

# GAS CHROMATOGRAPHY IN ADSORPTION AND CATALYSIS

## TADEUSZ PARYJCZAK

Professor of Chemistry, Institute of General Chemistry, Technical University of Łódź

## **ELLIS HORWOOD LIMITED**

Publishers · Chichester

Halsted Press: a division of

JOHN WILEY & SONS

New York · Chichester · Brisbane · Toronto

PWN-Polish Scientific Publishers

Warszawa

English edition first published in 1986 in coedition between

#### **ELLIS HORWOOD LIMITED**

Market Cross House, Cooper Street, Chichester, West Sussex, PO19 1EB, England and

#### PWN — POLISH SCIENTIFIC PUBLISHERS

Warsaw, Poland

The Horwood publisher's colophon is reproduced from James Gillison's drawing of the ancient Market Cross, Chichester

Translated by Peter Senn from the Polish

Chromatografia gazowa w badaniach adsorpcji i katalizy, Państwowe Wydawnictwo Naukowe, Warszawa 1975; subsequently subjected to minor revision

#### **DISTRIBUTORS:**

Australia, New Zealand, South-east Asia:

JACARANDA WILEY LTD

G.P.O. Box 859, Brisbane, Queensland 4001, Australia

#### Canada:

JOHN WILEY & SONS CANADA LIMITED

22 Worcester Road, Rexdale, Ontario, Canada

Europe, Africa:

JOHN WILEY & SONS LIMITED

Baffines Lane, Chichester, West Sussex, England

Albania, Bulgaria, Cuba, Czechoslovakia, German Democratic Republic, Hungary, Korean People's Democratic Republic, Mongolia, People's Republic of China, Poland, Romania, the U.S.S.R., Vietnam, Yugoslavia:

ARS POLONA — Foreign Trade Enterprise

Krakowskie Przedmieście 7, 00-068 Warszawa, Poland

North and South America and the rest of the world:

Halsted Press: a division of

JOHN WILEY & SONS

605 Third Avenue, New York, N.Y. 10158, U.S.A.

#### British Library Cataloguing Publication Data

Paryjczak, T.

Gas chromatography in adsorption and catalysis. —
(Ellis Horwood series in physical chemistry)

1. Gas chromatography 2. Chemistry, Physical and theoretical

I. Title II. Chromatografia gazowa w badaniach

adsorpcji i katalizy. English

541.3'028 QD79. C45

ISBN 0-85312-219-9 (Ellis Horwood Limited)

ISBN 0-470-20131-2 (Halsted Press)

#### LIBRARY OF CONGRESS Card No. 85-936

Copyright notice: © PWN - Polish Scientific Publishers, Warszawa, 1986

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, mechanical, photocopying, recording or otherwise, without the permission of Polish Scientific Publishers

Printed in Poland

GAS CHROMATOGRAPHY IN ADSORPTION AND CATALYSIS



### ELLIS HORWOOD SERIES IN PHYSICAL CHEMISTRY

Editor: Professor T. J. Kemp, Department of Chemistry and Molecular Science, University of Warwick

Ball, M. A. and Strachan, A. N. Bodor, G. Buxton, G. V. and Salmon, G. A.

Chemistry and Reactivity of Solids The Structural Investigation of Polymers Pulse Radiolysis and its Applications in Chemistry Structures and Approximations for Electrons in Molecules

Organic Photochemistry

Cook, D. B. Coyle, J. D. Devonshire, R. Gray, G. W. and Winsor, P. A. Harriman, A. Horvath, A. L. Ignatowicz, S. and Kobendza, A. Jaycock, M. J. and Parfitt, G. D.

Physical Photochemistry Liquid and Plastic Crystals, Vols. I and II Inorganic Photochemistry Handbook of Aqueous Electrolyte Solutions Semiconducting Thin Films of AIBVI Compounds Chemistry of Interfaces Chemistry of Colloids

Jaycock, M. J. and Parfitt, G. D. Ladd, M. F. C. Ladd, M. F. C. Mills, A. and Darwent, J. R.

Structure and Bonding in Solid State Chemistry Symmetry in Molecules and Crystals Photochemical and Photoelectrical Conversion of Solar Energy Adsorption

Ościk, J. Paryjczak, T. Rest, I. R. and Dunkin, A. J. Snatzke, G.

Gas Chromatography in Adsorption and Catalysis Cryogenic Photochemistry Optical Rotary Dispersion and Circular Dichroism Southampton Electrochemistry Group Instrumental Methods in

Wan, J. K. S. and Depew, M. C.

Electrochemistry Polarization and Magnetic Effects in Chemistry

Wiseman, P.

Petrochemicals

# List of the More Important Symbols

|   | a   | - quantity of adsorbed substance                              |
|---|---|---|
|   | $a_{\rm A}$ , $a_{\rm B}$                                     | - quantity of adsorbed component A and B                      |
|   | $a_{\mathbf{m}}$  | - quantity of substance adsorbed in the monolayer - the       |
|   |   | monolayer capacity  |
| - | $a_{\rm mg}$  | - quantity of poison required to cover the catalyst surface   |
|   |   | with a monolayer  |
|   | A   | - constant characterizing the eddy diffusion coefficient in   |
|   |   | the van Deemter equation                                      |
|   | $A_0$   | - activity of an unpoisoned catalyst                          |
|   | $A_{\mathbf{g}}$  | - activity of a poisoned catalyst                             |
|   | $egin{aligned} A_{\mathbf{g}} \ b_{\mathbf{g}} \end{aligned}$ | - adsorption coefficient of a poison at active sites          |
|   | B   | - constant characterizing the molecular diffusion coefficient |
|   |   | in the van Deemter equation                                   |
|   | В   | - the distance between atomic centres or groups of atoms      |
|   |   | and the centre of surface atoms of graphite under             |
|   |   | equilibrium conditions  |
|   | $B_{11}$  | - second virial coefficient for the sorbate                   |
|   | $B_{12}$  | - second virial coefficient of sorbate vapour (1) and carrier |
|   |   | gas (2)   |
|   | c   | - concentration of adsorbate in the mobile phase              |
|   | $c_{\rm A}^{\rm o},c_{\rm B}^{\rm o}$                         | - initial concentrations of components A and B in the         |
|   |   | gaseous mixture   |
|   | $c_{\rm A}, c_{\rm B}$  | - concentrations of components A and B in the gaseous         |
|   | _   | phase   |
|   | $c_x$   | — mole fraction of adsorbate in the carrier gas               |
|   | $c_{\rm s}$   | - concentration of adsorbate in the adsorption layer          |
|   |   |   |

| $c_{\mathbf{a}\mathbf{v}}$ | — average concentration of adsorbate in the gaseous phase     |
|----------------------------|---|
| $c_{\mathbf{g}}$           | — resistance to mass transfer in the gaseous phase            |
| $c_{\mathbf{k}}$           | — expression characterizing the kinetics of adsorption        |
| $\tilde{C}$                | - constant characterizing the resistance to mass transfer     |
|                            | in the van Deemter equation                                   |
| C                          | — constant in the BET equation                                |
| $C_{\mathbf{k}}$           | — constant C in the van Deemter equation after having         |
| C <sub>K</sub>             | taken the "wall" effect into account                          |
| d                          | - density   |
| $d_{p}$                    | — average diameter of particles in the column packing         |
| $d_{\mathbf{p}}$           | — edge of metal crystallite                                   |
| $d_{\varepsilon}$          | — dispersion of metal   |
| -                          | — molecular diffusion coefficient of adsorbate in the carrier |
| $D_{\mathbf{g}}$           |   |
| D                          | gas   |
| $D_1$                      | — diffusion coefficient in the liquid phase                   |
| $D_{ m ef}$                | — effective diffusion coefficient                             |
| $D_{\mathbf{K}}$           | — Knudsen diffusion coefficient                               |
| $D_{\rm s}$                | — surface diffusion coefficient                               |
| E                          | — activation energy   |
| $E_{\mathtt{d}}$           | — activation energy of desorption                             |
| $E_{\mathtt{p}}$           | - porosity of column packing particles                        |
| $E_{\sf pack}$             | - porosity of column packing                                  |
| $F_{c}$                    | - volumetric flow rate of carrier gas through the column      |
| $F_{\mathbf{c}}^{0}$       | - volumetric flow rate of carrier gas corrected to normal     |
|                            | conditions  |
| $F_{\mathrm{m}}$           | - volumetric flow rate of gas through the flow-meter          |
| $F_{\rm cal}$              | - volumetric flow rate of gas during calibration              |
| $F_{ m ads}$               | - volumetric flow rate of adsorbate                           |
| $F_{cx}$                   | - average volumetric flow rate of the mobile phase in the     |
|                            | presence of adsorbate   |
| $G_{0}$                    | — quantity of substance introduced into the reactor           |
| $\Delta G^\Theta$          | change in the standard energy of a system during ad-          |
|                            | sorption  |
| $\bar{h}$                  | — Planck's constant   |
| h                          | - height measured (perpendicular to the time axis) from the   |
|                            | baseline to a point on the chromatogram                       |
| H                          | — height equivalent to a theoretical plate (HETP)             |
| $H_{M}$                    | — peak height at maximum $c_{\rm g}$                          |
| $\Delta H^{\Theta}$        | - change in the standard enthalpy during adsorption           |
| <b>ы</b>                   | change in the standard enthalpy during adsorption             |
|                            |   |

| $\boldsymbol{j}$                                 | - pressure gradient correction factor  |
|--|--|
| k  | — detector constant  |
| k  | Boltzmann constant   |
| $k_{\bullet}$                                    | - adsorption rate constant   |
| $k_{\rm d}$                                      | - desorption rate constant   |
| $k_n$  | - rate constant for irreversible activated adsorption  |
| $k_{\rm f}$                                      | — coefficient of mass transfer from gas to particle surface  |
| $k_1, k_2$                                       | — rate constants of reactions  |
| $k_{\text{ef}}$                                  | — effective rate constant of a reaction  |
| $k_{\text{hom}}$                                 | — rate constant of a homogeneous reaction  |
|  | - Henry's constant   |
|  |  |
| $K_0$  | — Henry's constant during the adsorption of a molecule not forming a complex on the surface of a solid |
| <i>v v v</i>                                     | - adsorption equilibrium constants   |
| $K_{\mathbf{A}}, K_{\mathbf{B}}, K_{\mathbf{C}}$ |  |
| $K_{\mathbf{v}}$                                 | — effective Henry's constant for substrate A   |
|  | — volume partition coefficient   |
| $K_{p}$  | — partition coefficient  |
| $K_{s}$  | — adsorption coefficient at the solid-liquid partition bound-  |
| <b>1</b> 2                                       | ary  |
| $K_{\mathbf{L}}$                                 | - adsorption coefficient at the liquid-gas partition bound-  |
| 72   | ary  |
| $K_{AB}$   | — stability constant of a complex  |
| $l_0$  | — length of recorder tape from the instant of sample in-   |
| •  | jection to the outflow of carrier gas  |
| $l_{\mathbf{h}}$                                 | - length of recorder tape from the instant of sample in-   |
|  | jection to the outflow of adsorbate at concentration $c$   |
|  | (to the appropriate deflection $h$ )   |
| L  | — length of column   |
| m  | — mass of adsorbent or catalyst in the column  |
| $m_{\rm L}$                                      | — mass of a unit length of adsorbent layer   |
| $\Delta m_{\mathbf{A}}$                          | — quantity of reacted substance A in the microreactor  |
| $m_{g}$  | - quantity of poison introduced into the microreactor  |
| $m_{\rm st}$                                     | — mass of standard   |
| $Me_s$   | — surface atoms of a metal which are available for chemi-  |
|  | sorption   |
| M  | — molecular weight (relative molecular mass)   |
| n  | — order of reaction  |
| $n_{\mathbf{a}}$                                 | — number of atoms or chemisorbed molecules on the surface  |
|  | of a metal   |
|  |  |

|                    | number of males of adsorbate in the sample                     |
|--------------------|--|
| $n_{s}$            | — number of moles of adsorbate in the sample                   |
| $n_{ m L}$         | — number of moles of test substance in the liquid phase        |
| $n_{\mathbf{g}}$   | — number of moles of test substance in the gaseous phase       |
| N                  | — number of theoretical plates in the column                   |
| $N_{\mathbf{a}}$   | — number of active sites                                       |
| $N_A$              | — Avogadro's number  |
| $N_{g}$            | — number of adsorbate molecules in the gas space of the column |
| $N_0$              | — constant dependent on the number of active sites per unit    |
| *10                | of surface   |
| $N_{ m L}$         | - number of moles of stationary liquid phase per unit of       |
|                    | volume   |
| $N_{\mathfrak{t}}$ | - number of adsorbed molecules                                 |
| $N_{\infty}$       | — monolayer capacity   |
| p                  | - vapour pressure of adsorbate at the temperature of           |
|                    | measurement  |
| $p_{\rm s}$        | — saturated vapour pressure of adsorbate at the temperature    |
|                    | of measurement   |
| $p_i$              | — column inlet pressure  |
| $p_{o}$            | — column outlet pressure                                       |
| $p_{c}$            | — mean column pressure   |
| $p_{b}$            | — barometric pressure  |
| $p_{\mathbf{m}}$   | — gas pressure in the flow-meter                               |
| $p_{A}, p_{B}$     | — partial pressures of components A and B                      |
| $p_{\rm eq}$       | — equilibrium pressure   |
| q                  | — cross-sectional area of the column                           |
| $q_{ m st}$        | — isosteric heat of adsorption                                 |
| $q_{\mathrm{stA}}$ | — isosteric heat of adsorption of substance A                  |
| $q_{int}$          | — integral heat of adsorption                                  |
| $q_{ m d}$         | — differential heat of adsorption                              |
| $q_0$              | - differential heat of adsorption at zero packing of ad-       |
|                    | sorbent surface  |
| $Q_1$              | — heat of adsorption in the first layer                        |
| $Q_{c}$            | — heat of condensation of adsorbate                            |
| <b>r</b> .         | — column radius  |
| R                  | — gas constant   |
| <b>S</b>           | — specific surface area  |
| $S_{ m st}$        | - specific surface area of standard                            |
| $S_{\mathtt{ads}}$ | - adsorption surface area                                      |
|                    |  |

| $S_{\rm peak}$      | — peak area   |
|---------------------|---|
| $S_{\rm peakst}$    | - peak area of standard                                     |
| $S_{v}$             | - surface area of sorbent per unit volume of column         |
| $\Delta S^{\Theta}$ | - change in standard entropy during adsorption              |
| t                   | — time  |
| $t_{\rm R}$         | - uncorrected retention time                                |
| $t_{\mathbf{M}}$    | — carrier gas retention time                                |
| $t_{\rm R}'$        | — adjusted retention time                                   |
| $t_0$               | — duration of a pulse of gas at concentration $c_0$ being   |
|                     | adsorbed  |
| $T_{\mathtt{c}}$    | column temperature  |
| $T_{ m m}$          | — temperature of gas in the flow-meter                      |
| $T_{ m ch}$         | — characteristic temperature at $u_A = u_p$                 |
| t'Ralkene           | — adjusted retention times of an alkene and an alkane       |
| t'Ralkane           | — adjusted retention times of an arkene and an arkane       |
| $t_{\rm max}$       | - time required for complete catalyst regeneration          |
| и                   | — linear velocity of carrier gas                            |
| $u_{\rm c}$         | - linear migration velocity of adsorbate at concentration c |
|                     | along the column  |
| $u_{A}$             | - linear velocity of substance A along the column           |
| $u_{\text{opt}}$    | — optimum linear velocity                                   |
| $u_{p}$             | - rate of temperature field shift (thermodesorption)        |
| $\bar{u}_{ m mol}$  | - average thermal velocity of adsorbate molecules           |
| $u_1'$              | — first moment  |
| $u_2$               | - second central moment                                     |
| V                   | - volume of mobile phase per unit length of column          |
| $V_{s}'$            | - volume of adsorption layer per unit length of column      |
| $V_{\rm cat}$       | — volume of catalyst  |
| $V_{\mathbf{R}}$    | - uncorrected retention volume                              |
| $V_{\mathrm{R}}'$   | — adjusted retention volume                                 |
| $V_{\mathbf{N}}$    | — net retention volume                                      |
| $V_{\rm R}^{\rm O}$ | - corrected retention volume                                |
| $V_{\mathbf{M}}$    | - retention volume of unsorbed gas (gas hold-up)            |
| $V_{g}$             | - specific retention volume                                 |
| $V_{g(c)}$          | — specific retention volume for adsorbate concentration $c$ |
| $V_{s}$             | — "net retention volume" — $V_{\rm g}/S$                    |
| $V_{\rm m}$         | - volume of adsorbate equivalent to a monolayer             |
| $V'_{\mathbf{R_A}}$ | - adjusted retention volume of substance A if there is no   |
|                     | chemical reaction   |
|                     |   |

| V'RA react          | - adjusted retention volume of substance A if a chemical       |
|---------------------|--|
| 7. 1000             | reaction takes place   |
| $V_{ m Aeq}$        | - volume of carrier gas required for the complete transfer     |
|                     | of A from plate N to plate $N+1$                               |
| $\Delta V'$         | — volume of gas adsorbed in unit time                          |
| $V_1^{\infty}$      | - solute molar volume at infinite dilution in stationary phase |
| $V_1^0$             | — solute bulk molar volume                                     |
| W                   | — peak width at base   |
| w                   | — recorder tape speed  |
| $\overline{w}$      | - rate of reaction in the microreactor for an average con-     |
|                     | centration of reagent in a pulse                               |
| $\boldsymbol{Z}$    | - number of collisions between the molecules of adsorbate      |
|                     | and the adsorbent surface (in the column)                      |
| $Z_{\mathbf{a}}$    | - number of collisions leading to adsorption of molecules      |
| z                   | - distance from the centre of the molecular mass of the        |
|                     | adsorbate to the principal plane of the solid (assuming        |
|                     | a flat surface)  |
| $\Phi$ , $\Psi$     | - normal Euler angles determining the orientation of           |
|                     | molecules with respect to the adsorbent surface                |
| ν                   | - angle between the principal axis of the molecule and the     |
|                     | axis perpendicular to the surface                              |
| α                   | — quantity of adsorbed substance per unit surface area or      |
|                     | surface concentration of the adsorbed substance                |
| α                   | - coefficient accounting for the probability of adsorption     |
|                     | during a collision between an adsorbate molecule and           |
|                     | the surface (so-called condensation coefficient)               |
| α                   | - total polarizability of an adsorbate molecule                |
| α                   | <ul> <li>degree of conversion</li> </ul>                       |
| $\alpha_0$          | - degree of transformation of reacting substance on an         |
| •                   | unpoisoned catalyst  |
| β                   | — rate of programmed heating                                   |
| λ                   | - constant characterizing the statistical heterogeneity of the |
|                     | column packing   |
| λ                   | — energy of desorption   |
| $\chi(\varepsilon)$ | - differential distribution of adsorption energy               |
| Δλ                  | - heat of adsorption per carbon atom in a hydrocar-            |
|                     | bon  |
| γ                   | - structural factor describing the labyrinth of gas flow       |
|                     | channels in the column   |
|                     |  |

| v | X/1 |
|---|-----|
| Λ | V.I |

## List of the More Important Symbols

| $\gamma_p$                                | - transmission coefficient   |
|---|--|
| γ   | <ul> <li>activity coefficient</li> </ul>                               |
| $\gamma^{\infty}$                         | <ul> <li>activity coefficient at infinite dilution</li> </ul>          |
| ε   | — that part of the column cross-section not occupied by                |
|   | the stationary phase   |
| 0   | <ul> <li>density of adsorbate in the free gaseous phase</li> </ul>     |
| $\varrho_0$                               | — apparent particle density  |
| $\varrho_{\rm p}$                         | — that part of the column cross-section not occupied by                |
| $(1-\varepsilon)$                         |  |
| 0   | the stationary phase   |
| $oldsymbol{	heta}$ and $oldsymbol{	heta}$ | - coverage of the adsorbent surface with adsorbate mole-               |
|   | cules  |
| $\theta_{A}$                              | — coverage of active sites by molecules of A                           |
| $\mu$                                     | — chemical potential   |
| $\Delta \mu^{\Theta}$                     | <ul> <li>standard change of chemical potential of adsorbate</li> </ul> |
| $v_{\mathbf{g}}$                          | - number of poison molecules which can be adsorbed at                  |
|   | an active site on the catalyst surface                                 |
| $\sigma$                                  | <ul> <li>standard deviation</li> </ul>                                 |
| τ   | - mean hold-up time of an adsorbate molecule at an active              |
|   | site   |
| $\Phi_{(z)}$                              | - potential energy of adsorbate-adsorbent interaction                  |
| φ <sub>C</sub>                            | - potential energy of the interaction between a lattice                |
| 7 CA                                      | carbon atom (graphite black) and an atom or molecule                   |
|   | of adsorbate   |
| <b>v</b>                                  | - stoichiometry of interaction between the adsorbate and               |
| χ   | surface atoms of a metal   |
| 1/4                                       | — function describing the type of pulse introduced into the            |
| $\psi_{(t)}$                              | microreactor   |
|   |  |
| $\omega_{1/2}$                            | — peak width at half the height  |
| ω   | - average area occupied by one surface atom of a metal                 |
| $\omega_{m}$                              | - surface area occupied by one adsorbate molecule in the               |
| \   | monolayer, or sitting surface  |

## Contents

| List of the More Important Symbols                         | X  |
|--|----|
| Introduction   | 1  |
| References   | 5  |
| Chapter 1 Introduction to the Use of Gas Chromatography in | 4. |
| Physicochemical Research                                   | 7  |
| 1.1 General  | 7  |
| The Carrier Gas  | 9  |
| Injection System   | 11 |
| The Sample Size  | 12 |
| Columns  | 13 |
| Column Temperature Control                                 | 14 |
| Measurement of Retention Time                              | 15 |
| Detectors  | 16 |
| 1.2 Techniques Used in Gas Chromatography                  | 19 |
| The Elution Technique                                      | 19 |
| Frontal Analysis   | 23 |
| The Elution-on-a-Plateau Technique                         | 24 |
| The Displacement Technique                                 | 25 |
| The Thermodesorption Technique                             | 27 |
| 1.3 Elements of Theory                                     | 27 |
| Theories   | 27 |
| The Number of Theoretical Plates                           | 29 |
| Broadening of Chromatographic Peaks                        | 30 |
| Correction of Peaks for Diffusion                          | 37 |
| 1.4 The Statistical Moments Method in Gas Chromatography   | 39 |
| 1.5 General Comments on the Precision and Accuracy of      |    |
| Chromatographic Measurements                               | 42 |
|  |    |

|    | 1.6  | Examples of Chromatographic Apparatus for Studying                         |      |
|----|------|--|------|
|    |      | Physicochemical Phenomena  | 43   |
|    |      | References   | 4    |
| Ch | apte | r 2 The Nature of Adsorption   | 50   |
|    |      | Physical Adsorption  | . 50 |
|    |      | Investigation of Irreversible and Reversible Adsorption                    | 50   |
|    |      | Investigation of the Co <sub>3</sub> O <sub>4</sub> -H <sub>2</sub> System | 5    |
|    |      | General Adsorption, Chemisorption  | 59   |
|    |      | Study a of Metal/ Support-Oxygen System                                    | 60   |
|    |      | Investigation of the Properties of Different Forms of a Catalyst           | 60   |
|    |      | Application of the Displacement Technique                                  | 62   |
|    |      | Investigation of Slow Sorption Processes on Fe/SiO <sub>2</sub> Catalysts  | 6.   |
|    |      | References   | 67   |
| Ch | apte | r 3 The Heterogeneous Surfaces of Adsorbents and Catalysts                 | 69   |
|    | 3.1  | Introduction   | 69   |
|    | 3.2  | A Method to Determine the Adsorption Energy Distribution                   |      |
|    |      | from the Pressure Relationships of Retention Data                          | 70   |
|    | 3.3  | Adamson's Method for Analysing the Pressure Relationships                  |      |
|    |      | of Retention Volumes   | 76   |
|    | 3.4  | The Laplace and Stieltjes Transformation Methods in                        |      |
|    |      | Chromatographic Data Analysis  | 7    |
|    | 3.5  | Determination of the Differential Energy Distribution                      |      |
|    |      | Function $\chi(\varepsilon)$ — an Example                                  | 80   |
|    |      | References   | 82   |
| Ch | apte | r 4 Determination of the Adsorption Isotherm                               | 84   |
|    | 4.1  | Introduction   | 84   |
|    | 4.2  | Theoretical Principles   | 85   |
|    |      | Ideal Chromatography. Elution at Infinite Dilution                         | 85   |
|    |      | Determination of Adsorption and Equilibrium Pressure from                  |      |
|    |      | the Chromatogram for Ideal Gas Chromatography                              | 91   |
|    |      | Non-Linear, Non-Ideal Gas Chromatography                                   | 93   |
|    | 4.3  | Methods of Determining the Adsorption Isotherm                             | 97   |
|    |      | The Peak Maxima Method   | 97   |
|    |      | Elution by Characteristic Point (ECP) Method                               | 98   |
|    |      | Frontal Analysis by Characteristic Point (FACP) Method                     | 101  |
|    |      | Flution-on-a-Plateau (FP) Method   | 106  |

| ~        | ••  |
|----------|-----|
| Contents | VII |

|        | Schay's Method   | 107 |
|--------|--|-----|
|        | Determination of the Adsorption Isotherm of Gaseous            |     |
|        | Mixtures   | 109 |
| 4.4    | Determination of the Porosity of Solids                        | 115 |
| 4.5    | General Remarks  | 122 |
|        | References   | 123 |
|        |  |     |
| Chapte | er 5 Determination of the Specific Surface Areas of Solids     | 128 |
|        | Introduction   | 128 |
| 5.2    | Chromatographic Methods of Determining the Specific Sur-       |     |
|        | face Areas of Solids   | 128 |
|        | The Heat Desorption Method                                     | 129 |
|        | Methods Involving the Determination of the Adsorption          |     |
|        | Isotherm from the Extended Chromatogram Boundary               | 138 |
|        | Schay's Frontal Method   | 138 |
|        | The Retention Volume Method                                    | 139 |
|        | A Method Based on the Change in Peak Shape with Change         |     |
|        | in Sample Size   | 146 |
|        | Determination of the Specific Surface Area by the Adsorbed     |     |
|        | Liquid Phase Method  | 149 |
|        | Determination of the Specific Surface Area from the Second     |     |
|        | $B_{2S}$ and Third $B_{3S}$ Virial Coefficients                | 153 |
|        | Catalyst Surface Area Measurements under Reaction Con-         |     |
|        | ditions  | 155 |
|        | Survey of the Chromatographic Techniques for Determining       |     |
|        | the Specific Surface Areas of Solids                           | 156 |
|        | References   | 158 |
|        |  |     |
| Chapte | r 6 Determination of the Dispersion and Selective Surface Area | J   |
|        | of Metals and Metal Oxides in Compound Catalysts               | 163 |
| 6.1    | Principles   | 163 |
|        | Determination of the Dispersion and Specific Surface Area      | 100 |
| 0.2    | of a Supported Metal   | 169 |
| 6.3    | The Pulse Technique  | 175 |
| 6.4    | The Frontal Method   | 178 |
|        | The Gas-Titration Method                                       | 178 |
|        | Determination of the Selective Surface Area of Metal Oxides    | 170 |
| 2.0    | in Compound Catalysts  | 184 |
|        |  | 104 |

viii Contents

|     | 6.7  | Temperature-Programmed Desorption (TPD)                   | 18  |
|-----|------|---|-----|
|     |      | Thermodesorption of Hydrogen from Group VIII Metals       | 192 |
|     |      | Thermodesorption of Carbon Monoxide from the Surface of   |     |
|     |      | Group VIII Metals   | 19  |
|     |      | References  | 199 |
|     |      |   |     |
| Cha | apte | r 7 Determination of Catalyst Surface Acidity             | 206 |
|     | 7.1  | Introduction  | 206 |
|     | 7.2  | Methods of Determining Surface Acidity                    | 207 |
|     |      | Chromatographic Determination of Surface Acidity          | 209 |
|     |      | References  | 215 |
| CI. |      |   |     |
| Cna | apte | r 8 Determination of the Heat and Other Thermodynamic     | 210 |
|     | 0 1  | Functions of Adsorption                                   | 219 |
|     |      | Introduction  | 219 |
|     | 8.2  | The Theoretical Basis for Determining the Heat of Ad-     |     |
|     |      | sorption  | 220 |
| ١.  | 8.3  | Determination of Other Thermodynamic Functions of         |     |
|     |      | Adsorption  | 229 |
|     | 8.4  | A More Detailed Discussion of the Chromatographic De-     |     |
|     |      | termination of the Isosteric Heat of Adsorption           | 233 |
|     |      | References  | 237 |
| Cha | pte  | r 9 Interaction of Molecules in the Adsorbent Layer       | 242 |
|     | -    | Introduction  | 242 |
| (   | 9.2  | The Classification of Molecules and Adsorbents            | 244 |
|     |      | The Classification of Molecules                           | 244 |
|     |      | The Classification of Adsorbents                          | 244 |
| (   | 9 3  | Adsorbate-Adsorbent Interactions                          | 245 |
|     |      |   | 254 |
| , - |      |   | 258 |
|     |      | References  | 230 |
| Cha | ptei | 10 The Study of Diffusion Processes                       | 261 |
| . ] | 10.1 | Introduction  | 261 |
|     |      | Determination of the Diffusion Coefficient in the Gaseous |     |
|     |      |   | 262 |
| 1   | 0.3  | Determination of the Effective Diffusion Coefficient in   |     |
|     |      |   | 263 |
|     |      |   | 260 |

|         | 11 The Study of Catalytic Reactions                                   | 271 |
|---------|---|-----|
| 11.1    | Introduction  | 271 |
|         | Reversible Reactions  | 274 |
|         | $A \rightleftharpoons B$ Reactions                                    | 274 |
|         | $A \rightleftharpoons 2B$ Reactions                                   | 275 |
|         | $A \rightleftharpoons B+C$ Reactions                                  | 276 |
|         | $A \rightleftharpoons B+C$ Reactions under Thermochromatographic Con- |     |
|         | ditions   | 280 |
|         | $A+B \rightleftharpoons AB$ Reactions                                 | 281 |
| 11.3    | Irreversible Reactions  | 284 |
|         | A -> B Reactions under Ideal Linear Chromatography                    |     |
|         | Conditions  | 284 |
|         | $nA \rightarrow B$ Reactions under Ideal Gas Chromatography           |     |
|         | Conditions  | 287 |
|         | $A \rightarrow B$ Reactions in which Adsorption Equilibrium is        |     |
|         | Established Slowly  | 290 |
|         | A -> B Reactions with Allowance for Diffusion and the                 |     |
|         | Kinetics of Adsorption  | 292 |
|         | The Application of the Plate Theory to Catalytic Processes            |     |
|         | Taking Place under Chromatographic Conditions                         | 293 |
| 11.4    | The Kinetics of Reactions at Heterogeneous Surfaces                   |     |
|         | Proceeding in a Microreactor  | 293 |
| 11.5    | The Radiochromatographically Determined Kinetics of                   |     |
|         | Complex Reactions Taking Place in a Microreactor                      | 294 |
| 11.6    | Gas Chromatography in the Study of Catalyst Poisoning                 | 296 |
|         | Examples of Catalytic Reactions Investigated by Chroma-               |     |
|         | tographic Methods   | 298 |
| 11.8    | General Remarks on the Study of Catalytic Reactions by                |     |
|         | Chromatography  | 308 |
|         | References  | 309 |
| Chantar | 12 Microreactor Techniques  | 316 |
|         | Introduction  | 316 |
|         | Microreactors   | 319 |
|         | Methods of Connecting the Microreactor to the Chromato-               | 313 |
| 12.3    | graphic Apparatus   | 326 |
|         |   | 334 |
|         | References  |     |
|         | Index   | 337 |
| Subject | Index   | 341 |
|         |   |     |