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GRADUATE COLLEGE

CONTINUOUS HYDROGEN REDUCTION OF COPPER FROM ITS SULFATE SOLUTION: KINETIC STUDY IN A PLUG FLOW REACTOR

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

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By

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CONTINUOUS HYDROGEN REDUCTION OF COPPER FROM ITS SULFATE SOLUTION: KINETIC STUDY IN A PLUG FROM REACTOR

APPROVED BY

R.D. Daniels

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DISSERTATION COMMITTEE

To my (Late) Father

Who Appreciated the Value of Education

ABSTRACT

Hydrometallurgical processes for recovering pure metals from their salt solutions by hydrogen reduction, are currently practiced in batch operations only.

The objective of this investigation was to explore the reaction kinetics for an acidic copper sulfate-hydrogen system in a continuous, tubular reactor. An aqueous copper sulfate solution of 0.19 molar (in some experiments 0.38 molar) feed concentration, was introduced at the top of the reactor while hydrogen was sparged at the bottom of the reactor, for countercurrent operation. The bottom (liquid-solid) and overflow (gas-liquid) products were separated in high pressure separators. Due to process requirements, the upper part of the reactor had to be utilized as a preheater; consequently, the experimental runs at constant temperature could not be obtained.

Experimental studies were made in the temperature range of 250°F (121°C) - 450°F (232°C), feed pH of 4.45 - 1.40, for total system pressures of either 500 psig (35 atmospheres) or 400 psig (28.2 atmosphere). Results indicate that the rate of reaction increases with temperature up to a certain point and then levels off or slightly

decreases as the temperature is further increased. Dependency of the process on feed pH (less than 1.80), for obtaining pure copper (without cuprous oxide contamination), from acidic sulfate solution, was observed. Even though hydrogen solubilities decrease with decrease in total pressure, corresponding decreases in conversions were not observed. In the range of study of residence times, 10-30 minutes, no appreciable change in conversions due to a change in residence time were observed. In agreement with previous investigators, acid addition (in the form of H_2SO_4) to the feed retarded the rate of reaction, whereas addition of sulfate (in the form of sodium sulfate) increased the rate.

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Krishna Murthy Sista

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CHAPTER I

INTRODUCTION

Hydrometallurgical processes for recovering pure metals from their natural ores or from scrap are particularly attractive from the standpoint of lower energy requirements and lesser environmental effects. One version of this class of processes is gaseous reduction, whereby metals are precipitated from leach solutions by direct contacting with reducing gases such as hydrogen, sulfur dioxide and carbon monoxide. For the same fuel consumption, hydrogen reduction has the potential of producing two to six times as much metal as the competing electrowinning process. To date, gaseous reduction has been practiced commercially only in batch operations. The continuous process offers the prospect of significantly lower capital and operating costs and better product quality.

Among the metals, copper, nickel and cobalt have attracted the most attention of the extractive metallurgical industry. For thermodynamic reasons nickel and cobalt can be effectively precipitated by hydrogen reduction only from alkaline solutions, whereas copper can be precipitated from acidic as well as alkaline solutions. However, for

copper, reduction from the acidic medium is faster and the product quality is better than when extracted from alkaline solutions. Copper is generally extracted in the sulfate form from oxide ores or scraps when leaching.

Even though hydrogen reduction of copper has been practiced in industry by the batch process, very little information concerning the kinetics of the reduction is available in the literature; to be sure it is inadequate for translation to continuous commercial operation. Even if proprietary know-how for batch system was released, it would not be sufficient to leap frog bench scale and pilot plant sequences because the operating requirements and attendant problems in batch and continuous systems are quite different. In this work an attempt was made to conduct relevant experiments in a tubular reactor to ascertain the kinetics of the continuous reduction for copper from acidic sulfate medium. The results were then compared with the available information on batch system.

CHAPTER II

THEORETICAL BACKGROUND

The reduction of metals from its aqueous salt solutions results from electron exchange between the reducing agent and the reduced species. Electrolytic, cementation and gaseous reduction processes are common in this respect. In electrolytic process the electrons are supplied by the applied voltage; in cementation and gaseous reduction the electrons are supplied by lower electron affinity metal and the reducing gas, respectively. As a result gaseous reduction may be treated thermodynamically from an electrochemical view point.

It should be recalled that "oxidation" is defined as the loss of electrons by an atom, molecule or ion and "reduction" is the gain of electrons by such particles. Oxidation is often defined as an increase in oxidation number, and similarly reduction is defined as decrease in oxidation number. It is standard convention to write the reaction equation from left to right; for example

$$Cu^{++} + e = Cu^{+} \qquad \text{(II-1)}$$

is termed as a reduction reaction, whereas

$$Cu^{+} = Cu^{++} + e \qquad \text{(II-2)}$$

is termed as oxidation reaction. In equation (II-2) cuprous ion loses one electron in being oxidized to cupric ion; the cuprous ion is called the reducing agent or reductant. Similarly from equation (II-1), cupric ion gains one electron in being reduced to cuprous ion. The cupric ion is called oxidizing agent or oxidant, so the above equation may be written in general form

$$\text{Oxidant} + ne = \text{Reductant} \qquad \text{(II-3)}$$

Equation (II-3) is termed a redox couple. A redox reaction is the interaction and exchange of electrons between two redox couples. Hydrogen reduction of copper from its aqueous solution is in itself a redox reaction and can be cited as an example, the over all reaction being

$$Cu^{++} + H_2 = Cu^{\circ} + 2H^{+} \qquad \text{(II-4)}$$

which in terms of redox couple can be written as

$$Cu^{++} + 2e = Cu^{\circ} \qquad \text{(II-5)}$$

$$2H^{+} + 2e = H_2 \qquad \text{(II-6)}$$

Equations (II-5) and (II-6) in electrochemical terminology is referred to as half-cell reactions.

The reactivity of a redox couple (or half-cell reaction) is determined by its tendency to gain or lose

electrons. The measure of this tendency is the "Potential", and the difference in these potentials for two couples are related to the equilibrium constant of the redox reaction. IUPAC (Stockholm)* recommended and adopted as standard to write the half-cell reaction as

$$\text{Oxidant} + ne = \text{Reductant} \qquad E^\circ \text{ volts} \qquad \text{(II-7)}$$

where E° is the standard potential of the half-cell reaction. For cupric reduction the equation will be

$$Cu^{++} + 2e = Cu^\circ \qquad E^\circ = +0.34 \text{ volts} \qquad \text{(II-8)}$$

It is common practice some times to write the above equation as

$$Cu^\circ = Cu^{++} + 2e \qquad E^\circ = -0.34 \text{ volts} \qquad \text{(II-9)}$$

Equation (II-9) is representative of an oxidation from left to right. As a result the potential in equation (II-9) is referred to as "Oxidation potential". By the same token the potential in equation (II-8) may be referred to as "Reduction potential". Use of either of these alternative forms is valid so long as consistency is maintained.

Equation (II-4) is the overall reaction taking place between cupric ion and hydrogen molecule, giving

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*International Union of Pure Applied Chemistry, meeting took place in Stockholm in 1953.

copper and hydrogen ion. The extent to which the reaction will proceed is given by the equilibrium constant K, which is defined as

$$K = \frac{[Cu^{\circ}][H^{+}]^{2}}{[Cu^{++}][H_2]} \qquad \text{(II-10)}$$

The quantities in the square brackets are the activities of the respective species. This thermodynamic equilibrium constant, K, is related to the free energy change ΔG by

$$\Delta G = \Delta G^{\circ} + RT \ln K \qquad \text{(II-14)}$$

Where ΔG° is the standard free energy change (at unit activity of reactants and products). R is the gas constant and T is the absolute temperature in appropriate units. The reaction given in equation (II-4) may be visualized as a perfectly reversible electrochemical cell in which case the work obtainable from this cell would be nEF, where n is the number of Faradays passing through the cell to complete the reaction, E is the potential of the cell in volts and F is the Faraday equivalent (96,487 coulombs). The reversible work must equal the free energy change of the reaction

$$\Delta G = -nEF \qquad \text{(II-12)}$$

Thus the equlibrium constant K is related to the potential E by

$$\Delta G = -nE^{\circ}F + RT \ln K \qquad \text{(II-13)}$$

or

$$E = E^\circ - \frac{RT}{nF} \ln K \qquad \text{(II-14)}$$

Equation (II-14) is usually referred to as Nernst equation after the physical chemist Nernst, who first used it to express the relationship between the potential of a metal-metal ion electrode and the concentration of the metal ion in solution. At equilibrium E=0 since $\Delta G = 0$ and equation (II-14) reduces to

$$E^\circ = \frac{RT}{nF} \ln K \qquad \text{(II-15)}$$

The potential for the overall reaction given by equation (II-4) can be obtained by combining the potentials of the individual redox couple

$$Cu^{++} + 2e = Cu^\circ \qquad E^\circ_{Cu} = 0.34 \text{ volts} \qquad \text{(II-16)}$$

$$2H^+ + 2e = H_2 \qquad E^\circ_{H_2} = 0.00 \text{ volts} \qquad \text{(II-17)}$$

$$E_{(overall)} = (E_{Cu} - E_{H_2}) \qquad \text{(II-18)}$$

Since a decrease in free energy of the system is the characteristic criterion for spontaneous reaction, and since $\Delta G = -nEF$, $E_{(overall)}$ must be positive for the reaction to take place spontaneously. As a result it is necessary that $E_{Cu} \geq E_{H_2}$ all the time, which is generally the case for all pH values in the case of copper. As a general rule for any metal reduction the above criterion should be satisfied, i.e.,

$$E_M \geq E_{H_2} \qquad \text{(II-19)}$$

or in terms of "oxidation potentials"

$$E_M \leq E_{H_2} \qquad \text{(II-20)}$$

Using equations (II-14), (II-16) and (II-17) and using definitions of oxidation potential and equilibrium constants $K_{Cu} = \frac{[Cu^{++}]}{[Cu^{\circ}]}$ and $K_{H_2} = \frac{[H^+]^2}{[H_2]}$ and noting that n=2

$$E_{Cu} = E^{\circ}_{Cu} - \frac{RT}{2F} \ln [Cu^{++}] + \frac{RT}{2F} \ln [Cu^{\circ}] \qquad \text{(II-21)}$$

$$E_{H_2} = E^{\circ}_{H_2} - \frac{RT}{F} \ln [H^+] + \frac{RT}{2F} \ln [H_2] \qquad \text{(II-22)}$$

where $[Cu^{++}]$, $[Cu^{\circ}]$, $[H^+]$ and $[H_2]$ are activities of cupric ion, metallic copper, hydrogen ion and hydrogen respectively. In equation (II-21) the last term on the right hand side vanishes as the activity of pure metal is unity and the second term can be expressed in terms of the metal ion concentration and activity coefficient. In equation (II-22) the second term on the right hand side can be expressed in terms of pH, since $pH = -\log_{10}[H^+]$. The last term may be expressed in terms of partial pressure of hydrogen assuming that hydrogen behaves as an ideal gas and forms an ideal solution in the concentration range of interest. Figure II-1 is the plot of oxidation potential versus pH for hydrogen pressures of 1, 30 and 200 atmospheres at 25°C.

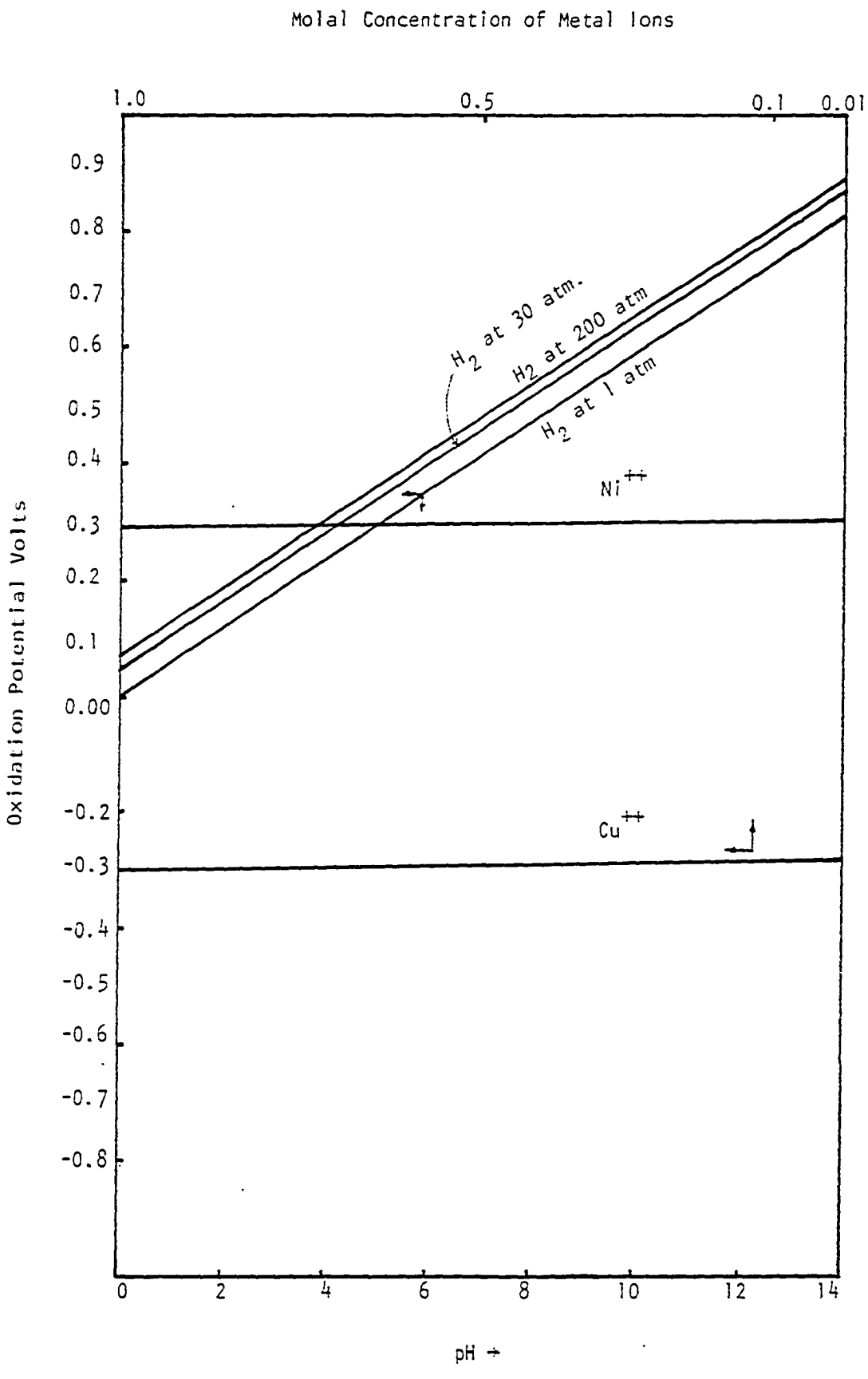


FIGURE II-1. Oxidation potentials of 1 and 1.0×10^{-2} molar copper and nickel solutions, and hydrogen potentials at varying pH (25°C).

Similarly metal ion concentrations from 1.0 to 0.01 moles/liter are plotted against the oxidation potentials and are represented in the same Figure II-1. Equation (II-21) and (II-22) were used in constructing Figure II-1. As shown in equation (II-20), it is thermodynamically possible to reduce a metal from solution by hydrogen if the E_{H_2} line in Figure (II-1) lies above the E_M line. Thus it is clearly possible to reduce cupric ions to copper at all normal pH values. To exemplify the importance of thermodynamic considerations, it is seen from Figure (II-1) that to reduce nickel it is necessary to maintain the pH above a certain value (for instance above 4.2 for hydrogen pressures of 30 atmospheres) at all times during reduction. As a result nickel is preferably reduced from ammoniacal solutions. However, this problem does not arise in the case of copper. Also, for the reaction $Cu^{++} + H_2 \rightleftarrows Cu^{\circ} + 2H^{+}$, the equilibrium constant K at 25°C is calculated to be 3.1701058×10^{11}. Equilibrium constant values and heat of reaction values at different temperatures are presented in Table II-1. From the foregoing thermodynamic considerations it is clear that hydrogen reduction of cupric ion to metal should proceed almost to completion at 25°C under a pressure of one atmosphere. (In fact, the equilibrium, conversion even at 250°C is virtually complete.) That it does not proceed appreciably under these conditions shows that the kinetic factors must be considered to evaluate the rate at which the reaction proceeds.

TABLE II-I

Heat of Reaction and Equilibrium Constant Values at Different Temperatures for the Reaction

$$Cu^{++} + H_2 \rightleftarrows Cu^{\circ} + 2H^{+}$$

Temperature °C	Heat of Reaction ΔH in Kcal/mole	Equilibrium Constant K
25	-15.36	3.170×10^{11}
125	-15.26	4.682×10^{8}
150	-15.23	1.485×10^{8}
175	-15.21	5.358×10^{7}
200	-15.18	2.152×10^{7}
250	-15.16	9.476×10^{6}

Kinetic factors very much depend on the mechanism by which the reaction proceeds. In homogeneous reactions, the respective reactants are available freely to combine in a common media to form the products. Reaction may proceed in several steps, forming intermediate complexes before obtaining the product. Each individual step may proceed at different rates and the slowest step controls the overall reaction. In heterogeneous reactions, the reaction takes place in the gas-liquid, liquid-solid or gas-solid interphases. Thus the heterogeneous reactions are controlled by either mass transfer rate or by chemical reaction rate depending on which ever is slowest. Both homogeneous and heterogeneous reactions are subclassified as (a) catalytic in which the motivating species (a catalyst) is required to enhance the rate, (b) non-catalytic in which the reactants react at a fast enough rate without any external help. Reduction of nickel from its aqueous solution is an example of heterogeneous catalytic reaction. Precipitated nickel acts as catalyst and the rate of reduction is proportional to the precipitated nickel and/or seed (nickel) externally added before the start of the reaction. On the other hand reduction of copper from its aqueous solution was considered for some time as a non-catalytic homogeneous reaction, but recent studies (7, 20 and 27) indicate it to be a catalytic homogeneous reaction, the cuprous ion formed in the intermediate step acting as

a catalyst. The reaction takes place in the liquid phase, and at low hydrogen partial pressures the reaction is influenced by diffusional mass transfer of hydrogen into the solution. However by increasing the partial pressure of hydrogen and sufficient agitation, the influence of mass transfer can be eliminated.

A copper sulfate solution, when heated, hydrolyses and precipitates copper basic salts, probably by the following reaction

$$3\ CuSO_4 + 4H_2O \rightleftarrows Cu_3SO_4(OH)_4 + 2H_2SO_4 \qquad \text{(II-23)}$$

How the basic salt reacts, when contacted with hydrogen is not resolved, but from the observations of previous investigators, the following mechanism seems probable

$$Cu_3SO_4(OH)_4 + \frac{3}{2}\ H_2 = \frac{3}{2}\ Cu_2O + H_2SO_4 + \frac{5}{2}\ H_2O \qquad \text{(II-24)}$$

$$Cu_3SO_4(OH)_4 + 3H_2 = 3Cu + H_2SO_4 + 4H_2O \qquad \text{(II-25)}$$

When the acidity of the solution is increased, either by formation of H_2SO_4 during reduction or by external addition, the cuprous oxide formed redissolves into the solution probably by the following reaction

$$Cu_2O + 2H^+ \rightleftarrows Cu^{++} + Cu^\circ + H_2O \qquad \text{(II-26)}$$

During hydrogen reduction of copper from its aqueous sulfate solution, the above reactions may take place to some extent along with the principal, homogeneous

reaction. The extent of these reactions depends mainly on the conditions of operation and acidity of the solution, if the reduction is carried out in the acidic medium. By properly adjusting the acidity of the feed solution, the hydrolysis reaction given by equation (II-23) and subsequent complicated solid phase heterogeneous reactions may be eliminated. Homogeneous reduction of copper by hydrogen from aqueous solution presumably takes place by homonucleation and crystal growth, and atom by atom deposition on the nucleus formed. Homonucleation is the process in which the metal nucleus is formed directly from metal atoms produced by chemical reduction in the bulk solution, possibly by the following mechanism suggested by Courtney (6).

$$8\ Cu^{+} \xrightarrow{\text{Fast}} 4\ Cu^{\circ} + 4\ Cu^{++} \qquad \text{(II-27)}$$

$$Cu^{\circ} + Cu^{+} \xrightarrow{\text{Fast}} Cu^{\circ}\cdot Cu^{+} \quad \text{(adsorption)} \qquad \text{(II-28)}$$

$$Cu^{\circ}\cdot Cu^{+} + Cu^{+} \xrightarrow{\text{Slow}} 2Cu^{\circ} + Cu^{++} \qquad \text{(II-29)}$$

$$Cu^{\circ} \xrightarrow[\text{Growth}]{\text{Fast}} \text{microscopic particle} \qquad \text{(II-30)}$$

The microscopic particle thus formed, if allowed, can overgrow and start agglomerating with other crystals. Over growth and agglomeration, as well as undergrowth are not desirable in industry; particle size can be regulated by controlling the reaction, by means of additives like polyacrylic acid.

CHAPTER III

REVIEW OF LITERATURE

The precipitation of pure metal powders, by gaseous reduction from their salt solution, though a new art compared to its hydrometallurgical counterpart cementation (a process by which a metal is precipitated by displacement using another metal), has been known for more than a century. The precipitation of different metal powders by gaseous reduction is covered by many publications and patents. This chapter of the text will be limited to the review of only the literature most pertinent to this investigation.

N.N. Beketov in 1859, is reported to be the first to study the effect of hydrogen on some metal salt solutions at different pressures. During the experimental study he observed certain peculiarities which forced him to pay attention to the nature of the reaction itself, i.e.; to the effect of pressure on the chemical action of gases. In particular, Beketov found that hydrogen under a pressure of 10 atmospheres, deposited silver from its salt solutions of chloride, nitrate and sulfate. Same experiments conducted under atmospheric conditions failed to separate

the metal, even after several days of exposure. From these experiments he concluded that the action of hydrogen depended on the gas pressure and the concentration of the solution. Based on Beketov's experiments, Tammann and Nernst in 1892, attempted unsuccessfully to precipitate copper from copper sulfate solution under hydrogen pressures up to forty atmospheres. Most of their experiments terminated in ruptures of the reactor, and the few which withstood the severe pressure conditions of the experiments failed to precipitate copper. No further attempts were made up until 1908, when Vladimir Ipatieff (13) based on his experience with high pressure hydrogenation of organic compounds, reinitiated the work of hydrogen reduction of metal salt solutions. He almost repeated the work of earlier investigators and attempted to reduce copper from aqueous sulfate solution. Even though the experiments survived the severe pressures of 200, 580 and 600 atmospheres respectively, they failed to precipitate the metal even after continued exposure for several days. The experiments proved to be unsuccessful, even with other salts of copper, as well as other metal salts like nickel, cobalt and cadmium. All these experiments like earlier workers were attempted at ambient temperatures. In his subsequent experiments he decided to apply heat to increase the temperature of the reaction. The results were dramatic and deposits of copper, copper oxide and copper

basic salts were observed to have formed in the autoclave when experiments were conducted at 90°C and 25 atmospheres pressure. The composition of the deposit varied depending upon the experimental conditions and duration. The experiments conducted at 90°C and 25 atmospheres deposited basic salt of copper of composition $CuSO_4 \cdot 2Cu(OH)_2$ (antlerite) first, followed by cuprous oxide. Crystals of copper along with cuprous oxide separated out after 40 to 50 hours, and only after seven days complete conversion, to metallic copper was observed. However, beautiful crystals of copper precipitated out under 100 atmospheres and 200°C. Ipatieff concluded from his observations, that formation of basic salt and metal oxide are by hydrolysis of the salt, whereas precipitation of metal by hydrogen was a separate reaction. To support his conclusions, he added sulfuric acid to suppress the hydrolysis reaction. Further experiments conducted at elevated temperatures and atmospheric pressure failed to separate any metal from its solution, thus the cooperative action of temperature and pressure is essential. He concluded from his experimental observations that a set of "critical" temperature and minimum pressure exists without which, it is not possible to precipitate metals from their respective salt solutions by hydrogen reduction, i.e., readily and rapidly to completion. As various metals have different electrode potentials, and "critical" temperatures and pressures are

different, it would be possible to separate metals selectively from solution containing different metal ions, precipitating the metal with the lowest electrode potential first. In order to prevent hydrolysis of other salts, reduction may have to be carried out in acidic media.

The work of Ipatieff and others remained academic up until the nineteen fifties when Chemical Construction Corporation initiated research on hydrometallurgy of copper, nickel and cobalt, including hydrogen reduction, for commercialization. This research resulted in many patents. A paper was published by F.A. Schaufelberger (26) giving basic and important qualitative information about the process of hydrogen reduction of metal salt solutions. The reduction of copper or any other metal depends on temperature, partial pressure of hydrogen, metal and hydrogen ion concentrations in solution. Increase in temperature, partial pressure of hydrogen and metal ion concentration enhances the rate of reduction, whereas hydrogen ion concentration retards the rate. As the reduction proceeds metal ions in solution are depleted, generating hydrogen ions and precipitating the metal. As a result, the rate of reduction drops rapidly and levels off at a particular metal ion concentration. Addition of buffers like ammonia to neutralize the generated hydrogen ions helps in improving the conversion to a greater extent. On the other hand neutralizing agents like ammonia have a counter effect,

forming complexes with the metal ion and making reduction more difficult in the way of lower conversions. As a result the initial ratio of ammonia to metal ion concentration in the solution, plays a very important role in reduction from ammoniacal solutions. Sulfates acts as suppressant for hydrogen ions to some extent, forming more stable bisulfate ions in solution when reducing from acidic solutions. Controlling the acidity is also important to prevent precipitation of sulfides. Addition of seed to aid nucleation, though required for nickel and cobalt, is not necessary in the case of copper reduction either from ammoniacal or acidic solutions. However the reduction rates are much faster in acidic medium than in ammoniacal solutions.

Most of the other contributions in hydrogen reduction came from the University of British Columbia, Vancouver, during the same period. MacGregor and Halpern (18) studied the kinetics of the reduction of cupric perchlorate and sulfate salt aqueous solutions by molecular hydrogen to metallic copper. Based on their experimental observations, they proposed a mechanism and derived a rate equation for reduction in perchlorate solutions.

$$Cu^{++} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+ \qquad \text{(III-1)}$$

$$CuH^+ + Cu^{++} \xrightarrow{k_2} 2Cu^+ + H^+ \qquad \text{(III-2)}$$

$$2Cu^{+} \xrightarrow{\text{Fast}} Cu^{\circ} + Cu^{++} \qquad \text{(III-3)}$$

and the rate equation

$$-\frac{d(H_2)}{dt} = \frac{k_1 [H_2] [Cu^{++}]^2}{[Cu^{++}] + (k_{-1}/k_2)[H^{+}]} \qquad \text{(III-4)}$$

In the rate equation, $[Cu^{++}]$ is the cupric ion concentration, $[H_2]$ is the concentration of hydrogen in solution and $[H^{+}]$ is the hydrogen ion concentration. k_1 and k_{-1} are the forward and reverse rate constants of equation (III-1). $[CuH^{+}]$ is the intermediate formed during the reaction and is assumed to be present in at least negligible quantities at all times. (This assumption is the stationary state hypothesis which is used in deriving the rate equation). The inverse dependence of rate of the reduction on hydrogen ion concentration is evident from equation (III-4). Even though the catalytic action of cuprous ions were observed in many other reactions, it was interpreted that there was no indication of cuprous effect in this reaction even though it formed in appreciable quantities. In fact equation (III-3) indicates that precipitation of copper takes place via disproportionation of cuprous ions formed in the process. A value of 1.3 for (k_{-1}/k_2) estimated at 160°C and the value of 0.25 at 110°C reported earlier by Halpern, MacGregor and Peters (11), indicate that the reverse reaction becomes increasingly important as the temperature is increased, which seems to be in agreement

with the small apparent effect of temperature on the overall rate. The activation energy of 26,600 cal/mole (for the forward reaction of equation (III-1)), with a frequency factor of $1x10^{13}$, was obtained. Even though the reductions from sulfate solutions was found to be qualitatively similar to those from perchlorate solutions and to the results reported by Schaufelberger, two important qualitative differences relative to perchlorate solutions were observed. (1) The rates of reduction under comparable conditions were appreciably faster, and (2) the final slowing down of the reduction occurred at a considerably lower copper concentration. In fact the reaction was so fast that no quantitative analysis of the kinetics in sulfate solution was attempted. Qualitatively the higher rates obtained in sulfate solutions were attributed to the undissociated $CuSO_4$ complex, which activates hydrogen about 6.5 times as rapidly as the uncomplexed Cu^{++} ion. Addition of inert sulfate salt (i.e., Na_2SO_4) increased the initial rate of reduction as well as yielding a higher conversion. The product obtained from sulfate solutions was a loose network of fine needles or filaments, whereas for perchlorate it was porous powder made up of globular particles of indefinite shape and varying sizes.

McDuffie, et al (20) while conducting experiments for disposal of the mixture of hydrogen and oxygen created by the radiolytic decomposition of water, in aqueous homogeneous nuclear (fission) reactors observed that the

reaction occurs only in the liquid phase in the presence of cupric ion. They further observed that the rate of pressure decrease of the gaseous phase was directly proportional to the hydrogen pressure; they inferred that the rate controlling reaction in solution must be first order in dissolved hydrogen. The overall reaction appeared to be a slow reduction of the cupric catalyst by dissolved hydrogen followed by a rapid regenerative oxidation of the reduced species. The reactions carried out in cupric perchlorate and cupric sulfate solutions gave results agreeing with MacGregor's and Halpern's results when extrapolated to their experimental conditions. Except in the case of perchlorate solution, they did not find any rate dependency on hydrogen ion concentration at an experimental temperature of 250°C. Similarly for sulfate solutions the ratio (k_{-1}/k_2) was negligible, giving a value of 0.0258. From these observations it was concluded that the reaction between CuH^+ and H^+ to regenerate Cu^{++} and H_2 is relatively unimportant compared with the reaction between the postulated CuH^+ and another Cu^{++} ion. This observation however, does not disprove the mechanism suggested by MacGregor and Halpern since no information is available concerning the effect of temperature on the component reactions.

Dunning and Potter (7) carried out experiments at 1 to 3.30 atmospheres hydrogen (at 20°C) and 145°C. Solutions of cupric sulfate in sulfuric acid were heated in thick

walled tubes with hydrogen. The disappearance of cupric species was observed spectrophotometrically. They observed an accelerating autocatalytic range, followed by a steady disappearance of cupric species. Analysis of the rate curves gave the relation

$$-d[Cu^{++}]/dt = r_{10} + \text{slope}\ ([Cu^{++}]_o - [Cu^{++}]) \quad \text{(III-5)}$$

where r_{10} is the finite initial rate, and the second term describes the autocatalytic rate, with $[Cu^{++}]_o$ the initial cupric concentration and $[Cu^{++}]$ the cupric concentration at any time t. The effects of cupric concentration, hydrogen pressure, sulfuric acid concentration and ionic strength on the initial and autocatalytic rates were determined. Both rates were first order with hydrogen pressure and inversely proportional to the acid concentration. However, when nucleated copper was added, the autocatalytic part of the reaction disappeared. On the other hand, when metallic platinum was added the induction period was still present indicating that copper did not act as a heterogeneous catalyst. This behavior was attributed to cuprous species, which upon addition of metallic copper attained the equilibrium $Cu(metal) + Cu^{++} \rightleftarrows 2Cu^{+}$, rapidly, thus producing a higher concentration of the cuprous species and a higher initial rate than when the cuprous is produced by reduction of cupric species. After nucleation of metallic copper has taken place, the cuprous

concentration decreases in proportion to the amount of metallic copper precipitated, and hence the overall rate which is mainly controlled by the cuprous rate decreases.

It was found that at 145°C, for the initial rate (r_1)

$$r_1 = \frac{0.315\ [H_2][Cu^{++}]^2}{[Cu^{++}] + 0.105\ [H^+]} \quad \text{mole/liter (min)} \qquad \text{(III-6)}$$

and for the autocatalytic rate (r_2)

$$r_2 = \frac{71\ [H_2][Cu^{++}]^2[Cu^+]}{[Cu^{++}] + 0.90\ [H^+]} \quad \text{mole/(liter)(min)} \qquad \text{(III-7)}$$

where $[Cu^{++}]$, $[Cu^+]$, $[H^+]$ and $[H_2]$ are the concentrations (mole/liter) of cupric, cuprous, hydrogen ions and molecular hydrogen respectively. This experimental observation was claimed to be the first evidence for the activation of molecular hydrogen by cuprous ion in aqueous solution. It seems that cuprous is about 100 times more active than cupric ion. The activation energies of 9.3 Kcal/mole and 24.0 Kcal/mole were reported for cuprous and cupric reactions respectively. A possible reaction scheme

$$Cu^{++} + H_2 \rightleftarrows CuH^+ + H^+ \qquad \text{(III-8)}$$

$$CuH^+ + Cu^{++} \rightleftarrows 2Cu^+ + H^+ \qquad \text{(III-9)}$$

followed by

$$Cu^{+} + H_2 \rightleftarrows CuH + H^{+} \qquad \text{(III-10)}$$

$$CuH + Cu^{++} \rightleftarrows Cu^{+} + CuH^{+} \qquad \text{(III-11)}$$

was suggested.

Von Hahn and Peters (27) conducted additional experiments to investigate further the effect of cuprous ions on molecular hydrogen and on overall cupric reduction from sulfate solutions. Concentration of cuprous ions in solution during hydrogen reduction of cupric sulfate, were measured by tapping solution samples at predetermined intervals of time and reacting with dichromate solution. The excess unreacted dichromate in the sample was determined spectrophotometrically. The cuprous concentrations were calculated by difference. Precautionary measures were taken in the equipment set up to prevent disproportionation of cuprous ions to metallic copper and cupric ion by rapid cooling during sampling. It was observed by them that cuprous ion concentration in the solution increased with time for a while, reached a maximum and then started decreasing. From the observed rate data, they arrived at a mechanism, which was proposed earlier by Dunning and Potter.

$$Cu^{++} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^{+} + H^{+} \qquad \text{(III-12)}$$

$$CuH^+ + Cu^{++} \xrightarrow{k_2} 2Cu^+ + H^+ \qquad \text{(III-13)}$$

$$Cu^+ + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CuH + H^+ \qquad \text{(III-14)}$$

$$CuH + Cu^{++} \xrightarrow{k_4} CuH^+ + Cu^+ \qquad \text{(III-15)}$$

$$2Cu^+ \overset{\text{Fast}}{\rightleftharpoons} Cu^\circ + Cu^{++} \qquad \text{(III-16)}$$

The mechanism leads to the rate equation, after using the stationary state hypothesis for CuH^+ and CuH

$$r = \frac{k_1 [Cu^{++}]^2 [H_2]}{[[Cu^{++}] + (k_{-1}/k_2)[H^+]]} + \frac{k_3 [Cu^+][Cu^{++}]^2[H_2]}{[[Cu^{++}] + (k_{-1}/k_2)[H^+]][[Cu^{++}] + (k_{-3}/k_4)[H^+]]}$$

$$= R_{cu^{++}} + R_{cu^+} \qquad \text{(III-17)}$$

Initially the rate is predominated by the cupric effect. As the reaction progresses, the cuprous ions present increase and the reaction is dominated by the presence of cuprous ions. Additional experiments (28) conducted using Deuterium exchange gave almost the same results. This experiment confirmed the hydrogen ion effect on the overall reaction of cupric ions with molecular hydrogen. It was found in general that the cuprous effect is more predominant in sulfate solutions than in

perchlorate solutions. This cuprous ion effect was attributed to the reverse reaction of equation (III-14) being higher than equation (III-15) in sulfate solution, which is exactly the opposite for perchlorate solutions. However, this explanation was not substantiated.

Yet another totally different rate equation was obtained by Gen-ichi Nakazava (22), of Tokyo Laboratory. Experiments were conducted in batch autoclaves. Reduction reactions were carried out on cupric sulfate solutions with molecular hydrogen. Ammonium sulfate as a buffer for neutralizing hydrogen ions and acryl compound as an antiplating agent were used. It was observed that the antiplating agent affected the reduction rate (increasing with addition of antiplating agent) and physical properties of the product. Addition of ammonium sulfate increased the rate in proportion to the amount added. A very little increase in rate was also observed when metallic copper in the form of seed was added. From these observations the rate equation was derived as

$$-\frac{d[Cu^{++}]}{dt} = k_1 [Cu^{++}][H_2][(NH_4)_2SO_4] - k_2 f[H^+] \qquad \text{(III-18)}$$

where k_1 and k_2 are rate constants and $[Cu^{++}]$, $[H_2]$ and $[(NH_4)_2SO_4]$ are concentrations of cupric, hydrogen and ammonium sulfate in solution, respectively. However, one disadvantage of equation (III-18) is that, the first term on the right hand side vanishes for zero concentration of

ammonium sulfate, and the reaction will depend only on hydrogen ion concentration.

Work initiated at University Engineers in 1964 resulted in development of continuous tubular reactor. Work of Brown (4) was mainly concerned with crystal growth; however, he could reproduce the work of previous workers in copper reduction from their salt solution. Copper and copper oxide were precipitated from cupric sulfate solutions at temperatures of 135 to 200°C at hydrogen partial pressures of 60 to 80 atmospheres in less than 2 hours. Brown observed that pure copper could be precipitated alone in relatively short periods of time at a particular temperature and pressure. However, these results were not conclusive. The reaction "triggering" temperature varied slightly for 1 molar to 0.1 molar solutions of copper sulfate, but it increased below 0.1 molar concentrations in inverse proportion to the concentration.

Conner (5) made a thermodynamic analysis of the equilibrium constants for this system in the temperature range of 120°C to 140°C and 27 to 53 atmospheres hydrogen pressures. The medium was acidic and in few cases were buffered with ammonium sulfate. It was concluded that the reaction was basically a homogeneous reaction taking place in the liquid phase. The reaction tends to be more irreversible with increasing pressure and temperature.

Kieswetter (14) studied the reduction of cupric sulfate by hydrogen in the presence and absence of ammonia in batch reactors. He devised a special rocking mechanism for the reactors to get enough agitation for proper distribution and mixing of hydrogen with the solution. The conclusions from his observations were, that the initial rates of reduction were much faster in sulfate solutions in the absence of ammonia than in its presence. An induction period similar to that observed by Dunning and Potter was observed in this case also and was attributed to two probable factors, (1) the time required for the reactors to reach reaction temperature, and (2) the time required for hydrogen to go into solution. For reduction in presence of ammonia, the ratio of ammonia to copper of 1 and 4 gave better rate than the previously suggested ratio of 2 by others. Acid neutralized ammoniacal leach solutions give better yields and the advantages are greater at lower temperature reduction.

Neskora (23), built and studied the continuous reduction of metal solution by hydrogen. The experiments were conducted in a tubular concurrent flow reactor. The quantitative results were not satisfactory as far as the kinetic aspects of the copper runs were concerned, even though very good crystals of copper were precipitated. Qualitatively the results proved the feasibility of the process. Different problems encountered in this process,

generally not anticipated in the batch reactors, were the precipitation of basic salts at elevated temperatures which virtually eliminated the preheating of the feed before entering the reactor. However, based on the observations made it was concluded that, the sulfuric acid pretreatment of ammoniacal copper sulfate solutions increased the reaction rates by factor of 20 to 80. The activation energy for the hydrolysis formation reaction is 12 $\pm$ 2 kilocalories per mole. The rate limiting step for copper reduction by the heterogeneous mechanism is the reduction of the intermediate basis salt.

CHAPTER IV

EXPERIMENTAL EQUIPMENT

The experimental set up was a modification of the system originally built by Neskora (23). It consisted of a vertical, tubular reactor with associated feed and product separation systems. The complete system with its accessories is shown schematically in Figure IV-1.

Feed System

The feed solution, to be processed, was contained in a 15-gallon polypropylene accumulator (A-1), mounted on a Detecto platform scale graduated to 50 grams division. The bottom fill-level of the accumulator was connected to the suction of a 1/4 horse power Teel centrifugal circulating pump (P-1) through a 3/4 inch (19 mm) diameter flexible PVC tubing. The discharge of the circulating pump was divided into three branches: (1) Feed to the suction side of the high pressure pump (P-2), (2) a recirculation line through a Jamesbury ball valve back to the accumulator, and (3) a drain line, provided with a Jamesbury ball valve, for removing feed after the run or for emergency dumps. The high pressure pump, a 1/2 horse power Milton Roy recipro-

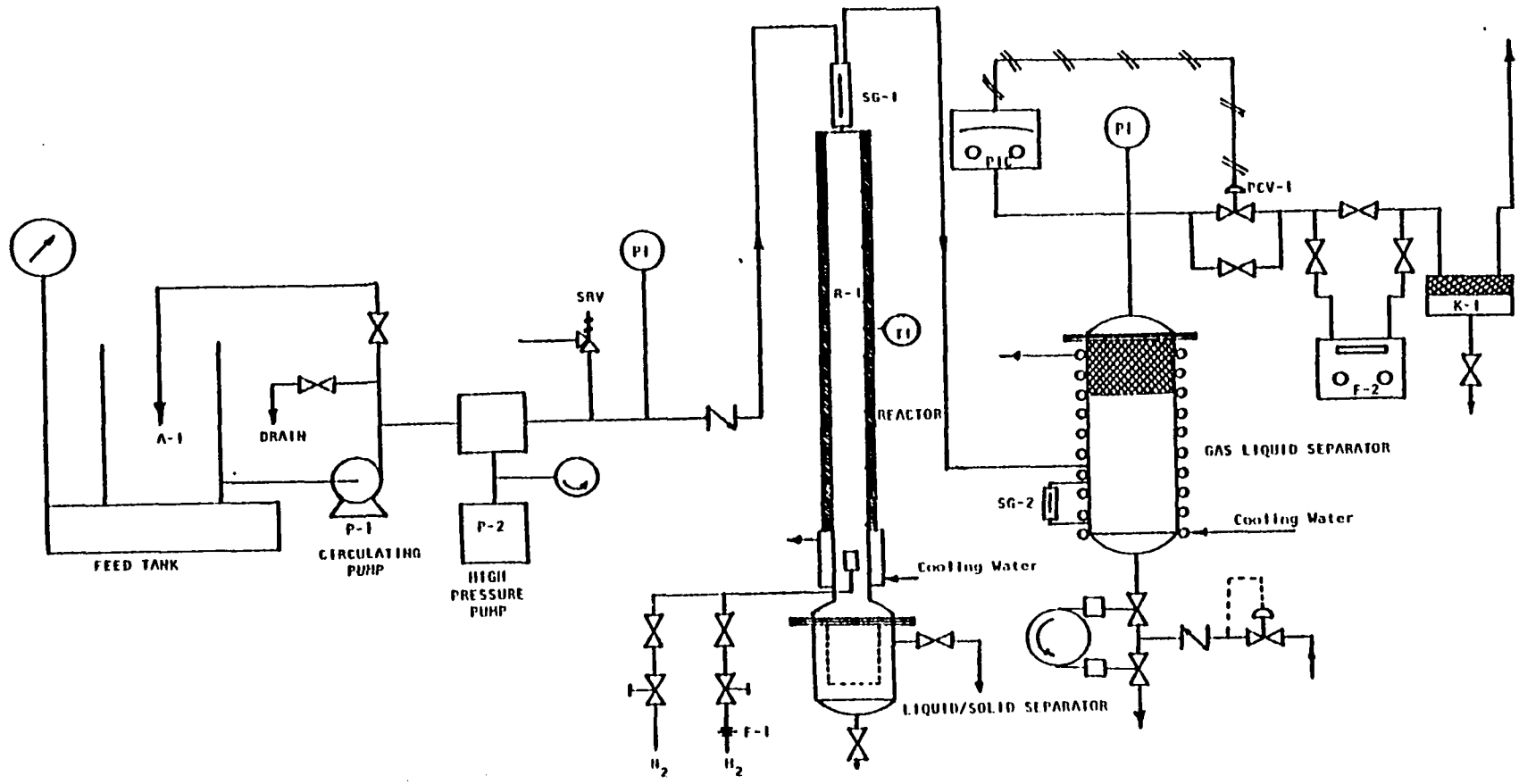
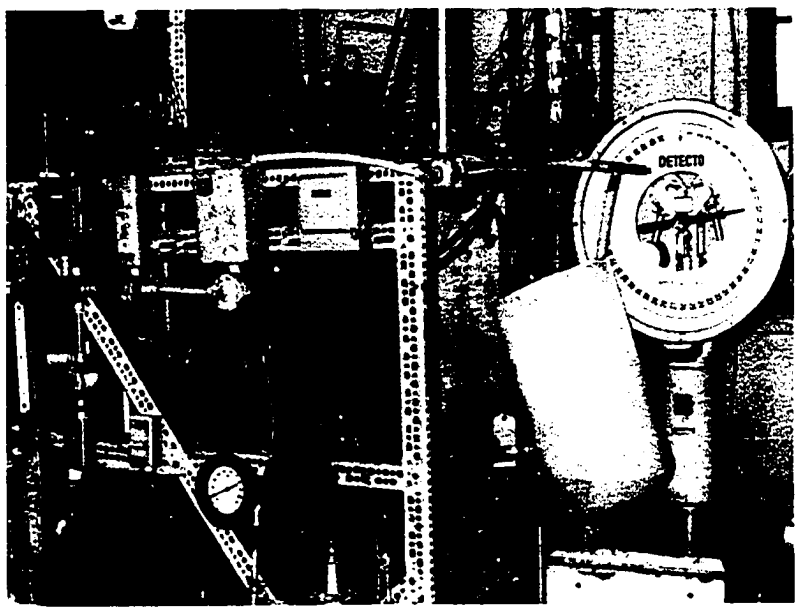


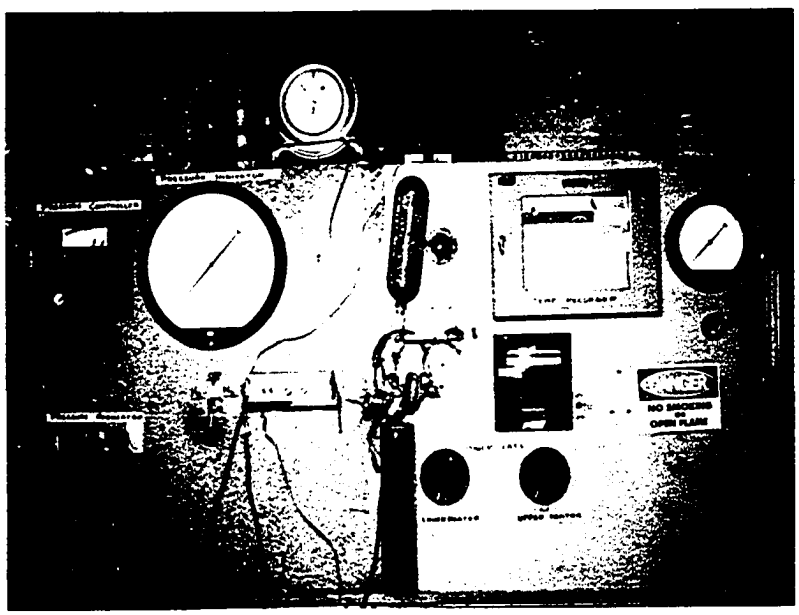
FIGURE IV-1. Schematic diagram for continuous hydrogen reduction process.

cating diaphragm pump, received the feed from the circulating pump through a 1/2 inch (13 mm) diameter flexible PVC tubing. The Milton Roy pump was constructed from carpenter stainless 20 material. The discharge from the high pressure pump feeds directly to the top of the reactor. An Ashcroft dial pressure indicator and an Anderson Greenwood 316 stainless steel safety relief valve were provided on the discharge line of the high pressure pump.

Hydrogen was stored in a regular "K" type bottle equipped with a Victor pressure regulator; it was introduced into the reactor through 1/4 inch (6.3 mm), 304 stainless steel, high pressure tubing. The flow of hydrogen to the reactor was measured by a DP (differential pressure) cell (F-1) and was controlled by a manually operated 1/4 inch (6.3 mm) Nupro needle valve. Hydrogen was introduced to the reactor through a sparger located inside the reactor below the jacketed cooler. A three way Republic valve was incorporated in the hydrogen line downstream from the DP cell. Nitrogen which was used to purge or pressure test the reactor, was introduced to the reactor through the same line as hydrogen at the three way valve. The feed system is photographically shown in Figure IV-2.



Feed System



Control Panel

FIGURE IV-2: Continuous Hydrogen Reduction Feed System and Control Panel.

Reactor System

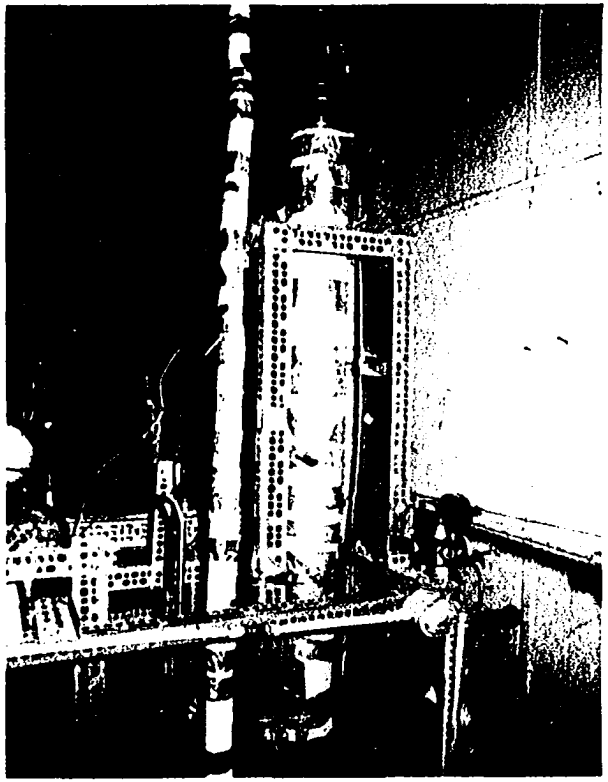
The vertical countercurrent flow reactor was constructed from titanium pipe 6 feet (1.83 meters) in length, 1 1/2 inch (38 mm) in outer diameter and 1/8 inch (3.2 mm) in wall thickness. The top end of the reactor was reduced to 3/4 inch (19 mm), by appropriate stainless steel Swagelok fittings. The sight glass (SG-1) is mounted just above the reactor; it is connected to the 3/4 inch (19 mm) reducer nipple. The lower end of the reactor was directly connected to the top part of the liquid-solid separator. Right above this connection, a cooling jacket about 12 inch (305 mm) long was provided to cool the reactor products before entering the separator. The rest of the reactor length was wrapped evenly with two electrical resistance wire, tape heaters of 960 watts each. These heaters were connected to two separate 200-volt single phase powerstat variacs, respectively, for controlling the heat input to the reactor. Nine J-type thermocouples, four on each side 8 inches (200 mm) apart and one in the middle of the reactor, were provided. The thermocouple output was recorded with a 24 point, Honeywell-Brown Electronik, temperature recorder. The reactor was insulated first by wrapping asbestos tape, one inch (25 mm) wide and 1/8 inch (3.2 mm) thick over the heaters. A 2 inch (50 mm) thickness of fiberglass pipe form insulation was then installed over the asbestos tape. The feed line

to the reactor from the high pressure pump and the outlet for the gaseous products from the reactor to the gas-liquid separator were connected just above the sight glass (SG-1) via a "T" connection. The lines were fabricated from 1/4 inch (6.3 mm) stainless steel, high pressure tubing. The reactor system is shown photographically in Figure IV-3.

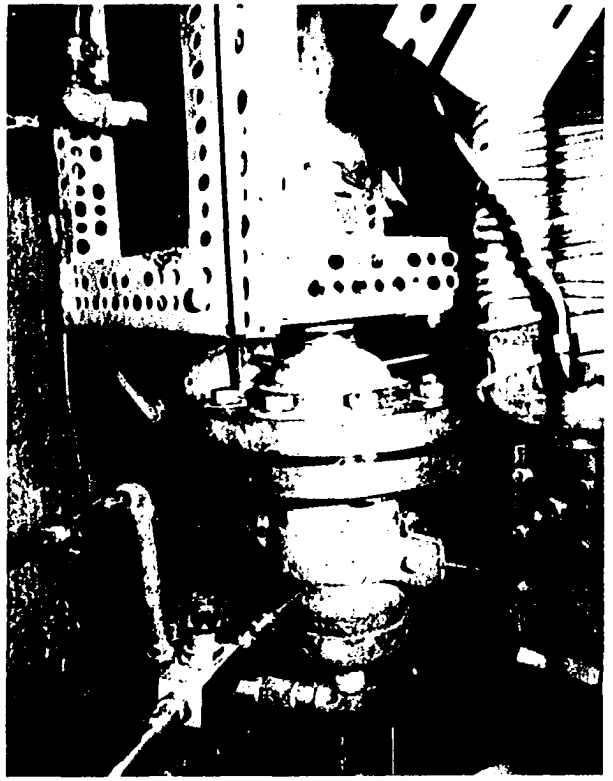
Product Separation System

The product separation system consists of two components: (1) a liquid-solid separator directly below the reactor, and (2) gas-liquid separator connected to the top vent line of the reactor.

Liquid-solid separator: The outerbody of the liquid solid separator was constructed from 7 1/2 inch (190 mm) long, schedule 40, 4 inch (100 mm) nominal diameter, 304 stainless steel pipe. One 300 psi rated, 4 inch (100 mm) stainless steel slip-on flange conforming to ANSI standards, was welded to the top end of the pipe. The flange was positioned in such a way that the concave weld joint would serve as a seat for the filter basket. The lower end of the pipe was welded to a standard, 4 inch (100 mm) stainless steel cap. The lid for the separator, consisting of a cap welded to the second flange, was connected to the reactor lower end with appropriate Swagelok fittings. The filter basket fabricated from 1/16 inch (1.6 mm) thick perforated stainless steel sheet was



Reactor System



Product Separators

FIGURE IV-3: Continuous Hydrogen Reduction Reactor and Product Separators.

provided with a ring around the basket at the top to fit securely into the concave seat of the body. Inside the basket a filter bag (+ 10μ) was provided. A 3 inch (75 mm) long, 1/4 inch (6.3 mm) diameter, high pressure stainless steel tubing, welded to the separator body at a distance of 2 inches (50 mm) from the flange center and provided with an 1/4 inch (6.3 mm) on-line filter and Nupro needle valve, was used for sample collection and for continuously draining the product filtrate. For draining the separator and reactor after completion of run and during an emergency, a 3/4 inch (19 mm) tap was provided at the bottom of the separator, with an appropriate Jamesbury stainless steel ball valve. The liquid-solid separator is shown photographically in Figure IV-3.

Gas-Liquid Separator: The gas-liquid separator was constructed from a 15 inch (380 mm) section of 4 inch (100 mm), Schedule 80, 316 stainless steel pipe. The separator includes a set of 600 psi rated weldneck stainless steel flanges at the upper end and a weld cap at the lower end. The separator section below the flanges was fitted with appropriate connections for gas-liquid product inlet, a liquid level sight glass and a liquid removal system. Cooling water was circulated through thirty feet of copper tubing wrapped around the lower separator section to cool down the product gas and the entrained liquid. The separator section above the flanges was

packed with aluminum shavings to remove entrained liquid from the gas product prior to depressurization.

The products from the reactor entered the separator approximately three inches below the separator flange assembly. A Penberthy liquid level sight glass was installed on the lower separator section to provide a visual means for monitoring the entrapped liquid level in the separator. The accumulated separator liquid was periodically removed through a cycling ball valve system located on the bottom of the separator. The cycling ball valve system, composed of two pneumatically activated 316 stainless steel ball valves, was connected by a short teflon lined section of stainless steel pipe. The valves were installed in a vertical position below the separator and were alternately opened and closed with a variable speed cam actuator. The actuator was designed to ensure that only one of the two valves could be opened at a time. The cycle began with both valves closed. As the cam actuator rotated to open the top valve, the section between the ball valves would be filled with liquid. Continued rotation of the cam actuator closed the top valve, and after a short time lapse, opened the bottom ball valve to drain the liquid from the section between the ball valves. The cycle was completed with the closing of the bottom valve. The section between the ball valves was purged automatically with nitrogen when the lower valve was

opened. This purging was accomplished by the use of a Grove pressure regulator and check valve combination.

The product gases removed from the top of the separator were depressurized through a, Research control, pressure control valve (PCV-1), shown in Figure IV-1. The pressure control valve also maintained the desired system operating pressure through a control sequence employing a Honeywell-Brown pressure indicator controller (PIC). The pressure indicator controller sensed the high pressure separator pressure and pneumatically controlled the pressure control valve to maintain the desired system pressure. A Grove small volume, pressure regulator was provided parallel to the pressure control valve to gain better control on the reactor pressure. The indicated pressure of the Honeywell-Brown pressure controller was supplemented by a more acurate, Heise, pressure indicator calibrated in one pound per square inch divisions. Both the pressure controller and pressure indicator are shown on the left side of the control panel in Figure IV-2.

Depressurized gas from PCV-1, was passed through a, 1/4 inch (6.3 mm) Nupro, needle valve to a Precision Scientific wet test meter (F-2), then through a knockout pot (K-1) before venting to the atmosphere. A bypass, with a Whitey globle valve, was provided for prerun and emergency purposes.

Auxiliary System: Special precautions were taken to handle highly explosive and flammable hydrogen, apart from the precautions taken to handle the high pressure system in this investigation. All the electrical motors used were explosion proof and wiring was sealed in conduits. A Dayton, exhaust fan 24 inches in diameter, having a capacity of 5000 cubic feet per minute, was used to purge air continuously from the laboratory to preclude any accumulation of explosive gases.

The utilities required during the operation included a 110-volt, single phase and 220-volt, three phase electrical circuits, domestic cooling water and compressed air at 120 psig for the instruments. All the utilities and the required hardware for normal functioning and cleaning of the system were available in the existing facilities.

CHAPTER V

EXPERIMENTAL WORK

Process Description

In this study, aqueous copper sulfate solution was contacted with, and was reduced by, hydrogen in a counter-current, vertical, tubular, plug-flow reactor by flowing the solution from the top and hydrogen from the bottom of the reactor. For better contact surface area and dissolution in the solution, hydrogen was passed through a sparger. The reaction products containing liquid and solids were separated in a high pressure separator, located immediately below the reactor; the liquid product was continuously removed to maintain the desired liquid level in the reactor. The excess and unreacted hydrogen, along with entrained liquid, exited from the top of the reactor and entered another separator before venting to the atmosphere after passing through a wet test meter. The investigation covered a temperature range of 250°F (121°C) to 450°F (232°C) with flow rates of 40 cc/min to 100 cc/min at 500 psig (34 atmospheres) and 400 psig (27 atmospheres) total pressures. For some of the runs the

feed was pretreated with either sulfuric acid, or sodium sulfate or both. Since the liquid feed could not be pre-heated prior to entering the reactor because of precipitation of basic salts at elevated temperatures, part of the reactor had to serve as a preheater. Thus, it was not possible to operate the reactor isothermally. As a result, experimental runs were a combination of non-isothermal and isothermal processing.

Experimental Procedure

The sequence of events for a total run consisted of feed preparation, equipment check-out, experimental run, shutdown, and analysis of the product solution for conversion.

Feed Preparation: In all runs reagent grade chemicals were used. The copper sulfate ($CuSO_4 \cdot 5H_2O$), sodium sulfate ($Na_2SO_4 \cdot 10H_2O$) and sulfuric acid (H_2SO_4) were obtained either from J.T. Baker, Mallinkrodt or Fisher Scientific Company. Deionized water required for the feed was prepared by using an ion exchange demineralizer (universal) cartridge obtained from the Illinois Water Treatment Company.

A weighed amount of copper sulfate was transferred into a calibrated 5-gallon polypropylene carboy graduated in 1 liter divisions. A measured amount of deionized water was added to dissolve the copper sulfate(and in some runs,

weighed amount of sodium sulfate and/or sulfuric acid, prediluted in deionized water, were added to the calibrated carboy). After all the reagents were added, the carboy was filled to the required mark by adding additional deionized water, and the contents were mixed throughly. If the feed required was more than 5 gallons, the contents were transferred to another carboy and the procedure was repeated as described. Care was exercised to insure that the water used was of high quality and did not precipitate copper out. (When copper sulfate was added to ordinary tap water, a turbid solution is observed, which may be due to the presence of chlorine in the water reacting with copper and precipitating it as copper chloride.)

Prerun Checkup: Because of operation at elevated pressures, each time the reactor system was opened (which was the case for every run) and was reassembled, the complete system had to be pressure checked. The reactor and liquid-solid separator were filled with water and then were pressurized to 500 psig (34 atmospheres) with nitrogen. All the gas lines were checked for leaks by a soap bubble test. The liquid lines were checked for leaks by visual inspection. The pressure was retained for one hour, and if the pressure held, the equipment was assumed to be tight in which case it was depressurized and the reactor was drained. (If the pressure started to drop more careful inspection was carried out until a leak

was found.) Having established the readiness of the equipment, hydrogen and nitrogen bottle pressures were checked to make sure they were adequate for the experimental run. Similarly, the utility water and air supplies and the sufficiency of the recorder chart paper were checked.

Experimental Run: The feed was transferred to the accumulator and the cooling water and air supply lines were connected. The laboratory heater, or air conditioner, was shut off to eliminate any possible ignition sources, and the room exhaust fan was activated. Then the circulation pump and, the high pressure pump were started, and hydrogen was allowed to flow into the reactor. Once the reactor was filled to the liquid level at the preset mark on the sight glass, the outlet valve on the separator was opened and was adjusted to maintain the level in the reactor. Then the reactor heaters were activated, and the temperatures were recorded on the chart. When the pressure in the reactor reached the preset level, the hydrogen flow to the reactor was cut back to the required point needed for the run by monitoring the needle valve on the hydrogen line. The temperature was allowed to come to a steady preset value, which was maintained for approximately one hour before taking any samples. Once the run attained steady state, the hydrogen exhaust was routed through the wet test meter by monitoring the valves.

Samples of the feed and the product solution coming out of the separator were collected in 10 cc sample bottles. The product solution was collected every 10 minutes while recording the hydrogen exhaust rate. The total run duration for each experiment was 60 minutes, which was established by experience to be adequate for the liquid product separator to reach steady state. Once steady conditions were obtained, the conversion remained constant with time.

Shut-down and Post-run Procedures: Once the samples were collected, the feed from the accumulator was drained and then after thoroughly washing and rinsing the reactor system, it was filled with deionized water by maintaining flow during the process of change over. The power to the heaters and hydrogen supply to the reactor were cut off after ensuring that no copper sulfate solution remained in the reactor. After the reactor temperature dropped below its normal boiling temperature, the feed water was shut off and the reactor was depressurized. Then, the cooling water and air supply lines were disconnected, and the prerun start-up procedure was effected in the reverse order. Finally, the reactor was purged with nitrogen.

After allowing the reactor to cool down to room temperature, the liquid-solid separator was disconnected and the accumulated product was filtered and was washed,

first with water, and then with acetone. The sight glass at the top of the reactor was disconnected, the reactor was thoroughly brushed with an infant, feed bottle brush and then was washed with deionized water. The product disengaged from the reactor walls was separated from the wash water by filtering and washing. The reactor and the separator were allowed to dry before the separator and the sight glass were reassembled to the reactor, following which the lines were pressure checked. After the pressure check the reactor and the system was ready for the next run.

Product Analysis

The product filtrate samples collected were quantitatively analyzed using iodometry for unreacted copper present in the solution. The difference between the initial (feed) concentration of copper in the feed and the product solution were taken as the conversion to copper, including cuprous oxide and copper basic salts.

pH Measurement: pH of the feed and product samples were measured by an ionalyzer (orion research) pH meter.

Specific Gravity of Feed: Specific gravity of the feed was measured by using a specific gravity bottle to determine the volumetric feed rate to the reactor.

Iodimetric Titration of Feed and Product Solutions(25): The procedure followed for all the samples was:

1. Take 5 cc of the solution to be analyzed in a 250 cc conical flask.
2. Add a few drops of 4N. Ammonium Hydroxide till the solution attains a deep blue color and/or pale blue color precipitate appears.
3. Add 5 ml of glacial acidic acid and dilute with deionized water to about 50 cc.
4. Add one or two crystals of ammonium bifluoride and thoroughly mix the solution. The solution should be clear.
5. Add few crystals of potassium iodide and immediately cork the conical flask to prevent air oxidation of the iodine released. Cupric ions will react with potassium iodide to form cuprous iodide (white precipitate), releasing stoichiometric amount of iodine.
6. Allow the reaction to proceed for about 2 minutes. Then titrate against the already standardized sodium thiosulfate solution. During titration the solution should be agitated, but very slowly, so that dissolved iodine in the solution does not get disturbed.

7. When the solution turns to pale yellow, the iodine is essentially consumed. Add 3 to 4 cc of starch solution and titrate with sodium thiosulfate. Just before the end point, add potassium thiocyanate and titrate to the end point. The solution containing cuprous iodide precipitate should turn to a white color.
8. Note the volume of sodium thiosulfate consumed and from that calculate the copper concentration as follows:

$$Cu^{++} \text{ concentration in grs/lit} = \frac{V \times M \times N}{C}$$

where V = Volume of thiosulfate consumed

M = molecular weight of the copper ions (=63.54)

C = Volume of the sample solution taken (5cc for most cases)

N = Normality of the thiosulfate solution.

CHAPTER VI

LIMITATIONS AND PROBLEMS ENCOUNTERED

The investigation had to be limited to a very narrow range of operating conditions due to various factors. The temperature had to be limited to, 250°F (121°C) to 450°F (232°C) range due to hydrodynamic and heat transfer limitations. Since the wattage capacity of the tape-heaters is dependent on the tape length, and the tape length is limited by the reactor length, the maximum heat input to the reactor was fixed. Alternate means for heating were rejected for various reasons. Nichrome wire, for instance, could have been used to provide more wattage, but previous experience in this laboratory exposed problems like breaking and fusing of the wire, with subsequent penetration of the heating wire into the containment walls, which posed a dangerous situation. Heating oil could give more uniform heat input if sophisticated controls are used, but based on previous experience in this laboratory heating oil was not considered feasible for short duration runs because of long heat-up times for the oil. Sand bath heaters are reliable but effective only for heating short lengths.

Because of these limitations on the heating method, liquid flow rates to the reactor above 100 cc/min could not be employed. Above 100 cc/min, the temperature profiles were erratic, and at 100 percent heating capacity the maximum temperature that could be obtained was 450°F (232°C). At the other extreme, flows below 40 cc/min gave improper distribution of hydrogen and, as a result, erratic conversions.

The pressure was limited to 500 psig (34 atmospheres), because the liquid-solid separator was only rated for 600 psig (40 atmospheres) pressure.

The possibility of varying the residence time (or reactor length) at a fixed feed rate by providing intermediate taps along the length of the reactor would have generated valuable additional data, but it could not be provided in this case for the following reasons:

1. The reactor being titanium (for corrosion resistance) it is difficult to provide taps welded to the reactor walls.
2. Analysis of the data obtained from intermediate taps would have been difficult due to non-isothermal nature of the part of the reactor.
3. Clogging of the taps due to deposition of metal.

Hydrolysis and precipitation of basic copper sulfate at elevated temperature in the absence of hydrogen prevented preheating the feed before entering the reactor. Thus, as mentioned before, the reactor had to be operated non-isothermally.

The most aggravating operating problem was the sticking of the metal product to the reactor walls. Different coatings and additives were tried, but unsuccessfully, as detailed in Appendix D.

The aforementioned operating problems precluded covering the range of variables that should have been investigated in order to perform a complete kinetic study.

CHAPTER VII

EXPERIMENTAL OBSERVATIONS

A brief description of the experiments with pertinent observations are presented in this chapter. As mentioned in earlier chapters, since the reactor had to be operated partly isothermally and partly non-isothermally (as a preheater), it is difficult to assign one particular temperature for the experiment. To distinguish among runs and to have a common basis for comparison, the average isothermal portion of the reactor temperature is reported here as the temperature of operation. Except for run #39 and #40, all runs were made at a total pressure of 500 psig.

Run #1 and 2

These two runs were made to check the operability of the experimental apparatus over a prolonged period to determine the degree to which changing temperatures could be monitored. The experiments were conducted at 100 grs/min flow rate (residence time of about 11 minutes) with a feed concentration of 22.4 grs (Cu^{++})/liter (0.3523 molar conc), in the temperature range of 300°F (148.8°C) to 450°F (232°C) for 8 hours. The reactor

temperature profiles for this run are shown in Figure VII-1. The conversions obtained were in the range of 30 percent for the 300°F (148.8°C) run to 78 percent for the 400°F (204.4°C) run. The conversion was higher at 400°F (204.4°C) (78 percent) than at 450°F (232°C) for which a conversion of 76.5 percent, was obtained. Following this latter run, the reactor was opened and was found to be filled with copper and probably cuprous oxide. At that time it was reasoned that the lower conversion, of 76.5 percent, at 450°F (232°C) than at 400°F (204.4°C) was due to a lack of adequate hydrogen distribution through the liquid because of copper buildup in the reactor, which in some sections covered the entire cross section of the reactor. Based on this observation and particularly because of the large amounts of feed required for runs of long duration, the decision was made to investigate only one set of operating variables between each cleansing of the reactor system and to limit the duration of each run to less than 2 hours.

Run #3 and 4

Run #3 was conducted at 400°F (204.4°C) with a temperature profile as shown in Figure VII-2. The average flow rate was 93 grs/min (residence time about 12.5 min), the liquid feed concentration was 22.98 grs(Cu^{++})/liter (0.3616 molar conc), and the feed rate of hydrogen was 25 percent in excess over the stoichiometric. The run duration

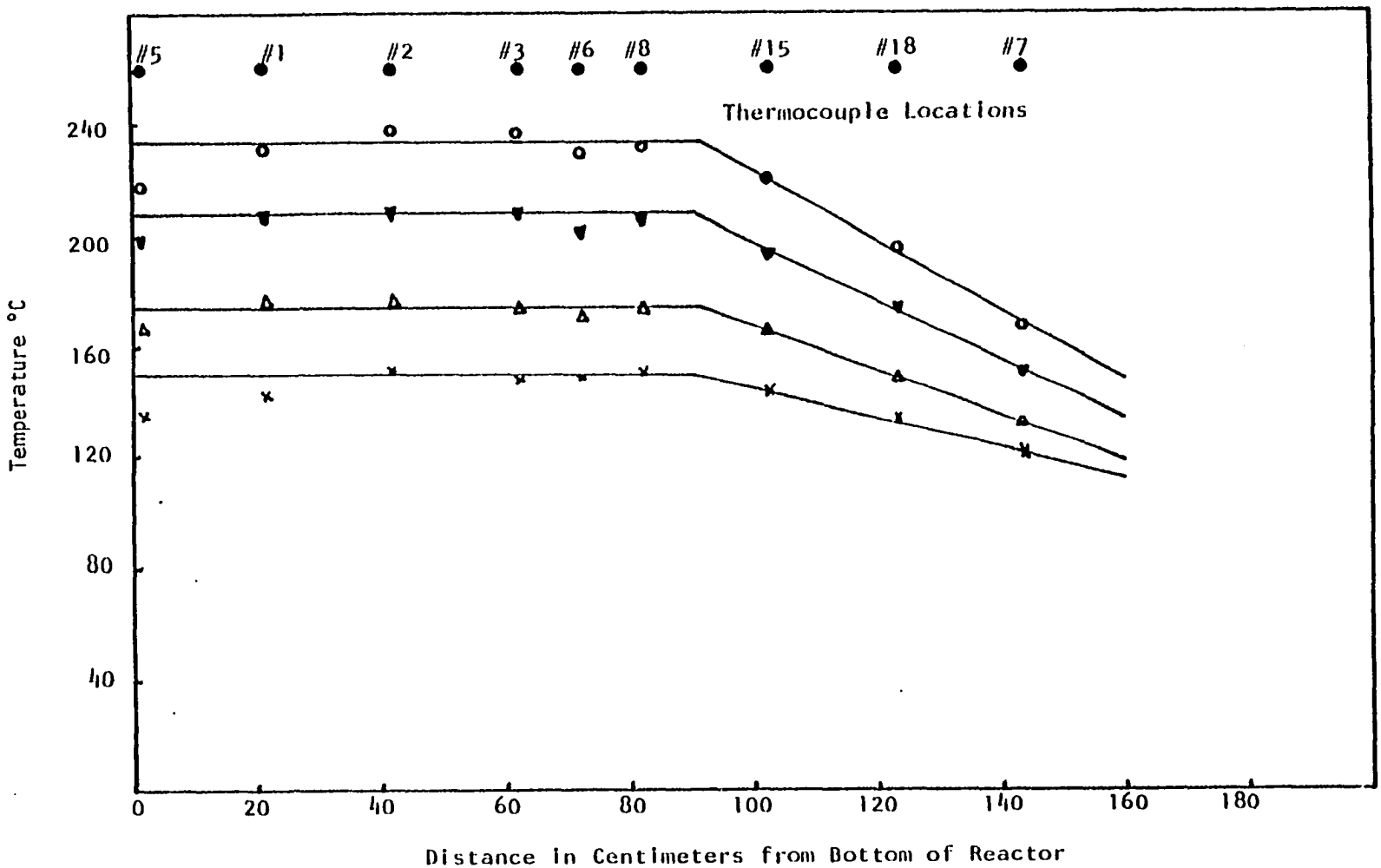


FIGURE VII-1. Temperature profile in the reactor for run #2.

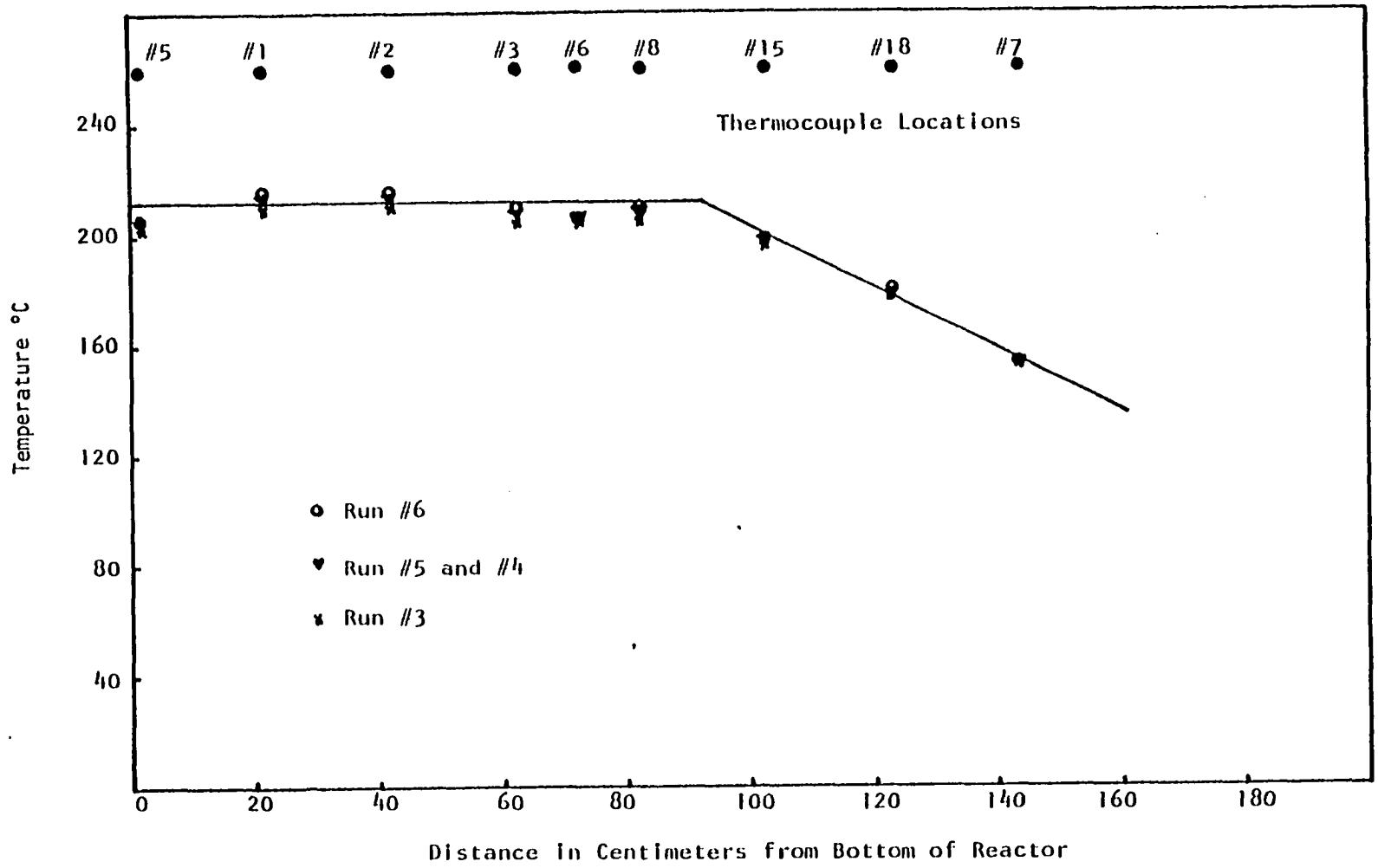


FIGURE VII-2. Temperature profile in the reactor for run #3, #4, #5 and #6.

was one hour, excluding the prerun and postrun periods. The conversion obtained was 79 percent. Even though the run was smooth, metallic copper and probably cuprous oxide in the form of very fine crystals was found to be sticking very loosely to the reactor walls. The solid product from the separator was spongy.

The objective of run #4 was to check if stoichiometric amounts of hydrogen would make any significant difference and also to see if mechanical tapping of the reactor periodically would loosen the copper from the walls of the reactor and thus eliminate the sticking problem. Experimental conditions for run 4, were the same as run 3. The conversion obtained was 75.5 percent (for a residence time of about 11.6 minutes). Tapping the reactor did not help much; a compact mass of copper was found adhering around the sparger and protruding from the reactor walls.

Run #5 and 6

These runs were made under conditions similar to runs #3 and 4, except that the feed concentration was lowered to approximately 12.0 grs(Cu^{++})/liter (0.188 molar conc). Run #5 was made with 25 percent excess hydrogen over stoichiometric and run #6 was made with a stoichiometric amount of hydrogen. Conversion of 72 percent were obtained in both the cases.

Run #7

This run was made by injecting live steam into the reactor for direct contact heating. The objective was to check if the external electrical heating can be contributing in any way to the sticking of copper to the reactor walls. A special dip pipe to inject steam was provided at the top of the reactor and was incorporated in the sight glass assembly. The dip pipe was always immersed in the solution during operation. A "mini-boiler" to provide the steam requirements was designed and fabricated in the laboratory. The steam pressure was maintained slightly above the operating pressure of the reactor. The quantity of steam injected to the reactor was maintained such that an operating isothermal temperature of 300°F (176.6°C) was maintained. See temperature profile in Figure VII-3. The run was smooth but copper was found sticking to the walls of the reactor, as in earlier experiments, dispelling the doubts about the external electrical heating causing the sticking problem. This method of heating was discontinued in the later runs since the required instrumentation for accurate control of the system was not available.

Run #8 and 9

These runs were made at 350°F (176.6°C) (see temperature profile in Figure VII-4) with flow rates of 77.5 grs/min (residence time 15.1 minutes) and with feed concentrations of 12.81 grs(Cu^{++})/liter (0.2016 molar conc)

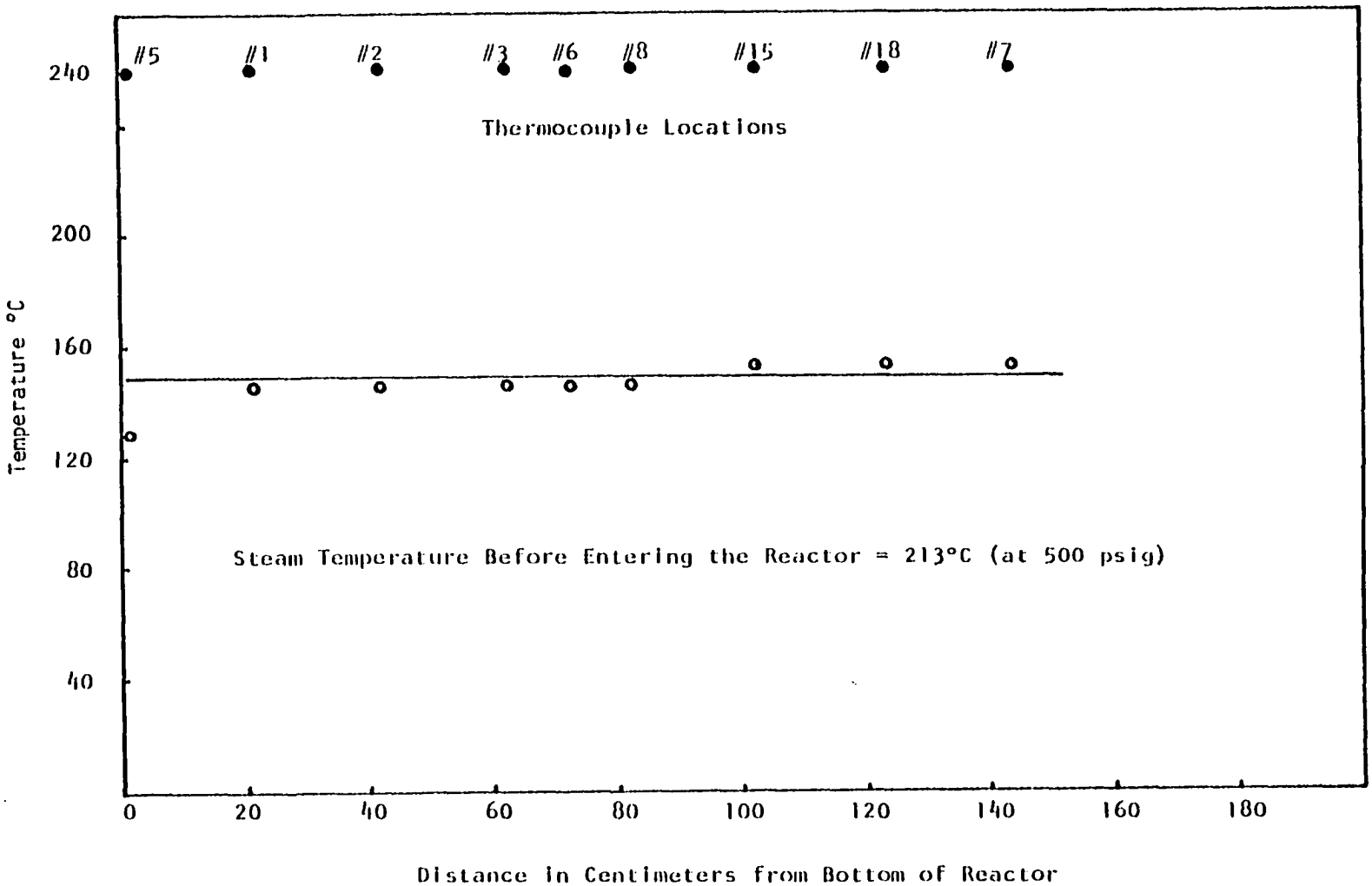


FIGURE VII-3. Temperature profile in the reactor for run #7.

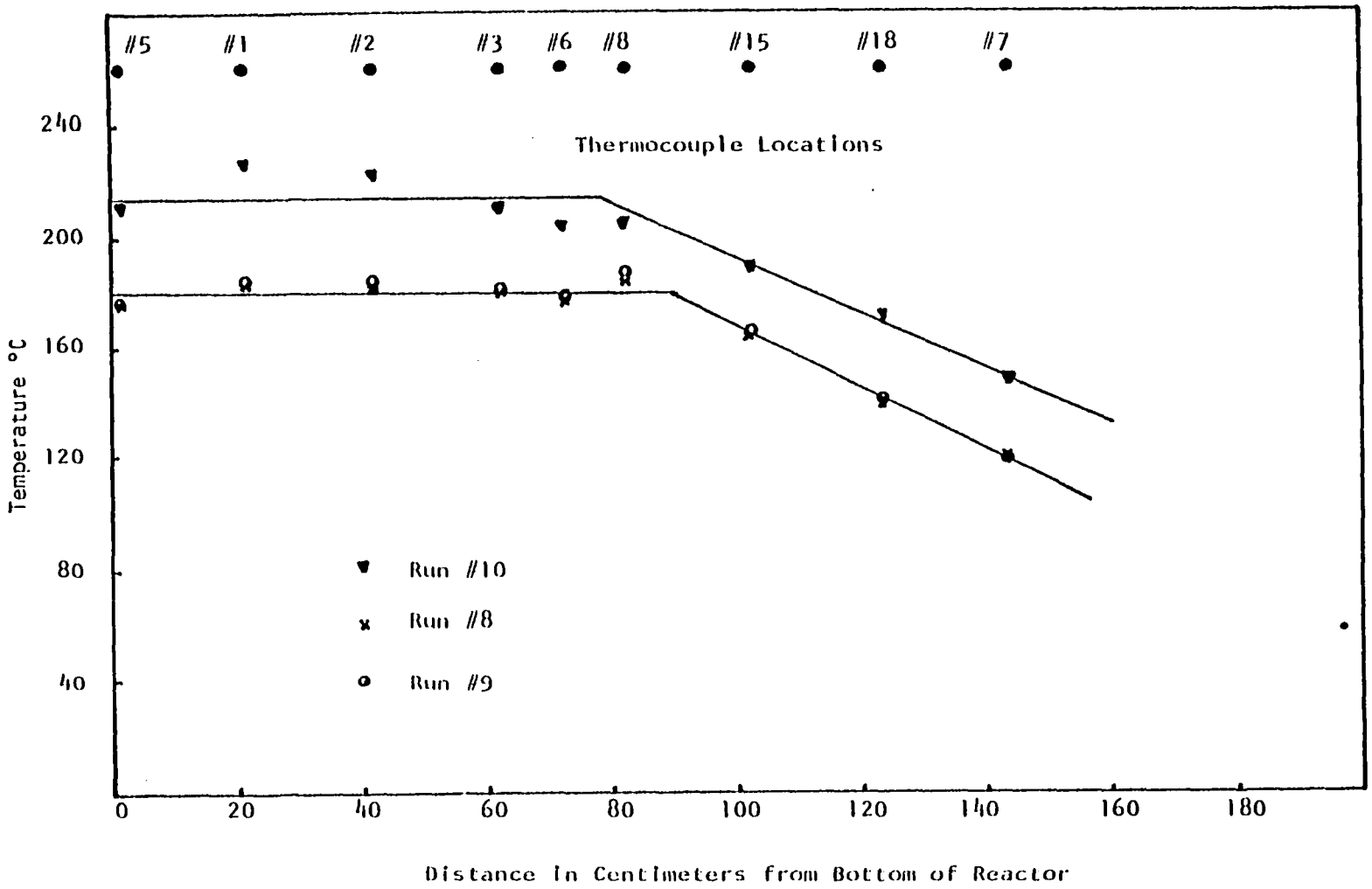


FIGURE VII-4. Temperature profile in the reactor for run #8, #9 and #10.

and 11.42 grs (Cu^{++})/liter (0.1797 molar conc) respectively. Run #8 was made using freshly made feed whereas run #9 was made using spent solution (of previous runs) made up to the required feed concentration by adding copper sulfate. Both of these runs appeared overtly to be similar to the previous seven runs described above. However, when the sight glass was dismantled from the reactor, sparkling violet crystals were observed sticking to the steam dip pipe, which had been installed for the purposes of run #7. These crystals, upon examination under a microscope looked like ruby crystals. Upon further analysis by x-ray diffraction they were identified as cuprous oxide, Cu_2O. A report of Southwest Metallurgical Consultants is presented in Table VII-1. The product obtained from the separator for run #9 was partly oxidized and mud-like. No possible explanation could be given for this phenomena.

Run #10, 11 and 12

The objective of these runs was to check if addition of acid, or lowering the pH, will prevent formation of Cu_2O. In addition, the experiments were conducted at three different temperatures to ascertain if temperature has any influence on the formation of cuprous oxide. The pH of feed was lowered from 3.8 (natural pH of aqueous copper sulfate solution) to 2.4 by adding sulfuric acid to the solution. Runs #10, 11 and 12 were conducted at

TABLE VII-1

X-RAY ENERGY SPECTROSCOPY AND X-RAY DIFFRACTION ANALYSIS

REPORT OF SOUTHWEST METALLURGICAL CONSULTANTS INC.

Sample No. 1 identified as Run No. 34

Major Element	Minor Elements	Trace Elements
Copper	Aluminum Iron Silicon	Chromium Nickel

Note: No Cu_2O as identified in Sample No. 3 was found.

Sample No. 2 identified as Run No. 17

Major Element	Minor Element	Trace Elements
Copper	Sulphur	Aluminum Iron Silicon

Sample No. 3 identified as Ruby Copper

Major Elements	Minor Element	Trace Element
Copper Oxygen	--	Aluminum

Note: X-ray diffraction identified the crystal structure as Cu_2O(cuprite) oxide. A trace of metallic copper and CuS were found.

400°F (204.4°C), 350°F (176.6°C) and 450°F (232°C) respectively (temperature profiles are shown in Figure VII-5). In all three cases cuprous oxide was found deposited on the dip pipe.

Run #13, 14, 15 and 16

The objective of these runs was to obtain the temperature effect on conversions while holding the other parameters constant. The experiments were conducted with average flow rates of 77.5 grs/min (residence time 15.11 min), 72.50 grs/min (residence time 16.15 min), 71.66 grs/min (residence time 16.43 min) and 75.0 grs/min (residence time 15.62 min) respectively, with feed concentrations of 12.3, 12.81, 12.3 and 11.55 grs(Cu^{++})/liter (corresponds to 0.1935, 0.2016, 0.1935 and 0.1817 molar concentrations respectively). Run #13, 14, 15 and 16 were made at average temperatures of 350°F (176.6°C), 400°F (204.4°C), 450°F (232°C) and 300°F (148.8°C) respectively. The temperature profile is shown in Figure VII-6. The conversions obtained were 70, 73.5, 70.4 and 45.7 percent, respectively. Cuprous oxide deposits on the dip pipe were observed in these runs also as before.

Run #17, 18, 22 and 31

These runs were made to obtain data at lower temperature levels. Run #17, 18, 22 and 31 were conducted at flow rates of 75 grs/min, 118.3 grs/min, 58.3 grs/min

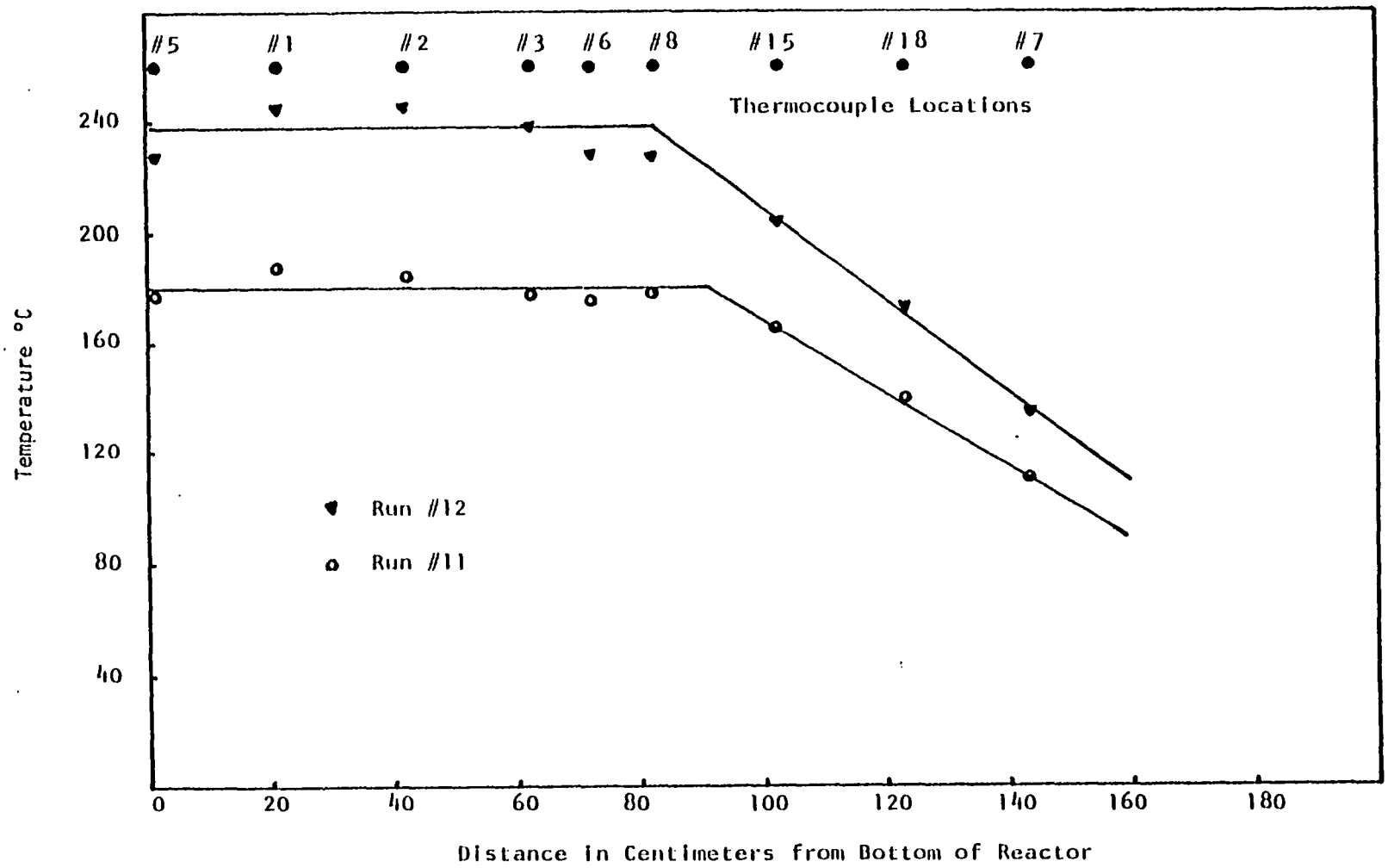


FIGURE VII-5: Temperature profile in the reactor for run #11 and #12.

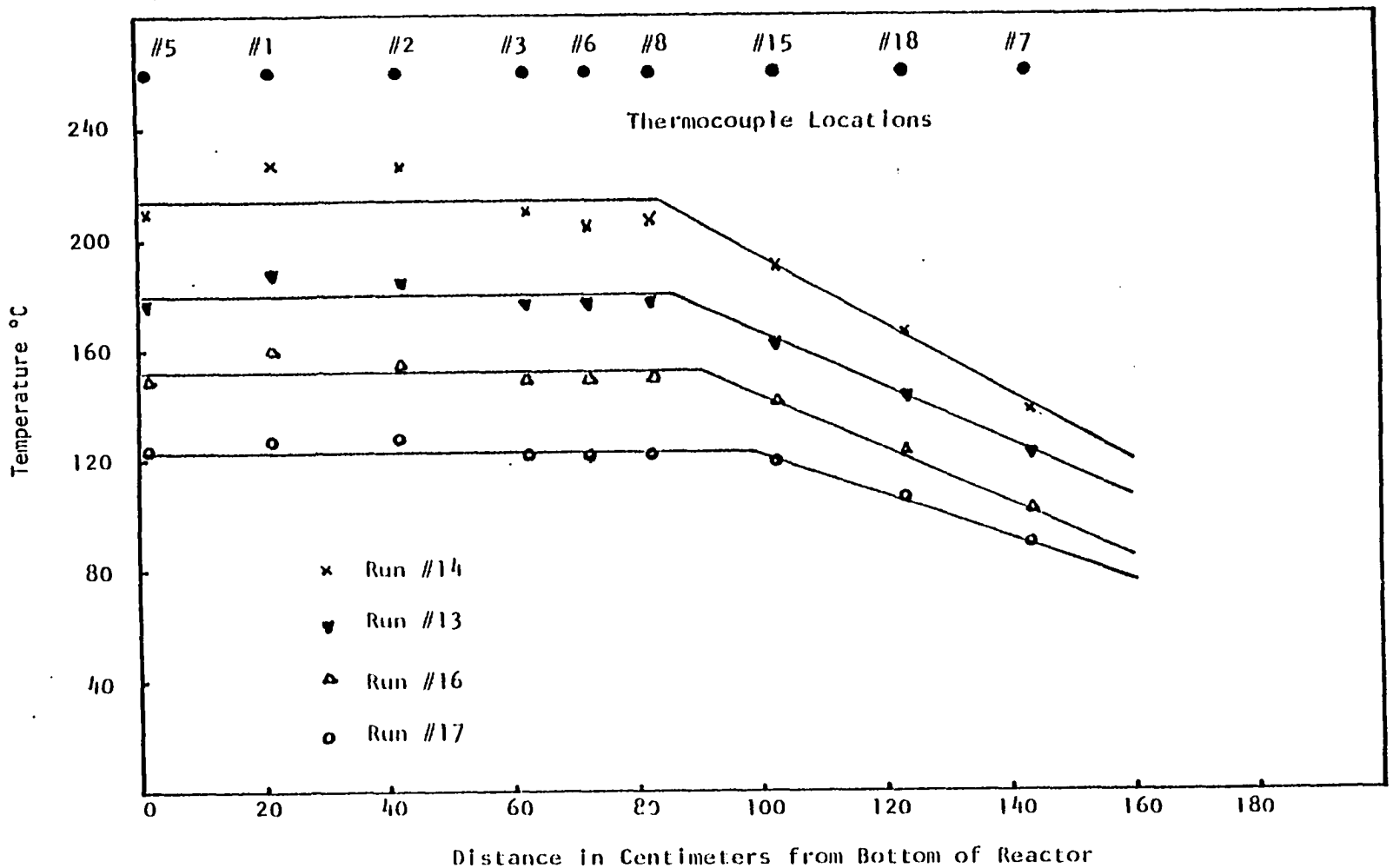


FIGURE VII-6. Temperature profile in the reactor for run #13, #14, #16 and #17.

and 41.6 grs/min (corresponds to 15.62, 9.9, 20.08 and 28.12 mins residence time) respectively. The feed concentrations were 12.43, 11.8, 11.74 and 12.13 grs(Cu^{++})/liter (corresponds to 0.1956, 0.1857, 0.1847 and 0.1909 molar concentrations). The experiments were performed at average temperatures of 250°F (121°C) (see temperature profiles in Figures VII-6, VII-7, VII-8 and VII-10). In all cases a green precipitate of basic copper sulfate was observed to have been deposited on the reactor walls. A report of Southwest Metallurgical Consultants is presented in Table VII-1.

Run #20 and 21

These runs were made at a flow rate of 120 and 115 grs/min (corresponds to 9.69 and 10.18 minutes residence time) respectively. Feed concentrations were 12.0 and 11.74 grs(Cu^{++})/liter (which corresponds to 0.1888 and 0.1847 molar concentration). The average temperatures were 350°F (176.6°C) and 300°F (148.8°C). See Figure VII-7 for the temperature profile. The observations made in earlier runs, namely formation of cuprous oxide and deposition of product copper and cuprous oxide on the reactor walls, were observed in these runs too. The conversions obtained were 52 and 21.7 percent respectively.

Run #24, 25 and 26

These runs were made to obtain data at different flow rates (57.5, 58.33 and 58.33 which correspond to 20.37,

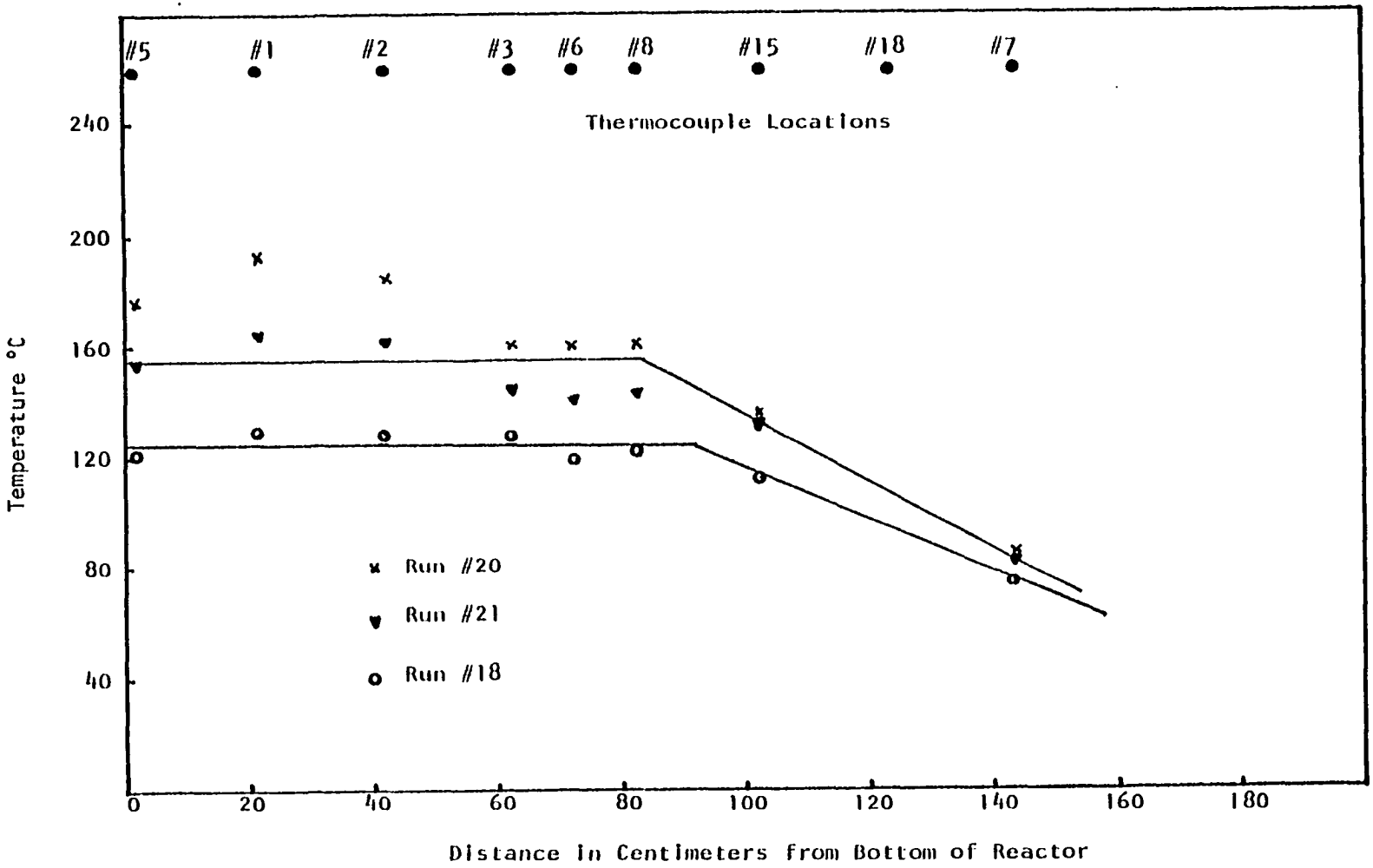


FIGURE VII-7. Temperature profile in the reactor for run #18, #19 and #20.

20.08 and 20.08 min residence time) respectively. Feed concentrations were 11.87, 12.38 and 13.78 grs(Cu^{++})/liter (corresponds to 0.1868, 0.1948 and 0.2168 molar concentration) and different temperatures. (Average temperatures were 350°F (176.6°C), 400°F (204.4°C) and 300°F (148.8°C) respectively.) The temperature profiles for these runs are shown in Figure VII-8. The observations were similar to those of earlier runs. The conversions obtained were 72, 76.3 and 52.8 percent respectively.

Run #27

This run was made to obtain data at an average temperature of 350°F (176.6°C). The temperature profile is shown in Figure VII-9 at a constant feed concentration of 11.62 grs(Cu^{++})/liter (0.1828 molar concentration) and at a flow rate of 80.8 grs/min (residence time 14.47 min). The conversion obtained was 63 percent.

Run #28

This run was made at an average temperature of 300°F (148.8°C). The temperature profile is shown in Figure VII-9. The feed concentration was 11.87 grs(Cu^{++})/ liter (0.1868 molar concentration). The experiment was conducted at a flow rate of 96.6 grs/min (residence time 12.1 min). The conversion obtained was 38.7 percent.

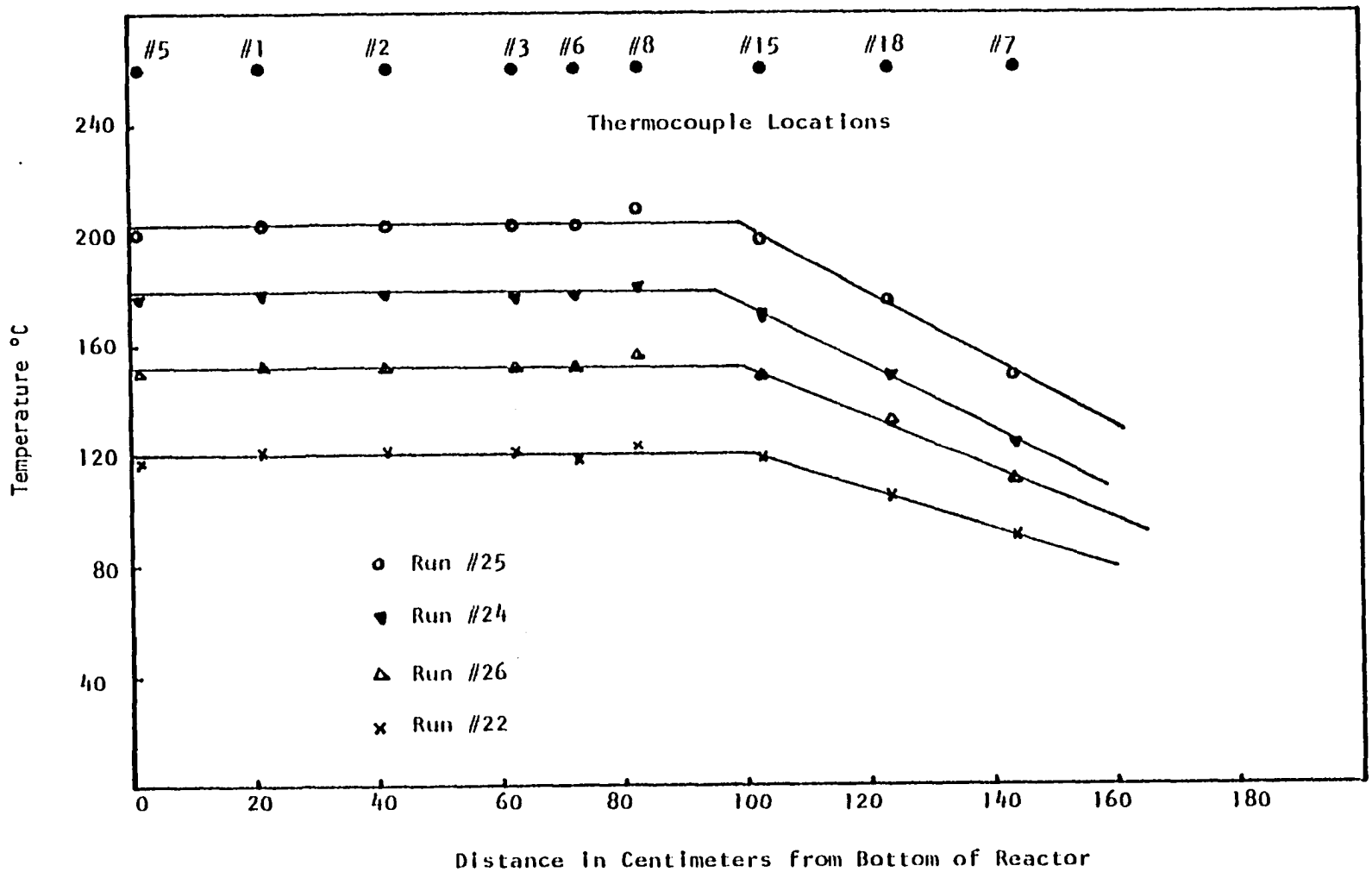


FIGURE VII-8. Temperature profile in the reactor for run #22, 24, 25 and 26.

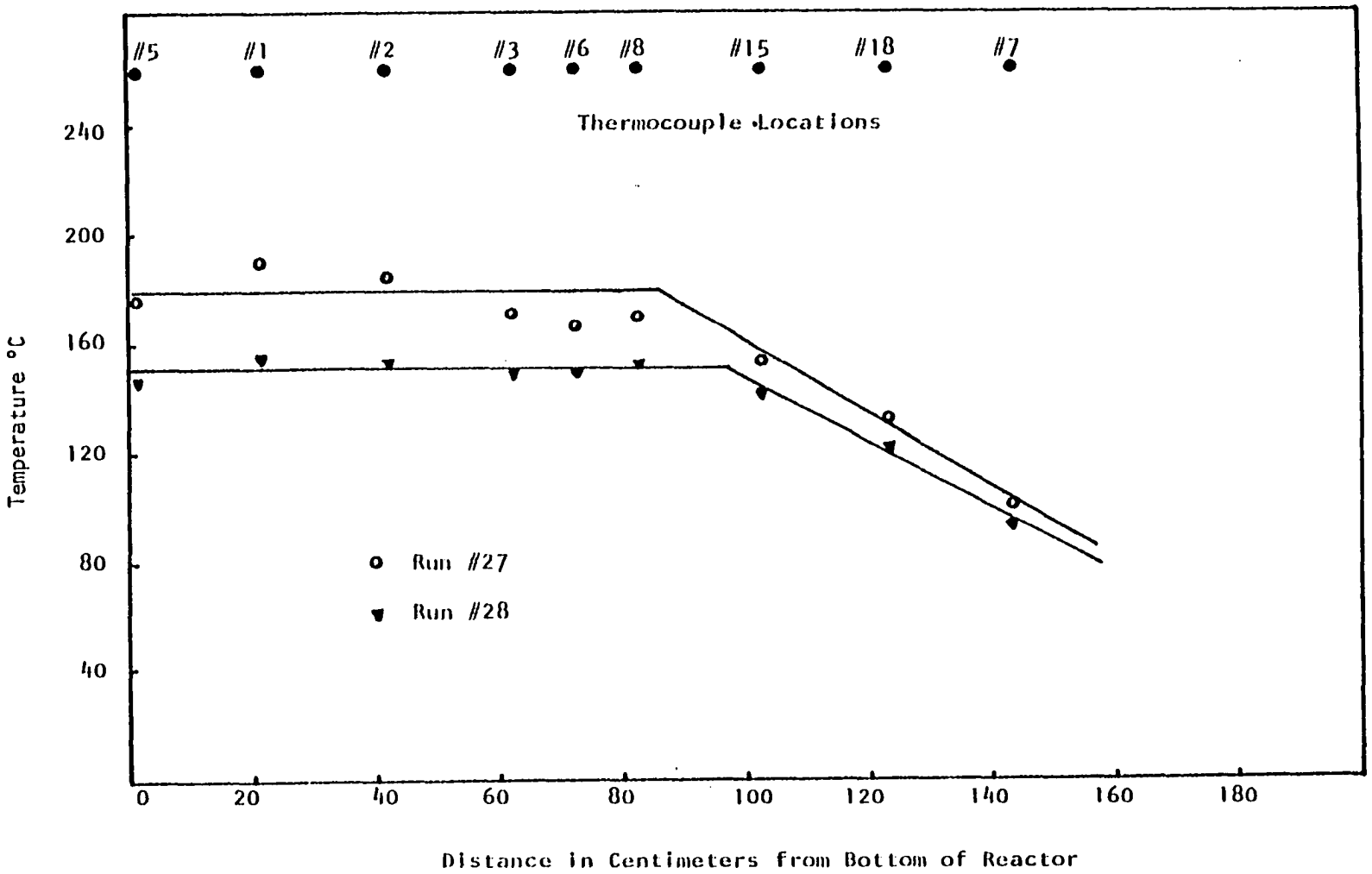


FIGURE VII-9. Temperature profile in the reactor for run #27 and #28.

Run #29, 30 and 32

These runs were made at a flow rate of 40.8, 39.1 and 40 grs/min (residence time 28.69, 29.96 and 29.29 min) respectively. The average temperatures were 300°F (148.8°C), 350°F (176.6°C) and 400°F (204.4°C) respectively. The temperature profiles are shown in Figure VII-10. The feed concentration was 12.13 grs(Cu^{++})/liter (0.1909 molar concentration) for all three runs. The conversions obtained were 26, 72.6 and 73.7 percent respectively.

Run #33, 34, 35 and 36

These runs were made to find the effect of acid addition on conversion, and to utilize these data to check the theoretical equations proposed by other investigators. The experiments were carried out at an average temperature of 350°F (176.6°C). The temperature profile is shown in Figure VII-11. The flow rates were 56.6, 55.0, 58.33 and 54.1 grs/min (residence times 20.67, 21.29, 20.08 and 21.63 minutes) respectively. The feed concentrations were 11.49, 12.25, 12.25 and 12.25 grs(Cu^{++})/liter (0.1808, 0.1927, 0.1927, 0.1927 molar concentrations) respectively. The added acid concentrations in the feed were 15.77, 31.54, 63.08 and 7.89 grs(H_2SO_4)/liter. The conversions obtained were 55.6, 51.0, 30.2 and 61.4 percent respectively. In the case of run 34 and 35, there were no deposits of cuprous oxide observed. The product deposited on the reactor walls, as well as steam dip pipe was pure copper. Run #34

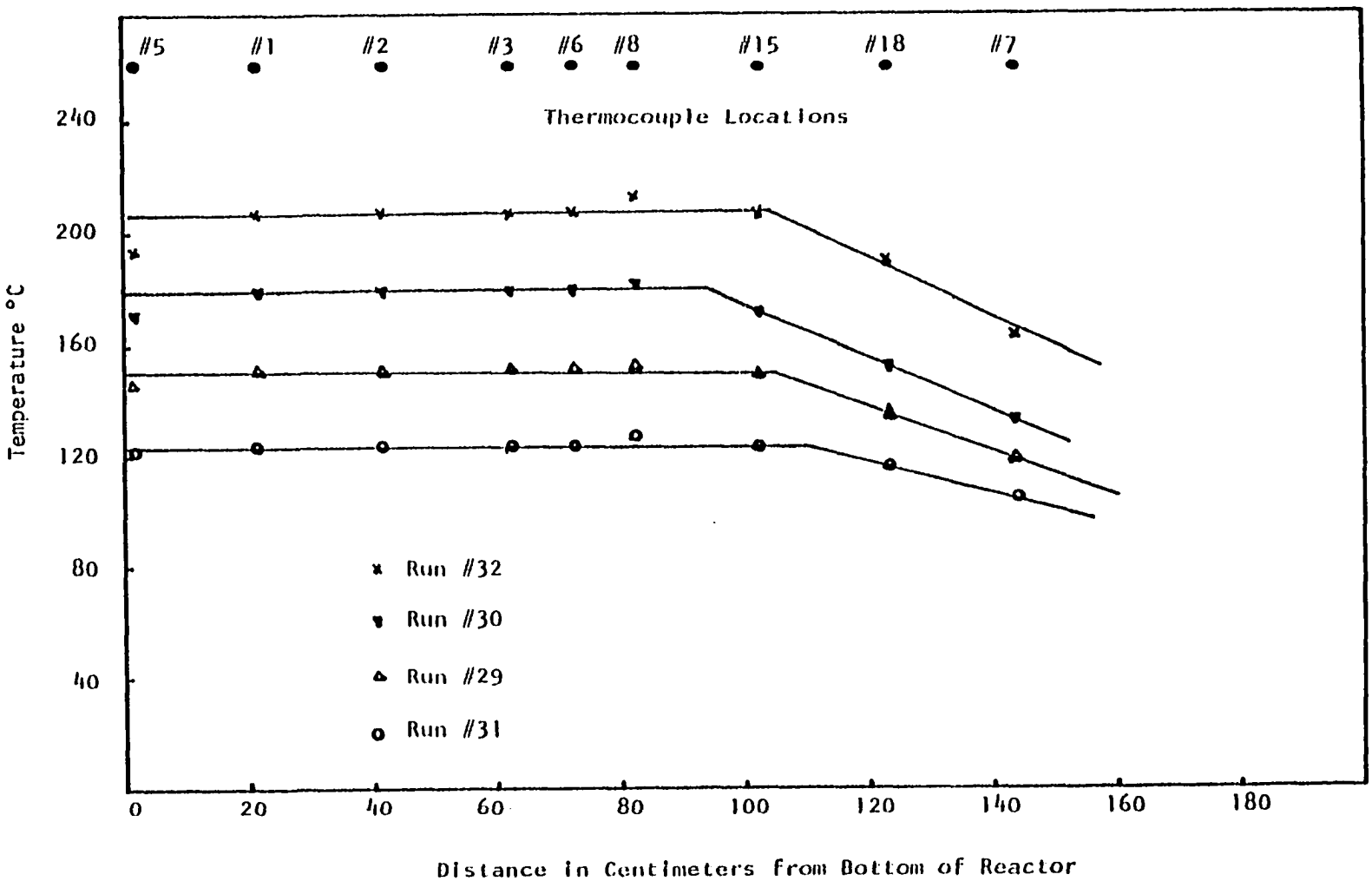


FIGURE VII-10. Temperature profile in the reactor for run #29, #30, #31 and #32.

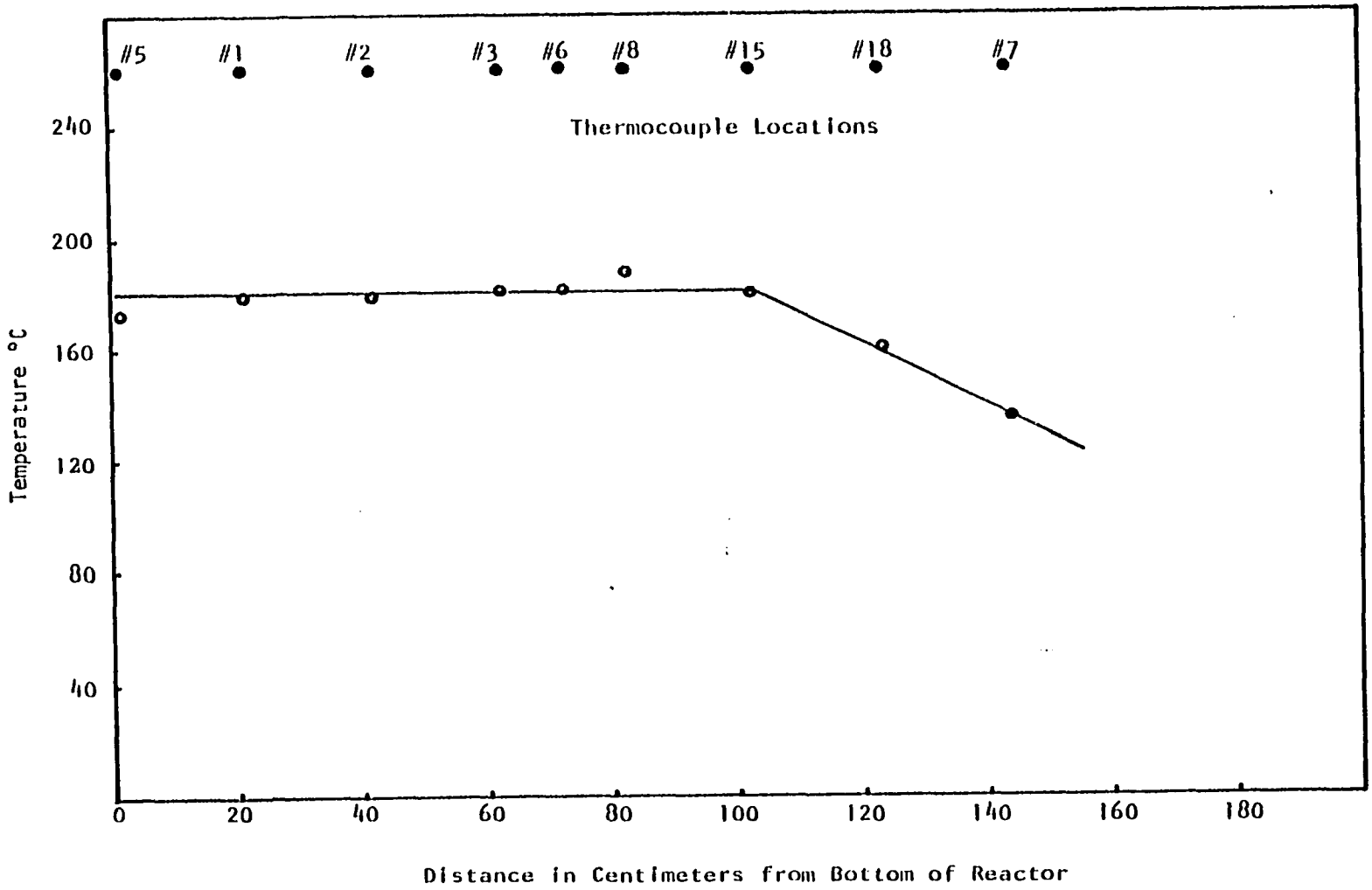


FIGURE VII-11. Temperature profile in the reactor for run #33, #34, #35 and #36.

was analyzed by x-ray diffraction and no trace of cuprous oxide was indicated. In Table VII-1 the report of the Southwest Metallurgical Consultants is presented.

Run #37 and 38

These runs were made to test the effect of addition of sodium sulfate in the presence or absence of acid. Run #37 was conducted with addition of sodium sulfate to the copper sulfate solution in the stoichiometric amount. The feed concentration was 11.87 grs(Cu^{++})/liter (0.1868 molar concentration) and the concentration of sodium sulfate was 60.74 grs($Na_2SO_4 \cdot 10H_2O$)/liter. The average temperature was 350°F (176.6°C). The temperature profile is shown in Figure VII-12. The experiment was conducted at a flow rate of 62.5 grs/min (residence time 17.74 min). Run #38 was made with addition of 31.5 grs (H_2SO_4)/liter of acid and stoichiometric amounts of sodium sulfate to provide enough sulfate ions to combine with the hydrogen ions generated during the reduction as well as with the acid added. The feed concentration was 12.25 grs(Cu^{++})/liter (0.1928 molar concentration), sodium sulfate added amounted to 164.44 grs($Na_2SO_4 \cdot 10H_2O$)/liter. The average temperature was 350°F (176.6°C); the temperature profile is shown in Figure VII-12. The experiment was conducted at a flow rate of 68.33 grs/min (residence time 17.14 min). In run 37, most of the product was cuprous oxide and very little copper was observed in the separator

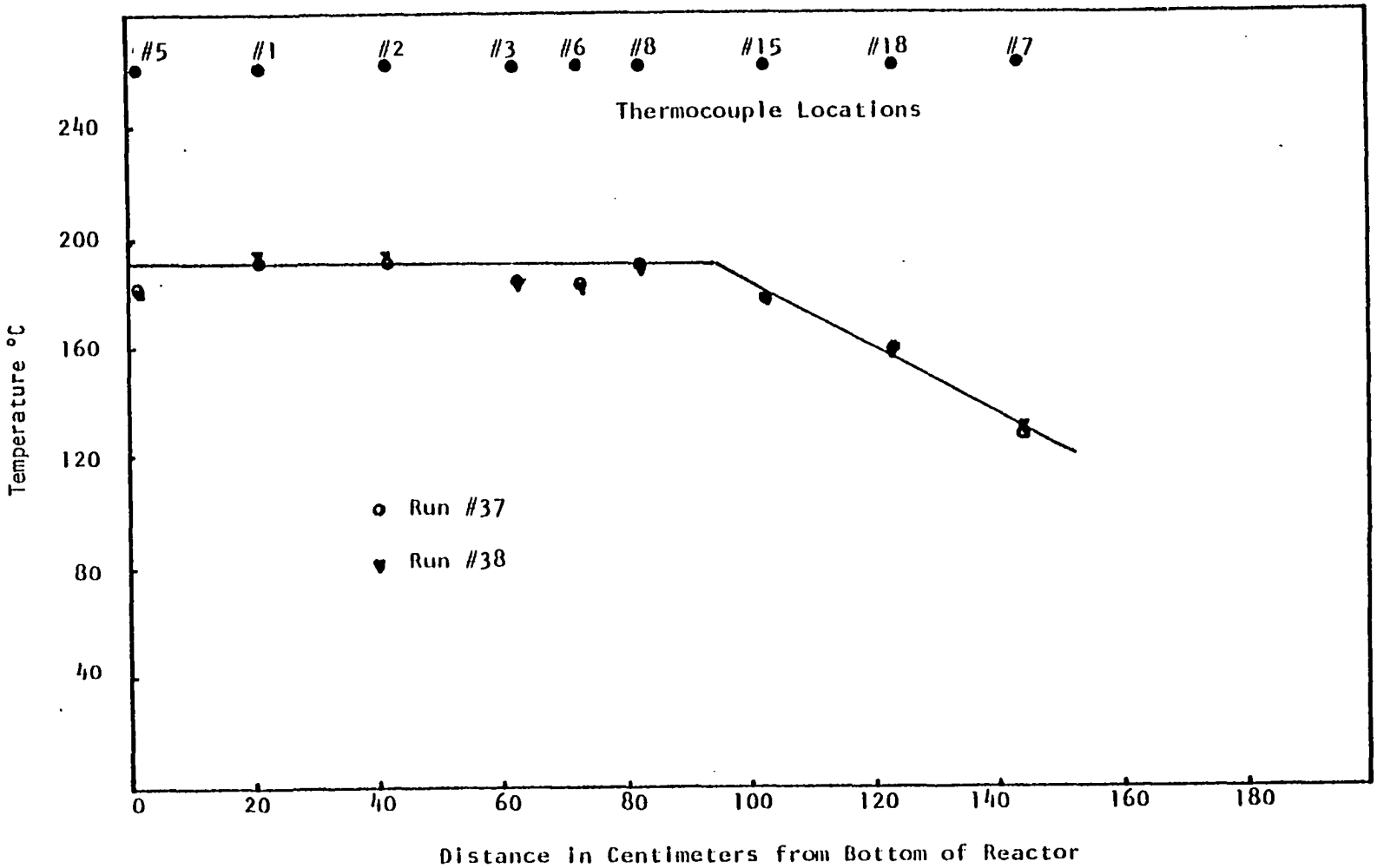


FIGURE VII-12. Temperature profile in the reactor for run #37 and #38.

or on the reactor walls. In the case of run 38 the product obtained was pure copper and no trace of cuprous oxide was found. The conversions obtained were 90 and 80 percent respectively.

Run #39 and 40

These two runs were made at a total pressure of 400 psig. The average temperatures were 350°F (176.6°C) and 300°F (148.8°C) respectively. The temperature profile is shown in Figure VII-13. The feed concentrations were 12.13 and 11.74 grs(Cu^{++})/liter (0.1909 and 0.1847 molar concentrations). The experiments were conducted at flow rates 59.16 and 53.73 grs/min (residence time 19.8 and 21.79 minutes) respectively. The objective was to check if lowering the total pressure will have effect on conversion since, at a given temperature, the partial pressure of hydrogen will decrease with total pressure. The conversions obtained were 71.6 and 53.2 percent respectively. The observations made in earlier runs - cuprous oxide formation and product sticking to the reactor walls - were observed in these runs too.

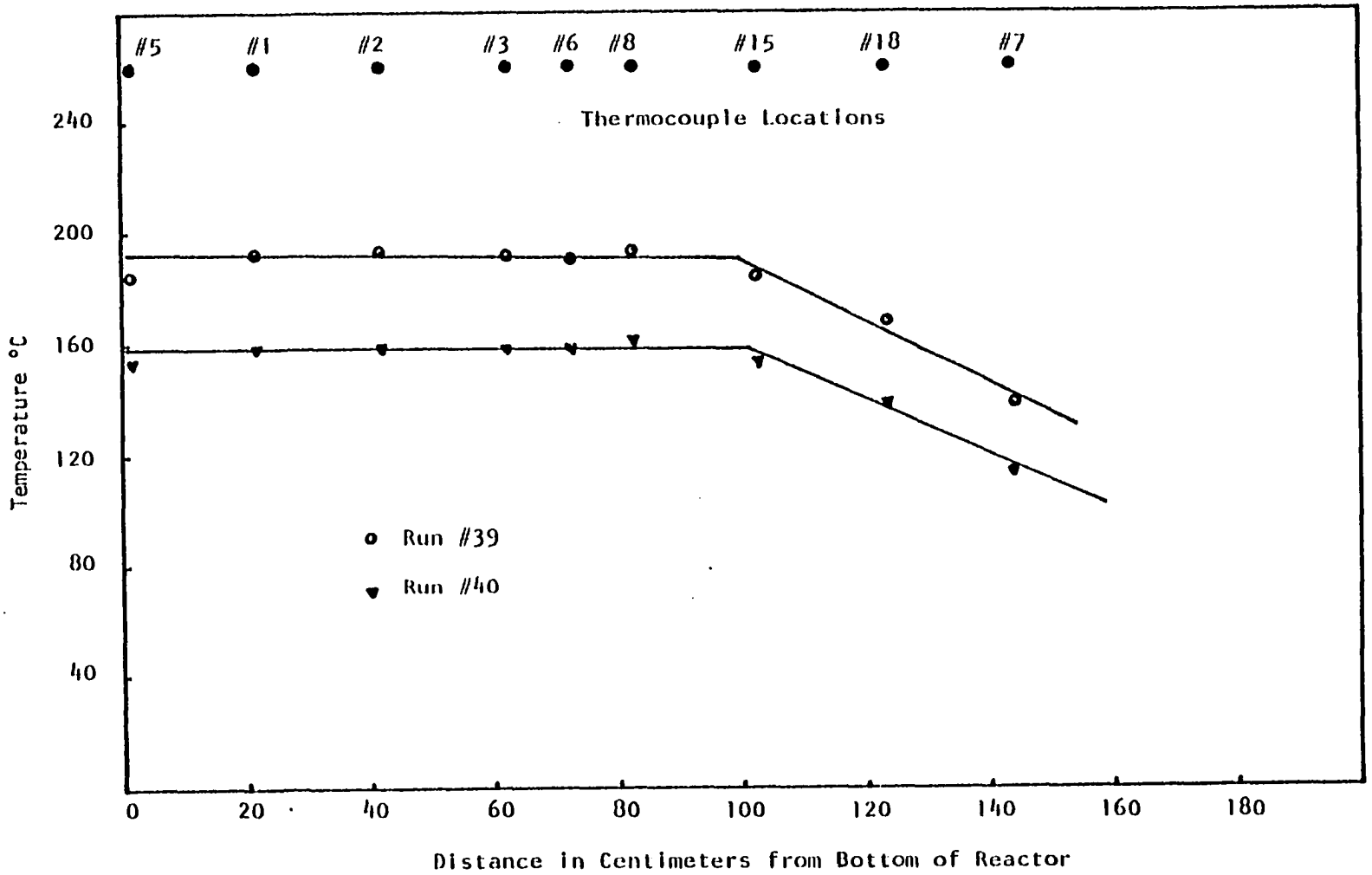


FIGURE VII-13. Temperature profile in the reactor for run #39 and #40.

CHAPTER VIII

METHOD OF DATA ANALYSIS

In this study the kinetic parameters, activation energy and frequency factor, could not be obtained directly by integral rate data analysis for two reasons. (1) The experiments could not be conducted at isothermal conditions, and (2) the rate equation is so involved that a simple analytical integrated equation is not possible. The rate equation in the differential form was integrated numerically using a fourth order Runge-Kutta approximation. Fully developed plug flow (no axial diffusion) was assumed for the analysis. It was further assumed that there were no diffusional effects and that the hydrogen concentration in the solution was constant. This technique was used for both non-isothermal and isothermal regions.

Consider a tubular, plug flow reactor shown in Figure VIII-1, where FA_o is the volumetric flow rate of the fluid, C_A is the concentration of species A at a distance Z in the reactor and $(C_A + \Delta C_A)$ is the concentration of the species A at a distance $Z + \Delta Z$. If the species is reacting

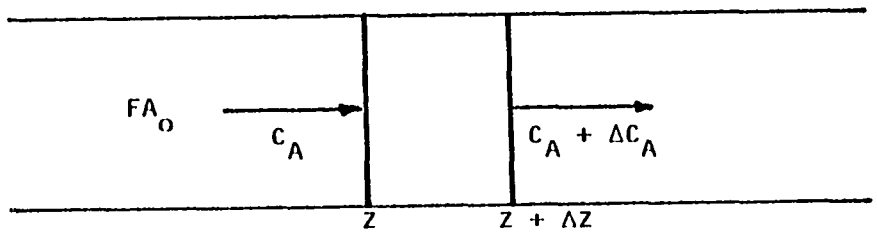


FIGURE VIII-1. Tubular plug flow reactor.

at a rate r (mole/volume) then the material balance around the differential element would yield

$$(FA_o) \cdot C_A - FA_o(C_A + \Delta C_A) = A(Z-(Z+\Delta Z))\cdot r \qquad \text{(VIII-1)}$$

or $$- FA_o \cdot \Delta C_A = A \cdot \Delta Z \cdot r \qquad \text{(VIII-2)}$$

taking the limits,

$$FA_o dC_A = -A \cdot r \cdot dZ \qquad \text{(VIII-3)}$$

C_A can be represented as $C_{Ao}(1-x)$ where C_{Ao} is the initial concentration at Z=0 and x is the conversion to products at Z.

then

$$FA_o \cdot d[C_{Ao}(1-x)] = -A \cdot r \cdot dZ \qquad \text{(VIII-4)}$$

$$FA_o \cdot C_{Ao} \cdot dx = A \cdot r \cdot dZ \qquad \text{(VIII-5)}$$

or $$\frac{dx}{dZ} = \frac{A \cdot r}{FA_o \cdot C_{Ao}} \qquad \text{(VIII-6)}$$

Equation (VIII-6) was used after substituting appropriate terms for the reaction rate (r) for evaluating the conversions at different locations along the length of the reactor.

The rate equation proposed by von Hahn seems to be the latest. Since it includes the cuprous ion effect it supposedly is complete. von Hahn's equation was substituted

for "r" in equation (VIII-6) to perform the calculations with the data obtained in this study. To do so required calculating the hydrogen solubility in the aqueous solution, the hydrogen ion concentration, and the cuprous ion concentration. Hydrogen solubilities were calculated using the equation proposed by Scott Conner (5) in his thesis:

$$\log_{10}S = -A_o + B_o(P) - C_o(P^2) + D_o(P^3) \qquad \text{(VIII-7)}$$

where S is the solubility of hydrogen in water in ml H_2·STP/10 grs·H_2O (to be multiplied by 0.004458 to convert to gr. moles H_2/1000g H_2O) and A_o, B_o, C_o and D_o are constants for a given temperature. The values, however, change from one temperature to another; some of these values are presented in Appendix (C). Figure VIII-2 shows the change in partial pressure with temperature at a total pressure of 500 psig. Figure VIII-3 represents the variation of solubility with temperature at 500 psig and 400 psig total operating pressures, calculated by equation (VIII-7). The calculated values agrees well with other published data.

Hydrogen ion concentrations, were calculated using the second dissociation constant values of sulfuric acid at the reaction temperatures, as given by Marshall and Jones (19).

$$\log_{10}K_i = 56.889 - (19.8858)\log_{10}(T) - (2307.9/T) - (0.006473T) \qquad \text{(VIII-8)}$$

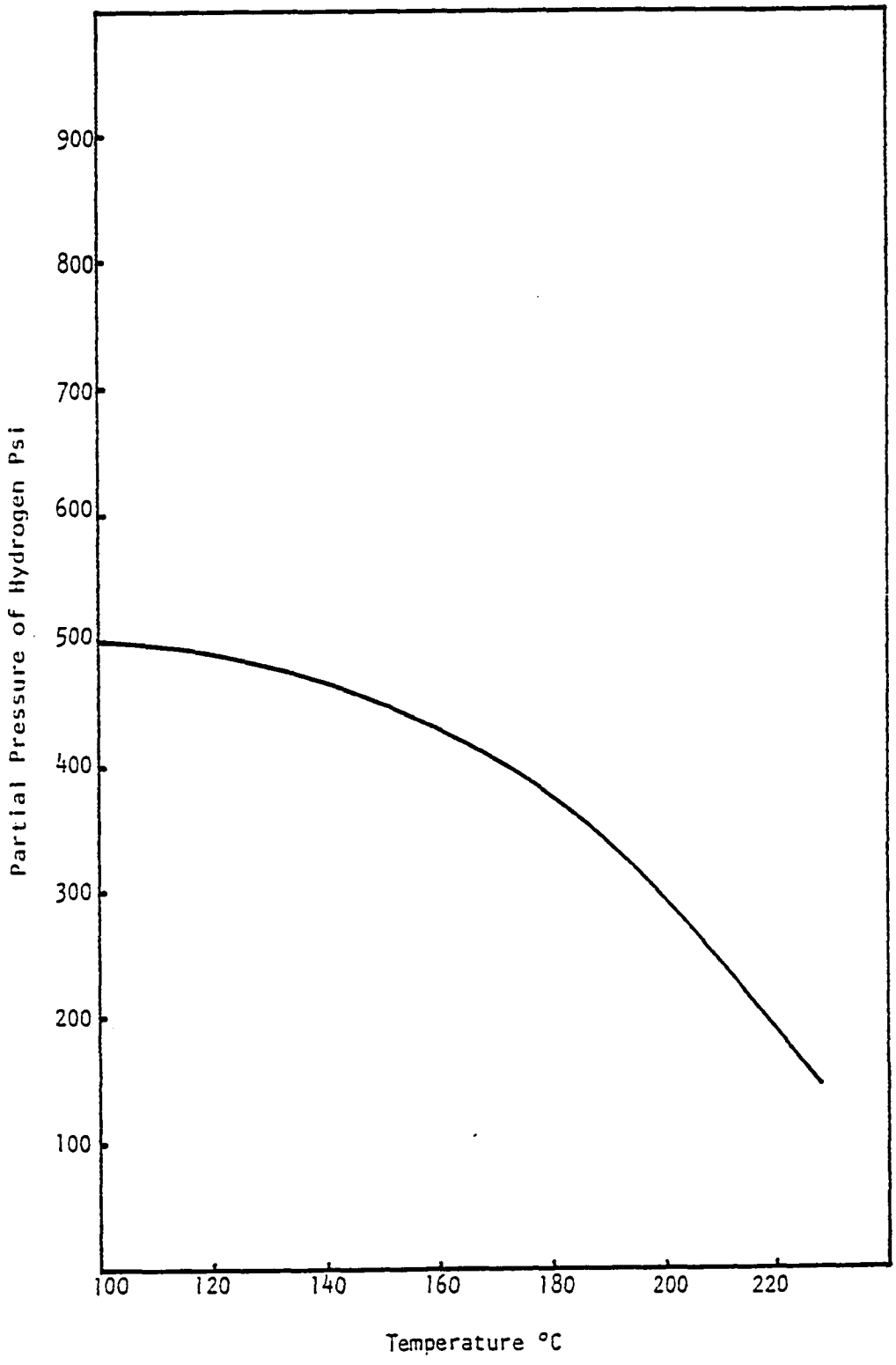


FIGURE VIII-2. Relation of partial pressure of hydrogen to temperature at total pressure of 500 psig.

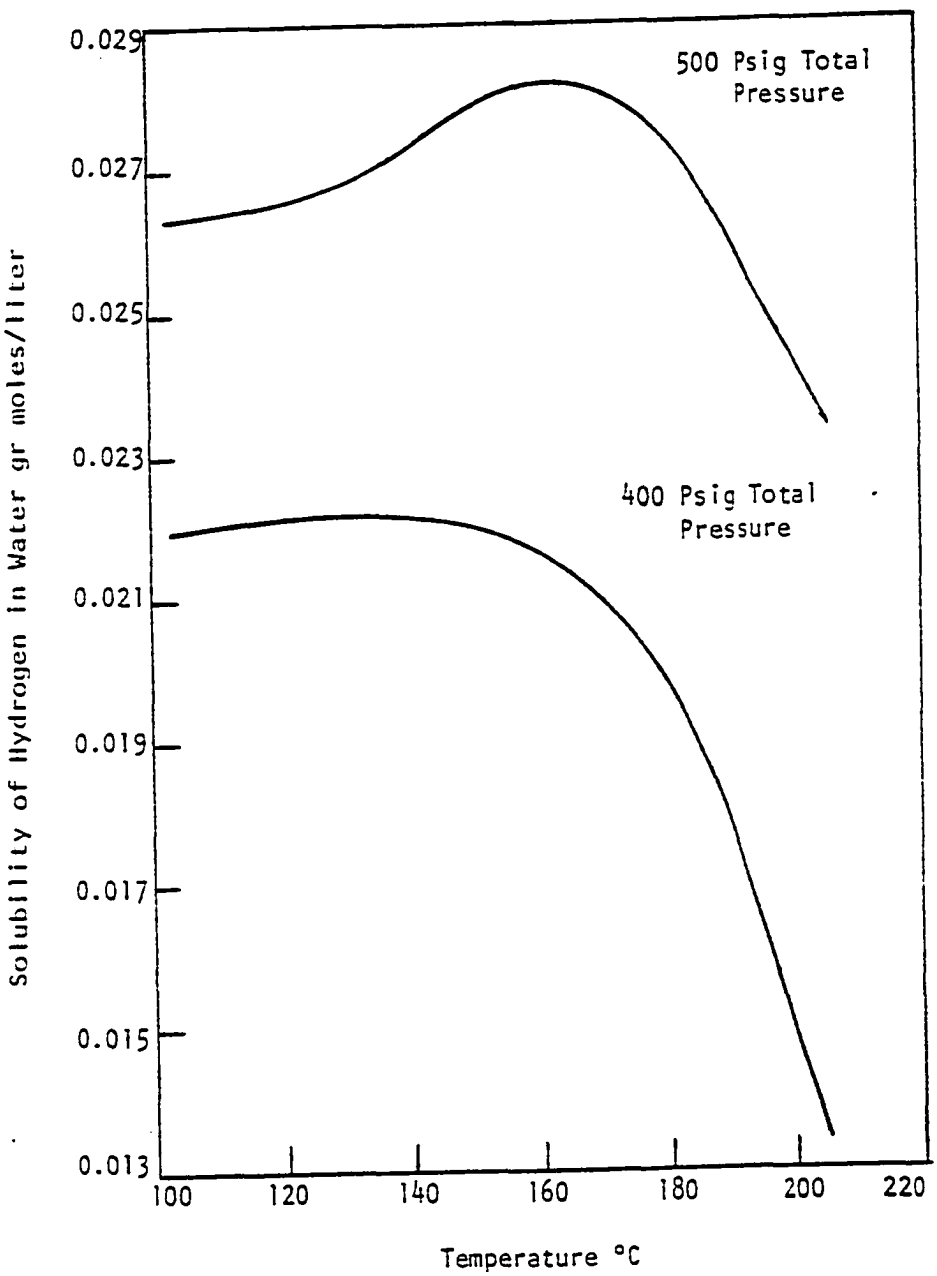


FIGURE VIII-3. Solubility of hydrogen at different temperatures.

where K_i is the dissociation constant (at zero ionic strength) and T is the absolute temperature in °K. Utilizing the K_i value obtained from equation VIII-8, the hydrogen ion concentration at any time is calculated as follows.

Let x be the conversion of cupric ions to products at any time t; then the total hydrogen ion concentration at t would be

$$H^+ = (2AC + Cu_o^{++} \cdot x) \quad \text{(before disproportionation)} \tag{VIII-9}$$

and $$H^+ = (2AC + (Cu_o^{++} \cdot x) + 2Cu^o) \quad \text{(after disproportionation)} \tag{VIII-10}$$

If y is the conversion of H^+ to HSO_4^- (bisulfate) then the concentration (before disproportionation) of

$$H^+ = (2AC + Cu_o^{++} \cdot x)(1-y) \tag{VIII-11}$$

$$SO_4 = (AC + Cu_o^{++} + AN) - (2AC + Cu_o^{++} \cdot x)y \tag{VIII-12}$$

$$HSO_4^- = (2AC + Cu_o^{++} \cdot x)y \tag{VIII-13}$$

where Cu_o^{++} = initial concentration of cupric ions;
AC = initial free acid added;
AN = any other salt added containing sulfate (i.e., Na_2SO_4)
SO_4^{--} = sulfate ions present in solution
HSO_4^- = bisulfate formed
Cu^o = metallic copper

at equilibrium

$$\bar{K} = \frac{(H^+)(SO_4^{--})}{(HSO_4)^-} = \frac{(1-y)x[(AC + Cu_o^{++}\cdot x + AN) - (2AC + Cu_o^{++}\cdot x)y]}{y} \qquad \text{(VIII-14)}$$

$$\bar{K}y = (AC + Cu_o^{++} + AN)(1-y) - y(2AC + Cu_o^{++}\cdot x)(1-y) \qquad \text{(VIII-15)}$$

$$\therefore (2AC + Cu_o^{++}\cdot x)y^2 - [(2AC + Cu_o^{++}\cdot x) + (AC + Cu_o^{++} + AN) + \bar{K}]y + (AC + Cu_o^{++} + AN) = 0 \qquad \text{(VIII-16)}$$

$$y = \frac{b \pm \sqrt{b^2 - 4ac}}{2a} \qquad \text{(VIII-17)}$$

where $b = [(2AC + Cu_o^{++}\cdot x) + (AC + Cu_o^{++} + AN) + \bar{K}]$ (VIII-18)

$$a = (2AC + Cu_o^{++}\cdot x) \qquad \text{(VIII-19)}$$

$$c = (AC + Cu_o^{++} + AN) \qquad \text{(VIII-20)}$$

of the two roots,, $\frac{b + \sqrt{b^2 - 4ac}}{2a}$ is always equal to or greater than unity; hence it was discarded since y cannot be more than one. Therefore,

$$y = \frac{b - \sqrt{b^2 - 4ac}}{2a} \qquad \text{(VIII-21)}$$

The value of y from equation (VIII-21) is substituted in equation (VIII-11) to obtain the H^+ concentration. Sulfate ions to some extent will be locked up with cupric ions forming a complex; as a result the calculated hydrogen ion

concentration will be less than the actual. The extent of sulfate complexing with cupric ion is not known; in this study its contribution was not accounted for in the hydrogen ion concentration calculations.

Cuprous ion concentrations were calculated using the equilibrium constant $K_{cu^+} = \frac{(Cu^+)^2}{(Cu^{++})}$ given by von Hahn, at 160°C. ($K_{cu^+} = 3.8462 \times 10^{-2}$) for the reaction, $Cu^{++} + Cu^o \rightarrow 2Cu^+$ according to van't Hoff's equation,

$$\left[\frac{\partial(\ell n K)}{\partial T}\right]_P = \frac{\Delta H}{RT^2} \qquad \text{(VIII-22)}$$

Upon integration

$$\ell n\ K(T_2) - \ell n\ K(T_1) = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \text{(VIII-23)}$$

where K(T) is the equilibrium constant at temperature T

T_2 and T_1 are the absolute temperatures in appropriate units

ΔH is the heat of reaction (assumed constant)

R is the gas constant.

Generally, the heat of reaction is a function of temperature, but in this work it was assumed constant in the range of this study. The heat of reaction was calculated using the heat of formations taken from Gedansky et al (9):

Heat of formations at 25°C

Cu^+ (aq) = 17.2 Kcal/mole

Cu^{++} (aq) = 15.6 Kcal/mole

$$\therefore \Delta H_r(25°C) = \Delta H_f(Cu^{+}) - \Delta H_f(Cu^{++})$$

$$\Delta H_r = 2x17.2 - 15.6 = 18.8 \text{ Kcal/mole}$$

$$= 18{,}800 \text{ calories/per mole of } Cu^{++}$$

if C_p is assumed to be 1.0 for the solution, then $\Delta H_r(160°C)$ = 18,800 + 1x(160-25) = 18,935 cal/mole. Hence the assumption of constant heat of reaction is acceptable. From the values of the heat of reaction, and the equilibrium constant at 160°C, the expression for the equilibrium constant at any temperature, using equation (VIII-23) was derived:

$$\ell n(K_{cu}+) = 18.436033-(9393.55/T) \qquad \text{(VIII-24)}$$

where $$(K_{cu}+) = \frac{(Cu^{+})^2}{(Cu^{++})} \qquad \text{(VIII-25)}$$

T = absolute temperature in °K

Cu^{+} = cuprous ion concentration in solution mole/lit

Cu^{++} = cupric ion concentration in solution mole/lit

from equation (VIII-25)

$$Cu^{+} = [(K_{cu}+)\cdot(Cu^{++})]^{1/2} \qquad \text{(VIII-26)}$$

Representative values for the heat of reaction, ΔH, and the equilibrium constant, K_{cu}, are:

Temperature, °C	ΔH, Kcal/mole Cu^{++}	K_{cu^+}
125	18.900	5.708×10^{-3}
150	18.925	2.303×10^{-2}
175	18.950	7.952×10^{-2}
200	18.975	2.408×10^{-1}
225	19.000	6.527×10^{-1}
250	19.025	1.608

It is apparent from the above that the equilibrium conversion increases with temperature which is as would be expected since ΔH is positive.

CHAPTER IX

RESULTS AND DISCUSSION

In Chapter VIII experimental observations were presented, which give an insight, at least, to some of the problems and advantages of the continuous hydrogen reduction of copper from acidic sulfate solutions. To prevent plugging in the pipe sections of the feed line by basic copper sulfate precipitate, preheating of the feed before introducing to the reactor was avoided in the study*.

*Several preliminary runs were made in which a section of the liquid feed line to the top of the reactor was wrapped with nichrome wire. Thereby the preheater consisted of a vertical 1/4 inch (0.63 cm) O.D. stainless steel tubing, 54 inches (137 cm) in length. The feed (copper sulfate dissolved in water without any sulfuric acid added) was preheated to 200°F (93°C) at flow rates (upward, vertical) up to 100 cc/min. Over a period of 3 or more hours of continuous operation, the unheated horizontal section (10 inches or 25.4 cm in length) of the feed line between the preheater and the top of the reactor became uniformly coated around its periphery with basic salts, and thereafter the build-up of solids in this section was quite rapid. Obviously, the wall temperature of the tubing on which the deposit just occurred was several hundred degrees higher than the 200°F (93°C) bulk temperature of the preheated feed, which could have been the principal reason for precipitation of the basic salts in the first instance. Furthermore, the small inside diameter of the tubing (1/8 inch or 0.32 cm) increased the tendency for bridging and eventually plugging. Although different heating methods, lowering the pH of the feed with sulfuric acid, and modifications of the preheater configuration might have eliminated the precipitation problem, it was decided at this point to operate without a preheater.

For this reason part of the reactor was utilized as a preheater in which the feed was being heated to the isothermal reaction temperature. During this preheating phase, as the temperature was increasing, some reaction was taking place at the same time. As a result the preheater portion of the reactor was operating under non-isothermal conditions. As mentioned earlier in Chapter VII, it is difficult to report one single temperature for the run. For identification purposes and reporting on a common basis, the isothermal portion of the reactor temperatures are indicated as temperature of the run in the discussion of this chapter. It is also to be noted that the residence times reported here are based on the total reactor length; as a consequence the conversions obtained will be less than the conversions obtained for the same residence time when the total reactor is operated under isothermal conditions. The same arguments apply in attempting to strike comparisons with batch data on isothermal runs reported by others.

The experiments totaling forty runs were carried out for different temperatures ranging from 250°F (121°C) to 450°F (232°C), different flow rates ranging from 40 grs/min to 120 grs/min (which corresponds to approximate residence times of 30 to 10 minutes). The runs for the above parameters were made using pure synthetic copper sulfate solutions at their "natural" pH values for the aqueous solution at that particular concentration. This

natural pH ranged between 4.4 to 3.5. Four runs were made with varying acid content, and pH, for fixed temperature and flow rate conditions. Two runs were made using sodium sulfate, with and without acid addition. All the above runs were made at a total pressure of 500 psig. The last two runs were made at 400 psig total pressure for two different temperature conditions.

The experimental results of run #2 for a nominal residence time of 11.4 minutes, run #13, 14, 15, 16 and 17 for an average residence time of 15.5 minutes, Run #22, 23, 24 and 25 for a residence time of 20.3 minutes, for various temperatures are plotted against conversion in Figures IX-1, IX-2 and IX-3. The results indicate that the conversion to copper increases with temperature at a given residence time; in other words the rate of reaction increases with temperature. However, at higher temperatures an apparent equilibrium was reached and no further increase in conversion was observed by increasing the temperature. However, this apparent equilibrium may not be a true thermodynamic equilibrium as shown in Table II-1 which indicates that the reaction should proceed practically to completion even at 250°C. Thus, this apparent equilibrium may be associated with kinetic factors. In Figures IX-1 and IX-2, the equilibrium is reached at

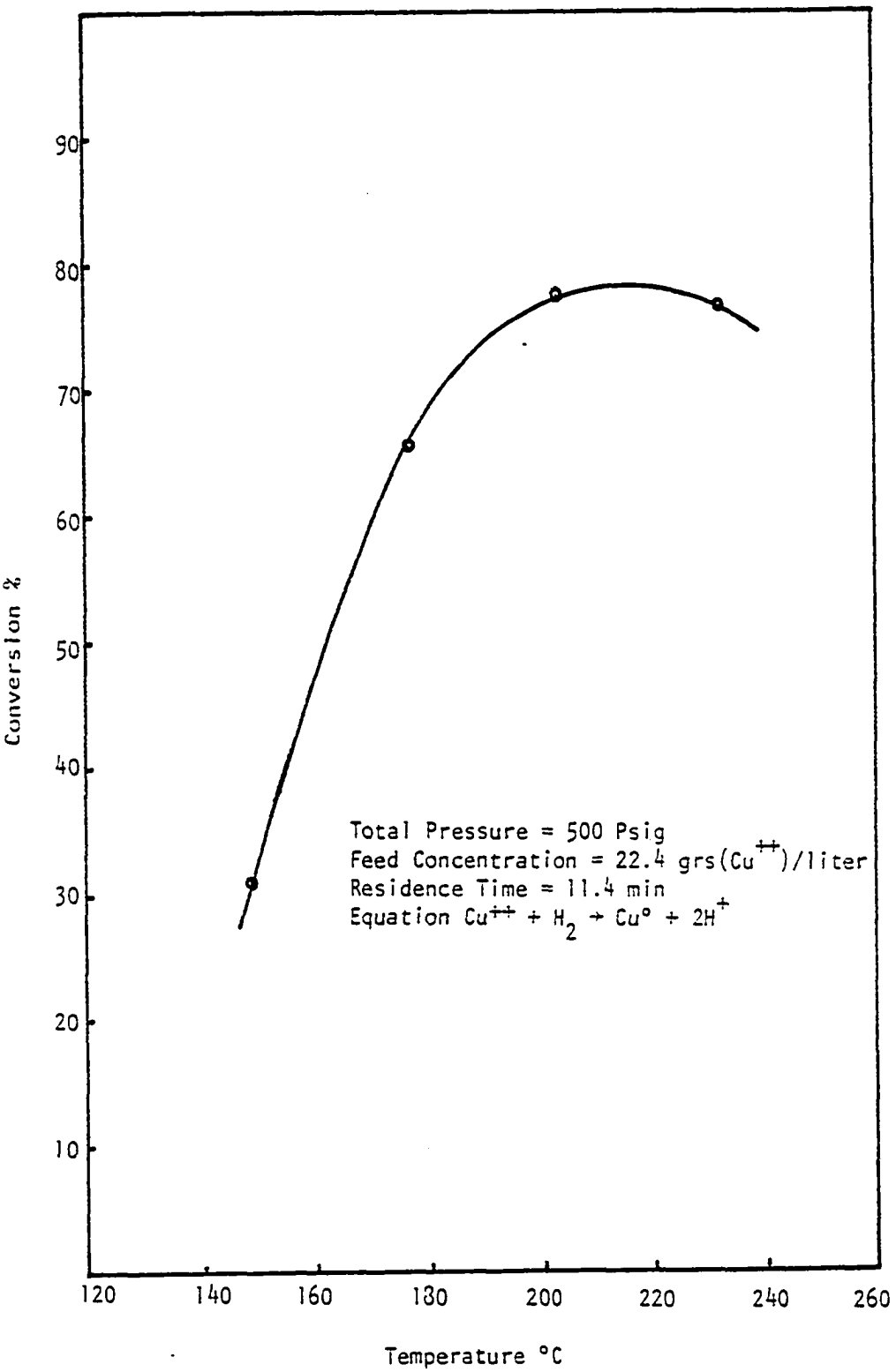


FIGURE IX-1. Change in conversion with temperature at residence time 11.4 minutes.

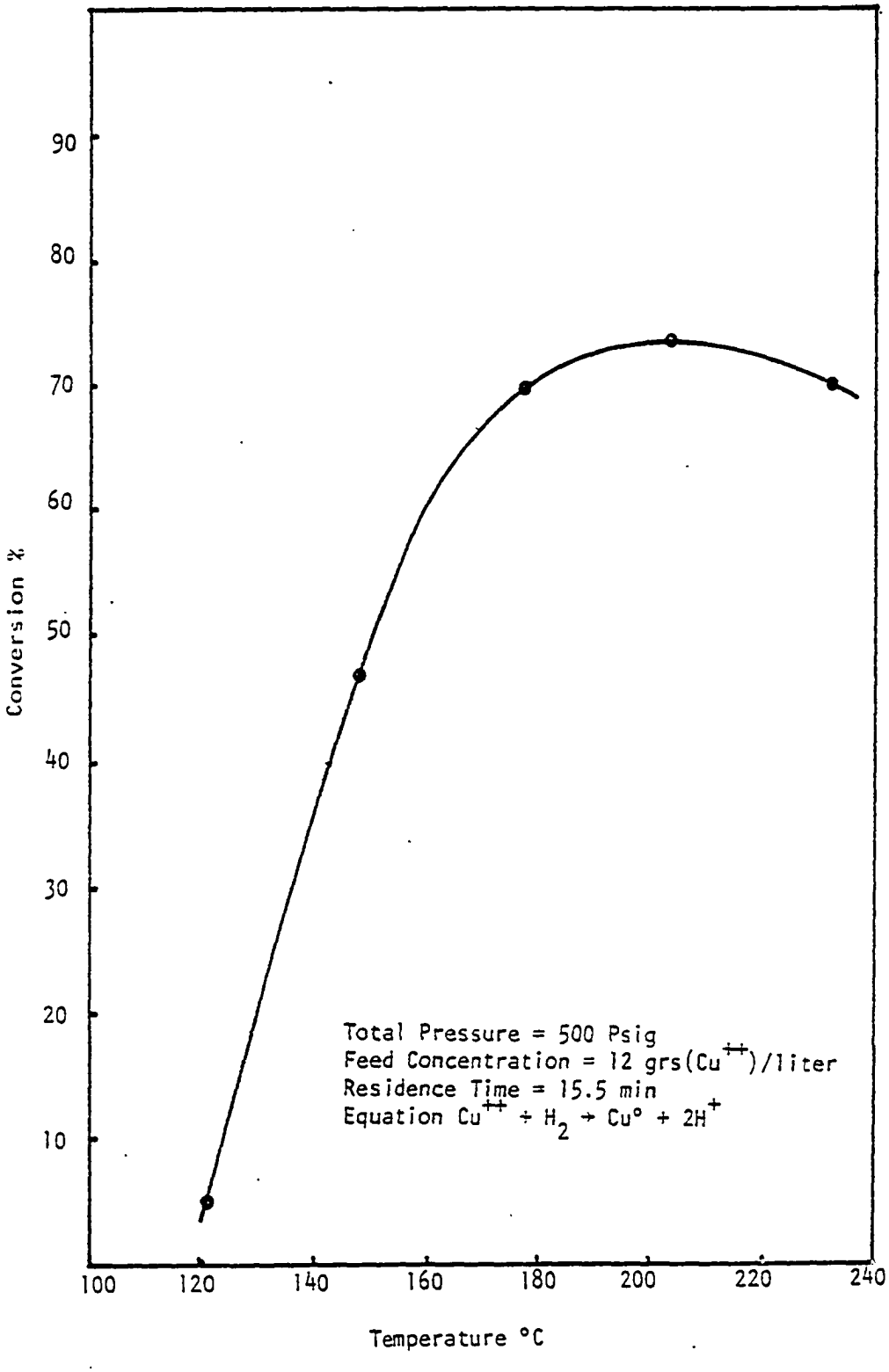


FIGURE IX-2. Change in conversion with temperature at residence time 15.5 minutes.

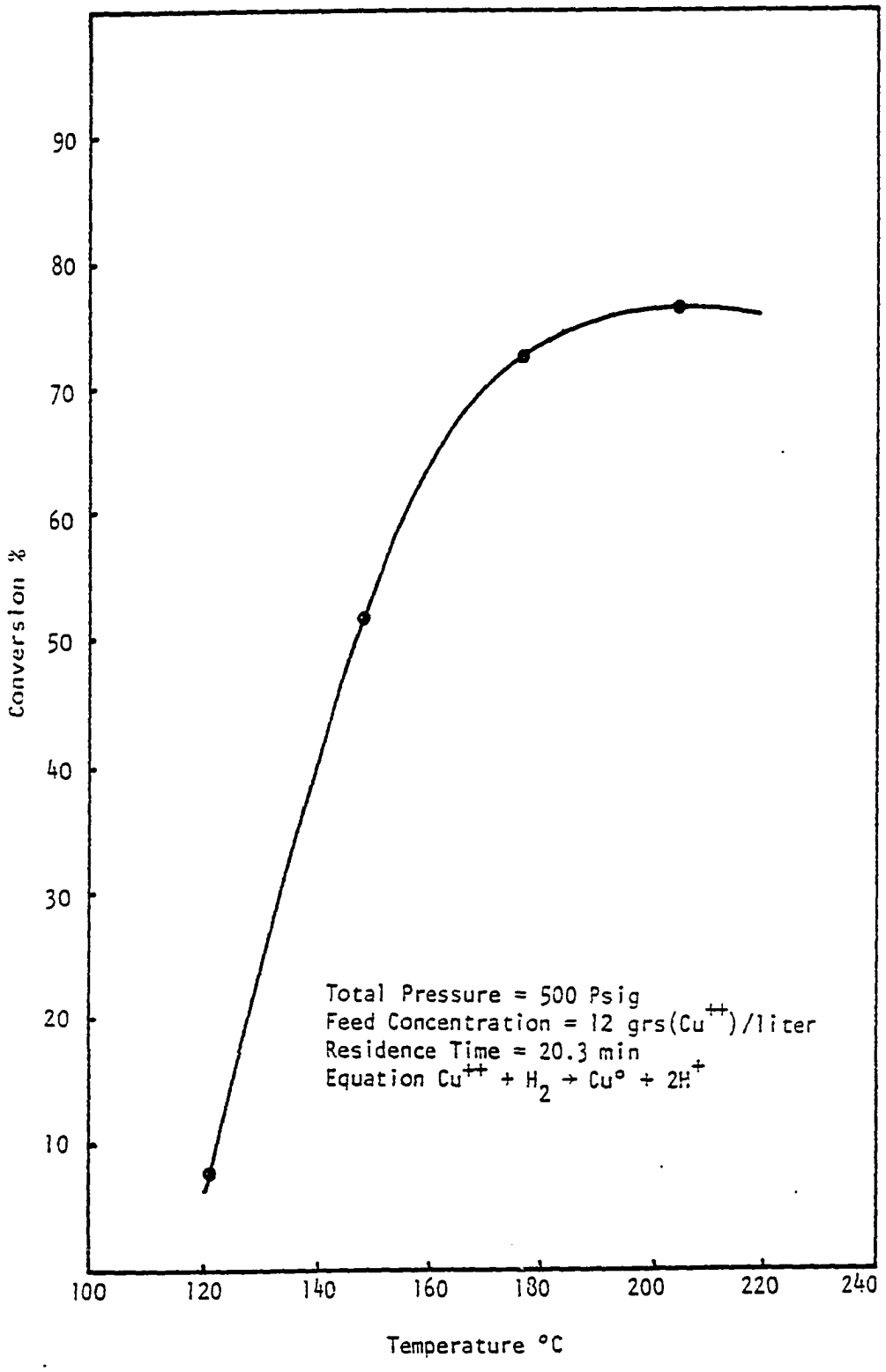


FIGURE IX-3. Change in conversion with temperature at residence time 20.3 minutes.

400°F (204.4°C) with a conversion* of 77 and 74 percent respectively. A slight drop in conversion was observed at 450°F (232°C). This behavior of leveling off or reaching apparent equilibrium could possibly be due to a pronounced increase in the rate constant (k_{-1}) of the reverse reaction (given in equation IX-1 below) with increase in temperature, and in which case it would compete effectively with the forward reaction at elevated temperatures.

$$Cu^{++} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu^{\circ} + 2H^{+} \qquad \text{(IX-1)}$$

Similar observations were also made by McGregor and Halpern (18), in their batch reduction experiments using copper perchlorate solutions.

In Figure IX-4, residence time is plotted against conversion for average temperatures of 300°F (148.8°C), 350°F (176.6°C) and 400°F (204.4°C). Increase in conversions with increase in residence times can be noticed for average temperatures of 300°F (148.8°C) and to a lesser

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*In Figures IX-1 thru IX-11 the ordinate "conversion" measures the conversion of cupric ions to basic salts, cuprous oxide and copper. For most of the runs more than 75 percent of the total conversion was to copper; in fact in runs #34, 35 and 38 (as discussed later) for which enough sulfuric acid was added to drop the pH of the feed to 1.8, the conversion was essentially 100 percent to pure copper.

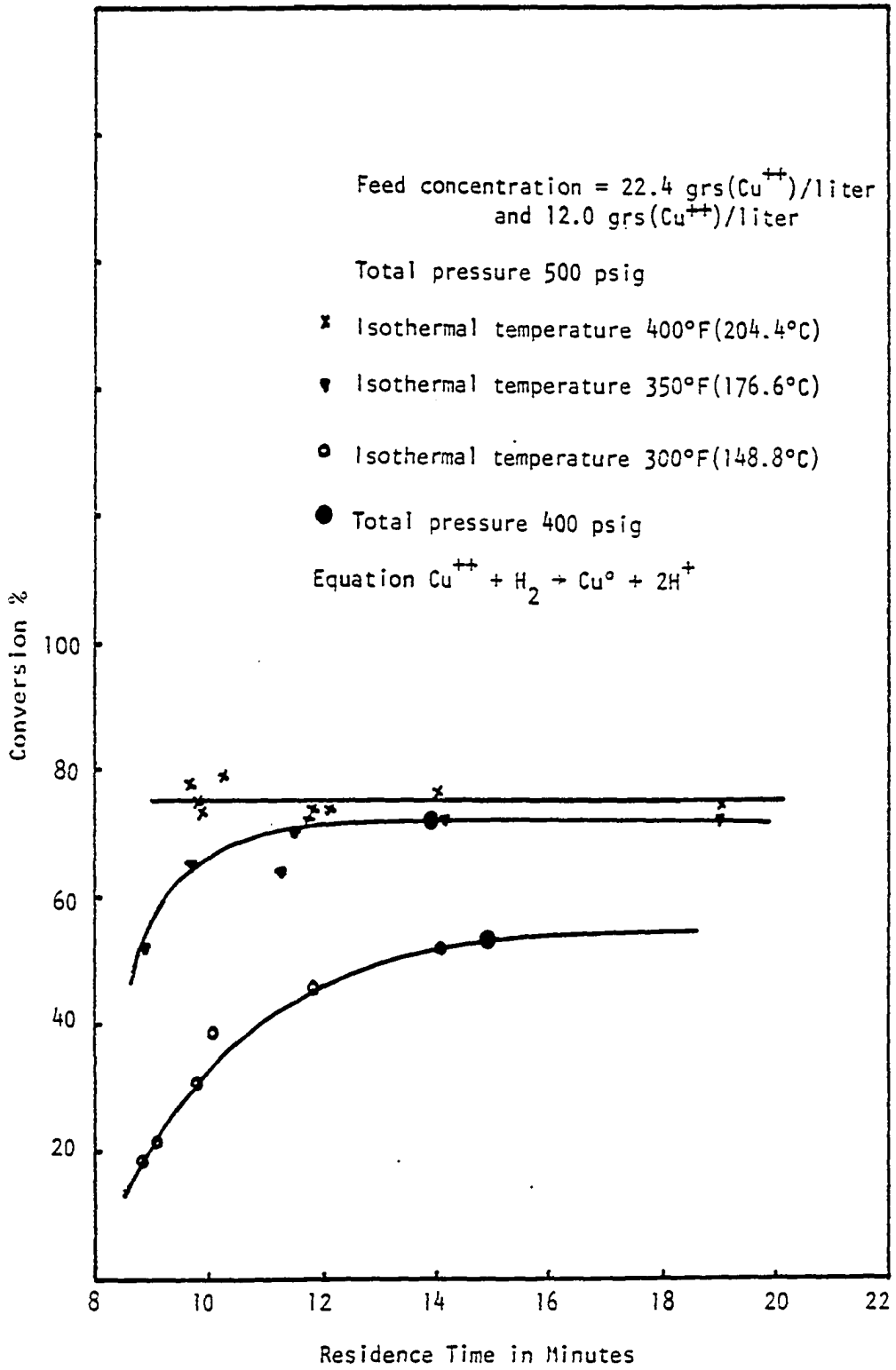

FIGURE IX-4. Effect of residence time on conversion.

extent for 350°F (176,6°C). At 400°F (204.4°C) the conversion appears to be independent of residence time, at least for times greater than 10 minutes. For 350°F (176.6°C), the "cut off" residence time, beyond which the conversion does not change appreciably, can be taken as 15 minutes, and for 400°F (204.4°C), the "cut off" falls below the experimental range studied here. The leveling off takes place as a result of acid formation in the reaction, as given by equation IX-1, which retards the forward reaction. Below the "cut off" point, as expected, the reaction rates increase with increase in temperature, as reflected by the higher conversions demonstrated in Figure IX-4. For a residence time of 10 min, the conversion at 400°F (204.4°C) is 75 percent, whereas at 350°F (176.6°C) the conversion is 55 percent and at 300°F (148.8°C) the conversion is only 20 percent. From a practical standpoint, it would appear that operating at high throughputs and at 400°F is desired. However, the economics will depend on heat duty which certainly becomes more costly at higher temperatures.

Decreasing the total pressure from 500 psig to 400 psig did not produce any change in conversions as can be seen from Figures IX-4 and IX-5. In fact the conversions fall right on the 500 psig lines for 300°F (148.8°C) and 350°F (176.6°C) temperatures as shown by the solid black circles on Figure IX-4. This result indicates that the decrease in hydrogen partial pressures involved here,

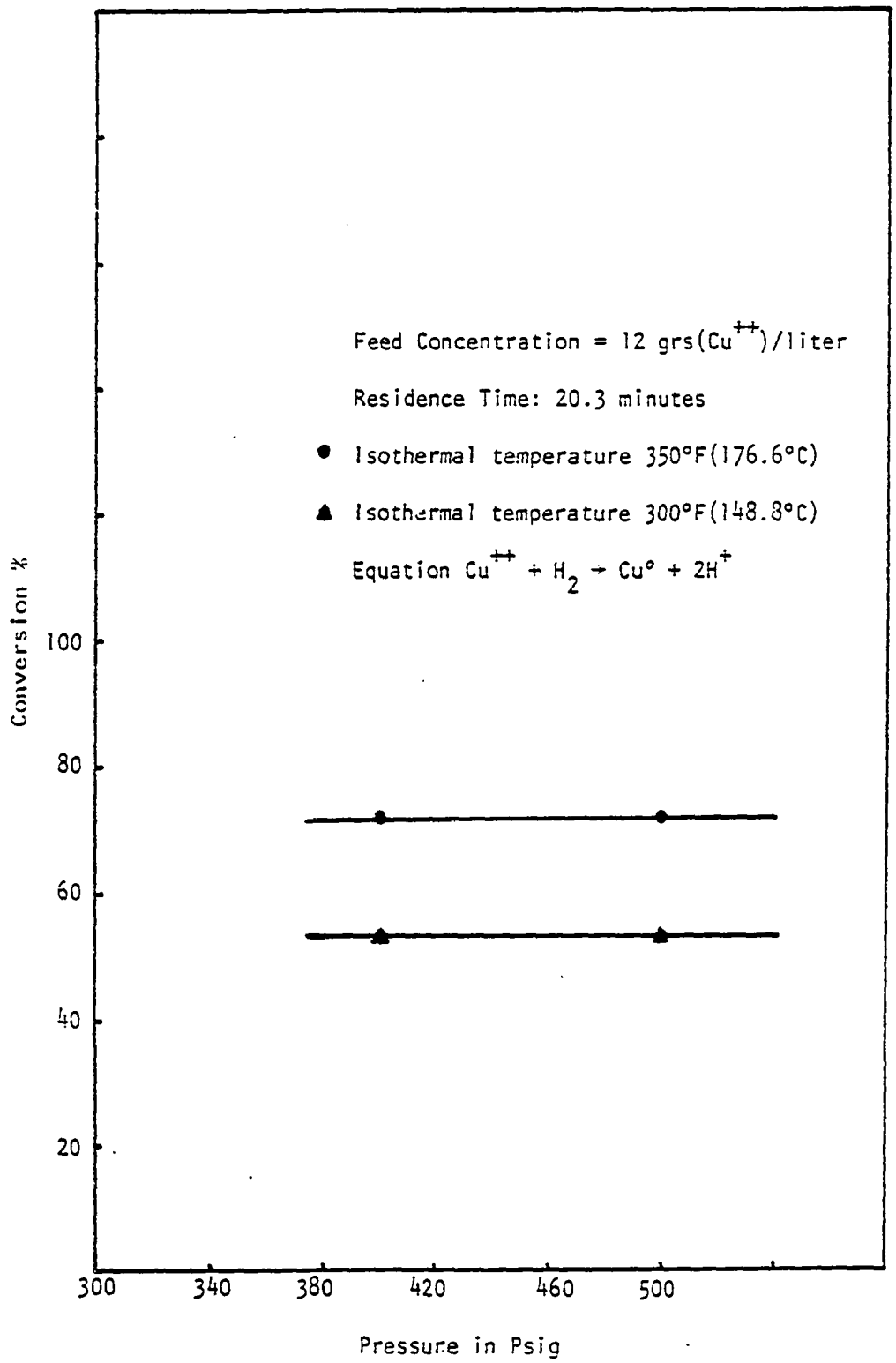

FIGURE IX-5. Effect of pressure on conversion.

has little effect on conversion. (Recall that a 25% excess of hydrogen over the stoichiometric amount was used.) This lack of effect is observed in spite of the fact that the solubility of hydrogen goes down from 0.028 moles/liter at 500 psig total pressure and 350°F (176.6°C) to 0.0205 moles/liter at 400 psig total pressure and 350°F.

Decreasing the pH of the feed has an adverse effect on conversion as shown in Figure IX-6. The drop in conversion between pH 2.2 to 1.6 is gradual and almost follows a straight line. This behavior may be explained in terms of the change in pH with hydrogen ion concentration. Since the pH is equal to $-\log_{10}[H^+]$, at higher hydrogen ion concentrations, the change felt in pH due to a change in hydrogen ion concentration will be smaller than the change felt at lower hydrogen ion concentration. This fact is evident from experimental runs #33, 34, 35 and 36. When 7.89, 15.77, 31.54 and 63.08 grs (H_2SO_4)/liter, respectively, were added to the feed, the pH's registered were 2.2, 1.9, 1.55 and 1.4 respectively. When conversion was plotted against acid added to the feed, the relation obtained was a straight line as shown in Figure IX-7. When the acid added was 7.89 grs (H_2SO_4)/liter the conversion obtained was 62 percent at an average temperature of 350°F (176.6°C); whereas at the same conditions, when the acid content was increased to 63.08 grs (H_2SO_4)/liter (eight fold increase), the conversion dropped, by 50 percent, to 30 percent conversion. This drop in conversion with acid

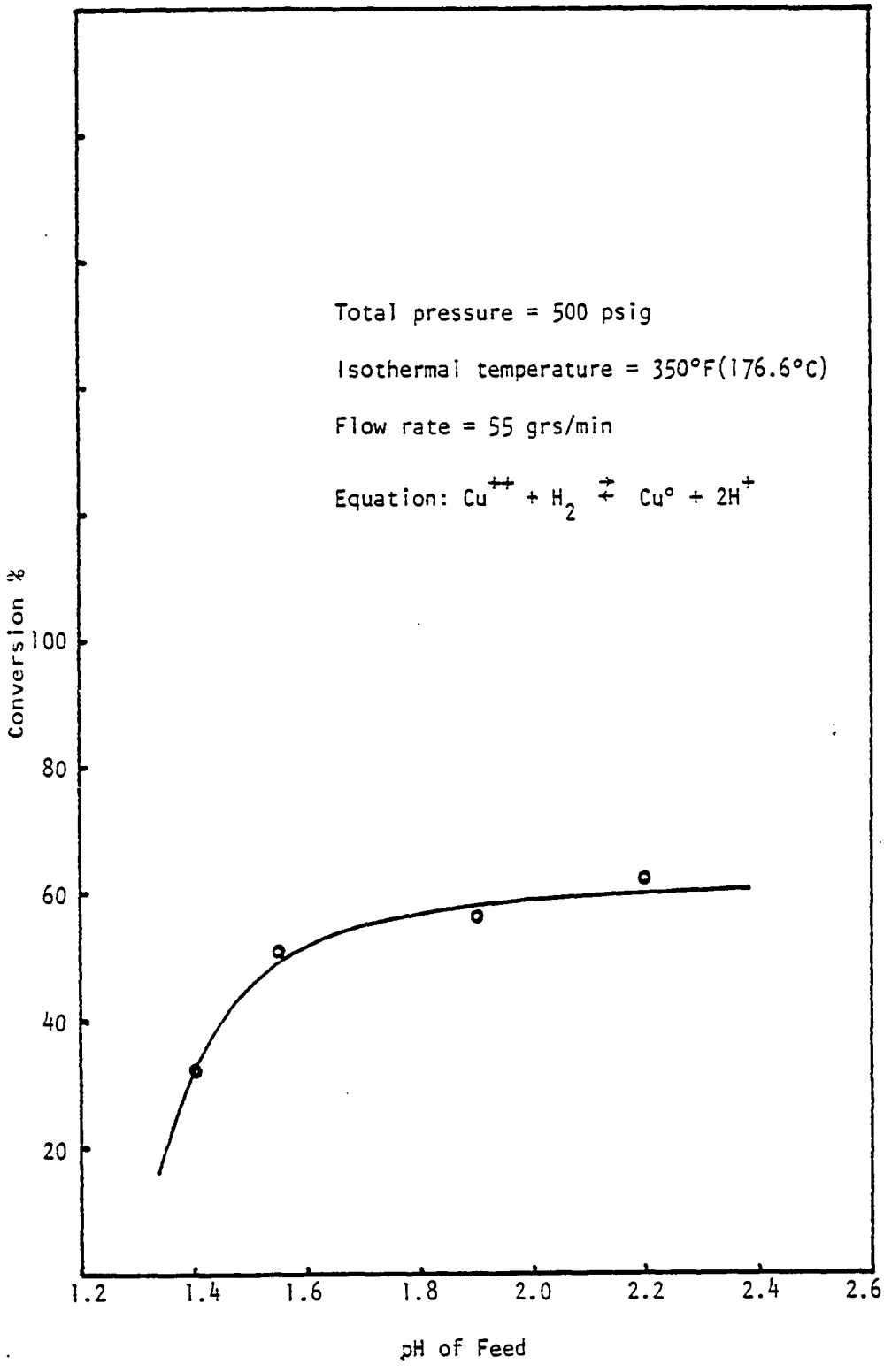

FIGURE IX-6. Effect of pH on conversion.

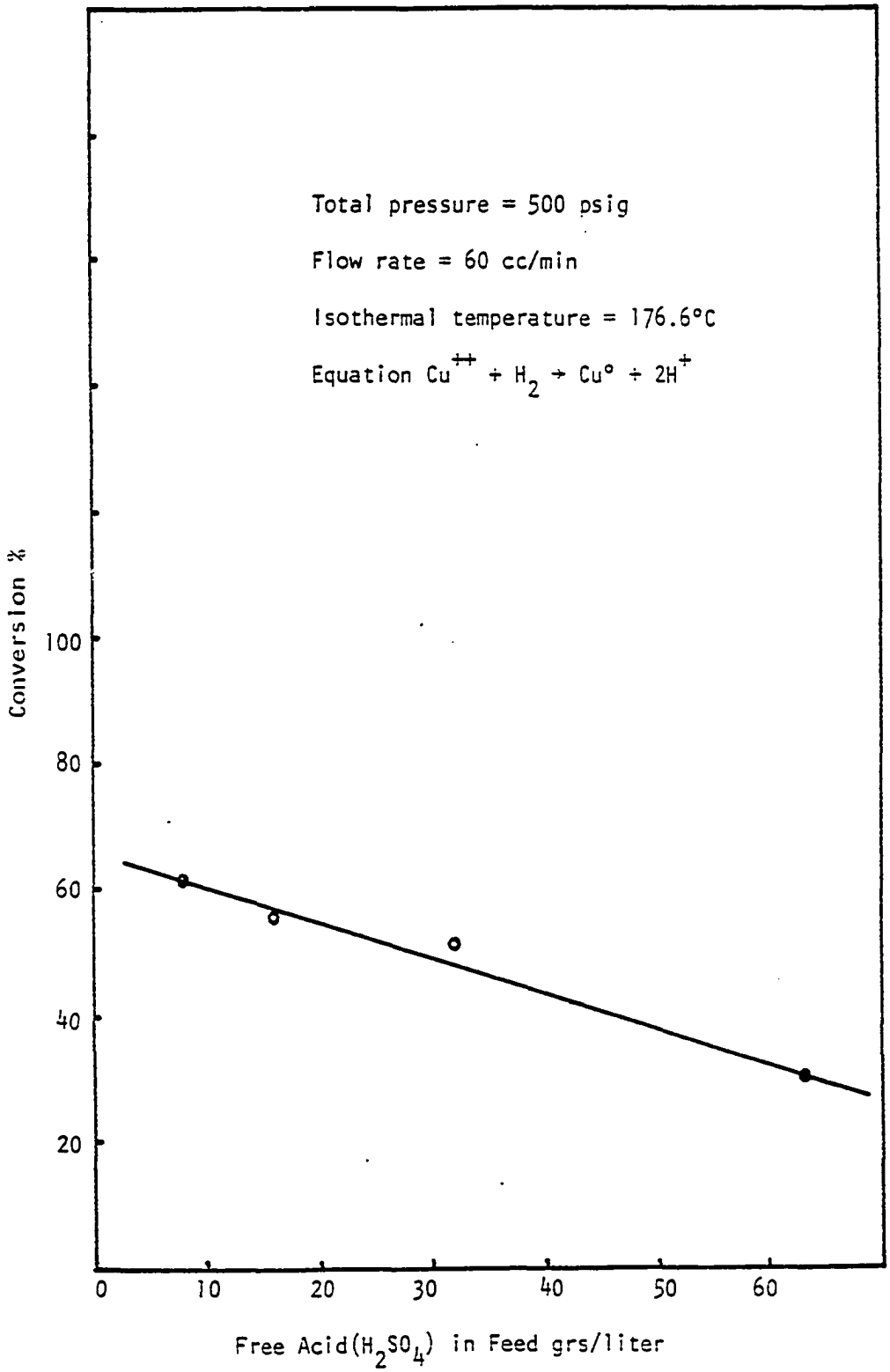

FIGURE IX-7. Effect of acid concentration on conversion.

addition is again explained in terms of equation IX-1 where the presence of hydrogen ion concentration opposes the forward reaction.

The flow rate of hydrogen seems to have no effect on conversion, as can be seen from experimental runs, #3, 4, 5 and 6, presented in Table IX-1 and shown in Figure IX-8. This behavior is expected since the hydrogen solubility in the liquid phase is purely dependent on the partial pressure of hydrogen and the temperature. This result also proves that the reaction under study, at the operating conditions, was not mass transfer controlled and also that the reaction was purely a homogeneous reaction taking place in the liquid phase. If the reaction were heterogeneous, taking place at the liquid and gas interface, then the mass transfer coefficient would increase with increase in flow rate, and hence an increase in conversion would have been expected.

Runs #5 and 6 when compared with 3 and 4 (see Table IX-1), indicate that the conversion, and therefore the reaction rate, is almost independent of initial concentration of cupric ions. However, this result seems contrary to expectations, since the kinetic equations suggested by various investigators indicate a dependency of rate on cupric ion concentration. A possible explanation could be that the initial rates are so fast that the effect of concentration on the rate is not felt unless the

TABLE IX-1

SUMMARY OF EXPERIMENTAL RUNS

Run #	Feed conc grs(Cu^{++})/liter	Free acid (H_2SO_4) added grs/liter	Sodium Sulfate ($Na_2SO_4 \cdot 10H_2O$) added grs/liter	Feed pH at 25°C	Feed rate grs/min	Reactor Total Pressure Psig	Isothermal Section Temperature °C	DP Cell Setting	Residence Time of Liquid in Reactor Minutes	Product pH	Product Gas rate SCFM	Conversion %
2	22.4	--	--	3.65	102.5	500	148.8	1.6	11.43	1.35	0.03133	30.6
2	22.4	--	--	3.65	103.3	500	174.4	1.6	11.34	1.00	0.01958	65.5
2	22.4	--	--	3.65	102.5	500	208.8	1.6	11.34	0.92	0.01370	77.6
2	22.4	--	--	3.65	101.6	500	232.2	1.6	11.53	0.92	0.01125	76.5
3	22.98	--	--	3.6	93.3	500	204.4	1.7	12.55	0.80	0.01841	79.2
4	22.73	--	--	3.5	100.83	500	204.4	1.25	11.62	1.00	0.00985	75.1
5	12.35	--	--	3.8	100.0	500	204.4	0.9	11.71	1.15	0.00952	73.6
6	11.99	--	--	3.8	98.7	500	204.4	0.6	11.87	1.10	0.00548	72.2
7	11.68	--	--	3.50	75.9	500	148.8	0.6	15.43	0.90	0.00560	Not Recorded
8	12.81	--	--	3.2	77.9	500	176.6	0.58	15.03	0.80	0.00516	83.3
9	11.42	--	--	3.2	77.5	500	176.6	0.55	15.11	0.85	0.00528	89.0
10	11.93	3.00	--	2.4	75.00	500	204.4	0.60	15.62	0.75	0.00620	74.7
11	11.93	3.00	--	2.5	81.66	500	176.6	0.60	14.34	1.00	0.0078	70.57
12	12.30	3.00	--	2.4	80.0	500	232.2	0.60	14.63	0.95	0.0076	69.43
13	12.30	--	--	3.85	77.5	500	176.6	0.60	15.11	1.00	0.00796	70.4
14	12.81	--	--	3.90	72.50	500	204.4	0.60	16.15	1.00	0.00541	73.53
15	12.30	--	--	3.90	71.66	500	232.2	0.60	16.43	1.00	0.00610	70.40
16	11.55	--	--	4.00	75.00	500	148.8	0.60	15.62	1.00	0.00968	45.71
17	12.43	--	--	3.90	75.00	500	121.1	0.60	15.62	1.90	0.03153	5.07
18	11.80	--	--	3.60	118.30	500	121.1	0.70	9.90	2.00	0.017616	5.34
19	12.13	--	--	3.60	121.66	500	148.8	0.70	9.63	1.40	0.01456	17.90
20	12.00	--	--	3.60	120.83	500	176.6	0.70	9.69	0.85	0.00796	52.16
21	11.74	--	--	3.60	115.00	500	148.8	0.90	10.18	1.25	0.01893	21.72
22	11.74	--	--	4.1	58.33	500	121.1	0.45	20.08	2.00	0.01158	7.58
23	12.13	--	--	4.00	56.66	500	154.4	0.45	20.67	1.10	0.00623	31.57
24	11.87	--	--	3.80	57.50	500	176.6	0.50	20.37	0.85	0.00531	72.03

TABLE IX-1 (Continued)

SUMMARY OF EXPERIMENTAL RUNS

Run #	Feed conc grs(Cu^{++})/liter	Free acid (H_2SO_4) added grs/liter	Sodium Sulfate ($Na_2SO_4 \cdot 10H_2O$) added grs/liter	Feed pH at 25°C	Feed rate grs/min	Reactor Total Pressure Psig	Isothermal Section Temperature °C	DP Cell Setting	Residence Time of Liquid in Reactor Minutes	Product pH	Product Gas rate SCFM	Conversion %
25	12.38	--	--	3.80	58.33	500	204.4	0.50	20.08	0.80	0.00506	76.33
26	13.78	--	--	3.60	58.33	500	148.8	0.50	20.08	0.90	0.00736	51.81
27	11.62	--	--	3.60	80.83	500	176.6	0.70	14.49	0.80	0.00818	63.77
28	11.87	--	--	3.60	96.66	500	148.8	0.70	12.11	0.95	0.01341	38.75
29	12.13	--	--	3.65	40.83	500	148.8	0.40	28.69	1.10	0.00620	26.38
30	12.13	--	--	3.65	39.1	500	176.6	0.40	29.96	0.70	0.00591	72.63
31	12.13	--	--	3.90	41.66	500	121.1	0.40	28.12	2.30	0.01051	5.27
32	12.13	--	--	3.90	40.00	500	204.4	0.40	29.29	0.90	0.00581	73.70
33	11.49	15.77	--	1.90	56.66	500	176.6	0.50	20.67	1.70	0.00668	55.61
34	12.25	31.54	--	1.55	55.00	500	176.6	0.50	21.29	1.40	0.00713	51.02
35	12.25	63.08	--	1.40	58.33	500	176.6	0.50	20.08	1.20	0.00851	30.20
36	12.25	7.89	--	2.20	54.16	500	176.6	0.50	21.63	1.80	0.00636	61.47
37	11.87	--	60.74	4.45	62.50	500	176.6	0.50	18.74	1.55	0.00701	90.31
38	12.25	31.54	164.44	1.80	68.33	500	176.6	0.50	17.14	1.60	0.00545	80.24
39	12.13	--	--	4.4	59.16	400	176.6	0.50	19.80	2.00	0.00593	71.64
40	11.74	--	--	4.3	53.75	400	148.8	0.50	21.79	2.10	0.00778	53.23

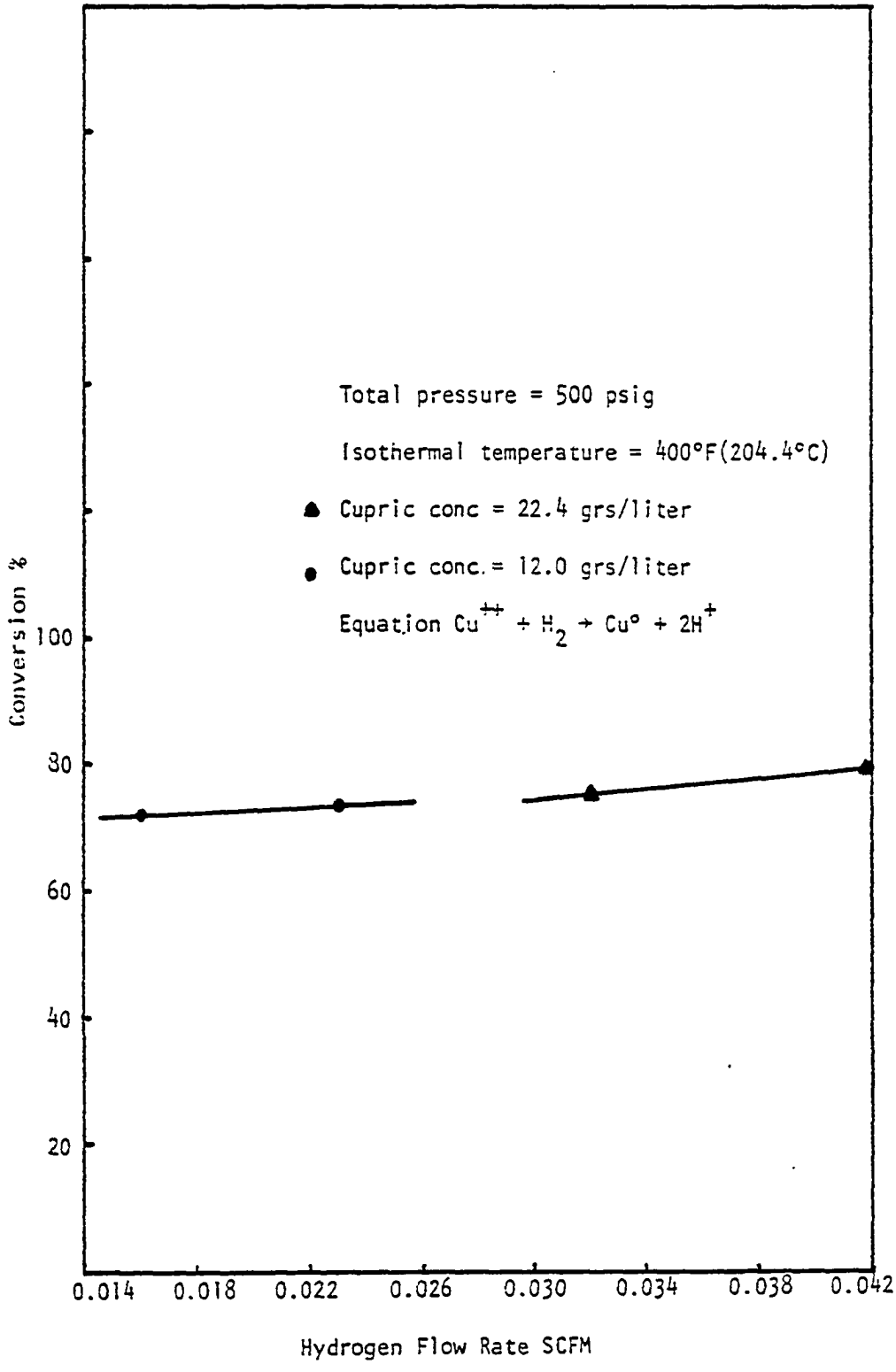

FIGURE IX-8. Effect of hydrogen flow on conversion.

feed concentration drops to a certain level, at which point the hydrogen ions produced in the reaction take over and retard the reaction. This explanation is somewhat supported by the experimental results of MacGregor and Halpern (18) and the results of von Hahn and Peters (27).

The presence of cuprous oxide observed in the runs made with feed solutions having a pH of more than 1.8 may be due to the following:

1. Formation of the basic salt of copper sulfate, which in turn reacts with the incoming hydrogen to form cuprous oxide and sulfuric acid as explained in Chapter II and given by equations (II-23) and (II-24).

$$3CuSO_4 + 4H_2O \rightleftarrows Cu_3SO_4(OH)_4 + 2H_2SO_4 \qquad \text{(II-23)}$$

$$Cu_3SO_4(OH)_4 + \frac{3}{2} H_2 \rightleftarrows \frac{3}{2} Cu_2O + H_2SO_4 + \frac{5}{2} H_2O \qquad \text{(II-24)}$$

The formation of copper in the later part of the reactor may take place as per equations (II-25) and (II-26)

$$Cu_3SO_4(OH)_4 + 3H_2 \rightleftarrows 3Cu + H_2SO_4 + 4H_2O \qquad \text{(II-25)}$$

$$Cu_2O + 2H^+ \rightleftarrows Cu^{++} + Cu^\circ + H_2O \qquad \text{(II-26)}$$

However, the possibility of formation of cuprous oxide by this method seems less likely since reaction (II-24) is a heterogeneous reaction involving solid and gas phases. This argument may be supported to some extent by noting that no cuprous oxide or copper were found at low temperatures, 250°F (121°C); only basic copper sulfate was formed.

2. Freshly formed copper reacting with incoming aqueous copper sulfate solution to form cuprous oxide and sulfuric acid was explained by Biswas and Reid (3):

$$Cu^{\circ} + CuSO_4 + H_2O \rightarrow Cu_2O + H_2SO_4 \qquad \text{(IX-1)}$$

They have experimentally observed that the above reaction takes place between copper and aqueous copper sulfate solution when the pH of the solution is maintained above 1.9. It was observed by these authors, that the reaction (IX-1) could be totally prevented at a pH lower than 1.7.

3. The cuprous ions, formed in the intermediate step of the reaction between hydrogen and cupric ion, react with hydroxyl ions present in the aqueous medium according to

$$2Cu^{+} + 2OH^{-} \rightarrow Cu_2O + H_2O \qquad \text{(IX-2)}$$

It is well known that reaction (IX-2) competes effectively with the disproportionation reaction

$$2Cu^{+} \rightleftarrows Cu^{\circ} + Cu^{++} \qquad \text{(IX-3)}$$

at higher pH values.

There is every possibility that the formation of cuprous oxide at the top of the reactor observed in this study may be taking place by both mechanisms as explained in reasons (2) and (3) above.

The pH requirement of less than 1.8 to obtain pure copper was observed in this study, as can be seen from runs

34, 35 and 38. The pH of these runs were 1.55, 1.4 and 1.8 respectively as presented in Table IX-1. This observation implies that, though higher acidity retards the reaction, its presence is important to prevent cuprous oxide formation.

Addition of neutral salts, like sodium sulfate increases the rate of reaction as can be seen from the results of run #37 and 38 given in Table IX-1. The reason is that the sulfate ions react with hydrogen ions, generated in the reduction reaction, to form more stable bisulfate ions.

$$H^{+} + SO_4^{--} \rightarrow HSO_4^{-} \qquad \text{(IX-4)}$$

However, pH requirement of 1.8 for obtaining pure copper was noticed in these experiments also.

In Table IX-2, some of the results obtained in this study were compared with the batch data of Kieswetter, Jr. (14), under almost similar conditions. The lower conversion values, of this study, compared to Kieswetters, can be accounted for by the non-isothermal portion of the reactor being included in the residence time calculations. Otherwise, the values seem to agree very well. A similar comparison with results of Neskora (23) are presented in Table IX-3. As can be seen the results of Neskora (23) are totally different and cannot be compared on a common basis. However the high conversions of 20.9, 35.7 and 75 percent reported for residence times 0.8, 1.5 and 1.9

TABLE IX-2

COMPARISON OF RESULTS OF THIS STUDY WITH KIESWETTERS(14)

Residence Time Minutes	This Study		Kieswetter's	
	Temperature °C	Conversion %	Temperature °C	Conversion %
10	148.8	21.0	150.0	35.0
20	148.8	51.0	150.0	58.0
10	176.6	56.0	170.0	72.0
20	176.6	72.0	170.0	81.0

TABLE IX-3

COMPARISON OF RESULTS OF THIS STUDY WITH NESKORA'S(23)

	This Study		Neskora's		
Residence Time Minutes	Temperature °F	Conversion %	Residence Time Minutes	Temperature °F	Conversion %
10	300	21.0	0.8	292.0	20.9
12.6	300	36.0	1.5	303.0	35.7
22.0	300	53.0	1.90	287.0	75.0

minutes, respectively, appear questionable. Neskora's high conversions could be the result of formation of basic salts in the preheater which would be included in the depletion terminology used by Neskora in place of conversion. Secondly, Neskora started each experimental run with the reactor filled with water at the time the feed solution was first introduced. This prerun water diluted the feed in the system, which could have been erronously taken as the depletion of solution due to reaction, even though the dilution effects were taken into account (but probably not adequately) in the case of the product separator.

As explained in Chapter VIII, the activation energy and frequency factors could not be calculated directly using the integral rate data. Von Hahn's rate equation (Equation III-17) was chosen for calculation purposes because this equation takes into account the catalytic effect of the cuprous ions. Many investigators reported the catalytic action of the cuprous ions for the reaction under study. The results obtained by computer calculations (see Appendix E for the computer program) utilizing rate equation (A-25) (see Appendix A) substituted in equation (VII-6), the conversions were calculated for different residence times at the experimental conditions. Activation energies of 22.4 Kcal/mole for k_1 and 15.3 Kcal/mole for k_3 given by von Hahn and Peters were used

in the equation (A-25). Cuprous ion concentrations were calculated using equation (VII-24), hydrogen ion concentration by equation (VII-11). The simulated and experimental results are compared in Figures IX-9, IX-10 and IX-11. In each case the results obtained by simulation were higher than those experimentally observed. However, simulated lines were parallel to the experimentally observed results in all cases. A similar shift was noticed when MacGregor and Halpern's data were simulated using the rate equation given by equation (A-25), as shown in Figures IX-12, IX-13 and IX-14. This shift and the higher values obtained in the simulation may be due to the fact that von Hahn and Peters used magnesium sulfate in place of sodium sulfate as the neutral sulfate supplying salt. Also the hydrogen ion concentrations calculated may be in error as the effect of complexing of cupric ions with sulfate was neglected in this study, as mentioned in Chapter VIII. Equation (A-25) is a modified version of von Hahn and Peters equation. In their equation some discrepancies were found during this study and a detailed account is given in Appendix A. The rate equation given by von Hahn and Peters when used did not reproduce their own data, whereas the modified version reproduced their data very well as is shown in Figure IX-15. Even though the modified version is mathematically consistant, there are some physical inconsistancies, which

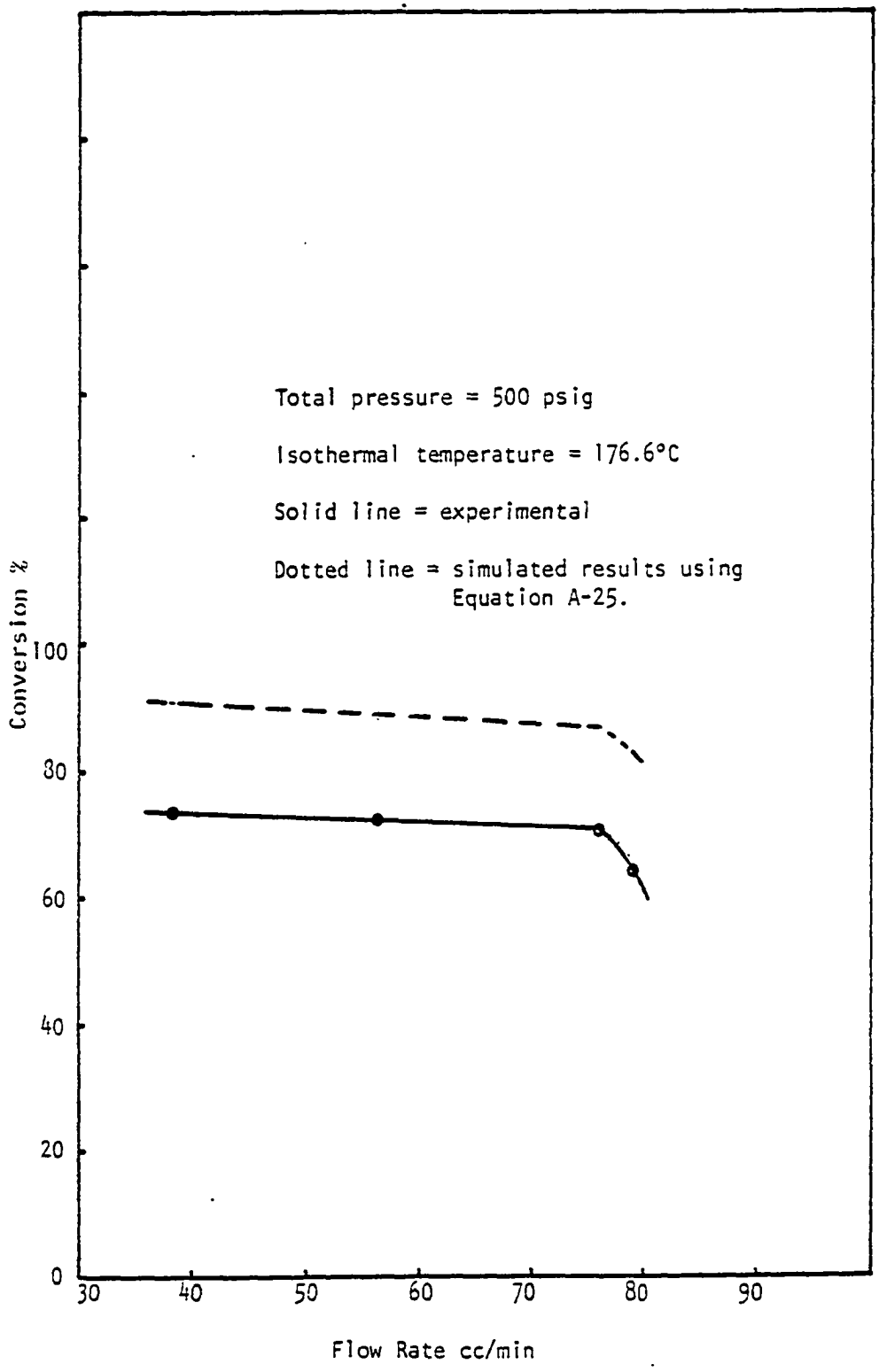

FIGURE IX-9. Comparison of experimental and simulated results for isothermal temperature 176.6°C.

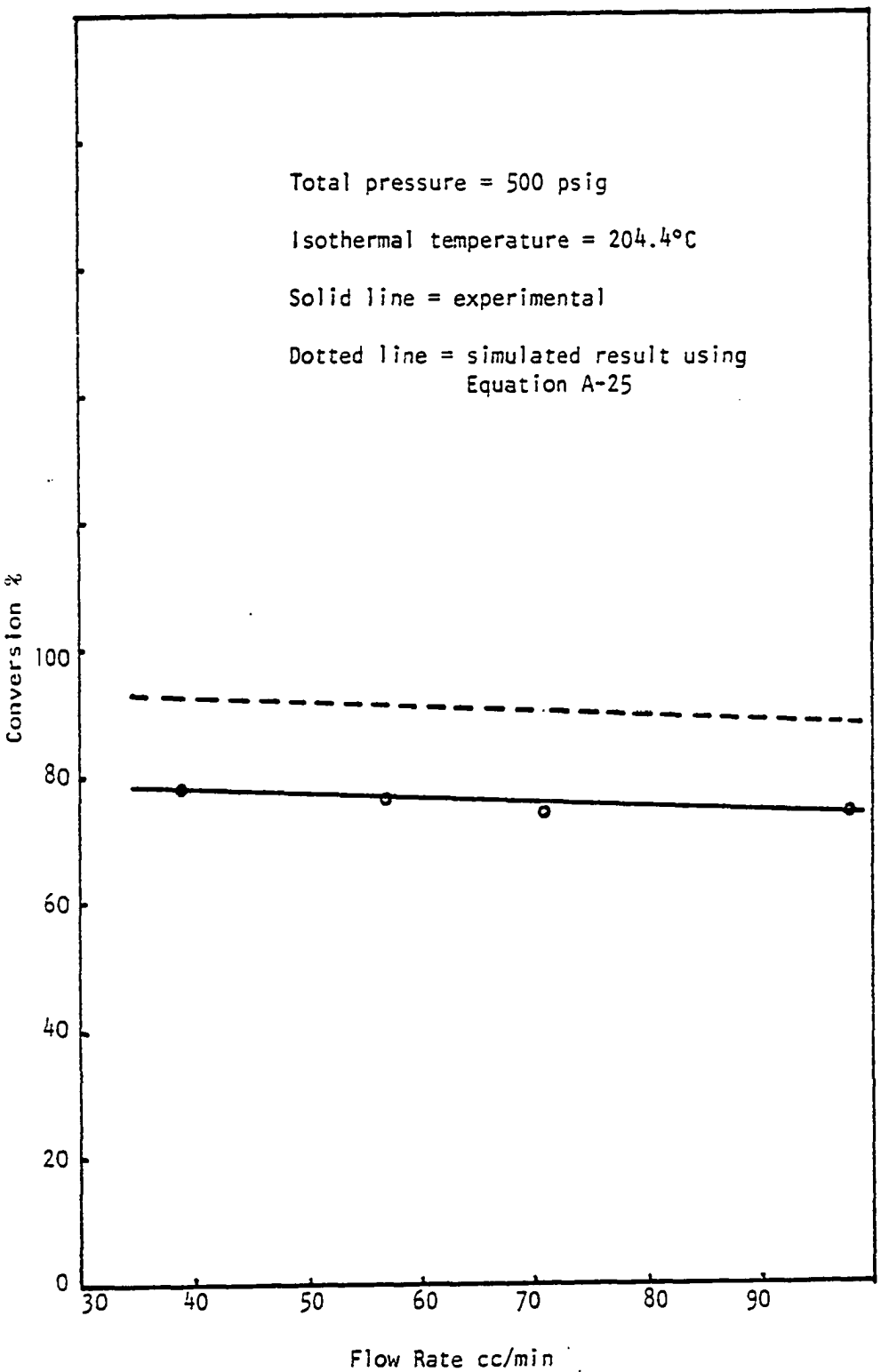

FIGURE IX-10. Comparison of experimental and simulated results for isothermal temperature 204.4°C.

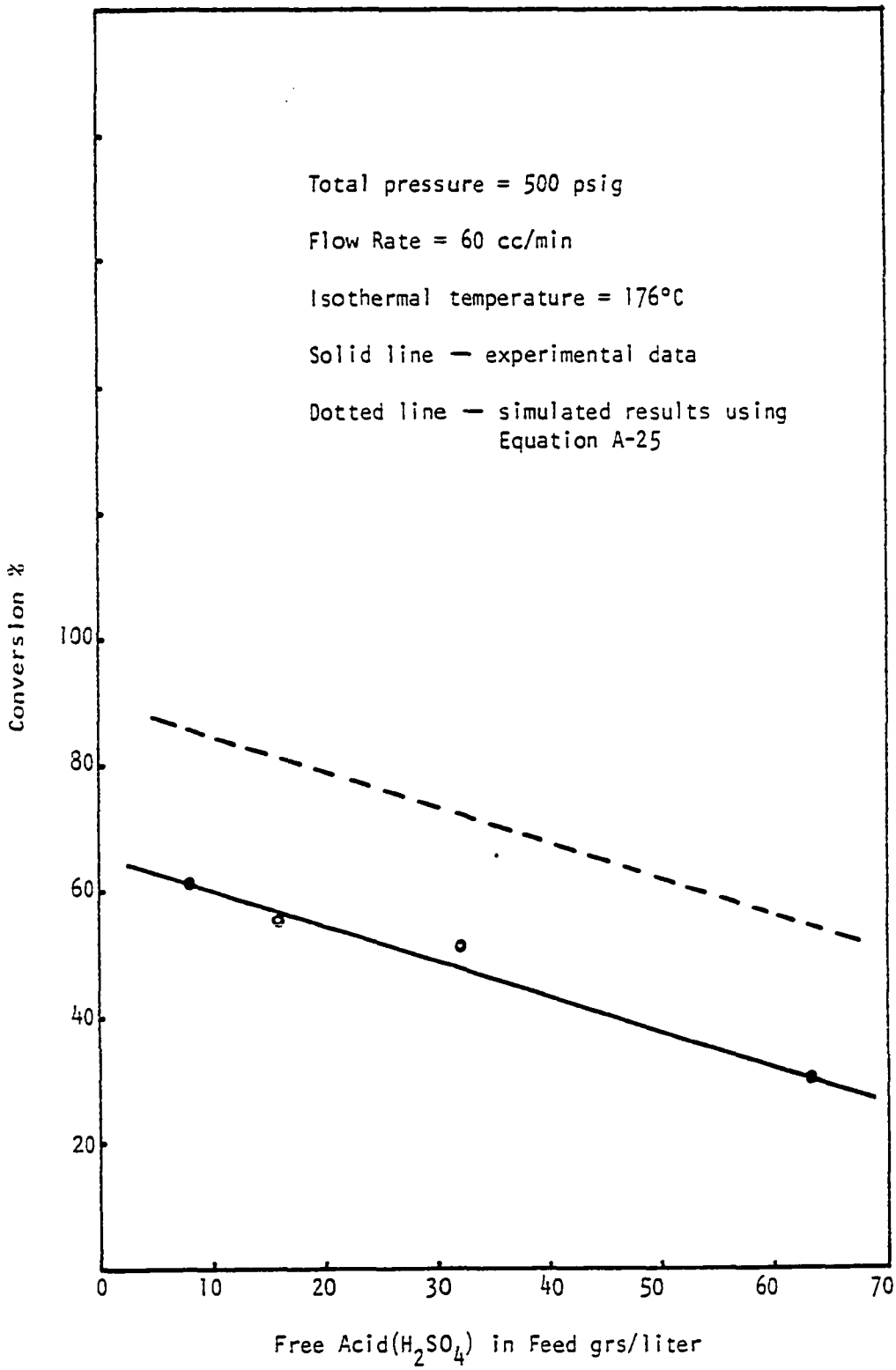

FIGURE IX-11. Comparison of experimental and simulated results for different acid(H_2SO_4) concentration in feed.

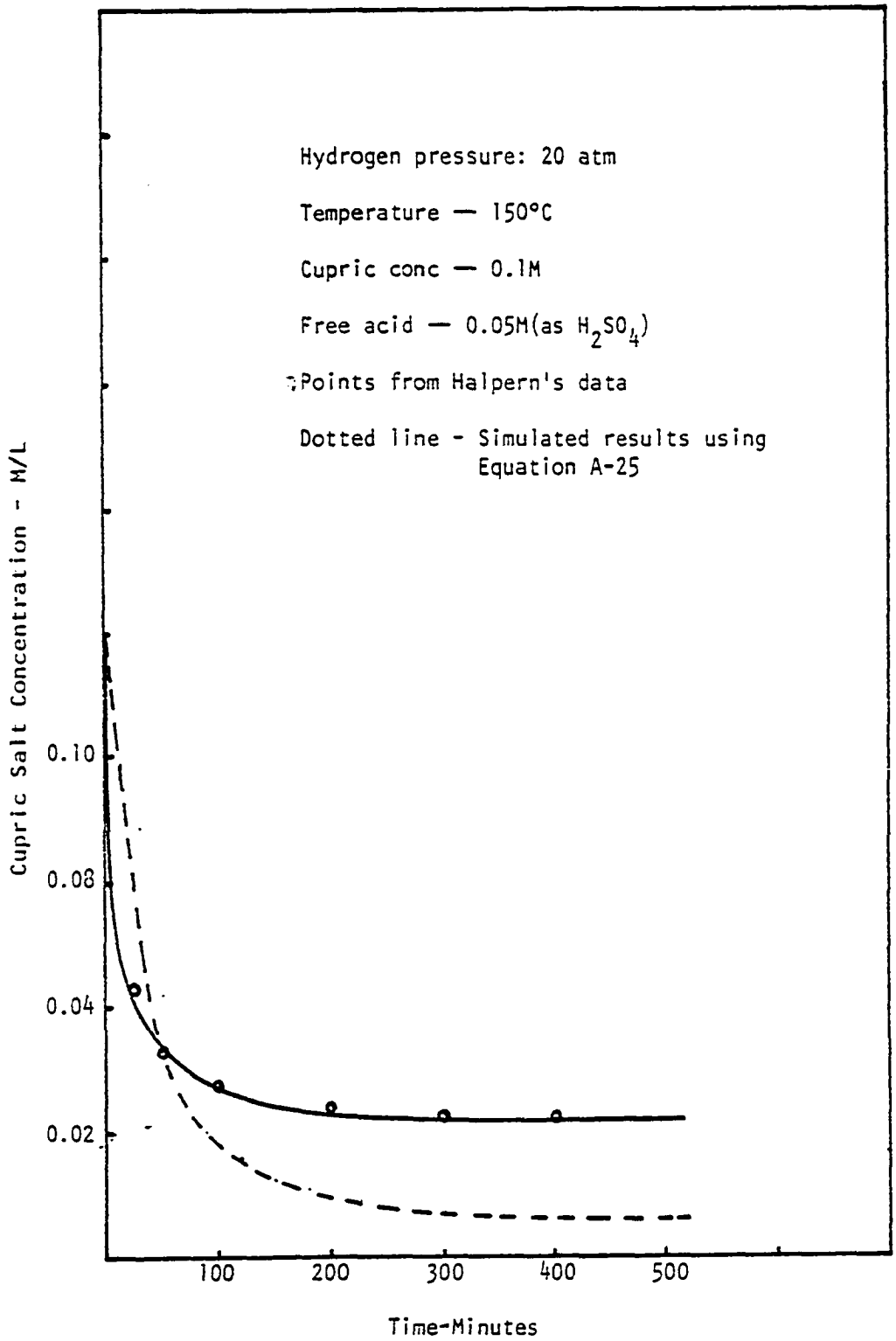

FIGURE IX-12. Comparison of Halpern's experimental data with simulated results at 150°C.

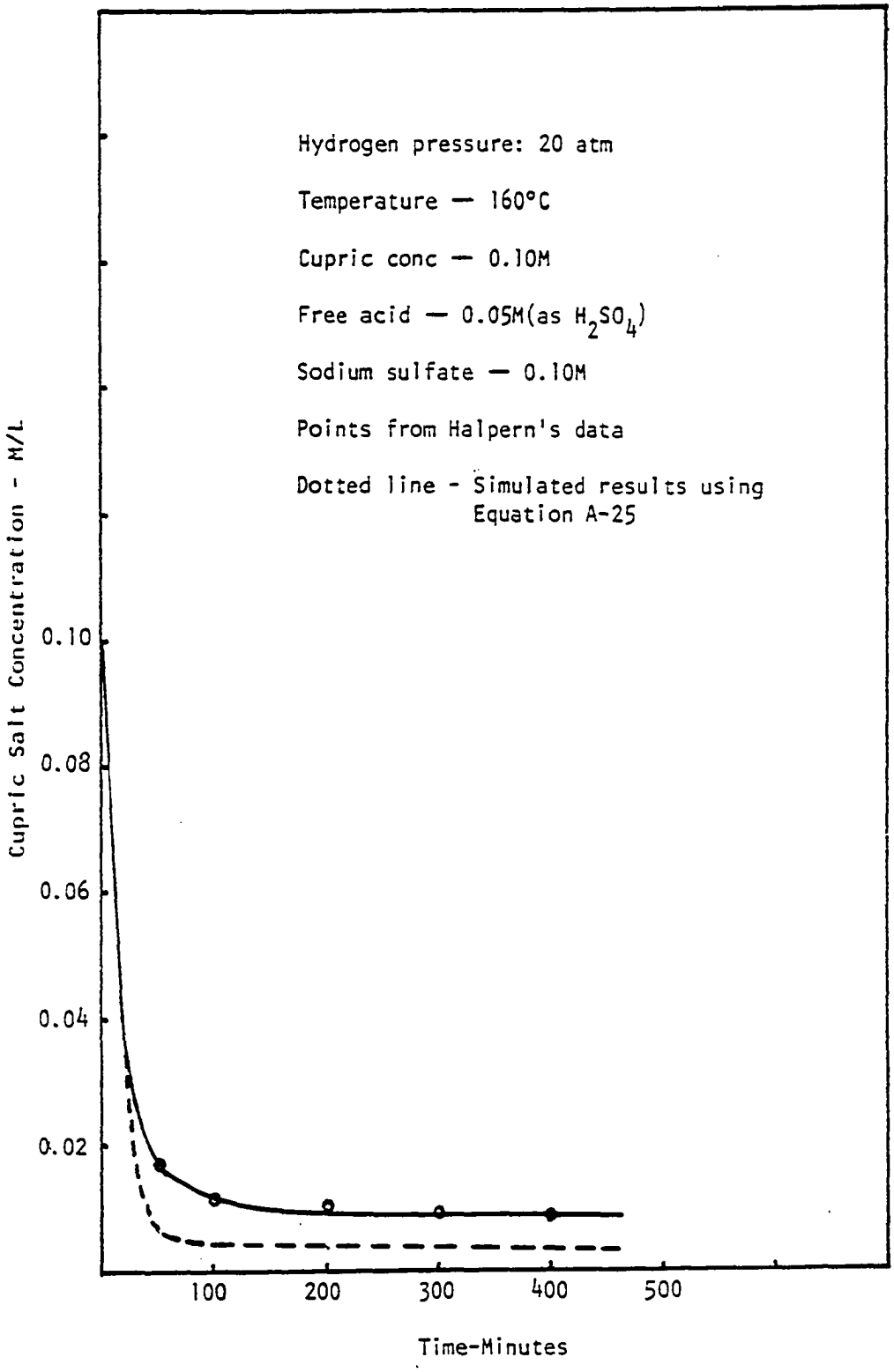

FIGURE IX-13. Comparison of Halpern's experimental data with simulated results at 160°C.

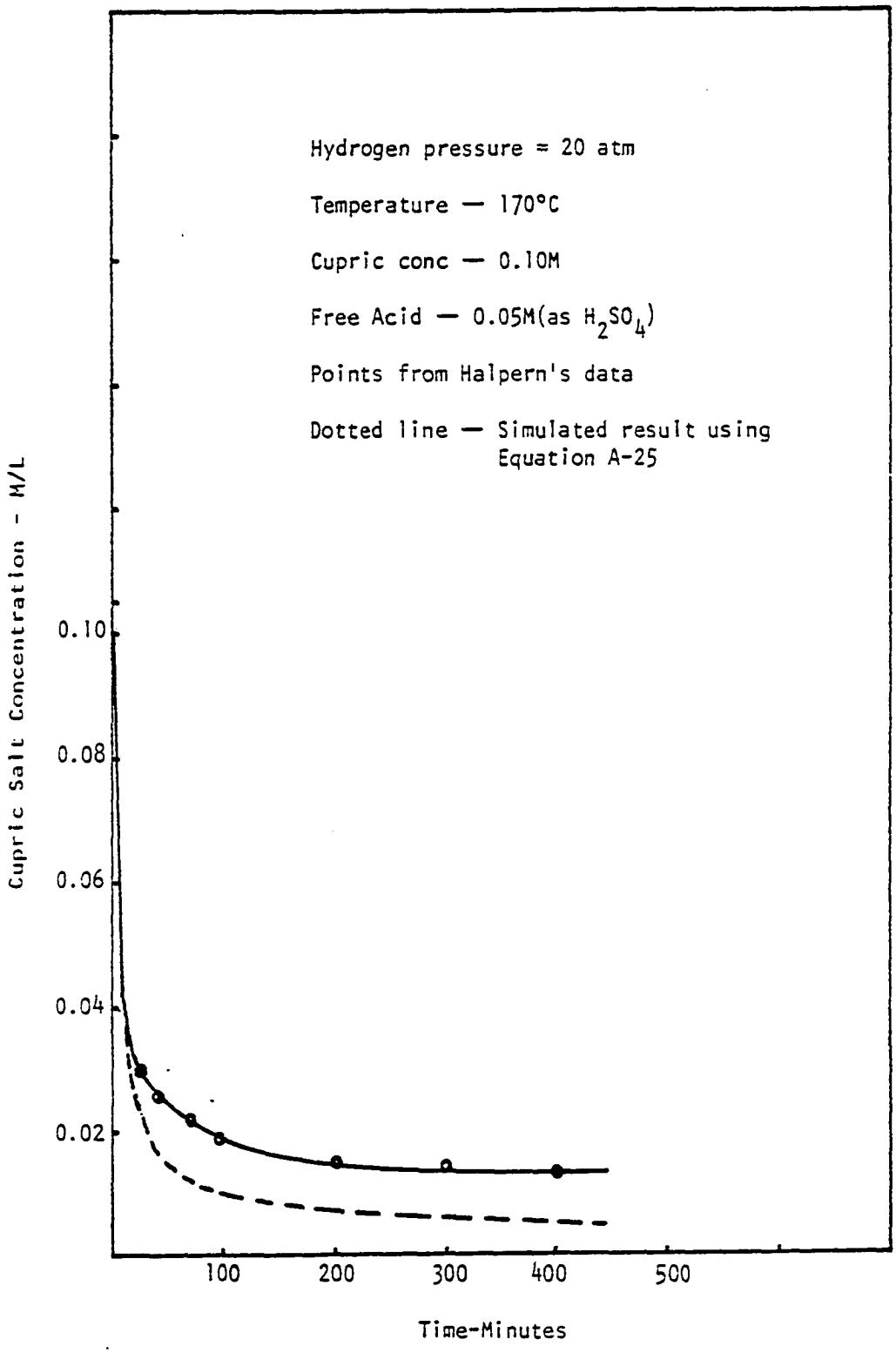

FIGURE IX-14. Comparison of Halpern's experimental data with simulated results at 170°C.

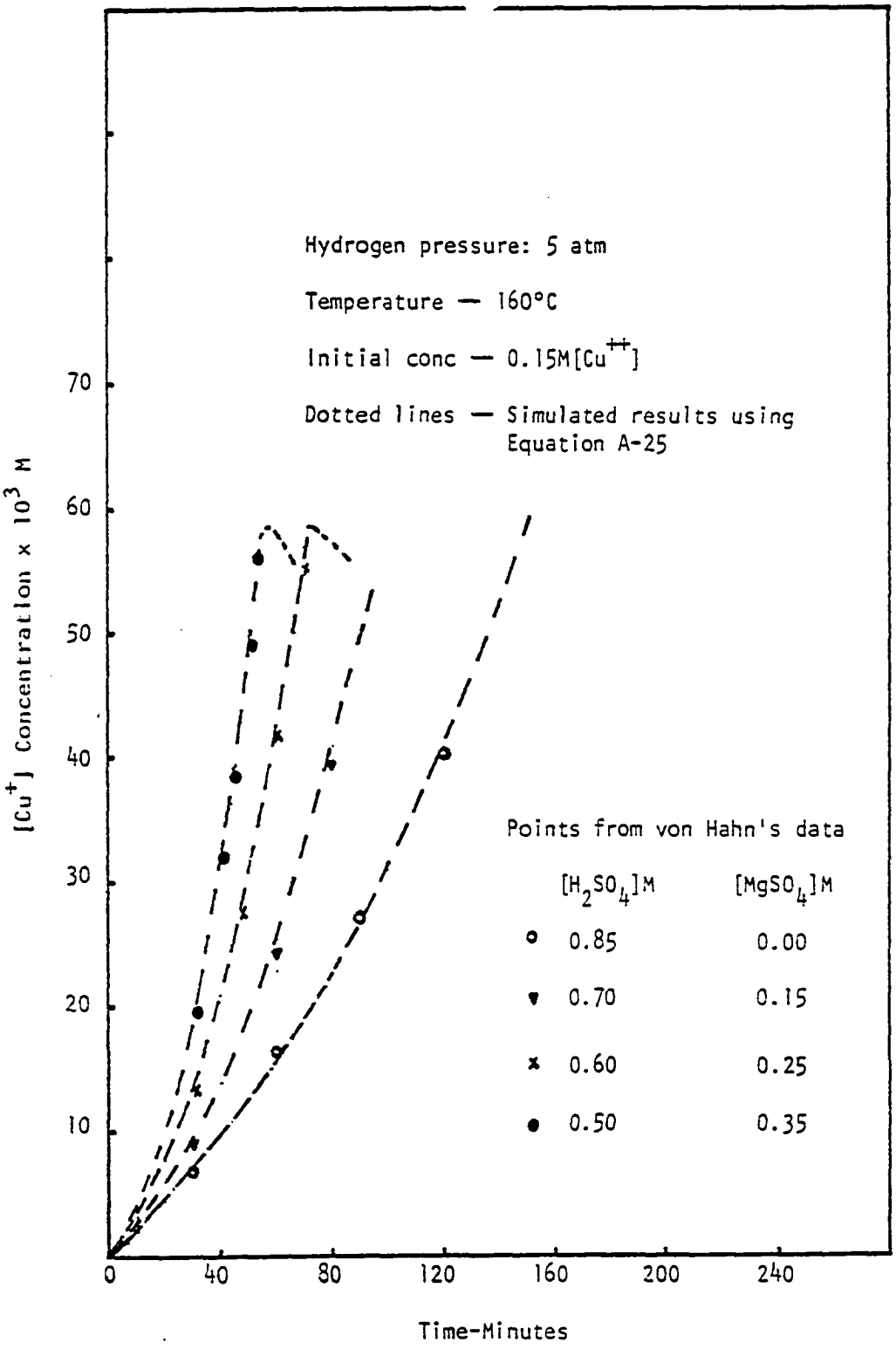

FIGURE IX-15. Comparison of von Hahn's experimental data with simulated results.

indicate that the mechanism proposed by von Hahn and Peters is deficient. For example in equation (A-25), a negative sign in the denominator can be obtained only when the parameter $(\frac{k_{-3}}{k_4})$ is negative, when derived from the mechanism given by von Hahn and Peters, which is a physical inconsistancy. However, no attempt to correct the mechanism was made in this study.

CHAPTER X

CONCLUSIONS

The results of this investigation show that copper can be precipitated effectively from acidic sulfate solution by hydrogen reduction in a continuous tubular reactor.

Unlike the batch process, the continuous process requires careful control of feed temperature and pH to prevent premature precipitation of basic copper sulfate. To prevent formation of cuprous oxide during reduction the pH of the feed should be maintained below 1.8.

As demonstrated for a residence time of about 10 minutes, at least 72% of the copper can be reduced from the solution at an average temperature of 400°F (204.4°C) and a total pressure of 500 psia. (Note from Figure IX-4, that at 400°F, the residence time could probably be reduced substantially below 10 minutes without reducing the conversion.) Additives like sodium sulfate enhance the rate and hence the conversion. When used in combination with sulfuric acid very good conversions to copper, free of cuprous oxide, could be obtained.

While very low temperatures like 250°F (121°C) are not suitable for continuous operations, very high temperatures are not desirable either, as the increase in yield is negligible at temperatures higher than 400°F (204.4°C). Residence times longer than 10 minutes may not be practical, from an economic viewpoint. Furthermore, the conversions are almost constant beyond residence time of 10 minutes. All that longer residence times achieve, then, are overgrowth of crystals and agglomeration which may not be desirable for the end use intended for the products.

The problem of product sticking to the reactor walls must be solved before further progress can be made on the continuous hydrogen reduction process.

The only kinetic equation available, which was proposed by von Hahn and Peters, was not applicable to the results as was demonstrated in this study. For simulation and optimization of the continuous process, a better kinetic equation must be developed.

NOMENCLATURE

A	Area of cross section of pipe, cm^2
A_o	Empirical constant in Equation VIII-7
AC	Initial free acid concentration, gr moles (H_2SO_4)/liter
AN	Inert sulfate added to feed, gr moles/liter
B_o	Empirical constant in Equation VIII-7
C	Volume of the sample solution for analysis, cc
C_A	Concentration of species A in solution, gr moles/liter
C_o	Empirical constant in Equation VIII-7
D_o	Empirical constant in Equation VIII-7
E	Electrode potential, volts
e	Electron
F	Faraday equivalent, 96,496 columbs
FA_o	Volumetric flow rate of fluid, cc/min
G	Free energy, Kcal/gr mole
ΔH	Heat of reaction, Kcal/gr mole
H_2	Hydrogen as gas or in solution
H^+	Hydrogen ion concentration in solution, gr mole/liter
HSO_4^-	Bisulfate ion concentration in solution gr moles/liter

K	Equilibrium constant
k_1, k_2, etc.	Rate constants in appropriate units
M	Molecular weight of copper
N	Normality of thiosulfate solution, gr equivalents/liter
R	Universal gas constant in appropriate units
r	Rate of reaction in appropriate units
S	Solubility of hydrogen in water
SO_4^{--}	Sulfate ions in solution, gr mole/liter
T	Absolute temperature, °K
V	Volume of thiosulfate consumed in analysis, cc
x	Conversion of cupric ions to product
y	Conversion of H^+ to HSO_4^-
Z	Length of pipe, cm

REFERENCES

1. Amdur, I. and Hammes, G.G., Chemical Kinetics, Principles and Selected Topics, McGraw-Hill Book Company, New York, 1966.

2. Balzhiser, R.E., Samuels, M.R. and Eliassen, J.D., Chemical Engineering Thermodynamics, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1972.

3. Biswas, A.K. and Reid, J.G., "Production of High Purity Copper by Cementation on Iron", paper presented at C.I.M. Conference of Metallurgists, Halifax, Nova Scotia, August 27-30, 1972.

4. Brown, R.L., "Steady State Crystallization from Solutions of Metal Salts Under Hydrogen Atmospheres at Elevated Temperatures and Pressures", M.S. Thesis, University of Oklahoma, Norman, Oklahoma, 1965.

5. Conner, H.S., "Equilibrium Thermodynamics of Copper Displacement from Copper Salt Solutions Under Hydrogen Atmospheres at Elevated Temperatures and Pressures", M.S. Thesis, University of Oklahoma, Norman, Oklahoma, 1965.

6. Courtney, W.G., "Nucleation of Copper Metal from Aqueous Solution", The Journal of Physical Chemistry, 60, 1956, p. 1461.

7. Dunning, W.J. and Potter, P.E., "Some Evidence for the Homogeneous Catalytic Activation of Molecular Hydrogen by the Cuprous Ion in Aqueous Solution", Proceeding of the Chemical Society (London), 1960, p. 244.

8. Evans, D.J.I., "Production of Metals by Gaseous Reduction from Solution - Processes and Chemistry", Advances in Extractive Metallurgy, Proceedings of a Symposium held in London, April 17-20, 1967, The Institution of Mining and Metallurgy, American Elsevier Publishing Company, Inc., New York.

9. Gedansky, L.M., Woolley, E.M. and Hepler, L.G., "Thermochemistry of Compounds and Aqueous Ions of Copper", Journal of Chemical Thermodynamics, 2, 1970, p. 561.

10. Hahn, E.A. and Peters, E., "The Kinetics and Mechanism of the Cu^{++} Catalyzed Reduction of Cr by Hydrogen in Aqueous Solutions", Canadian Journal of Chemistry 39, 1961, p. 162.

11. Halpern, J., MacGregor, E.R. and E. Peters, "The Nature of the Activated Intermediate in the Homogeneous Catalytic Activation of Hydrogen by Cupric Salts", Journal of Physical Chemistry, 60, 1956, p. 1455.

12. Halpern, J., "Some Aspects of the Physical Chemistry of Hydrometallurgy", Journal of Metals, February 1957, p. 280.

13. Ipatieff, V.N., "Early Work on the Displacement of Metals and Metal Oxides", Journal of Chemical Education, March 1953, p. 110.

14. Kieswetter, Jr., O., "Reduction of Cupric and Nickelous Ions from Aqueous Copper and Nickel Sulfate Solutions by Hydrogen", Ph.D. Thesis, University of Oklahoma, Norman, Oklahoma, 1973.

15. Kunda, W. and Evans, D.J.I., "Hydrogen Reduction of Copper to Powder from the Ammine Carbonate System", Modern Developments in Powder Metallurgy, Vol. IV, Plenum Press, New York 1966.

16. Lapidus, L., Digital Computation for Chemical Engineers, McGraw-Hill, New York, 1962.

17. Levenspiel, O., Chemical Reaction Engineering, 5th ed., John Wiley and Sons, New York, 1967.

18. MacGregor, E.R. and Halpern, J., "The Reduction of Cupric Salts in Aqueous Perchlorate and Sulfate Solutions by Molecular Hydrogen", Trans. Met. Soc. of A.I.M.E. 212, April 1958, p. 244.

19. Marshall, W.L. and Jones, E.V., "Second Dissociation Constant of Sulfuric Acid from 25 to 350° Evaluated from Solubilities of Calcium Sulfate in Sulfuric Acid Solutions", The Journal of Physical Chemistry, 70(2), December 1966, p. 4028.

20. McDuffie, H.F., Compere, E.L., Stone, H.H., Woo, L.F. and Secoy, C.H., "Homogeneous Catalysis for Homogeneous Reactors. Catalysis of the Reaction Between Hydrogen and Oxygen", The Journal of Physical Chemistry, 62, September 1958, p. 1030.

21. Meddings, B. and Mackiw, V.N., "The Gaseous Reduction of Metals from Aqueous Solutions", Unit Processes in Hydrometallurgy, Vol. 24, Gordon and Breach, Science Publishers, Inc., New York, 1963.

22. Nakazava, G.I., "Study on the Precipitation of Copper Powder from Aqueous Cupric Sulfate Solution by Hydrogen Pressure Reduction", Zairyo, 14 (144), 1965, p. 725.

23. Neskora, D.R., "Copper and Nickel Production by Continuous Steady-State Hydrogen Reduction from Aqueous Ionic Salt Solutions", Ph.D. Thesis, University of Oklahoma, Norman, Oklahoma, 1973.

24. Peters, E. and Halpern, J., "Effect of Complexing on the Homogeneous Catalytic Activation of Hydrogen by Cupric Salt", Canadian Journal of Chemistry 34, 1956, p. 554.

25. Pierce, W.C., Haenisch, E.L. and Sawyer, D.T., Quantitative Analysis, 4th edition, John Wiley, New York, 1958.

26. Schaufelberger, F.A., "Precipitation of Metal from Salt Solution by Reduction with Hydrogen", Journal of Metals 8, May 1956, p. 695.

27. von Hahn, E.A. and Peters, E., "Role of Copper (I) in the Kinetics of Hydrogen Reduction of Aqueous Cupric Sulfate Solutions", The Journal of Physical Chemistry, 69(2), February 1965, p. 547.

28. von Hahn, E.A. and Peters, E., "Kinetics of Copper (II) and Copper (I) - Catalyzed Deuterium Exchange in Sulfuric and Perchloric Acid Solutions", The Journal of Physical Chemistry, 75(4), 1971, p. 571.

29. Wadsworth, M.E., "Reduction of Metals in Solution", Trans. Met. Soc. of A.I.M.E., 245, July 1969, p. 1381.

APPENDIX A

DERIVATION OF RATE EQUATION PROPOSED BY VON HAHN AND THE DISCREPANCY THEREOF

The mechanism suggested was

$$Cu^{++} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+ \qquad \text{(A-1)}$$

$$CuH^+ + Cu^{++} \xrightarrow{k_2} 2Cu^+ + H^+ \qquad \text{(A-2)}$$

$$Cu^+ + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CuH + H^+ \qquad \text{(A-3)}$$

$$CuH + Cu^{++} \xrightarrow{k_4} CuH^+ + Cu^+ \qquad \text{(A-4)}$$

and

$$2Cu^+ \underset{K}{\overset{\text{Fast}}{\rightleftharpoons}} Cu^{++} + Cu^\circ \qquad \text{(A-5)}$$

Writing the rate of depletion of cupric ions

$$-\frac{d(Cu^{++})}{dt} = k_1(Cu^{++})(H_2) - k_{-1}(CuH^+)(H^+) + k_2(CuH^+)(Cu^{++}) + k_4(CuH)(Cu^{++}) \qquad \text{(A-6)}$$

and

$$\frac{d(CuH^+)}{dt} = k_1(Cu^{++})(H_2) - k_{-1}(CuH^+)(H^+) - k_2(CuH^+)(Cu^{++})$$

$$+ k_4(CuH)(Cu^{++}) \qquad \text{(A-7)}$$

Assuming stationary state hypothesis for CuH^+

$$\therefore \quad \frac{d(CuH^+)}{dt} = 0$$

Applying the above condition to equation (A-7) will lead to

$$(CuH^+) = \frac{k_1(Cu^{++})(H_2) + k_4(CuH)(Cu^{++})}{\left[k_{-1}(H^+) + k_2(Cu^{++})\right]} \qquad \text{(A-8)}$$

Substituting the value of (CuH^+) from equation (A-8) into equation (A-6)

$$-\frac{d(Cu^{++})}{dt} = k_1(Cu^{++})(H_2) - k_{-1}(H^+)\ \frac{k_1(Cu^{++})(H_2) + k_4(CuH)(Cu^{++})}{\left[k_{-1}(H^+) + k_2(Cu^{++})\right]}$$

$$+ k_2(Cu^{++})\ \frac{k_1(Cu^{++})(H_2) + k_2(CuH)(Cu^{++})}{\left[k_{-1}(H^+) + k_2(Cu^{++})\right]}$$

$$+ k_4(CuH)(Cu^{++}) \qquad \text{(A-9)}$$

After expansion and cancellations

$$-\frac{d(Cu^{++})}{dt} = \frac{2k_1(Cu^{++})^2(H_2) + 2k_4(Cu^{++})^2(CuH)}{\left[(Cu^{++}) + \frac{k_{-1}}{k_2}(H^+)\right]} \qquad \text{(A-10)}$$

$$\frac{d(CuH)}{dt} = k_3(Cu^+)(H_2) - k_3(CuH)(H^+) - k_4(CuH)(Cu^{++})$$

(A-11)

Assuming stationary state hypothesis for (CuH)

$$\therefore \frac{d(CuH)}{dt} = 0$$

Applying the above assumption to equation (A-11) will lead to

$$CuH = \frac{k_3(Cu^+)(H_2)}{\left[k_4(Cu^{++}) + k_{-3}(H^+)\right]} \qquad \text{(A-12)}$$

Substituting (A-12) into equation (A-10) and rearranging

$$-\frac{d(Cu^{++})}{dt} = \frac{2k_1(Cu^{++})^2(H_2)}{\left[(Cu^{++}) + \frac{k_{-1}}{k_2}(H^+)\right]} + \frac{2k_3(Cu^{++})^2(H_2)(Cu^+)}{[(Cu^{++}) + \frac{k_{-1}}{k_2}(H^+)][Cu^{++} + \frac{k_{-3}}{k_4}(H^+)]}$$

(A-13)

The above equation (A-13) is valid up to the point where disproportionation begins.

If equations A-1 to A-4 are balanced, then it will be seen that for every two cupric ions reacted one hydrogen reacts.

$$\therefore -\frac{d(H_2)}{dt} = -\frac{1}{2}\frac{d(Cu^{++})}{dt} \qquad \text{(A-14)}$$

From equation (A-14) and equation (A-13)

$$-\frac{d(H_2)}{dt} = \frac{k_1(Cu^{++})^2(H_2)}{\left[Cu^{++} + \frac{k_{-1}}{k_2}(H^+)\right]} + \frac{k_3(Cu^{++})^2(H_2)(Cu^+)}{[(Cu^{++}) + \frac{k_{-1}}{k_2}(H^+)][(Cu^{++}) + \frac{k_{-3}}{k_4}(H^+)]} \qquad (A\text{-}15)$$

Equation (A-15) like equation (A-13) is valid only upto the initiation of disproportionation. After disproportionation begins

$$-\frac{d(H_2)}{dt} = -\frac{d(Cu^{++})}{dt} \qquad (A\text{-}16)$$

So, after disproportionation

$$-\frac{d(Cu^{++})}{dt} = \frac{k_1(Cu^{++})^2(H_2)}{\left[Cu^{++} + \frac{k_{-1}}{k_2}(H^+)\right]} + \frac{k_3(Cu^{++})^2(H_2)(Cu^+)}{[(Cu^{++}) + \frac{k_{-1}}{k_2}(H^+)][(Cu^{++}) + \frac{k_{-3}}{k_4}(H^+)]} \qquad (A\text{-}17)$$

von Hahn and Peters (27) in their paper, plotted $-\frac{dH_2}{dt}$ vs Cu^+ (Figure 2 in their paper) and obtained straight lines. (see Figure A-1). They contended that the intercepts represent the rate part due to cupric ion alone, i.e.

$$I = \frac{k_1(Cu^{++})^2(H_2)}{\left[Cu^{++} + \frac{k_{-1}}{k_2}(H^+)\right]} \qquad (A\text{-}18)$$

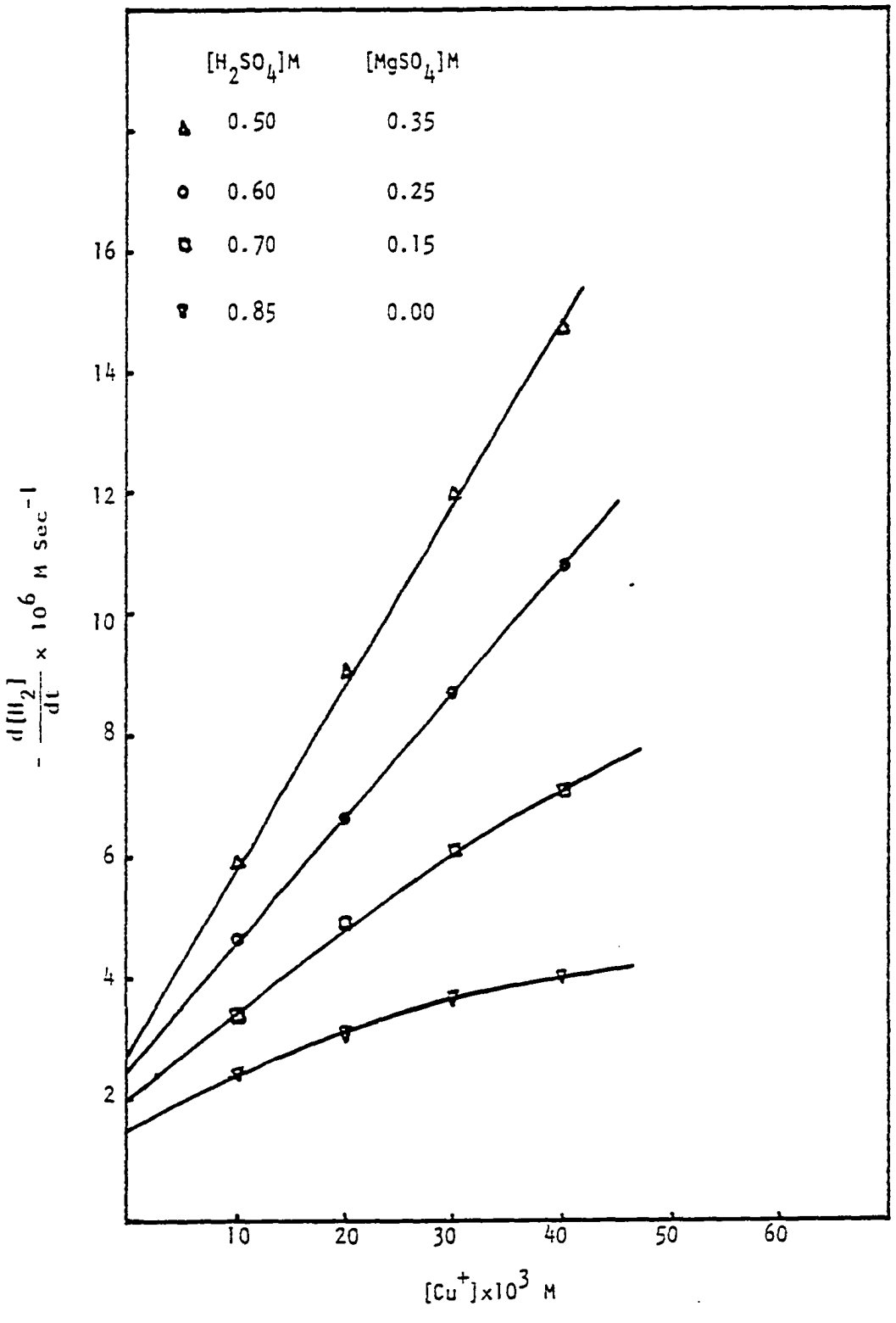

FIGURE A-1. Rate vs Cu^{+} as a function of acidity (From vonHahn and Peters)

and the slope as

$$S = \frac{k_3(Cu^{++})^2(H_2)}{[(Cu^{++}) + \frac{k_{-1}}{k_2}(H^+)][\frac{k_{-3}}{k_4}(H^+) + Cu^{++}]} \qquad (A\text{-}19)$$

So far, so good; but then they devided I by S and obtained

$$\frac{I}{S} = \frac{k_1}{k_3} \times \frac{k_{-3}}{k_4}(H^+) + \frac{k_1}{k_3}(Cu^{++}) \qquad (A\text{-}20)$$

This result is not valid, because the intercept I has a particular value when Cu^+ is zero.

i.e. $$I = \frac{k_1(Cu_o^{++})^2(H_2)}{[(Cu_o^{++}) + \frac{k_{-1}}{k_2}(H^+)]}$$

Where Cu_o^{++} is the initial concentration at which Cu^+ is zero.

Note that S can be taken at any point along the straight line, at which the cuprous concentration is Cu^+ and cupric concentration is Cu^{++}. Therefore, the valve of I/S cannot be that which is given by von Hahn and Peters in their paper.

For a given line, the slope remains constant,

i.e., $S_1 = S_2$

$$\text{or } \frac{k_3(Cu_1^{++})^2(H_2)}{[(Cu_1^{++}) + \frac{k_{-1}}{k_2}(H_1^+)][Cu_1^{++} + \frac{k_{-3}}{k_4}(H_1^+)]} =$$

$$\frac{k_3(Cu_2^{++})^2(H_2)}{[(Cu_2^{++}) + \frac{k_{-1}}{k_2}(H_2^+)] + [Cu_2^{++} + \frac{k_{-3}}{k_4}(H_2^+)]} \qquad (A\text{-}21)$$

If it is assumed that $Cu_1^{++} > Cu_2^{++}$, then $H_2^{+} > H_1^{+}$ and if it is assumed that the concentration of hydrogen is constant, then

$$\frac{(Cu_1^{++})^2}{[(Cu_1^{++}) + \frac{k_{-1}}{k_2}(H_1^{+})][Cu_1^{++} + \frac{k_{-3}}{k_4}(H_1^{+})]} = \frac{(Cu_2^{++})^2}{[(Cu_2^{++}) + \frac{k_{-1}}{k_2}(H_2^{+})][(Cu_2^{++}) + \frac{k_{-1}}{k_4}(H_2^{+})]} \qquad \text{(A-22)}$$

Modification I

If equation (A-22) is valid, then, since $Cu_1^{++} > Cu_2^{++}$ the dominator $[Cu_2^{++} + \frac{k_{-1}}{k_2}(H_2^{+})][Cu_2^{++} + \frac{k_{-3}}{k_4}(H_2^{+})]$ should be proportionately lower than $[Cu_1^{++} + \frac{k_{-1}}{k_2}(H_1^{+})][Cu_1^{++} + \frac{k_{-3}}{k_4}(H_1^{+})]$. But as Cu_2^{++} is decreasing, H_2^{+} is increasing due to release of H^{+} ions in the reaction. Therefore, $[Cu_2^{++} + \frac{k_{-1}}{k_2}(H_2^{+})][Cu_2^{++} + \frac{k_{-3}}{k_4}(H_2^{+})]$ will never be proportionately lower than $[Cu_1^{+} + \frac{k_{-1}}{k_2}(H_1^{+})][Cu_1^{+} + \frac{k_{-3}}{k_4}(H_1^{+})]$, such that equation (A-22) will be satisfied, unless one of the terms contains a negative sign. That is

either $[Cu_2^{++} + \frac{k_{-1}}{k_2}(H_2^{+})][Cu_2^{++} - \frac{k_{-3}}{k_4}(H_2^{+})$ (A-23)

or $[Cu_2^{++} - \frac{k_{-1}}{k_2}(H_2^{+})][Cu_2^{++} + \frac{k_{-3}}{k_3}(H_2^{+})]$ (A-24)

Similarly for the Cu_1^{++} case, equation (A-23) and (A-24) can be proved by taking numerical values and substituting in equation (A-22). For arguments sake consider equation (A-23). It leads to the original equation (A-15) in the form

$$-\frac{d(H_2)}{dt} = \frac{k_1(Cu^{++})^2 (H_2)}{Cu^{++} + \frac{k_{-1}}{k_2}(H^+)} + \frac{k_3(Cu^{++})^2 (H_2)(Cu^+)}{[Cu^{++} + \frac{k_{-1}}{k_2}(H^+)][Cu^{++} - \frac{k_{-3}}{k_4}(H^+)]} \qquad \text{(A-25)}$$

From the proposed mechanism given by equation A-1 to A-5, it is not possible to obtain equation (A-25), until the ratio $(\frac{k_{-3}}{k_4})$ bears a negative sign. That means either k_{-3} or k_4 should bear a negative sign which is physically absurd.

Modification II

Considering equation (A-22) again, this time it will be assumed that (k_{-3}/k_4) varies such that equation (A-22) is satisfied. Therefore equation (A-22) can be written as:

$$\frac{(Cu_1^{++})^2}{[(Cu_1^{++}) + \frac{k_{-1}}{k_2}(H_1^+)][(Cu_1^{++}) + \left(\frac{k_{-3}}{k_4}\right)_1 (H_1^+)]} = \frac{(Cu_2^{++})^2}{[(Cu_2^{++}) + \frac{k_{-1}}{k_2}(H_2^+)][(Cu_2^{++}) + (\frac{k_{-3}}{k_4})_2 (H_2^+)]} \qquad \text{(A-26)}$$

on expansion and manipulation equation (A-26) reduces to

$$\left(\frac{k_{-3}}{k_4}\right)_2 = (k_{-3}/k_4)_1 \frac{[(Cu_2^{++})^2 \cdot (H_1^+)^2 \cdot (\frac{k_{-1}}{k_2}) + (Cu_2^{++})^2 (Cu_1^{++}) \cdot (H_1^+) + (\frac{k_{-1}}{k_2})[(Cu_1^{++}) \cdot (H_1^+)(Cu_2^{++})^2 - (Cu_1^{++})^2 (Cu_2^{++})(H_2^+)]]}{[(Cu_1^{++})^2 \cdot (\frac{k_{-1}}{k_2}) \cdot (H_2^+)^2 + (Cu_1^{++})^2 (Cu_2^{++})(H_2^+)]}$$

(A-27)

equation (A-27), indicates the dependency of $\left(\frac{k_{-3}}{k_4}\right)$ on cupric ion, hydrogen ion concentration and $\left(\frac{k_{-1}}{k_2}\right)$. This result seems likely and open to arguments. Surprisingly both Modification I and Modification II, reproduces von Hahn's experimental data equally well when used in the simulator. Further investigation and careful analysis is required, including possible changes in the mechanism to resolve this discrepency.

APPENDIX B

CALIBRATIONS

For the DP Cell

The reactor system was filled with water and the system was pressurized to 500 psig with hydrogen. The continuously fed hydrogen was routed through the wet test meter to the vent. For each DP cell setting, the flow was recorded for 30 minutes for low flow rates and for 15 minutes for higher flow rates. The average flow rate over the time period was taken as the flow rate of hydrogen for that DP setting. The calibration is graphically presented in Figure B-1.

For Skin Temperature with Fluid Temperatures

A dip leg of 6.5 mm diameter, made out of stainless steel and sealed at one end, was inserted into the reactor. The dip leg was long enough to cover the length of the reactor. It was filled with heating oil and a flexible thermocouple was inserted into the dip leg to read the fluid temperature. The reactor was filled with water and pressurized to 500 psig with nitrogen. At a fixed flow rate, the skin temperature and the corresponding

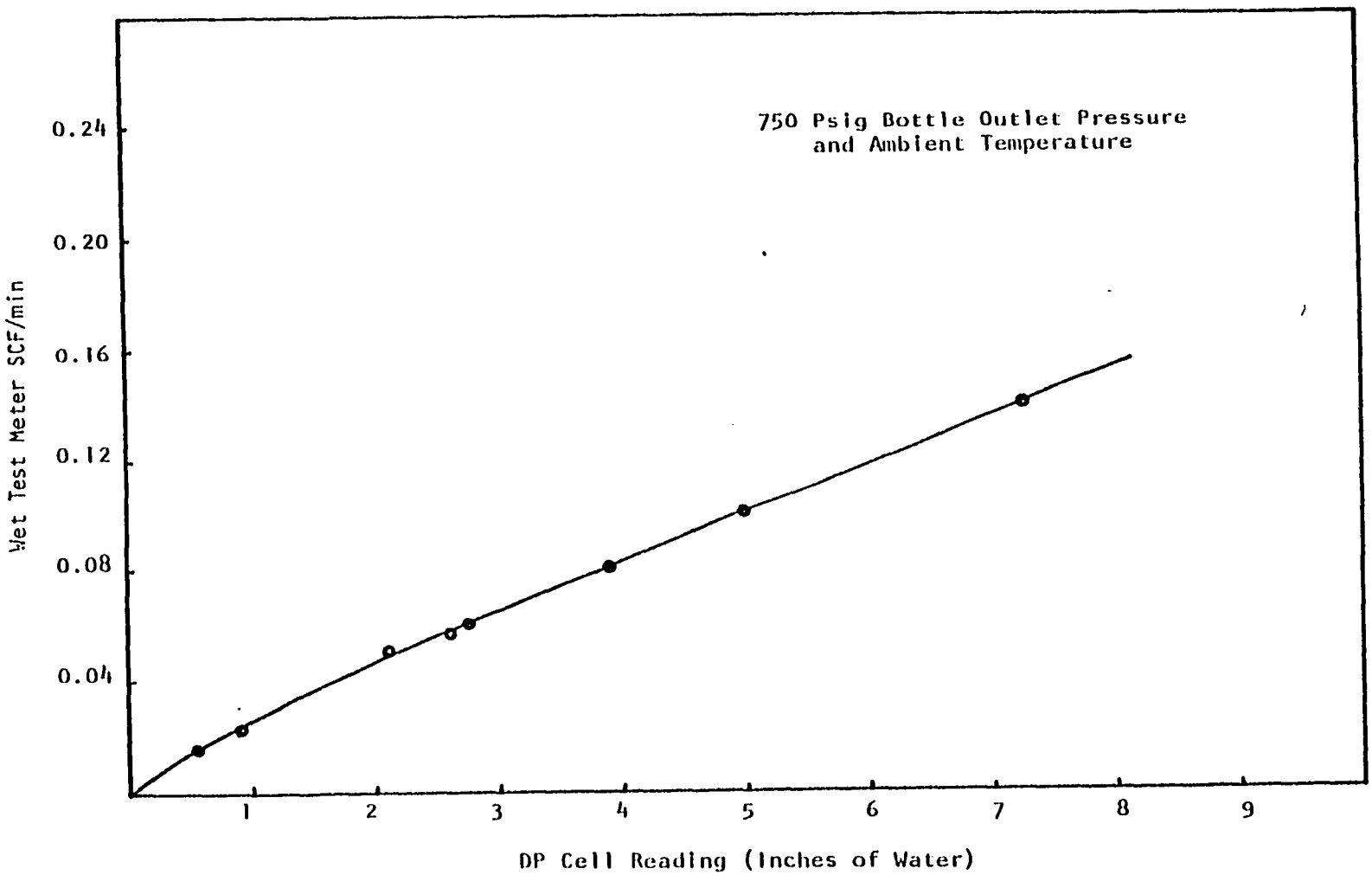

FIGURE B-1. Calibration of DP cell.

fluid temperatures at different points of the reactor were recorded by moving the dip leg thermocouple to the appropriate point. This procedure was repeated for different flow rates, ranging from 60 cc/min to 128 cc/min, and temperatures, ranging from 150°C to 235°C. The correspondence of skin temperatures to fluid temperatures are represented in Figures B-2 and B-3.

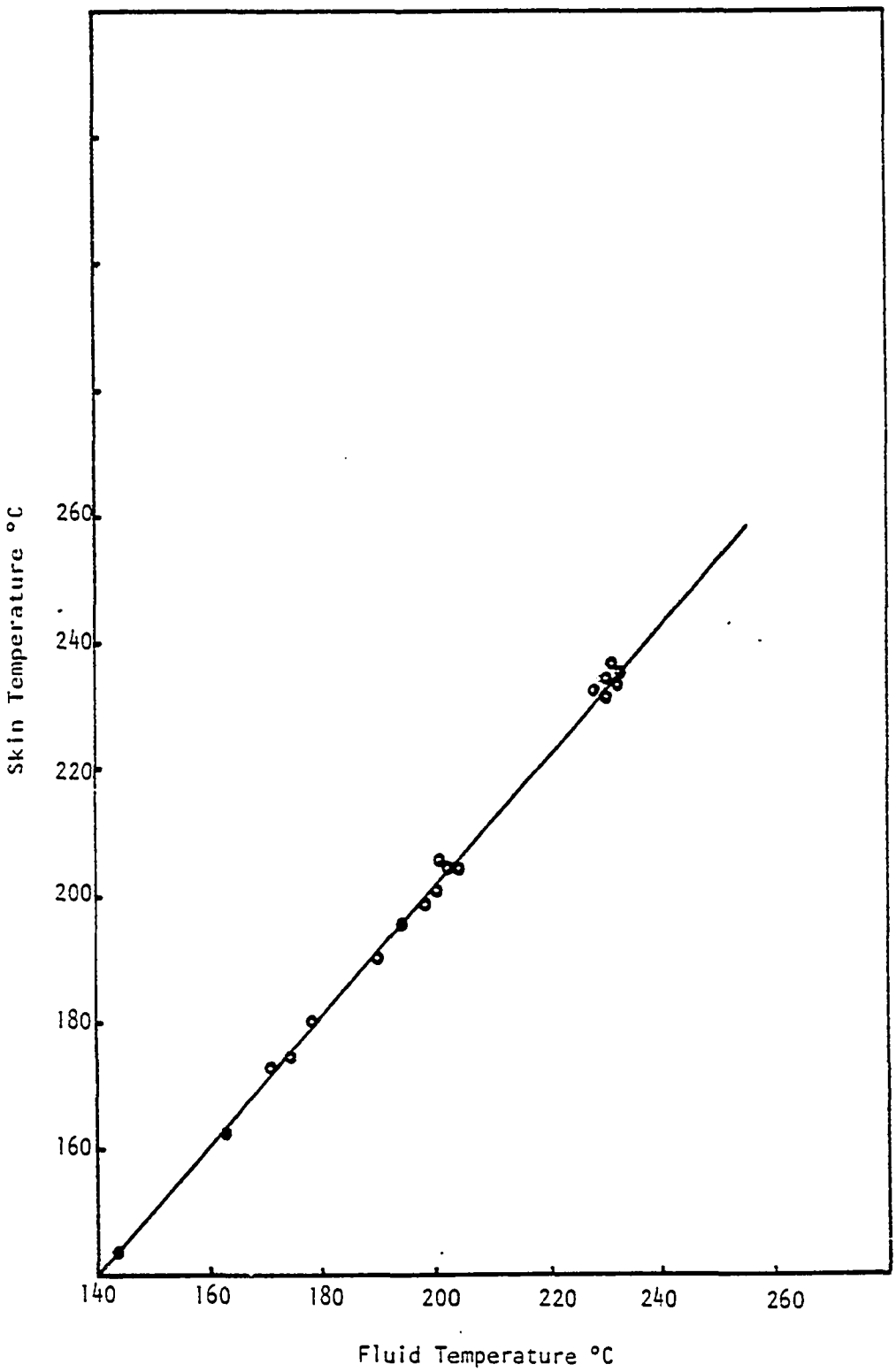

FIGURE B-2. Relation between reactor skin and fluid temperatures.

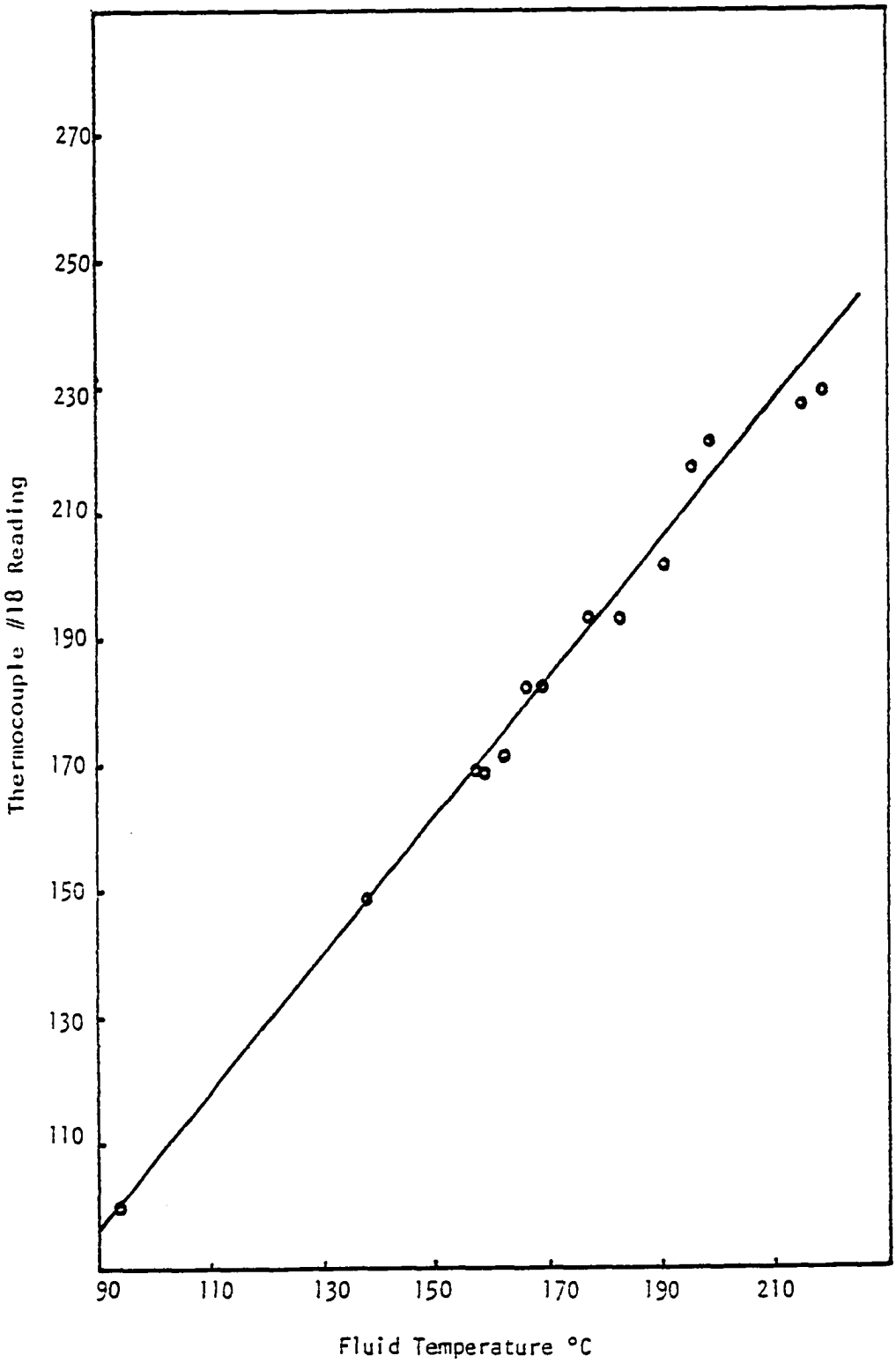

FIGURE B-3. Relation between reactor skin and fluid temperatures for thermocouple #18.

APPENDIX C

SOLUBILITY OF HYDROGEN

The solubility of hydrogen in water at different temperatures and partial pressures of hydrogen are calculated using an equation provided in Scott Conner's Thesis (5). Even though the solubility of hydrogen in aqueous solutions are to be used for computations, lack of data forced the author to use solubilities in water. In the non-isothermal region, the solubilities are taken at the arithmetic average temperatures.

TABLE C-1

SOLUBILITY OF HYDROGEN IN THE ISOTHERMAL REGION

Temperature °F/°C	Vapor Pressure of H_2O Psia	Partial Pressure of H_2 Psig	Solubility of Hydrogen gr mole H_2/liter water
400/204.5	247.31	267.39	0.0235
350/176.7	134.63	380.07	0.0277
300/148.9	67.01	447.7	0.0278
250/121.1	29.82	484.88	0.0264

TABLE C-2.

SOLUBILITY OF HYDROGEN IN THE NON-ISOTHERMAL REGION

Isothermal temperature	40 cc/min			60 cc/min			75 cc/min			100 cc/min			120 cc/min		
	Non-isothermal average temperature	Partial Pressure of H_2	Solubility of Hydrogen	Non-isothermal average temperature	Partial Pressure of H_2	Solubility of Hydrogen	Non-isothermal average temperature	Partial Pressure of H_2	Solubility of Hydrogen	Non-isothermal average temperature	Partial Pressure of H_2	Solubility of Hydrogen	Non-isothermal average temperature	Partial Pressure of H_2	Solubility of Hydrogen
400/204.5	180.83°C	368.7	0.0274	172.5°C	393.7	0.0280	164.6°C	414.7	0.0281	172.5°C	393.7	0.0280			
350/176.7	151.6°C	443.5	0.0280	146.1°C	451.7	0.0276	143.8°C	455.7	0.0274	135	468.7	0.0270			
300/148.9	132.2	473.2	0.0270	129.4	476.7	0.0269	121.1	484.7	0.0264	118.3	487.7	0.0266			
250/121.1	112.7	491.7	0.0267	103.0	498.7	0.0263	103.0	498.7	0.0263				98.8	501.0	0.0263

APPENDIX D

TECHNIQUES TRIED TO PREVENT COPPER FROM ADHERING TO THE REACTOR SURFACES

Two different methods, additives or coatings, were tried to prevent sticking of copper to the reactor walls.

Additives Mixed in the Feed Solution

Polyacrylic acid: A concentration of 0.008 grs/gr of copper was added to the copper sulfate solution containing 24 grs (Cu^{++})/liter, in solution. The experiment was carried out in the same manner as the regular runs. The temperature in the isothermal section was 176.6°C; the flow rate was 80 cc/min; and the pressure was 500 psig. The product obtained in the filter bag of the solid-liquid separator was a mixture of copper and cuprous oxide; it was finer than the product of experiments without polyacrylic acid. Product copper was found deposited on the reactor walls as before. The experiment proved that polyacrylic acid is not suitable for acidic copper sulfate solution as a anti-sticking agent. However, it does control the particle size.

Stearic acid: A similar experiment, like the above was carried out with addition of stearic (instead of polyacrylic acid.) The agent was in powder form and was highly insoluble. The results of the experiment were not encouraging.

Coatings for the Reactor Walls

The coatings were evaluated in the form of test plugs or actually coated on small tubular reactors. No coating was tried on the actual continuous reactor.

TFE (crown product): A mild steel plug was coated with TFE and put into a "bomb" containing copper sulfate solution of 23 grs (Cu^{++})/liter concentration. Hydrogen was pumped into the bomb to a pressure of 450 psig and heated to 205°C. The contents were allowed to remain at that temperature for half hour and then were cooled rapidly to room temperature. The plug was partially stripped of its coating, and in some places the plug was pitted.

FEP: A mild steel plug was coated with FEP and put in a bomb containing copper sulfate solution of 24 grs (Cu^{++})/ liter concentration. Hydrogen was pumped into the bomb to a pressure of 450 psig and heated to 215°C. The contents were allowed to remain at that temperature for one hour and 50 minutes and then were cooled rapidly to room temperature. There was no change in the color of the coating, which was green, but formation of blisters at different places were

observed. No copper was sticking to the plug, but the coating was not suitable because of formation of blisters.

PPS (Ryton): A mild steel plug was coated with PPS (A Phillips Petroleum Product), and the experiment was carried out as outlined in the preceding paragraph. The coating appeared to have survived this short experiment, but on prolonged heating for 18 hours, blisters appeared on the plug. There was discoloration from the original black to a military brown; a black deposit also appeared on the bomb wall. Similar experiments were carried out using plugs treated differently (treatments were done by Phillips Petroleum and supplied) but none of them withstood the test beyond 18 hours.

Dow-Corning's conformal coating (R-4-3117): A Hastelloy C bomb was coated with Dow-corning conformal coating(R-4-3117). After allowing the coating to cure, the bomb was filled with copper sulfate solution, was pressurized with hydrogen to 450 psig and was heated to 205°C. The bomb was allowed to remain at that temperature for one hour and then was cooled. Copper was sticking to the walls and some places blisters of the coating appeared.

Dow-Corning GP77 varnish: A stainless steel bomb was coated with Dow-corning GP77 varnish and cured for 6 hours at 150°C (as per the Dow-Corning's instructions). The experiment was repeated as described in the preceding paragraph. At the end of the experiment, the bomb was

found to be completely stripped of its coating and the copper product was contaminated, probably with the varnish.

Phenolic coating (tan color): A bomb was coated with Phenolic coating and subjected to the experiment described above. The coating was discolored, from tan to ash, and blisters appeared on the wetted portion of the bomb. Copper was sticking to the walls.

APPENDIX E

COMPUTER PROGRAM

```
      $JOB
      C       COMPUTER PROGRAM FOR SIMULATING CONTINUOUS HYDROGEN REDUCTION OF
      C       COPPER AT 500 PSIG TOTAL PRESSURE
 1            DIMENSION X(1)
 2            COMMON H,N,FAO,CUO,C,TF,TI,AH2,T,AC,AN2,CUPO,HY,XAC,CU
 3            EXTERNAL AUX
 4            READ(5,1)FAO,CUO,C,TF,TI,AH2,AC,AN2,CUPO,HY,XAC
 5          1 FORMAT(F6.2,F9.7,F6.4,F6.2,F6.2,F6.4,F6.4,F6.4,3F8.6)
 6            WRITE(6,13)FAO,CUO,C,TF,TI,AH2,AC,AN2,CUPO,HY,XAC
 7         13 FORMAT(F6.2,1X,F9.7,1X,F6.4,1X,F6.2,1X,F6.2,1X,F6.4,1X,F6.4,F6.4,
           11X,F8.6,1X,F8.6,1X,F8.6)
 8            H=2.0
 9            N=76
10            Z=0.00
11            X(1)=0.00
12            T=(TI+460)/1.8
13            PRINT 5,T,Z,X(1),CUPO,HY,CU
14            DO 6 I=1,N
15            T=(((C*Z/2.54)+TI)+460)/1.8
16            IF(T.GE.TF) T=TF
17            CALL RKK4(Z,X,N,H,AUX)
18          6 PRINT 5,T,Z,X(1),CUPO,HY,CU,XAC
19          5 FORMAT (3X,'T= ',F6.2,1X,'Z= ',F6.2,1X,'X(1)= ',F8.6,1X,'CUPO=',
           1F8.6,1X,'HY=',F8.6,1X,'CU=',F8.6,1X,'AFTER COOLING X(1)=',F8.6)
20            STOP
21            END
```

```
      SUBROUTINE AUX(Z,X,F,NE)
      DIMENSION X(1),F(1)
      COMMON H,N,FAO,CUO,C,TF,TI,AH2,T,AC,AN2,CUPO,HY,XAC,CU
      AB1=EXP(-22000/(1.987*T))
      RK1=(0.545080E+09)*(AB1)*(120)
      AB2=EXP(-15300/(1.987*T))
      RK3=(0.529596E+07)*(AB2)*(120)
      RK4=(RK3)/(RK1)
      D3=(AC+CUO+AN2)
      A1=0.163738
      A2=0.110267
      A3=0.100609E-01
      AS2=(AC)/((D3)*(CUO))
      RK2=(RK4)*(1+(A1*AS2)-(A2*(AS2**2))+(A3*(AS2**3)))
      EK2=18.436033-(9393.55/T)
      EK1=EXP(EK2)
      EK=(EK1)**(0.5)
      IF(T-428)7,7,8
    7 AH2=0.0254+0.00005*(T-373)
      GO TO 11
    8 IF(T-447)9,9,10
    9 AH2=0.0281
      GO TO 11
   10 AH2=0.0281+(0.148387E-03)*(447-T)
   11 B1=(RK1)*(CUO)*((1-X(1))**2)*(AH2)
      RKR1=(26.311541)*EXP(-4500/(1.987*T))
      QK2=56.889-(19.8858)*ALOG10(T)-(2307.9/T)-(0.006473)*T
      QK1=(10.0)**(QK2)
      D5=2*AC
      D6=(D5+D3+QK1)
      IF(D5-0.0)19,19,20
   19 HYC=0.0
      GO TO 21
```

```
55        20 Y=(D6-(((D6**2)-(4*D5*D3))**0.5))/(2*D5)
56           HYO=D5*(1-Y)
57        21 AA=(HYO+((0.1)*CUO))
58           IF(AA-0.0)30,30,31
59        30 RKR2=-(RKR1)
60           GO TO 32
61        31 BB=(HYO+((0.2)*CUO))
62           DD=CUO*((0.648*BB)-(0.576*AA))
63           EE=(RKR1)*((0.81*(BB**2))-(0.64*(AA**2)))
64           CC=(DD+EE)
65           RKR2=-(RKR1)*((DD)/(CC))
66        32 X1=1-(((4.+(EK1/CUO))**0.5)-(EK1/CUO)**0.5)/2.)**2.
67           IF(X(1)-X1)12,12,14
68        12 CU=0
69           D1=(2*AC+CUO*X(1))
70           D2=(D1+D3+QK1)
71           IF(D1-0.0)22,22,23
72        22 HY=0.0
73           GO TO 24
74        23 Y=(D2-(((D2**2)-(4*D1*D3))**0.5))/(2*D1)
75           HY=D1*(1-Y)
76        24 CUPO=CUO-CUO*(1-X(1))-CU
77           B3=(RKR1)*HY
78           C3=(RKR2)*HY
79           IF(HY-0)2,2,4
80         2 B3=0
81           HY=0.0
82         4 B2=(((CUO)*(1-X(1)))+B3)
83           B4=B1/B2
84           C2=(CUO*(1-X(1))+C3)
```

```
      C4=(RK2*CUPO)/(C2)
      F(1)=((7.9173045)/(FAO))*(B4*(1+C4))
      GO TO 18
   14 CU=CUO-CUO*(1-X(1))-(EK)*((CUO*(1-X(1)))**0.5)
      D1=2*AC+CUO+CU-CUO*(1-X(1))
      D2=(D1+D3+QK1)
      IF(D1-0.0) 25,25,26
   25 HY=0.0
      GO TO 27
   26 Y=(D2-(((D2**2)-(4*D1*D3))**0.5))/(2*D1)
      HY=D1*(1-Y)
   27 CUPO=CUO-CUO*(1-X(1))-CU
      B3=(RKR1)*HY
      C3=(RKR2)*HY
      IF(HY-0) 15,15,16
   15 B3=0.0
      C3=0
      HY=0.0
   16 B2=(((CUO)*(1-X(1)))+B3)
      B4=B1/B2
      C2=(CUO*(1-X(1))-C3)
      C4=(RK2*CUPO)/(C2)
      F(1)=((7.9173045)/(FAO))*(B4*(1+C4))/2
   18 CUAC=CUO*(1-X(1))+((0.5)*CUPO)
      XAC=(1-(CUAC/CUO))
      RETURN
      END

      SUBROUTINE RKK4(Z,X,N,H,AUX)
      REAL K0,K1,K2,K3
```

```
      DIMENSION K0(1),K1(1),K2(1),K3(1),X1(1),X(1)
      A=2.0
      B=H/6.0
      C=0.5*H
      CALL AUX(Z,X,K0,N)
      Z1=Z+C
      X1(1)=X(1)+C*K0(1)
      CALL AUX(Z1,X1,K1,N)
      X1(1)=X(1)+C*K1(1)
      CALL AUX(Z1,X1,K2,N)
      Z=Z+H
      X1(1)=X(1)+H*K2(1)
      CALL AUX(Z,X1,K3,N)
      X(1)=X(1)+B*(K0(1)+A*K1(1)+A*K2(1)+K3(1))
      RETURN
      END
```

Nomenclature used in Computer Program

H = Incremental length

N = Total number of segments

C = Slope of the non-isothermal temperature section, °F/inch

CUO = Initial concentration of feed, gr moles(Cu^{++})/liter

FAO = Flow rate in, cc/min

TF = Isothermal section temperature, °K

TI = Temperature at the zero length, °F

AC = Acid concentration, gr moles(H_2SO_4)/liter

AH2 = Concentration of hydrogen in solution, gr moles/liter

AN2 = Concentration of inert sulfate added (in the form Na_2SO_4 etc), gr moles/liter

CUPO = Cuprous ion concentration, gr moles/liter

HY = Hydrogen ion concentration, gr moles/liter

Z = Length of the reactor, cm

X(1) = Conversion of cupric ions to products