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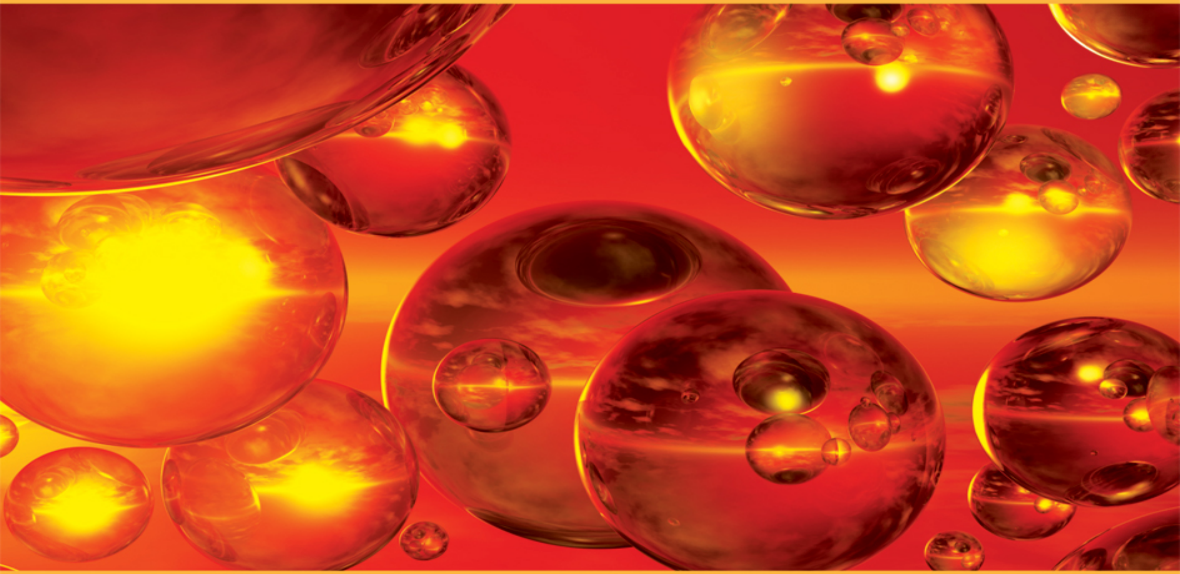
CHEMICAL THERMODYNAMICS SET



Volume 2

Modeling of Liquid Phases

Michel Soustelle

iSTE

WILEY

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Chemical Thermodynamics Set

coordinated by
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 in the series is devoted to the study of liquid phases.

Chapter 1 describes the modeling of pure liquids, either using the radial distribution function or partition functions. The different models presented herein range from the very simplest to the most complex. The results yielded by these models are then compared, both to one another and to the results found experimentally.

The second chapter describes the tools used for macroscopic modeling of solutions. The use of limited expansions of the activity coefficient logarithm is presented, before we define simple solution models such as the ideal dilute solution, regular solutions and athermal solutions, on the basis of macroscopic properties.

Next, in Chapter 3, we present a number of solution models with microscopic definition, including random distribution models and models integrating the concepts of local composition and combinatorial excess entropy.

The fourth chapter deals with the modeling of ionic solutions combining the term due to the electrical effects, found using the Debye and Hückel model, with the terms of local composition and combinatorial excess entropy found in the previous chapter.

Chapter 5 presents the various experimental methods for determining the activity or the activity coefficient of a given component in a solution.

Finally, three appendices are provided, which recap a few notions about statistical methods of numerical simulation (Appendix 1), and offer some reminders about the properties of solutions (Appendix 2) and statistical thermodynamics (Appendix 3) – subjects which were discussed in detail in the first volume of this series.

Michel SOUSTELLE
Saint-Vallier,
April 2015

Notations and Symbols

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

A:	area of a surface or an interface.
$A_{\mathrm{H}}^{(12)}$:	Hamaker constant between two media 1 and 2.
$\mathbb{A}$:	affinity.
$\tilde{\mathsf{A}}$:	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.

$\mathrm{d}_e S$: entropy exchange with the outside environment.

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

$\mathrm{d}_i S$: internal entropy production.

$\mathrm{d}\omega$: 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.
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_{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_{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.
$g(\text{r})$:	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_I:	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.
$K_{i,j}(\mathsf{E}_p)$:	thermodynamic coefficient associated with the set of variables $\mathtt{E}p$. X_j is its definition variable and Y_i its definition function.
$K_i^{(Tr)}$:	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 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 fugacity values.
$K_r^{(P)}$:	equilibrium constant relative to partial pressure values.
K_r:	equilibrium constant.
K_s:	solubility product.
k:	wavenumber.
$\mathrm{k_B}$:	Boltzmann's constant.
L_t:	latent heat accompanying the transformation t.
l_c:	capillary length.
M:	molar mass.
$\mathtt{M}$:	magnetic moment or Madelung constant.
m_{s}:	mass of solute s in grams per kg 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.
$\mathrm{N_a}$:	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 ε_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 α.
$<n>$:	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_ϕ:	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.
s:	parameter of order of an alloy.

s_i^0: molar entropy of pure component i.

T: temperature.

T_c^{mix}: critical temperature of the mixture.

T^*: second-order transition temperature.

T_r^{mix}: relative temperature of the mixture.

$T_{(Az)}$: boiling point of azeotropic solution.

T_c: critical temperature.

T_F: Fermi temperature.

$T_{i(Eb)}$: boiling point of pure i.

$T_{i(F)}$: melting point of pure i.

T_s: sublimation temperature.

T_v: vaporization temperature.

U_m^{xs}: excess molar internal energy.

U_m^{mix}: mixing molar internal energy.

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

$\overline{U}_i^{mix}$: partial mixing molar internal energy of component i.

U, $\overline{U}_i$: internal energy, partial molar internal energy of i.

U_{el}: contribution of free electrons to the molar internal energy.

$\tilde{U}$: internal electrochemical energy.

U_m: molar internal energy.

U_R: crosslink internal energy.

u_+, u_-: ionic mobilities of the cation and anion.

u_i^0: molar internal energy of pure component i.

V, $\overline{V}_i$:	volume, partial molar volume of *i*.
V_c:	critical volume.
V_G:	Gibbs variance.
V_m:	molar volume.
v_c:	volume of the unitary element of a liquid.
v_D:	Duhem variance.
v_f:	free volume per molecule.
v_∞:	volume of influence around a molecule.
v_i^0 :	molar volume of pure component *i*.
v:	quantum vibration number.
v_m:	molecular volume.
v_M:	molar volume of solid at melting point.
v_{mono}:	volume of monolayer of adsorbed gas.
v_{xi}:	component along *Ox* axis of the velocity of a particle *i*.
W_{12}:	energy per square meter of interaction between the surfaces of phases 1 and 2.
w_i:	mass fraction of the component *i*.
w_{ij}:	energy of exchange between atoms *i* and *j*.
$x_k^{(\alpha)}$:	molar fraction of component *k* in phase α.
x, y, z:	coordinates of a point in space.
x_i:	molar fraction of the component *i* in a solution.
$<y>$:	mean value of *y*.
Y_i and X_i:	conjugal intensive and extensive values.
$y_{i,j}$:	Mayer function.
y_i:	molar fraction of component *i* in a gaseous phase.
Z:	compressibility coefficient.

Z_i:	compressibility coefficient of gas *i*.
Z^{mix}:	compressibility coefficient of the mixture of gases.
Z_{AB}:	molecular partition function of interaction between molecules.
Z_C:	canonical partition function.
$Z_{C(\mathrm{A})}$:	canonical partition function of component A.
$Z_{C(I)}$:	canonical partition function of interaction.
$Z_{C(t)}$:	canonical partition function of translation.
z:	molecular partition function, altitude of a point or coordination index, number of nearest neighbors.
z_e:	electron molecular partition function or electrovalence of ion *i*.
z_i:	number of molecules that are near neighbors of a molecule *i*.
z_{int}:	contribution of internal motions to the molecular partition function.
z_n:	molecular partition function of nuclei.
z_{pf}:	molecular partition function of a perfect gas.
z_r:	rotational molecular partition function.
z_t:	translational molecular partition function.
$z_{t(pf)}$:	translational molecular partition function of a perfect gas.
z_v:	vibrational molecular partition function.
α:	coefficient of dissociation of a weak electrolyte or linear dilation coefficient at pressure *P* or relative volatility or Lagrange multiplier relating to the number of objects of a collection or polarizability of a molecule.
α_{a}:	apparent dissociation coefficient of a weak electrolyte.
β:	Lagrange multiplier relating to the energy of the objects in a collection or volumetric dilation coefficient at pressure *P*.
$\Gamma(E_P)$:	characteristic function with the set E_P as canonical variables.

Γ_k :	coefficient of activity of a group.
Γ:	characteristic function.
Γ_i:	surface excess or surface concentration of component *i*.
$\Gamma_{i,j}$:	excess surface or surface concentration of component *i* in relation to *j*.
γ :	coefficient of activity of the component *i* irrespective of the reference state or Grüneisen parameter or structure coefficient whose value is $\sqrt{2}$ for cubic crystal lattices with centered faces.
γ_0:	activity coefficient of a solvent.
γ_i:	activity coefficient of the species *i* or Grüneisen factor of phonon *i*.
$\gamma_i^{(I)}$:	activity coefficient of component *i*, pure-substance reference.
$\gamma_i^{(II)}$:	activity coefficient of component *i*, infinitely dilute solution reference.
$\gamma_i^{(III)}$:	activity coefficient of component *i*, molar solution reference.
$\gamma_{\pm}$:	mean activity coefficient of ions in an ionic solution.
γ_s:	activity coefficient of a solute.
$\Delta\sigma$:	spreading of a liquid.
$\Delta_r A_T^0$:	standard value at temperature *T* of *A* associated with the transformation *r*.
$\Delta_r A$:	value de *A* associated with the transformation *r*.
$\delta_{i,j}$:	Kronecker delta.
δ:	coefficient of pressure increase at volume *V*.
$\varepsilon_{\mathrm{A(A)}}$:	network energy of an atom of A in network A.
ε_i^j :	Wagner interaction coefficient.

ε : electrical permittivity of the medium.

ε_0 : electrical permittivity of a vacuum.

ε_{attr}: energy of attraction between molecules.

ε_c: kinetic energy of a molecule.

$\varepsilon_{\mathrm{C\text{-}H}}$: energy of the C-H bond.

ε_d: energy from the dispersion effect between molecules.

ε_F: Fermi energy.

$\varepsilon_{i(e)}$: electronic energy of a molecule *i*.

$\varepsilon_{i(I)}$: interactional energy of a molecule *i*.

$\varepsilon_{i(n)}$: nuclear energy of a molecule *i*.

$\varepsilon_{i(r)}$: rotational energy of a molecule *i*.

$\varepsilon_{i(t)}$: translational energy of a molecule *i*.

$\varepsilon_{i(v)}$: vibrational energy of a molecule *i*.

$\varepsilon_{i,j}$: energy of interaction between two molecules *i* and *j* or pair energy between atoms *i* and *j*.

$\varepsilon_{\mathrm{mm}}$: switch.

ε_o: energy due to the effect of orientation between molecules.

ε_p: potential energy of a molecule.

ε_{rep}: repulsion energy between molecules.

η: viscosity.

η_{ij} : Warren and Cowley's order parameter.

Θ_{D}: Debye's vibration temperature.

Θ_{E}: Einstein's vibration temperature.

Θ_{r}: characteristic rotation temperature.

θ: overlap fraction.

θ_i:	surface fraction of a component.
λ:	linear dilation coefficient.
λ_{0+}, λ_{0-}:	equivalent ionic conductivities of the cation and anion.
λ_A :	absolute activity of component A.
λ_ι :	lateral chemical potential of component *i*.
Λ:	equivalent conductivity of an electrolyte or thermal wavelength of a molecule.
Λ_0:	maximum equivalent conductivity of an electrolyte.
μ_i, $[\mu_i]$, $\overline{\mu}_i$:	chemical potential of the component *i*, dipolar electrical moment of molecule *i*, generalized chemical potential.
$\mu_i^{(L)}, \mu_i^{(G)}$:	chemical potential of component *i* in liquid/gaseous state, respectively.
$\tilde{\mu}$:	electrochemical potential.
ν:	vibration frequency.
$\nu_{k(\rho)}$:	algebraic stoichiometric number of component A_k in reaction ρ.
ν_D:	Debye's maximum frequency.
ν_e:	stoichiometric coefficient of electrons in an electrochemical reaction.
ξ:	reaction extent.
Π_d:	disjunction pressure.
ρ:	density of molecules in a spherical crown of radius *r* or volumetric density of electrical charges or density.
$\rho(r)$:	density of molecules in an enclosure.
σ:	surface energy or symmetry number.
σ_e:	surface density of electrical charges.
σ^*:	surface tension.
τ_+, τ_-:	cationic and anionic transport numbers.

Φ :	practical osmotic coefficient; expansion pressure.
Φ_i :	coefficient of fugacity of component *i* in a gaseous mixture.
ϕ:	coefficient of conductivity of a strong electrolyte or number of Phases.
ϕ_i :	coefficient of fugacity of gas *i* in a mixture or volume fraction of a component.
ϕ^0 or ϕ_i^0 :	coefficient of fugacity of a pure gas.
χ_i :	calorimetric coefficient relative to the variable x_i.
χ:	electrical conductivity.
χ_T:	coefficient of compressibility at temperature *T*.
Ψ_i **:**	electrostatic potential of ionic atmosphere.
$\Psi(r)$:	electrostatic potential.
Ψ_{km} :	energy term between two groups.
Ψ:	wavefunction.
Ω_{BE}:	number of complexions in Bose-Einstein statistics.
Ω_{C}:	number of complexions in Fermi-Dirac statistics.
Ω:	number of complexions.
ω_i:	set of position coordinates of molecule *i*.
ω_x:	rotational velocity component in direction *Ox*.

1

Pure Liquids

This chapter will be given over to atomic and molecular liquids. A pure molecular liquid is a liquid comprising only one type of non-dissociated molecules. The study of liquids is more difficult than that of gases and solids because they are in an intermediary state, structurally speaking. Indeed, as is the case with solids, we can imagine that in liquids (and this is confirmed by X-ray diffraction), the interactions between molecules are sufficiently powerful to impose a sort of order within a short distance of the molecules. However, the forces involved in these interactions are sufficiently weak for the molecules to have relative mobility and therefore for there to be disorder (no form of order) when they are far apart, as is the case with gases.

1.1. Macroscopic modeling of liquids

In the areas where liquids are typically used, far from the critical conditions, it is often possible to consider liquids to be incompressible – meaning that $(\partial V / \partial P)_T \cong 0$ – but dilatable. The order of magnitude of a dilation coefficient is 10^{-3} degrees^{-1}, whereas that of the compressibility coefficient is 10^{-4}atm^{-1}.

As we approach the critical conditions, this approximation is no longer possible, and the properties of the liquid tend more to be governed by an equation of state. Whilst the "cubic" equations of state for gases do include critical conditions, it is accepted that the properties of liquids often necessitate equations of state that take account of the intervention of forces when more than two bodies are concerned. Additionally, the third- and

Modeling of Liquid Phases, First Edition. Michel Soustelle.

fourth coefficients of the virial, which can no longer be ignored in the case of liquids, become necessary when these types of forces are at work.

Certain equations of state specific to liquids have been put forward in the literature, including Rocard's, which is written thus:

$$P = \frac{\mathrm{R}TV^2}{(V - b/3)^3} - \frac{a}{V^2} \qquad [1.1]$$

In addition, this equation, expressed as the expansion of the virial, assumes the form:

$$PV = RT\left\{\begin{array}{l} 1 + \left(b - \dfrac{a}{RT}\right)\dfrac{1}{V} + \left(\dfrac{ab}{RT} - \dfrac{b^2}{3}\right)\dfrac{1}{V^2} \\ + \left(\dfrac{b^3}{27} - \dfrac{ab^2}{3RT}\right)\dfrac{1}{V^3} + \dfrac{ab^3}{3RT}\dfrac{1}{V^4} \end{array}\right\} \qquad [1.2]$$

This equation does indeed include the third and fourth coefficients of the virial.

The heat capacities at constant volume and constant pressure are practically identical, around 0.5cal/g, or 2.1kJ/kg.

1.2. Distribution of molecules in a liquid

On a structural level, liquids are classified into two categories: *associated liquids* and *non-associated liquids*.

A liquid is said to be *non-associated* if the intra-molecular degrees of freedom (rotational, vibrational, electronic and nuclear) are not majorly disturbed by the proximity of neighboring molecules. These liquids can be treated, as is the case with gases, with independence between the internal motions and the translation of the molecules.

A liquid is said to be *associated* if, unlike in the previous case, the molecule's internal degrees of freedom are disturbed by the proximity of other molecules. This disturbance may be so great that, in practical terms, we need to consider associations between molecules, coming together to form dimers, trimers, etc. The new bonds that need to be taken into account are usually hydrogen bonds, whose energy is 4-5 times less than that involved in typical chemical bonds, but which are 4-5 times stronger than intermolecular bonding by van der Waals forces. When the temperature rises, these bonds are broken and, particularly when the thermal agitation energy (k_BT) is much greater than the energy in the hydrogen bond, the molecules separate and regain individuality when they are near to the gaseous state.

These associations lend associated liquids very special properties, such as anomalies of the dilation coefficient, high viscosity, low surface tension and a high boiling point. Liquid water belongs to this category. The best way of dealing with these liquids in thermodynamics is to consider them no longer as pure liquids, but rather to treat them as associated solutions, with dimeric, trimeric (etc.) molecules – see section 2.5.

1.2.1. *Molecular structure of a non-associated liquid*

Hereinafter, we shall focus only on non-associated liquids, and we shall suppose the molecules are spherical. A non-associated liquid is characterized by a local order, or short-distance order. The best illustration of this is of liquid metals. In Figure 1.1, which gives a 2-dimensional image of the arrangement of spherical molecules in a liquid, we can see that the molecules are relatively close together, and that around each molecule, there is an area of order which is illustrated by the circles superimposed on the figure. The short-distance arrangement, within the circles, is almost identical to the molecular arrangement in a solid crystal but, unlike with a crystal, there is no long-distance order. The two circles on Figure 1.1 exhibit no periodicity.

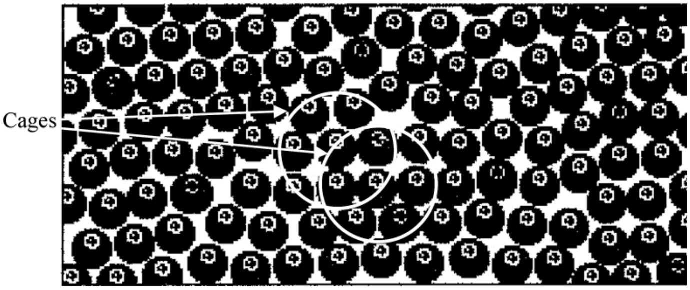

Figure 1.1. *Two-dimensional diagram of the distribution of molecules in a liquid*

The second difference between a crystal and a liquid is that in the latter, the molecules are in perpetual motion, so Figure 1.1 is representative of the situation only at a given time. Unlike with a solid crystal, the distribution of those molecules would be different an instant later, although we would find similar zones of ordered arrangement.

Hence, in order to accurately describe a liquid, we cannot content ourselves with merely describing the position of a few appropriately-chosen neighboring molecules, as we can with the lattice of the crystal. We would have to define the positions of each of the molecules at every moment in time. In view of the impossibility of the task in a medium with normal dimensions (around a mole, which contains 10^{23} molecules), we use statistical methods using so-called *correlation functions*. The paired correlation function which we intend to examine constitutes the first level of this description.

1.2.2. *The radial distribution function*

Throughout this chapter, we shall suppose that the interactions between N particles of a liquid medium are additive and paired, meaning that the internal energy due to these interactions is merely the sum of the interactions between molecules, two by two. Thus, the internal energy is the sum of the energies between the molecules taken two by two $\varepsilon_{i,j}\left(r_{i,j}\right)$. This energy depends only on the distance between the two molecules. Hence, we have:

$$U(1,2,\dots N)=\sum_{i<j}^{N}\varepsilon_{i,j}\left(r_{i,j}\right) \qquad [1.3]$$

Consider a molecule chosen at random in the structure (Figure 1.2). Let d$N(r)$ signify the number of molecules whose centers are situated in the crown between the two spheres centered on the chosen molecule, with radii r and r+dr and volume $4\pi\, r^2$dr. The density of molecules in the crown $\rho(r)$, i.e. the number of molecules situated in the crown per unit volume of that spherical crown, at a distance r from the central molecule, is such that:

$$\rho(r)=\left(\frac{\mathrm{d}N(r)}{\mathrm{d}V(r)}\right)_r=\frac{1}{4\pi r^2}\frac{\mathrm{d}N(r)}{\mathrm{d}r} \qquad [1.4]$$

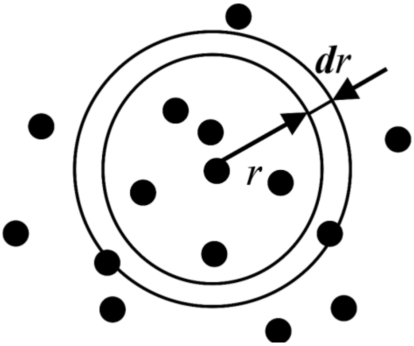

Figure 1.2. *Arrangement of molecules of liquid around the center of a cage*

The volumetric density ρ is defined as the ratio of the total number of molecules in the liquid in question to the volume of that liquid, i.e.:

$$\rho = \frac{N}{V} \qquad [1.5]$$

We define the paired correlation factor or the radial distribution function *g(r)* by the relation:

$$g(r) = \frac{\langle \rho(r) \rangle}{\rho} \qquad [1.6]$$

As we can see, this function is the ratio of the mean value of the local density of molecules (mean calculated at the positions, at a given time and over a period of time) to the volumetric density of molecules. The correlation factor *g(r)* is proportional to the probability of finding a molecule at a distance r + dr from another molecule. Thus, we can write the relation:

$$g(r) = \frac{1}{\rho N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta_{i,j} \left[r - r_{i,j} \right] \right\rangle \qquad [1.7]$$

where $\delta_{i,j}$ is the Kronecker delta, such that: $\begin{cases} \delta_{i,j} = 0 \text{ if } i \neq j \\ \delta_{i,j} = 1 \text{ if } i = j \end{cases}$

This ratio [1.7] quantifies the local structure – in other words, the way in which the molecules are arranged in relation to one another.

1.2.3 *The curve representative of the radial distribution function*

By combining relations [1.4] and [1.6], we see that the mean number of molecules in the coronal volume between the spheres with radii r and $r + \mathrm{d}r$ will be:

$$\left\langle \mathrm{d}N(r) \right\rangle = 4\pi \rho r^2 g(r)\,\mathrm{d}r \qquad [1.8]$$

In the solid crystal, only certain distances exist, and the representative curve for the function $g(r)$ exhibits extremely slender peaks for these distances.

In the case of the liquid, the curve representing the function $g(r)$ has the shape shown in Figure 1.3. We obtain a first peak with a breadth $\Delta r/r$ of several %, which represents the distance between the first neighbors. The next peaks, which represent the second, third (etc.) neighbors, are heavily damped because of the disorder over a long distance. The function $g(r)$ tends toward 1 at a long distance, there is no longer order and therefore, on average, we always find the same number of molecules per unit volume as are present in the overall liquid.

Figure 1.3 can be obtained by neutron diffraction or hard, very penetrating X-ray diffraction, such as those produced by synchrotron sources.

In principle, the distribution $g(r)$ is null for distances less than 0.5 Ä, because there is no chance of finding two molecules that close together, given that the order of magnitude of a molecule's diameter is between 1 and 3 Ä. Around values between 3 and 5 Ä, molecules may be found, and the local density is greater than the overall density. Thus, $g(r)$ is greater than 1. Between the first series of neighbors and the second, there are few molecules, and the factor $g(r)$ drops back below 1. The second maximum corresponds to the second neighbors, which are less precisely localized, and therefore have lower local densities – hence the damping effect seen here.

The more the peaks are damped, the more negligible the influence of the central atom. Thus, it is easy to understand that we can often content ourselves with the influence of the nearest neighbors, i.e. those which correspond to the first peak.

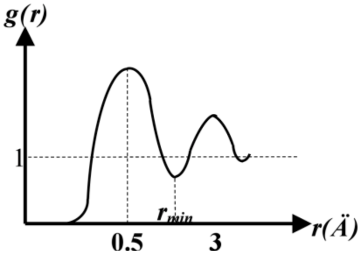

Figure 1.3. *Paired distribution function for a liquid*

We can see that, apart for a few exceptions, the local order and the intermolecular distances of the maxima are the same in the solid and the corresponding liquid. The peaks shown in the solid are very slender, but the first peak is situated at the same value of r.

Diagrams such as Figure 1.3 are very useful, because they enable us to calculate two statistical values:

– the mean distance of the first neighbors. This value is given by the first maximum point on the curve. The breadth of the peaks shows the variation of the distances around the mean value due to the ordering of the molecules and to their agitation;

– the mean value of the number of first neighbors. To calculate this, we decide that the first neighbors are those which are found at distances between 0 and r_{min}. This value is the abscissa of the minimum which follows the first maximum (see Figure 1.3) on the plot of $g(r)$. Thus, for the number of first neighbors, we can write:

$$z = \int_0^{r_{\min}} \mathrm{d}N(r) = 4\pi\rho \int_0^{r_{\min}} r^2 g(r)\,\mathrm{d}r \qquad [1.9]$$

In a liquid, unlike with a crystal, this number may not necessarily be an integer.

1.2.4. *Calculation of the macroscopic thermodynamic values*

We shall show that, like the partition function, the radial distribution function contains all the information pertaining to the thermodynamic definition of the liquid. Therefore, it can be used to calculate the macroscopic values such as the internal energy, the pressure, an equation of state or the heat capacities.

On the basis of relation [1.8], we can write the differential of the internal energy due to the interactions in the form:

$$\mathrm{d}u = \frac{4\pi r^2 \rho g(r)\varepsilon(r)\,\mathrm{d}r}{2} \qquad [1.10]$$

Hence, by integrating over the whole volume:

$$\frac{U - U_{pf}}{\mathrm{R}T} = \frac{\rho}{2\mathrm{k_B}T}\int_0^\infty 4\pi r^2 g(r)\varepsilon(r)\,\mathrm{d}r \qquad [1.11]$$

U_{pf} denotes the internal energy of a fluid with no interaction, i.e. the molar internal energy of the perfect gas which, according to the theorem of equal distribution of energy, has the value:

$$U_{pf} = \frac{3\mathrm{R}T}{2} \qquad [1.12]$$

From this, we can deduce the internal energy:

$$\frac{U}{\mathrm{R}T} = \frac{3}{2} + \frac{\rho}{2\mathrm{k_B}T}\int_0^\infty 4\pi r^2 g(r)\varepsilon(r)\,\mathrm{d}r \qquad [1.13]$$

As we have the expression of the internal energy, which is a characteristic function in variables *V* and *S*, we have all the necessary information to define the phase.

To calculate the pressure, we need to have the differential of the internal energy in variables *P* and *T*, an expression which is of the form:

$$\mathrm{d}U = T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T - \left[P + \left(\frac{\partial P}{\partial T}\right)_V\right]\mathrm{d}V \qquad [1.14]$$

Then, we calculate the pressure on the basis of the derivative of the internal energy in relation to the volume, which gives us:

$$\frac{P}{\rho \mathrm{R}T}=1-\frac{2\pi \mathrm{N}_{\mathrm{a}}^{2}\rho}{3\mathrm{k}_{\mathrm{B}}T}\int_{0}^{\infty} r^{2}g(r)\left[\frac{\mathrm{d}\varepsilon(r)}{\mathrm{d}r}\right]\mathrm{d}r \qquad [1.15]$$

By substituting the value of r found in relation [1.5], written for one mole, back into the above expression, then it is easy to write the equation of state:

$$PV=n\mathrm{N}_{\mathrm{a}}\left\{1-\frac{2\pi \mathrm{N}_{\mathrm{a}}^{2}\rho}{3\mathrm{k}_{\mathrm{B}}T}\int_{0}^{\infty} r^{2}g(r)\left[\frac{\mathrm{d}\varepsilon(r)}{\mathrm{d}r}\right]\mathrm{d}r\right\}RT \qquad [1.16]$$

Similarly, the material derivative of the internal energy in relation to the temperature enables us to easily calculate the heat capacity at constant volume.

We can now calculate all the other functions, particularly the compressibility at constant temperature χ_T, which gives us:

$$\chi_{T}=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T}=\frac{1+\mathrm{N}_{\mathrm{a}}\int_{V}[g(r)-1]4\pi r^{2}dr}{\mathrm{R}T} \qquad [1.17]$$

Thus, we have shown that knowing the radial distribution function enables us to completely define the phase in thermodynamic terms.

We know that a second way of calculating the macroscopic values is to use the canonical partition function. This is the method that we shall use from hereon in. To do so, we must construct a structure of the liquid, in order to be able evaluate the terms of interaction in the canonical partition function. Various techniques are used. We shall describe four such techniques: Guggenheim's and Mie's models, extrapolated respectively from the gas and solid models, the Lennard-John and Devonshire cellular model and the cell/vacancy model.

1.3. Models extrapolated from gases or solids

In light of the proximity of the structure of liquid, firstly to that of a gas (in terms of the mobility of the molecules and the disorder at long distance) and secondly to that of a solid (in terms of the presence of an order over a short distance and figures of X-ray diffraction), the earliest models developed were extrapolations either from a model of a gas or from one of a solid. These models can be used to calculate the radial distribution function and the canonical partition function. As we know that only one of the two is necessary, in our discussion below, we shall restrict ourselves to calculating the canonical partition function.

1.3.1. *Guggenheim's smoothed potential model*

This model [GUG 32] is extrapolated from the imperfect gas model, which can be used to calculate the second coefficient of the virial (see section A.3.4 in Appendix 3). The canonical partition function then takes the form of equation [A.3.41].

From this, we deduce the configuration integral due to the interactions and to the volume, in this case the volume of slightly imperfect gases:

$$I_I = \frac{V^N}{N!}\left(1 - \frac{N^2 B_{\mathrm{AA}}(T)}{V}\right)^N \qquad [1.18]$$

Using the notation v_m to represent the volume per molecule (V/N), or the molecular volume (which must not be confused with the volume of a molecule), and using Stirling's approximation [A.3.1], this expression takes the following equivalent form:

$$I_I = \exp(N)\left(v_m - B_{\mathrm{AA}}(T)\right)^N \qquad [1.19]$$

According to relation [A.3.40], the term B_{AA} is a function only of the temperature.

We can use such an expression for a highly-imperfect gas or a liquid, supposing that the term B_{AA} is also a function of the volume. The difference v_m-$B_{\mathrm{AA}}(T,v_m)$ will therefore represent the free volume per molecule v_f and the above relation will then be written:

$$I_I = \exp(N)\left(v_f(v_m)\right)^N \qquad [1.20]$$

Supposing the potential function to be more or less constant, an initial model of the liquid state was proposed.

Thus, we suppose that each molecule moves through a uniform field of potential, the lattice energy, $(-\varepsilon)$ (attractive) which will be determined by the mean number of near neighbors at a given distance from the molecule, and will essentially be a function of the number of molecules per unit volume, i.e. a function of the volume per molecule v_m. The contribution of the interactions to the canonical function can thus be written by supplementing it with the exponential term corresponding to that uniform potential. Thus, we obtain:

$$I_I = \exp(N)\left(v_f(v_m)\right)^N \left[\exp\left(\frac{\varepsilon(v_m)}{\mathrm{k_B}T}\right)\right]^N \qquad [1.21]$$

This can also be written as:

$$I_I = \left[\exp(1) v_f(v_m) \exp\frac{\varepsilon(v_m)}{\mathrm{k_B}T}\right]^N \qquad [1.22]$$

Hence, in light of relation [A.3.42], and with Stirling's approximation applied, the canonical partition function for the fluid will be written thus:

$$\begin{aligned}\ln Z_C &= \frac{N\varepsilon(v_m)}{\mathrm{k_B}T} + N\ln\left(\frac{\left(2\pi m \mathrm{k_B}T\right)^{3/2} v_f(v_m)}{\mathrm{h}^3}\right) \\ &+ N + N\ln z_{\text{int}} - N\ln N\end{aligned} \qquad [1.23]$$

On the basis of relations [1.23] and [A.3.48], we can calculate the Helmholtz energy F:

$$\begin{aligned}\frac{F}{N} &= -\varepsilon(v_m) - \mathrm{k_B}T\ln\left(\frac{\left(2\pi m \mathrm{k_B}T\right)^{3/2} v_f(v_m)}{\mathrm{h}^3}\right) \\ &- \mathrm{k_B}T - \mathrm{k_B}T\ln z_{\text{int}}\end{aligned} \qquad [1.24]$$

From this, we deduce the pressure:

$$P=-\left(\frac{\partial F}{\partial V}\right)_{T,N}=\frac{\partial \varepsilon(v_m)}{\partial v_m}+\mathrm{k_B}T\frac{\partial \ln v_f(v_m)}{\partial v_m} \qquad [1.25]$$

Most of the time, the properties of the liquid are insensitive to variations in pressure and it is therefore correct to consider the pressure to be zero. Thus, we shall have:

$$\frac{\partial \varepsilon(v_m)}{\partial v_m}+\mathrm{k_B}T\frac{\partial \ln v_f(v_m)}{\partial v_m}\cong 0 \qquad [1.26]$$

Hence, the compressibility factor $Z = PV/\mathrm{R}T$ is essentially null regardless of the volume.

The molecular Gibbs energy is:

$$\begin{aligned}\frac{G}{N}&=\frac{F}{N}+P\frac{V}{N}\\&=-\varepsilon-\mathrm{k_B}T\ln\frac{\left(2\pi m\mathrm{k_B}T\right)^{3/2}v_f}{\mathrm{h}^3}-\mathrm{k_B}T-\mathrm{k_B}T\ln z_{\text{int}}+Pv_m\end{aligned} \qquad [1.27]$$

The molecular internal energy is given by:

$$\frac{U}{N}=-T^2\left(\frac{\partial(F/T)}{\partial T}\right)=-\varepsilon+\frac{3}{2}\mathrm{k_B}T+\frac{U_{\text{int}}}{N} \qquad [1.28]$$

Thus, the molecular enthalpy is:

$$\frac{H}{N}=\frac{U}{N}+P\frac{V}{N}=-\varepsilon+\frac{3}{2}\mathrm{k_B}T+\frac{U_{\text{int}}}{N}+Pv_m \qquad [1.29]$$

The molecular entropy is given by:

$$\begin{aligned}\frac{S}{N}&=-\frac{\partial\frac{F}{N}}{\partial T}=\mathrm{k_B}\ln\left(\frac{\left(2\pi m\mathrm{k_B}T\right)^{3/2}v_f v_m)}{\mathrm{h}^3}\right)\\&+\frac{5}{2}\mathrm{k_B}+\mathrm{k_B}T\frac{\partial \ln v_f}{\partial T}+\mathrm{k_B}\ln z_{\text{int}}\end{aligned} \qquad [1.30]$$

In view of the variation of the free volume with temperature (see section 1.3.3) and of the independence of the volume from pressure ($\chi_T \approx 0$), we find:

$$\frac{S}{N} = \mathrm{k_B} \ln\left(\frac{\left(2\pi m \mathrm{k_B} T\right)^{3/2} v_f)}{\mathrm{h}^3}\right) - \mathrm{k_B} \ln\frac{1}{v_m} + \frac{5}{2}\mathrm{k_B} + \mathrm{k_B} \ln z_{\mathrm{int}} \qquad [1.31]$$

In relations [1.27], [1.28] and [1.29], the pressure can be taken to be null, in keeping with relation [1.26].

1.3.2. *Mie's harmonic oscillator model*

This time referring to the local order in a liquid similar to that of a solid, the potential function is given a form very similar to that of a harmonic oscillator. Thus, a second model of the liquid state [MIE 03] was put forward. Beginning with the quasi-crystalline model of a liquid, we suppose that each molecule is in a field of potential whose minimum is $\varepsilon_0(v_m)$, and that the molecule moves through that field corresponding to a three-dimensional harmonic oscillator of frequency ν, which is also a function of the volume per molecule v_m. We use the symbol r to denote the distance from the center of the molecule to the center of the cavity where the minimum potential is in force. At that distance, the molecule would have a potential energy $-(\varepsilon_0 + \mathrm{k_B}T) + \frac{m(2\pi\nu)^2 r^2}{2}$ so, if we integrate for all possible positions of the molecule, the configuration integral for the partition function is found to be:

$$I_I = \exp\left[N\frac{(\varepsilon_0 + \mathrm{k_B}T)}{\mathrm{k_B}T}\right]\left[\int_0^\infty 4\pi r^2 \exp\left(-\frac{m(2\pi\nu)^2 r^2}{2\mathrm{k_B}T}\right)\mathrm{d}r\right]^N \qquad [1.32]$$

After integration, this gives us:

$$I_I = \left\{\exp\left[\frac{(\varepsilon_0 + \mathrm{k_B}T)}{\mathrm{k_B}T}\right]\left(\frac{\mathrm{k_B}T}{2\pi m\nu^2}\right)^{3/2}\right\}^N \qquad [1.33]$$

Using approximation [A.3.31] for the vibration, the complete canonical partition function is then written:

$$Z_C = \left[z_{\text{int}} \left(\frac{2\pi m \mathrm{k_B} T}{\mathrm{h}^2} \right)^{3/2} \left(\frac{\mathrm{k_B} T}{\mathrm{h}\nu} \right)^3 \right]^N I_1 \tag{1.34}$$

Hence, if we take relation [1.33] into account:

$$Z_C = \left[z_{\text{int}} \left(\frac{2\pi m \mathrm{k_B} T}{\mathrm{h}^2} \right)^{3/2} \right]^N \left\{ \exp\left[\frac{(\varepsilon_0 + \mathrm{k_B} T)}{\mathrm{k_B} T} \right] \left(\frac{\mathrm{k_B} T}{2\pi m \nu^2} \right)^{3/2} \right\}^N \tag{1.35}$$

By switching to logarithms, we obtain:

$$\ln Z_C = \frac{N \varepsilon_0 (v_m)}{\mathrm{k_B} T} + 3N \ln\left(\frac{\mathrm{k_B} T}{\mathrm{h}\nu(v_\mathrm{m})} \right) + N + N \ln z_{\text{int}} \tag{1.36}$$

This is the partition function of the liquid, given by Mie’s 3D harmonic oscillator model.

Based on relations [1.36] and [A.3.48], we find that the Helmholtz energy per molecule is:

$$\frac{F}{N} = -\varepsilon_0 - 3\mathrm{k_B} T \ln\left(\frac{\mathrm{k_B} T}{\mathrm{h}\nu} \right) - \mathrm{k_B} T - \mathrm{k_B} T \ln z_{\text{int}} \tag{1.37}$$

In the same way as we did above, we deduce the expressions for the different functions:

$$P = -\frac{\partial F}{\partial V} = \frac{\partial \varepsilon_0}{\partial v} - 3\mathrm{k_B} T \frac{\partial \ln v_f}{\partial v_m} \cong 0 \tag{1.38}$$

$$\frac{G}{N} = -\varepsilon_{0N} - 3\mathrm{k_B} T \ln \frac{\mathrm{k_B} T}{\mathrm{h}\nu} - \mathrm{k_B} T - \mathrm{k_B} T \ln z_{\text{int}} + P v_m \tag{1.39}$$

$$\frac{U}{N} = -\varepsilon_0 + 3\mathrm{k_B} T + \frac{U_{\text{int}}}{N} \tag{1.40}$$

$$\frac{H}{N}=-\varepsilon_0+3\mathrm{k_B}T+\frac{U_{\mathrm{int}}}{N}+Pv_m \qquad [1.41]$$

In all these relations, the term Pv_m is negligible.

The entropy per molecule is given by:

$$\frac{S}{N}=-\frac{\partial\left(\frac{F}{N}\right)}{\partial T}=3\mathrm{k_B}\ln\left(\frac{\mathrm{k_B}T}{\mathrm{h}\nu}\right)+4\mathrm{k_B}+\mathrm{k_B}\ln z_{\mathrm{int}} \qquad [1.42]$$

This expression is independent of the volume.

Thus, we obtain two different series of expressions. We usually use the smoothed potential model we link the properties of gases to those of liquids, and the harmonic oscillator model to link the properties of liquids to those of solids.

NOTE 1.1.– Relations [1.24] and [1.37] may be identical for a certain temperature and a certain volume per molecule, identifying ε with ε_0 and attributing the following value for the molecular volume:

$$v_m=\left(\frac{\mathrm{k_B}T}{2\pi m\nu^2}\right)^{3/2} \qquad [1.43]$$

1.3.3. *Determination of the free volume on the basis of the dilation and the compressibility*

The free volume of the liquid, which we need to know in order to exploit Guggenheim's model, can be determined by a variety of methods: velocity of propagation of sound, vapor pressure, measurements of dilatation and compressibility. We have chosen to discuss this latter method.

In view of their definitions, the volumetric dilation coefficient and compressibility coefficient enable us to write:

$$\frac{\beta}{\chi_T}=-\frac{(\partial V/\partial T)_{P,N}}{(\partial V/\partial P)_{T,N}}=\left(\frac{\partial P}{\partial T}\right)_{V,N} \qquad [1.44]$$

In light of relation [1.26] (with ε and v_f being functions only of v_m), we can write:

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \mathrm{k_B}\frac{\partial \ln v_f}{\partial v_m} \qquad [1.45]$$

However, if we consider that the molecules are arranged in a cubic lattice with centered faces, spaced the length a apart, we can take the following value for the free volume for the molecules:

$$v_f = \frac{4\pi}{3}(a-D)^3 \qquad [1.46]$$

Using relation [1.51], which we shall demonstrate later on (see relations [1.50] and [1.51] in section 1.4), we can write:

$$\frac{\partial \ln v_f}{\partial v_m} = \frac{\left(\frac{4\pi}{3}\sqrt{2}\right)^{1/3}}{v_m^{2/3} v_f^{1/2}} \qquad [1.47]$$

By substituting this value back into equations [1.44] and [1.45], we find the value of the molecular free volume:

$$v_f = \frac{4\pi\sqrt{2}\mathrm{k_B^{1/3}}\chi_T^3}{3v_m^2\beta^3} \qquad [1.48]$$

If, for β and χ_T, we take orders of magnitude of, respectively, $10^{-3}\mathrm{K}^{-1}$ and $10^{-4}\mathrm{atm}^{-1}$, we obtain, e.g. for chloroform:

$$\mathrm{N_a} v_f = 0.44\ \mathrm{cm^3/mole} \qquad [1.49]$$

This value is perfectly acceptable.

1.4. Lennard-Jones and Devonshire cellular model

This model [LEN 37] is based on Figure 1.4. Each molecule is inside a spherical cage – the cell – whose radius is a. This sphere is the molecule's mean sphere of influence.

The energy of interaction between two molecules is expressed by Lennard-Jones' relation [A.3.44]. This interaction is limited to the molecule's z nearest neighbors.

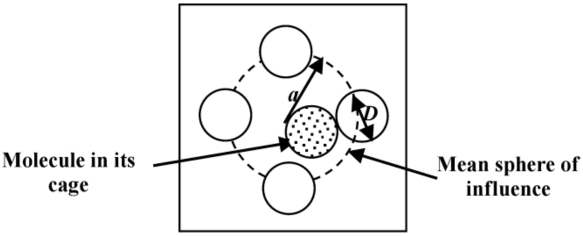

Figure 1.4. *Cage and molecules of liquid*

This number z is the coordination index linked to the cell geometry. We shall suppose that the molecules occupy the sites of a cubic lattice with centered faces, and therefore the coordination index is $z = 12$.

The volume of liquid is divided into cells centered on each molecule, whose near neighbors occupy the medium from the vertices of a cube with side length $2a/\sqrt{2}$. Each molecule which is a near neighbor of the original one thus belongs to four cells, and each cell contains 1 + 12/4 = 4 molecules. Hence, the volume of the cell is such that:

$$4v_m = 8a^3 / \left(\sqrt{2}\right)^3 \tag{1.50}$$

and therefore:

$$a^3 = v_m\sqrt{2} \tag{1.51}$$

The translational canonical partition function with interactions can be written, on the basis of expression [A.3.38], taking account only of the z molecules that are near neighbors of each molecule i.

$$Z_{C(t)} = \frac{1}{N!}\left(\frac{z_{pf}}{V}\right)^N \iint_V\ldots\int \exp - \frac{\sum_{i=1}^{N}\sum_{j=1}^{z}\varepsilon_{i,j}\left(\omega^N\right)}{\mathrm{k_B}T}\left(\mathrm{d}\,\omega\right)^N \tag{1.52}$$

On the basis of relation [A.3.24], using $\varepsilon\left(\omega^N\right)$ to denote the double sum appearing in the previous relation, the canonical partition function becomes:

$$Z_{C(t)} = \frac{1}{N!}\left[\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}}\right]^{-3N} \iiint\limits_{V}\cdots\int\limits_{V} \exp\left(-\frac{\varepsilon\left(\omega^N\right)}{\mathrm{k_B}T}\right)(\mathrm{d}\omega)^N \qquad [1.53]$$

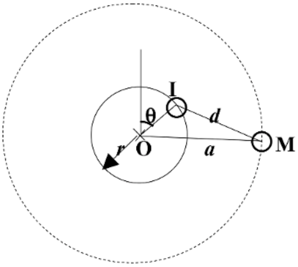

Figure 1.5. *Distance between a molecule and one of its near neighbors*

We shall now evaluate the double sum $\varepsilon\left(\omega^N\right)$. The near neighbors of a molecule i are, in fact, situated at different distances d_{ij} from it, and those distances change over time. Rather than moving both the molecule i and its near neighbors at once, we shall suppose that the center of the cell is stationary, that the molecule i moves in concentric circles of radius r around that center, and that the near neighbors are affixed to a concentric sphere with radius a. The radius r varies between 0 and a. Consider the plane passing through the molecule i at point I, one of its near neighbors at M and the center of the cell O (Figure 1.5).

In order to simplify the multiple integration appearing in expression [1.53], we shall create spherical symmetry and average the distance from the atom i along a radius r to all its near neighbors. The energy $\varepsilon\left(\omega^N\right)$ can be written:

$$\varepsilon\left(\omega^N\right) = \frac{Nz}{2}\varepsilon(a) + \frac{z}{2}\sum_{i=1}^{N}\left[\langle\varepsilon(d)\rangle - \varepsilon(a)\right] \qquad [1.54]$$

$\langle \varepsilon(d) \rangle$ is the mean mutual energy between the atom *i* and a near neighbor when the atom *i* is on the disc of radius *r*. This energy is a function of the distance, which is given by the following equation (see Figure 1.5):

$$d = \sqrt{r^2 + a^2 + 2ar\cos\theta} \qquad [1.55]$$

The mean energy is:

$$\langle \varepsilon(d) \rangle = \int_0^{\pi} \varepsilon(d)\sin\theta\,\mathrm{d}\theta \qquad [1.56]$$

Using relation [A.3.44] for the potential energy of interaction and substituting into it the value given by relation [1.55], we find:

$$\langle \varepsilon(d) \rangle = \frac{Nz\varepsilon_0}{2}\left[\left(\frac{d_0}{a}\right)^{12}\mathrm{l}\left(\frac{d^2}{a^2}\right) - 2\left(\frac{d_0}{a}\right)^{6}\mathrm{m}\left(\frac{d^2}{a^2}\right)\right] \qquad [1.57]$$

with the following meaning for the functions “l” and “m” that appear in equation [1.57]:

$$\mathrm{l} = \frac{a^2}{d^2}\left\{\begin{pmatrix} 1 + 12\dfrac{d^2}{a^2} + 50\left(\dfrac{d^2}{a^2}\right)^2 \\ +12\left(\dfrac{d^2}{a^2}\right)^3 + \left(\dfrac{d^2}{a^2}\right)^4 \end{pmatrix}\left(1 - \frac{d^2}{a^2}\right)^{-10} - 1\right\} \qquad [1.58]$$

$$\mathrm{m} = \frac{a^2}{d^2}\left\{\left(1 + \frac{d^2}{a^2}\right)\left(1 - \frac{d^2}{a^2}\right)^{-4} - 1\right\} \qquad [1.59]$$

Figure 1.6 shows two curves illustrating the variations of our potential energy as a function of the ratio *d*/*a* for two values of the ratio d_0/a equal to 0.942 (part *a*) and 0.681 (part *b*). *A posteriori*, these two functions provide a justification: the first, for the approximation of the smoothed potential theory, as the potential energy is practically constant (part *a*), and the second, for the approximation of the 3D oscillator theory, with the potential energy showing a near-parabolic shape as a function of the distance (part *b*).

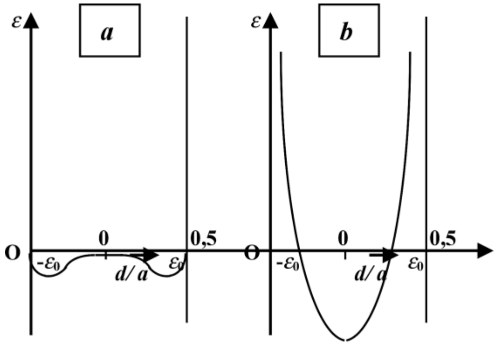

Figure 1.6. *Potential for interaction of a molecule in a liquid according to Lennard-Jones and Devonshire. a) for $d_0/a = 0.942$; b) $d_0/a = 0.681$*

By substituting expression [1.57] back into relation [1.53], the contribution of the translational motion to the canonical partition function can be written as:

$$Z_{C(t)} = \frac{1}{N!}\left[\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}}\right]^{-3N}\left[2\pi N a^3 \int_0^{a/2} \exp\left(\frac{\langle \varepsilon(d)\rangle - \varepsilon(a)}{\mathrm{k_B} T}\right) \mathrm{d}x\right]^N \qquad [1.60]$$

According to Lennard-Jones and Devonshire, the integration limit in equation [1.60] is of no importance, because the greater part of the contribution is made by small distances, particularly where $d < a/2$.

If we set $x = d/a$, then the logarithm of the translational partition function is:

$$\ln Z_{C(t)} = N \ln \frac{\left(2\pi m \mathrm{k_B} T\right)^{3/2}}{\mathrm{h}^3} + N$$
$$+N \frac{6\varepsilon_0 \left[-2\left(\frac{d_0}{a}\right)^6 + \left(\frac{d_0}{a}\right)^{12}\right]}{\mathrm{k_B} T} + N \ln\left(2\pi a^3\right) + N \ln\left[\eta(\varepsilon_0, d_0)\right] \qquad [1.61]$$

We have chosen $z = 12$, and $\eta(\varepsilon_0, d_0)$ denotes the function defined by:

$$\eta(\varepsilon_0, r_0) = \int_0^{1/2} x^{1/2} \exp\left[\frac{\varepsilon_0}{\mathrm{k_B}T} \left\{ \begin{array}{l} \left(\dfrac{d_0}{a\gamma}\right)^{12} \mathrm{l}(x) \\ -2\left(\dfrac{d_0}{a\gamma}\right)^{6} \mathrm{m}(x) \end{array} \right\} \right] \mathrm{d}x \qquad [1.62]$$

d_0/a	$\dfrac{\varepsilon_0}{\mathrm{k_B}T} = -9$	$\dfrac{\varepsilon_0}{\mathrm{k_B}T} = -10$
0.942	0.00180	0.00161
0.918	0.00295	0.00269
0.891	0.00515	0.00478
0.858	0.00964	0.00916
0.818	0.01957	0.01920
0.765	0.0437	0.0445
0.730	0.0676	0.0700
0.681	0.1069	0.1125

Table 1.1. *Values of the function* $\eta(\varepsilon_0, d_0)$

The energy $\varepsilon(a)$ is given by:

$$\varepsilon(a) = \varepsilon_0 \left[-2\left(\frac{d_0}{a}\right)^6 + \left(\frac{d_0}{a}\right)^{12} \right] \qquad [1.63]$$

Table 1.1 gives a few values, which are easy to calculate automatically, for this function for two values of the ratio $\varepsilon_0/\mathrm{k_B}\mathrm{T}$ and different values of the ratio d_0/a.

Thus, if we accept the hypothesis of a cubic stack with centered faces, i.e. $\gamma = \sqrt{2}$, and if we know the molecular volume, the translational partition function contains only two parameters linked to the substance: d_0 and ε_0, which are the two parameters that play a part in the expression [A.3.44] (in Appendix 3) of the Lennard-Jones interaction potential.

In order to compare the result to other models and to experimental results, we need to deduce the expressions of the thermodynamic functions. From relation [A.3.48], we deduce the expression of the molecular Helmholtz energy function:

$$\begin{aligned}\frac{F}{N} &= -\mathrm{k_B}T\ln\frac{\left(2\pi m\mathrm{k_B}T\right)^{3/2}}{\mathrm{h}^3} - \mathrm{k_B}T - \frac{6\varepsilon_0\left[-2\left(\dfrac{d_0}{a}\right)^6+\left(\dfrac{d_0}{a}\right)^{12}\right]}{\mathrm{k_B}T} \\ &\quad -\mathrm{k_B}T\ln\left(2\pi a^3\right) - \mathrm{k_B}T\ln z_{\mathrm{int}} - \mathrm{k_B}T\ln 2\sqrt{2}\pi\eta(\varepsilon_0,d_0)v_m\end{aligned} \qquad [1.64]$$

Here, z_{int} represents the contribution of all other internal motions of the molecule to the molecular partition function (rotations, vibrations, electronic and nuclear spin motions). For atomic liquids, this term can be taken as being equal to 1.

Based on the Helmholtz energy, it is easy to obtain the other thermodynamic functions such as:

$$PV_m = V_m\frac{\partial F}{\partial V} \qquad [1.65]$$

Thus:

$$PV_m = \mathrm{R}T\left\{\begin{array}{l} 1+\dfrac{12\varepsilon(a)}{\mathrm{k_B}T}\left[2\left(\dfrac{d_0}{a\gamma}\right)^6-4\left(\dfrac{d_0}{a\gamma}\right)^{12}\right] \\ -48\dfrac{\varepsilon(a)}{2\mathrm{k_B}T}\left[\left(\dfrac{d_0}{a\gamma}\right)^{12}\dfrac{\eta_l(\varepsilon_0,d_0)}{\eta(\varepsilon_0,d_0)}-2\left(\dfrac{d_0}{a\gamma}\right)^6\dfrac{\eta_m(\varepsilon_0,d_0)}{\eta(\varepsilon_0,d_0)}\right]\end{array}\right\} \qquad [1.66]$$

$\eta_l(\varepsilon_0,d_0)$ and $\eta_m(\varepsilon_0,d_0)$ being two functions, such as $\eta(\varepsilon_0,d_0)$, of the two variables d_0 and ε_0. They can be calculated numerically using the relations:

$$\eta_l(\varepsilon_0,r_0) = \int_0^{1/2} x^{1/2}\,\mathrm{l}(x)\exp\left[\frac{12\varepsilon_0}{\mathrm{k_B}T}\left\{\begin{array}{l}\left(\dfrac{d_0}{a\gamma}\right)^{12}\mathrm{l}(x) \\ -2\left(\dfrac{d_0}{a\gamma}\right)^6\mathrm{m}(x)\end{array}\right\}\right]\mathrm{d}x \qquad [1.67]$$

$$\eta_m(\varepsilon_0, r_0) = \int_0^{1/2} x^{1/2}\, \mathrm{m}(x) \exp\left[\frac{12\varepsilon_0}{\mathrm{k_B}T}\left\{\begin{array}{l}\left(\dfrac{d_0}{a\gamma}\right)^{12} \mathrm{l}(x) \\ -2\left(\dfrac{d_0}{a\gamma}\right)^{6} \mathrm{m}(x)\end{array}\right\}\right] \mathrm{d}x \qquad [1.68]$$

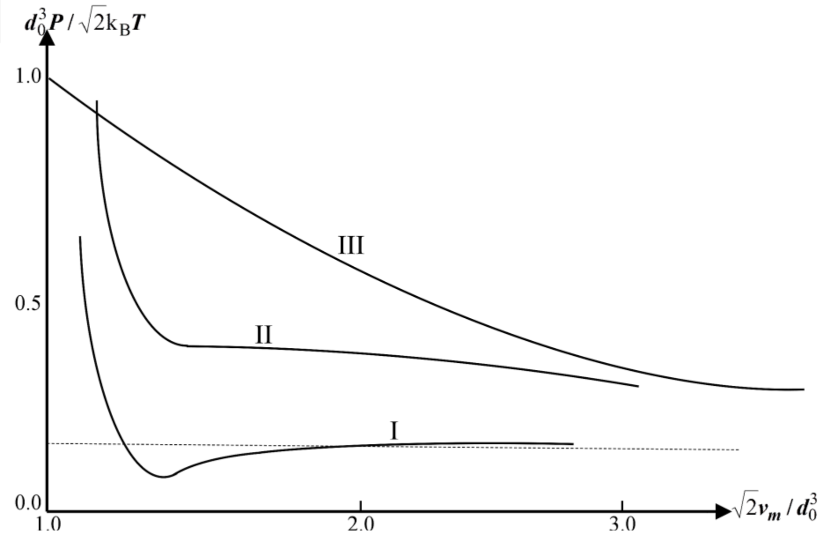

Figure 1.7. *Isotherms calculated using the Lennard-Jones and Devonshire model*

NOTE 1.2.– In expression [1.60], by comparison with the translational canonical partition function for a perfect gas (relation [A.3.26]), we can define the free volume of the molecules as:

$$\begin{aligned} v_f &= 2\pi a^3 \int_0^{1/2} \exp\left(\frac{\langle \varepsilon(d)\rangle - \varepsilon(a)}{\mathrm{k_B}T}\right) \mathrm{d}x \\ &= 2\pi\eta(\varepsilon_0, d_0)\gamma v_m = 2\sqrt{2}\pi\eta(\varepsilon_0, d_0) v_m \end{aligned} \qquad [1.69]$$

Figure 1.7 shows a few forms of isotherms in the representation $d_0^3 P/\sqrt{2}\mathrm{k_B}T$ as a function of $\sqrt{2}v_m/d_0^3$. Curve (III) is that of a perfect gas, curve (II) is obtained for $12\varepsilon_0/\mathrm{k_B}T = -9$, and curve (I) for

$12\varepsilon_0 / \mathrm{k_B}T = -10$. It is noteworthy that curve (II) seems very similar to the critical isotherm which is given by:

$$T_c = -\frac{4\varepsilon_0}{3\mathrm{k_B}} \qquad [1.70]$$

The values obtained for certain liquids (see Table 1.2) show a satisfactory degree of accordance with their experimental values.

Substances	d_0 (Ä)	$-\varepsilon_0$ (10^{-22} joules/molecule)	T_c calculated	T_c observed
H_2	35.3	4.25	41	33
Ne	29.2	4.89	47	44.47
N_2	72.5	13.25	128	126
A	56.2	16.5	160	150.66

Table 1.2. *Values of the critical temperature, found experimentally and calculated by the Lennard-Jones and Devonshire model*

It is a fairly laborious task to rigorously calculate the critical volume, but from Figure 1.7, it seems we can choose the critical volume such that:

$$\frac{\sqrt{2}v_c}{d_0^3} = 2 \text{ so that } v_c = d_0^3\sqrt{2} \qquad [1.71]$$

We can see that this value is far too low. Indeed, it yields a value of 0.7 for $d_0^3 P / \sqrt{2}\mathrm{k_B}T$, instead of 0.3, which is the result found experimentally.

Thus, the Lennard-Jones and Devonshire cellular model can be used to calculate thermodynamic functions with only two adjustable parameters. In section 1.7, however, we shall demonstrate that the results obtained are very approximate, so there is a necessity to perfect the model. This was the purpose of the cellular and vacancies model developed by Ono and Eyring.

1.5. Cellular and vacancies model

Whilst it does represent real progress in relation to the previous two models, the Lennard-Jones and Devonshire model discussed above has a serious shortcoming–it is incapable of taking account of two dynamic properties of liquids: the phenomena of viscosity and self-diffusion. In order to take account of these properties, Ono [ONO 47] introduced the concept of vacancies, comparable to that which takes account of conductivity and diffusion in the solid phase. Ono considers that certain sites in the pseudo-lattice, or if you prefer, certain cells described in the above model, are not occupied, forming what we call vacancies. Thus, on average, over time, a molecule *i* will be surrounded by z_i first neighbors in accordance with:

$$z_i = y_i z \qquad [1.72]$$

y_i appears as the fraction of first-neighbor sites occupied around the molecule *i*. Therefore, y_i is a short-distance order index, whose value is zero when the central molecule *i* is surrounded only by holes (i.e. no molecules), and 1 if all the cells neighboring the central molecule are occupied (see section 3.2.1). Its spatial mean would be $<y_i>$, and would correspond to the mean value of the number of first neighbors $<z_i>$ determined by the first maximum of the radial distribution function demonstrated by X-ray diffraction. The number z, which is the coordination index, is in fact that maximum possible number of first neighbors, given by the chosen structure; that value is often taken to be equal to 12 for cubic cells with centered faces.

In order to take account, individually, of the environs of each molecule, we divide the liquid volume V into L cells ($L \geq N$) with respective volumes τ_1, τ_2 … τ_L. The configuration integral, which is expressed over the whole of the volume V, and plays a part in relation [1.53], will be replaced by a sum of partial integrals, each of which corresponds to an individual cell. Relation [1.53] then becomes:

$$Z_{C(t)} = \frac{1}{N!}\left[\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}}\right]^{-3N} \sum_{l_1=1}^{L} \cdots \sum_{l_n=1}^{L} \int_{\tau_1} \cdots \int_{\tau_N} \exp\left(-\frac{\varepsilon\left(\omega^N\right)}{\mathrm{k_B} T}\right) \left(\mathrm{d}\omega\right)^N \qquad [1.73]$$

The sum contains L^N terms which correspond to L different cells, in relation to which the coordinates of the different molecules are expressed. Because each cell is supposed to be sufficiently small to contain at most one molecule, and sufficiently large so that the intermolecular forces are practically no longer felt beyond the immediately adjacent cells, the sums in expression [1.73] contain only $L!/(L\text{-}N)!$ non-null terms.

The energy $\varepsilon\left(\omega^N\right)$ in expression [1.71] will therefore be rewritten, instead of expression [1.54], in the form:

$$\varepsilon\left(\omega^N\right)=\sum_{i=1}^{N}\frac{z_i}{2}\varepsilon(a)+\sum_{i=1}^{N}\frac{z_i}{2}\left[\langle\varepsilon(d_i,y_i)\rangle-\varepsilon(a)\right] \qquad [1.74]$$

The distance d_i is given, for each cell, by a relation similar to expression [1.55], namely:

$$d_i=\sqrt{r_i^2+a^2+2ar_i\cos\theta} \qquad [1.75]$$

We use the notation v_c to denote the volume of a given cell, and for the cubic lattice with centered face, we have:

$$v_c=\frac{a^3}{\sqrt{2}} \qquad [1.76]$$

Note that this cellular volume differs from the molecular volume $v_m = V/N$, because we no longer always have a molecule in each cell.

NOTE 1.3.– The volumes v_c and v_m have a known ratio, because we have:

$$\frac{v_c}{v_m}=\langle y_i\rangle=\frac{N}{L} \qquad [1.77]$$

Hence, instead of relation [1.61], the translational canonical partition function is written as:

$$Z_{C(t)}=\frac{1}{N!}\left[\frac{\mathrm{h}}{\left(2\pi m\mathrm{k_B}T\right)^{1/2}}\right]^{-3N}\sum_{l_1=1}^{L}\cdots\sum_{l_N=1}^{L}\left[\prod_{i=1}^{N}\exp\left(-\frac{z_i\varepsilon(a)}{2\mathrm{k_B}T}\right)\mathrm{j}(y_i)\right] \qquad [1.78]$$

The function $j(y_i)$ is homogeneous with a volume. It is defined by:

$$j(y_i) = \int_{\tau_i} 4\pi r_i^2 \left\{ \exp \frac{-zy_i\left[\langle \varepsilon(d_i, y_i)\rangle\right] - \varepsilon(a)}{2k_B T} \right\} \mathrm{d}r_i \qquad [1.79]$$

If all the sites are occupied, $y_i = 1$ and $j(y_i)$ is identified with the free volume logarithm v_f from relation [1.69]. If $y_i = 0$, then $j(0)$ is the logarithm of the volume of the cell v_c.

We can see that the function $j(y_i)$ is not a simple expression, and the various authors have been led to simplify it by a linear form of y_i as a function of the logarithm of v_f and v_c so as to satisfy the boundary values of $j(y_i)$. Thus, Ono proposed the expression:

$$j(y_i) = y_i \ln\left(v_f\right) + \left(1 - y_i\right)\ln v_c \qquad [1.80]$$

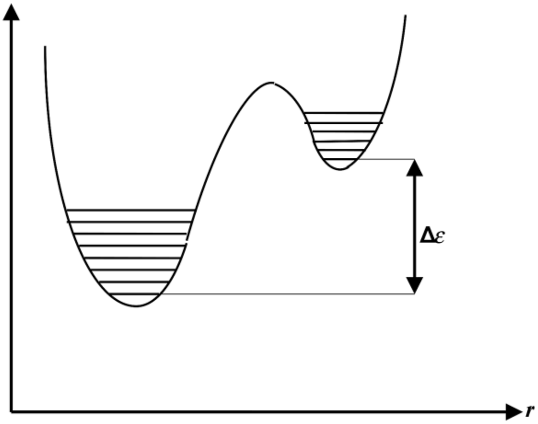

Figure 1.8. *Potential energy curve for a molecule occupying a more favorable position than a neighboring vacancy (from [REE 64])*

Eyring and his collaborators [REE 64] put forward the formula:

$$j(y_i) = y_i \ln\left(v_f g_i\right) + \left(1 - y_i\right)\ln v_c \qquad [1.81]$$

Eyring's function differs from Ono's only by the introduction of a factor g, known as the *degeneration factor*, which is introduced because it is natural to suppose that, of all the places that are available, on average, for a molecule, some are more favorable than others, energetically speaking, simply because of the organization of the other molecules. This difference in energy between the most probable place and a less-probable near neighbor (see Figure 1.8) must be proportional to the interaction energy $z\varepsilon(a)/2$, and inversely proportional to the number of vacancies $n_h = z\left(1-\langle y_i\rangle\right)$. Thus, this energy difference would be of the form:

$$\Delta\varepsilon = \frac{kz\varepsilon(a)}{2n_h} = \frac{k\varepsilon(a)}{2\left(1-\langle y_i\rangle\right)} \qquad [1.82]$$

k is an adjustable constant of proportionality. Thus, the degeneration factor due to the vacancies present around a molecule would be written as:

$$\begin{aligned} g &= 1 + z\left(1-\langle y_i\rangle\right)\exp\left[\frac{\Delta\varepsilon}{\mathrm{k_B}T}\right] \\ &= 1 + z\left(1-\langle y_i\rangle\right)\exp\left[\frac{k\varepsilon(a)}{2\mathrm{k_B}T\left(1-\langle y_i\rangle\right)}\right] \end{aligned} \qquad [1.83]$$

The authors show that if we take account of relation [1.81], using the Bragg-Williams approximation ($\Delta\varepsilon = 0$ in g, see section 3.1.2) and Stirling's approximation [A.3.1], the translational canonical partition function [1.78] assumes the form:

$$\begin{aligned} \ln Z_{C(t)} = -3N\ln\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B}T\right)^{1/2}} + \frac{v_c N}{v_m}\Bigg\{\left[-\frac{z\varepsilon(a)}{2\mathrm{k_B}T}\right] + \ln\frac{v_f}{v_c} \\ + \ln\left[1 + \frac{v_m - v_c}{v_m}\exp - \frac{k v_m \varepsilon(a)}{2(v_m\text{-}v_c)\mathrm{k_B}T}\right] \\ + N\ln v_m + \left(1-\frac{v_m}{v_c}\right)N\ln\left(1-\frac{v_c}{v_m}\right)\Bigg\} \end{aligned} \qquad [1.84]$$

Using this expression, the thermodynamic functions – particularly the Helmholtz energy – can be calculated.

1.6. Eyring's semi-microscopic formulation of the vacancy model

The expressions used by Eyring in the vacancy model become complicated and tricky to calculate numerically. In order to remedy this situation, Eyring and his collaborators [EYR 61] adapted the vacancy model to a semi-microscopic model, by replacing Lennard-Jones' interaction functions with macroscopic values, involving the molar volume of the solid $v^{0(sol)}$ at its melting point and that of the liquid $v^{0(liq)}$ at the temperature of study. Observing (except for a few very rare cases, one of which is water, which is not a non-associated liquid) a significant increase (around a twofold increase) in the molar volume upon transitioning from the solid state to the liquid state, the authors model a liquid as being a two-component solution:

- molecules, which behave like a molecule in a solid, i.e. three vibrational degrees of freedom. This is the model of the short-distance lattice aspect;
- vacancies, which behave like a gas, and therefore have three translational degrees of freedom, which we shall suppose to be perfect, with non-localized objects that are free to move around, which will create disorder over a long distance and mobility of the species.

Of course, the movement of a vacancy is, in fact, the movement of a molecule neighboring that vacancy.

Solids, just below their melting point, are assumed to contain no vacancies. If there are any, they are few in number in relation to the molecules. In a liquid, on the other hand, the number of vacancies is of the same order of magnitude as the number of molecules. If N denotes the number of molecules behaving like a solid, the number of vacancies would be:

$$N_L = N\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}} \qquad [1.85]$$

Thus, the total number of cells would be:

$$N_c = N_L + N = N\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}} \qquad [1.86]$$

Hence, the fraction of sites with molecules would be:

$$x_s = \frac{N}{N_c} = \frac{v^{0(sol)}}{v^{0(liq)}} \qquad [1.87]$$

and the fraction of sites with vacancies would be:

$$x_L = \frac{N_L}{N_c} = \frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}} \qquad [1.88]$$

The mean number of vacancies neighboring a molecule (z is the coordination index of the lattice) would be:

$$\langle n_L \rangle = z\frac{x_L}{x_s} = z\frac{v^{0(sol)}}{v^{0(liq)}} \qquad [1.89]$$

By applying relation [A.3.36] to both components of the solution, we can calculate the canonical partition function on the basis of that of the localized molecules and non-localized vacancies, so that:

$$Z_C = Z_{C(s)}.Z_{C(L)} \qquad [1.90]$$

As the vacancies behave like a perfect gas with three translational degrees of freedom, we have:

$$Z_{C(L)} = \left\{\left[\frac{\mathrm{h}}{(2\pi m \mathrm{k_B} T)^{1/2}}\right]^{-3}\left(v^{0(liq)} - v^{0(sol)}\right)\right\}^{N\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}}} \left\{\left(N\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(liq)}}\right)!\right\}^{-1} \qquad [1.91]$$

For molecules which behave like a solid, with three vibrational degrees of freedom, if we ignore the residual vibration, we have:

$$Z_{C(s)} = \frac{g}{\left[1 - \exp\left(-\frac{\mathrm{h}\nu}{\mathrm{k_B}T}\right)\right]^3} \qquad [1.92]$$

The degeneration coefficient is calculated in a similar manner to that used to obtain relation [1.85]. Its value is:

$$g = 1 + n \exp\left[-\frac{\Delta\varepsilon}{\mathrm{k_B}T}\right] \qquad [1.93]$$

If $\Delta_S U$ is the Helmholtz energy of sublimation of the solid, the variation in energy $\Delta\varepsilon$ (Figure 1.8) will be proportional to the sublimation energy and inversely proportional to the number of vacancies N_L. We can write this in a similar manner to expression [1.82]:

$$\Delta\varepsilon = \frac{k \Delta_s U v^{0(sol)}}{v^{0(liq)} - v^{0(sol)}} \qquad [1.94]$$

The partition function of the molecules with solid behavior would therefore be:

$$Z_{C(s)} = \left\{ \frac{\exp\left(\frac{\Delta_s U}{\mathrm{R}T}\right)}{\left[1 - \exp\left(-\frac{\mathrm{h}\nu}{\mathrm{k_B}T}\right)\right]^3} \left(1 + \langle n \rangle \frac{v^{0(liq)} - v^{0(sol)}}{v^{0(sol)}} \exp - \frac{k \Delta_s U v^{0(sol)}}{\mathrm{R}T\left(v^{0(liq)} - v^{0(sol)}\right)}\right) \right\}^{\frac{N v^{0(sol)}}{v^{0(liq)}}} \qquad [1.95]$$

Using expressions [1.90], [1.91] and [1.95] for the overall partition function, and after application of Stirling's approximation, we find:

$$\ln Z_C = \frac{N v^{0(sol)}}{v^{0(liq)}} \left\{ \begin{aligned} & \frac{\Delta_s U}{\mathrm{R}T} - 3\ln\left[1 - \exp\left(-\frac{\mathrm{h}\nu}{\mathrm{k_B}T}\right)\right] + \\ & \ln\left(1 + z\frac{v^{0(liq)} - v^{0(sol)}}{v^{0(liq)}}\exp - \frac{k\Delta_s U v^{0(sol)}}{\mathrm{R}T\left(v^{0(liq)} - v^{0(sol)}\right)}\right) \end{aligned} \right\} + \frac{N\left(v^{0(liq)} - v^{0(sol)}\right)}{v^{0(liq)}}\left[-3\ln\frac{\mathrm{h}}{\left(2\pi m \mathrm{k_B} T\right)^{1/2}} + \ln\frac{e v^{0(liq)}}{N}\right] \quad [1.96]$$

We can see that the canonical partition function, and therefore all the thermodynamic functions (particularly the Helmholtz energy) depend only on the single adjustable parameter *k* defined in expression [1.94]. Hence, this model is a simple and powerful tool.

The model we have just looked at is that which applies to atomic liquids, such as argon, for instance. Eyring and his collaborators carried out parallel tests, applied to the cases of molten salts and liquid metals.

NOTE 1.4.– It is worth noting that Eyring's model, for the partition function (relation [1.90]) is tantamount to mixing Guggenheim's (section 1.3.1) and Mie's (section 1.3.2) models. These models gave a good account of the properties of liquids respectively in the vicinity of a gaseous state and of a solid state.

1.7. Comparison between the different microscopic models and experimental results

A variety of comparisons have been offered by the different creators of models: comparisons between a model and the experimental results, comparisons between different models, and comparisons between results produced by a model and those produced by simulation calculations. Indeed, the calculation methods used for statistic simulation lend themselves very well to this type of problem. Examples include the static Monte Carlo method, based on equation [1.3], or the molecular dynamics method, based on the fundamental law of dynamics (see Appendix 1).

In terms of comparison with experimental values, we shall give the example of the variation in heat capacity at constant volume as a function of the temperature calculated by Eyring's semi-microscopic method. Remember that it is a cellular model including vacancies and a degeneration coefficient (see section 1.6). Figure 1.9 illustrates such a comparison and exhibits good accordance between the results obtained by the model and the experimental results.

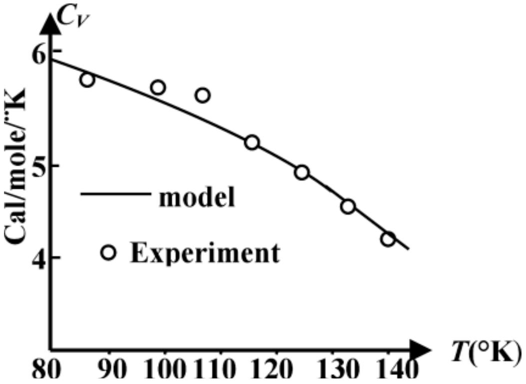

Figure 1.9. *Comparison between the observed values of the heat capacity at constant volume and those calculated using the cellular and vacancies model by Eyring et al. [EYR 61]*

Figure 1.10 shows the comparison of the result of the same model of the radial distribution function curve for argon at a temperature of 84.4K, against the experimental result. Once again, we see excellent accordance.

Certain comparisons are made between the measured values and those calculated by a model, for the critical values – particularly the critical temperature and critical pressure, using the conditions:

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \qquad \left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \qquad [1.97]$$

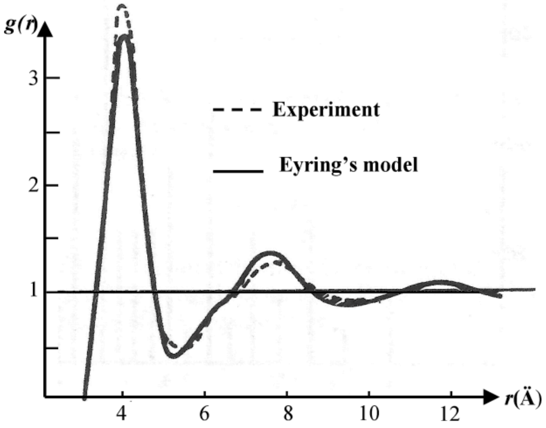

Figure 1.10. *Comparison between the experimental value and that calculated by Eyring's model for the radial distribution function of Argon at 84.4K (data from [YOO 81])*

Substance	T_c (°K)		P_c (atm)	
	Calculated	Observed	Calculated	Observed
Neon	55.41	44.47	37.65	26.86
Argon	154.44	150.66	58.72	48.00
Krypton	208.33	210.60	69.68	54.24
Xenon	287.80	289.80	74.89	58.20

Table 1.3. *Comparison of the observed values and those calculated by the Eyring model, for the temperature and the critical pressure (data from [EYR 58])*

Certain data appear in Table 1.2 for Lennard-Jones and Devonshire's model (see section 1.4). Others are given for the solids of rare gases in Table 1.3, and pertain to Eyring's model (see section 1.5).

Note that both models yield satisfactory results on this point. However, it is important to apply the comparison to several types of results. For example, Figure 1.11 shows that, for the representation of the distribution function, Lennard-Jones and Devonshire's model, Eyring's model and the calculations performed by numerical simulation are very similar. Meanwhile, Figure 1.12, which gives the variation of the compressibility coefficient as a function of a reduced volume, illustrates the significant behavioral difference between the molecular dynamics simulation and Eyring's model, on the one hand, and Lennard-Jones/Devonshire's, Guggenheim's (see section 1.3.1) and Mie's model (see section 1.3.2), on the other. It seems that the important point which divides Eyring's model from that of Lennard-Jones and Devonshire is more the introduction of the degeneration coefficient than the variability of the number of molecules that are near neighbors of a given molecule (z_i).

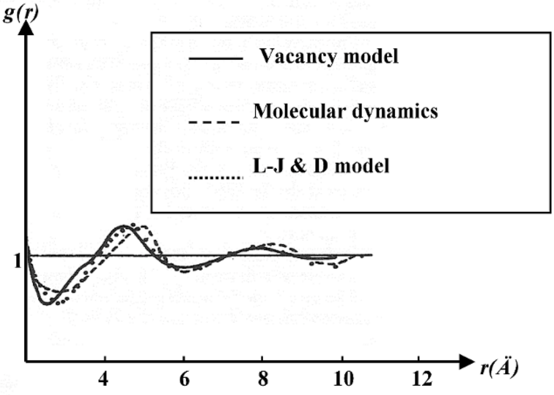

Figure 1.11. *Comparison of the curve of the radial distribution function between the calculations of molecular dynamics and different models (according to [YOO 81])*

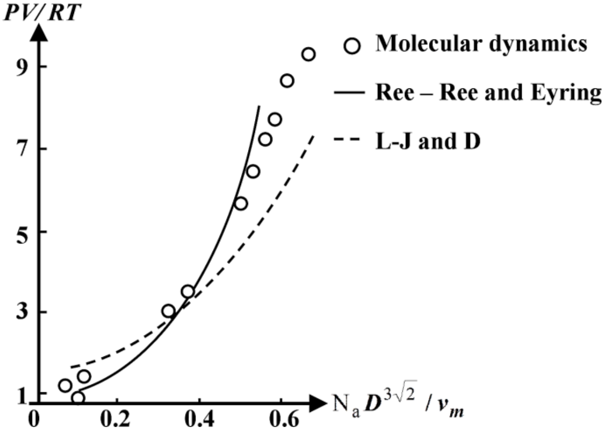

Figure 1.12. *Comparison of the results obtained on the compressibility factor (data from [REE 64])*

Thus, we can see that it is important to examine the validity of a model by comparing several results produced by that model. Additionally, a good model of the structure of liquids must also satisfy the interpretation of properties other than the mere thermodynamic values that are of interest to us here, e.g. surface tension, viscosity and self-diffusion. The major advantage of Eyring's cellular and vacancy model with a degeneration coefficient is that it also takes account of the dynamic properties of liquids.

2

Macroscopic Modeling of Liquid Molecular Solutions

The representation of solutions must give the expressions either for the molar excess Gibbs energy or the activity coefficients, using a given convention for each component as a function of the variables of the problem, which are usually the pressure, temperature and the composition of the solution. In this chapter, we shall only discuss the case of liquid molecular solutions. In such solutions, usually, the pressure is no longer a variable of the system.

A distinction must be drawn between macroscopic representations and simulations using a microscopic model.

The advantage of a representation is that we have an expression for the excess Gibbs energy or the activity coefficients, as a function of the solution's composition and possibly of the temperature, based on experience, which can be used in expressing the law of action of the masses or in constructing phase diagrams.

The advantage of a microscopic model is that it shows the same qualities as the representation, with an added predictive element and a physical meaning for the different properties that are involved.

We often work with binary solutions, which are obviously simpler, but significant efforts are being invested in modeling solutions with more than two components, based on the knowledge of binary solutions formed with

Modeling of Liquid Phases, First Edition. Michel Soustelle.

different pairs of components of the solution. Another interesting method is the modeling of binary solutions using the functional groups of the molecules.

In this chapter, we shall discuss macroscopic models. The next chapter (Chapter 3) will describe microscopic models.

The expressions of the activity coefficients, given to represent a solution, must be self-consistent, and in particular, they must satisfy relation [A.2.23], which is derived from the Gibbs–Duhem relation.

2.1. Macroscopic modeling of the Margules expansion

A helpful and simple representation of a non-perfect solution is given by a limited expansion.

Consider a solution with two components, 1 and 2. It is always possible to represent it by expanding the logarithm of the activity coefficient for component 1 in reference (I), in a MacLaurin series of the molar fraction x_2 of the other component – for example:

$$T \ln \gamma_1^{(I)} = A_1 + \alpha_1 x_2 + \beta_1 x_2^2 + \delta_1 x_2^3 + \varepsilon_1 x_2^4 + \ldots \qquad [2.1]$$

and, absolutely symmetrically for the second component:

$$T \ln \gamma_2^{(I)} = A_2 + \alpha_2 x_1 + \beta_2 x_1^2 + \delta_2 x_1^3 + \varepsilon_2 x_1^4 + \ldots \qquad [2.2]$$

These expansions are known as *Margules expansions*.

Conventionally, the activity coefficient of a component tends toward 1 if the molar fraction of the other component tends toward zero, so the limited expansion does not contain a constant term.

$$A_1 = A_2 = 0 \qquad [2.3]$$

In addition, according to relation [A.2.23], we should have:

$$x_1 \, \mathrm{d} \ln \gamma_1 + x_2 \, \mathrm{d} \ln \gamma_2 = 0 \qquad [2.4]$$

From this, we can easily deduce the following relations, if we examine the first five terms in the expansion:

$$\alpha_1 = \alpha_2 = 0 \qquad [2.5]$$

$$\frac{\beta_1}{2} = \frac{\beta_2}{2} + \frac{\varepsilon_2}{2} + \frac{\delta_2}{3} \text{ and } \frac{\beta_2}{2} = \frac{\beta_1}{2} + \frac{\varepsilon_1}{2} + \frac{\delta_1}{3} \qquad [2.6]$$

$$\frac{\varepsilon_1}{4} = -\frac{\varepsilon_2}{4} - 2\frac{\delta_2}{3} \text{ and } \frac{\varepsilon_2}{4} = -\frac{\varepsilon_1}{4} - 2\frac{\delta_1}{3} \qquad [2.7]$$

$$\delta_1 = \delta_2 \qquad [2.8]$$

Thus, the Margules expansion contains no constants or first-degree terms. The first non-zero term is the second-degree one.

It is worth noting that, if we look at an expansion with two non-null coefficients β_i and δ_i, we can write, for component 1, for instance:

$$\frac{T \ln \gamma_1}{x_2^2} = \beta_1 + \delta_1 x_2 \qquad [2.9]$$

We can attempt to plot a straight line on the experimental points in a representation $T \ln \gamma_1 / x_2^2$ as a function of x_2. If the representation is properly linear, we can easily determine the two coefficients. The ordinate at the origin of this straight line is β_1 and its slope is δ_1.

2.2. General representation of a solution with several components

Still with the aim of having mathematical expressions for the representation of the solution, Redlich and Kister offered a representation that provides an expansion of the excess Gibbs energy, a pure-substance reference in the same state of segregation as the solution (reference (I)), the equivalent of the Margules expansion for the activity coefficients. For a two-component solution, the polynomial expansion up to order *m* is written:

$$G_m^{xs} = x_1 x_2 \sum_{k'=0}^{m} L_{12}^{(k')} \left(x_1 - x_2\right)^{k'} \qquad [2.10]$$

The coefficients $L_{12}^{(k')}$ are parameters which reflect atomic interactions. Because the exponents *k*' are odd and even integers, it is internationally agreed to write the differences $\left(x_1 - x_2\right)$ in alphabetical order of the chemical symbols of the components, written as subscripts next to the molar fractions.

For a solution containing a given number of components, relation [2.10] becomes:

$$G_m^{xs} = \sum_{i \neq j} x_i x_j \sum_{k'=0}^{m} L_{ij}^{(k')} \left(x_i - x_j\right)^{k'} \qquad [2.11]$$

The alphabetical convention applies to all the couples *i, j*.

2.3. Macroscopic modeling of the Wagner expansions

The *Wagner expansion* is another form of limited expansion, this time used to represent the logarithms of the activity coefficients for the solutes in a solvent, as reference (II) – an infinitely-dilute solution.

2.3.1. *Definition of the Wagner interaction coefficients*

Consider a solution containing the components 1, 2, …, *i*, …*j*, …. Suppose that this solution is diluted in solvent 1. In order to express the variations of the activity coefficients for the solutes as a function of the molar fractions x_i ($i \neq 1$), which are much smaller than 1, let us take the expansion of $\ln \gamma_i^{II}$ into a Taylor series in the vicinity of 1:

$$\ln \gamma_i^{II} = \ln \gamma_i^{(II)\infty} + \sum_{j=2}^{N} x_j \left(\frac{\partial \ln \gamma_i^{II}}{\partial x_j} \right)_{\infty} + \ldots \qquad [2.12]$$

If, in that expansion, we content ourselves with the first two terms, we can write:

$$\ln \gamma_i^{II} = \ln \gamma_i^{(II)\infty} + \sum_{j=2}^{N} x_j \varepsilon_i^j \qquad [2.13]$$

$\gamma_i^{(II)\infty}$ is the value of the activity coefficient of the solute *i* if the solution is very dilute – i.e. when all the molar fractions x_j of the other solutes are null.

ε_i^j is called the *Wagner coefficient of interaction of solute* i *with solute* j. Thus, it is defined as:

$$\varepsilon_i^j = \left(\frac{\partial \ln \gamma_i^{II}}{\partial x_j} \right)_\infty \qquad [2.14]$$

By simply applying relation [A.2.27] (see Appendix 2), we can show that the matrix of Wagner coefficients is symmetrical, so:

$$\varepsilon_i^j = \varepsilon_j^i \qquad [2.15]$$

We can show, by application of relation [A.2.23] (see Appendix 2), that the activity coefficient of the solvent obeys the relation:

$$\ln \gamma_1^{II} = -\frac{1}{2} \sum_{i,j} x_i x_j \varepsilon_i^j \qquad [2.16]$$

This Wagnerian representation is widely used for metal alloys with low degrees of addition of the alloyed elements.

2.3.2. *Example of a ternary solution: experimental determination of Wagner's interaction coefficients*

Consider the ternary system constituted by solvent 1 and the two solutes 2 and 3. According to relation [2.16], we have:

$$\ln \gamma_2^{II} = \ln \gamma_2^{(II)\infty} + x_2 \varepsilon_2^2 + x_3 \varepsilon_2^3 \qquad [2.17]$$

$$\ln \gamma_3^{II} = \ln \gamma_3^{(II)\infty} + x_2 \varepsilon_3^2 + x_3 \varepsilon_3^3 \qquad [2.18]$$

We can distinguish two types of Wagner coefficients:

– the diagonal coefficients ε_2^2 and ε_3^3;

– the symmetrical coefficients, which are equal according to expression [2.15]: $\varepsilon_2^3 = \varepsilon_3^2$.

Let us first determine the diagonal terms – e.g. ε_2^2. By definition:

$$\varepsilon_2^2 = \left(\frac{\partial \ln \gamma_2^{II}}{\partial x_2} \right)_\infty \qquad [2.19]$$

As this term does not depend on the presence of component 3, we can operate in the binary system 1-2, and simply measure the tangent to the origin of the curve giving $\ln \gamma_2^{II}$ as a function of x_2 in that binary system. The slope of the tangent is ε_2^2.

The same process can be used to obtain the other symmetrical coefficient, this time considering the binary system 1-3, so ε_3^3.

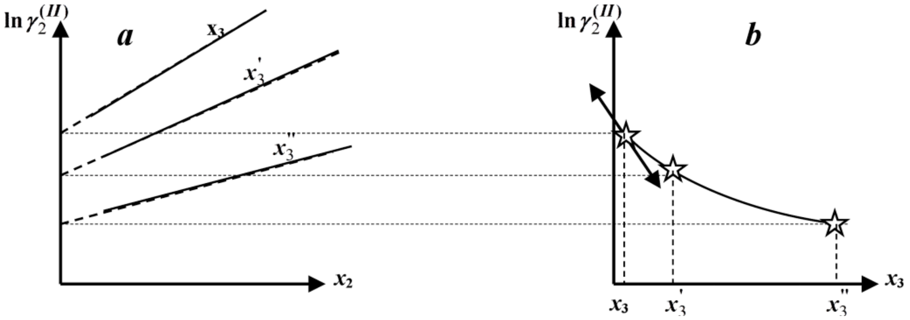

Figure 2.1. *Obtaining of the Wagner interaction coefficients for a ternary system*

Let us now examine the case of the mixed term ε_2^2. By definition, we have:

$$\varepsilon_2^3 = \left(\frac{\partial \ln \gamma_2^{II}}{\partial x_3} \right)_\infty \qquad [2.20]$$

For different values of x_3, we plot (Figure 2.1(a)) the experimental curve of the variations of $\ln \gamma_2^{II}$ as a function of x_2. By extrapolation to $x_2 = 0$, we obtain the values of $\ln \gamma_2^{II}$ at $x_2 = 0$ for different values of x_3. We report (Figure 2.1(b)) those values as a function of x_3, and by extrapolation, we obtain the tangent to the origin – i.e. ε_2^3.

2.4. Dilute ideal solutions

Below, we shall examine a category of solution which is a limit category, known as *dilute ideal solutions*. These solutions must not be confused with perfect solutions, although they do have a certain number of properties in common. For this reason, we shall never use the term "ideal solution" to speak of a perfect solution, as some authors do.

2.4.1. *Thermodynamic definition of a dilute ideal solution*

If, in a solution, all the components bar one – the solvent – are very dilute, the number of molecules of solute is so low that they have no effect on the behavior of the solvent, which could be said to exhibit perfect behavior. In this case, we say that we have a *dilute ideal solution*. Because of the distinction between solvent and solute, we shall use convention (II) – the infinitely dilute solution reference – to express the activity coefficients.

We know that for the solvent, conventions (I) and (II) are identical, and as, hypothetically, it should exhibit perfect behavior, we will have:

$$\gamma_0^{(I)} = \gamma_0^{(II)} = 1 \qquad [2.21]$$

Let us apply relation [A.2.23] (see Appendix 2) to the set of components:

$$x_0 \, \mathrm{d} \ln \gamma_0^{(II)} + \sum_s x_s \, \mathrm{d} \ln \gamma_s^{(II)} = 0 \qquad [2.22]$$

From this, we deduce that $\gamma_s^{(II)} = \text{constant}$. Yet we know, because of the convention chosen, that if the solution is in its reference state, $\gamma_s^{\infty(II)} = 1$. Hence, the value of the constant is 1, and the activity coefficients for all the components will be $\gamma_s^{(II)} = 1$ at any temperature.

2.4.2. *Activity coefficients of a component with a pure-substance reference*

With regard to the solvent, we already know its activity coefficient in convention (I) (pure-substance reference), through expression [2.21]. Similarly as above, by applying relation [A.2.23] (see Appendix 2), we deduce that for all solutes, the activity coefficient in reference (I) is a constant. This constant is independent of the composition, but its value is not 1 because the reference state does not overlap the domain of definition of reference (I). However, given that, in reference (II), the activity coefficient for the solute is 1, we can apply relation [A.2.21] (see Appendix 2). From this, we deduce that the constant is Henry's constant K_{sH} :

$$\gamma_s^{(I)} = K_{sH} \qquad [2.23]$$

It is only in the particular case of a perfect solution that this constant has a value of 1.

Thus, the perfect solution appears to be a special case of the ideal dilute solution – for which Henry's constant is equal to 1 – but the two must not be confused.

2.4.3. *Excess Gibbs energy of an ideal dilute solution*

According to expression [A.2.31] (see Table A.2.2 in Appendix 2), we immediately obtain:

$$G_m^{xs} = \mathrm{R}T\sum_s x_s \ln \gamma_s^{(I)} = \mathrm{R}T\sum_s x_s \ln K_{sH} \qquad [2.24]$$

This excess Gibbs energy is non-null, but in that excess Gibbs energy, there is no contribution from the solvent ($\gamma_0^{(I)} = 1$).

We can see that because the excess Gibbs energy is not null, we have another reason to avoid confusing an ideal dilute solution with a perfect solution.

2.4.4. Enthalpy of mixing for an ideal dilute solution

In view of the definition of an ideal dilute solution, we can write that:

$$\frac{\partial \ln \gamma_s^{(II)}}{\partial T} = 0 \qquad [2.25]$$

Thus, given relation [A.2.24] (see Appendix 2), we have:

$$\overline{H_i} = \overline{H_i^{\infty}} \qquad [2.26]$$

where, for the solvent:

$$\overline{H_i} = h_0^0 \qquad [2.27]$$

The partial molar enthalpy of the solvent is identical to its molar enthalpy in the pure state in the same state of aggregation as the solution.

and for the solutes:

$$\frac{\partial \ln \gamma_s^{(I)}}{\partial T} = \frac{h_s^0 - \overline{H_s}}{\mathrm{R}T^2} = \frac{h_s^0 - \overline{H_s^{\infty}}}{\mathrm{R}T^2} \qquad [2.28]$$

The difference:

$$h_s^0 - \overline{H_s^{\infty}} = A_s \qquad [2.29]$$

does not depend on the composition. The molar enthalpy of mixing therefore, according to equation [A.2.17] (see Appendix 2), is:

$$H_m^{mix} = \sum_s x_s A_s \qquad [2.30]$$

and the corresponding molar value is:

$$\overline{H_s^{mix}} = A_s \qquad [2.31]$$

Thus, the constant A_s appears as the partial molar enthalpy of mixing of the solute s in the solution, which enables us to write the following, in light of relation [2.29]:

$$\overline{H_s^\infty} = h_s^0 - \overline{H_s^{mix}} \quad [2.32]$$

2.4.5. *Excess entropy of a dilute ideal solution*

Given equations [2.30] and [2.24], we can write:

$$S_m^{xs} = \frac{H_m^{mix} - G_m^{xs}}{T} = \frac{\sum_s x_s \overline{H_s^{mix}} - \mathrm{RT}\sum_s x_s \ln K_{sH}}{T} \quad [2.33]$$

This function, which does not contain any terms pertaining to the solvent either, is non null. Here, again, it is important to avoid confusing the representation of the ideal dilute solution with that of the perfect solution.

2.4.6. *Molar heat capacity of an ideal dilute solution at constant pressure*

If we neglect the variations of the enthalpy values with temperature (which is often acceptable within a reasonable temperature range), we have:

$$C_P^{xs} = \frac{\partial H^{mix}}{\partial T} = 0 \quad [2.34]$$

Thus, the excess heat capacity at constant pressure of dilute ideal solutions is practically non-existent, which means that – like perfect solutions – dilute ideal solutions obey Kopp's law of additivity given by relation [A.2.14] in Table A.2.1 from Appendix 2.

2.5. Associated solutions

A number of solutions exhibit significant differences from perfection, due largely to the forces of attraction that are exerted between certain species in solution. The idea of the model of an associated solution is to average the properties of the solution by replacing the initial components with classes of components that include the initial components but also associated species (dimers, trimers, etc., associations between different molecules, or dissociated species), resulting from the condensation of the initial species, at equilibrium with them and with one another. We then consider that the new solution thus defined has perfect behavior.

The associated and dissociated species can be revealed experimentally, because the forces of attraction are sufficiently strong to be detected by certain techniques, such as infrared spectroscopy.

This method is commonly used, for example, for the study of so-called "weak" electrolytes, where the dissociation of the molecules into ions is considered to be incomplete, and there is thought to be an equilibrium between the ions and the non-dissociated molecules. This model is also at the root of the quasi-chemical method of dealing with solutions (see Chapter 3).

The superposition of one or more equilibrium states between the newly-defined species enables us to calculate the activity coefficients or the partial molar Gibbs energy values for the initial components.

2.5.1. *Example of the study of an associated solution*

In order to illustrate the model of the associated solution, we shall take the example of a binary solution obtained by mixing n_{A} moles of a component A and n_{B} moles of another component B, and suppose that the forces of attraction between two molecules of A are strong in comparison to $\mathrm{k_B}T$, and in comparison to those that are exerted between two molecules of B, and between a molecule of A and a molecule of B. This property leads us to a second description of the solution, in which we accept that two molecules of A can come together to yield a dimer molecule A_2, in equilibrium with the monomer A.

We describe the solution under examination from two different points of view:

One option is to consider it to be a non-perfect solution, with n_A moles of A and n_B moles de B (initial quantities), with the molar fractions x_A and x_B respectively, given by:

$$x_\text{A} = \frac{n_\text{A}}{n_\text{A} + n_\text{A}} \quad \text{and} \quad x_\text{B} = \frac{n_\text{B}}{n_\text{A} + n_\text{A}} = 1 - x_\text{A} \qquad [2.35]$$

The chemical potentials will be μ_A and μ_B, and the activity coefficients γ_A and γ_B. This is the first description of the solution.

Alternatively, we can consider the solution to be a *perfect* solution, with n'_A moles of monomer A, n'_{A_2} moles of dimer A_2 and n'_B moles of B with the molar fractions:

$$x'_\text{A} = \frac{n'_\text{A}}{n'_\text{A} + n'_{\text{A}_2} + n'_B} \text{ ; } x'_{\text{A}_2} = \frac{n'_{\text{A}_2}}{n'_\text{A} + n'_{\text{A}_2} + n'_B}$$

$$\text{and } x'_\text{B} = \frac{n'_\text{B}}{n'_\text{A} + n'_{\text{A}_2} + n'_B} \qquad [2.36]$$

The chemical potentials will be μ'_A μ'_{A_2} and μ'_B.

In this solution, we have a state of chemical equilibrium:

$$2\text{A} = \text{A}_2 \qquad [2.\text{R}1]$$

This imposes the condition on the affinity:

$$\mathsf{A} = 2\mu'_\text{A} - \mu'_{\text{A}_2} = 0 \qquad [2.37]$$

Furthermore, the law of conservation of the elements imposes the following relations between the amounts:

$$n_B = n'_B \qquad [2.38]$$

$$n_\text{A} = n'_\text{A} + 2n'_{\text{A}_2} \qquad [2.39]$$

Using the symbol α to denote the extent of the equilibrium, we shall write that the amounts of the species containing A in the second solution will be:

$$n'_{\mathrm{A}} = n_{\mathrm{A}}(1-\alpha) \qquad [2.40]$$

$$n'_{\mathrm{A}_2} = n_{\mathrm{A}}\alpha / 2 \qquad [2.41]$$

The sum of equations [2.40] and [2.41] does indeed produce relation [2.39].

This is the second description of the solution.

NOTE 2.1.– between the two descriptions, the molar fractions of B are not the same in the two cases, although the numbers n_{B} and n'_B are equal.

2.5.2. *Relations between the chemical potentials of the associated solution*

We shall now establish a relation between the chemical potentials of the different components of the second description as a function of those from the first description.

The Gibbs energy of the solution does not depend on the way in which it is described. Let us write the expression of that Gibbs energy in both descriptions, and equal those expressions, which gives us:

$$G = n_{\mathrm{A}}\mu_{\mathrm{A}} + n_{\mathrm{B}}\mu_{\mathrm{B}} = n'_{\mathrm{A}}\,\mu'_{\mathrm{A}} + n'_{\mathrm{A}_2}\,\mu'_{\mathrm{A}_2} + n'_{\mathrm{B}}\,\mu'_{\mathrm{B}} \qquad [2.42]$$

If we look at relation [2.38], we can deduce:

$$\mu_{\mathrm{B}} = \mu'_{\mathrm{B}} \qquad [2.43]$$

and in light of relations [2.37] and [2.39], we deduce:

$$\mu'_{\mathrm{A}} = \mu_{\mathrm{A}} \qquad [2.44]$$

$$\mu'_{\mathrm{A}_2} = 2\mu_{\mathrm{A}} \qquad [2.45]$$

2.5.3. *Calculating the extent of the equilibrium in an associated solution*

The law of mass action, written for equilibrium [2.R1] (with a solution considered to be perfect) gives us:

$$K = \frac{x'_{A_2}}{(x'_A)^2} = \frac{n_A \alpha / 2}{n_A^2 (1-\alpha)^2} [n_A (1 - \alpha/2) + n_B] \qquad [2.46]$$

However, the equilibrium constant can be expressed on the basis of the partition functions, according to relation [A.3.50] from Appendix 3, which gives us:

$$K = \frac{z^0_{m(A_2)}}{\left(z^0_{m(A)}\right)^2} \exp\left(-\frac{\Delta_r h^0(T)}{RT} \right) \qquad [2.47]$$

In this relation, $\Delta_r h^0(T)$ is the fundamental energy level of vibration of the molecule A_2.

Thus, by combining expressions [2.46] and [2.47], we can determine α.

2.5.4. *Calculating the activity coefficients in an associated solution*

Although it is not necessary in order to study our solution, we shall calculate the activity coefficients for the components in the first description.

If we use reference (I) – the pure substance reference – we can write:

$$\mu_A = g_A^0 + RT \ln \gamma_A^{(I)} x_A \qquad [2.48]$$

and

$$\mu'_A = g_A^0 + RT \ln x'_A \qquad [2.49]$$

Using expression [2.47], we obtain

$$\gamma_A^{(I)} = \frac{x'_A}{x_A} \qquad [2.50]$$

In the same way, for component B, we find:

$$\gamma_{\mathrm{B}}^{(I)} = \frac{x'_{\mathrm{B}}}{x_{\mathrm{B}}} \qquad [2.51]$$

Using relations [2.35], [2.36], [2.41] and [2.50], equation [2.50] becomes:

$$\gamma_{\mathrm{A}}^{(I)} = \frac{(n_{\mathrm{A}} + n_{\mathrm{B}})(1-\alpha)}{n_{\mathrm{A}}(1-\alpha/2) + n_{\mathrm{B}}} \qquad [2.52]$$

Similarly, for B, we find:

$$\gamma_{\mathrm{B}}^{(I)} = \frac{(n_{\mathrm{A}} + n_{\mathrm{B}})}{n_{\mathrm{A}}(1-\alpha/2) + n_{\mathrm{B}}} \qquad [2.53]$$

Thus, the two activity coefficients we are seeking can be expressed as a function of the extent of the equilibrium [2.R1].

2.5.5. *Definition of a regular solution*

Consider a solution with N components. It is said to be *regular* if its molar mixing entropy is identical to that of a perfect solution, given by expression [A.2.10] (see Table A.2.1 in Appendix 2).

By comparing this expression with the general formula for the molar entropy of mixing of a solution:

$$S^{\mathrm{mix}} = \mathrm{R}\sum_{i=1}^{N} x_i \left(-T\frac{\partial \ln \gamma_i^{(I)}}{\partial T} - \ln \gamma_i^{(I)} - \ln x_i \right) \qquad [2.54]$$

In view of expression [A.2.10], regardless of the composition, we obtain:

$$\sum_{i=1}^{N} x_i \left(T\frac{\partial \ln \gamma_i^{(I)}}{\partial T} + \ln \gamma_i^{(I)}\right) = 0 \qquad [2.55]$$

In order for this equation to be satisfied, we must have the following for any component i:

$$x_i \left(T\frac{\partial \ln \gamma_i^{(I)}}{\partial T} + \ln \gamma_i^{(I)} = 0 \qquad [2.56]$$

Thus, by integrating:

$$T \ln \gamma_i^{(I)} = \Re_i(x) \qquad [2.57]$$

The value thus defined, $\Re_i(x)$, is thus temperature-independent (we have discounted the influence of the pressure on liquid solutions). It depends only on the composition x.

Based on the definition we have just given, it is obvious that the excess entropy of a regular solution is null, as are the excess partial molar entropies of each it its components – i.e.:

$$S^{\text{xs}} = 0 \quad \text{and} \quad \overline{S_i^{\text{xs}}} = 0 \qquad [2.58]$$

As the entropy of mixing of a regular solution is identical to that of a perfect solution, we can deduce that the molar heat capacity obeys Kopp's law of additivity (see expression A.2.14 in Table A.2.2, Appendix 2).

We can see that the regular solution model does not give us the variations of the activity coefficient with the amounts of substance. In fact, it is a family of models which includes several possible subsets – each one defined by a relation $\Re_i(x)$. We shall come across two of these subsets in our study: the Van Laar equation (see Table 3.3) and the Hildebrand-strictly-regular solution model, which we shall touch on.

2.5.6. *Strictly-regular solutions*

A group of solutions known as *strictly-regular solutions* is of significant interest for a number of reasons:

– it yields the most mathematically simple form of a non-perfect and non-dilute ideal solution;

– it demonstrates that complete knowledge of the solution includes all the phenomena that are typically superposed on the model artificially. Hence, in certain cases, it includes the phenomenon of demixing, and the existence of azeotropic mixtures;

– in practical terms, it is applicable in numerous cases in metallurgy with mixtures of liquid metals, and in chemistry with solutions of homologous compounds. It is found in the modeling of other phenomena such as the concept of order/disorder in alloys, or the isotherm of non-"Langmuirian" adsorption of a gas on a solid;

– we have a microscopic model of strictly-regular solutions, as we do for perfect solutions, which enables us to demonstrate an initial cause of imperfection of the solutions.

2.5.7. *Macroscopic modeling of strictly-regular binary solutions*

Let us take the Margules expansion, limited to the first non-zero term. In light of relations [2.2] to [2.5], assuming that $\beta_1 = \beta_2 = \frac{B}{T}$, where *B* is a parameter independent of the temperature and of the composition, the activity coefficients will be written as:

$$\ln \gamma_1^{(I)} = \frac{B}{T} x_2^2 \quad \text{and} \quad \ln \gamma_2^{(I)} = \frac{B}{T} x_1^2 \qquad [2.59]$$

In view of the definition of *B*, it is clear, given [2.57], that such a solution is regular.

Note that the function of the pressure is not specified, and therefore the model includes all solutions defined by these two equations, whatever the function *B(P)* and, in particular, *B* can very well be independent of the pressure.

The solutions that we have just defined constitute a family of regular solutions, known as *strictly-regular solutions in the sense of Hildebrand*.

In these solutions, the two components play a perfectly symmetrical role.

As strictly-regular solutions are, by definition, regular, we can deduce that the entropy of mixing is the same as that of a perfect solution and therefore that the excess entropy is null.

We shall now calculate the other main thermodynamics involved in strictly-regular solutions.

The excess partial molar Gibbs energy of a component is obtained directly on the basis of the activity coefficient:

$$\overline{G_1^{\mathrm{xs}}} = \mathrm{R}T\ln\gamma_1 = \mathrm{R}Bx_2^2 \quad \text{and} \quad \overline{G_2^{\mathrm{xs}}} = \mathrm{R}T\ln\gamma_2 = \mathrm{R}Bx_1^2 \qquad [2.60]$$

The total molar excess Gibbs energy will therefore be:

$$G_m^{\mathrm{xs}} = x_1\overline{G_1^{\mathrm{xs}}} + x_2\overline{G_2^{\mathrm{xs}}} = \mathrm{R}Bx_1x_2 \qquad [2.61]$$

As the excess entropy is null by definition, the excess enthalpy is equal to the excess Gibbs energy, and thus for the partial molar values, we would have:

$$\overline{H_1^{\mathrm{xs}}} = \overline{G_1^{\mathrm{xs}}} = \mathrm{R}Bx_2^2 \quad \text{and} \quad \overline{H_2^{\mathrm{xs}}} = \overline{G_2^{\mathrm{xs}}} = \mathrm{R}Bx_1^2 \qquad [2.62]$$

and for the molar excess enthalpy:

$$H_m^{\mathrm{xs}} = x_1\overline{H_1^{\mathrm{xs}}} + x_2\overline{H_2^{\mathrm{xs}}} = \mathrm{R}Bx_1x_2 \qquad [2.63]$$

As the enthalpy of mixing for a perfect solution is zero, the enthalpy of mixing for a strictly-regular solution is identical to its excess enthalpy, so for the the partial molar values:

$$\overline{H_1^{\mathrm{mix}}} = \overline{H_1^{\mathrm{xs}}} = \mathrm{R}Bx_2^2 \quad \text{and} \quad \overline{H_2^{\mathrm{mix}}} = \overline{H_2^{\mathrm{xs}}} = \mathrm{R}Bx_1^2 \qquad [2.64]$$

and for the molar enthalpy of mixing:

$$H_m^{\mathrm{mix}} = x_1\overline{H_1^{\mathrm{mix}}} + x_2\overline{H_2^{\mathrm{mix}}} = \mathrm{R}Bx_1x_2 \qquad [2.65]$$

We can see that the plot of the mixing enthalpy is a parabola (see Figure 2.2) as a function of the molar fraction of a component because:

$$\frac{H_m^{\mathrm{mix}}}{\mathrm{R}B} = x_1(1-x_1) \qquad [2.66]$$

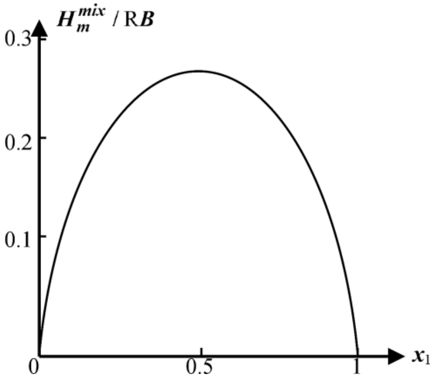

Figure 2.2. *Parabolic form of mixing enthalpy for a strictly-regular solution*

The Gibbs energy can immediately be deduced from the definition:

$$G^{\mathrm{mix}} = H^{mix} - TS^{\mathrm{mix}} \tag{2.67}$$

In the knowledge that the mixing enthalpy is the same as that for a perfect solution, we find the following for the molar Gibbs energy of mixing:

$$G_m^{\mathrm{mix}} = \mathrm{R}Bx_1x_2 + \mathrm{R}T(x_1 \ln x_1 + x_2 \ln x_2) \tag{2.68}$$

and for the partial molar values:

$$\overline{G_1^{\mathrm{mix}}} = \mathrm{R}Bx_2^2 + \mathrm{R}Tx_1 \ln x_1 \quad \text{and} \quad \overline{G_2^{\mathrm{mix}}} = \mathrm{R}Bx_1^2 + \mathrm{R}Tx_2 \ln x_2 \tag{2.69}$$

As we saw earlier, because a strictly-regular solution is a regular solution, it obey's Kopp's law of additivity (see relation A.2.14 in Table A.2.1, Appendix 1) for the molar heat capacities.

We can easily calculate the expression of the activity of a component at temperature T. Immediately, we find:

$$a_2^{(I)} = \gamma_2^{(I)} x_2 = x_2 \exp\left(\frac{B}{T}(1 - x_2)^2\right) \tag{2.70}$$

The relation is absolutely symmetrical for component 1.

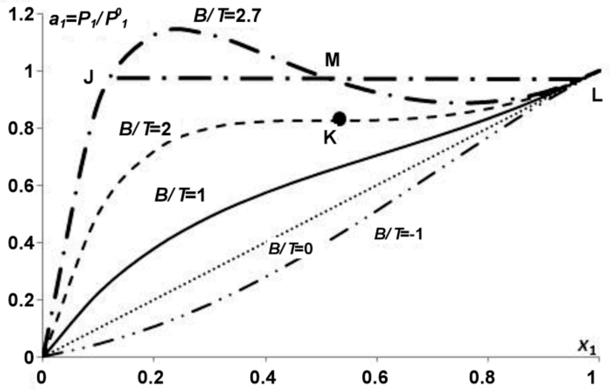

Figure 2.2. *Activity (in convention I) of a component of a strictly regular solution as as a function of the composition*

Figure 2.3 illustrates the activity of a strictly-regular solution as a function of the composition. We can see that the solution displays positive deviation in relation to Raoult's law if $B/T < 0$, and negative deviation if $B/T > 0$. If B/T is greater than 2, the inflection point indicates demixing into two solutions, whose compositions are given by the endpoints of the plateau. The activities on either side of the plateau correspond to a metastable phase.

The curves for the second component are, obviously, symmetrical.

NOTE 2.2.– the strictly-regular solution becomes a perfect solution if the parameter B is 0 for all compositions ($B/T = 0$). The corresponding curve in Figure 2.3 is Raoult's straight line.

2.5.8. *Extension of the model of a strictly-regular solution to solutions with more than two components*

Certain authors prefer to choose relation [2.89] from the expression of the excess Gibbs energy as the definition for strictly-regular solutions. This second definition is rigorously identical to that which we have chosen (relation [2.87]), because relation [A.2.32] (see Table A.2.2 in Appendix 2) links the activity coefficients and the partial molar Gibbs energy values.

On the basis of this definition, we can extend the concept of a strictly-regular solution to systems with more than two components, but preserve the symmetry that is present in binary systems. For instance, for a system with N components, we can say that a solution is strictly regular if its excess molar Gibbs energy takes the form:

$$G^{xs} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \lambda_{ij} x_i x_j \qquad [2.71]$$

The coefficients λ_{ij} are positive coefficients, independent of the temperature and composition.

By application of this relation to a two-component system, obviously, we obtain relation [2.60], with:

$$\lambda_{12} = \mathrm{R}B \qquad [2.72]$$

For a system with three components 1, 2 and 3, we find:

$$G^{xs} = \lambda_{12} x_1 x_2 + \lambda_{13} x_1 x_3 + \lambda_{23} x_2 x_3 \qquad [2.73]$$

Based on the derivative of this function in relation to one of the quantities of matter, we immediately obtain the activity coefficient of that component. For example, for the three-component solution, we obtain:

$$\mathrm{R}T \ln \gamma_1^{(I)} = \frac{\partial G^{xs}}{\partial n_1} = \mathrm{R}T\left(\lambda_{12} x_2 + \lambda_{13} x_3\right) \qquad [2.74]$$

Multicomponent strictly-regular solutions constitute an excellent model for mixtures of molecules of the same polymer in different states of polymerization, which is understandable in view of the similitude of the molecules involved.

2.6. Athermic solutions

Alongside regular solutions (see section 2.5.1), we can define *athermic solutions*, which are primarily found when amorphous or molten polymers are dissolved in solvents.

2.6.1. *Thermodynamic definition of an athermic solution*

In the same way as we defined a regular solution as one which has the same entropy of mixing as a perfect solution, we shall define an athermic solution as one which has the same enthalpy of mixing as a perfect solution – i.e. zero. Of course, its excess molar enthalpy is also null.

2.6.2. *Variation of the activity coefficients with temperature in an athermic solution*

By applying the above property of definition to expressions [A.2.24] and [A.2.8] for a perfect solution, we deduce:

$$\sum_{i=1}^{N} \frac{\partial \ln \gamma_i^{(I)}}{\partial T} = 0 \qquad [2.75]$$

As the activity coefficients do not depend on the temperature, they will be functions only of the composition and perhaps of the pressure. Therefore, this type of solutions is referred to as *athermic*.

$$\gamma_i^{(I)} = \gamma_i^{(I)}(P, x) \qquad [2.76]$$

Instantly, we can derive the following equality from this:

$$\overline{H_i} = h_i^0 \qquad [2.77]$$

Thus, the partial molar enthalpy of each component is identical to its molar enthalpy when it is pure (in the same state of aggregation).

2.6.3. *Molar entropy and Gibbs energy of mixing for an athermic solution*

Using the general expression of the excess entropy [A.2.33], for the excess molar entropy of an athermic solution, we obtain:

$$S_m^{xs} = -\mathrm{R} \sum_{i=1}^{N} x_i \ln \gamma_i^{(I)} \qquad [2.78]$$

Hence, the molar entropy of mixing is:

$$S_m^{mix} = -\mathrm{R}\sum_{i=1}^{N} x_i \left(\ln \gamma_i^{(I)} + \ln x_i\right) \qquad [2.79]$$

As the molar enthalpy of mixing is null, the molar Gibbs energy of mixing is given by:

$$G_m^{mix} = -TS_m^{mix} = \mathrm{R}T\sum_{i=1}^{N} x_i \left(\ln \gamma_i^{(I)} + \ln x_i\right) \qquad [2.80]$$

2.6.4. *Molar heat capacity of an athermic solution*

The excess molar heat capacity is written simply as:

$$C_P^{xs} = \frac{\partial H_m^{xs}}{\partial T} = 0 \qquad [2.81]$$

Thus, the molar heat capacity is the same as that for a perfect solution and therefore obeys Kopp's additivity law [A.2.14]. This law can be said to be fairly widely applicable, because we have seen it at work with perfect solutions, regular solutions, athermic solutions and approximately with dilute ideal solutions.

NOTE 2.3.– a solution which is both regular and athermic is a perfect solution, because these two solutions have the same enthalpy and the same entropy, and therefore the same Gibbs energy. Hence, they are identical.

In this chapter, we have examined a number of simple analytical models which are extremely useful for the study of equilibrium states. However, these models involve parameters with unknown physical meaning. In addition, they are often not sufficiently accurate. For that reason, it is worth considering the modeling of solutions by a microscopic description.

3

Microscopic Modeling of Liquid Molecular Solutions

The purpose of modeling liquid solutions is to understand the structure and the properties of the medium, and to help predict certain behaviors by giving expressions for the molar Gibbs energies or activity coefficients. These data can then be used in practical applications such as the establishing of chemical equilibrium states or the plotting of phase diagrams.

Solutions are complex media, and usually the model needs to be "calibrated" on experiments in order to determine certain constants. The advantage to using a model, in terms of the predictive aspect, is obviously that it requires a minimal number of terms to be determined, and therefore a minimal number of experiments, to calibrate it. Nevertheless, this number must be sufficiently high for the model to represent reality as closely as possible.

In the existing body of literature, a great many different microscopic models are put forward. Hence, it is impossible to discuss all of them here. Instead, we shall limit ourselves to a presentation of the most widely-used models, which are practical and illustrate modern ideas by way of the approaches and hypotheses that they implement. Certain models will not be examined in detail because, whilst they were groundbreaking when they were first published, today they are known to be specific cases of other,

Modeling of Liquid Phases, First Edition. Michel Soustelle.

more general, models. We shall content ourselves with listing these models in Table 3.3.

3.1. Models of binary solutions with molecules of similar dimensions

Suppose we have a binary liquid solution – a mixture of two components A and B, which contains n_A moles of component A and n_B moles of component B, which equates to N_A molecules of A and N_B molecules of B. This solution satisfies the following six conditions:

1) There is an order over a short distance, and the short-distance lattice is the same for the solution as for the two liquids A and B. Thus, these three liquids exhibit the same coordination number z (e.g. 12 for the hexagonal or cubic lattice with centered faces).

2) The molar volumes v_A^0 and v_B^0 of the two pure liquids are sufficiently close. Certain authors have evaluated that this condition was acceptable if the ratio of the radii of the two molecules A and B, which are supposed to be spherical, was no greater than 1.25;

3) The free volumes $v_{f(\mathrm{A})}$ and $v_{f(\mathrm{B})}$ of the two pure liquids (see section 1.3.1) are near to one another (to within 30%);

4) The molar volumes and the free volumes of the two liquids are not altered by the operation of mixing, and therefore the mixing volume is null, which means that the volume of the solution is given by the additive law:

$$V = n_\mathrm{A} v_\mathrm{A}^0 + n_\mathrm{B} v_\mathrm{B}^0 \qquad [3.1]$$

5) The potential energy of interaction E_I can be considered to be the sum of the contributions of the closest neighboring pairs of molecules;

6) The model of the liquid chosen is Guggenheim's smoothed potential model (see section 1.3.1), both for the pure liquids and for the solution, and we use $\varepsilon_{\mathrm{A(A)}}$ and $\varepsilon_{\mathrm{B(B)}}$ to represent the values of the lattice energy ε which appears in expression [1.22], respectively for each of the pure liquids A and B.

The mean energy of interaction of two molecules of A is $-2\varepsilon_{\text{A(A)}}/z$, and similarly for two molecules of B it is $-2\varepsilon_{\text{B(B)}}/z$. Hence, we can say that the energy levels of pairs of molecules A-A and pairs de molecules B-B are, respectively:

$$\varepsilon_{\text{AA}} = -\frac{2\varepsilon_{\text{A(A)}}}{z} \text{ and } \varepsilon_{\text{BB}} = -\frac{2\varepsilon_{\text{B(B)}}}{z} \qquad [3.2]$$

NOTE 3.1.– As we are essentially interested in the mixing values, the pure liquid model chosen has no impact on the results.

Let us define an energy value, called the *exchange energy* w_{AB}, such that, if we begin with the two pure liquids A and B, the exchange of a molecule of A and a molecule of B between the two liquids increases the energy of the system by the amount $2w_{\text{AB}}$. During this process, z A-A pairs and z B-B pairs have been destroyed, and $2z$ A-B pairs have been created.

Thus, the mean potential energy of the pairs A-B will be:

$$\varepsilon_{AB} = \left(-2\varepsilon_{\text{A(A)}} - 2\varepsilon_{\text{B(B)}} + 2w_{\text{AB}}\right)/2z = \left(-\varepsilon_{\text{A(A)}} - \varepsilon_{\text{B(B)}} + w_{\text{AB}}\right)/z \qquad [3.3]$$

In view of equations [3.2] and [3.3], the exchange energy is:

$$w_{\text{AB}} = z\left(\varepsilon_{\text{AB}} - \frac{\varepsilon_{\text{AA}} + \varepsilon_{\text{BB}}}{2}\right) \qquad [3.4]$$

The property w_{AB} will be temperature-independent, so long as the type of environment of a molecule and therefore z are not altered.

NOTE 3.2.– The energy of interaction between a molecule of A and a molecule of B in the solution can be written as $\varepsilon_{\text{AB}} = -2\varepsilon_{\text{AB(AB)}}/z$. Thus, the exchange energy can be written as follows, if we take account of relation [3.3]:

$$w_{\text{AB}} = \varepsilon_{\text{A(A)}} + \varepsilon_{\text{B(B)}} - 2\varepsilon_{\text{AB(AB)}}$$

We can establish a general form of the configuration integral in the case of interactions by pairs.

If we look again at relations [A.3.25] and [A.3.37], we can write the following formula for the translational partition function of a substance A:

$$Z_{C(t)_\mathrm{A}} = \frac{1}{N_\mathrm{A}!}\left(\frac{2\pi m_\mathrm{A} \mathrm{k_B} T}{\mathrm{h}^2}\right)^{-3N_\mathrm{A}} \int .. \int\int \exp\left(-\frac{E_I}{\mathrm{k_B}T}\right) \mathrm{d}\,\omega_\mathrm{A}^{N_\mathrm{A}} \qquad [3.5]$$

where ω_A is the set of position coordinates of the N_A molecules of A in a given configuration.

The integral of equation [3.5] is thus extended to all configurations of the N_A molecules de A.

Similarly, for a binary mixture of two species A and B, we can write the canonical partition function of translation in the form:

$$\begin{gathered} Z_{C(t)} = \frac{1}{N_\mathrm{A}!}\frac{1}{N_\mathrm{B}!}\left(\frac{2\pi m_\mathrm{A} \mathrm{k_B} T}{\mathrm{h}^2}\right)^{-3N_\mathrm{A}} \left(\frac{2\pi m_\mathrm{B} \mathrm{k_B} T}{\mathrm{h}^2}\right)^{-3N_\mathrm{B}} \\ \int .. \int\int \exp\left(-\frac{E_I}{\mathrm{k_B}T}\right) \mathrm{d}\,\omega_\mathrm{A}^{N_\mathrm{A}}\, \mathrm{d}\,\omega_\mathrm{B}^{N_\mathrm{B}} \end{gathered} \qquad [3.6]$$

This time, the integral is extended to all configurations of N_A molecules of A and N_B molecules of B (the extension to solutions with more than two components is obvious).

We shall use $Z_{\mathrm{A}(pf)}$ to denote the canonical partition function of the pure component A without interaction, i.e. the perfect gas; similarly, $Z_{\mathrm{B}(pf)}$ denotes that of component B. The canonical partition function of translation of the solution can be written as:

$$Z_{C(t)} = \frac{1}{N_\mathrm{A}!}\frac{1}{N_\mathrm{B}!}\frac{Z_{\mathrm{A}(pf)}}{\mathrm{V}}\frac{Z_{\mathrm{B}(pf)}}{\mathrm{V}} \int .. \int\int \exp\left(-\frac{E_I}{\mathrm{k_B}T}\right) \mathrm{d}\,\omega_\mathrm{A}^{N_\mathrm{A}}\, \mathrm{d}\,\omega_\mathrm{B}^{N_\mathrm{B}} \qquad [3.7]$$

The problem of modeling of the solution involves being able to express the configuration integral of the mixture, whose value is:

$$I_{\mathrm{AB}} = \frac{1}{N_{\mathrm{A}}!} \frac{1}{N_{\mathrm{B}}!} \int .. \int \int \exp\left(-\frac{E_I}{\mathrm{k_B} T} \right) \mathrm{d}\,\omega_{\mathrm{A}}^{N_{\mathrm{A}}}\, \mathrm{d}\,\omega_{\mathrm{B}}^{N_{\mathrm{B}}} \qquad [3.8]$$

For each configuration, the solution comprises a certain number of pairs A-A, pairs B-B and mixed pairs A-B.

Let us look at a particular configuration of the solution in which the number of mixed pairs A-B is zX.

Thus, the number of neighbors of a molecule of A which are not molecules of B is $z(N_{\mathrm{A}} - X)$. Hence, the number of pairs A-A is $z(N_{\mathrm{A}} - X)/2$ and, by the same token, the number of pairs B-B is $z(N_{\mathrm{B}} - X)/2$. Therefore, the total number of pairs N_p of the three species is:

$$N_p = \frac{z}{2}\left(N_{\mathrm{AA}} + N_{\mathrm{BB}} + N_{\mathrm{AB}} \right) = \frac{z}{2}(N_{\mathrm{A}} + N_{\mathrm{B}}) \qquad [3.9]$$

For this particular configuration, characterized by the value of *X*, the potential energy of the solution, due to the interactions, will be:

$$\begin{aligned} E_I = {} & \frac{z(N_{\mathrm{A}} - X)}{2}\left(-\frac{2\varepsilon_{\mathrm{A(A)}}}{z} \right) + \frac{z(N_{\mathrm{B}} - X)}{2}\left(-\frac{2\varepsilon_{\mathrm{B(B)}}}{z} \right) \\ & + zX \frac{(-\varepsilon_{\mathrm{A(A)}} - \varepsilon_{\mathrm{B(B)}} + \varepsilon_{\mathrm{AB}})}{z} \end{aligned} \qquad [3.10]$$

Thus:

$$E_I = -N_{\mathrm{A}}\varepsilon_{\mathrm{A(A)}} - N_{\mathrm{B}}\varepsilon_{\mathrm{B(B)}} + Xw_{\mathrm{AB}} \qquad [3.11]$$

This relation can also be written as follows, taking account of expressions [3.2] and [3.8]:

$$E_I = \frac{zN_{\mathrm{A}}\varepsilon_{\mathrm{AA}}}{2} + \frac{zN_{\mathrm{B}}\varepsilon_{\mathrm{BB}}}{2} + Xz\left(\varepsilon_{\mathrm{AB}} - \frac{\varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}}}{2} \right) \qquad [3.12]$$

Note in passing that, if x_A and x_B are, respectively, the molar fractions of the components A and B, the internal energy per mole of solution ($N_\mathrm{A}+N_\mathrm{B}=\mathrm{N_a}$), which is also its enthalpy, because the volume of mixing is null, is:

$$U_m = H_m = \mathrm{N_a}\left[\frac{zx_\mathrm{A}\varepsilon_\mathrm{AA}}{2}+\frac{zx_\mathrm{B}\varepsilon_\mathrm{BB}}{2}\right]+Xz\left(\varepsilon_\mathrm{AB}-\frac{\varepsilon_\mathrm{AA}+\varepsilon_\mathrm{BB}}{2}\right) \qquad [3.13]$$

By substituting expression [3.12] back into equation [3.8], the exchange integral becomes:

$$I_\mathrm{AB} = \exp\left(\frac{N_\mathrm{A}\varepsilon_\mathrm{AA}+N_\mathrm{B}\varepsilon_\mathrm{BB}}{\mathrm{k_B}T}\right) \frac{\int\ldots\int \exp\left(-\frac{Xw_\mathrm{AB}}{\mathrm{k_B}T}\right)(\mathrm{d}\omega_\mathrm{A})^{N_\mathrm{A}}(\mathrm{d}\omega_\mathrm{B})^{N_\mathrm{B}}}{N_\mathrm{A}!N_\mathrm{B}!} \qquad [3.14]$$

In order to calculate the integral of expression [3.14], we define the value Y by relation:

$$\exp\left(-\frac{Yw}{\mathrm{k_B}T}\right)\int\ldots\int(\mathrm{d}\omega_\mathrm{A})^{N_\mathrm{A}}(\mathrm{d}\omega_\mathrm{B})^{N_\mathrm{B}} = \int\ldots\int\exp\left(-\frac{Xw}{\mathrm{k_B}T}\right)(\mathrm{d}\omega_\mathrm{A})^{N_\mathrm{A}}(\mathrm{d}\omega_\mathrm{B})^{N_\mathrm{B}} \qquad [3.15]$$

As, according to hypothesis 3, the free volumes $v_{f(A)}$ and $v_{f(B)}$ are very close, we can replace the arithmetic mean with the geometric mean, and use the following approximation:

$$\frac{N_A v_{f(A)}+N_2 v_{f(B)}}{N_A+N_B} \cong \left({v_{f(A)}}^{N_A}{v_{f(B)}}^{N_B}\right)^{\left(\frac{1}{N_A+N_B}\right)} \qquad [3.16]$$

In light of relation [3.16], we can integrate the left-hand side of expression [3.15], and we obtain:

$$\begin{gathered}I_{\mathrm{AB}}=\left[\exp(1)v_{f(A)}\exp\left(\frac{\varepsilon_{\mathrm{A(A)}}}{\mathrm{k_B}T}\right)\right]^{N_\mathrm{A}}\left[\exp(1)v_{f(B)}\exp\left(\frac{\varepsilon_{\mathrm{B(B)}}}{\mathrm{k_B}T}\right)\right]^{N_\mathrm{B}}\\ \frac{\left(N_\mathrm{A}+N_\mathrm{B}\right)!}{N_\mathrm{A}!N_\mathrm{B}!}\exp\left(-\frac{Yw}{\mathrm{k_B}T}\right)\end{gathered}\tag{3.17}$$

The configuration integral I_{AB} can be broken down into three terms: an interaction integral for the pure liquid A (term given by relation [1.22]), an interaction integral for the pure liquid B and a mixing integral I_{AB}^{mix} which is:

$$I_{\mathrm{AB}}^{mix}=\frac{\left(N_\mathrm{A}+N_\mathrm{B}\right)!}{N_\mathrm{A}!N_\mathrm{B}!}\exp\left(-\frac{Yw}{\mathrm{k_B}T}\right)\tag{3.18}$$

The composition Y appears as the fictitious number of mixed pairs that would yield the right value of the partition function if the molecules were distributed at random.

NOTE 3.3.– As pointed out earlier, the choice of the model of a pure liquid is no longer relevant in the expression of the integral of mixing.

The integral of mixing is the contribution of the mixing to the system's overall partition function.

We can now calculate the Helmholtz energy of mixing and the Gibbs energy of mixing, which are equal because the volume of mixing is null, with the following formula:

$$\begin{aligned}G^{mix}&=F^{mix}=-\mathrm{k_B}T\ln I_{\mathrm{AB}}^{mix}=Yw_{AB}-\mathrm{k_B}T\,\ln\frac{\left(N_\mathrm{A}+N_\mathrm{B}\right)!}{N_\mathrm{A}!N_\mathrm{B}!}\\&=Yz\left(\varepsilon_{\mathrm{AB}}-\frac{\varepsilon_{\mathrm{AA}}+\varepsilon_{\mathrm{BB}}}{2}\right)-\mathrm{k_B}T\,\ln\frac{\left(N_\mathrm{A}+N_\mathrm{B}\right)!}{N_\mathrm{A}!N_\mathrm{B}!}\end{aligned}\tag{3.19}$$

Using Stirling's approximation, this Gibbs energy of mixing takes the form:

$$G^{mix} = F^{mix} = Yw_{AB}$$
$$-\mathrm{k_B}T\left[N_{\mathrm{A}} \ln \frac{N_{\mathrm{A}}}{(N_{\mathrm{A}} + N_{\mathrm{B}})} + N_{\mathrm{B}} \ln \frac{N_{\mathrm{B}}}{(N_{\mathrm{A}} + N_{\mathrm{B}})} \right] \quad [3.20]$$

Thus, we need to calculate the value Y. In order to do so, we write $\langle X \rangle$ for the value of X at equilibrium, which is such that:

$$\langle X \rangle \int \ldots \int \exp\left(-\frac{w_{\mathrm{AB}}}{\mathrm{k_B}T} \right) (\mathrm{d}\,\omega_{\mathrm{A}})^{N_{\mathrm{A}}} (\mathrm{d}\,\omega_{\mathrm{B}})^{N_{\mathrm{B}}}$$
$$= \int \ldots \int X \exp\left(-\frac{Xw_{\mathrm{AB}}}{\mathrm{k_B}T} \right) (\mathrm{d}\,\omega_{\mathrm{A}})^{N_{\mathrm{A}}} (\mathrm{d}\,\omega_{\mathrm{B}})^{N_{\mathrm{B}}} \quad [3.21]$$

By deriving equation [3.15] in relation to temperature, we can verify the expression:

$$\langle X \rangle = Y - T\left[\frac{\partial Y}{\partial T} \right] = \frac{\partial [Y/T]}{\partial (1/T)} \quad [3.22]$$

Thus, ultimately, calculation of the partition function of our model of a solution boils down to determining $\langle X \rangle$ and then Y using expression [3.22]. Finally, by feeding the value Y thus obtained back into expression [3.20], we find the value of the Gibbs energy of mixing.

3.1.1. *The microscopic model of a perfect solution*

We have already given (see relation [A.2.28] and Table A.2.1 in Appendix 2) the macroscopic representation of a perfect solution and the resulting properties. Now, we are going to construct a microscopic model, to see which hypotheses yield the same expression for the Gibbs energy of mixing given by expression [A.2.6] (see Table A.2.1).

We return to the previous model (section 3.1), and we shall now determine Y by adding a seventh hypothesis to our model: the exchange energy is null, i.e.:

$$w_{\mathrm{A}B} = \frac{2\varepsilon_{\mathrm{AB}} - \varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}}}{z} = 0 \qquad [3.23]$$

Thus, by substituting this value into relation [3.13], we see that the total enthalpy is equal to the sum of the enthalpies of the two pure liquids, and therefore the enthalpy of mixing is zero. This means that our two solutions are mixed with no alteration of the energy – i.e. with no thermal effect.

With our new hypothesis, relation [3.18] becomes:

$$I_{\mathrm{AB}}^{mix} = \frac{\left(N_{\mathrm{A}} + N_{\mathrm{B}}\right)!}{N_{\mathrm{A}}!N_{\mathrm{B}}!} \qquad [3.24]$$

The Helmholtz energy of mixing is the same as the Gibbs energy of mixing (as the mixing volume is null), and in light of relation [3.19] $(\mathrm{w}_{\mathrm{AB}} = 0)$, we calculate:

$$G^{mix} \cong \mathrm{k}_B T\left(N_{\mathrm{A}} \ln \frac{N_{\mathrm{A}}}{N_{\mathrm{A}} + N_{\mathrm{B}}} + N_{\mathrm{B}} \ln \frac{N_{\mathrm{B}}}{N_{\mathrm{A}} + N_{\mathrm{B}}} \right) \qquad [3.25]$$

In order to find the molar value, we make $N_{\mathrm{A}} + N_{\mathrm{B}} = \mathrm{Na}$ and $n_{\mathrm{A}} + n_{\mathrm{B}} = 1$, so that $x_{\mathrm{A}} = n_{\mathrm{A}}$ and $x_{\mathrm{B}} = n_{\mathrm{B}}$. Thus, the molar Gibbs energy of mixing is:

$$G_m^{mix} \cong F_m^{mix} = \mathrm{R}T\left(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\right) \qquad [3.26]$$

We can see that this relation is indeed identical to expression [A .6] (see Table A.2.1 in Appendix 2). Thus, we have here a model of the perfect solution, and note that this solution is not, as might be imagined, a solution in which there are no inter-molecular interactions, as is the case with a perfect gas. Rather, it is a solution in which the energy of interaction $\varepsilon_{\mathrm{AB}}$ between two molecules of A and of B is the arithmetic mean of the energies of the A-A and B-B pairs because, in view of relations [3.4] and [3.23], we obtain:

$$\varepsilon_{\mathrm{AB}} = \frac{\varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}}}{2} \qquad [3.27]$$

Of course, as is often the case in modeling, we have established a model of a perfect solution, but there is nothing to say that this is the only possible model.

3.1.2. *Microscopic description of strictly-regular solutions*

We shall now return to our model of a solution given in section 3.1, with the six hypotheses upon which it is founded, but exclude hypothesis 7, given by equation [3.23]. The exchange energy w_{AB} is no longer null.

NOTE 3.4.– Whilst we continue to state the hypothesis of a random distribution of the molecules of A and B, this hypothesis appears to contradict the existence of an exchange energy, whose presence means that the minimum of the Helmholtz energy cannot correspond exactly to the random distribution. We get around the contradiction by accepting that the short-distance order that would be caused by this exchange energy is annihilated by the thermal agitation. In other words, we accept the condition:

$$w_{\mathrm{AB}} << \mathrm{k_B} T \tag{3.28}$$

Thus, let us write the random distribution of the mixed pairs A-B. Around a molecule of A, there are, on average, zx_B molecules of B, so the mean number of such pairs will be given by:

$$z\langle X\rangle = N_{\mathrm{A}} z x_{\mathrm{B}} = N_{\mathrm{B}} z x_{\mathrm{A}} \tag{3.29}$$

This enables us to write:

$$\langle X\rangle^2 = N_{\mathrm{A}} N_{\mathrm{B}} x_{\mathrm{A}} x_{\mathrm{B}} = N_{\mathrm{A}} N_{\mathrm{B}} \left(1 - \frac{N_{\mathrm{A}}}{N_{\mathrm{A}} + N_{\mathrm{B}}}\right)\left(1 - \frac{N_{\mathrm{B}}}{N_{\mathrm{A}} + N_{\mathrm{B}}}\right) \tag{3.30}$$

Thus:

$$\langle X\rangle^2 = \left(N_{\mathrm{AA}} - \langle X\rangle\right)\left(N_{\mathrm{BB}} - \langle X\rangle\right) \tag{3.31}$$

Thus, $\langle X\rangle$ is independent of the temperature. This is what is known as the *zero-order approximation* or the *Bragg–Williams approximation*.

This temperature-independence of $\langle X \rangle$ means that, in light of relation [3.22], we can write:

$$\langle X \rangle = Y \tag{3.32}$$

and, using relation [3.29], we deduce from this that:

$$\langle X \rangle = Y = \frac{N_\mathrm{A} N_\mathrm{B}}{N_\mathrm{A} + N_\mathrm{B}} \tag{3.33}$$

The integral of mixing is obtained from relation [3.18]. It is of the same form as relation [3.18]. It will be the product of two terms: one identical to that in relation [3.24], pertaining to the perfect solution, and the other comprising the exponential, which will, in fact, be the excess term. According to equation [3.33], this term is:

$$G^{xs} = Y w_\mathrm{AB} = \frac{\mathrm{N_a} n_\mathrm{A} n_\mathrm{B}}{n_\mathrm{A} + n_\mathrm{B}} w_\mathrm{AB} \tag{3.34}$$

and for the corresponding molar value ($n_\mathrm{A}+n_\mathrm{B}=1$), we obtain:

$$G_m^{xs} = \mathrm{N_a} x_\mathrm{A} x_\mathrm{B} w_{AB} \tag{3.35}$$

As Y is independent of the temperature, the excess entropy is null, and we find the following molar enthalpy:

$$H_m^{xs} = -T^2 \frac{\partial \left(G_m^{xs} / T \right)}{\partial T} = \mathrm{N_a} x_\mathrm{A} x_\mathrm{B} w_\mathrm{AB} \tag{3.36}$$

Thus, we see all the properties of the strictly-regular solution (section 2.5.6) and by identification between equations [3.35] and [2.61], we can deduce:

$$B = \frac{\mathrm{N_a} w_{AB}}{\mathrm{R}} \tag{3.37}$$

The difference between a strictly-regular solution and a perfect solution lies in the exchange energy, which is null in the case of the latter.

NOTE 3.5.– the null excess entropy is due to the temperature-independence of Y, which means, in view of relation [3.22], that the equilibrium value $\langle X \rangle$ is also independent of T, and we have shown that the random distribution of the molecules satisfies this condition. There is nothing to show that only this distribution leads to a null excess entropy, which explains why not all regular solutions are *strictly* regular.

Certain authors work differently to construct the model. They accept the hypothesis of random distribution of the molecules. They then deduce that the excess entropy is null. Knowing the excess enthalpy, given by relation [3.13], they then calculate the Gibbs energy, applying relation [3.36] in reverse. Integration is then performed, making the hypothesis that, if the temperature tends toward infinity, the mixture behaves like a perfect solution, which is to say that its excess enthalpy is null. In fact, this way of working seems much simpler, and it does yield the right result. However, the assertion that the mixture behaves like a perfect solution if the temperature tends toward infinity is not easily conceived of. Thus, we prefer the previous construction. This presentation also has the advantage of being able to be used in the case of another model (see section 3.2.4).

3.1.3. *Microscopic modeling of an ideal dilute solution*

Let us look again at the above model of a strictly-regular solution (section 3.1.2). If the number of molecules of B is small in relation to that of A – in other words, if the solution is very dilute in terms of B content – then relation [3.33] gives us:

$$\langle X \rangle = Y \cong N_{\mathrm{B}} \qquad [3.38]$$

Relation [3.34] yields:

$$G^{xs} = \mathrm{N_a} n_{\mathrm{B}} w_{\mathrm{AB}} \qquad [3.39]$$

The activity coefficient of B in convention (I) thus satisfies the equality:

$$-\mathrm{R}T \ln \gamma_{\mathrm{B}}^{(I)} = \frac{\partial G^{xs}}{\partial n_B} = \mathrm{N_a} w_{\mathrm{AB}} \qquad [3.40]$$

Therefore, we can deduce that:

$$\gamma_{\mathrm{B}}^{(I)} = \exp - \frac{\mathrm{N_a} w_{\mathrm{AB}}}{\mathrm{R}T} \tag{3.41}$$

This activity coefficient is independent of the composition of the solution; it depends only on the temperature.

The excess molar Gibbs energy is thus:

$$G^{xs} = \mathrm{N_a} w_{\mathrm{AB}} = -\mathrm{R}Tn_{\mathrm{B}} \ln \gamma_{\mathrm{B}}^{(I)} \tag{3.42}$$

In this excess Gibbs energy, the solvent makes no contribution at all. This tells us that $\gamma_{\mathrm{A}}^{(I)} = 1$. Consequently, as with the solvent, conventions (I) and (II) are identical. We deduce that:

$$\gamma_{\mathrm{A}}^{(I)} = \gamma_{\mathrm{A}}^{(II)} = 1 \tag{3.43}$$

In convention (II), therefore, the activity coefficient of the solute B is also constant, and as with the infinitely-dilute solution, the value of this constant is 1. From this, we deduce that:

$$\gamma_{\mathrm{B}}^{(II)} = 1 \tag{3.44}$$

Here, we encounter all the characteristics of the ideal dilute solution studied in section 2.4.

Henry's constant is therefore given, on the basis of relation [2.23], by:

$$K_{\mathrm{B}H} = \gamma_{\mathrm{B}}^{(I)} = \exp\left(-\frac{\mathrm{N_a} w_{\mathrm{AB}}}{\mathrm{R}T} \right) \tag{3.45}$$

Thus, the ideal dilute solution is the particular case of the strictly-regular solution wherein there is a very small proportion of one of the components.

From expression [A.2.21], we deduce the physical meaning of the chemical potential of the solute for the reference state (II):

$$\mu_s^{\infty} = g_s^0 - \mathrm{N_a} w_{\mathrm{AB}} \tag{3.46}$$

The chemical potential of reference state (II) is that of reference state (I) less the molar exchange energy.

The most general of the three models of solutions that we have just examined is that of the strictly-regular solution. The other two models seem to be two particular cases; that of the perfect solution if we make $w_{AB} = 0$ and that of the ideal dilute solution if we make $n_A >> n_B$. In all these models, we assumed a random distribution of the molecules, which is a fairly restrictive hypothesis, as we mentioned in our discussion of the strictly-regular solution. It is this hypothesis which we are going to examine in greater detail in the next section.

3.2. The concept of local composition

In the model of strictly-regular solutions, we have indicated a contradiction in the fact that the A-B bond involved a different amount of energy than the A-A and B-B bonds, but admitted that this difference did not prevent random distribution of the pairs A-B – in other words, the local composition of the liquid around a molecule of A or a molecule of B was the same as the overall composition. Now, we shall refine our models by examining local distributions different to the overall composition.

3.2.1. *The concept of local composition in a solution*

In reality, the exchange energy has consequences for the local distribution of the molecules. Indeed, it is easy to see that if there is a stronger force of attraction between a molecule of A and a molecule of B than there is between two molecules of A or between two molecules of B, then a molecule of A will tend to be surrounded by molecules of B, and therefore the composition of the immediate environment of the molecule of A will not be the same as the overall composition of the solution – it will be richer in molecules of B. The opposite effect would be observed if the two molecules A and B had a lesser force of attraction than two molecules of A and two molecules of B. This is the *concept of local composition*, first expressed by Wilson.

In order to describe this concept of local composition, we use a nomenclature that enables us to clearly distinguish, every time, between the central molecule and its closest neighboring molecules.

N_{ij} denotes the number of molecules of i around a molecule of j, and we define the conditional probability P_{ij} that a molecule of i will be located in the environs of a molecule of j by the expression (where N denotes the number of components in the solution):

$$P_{ij} = \frac{N_{ij}}{\sum_{i=1}^{N} N_{ij}} \quad [3.47]$$

Note that this probability also represents the local molar fraction.

Evidently, we have:

$$\sum_{i=1}^{N} P_{ij} = 1 \quad [3.48]$$

Thus, for a binary solution, we distinguish:

– P_{AA} : local molar fraction of the molecules of A around a molecule of A;

– P_{BA} : local molar fraction of the molecules of B around a molecule of A;

– P_{BB} : local molar fraction of the molecules of B around a molecule of B;

– P_{AB} : local molar fraction des molecules of A around a molecule of B;

with the equalities:

$$P_{\text{AA}} + P_{\text{BA}} = 1 \quad [3.49a]$$

and $$P_{\text{BB}} + P_{\text{AB}} = 1 \quad [3.49b]$$

We shall suppose that it is always possible to define a weighting factor k_{ij} such that the local composition is the overall composition weighted by that factor. In other words, we shall define the factors k_{ij} by way of the following relations – e.g. for a binary solution (x_A and x_B are the overall molar fractions of the two components in the solution):

$$\frac{P_{BA}}{P_{AA}} = \frac{x_B}{x_A} k_{BA} \qquad [3.50a]$$

$$\frac{P_{AB}}{P_{BB}} = \frac{x_A}{x_B} k_{AB} \qquad [3.50b]$$

By combining equations [3.49a], [3.49b], [3.50a] and [3.50b], we obtain:

$$P_{AA} = \frac{x_A}{x_A + x_B k_{BA}} \qquad [3.51]$$

and by substituting the result back into expression [3.50a], we find:

$$P_{BA} = \frac{x_B k_{BA}}{x_A + x_B k_{BA}} \qquad [3.52]$$

Similarly, around molecule B, we find:

$$P_{BB} = \frac{x_B}{x_B + x_A k_{AB}} \qquad [3.53]$$

and:

$$P_{AB} = \frac{x_A k_{AB}}{x_B + x_A k_{AB}} \qquad [3.54]$$

NOTE 3.6.– If the arrangement of the molecules of A and B is random, obviously we have $P_{AB} = x_A$ and $P_{BA} = x_B$, and therefore $k_{AB} = k_{BA} = 1$.

3.2.2. *Energy balance of the mixture*

We shall now recalculate the energy of mixing of N_A molecules of A and N_B molecules of B in that context of local composition, by finding the energy balance of that mixture. We suppose that in pure liquid A, a molecule of A has a coordination number z_A, meaning that it is surrounded by z_A molecules, which exert an influence on it in energetic terms. Similarly, in pure liquid B, the coordination number is z_B. In solution, we use z'_A and z'_B respectively to denote the coordination numbers of the molecules of A and the molecules of B in the solution. There is no reason, *a priori*, for all these coordination numbers to be equal, which runs counter to the hypothesis we have employed up until now.

The interaction between two molecules that are not immediate neighbors is ignored.

In order to extract a molecule of A from the pure liquid A, we must break z_A A-A bonds and therefore provide the energy $z_A\ \varepsilon_{AA}$. We place that molecule in the pure liquid B. This transfer forms new bonds and therefore releases the energy $z'_A\ (y_{AA}\varepsilon_{AA} + y_{BA}\varepsilon_{BA})$. The variation in energy due to the transfer of a molecule of A from the pure liquid A into liquid B will therefore be: $z_A\ \varepsilon_{AA} - z'_A\ (y_{AA}\varepsilon_{AA} + y_{BA}\varepsilon_{BA})$. Obviously, we can calculate a symmetrical expression for the transfer of a molecule of B from liquid B into liquid A. The variation in internal energy to form a mole of mixture, therefore, will be:

$$U_m^{mix} = \frac{\mathrm{Na}}{2}\left\{\begin{array}{l} x_A\left[z_A\varepsilon_{AA} - z'_A\left(y_{AA}\varepsilon_{AA} + y_{BA}\varepsilon_{BA}\right)\right] \\ +x_B\left[z_B\varepsilon_{BB} - z'_B\left(y_{BB}\varepsilon_{BB} + y_{AB}\varepsilon_{AB}\right)\right] \end{array}\right\} \qquad [3.55]$$

Taking account of relations [3.50a], [3.50b], [3.53] and [3.54], we find the following for the excess- or mixing molar internal energy:

$$U_m^{xs} = \frac{\mathrm{Na}}{2}\left[\frac{x_A x_B K_{BA} z'\ \left(\varepsilon_{BA} - \varepsilon_{AA}\right)}{x_A + x_B K_{BA}} + \frac{x_A x_B K_{AB} z'_B\left(\varepsilon_{AB} - \varepsilon_{BB}\right)}{x_B + x_A K_{AB}}\right] \qquad [3.56]$$

Based on our knowledge of the internal mixing energy, we calculate the Helmholtz energy using the relation:

$$\frac{\partial\left(\dfrac{F_m^{xs}}{T}\right)}{\partial(1/T)} = U_m^{xs} \qquad [3.57]$$

Integration gives us:

$$\left(\frac{F_m^{xs}}{T}\right)-\left(\frac{F_m^{xs}}{T}\right)_{T=T_{\text{lim}}}=\int_{1/T_{\text{lim}}}^{1/T} U_m^{xs}\,\mathrm{d}\left(\frac{1}{T}\right) \qquad [3.58]$$

If T_{lim} is infinite, at this temperature F/T_m becomes independent of the temperature because the mixture is identical to a mixture of perfect gases without interaction between molecules, but F/T_m may depend on the composition or the density of the liquid.

Finally, the modeling of the solution, i.e. the establishing of the excess molar Helmholtz energy function, involves expressing the value of the coefficients k_{ij} from relation [3.56], and most of the existing models differ only in this evaluation.

3.2.3. *Warren and Cowley's order parameter*

For a solution containing molecules *i* and *j*, Warren and Cowley defined an order parameter η_{ij} as being:

$$\eta_{ij}=1-\frac{\text{nb of molecules of } i \text{ around a molecule of } j}{\text{mean nb of molecules of } i \text{ around a molecule of } j} \qquad [3.59]$$

In the case of a binary mixture, therefore, we would have:

$$\eta_{\text{AB}}=1-\frac{P_{\text{AB}}}{x_{\text{A}}}$$

with the condition:

$$0<\eta_{\text{AB}}\leq 1 \qquad [3.60]$$

and in parallel:

$$\eta_{\text{BA}}=1-\frac{P_{\text{BA}}}{x_{\text{B}}} \text{ and } 0<\eta_{\text{BA}}\leq 1 \qquad [3.61]$$

We can obviously deduce that:

$$P_{\mathrm{BA}} = x_{\mathrm{B}}\left(1-\eta_{\mathrm{BA}}\right) \qquad [3.62a]$$

and $$P_{\mathrm{AB}} = x_{\mathrm{A}}\left(1-\eta_{\mathrm{AB}}\right) \qquad [3.62b]$$

NOTE 3.7.– if the distribution of the molecules is random, then $P_{\mathrm{AB}} = x_{\mathrm{A}}$ and $\eta_{\mathrm{BA}} = 1$.

The two order parameters η_{AB} and η_{BA} are connected; indeed, the number of pairs A-B can be expressed in two ways, such that:

$$N_{\mathrm{BA}} N_{\mathrm{A}} = N_{\mathrm{AB}} N_{\mathrm{B}} \qquad [3.63]$$

Hence:

$$z'_{\mathrm{A}} P_{\mathrm{BA}} N_{\mathrm{A}} = z'_{\mathrm{B}} P_{\mathrm{AB}} N_{\mathrm{B}} \qquad [3.64]$$

By introducing the values of P_{BA} and P_{AB} in equations [3.62a] and [3.62b], we find:

$$z'_{\mathrm{A}} x_{\mathrm{B}} N_{\mathrm{A}} (1-\eta_{\mathrm{BA}}) = z'_{\mathrm{B}} x_{\mathrm{A}} N_{\mathrm{B}} (1-\eta_{\mathrm{AB}}) \qquad [3.65]$$

If we note that we have the equality:

$$x_{\mathrm{B}} N_{\mathrm{A}} = x_{\mathrm{A}} N_{\mathrm{B}} = \frac{N_{\mathrm{A}} N_{\mathrm{B}}}{N_{\mathrm{A}} + N_{\mathrm{B}}} \qquad [3.66]$$

We obtain:

$$z'_{\mathrm{A}} \eta_{\mathrm{BA}} - z'_{\mathrm{B}} \eta_{\mathrm{AB}} = z'_{\mathrm{B}} - z'_{\mathrm{B}} \qquad [3.67]$$

Hence, the two parameters of opposite orders are not independent.

If the coordination numbers of two types of molecules are the same in the solution ($z'_{\mathrm{A}} = z'_{\mathrm{B}}$), then the two Warren–Cowley order parameters are also equal ($\eta_{\mathrm{AB}} = \eta_{\mathrm{BA}}$).

There is an obvious relation between the order parameters and the weighting factors k_{ij}; indeed, according to equations [3.51], [3.52], [3.62a] and [3.62b], we can write:

$$\eta_{\mathrm{BA}} = 1 - \frac{k_{\mathrm{BA}}}{x_{\mathrm{A}} + x_{\mathrm{B}} k_{\mathrm{BA}}} \text{ and } \eta_{\mathrm{AB}} = 1 - \frac{k_{\mathrm{AB}}}{x_{\mathrm{A}} k_{\mathrm{AB}} + x_{\mathrm{B}}} \qquad [3.68b]$$

This expression shows that if $\eta_{\mathrm{AB}} = 0$ or $k_{\mathrm{AB}} = 1$, the distribution of molecules A and B is random.

If $\eta_{\mathrm{AB}} > 0$ or $k_{\mathrm{AB}} < 1$, this means that $P_{\mathrm{AB}} < x_{\mathrm{A}}$. Thus, on average, there are fewer mixed pairs than in the disordered solution, so there is a tendency toward dissociation of the pairs A-B. On the contrary, if $\eta_{\mathrm{AB}} < 0$ or $k_{\mathrm{AB}} > 1$, that would mean that there is a certain tendency toward the association of molecules of A with molecules of B.

3.2.4. *Model of Fowler & Guggenheim's quasi-chemical solution*

Let us return to our binary solution formed of two components A and B. With the exchange energy being given by w_{AB}, we can write that the system's partition function of exchange is the sum of all the values of *X*, with each energy state being weighted by a degeneration $g(X)$, so that:

$$I_{\mathrm{AB}} = \sum_{X} g(X) \exp\left[-\frac{\left(2zXw_{\mathrm{AB}} - zN_{\mathrm{AA}}\varepsilon_{\mathrm{AA}} - zN_{\mathrm{BB}}\varepsilon_{BB}\right)}{z\mathrm{k}_{\mathrm{B}}T} \right] \qquad [3.69]$$

g(*X*) is the number of arrangements which are possible for a given level of energy. For a given value of *X*, the different pairs of atoms may be arranged in accordance with the number of possibilities, proportional to:

$$\frac{(zN/2)!}{\left[z(N_{\mathrm{A}} - X)/2\right]!\left[z(N_{\mathrm{B}} - X)/2\right]!\left[zN_{\mathrm{AB}}/2\right]!\left[zN_{\mathrm{BA}}/2\right]!}$$

Thus, we can write:

$$g(X) = k\frac{(zN/2)!}{\left[z(N_{\mathrm{A}} - X)/2\right]!\left[z(N_{\mathrm{B}} - X)/2\right]!\left[zN_{\mathrm{AB}}/2\right]!\left[zN_{\mathrm{BA}}/2\right]!} \qquad [3.70]$$

In this expression, the first and second term in the denominator, respectively, are relative to the numbers of pairs A-A and B-B, and the third and fourth term respectively relate to the numbers of pairs A-B and B-A.

We have introduced a coefficient of proportionality, because the A-B bonds are not totally independent of one another. Figure 3.1 shows an example of this non-independence. Indeed, suppose that on the lattice (which we shall take to be flat for the purpose of simplicity), we have placed the molecules A_a, B_b, and B_c respectively on sites a, b and c. If we place a molecule B on site d, it is clear that the bond between sites a and d is necessarily a mixed bond A_aB_d. In other words, the pairs are not distributed entirely randomly. The coefficient *k* depends on the lattice chosen to represent the cell.

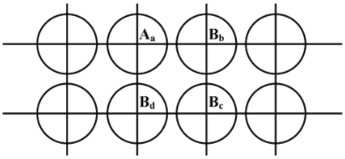

Figure 3.1. *Dependency of the pairs*

Suppose we use $g_a(X)$ to denote the possible number of arrangements of pairs when they are distributed "at random". According to equation [3.70], we have:

$$g_a(X) = k\frac{(zN/2)!}{\left[z\left(N_\text{A}-X^*\right)/2\right]!\left[z\left(N_\text{B}-X^*\right)/2\right]!\left[zN^*_\text{AB}/2\right]!\left[zN^*_\text{BA}/2\right]!} \qquad [3.71]$$

However, we know that, for a random distribution, this number is:

$$g_a(X) = \frac{N!}{[N_\text{A}]![N_\text{B}]!} \qquad [3.72]$$

By multiplying and dividing relation [3.70] by the values of $g(X)$ given respectively by relations [3.72] and [3.71], which are equal, we obtain:

$$g(X) = \frac{\left[z\left(N_\text{A}-X^*\right)/2\right]\left[z\left(N_\text{B}-X^*\right)/2\right]!\left[zX^*/2\right]!\left[zX^*/2\right]!}{\left[z\left(N_\text{A}-X\right)/2\right]!\left[z\left(N_\text{B}-X\right)/2\right]!\left[zX/2\right]!\left[zX/2\right]!}\frac{N!}{[N_\text{A}]![N_\text{B}]!} \qquad [3.73]$$

To simplify the calculations, we apply Boltzmann's law (see Appendix 3), whereby the sum of all the states in equation [3.69] can be replaced by its maximum value.

In this case, the number of mixed pairs $z\langle X\rangle$ will be such that:

$$\frac{\partial \ln\{I_{\mathrm{AB}}\}}{\partial X}=0 \qquad [3.74]$$

$\langle X\rangle$ is the value of X which satisfies relation [3.74].

We obtain:

$$\langle X\rangle^2=\left(N_{\mathrm{A}}-\langle X\rangle\right)\left(N_{\mathrm{B}}-\langle X\rangle\right)\exp-\frac{2w_{\mathrm{AB}}}{\mathrm{k_B}T} \qquad [3.75]$$

A laborious calculation performed by Christian in 1975 gives us:

$$\langle X\rangle=\frac{2N_{\mathrm{A}}N_{\mathrm{B}}}{\left(N_{\mathrm{A}}+N_{\mathrm{B}}\right)\beta_q+1} \qquad [3.76]$$

If we introduce the molar fractions defined by:

$$x_{\mathrm{A}}=\frac{n_{\mathrm{A}}}{\left(n_{\mathrm{A}}+n_{\mathrm{B}}\right)}=\frac{N_{\mathrm{A}}}{\left(N_{\mathrm{A}}+N_{\mathrm{B}}\right)} \text{ and } x_{\mathrm{B}}=\frac{n_{\mathrm{B}}}{\left(n_{\mathrm{A}}+n_{\mathrm{B}}\right)}=\frac{N_{\mathrm{B}}}{\left(N_{\mathrm{A}}+N_{\mathrm{B}}\right)} \qquad [3.77]$$

Thus, for a mole of mixture $\left(N_{\mathrm{A}}+N_{\mathrm{B}}=\mathrm{N_a}\right)$, we have:

$$\langle X\rangle=\frac{2\mathrm{N_a^2}x_{\mathrm{A}}x_{\mathrm{B}}}{\mathrm{N_a}\beta_q+1} \qquad [3.78]$$

The term β_q is defined by:

$$\beta_q=\frac{\left\{1+4N_{\mathrm{A}}N_{\mathrm{B}}\left[\exp-\dfrac{2w_{\mathrm{AB}}}{z\mathrm{k_B}T}-1\right]\right\}^{1/2}}{N_{\mathrm{A}}+N_{\mathrm{B}}} \qquad [3.79]$$

$$=\left\{\left(1-2x_{\mathrm{A}}\right)^2+4x_{\mathrm{A}}x_{\mathrm{B}}\exp-\frac{2w_{\mathrm{AB}}}{z\mathrm{k_B}T}\right\}^{1/2}$$

By substituting expression [3.78] into equation [3.22], we obtain:

$$Y = \frac{N_A N_B}{N_A + N_B} \frac{z k_B T}{2w_{12}} \int_0^{2w_{AB}/z k_B T} \frac{2}{\beta_q - 1} d\left(\frac{2w_{AB}}{z k_B T}\right) \tag{3.80}$$

The lower bound of the integral of expression [3.80] is determined as follows: if $T \to \infty$, we must observe a random distribution (because then $w_{12} << k_B T$), in which Y is more or less equal to $\langle X \rangle$, according to relation [3.22], and where the difference $Y - \langle X \rangle$ is finite. Thus, Y / T tends toward zero if $1/T$ tends toward zero. In view of the definition of β_q (relation [3.79]), we have:

$$\exp\left(\frac{2w_{AB}}{z k_B T}\right) = \frac{\beta_q^2 - (1 - 2x_A)}{4 x_A x_2} \tag{3.81}$$

Thus:

$$d\left(\frac{2w_{AB}}{z k_B T}\right) = \frac{2\beta_q \, d\beta_q}{\left(\beta_q - 1 + 2x_A\right)\left(\beta_q + 1 - 2x_A\right)} \tag{3.82}$$

By introducing this into expression [3.80], we find:

$$\frac{Y}{N_A N_B} = \frac{z k_B T}{2w_{AB}} \left(x_A \ln \frac{\beta_q - 1 + 2x_A}{2x_A} + x_B \ln \frac{\beta_q + 1 - 2x_A}{2x_B} - \ln \frac{\beta_q + 1}{2} \right) \tag{3.83}$$

In the knowledge that:

$$(N_A + N_B = 1) \tag{3.84}$$

By feeding this back into relation [3.20], we obtain the excess molar Gibbs energy:

$$G^{xs} = \frac{1}{2} z R T \left[x_B \ln \frac{\beta_q + x_B - x_A}{x_B\left(\beta_q + 1\right)} + x_A \ln \frac{\beta_q + x_A - x_B}{x_A\left(\beta_q + 1\right)} \right] \tag{3.85}$$

Note that, as was the case with the strictly-regular solutions model, our new model preserves a result that is symmetrical in relation to the two components A and B.

Figure 3.2 shows the difference between the excess molar Gibbs energy of the strictly-regular solution and that of this model for the values $T = 800$ K, $z = 12$ and $Naw_{AB} = 30$ kJ. The two curves reach their minimum point at $x_A = x_B = 0.5$.

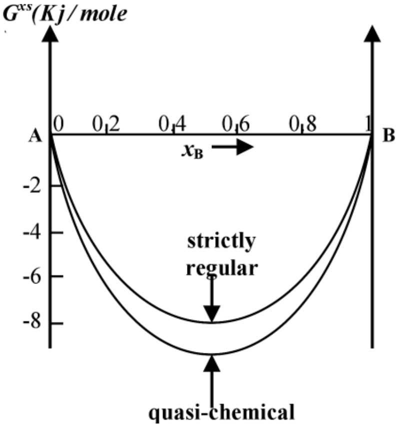

Figure 3.2. *Comparison of the excess Gibbs energies of a strictly-regular solution and the quasi-chemical model (reproduced from [DES 10], p.62 – see Bibliography)*

We can see that the solution is no longer regular.

The activity coefficients of the two components become the following, by derivation of the excess Gibbs energy in relation to n_i, remembering that β_q, x_A and x_B are functions of N_A and N_B (the calculation is complicated but yields a direct result):

$$\gamma_A^{(I)} = \left(\frac{\beta_q + x_A - x_B}{x_A \left(\beta_q + 1 \right)} \right)^{z/2} \quad [3.86]$$

$$\gamma_B^{(I)} = \left(\frac{\beta_q + x_B - x_A}{x_B \left(\beta_q + 1 \right)} \right)^{z/2} \quad [3.87]$$

The solution thus modeled is called Fowler and Guggenheim's quasi-chemical model.

This model may be calibrated on an experiment with a single adjustable parameter β_q. Based on the knowledge of the values of the activity coefficients at a given temperature T, for a given composition, using relations [3.86] and [3.87], we calculate $G_{\grave{u}}^{xs}$; then, we use relation [3.85] to deduce β_q and, with equation [3.79], we obtain the ratio w_{AB}/z – i.e. the difference $\varepsilon_{\mathrm{AB}} - \frac{\varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}}}{2}$.

Let us calculate Warren and Cowley's parameter for Fowler and Guggenheim's quasi-chemical model.

If we attempt to link our results to the values introduced in sections 3.1 and 3.2.3, we immediately find:

$$z'_{\mathrm{A}} = z'_{\mathrm{B}} = z \qquad [3.88]$$

$$\langle X \rangle = N_{\mathrm{A}} y_{\mathrm{AB}} = N_{\mathrm{A}} y_{\mathrm{BA}} = N_{\mathrm{B}} x_{\mathrm{A}} = N_{\mathrm{A}} x_{\mathrm{B}} = N_{\mathrm{AB}} / z \qquad [3.89]$$

$$\eta_{\mathrm{AB}} = \eta_{\mathrm{BA}} = \eta = 1 - \frac{x_{\mathrm{AB}}}{x_{\mathrm{A}} x_{\mathrm{B}}} \qquad [3.90]$$

By substituting this last relation into equations [3.76] and [3.81], we obtain:

$$\eta = 1 - \frac{2 z x_{\mathrm{A}} x_{\mathrm{B}}}{\beta_q - 1} \qquad [3.91]$$

β_q is defined, as usual, by relation [3.79].

Thus, the activity coefficients expressed by relations [3.86] and [3.87] can be written in the form:

$$\ln \gamma_{\mathrm{A}} = \frac{z}{2} \ln\left(\frac{1 - x_{\mathrm{B}}(1-\eta)}{x_{\mathrm{A}}} \right) \qquad [3.92]$$

$$\ln \gamma_{\mathrm{B}} = \frac{z}{2}\ln\left(\frac{1 - x_{\mathrm{A}}(1-\eta)}{x_{\mathrm{B}}}\right) \qquad [3.93]$$

Figure 3.3 shows the variations of Warren and Cowley's order parameter for Fowler and Guggenheim's quasi-chemical model, for the following values of the parameters: $T = 800$ K, $N_a w_{AB} = 30$ kJ and $z = 12$. The result obtained respects the symmetry of the model with a minimum for the composition $x_A = x_B = 0.5$.

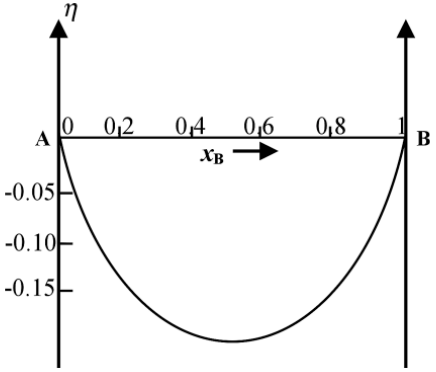

Figure 3.3. *Variation of the degree of order as a function of the composition of a binary solution in Fowler and Guggenheim's quasi-chemical model (reproduced from [DES 10], p.87)*

NOTE 3.8.– The values k_{AB} and k_{BA} defined by expressions [3.50a] and [3.50b] are linked to one another by:

$$(1-\eta) = \frac{x_{\mathrm{A}} k_{\mathrm{AB}}}{x_{\mathrm{B}}\left(x_{\mathrm{B}} k_{\mathrm{AB}} - x_{\mathrm{A}}\right)} = \frac{x_{\mathrm{B}} k_{\mathrm{BA}}}{x_{\mathrm{A}}\left(x_{\mathrm{A}} k_{\mathrm{BA}} - x_{\mathrm{B}}\right)} \qquad [3.94]$$

Thus, in Fowler and Guggenheim's quasi-chemical model, the two weighting factors k_{AB} and k_{BA} depend on the composition.

There are several models of solutions which use this concept of overall composition – Wilson's, in particular. Given the restricted reach of these models, we have chosen to use the concept of local composition only in the context of the much more widely-applicable models UNIQUAC (see section 3.5) and UNIFAC (see section 3.6).

3.3. The quasi-chemical method of modeling solutions

If we examine relation [3.31], it is exactly as though we had applied the law of mass action to a chemical equilibrium, which can be written as:

$$\text{A-A+B-B} = 2\ \text{A-B} \qquad [3R.1]$$

The constant in this equilibrium would be equal to 1, meaning that it is independent of the temperature.

Similarly, by examining relation [3.75], we are led to write a law of mass action of the same equilibrium [3R.1], but this time with an equilibrium constant of:

$$K = \exp-\left(\frac{2w_{\mathrm{AB}}}{\mathrm{k_B}T}\right) \qquad [3.95]$$

It is because of these similarities that Fowler and Guggenheim's model is known as the quasi-chemical model.

Generalizations of this model have been put forward. Remembering that we have only taken account of the energies of interaction between near neighbors, we can extrapolate, by writing that the energy which is involved in the constant could be considered to be the sum of the energies between first neighbors, between second neighbors, etc., which would lead to a constant K appearing as the sum of the exponential terms, in the form:

$$K = \exp-\left(\frac{2w_{\mathrm{AB}}}{\mathrm{k_B}T}\right) + \exp-\left(\frac{3w_{\mathrm{AB}}}{\mathrm{k_B}T}\right) + \exp-\left(\frac{4w_{\mathrm{AB}}}{\mathrm{k_B}T}\right) + \ldots \qquad [3.96]$$

Thus, we can understand why the solution given by relation [3.31], which is the Bragg–Williams approximation, is also called the *zero-order approximation*, whereas Fowler and Guggenheim's, given by relation [3.75], is called the *1st-order approximation*. Similarly, we can have 2nd-order, 3rd-order approximations, etc.

As we can see, this quasi-chemical method is not dissimilar to the associated-solutions model discussed in section 2.5. This method has been rendered more generally applicable by writing what are known as *quasi-equilibria* – i.e. equilibria of the same type as above, but between fictitious entities which might be atoms, molecules, vacancies, etc. – in fact, any entities the user cares to define. Thus, we can find pairs of molecules, trios, or even functional groups (parts of molecules), or clusters (groups of atoms or molecules).

A generalization of Guggenheim's quasi-chemical method has been constructed in order to find the number of possibilities of configurations between groups of elements for each pair in a binary solution of N_A molecules of component A and N_B molecules of components B (here, the term "molecule" is used in a generic sense to speak of the elementary units involved in the processes). The units that come together in pairs may be true molecules, fragments of molecules, surfaces of molecules, parts of the surface of molecules, etc. The distinction is maintained between those elements which belong to component A and those belonging to component B. We suppose that the canonical partition function of mixing is of the form:

$$Z_C^{mix} = \sum_k g(a_k, b_k ..) \exp\left(-\frac{U(a_k, b_k, ...)}{\mathrm{R}T} \right) \qquad [3.97]$$

$g(a_k, b_k ...)$ is the statistical weight of a configuration of elements in the volume defined by a series of particular values a_k, b_k of the configuration variables a, b, etc. These variables may be the volumic compositions, the local volumic compositions, the global or local surfacic compositions, depending on the elements in question.

$U^{mix}(a_k, b_k, ...)$ is the configuration energy of mixing, which is a function of the configuration variables.

Generally speaking, we do not know an exact solution to the problem. The quasi-chemical method gives an approximate value for our unknown: the total number of all the configurations.

We know from Boltzmann's law (see section 2.1.1) that in the sum involved in relation [3.97], one of the terms is much greater than the others, and that therefore the sum can be replaced by this maximum term. Hence, we can replace relation [3.97] with:

$$Z_C^{mix} = g(a, b ..) \exp\left(-\frac{U^{mix}(a, b, ...)}{\mathrm{R}T} \right) \qquad [3.98]$$

$g(a,b..)$ and U^{mix} $(a,b,...)$ are the values of g and U^{mix} which correspond to the most probable configuration – i.e. to the values a, b, … of the configuration variables which yield the maximum Z_C^{mix}.

The hypothesis of the quasi-chemical method is to assume that the statistical weight g of the solution, i.e. the number of configurations with energy U^{mix} that yields the maximum value of Z_C^{mix}, is given by the following equilibrium:

Pair of elements belonging to A + Pair of elements belonging to B = Mixed pair

The law of mass action applied to this quasi-chemical equilibrium is written as:

$$g(a,b,...) = h(N_{\mathrm{A}}, N_{\mathrm{B}})g_{\mathrm{A}}(a,b,...)g_{\mathrm{B}}(a,b,...) \qquad [3.99]$$

$g_{\mathrm{A}}(a,b,...)$ denotes the number of configurations with energy U^{mix} which have the maximum number of homogeneous pairs A-A, and similarly $g_{\mathrm{B}}(a,b,...)$ for the pairs B-B. The method postulates that $h(N_{\mathrm{A}}, N_{\mathrm{B}},)$ is contingent only upon the amounts of each of the components N_{A} and N_{B} present. The function $h(N_{\mathrm{A}}, N_{\mathrm{B}},)$ appears as a corrective factor, because the simple product $g_{\mathrm{A}}g_{\mathrm{B}}$ would yield too high a number of configurations with the energy U.

The solution must satisfy the boundary condition, which is that if the temperature increases indefinitely, U^{mix} tends toward zero, and therefore we must find the number of configurations wherein the elements are distributed at random. For this purpose, we choose a reference model which satisfies that boundary condition. Guggenheim chose molecules comprising pairs of spheres of equal dimensions, distributed at random, which we examined in section 3.2.4, whereas in the UNIQUAC model, it is Staverman's athermic solution for molecules of diverse shapes and sizes, distributed at random (see section 3.5) which is chosen. Suppose that we know the functions $g_{\mathrm{A}}^{*}(a,b...)$ $g_{\mathrm{B}}^{*}(a,b...)$ and $g^{*}(a,b...)$ in this referential model.

To solve relation [3.99], we shall use a two-step process: firstly, we shall calculate the function $h(N_A, N_B,)$, and then use the result in expression [3.99].

In order to determine $h(N_A, N_B,)$, we must remember that this function depends not on the configurations but only on the amounts of the two components. Thus, we shall choose a solution of g that satisfies our boundary condition, which we know how to calculate. Clearly, the simplest such solution is that which we chose as a reference, for which the values are marked with a subscript a (e.g. g_a). This is the Bragg–Williams zero-order approximation. It obeys the following equation (random distribution):

$$g_a(a,b,...) = g_{\mathrm{aA}}(a,b,...)g_{\mathrm{aB}}(a,b,...) \qquad [3.100]$$

As the chosen reference solutions are temperature-independent, the reference solution will be such that the function Z_C^{mix} in equation [3.100], when $U^{mix} = 0$, is maximal. Thus, we shall write the system of equations which makes all the partial differentials of g in relation to the configuration variables equal to 0:

$$\frac{\partial \ln g_a}{\partial a_k} = \frac{\partial \ln g_{a\mathrm{A}}}{\partial a_k} + \frac{\partial \ln g_{a\mathrm{B}}}{\partial a_k} = 0 \qquad [3.101a]$$

$$\frac{\partial \ln g_a}{\partial b_k} = \frac{\partial \ln g_{a\mathrm{A}}}{\partial b_k} + \frac{\partial \ln g_a}{\partial b_k} = 0 \qquad [3.101b]$$

The resolution of this system leads us to the particular functions of the configuration variables $a_a(N_\mathrm{A}, N_\mathrm{B})$, $b_a(N_\mathrm{A}, N_\mathrm{B})$, …, which enables us, on the basis of the values $g_\mathrm{A}^*(a,b...)$, $g_\mathrm{B}^*(a,b...)$ and $g^*(a,b,...)$, to calculate the particular functions $g_{a\mathrm{A}}(N_\mathrm{A}, N_\mathrm{B})$, $g_{a\mathrm{B}}(N_\mathrm{A}, N_\mathrm{B})$ and $g_a(N_\mathrm{A}, N_\mathrm{B})$, and then, because h is independent of the model, we can use relation [3.99] to deduce the following from those functions:

$$h(N_\mathrm{A}, N_\mathrm{B}) = \frac{g_a}{g_{a\mathrm{A}} g_{a\mathrm{B}}} \qquad [3.102]$$

Then, we move on to the second phase, searching for the so-called 1st-order approximation or Guggenheim's quasi-chemical approximation, characterized by the relation:

$$g\ (a,b,...)\exp\left(-\frac{U^{mix}(a,b,...)}{\mathrm{R}T}\right)=g_{\mathrm{A}}(a,b,...)g_{\mathrm{B}}(a,b,...) \qquad [3.103]$$

Now we shall cancel out the derivatives:

$$\frac{\partial \ln g}{\partial a_k}-\frac{U^{mix}(a,b,...)}{\mathrm{R}T}=\frac{\partial \ln g_{\mathrm{A}}}{\partial a_k}+\frac{\partial \ln g_{\mathrm{B}}}{\partial a_k}=0 \qquad [3.104a]$$

$$\frac{\partial \ln g}{\partial b_k}-\frac{U^{mix}(a,b,...)}{\mathrm{R}T}=\frac{\partial \ln g_{\mathrm{A}}}{\partial b_k}+\frac{\partial \ln g_{\mathrm{B}}}{\partial b_k}=0 \qquad [3.104b]$$

We deduce the functions $a(N_{\mathrm{A}},N_{\mathrm{B}})$ and $b(N_{\mathrm{A}},N_{\mathrm{B}})$, which enables us to calculate the functions $g_{\mathrm{A}}(N_{\mathrm{A}},N_{\mathrm{B}})$ and $g_{\mathrm{B}}(N_{\mathrm{A}},N_{\mathrm{B}})$, and then by using expression [3.99], we can calculate the function $g(N_{\mathrm{A}},N_{\mathrm{B}})$, which is the approximate solution to our problem.

If the solution has more than two components, we write as many relations akin to [3.99] as there are pairs of components. For example, for a solution with three components, we shall have the following three equilibria:

Pair A-A + Pair B-B = Pair A-B
Pair A-A + Pair C-C = Pair A-C
Pair B-B + Pair C-C = Pair B-C

Hence, for N components, we would have $N(N\text{-}1)/2$ equilibrium states.

Thus, the quasi-chemical method offers an approximate solution whose validity has been proven by Chang, with some extremely arduous work.

3.4. Difference of the molar volumes: the combination term

In the models discussed hitherto, we have always assumed that the molar volumes of the two components of the solution were very similar, so that the imperfection of the solution was attributed solely to interactions between the molecules. This hypothesis, though, is clearly not true in all cases – particularly in solutions of a polymer in a solvent – e.g. a solution of polystyrene in acetone, where the difference between the molar volumes is very significant: acetone has a molar volume of 73 cm^3/mole, whilst that of polystyrene is, on average, 3333 cm^3/mole. In order to take account of this fact, we introduce the concept of combinatorial excess entropy, which is linked to the distributions of the molecules in the space.

3.4.1. *Combinatorial excess entropy*

Flory and Huggins, simultaneously but independently of one another, constructed a term representing the excess entropy known as the *conformation term* or the *combinatorial excess entropy*. We shall now present their reasoning process for a mixture of small molecules, of a solvent A, and large one-dimensional molecules making up the solute B. The hypothesis at the heart of the model is still the pseudo-lattice, whose mesh is defined as follows: the molecule of component A (the smallest molecules) determines the acceptable dimension on each site of the lattice – its base volume. The larger molecules of polymer (component B) are virtually divided into sequences of the same volume as the small molecule, so that the large molecule contains ν_s sequences such that ν_s is equal to the ratio of the molar volumes of the two pure components:

$$\nu_s = \frac{v_2^0}{v_1^0} \qquad [3.105]$$

A molecule of B occupies the ν_s sites of the pseudo-lattice. If the solution contains N_A molecules of component A (the solvent) and N_B molecules of component B (the polymer), the number of sites in the lattice is:

$$N_0 = N_A + \nu_s N_B \qquad [3.106]$$

NOTE 3.9.– Nothing in the reasoning process suggests that the sequence of polymer chosen must correspond to a unit of monomer. The choice of sequencing relates only to the volume of the molecule of solvent. The sequence of polymer chosen may contain more or less than a monomer unit.

We shall now construct the lattice in order to calculate the number of complexions Ω, i.e. the number of possibilities for placing N_A molecules of A and N_B molecules of B. Then, we shall use Boltzmann's formula [2.41] to calculate the corresponding entropy term.

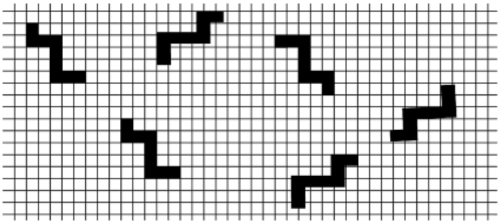

Figure 3.4. *Distribution of the molecules of solvent and polymer on the pseudo-lattice*

To construct the lattice in space, at each site, we place either a molecule of solvent or a sequence of a polymer chain, in the knowledge that those sequences are connected to one another. Figure 3.4 gives a 2D representation of the solution. Each grid square represents a site in the lattice which contains either a molecule of solvent A (in which case the square is white) or a sequence of the solute B (in which case the square is black).

Each site is surrounded by z adjacent neighbors (z is the coordination number of the lattice). If we examine the closest neighboring sites of a sequence of polymer, there are two sites which must, inevitably, contain another sequence (if we discount the ends of the chains, of which there are very few, in relative terms). Hence, there are only z-2 neighboring sites that can be occupied by molecules of solvent A, and therefore able to interact in the mixture (interaction between sequences of polymer of two different chains also takes place in the pure polymer, and is not included in the mixing value). We suppose that the molecules of A and B are randomly distributed. Note that the entropic term of local composition which we encountered above is not brought into play; instead we restrict ourselves just to the combinatorial term. Thus, we have only one term of the excess Gibbs energy due to the distribution imposed by the volumes.

We shall break down the number of possibilities of placing N_B molecules of polymer on $\nu_s N_B$ sites in a lattice containing N_0 sites. The remaining sites, obviously, are occupied by the N_A molecules of solvent.

Suppose that we have already put i molecules of polymer in place on the lattice. Let Ω_{i+1} be the number of possibilities to place the $(i+1)^{\text{th}}$ molecule of polymer. We can calculate Ω_{i+1} by considering each of its segments, one by one. Because the first i molecules are occupying $i\nu_s$ sites, there are $N_0 - i\nu_s$ places to put the first segment in place. The probability of a site closely neighboring this first segment being free is:

$$p_0 = \frac{\left(N_0 - i\nu_s - 1\right)}{N_0} \cong \frac{\left(N_0 - i\nu_s\right)}{N_0} \qquad [3.107]$$

Because there are z sites neighboring this first segment, on average there are pz possibilities to place the second segment. That second segment has z-1 free neighboring sites, and the probability of those z-1 sites being vacant is:

$$p_1 = \frac{\left(N_0 - i\nu_s - 2\right)}{N_0} \cong \frac{\left(N_0 - i\nu_s\right)}{N_0} \cong p_0 \qquad [3.108]$$

Hence, the number of possibilities to place the third segment is $p_0(z-1)$. By the same reasoning, the same probability p_0 that the neighboring sites will be occupied is valid for the addition of any segment, provided we have:

$$N_0 >> \nu_s \qquad [3.109]$$

Thus, the number of possibilities of placing the ν_s segments of the $(i+1)^{\text{th}}$ polymer molecule on the lattice is:

$$\Omega_{i+1} = \left(N_0 - i\nu_s\right) p_0^{\nu_s - 1} z(z-1)^{\nu_s - 2} \qquad [3.110]$$

If z is not too small and ν_s is sufficiently large, we can replace $z(z-1)^{\nu_s - 2}$ with $(z-1)^{\nu_s - 1}$. By doing so, we obtain:

$$\Omega_{i+1} = \left(N_0 - i\nu_s\right) p_0^{\nu_s - 1} z(z-1)^{\nu_s - 1} \qquad [3.111]$$

In light of expression [3.107] for p_0, this gives us:

$$\Omega_{i+1} \cong \left(N_0 - i\nu_s\right)^{\nu_s} (\frac{z-1}{N_0})^{\nu_s - 1} \qquad [3.112]$$

noting that with the condition [3.109], we can write:

$$\begin{gathered} \frac{\left(N_0 - i\nu_s\right)!}{\left[N_0 - (i+1\nu_s)\right]!} = \\ \left(N_0 - i\nu_s\right)\left(N_0 - i\nu_s - 1\right)\ldots\left(N_0 - (i+1)\nu_s + 1\right) \cong \left(N_0 - i\nu_s\right)^{\nu_s} \end{gathered} \qquad [3.113]$$

By substituting this back into equation [3.112], we find:

$$\Omega_{i+1} \cong \frac{\left(N_0 - i\nu_s\right)!}{\left[N_0 - (i+1)\nu_s\right]!}(\frac{z-1}{N_0})^{\nu_s - 1} \qquad [3.114]$$

This can also be written as:

$$\Omega_{i+1} \cong \frac{\left[N_0 - (i-1)\nu_s\right]!}{\left(N_0 - i\nu_s\right)!}(\frac{z-1}{N_0})^{\nu_s - 1} \qquad [3.115]$$

However, the number of complexions or number of possibilities of placing the N_{B} molecules of polymer will be such that:

$$\Omega = \frac{1}{N_{\mathrm{B}}!}\prod_{i=1}^{N}\Omega_{i+1} \qquad [3.116]$$

The division by $N_{\mathrm{B}}!$ stems from the indiscernibility of the molecules of polymer.

If we feed expression [3.115] back into relation [3.116], we can separate the product into two groups in the form:

$$\Omega \cong \left[\frac{1}{N_{\mathrm{B}}!}\left(\frac{z-1}{N_0}\right)^{N_{\mathrm{B}}\left(\nu_s - 1\right)}\right]\left[\prod_{i=1}^{N_{\mathrm{B}}}\frac{\left[N_0 - (i-1)\nu_s\right]!}{\left(N_0 - i\nu_s\right)!}\right] \qquad [3.117]$$

We can show that the second factor in the above relation can be written as:

$$\prod_{i=1}^{N_\mathrm{B}} \frac{\left[N_0-(i-1)\nu_s\right]!}{\left(N_0-i\nu_s\right)!}=\frac{N_0!}{\left(N_0-N_\mathrm{B}\nu_s\right)!} \qquad [3.118]$$

Thus, the number of complexions will be:

$$\Omega \cong \frac{\left(N_\mathrm{A}+N_\mathrm{B}\nu_s\right)!}{N_\mathrm{A}!N_\mathrm{B}!}\left(\frac{z-1}{N_\mathrm{A}+N_\mathrm{B}\nu_s}\right)^{N_\mathrm{B}\left(\nu_s-1\right)} \qquad [3.119]$$

By switching to logarithms and applying Stirling's approximation, we find:

$$\begin{aligned}\ln\Omega &\cong N_\mathrm{A}\ln\frac{N_\mathrm{A}+N_\mathrm{B}\nu_s}{N_1}+N_2\ln\frac{N_\mathrm{A}+N_\mathrm{B}\nu_s}{N_2}\\ &+N_\mathrm{B}\left(\nu_s-1\right)\left[\ln(z-1)-1\right]\end{aligned} \qquad [3.120]$$

Thus, if we substitute equation [3.120] back into Boltzmann's relation, we find the entropy term of conformation:

$$S^{(C)} \cong \mathrm{R}\left\{\begin{aligned}&n_\mathrm{A}\ln\frac{N_\mathrm{A}+N_\mathrm{B}\nu_s}{N_\mathrm{A}}+n_2\ln\frac{N_\mathrm{A}+N_\mathrm{B}\nu_s}{N_\mathrm{B}}\\ &+n_\mathrm{B}\left(\nu_s-1\right)\left[\ln(z-1)-1\right]\end{aligned}\right\} \qquad [3.121]$$

If we denote the volumic fraction of component i as:

$$\Phi_i=\frac{N_i}{N_\mathrm{A}+N_\mathrm{B}\nu_s} \qquad [3.122a]$$

the conformation entropy can be written as:

$$S^{(C)} \cong -\mathrm{R}\left\{n_\mathrm{A}\ln\Phi_\mathrm{A}+n_\mathrm{B}\ln\Phi_\mathrm{B}-n_\mathrm{B}\left(\nu_s-1\right)\left[\ln(z-1)-1\right]\right\} \qquad [3.122b]$$

However, the conformation entropy of the pure solvent on the lattice is zero (there is only one configuration with one molecule per site), and that of the polymer is given by relation [3.121] with $N_\mathrm{A} = 0$ – i.e.:

$$S_p \cong \mathrm{R}n_\mathrm{B}\left\{\ln \nu_s + (\nu_s - 1)[\ln(z-1) - 1]\right\} \qquad [3.123]$$

Thus, the conformation entropy of mixing of the solution is:

$$S^{mix(C)} = S^{(C)} - S_p \cong -\mathrm{R}\left\{n_\mathrm{A} \ln \Phi_\mathrm{A} + n_\mathrm{B} \ln \Phi_\mathrm{B}\right\} \qquad [3.124]$$

If we subtract the entropy of mixing from the perfect solution given by relation [A.2.10], we obtain the following for the molar excess conformation entropy:

$$S_m^{xs(C)} \cong -\mathrm{R}\left\{x_\mathrm{A} \ln \frac{\Phi_\mathrm{A}}{x_\mathrm{A}} + x_\mathrm{B} \ln \frac{\Phi_\mathrm{B}}{x_\mathrm{B}}\right\} \qquad [3.125]$$

We use this expression for a model of an athermic solution, defined in Chapter 2 (see section 2.6).

3.4.2. *Flory's athermic solution model*

Flory's model applies to an athermic solution, meaning that the excess molar enthalpy is null, so the excess molar Gibbs energy is simply written as follows, in light of relation [3.125]:

$$G_m^{xs} = -TS_m^{xs} = \mathrm{RT}\left\{x_\mathrm{A} \ln \frac{\Phi_\mathrm{A}}{x_\mathrm{A}} + x_\mathrm{B} \ln \frac{\Phi_\mathrm{B}}{x_\mathrm{B}}\right\} \qquad [3.126]$$

For a binary solution, we use the excess partial molar Gibbs energy to deduce the activity coefficient of a component *i*:

$$\ln \gamma_i^{(I)} = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i} = \ln \frac{v_i^0}{V_m} + 1 - \frac{v_i^0}{V_m} \qquad [3.127]$$

ν_s	$\gamma_A^{\infty(I)}$	$\gamma_B^{\infty(I)}$
10	0.245	0.0012
100	2.7×10^{-2}	10^{-40}
1000	2.7×10^{-3}	10^{-430}

Table 3.1. *Values of activity coefficients with infinite dilution of a polymer (B) in a solvent (A) as a function of the "length" ν_s of that polymer*

In particular, at infinite dilution, we obtain the activity coefficient of each of the two components of a binary by making $n_B = 0$ for that of component A and $n_A = 0$ for that of component B. This gives us:

$$\ln\gamma_A^{\infty(I)} = \ln\frac{v_1^0}{v_2^0} + 1 - \frac{v_1^0}{v_2^0} = \ln\frac{1}{v_s} + 1 - \frac{1}{v_s} \quad [3.128]$$

$$\ln\gamma_B^{\infty(I)} = \ln\frac{v_2^0}{v_1^0} + 1 - \frac{v_2^0}{v_1^0} = \ln v_s + 1 - v_s \quad [3.129]$$

In this model, we have not taken account of the energetic interactions between the molecules. For precisely this reason, such as model is well suited for solutions of polymers, as the intermolecular energy values are very low indeed in these solutions. Table 3.1 shows that the deviation from ideal state grows very rapidly as the "polymer chain length" ν_s increases.

3.4.3. *Staverman's corrective factor*

In the above model, we chose linear polymer molecules and molecules of solvent which are much smaller than those of the polymer, so that every part of the polymer was in the vicinity of molecules of solvent.

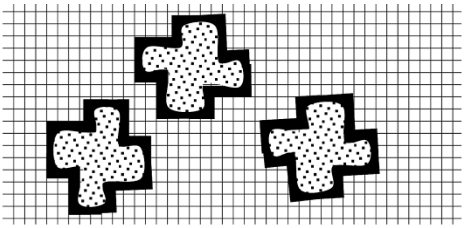

Figure 3.5. *Exclusion of sites available for the solvent due to the closure of the polymer molecule*

Staverman examined the problem of representing a solution in which the molecules are no longer linear, and therefore a certain amount of the molecule would not be exposed to the molecules of solvent, because they would be isolated inside the molecule of solute. These imprisoned sites receive no molecules of solvent. Figure 3.5 gives a 2D representation of the exclusion of certain sites (shaded) which are no longer able to receive molecules of solvent as near neighbors. This introduces a corrective factor relating to the surface of the molecule.

3.4.3.1. *The concept of structural parameters*

We shall now introduce two fundamental parameters of the molecules which are used in the models of molecular solutions discussed below. These two parameters are:

– the ratio of the van der Waals volume of the molecule to the van der Waals volume of a standard molecule or segment:

$$r_i = \frac{V_{w(i)}}{V_{w(st)}} \qquad [3.130]$$

– the ratio of the area of the molecule to the area of a standard molecule or segment:

$$q_i = \frac{\Sigma_{w(i)}}{\Sigma_{w(st)}} \qquad [3.131]$$

The choice of standard is arbitrary. Frequently, we use the Abrams and Prausnitz standard [ABR 95]: a linear molecule of polyethylene of infinite length, which conforms to the following equation:

$$r_{st} - 1 = \frac{z}{2}\left(r_{st} - q_{st}\right) \quad \text{where } z = 10 \qquad [3.132]$$

This gives us:

$$V_{w(st)} = 15.17\ \text{cm}^3/\text{mole} \ \text{ and } \ \Sigma_{w(st)} = 2.5\times10^9\ \text{cm}^2/\text{mole} \qquad [3.133]$$

Thus, the structural parameters are calculated on the basis of the two relations:

$$r_i = V_{w(i)} / 15{,}17 \text{ and } q_i = \Sigma_{w(i)} / 2.5 \times 10^9 \qquad [3.134]$$

Table 3.2 gives the values of the structural parameters of a several molecules, calculated by Abrams and Prausnitz on the basis of the van der Waals volumes and the areas published by Bondi in 1968.

Based on the structural parameters, we define:

– the volumic fraction of a component *i* by:

$$\Phi_i = \frac{N_i r_i}{\sum_{i=1}^{N} N_i r_i} = \frac{x_i r_i}{\sum_{i=1}^{N} x_i r_i} \qquad [3.135]$$

– the areic fraction of a component *i* by:

$$\theta_i = \frac{N_i q_i}{\sum_{i=1}^{N} N_i q_i} = \frac{x_i q_i}{\sum_{i=1}^{N} x_i q_i} \qquad [3.136]$$

Fluid	r_i	q_i
Water	0.92	1.40
Carbon dioxide	1.30	1.12
Ethane	1.80	1.70
Benzene	3.19	2.40
Toluene	3.87	2.93
Aniline	3.72	2.83
n-Octane	5.84	4.93
Acetone	2.57	2 .34
Dimethylamine	2.33	2.09
Acetaldehyde	1.90	1.80
Polyethylene	$0.67\nu_s$	$0.54\nu_s$

Table 3.2. *Values of the structural parameters for various molecules*

3.4.3.2. *Staverman's model*

Staverman uses Flory's model as a starting point, but introduces a form factor in the number of complexions, taking account of the fact that the molecules are only in contact at their surfaces. This enables him to construct a new expression for number of possibilities of introducing the molecule of polymer and the molecules of solvent. Thus, the excess molar entropy term of conformation is altered, and becomes:

$$S_m^{xs(C)} \cong -\mathrm{R}\left\{\sum_{i=1}^{N} x_i \ln\frac{\Phi_i}{x_i} + \frac{z}{2}\sum q_i x_i \ln\frac{\theta_i}{\Phi_i}\right\} \qquad [3.137]$$

We can see that the form factor is illustrated by the ratio θ_i / Φ_i.

Using the concepts which we have introduced, we shall now present one of the most popular models of solution: the UNIQUAC model.

3.5. Combination of the different concepts: the UNIQUAC model

The UNIQUAC (Universal Quasi-Chemical) model was introduced by Abrams and Prausnitz (1975), using Guggenheim's quasi-chemical model and applying the concepts of conformation with Staverman's relation and Wilson's local-composition model.

This model, which yields excellent results for polar and non-polar molecular liquids, is especially well suited for the study of liquid/ vapor equilibrium and the equilibrium between two liquids that are not completely miscible. Regardless of the number of components of the solution, the application of this model only requires the knowledge of two adjustment parameters per binary system, which can be deduced from the solution. The model is so widely applicable that it actually contains a number of previously classic models such as the models put forward by Van Laar, Wilson, Renon *et al.* (the NRTL – Non Random Two Liquids – model), Scatchard and Hildebrand, Flory and Huggins as special cases. In addition, it lends a physical meaning to the first three coefficients β_i, δ_i and ε_i in the Margules expansion (equation [2.1]).

The model is founded on the following hypotheses:

– we accept the existence of a pseudo-lattice in space, which occupies the whole of the volume. The vacancies in the liquid will not be taken into consideration, either in the pure liquids or in the solution;

– the coordination number of the lattice is the same around an element of A as it is around an element of B, and it is also the same as in each of the pure liquids of which the solution is composed. Thus, for example, for a binary solution, we would have:

$$z_{\mathrm{A}} = z_{\mathrm{B}} = z'_{\mathrm{A}} = z'_{\mathrm{B}} \qquad [3.138]$$

– the interacting elements chosen are segments of the surface of each molecule. Each molecule may present different surface elements;

– the fragments of components are chosen in such a way that their dimensions, volume and surface area are practically the same. As we saw above that vacancies are not taken into account, this means that the mixing volume is null, and therefore that we can treat the internal energy and enthalpy of mixing as one and the same thing, and do likewise for the Helmholtz energy and the Gibbs energy of mixing;

– although the interacting surface elements may be different in nature from one point in the solution to another, we shall make the hypothesis that the energies of interaction are mean values, which depend only on the origin of the elements. Thus, for instance, for a binary system, we would have the energy $\varepsilon_{\mathrm{BA}} = \varepsilon_{\mathrm{AB}}$ between two surface elements, one of which belongs to the molecule of component A and the other to the molecule of component B, $\varepsilon_{\mathrm{AA}}$ between two elements belonging to two molecules of component A and $\varepsilon_{\mathrm{BB}}$ between two elements belonging to two molecules of component B.

The states will be characterized by the local areic fractions:

θ_{AA} denotes the surface fraction of surface elements derived from A around a surface element derived from A. We can immediately deduce the mean of the other symbols: θ_{BB}, θ_{AB} and θ_{BA}. Of course, the balance around any surface element gives us:

$$\theta_{\mathrm{AA}} + \theta_{\mathrm{BA}} = 1 \qquad [3.139]$$

$$\theta_{\text{BB}} + \theta_{\text{AB}} = 1 \tag{3.140}$$

Thus, as configuration variables, we can choose a value belonging to each of the two pairs θ_{AA} or θ_{BA}, on the one hand, and θ_{BB} or θ_{AB} on the other.

In light of our last hypothesis concerning the energies of interaction, the internal energy of mixing will be given by the expression:

$$\begin{gathered} U^{mix} - U_0^{mix} = -\frac{z}{2} q_{\text{A}} N_{\text{A}} \left(\theta_{\text{AA}} \varepsilon_{\text{AA}} + \theta_{\text{BA}} \varepsilon_{\text{BA}}\right) \\ -\frac{z}{2} q_{\text{B}} N_{\text{B}} \left(\theta_{\text{BB}} \varepsilon_{\text{BB}} + \theta_{\text{AB}} \varepsilon_{\text{AB}}\right) \end{gathered} \tag{3.141}$$

For the sake of ease, we shall set:

$$u_{ij} = \frac{z}{2} \varepsilon_{ij} = u_{ji} \tag{3.142}$$

This gives us the following expression for the internal energy of mixing:

$$\begin{gathered} U^{mix} - U_0 = -q_{\text{A}} N_{\text{A}} \left(\theta_{\text{AA}} u_{\text{AA}} + \theta_{\text{BA}} u_{\text{BA}}\right) \\ -q_{\text{B}} N_{\text{B}} \left(\theta_{\text{BB}} u_{\text{BB}} + \theta_{\text{AB}} u_{\text{AB}}\right) \end{gathered} \tag{3.143}$$

We shall express the canonical partition function of mixing by using Guggenheim's quasi-chemical method (see section 3.3), applied with Staverman's athermic model as a reference, where the excess entropy is given by relation [3.137].

In Staverman's model, the statistical weights of the homogeneous elements g_1^* and g_2^* are given by:

$$g_1^* = \frac{\left(q_1 N_1 \theta_{11} + q_2 N_2 \theta_{12}\right)!}{\left(q_1 N_1 \theta_{11}\right)! \left(q_1 N_1 \theta_{21}\right)!} \tag{3.144}$$

$$g_2^* = \frac{\left(q_2 N_2 \theta_{22} + q_1 N_1 \theta_{21}\right)!}{\left(q_2 N_2 \theta_{22}\right)! \left(q_2 N_2 \theta_{12}\right)\ !} \tag{3.145}$$

With the zero-order approximation, calculation leads us to:

$$\theta_{\mathrm{AA}}^{(0)} = \frac{q_{\mathrm{A}} N_{\mathrm{A}}}{q_{\mathrm{A}} N_{\mathrm{A}} + q_{\mathrm{B}} N_{\mathrm{B}}} = \theta_{\mathrm{AB}}^{(0)} = \theta_{\mathrm{A}} \qquad [3.146]$$

$$\theta_{\mathrm{BA}}^{(0)} = \frac{q_{\mathrm{B}} N_{\mathrm{B}}}{q_{\mathrm{A}} N_{\mathrm{A}} + q_{\mathrm{B}} N_{\mathrm{B}}} = \theta_{\mathrm{BB}}^{(0)} = \theta_{\mathrm{B}} \qquad [3.147]$$

θ_i is the areic fraction of the molecule *i*. It is given by relation [3.136].

The application of the 1st-order approximation yields:

$$\theta_{\mathrm{AA}} = \frac{\theta_{\mathrm{A}}}{\theta_{\mathrm{A}} + \theta_{\mathrm{B}} \exp\left(-\frac{u_{\mathrm{BA}} - u_{\mathrm{AA}}}{\mathrm{R}T}\right)} \qquad [3.148]$$

$$\theta_{\mathrm{BB}} = \frac{\theta_{\mathrm{B}}}{\theta_{\mathrm{B}} + \theta_{\mathrm{A}} \exp\left(-\frac{u_{\mathrm{AB}} - u_{\mathrm{BB}}}{\mathrm{R}T}\right)} \qquad [3.149]$$

After calculating the partition function using relation [3.97], we deduce the excess molar Gibbs energy using the relation:

$$G_m^{xs} \cong F_m^{xs} = -\frac{\mathrm{R}T \ln Z}{n_{\mathrm{A}}} \qquad [3.150]$$

We can see that this molar Gibbs energy can be expressed as the sum of two terms:

$$G_m^{xs} = G_m^{xs(\mathrm{Com})} + G_m^{xs(\mathrm{Res})} \qquad [3.151]$$

One of them, $G_m^{xs(\mathrm{Com})}$, is drawn from Staverman's athermic solution, from which it draws its name – the *conformation term*:

$$G_m^{xs(\mathrm{Com})} = \mathrm{R}T \left[\begin{array}{l} x_{\mathrm{A}} \ln \frac{\Phi_{\mathrm{A}}}{x_{\mathrm{A}}} + x_{\mathrm{B}} \ln \frac{\Phi_{\mathrm{B}}}{x_{\mathrm{B}}} \\ + \frac{z}{2} \left(q_{\mathrm{A}} x_{\mathrm{A}} \ln \frac{\theta_{\mathrm{A}}}{\Phi_{\mathrm{A}}} + q_{\mathrm{B}} x_{\mathrm{B}} \ln \frac{\theta_{\mathrm{B}}}{\Phi_{\mathrm{B}}} \right) \end{array} \right] \qquad [3.152]$$

The other term, $G_m^{xs(\mathrm{Res})}$, is called the *residual term*. Its value is:

$$G_m^{xs(\mathrm{Res})} = \mathrm{R}T\left[-q_\mathrm{A} x_\mathrm{A} \ln\left(\theta_\mathrm{A} + \theta_\mathrm{B}\tau_\mathrm{BA}\right) - q_\mathrm{B} x_\mathrm{B} \ln\left(\theta_\mathrm{B} + \theta_1 \tau_\mathrm{AB}\right)\right] \qquad [3.153]$$

In this latter expression, the different symbols have the following meanings:

$$\tau_\mathrm{BA} = \exp\left(-\frac{u_\mathrm{BA} - u_\mathrm{AA}}{\mathrm{R}T}\right) = \exp\left(-\frac{a_\mathrm{BA}}{T}\right) \qquad [3.154a]$$

$$\tau_\mathrm{AB} = \exp\left(-\frac{u_\mathrm{AB} - u_\mathrm{BB}}{\mathrm{R}T}\right) = \exp\left(-\frac{a_\mathrm{AB}}{T}\right) \qquad [3.154b]$$

Φ_i is given by relation [3.122], which can be written in the form:

$$\Phi_i = \frac{x_i r_i}{\sum_{j=1}^{N} x_j r_j} \qquad [3.155]$$

We can easily calculate the activity coefficients for the components of a binary solution:

$$\begin{aligned} \ln \gamma_\mathrm{A}^{(I)} &= \ln \frac{\Phi_\mathrm{A}}{x_\mathrm{A}} + \frac{z}{2} q_\mathrm{A} \ln \frac{\theta_\mathrm{A}}{\Phi_\mathrm{A}} + \Phi_\mathrm{B}\left(l_\mathrm{A} - \frac{r_\mathrm{A}}{r_\mathrm{B}} l_\mathrm{B}\right) \\ &- q_\mathrm{A} \ln\left(\theta_\mathrm{A} + \theta_\mathrm{B}\tau_\mathrm{BA}\right) \\ &+ \theta_\mathrm{B} q_\mathrm{A}\left(\frac{\tau_\mathrm{BA}}{\theta_\mathrm{A} + \theta_\mathrm{B}\tau_\mathrm{BA}} - \frac{\tau_\mathrm{AB}}{\theta_\mathrm{B} + \theta_\mathrm{A}\tau_\mathrm{AB}}\right) \end{aligned} \qquad [3.156]$$

where:

$$l_i = \frac{z}{2}\left(r_i - q_i\right) - \left(r_i - 1\right) \qquad [3.157]$$

with a symmetrical expression for component B.

In the view of the model's developers, any value of the coordination number z between 6 and 12 has practically no impact on the results. Thus, they chose the value:

$$z = 10 \qquad [3.158]$$

For a solution with N components, the above results can be extrapolated, and we obtain the following results:

$$G_m^{xs(\text{Com})} = \text{R}T\left[\sum_{i=1}^{N} x_1 \ln\frac{\Phi_i}{x_i} + \frac{z}{2}\left(\sum_{i=1}^{N} q_i x_i \ln\frac{\theta_i}{\Phi_i}\right)\right] \qquad [3.159]$$

$$G_m^{xs(\text{Res})} = \text{R}T\left[-\sum_{i=1}^{N} q_i x_i \ln\sum_{j=1}^{N} \theta_j \tau_{ji}\right] \qquad [3.160]$$

$$\tau_{ji} = \exp\left(-\frac{u_{ji} - uii}{\text{R}T}\right) = \exp\left(-\frac{a_{ji}}{T}\right) \qquad [3.161]$$

The activity coefficients of each of the components are also divided into a conformation term and a residual term, and we have:

$$\ln \gamma_i^{(I)(\text{Com})} = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_{j=1}^{N} x_j l_j \qquad [3.162]$$

$$\ln \gamma_i^{(I)(\text{Rés})} = q_i \ln\left(1 - \sum_{j=1}^{N} \theta_j \tau_{ji} - \sum_{j=1}^{N} \frac{\theta_j \tau_{ji}}{\sum_{k=1}^{N} \theta_k \tau_{kj}}\right) \qquad [3.163]$$

$$\ln \gamma_i^{(I)} = \ln \gamma_i^{(I)(\text{Com})} + \ln \gamma_i^{(I)(\text{Res})} \qquad [3.164]$$

We can see that the UNIQUAC model requires only two adjustable parameters for each pair of components: the differences: $u_{ij} - u_{jj}$ and $u_{ji} - u_{ii}$ (or a_{ij} and a_{ji}). However, we shall take the precaution of not involving too many parameters. For a system with N components, there are only

$N(N-1)/2$ binary systems and therefore the same number of pairs of adjustable parameters.

Name of model	Approximations about equation [3.152]	Approximations about equation [3.153]
Flory–Huggins athermic model	$q_1 = r_1$ and $q_2 = r_2$	$u_{21} = u_{11}$ and $u_{12} = u_{22}$
Wilson 2-parameter model	$q_1 = r_1$ and $q_2 = r_2$	$q_1 = q_2 = 1$
NRTL model	$G_m^{xs(\mathrm{Com})} = 0$	$(q_1)^{-1} = (q_2)^{-1} = \alpha_{12}$
Van Laar's model	$G_m^{xs(\mathrm{Com})} = 0$	Expansion of $(\Delta u / \mathrm{R}T)$, limited to the 3rd term
Scatchard–Hildebrand model	$G_m^{xs(\mathrm{Com})} = 0$	Expansion of $(\Delta u / \mathrm{R}T)$ limited to the 3rd term
Margulès 3-term model	$G_m^{xs(\mathrm{Com})} = 0$	Expansion of $(\Delta u / \mathrm{R}T)$ limited to the 4th term
Flory–Huggins non-athermic model	$q_1 = r_1$ and $q_2 = r_2$	Expansion of $(\Delta u / \mathrm{R}T)$ limited to the linear term

Table 3.3. *Particular models of solutions included in the UNIQUAC model*

The model's creators showed that a certain number of classic models of solutions published previously were actually included in the UNIQUAC model, as they appear to be particular cases. By way of certain approximations performed on equations [3.152], [3.153] and [3.154], we obtain the expressions of the excess molar Gibbs energy for these different models. Table 3.3 lists some of these simplifications.

3.6. The concept of contribution of groups: the UNIFAC model

The UNIQUAC method requires complete calculation in each specific case. Now, though, we are going to examine the concept of the contribution of groups, which can be used to calculate certain properties of the molecules *a priori*, using relatively small databases, and the application to a model to calculate the excess Gibbs energy *a priori*.

3.6.1. *The concept of the contribution of groups*

The concept of the contribution of groups is based on the idea of additivity. Some of the properties of a molecule can be expressed by a weighted linear combination of the contributions of the groups of atoms making up the molecule.

Thus, for example, we can calculate the values of the parameters r_i and q_i of the volumic fraction and areic fraction of a molecule, as being the weighted combined of values of those same properties attributed to groups of atoms. Thus, for the volumic fraction parameter r_i, we would write:

$$r_i = \sum_k \nu_k^{(i)} R_k \qquad [3.165]$$

$\nu_k^{(i)}$ is the number of groups of nature *k* present in the molecule *i*, and R_k is the parameter of the volumic fraction attributed to group *k* (defined on the basis of equation [3.134], as was the case for molecules). The sum is extended to all the groups of which the molecule is composed.

Similarly, for the parameter of the areic fraction q_i, we shall have:

$$q_i = \sum \nu_k^{(i)} Q_k \qquad [3.166a]$$

To do this, we have divided the molecules into groups of atoms, which are, themselves, divided into subgroups. Each subgroup is assigned a value R_k and a value Q_k. Table 3.4 gives the contributions of a number of groups. Each first term of an organic series constitutes a group.

The values calculated by relations [3.165] and [3.166] can be used in the UNIQUAC model (see section 3.5) if the molecular values are not available.

3.6.2. *The UNIFAC model*

Models known as group models have been created, based on the following observation: the number of systems – even just the number of binary systems – is extremely high, and new ones are being discovered all the time; meanwhile, the number of functional groups of which these molecules are composed is far less.

Group	Subgroup	R_k	Q_k
CH_3	CH_3	0.9011	0.8480
	CH_2	0.6744	0.5400
	CH	0.4469	0.2281
	C	0.2195	0
C=C	CH_2=CH	1.3454	1.1760
	CH=CH	1.1167	0.8670
	CH_2=C	1.1173	0.9880
	CH=C	0.8886	0.6760
	C=C	0.6605	0.4850
ACH	ACH	0.5313	0.4000
	AC	0.3652	0.1200
OH	OH	1.0000	1.2000
CH_3OH	CH_3OH	1.4311	1.4320
ACOH	ACOH	0.8952	0.6800
CH_2CO	CH_3CO	1.6724	1.4880
	CH_2CO	1.4457	1.1800
CHO	CHO	0.9980	0.9480
COOH	COOH	1.013	1.2240

Table 3.4. *Functional groups and subgroups and structural parameters for the UNIFAC model ("AC" represents a carbon belonging to an aromatic ring)*

The UNIFAC model (UNIQUAC Functional Group Activity Coefficient), which was put forward by Fredenslund, Jones and Prausnitz in 1975, is a group model where the idea is to use the existing data on equilibrium states to predict the properties of systems for which no experimental data are available. Thus, it is an entirely predictive model which, unlike the models discussed above, does not require us to determine parameters by calibrating the experimental results found for partial systems (in contrast to the UNIQUAC model, which requires the data from binary systems in order to deduce the properties of more complex systems).

The group-model method requires us to work back from experimental results to determine parameters which are characteristic of the interactions between pairs of structural groups, and then inject that knowledge back into models to obtain the properties of new systems containing those same structural groups.

The idea underlying the UNIFAC model is the consideration that a solution of molecules *i*, *j*, etc. behaves like a solution of the functional groups *k*, *m*, etc. making up those molecules.

For example, a mixture of linear alkane molecules involves three types of interactions: CH_3–CH_3, CH_3–CH_2 and CH_2–CH_2. The properties of any given mixture of alkanes must be able to be deduced from the properties linked to the three types of interactions at play. Of course, this whole construct is founded on a hypothesis which stipulates that the interactions between groups do not depend on the environment of these groups in their respective molecules. Yet, indubitably, it is this hypothesis which is the main source of errors that become apparent when the calculation results are contrasted with experimental data. For example, we can see that, in a complex system, the results given by the wholesale use of UNIFAC are much poorer than those given by the use of the UNIQUAC model. For this reason, the UNIFAC model is not used wholesale to model a complex system; instead, essentially, it is used to obtain the necessary data on binary systems for which no experimental data are available. These data are then fed back into a UNIQUAC-type model (see section 3.5).

Thus, we shall apply the UNIQUAC model to this solution of functional groups.

From this, we deduce that the activity coefficient for a component *i* obeys relation [3.164], meaning that its logarithm will be the sum of two contributions – one conformation contribution, pertaining to the entropy, due to the arrangement of the molecules within the volume, and the other residual, relating to the enthalpy and due to the different interactions between pairs of molecules.

The conformation contribution is written by following relation [3.162] – indeed, the arrangement of functional groups obeys the same laws as that of entire molecules, in view of the unavoidable intramolecular bonds between the functional groups in the same molecule.

The residual contribution is obtained by considering a functional-group solution.

The values corresponding to the functional groups will be written with the same letter as the same value in a solution of molecules, but in uppercase. Thus, the coefficient of activity of the group *k* will be Γ_k, its volume parameter R_k, its surface parameter Q_k, its molar fraction X_k. In the energy exponential of relation [3.153], the letter τ would be replaced by Ψ_{km}, its surface fraction θ would be replaced by Θ_k. Only the term a in the equivalent relations [3.154] would retain the same notation, a_{km}. By transposition of relation [3.163] to the group solution, the residual activity coefficient Γ_k for a group *k* will be written as:

$$\mathrm{R}T \ln \Gamma_k = Q_k \left[1 - \ln \sum_k \Theta_k \Psi_{km} - \sum_k \frac{\Theta_k \Psi_{km}}{\sum_k \Theta_k \Psi_{km}} \right] \qquad [3.166b]$$

The different entities are defined, as before, for the groups this time by:

The surface fraction of the group *k*:

$$\Theta_k = \frac{X_k Q_k}{\sum_k X_k Q_k} \qquad [3.167]$$

The energy term between the groups *k* and *m*:

$$\Psi_{km} = \exp\left(-\frac{a_{km}}{T} \right) \qquad [3.168]$$

The molar fraction of the group *k*:

$$X_k = \frac{\sum_i \nu_k^{(i)} x_i}{\sum_i \sum_k \nu_k^{(i)} x_i} \qquad [3.169]$$

Of course, that same coefficient of residual activity of the group is, by definition:

$$\mathrm{R}T\ln\Gamma_k = \mu_k - \mu_k^0 \qquad [3.170]$$

In this expression, μ_k is the chemical potential of the group k in the group solution studied, and μ_k^0 is the chemical potential of component k in a hypothetical substance in which the component k is pure. Evidently, such a substance can neither be formulated nor conceived. However, we are able to conceive a pure solution of i, considered to be a solution of its groups, in which the group k has a chemical potential $\mu_k^{(i)}$ and we can write the following for the chemical potentials and the residual activity coefficients:

$$\mu_k - \mu_k^{(i)} = \left(\mu_k - \mu_k^0\right) - \left(\mu_k^{(i)} - \mu_k^0\right) = \mathrm{R}T\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \qquad [3.171]$$

$\Gamma_k^{(i)}$ is the coefficient of residual activity of the component k in a pure solution of “component” i.

In addition, the residual chemical potential of component i is given by the linear combination of the chemical potentials of the different groups, in accordance with:

$$\mu_i = \sum_k \nu_k^{(i)}\mu_k \qquad [3.172]$$

Similarly, for the pure solution of i:

$$g_i^0 = \sum_k \nu_k^{(i)}\mu_k^{(i)} \qquad [3.173]$$

This gives us the coefficient of residual activity of component i (using convention (I) – pure substance) in the solution at hand:

$$\mathrm{R}T\ln\gamma_i^{(\mathrm{Res})} = \mu_i - g_i^0 = \mathrm{R}T\sum_k \nu_k^{(i)}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \qquad [3.174]$$

The term $\ln\Gamma_k$ is calculated on the basis of relation [3.166]; the term $\ln\Gamma_k^{(i)}$ is also calculated on the basis of the same relation [3.166], but introducing the elements for pure i – in particular, the molar fraction of the group k is $X_k^{(i)}$ in the pure component i and is given by expression [3.169], making $x_i = 1$. This term is then fed back into relation [3.167] and the interactions to be taken into account in expression [3.166] exist only between groups belonging to the component i.

Groups	CH_2	ACH	$ACCH_2$	OH	CH_3OH	ACOH	CH_2CO	CHO	COOH
CH_2	0	61.13	76.5	986.5	697.2	0133.3	476.4	677	663.50
ACH	-11.12	0	167	636.1	637.3	1329	25.77	347.3	537.4
$ACCH_2$	-69.7	-146	0	803.2	603.3	884.9	-52.1	586.8	872.3
OH	156.4	89.6	25.82	0	-137.1	-259.7	84	-203.6	199
CH_3OH	16.51	-50	-44.5	249.1	0	-101.7	23.39	306.4	-202.0
ACOH	275.8	25.34	244.2	-451.6	-265.2	0	-356.1	-271.1	408.9
CH_2CO	26.76	140.1	365.8	164.5	108.7	-133.1	0	-37.36	669.4
CHO	505 .7	23.39	106.0	529	-340.2	-155.6	128	0	497.5
COOH	315.3	62.35	89.86	-151	339.80	-11.00	-297.8	-165.5	0

Table 3.5. *Energy interaction terms of groups, expressed in Kelvin*$^{-1}$
("AC" represents an aromatic carbon)

All of the activity coefficient of the component i in the solution, therefore, is given by relation [3.164], in which the terms are given by relations [3.162] (with [3.156]) and [3.173] (with [3.166]).

We can easily calculate the excess molar Gibbs energy and the excess molar enthalpy, using:

$$G_m^{xs} = \mathrm{R}T\left\{\sum_i\sum_k x_i \nu_k^{(i)}\left[\ln\Gamma_k - \ln\Gamma_k^{(i)}\right]\right\} \qquad [3.175]$$

$$H_m^{xs} = -\mathrm{R}T\left\{\sum_i\sum_k x_i \nu_k^{(i)}\left[T\left(\frac{\partial \ln\Gamma_k}{\partial T}\right)_{P,n} - T\left(\frac{\partial \ln\Gamma_k^{(i)}}{\partial T}\right)_{P,n}\right]\right\} \qquad [3.176]$$

The calculations are conducted using values of the structural parameters of the groups and the energy terms of pairs of groups a_{km}. The initial data, drawn from the study of numerous liquid/vapor and liquid/liquid equilibria, were provided by Gmehling in 1979. A few examples of structural parameters and energy terms a_{km} (in Kelvin^{-1}) between two groups k and m are listed in Tables 3.4 and 3.5 respectively.

3.6.3. *The modified UNIFAC model (Dortmund)*

The UNIFAC model discussed in the previous section does suffer from a number of shortcomings, particularly for values of the activity coefficients in infinite dilution, the enthalpies of mixing and the values obtained for highly-asymmetrical systems. In order to improve the data, adjustments were made in three directions (1987):

– a refinement of the functional groups, and therefore of their number. The UNIFAC Consortium (Dortmund Data Bank), a user group, now produces 92 groups instead of the 67 that were included in the first system. The result of this is that we are better able to take account of the groups' environments;

– an increase in the number of binary systems studied experimentally, with a view to refining the energy values;

– better integration of the variation of the results with temperature, by writing the energy parameter in the form:

$$a_{km} + b_{km}T + c_{km}T^2 \qquad [3.177]$$

Obviously, the consequence of this is the provision of four extra parameters per pair (b_{km}, c_{km}, b_{mk} and c_{mk}).

All of these improvements were brought together in the creation of a new model, called the Dortmund modified UNIFAC model, which is characterized, for each binary system, by four structural parameters and six energy parameters contained in a database.

The UNIFAC consortium also gives its subscribers a piece of software capable of calculating various thermodynamic values on the basis of the model and its database.

3.6.4. *Use of the UNIFAC system in the UNIQUAC model*

Although the UNIFAC model is totally predictive, it is rarely used for systems with more than two components because, as indicated above, the results given in such cases by the UNIQUAC model are often of better quality. On the other hand, UNIQUAC requires us to know two parameters per pair of components: the energy parameters, drawn from experimentation.

Occasionally, when using it, we do not have the necessary data for all the pairs that it is necessary to consider. Therefore, we use the UNIFAC model to provide the data corresponding to certain pairs for which we have no experimental data. It is then necessary to transfer parameters from the UNIFAC model to the UNIQUAC model. This is what we shall now examine.

Remember that the use of UNIQUAC requires parameters τ_{km} and τ_{mk}, which are at play in relation [3.153] – in fact, by relations [3.154a] and [3.154b], the energies a_{km} and a_{mk}. It should be noted that, in spite of the similitude of the notations, these values are not those that are given by the group data (e.g. in Table 3.5) which are group values, whereas those required by UNIQUAC are mean values per molecule. In order to switch from one to another, we proceed as follows.

For the binary system in question, we calculate the values of $\mathrm{R}T\ln\gamma_i^{(\mathrm{Res})}$ for each of the two components, on the basis of the UNIFAC system and relation [3.174], for different values θ_i, i.e. the composition of the binary solution defined by the quantities NA and NB of molecules of the two components and relation [3.136]. We then adjust the two curves $\mathrm{R}T\ln\gamma_{\mathrm{A}}^{(\mathrm{Res})}(\theta_{\mathrm{A}})$ and $\mathrm{R}T\ln\gamma_{\mathrm{B}}^{(\mathrm{Res})}(\theta_{\mathrm{B}})$ on the UNIQUAC model on the basis of relation [3.161] by choosing appropriate values τ_{AB} and τ_{BA}. These latter values, or the corresponding energies a_{AB} and a_{BA}, are then used with UNIQUAC to study the complex system containing the pair A-B.

In this chapter, we have examined a number of models based on what is known as the G^{xs} method. They share a common characteristic: they do not take account of any possible vacancies in the liquid, i.e. non-null excess volumes. Another method, based on equations of state, gives better results in certain cases, particularly when one of the components of the solution is in a hypercritical state and in the vicinity of the critical region of the solution. These models are described in the chapters devoted to mixtures of gases.

4

Ionic Solutions

Ionic solutions are set apart from molecular solutions by the intervention of Coulombian forces between electrical charges – forces which decrease far more slowly with increasing distance than do the van der Waals forces which exist between molecules. An important consequence of this difference is that for ionic solutions, we can no longer content ourselves with the two-body interactions between near neighbors. This means that, in the case of ionic solutions, the approximation of the ideal dilute solution model (see sections 2.4 and 3.1.3) is acceptable only for much lower concentrations than in the case of molecular solutions. In other words, for an identical level of concentration, an ionic solution is more imperfect than a molecular solution.

Numerous models of ionic solutions have been put forward in the existing body of literature. The most important of these models, which is actually found to be included in all the others, is Debye and Hückel's, which attributes the imperfection solely to the electrostatic forces between the ions but, in spite of this, is acceptable only for fully-dissociated strong electrolytes and very-dilute solutions. Then, we shall cite Pitzer's model (1973), which combines Debye and Hückel's model with a virial-type expansion, and is therefore able to extend the range of concentrations examined. Beuner and Renon's model (1978) builds on Pitzer's, extending it to solutions containing neutral molecules such as SO_2, NH_3, CO_2 or H_2S. The most recent models take account of the concept of local composition (see section 3.2). In this category, we can cite the NRTL electrolyte model introduced by Chen (1979). Finally, other models have expressed the intermolecular interactions over short distances by a

Modeling of Liquid Phases, First Edition. Michel Soustelle.

UNIQUAC simulation (see section 3.5), and even the UNIFAC version (see section 3.6).

The objective of all the improvements made to modeling has always been to find models that cover ranges of increasingly high concentrations, which are usable both for weak electrolytes and strong electrolytes, i.e. introducing models of solutions that are mixtures of ions and molecules.

In this context, we can agree that the interaction energy can be considered to be the sum of two contributions, in the form:

$$w = w^{(\mathrm{e}l)} + w^{(\mathrm{Mol})} \qquad [4.1]$$

The first term $w^{(\mathrm{e}l)}$ is a contribution due to the electrical charges, connected to long-distance interactions; the second term $w^{(\mathrm{Mol})}$ corresponds to intermolecular forces over a short distance and pertains to the molecules and the ions independently of their charges.

In general, the first term yields Debye and Hückel's model (see section 4.2).

The second term can be expressed in a variety of forms, such as the form of a virial involving the two-way and three-way interaction terms of the molecules (etc.) as found in Pitzer model (see section 4.3), and yield an excess Gibbs energy in the form:

$$G^{xs} = G^{xs(\mathrm{elec})} + G^{xs(\mathrm{Virial})} \qquad [4.2]$$

Another possibility is that the excess Gibbs energy can take the form of a sum of two terms such that:

$$G^{xs} = G^{xs(\mathrm{elec})} + G^{xs(\mathrm{UNI})} \qquad [4.3]$$

– a term of electrostatic interaction, the basis for which is still Debye and Hückel's model, which pertains only to the ions;

– a "UNIQUAC" or "UNIFAC" term, concerning both the ions and the molecules, which is of the same nature as that which we encountered in the molecular models (see sections 3.5 and 3.6);

Relations [4.2] and [4.3] are transposed to give relations [4.4] and [4.5] in terms of activity coefficients:

$$\ln \gamma_i = \ln \gamma_i^{(\text{elec})} + \ln \gamma_i^{(\text{Virial})} \qquad [4.4]$$

$$\ln \gamma_i = \ln \gamma_i^{(\text{elec})} + \ln \gamma_i^{(\text{UNI})} \qquad [4.5]$$

In what follows, we have chosen to show the progression of the modeling of ionic solutions, focusing at length on Debye and Hückel's essential model, Pitzer's model (which is very widely used in industrial circles) and the extension of the UNIQUAC and UNIFAC models to mixture of ions and molecules.

4.1. Reference state, unit of composition and activity coefficients of ionic solutions

The molecular models that we have discussed (see Chapters 2 and 3) all yielded activity coefficients in reference (I), pure substance reference, and the compositions were always expressed in molar fractions. In the case of ionic solutions, firstly the distinction between solvent and solute is often very clear, and secondly as the notion of a pure ion is illusory, usually the activity coefficients of the components of an ionic solution are expressed in reference (II), the infinitely-dilute solution, or even more frequently, in reference (III), the molar concentration. As is suggested by relations [4.4] and [4.5], we shall add terms put in place in the case of molecular solutions and purely ionic solutions. Thus, in order to perform this addition, we need to be able to switch, for the molecular components, from an activity coefficient in reference (I) to an activity coefficient in reference (II) or (III). Relation [A.2.21] is used to switch from $\gamma_s^{(I)}$ to $\gamma_s^{(II)}$, and given that we can write:

$$\frac{\mu_s^{\infty} - g_s^0}{\mathrm{R}T} = \ln \gamma_s^{(I)\infty} \qquad [4.6]$$

relation [A.2.21] is transformed into:

$$\gamma_s^{(II)} = \gamma_s^{(I)} / \gamma_s^{(I)\infty} \qquad [4.7]$$

This relation will enable us to add terms of the same nature into a sum of activity coefficients such as relation [4.4]. As we can see, the electrostatic term is given directly in convention (II), whereas the combination and residual terms are, as we have seen (in section 3.5), obtained in convention (I).

Additionally, in normal usage, the composition of an ionic solution is very frequently expressed in terms of molality (M_s : number of moles per kg of solvent) or concentration (moles per liter of solution), rather than molar fraction.

We find the molar fractions on the basis of the molalities using the relation:

$$\mathsf{M}_s = \frac{n_s}{m_0} = \frac{n_s}{n_0 M_0} = \frac{x_s}{x_0 M_0} \qquad [4.8]$$

The chemical potential of the component *s* becomes:

$$\mu_s = \mu_s^\infty + \mathrm{R}T \ln \gamma_s^{(II)} x_0 M_0 \mathsf{M}_s = \mu_s^\infty + \mathrm{R}T \ln M_0 + \mathrm{R}T \ln \mathsf{M}_s \gamma_s^{(m)} \qquad [4.9]$$

We find the following equivalences, in light of relation [4.8]:

$$\gamma_s^{(m)} = \gamma_s^{(II)} x_0 \qquad \text{and} \qquad \mu_s^{(m)} = \mu_s^\infty + \mathrm{R}T \ln M_0 \qquad [4.10]$$

M_0 is the molar mass of the pure solvent and x_0 its molar fraction, practically equal to 1 for dilute solutions.

If, now, the unit of composition is the concentration (molarity in moles per liter), with v_0 denoting the volume of solvent, then if the solution is sufficiently dilute we find:

$$c_s \cong \frac{x_s}{v_0 x_0} \qquad [4.11]$$

and therefore the chemical potential of the solute becomes:

$$\mu_s = \mu_s^\infty + \mathrm{R}T \ln x_s v_0 c_s \gamma_s^{(II)} = \mu_s^{(III)} + \mathrm{R}T \ln c \gamma_s^{(III)} \qquad [4.12]$$

For the activity coefficient in reference (III), the molar solution:

$$\gamma_s^{(III)} = \gamma_s^{(II)} x_0 \cong \gamma_s^{(II)} \text{ and } \mu_s^{(III)} = \mu_s^{(II)} v_0 \qquad [4.13]$$

We shall also see in section 4.2.11 how to switch from using concentrations to using molalities.

4.2. Debye and Hückel's electrostatic model

The purpose of Debye and Hückel's electrostatic model is to give an account of the contribution of the effect of charges on the properties of solutions. When it was first published, this model was considered a model of an ionic solution in itself, but applicable only to sufficiently dilute solutions of strong electrolytes, which are fully dissociated – in practice, with ionic strengths less than 0.01 mole/l. A resurgence of interest in this model occurred when it was understood that the interactions due to the charges were not the only interactions at play in solutions, and that the model needed to be used in conjunction with another, integrating the molecular interactions over short distances. Debye and Hückel's model has thus become the standard way to express the contribution of the electrical charges to the properties of any solution containing ions.

Numerous publications have given developments of Debye and Hückel's theory, some of them more condensed than others, and some more rigorous than others. In view of the importance of this model, which is used unanimously in all models of ionic solutions, we have chosen to base our presentation here on that given by Fowler and Guggenheim. Indeed, the method developed by these authors shows numerous advantages, including the fact that it is extremely rigorous in regard to the fundamental hypotheses – particularly hypothesis 4 (see section 4.2.5.4). This development also establishes criteria of self-consistency which must be respected by the accepted approximations. We have chosen to present this model by using the concentrations (molarities) in moles/liter to express the composition of the solutions. We shall see later on (in section 4.2.11) what becomes of the expressions derived from the model when the compositions are expressed in molalities (moles/kilo). In addition, if we use the SI units, the expressions of electrostatics will respect this system, in which the electrical permittivity of the medium is given by:

$$\varepsilon = \varepsilon_0 D \qquad [4.14]$$

D is the relative permittivity or dielectric constant of the medium: it is a dimensionless property whose value is around 80, for example, in the case of water at ambient temperature. ε_0 is the electrical permittivity of a vacuum. Its value is 8.85 × 10^{-11} SI, which equates to around $10^{-9} / 36\pi$.

4.2.1. *Presentation of the problem*

Thus, we consider an encompassing solution, in a continuum with dielectric constant *D* (which, as we shall see, will be that of the solvent). This solution contains *s* types of ions $1,2,...,i,...,s$ with positive or negative electrovalences $z_1, z_2, ..., z_i, ..., z_s$ at the concentrations (molarities) $c_1^0, c_2^0, ..., c_i^0, ..., c_s^0$ meaning that the volume *V* contains $N_1, N_2, ..., N_i, ..., N_s$ ions or $n_1, n_2, ..., n_i, ..., n_s$ ions-moles of each type. Each ion *i* carries the charge $z_i e$, where *e* is the elementary charge, which is 1.602×10^{-19} Coulombs. The electrical neutrality of the collection is expressed by any one of
the following three equations:

$$\sum_s N_i z_i = 0 \text{ or } \sum_s n_i z_i = 0 \text{ or } \sum_{i=1}^{s} c_i^0 z_i = 0 \qquad [4.15]$$

The overall density of an ion *j* in the volume of the solution is $N_j V = \mathrm{N_a} c_j^0 / 1000$ (if the concentration is expressed in moles per liter). If we choose an elementary volume $\delta\omega$ at a point M of the solution in the vicinity of any ion *k* (Figure 4.1), then following thermal agitation, at all times, ions of the different species enter into that element, so that at a given time, there may be an excess of positive or negative charges. The local density of ions *j* around the point M will be $\delta N_j / \delta\omega = \mathrm{N_a} c_j^{(M)} / 1000$ (where $c_j^{(M)}$ is the concentration in molecules per liter around the point M). Nonetheless, on average, over time, the local concentration of an ion *j* is not equal to its overall concentration in the solution. Thus, if the point M is a neighbor of a cation, it is probable that the density of anions present will, on average, be greater at point M. Put differently, the electrostatic forces over a long distance lead to an ordered structure of the solution, the effect of which is that the concentration of a species at any given point is not equal to its overall concentration in the solution. We recognize the concept of local composition, as described in Chapter 3. We write the following for the concentration of ions *j* at point M:

$$c_j^0 = c_j^{(M)} g_{kj}(r_{kj}, z_k z_j T) \qquad [4.16]$$

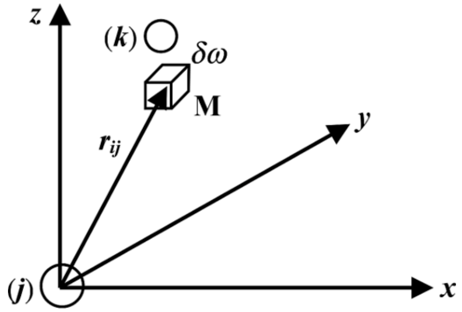

Figure 4.1. *Ion j in the vicinity of an ion i*

The function $g_{kj}(r_{kj}, z_k z_j T)$ is a distribution function which depends on the two species *k* and *j*, on the interactions between those species and particularly, on how far apart they are r_{kj}, but also on the temperature, because thermal agitation works against the ordering of the solution. The distribution function will generally tend toward zero if the repulsion between the ions *k* and *j* is strong, whereas if there is a strong force of attraction between those two ions, this function will tend to have a high value.

At a point M, the charge density would be:

$$\rho = \sum_{i=1}^{s} c_i^{(M)} z_i e = c_+^{(M)} \sum_i z_i^+ e - c_-^{(M)} \sum_i \left| z_i^- \right| e \qquad [4.17]$$

We shall use the notation $c_+^{(M)}$ and $c_-^{(M)}$ to denote the local concentrations of positive and negative charges at that point M.

4.2.2. *Notations*

To clarify our arguments, in this presentation of Debye and Hückel's model, we shall use a particular system of notation, which we shall begin by presenting here.

Suppose we have a value Q that quantifies a property of the collection of ions and is dependent on their distribution within the volume, i.e. on the configuration of the system. Just as we have done up until now, we shall use (Q) to represent the mean value of Q across all possible configurations. If w denotes the potential interaction energy of the system, then by virtue of the first mean value theorem, we shall have:

$$\langle Q\rangle \int_V \ldots \int \exp\left(-\frac{w}{\mathrm{k_B}T}\right)(\mathrm{d}\omega)^N = \int_V \ldots \int Q \exp\left(-\frac{w}{\mathrm{k_B}T}\right)(\mathrm{d}\omega)^N \qquad [4.18]$$

We use the notation $\langle Q\rangle_\alpha$ for the mean value of Q across all possible configurations around an ion α when that ion α is held still in a given position. Thus, we shall have:

$$\langle Q\rangle_\alpha \int_V \ldots \int \exp\left(-\frac{w}{\mathrm{k_B}T}\right)(\mathrm{d}\omega)^{N-1} = \int_V \ldots \int Q \exp\left(-\frac{w}{\mathrm{k_B}T}\right)(\mathrm{d}\omega)^{N-1} \qquad [4.19]$$

The integrations are then performed on the coordinates of all the ions other than the ion α.

4.2.3. *Poisson's equation*

Hereinafter, we shall suppose that we can define, at each point of the solution, for any configuration at all, an electrostatic potential Ψ and a charge density ρ which obey Poisson's equation. Thus, in light of relation [4.16], at a coordinate point r which is not occupied by an ion, we would have:

$$\nabla^2 \Psi(r) = -\frac{\rho(r)}{\varepsilon_0 D} \qquad [4.20]$$

If we now average this expression over all configurations with the fixed ion k, in light of the notations introduced in section 4.2.2, we shall have:

$$\nabla^2 \langle \Psi(r)\rangle_k = -\frac{\langle \rho(r)\rangle_k}{\varepsilon_0 D} \qquad [4.21]$$

4.2.4. *Electrical potential due to the ionic atmosphere*

We have agreed (expression [4.1]) that the interaction energy could be considered to be the sum of an energy due to the electrical charges and an energy due to the molecular interactions in proximity. We now suppose that, if the molecular interactions were the only forces at play, the solution would be accurately represented by the model of an ideal dilute solution (see section 3.1.3) and that the deviation from this model is due merely to the long-distance interactions $w^{(\mathrm{C}h)}$ caused by the electrical charges.

Because our solution is dilute, the energy $w^{(\mathrm{mol})}$ is, in fact, due only to the molecular interactions (short distance) between molecules of solvent and ions of solute, and therefore is independent of the different relative configurations of the ions.

The Helmholtz energy of the real solution with the charged ions would exceed that of the hypothetical solution, wherein the ions are not charged with an amount $F^{(Ch)}$ such that:

$$F^{(\mathrm{Ch})} = -\mathrm{k_B}T\ln\int\ldots\int\exp\left(-\frac{w^{(\mathrm{Ch})}}{\mathrm{k_B}T}\right)\prod_i\left(\mathrm{d}\omega_i\right)^{N_i} + N\mathrm{k_B}T\ln V \qquad [4.22]$$

In addition, the interaction energy due to the electrical charges can, itself, be broken down into two terms:

– the energy $w^{(\mathrm{Sel}f)}$ due to the charging of each ion in the absence of all the other charges;

– the energy $w^{(elec)}$ due to the electrical interactions between the ions:

$$w^{(\mathrm{Ch})} = w^{(\mathrm{Self})} + w^{(elec)} \qquad [4.23]$$

The Helmholtz energy $F^{(\mathrm{Ch})}$ can thus be written:

$$\mathrm{F}^{(\mathrm{Ch})} = w^{(\mathrm{Self})} + F^{(elec)} \qquad [4.24]$$

We can therefore write the excess Helmholtz energy due only to the electrical interactions in the form:

$$F^{(elec)} = -\mathrm{k_B}T\ln\int\ldots\int\exp\left(-\frac{w^{(elec)}}{\mathrm{k_B}T}\right)\prod_i(\mathrm{d}\omega_i)^{N_i} + N\mathrm{k_B}T\ln V \qquad [4.25]$$

Let us derive relation [4.24] in relation to the charge of the ion k: $e|z_k|$, after having used expression [4.25]. We have:

$$\frac{\partial w^{(\mathrm{Self})}}{e\partial|z_k|}+\frac{\partial F^{(elec)}}{e\partial|z_k|}=\frac{\int\ldots\int\frac{\partial w^{(\mathrm{Ch})}}{e\partial|z_k|}\exp\left(-\frac{w^{(\mathrm{C}h)}}{\mathrm{k_B}T}\right)(\mathrm{d}\omega)^N}{\int\ldots\int\exp\left(-\frac{w^{(\mathrm{Ch})}}{\mathrm{k_B}T}\right)(\mathrm{d}\omega)^N}=\left\langle\frac{\partial w^{(\mathrm{Ch})}}{e\partial|z_k|}\right\rangle \qquad [4.26]$$

The value $\left\langle\frac{\partial w^{(\mathrm{Ch})}}{e\partial|z_k|}\right\rangle$ is the mean increase in energy of the ensemble of particles per unit charge of k. Thus, this mean is equal to the electrostatic potential at the point occupied by the ion k and therefore, in view of our system of notation (see section 4.2.2), we can replace relation [4.26] by:

$$\frac{\partial w^{(\mathrm{Self})}}{e\partial|z_k|}+\frac{\partial F^{(\mathrm{elec})}}{e\partial|z_k|}=\langle\Psi(0)\rangle_k \qquad [4.27]$$

However, $\partial w^{(\mathrm{Self})}/e\partial|z_k|$ is the fraction of the electrostatic energy in k due to the ion k itself, and therefore this term is independent of the other ions. If we subtract that term from $\langle\Psi(0)\rangle_k$, we obtain the fraction of the mean electrostatic energy occupied by k and due to all the other ions. This is what is known as the *potential due to the ionic atmosphere*. It is written as Ψ_k, so:

$$\Psi_k=\langle\Psi(0)\rangle_k-\frac{\partial w^{(\mathrm{Self})}}{e\partial|z_k|} \qquad [4.28]$$

and therefore, we find the following for the contribution $F^{(\text{elec})}$:

$$\frac{\partial F^{(\text{elec})}}{e\partial\left|z_k\right|}=\varPsi_k \qquad [4.29]$$

If we take into account the contribution of each ion *i* in the set of ions, we can always write:

$$\mathrm{d}F^{(\text{elec})}=e\sum_i \varPsi_i\,\mathrm{d}\left|z_i\right| \qquad [4.30]$$

Each term $\varPsi_i$ is a function of all the charges z_1, z_2, …, z_i, … z_s of all the ions.

However, the Helmholtz energy is a function of state, so we can apply Schwartz's equation, meaning that we have:

$$\frac{\partial \varPsi_k}{\partial\left|z_j\right|}=\frac{\partial \varPsi_j}{\partial\left|z_k\right|}\ldots \qquad [4.31]$$

This relation will be extremely useful because, as it is very general, it can be used to test the self-consistency of any approximate expression of the potentials $\varPsi_i$.

4.2.5. *Debye and Hückel's hypotheses*

Debye and Hückel's model is an approximate evaluation of the potentials $\varPsi_i$ and of $\rho(r)$, in order to solve Poisson's equation [4.24]. This model is founded on five hypotheses.

4.2.5.1. *Hypothesis 1: shape of the ions and nature of the medium*

The ions are all considered to be hard spheres with the same radius *a* and different charges. The medium in which they are bathed is considered as a continuum with the dielectric constant *D* chosen as being that of the pure solvent, independently of the presence of the ions.

4.2.5.2. *Hypothesis 2: pairwise interactions*

We suppose that the energy $w^{(\text{elec})}$, which is due to mutual electrostatic interactions between the ions, is the sum of all the potential energies of interaction of the pairs of ions which it is possible to envisage on the basis of the ions present in the solution. We write this condition as:

$$w^{(\text{elec})} = \sum_{k=1}^{s} \sum_{j \neq k} \varepsilon_{kj} \qquad [4.32]$$

If we take account of relation [4.14], the pairwise energies ε_{kj} are such that:

$$\varepsilon_{kj} = \frac{|z_k||z_j|e^2}{4\pi\varepsilon_0 D r_{kj}} \text{ for } r_{kj} \geq a \qquad [4.33]$$

and

$$\varepsilon_{kj} = \infty \text{ for } r_{kj} < a \qquad [4.34]$$

This last condition simply expressed the fact that the centers of two ions cannot come any closer to one another than a distance $2a$.

4.2.5.3. *Hypothesis 3: Boltzmann distribution*

The third hypothesis is to accept that the distribution function of the ions, $g_{kj}(r_{kj}, z_k z_j T)$, in the space is such that at the distance r_{kj} (greater than or equal to $2a$) of an ion k, the concentration of ions j is given by:

$$c_j = c_j^0 \exp\left(-\frac{\varepsilon_{kj}}{\mathrm{k_B} T}\right) \text{ or } \delta N_j = \frac{N_j}{V} \delta\omega \exp\left(-\frac{\varepsilon_{kj}}{\mathrm{k_B} T}\right) \qquad [4.35]$$

This is the form of Boltzmann's distribution.

NOTE 4.1.– The energy ε_{kj} has multiple meanings. Indeed, it is:

– the mean Helmholtz energy of an ion j at a distance r_{kj} from an ion k;

– the work needed to bring an ion *j* from an infinite distance to the distance r_{kj} from the ion *k* (this work is averaged over all the configurations of the other ions);

– the potential energy, whose derivative gives the mean force exerted between two ions *k* and *j*, set a distance r_{kj} apart.

From this third meaning, we can deduce:

$$\varepsilon_{kj} = \varepsilon_{jk} \tag{4.36}$$

This expression is not clear for an energy averaged over all the configurations.

Based on the expressions [4.35] and [4.17], we can calculate the charge density at the distance *r* from the ion *k*. We can then easily calculate:

$$\langle \rho(r) \rangle_k = \sum_{j \neq k} z_j e \frac{\delta N_j}{\delta \omega} = \frac{e}{V} \sum_{j \neq k} |z_j| N_j \exp\left(-\frac{\varepsilon_{kj}}{\mathrm{k_B} T} \right) \tag{4.37}$$

By substituting this back into Poisson's relation [4.21], we obtain:

$$\nabla^2 \left(\langle \Psi(r) \rangle_k \right) = -\frac{e}{\varepsilon_0 D V} \sum_{j \neq k} |z_j| N_j \exp\left(-\frac{\varepsilon_{kj}}{\mathrm{k_B} T} \right) \tag{4.38}$$

It is envisageable to solve this equation when we know the relation that exists between $\langle \Psi(r) \rangle_k$ and ε_{kj}.

4.2.5.4. *Hypothesis 4: relation between $\langle \Psi(r) \rangle_k$ and ε_{kj}*

Debye posits a fundamental approximation which is a relation between the mean energy ε_{kj} and the mean potential $\langle \Psi(r) \rangle_k$, and accepts that we have:

$$\varepsilon_{kj} = e |z_j| \langle \Psi(r) \rangle_k \tag{4.39}$$

Using equation [4.36], we can deduce that:

$$\left|z_j\right|\left\langle \Psi(r)\right\rangle_k = \left|z_k\right|\left\langle \Psi(r)\right\rangle_j \qquad [4.40]$$

Irrespective of the pair of ions in question, this relation [4.41] can only be verified if:

$$\frac{\left\langle \Psi(r)\right\rangle_k}{\left|z_k\right|} = \frac{\left\langle \Psi(r)\right\rangle_j}{\left|z_j\right|} = \ldots \qquad [4.41]$$

If we feed relation [4.39] back into expression [4.38] we obtain Debye's equation:

$$\nabla^2\left(\left\langle \Psi(r)\right\rangle_k\right) = -\frac{e}{\varepsilon_0 DV}\sum_{j\neq k}\left|z_j\right| N_j \exp\left(-\frac{e\left|z_j\right|\left\langle \Psi(r)\right\rangle_k}{\mathrm{k_B}T}\right) \qquad [4.42]$$

To simplify the notations, we shall write $\Psi(r)$ instead of $\left\langle \Psi(r)\right\rangle_k$ and rewrite relation [4.42] in the form:

$$\nabla^2\left(\Psi(r)\right) = -\frac{e}{\varepsilon_0 DV}\sum_{i}\left|z_i\right| N_i \exp\left(-\frac{e\left|z_i\right|\Psi(r)}{\mathrm{k_B}T}\right) \qquad [4.43]$$

The relation is often called the Poisson–Boltzmann relation.

4.2.5.5. *Hypothesis 5: primacy of thermal agitation*

Although equation [4.43] can be solved, Debye's final hypothesis, the aim of which is to simplify this resolution, is to consider the case where the thermal agitation energy is much greater than the interaction energy:

$$\varepsilon_{kj} << \mathrm{k_B}T \qquad [4.44]$$

On the basis of equation [4.39], the above equation can be expressed by the inequality:

$$e\left|z_j\right|\Psi(r) << \mathrm{k_B}T \qquad [4.45]$$

This approximation enables us to replace the exponential in relation [4.43] with a limited expansion, which Debye limits to the second term – i.e.:

$$\exp\left(-\frac{e\left|z_j\right|\left\langle\Psi(r)\right\rangle_k}{\mathrm{k_B}T}\right)\approx 1-\frac{e\left|z_j\right|\left\langle\Psi(r)\right\rangle_k}{\mathrm{k_B}T}=1-\frac{e\left|z_j\right|\Psi(r)}{\mathrm{k_B}T} \qquad [4.46]$$

Indeed, we can easily see that the first term of the expansion disappears in expression [4.43], because of electrical neutrality, which imposes the following condition:

$$\sum_{i=1}^{s} N_i z_i = 0 \qquad [4.47]$$

Thus, we can write the Poisson–Boltzmann equation [4.43] can be written in the form:

$$\nabla^2\left(\Psi(r)\right)=\kappa^2\Psi(r) \qquad [4.48]$$

κ denotes a constant defined by:

$$\kappa^2=\frac{e^2}{\varepsilon_0 D V \mathrm{k_B}T}\sum_{i=1}^{s} N_i z_i^2=\frac{\mathrm{N_a}e^2}{\varepsilon_0 D V \mathrm{k_B}T}\sum_{i=1}^{s} n_i z_i^2 \text{ where } \kappa>0 \qquad [4.49]$$

If we use the concentrations to measure the composition of the solution, and if these concentrations are expressed in mole/l, rather than in mole/m^3, relation [4.49] is written as:

$$\kappa^2=\frac{\mathrm{N_a}e^2}{1000\,\varepsilon_0 D \mathrm{k_B}T}\sum_{i=1}^{s} c_i^0 z_i^2 \qquad [4.50]$$

In this new definition of the constant κ^2, we see the appearance of the ionic strength I as defined by relation [A.2.49]. Thus, this constant can also be written as:

$$\kappa^2=\frac{2\mathrm{N_a}e^2}{1000\,\varepsilon_0 D \mathrm{k_B}T}I \qquad [4.51]$$

We shall now easily be able to integrate equation [4.48] by using the spherical coordinates.

4.2.6. *Debye and Hückel's solution for the potential due to the ionic atmosphere*

In spherical coordinates and spherical symmetry, the Laplacian contains only the radial term, which is:

$$\nabla^2\left(\Psi(r)\right)=\frac{1}{r^2}\frac{\mathrm{d}\left(r^2\dfrac{\mathrm{d}\Psi(r)}{\mathrm{d}r}\right)}{\mathrm{d}r} \tag{4.52}$$

Thus, in light of equation [4.41], the equation to be solved is:

$$\frac{\mathrm{d}^2\Psi(r)}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}\Psi(r)}{\mathrm{d}r}=\kappa^2\Psi(r) \tag{4.53}$$

Equation [4.53] is a second-order differential equation, which implies that the solution must satisfy boundary conditions to set the two integration constants.

The first condition is that the potential $\Psi(r)$ and the field, i.e. the derivative of the potential $\dfrac{\mathrm{d}\Psi(r)}{\mathrm{d}r}$, become null as r tends toward infinity.

The second condition is that the electrical induction be constant at the boundary between the inside and the outside of the ion, meaning that for $r=a$.

The solution of equation [4.53], which remains finite as r tends toward infinity, will be of the form:

$$\Psi(r)=\frac{K}{r}\exp\left(-\kappa r\right) \tag{4.54}$$

K is a constant determined by the continuity of induction. The radial component of the electrical induction for $r \geq a$, according to relation [4.54], is:

$$4\pi\varepsilon\left(\frac{\partial \Psi(r)}{\partial r}\right)_{r=a+\varepsilon} = \frac{4\pi\varepsilon_0 DK}{r^2}(1-\kappa r)\exp(-\kappa r) \qquad [4.55]$$

However, in the vicinity of the boundary, within the ion, induction is due only to the charge on the ion, and therefore its value is:

$$D\left(\frac{\partial \Psi(r)}{\partial r}\right)_{r=a-\varepsilon} = \frac{e|z_k|}{a^2}. \qquad [4.56]$$

Let us write the continuity of the induction for $r = a$, which is:

$$\frac{4\pi\varepsilon_0 DK}{a^2}(1-\kappa a)\exp(-\kappa a) = \frac{4\pi e|z_k|}{4\pi a^2} \qquad [4.57]$$

By drawing K from expression [4.57] and substituting it back into relation [4.54], we obtain the potential as a function of r:

$$\Psi(r) = \frac{e|z_k|}{4\pi\varepsilon_0 Dr(1+\kappa a)}\exp\left[-\kappa(r-a)\right] \qquad [4.58]$$

and in particular, for $r = a$, this solution is:

$$\Psi(a) = \frac{e|z_k|}{4\pi\varepsilon_0 Da(1+\kappa a)} \qquad [4.59]$$

If we now subtract from $\Psi(a)$ the potential due to the ion k for $r = a$, we obtain the potential Ψ_k due to the other ions, i.e. the potential due to the ionic atmosphere:

$$\Psi_k = \frac{e|z_k|}{4\pi\varepsilon_0 Dr(1+\kappa a)} - \frac{e|z_k|}{4\pi\varepsilon_0 Da} = -\frac{e|z_k|}{4\pi\varepsilon_0 D}\frac{\kappa}{1+\kappa a} \qquad [4.60]$$

4.2.7. *Charge and radius of the ionic atmosphere of an ion*

Consider a sphere centered on an ion *k* with radius *r*. The areic charge density at the surface of the sphere is calculated on the basis of the mean charge density:

$$\sigma_S(r) = 4\pi r^2 \langle\sigma\rangle_k \tag{4.61}$$

By taking account of Poisson's law and of expression [4.48], we find the following for the areic density:

$$\sigma_S(r) = 4\pi r^2 \varepsilon_0 D \kappa^2 \Psi(r) \tag{4.62}$$

However, $\Psi(r)$ is provided by expression [4.58], which gives us an areic charge density on the sphere of:

$$\sigma_S(r) = \frac{r\kappa^2 e|z_k|}{1+\kappa a}\exp(\kappa a)\exp(-\kappa r) \tag{4.63}$$

If we study this function of *r*, we see that it exhibits a maximum for:

$$\frac{\mathrm{d}\left[r\exp(-\kappa r)\right]}{\mathrm{d}r} = 0 \tag{4.64}$$

By solving equation [4.64], we find that this maximum is obtained by:

$$r_A = 1/\kappa \tag{4.65}$$

This radius r_A is known as the radius of the ionic atmosphere around an ion *k*. It is the distance at which we find the maximum of the electrical density of the ionic atmosphere of the ion *k*.

Figure 4.2 shows the shape of the areic distribution as a function of *r* for two values of the ionic strength (*I* = 1 and *I* = 10^{-2} moles/l). We can see that the maximum point of the curve shifts toward larger radii if the ionic strength decreases, and that the amplitude of the corresponding peak also decreases.

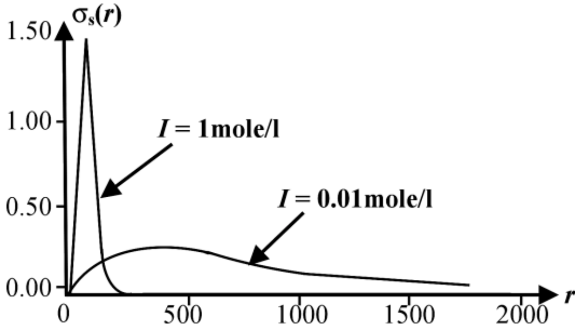

Figure 4.2. *Distribution of net charge around an ion k*

In water at 25°C, we calculate (in meters):

$$r_A = \frac{30.8 \times 10^{-9}}{\sqrt{I}} \qquad [4.66]$$

Table 4.1 gives the value of the radius of the ionic atmosphere for these two values of the ionic strength.

Ionic strength (moles/l)	Radius r_A(nm)
0.01	308
1	30.8

Table 4.1. *Radius of the ionic atmosphere for a few values of the ionic strength*

If, for the radius of the ion, we choose the value of 30 nm, this means that for an ionic strength of 1 mole/l, in water at ambient temperature, the radius of the ionic atmosphere is of the order of magnitude of the radius of the ion, so:

$$\text{for } I = 1 \text{ mole/l} \quad r_A = \frac{1}{\kappa} = a \qquad [4.67]$$

Note that, as κ is proportional to the square root of V, the radius of the ionic atmosphere will increase with the square root of the volume and therefore of the dilution.

4.2.8. *Excess Helmholtz energy and excess Gibbs energy due to charges*

Considering condensed solutions, we ignore the variations in volume, and therefore we can treat the excess Gibbs energy due to the charges as the same thing as the corresponding Helmholtz energy, and returning to relation [4.30], we write:

$$\mathrm{d}G^{(\mathrm{elec})} \approx \mathrm{d}F^{(\mathrm{elec})} = e\sum_i \Psi_i \,\mathrm{d}\left|z_i\right| \tag{4.68}$$

In order to integrate this equation, we shall imagine a virtual path which consists of progressively charging the ions. A point on that path would be characterized by a fractional extent of the charge λ between 0 and 1. At that point, the charge of the ion i would be $\lambda e\left|z_i\right|$, and we integrate relation [4.68] in relation to λ:

$$G^{(\mathrm{elec})} = \int_0^1 \sum_i N_i \Psi_i(\lambda) e\left|z_i\right| \mathrm{d}\lambda \tag{4.69}$$

Of course, the envisaged path is purely a calculation ploy, because a charge less than the elementary charge is inconceivable.

Integration is done in the following manner:

$$G^{(\mathrm{elec})} = -\sum_i \frac{N_i z_i^2 e^2 \kappa}{4\pi\varepsilon_0 D}\int_0^1 \frac{\lambda^2\,\mathrm{d}\lambda}{1+\lambda\kappa a} = -\mathrm{Na}\sum_i \frac{n_i z_i^2 e^2 \kappa}{12\pi\varepsilon_0 D}\tau(\kappa a) \tag{4.70}$$

The function $\tau(x)$ is defined by:

$$\tau(x) = \frac{3}{x^3}\left[\log(1+x) - x + \frac{x^2}{2}\right] \tag{4.71}$$

which, when x is smaller than 1, we can expand into:

$$\tau(x) = 1 - \frac{3}{4}x + \frac{3}{5}x^2 - \frac{3}{6}x^3 + \frac{3}{7}x^4 - \ldots \tag{4.72}$$

Table 4.2 contains several values of the function $\tau(x)$.

NOTE 4.2.– From the approximation which we have just added, we can see that the expression envisaged for the excess Gibbs energy is only acceptable for $\kappa a << 1$. This means that, for a given radius (around 30 nm), our Gibbs energy is acceptable only for values of κ such as $3\times10^{-10}; (\kappa << 1)$, which corresponds to an ionic strength less than 1 mole/l. However, this restriction is not a true restriction because, for such values of the ionic strength, it has certainly been a long time since Debye's hypotheses have been proved to be unacceptable.

Thus, we can keep only the first term in expansion [4.72] and write the following for the excess Gibbs energy:

$$G^{(\mathrm{elec})} = -\sum_i \frac{N_i z_i^2 e^2 \kappa}{12\pi\varepsilon_0 D} = -\frac{1}{3}\sum_i \left(\frac{N_i z_i^2 e^2}{\varepsilon_0 D}\right)^{3/2} \frac{1}{\sqrt{4\pi V \mathrm{k_B} T}} \qquad [4.73]$$

By switching to concentrations in moles per liter, we find:

$$G^{(\mathrm{elec})} = -\mathrm{N_a}\sum_i \frac{n_i z_i^2 e^2 \kappa}{12\pi\varepsilon_0 D} = -\frac{1}{3\sqrt{4\pi V \mathrm{k_B} T}} \left(\sum_i \frac{\mathrm{N_a} c_i^0 z_i^2 e^2 V}{1000\varepsilon_0 D}\right)^{3/2} \qquad [4.74]$$

By revealing the ionic strength *I*, we obtain the following for the electrostatic excess Gibbs energy:

$$G^{(\mathrm{elec})} = -\frac{2\sqrt{2}}{3\sqrt{4\pi V \mathrm{k_B} T}} \left(\frac{\mathrm{N_a} e^2 V I}{1000\varepsilon_0 D}\right)^{3/2} \qquad [4.75]$$

Thus, we shall use the formulae [4.75] and [4.76], drawn from the first form of relation [4.66]:

$$G^{(\mathrm{elec})} = -\frac{1}{3}\frac{\mathrm{N_a}\kappa V e^2}{1000.4\pi\varepsilon_0 D}\left(\sum_i c_i^0 z_i^2\right)^{1/2} = -\frac{2\mathrm{N_a} V \kappa e^2}{3000.4\pi\varepsilon_0 D}\sqrt{I} \qquad [4.76]$$

4.2.9. *Activity coefficients of the ions and mean activity coefficient of the solution*

By deriving equation [4.70] in relation to the amount of component *k* in the solution, we can calculate the excess partial molar Gibbs energy of the ion *k* due to electrical charges:

$$\begin{aligned} \mathrm{R}T \ln \gamma_{k(c)}^{(II)} &= \mu_k^{(\mathrm{elec})} = \frac{\partial G^{(\mathrm{elec})}}{\partial n_k} \\ &= -\frac{z_k^2 e^2 \mathrm{N_a}}{8\pi\varepsilon_0 D} \frac{\kappa}{1+\kappa a} + \frac{\sum_i N_i z_i^2 e^2}{12\pi\varepsilon_0 D} \frac{\kappa}{2V} v_{m(k)} \sigma(\kappa a) \end{aligned} \qquad [4.77]$$

This gives us the activity coefficient of the ion *k*:

$$\ln \gamma_{k(c)}^{(II)} = -\frac{z_k^2 e^2}{8\pi\varepsilon_0 D \mathrm{k_B} T} \frac{\kappa}{1+\kappa a} + \frac{\kappa^3}{24\pi\varepsilon_0 D V} V_{m(k)} \sigma(\kappa a) \qquad [4.78]$$

$\sigma(x)$ is the function defined by:

$$\sigma(\mathrm{x}) = \frac{3}{\mathrm{x}^3}\left[1 + x - \frac{1}{1+x} - 2\ln(1+x)\right] \qquad [4.79]$$

or

$$\sigma(\mathrm{x}) = 1 - 3\frac{2}{4}x + 3\frac{2}{5}x^2 - 3\frac{2}{6}x^3 + 3\frac{2}{7}x^4 - .. \qquad [4.80]$$

A number of values of $\sigma(x)$ are given in Table 4.2. We can see that at a very high level of dilution, if $\kappa a << 1$ the function $\sigma(\kappa a)$ tends toward 1 and in the conditions we chose previously, the activity coefficient is such that:

$$\ln \gamma_{k(c)}^{(II)} = -\frac{z_k^2 e^2}{8\pi\varepsilon \mathrm{k_B} T} \frac{\kappa}{1+\kappa a} = -\frac{z_k^2 e^2}{2D\varepsilon_0 \mathrm{k_B} T} \frac{\sqrt{\dfrac{2N_a e^2 I}{1000\,\varepsilon_0 D \mathrm{k_B} T}}}{1 + a\sqrt{\dfrac{2N_a e^2 I}{1000\,\varepsilon_0 D \mathrm{k_B} T}}} \qquad [4.81]$$

This function is usually written in the form of the decimal logarithm:

$$\log \gamma_{k(c)}^{(II)} = -Bz_k^2 \frac{\sqrt{I}}{1+Aa\sqrt{I}} \quad [4.82]$$

x^2	x	$\tau(x)$	$\sigma(x)$
0.0000	0.0000	1.000	1.000
0.001	0.0316	0.976	0.954
0.002	0.0447	0.967	0.936
0.003	0.0557	0.960	0.922
0.004	0.0633	0.954	0.912
0.005	0.0707	0.949	0.902
0.006	0.0775	0.945	0.893
0.007	0.0837	0.941	0.886
0.008	0.0894	0.937	0.879
0.009	0.0947	0.934	0.871
0.010	0.1000	0.931	0.866
0.100	0.3162	0.811	0.659
0.200	0.4472	0.752	0.569

Table 4.2. *Table of values of functions $\tau(x)$ and $\sigma(x)$*

with the following meanings, for the term B (sometimes called Debye and Hückel's constant) and the term A:

$$B = 2.303 \frac{e^2 \sqrt{\dfrac{2N_a e^2}{1000\,\varepsilon_0 D \mathrm{k_B} T}}}{2D\varepsilon_0 \mathrm{k_B} T} \quad [4.83]$$

$$A=\sqrt{\frac{2N_a e^2}{1000\,\varepsilon_0 D \mathrm{k_B} T}} \qquad [4.84]$$

Let us recap the values of the electrostatic constants:

$$\varepsilon_0=\frac{1}{36\pi 10^9} \text{ and } e=1{,}602.10^{-19}C \qquad [4.85]$$

The law [4.82] is called Debye and Hückel's extended law (as opposed to the limit law, which we shall see in section 4.2.13).

At 25°C, by choosing to use the dielectric constant of water for aqueous solutions ($D=78.54$), we calculate:

$$B=0.511\ \mathrm{l}^{1/2}\mathrm{mole}^{-0.5} \qquad [4.86]$$

$$A=0.3287\times 10^{10}\,\mathrm{l}^{0.5}\mathrm{mole}^{-0.5}\mathrm{m}^{-1} \text{ if } a \text{ is in meters.} \qquad [4.87]$$

NOTE 4.3.– It is worth noting that if we choose the value of the radius as $a=3.04\times 10^{-10}\ \mathrm{m}$, we find $Aa\approx 1\mathrm{l}^{0.5}\mathrm{mole}^{-0.5}$, and relation [4.82] is then rewritten as:

$$\log \gamma_{k(c)}^{(II)}=-Bz_k^2\frac{\sqrt{I}}{1+\sqrt{I}} \qquad [4.88]$$

The "electrostatic" chemical potential of the solvent is calculated, for instance, as follows:

$$\mu_0^{(\mathrm{elec})}=\frac{\partial G^{(\mathrm{elec})}}{\partial n_0}=\frac{\partial G^{(\mathrm{elec})}}{\partial \kappa}\frac{\partial \kappa}{\partial V}\frac{\partial V}{\partial n_0} \qquad [4.89]$$

Using relation [4.77], we obtain:

$$\mu_0^{(\mathrm{elec})}=\frac{\sum_i N_i z_i^2 e^2}{12\pi\varepsilon_0 D}\frac{\kappa}{2V}v_{\mathrm{m}(0)}\sigma(\kappa a) \qquad [4.90]$$

In the context of very dilute solutions, $\sigma(\kappa a) \approx 1$, this potential becomes:

$$\mu_0^{(\text{elec})} = \frac{\sum_i N_i z_i^2 e^2}{12\pi\varepsilon_0 D} \frac{\kappa}{2V} v_0^0 \qquad [4.91]$$

v_0^0 is the molar volume of the pure solvent. The solvent's activity coefficient can thus be calculated, and we shall verify that it satisfies the Gibbs–Duhem relation.

We know that it is impossible to determine the coefficients of the individual ions by experimentation, but that we can determine the mean coefficient $\gamma_{\pm(c)}^{(II)}$ of the solution. In light of electric neutrality:

$$\nu_+ z_+ + \nu_- z_- = 0 \qquad [4.92]$$

Using relation [A.2.45] for the mean activity coefficient, we can easily calculate:

$$\ln \gamma_{\pm(c)}^{(II)} = -\frac{z_+ |z_-| e^2}{8\pi\varepsilon_0 D \mathrm{k_B} T} \frac{\kappa}{1 + \kappa a} \qquad [4.93]$$

With $D = 78.54$ for water at 25°C, we calculate the following, with a being in meters:

$$\log \gamma_{\pm(c)}^{(II)} = -0.511 z_+ |z_-| \frac{\sqrt{I}}{1 + 0.3287 \times 10^{-10} a\sqrt{I}} \qquad [4.94]$$

Although the dielectric constant varies with temperature, the product DT which is the only one that plays a role practically does not change between 18 and 25°, and therefore the values of the coefficients A and B do not either.

4.2.10. *Self-consistency of Debye and Hückel's model*

Any model of an ionic solution must satisfy two categories of self-consistency criteria: thermodynamic criteria and electrostatic criteria.

4.2.10.1. *Thermodynamic criteria*

We have already checked, at the end of section 4.2.9, that the Gibbs–Duhem relation was verified. With regard to the other criteria:

– the model must satisfy the symmetry of the characteristic matrix:

$$\frac{\partial \mu_i}{\partial n_j} = \frac{\partial \mu_j}{\partial n_i} \qquad [4.95]$$

If we apply this relation to the expression of the chemical potential, given by relation [4.77], we note that this relation is respected, provided we take both terms from equation [4.77], because the first term on its own is not able to satisfy this criterion. Certainly, the second term may be numerically negligible, but it cannot be taken as equal to zero. Hence, Debye and Hückel’s model satisfies this criterion.

– the terms in the diagonal of the characteristic matrix must be positive:

$$\frac{\partial \mu_i}{\partial n_i} > 0 \qquad [4.96]$$

We can see, from relation [4.70], that Debye and Hückel’s model satisfies this criterion.

– the excess Gibbs energy must be homogeneous of degree 1 (like all extensive values) in relation to the amounts of material.

If we examine relation [4.50], we can see that κ is of degree ½ in relation to the concentrations and that $\sqrt{I}$ is also of degree ½, and therefore, in relation [4.76], the “electrical” excess Gibbs energy is of degree 1 and the function is homogeneous because each quantity N_i is the product:

$$N_i = N_a n x_i \qquad [4.97]$$

and therefore the quantity n can be factorized.

4.2.10.2. *Electrostatic criteria*

We have three electrostatic criteria to satisfy.

The first criterion needing to be respected is the proportionality between the potential due to the ionic atmosphere and the charge. Relation [4.58] shows that Debye and Hückel's solution satisfies this criterion.

We have encountered the criterion given by relation [4.31] that must be satisfied by the potential of the ionic atmospheres of the ions. Let us now examine whether Debye and Hückel's solution conforms to this criterion. By writing:

$$\frac{\partial \Psi_k}{\partial z_j} = \frac{\partial \Psi_k}{\partial \kappa} \frac{\partial \kappa}{\partial z_j} \qquad [4.98]$$

Fowler and Guggenheim show that the derivative $\partial \Psi_k / \partial z_j$ contains the product $z_j z_k$, and also only depends on z_j and z_k by way of the coefficient κ, and therefore this derivative is symmetrical in relation to j and k, and thus the criterion [4.31] is verified.

The third criterion is that the solution must respect electrical neutrality. To determine this, we calculate the overall charge of the atmosphere surrounding an ion k. We shall consider two spheres centered on the ion k, with respective radii r and $r + \mathrm{d}r$. The electrical charge contained in the volume between these two spheres is:

$$\mathrm{d}q_k = \sigma_S(r)\,\mathrm{d}r \qquad [4.99]$$

By integrating this equation between $r = a$ and an infinite value of r, we obtain the charge of the whole of the ionic atmosphere surrounding the ion k, meaning that the electrical charge of the whole solution decreases by that of the ion k. Thus, we have:

$$q_k = \int_a^\infty \sigma_S(r)\,\mathrm{d}r \qquad [4.100]$$

Returning to expression [4.63] for the areic charge, we calculate that this overall charge is:

$$q_k = -|z_k|\,e \qquad [4.101]$$

Thus, the charge surrounding the ion *k* is precisely the opposite of the charge on that ion, which shows that Debye and Hückel's law respects the condition of electrical neutrality.

We have gone into detail in our examination of the respect of these criteria, because we shall see that certain corrections, proposed to improve the model's conformity to experience, yield solutions which no longer respect all these criteria.

4.2.11. *Switching from concentrations to molalities*

Up until now, we have chosen to quantify the composition of solutions in concentrations (molarities) expressed in moles/liter. Very often, users of Debye and Hückel's model use molality values M_i, which are expressed in moles per kilogram of solvent. Between these two values, if the solution is sufficiently dilute (which is the case in the domain of validity of Debye and Hückel's model) to enable us to treat the volume of the solution and that of the solvent as one and the same thing, we can write:

$$\frac{\mathsf{M}_i \rho_0}{1000} = C_i \qquad [4.102]$$

The coefficient 1000 stems from the fact that the molality is given in moles/kg and the molarity in moles/l, rather than in moles/m^3.

If we work on the basis of the second expression of the "electrical" excess Gibbs energy given by relation [4.76], using expression [4.102], we obtain:

$$G^{(\mathrm{elec})} = -\frac{1}{3\sqrt{4\pi V \mathrm{k_B} T}} \left(\sum_i \frac{\mathrm{N_a} \mathsf{M}_i z_i^2 e^2 M_0}{1000 \varepsilon_0 D} \right)^{3/2} \qquad [4.103]$$

Thus, we define an ionic strength in terms of molality, which is expressed, similarly to definition [A.2.49], by:

$$I_M = \frac{1}{2} \sum_{i=1}^{s} \mathsf{M} z_i^2 \qquad [4.104]$$

Thus, the "electrical" excess Gibbs energy can be written:

$$G^{(\text{elec})} = -\frac{2\sqrt{2}}{3\sqrt{4\pi V \mathrm{k_B} T}} \frac{\mathrm{N_a} M_0 e^2 I_M^{3/2}}{1000 \varepsilon_0 D} \qquad [4.105]$$

Similarly, on the basis of expression [4.50], using relations [4.102] and [4.104], we write the coefficient κ^2 in the form:

$$\kappa^2 = \frac{2\mathrm{N_a} \rho_0 e^2}{1000\, \varepsilon_0 D \mathrm{k_B} T} I_M \qquad [4.106]$$

and for the activity coefficient linked to the molality values, we find:

$$\log \gamma_{i(m)}^{(II)} = -B\sqrt{\rho_0} \frac{\sqrt{I_M}}{1 + A\rho_0 a\sqrt{I_M}} \qquad [4.107]$$

For water, though, we apparently have $\rho_0 = 1\ \text{kg/dm}^3$ at normal temperature, so relation [4.82] with the values of the coefficients *B* and *A* given by equations [4.86] and [4.87], is conserved, with the ionic strength relative to the concentrations being replaced by the ionic strength relative to the molality values I_M.

Thus, equation [4.82] applies indifferently, whether the compositions are expressed in molarity or molality. The ionic strength is expressed, in each case, with the same unit of composition.

In addition, we can express the activity coefficient in any one of the conventions, but using relations [4.10] and [4.13], if the solution is sufficiently dilute, the values of the different coefficients become the same, because we find:

$$\gamma_i^{(III)} \approx \gamma_i^{(II)} \approx \gamma_i^{(m)} \qquad [4.108]$$

Definitively, all the activity coefficients are given by relation [4.82] with, in an aqueous solution, the values of the coefficients *B* and *A* given by equations [4.86] and [4.87], and choosing *I* or I_M depending on whether the compositions are expressed in molarity (or concentration) or molality. The same is true for the mean activity coefficients, using relations [4.86] or [4.87]. Thus, we no longer make the distinction between the different activity coefficients, simply writing them as γ_i , and similarly for the mean activity coefficients, which we shall denote by $\gamma_\pm$.

4.2.12. *Debye and Hückel's law: validity and comparison with experimental data*

Experience tells us that ionic solutions only behave like ideal dilute solutions ($\gamma_\pm = 1$) below a concentration of 10^{-4} moles per liter, whereas for a molecular solution, such behavior is acceptable below 10^{-2} moles per liter.

Figure 4.3 shows a comparison of the variations of the mean activity coefficient of magnesium chloride as a function of the ionic strength. The points are obtained experimentally and the downward curve is obtained by application of Debye and Hückel's law. The figure demonstrates that the model begins to deviate from the experimental values long before the ionic strength reaches one. In particular, for most electrolytes, the real curve exhibits an extremum which Debye and Hückel's model never shows.

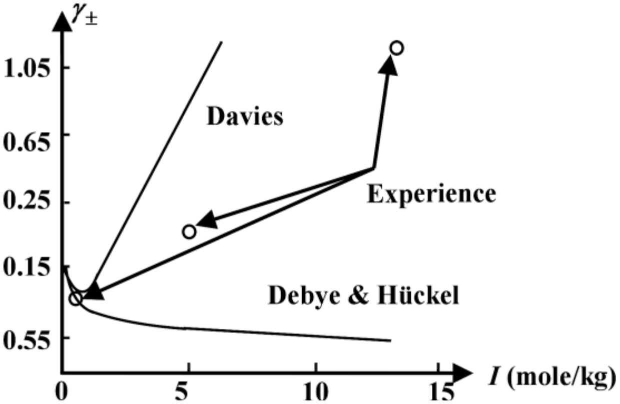

Figure 4.3. *Variations of the mean activity coefficient of magnesium chloride with the ionic strength*

In practice, we consider that Debye and Hückel's law, expressed by relation [4.82], and in particular using its form [4.88] in water, can only be used for solutions in which the ionic strength is no greater than 10^{-2}mol/l, although in certain cases, ionic strengths of 10^{-1}mol/l can also yield acceptable results. Certain authors prefer to adjust the law [4.82] by adjusting two experimental conditions:

– the extrapolation for an ionic strength of zero for which the mean activity coefficient is one;

– the radius of the ion *a* with the experimental curve.

By this method, we are able to apply the formula [4.82] to a broader range of ionic strengths. However, the values thus determined for *a* still need to be acceptable in terms of the physical meaning. Indeed, certain experiments yield very low values of the radius *a* – sometimes zero, and sometimes even negative values are required. The true value of *a* must be no lower than the ionic radius determined in a crystal of a corresponding salt.

Nevertheless, let us remember that Debye and Hückel's law supposes the ions are spherical, which can be accepted for sufficiently dilute solutions in which the radius of the ionic atmosphere is larger than *a* and therefore in which the ions are relatively far removed from one another. If the ions come closer together, the hypothesis of sphericity becomes trickier to accept for a large number of types of ions – particularly for polyatomic ions.

4.2.13. *Debye and Hückel's limit law*

For very significant degrees of dilution ($10^{-4} < I < 10^{-3}$), the denominator term in law [4.82] becomes much smaller than 1, and we obtain what is known as Debye and Hückel's limit law.

This limit law is written as:

$$\log \gamma_i = -Bz_i^2 \sqrt{I} \qquad [4.109]$$

The curve giving the mean activity coefficient, calculated using this limit law, is tangential to the origin of the complete curve given by equation [4.82], as illustrated by Figure 4.4, and can be used for the extrapolation of the real curve at infinite dilution.

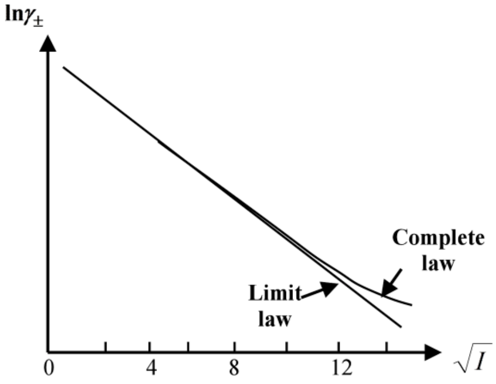

Figure 4.4. *Comparison of the complete law and Debye and Hückel's limit law*

The fact that this limit law can be obtained numerically by making $a = 0$ in expression [4.82] does not mean that it must be attributed to an approximation in which the ions are assimilated to single-point charges. This approximation, which is sometimes presented, is totally erroneous, because it is easy to show that a collection of electrically-charged points is completely unstable; indeed, it is the existence of a non-null radius a which lends stability, because two ions can never come together completely, as is demonstrated by the second form [4.34] of the potential function.

4.2.14. *Extensions of Debye and Hückel's law*

The limits exhibited by Debye and Hückel's law in its application to real-world cases have led many researchers to attempt to improve it. These improvements were first made in the strict framework of the law [4.82], before branching out in a new direction, integrating the molecular interactions that we shall see in sections 4.3 and 4.4.

One of the earliest methods involved adding one or more adjustable parameters to the law [4.82]. Thus, Hückel, taking account of a variation in the medium's dielectric constant with changing ionic strength, was led to propose the following relation:

$$\log \gamma_i = -Bz_i^2 \frac{\sqrt{I}}{1 + ga\sqrt{I}} + KI \qquad [4.110]$$

This relation is able to represent the minimum of the curve in Figure 4.3. Unfortunately, the term K cannot be calculated *a priori*, and must be determined experimentally, which takes away from the advantage of this type of formula.

Along the same lines, after numerous measurements, Davies proposed to determine the mean activity coefficient of aqueous solutions (at standard temperature) using the following relation:

$$\log \gamma_{\pm} = -0.511 z_{+} \left| z_{-} \right| \frac{\sqrt{I_m}}{1+\sqrt{I_m}} - 0.3 I \qquad [4.111]$$

He proposed a second version of the relation:

$$\log \gamma_{\pm} = -B_m z_{+} \left| z_{-} \right| \frac{\sqrt{I_m}}{1+C_1 A_m a \sqrt{I_m}} + C_2 \qquad [4.112]$$

He drew up lists of values of the constants C_1 and C_2 for each family of electrolytes.

Figure 4.3 gives the result obtained by that model for magnesium chloride. We can see that whilst the model does show the minimum of the curve, it quickly deviates from the experimental results and, therefore, is hardly any better than Debye and Hückel's original model.

A second way of improving Debye and Hückel's model was to review some of its hypotheses, making them less stringent.

An initial attempt was made by modifying hypothesis 5 (see section 4.2.5.5), increasing the number of terms chosen in the serial expansion of expression [4.46] or indeed by solving the complete Poisson–Boltzmann equation with the exponential term, which is possible. Of course, the expressions obtained are complex, but they all manifest a major shortcoming: they no longer satisfy the electrostatic criterion represented by relation [4.41], which greatly takes away from their interest.

A second way to improve was to keep certain terms (at least two) in the expansion [4.72], but we have already pointed out in section 4.2.8 that the degree of accuracy obtained became illusory in relation to the other hypotheses.

A third way of improving the law was attempted by Bjerrum, who introduced interactions between the ions in the form of associated species between ions that are sufficiently close. We can also introduce terms linked to the shapes of the ions by introducing parameters resulting from the associations between the anions and cations present in the solution. Using this technique, Guggenheim was able to develop a law with multiple parameters, which can be deduced from the experimental behaviors of pure salts.

It is clear that, ultimately, these latter attempts consist of taking account of the interactions between the ions over short distances. This observation has led to a new general way of modeling ionic solutions: now we no longer modify the law [4.82] or its derivatives, but instead superpose on the effects of the electrostatic interactions, represented by that law, the effects due to the molecular interactions over short distances, as found in non-ionic solutions. It is this method which we are going to discuss in sections 4.3 and 4.4 below – a method which enables us to move away from just strong electrolytes, to take account of mixtures of ions and neutral molecules, and therefore weak electrolytes.

4.3. Pitzer's model

Pitzer's model is a semi-empirical model based on Debye and Hückel's extended law [4.82], where additional terms have been introduced in order to take account of the effects of the ionic strength on the binary interactions over a short distance.

Although we noted that this operation rendered the model non-self-consistent, in order to improve its conformity to experimental results, Pitzer proposed an expansion of the exponential of relation [4.43], limited to the first three terms instead of two, as Debye and Hückel did in relation [4.46], so:

$$\exp\left(-\frac{w}{\mathrm{k_B}T}\right) \cong 1-\frac{w}{\mathrm{k_B}T}-\left(\frac{w}{\mathrm{k_B}T}\right)^2 \qquad [4.113]$$

If λ_{ij} and μ_{ijk} respectively denote the terms describing the pairwise interactions between the species i and j and the three-way interactions between the species i, j and k, expressed in kg^2.mole^{-2} and kg^{3}mole^{-3}, the excess Gibbs energy is written as:

$$\frac{G^{xs}}{\mathrm{R}T}=\frac{G^{(\mathrm{elec})}}{\mathrm{R}T}+\sum_i\sum_j\lambda_{ij}\mathsf{M}_i\mathsf{M}_j+\sum_i\sum_j\sum_k\mu_{ijk}\mathsf{M}_i\mathsf{M}_j\mathsf{M}_k \qquad [4.114]$$

$\frac{G^{(\mathrm{elec})}}{\mathrm{R}T}$ is the term expressing the long-distance electrostatic interactions between the ions. It is a function of the temperature and of the ionic strength. This function stems directly from Debye and Hückel's hard-sphere model (see section 4.2). With the new hypotheses chosen by Pitzer, it is expressed thus as a function of the ionic strength:

$$\frac{G^{(\mathrm{elec})}}{\mathrm{R}T}=-x_0M_0B_m\frac{4I}{b}\ln\left(1+b\sqrt{I}\right) \qquad [4.115]$$

B_m is Debye and Hückel's constant, expressed in relation to the molality values and given, as is shown by the comparison of relations [4.82] and [4.107], by:

$$B_m=B\sqrt{\rho_0} \qquad [4.116]$$

The parameter B is given by relation [4.86]. The term b is an adjustable parameter which has been optimized and taken as equal to 1.5kg$^{1/2}$.mole$^{-1/2}$ for all temperatures and all solutes. It is theoretically linked to the distance beyond which the forces of repulsion between the ions become significant. ρ_0 is expressed in kg/dm^3.

NOTE 4.4.– In ionic solutions containing molecular species, the parameters λ_{ij} must include the molecule-molecule interactions of the ions, excluding the effect of charge, and molecule-ion interactions. The parameter μ_{ijk} must include the molecule-molecule-molecule interactions (again including the ions but excluding the effect of charge).

We consider that the solution contains n_c types of cations numbered 1, 2, …c,… n_c and n_a types of anions numbered 1, 2, …a, … n_a. We shall rewrite relation [4.114] to separately introduce the terms linked to cations and anions. The excess Gibbs energy becomes:

$$\begin{aligned}\frac{G^{xs}}{\mathrm{R}T}=&-\frac{4x_0M_0B_mI}{b}\ln\left(1+b\sqrt{I}\right)+2\sum_a\sum_c \mathsf{M}_a\mathsf{M}_c\left[B_{ca}+\left(\sum_c z_c\mathsf{M}_c\right)\right]C_{ca}\\&+\sum_c\sum_{c'}\mathsf{M}_c\mathsf{M}_{c'}\left[\varphi_{cc'}+\frac{1}{2}\sum_a\mathsf{M}_a\psi_{cc'a}\right]\\&+\sum_a\sum_{a'}\mathsf{M}_a\mathsf{M}_{a'}\left[\left[\varphi_{aa'}+\frac{1}{2}\sum_c\mathsf{M}_c\psi_{caa'}\right]\right]\end{aligned}\qquad[4.117]$$

This relation exhibits the advantage of introducing adjustable parameters with experimental data: B_{ca}, C_{ca}, $\varphi_{cc'}$ and $\varphi_{aa'}$.

The terms B_{ca} are given by:

$$B_{ca}=\beta_{ca}^{(0)}+\beta_{ca}^{(1)}f\left(\alpha_{ca}^{(1)}\sqrt{I}\right)+\beta_{ca}^{(2)}f\left(\alpha_{ca}^{(2)}\sqrt{I}\right)\qquad[4.118]$$

The coefficients $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and $\beta_{ca}^{(2)}$ are assimilated to second-order virial coefficients, expressing the short-distance effects between the ions c and a. They are expressed in kg/mole. The function $f(y)$ is defined by:

$$f(y)=\frac{2\left[1-(1+y)\exp(-y)\right]}{y^2}\qquad[4.119]$$

The second-order virial coefficients have the following properties:

$$\begin{cases}\beta_{ij}=\beta_{ji} & [4.120]\\ \beta_{ij}=\beta_{ji}=0 \text{ if } i \text{ and } j \text{ have the same sign} & [4.121]\end{cases}$$

NOTE 4.5.– The London forces of repulsion prevent interactions between ions over a short distance.

The parameters C_{ca} are given by the expression:

$$C_{ca} = \frac{C_{ca}^{*}}{2\sqrt{z_a z_c}} \qquad [4.122]$$

The parameters $\varphi_{cc'}$ and $\varphi_{aa'}$ are also functions of the ionic strengths given by:

$$\varphi_{cc'} = \varphi_{c'c} = \beta_{cc'}^{(0)} + \beta_{cc'}^{(1)}(I) \qquad [4.123]$$

and

$$\varphi_{aa'} = \varphi_{a'a} = \beta_{aa'}^{(0)} + \beta_{aa'}^{(1)}(I) \qquad [4.124]$$

The coefficients $\beta_{cc'}^{(0)}$ and $\beta_{cc'}^{(1)}$ are functions of the ionic strength and of the charges on the ions. We have seen that these coefficients are null if they refer to cations or anions of the same charge ($z_a = z_{a'}$ or $z_c = z_{c'}$).

Thus, the new form [4.117] of the excess Gibbs energy brings into play various parameters that are adjustable to each ionic solution studied. These parameters may be classified into two categories:

– so-called “binary” parameters. This category includes the parameters: $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and $\beta_{ca}^{(2)}$, $\alpha_{ca}^{(1)}$ and $\alpha_{ca}^{(2)}$, C_{ca}^{*}, which characterize binary solutions (with an anion *a* and a cation *c* in addition to the solvent);

– so-called “ternary” parameters, which include the parameters $\beta_{cc'}^{(0)}$ and $\beta_{cc'}^{(1)}$, $\psi_{caa'}$ and $\psi_{cc'a}$.

NOTE 4.6.– the parameters $\beta_{cc'}^{(0)}$ and $\beta_{cc'}^{(1)}$, which relate to pairwise interactions, are described as “ternary” because they characterize ternary solutions with an anion or a cation in common, as the electrolytes: mixtures of *ac* and *a'c* or of *ac* and *ac'*.

Pitzer’s model, as we have just described it, can be used for solutions whose ionic strength can be up to 6M.

For lower ionic strengths, it is possible to use simplified forms. In particular, we can often simplify the model by setting $\beta_{ca}^{(2)} = 0$ for any couple *ca*.

The coefficients $\alpha_{ca}^{(1)}$ are such that, frequently, we can use the following values:

– $\alpha_{ca}^{(1)} = 2$ for all the electrolytes *ca* except those of the type 2-2(z_c and $\left|z_a\right|$, which are different from 2);

– $\alpha_{ca}^{(1)} = 12$ for all the electrolytes *ca* of the type 2-2 ($\left|z_a\right| = z_c = 2$).

Therefore, in the highly-simplified version, there are now only three types of parameters to identify – namely $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and C_{ca}^{*}. In these circumstances, relation [4.118] can be simplified to:

– if $\alpha_{ca}^{(1)} = 2$ – i.e. for all electrolytes *ca* except those of type 2-2:

$$B_{ca} = \beta_{ca}^{(0)} - \beta_{ca}^{(1)} \frac{1 - 3\exp\left(2\sqrt{I}\right)}{2I} \qquad [4.125]$$

– if $\alpha_{ca}^{(1)} = 12$ – i.e. for all electrolytes *ca* of type 2-2:

$$B_{ca} = \beta_{ca}^{(0)} - \beta_{ca}^{(1)} \frac{1 - 13\exp\left(-12\sqrt{I}\right)}{77I} \qquad [4.126]$$

For example, for a solution with only one electrolyte (a cationic species and an anionic species), it is easy to see that the excess Gibbs energy assumes the simplified form:

$$\frac{G^{xs}}{\mathrm{R}T} = -\frac{4B_m I}{b} \ln\left(1 + b\sqrt{I}\right) + 2\mathsf{M}_a \mathsf{M}_\mathrm{c}\left[B_{ca} + z_c \mathsf{M}_\mathrm{c} C_{ca}\right] \qquad [4.127]$$

The parameter C_{ca} conforms to definition [4.125], and the parameter B_{ca}, depending on the type of electrolyte, conforms to one or other of relations [4.125] or [4.126].

The activity coefficients of the ions can be calculated in the following way:

$$\mathrm{R}T\ln\gamma_i^{(I)} = \frac{\partial G^{xs}}{\partial n_i} = \frac{\partial G^{xs}}{\partial \mathsf{M}_i}\frac{\partial \mathsf{M}_\mathrm{i}}{\partial n_i} = \frac{1}{M_0 n_0}\frac{\partial G^{xs}}{\partial \mathsf{M}_i} \qquad [4.128]$$

n_0 is the amount of solvent of molar mass M_0.

Additionally, Pitzer's model has been extended by Beuter and Renon to apply to solutions containing dissolved molecular species stemming from gases.

4.4. UNIQUAC model extended to ionic solutions

The extension of the UNIQUAC model to ionic solutions was first envisaged by Sander *et al.* in 1986. The basic idea is to think of the excess Gibbs energy of an ionic solution as being the sum of two contributions:

– the term $G^{xs(elec)}$ drawn from Debye and Hückel's model, to take account of the long-distance electrostatic interactions between the ions (see section 4.2);

– the UNIQUAC term as it is used for molecular solutions (see section 3.5), in order to take account of the short-distance interactions between molecules, between molecules and ions and between ions.

Thus, from the excess Gibbs energy of the solution, we write:

$$G^{xs} = G^{xs(ion)} + G^{xs(\mathrm{U}NI)} \qquad [4.129]$$

For a given species *i*, this relation results in a relation between the activity coefficients, given by:

$$\ln\gamma_i^{(II)} = \ln\gamma_i^{(II)(ion)} + \ln\gamma_i^{(II)(UNI)} \qquad [4.130]$$

Normally, the UNIQUAC model leads to the activity coefficients with the pure-substance reference $\ln\gamma_i^{(I)(UNI)}$. To switch to the activity coefficient for reference II – the infinitely-dilute solution – we use relation [4.2], so equation [4.130] is reformulated as:

$$\ln \gamma_i^{(II)} = \ln \gamma_i^{(II)(elec)} + \ln \frac{\gamma_i^{(I)(UNI)}}{\gamma_i^{(I)\infty(UNI)}} \tag{4.131}$$

The term $\gamma_i^{(I)\infty(UNI)}$ is the activity coefficient of the species *i* in infinite dilution. Thus, it is calculated by the UNIQUAC model by taking a molar fraction of one unit for the solvent (and therefore a molar fraction of zero for all the other components), so that:

$$\ln \gamma_i^{(I)\infty(UNI)} = \lim_{x_0 \to 1} \ln \gamma_i^{(I)(UNI)} \tag{4.132}$$

Thus, definitively, the parameters of the model are:

– the parameters *B* and *A* (often taken as equal to 1.5) used by Debye and Hückel as a function of the temperature;

– the parameters linked to the UNIQUAC model, i.e. the structural parameters r_i and q_i and the energy parameters a_{ij} and a_{ji} for each pair of components.

The number of parameters needed for this model, therefore, is less than that needed for Pitzer’s model.

The problem with electrolytes is that of the nature of the species that are actually present in the solution, which may be very different to those introduced when making up the solution. Indeed, we may see more or less complete dissociations, reactions with the solvent (water, for example), solvation of ions as introduced by Lu and Maurer (1993). These equilibrium states introduce new relations between the activity coefficients. For example, for the solvation of a cation c, the equilibrium is written as:

$$hc\mathrm{H_2O} + \mathrm{c} = \mathrm{c}\left(\mathrm{H_2O}\right)_{hc}$$

This equilibrium introduces the expression of the law of mass action, which is the relation:

$$K_a = \frac{x_{hc}}{x_c x_0^{hc}} \frac{\gamma_{hc}^{(II)}}{\gamma_c^{(II)} \gamma_0^{hc}} \tag{4.133}$$

In such cases, only an iterative method can be used to calculate the activity coefficients because, in order to find the molar fractions, we must already know the activity coefficients to use relations such as [4.133].

The UNIQUAC part of the model can be extended to the UNIFAC version in order to enhance the model's predictive capability.

This type of model can obviously be used for ionic solutions "with no solvent" such as pure salts in the molten state.

5

Determination of the Activity of a Component of a Solution

In this chapter, we shall examine the methods for determining the activities, or the activity coefficients of the components of a condensed liquid solution whose composition is known. Note in passing that this determination of the activity may soon yield that of the chemical potential of the same component, if we know the chemical potential of that component in the reference solution.

Remember that the activity and the activity coefficient of component of a solution depend simultaneously on the composition of the solution and its temperature. Consequently, a determination of the activity of a component is valid only at a given temperature and for a known composition of the solution.

Remember, also, that there are several activities for the same component depending on the convention chosen to define it (see section A.2.5), namely:

– convention (I) – pure-substance reference;

– convention (II) – infinitely-dilute solution reference;

– convention (III) – molar solution reference for all solutes.

Hence, if it is not universal, each method must specify the convention in the context of which the determination is performed.

Modeling of Liquid Phases, First Edition. Michel Soustelle.

The methods for determining the activities (or the activity coefficients) can be divided into two main categories:

– experimental methods, which are our focus in this chapter;

– methods using a model of a solution – methods which stem directly from the study of different models (see Chapters 2, 3 and 4).

The experimental methods which we are about to examine are based on the properties of the solutions – specifically on their behavior in a system at physicochemical equilibrium. The component whose activity we wish to measure is involved in a physical, chemical or electrochemical equilibrium, and the only unknown activity is that for which we are searching. Certain methods apply more to molecular solutions than to ionic solutions, whereas others are reserved for conductive solutions (ionic solutions or electrical conductors), and others are valid for all types of solutions.

5.1. Calculation of an activity coefficient when we know other coefficients

Before discussing experimental methods *per se* for determining the activity, we shall examine two methods which are, in fact, calculation methods based on knowledge of either the activity of the other species in the solution or the activity of the species in question at a different temperature to the desired conditions.

5.1.1. *Calculation of the activity of a component when we know that of the other components in the solution*

Suppose that, for all compositions between a known state (generally the reference state) and the composition under examination, we know the activities (or activity coefficients) of all the components of a solution in the same frame of reference, except for one of them, and we are going to calculate the unknown activity of that component for the chosen composition. This method is founded on the Gibbs–Duhem relation, which is valid regardless of the convention adopted. Thus, we obtain the activity (or the activity coefficient) in the chosen convention for the known values.

For the activity coefficients, at constant temperature and pressure and for a solution with N components (see equation A.2.23), this relation is written as:

$$\sum_{i=1}^{N} x_i \,\mathrm{d}\ln\gamma_i = 0 \qquad [5.1]$$

In light of relation [5.1], if we wish to determine the activity coefficient γ_j of the component j whose molar fraction is x_j, we shall write:

$$\mathrm{d}\ln\gamma_j = -\sum_{k\neq j} \frac{x_k}{x_j}\,\mathrm{d}\ln\gamma_k \qquad [5.2]$$

This relation is integrated between two states p and q. Each state is characterized by a composition of the solution:

$$\int_p^q \mathrm{d}\ln\gamma_j = -\sum_{k=j} \int_p^q \frac{x_k}{x_j}\,\mathrm{d}\ln\gamma_k \qquad [5.3]$$

In general, the lower bound p is chosen as the reference state, which gives a value of 1 for the activity coefficient γ_j, and the upper bound q is taken as the solution in which we are seeking the coefficient. In convention (I), the pure-substance reference, this gives us:

$$\int_1^{\gamma_j^{(I)}} \mathrm{d}\ln\gamma_j^{(I)} = -\sum_{k\neq j} \int_1^q \frac{x_k}{x_j}\,\mathrm{d}\ln\gamma_k^{(I)} \qquad [5.4]$$

Integration yields:

$$\ln\gamma_j^{(I)} = -\sum_{k\neq j} \int_1^q \frac{x_k}{x_j}\,\mathrm{d}\ln\gamma_k^{(I)} \qquad [5.5]$$

In convention (II), for the solvent, in the infinitely-dilute solution reference (which is to say, pure solvent), the relation is identical to the previous one:

$$\ln\gamma_0^{(II)} = -\sum_{k\neq 0} \int_1^q \frac{x_k}{x_0}\,\mathrm{d}\ln\gamma_k^{(II)} \qquad [5.6]$$

In convention (II), for the solvent, in the infinitely-dilute solution reference, the relation becomes:

$$\ln \gamma_s^{(II)} = -\sum_{k \neq s} \int_0^q \frac{x_k}{x_s} \mathrm{d} \ln \gamma_k^{(II)} \qquad [5.7]$$

Expressions [5.5], [5.6] and [5.7] are usually used by numerical integration.

5.1.2. *Determination of the activity of a component at one temperature if we know its activity at another temperature*

If we know an activity coefficient at a certain temperature, it is possible to obtain the value for another temperature, knowing the dissolution enthalpy of the component as a function of the composition and the temperature.

Let us employ the terms $\overline{H_i^*}$ and $\overline{H_i^x}$ respectively to denote the partial molar enthalpies of the component *i* in the reference solution and in the solution under study, for which the molar fraction of the component *i* is *x*. The application of Helmholtz's second relation to the chemical potential of a component *i* (which is the partial molar Gibbs energy of that component) is written:

$$\frac{\partial(\mu_{\mathrm{i}} / T)}{\partial T} = -\frac{\overline{H_i^x} - \overline{H_i^*}}{T^2} = \mathrm{R} \frac{\partial \ln \gamma_i^{(*)}}{\partial T} \qquad [5.8]$$

From this, we deduce the variation of the activity coefficient of that component:

$$\frac{\partial \ln \gamma_i^{(*)}}{\partial T} = \frac{\overline{H_i^*} - \overline{H_i^x}}{\mathrm{R} T^2} \qquad [5.9]$$

If we consider a solvent, regardless of the reference state, or a solute in the pure-substance reference (I), the above relation is written:

$$\frac{\partial \ln \gamma_i^{(I)}}{\partial T} = \frac{h_i^0 - \overline{H_i^x}}{\mathrm{R} T^2} \qquad [5.10]$$

The difference $h_i^0 - \overline{H_i}$ appears as the opposite of the partial molar enthalpy of dissolution $\overline{\Delta_{diss} H_i^x}$ of substance *i* from the pure state to the state of composition *x*.

If, for a solute, we choose reference (II) – the infinitely-dilute solution – then relation [5.9] is written as:

$$\frac{\partial \ln \gamma_i^{(II)}}{\partial T} = \frac{\overline{H_i^\infty} - \overline{H_i^x}}{\mathrm{R}T^2} \qquad [5.11]$$

The numerator in the right-hand fraction can also be written as:

$$\overline{H_i^\infty} - \overline{H_i^x} = \left(\overline{H_i^\infty} - h_i^0\right) - \left(\overline{H_i^x} - h_i^0\right) = \overline{\Delta_{diss} H_i^\infty} - \overline{\Delta_{diss} H_i^x} \qquad [5.12]$$

Thus, we find the difference between the variation of the partial molar enthalpy of dissolution of the pure substance in an infinitely-dilute solution and that of dissolution of the same pure substance in a solution of the chosen composition. These two values are given (Figure 5.1) on the curve representing the enthalpy of dissolution of the component as a function of its molar fraction. The first value $\overline{\Delta_{diss} H_i^\infty}$ is the slope of the tangent to the origin of the curve, and the second value $\overline{\Delta_{diss} H_i^x}$ is the slope of the tangent to the same curve at abscissa point *x*.

It is possible to integrate the different expressions [5.11] and [5.12] if we know the variations of the enthalpies of dissolution with temperature.

Usually, these enthalpies are considered to be constants within a reasonable range of temperature, so between two temperatures *T* and *T*', we can integrate relation [5.9] in the different cases in the form:

$$\ln \gamma_{i(T)}^{(*)} - \ln \gamma_{i(T')}^{(*)} = \frac{\overline{H_i^*} - \overline{H_i^x}}{\mathrm{R}} \left(\frac{1}{T'} - \frac{1}{T} \right) \qquad [5.13]$$

The partial molar enthalpies $\overline{H_i^*}$ and $\overline{H_i^*}$ or the enthalpies of dissolution $\overline{\Delta_{diss} H_i^x}$ and $\overline{\Delta_{diss} H_i^\infty}$ are therefore constants, and one of the values of the activity coefficient $\gamma_{i(T')}^{(*)}$ is known in the same composition.

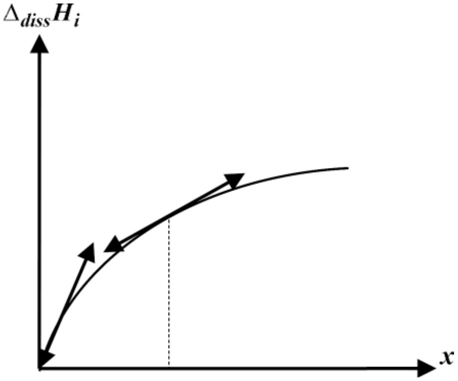

Figure 5.1. *Enthalpy of dissolution of a species as a function of the molar fraction*

5.2. Determination of the activity on the basis of the measured vapor pressure

The vapor pressure methods derive directly from the properties of the equilibrium between the condensed solution and the vapor – a consequence of the equality of the chemical potentials of the component in question in the solution and in the gaseous phase at equilibrium with it. This equality gives us a very general relation between fugacity coefficient of component i in the gaseous phase $\Phi_i^{(G)}$, the total pressure, the activity $a_i^{(L)}$ of the component in the solution and an equilibrium constant $K_i^{(LV)}$:

$$\frac{\Phi_i^{(G)} P}{a_i^{(L)}} = K_i^{(LV)} \qquad [5.14]$$

In experimental terms, these methods only require measurements of the pressure and the composition of the gaseous phase.

We can distinguish two approaches:

– one, known as the direct method, which is primarily used with a pure-substance reference convention, meaning either for a component in a solution, for which we choose convention (I), or for the solvent of a solution, for which we choose convention (II);

– the other, which is based on the measurement of Henry’s constant, and is mainly used for solutes with the choice of convention (II).

5.2.1. *Measurement by the direct method*

For this method, we choose to adopt convention (I). Thus, the equilibrium constant for the liquid/vapor equilibrium is the same as the saturating vapor pressure of the pure liquid in question P_i^0, which is expressed by:

$$\frac{\Phi_i^{(G)} P}{a_i^{(L)(I)}} = K_i^{(LG)(I)} = P_i^0 \qquad [5.15]$$

In order for us to use this method, we need the pure component *i* and the solution to be in the same physical state so as to preserve the same standard state. Such is often the case, for example, with aqueous solutions of salts in which the water and the solution are in the same state, which cannot be said for the salt. Particular caution must be exercised with solid solutions: the solution and the solid *i* under examination must crystallize in the same crystalline system.

The simplest case of the use of the direct method is found when the component being studied is much more volatile than the others, so that it alone practically constitutes the gaseous phase, which is then said to be pure. The conditions then allow us to treat fugacity and pressure as one and the same thing. Relation [5.15] then directly gives us:

$$\gamma_i^{(L)(I)} = \frac{P}{x_i^{(L)} P_i^0} \qquad [5.16]$$

The pressure P is often not very different from the saturating vapor pressure of the pure substance P_i^0. To improve the accuracy, therefore, it is preferable to work with a differential measurement. We use a pressure-differential sensor, which measures the difference in pressure that exists between two tanks placed in a thermostatic chamber at the chosen temperature. In one tank, equilibrium is established between the pure component and the vapor phase, and in the other, that equilibrium is established between the solution and the vapor phase. The saturating vapor pressure of the pure gas is measured using an absolute pressure sensor in relation to the first chamber, or read from thermodynamic tables.

When two components are notably present in the gaseous phase but it can be considered to exhibit perfect behavior both as a gas and as a solution, relation [5.15] gives us:

$$\gamma_i^{(L)(I)} = \frac{x_i^{(G)} P}{x_i^{(L)} P_i^0} \tag{5.17}$$

In addition to the above measurements, the method requires us to know the composition of the gaseous phase, which can be found using a mass spectrometer.

More generally, we can use the Lewis relation to characterize the fugacity of the component *i* in the gaseous phase on the basis of its fugacity coefficient in the pure state $\Phi_i^{0(G)}$. That relation is:

$$\Phi_i^{(G)} = \Phi_i^{0(G)} x_i^{(G)}$$

Relation [5.15] then becomes:

$$\gamma_i^{(L)(I)} = \frac{\Phi_i^{0(G)} x_i^{(G)} P}{x_i^{(L)} P_i^0} \tag{5.18}$$

The fugacity coefficient of the pure gas is supposed to be known or determined separately.

5.2.2. *Method using the vaporization constant in reference II*

If we adopt convention (II) for a solute, the expression of the liquid/vapor equilibrium for the component *i* is written as follows at a given temperature:

$$\frac{\Phi_i^{(G)} P}{\gamma_i^{(L)(II)} x_i^{(L)}} = K_i^{(LV)} \tag{5.19}$$

If the gaseous mixture can be considered to be perfect, the equilibrium constant is the product of the saturating vapor pressure by Henry's constant

($K_{iH}^{(L)}$) of the component i, and relation [5.19] gives us the following for equilibrium:

$$\frac{P_i}{\gamma_i^{(L)(II)} x_i^{(L)}} = K_i^{(LV)} = P_i^0 K_{iH} \qquad [5.20]$$

If the solution were perfect, it would obey Henry's law, and would therefore satisfy the equation:

$$\frac{P_i}{x_i^{(L)}} = P_i^0 K_{iH} \qquad [5.21]$$

This means that the constant K_{iH} is the limit, as the context $x_i^{(L)}$ tends toward zero – in other words, if $\gamma_i^{(L)}$ is equal to 1, with the ratio $\frac{P_i}{P_i^0 x_i^{(L)}}$, so:

$$K_{iH} = \lim_{x_i^{(L)} \to 0} \frac{P_i}{P_i^0 x_i^{(L)}} \qquad [5.22]$$

We determine the value of the ratio $\frac{P_i}{P_i^0 x_i^{(L)}}$ at various decreasing values of $x_i^{(L)}$, and extrapolate the curve obtained at $x_i^{(L)} = 0$. The ordinate value than gives us the constant K_{iH}.

The extrapolation is illustrated in Figure 5.2. The slope of the curve must be horizontal. Otherwise, the measurements of the ratio $\frac{P_i}{P_i^0 x_i^{(L)}}$ have not been taken for sufficiently low values of the molar fraction of i in the liquid and thus found the validity of the limit law with a sufficient degree of accuracy.

We can then feed that extrapolated value back into equation [5.20] and deduce the activity coefficient of the component i in convention (II):

$$\gamma_i^{(L)(II)} = \frac{P_i}{x_i^{(L)} P_i^0 K_{iH}} = \frac{x_i^{(G)} P}{x_i^{(L)} P_i^0 K_{iH}} \qquad [5.23]$$

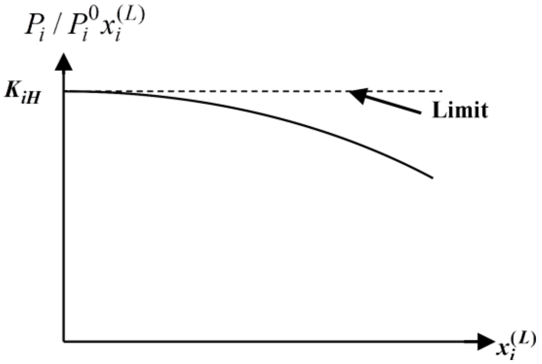

Figure 5.2. *Determination of Henry's constant*

As before, this law is easier to use when the component i is practically pure in the gaseous phase ($x_i^{(G)} = 1$), which is rare. If not, then a measurement of the composition of the gaseous phase is needed.

5.3. Measurement of the activity of the solvent of the basis of the colligative properties

A colligative property is a property of a solvent which depends solely on its molecular constitution rather than on the nature of the solutes in that solution. The existence of colligative properties is the consequence of the major dilution of the solute by the solvent.

Thus, these methods are used to determine the activities of solvents. Hence, we always use the pure-solvent reference, irrespective of the convention chosen for the solution. Therefore, this convention no longer needs to be explicitly stated.

Note that the method using the vapor pressures (see section 5.2.1) is already a colligative method.

5.3.1. *Use of measuring of the depression of the boiling point – ebullioscopy*

We suppose that the solute has a very low vapor pressure in comparison to that of the solvent. We can consider that the gaseous phase is pure and contains only the vapor of the solvent. In the presence of the solute, the solvent's boiling point is lowered. To calculate this depression, we write the equilibrium, which is expressed by the equality of the chemical potentials of the solvent in both phases, with the gaseous phase being under partial pressure of 1 atmosphere from the solution (at boiling point). Thus, we find the expression:

$$\frac{\partial \ln \gamma_0 x_0^{(L)}}{\partial T} = -\frac{\Delta_v h_0^0}{\mathrm{R}T^2} \qquad [5.24]$$

To begin with, we can suppose that the vaporization enthalpy $\Delta_v h_0^0$ is independent of the temperature. This being the case, it is easy to integrate this expression between the boiling point of the pure solvent $T_{0(Boil)}$ and the boiling point of the solution T. If we use $\Delta T_{(Boil)}$ to denote the difference between $T - T_{0(Boil)}$, we find:

$$\ln \gamma_0 \cong -\frac{\Delta_v h_0^0 \Delta T_{(Boil)}}{\mathrm{R}T_{0(Boil)}^2} - \ln\left(1 - \sum_s x_s^{(L)}\right) \qquad [5.25]$$

Thus, this relation enables us to determine the activity coefficient of the solvent at temperature T, which is not hugely different from $T_{0(Boil)}$.

If the solution is sufficiently dilute, the sum of the molar fractions of the solutes is much less than 1 and we can content ourselves with the first term of the expansion of the logarithm, and write:

$$\ln \gamma_0 \cong -\frac{\Delta_v h_0^0 \Delta T_{(Boil)}}{\mathrm{R}T_{0(Boil)}^2} - \sum_s x_s^{(L)} \qquad [5.26]$$

Now, if the enthalpy of vaporization depends on the temperature, it is sufficient to take it into account by integrating relation [5.24]. Note that this precaution is actually very rarely necessary, because the boiling points of the solvent and the solution are only a few degrees apart.

For the moment, we shall restrict ourselves to applying relation [5.26] to molecular solutions. We shall discuss the application to ionic solutions in the next section (see section 5.3.2), with regard to the cryoscopic method.

5.3.2. *Use of measuring of the depression of the freezing point – cryoscopy*

In a very similar manner to ebullioscopy, which we have just discussed, we can determine the activity, or the activity coefficient, of a solvent by cryoscopy, i.e. by looking at the depression of the freezing point of the solvent $\Delta T_{(F)}$ owing to the presence of the solutes. If the solvent is pure in the solid phase, in the same conditions and with the same hypotheses, we establish a relation similar to relation [5.25] which, in the case of cryoscopy, is written as:

$$\ln \gamma_0 \cong -\frac{\Delta_F h_0^0 \Delta T_{(F)}}{\mathrm{R} T_{0(F)}^2} - \ln\left(1 - \sum_s x_s^{(L)}\right) \qquad [5.27]$$

Thus, we obtain the activity coefficient at a temperature T which is not hugely different from the melting point of the pure solvent $T_{0(F)}$.

As before, if the solution is sufficiently dilute, the sum of the molar fractions of the solutes is smaller than 1, and we can content ourselves with the first term in the expansion of the logarithm and write:

$$\ln \gamma_0 \cong -\frac{\Delta_F h_0^0 \Delta T_{(F)}}{\mathrm{R} T_{0(F)}^2} - \sum_s x_s^{(L)} \qquad [5.28]$$

This relation is easily applicable for molecular solutions.

In the case of ionic solutions, a factor called the *Van't Hoff factor*, due to the dissociation of the electrolyte, comes into play in the sum of the molar fractions of the solutes. Thus, the situation is complex for weak electrolytes with incomplete dissociation, for which the dissociation coefficient is unknown. In order to resolve this impasse, it is possible to perform measurements using both ebullioscopy and cryometry at once.

Let us take the example of a molecule of solute s which dissociates, giving rise to ν_s ions, and let α_s be its degree of ionization. If we initially consider n_s moles of non-dissociated solute, the total amount of solute $n_{t(s)}$ after partial dissociation will be the sum of the amount of non-dissociated species and that of the ions:

$$n_{t(s)} = n_s\left(1 - \alpha_s\right) + \alpha_s n_s \nu_s = n_s\left[1 + \left(\nu_s - 1\right)\alpha_s\right] \qquad [5.29]$$

In this case, the sum of the molar fractions of the solutes will be:

$$\sum_s x_s = \sum_s \frac{n_s\left[1+(\nu_s-1)\alpha_s\right]}{n_0+n_s\left[1+(\nu_s-1)\alpha_s\right]} \tag{5.30}$$

If the solution is sufficiently dilute, the second term in the denominator of the above fraction is smaller than n_0 (the amount of solvent) and therefore the sum of the molar fractions is approximately:

$$\sum_s x_s \cong \sum_s x_s\left[1+(\nu_s-1)\alpha_s\right] \tag{5.31}$$

For each dissociable solute, we see the emergence of a factor i_s defined by:

$$i_s = \left[1+(\nu_s-1)\alpha_s\right] \tag{5.32}$$

This factor i_s is known as the *Van't Hoff factor*.

The relation found by ebullioscopy therefore involves the mean activity coefficient. According to expression [5.26], it is written thus:

$$\ln\gamma_{\pm} \cong -\frac{\Delta_v h_0^0 \Delta T_{(Eb)}}{\mathrm{R}T_{0(Eb)}^2} - \sum_s i_s x_s^{(L)} \tag{5.33}$$

If the solution contains only one electrolyte, then relation [5.33] can be simplified to:

$$\ln\gamma_{\pm} \cong -\frac{\Delta_v h_0^0 \Delta T_{(Eb)}}{\mathrm{R}T_{0(Eb)}^2} - i_s x_s^{(L)} \tag{5.33a}$$

Similarly, on the basis of cryoscopic measurements, relation [5.28] gives us:

$$\ln\gamma_{\pm} \cong -\frac{\Delta_F h_0^0 \Delta T_{(F)}}{\mathrm{R}T_{0(F)}^2} - \sum_s i_s x_s^{(L)} \tag{5.34}$$

In the case of the dissolution of a single electrolyte, relation [5.34] can be simplified to:

$$\ln \gamma_{\pm} \cong -\frac{\Delta_F h_0^0 \Delta T_{(F)}}{\mathrm{R} T_{0(F)}^2} - i_s x_s^{(L)} \qquad [5.34a]$$

Thus, we have two equations [5.33a] and [5.34a] and two unknowns: the coefficient of dissociation α_s and the mean activity coefficient $\gamma_{\pm}$. Obviously, this coefficient will be obtained for a mean temperature between the solvent's freezing and boiling points.

NOTE.– In the case of strong electrolytes (α_s = 1), the *Van't Hoff factor* is equal to the number of ions ν_s supplied by the dissociation of that electrolyte.

5.3.3. *Use of the measurement of osmotic pressure*

Remember that the osmotic pressure is the pressure difference between a solution and its solvent, separated by a semi-permeable membrane, which allows the solvent, but not the solute, to pass through (see Figure 5.3).

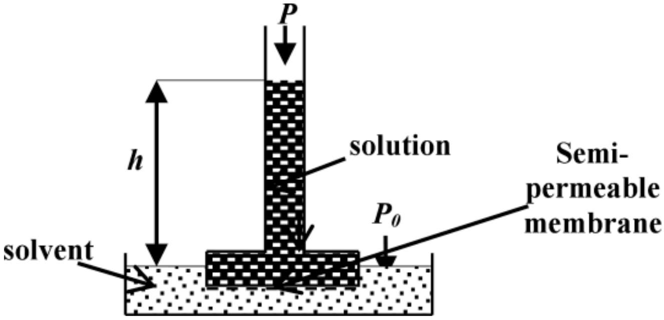

Figure 5.3. *Osmotic pressure*

Taking account of the variation of the chemical potential with the pressure, we can show that for sufficiently dilute, wherein the partial molar volume of the solvent in the solution can be treated as the same as its molar volume in the pure state, the equality of the solvent's chemical potential in both phases gives us the relation:

$$\ln \gamma_0 = -\frac{\Pi v_0}{\mathrm{R}T} - \ln x_0 \qquad [5.35]$$

In this relation, Π is the osmotic pressure, i.e. the difference between the pressure P over the solution and the pressure P_0 over the solvent (see Figure 5.3).

If the solution contains several solutes with the molar fraction x_s, this expression can also be written as follows, for a dilute solution:

$$\ln \gamma_0 = -\frac{\Pi v_0}{\mathrm{R}T} + \sum_s x_s \qquad [5.36]$$

In order for the accuracy to be sufficient, the osmotic pressure – i.e. the height h measured in Figure 5.3 – must be significant. This result is easy to obtain with solutions of polymers, for which numerous semi-permeable membranes are available. It is more difficult to find a good membrane for smaller molecules of solutes. Nevertheless, often, the measurement is significant because, for instance, for an aqueous solution of sodium chloride of 0.1 molar concentration, at 25°C, the osmotic pressure reaches 4.61×10^5 Pa.

5.4. Measuring the activity on the basis of solubility measurements

The solubility which results from an equilibrium of a component between two phases – one the pure phase of one of the components, and the other the solution – can also be used to determine the activity or the activity coefficient of a component in a solution. In general, it pertains mainly to solutes, but it is also applicable to solutions for which the concept of a solvent is no longer clear. The two phases including the component in questions are usually the pure solid phase on the one hand, and the liquid solution on the other.

Nevertheless, we shall distinguish between two cases, depending on whether the solution is molecular or ionic, i.e. whether the species in solution is identical to that of the solid, or whether it has undergone alterations as it dissolved.

5.4.1. *Measuring the solubilities in molecular solutions*

The molecule of the component in pure phase and that of the solution are identical; thus, there is a simple equilibrium between the two phases, so the chemical potentials of the component concerned are equal for both phases. Thus, we find the following relation, which is valid regardless of the convention chosen for the solution:

$$\ln \gamma_i^{(L)} = \frac{\Delta_F h_i^0}{\mathrm{R}} \left(\frac{1}{T_{i(F)}} - \frac{1}{T} \right) - \ln(1 - \sum_{j \neq i} x_j^{(L)}) \qquad [5.37]$$

If the solution has a very high content of component 0 (as is the case with a solvent), this relation is simplified, for that solvent, to:

$$\ln \gamma_0^{(L)} = \frac{\Delta_F h_0^0}{\mathrm{R}} \left(\frac{1}{T_{0(F)}} - \frac{1}{T} \right) + \sum_{j \neq 0} x_j^{(L)} \qquad [5.38]$$

Thus, relations [5.37] or [5.38] enable us to calculate the activity coefficient of a component if we know the composition of the solution, the temperature of solubility equilibrium chosen, the melting point of the pure component in its natural phase and its standard enthalpy of melting at the temperature in question.

5.4.2. *Measuring the solubilities in ionic solutions*

We shall only envisage the case of complete dissociation of the electrolyte, which is true for all salts and most other species with low solubility at the solubility equilibrium, because then the solutions are very dilute.

The species in solution (the ions) result from this dissociation upon dissolution. The equilibrium between the solid and the solution, therefore, is characterized by a solubility product K_s. If S denotes the solubility measured by the amount of solid which has passed into solution (as opposed to the amount of ions in the solution), and if the dissociation of a molecule of solid yields ν_+ cations and ν_- anions, we can show that writing the equilibrium gives us the following relation:

$$S = \frac{C^{onst.}}{\gamma_\pm} \qquad [5.39]$$

$\gamma_\pm$ is the mean activity coefficient and the constant, which depends only on the temperature, is linked to the solubility product by:

$$C^{onst.} = \left(\frac{K_s}{\nu_+^{\ \nu_+} \nu_-^{\ \nu_-}} \right)^{1/(\nu_+ + \nu_+)} \qquad [5.40]$$

If we switch to a logarithmic system, relation [5.39] is rewritten as:

$$\ln \gamma_\pm = \ln C^{onst.} - \ln S \qquad [5.41]$$

The mean activity coefficient tends toward 1 when the ionic strength of the solution tends toward 0. Thus, we deduce relation [5.42]:

$$\ln C^{onst.} = \lim_{I \to 0} \left(\ln S \right) \qquad [5.42]$$

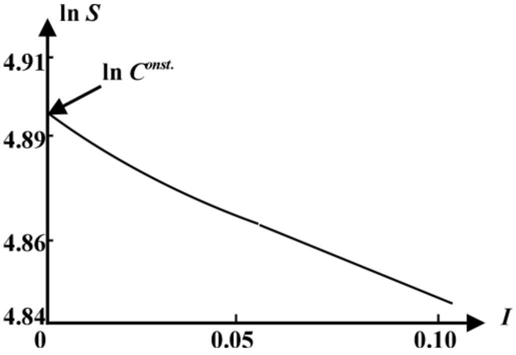

Figure 5.4. *Solubility of silver nitrate as a function of the ionic strength (reproduced from [POP 30])*

Thus, by measuring the solubility S at different ionic strengths I and extrapolating the curve at an ionic strength of zero (Figure 5.4), we obtain the value of the constant $C^{onst.}$ in relation [5.41], because then the mean activity coefficient tends toward 1. From this we deduce the value of the solubility product K_s by relation [5.40], and that of the mean activity coefficient, regardless of the value of the ionic strength, by relation [5.41].

5.5. Measuring the activity by measuring the distribution of a solute between two immiscible solvents

If we know the activity coefficient $\gamma_i^{(\alpha)}$ of a component in a phase (α), for example, and the partition coefficient $K_i^{(\alpha\beta)}$ of that component between that phase α and another phase β which is immiscible with it, then it is easy, by describing the equality of the chemical potentials of the component i between the two phases, to obtain the other activity coefficient $\gamma_i^{(\beta)}$ using the relation:

$$\gamma_i^{(\beta)} = \frac{K_i^{(\alpha\beta)} \gamma_i^{(\alpha)} x_i^{(\alpha)}}{x_i^{(\beta)}} \tag{5.43}$$

Thus, it is only necessary to know the molar fractions $x_i^{(\alpha)}$ and $x_i^{(\beta)}$ of the component in the two phases at equilibrium and of the activity coefficient in phase α to obtain $\gamma_i^{(\beta)}$. Relation [5.43] is independent of the reference state chosen.

5.6. Activity in a conductive solution

If the solution at hand is able to conduct electrical current, the panoply of methods that can be used is enriched with a set of electrochemical methods. These methods can be used in the case of ionic solutions used as electrolytes.

5.6.1. *Measuring the activity in a strong electrolyte*

In a strong electrolyte, we may be led to measure either the absolute activity of an ion or the mean activity of the electrolyte.

5.6.1.1. *Measuring the absolute activity of an ion*

The measurement of the absolute activity of an ion of a strong electrolyte (salts, strong acids and bases) is based on the complete dissociation of that electrolyte into ions, and uses the measurement of the electromotive force of a cell involving that ion.

In principle, we use the fact that electrode potentials are linear functions of the logarithm of the ion activity if the cell's behavior is reversible.

Thus, it is sufficient to construct a battery formed of an active electrode of the ion under study – the measuring electrode – and a reference electrode. In general, the liquids in which the electrodes are bathed are connected by a siphon, filled with a concentrated electrolyte in order to minimize the junction potentials.

For example, in order to measure the activity of the hydrogen ion, we can construct a system containing a mercurous-chloride electrode (the reference electrode) and a hydrogen electrode (the measuring electrode), connected by a junction siphon (see Figure 5.6).

The potential, in this case, is measured at 25°C, and obeys the relation:

$$E_{\text{abs}} = 0.252 - 0.06 \ln \left| \text{H}^+ \right| \qquad [5.44]$$

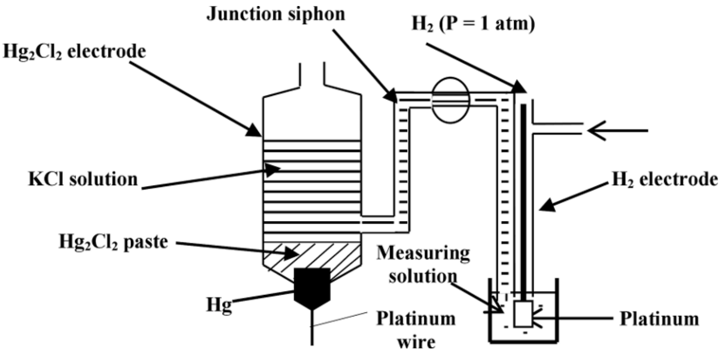

Figure 5.5. *Measuring the activity of the protons in a solution*

Thus, by measuring this potential, we are able to measure the activity of the solutions in terms of protons.

A variant of this method is to create a concentration cell by taking two identical electrodes, immersed in two solutions with different activities, one of which is known.

For example, we immerse two silver electrodes in two solutions of Ag^+ ions – one in which the activity of the silver is known (solution 2) and the other being the solution in which we wish to measure the activity in silver ions (solution 1). The potential of the cell thus constituted will be:

$$E_{\text{abs}} = e_{Ag}^{0} + 0.06 \ln \left| Ag^{+} \right|_{2} - e_{Ag}^{0} - 0.06 \ln \left| Ag^{+} \right|_{1} \qquad [5.45]$$

Thus:

$$E_{\text{abs}} = 0.06 \ln \frac{\left| Ag^{+} \right|_{2}}{\left| Ag^{+} \right|_{1}} \qquad [5.46]$$

This relation enables us to measure the activity of the unknown solution without needing to know the value of the standard potential of silver e_{Ag}^{0}.

In practice, the true value of the activity of an ion is difficult to find because of the error introduced by the junction siphon. Although the assembly attempts to minimize the junction potential, our calculation supposes that the potential is null, and the true value of the activity coefficient of the ion is tainted with an error.

5.6.1.2. *Measurement of the mean activity coefficient of a strong electrolyte*

In order to obtain more accurate results, it is preferable to use cells with no junction, but in that case, the method of measuring the activity coefficients of strong electrolytes will yield only the mean activity coefficient.

If we know the standard potential of a carefully-chosen cell (which may be determined experimentally or calculated on the basis of the electrode standard potential tables), then we can calculate the mean activity coefficient at any concentration.

We shall demonstrate the method with the example of measuring the mean activity coefficient of a zinc chloride solution of concentration *c*. For that purpose, we create the following cell with no junction:

$\mathrm{Zn} / \mathrm{ZnCl_2}$ (solution) / AgCl (dissolved), Ag

The cell's emf would be:

$$E_{\text{abs}} = E^0 - \frac{\mathrm{R}T}{2\mathrm{F}} \ln \left|\mathrm{Zn}^{++}\right| \left|\mathrm{Cl}^-\right|^2 \tag{5.47}$$

This involves only the product of the activities $\left|\mathrm{Zn}^{++}\right|\left|\mathrm{Cl}^-\right|^2$ rather than the individual activities of the ions, which would be:

$$\left|\mathrm{Zn}^{++}\right| = [Zn]\,\gamma_{Zn^{++}} = c\gamma_{Zn^{++}} \text{ and } \left|\mathrm{C}l^-\right| = \left[\mathrm{C}l^-\right]\gamma_{Cl^-} = 2c\gamma_{Cl^-} \tag{5.48}$$

By combining relations [5.47] and [5.48], the emf of the chain becomes:

$$E_{\text{abs}} = E^0 - \frac{\mathrm{R}T}{2\mathrm{F}} \ln 4c^2 - \frac{\mathrm{R}T}{2\mathrm{F}} \ln \gamma_{\mathrm{Zn}^{++}} \gamma_{Cl^-}^2 \tag{5.49}$$

However, the mean activity coefficient is defined by:

$$\gamma_\pm^3 = \gamma_{Zn^{++}} \gamma_{Cl^-}^2 \tag{5.50}$$

Relation [5.49] can thus be written in the form:

$$E_{\text{abs}} = E^0 - \frac{\mathrm{R}T}{2\mathrm{F}} \ln 4c^3 - \frac{3\mathrm{R}T}{2\mathrm{F}} \ln \gamma_\pm \tag{5.51}$$

If we know the standard cell potential E^0 and the concentration *c*, we can deduce the mean activity of the ions using the relation derived from the one above:

$$\ln \gamma_\pm = \frac{2\mathrm{F}}{\mathrm{R}T}\left(E^0 - E_{\text{abs}}\right) - \ln \frac{4c^2}{3} \tag{5.52}$$

Let us stress the fact that it is advisable to create cells without junctions, because no matter how perfect those junctions may be, they cause significant errors of up to 50% on the value of the cell emf.

5.6.2. *Determination of the mean activity of a weak electrolyte on the basis of the dissociation equilibrium*

Suppose that we know the dissociation constant of the weak electrolyte AH and its dissociation coefficient α at the chosen concentration *c*. The dissociation constant is written:

$$K = \frac{\alpha^2 c}{1-\alpha}\frac{\gamma_{\pm}}{\gamma_{AH}} \qquad [5.53]$$

Hypothesize that we are dealing with a sufficiently dilute solution of electrolyte AH. We know that when the concentration decreases, solutions of neutral molecules approach the ideal state much more quickly than do those containing ions. Hence, we shall set $\gamma_{\mathrm{AH}} = 1$. Then, we immediately obtain:

$$\gamma_{\pm} = \sqrt{\frac{K(1-\alpha)}{\alpha^2 c}} \qquad [5.54]$$

This simplification means that we now only have one unknown value – the mean activity coefficient of the ions in the solution. Such an approximation is correct provided the concentration of electrolyte is no greater than 10^{-1}-10^{-2} moles per liter.

Appendices

Appendix 1

Statistical Methods of Numerical Simulation

The purpose of this appendix is not to give readers a grounding in statistical simulation, but rather to enable future thermodynamicists to conduct a dialog with simulation specialists. We wish to demonstrate the physics which lies behind each simulation, and its reach, so that it is possible to appreciate the thermodynamic results of a simulation that the reader has conducted in complete collaboration with the specialists.

The objective of a simulation is to generate particle motion by using appropriate algorithms and to obtain an adequate distribution function, and thus, the macroscopic properties. In thermodynamics, we use this method to calculate the energy of interaction of a collection of molecules, the part of configuration of the translational partition function and the radial distribution function.

A.1.1. The physical bases of simulation

A simulation, whatever the method employed, is based on physical hypotheses. In the case of the molecular simulation, there are two fundamental hypotheses:

– the first pertains to the link between the internal energy of the set of molecules and the interactions which exist between them. One of the most commonly chosen hypotheses is to consider only the sum of the pairwise

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interactions between the molecules, excluding interactions involving more than two substances. In the case of the internal energy of configuration, it obeys the relation:

$$U_I(1,2,\ldots N)=\sum_{i<j}^{N}\varepsilon_{i,j}\left(r_{i,j}\right) \qquad \text{[A.1.1]}$$

Thus, we can calculate the configuration part of the canonical partition function of translation, which is:

$$I_I=\sum_{i<j}^{N}\exp\left[-\frac{\varepsilon_{i,j}\left(r_{i,j}\right)}{\mathrm{k_B}T}\right] \qquad \text{[A.1.2]}$$

We can also obtain the radial distribution function given by:

$$g(r)=\frac{1}{\rho N}\sum_{i=1}^{N}\sum_{j=1}^{N}\delta_{i,j}\left(r-r_{i,j}\right) \qquad \text{[A.1.3]}$$

– the second fundamental hypothesis is the choice of the potential function of interactions between molecules. In the hypothesis chosen in relation [A.1.1], it is the choice of the function $\varepsilon_{i,j}\left(r_{i,j}\right)$.

A variety of laws have been encountered for the potential of attraction:

– the Lennard-Jones potential in $1/d^6$, which relates to the van der Waals forces between molecules and stems from electrostatic forces between electrical dipoles. This potential is used for real gases and liquids;

– the Coulombian potential in $1/d$, stemming from the electrostatic forces between two points or two conductive spheres, used between ions in an ionic solution;

– the ion-dipole potential in $1/d^2$ of electrostatic nature between a conductive sphere and an electric dipole, which is useful, for instance, for examining the solvation of ions in a dipolar medium such as water;

– the potential for interaction between a molecule and a surface, in $1/d^3$, used for physical adsorption, which is the resultant of the different Lennard-Jones potentials.

For the repulsion potential, we normally use a potential in $d^{1/n}$, frequently with $n = 12$, which expresses the repulsion to the interpenetration of the electron clouds, which is therefore used for ions as well as molecules. To avoid an integral which diverges as the distance tends toward zero, we often adopt the approximation of a hard sphere, which gives an infinite potential for a protection distance less than or equal to D which is the minimum approach distance.

Of course, the overall potential requires the combination of potential of attraction and a potential of repulsion in order to represent the possibility of a position of equilibrium.

A.1.2. Construction of the sample

If we consider a system containing, for example a mole of liquid, this represents around 10^{24} molecules, which represents $10^{24} \times 10^{24}/2$, which is around 10^{48} couples of molecules that need to be taken into account in relation [A.1.1], for all combinations of relative positions of those couples (the configurations of the system). There is no computer system, no modern memory, that is capable of storing such a phenomenal amount of information. Therefore, we need to perform the simulation on a much smaller sample, whilst remaining faithful to the behavior of the real system. The sample adopted, therefore, needs to satisfy two fairly contradictory conditions:

– it should not contain too many elements in order to be manageable;

– it should contain enough elements for it to still be representative of the system.

In order to resolve this dilemma, we use a variety of techniques:

– limiting the distance over which the interactions between molecules are taken into account, by truncating the potential function;

– eliminating the edge effects, which can become very significant, relatively speaking, in a small system;

– testing the validity of the calculation at every step to limit its duration.

A.1.2.1. *Truncation of the potential function*

The curve showing the potential function generally tends toward zero when the distance between two elements increases, as is shown by Figure A.1.1. This means that, if we accept a slight degree of error, we can take account only of a molecule's interactions with its fairly close neighbors, that is, if the distance $r_{i,j}$ between two elements is less than a given distance r_c, called the *cutoff distance* (Figure A.1.2), so:

$$\begin{aligned} &\text{if } r_{i,j} \le r_c \text{ then } \varepsilon = \varepsilon_{\mathrm{i,j}} \\ &\text{if } r_{i,j} > r_c \text{ then } \varepsilon = 0 \end{aligned} \qquad \text{[A.1.4]}$$

We then compile what are called Verlet lists which, for each element in the sample, give the list of all the elements j which are at a distance less than a certain minimum distance r_m (Figure A.1.2), so as to be able to perform multiple steps of calculation without changing the list relative to a particle.

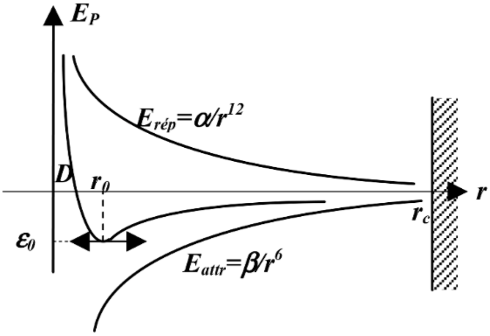

Figure A.1.1. *Lennard-Jones potential and cutoff radius*

The minimum radius r_m is such that:

$$r_m = r_c + 2k\Delta t \qquad \text{[A.1.5]}$$

In this formula, k is the number of times we use the list without changing it, Δt is the step increment (see section A.1.3.1). It is advisable to take the size of the sample for the calculation as that which contains N_{smpl} elements, which is given by:

$$N_{\text{smpl}} = \frac{4\pi}{3}\rho r_m^3 \qquad [A.1.6]$$

Here, ρ is the density of the real system in terms of molecules.

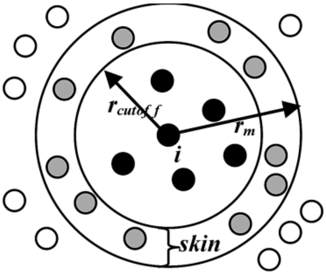

Figure A.1.2. *Cutoff radius and Verlet list*

A.1.2.2. *Limitation of edge effects*

When we choose a set with a small number of elements, the edge effects are very significant, meaning that a high proportion of the elements are near to the boundary of the system, and this poses two problems:

– during the course of a displacement, an element may stray out of the domain, and therefore we are no longer working with a constant number of particles. We remedy this problem by using what is known as the *periodic boundary condition*;

– an element near to the edge of the domain no longer inhabits its “normal” environment. We correct this effect by using the *minimum-image convention*.

A.1.2.2.1. *Periodic boundary condition*

Let us consider that the system in question is delimited by a cube of side length a. We can construct the cubes adjacent to that initial cell by exactly reproducing the composition of the initial cell. Figure A.1.3 offers a 2D representation of the stack thus created. The three Cartesian axes can be used to write, for example, that the central cell in our study is such that its boundaries have the abscissa values $X = a/2$ and $X = -a/2$, and similarly in the other two directions. During the displacement of the elements, one of them (A) near to the boundary may leave the central cell, crossing that boundary. So as to work with a constant number of elements, we shall use the Born and von Karman method, which consists of bringing in a corresponding element (B) across the opposite boundary, i.e. setting the following condition, for example, along the abscissa axis:

$$\begin{aligned} &\text{if } x_{\text{j}} < -a/2 \text{ then } x_{\text{j}} = x_{\text{j}} + a \\ &\text{if } x_{\text{j}} > a/2 \text{ then } x_{\text{j}} = x_{\text{j}} - a \end{aligned} \qquad [\text{A.1.7}]$$

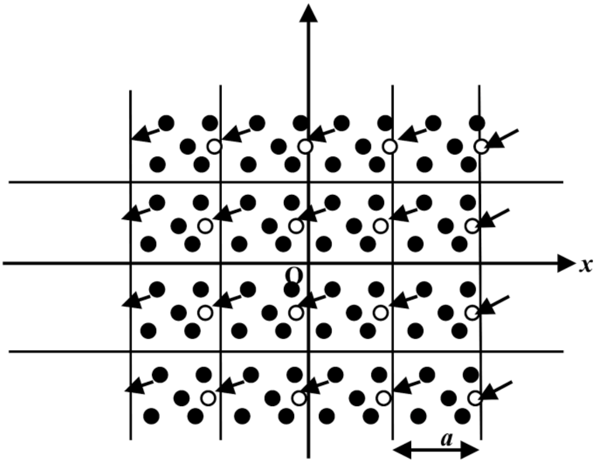

Figure A.1.3. *Born–von Karman periodic boundary condition*

A.1.2.2.2. *Minimum-image convention*

If an element A is too close to the border of its environment, there is a risk that it will not be complete. In order to correct this effect, we apply the minimum-image convention, which consists of including in the Verlet list for that element A, and in the calculation (Figure A.1.4), the elements neighboring A, situated in adjacent copies of the calculation cell, such as B.

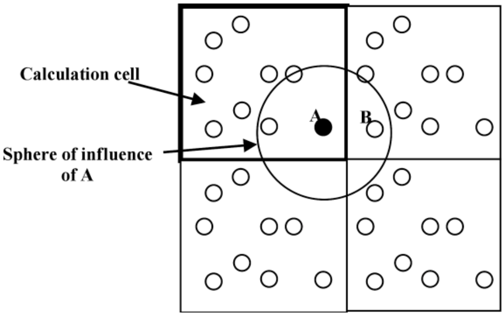

Figure A.1.4. *Minimum-image convention*

A.1.2.3. *Estimation of the duration of the calculation*

All of these calculation methods work on a step-by-step basis. A step has an increment, denoted by Δ*t*. In general, we begin with an initial configuration – e.g. the compact stack represented in two dimensions in Figure A.1.5 – and then, by successive displacements, at each step, we obtain a succession of configurations. One problem that arises during the calculation is knowing the number of steps after which the calculation should be halted in order to be representative of the state of the true system.

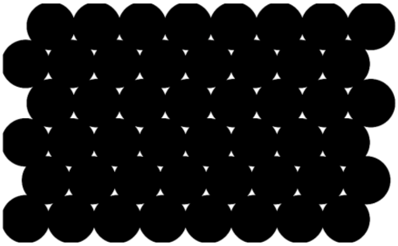

Figure A.1.5. *The initial compact hexagonal stack*

To determine this number of steps, we use a coefficient called the *self-correlation coefficient* on *g(r)*, for example.

The self-correlation coefficient measures how the value of x at step $t + \Delta t$ is connected to the previous value of x at step t; or, if readers prefer to think of it this way, it measures the influence of the previous state on the present state. This function is calculated by relation [A.1.8], which gives a curve that begins at 1 in the initial state and tends toward zero after a relatively long period of time (see Figure A.1.6). We need only set the acceptable error to determine the stopping point of the calculation.

$$C(t)=\frac{\sum_{k}^{M}\left[x(t_k)-\langle x\rangle\right]\left[x(t_{k+\Delta t})-\langle x\rangle\right]}{\sum_{k}^{M}\left[x(t_k)-\langle x\rangle\right]^2} \qquad [A.1.8]$$

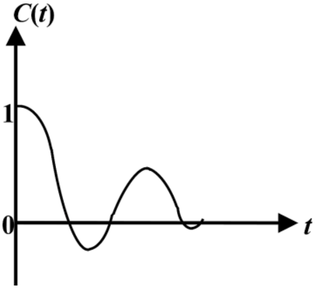

Figure A.1.6. *Self-correlation function*

A.1.3. The main calculation methods

There are two types of calculation methods: *static methods*, which lead to a state deemed to be stable, and *dynamic methods*, which show the system's evolution over time until it reaches a stable configuration.

A.1.3.1. *The Monte-Carlo method*

The Monte-Carlo method is a static statistical simulation method.

In this method, we begin with an initial configuration and the total energy of the system U_1 is calculated on the basis of relation [A.1.1]. Then, each element is shifted in the three directions of small amplitudes Δx, Δy and Δz. This amplitude is chosen as around 10% of the molecular diameter. Thus, each element has a new position, which gives a new configuration, for which we calculate the new energy U_2. If U_2 is less than U_1, the new configuration is accepted and the coordinates of the elements are saved to memory. If the new energy U_2 is greater than U_1, we calculate the ratio Π defined by:

$$\Pi = \exp\left(-\frac{U_2}{\mathrm{k_B}T}\right) / \exp\left(-\frac{U_1}{\mathrm{k_B}T}\right) \qquad [A.1.9]$$

This ratio is compared with a random number λ between zero and one. If λ is smaller than Π, the new configuration is refused and the first configuration is saved to memory again. If λ is larger than Π, the new configuration is accepted and saved to memory. Then, we carry out a new calculation step. All the elements are again shifted by the same distances as before, and the new value of Π is compared to a new random number λ', and so on. Thus, we find around 10^5 to 10^6 configurations.

The increments, Δx, Δy and Δz, of displacement must not be too large, otherwise few solutions are accepted, nor too small, which would lead to too high a number of acceptable solutions.

A.1.3.2. *The molecular dynamics method*

In this method, the evolution over time of the system with of N elements is studied on the basis of the fundamental law of dynamics:

$$\vec{F} = m\vec{a} \qquad [A.1.10]$$

The calculation step, in this method, is a period of time. The forces on each element are calculated at each step, with:

$$\vec{F}_i = -\frac{\partial}{\partial r_i}\left[\sum_{i<j} \varepsilon_{i,j}(r_{i,j})\right] \qquad [A.1.11]$$

For this, we use an appropriate algorithm, of which one of the best known is attributable to Verlet. In this algorithm, the displacement of a particle $\vec{r_i}$ at time $t + \Delta t$ is chosen on the basis of the previous two displacements at time t and $t - \Delta t$. Thus, we obtain the positions and velocities of all the elements at each step of the calculation. Based on those data inscribed in memory, we can calculate the radial distribution function using relation [A.1.3].

Appendix 2

Reminders of the Properties of Solutions

A.2.1. Values attached to solutions

Consider a solution comprising N components which contains n_1 moles of component 1, n_2 moles of component 2, …, n_i moles of component i, etc.

The molar fraction of component i is x_i, defined by:

$$x_i = \frac{n_i}{\sum_{i=1}^{N} n_i} \text{ where } 0 \le x_i \le 1 \text{ and } \sum_{i=1}^{N} x_i = 1 \qquad [\text{A.2.1}]$$

We use μ_i to denote the chemical potential of component i.

This solution is completely characterized by the knowledge of the function the Gibbs energy G, which is written as follows, in differential form:

$$\mathrm{d}G = -S\,\mathrm{d}T + P\,\mathrm{d}V + \sum_{i=1}^{N} \mu_i\,\mathrm{d}n_i \qquad [\text{A.2.2a}]$$

In order to find this function, we only need to know the chemical potentials, because they are the partial molar Gibbs energies, and we have:

$$G = \sum_{i=1}^{N} \mu_i n_i \qquad [\text{A.2.2b}]$$

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A.2.2. *Peculiar values and mixing values*

Generally speaking, an extensive value – e.g. the volume of a solution – is not the simple sum (weighted or otherwise) of the volumes of substances introduced when making up the solution. Usually, an extra term is added which is attributable solely to the mixing of the substances, called the corresponding mixing value.

A.2.2.1. *Definitions*

Consider a partial molar value $\overline{J_i}$. In a uniform solution, that value is a function of the variables temperature and composition. If we examine a mole of the overall solution, taking as composition variables the molar fractions x_i, it is always possible to decompose that function into the sum of two functions such that one depends only on the temperature (we ignore the influence of pressure on a liquid solution) – this is the peculiar function $\overline{J_i}^{pec}$ – and the other is a function of all the variables of temperature and composition, and is known as the mixing function $\overline{J_i}^{mix}$. This decomposition is written thus:

$$\overline{J_i} = \overline{J_i}^{pec}(T) + \overline{J_i}^{mix}(T, x_1 x_2 \ldots x_N) \qquad [A.2.3]$$

As a peculiar value, we choose the molar value of the pure substance *i* in the same state of agglomeration as the solution. The decomposition [A.2.3] is then written:

$$\overline{J_i} = j_i^0(T) + \overline{J_i}^{mix}(T, x_1 x_2 \ldots x_N) \qquad [A.2.4]$$

j_i^0 denotes the molar value of the pure property:

The operation [A.2.4] can also be applied to any linear combination of partial molar values, and in particular to the combination:

$$J_i = \sum_{i=1}^{N} n_i \overline{J_i} \qquad [A.2.5]$$

Mixing value	Definition	Expression
Gibbs energy	$G_m^{mix} == \sum_{i=1}^{N} x_i\left(\mu_i - g_i^0\right)$ [A.2.6]	$G_m^{mix} = \mathrm{R}T\sum_{i=1}^{N} x_i \ln x_i$ [A.2.7]
Helmholtz energy	$H_m^{mix} = \sum_{i=1}^{N} x_i\left(\overline{H_i} - h_i^0\right)$ [A.2.8]	$H_m^{mix} = 0$ [A.2.9]
Entropy of mixing	$S_m^{mix} = \sum_{i=1}^{N} x_i\left(\overline{S_i} - s_i^0\right)$ [A.2.10]	$S_m^{mix} = -\mathrm{R}\sum_{i=1}^{N} x_i \ln x_i$ [A.2.11]
Mixing volume	$V_m^{mix} = \sum_{i=1}^{N} x_i\left(\overline{V_i} - v_i^0\right)$ [A.2.12]	$V_m^{mix} = 0$ [A.2.13]
Specific heat capacity at constant pressure	$C_{P_m}^{mix} = \sum_{i=1}^{N} x_i\left(\overline{C_{P_i}} - c_{P_i}^0\right)$[A2.14]	$C_P = \sum_{i=1}^{N} c_{P(i)}^0$ [A.2.15]

Table A.2.1. *Definitions of the mixing properties and values for a perfect solution*

We use J_m^{mix} to denote the molar value of mixing of the solution, defined by:

$$J_m^{mix} = \sum_{i=1}^{N} x_i\left(\overline{J_i} - j_i^0\right) \quad [A.2.16]$$

The second column in Table A.2.1 gives the definitions of several molar values of mixing.

A.2.3. Characterization of the imperfection of a real solution

A perfect solution is defined as a solution in which the chemical potential of each of the components obeys the relation:

$$\mu_i = g_i^0 + \mathrm{R}T \ln x_i \qquad [A.2.17]$$

From this definition, we deduce a certain number of classic properties of the perfect solution. Table A.2.1 gives a few molar values of mixing for a perfect solution.

Two methods have been distinguished. What they have in common is that they characterize a real solution by its difference from a perfect solution:

– the first method, from Lewis' school of thought, introduces the activity coefficients;

– the second method uses the excess values, in particular the excess Gibbs energy.

A.2.4. Activity coefficients

Lewis refers to the expression [A.2.17] of the chemical potential, attempting to preserve its form. In order to do so, he introduces an activity coefficient γ, which is a function of the temperature and of the composition of the solution, writing the chemical potential of a component *i* of the solution in the form:

$$\mu_i = \mu_i^0 + \mathrm{R}T \ln \gamma_i x_i \qquad [A.2.18]$$

A.2.5. Activity coefficients and reference states

The product of the activity coefficient and the molar fraction is called the activity of the component *i* in the solution. The activity in a real solution plays the same thermodynamic role as the molar fraction does in a perfect solution:

$$a_i = \gamma_i x_i \qquad [A.2.19]$$

The reference chosen for convention (I) is components in the pure state in the same state of segregation as the solution (this reference is called the *pure-substance reference*), in which case, $\gamma_i^{(I)} = 1$. We chose to use it in section A.2.2 for the mixing values. In these conditions, the chemical potential of the reference state is the molar Gibbs energy of the pure *i*, and then the chemical potential is written:

$$\mu_i = g_i^0(T) + \mathrm{R}T \ln \gamma_i^{(I)} x_i \qquad \text{[A.2.20]}$$

This reference is mainly used when all the components in a solution play the same role, and in particular, have comparable molar fractions. For example, this convention is chosen when the data cover a broad spectrum of composition, possibly ranging from one pure substance to another.

Convention (II), called the *infinitely-dilute solution reference*, distinguishes, among the components of the solution, that (or those) present in a high proportion, called the solvent(s), and those which are present in lower proportions, called the solutes. The reference state is different for these two categories of components:

– for a solvent, we choose its pure state (in the same state of segregation as the solution) as a reference, and therefore its chemical potential will obey relation [A.2.20]. For a solvent, convention (II) is the same as convention (I);

– for a solute, the reference state is an imaginary solution in which all the solutes are infinitely dilute. The reference chemical potential is therefore that of the solute in this imaginary solution, and is written as μ_s^∞ for a solute *s*. The activity coefficient is equal to 1 in this imaginary solution and the chemical potential will then be written, for all solutes (accepting that the activity tends toward 1 if the molar fraction tends toward the composition of the reference state):

$$\mu_s = \mu_s^\infty(T) + \mathrm{R}T \ln \gamma_s^{(II)} x_s \qquad \text{[A.2.21]}$$

The activity coefficients of a solute in reference (I) – pure substance – and (II) – infinitely-dilute solution – are linked to one another because the chemical potential of the solute does not depend on the convention chosen.

From this, we deduce:

$$\ln \frac{\gamma_s^{(I)}}{\gamma_s^{(II)}} = \frac{\mu_s^{\infty}(T) - g_s^0(T)}{\mathrm{R}T} = \ln K_{iH} \qquad [A.2.22]$$

Thus, the constant K_{iH} linking the activity coefficients expressed in the two conventions: the pure-substance reference and the infinitely-dilute solution reference do not depend on the composition of the solution, but instead depends on the temperature by means of (amongst others) the chemical potentials of the reference states. The value K_{iH} is called Henry's constant. This constant can be determined, in particular, on the basis of the measured vapor pressure at equilibrium between the solution and the vapor phase (see section 5.2.2).

A.2.5.1. *Relation between the activity coefficients of the components of a solution*

Let us place ourselves in the context of any given convention. The Gibbs–Duhem relation applies to chemical potentials which, at constant temperature, obey the relation:

$$\sum_{i=1}^{N} x_i \,\mathrm{d}\mu_i = 0 \qquad [A.2.23]$$

From this, we deduce:

$$\sum_{i=1}^{N} x_i d \ln \gamma_i = 0 \qquad [A.2.24]$$

Thus, if, for each composition of the solution, we know the activity coefficients of all the components in a convention, except for one of them, relation [A.2.24] can be used to calculate the unknown activity coefficient in the same convention (see section 5.1.1).

A.2.5.2. *Influence of the different variables on the activity coefficients*

A.2.5.2.1. *Temperature*

If $\overline{H_i^0}$ is the partial molar enthalpy of component *i* in the reference state at temperature *T*, we can show that:

$$\frac{\partial \ln \gamma_i}{\partial T} = \frac{\overline{H_i^0} - \overline{H_i}}{\mathrm{R}T^2} \qquad [A.2.25]$$

This relation [A.2.24] gives us the variation of the activity coefficient at constant composition when the temperature changes.

The numerator in expression [A.2.25] reveals a difference which represents the enthalpy of transport, at constant temperature, of a mole of *i*, from the real solution under study to the solution in the reference state. We must imagine that the transport takes place with a large amount of solutions so it does not alter the compositions of the two solutions. If we adopt convention I, it is clear that this difference is the opposite of the enthalpy of mixing (because then $\overline{H_i^{0(I)}} = h_i^0$).

A.2.5.2.2. *Influence of the composition on the activity coefficients*

If a solution is perfect, it obeys Raoult's law, which is written as:

$$a_i^{(I)} = x_i \qquad [A.2.26]$$

This law is represented by Raoult's straight line, which is the first bisector in the system of axes ($a_i^{(I)}, x_i$).

An ideal dilute solution is defined by an activity coefficient in reference (II) equal to 1. Its activity coefficient in reference (I) will therefore be given by relation [A.2.22]. Thus, the activity of *i* in convention (I) in an infinitely-dilute ideal solution is:

$$a_i^{(I)} = K_{iH} x_i \qquad [A.2.27]$$

This is Henry's law. This law is represented by Henry's straight line, whose slope is K_{iH} in the system of axes ($a_i^{(I)}, x_i$). Henry's constant K_{iH} is independent of the composition and has a very clear value when the temperature is constant (see relation [A.2.22]).

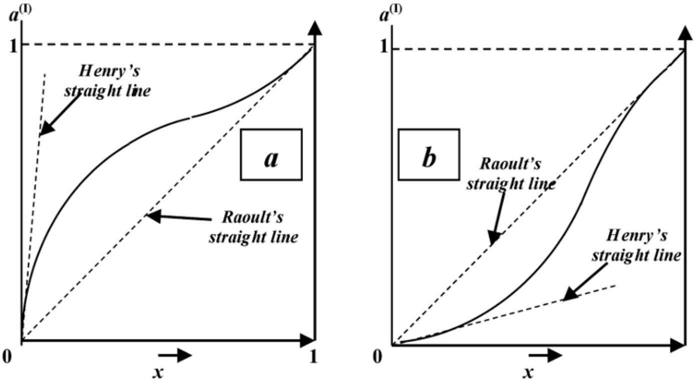

Figure A.2.1. *Activity curve of a component as a function of its molar fraction for a) a component with positive deviation and b) a component with negative deviation*

For a real solution, the activity, in the pure-substance reference, of a component tends toward 1 when its molar fraction tends toward 1. It tends toward 0, along Henry's straight line, when its molar fraction tends toward 0. Thus, the curve showing its activity, in the pure-substance reference, as a function of its molar fraction, is tangential to Raoult's straight line at the point $x = 0$. It is tangential to Henry's straight line at the point $x = 1$.

A solution is said to show positive deviation if its activity coefficient in the pure-substance reference is greater than 1($\gamma^{(I)} > 1$), the curve is above Raoult's straight line. This solution is said to show negative deviation if its activity coefficient in the pure-substance reference is less than 1($\gamma^{(I)} < 1$), with the curve below Raoult's straight line.

Besides, we can show the inter-relation between the activity coefficients of two components in a solution:

$$\frac{\partial \ln \gamma_i}{\partial x_k} = \frac{\partial \ln \gamma_k}{\partial x_i} \qquad \text{[A.2.28]}$$

This relation stems from a similar relation between the chemical potentials, which is the consequence of the symmetry of the characteristic matrix.

A.2.6. Excess values

We can show that the activity coefficient of a component in a perfect solution in the infinitely-dilute solution reference is also 1 at all temperatures and in all compositions.

$$\gamma_i^{(I)} = \gamma_i^{(II)} = 1 \qquad \text{[A.2.29]}$$

NOTE.– Henry's constant for a perfect solution has a value of 1.

Consider an extensive property *J* of a solution and use J^{pf} to denote the value of that property in given conditions of temperature and pressure if that solution were perfect. We speak of the excess value of *J*, denoted by J^{xs} and defined by:

$$J^{xs} = J - J^{pf} \qquad \text{[A.2.30]}$$

J^{xs} is indeed characteristic of the difference between our real solution and a perfect solution.

As this value is extensive, it has corresponding partial molar values pertaining to each component in the solution, which are defined by:

$$\overline{J^{xs}} = \left(\frac{\partial J^{xs}}{\partial n_i}\right)_{P,T,n_{j\neq i}} \qquad \text{[A.2.31]}$$

Table A.2.2 presents a few excess values, along with the corresponding excess partial molar values.

This table also demonstrates the equivalence between the two approaches to the modeling of real solutions: Lewis' approach based on the activity coefficients, and the approach based on the excess values.

Property	Excess molar value	Excess partial molar value
Gibbs energy	$G_m^{xs} = \mathrm{R}T\sum_{i=1}^{N} x_i \ln \gamma_i^{(I)}$ [A.2.32]	$\overline{G_i^{xs}} = \mathrm{R}T \ln \gamma_i^{(I)}$ [A.2.33]
Entropy	$S_m^{xs} = \mathrm{R}\sum_{\mathrm{i=1}}^{\mathrm{N}}\left[x_i\left(-T\dfrac{\partial \ln \gamma_i^{(I)}}{\partial T} - \ln \gamma_i^{(I)}\right)\right]$ [A.2.34]	$\overline{S_i^{xs}} = \mathrm{R}\left(-T\dfrac{\partial \ln \gamma_i^{(I)}}{\partial T} - \ln \gamma_i^{(I)}\right)$ [A.2.35]
Enthalpy	$H_m^{xs} = -\mathrm{R}\sum_{\mathrm{i=1}}^{\mathrm{N}}\left[x_i T^2 \dfrac{\partial \ln \gamma_i^{(I)}}{\partial T}\right]$ [A.2.36]	$\overline{H_i^{xs}} = -\mathrm{R}T^2 \dfrac{\partial \ln \gamma_i^{(I)}}{\partial T}$ [A.2.37]
Specific heat capacity	$C_p^{xs} = \mathrm{R}\sum_{\mathrm{i=1}}^{\mathrm{N}}\left[x_i\left(-T\dfrac{\partial^2 \ln \gamma_i^{(I)}}{\partial T^2} - 2\dfrac{\partial \ln \gamma_i^{(I)}}{\partial T}\right)\right]$ [A.2.38]	

Table A.2.2. *Excess values and excess partial molar values*

A.2.7. Ionic solutions

Ionic solutions exhibit several peculiarities in comparison to molecular solutions. The main source of these differences is to be found in the existence of inter-ion forces that are much stronger than those that exist between molecules – particularly over a long distance.

A.2.7.1. *Composition of an ionic solution and reference state*

To express the composition of the ionic solutions, we usually use the concentration (or molarity) c_i of a component i in a phase. This is the quotient of the amount of that component by the volume of the phase, so:

$$c_i = \frac{n_i}{V} \qquad [A.2.39]$$

The concentration is often expressed in moles/liter. For solutions in which the proportion of one of the components is much greater than the others (often that component is called the solvent), we frequently treat the volume of the phase as the same thing as the volume of the component introduced in the highest quantity when making up the solution. Its concentration is often considered constant, with the addition of a small amount of another component.

The reference state is usually defined by convention (III), which makes the distinction between solvent and solute:

– for the solvent, the reference (III) convention is identical to reference (I) – the pure substance – and therefore the chemical potential of the solvent is always given by relation [A.2.20] ;

– for the solute, we shall agree to choose that the activity coefficient of an ion tends toward 1 as its concentration tends toward zero, which gives us the following convention:

$$\gamma_s \to 1 \text{ if } c_s \to 0 \qquad [A.2.40]$$

A.2.7.2. *Chemical potential of an ion*

In spite of the difficulty, in the case of ions, of defining a derivation in relation to one of the components whilst preserving the values of the other constants, we can show that it is exactly as if we had chosen the usual relation to express the chemical potential:

$$\mu_i = \mu_i^0 + \mathrm{R}T \ln \gamma_i c_i \qquad [A.2.41]$$

The potential μ_i^0 is, of course, that of the reference state.

A.2.7.3. *Relation between the activities of the ions and the overall activity of the solutes*

Consider the dissolution of an electrolyte with the chemical formula $A_{\nu_+}B_{\nu_-}$. Suppose that it is a strong electrolyte; it dissociates completely. Its Gibbs energy is written as:

$$G = n_0\mu_0 + n_s\left(\nu_+\mu_\mathrm{A} + \nu_-\mu_{\substack{0\\A}}\right) \qquad [A.2.42]$$

However, we know that the chemical potential of the solute is also:

$$\mu_s = \nu_+\mu_\mathrm{A} + \nu_-\mu_\mathrm{B} \qquad [A.2.43]$$

From this, we deduce:

$$\gamma_s c_s = \left(\gamma_\mathrm{A} c_\mathrm{A}\right)^{\nu_+}\left(\gamma_\mathrm{B} c_\mathrm{B}\right)^{\nu_-} \qquad [A.2.44]$$

This equation links the molecular point of view about the solution to the ionic point of view.

A.2.7.4. *Mean concentration and mean activity coefficient of the ions*

The methods for precisely measuring the activity coefficients (see section 5.6.1.1) are incapable of giving us the activity coefficients of the individual ions. Thus, it has proved helpful, for an electrolyte $A_{\nu_+}B_{\nu_-}$, to introduce the concept of the mean activity coefficient defined by:

$$\gamma_\pm = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/(\nu_+ + \nu_-)} \qquad [A.2.45]$$

The mean activity coefficient obeys the same convention as the individual activity coefficients.

We can also define a mean concentration by a similar relation. If c is the molar concentration of solute, the concentrations of the different ions (for fully-dissociated strong electrolytes) would be:

$$c_+ = \nu_+ c \text{ and } c_- = \nu_- c \qquad [A.2.46]$$

and the mean concentration would be:

$$c_{\pm} = c\left(\nu_{+}^{\nu_{+}}\nu_{-}^{\nu_{-}}\right)^{1/(\nu_{+}+\nu_{-}))} \qquad [A.2.47]$$

A.2.7.5. *Activity coefficient of an individual ion*

We have already mentioned how difficult it is to determine the individual activity coefficients for the ions by experimentation. It is obvious that if we were able to determine the activity coefficient of a single individual ion, then little by little we could – on the basis of the mean activity coefficient, which we are able to measure (see section 5.6.1.2) – deduce that of all the other ions. In order to do so, MacInnes exploited the fact that in potassium chloride, the chloride ion and the potassium ion have the same charge in absolute value, have the same electron structure and therefore the same size, roughly the same mobility and masses that are not hugely different. MacInnes deduces from this that they should have approximately the same activity coefficient. In light of that result, we deduce, from the mean activity coefficient of potassium chloride, that of the separate ions, using the relation:

$$\gamma_{\mathrm{Cl}^-} = \gamma_{\mathrm{K}^+} = \gamma_{\pm}^2 \qquad [A.2.48]$$

By the same hypothesis, the results obtained for a set of ions show that monovalent ions have approximately the same activity coefficient, and that the activity coefficients are primarily influenced by the electrovalences of the ions and by the presence of other ions, which gives rise to the concept of ionic strength.

A.2.7.6. *Concept of ionic strength*

The activity coefficient of the ions is influenced by the presence of other ions. Experience shows us that the important value is the ionic strength, defined by:

$$I = \frac{1}{2}\sum_{i} c_i z_i^2 \qquad [A.2.49]$$

The sum is extended to all the ions present in the solution.

Appendix 3

Reminders on Statistical Thermodynamics

The purpose of this appendix is to recap, but not demonstrate, a few results of statistical thermodynamics which are used in this second volume. The detail and expansion of these concepts are presented in the first volume of the collection [SOU 15].

We know that a microscopic approach to a phase considers it as a collection of molecules-objects whose energies are distributed in accordance with a statistical law. The state of a collection of molecules-objects is constantly changing but, over time, the collection goes through a certain type of distribution in which the molecules-objects may be in a variety of different states. We use the term number of complexions for the number of distributions of molecules-objects between the different states that they are liable to assume. Out of all the possible distributions, there is one that corresponds to the maximum number of complexions. Boltzmann's principle accepts that the number of complexions corresponding to the most probable type of distribution is practically equal to the total number of complexions, and vice versa. The state of the collection is then always that which corresponds to the maximum number of complexions.

Most of the calculations in statistical thermodynamics are based on Stirling's approximation, which enables us to simplify the expression of the factorial logarithm n if the number n is large. It is written thus:

$$\ln n! \cong n \ln n - n \cong n \ln n \qquad [A.3.1]$$

Modeling of Liquid Phases, First Edition. Michel Soustelle.

A.3.1. The three statistical distributions

Each element in the collection has an energy ε_i, and the number of elements which have that energy is n_i. The total number of elements will be N, such that:

$$N = \sum_i n_i \qquad [A.3.2]$$

Hence, the total energy is:

$$E = \sum_i n_i \varepsilon_i \qquad [A.3.3]$$

The number of complexions, i.e. of configurations of the collection of elements, is represented by Ω.

The mean energy of an element is $\langle \varepsilon \rangle$, and by applying relation [2.2], we find:

$$\langle \varepsilon \rangle = \frac{E}{N} \qquad [A.3.4]$$

Thus, for the number of objects in the state i, we find:

$$n_i = g_i \exp(-\alpha)\exp(-\beta\varepsilon_i) \qquad [A.3.5]$$

where g_i is the statistical weight or the coefficient of degenerescence or the multiplicity of the energy level ε_i. It is the number of different states with the same energy ε_i.

The coefficient β is a universal value which is:

$$\beta = \frac{1}{\mathrm{k_B} T} \qquad [A.3.6]$$

$\mathrm{k_B}$ is Boltzman’s constant (the quotient of the joule constant, R, by Avogadro’s number $\mathrm{N_a}$).

Depending on the nature of the molecule-object, three kinds of statistics have been developed.

A.3.1.1. *Maxwell–Boltzmann statistics*

Maxwell–Boltzmann statistics applies to objects for which there is no room to resort to quantum mechanics, i.e. fairly large and easily-discernible objects. This branch of statistics is also applicable to discernible or localized quantum objects, such as the "molecules" distributed at the nodes of a crystalline lattice.

The coefficient α from relation [A.3.5] is given, in this case, by:

$$\exp(-\alpha) = \frac{N}{\sum_i g_i \exp(-\beta\varepsilon_i)} \qquad [A.3.7]$$

The distribution law becomes:

$$n_i = \frac{N g_i \exp(-\beta\varepsilon_i)}{\sum_i g_i \exp(-\beta\varepsilon_i)} \qquad [A.3.8]$$

β is defined by relation [A.3.6].

A.3.1.2. *Bose–Einstein quantum statistics*

Bose–Einstein quantum statistics applies to non-localized quantum objects, i.e. which are indiscernible and have integer spin (most of the molecules and the ions, the atoms). The distribution of the objects obeys the expression:

$$(n_i)_{BE} = \frac{g_i \exp(-\alpha - \beta\varepsilon_i)}{1 - \exp(-\alpha - \beta\varepsilon_i)} \qquad [A.3.9]$$

The value of the coefficient α is difficult to determine. We shall come back to this point later on (relation [A.3.11]).

A.3.1.3. *Fermi–Dirac quantum statistics*

Fermi–Dirac quantum statistics applies for non-localized quantum objects, meaning indiscernible objects with fractional spin (some molecules and ions, and electrons). The distribution of the objects obeys the expression:

$$(n_i)_{BE} = \frac{g_i \exp(-\alpha - \beta\varepsilon_i)}{1 + \exp(-\alpha - \beta\varepsilon_i)} \quad [A.3.10]$$

The value of the coefficient α is as difficult to calculate as in the previous case.

For the two branches of statistics for non-discernible objects, we content ourselves, for that coefficient α, with a limited expansion of the form:

$$\exp(-\alpha_{\mathrm{A}}) = a_0 + a_1 \frac{N_{\mathrm{A}}}{z_{\mathrm{A}}} + a_2 \left(\frac{N_{\mathrm{A}}}{z_{\mathrm{A}}}\right)^2 + a_3 \left(\frac{N_{\mathrm{A}}}{z_{\mathrm{A}}}\right)^3 + \ldots \quad [A.3.11]$$

Laborious calculations show that the coefficients a_{i} in this expansion are:

$$a_0 = 0\,;\ a_1 = 1\,;\ a_2 = \pm\frac{1}{2^{3/2}}\,;\ a_3 = \frac{1}{4} - \frac{1}{3^{3/2}}\,;\ \ldots \quad [A.3.12]$$

In the coefficient a_2, the + sign applies for Fermi–Dirac statistics, and the – sign applies for Bose–Einstein statistics.

A.3.1.4. *Classic limit case*

The three quantical statistics (MB, BE and FD) come together to form one, called the classic limit case, if the following condition is fulfilled:

$$\exp(-\alpha) << 1 \quad [A.3.13]$$

Thus, α must be large.

In these conditions, the three laws come together in the form:

$$n_i = g_i \exp(-\alpha - \beta\varepsilon_i) \quad [A.3.14]$$

We can see that this limit case maintains the formula of the Maxwell–Boltzmann distribution. Thus, α is determined by the relation:

$$\exp(-\alpha_{\mathrm{A}}) \cong \frac{N_{\mathrm{A}}}{z_{\mathrm{A}}} \tag{A.3.15}$$

We can show that in this case, we also have the condition:

$$N << g_i \tag{A.3.16}$$

i.e. if the number of particles is much less than the number of possible states.

A.3.2. Partition functions of a molecule object

A.3.2.1. *Definition*

The partition function of a molecule object of a collection is the sum z defined by:

$$z = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{\mathrm{k_B}T}\right) = \sum_i g_i \exp\left(-\varepsilon_i \beta\right) \tag{A.3.17}$$

The sum is extended to all the levels of energy that the object may attain.

A.3.2.2. *Independence of the energies*

The complete partition function for a system includes terms that refer to the various forms of energy: nuclear, electronic, vibration of the molecules, their rotation, their translation and the energy of interaction between the different molecules.

To simplify, we accept that these different forms of energy, for a molecule, are independent.

In these conditions, we can write the total energy of a molecule as the sum of the different contributions of the forms of energy – nuclear

ε_n, electronic ε_e, vibrational ε_v, rotational ε_r, translational ε_t and interactional ε_I, so that:

$$\varepsilon = \varepsilon_n + \varepsilon_e + \varepsilon_v + \varepsilon_r + \varepsilon_t + \varepsilon_I \qquad [A.3.18]$$

The molecule's partition function becomes:

$$\begin{gathered} z = \sum_{i_n} \exp\left(-\frac{\varepsilon_{i_n}}{\mathrm{k_B}T}\right) \sum_{i_e} \exp\left(-\frac{\varepsilon_{i_e}}{\mathrm{k_B}T}\right) \sum_{i_v} \exp\left(-\frac{\varepsilon_{i_v}}{\mathrm{k_B}T}\right) \\ \sum_{i_r} \exp\left(-\frac{\varepsilon_{i_r}}{\mathrm{k_B}T}\right) \sum_{i_t} \exp\left(-\frac{\varepsilon_{i_t}}{\mathrm{k_B}T}\right) \sum_{i_I} \exp\left(-\frac{\varepsilon_{i_I}}{\mathrm{k_B}T}\right) \end{gathered} \qquad [A.3.19]$$

Thus, we reveal partial partition functions, which are afferent to the different forms of energy:

$$z_n = \sum_{i_n} \exp\left(-\frac{\varepsilon_{i_n}}{\mathrm{k_B}T}\right), z_e = \sum_{i_e} \exp\left(-\frac{\varepsilon_{i_e}}{\mathrm{k_B}T}\right), z_v = \sum_{i_v} \exp\left(-\frac{\varepsilon_{i_v}}{\mathrm{k_B}T}\right)$$

$$z_r = \sum_{i_r} \exp\left(-\frac{\varepsilon_{i_r}}{\mathrm{k_B}T}\right), z_t = \sum_{i_t} \exp\left(-\frac{\varepsilon_{i_t}}{\mathrm{k_B}T}\right), z_I = \sum_{i_I} \exp\left(-\frac{\varepsilon_{i_I}}{\mathrm{k_B}T}\right) \qquad [A.3.20]$$

The overall partition function then assumes the form of a product of the partial partition functions:

$$z = z_n z_e z_v z_r z_t z_I \qquad [A.3.21]$$

Sometimes, we use the hypernym *internal contribution* to speak of the product:

$$z_{\text{int}} = z_n z_e z_v z_r \qquad [A.3.22]$$

It is the product of all the contributions other than those of translation and interaction.

Thus, obviously, the overall molecular partition function becomes:

$$z = z_{\text{int}} z_t z_I \qquad [A.3.23]$$

A.3.2.3. *Partial molecular partition functions, relating to the different motions*

By applying definition [A.3.20], we can calculate the contributions of each of the motions of the molecule to the molecular partition function.

A.3.2.3.1. *Translation*

The molecule has three degrees of freedom for translation. We can show that if it is subject to no other constraint than having to remain in the volume V, the contribution of translation is:

$$z_t = V\left(\frac{2\pi m \mathrm{k_B} T}{\mathrm{h}^2}\right)^{3/2} \qquad \text{[A.3.24]}$$

For the perfect gas, with no interaction ($z_I = 1$) between the molecules, the molecular partition function can be written as follows, in light of relation [A.3.24]:

$$z_{pf} = V\left(\frac{2\pi m \mathrm{k_B} T}{\mathrm{h}^2}\right)^{3/2} z_{\mathrm{int}} \qquad \text{[A.3.25]}$$

Thus, the translational partition function of the perfect gas is:

$$z_{t(pf)} = V\left(\frac{2\pi m \mathrm{k_B} T}{\mathrm{h}^2}\right)^{3/2} \qquad \text{[A.3.26]}$$

A.3.2.3.2. *Rotation with moment of inertia I*

A molecule may have two or three degrees of freedom for rotation. We distinguish three families of molecules.

For homonuclear diatomic molecules (i.e. where the two atoms are identical), the partition function per degree of freedom is:

$$z_r = \frac{4\pi^2 I \mathrm{k_B} T}{\mathrm{h}^2} \qquad \text{[A.3.27]}$$

For heteronuclear diatomic molecules, the partition function per degree of freedom is:

$$z_r = \frac{4\pi^2 I \mathrm{k_B} T}{\mathrm{h}^2} \qquad [A.3.28]$$

In the case of complex molecules, the partition function per degree of freedom is:

$$z_r = \frac{8\pi^2 \left(2\pi \mathrm{k_B} T\right)^{3/2} \sqrt{I_1 I_2 I_3}}{\sigma \mathrm{h}^2} \qquad [A.3.29]$$

where σ is a coefficient of symmetry which depends on the complexity of the molecule, whose value is at most a few units.

A.3.2.3.3. *Vibration of frequency* ν

We can show that the partition function of one degree of freedom of frequency ν is given by:

$$z_\nu = \frac{\exp\left[-\frac{\mathrm{h}\nu}{2\mathrm{k_B}T}\right]}{1-\exp\left[-\frac{\mathrm{h}\nu}{\mathrm{k_B}T}\right]} \qquad [A.3.30]$$

Note that if $\frac{\mathrm{h}\nu}{\mathrm{k_B}T} >> 1$, we can content ourselves with a simpler form:

$$z_\nu \approx \frac{\mathrm{k_B}T}{\mathrm{h}\nu} \qquad [A.3.31]$$

A.3.3. Canonical partition function

To use statistics for the characterization of the phases, it is interesting to construct the canonical ensemble.

A.3.3.1. *Canonical ensemble*

A so-called *canonical ensemble* is an ensemble, comprising replicas of the system under examination. Each element is closed, so the number of molecules N is identical in every element of the ensemble. This number is constant because there is no exchange of matter between the elements, or between those elements and the outside world. The volume V is the same for all the elements. The elements are in thermal contact with one another, and can thus exchange energy. Their temperature T is identical. Each element has an energy E_j. The total energy of the canonical ensemble would be E_C. This energy is constant because the ensemble is isolated from the outside.

A.3.3.2. *Canonical partition functions*

Similarly, as for molecules, we define the partition function for the canonical ensemble by the sum:

$$Z_C = \sum_j \exp\left(-\beta E_j\right) \quad [A.3.32]$$

This sum is extended to all the elements in the ensemble.

A.3.3.3. *Canonical partition function and molecular partition functions*

We can link the canonical partition function, firstly to the molecular canonical functions, and secondly to the thermodynamic functions which define the phase on the macroscopic level (*U, F, G, S,* etc.). These two types of relation use the canonical partition function to form the link between the microscopic definition of the phase and its macroscopic thermodynamic properties.

In order to calculate the canonical partition function on the basis of the molecular functions, we distinguish two cases, depending on whether the molecules are discernible or indiscernible.

A.3.3.3.1. *Case of collections of discernible molecules*

If the molecules are all identical and discernible, we show that we can use the expression:

$$Z_C = z^N \quad [A.3.33]$$

If the phase comprises several types of molecules – N_{A} molecules of A, in N_{B} molecules of B, etc., the canonical partition function becomes:

$$Z_C = z_{\mathrm{A}}^{N_{\mathrm{A}}}.z_{\mathrm{B}}^{N_{\mathrm{B}}}.... \qquad [A.3.34]$$

A.3.3.3.2. *Case of collections of indiscernible molecules*

If the molecules are all identical and indiscernible, we show that we can use the expression:

$$Z_C = \frac{z^N}{N!} \qquad [A.3.35]$$

If the phase comprises several types of molecules – N_{A} molecules of A in N_{B} molecules of B, etc. – the canonical partition function becomes:

$$Z_C = \frac{z_{\mathrm{A}}^{N_{\mathrm{A}}}}{N_{\mathrm{A}}!}.\frac{z_{\mathrm{B}}^{N_{\mathrm{B}}}}{N_{\mathrm{B}}!}... \qquad [A.3.36]$$

In the case that the medium under examination is a mixture of several phases α, β, γ, etc., the canonical partition function of the ensemble is the product of the canonical partition functions of the different phases, in accordance with:

$$Z_C = Z_C^{(\alpha)}.Z_C^{(\beta)}.Z_C^{(\gamma)}.. \qquad [A.3.37]$$

Each canonical partition function for each of the phases obeys one of the relations [A.3.33], [A.3.34], [A.3.35] or [A.3.36].

A.3.4. Interactions between molecules

Let us consider the mixture of N independent molecules, with no interaction between them. This collection is treated as an assembly of non-discernible quantum particles in the classic limit case of validity of relation [A.3.13].

If we use the notation ω_i to denote the set of position coordinates $(x_1, x_2, x_3)_i$ of the particle i, between two particles i and j there is an energy of interaction $\varepsilon_{i,j}$, and we suppose that the interaction energy only contains terms such as $\varepsilon_{i,j}$, although many molecules interact mutually. This hypothesis is known as the pairwise interaction model. The configuration integral thus takes the form:

$$I_I = \int\limits_{Nv_f} \int ... \int \prod_{i<j} \exp - \frac{\varepsilon_{i,j}}{\mathrm{k_B} T} (\mathrm{d}\omega)^N \qquad [A.3.38]$$

The integrals are extended to the available volume for the molecules, so Nv_f.

We suppose that there is a zone of interaction for the molecule, the sphere of influence, and that there is only one molecule *j* which is within the sphere of influence of a molecule *i*. Thus, by ignoring the volume of those molecules in relation to the total volume, we establish a term of interaction in the molecular partition function of the form:

$$I_I = \exp - \frac{N^2 B_{AA}(T)}{V} \qquad [A.3.39]$$

The term $B_{AA}(T)$ being given by the expression, a function of the distance *r* between two molecules:

$$B_{AA}(T) = -\frac{1}{2} \int_0^{\infty} 4\pi r^2 \left[\exp\left(-\frac{\varepsilon_{AA}}{\mathrm{k_B} T} \right) - 1 \right] \mathrm{d}r \qquad [A.3.40]$$

Usually, we content ourselves with a limited expansion of this contribution in the form:

$$I_I \approx 1 - \frac{N^2 B_{AA}(T)}{V} \qquad [A.3.41]$$

For a collection of *N* molecules of gas (indiscernible molecules), this gives us a canonical partition function which has the expression:

$$Z_C \approx \frac{z_{pf}^N}{N!} \left[1 - \frac{N^2 B_{AA}(T)}{V} \right]^N$$

$$= \frac{\left[\left(\frac{2\pi m \mathrm{k_B} T}{\mathrm{h}^2} \right)^{3/2} \right]^N z_{\mathrm{int}}^N V^N}{N!} \left[1 - \frac{N^2 B_{AA}(T)}{V} \right]^N \qquad [A.3.42]$$

The second coefficient of the virial is therefore:

$$B_2(T) = \mathrm{N_a} B_{AA}(T) \qquad [A.3.43]$$

The energy $\varepsilon_{\mathrm{AA}}$ of interaction between two molecules may take a variety of forms, particularly the Lennard-Jones form, which is due to the van der Waals forces:

$$\frac{\varepsilon_{\mathrm{AA}}}{\varepsilon_0} = -2\left(\frac{d_0}{d}\right)^6 + \left(\frac{d_0}{d}\right)^{12} \qquad [A.3.44]$$

where d_0 is the distance between two molecules which corresponds to the minimum.

Up until now, we have defined an energy of interaction between molecules ε_{ij}. It is possible to work another way, considering the molecules without interaction and introducing a term representing the overall energy of interaction E_I.

The configuration integral is written, at the level of the canonical partition function, by replacing the formula [A.3.38] by:

$$I_I = \int .. \int \int \exp\left(-\frac{E_I}{\mathrm{k_B} T}\right) \mathrm{d}\,\omega^N \qquad [A.3.45]$$

A.3.5. Canonical partition functions and thermodynamic functions

We can demonstrate the following formulae to express the thermodynamic functions on the basis of the canonical partition function.

For the internal energy:

$$U(T) - U(0) = -\sum_{\mathrm{A}} \frac{\partial \ln Z_{C(\mathrm{A})}}{\partial \beta} = \mathrm{k_B} T^2 \sum_{\mathrm{A}} \frac{\partial \ln Z_{C(\mathrm{A})}}{\partial T} \qquad [A.3.46]$$

For the entropy:

$$S = \mathrm{k_B}\left[\ln Z_C - \frac{1}{T}\frac{\partial \ln Z_C}{\partial \ln \beta}\right] \qquad [A.3.47]$$

For the Helmholtz energy function:

$$F(T) - F(0) = -\frac{\sum\limits_{\mathrm{A}} \ln Z_{C(\mathrm{A})}}{\beta} = -\mathrm{k_B}T\sum_{\mathrm{A}} \ln Z_{C(\mathrm{A})} \qquad [A.3.48]$$

NOTE (on the molar values).– In the expressions of the molecular and canonical partition functions, we worked for a certain number of molecules – a number of particles symbolized by N_{A} for component A.

To obtain the molar values of the thermodynamic functions, it is wise to choose Avogadro's number ($\mathrm{N_a}$) as the value of N_{A}.

To obtain the value of a function for an amount n_{A} (in moles) of the component, then for N_{A} we use the product $n_{\mathrm{A}}\ \mathrm{N_a}$.

A.3.6. Equilibrium constants in the liquid phase and partition functions

As the thermodynamic constants – particularly the Gibbs energies – can be expressed on the basis of the partition function, the same must be true of the equilibrium constants.

The equilibrium constant of a reaction is expressed on the basis of the partition functions of the reagents and products, in the case of liquid perfect solutions of dilute ideal solutions, by the expression:

$$K_x = \prod_i \left(z^0_{m(i)}\right)^{\nu_i} \exp\left(-\frac{\Delta_r h^0(T)}{\mathrm{R}T}\right) \qquad [A.3.49]$$

The term $z^0_{m(i)}$ is the molecular partition function of the component i, the partition function expressed in relation to a molecule, so:

$$z^0_{m(i)} = \frac{z_i}{N} = \frac{z_i}{n\mathrm{N_a}} \qquad [A.3.50]$$

The term $\Delta_r h^0(T)$ is the linear combination, weighted by the stoichiometric numbers, of the residual vibrational energies of each of the substances.

Thus, if each component has k_i vibrational degrees of freedom with the fundamental frequency $\nu_{k_i}^0$, we would have:

$$\Delta_r u^0(0) = \frac{\mathrm{N_a h}}{2} \sum_i (a_i \sum_{k_i} \nu_{k_i}^0) = \Delta_r h^0(0) \qquad \text{[A.3.51]}$$

If the solution is not perfect, this term is joined by the energy of interaction of mixing at the temperature of 0 K.

Bibliography

[ABR 95] ABRAMS D.S., PRAUSNITZ J.M., *AICHE Journal*, vol. 21, no. 1, p. 116, 1995.

[ATK 90] ATKINS P.W., *Physical Chemistry,* Oxford University Press, Oxford 1990.

[BEN 12] BEN-NAIM A., *Entropy and the Second Law*, World Scientific Publishing Company, New Jersey, 2012.

[BER 97] BERNACHE-ASSOLLANT D., COURNIL M., *Equilibres en solution*, Masson, Paris 1997.

[BES 84] BESSON J., *Précis de thermodynamique et de cinétique électrochimiques*, Ellipses, Paris, 1984.

[DEF 51] DEFAY R., PRIGOGINE I., *Tension superficielle et adsorption*, Edition Desoer, Liège, 1951.

[DEM 93] DEMANGE H., GERMAIN G., NOTIN M., *Comprendre et appliquer la thermodynamique*, Masson, Paris, 1973.

[DEN 68] DENBIGH K., *The Principles of Chemical Equilibrium*, University Press, Cambridge, 1968.

[DES 10] DESRE P., HODAJ F., *Thermodynamique des matériaux – Equilibres de phase et métastabilité*, EDP Sciences, Paris, 2010.

[EMS 51] EMSCHWILLER G., *Chimie Physique*, P.U.F. France, Paris, 1951.

[EYR 58] EYRING H., REE T., HIRAI N., “Significant-Structures in the Liquid State I”, *Proc. Natl. Acad. Sci.,* vol. 44, pp. 683–688, 1958.

[EYR 61] EYRING H., REE T., “Significant Liquid-Structures VI: the vacancy theory of Liquids”, *Proc. Natl. Acad. Sci. USA*, p. 47, 1961.

Modeling of Liquid Phases, First Edition. Michel Soustelle.

[FOW 49] FOWLER R., GUGGENHEIM E.A., *Statistical Thermodynamics*, Cambridge University Press, London, 1949.

[GER 59] GERMAIN J.E., *Catalyse hétérogène*, Dunod, Paris, 1959.

[GIL 63] GILBERT J., *Chimie-Physique I: Atomistique et liaison chimique,* Masson, Paris, 1963.

[GLA 41] GLASSTONE S.N., LAIDLER K.J., EYRING H.W., *The Theory of Rate Processes,* Mac Graw Hill Book Company, New York, 1941.

[GOK 96] GOKCEN N.A., REDDY R.G., *Thermodynamics*, Plenum Press, New York and London, 1996.

[GRE 99] GREINER W., *Mécanique quantique – une introduction,* Springer, Berlin, 1999.

[GUG 32] GUGGENHEIM E.A., "On the statistical-mechanics of dilute and of perfect solutions", *Proc. Roy. Soc. A.,* London, vol. 135, no. 181, 1932.

[HIL 56] HILL T.L., *Statistical Mechanics*, McGraw-Hill, NewYork, 1956.

[INF 06] INFELTA P., GRAETZEL M., *Thermodynamique, Principes et Applications*, Brown Walker Press 2006.

[KLO 08] KLOTZ I.M., ROSENBERG R.W., *Chemical Thermodynamics Basic Concepts and Methods*, 7th edition, Wiley and Son, 2008.

[KRÖ 74] KRÖGER F.A., *The Chemistry of Imperfect Crystals,* North Holland Publishing Company, Amsterdam, 1974.

[LAL 06] LALAUZE R., *Physico-chimie des interfaces solide-gaz 1*, Hermès–Lavoisier, Paris 2006.

[LE 05] LE GORREC B., Thermodynamique et cinétique électrochimique expérimentale, available at: www.minatec.grenoble-inp.fr/Cours, A.pdf, 2005.

[LEN 37] LENNARD JONES J.E., DEVONSHIRE A.F., "Critical Nenonena in gases I", *Proc. Roy. Soc.*, London, vol. A163, p. 53, 1937.

[MAR 95] MARCHAND A., PACAULT A., *La thermodynamique mot à mot*, De Boeck Université, Bruxelles, 1995.

[MC 99] MC QUARRIEN D.A., SIMON J.D., *Molecular Thermodynamics*, University Science Book, Sausalito (US), 1999.

[MET 46] METZGER E., "Loi de variation de la tension superficielle avec la temperature", *Journal de Physique*, EDP Sciences, available at http://dx.doi.org/10.1051/physrad.01946007010030300, 1946.

[MIE 03] MIE G., “Zur kinetischen Theorie der einatomigen Körper”, *Ann. Phys.*, vol. 11, p. 657, 1903.

[ONO 47] ONO S., *Mem. Fac. Eng. Kyushu Univ.*, vol. 10, p. 190, 1947.

[PAC 63] PACAULT A., *Eléments de thermodynamique statistique*, Masson, Paris, 1963.

[POP 30] POPOFF S., NEUMAN E.W., *J. Phys. Chem.*, vol. 34, p. 1853, 1930.

[PRI 46] PRIGOGINE I., DEFAY R., *Thermodynamique chimique*, Dunod, Paris, 1946.

[PRI 66] PRINCE A., *Alloy phase equilibria*, Elsevier Publishing Company, Amsterdam, London, New York, 1966.

[REE 64] REE T.S., REE T., EYRING H., *Proc. Ntl. Acad. Sci. USA*, p. 51, 1964.

[REI 87] REID R.C., PRAUSNITZ J.M., POLING B.E., *Properties of Gas and Liquids*, McGraw-Hill, New York, 1987.

[REN 71] RENON H., *Calcul sur ordinateur des équilibres liquide – vapeur et liquide – liquide,* Editions Technip, Paris, 1971.

[SOR 81] SORENSEN O.T., *Non-Stoichiometric Oxides*, Academic Press, New York, 1981.

[SOU 68] SOUCHAY P., *Thermodynamique chimique*, Masson, Paris, 1968.

[SOU 73] SOUSTELLE M., GARDET J.J, GUJLHOT B., *Diagrammes de phases et stœchiométrie*, Masson, Paris, pp. 33–50, 1973.

[SOU 90] SOUSTELLE M., *Modélisation macroscopique des transformations physico-chimiques,* Masson, Paris, 1990.

[SOU 93] SOUSTELLE M., *Défauts ponctuels dans les solides* in *Chimie – physique du frittage*, Hermès, Paris, pp. 21–90, 1993.

[SOU 10] SOUSTELLE M., *Handbook of Heterogeneous Kinetics*, ISTE Ltd, London, and John Wiley & Sons, New York, 2010.

[SOU 11] SOUSTELLE M., *Cinétique chimique: éléments fondamentaux*, Hermes-Lavoisier, Paris, 2011.

[SOU 15] SOUSTELLE M., *Phase Modeling Tools*, ISTE Ltd, London, and John Wiley & Sons, New York, 2015.

[YOO 81] YOON B.J., JHON M.S., EYRING H., *Proc. Natl. Acad. Sci.*, vol. 78, pp. 6588–6591, 1981.

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