CONTENTS

Preface xiii
General Introduction xv
Lists of Constants xvii
List of Symbols xix

1 Surfaces—An Introduction 1
   1.1 Historical Perspective, 1
   1.2 Surfaces and Interfaces—Classification of Properties, 3
   1.3 External Surfaces, 5
      1.3.1 Surface Concentration, 5
      1.3.1.1 Clusters and Small Particles, 6
      1.3.1.2 Thin Films, 8
      1.3.2 Internal Surfaces—Microporous Solids, 10
   1.4 Clean Surfaces, 12
   1.5 Interfaces, 13
      1.5.1 Adsorption, 13
      1.5.2 Thickness of Surface Layers, 15
   1.6 The Techniques of Surface Science, 15
   1.7 Summary and Concepts, 17
   1.8 Problems, 17
   References, 18

2 The Structure of Surfaces 36
   2.1 Introduction, 36
   2.2 Surface Diffraction, 42
   2.3 Notation of Surface Structures, 43
      2.3.1 Abbreviated Notation of Simple Surface Structures, 45
      2.3.2 Notation of High-Miller-Index, Stepped Surfaces, 47
2.4 The Structure of Clean Surfaces, 48
2.4.1 Bond-Length Contraction or Relaxation, 48
2.5 Reconstruction, 50
2.5.1 Atomic Steps and Kinks, 52
2.6 The Structure of Adsorbed Monolayers, 54
2.6.1 Ordered Monolayers and the Reasons for Ordering, 54
2.6.2 Adsorbate-Induced Restructuring, 55
2.6.3 Atomic Adsorption and Penetration into Substrates, 58
2.6.4 Metals on Metals: Epitaxial Growth, 60
2.6.5 Growth Modes at Metal Surfaces, 60
2.6.6 Molecular Adsorption, 60
2.6.6.1 Ethylene, 62
2.6.6.2 Benzene, 66
2.6.7 Coadsorbed Monolayers, 67
2.6.8 Physisorbed Monolayers, 72
2.7 Summary and Concepts, 74
2.8 Problems, 74
References, 75

3 Thermodynamics of Surfaces 271
3.1 Introduction, 271
3.2 Definition of Surface Thermodynamic Functions, 272
3.3 Work Needed to Create a Surface of a One-Component System: Surface Tension, 273
3.3.1 The Surface Free Energy Is Always Positive, 275
3.3.2 Temperature Dependence of the Specific Surface Free Energy, 277
3.3.3 Surface Heat Capacity, 277
3.3.3.1 Experimental Estimates, 277
3.3.3.2 Theoretical Estimates, 278
3.4 The Surface Energy and Surface Composition of Two-Component Systems, 282
3.4.1 The Wagner Experiment, 284
3.4.2 Surface Segregation in Binary Alloy Systems, 285
3.4.3 Surface Composition of Alloys from Model Calculations, 289
3.5 Surfaces When No Bulk Phase Exists: Two-Dimensional Phases, 291
3.5.1 Monomolecular Films, 291
3.6 Metastable Surface Phases, 292
3.7 Curved Surfaces, 293
3.7.1 Capillary Rise, 294
3.7.2 The Vapor Pressure of Curved Surfaces, 295
3.7.3 The Contact Angle and Adhesion, 296
3.7.4 Nucleation, 298
3.8 Thermodynamics of Adsorbed Monolayers, 301
3.8.1 Heat of Adsorption, 301
3.8.2 Two-Dimensional Phase Approximation, 302
3.8.3 Adsorption Isotherms, 302
3.8.4 Integral and Differential Heats of Adsorption, 307
3.8.5 Molecular and Dissociative Adsorption, 308
3.9 Summary and Concepts, 313
3.10 Problems, 314
References, 315

4 Dynamics at Surfaces

4.1 Introduction, 319
4.2 Surface Atom Vibrations, 319
  4.2.1 The Harmonic Oscillator Model, 319
  4.2.2 Vibrational Modes of Surface Atoms, 322
  4.2.3 Surface Mean-Square Displacements, 322
  4.2.4 Vibrations of Adsorbed Atoms and Molecules, 324
4.3 Elementary Processes of Gas–Surface Interaction, 329
  4.3.1 Adsorption. Energy Accommodation Coefficients, 331
  4.3.2 Sticking Probability, 333
  4.3.3 Models of Energy Transfer and Adsorption, 336
  4.3.4 Surface Diffusion, 340
  4.3.5 Mechanisms of Surface Diffusion, 343
  4.3.6 Desorption, 347
  4.3.7 Surface-Structure Sensitivity of Thermal Desorption, 349
  4.3.8 Collision-Induced Desorption, 350
  4.3.9 Electron-Beam-Induced Desorption, 351
  4.3.10 Photon-Stimulated Desorption, 351
  4.3.11 Ion-Beam-Induced Desorption and Sputtering, 351
4.4 Summary and Concepts, 352
4.5 Problems, 352
References, 354

5 Electrical Properties of Surfaces

5.1 The Surface Electron Potential, 362
5.2 The Surface Space Charge, 363
  5.2.1 The Surface Space Charge at the Solid–Vacuum Interface, 363
  5.2.2 Surface Space Charge at the Solid–Liquid Interface, 365
5.3 The Work Function, 366
  5.3.1 Effect of Surface Roughness on Work Function, 367
  5.3.2 Change of Work Function with Particle Size, 367
5.4 Adsorption-Induced Charge Transfer at Surfaces: Metals and Insulators, 369
  5.4.1 Charge Transfer at the Solid–Solid Interface, 375
  5.4.2 Gas-Phase Ion Production by Surface Ionization: Emission of Positive and Negative Ions, 376
5.5 Surface Electron Density of States, 378
5.6 Electron Excitation at Surfaces, 379
  5.6.1 Thermal Emission of Electrons from Surfaces, 380
5.7 Electron Emission from Surfaces by Incident Electron or Photon Beams, 382
7.6 Most Frequently Used Catalyst Materials, 459
7.7 Surface-Science Approach to Catalytic Chemistry, 461
  7.7.1 Techniques to Characterize and Study the Reactivity of Small-Area Catalyst Surfaces, 463
    7.7.1.1 High-Pressure Reactors, 463
    7.7.1.2 Comparison of the Reactivities of Small- and Large-Surface-Area Catalysts, 464
7.8 Case Histories of Surface Catalysts, 465
  7.8.1 Ammonia Synthesis, 465
    7.8.1.1 Thermodynamics and Kinetics, 465
    7.8.1.1.1 Kinetics, 466
    7.8.1.2 Catalyst Preparation, 466
    7.8.1.3 Activity for Ammonia Synthesis Using Transition Metals Across the Periodic Table, 467
    7.8.1.4 Surface Science of Ammonia Synthesis, 467
      7.8.1.4.1 Structure Sensitivity of Ammonia Synthesis, 467
      7.8.1.4.2 Kinetics of Dissociative Nitrogen Adsorption, 470
      7.8.1.4.3 Effects of Aluminum Oxide in Restructuring Iron Single-Crystal Surfaces for Ammonia Synthesis, 471
      7.8.1.4.4 Characterization of the Restructured Surfaces, 472
      7.8.1.4.5 Effect of Potassium on the Dissociative Chemisorption of Nitrogen on Iron Single-Crystal Surfaces in UHV, 475
      7.8.1.4.6 Temperature-Programmed Desorption Studies of Ammonia from Iron Surfaces in the Presence of Potassium, 477
      7.8.1.4.7 Effects of Potassium on Ammonia Synthesis Kinetics, 478
      7.8.1.4.8 Effects of Potassium on the Adsorption of Ammonia on Iron Under Ammonia Synthesis Conditions, 480
    7.8.1.5 Mechanism and Kinetics of Ammonia Synthesis, 482
  7.8.2 Hydrogenation of Carbon Monoxide, 483
    7.8.2.1 Thermodynamics, 483
    7.8.2.2 Catalyst Preparation, 488
    7.8.2.3 Methanation. Kinetics, Surface Science, Mechanisms, 489
    7.8.2.4 Promotion of the Rates of C—O Bond Hydrogenation by the Oxide–Metal Interface, 491
    7.8.2.5 Methanol Production. Kinetics, Surface Science, and Mechanisms, 494
    7.8.2.6 Production of Higher-Molecular-Weight Hydrocarbons. Kinetics, Surface Science, and Mechanisms, 495
7.8.2.7 Formation of Oxygenated Hydrocarbons from CO and H₂ and Organic Molecules, 500
7.8.3 Hydrocarbon Conversion on Platinum, 500
  7.8.3.1 Introduction, 500
  7.8.3.2 Structure Sensitivity of Hydrocarbon Conversion Reactions on Platinum Surfaces, 503
  7.8.3.3 Carbonaceous Overlayers, 505
  7.8.3.4 Catalysis in the Presence of a Strongly Adsorbed Overlayer, 507
  7.8.3.5 Structure Modifiers, 509
    7.8.3.5.1 Site Blocking by Sulfur, 509
    7.8.3.5.2 Ensemble Effect in Alloy Catalysis and the Creation of New Sites by Alloys, 510
  7.8.3.6 The Building of Improved Platinum and Other Metal Catalysts, 512
7.9 Summary and Concepts, 513
7.10 Problems, 513
References, 515

8 Mechanical Properties of Surfaces 596
  8.1 Introduction, 596
  8.2 Historical Perspective, 597
  8.3 Hardness, 597
  8.4 Mechanical Forces Required to Break a Chemical Bond, 600
  8.5 Adhesion, 602
  8.6 Surfaces in Relative Motion. Tribology, 603
    8.6.1 Friction and Sliding, 603
    8.6.2 Heating by Friction, 605
    8.6.3 Applications of Friction, 605
    8.6.4 Lubrication, 606
  8.7 Solid Lubricants. Coatings, 609
    8.7.1 Coatings: Mechanical Protection, 610
    8.7.2 Coatings: Chemical Protection, 611
  8.8 Crack Formation and Propagation. Fracture, 611
  8.9 Summary and Concepts, 613
  8.10 Problems, 613
References, 614

Answers to the Problems 619

Index 643