

CATALYSED CYANIDATION OF GOLD

by

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A thesis submitted for the degree of Doctor of Philosophy of the
University of London
and for the
Diploma of Imperial College of Science, Technology and Medicine

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August 1992



Abstract

A study was carried out to investigate the possibility of using an additional and recyclable oxidizing organic agent (i.e., an organic catalyst) during the cyanidation of gold. Normally, the cyanidation process uses oxygen in the form of air or bulk oxygen as the reagent to accomplish the needed gold oxidation, but in many circumstances it suffers from low kinetic rates mainly because of the low solubility of oxygen in water; thus the idea of introducing a liquid-phase catalyst to enhance the rate of dissolution of gold.

A literature survey was firstly performed in the search for a suitable reagent to act as required. Anthraquinone-2-sulphonic acid (AQ) was identified as a theoretically possible reagent and thermodynamic calculations confirmed this initial assumption. Spectrophotometric identification of both reduced and oxidized species was experimentally seen as possible, along with "in-situ" production of hydrogen peroxide from the oxidation of the reduced AQ. The cyanidation process was reviewed, including oxygen reduction, cyanide oxidation and a thorough examination on the rate of the dissolution of gold reported in the literature.

The effect of AQ addition on the rate of gold dissolution was studied by means of a rotating disc. The parameters studied were the concentration of cyanide, AQ and oxygen in the leaching solution, rotating speed and temperature. The rate was found to increase by around 25 to 30% when 3.00mM AQ is present in a 0.03M KCN leaching solution, in a normally aerated solution. The AQ concentration remains the same throughout the process, meaning that it is acting as a catalyst. If, however, the solution is saturated with oxygen, the

positive effect of the AQ on the rate of dissolution of gold was seen to be negligible.

The actual ability of AQ to oxidize gold in a cyanide solution was tested under an oxygen-free atmosphere. A high-surface area metallic sponge was also used, and from these experiments the oxidation of gold by the AQ was found to most probably obey a 2:1 (Au:AQ) relationship.

The behaviour of the AQ during the cyanidation of gold was studied in terms of a mechanism of molecular adsorption on the metal surface, which appears to explain many of the results obtained. Moreover, unlike the case of other oxidizing agents also used in the cyanidation process (such as inorganic peroxides) AQ did not increase the rate of oxidation of the cyanide.

Acknowledgements

I would like to thank:

Dr. A.J.Monhemius for suggesting the basis of this research and for his supervision.

Prof. A.R.Burkin for his kind attention and valuable suggestions.

Mr. John Burgess, for his extreme help throughout the period of my staying in the hydrometallurgy group. Thanks are also due to Mr. Vick Harris and Mr. Ron Walker for their cooperation, specially during some more difficult times.

My father, mother and sister, who, in spite of the distance, did not measure efforts to encourage and support me. Their selfless love, caring and attention is an example that I take to my life.

My friends and colleagues from the "hydro group": Diane, Elia, Themis, Veronica, Ayhan and Luis. Their constant cooperation - discussing, helping and suggesting in different (and sometimes hard) situations - I will always remember with happiness and gratitude.

The Brazilian government, through the Brazilian Research Council - CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), for the financial support, which I fully appreciate.

And last, but by no means least, my wife Luciane. Words are not enough to express my gratitude for her love, support, encouragement and confidence in me, specially during the not so easy periods that we both faced together. Needless to say, without her this work might have not been completed.

To my father, mother,
Luciane and Roberta,
with love.

"... for Nature herself, in my opinion, makes it clear that whereas the production of gold is laborious, the guardian of it is difficult, the zest for it is very great, and that its use is halfway between pleasure and pain."

Diodorus Siculus, in "Bibliotheca Historica", 60 BC.

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CHAPTER I

INTRODUCTION

1.1-General overview

Gold is one of the most valuable and sought after metals, probably because, among other properties, of its shining aspect and inertness, which has rendered it suitable for the manufacture of jewellery and coins throughout many centuries. Without doubt, the search for gold has played a major role in the history of mankind. The Egyptians were the main gold users from the pre-Christian era (3200 BC) until around 1300 BC, but it probably became a medium of exchange as early as 3400 BC, although there is some uncertainty about this date^[1,2]. Agricola^[3], in his well-known early work, mentions that many called "gold (and silver) the scourge of mankind because they are the cause of destruction and ruin to their possessors". He was, however, ready to point out that this was an unjustifiable badge indeed, for "it is not metals that are to be condemned, but our vices, such as anger, cruelty and discord". It was the adoption of gold as a monetary standard by the British government in 1816 that caused the so-called "gold fever", leading to new territorial explorations and discoveries in many parts of the world, such as America and Africa^[4].

Besides being a highly valuable commodity, gold offers the advantage over other precious metals, such as platinum for instance, of being widely distributed in many geological environments and in amounts that render attractive the investment to extract it. Much investigation

has been performed to adapt new technologies to overcome the challenge of working with almost any type of ore^[5,6,7,8]. Its main uses nowadays are found (in decreasing order of importance) in jewellery (more than 50%), coins (around 17%), electronic devices, dental alloys and others^[4].

Most of the gold processed in the world today is obtained by the cyanidation process (outlined in a following chapter), a technique known since the end of the last century, when in 1887 a British patent was granted to John Steward MacArthur. For the development of this work he also received assistance and support from the brothers Robert and William Forrest (both MD), who were the ones that actually made the discovery in the first place in their clinic in Glasgow^[9]. The patent, named "Process of Obtaining Gold and Silver From Ores", soon became known as the cyanidation process following its successful industrial application. Some important reviews concerning the cyanidation process and its main characteristics have been published^[7,11,12,13].

With the implementation of the cyanidation process, the world gold output increased more than four times in the period from 1901 to 1950 compared to the period from 1851 to 1900. The total cumulative world production of gold today exceeds 10^5 t; the present annual production reaches 1700 t^[2]. South Africa is the largest producer, where more than 300 thousand people are involved in the production of gold. Also, around 40% of the reserves known today are found in the Republic of South Africa; 35% in Brazil (Serra Pelada and Morro Velho); 15% in the Soviet Union, these being followed by the USA, Australia, New Guinea (Ok Tedi), Zimbabwe and Ghana, with 1 to 4% each^[2].

The search for an alternative reagent to cyanide led to the development of processes using thiourea, thiosulphates, bromine and thiocyanate, to overcome, among others, difficulties that have arisen with the depletion of the high-grade ores and with the exploitation of the so-called refractory gold ores (those which cannot be easily extracted by the conventional cyanidation process)^[10,14,15,16,17]. Moreover, there is the environmental problem that may be caused by the disposal of cyanide (since it is a highly poisonous chemical). In spite of these facts, however, to date the cyanide process for gold extraction still keeps its overwhelming dominance it has acquired over the past one hundred years.

As will be seen in later chapters, the basic aspects of the cyanidation process have been established. These revealed that the rate of gold dissolution is controlled by the concentration of cyanide and/or oxygen in solution, depending on the relative concentration of each, and that the optimum strength of cyanide solution is best determined by experiment. In order to form soluble cyanide complexes, the gold must be simultaneously oxidized; this operation is normally performed by introducing compressed air to use oxygen as the oxidizing agent. Without an oxidizing agent, gold dissolution is not possible even in a cyanide solution. Under many circumstances the gold dissolution may be hampered by slow rates, or even stop altogether, mainly because of the low solubility of oxygen in water. This situation is aggravated at high altitudes, with increasing temperature and during certain industrial practices, such as heap leaching for instance, where oxygen may be almost totally absent towards the bottom of the heap.

Much research has been carried out to overcome the problems of oxygen deficiency, and suggestions include the introduction of oxygen in an already dissolved form, such as adding inorganic

peroxides^[18,19,20], or introducing compressed air into the leaching heaps^[21]. As may be seen from this, it is believed to be highly important in practice to maintain an air-saturated situation during the whole stage of cyanide leaching. In the former case, while the addition of peroxides may prove useful in some circumstances, the fact is that peroxides are also able to oxidize cyanide to cyanate^[19] (which is unable to act as a complexing agent for gold), and therefore this addition must be performed with care; if not, this may lead to an increased cyanide consumption, which may render the process uneconomic. Moreover, hydrogen peroxide is believed to be a product of the reaction between gold, aqueous cyanide and oxygen, the reaction being



This means that too large an addition of hydrogen peroxide may lead to a shift in equilibrium to the left hand side of the reaction and therefore inhibit the dissolution reaction^[29]. The use of injected air may also be useful in some cases, by considerably shortening the leaching time of the gold ore, but the costs necessary to implement the facilities as well as the effect on cyanide oxidation must again be considered. The present work was developed concerning this aspect of the gold cyanidation process: the low rates observed caused by low oxygen availability, or total lack of it, during the leaching stage of this operation.

1.2 - Objective of this research

The objectives of this research may be summarised as follows:

1-to search for and identify a suitable organic compound that, if added to the gold cyanidation system, would speed up the rate of dissolution of the metal, by being an additional (besides the oxygen) oxidizing agent present in the solution (and, preferably, being not too harmful to the cyanide). At the same time, it would act without changing or being affected permanently by the reaction, playing thus the role of a catalyst.

2-once identified and thermodynamically seen as feasible, to investigate the behaviour of the catalyst by performing practical tests on a bench scale under various experimental conditions. This would lead to the demonstration (or not) of the practical usefulness of the catalyst and of its main characteristics during the cyanidation of gold.

3-to demonstrate quantitatively that the catalyst is actually able to oxidize gold in a cyanide solution.

4-identify and demonstrate (if possible) the basic mechanism through which the catalyst is accomplishing its role.

As will be discussed in following chapters, catalysts are encountered in a wide range of applications and have been tested and used, both in industry and laboratory, for some time in many different fields. However, it is in this work that, for the first time, the implementation of an organic aqueous reagent to enhance catalytically the rate of the

dissolution of gold is conceived and tested to see whether it can be conveniently used in a hydrometallurgical process.

1.3-Investigation approach

The approach taken was, initially, to engage in a detailed literature survey in the search for a suitable catalyst. As will be seen, this proved not to be a straightforward task, and a large amount of information had to be gathered from different fields of research. This pointed to **Anthraquinone-2-sulphonic acid (AQ)** as a convenient and thermodynamically possible reagent to act as required. A review of the gold cyanidation process, including oxygen reduction, cyanide oxidation, thermodynamic and kinetic aspects, are also shown. The study of gold dissolution in cyanide (KCN) with the aid of a gold rotating disc electrode followed, when parameters such as AQ and KCN concentration, as well as oxygen partial pressure, rotating speed and four different temperatures were investigated. Work was also carried out under an inert atmosphere (nitrogen), not only with the rotating disc but employing a high surface-area metallic sponge (gold-plated) and a flow-through cell connected to a UV-visible spectrophotometer. This equipment allowed the simultaneous and quantitative measurement of AQ decay due to its reduction when performing the oxidation of gold (when the actual possibility of AQ oxidizing gold could be demonstrated). "In-situ" hydrogen peroxide generation (through the oxidation of the reduced AQ) was also examined. In the light of these experimental results and of work in similar fields, a hypothesis describing the adsorptive behaviour of AQ during cyanidation and a mechanism to explain the results obtained as well as the role played by AQ in the process was proposed. Finally, through an electrochemical study, the diffusion coefficient of the

quinone used was determined (this value was used to calculate the theoretical rate value of dissolution from a rotating gold disc) and the results of tests carried out with ores, as well as carbon adsorption tests, were also reported.

CHAPTER II

CATALYSIS FOR THE CYANIDATION OF GOLD

2.1-Introduction

Catalysis is recognized nowadays as being a huge subject. It was the Swedish chemist Jons Jakob Berzelius (1779-1848) who first identified it as a special phenomenon, in 1835. He introduced the concept of "catalytic force", ascribing the occurrence to a special property, characteristic to certain agents. It was, however, only in the beginning of this century that Wilhelm Ostwald recognized the real aspect of a catalyst, putting aside the initial concept that catalytic reactions were brought up by a special kind of force. Ostwald defined a catalyst as "a substance which augments the rate of a chemical reaction without itself being consumed or altering the position of final thermodynamic equilibrium of the reactions involved"[22,84] (his work on this subject earned him a Nobel prize in 1909). Since then, the subject has been widely investigated in many different fields[23...26]. The word "catalysis" is a combination of two Greek words meaning "to break down". In principle, a catalyst may either refer to a substance that increases or decreases the rate of a chemical reaction, although in the latter case it is most commonly referred to as an inhibitor or a negative catalyst. Examples of this type of catalyst are rare, since in most circumstances what is initially presumed to be an inhibitor is, on closer examination, actually being consumed during the process[26]. One of the main areas where catalytic processes play a very significant role is petroleum refining, as in catalytic cracking and

hydrodesulphurisation, for instance, as well as in making gasoline and fuel oils^[84].

In a broad sense, catalytic processes may be separated into homogeneous catalysis, where all the substances involved are in the same physical phase, e.g., gas or miscible liquids, and heterogeneous catalysis, where frequently the catalyst is a solid and the reactants are in another phase when in contact with the catalyst. It is noteworthy that a particular feature of the present study, which distinguishes it from most other catalytic applications, is that, although the process may be still regarded as heterogeneous catalysis, the catalyst is not in the solid state, but rather, as will be seen, it is dissolved in the leaching solution of a hydrometallurgical process. The solid, in this case the gold sample, has its dissolution rate increased by the oxidative properties of the catalyst, which, in turn, keeps the same initial concentration throughout the process.

Since the primary aim of this research was to look for an organic compound (or compounds) that could be conveniently used as catalytic oxidizing agents for the cyanidation of gold, it was found that the most similar processes that could provide relevant information were:

(1) processes that deal with the precipitation of metals dissolved in aqueous solutions through gaseous reduction, employing an organic catalyst to enhance the overall kinetics of the process. It is evident that in this case what is attempted is exactly the opposite to the objective of the present investigation, namely to dissolve the metal into solution. Nevertheless, this path was followed since the information provided by the related works could well prove relevant, concerning the basic chemical and thermodynamic features of the reagents used.

(2) processes related to gas purification with liquids (washing) which are carried out with the aid of organic compounds as catalysts in liquid phase oxidative regimes, since it was known beforehand that there are a number of processes which employ organic compounds (e.g., hydroquinone) as catalyst or oxygen carriers for the oxidation of hydrogen sulphide (H_2S) to elemental sulphur. This idea was conceived as early as 1921 when a British patent (168,504) was granted to Evans and Stanier, whose process employed certain organic dye stuffs^[27].

(3) finally, those processes where the rate of leaching is improved by the addition of an organic catalyst, even if not specifically acting as an additional oxidizing agent, for, as stated earlier, catalysed oxidative leaching is not commonly encountered in the literature.

In the next section, the basic studies relating to the topics listed above are reviewed. It is emphasized that this review does not intend to be exhaustive; as stated in an earlier part of this section, catalysis is a broad domain, and without doubt much additional research has been performed. However, the aim here was to gather data to be used in a very focused perspective, i.e., to the cyanidation of gold. As will be seen, the information collected was able to be used to shape the foundation upon which the present investigation was then based.

2.2 - The search for a suitable catalyst

The practice of reducing metals from solution with the aid of gaseous compounds is relatively common and frequently referred to in the hydrometallurgical literature. Hydrogen is the most widely used

reducing agent, although carbon monoxide and sulphur dioxide have also achieved some attention^[28,29]. One of the difficulties faced by this type of process is that the formation of a new (solid) phase in the solution usually necessitates catalytically active surfaces, to serve as nucleating sites. In this respect, Meddings and Mackiw^[30] worked on the gaseous precipitation of some metal ions, including the reduction of silver, copper, cobalt and nickel, but it was with this latter element that the use of anthraquinone as an organic catalyst was reported. They found that a component such as anthraquinone (and structurally related compounds) accelerated the rate of nickel reduction with gaseous hydrogen from aqueous solution. It is believed that the anthraquinone increases the effective area of sites, or "active centres", where the reaction between the hydrogen molecules and nickel seed surfaces may take place; however, the exact mechanism through which this outcome is actually achieved was regarded as not very clear. They noticed that, surprisingly enough, the catalytic effect of anthraquinone was not observed in the hydrogen reduction of cobalt solutions.

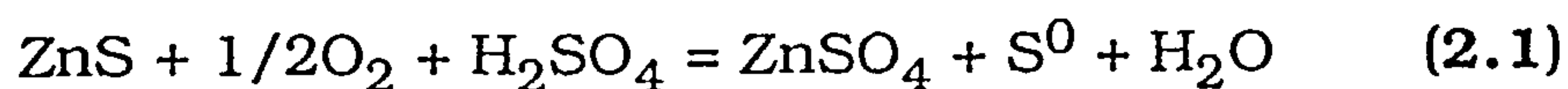
In a similar manner, Mackiw et al.^[31] studied the reduction of metallic nickel, with hydrogen under pressure, from ammoniacal nickel sulphate solution, employing ferrous sulphate as a catalyst required to initiate the first reduction, which is then accelerated by the continuous formation of nickel nuclei (autocatalysis). While the ferrous salt was termed as a catalyst, it would be probably better described as a seed, which is responsible for the reaction starting up. The process was conducted in mechanically agitated autoclaves, where hydrogen was injected under pressure at temperatures of around 180°C. The same technique is also dealt with by Meddings^[32] in a more recent paper where the commercial application of the process is described. Hydrogen gas is injected into the autoclave and the nickel solution is

nucleated by ferrous sulphate, which is added before the hydrogen. This results in a very rapid reduction and the "formation of a very fine nickel powder"^[32].

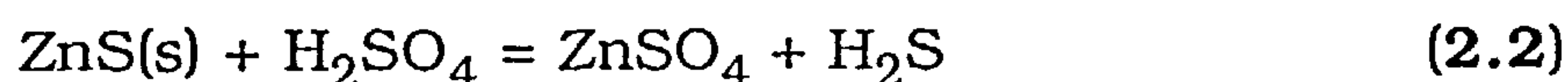
The catalytic effect of anthraquinone is again described by Meddings and Evans^[33,34], who patented a process for producing individual phosphorus particles "completely enclosed in a metal coating". Although a catalyst was not necessary for the reduction of the phosphorus particles, the addition of a small amount (about 0.01 to 1.00 g/l) of a member of the group of anthraquinone compounds, to act as a catalyst, was claimed to be necessary "to produce a uniform and continuous coating of the metal on the individual phosphorus particles". According to the results obtained in these works, the usual problem that is to initiate the reducing reaction may be conveniently solved by adding the aforementioned catalyst, which acts as a nucleating agent.

The catalytic ability of certain substances such as copper salts, platinum and charcoal to increase the reduction rate of dissolved elements by gases has long been recognized. This feature was quoted as early as 1931 by Lamb and Elder^[35] as a way to overcome the low rate at which gaseous oxygen establishes its potential on inert electrodes. George^[36] used cupric ions (perchlorate) to catalyse the oxidation of ferrous ions by molecular oxygen, although the effect was reported to be small. In phosphoric acid solutions, Cher and Davidson^[37] reported a substantial catalytic effect of added cupric ions on the rate of Fe^{2+} oxidation by oxygen; Hoffman and Davidson^[38] also found evidence that cupric ions may enhance the rate of Fe^{2+} oxidation in sulphuric acid solutions. Scott and Dyson^[39] studied the influence of catalytic agents, such as copper, bismuth, ruthenium, molybdenum and iron, on the oxidation of ZnS, under pressure leaching conditions.

According to this work, the reaction



proceeds at rather slow rate. This can be greatly increased by the addition of certain cations such as those mentioned above. More recently, Corriou et al.^[40] showed that the leaching of zinc sulphide in aqueous sulphuric acid was inhibited by hydrogen sulphide (formed during the process) but accelerated by the presence of activated carbon. Earlier, Jan et al.^[41] had already stated that the rate-controlling step for zinc sulphide dissolution in sulphuric acid is determined by the oxidation of the hydrogen sulphide to elemental sulphur, according to the following proposed mechanism:



Accordingly, Corriou and colleagues noticed that the addition of hydrogen sulphide inhibits the solubilization of ZnS, which could even be blocked altogether by introducing an excess of H₂S under a partial pressure of 10⁶ Pa even at a temperature of 180°C. On the other hand, they detected an enhancement of the dissolution rate of ZnS by a factor of 10 at 130°C when only 1g of activated carbon was introduced into the reactor. They proposed that the adsorptive character of the carbon was sufficient to accelerate the ZnS dissolution by removing the hydrogen sulphide in the first step of the process (reaction 2.2) and, therefore, displacing the chemical equilibrium to the right.

Thomas and Ingraham^[42] used activated carbon to catalyse heterogeneously the oxidation of ferrous ion by oxygen from air in sulphuric acid solutions. The rate of the reaction is said to increase by

more than 2000 times if activated carbon is used. The experimental results were explained by the expected behaviour for a surface reaction in which the surface is covered with oxygen, acid, ferrous and ferric ions. They assumed that ferrous and ferric ions compete equally to be adsorbed on selected sites, with the hydrogen (from the acid) also being adsorbed but "more strongly than the other reactants"^[42]. This was further used to explain the fact that when the sulphuric acid concentration is over a critical value, the increased adsorption of acid decreases the adsorption of other reactants, thus decreasing the rate of ferrous oxidation. It was also noticed that, since quinone type compounds may be successfully used to produce hydrogen peroxide^[43,44], which in turn can oxidize ferrous ion, hydroquinone was added to aerated acidic ferrous sulphate solutions; under these conditions, however, hydroquinone was not only found to be of little use as a catalyst, but also interfered to some extent with the catalytic effect of carbon. While no explanation was provided for this behaviour, it may be postulated that the hydroquinone might have also been oxidized by the available oxygen, thus decreasing the oxidation of the ferrous ions.

The catalytic effect of charcoal in the aerobic oxidation of Fe^{2+} ions in dilute HCl (0.1N - 4.0N) was also investigated by Posner^[45,46]. He concluded that the increase in the rate of oxidation is directly proportional to the catalyst concentration and its specific area.

Other and more complicated types of organic (homogeneous) catalyst have also been described. In order to speed up the rate of oxidation of some sulphide compounds (hydrogen sulphide to sulphur, thiosulphate and sulphate) by oxygen in aqueous solutions, Hoffmann and Lim^[47] investigated the effects of cobalt(II), nickel(II) and copper(II) 4,4',4'',4'''-tetrasulphophthalocyanine (TSP^{2-}) with varying

degrees of success (phthalocyanines are macrocyclic compounds, which readily form square planar complexes in which the metal atom is located in the plane of the ring and is bonded by four nitrogen atoms)^[47]. CoTSP²⁻ was reported to be an effective homogeneous catalyst for the oxidation of hydrogen sulphide in aqueous solution, with additions of ppb quantities resulting in a rate increase by a factor of 10^4 ; CuTSP²⁻ and NiTSP²⁻, however, were found to be less effective catalysts.

The catalysed oxidation of organic compounds by non-organic elements has also been reported. Heitler et al.^[48], for instance, studied the oxidation of ethanol by hydrogen peroxide, catalysed by ferric ion (ferric perchlorate). The conditions were acidic, and it was found that no oxidation of ethanol could be detected in the absence of ferric perchlorate, which was presumed to be acting as a catalyst. The oxidation kinetics of hydroquinone by oxygen was studied by Astanina and co-workers^[49], in aqueous solutions containing Fe²⁺ as catalyst at 30-50°C. The results were reported in terms of the hydroquinone effect on the Fe²⁺ oxidation; hydroquinone inhibits the oxidation of ferrous ions by reducing Fe³⁺ to Fe²⁺. It is suggested that the catalytic effect of Fe is related to the Fe²⁺ $\leftrightarrow$ Fe³⁺ valence change, which serves to transfer electrons from hydroquinone to oxygen.

By taking a slight shift in the course of the inquiry, it is realized that many investigations on processes for gas purification with the aid of an organic compound to be used as a catalyst and/or oxygen carrier (as well as with heterogeneous solid catalysts) have been carried out. Most of them deal with the oxidation of hydrogen sulphide (H₂S) to elemental sulphur^[27,50,51,52,58,64]. However, attention here will be drawn to those processes related to the first category, i.e., those in which organic compounds are the main agents of a liquid phase

homogeneous or heterogeneous catalytic oxidation process, to comply with the primary purpose of this investigation.

As stated earlier, the possibility of using organic compounds as catalysts or oxygen carriers for the oxidation of hydrogen sulphide was conceived in the early 20's, in the U.K.^[27]. The processes normally in operation nowadays employ moderately alkaline solutions containing water-soluble salts of quinone-type compounds which are capable of, directly or indirectly (see later), oxidizing the hydrosulphide ions to elemental sulphur. These quinone-type compounds, when in their reduced state, may be readily reoxidized by simple contact with air. This mechanism, thus, allows them to be constantly reused in a cyclic (catalytic) process.

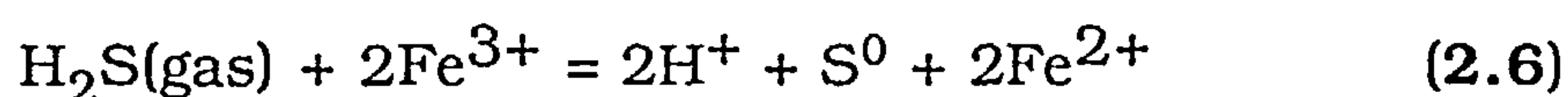
The Perox catalytic wet purification process was first developed in Germany, shortly after the 2nd World War^[27,53,54]. The absorption of H₂S is carried out in aqueous ammonia solution containing around 0.3 g/l of an organic catalyst, which is normally hydroquinone. This is followed by the oxidation of ammonium hydrosulphide to elemental sulphur by contact with air. At this stage it is reported that "the catalyst does its work in speeding up the oxidizing reaction":



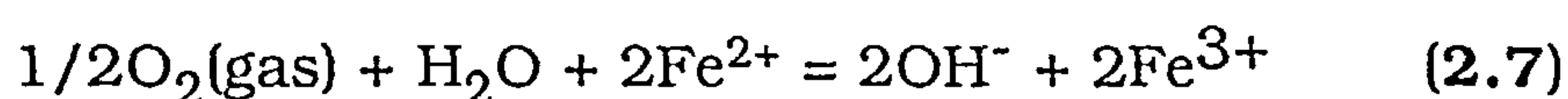
The sulphur, produced as a fine precipitate and carried forward with the air, aqueous ammonia solution and the catalyst, may be used for sulphuric acid manufacture or for agricultural ends. The catalytic washing medium, after being separated from the sulphur, is returned to the circuit. Not much information is provided on the exact mechanism of the role played by the catalyst, but the addition of small amounts of a quinone-type compound is said to produce "rapid

oxidation of hydrogen sulphide without diminishing the washing properties of the solution"^[54].

Hardison^[55] described a one step process (called "LO-CAT", as a trade mark) for removing H₂S from gas streams and producing elemental sulphur. It consists of a liquid phase oxidation method that employs an aqueous solution of iron, kept in solution by an organic chelating agent. The organo-metallic catalyst oxidizes the H₂S, leading to the reduction of iron; this is recirculated to an oxidizer to be regenerated (oxidized) by contact with air; it can then be reused. The overall reaction is



and for the iron regeneration



It is interesting to note that neither ferrous nor ferric ions are stable in neutral or alkaline solution. The precipitation is prevented by the complexation of the iron with the organic chelate, capable of holding both forms of iron in solution.

It is also reported that the LO-CAT process has been under development since 1972 and that it shows considerable advantages over other processes, such as Stretford and Takahax. The latter employs naphthoquinone compounds^[56,57] (normally 1,4-naphthoquinone, 2 sulphonic acid) as oxygen carriers, dissolved in alkaline aqueous media. The overall scheme of the Takahax process is basically the same as the Perox and LO-CAT previously described, although it is claimed that the oxidation of hydrosulphide to elemental sulphur occurs at a higher rate than in other processes. There are

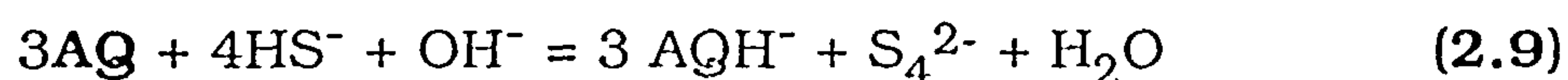
about one hundred units in operation in Japan, mainly in gas works, steel and chemical plants.

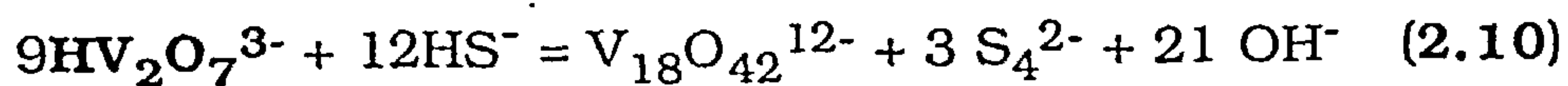
The Stretford process is described by Pylant^[59] as highly effective for removal of hydrogen sulphide from various gas streams. As will be seen later, this process provided interesting information, which helped considerably in the decision to use an organic catalyst in the leaching cyanidation of gold. The Stretford process was originally developed by the North Western Gas Board and the Clayton Aniline Co. of England to remove H₂S from coal gas, but it proved later to be also suitable for the desulphurisation of other gas streams, such as refinery gases and natural gas^[27,63,64,73]. It is reported that this method involves the spraying of the gas stream with an aqueous solution of anthraquinone sulphonic acid salts, which react with the H₂S, forming the corresponding hydroquinone. This solution is sent to an oxidation tower where the hydroquinone is reoxidized to its original state; it is then ready for another cycle. More recently, Thompson^[60] studied this process and described it in more detail. Basically, it comprises the following steps:

-Hydrogen sulphide dissolves in an alkaline solution producing hydrosulphide ions:



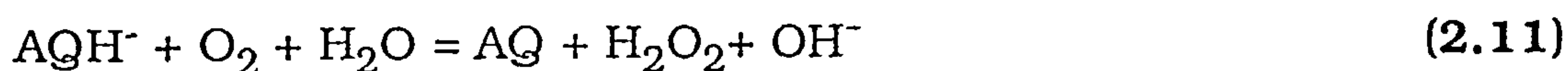
-In the absorber and reactor vessels the hydrosulphide ions are oxidized to form polysulphides (such as S₄²⁻) and the two oxidizing agents, vanadium (V) salts and anthraquinone derivatives (AQ), are reduced:





In earlier processes, anthraquinone-2,7-disulphonic acid (AQ27DA) was used as the oxidation catalyst, but it has been demonstrated elsewhere^[61] that various other substituted anthraquinones have at least as good as or superior activity to AQ27DA.

-In the oxidizer the reduction of oxygen with the anthraquinol (AQH) leads to the production of H_2O_2 , as follows:



This hydrogen peroxide can achieve the oxidation of the polysulphide ions to form elemental sulphur:



and it also reoxidises the vanadium reduced in the first step (reaction (2.10))



although the regenerated anthraquinone is also said to be able to oxidize the reduced vanadate^[27]. The air bubbled serves also to recover the sulphur produced by froth flotation, since the nature of elemental sulphur is hydrophobic.

Therefore, it may be inferred from the foregoing that to be an effective oxygen-reduction catalyst, the anthraquinone derivative must yield the maximum of hydrogen peroxide in the oxidizing vessel. Early Stretford plants used solutions that contained only anthraquinone derivatives,

and they had low throughput rates because of the slow reaction kinetics between AQ and HS^- ions (reaction (2.9))^[60,73]. The addition of vanadium (V) salts to the process has greatly improved its oxidation kinetics, probably due to the role of intermediate thiovanadates, formed during the reduction of V(V) to V(IV). It is also interesting to note that, while the vanadium readily reacts with the hydrosulphide, it will not be regenerated without the presence of the anthraquinone^[27].

Analysis of the information collected from the works quoted above leads to the initial assumption that compounds such as anthraquinone derivatives might prove useful as cyclic oxidizing agents in systems where the overall rate may be improved by an adequate supply of oxygen. This postulation is applied to the particular situation of the cyanidation of gold, where the anthraquinone may play the role of an additional oxidizing agent, while at the same time not only being continuously regenerated but also yielding "in-situ" hydrogen peroxide. This, as seen earlier, has been regarded as useful in the cyanidation process by some investigators^[18,19].

2.3 - Anthraquinone: a catalyst for the cyanidation of gold

Anthraquinones were originally obtained by the oxidation of anthracene; the suffix "anthra", from the Greek "coal", indicates its origin, since anthracene was first obtained from this source^[65]. Quinones are substances in which two hydrogen atoms of the benzene structure are replaced by two oxygen atoms, as in FIGURE 2.3.1. The products are distinguished as "ortho" and "para" quinones, according to the relative positions of the oxygen atoms (no "meta"- quinone has been isolated).

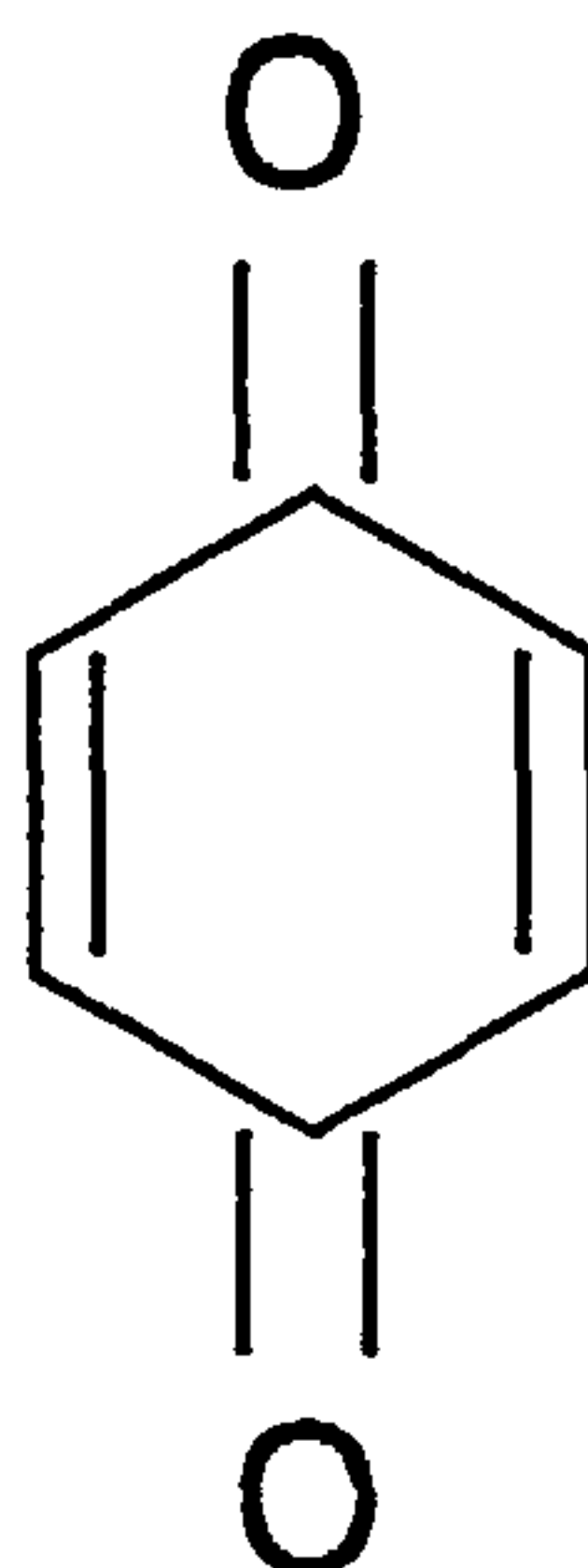


FIGURE 2.3.1 - Quinone molecular structure (para-quinone)

The quinone structure plays an important role in theories concerning the relationship of chemical constitution to colours. The most important characteristic reaction of quinone-type compounds is the reduction to the corresponding dihydroxy form, which is depicted in FIGURE 2.3.2:

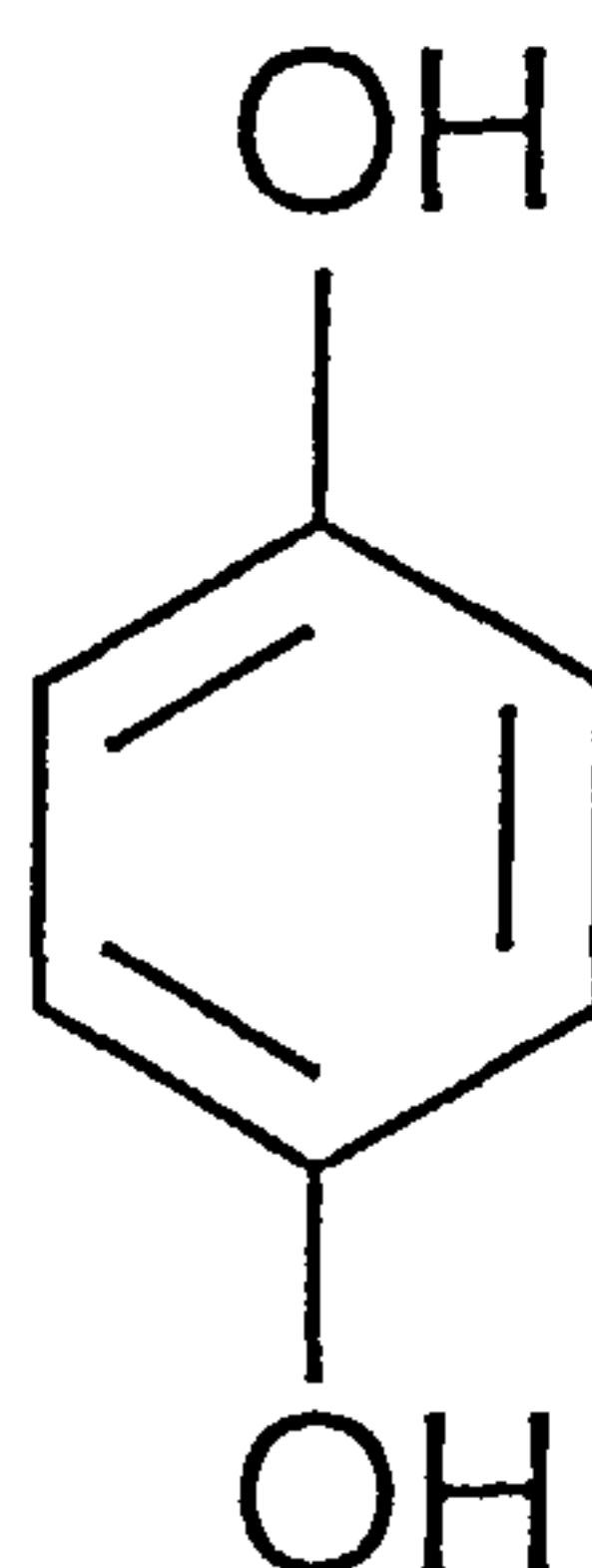


FIGURE 2.3.2 - Hydroquinone molecular structure

Anthraquinones, also called 9,10-anthraquinones, contain the two oxygen atoms bonded on an anthracene structure, as shown in FIGURE 2.3.3:

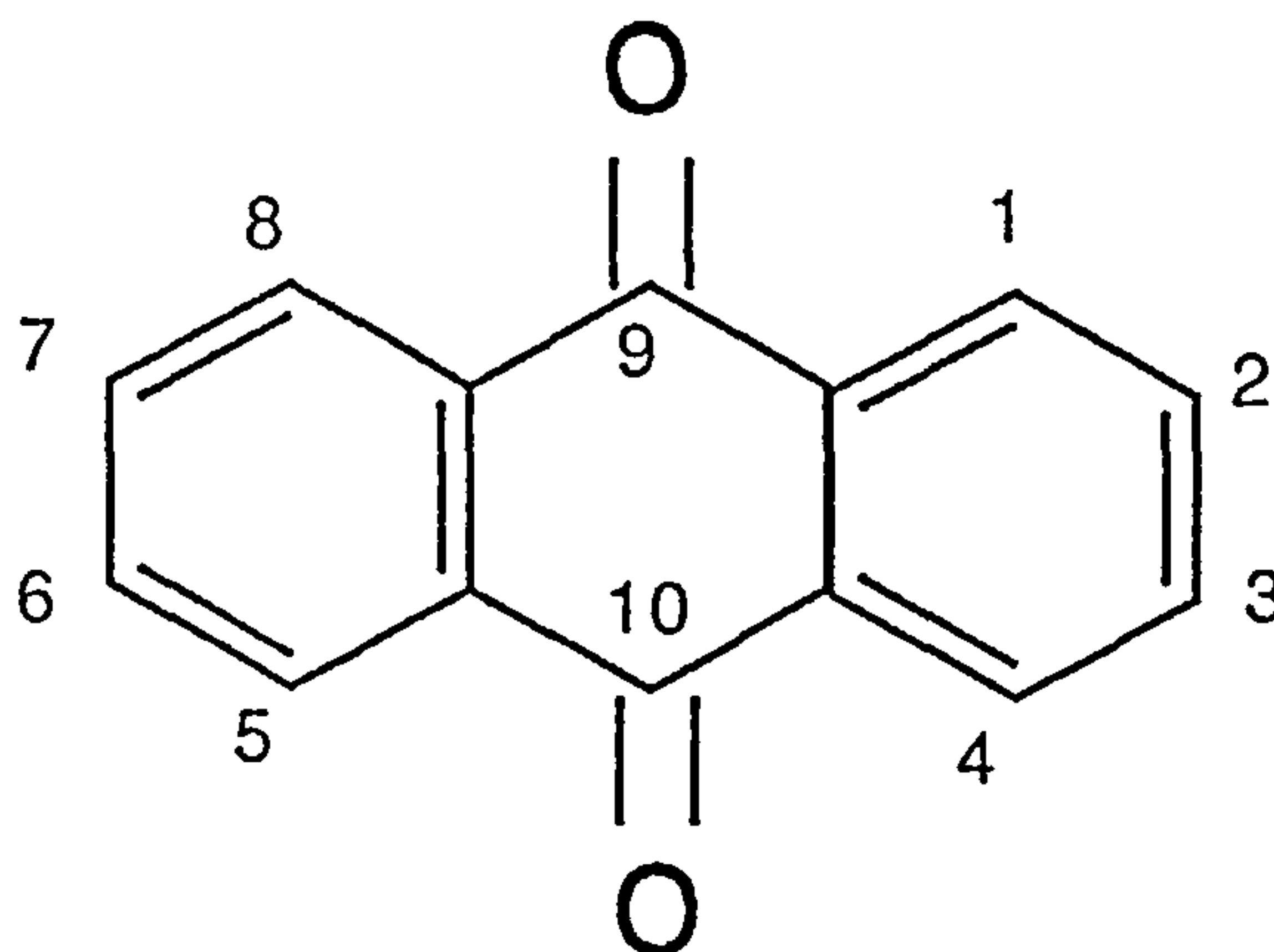
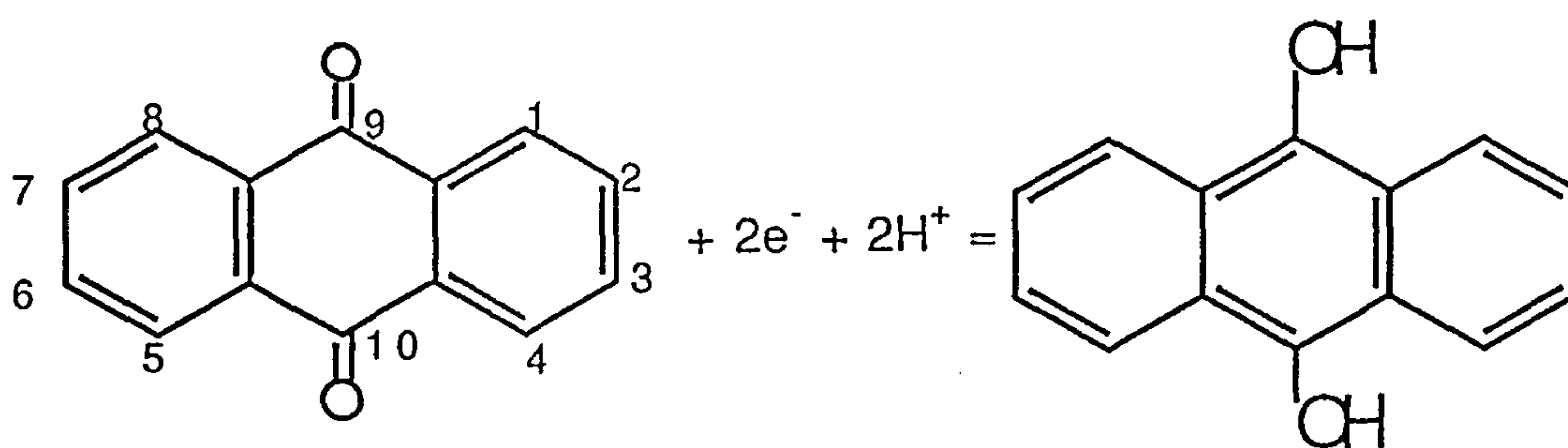


FIGURE 2.3.3 - 9,10-Anthraquinone molecular structure

When aromatic hydrocarbons or their derivatives are treated with H_2SO_4 , they yield sulphonic acids in which a hydrogen of the benzene nucleus is replaced by the sulphonic group SO_3H^- . Anthraquinone sulphonic acids are important intermediates in the preparation of dye-stuffs. The sulphonation of anthraquinone and its derivatives is regarded as highly important because it imparts water solubility to the almost totally insoluble anthraquinone, as well as an affinity for wool and silk^[65,66].

The anthraquinone displayed in Figure 2.3.3 is the most important quinone derivative of anthracene and is the source of a large class of dyes and pigments. Each of the functional groups can be reduced to a hydroxy group. This is regarded as an electron transfer followed by a protonation. When both groups are reduced a quinol is produced, as in equation 2.14:

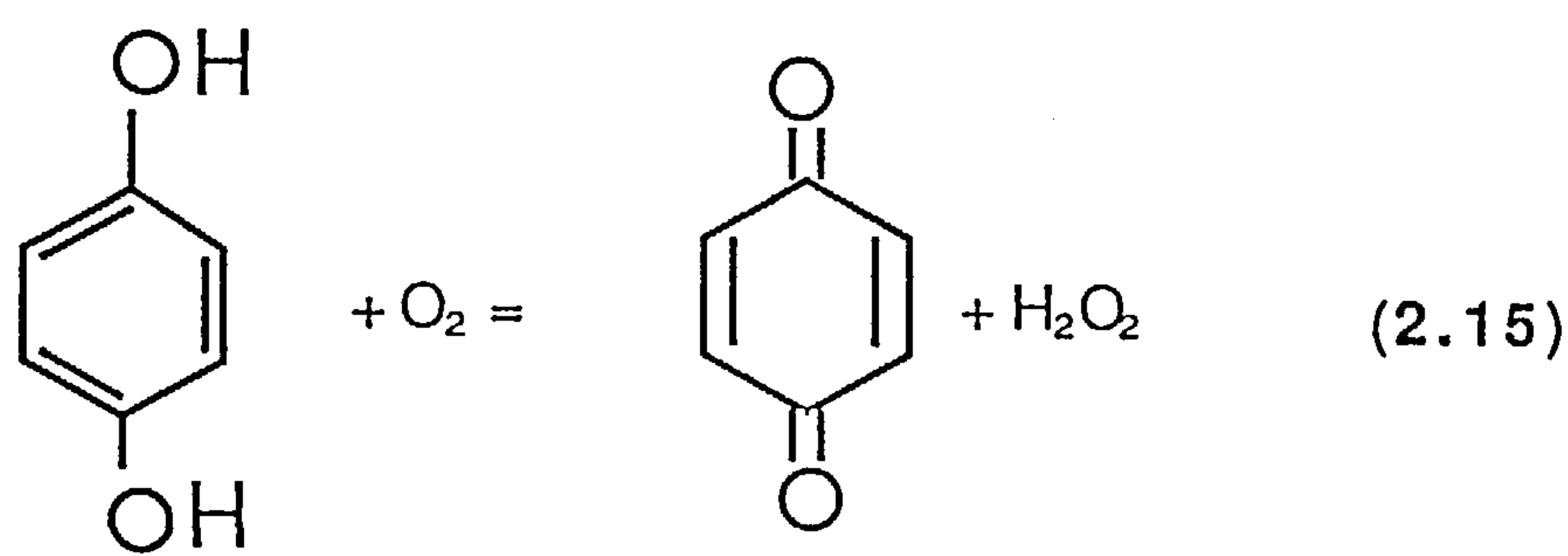


The reduction, however, is not so straightforward, but is seen as a complex phenomenon and commonly described as proceeding through nine possible intermediate species^[67,68]. The back oxidation of the reduced species not only leads to the regeneration of the original quinone, but also to the formation of hydrogen peroxide (see below).

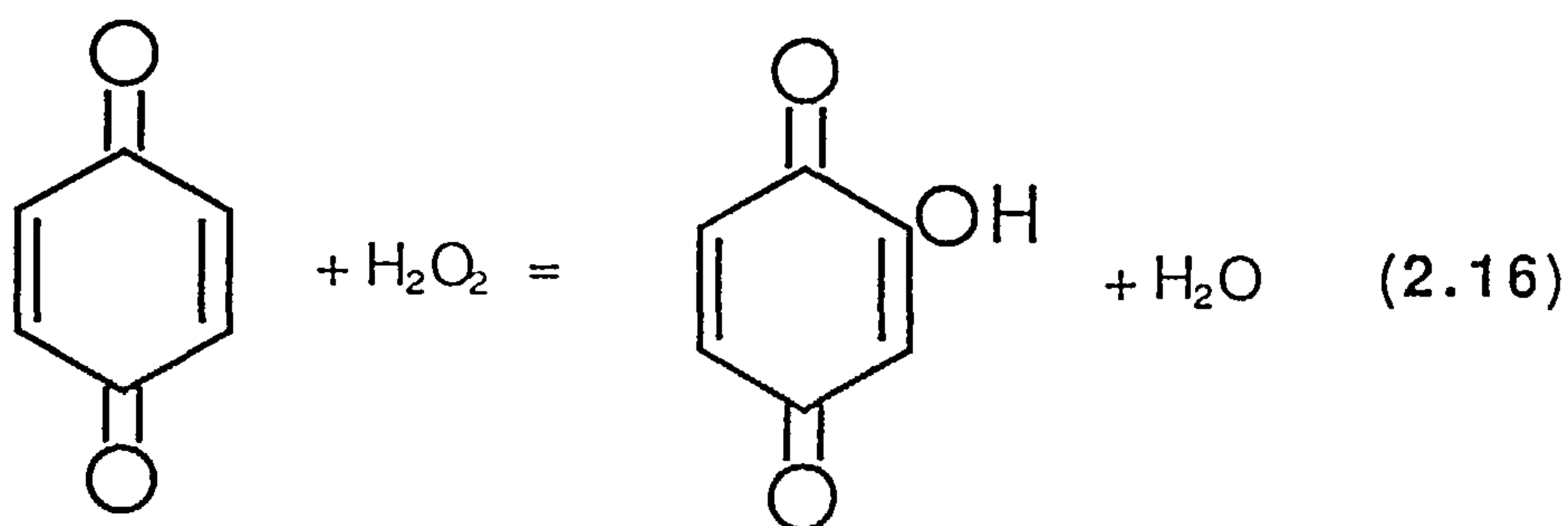
Filson and Walton^[69], in the mid 30's, discovered in pioneering work that anthraquinone and certain quinone type compounds form hydrogen peroxide in a cyclic autoxidation process. The first commercial process based on the oxidation and reduction of 2-ethylanthraquinone was developed in Germany and led to the production of concentrated hydrogen peroxide. Later, Atherton and Turner^[70] investigated the production of hydrogen peroxide in a solution of caustic soda by the oxidation of anthraquinone or equivalent dye. This had been previously reduced by the passage of hydrogen in the presence of a heterogeneous catalyst (nickel particles). Nowadays, hydrogen from the cracking of butane is used to reduce the quinone with palladium as a heterogeneous catalyst in free suspension (producing the corresponding anthraquinol). Hydrogen peroxide is extracted from the oxygenated organic solution in countercurrent columns, where its concentration in the working solution drops to about 20%^[71,72]. A major feature of this method of production is that, after oxidation, the quinone type compound can be reduced and then

again oxidized to produce hydrogen peroxide; as a consequence, the organic agent is continuously recycled during the process.

Many aromatic compounds such as hydroquinone, dihydroxymaleic acid and anthraquinone dyes may form hydrogen peroxide on autoxidation, although in most cases H_2O_2 disappears by back reaction as fast as it is formed. This reaction is complex and depends on the structure of the autoxidized compound. The first step is, probably the formation of quinone and hydrogen peroxide^[44] as:

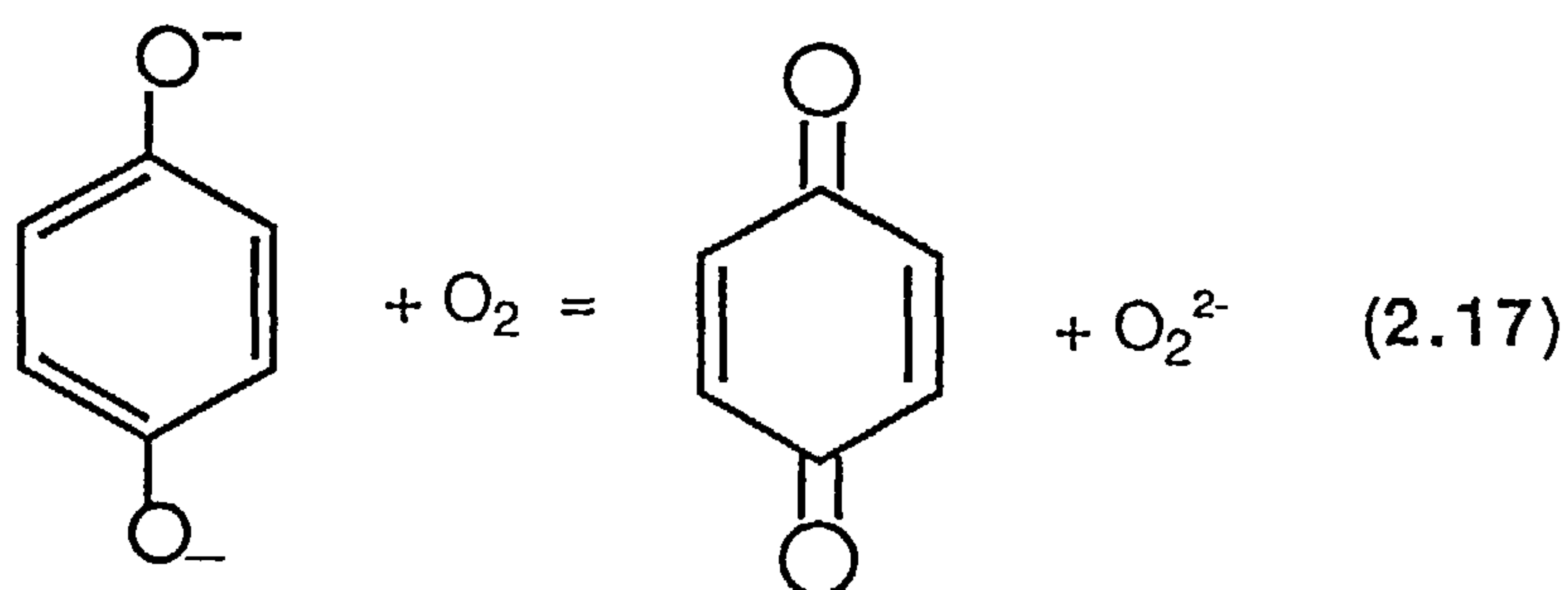


The reaction between the quinone formed and the hydrogen peroxide proceeds rapidly with the formation of water and hydroxyquinone:



thus consuming all the hydrogen peroxide that had been formed. However, if the reactive hydrogen atoms attached to the benzene

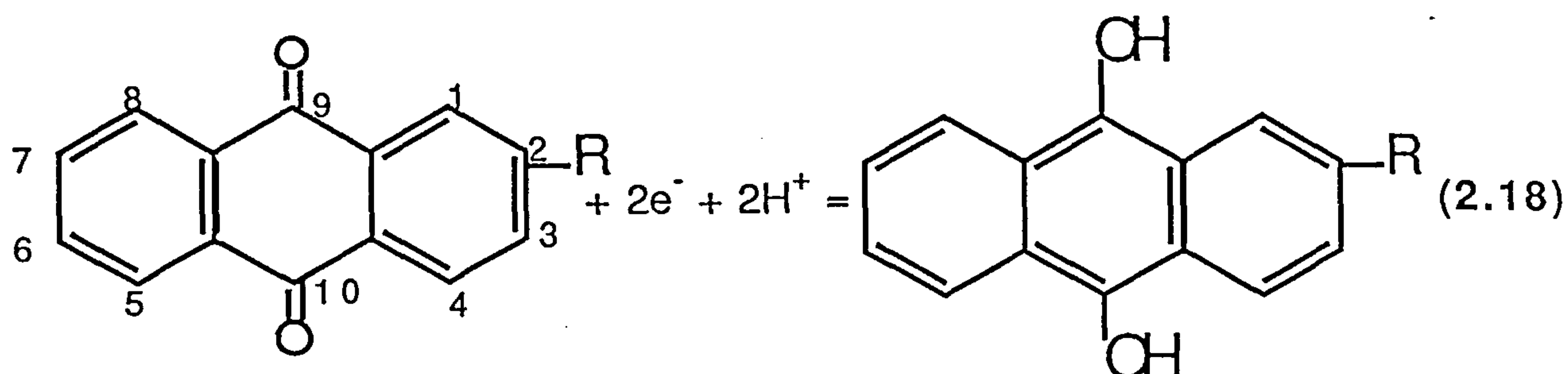
nucleus are replaced by inactive atoms or groups, no reactions take place after the autoxidation and then the hydrogen peroxide can be separated. In these circumstances the autoxidation of anthraquinone sulphonic acid, for example, results in a quantitative formation of hydrogen peroxide and the related quinone-type structure. It is believed that the reaction takes place first with the formation of a double charged anion of the quinone, which then reacts with oxygen to form the peroxide ion:



The use of products containing sulphonic acid groups is preferred and commonly used in industrial operations because of their relatively high solubilities in water, although the possibility of using other quinone-type compounds has also been mentioned^[44,61].

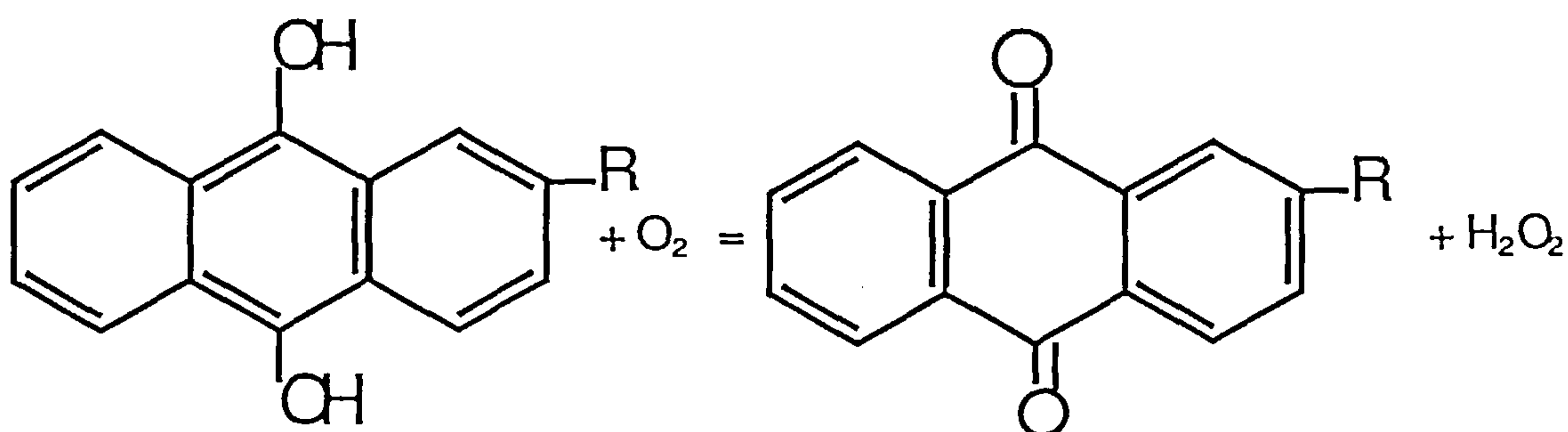
Generically, thus, the main reactions representing the production of hydrogen peroxide from the autoxidation of an anthraquinone derivative may be illustrated in the following way:

-hydrogenation of the anthraquinone



-oxidation of the anthraquinol (or anthrahydroquinone)

(2.19)



At the same time, it is worth noting that, while the process described above already occurs on an industrial scale, the "in-situ" production of hydrogen peroxide in **aqueous** solution should not be regarded as a merely academic possibility. Keita and Nadjo^[78] have already proposed that the reduction of anthraquinone derivatives into the corresponding anthraquinol (in aqueous solution), followed by the reduction of oxygen to hydrogen peroxide by the anthraquinol, may be an attractive possibility for the synthesis of small amounts of hydrogen peroxide. In this way, reactions whose rates are enhanced by the addition of small

amounts of hydrogen peroxide, or reactions controlled by the availability of oxygen, may well be benefited by this cyclic mechanism; this situation is particularly interesting in the case of the cyanidation of gold.

As outlined in the first chapter of this work, the rate of gold dissolution in the cyanidation process can be often hampered by a small availability of oxygen. The introduction of a supplementary oxidizing agent, namely hydrogen peroxide, to overcome this difficulty has been suggested. In the present work, however, instead of the addition of peroxide, it is proposed that anthraquinone-2-sulphonic acid (AQ) might be also useful if added to the gold cyanidation process. The major advantage of using this organic reagent is that it will not only act as an additional oxidizing agent, but its concentration will remain constant during the process. While this mechanism is described in more detail in a later chapter, its basic features may be generically represented by the following steps:

1-reduction of the anthraquinone to anthraquinol by the metallic gold (which, being oxidized, is taken into solution by the complexing agent - in this case cyanide).

2-oxidation of the anthraquinol by oxygen, with the regeneration of the original anthraquinone and simultaneous production of hydrogen peroxide.

3-the cycle starts again, this time with the hydrogen peroxide formed "in-situ" as an additional oxidizing agent.

The AQ concentration is, therefore, kept constant throughout the process. Moreover, as will be seen later, an additional characteristic of this cyclic mechanism is that AQ does not increase the rate of cyanide oxidation, which occurs at the same rate as when oxygen is the sole

oxidizing agent used.

2.4-Thermodynamics

2.4.1-Quinones

While equilibrium information about reactions taking place in solution is commonly summarized in potential-pH diagrams (Pourbaix diagrams), as a convenient means of visualizing the overall thermodynamic aspect of a system, little use has been made of this approach for organic compounds. However, Bayley and Ritchie^[74,75], in one of the few works specifically aimed at the construction of Pourbaix diagrams in the field of organic chemistry, have presented this type of diagram for certain organic oxidation-reduction reactions, including the study of some quinone type compounds. In their investigation some quinones were sulphonated in order to give them the required solubility in aqueous electrolytes. The Eh-pH diagram for 1,4 benzoquinone (para-quinone) is depicted in FIGURE 2.4.1. It should be noted that the numbers that appear by the lines of the diagram correspond to the equations involved in the calculation (which are reported in Appendix III) and not to equations shown in the text.

In this diagram, the oxidation-reduction intermediate species (the so-called semi-quinones) involved in the reactions have been neglected because they are said to be metastable and present only in very low concentrations^[74].

The equation represented in the acid region, up to a pH of approximately 9.8, corresponds to the reaction



from which the relationship

$$E = E^0 - \frac{0.0591}{2} \log \frac{(QH_2)}{(Q)(H^+)^2} \quad \text{eq.2.4.1}$$

may be written, with the symbols in brackets representing the activity of each species (which in dilute solutions may be considered as approximately equal to the molal concentration).

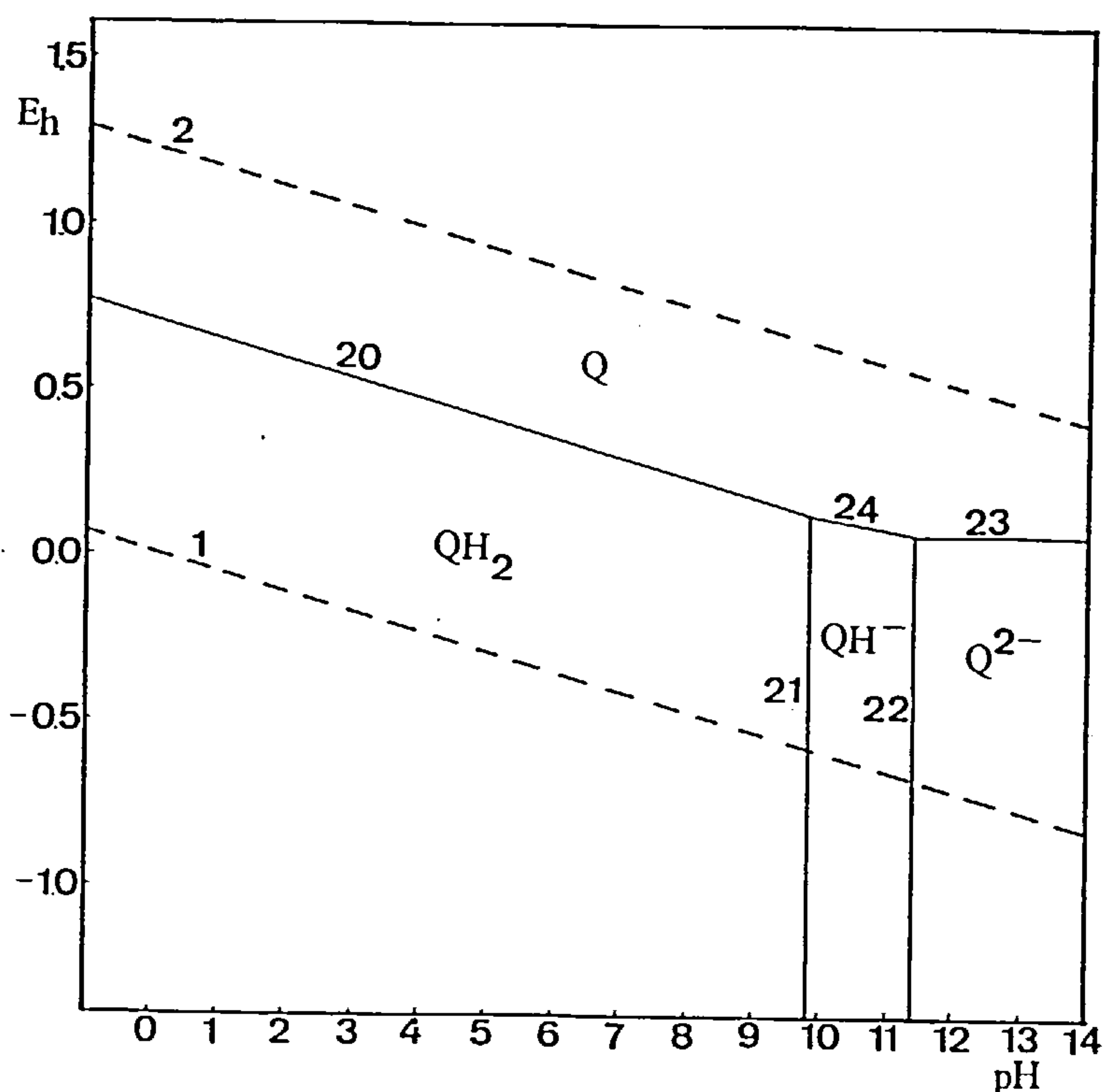


Figure 2.4.1- Eh-pH diagram for 1,4-benzoquinone, after Bailey and Ritchie^[75] (equations given in Appendix III).

Since $E^0=0.6998$ V (SHE)^[74], and assuming equal concentrations of oxidized and reduced species,

$$E = 0.6998 - 0.0591\text{pH} \quad \text{eq. 2.4.2}$$

As the pH increases, the quinone is reported to undergo two successive deprotonations, at around pH values of 9.9 and 11.5 respectively^[76], as shown in the diagram above. The quinone reactions to give these two new species may be represented as



and



For reaction (2.21), the following relationship holds

$$E = E^0 - \frac{0.0591}{2} \log \frac{(QH^-)}{(Q)(H^+)} \quad \text{eq. 2.4.3}$$

giving an equation of slope -0.0296 V per pH unit

$$E = 0.4530 - 0.0296 \text{ pH} \quad \text{eq. 2.4.4}$$

The second reaction, (2.22), is of course represented by a horizontal line with the second deprotonation occurring at pH=11.5^[76].

While the diagram depicted in Figure 2.4.1 is for 1,4-benzoquinone, it is believed that most similar quinone type compounds should follow this same basic pattern^[75]. The Pourbaix diagram for AQ, shown next, confirms this assumption.

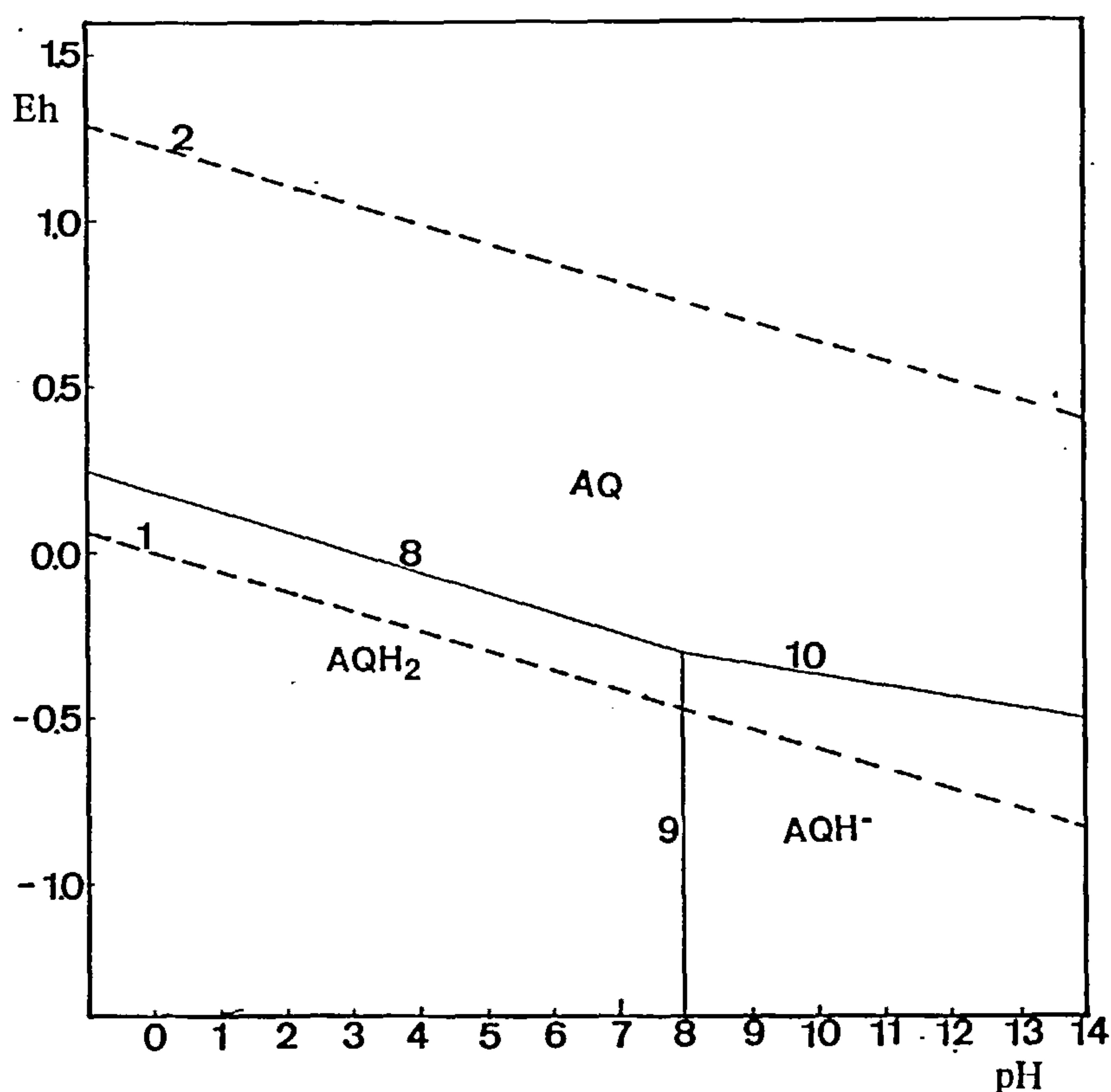


Fig. 2.4.2 - Eh-pH diagram for the system AQ - water, at 298K.

Moreover, it is worth noting that in strong alkaline solutions (pH above around 9.5) quinone type compounds begin to decompose, with the exception of those having an additional benzene ring. As seen earlier, this ring also prevents the hydrogen peroxide, formed by the so-called autoxidation of quinones, from reacting with the autoxidized compound, thus allowing it to be readily isolated. This characteristic applies, for example, to the anthraquinone-2-sulphonic acid employed in this work, which is reported as being stable over the entire pH range from 0-14^[75].

Although some conflicting information exists concerning thermodynamic values of organic compounds, the data used to draw this Pourbaix diagram were taken from the extensive compilation by Clark^[77] and the works carried out by Bayley and co-workers^[75], and are consistent with the fact that equilibrium diagrams of quinone type compounds follow the same basic format.

In the present case, the second deprotonation, shown earlier in the diagram for 1,4-benzoquinone, was not considered because this semiquinone is said to form only to a small extent in alkaline aqueous solution of anthraquinone-2-sulphonate. Ionization of $-\text{SO}_3\text{Na}$ has also been neglected^[77]. Thermodynamic data and the equations related to the construction of this diagram are reported in Appendix III.

2.4.2-Hydrogen peroxide

While a number of theoretically feasible processes for the production of hydrogen peroxide are quoted in the literature (e.g., from the oxidation of hydrocarbons; from inorganic peroxides, such as reacting barium peroxide with sulphuric acid to produce hydrogen peroxide and barium sulphate; electrolytic means)^[44], it is through the cyclic concept of the autoxidation of quinone-type compounds that most of the hydrogen peroxide is commercially produced (see former section).

Hydrogen peroxide is a metastable compound and its decomposition is also catalysed by trace levels of some metals in solution. Because of that, commercial hydrogen peroxide is stabilised with additives (strong chelating agents; the peroxy stabilizers) which slow down the decomposition kinetics by lowering the thermodynamic activities of those metals to almost zero. The Eh-pH diagram of the hydrogen

peroxide and water system is depicted in FIGURE 2.4.3.

Hydrogen peroxide may be formed under line 3 by the reduction of oxygen in solution as



Above line 4, it may be formed by the oxidation of water, according to

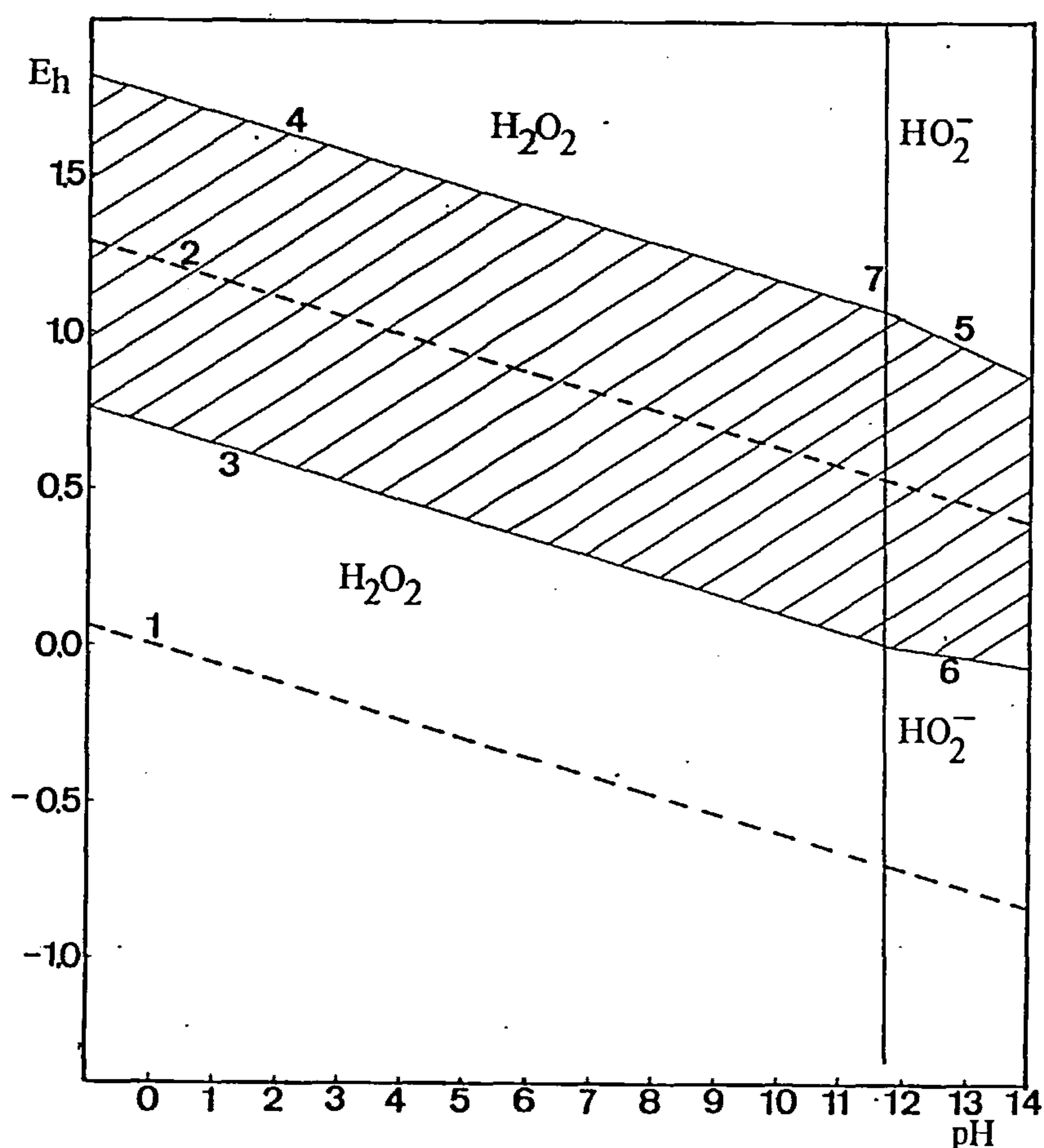


Fig.2.4.3 - Eh-pH diagram of the system hydrogen peroxide/water at 298K (shaded area represents the domain of double instability); $[\text{H}_2\text{O}_2] = 10^{-1}\text{M}$.

Within the region enclosed by these lines, H_2O_2 is unstable and reducible to H_2O , or unstable and oxidizable to oxygen; this, then, is a unique domain of double instability of H_2O_2 , which, within this region, may decompose chemically into H_2O and O_2 , as



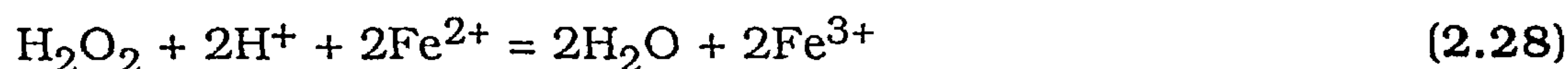
Under line 4 hydrogen peroxide acts as an oxidant with the formation of water; it will oxidize, for example, ferrous ions to ferric:



and



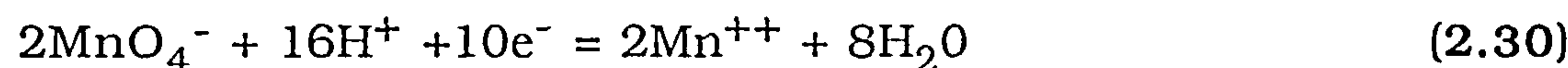
yielding



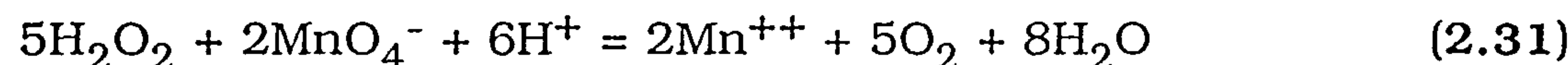
In the region above line 3, it will act as a reducing agent with the formation of oxygen; permanganate ions will be reduced, for example, into manganous according to:



and



to give



Therefore, if a hydrogen peroxide solution is contacted with a mineral whose electrode potential lies below line 3, it will act as an oxidant (reduction of H_2O_2).

A comparison of the peroxide Eh-pH diagram (Fig.2.4.3) with that of



the AQ (Fig.2.4.2) shows that hydrogen peroxide is thermodynamically stable with either AQ or AQH⁻, in the pH region where the cyanide leaching of gold is normally conducted (10.5 to 11.5).

2.5-Summary

A literature survey was carried out with the aim of discovering a suitable liquid-phase organic catalyst that might contribute as a supplementary and recyclable oxidizing agent (acting, therefore, as an oxidative catalyst) during the leaching of gold in the cyanidation process. Anthraquinone-2-sulphonic acid (AQ) was identified, at least theoretically, as a suitable reagent to do this. Other quinones could probably be also used, but AQ has the advantage of being soluble in water, besides being easily obtained and commonly used for the production of hydrogen peroxide.

CHAPTER III

REVIEW OF GOLD CYANIDATION

3.1-Introduction

Gold may occur in nature in native form, with iron sulphides, arsenic and antimony minerals, as tellurides, selenides and with carbonaceous ores. It is usually associated mainly with silver, copper, lead and the platinum-group metals. The amount of gold in ores varies considerably; nowadays, the gold content in an ore may reach an amount as low as 1 gram per tonne (and sometimes even less), but economical factors such as mine site and local governmental policies must be also obviously considered.

As seen in Chapter I of this work, the metallurgy of gold received a major impulse when John MacArthur, in the last century, patented a process in which a solution of KCN was used to dissolve gold from ores, by forming highly stable cyanide-gold complexes. This process is recognized as highly effective and is, certainly, the most widely used to process gold ores. In recent years, however, there has been an emergence of different lixiviants to overcome the challenge of working with different ores and/or refractory ones, or even to deal with environmental problems arising from the disposal of the toxic cyanide^[10,21,85,86].

It may be said that the main advantages of the cyanidation process are that gold is reasonably selectively dissolved by cyanide; silver is also

recovered; it is a relatively simple process, besides incorporating a great deal of industrial experience and technological improvements (compared to other reagents which are still being evaluated, such as thiourea or bromine^[85,87]),

On the other hand, cyanide is ineffective and/or not economically adequate to be used with certain "refractory" minerals such as those containing carbon or some sulphide minerals such as arsenopyrite, pyrite or stibnite. These ores usually must undergo a pretreatment, involving flotation, oxidative roasting or pressure leaching. Cyanide is also a highly toxic chemical and, therefore, must be disposed of with extreme care to avoid environmental problems; the cyanide leaching process suffers from slow kinetics mainly caused by the low solubility of oxygen in water. This latter hindrance is worsened at high altitudes, with increasing temperature and in heap leaching operations, where the gold at the bottom of the heap might not be leached at all due to lack of oxygen.

In order to dissolve, gold must be both oxidized and complexed, to allow the reaction to proceed. To overcome the problem of low oxygen supply, much research has been undertaken. Suggestions include, as mentioned previously, the injection of compressed air into the heap and/or the introduction, into the leaching solution, of an oxidizing agent which carries the oxygen in an already dissolved form, such as inorganic peroxides. In this particular situation, the addition of an oxidizing agent that may be cyclically regenerated might well prove useful. FIGURE 3.1 overleaf displays a typical flowsheet for the cyanidation process.

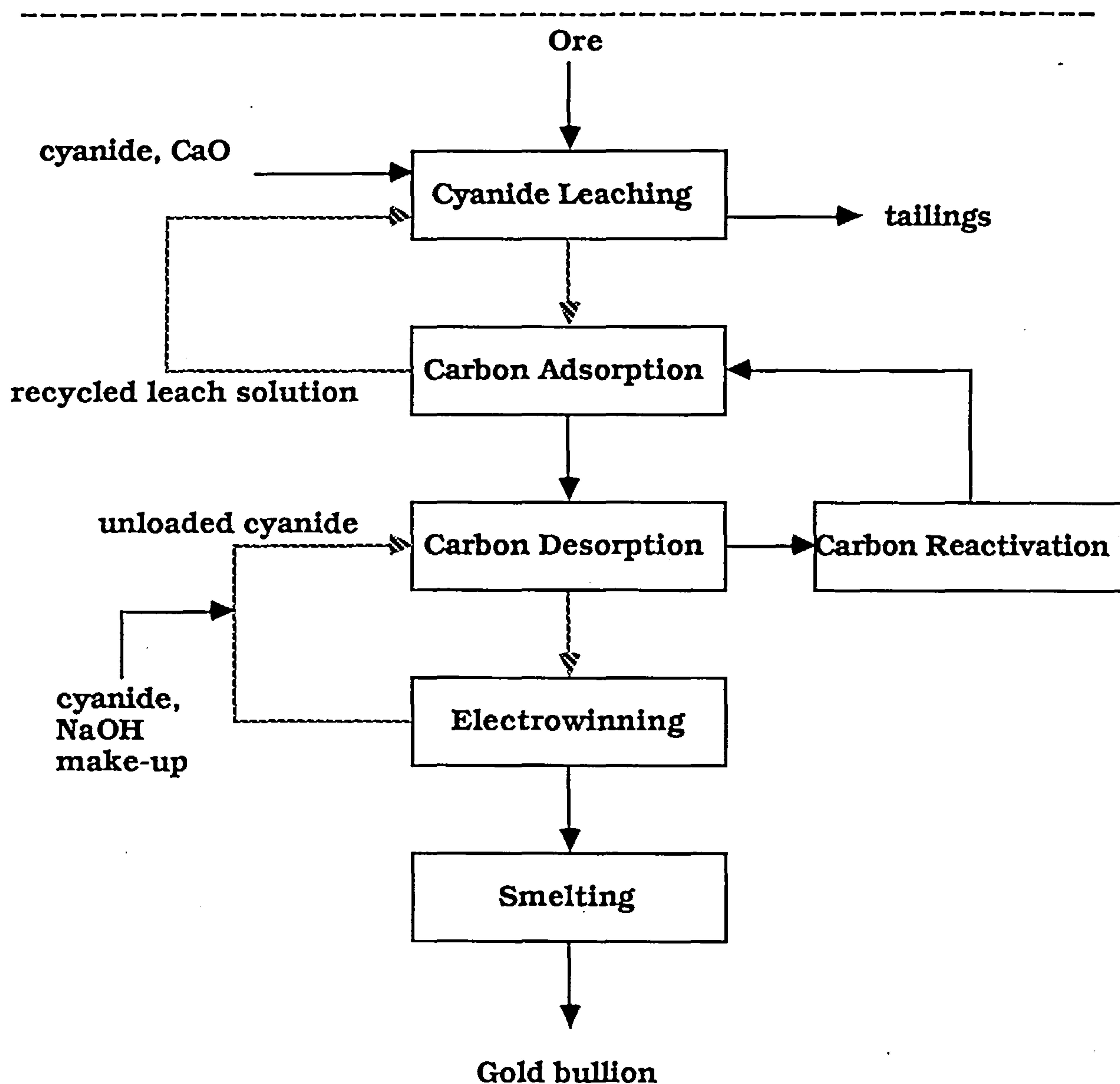


Figure 3.1 - Simplified flow-sheet of the cyanidation process for gold recovery.

The mechanistic steps involved during the dissolution of gold have been investigated employing mainly electrochemical techniques^[89...92]. Some research has been focused also on the understanding of the mechanism for the electrodeposition (gold reduction) from highly

concentrated cyanide solutions, since gold plating baths are normally operated under these conditions^[93,94]. In all these studies, a mechanistic path for the oxidation of gold and cyanide adsorption on the surface of the metal has been proposed. Basically, it has been demonstrated that the rate of gold dissolution in dilute cyanide solutions is controlled either by the amount of the cyanide or oxygen in solution, depending on the relative concentration of each. Some workers have also postulated that an excess of oxygen leads to passivation of the gold surface and, therefore, to a sharp decrease in the rate of metal dissolution, if the cyanide concentration is not increased accordingly. This mechanism was explained by the theory of the adsorptive nature of the cyanide and oxygen reacting on the gold surface. Nevertheless, there has been controversy regarding some fundamental points, as for example the optimum cyanide concentration capable of providing the highest rates of gold dissolution and the exact role played by hydrogen peroxide, either formed during the reduction of oxygen on the surface of the metal or added as an auxiliary oxidizing agent^[19,29]. With the advent of the technique of the rotating disc applied to the study of metal dissolution, during the fifties, many of the main features of the gold dissolution have been clarified. However, the actual pathway through which the oxidation of gold (and the counter part reduction of oxygen) is accomplished in alkaline cyanide solutions is still regarded as a complex phenomenon.

It is generally accepted nowadays that the dissolution of gold in aerated cyanide solution (KCN, for example) takes place according to one, or a combination, of the following simplified reactions (without taking into account the fact that intermediate species, normally highly reactive, might be formed during the process):



Reaction 3.1 was first proposed by Elsner, whereas the other two were suggested by Bodländer (these, as can be readily seen, in combination give the single Elsner equation)^[9,29].

The dissolution process is considered to be, most probably, an electrochemical reaction, with the cathodic and anodic zones of the metal linked as in a short circuit, as schematically shown in FIGURE 3.2 overleaf. At one part, the anode, the metallic surface is oxidized by giving up electrons to the oxidant (chiefly oxygen, under normal conditions) which in its turn is reduced on the cathodic part of the gold. Although this mechanism was established by the important work carried out by Kudryk and Kellog^[90], the dissolution of gold in cyanide had already been proposed to be a corrosion process by Brööntra^[96] (the first to suggest this type of mechanism) and also Thompson, in earlier works^[95].

It may be seen that, since the reduction of oxygen is the reaction responsible for the oxidation of gold and its subsequent complexation by the cyanide in solution, there will be no driving force for the process if no oxygen (air) is available in the leaching solution. However, as will be seen in the following chapter, it has been demonstrated in this work that even in the absence of oxygen it is possible to accomplish the dissolution of gold when a suitable oxidizing agent, such as anthraquinone-2-sulphonic acid (AQ), is present. Apart from oxygen (and hydrogen peroxide) this is the first time that an alternative oxidizing agent has been successfully demonstrated for the gold cyanidation process.

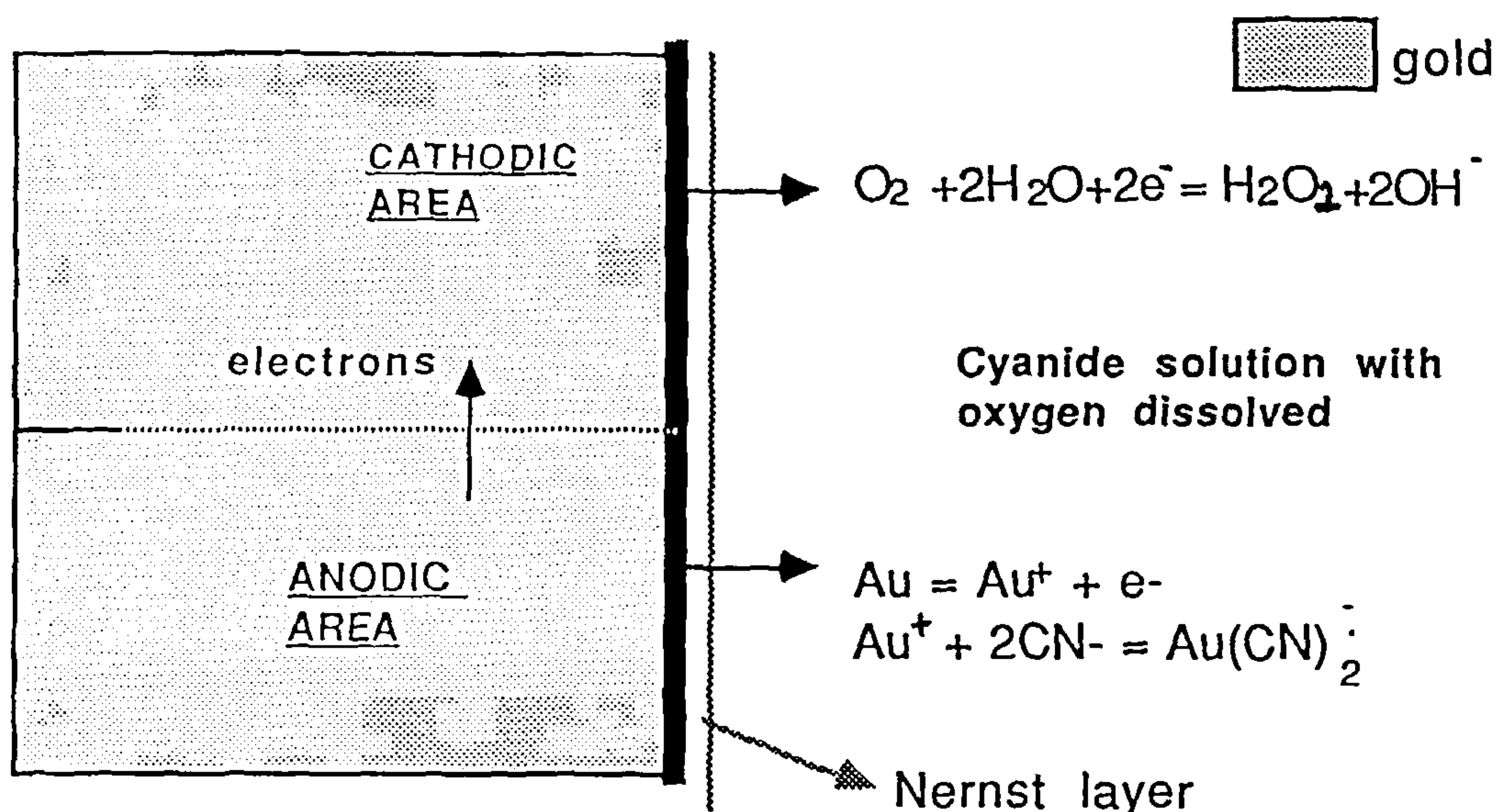


Figure 3.2 - Schematic electrochemical corrosion of gold in cyanide solution.

3.2-Thermodynamic considerations

Thermodynamically, neither aurous nor auric ions are stable in water if no complexing agents are present. FIGURE 3.3 displays the well known Eh-pH diagram for the system gold-water at 25°C. The activity of dissolved gold species is equal to 10^{-4} M. The two dashed lines delineate the region of water stability and the numbers appearing by each line correspond to the reactions given in Appendix III. Thermodynamic data used in both diagrams shown in this section were taken from Bard^[98], and the equations used for their construction are also given in Appendix III.

As may be seen from the figure, metallic gold occupies a large area of predominance, which includes the whole region of water stability. While in the diagram only $Au(OH)_3$ is shown, at stronger oxidizing potentials AuO_2 may also appear; these highly oxidized species, however, are solely a thermodynamic possibility, since they lie in a

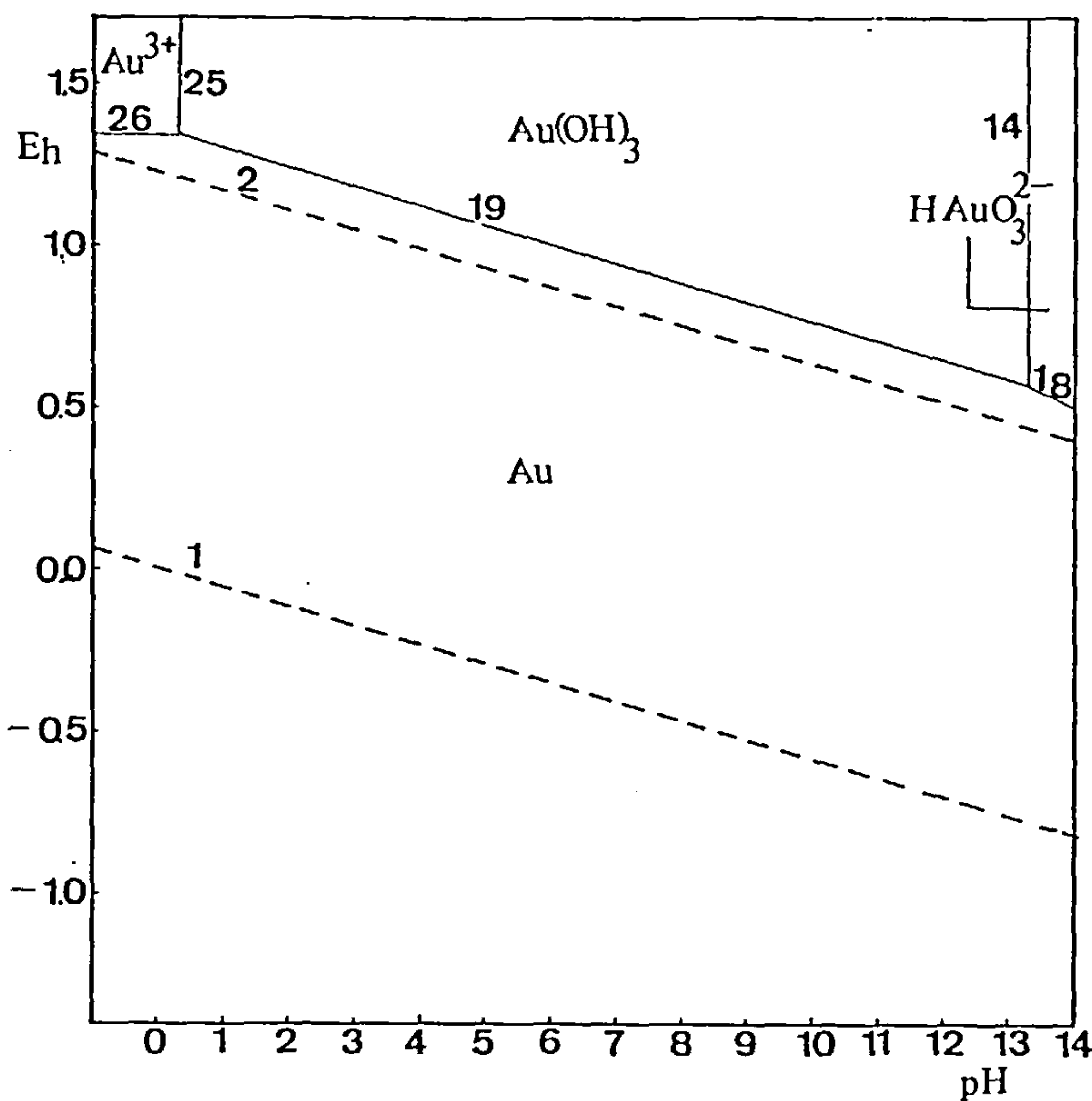


FIGURE 3.3-Eh-pH diagram for the system Au-H₂O at 298K; [Au]=10⁻⁴ M.

zone where water is no longer stable.

The introduction of a complexing agent, such as cyanide, in the gold-water system, greatly changes the regions of stability from the original diagram. The Eh-pH diagram for gold in the presence of cyanide ions is depicted in FIGURE 3.4.

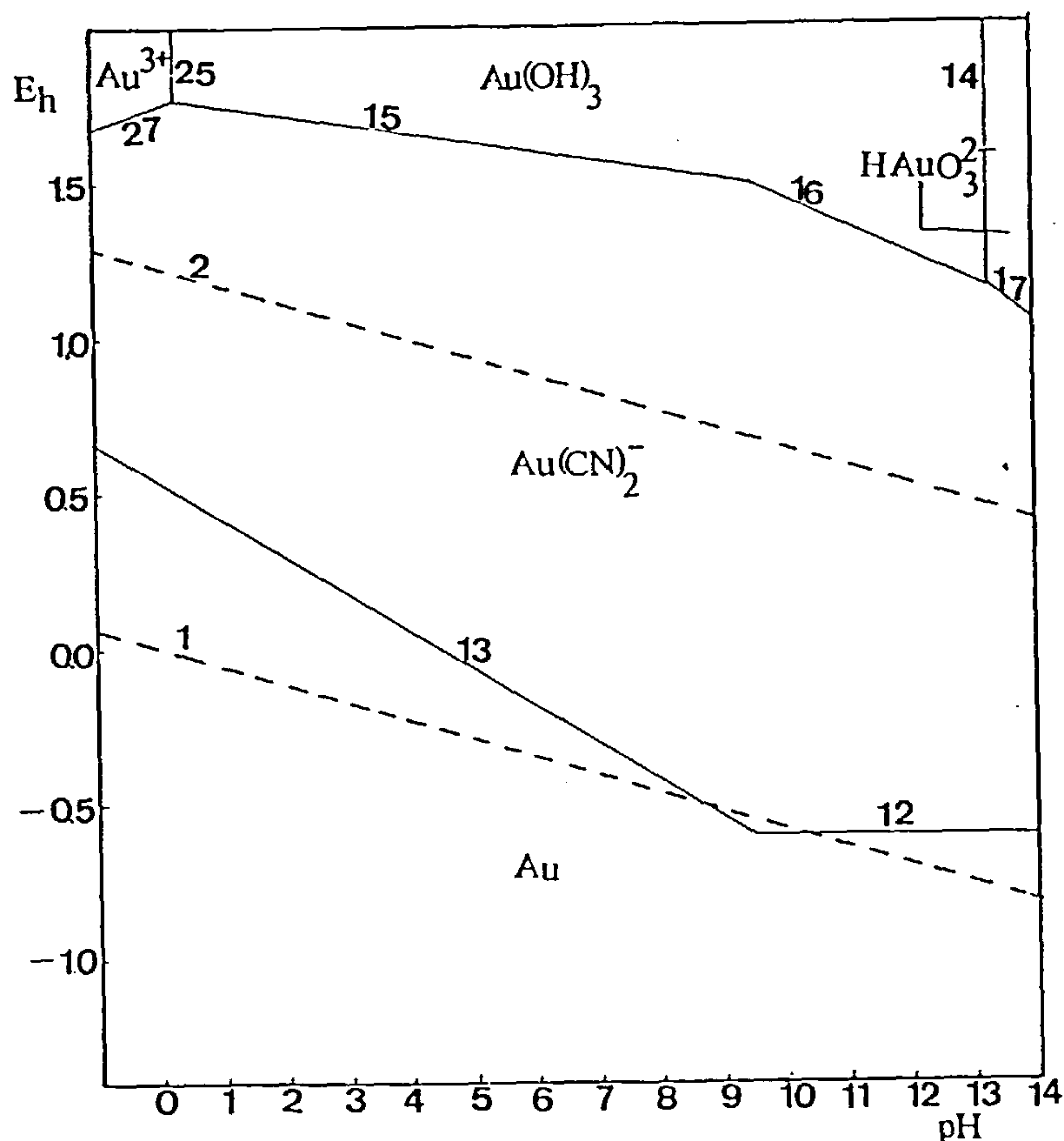


Figure 3.4 - Eh-pH diagram for the system Au-CN-H₂O at 298K; [Au]=10⁻⁴M; [CN⁻]=10⁻¹M.

The formation of the complex Au(CN)_2^- brings about the possibility of dissolving gold in a vast region, with oxygen being able to act as an appropriate oxidizing agent as shown by equation 3.1,



Nevertheless, since HCN is a weak acid, with dissociation constant K_a given by:

$$K_a = \frac{[H^+].[CN^-]}{[HCN]} = 4.93 \times 10^{-10}$$

too low a pH would considerably decrease the concentration of the cyanide ion (the complexing agent) with deleterious effects on the gold dissolution, besides forming the highly toxic HCN. Normally, the gold cyanidation process is conducted in the pH region from 10.0 to 11.5.

At this point, it is useful to recall the hydrogen peroxide and AQ equilibria in aqueous solution, seen in the former chapter, and to superimpose these on the gold-cyanide diagram in order to visualize the relative positions of species in this system. FIGURE 3.5 depicts the complexation of gold with cyanide and the region of stability of H_2O_2 and AQ.

The diagram indicates that it is thermodynamically possible for AQ to act as an oxidizing agent for the gold-cyanide system over a pH range from about 8.0 upwards, and also indicates the region where AQ, H_2O_2 and $Au(CN)_2^-$ may coexist.

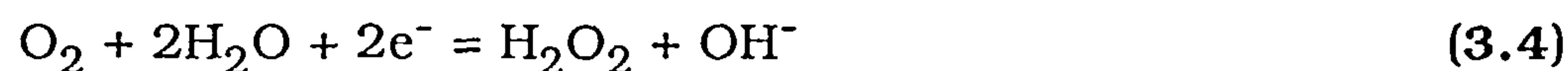
As seen earlier in this work, it is reasonably established that the reactions by which gold dissolves in cyanide solution can be either



or



The reduction of oxygen (see following section) involves the formation of hydrogen peroxide, according to



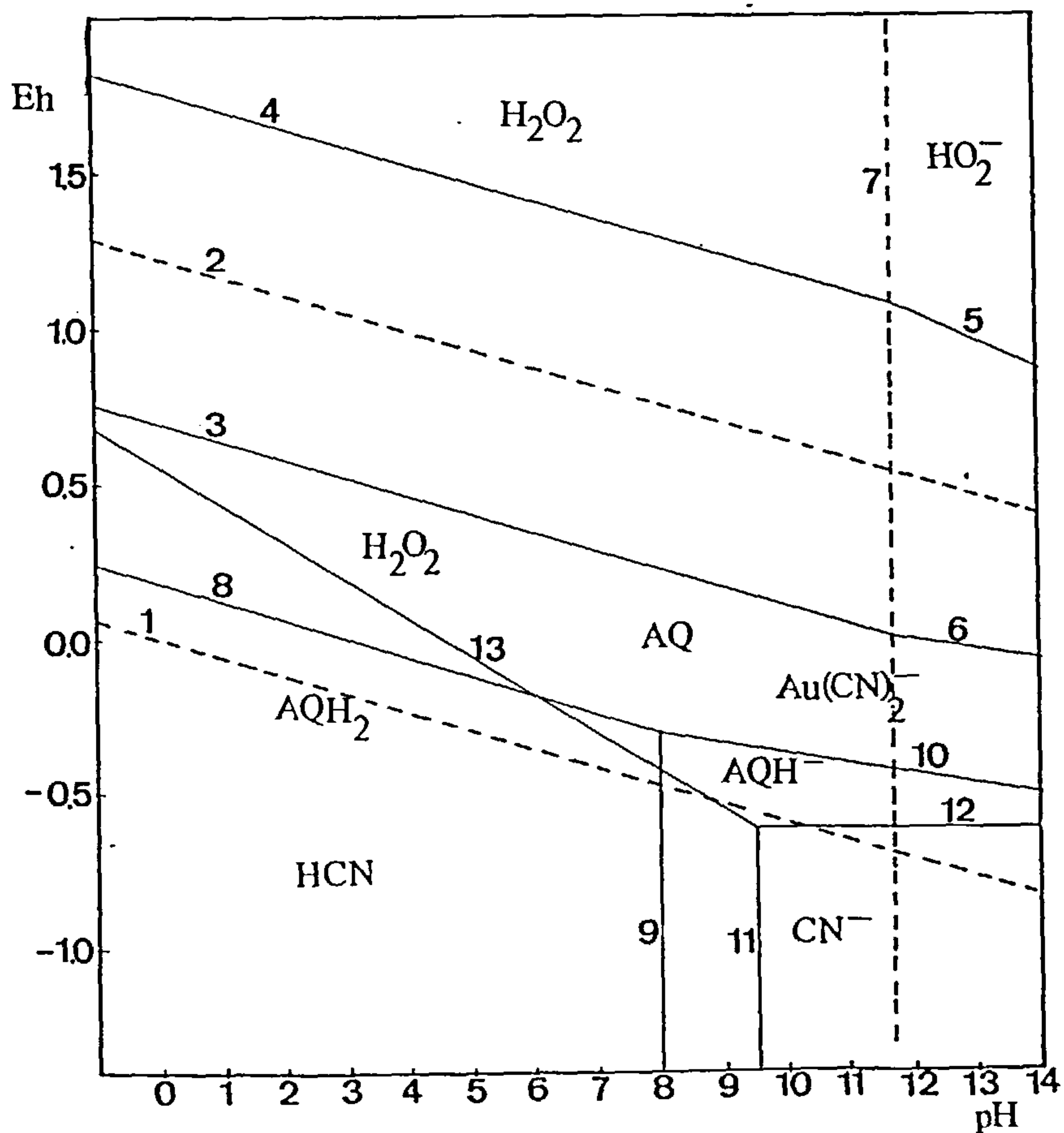
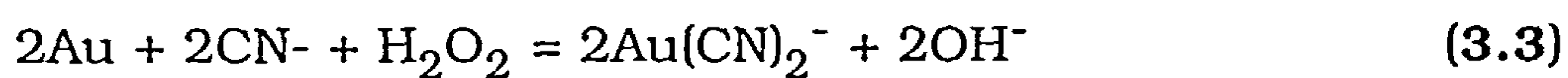


Figure 3.5 - Superimposed Eh-pH diagram for the system Au-CN-H₂O₂-AQ-H₂O at 298K; [Au]=10⁻⁴M; [CN]=10⁻¹M; [H₂O₂]=10⁻¹ M.

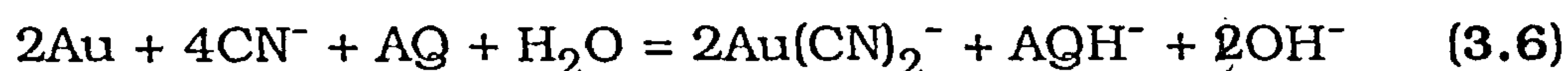


Hydrogen peroxide is a strong enough oxidant to oxidize gold and promote the formation of the soluble complex $\text{Au}(\text{CN})_2^-$ by the reaction



Therefore, the dissolution of gold may take place according to

equations 3.1, 3.2 and 3.3 above. However, it has been demonstrated in this work (see Chapter V) that a leaching system consisting of cyanide + AQ, even in the complete absence of oxygen, is capable of achieving the dissolution of gold. This fact suggests that AQ is acting as the oxidizing agent, and the dissolution proceeds as



with the reduction step being



where the AQH^- is the so-called anthraquinol sulphonic acid.

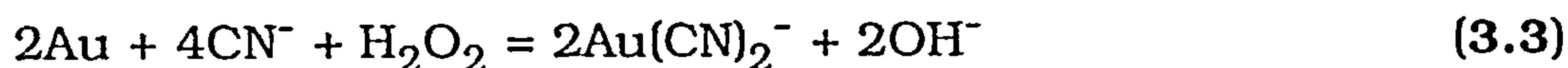
In the previous chapter, it was seen that the oxidation of reduced anthraquinone derivatives is an industrial process for the production of hydrogen peroxide. Moreover, the "in-situ" synthesis of hydrogen peroxide, in an aqueous solution, has actually been suggested as a possibility in systems where air (or oxygen) is continuously flowing through a solution where anthraquinone derivatives are previously reduced^[44,78].

Under normal circumstances, gold cyanidation is carried out in a well aerated solution, which would allow the back-oxidation of the anthraquinol formed in equation 3.7 to proceed as



The regenerated AQ thus formed may take part again in the process through equation 3.6, whereas the "in-situ" formed hydrogen peroxide follows a similar path through equation 3.3. This sequence of reactions indicates that the dissolution of gold in aerated cyanide and

in the presence of AQ as a catalytic oxidizing agent may be represented as:



The oxidation step shown in equation 3.8 above may continuously generate both oxidizing agents, leading to an increase in the rate of gold oxidation, as demonstrated in the following chapter.

3.3-Oxygen reduction on the gold surface

As seen from the discussion above, without any other oxidizing agent, the reduction of oxygen is the counter electrode reaction responsible for oxidation of gold. The reduction of oxygen has been studied on different types of surfaces^[99,100,101] and a comprehensive review has been published recently by Schiffrin^[102]. The importance of this reaction, apart from playing a role in the corrosion of gold, and other metals, is also related to the conversion of chemical energy into electrical energy, the production of hydrogen peroxide and the recovery of oxygen from air^[103].

The cathodic reduction of oxygen is seen as a complex electrochemical process, and many possible paths have been proposed to account for the formation of hydrogen peroxide and intermediate species. Pillai and Bockris^[104] have proposed some seventeen different mechanisms and kinetic parameters for the reduction of oxygen to fit their experimental observations, as for example,

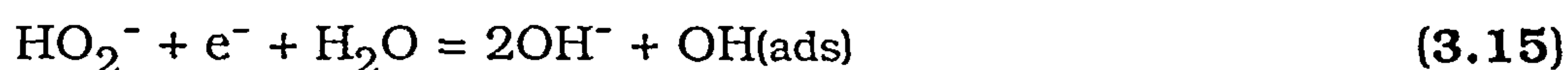


However, the formation of hydrogen peroxide as an intermediate in the reduction of oxygen is generally accepted nowadays, with its presence assimilated in many proposed mechanisms^[105].

Zurilla et al.^[106], using a rotating ring-disc gold electrode, examined the reduction of oxygen and proposed the following mechanism, involving the adsorption of species:



A very similar mechanism is proposed by Adzic et al.^[107], who compared the influence of crystal orientation on the reduction of oxygen on the surface of gold. They also put forth the further reduction of HO_2^- as



Wrobleva et al.^[108], also employing the rotating ring-disc technique, studied the reaction by considering a generic scheme for oxygen reduction, which is illustrated in FIGURE 3.6.

A similar path was considered by Tarasevich^[109] as the probable reactions of oxygen as shown in FIGURE 3.7.

From the outlined, it may be seen that, while the reduction of oxygen is recognized as a complex phenomenon, the overall reaction may be generically considered as following two basic paths. Direct reduction to water, involving four electrons and four protons as



or a two step reaction, with the formation of hydrogen peroxide as an intermediate, which, on the gold surface, may undergo a further catalytic decomposition^[110] to give water as the final product:



Oxygen in solution is initially adsorbed on the electrode surface and then it is reduced either to water or hydrogen peroxide (which in its turn can decompose into water and elemental oxygen).

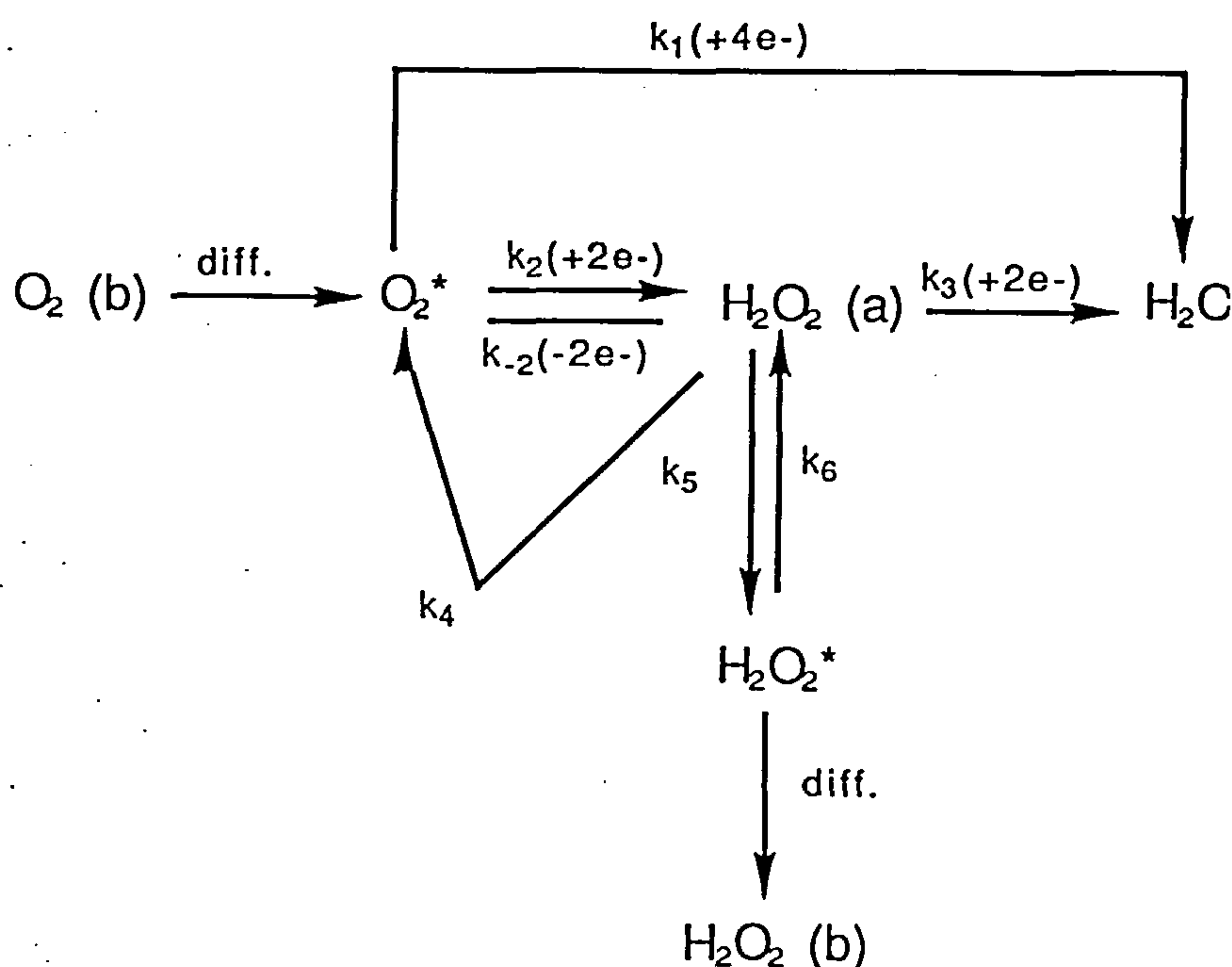


Figure 3.6- Schematic illustration of oxygen reduction (b-bulk; *-surroundings of the electrode; a-adsorbed species)(after Wroblowa et al.^[108]).

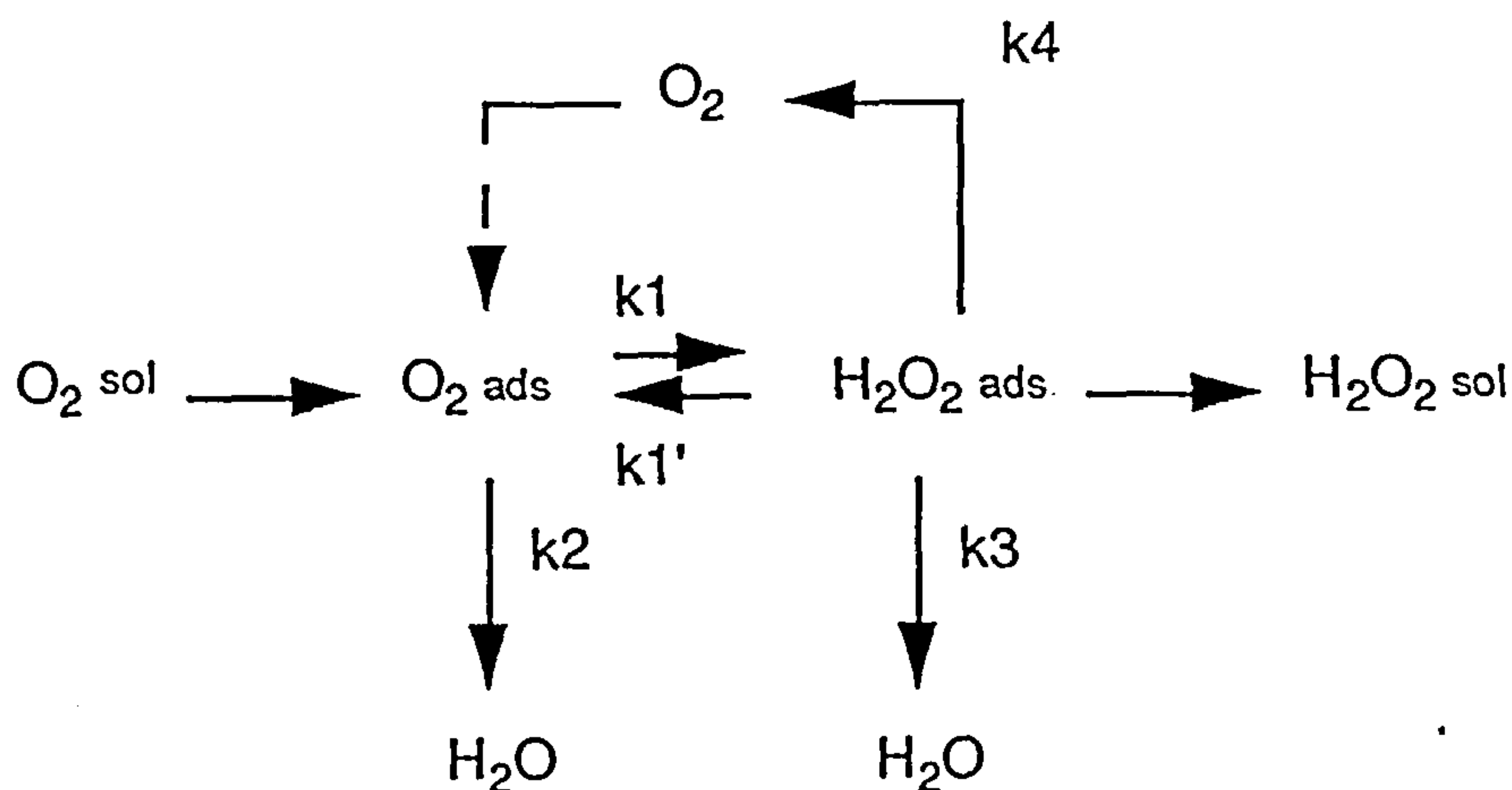


Figure 3.7 - Probable paths for oxygen reaction on the surface of an electrode (after Tarasevich^[109]).

3.4-Cyanide oxidation

Free CN^- is the ionic species that makes possible the solubilization of gold in a thermodynamically vast region, by forming the cyano-complex $Au(CN)_2^-$, as seen in FIGURE 3.4. The complex has a formation constant, in aqueous solution, of $\beta_2 = 10^{37} \text{ M}^{-2}$ [111]. The ability of cyanide to form soluble complexes extends to some 28 other elements, including silver, zinc, copper and iron. FIGURE 3.8 below depicts the potential-pH diagram for the system cyanide-water. As in the former section, thermodynamic data were taken from Bard^[98], and the equations related to each line (which correspond to the numbers seen by them) are given in Appendix III.

As seen earlier, (section 2) HCN is a weak acid, and at low pH values the well known hydrolysis of cyanide occurs as^[112]



with the formation of the toxic hydrogen cyanide. Therefore, the cyanidation of gold must be conducted in alkaline media to keep the complexing agent (CN^-) always available in solution (and, of course, to avoid the formation of HCN). It is interesting to note that, as seen from the diagram below, cyanide is not thermodynamically stable in water at 25°C . The decomposition to cyanogen or cyanate was extensively investigated by Gauguin in an early work^[113], and the reactions are commonly represented by



or

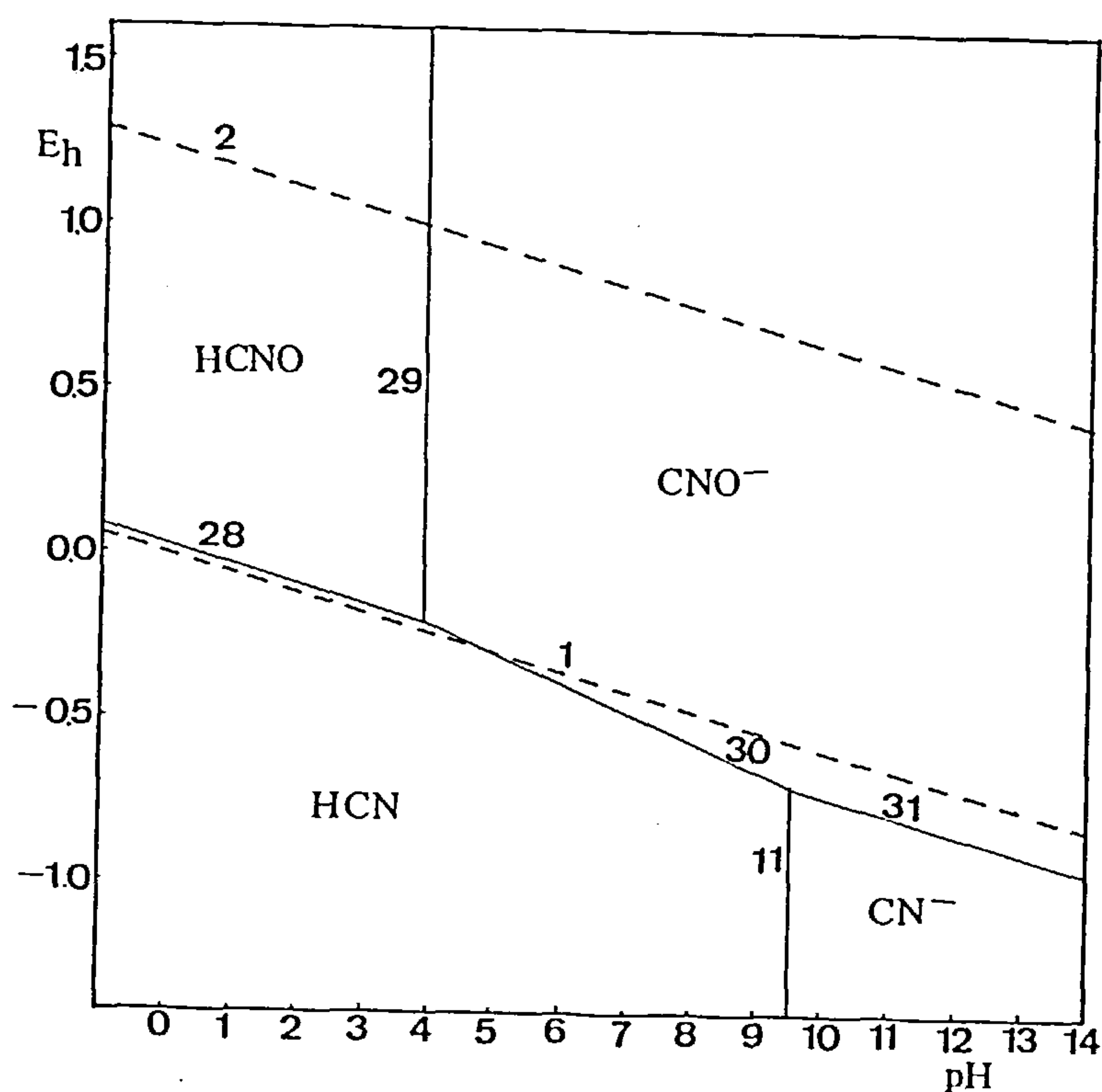
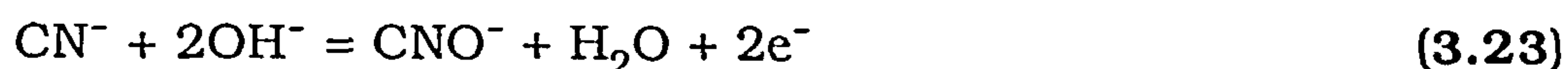


Figure 3.8 -Eh-pH diagram for the system cyanide - water at 298K, $[\text{CN}^-] = 10^{-1}\text{M}$.

In alkaline solutions, however, the latter reaction is more likely to occur, since the gaseous cyanogen will decompose into cyanate and cyanide^[114]. Whatever the reaction, though, the kinetic rate involved is slow in the absence of a heterogeneous catalyst. If, on one hand, this fact makes possible the use of cyanide in the hydrometallurgy of gold, on the other, solutions containing cyanide must be oxidized before being discharged to avoid the contamination of the environment. A review by Kuhn deals with the basic aspects of treating cyanide-containing effluent streams^[115]. In industry, this operation is usually carried out chemically, by treating the cyanide solution with chlorine, sodium hypochlorite or Caro's acid^[116]. A possible alternative oxidation method, which has also received attention lately, is to treat the cyanide waste by electrolysis using metallic electrodes. This route may be interesting, since it would avoid handling and storage of the chemical used when treating large amounts of strong cyanide solutions^[117,118].

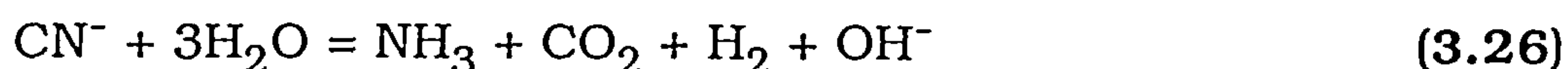
The rate of cyanide oxidation is higher when a heterogeneous catalyst, such as activated carbon, is present in the system^[119]. The oxidation not only produces cyanate but also consumes some oxygen, as shown by the suggested mechanism:



giving

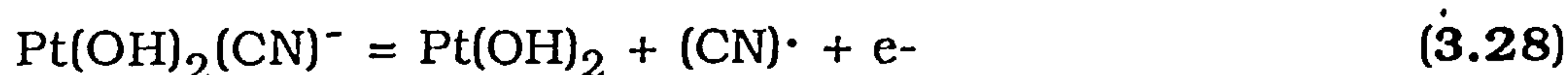
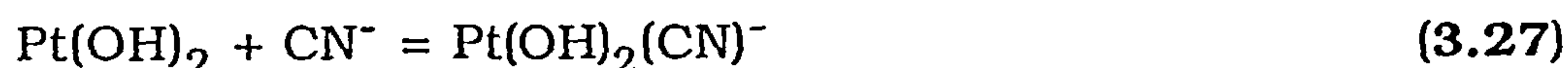


At high temperatures ($\sim > 70^\circ\text{C}$) further cyanide is lost with the formation of ammonia, hydrogen and carbon dioxide,



The effect of the activated carbon on the rate of this reaction is reported to be negligible^[119].

On platinum electrodes, Sawyer^[120] suggested a mechanism involving the catalytic effect of a platinum oxide film ($\text{Pt}(\text{OH})_2$), represented by



As the cyanide concentration increases, the platinum oxide is "poisoned" by forming $\text{Pt}(\text{CN})_2$ according to



The modified surface is said to be less effective as a catalyst and to inhibit the oxidation of the cyanide ion. This mechanism leads to a unique situation where the very ion that is being oxidized is also "poisoning the electrode responsible for its own oxidation"^[120].

A different mechanism was suggested by Tamura et al.^[121], who also studied the oxidation of cyanide on a platinum electrode and proposed five different reactions. However, the path represented by



was considered to fit reasonably for the consecutive intermediate

reactions involved in the oxidation of cyanide. Also, hydrogen peroxide was added in a 1:1 ratio to a solution containing cyanide, with stirring provided by a magnetic follower. Under these conditions, it was found that within one hour hydrogen peroxide could oxidize more than 50% of the cyanide present. In further study^[122], they also investigated the mechanism of the electrochemical oxidation of cyanide on a graphite electrode and suggested two possible mechanisms to account for the observed variation of pH.

In most of these studies, the cyanide content was measured with a cyanide-ion selective electrode. This is a method which has attracted widespread interest, since it enables the direct detection of cyanide in solution and at concentrations as low as 10^{-6}M ^[123]. In this work, a Russel cyanide-selective electrode, model 94-4096, was also used to detect cyanide variation during experiments. Data obtained to draw the calibration curves and the description of this method of determination are reported in Appendix IV.

3.5-Gold cyanidation kinetics

Some years after the discovery of the cyanide process, research was carried out in an attempt to understand better the chemistry of the process. One of the initial investigations was performed by Barsky and co-workers, in the early thirties^[124]. Their search for a definite decision concerning the equation (or equations) representing the reactions involved led to the conclusion that Bodländer's equations (3.2 and 3.3) are the true reactions taking place when gold and/or silver are dissolved in cyanide solution. In later work, however, it was verified that equation 3.2 is the more important of the two^[9]. It is stated that even though Elsner's equation 3.1 results in the same final

products, it does not consider the intermediate formation of hydrogen peroxide, which plays an important role in the whole process. This is indeed a debatable point, since hydrogen peroxide is said both to have no effect or to provoke a slight increase in the rate of gold dissolution during cyanidation, if added in small amounts^[11,29,125]. Additionally, the rate of dissolution of gold (and silver) was investigated by Barsky et al. and an initial evaluation of the most suitable cyanide concentration was made. The rate of dissolution of pure gold was then measured in solutions within the range from zero to 0.50% (0.10M) NaCN. The apparatus used in these experiments consisted of a piece of gold foil suspended in the cyanide solution by means of a fine thread which, in its turn, was attached to an analytical balance. In this way, the rate of gold dissolution could be measured without removing the gold from solution. The oxygen was supplied by air bubbles coming upwards from the bottom of the reactor. In all trials no alkali was added and the pH is reported to have been kept above 9.0, which was considered to be an appropriate value for the investigation. Because of reproducibility problems, the average values of several tests under the same experimental conditions had to be used to draw conclusions. The maximum rate of gold dissolution was found for a 0.01M (0.05%) NaCN solution and reached $4.6 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$. Higher cyanide concentrations (0.10M, 0.05M and 0.02M) did not give higher dissolution rates, with some values actually being slightly lower (but by not more than 10%). The solubility of oxygen in solutions of distilled water and increasing NaCN concentrations was also determined. They concluded that oxygen solubility is not affected by cyanide concentrations up to 0.41M (2.00%). The effect of alkalinity on the rate was investigated by adding lime and sodium hydroxide. In the first case, there was a sharp decrease in the rate for pH values above 10.7; in the case of NaOH, no significant variation was observed for pH up to 12.5. Although an attempt was made to clarify this difference in

behaviour, no adequate explanation could be provided.

Two years later Beyers^[126] published a comprehensive investigation of the rate of gold (and silver) dissolution in cyanide solutions of different concentrations, varying also the dissolved oxygen concentration and studying the effects of different types of metal impurities in the solution. These experiments were performed in a rather different way from the previous one. Strips of the metal with a defined total surface area of 0.90 cm^2 each were placed in KCN solutions. Tests were carried out with the following concentrations of the salt: 0.0015M, 0.003M, 0.0075M, 0.015M, 0.023M and 0.03M. The metal dissolution was performed in special bottles, which were agitated by revolving them for two hours. The rate of gold dissolution was found to increase if the cyanide concentration was raised from 0.0015M (0.01%) to 0.03M (0.20%). The average value for the rate of dissolution with KCN 0.03M was reported to be $5.8 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$. Also, the rate of gold dissolution, in solutions of constant cyanide concentration, was found to decrease as the dissolved oxygen increased from around 6.0 to 30 ppm, and when the gas mixture was not directly striking the gold strips. The highest average rate reported in a 0.01M NaCN solution was $1.74 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$, with 11.5% of oxygen in the gas mixture bubbling through the solution. When the gas was directly impinging on the gold surface the average rate was found to be $3.43 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$, which increased with increasing oxygen content, although this relation was not directly proportional.

Fahrenwald and Newton^[127] chose a different type of equipment. They used a piece of gold foil in a triangular shape and a revolving steel cylinder as a reactor to investigate the effect of both cyanide and oxygen content on the rate of the metal dissolution. The reactor was kept rotating at 6 rpm. Under these experimental conditions the rate

of Au dissolution was found to increase with the oxygen partial pressure, if the cyanide concentration was also increased accordingly (cyanide content varied from 0.002M to 0.104M). Although the values are only reported in graphical form, which makes them rather difficult to examine since the figures are not very clear, for a $pO_2 = 0.21$ atm and KCN 0.01M the rate reported reached $2.12 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$.

Kameda^[125] investigated the dissolution of gold in cyanide by suspending a gold plate within the leaching solution. A current of air provided the oxygen necessary for the reaction, as well as the stirring. He could detect the formation of hydrogen peroxide during the dissolution process, which led him to affirm that Bodländer's equations describe the reactions involved in the dissolution. Even though it was recognized that the stirring method used did not strictly represent the stirring velocity, it was suggested that the dissolution rate is only slightly dependent on this parameter.

The effect of oxygen content was investigated by passing nitrogen, air and oxygen in different experiments. Two dissolution rates were considered because the rate had a tendency to decrease in the beginning and increase steadily later, being twice the initial rate after 6 to 8 hours. This outcome was explained as being due to a passivation of the gold at the beginning of the process, and the rates observed suggested that it was nearly proportional to the oxygen concentration in solution. The maximum rate was obtained with 0.005M KCN, reaching $1.97 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ initially, and $2.40 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ later in the process. For 0.01M KCN these values were $1.20 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ and $2.40 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ respectively (the latter did not change from KCN concentrations of 0.005M onwards).

As stated before, Thompson^[95] demonstrated the corrosion character

of the dissolution of gold during cyanidation. He postulated that with sufficient excess of cyanide ions "oxygen is the controlling reagent in the cyanide process". A film formed on the gold surface during dissolution was detected, but no explanation was given concerning its electrochemical and/or chemical properties. Moreover, it was reported that this film did not appear to impair the rate of dissolution of the gold leaf used in these experiments. More recently, however, the formation of an insoluble film on the surface of a rotating gold disc was mentioned as a probable cause for lower experimental rates compared to those expected theoretically, although the difference was not specified quantitatively^[128].

Cathro^[129] studied the effect of oxygen on the dissolution of gold in 0.04M KCN at 30°C. He used gold spheres for his first set of experiments (achieving poor levels of reproducibility) and a fixed gold disc later, with the solution being stirred by a glass turbine. It was shown that, at low agitation levels, the rate of gold dissolution is proportional to the oxygen content, whereas at higher speeds the relationship is not linear, with the rate even decreasing if the oxygen concentration is about 20ppm or more. The rate of gold dissolution in an aerated solution was found to be around $2.82 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ at 3.3 Hz (200 rpm) and about $7.0 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ at 10 Hz (600rpm), this being the highest rate found amongst the works reviewed. Basically, it was concluded that the rate of gold dissolution does not appear to be controlled by the diffusion of oxygen, even in the region where the cyanide concentration is well above the theoretical value required, probably because of the gold becoming passive. Therefore, it was proposed that the rate of gold dissolution is, in this situation, apparently being controlled by the anodic reaction (oxygen reduction); it was recommended that to obtain the best results the cyanide concentration must be increased "over the value possible if the gold

did not become passive"^[129].

Kakovsky^[130] reported values for the rate of gold dissolution using a rotating disc of this metal, in one of the first studies employing this technique. The exact experimental conditions and, in particular, the treatment applied to the disc surface were not reported. For low rotating speeds (up to 2.5Hz) and under an oxygen partial pressure of 0.21 atm, the rate was found to be about $1.5 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ with 0.01M KCN. Under these experimental conditions, the rate of dissolution was found to follow Levich's equation. For higher rotating speeds, the rate was practically independent of agitation if $p\text{O}_2=0.21\text{atm}$, but decreased at $p\text{O}_2=1.0\text{atm}$, remaining unchanged for values up to around 18Hz. The rate found at 6.1Hz was ca. $2.20 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$, with 0.01M KCN and $p\text{O}_2= 0.21 \text{ atm}$. However, at $p\text{O}_2=1.0 \text{ atm}$, the rate was found to increase to ca. $5.40 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$.

In this same work, the effect of alkalinity was studied and it was found that if the pH was raised to up to 13 a linear decrease in the rate of gold dissolution occurred. Beyond this pH the rate decreased more dramatically; this result was explained by "the kinetic difficulties in relation to the reduction of oxygen".

Dorin and Woods^[131] investigated the leaching rates of gold, silver, palladium and platinum in cyanide solutions. For gold, it was reported that the rate is at a maximum in "the region of pH 10", declining steeply for higher values. With the electrode rotated at 4Hz and cyanide (NaCN) concentration at 0.02M, the highest rate for gold dissolution was found to be about $3.5 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$, which was considered to be an expected value "from general knowledge of conventional leaching processes". It was also stated that the electrodes

were polished with 5 μm alumina paste, cleaned ultrasonically after each polishing process and etched at room temperature with 1M NaCN, in order to achieve reproducible results.

Although investigating the leaching of gold (and also silver) with thiourea, Chen et al.^[132] reported values for the dissolution of gold in cyanide solution, for the sake of comparison. It was found that in an aerated solution of 0.1M NaCN (an unusually high concentration) the rate was $1.8 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$.

Deventer and Lorenzen^[133] investigated the galvanic interaction during gold cyanidation caused by the presence of mild steel, pyrite, haematite and galena. The rotating disc technique was chosen and a careful polishing procedure was needed to achieve reproducibility within 6%. The leaching experiments were all carried out with KCN at a concentration of 0.003M, apart from when examining the influence of mild steel, where this concentration was 0.004M. The rotating speed was kept at 100 rpm (1.7 Hz) in all runs, the temperature at 20°C and pH at 10.4. The rate values experimentally found for gold only (without any interaction) were reported to be $0.60 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ when the cyanide concentration was 0.004M; and $0.42 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ for a cyanide concentration of 0.003M.

In summary, the rates from the studies quoted above, with their respective experimental conditions, may be seen in TABLE 5.1 overleaf. In addition, while the details of the experimental investigation using a rotating disc, as well as the discussion of the results obtained in the present work are described in a following chapter, these rates are also presented in the same table for comparison.

Researcher	rate reported (10 ⁹)(mol/cm ² .s)	[CN] (M)	[O ₂] (mg/l)	Method of investigation
Barsky ^[124]	4.60	0.01	8.2	Au foil suspended in solution.
Beyers ^[126]	5.80	0.03	8.2	Au strips in shaped revolving bottles filled with CN solution.
idem	1.74	0.01	8.2	Au foil suspended with glass clamp (gas not striking the metal)
idem	3.43	0.01	8.2	idem (gas striking the metal)
Fahrenwald [127]	2.12	0.01	8.2	triangular shaped Au foil in a revolving steel reactor
Kameda ^[125]	1.97 (initial)	0.005	8.2	suspended Au plates with air current providing both O ₂ and stirring
	2.40 (final)	0.005	8.2	idem
	1.20 (initial)	0.01	8.2	idem
	2.40 (final)	0.01	8.2	idem
Cathro ^[129]	2.82 (3.3 Hz)	0.04	8.2	fixed Au disc; stirring
	7.00 (10.0 Hz)	0.04	8.2	with glass turbine (30°C)
Kakovskii ^[130]	1.50 (2.5 Hz)	0.01	8.2	rotating disc
	2.20 (6.1 Hz)	0.01	8.2	idem
	5.40 (6.1 Hz)	0.01	41.0	idem
Dorin/Woods [131]	3.50 (4.0 Hz)	0.02	deaerated	rotating disc electrode; potential corresponding to corrosion pot. in aerated solution.
Chen ^[132]	1.80 (2.0 Hz)	0.10	8.2	rotating disc
Deventer ^[133]	0.60 (1.7 Hz)	0.004	8.2	rotating disc
	0.42 (1.7 Hz)	0.003	8.2	rotating disc
this work	3.59 (10 Hz)	0.01	41.0	rotating disc
	2.67 (10 Hz)	0.01	8.2	idem
	1.63 (2.5 Hz)	0.01	8.2	idem

TABLE 3.1 - Rates of dissolution of gold reported by various investigators.

From the text and table, the variety of methods that have been employed to investigate the kinetics of gold dissolution in cyanide is apparent; also, even though all the rates fall in the same order of magnitude (10^{-9}), some of them differ quite considerably. It must be stressed, however, that the comparison of these results is not a simple task, since the methods of investigation obviously differ one from another. Moreover, even when the same approach is used, as in the case of the rotating disc, the experimental procedure is not always detailed, including the metal surface preparation, which is considered as highly important for this type of experiment^[134,135]. The rates reported are, most probably, correct for the procedure adopted in each one of the experiments. It is noticeable that the results obtained with a rotating disc, including those from the present work, are in good agreement, considering that the experimental conditions were not always exactly the same.

3.6 - Summary

The cyanidation process for recovering gold has been reviewed and the possibility of using AQ as an oxidizing agent demonstrated. With the aid of Eh-pH diagrams the region where AQ, H_2O_2 and $Au(CN)_2^-$ may coexist was established. Moreover, it was seen that in fact, it is thermodynamically possible for AQ to act as an oxidizing agent for the gold-cyanide system over a pH range from approximately 8.0 upwards, and reactions representing the paths involved were suggested. Following that, a review of work dealing with oxygen reduction and cyanide oxidation, as well as with gold cyanidation kinetics was presented. It is noticed that somewhat surprisingly not much work on the rate of gold dissolution under strictly defined hydrodynamic conditions has been reported in the literature. Also kinetic results obtained in the present work were included for comparison.

CHAPTER IV

EXPERIMENTAL ANTHRAQUINONE IDENTIFICATION

4.1-Chemical reduction

The changes in the concentration of anthraquinone in aqueous solution can be detected by ultra-violet spectroscopy at a wavelength of 330nm. Non-aqueous solutions with concentrations below $3.0 \times 10^{-4}\text{M}$ are normally investigated by this technique^[79,82,83]. Measurement of the absorption of UV and visible radiation by species in solution is a widely used method for quantitative analysis. However, in order to make such determinations it is first necessary to construct a calibration curve of absorbance 'versus' concentration, according to the Beer-Lambert's law.

The equipment used for such determination was a Perkin-Elmer double beam spectrophotometer model 124. The absorbance of the standard solutions with different AQ contents were measured to fit a straight line, as required by the Beer-Lambert's law. The calibration curve may be seen in FIGURE 4.1; (path length 10mm and the pH adjusted to 11.0 with sodium hydroxide) and the table with the exact figures is reported in Appendix II.

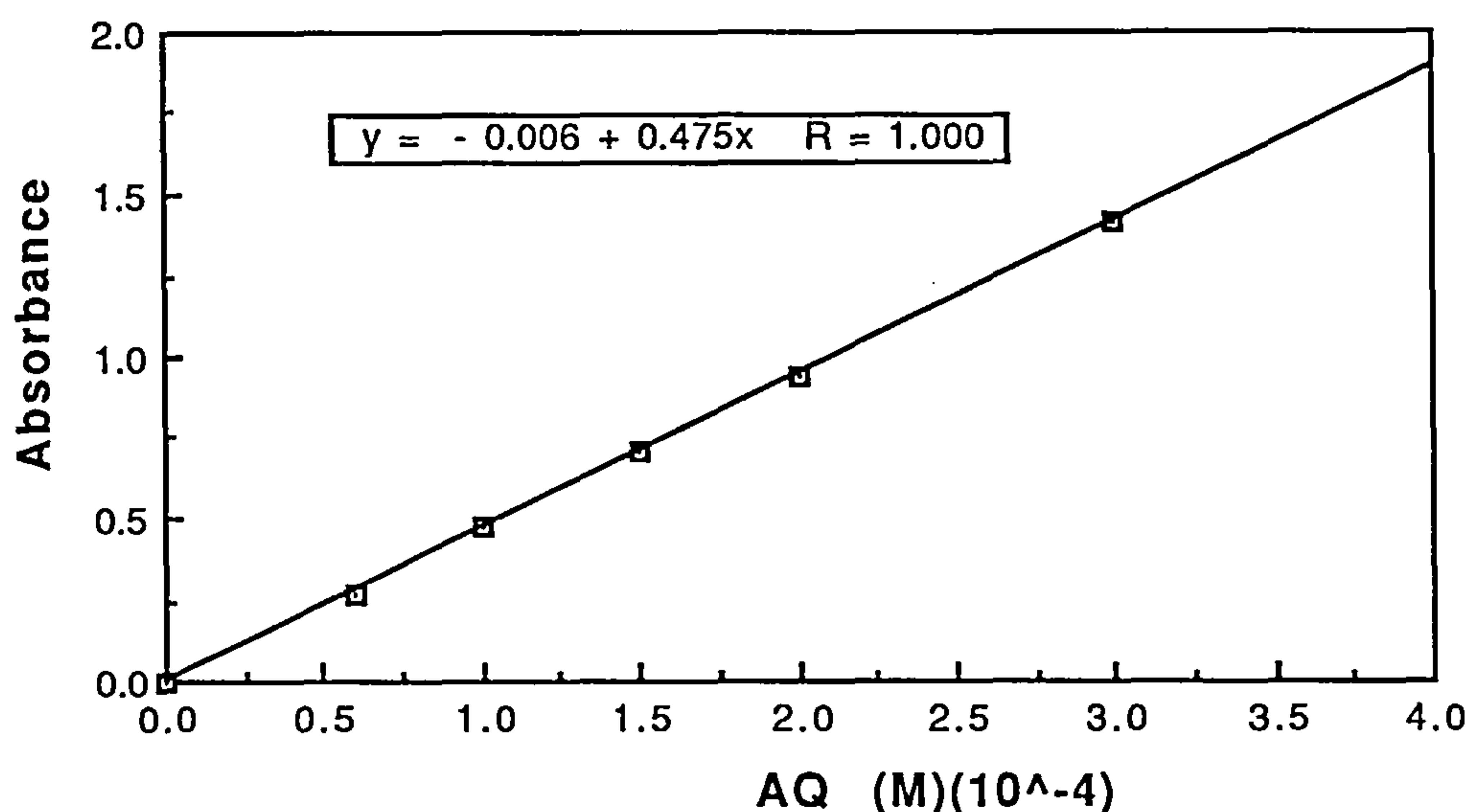


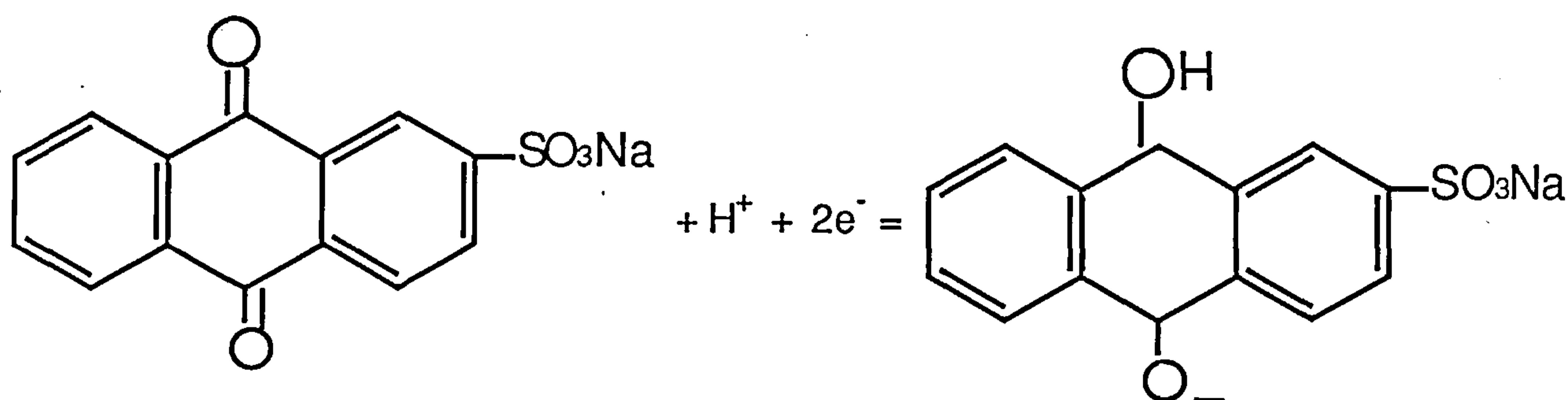
Fig 4.1-Calibration curve for AQ at pH 11.0, path length 10mm and $\lambda=330\text{nm}$.

From the data obtained using the calibration curve it is possible to calculate the molar absorption coefficient of the anthraquinone under investigation. This was found to be **476.6 m²/mol**, which is close to the value of 460.3 m²/mol taken from the literature for a similar compound (anthraquinone 2,6 disulphonate^[60]).

Most quinones may be chemically reduced to their hydroquinones with agents such as sulphurous acid or hydrogen iodide. These are, however, unable to reduce anthraquinone, whose reduction must be performed with sodium hyposulphite (Na₂S₂O₄), (which is a more powerful reducing agent than sulfurous acid, hydrogen iodide or stannous chloride) with additions of zinc powder. Anthraquinone when reduced by this method yields a compound (anthrahydroquinone) which in aqueous solution has a characteristic reddish colour; this anthrahydroquinone is very rapidly reoxidized even by atmospheric oxygen.

The UV-visible spectra of the AQ during its reduction with sodium hyposulphite is shown in FIGURE 4.2, overleaf. These spectra clearly shows the disappearance of the peak at $\lambda=330\text{nm}$ as the reduction proceeds, and the emergence of one at $\lambda=400\text{nm}$, which characterizes the reduced species (probably the monoprotonated quinol AQH^- , as seen from the Eh-pH diagram shown earlier).

Full reduction was achieved in less than 30 minutes. The experiment was carried out in a conventional reactor with 100ml of solution and under an oxygen-free nitrogen atmosphere. Samples were taken every quarter of an hour and taken to be scanned in the UV-visible spectrophotometer; the cuvette used had a 10mm optical path length. AQ was dissolved in KCN 0.03M; during the course of the experiment an increase of pH was observed, which is indicative that a consumption of protons occurred, according to eq.4.1 below



It is possible that some AQH^- might have been back-oxidized during the transfer from the reactor to the cuvette, but this fact did not prevent the peak at $\lambda=330\text{nm}$ from almost completely disappearing. The solution containing the AQ, which is colourless at this concentration, changed, as expected, to a typical reddish colour, detected at $\lambda=400\text{nm}$.

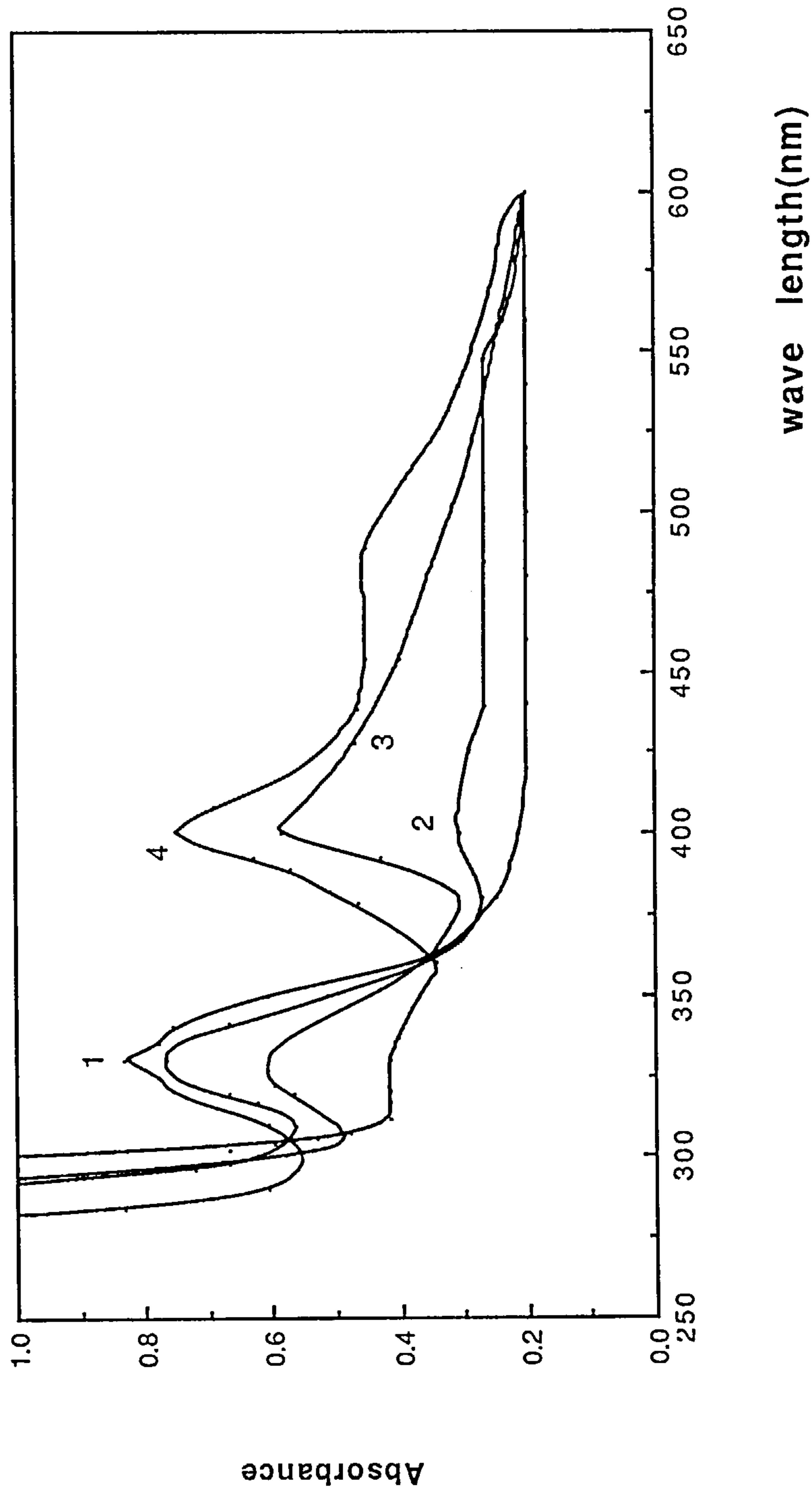


Figure 4.2 - UV-visible spectra of AQ, showing gradual decrease of peak at $\lambda=330\text{nm}$ (oxidised species) and emergence of peak at $\lambda=400\text{nm}$ (reduced species) as AQ reduction proceeds (curves 1 to 4). Cuvette length=10mm; initial AQ conc.= $1.7 \times 10^{-4}\text{M}$ dissolved in KCN; reduced with $\text{Na}_2\text{S}_2\text{O}_4$.

From the results obtained in this experiment it is clear that if AQ is being consumed, or reduced, in an aqueous solution the reaction is conveniently monitored by observing the decrease of the absorbance intensity at $\lambda=330\text{nm}$. The back-oxidation of the AQH^- (to regenerate the original AQ) is easily accomplished by replacing the nitrogen by an air or oxygen flow.

4.2-Electrochemical reduction, with detection of H_2O_2

While the AQ may be readily reduced by the method described above, for the determination of hydrogen peroxide produced "in-situ" (from the oxidation of the reduced AQ) an electrochemical method was preferred in order to avoid any variation in the composition of the solution that could interfere with the method used for quantitative determination and mask the actual concentration of the peroxide. The equipment used for this end was a conventional electrochemical cell, which is schematically represented in FIGURE 4.3 overleaf.

The solution (210ml) containing anthraquinone dissolved in water was pumped through a flow-cell in the spectrophotometer, by means of a peristaltic pump. Because of the extreme rapidity with which the oxidation of anthrahydroquinone occurs, the connexions between the reactor and the flow-cell had to be carefully made with thin glass tubing; the exception was, of course, the section passing through the pump and the small connexions to and out of the flow-cell. In these parts tygon tubing (BDH-Tygon Masterflex 6409-16) with very low oxygen permeability was used. With this care taken, very little oxygen could permeate and reoxidize the reduced anthraquinol in the path between the reactor and the flow-cell.

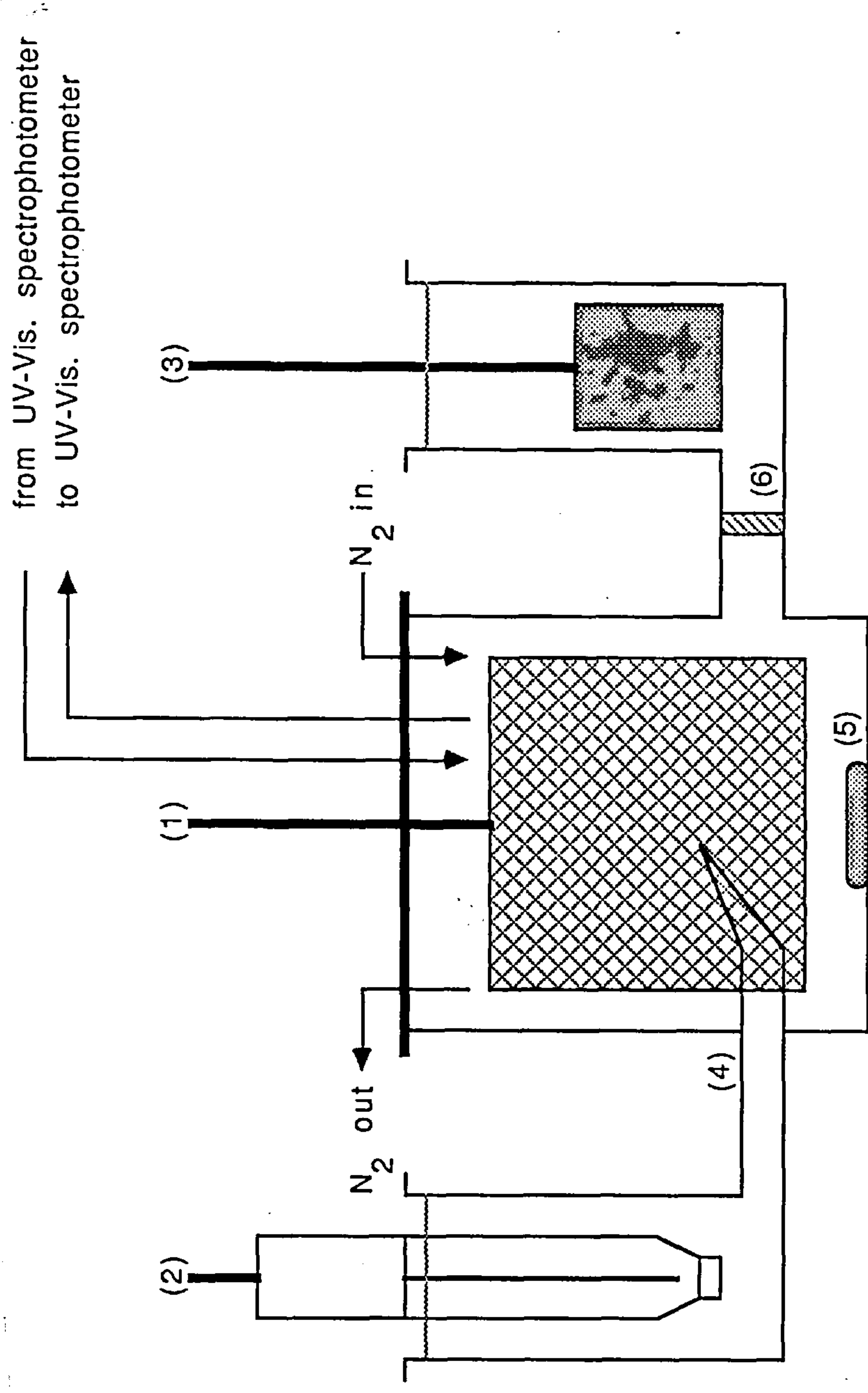


Figure 4.3 - Electrochemical cell used to reduce an aqueous solution of AQ; supporting electrolyte 0.5M K_2SO_4 ; pH adjusted to 11.0 with KOH; 1-working electrode (titanium grid); 2-reference electrode (Ag-AgCl); 3-counter electrode (platinum); 4-Luggin probe; 5-magnetic follower; 6-frit.

The temperature was kept at 298K with the aid of a water bath. The cathode consisted of a titanium grid, the counter electrode was a platinum foil and a 0.5M solution of K_2SO_4 was used as the supporting electrolyte. Stirring was provided by a magnetic follower and the pH was adjusted with KOH to around 11.0. From the Eh-pH diagram shown earlier in FIGURE 2.4.2 it may be seen that thermodynamically a potential of -0.5 V (SHE) is sufficient to drive the reduction of the anthraquinone. This was, therefore, the potential applied to the electrodes, by means of a potentiostat Princeton model 363 controlled by a Parc Universal Programmer, model 175. The initial anthraquinone concentration was 3.0×10^{-4} M.

The experiment was repeated four times to check for reproducibility and was carried out in the following way: by comparing the variation of absorbance at $\lambda=330\text{nm}$ it was possible to follow the decay of AQ (i.e., its reduction to AQH^-) as previously described. When a suitable amount of AQH^- was formed (a typical value being 0.80×10^{-4} M), the applied potential was removed and the nitrogen was replaced by an air flow. The solution, which was turning to the reddish colour characteristic of the reduced species, almost instantaneously recovered the original colourless form, with the absorbance peak at $\lambda=330\text{nm}$ also returning to its previous intensity, confirming that AQ may be easily regenerated to its initial concentration. Hydrogen peroxide was then quantitatively analysed by the method suggested by Bayley and Boltz^[80] (and described in Appendix IV). The result of this experiment indicated that hydrogen peroxide was formed in a molar relation of 1:1 with regard to AQH^- . Also, the pH was found to increase during the course of the reaction, suggesting that the reduction proceeds via a proton consumption, as shown previously in equation 4.1. Typical values are reported below.

An initial AQ concentration of 3.0×10^{-4} M was allowed to fall to 2.20×10^{-4} M, which could theoretically yield 0.8×10^{-4} M (3.0×10^{-4} M - 2.20×10^{-4} M) of hydrogen peroxide. In this case, however, the quantity actually found through analysis was 1.08×10^{-4} M, which suggests that the absorbance corresponding to 2.20×10^{-4} M was in fact lower (it should be 3.0×10^{-4} M - 1.08×10^{-4} M = 1.92×10^{-4} M). This difference may be ascribed to the fact that, in spite of the care taken to avoid oxygen, some AQH⁻ formed in the reactor (actually 12.7%) was still reoxidized while passing between the reactor and the spectrophotometer. In fact, previous tests had demonstrated the extreme rapidity in which AQH₂ is reoxidized: AQ was electrochemically reduced (in a Ti electrode) to AQH₂, under a nitrogen atmosphere and the concentration of both species was monitored as previously described. It was verified that complete oxidation of the full AQH₂ occurs in less than 40 seconds, after the inert atmosphere is replaced by an air flow or a 1:1 mixture of oxygen and nitrogen. Nevertheless, this did not prevent the experiment from showing that dilute aqueous solutions of AQ, when reduced, may quantitatively yield "in-situ" hydrogen peroxide, by reacting with oxygen.

4.3-Determination of AQ diffusion coefficient: an electrochemical study

The expression known as the Levich equation, which relates the limiting current density on an electrode with the rotating speed, provides an excellent test that the current is entirely mass transport controlled (that is, for those potentials where the concentration on the electrode surface of the diffusing species is zero). The slope of the plot $I_l \times \omega^{1/2}$ (limiting current density 'versus' the square root of the rotating speed) should be linear and pass through the origin^[136]. The

slope of the above mentioned plot may be used to estimate the diffusion coefficient of the electroactive species. The equation is written as:

$$I_l = 0.62 \times n \times F \times D^{2/3} \times \nu^{-1/6} \times \omega^{1/2} \times C^0$$

where

I_l = limiting current density (A/m²)

n = number of electrons involved in the reaction investigated

F = Faraday constant (C.mol⁻¹)

D = diffusion coefficient (m².s⁻¹)

ν = kinematic viscosity (m².s⁻¹)

ω = rotating speed of the disc (s⁻¹)

C_0 = concentration of the electroactive species in the bulk of the solution (M)

In the present case, a platinum rotating disc (area = 3.85×10^{-5} m²) was used as the working electrode. The remaining equipment was as described in the previous section, and may be schematically seen in FIGURE 4.4 overleaf.

The current values are taken from the limiting current in the sweep from a potential where the species is thermodynamically stable to the potential of interest. FIGURE 4.5 shows the current-potential curves obtained under different rotating speeds.

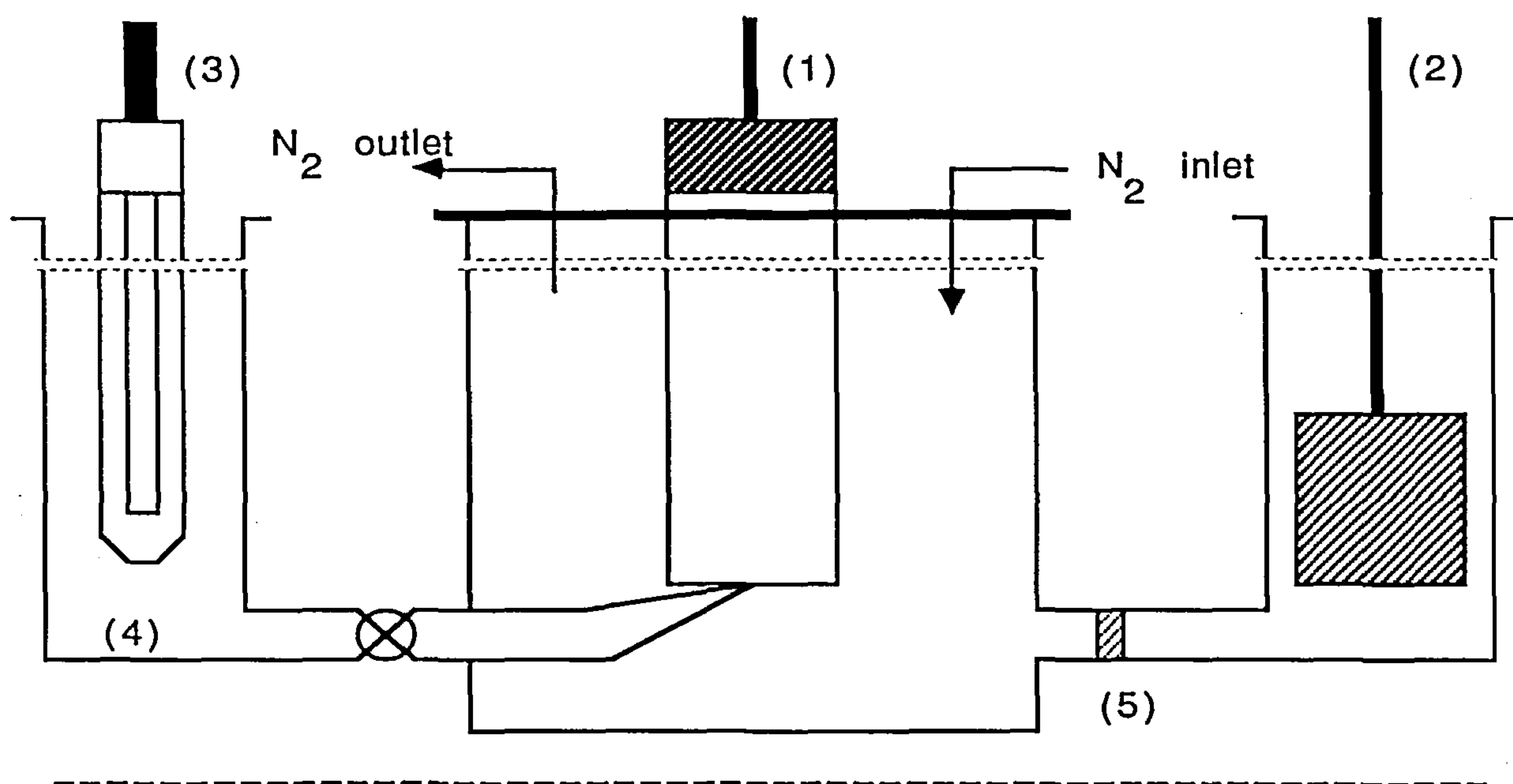


Figure 4.4 - Schematic representation of the cell used for the determination of AQ diffusion coefficient: (1) working electrode (platinum rotating disc); (2) counter electrode (platinum); (3) reference electrode (Ag-AgCl); (4) Luggin probe; (5) glass frit.

The experiments were performed in a conventional split-top round bottom reactor. The solution was previously thoroughly deaerated by bubbling oxygen-free nitrogen for at least one hour. The system comprised of 0.5M K₂SO₄ as the supporting electrolyte, 0.03M KCN and 6.0×10^{-4} M AQ.

It may be seen in FIGURE 4.5 that the limiting current is well defined, and these values were taken to draw the Levich plot in FIGURE 4.6. In this plot the values in the abscissa are the square root of the angular speed of the disc (ω , in s⁻¹), which is related to the frequency f (r.p.s., or Hz) by: $\omega = 2 \pi f$.

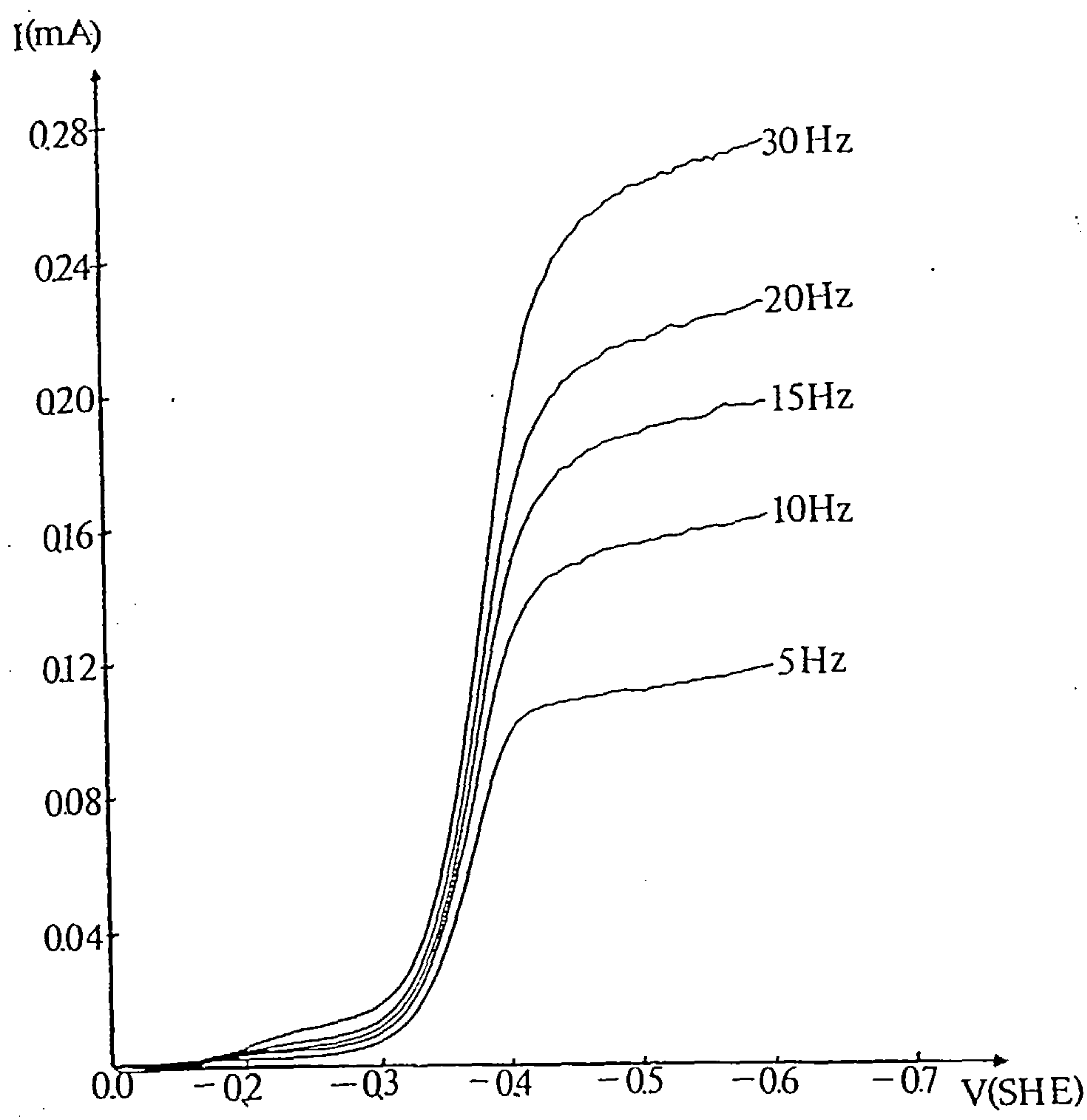


Figure 4.5 - Current-potential curves on a platinum disc electrode for the reduction of 6.0×10^{-4} M AQ (supporting electrolyte 0.5M K_2SO_4 , 0.03M KCN at a scan rate of 0.050 V.s^{-1}).

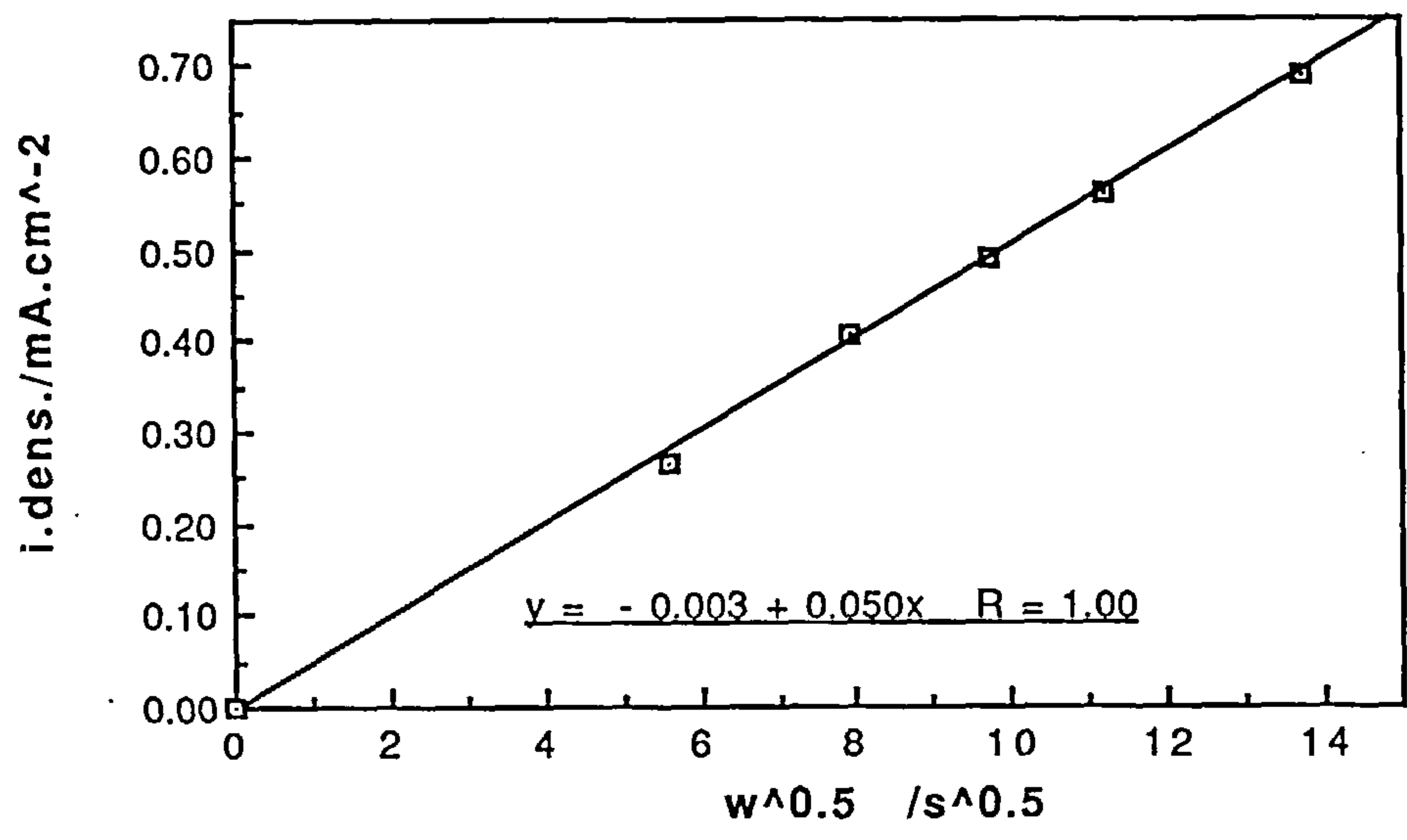
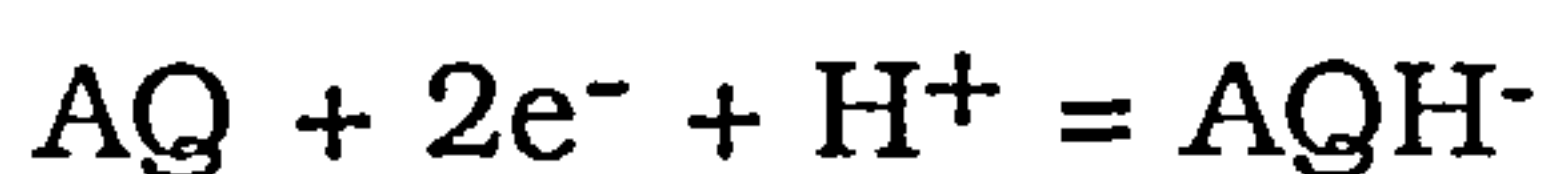


Figure 4.6 - Limiting diffusion current density versus rotational speed. System: 0.5M K_2SO_4 , 0.03M KCN, 6.0×10^{-4} M AQ.

From the slope of the plot in FIGURE 4.6, which is 0.05, and considering the total reduction



the Levich equation may be used to evaluate the diffusion coefficient of the electroactive species (AQ)

$$0.05 = 0.62 \times 2 \times 96490000 \times D^{2/3} \times 10^{1/3} \times 6 \times 10^{-7}$$

$$\text{therefore } D = 5.81 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$$

This value may be compared with that from data obtained by chronoamperometry. In this type of experiment, the potential of the working electrode is changed instantaneously and the current-time response recorded, as shown in FIGURE 4.7 overleaf.

A potential-time profile was then applied to the working electrode from an initial potential, chosen such that no AQ reduction, or indeed any other reaction occurred. At the time $t=0$, the potential was changed to the value (in this case equal to -0.5 V, where the AQ is no longer thermodynamically stable) where the reduction occurs at a diffusion controlled rate.

FIGURE 4.7 shows that the current decayed exponentially with time, which agrees with the Cottrell equation below (i.e. the current falls with $t^{-1/2}$):

$$|I| = (n.F.D^{1/2}.C^0) / \pi^{1/2}.t^{1/2}$$

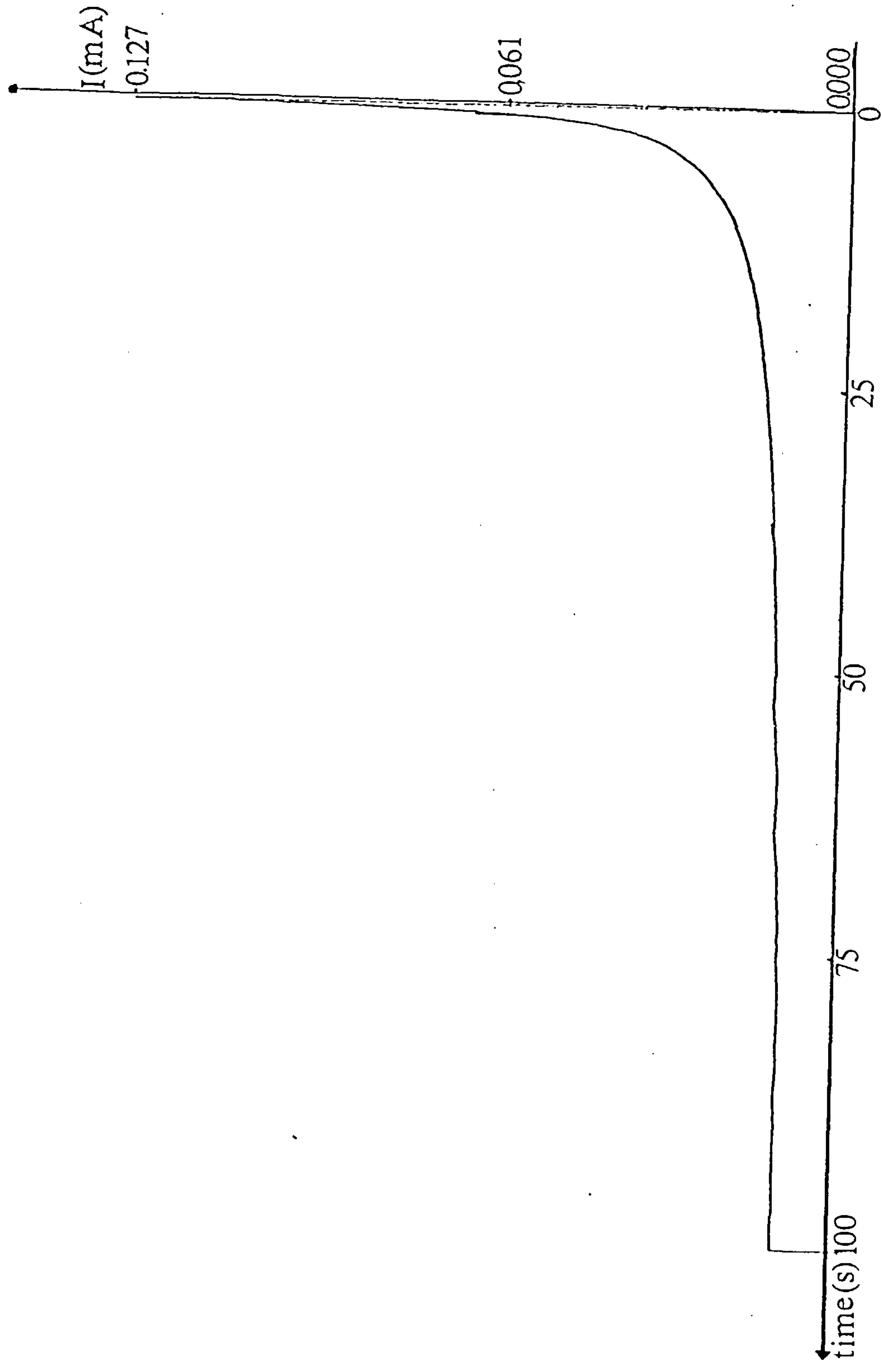


Figure 4.7 - Current 'versus' time response for a potential step experiment (chronoamperometry), with stationary (Pt) electrode. Potential: -0.5 V (SHE); solution: 0.1M K_2SO_4 , 0.03M KCN and 6×10^{-4} M AQ.

The region of the plot $i.t^{1/2}$ 'versus' $t^{1/2}$ where the value of $i.t^{1/2}$ begins to be independent of time corresponds to the diffusion controlled region. This value may be used to calculate the diffusion coefficient of the species with the Cottrell equation. The plot may be seen in FIGURE 4.8.

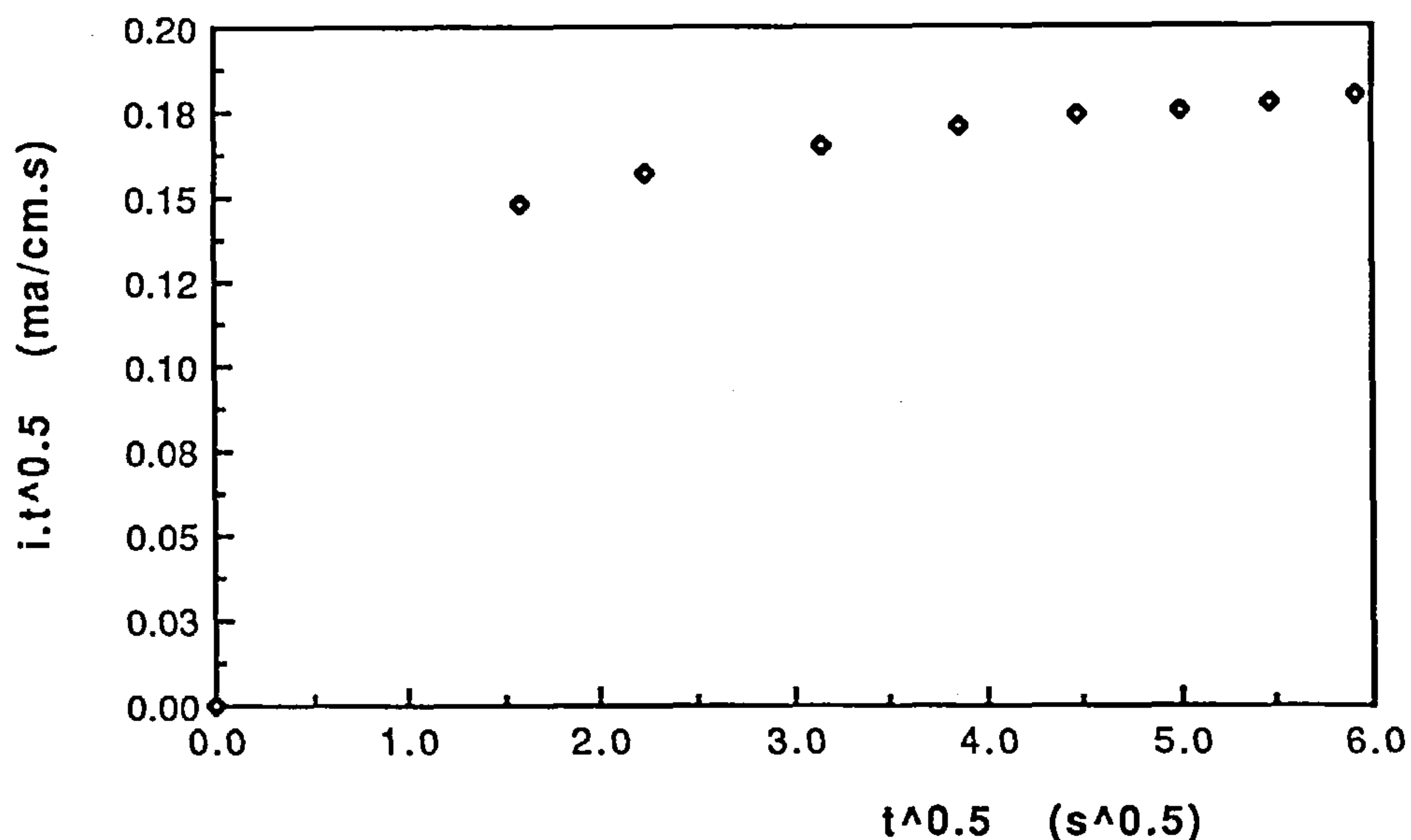


Figure 4.8 - Plot of $i.t^{1/2}$ 'versus' $t^{1/2}$ from chronoamperometric data for $6.0 \times 10^{-4} \text{ M AQ}$.

Taking the value of 0.16 mA/cm.s, which is found shortly after the beginning of the horizontal region and substituting in the Cottrell equation, the following coefficient is obtained:

$$D = 5.99 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$$

which agrees quite well with the value obtained with the Levich equation.

These data may, for example, be used to calculate theoretically the

rate of gold dissolution when the AQ is regarded as the active species in the Levich equation (as for example the value obtained in Chapter V, section 5.3.4).

4.4-Summary

Characterization of both oxidized and reduced species, needed for a future mechanistic study of the role played by the AQ in the cyanidation of gold, was successfully achieved. Chemical and electrochemical techniques were used. The molar absorption coefficient for the AQ under investigation was evaluated. Moreover, since the reduced AQ (anthraquinol) is capable of producing hydrogen peroxide, by reacting with oxygen and simultaneously regenerating the original AQ, this reaction (with quantitative detection of hydrogen peroxide) was also examined. Finally, through an electrochemical study, the diffusion coefficient of the AQ used was evaluated.

CHAPTER V

GOLD DISSOLUTION IN CATALYSED CYANIDE SOLUTIONS

5.1-Introduction

A series of tests were performed to investigate the behaviour of the rate of gold dissolution in the system $\text{KCN} + \text{O}_2$ when additions of 9,10-anthraquinone-2-sulphonic acid (AQ) were made. The practical viability of using AQ as a useful aid in the cyanidation of gold was studied with a rotating disc system. The disc consisted of a thin planar gold surface, large enough in diameter so that any edge effect could be neglected with respect to the total surface area.

Nernst was the first to establish the grounds for a formal interpretation of the steps involved in heterogeneous reactions. He initially assumed that the chemical processes occurring at the liquid/solid interface are always faster than at least one of the transport processes. Therefore the reaction would be always "transport controlled" (later, it was demonstrated that this assumption, which caused considerable controversy at the time of its postulation, in the beginning of this century, was not entirely correct^[134]).

It is generally accepted that the general course of a heterogeneous reaction occurring between a solid and a solution may be interpreted as follows:

1-transfer of oxygen (in the present case) from the gas phase to the liquid

2-transfer of reactants from the bulk of the solution to the interface

3-adsorption and reaction at the surface, and desorption of products.

4-transfer of products away from the solid boundary into the bulk of the solution.

The first, second and the fourth steps are the transport processes, whereas the third is the chemical one.

While Nernst considered just one thin layer of solution adherent to the solid surface, where the concentration of species would vary linearly, it was shown later by Levich^[128,136] that two boundary layers could actually be characterized. One, not adjacent to the solid surface (the rotating disc surface, for instance), was called by "hydrodynamic boundary layer", in which the velocity of the fluid equals that of the bulk value; and the other, around a thousand times smaller than the first one, called "diffusion boundary layer", where there is a concentration gradient of any particular species, and thus mass transfer is accomplished by molecular diffusion only. It has been also demonstrated by Levich^[128] that, if the surface area of the rotating disc in contact with the (leaching) solution is considerably greater than the thickness of the disc, the magnitudes of both the hydrodynamic and diffusion boundary layers have constant values over the entire surface of the disc. Therefore, in the rotating disc system all points on the surface are uniformly accessible to the flowing liquid, rendering it quite appropriate for most investigations. Moreover, Levich proposed an equation which may predict the mass flux of solution to the disc surface, which is

$$j = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} C_0 \quad (5.1.1)$$

where

j is the mass flux of a species onto the surface of the rotating disc ($\text{mol.cm}^{-2}.\text{s}^{-1}$)

D the diffusion coefficient of the active species ($\text{cm}^2.\text{s}^{-1}$)

ν the kinematic viscosity of the liquid (viscosity/density) ($\text{cm}^2.\text{s}^{-1}$)

ω the angular velocity of the disc (s^{-1})

C_0 concentration of the active species in the bulk of the solution (mol.cm^{-3}).

The equation above, known as the Levich equation, is also employed as a test to confirm whether the dissolution occurring at the disc surface is entirely transport controlled, for, if this is the case, a plot of j versus $\omega^{1/2}$ will be linear passing through the origin^[136]. The diffusion coefficient of the active species may be calculated from the slope of this plot. In the case where the transport of the species is the rate-determining step, the Levich equation describes the dependence of the metal dissolution with the rotating speed. If, however, the process is other than transport controlled the equation cannot be applied. It is also worth noticing that the Levich equation applies only to a laminar regime, i.e., in the case of the rotating disc system, to flows characterized by a Reynolds number (R_e ; dimensionless) below about 10^5 . In this case, this number is defined as:

$$R_e = (\omega.R_0^2)/\nu \quad (5.1.2)$$

where R_0 the radius of the disc (cm)

In practical terms, however, because of the vortex build-up near the disc, for the application of the theory in laboratory experiments, a typical upper limit for the rotating speed is 160 Hz and a minimum

theoretical value is taken as 1.6 Hz^[136].

5.2-Experimental

5.2.1 - Apparatus and Method

In order to investigate the dissolution rate, a pure gold (99.9%) disc (area= $1.539 \times 10^{-4} \text{ m}^2$) was coated with an epoxy resin sheath, resistant to chemical attack, in such a way that only one surface of the metal was exposed to the leaching solution. The disc length was 10 cm and the bottom tip was detachable (by unscrewing) to make the polishing step easier. FIGURE 5.2.1 schematically represents the rotating disc employed in the tests,

The disc was rotated by a precise motor (Oxford Electrodes) at a constant angular velocity. A picture of the equipment used for these experiments may be seen in FIGURE 5.2.2.

A number of initial experiments had to be rejected, mainly because of poor repeatability which at times yielded unexpected results. The reason for this outcome was most probably the preparation applied on the disc surface shortly before each experiment. In spite of the care taken, leaching tests with a rotating disc (particularly of soft metals like gold) may lead to disappointing results. Nevertheless, it is perhaps useful to recall that problems of lack of repeatability and of experimental difficulties are often mentioned in the literature^[129,135,137,138].

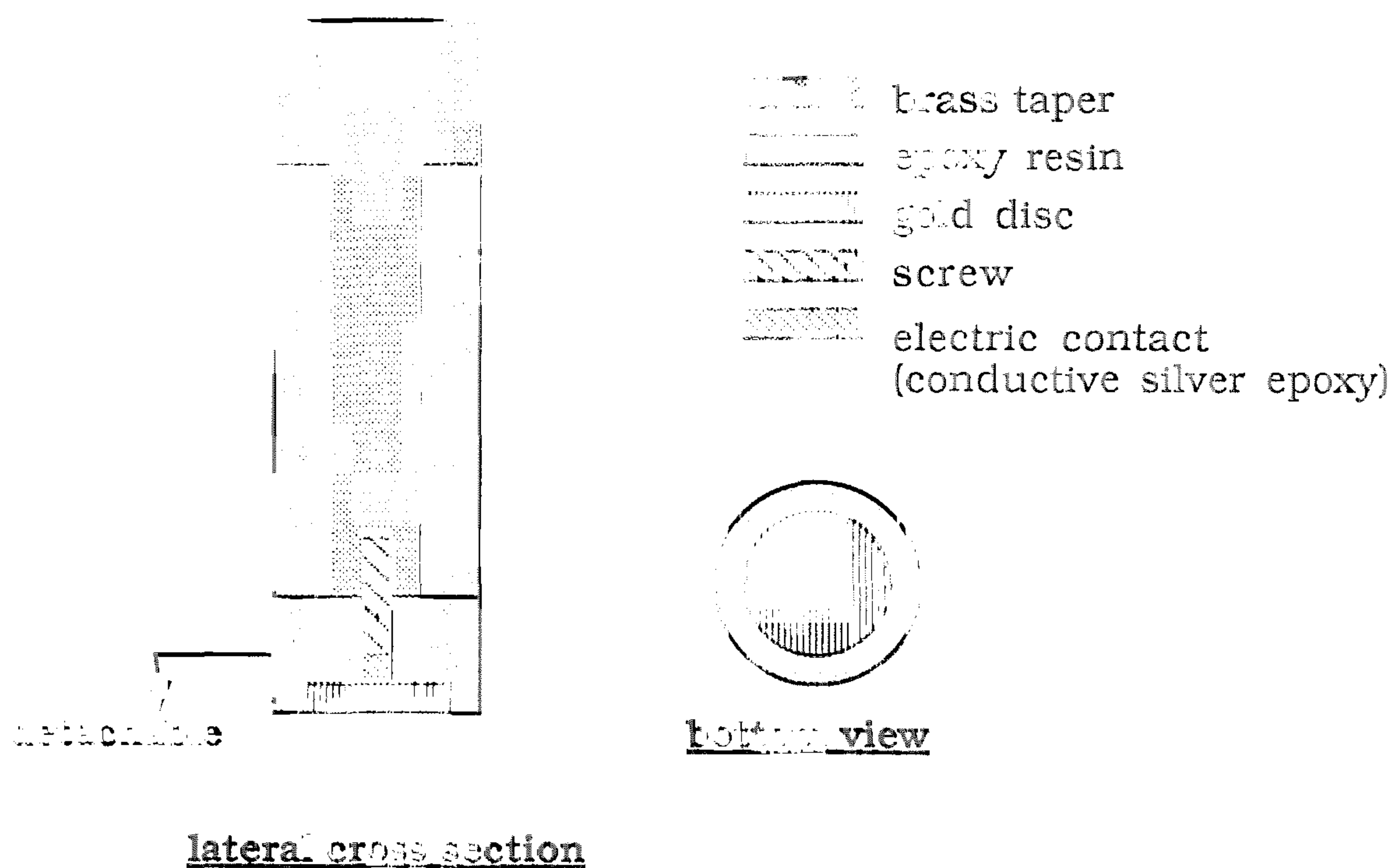


Figure 5.2.1 - Schematic representation of the rotating disc employed in the experiments.

Many disc polishing procedures were tried. The one that best fulfilled the requirements was polishing with diamond compounds (Hyprez Five Star Diamond Compound) of 1.0μ , placed on a silk cloth and using a water soluble liquid type polishing lubricant. The gold disc with a mirror like appearance was then rinsed and immersed in a chromic sulphate ($K_2Cr_2O_7 + H_2SO_4$) solution for about 20 seconds; afterwards the disc was thoroughly rinsed again with double distilled water and was then considered to be suitable for the experiment. In earlier experiments, a further electrolytic cycling (from the oxygen to the hydrogen region and vice-versa) was applied to the disc in a neutral solution ($0.5M K_2SO_4 + 0.01M NaOH$), but the subsequent leaching results did not display appreciable difference compared to those where this cycling was not applied. Therefore the procedure for the

otherwise stated. The amount of gold dissolved from the disc was analysed by atomic absorption in all cases (Perkin Elmer 1100B).

The rates of gold dissolution were calculated from the slopes of the plots: amount of gold dissolution (mg) 'versus' time (h). All the results considered could be fitted linearly, with a correlation factor equal to or greater than 0.980 in most cases. FIGURE 5.2.4 illustrates a typical dissolution profile obtained from tests performed with the rotating gold disc.

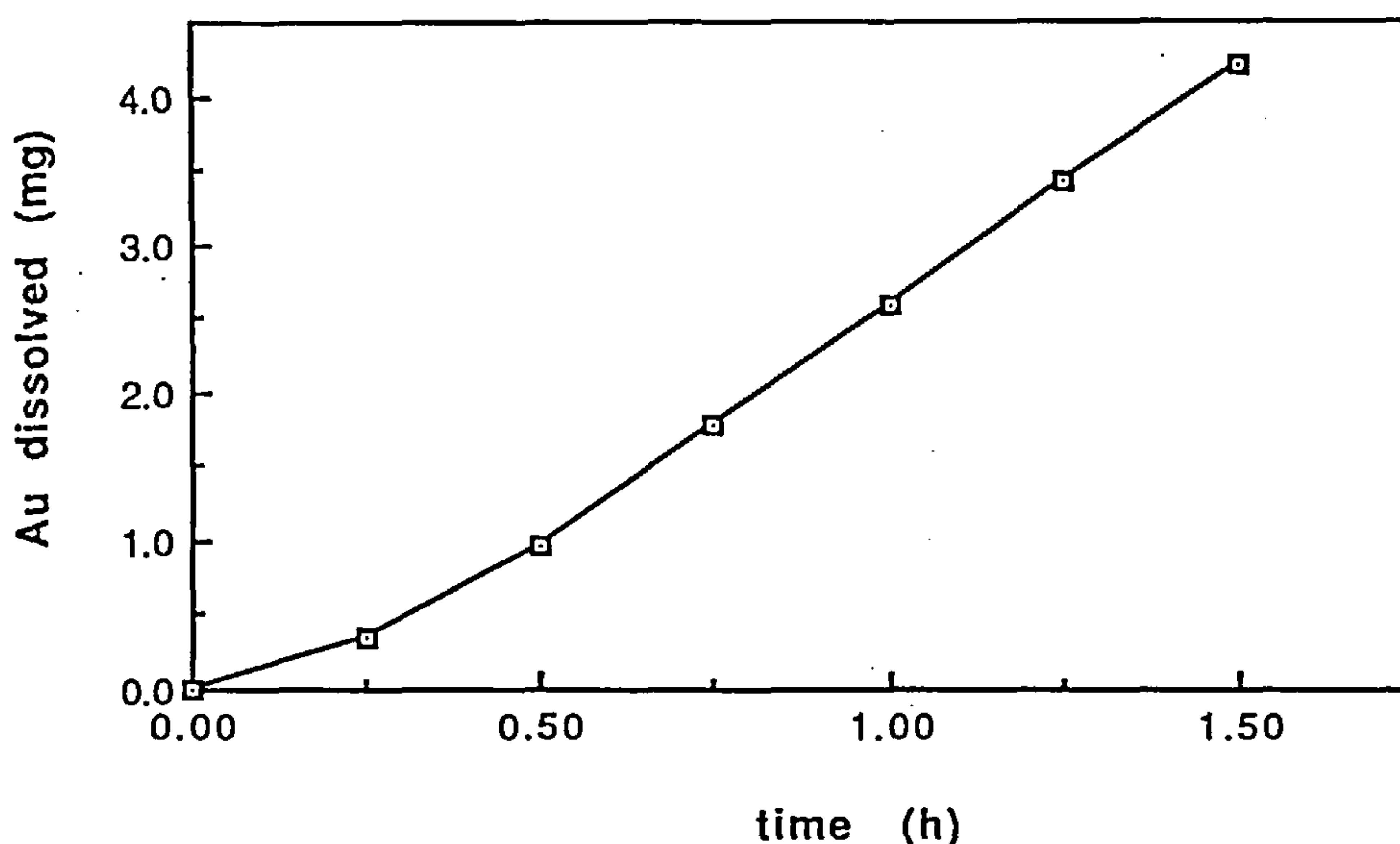


Figure 5.2.4-Dissolution of gold from a rotating disc in an aerated cyanide solution (0.01M KCN; $f=10.0$ Hz; no AQ).

5.2.2 - Standard solutions

The standard solutions used to calibrate the atomic absorption equipment were prepared as follows: a 1000 ppm gold chloride atomic spectroscopy standard solution (BDH) was diluted firstly to 100 ppm; thereafter, this solution was diluted again to fit the standard range required for each analysis (normally standard solutions were

prepared to 5, 15 and 20 ppm). Dilution was made with a solution of the same composition to that used in the leaching trials (cyanide and AQ) to minimise background effects.

Results giving the amount of gold dissolved with time were calculated using the equation below:

$$M_t = C_t (V_{t-1} - S_{t-1}) + \sum_{i=t-1}^0 S_i C_i \quad (5.2.1)$$

where

M_t is the amount of gold dissolved at time t (mg)

C_t the atomic absorption reading in time t (mg/l)

V_t the solution volume in the reactor in time t (l)

S_t the volume of the sample taken (l)

In the evaluation of the rates obtained experimentally, the use of this equation is important to make allowance for the decrease in volume at each sample withdrawal.

The tables with the complete set of results obtained from all the experiments are presented in Appendix II. An oxygen partial pressure of 2.13×10^4 Pa ($[O_2]=8.2$ mg/l) was obtained by bubbling air through the leaching solution, whereas for a $pO_2 = 1.01 \times 10^5$ Pa ($[O_2]=41.0$ mg/l)^[172,173] the gas flow was changed to full oxygen, and kept for at least 30 minutes before starting the experiment (previous tests had shown that there was no significant change in the rate when the initial bubbling time was equal to or greater than 15 minutes). In the case of experiments performed under an oxygen-free atmosphere, nitrogen was flushed through the solution for at least 45 minutes, after which the run was started. The nitrogen stream was kept flowing over the

solution during the time of the experiment and the lid was sealed with silicon rubber to avoid any oxygen leaking in. In all these trials, the oxygen concentration was checked periodically with a dissolved oxygen probe Kent model EIL 7135. The temperature was kept constant within 0.5°C, with the aid of a water bath.

5.2.3 - Materials

Reagent grade potassium cyanide was used in all trials with no further purification. The salt was dissolved in double distilled water and the solutions were freshly prepared shortly before each experiment to avoid cyanide depletion due to oxidation to cyanate. Analytical grade (BDH) 9,10-anthraquinone-2-sulphonic acid ("silver salt") (AQ) was used as the organic catalyst. A stock solution of 0.015 M AQ in 0.001 M KOH (analytical grade-BDH) was previously prepared and diluted accordingly to give the concentration required for each experiment.

For the detection of a possible build-up of hydrogen peroxide in solution (see later), the method suggested by Bayley and Boltz^[80] was used, with the following reagents and concentration: analytical (BDH) standard iron (II) solution (ammonium iron sulphate-Mohr's salt), 0.21 g/l; analytical (BDH) 1,10-Phenanthroline solution, 0.50 g/l. At this concentration, this reagent needs to be gently warmed and stirred for some minutes to achieve complete dissolution. The buffer used was sodium acetate-acetic acid solution, and, from previous trials, it was found that the method does not suffer from interferences of AQ, if this compound is present in the concentrations used in this work. This method of determination is fully described in Appendix IV.

Free cyanide was measured with a cyanide-ion selective electrode with the calibration curve fitting linearly to concentrations as low as 10^{-6}M . Values obtained from a typical calibration curve are shown in TABLE 4.2.1 (additional data and a full description of the method of determination of cyanide with a selective electrode is given in Appendix IV).

Cyanide conc. (10^{-6})(M)	Pot. reading (mV)
1.00	-3.70
2.00	12.70
4.00	32.2
6.00	42.50
9.90	55.00
29.0	81.00
48.0	92.00

Table 5.2.1 - Typical values obtained for the calibration curve for the cyanide-ion selective electrode (plot is in semi-logarithmic paper).

Experiments were carried out in order to study the behaviour of gold dissolution when various amounts of AQ were added to different concentrations of the leaching solution (KCN) and of oxygen partial pressure, as well as under an oxygen-free atmosphere. The effect of the rotating speed was also investigated under different experimental conditions and the temperature was changed from 25°C to 55°C in some experimental conditions; in this way, activation energy values could be evaluated. The pH was not adjusted with any alkali (apart from the KOH used to prepare the AQ stock solution) and remained in the region between 10.4 and 11.5 (which is the pH range actually used during the cyanidation of gold). The dissolution potential observed on

the gold surface (and measured against a Ag-AgCl reference electrode) typically changed during the course of the experiment from -420 mV to -380 mV (SHE) for a conventional aerated solution, and from -250 mV to -300 mV (SHE) when AQ was added to the leaching solution.

In order to investigate previously the effect of AQ on cyanide, the following test was also performed: different AQ concentrations (up to 22mM) were added to shaking bottles covered with parafilm (to avoid the effect of oxygen), containing aqueous 0.01M KCN, and at the constant temperature of 25°C. The cyanide contents were analysed with the selective electrode, in the way described in Appendix IV. Samples were collected at regular intervals and at the end of 24 hours of test there was no detectable cyanide oxidation. This is an important result, and indicates that AQ will not interfere with the cyanide oxidation during the dissolution of gold.

5.3 - Results

5.3.1 - Repeatability

The repeatability^[97] of the measured rate was examined by performing a series of seven experiments under similar conditions. These results are illustrated in TABLE 5.3.1.

The values ranged from 2.84 to 3.02 x 10⁻⁹ mol/cm².s. The **standard deviation**, in this case given by

$$\sigma = \sum \left[\frac{(Au_i - Au_{\text{mean}})^2}{6} \right]^{\frac{1}{2}} \quad (5.3.1)$$

and which measures the dispersion of the data in absolute values, was found to be $0.0247 \times 10^{-9} \text{ mol/cm}^2\text{s}$. The **mean** value was $2.86 \times 10^{-9} \text{ mol/cm}^2\text{s}$ with an average deviation of 4.01%, which was regarded as an acceptable figure (below 5%).

test	rate(mol/cm ² .s) J x 10 ⁹	deviation from mean (%)
Au-1	2.99	+4.65
Au-2	2.86	-0.10
Au-3	2.70	-5.50
Au-4	2.63	-7.95
Au-5	2.96	+3.60
Au-6	3.02	+5.70
Au-7	2.84	+0.60
mean	2.86	4.01

Table 5.3.1 - Repeatability of the measured rate (0.03M KCN; f=10Hz; no AQ; air only).

The gold surface was examined microscopically at the end of each of these tests and no indication of uneven attack or pitting was observed. The linearity of the plot between the amount of gold dissolved and time, reported earlier, was also an indication that the metal surface area was constant throughout the leaching trials.

5.3.2 - Effect of cyanide concentration and pO₂

The influence of KCN concentration, with no AQ added, on the rate of

gold dissolution was initially investigated to serve as a parameter for comparison with the tests when the catalyst was added. The KCN concentration was varied within the range from 0.0025 M to 0.09 M. The disc rotating speed was kept at 10.0 Hz in all tests (the effect of changing the rotating speed is shown later) and $pO_2 = 2.13 \times 10^4$ Pa (air only). The results are summarized in FIGURE 5.3.1. The amount of gold dissolved with 0.0025M KCN was negligible and could not be detected by the atomic absorption method employed in the analysis.

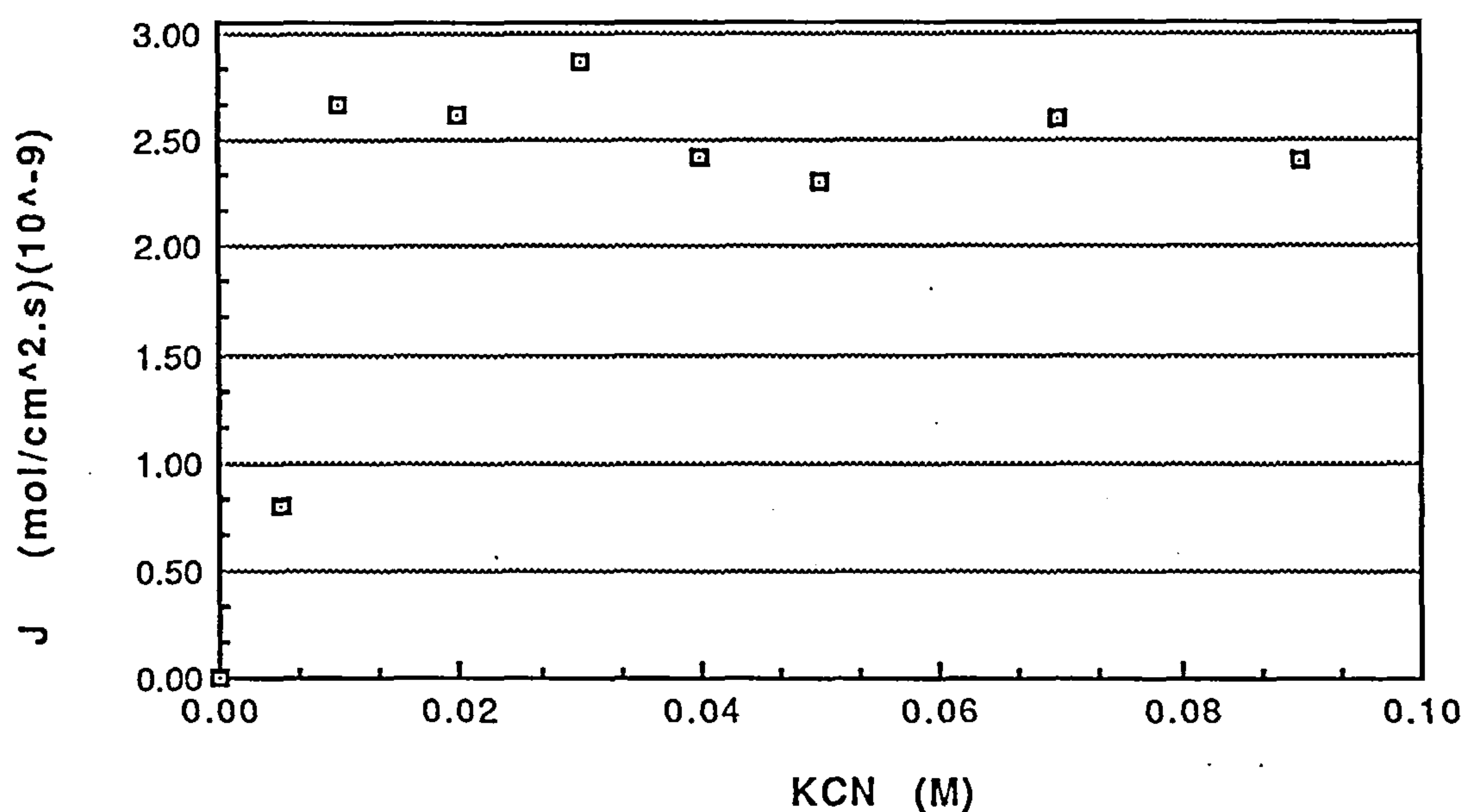


Figure 5.3.1 - Variation of the rate of gold dissolution with cyanide concentration, under normal aerated solution, and no AQ added.

It can be seen that for KCN concentrations above 0.01M there is no significant further increase in the rate of gold dissolution (actually, a slight decrease in the rate is observed at high cyanide concentrations). Therefore, it is evident that, as expected^[125,126] the rate is independent of the cyanide concentration for values equal to or

greater than 0.01M and depends on the availability of oxygen only (for oxygen coming from air). While the results may appear straightforward, these tests are important because, as the aim of this work is to increase the oxidizing efficiency of the leaching solution, early tests must necessarily be performed in the region where the rate is not dependent on the cyanide concentration.

To further investigate this point, tests were carried out by bubbling pure oxygen through the leaching solution in order to give an oxygen concentration of around 1.28 mM (42.0 mg/l). The results for these tests may be seen in FIGURE 5.3.2.

In fact, for a higher oxygen partial pressure the rate of gold dissolution increases considerably compared with the previous value. While not immediately obvious from the figure, it is also noticeable that for a higher oxygen concentration in solution, the cyanide concentration beyond which there is no further increase in the rate is switched from 0.01M (the optimum value when air only is flowing) to 0.05M.

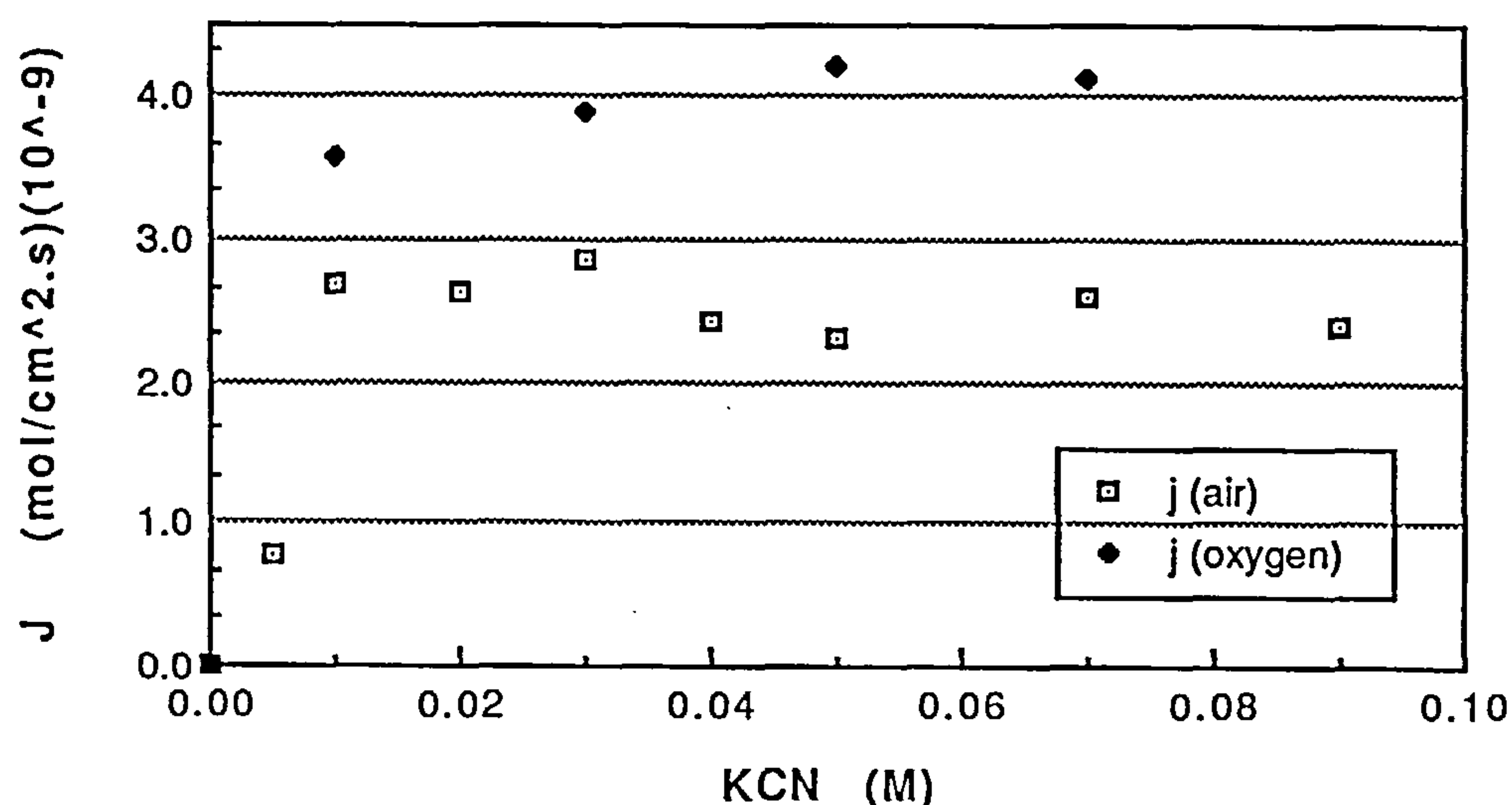


Figure 5.3.2 - Gold dissolution rate dependence on cyanide concentration showing effect of two different oxygen concentrations.

5.3.3 - Effect of anthraquinone

A number of test were performed to investigate the effect on the rate, of AQ additions to a cyanide solution, initially bubbled with air only. The AQ concentration was varied within the range from 0.30mM to 6.00mM, the KCN concentration was kept at 0.03M and the disc rotation speed at 10 Hz in all cases. The results of these tests are depicted in FIGURE 5.3.3.

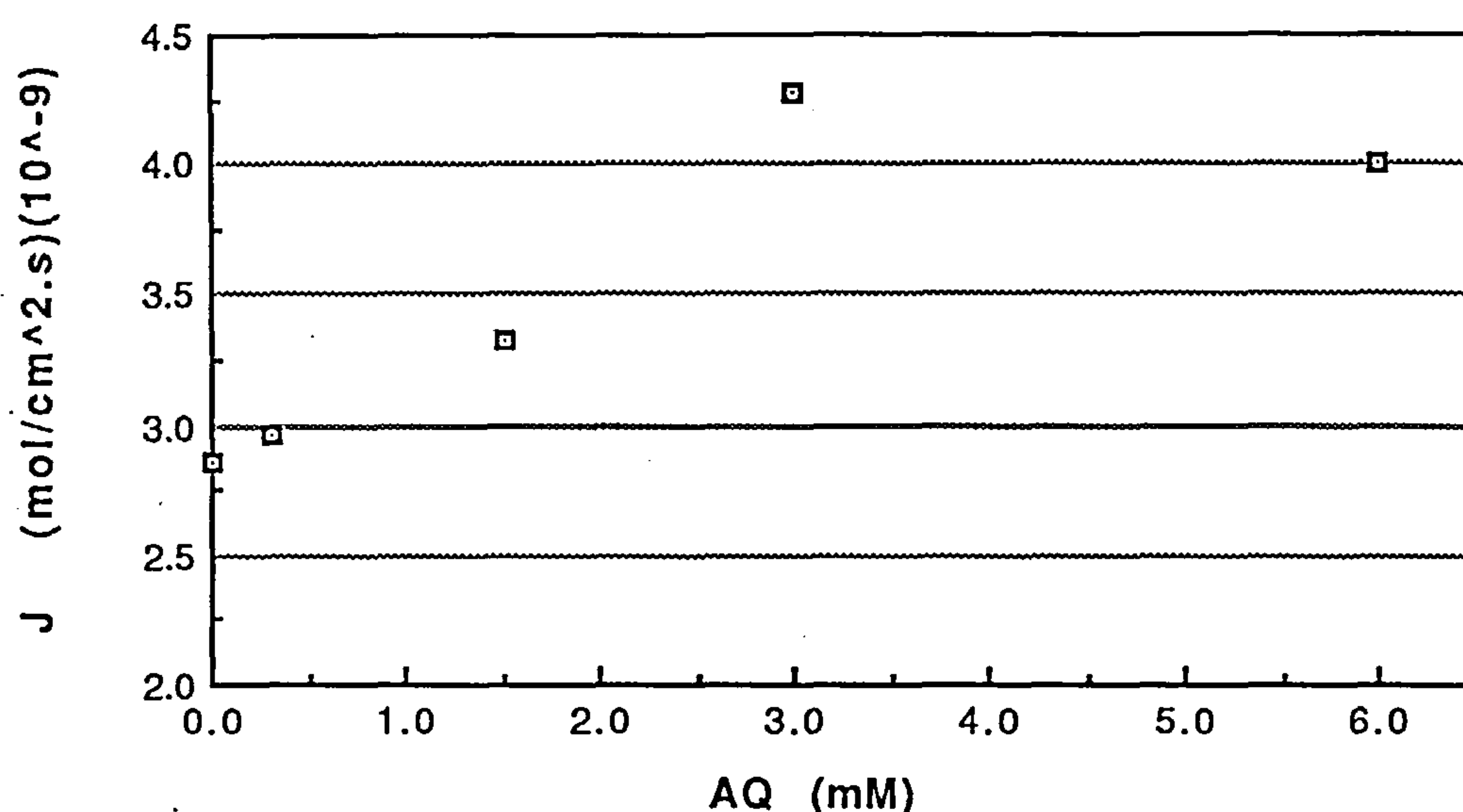


Figure 5.3.3 - Rate variation of gold dissolution with AQ additions (KCN 0.03M, air only)

It is clear from the figure that as the concentration of AQ in the leaching solution increases, the rate accordingly attains higher values, up to a limiting AQ concentration of 3.00mM; beyond this point additions of AQ do not cause further enhancement of the rate of gold dissolution (in fact, the rate suffers a small decrease). In order to obtain a clearer view of this picture, a new series of experiments was carried out. In each of them, the AQ concentration was maintained at

three different levels, 1.50mM, 3.00mM and 6.00mM, while the cyanide concentration varied from 0.0025M to 0.09M. These results are reported in FIGURE 5.3.4, where the rate values when no AQ was present may also be seen. Air only was flushing and the disc rotation speed was kept at 10 Hz.

It was confirmed that there is a significant increase in the rate of gold dissolution when AQ is added to an aerated cyanide solution. Moreover, the highest rates were attained not for a KCN concentration of 0.01M ($2.67 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$), as was the case when there was no AQ, but rather at 0.03M KCN ($4.24 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$). Beyond this point (KCN 0.03M), however, no significant difference in the rate was observed. This is more clearly seen in FIGURE 5.3.5, which shows results from tests changing cyanide concentration, both with no AQ and 3.00mM AQ only.

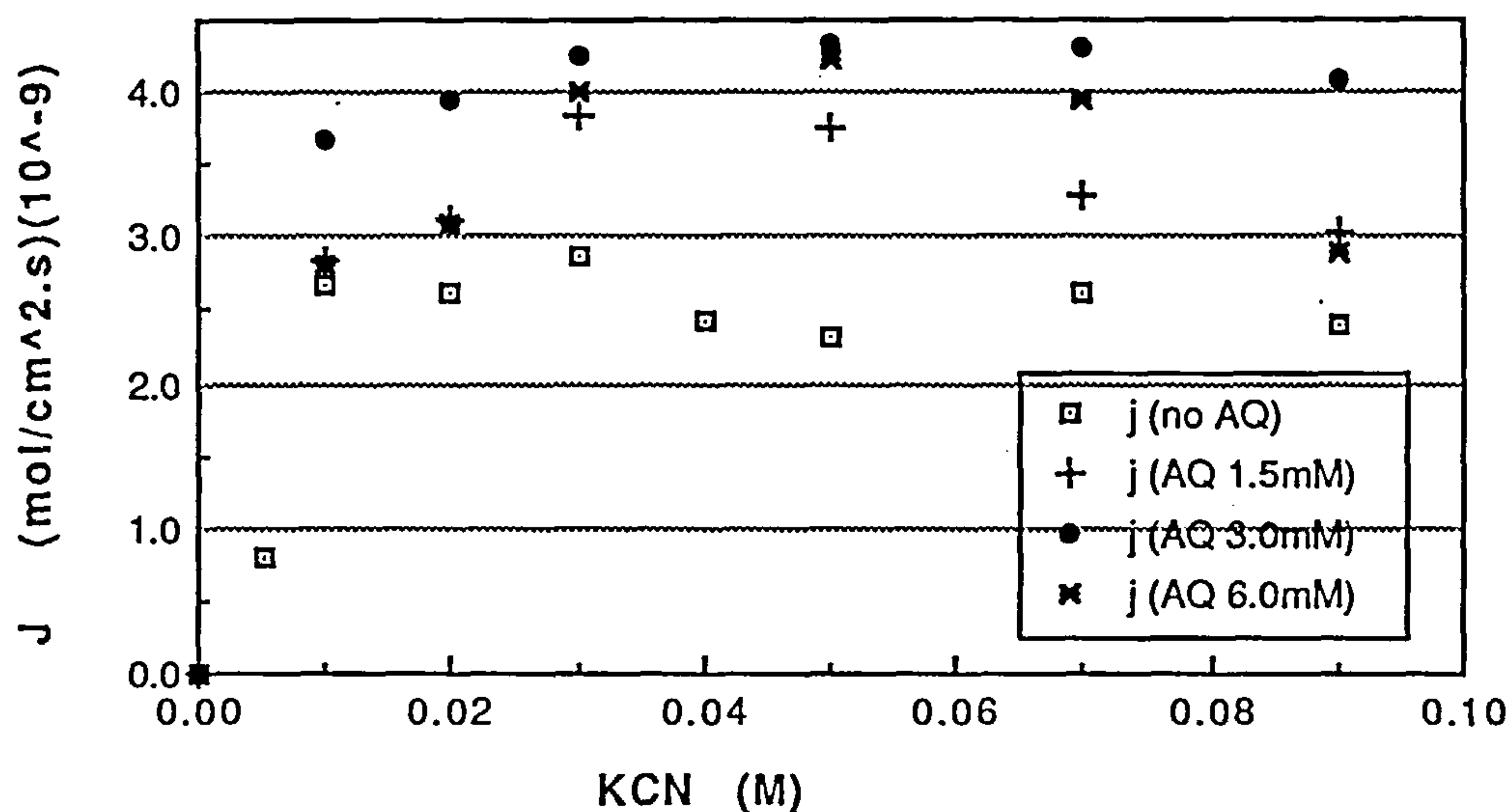


Figure 5.3.4 - Au dissolution rate dependence on KCN and AQ concentration (air only).

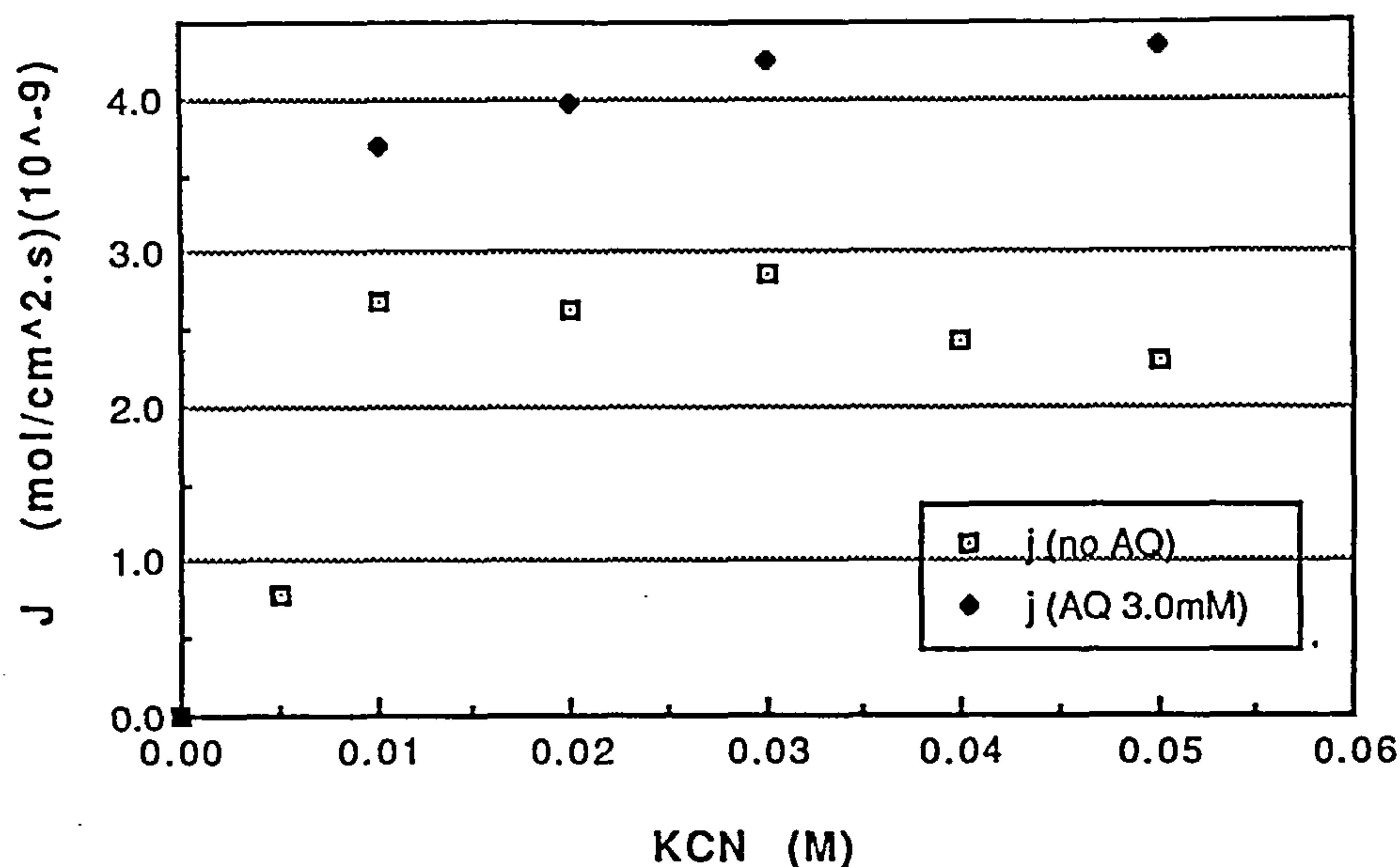


Figure 5.3.5 - Variation of gold dissolution rate with KCN concentration, showing influence of 3.00mM AQ addition (air only).

The influence on the rate of gold dissolution of the three AQ concentrations used in the above tests, 1.50mM, 3.00mM and 6.00mM, was also investigated again at various cyanide concentrations, but under a full oxygen atmosphere. These results are shown in FIGURE 5.3.6, where the results obtained when no AQ was added also appear.

It may be seen that the marked effect of AQ on the rate when air only is bubbling (see FIGURE 5.3.4 and 5.3.5) is considerably diminished by the greater availability of oxygen in solution. The highest rates were once more observed for cyanide concentrations in the region of 0.03M. Also, it is interesting that at higher KCN concentrations the rate is slightly decreased if AQ is present in the system.

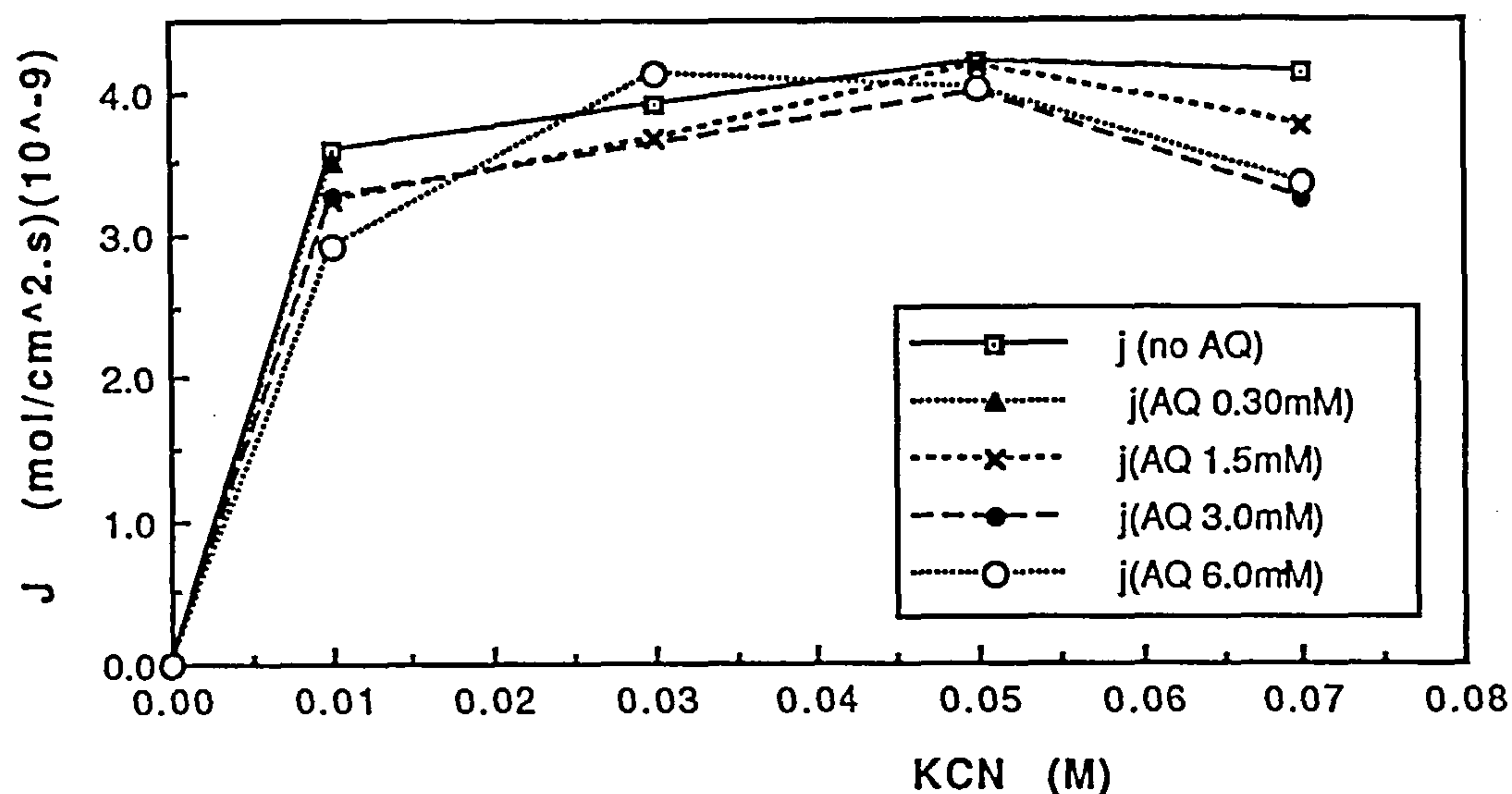


FIGURE 5.3.6 - Au dissolution rate variation with KCN and AQ concentrations with oxygen flowing.

5.3.4 - Effect of the rotating speed

All tests mentioned above were performed at a fixed rotating speed of 10 Hz. Thus, the influence of changing the rotating speed on the rate of gold dissolution was initially examined under the following experimental conditions: KCN 0.01M, air only and no AQ added. The value of 0.01M was chosen for this set of trials because it had already been seen that, for an aerated solution, the rate is independent of the cyanide concentration for values at or above this one.

Three different rotating speeds were initially used (in Hz): 2.5, 6.1 and 10.0. It should be noticed that, while theoretically lower rotating speeds may be investigated, the equipment used for the tests does not keep a strictly uniform rotation for values below 2.5 Hz. The results are shown in FIGURE 5.3.7, which is a plot of the rate measured against the square root of the rotating speed (Levich plot). As seen in a

former section, this is a good test to demonstrate whether the reaction is entirely mass transport controlled or not. In such a case, the plot must be linear and pass through the origin.

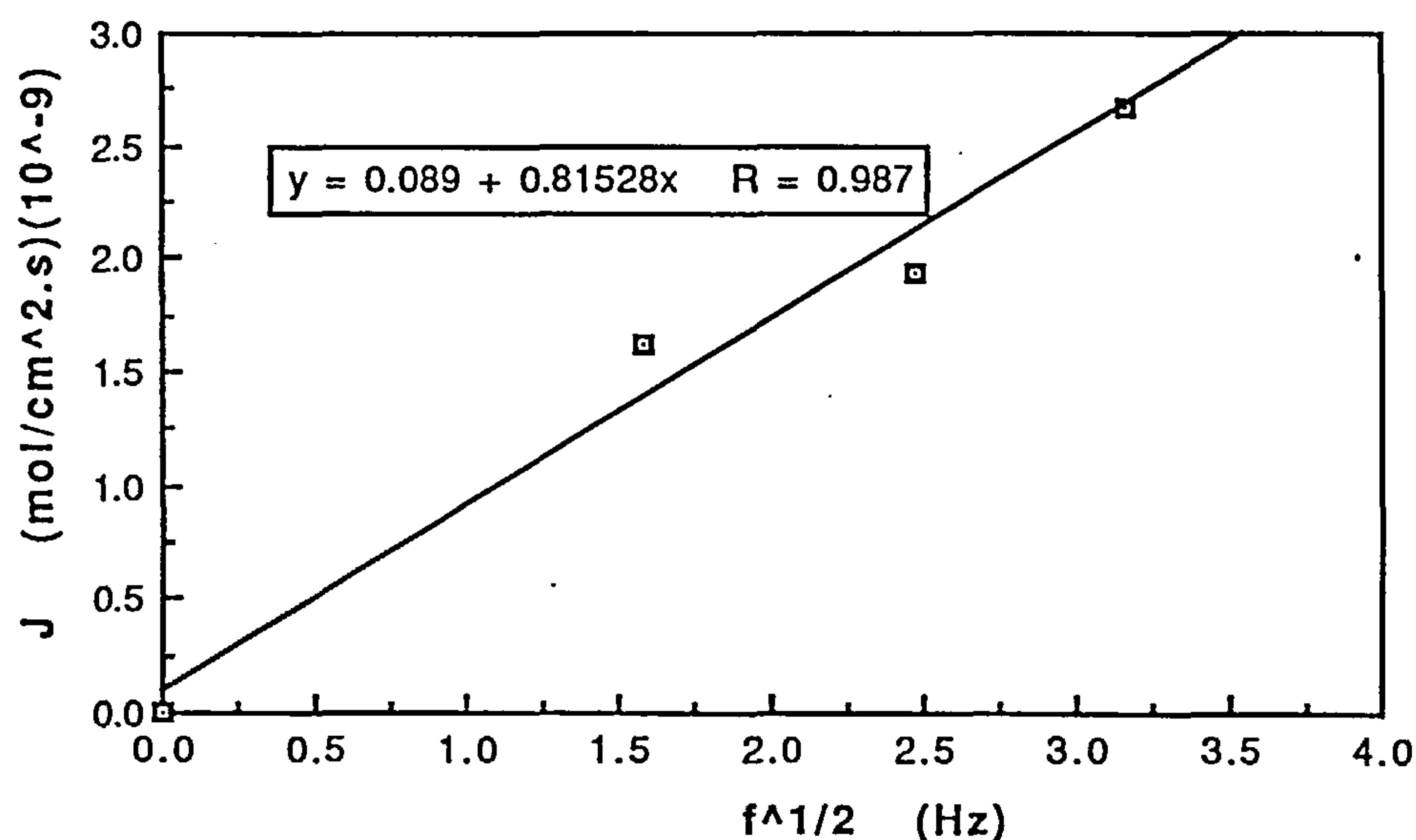


Figure 5.3.7 - Gold dissolution rate dependence on square root of rotating speed, showing linear region only (KCN 0.01M; no AQ; air only).

From this figure, it may be seen that the plot in this region fits reasonably well to a straight line. This means that, in this region, the rate of gold dissolution is mass transport controlled, i.e., it depends on the transport of species to the gold surface. If, however, higher rotating speeds are used, the plot deviates from linearity, as also pointed out in the literature^[130]. This may be seen in FIGURE 5.3.8, where the results from five different rotating speeds are plotted.

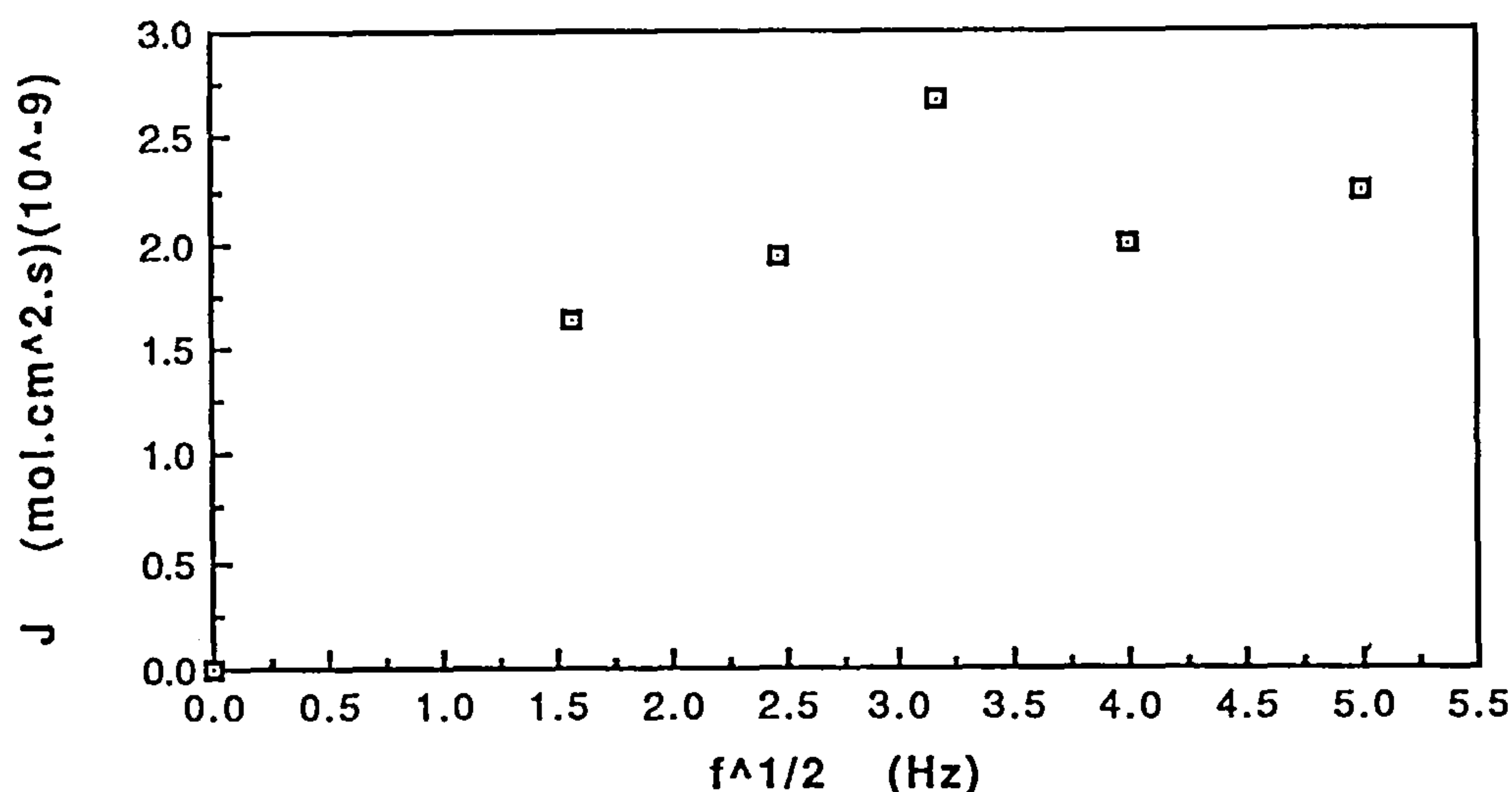


Figure 5.3.8 - Gold dissolution rate dependence on square root of rotating speed (KCN 0.01M; no AQ; air only).

A similar set of experiments were then performed to explore the effect of changing the rotating speed in a system of KCN 0.01M, and AQ 3.00mM (and air only). The rotating speeds used were (in Hz): 2.5, 6.1, 10.0 and 16.0. Also, an investigation using two different rotating speeds, 2.5 and 10.0 Hz, was carried out with the same cyanide concentration (0.01M), but with no AQ and with pure oxygen flushing the system. These results are shown in FIGURE 5.3.9 where the values obtained for the former experiment (with air only) are also displayed. The figure shows that for the system with AQ and air only, the behaviour is similar to when no AQ is present, in the sense that the rate of gold dissolution is mass transport controlled up to a rotating speed of 10.0 Hz. Beyond this point, it probably turns to be controlled by the chemical reaction occurring at the disc surface. Furthermore, it is also noticeable that the slope of the straight line for the experiments with AQ is over 30% above than that obtained when the leaching solution is cyanide and oxygen (from air) only. This situation

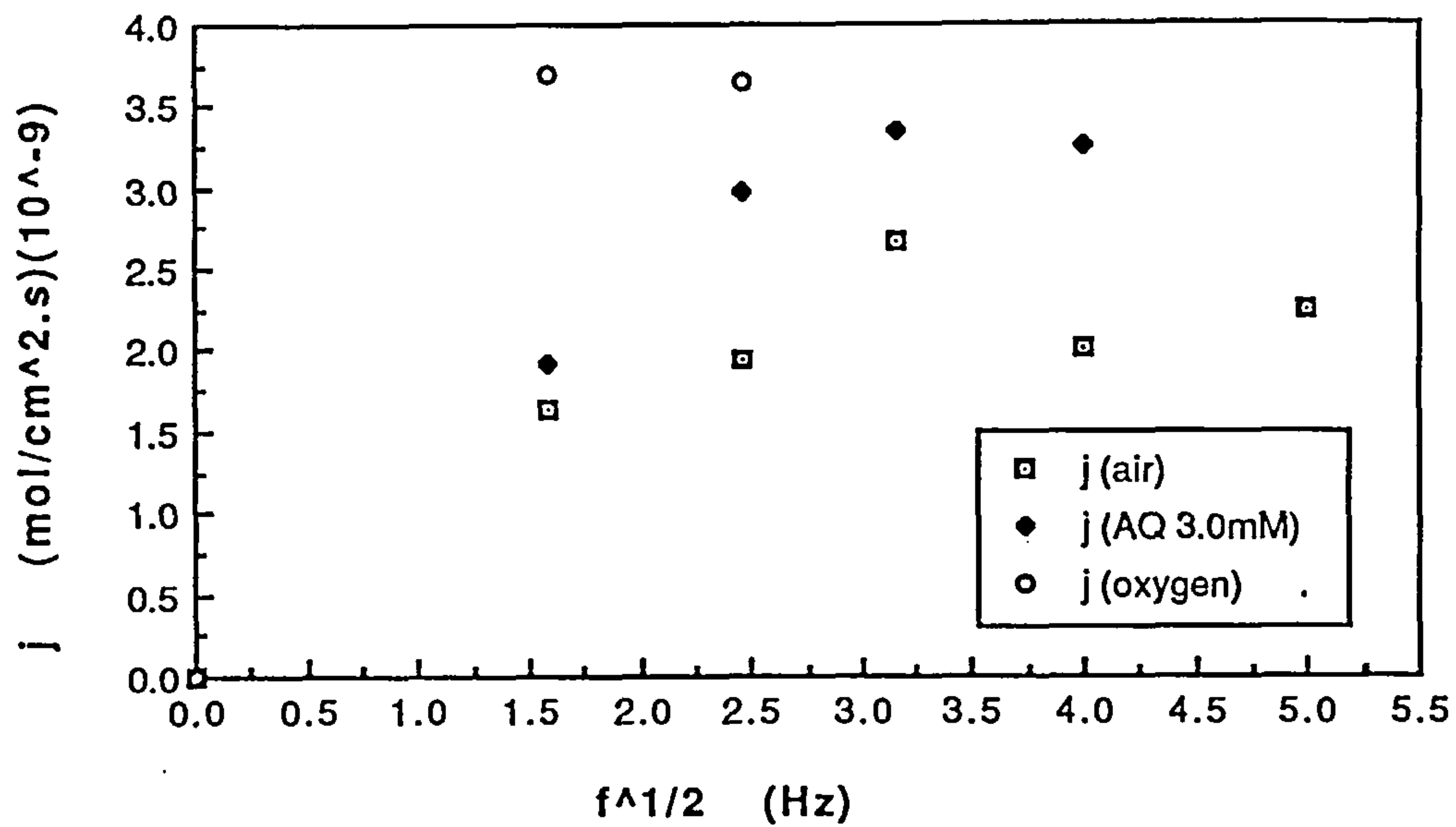


Figure 5.3.9 - Gold dissolution rate dependence on the square root of the rotating speed, at 0.01M KCN, showing the effect of flushing air, oxygen and adding 3.0 mM AQ.

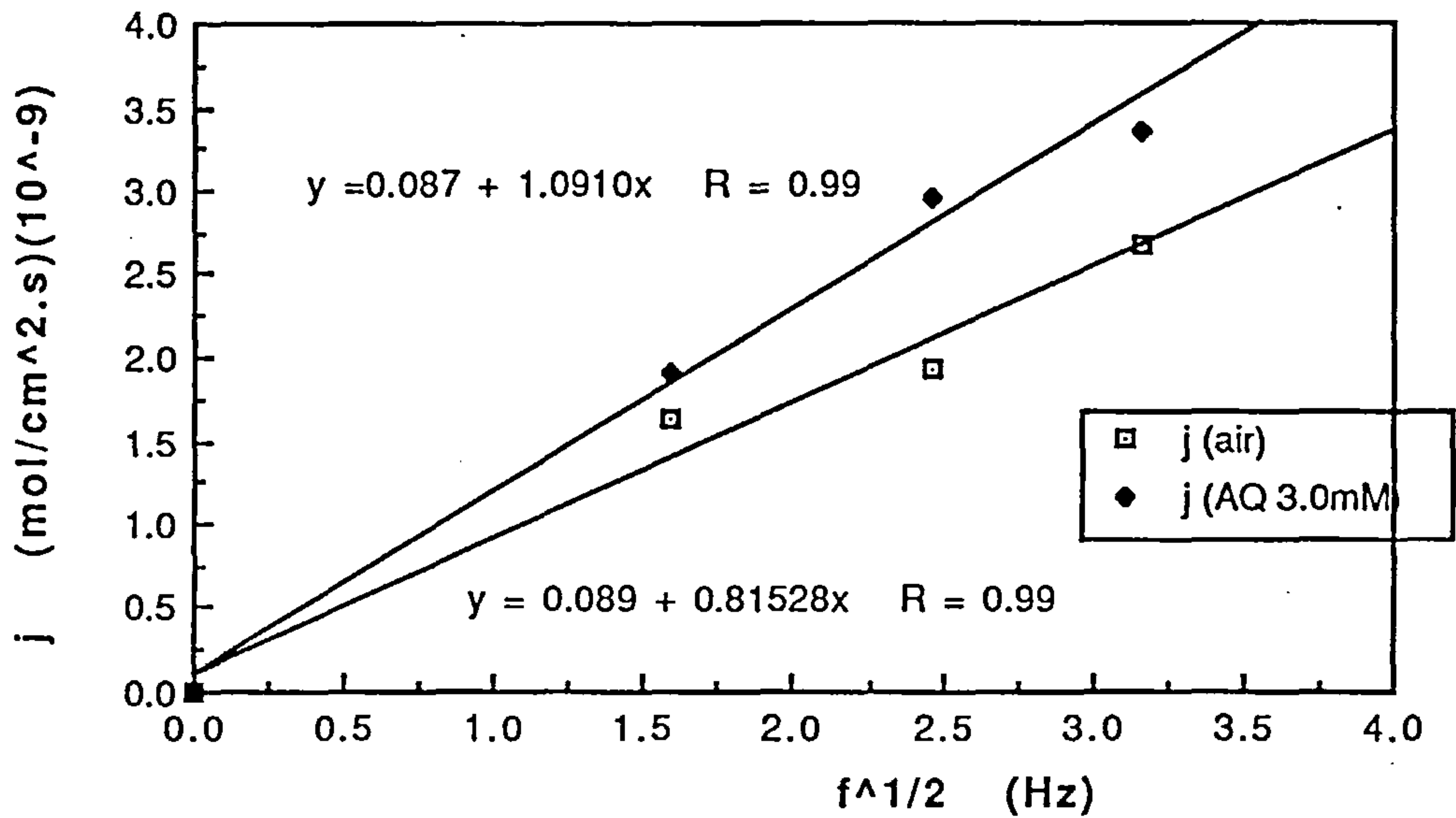


Figure 5.3.10 - Linear region of gold dissolution rate dependence on square root of rotating speed, at 0.01M KCN, air flushing, with and with no AQ (3.0mM).

is better seen in FIGURE 5.3.10 where only the points up to 10.0 Hz were plotted.

For the case where pure oxygen is flowing, the transport step from the gas phase into the liquid, and then to the disc surface, is overcome at lower rotating speeds than in the case for air only; this outcome may be seen in FIGURE 5.3.9, where the results for oxygen only do not follow the Levich equation. This behaviour is in agreement with that reported in the literature for experiments under similar conditions^[130], and indicates that in this case (where oxygen is present at higher concentration), the chemical reaction occurring on the gold surface, rather than the transport step, is more likely to control the dissolution process.

Theoretical rate values may be obtained from the Levich equation for different concentrations of cyanide, oxygen and AQ. These are shown in TABLE 5.3.2, and may be compared with the results obtained experimentally. For the calculation, typical diffusion coefficients for cyanide and oxygen^[174] were taken as $10^{-5} \text{ cm}^2.\text{s}^{-1}$ and $2.2 \times 10^{-5} \text{ cm}^2.\text{s}^{-1}$ respectively; for the AQ, the diffusion coefficient used, $5.81 \times 10^{-6} \text{ cm}^2.\text{s}^{-1}$, was obtained experimentally in the way described in Chapter IV; kinematic viscosity of the solvent (water) was assumed to be $10^{-2} \text{ cm}^2.\text{s}^{-1}$. The value for "Co" in the Levich equation depends on which of the species involved in the process is the rate controlling; i.e. which is the one whose availability controls the dissolution rate.

It may be seen from the table that the theoretically calculated values are higher than those obtained experimentally. The difference between the experimental and calculated values has already been mentioned in previous work, and has been attributed either to the possible formation of an insoluble film of reaction products on the metal surface or to an approximation in the equation made by

rate contr. species	observed rate (mol/cm ² .s)	theoret. rate (mol/cm ² .s)
CN ⁻ conc. (M)	with 1.27mM O ₂ ; J x 10 ⁹	J x 10 ⁹
0.010	3.64	9.80
0.030	3.90	29.40
0.050	4.21	49.00
rate contr. species	observed rate (mol/cm ² .s)	theoret. rate (mol/cm ² .s)
O ₂ conc. (mM)	with 0.03M KCN; J x10 ⁹	J x 10 ⁹ .
0.256	2.86 (no AQ)	3.50
	3.09 (0.3 mM AQ)	
	3.30 (1.5 mM AQ)	
	4.28 (3.0 mM AQ)	
	4.00 (6.0 mM AQ)	
	with 0.05M KCN	
1.280	4.21 (no AQ)	17.00
	4.18 (1.5 mM AQ)	
	4.00 (3.0 mM AQ)	
	4.03 (6.0 mM AQ)	
rate contr. species	observed rate (mol/cm ² .s)	theoret.rate(mol/cm ² .s)
AQ conc. (mM)	J x 10 ⁹	J x 10 ⁹
1.50	2.85 (0.01M KCN; air only)	4.10
	3.23 (0.01M KCN; oxygen)	
	3.83 (0.03M KCN; air only)	
	3.66 (0.03M KCN; oxygen)	
	4.18 (0.05M KCN; oxygen)	
3.00	4.28 (0.03M KCNl; air only)	8.19
	4.34 (0.05M KCN; air only)	
	1.50 (0.01M KCN; nitrogen)	
6.00	4.00 (0.03M KCN; air only)	16.40
	4.12 (0.03M KCN; oxygen)	
	2.12 (0.01M KCN; nitrogen)	

Table 5.3.2 - Experimental and theoretical values for gold dissolution from a rotating disc (calculation using the Levich equation) (f=10 Hz).

Levich^[125,132]. In any case, though, this is an indication that the reactants or the reaction products may be adsorbing on the surface and imposing an additional diffusion barrier, leading to slower rate than predicted. It is interesting to note, however, that when using oxygen from air only (0.256 mM; 8.2 ppm) the theoretical rate is comparable to the experimental one, when AQ is also present in the system. With 3.0mM AQ the experimental value is actually higher than the theoretical one. In spite of the diffusional barrier that might be forming, this suggests that the disagreement between practical and theoretical values is cancelled because of the additional oxidizing agent (in this case the AQ) and leads to a rate value equivalent to that predicted by the Levich equation. Also, when considering AQ as the rate controlling species, the theoretical rate is equivalent to that actually observed in practice for 1.5mM AQ, 0.05M KCN and full oxygen.

5.3.5 - Experiments with no oxygen

5.3.5.1 - Rotating disc

To further investigate the role played by AQ at the gold surface, and its ability to act as a suitable oxidizing agent for the cyanide system, a number of experiments under a nitrogen atmosphere were carried out, as described in section 5.2.1. In this case, AQ is the sole oxidizing agent, and, therefore, the cyclic oxidation $\leftrightarrow$ reduction path no longer takes place. The results are seen in FIGURE 5.3.11, where the amount of gold dissolved is plotted against time. These experiments were important because they demonstrated that in an aqueous cyanide solution gold may be actually oxidized by an oxidant other than oxygen or hydrogen peroxide (this is the first time that a different and

recyclable oxidant has been successfully demonstrated in the gold cyanidation process). An interesting effect is observed: the gold dissolved increases with AQ concentration, but only up to a point, beyond which the AQ effect starts to influence in the opposite way (i.e., less gold dissolves with higher AQ concentrations). In the figure, this may be noticed by comparing the curve for 6.00 mM and 12.00 mM AQ, where the amount of gold dissolved is higher in the former instance.

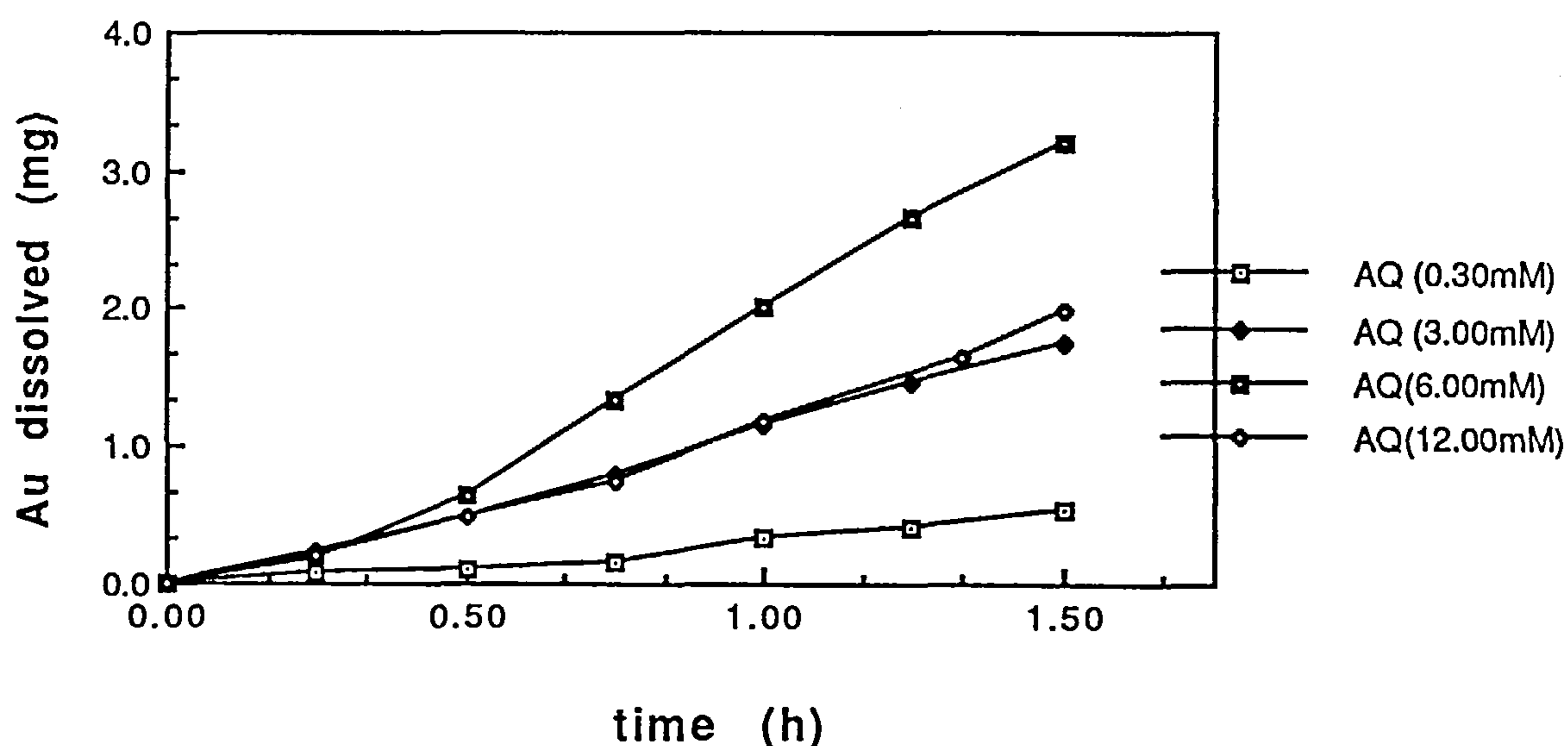


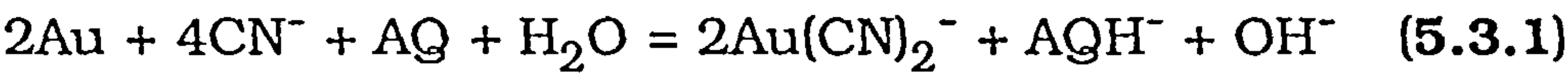
Figure 5.3.11 - Amount of gold dissolved with time, under an oxygen free atmosphere and different AQ concentrations (0.01M KCN; $f=10.0$ Hz).

The actual rates obtained may be seen in TABLE 5.3.3, where the value for the experiment with no AQ and normally aerated leaching solution is also shown for comparison.

J (mol/cm ² .s)(10 ⁻⁹)	AQ (mM)
2.67	air
0.33	0.30
1.10	3.00
2.12	6.00
1.23	12.00

Table 5.3.3 - Variation of the rate of gold dissolution in a 0.01M KCN, normally aerated solution, and with different additions of AQ (tests with AQ carried out in a oxygen-free solution).

It should be pointed out that an initial test was carried out under nitrogen but with no AQ, to test for any oxygen leaking into the reactor; under this experimental condition, as expected, no detectable gold was dissolved. Therefore, the results seen in FIGURE 5.3.11 suggest that the oxidation reaction necessary for the process was due to the AQ as



This means that, with AQ present in the system, gold dissolution is possible, even in the complete absence of oxygen.

The tests shown in FIGURE 5.3.11 were with 0.01M KCN. However, on increasing the cyanide concentration, the point where the rate starts to decrease shifts toward higher AQ concentrations. This outcome may be seen in FIGURE 5.3.12, which depicts the situation where different AQ and cyanide concentrations are used, always under

an oxygen-free atmosphere.

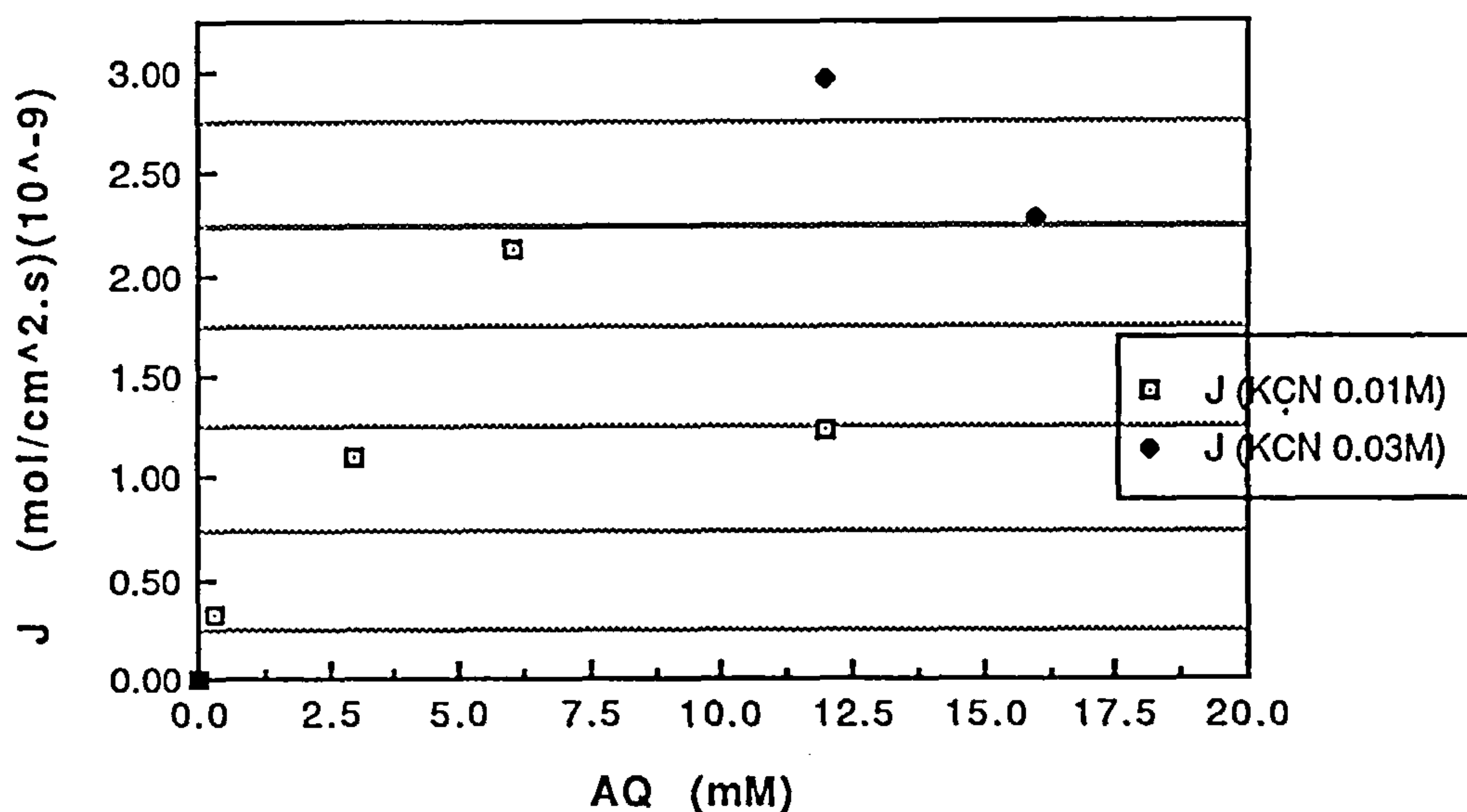


Figure 5.3.12 - Gold dissolution rate dependence on KCN and AQ concentration, in an oxygen-free solution ($f=10$ Hz).

As will be seen, these results suggest that a mechanism of adsorption may be occurring at the gold surface, where the reagents responsible for different reactions would be displacing each other, according to their respective concentration, leading to the behaviour observed. This subject, along with the analysis of the results given above, is treated in more detail in section 5.4.

5.3.5.2 - High-surface area metallic sponge

The consumption of AQ during the oxidation of gold was quantitatively investigated with a high surface area Ni-Cr sponge. This sponge, with a surface area of $8.56 \times 10^{-3} \text{ m}^2$ was previously plated with gold under the conditions detailed in Appendix I. The advantage of using this type of material was that the larger amount of gold available consumed

more AQ, so that it was feasible quantitatively to measure the AQ decay. A 0.01M KCN solution, with $1.34 \times 10^{-4}\text{M}$ AQ was thoroughly deaerated with nitrogen and connected to a flow-cell in a UV-visible spectrophotometer by means of glass tubing and a peristaltic pump, in a manner similar to that described in Chapter IV for the electrochemical reduction of AQ. The wavelength was 330nm and thus any AQ variation could be detected by the absorbance reading. Stirring was provided by a magnetic follower. FIGURE 5.3.13 below represent the profile of AQ decay during 90 minutes of test.

The absorbance did not decrease totally to zero probably because of some leak of oxygen into the circuit, in spite of the care taken to avoid this problem. The solution, colourless at the beginning of the experiment, turned to a reddish aspect, characteristic of the reduced species. It is interesting to note that, in this case, the reduction was accomplished by the gold plated on the electrode.

The analysis (atomic absorbance) of gold content in the final solution was, for a ten times diluted sample, 16.1 mg/l. If the reaction is represented by equation 5.3.1, the initial AQ concentration could theoretically oxidize $2.68 \times 10^{-4}\text{M}$ of gold. The value actually obtained was $2.00 \times 10^{-4}\text{M}$, which, considering the oxygen leak mentioned above, may be regarded as an acceptable approximation to indicate that AQ was almost totally reduced during the process and that the stoichiometry of the reaction is indeed the one indicated by equation 4.3.1. After the period allowed for the reaction (90 minutes), air was admitted into the reactor, causing, as expected, the prompt regeneration of the original AQ.

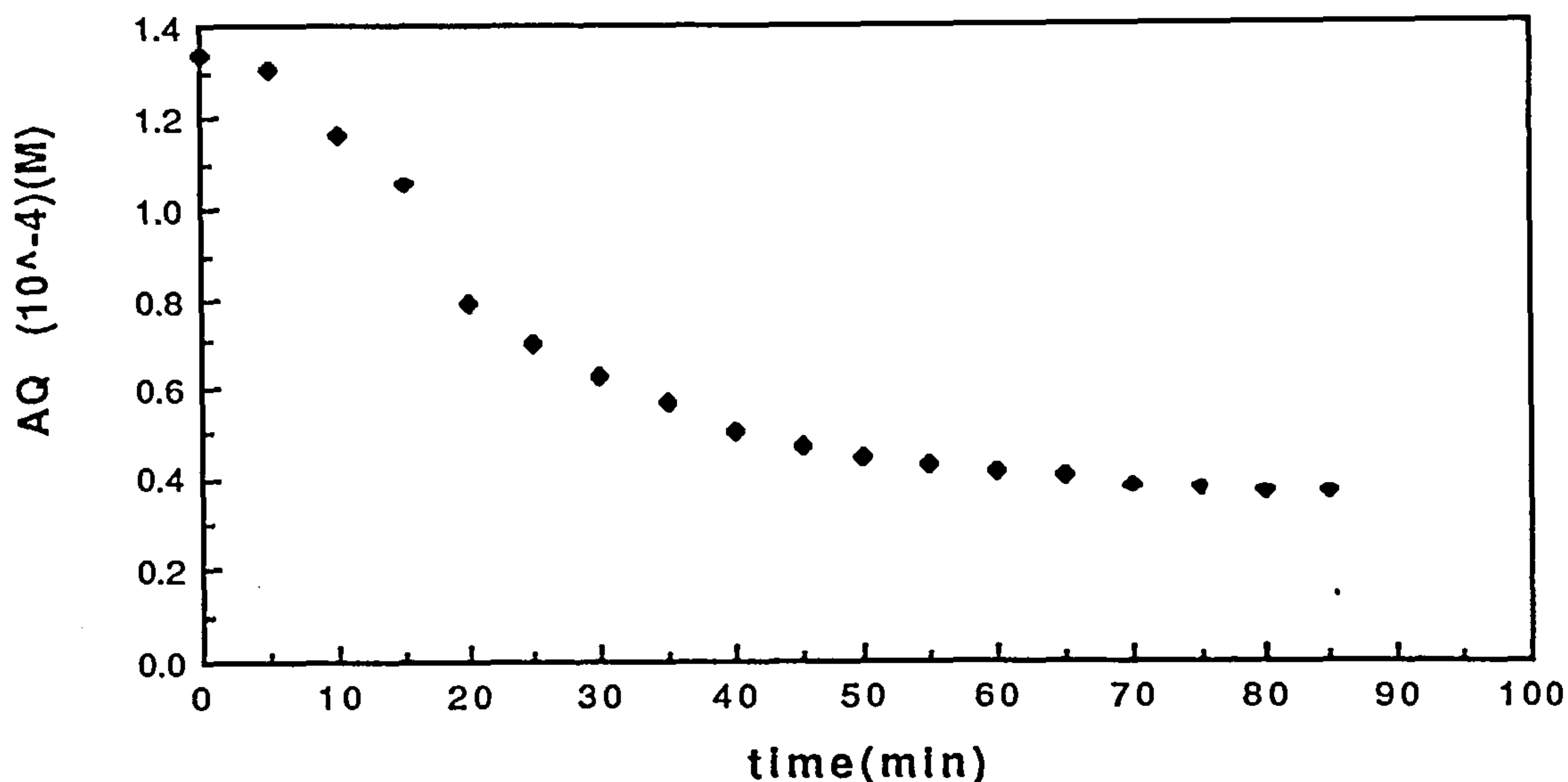


Figure 5.3.13 - AQ consumption (reduction) while oxidizing Au in 0.01KCN, under nitrogen atmosphere ($\lambda=330\text{nm}$; path length 10mm).

5.3.5.3 - "In-situ" hydrogen peroxide generation

While the "in-situ" production of hydrogen peroxide had already been demonstrated by the experiment described in Chapter IV, further tests were run to investigate quantitatively this mechanism, this time during the dissolution of gold from the rotating disc. The first test was carried out normally, under nitrogen, when after 2 hours the disc was raised from the leaching solution in order to stop the dissolution process. Thereafter, the nitrogen was replaced by an air flow, for at least 15 minutes. This procedure would, thus, allow the oxidation of the reduced AQ with simultaneous generation of hydrogen peroxide, according to equation 3.8. The leaching solution was then again thoroughly deaerated with nitrogen, the gold disc lowered and the experiment carried out normally for more 90 minutes. The results obtained from this type of test may be seen in FIGURE 5.3.14 below.

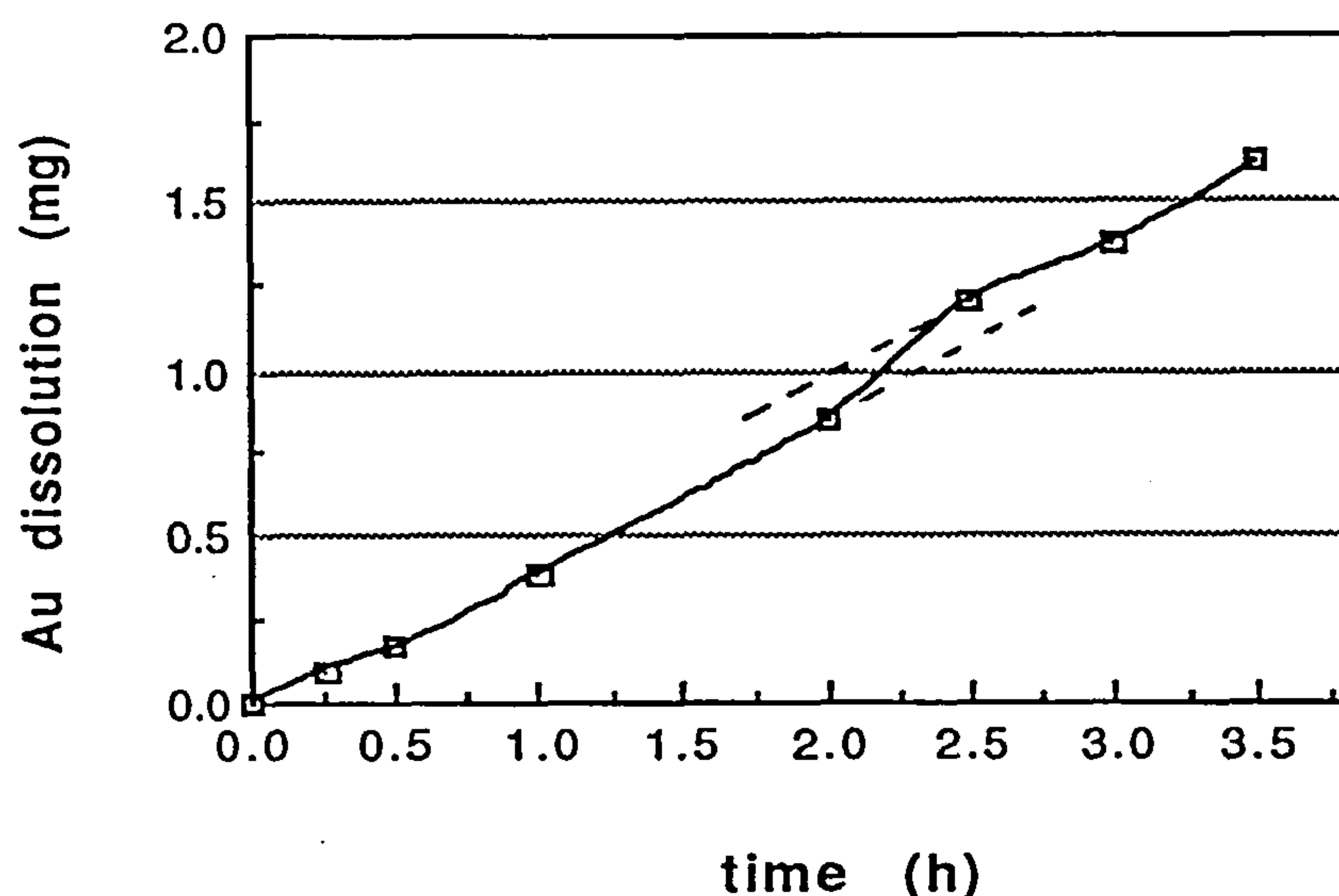


Figure 5.3.14 - Amount of gold dissolved with time, under an oxygen-free atmosphere, with AQ regeneration with air at $T=2.0h$ (0.01M KCN; 0.60mM AQ; $f=10$ Hz).

While not immediately obvious, it may be noticed from the figure that there occurred a slight deviation in the curve from 2.0h (which was the moment the experiment stopped and air was allowed in the reactor) to 2.5h (when the experiment had started again, under a nitrogen flux). The increase observed was

$$1.20\text{mg} - 0.85\text{mg} = \mathbf{0.35 \text{ mg of gold}}$$

which corresponds to 0.008mM (since the volume of the reactor was 0.225l).

The AQ present in the leaching solution (0.60mM) could theoretically dissolve 1.2mM of gold. The analysed amount of 0.019mM of gold (corresponding to 0.85mg) indicates that 0.0095mM (0.019mM/2) of

the AQ had been converted to the corresponding anthraquinol. This amount, through oxidation (equation 3.8), would provoke the regeneration of the original AQ plus the the formation of 0.0095mM of hydrogen peroxide. This concentration, according to equation 3.3, would stoichiometrically dissolve 0.019mM of gold, which is higher than the dissolution actually detected. This outcome may suggest that the "in-situ" hydrogen peroxide formed by the regeneration of the AQ was only partially used to oxidize the gold and probably did not take further role in the second part of the experiment, i.e., in this period the oxidation was carried out again by the AQ alone. This may be more clearly seen by analysing the rate values in the first part of the experiment (up to 2.0h only) and the rate from 2.5h onwards, which are shown in TABLE 5.3.4:

period considered(h)	rate (mol/cm ² .s)(10 ⁻⁹)
from 0 to 2.0	0.40
from 2.5 to 3.5	0.41

Table 5.3.4 - Rates of gold dissolution in an oxygen-free solution, showing values before and after AQ regeneration (0.01M KCN; 0.60mM AQ).

As may be seen, after the initial increase observed from 2.0 to 2.5h, the rate is the same as when the experiment started and no hydrogen peroxide had been generated. This suggests that, as seen above, in the second part of the test AQ was again the sole oxidizing agent in the process. The produced hydrogen peroxide that was not consumed to oxidize the gold was probably decomposed (hydrogen peroxide is unstable in alkaline solution, particularly without any stabilizer^[29]).

To further investigate these results, a similar set of experiment was then carried out at lower AQ concentration (0.12mM). This test ran for 2.5h under nitrogen before stopping to allow "in-situ" hydrogen peroxide generation by reaction with air. Nitrogen was again introduced in the reactor for 45 minutes before restarting the experiment, which was then carried on up to 3.75h. The results may be seen in FIGURE 5.3.15, and are of a similar profile to those obtained earlier (FIGURE 5.3.14). Gold dissolved is, as expected, not as high as the previous test, since in this case the AQ concentration is lower. Again the increase in the gold dissolved, observed at 2.5h, was

$$0.79\text{mg} - 0.59\text{mg} = 0.20\text{mg of gold}$$

which corresponds to 0.005mM. Following the same reasoning as before, 0.12mM AQ would theoretically dissolve 0.24mM of Au. The analysed 0.013mM (0.59mg) indicates that 0.0065mM AQ had been converted to anthraquinol.

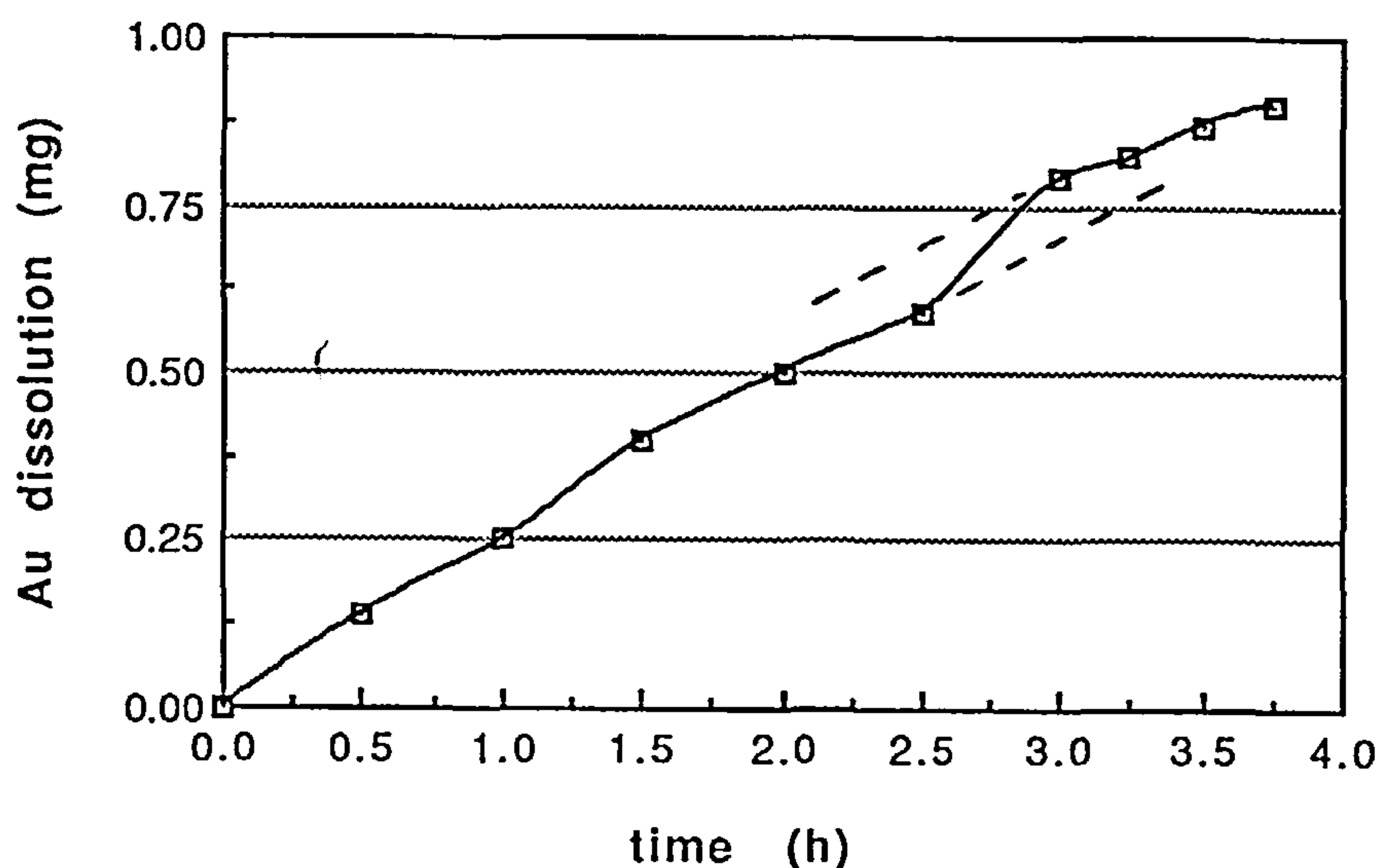


Figure 5.3.15 - Amount of gold dissolved with time, under an oxygen-free atmosphere, with AQ regeneration with air at T=2.5h (0.01M KCN; 0.12mM AQ; f=10Hz).

This regenerates AQ and produces 0.0065mM H₂O₂, which could theoretically oxidise 0.013mM of Au. This result again indicates that the peroxide, while taking part in the oxidation of gold, was but partially used for this end. This may be also seen in TABLE 5.3.5, where the rates observed before and after the AQ regeneration are displayed. These are approximately the same and also in agreement with the results obtained in the former experiment (i.e., in both cases the rates observed in the second part of the experiment are equivalent).

period considered(h)	rate (mol/cm ² .s)(10 ⁻¹⁰)
from 0 to 2.5	2.20
from 3.0 to 3.75	2.26

Table 5.3.5 - Rates of gold dissolution in an oxygen-free solution, showing values before and after AQ regeneration (0.01M KCN; 0.12mM AQ).

5.3.6 - Effect of temperature

All tests mentioned so far were performed at a constant temperature of 25°C. In order to investigate the effect of the temperature and evaluate the activation energy involved, a number of tests were carried out at three additional temperatures: 35°C, 45°C and 55°C. In all cases a water bath was used. For each set of temperature the experiemental conditions were changed as seen in TABLE 5.3.6:

set No.	1	2	3*	4	5
AQ(mM)	12.0	1.5	no	no	no
KCN(M)	0.03	0.03	0.03	0.03	0.01
gas	nitrogen	air	oxygen	air	oxygen

Table 5.3.6 - Experimental conditions of tests investigating the effect of temperature (f=10Hz).

Results are presented as plots of log rate (J) versus 1/T (the Arrhenius plot), from the equation:

$$\ln J = \ln A - \frac{1}{T} \frac{E_a}{R}$$

(5.3.3)

These are straight lines, and the activation energy (E_a) may be then calculated from their slopes ($- E_a / R$). Full details of the amount of gold dissolution found in each experiment, as well as of the calculations performed to obtain the activation energy, are reported in the tables of Appendix II.

Activation energies may vary considerably for different types of reactions, but there is a general rule of thumb that if the activation energy is not much higher than 20kJ/mol, the rate of the reaction is probably controlled by diffusion or another transport mechanism (rather than by a slow chemical process); for rates controlled by a chemical reaction, the activation energy may be of the order of 60 to above 100kJ/mol [140,141]. It is important to note, however, that in spite of being a useful parameter, the activation energy alone cannot

*in this set two additional temperatures were used: 40 and 50°C

strictly define the mechanism of a reaction, which often may prove to be a complex problem^[142].

FIGURE 5.3.16 is the Arrhenius plot for the results obtained from experiments carried out with conventional aerated solutions, and with plenty of cyanide to form the soluble gold complex. In this case, the availability of oxygen (the oxidizing agent) was controlling the rate of gold dissolution. The rate of reaction increases with temperature, but this effect is not marked. The activation energy obtained, **18.7 kJ/mol**, indicates that under these experimental conditions the dissolution rate is probably diffusion controlled, a fact already suggested in the literature^[143]. Activation energy values reported for the dissolution of gold in cyanide solutions vary from around 14.3 to 25.4 kJ/mol^[96]. The Arrhenius plots for the remaining experimental conditions are shown in FIGURES 5.3.17... 20 on the following pages.

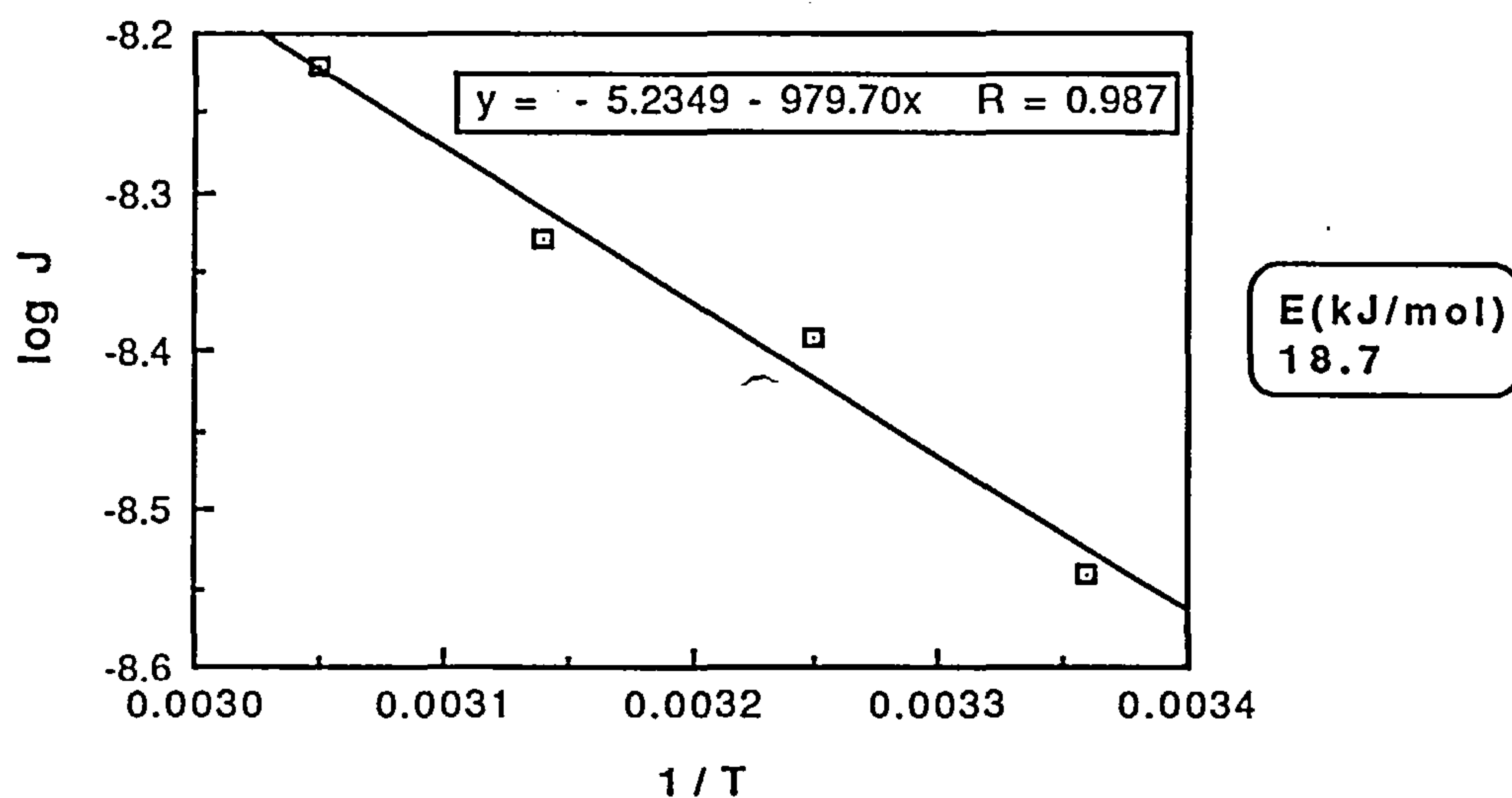


Figure 5.3.16 - Arrhenius plot for gold dissolution from a rotating disc in 0.03M KCN, no AQ and air only ($f=10.0\text{Hz}$).

It may be seen that, as the oxidizing agents are supplied in larger quantities (by adding AQ, FIGURES 5.3.17 and 5.3.18, or flushing the solution with pure oxygen, FIGURES 5.3.19 and 5.3.20), the activation energy tends to increase, moving to a region slightly out of the pure diffusion control, but without coming to the range where the chemical reactions are more likely to control the kinetic rate. Possibly, this change is caused by the fact that, unlike the case where the oxidizing agent is the oxygen from air only, the AQ and the oxygen only are already dissolved (and thus, present in a larger amount and more readily available) in solution for the oxidation of gold. This means that, when oxygen from air only is present, the dissolution step from the gas phase into the leaching solution and its further transport to the surface of the rotating disc is more likely to control the dissolution process than when AQ and/or oxygen only are the oxidizing agents, already dissolved in the leaching solution.

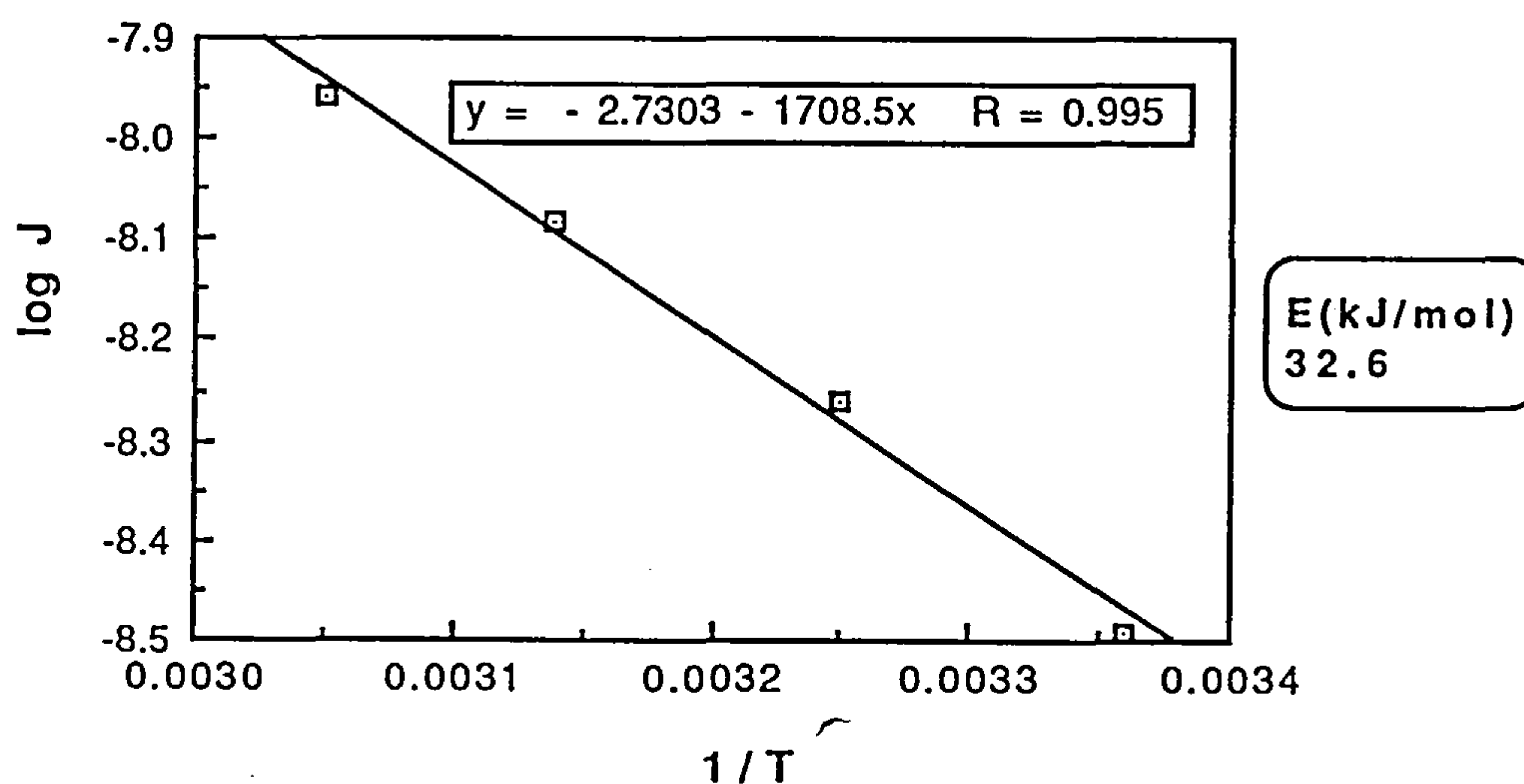


Figure 5.3.17 - Arrhenius plot for gold dissolution from a rotating disc in 0.03M KCN, 1.5mM AQ and air only ($f=10.0\text{Hz}$).

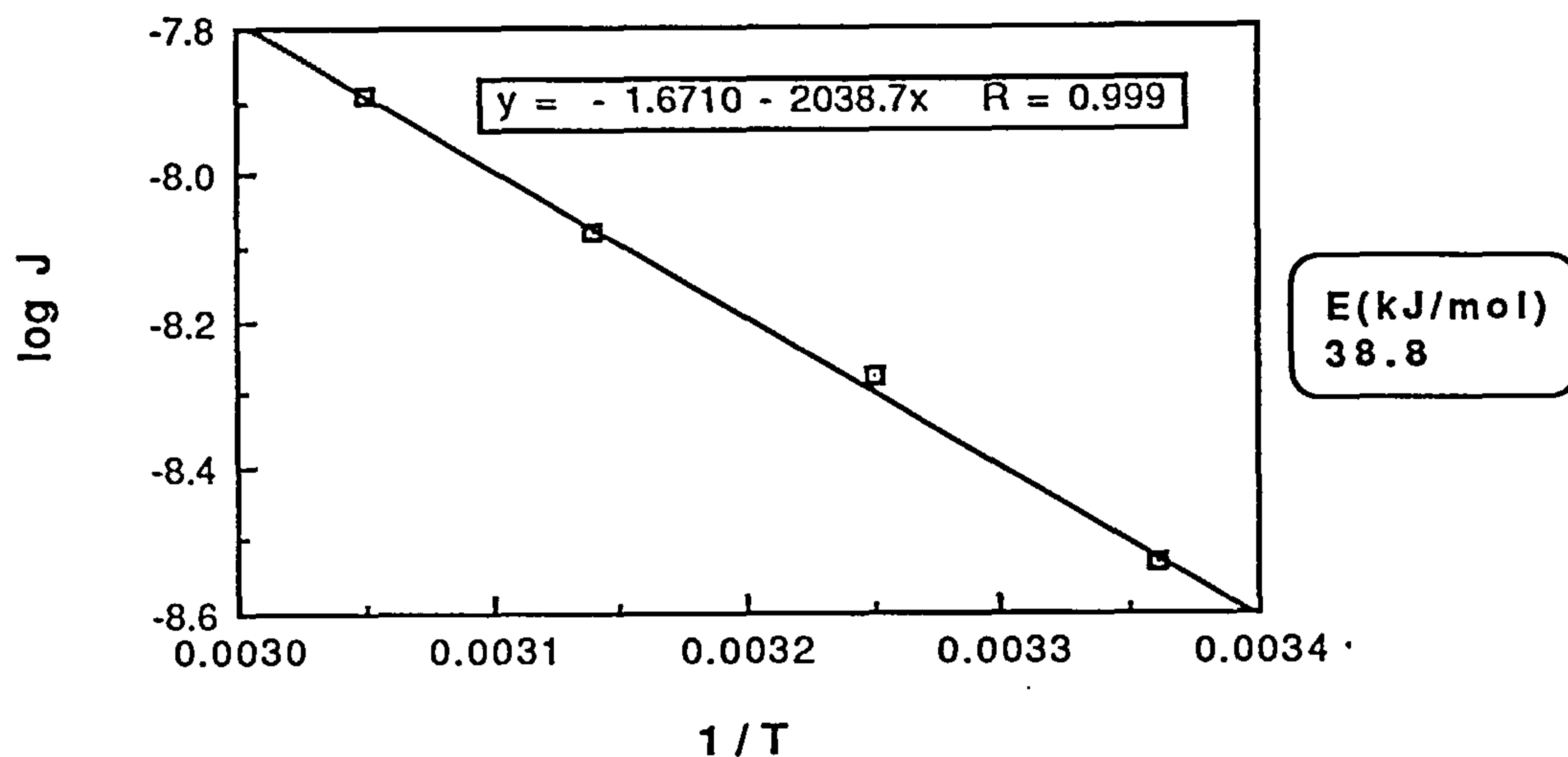


Figure 5.3.18 - Arrhenius plot for gold dissolution from a rotating disc in 0.03M KCN, 12mM AQ and nitrogen (f=10.0Hz).

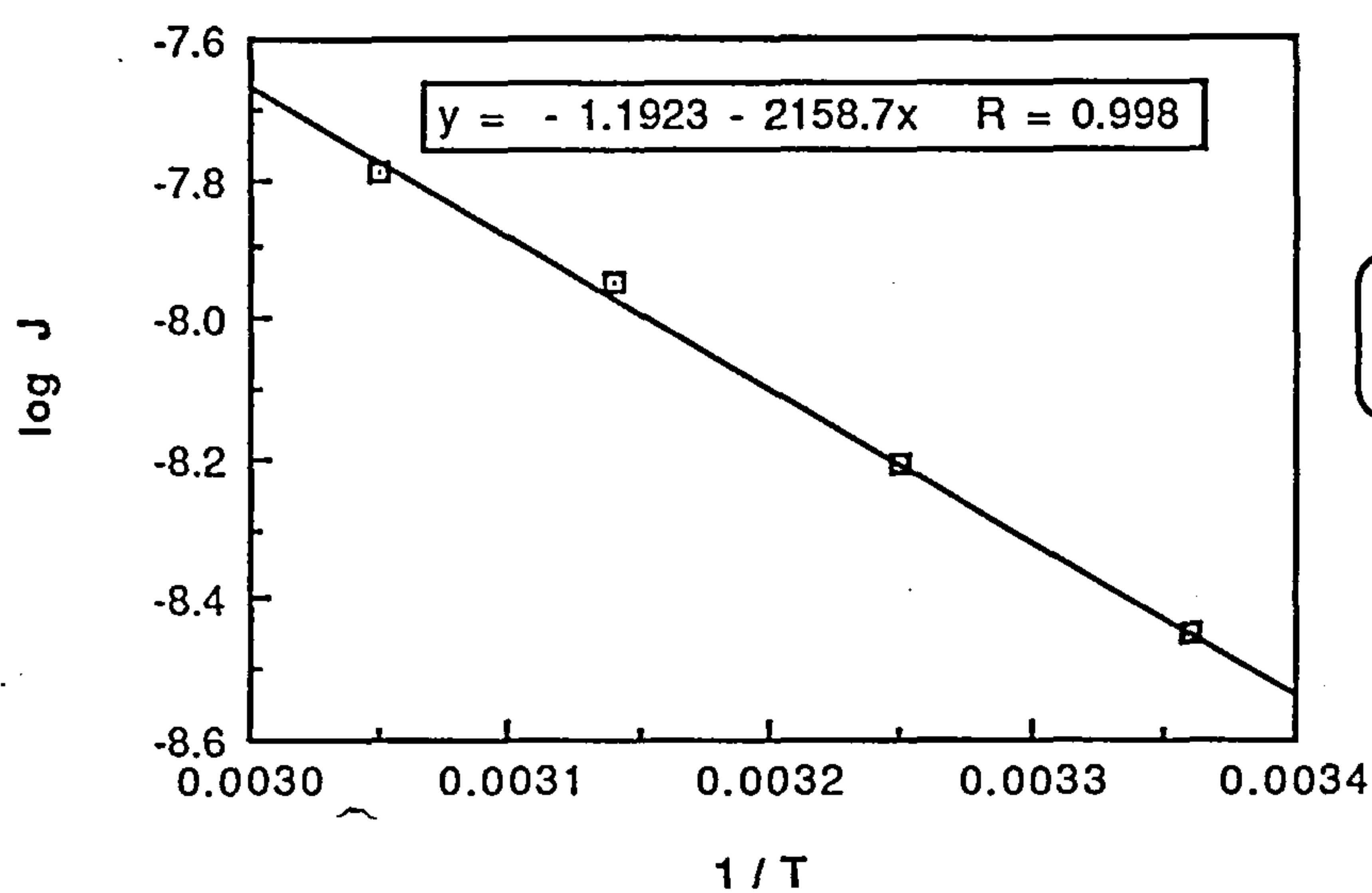


Figure 5.3.19 - Arrhenius plot for gold dissolution from a rotating disc in 0.01M KCN, no AQ and full oxygen (f=10.0Hz).

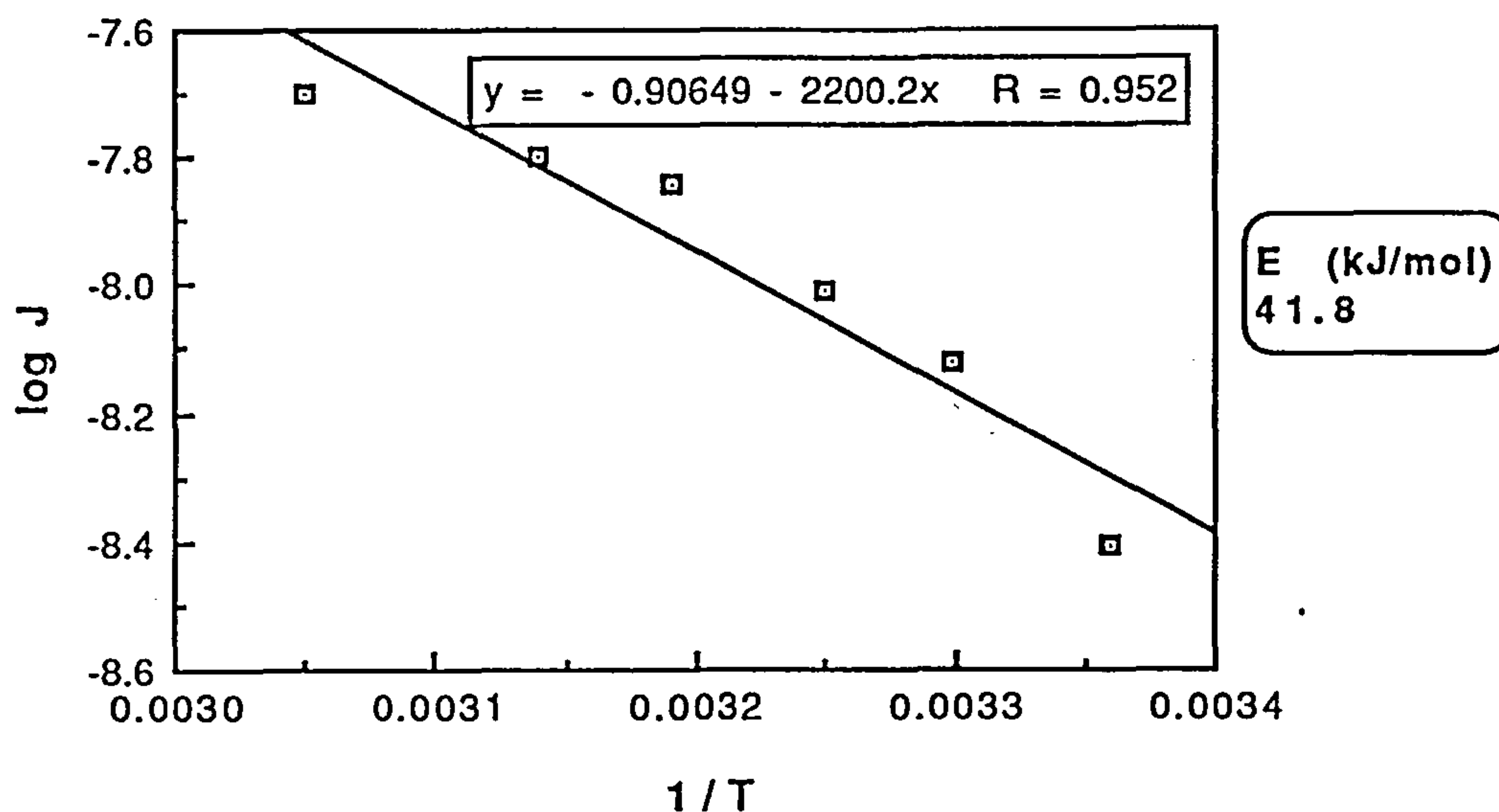


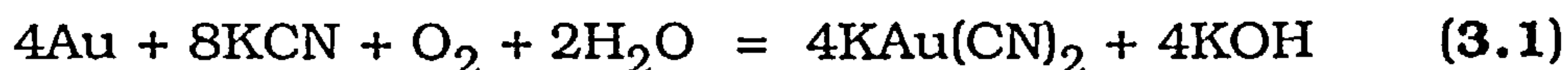
Figure 5.3.20 - Arrhenius plot for gold dissolution from a rotating disc in 0.03M KCN, no AQ and full oxygen (f=10.0Hz).

These higher values of the activation energy are also an indication that a different mechanism from that suggested by the activation energy obtained in Figure 5.3.16 is occurring in these further experimental conditions. While not yet lying in the region characterized by chemical control, a process other than pure diffusional is probably controlling the reaction rate on the gold surface.

5.4 - Discussion

5.4.1 - Introduction

As seen in Chapter III, it is generally accepted that gold dissolves in dilute cyanide solutions predominantly according to the following direct equation, first proposed by Elsner:



Under conventional circumstances, the reduction of oxygen is the reaction responsible for the oxidation of gold. Although, as has been seen, there has been some controversy on the number of electrons involved in this reaction, as well as the reaction paths occurring, some mechanisms have been proposed which involve the production of hydrogen peroxide, as



Hydrogen peroxide may also act as an additional oxidant for gold as



In the previous section, it was observed, as reported in the literature, that for strong cyanide solutions, i.e., for concentrations above 0.01M, with conventionally aerated solutions, there is no corresponding increase in the rate of gold dissolution. If, however, the oxygen concentration is increased to around 1.28 mM (1.01×10^5 Pa), the cyanide concentration above which the rate is independent is increased to 0.03M^[130]. These results are shown in FIGURE 4.3.2. It was also shown that it is possible for AQ to act as an oxidizing agent in the cyanidation of gold.

As seen in Chapter II, the reduction of AQ is not a straightforward reaction, and it has been suggested^[67] that it can proceed through up to nine intermediate species. However, for the moment, it will be assumed that, in alkaline media, this reaction proceeds as:



where AQH^- represents the reduced form of AQ, the so-called anthraquinol sulphonic acid. While the reoxidation of this species leads, as thoroughly described in the literature^[44,65,71], to the "in-situ" production of hydrogen peroxide, the approach given here is unusual, since the AQ is being reduced on the gold surface, and not by means of a gaseous reductant (normally hydrogen, with the aid of a heterogeneous catalyst) as is the common industrial process. The hydrogen peroxide produced in reaction 5.4.1 may act as a supplementary oxidant, as in reaction 3.3

The results reported in the previous section showed that when AQ is added to cyanide leaching solutions a noticeable increase in the rate of gold dissolution is observed, up to a concentration of 3.0mM AQ, as shown in FIGURES 5.3.3, 5.3.4 and 5.3.5. Above this AQ concentration the rate either does not increase further or actually decreases. While the rate enhancement may be attributed to the system outlined above, the picture is probably better understood by examining a mechanism of molecular adsorption on the metal surface, as explained in the following section. Moreover, it will be seen that the reason why higher AQ concentrations did not further increase the rate of gold dissolution may also be explained by this interpretation.

5.4.2 - On the role of anthraquinone during gold cyanidation

5.4.2.1 - Adsorption on electrodes

The adsorption of species on an electrode surface is often mentioned in the literature dealing with mechanistic aspects of heterogeneous

reactions^[29,144]. The build-up of adsorbed species may inhibit or accelerate the reaction on the solid surface. In the former case, for example, if the adsorption does not occur over the entire surface, the reaction will proceed only at the uncovered fraction (and at a slower pace, or even stop altogether on the "poisoned" fraction)^[144]. If the latter case applies, the overall rate will be enhanced, even if the adsorption is only locally observed.

In the case of the dissolution of gold in cyanide solutions, it has been suggested by a number of researchers^[89,129,145,146] that an increase in the oxygen concentration in the leaching solution may cause passivation of the gold surface, if the cyanide concentration is not increased "over the value possible if gold did not become passive"^[129]. This leads to a sharp decrease in the rate of the metal dissolution, caused by the retardation of the anodic process. The prevention of this situation may be achieved by an increase in the cyanide concentration. This was explained by the theory of the adsorptive nature of the cyanide and oxygen reacting on the gold surface^[145]. The mentioned increase in the cyanide concentration would displace, from the gold surface, some of the adsorbed oxygen, decreasing in this way the degree of passivation caused by the local excess of oxygen. Similarly, if the oxygen concentration is increased in the leaching solution, it will compete anew with cyanide for adsorption sites on the gold surface, eventually increasing the magnitude of the gold passivation (and thus slowing down the rate of dissolution).

The mechanism of the reduction of anthraquinone on the surface of some metals (including gold) has been investigated by Zolotova and co-workers^[147]. They described it as following a path of adsorption first and chemical reaction in a subsequent step, according to



in both neutral and alkaline solution. The subsequent formation of hydrogen peroxide by the oxidation of AQH_2 is well documented, as seen before, and was extensively studied by James et al. in a series of papers published in the thirties^[148].

While the adsorption occurs only at the first stage of the reaction, the mechanism indicates that, in order that it may be reduced, AQ molecules will have to "compete" with oxygen and cyanide for sites on the gold surface. Therefore it may be postulated that the character of the mechanism of the gold dissolution in the leaching system comprising cyanide + oxygen + anthraquinone is regulated by the adsorptive nature of each one of these components. By analyzing the interaction among them it is possible, in the light of previous work and from the results seen earlier, to understand the action of the anthraquinone in the cyanide leaching system for gold dissolution.

5.4.2.2 - The dissolution of gold in the system $\text{KCN} + \text{O}_2 + \text{AQ}$

When the oxygen partial pressure over the leaching solution is provided by the bubbling of air (oxygen conc.= 8.2 mg/l; 0.27mM) experimental results indicate that AQ may be adsorbed on the gold surface and therefore act as an additional oxidant in the manner explained earlier. Typical results showed that in a conventionally aerated solution of 0.01M KCN, and with a rotating speed of 10 Hz, the rate of gold dissolution is $2.67 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$ (FIGURE 5.3.1) while with the addition of 3.00mM AQ the rate attains $3.35 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$, (FIGURE 5.3.9) an increase of around 25%.

However, when the oxygen concentration in solution is increased to 1.28 mM (41 mg/l) it was seen (FIGURE 5.3.6) that not only cyanide ions will be displaced from the gold surface^[145], but also the adsorption of anthraquinone will be considerably hampered, preventing, thus, the cyclic mechanism explained above from taking place. This may well explain why the effect of AQ on the rate of gold dissolution was negligible, or even overshadowed, when the oxygen concentration was increased from 8.2 mg/l to 41.0 mg/l. Thus for a solution of 0.01M KCN, and oxygen concentration 41.0 mg/l, the rate of gold dissolution was found to be $3.56 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$; under similar experimental conditions, but with 3.00mM AQ added, not only the rate increase mentioned above did not occur but actually a slight decrease to $3.26 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$ was observed.

This picture may be clarified by further examination. As seen from the results reported in FIGURE 5.3.3 and 5.3.5 if the oxygen concentration in the leaching solution is 0.27mM, additions of AQ up to a concentration of 3.0 mM are capable of enhancing the rate of gold dissolution; beyond this point, however, further additions did not cause the rate to increase. This fact can also be understood by the nature of the process occurring on the metal surface.

The reduction of AQ on the gold surface is considered to be of an adsorptive nature, with the acceptance of the protons being the second and slower^[147] stage of the reaction. When the AQ concentration in the aerated cyanide solution is increased beyond a certain point, the experimental results suggest that AQ will compete for sites on the gold surface, either displacing the oxygen or the cyanide ions. It is clear that in both cases the rate of gold dissolution will be impaired. In an extreme situation, with increasing AQ concentration, the rate may even decrease (as seen from the

experimental results), for if the surface of the electrode is well covered with AQ, the oxygen arriving from the bulk will, from the beginning, be reduced to hydrogen peroxide by the reduced AQ itself (AQH_2 , which appears by the AQ reduction on the gold surface), rather than being reduced by oxidizing the gold, as would be the case were the oxygen in solution appearing in a higher concentration (at 1.27mM, for instance; see below). The results observed in practice actually suggest this type of mechanism: for a 0.03M KCN solution, for example, as the AQ concentration increases, the rate also increases from 2.86, 2.97 (0.30mM AQ), 3.42 (1.50mM AQ), 4.26 (3.00mM AQ), but decreases to $4.00 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$ with further (6.00mM) AQ addition. While the difference between these two latter results is close to the experimental error, it indicates that the tendency of the rate to increase is no longer observed.

A similar situation would, probably, happen to the cyanide ions, but not in the present case since it was shown from the results of FIGURE 5.3.1 that the cyanide concentration is above the value where it would be the rate limiting species for gold dissolution. It is interesting to note, though, that if an additional oxidizing agent is introduced into the leaching solution (by adding AQ or bubbling pure oxygen through the solution), the rate again becomes dependent on the cyanide content. This is seen in FIGURE 5.3.4, where with 3.00mM AQ, the rate of $3.68 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$ for 0.01M KCN was found to increase to $4.24 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$ when the cyanide concentration was increased to 0.03M.

A comparison of the present system with work performed in similar fields is useful for further analysis.

The properties of electrodes which have adsorbed species on their

surface have received considerable attention in the last ten years or so, because an electrode coated in this manner may acquire unusual properties. Complicated cases have been reported involving electrodes coated with hydroquinone-quinone derivatives, due to their selective and cyclic oxidative character, which render them interesting for applications involving electrocatalysis [149,150].

The direct reduction of oxygen on metallic electrodes covered with quinone derivatives compounds was investigated by Calabrese and co-workers [151,152]. They described the catalysed reduction of oxygen to hydrogen peroxide, according to the mechanism schematically shown in FIGURE 5.4.1 (this mechanism, in a slight different situation, had previously been proposed by Degrand et al. [153]).

This reaction, i.e., the direct reduction of oxygen to hydrogen peroxide on electrodes covered with quinone derivatives, is reported to be efficient and may be sustained for a long time to generate significant concentrations of hydrogen peroxide [152]. Information given on tests that have been carried out for over 5 hours [151] indicate that there were low losses of adsorbed species ($[AQ/AQH_2]_{ads}$).

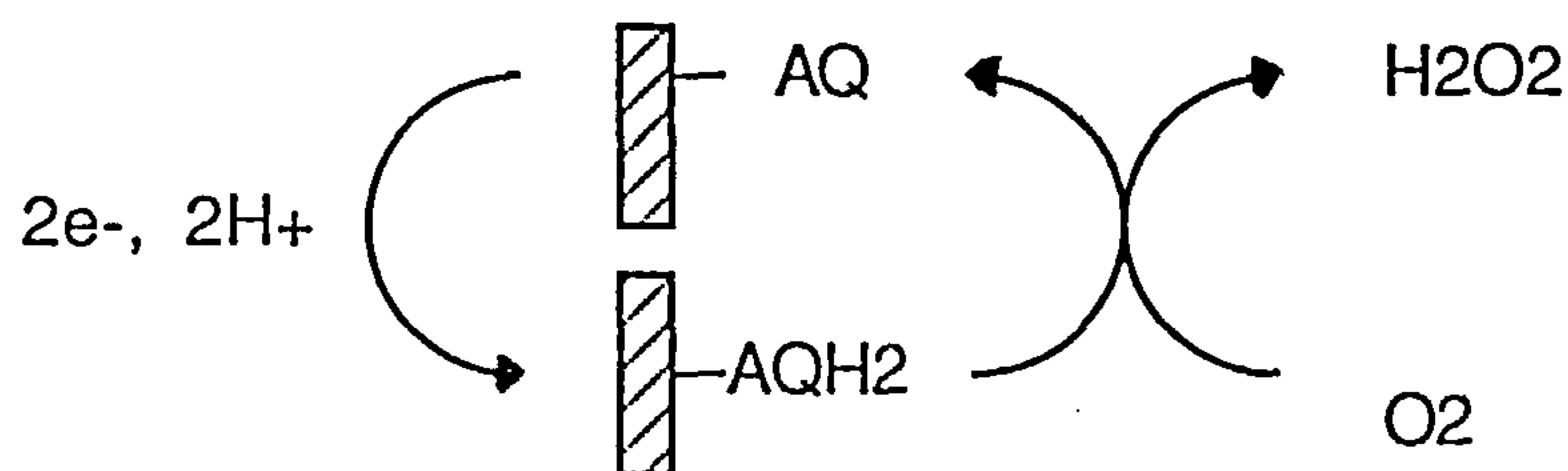


Figure 5.4.1: Schematic electrochemical reduction of oxygen to hydrogen peroxide, with cyclic regeneration of quinone derivatives adsorbed on a metallic electrode (after Calabrese et al. [151]).

It was further indicated by the same authors that the oxidation of the reduced adsorbed quinol occurs at a high rate. Earlier, James and Weissberg^[154] had already reported that the velocity of this oxidation is approximately directly proportional to the oxygen partial pressure, with quantitative formation of the related quinone and hydrogen peroxide. In the case of the present study, the high rate of oxidation of the adsorbed quinol would prevent the gold from being oxidized by the oxygen arriving at the metal surface. This effect is an additional indication that too high an AQ concentration may be deleterious for the rate of gold dissolution, by consuming increasing quantities of oxygen, which would otherwise be used for the oxidation of gold.

In fact, as seen in section 5.3, if the AQ concentration is increased beyond the point which it produces the maximum rate of gold dissolution (under air only, i.e., $[O_2]=0.27\text{mM}$), there is no further effect and an indication that the rate starts to decrease may be observed. Typical practical values for 0.03M KCN were found to be $4.28 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ with 3.00 mM AQ and $4.00 \times 10^{-9} \text{ mol.cm}^{-2}.\text{s}^{-1}$ with 6.00 mM AQ. This phenomenon, however, is unlikely to stop the gold dissolution altogether, for even in the absence of oxygen the necessary gold oxidation to render it amenable to complexation by the cyanide will be carried out by the AQ alone, although, probably, at a slower pace. It should be noted that the maximum AQ concentration available is limited by its low solubility. It was seen experimentally that solutions with concentrations used as the stock solutions in this work (15 mM) were already difficult to dissolve and needed gentle warming and stirring.

The role of AQ in the cyanidation of gold can be further clarified by performing experiments under an oxygen-free atmosphere, such as that attained by bubbling nitrogen through the solution, as explained

before. The result of the test with the high-surface area gold-plated metallic sponge revealed, to a reasonable approximation, that, as previously suggested, according to the stoichiometry of the process, 1 mole of AQ is needed for the dissolution of 2 moles of gold. This experiment demonstrated that the consumption of AQ (reduction) while oxidizing gold could be quantitatively followed, as well as its prompt regeneration when the solution is saturated with air and/or oxygen. It is thus experimentally confirmed that AQ may be quantitatively reduced by gold, in an aqueous cyanide solution, with the obvious benefit that gold is oxidized to form the cyano-complex.

The results obtained from experiments with a gold disc, under nitrogen, additionally suggest that an adsorption mechanism is taking place on the metal surface. As seen from the results, at 0.01M KCN, the rate of gold dissolution was enhanced with AQ concentration, up to a point beyond which it started to decrease: $2.12 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$, with AQ 6.00 mM, but $1.23 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$ with AQ 12.00 mM, as may be seen in FIGURE 5.4.2.

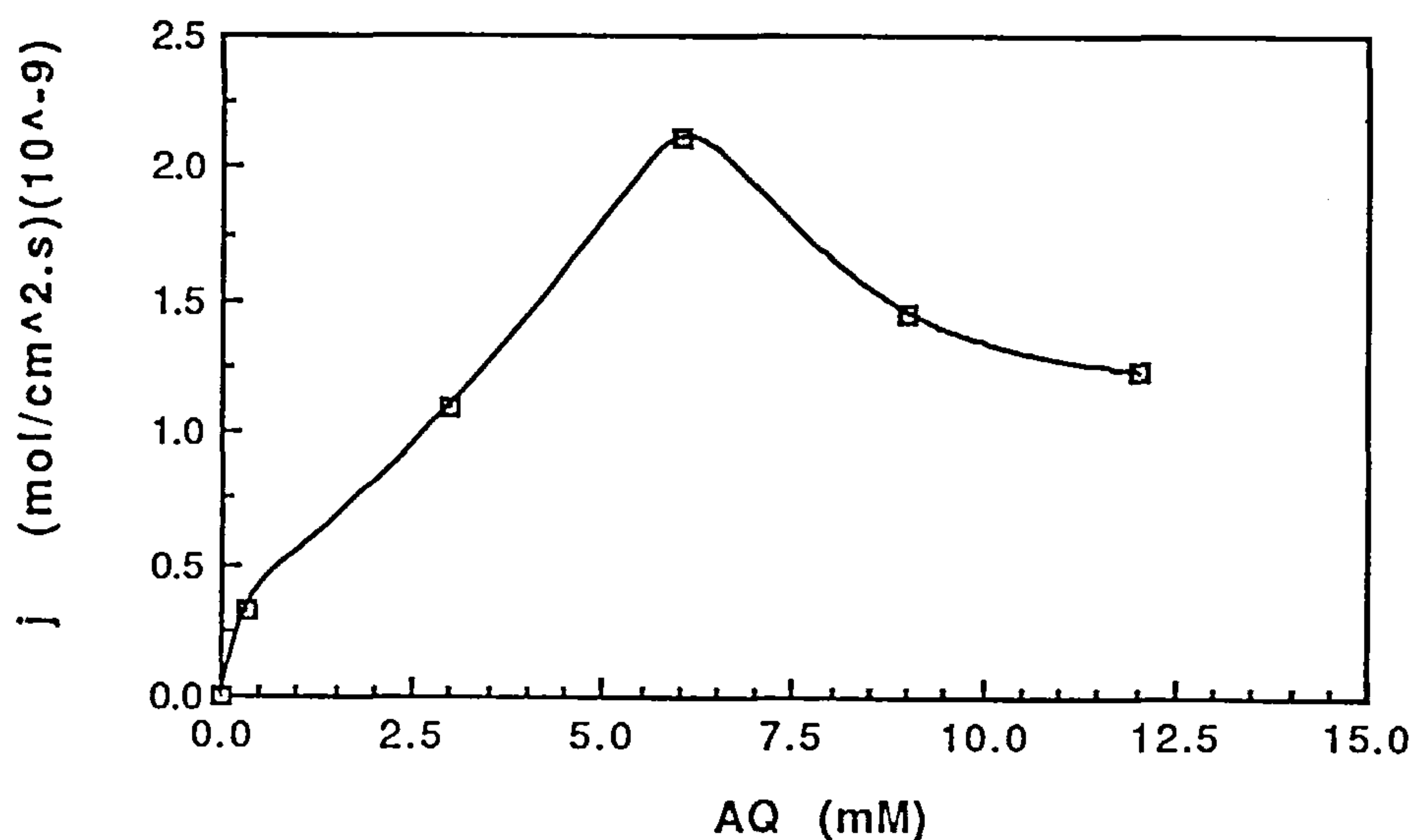


Figure 5.4.2 - Gold dissolution rate dependence on AQ concentration, in an oxygen-free 0.01M KCN solution (f=10.0 Hz).

This is, indeed, a similar situation to that of the conventional aerated solutions, with the difference that, in the presence of air the maximum rate was achieved with AQ 3.00 mM. It is also noteworthy that, under nitrogen, with AQ concentrations up to 6.00 mM the dissolution rate will not increase if the cyanide content exceeds 0.01M. (e.g.: at 3.00 mM AQ: the rate of dissolution of gold was found to be 1.10×10^{-9} mol.cm².s⁻¹ with 0.01M KCN and 1.09×10^{-9} mol.cm².s⁻¹ with 0.02M KCN; at 6.00 mM AQ: the rate was 2.12×10^{-9} mol.cm².s⁻¹ with both 0.01M and 0.02M KCN). However, for higher AQ concentration, 12.00 mM for instance, the rate is benefited by an increase in the cyanide concentration (e.g: at 12.0 mM AQ the rate reaches 2.97×10^{-9} mol.cm².s⁻¹ with 0.03M KCN). Typical experimental values are shown in TABLE. 5.4.1.

AQ conc. (mM)	j(mol/cm ² .s)(10 ⁻⁹)
3.00	1.10(KCN 0.01M)
	1.09(KCN 0.02M)
6.00	2.12(KCN 0.01M)
	2.12(KCN 0.02M)
12.00	1.23(KCN 0.01M)
	2.97(KCN 0.03M)
16.00	2.29(KCN 0.03M)
	2.52(KCN 0.04M)

Table 5.4.1- Typical experimental values for the rate of gold dissolution obtained with different AQ and cyanide concentrations, under an oxygen-free atmosphere (f=10.0 Hz).

It may be observed that the rates under these conditions were lower than those obtained with the normal aerated solutions, indicating that,

while being a useful oxidizing agent for the system, AQ alone is less efficient than oxygen itself. Furthermore, the fact that the rate decreases if the AQ concentration passes beyond the point of maximum benefit indicates that cyanide and AQ may start to "compete" for selected sites on the gold surface. If, however, the cyanide concentration is raised at the onset of the falling rate, this will no longer decrease (for example, with AQ 12.00mM and 0.01M KCN, the rate was $1.23 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$, whereas, as seen above, for the same AQ and 0.03M KCN, it reached $2.97 \times 10^{-9} \text{ mol.cm}^2.\text{s}^{-1}$).

The cyclic character of the anthraquinone reduction/oxidation is recognized as an important reaction that may bring about interesting and sometimes unexpected features. In this respect, a similar mechanism, though in a quite different environment, has been proposed by Dimmel^[155], who suggested that reactions occurring during wood pulping with anthraquinone are responsible for the lignin fragmentation of the woody tissue. The anthrahydroquinone (AQH₂, or anthraquinol) reduces the wood lignin and the anthraquinone (AQ) that is regenerated oxidizes the carbohydrates present.

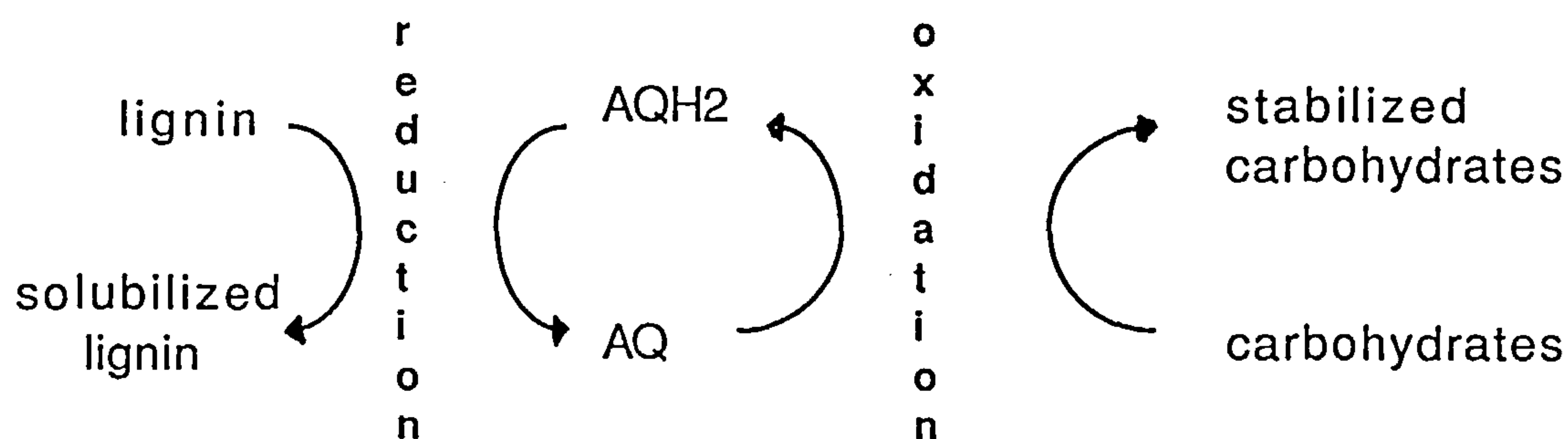


Figure 5.4.3 - Cyclic redox reactions schematically showing the catalytic effect of anthraquinone in wood pulping (after Dimmel^[155]).

This redox cyclic mechanism is used to explain the catalytic effect of the anthraquinone during the process, and is schematically depicted in FIGURE 5.4.3. Moreover, it is interesting to note that since the oxidation of AQH₂ is accomplished by the wood lignin, and not by oxygen, there is no mention of hydrogen peroxide formation.

As mentioned earlier, the effect of adsorbed substances on metal electrodes has been the subject of much research. The adsorption of impurities onto a platinum electrode is a well-known example of how normally observed hydrogen reactions may be inhibited^[144,156]. The adsorption of organic molecules on metallic electrodes is an accepted explanation for the inhibitions of reactions that may occur at the metal surface, due to the insulating nature of the adsorption^[144]. Decker and Parkinson^[157] investigated the subject using sulphonate anthraquinones in aqueous solution to prevent the photocorrosion of GaAs electrodes. The adsorption of the redox couple $AQ \leftrightarrow AQH_2$ at the metallic electrode–electrolyte interface was found to play a definitive role in stabilizing the metal (in this case a semiconductor) against photocorrosion. They have also postulated that if the concentration of the adsorbing species in the bulk of the solution is high enough, stabilization is even stronger. There may even come a point where if the adsorbed layer gets too thick it will become "protective", by insulation of the metal.

A similar picture may be visualized in the present case where the AQ adsorbed on the gold surface establishes the redox couple $AQ \leftrightarrow AQH_2$ at the gold-cyanide leaching solution interface. FIGURE 5.4.4. attempts to illustrate schematically the gold surface being leached in an aerated solution of cyanide plus AQ.

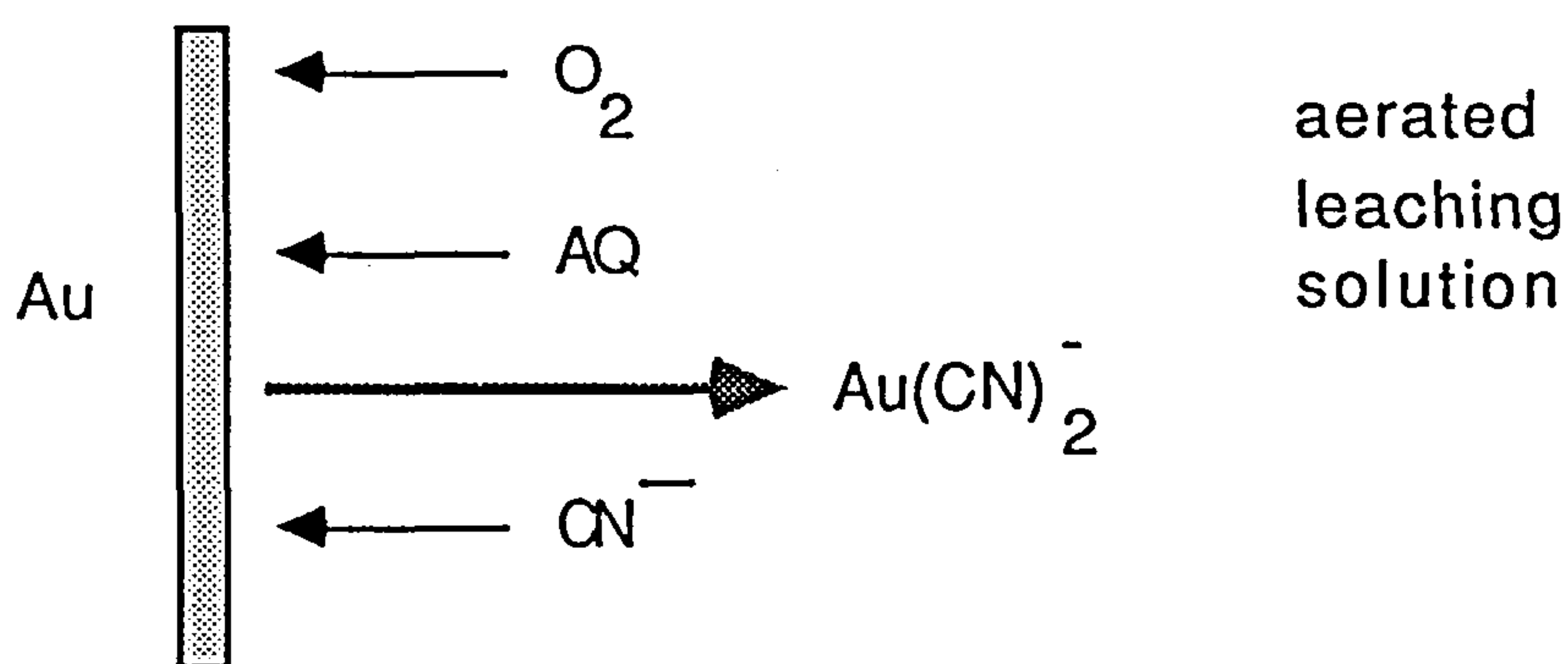


Figure 5.4.4 - Schematic illustration of gold being dissolved in an aerated cyanide solution containing AQ.

As seen from the experimental results, if the AQ concentration is increased beyond a certain point of maximum benefit, the otherwise useful addition of AQ starts to influence in the opposite direction. This is probably because of a "protective" AQ layer on the metal surface (i.e., AQ may displace either the oxygen or cyanide, depending on the concentration of these reagents).

The way in which AQ molecules are adsorbed on metallic surfaces has been investigated by Soriaga and Hubbard^[165], by means of a thin-layer electrochemical technique. The results of their investigation indicate that the AQ may be categorized as a compound which always adsorbs in the flat orientation (i.e., the ring is approximately parallel to the electrode surface), for concentrations above 10^{-4}M (this position is in contrast to the so-called "edgewise" orientation, in which the ring is perpendicular to the surface). This situation is schematically seen in FIGURE 5.4.5:

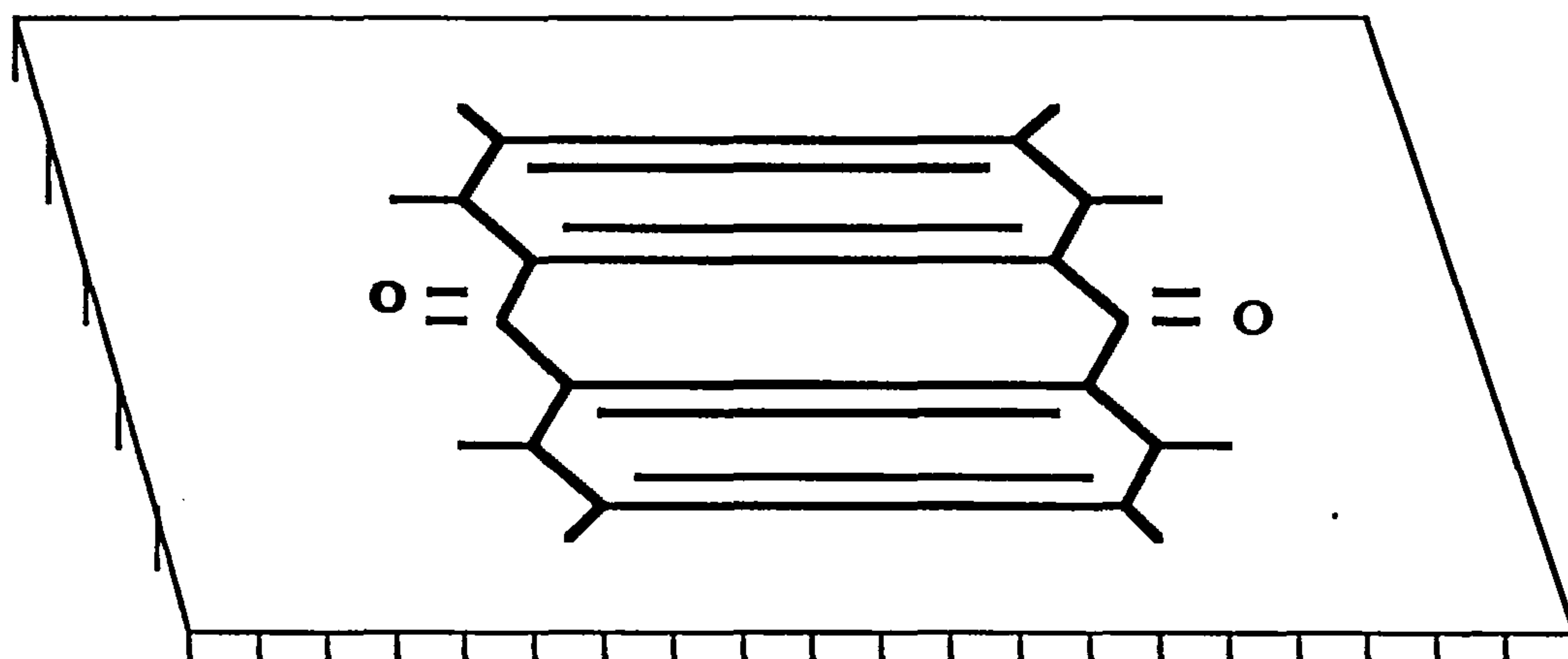


Figure 5.4.5 - Schematic representation of a quinone type molecule adsorbing on a metallic surface (after Soriaga^[165]).

Also, the possibility that the compound adsorbs in another orientation has been found to be very unlikely^[165]. This situation highlights the fact that, in order to adsorb on the gold surface, AQ molecules will always occupy a large area (in Soriaga's work, this area was experimentally found to be around 130 Å²). Furthermore, AQ is indeed a large molecule; both in the flat position, it will cover, for instance, nearly three times more than the area occupied by a hydroquinone molecule, which has only one benzene ring in its structure^[165]. This suggests that, as the AQ concentration increases, the sites left for cyanide and oxygen to adsorb on the metallic surface will be increasingly obstructed by the large area occupied by the AQ.

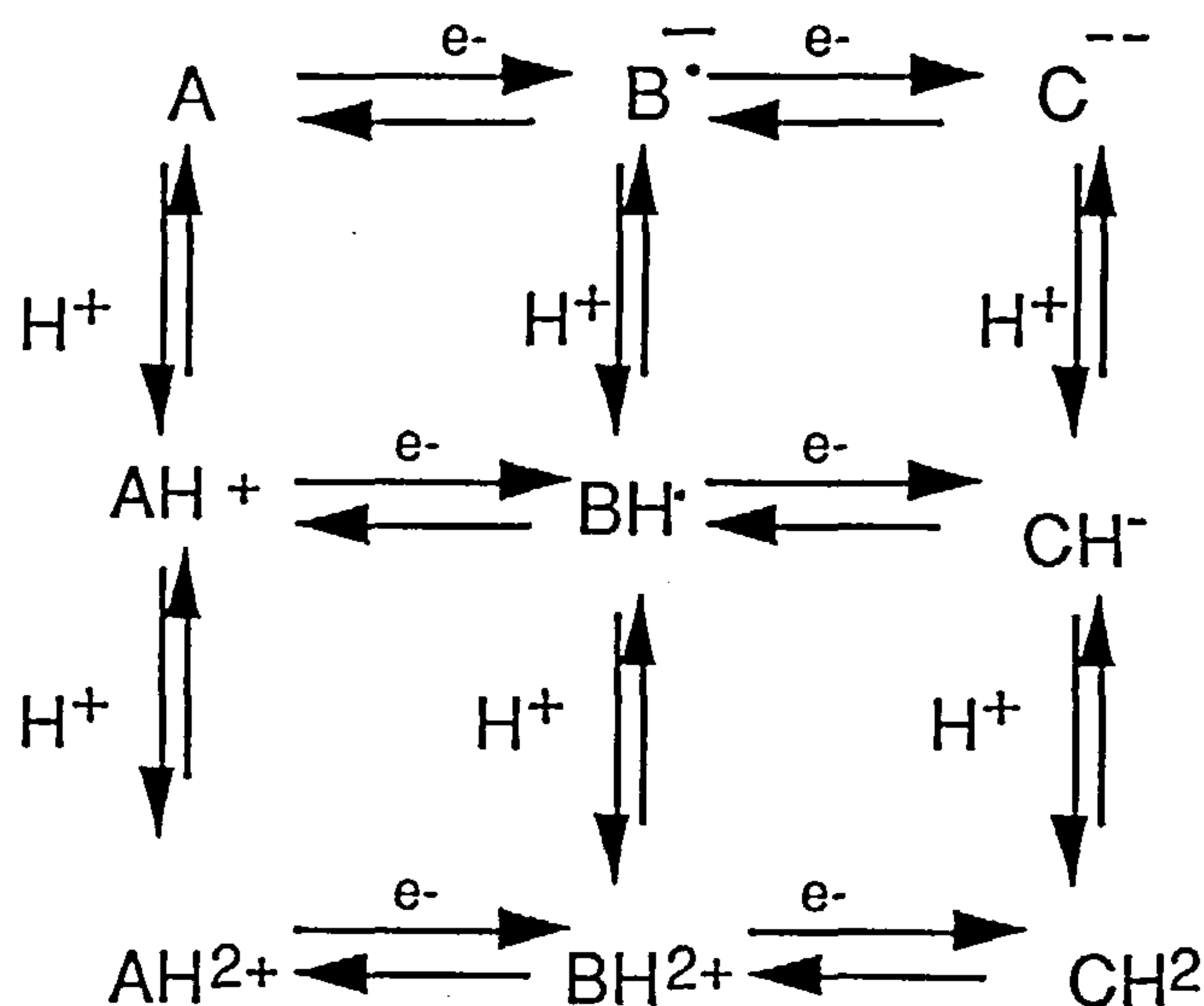
In a similar line of study, Bailey and co-workers^[158] investigated a series of hydrogen substituted anthraquinones in the preparation and protection of surface modified electrodes, to be used in batteries in strong acid media. The stability of the films were tested by cyclic

voltammetry and for chemical durability. Even though the redox stability was found to be highly satisfactory, the films produced in Bailey's work were not considered to be suitable for protection of the electrodes, since they were not able to endure the extremely low pH of the working solution. This situation is, of course, unlikely to be found during the dissolution of gold in the present leaching system, since the pH is always maintained well alkaline.

At this point, it is relevant to note that the mechanism of the electrochemical oxidation/reduction of quinone derivatives has received considerable attention. It is generally accepted that the formation of intermediate species is very likely to occur^[67,159,160]. The reduction $\leftrightarrow$ oxidation path of quinone/ anthraquinone derivatives is seen as complex and is commonly described by a scheme of nine possible species^[67,153,160,161], as shown in FIGURE 5.4.5 overleaf. These intermediate species are reported to be highly reactive^[162]. However, it is believed that the preferred path for the transition states in basic solutions is most probably the one represented by the top line on the figure^[68].

The overall picture of the reactions occurring at the gold surface when the leaching system is comprised of cyanide + oxygen + anthraquinone may lead to the assumption that if the AQ concentration is high enough, a build-up of hydrogen peroxide is likely to occur (because of the continuous reduction of the oxygen to peroxide by the anthraquinol). However, this is not necessarily so, since hydrogen peroxide is very unstable in some conditions, particularly in alkaline solutions and/or without the presence of a peroxy stabilizer^[29]. Moreover, even if the peroxide is not promptly decomposed, it may be readily consumed by acting as an additional oxidizing agent for the process. To verify quantitatively this assumption, the detection of

hydrogen peroxide in the leaching solutions of some of the experiments presented was attempted using the aforementioned sensitive method suggested by Bayley and Boltz^[80]; but all the analyses failed to detect any peroxide present in solution.



where

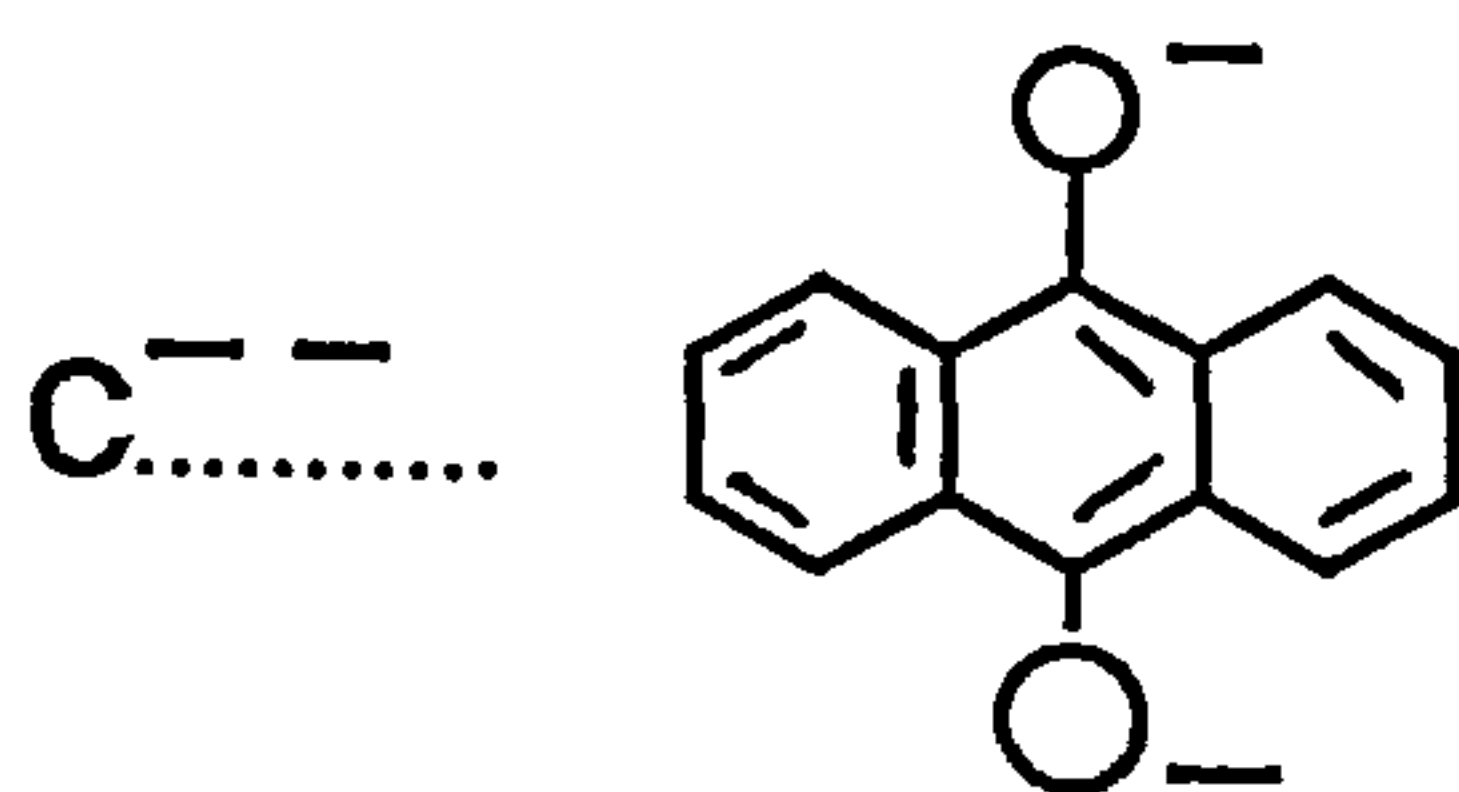
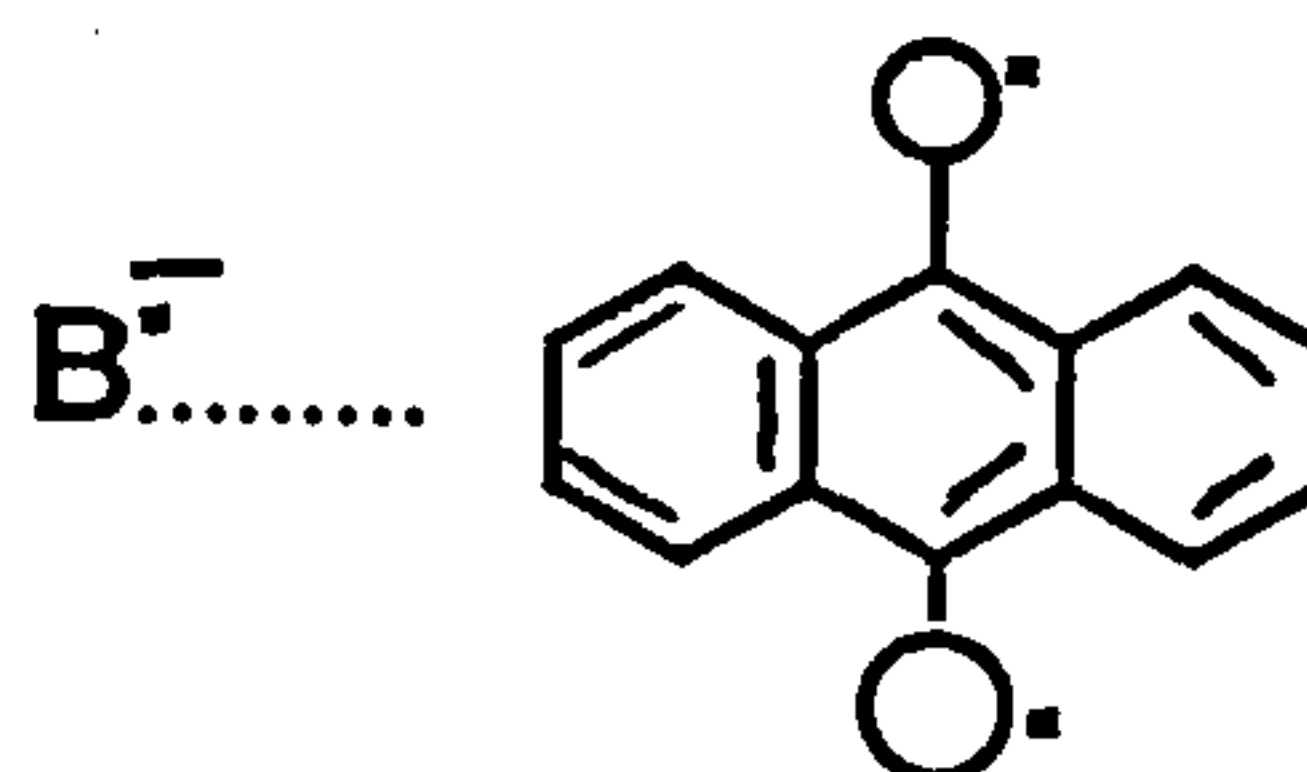
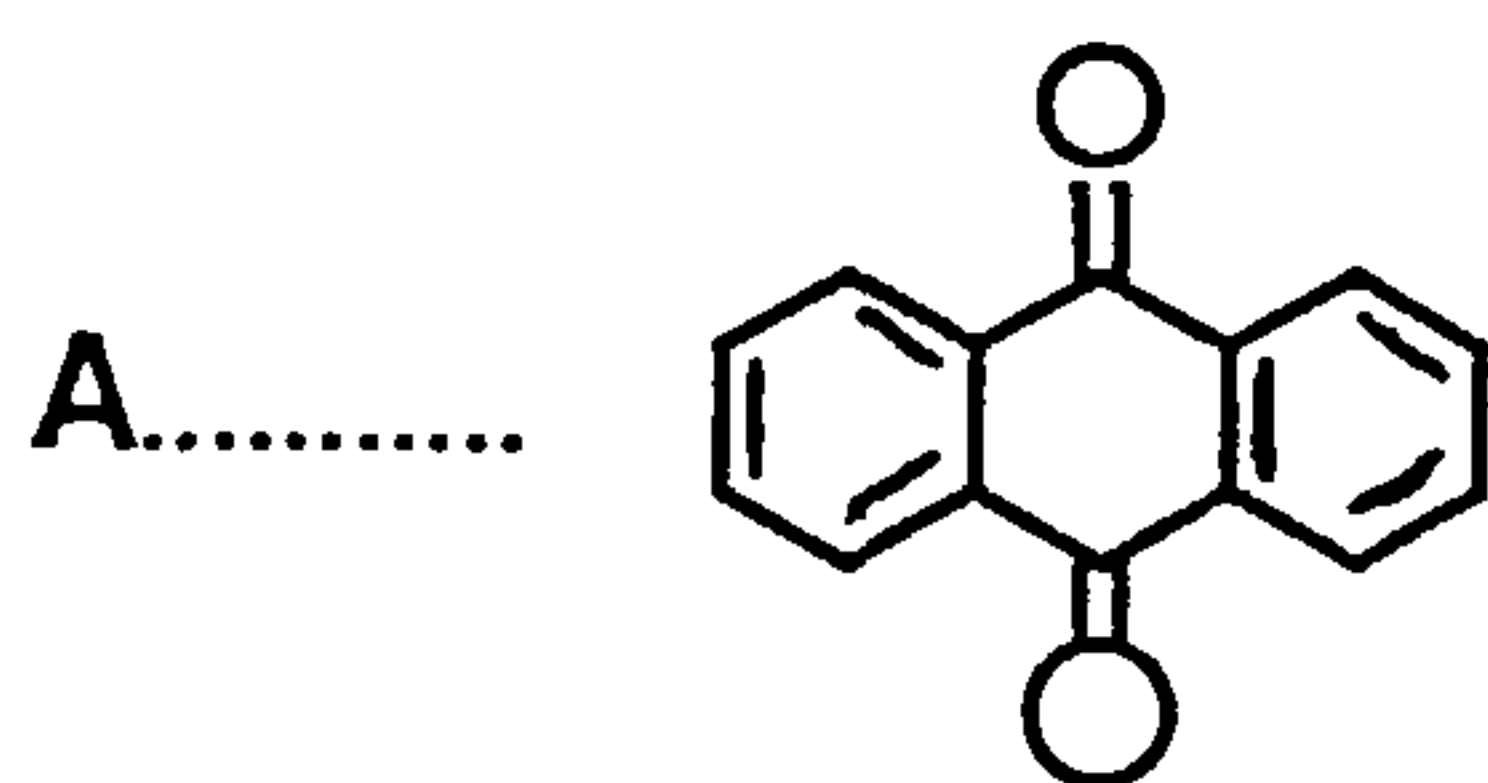


Figure 5.4.6 - Scheme representing the formation of the possible intermediates in the reduction/oxidation path of quinone derivatives.

As explained before, cyanide depletion was measured with a cyanide-sensitive electrode. No increase in the rate of cyanide oxidation was observed when AQ was added to the leaching solutions; also, the same outcome was observed in specific tests to investigate the oxidation of cyanide by AQ, as already mentioned earlier in this work. Even though AQ is a possible and useful oxidant to the process, this indicates that it will not oxidize cyanide under usual experimental conditions. This is unlike the situation when other suggested compounds are added to the cyanide solution to improve the rate of gold dissolution (such as inorganic peroxides, or compressed air/oxygen). This experimental fact is indeed an important one, and discloses a further attractive characteristic of AQ.

5.4.2.3 - Relationship determination of the area occupied by the adsorbing species on the gold surface

A situation where two or more substances are adsorbed on the same surface, i.e., when they are competing with each other for a limited number of sites, is referred to as "competitive adsorption"[163]. This may be mathematically analysed by expressions commonly referred to as "adsorption isotherms"

Adsorption isotherms are semi-empirical equations that relate the amount of a substance adhered to a surface with its concentration in solution, at a fixed temperature. A widely used isotherm is the so-called "Langmuir isotherm" obtained in 1916 by Irving Langmuir. The equation can only be applied for models satisfying the following conditions: 1-there is a homogeneous surface; 2-the forces among the adsorbed molecules is negligible; 3-the surface becomes saturated by a unimolecular layer of adsorbed molecules.

The Langmuir isotherm is usually written as

$$\theta = \frac{K [A]}{1 + K[A]} \quad (5.4.1)$$

where θ is the fraction of the surface covered by the adsorbed molecule

$[A]$ the concentration of the molecule in solution

K a constant relating to the adsorption and desorption process

At very low concentrations, that is, if $[A] \ll 1$, the product $K[A]$ may be neglected with respect to unity; equation 1 then reduces to a direct proportionality between θ and $[A]$:

$$\theta = K[A] \quad (5.4.2)$$

At higher concentrations, the value of $K[A]$ becomes considerably more significant than unity. If equation 5.4.1 is rewritten as

$$1 - \theta = \frac{1}{1 + K[A]} \quad (5.4.3)$$

it is possible to perceive that, when unity value may be neglected, this equation is reduced to

$$1 - \theta = \frac{1}{K[A]} \quad (5.4.4)$$

In the present case, when the system is comprised by cyanide + oxygen + AQ, experimental results indicate that these three reagents are probably competing for reacting sites on the gold surface. The analysis is more conveniently carried out, however, if the cases when

there are only two reagents in solution are treated separately.

When cyanide and oxygen (from air) are reaching the gold surface, the fraction covered by the cyanide molecules may be called θ_{CN} and that covered by the oxygen from air may be called θ_{O_2} . In this case, the empty fraction is represented by $1 - \theta_{\text{CN}} - \theta_{\text{O}_2}$.

The rate of adsorption (α^a) is proportional to the bare fraction and to the concentration of the reagent in solution; thus, it may be written as

$$\alpha_{\text{CN}}^a = k_{\text{CN}}^a [\text{CN}] [1 - \theta_{\text{CN}} - \theta_{\text{O}_2}] \quad (5.4.5)$$

and

$$\alpha_{\text{O}_2}^a = k_{\text{O}_2}^a [\text{O}_2] [1 - \theta_{\text{CN}} - \theta_{\text{O}_2}] \quad (5.4.6)$$

The rate of desorption (α^d) would be only proportional to the covered region of the solid, i.e.,

$$\alpha_{\text{CN}}^d = k_{\text{CN}}^d \theta_{\text{CN}} \quad (5.4.7)$$

and

$$\alpha_{\text{O}_2}^d = k_{\text{O}_2}^d \theta_{\text{O}_2} \quad (5.4.8)$$

At equilibrium the adsorption and desorption rate should be the same, and thus for the cyanide case for instance it follows that

$$\alpha_{\text{CN}}^a = \alpha_{\text{CN}}^d \quad (5.4.9)$$

$$k_{\text{CN}}^{\text{a}}[\text{CN}][1 - \theta_{\text{CN}} - \theta_{\text{O}_2}] = k_{\text{CN}}^{\text{d}} \theta_{\text{CN}} \quad (5.4.10)$$

and

$$\frac{\theta_{\text{CN}}}{1 - \theta_{\text{CN}} - \theta_{\text{O}_2}} = \frac{k_{\text{CN}}^{\text{a}}[\text{CN}]}{k_{\text{CN}}^{\text{d}}} \quad (5.4.11)$$

Since

$$\frac{k_{\text{CN}}^{\text{a}}}{k_{\text{CN}}^{\text{d}}} = K_{\text{CN}} \quad (5.4.12)$$

and therefore

$$\frac{\theta_{\text{CN}}}{1 - \theta_{\text{CN}} - \theta_{\text{O}_2}} = K_{\text{CN}}[\text{CN}] \quad (5.4.13)$$

A similar reasoning may be taken with the oxygen, which would then yield

$$\frac{\theta_{\text{O}_2}}{1 - \theta_{\text{CN}} - \theta_{\text{O}_2}} = K_{\text{O}_2}[\text{O}_2] \quad (5.4.14)$$

Equations 5.4.13 and 5.4.14 can be solved as two simultaneous equations to give the fraction of the region covered by cyanide and oxygen as

$$\theta_{\text{CN}} = \frac{K_{\text{CN}}[\text{CN}]}{1 + K_{\text{CN}}[\text{CN}] + K_{\text{O}_2}[\text{O}_2]} \quad (5.4.15)$$

$$\theta_{\text{O}_2} = \frac{K_{\text{O}_2}[\text{O}_2]}{1 + K_{\text{CN}}[\text{CN}] + K_{\text{O}_2}[\text{O}_2]} \quad (5.4.16)$$

The equations indicate that the part covered by one reagent will be reduced if the concentration of the other is increased. Both equations reduce to equation 5.4.1 if $[O_2]=0$ (or $[KCN]=0$), in which case the oxygen (or the cyanide) cannot be adsorbed on the metal surface. As seen earlier, experimental results and related literature indicate that the adsorption of the reacting species on the gold surface may be indeed the situation occurring during the process of gold dissolution; a case that may be characterized as competitive adsorption. The interesting point here is that, unlike the cases normally found in the literature^[164], both reagents are needed for the reaction occurring on the metal surface (dissolution of gold) to proceed. Assuming that the rate of reaction is proportional to θ , this means that if the concentration of one of the reagents decreases, or even drops to zero altogether, the other may completely cover the surface, but the dissolution reaction will no longer occur.

From the stoichiometry of the gold dissolution reaction (reaction 3.2), and assuming initially that the area occupied by each molecule is approximately equivalent, it may be seen that, for maximum rate, the fraction occupied by the cyanide should correspond to four times that occupied by the oxygen. Therefore

$$4\theta_{O_2} = \theta_{CN} \quad (5.4.17)$$

and, relating equations 5.4.15 and 5.4.16 it follows that

$$\frac{\theta_{CN}}{\theta_{O_2}} = \frac{K_{CN}[CN]}{K_{O_2}[O_2]} \quad (5.4.18)$$

and

$$4K_{O_2}[O_2] = K_{CN}[CN] \quad (5.4.19)$$

$$\frac{K_{O_2}}{K_{CN}} = \frac{[CN]}{4 \times [O_2]} \quad (5.4.20)$$

Experimentally, it has been shown that for a normally aerated solution the maximum rate was obtained with 0.01M KCN. Therefore

$$\frac{K_{O_2}}{K_{CN}} = \frac{0.01}{4 \times 0.27 \times 10^{-3}} \quad (5.4.21)$$

$$K_{O_2} = 9.26 K_{CN}$$

A similar path may be followed when the leaching solution is saturated with pure oxygen. For maximum rate of dissolution, the relationship between the fractions covered will be

$$4\theta'_{O_2} = \theta_{CN} \quad (5.4.22)$$

and from equations 5.4.20 and 5.4.21

$$\frac{9.26K_{CN}}{K_{CN}} = \frac{[CN]}{4 \times 1.28 \times 10^{-3}} \quad (5.4.23)$$

$$\text{and } [CN] = 0.047M$$

The value actually found experimentally was 0.05M, which may be accepted as a good approximation. If the cyanide concentration is increased beyond this point, there will be no further enhancement to

the dissolution rate of gold (a fact actually observed experimentally), probably because the cyanide will displace oxygen from sites on the metal surface (actually, a slight decrease has been observed for higher cyanide concentrations).

Analogously, when the solution is under an oxygen-free atmosphere, similar arguments may be used to deal with the case where the reagents are cyanide and AQ. The fraction covered by each reagent is then given by

$$\theta_{AQ} = \frac{K_{AQ}[AQ]}{1 + K_{CN}[CN] + K_{AQ}[AQ]} \quad (5.4.24)$$

$$\theta_{CN} = \frac{K_{CN}[CN]}{1 + K_{CN}[CN] + K_{AQ}[AQ]} \quad (5.4.25)$$

It is clear that, again, as the AQ concentration increases it would displace cyanide from the surface of the metal. Since in this case (no oxygen) the dissolution process depends on the presence of those two reagents, the rate will fall, as observed experimentally.

Assuming initially that the rate of dissolution is proportional to θ and that the areas occupied by the AQ and CN species are approximately the same, the stoichiometry of the reaction (equation 3.6) indicates that the following relationship should prevail:

$$4\theta_{AQ} = \theta_{CN} \quad (5.4.26)$$

and from equations 5.4.24 and 5.4.25

$$\frac{\theta_{\text{CN}}}{\theta_{\text{AQ}}} = \frac{K_{\text{CN}}[\text{CN}]}{K_{\text{AQ}}[\text{AQ}]} \quad (5.4.27)$$

$$\frac{4}{1} = \frac{K_{\text{CN}}[\text{CN}]}{K_{\text{AQ}}[\text{AQ}]} \quad (5.4.28)$$

$$\frac{K_{\text{AQ}}}{K_{\text{CN}}} = \frac{[\text{CN}]}{4 \times [\text{AQ}]} \quad (5.4.29)$$

Experimentally, it has been seen that the with 0.01M KCN the corresponding AQ concentration at maximum rate was 6.0mM. Therefore equation 5.4.27 becomes

$$\frac{K_{\text{AQ}}}{K_{\text{CN}}} = \frac{0.01}{4 \times 6 \times 10^{-3}} \quad (5.4.30)$$

which gives $K_{\text{AQ}} = 0.42K_{\text{CN}}$

When the cyanide concentration is increased to 0.03M, equation 5.4.29 may be written as

$$\frac{0.42K_{\text{CN}}}{K_{\text{CN}}} = \frac{0.03}{4 \times [\text{AQ}]} \quad (5.4.31)$$

and $[\text{AQ}] = 18 \text{ mM}$

This value, however, does not exactly correspond to that obtained experimentally, which was found to be 12mM. A possible cause for this discrepancy may be that AQ is in fact a large molecule (as seen earlier

in this Chapter). Thus, the relationship between the area occupied by the AQ and CN molecules should be different than the one considered in equation 5.4.26.

The correct relationship may be then found from the results obtained in practice. Assuming initially an unknown value R , equation 5.4.26 becomes

$$R \theta_{AQ} = \theta_{CN} \quad (5.4.32)$$

and from equation 5.4.30

$$\frac{K_{AQ}}{K_{CN}} = \frac{[CN]}{R \times [AQ]} \quad (5.4.33)$$

For 0.01M KCN, the maximum rate was obtained with 6.0mM AQ. Therefore

$$\frac{K_{AQ}}{K_{CN}} = \frac{0.01}{R \times 6 \times 10^{-3}} \quad (5.4.34)$$

and $K_{AQ} = 1.67 R K_{CN}$

If the cyanide concentration is increased to 0.03M, the corresponding AQ concentration was found experimentally to be 12mM; and then, rewriting equation 5.4.34, the value for R may be obtained.

$$\frac{1.67 R K_{CN}}{K_{CN}} = \frac{0.03}{R \times 12 \times 10^{-3}} \quad (5.4.35)$$

and thus

$$R^2 = 1.50 \Rightarrow R = 1.22$$

This means that, in the present circumstances, the relationship between the fraction covered by the cyanide and AQ is not the one initially considered in equation 5.4.26, but may be given by

$$\theta_{\text{KCN}} = 1.22 \theta_{\text{AQ}} \quad (5.4.36)$$

This equation indicates that, while the stoichiometry shows that for the dissolution of gold four molecules of cyanide are needed for each AQ, the region occupied by these molecules on the metal surface should be almost equivalent.

With regard to this result, it is interesting to recall the fact seen earlier that AQ molecules are reported^[165] as always adsorbing in the flat orientation (i.e., parallel to the surface), for concentrations above 10^{-4} M (FIGURE 5.4.5). The mathematical relation obtained above, thus, shows that the experimental results display agreement with this observation, and corroborates also the fact that the proposed mechanism of competitive adsorption is probably able to explain most of the results obtained.

From the results, as the AQ concentration increases, the space covered by this molecule will continuously grow. This will probably result in displacement of cyanide and/or oxygen molecules, leading to a decrease in the rate of gold dissolution (as actually observed). This decrease is avoided by an increase of either one of the other two reactants (cyanide and oxygen). A situation may be reached, for example, when the initial air flow is replaced by full oxygen. In this

situation, AQ molecules will no longer be able to adsorb on the gold surface. The reaction, thus, proceeds on its course, and the presence or not of AQ makes no difference to the final rate of dissolution.

5.5 -Summary

In this chapter, the experimental part of the study of gold dissolution in the system comprised by AQ + oxygen + cyanide is described and discussed in detail. The rotating disc technique was described and it was seen that the polishing procedure applied to the gold surface played a relevant role, if reliable and reproducible results are to be achieved. Tests were performed under various experimental conditions. A high-surface area metallic sponge (gold-plated) was also used to study the reduction of AQ by gold, as well as the stoichiometry ruling the reaction. The experimental results together with analysis of work in similar fields, led to the postulation that an adsorption mechanism might be occurring on the gold surface, which then explains the results obtained when AQ is introduced. Moreover, experiments under an oxygen-free atmosphere also demonstrated that, if AQ is part of the cyanidation system, the dissolution of gold is possible **even in the absence of oxygen**; in this case, the required gold oxidation is performed by the AQ. Finally, a semi-empirical mathematical model was applied to disclose the probable relationships for the fraction of the metal surface occupied by each adsorbing molecule.

CHAPTER VI

CONCLUSIONS

6.1-Summary of results

This study of gold cyanidation has opened a new operational possibility in the hydrometallurgy of gold. It has revealed, for the first time, that it is possible to use an additional and recyclable oxidizing agent (i.e., a catalyst) that may speed up the rate of gold dissolution in the cyanidation process.

Initially, through a literature survey it was perceived that, while the use of catalytic agents is widely applied in different fields, information specifically dealing with catalysed oxidative leaching with organic compounds is rare. In spite of this fact, useful material could be collected from work related to liquid gas purification, performed with the aid of organic compounds as oxidative catalysts. From this investigation, the organic reagent **anthraquinone-2-sulphonic acid (AQ)** ("silver salt") was identified as a possible suitable catalyst. Quinones have been applied as convenient oxidants in synthetic organic chemistry and oxidations by anthraquinones in alkaline solution is of considerable interest. However, the interesting feature here is that the oxidizing properties of the reagent are being investigated not in organic synthesis but in a system of hydrometallurgical interest.

A review of the cyanidation process, which included oxygen reduction,

cyanide oxidation and the thermodynamic and kinetic aspects of the process was also carried out. Thermodynamic calculations for the system Au-CN-H₂O₂-AQ in aqueous solution indicated that, at least theoretically, AQ could indeed act as an additional and recyclable oxidizing agent, over a pH range from approximately 8.0 upwards. From a kinetic view point, it was somewhat surprising to find that not much work on the rate of gold dissolution, under strictly defined hydrodynamic conditions, has been reported in the literature.

The characterization of reduced and oxidized AQ species in aqueous solution was shown to be possible by use of a flow-through cell in a UV-spectrophotometer, if certain precautions are taken because the reduced form oxidizes with extreme rapidity. The reduction was performed by chemical and electrochemical means. It was also possible to produce hydrogen peroxide "in-situ", from the oxidation of the anthraquinol, and the reaction probably follows a 1:1 molar relationship (anthraquinol:hydrogen peroxide). In an electrochemical study, the diffusion coefficient of the AQ in aqueous solution was determined. The cyclic oxidation/reduction reaction undergone by the AQ is not regarded to follow a straightforward path, but rather to pass through up to nine possible intermediate and highly reactive species. During the course of the reduction step, an increase in pH is observed, which is an indication that a consumption of protons occurs. Thus, without considering the intermediate species, the reduction of AQ in aqueous alkaline solution may be represented by



Moreover, experimental results from tests specifically dealing with gold dissolution (rotating disc and high-surface area metallic sponge) as well as the analysis of work in similar fields indicate that:

1-the rate of gold dissolution in the cyanidation process may be definitely enhanced by about 30% with the addition of AQ, at concentration up to 3.0mM in a 0.03M KCN solution.

2-the influence of AQ on the rate is negligible if the leaching solution is saturated with oxygen, instead of using air only.

3-in rotating disc experiments, the rate of dissolution of gold is transport controlled up to a rotating speed of 10.0 Hz, if the solution is not saturated with oxygen. If it is saturated with oxygen, the rate does not increase at speeds above 2.5 Hz.

4-tests performed under an oxygen-free atmosphere demonstrated that, in dilute cyanide solutions, AQ is indeed able to oxidize gold, (therefore, gold dissolution is possible even with no oxygen in the leaching solution). Apart from oxygen and hydrogen peroxide, this is the first time that an alternative (and **recyclable**) oxidizing agent has been successfully used in the cyanidation process.

AQ may be quantitatively reduced by gold in a cyanide solution and the stoichiometry of the reaction indicates that a 1:2 (AQ:Au) relationship holds, which may be represented by

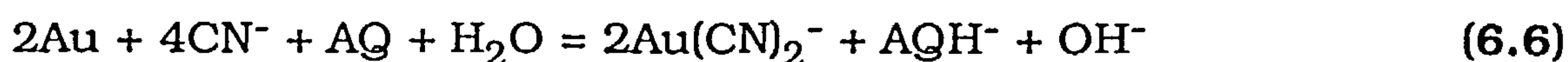
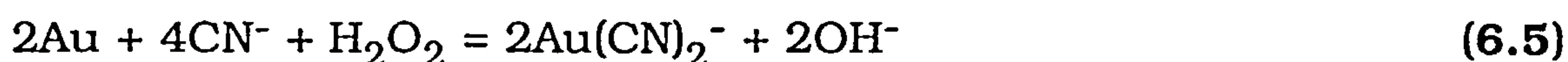
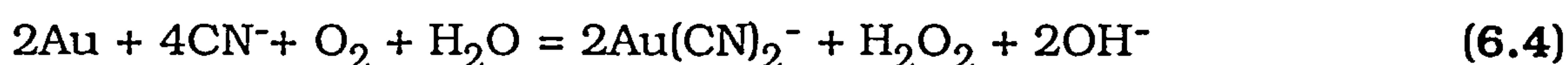


In a conventional aerated solution, the anthraquinol is oxidized with "in-situ" production of hydrogen peroxide according to



and the peroxide is also able to act as an additional oxidizing agent

(even if, as seen, this hydrogen peroxide is only partially used to further oxidize the gold). These reactions show that **AQ is not only capable of oxidizing gold in a cyanide solution but also it may be continuously regenerated**, which is probably the most interesting characteristic introduced in the system. The overall proposed reactions for the dissolution of gold in an aerated cyanide solution in the presence of AQ as a catalytic oxidizing agent may then be written as:



with equation 6.3 continuously generating both oxidizing agents (AQ and H_2O_2).

While the rate enhancement may be attributed to the presence of an additional oxidizing agent in the leaching solution (as described above), the action of AQ is probably better described by a mechanism of molecular adsorption on the metal surface. The nature of the reduction of AQ on the gold surface has been reported to involve a path of adsorption followed by chemical reaction. Cyanide and oxygen are also adsorbed as part of the mechanism occurring on the gold surface. This indicates that, to be reduced, AQ molecules need to "compete" with the other reagents for sites on the gold surface. Therefore, the character of the mechanism of gold dissolution in the leaching system comprised of AQ + cyanide + oxygen seems to be regulated by the adsorptive nature of these reagents. The proposed mechanism, thus, appears to explain many of the results obtained in the cyanidation of gold when AQ is present as an additional reagent, both in aerated or oxygen-free solutions (a case that may be

characterized as "competitive adsorption"). A semi-empirical mathematical model determined the probable relationship between the area occupied by each species.

5-beyond the AQ concentration that yields maximum rate of gold dissolution, further addition not only causes no further benefit, but also can cause the rate to actually start to decrease. This situation probably occurs because, with sufficient cyanide concentration, the adsorbed AQ prevents the oxygen from coming into contact with the gold (this oxygen would otherwise be used to oxidize gold). In this situation, the oxygen may be primarily reduced by the anthraquinol (to form hydrogen peroxide), without taking part in the gold oxidation. With the solutions fully saturated with oxygen, the opposite situation probably occurs, i.e., the greater oxygen availability prevents the AQ from adsorbing on the gold surface; evidence for such a situation comes from the negligible effect of AQ when air is substituted by an oxygen flow. Analysis of results from tests under nitrogen also suggest that this adsorption mechanism is able to explain the behaviour of AQ during gold cyanidation.

6-while significant quantities of gold were dissolved when AQ was the sole oxidizing agent in the leaching solution, the rates of gold dissolution obtained in this situation are lower than those with oxygen (air). This indicates that, in spite of being a possible and useful oxidizing agent for the cyanidation process, AQ alone is less efficient than oxygen itself. If, on one hand, this may be regarded as a drawback, on the other it may prove to be an important feature since, unlike other suggested oxidizing agents (such as inorganic peroxides, for instance), AQ will not increase cyanide oxidation of itself (a fact which was indeed observed experimentally).

7-it is reported that the intermediate species formed during the cyclic AQ oxidation/reduction reaction are highly reactive. This fact may further indicate that the more AQ is adsorbed on the gold surface (which occurs by increasing in the AQ concentration) the faster oxygen will be reduced (to hydrogen peroxide) and, therefore, not participate in the oxidation of the metal. This, of course, causes the rate to decrease, as was demonstrated experimentally (i.e., increasing AQ concentration affects the rate negatively).

8-in using the rotating disc technique, it has been observed that it is important to pay special attention to the preparation of the metal disc surface (polishing procedure) before each experiment to achieve reproducible and reliable results.

9-at high AQ concentrations, an anticipated build-up of hydrogen peroxide (caused by the reaction of oxygen with the reduced anthraquinone) was not detected experimentally and is unlikely to occur, because of the unstable character of H_2O_2 in alkaline solutions (particularly in the absence of peroxy stabilizers) and/or the fact that the locally produced peroxide is readily consumed by oxidizing the gold disc.

10-with the normally aerated cyanide solutions, the activation energy obtained suggests that the dissolution rate is probably diffusion controlled, which is in agreement with the literature. Higher values of activation energy (although not yet lying in the region of pure chemical control), however, are obtained for experimental conditions where the oxidizing agent (AQ and/or oxygen) is present in larger amounts in the leaching solutions. This fact indicates that, under these conditions, a process other than pure diffusion controls the gold dissolution rate.

6.2-Suggestion for further work

It seems that other systems of hydrometallurgical interest, which are in need of an additional oxidizing agent to increase reaction rates, will benefit from the use of catalysts, as proposed in this work. While evident that each situation must be carefully examined before any attempt to use an additional reagent, the role played by the AQ as seen in this work may be regarded as a starting point for future investigations. Other quinone-type compounds may be tested, since their oxidizing properties and cyclic oxidation/reduction character, already employed in organic chemistry, may prove useful also in the hydrometallurgical field.

In the specific case of the cyanidation of gold, the addition of AQ to the leaching of ores, particularly during heap leaching practices, opens an interesting possibility for increasing the efficiency of gold extraction. Extreme situations, such as high ambient temperatures and/or altitudes and the leaching of high heaps (where oxygen deficiency may be a serious hindrance at the bottom of the heap) can also be investigated with AQ additions at various concentrations.

Detailed research into the rates of gold dissolution from different types of ores is also required (preliminary results are given in Appendix V). From such a study, the effect of foreign substances on the role played by the AQ may be clarified and the most ideal ore type and practical conditions to be used with the catalyst would be established. The economic aspect of adding a further reagent to the process is of course also relevant to investigate the viability of using AQ in each particular case. The effect of AQ during the adsorption step on activated carbon is another interesting aspect to be investigated, since, besides the gold, AQ will most probably adsorb on the carbon as

well (some tests on carbon adsorption may be also seen in the second part of Appendix V).

Finally, it is perhaps not too much to stress the importance of the catalytic concept, as used in this work, and that it could be more often considered and investigated in other systems of hydrometallurgical interest. The door has been opened.

APPENDIX I

Experimental conditions used to gold plate the high surface area metallic (Ni-Cr) sponge

This metallic sponge is manufactured by a technique known as electroless nickel plating of expanded, reticulated polyurethane. This technique involves a chemical reduction of nickel salts with formaldehyde on a surface previously activated by treatment with palladium and tin salts (PdCl_2 and SnCl_2)^[170]. A thin layer (around $0.3\ \mu\text{m}$) of nickel is thus obtained, which is enough to give electrical conductivity to the foam. Electroplating of Ni is then used to produce the final sponge, followed by chemical dissolution of the plastic foam. The original geometry is not altered and the electrode ends up with good mechanical properties and lightness. The specific surface of the electrode will depend on the initial foam matrix and on the galvanic deposition procedures. A typical magnified aspect of the electrode used is seen in FIGURE 1 overleaf.

In order to plate the gold on this metallic sponge, the following experimental conditions were used:

cathodic potential applied on electrode: - 1.0 V (SHE)

$\text{KAu}(\text{CN})_2$ initial concentration: $1 \times 10^{-2}\ \text{M}$

supporting electrolyte: 1M KCl

A magnified picture of the electrode seen in FIGURE 1, after being gold plated, is shown in FIGURE 2.

While it cannot be guaranteed that the entire surface is covered with gold, it may be seen that the plating is uniform and suitable for the experiment described in Chapter V.

APPENDIX II

Complete table of results from data arising from the experimental investigation on gold dissolution.

			Au - 1				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	2.99E-09
1.27	.3487	0.44	0.00	0.005	0.44	0.25	
2.52	.3424	0.86	0.01	0.005	0.87	0.50	Experim. conditions
7.80	.3347	2.61	0.02	0.005	2.63	1.00	f=10 Hz
9.72	.3284	3.19	0.06	0.005	3.25	1.25	0.03M KCN
12.38	.3220	3.99	0.11	0.005	4.09	1.50	air only
							no AQ
			Au - 2				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time(h)	Rate(mol/cm2.s)
0.00					0.00	0.00	2.86E-09
1.29	.3492	0.45	0.00	0.005	0.45	0.25	
2.73	.3433	0.94	0.01	0.005	0.94	0.50	Experim. conditions
5.04	.3375	1.70	0.02	0.005	1.72	0.75	f=10 Hz
8.01	.3317	2.66	0.05	0.005	2.70	1.00	0.03M KCN
10.95	.3258	3.57	0.09	0.005	3.65	1.25	air only
13.77	.3200	4.41	0.14	0.005	4.55	1.50	no AQ
			Au - 3				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time(h)	Rate(mol/cm2.s)
0.00					0.00	0.00	2.70E-09
0.30	.3492	0.11	0.00	0.005	0.11	0.25	
1.82	.3433	0.62	0.00	0.005	0.63	0.50	Experim. conditions
4.20	.3375	1.42	0.01	0.005	1.43	0.75	f=10 Hz
7.02	.3317	2.33	0.03	0.005	2.36	1.00	0.03M KCN
9.93	.3258	3.24	0.07	0.005	3.30	1.25	air only
12.69	.3200	4.06	0.12	0.005	4.18	1.50	no AQ
			Au - 4				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time(h)	Rate(mol/cm2.s)
0.00					0.00	0.00	2.64E-09
0.38	.3492	0.13	0.00	0.005	0.13	0.25	
1.81	.3433	0.62	0.00	0.005	0.62	0.50	Experim. conditions
4.18	.3375	1.41	0.01	0.005	1.42	0.75	f=10 Hz
7.02	.3317	2.33	0.03	0.005	2.36	1.00	0.03M KCN
9.80	.3258	3.19	0.07	0.005	3.26	1.25	air only
12.27	.3200	3.93	0.12	0.005	4.04	1.50	no AQ
			Au - 5				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time(h)	Rate(mol/cm2.s)
0.00					0.00	0.00	2.97E-09
0.27	.3492	0.10	0.00	0.005	0.10	0.25	
1.17	.3433	0.40	0.00	0.005	0.40	0.50	Experim. conditions
3.38	.3375	1.14	0.01	0.005	1.15	0.75	f=10 Hz
6.70	.3317	2.22	0.02	0.005	2.24	1.00	0.03M KCN
10.36	.3258	3.38	0.06	0.005	3.43	1.25	air only
14.39	.3200	4.61	0.11	0.005	4.71	1.50	no AQ

			Au - 6				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time(h)	Rate(mol/cm2.s)
0.00					0.00	0.00	3.02E-09
1.30	.3492	0.45	0.00	0.005	0.45	0.25	
2.61	.3433	0.90	0.01	0.005	0.90	0.50	Experim. conditions
5.58	.3375	1.88	0.02	0.005	1.90	0.75	f=10 Hz
8.50	.3317	2.82	0.05	0.005	2.87	1.00	0.03M KCN
11.44	.3258	3.73	0.09	0.005	3.82	1.25	air only
14.48	.3200	4.63	0.15	0.005	4.78	1.50	no AQ
			Au -7				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.84E-09
1.30	0.2492	0.32	0.00	0.005	0.32	0.25	
3.80	0.2433	0.92	0.01	0.005	0.93	0.50	Experim. conditions
7.06	0.2375	1.68	0.03	0.005	1.70	0.75	f=10 Hz
10.93	0.2317	2.53	0.06	0.005	2.59	1.00	0.03M KCN
15.19	0.2258	3.43	0.12	0.005	3.55	1.25	air only
19.64	0.2200	4.32	0.19	0.005	4.51	1.50	no AQ
			Au -8				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.84E-09
0.53	.3492	0.19	0.00	0.005	0.19	0.25	
2.95	.3433	1.01	0.00	0.005	1.02	0.50	Experim. conditions
5.79	.3375	1.95	0.02	0.005	1.97	0.75	f=10 Hz
8.42	.3317	2.79	0.05	0.005	2.84	1.00	0.05M KCN
10.86	.3258	3.54	0.09	0.005	3.63	1.25	air only
13.07	.3200	4.18	0.14	0.005	4.32	1.50	no AQ
			Au -9				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.61E-09
0.83	.3492	0.29	0.00	0.005	0.29	0.25	
2.85	.3433	0.98	0.00	0.005	0.98	0.50	Experim. conditions
5.37	.3375	1.81	0.02	0.005	1.83	0.75	f=10 Hz
7.77	.3317	2.58	0.05	0.005	2.62	1.00	0.07M KCN
10.11	.3258	3.29	0.08	0.005	3.38	1.25	air only
12.23	.3200	3.91	0.13	0.005	4.05	1.50	no AQ
			Au -10				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.40E-09
0.45	.3492	0.16	0.00	0.005	0.16	0.25	
2.40	.3433	0.82	0.00	0.005	0.83	0.50	Experim. conditions
4.77	.3375	1.61	0.01	0.005	1.62	0.75	f=10 Hz
7.07	.3317	2.35	0.04	0.005	2.38	1.00	0.09M KCN
9.21	.3258	3.00	0.07	0.005	3.07	1.25	air only
11.03	.3200	3.53	0.12	0.005	3.65	1.50	no AQ
			Au -11				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.62E-09
0.94	.3492	0.33	0.00	0.005	0.33	0.25	
3.25	.3433	1.12	0.00	0.005	1.12	0.50	Experim. conditions
5.79	.3375	1.95	0.02	0.005	1.97	0.75	f=10 Hz
8.13	.3317	2.70	0.05	0.005	2.74	1.00	0.02M KCN
10.19	.3258	3.32	0.09	0.005	3.41	1.25	air only
12.27	.3200	3.93	0.14	0.005	4.07	1.50	no AQ

			Au -12				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.42E-09
0.98	.3492	0.34	0.00	0.005	0.34	0.25	
2.83	.3433	0.97	0.00	0.005	0.98	0.50	Experim. conditions
4.88	.3375	1.85	0.02	0.005	1.67	0.75	f=10 Hz
7.06	.3317	2.34	0.04	0.005	2.39	1.00	0.04M KCN
9.34	.3258	3.04	0.08	0.005	3.12	1.25	air only
11.65	.3200	3.73	0.13	0.005	3.85	1.50	no AQ
			Au -13				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.64E-09
1.38	.3492	0.48	0.00	0.005	0.48	0.25	
3.67	.3433	1.26	0.01	0.005	1.27	0.50	Experim. conditions
5.97	.3375	2.01	0.03	0.005	2.04	0.75	f=10 Hz
8.24	.3317	2.73	0.06	0.005	2.79	1.00	0.05M KCN
10.41	.3258	3.39	0.10	0.005	3.49	1.25	air only
12.68	.3200	4.06	0.15	0.005	4.21	1.50	no AQ
			Au -14				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.67E-09
1.44	0.2492	0.36	0.00	0.005	0.36	0.25	
3.99	0.2433	0.97	0.01	0.005	0.98	0.50	Experim. conditions
7.36	0.2375	1.75	0.03	0.005	1.77	0.75	f=10 Hz
10.88	0.2317	2.52	0.06	0.005	2.58	1.00	0.01M KCN
14.60	0.2258	3.30	0.12	0.005	3.42	1.25	air only
18.20	0.2200	4.00	0.19	0.005	4.20	1.50	no AQ
			Au -14a				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	7.94E-10
0.38	0.2492	0.09	0.00	0.005	0.09	0.25	
0.85	0.2433	0.21	0.00	0.005	0.21	0.50	Experim. conditions
1.55	0.2375	0.37	0.01	0.005	0.37	0.75	f=10 Hz
2.60	0.2317	0.60	0.01	0.005	0.62	1.00	0.005M KCN
4.04	0.2258	0.91	0.03	0.005	0.94	1.25	air only
5.79	0.2200	1.27	0.05	0.005	1.32	1.50	no AQ
			Au -15				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time(h)	Rate(mol/cm2.s)
0.00					0.00	0.00	3.02E-09
1.09	.3492	0.38	0.00	0.005	0.38	0.25	
3.30	.3433	1.13	0.01	0.005	1.14	0.50	Experim. conditions
6.49	.3375	2.19	0.02	0.005	2.21	0.75	f=10 Hz
9.24	.3317	3.06	0.05	0.005	3.12	1.00	0.03M KCN
12.10	.3258	3.94	0.10	0.005	4.04	1.25	air only
13.87	.3200	4.44	0.16	0.005	4.60	1.50	0.30mM AQ
			Au -16				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.92E-09
1.00	.3492	0.35	0.00	0.005	0.35	0.25	
3.99	.3433	1.37	0.01	0.005	1.37	0.50	Experim. conditions
7.01	.3375	2.37	0.02	0.005	2.39	0.75	f=10 Hz
9.81	.3317	3.25	0.06	0.005	3.31	1.00	0.03M KCN
11.07	.3258	3.61	0.11	0.005	3.72	1.25	air only
13.70	.3200	4.38	0.16	0.005	4.55	1.50	0.30mM AQ

			Au -17				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.34E-09
0.99	.3492	0.35	0.00	0.005	0.35	0.25	
3.00	.3433	1.03	0.00	0.005	1.03	0.50	Experim. conditions
6.61	.3375	2.23	0.02	0.005	2.25	0.75	f=10 Hz
9.50	.3317	3.15	0.05	0.005	3.21	1.00	0.03M KCN
12.66	.3258	4.12	0.10	0.005	4.23	1.25	air only
15.73	.3200	5.03	0.16	0.005	5.20	1.50	0.30mM AO
			Au -18				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	3.32E-09
1.47	.2499	0.37	0.00	0.005	0.37	0.25	
5.45	.2449	1.33	0.01	0.005	1.34	0.50	Experim. conditions
12.54	.2398	3.01	0.03	0.005	3.04	1.00	f=10 Hz
18.72	.2347	4.39	0.10	0.005	4.49	1.50	0.03M KCN
25.13	.2296	5.77	0.19	0.005	5.96	2.00	air only
			Au -19				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time(h)	Rate(mol/cm2.s)
					0.000	0.00	3.20E-09
0.13	.3492	0.05	0.00	0.005	0.046	0.25	
0.87	.3434	0.30	0.00	0.005	0.299	0.50	Experim. conditions
6.94	.3367	2.34	0.01	0.005	2.342	1.00	f=10 Hz
9.91	.3309	3.28	0.04	0.005	3.319	1.25	0.03M KCN
12.55	.3250	4.08	0.09	0.005	4.168	1.50	air only
							1.50mM AO
			Au -20				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.28E-09
2.29	.3492	0.80	0.00	0.005	0.80	0.25	
6.40	.3433	2.20	0.01	0.005	2.21	0.50	Experim. conditions
10.21	.3375	3.44	0.04	0.005	3.49	0.75	f=10 Hz
13.68	.3317	4.54	0.09	0.005	4.63	1.00	0.03M KCN
17.13	.3258	5.58	0.16	0.005	5.75	1.25	air only
20.45	.3200	6.54	0.25	0.005	6.79	1.50	3.00mM AO
			Au -21				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.00E-09
2.12	.3492	0.74	0.00	0.005	0.74	0.25	
5.96	.3433	2.05	0.01	0.005	2.06	0.50	Experim. conditions
9.14	.3375	3.08	0.04	0.005	3.12	0.75	f=10 Hz
12.37	.3317	4.10	0.09	0.005	4.19	1.00	0.03M KCN
15.86	.3258	5.17	0.15	0.005	5.31	1.25	air only
19.43	.3200	6.22	0.23	0.005	6.44	1.50	6.00mM AO
			Au -22				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.67E-09
0.43	.3448	0.15	0.00	0.005	0.15	0.25	
2.73	.3397	0.93	0.00	0.005	0.93	0.50	Experim. conditions
6.51	.3345	2.18	0.02	0.005	2.19	0.75	f=10 Hz
10.31	.3293	3.39	0.05	0.005	3.44	1.00	0.01M KCN
13.94	.3242	4.52	0.10	0.005	4.62	1.25	air only
16.84	.3190	5.37	0.17	0.005	5.54	1.50	3.00mM AO

			Au-23				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.24E-09
1.90	.3492	0.66	0.00	0.005	0.66	0.25	
6.14	.3433	2.11	0.01	0.005	2.12	0.50	Experi ~~m~~ . conditions
9.88	.3375	3.33	0.04	0.005	3.37	0.75	f=10 Hz
13.25	.3317	4.39	0.09	0.005	4.48	1.00	0.03M KCN
16.68	.3258	5.43	0.16	0.005	5.59	1.25	air only
20.32	.3200	6.50	0.24	0.005	6.74	1.50	3.00mM AQ
			Au -24				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.34E-09
0.89	.3492	0.31	0.00	0.005	0.31	0.25	
4.61	.3433	1.58	0.00	0.005	1.59	0.50	Experi ~~m~~ . conditions
9.12	.3375	3.08	0.03	0.005	3.11	0.75	f=10 Hz
12.80	.3317	4.25	0.07	0.005	4.32	1.00	0.05M KCN
16.45	.3258	5.36	0.14	0.005	5.49	1.25	air only
20.26	.3200	6.48	0.22	0.005	6.70	1.50	3.00mM AQ
			Au -25				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.31E-09
1.44	.3492	0.50	0.00	0.005	0.50	0.25	
5.78	.3433	1.99	0.01	0.005	1.99	0.50	Experi ~~m~~ . conditions
9.96	.3375	3.36	0.04	0.005	3.40	0.75	f=10 Hz
13.42	.3317	4.45	0.09	0.005	4.54	1.00	0.07M KCN
16.67	.3258	5.43	0.15	0.005	5.58	1.25	air only
20.34	.3200	6.51	0.24	0.005	6.75	1.50	3.00mM AQ
			Au -26				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.09E-09
1.90	.3492	0.66	0.00	0.005	0.66	0.25	
6.33	.3433	2.17	0.01	0.005	2.18	0.50	Experi ~~m~~ . conditions
10.36	.3375	3.50	0.04	0.005	3.54	0.75	f=10 Hz
13.42	.3317	4.45	0.09	0.005	4.54	1.00	0.09M KCN
16.37	.3258	5.33	0.16	0.005	5.49	1.25	air only
19.25	.3200	6.16	0.24	0.005	6.40	1.50	3.00mM AQ
			Au -27				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.96E-09
1.50	.3492	0.52	0.00	0.005	0.52	0.25	
5.52	.3433	1.90	0.01	0.005	1.90	0.50	Experi ~~m~~ . conditions
9.24	.3375	3.12	0.04	0.005	3.15	0.75	f=10 Hz
12.48	.3317	4.14	0.08	0.005	4.22	1.00	0.02M KCN
15.65	.3258	5.10	0.14	0.005	5.24	1.25	air only
18.60	.3200	5.95	0.22	0.005	6.17	1.50	3.00mM AQ
			Au -28				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	2.85E-09
0.01	.3492	0.00	0.00	0.005	0.00	0.25	
1.18	.3433	0.40	0.00	0.005	0.40	0.50	Experi ~~m~~ . conditions
3.83	.3375	1.29	0.01	0.005	1.30	0.75	f=10 Hz
7.02	.3317	2.33	0.03	0.005	2.35	1.00	0.01M KCN
10.22	.3258	3.33	0.06	0.005	3.39	1.25	air only
13.20	.3200	4.22	0.11	0.005	4.34	1.50	1.50mM AQ

			Au -28a				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.11E-09
0.88	.3492	0.31	0.00	0.005	0.31	0.25	
3.08	.3433	1.06	0.00	0.005	1.06	0.50	Experim. conditions
5.84	.3375	1.97	0.02	0.005	1.99	0.75	f=10 Hz
8.69	.3317	2.88	0.05	0.005	2.93	1.00	0.02M KCN
11.72	.3258	3.82	0.09	0.005	3.91	1.25	air only
14.80	.3200	4.73	0.15	0.005	4.89	1.50	1.50mM AQ
			Au -29				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0					0.00	0.00	3.83E-09
1.72	.3492	0.60	0.00	0.005	0.60	0.25	
5.70	.3433	1.96	0.01	0.005	1.97	0.50	Experim. conditions
9.24	.3375	3.12	0.04	0.005	3.16	0.75	f=10 Hz
12.32	.3317	4.09	0.08	0.005	4.17	1.00	0.03M KCN
15.29	.3258	4.98	0.14	0.005	5.13	1.25	air only
18.02	.3200	5.77	0.22	0.005	5.99	1.50	1.50mM AQ
			Au -30				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.76E-09
1.27	.3492	0.44	0.00	0.005	0.44	0.25	
5.11	.3433	1.75	0.01	0.005	1.76	0.50	Experim. conditions
8.53	.3375	2.88	0.03	0.005	2.91	0.75	f=10 Hz
11.45	.3317	3.80	0.07	0.005	3.87	1.00	0.05M KCN
14.62	.3258	4.76	0.13	0.005	4.89	1.25	air only
17.80	.3200	5.70	0.20	0.005	5.90	1.50	1.50mM AQ
			Au -31				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.28E-09
1.58	.3492	0.55	0.00	0.005	0.55	0.25	
5.43	.3433	1.86	0.01	0.005	1.87	0.50	Experim. conditions
8.56	.3375	2.89	0.04	0.005	2.92	0.75	f=10 Hz
11.05	.3317	3.67	0.08	0.005	3.74	1.00	0.07M KCN
13.29	.3258	4.33	0.13	0.005	4.46	1.25	air only
15.40	.3200	4.93	0.20	0.005	5.13	1.50	1.50mM AQ
			Au -32				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.05E-09
1.56	.3492	0.54	0.00	0.005	0.54	0.25	
5.55	.3433	1.91	0.01	0.005	1.91	0.50	Experim. conditions
8.70	.3375	2.94	0.04	0.005	2.97	0.75	f=10 Hz
10.74	.3317	3.56	0.08	0.005	3.64	1.00	0.09M KCN
12.56	.3258	4.09	0.13	0.005	4.22	1.25	air only
14.17	.3200	4.53	0.20	0.005	4.73	1.50	1.50mM AQ
			Au -33				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	3.60E-09
0.46	.3492	0.16	0.00	0.005	0.16	0.25	
2.98	.3433	1.02	0.00	0.005	1.02	0.50	Experim. conditions
6.67	.3375	2.25	0.02	0.005	2.27	0.75	f=10 Hz
10.28	.3317	3.41	0.05	0.005	3.46	1.00	0.01M KCN
13.55	.3258	4.41	0.10	0.005	4.52	1.25	Oxygen
16.51	.3200	5.28	0.17	0.005	5.45	1.50	

Au -33a							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	7.97E-10
	0.25	0.00	0.00	0.01	0.00	0.25	
	0.24	0.00	0.00	0.01	0.00	0.50	Experm. conditions
0.28	0.24	0.07	0.00	0.01	0.07	0.75	f=10 Hz
1.05	0.23	0.24	0.00	0.01	0.24	1.00	0.0025M KCN
2.28	0.23	0.51	0.01	0.01	0.52	1.25	air only
3.84	0.22	0.84	0.02	0.01	0.86	1.50	3.00mM AQ
Au -33b							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	3.35E-09
1.06	.2492	0.26	0.00	0.005	0.26	0.25	
4.16	.2433	1.01	0.01	0.005	1.02	0.50	Experm. conditions
9.25	.2375	2.20	0.03	0.005	2.22	0.75	f=10 Hz
14.28	.2317	3.31	0.07	0.005	3.38	1.00	0.01M KCN
18.64	.2258	4.21	0.14	0.005	4.35	1.25	air only
21.72	.2200	4.78	0.24	0.005	5.02	1.50	3.00mM AQ
Au -34							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	3.52E-09
0.37	.3497	0.13	0.00	0.005	0.13	0.25	
1.82	.3443	0.63	0.00	0.005	0.63	0.50	Experm. conditions
4.92	.3390	1.67	0.01	0.005	1.68	0.75	f=10 Hz
8.89	.3337	2.97	0.04	0.005	3.00	1.00	0.01M KCN
12.86	.3283	4.22	0.08	0.005	4.30	1.25	oxygen
16.26	.3230	5.25	0.14	0.005	5.40	1.50	
Au -35							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	4.21E-09
2.24	.3492	0.78	0.00	0.005	0.78	0.25	
6.38	.3433	2.19	0.01	0.005	2.20	0.50	Experm. conditions
9.80	.3375	3.31	0.04	0.005	3.35	0.75	f=10 Hz
13.23	.3317	4.39	0.09	0.005	4.48	1.00	0.05M KCN
16.70	.3258	5.44	0.16	0.005	5.60	1.25	oxygen
20.317	.3200	6.50	0.24	0.005	6.74	1.50	
Au -36							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	4.12E-09
2.73	.3492	0.95	0.00	0.005	0.95	0.25	
7.01	.3433	2.41	0.01	0.005	2.42	0.50	Experm. conditions
10.51	.3375	3.55	0.05	0.005	3.60	0.75	f=10 Hz
13.85	.3317	4.59	0.10	0.005	4.69	1.00	0.07M KCN
17.01	.3258	5.54	0.17	0.005	5.71	1.25	oxygen
19.84	.3200	6.35	0.26	0.005	6.60	1.50	
Au -37							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	3.90E-09
1.07	.3492	0.37	0.00	0.005	0.37	0.25	
5.06	.3433	1.74	0.01	0.005	1.74	0.50	Experm. conditions
8.63	.3375	2.91	0.03	0.005	2.94	0.75	f=10 Hz
11.85	.3317	3.93	0.07	0.005	4.00	1.00	0.03M KCN
14.95	.3258	4.87	0.13	0.005	5.00	1.25	oxygen
18.38	.3200	5.88	0.21	0.005	6.09	1.50	

Au -38							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
0.00					0.00	0.00	3.64E-09
0.58	.2492	0.14	0.00	0.005	0.14	0.25	
4.45	.2433	1.08	0.00	0.005	1.09	0.50	Experim. conditions
8.97	.2375	2.13	0.03	0.005	2.16	0.75	f=10 Hz
14.03	.2317	3.25	0.07	0.005	3.32	1.00	0.01M KCN
19.25	.2258	4.35	0.14	0.005	4.49	1.25	oxygen
22.77	.2200	5.01	0.24	0.005	5.25	1.50	
Au -39							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.08E-09
0.51	.3492	0.18	0.00	0.005	0.18	0.25	
2.50	.3433	0.86	0.00	0.005	0.86	0.50	Experim. conditions
5.65	.3375	1.91	0.02	0.005	1.92	0.75	f=10 Hz
9.14	.3317	3.03	0.04	0.005	3.08	1.00	0.02M KCN
12.01	.3258	3.91	0.09	0.005	4.00	1.25	air only
13.80	.3200	4.42	0.15	0.005	4.56	1.50	6.00mM AQ
Au -40							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.99E-09
1.01	.3492	0.35	0.00	0.005	0.35	0.25	
3.46	.3433	1.19	0.01	0.005	1.19	0.50	Experim. conditions
6.90	.3375	2.33	0.02	0.005	2.35	0.75	f=10 Hz
10.41	.3317	3.45	0.06	0.005	3.51	1.00	0.02M KCN
15.19	.3258	4.95	0.11	0.005	5.06	1.25	air only
18.98	.3200	6.07	0.18	0.005	6.26	1.50	6.00mM AQ
Au -41							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.94E-09
1.20	.3492	0.42	0.00	0.005	0.42	0.25	
4.58	.3433	1.57	0.01	0.005	1.58	0.50	Experim. conditions
8.16	.3375	2.75	0.03	0.005	2.78	0.75	f=10 Hz
11.63	.3317	3.86	0.07	0.005	3.93	1.00	0.07M KCN
15.12	.3258	4.93	0.13	0.005	5.05	1.25	air only
18.67	.3200	5.98	0.20	0.005	6.18	1.50	6.00mM AQ
Au -42							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.90E-09
0.68	.3492	0.24	0.00	0.005	0.24	0.25	
2.68	.3433	0.92	0.00	0.005	0.92	0.50	Experim. conditions
5.53	.3375	1.87	0.02	0.005	1.88	0.75	f=10 Hz
8.40	.3317	2.79	0.04	0.005	2.83	1.00	0.09M KCN
11.05	.3258	3.60	0.09	0.005	3.69	1.25	air only
13.50	.3200	4.32	0.14	0.005	4.46	1.50	6.00mM AQ
Au -43							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.81E-09
0.00	.3492	0.00	0.00	0.005	0.00	0.25	
0.22	.3433	0.08	0.00	0.005	0.08	0.50	Experim. conditions
0.99	.3375	0.33	0.00	0.005	0.33	0.75	f=10 Hz
3.08	.3317	1.02	0.01	0.005	1.03	1.00	0.01M KCN
6.15	.3258	2.00	0.02	0.005	2.03	1.25	air only
9.43	.3200	3.02	0.05	0.005	3.07	1.50	6.00mM AQ

			Au -44				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.22E-09
2.04	.3495	0.71	0.00	0.005	0.71	0.25	
5.93	.3440	2.04	0.01	0.005	2.05	0.50	Experim. conditions
9.33	.3385	3.16	0.04	0.005	3.20	0.75	f=10 Hz
12.68	.3330	4.22	0.09	0.005	4.31	1.00	0.05M KCN
16.33	.3275	5.35	0.15	0.005	5.50	1.25	air only
20.47	.3220	6.59	0.23	0.005	6.82	1.50	6.00mM AQ
			Au -45				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.53E-09
2.00	.3492	0.70	0.00	0.005	0.70	0.25	
4.02	.3433	1.38	0.01	0.005	1.39	0.50	Experim. conditions
7.26	.3375	2.45	0.03	0.005	2.48	0.75	f=10 Hz
10.53	.3317	3.49	0.07	0.005	3.56	1.00	0.03M KCN
14.00	.3258	4.56	0.12	0.005	4.68	1.25	oxygen
17.05	.3200	5.46	0.19	0.005	5.65	1.50	0.30mM AQ
			Au -46				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time(h)	J(mol.cm-2.s-1)
0.00					0.00	0.00	3.49E-09
0.82	.3492	0.29	0.00	0.005	0.29	0.25	
3.73	.3433	1.28	0.00	0.005	1.28	0.50	Experim. conditions
6.69	.3375	2.26	0.02	0.005	2.28	0.75	f=10 Hz
8.93	.3317	2.96	0.06	0.005	3.02	1.00	0.03M KCN
13.20	.3258	4.30	0.10	0.005	4.40	1.25	oxygen
16.90	.3200	5.41	0.17	0.005	5.57	1.50	0.30mM AQ
			Au -47				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.23E-09
0.77	.3492	0.27	0.00	0.005	0.27	0.25	
3.36	.3433	1.15	0.00	0.005	1.16	0.50	Experim. conditions
6.66	.3375	2.25	0.02	0.005	2.27	0.75	f=10 Hz
9.77	.3317	3.24	0.05	0.005	3.29	1.00	0.01M KCN
12.48	.3258	4.07	0.10	0.005	4.17	1.25	oxygen
14.82	.3200	4.74	0.17	0.005	4.91	1.50	1.50mM AQ
			Au -48				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.18E-09
3.22	.3492	1.12	0.00	0.005	1.12	0.25	
7.21	.3433	2.48	0.02	0.005	2.49	0.50	Experim. conditions
10.53	.3375	3.55	0.05	0.005	3.61	0.75	f=10 Hz
13.78	.3317	4.57	0.10	0.005	4.68	1.00	0.05M KCN
17.15	.3258	5.59	0.17	0.005	5.76	1.25	oxygen
20.49	.3200	6.56	0.26	0.005	6.82	1.50	1.50mM AQ
			Au -49				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.76E-09
3.91	.3492	1.36	0.00	0.005	1.36	0.25	
7.87	.3433	2.70	0.02	0.005	2.72	0.50	Experim. conditions
10.91	.3375	3.68	0.06	0.005	3.74	0.75	f=10 Hz
13.64	.3317	4.52	0.11	0.005	4.64	1.00	0.07M KCN
16.15	.3258	5.26	0.18	0.005	5.44	1.25	oxygen
18.52	.3200	5.93	0.26	0.005	6.19	1.50	1.50mM AQ

			Au -50				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.66E-09
1.40	.3492	0.49	0.00	0.005	0.49	0.25	
4.90	.3433	1.68	0.01	0.005	1.69	0.50	Experim. conditions
8.31	.3375	2.80	0.03	0.005	2.84	0.75	f=10 Hz
11.40	.3317	3.78	0.07	0.005	3.85	1.00	0.03M KCN
14.44	.3258	4.70	0.13	0.005	4.83	1.25	oxygen
17.20	.3200	5.50	0.20	0.005	5.71	1.50	1.50mM AQ
			Au -51				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.26E-09
0.74	.3492	0.26	0.00	0.005	0.26	0.25	
2.83	.3433	0.97	0.00	0.005	0.98	0.50	Experim. conditions
6.05	.3375	2.04	0.02	0.005	2.06	0.75	f=10 Hz
9.35	.3317	3.10	0.05	0.005	3.15	1.00	0.01M KCN
12.40	.3258	4.04	0.09	0.005	4.13	1.25	oxygen
15.13	.3200	4.84	0.16	0.005	5.00	1.50	3.00mM AQ
			Au -52				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.00E-09
3.23	.3492	1.13	0.00	0.005	1.13	0.25	
7.06	.3433	2.42	0.02	0.005	2.44	0.50	Experim. conditions
10.18	.3375	3.44	0.05	0.005	3.49	0.75	f=10 Hz
13.19	.3317	4.38	0.10	0.005	4.48	1.00	0.05M KCN
16.32	.3258	5.32	0.17	0.005	5.49	1.25	oxygen
19.70	.3200	6.30	0.25	0.005	6.55	1.50	3.00mM AQ
			Au -53				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.25E-09
2.75	.3492	0.96	0.00	0.005	0.96	0.25	
6.38	.3433	2.19	0.01	0.005	2.20	0.50	Experim. conditions
9.28	.3375	3.13	0.05	0.005	3.18	0.75	f=10 Hz
11.65	.3317	3.86	0.09	0.005	3.96	1.00	0.07M KCN
13.76	.3258	4.48	0.15	0.005	4.63	1.25	oxygen
15.70	.3200	5.02	0.22	0.005	5.24	1.50	3.00mM AQ
			Au -54				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.92E-09
0.56	.3492	0.20	0.00	0.005	0.20	0.25	
1.40	.3433	0.48	0.00	0.005	0.48	0.50	Experim. conditions
3.02	.3375	1.02	0.01	0.005	1.03	0.75	f=10 Hz
6.02	.3317	2.00	0.02	0.005	2.02	1.00	0.01M KCN
10.22	.3258	3.33	0.06	0.005	3.38	1.25	oxygen
14.70	.3200	4.70	0.11	0.005	4.81	1.50	6.00mM AQ
			Au -55				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.12E-09
0.90	.3492	0.31	0.00	0.005	0.31	0.25	
4.20	.3433	1.44	0.00	0.005	1.45	0.50	Experim. conditions
8.00	.3375	2.70	0.03	0.005	2.73	0.75	f=10 Hz
11.60	.3317	3.85	0.07	0.005	3.91	1.00	0.03M KCN
15.35	.3258	5.00	0.12	0.005	5.12	1.25	oxygen
19.55	.3200	6.26	0.20	0.005	6.46	1.50	6.00mM AQ

Au -56							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.03E-09
2.18	.3492	0.76	0.00	0.005	0.76	0.25	
6.06	.3433	2.08	0.01	0.005	2.09	0.50	Experim. conditions
9.60	.3375	3.24	0.04	0.005	3.28	0.75	f=10 Hz
12.75	.3317	4.23	0.09	0.005	4.32	1.00	0.05M KCN
16.00	.3258	5.21	0.15	0.005	5.37	1.25	oxygen
19.30	.3200	6.18	0.23	0.005	6.41	1.50	6.00mM AQ
Au -57							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.36E-09
0.93	.3492	0.33	0.00	0.005	0.33	0.25	
3.85	.3433	1.32	0.00	0.005	1.33	0.50	Experim. conditions
7.42	.3375	2.50	0.02	0.005	2.53	0.75	f=10 Hz
10.46	.3317	3.47	0.06	0.005	3.53	1.00	0.07M KCN
13.00	.3258	4.23	0.11	0.005	4.35	1.25	oxygen
15.53	.3200	4.97	0.18	0.005	5.15	1.50	6.00mM AQ
Au -58							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.94E-09
1.24	0.2492	0.31	0.00	0.005	0.31	0.25	
2.60	0.2433	0.63	0.01	0.005	0.64	0.50	Experim. conditions
4.58	0.2375	1.09	0.02	0.005	1.11	0.75	f=6.1Hz
7.35	0.2317	1.70	0.04	0.005	1.74	1.00	0.01M KCN
10.34	0.2258	2.33	0.08	0.005	2.41	1.25	air only
13.86	0.2200	3.05	0.13	0.005	3.18	1.50	
Au -59							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.63E-09
2.42	0.2490	0.60	0.00	0.005	0.60	0.50	
6.40	0.2430	1.55	0.01	0.005	1.57	1.00	Experim. conditions
10.95	0.2370	2.59	0.04	0.005	2.64	1.50	f=2.5Hz
15.99	0.2310	3.69	0.10	0.005	3.79	2.00	0.01M KCN
21.29	0.2250	4.79	0.18	0.005	4.97	2.50	air only
Au -60							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.00E-09
1.09	0.2492	0.27	0.00	0.005	0.27	0.25	
2.86	0.2433	0.70	0.01	0.005	0.70	0.50	Experim. conditions
4.94	0.2375	1.17	0.02	0.005	1.19	0.75	f=16.0Hz
7.80	0.2317	1.81	0.04	0.005	1.85	1.00	0.01M KCN
10.40	0.2258	2.35	0.08	0.005	2.43	1.25	air only
14.30	0.2200	3.15	0.14	0.005	3.28	1.50	
Au -61							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.24E-09
1.17	0.2492	0.29	0.00	0.005	0.29	0.25	
2.99	0.2433	0.73	0.01	0.005	0.73	0.50	Experim. conditions
5.72	0.2375	1.36	0.02	0.005	1.38	0.75	f=25.0Hz
8.61	0.2317	1.99	0.05	0.005	2.04	1.00	0.01M KCN
12.21	0.2258	2.76	0.09	0.005	2.85	1.25	air only
15.60	0.2200	3.43	0.15	0.005	3.59	1.50	

			Au -62				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.69E-09
1.43	0.2492	0.36	0.00	0.005	0.36	0.25	
5.10	0.2433	1.24	0.01	0.005	1.25	0.50	Experim. conditions
10.20	0.2375	2.42	0.03	0.005	2.46	0.75	f=2.5Hz
15.28	0.2317	3.54	0.08	0.005	3.62	1.00	0.01M KCN
20.36	0.2258	4.60	0.16	0.005	4.76	1.25	oxygen
24.63	0.2200	5.42	0.26	0.005	5.68	1.50	
			Au -63				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.91E-09
0.52	0.2492	0.13	0.00	0.005	0.13	0.25	
2.15	0.2433	0.52	0.00	0.005	0.53	0.50	Experim. conditions
3.83	0.2375	0.91	0.01	0.005	0.92	0.75	f=2.5Hz
6.81	0.2317	1.58	0.03	0.005	1.61	1.00	0.01M KCN
10.01	0.2258	2.26	0.07	0.005	2.33	1.25	air only
13.23	0.2200	2.91	0.12	0.005	3.03	1.50	3.00mM AQ
			Au -64				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.96E-09
1.48	0.2492	0.37	0.00	0.005	0.37	0.25	
4.71	0.2433	1.15	0.01	0.005	1.15	0.50	Experim. conditions
8.65	0.2375	2.05	0.03	0.005	2.08	0.75	f=6.1Hz
12.68	0.2317	2.94	0.07	0.005	3.01	1.00	0.01M KCN
16.50	0.2258	3.73	0.14	0.005	3.86	1.25	air only
19.90	0.2200	4.38	0.22	0.005	4.60	1.50	3.00mM AQ
			Au -65				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.24E-09
1.22	0.2492	0.30	0.00	0.005	0.30	0.25	
4.58	0.2433	1.11	0.01	0.005	1.12	0.50	Experim. conditions
9.35	0.2375	2.22	0.03	0.005	2.25	0.75	f=16.0Hz
13.93	0.2317	3.23	0.08	0.005	3.30	1.00	0.01M KCN
17.86	0.2258	4.03	0.15	0.005	4.18	1.25	air only
21.39	0.2200	4.71	0.23	0.005	4.94	1.50	3.00mM AQ
			Au -66				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	3.31E-10
0.30	0.2485	0.07	0.00	0.005	0.07	0.25	
0.40	0.2420	0.10	0.00	0.005	0.10	0.50	Experim. conditions
0.62	0.2355	0.15	0.00	0.005	0.15	0.75	f=10.0Hz
1.40	0.2290	0.32	0.01	0.005	0.33	1.00	0.01M KCN
1.76	0.2225	0.39	0.01	0.005	0.41	1.25	nitrogen
2.40	0.2160	0.52	0.02	0.005	0.54	1.50	0.30mM AQ
			Au -67				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.10E-09
0.94	0.2485	0.23	0.00	0.005	0.23	0.25	
2.03	0.2420	0.49	0.00	0.005	0.50	0.50	Experim. conditions
3.33	0.2355	0.78	0.01	0.005	0.80	0.75	f=10.0Hz
4.90	0.2290	1.12	0.03	0.005	1.15	1.00	0.01M KCN
6.39	0.2225	1.42	0.06	0.005	1.48	1.25	nitrogen
7.72	0.2160	1.67	0.09	0.005	1.76	1.50	3.00mM AQ

			Au -68				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.12E-09
0.78	0.2485	0.19	0.00	0.005	0.19	0.25	
2.69	0.2420	0.65	0.00	0.005	0.65	0.50	Experi ^m . conditions
5.56	0.2355	1.31	0.02	0.005	1.33	0.75	f=10.0Hz
8.57	0.2290	1.96	0.05	0.005	2.01	1.00	0.01M KCN
11.58	0.2225	2.58	0.09	0.005	2.66	1.25	nitrogen
14.10	0.2160	3.05	0.15	0.005	3.19	1.50	6.00mM AQ
			Au -69				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.23E-09
0.80	0.2492	0.20	0.00	0.005	0.20	0.25	
1.99	0.2433	0.48	0.00	0.005	0.49	0.50	Experi ^m . conditions
3.10	0.2375	0.74	0.01	0.005	0.75	0.75	f=10.0Hz
5.01	0.2317	1.16	0.03	0.005	1.19	1.00	0.01M KCN
7.12	0.2258	1.61	0.05	0.005	1.66	1.33	nitrogen
8.66	0.2200	1.91	0.09	0.005	2.00	1.50	12.00mM AQ
			Au -70				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.09E-09
0.99	0.2492	0.25	0.00	0.005	0.25	0.25	
2.77	0.2433	0.67	0.00	0.005	0.68	0.50	Experi ^m . conditions
3.92	0.2375	0.93	0.02	0.005	0.95	0.75	f=10.0Hz
5.05	0.2317	1.17	0.04	0.005	1.21	1.00	0.02M KCN
6.50	0.2258	1.47	0.06	0.005	1.53	1.33	nitrogen
7.89	0.2200	1.74	0.10	0.005	1.83	1.50	3.00mM AQ
			Au -71				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.11E-09
0.93	0.2492	0.23	0.00	0.005	0.23	0.25	
2.60	0.2433	0.63	0.00	0.005	0.64	0.50	Experi ^m . conditions
5.20	0.2375	1.24	0.02	0.005	1.25	0.75	f=10.0Hz
8.34	0.2317	1.93	0.04	0.005	1.98	1.00	0.02M KCN
11.60	0.2258	2.62	0.09	0.005	2.70	1.25	nitrogen
14.22	0.2200	3.13	0.14	0.005	3.27	1.50	6.00mM AQ
			Au -72				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.97E-09
1.16	0.2492	0.29	0.00	0.005	0.29	0.25	
4.89	0.2433	1.19	0.01	0.005	1.20	0.50	Experi ^m . conditions
8.88	0.2375	2.11	0.03	0.005	2.14	0.75	f=10.0Hz
12.77	0.2317	2.96	0.07	0.005	3.03	1.00	0.03M KCN
16.88	0.2258	3.81	0.14	0.005	3.95	1.25	nitrogen
19.42	0.2200	4.27	0.22	0.005	4.50	1.50	12.00mM AQ
			Au -73				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.29E-09
1.14	0.2492	0.28	0.00	0.005	0.28	0.25	
3.94	0.2433	0.96	0.01	0.005	0.96	0.50	Experi ^m . conditions
7.15	0.2375	1.70	0.03	0.005	1.72	0.75	f=10.0Hz
9.90	0.2317	2.29	0.06	0.005	2.35	1.00	0.03M KCN
12.97	0.2258	2.93	0.11	0.005	3.04	1.25	nitrogen
15.31	0.2200	3.37	0.18	0.005	3.54	1.50	16.00mM AQ

			Au -74				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	2.52E-09
1.33	0.2492	0.33	0.00	0.005	0.33	0.25	
5.04	0.2433	1.23	0.01	0.005	1.23	0.50	Experim. conditions
8.56	0.2375	2.03	0.03	0.005	2.06	0.75	f=10.0Hz
11.41	0.2317	2.64	0.07	0.005	2.72	1.00	0.04M KCN
14.06	0.2258	3.17	0.13	0.005	3.31	1.25	nitrogen
17.00	0.2200	3.74	0.20	0.005	3.94	1.50	16.00mM AQ
			Au -75				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.45E-09
0.78	0.2485	0.19	0.00	0.005	0.19	0.25	
2.15	0.2420	0.52	0.00	0.005	0.52	0.50	Experim. conditions
3.95	0.2355	0.93	0.01	0.005	0.94	0.75	f=10.0Hz
6.47	0.2290	1.48	0.03	0.005	1.52	1.00	0.01M KCN
8.35	0.2225	1.86	0.07	0.005	1.92	1.25	nitrogen
9.87	0.2160	2.13	0.11	0.005	2.24	1.50	9.00mM AQ
			Au -76				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	first 2hours
0.39	0.2496	0.10	0.00	0.005	0.10	0.25	4.00E-10
0.70	0.2442	0.17	0.00	0.005	0.17	0.50	
1.58	0.2385	0.38	0.01	0.005	0.38	1.00	2.25h onwards
3.60	0.2321	0.84	0.01	0.005	0.85	2.00	4.12E-10
4.40	0.2267	1.00	0.03	0.005	1.03	2.25	
5.16	0.2214	1.14	0.05	0.005	1.20	2.50	Experim. conditions
6.00	0.2157	1.29	0.08	0.005	1.37	3.00	f=10.0Hz
7.20	0.2100	1.51	0.11	0.005	1.62	3.50	0.01M KCN
							nitrogen initially
							0.60mM AQ
			Au -77				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.10E-08
12.20	0.2500	3.05	0.00	0.005	3.05	0.25	Experim. conditions
25.00	0.2450	6.13	0.06	0.005	6.19	0.50	f=10.0Hz
37.75	0.2400	9.06	0.19	0.005	9.25	0.75	0.01M KCN
49.00	0.2350	11.52	0.37	0.005	11.89	1.00	air only / 55 C
							1.5mM AQ
			Au-78				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	8.37E-09
13.30	0.2500	3.33	0.00	0.005	3.33	0.25	Experim. conditions
22.50	0.2450	5.51	0.07	0.005	5.58	0.50	f=10.0Hz
30.25	0.2400	7.26	0.18	0.005	7.44	0.75	0.03M KCN
38.50	0.2350	9.05	0.33	0.005	9.38	1.00	nitrogen ; 45 C
							12mM AQ
			Au-79				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.30E-08
20.00	0.2500	5.00	0.00	0.005	5.00	0.25	Experim. conditions
34.30	0.2450	8.40	0.10	0.005	8.50	0.50	f=10.0Hz
46.65	0.2400	11.20	0.27	0.005	11.47	0.75	0.03M KCN
59.75	0.2350	14.04	0.50	0.005	14.55	1.00	nitrogen; 55 C
							12mM AQ

Au-80							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	5.29E-09
7.80	0.2500	1.95	0.00	0.005	1.95	0.25	Experm. conditions
14.43	0.2450	3.54	0.04	0.005	3.57	0.50	f=10.0Hz
19.70	0.2400	4.73	0.11	0.005	4.84	0.75	0.03M KCN
23.65	0.2350	5.56	0.21	0.005	5.77	1.00	nitrogen; 35 C
							12mM AO
Au-81							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	5.53E-09
6.80	0.2500	1.70	0.00	0.005	1.70	0.25	Experm. conditions
13.70	0.2450	3.36	0.03	0.005	3.39	0.50	f=10.0Hz
20.00	0.2400	4.80	0.10	0.005	4.90	0.75	0.03M KCN
24.40	0.2350	5.73	0.20	0.005	5.94	1.00	air only; 35 C
							1.5mM AO
Au-82							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	8.41E-09
10.38	0.2500	2.60	0.00	0.005	2.60	0.25	Experm. conditions
20.50	0.2450	5.02	0.05	0.005	5.07	0.50	f=10.0Hz
28.00	0.2400	6.72	0.15	0.005	6.87	0.75	0.03M KCN
38.50	0.2350	9.05	0.29	0.005	9.34	1.00	air only; 45 C
							1.5mM AO
Au-83							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	9.76E-09
7.88	0.2500	1.97	0.00	0.005	1.97	0.25	Experm. conditions
17.20	0.2450	4.21	0.04	0.005	4.25	0.50	f=10.0Hz
28.70	0.2400	6.89	0.13	0.005	7.01	0.75	0.03M KCN
44.80	0.2350	10.53	0.27	0.005	10.80	1.00	oxygen; 35 C
							no AO
Au-84							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.65E-08
13.02	0.2500	3.26	0.00	0.005	3.26	0.25	Experm. conditions
30.65	0.2450	7.51	0.07	0.005	7.57	0.50	f=10.0Hz
52.15	0.2400	12.52	0.22	0.005	12.73	0.75	0.03M KCN
73.75	0.2350	17.33	0.48	0.005	17.81	1.00	oxygen; 45 C
							no AO
Au-85							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.93E-08
5.60	0.2500	1.40	0.00	0.005	1.40	0.10	Experm. conditions
14.00	0.2450	3.43	0.03	0.005	3.46	0.20	f=10.0Hz
31.75	0.2400	7.62	0.10	0.005	7.72	0.40	0.03M KCN
43.35	0.2350	10.19	0.26	0.005	10.44	0.50	oxygen; 55 C
							no AO

			Au-86				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.08E-09
3.20	0.2500	0.80	0.00	0.005	0.80	0.25	Experim. conditions
7.75	0.2450	1.90	0.02	0.005	1.91	0.50	f=10.0Hz
12.84	0.2400	3.08	0.05	0.005	3.14	0.75	0.03M KCN
18.17	0.2350	4.27	0.12	0.005	4.39	1.00	air only; 35 C
							no AQ
			Au-87				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	4.69E-09
3.25	0.2488	0.81	0.00	0.005	0.81	0.25	Experim. conditions
8.31	0.2425	2.02	0.02	0.005	2.03	0.50	f=10.0Hz
14.46	0.2363	3.42	0.06	0.005	3.47	0.75	0.03M KCN
21.46	0.2300	4.94	0.13	0.005	5.07	1.00	air only; 45 C
							no AQ
			Au-88				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	6.07E-09
2.02	0.2488	0.50	0.00	0.005	0.50	0.10	Experim. conditions
4.55	0.2425	1.10	0.01	0.005	1.11	0.20	f=10.0Hz
10.45	0.2363	2.47	0.03	0.005	2.50	0.40	0.03M KCN
13.87	0.2300	3.19	0.09	0.005	3.28	0.50	air only; 55 C
							no AQ
			Au-89				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	6.20E-09
4.72	0.2488	1.17	0.00	0.005	1.17	0.25	Experim. conditions
12.69	0.2425	3.08	0.02	0.005	3.10	0.50	f=10.0Hz
19.86	0.2363	4.69	0.09	0.005	4.78	0.75	0.01M KCN
28.13	0.2300	6.47	0.19	0.005	6.66	1.00	oxygen; 35 C
							no AQ
			Au-90				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.12E-08
10.49	0.2488	2.61	0.00	0.005	2.61	0.25	Experim. conditions
24.38	0.2425	5.91	0.05	0.005	5.96	0.50	f=10.0Hz
38.40	0.2363	9.07	0.17	0.005	9.25	0.75	0.01M KCN
50.35	0.2300	11.58	0.37	0.005	11.95	1.00	oxygen; 45 C
							no AQ
			Au-91				
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.64E-08
5.65	0.2488	1.41	0.00	0.005	1.41	0.10	Experim. conditions
13.88	0.2425	3.37	0.03	0.005	3.39	0.20	f=10.0Hz
29.65	0.2363	7.00	0.10	0.005	7.10	0.40	0.01M KCN
36.83	0.2300	8.47	0.25	0.005	8.72	0.50	oxygen; 55 C
							no AQ

Au-92							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	7.53E-09
2.87	0.2500	0.72	0.00	0.005	0.72	0.10	Experim. conditions
6.58	0.2450	1.61	0.01	0.005	1.63	0.20	f=10.0Hz
13.44	0.2400	3.23	0.05	0.005	3.27	0.40	0.03M KCN
16.77	0.2350	3.94	0.11	0.005	4.06	0.50	oxygen; 30 C
							no AQ
Au-93							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	1.43E-08
5.12	0.2488	1.27	0.00	0.005	1.27	0.10	Experim. conditions
9.66	0.2425	2.34	0.03	0.005	2.37	0.20	f=10.0Hz
21.95	0.2363	5.19	0.07	0.005	5.26	0.40	0.03M KCN
34.45	0.2300	7.92	0.18	0.005	8.11	0.50	oxygen; 40 C
							no AQ
Au-94							
mg/l	vol. (l)	m (mg)	m.aliq.(mg)	sample vol.(l)	final amount(mg)	time (h)	Rate(mol/cm2.s)
					0.00	0.00	first 2.5 hours
0.56	0.2493	0.14	0.00	0.005	0.14	0.50	2.20E-10
1.01	0.2437	0.25	0.00	0.005	0.25	1.00	
1.65	0.2380	0.39	0.01	0.005	0.40	1.50	3.0h onwards
2.17	0.2323	0.50	0.02	0.005	0.52	2.00	2.26E-10
2.48	0.2267	0.56	0.03	0.005	0.59	2.50	
3.39	0.2210	0.75	0.04	0.005	0.79	3.00	Experim. conditions
3.55	0.2157	0.77	0.06	0.005	0.82	3.25	f=10.0Hz
3.80	0.2103	0.80	0.07	0.005	0.87	3.50	0.01M KCN
3.96	0.2050	0.81	0.09	0.005	0.90	3.75	nitrogen initially
							0.12mM AQ

	A	B	C	D	E	F	G
1	t (C)	T(K)	1/T	J	log J	E(kJ/mol)	Exp. Conditions
2	55	328	3.05E-03	1.30E-08	-7.89	38.9	
3	45	318	3.14E-03	8.37E-09	-8.08		KCN: 0.03M
4	35	308	3.25E-03	5.29E-09	-8.28		AQ:120 mM
5	25	298	3.36E-03	2.97E-09	-8.53		nitrogen
6							
7	t (C)	T(K)	1/T	J	log J	E(kJ/mol)	Exp. Conditions
8	55	328	3.05E-03	1.10E-08	-7.96	32.6	
9	45	318	3.14E-03	8.41E-09	-8.08		KCN: 0.03M
10	35	308	3.25E-03	5.53E-09	-8.26		AQ:1.5 mM
11	25	298	3.36E-03	3.20E-09	-8.49		air only
12							
13	t (C)	T(K)	1/T	J	log J	E(kJ/mol)	Exp. Conditions
14	55	328	3.05E-03	1.99E-08	-7.70	42.0	
15	45	318	3.14E-03	1.60E-08	-7.80		
16	40	313	3.19E-03	1.43E-08	-7.84		
17	35	308	3.25E-03	9.68E-09	-8.01		KCN: 0.03M
18	30	303	3.30E-03	7.53E-09	-8.12		no AQ
19	25	298	3.36E-03	3.90E-09	-8.41		oxygen
20							
21	t (C)	T(K)	1/T	J	log J	E(kJ/mol)	Exp. Conditions
22	55	328	3.05E-03	6.07E-09	-8.22	18.7	
23	45	318	3.14E-03	4.70E-09	-8.33		KCN: 0.03M
24	35	308	3.25E-03	4.08E-09	-8.39		no AQ
25	25	298	3.36E-03	2.86E-09	-8.54		air only
26							
27	t (C)	T(K)	1/T	J	log J	E(kJ/mol)	Exp. Conditions
28	55	328	3.05E-03	1.64E-08	-7.79	41.2	
29	45	318	3.14E-03	1.12E-08	-7.95		KCN: 0.01M
30	35	308	3.25E-03	6.20E-09	-8.21		no AQ
31	25	298	3.36E-03	3.58E-09	-8.45		oxygen

Data used to construct the calibration curve used in Chapter IV to evaluate AQ concentration according to Beer-Lambert's law.

optical path length = 10mm
wavelength = 330nm

AQ (M) (10 ⁻⁴)	Absorbance
3.0	1.42
2.0	0.94
1.5	0.71
1.0	0.47
0.6	0.27

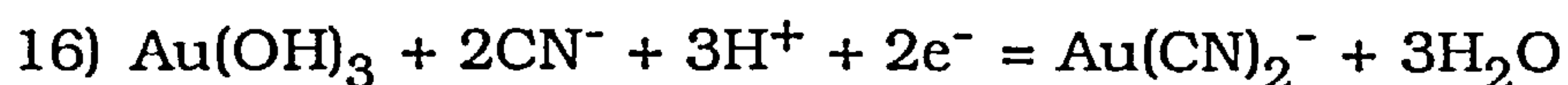
From these data the molar absorption coefficient (ε) may be calculated with Beer-Lambert's law:

$$A = \epsilon \cdot l \cdot c$$

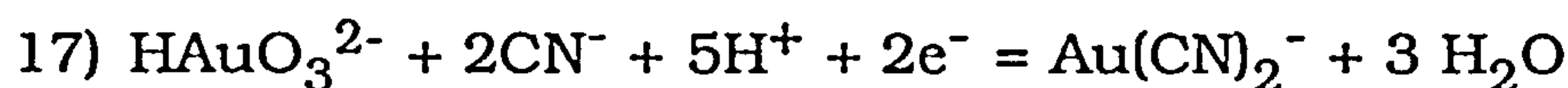
Since l = 10mm, the molar absorption coefficient of the AQ was found to be 476.6 m²/mol.

APPENDIX IIIThermodynamic data and equations used to draw the Eh-pH diagrams.

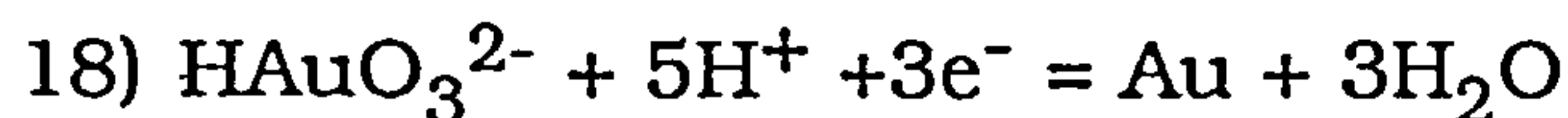
- 1) $2\text{H}^+ + 2\text{e}^- = \text{H}_2$
 $E = -0.0591 \text{ pH}$
- 2) $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$
 $E = 1.23 - 0.0591 \text{ pH}$
- 3) $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$
 $E = 0.72 - 0.0591 \text{ pH}$
- 4) $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$
 $E = 1.73 - 0.0591 \text{ pH}$
- 5) $\text{HO}_2^- + 3\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$
 $E = 2.08 - 0.09 \text{ pH}$
- 6) $\text{O}_2 + \text{H}^+ + 2\text{e}^- = \text{HO}_2^-$
 $E = 0.32 - 0.0296 \text{ pH}$
- 7) $\text{HO}_2^- + \text{H}^+ = \text{H}_2\text{O}_2$
 $\text{pH} = 11.7$
- 8) $\text{AQ} + 2\text{H}^+ + 2\text{e}^- = \text{AQH}_2$
 $E = 0.187 - 0.0591 \text{ pH}$
- 9) $\text{AQH}^- + \text{H}^+ = \text{AQH}_2$
 $\text{pH} = 8.0$
- 10) $\text{AQ} + \text{H}^+ + 2\text{e}^- = \text{AQH}^-$
 $\text{pH} = 0.04 + 0.0296 \text{ pH}$
- 11) $\text{CN}^- + \text{H}^+ = \text{HCN}$
 $\text{pH} = 9.5$
- 12) $\text{Au}(\text{CN})_2^- + \text{e}^- = 2\text{CN}^- + \text{Au}$
 $E = -0.60 \text{ V}$
- 13) $\text{Au}(\text{CN})_2^- + 2\text{H}^+ + \text{e}^- = \text{Au} + 2\text{HCN}$
 $E = 0.52 - 0.118 \text{ pH}$
- 14) $\text{HAuO}_3^{2-} + 2\text{H}^+ = \text{Au}(\text{OH})_3$
 $\text{pH} = 13.3$
- 15) $\text{Au}(\text{OH})_3 + 2\text{HCN} + \text{H}^+ + 2\text{e}^- = \text{Au}(\text{CN})_2^- + 3\text{H}_2\text{O}$
 $E = 1.78 + 0.0296 \text{ pH}$



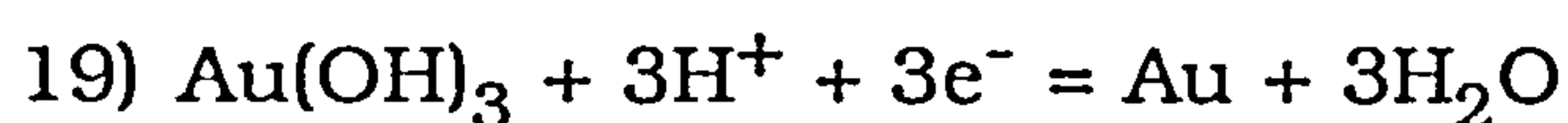
$$E=2.34 - 0.089 \text{ pH}$$



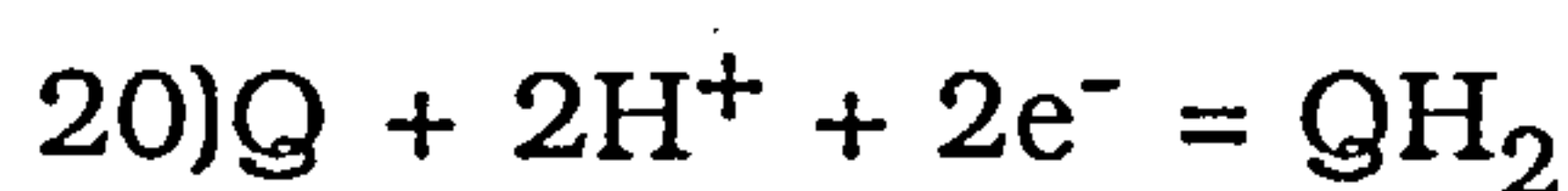
$$E=3.13 - 0.148 \text{ pH}$$



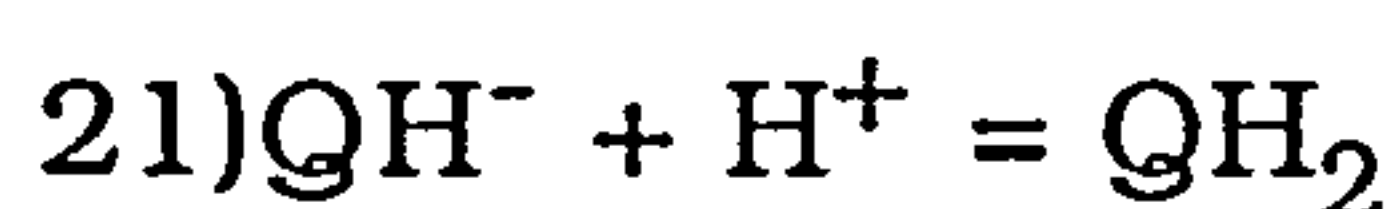
$$E=1.89 - 0.099 \text{ pH}$$



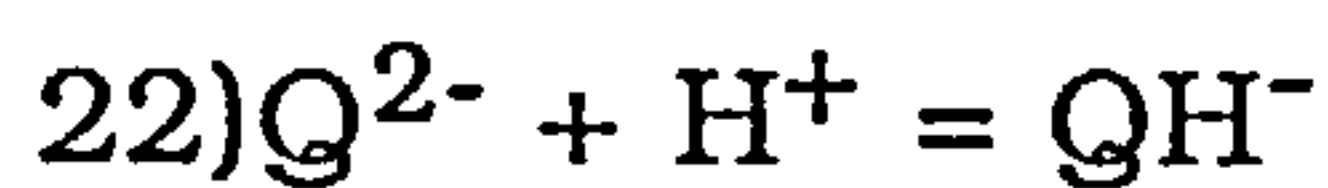
$$E= 1.36 - 0.0591 \text{ pH}$$



$$E=0.6998 - 0.0591 \text{ pH}$$



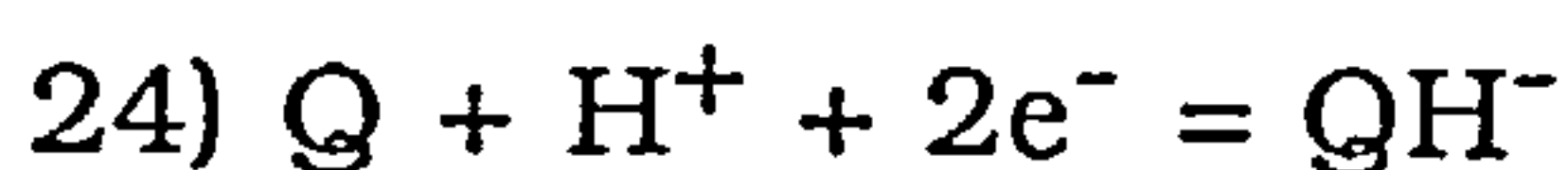
$$\text{pH} = 9.85$$



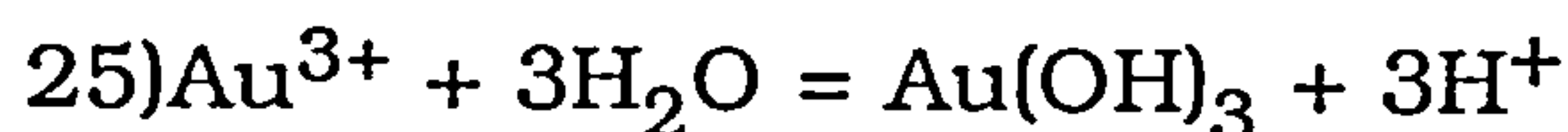
$$\text{pH} = 11.4$$



$$E= 0.08 \text{ V}$$



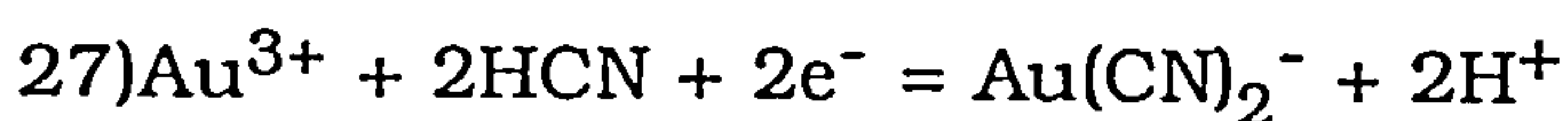
$$E=0.453 - 0.0296 \text{ pH}$$



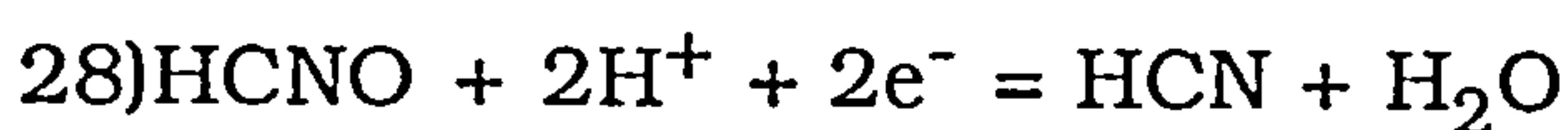
$$\text{pH} = 1.32$$



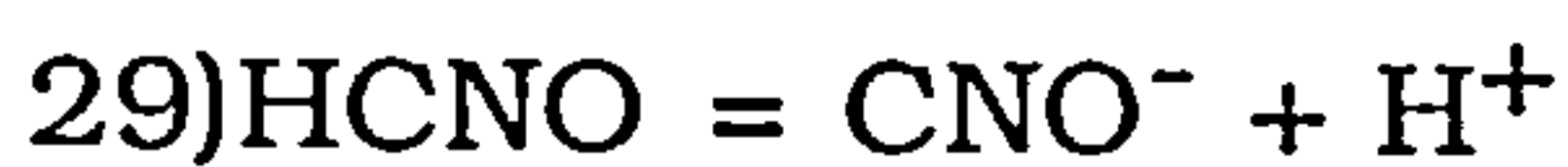
$$E=1.44 \text{ V}$$



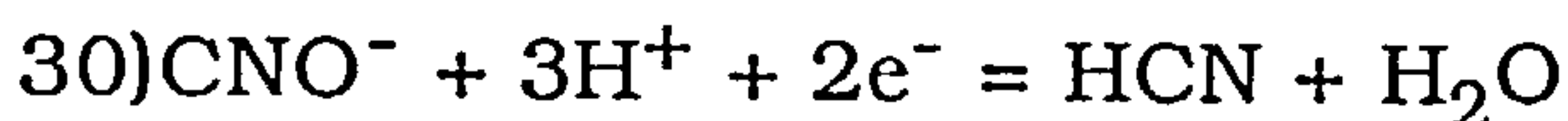
$$E=1.90 + 0.0591 \text{ pH}$$



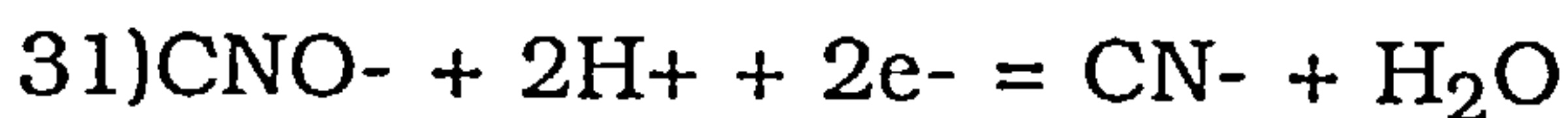
$$E=0.022 - 0.0591 \text{ pH}$$



$$\text{pH}=3.9$$



$$E=0.137 - 0.089 \text{ pH}$$



$$E=-0.143 - 0.0591 \text{ pH}$$

Thermodynamic data used in the calculations (taken from Bard^[98]).

species	ΔG° (kJ/mol)
H ₂ O	-237.178
O ₂	0
H ₂ O ₂	-134.1
HO ₂ ⁻	-67.4
HCN	112.0
Au(CN) ₂ ⁻	286.0
CN ⁻	166.0
Au ₃ ⁺	433.8 ¹
Au(OH) ₃ (s)	-317.0
HAuO ₃ ²⁻	-142.0
HCNO	-121.0
CNO ⁻	-98.7

E _o (V)	pK
0.1870 (AQH ₂ /AQ)	8.0 ²
0.6998 (QH ₂ /Q)	9.90 ³
0.4530 (QH ⁻ /Q)	11.40 ³
0.080 (Q ²⁻ /Q) ³	

¹from Latimer^[171]

²from Clark^[77]

³from Bailey^[74]

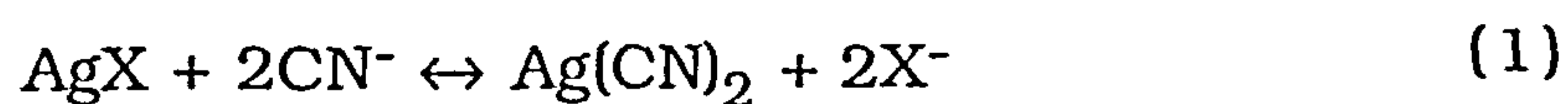
APPENDIX IV

1-Cyanide determination with an ion-selective electrode

During the course of this work, cyanide analysis was carried out with a cyanide ion-selective electrode. This is a quick and accurate method for cyanide determination. Here, some basic aspects and guidelines are given for the successful application of this technique.

Principle of operation

The determination is based on the behaviour of the sensing part of the cyanide electrode. This is found on the bottom tip of the electrode and consists of a membrane layer of a silver halide compound, merged with an appropriate supporting material, which may be silicone, rubber or a mixture of inorganic salts^[166]. When this membrane comes into contact with a cyanide solution, silver ions dissolve from the membrane surface by complex formation as^[123,166]:



As a consequence, silver ions within the membrane will move to replace the complexed ions; this determines a difference in potential that corresponds to the concentration of cyanide in solution. The potential is then measured against a constant standard electrode with a pH/Eh meter and is determined by the Nernst equation:

$$E = E_0 - S \log [\text{CN}^-]$$

where E is the potential reading
 E_0 the standard electrode potential
 S the slope of the equation
 $[CN^-]$ cyanide ion concentration in the solution

Strictly, the term $[CN^-]$ should be replaced by the cyanide activity, which is related to the cyanide ion concentration by the activity coefficient, γ . This coefficient is variable and depends on the total ionic strength present in solution. However, if the ionic strength is very high and constant with respect to the concentration of the ion being measured, γ may be considered as constant and therefore the activity becomes direct proportional to the concentration. For this reason, it will be seen that an ionic strength adjustor (ISA) solution is always added to both the standard and sample cyanide solutions. In this way the background ionic strength is kept high and constant relatively to the ion (cyanide) that is being measured. In the case of the cyanide-sensitive electrode, the ISA solution normally recommended is 10M NaOH^[123].

Reagents

Cyanide determination is carried out with the aid of a calibration curve (see below). In order to construct this curve, a number of reagents must be initially prepared:

A—at least 100ml of the ISA solution, which, as seen above, consists of 10M NaOH. This is, of course, a very strong corrosive alkaline solution and therefore should be handled with extreme care. It is also recommended that this solution be kept in a plastic bottle.

B-a standard 10^{-2} M cyanide solution (0.65g of KCN, for example, to 1 litre of distilled water), **freshly prepared every week**. Add 1ml of ISA solution to every 100ml of standard solution.

C-100ml of a 10^{-3} M cyanide solution, which is prepared by diluting the above 10^{-2} M standard solution. Add 1ml ISA to each 100ml prepared. This solution must be prepared daily.

Apparatus

A METROHM model 654 pH meter was used for all potentiometric measurements. The cyanide-selective electrode was a Russell cyanide electrode model 94-4096 and a double junction calomel electrode (Russell, type CRL/DJ/ NaNO_3) was used as the reference electrode (if this is not available a Ag-AgCl electrode may be also used).

Range of determination

It is theoretically possible to use the cyanide electrode in solutions containing cyanide within the range from 10^{-1} M to 10^{-6} M[167]. However, it has to be considered that measurements in solutions containing more than 10^{-3} M CN^- considerably shorten the electrode life and should only be carried out occasionally. It is advisable, whenever possible, to dilute samples to below this concentration.

Procedure

For cyanide determinations within the range from 10^{-6} M to 4×10^{-5} M

approximately, proceed as follows (obs.: as stated above, it is always better to analyse low cyanide concentrations. Therefore, the procedure described here may be followed even if the sample considered is above the higher concentration limit of $4 \times 10^{-5} \text{M}$; in this case the sample needs, of course, only to be diluted to within the acceptable range).

- 1-add 100ml of distilled water and 1ml of ISA to a beaker and stir with the aid of a magnetic follower.
- 2-place both electrodes in this solution.
- 3-add increments of the reagent described in item C above according to TABLE 1 and note the potential reading after each addition (allow around 2 minutes for a stable reading).

vol.added of reagent C (ml)	conc. in beaker ($\text{M} \times 10^{-6}$)
0.1	1.0
0.1	2.0
0.2	4.0
0.2	6.0
0.4	9.9
2.0	29.0
2.0	48.0

Table 1 - Guide values used to construct the calibration curve for cyanide determination with a cyanide-selective electrode.

4-plot the values of concentration (log axis) and potential (linear axis) on a semilogarithmic paper (supplemental practical data is given on the last page of this appendix). A typical plot is shown in FIGURE 1.

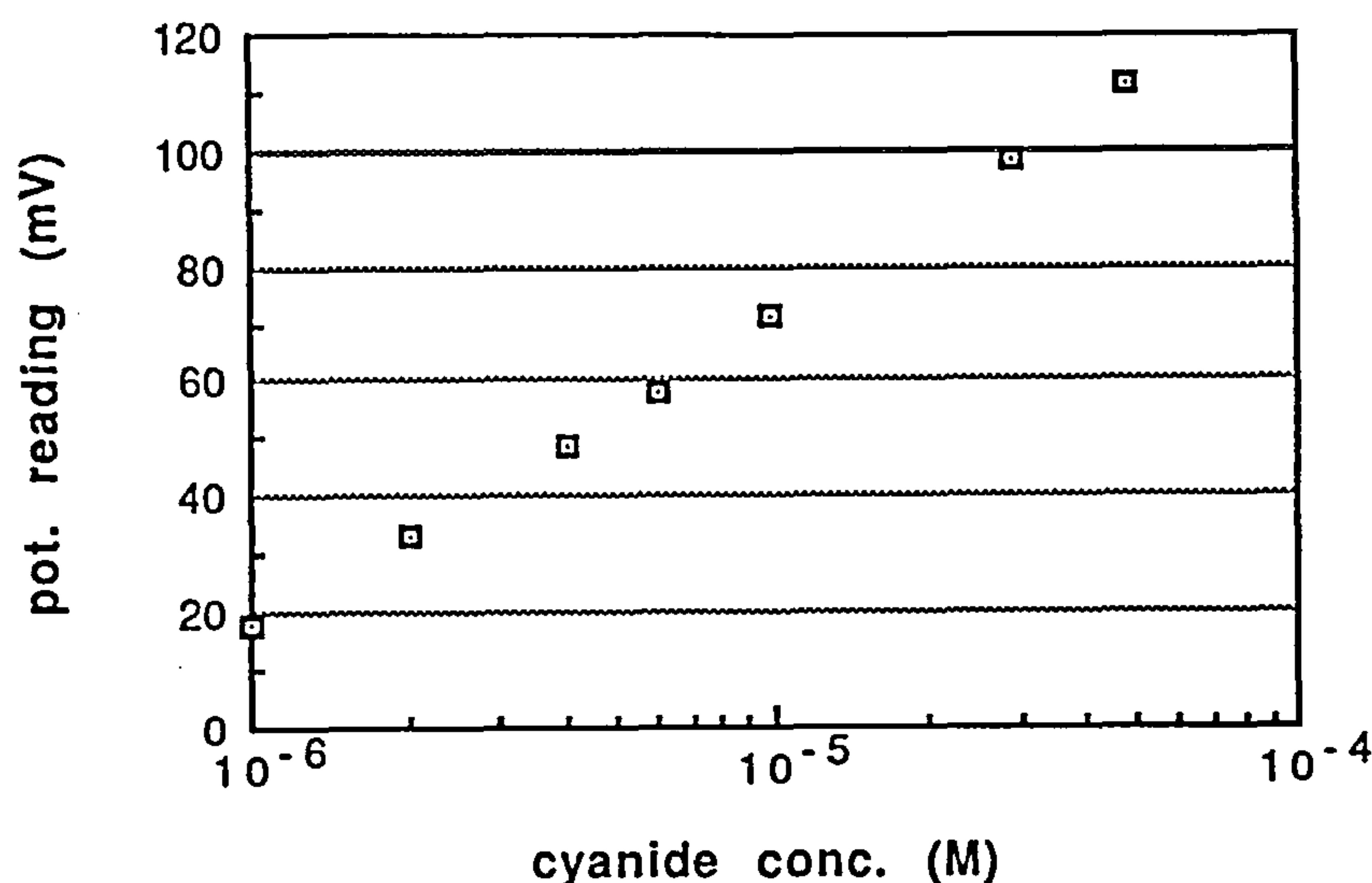


Figure 1 - Typical calibration curve for cyanide determination with an ion selective electrode.

5-rinse and completely dry both electrodes.

6-add 1ml of ISA to each 100ml of the sample to be measured.

7-place sample solution, prepared as in item 6 above, in a beaker and insert both electrodes.

8-stir with the magnetic follower and wait for a stable reading. Response time does not normally exceed 1 minute.

9-the cyanide concentration in the sample is given from the measured potential compared with the calibration curve.

General precautions

1-all samples and standards should be kept at the same temperature. For intermittent use, the electrode can work in the temperature range from 5°C to 100°C. Some stirring plates generate heat while stirring, and thus it is advisable to use an insulator between the beaker and the

stirring plate.

2-stirring should not be allowed to cause vortexing in the beaker.

3-to obtain the best precision, the beaker used should be covered with Parafilm.

Cyanide-selective electrode calibration data		
	1	
Vol.added (ml)	Conc. (M)(ee-6)	Pot read. (mV)
0.10	1.00	-12.50
0.10	2.00	-22.00
0.20	4.00	-38.50
0.20	6.00	-47.00
0.40	9.90	-59.80
2.00	29.00	-87.00
2.00	48.00	-99.00
	2	
Vol.added (ml)	Conc. (M)(ee-6)	Pot read. (mV)
0.10	1.00	-14.50
0.10	2.00	-29.00
0.20	4.00	-43.50
0.20	6.00	-52.50
0.40	9.90	-64.30
2.00	29.00	-91.50
2.00	48.00	-102.50
	3	
Vol.added (ml)	Conc. (M)(ee-6)	Pot read. (mV)
0.10	1.00	-4.00
0.10	2.00	-16.50
0.20	4.00	-31.50
0.20	6.00	-41.50
0.40	9.90	-53.00
2.00	29.00	-80.50
2.00	48.00	-94.00
	4	
Vol.added (ml)	Conc. (M)(ee-6)	Pot read. (mV)
0.10	1.00	12.00
0.10	2.00	22.50
0.20	4.00	39.60
0.20	6.00	49.20
0.40	9.90	61.20
2.00	29.00	88.00
2.00	48.00	100.00
	5	
Vol.added (ml)	Conc. (M)(ee-6)	Pot read. (mV)
0.10	1.00	11.50
0.10	2.00	25.30
0.20	4.00	41.30
0.20	6.00	51.20
0.40	9.90	64.00
2.00	29.00	92.00
2.00	48.00	104.00

2-Hydrogen peroxide determination with 1,10-phenanthroline^[80]

This is a differential spectrophotometric method applied to the determination of hydrogen peroxide in the 0.03 to 2.50 mg/l concentration range. The method involves the oxidation of Fe^{2+} to Fe^{3+} with hydrogen peroxide and subsequent addition of the phenanthroline to react with the excess of Fe^{2+} which was not oxidized by the peroxide. Two volumetric flasks are filled with sufficient volume of Fe^{2+} solution, but to only one of them is the solution containing the hydrogen peroxide added. This solution (with the hydrogen peroxide) is then the reference cell and the other is used in the sample cell to determine the difference in absorbance, measured at 510 nm, as given in the equation below:

$$(2/a) (A_1 - A_2) = (V \cdot M/V_f)$$

where	$(A_1 - A_2)$	absorbance measured in the conditions stated above
a		molar absorptivity of the complex Fe^{2+} -1,10 phenanthroline
V		volume of the solution containing hydrogen peroxide added to the volumetric flask
V_f		final volume of both coloured solution
M		molar hydrogen peroxide concentration

Reagents

-Standard iron (II) solution (ammonium iron sulphate - Mohr's salt):
0.21 g/l

-1,10 - Phenanthroline solution: 0.5 g/l

-sodium acetate - acetic acid solution (buffer): 0.01M each.

Procedure

To both 50 ml volumetric flasks, a sufficient volume of the iron (II) solution is added. The desired volume of the solution containing the hydrogen peroxide to be determined is then added to **one** of the two flasks (OBS.: it is noteworthy that, at this point, all the hydrogen peroxide present in this solution will oxidize the iron (II) to iron (III), which then will make possible the difference in absorbance). Ten ml of the sodium acetate-acetic acid buffer and 5 ml of the colour forming reagent (phenanthroline) are added to both flasks; the volume is then completed to the graduation mark and the solutions are left for around 15 minutes, to allow the colour to develop.

The flask containing the hydrogen peroxide is used as the reference cell and the absorbance measured (at $\lambda = 510$ nm) with the other solution is used to give $A_1 - A_2$, as in the equation above. The concentration of hydrogen peroxide in the sample may be then calculated. The molar absorptivity of the complex is reported as being 11100 l/mole.cm^[80].

It is important to note that when the equation above is used, the result obtained is the concentration of the original solution, i.e., the one used to prepare the sample to be analysed. On the other hand, if the factor V/V_f is not used, that is, when the equation becomes

$$2/a (A_1 - A_2) = M$$

the result obtained is the concentration of hydrogen peroxide in the sample solution itself.

APPENDIX V

1-Results of tests carried out with ores

Some tests were carried out to investigate the effect of AQ addition on the cyanide leaching of gold from ores. TABLE 1 below displays the gold content in each one of the ores tested, which were all of oxidised type.

ore #	Au content (g/t)
01	6.90
50	18.66
176	81.8
1006	8.71

Table 1 - Gold content in the ores tested

Experimental

All leaching tests were carried out in a conventional round-bottom split-top glass reactor, with 200 or 400 ml of solution. Pulp density was kept at 30% (percentage of solids in the slurry) in all cases and representative samples of the ores were taken by riffing. Lime (CaO) was always added when necessary to keep the pH between 10.6 and 12.0. The pulp was agitated with the aid of a glass stirrer adapted to an

electric motor and air was continuously injected by means of a glass frit. All tests were carried out at room temperature (18-22°C). Samples of 5 ml each approximately were collected at predetermined intervals, vacuum filtered and analysed by atomic absorption for their gold content.

Results

1- ore # 1 (6.9 gAu/t ore) - The experimental conditions used to run tests with this ore are shown in TABLE 2 below:

Test No.	KCN (M)	AQ (mM)
1	0.015	---
2	0.015	1.6
3	0.015	8.0
4	0.040	8.0
5	0.040	---
6	0.015	8.0 ¹

Table 2 - Experimental conditions of tests for ore # 1.

The results for this ore may be seen in FIGURE 1 and 2, which are plots of % Au dissolved against time. Samples were collected at different intervals in each case and tests were normally run for 24 hours, although one of them (test 4) was stopped after 18 h 30 min. FIGURE 1 displays the tests with 0.015M KCN whereas FIGURE 2

¹ test carried out under nitrogen

those with 0.04M KCN. The results with the exact figures for the experiments are reported in TABLE 6 on the last page of this Appendix.

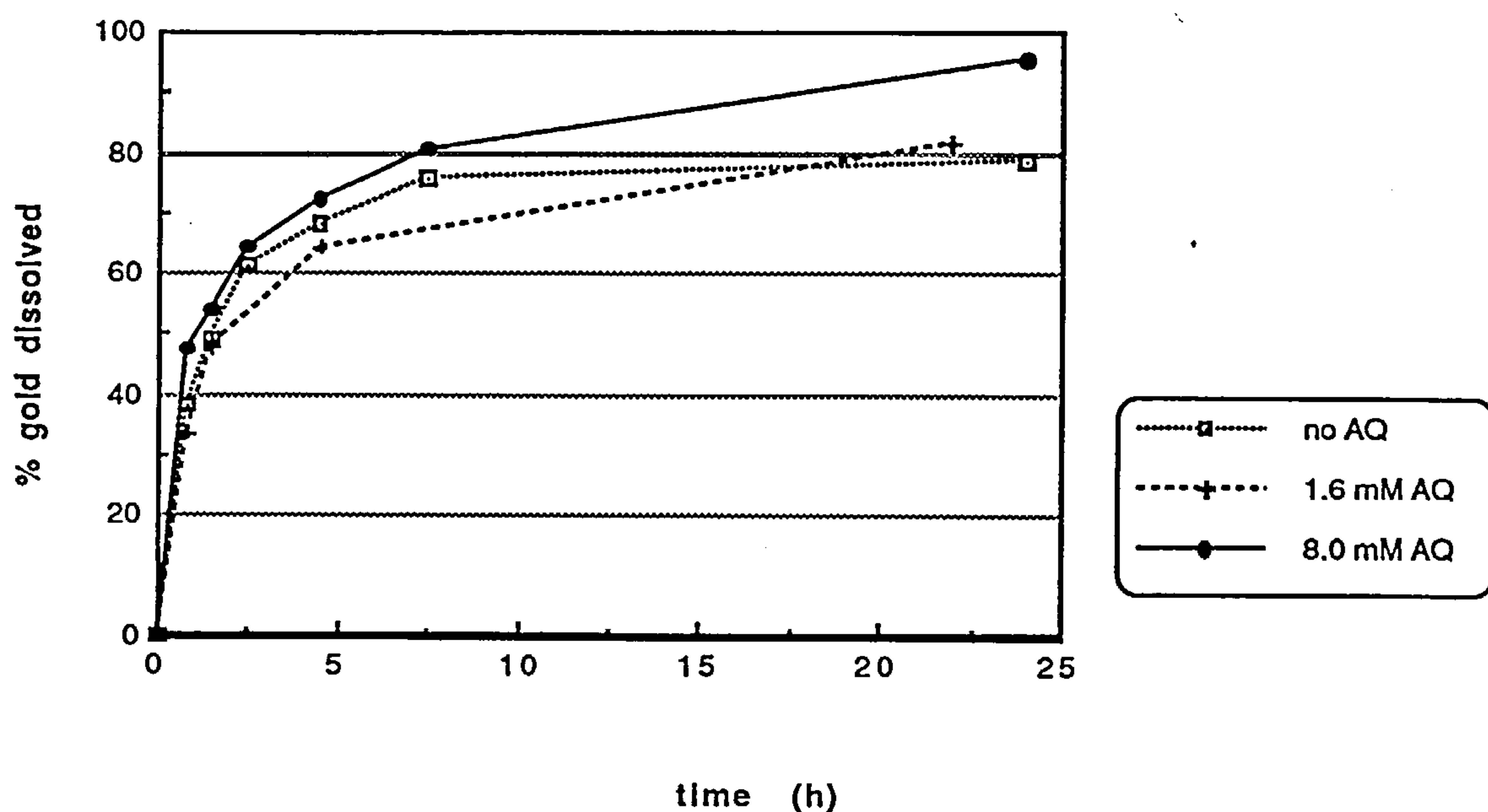


Figure 1 - Amount of gold dissolved with time from ore # 1, with 0.015M KCN, showing effect of two AQ concentrations.

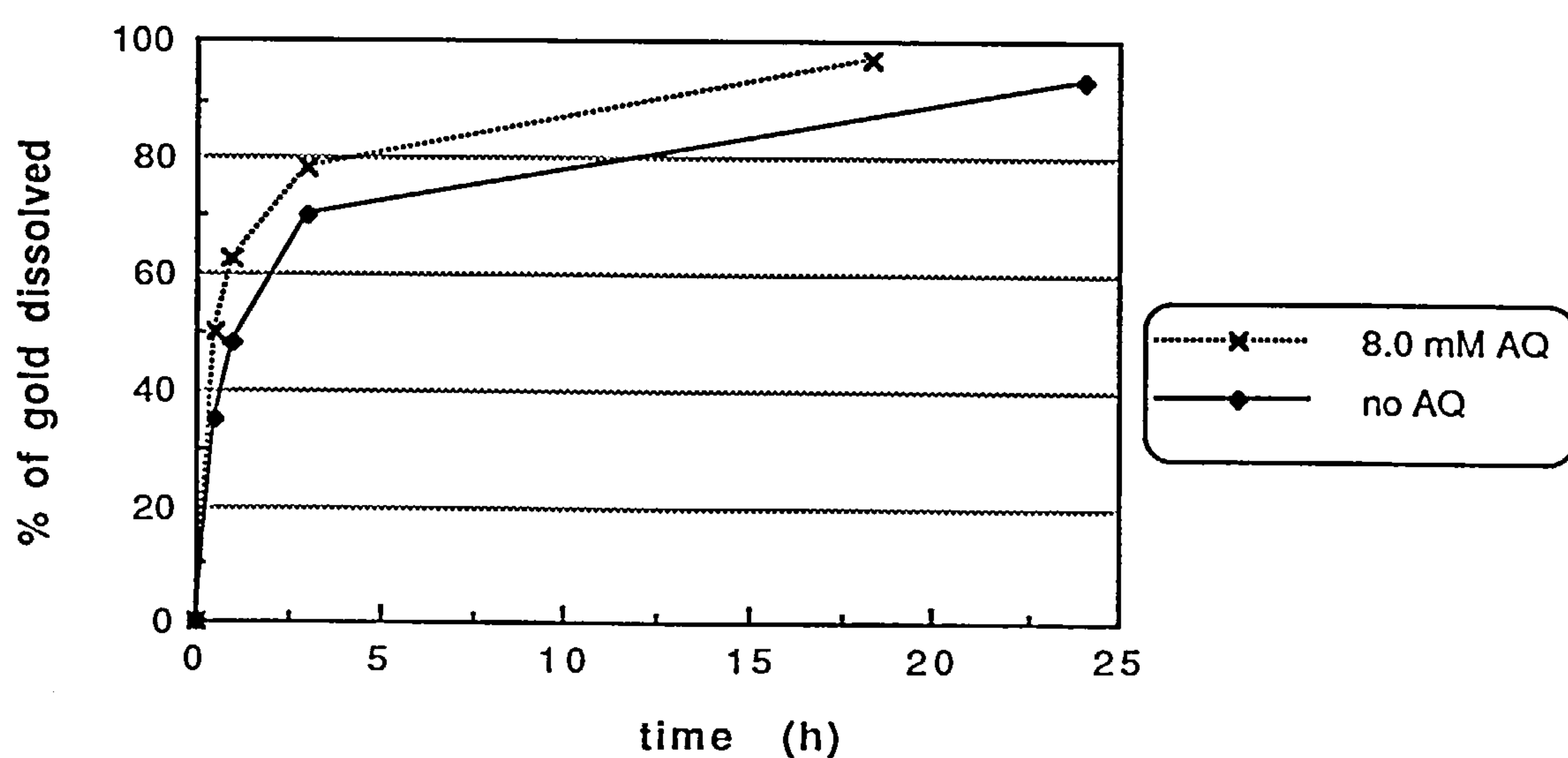


Figure 2 - Amount of gold dissolved with time from ore # 1, with 0.04M KCN, showing effect of AQ.

It may be seen from the figures that there was a positive effect on the gold dissolution when AQ was added to solutions containing both cyanide concentrations. The effect observed with 1.6mM AQ, however, is less pronounced than that with 8.0mM AQ. It may be seen that in the former case (1.6mM AQ) gold dissolution was actually less over most of the time, although the final amount was higher than the experiment carried out with no AQ. It is also interesting to note that this higher value (81.2%) was achieved in 22 hours, which was a level not reached by the experiment without AQ even after 24 hours of leaching (78.3%). With 8.0mM AQ the amount of gold dissolved was always higher, reaching 94.9% after 24 hours, and still showing a slight upward tendency.

When the leaching was performed with a higher KCN concentration, the influence of the AQ was always positive, with the final amount reaching 97.0% after 18 h 30 min compared to 92.8% after 24 h of test without AQ. The AQ effect was more marked in this case possibly because the cyanide concentration was higher, and therefore the rate was being controlled by the availability of oxidant in the solution (which in this case was supplied in more quantity by the presence of AQ).

The ability of AQ to oxidize gold from an ore in a cyanide solution was also tested under an oxygen-free atmosphere (test 6). Nitrogen was allowed to flush for 45 minutes before starting the experiment, which lasted for 7 h 30 min. The leaching solution was 0.015M KCN, 8.0mM AQ and lime was also added to keep the pH within 10.8 and 12.5 during the experiment. The results of this test are displayed in FIGURE 3.

It may be seen that, while the amount dissolved after 7 h 30 min. was

lower than the one obtained with air, and AQ + air (64.5% for test 6, 75.4% for test 1 and 80.4% for test 3), with AQ in the leaching solution it is possible to dissolve gold from the ore, even in the complete absence of oxygen. The reduced AQ is, of course, promptly regenerated by contact with air.

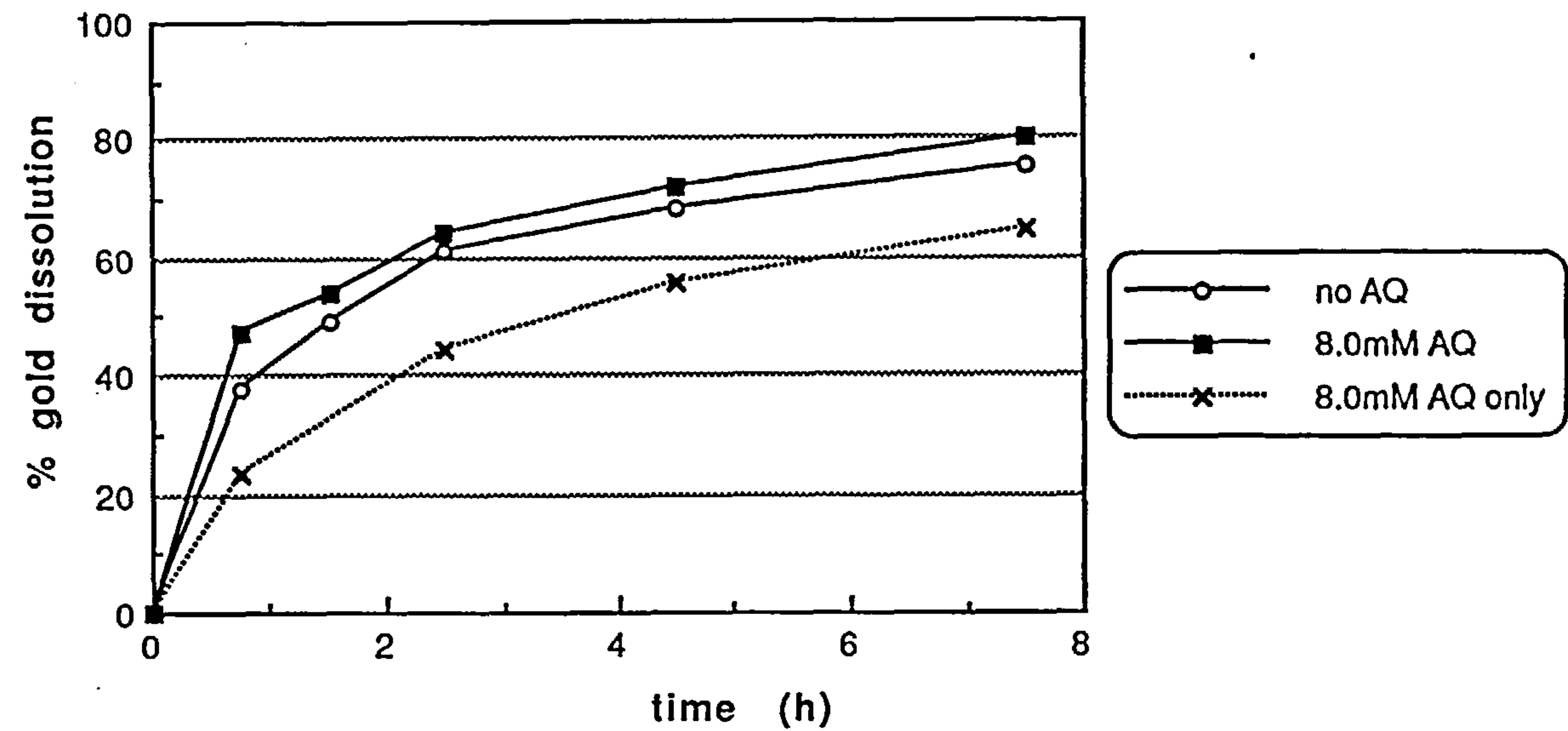


Figure 3 - Amount of gold dissolved with time from ore # 1, with 0.015M KCN, showing results (1) with air only, (2) 8.0mM AQ with air and (3) 8.0mM AQ in an oxygen-free solution.

2- ore # 50 (18.66 g Au/t ore) - The experimental conditions for tests with this ore are seen in TABLE 3:

Test No.	KCN (M)	AQ (mM)
7	0.04	---
8	0.04	16.0

Table 3 - Experimental conditions of tests for ore # 50

The experimental procedure followed basically the same pattern as the one described earlier and the results are shown in FIGURE 4.

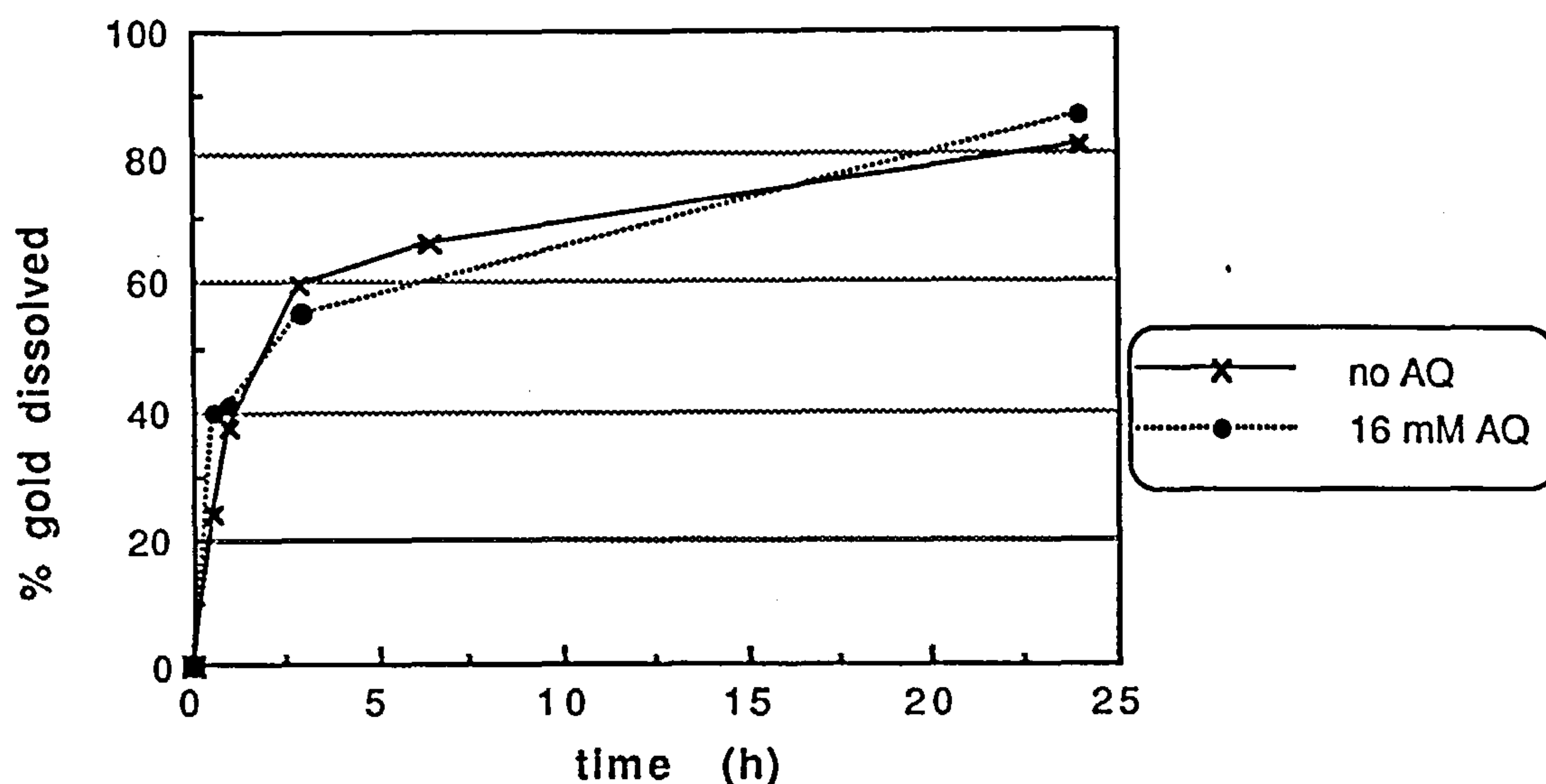


Figure 4 - Amount of gold dissolved with time from ore # 50, with 0.04M KCN, showing effect of 16mM AQ addition.

In this case, the marked positive effect caused by the AQ, which was observed with the previous ore, did not occur, even though the cyanide concentration was relatively high. However, it is interesting that the amount dissolved in the test with AQ was usually higher during the experiment, and the final amount reached **86.6%** compared to **81.3%** for the test without the AQ. Also, according to the mechanism discussed earlier, it is possible that a lower AQ concentration might yield better results.

3- ore # 176 (81.8 g Au/t ore) - Tests with this ore were carried out under the following experimental conditions:

Test No.	KCN (M)	AQ (mM)
9	0.04	--
10	0.04	16.0

Table 4 - Experimental conditions of tests for ore # 176

The results obtained in these tests are shown in FIGURE 5.

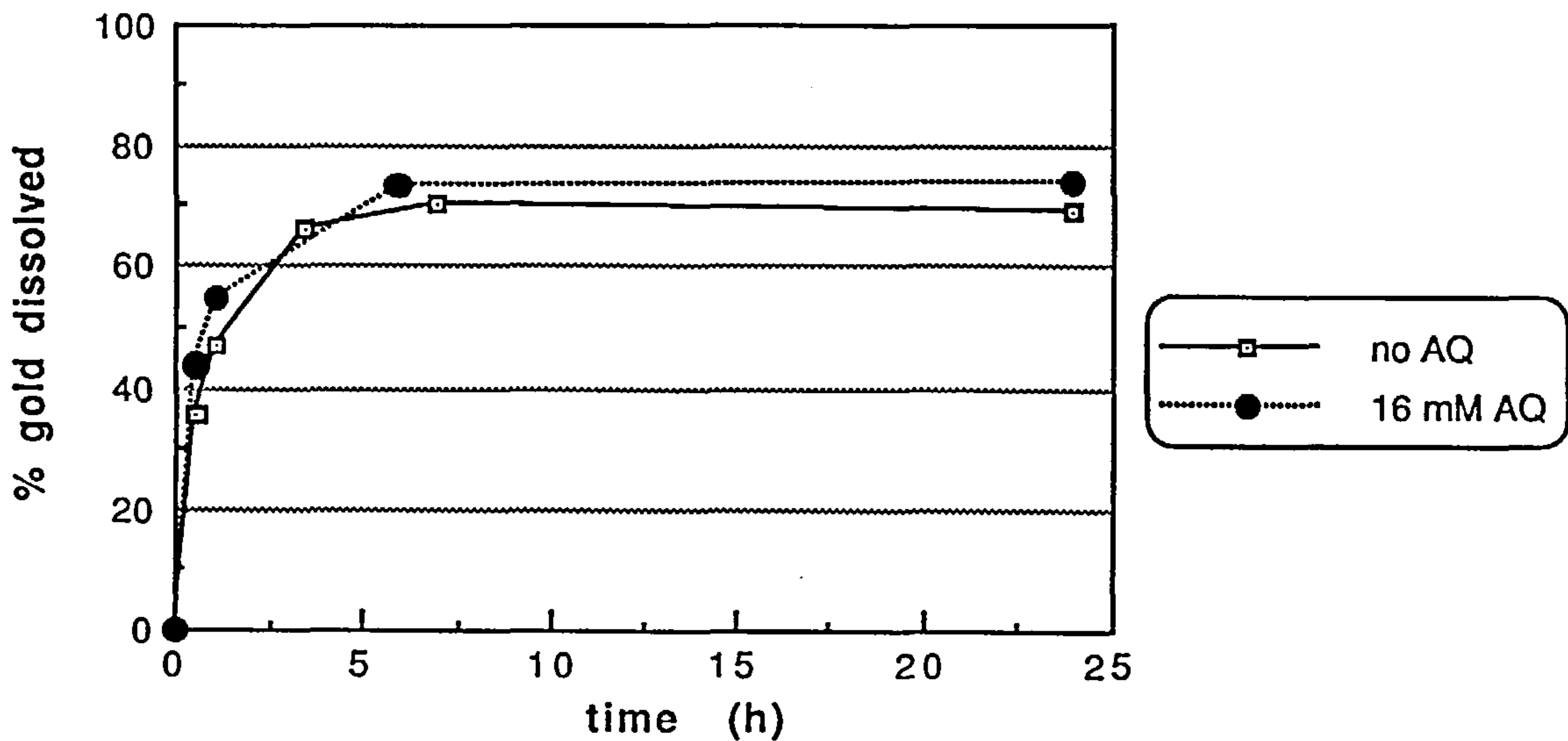


Figure 5 - Amount of gold dissolved with time from ore # 176, with 0.04M KCN, showing effect of 16mM AQ addition.

The final amount obtained when AQ is present in the leaching solution was again higher (73.7%) than when the oxidant was oxygen from air only (69.0%). Moreover, the amount of gold dissolved was always higher with AQ. It is also important to note that this AQ concentration is in its limit of solubility in aqueous solution.

4 - ore # 1006 (8.71 g Au/t ore) - TABLE 5 shows the experimental conditions for tests performed with this ore.

Test No.	KCN (M)	AQ (mM)
11	0.04	---
12	0.04	16.0

TABLE 5 - Experimental conditions for tests with ore # 1006

The results are reported in FIGURE 6 below.

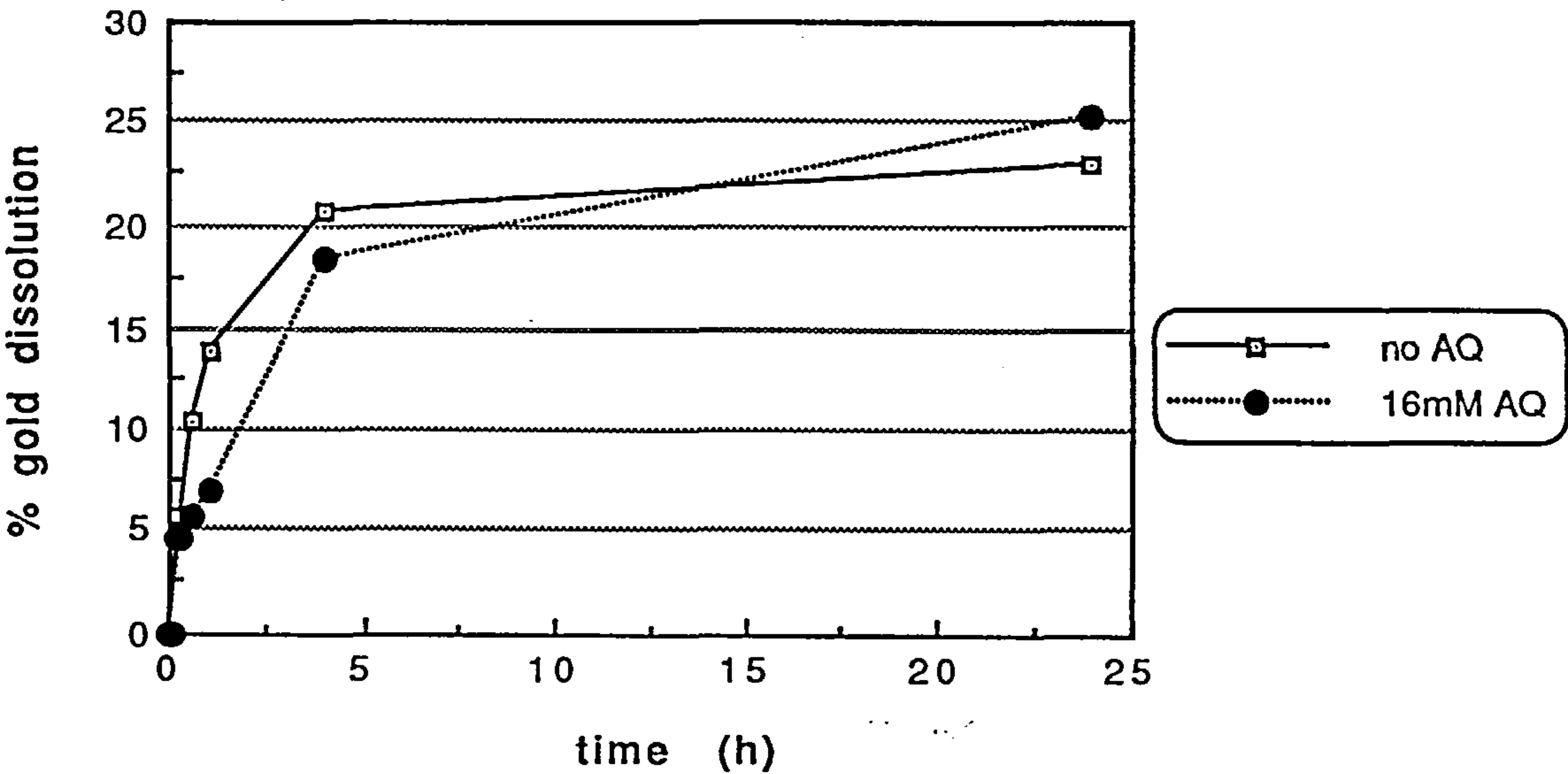


Figure 6 - Amount of gold dissolved with time from # 1006, with 0.04M KCN, showing effect of 16mM AQ addition.

In this test, the AQ had only a minor effect, reflected in the final amount dissolved, which was found to be 25.3% against 23.0% obtained in the test with no AQ. In the remaining part of the test, however, the presence of the AQ had in fact a negative effect on the dissolution of gold (which may be caused because the AQ concentration was too high).

Conclusions

While this tests did not show conclusive evidence of the usefulness of AQ, encouraging results were obtained in some cases. The best result was undoubtedly achieved in the first ore tested, with an interesting increase in the amount of gold dissolved, as seen in Figures 1 and 2. An important aspect was the dissolution of gold even in the absence of oxygen, if AQ is present in the leaching solution. As observed earlier in this work, a process such as heap leaching, for instance, may be considerably benefited by this fact, since it may suffer from a lack of oxygen towards the bottom of the heap. It is also noteworthy that all tests were carried out with air continuously being injected; this is a situation where the oxygen is more easily available, which may not be always the case found in industrial scale.

On the other hand, for the other ores investigated, the effect of AQ on the gold dissolution was not immediately positive. Although for ore # 176, the dissolution of gold was always higher when AQ was present, for the two remaining situations the effect of AQ cannot be considered obvious. Nevertheless, it is worth noticing that, if AQ was added, the final amount of gold dissolution was higher in all cases. Also, as noted earlier, the effect of AQ may turn to be more beneficial if lower concentrations are used.

As a final remark, it may be said that the effect caused by the AQ in the cyanidation process appears to be attractive. Surely, additional investigation with different ores, including heap leaching tests, changing AQ and cyanide concentration, as well as temperature, is useful for a further understanding of the system.

Table 6 - Overall results of tests carried out with the ores

		TEST 1		
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.015M KCN
0.75	1.31	0.26	37.70	no AQ
1.50	1.72	0.34	49.30	100g ore #01
2.50	2.19	0.42	60.90	200 ml
4.50	1.54	0.47	68.10	
7.50	2.88	0.52	75.40	
24.00	3.08	0.54	78.30	
		TEST 2		
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.015M KCN
0.75	1.14	0.23	33.30	1.6mM AQ
1.50	1.70	0.33	47.80	100g ore #01
4.50	2.40	0.44	63.80	200 ml
22.00	3.09	0.56	81.20	
		TEST 3		
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.015M KCN
0.75	1.63	0.65	47.10	8.0mM AQ
1.50	1.88	0.73	53.90	200g ore #01
2.50	2.32	0.88	63.80	400 ml
4.50	2.67	0.99	71.70	
7.50	3.09	1.11	80.40	
24.00	3.74	1.31	94.90	
		TEST 4		
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.04M KCN
0.50	1.73	0.69	50.00	8.0mM AQ
1.00	2.21	0.86	62.30	200g ore #01
3.00	2.85	1.08	78.30	400 ml
18.50	3.61	1.34	97.00	
		TEST 5		
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.04M KCN
0.50	1.19	0.48	34.80	no AQ
1.00	1.69	0.66	47.80	200g ore #01
3.00	2.57	0.97	70.30	400 ml
24.00	3.46	1.28	92.80	
		TEST 6		
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.015M KCN
0.75	0.80	0.32	23.20	8.0 mM AQ
2.50	1.57	0.61	44.20	200g ore #01
4.50	2.04	0.77	55.80	400 ml
7.50	2.40	0.89	64.50	nitrogen

TEST 7				
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.04M KCN
0.50	2.21	0.44	23.50	no AQ
1.00	3.60	0.70	37.40	100g ore #50
3.00	5.91	1.12	59.90	200 ml
6.50	6.69	1.24	66.30	
24.00	8.45	1.52	81.30	
TEST 8				
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.04M KCN
0.50	3.68	0.74	39.60	16mM AQ
1.00	3.93	0.77	41.20	100g ore #50
3.00	5.44	1.03	55.10	200 ml
24.00	8.77	1.62	86.60	
TEST 9				
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.04M KCN
0.50	14.62	2.92	35.70	16mM AQ
1.00	19.44	3.79	46.30	100g ore #176
3.30	28.43	5.40	66.00	200 ml
7.00	31.06	5.75	70.30	
24.00	31.30	5.64	69.00	
TEST 10				
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.04M KCN
0.50	17.82	3.56	43.50	16mM AQ
1.00	22.87	4.46	54.50	100g ore #176
6.00	34.51	6.00	73.40	200 ml
24.00	32.57	6.03	73.70	
TEST 11				
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.04M KCN
0.25	0.26	0.05	5.70	no AQ
0.50	0.44	0.90	10.30	100g ore #1006
1.00	0.64	0.12	13.80	200 ml
4.00	0.99	0.18	20.70	
24.00	1.13	0.20	23.00	
TEST 12				
time (h)	mg/l	total amount (mg)	% Au dissolved	Exp. cond.
0.00	0.00	0.00	0.00	0.04M KCN
0.25	0.19	0.04	4.60	16mM AQ
0.50	0.22	0.05	5.70	100g ore #1006
1.00	0.32	0.06	6.90	200 ml
4.00	0.90	0.16	18.40	
24.00	1.25	0.22	25.30	

2-Carbon adsorption tests

After leaching the ore with cyanide, the following stage of the process is usually the adsorption of the loaded solution on activated carbon, as seen earlier in Figure 3.1. Since the AQ present in the solution may also adsorb, some tests were carried out to investigate basically three points:

1-if AQ is adsorbed;

2-if the presence of AQ interferes with the adsorption and/or desorption of gold;

3-in case AQ is adsorbed, if it is possible to perform its desorption from the carbon.

Experimental

All tests were carried out in a tall 400ml beaker, placed on a stirring plate and vigorously agitated with the aid of a magnetic follower. "Eurocarb" activated carbon (Eurocarb Products Ltd., Bristol, England), grade # 8 x 16, was used in all tests. Before running the experiment, the carbon was washed with a dilute solution of HCl: water (1:3) for at least 30 minutes and then thoroughly dried. For all the experiments, the carbon content was kept in a concentration of 20 g/l. The solution containing gold was synthetically prepared by diluting a standard gold chloride (BDH) solution (originally with a concentration of 1000 ppm); cyanide and AQ were added as required to each experiment. Samples of 5 ml each were collected at determined intervals. The gold content in each sample was analysed by atomic absorption. The AQ concentration was measured with the aid of a UV-visible spectrophotometer, following the method described previously (Chapter II).

Results

The first two tests were carried out to investigate whether the AQ also adsorbs and whether its presence prevents (or interferes in any form) the gold from adsorbing on the activated carbon. Both tests ran for 1 hour. The experimental conditions are reported in TABLE 7 below.

Test No.	Au conc.(ppm)	AQ (mM)	KCN (M)	Temp. (°C)
1	20	3.0	0.005	22
2	20	no	0.005	22

Table 6 - Experimental conditions of tests investigating the effect of AQ on gold adsorption from a cyanide solution.

FIGURE 7 displays the adsorption of gold and AQ on the carbon from test No 1.

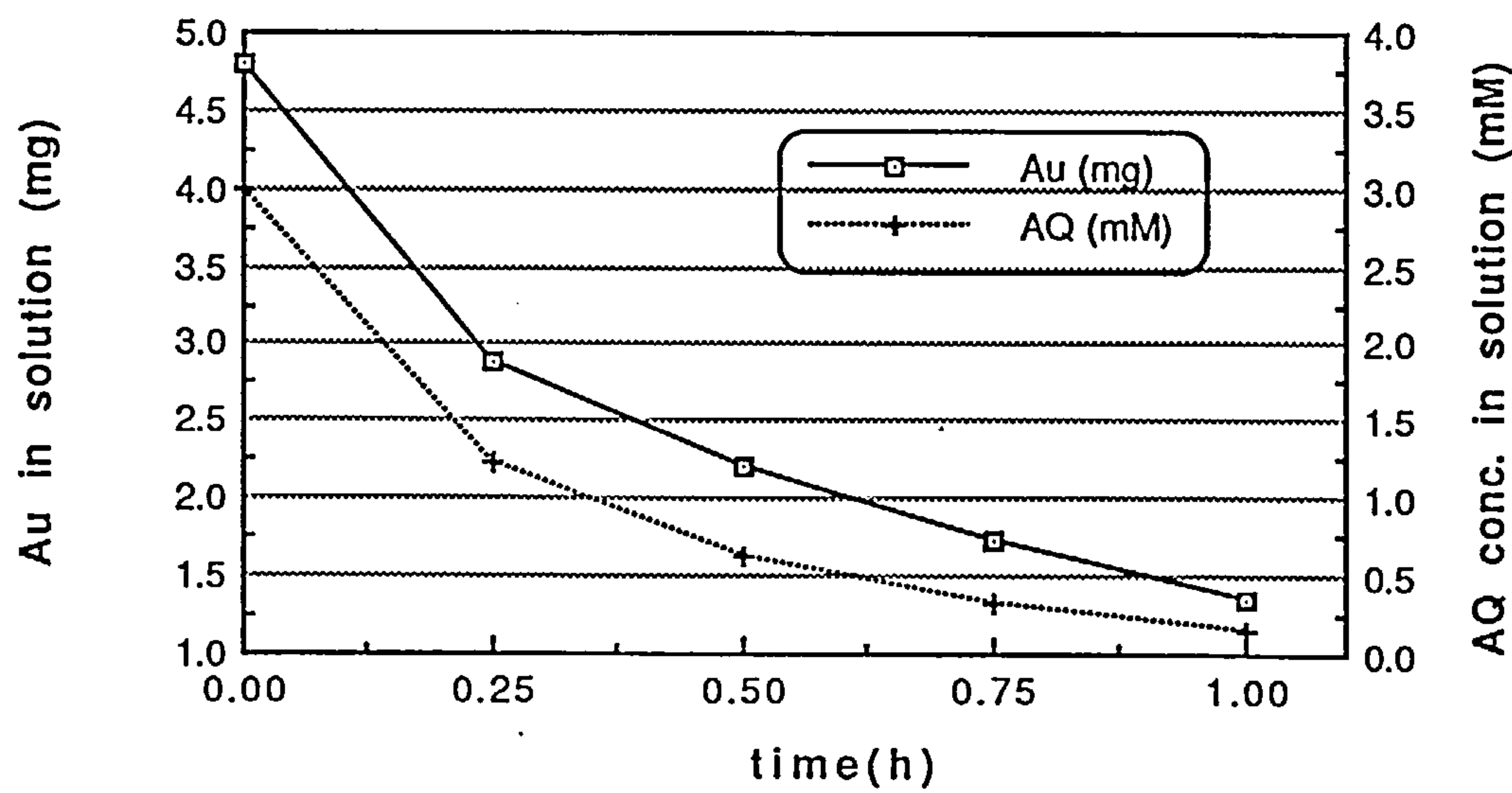


Figure 7 - Gold and AQ adsorption on carbon from test No.1.

It may be seen that, in these experimental conditions, the AQ is indeed adsorbed on the carbon. After one hour of test almost all the AQ initially present had been taken out of the solution, and this uptake follows a similar profile of that of the gold itself. The results concerning the amount of gold adsorbed from both tests may be seen in FIGURE 8.

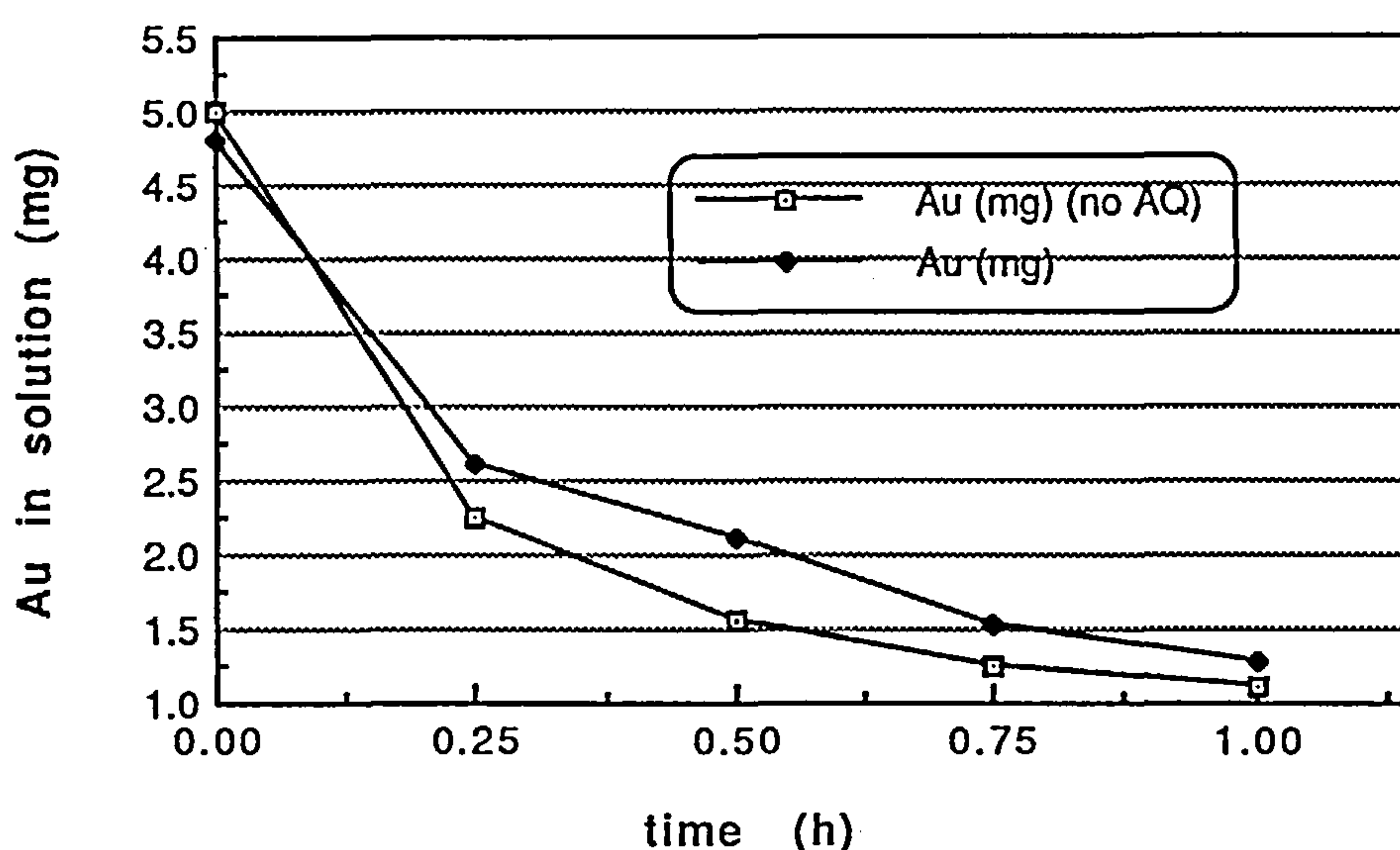


Figure 8 - Gold adsorption on carbon, from tests with and with no AQ in solution.

It may be seen that, although the amount of gold left in solution was slightly higher for the test with the AQ, the final difference between the two tests is not appreciable (1.10 mg with no AQ; 1.28 mg with AQ). This indicates that the presence of the AQ in the leaching solution **does not** prevent the gold from adsorbing on the activated carbon.

The bare solution was vacuum filtered, the carbon loaded from both tests allowed to dry gently overnight and then submitted to the

desorption step (tests No. 3 and 4). This was performed in the following experimental conditions: 75°C, 0.01M KCN and with an addition of 20% v/v of ethanol. The results showing the gold desorbed from the loaded carbon are seen in FIGURE 9, where the adsorption results are also seen.

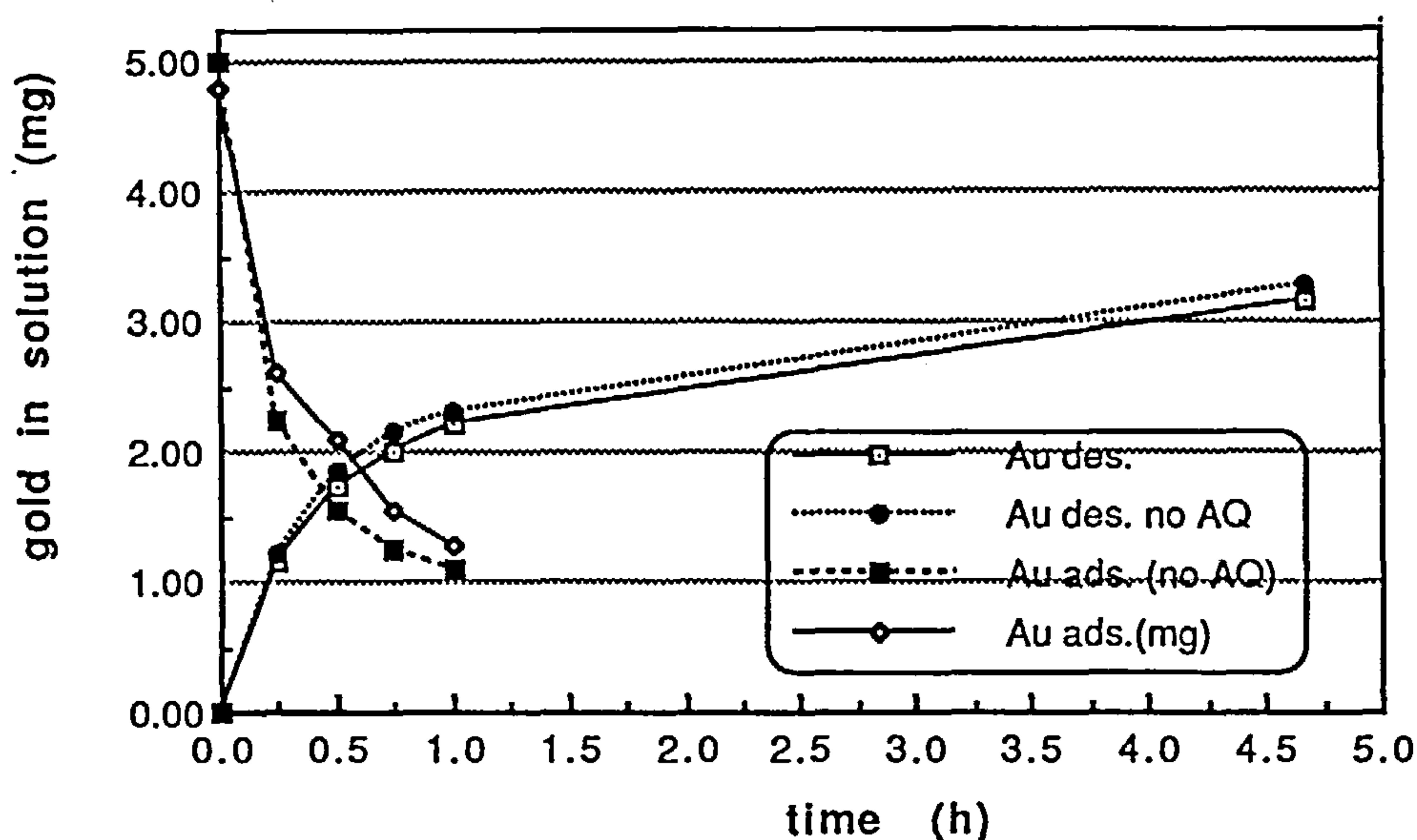


Figure 9 - Desorption of gold from carbon loaded in solutions with and with no AQ (tests No. 3 and 4, respectively) (T=75°C; 0.01M KCN; ethanol 20% v/v) (adsorption results also seen).

It may be seen that the presence of the AQ did not change the behaviour of the desorption step either. The results indicate that the desorption process takes place equally, regardless if the carbon was loaded in solutions containing or not the AQ. It is also seen that, for both cases, the desorption step has lower kinetic rates compared to that of the adsorption.

For the carbon loaded in the solution containing the AQ (test No.3), the amount of AQ desorbed was also measured. The results are

depicted in FIGURE 10, where the curve for AQ adsorption is also plotted.

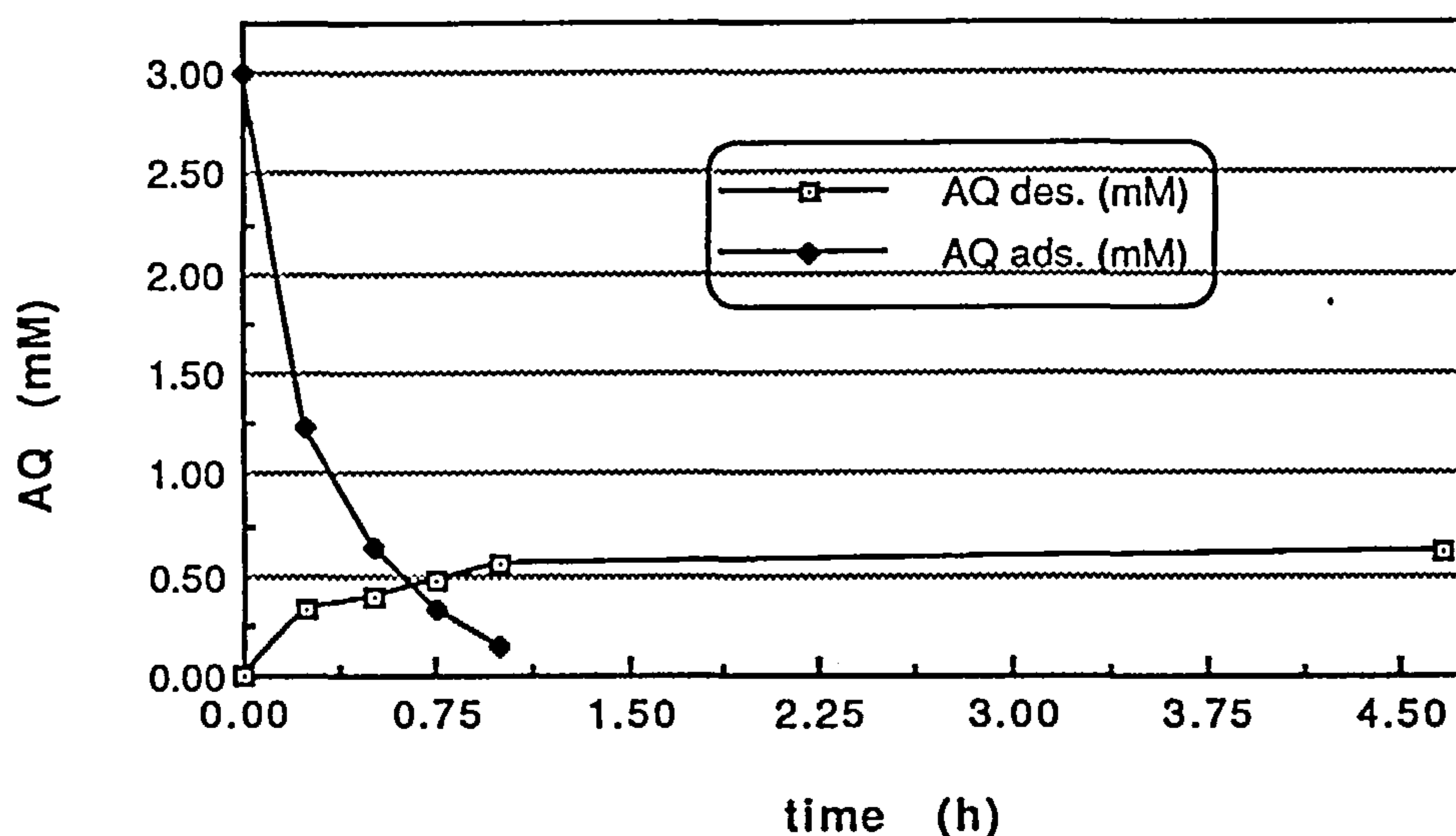


Figure 10 - Adsorption and desorption tests for AQ (des.: 75°C; 0.01M KCN; 20% v/v ethanol)

The results show that, unlike the gold, only about 20% of the original AQ could be recuperated after more than 4.5h of test, in this experimental condition. While the graph displays a slight upward tendency for the desorption curve, it seems that an adsorption/desorption equilibrium was attained and that a further considerable increase in the AQ desorbed is not likely to occur.

To investigate further the desorption step of AQ, two additional tests were carried out. The first, in the same conditions as test No.1 above (to load the AQ onto the carbon); the second as shown in Figure 10, but increasing the temperature to 85°C. The results are shown in FIGURE 11. The results for AQ desorption at 75°C are also shown.

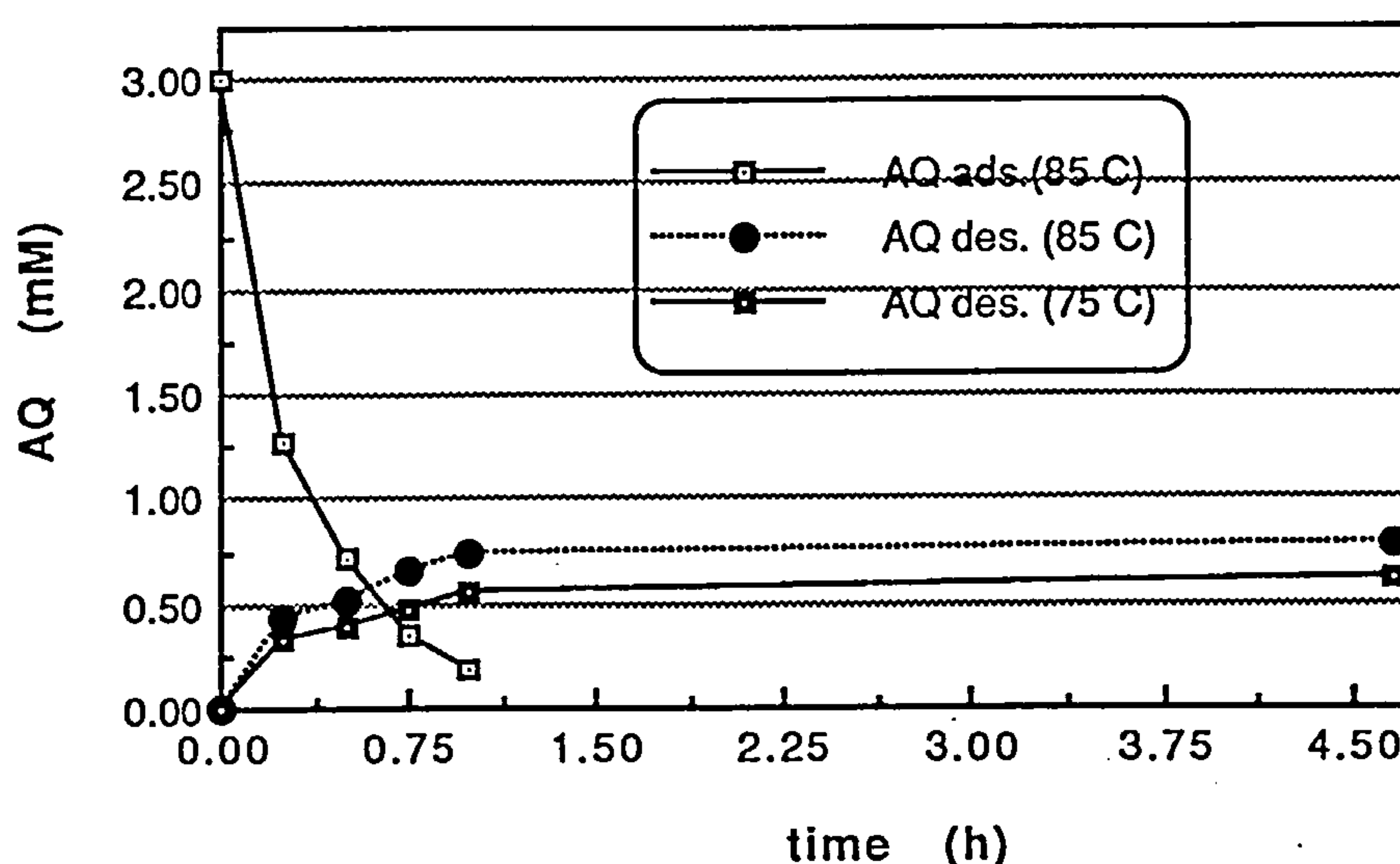


Figure 11- Adsorption and desorption results for AQ at 85°C, compared with desorption at 75°C (0.01M KCN; 20% v/v ethanol).

Although the difference between the tests at 75°C and 85°C is not pronounced, it may be seen that about 40% (20% more than the test at 75°C) of the original AQ could be recuperated. This is an interesting result and indicates that, with increasing temperatures, AQ may be more easily desorbed from the activated carbon.

Conclusions

The basic conclusions that may be taken from these carbon adsorption tests are:

- 1-if AQ is present in the original leaching solution, it will be adsorbed on the activated carbon, together with the dissolved gold;
- 2-the presence of the AQ does not prevent the gold from also adsorbing. The kinetic rate of adsorption involved in both cases (with and with no AQ) is approximately the same.

3-in a 0.01M KCN solution, with 20% v/v ethanol and at 75°C, the desorption of AQ from the activated carbon does not proceed largely. An increase in temperature to 85°C has a beneficial effect, leading to a desorption around 20% higher than in the former instance. Even at this higher temperature, however, the amount desorbed is still below 50% of the original AQ concentration.

Concerning this latter aspect, while the results for the AQ desorption are not ideal, it is suggested that a change in the experimental conditions might be favorable for a higher desorption of the AQ. This step may be carried out, for instance, in acidic media and at high temperature, since, as seen, the desorption is helped if the temperature is increased. Further investigation of this point is certainly needed, in order to take fully advantage of the improvements caused by the AQ when added to the gold cyanidation process.

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