

CHEMICAL KINETICS

EDITED BY

C.H. BAMFORD

M.A., Ph.D., Sc.D. (Cantab.), F.R.I.C., F.R.S.
*Formerly Campbell-Brown Professor of Industrial Chemistry,
University of Liverpool*

The late C.F.H. TIPPER

Ph.D. (Bristol), D.Sc. (Edinburgh)
*Senior Lecturer in Physical Chemistry,
University of Liverpool*

AND

R.G. COMPTON

M.A., D.Phil. (Oxon.)
*Lecturer in Physical Chemistry,
University of Liverpool*

VOLUME 19

SIMPLE PROCESSES AT THE
GAS—SOLID INTERFACE



ELSEVIER

AMSTERDAM—OXFORD—NEW YORK—TOKYO

1984

Contents

Preface	ix
<i>Chapter 1 (M.A. Morris, M. Bowker and D.A. King)</i>	
Kinetics of adsorption, desorption and diffusion at metal surfaces	1
1. Introduction.	1
1.1 The development of the science of solid surfaces.	1
1.2 The gas—solid surface interaction potential.	3
1.3 Order—disorder phenomena in adsorbed layers	6
1.3.1 Dipole—dipole interactions	7
1.3.2 Indirect coupling interaction	7
1.3.3 Direct coupling	7
1.3.4 Substrate atom sharing interactions.	8
1.3.5 Importance of lateral interactions.	8
1.4 Adsorbate-induced static displacements of substrate atoms	9
2. Experimental techniques.	10
2.1 Surface crystallography, chemical composition and electronic structure	10
2.1.1 Low energy electron diffraction (LEED)	10
2.1.2 Auger electron spectroscopy (AES).	13
2.1.3 Photoemission.	15
2.1.4 Vibrational spectroscopies.	16
2.2 Adsorption kinetics and absolute coverages	17
2.2.1 Uptake techniques.	17
2.2.2 Temperature-programmed desorption	20
2.2.3 Radiotracer techniques.	21
2.2.4 Nuclear reaction method.	21
2.2.5 Microbalance techniques.	22
2.2.6 Relative coverage measurement techniques.	23
2.2.7 Reflection detector techniques.	24
2.2.8 Absolute random flux technique.	26
2.3 Desorption kinetics	27
2.3.1 Temperature-programmed desorption	27
2.3.2 Isothermal desorption.	29
2.3.3 Electron-, photon-, ion- and field-stimulated desorption	29
2.4 Surface diffusion.	31
2.4.1 Scanning methods	31
2.4.2 Field emission and field ion microscopies	34
2.4.3 Other methods	39
3. Adsorption kinetics	41
3.1 The data base	41
3.1.1 Zero coverage sticking probabilities.	41
3.1.2 Variations of s with surface coverage	55
3.2 Mechanisms and rate laws in adsorption.	57
3.2.1 Energy accommodation and trapping.	58
3.2.2 Precursor states in reactive gas—solid interactions.	62

3.2.3 Models for adsorption kinetics	64
3.2.4 Activated adsorption	82
4. Desorption kinetics	84
4.1 Theory and analysis of desorption spectra	86
4.1.1 Theoretical aspects of thermal desorption.	86
4.1.2 Integral order desorption with coverage-independent parameters	90
4.1.3 Systems with variable desorption energies.	94
4.1.4 Systems with variable pre-exponentials	97
4.1.5 Desorption order	98
4.1.6 The effect of precursor states.	101
4.1.7 The influence of lateral interactions	104
4.2 The data base	108
4.2.1 Crystal plane orientation.	108
4.2.2 Surface cleanliness	108
4.2.3 Temperature-programmed reaction spectroscopy	122
4.3 The desorption data bank	125
4.4 Interstate conversion	141
5. Surface diffusion.	142
5.1 Introduction.	142
5.2 Results	149
5.3 Summary	163
References	163

Chapter 2 (B.A. Joyce and C.T. Foxon)

Adsorption, desorption and migration on semiconductor surfaces.	181
1. Introduction.	181
1.1 Justification for the subject matter	181
1.2 The "charge-transfer" model	182
2. Experimental approach.	183
2.1 Surface crystallography. Diffraction techniques.	183
2.1.1 Low energy electron diffraction (LEED)	183
2.1.2 Reflection high energy electron diffraction (RHEED).	187
2.2 Surface compositional analysis. Auger electron spectroscopy (AES)	189
2.3 Surface electronic structure. Photoelectron spectroscopies	190
2.4 Surface kinetic measurements	192
2.4.1 Modulated molecular beam methods	193
2.4.2 Thermal desorption	195
3. Atomically clean semiconductor surfaces.	197
3.1 Electronic structure of semiconductor surfaces	197
3.1.1 Self-consistent pseudo-potential calculations.	199
3.1.2 Realistic tight-binding calculations	200
3.2 Crystallography of semiconductor surfaces. Relaxation and reconstruction	200
3.3 Preparation of clean surfaces	201
3.3.1 Silicon.	202
3.3.2 Gallium arsenide	204
3.4 Determination of the crystallographic and electronic structure of clean semiconductor surfaces.	206
3.4.1 Si{100}	206
3.4.2 Si{111}	210
3.4.3 GaAs{110}	215
4. Gas—semiconductor surface interactions	221

4.1	Adsorption of hydrogen on silicon	221
4.1.1	Introduction and survey of early work	221
4.1.2	Hydrogen atom adsorption on Si {111}	223
4.1.3	Hydrogen atom adsorption on Si {110}	227
4.1.4	Hydrogen atom adsorption on Si {100}	229
4.1.5	Direct observation of hydride surface phases	230
4.1.6	Theoretical considerations	231
4.1.7	Conclusions	232
4.2	Oxygen adsorption on silicon	233
4.3	Chlorine adsorption on silicon	242
4.4	Oxygen adsorption on GaAs	246
4.4.1	Oxygen adsorption on clean {110} GaAs surfaces	247
4.4.2	Oxygen adsorption on other orientations	252
5.	Metal interactions with semiconductor surfaces	253
5.1	Introduction	253
5.2	Metal—semiconductor interfaces	254
5.2.1	Gold—silicon	255
5.2.2	Silver—silicon	258
5.2.3	Group III metals (Al, Ga, In)—silicon	259
5.2.4	Caesium—silicon	260
5.2.5	Metals—Group III—V compounds	260
5.2.6	Mechanisms of metal—semiconductor interface interactions	269
5.2.7	“Classical” models of metal desorption from semiconductor surfaces	270
5.3	Semiconductor—semiconductor interfaces	275
5.4	Interaction of Group V elements with GaAs surfaces	277
	References	280

Chapter 3 (J. Cunningham)

	Radiation and photoeffects at gas/solid interfaces	291
1.	General introduction	291
1.1	Scope	291
1.2	Origins of radiation sensitivity	293
1.2.1	Collective-electron models	293
1.2.2	Active-site models and their sensitivity to radiation	296
1.2.3	Combinations of collective-electron and active-site models	301
1.2.4	Surface-state models	303
1.3	Spectroscopic aspects of irradiated gas/solid interfaces	310
1.3.1	Electron spectroscopy of surfaces	311
2.	Photoeffects at gas/solid interfaces	325
2.1	Photophysical effects	327
2.1.1	Experimental aspects	327
2.1.2	Results and interpretations	333
2.2	Photochemical effects	354
2.2.1	Experimental aspects	354
2.2.2	Results and interpretations	359
2.2.3	Modifying effects of surface dopants	394
3.	Effects induced by irradiation with high-energy photons or particles	397
3.1	Energy deposition and localisation at the gas/solid interface	398
3.2	Experimental aspects	399
3.3	Results and interpretations	401
3.3.1	Effects on adsorption—desorption processes during irradiation	401
3.3.2	Chemical effects during irradiation	405

3.3.3 Effects persisting at the interface after irradiation 413

4. Perspectives and prospectus. 417

References 419

Index 429