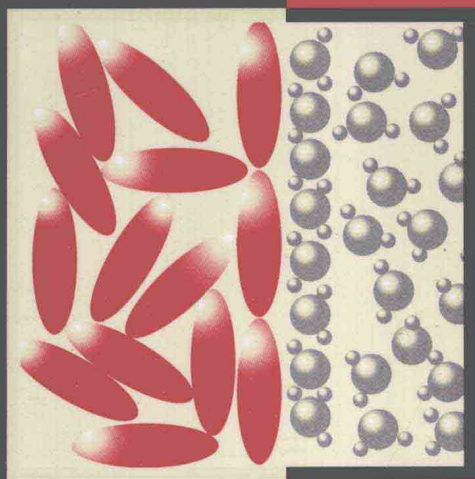


LIQUID INTERFACES IN CHEMISTRY AND BIOLOGY



ALEXANDER G. VOLKOV
DAVID W. DEAMER
DARRELL L. TANELIAN
VLADISLAV S. MARKIN

LIQUID INTERFACES IN CHEMISTRY AND BIOLOGY

Alexander G. Volkov
David W. Deamer

Department of Chemistry and Biochemistry, University of California,
Santa Cruz, California

Darrell L. Tanelian
Vladislav S. Markin

Department of Anesthesiology and Pain Management, University of Texas,
Southwestern Medical Center, Dallas, Texas



A Wiley-Interscience Publication

JOHN WILEY & SONS, INC.

New York • Chichester • Weinheim • Brisbane • Singapore • Toronto

This text is printed on acid-free paper. ☺

Copyright © 1998 by John Wiley & Sons, Inc. All rights reserved.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (508) 750-8400, fax (508) 750-4744. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012, (212) 850-6011, fax (212) 850-6008, E-Mail: PERMREQ @ WILEY.COM.

Library of Congress Cataloging-in-Publication Data:

Liquid interfaces in chemistry and biology / Alexander G. Volkov ...

[et al.].

p. cm.

“A Wiley-Interscience publication.”

Includes bibliographical references (p. –) and index.

ISBN 0-471-14872-5 (cloth : acid-free paper)

1. Surface chemistry. 2. Liquid-liquid interfaces I Volkov,

Alexander G. (Alexander George)

QD509.L54L55 1998

541.3'3—dc21

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

LIQUID INTERFACES IN CHEMISTRY AND BIOLOGY

PREFACE

Phenomena involving interfaces have fascinated man since the beginning of recorded history. Over 2000 years ago ancient philosophers contemplated the interface between oil and water. Pliny the Elder (23–79 B.C.) documented his observations in the treatise “*Historie Naturalis*” and noted that waves could be dampened by pouring oil into water (Pliny, 1962). The mechanism underlying this effect is still not clear even today.

Titus Lucretius Carus (99–55 B.C.) discussed the ability of various liquids to mix with one another in his book “*De Rerum Natura*” and “crying teardrops of wine” were described in which droplets of alcohol-containing fluids appear to crawl up the side of a glass (Lucretius, 1953). In physical chemistry this is known as the Marangoni effect. Leonardo da Vinci (1452–1519) repeated Pliny the Elder’s experiments with wave dampening and described the rise of a liquid in a small bore tube. This became known as capillarity because the tubes that were used were as fine as a hair. (The word *capillus* means hair in Latin.)

These and many other observations over time have culminated in the field known as surface science, which seeks to understand the physics and chemistry of interfaces. In most experimental situations only processes occurring in bulk phases are considered while those taking place at the interface between different phases go largely unnoticed. Yet the interfacial region can have totally unexpected properties, not intuitively apparent from a knowledge of bulk phase properties. Examples of interfacial phenomena include the ability to produce large ($10 \times 10^6 \text{ V m}^{-1}$) electrical fields at an interface due to asymmetric charge and dipole distribution; dramatic effects on solute distribution in a bulk phase due to differences in the energies required to partition a solute between the two phases; and development of catalytic sites at the interface of a dispersed two-phase system which allows reactions to take place that would not proceed in the bulk phases alone.

Processes occurring at the interface between two immiscible liquids are fundamental to life since cells and organelles are defined by membranes consisting of lipid bilayers that separate fluid compartments. Virtually all energy conversion processes in living organisms occur at these interfaces. The properties of liquid–liquid interfaces are also fundamental to a variety of industries including pharmaceuticals,

cosmetics, paints, detergents, oil extraction processes, and mining.

Despite their obvious interest and significance, liquid–liquid interfaces are often poorly understood. This may stem from the fact that the field is relatively new, and until recently there has been little appreciation of the importance of interfaces to chemistry and biology. For these reasons we have dedicated this book to presenting the fundamental concepts and principal applications of surface science.

This book begins with a discussion of the thermodynamics of liquid interfaces. In Part A we introduce the principles of classical thermodynamics, discuss the measurement of interfacial tension, and present adsorption at liquid interfaces according to Gibbs and Hansen's methods. Special attention is given to electrified interfaces in Part B, which includes interfacial potentials, electrocapillarity, and ion resolution. Part C addresses the structure of interfaces, focusing on specific models of interfacial adsorption and a detailed presentation of the electric double layer. In this section the reader will learn about laser photochemistry at liquid interfaces and recent methods for visualizing interface structure by molecular dynamics. The chemistry of interfacial catalysis is presented in Part D, which includes the theory of ion transfer across interfaces, electrolysis and electrocatalysis at ITIES, and biochemical reactions and photoelectrochemistry with environmental applications. Part E is devoted to biological membranes and presents the topics of membrane thermodynamics, transport, and mechanics. In it we first introduce the structure and properties of biological membranes, then focus on membrane electrostatics and transport of ions and non-electrolytes. The mechanical properties of membranes are presented together with practical applications such as membrane self-organization, electroporation, membrane fusion, and mechanosensitivity. Tables of fundamental constants, useful relations, and quantities can be found in the appendix.

In summary, this book presents both the theory of surface science and its applications in modern biology and chemistry. The authors intend this basic text to be used as an introduction to surface science for scientists and engineers, as a textbook for students, and as reference resource for experts in the field.

LIQUID INTERFACES IN
CHEMISTRY AND
BIOLOGY

CONTENTS

PREFACE

A. THERMODYNAMICS OF INTERFACES

1. Introduction to classical thermodynamics / 2

- 1.1. Basic concepts and definitions / 2
- 1.2. Thermodynamic potentials / 11
- 1.3. Generalization of thermodynamic potentials / 16
- 1.4. Chemical potential / 24
- 1.5. Multicomponent systems / 32
- 1.6. External field / 43
- 1.7. Surfaces / 47
- 1.8. Irreversible processes / 63

2. Measurement of interfacial tension / 69

3. Adsorption at liquid interfaces / 78

- 3.1. Gibbs method for planar interfaces / 78
- 3.2. Hansen's method / 87
- 3.3. Other definitions of surface excesses / 99
- 3.4. Volume and entropy of interface formation / 102
- 3.5. Curved interfaces / 111
- 3.6. Variables of the system / 120

B. ELECTRIFIED INTERFACES

4. Interfacial potentials / 130

- 4.1. Boundary potential difference / 130
- 4.2. Standard potentials and standard Gibbs free energies / 132

- 4.3. Distribution potentials / 136
- 4.4. Incomplete dissociation of the salt / 139
- 4.5. Complex formation in one of the phases / 140
- 4.6. The Donnan potential / 142
- 4.7. The Nernst potential / 144
- 4.8. The oxidation–reduction interfacial potential: Gibbs free energy of electron and ion transport coupling / 144
- 4.9. The mixed potential / 146
- 4.10. The adsorption potential / 149
- 4.11. Verification of the thermodynamic theory of interfacial potentials / 150
- 4.12. Measurement of interfacial potentials: the tetraphenylborate hypothesis / 151
- 4.13. Methods for measuring the interfacial potential difference / 153
- 4.14. Hung’s method of Galvani-potentials calculation: small systems and the effect of volumes / 160
- 4.15. Interfacial potential measurements as a tool for studying mechanisms of enzymatic and catalytic reactions / 161

5. Electrocapillarity / 167

- 5.1. The electrocapillary equation / 167
- 5.2. Particular cases of the electrocapillary equation / 173
- 5.3. Thermodynamic charge at the interface / 176
- 5.4. Polarizable interface / 177
- 5.5. Non-polarizable interface / 183

6. Energetics of extraction / 192

- 6.1. Electrostatic contribution to the solvation energy / 195
- 6.2. The Born model / 198
- 6.3. Non-linear dielectric effects / 200
- 6.4. Other approaches to the saturation problem / 204
- 6.5. The non-local electrostatic method / 208
- 6.6. Statistical solvent models / 210
- 6.7. Contribution of the solvophobic effect to the resolution energy / 214
- 6.8. The total resolution energy / 215
- 6.9. Dipole resolution / 217

C. STRUCTURE OF INTERFACES

7. Interfacial structures and electrical double layers / 222

- 7.1. The modified Verwey–Niessen (MVN) model / 223

- 7.2. Potentials of zero free charge and zero thermodynamic charge / 229
- 7.3. Measuring the capacitance of the electrical double layer / 239
- 7.4. Parsons–Zobel dependencies / 243
- 7.5. Potential discontinuities in the compact layer / 245
- 7.6. Specific adsorption: ionic association and ligand binding / 249
- 7.7. Adsorption isotherm and structure of the interface / 256
- 7.8. Roughness of the interface between two immiscible electrolyte solutions / 266
- 7.9. Image forces / 270
- 7.10. Drawbacks and development of MVN and the Gouy–Chapman–Stern theories / 278
- 7.11. Effects of variable dielectric permittivity / 282
- 7.12. Non-local electrostatics / 285
- 7.13. Electric double layer with hydration forces / 287
- 7.14. Modified Poisson–Boltzmann (MPB) model / 294
- 7.15. Ionic plasma in a continuous dielectric next to a charged interface / 301
- 7.16. Ion–dipole plasma at a charged interface / 303
- 7.17. The Monte Carlo method and the double layer / 309
- 7.18. Computer simulations of ITIES / 313
- 7.19. Molecular dynamics and the structure of interfaces / 319

D. CHEMISTRY AT LIQUID INTERFACES

8. Interfacial catalysis / 324

- 8.1. Oil–water interface as a model of membranes / 324
- 8.2. Multielectron reactions at interfaces / 325
- 8.3. Solvent reorganization energy / 329
- 8.4. Selective catalytic properties of liquid interfaces / 331
- 8.5. Charge transfer reactions at oil–water interfaces / 333
- 8.6. Examples of chemical reactions at liquid interfaces / 334
- 8.7. Chlorophyll as a catalyst of electron transfer reactions in bilayers and at the liquid hydrocarbon–water interface / 338
- 8.8. Porphyrins as interfacial catalysts / 342
- 8.9. Reduction of porphyrin at the octane–water interface controlled by specific adsorption / 347
- 8.10. Coupling of two redox reactions at the octane–water interface / 351
- 8.11. Enzyme complexes of the mitochondrial respiratory chain / 355
- 8.12. ATPase / 359

9. Light energy conversion at liquid–liquid interfaces: artificial photosynthetic systems / 361

- 9.1. Structure and composition of the oxygen-evolving complex *in vivo* / 362
- 9.2. Thermodynamics of water oxidation / 362
- 9.3. Kinetic aspects of multielectron reactions / 365
- 9.4. Molecular mechanism of oxygen evolution *in vivo* / 368
- 9.5. Photoinduced charge transfer across an oil–water interface / 369
- 9.6. Artificial photosynthesis at the oil–water interface in the presence of chlorophyll / 370
- 9.7. Water photo-oxidation / 379

E. MEMBRANES

10. Membrane thermodynamics and electrostatics / 406

- 10.1. Structure and properties of biological membranes / 406
- 10.2. Membrane electrostatics / 410
- 10.3. Consecutive stages of membrane ion transport / 417
- 10.4. Mechanisms of passive permeation of ions and dipoles through membranes / 422
- 10.5. Facilitated transport—mobile carriers and channels / 433
- 10.6. Coupled transport and membrane equilibrium / 435

11. Mechanics of interfaces / 452

- 11.1. Definition of surface tension at a non-spherical interface / 452
- 11.2. Elastic properties of interfaces and the shape of vesicles / 464
- 11.3. Edge energy and pores in membranes / 475
- 11.4. Membrane fusion / 483

Bibliography / 492

APPENDIX / 544

INDEX / 547

A

THERMODYNAMICS OF INTERFACES

INTRODUCTION TO CLASSICAL THERMODYNAMICS

1.1. BASIC CONCEPTS AND DEFINITIONS

The physical properties of liquid–liquid interfaces are modulated by temperature, pressure, and other thermodynamic variables. For this reason we begin with a chapter that outlines basic thermodynamic principles, and illustrate the principles with specific theoretical and experimental examples related to liquid–liquid interfaces.

Thermodynamics deals with the most general properties of macroscopic systems at equilibrium, and processes of transition between different equilibrium states. No special hypotheses about the structure of matter or the nature of heat are involved. Thermodynamic systems consist of large numbers of particles. Depending on its interaction with the environment, a given thermodynamic system can exist in any of four states. A system is called *isolated* if it does not exchange matter or energy with the environment. If the system exchanges only energy with the environment, it is called *closed*, and if the system can exchange both matter and energy, it is called *open*. Some thermodynamic systems cannot exchange heat with the environment, and are referred to as *adiabatically isolated*, or simply *adiabatic systems*.

Thermodynamic systems can be either homogeneous, or heterogeneous if they contain several physically homogeneous phases. They are characterized by properties called macroscopic parameters. Parameters can be *extensive* (additive) such as volume or weight, or *intensive*, such as density, pressure, and polarizability. Parameters determined by bodies that are not part of the system are called *external parameters*, and parameters determined by movement and distribution in space of particles included in the system, are called *internal parameters*.

A given thermodynamic system is determined by a set of independent parameters

necessary to define the equilibrium state of the system. Processes that occur in the system can change the number of parameters. If in a certain process all parameters change very slowly, so that the system is near equilibrium at all times, the process is called an *equilibrium* or *quasistatic* process. In nonequilibrium processes the individual parts are not in equilibrium with one another, and the number of parameters necessary to describe the system becomes infinite because all points of the system are essentially different.

Quantities that are independent of the previous history of a system and are completely determined by its current state, are called the *functions of state*. One of the most important functions of state is the total energy of the system, which can be divided into external and internal portions. The external energy includes both the kinetic energy and the potential energy of a system in a field of external forces, and all other energy is internal energy.

Two or more systems can exchange energy via work or by exchange of heat. The energy transferred by changing external parameters is called *work* W , and the energy transferred without changing any external parameters is called *heat* Q . By convention, the work W is considered positive if it is done *by the system* on external bodies. The heat Q is considered positive if the energy is transferred from the external environment to the system without changing its external parameters.

Each external parameter a is coupled to a generalized force A , so that the work performed by the system at an infinitely small change of this parameter is equal to

$$\delta W = A da. \quad (1.1)$$

The generalized force A_i is a function of external parameters a_i and of the temperature T . If two or more external parameters are involved in the change, then

$$\delta W = \sum_i A_i da_i. \quad (1.2)$$

The volume of the system V is one example of an external parameter, and a generalized force related to it is pressure P . In this case

$$\delta W = P dV. \quad (1.3)$$

The work W_{ne} performed by a system undergoing a nonequilibrium transition from one state to another is always less than the work W_{eq} of an equilibrium transition

$$W_{ne} < W_{eq}. \quad (1.4)$$

Equations of State. In the state of thermodynamic equilibrium all internal parameters of the system are functions of external parameters and temperature. If a generalized force A_n is an internal parameter linked to an external parameter a_n , then the equations

$$A_k = A_k(a_1, \dots, a_n; T) \quad (1.5)$$

are called the thermal equations of state. If an internal parameter is the internal energy U , then the equation

$$U = U(a_1, \dots, a_n; T) \quad (1.6)$$

is called the equation of energy or the caloric equation of state.

The total number of these equations is equal to the number of degrees of freedom of the system, or the number of independent variables that determine this state.

Simple systems play a special role in thermodynamics. These are single-phase systems with a constant number of particles. The state of such systems is determined by a single external parameter, for example by the volume V and by the temperature T . They are described by one thermal and one caloric equation of state

$$P = P(V, T), \quad (1.7)$$

$$U = U(V, T). \quad (1.8)$$

For example, in the elementary case of an ideal gas, the thermal equation of state is the familiar Clapeyron equation:

$$PV = nRT, \quad (1.9)$$

where n is the number of moles of the gas and R is the gas constant, equal to $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$. It is impossible to derive the equation of state from general principles of thermodynamics. Instead, this equation must be determined either experimentally or by methods of statistical physics based on specific models.

Even if we cannot determine an explicit thermal equation of state, the mere fact of its existence leads to important conclusions. For instance, suppose we solve the equation of state (1.7) for the volume:

$$V = V(P, T). \quad (1.10)$$

Any change of the variables P and T produces a change in volume which can be presented as a differential:

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT. \quad (1.11)$$

The coefficients in front of differentials of pressure dP and temperature dT play a very important role in thermodynamics. These are partial derivatives which describe the change of volume in thermodynamic processes. The first coefficient $(\partial V / \partial P)_T$ gives the isothermal change of volume related to changes of pressure at constant temperature, and characterizes the isothermal compressibility of the material.

The second coefficient $(\partial V / \partial T)_P$ gives the change of volume with temperature at constant pressure and thereby characterizes volumetric expansion of the body. Obviously, each of these coefficients depends on temperature and pressure.

A similar relationship exists between pressure and temperature. The partial derivative $(\partial P/\partial T)_V$ characterizes the rate of change of pressure with temperature at constant volume. However, this value is not independent, but can be expressed by the previous two derivatives. If we assume volume in (1.11) to be constant ($dV = 0$) it follows that

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}. \quad (1.12)$$

By changing the order of differentiation, one can find

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (1.13)$$

or

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1. \quad (1.14)$$

In this way we can define useful coefficients that describe relationships between the volume, temperature, and pressure in thermodynamic processes. For instance, the coefficient of thermal expansion is the ratio of the derivative $(\partial V/\partial T)_P$ to the volume V_0 at a given pressure at 0°C (273.15 K):

$$\alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T}\right)_P. \quad (1.15)$$

Specifying a volume V_0 that corresponds to a particular temperature 0°C is required only for gases. For liquid and solid bodies, which expand much less as T increases, the index “0” can be omitted without loss of accuracy.

Other useful thermal coefficients include compressibility

$$\beta = -\frac{1}{V_0} \left(\frac{\partial V}{\partial P}\right)_T \quad (1.16)$$

and thermal coefficient of pressure

$$\gamma = \frac{1}{P_0} \left(\frac{\partial P}{\partial T}\right)_V. \quad (1.17)$$

Using the identity (1.14) one can find the relationship between the coefficients

to be

$$\alpha = P_0 \beta \gamma. \quad (1.18)$$

If the volume and pressure are referred to the zero temperature, the same quantities are called the thermodynamic coefficients of expansion, compression, and pressure:

$$\alpha_t = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P, \quad \beta_t = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad \gamma_t = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V. \quad (1.19)$$

These are related by an equation similar to (1.18).

Sometimes the isothermal modulus of compression is used instead of the coefficient of compression

$$K_T = -V \left(\frac{\partial P}{\partial V} \right)_T = - \left(\frac{\partial P}{\partial \ln V} \right)_T. \quad (1.20)$$

The isothermal modulus of compression K_T is always positive since any body is compressible to a certain degree. However, the coefficient of thermal expansion α can have any sign. It is known, for example, that for water in the range from 0 to 4 °C it is negative.

The First Principle of Thermodynamics. The first principle of thermodynamics is that the internal energy of a system is a function of its state, and can only be changed by external influences. The change of internal energy ΔU is equal to the sum of heat transferred to the system and the work performed *on this system*. If W is defined as the work performed *by the system*, then the first principle can be expressed mathematically as

$$Q = \Delta U + W. \quad (1.21)$$

Therefore the first principle reflects the law of energy conservation. The first principle also states that it is impossible to build an operating engine that could perform more work than the energy transferred to the system from outside. Such an engine is called a perpetual motion machine of the first kind.

For an elementary process, when an infinitesimal amount of heat δQ is transferred, an infinitesimal amount of work δW is performed and the internal energy undergoes an infinitesimal change dU , the equation of the first principle can be expressed as follows

$$\delta Q = dU + \delta W. \quad (1.22)$$

Thus, if the system has passed from the known state 1 to the known state 2, it is