Volume 3

# Thermodynamic Modeling of Solid Phases

**Michel Soustelle**

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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, 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;

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

This volume of the set is devoted to modeling of solid phases.

Chapter 1 discusses the modeling of pure solids. Oscillator models (Einstein's and Debye's) are used to calculate canonical partition functions for four types of solid: atomic, ionic, molecular and metallic. These canonical partition functions can be employed, first to calculate the specific heat capacities at constant volume, and second to determine the expansion coefficients with the Grüneisen parameters.

Chapter 2 looks at the modeling and characterization of solid solutions. Following a qualitative description of the different types of solid solution of substitution and insertion, the short-distance and long-distance order coefficients are introduced. Simple solution models are briefly described and the thermodynamics of the order/disorder transformations in alloys is presented. The chapter ends with the experimental determination of the activity coefficients of the components of a solid solution.

The third chapter deals with non-stoichiometry of solids, and therefore point defects in pure solids. Equilibria between defects are discussed in the context of quasi-chemical phenomena.

The fourth and final chapter looks at the question of point defects in solid solutions that are slightly or highly concentrated. The role of doping of insulating and semiconductive ionic materials is discussed, as is the description of models of gas dissolution in solids. The chapter finishes with an examination of the methods used to calculate the equilibrium constants of point-defect creation.

Two appendices are given at the end of the book, discussing the Lagrange multiplier method and a method for solving Schrödinger's equation.

Michel SOUSTELLE
Saint-Vallier,
July 2015

# Notations and Symbols

$\{gas\}$ pure, $\{\{gas\}\}$ in a mixture, $(liquid)$ pure, $((liquid))$ in solution, $\langle solid \rangle$ pure, $\langle\langle solid \rangle\rangle$ in solution

| | |
|---|---|
| $A$: | area of a surface or an interface. |
| $A_H^{(12)}$ : | Hamaker constant between two media 1 and 2. |
| A: | affinity. |
| $\widetilde{A}$ : | electrochemical affinity. |
| $A_M$: | molar area. |
| $A_m$: | molecular area. |
| $a$: | cohesion pressure of a gas or radius of the unit cell of a liquid. |
| A, B, …: | components of a mixture. |
| $a^{mix}$ and $b^{mix}$: | mixing terms of the constants in a state equation. |
| $B'_i$: | $i^{th}$ coefficient of the virial in the pressure expansion. |
| $B_i$: | $i^{th}$ coefficient of the virial. |
| $b$: | covolume of a gas or cosurface of an adsorbed gas. |
| $C$: | concentration or concentration in a potential-pH plot. |
| $C_P^{xs}$ : | molar heat capacity of excess at constant pressure. |

$C_i$:            molar concentration (or molarity) of component $i$.

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

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

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

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

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

$C_V, C_P$:       heat capacity at constant volume and constant pressure, respectively.

$c$:              capacity of a capacitor or number of independent components.

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

$D(T/\Theta_D)$:  Debye's function.

$d$:              distance between two liquid molecules.

$d_e S$:          entropy exchange with the outside environment.

$d_i$:            degree of oxidation $i$ of an element A.

$d_i S$:          internal entropy production.

$d\omega$:        elementary volume.

$E$:              energy of the system.

E:                Young's modulus.

$E(T/\Theta_E)$:  Einstein's function.

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

$E^0$:            standard electrical potential or standard electromotive force (emf) of an electrochemical cell.

$E_{abs}$:        reversible emf of an electrochemical cell.

$Eb$:             balance equation.

$\langle E \rangle$ :            mean total energy of an element in the canonical ensemble.

$E_C$:            total energy of the canonical ensemble.

$E_I$:            potential energy due to interactions.

$E_j$:            energy of an element $j$ of the canonical ensemble.

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

$\mathrm{E}_p$:            set of variables with $p$ intensive variables chosen to define a system.

$e$:            relative emf of an electrode.

$e^0$:            standard emf of an electrode.

$e_0$:            equi-activity- or equiconcentration emf of an electrode.

$e_{\mathrm{abs}}$:            absolute emf of an electrode.

$F$:            Helmholtz energy.

$F_m^{mix}$ :            molar excess Helmholtz energy.

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

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

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

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

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

$F_m$:            molar Helmholtz energy.

$\mathscr{F}$:            faraday.

$f_{\mathrm{het}}$ :            heterogeneous wetting function.

$f_i$:            fugacity of the component $i$ in a gaseous mixture.

$f_i^0$ :            molar Helmholtz energy of pure component $i$.

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

$G_m^{xs}$ :                      excess Gibbs energy.

$\tilde{G}_\sigma$ :                      electrocapillary Gibbs energy.

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

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

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

$G_m$ :                      molar Gibbs energy.

$G_m^{mix}$ :                      molar Gibbs energy of mixing.

$g$:                      osmotic coefficient *or* acceleration due to gravity or degeneration
                      coefficient or multiplicity or statistical mass.

$g_i^0$ :                      molar Gibbs energy of pure component $i$.

$g_a$:                      statistical weight of fundamental electron level of nucleus a.

$g_i$:                      coefficient of multiplicity of state $i$.

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

$g(r)$:                      radial distribution function.

$g(v_x)$:                      distribution of velocity components along $Ox$ axis.

$g^*$:                      molar Gibbs energy of gas $i$ at 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.

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

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

$\mathcal{H}$:                      magnetic field.

$\tilde{H}$ :                electrochemical enthalpy.

$H_m^{xs}$ :                molar excess enthalpy.

$H_m^{mix}$ :                molar mixing enthalpy.

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

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

$h_{sp}$:                Harkins spreading coefficient of a liquid on another.

$I$:                ionic strength of a solution of ions.

$I_m$ :                ionic strength in relation to molality values.

$I, I_1, I_2, I_3$:                moments of inertia.

$I_t$:                integral of configuration of the canonical distribution function of translation.

$i$:                Van't Hoff factor.

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

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

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

$J_i^*$ :                value of $J$ relative to component $i$ in a perfect solution.

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

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

$j$:                         rotational quantum number.

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

$K_i^{(\alpha\beta)}$ :           constant of change of equilibrium for phase transition Tr for component $i$.

$K_{ij}$ :                       weighting factor of local composition.

$K_{ads}$:                   equilibrium adsorption constant.

$K_{AX}$:                   solubility product of solid AX.

$K_i^{(\alpha\beta)}$ :            coefficient of sharing of compound $i$ between the two phases $\alpha$ and $\beta$.

$K_d$:                       dissociation constant.

$K_{fe}$:                    adsorption equilibrium function.

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

$K_r^{(f)}$ :                 equilibrium constant relative to fugacity values.

$K_r^{(P)}$ :                equilibrium constant relative to partial pressure values.

$K_r$:                       equilibrium constant.

$K_s$:                       solubility product.

$k$:                         wavenumber.

$k_B$:                       Boltzmann's constant.

$L_t$:                       latent heat accompanying the transformation $t$.

$l_c$:                       capillary length.

$M$:                         molar mass.

M:                         magnetic moment or Madelung constant.

| | |
|---|---|
| $m_s$ : | mass of solute s in grams per kilo of solvent. |
| $m$: | total mass. |
| $m_i$: | mass of component $i$. |
| $N$: | number of components of a solution or a mixture of gases or involved in a reaction or number of molecules of a collection. |
| $N_a$: | Avogadro's number. |
| $N_A$: | number of molecules of component A. |
| $N_C$: | number of elements in the canonical collection. |
| $N_c$: | total number of cells of a liquid. |
| $n_i$: | number of objects $i$ in the system with energy $\varepsilon_i$ or number of moles of component $i$. |
| $n$: | translational quantum nimber or total number of moles in a solution or a mixture. |
| $n^{(\alpha)}$: | total number of moles in a phase $\alpha$. |
| $<n>$: | mean number of neighboring vacancies of a molecule in a liquid. |
| $N_L$: | total number of vacancies in a liquid. |
| $P_c^{mix}$ : | critical pressure of the mixture. |
| $P$: | pressure of a gas. |
| $P_i^{subl}$ : | sublimating vapor pressure of component $i$. |
| $P_i^{vap}$  $P_i^0$ : | saturating vapor pressure of component $i$. |
| $P_r^{mix}$ : | relative pressure of the mixture. |
| $P_c$: | critical pressure. |
| $P_i$: | partial pressure of component $i$. |
| $P_j$: | proportion of number of elements in a state $j$. |
| $p$: | number of external physical variables $or$ spreading parameter. |
| $p_F$: | Fermi pulse. |

$Q$:                        heat involved.

$Q_a$:                      reaction quotient in terms of activity.

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

$Q_r$:                      reaction quotient of transformation $r$.

$Q_V$:                      transformation heat at constant volume.

$q_\phi$:                    equilibrium heat of adsorption.

$q_d$:                      differential heat of adsorption.

$q_i$:                      volumetric fraction parameter.

$q_{isost}$:                isosteric heat of adsorption.

$\Re$ :                     reaction rate

R:                        perfect gas constant.

$R$:                        mean curvature radius of a surface or rate of reflux of distillation.

$r_A$:                      radius of the ionic atmosphere.

$r_0$:                      minimum distance of energy between two molecules.

$r_c$:                      radius of a cylindrical tube.

$r_i$:                      volumetric fraction parameter.

$r_K$:                      Kelvin radius.

$S_m^{mix}$ :               molar mixing entropy.

$\overline{S}_i^{xs}$ :     partial excess molar entropy of component $i$.

$\overline{S}_i^{mix}$ :    partial mixing molar entropy of component $i$.

S:                        oversaturation of a solution.

$\overline{S}_i$ :          entropy or partial molar entropy of $i$.

$\tilde{S}$ :               electrochemical entropy.

$S_m^{xs}$                  excess molar entropy.