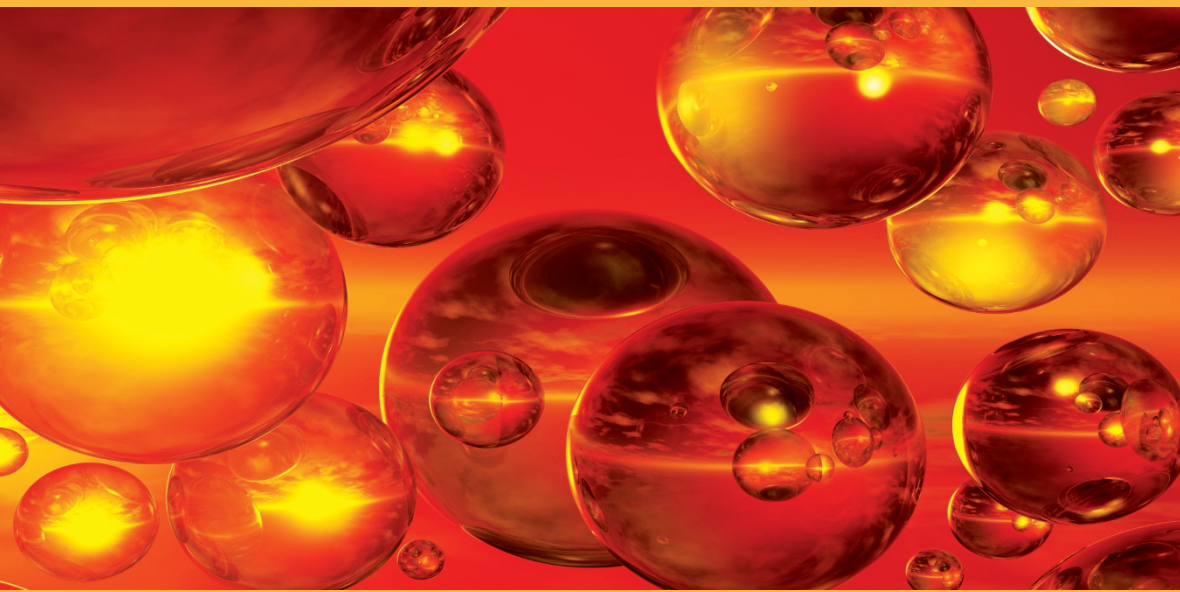


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CHEMICAL THERMODYNAMICS SET



Volume 7

Thermodynamics of Surfaces and Capillary Systems

Michel Soustelle

ISTE

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Thermodynamics of Surfaces and Capillary Systems

Chemical Thermodynamics Set

coordinated by
Michel Soustelle

Volume 7

**Thermodynamics of Surfaces
and Capillary Systems**

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Preface

This book – an in-depth examination of chemical thermodynamics – is written for an audience of engineering undergraduates and Masters students in the disciplines of chemistry, physical chemistry, process engineering, materials, etc., and doctoral candidates in those disciplines. It will also be useful for researchers at fundamental- or applied-research labs, dealing with issues in thermodynamics during the course of their work.

These audiences will, during their undergraduate degree, have received a grounding in general thermodynamics and chemical thermodynamics, which all science students are normally taught. This education will undoubtedly have provided them with the fundamental aspects of macroscopic study, but usually the phases discussed will have been fluids exhibiting perfect behavior. Surface effects, the presence of an electrical field, real phases, the microscopic aspect of modeling, and various other aspects, are hardly touched upon (if at all) during this early stage of an academic career in chemical thermodynamics.

This set of books, which is positioned somewhere between an introduction to the subject and a research thesis, offers a detailed examination of chemical thermodynamics that is necessary in the various disciplines relating to chemical or material sciences. It lays the groundwork necessary for students to go and read specialized publications in their different areas. It constitutes a series of reference books that touch on all of the concepts and methods. It discusses both scales of modeling: microscopic (by statistical thermodynamics) and macroscopic, and illustrates the link between them at every step. These models are then used in the study of solid,

liquid and gaseous phases, either of pure substances or comprising several components.

The various volumes of the set will deal with the following topics:

- phase modeling tools: application to gases;
- modeling of liquid phases;
- modeling of solid phases;
- chemical equilibrium states;
- phase transformations;
- electrolytes and electrochemical thermodynamics;
- thermodynamics of surfaces, capillary systems and phases of small dimensions.

Appendices in each volume give an introduction to the general methods used in the text, and offer additional mathematical tools and some data.

This series owes a great deal to the feedback, comments and questions from all my students at the *Ecole Nationale Supérieure des Mines* (engineering school) in Saint Etienne who have “endured” my lecturing in thermodynamics for many years. I am very grateful to them, and also thank them for their stimulating attitude. This work is also the fruit of numerous discussions with colleagues who teach thermodynamics in the largest establishments – particularly in the context of the “Thermodic” group, founded by Marc Onillion. My thanks go to all of them for their contributions and kindness.

This seventh instalment is devoted to the study of surface phenomena and to the properties of phases with small dimensions. Chapter 1 looks at the system composed of the interface between a pure liquid and its vapor. A thermodynamic approach is used to determine the influence of the temperature and pressure on the surface tension and its consequences for the specific heat capacities and the latent heats. Chapter 2 describes the modeling and properties of the interfaces between a liquid and a liquid solution or a gaseous mixture. An example of a model of the interface is studied with the model of the strictly-regular solution. Chapter 3 examines the surfaces of solids and solid–solid and solid–liquid interfaces. It closes with the study of electro-capillary phenomena. Chapter 4 deals with small-

volume phases, droplets or solids of small dimensions. The thermodynamic values are determined on the basis of Reiss' potential functions. The chapter concludes with a thermodynamic study of the phenomenon of nucleation of a condensed phase. In Chapter 5, we study firstly the thermodynamics of cylindrical capillary, and secondly the properties of thin liquid films. Chapters 6 and 7, respectively, discuss the phenomena of physical adsorption and chemical adsorption of gases by solid surfaces. Finally, in an appendix, we present the application of physical adsorption to the determination of the specific areas of solids and their porosity.

Michel SOUSTELLE
Saint-Vallier
April 2016

Notations and Symbols

A :	area of a surface or an interface.
$A_H^{(12)}$:	Hamaker constant between two media 1 and 2.
\mathcal{A} :	affinity.
$\tilde{\mathcal{A}}$:	electrochemical affinity.
A_M :	molar area.
A_m :	molecular area.
a :	pressure of cohesion of a gas or radius of the elementary cell of a liquid.
A, B, \dots :	components of a mixture.
b :	cosurface of an adsorbed gas.
\mathcal{E}_p :	set of variables with p intensive variables chosen to define a system.
F :	Helmholtz energy.
f_{het} :	heterogeneous wetting function.
\tilde{G}_σ :	electrocapillary Gibbs energy.
h_t :	spreading coefficient.
h :	Planck's constant.
H_{spr} :	Harkins spreading coefficient of one liquid over another.

$K_{i,j}(\mathcal{E}_p)$:	thermodynamic coefficient associated with the set of variables \mathcal{E}_p . X_j is its definition variable and Y_i is its definition function.
K_{ads} :	equilibrium constant of adsorption.
K_{fe} :	equilibrium function of adsorption.
k_B :	Boltzmann's constant.
l_c :	capillary length.
M :	molar mass.
N_a :	Avogadro's number.
N_A :	number of molecules of component A.
P :	pressure of a gas.
p :	spreading parameter.
q_ϕ :	equilibrium heat of adsorption.
q_d :	differential heat of adsorption.
q_{isost} :	isosteric heat of adsorption.
R :	perfect gas constant.
R :	mean radius of curvature of a surface.
r_c :	radius of a cylindrical tube.
r_K :	Kelvin radius.
T :	temperature.
v_{mono} :	volume of a monolayer of adsorbed gas.
$x_k^{(\alpha)}$:	molar fraction of the component k in the α phase.
x_i :	molar fraction of the component i in a solution. Y_i and X_i : conjugate intensive and extensive values.
$y_{i,j}$:	Mayer function.
$\Gamma(\mathcal{E}_p)$:	characteristic function with the set \mathcal{E}_p as canonical variables.
Γ :	characteristic function.

Γ_i :	excess surface or surface concentration of component i .
Γ_{ij} :	excess surface or surface concentration of component i in relation to j .
$\gamma_i^{(I)}$:	activity coefficient of component i in the pure-substance reference.
$\gamma_i^{(II)}$:	activity coefficient of component i in the infinitely dilute-solution reference.
$\gamma_i^{(III)}$:	activity coefficient of component i in the molar-solution reference.
$\Delta\sigma$:	spreading on a liquid.
$\Delta_r(A)$:	value of A associated with the transformation r .
θ :	fraction of coverage.
θ_i :	surface fraction of a component.
σ :	surface energy.
σ_e :	surface density of electrical charges.
σ^* :	surface tension.

Liquid Surfaces

An interface constitutes an extensive, two-dimensional defect in a system. Given that at least one of the intensive values of that system (as is often the case, for example, with the refractive index) evidently undergoes a discontinuity at that interface, the interface separates two distinct phases. Hence, the system is heterogeneous. The presence of that defect, at least in its vicinity, leads to the modification of the properties of the two phases thus separated. This leads us to model the system considering three phases: two so-called massive (or bulk) phases, which are the phases separated by the interface, and a superficial (surface) phase constituting a layer of a certain thickness, containing the modified properties of the two massive phases. Unlike the two massive phases, which each have their own thermodynamic properties with their own specific thermodynamic coefficients, the surface phase has thermodynamic properties that are dependent on the properties of the two phases surrounding it. Thus, we say that the *surface phase is not autonomous*.

It is common to speak of the surface of a liquid, but in fact this is a misuse of language. In reality, that surface is never isolated from another phase, so in nature we only ever actually find interphases. For example, if the liquid is placed in a vacuum, it vaporizes spontaneously (and least in part), and we see the presence of an interphase between the liquid and its vapor which, in the case of a pure substance, have the same composition but different molecular densities. In this particular case of the equilibrium between a pure substance and its vapor, we sometimes speak of the surface of the liquid, and the properties of that interface are qualified as being the properties of the surface of the liquid. This chapter will be devoted to interfaces between a pure liquid and its vapor.

The different molecular densities of the two bulk phases will lead to anisotropic bond forces in the surface phase. Indeed, the molecules of the liquid which are at the surface are on half of the space in the vicinity of other molecules placed at greater distances, and therefore create an intermolecular force field which also undergoes a discontinuity.

The interface between a pure liquid and its vapor is characterized by easy mechanical deformation and easy variation of its areas. Indeed, we simply need to tilt a recipient to extend the area of the interface separating two fluid phases – i.e. increase the quantity of material making up that interface. This augmentation in the area of the liquid–vapor interface takes place without deformation, because the stresses likely to be engendered are quickly relaxed because the shearing modulus of a liquid is zero.

NOTE.– It is impossible to construct an interface between two pure liquids because reciprocal dissolution, even slight, leads to an interface between two solutions, which will be discussed in Chapter 2.

1.1. Mechanical description of the interface between a liquid and its vapor

Numerous experiments in mechanics show the existence of forces acting on the surface of the liquid in the presence of its vapor. The resultant of those forces seems to be parallel to the surface and tends to reduce the area of the interface.

1.1.1. Gibbs' and Young's interface models

To apply mechanics and thermodynamics to interfaces, it is useful to have a model of that interface. The simplest model is Gibbs', whereby the interface is considered to be reduced to the surface of separation of the two phases, with no thickness. In that model, the discontinuity of an intensive value upon the changing phase is sudden, as illustrated by Figure 1.1, which shows the discontinuity of the density on phase change. In order to take account of a certain number of phenomena which we encounter in the study of systems with multiple components, such as adsorption, segregation or surface excess, it is necessary to accept that the surface contains a certain amount of virtual material (a certain number of moles) of each of the species involved.

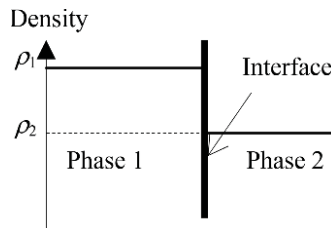


Figure 1.1. *Discontinuity in density in Gibbs' model*

A second, more elaborate, model is Young's layered model. In this model, the interface has a certain thickness or depth, d , which is unknown but is likely to be small (see Figure 1.2(a)), at around a few atomic layers, except in the vicinity of the critical point for the liquid–vapor interface.

In Young's model, we cut that surface perpendicularly with a plane AB whose breadth is δl . Figure 1.2(b) illustrates the different forces acting on the left-hand side of the plane AB (with the right-hand side being subject to the same symmetrical forces).

- Between A and A', the force is exerted by the hydrostatic pressure P'' of the lower phase;
- Between B' and B, the force results from the hydrostatic pressure P' in the upper phase;
- Between A' and B', the forces are distributed in accordance with an unknown law.

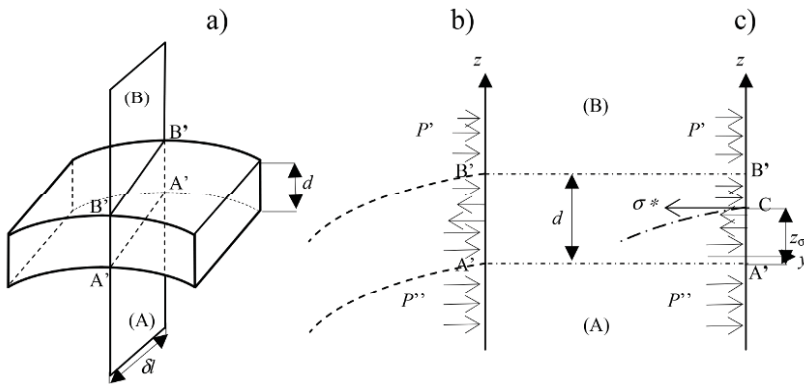


Figure 1.2. *Representation of an interface in Young's model*

Young models the system (see Figure 1.2(c)) as the existence, between B' and A', of a *surface tension* σ^* tangent to a point C, at a distance z_c from A' and such that the equivalences of the forces and the moments in relation to A' are assured between the two representations 1.2b and 1.2c, which we can express for the forces along the z axis by:

$$\sum_z (\bar{F}_z)_b = \sum_z (\bar{F}_z)_c \quad [1.1]$$

and for the moments in relation to A', by:

$$\sum_z (\bar{M}_{A'})_b = \sum_z (\bar{M}_{A'})_c \quad [1.2]$$

Between A and C, the forces are due to the pressure P' , and between C and B they are due to the pressure P'' .

1.1.2. Mechanical definition of the surface tension of the liquid

Let us look again at Young's model for the interface between a pure liquid phase and its vapor. If we extend the free surface of the liquid over a breadth δx (Figure 1.3), the variation in the area of that surface is:

$$dA = \delta x \cdot \delta l \quad [1.3]$$

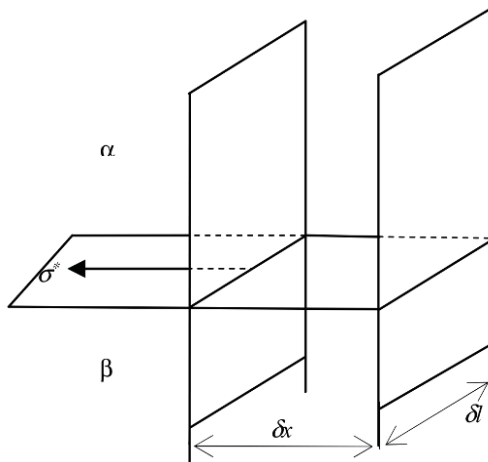


Figure 1.3. Extension of a portion of surface of a liquid

The force exerted against the surface tension is:

$$F = \sigma^* \delta l \quad [1.4]$$

The work which must be injected is the product of that force by the displacement δx . That work will be:

$$dW = F \delta x = \sigma^* \delta l \cdot \delta x = \sigma^* dA \quad [1.5]$$

The term σ^* is called the *surface tension* or *interfacial tension* of the liquid. This value is expressed in Newtons per meter, as shown by relation [1.4].

1.1.3. Influence of the curvature of a surface – Laplace's law

Consider an element $d\bar{S}$ of a curved interface with radii of primary curvatures (in two orthogonal directions) R_1 and R_2 (see Figure 1.4). Each boundary line of that element is subject to forces of surface tension exerted by the rest of the interface.

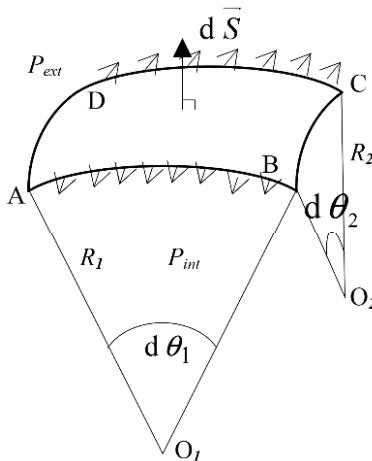


Figure 1.4. Radii of curvature of a curved surface

At mechanical equilibrium, the resultant of these forces is canceled out by the forces exerted on the surface by the pressure P_{int} inside the curve and P_{ext} outside of it. As the tangential components, two by two, cancel one

another out, it is easy to calculate the normal components. Thus, for instance, on the side AB, the force experienced by the surface element is:

$$-R_1 d\theta_1 \sigma^* \sin \frac{d\theta_2}{2} \approx -\frac{1}{2} R_1 d\theta_1 \sigma^* d\theta_2 \quad [1.6]$$

The projection of the resultant of all the components, which takes the value of 0, is written:

$$-R_1 d\theta_1 d\theta_2 \sigma^* - R_2 d\theta_2 d\theta_1 \sigma^* + (P_{\text{int}} - P_{\text{ext}}) R_1 d\theta_1 R_2 d\theta_2 = 0 \quad [1.7]$$

From this, we deduce:

$$P_{\text{int}} - P_{\text{ext}} = \sigma^* \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad [1.8]$$

This is Laplace's law, which gives the expression of the discontinuity in pressure on either side of a curved interface as a function of the surface tension and of the primary radii of curvature of that curved surface.

This law can be expressed in a different form, if we define the mean radius of curvature R by the relation:

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{2}{R} \quad [1.9]$$

Laplace's law becomes:

$$P_{\text{int}} - P_{\text{ext}} = \frac{2\sigma^*}{R} \quad [1.10]$$

Two particular cases of relation [1.8] are often used.

For a spherical surface, such as a drop of liquid, the primary radii of curvature are equal to the radius r of the sphere:

$$R_1 = R_2 = r \quad [1.11]$$

and Laplace's law becomes:

$$P_{\text{int}} - P_{\text{ext}} = \frac{2\sigma^*}{r} \quad [1.12]$$

If we now consider a cylindrical surface with radius r , the primary radii are:

$$R_1 = r \quad [1.13a]$$

$$R_2 \text{ is infinite} \quad [1.13b]$$

and Laplace's law then takes the form:

$$P_{\text{int}} - P_{\text{ext}} = \frac{\sigma^*}{r} \quad [1.14]$$

We shall use relations [1.12] and [1.14] in Chapters 4 and 5, which are devoted to the study of phases of small dimensions.

1.2. Thermodynamic approach to the liquid–vapor interface

Considering that the surface work is given by the product of the area by an intensive value σ called the *surface energy*, here we shall discuss a thermodynamic approach to the study of interfaces which, amongst other things, will help us distinguish, in liquids, between the surface tension σ^* as defined by relation [1.5] on the basis of mechanics and the surface energy σ derived from thermodynamics.

1.2.1. Potential functions

Let us look again at the layered model shown in Figure 1.2(a), whereby the interface is defined using three volumes: that of the liquid phase, known as the α phase; that of the vapor phase, known as the β phase; and that of the interfacial layer, called the γ phase. The total volume of the system is the sum of those three volumes:

$$V = V^{(\alpha)} + V^{(\beta)} + V^{(\gamma)} \quad [1.15]$$