Physical Chemistry

of Surfaces

Third Edition

ARTHUR W. ADAMSON

Department of Chemistry, University of Southern California
Los Angeles, California

Preface

The character of this edition is much the same as that of the previous ones. I hope that it will continue to serve as a textbook for senior and graduate level courses, both of academic and of industrial venue. As before, it is assumed that students have completed the usual undergraduate year course in physical chemistry. I hope, too, that professional chemists will continue to find the book useful both for its references and as an entreé into a field that is too often neglected in formal training.

It is now 16 years since the first edition appeared, and I will not resist a brief retrospective glance. Much has happened; much has evolved. The first edition (1960) was largely classical in content and approach. There was much appreciation of the contributions of the great American and European schools. My own high people were N. K. Adam, E. Rideal, J. Schulman, J. W. McBain, W. D. Harkins, and I. Langmuir.

The second edition (1967) improved the general level and style (greatly, I am told). It also recognized those newer developments that were of textbook status. These were found particularly in the areas of solution surface chemistry and contact angle phenomena, and, to some extent, in the then emerging field of high vacuum surface physics and spectroscopy. The treatment of physical adsorption grew in sophistication. More attention was given to surface statistical thermodynamics.

This edition brings yet more emphasis on the molecular approach. There is now a veritable alphabet soup of phenomena: AES, APS, EIS, LEED, SIMS, to name a few. The growing bridge between such studies and heterogeneous catalysis is noticed. All chapters have been updated with respect to the literature, although this is now vast and I must apologize in advance for the major omissions that undoubtedly have occurred. New problems have been added, and the ordering of such problem sections has been brought into approximate parallel with that of subjects in the chapter. The book is some 10% longer; it is long enough.

The future looks exciting. I see great extensions of excited state studies, both photochemical and photophysical, to molecules residing at an interface. The fields of homogeneous and heterogeneous catalysis should come even closer as the ability to prepare surfaces with predesired structures becomes less of an art. Molecular biology is drawing more and more on interface chemistry and physics.

Less happily, we may see molecular and phenomenological surface chemistry become relatively distinct disciplines. The former will be a magnet attracting new investigators from all fields; the latter, however, will remain both a fundamental subject and one that is essential in a host of applied areas. Having no wish to encourage such separation, I have not anticipated it in the present writing. Nor have I accepted the awkward SI system of units—a system in no way designed to be either convenient or relevant to physical chemistry.

Much of this edition was prepared during a pleasant stay at the University of Hawaii. The hospitality of the Department of Chemistry and of Professor R. L. Pecsok in particular is gratefully appreciated. Many thanks go to the numerous colleagues who kindly sent me reprint collections; their suggestions were taken seriously and were largely followed.

I am especially indebted to students Patrick Hu and James Tse and to colleagues W. Wade and Vida Slawson for their reading of the galleys; the book is distinctly more errorfree because of their efforts. The many hours spent by my wife, Virginia, in reading proofs has made the book (if not the subject) partly hers.

ARTHUR W. ADAMSON

Los Angeles, California
April 1976

Contents

ix

CHAPTER I

Capillarity

1. Surface Tension and Surface Free Energy

The material of this book, according to its title, deals with the physical chemistry of surfaces. Although an obvious enough point, it is perhaps worth noting that in reality we will always be dealing with the *interface* between two phases and that in general the properties of an interface will be affected by changes in either of the two phases involved.

The types of interfaces possible can be summarized in a formal way in terms of the three states of matter—solid, liquid, and gas:

<div align="center">

gas–liquid
gas–solid
liquid–liquid
liquid–solid
solid–solid

</div>

A general prerequisite for the stable existence of an interface between two phases is that the free energy of formation of the interface be positive; were it negative or zero, the effect of accidental fluctuations would be to expand the surface region continuously and to lead to eventual complete dispersion of one material into the other. Examples of interfaces whose free energy per unit area is such as to offer no opposition to dispersive forces would be those between two dilute gases or between two miscible liquids or solids. Even in the case of two immiscible liquids, the presence of a suitable third component can so affect the interfacial free energy that spontaneous emulsification occurs (see Section XII-5).

The topic of capillarity concerns interfaces that are sufficiently mobile to assume an equilibrium shape. The most common examples are meniscuses and drops formed by liquids in air or in another liquid and thin films such as that forming a soap bubble. Because it deals with equilibrium configurations, capillarity occupies a place in the general framework of
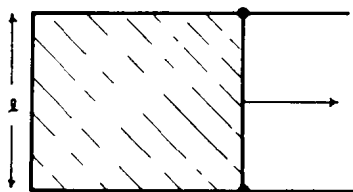
Fig. I-1

thermodynamics—it deals with the macroscopic and statistical behavior of interfaces rather than with the details of their molecular structure.

Although referred to above as a free energy per unit area, surface tension may equally well be thought of as a force per unit length. Two examples serve to illustrate these viewpoints. Consider, first, a soap film stretched over a wire frame, one end of which is movable (Fig. I-1). Experimentally one observes that a force is acting on the movable member in the direction opposite to that of the arrow in the diagram. If the value of this force per unit length is denoted by γ, then the work done in extending the movable member a distance dx is

$$\text{Work} = \gamma l dx \qquad (I\text{-}1)$$

Equation I-1 could be equally well written as

$$\text{Work} = \gamma d\mathcal{A} \qquad (I\text{-}2)$$

where $d\mathcal{A} = ldx$ and thus gives the change in area. In this second formulation, γ appears to be an energy per unit area. Customary units, then, may either be erg/cm^2 or dyne/cm; these are identical dimensionally.

A second illustration involving soap films is that of the soap bubble. We will choose, here, to think of γ in terms of energy per unit area. In the absence of fields, such as gravitational, a soap bubble is spherical, this being the shape of minimum surface area for a given enclosed volume. Consider a soap bubble of radius r, as illustrated in Fig. I-2. Its total surface free energy is $4\pi r^2 \gamma$ and, if the radius were to decrease by dr, then the change in surface free energy would be $8\pi r \gamma dr$. Since shrinking decreases the surface energy, the tendency to do so must be balanced by a pressure difference across the film ΔP, such that the work against this pressure difference $\Delta P 4\pi r^2 dr$ is just equal to the decrease in surface free energy. Thus,

$$\Delta P 4\pi r^2 dr = 8\pi r \gamma dr \qquad (I\text{-}3)$$

or

$$\Delta P = 2\gamma/r \qquad (I\text{-}4)$$

One thus arrives at the important conclusion that the smaller the bubble, the greater the pressure of the air inside as compared to that
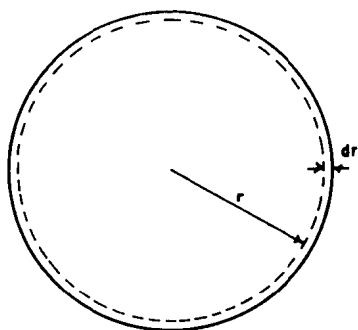
Fig. I-2

outside. This conclusion is easily verified experimentally by arranging two bubbles with a common air connection, as illustrated in Fig. I-3. The arrangement is unstable, and the smaller of the two bubbles will shrink while the other enlarges. Note, however, that the smaller bubble does not shrink indefinitely; once its radius is equal to that of the tube the radius will begin to increase with further shrinkage and a stage must be reached such that the two radii become equal, as shown by the dotted lines. This final state is now one of mechanical equilibrium.

It might be noted that common usage defines γ as the surface tension for *one* interface. Because of this, it would be better to use the quantity 2γ instead of γ in the equations above when they *are applied to soap or other two-sided films.*

The examples above illustrate the point that equilibrium surfaces may be treated mathematically, using either the concept of surface tension or the (mathematically) equivalent concept of surface free energy. (The derivation of Eq. I-4 from the surface tension point of view is given as an exercise at the end of the chapter.) This mathematical equivalence holds
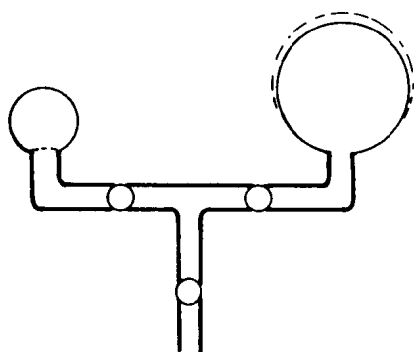

Fig. I-3. Illustration of the equation of Young and Laplace.