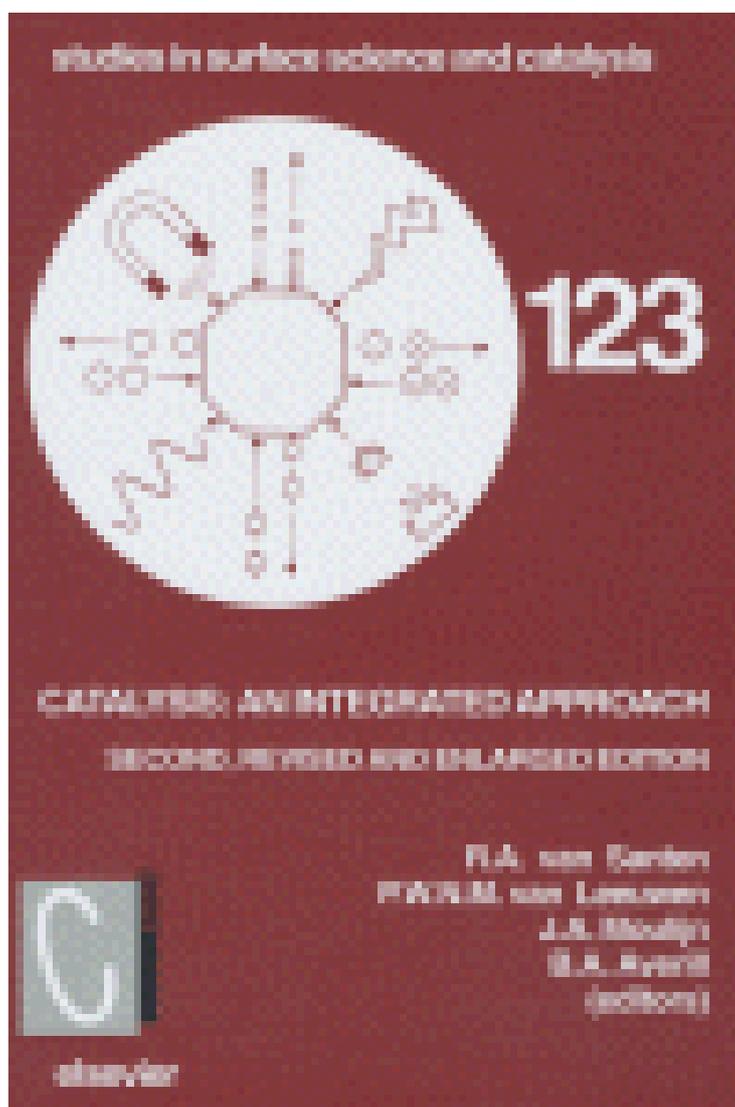


# Catalysis: An Integrated Approach, 2<sup>nd</sup> Edition

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# Preface

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This book has undergone a thorough revision. The first reason was that, in our opinion, biocatalysis could no longer be left out of the integrated approach that is our aim with this book. Several chapters have been extended by incorporation of biocatalytic details. One new chapter has been written especially for this book (Chapter 7, Biocatalysis), whereas extensive biocatalytic sections have been added to other chapters (e.g. Chapter 1.3, Biocatalysis, and Chapter 4.5 & 4.6, Bonding and Elementary Steps in Catalysis).

The other major reason for a revision was the development of catalysis science in general, which necessitated rewriting sections or complete chapters. There is virtually no chapter left untouched by this revision operation. Special chapters on catalyst characterization (Chapter 12) and on adsorption methods (Chapter 13) highlight these new insights. Adding biochemistry to this bunch of flowers has added a new scent, or, to change the metaphor, taught us to communicate in a new language, which we all enjoyed learning. And also, pasting together all these bits and ends proved to be more time consuming than was originally envisaged.

The NIOK Integrated book is one of the most concrete signs of a research school which, since it first came into being, has grown into one of Europe's leading institutes. We repeat our wish that it may continue to be of service to teachers, students and other scholars in catalysis.

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# Preface to the first edition

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Catalysis is a fascinating science for those who are actively involved in it, but perhaps even more so for those who know only a little about it. Chemical reactions, for which one would expect half-life times as long as centuries, can be accomplished in minutes to hours with the magic power of a mysterious black box containing a catalyst. Most of our liquid fuels and some 80% of our chemical products are manufactured with the aid of catalytic conversions. In the near future most of our automotive exhaust gases will be cleaned by a catalyst. The ever-increasing yield of fuel from a barrel of crude oil, the continuing increase of the quality of our polymeric materials, the steadily decreasing production cost of bulk and fine chemicals, etc., can be ascribed, to a great extent, to improvements in catalytic systems. Nevertheless, to the layman catalysis does not play a glamorous role, or at least it didn't until the catalytic converter in automobiles entered his life. Even to the modern chemist who is not familiar with it, catalysis has the aura of an empirical discipline, containing some of the ingredients of a black art. Indeed, entirely new catalysts and processes have been discovered mostly by accident, but the majority of the enormous improvements in catalyst performance which we have seen have been brought about by progress in the underlying sciences.

To a large extent catalysis is concerned with the transformations of organic molecules. Nevertheless, the subject is not the realm of organic chemists but rather that of catalysis specialists who are interested in the (often simple) conversions of basic organic molecules while using highly complex catalyst systems. Apart from a large body of acid-base catalysis and catalysis by 'organic' catalysts, heterogeneous and homogeneous (metal) catalysts have been developed in isolation from organic chemistry. There are several factors which have a bearing on this: (i) the synthesis of a catalytic material requires a knowledge of inorganic and organometallic chemistry, surface science, and spectroscopic techniques; (ii) the industrial importance of catalysis ensured that a great deal of the empirical development of the catalysts was not readily available to the scientific community, which concentrated its efforts on more fundamental aspects of the catalyst; (iii) industrial catalysis deals with simple organic molecules, the synthesis of which, quite justifiably, did not attract the interest of modern organic chemists; and (iv) the differing requirements imposed by the industrial manufacture and small-scale laboratory synthesis of chemicals made the gap even

larger. In this book we will concentrate on industrially relevant reactions which are catalyzed by heterogeneous and homogeneous catalysts. This is a somewhat arbitrary choice, but some choice is necessary. Unfortunately, this leaves large areas of industrial biocatalysis and catalysis science uncovered. In keeping with this industrial focus, the topic of catalytic reaction engineering has been included. In industrial applications reaction engineering forms an integral part of catalysis; the constraints of the catalyst material are determined by chemical and reactor engineering aspects, and the related problems have to be solved in close harmony.

Clearly, catalysis is a multidisciplinary activity and this is reflected in the present book. We have chosen a novel combination of basic disciplines which we hope will be of value to our readers. Homogeneous catalysis by metal complexes is treated jointly with heterogeneous catalysis using metallic and non-metallic solids. In both areas the high degree of sophistication of spectroscopic techniques and theoretical modelling has led to an enormous increase in our understanding at the molecular level. This holds for the kinetics of the reactions and the reactivities of the catalysts, as well as for the syntheses of the catalytic materials. In homogeneous catalysis, the time span between the discovery of a new catalytic process and the delineation of the reaction mechanism on a molecular level has usually been relatively short. Hence, while homogeneous catalysis with organometallics is a young branch of catalysis science, its rapid development can be ascribed to a successful molecular approach in the early stages of its development. Heterogeneous catalysis has to a great extent been developed within the context of catalytic reaction engineering. The more recent advances in surface science have contributed to an understanding of the catalytic materials and processes on a molecular level. It therefore seems timely to deal with the organometallic chemistry of heterogeneous and homogeneous catalysis in a concerted manner. The analogies between the bonding of discrete complexes on surfaces and in solution has been noted many times. Many studies have been published on the analogies and differences between bonding in cluster compounds and metal surfaces. There are, however, also fundamental differences between elementary events on metal surfaces and elementary steps on isolated metal complexes. The study of the basic principles is refreshing and inspiring to both worlds.

### *Outline*

The *introductory section* (Chapter 1) presents a brief survey of the history of industrial heterogeneous and homogeneous catalysis. The survey shows that the availability of the feedstocks has had a decisive influence on the catalysts that have been developed. In some instances the chemical 'leads' for new catalysts have lain dormant in the literature for a number of years before they were developed into industrial processes. Subsequently (Chapter 2) a very limited selection of

current industrial catalytic processes is described. These include the industrial context of the features to be discussed later in the sections on fundamental and applied catalysis. A broad spectrum of important catalytic applications is presented. Each summary contains the basic chemistry, some engineering aspects, feedstock sources and product utilisation. In Chapter 3 the kinetic principles are treated, since in a way they form the basis for catalysis.

The section on *fundamental catalysis* starts off (Chapter 4) with a description of the bonding in complexes and to surfaces. The elementary steps on complexes and surfaces are described as they are relevant to catalysis. The chapter on heterogeneous catalysis (Chapter 5) deals with the mechanistic aspects of three groups of important reactions: syn-gas conversions, hydrogenation, and oxidation. These three reactions give us an opportunity to present the main principles of metal and metal oxide catalysis. Likewise, in the chapter on homogeneous catalysis (Chapter 6) we concentrate on only three reactions, representing examples from three areas: hydroformylation, polymerization, and asymmetric catalysis. Identification by *in-situ* techniques has been included, since it was felt to be more appropriate to outline this here than to devote separate chapters to the preparation and characterization of organometallic catalysts (*vide infra* for heterogeneous catalysts).

Many constraints on the industrial use of a catalyst have a macroscopic origin. In *applied catalysis* (Chapter 7) we show how catalytic reaction engineering deals with such macroscopic considerations. The transport and kinetic phenomena in both model reactors and industrial reactors are outlined.

The section on *catalyst preparation* (Chapters 8 and 9) is concerned with the preparation of catalyst supports, zeolites, and supported catalysts, with an emphasis on general principles and mechanistic aspects. For the supported catalysts the relation between the preparative method and the surface chemistry of the support is highlighted. The molecular approach is maintained throughout.

The first chapter (Chapter 10) in the section on *catalyst characterization* summarizes the most common spectroscopic techniques used for the characterization of heterogeneous catalysts, such as XPS, Auger, EXAFS, etc. Temperature programmed techniques, which have found widespread application in heterogeneous catalysis both in catalyst characterization and the simulation of pretreatment procedures, are discussed in Chapter 11. A discussion of texture measurements, theory and application, concludes the section on the characterization of solid catalysts (Chapter 12).

The final chapter (Chapter 13) gives an outline of *current trends* in catalysis. Two points of view are adopted: the first one focuses on developments in process engineering. Most often these have their origin in demands by society for better processes. The second point of view draws attention to the autonomous developments in catalysis, which is becoming one of the frontier sciences of physics and chemistry.

*Final remarks*

The main theme of the book is the molecular approach to industrial catalysis. The integrated way in which the subject matter has been treated involves many disciplines; as a consequence, the writing of the book has been entrusted to a number of authors. The editors envisaged a careful planning and harmonization of the contents of the chapters. The latter is important, because a rigorous selection of subject matter is necessary in order to keep the size of the book within the limits of a practicable textbook.

The editors have enjoyed working together on this project. We have learned a great deal about our mutual fields while discussing which essential elements should be included and what reactions should serve as instructive examples. The order of the editors' names does not in any way reflect the outcome of these discussions, nor the magnitude of our efforts! We are very grateful to our authors, who have contributed a number of very good chapters. Some of them were well in time with their responses, while others enjoyed the privilege of having written the most up to date contributions!

When we started putting together the national course on catalysis, on which this book is based, we were a loosely organised foundation for the promotion of catalysis. In the meantime we have organised ourselves into the Netherlands Institute for Catalysis Research, NIOK. We express our wish that this book may contribute in shaping the new Dutch School of Catalysis by providing a broad, general training for our Ph.D. students in the essential elements of catalysis.

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## Chapter 1

# History of catalysis

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### 1.1 INTRODUCTION

The name 'catalysis' was coined by Berzelius in 1836. He concluded that besides 'affinity' a new force is operative, the 'Catalytic Force'. Reaction occurred by catalytic contact. The word 'catalysis' stems from the Greek: it has the sense of 'down' and 'loosen'. At that time affinity was known as a chemical driving force, but no understanding existed, on a molecular level, of reaction rates. Catalysis—as a tool for carrying out reactions—had already been exploited much earlier. It has been applied for thousands of years in processes such as fermentation. An interesting example is the production of sulphuric acid. In the Middle Ages this was synthesised in small quantities in glass equipment by burning sulphur with nitric acid in humid air. In 1746 lead was used as a construction material for the reaction chambers and larger production volumes became possible. In 1793 Clement and Desormes showed that the quantity of nitre could be much reduced by admitting additional air to the reactor. They were aware of the fact that the nitrous vapours are only intermediates and that the oxidising agent is air. Their conclusion was correct, and nitre is what we would nowadays call a catalyst.

At the end of the eighteenth and the beginning of the nineteenth century the influence of metals and oxides on the decomposition of several substances was studied by many scientists. It was noticed that contact with different substances gives very different products. An example is the decomposition of alcohol: in the presence of copper or iron, carbon and an inflammable gas are produced. In the presence of pumice stone decomposition into ethene and water was observed. In other words, selectivity was demonstrated. Many other important milestones can be mentioned: we limit ourselves to a few. Thenard investigated the dissociation of ammonia in contact with metals. In 1813 he found that the

dissociation occurs over various metals, provided they are hot. Later he systematically studied the dissociation of hydrogen peroxide. He concluded that some of the solids studied changed and others did not. Humphry Davy performed systematic investigations with the objective of developing a miner's safety lamp. He discovered that the oxidation of coal gas is catalysed by platinum. He found that palladium was also active, whereas copper, silver and gold did not show any catalytic activity. Davy found that the platinum wires he used had to be hot and, as a consequence, he concluded that the action of platinum was to heat the reacting mixture. The fact that only platinum and palladium were active was explained on the basis of their low heat capacity and low thermal conductivity. Later it was found that finely dispersed platinum is active even at room temperature and Davy's explanation was thus not correct. Platinum catalyses the combustion of the components of coal gas, in particular CO and CH<sub>4</sub>, which in the absence of a catalyst can lead to an explosion. Copper and silver are also active in the oxidation of CO, but they are not sufficiently active in CH<sub>4</sub> oxidation. Of course, depending on the construction, a wire can function as a flame arrester in which radical terminations take place and, as a consequence, explosions are avoided.

In 1834 Faraday proposed that the reactants have to adsorb simultaneously at the surface, but he did not really explain the catalytic action. Of course, neither did Berzelius give an explanation, but he nicely generalised many results in a simple description. Later, Ostwald gave the definition that a catalyst does not influence the thermodynamic equilibrium of reactants and products but affects the rates of the chemical reactions. The conclusions of Berzelius and Faraday proved to be correct.

Industrial catalysis, based on man-made catalysts, developed its own history which is briefly summarised in Section 1.2. The roots of biocatalysis and biocatalytic processes are completely different, notwithstanding the early recognition that fermentation processes are in essence of a catalytic nature. The relationship between biocatalysis and organic chemistry is close. It is really quite recently that biocatalysis and man-made catalysis have become part of the same context. This is mainly the result of increasing interest in catalytic applications to fine chemicals.

An historical review of biocatalysis is given in Section 1.3.

## 1.2 INDUSTRIAL CATALYSIS

Industrial catalysis is an old practice. Catalysts have always been used in the production of wine and beer. Among the first industrial catalytic processes are a few inorganic oxidation processes, viz. the Deacon process (oxidation of HCl into Cl<sub>2</sub>) and the production of sulphuric acid. These processes were developed

before a scientific basis of chemical reactivity was established. Only after the formulation of the theory of chemical equilibria by van 't Hoff did a framework for catalyst development become available. This had a major impact on the development of a process for the synthesis of ammonia at the beginning of the twentieth century, allowing a systematic, scientifically based search for a good catalyst to be performed. It also initiated the development of chemical process engineering as we know it today.

### *1.2.1 Sulphuric Acid*

The production of sulphuric acid was commercialised in the mid-18th century. In the so-called lead chamber process the oxidation of  $\text{SO}_2$  into  $\text{SO}_3$  was catalysed by  $\text{NO}$ . The acid produced is not very concentrated. The raw material used was elemental sulphur from Sicily. Later, pyrite was used because of its lower price. One of the consequences was a much higher impurity level in the feed to the reactor. As early as 1831 a process was patented in which  $\text{SO}_2$  was oxidised in the presence of finely divided platinum. The commercial application, however, was strongly delayed due to technical difficulties, the major one being catalyst poisoning.

In the First World War the explosives industry demanded highly concentrated sulphuric acid, which required a different technology. A logical way to go was to use the heterogeneous metal catalysts which had just been developed at that time. Initially, platinum supported on silica or asbestos was used as a catalyst. Subsequently, platinum was substituted by  $\text{V}_2\text{O}_5$ -based catalysts because of the high price of the precious metal and the fact that it is easily poisoned by the pollutants present in the raw material, such as arsenic. The raw material has also changed. Nowadays, it is once again mainly elemental sulphur, which, to a considerable degree, is a product of the hydrotreatment of oil.

### *1.2.2 Ammonia Synthesis*

Initially, the source of ammonia was coke oven gas and Chile saltpetre. In Germany, in particular, it was recognised as early as the turn of the 20th century that insufficient ammonia was available for agricultural needs. Moreover, the use of ammonia for the manufacture of explosives increased dramatically due to the beginning of the First World War. Extensive efforts were made by teams in many countries, but particularly in Germany, to synthesise  $\text{NH}_3$  directly from  $\text{N}_2$ . Non-catalysed routes were discovered and were commercialised, but they were very inefficient. The breakthrough was the development of a catalytic process.

In 1905 Haber reported a successful experiment in which he succeeded in producing  $\text{NH}_3$  catalytically. However, under the conditions he used (1293 K) he

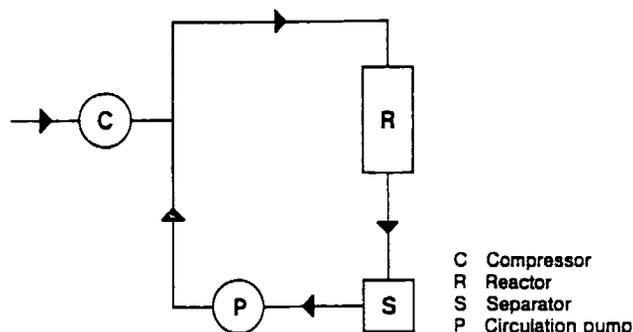


Fig. 1.1. Process scheme for the production of ammonia according to Haber.

found only minor amounts of  $\text{NH}_3$ . He extrapolated his value to lower temperatures (at 1 bar) and concluded that a temperature of 520 K was the maximum temperature for a commercial process. This was the first application of chemical thermodynamics to catalysis, and precise thermodynamic data were not then known. At that time Haber regarded the development of a commercial process for ammonia synthesis as hopeless and he stopped his work. Meanwhile, Nernst had also investigated the ammonia synthesis reaction and concluded that the thermodynamic data Haber used were not correct. He arrived at different values and this led Haber to continue his work at higher pressures. Haber tried many catalysts and found that a particular sample of osmium was the most active one. This osmium was a very fine amorphous powder. He approached BASF and they decided to start a large program in which Bosch also became involved.

The process development studies were carried out in a systematic way. A good catalyst had to be formulated; the reactor was to be scaled up; and an integrated process had to be designed, including the production of sufficiently pure synthesis gas. Haber envisaged the process scheme given in Fig. 1.1.

Systematic studies were carried out in order to discover a suitable catalyst. Iron catalysts were especially tried, because it was known that iron catalyses the decomposition of ammonia, which is the reverse of the reaction being studied. It was discovered that iron alone was only slightly active but its activity could be improved (promoted) or worsened (poisoned) by additives. In their studies over 10 000 catalysts were prepared and over 4000 were tested.

When the laboratory studies gave promising results, scale-up studies commenced. The major problem was the construction of a reactor which was able to withstand the reaction conditions. Because of the high pressure, high-strength carbon steel was used; however, this steel is corroded by  $\text{H}_2$  under the severe reaction conditions used, and consequently loses its strength. Bosch designed a reactor which contained an outer wall of high carbon steel, lined internally with soft, low carbon steel (Fig. 1.2). The catalyst was also heated internally, so that the external wall was continuously kept at a low temperature.

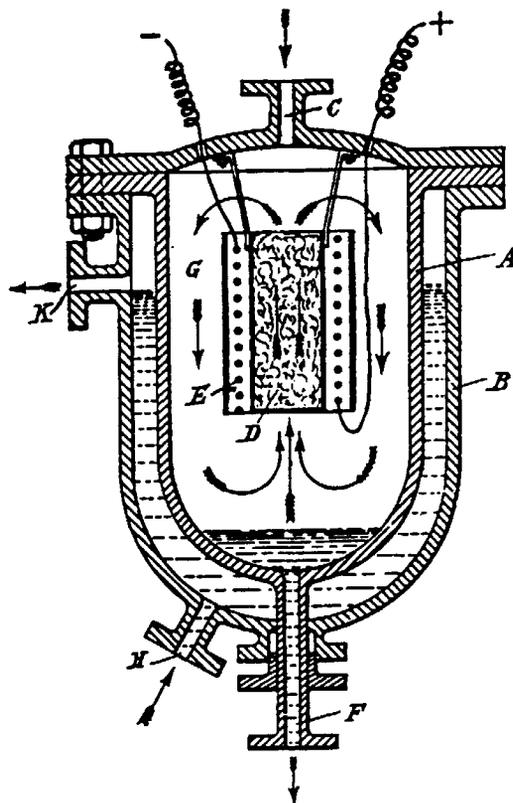
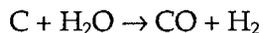
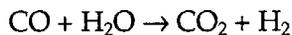


Fig. 1.2. Reactor for the synthesis of ammonia (BASF 1910).

Very pure, electrically generated  $\text{H}_2$  was available for the pilot studies, but for a commercial plant, this was of course not practical. The solution was found in coal gasification:



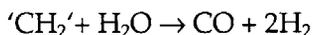
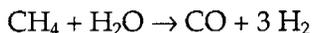
followed by the water-gas shift reaction:



Haber received the Nobel prize in 1919 for his work on ammonia synthesis. Bosch was awarded the 1931 Nobel prize for his achievements in high-pressure technology.

Up to the 1950s, the technology for ammonia synthesis did not change very much. Fundamental changes became possible in the '60s. These changes were of both a chemical and a technological nature.

Technically, the most attractive hydrocarbons for the production of  $H_2$  are methane and, to a lesser extent, oil (' $CH_2$ ')



These reactions are carried out catalytically using nickel catalysts. However, a side reaction is carbon deposition. Since the rate of this side reaction increases with pressure, the production of synthesis gas at high pressure was not feasible. The addition of promoters, which catalyse the carbon steam reaction, suppresses carbon deposition, thus allowing higher pressures. This made a revolution possible in the ammonia synthesis industry. At the same time progress in the development of centrifugal compressors enabled large, single-train plants to be constructed. These developments have led to much more efficient ammonia plants. Figure 1.3 illustrates the process development since the beginning of commercial ammonia production by nitrogen fixation.

Still further process improvements may be possible, but potential improvements should be analysed by considering the whole process integrally.

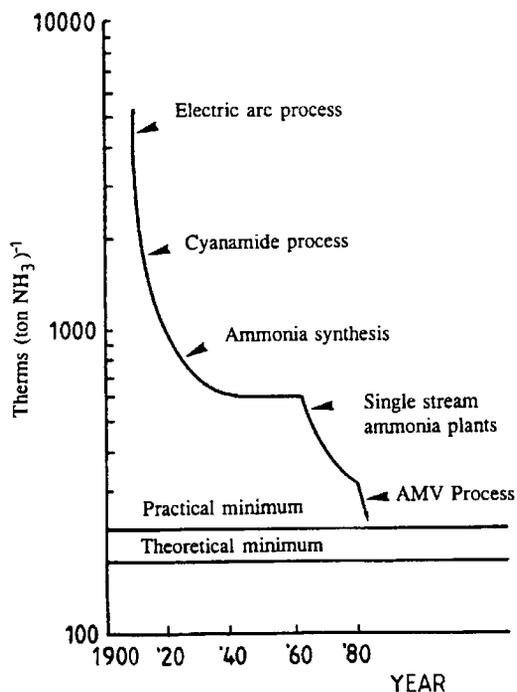


Fig. 1.3. Efficiency of nitrogen fixation [1].