

Contents

Preface	xix
I. General Introduction	1
II. Capillarity	4
1. Surface Tension and Surface Free Energy	4
2. The Young–Laplace Equation	6
3. Some Experiments with Soap Films	8
4. The Treatment of Capillary Rise	10
A. Introductory Discussion	10
B. Exact Solutions to the Capillary Rise Problem	12
C. Experimental Aspects of the Capillary Rise Method	16
5. The Maximum Bubble Pressure Method	17
6. Detachment Methods	19
A. The Drop Weight Method	19
B. The Ring Method	21
C. Wilhelmy Slide Method	23
7. Methods Based on the Shape of Static Drops or Bubbles	26
A. Pendant Drop Method	27
B. Sessile Drop or Bubble Method	27
C. Sources of Other Deformed Shapes	30
8. Dynamic Methods of Measuring Surface Tension	33
A. Flow Methods	33
B. Capillary Waves	34
C. Maximum Bubble Pressure Method	35
9. Surface Tension Values as Obtained by Different Methods	35
10. Problems	40
General References	43
Textual References	43

III. The Nature and Thermodynamics of Liquid Interfaces	48
1. One-Component Systems.....	48
A. Surface Thermodynamic Quantities for a Pure Substance.....	48
B. The Total Surface Energy, E^S	51
C. The Effect of Curvature on Vapor Pressure and Surface Tension.....	53
D. The Effect of Pressure on Surface Tension.....	55
2. Structural and Theoretical Treatments of Liquid Interfaces.....	56
A. Further Development of the Thermodynamic Treatment of the Surface Region.....	58
B. Calculation of the Surface Energy and Structure of Interfaces.....	61
3. Orientation at Interfaces.....	63
4. The Surface Tension of Solutions.....	65
A. Binary Solutions.....	65
B. The Surface Tension of Polymeric Systems.....	69
5. Thermodynamics of Binary Systems: The Gibbs Equation.....	71
A. Definition of Surface Excess.....	71
B. The Gibbs Equation.....	73
C. The Dividing Surface.....	74
D. Other Surface Thermodynamic Relationships.....	76
6. Determination of Surface Excess Quantities.....	77
A. Experimental Methods.....	77
B. Historical Footnote and Commentary.....	79
C. Theoretical Calculation of Surface Excess Quantities.....	79
7. Gibbs Monolayers.....	80
A. The Two-Dimensional Ideal-Gas Law.....	82
B. Nonideal Two-Dimensional Gases.....	83
C. The Osmotic Pressure Point of View.....	86
D. Surface Elasticity.....	89
E. Traube's Rule.....	90
F. Some Further Comments on Gibbs Monolayers.....	91
8. Problems.....	92
General References.....	96
Textual References.....	96
IV. Surface Films on Liquid Substrates	101
1. Introduction.....	101
2. The Spreading of One Liquid on Another.....	104
A. Criteria for Spreading.....	104
B. Empirical and Theoretical Treatments.....	107
C. Kinetics of Spreading Processes.....	110
D. The Marangoni Effect.....	111
E. Lenses—Line Tension.....	112
3. Experimental Techniques for the Study of Monomolecular Films.....	113
A. Measurement of π	114
B. Surface Potentials.....	116

C. Measurement of Surface Viscosity	118
D. Optical Properties of Monolayers	126
E. Microscopic Evaluation of Monolayers	128
F. Diffraction Studies	130
4. States of Monomolecular Films	131
A. Gaseous Films	131
B. Gas-Liquid Transitions	132
C. Condensed Phases	133
D. The Solid State	135
E. Monolayer Collapse	136
F. Domain Shapes and Interactions	136
5. Mixed Films	140
6. Evaporation Rates through Monomolecular Films	146
7. Dissolution of Monolayers	148
8. Reactions in Monomolecular Films	151
A. Kinetics of Reactions in Films	151
B. Kinetics of Formation and Hydrolysis of Esters	152
C. Other Chemical Reactions	155
9. Problems	156
General References	158
Textual References	158
V. Electrical Aspects of Surface Chemistry	169
1. Introduction	169
2. The Electrical Double Layer	169
3. The Stern Layer	175
4. The Free Energy of a Diffuse Double Layer	179
5. Repulsion between Two Planar Double Layers	180
6. The Zeta Potential	183
A. Electrophoresis	183
B. Electroosmosis	185
C. Streaming Potential	187
D. Sedimentation Potential	188
E. Interrelationships in Electrokinetic Phenomena	188
F. Potential, Surface Charge, and Colloidal Stability	189
7. Electrocapillarity	192
A. Thermodynamics of the Electrocapillary Effect	195
B. Experimental Methods	197
C. Results for the Mercury-Aqueous Solution Interface	199
D. Effect of Uncharged Solutes and Changes of Solvent	200
E. Other Electrocapillary Systems	202
8. The Electrified Solid-Liquid Interface	202
A. Electrode-Solution Interface	203
B. Electrochemistry in Dispersed Phases	204
C. Photoelectrochemistry; Solar Energy Conversion	204
9. Types of Potentials and the Meaning of Potential Difference When Two Phases Are Involved	205
A. The Various Types of Potentials	205

B. Volta Potentials, Surface Potential Differences, and the Thermionic Work Function	208
C. Electrode Potentials	209
D. Irreversible Electrode Phenomena	212
10. Problems	215
General References	217
Textual References	218
VI. Long-Range Forces	225
1. Introduction	225
2. Forces between Atoms and Molecules	226
3. Long-Range Forces	232
A. The Microscopic Approach	232
B. The Retarded Dispersion Interaction	234
C. Experimental Measurements	236
4. Long-Range Forces in Solution	239
A. Dispersion Forces in Condensed Media	240
B. Electric Double-Layer Repulsion	240
C. Forces Due to Solvent Structure	243
D. Thin-Film Viscosity	246
5. Forces in Biological Systems	246
6. The Disjoining Pressure	247
7. Anomalous Water	248
8. Dipole-Induced Dipole Propagation	248
9. Problems	250
General References	252
Textual References	252
VII. Surfaces of Solids	257
1. Introduction	257
A. The Surface Mobility of Solids	257
B. Effect of Processing on the Condition of Solid Surfaces	259
2. Thermodynamics of Crystals	259
A. Surface Tension and Surface Free Energy	259
B. The Equilibrium Shape of a Crystal	261
C. The Kelvin Equation	262
3. Theoretical Estimates of Surface Energies and Free Energies	263
A. Covalently Bonded Crystals	263
B. Rare-Gas Crystals	264
C. Ionic Crystals	267
D. Molecular Crystals	269
E. Metals	269
4. Factors Affecting the Surface Energies and Surface Tensions of Actual Crystals	271
A. State of Subdivision	271
B. Deviations from Ideality	271
C. Fractal Surfaces	272
D. Dislocations	275

5. Experimental Estimates of Surface Energies and Free Energies . . .	278
A. Methods Depending on the Direct Manifestation of Surface Tensional Forces	278
B. Surface Energies from Heats of Solution	280
C. Relative Surface Tensions from Equilibrium Crystal Shapes	280
D. Dependence of Other Physical Properties on Surface Energy Changes at a Solid Interface	281
6. Reactions of Solid Surfaces	282
7. Problems	285
General References	287
Textual References	287
VIII. Surfaces of Solids: Microscopy and Spectroscopy	293
1. Introduction	293
2. The Microscopy of Surfaces	293
A. Optical and Electron Microscopy	293
B. Scanning Probe Microscopies	294
C. Field Emission and Field Ion Microscopies	299
D. Low-Energy Electron Diffraction (LEED)	302
3. Spectroscopic Methods	306
A. Auger Electron Spectroscopy (AES)	306
B. Photoelectron Spectroscopy (XPS, ESCA)	308
C. Ion Scattering (ISS, LEIS)	308
4. Other Techniques	311
5. Problems	312
General References	318
Textual References	319
IX. The Formation of a New Phase-Nucleation and Crystal Growth	328
1. Introduction	328
2. Classic Nucleation Theory	329
3. Experimental Nucleation Studies	336
A. One-Component Systems	336
B. Binary Systems and Solutions	338
4. Crystal Growth	339
5. Epitaxial Growth and Surface Nucleation	341
6. Problems	342
General References	343
Textual References	343
X. The Solid-Liquid Interface—Contact Angle	347
1. Introduction	347
2. Surface Energies from Solubility Changes	347
3. Surface Energies from Immersion, Adsorption, and Engulfment Studies	348
A. Enthalpy of Immersion	348

B. Surface Energy and Free Energy Changes from Adsorption Studies	350
C. Engulfment	352
4. Contact Angle	352
A. Young's Equation	352
5. Contact Angle Hysteresis	355
A. Heterogeneous Surfaces	355
B. Surface Roughness	358
C. Liquid-Surface Interactions: Surface Changes and Autophobicity	359
D. Dynamic Contact Angles	361
6. Experimental Methods and Measurements of Contact Angle	362
A. Experimental Methods to Measure Contact Angle	362
B. Results of Contact Angle Measurements	364
7. Theories of Contact Angle Phenomena	372
A. Thermodynamics of the Young Equation	372
B. Semiempirical Models: The Girifalco-Good-Fowkes-Young Equation	375
C. Potential-Distortion Model	377
D. The Microscopic Meniscus Profile	378
8. Problems	380
General References	382
Textual References	383
 XI. The Solid-Liquid Interface—Adsorption from Solution	390
1. Adsorption of Nonelectrolytes from Dilute Solution	390
A. Isotherms	391
B. Self-Assembling Monolayers	394
C. Multilayer Adsorption	397
2. Polymer Adsorption	398
3. Irreversible Adsorption	404
4. Surface Area Determination	405
5. Adsorption in Binary Liquid Systems	406
A. Adsorption at the Solid-Solution Interface	406
B. Heat of Adsorption at the Solid-Solution Interface	411
6. Adsorption of Electrolytes	412
A. Stern Layer Adsorption	412
B. Surfactant Adsorption	414
C. Counterion Adsorption-Ion Exchange	416
7. Photophysics and Photochemistry of the Adsorbed State	418
A. Photophysics of Adsorbed Species	418
B. Photochemistry at the Solid-Solution Interface	419
8. Problems	420
General References	422
Textual References	422

XII. Friction, Lubrication, and Adhesion	431
1. Introduction	431
2. Friction between Unlubricated Surfaces	431
A. Amontons' Law	431
B. Nature of the Contact between Two Solid Surfaces	432
C. Role of Shearing and Plowing—Explanation of Amontons' Law	434
D. Static and Stick-Slip Friction	436
E. Rolling Friction	437
3. Two Special Cases of Friction	437
A. Use of Skid Marks to Estimate Vehicle Speeds	437
B. Ice and Snow	438
4. Metallic Friction—Effect of Oxide Films	439
5. Friction between Nonmetals	440
A. Relatively Isotropic Crystals	440
B. Layer Crystals	440
C. Polymers	441
6. Some Further Aspects of Friction	442
7. Friction between Lubricated Surfaces	443
A. Boundary Lubrication	443
B. The Mechanism of Boundary Lubrication	447
C. Forces and Friction between Smooth Surfaces	450
8. Adhesion	452
A. Ideal Adhesion	452
B. Polymer Adhesion	455
C. Practical Adhesion	455
9. Problems	458
General References	459
Textual References	459
XIII. Wetting, Flotation, and Detergency	465
1. Introduction	465
2. Wetting	465
A. Wetting as a Contact Angle Phenomenon	465
B. Wetting as a Capillary Action Phenomenon	469
3. Water Repellency	470
4. Flotation	471
A. The Role of Contact Angle in Flotation	473
B. Flotation of Metallic Minerals	476
C. Flotation of Nonmetallic Minerals	478
5. Properties of Association Colloids—Micelles	479
6. Detergency	484
A. General Aspects of Soil Removal	484
B. Factors in Detergent Action	486
C. Adsorption of Detergents on Fabrics	487
D. Detergents in Commercial Use	488
7. Problems	489

General References	491
Textual References	491
XIV. Emulsions, Foams, and Aerosols	500
1. Introduction	500
2. Emulsions—General Properties	501
3. Factors Determining Emulsion Stabilization	503
A. Macroscopic Theories of Emulsion Stabilization	504
B. Specific Chemical and Structural Effects	505
C. Long-Range Forces as a Factor in Emulsion Stability	506
D. Stabilization of Emulsions by Solid Particles	510
4. The Aging and Inversion of Emulsions	510
A. Flocculation and Coagulation Kinetics	511
B. Inversion and Breaking of Emulsions	513
5. The Hydrophile–Lipophile Balance	513
6. Microemulsions	516
7. Foam Structure	519
8. Foam Drainage	521
A. Drainage of Single Films	521
B. Drainage of Foams	523
9. Foam Stability	524
10. Aerosols	525
11. Problems	526
General References	527
Textual References	528
XV. Macromolecular Surface Films, Charged Films, and Langmuir–Blodgett Layers	537
1. Introduction	537
2. Langmuir Films of Polymers	537
A. Adsorption and Phase Behavior	537
B. Dynamics and Rheology	541
3. Langmuir Films of Proteins	542
4. Films of Other Biological Substances	544
5. Membranes, Bilayers, and Vesicles	548
6. Films at Liquid–Liquid Interfaces and on Nonaqueous Liquid Surfaces	551
7. Charged Films	553
A. Equation of State for Charged Films	553
B. Influence of Subphase pH on the State of Monomolecular Films	557
8. Langmuir–Blodgett Films	557
A. Structure and Characterization of LB Films	558
B. Mixed LB Films and Films of Polymers and Colloids	560
C. Studies of the LB Deposition Process	562
9. Problems	562
General References	563
Textual References	563

XVI. The Solid-Gas Interface—General Considerations	571
1. Introduction	571
2. The Surface Area of Solids	572
A. The Meaning of Surface Area	572
B. Surfaces as Having a Fractal Geometry	574
C. Methods Requiring Knowledge of the Surface Free Energy or Total Energy	576
D. Rate of Dissolving	577
E. The Mercury Porosimeter	577
F. Other Methods of Surface Area Determination	580
3. The Structure and Chemical Nature of Solid Surfaces	581
4. The Nature of the Solid-Adsorbate Complex	582
A. Effect of Adsorption on Adsorbate Properties	582
B. Effect of the Adsorbate on the Adsorbent	589
C. The Adsorbate-Adsorbent Bond	591
5. Problems	592
General References	593
Textual References	594
 XVII. Adsorption of Gases and Vapors on Solids	 599
1. Introduction	599
2. The Adsorption Time	601
3. The Langmuir Adsorption Isotherm	603
A. Kinetic Derivation	604
B. Statistical Thermodynamic Derivation	606
C. Adsorption Entropies	609
D. Lateral Interaction	613
E. Experimental Applications of the Langmuir Equation	615
4. Experimental Procedures	615
5. The BET and Related Isotherms	617
A. Derivation of the BET Equation	618
B. Properties of the BET Equation	620
C. Modifications of the BET Equation	621
6. Isotherms Based on the Equation of State of the Adsorbed Film	622
A. Film Pressure-Area Diagrams from Adsorption Isotherms	623
B. Adsorption Isotherms from Two-Dimensional Equations of State	623
7. The Potential Theory	625
A. The Polanyi Treatment	625
B. Isotherms Based on an Assumed Variation of Potential with Distance	627
C. The Polarization Model	629
8. Comparison of the Surface Areas from the Various Multilayer Models	630
9. The Characteristic Isotherm and Related Concepts	631
10. Chemical Physics of Submonolayer Adsorption	634
11. Phase Transformations in the Multilayer Region	639
12. Thermodynamics of Adsorption	641

A. Theoretical Considerations	641
B. Experimental Heats and Energies of Adsorption	647
13. Critical Comparison of the Various Models for Adsorption	652
A. The Langmuir-BET Model	652
B. Two-Dimensional Equation of State Treatments	653
C. The Potential Model	654
14. Physical Adsorption on Heterogeneous Surfaces	655
A. Distribution of Site Energy Patches	655
B. Thermodynamics of Adsorption on Heterogeneous Surfaces	659
C. Point versus Patch Site Energy Distributions	660
D. Geometric Heterogeneity	660
15. Rate of Adsorption	661
16. Adsorption on Porous Solids—Hysteresis	662
A. Molecular Sieves	662
B. Capillary Condensation	664
C. Micropore Analysis	669
17. Problems	672
General References	676
Textual References	676

XVIII. Chemisorption and Catalysis **685**

1. Introduction	685
2. Chemisorption: The Molecular View	686
A. LEED Structures	686
B. Surface Microscopies	688
C. Spectroscopy of Chemisorbed Species	689
D. Work Function and Related Measurements	693
E. Programmed Desorption	694
3. Chemisorption Isotherms	698
A. Variable Heat of Adsorption	698
B. Effect of Site and Adsorbate Coordination Number	701
C. Adsorption Thermodynamics	702
4. Kinetics of Chemisorption	703
A. Activation Energies	703
B. Rates of Adsorption	705
C. Rates of Desorption	707
5. Surface Mobility	709
6. The Chemisorption Bond	712
A. Some General Aspects	712
B. Metals	715
C. Semiconductors	717
D. Acid-Base Systems	718
7. Mechanisms of Heterogeneous Catalysis	720
A. Adsorption or Desorption as the Rate-Determining Step	720
B. Reaction within the Adsorbed Film as the Rate-Determining Step	722

8. Influence of the Adsorption Isotherm on the Kinetics of Heterogeneous Catalysis	724
A. Unimolecular Surface Reactions	724
B. Bimolecular Surface Reactions	726
9. Mechanisms of a Few Catalyzed Reactions	728
A. Ammonia Synthesis	729
B. Fischer-Tropsch Reactions	730
C. Hydrogenation of Ethylene	733
D. Catalytic Cracking of Hydrocarbons and Related Reactions ..	734
E. Oxidation of CO	735
F. Photochemical and Photoassisted Processes at Surfaces	738
10. Problems	739
General References	742
Textual References	744
Index	757