

Table of Contents

Preface	xiii
Chapter 1. Adsorption Phenomena	1
1.1. The surface of solids: general points	1
1.2. Illustration of adsorption	2
1.2.1. The volumetric method or manometry	3
1.2.2. The gravimetric method or thermogravimetry.	4
1.3. Acting forces between a gas molecule and the surface of a solid.	4
1.3.1. Van der Waals forces	4
1.3.2. Expression of the potential between a molecule and a solid.	6
1.3.3. Chemical forces between a gas species and the surface of a solid . .	7
1.3.4. Distinction between physical and chemical adsorption	8
1.4. Thermodynamic study of physical adsorption.	8
1.4.1. The different models of adsorption	8
1.4.2. The Hill model	9
1.4.3. The Hill-Everett model	10
1.4.4. Thermodynamics of the adsorption equilibrium in Hill's model . .	10
1.4.4.1. Formulating the equilibrium	10
1.4.4.2. Isotherm equation	11
1.4.5. Thermodynamics of adsorption equilibrium in the Hill-Everett model	12
1.5. Physical adsorption isotherms	13
1.5.1. General points.	13
1.5.2. Adsorption isotherms of mobile monolayers	15
1.5.3. Adsorption isotherms of localized monolayers	15
1.5.3.1. Thermodynamic method	16
1.5.3.2. The kinetic model	17
1.5.4. Multilayer adsorption isotherms	18
1.5.4.1. Isotherm equation	18

1.6. Chemical adsorption isotherms	23
1.7. Bibliography	27
Chapter 2. Structure of Solids: Physico-chemical Aspects	29
2.1. The concept of phases	29
2.2. Solid solutions	31
2.3. Point defects in solids	33
2.4. Denotation of structural members of a crystal lattice.	34
2.5. Formation of structural point defects	36
2.5.1. Formation of defects in a solid matrix	36
2.5.2. Formation of defects involving surface elements	37
2.5.3. Concept of elementary hopping step	38
2.6. Bibliography	38
Chapter 3. Gas-Solid Interactions: Electronic Aspects	39
3.1. Introduction	39
3.2. Electronic properties of gases	39
3.3. Electronic properties of solids	40
3.3.1. Introduction	40
3.3.2. Energy spectrum of a crystal lattice electron.	41
3.3.2.1. Reminder about quantum mechanics principles	41
3.3.2.2. Band diagrams of solids.	45
3.3.2.3. Effective mass of an electron.	52
3.4. Electrical conductivity in solids	55
3.4.1. Full bands	55
3.4.2. Partially occupied bands	56
3.5. Influence of temperature on the electric behavior of solids	57
3.5.1. Band diagram and Fermi level of conductors	57
3.5.2. Case of intrinsic semiconductors	61
3.5.3. Case of extrinsic semiconductors	62
3.5.4. Case of materials with point defects.	64
3.5.4.1. Metal oxides with anion defects, denoted by MO_{I-x}	65
3.5.4.2. Metal oxides with cation vacancies, denoted by $M_{I-x}O$	66
3.5.4.3. Metal oxides with interstitial cations, denoted by $M_{I+x}O$	67
3.5.4.4. Metal oxides with interstitial anions, denoted by MO_{I+x}	67
3.6. Bibliography	68
Chapter 4. Interfacial Thermodynamic Equilibrium Studies	69
4.1. Introduction	69
4.2. Interfacial phenomena	70
4.3. Solid-gas equilibriums involving electron transfers or electron holes	71
4.3.1. Concept of surface states	72

4.3.2. Space-charge region (SCR)	73
4.3.3. Electronic work function	77
4.3.3.1. Case of a semiconductor in the absence of surface states	77
4.3.3.2. Case of a semiconductor in the presence of surface states	78
4.3.3.3. Physicists' and electrochemists' denotation systems	79
4.3.4. Influence of adsorption on the electron work functions	80
4.3.4.1. Influence of adsorption on the surface barrier V_S	80
4.3.4.2. Influence of adsorption on the dipole component V_D	90
4.4. Solid-gas equilibriums involving mass and charge transfers	91
4.4.1. Solids with anion vacancies	92
4.4.2. Solids with interstitial cations	94
4.4.3. Solids with interstitial anions	94
4.4.4. Solids with cation vacancies	96
4.5. Homogenous semiconductor interfaces	97
4.5.1. The electrostatic potential is associated with the intrinsic energy level	103
4.5.2. Electrochemical aspect	104
4.5.3. Polarization of the junction	107
4.6. Heterogenous junction of semiconductor metals	107
4.7. Bibliography	108
Chapter 5. Model Development for Interfacial Phenomena	109
5.1. General points on process kinetics	109
5.1.1. Linear chain	111
5.1.1.1. Pure kinetic case hypothesis	114
5.1.1.2. Bodenstein's stationary state hypothesis	118
5.1.1.3. Evolution of the rate according to time and gas pressure	119
5.1.1.4. Diffusion in a homogenous solid phase	121
5.1.2. Branched processes	125
5.2. Electrochemical aspect of kinetic processes	126
5.3. Expression of mixed potential	133
5.4. Bibliography	136
Chapter 6. Apparatus for Experimental Studies: Examples of Applications	137
6.1. Introduction	137
6.2. Calorimetry	138
6.2.1. General points	138
6.2.1.1. Theoretical aspect of Tian-Calvet calorimeters	139
6.2.1.2. Seebeck effect	139
6.2.1.3. Peltier effect	140
6.2.1.4. Tian equation	140

6.2.1.5. Description of a Tian-Calvet device	142
6.2.1.6. Thermogram profile	144
6.2.1.7. Examples of applications	146
6.3. Thermodesorption	156
6.3.1. Introduction	156
6.3.2. Theoretical aspect	157
6.3.3. Display of results	161
6.3.3.1. Tin dioxide	161
6.3.3.2. Nickel oxide	163
6.4. Vibrating capacitor methods	172
6.4.1. Contact potential difference	172
6.4.2. Working principle of the vibrating capacitor method	176
6.4.2.1. Introduction	176
6.4.2.2. Theoretical study of the vibrating capacitor method	176
6.4.3. Advantages of using the vibrating capacitor technique	179
6.4.3.1. The materials studied	179
6.4.3.2. Temperature conditions	179
6.4.3.3. Pressure conditions	181
6.4.4. The constraints	181
6.4.4.1. The reference electrode	181
6.4.4.2. Capacitance modulation	182
6.4.5. Display of experimental results	182
6.4.5.1. Study of interactions between oxygen and tin dioxide	184
6.4.5.2. Study of interactions between oxygen and beta-alumina	185
6.5. Electrical interface characterization	187
6.5.1. General points	187
6.5.2. Direct-current measurement	189
6.5.3. Alternating-current measurement	191
6.5.3.1. General points	191
6.5.3.2. Principle of the impedance spectroscopy technique	191
6.5.4. Application of impedance spectroscopy – experimental results	196
6.5.4.1. Protocol	196
6.5.4.2. Experimental results: characteristics specific to each material	197
6.5.5. Evolution of electrical parameters according to temperature	202
6.5.6. Evolution of electrical parameters according to pressure	208
6.6. Bibliography	212
Chapter 7. Material Elaboration	215
7.1. Introduction	215
7.2. Tin dioxide	216
7.2.1. The compression of powders	216
7.2.1.1. Elaboration process and structural properties	216

7.2.1.2. Influence of the morphological parameters on the electric properties	217
7.2.2. Reactive evaporation.	219
7.2.2.1. Experimental device	219
7.2.2.2. Measure of the source temperature	222
7.2.2.3. Thickness measure	222
7.2.2.4. Experimental process	224
7.2.2.5. Structure and properties of the films	224
7.2.3. Chemical vapor deposition: deposit contained between 50 and 300 Å.	236
7.2.3.1. General points.	236
7.2.3.2. Device description	238
7.2.3.3. Structural characterization of the material	242
7.2.3.4. Influence of the experimental parameters on the physico-chemical properties of the films.	245
7.2.3.5. Influence of the structure parameters on the electric properties of the films	250
7.2.4. Elaboration of thick films using serigraphy	252
7.2.4.1. Method description.	252
7.2.4.2. Ink elaboration	253
7.2.4.3. Structural characterization of thick films made with tin dioxide	254
7.3. Beta-alumina	255
7.3.1. General properties	255
7.3.2. Material elaboration	257
7.3.3. Material shaping	261
7.3.3.1. Mono-axial compression	261
7.3.3.2. Serigraphic process.	262
7.3.4. Characterization of materials	263
7.3.4.1. Physico-chemical characterization of the sintered materials	263
7.3.4.2. Physico-chemical treatment of the thick films.	266
7.3.5. Electric characterization.	273
7.4. Bibliography	275
Chapter 8. Influence of the Metallic Components on the Electrical Response of the Sensors	277
8.1. Introduction	277
8.2. General points.	278
8.2.1. Methods to deposit the metallic parts on the sensitive element	278
8.2.2. Role of the metallic elements on the sensors' response	279
8.2.3. Role of the metal: catalytic aspects	282
8.2.3.1. Spill-over mechanism	283

8.2.3.2. Reverse spill-over mechanism	284
8.2.3.3. Electronic effect mechanism	284
8.2.3.4. Influence of the metal nature on the involved mechanism.	286
8.3. Case study: tin dioxide	288
8.3.1. Choice of the samples	288
8.3.2. Description of the reactor	289
8.3.3. Experimental results	291
8.3.3.1. Influence of the oxygen pressure on the electric conductivity .	291
8.3.3.2. Influence of the reducing gas on the electric conductances . .	295
8.4. Case study: beta-alumina	296
8.4.1. Device and experimental process	297
8.4.2. Influence of the nature of the electrodes on the measured voltage .	298
8.4.2.1. Study of the different couples of metallic electrodes	299
8.4.2.2. Electric response to polluting gases	301
8.4.3. Influence of the electrode size	303
8.4.3.1. Description of the studied devices	303
8.4.3.2. Study of the electric response according to the experimental conditions	304
8.5. Conclusion.	306
8.6. Bibliography	307
Chapter 9. Development and Use of Different Gas Sensors	309
9.1. General points on development and use	309
9.2. Examples of gas sensor development	310
9.2.1. Sensors elaborated using sintered materials	310
9.2.2. Sensors produced with serigraphed sensitive materials	312
9.3. Device designed for the laboratory assessment of sensitive elements and/or sensors to gas action	316
9.3.1. Measure cell for sensitive materials	317
9.3.2. Test bench for complete sensors	319
9.3.3. Measure of the signal	319
9.3.3.1. Measure of the electric conductance	319
9.3.3.2. Measure of the potential.	322
9.4. Assessment of performance in the laboratory	322
9.4.1. Assessment of the performances of tin dioxide in the presence of gases	322
9.4.2. Assessment of beta-alumina in the presence of oxygen	327
9.4.2.1. Device and experimental process	327
9.4.2.2. Electric response to the action of oxygen.	327
9.4.3. Assessment of the performances of beta-alumina in the presence of carbon monoxide	329
9.4.3.1. Measurement device	329

9.4.3.2. Electric results	329
9.5. Assessment of the sensor working for an industrial application	332
9.5.1. Detection of hydrogen leaks on a cryogenic engine	333
9.5.1.1. Context of the study	333
9.5.1.2. Study of performances in the presence of hydrogen	333
9.5.1.3. Test carried out in an industrial environment	337
9.5.2. Application of the resistant sensor to atmospheric pollutants in an urban environment	341
9.5.2.1. Measurement campaign conducted at Lyon in 1988	342
9.5.2.2. Measurement campaign conducted at Saint Etienne in 1998 . .	345
9.5.3. Application of the potentiometric sensor to the control of car exhaust gas	347
9.5.3.1. Strategy implemented to control the emission of nitrogen oxides	347
9.5.3.2. Strategy implemented to control nitrogen oxide traps	349
9.5.3.3. Results relative to the nitrogen oxides traps	350
9.6. Amelioration of the selectivity properties	352
9.6.1. Amelioration of the selective detection properties of SnO ₂ sensors using metallic filters	352
9.6.1.1. Development of a sensor using a rhodium filter	352
9.6.1.2. Development of a sensor using a platinum filter	354
9.6.2. Development of mechanical filters	356
9.6.2.1. Development of a sensor detecting hydrogen	356
9.6.2.2. Development of a protective film for potentiometric sensors .	356
9.7. Bibliography	359
Chapter 10. Models and Interpretation of Experimental Results	361
10.1. Introduction	361
10.2. Nickel oxide	362
10.2.1. Kinetic model	365
10.2.2. Simulation of a kinetic model using analog electric circuits . . .	370
10.2.2.1. Simulation of the curves displaying a maximum	370
10.2.2.2. Simulation of the curves displaying a plateau	377
10.2.3. Physical significance of the measured electric conductivity . . .	380
10.3. Beta-alumina	380
10.3.1. Physico-chemical and physical aspects of a phenomenon taking place at the electrodes	380
10.3.1.1. Oxygen species present at the surface of the device	380
10.3.1.2. Origin of the electric potential	384
10.3.2. Expression of the model	385
10.3.2.1. The electrode potential	385
10.3.2.2. Expression of the coverage degree	389

10.3.2.3. Expression of the theoretical potential difference at the poles of the device.	394
10.3.3. Simulation of the results obtained with oxygen	395
10.3.3.1. Behavior as a function of temperature and pressure.	395
10.3.3.2. Behavior as a function of electrode size.	397
10.3.3.3. Evolution of the surface potential	399
10.3.4. Simulation of the phenomenon in the presence of CO	401
10.3.4.1. Description of the mechanisms considered.	401
10.3.4.2. Oxidation mechanisms of carbon monoxide	402
10.3.4.3. Results of the simulation.	405
10.4. Tin dioxide.	409
10.4.1. Introduction	409
10.4.2. Proposition for a physico-chemical model	410
10.4.3. Phenomenon at the electrodes and role of the thickness of the sensitive film	415
10.4.3.1. Calculation of the conductance G as a function of the thickness of the film	416
10.4.3.2. Mathematical simulation.	423
10.5. Bibliography.	428
Index	431