

Contents

✓ I. Capillarity	1
✓ 1 Surface Tension and Surface Free Energy	4
✓ 2 The Equation of Young and Laplace	6
3 Some Experiments with Soap Films	9
4. The Treatment of Capillary Rise	9
A. Introductory Discussion	12
B. Exact Solution to the Capillary Rise Problem	17
C. Experimental Aspects of the Capillary Rise Method	18
D. Variations in the Capillary Rise Method	18
5. The Maximum Bubble Pressure Method	21
✓ 6 The Drop Weight Method	24
✓ 7 The Ring Method	26
✓ 8. Wilhelmy Slide Method	28
9. Methods Based on the Shape of Static Drops or Bubbles	28
A. Sessile Drop or Bubble Method	30
B. Pendant Drop Method	37
10. Dynamic Methods of Measuring Surface Tension	37
A. Flow Methods	40
B. Capillary Waves	41
11. Miscellaneous Methods of Surface Tension Measurement	42
✓ 12. Surface Tension Values as Obtained by Different Methods	46
13. Problems	49
General References	49
Textual References	49
✓ III The Nature and Thermodynamics of Liquid Interfaces	53
1. One-Component Systems	53
A. Surface Thermodynamic Quantities and the Temperature Dependence of the Surface Free Energy	56
B. The Total Surface Energy, E^s	58
C. Change in Vapor Pressure for a Curved Surface	60
D. Effect of Curvature on Surface Tension	60
E. Effect of Pressure on Surface Tension	61
F. Effects of Other Variables	61
✓ 2 The Structural and Theoretical Treatment of Liquid Interfaces	61
A. Further Development of the Thermodynamic Treatment of the Surface Region	61
B. Calculation of the Surface Energy and Free Energy of Liquid	61
3. Orientation at Interfaces	71

4.	The Surface Tension of Solutions	
5.	Thermodynamics of Binary Systems—the Gibbs Equation	
	A. Definition of Surface Excess	
	✓ B. The Gibbs Equation	
	C. Alternate Methods of Locating the Dividing Surface	
	D. Limiting Relationships between the Various Surface Excess Quantities	
	E. The Thermodynamics of Surfaces Using the Concept of a Surface Phase	
6.	Verification of the Gibbs Equation—Direct Measurements of Surface Excess Quantities	
	A. The Microtome Methods for Measuring Γ	
	B. The Tracer Method for Measuring Surface Excess	
	C. An Apparent Violation of the Gibbs Equation	
7.	Gibbs Monolayers	
	A. The Two-Dimensional Ideal Gas Law	
	B. Nonideal Two-Dimensional Gases	
	C. The Osmotic Pressure Point of View	
	D. Traube's Rule	
	E. Some Further Comments on Gibbs Monolayers	
8.	Problems	
	General References	
	Textual References	
III.	Surface Films on Liquid Substrates	
1.	Introduction	
2.	The Spreading of One Liquid on Another	
	A. Criteria for Spreading	
	B. Kinetics of Spreading Processes	
	C. Lenses	
3.	Experimental Techniques for the Study of Monomolecular Films	
	A. Measurement of π	
	B. Surface Potentials	
	C. Surface Viscosities	
	D. Optical Properties of Monolayers	
	E. The Ultramicroscope	
	F. Electron Microscopy and Diffraction	
	G. Other Techniques	
4.	States of Monomolecular Films	
5.	Correspondence between π and a Three-Dimensional Pressure	
6.	Further Discussion of the States of Monomolecular Films	
	A. Gaseous Films	
	B. The Liquid Expanded State	
	C. Intermediate and L_2 Films	
	D. The Solid State	
	E. Viscosities of Monolayers	
	F. Effect of Changes in the Aqueous Substrate	

CONTENTS

xiii

G. General Correlations between Molecular Structure and the Type of Film Formed	155
7. Mixed Films	157
8. Evaporation Rates through Monomolecular Films	160
9. Reactions in Monomolecular Films	164
A. Kinetics of Reactions in Films	164
B. Kinetics of Formation and Hydrolysis of Esters	167
C. Reactions at a Double Bond	170
D. Other Chemical Reactions	171
E. Rate of Dissolving of Monolayers	172
10. Protein and Polymer Films	173
A. Spreading Techniques	174
B. Physical Properties of Protein Films	175
C. Reactions of Protein Films	179
D. Protein Films at Oil-Water Interfaces	180
E. Polymer Films	181
11. Films at Liquid-Liquid Interfaces and on Liquid Surfaces Other than Water	182
12. Charged Films	184
A. Equation of State of a Charged Film	184
B. Interfacial Potentials	189
13. Capillary Waves	191
14. Films Deposited on Solids	195
A. Built-Up Films	195
B. Monolayers	196
15. Problems	198
General References	201
Textual References	201
 IV. Electrical Aspects of Surface Chemistry	 209
1. Introduction	209
2. The Electrical Double Layer	210
3. The Stern Treatment of the Electrical Double Layer	214
4. The Free Energy of a Diffuse Double Layer	217
5. Repulsion between Two Plane Double Layers	218
6. The Nature of the Different Parts of the "Double" Layer	219
7. Further Treatment of the Stern and Diffuse Layers	222
8. The Zeta Potential	223
A. Electrophoresis	224
B. Electroosmosis	225
C. Streaming Potential	227
D. Sedimentation Potential	228
E. Further Developments in the Theory of Electrokinetic Phenomena	229
F. General Observation on ζ Potentials—Stability of Colloids	229
9. Electrocapillarity	231
A. Thermodynamics of the Electrocapillary Effect	234
B. Experimental Methods	237

CONTENTS

C. Results for the Mercury–Aqueous Solution Interface	
D. Effect of Uncharged Solutes and Changes of Solvent	
E. Other Electrocapillary Systems.	
F. The Potential Difference between Two Phases	
10. Types of Potentials and the Meaning of Potential Differences When Two Phases are Involved.	
A. The Various Types of Potentials	
B. Volta Potentials, Surface Potential Differences, and the Thermionic Work Function	
C. Electrochemical and Electrode Potentials	
D. Irreversible Electrode Phenomena	
11. Problems	
General References	
Textual References	
V. Surfaces of Solids	
1. Introduction	
A. The Surface Mobility of Solids—Sintering.	
B. Effect of Past History on the Condition of Solid Surfaces	
2. Thermodynamics of Crystals	
A. Surface Tension and Surface Free Energy	
B. The Equilibrium Shape of a Crystal	
C. The Kelvin Equation	
3. Theoretical Estimates of Surface Energies and Free Energies	
A. Covalently Bonded Crystals	
B. Rare Gas Crystals	
C. Ionic Crystals	
D. Molecular Crystals	
E. Metals	
4. Factors Affecting the Surface Energies and Surface Tensions of Actual Crystals	
A. State of Subdivision	
B. Deviations from Ideal Considerations.	
C. Dislocations	
D. Surface Heterogeneity	
5. Experimental Estimates of Surface Energies and Free Energies	
A. Methods Depending on the Direct Manifestation of Surface Tensional Forces	
B. Surface Energies and Free Energies from Heats of Solutions	
C. Relative Surface Tensions from Equilibrium Shapes of Crystals	
D. Dependence of Other Physical Properties on Surface Energy Changes at a Solid Interface.	
6. Experimental Methods for Determining Surface Structure	
A. Low Energy Electron Diffraction.	
B. Field Emission and Field Ion Microscopy	
C. Other Methods.	
7. Reactions of Solid Surfaces	
8. Problems.	

CONTENTS

xv

General References	312
Textual References	312
VI. Long Range Forces	317
1. Forces between Atoms and Molecules	317
2. Qualitative Evidence for Long Range Forces	322
A. Evidence for Deep Surface Orientation	322
B. Apparent Long Range Interaction between Macromolecules	323
C. Entropy Considerations in the Case of Highly Asymmetric Molecules	326
3. Long Range Forces	329
A. Dispersion or van der Waals Force	329
B. Electrical Double Layer Interactions	333
C. Dipole-Induced Dipole Propagation	334
4. Experimental Verification of Long Range Forces	335
A. Direct Measurement of Long Range van der Waals Attraction	335
B. The Balance of Forces in a Soap Film	337
C. Flocculation of Lyophobic Colloids	337
5. Problems	339
General References	342
Textual References	342
VII. The Solid-Liquid Interface—Contact Angle—Nucleation	345
1. Introduction	345
2. Surface Free Energies from Solubility Changes	346
3. Surface Energy and Free Energy Differences from Immersion and Adsorption Studies	348
A. Heat of Immersion	348
B. Surface Energy and Free Energy Changes from Adsorption Studies	350
4. Contact Angle Phenomena	352
A. Contact Angles	352
B. Measurement of Contact Angle	355
C. Nonuniform Surfaces	357
D. Hysteresis in Contact Angle Measurements	359
E. Results of Contact Angle Measurements	363
5. Some Theoretical Aspects of Contact Angle Phenomena	369
A. Thermodynamics of the Young and Dupré Equation	369
B. Semiempirical Models for Contact Angle Phenomena	372
★ <u>B</u> The Formation of a New Phase—Nucleation and Crystal Growth	375
<u>A</u> Classical Nucleation Theory	375
B. Results of Nucleation Studies	382
C. Crystal Growth	385
D. Some Further Remarks on Nucleation Theory	387
7. Problems	388
General References	391
Textual References	391

VIII. The Solid-Liquid Interface. Adsorption from Solution	397
1. Adsorption of Nonelectrolytes from Dilute Solution	397
A. Adsorption Isotherms.	398
B. Qualitative Results of Adsorption Studies—Traube's Rule.	402
C. Multilayer Adsorption	407
2. Adsorption of Polymers	409
3. Surface Area Determination	412
④ 4. Adsorption in Binary Liquid Systems	414
A. Adsorption at the Solid-Solution Interface.	414
B. Interrelations between Adsorption at Different Interfaces	418
C. Heat of Adsorption at the Solid-Solution Interface	422
5. Adsorption of Electrolytes	423
A. Stern Layer Adsorption	423
B. Counterion Adsorption—Ion Exchange	427
6. Problems.	429
General References	432
Textual References	432
IX. Friction and Lubrication; Adhesion.	437
1. Introduction	437
2. Friction between Unlubricated Surfaces	437
A. Amontons' Law	437
B. Nature of the Contact between Two Solid Surfaces.	438
C. Role of Shearing and Plowing; Explanation of Amontons' Law	441
D. Static and "Stick-Slip" Friction	444
3. Two Special Cases of Friction.	445
A. Use of Skid Marks to Estimate Vehicle Speeds.	445
B. Ice and Snow	446
4. Metallic Friction—Effect of Oxide Films	447
5. Friction between Nonmetals	449
A. Relatively Isotropic Crystals.	449
B. Layer Crystals.	449
C. Plastics	450
6. Some Further Aspects of Friction	451
7. Friction between Lubricated Surfaces	453
A. Boundary Lubrication	453
B. The Mechanism of Boundary Lubrication	457
8. Adhesion.	465
A. Ideal Adhesion.	465
✓ B. Practical Adhesion	466
9. Problems.	468
General References	470
Textual References	470
⑩ X. Wetting, Flotation, and Detergency	473
1. Introduction	473
② Wetting	473
A. Wetting as a Contact Angle Phenomenon	473
B. Wetting as a Capillary Action Phenomenon	475

D. Surface Areas from the Electrical Potential of an Adsorbed Layer	5
E. The Mercury Porosimeter	5
F. Other Methods of Surface Area Estimation	5
3. The Structural and Chemical Nature of Solid Surfaces	5
4. The Nature of the Solid-Adsorbate Complex	5
A. Effect of Adsorption on Adsorbate Properties	5
B. Effect of the Adsorbate on the Adsorbent	5
C. The Adsorbate-Adsorbent Bond	5
5. Problems	5
General References	5
Textual References	5
XIII. Adsorption of Gases and Vapors on Solids	
1. Introduction	
2. The Adsorption Time	
3. The Langmuir Adsorption Isotherm	
A. Kinetic Derivation	
B. Statistical Thermodynamic Derivation	
C. Adsorption Entropies	
D. Lateral Interaction	
E. Experimental Applications of the Langmuir Equation	
4. Experimental Procedures	
5. The BET and Related Isotherms	
A. Derivation of the BET Equation	
B. Properties of the BET Equation	
C. Modifications of the BET Equation	
6. Isotherms Based on the Equation of State of the Adsorbed Film	
A. Types of Force-Area Diagrams from Adsorption Isotherms	
B. Adsorption Isotherms from Two-Dimensional Equations of State	
7. The Potential Theory	
A. The Polanyi Treatment	
B. Correspondence between the Potential Theory and that of a Two-Dimensional Film	
C. Isotherms Based on an Assumed Variation of Potential with Distance	
D. The Polarization Model	
8. Comparison of the Surface Areas from the Various Multilayer Models—The Characteristic Isotherm	
9. Surface Areas from Submonolayer Adsorption	
10. Adsorption Steps and Phase Transformations	
11. Thermodynamics of Adsorption	
A. Theoretical Considerations	
B. Experimental Heats and Entropies of Adsorption	
12. Critical Comparison of the Various Models for Adsorption	

CONTENTS

xix

A. The Langmuir-BET Model	620
B. Two-Dimensional Equation of State Treatments	622
C. The Potential Model	622
13. Adsorption on Heterogeneous Surfaces	625
A. Site Energy Distributions	625
B. Thermodynamics of Adsorption on Heterogeneous Surfaces	632
14. Rate of Adsorption	634
15. Adsorption on Porous Solids—Hysteresis.	634
A. Molecular Sieves	634
B. Capillary Condensation	637
16. Problems	641
General References	643
Textual References	644
XIV. Chemisorption and Catalysis	649
1. Introduction	649
2. Chemisorption Isotherms.	650
A. Variable Heat of Adsorption.	650
B. Effect of Site and Adsorbate Coordination Number.	654
C. Adsorption Thermodynamics	656
3. Kinetics of Chemisorption	656
A. Activation Energies.	656
B. Rates of Adsorption	660
C. Rates of Desorption	663
D. Flash Desorption Studies	664
E. Other Kinetic Techniques	665
4. Surface Mobility	666
5. The Chemisorption Bond.	668
A. The Localized Bond Approach	668
B. Metals	671
C. Semiconductors	674
D. Acid-Base Systems.	676
6. Mechanisms of Heterogeneous Catalysis	678
A. Adsorption or Desorption as the Rate-Determining Step	678
B. Reaction within the Adsorbed Film as the Rate-Determining Step	680
7. Influence of the Adsorption Isotherm on the Kinetics of Heterogeneous Catalysis	682
A. Unimolecular Surface Reactions	683
B. Bimolecular Surface Reactions	685
C. Effect of Isotherm Complexities	686
8. Mechanisms of a Few Catalyzed Reactions	686
A. Ammonia Synthesis.	686
B. Fischer-Tropsch Type Reactions	688
C. Hydrogenation of Ethylene	690
D. Catalytic Cracking of Hydrocarbons and Related Reactions	691
9. Problems.	692

General References	694
Textual References	694
Author Index	699
Subject Index	721