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THE DISSOLUTION OF PLATINUM-IRON ALLOYS
IN OXYGENATED ACID CHLORIDE SOLUTIONS

BY

JOHN WILFRED SCOTT

B.Sc., Queens University, 1968

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Department of Metallurgy

The University of British Columbia
Vancouver 8, Canada

Date August 10th, 1972

ABSTRACT

The dissolution of platinum from platinum iron alloys in oxygenated hydrochloric acid/sodium chloride solutions has been investigated using an autoclave technique.

The dissolution rate was found to be dependent on alloy composition, acid concentration, and oxygen pressure. The dissolution followed typical corrosion kinetics and analysis of the results indicated that the cathodic reduction of oxygen was the rate controlling step in the dissolution reaction, at high chloride ion concentrations. An apparent activation energy of 16.8 kcal per mole was found for the dissolution of PtFe alloys, and 19 kcal per mole for pure Pt sheet.

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INTRODUCTION

I. General

The extraction and recovery of platinum and the associated metals of the platinum group from ores and industrial scrap is of increasing importance as world demand grows. Present extraction and recovery processes are all based on the old and proven aqua regia dissolution as a first step, followed by classical chemical separations of the various metals. As the aqua regia process is expensive, slow and generally limited to a series of batch operations, an investigation into the possibilities of applying modern high-temperature, high-pressure autoclave techniques to the dissolution of platinum was thought to be interesting. This type of processing would be generally applicable to both ore concentrates and industrial scrap material, with perhaps a further use in recovering platinum values from low grade deposits not presently economical to exploit. A general review of the mineralogy and extractive metallurgy of platinum shows that the native metal is most commonly the starting material available for extraction. The principles of metallic corrosion should apply to the chemical dissolution of the native platinum, as it is a metal or metal alloy. As part of the introduction to this work then, it was necessary to look at the mineralogy of platinum occurrence, the chemical

and electrochemical corrosion of platinum and the commonly used recovery processes, as well as reviewing previous attempts at dissolving platinum under pressure.

II. Mineralogy of Platinum Metal Deposits

The platinum metals occur mainly as platinum minerals associated with nickel-copper sulfides or copper sulfides in lodes, or as platinum metal alloys disseminated in ultrabasic rock and in placer deposits derived from these rocks.¹

(i) Lode Deposits

Platinum ores in lode deposits may be classified into three main types, according to the relative concentration and form of the contained platinum metals.

In the Sudbury type of deposit, the platinum metals are produced as a by-product in nickel and copper production. The platinum metals are contained in nickel-copper, copper or copper-cobalt sulfides that are related to basic or ultrabasic rocks. In this type of deposit there are no native platinum metals or alloys. The platinum minerals are sperrylite (PtAs_2), michenerite $[(\text{Pt}, \text{Pd})(\text{Bi}, \text{Te})]$, froodite (PdBi_2), and minor unnamed minerals.

The Merensky type of deposit consists of platinum-bearing copper-nickel sulfides in which the platinum values are high enough to constitute the principal ore mineral. The platinum occurs mainly as sperrylite and cooperite $[(\text{Pt}, \text{Ni}, \text{Pd})(\text{S})]$ in lenses of peridotite or chromite in the host ultrabasic rock. Small amounts of native platinum metal alloys are also present.

The third important type of deposit is a concentration of native platinum metal alloys disseminated in peridotites and sometimes in perknites. Most of these deposits are in dunite which is commonly altered to serpentine. This type of deposit is the source of the Uralian placers, the Goodnews Bay deposit, and the Tulameen placers. Most of these deposits are either too small or too low grade for direct mining, although some high grade concentrations in masses of chromite in dunite have been found. The Transvaal deposits of platiniferous iron-rich dunite are mined for platinum occurring in this way.

There are also a number of minor platinum metal occurrences, for example in gold ores, in platinum bearing meteorites and in contact metamorphic copper ores.

(ii) Placer Deposits

Platinum placers are alluvial deposits that contain economic amounts of native platinum metal alloys. The two types of alloys may be typified as 'platinum' and 'osmiridium' with the two often occurring together. 'Platinum' consists mostly of that metal, but contains all the other platinum metals in varying amounts. 'Osmiridium' consists dominantly of iridium and osmium but also includes ruthenium, rhodium and platinum. Both these alloys can also contain base metals such as iron or copper; either as minerals or alloys, in varying amounts.

Platinum placers are derived from dunites, serpentinite, or perknites in which the native platinum metals are very highly disseminated. As in gold placers, the platinum placers are assumed to be close to their bedrock sources in the absence of extensive glaciation.

The major placer deposit in British Columbia is in the Tulameen area near Princeton. This series of post-glacial stream and terrace placers is derived from a large intrusive mass of pyroxenite and gabbro containing two smaller bodies of peridotite. The peridotite is considered a more important source rock than the pyroxenite. The platinum occurs in these placers as small rounded grains of platinum rich alloy, with small pits and some adhering chromite and magnetite. Dana² has given the composition of the naturally occurring Fe-Pt alloys, known as polyxene and ferrian (ferroplatinum). Polyxene is 80-90% platinum and 3-11% iron while ferrian is about 28% iron. An assay of two types of platinum found in the Tulameen Placer deposits gave the following results:

	<u>Magnetic</u>	<u>Non-magnetic</u>
% Pt	78.4	68.2
% Fe	7.87	9.8

The weighted average was 72.0% platinum and 8.6% iron. If the Fe-Pt ratio is taken as indicating an alloy composition, these assays would put the Fe-Pt alloy from the Tulameen area as being somewhere in between FePt and FePt₃. These two alloys are intermetallic compounds, as shown in the phase diagram Figure 1. These alloys should be more easily dissolved than pure Pt and as they occur commonly in this particular deposit the investigation of their dissolution properties should prove of more practical value than similar investigations on pure Pt.

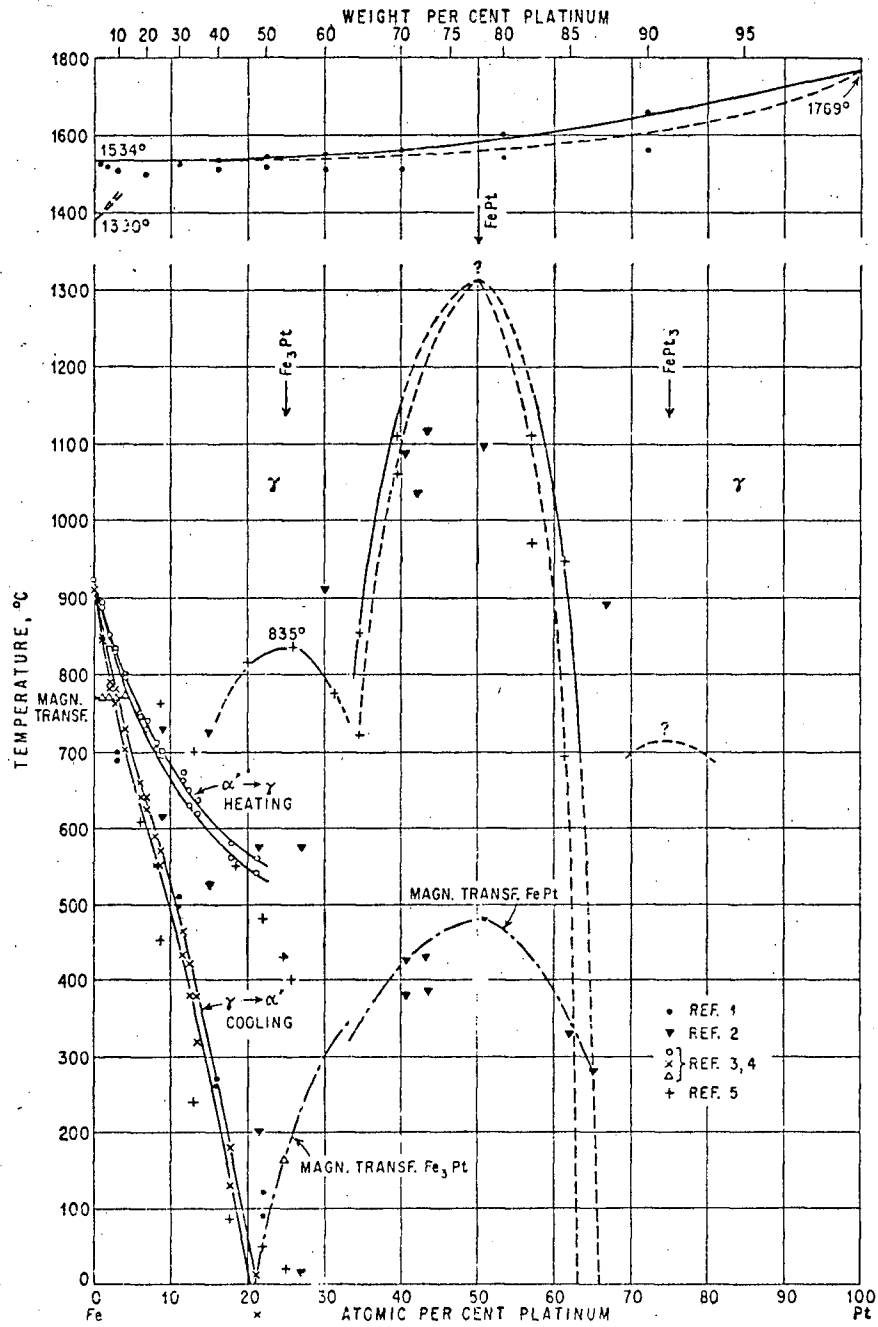


Fig. 1. Phase diagram of the Fe-Pt system

III. Extractive Metallurgy of Platinum

The extractive metallurgy of platinum is essentially the same whether the concentrate is produced as a by-product in Cu-Ni production or as a primary metal value from placer or lode deposits. Platinum metal concentrates derived from Cu-Ni sulfide ores are produced from matte anodes as anode slimes. The copper and nickel are dissolved electrolytically from the anode in an acid sulfate bath. The anode slimes are collected in anode bags, then removed and washed. The washed slimes are roasted to remove sulfur, ground to - 40 mesh, then leached in hot sulfuric acid to remove residual copper and nickel. The residual slimes concentrate is washed and filtered and sent to a platinum refinery.

In placer and lode platinum operations the platinum metals are concentrated by gravity techniques, usually a dredging operation in placer mines, followed by tabling. Flotation has also been used in some lode operations. The resulting concentrates from either type of deposit are then sent to the platinum refinery.

In most platinum refineries the steps followed are almost the same; the following description is of the Engelhard³ refinery process which is probably typical of the industry. The bulk concentrate is first leached in hot aqua regia. This is done in glass lined vessels as follows: Five hundred pounds of concentrate are heated to 80°C in five hundred gallons of 5:1 concentrated hydrochloric acid. One hundred gallons of nitric acid is added over a period of eleven hours, then the residue is filtered off. The solution, which is rich in dissolved platinum, palladium and gold, is evaporated to drive off

nitrate, then redissolved in HCl and sent to an ammonium chloride precipitation. This precipitates an impure platinum ammonium chloride, which is calcined to platinum metal, then redissolved in aqua regia and reprecipitated as pure platinum ammonium chloride. This precipitate is then calcined to produce commercial platinum sponge. The solution after the first precipitation is treated to extract the other platinum metals, (i.e. iridium, osmium, rhodium and ruthenium).

Most recovery operations for scrap platinum either in catalysts or in metal form are based on a similar procedure. They differ only in minor details and are applicable to platinum recovery from catalysts, and other sources of contained platinum metal.

IV. Literature Review on Platinum Corrosion

(i) Anodic Dissolution of Platinum

The extensive use of platinum as an anode in electrolytic cells and for cathodic protection in sea water as well as its use in polarographic analyses has led to some investigations of corrosion under anodic conditions. Even though the platinum has been considered to be "inert", it is slowly attacked and eventually has to be replaced. Llopis and Sancho⁴ found that the anodic corrosion of platinum requires high over potentials and can only be studied in the presence of complex-forming ions. In HCl and chloride solutions, platinum dissolves as $\text{PtCl}_6^{=}$ at the anode. The nature of the platinum surface has some effect on the corrosion characteristics, with platinized titanium anodes being more susceptible than solid platinum anodes. For platinized titanium in sea water,⁵ consumption rates of from 6-50 mg/Ampere/year have been

reported, while under similar conditions pure platinum anodes were uniformly consumed at a rate of 6-7 mg/ampere/year over a wide range of current density. In an electrolysis cell for the production of sodium hypochlorite for sewage treatment platinum consumption rates of 50-100 mg/ampere/year were reported,⁶ and could be controlled by controlling the anode potential. The platinum loss was postulated to be related to a potential dependent change in surface structure, corresponding to the formation of platinum oxide. On platinized titanium anodes⁵ in acidified chloride solutions, this anodically formed oxide dissolved at open circuit.

A recent study of the passivation of platinum in 1-8 M HCl and 1-5 M NaCl solutions showed rapid corrosion below the passivation potential. This potential was $[H^+]$ independent, thus ruling out direct oxide formation as the cause of passivation. It was concluded that passivation is due to the formation of a series of adsorption complexes, with a final surface of $PtO_x \cdot nHOH$.

In HCl solutions prior to passivation,⁴ platinum dissolves to form $PtCl_6^{=}$. The rate of corrosion increases with temperature, chloride ion concentration and acidity. The activation energy for dissolution was found to be 25 Kcal/mole corresponding to a highly irreversible step. Superimposed alternating current increases corrosion by minimizing concentration polarization effects.

(ii) Chemical Dissolution of Platinum

Platinum is a very noble metal, and extreme conditions must be used to dissolve it chemically. According to the Pourbaix diagram,⁹

(Fig. 3) platinum is stable in aqueous solutions of all pH's, in the absence of complexing agents, except under certain very low pH and highly oxidizing conditions. At room temperature platinum is unattacked by water, caustic alkalis and acids and attacked slowly by oxidizing agents, except when complexes are formed.

The best known and most commonly used reagent for dissolving platinum is aqua regia. This acid combines the oxidizing power of nitric acid with the complexing power of hydrochloric acid and dissolves platinum as chloroplatinic acid, H_2PtCl_6 . Pure HCl hardly attacks platinum, but if it contains dissolved chlorine or oxygen the combination of oxidizing and complexing actions will dissolve the metal.

Some platinum alloys, especially those with iridium, are insoluble in aqua regia, and must be dissolved by some other method. Some methods¹⁰ which have been used are closed tube fusions with salts, closed tube dissolutions with HCl and added oxidizing agents, and open boat chlorinations both with and without added salt. Fusion with base metals followed by acid attack has also been used as a method of dissolving resistant platinum metal alloys and is the basis of the classical fire assay techniques.

Tronev¹¹ studied the dissolution of the platinum metals in hydrochloric acid under high air pressures. He found that acid concentration, particle size of the platinum, over-pressure of air and temperature were the important variables in increasing the dissolution rate. He proposed a mechanism of dissolution involving a free chlorine molecule produced from the HCl oxygen reaction.

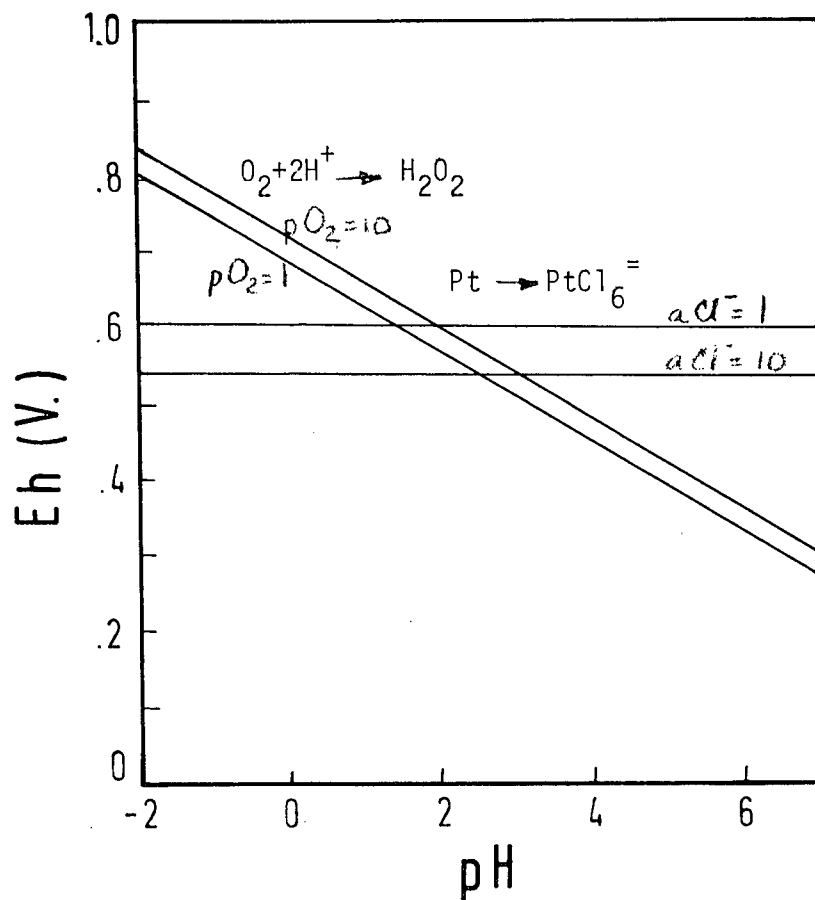


Fig. 2. Eh-pH diagram for the systems $O_2-H_2O_2$ and $Pt-PtCl_6^{=}$ at 25°C, as a function of pO_2 and $a[Cl^-]$

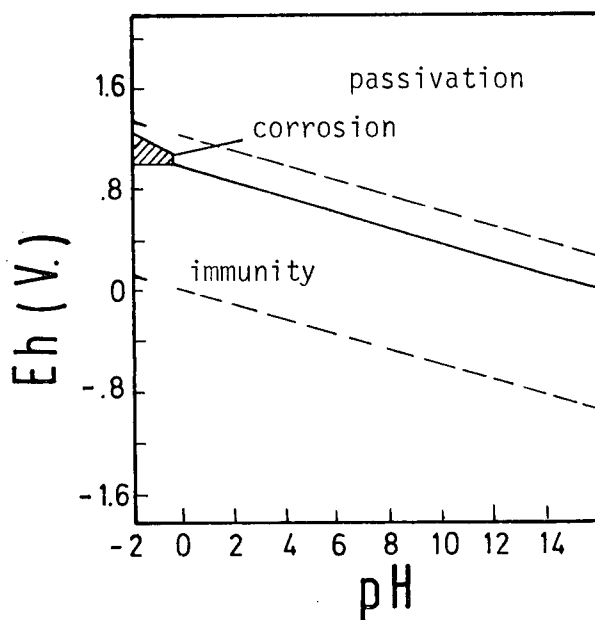
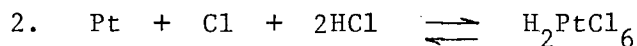
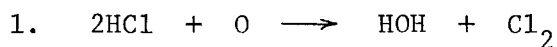
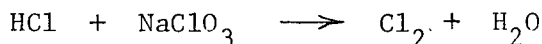
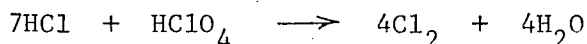


Fig. 3. Simplified Pourbaix diagram for the system $Pt-H_2O$

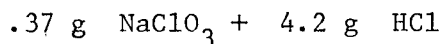
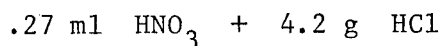


As the equilibrium in equation 1 goes to the right as the temperature rises, this mechanism gives an increasing rate with increasing temperature and hence fits his results. Tronev made no attempt to further characterize the dissolution reaction, simply stating his results in tabular form.

Wichers, Schlecht and Gordon¹² developed a closed tube method of dissolving refractory platiniferous materials. They felt that temperature could be the controlling factor in the inertness of iridium and other platinum alloys to aqua regia in open vessels. They assumed the same type of reaction as Tronev, i.e.



They found that some HCl was necessary for attack to occur, using LiCl as a source of chloride ion. They also found a maximum attack on irido-platinum alloys with the following mixtures at temperatures from 100°C to 150°C.

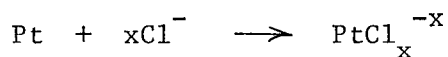


The authors concluded that the pressure developed, which could go as high as 4000 psi, was unimportant as it was controlled by the reaction mixtures. Interestingly enough, they also mention that Tronev's work on dissolving platinum under air pressure is equivalent to their added oxidant method of producing chlorine, with increasing air pressure being regarded as increasing the chlorine concentration.

(iii) Corrosion Mechanism for Platinum in Oxygenated Acid Chloride Solutions

(a) Anodic Platinum Dissolution

Llopis⁷ has reviewed the literature on the anodic dissolution mechanism of platinum in chloride solutions. As mentioned above, Pt dissolves as $\text{PtCl}_6^{=}$ at the anode below the oxide formation potential. The mechanism proposed can be expressed in the form of two consecutive reactions:



The first reaction corresponds to specific adsorption of the anions on the metal surface with complex formation, the second to ionization

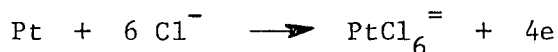
and desorption of the adsorbed complex. The adsorption of halide ions has been shown to depend on the presence of adsorbed oxygen, and vice versa. However, it appears that over the range of 0.35 to 0.75 volts, Pt displays an entirely gas-free surface, with adsorption of oxygen leading to oxide formation at potentials above 1.5 volts.⁷ For hydrochloric acid and NaCl solutions up to 3 M HCl, it appears that a potential of at least 1.2 volts is required for any passivation to occur.

The chloride ion dependence of the Pt dissolution rate was found to follow the rate law:

$$\text{Rate} = k [\text{Cl}^-]^{0.9}$$

which supports a Cl^- one electron transfer step at the Pt surface as the rate limiting step.

The overall electrode half-reaction for Pt dissolution at 25°C in chloride solutions is:

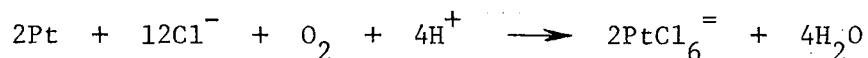


$$E = 0.72 + 0.015 \log a(\text{PtCl}_6^{=}) - 0.089 \log a(\text{Cl}^-)$$

and depends only on the activity of $\text{PtCl}_6^{=}$ [$a(\text{PtCl}_6^{=})$] and the activity of Cl^- [$a(\text{Cl}^-)$] at 25°C.

(b) Cathodic Reduction Reaction and Eh-pH Relationship

For Pt corrosion by oxygen saturated acid solutions, the reduction of molecular oxygen to water will be the cathodic reaction. Therefore an overall electrochemical corrosion reaction for the dissolution would be:



As both the half reactions are oxidation-reduction type of reactions we can calculate Eh-pH or Pourbaix type diagrams to represent the thermodynamic equilibria of the various species. For the anodic process the potential is described by:

$$E = 0.72 + .015 \log a\text{PtCl}_6^- - .089 \log a\text{Cl}^-$$

at 25°C. This potential is independent of pH and gives a straight horizontal line on a Pourbaix diagram. For higher temperatures various methods of calculation have been proposed for the construction of Eh-pH diagrams. However none have been calculated for the Pt-Cl-PtCl₆⁻ system. The Eh-pH diagrams for the Pt-PtCl₆⁻ and O₂-H₂O₂ reactions at 25°C and for various O₂ pressures and Cl⁻ activities are shown below (Fig. 2). This diagram shows that thermodynamically it is possible for corrosion of platinum to occur with the reduction of oxygen to hydrogen peroxide as the cathodic reaction.

V. Theory of Corrosion

Electrochemical Theory

The basic premise of the electrochemical theory of corrosion is that the overall chemical reaction is divided into two largely independent processes.

1. Anodic dissolution of metal - the transfer of metal into solution as hydrated or complexed ions, with the loss of a number of electrons to the metal.
2. Cathodic reduction - the gain of electrons from the metal by depolarizers which are atoms, molecules or ions in the solution capable of reduction.

Naturally for the different processes to occur independently at different parts of the surface there must be a heterogeneous surface structure. This is known as the local cell theory. If the corrosion is considered to be analogous to a galvanic cell, the anodic and cathodic areas on the surface may be due to a number of factors acting together or independently. Surface heterogeneities are classified as macroscopic, microscopic, or submicroscopic. Macro-couples are formed by coupling different metals, or differential aeration, and lead to definite areas of local corrosion. Micro-couples may be formed by such things as solid solution segregation, grain boundaries and crystal anisotropy leading to microscale corrosion such as intergranular corrosion, structurally selective corrosion and pitting corrosion. A good basic example is metallographic etching. Submicroscopic corrosion couples exist on metal surfaces within groups of atoms and are caused by factors like substitutional impurity atoms, surface topography, and thermal oscillations of atoms in

the lattice. These submicro-couples are very unstable and lead to uniform surface dissolution by changing a certain point from anodic to cathodic rapidly and frequently.

In the case of an ultra pure metal with no impurities or heterogeneities, corrosion would be impossible by the local cell theory. The theory for corrosion of ultra pure metals was first suggested by Wagner and Traud¹³ in 1938. The basis of this theory is that for corrosion to occur, spatially separated anodic and cathodic areas are not necessary. The necessary and sufficient condition for corrosion is that the metal dissolution and some cathodic reduction reaction proceed simultaneously on the surface. For this to happen the potential difference across the interface must be more positive than the equilibrium potential of the $M \rightarrow M^{n+} + ne$ and more negative than the equilibrium potential of the reduction reaction $A + ne^- \rightarrow D$ involving a solution species.

Hoar¹⁴ recognizes three general situations of corrosion attack.

1. Base metal - the metal dissolves to an etched surface, and cathodic reduction occurs on the same surface over a period of time. At any instant the number of active anode sites (i.e. Kinks, edges) is relatively small, and these sites are constantly changing and giving a uniform dissolution. In this case the whole surface acts as anode and cathode so we may take their respective areas as being equal.
2. Metal dissolving in well defined zones - for example at oxygen starved areas or at obvious heterogeneities or inclusions.
3. Metal pitting - that is often due to a passivating film and the anode area is negligible compared to the cathode area.

Alloy Corrosion

When a homogeneous binary alloy is dissolved, there are two possible modes of dissolution.

1. Simultaneous dissolution of the two metals in the alloy,
2. Preferential dissolution of the less noble metal with surface enrichment of the noble metal.

In an alloy consisting of a noble metal and an active metal, in solid solution, it has been found¹⁵ that there is a more or less sharp increase in corrosion resistance at a certain ratio of alloy components. Normally, this increase in stability occurs at an atom ratio of $n/8$ where n is an integer from 1-6. For a Cu-Au system in hot nitric acid this occurred at $n = 4$. The simplest explanation of this phenomenon is surface enrichment, however, intermetallic compound formation may play a part as well. If an active phase is finely dispersed in a noble matrix, it will be dissolved out and surface enrichment will occur. If the active phase is continuous or in excess this cannot happen, as a small number of noble atoms will probably be detached along with the large number of active atoms. Surface enrichment should only occur in dilute heterogeneous alloys, however a homogeneous alloy may be regarded as a heterogeneous alloy in the finest possible state of dispersion and therefore surface enrichment could control the dissolution.

In a binary alloy corroding in a system in which both components can dissolve, the situation is far from clear. It is apparent that the corrosion rate of the noble component is raised while that of the less noble component is lowered. In an ideal situation the corrosion potential would vary between that of the base and noble components linearly with the composition. As was shown above for the Cu-Au alloys

this is not the case, and deviations are due to solid state interactions and non-ideal solution behavior. Uhlig¹⁶ made an attempt to explain the passivation phenomena in stainless steels and corrosion behavior in some binary alloys through the use of electron theory. In particular he related the number of unpaired d electrons to the ability to adsorb oxygen at the surface. Leidheiser¹⁷ explained the corrosion behavior of certain stainless steel alloys on the basis of a nearest neighbour theory and a rate controlling nucleation step. He proposed that a noble metal (slow corroding atom) is unaffected in its rate of active anode site nucleation, while the ability of a base metal atom to nucleate an active anode site is reduced to a negligible value by having a noble nearest neighbour (or is unaffected if it has all the same nearest neighbours), thereby reducing the rate of dissolution to one controlled by the noble metal. This theory assumes no ordering and a statistical distribution of different atoms, allowing the calculation of most likely nearest neighbours from a probability function. This type of analysis could apply to iron platinum alloys but only in the dilute platinum region.

EXPERIMENTAL

I. Materials and Reagents

(i) Materials

The materials used in this investigation were pure platinum rolled sheet as supplied by Engelhard, purified Armco iron powder and iron platinum alloys made from these two materials.

(ii) Reagents

All reagents used were reagent grade. Deionized water was used for all solutions. The oxygen was cylinder grade, supplied by Canadian Liquid Air.

II. Alloy Preparation

The Armco iron powder was reduced under cracked ammonia at 700°C for four hours to remove any surface oxide, then cooled under the reducing gas. The platinum sheet was cleaned in aqua regia, washed, degreased with acetone, and dried in an air blast. Stoichiometric proportions of the two metals, platinum and freshly reduced iron, were then weighed into a 10 cc recrystallized alumina crucible. This small crucible was then placed in a tight fitting graphite susceptor crucible, and placed in alumina powder in a larger crucible. The crucible assembly was then placed inside a Vycor tube and the metal.

melted under a helium atmosphere in an induction furnace. After melting the metal was well stirred by magnetic induction and then allowed to cool slowly under helium. The resulting alloy button was then annealed under cracked ammonia at 700°C for twelve hours to ensure homogenization. After annealing the samples were cleaned and polished by standard metallographic techniques through 3-0 carborundum papers and on the 6 μ and 1 μ diamond dust wheels.

III. Autoclave Design

A titanium autoclave (Fig. 4) of 2000 ml capacity, manufactured by the Parr Instrument company was used for the leaching experiments. This series 4500 autoclave as supplied had the head, cylinder and inner wetted parts of titanium with the external valves and fittings of stainless steel. As the leaching experiments were to be done in hot acid chloride solutions the stainless steel sampling tube and valve had to be replaced. An all titanium sampling tube and a Teflon-titanium sampling valve were fabricated and fitted. In order to protect the titanium cylinder a tight fitting glass liner was used, and a protective glass tube was fitted over the thermowell.

The reactor contents were stirred by a large magnetic stirrer bar on the bottom of the glass liner, which was protected with a thin Teflon sheet. This was found to be the only practical method of stirring as the top stirring arrangement proved to be susceptible to corrosion and leakage.

The autoclave was heated by a 1500 watt electric heater built into an insulated steel shell. The autoclave slides into the heater and rests on the magnetic stirrer at the bottom. Automatic temperature

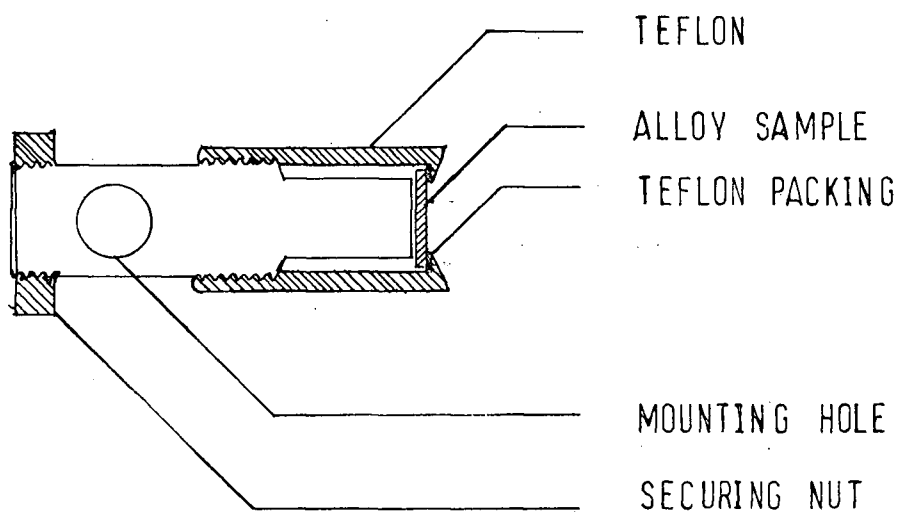
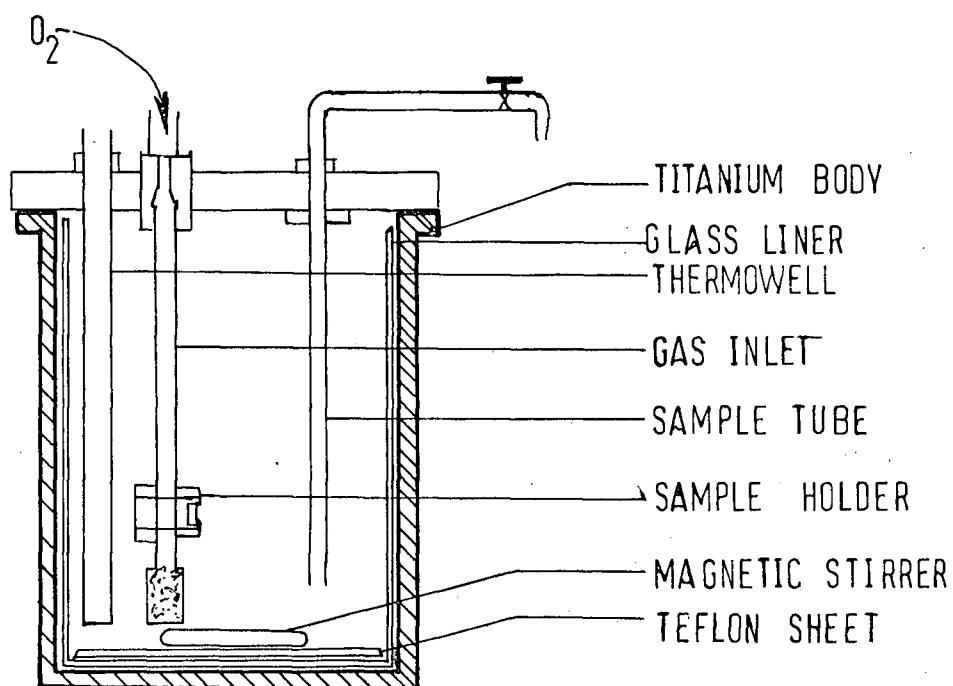


Fig. 4. Schematic diagram of the Parr autoclave and the machined Teflon sample holder

control was achieved with a Thermistemp temperature controller Model 71 (Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio). The thermistor probe was of iron constantan and slid into the thermistor well in the autoclave. A second thermocouple was used to follow and record the temperature variation. The temperature was controlled to within 1°C.

The pressure gauge used had a 4 1/2" dial graduated from 0-1000 psi in 5 lb/in.² subdivisions. This was connected on the pressure side of the gas exit tube valve.

The oxygen cylinder was connected to the autoclave with high pressure woven wire tubing. A check valve was installed before the inlet valve on the head of the autoclave to prevent accidental backflow of corrosive gas or liquid.

The sample tube inside the autoclave was made of Teflon with a fritted glass filter on the end. The internal pressure forces the sample through this tube and out the sampling valve. A small cold water cooler was used on the sampling tube outside the autoclave to prevent flashing of the high temperature liquid.

The sample holder (Fig. 4) was constructed of Teflon in such a manner as to maintain a constant surface area exposed to the solution. A Teflon cylinder was machined on one end to provide a restraining lip to hold the sample. The sample was pressed against the lip by a threaded rod, the edges being sealed by using a ring of soft Teflon valve packing on the restraining lip. The sample holder was supported on the sample tube inside the autoclave with the exposed face held at an angle to the flow of the solution. This arrangement of sample positioning worked very well and gave no evidence of uneven leaching

or stagnant pockets of gas on the sample surface.

IV. Analytical Method

The dissolution rate of the alloys was followed by determining the concentration of Pt (IV) in solution. A colorimetric method utilizing the colored $\text{Sn}^{(\text{II})}$ -Pt chloro-complex was used. The method is described in detail by Beamish.¹⁰ The optimum concentration range is from 3-25 ppm platinum, however the system conforms to Beer's law fairly well up to about 60 ppm. The procedure used was as follows. A solution 1.0 M in HCl was prepared. A 15 ml sample aliquot was put in a 25 cc volumetric flask, and 2.5 ml of concentrated HCl was added. Then 5 ml of the SnCl_2 solution was added and the volume diluted to the mark with deionized water. The flask was shaken and the colour allowed to develop for fifteen minutes. The transmittance of the sample was measured at 403 millimicrons in a Beckman DU spectrophotometer using glass cells. A blank sample was prepared from the SnCl_2 solution and deionized water and used as a reference. A standard sample containing 10 ppm platinum was prepared from H_2PtCl_6 solution and measured against the reference to calibrate the transmittance curves. The platinum content was calculated from the curves using Beer's law. The total amount of dissolved platinum was calculated from the known volume of solution and the concentration determined spectrophotometrically. The iron concentration was checked by using an Ortho-phenanthroline method as described by Bath.¹⁸

V. Experimental Procedure

The alloy buttons were polished and mounted in the sample holder. The excess Teflon packing was carefully trimmed away to give a circular surface area and the sample holder was washed and mounted on the autoclave sample tube. The leaching solution was made up by adding the proper amounts of reagent grade NaCl and concentrated HCl to deionized water and making the total volume up to 1500 ml. The autoclave was then assembled and placed inside the heating jacket. The temperature controller was set and the autoclave flushed through with oxygen. When the autoclave reached the desired temperature the stirrer was started and the oxygen pressure raised to the desired pressure. The oxygen pressure was constantly maintained at the desired pressure. Samples were taken at regular intervals, using 10 cc to flush the sampling line and keeping a 25 cc sample for colorimetric analysis.

At the end of each run, the alloy button was removed from the sample holder, washed, dried and examined microscopically. Photographs were taken after some runs and electron probe photographs were also taken to further reveal surface structure.

RESULTS

The dissolution data obtained are presented in graphical form; the numerical results are tabulated in the appendix.

The rate curves are calculated from analytical results and are corrected for initial surface area and reaction volume changes due to sample removal.

I. Dissolution of Fe-Pt Alloys

The dissolution curves are all based on the total amount of dissolved platinum after certain time intervals. These values were then used to calculate the amount of dissolution per unit initial surface area. All the dissolution curves found were linear after a short initial non-linear portion.

(i) A typical dissolution curve for an Fe-Pt alloy is given in Fig. 5. As noted above the curve is linear, apart from a slight initial curvature. This curvature may be due to polishing effects on the surface or to a deficiency in the analytical technique at low platinum concentrations.

(ii) The curves in Fig. 6 compare the leaching rates for Pt sheet, Fe-Pt, and Fe_3Pt alloys. The curves for the Pt sheet, Fe-Pt and Pt_3Fe are again linear, however, no platinum dissolved from a Fe_3Pt alloy, and the results were not plotted.

(iii) The effect of temperature on the leaching rate of FePt is given in Fig. 7. The rate increased with temperature as expected. An Arrhenius type plot of this data is presented in Fig. 8 from which an apparent activation energy for dissolution of 16 kcal/mole is found. This high an apparent activation energy would indicate chemical control rather than diffusion control.¹⁹

(iv) A series of curves showing the temperature effect on the leaching rate of pure platinum sheet is given in Fig. 9. As for the Fe-Pt alloy an Arrhenius plot of this data is given in Fig. 10. An apparent activation energy of 20 kcal/mole is found, again indicating chemical control.

II. Effect of Acid Concentration

The effect of varying the H^+ concentration at a constant Cl-ion concentration (3 M) on the dissolution of Pt from Fe-Pt alloy is given in Fig. 11. The acid concentration was limited to 3 M because of the danger of autoclave corrosion. A plot of the rate of dissolution versus acid concentration is given in Fig. 12. This is a curve, however a plot of rate of dissolution versus $[H^+]^2$ (Fig. 12) is linear.

III. Effect of Oxygen Pressure

The effect of oxygen pressure on the rate of dissolution of Fe-Pt alloy in 2 M HCl at 150°C is given in Fig. 13. All the curves are again linear, and the rate increases with increasing O_2 partial pressure. A plot of O_2 partial pressure versus dissolution rate (Fig. 14) is also linear. As the solubility of O_2 in aqueous solutions

is proportional to pressure,²⁰ this plot therefore gives the variation in reaction rate (dissolution rate) as a function of O_2 concentration as well as pressure.

IV. Effect of Chloride Ion Concentration

The effect of increasing the chloride ion concentration through the addition of NaCl to 2 M HCl solution is shown in Fig. 15. Increased Cl^- ion leads to an increase in rate, but a saturation type of curve is obtained when a rate versus (Cl^-) plot (Fig. 16) is made.

Estimate of Errors in Results

The calculated error in the raw data used to obtain dissolution rates is $\pm 5\%$. This is composed of a $\pm 1\%$ accuracy in analytical results and a $\pm 4\%$ error in the calculated surface area of the sample. The actual errors in the derived rate values are than $\pm 5\%$ plus an error incurred in drawing a straight line through the scattered experimental points. Repeated experiments gave identical rates of dissolution, using the line drawing technique.

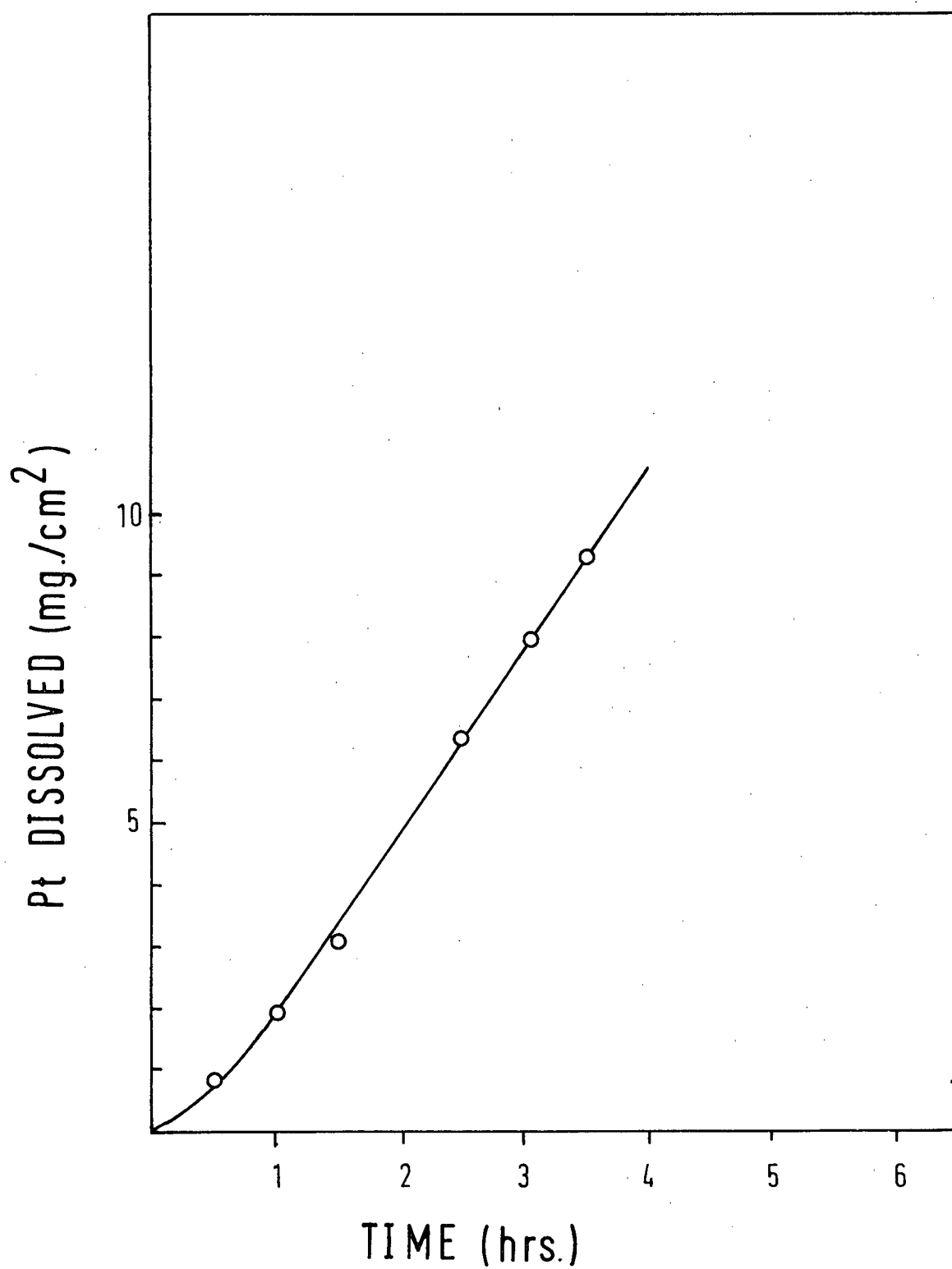


Fig. 5. A typical dissolution curve for Pt-Fe alloy at 700 psig O_2 , 2 M HCl and $150^\circ C$

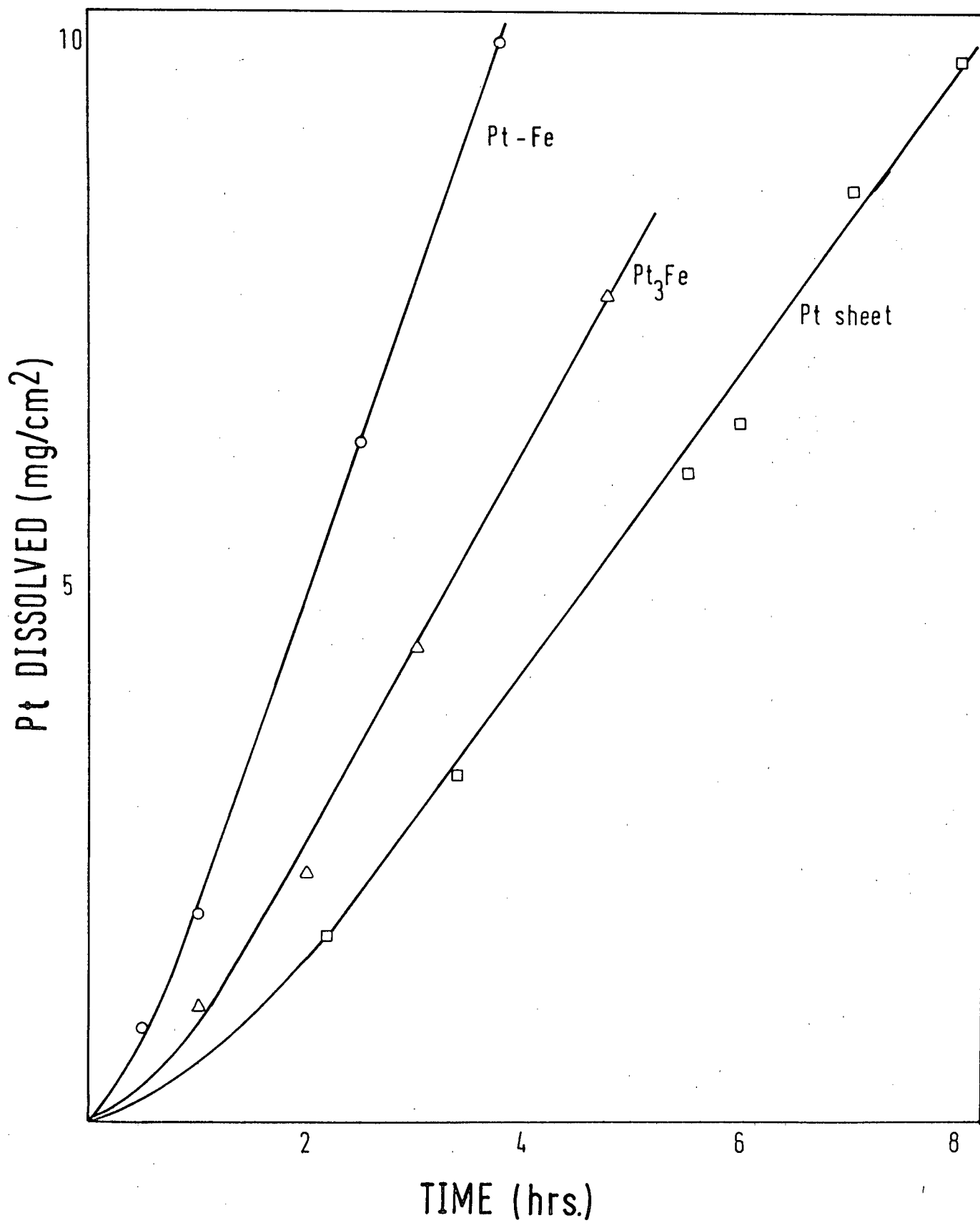


Fig. 6 Comparative Dissolution rates for PtFe, Pt₃Fe and Pt sheet under similar leaching conditions.

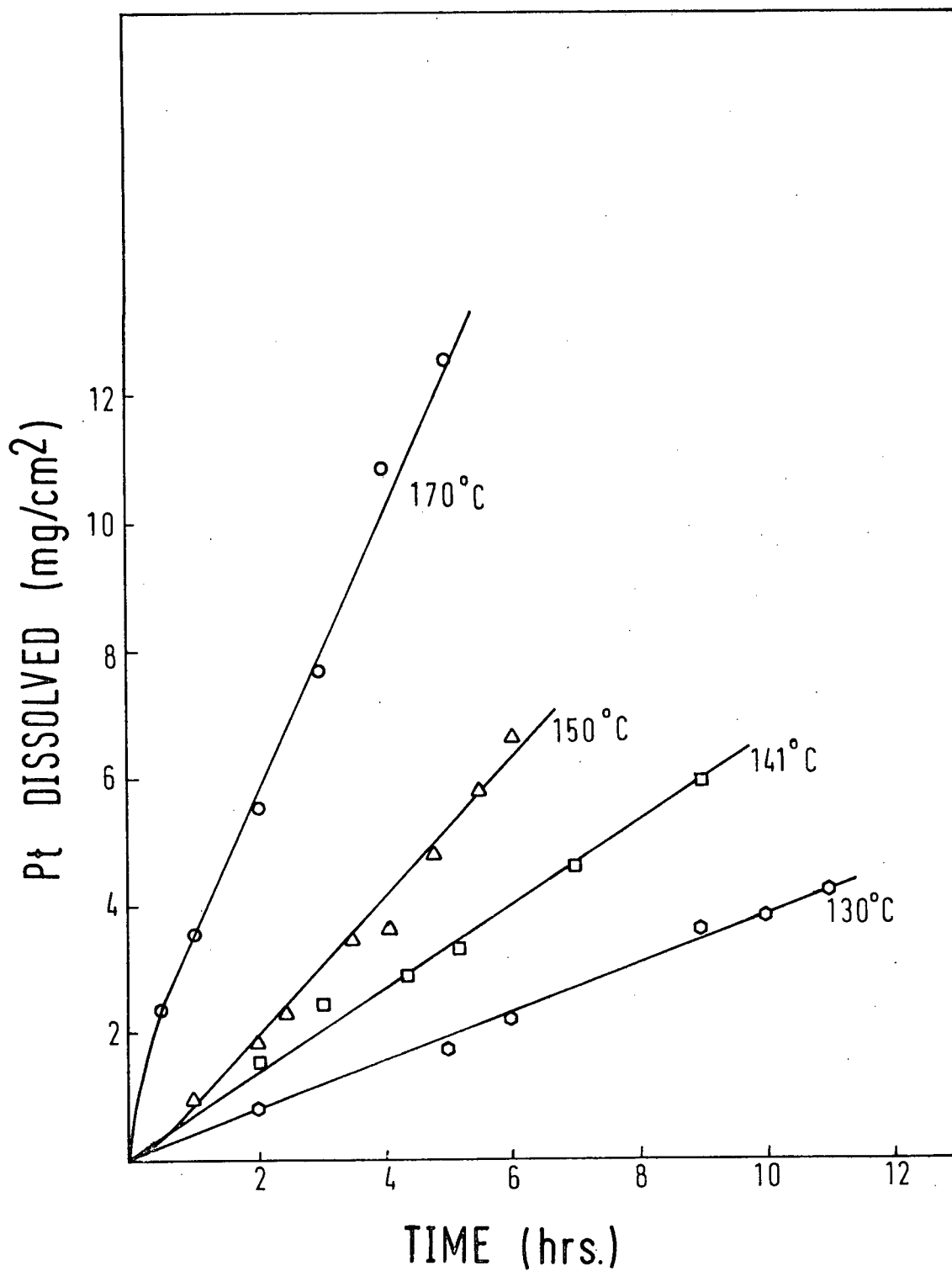


Fig. 7. The effect of temperature on the dissolution rate of PtFe alloy at 1 M HCl and 700 psig O₂

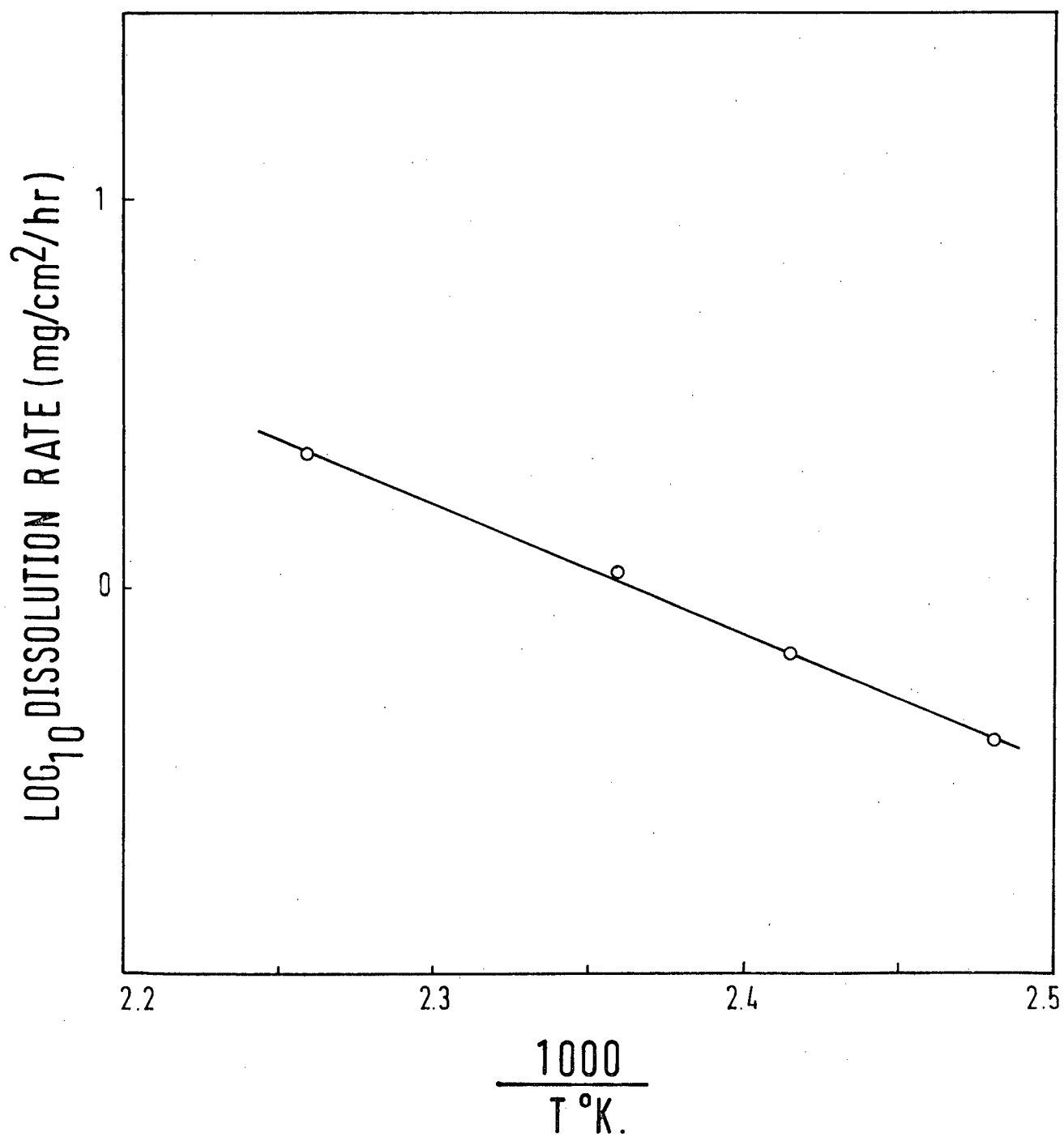


Fig. 8. Arrhenius plot for the dissolution of PtFe alloy

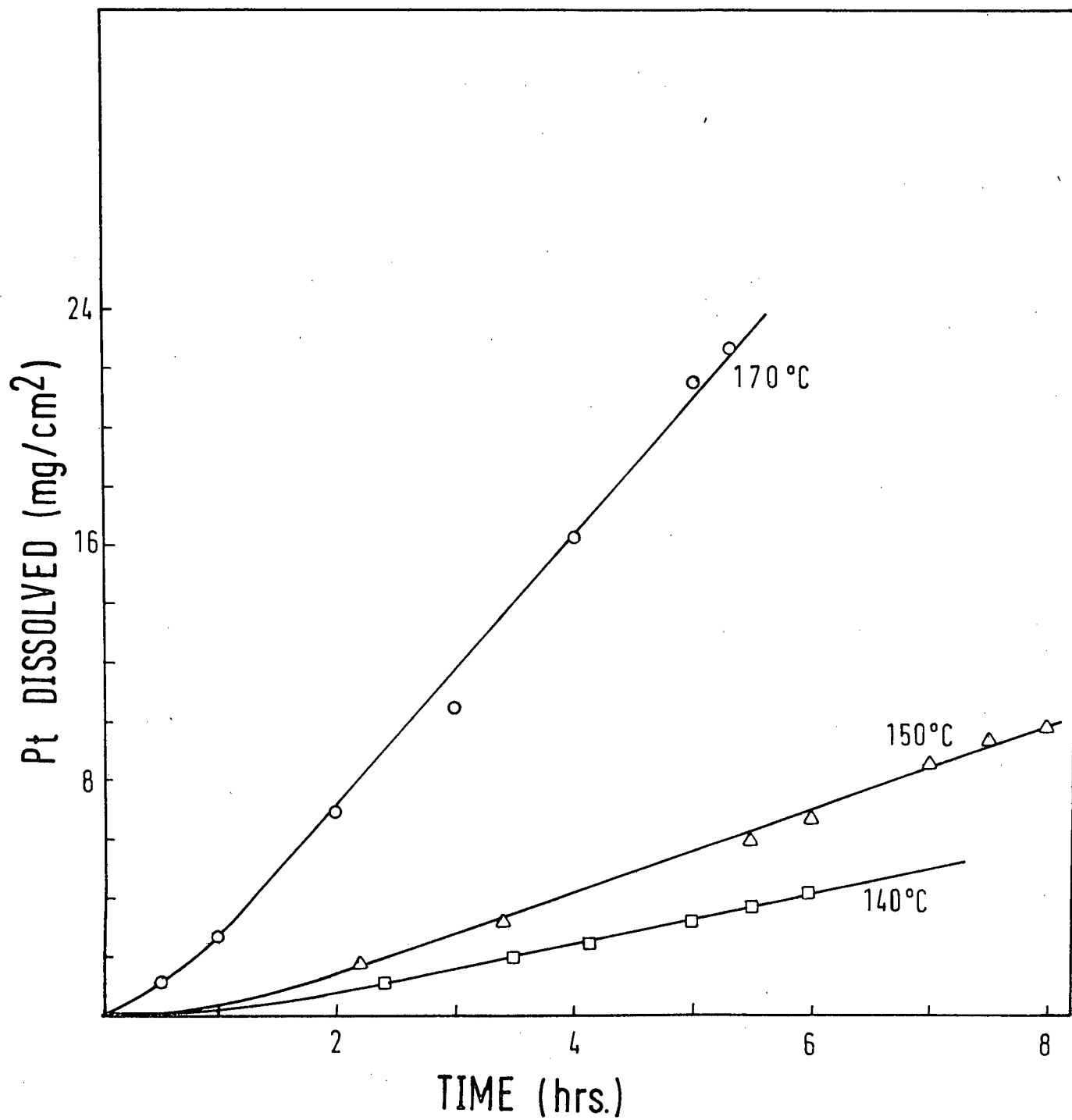


Fig. 9. The effect of temperature on the dissolution rate of pure Pt sheet at 2 M HCl and 700 psig O₂

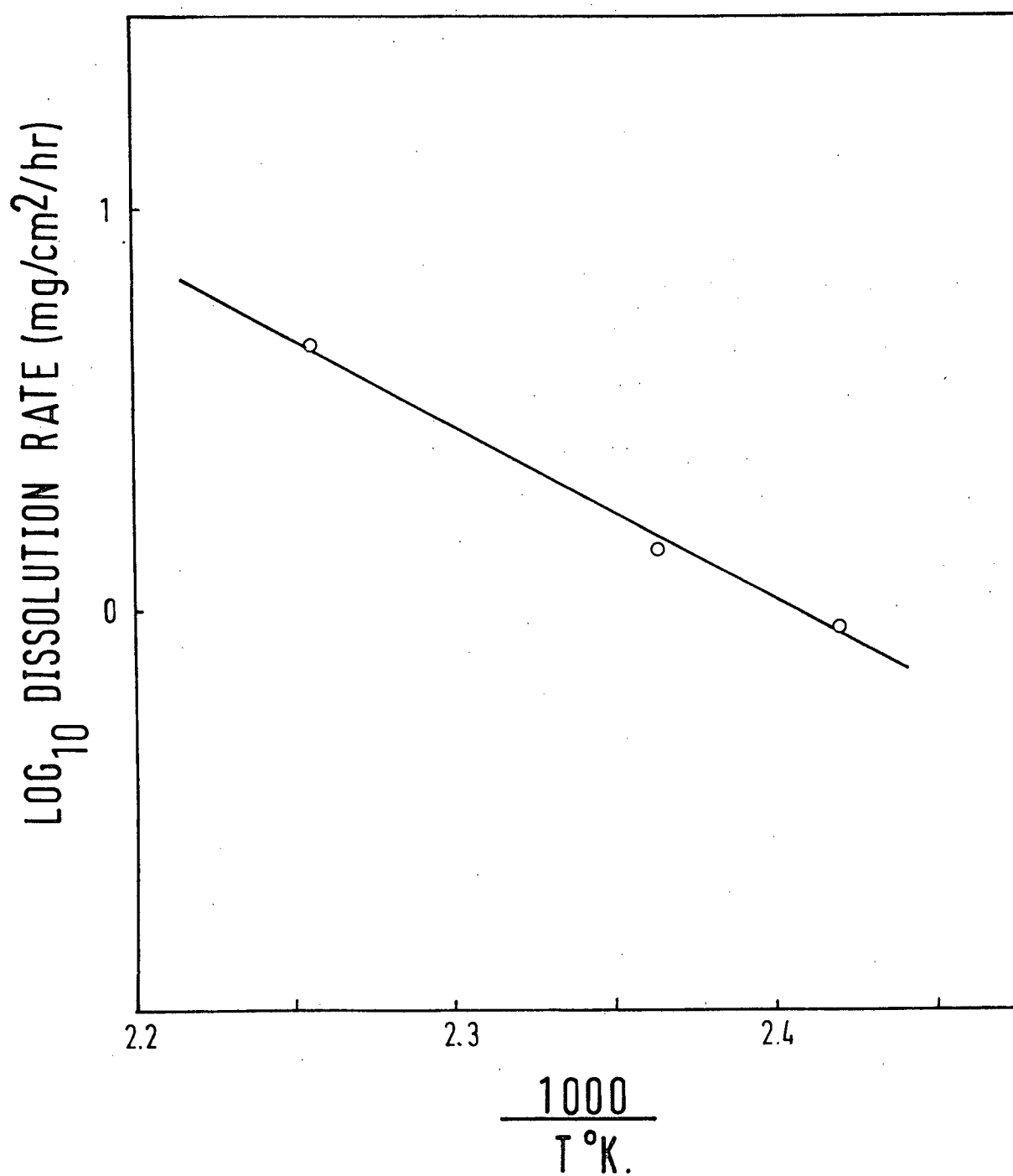


Fig. 10. Arrhenius plot for the dissolution of Pt sheet

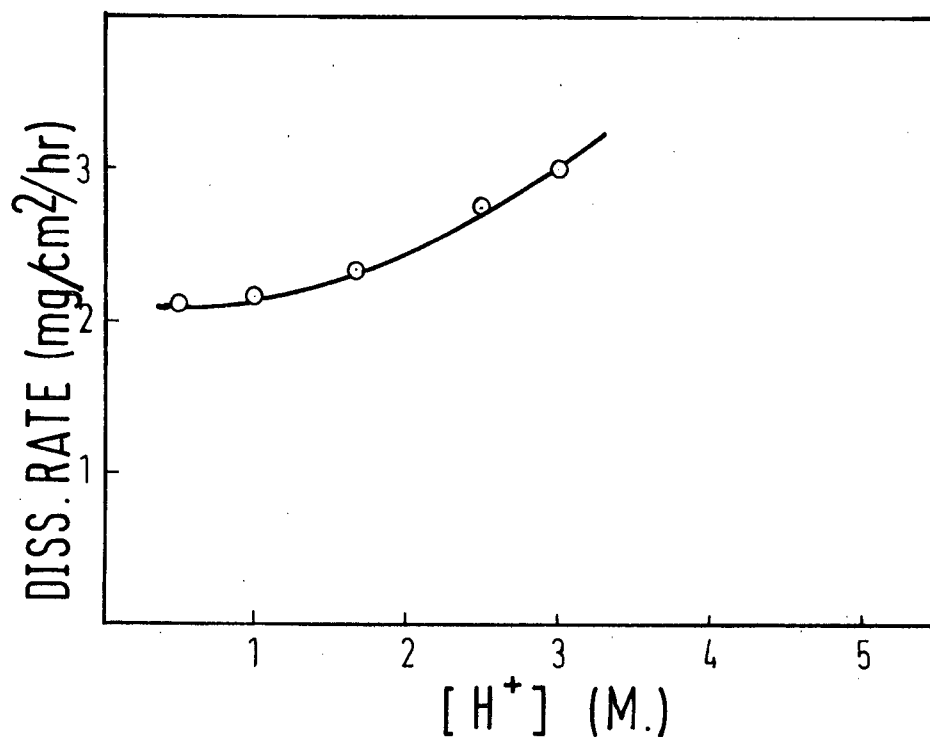


Fig. 11. The effect of HCl concentration on the dissolution rate of PtFe alloy at 3 M total Cl⁻ concentration, 150°C and 500 psig O₂

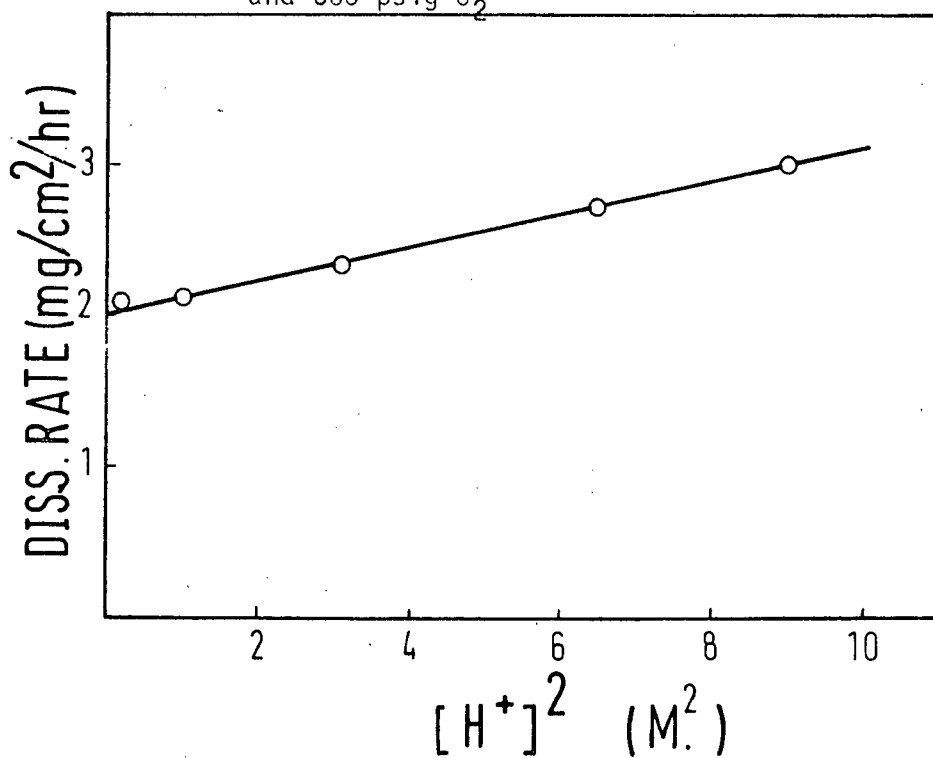


Fig. 12. Dissolution rate vs. [H⁺]² for PtFe alloy

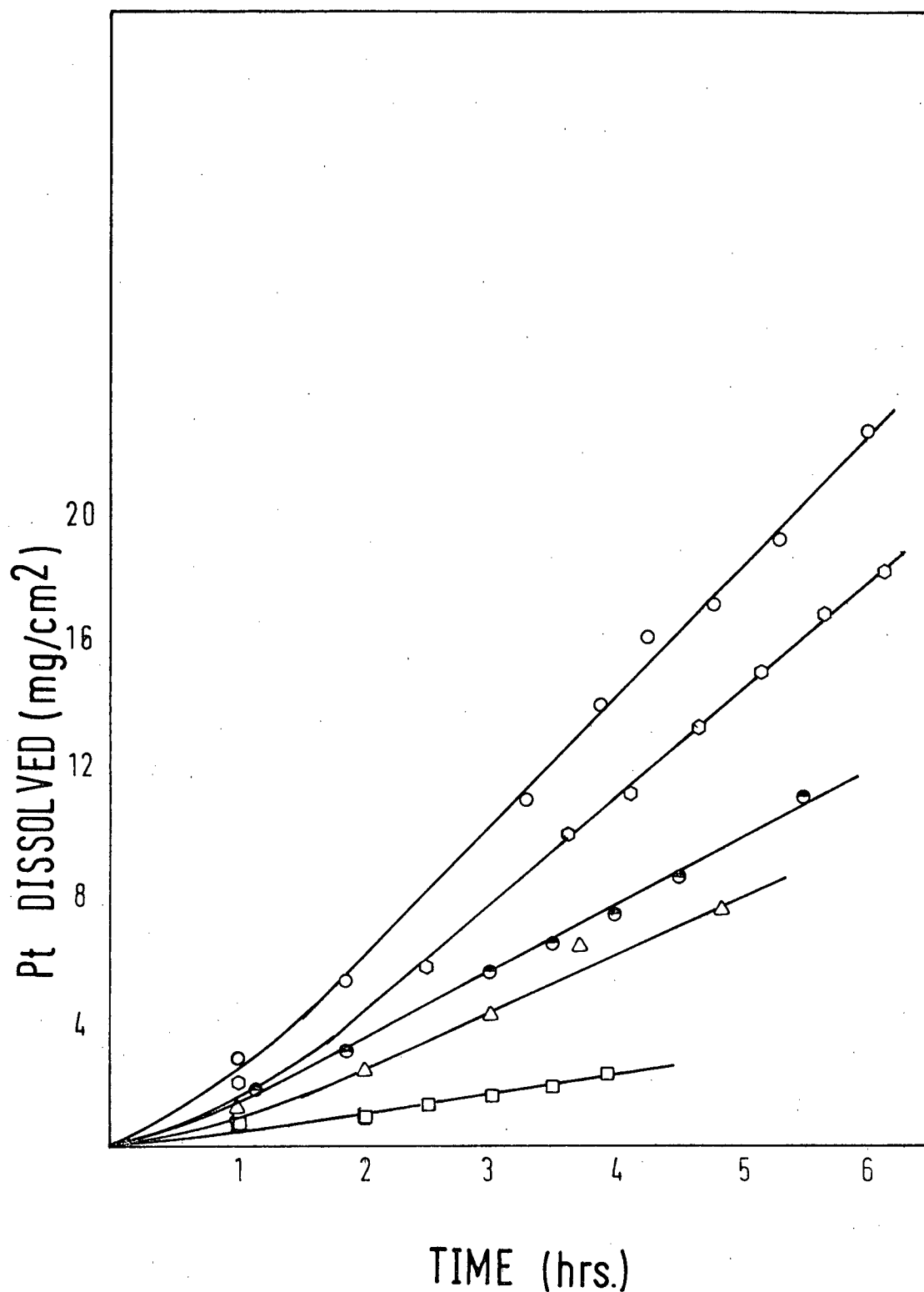


Fig. 13. The effect of oxygen pressure on the dissolution rate of PtFe alloy at 150°C and 2 M HCl

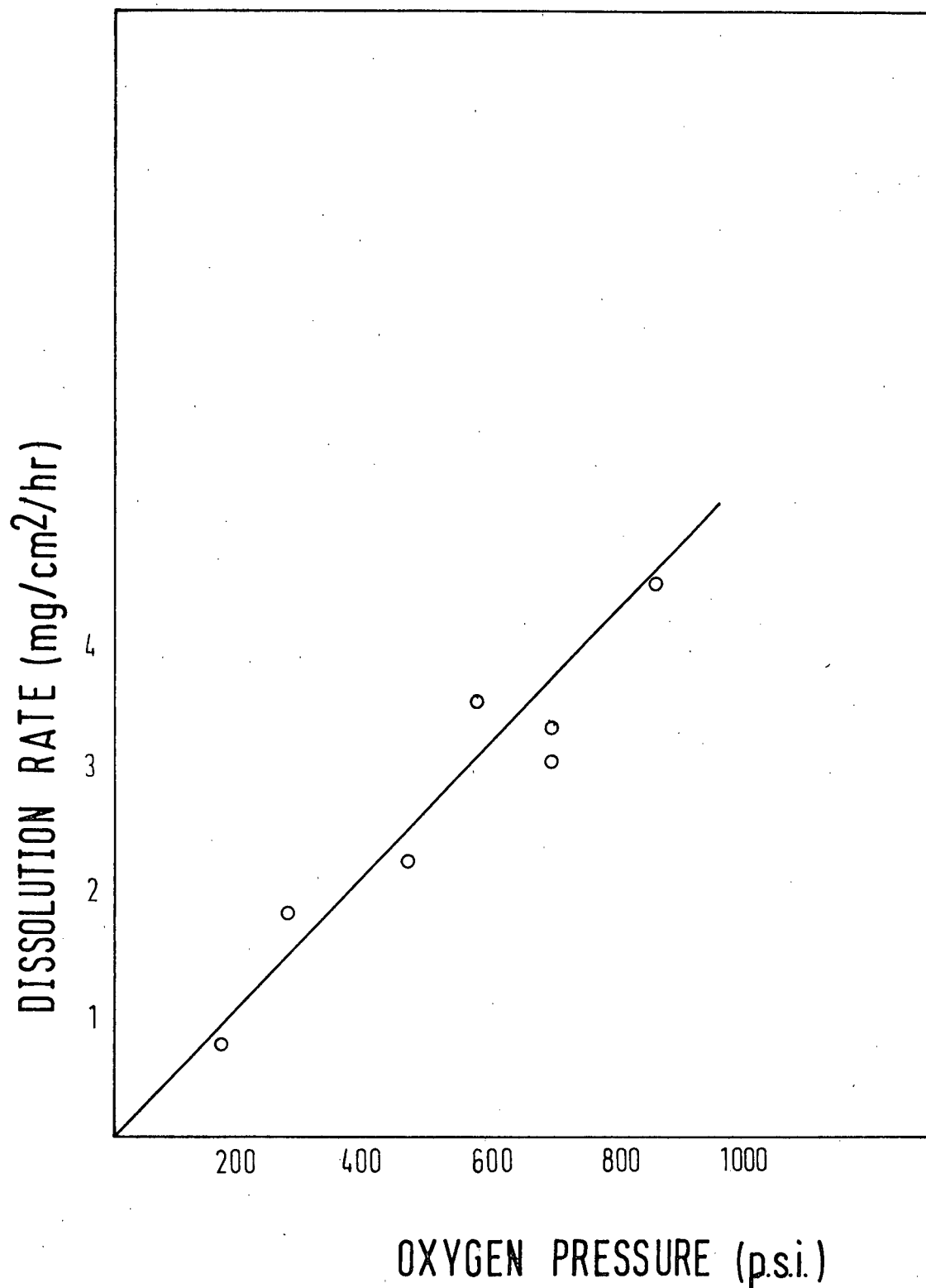


Fig. 14. Dissolution rate vs. pO_2 for PtFe alloy dissolution

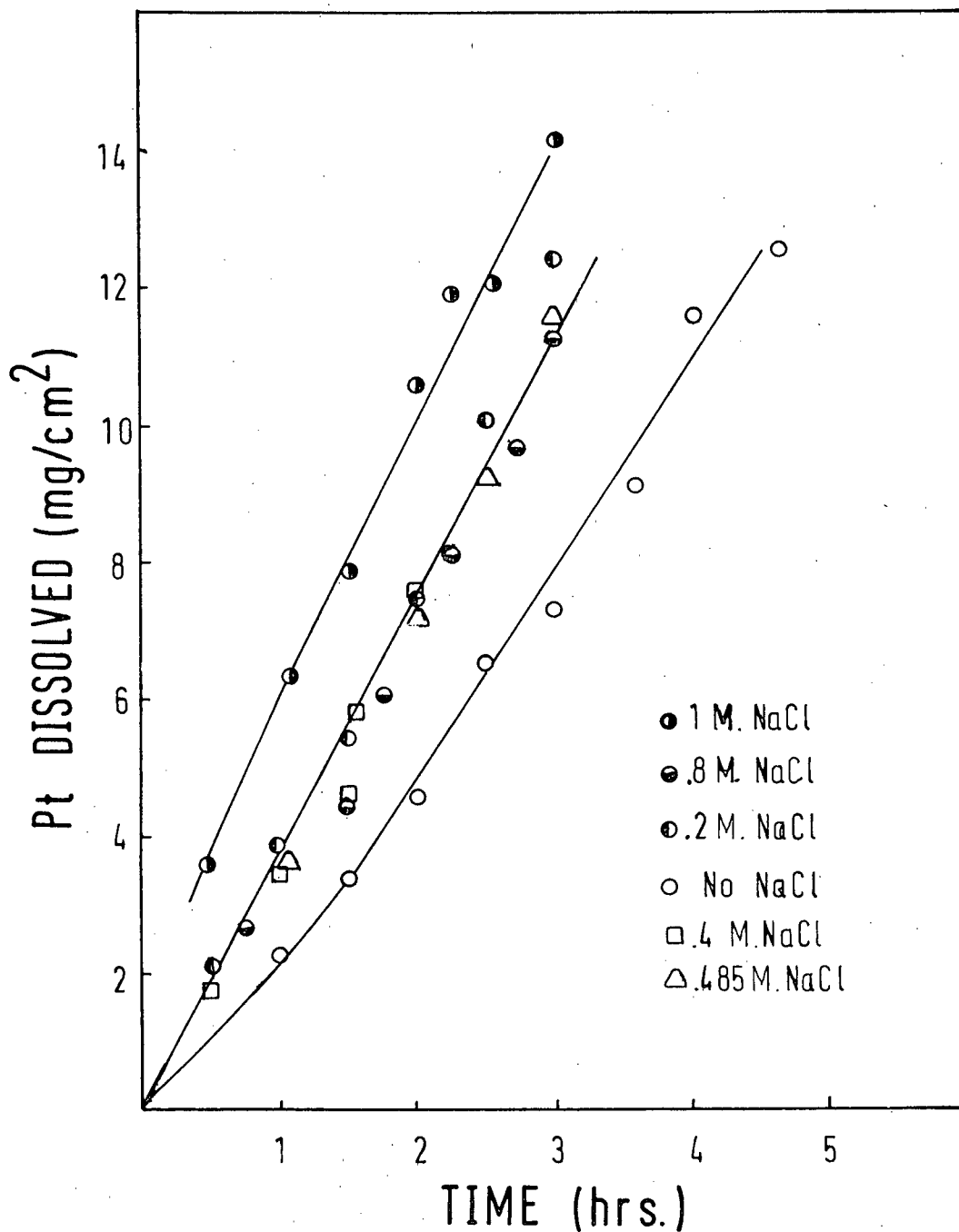


Fig. 15. The effect of $[Cl^-]$ on the dissolution rate of PtFe alloy at 500 psig O_2 and 2 M HCl

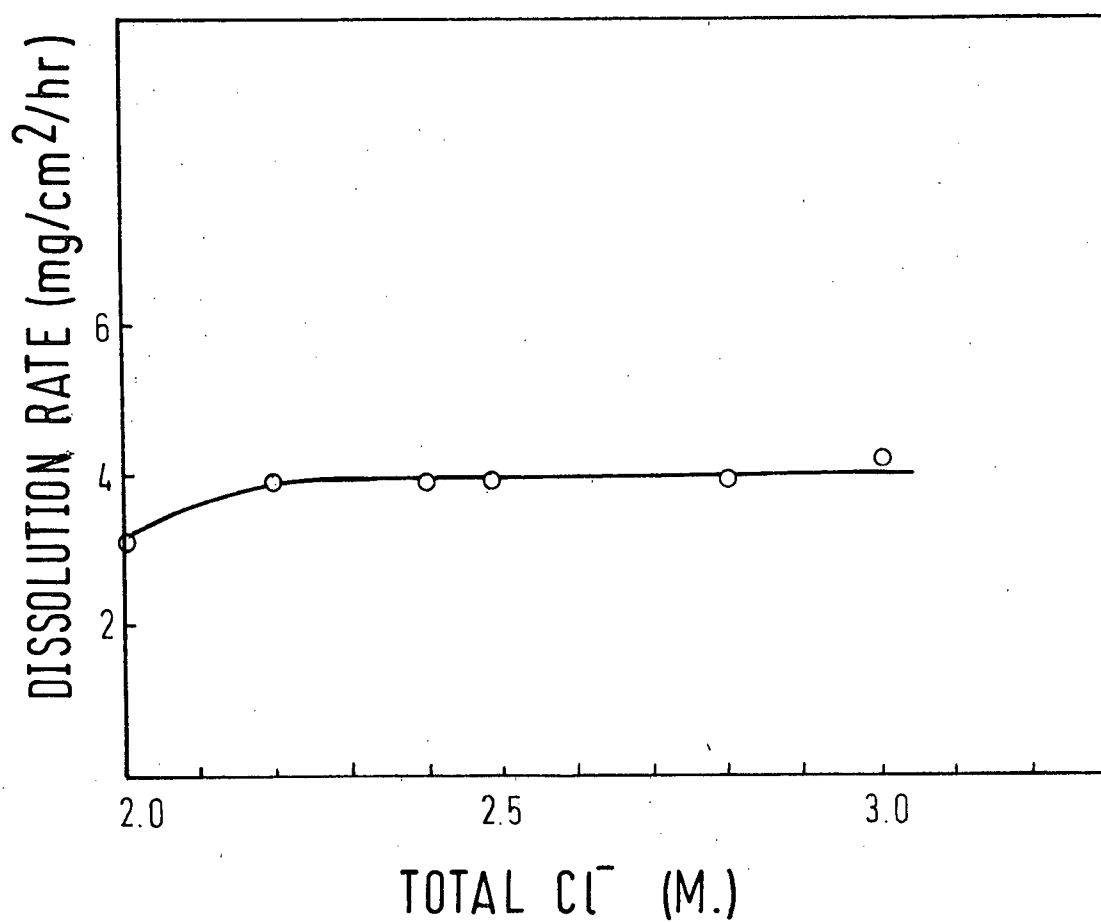


Fig. 16. Dissolution rate vs. total Cl⁻ concentration for PtFe alloy

DISCUSSION

I. Linear Dissolution Curves

In all instances in this study, the dissolution rate of the platinum from both pure Pt and Fe-Pt alloys was linear with time. Microscopic examination of the surface showed general uniform corrosion (Fig. 17) with some preferential grain boundary corrosion. However, electron microprobe analysis of the leached surface showed no preferential dissolution of Fe from the Fe-Pt alloys at greater than 50 at % Pt. Therefore in the following discussion it is assumed that the alloy dissolved uniformly over the exposed portion of the sample, with Fe and Pt dissolving at the same rate. The linear rates of corrosion indicate²¹ that the surface area of the specimen remained essentially constant over the duration of the leaching experiments and also that the reactant concentrations remained unchanged. The small amounts of Pt dissolved in all cases tend to support these assumptions, as not enough would dissolve to appreciably change the surface.

II. Activation Energies and Stirring Effects

The apparent activation energies for the dissolution of Pt from both Fe-Pt alloys (15.6 kcal/mole) and pure Pt sheet (19.8 kcal/mole)

are high enough that it appears the reaction is chemically controlled.¹⁹ A two fold increase in the stirring rate had no effect on the rate of Pt dissolution, therefore chemical reaction control is definitely indicated. The chemical reaction which is rate controlling must occur at the surface, as the rate is dependent on initial surface area.

The activation energies of both the cathodic reduction reaction and the anodic dissolution of Pt in chloride solution are close to the values found for dissolution of Pt in the autoclave.

The activation energy for oxygen reduction at a platinum surface is in the neighborhood of 20-25 kcal/mole. This value is found by using the magnitude of the exchange current density (10^{-10} amps/cm²) and calculating the activation energy by a modification of the Tafel equation.²² The activation energy for the anodic dissolution of Pt in all solutions was found to be 20 kcal/mole.⁷ The decrease in activation energy for the dissolution of the Fe-Pt alloy is probably an effect of lowering the corrosion potential and/or providing more easily corrodable sites at the surface.

III. Kinetic Analysis

The kinetics of corrosion of metals has been presented by Habashi²³ in the following fashion.

For the cathodic half-reaction, when first-order kinetics are followed, the rate law is:

$$V_c = k_c A_c [D]$$

where V_c = the reaction velocity

k_c = the cathodic velocity constant

A_c = the surface area of the cathodic zone

$[D]$ = concentration of the depolarizer.

Similarly, the rate law for the anodic half-reaction is given by:

$$V_a = k_a A_a [C]$$

where V_a = the reaction velocity

k_a = the anodic velocity constant

A_a = the surface area of the anodic zone

$[C]$ = concentration of complexing agent.

At the steady state, the rate of the cathodic reaction is equal to the rate of the anodic reaction; and this rate is equal to the corrosion rate, i.e.

$$V = k_c A_c [D] = k_a A_a [C]$$

however since $A = A_c + A_a$ where A is the total surface area available for corrosion, the rate equation can be written:

$$V = \frac{k_c k_a A [D] [C]}{k_c [D] + k_a [C]}$$

At a relatively low concentration of D and a high C concentration the rate equation simplifies to

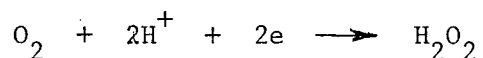
$$V = k_c A[D]$$

indicating a cathodically controlled corrosion reaction. Similarly at a high concentration of D and a low concentration of C, the rate equation becomes:

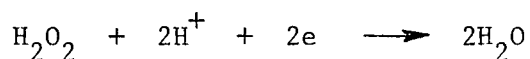
$$V = k_a A[C]$$

and the corrosion is anodically controlled.

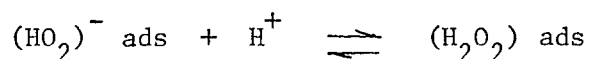
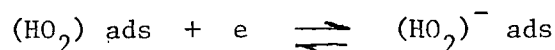
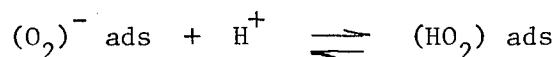
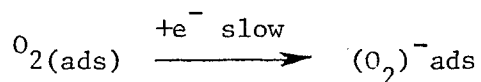
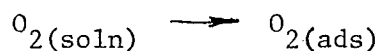
For metal corrosion in acid oxygenated solutions the cathodic reduction of oxygen is the most likely 'depolarization' reaction. Hoare²⁴ has reviewed the literature on the oxygen reduction reaction at platinum electrodes. This reaction is generally believed to occur in two steps both involving a 2-electron transfer. The first step is:



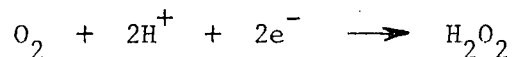
followed by a second catalytic step on the surface:



The reaction mechanism for the first step is believed to be as follows, with the first one-electron transfer reaction involving adsorbed molecular oxygen being rate determining:



after which the adsorbed peroxide molecule either desorbs or reacts further. The second reaction step is believed to be catalyzed somehow by the surface and a detailed mechanism has not yet been proposed. However, the rate of this second reaction has been found to be an order of magnitude larger than the first reaction rate. Hoare also noted that on alloys of Pt, the same overall reaction mechanism is observed, however the rates are generally enhanced, due to a better electron transfer, an improvement in catalytic ability, or a decrease in inhibiting anion adsorption. In this case, taking the first reduction reaction to H_2O_2 as being the rate controlling step, we get:



Under the conditions for determining the oxygen dependence of the dissolution reaction, the H_2O_2 concentration is regarded as being

small as it is a quickly reduced intermediate.

The effect of chloride ion concentration on the dissolution rate of the PtFe alloy is given in Figs. 15 and 16. As shown in Fig. 16 it is apparent that there is no increase in dissolution rate with increasing chloride ion concentration above 2 M. This leads to the conclusion that the dissolution reaction is in fact cathodically controlled, and therefore only the oxygen pressure and hydrochloric acid concentration will have an effect on the dissolution rate. As the situation is one where the concentration of complexing agent (Cl^-) is high with respect to the depolarizer (O_2, H^+); according to the kinetic derivation given above, the overall dissolution rate should correspond to a rate law of the form:

$$V = k_c A[D]$$

where V is the dissolution rate, k_c is a cathodic rate constant, A is the surface area and $[D]$ is the concentration of depolarizer.

The effect of oxygen pressure on the dissolution rate, determined at a constant hydrochloric acid concentration of 2 M is shown in Figs. 13 and 14. The plot of dissolution rate vs. $p\text{O}_2$ (Fig. 14) shows a linear dependence of the rate on the oxygen pressure. As oxygen follows Henry's law in this temperature and pressure range, this dependence is equivalent to a linear dependence on the O_2 concentration in solution. As the dissolution rate is given in $\text{mg dissolved/cm}^2/\text{hour}$ we can write a specific rate expression.

$$V = k_c' p\text{O}_2 \tag{1}$$

where V is the dissolution rate per unit area and k_c' is a rate constant describing the linear dependence of the dissolution rate on oxygen pressure. Therefore, for the specific conditions of high (> 2 M) chloride ion concentration and a constant acid concentration, the dissolution rate follows standard corrosion kinetics. The numerical value of the rate constant is:

$$k_c' = 0.00517 \text{ mg/cm}^2 \text{ hr psi}$$

and the rate law is:

$$V = 0.00517 p_{O_2} \text{ mg/cm}^2 \text{ hr}$$

The effect of the acid concentration on the dissolution rate is more complex. The acid dependence of the rate was determined at high (3 M) total chloride ion concentration and at constant oxygen pressure. As shown in Fig. 11, the rate dependence on the acid concentration is non-linear. However, a plot of (acid concentration)² vs. dissolution rate (Fig. 12) is linear over a region from 1.0 M HCl to 3.0 M HCl. Below 1 M HCl the rate drops off sharply and should become zero at zero acid concentration.

Therefore over the region from 1 M HCl to 3 M HCl a rate law for the dissolution may be written:

$$V = k_c'' ([H^+]^2 + C) \quad (2)$$

where V = dissolution rate
 k_c'' = rate constant
 $[H^+]$ = acid concentration
 C = integration constant.

Numerically, k_c'' is the slope of the Rate vs. $[H^+]^2$ curve and $k_c''C$ is the zero intercept of the straight line extrapolated to zero. At constant $[H^+]$ the rate law was found to be:

$$V = k_c' pO_2$$

therefore for a situation where both the acid concentration and pO_2 are changing, the rate law will be:

$$V = k_c''' (k_c'' [H^+]^2 + k_c'' C) pO_2 \quad (3)$$

which simplifies to

$$V = k_c [H^+]^2 pO_2 + k_c C pO_2 \quad (4)$$

where $k_c = k_c''' k_c''$

Therefore k_c is a rate constant for the overall cathodic reaction in the rate law (4) which is valid in the region $1\text{ M} < [H^+] < 3\text{ M}$.

The anodic half reaction of the dissolution was not rate controlling under the experimental conditions used in the autoclave, therefore, no experimental data are available for calculating a rate constant for

the anodic half reaction or the overall dissolution reaction.

Chemodanov et al.⁸ have shown that at low Cl^- concentrations, from about 0.01 to 0.5 M, the rate dependence of the anodic Pt dissolution on chloride ion concentration in acid solution is of the form

$$V = k_a A [\text{Cl}^-]^{0.9}$$

where k_a is an anodic rate constant, A is the surface area and $[\text{Cl}^-]$ is the chloride ion concentration. If this dependence on chloride ion is valid for the dissolution from PtFe alloys, a rate law describing the overall dissolution rate would have the form:

$$V = \frac{[k_c [\text{H}^+]^2 \text{pO}_2 + k_c \text{CpO}_2] k_a [\text{Cl}^-]^{0.9}}{(k_c [\text{H}^+]^2 \text{pO}_2 + k_c \text{CpO}_2) + k_a [\text{Cl}^-]^{0.9}}$$

in a region where both the anodic and cathodic reactions are rate controlling to some extent. In the dissolution experiments done in the autoclave this region was not studied, therefore, no numerical values for the rate constants or experimental evidence for the validity of the proposed rate law is available.

CONCLUSIONS

1. Platinum-iron alloys at platinum concentrations of 50 atom percent or greater dissolve homogeneously in oxygenated hydrochloric acid solutions.
2. The rate of platinum dissolution from platinum-iron alloys follows corrosion kinetics at chloride ion concentrations greater than 2 M, with the rate controlling step being cathodic oxygen reduction. The rate is dependent on acid concentration, temperature, oxygen pressure and alloy composition.

SUGGESTIONS FOR FURTHER WORK

1. An investigation of the dissolution rate under anodic corrosion control would add to the detail of the dissolution mechanism. This work would have to be done using an electrochemical technique, as the corrosion problems in the autoclave are serious.
2. A series of experiments on other PtFe alloys at concentrations both below 50 atom percent and in a solid solution regime rather than at intermetallic compound compositions could lead to better understanding of both alloy corrosion and the de-alloying type of phenomena.

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TABLE 1. Alloy Comparison

Alloy	pO_2	[HCl]/M	Dissolution rate (mg/cm ² /hr)
Pt	700 psig	2	1.4
Pt ₃ Fe	600 psig	3	1.9
PtFe	700 psig	2	2.9

TABLE 2. Effect of Temperature on Dissolution Rate

Alloy	Temperature (°C)	Dissolution rate	
Pt-Fe	130	0.40	(1 M HCl 700 psig)
"	141	0.675	
"	150	1.10	
"	170	2.20	
Pt	140	0.90	(2 M HCl 700 psig)
"	150	1.40	
"	170	4.60	

TABLE 3. Effect of $[H^+]$ on Dissolution Rate of Fe-Pt

$[H^+]$ (M)	Dissolution rate
0.5	1.85
1.0	2.185
1.6	2.33
2.5	2.70
3	2.97

TABLE 4. Effect of Oxygen Pressure on Dissolution Rate $[H^+] = 2$ M,
 $T = 150^\circ\text{C}$

pO_2 (psi)	Dissolution rate ($\text{mg}/\text{cm}^2/\text{hr}$)
170	0.75
270	1.80
470	2.40
670	3.25
870	4.45

TABLE 5. Effect of Chloride Ion on Dissolution Rate.

$[\text{H}^+] = 2 \text{ M}$, $p\text{O}_2 = 500 \text{ psig}$

Total $[\text{Cl}^-]$ (M)	Dissolution rate ($\text{mg}/\text{cm}^2/\text{hr}$)
2.0	3.1
2.2	3.9
2.4	3.9
2.485	3.9
2.8	3.9
3.0	4.2