REMOVAL OF NITRILO-TRIACETIC ACID IN WASTE WATER BY WET AIR OXIDATION PROCESS

by

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ABSTRACT

The wet air oxidation process or Zimmermann process is a method to remove suspended solids from waste waters by combining the waste stream and air under some suitable conditions so that liquid water is present.

Theoretically the waste organic is oxidized to carbon dioxide and water and thus removed by conversion to a harmless gas, but practically there are some problems with incomplete combustion and tar formation as in the case of volatile organic substances (e.g. phenol).

This project was undertaken to continue the study of oxidation in liquid-phase, but with a non-volatile substance. Sodium nitrilotriacetate(NTA) was chosen as the non-volatile substance in order to complete the investigation for both volatile and non-volatile components. It was chosen because it is currently allowed in Canada as a phosphate substitute in detergents, and because of its interesting chemistry.

This study was carried out in a non-agitated reactor at temperatures of 200,225, and 250°C. Pressure was varied from 800 to 2200 psig, residence time from 0.25 to 2 hours, and NTA concentration from 10 to 100 ppm. Conversions of 90% were achieved at 250°C and 1500 psig or higher.

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NOMENCLATURE

a	bubble surface per unit volume, cm^2/cm^3
C_m	measured concentration in effluent, g-mole/liter, see page 69
C^o_{NTA}	inlet concentration of NTA, g-mole/liter (for calculation), mg/liter (for experimental works)
C_R , C_{NTA}	true reactor concentration of NTA, g-mole/liter (for calculation), mg/liter (for experimental works)
C_{O_2}	oxygen concentration in solution, g-mole/liter
$C^*_{O_2}$	oxygen concentration at saturation in solution, g-mole/liter, see equation (3)
COD	Chemical Oxygen Demand
D	diffusivity, cm^2/sec
E	activation energy, cal/g-mole
H	Henry's law constant, atm-liter/mole, or atm/mole-fr
k_L	mass transfer coefficient, cm/hr
k_R	reaction rate constant, moles/hr-liter
k_{R_o}	Arrhenius'equation constant
L	liquid flow rate, liter/hr

m_1	an exponent in equation (1)
m_2	an exponent in equation (1)
n	number of moles of air, moles/hr
n'	concentration of NTA, mg/liter, see page 64
P^o, $P^o_{H_2O}$	water vapor pressure, atm or psia
P, P_T	total pressure, atm or psia
ppm	mg/liter
Q	gas flow rate, ft^3/hr
R	gas constant, liter-atm/g-mole - °K
S	stoichiometric ratio, moles NTA/moles O_2
T	operating temperature, °C (for experimental) °K (for calculation)
V_R	reactor volume, liter
x	moles of water vapor, moles/hr, see page 69
y	amouht of liquid in gas-phase, liter/hr
ρ	liquid density, g/cm^3
τ	reactor residence time, hr
μ	liquid viscosity, centipoise
ΔC	change in concentration, g-mole/liter
Re	Reynolds number, dimensionless
Sc	Schmidt number, dimensionless
NTA	nitrilotriacetic acid
Na_3NTA	trisodium salt of NTA
EDTA	ethylenedinitrilo tetraacetic acid
Ph	phenol, see Figure 13

I . INTRODUCTION

From the earliest days, pollution of the human environment has meant many things to different people. It is cleanliness in the environment, it is an orderly and tidy arrangement of the neighborhood, or it is something that can promote the spread of disease.

In our modern world with a tremendous growth of population and industries, man's relation with his environment will become more and more important. He will be affected by many conditions. The contact with air, water, and soil can injure his health, cause economic losses, bring nuisance and inconvenience, and in general have a detrimental effect on his well-being. Yet he cannot escape these contacts. They are essential throughout his existance. He therefore must find the ways to control these conditions so that he can live unharmed and in comfort.

Thus, the environment cannot be entirely free of pollutants or other unnatural conditions. The air cannot be maintained free of all obnoxious ingredients, nor can water be of the same quality as before man inhabited the earth.

Concerning only water pollution, it is clear that the seriousness of this problem and its impact on environmental health is presently the focus of international attention. Never was there a time in the history of man when he was so deeply concerned with the quality of water. Much legislation has been passed and appropriations have been made to restore the quality of man's environment. The chemical industry, accused of being a main contributor to pollution, is undertaking expensive programs designed to limit emissions and improve disposal of industrial wastes as well as to ensure fitness and appropriateness in the use of industrial products.

Detergents are one of the major sources of water pollution. About fifteen years ago, the use of synthetic detergents began to grow due to their superiority over soaps for washing and cleaning. This caused difficulties in sewage treatment, and led to a new form of water pollution, the main visible effect of which was the formation of objectionable quantities of foam on rivers, lakes, and streams. This has since been cleaned up by changing the formula of the detergent so that the ingredients break down or are digested by biological action. The result is no visible detergent effects on bodies of water, but the hidden biological damage called "eutrophication" is the subject of much controversy.

Most of the major detergent manufacturers have been using phosphates because they serve the following functions: soften water by sequestering hardness ions, increase the efficiency of the surface active agent, furnish necessary alkalinity for cleaning and provide resistance to change in alkalinity during washing, reduce redeposition of dirt by keeping the dirt particles in suspension, and emulsify oil and greasy soils.[1] However because they hasten eutrophication which is the process of fertilization of water when phosphorous and other nutrients accumulate in waterways the detergent manufacturers have the goal of finding a substitute for the phosphates.

A very promising substitute for the phosphates in term of cleaning has been identified. It is the sodium salt of nitrilotriacetic acid, $N-(CH_2COONa)_3$, better known as NTA. NTA is a good water softener and can also function to suspended soil. It contains three carboxyl groups and a basic nitrogen in a relatively simple symmetrical molecule commercially produced from ammonia, formaldehyde and hydrogen cyanide.[2] It was being considered as a component of detergents as long ago as 1967. When NTA became available in sufficient quality and at a low price, it was substituted to some extent for phosphate in detergents, for example Lever Brothers Company switched a relatively low-volume brand, SUNLIGHT, to an all-NTA formula and built an advertising campaign around the benefit "phosphate free".[3] But the complete substitution did not occur because not enough NTA was produced for complete substitution accordingly additional manufacturing plants were being built to increase the supply. Work on these plants was not completed because it was found that NTA absorbs moisture and hence the detergent would lump in the box if NTA completely replaced the phosphates; because toxicity of mercury and cadmium are considerably increased when they chelated with NTA;[4] and because of the possibility of cancer-causing problem with NTA investigated by Epstein and Jones.[5]

NTA as a substitute for phosphates thus has been discontinued in the U.S.A. until further testing gives evidence that it is safe in the environment. Since then, many studies have been carried out. Many have found that NTA is biodegradable to natural products, and that NTA would be removed in "well-operated activated sludge wastewater treatment plants".[2,4] It was also found that NTA can be oxidized in the presence of 5% Pd/C at pH 8.5 (90°C for 10 hours) to final forms of CO_2 and H_2O.[5]

The object of this project came about following the fact that many organic compounds can be oxidized readily when combined with air at elevated temperatures and pressures. This study came about following the interest in the oxidation of a non-volatile substance like NTA which combines with our previous work[14] on a volatile substance (phenol) to give a complete investigation of two kinds of organic substances in a contiuous process in a non-agitated reactor at elevated temperatures and pressures.

II . LITERATURE SURVEY

1. BACKGROUND OF WET AIR OXIDATION PROCESS

The Wet Air Oxidation process or Zimmermann process is a method of combustion in which, in a continuous operation under pressure, organic matter is oxidized with air while it is dissolved or suspended in water.

This process was first discovered in 1944 by Zimmermann[6] but was not developed until 1957 when he carried out this process in a pilot plant. He found that many kinds of materials were oxidized successfully using WAO, such as paper mill effluents, sewage, slaughter house effluent, dairy wastes, and oil refinery wastes[7]. He also found that 80% of the total Chemical Oxygen Demand (COD) was removed from the sludge as long as the reactor pressure was 1200 psig. The degree of COD removal was dependent on the temperature at which the oxidation took place, the residence time in the reactor, the concentration of oxidizable material in sludge, and the quantity of air, but excess air to the reactor was not necessary.

In 1960, Zimmermann[8] discussed in more detail the effect of the temperature as he found that between 250°C and 330°C a rise of 15 degrees in reactor temperature permitted at least twice the volume of feed liquor to be oxidized in the same time. But it was also necessary to raise the reactor pressure when the temperature was increased in order to maintain some water in the liquid phase. Some results from his work showed that at 250°C and 1500 psig, the COD was reduced very much the same as at 250°C and 1200 psig even though the flow rate had been increased, but at 250°C and 1800 psig, the percentage of COD reduction was higher (85% compared to 80%) than at 1200 psig even after the flow rate had been doubled. Therefore, higher pressure could make the residence time in the reactor decrease, making the process equipment more compact.

In other papers [9,10], Zimmermann stressed the potential industrial applications of his process as a means of pollution control. It should be interesting also to note that this process has the capacity to produce steam and electric energy to operate the process itself and thus can solve today's problems of energy crisis while concerning about pollution problems.

2. APPLICATIONS TO WET AIR OXIDATION PROCESS

The removal of phenol in waste waters using the Wet Air Oxidation process was first attempted by Shmidt[11]. A batch-type, agitated reactor was used with a temperature range from 150°C to 300°C, pressure from 1075 psig to 2275 psig, contact time from 30 minutes to 2 hours, and feed concentration from 10 to 50 grams of phenol per liter. Shmidt's results showed that there was a considerable increase in the conversion of phenol between 150°C and 225°C but a relatively small increase for further temperature increase. This was in agreement with Zimmermann's results. But the end product, which contained carbon monoxide as well as carbon dioxide, formic acid, acetic acid, and other fatty acids, was different from Zimmermann's. This may have resulted from the limited supply of oxygen in Shmidt's studies.

The purified water, he found, was a transparent, colorless (at 250-300°C) or dark (at 150-200°C) liquid with an odor of acetic acid but he didn't state the cause of this discoloration. He also determined the oxidation of volatile acids by making some runs with acetic acid solution and found that it had a high resistance to oxidation. This agreed with Zimmermann's results that if the reactions were such that a considerable amount of phenol was converted to acetic acid, the acid would not be oxidized to any appreciable extent in this type of reactor so that further treatment of the waste stream would be necessary.

Again in a batch-type reactor, Stepanyan et al[12] studied the liquid-phase oxidation of phenol, methanol, and formaldehyde as well as a mixture of the three under conditions of 40 atm pressure, 200°C , and with contact time varied from 0 to 240 minutes. In the oxidation of phenol solution over a period of 90 minutes, 94.7% of the COD was reduced with a feed concentration of 25 g of phenol per liter. There were no details of the various oxidation reactions but the oxidation of more than one organic compound solution in water could be successful to a considerable extent as they found that 80% of reduction in COD was achieved for a solution of phenol, methanol and formaldehyde in water which made the Wet Air Oxidation process more promising in the purification of waste water.

The Wet Air Oxidation process was used in studying the kinetics of the oxidation of phenol with oxygen by Shibaeva and Metelitsa[13]. They found that it was a function of hydrogen ion concentration and the reaction order with respect to phenol was : first order at pH = 3.0-5.5 and zero-order at lower pH (2.0-0.7). The mechanism for the oxidation of phenol with oxygen was also investigated so that the rate constant of the reaction between phenol molecule and oxygen was calculated.

The oxidation of phenol was again studied by Pruden and Ferguson[14] using the WAO process in an continuous, non-agitated reactor at temperatures of 200 and 250°C, pressures of 800-2200 psig, and residence times of 0.25-2.0 hrs.

Phenol feed concentration was either 1400 or 3000 mg/1. They found that the pressure near the vapor pressure of water at certain temperatures are not suitable for the Wet Air Oxidation plants as in the Zimmermann's case, and that there was a trade-off between pressure and residence time in the high conversion range. A high percentage of conversion (more than 90%) was achieved for conditions at the highest pressure and either temperature. However for low concentrations of phenol (less than 1 mg/1) in the effluent the Wet Air Oxidation process may be undesirable or their type of reactor was not suitable, but this confirmed Shmidt's results that low phenol in the effluent did not mean low COD.

Day et al[15] in a study of the oxidation of propionic acid solutions using the Wet Air Oxidation process found that the oxidation occured homogeneously in the liquid phase and was kinetically controlled between 232°C and 288°C They also made investigations of surface effects and a possible gas-phase reaction but statistical significance tests indicated a negligible influence of the reactor on the oxidation rate and so that the rate was not affected by the gas-phase volume, thus the oxidation appeared to proceed in the liquid-phase as Zimmermann indicated.

The gas-phase oxidation was studied again by Kramarenko[16], who studied the mechanism and the kinetics of the combustion process of substances suspended or dissolved in water under condition of incomplete evaporation in an agitated reactor of a constant volume at temperature of 280-340°C, pressure of 1097-2340 psig. One of their findings agreed with Zimmermann's in the oxidation in liquid-phase of non-volatile substances, soluble or non-soluble in water, as they tested pyrogallic acid (non-volatile and soluble) and charcoal (non-volatile and insoluble) but the other study on the oxidation of volatile substances indicated that the oxidation was in the gas-phase as they tested ethyl alcohol (volatile and soluble) and isO-octane (volatile and non-soluble). This conclusion came about by the fact that there was an accumulation of vapors of volatile substances at the moment when the temperature reaches the ignition level and that an increase in the rate of heating of the system also resulted in a decrease of the amount of substances subjected to low-temperature oxidation in the liquid-phase. Based on these facts, they concluded that the mechanism and kinetics of the combustion process of substances with air at certain temperatures and pressures were dependent on the solubility of the combustible material in water and its volatility. But the conclusions regarding the oxidation of volatile substance occuring in the gas-phase seems to be vague since the studies of Shmidt[11], Shibaeva[13], and Pruden et al[14] on phenol (volatile substance) proved that it occured also in liquid-phase.

A recent investigation of the Wet Oxidation destruction of shipboard waste streams by Schatzberg et al[17] reported that shipboard waste streams including laundry, shower, galley, and sanitary waste (which are pollutants not only because they lower the oxygen content of water containing marine life but also because they are in various stages of decay and carry disease-causing organism) can be treated by wet oxidation conditions in 10 minutes. This was found to destroy all living organisms and convert a large percentage of organic waste to carbon dioxide and water and a small percentage of inoffensive, soluble, easily biodegradable, low molecular weight organic compounds. They concluded that an eight-fold increase in reduction of percent COD was found between 150 to 260°C but a leveling-off effect was observed above 260°C due to reduced partial pressure of oxygen as a result of higher steam pressure, consequently the WAO was not practical above 260°C. This agreed with the findings of Zimmermann[8], Shmidt[11], and Pruden[14] as discussed earlier.

The effect of pH was also studied[17] and it was shown that no advantage was realized by reducing the initial pH to 2, but the addition of catalyst appeared to enhance the Wet Oxidation process since the main advantage of catalysts was to permit operation of the process at lower temperature and hence lower pressure. This could result in the use of a lighter reaction pressure vessel and air compressor without loss of effectiveness, but the catalyst itself may be a pollutant when discharged if it were dissolved or suspended in aqueous medium.

Pope[18] when studying the Zimmermann process also used a combination of metal oxides as a catalyst in addition to elevated temperatures and pressures to achieve the oxidation. He found that the catalytic process was good for a variety of organics such as acetic acid which were not readily oxidized by the Zimmermann process but he did not have any run without catalyst to prove that the catalytic process was better than the Zimmermann process and he ignored the fact that catalyst may be a pollutant when dissolved or suspended in the aqueous solution.

In a more detailed study of the Wet Air Oxidation process with cost analysis by Pradt[19], it was found that at 370°C nearly complete oxidation occured for most substances. He suggested that pure oxygen should be used rather than compressed air since it would give lower cost for the Wet Oxidation plant but still he did not mention whether it should be convenient to handle in a case of continuous process and at high operating pressures. A flow sheet for a biotreatment facility which incorporated Wet Oxidation was proposed since disposal of waste activated sludge is perharps the most difficult, expensive and frustrating aspect of biotreatment of industrial wastes.

The Wet Air Oxidation process thus appears to be very promising since the industry trend to modify process design so as to discharge a smaller volume of more highly concentrated waste will make Wet Air Oxidation more attractive.

3. SOLUBILITY AND DIFFUSIVITY :

The solubility and diffusivity data of oxygen in waste liquid at the high temperature and pressure are required in order to study mass transfer in the reacting system.

Himmelblau[20] has studied the solubility of gases at high temperature and found that Henry's law constant, H , for oxygen in water goes through a maximum ($H = 7\times10^4$ atm/mole-fr) at 94°C, with a value of 4×10^4 at 203°C and 21°C.

St. Denis and Fell[21] recently reported that the diffusivity, D , of oxygen in water appears to be a linear temperature relationship up to 60°C, the temperature limit of the data as they plotted D versus T/μ . The diffusivity at 250°C can be extrapolated using this method and it is obvious that, for temperature above 94°C, the mass transfer coefficient and driving force for the mass transfer steadily increase with temperature. Thus, at normal Wet Air Oxidation conditions, special design precautions for high rate of mass transfer and the mechanical mixing in a bubbling reactor may not be necessary.

4. ANALYSIS OF NTA

There are several methods to determine nitrilotriacetic acid, such as the polarograhic method, colorimetric methods, potentiometric method, and gas chromatography method. For each of these methods, there are several approaches, newly invented or just modifications of each other. The reason for having different techniques in the determination of NTA are due to the convenience of equipment, the sewage conditions and mainly the interference of metals, naturally occuring chelating agents such as aminoacids, and synthetic chelating agents such as EDTA and triphosphate.

The following descriptions are summarized from recently published papers. These methods were studied in order to chose the most effective NTA analysis for this project.

A. POLAROGRAPHIC METHOD

a. Method of Afghan and Goulden[22] (1971)

This differential polarographic method is applicable to the determination of NTA in natural and polluted waters and in sewage samples in the range of NTA concentrations of 0.01 to 3.0 mg/l. Higher concentrations can de determined by dilution of the sample. This method can be also used in the determination of NTA in detergents.

It is based on the formation of bismuth-NTA complex at a pH of 3 which is analysed using differential cathode-ray polarography. It utilizes a two-cell operation in which the signals from the sample solution and the blank solution are balanced, thus eliminating all cell currents not of interest in the analysis. Therefore, full use of current sensitivity of the instrument is made to measure very small quantities of NTA.

There are no known interferences from aminopolycarboxylic acids, amino acids, and pyro-, hexameta-, and tripoly phosphate. Interference from a large excess of iron III can be eliminated by adding hydroxylamin hydrochloride or ascorbic acid (vitamin C) in order to reduce iron III to iron II.

The coefficient of variation at 50 and 100 mg/1 NTA were ± 3.8 and 8.9 respectively, but it should be noted that the David Differential Cathode Ray polarograph type A-1660 used in this method was very expensive and the procedure was quite complex.

b . Method of Haberman[23] (1971)

This method is based on the conversion of the trisodium salt of NTA to a polarographically active complex with iron III in 1 M NaCl, 0.1 M acetic acid, and 0.1 M sodium acetate buffer. Anion exchange concentration and differential polarography were used to increase the sensitivity. A cation exchange column pretreatment was used as a precaution against interfering cations, and isotope dilution analysis with NTA-^{14}C was used to determine the variability of the concentration step.

The technique was evaluated for NTA samples from river water and sewage from 0.0257 to 2.57 ppm with anion exchange concentration.

No evidence of interference was detected in distilled water solution with a ten-fold molar ratio of EDTA, EHDP, citrate, phosphate, carbonate or sulphate to 2.57 ppm Na_3NTA.

The relative standard derivation was approximately 10% except for the lowest concentrations.

c. Method of Afghan, Goulden and Ryan[24]

This method is based on the formation of a bismuth-NTA complex which is analyzed using a twin cell oscillographic DC polarograph. It is an automated method for the determination of NTA in natural water, detergents and sewage samples. It may be operated at the rate of 15 samples per hour and it can be used to detect levels of NTA as low as 10 mg/l.

There is no interference due to metal ions like antimony, arsenic, cadmium, chromidium III, cobalt, copper, iron II , nickel, vanadium, zinc, and indium. Iron III may interfere, but this can be eliminated by adding hydroxylamine hydrochloride to reduce iron II which does not interfere. The coefficient of variation at 100 mg/l was found to be 1.3%

There were several other polarographic methods[26,27,28,29] but none were suitable and effective like those described above.

B. COLORIMETRIC METHOD

a. Method of Thompson and Duthie[25] (1968)

This is a compleximetric, colorimetric procedure involving the reaction of sequesterants with a zinc-zincon reagent. The minimum detectable concentration is 0.2 mg/l Na_3NTA, and the maximum level measurable without sample dilution is 10 mg/l Na_3NTA.

In this method, an ion exchange step is required to remove interfering cations prior to the reaction : Ca and Mg are removed easily and do not interfere; Co, Zn, Ni, and Pb have negligible interference at up to 5 mg/l in the original sample; Fe and Cu may interfere at 5 mg/l; color and turbidity which absorb at 620 mμ will be negative interferences if not removed in sample preparation, but color is not normally significant in laboratory samples and turbidity can be removed by filtration prior to ion exchange; polyphosphates do not interfere; fatty acids give a slight positive interference.

In spite of some positive and negative interferences, this method has been quite satisfactory for laboratory studies of NTA, especially at low concentrations.

b. Method of Vanwelssenaers and Chinckemaille[30] (1971)

This method is based on the colorimetric measurement of the blue-green color of the nickel-NTA chelate. It is automated by the use of a technicon Auto-Analyzer and can operate at a rate of 15 samples per hour.

It was found that iron III and copper II cause no error in this method since their level in detergents is so low (5-20 ppm) and hence the interference of these ions cannot be observed. The nickle-EDTA complex absorbs at 600 mm and would therefore interfere with the method, but EDTA is not usually present in detergents already containing NTA.

The standard deviation was 0.17% and the relative standard deviation was 0.61% on an average result of 28.61% Na_3NTA.

c. Method of Longman, Stiff, and Gardiner[31] (1971)

This is a modification of the zinc-zincon method described by Thompson and Duthie[25] who published a modification of the original procedure of Rush and Yoe[32] (1954).

In this method, an ion exchange column with a cotton-wool plug was used and an aqueous slurry of Chex-100 resin was introduced into this column where the filtered samples were eluted at the rate of 1 ml per min., and the eluate was collected to be mixed with zinc-zincon reagent for absorbance measurement.

There was generally good agreement between the amount of NTA added and the amount of NTA found in various samples. The presence of iron had no effect upon NTA recovery.

Again, there were several other methods[32,33,34,35] in the determination of NTA, but none were suitable and effective as those described above.

C. TITRATION METHOD

The following are two techniques in a number of studies[36,37,38,39] concerning the determination of NTA based on the titration method

a. Method of Clinckemaille[36] (1969)

This method is based on the titration of NTA with copper II chloride in the present of chrome azurol

S as indicator. The phosphates are removed by precipitation with tin II. Chrome azurol S has previously been used in the titration of copper II with EDTA.

Tin II ions do not displace copper from the copper-NTA complexes and thus do not interfere. No interference on Calcium and Magnesium was found.

It was calculated that the amount of NTA found was 98% of the theoretical maount of NTA present. The standard deviation calculated from the results of 5 determinations was 0.06% absolute on an average value of 9.31% NTA.

b. Method of Rechnitz and Kenny[37] (1970)

This method is based on the potentiometric titration of NTA with copper II using a solid membrance copper ion selective electrode.

It was found that NTA can be titrated in the presence of triphosphate without prior separation. The possibility of the determination of NTA in commercial detergent samples containing phosphates and sulphonates was also studied.

It was shown that NTA may be titrated

directly in NH_3-Na_4NO_3 buffer (pH = 9.6) at concentrations as low as $5x10^{-5}$ M but no precision and accuracy were recorded.

D. GAS CHROMATOGRAPHIC METHOD

a. Method of Murray and Povoledo[40] (1971)

This method is based on the well-known chemical property of esterification of NTA to give a volatile derivative that can be measured by gas chromotograghy using methyl heptadecanoate as an internal standard.

This method does not depend on chelation properties, is free of interference from substances present in natural waters, and permits the measurement of NTA in concentrations from 25 mg/l upward with a coefficient of variation of ± 4 %.

b. Method of Lars Rudding[41] (1971)

NTA is first adsorbed on an ion exchange resin and is then eluted with hydrochloric acid. The HCl solution is evaporated and the NTA is esterified using a solution of boron trifluoride in 2-chloroethane. The resulting NTA tri-(2 chloroethylester) is determined by means of gas chromatography.

It was found that there was no interference from metal ions at the concentrations normally occuring in sewage. The possible interference from carbonates was avoided by buffering the sample to pH 5.

The results have shown that NTA added to sewage could be recovered and determined with a satisfactory precision.

c. Method of Chan and Fox[42] (1971)

This method is based on the ease of the esterification of NTA with alcohol. The esters formed have sufficient volatility to permit gas chromatography separation and determination. The NTA is first concentrated on an anion exchange resin, eluted with formic acid and followed by propyl alcohol esterification.

This method is sensitive, specific, and free from the interferences of metals and common fatty acids.

The sensitivity of the method is in the order of 0.01 mg/l (injected) under normal instrument operation conditions.

At the level of 20 mg/1, the standard deviation calculated was 1.3 mg/1, coefficient of variation ± 6.3 %.

d. Method of Longbottom[43] (1972)

This method uses a high efficiency ion exchange chromatograph to detect various amine derivatives. Accordingly, ion exchange chromatography was investigated as a way of separating NTA from other amino acid chelates. By this method NTA was measured over a wide range of sample pH values. Possible interferences from metallic ion were overcome by converting all metal-NTA chelates to the analyzable ferric chelate. The method has been applied to the analysis of sewage samples and solutions of detergent formulations with sensitivity of 1.0 mg/1

At the 1.0 mg/1 level, the deviation was ± 0.02 mg/1, but at 0.2 mg/1 the standard deviation was 0.05 mg/1

Many other gas chromatographic methods in the determination of NTA[44,45,46] were found but these were too complex to study.

From the above description of four

principal methods in the determination of NTA, the colorimetric zinc-zincon method of Thompson and Duthie[25] was chosen as an unique method of NTA analysis for this project with the reasons of its simplicity and its sensitivity, and also because a good spectrophotometer was available.

In spite of some suffering from interference with metals, notably Fe^{+3}, which are more likely than zinc to chelate with NTA and from the inaccuracy in the presence of other chelates or high chloride ion concentrations, the zinc-zincon method was judged the most promising because of its simplicity and its sensitivity. It has been most widely used for the analysis of NTA in lake and river waters[31].

III. THEORY

In order for the reaction to occur, oxygen from the gas bubbles has to diffuse through a gas interface, then a liquid interface to the bulk liquid where it reacts with NTA. These obstacles can be referred to as the gas phase resistance, the liquid phase resistance, and chemical reaction. But earliers workers[47] have shown that the gas phase resistance can be neglected, so that the problem can be formulated in term of the other two.

The rate for chemical reaction is expressed in power law form:

$$\text{rate} = \frac{dC_{NTA}}{dt} = \frac{\text{g-moles}}{\text{hr-liter}} = -k_R\, C_{O_2}^{m_1}\, C_{NTA}^{m_2} \qquad (1)$$

where C_{O_2}, C_{NTA} are the concentrations of oxygen and NTA respectively in the liquid phase in g-moles/liter; k_R is the reaction rate constant; m_1 and m_2 are orders in oxygen and in NTA.

Assuming first-order in both oxygen and in NTA (i.e. $m_1 = m_2 = 1$), the chemical reaction rate becomes:

$$\frac{dC_{NTA}}{dt} = -k_R\, C_{O_2}\, C_{NTA} \qquad (2)$$

Also, assuming that mass transfer is much faster than chemical reaction, then $C_{O_2} = C^*_{O_2}$, where $C^*_{O_2}$ is the oxygen concentration at saturation.

Thus (2) becomes:

$$\frac{dC_{NTA}}{dt} = -k_R \, C^*_{O_2} \, C_{NTA} \tag{3}$$

The chemical reaction rate constant, k_R, is defined by Arrhenius' equation as:

$$k_R = k_{R_o} \, e^{-E/RT} \tag{4}$$

where k_{R_o} is Arrhenius' equation constant, E is the activation energy in cal/g-mole, R is the gas constant in liter-atm/g-mole °K, and T is the absolute temperature in °K

The partial pressure of oxygen, P_{O_2} in atm, is defined by Henry's law :

$$P_{O_2} = H \, C^*_{O_2} \tag{5}$$

where H is Henry's law constant, liter-atm/g-mole.

During the period in which the air is in the reactor there is an amount of water vapor transferred into the bubbles (bubble formation and rise). It was found[48] that the gas was nearly saturated with water vapor on leaving the vessel, therefore the saturation concentration of oxygen, $C^*_{O_2}$, can be found from the equation :

$$C^*_{O_2} = \frac{0.21\ (P_T - P^o_{H_2O})}{H} \qquad (6)$$

From (4) and (6), (3) becomes:

$$\frac{dC_{NTA}}{dt} = -k_{R_o} \cdot \frac{0.21\ (P_T - P^o_{H_2O})}{H} \cdot C_{NTA} \cdot e^{-E/RT}$$

or:

$$\frac{dC_{NTA}}{dt} = \frac{\Delta C_{NTA}}{\Delta t} = \frac{C_{NTA,\ out} - C_{NTA,\ in}}{\tau}$$

$$= -k_{R_o} \cdot \frac{0.21\ (P_T - P^o_{H_2O})}{H} \cdot C_{NTA} \cdot e^{-E/RT}$$

where τ is residence time, in hours;and ΔC_{NTA} is the change in concentration of NTA, in moles/liter.

By rearranging:

$$\frac{0.21\ k_{R_o}\ e^{-E/RT}}{H} = -\frac{\Delta C_{NTA}}{\tau \cdot (P_T - P^o_{H_2O}) \cdot C_{NTA}} \qquad (7)$$

The left-hand side of the above expression should be constant with constant temperature. It follows that the right-hand side term would be constant for different runs of different pressure, residence time, and feed concentration if the assumptions were correct.

A similar expression to (7) can be found for different order in oxygen and in NTA. But for this project, the assumption of first-order in both components was suitable, and this is the first theoretical basis for the experimental runs to be made in order to ensure that oxidation could be carried out successfully.

If the reaction rate were controlled only by mass transfer of oxygen to the reaction side (i.e. if the chemical reaction is very fast), the rate can be expressed mathematically as :

$$\text{rate} = k_L\, a\, S\,(C^*_{O_2} - C_{O_2}) \qquad (8)$$

where k_L is mass transfer coefficient; a is the bubble surface per unit volume, cm^2/cm^3; S is the stoichiometric ratio, moles NTA per moles O_2 .

By material balance the rate can be expressed as :

$$\text{rate} = \frac{L}{V_R} \cdot \Delta C_{NTA} \qquad (9)$$

where L is liquid flow rate, liter/hr; V_R is reactor volume, liter. This equation can be used with equations (8) and (2) to obtain an equation where the effects of mass transfer and chemical reaction must be considered.

Because the gas-holdup in the non-agitated reactor is small (2%), the residence time, τ, in the reactor is:

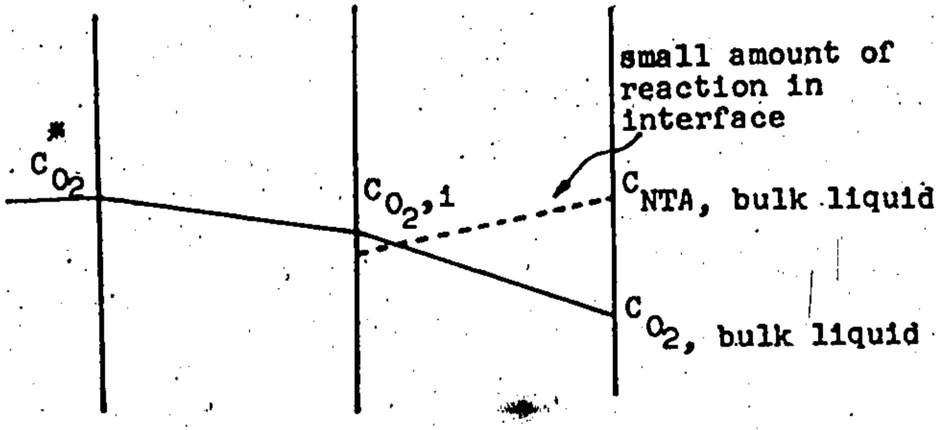
$$\tau = \frac{V_R}{L} \tag{10}$$

Eliminate C_{O_2} in (2) and (8), then combine with (9) and (10) to get:

$$\frac{\tau C_{O_2}^{*}}{\Delta C_{NTA}} = \frac{1}{k_R\ C_{NTA}} + \frac{1}{k_L\ a\ S} \tag{11}$$

which has been derived by Levenspiel[49].

The above simple theory was used since there is no information available at the present time for the diffusivities of NTA and oxygen in water at high temperature. No consideration has been made of reaction taking place in the interface or very small amounts of reaction in the interface as in the model in the following figures:



(note : $C_{O_2,i}$ is C_{O_2} at interface)

IV. EXPERIMENTAL

A. APPARATUS

A small-scale pilot plant was designed based on sketches in Zimmermann's paper[7] with some modifications to suit the scale of operation (Figure 1).

a. MAIN EQUIPMENT

1. *Air compressor* was a two-stage, diaphragm type, model Q-07038, supplied by PPI (pressure Products Industries). Its maximum suction and discharge pressures were 65 psig and 5000 psig respectively, with a maximum flow rate of 2.09 SCFM. This flow rate was regulated by a needle valve and a rotameter in the discharge line.

2. *Liquid pump* was a pulsafeeder diaphragm type metering pump, positive displacement, model CP-3, supplied by Interpace Corporation, Lapp Insulation division, Le Roy, New York. Its maximum capacity was 0 and 242.8 USGPH corresponding to output pressures of 5000 and 50 psig respectively. The output was regulated from zero to maximum by adjusting the slave piston stroke-length.

3. *Non-agitated reactor* was made of 316 stainless steel, and had a capacity of 1 liter. It was

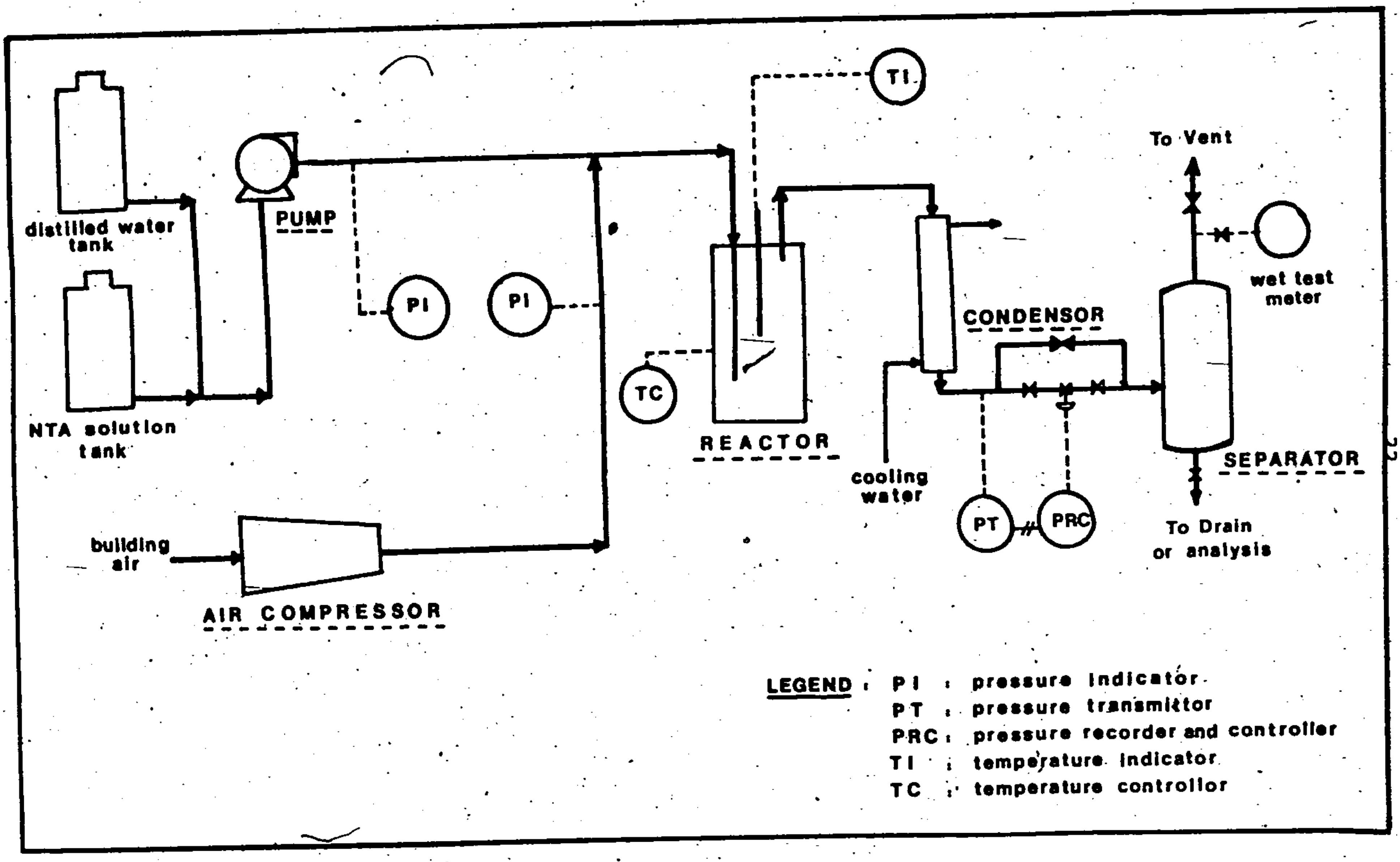


Figure 1: Schematic diagram of apparatus

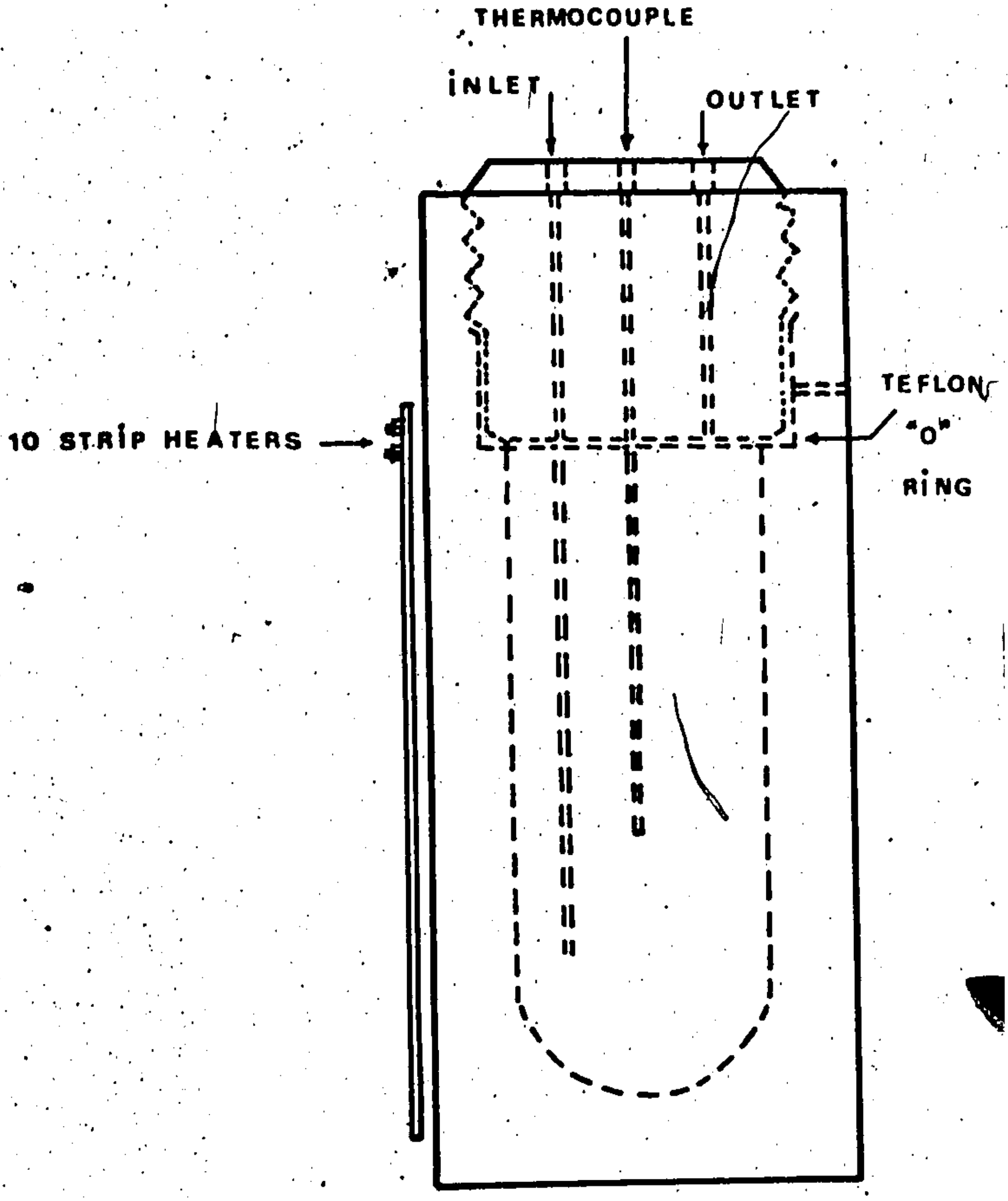
made to our specifications by PPI, Hatboro, Penn. Maximum pressures and temperatures were to 7500 psig and 350°C respectively. It was designed to run full of liquid with liquid and gas entering and leaving through top inlet and outlet connections as shown in Figure 2. The reactor internal temperature was maintained by 10 electrical strip heaters connected in series, and measured by a thermocouple which was also placed through a top connection (see Fig. 2)

4. Condenser was made by the department machine shop. It contains a LP stainless tube and a shell of 4 inches ID copper pipe. Cold water in the shell was allowed to flow counter-current to the process stream.

5. Separator was a stainless steel cylinder of 23 inches height and 8 inches outside diameter. A thermocouple was installed to read the liquid temperature in the bottom of the separator.

b. CONTROL DEVICES

1. Temperature controller for reactor: was a Brown Pyr-o-vane, supplied by Honeywell Control Limited, which could control up to 1400°F and had a manual pointer to set the desired temperature. It was connected to a series of 10 electric strip heaters which were model SE 1202, 25 watts each, supplied by Canadian Chromalox Limited, Toronto



REACTOR

10" HIGH

5" O.D.

3" I.D.

ONE-LITER VOLUME

2. Temperature indicator and recorder was an Electronik 16 multi-point strip chart recorder, supplied by Honeywell controls Ltd. It had a continuous balance servo potentiometer which automatically measured the temperature in up to 12 points. The temperature range of the instrument was 0 - 400°C.

3. Pressure control system was a basic Pneumatik Tel-O-set control system, supplied by Honeywell Controls Ltd., which consisted of three units:

- a transmitter measured the process variable and sent a proportional air pressure to the receiver and the controller, it was a non-indicating type, model 738 N 1H3, range 0-1400 psig.
- a receiving control station recorded or indicated the process variable, transmitted a set point pressure to the controller, and incorporated provisions for manual-automatic switching and manual regulation of air-to-valve pressure. It was a model 51311 (single pen).
- a controller compared the process variable signal with the set point signal and positioned the final control element to maintain the process variable at the desired set point. It was a two-mode PI controller, model 52201.

4. Wet test meter was used to check the air flow rate independent of the rotameter in the discharge line of

the compressor. It was a " Precision " type, No. 11-166-5, capacity of 1/10 cubic foot, supplied by Fisher Scientific Co. Ltd, Ottawa, Ont.

5. Hand pump was used for hydraulic pressure testing of the system before operating. It was a model OH-100-15, supplied by PPI.

6. Control valve was a 1/4 in. Research control valve supplied with various trims with a C_v value of 0.00012 to 0.0013 . We used a trim with C_o value of 0.0006 .

c. OTHER EQUIPMENT

1. Tubings, valves, fittings were 1/4 in. LP (low pressure) 316 stainless steel, supplied by PPI, Hatboro, Penn.

2. Feed tanks were polyethylene bottles of 13-gallon capacity with spigot, No. 137586-13, supplied by Canadian Laboratory Supplies Ltd., Montreal.

B. CHEMICALS

1. Nitrilo-triacetic acid (trisodium salt)
supplied by Sigma Chemical Company,
3500 Dekalb St. St. Louis, Miss. USA

2. Dowex 50W-X8 resin (20-50 mesh) supplied

by Alchem Ltd., Burlington, Ont.

3. Zinc sulphate (crystal), boric acid (crystal) Potassium chloride (crystal) supplied by by J.T.Baker Chemical Co. Phillipsburg, N.J.
4. Sodium hydroxide solution (10 N), Zincon reagent, hydrochloric acid solution (2N) supplied by Fisher Scientific Co., Ottawa, Ont
5. Sodium hydroxide (1N) supplied by BDH Chemicals, Montreal.

C. EQUIPMENT FOR ANALYSIS

1. Spectrophotometer was a B&L Precision spectrophotometer, model No. 14-385-680 with 14-385-621 digital readout accessory. The unit was complete with light source and power supply; quatz-iodine, deuterium, and mercury lamps; 1 set of 10 mm square silica cuvets, dust cover, and reference manual. The range switch could be selected from these photometric ranges: - 10% and 100% transmittance and 0.0 to 2.0, 0.5 to 2.5, and 1.0 to 3.0 absorbance at full scale values. Two lamps covered the whole 190 mμ to 700 mμ wavelength range.

2. pH meter was a Fisher Accumet pH meter, mode 220, model 13-637-20.

3. Stirrer was a magnetic stirrer, model PC-353, Corning. Stirring range was 80-1400 rpm.

D. ASSEMBLY AND CALIBRATION

1. Assembly The assembly was done mainly by the machine shop staff. A hand pump was used to check for leaks at high pressure. The whole system was safe if it was operated below 5000 psig which is the limit pressure for both reactor and compressor.

2. Compressor calibration The compressor was 3-years old, and it broke down once due to failure of the "O" ring seals in the high pressure chamber. Therefore its effectiveness was different than when it was new. Also condensate in the compressor flowed out through the rotameter which affected the rotameter calibration curve. The original curve for the compressor calibration, supplied by PPI was not used, and should not be used by future workers. The actual calibration for each run was done with a wet test meter to ensure an accurate gas flow rate, which could fluctuate due to the change in atmospheric pressure and in daily room temperature change. A sample calculation of this calibration can be seen in detail in the appendix.

Another problem when operating the compressor was that it made too much noise. A plywood box with access door around the compressor was ~~thus~~ constructed and lined with fiber glass insulation to solve this problem.

There was also a fan in one wall of the box to cool off the compressor due to a long period of operation.

3. Pump calibration There was a pump calibration curve supplied by Interpace Corporation, Lapp Insulator Division, LeRoy, N.Y., but it was checked and shown somewhat different because the pump was three-years old. A new calibration curve was made and checked again from time to time for each run by allowing the reactor to fill with liquid, then collecting the effluent liquid through the separator while taking the time period.

4. Temperature calibration The temperature inside the reactor was recorded through a thermocouple which was previously checked. The temperature control was indirect: that is the reactor skin temperature was controlled to give the correct internal temperature. This was done to prevent burn-out of the heaters during startup, and to make the system failsafe.

E. PROCEDURE

The heaters were turned on and left on at all time to avoid any leaks in the Teflon seal ring caused by alternate heating and cooling. The operation procedure was as follows:

1. The NTA solution was prepared: since NTA concentrations used in this study were small (10-100 ppm), care

was taken in weighing and diluting. For example, in order to have 50 liters of 20 ppm NTA concentration solution, 1 g of NTA powder was weighed in a small beaker (50 ml), dissolved in distilled water; transferred with rinsing to a volumetric flask and diluted to 1 liter. This was then transferred to the NTA feed tank and another 49 liters of distilled water were added using the same flask. This sample concentration was checked by analysis to ensure that it was 20 ppm as desired.

2. The liquid feed rate was selected and distilled water was allowed to flow in the reactor first to avoid tar deposits in the reactor which could occur, since the reactor was hot and the first water entering the reactor was vaporized.

3. The desired operating pressure was set using the manual switch of the pressure controller then the compressor was started with all the air discharged through the bleed rotameter. This was continued for 10 or 15 minutes, then the discharge valve was opened to let the air go through the reactor and the air flow rate was adjusted from the bleed valve. The bypass valve in diagram 1 was closed at this point.

4. After the desired pressure was reached, the

pressure control was switched back to "automatic". In order to reach the constant desired pressure of the system the pressure controller or bleed valve was adjusted if necessary. While doing this, the air flow rate might be changed, requiring adjustments to the pressure controller and bleed valve again, and also measurement of the air flow rate with the wet test meter until steady state was reached.

5. While doing the above part, the desired temperature was set and adjusted.

6. When the desired temperature and pressure were reached, the NTA feed was started.

7. After five or six residence times, the effluent liquid was collected for analysis. This was repeated one or two residence times thereafter.

8. The feed was switched back to distilled water at high rate to clean the reactor for the next run and to avoid any NTA charring on the reactor walls when depressuring the reactor.

9. The whole system was finally shut off as follows:

- liquid pump power was turned off.

- bypass valve was opened to depressure the reactor.
- pressure controller was slowly set to zero-pressure mark.
- bleed valve was opened, discharge valve was closed.
- compressor was allowed to run 10 minutes before power was turned off.

F. ANALYSIS

The zinc-zincon method[25] was used for NTA analysis. A detailed procedure is given in the Appendix. The departure from the published analysis method was to have a calibration curve of NTA concentration versus absorbance as in Figure 3A, then each sample concentration could be read directly from this curve according to its absorbance.

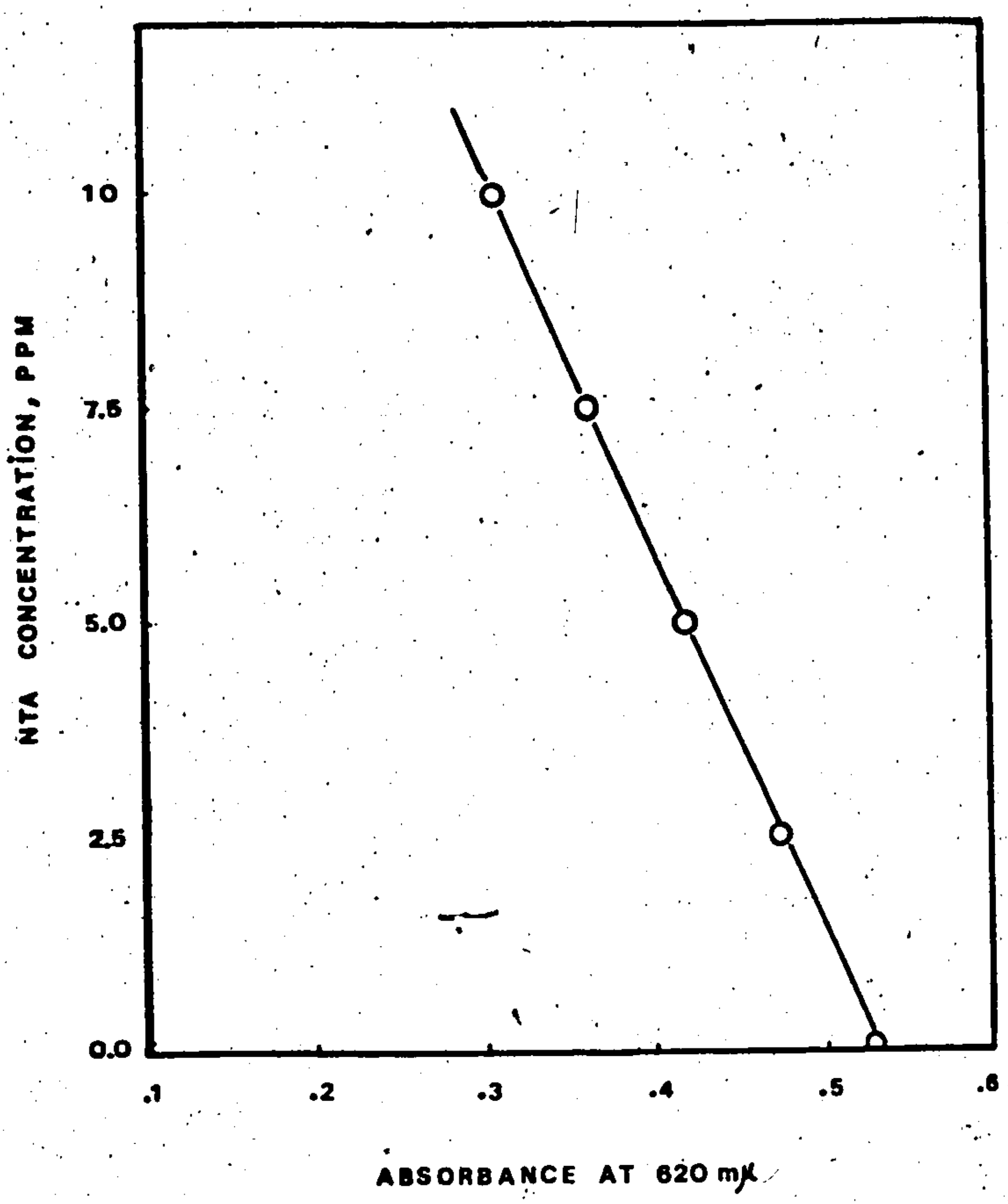


Figure 3A: Calibration curve for the determination of NTA

V. RESULTS AND DISCUSSION

1. ANALYSIS

The determination of NTA was an important first problem for this project since it is hard to find a reliable method which is simple, easy to work with, and which does not require expensive equipment but should give good results even at low concentrations of NTA. The method of Thompson and Duthie[25] was found to be suitable for our requirement because of its simplicity and sensitivity, and the availability of a good spectrophotometer.

The determination of NTA by Thompson and Duthie's method was studied for NTA in both the acid and sodium form.

a. Analysis of NTA in acid form, $N(CH_2COOH)_3$

The data of NTA concentrations versus absorbance in Table 6 were obtained using the Thompson and Duthie procedure on triplicate samples, and were plotted in Figure 3B, Curve A. The curve is not linear, even in the range of low concentrations, 0 - 10 ppm, which is unexpected since there should be a linear relationship between concentration and absorbance.

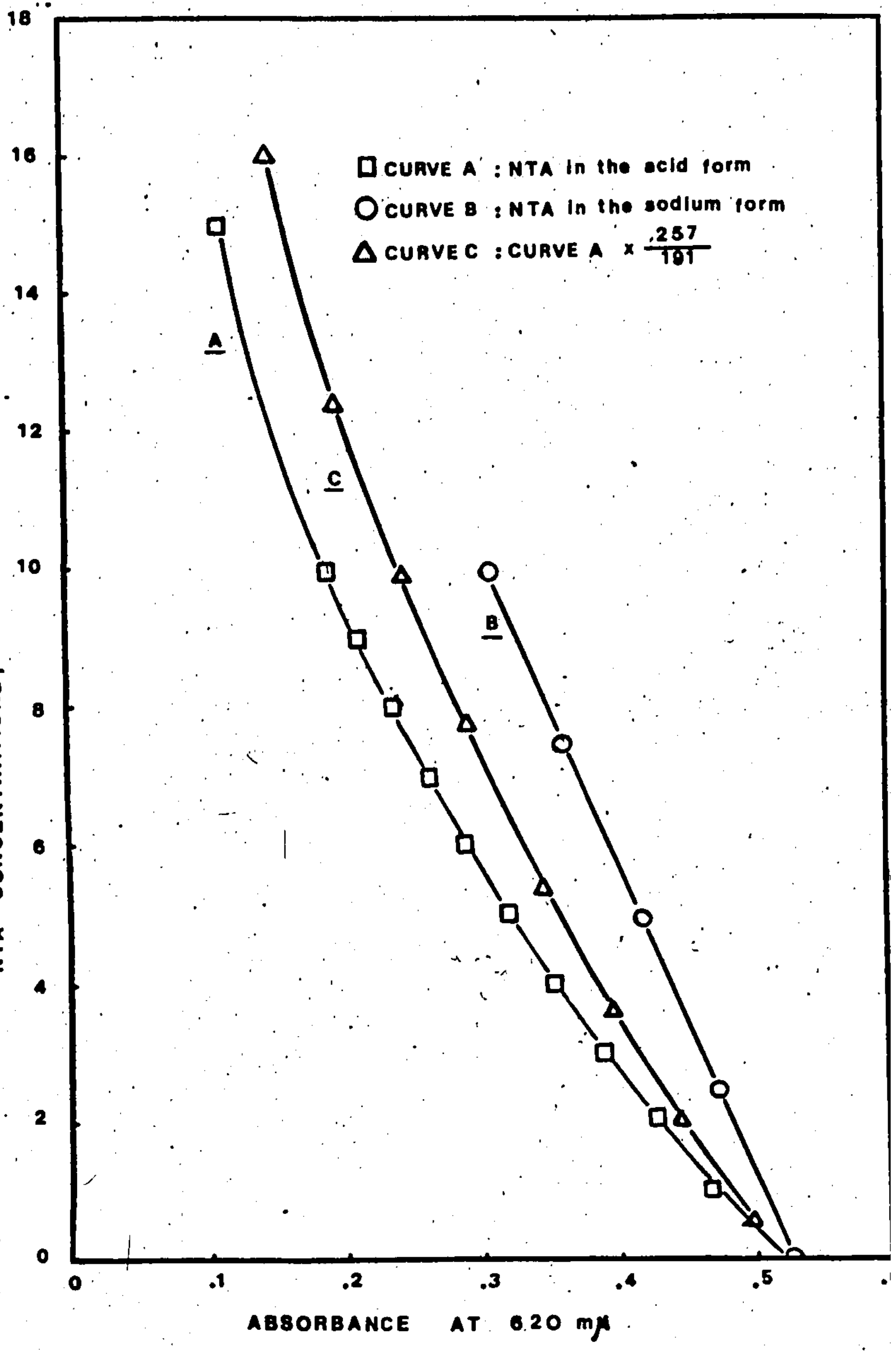


Figure 3B: Calibration curves for the determination of NTA

The formula given by Thompson and Duthie,

$$\text{sample conc.} = \frac{\text{Blank abs.} - \text{sample abs.}}{\text{Blank abs.} - \text{abs. of 5 mg/1 NTA}} \times 5 ,$$

to caloulte NTA concentration without direct reading from a calibration curve was found to be somewhat inaccurate so that it was not applied to any further determination of NTA concentration, and direct reading from the calibration curve (Figure 3B) was used instead.

b. Analysis of NTA in sodium form, $N(CH_2COONa)_3$

The same routine of Thompson and Duthie's method was repeated in the determination of NTA in sodium form. The data in Table 7 were also obtained using the zinc-zincon procedure with triplicate samples to minimize the error in absorbance reading, and were plotted in Figure 3B Curve B. It is evident that there was a linear relationship between NTA concentration and absorbance as Thompson and Duthie indicated.

c. Relationship of Curve A and Curve B in Figure 3B

The different of Curve A and Curve B in the determination of NTA in acid form and in sodium form using the same buffer solution and zinc-zincon reagent was first assumed to be due to the different molecular weights of NTA in acid form (molecular weight = 191) and in sodium form.(molecular weight = 257). Therefore Curve C was plotted from Curve A with a correction factor of $\frac{257}{191}$. The plot of Curve C in Figure 3B showed that the difference of Curve A and Curve B was not only because of different molecular weights but might be also in the different chemistry and physical properties of NTA in both forms.

2. EXPERIMENTAL RUNS

The first four runs were made at different pressure, liquid flow rate and with no air flow rate in order to ensure that there was no reaction in the absence of air. The conversion in these runs was zero as expected.

The next 50 runs were made at different temperatures, pressures, residence times, and with an air flow rate of 0.5 ft^3/hr (at conditions). The air feed rate was chosen on the basis of studies in a similar bubbling reactor at atmospheric pressure, and because the presence of a large amount of excess oxygen was desired.

Runs at 200°C and 250°C with feed concentration of 20 ppm at different pressures and residence times are summarized in Figures 4 and 5. It can be seen from these

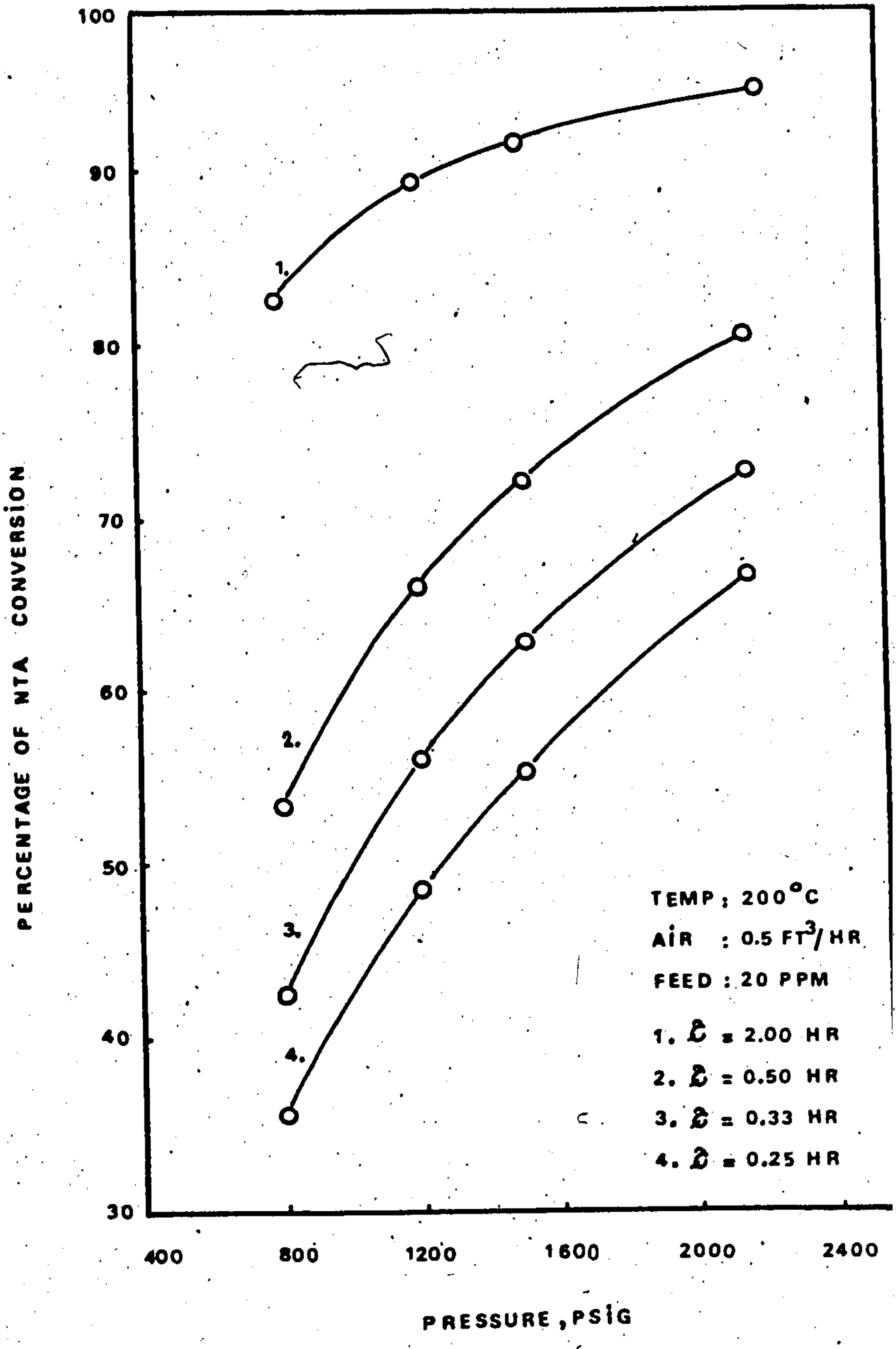


Figure 4: Conversion versus pressure for 200°C and 20 ppm feed

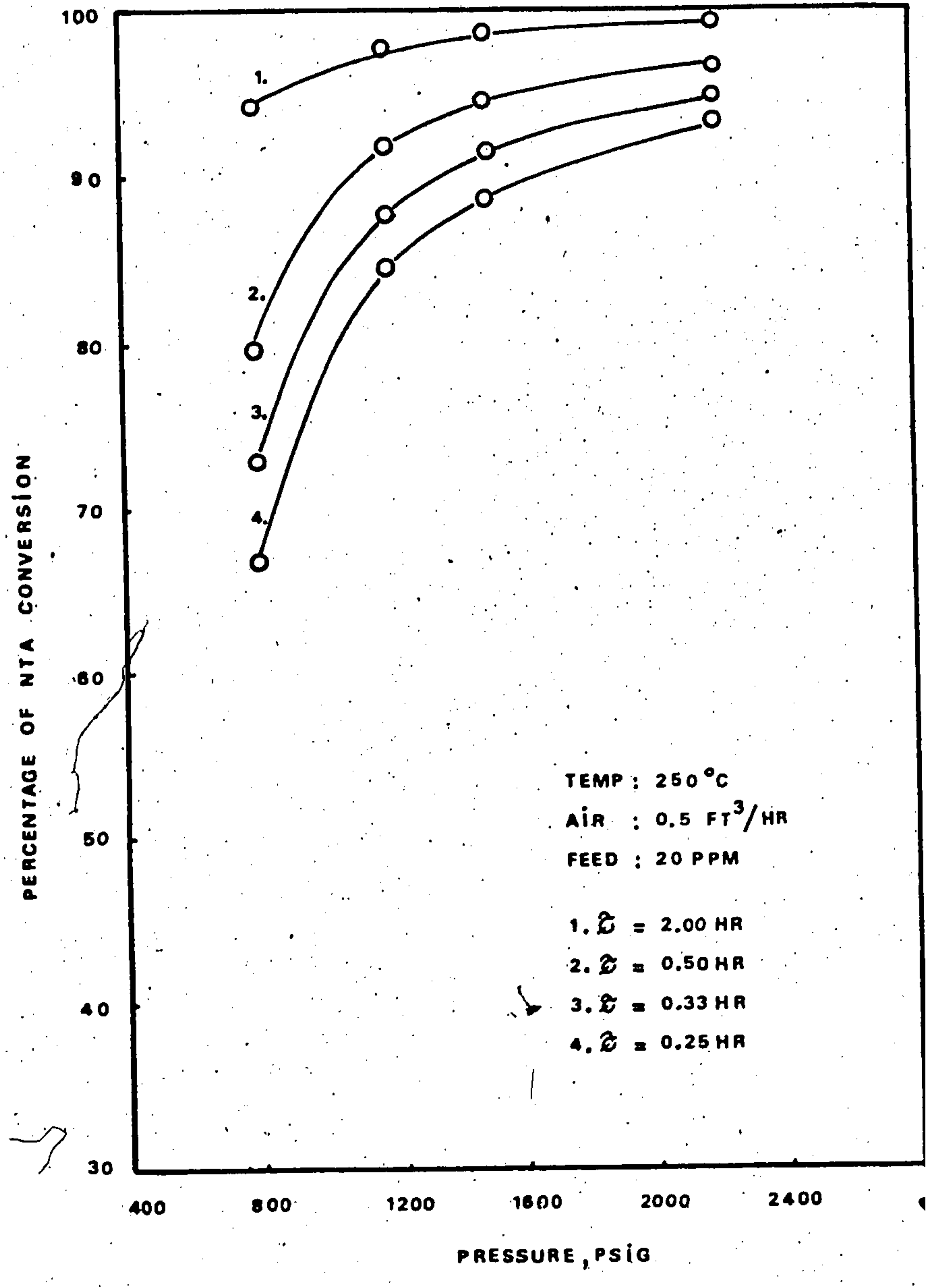


Figure 5 : Conversion versus pressure for 250° C and 20 ppm feed

figures that the percentage of NTA reacted is higher at higher temperature. The temperature of 250°C is more effective for the wet air oxidation process.

It is obvious from these runs that pressure is an important parameter. In order to have an understanding about the effect of pressure in this process, equations (6) and (11) in the theory section can be recalled as follows:

$$C^{*}_{O_2} = \frac{0.21\,(P_T - P^{o}_{H_2O})}{H} \qquad (6)$$

and

$$\frac{\mathfrak{C}\, C^{*}_{O_2}}{\Delta C_{NTA}} = \frac{1}{k_L\, a\, S} + \frac{1}{k_R\, C_{NTA}} \qquad (11)$$

by substituting (6) into (11) :

$$\frac{\mathfrak{C} \times 0.21\,(P_T - P^{o}_{H_2O})}{\Delta C_{NTA}\; H} = \frac{1}{k_L a S} + \frac{1}{k_R C_{NTA}} \qquad (12)$$

or the conversion term, $\frac{\Delta C_{NTA}}{C^{o}_{NTA}}$, can be derived from (12) :

$$\frac{\Delta C_{NTA}}{C^{o}_{NTA}} = \frac{\dfrac{0.21\,\mathfrak{C}\,(P_T - P^{o}_{H_2O})}{H\, C^{o}_{NTA}}}{\dfrac{1}{k_L a\, S} + \dfrac{1}{k_R\, C_{NTA}}} \qquad (13)$$

where C^o_{NTA} and C_{NTA} are the inlet concentration and true concentration of NTA in the reactor respectively (see detailed calculation of C_{NTA} in appendix : they are different because some water is vaporized in the reactor, increasing the reactor concentration over the outlet concentration).

Assuming that k_L in equation (13) is constant by keeping the air flow rate the same for all runs at one temperature with different pressures and residence time (this can be maintained since the volumetric air flow rate of 0.5 ft^3/hr provided a large excess of oxygen and good liquid mixing), the effect of pressure decrease will be large when total pressure, P_T , approaches the water vapor pressure, $P^o_{H_2O}$, (this makes the numerator in equation (13) go to zero); and the effect of NTA concentration, C_{NTA} , will increase as C_{NTA} approaches zero this makes the term $(1/k_R C_{NTA} + 1/k_L a\ S)$ go to infinity no matter what value of k_L a S.

Figures 6 and 7 show the effect of residence time. The vapor pressure of water at 200°C and 250°C is 225 and 576 psia (Table 5) respectively. It is clear that the wet air oxidation process is not effective when the system pressure approaches the vapor pressure of water at system conditions, especially at temperatures below 200°C.

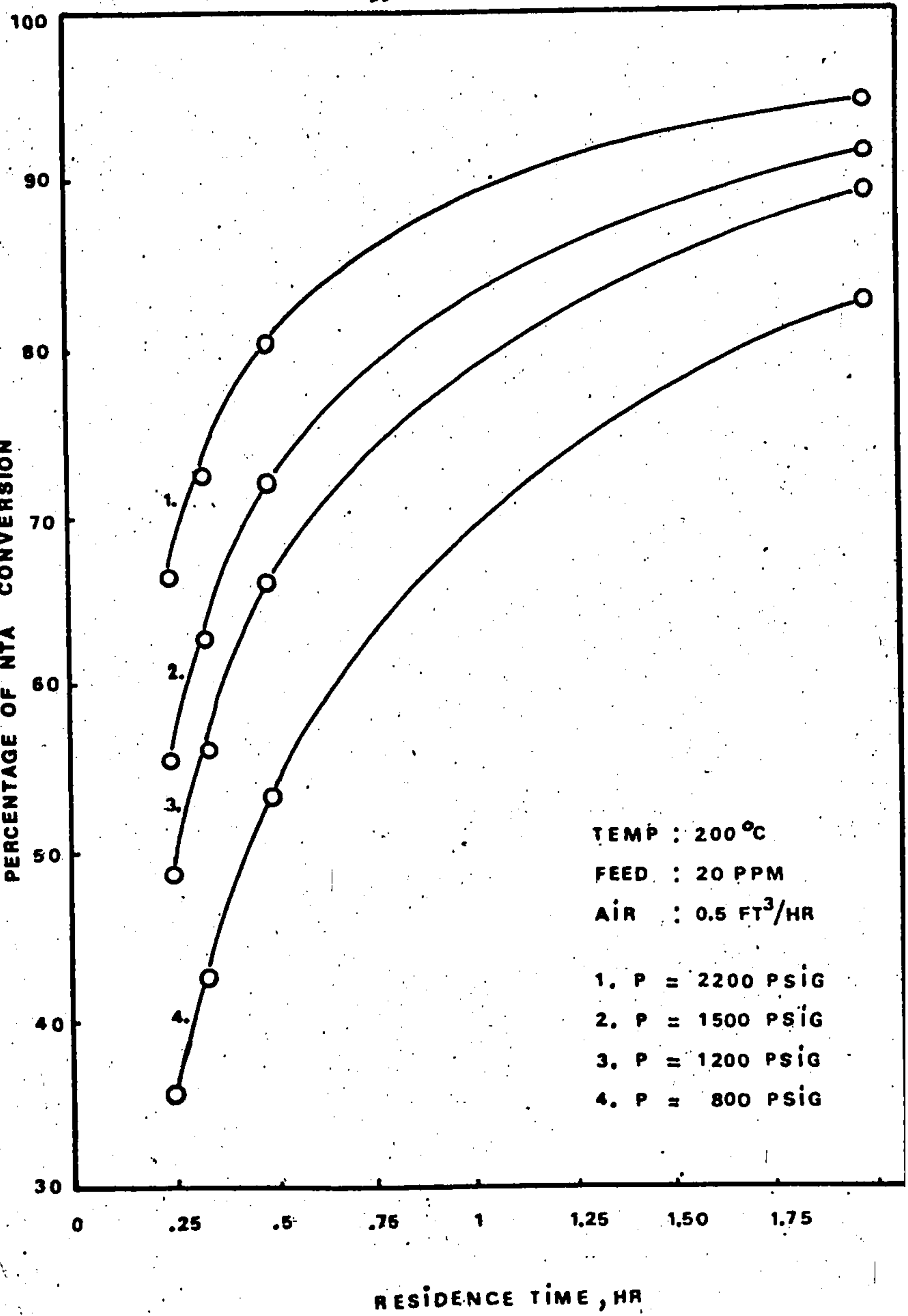


Figure 6: Conversion versus residence time with pressure as parameter

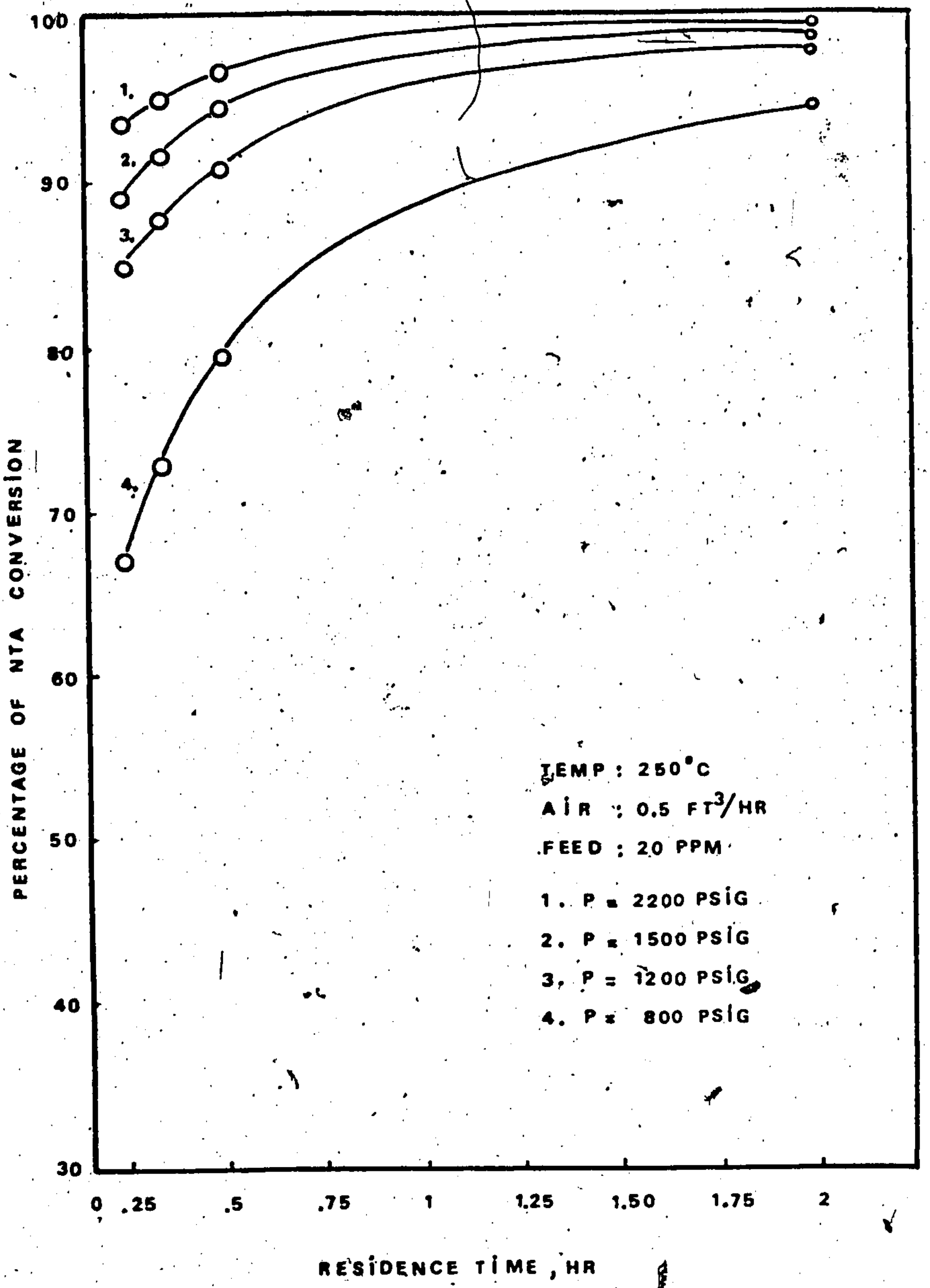


Figure 7 : Conversion versus residence time with pressure as parameter

Also from Figure 7 at 250°C and above 1500 psig, the NTA conversion is almost constant over the residence time of 0.5 hour or higher, while at lower pressure, the conversion drops sharply as residence time decreases. This shows the the reaction occurs more rapidly at higher pressure and that the residence time could likely be reduced to just a few minutes without experiencing a significant drop in conversion.

From these runs, a plot of $\frac{\tau C^*_{O_2}}{\Delta C_{NTA}}$ versus $\frac{1}{C_{NTA}}$ in equation (11) for three different temperatures of 200, 225, and 250°C is truly a straight line (Figures 9, 10, and 11 respectively) and this agrees with the assumption of constant k_L and first order in both NTA and oxygen.

Note that the NTA concentration in the reactor, C_{NTA} for Figures 8, 9, and 10 was computed from the effluent concentration assuming that the exit gas was saturated with water vapor, and that NTA vapor in the exit gas was in equilibrium with the NTA liquid concentration in the reactor. A least square fitting of data gave three values of the chemical rate constant k_R for three temperatures, and a plot of $\ln k_R$ versus $\frac{1}{T}$ in Figure 11 is a straight line which shows that the data are consistent with the Arrhenius equation for variation with temperature. From

Figure [illegible]: Plot of equation 11 to determine mass transfer product and reaction rate constant at 200°C

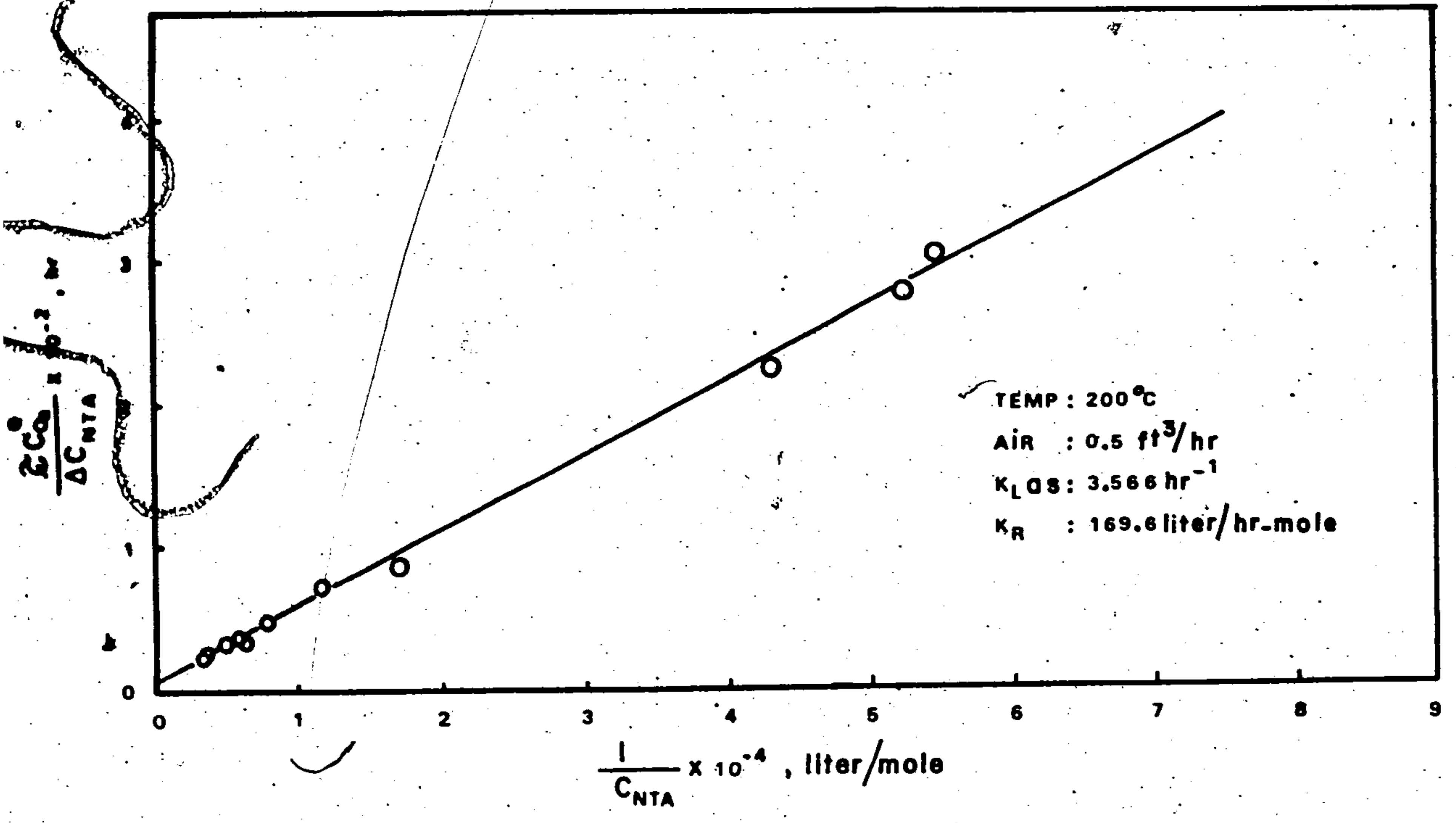


Figure 9 : Plot of equation 11 to determine mass transfer product and reaction rate constant at 225°C

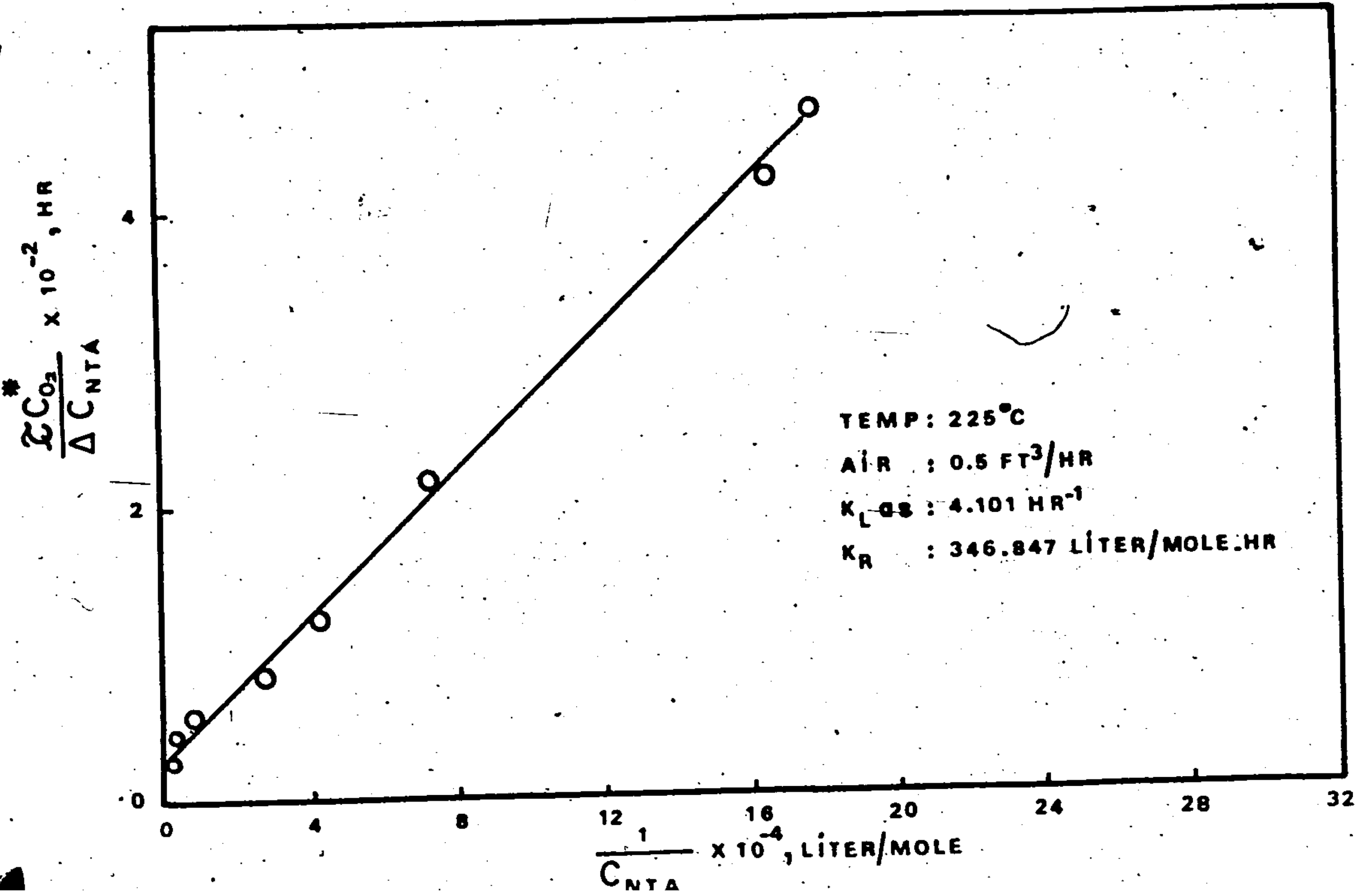
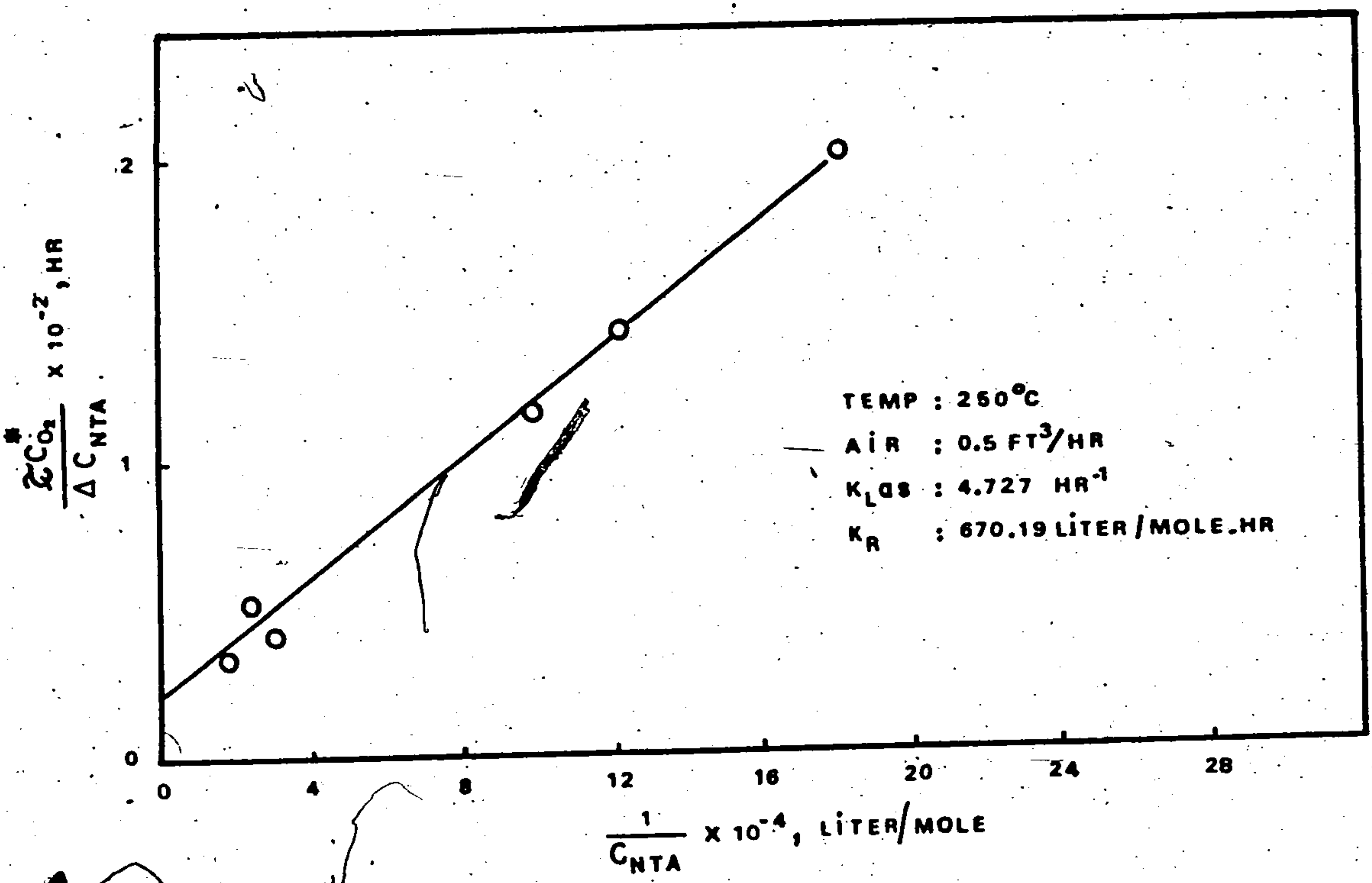


Figure 10: Plot of equation 11 to determine mass transfer product and reaction rate constant at 250°C



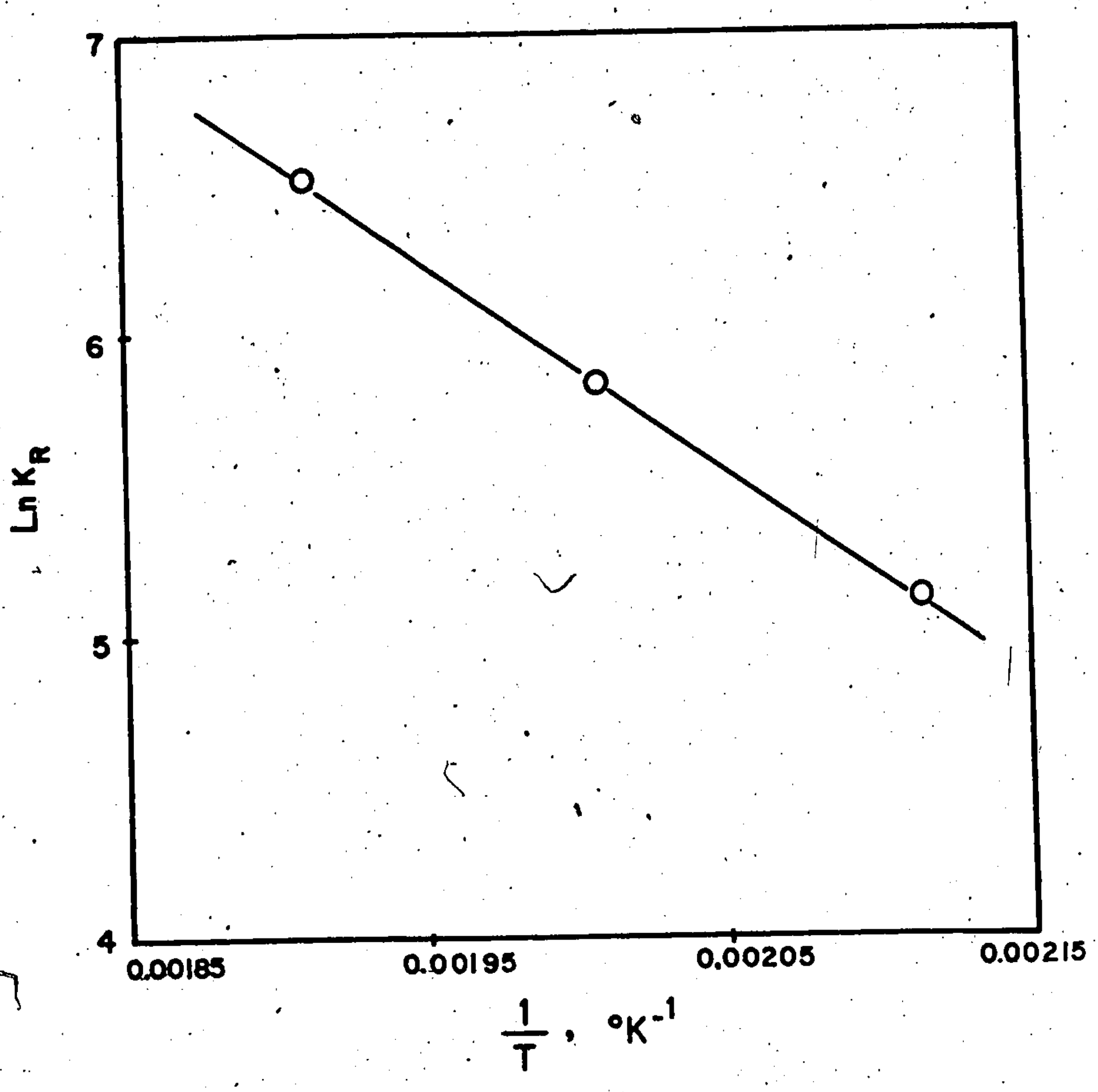


Figure 11: Reaction rate constant versus temperature

the slope of this line, an activation energy of 13000 cal/mole was calculated, which is reasonable for this type of reaction[49]. Ploos Van Amstel [50] found that the activation energy of the oxidation of both activated and primary sludges was 2300 cal/mole. Shibaeva et al[17] found that the activation energy for oxidation of phenol was 25000 cal/mole while in the same study of oxidation of phenol, Pruden and Ferguson[14] only got a value of 10800 cal/mole but this is more reasonable according to Levenspiel[49]. The high value of the activation energy obtained in this project was consistent with the model assumption that the reaction is not controlled by mass transfer through the air-water interface as discussed earlier in theory section.

In the theory section, it is obvious that there was no proof of the first order reaction in both NTA and O_2, only that the model works for the concentration range (10 - 100 ppm) and is consistent with first order. This can be true, however, since the mass transfer rates were much higher than required to supply the needed oxygen when compared with the previous work on phenol by Pruden and Ferguson[14]. Their data were plotted in Figure 12 according to the rate equation (neglecting mass transfer), and proved to be first order. In addition to this certainly many other previous workers proved that the reaction behaved

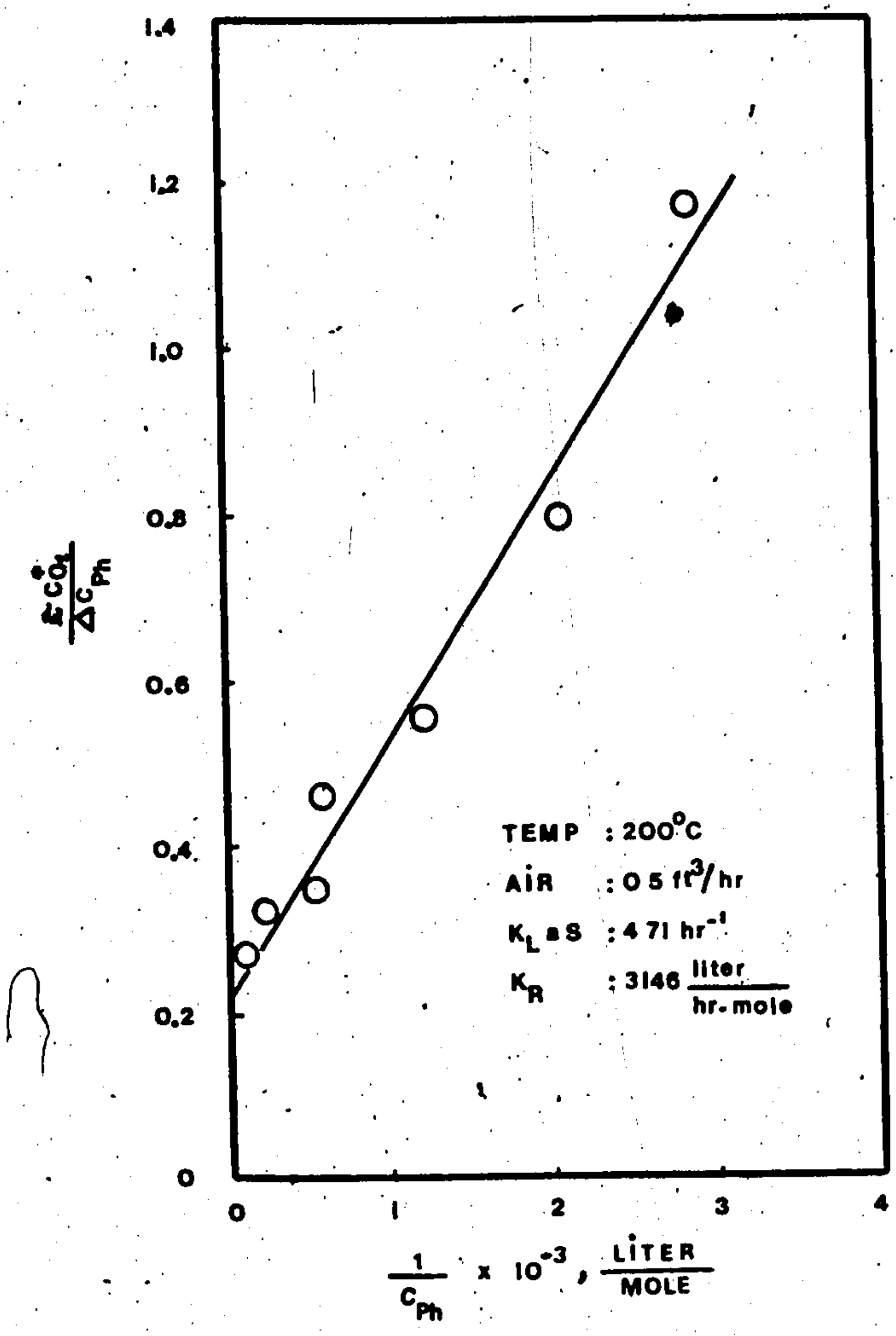


Figure 12 : Plot of equation 5[14] to detemine mass transfer product and rate constant at 200°C

like first order; Ploos Van Amstel[50], studying the oxidation of glucose solutions and real sludges, found that the rate of oxidation was first order in both oxygen and substance oxidized. Weygandt[51] found also that the rate was first order in an organic compound and in oxygen as he oxidized primary, secondary, and tertiary alcohols; Shibaeva et al[13] confirmed that the rate of oxidation of phenol was first order in both oxygen and phenol, and so did Pruden and Ferguson[14].

The variation of k_L a S values with temperature $\left(\frac{k_L, 225^\circ C}{k_L, 200^\circ C} = 1.15 \; ; \; \frac{k_L, 250^\circ C}{k_L, 200^\circ C} = 1.32\right)$ obtained by least square fitting of the data are quite consistent when compared with the theoretical values which were calculated from Sherwood's equation[51] combined with Stokes-Einstein's equation[52] $\left(\frac{k_L, 225^\circ C}{k_L, 200^\circ C} = 1.136 \; ; \; \frac{k_L, 250^\circ C}{k_L, 200^\circ C} = 1.27\right)$ This again ensures that the experimental data were good.

Figure 13 is a plot of additional runs at a new air rate (1.0 ft^3/hr at conditions) at 250°C. Using least square fitting of the data, the value of k_La S at 250°C was calculated to be 6.13 hr^{-1} which is higher than that of 4.73 hr^{-1} at the same temperature and lower air rate (0.5 ft^3 per hour) as expected.

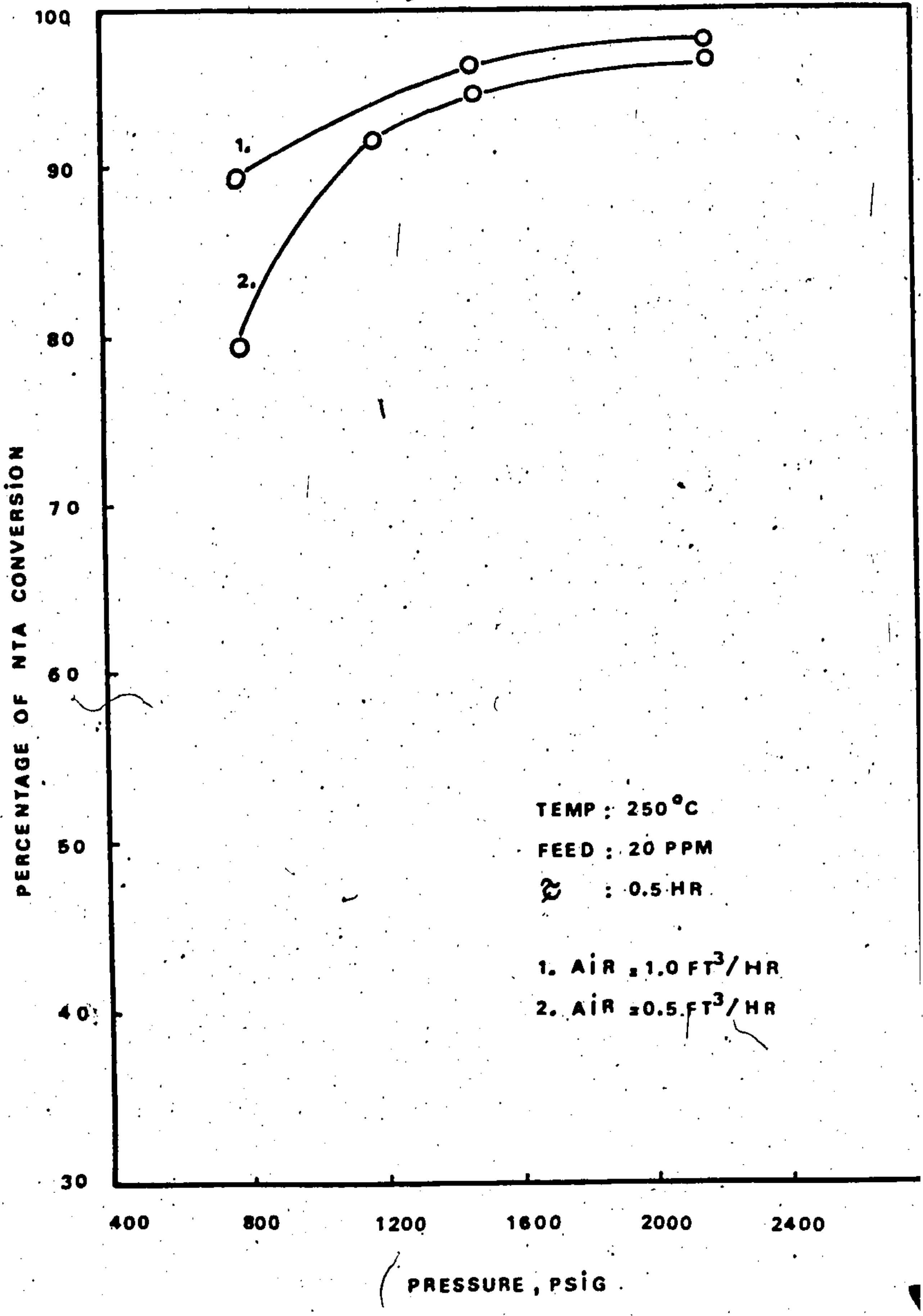


Figure 13 : Effect of air rate on conversion for τ = 0.5 hour

3. EQUIPMENT

There were a few problems for the process equipment. One of them was the leaks from the reactor "O" ring which failed due to the sudden changes of the temperature. To avoid this problem, the heater was kept on at all times and the pressure was changed gradually.

Another problem was the failure of the "O" ring seal in the high pressure chamber of the compressor. This forced the oil in the oil side out through a safty valve and no air was compressed to the system even at high pressure. This was overcome and avoided by changing the compressor conditions gradually, and by allowing the compressor to run for 20 minutes with no load while making sure that the oil ran continuously in both chambers before compressing the air to the reactor. These equipment problems are mentioned in this section because they were the major problems which were overcome.

VI . CONCLUSIONS

1. The Wet Air Oxidation process using a simple non-agitated reactor has been applied to the continuous oxidation of NTA in dilute solution and has been shown to be effective in converting up to 90 % of NTA, mostly to CO_2 and water at temperature of $250^{\circ}C$ and pressure of 1500 psig or higher.

2. The effects of pressure, temperature, and residence time on the reaction have been shown but the complex reaction mechanism was not investigated deeply.

3. The effects of mass transfer and chemical reaction also have been studied using mathematical models and plots on these models.

4. The expression involving $1/k_La.S$ and $1/k_R.C_{NTA}$ shows that the mass transfer controlled at high concentration of NTA and $1/k_R.C_{NTA}$ can be neglected, and that chemical reaction controlled at low concentration, so that $1/k_La.S$ can be neglected. This supports the earlier thesis that "no mixer may be required" with the qualification that the reaction concentration, determined by pressure, temperature, and residence time be sufficiently low.

5. The true concentration was estimated to be about 10% higher than that of the effluent.

6. The application to the process in a continuous flow system is both feasible and workable based on the results of this work. It is therefore possible for industries to reduce the concentrations of effluent organic pollutants by using this process in series to meet the requirement of goverment due to the present pollution problems.

7. Various determinations of NTA were studied and the zinc-zincon method of Thompson and Duthie[25] was proved to be suitable, especially for laboratory works, but some improvements were made and recommended for further studies in NTA as follows :

a. Care must be taken in the preparation of the buffer solution and the zinc-zincon reagent, and these must be made up once a week to avoid any change in color due to the light and temperature changes of the surrounding which cause the color to fade with time (red color of zinc-zincon reagent will change into light yellow if kept over a few weeks).

b. Standard solutions or sample solutions should be triplicated in preparing and reading their absorbances, and an average value is calculated. The spectrophotometer should be standardized with a blank solution (distilled water) before reading other solutions.

c. A calibration curve should be made and repeated every week to determine the NTA concentration instead of the calculation formula given by Thompson and Duthie[25].

d. NTA samples should be analyzed as soon as possible within a week or kept in the dark at all times. For best results and convenience, samples should be collected and analyzed at the end of the week.

e. Samples with concentration higher than 10 ppm should be diluted to 10 ppm or lower before making analysis.

8. It was found also that the acid form of NTA could not be determined accurately by the zinc-zincon method since the concentration did not behave linearly with absorbance (see Figure 3B) as expected, and thus this method is only good for the sodium form of NTA.

VII. APPENDIX

1. TABULATED DATA

All experimental runs are tabulated in Tables 1, 2, 3, and 4.

Vapor pressure of water and partial pressure of oxygen versus temperatures are tabulated in Table 5.

NTA concentrations in the acid form and in the sodium form versus absorbance at 620 mμ are tabulated in Tables 6 and 7 respectively.

TABLE 1

SUMMARY OF RUNS 1 TO 4

No air flow rate

Run No.	Inlet Concentration (ppm)	Outlet Concentration (ppm)	% Conversion	Temperature (°C)	Pressure (psig)	Liquid Flow rate (l/hr)
1	10	10	0	200	800	.5
2	20	20	0	200	1200	2
3	20	20	0	250	1500	3
4	100	100	0	250	2200	4

TABLE 2

SUMMARY OF RUNS 5 TO 60

Air flow rate = 0.5 ft^3/hr at conditions

Run No.	Inlet Concentration (ppm)	Outlet Concentration (ppm)	% Conversion	Temperature (^oC)	Pressure (psig)	Liquid Flow rate (l/hr)
5	10	4.50	55.00	200	800	2
6	10	1.97	80.30	200	2200	2
7	10	1.58	84.20	250	800	2
8	10	0.36	96.40	250	2200	2
9	20	3.45	22.75	200	800	.5
10	20	2.18	89.10	200	1200	.5
11	20	1.70	91.50	200	1500	.5
12	20	1.12	94.40	200	2200	.5
13	20	1.17	94.15	250	800	.5
14	20	0.46	97.70	250	1200	.5
15	20	0.31	98.45	250	1500	.5
16	20	0.18	99.05	250	2200	.5
17	20	9.35	53.23	200	800	2
18	20	6.80	66.00	200	1200	2
19	20	5.60	72.00	200	1500	2
20	20	3.95	80.25	200	2200	2
21	20	4.10	79.50	250	800	2
22	20	1.64	91.80	250	1200	2
23	20	1.14	94.30	250	1500	2
24	20	0.71	96.45	250	2200	2

TABLE 2 (continued)

Run No.	Inlet Concentration (ppm)	Outlet Concentration (ppm)	% Conversion	Temperature (°C)	Pressure (psig)	Liquid Flow rate (1/hr)
25	20	11.50	42.50	200	800	3
26	20	8.80	56.00	200	1200	3
27	20	7.45	62.75	200	1500	3
28	20	5.50	72.50	200	2200	3
29	20	5.45	72.75	250	800	3
30	20	2.45	87.75	250	1200	3
31	20	1.74	91.30	250	1500	3
32	20	1.03	94.85	250	2200	3
33	20	12.90	35.50	200	800	4
34	20	10.30	48.50	200	1200	4
35	20	8.95	55.25	200	1500	4
36	20	6.75	66.25	200	2200	4
37	20	6.66	66.70	250	800	4
38	20	3.14	84.30	250	1200	4
39	20	2.25	88.75	250	1500	4
40	20	1.35	93.25	250	2200	4
41	100	61.50	39.50	200	800	3
42	100	42.20	97.30	200	1500	3
43	100	32.30	67.70	200	2200	3

TABLE 2 (continued)

Run No.	Inlet Concentration (ppm)	Outlet Concentration (ppm)	% Conversion	Temperature (°C)	Pressure (psig)	Liquid Flow rate (1/hr)
44	100	25.20	74.80	250	800	3
45	100	9.50	90.50	250	1500	3
46	100	5.70	94.30	250	2200	3
47	100	70.50	29.50	200	800	4
48	100	49.80	50.20	200	1500	4
49	100	39.00	61.00	200	2200	4
50	100	33.20	66.80	250	800	4
51	100	12.65	87.35	250	1500	4
52	100	7.71	92.29	250	2200	4
53	10	2.95	70.50	225	800	2
54	10	0.98	90.20	225	2200	2
55	20	0.68	96.60	225	1200	.5
56	20	0.54	97.30	225	1500	.5
57	20	7.96	60.20	225	800	3
58	20	5.26	73.70	225	1200	3
59	100	26.44	73.56	225	1500	4
60	100	18.22	81.78	225	2200	4

TABLE 3

SUMMARY OF RUNS 61 TO 66

Air flow rate = 1.0 ft^3/hr at conditions

Run No.	Inlet Concentration (ppm)	Outlet Concentration (ppm)	% Conversion	Temperature (°C)	Pressure (psig)	Liquid Flow rate (l/hr)
61	20	2.71	86.45	250	800	4
62	20	1.14	94.30	250	1500	4
63	20	0.91	95.45	250	2200	4
64	20	2.10	89.50	250	800	2
65	20	0.80	96.00	250	1500	2
66	20	0.40	98.00	250	2200	2

TABLE 4

Reproductive data

SUMMARY OF RUNS 67 TO 70

Air flow rate = 0.5 ft^3/hr at conditions

Run No.	Inlet Concentration (ppm)	Outlet Concentration (ppm)	% Conversion	Temperature (°C)	Pressure (psig)	Liquid Flow rate (1/hr)
67	10	4.48	55.20	200	800	2
68	20	2.19	89.50	200	1200	.5
69	20	1.76	91.20	250	1500	3
70	100	7.68	92.32	250	2200	4

TABLE 5

TEMPERATURE °C	VAPOR PRESSURE OF WATER (psia)
200	225
225	366
250	576

PRESSURE P_{total} (psig)	TEMPERATURE ° C	PARTIAL PRESSURE OF OXYGEN (psia) $P_{O_2} = 0.21(P_{total} - P_{H_2O})$
800	200 225 250	124 94 50
1200	200 225 250	208 178 134
1500	200 225 250	271 241 197
2200	200 225 250	418 388 344

TABLE 6

NTA CONCENTRATION , ppm (acid form)	ABSORBANCE AT 620 mμ
0	0.530
1	0.470
2	0.430
3	0.385
4	0.350
5	0.325
6	0.285
7	0.265
8	0.240
9	0.210
10	0.190
15	0.110
20	0.090

TABLE 7

NTA CONCENTRATION , ppm (sodium form)	ABSORBANCE AT 620 mμ
0.0	0.530
2.5	0.475
5.0	0.420
7.5	0.360
10.0	0.310

2. CALCULATIONS

a. Calculation of theoretical oxygen demand for complete oxidation of NTA

The balanced equation for the complete oxidation of trisodium nitrilotriacetate (NTA) is:

$$N\,(CH_2COONa)_3 + 6O_2 \longrightarrow 6\,CO_2 + 3\,H_2O + NO_3^- + Na^+$$

The molecular weight of NTA is 257. If concentration of NTA were n′ mg/l, the theoretical oxygen demand would be:

$$\text{oxygen demand} = \frac{n'}{257} \times 6 \times 32 = 0.747\,n'\,\text{mg/l}$$

b. Calculation of air requirement for complete reaction

The following is a sample calculation of air requirement for RUN 48 which has the conditions below :

NTA feed concentration = 100 mg/l
Liquid flow rate = 4 liter/hr
Temperature = 200° C
Pressure = 1500 psig
Air flow rate = .5 ft^3/hr

Other information :

Air contains 23.17% O_2, 76.83% N_2 (by weight)
Room temperature: 25 °C, 14.7 psia
Density of air at room temperature = 0.00141 g/cm^3

From b., theoretical oxygen demand = 0.747 x 100 = 74.7 mg/l

Oxygen requirement for given liquid flow rate

$$= 74.7 \times 4 = 298.8 \text{ mg/hr}$$

Air flow rate required $= \frac{298.8}{.2317} = 1289.6$ mg/hr $= 1.2896$ g/hr

or $= \frac{1.2896 \text{ g/hr}}{0.0014 \text{ g/cm}^3} = 914.61 \text{ cm}^3\text{/hr} = 0.03226 \frac{\text{ft}^3}{\text{hr}}$ at room temp.

Actual air supplied was $0.5 \times \frac{298}{473} \times \frac{1514.7}{14.7} = 32.45 \text{ ft}^3\text{/hr}$

Thus, there was a large amount of excess air present.

c. Adjustment of air flow rate

Suppose that it is required to have an air flow rate of 0.5 ft^3/hr at conditions:

Temperature = 200°C
Pressure = 1500 psig

It is necessary to know exactly the room temperature and atmospheric pressure at the time when the system is in operation. For example, they were read to be:

Room temperature = 23°C = 296°K
Atmospheric pressure = 745 mmHg = 14.4 psia.

Using ideal gas law, we have:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

or:

$$V_1 = V_2 \cdot \frac{P_2}{P_1} \cdot \frac{T_1}{T_2}$$

$$= 0.5 \times \frac{1524.4}{14.4} \times \frac{296}{473}$$

$$= 32.912 \text{ ft}^3\text{/hr} = 0.55 \text{ ft}^3\text{/min}$$

Thus, we adjusted the air flow rate so that the wet test meter indicated + 0.55 ft^3 per minute or more accurately 2.74 ft^3 per 5 minutes.

d. The Zinc- Zincon method for NTA analysis

A manual procedure for the zinc-zincon method[25] of NTA analysis is summarized as ~~follows~~

Step 1 Preparation of ion exchanger

Weigh 100 gram of Dowex 50W-X8 resin (100-200 mesh). Add 40 ml of 6N NaOH and 50 ml distilled water. Mix well with a magnetic stirrer for 10 min. Decant the supernatant liquid. Add 25 ml of NaOH and 50 ml distilled water. Mix again for 10 min. Decant the aqueous layer. Wash the resin with distilled water until the pH of this aqueous layer is 7.0 - 7.5. Filter the resin through a Buchner-funnel and air-dry the resin on the funnel for 20 minutes.

Step 2 Preparation of buffer

Dissolve 31 g boric acid and 37 g potassium chloride in 800 ml distilled water. Adjust pH of this solution to 9.2 with 6N NaOH. Dilute to 1 liter with distilled water.

Step 3 Preparation of zinc

Dissolve 0.44 g $ZnSO_4.7H_2O$ in 100 ml of 2N HCl. Dilute to 1 liter with distilled water.

Step 4 Preparation of zinc-zincon reagent

Dissolve 0.13 g zincon powder in 2 ml of 1N NaOH. Add 300 ml buffer (from step 2) and 15 ml zinc solution (from step 3). Dilute to 1 liter with distilled water. This reagent should be prepared every week and stored in the dark.

Step 5 Preparation of standards

Prepare NTA standard solutions of the following concentrations : 2.5, 5.0, 7.5, 10 mg/l with distilled water. Pipette 25 ml of each solution and 25ml of distilled water (blank) into five 50 ml beakers.

Step 6 Final step

Add 2.5 g resin and a stirring bar to each beaker. Cover with watch glass and stir on magnetic stir for 15 minutes. Filter through Whatman No. 40 filter paper into a second beaker. Pipette 15 ml of filtrate into a third 50 ml beaker and add 35 ml of zinc-zincon reagent (from step 4) by pipette. Read the absorbance of these coloured solutions against a water blank at 620 mμ.

A typical calibration curve of absorbance versus concentration is shown in Figure. 3A

Step 7 Preparation of sample solutions

For each sample, pipette 25 ml of each sample into a 50 ml beaker and follow step 6 in order to read the absorbance of this sample. Once, its absorbance is obtained from spectrophotometer, its concentration can be raed directly from calibration curve (figure3A). For example, if sample absorbance were 0.40, its concentration would be 6.0 ppm.

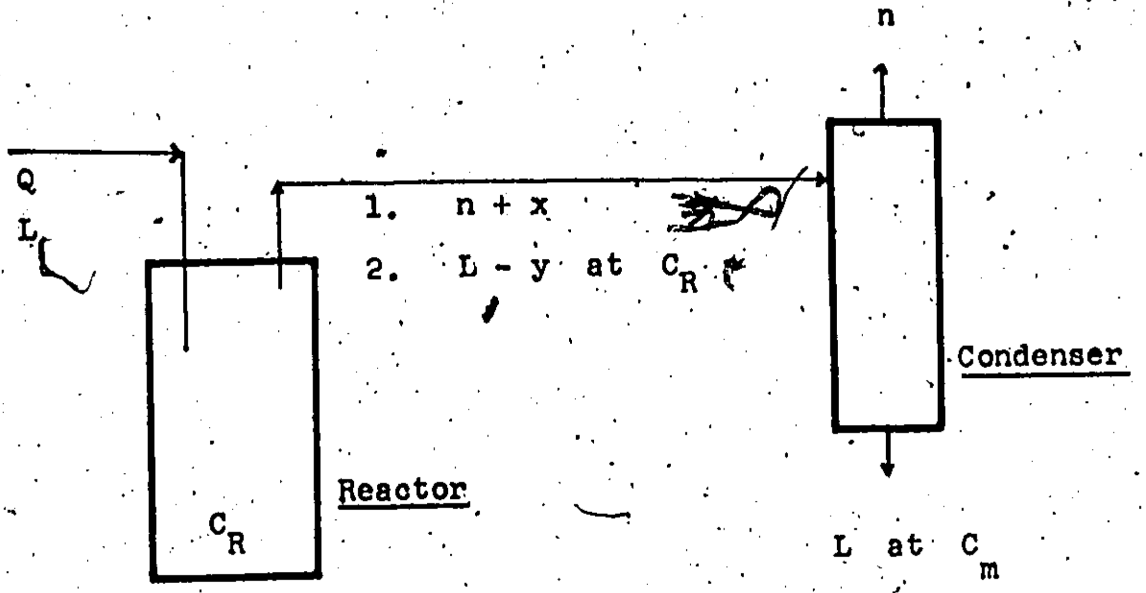
Remark After storing zinc-zincon reagent in the dark for more than 3 or 4 days, a new calibration curve should be made again. It should be renewed also when new reagent is made . For better results, repeat all steps over every week.

e. Calculation of true concentration in reactor

The true concentration for a non-volatile component in a high-temperature reactor can be computed as following with two assumptions:

a. Gas is saturated when leaving reactor at T and P

b. Only a portion of the gas is reacted



NOMENCLATURE

T : reactor temperature, °K
P : reactor pressure (total pressure), atm
C_R : true reactor concentration, mole/liter
C_m : measured concentration in effluent, mole/liter
L : liquid flow rate, liter/hr
Q : gas flow rate at condition, ft^3/hr
p^o : water vapor pressure at T
x : moles of water vapor entering condensor/hr
y : amount of liquid in gas phase, liter/hr
n : moles of air/hr

Mass balance on condensor with basis of 1 hour:

$$C_R (L - y) = C_m (L)$$

or:

$$C_R = C_m \frac{L}{L-y}$$

but:

$$\frac{x}{n} = \frac{p^o}{P - po}$$

or $$x = n . \frac{P^o}{P - P^o}$$

Ideal gas law gives:

$$n = \frac{PV}{RT} = \frac{P . Q . 28.316}{0.08206\ (T + 273)} \qquad (1\ ft^3 = 28.316\ liter)$$

then $$x = \frac{Q . 28.316}{0.08206} \times \frac{P}{T+273} \times \frac{P^o}{P - P^o}$$

Also, we have:

$$y = x . \frac{18}{1000} \ \frac{gm}{mole} . \frac{liter}{gm}$$

thus: $$C_R = C_m \left(\frac{L}{L - \frac{Q.28.316}{0.08206} . \frac{P}{T + 273} . \frac{P^o}{P-P^o} . \frac{18}{1000}} \right)$$

Note that the ratio inside the parentheses of the above expression is the correction factor of the true reactor concentrations.

A sample calculation of this correction factor with the following conditions is:

Liquid flow rate : $L = 2$ liter/hr
Gas flow rate : $Q = 0.5\ ft^3/hr$
Reactor pressure : $P = 800$ psig (55.42 atm)
Reactor temperature: $T = 200\ ^oC$
Vapor pressure at T: $P^o = 225$ psia (15.306 atm)

Correction factor $$= \frac{2}{2 - 0.5 \times \frac{28.316}{0.08206} \times \frac{55.42}{473} \times \frac{15.306}{55.42-15.306} \times \frac{18}{1000}}$$

$$= 1.0746$$

and similarily, we can get the following table for this correction factor.

Q ft^3/hr	T ^oC	L l/hr	P psig	Correction factor
0.5	200	2	800	1.0746
			1200	1.0657
			1500	1.0627
			2200	1.0592
		3	800	1.0485
			1200	1.0429
			1500	1.0410
			2200	1.0390
	250	3	800	1.3600
			1200	1.1730
			1500	1.1430
			2200	1.1170
		4	800	1.2470
			1200	1.1240
			1500	1.1030
			2200	1.0850

Thus, the true reactor concentrations are about 10% higher than that of the effluent.

f. Calculation of activation energy

Arrhenius' equation : $k_R = k_{R_o} e^{-e/RT}$

Taking ln both sides : $\ln k_R = \ln k_{R_o} - (E/R).\frac{1}{T}$

Therefore, the plot of $\ln k_R$ versus $\frac{1}{T}$ should be a straight line which has slope of $-E/R$, and intercept of $\ln k_{R_o}$

Figure 12 is a plot of $\ln k_R$ versus $\frac{1}{T}$ for different three temperature.

The slope is this line is $-6562.5\ {}^{\circ}K^{-1}$

Thus, the activation energy is = $6562.5 \times 1.98 = 13000$ cal/mole which is reasonable value for this type of reaction[49].

g. Comparison of mass transfer coefficients

The theoretical values of mass transfer coefficient can be estimated from Sherwood's equation:[52]

$$k_L \propto D \cdot Re^{0.5} \cdot Sc^{0.33}$$

or

$$k_L \propto D^{0.67} \frac{\rho^{0.17}}{\mu^{0.17}}$$

but, the Stokes-Einstein's equation[53] gives :

$$D \propto \frac{T}{\mu}$$

thus:

$$k_L \propto \frac{T^{0.67} \times \rho^{0.17}}{\mu^{0.84}}$$

From this relationship, we can calculate two ratios:

$$\frac{k_L \text{ at } T=225^{\circ}C}{k_L \text{ at } T=200^{\circ}C} = 1.136$$

and

$$\frac{k_L \text{ at } T=250^{\circ}C}{k_L \text{ at } T=200^{\circ}C} = 1.270$$

The experimental values of mass transfer coefficients can be estimated from intercepts of the straight lines in

Figures 8, 9 , and 10 :

Figure 8, at 200°C
$$\text{Intercept} = \frac{1}{k_L\, a\, S} = 0.28064$$
$$k_L\, a\, S = 3.566$$

Figure 9 , at 225°C
$$\text{Intercept} = \frac{1}{k_L\, a\, S} = 0.2438$$
$$k_L\, a\, S = 4.101$$

Figure 10, at 250°C
$$\text{Intercept} = \frac{1}{k_L\, a\, S} = 0.211517$$
$$k_L\, a\, S = 4.7227$$

Thus:
$$\frac{k_L \text{ at } 225^\circ\text{C}}{k_L \text{ at } 200^\circ\text{C}} = \frac{4.1011}{3.566} = 1.15$$

and
$$\frac{k_L \text{ at } 250^\circ\text{C}}{k_L \text{ at } 200^\circ\text{C}} = \frac{4.7277}{3.566} = 1.32$$

These results compare favorably with those estimated theoretically.

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