

Contents

I. General Introduction	1
II. Capillarity	4
1. Surface Tension and Surface Free Energy	4
2. The Equation of Young and Laplace	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	17
5. The Maximum Bubble Pressure Method	18
6. The Drop Weight Method	20
7. The Ring Method	23
8. Wilhelmy Slide Method	24
9. Methods Based on the Shape of Static Drops or Bubbles	27
A. Pendant Drop Method	28
B. Sessile Drop or Bubble Method	29
C. Deformed Interfaces	34
10. Dynamic Methods of Measuring Surface Tension	36
A. Flow Methods	37
B. Capillary Waves	38
11. Surface Tension Values as Obtained by Different Methods	39
12. Problems	39
General References	45
Textual References	46
III. The Nature and Thermodynamics of Liquid Interfaces	49
1. One-Component Systems	49
A. Surface Thermodynamic Quantities for a Pure Substance	49
B. The Total Surface Energy, E^s	52
C. Change in Vapor Pressure for a Curved Surface	54
D. Effect of Curvature on Surface Tension	55
E. Effect of Pressure on Surface Tension	56
2. The Structural and Theoretical Treatment of Liquid Interfaces	56
A. Further Development of the Thermodynamic Treatment of the Surface Region	59

B. Calculation of the Surface Energy and Free Energy of Liquids	61
3. Orientation at Interfaces	63
4. The Surface Tension of Solutions	65
5. Thermodynamics of Binary Systems—The Gibbs Equation	70
A. Definition of Surface Excess	70
B. The Gibbs Equation	72
C. Alternate Methods of Locating the Dividing Surface	73
D. The Thermodynamics of Surfaces Using the Concept of a Surface Phase	76
E. Other Surface Thermodynamic Relationships	77
6. Verification of the Gibbs Equation—Direct Measurements of Surface Excess Quantities	78
A. The Microtome Method for Measuring Surface Excess	79
B. The Tracer Method for Measuring Surface Excess	80
C. Ellipsometric Method for Measuring Surface Excess	82
7. Gibbs Monolayers	83
A. The Two-Dimensional Ideal Gas Law	84
B. Nonideal Two-Dimensional Gases	86
C. The Osmotic Pressure Point of View	88
D. Dynamic Surface Properties of Solutions	90
E. Traube's Rule	92
F. Some Further Comments on Gibbs Monolayers	93
8. Problems	93
General References	96
Textual References	97
IV. Surface Films on Liquid Substrates	100
1. Introduction	100
2. The Spreading of One Liquid on Another	103
A. Criteria for Spreading	104
B. Kinetics of Spreading Processes	109
C. Lenses	111
3. Experimental Techniques for the Study of Monomolecular Films	111
A. Measurement of π	112
B. Surface Potentials	114
C. Surface Viscosities	117
D. Optical Properties of Monolayers	121
E. The Ultramicroscope	124
F. Electron Microscopy and Diffraction	124
G. Other Techniques	124
4. States of Monomolecular Films	124
5. Correspondence between π and a Three-Dimensional Pressure	128
6. Further Discussion of the States of Monomolecular Films	128
A. Gaseous Films	128
B. The L_1 - G Transition	129
C. The Liquid Expanded State	130
D. Intermediate and L_2 Films	132

E. The Solid State	133
F. Effect of Changes in the Aqueous Substrate	134
G. Rheology of Monolayers	135
H. General Correlations between Molecular Structure and the Type of Film Formed	136
7. Mixed Films	139
8. Evaporation Rates through Monomolecular Films	143
9. Rate of Dissolving of Monolayers	146
10. Reactions in Monomolecular Films	148
A. Kinetics of Reactions in Films	148
B. Kinetics of Formation and Hydrolysis of Esters	150
C. Other Chemical Reactions	152
11. Films of Biological and Polymeric Materials	153
A. General Properties and Structure	153
B. Reactions of Protein Films	157
C. Films at the Oil-Water Interface	158
D. Polymer Films	160
12. Films at Liquid-Liquid Interfaces and on Liquid Surfaces Other than Water	161
13. Charged Films	162
A. Equation of State of a Charged Film	162
B. Interfacial Potentials	167
14. Capillary Waves	168
15. Films Deposited on Solids	172
A. Built-Up Films	172
B. Monolayers	173
16. Problems	174
General References	176
Textual References	176
 V. Electrical Aspects of Surface Chemistry	 185
1. Introduction	185
2. The Electrical Double Layer	185
3. Units—the SI System	189
A. Potential	190
B. Coulomb's Law and Equations of Electrostatics	190
4. The Stern Treatment of the Electrical Double Layer	191
5. Further Treatment of the Stern and Diffuse Layers	193
6. The Free Energy of a Diffuse Double Layer	195
7. Repulsion between Two Plane Double Layers	196
8. The Zeta Potential	198
A. Electrophoresis	199
B. Electroosmosis	200
C. Streaming Potential	202
D. Sedimentation Potential	203
E. Further Developments in the Theory of Electrokinetic Phenomena	204
F. General Observation of ζ Potentials—Stability of Colloids	204

9. Electrocapillarity	206
A. Thermodynamics of the Electrocapillary Effect	208
B. Experimental Methods	211
C. Results for the Mercury–Aqueous Solution Interface	212
D. Effect of Uncharged Solutes and Changes of Solvent	214
E. Other Electrocapillary Systems	217
10. The Electrified Solid–Liquid Interface	217
A. Electrode–Solution Interface	218
B. Silver Halide–Solution Interface	218
11. Types of Potentials and the Meaning of Potential Differences When Two Phases are Involved	219
A. The Various Types of Potentials	219
B. Volta Potentials, Surface Potential Differences, and the Thermionic Work Function	221
C. Electrode Potentials	222
D. Irreversible Electrode Phenomena	224
12. Problems	227
General References	229
Textual References	229
 VI. Long-Range Forces	 232
1. Introduction	232
2. Forces between Atoms and Molecules	233
3. The SI System	237
4. Long-Range Forces	238
A. Attraction Due to the Dispersion Effect	239
B. The Retarded Dispersion Attraction	240
C. Experimental Verification	241
5. Long-Range Forces in Solution	244
A. Dispersion Attraction in a Condensed Medium	244
B. Electrical Double Layer Repulsion	245
C. Other Experimental Approaches	247
6. The Disjoining Pressure	248
7. Dipole-Induced Dipole Propagation	249
8. Evidence for Deep Surface Orientation	251
9. Anomalous Water	253
10. Problems	254
General References	256
Textual References	257
 VII. Surfaces of Solids	 260
1. Introduction	260
A. The Surface Mobility of Solids	260
B. Effect of Past History on the Condition of Solid Surfaces	262
2. Thermodynamics of Crystals	263
A. Surface Tension and Surface Free Energy	263
B. The Equilibrium Shape of a Crystal	264
C. The Kelvin Equation	266

3. Theoretical Estimates of Surface Energies and Free Energies	266
A. Covalently Bonded Crystals	266
B. Rare Gas Crystals	267
C. Ionic Crystals	270
D. Molecular Crystals	273
E. Metals	273
4. Factors Affecting the Surface Energies and Surface Tensions of Actual Crystals	274
A. State of Subdivision	274
B. Deviations from Ideal Considerations	275
C. Dislocations	277
D. Surface Heterogeneity	280
5. Experimental Estimates of Surface Energies and Free Energies	280
A. Methods Depending on the Direct Manifestation of Surface Tensional Forces	280
B. Surface Energies and Free Energies from Heats of Solution	282
C. Relative Surface Tensions from Equilibrium Shapes of Crystals	283
D. Dependence of Other Physical Properties on Surface Energy Changes at a Solid Interface	284
6. Reactions of Solid Surfaces	285
7. Problems	287
General References	289
Textual References	290
VIII. Surfaces of Solids: Microscopy and Spectroscopy	294
1. Introduction	294
2. Microscopy of Surfaces	294
A. Optical and Electron Microscopy	294
B. Scanning Electron Microscope	299
C. Field Emission and Field Ion Microscopy	300
3. Low Energy Electron Diffraction (LEED)	305
4. Spectroscopic Methods	310
A. Auger Electron Spectroscopy (AES)	310
B. Photoelectron Spectroscopy (ESCA)	311
C. Ion Scattering (ISS, LEIS)	312
5. Problems	315
General References	316
Textual References	316
IX. The Formation of a New Phase—Nucleation and Crystal Growth	319
1. Introduction	319
2. Classical Nucleation Theory	320
3. Results of Nucleation Studies	325
4. Crystal Growth	327
5. Problems	329
General References	329
Textual References	329

X. The Solid-Liquid Interface—Contact Angle	332
1. Introduction	332
2. Surface Free Energies from Solubility Changes	332
3. Surface Energy and Free Energy Differences from Immersion, Adsorption, and Engulfment Studies	334
A. Heat of Immersion	334
B. Surface Energy and Free Energy Changes from Adsorption Studies	335
C. Engulfment	337
4. Contact Angle	338
A. Young's Equation	338
B. Nonuniform Surfaces	340
5. Experimental Methods and Results of Contact Angle Measurements	341
A. Measurement of Contact Angle	341
B. Hysteresis in Contact Angle Measurements	344
C. Results of Contact Angle Measurements	348
6. Some Theoretical Aspects of Contact Angle Phenomena	354
A. Thermodynamics of the Young Equation	354
B. Semiempirical Models—The Girifalco-Good-Fowkes-Young Equation	357
C. Potential-Distortion Model	359
D. The Microscopic Meniscus Profile	360
7. Problems	361
General References	364
Textual References	364
XI. The Solid-Liquid Interface—Adsorption from Solution	369
1. Adsorption of Nonelectrolytes from Dilute Solution	369
A. Adsorption Isotherms	370
B. Qualitative Results of Adsorption Studies—Traube's Rule	373
C. Multilayer Adsorption	377
2. Adsorption of Polymers	378
3. Surface Area Determination	381
4. Adsorption in Binary Liquid Systems	382
A. Adsorption at the Solid-Solution Interface	382
B. Heat of Adsorption at the Solid-Solution Interface	388
5. Adsorption of Electrolytes	388
A. Stern Layer Adsorption	389
B. Surface Areas from Negative Adsorption	393
C. Counterion Adsorption—Ion Exchange	394
6. Problems	396
General References	398
Textual References	399
XII. Friction and Lubrication—Adhesion	402
1. Introduction	402
2. Friction Between Unlubricated Surfaces	402
A. Amontons' Law	402

B. Nature of the Contact Between Two Solid Surfaces	403
C. Role of Shearing and Plowing—Explanation of Amontons' Law	405
D. Static and "Stick-Slip" Friction	407
E. Rolling Friction	408
3. Two Special Cases of Friction	409
A. Use of Skid Marks to Estimate Vehicle Speeds	409
B. Ice and Snow	410
4. Metallic Friction—Effect of Oxide Films	411
5. Friction Between Nonmetals	412
A. Relatively Isotropic Crystals	412
B. Layer Crystals	412
C. Plastics	413
6. Some Further Aspects of Friction	413
7. Friction Between Lubricated Surfaces	415
A. Boundary Lubrication	415
B. The Mechanism of Boundary Lubrication	417
8. Adhesion	424
A. Ideal Adhesion	424
B. Practical Adhesion	425
9. Problems	428
General References	429
Textual References	430
XIII. Wetting, Flotation, and Detergency	433
1. Introduction	433
2. Wetting	433
A. Wetting as a Contact Angle Phenomenon	433
B. Wetting as a Capillary Action Phenomenon	435
C. Tertiary Oil Recovery	436
3. Water Repellency	437
4. Flotation	438
A. The Role of Contact Angle in Flotation	439
B. Flotation of Metallic Minerals	443
C. Flotation of Nonmetallic Minerals	444
5. Detergency	446
A. General Aspects of Soil Removal	446
B. Properties of Colloidal Electrolyte Solutions	448
C. Factors in Detergent Action	452
D. Adsorption of Detergents on Fabrics	454
E. Detergents in Commercial Use	455
6. Problems	456
General References	458
Textual References	458
XIV. Emulsions and Foams	461
1. Introduction	461
2. Emulsions—General Properties	462

3. Factors Determining Emulsion Stability	464
A. Macroscopic Theories of Emulsion Stabilization	464
B. Specific Chemical and Structural Effects	466
C. Long-Range Forces as a Factor in Emulsion Stability	467
D. Stabilization of Emulsions by Solid Particles	470
4. The Aging and Inversion of Emulsions	470
A. Flocculation and Coagulation Kinetics	471
B. Inversion and Breaking of Emulsions	472
5. Spontaneous Emulsification—Micellar or Microemulsions	474
6. The Hydrophile–Lipophile Balance	475
7. Practical Aspects of Emulsions	477
8. Foams—The Structure of Foams	478
9. Foam Drainage	480
A. Drainage of Single Films	481
B. Drainage of Foams	483
10. The Stability of Foams	484
11. Foaming Agents and Foams of Practical Importance	486
12. Problems	486
General References	487
Textual References	488
XV. The Solid–Gas Interface—General Considerations	492
1. Introduction	492
2. The Surface Area of Solids	493
A. The Meaning of Surface Area	493
B. Methods Requiring Knowledge of the Surface Free Energy or Total Energy	495
C. Rate of Dissolving	496
D. The Mercury Porosimeter	498
E. Other Methods of Surface Area Estimation	501
3. The Structural and Chemical Nature of Solid Surfaces	502
4. The Nature of the Solid–Adsorbate Complex	503
A. Effect of Adsorption on Adsorbate Properties	503
B. Effect of the Adsorbate on the Adsorbent	510
C. The Adsorbate–Adsorbent Bond	512
5. Problems	512
General References	513
Textual References	514
XVI. Adsorption of Gases and Vapors on Solids	517
1. Introduction	517
2. The Adsorption Time	519
3. The Langmuir Adsorption Isotherm	521
A. Kinetic Derivation	521
B. Statistical Thermodynamic Derivation	523
C. Adsorption Entropies	526
D. Lateral Interaction	529
E. Experimental Applications of the Langmuir Equation	531
4. Experimental Procedures	531

5. The BET and Related Isotherms	533
A. Derivation of the BET Equation	535
B. Properties of the BET Equation	537
C. Modifications of the BET Equation	538
6. Isotherms Based on the Equation of State of the Adsorbed Film	539
A. Film Pressure–Area Diagrams from Adsorption Isotherms	539
B. Adsorption Isotherms from Two-Dimensional Equations of State	540
7. The Potential Theory	543
A. The Polanyi Treatment	543
B. Correspondence between the Potential Theory and That of a Two-Dimensional Film	545
C. Isotherms Based on an Assumed Variation of Potential with Distance	546
D. The Polarization Model	547
8. Comparison of the Surface Areas from the Various Multilayer Models	549
9. The Characteristic Isotherm and Related Concepts	551
10. Potential Theory as Applied to Submonolayer Adsorption	553
11. Adsorption Steps and Phase Transformations	556
12. Adsorption in the Case of a Nonwetting System	559
13. Thermodynamics of Adsorption	559
A. Theoretical Considerations	559
B. Experimental Heats and Entropies of Adsorption	565
14. Critical Comparison of the Various Models for Adsorption	570
A. The Langmuir–BET Model	570
B. Two-Dimensional Equation of State Treatments	571
C. The Potential Model	572
15. Adsorption on Heterogeneous Surfaces	573
A. Site Energy Distributions	574
B. Thermodynamics of Adsorption on Heterogeneous Surfaces	580
16. Rate of Adsorption	581
17. Adsorption on Porous Solids—Hysteresis	582
A. Molecular Sieves	582
B. Capillary Condensation	584
C. Micropore Analysis	590
18. Problems	591
General References	594
Textual References	595

XVII. Chemisorption and Catalysis 601

1. Introduction	601
2. Chemisorption—The Molecular View	602
A. LEED Structures	602
B. Spectroscopy of Chemisorbed Species	603
C. Work Function and Related Measurements	603
D. Flash Desorption	605

3. Chemisorption Isotherms	607
A. Variable Heat of Adsorption	607
B. Effect of Site and Adsorbate Coordination Number	610
C. Adsorption Thermodynamics	611
4. Kinetics of Chemisorption	611
A. Activation Energies	611
B. Rates of Adsorption	613
C. Rates of Desorption	615
5. Surface Mobility	616
6. The Chemisorption Bond	618
A. The Localized Bond Approach	618
B. Metals	621
C. Semiconductors	623
D. Acid-Base Systems	626
7. Mechanisms of Heterogeneous Catalysis	627
A. Adsorption or Desorption as the Rate-Determining Step	628
B. Reaction Within the Adsorbed Film as the Rate-Determining Step	629
8. Influence of the Adsorption Isotherm on the Kinetics of Heterogeneous Catalysis	631
A. Unimolecular Surface Reactions	632
B. Bimolecular Surface Reactions	633
C. Effect of Isotherm Complexities	634
9. Mechanisms of a Few Catalyzed Reactions	634
A. Ammonia Synthesis	634
B. Fischer-Tropsch Type Reactions	636
C. Hydrogenation of Ethylene	637
D. Catalytic Cracking of Hydrocarbons and Related Reactions	639
E. Photochemical and Photoassisted Processes at Surfaces	640
10. Problems	641
General References	642
Textual References	643
Index	649