

Introduction to Liquid State Chemistry

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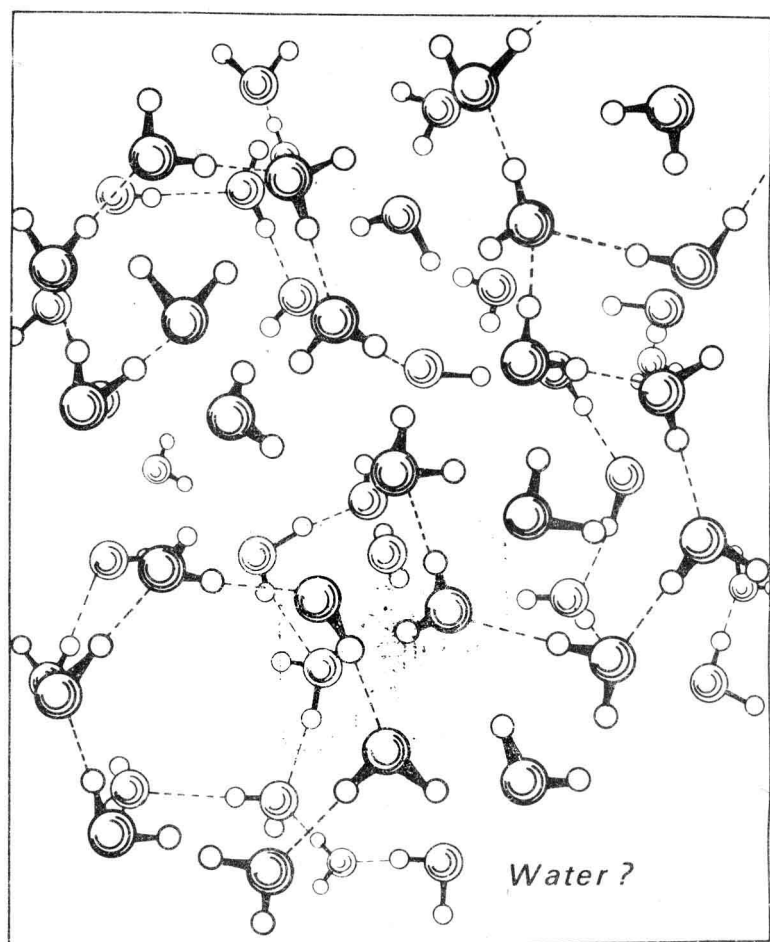
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Preface

Chemists have been working with liquids since the dawn of chemistry, so that much of chemistry is indeed 'liquid state chemistry' although this phrase is not in common use. Conversely, both 'solid state physics' and 'solid state chemistry' are recognized fields of science in which many advances have been achieved over the past decades. But, although in recent years the liquid state has been the subject of intense study, the several books that have been published treat mainly the physics of this state. Liquid argon is an admirable substance upon which test liquid state theories, almost as good as the old stand-by of hard spheres, but it is relatively little interest to chemists. Crude petroleum, sea water, aqueous acetone or molten cryolite, which are of more practical interest, cannot be handled by the theories of physics, unless simple models and far-reaching approximations and assumptions are introduced. It is the proper domain of the liquid state chemist to provide these, and with this the present book is concerned.

This introduction to liquid state chemistry applies the tools of statistical mechanics and thermodynamics to the equilibrium properties of liquids and liquid mixtures, so that reactions and interactions phenomenologically described can also be understood and made the basis for predictions regarding systems not yet studied. There are several broad areas of liquid state chemistry which are currently subject to extensive research but do not sufficiently share their concepts and approaches. These areas comprise *non-polar liquids*, such as form regular solutions, but may also have non-ideal entropies of mixing (e.g. petroleum, certain polymer solutions); *electrolyte solutions*, ranging from dilute aqueous solutions to molten hydrate salts, with organic solvents and inorganic non-aqueous solvents included; *molten salts*, which range from ideally ionic fluids to molecular melts and liquid or glassy network systems; *non-aqueous solvents* used by organic chemists as reaction media, ranging from the rather inert to those with highly pronounced donor or acceptor properties. and *liquid metals and alloys*, and their solutions in other liquids (e.g. in liquid ammonia or in molten salts). Discussions of these have rarely been brought together in one volume from a unified point of view based on common models, and extended as the need arises to cover specific requirements.

The great advances that have been made in the last two decades in deriving approximations of integral equations relating to correlation functions in fluids, and the simulation by computers of the equilibrium and dynamic behaviour of assemblies of particles, have revived the interest of liquid state scientists in

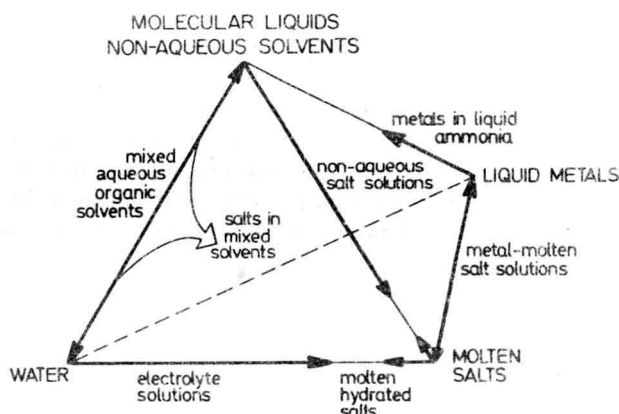
theoretical aspects. One of the major problems is the statement of the correct potential functions describing the interactions in the various types of fluids, and of approximating these according to well understood simplified models. However, this approach often disguises the lack of knowledge of the actual interactions by providing a too simplified model which is only capable of describing the properties of highly artificial model liquids rather than those of real liquids. Although the chemist is involved with real liquids, and usually with mixtures of real liquids, the theories cannot as yet provide detailed information about those properties which are required in order to make the best use of these liquids in practical applications. One must, therefore, revert to the phenomenology of these liquids and liquid mixtures, but this field has been somewhat neglected in recent years. In this book there is strong emphasis on the phenomenological aspects of liquids and liquid mixtures, with the understanding that not everything can be generalized and forced into the framework of simple phenomenological expressions, successful though these may be in describing some of the properties of some of the liquids and mixtures of interest. This is the reason that in many cases several phenomenological approaches are described in this book side-by-side, without the presumption of a decision on which is best among them.

This book provides also a considerable amount of factual knowledge so that the properties discussed and described by theoretical or phenomenological expressions are well illustrated. In many ways, the book provides a convenient source of information, in so far as its scope and size permit. The more extensive tables of properties are relegated to appendixes, so as not to break the continuity of the presentation. Among the properties displayed, much space has been devoted to solubilities and phase relationships, since these are often among the prime considerations of chemists in their decision on the suitability of a liquid or a liquid mixture for their purposes.

The book opens with a consideration of the liquid state as a disordered condensed phase, with thermal motion producing randomness, internal equilibrium and isotropic properties, and intermolecular forces producing cohesion and in some cases local order. The thermodynamic and statistical mechanical concepts and relationships used are briefly outlined, as are the phenomenological studies. Detailed considerations of transport properties and irreversible processes, as well as spectroscopic studies of liquids and mixtures, are excluded, although their results are frequently drawn upon to decide a point of discussion.

Pure liquids are discussed from two approaches: in the first, their physics is pursued as far as is profitable, treating the liquid either as a very dense gas (distribution function theories) or as a highly disordered solid (lattice theories); in the second, the structure and properties of actual liquids are described and compared with the results of the theoretical studies. The liquids are classified into atomic liquids (inert gases and metals); molecular liquids, with increasing degrees of interaction, culminating with water; and ionic liquids, that is molten salts, with varying degrees of ionicity. The relationships among these various kinds of liquids may be demonstrated by a schematic diagram.

LIQUIDS, MIXTURES AND SOLUTIONS



Liquid mixtures and solutions are subsequently discussed. Ideally, theories of the liquid state should provide potential functions which can be applied to dissimilar particles, leading to correlation functions involving all pairs of particles, the same and different, and finally to partition functions and free energies which are functions of the state of the system and the composition. Valiant attempts have been made in this direction, but a chemist is assisted more if it is permitted to take the macroscopic properties of the components of the mixture as granted, and information is then provided on how the properties of the mixture depend on those of the components at the given conditions and as a function of the composition. Heavy reliance is therefore put on the concept of excess functions. The systems are classified mainly according to the intermolecular forces: dispersion forces only (e.g. regular solutions); superposed dipole interactions (solutions of polar and hydrogen-bonded liquids); ion-dipole interactions and ion-ion interactions in a dielectric medium (electrolyte solutions); ionic interactions with no medium (molten salts); and electron-ion or -molecule interactions (solutions of metals). These interactions are usually regarded as 'physical interactions' since they are non-specific and non-directed, although in certain cases it is best to regard them as 'chemical', leading to definite association products, solvates or complexes.

It is hoped that practising chemists employing liquids as their reaction media, as well as advanced students of chemistry, will find this book a helpful introduction to the chemistry of the liquid state. They will gain an appreciation of the importance of this field of science and of its relationships to other fields of knowledge. They will then be able to apply a deeper comprehension to the problems of the liquid state in their work, and to extend their knowledge by studying more advanced texts and the current literature.

The author is indebted to many sources for the material in this book. These have been cited in the lists of references at the ends of tables, in figure-captions, and at

the ends of chapters. The more subtle influences on his mental picture of the chemistry of the liquid state, which has found expression in this book, is more difficult to acknowledge. The author has read, and it is hoped at least partly digested, the contents of many books. Following the preface is a list of such general references, which may also be of help to the reader. In his capacity as a university teacher the author had the opportunity of presenting some of the material in this book to his students, and he has profited from this experience too. Fruitful discussions with his graduate students and his colleagues, and in particular with Professor Arieh Ben-Naim, are acknowledged. The financial support of the Alexander von Humboldt Stiftung in the German Federal Republic, and the hospitality of Professor Franz Baumgärtner in his institute in the Kernforschungszentrum Karlsruhe, where a major part of this book was written, are also deeply appreciated. Last but not least, the loving patience of his wife and daughters, taxed by long absences caused by the need to concentrate on the writing of this book, is very gratefully recognized.

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Glossary of Symbols

Roman type letters are used for chemical species, *italicized* and Greek letters for physical quantities expressible in numerical terms, and heavy type letters for universal physical constants. Mathematical operators have their usual meaning (ln denotes natural, log denotes decadic logarithm), with the addition of $\langle \rangle$ for average quantity over a system and $\vec{}$ over a symbol designating a vector. Extensive thermodynamic quantities are normally in capital letters, molar quantities in lower case, while partial molar quantities have generally a subscript indicating the relevant component (occasionally a bar $\bar{}$ over the symbol if confusion would otherwise ensue). Superscripts for processes are normally in capital letters, superscripts and subscripts for states in lower case. Generally accepted and widely used symbols are preferred, however, to the systematic application of these generalizations, if in conflict.

The following list includes the main symbols used, their SI units and the equation or page (prefix p.) where the symbol is first defined or applied.

List of Principal Symbols — Latin Letters

A	Helmholz (free) energy (J)
AN	acceptor number (p. 109)
a	molar Helmholtz energy (J mol^{-1})
a	distance between centres of cells (m) (p. 78)
a	mean ionic diameter (m) (p. 230)
a_i	(relative) activity of component i (4.44)
$a(k)$	atomic scattering intensity (p. 50)
B_i	i th virial coefficient (B_2, B_3 , etc.) ($\text{m}^3 \text{mol}^{-1}$) $^{i-1}$ (1.44)
B	coefficient of linear term in Jones-Dole viscosity equation (6.19)
b	field-dependence coefficient of dielectric constant ($\text{m}^2 \text{V}^{-2}$) (1.32)
b	bound atom scattering length (m) (p. 50)
b	parameter in ionic association theory (6.109)
b	coefficient of the term in $\log \gamma_{\pm}$ linear in the ionic strength ($\text{dm}^3 \text{mol}^{-1}$) (6.88)
$b(i,j)$	set of graphs that contain at least one bridge point (p. 63)
b_j	coefficient of Redlich-Kister equation (4.65)
$b_j^{\prime}, b_j^{\prime\prime}$	coefficient of Margules equation (4.66), (4.67)

$b_{i(jk)}$	coefficient in Gibbs energy equation of molten salt mixtures (J mol^{-1}) (p. 274)
CAV_{ij}	contribution of dielectric cavity to potential energy between ions i and j (p. 241)
COR_{ij}	contribution of core repulsion to potential energy (p. 241)
C_p	heat capacity at constant pressure (JK^{-1})
C_2	total number of contact points of solute (p. 175)
C_{ij}	interaction parameter (J m^3) (p. 154)
c	speed of light in vacuum, $2.9979 \times 10^8 \text{ m s}^{-1}$
c_i	concentration of component i ($\text{M, dm}^3 \text{ mol}^{-1}$)
c_p	molar heat capacity at constant pressure ($\text{J K}^{-1} \text{ mol}^{-1}$) (1.20)
c_v	molar heat capacity at constant volume ($\text{J K}^{-1} \text{ mol}^{-1}$) (p. 12)
c_σ	orthobaric molar heat capacity ($\text{J K}^{-1} \text{ mol}^{-1}$) (p. 13)
c_{ij}	scaling factor of potential in molten salts (7.24)
D	bond dissociation energy (J) (p. 32)
D	electric displacement (C m^{-2}) (p. 219)
D	distribution ratio (p. 229, 316)
d	density, mass per unit volume (kg m^{-3}) (p. 10)
d	molecular size parameter (m) (p. 69)
d_{ij}	cation-anion distance in molten salts (m) (p. 260)
DN	donor number (kcal mol^{-1} , $1 \text{ cal} = 4.184 \text{ J}$) (p. 109)
E	energy (J), of electronic state, etc., internal energy
E	electric field intensity (V m^{-1})
E_A	electron affinity (J molecule^{-1})
E_F	Fermi energy (J) (p. 35)
E_κ	activation energy for conductance (J mol^{-1}) (3.14)
E_η	activation energy for viscosity, fluidity (J mol^{-1}) (3.14)
e	charge of proton, $1.6021 \times 10^{-19} \text{ C}$
e	molar expansibility ($\text{m}^3 \text{ K}^{-1} \text{ mol}^{-1}$) (p. 236)
F	Faraday constant, $9.6487 \times 10^4 \text{ C mol}^{-1}$
f	intermolecular force (N) (p. 21)
f	scaling factor for intermolecular potential (p. 25)
$f(r)$	direct correlation function (p. 52)
f_i	rational activity coefficient of component i (4.43)
GUR_{ij}	contribution of liquid structure to potential energy (p. 240)
G	Gibbs (free) energy (J)
G	affinity between particles (m^3) (2.6)
G	cavity surface-concentration of particles (p. 68)
G_j	group contribution to solubility parameter ($\text{J}^{1/2} \text{ cm}^{3/2}$)
δG^{HI}	Gibbs energy change for hydrophobic interactions (J mol^{-1}) (5.102)
g	scaling factor for molecular diameter (p. 25)
g	dipole correlation parameter (1.35, 3.4)
$g(r)$	pair correlation function (2.5)

$g^{(3)}$	triplet correlation function (p. 72)
g_i	molar Gibbs energy of component i (J mol^{-1})
g_p	coefficient in power series of Gibbs energy of electrolyte mixtures (6.118)
H	enthalpy (J)
\hat{H}	Hamiltonian function (1.71)
h	Planck's constant $6.6256 \times 10^{-34} \text{ J s}$
\bar{h}	molar enthalpy (J mol^{-1})
$b(r)$	total correlation function (p. 45)
I	ionization potential (J molecule^{-1})
I	ionic strength (mol kg^{-1} or M , mol dm^{-3}) (6.78)
$I(\theta)$	intensity of beam of radiation diffracted through angle θ
K	equilibrium constant (units according to reaction and concentration scales)
K	factor representing the reciprocal of the dielectric constant of a molten salt ($\text{C}^2 \text{ J}^{-1} \text{ m}^{-1}$) (3.7, 7.7)
K	scattering parameter (m^{-1}) (p. 317)
K_a	association constant for ion-pair (M , mol dm^{-3}) (6.105)
K_ϕ	equilibrium constant in terms of volume fraction
$K_{B(A)}$	Henry's law constant ($B = \text{solute}$, $A = \text{solvent}$) (Pa) (4.35)
k	Boltzmann's constant, $1.3805 \times 10^{-23} \text{ J K}^{-1}$
k	force constant (N m^{-1})
k	wave number (m^{-1}) (2.18)
k_F	Fermi wave number of electrons in metals (m^{-1})
k_p	packing factor (6.44)
k_s	salting (Setchenov) coefficient (M^{-1} , $\text{dm}^3 \text{ mol}^{-1}$) (6.55)
k_{ij}	deviation parameter (5.49)
L	length of edge of box containing particles (m) (p. 54)
L_i	partial molal relative heat content of component i (J mol^{-1}) (p. 212)
l_c	average intermolecular distance at critical state (m) (1.1)
(l)	liquid state
M	molar mass (kg mol^{-1})
m	mass of electron, $9.1066 \times 10^{-31} \text{ kg}$
m_i	molality of component i ($\text{mol (kg solvent)}^{-1}$)
N	Avogadro's number, $6.0225 \times 10^{23} \text{ molecule mol}^{-1}$
N	number of molecules
n	number of moles (mol)
n	refractive index (n_D when measured with sodium D line light) (1.30)
n	number of metallic bonds formed between two metal atoms (p. 309)
$n^{(1)}$	singlet distribution function (2.2)
$n^{(2)}$	pair distribution function (2.3)
$n^{(i)}$	i -particle distribution function (p. 61)
$n(r)$	radial distribution function

P	pressure (Pa)
P	molar polarization ($\text{m}^3 \text{mol}^{-1}$) (1.33)
P	probability that neighbouring sites are occupied (5.13)
P_σ	(saturated) vapour pressure (Pa)
p	momentum (kg m s^{-1})
p	probability that a neighbour of a molecule of type 1 is a molecule of type 2 (p. 139)
p_i	vapour pressure of component i (Pa) (4.32)
\vec{p}	momentum vector (Cartesian coordinates) (p. 37)
Q	(total) partition function (1.72)
$Q(b)$	integral function concerning ion-pairs (6.109)
q	internal partition function (p. 38)
q	quadrupole moment (C m^2) (p. 27)
q	geometric parameter for polymers (p. 167)
q	critical distance for association (m) (p. 243)
q_n	collective coordinate (2.47)
q_{ij}	electrical potential energy divided by kT (6.91)
R	gas constant, $8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$
R	specified distance between particles (m)
R	molar refractivity ($\text{m}^3 \text{mol}^{-1}$) (1.30)
R	width, relative to σ , of square-well potential (1.40)
R_{ij}	mole ratio in dilute reciprocal molten salt mixture (7.63)
r	distance between particles (m)
r	critical index of surface tension (p. 16)
r	ratio of (molar or free) volumes of components of mixture
$r_c(r_{c+}, r_{c-})$	(crystal) radius of ion (cation, anion) (m)
r_i	reaction field correction to dipole interaction (5.59)
$r_p(r_s)$	limit of primary (secondary) hydration of ions (m) (p. 215)
r_e	effective radius (m) (p. 215)
r^0	equilibrium distance between two neighbouring molecules (m)
\vec{r}	distance vector (Cartesian coordinates) (Fig. 2.1, p. 44)
r^N	set of N molecules at specified distances r from origin (p. 37)
S	entropy (J K^{-1})
S	overlap integral (p. 32)
S	structuredness (3.5)
S_{comm}	communal entropy (J K^{-1}) (1.3)
$S(k), S(K)$	structure factor (pp. 50, 317)
S_t	generalized limiting slope of properties of electrolyte solutions (units depend on property) (6.87)
S_γ	limiting slope of activity coefficient ($\text{kg}^{1/2} \text{mol}^{-1/2}$) (6.86)
T	temperature (K)
T_m	melting point (K)
T_b	normal boiling point (K)
T_t	triple point (K)
T_c	critical point (K)

T_0	ideal glass transition point (vanishing configurational entropy) (K) (p. 5)
T_g	glass transition temperature (K) (p. 6)
t	centigrade temperature ($^{\circ}\text{C}$)
t	ordinal number of a step in a sequence (p. 55)
t_s	generalized partial molar quantity of an electrolyte (7.87) (units depend on property)
U	internal energy (J)
U	potential energy of a system of particles (J)
u	molar internal energy (J mol^{-1})
$u(r)$	mutual pair-interaction energy of molecules (J molecule^{-1})
$\bar{u}(r)$	angle averaged mutual interaction energy (J molecule^{-1})
V	volume (m^3)
v	molar volume ($\text{m}^3 \text{mol}^{-1}$) (p. 11)
v_f	free volume ($\text{m}^3 \text{mol}^{-1}$) (p. 75)
W	work (J)
W_i	mass of a component i (kg)
w	interaction (exchange) energy (J molecule^{-1}) (p. 81) (4.121)
w_i	mass fraction of component i (4.1)
x	mole fraction of a specified component in a binary mixture
x'	equivalent fraction in molten salt mixture (7.5)
x_i	mole fraction of component i
x_{ij}	fraction of particles i and j which are neighbours
Y_m	generalized thermodynamic property of a mixture (units depend on property)
y	generalized molar thermodynamic function (units depend on properties) (p. 7)
y	mole fraction of an electrolyte in a binary electrolyte mixture (6.117)
y_i	partial molar generalized thermodynamic property (4.12)
γ_i	molar (concentration) activity coefficient (4.57)
$y(i,j)$	set of graphs (i,j) -irreducible and free from bridge points (p. 63)
Z	atomic number
Z	configurational partition function (1.75)
Z	coordination number for nearest-neighbours (2.28)
Z'	coordination number for next-nearest-neighbours (p. 60)
Z	compressibility factor (p. 90)
Z^z	generalized ion of charge z
z	charge of an ion (algebraic, in units of e)
z	composition descriptor (4.74)

List of Symbols – Greek Letters

α	polarizability ($\text{m}^3 \text{molecule}^{-1}$)
α	critical index of heat capacity (p. 16)

α	ratio of site occupancy probabilities (5.15)
α	degree of dissociation of an electrolyte (6.105)
α_j	(regular mixture) interaction coefficient (J mol^{-1}) (4.69)
α_j	solvent-sorting coefficient (6.65)
α_p	isobaric thermal expansibility (K^{-1}) (1.10)
α_o	orthobaric thermal expansibility (K^{-1}) (1.12)
α_{ij}	non-randomness parameter in Renon's equation (p. 173)
β	resonance integral (p. 33)
β	critical index of molar volume (p. 16)
β_j	temperature coefficient of interaction parameter ($\text{J K}^{-1} \text{mol}^{-1}$) (4.69)
Γ	surface excess of matter (mol m^{-2}) (1.23)
γ	critical index for pressure-derivative with volume (p. 16)
γ	coupling parameter (2.60)
γ_i	molal activity coefficient of component i (4.56)
γ_j	interaction coefficient of excess heat capacity ($\text{J K}^{-1} \text{mol}^{-1}$) (4.69)
Δ	change in a thermodynamic property for a process
δ	square root of cohesive energy density (solubility parameter) ($\text{J}^{1/2} \text{cm}^{-3/2}$) (p. 10) (5.31)
δ	critical index of pressure (p. 16)
δ	Kihara hard-core diameter (m) (p. 26)
δ	perturbation parameter relating to energies (4.103)
δ	size parameter in molten salts (7.14)
δ_i	molar dielectric decrement caused by component i ($\text{M}^{-1}, \text{dm}^3 \text{mol}^{-1}$) (p. 227)
ϵ_0	permittivity of vacuum $8.8542 \times 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1}$
ϵ	(relative) dielectric constant
ϵ	depth of potential-well (J molecule^{-1}) (1.40, 1.42)
ϵ	self interaction parameter (p. 307)
ϵ_h	minimum energy required for a molecule to enter a hole (J molecule^{-1}) (p. 84)
ζ	fraction of adduct (p. 187)
η	viscosity (Pa s^{-1})
η	reduced density $\pi/6\rho\sigma^3$ (p. 66)
η	electronegativity factor (J mol^{-1}) (p. 304)
θ	angle in polar coordinates
θ	critical index of $(\partial^2 p / \partial T^2)_o$ (p. 16)
θ	perturbation parameter pertaining to energies (4.105)
θ_E	characteristic Einstein temperature (K) (p. 85)
θ_{ai}	fraction of contact points of type a in component i (p. 175)
κ	specific conductance ($\Omega^{-1} \text{m}^{-1}$)
κ	reciprocal thickness of ionic atmosphere (m^{-1}) (6.70)
κ_S	adiabatic compressibility (Pa^{-1}) (1.17)
κ_T	isothermal compressibility (Pa^{-1}) (1.13)

Λ	ternary (reciprocal) ion mixing enthalpy in molten salts (J mol^{-1}) (7.50)
Λ	momentum partition function (reciprocal, per degree of freedom) (1.73)
Λ	interaction parameter in Wilson's equation (5.42)
λ	wavelength of radiation (m)
λ	scaling parameter (pp. 68, 232)
λ	equivalent conductivity ($\Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$)
λ	dispersion contribution to solubility parameter ($\text{J}^{1/2} \text{ cm}^{-3/2}$) (p. 179)
λ	coulomb interaction energy (J mol^{-1}) (7.20).
λ_i	absolute activity of component i (4.17)
λ_{ij}	short-range interaction parameter (6.95)
μ	chemical potential (J molecule^{-1}) (1.83)
μ	dipole moment (Debye, $3.33564 \times 10^{-30} \text{ C m}$)
μ_i	chemical potential of component i (J mol^{-1}) (4.14)
ν	vibration frequency (s^{-1})
$\nu(\nu_+, \nu_-)$	number of ions (cations, anions) into which electrolyte is dissociated
ν_{CT}	vibration frequency for charge transfer absorption band
ρ	number density (molecules m^{-3})
ρ	perturbation parameter pertaining to sizes (4.104)
ρ	size factor (p. 304)
ρ	electrical resistivity ($\Omega \text{ m}$) (p. 317)
ρ_0	number density of close-packed system $2^{1/2} \sigma^{-3}$ (molecule m^{-3})
ρ_i	perturbation parameter (7.9)
σ	molecular diameter (m)
σ	surface tension (N m^{-1}) (p. 13)
σ	scattering cross-section (p. 50)
σ	perturbation parameter pertaining to sizes (4.106)
σ	degree of order in a mixture (4.122)
$\sigma(\kappa a)$	parameter of Gibbs energy of solvent (6.81)
$\sigma_{\text{M}}(\sigma_{\text{X}})$	softness parameter of cation (anion) (7.27, 7.28)
τ	induction and orientation contribution to solubility parameter ($\text{J}^{1/2} \text{ cm}^{-3/2}$) (p. 179)
$\tau(\kappa a)$	parameter of Gibbs energy of electrolyte (6.75)
Φ	intermolecular virial function (J) (p. 40)
Φ	local volume fraction (5.39)
ϕ	volume fraction of a component (4.6)
ϕ	osmotic coefficient (6.11)
$\phi(i, j)$	interaction path (p. 63, Fig. 2.8)
$\phi(r)$	potential function for polarizable ions (J molecule^{-1}) (7.24)
ϕ	angle in polar coordinates
ϕ_i	volume fraction of component i (4.8)
ψ	wave function
ψ	RT times a generalized dimensionless function of electrolyte mixtures (J mol^{-1}) (6.124)

ψ_a	electrostatic potential due to ionic atmosphere (V) (6.72)
ψ_j	electrostatic potential caused by ion j (V)
$\psi(r/d)$	potential function for molten salts (J m molecule ⁻¹) (7.8)
ψ_{12}	binary interaction parameter (J mol ⁻¹) (5.56)
ξ	random number between 0 and 1 (p.55)
ξ	coupling parameter (p.67)
ξ	fraction of self-associated species (dimer) (p.184)
χ	interaction parameter for z-regular solutions (J mol ⁻¹) (5.45)
χ_i	electronegativity of i (kJ mol ⁻¹) ^{1/2} (p.304)
ω	acentric factor (3.1, 5.46)

Superscripts

^o	for standard state
[∞]	for (infinitely) dilute solutions
*	of pure component
*	of reference, for conformational substances (p.25)
'(")	designation of phases in equilibrium
'	equivalent fraction composition scale in molten salts (7.5)
~	equimolar binary mixture
~	reduced (divided by the relevant standard quantity)
E	excess function of mixing (p.144)
F	of fusion (negative sign : of freezing)
g	gaseous state
l	liquid state
M	change on mixing
s	solid state
tr	of transfer
V	of vaporization

Subscripts

c	at the critical state
h	of hydration
i	of component i
i(j,k)	of molecule i (j or k)
m	of a mixture
r	reduced, i.e. divided by the corresponding quantity for the critical, or another specified, state (p.13)
s	of surface
u	of unionized part of electrolyte (p.242)
σ	orthobaric state (liquid—vapour equilibrium line) (p.9)