Volume 1

Phase Modeling Tools

Applications to Gases

Michel Soustelle

Chemical Thermodynamics Set

coordinated by
Michel Soustelle

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Phase Modeling Tools

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, and will therefore be familiar with the fundamentals, such as the principles and the basic functions of thermodynamics, and the handling of phase- and chemical equilibrium states, essentially in an ideal medium, usually for fluid phases, in the absence of electrical fields and independently of any surface effects.

This set of books, which is positioned somewhere between an introduction to the subject and a research paper, 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;

– phase 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 *École 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 group "Thermodic", founded by Marc Onillion. My thanks go to all of them for their contributions and conviviality.

This volume is split into two parts. In the first part, Chapter 1 is dedicated to phase modeling tools and covers the modeling of a phase: constructing potential characteristic functions. Chapter 2 covers the microscopic approach and presents the characteristic matrices that group together thermodynamic coefficients, from different experimental data. Chapters 3, 4 and 5 cover tools used in the microscopic modeling of phases through the use of statistics of molecular objects and microcanonical and canonical spaces. The calculation of state functions from molecular data allow the characteristic functions of a phase to be calculated.

The second part covers the modeling of gaseous phases. In Chapter 7, we cover macroscopic and microscopic modeling of pure gases using state equations, generalized compressibility charts and the concept of fugacity. Microscopic modeling is an initial application of statistical thermodynamics by calculating the second virial coefficient. The eighth chapter describes the

models of gaseous mixtures, macroscopic and microscopic. Mixed models from models of condensed solutions and state equations are covered.

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Notations

$\{\mathbf{gas}\}$: pure gas

$\{\{\mathbf{gas}\}\}$: gas in mixture

$(\mathbf{liquid})$: pure liquid

$((\mathbf{liquid}))$: liquid in solution

$\langle\mathbf{solid}\rangle$: pure solid

$\langle\langle\mathbf{solid}\rangle\rangle$: solid in solution

Symbols

A : Area of a surface or interface

$A_H^{(12)}$: Hamaker constant between two media 1 and 2

A : affinity

$\tilde{A}$: electrochemical affinity

A_M : molar area

A_m : molecular area

a : cohesion pressure of a gas; radius of the unit cell of a liquid

A, B, ... : components of a mixture

a^{mix} and b^{mix} : terms for mixing of constants of a state equation

B'_i : i^{th} coefficient of the virial in the increase in pressure

B_i : i^{th} coefficient of the virial

b : co-volume of a gas, co-surface of an adsorbed gas

C : concentration, trace concentration of a voltage-pH diagram

C_P^{xs} : excess molar heat capacity at constant pressure

C_i : molar concentration (or molarity) of a component i

$C_\pm$: mean concentration of ions in an ionic solution

$C_{V(el)}$: contribution of free electrons of a metal to the molar heat capacity

$C_{v(r)}$: contribution of rotational movements to the heat capacity at constant volume

$C_{v(t)}$: contribution of translational movements to the heat capacity at constant volume

$C_{v(v)}$: contribution of vibrational movements to the heat capacity at constant volume

C_V, C_P : heat capacity at constant volume and pressure

c : capacity of a capacitor; number of independent components

D : dielectric constant of the medium; protection or contact diameter of a molecule

$D(T/\Theta_D)$: Debye function

d : distance between two liquid molecules

d_eS : exchange of entropy with the external environment

d_i : degree of oxidation i of an element A

d_iS : internal production of entropy

$d\omega$: element of volume

E : energy of the system

ε : Young's modulus

$E(T/\Theta_E)$: Einstein function

E_0 : internal energy associated with a reaction at temperature 0 K

E^0 : standard electric potential or standard electromotive force of an electrochemical cell

E_{abs} : reversible electrical voltage of an electrochemical cell

Eb : balanced equation

$\langle E \rangle$: total mean energy of an element of a canonical ensemble

E_C : total energy of canonical ensemble

E_I : potential energy due to interactions

E_j : energy of an element j of canonical ensemble

E_{kin} : molar kinetic energy of electrons in a metal

ε_p : set of variables at p intensive variables chosen to define a system

e : relative potential of an electrode

e^0 : standard electrical potential (or normal potential) of an electrode

e_0 : potential of equi-activity or equi-concentration of an electrode

e_{abs} : absolute potential of an electrode

F : Helmholtz free energy

F_m^{mix} : excess molar free energy

$\overline{F}_i^{xs}$: excess partial molar Helmholtz free energy of a component i

$\overline{F}_i^{mix}$: partial molar Helmholtz free energy of mixing of a component i

$\overline{F}_i$: Helmholtz free energy, partial molar Helmholtz free energy of a component i

F_{el} : contribution of free electrons to molar Helmholtz free energy

$\tilde{F}$: electrochemical Helmholtz free energy

f_{het} : heterogeneous spreading parameter

f_i : fugacity of component i in a gaseous mixture

F_m : molar Helmholtz free energy

$\mathscr{F}$: faraday

f_i^0 : molar Helmholtz free energy of a pure component i

f^0 or f_i^0 : fugacity of a pure gas i

G_m^{xs} : excess Gibbs free energy

$\tilde{G}_\sigma$: electro-capillary Gibbs free energy

$\tilde{G}$: electrochemical Gibbs free energy

$\overline{G}_i^{xs}$: excess partial molar Gibbs free energy of a component i

G : Gibbs free energy

G, $\overline{G}_i$, $[G]$: Gibbs free energy, partial molar Gibbs free energy of i, generalized Gibbs free energy

G_m : molar Gibbs free energy

G_m^{mix} : molar Gibbs free energy of mixing

$\overline{G}_i^{xs}$: excess partial molar Gibbs free energy of a component i

g : osmotic coefficient; acceleration of gravity; coefficients of degeneracy or multiplicity or statistical weight

g_i^0 : molar Gibbs free energy of a pure component i

g_a : statistical weight of fundamental electron level of the nucleus a

g_i : coefficient of multiplicity of state i

$g_{(e)}$: statistic weight of electron levels

$g(r)$: radial distribution function

$g(v_x)$: distribution of velocity components according to Ox

g^* : molar Gibbs free energy of gas i under a pressure of 1 atmosphere in a mixture

H_T^0 : standard molar enthalpy of formation at temperature T

H, $\overline{H}_i$: enthalpy, partial molar enthalpy of i

H : Hamiltonian

$H_{i,}$: resonance integral between two identical neighboring atoms

$H_{i,i}$: Coulombian integral between two identical neighboring atoms

H : magnetic field

$\tilde{H}$: electrochemical enthalpy

H_m^{xs} : excess molar enthalpy

H_m^{mix} : molar enthalpy of mixing

$\overline{H}_i^{xs}$: excess partial molar enthalpy of a component i

$\overline{H}_i^{mix}$: partial molar enthalpy of mixing of component i

h_t : spreading coefficient

h : stoichiometric coefficient of protons in an electrochemical reaction

h : Planck's constant

h_i^0 : molar enthalpy of a pure component i

$h_{\acute{e}t}$: spreading coefficient of a liquid on another Harkins liquid

I : ionic strength of an ionic solution

I_m : ionic strength reduced to molarities

I, I_1, I_2 I_3 : moments of inertia.

I_l : configuration integral of the canonical translational partition function

i : Van 't Hoff factor

$\overline{J}_i$: partial molar value of the variable J relative to component i

J_i^{mix} : value of mixing of size J relative to component i

$\overline{J_i^{mix}}$: partial molar value of mixing of size J relative to component i

J_i^* : size of J relative to component i in a perfect solution

$\overline{J}_i^*$: partial molar value of size J relative to component i in a perfect solution

j_i^0 : value of size J for the pure component i in the same segregation state

j : quantum rotation number

$K_{i,j}(E_p)$:   Thermodynamic coefficient associated with the set of variables ϵp, X_j is its variable of definition and Y_i its function of definition

$K_i^{(Tr)}$: equilibrium constant of the phase transformation Tr for component i

K_{ij} : local composition weighting factor

K_{ads} : adsorption equilibrium constant

K_{AX} : solubility product of solid AX

$K_i^{(\alpha\beta)}$: partition coefficient of compound i between both phases α and β

K_d : dissociation constant

K_{fe} : adsorption equilibrium function

$K_r^{(c)}$: equilibrium constant relative to concentrations

$K_r^{(f)}$: equilibrium constant relative to fugacities

$K_r^{(P)}$: equilibrium constant relative to partial pressures

K_r : equilibrium constant

K_s : solubility product

k : wave number

k_B : Boltzmann constant

L_t : latent heat accompanying the transformation t

l_c : capillary length

M : molar mass

M : magnetic moment; Madelung constant

m , m_s : mass of solute s in grams per kg of solvent

m : total mass

m_i : mass of component i

N : number of molecules in an ensemble

N_a : Avogadro's number

N_A : number of molecules of the component A

N_C : number of elements in the canonic ensemble

N_c : Total number of cells in a liquid.

n : total number of moles in a solution or a mixture; quantum translation number

n_i : number of objects i of system with energy ε_i.

$n^{(\alpha)}$: total number of moles in phase α

$<n>$: mean number of neighboring holes in a molecule in a liquid

n_i : number of moles of component i

N_L : total number of holes in a liquid

P_c^{mix} : critical pressure of a mixture

P : pressure of a gas

P_i^{subl} : sublimation vapor pressure of component i

P_i^{vap}, P_i^0 : saturation vapor pressure of component i

P_r^{mix} : relative pressure of the mixture

P_c : critical pressure

p_F : Fermi impulsion

P_i : partial pressure of component i

P_j : fraction of number of elements in a state j

p : number of external physical variables; spreading parameter

Q : heat balance

Q_a : reaction quotient in terms of activities

Q_P : heat of transformation at constant pressure ; reaction quotient in terms of partial pressure

Q_r : reaction quotient of transformation r

Q_V : heat of transformation at constant volume

q_ϕ : equilibrium heat of adsorption

q_d : differential heat of adsorption.

q_i : volumic fraction parameter

q_{isost} : isoteric heat of adsorption

$\Re$: reaction rate

R : ideal gas constant

R : radius of mean curvature of a surface; distillation reflux ratio

r_A : radius of ionic atmosphere

r_0 : distance of minimal energy between two molecules

r_c : radius of a cylindrical tube

r_i : parameter of volumic fraction

r_K : Kelvin's radius

s : parameter of order of an alloy

S_m^{mix} : molar entropy of mixing