

Insights into
CHEMICAL
ENGINEERING

DANCKWERTS

INSIGHTS INTO CHEMICAL ENGINEERING

(Selected Papers of P. V. Danckwerts)

by

P. V. DANCKWERTS

F.R.S., F.Eng., Foreign Ass. N.A.E.,

Emeritus Professor, University of Cambridge



PERGAMON PRESS

OXFORD · NEW YORK · TORONTO · SYDNEY · PARIS · FRANKFURT

U.K.	Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, England
U.S.A.	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
CANADA	Pergamon Press Canada Ltd., Suite 104, 150 Consumers Rd., Willowdale, Ontario M2J 1P9, Canada
AUSTRALIA	Pergamon Press (Aust.) Pty. Ltd., P.O. Box 544, Potts Point, N.S.W. 2011, Australia
FRANCE	Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
FEDERAL REPUBLIC OF GERMANY	Pergamon Press GmbH, 6242 Kronberg-Taunus, Hammerweg 6, Federal Republic of Germany

Copyright © 1981 P. V. Danckwerts

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic tape, mechanical, photocopying, recording or otherwise, without permission in writing from the publishers.

First edition 1981

British Library Cataloguing in Publication Data

Danckwerts, P. V.

Insights into chemical engineering.

1. Chemical engineering

I. Title

660.2 TP155 80-42316

ISBN 0-08-026250-3

In order to make this volume available as economically and as rapidly as possible the author's typescript has been reproduced in its original form. This method unfortunately has its typographical limitations but it is hoped that they in no way distract the reader.

Printed in Great Britain by A. Wheaton & Co. Ltd., Exeter

Insights into Chemical Engineering

(Selected Papers of P. V. Danckwerts)

Other Related Pergamon Titles of Interest

Books

ARIS & VARMA: The Mathematical Understanding of Chemical Engineering Systems (Selected Papers of Neal R. Amundson)

COULSON & RICHARDSON: Chemical Engineering (6 Vols all in SI units)

Volume 1: Fluid Flow, Heat Transfer and Mass Transfer, 3rd edition

Volume 2: Unit Operations, 3rd edition

Volume 3: Chemical Reaction Design, Biochemical Reaction Engineering including Computational Techniques and Control, 2nd edition

Volume 4: Solutions to the Problems in Volume 1

Volume 5: Solutions to the Problems in Volume 2

Volume 6:* Introduction to Chemical Engineering Design

Journals

Chemical Engineering Science

Computers & Chemical Engineering

International Journal of Heat and Mass Transfer

Letters in Heat and Mass Transfer

****In preparation***

Full details of all titles/free specimen copy of any Pergamon journal available on request from your nearest Pergamon office.

Foreword

It gives me great pleasure to be associated with this volume of some of the publications which Professor Danckwerts has made in chemical engineering science. His output over the past 30 years has been rich and varied and I was fortunate, as an undergraduate at Cambridge, to be one of those on whom some of his early ideas were tried out.

Many will associate him with the theory of mass transfer operations, particularly in the field of gas absorption, and this work represents a very significant contribution to chemical engineering. It is so well known and has been used so extensively in plant design that it needs no introduction from me.

Perhaps fewer will be familiar with his early work on mixing but this was an important attempt to quantify a very practical process of great industrial significance. The deceptively simple and elegant concepts of the scale and intensity of segregation to describe the degree of mixing were much debated at the time but were not taken up as quickly as they should have been. However, it is noteworthy that they are now being increasingly applied to great effect in widely ranging fields, polymer processing being a typical example, in which temperature or colour uniformity can be of great importance.

The concept of residence time distribution in continuous processes is another topic which Danckwerts pioneered and this has proved to be of great benefit in many areas, including reactor design, blending operations, and many more.

Whereas chemical engineers in industry owe much to his work, those in education have also a lot to be thankful for. Many of the concepts he developed appear to have been designed to stretch the minds of undergraduates and perhaps they were! Certainly many of the examination papers with which they inevitably became confronted contain questions which unmistakably stem from his work.

It is perhaps a little sad to reflect that the gulf between chemical engineering science as developed in the universities and chemical engineering practice is still so wide. Even the best-intentioned engineers in industry find great difficulty in using all but the very simple and approximate design procedures and they have to

rely heavily on expensive and time-consuming pilot plant work or the inclusion of extravagant safety factors. We should strive to do better and there are signs that we are now succeeding for, whereas over-exposure to computers at an early age tends to dull the brain, their widespread use in industry is clearly proving to be of great benefit insofar as they allow more realistic design procedures to be used. However, a necessary pre-requisite is a thorough understanding of the basic physical and chemical concepts of the system and it is to this that Danckwerts has made a lasting contribution.

His work has been basic but, more importantly, it has been objective basic in that it has had as its main purpose the development of a better understanding of some of the chemical engineering phenomena which provide a sound basis for plant design.

I feel sure that many will enjoy reading these original papers and come to reflect that they are much easier to understand than some of the mutilated 'interpretations' of his work which appear in many textbooks.

W L WILKINSON

President, Institution of Chemical Engineers

24 November 1980

Autobiographical Note

DANCKWERTS, Prof. Peter Victor, b 14 Oct. 1916, GC 1940; MBE 1943; FRS 1969; FI ChemE; Shell Professor of Chemical Engineering, Cambridge University, 1959-77. Educ. Winchester Coll.; Balliol Coll., Oxford; Massachusetts Inst. of Technology, BA(chemistry)Oxon, 1938; SM (Chemical Engineering Practice), MIT, 1948; MA Cantab 1948; Hon.D.Sc. Bradford, 1978. RNVR, 1940-46. Commonwealth Fund Fellow, MIT 1946-48; Demonstrator and Lecturer, Dept. of Chemical Engineering, Cambridge Univ., 1948-54; Deputy Director of Research and Development, Industrial Group, UK Atomic Energy Authority, 1954-56; Professor of Chemical Engineering Science, Imperial College of Science and Technology, 1956-59. MIChemE 1955 (President, 1965-66). For. Hon. Mem., Amer. Acad. of Arts and Scis, 1964; For. Associate, Nat. Acad. of Engineering, USA. 1978. E.V. Murphree Award, ACS. 1973. Address: The Abbey House, Abbey Road, Cambridge CB5 8HQ.

Born on 14 Oct. 1916, the son of a naval officer whose family were brought up in a state of genteel poverty, I attended various dame-schools and then went to a prep-school (= U.S. primary boarding school), a singular establishment in some ways reminiscent of Evelyn Waugh's Llanabbas Towers. Between the ages of 10 and 14 I wasted many dreary hours on Latin and even Greek, not to mention the dates of the kings of England. However, among the masters there were a few to whom I owe a debt for a thorough grounding in the writing of English and a basic appreciation of the principles of mathematics. The academic standards were not high and it was regarded as little short of a miracle when I got a place at

Winchester College (founded by William of Wykeham in 1382). This was a public school (= U.S. prep-school) which was unique in valuing intellectual at least as highly as athletic attainment. In spite of its notable classical tradition, it provided an excellent scientific education. Despite the long hours devoted to the ineffectual study of Latin and Greek, I got a remarkably good grounding in physics and chemistry, but for some reason made no progress in mathematics. However, my training in English was reinforced. Churchill used to say that he was regarded as a stupid boy at Harrow and was thus allowed to learn English instead of Latin. I was not so lucky, but at least I managed to avoid tackling Homer.

There was a scholarship, perhaps more closed than any other, for a Winchester scientist to study chemistry at Balliol College, Oxford (founded about 1260 by John de Balliol and Devorgilla, his wife). There were only two candidates in my year and I was the rank outsider. Nevertheless I won it, to universal dismay, and became a Scholar of Balliol, a notable title. I must say that I have been somewhat cynical about honours and awards ever since. Happy to escape from school I spent a year in Austria, that charmed country, living in Vienna and Salzburg, learning a fair amount of German and conceiving a passion for the Baroque and for the mountains.

Balliol was a college with a formidable tradition of raising the rulers (both political and executive) of Britain and other countries, but I had no contacts in such circles; I spoke once to Edward Heath but never to Denis Healey. The course in chemistry had a curious structure. It lasted four years but the all-important final examinations, which determined the pecking-order, took place in the summer of the third year. The fourth was spent on a light-hearted piece of research which meant that in one's final summer one was free to punt on the river, go to balls and otherwise lead the dolce vita. The year was 1939.

I cannot claim that I was particularly diligent during my first two years, either, so that in my third year it was necessary to do some serious work. I acquired some excellent text-books which I read from cover to cover, I studied the predilections of the examiners and tested myself on previous examination-papers. As a result I did rather well in my examinations, a result which I believe gave my tutor the idea that something was wrong with the system. It is true that I could have learned a great deal more than I did. Chemistry was an essentially literary subject at Oxford at that time. I was taught no physics and no mathematics. It was said that if an Oxford chemist encountered a differential coefficient in a book he turned the page; if he saw an integral sign he shut the book. Perhaps the most valuable parts of my intellectual heritage from Balliol were a sense of scientific rigour combined with scepticism - the latter summed-up in the imputations of the word "bogus".

In 1939 I joined a small chemical company, doing a job which - as I now recognise - should have been done by a chemical engineer (an almost unknown species in England in those days). By the summer of 1940 I had had enough; in order to have a go at the Germans who were supposed to be about to invade the country it was clearly necessary to get into the armed forces. I was interviewed at the Admiralty on a Wednesday and on the following Sunday, in the uniform

of a Sub-Lieutenant R.N.V.R., I was on my way North to train at the R.A.F. Bomb Disposal School. No one ever taught me the things a young naval officer should know, such as who and how to salute, and that the Loyal Toast was drunk sitting down. Moreover, my role throughout the war was non-combatant. Such an inconsequential chain of events is typical of war; however, my whole career has run on similar lines of chance and hazard.

I then went to the R.N. Torpedo School, H.M.S. Vernon, at Portsmouth. During a lecture by one of those rock-faced Chief Petty Officers about how to render safe enemy mines there was a sharp explosion. "Ah" said our instructor "they're trying-out one of those double depth-charge throwers". As it happened, two experts had been dismantling a recovered German magnetic mine, which had been booby-trapped. For some reason (probably bureaucracy in the Kriegsmarine) the Germans had not put the 1 kg booby-trap charge in a position where it would detonate the main 750 kg charge of explosive. Otherwise our course would have come to an abrupt end. As it was, the episode served as a salutary practical lesson.

I was posted to the Port of London in time for the Blitz, which began on 7 Sept. 1940. I became for a time the incumbent disposer of German parachute mines. These were magnetic mines and would have been infinitely more cost-effective if used as such to close British harbours to shipping. However, they were the biggest bombs the Germans had and in the pursuit of Schrecklicheit were dropped on land. As it turned out, the mechanism which was designed to detonate them if they dropped on land, rather than into water, was grossly inefficient and after each raid a number were found standing on the top floors of houses, hanging from trees and bridges, etc. There was a sporting chance of actuating the "bomb fuse" while trying to remove it, but usually it buzzed for 10-15 s before the explosion. Those were stirring times.

After many adventures abroad and a great deal of boredom I fetched up early in 1944 in Combined Operations Headquarters in Whitehall, where I was an Experimental Staff Officer. COHQ had been set up by Lord Louis Mountbatten in his usual princely style. It had assembled the prettiest girls from all three services and had a car-pool, a private cinema, the only all-ranks bar I encountered during the war and a canteen, run by society ladies, which served the best food in Whitehall. Many of the famous and the notorious passed through the HQ. I remember particularly our genius-in-residence, Geoffrey Pyke who invented Habbakuk, the giant iceberg ship, and the concept of Power-Driven Rivers; and the brilliant Marxist physicist J.D. Bernal, with whom I shared an office. Whatever may have transpired later about leftward security leaks he seemed to be genuinely surprised when the Hiroshima bomb was dropped.

So passed an agreeable year, devising and attending trials often involving large quantities of explosives, which caused either apathy among the assembled brass when nothing went off at all or indignation when the intensity of blast and missiles among the spectators was too great.

In 1946 I was "on the beach" and wondering about a job. At the

same time a friend advised me to apply for a Commonwealth Fund Fellowship (financed by the Commonwealth Fund of New York, based on the Harkness-Standard Oil fortune). I met an Oxford don who had spent the war in Washington and had heard of a profession called "chemical engineering". This happy combination of suggestions led me to a Fellowship for the study of Chemical Engineering at MIT (founded 1861 by William Barton Rogers). The Commonwealth Fund Fellowships were conceived on a generous scale. One was expected to own a car and to spend at least six months of the Fellowship travelling about the U.S.A.

My introduction to MIT was a considerable cultural shock. At Oxford I had been a scholar and a gentleman, in the Navy an officer and a gentleman. At MIT I was one of a multitude, mostly enjoying the GI Bill of Rights, who were being processed by a vast and somewhat impersonal machine working double shifts. I was bewildered by everything - "material balance" meant nothing to me, I didn't know what a differential equation was and (at the age of 30) I had never used a slide-rule. I scored zero on my first quizz and 100% on my last one. The principles were not so difficult; the main things I had to learn were how to apply them and put numbers into them, and how to adopt a commonsense and pragmatic attitude towards problems rather than a purely intellectual one. I believe these were the most important attributes of the MIT course and should properly be the basis of any engineering course in its extended sense. Of course, there are subjects such as mathematics, fluid mechanics and chemical thermodynamics which should be taught at a university if they are ever to be learned; but never should it be implied that they constitute the whole of an engineer's training.

The MIT Chemical Engineering Practice School was then at its prime and I spent six months divided between different locations from Bangor, Maine to Buffalo, working on the plants. We were a group of six, of whom I was the only non-U.S. citizen and the only owner of a car. It was a unique opportunity to become acclimatised to a country and its people, and I have felt at home in the U.S.A. ever since. The course was brilliantly conceived and executed. At each plant, apart from carrying out measurements and experiments we learned about the history and the state of the art of the process and about scientific topics related to it. In the Lackawanna Steel works, for instance, I learned more about the theory and the practical aspects of radiation than I could have done in any other way. Even Boltzmann, I like to think, could not have had a better intuitive appreciation of the meaning of "black-body radiation" than I acquired by peering into furnaces. One member of the group was Ray Baddour, who subsequently became head of the Chemical Engineering Department at MIT.

Returning to England in 1948 with a Master's Degree in Chemical Engineering Practice, I began to look around for a job. I found that invariably I had to explain to potential employers what a chemical engineer was - they had always got along perfectly well with chemists and mechanical engineers (in which they followed the highly-successful German model). Not feeling that I had the fortitude to revolutionise the British chemical industry, I was grateful for a chance to join the staff of the newly-formed Chemical Engineering Department at Cambridge University. This had been foisted on the University by an irresistible cash benefaction from the

Shell group of companies and had been judged unsuitable to join the department which housed the more traditional branches of engineering. It became, therefore, an independent and anomalous entity, not attached to any Faculty - a situation which continues to this day and carries many advantages as regards autonomy. The fact is that engineers don't understand chemistry and chemists don't understand engineering, and it is not uncommon for university departments of chemical engineering, both in the U.K. and in the U.S.A., to be happily independent of both.

The first Shell professor of chemical engineering was Terence Fox, a Cambridge mechanical engineer with a singularly rigorous cast of mind - just what was needed, in fact, to make the subject respectable in Cambridge eyes. He soon licked us all, staff and students, into shape. He was a brilliant teacher but never launched into original research.

During the years 1948-54, although there was plenty of teaching to be done, I sat on no committees and supervised only one graduate student. I look back on this as my period of "academic indolence", during which I had time to shove my feet up on the desk and actually think. Such "insights" as I have experienced originated mainly in this period, stimulated by summer visits to chemical plants. Alas, indolence is no longer in fashion in universities where, as in industry, one feels that the cult of busyness is antipathetic to thinking. University people sit on committees, travel the world, generate reams of administrative paper, go to conventions; all too seldom does one hear the cry "Eureka!". It was also true that "chemical engineering science" was in its infancy in those days; relatively few people had applied the methods of science to distinctively chemical engineering problems. The scene was very different from that of today when (dare I say it?) too many academics are pursuing too many non-problems. We had an almost virgin field to plough and very few competitors in launching some important new ideas.

In 1954 I joined the U.K. Atomic Energy Authority in a job which was essentially administrative and for which I was not qualified. It happened that the U.K., having launched the atomic energy project ("Tube Alloys") in 1940, having sold the idea to the Americans and having provided much of the expertise involved in the Manhattan Project, was abruptly cut-off from all communication with the U.S.A. by the McMahon Act of 1946. This was too much even for Clement Attlee's labour government who decided in 1947 (in an inner cabinet committee of four or five persons) to thumb their noses at the Americans and go it alone. We had, of course, a good number of people who had been among the mainstays of the Manhattan Project and knew how to go about the two routes for making a bomb - plutonium or enriched uranium. John Cockroft (later Lord) was put in charge of the research establishment at Harwell; William Penny (later Lord) in charge of the Atomic Weapons Research Establishment at Aldermaston. Christopher Hinton (later Lord) was my boss and with very close personal attention to detail built and commissioned the Springfields plant for the manufacture of extremely pure uranium; the Capenhurst plant for the enrichment of U_{235} by gaseous diffusion; and the Windscale plant which consisted of two air-cooled graphite-moderated reactors and the associated chemical facilities for the extraction of plutonium and the separation of

fission products and unchanged uranium. Hinton is, I believe, one of the great British engineers. Having had to learn the science and technique from scratch he succeeded by sheer brilliance and unremitting driving force to get his plants designed, built and commissioned on time. It was a reign of terror and the degree of hyperactivity was comparable with that associated with the Manhattan Project. Harwell soon became indistinguishable from a university campus and the hard facts required for the Industrial Group to carry out its job led to the need for a completely separate and dedicated R. and D. organisation to be set up. Such an experience, I imagine, is not unique to the Atomic Energy Authority. I was Deputy Director of this R. and D. organisation for two years which were fascinating, adventurous and precarious. It was in this job that I learnt the meaning of the phrase "empire building" - not without its analogues in academic life. I was mercifully released in 1959 by the offer of a chair of Chemical Engineering Science at Imperial College, London. Not long after I left our No.1 reactor went up in flames because of the uncontrolled release of Wigner energy from the graphite. One can imagine the kind of hullabaloo which would have ensued if this had happened in 1980; fortunately in those days the anti-nuclear hysteria had not yet incubated and the worst that happened was that a few hundred gallons of milk had to be thrown away.

My three years at Imperial College were indeed strenuous, but since I was a bachelor able to live five minutes from my work and with all the delights of London at my disposal they were not exiguous. My hero at this time, equal in stature to Hinton although very different in personality, was Prof. D.M. Newitt. Soldier, sailor, saboteur and a chemical engineer before the profession had become fashionable, he was humane and deeply sympathetic to his many third-world students. He could cap any story: e.g. "When I was sent to arrest Lawrence of Arabia ...". Imperial College is one of the richer anomalies of the English university system. Although for practical purposes autonomous it is officially one of the colleges of London University, which means a double ration of Faculty Boards, committees and so on. I have always favoured a unilateral declaration of independence to set up a University of South Kensington - Imperial College, the Royal College of Music, the Royal College of Art, the Royal College of Organists, the Royal School of Needlework, the Victoria and Albert Museum, the Science Museum, the Natural History Museum, the Geological Museum, the Royal Marsden Hospital - even perhaps the Albert Hall; most of these institutions having been founded on the profits (unique) of the Great Exhibition of 1851 and owing their foundation to Prince Albert.

In 1959 Terence Fox resigned from the Shell chair at Cambridge (he died the following year) and I felt (perhaps not for the first time) the firm guiding hand of Sir Harold Hartley, evergreen Balliol man, who was, among many other appointments, Brigadier General and controller of chemical warfare in the first world war, Vice-President of the L.M.S. Railway Co., Chairman of British European Airways and a Director of the "Times"; speech-writer to the Duke of Edinburgh, physical chemist extraordinary, energetic promoter of chemical engineering and éminence grise in general regarding the scientific and technological establishment. So I was impelled to Cambridge again, cheerfully leaving behind me a lot of unsolved questions about the succession at Imperial College.

In 1960-74 I held the chair and was head of the department at Cambridge. On the whole I think these were successful years, although the number of our students fluctuated wildly according to fashion and job opportunities. I cannot say that the reputation of the department's graduates (its primary product) or its research has suffered as a result.

Ill-health removed me from the scene for a large part of 1974. In 1975-6 I spent a year as Visiting Professor at North Carolina State University which was highly enjoyable but more of a holiday than a study-leave, I fear.

The Headship of the department had passed to John Davidson in 1975 and in 1977, when I decided to retire, he was elected to the Shell chair. I hope he will prove to have more staying-power than his two predecessors.

At the moment I continue to pursue my researches on gas-absorption in a modest way, act as Executive Editor of "Chemical Engineering Science", and am about to publish an account of the owners of the land on which my house stands - namely the site of Barnwell Priory (founded 1112, dissolved 1538, demolished 1578), who include the Royal Physician to Henry VIII, Edward VI, Mary and Elizabeth I, and also the winner of the Derby in 1786.

The general squalor of travelling conditions is such that I seldom leave Cambridge and never attend committees unless I am chairman (preferably in my own home). I leave it to others to decide whether it is irresponsible or wise to "opt out" before one is forced to retire.

General Introduction

The title of this book is somewhat pretentious, but a title was needed and I think it does in fact contain, here and there, certain ideas which were novel and thought-provoking at the time of their publication. Some of these have inspired a considerable literature and, I hope, proved useful to practical chemical engineers; others seem to have passed unnoticed and I am glad of an opportunity to give them a second airing here.

The papers which follow are selected from research work conducted at Cambridge and Imperial College, mainly during the years 1950-1954 and 1957-1973 (after which ill-health put an end to research for some time).

The bulk of the material is contained in SECTION B - "The Design of Gas Absorbers" - but I would like to think that I have provided some growing-points in other fields which I have not been able to follow-up personally.

In some cases papers of interest have had to be represented only by their Abstracts, in order to keep the number of pages within limits. Each section is provided with a commentary and I hope that these may encourage interested readers to refer to the originals of the missing papers. These commentaries are in no sense review articles because the proliferation of the literature subsequent to (and sometimes based on) the papers reproduced here has been enormous.

One particular paper, which I believe has been widely used in industry, but which has not been reproduced here because of its length and because it is essentially a review, is "The Absorption of Carbon Dioxide into Solutions of Alkalies and Amines" (The Chem. Engr Oct. 1966, pp. 245-280) which was written in collaboration with M.M.Sharma. Not all the papers published under my name appear here, nor is there a complete bibliography. I am afraid that reproduction of photographic plates in some of the papers may be unsatisfactory but the information they were intended to convey is duplicated to a large extent in the text.

My heartfelt thanks go to my co-authors (whose permission I have sought wherever possible). They did all the experimental work and much of the thinking. I must also thank publishers of the various journals for permission to reproduce papers.

Contents

AUTOBIOGRAPHICAL NOTE	ix
GENERAL INTRODUCTION	xvii
SECTION A: Mathematics of Diffusion	1
SECTION B: The Design of Gas Absorbers	45
SECTION C: Reactions of Carbon Dioxide with Bases and Catalysts in Aqueous Solution	181
SECTION D: Residence-Time Distributions and Related Topics	217
SECTION E: Mixtures and Mixing	259
SECTION F: Miscellaneous	299
SUBJECT INDEX	305
INDEX OF CO-AUTHORS	307