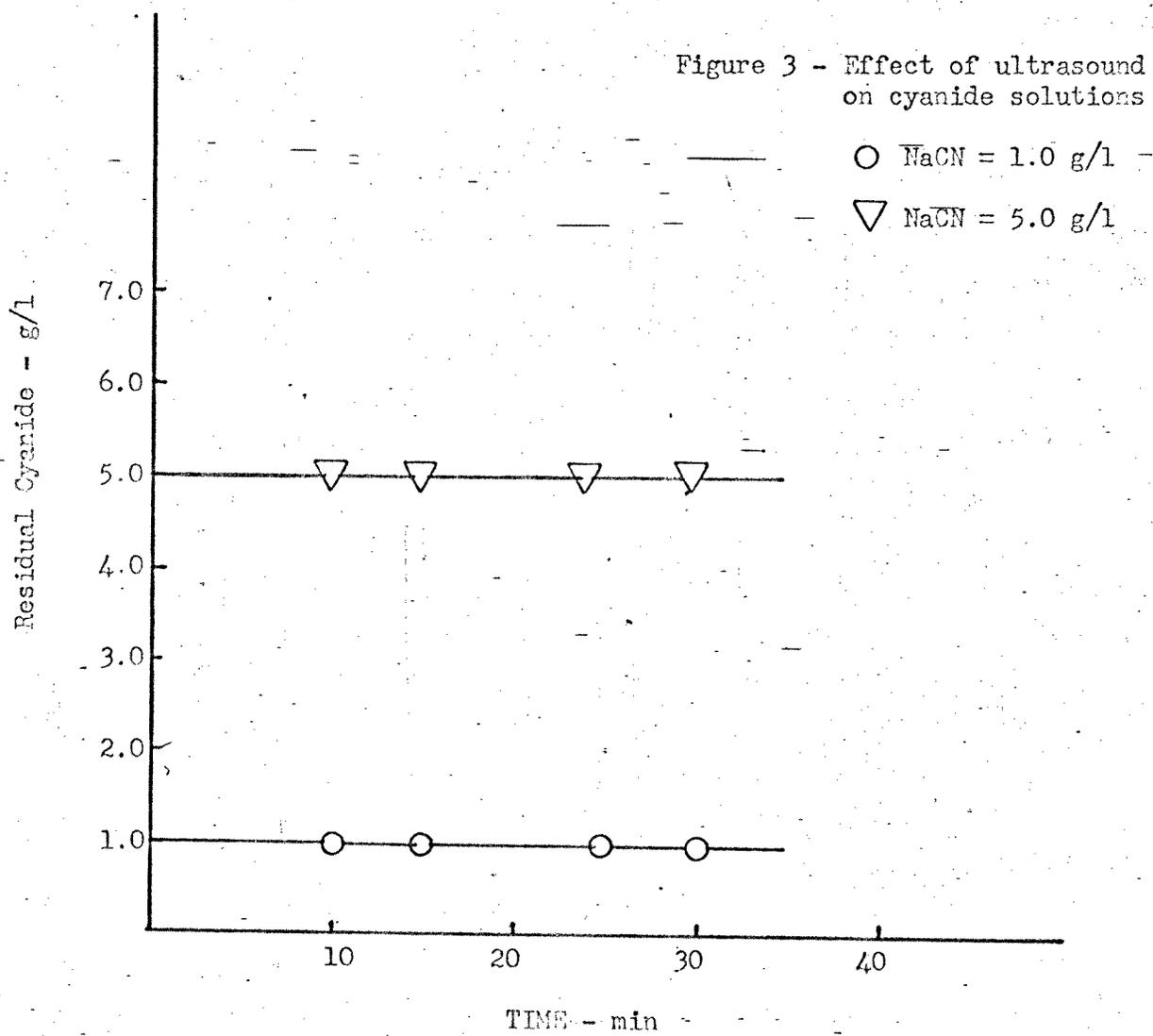


Figure 4 - Reaction of Sodium-Cyanide with
Hydrogen Peroxide

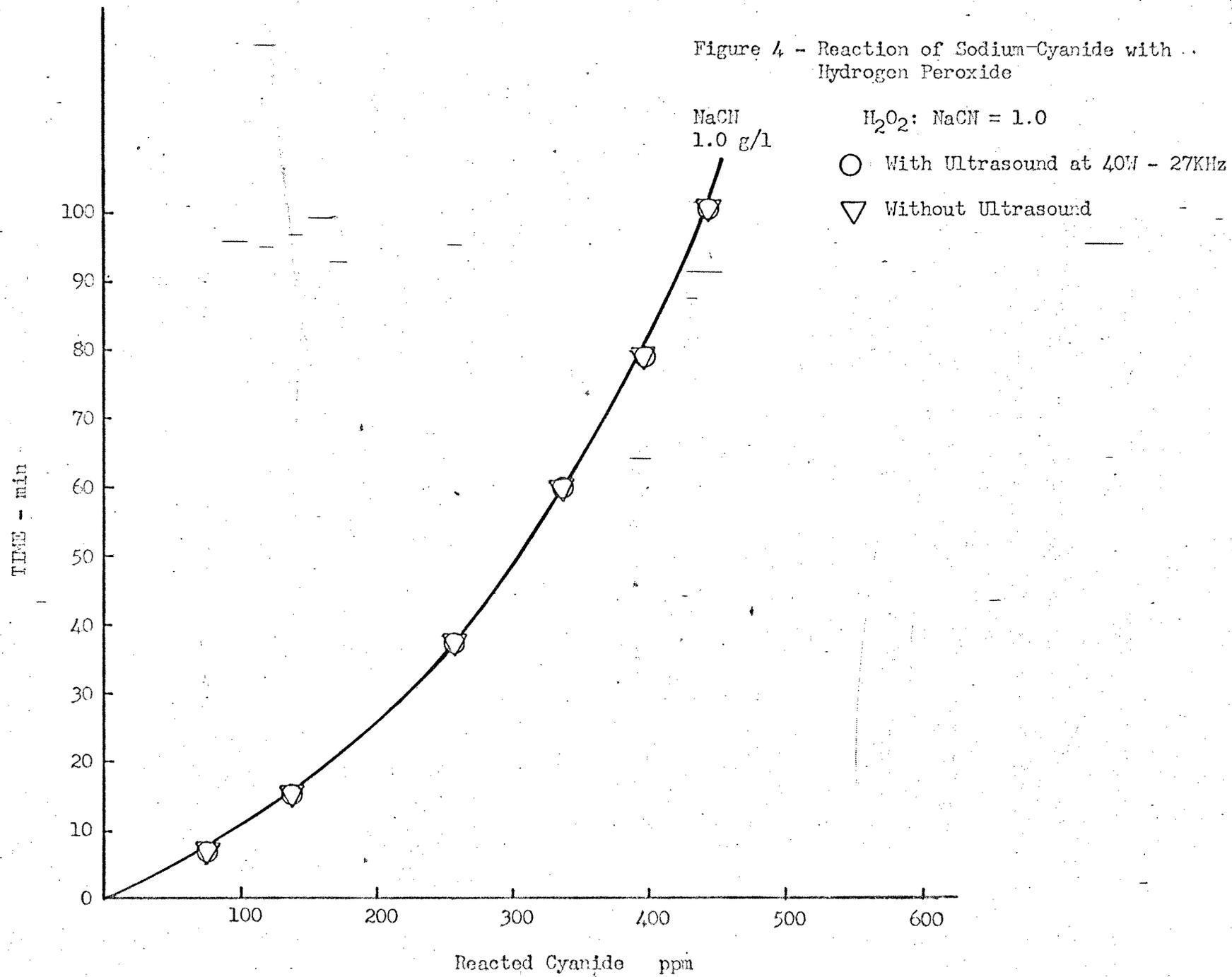


Figure 5 - Effect of power on reaction rate

NaCN = 0.5 g/l

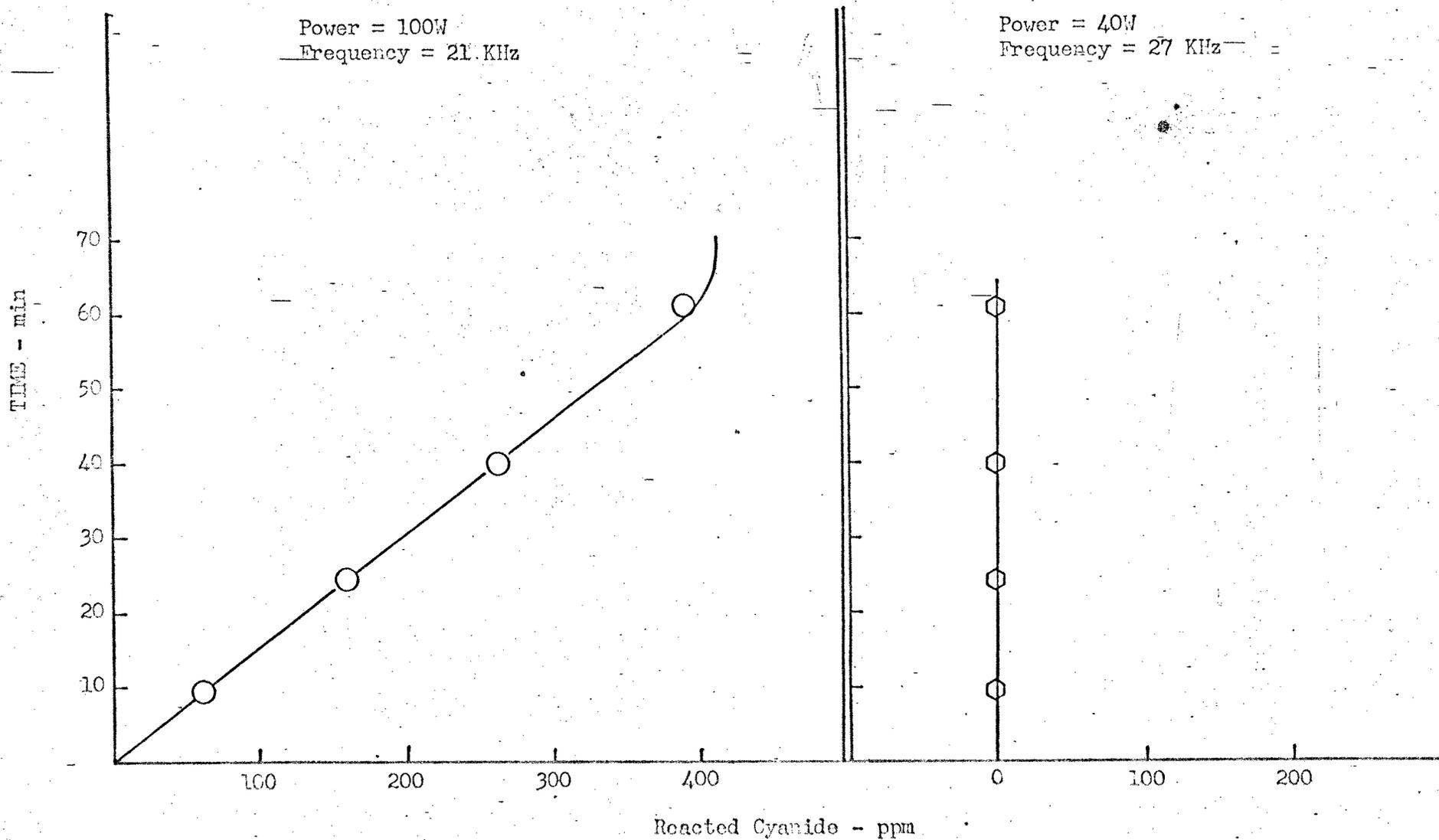


Figure 6 - Effect of Ultrasound at 100W - 21KHz with no aeration

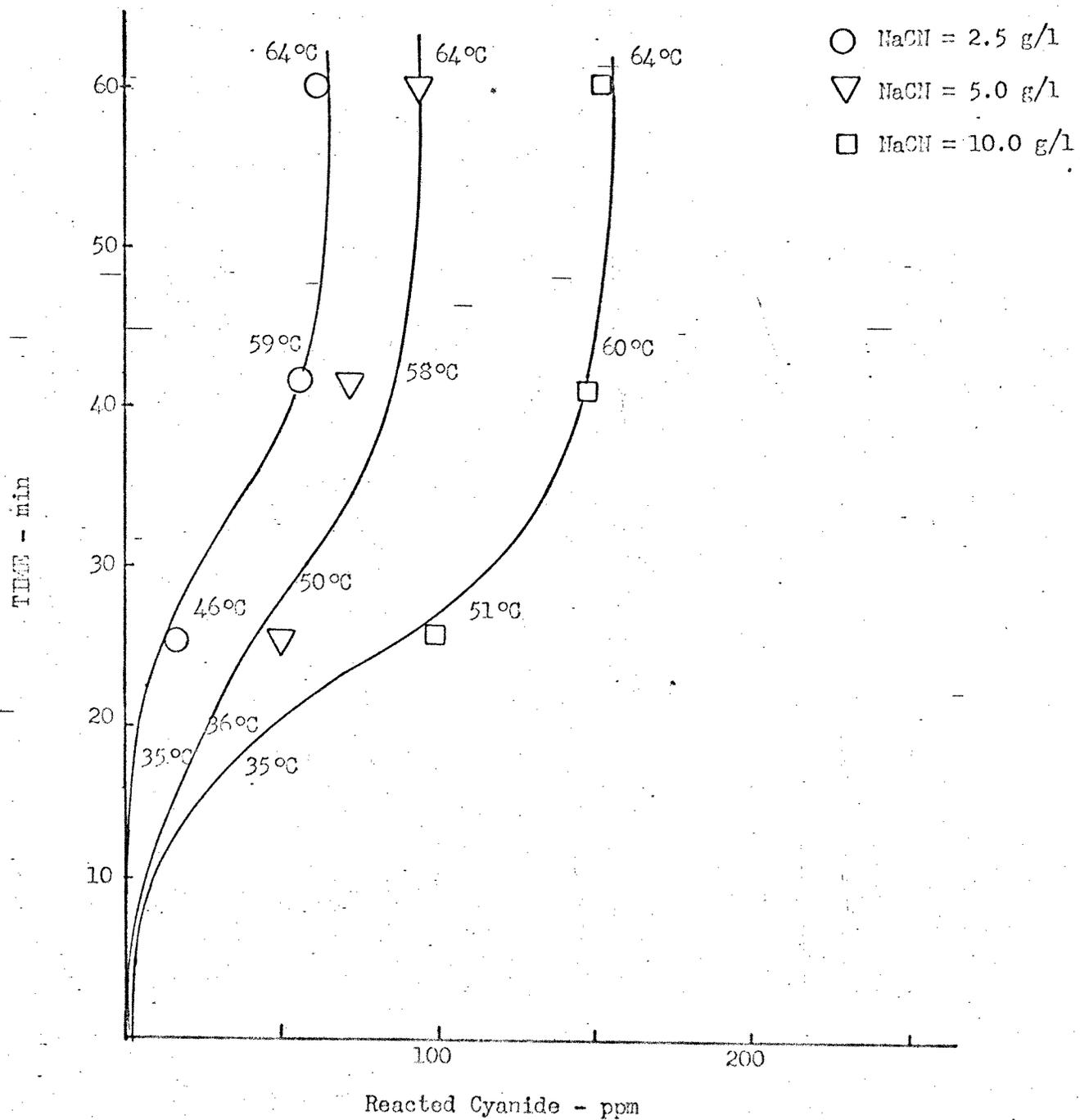


Figure 7 - Effect of Ultrasound at 100W - 21KHz with continuous aeration

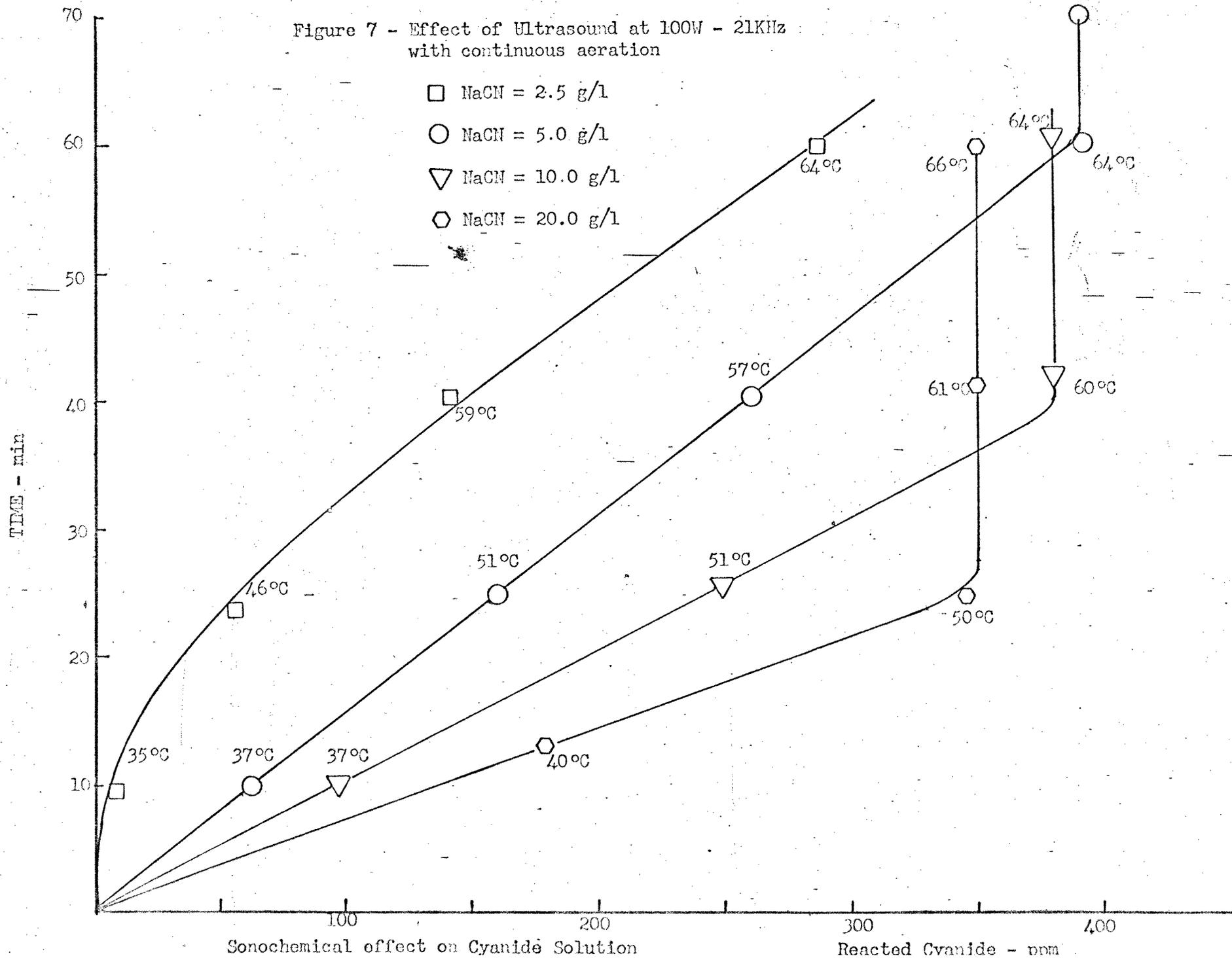


Figure 8 - Reaction of Sodium Cyanide with Hydrogen Peroxide - Without Ultrasound

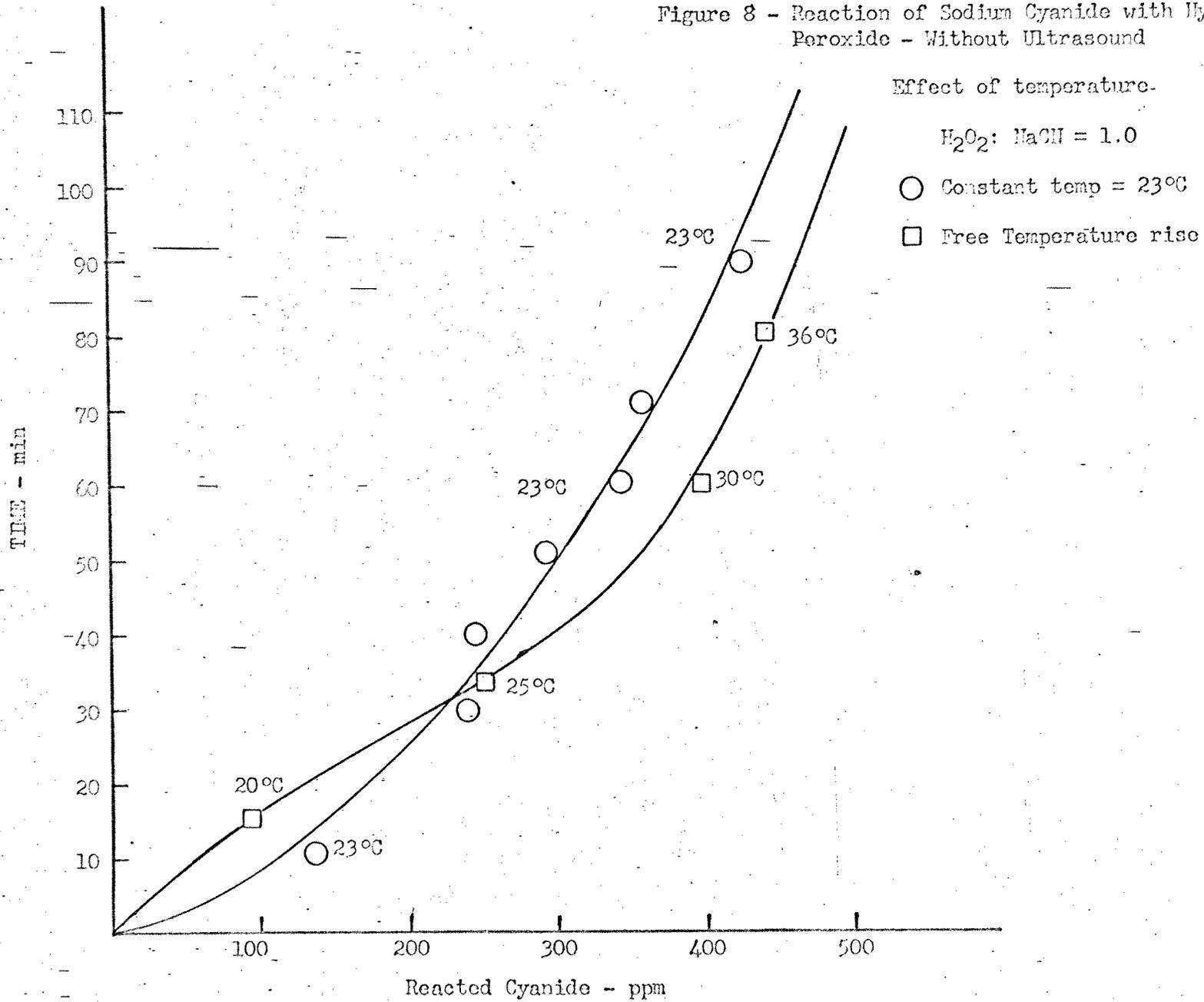
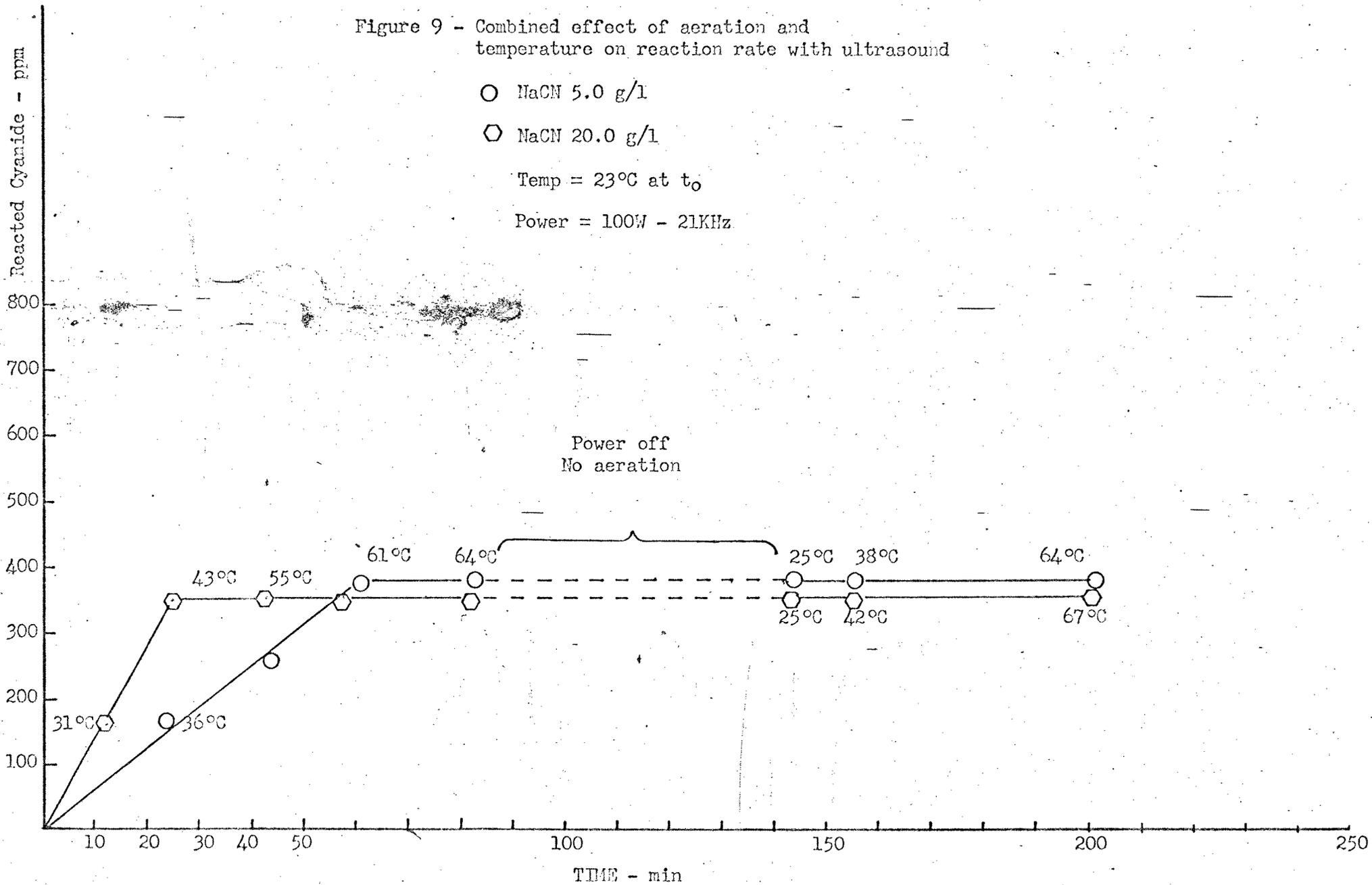


Figure 9 - Combined effect of aeration and temperature on reaction rate with ultrasound



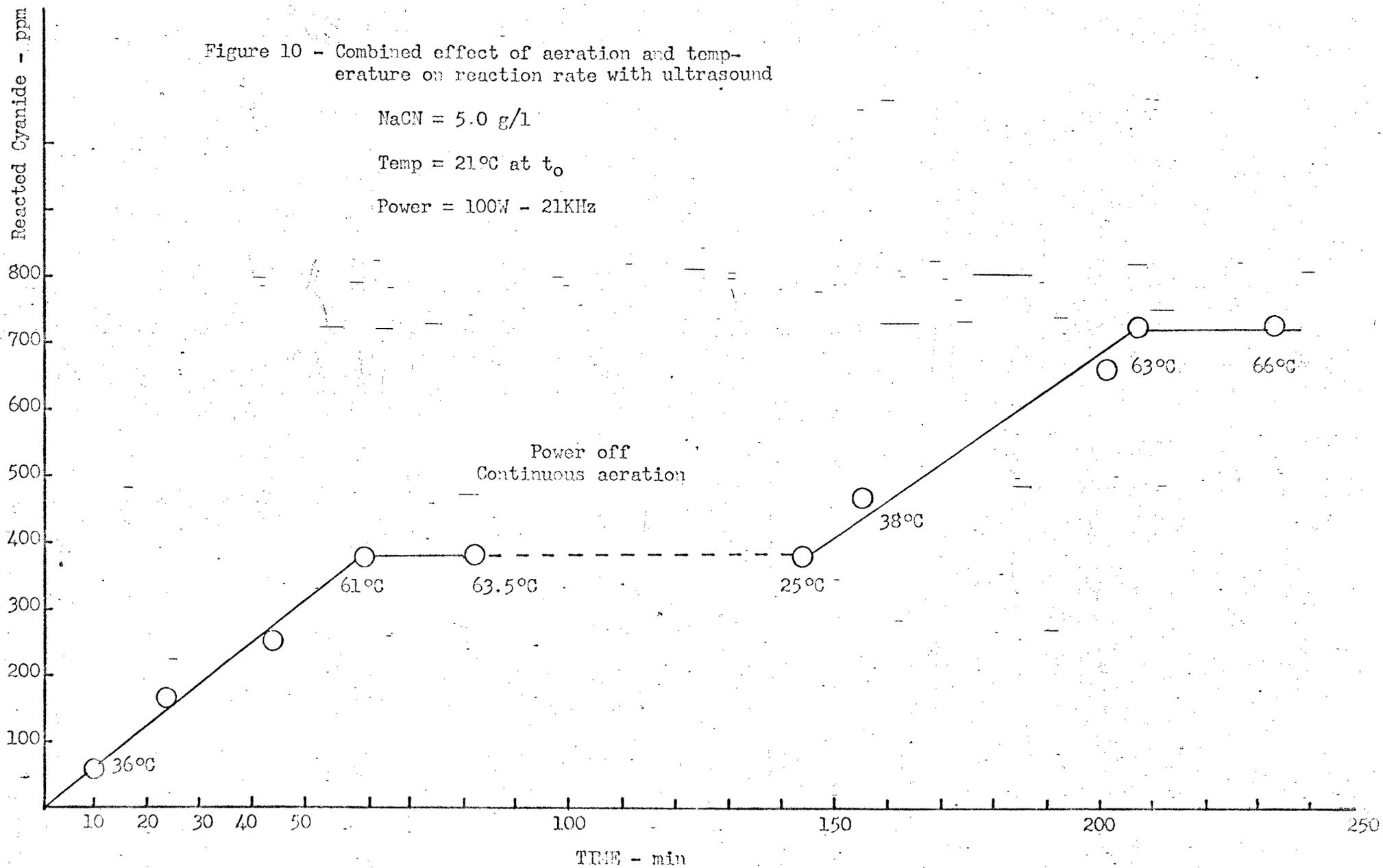
Sonochemical effect on Cyanide Solutions at 100W - 21KHz

Figure 10 - Combined effect of aeration and temperature on reaction rate with ultrasound

NaCN = 5.0 g/l

Temp = 21°C at t_0

Power = 100W - 21KHz



Discussion of Results

The net effect of ultrasonic radiation was found to be a function of several experimental parameters. In order to understand the overall effect of the process, each parameter was studied separately.

Effect of Power:

Transducers with power inputs of 40 and 100 watt and frequencies of 27 and 21 KHz respectively were investigated. No reaction took place at 40W in the cyanide solutions of initial concentrations of 1.0 and 5.0 g/l. Continuous aeration during radiation had no effect at that power, even though cavitation was visible during the process. (see Figure 3)

The amount of hydrogen peroxide generated in the solutions at 40W was nil or too small to start a chemical reaction.

To substantiate this conclusion, sodium cyanide and hydrogen peroxide solutions in a molar ratio of 1:1 were allowed to react at constant temperature and with constant aeration while exposed to the ultrasonic field at 40 W. The reaction rate was identical to that obtained from the same reacting solutions under the same conditions without ultrasonic radiation. (see Figure 4)

At a power of 100 W, a gradual decrease in residual cyanide concentration in solution was observed without any additions of hydrogen peroxide. The rate of cyanide disappearance was a

function of the initial cyanide concentration, temperature and aeration. The hydrogen peroxide required for the reaction was generated by the ultrasonic radiation of the solutions at that power. This is in agreement with the findings of S. C. Liu and H. Wu⁽⁷⁾ and V. Griffing⁽⁵⁾ on the formation of hydrogen peroxide and the oxidation effects by ultrasound in aqueous solutions. Figure 5 compares the effects of power at 40 and 100W on a 5 g/l cyanide solution.

Effect of Aeration:

The effect of aeration on the reaction rate is shown in Figure 6 and 7. It was found that solutions which were not aerated during ultrasonic radiation had a slower reaction rate. The reaction stopped after a maximum amount of cyanide, proportional to the initial solution concentration, had reacted. (see Figure 6)

Solutions which were constantly aerated during ultrasonic radiation showed a faster reaction rate, which was sustained for a longer period of time. (see Figure 7)

The oxygen content of the air dissolved in solutions was consumed in the formation of hydrogen peroxide, which in turn was used up in the reaction with cyanide. In the case of solutions which were not constantly aerated during radiation, the reaction proceeded to the extent of available dissolved air (or oxygen) then

stopped. In aerated solutions, a constant supply of bubbled air provided the required oxygen to replenish the consumed hydrogen peroxide and sustain the reaction.

(7)
S.C. Liu and H. Wu obtained similar results with the liberation of iodine from potassium iodide solutions by ultrasonic radiation. It was also observed in Figure 7 that the maximum amount of reacted cyanide decreased with the increase of initial cyanide concentration.

This was due to the fact that the solubility of air in aqueous solutions decreases with the increase of solute concentration. Consequently the amount of available dissolved air decreased in the more concentrated cyanide solutions.

Effect of Initial Cyanide Concentration:

Figure 6 and Figure 7 show the effect of initial cyanide concentration on the rate of reaction. The reaction was higher in both aerated and non aerated solutions, at the higher initial cyanide concentration values. The same effect was observed in the oxidation of cyanide with hydrogen peroxide solutions without ultrasonic radiation. (see Figure 1)

Effect of Peroxide to Cyanide Ratio on Reaction Rate:

Figure 2 shows that the reaction rate of hydrogen peroxide and sodium cyanide solutions decreased with their molar ratio, overcoming the effect of higher initial cyanide concentration. Comparison of

rates obtained with different peroxide to cyanide ratios and rates obtained by ultrasonic radiation showed that the amount of hydrogen peroxide generated by ultrasound was very small in relation to the cyanide present in solution.

Effect of Temperature:

Figure 8 shows the effect of temperature on the reaction rate of hydrogen peroxide and a 1.0 g/l cyanide solution. Although the reacting solutions were ultrasonically radiated at 40W, no chemical effects were observed from the ultrasound other than the heat effect.

It was found that the rate increased only slightly when the temperature was allowed to rise freely from 18°C to 36°C. After 80 min the amount of reacted cyanide at 36°C was only 20 ppm higher than the amount observed when the temperature was held constant at 23°C. An increase in temperature of batch processed solutions by ultrasonic radiation could not be avoided, due to the absorption of sound energy by the solution. Below 50°C the temperature did not appear to be a critical factor in most chemical reactions according to Weissler.
(15)

Figure 7 shows the effect of temperature rise caused by ultrasonic radiation on the maximum yield of reacted cyanide at different concentrations. The reaction stops almost suddenly when the solution temperature reaches 62 - 64°C in each case. The formation of hydrogen

peroxide in air containing water by ultrasound was found to decrease with temperature from 10 - 50°C according to Urasovskii and Polotskii.⁽¹⁴⁾

The combined effect of increased oxidation rate of cyanide with temperature and decrease in yield of hydrogen peroxide formed kept the reaction rate nearly linear until the critical temperature was reached.

Combined effect of aeration and temperature:

Figure 9 and Figure 10 show the combined effect of both aeration and temperature on the reaction rate. The ultrasonic radiation was applied in two cycles to 5 and 20 g/l cyanide solutions. Continuous aeration by bubbling air through the solutions was maintained during the first and second cycle. When the solutions reached the critical temperature and the reaction stopped at the end of the first cycle, the power was turned off and the solutions allowed to cool to room temperature for one hour.

The ultrasonic radiation was then resumed and the rate of reaction monitored during the second cycle.

No further reaction was observed in either solutions in the second cycle when no air was bubbled through the solutions between the two cycles. (see Figure 9)

By contrast, when aeration was maintained during the cooling period the reaction rate was restored and maintained during the second cycle, then stopped when the solution reached the critical temperature again.

Quantitative Evaluation of Results

Comparison of Figures 1, 2, 6 and 7 clearly showed that the reaction rates obtained from the effect of ultrasound on cyanide solutions were slower than those obtained from the action of hydrogen peroxide solutions and cyanide solutions in general. The reaction rates, however, decreased noticeably in Figure 2 as the ratio of H_2O_2 : NaCN decreased, suggesting that the lower reaction rate obtained with ultrasound was due to a very low H_2O_2 : NaCN ratio. This could be expected in light of the limit of solubility of air in aqueous solutions. In the case of irradiating 30 mls of 2.5, 5.0 and 10.0 g/l cyanide solutions at 100W without continuous aeration, the amount of dissolved oxygen and the equivalent hydrogen peroxide formed can be estimated as follows, assuming air saturation of these solutions before the application of ultrasound:

Average air concentration in solutions at 20°C	= 20 cc per liter
% oxygen in dissolved air	= 34%
Average amount of dissolved oxygen	= 6 cc per liter
Equivalent amount of hydrogen peroxide formed by ultrasound from reaction 5	= 18.75 mg per liter = 18.75 ppm
From reaction 7, the equivalent amount of oxidized cyanide	= 27 ppm

Based on Masson's mechanism of reaction of cyanide with peroxide, the amount of hydrolyzed cyanide by the catalytic effect of H_2O_2 would be: $0.25, \times 27$ = 7 ppm

Total amount of reacted cyanide = 34 ppm

From Figure 6, however, the total amount of reacted cyanide obtained was 2 to 3 times that value. This could only be explained on the basis that the hydrolysis of cyanide through the catalytic effect of H_2O_2 during ultrasonic radiation occurs at a much higher rate than that found by Masson's in conventional cyanide-peroxide reactions.

Based on equal amounts of hydrogen peroxide, the overall reaction yield by ultrasonic radiation improves the yield obtained by conventional cyanide peroxide reactions by 200 to 300 %.

CONCLUSIONS

- 1- Ultrasonic radiation has a chemical effect on sodium cyanide solutions. This effect is based on the generation of hydrogen peroxide in cyanide solutions during irradiation. The reaction includes a direct oxidation between the cyanide and peroxide and hydrolysis of the cyanide through the catalytic effect of hydrogen peroxide. The latter effect is greatly enhanced by ultrasound and increases the overall reaction yield by 200 - 300% over the yield normally obtained from equal amounts of hydrogen peroxide in conventional cyanide - peroxide reactions without ultrasonic radiation.
- 2- The parameters affecting the reaction rate are power, concentration of cyanide, time, temperature and aeration.
- 3- The chemical effect was obtained at 100W, while at 40W no reaction was observed in the cyanide solutions.
- 4- The sonochemical effect can be sustained by constantly bubbling air into the solution and maintaining the temperature below 60°C.

RECOMMENDATIONS

- 1- A study of actual rates of reaction during ultrasonic radiation is important in the evaluation of sonochemical effects. This requires controlled temperature operations only possible by a continuous recirculation of the reacting solutions through an external heat exchanger and back to the ultrasonic field.
- 2- Catalysts such as copper and silver known for their promotion of oxidation processes, can be investigated for their effect on oxidation reactions produced by ultrasonic radiation on cyanide solutions.
- 3- Methods to measure power input to the system should be developed to establish accurate power to reaction yield relationships.

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APPENDIX A

ANALYTICAL PROCEDURE

A) - Procedure:

- 1- Pipette a 10 ml sample into a 250 ml Erlenmeyer flask.
- 2- Add 100 ml of distilled or deionized water and 5 ml of potassium iodide 10% solution.
- 3- Titrate with 0.1 N standard silver nitrate solution until a faint yellowish turbidity persists after stirring.

B) - Calculations:

Free sodium cyanide g/l =

ml of silver nitrate x 0.1 x 9.8

C) - Discussion of the Method

Silver nitrate reacts with sodium cyanide to form soluble silver cyanide in solution. After all the cyanide had reacted, the silver ions then react with iodide ions to cause the solution to take on a yellow opalescent appearance due to the formation of finely dispersed silver iodide. The minimum detectable concentration by this method approaches 0.1 ppm cyanide.

APPENDIX B

REACTION APPARATUS ASSEMBLY
(see Figure 12)

The reaction tube consisted of a 25 mm ID pyrex tube 2 mm thick and 33 cm long, fixed vertically in position in the constant volume water bath. The bottom of the reaction tube was fixed at 30 mm from the bottom of the water bath and at equal distance from its walls at all times.

The water bath was made of a 50 mm ID 3/16" pyrex tubing, 30 cm long. A 7 x 7 cm, 3/16" glass plate was sealed to the lower end of the tubing with GE silicone sealant.

The transducer was epoxied to the outer side of the square plate, and lined up with the vertical center line of the tubing. The glass plate was held and pressed against the tubing with steel flanges. Sealsare .125 cork sheets were used to protect the glass plate between the flanges.

Aeration of the reacting solutions was achieved with a small air pump. The air was dried by passing through a U-tube filled with calcium chloride solution. In order to obtain the smallest possible air bubble size, a 10 mm glass tube with a sealed fine porosity fritted disc at its end was used to bubble the air through the reacting solution. The air flow was adjusted to a minimum by means of two air regulating valves. The same rate was kept constant for all runs.

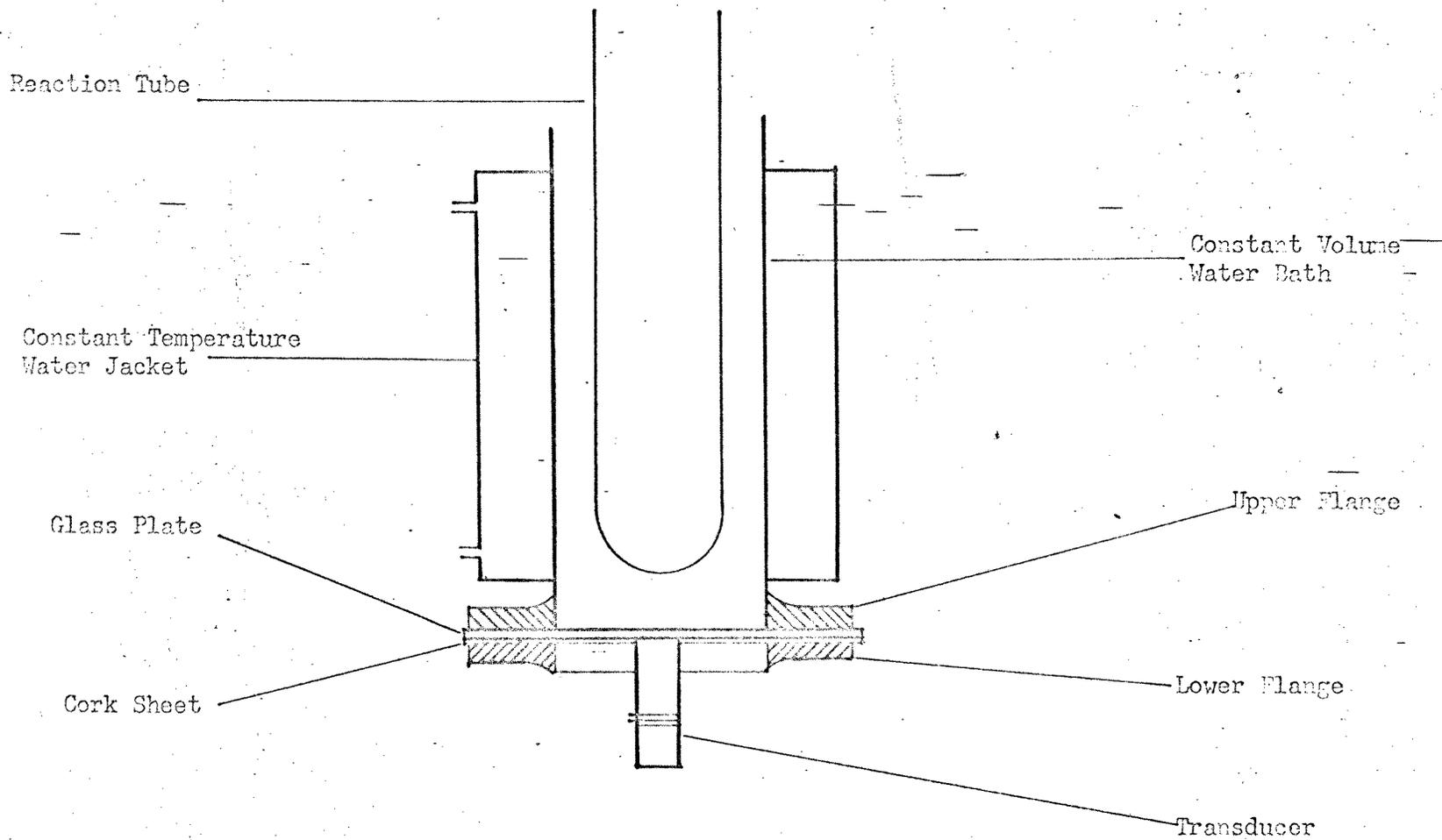


Figure 12 - Reaction Apparatus Assembly

The external water jacket was made of an 8 cm ID plexiglass 3/16" thick with an inlet and outlet for water circulation. The jacket was used to cool the constant volume water bath and the reacting tube as required.

A second air pump was used to air-cool the transducer through a 10 mm aluminum air nozzle during the test. Samples of the reacting solutions were taken from the open end of the reacting tube by means of a pipette and titrated with a burette graduated to 0.05 ml for a high precision titration.