

**Chemical
Reaction
Engineering**

Edited by

Dr. K. RIETEMA

FIRST EUROPEAN SYMPOSIUM ON CHEMICAL ENGINEERING

Chemical Reaction Engineering

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CHEMICAL REACTION ENGINEERING

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This 12th Meeting was organized by

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Sectie voor chemische technologie en bedrijfschemie

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SYLLABUS

CHEMICAL reaction engineering is a part of chemical engineering in general. It is a new branch of science which is still in the development stage.

It aims at controlling the chemical conversions on a technical scale and will ultimately lead to appropriate and successful reactor design.

An important part is played by various factors, such as flow phenomena, mass and heat transfer, and reaction kinetics. It will be clear that in the first place it is necessary to know these factors separately.

Yet this knowledge in itself is insufficient. The development of chemical conversions on a technical scale can only be understood from the relation and interaction between the above mentioned factors.

This relation and interaction will be the main theme of the symposium on "chemical reaction engineering".

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Opening Address

by Dr. Ir. J. C. VLUGTER

MESDAMES, MESSIEURS,

Ce m'est un grand honneur de pouvoir ouvrir le Premier Symposium Européen de la Fédération Européenne du Génie Chimique. Les associations organisatrices, l'Institut Royal des Ingénieurs et la Société Royale de Chimie aux Pays-Bas, sont très heureuses de constater qu'un si grand nombre de participants est venu à Amsterdam pour assister à la conférence.

Je vous souhaite la bienvenue à vous tous et j'espère que vous vous sentirez comme chez vous, non seulement pendant les discussions dans cette salle, mais aussi pendant tout votre séjour dans la charmante ville d'Amsterdam.

Sous ce rapport je tiens particulièrement à remercier Monsieur MORREN, Directeur du Bureau d'Enseignement de la ville d'Amsterdam et représentant de la Municipalité, de sa présence à cette ouverture, et à exprimer notre reconnaissance des facilités que les membres du Symposium reçoivent dans cette ville et de la réception de ce soir dans le Musée Municipal. Nous apprécions beaucoup, Monsieur MORREN, que vous ayez bien voulu nous accorder quelques heures de votre temps précieux.

Je me félicite de pouvoir saluer ici les présidents et les secrétaires des deux Sociétés Organisatrices et je me fais l'interprète du Comité d'Organisation du Symposium en les remerciant de la confiance qu'ils nous ont témoignée.

M'adressant maintenant à tous nos hôtes pour qui le français est la langue maternelle ou la seconde langue, je voudrais attirer l'attention sur le fait que c'était Monsieur JEAN GÉRARD qui, il y a environ cinq ans, a pris l'initiative de la fondation de la Fédération Européenne du Génie Chimique.

M. JEAN GÉRARD, nous le connaissions déjà bien avant cette date par la force stimulatrice qu'il exerçait chaque année dans l'organisation des congrès de la Société de Chimie Industrielle. Et avant la deuxième guerre mondiale il était le secrétaire énergique de l'Union Internationale de Chimie Pure et Appliquée. C'était donc avec tristesse que nous avons appris la mort soudaine de ce grand organisateur pendant les manifestations à grande envergure de la Société de Chimie Industrielle à Paris en novembre de l'an dernier. Les membres de la Fédération de Génie Chimique et de la Corrosion garderont un fidèle et profond souvenir de la personnalité de M. JEAN GÉRARD.

Nous sommes reconnaissants à Monsieur BIENAIMÉ, ex-président de la Société de Chimie Industrielle, d'avoir bien voulu accepter l'invitation à prendre la place de M. JEAN GÉRARD dans le Comité de Direction de notre Fédération.

MEINE DAMEN UND HERREN,

Weil es drei Konferenzsprachen gibt, will ich jetzt in deutscher Sprache fortfahren um unsere deutschen Teilnehmer herzlich zu begrüßen.

Es ist mir eine besondere Freude, Herrn Dr. BRETSCHNEIDER hier willkommen heißen zu können, der sich zusammen mit Herrn JEAN GÉRARD, der uns vor kurzem entrissen wurde, so erfolgreich angestrengt hat und noch immer bemüht ist, die Entwicklung der Europäischen Föderation zu fördern.

Opening address

Das Thema dieses Symposiums, die Chemische Reaktionstechnik, steht in Deutschland im Brennpunkt des technisch-wissenschaftlichen Interesses, wie es die zwei unlängst errichteten Fachausschüsse — „Chemische Reaktionstechnik“ der DECHEMA unter der Leitung von Prof. Patat und „Technische Reaktionsführung“ der Abteilung Verfahrenstechnik des Vereins Deutscher Ingenieure unter der Leitung von Prof. Wicke — beweisen. Wir haben denn auch vier wichtige Beiträge zu diesem Symposium aus Deutschland empfangen und es freut uns sehr, dass so viele deutsche Experten, darunter die Prominenten auf diesem Gebiet, nach Holland gekommen sind um ihren Teil an diesen Besprechungen zu haben.

And last but not least, Ladies and Gentlemen, I should like to say a few words of welcome to our English-speaking guests.

The organizing Dutch associations, the Royal Institute of Engineers and the Royal Dutch Chemical Society, have enjoyed the collaboration which has for quite some time existed with the corresponding English institutes, viz. The Institution of Chemical Engineers and The Society of Chemical Industry. This collaboration has led to two successful conferences, the first in London on "fluidization" and the second in Amsterdam on "oxidation processes"; and the third symposium, which will be held in London by the end of this month and which will deal with the "scaling-up of chemical plants and processes", again bids fair to be a success, considering the quality of the papers and the considerable interest it has aroused. Continuation of this collaboration is a matter of great appreciation to us. By contributing papers for this Symposium and through the presence of so many of you, you are taking an active part in the co-operation in this field between practically all the Western European countries.

In Paris at the end of last year Mr. ORIEL, as President of the Institution of Chemical Engineers, has spoken in favour of this Institution joining the European Federation, and it is hoped that it will be possible to announce the realization of this co-operation in the very near future.

I should like to say a word of welcome to Dr. FREETH, who, since the foundation of the European Federation, has done his utmost to voice the opinion of the English in the Committee of the Federation.

Finally, I should like to address the Dutch participants, who, because the congress is held in Amsterdam, of course constitute the larger part of the audience. Many of them have already taken part in the "spade-work" as regards both the organization and the scientific side and a number of them will be called upon to help also during the next two days.

Considering the work done so far to organize this Symposium I may say I feel confident as regards its further development.

In particular I should like to welcome the many students, who have come to attend in larger numbers than ever before. This is very valuable, because it gives evidence of the great interest shown by those of our juniors who, within not too long a time, will have to take over from the senior chemical engineers in universities and industry.

With these words I declare the Symposium, as far as the scientific side is concerned, open.

First Session

INTRODUCTORY PAPERS

Chairman: Dr. Ir. J. C. VLUGTER

Rapporteur: Dr. Ir. D. VAN ZONEN

Micro- and macro-kinetics

General Introduction to the Symposium

by Professor Dr. D. W. VAN KREVELEN*

"The development of any phenomenon in time has a fascination of its own and the laws which it follows have an attraction to those interested in the quantitative aspect of things."

SIR CYRIL HINSHELWOOD
in *The Structure of Physical Chemistry*

Résumé—La présent exposé donne un aperçu du développement historique de la cinétique chimique, suivi d'une discussion des facteurs "macrocinétiques" qui influencent le résultat final de réactions chimiques à différentes échelles. Il donne attention aux différents procédés technologiques et les problèmes y relatifs.

Finalemment il résume la façon dont certains facteurs influencent l'évolution et le résultat de conversions chimiques (conversion optimale, stabilité, sélectivité, etc.).

Zusammenfassung—Auf eine Übersicht der historischen Entwicklung der chemischen Kinetik folgt eine Besprechung der „makrokinetischen“ Faktoren, die das Endergebnis von in verschiedenen Masstäben durchgeführten chemischen Reaktionen beeinflussen. Die verschiedenen technologischen Verfahren und die damit verbundenen Probleme werden behandelt. Abschliessend werden die verschiedenartigen Einflüsse bestimmter Faktoren auf den Verlauf und das Ergebnis chemischer Umsetzungen (Umsetzungsgrad, Stabilität, Selektivität, usw.) zusammengefasst.

Summary—Following a survey of the historical development of chemical kinetics, a discussion is given of the "macrokinetic" factors which influence the ultimate result of chemical reactions on various scales. Attention is paid to the various technological performances and the problems involved, and finally a summary is given of the ways in which certain factors influence course and result of chemical conversions (optimum conversion, stability, selectivity, etc.).

INTRODUCTION

REACTION dynamics in its widest sense is based, on the one side, upon the fundamental principles of chemical kinetics, and, on the other, upon the principles underlying chemical engineering.

We will try to outline the development of reaction dynamics and then proceed to give a general background to the papers presented at this symposium.

The development of reaction dynamics may be divided into three stages.

The period before about 1915 may be called the "empirical-phenomenological"; some names dating from the beginning of this period [about 1870] that deserve mention are those of WILHELMY, BERTHELOT and especially VAN T'HOFF, who, in

* Central Laboratory, Staatsmijnen in Limburg, Netherlands.

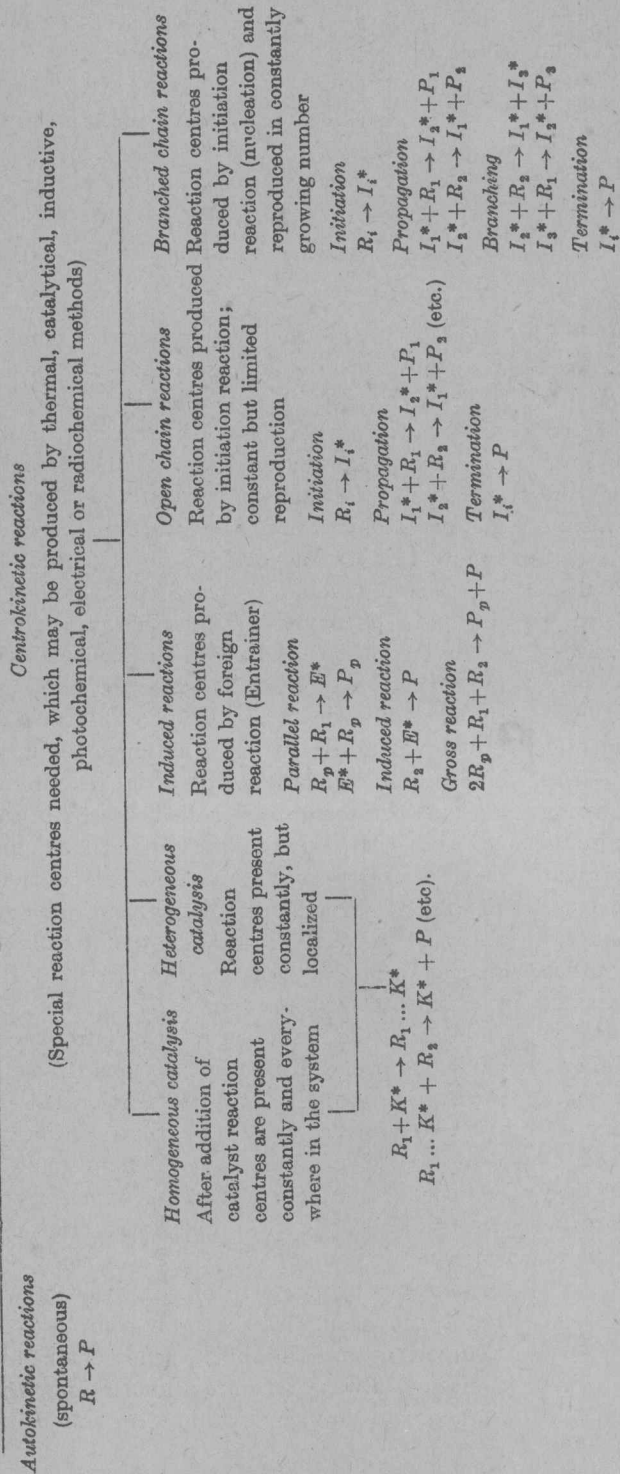
1884, wrote his *Études de dynamique chimique*. Thanks to this preparatory work Arrhenius could introduce the concepts "activation" and "activation energy" [1889]. The following years saw a large extension of experimental material [BODENSTEIN] and the germination of ideas which were far in advance of their time: such concepts as activation entropy [KOHNSTAMM, SCHEFFER and BRANDSMA, 1911], active complex [MARCELIN, 1912] and chain reaction [BODENSTEIN, 1913].

About 1915 a second, very fruitful, period begins, which I should like to call the "molecular-statistical" period, and in which interest is aroused above all in the mechanism of the activation of reacting molecules. On the one side the reaction-rate theory (homogeneous reactions) is correlated with the theory of molecular vibration [LINDEMANN, HINSHELWOOD], and on the other the theory of

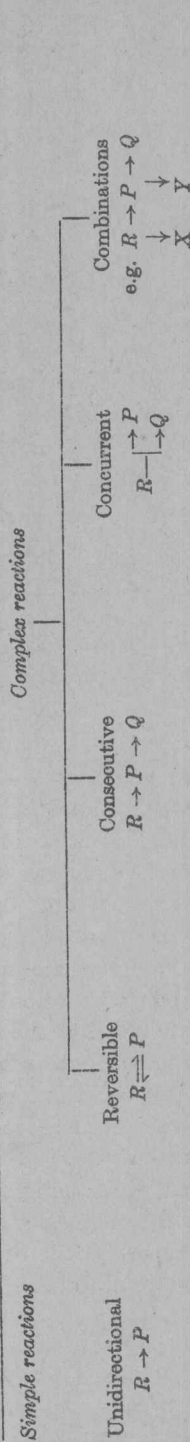
Table 1. Survey of classical chemical kinetics

A. ELEMENTARY KINETIC PROCESSES	
<p>1. Unimolecular process: $R \xrightleftharpoons[\text{deactivation}]{\text{activation}} \dots\dots A$</p> <p style="text-align: center;">(collisions)</p>	<p style="text-align: center;"> $\xrightarrow{\quad} \Sigma P_i$ </p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 0 auto;">Reaction products</div>
<p style="text-align: center;"> $\xrightarrow{\quad} TS$ </p>	<p style="text-align: center;"> $\xrightarrow{\quad} \Sigma P_i$ </p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 0 auto;">Transition state molecule, with energy so distributed that the necessary links can be broken</div>
<p style="text-align: center;"> $\xrightarrow{\quad} \dots\dots A$ </p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 0 auto;">Energized molecule possessing energy E distributed at random</div>	
<p style="text-align: center;"> $\xrightarrow{\quad} R$ </p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 0 auto;">Normal molecule</div>	
<p>2. Bimolecular process: $R_1 + R_2 \xrightarrow{\quad} \dots\dots$</p>	<p style="text-align: center;"> $\xrightarrow{\quad} \Sigma P_i$ </p>
<p>3. Trimolecular process: $R_1 + R_2 + M \xrightarrow{\quad} \dots\dots$</p>	<p style="text-align: center;"> $\xrightarrow{\quad} \Sigma P_i$ </p>

B. FUNDAMENTAL MECHANISMS (Arranged according to growing complexity)



C. GROSS REACTION TYPES (Arranged according to growing complexity)



branched reaction chains proves to shed a surprising new light on explosions and combustion reactions [SEMEŃOV, HINSHELWOOD, POLANYI, HIRSCHFELD]. LANGMUIR's idea of activated adsorption gave a new impulse to the interpretation and understanding of heterogeneous reactions—in particular catalytic reactions—[TAYLOR], while, finally, the quantum-statistical treatment of transition states (EYRING) provided an all-embracing view of rate processes.

Meanwhile, chemical kinetics had not become easier to understand. Since the discovery of chain reactions and the sometimes highly complicated relationships involved, since the discovery also that even the true unimolecular reactions derive their activation energy from collisions between at least two molecules, the significance of the concept "order of a reaction" as a regulating principle of kinetics has waned more and more. Although the elementary steps of any reaction mechanism are simple and, without an exception, of the orders 1, 2 or 3, the precise nature of these steps becomes clear only after the reaction mechanism has been unravelled.

Towards the end of the nineteen-thirties the beginning of a new period—the third—was heralded. This was characterized by a growing interest in technological aspects. DAMKÖHLER [1937] was one of the first to show the great influence of flow factors and boundary layer phenomena on the gross result of chemical reactions. Since this moment ever more attention has been paid to the effects of fluid flow, mixing, mass and heat transfer, and to the influence of the physical fine structure of reacting substances. FRANK KAMENETSKII uses the term "*macroscopic kinetics*" for this type of chemical dynamics, to distinguish it from classical molecular "*microkinetics*". This third period might be called the "*technological*"; it is the one in which we are working, and its problems are identical with those posed in the present symposium.

CHEMICAL KINETICS IN THE NARROWER SENSE (MICROKINETICS)

In trying, first and foremost, to form a general view of the advance of classical chemical kinetics,

we may start from a survey (Table I) in which our "scale of observation" becomes ever more embracing.

We distinguish into:

- A. Elementary kinetic processes (individual reaction steps).
- B. Fundamental mechanisms (series of molecular reaction steps, sum of elementary processes as mentioned under A).
- C. Gross reaction types (gross result of B).

On each of these "levels" an arrangement according to growing complexity can be made.

There are only three *elementary kinetic processes*, viz. unimolecular, bimolecular and trimolecular processes. However, each of these consists in an *activation* of the reactants, a *transition state*, and a *decomposition* into the reaction products. In principle it is now possible to calculate the rate of these elementary processes, thanks to the results of statistical and quantum mechanics.

The reaction mechanism is formed by a combination of a number of elementary processes. By the side of comparatively few "*autokinetic*" reactions (which are entirely spontaneous) there are a large number that require special reaction centres and may therefore be called "*centrokinetic*" reactions.* After their addition to the system these reaction centres may be present constantly and at all places throughout the system (*homogeneous catalysis*), or they may be present locally (*heterogeneous catalysis*), or be produced by parallel reactions (*entrainment* or *induced* reactions); in some cases the centres are formed from the reactants by special initiating reactions (free radicals, *chain reactions*). If during a reaction the number of centres increases steadily, the reaction is autocatalytic, or—in the case of chain reactions—a branched chain reaction (most explosions are of this type). The more complex a reaction mechanism, the more involved also the kinetic relationship expressing the rate of the reaction. One of the characteristics of the most complicated reaction mechanism—that of branched chains—is that it nearly always requires nucleation, ignition. Therefore a branched-chain reaction is also a

* The Greek word *κεντρον* (centre) means stimulus.

nucleation process. As soon as it starts it is self-accelerating.*

Finally, the class of gross reaction types comprises the simple and the complex conversions (reversible, consecutive, concurrent reactions, etc.).

A very detailed exposition of this whole field—with the problems involved—is given in the paper by LETORT [1]. In reaction engineering it is, in general, sufficient if the over-all kinetic relationship, with its temperature-dependence, and the heat-effect of the reaction are known. These data on the chemical kinetics are of particular importance in the calculation of the optimum temperature sequence to be chosen for the reaction; the papers by DENBIGH [9] and by VAN HEERDEN [10] give striking examples in this respect.

“MACROKINETICS” [14, 15]

Whereas the laboratory chemist who is interested in the reaction mechanism, in general attempts—and manages—to make the reaction proceed under such conditions of dispersion and homogenization that only the rate of the reaction proper is measured, the chemical engineer, who has to work on a much larger scale, immediately faces great difficulties if he tries to obtain the same degree of dispersion and homogenization. In addition, if the engineer wants to make the reaction proceed according to a fixed temperature programme, he encounters problems of an altogether different nature than those confronting the laboratory chemist. Problems of heat production and heat removal become highly important.

As reaction kinetics are ultimately based on the elementary kinetic processes, so reaction engineering is based on three elementary processes, viz. transfer of momentum, mass and heat. These processes, too, take place on various “scales”, viz.:

- I. The scale of the reactor dimensions.
- II. The scale of the dimensions of the “dispersion”, whether this comprises solid particles, drops of liquid or gas bubbles in heterogeneous phases, or

streaks and eddies in homogeneous phases.

- III. The scale of the length of molecular paths as these are encountered in very thin boundary layers and narrow pores.

Transport problems on the scale of the reactor dimensions

Let us first consider the transfer processes taking place on the largest of the three scales mentioned above. In this connection the first point that demands our attention is the way in which the reaction is carried out. Whereas the laboratory chemist mostly uses batch methods for reaction-rate measurement, working with closed flasks or flow methods with reactants flowing through narrow tubes, the chemical engineer often uses large continuous reactors, so that he faces the task of translating the kinetic data obtained with experimental apparatus into those applying to his own operating conditions. Fig. 1 provides a survey of the situation and of the problems involved.

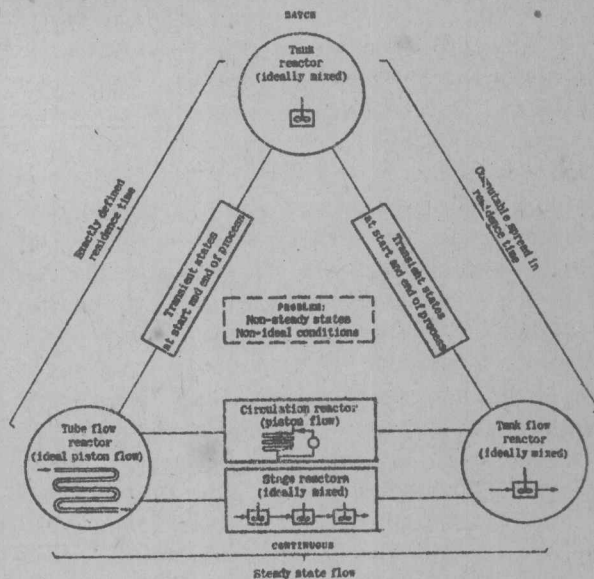


FIG. 1. Large-scale macrokinetic phenomena.

The transition from a batch process to a process carried out in an ideal tubular continuous reactor is relatively simple: both processes are characterized by a sharply defined residence time, so that the translation of batch kinetics into continuous

* Auto-acceleration in a broader sense is a characteristic of all reactions with a great exothermic heat effect.