Chapter 2
The Properties of Ions Constituting Ionic Liquids

Ions are defined as particles of atomic or molecular size that carry electrical charges. They may exist in gaseous phases as individual ions but in condensed phases (solids and liquids) they exist as electrically neutral combinations of positively charged cations and negatively charged anions. High temperature ionic liquids may consist of monatomic ions, such as Ca^{2+} or F^{-}, their anions (but hardly the cations) may also consist of a few atoms, such sulfate, $SO_4{}^{2-}$. At somewhat lower temperatures molten salts may consist of quaternary ammonium or phosphonium cations with a variety of anions, e.g., Bu_4N^+ $BF_4{}^{-}$. A class of ionic liquids, molten hydrated salts, on the contrary, consist of cations, such as $Mg(H_2O)_6{}^{2+}$, in which a monatomic cation is coordinated to water molecules. Finally, room temperature ionic liquids (RTILs) consist mostly of large organic cations, such as 1-ethyl-3-methylimidazolium, and polyatomic anions, such as bis(trifluoromethylsulfonyl)amide, $(CF_3SO_2)_2N^{-}$. The physical properties of ions are designated in this book by having the subscript $_I$ for the ion.

2.1 The Properties of Isolated Ions

Ions in an ideal gaseous state, termed isolated or bare ions, are devoid of interactions with other particles or their surroundings and are commonly monatomic or consist of relatively few atoms. Generalized ions are designated by $I^{z\pm}$, where z_I is an integral positive or negative number. The primary characteristics of isolated ions are the amount of electrical charge they carry and their mass. The amount of charge is given in terms of $z_I e$, where $e = 1.60218 \times 10^{-19}$ C is the elementary unit of the charge. The masses of ions are generally specified as their molar mass, M_I, that is, the mass of Avogadro's number, $N_A = 6.02214 \times 10^{23}$ mol^{-1}, of ions. The units of the molar mass, are kg·mol^{-1}. The molar masses of the ions constituting the ionic liquids dealt with in this book are shown in Table 2.1, and are, of course, additive,

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Table 2.1 The names, formulas, charge numbers, z_I, and molar masses, M_I, of common ions

Cations	z_I	M_I /kg·mol^{-1}
Lithium, Li^+	+1	0.006941
Sodium, Na^+	+1	0.02294
Potassium, K^+	+1	0.03910
Rubidium, Rb^+	+1	0.08547
Cesium, Cs^+	+1	0.13291
Copper(I), Cu^+	+1	0.06355
Silver, Ag^+	+1	0.10787
Thallium(I), Tl^+	+1	0.20438
Beryllium, Be^{2+}	+2	0.009012
Magnesium, Mg^{2+}	+2	0.02431
Calcium, Ca^{2+}	+2	0.04008
Strontium, Sr^{2+}	+2	0.08762
Barium, Ba^{2+}	+2	0.13733
Vanadium(II), V^{2+}	+2	0.05094
Chromium(II), Cr^{2+}	+2	0.05201
Manganese(II), Mn^{2+}	+2	0.05494
Iron(II), Fe^{2+}	+2	0.05585
Cobalt, Co^{2+}	+2	0.05893
Nickel, Ni^{2+}	+2	0.05869
Copper(II), Cu^{2+}	+2	0.06355
Zinc, Zn^{2+}	+2	0.06539
Cadmiun, Cd^{2+}	+2	0.11241
Tin(II), Sn^{2+}	+2	0.11871
Lead, Pb^{2+}	+2	0.2072
Aluminum, Al^{3+}	+3	0.02698
Scandium, Sc^{3+}	+3	0.04496
Vanadium(III), V^{3+}	+3	0.05094
Chromium(III), Cr^{3+}	+3	0.05201
Iron(III), Fe^{3+}	+3	0.05585
Gallium, Ga^{3+}	+3	0.06971
Yttrium, Y^{3+}	+3	0.08891
Indium, In^{3+}	+3	0.11482
Lanthanum, La^{3+}	+3	0.13891
Cerium(III), Ce^{3+}	+3	0.14012
Praseodymium, Pr^{3+}	+3	0.14091
Neodymium, Nd^{3+}	+3	0.14424
Promethium, Pm^{3+}	+3	0.147
Samarium(III), Sm^{3+}	+3	0.15036
Europium(III), Eu^{3+}	+3	0.15197
Gadolinium, Gd^{3+}	+3	0.15725
Terbium, Tb^{3+}	+3	0.15893
Dysprosium, Dy^{3+}	+3	0.16251

(continued)

Table 2.1 (continued)

Cations	z_I	M_I /kg·mol^{-1}
Holmium, Ho^{3+}	+3	0.164936
Erbium, Er^{3+}	+3	0.16726
Thulium, Tm^{3+}	+3	0.16893
Ytterbium(III), Yb^{3+}	+3	0.17304
Lutetium, Lu^{3+}	+3	0.17497
Thallium(III), Tl^{3+}	+3	0.20438
Bismuth, Bi^{3+}	+3	0.20898
Zirconium, Zr^{4+}	+4	0.09122
Tin(IV), Sn^{4+}	+4	0.11871
Cerium(IV), Ce^{4+}	+4	0.14012
Hafnium, Hf^{4+}	+4	0.17849
Thorium, Th^{4+}	+4	0.23204
Uranium(IV), U^{4+}	+4	0.23803
Cations of low- and room-temperature melting salts	z_I	M/kg·mol^{-1}
Ammonium, $NH_4{}^+$	+1	0.01804
Hydroxylaminium, $HONH_3{}^+$	+1	0.03404
Hydrazinium, $H_2NNH_3{}^+$	+1	0.03305
Guanidinium, $C(NH_2)_3{}^+$	+1	0.06008
Tetraalkylammonium, $[H(CH_2)_n]_4N^+$	+1	$0.01803 + 0.05611n$
Tetraalkylphosphonium, $[H(CH_2)_n]_4P^+$	+1	$0.03500 + 0.05611n$
1-Alkyl-3-methylimidazolium ($C_n$mim), $[H(CH_2)_n]C_4H_6N_2{}^+$	+1	$0.08307 + 0.01403n$
1-Alkylpyridinium (C_nPy^+), $[H(CH_2)_n]C_5H_5N^+$	+1	$0.07911 + 0.01403n$
1-Alkyl-1-methylpyrrolidinium(C_nMePyrr), $[H(CH_2)_n]C_5H_{11}N^+$	+1	$0.08506 + 0.01403n$
Tetraphenylphosphonium,Ph_4P^+	+1	0.33939
Tetraphenylarsonium, Ph_4As^+	+1	0.38334
Cations of hydrated molten salts	z_I	M/kg·mol^{-1}
$M(H_2O)_n{}^{z+}$ (M is a monatomic cation)	$+z$	$M_I + 0.01802n$
Anions	z_I	M/kg·mol^{-1}
Fluoride, F^-	−1	0.01899
Chloride, Cl^-	−1	0.03545
Bromide, Br^-	−1	0.07991
Iodide, I^-	−1	0.12691
Hydroxide, OH^-	−1	0.01701
Hydrosulfide,SH^-	−1	0.03307
Cyanide, CN^-	−1	0.02602
Cyanate, NCO^-	−1	0.04203
Thiocyanate, SCN^-	−1	0.05808
Azide, $N_3{}^-$	−1	0.04202
Hydrogenfluoride, $HF_2{}^-$	−1	0.03901
Triiodide, $I_3{}^-$	−1	0.38071
Metaborate, $BO_2{}^-$	−1	0.04281
Nitrite, $NO_2{}^-$	−1	0.04601
Nitrate, $NO_3{}^-$	−1	0.06201

(continued)

Table 2.1 (continued)

Cations	z_I	M_I /kg·mol^{-1}
Chlorate, ClO_3^-	−1	0.08345
Bromate, BrO_3^-	−1	0.12761
Iodate, IO_3^-	−1	0.17491
Perchlorate, ClO_4^-	−1	0.09945
Permanganate, MnO_4^-	−1	0.11894
Pertechnetate, TcO_4^-	−1	0.16301
Perrhenate, ReO_4^-	−1	0.25002
Tetrafluoroborate, BF_4^-	−1	0.08681
Trifluoromethyltrifluoroborate, $CF_3BF_3^-$	−1	0.14281
Tetracyanoborate, $B(CN)_4^-$	−1	0.11488
Formate, HCO_2^-	−1	0.04502
Acetate, $CH_3CO_2^-$	−1	0.05904
Benzoate, $PhCO_2^-$	−1	0.12112
Chloroacetate, $CH_2ClCO_2^-$	−1	0.09349
Trifluoroacetate, $CF_3CO_2^-$	−1	0.11302
Methylsulfonate, $CH_3SO_3^-$	−1	0.09510
Trifluoromethylsulfonate, $CF_3SO_3^-$	−1	0.14906
4-toluenesulfonate (tosylate) $CH_3C_6H_4SO_3^-$	−1	0.17121
Tetraphenylborate, BPh_4^-	−1	0.31923
Hexafluorophosphate, PF_6^-	−1	0.14496
Trifluoro-tris(pentafluoroethyl)phosphate (FAP), $PF_3(C_2F_5)_3$	−1	0.44503
Hexafluoroantimonate, SbF_6^-	−1	0.23574
Hydrogensulfate, HSO_4^-	−1	0.09707
Methylsulfate, $CH_3SO_4^-$	−1	0.11110
Ethylsulfate, $C_2H_5SO_4^-$	−1	0.12512
Octylsulfate, $C_8H_{17}SO_4^-$	−1	0.20931
Tetrachloroaluminate, $AlCl_4^-$	−1	0.17179
Tetrachloroferrate, $FeCl_4^-$	−1	0.20066
Dicyanamide (DCA), $N(CN)_2^-$	−1	0.06604
Difluorosulfonylamide (FSA), $N(FSO_2)_2^-$	−1	0.18014
Bis(trifluoromethylsulfonyl)amide (NTF2), $N(CF_3SO_2)_2^-$	−1	0.28015
Oxide, O^{2-}	−2	0.01600
Sulfide, S^{2-}	−2	0.03207
Carbonate, CO_3^{2-}	−2	0.06001
Sulfite, SO_3^{2-}	−2	0.08007
Sulfate, SO_4^{2-}	−2	0.09607
Selenate, SeO_4^{2-}	−2	0.14297
Chromate, CrO_4^{2-}	−2	0.11599
Molybdate, MoO_4^{2-}	−2	0.15994
Tungstate, WO_4^{2-}	−2	0.24785
Thiosulfate, $S_2O_3^{2-}$	−2	0.11212
Hexafluorosilicate, SiF_6^{2-}	−2	0.14208
Dichromate, $Cr_2O_7^{2-}$	−2	0.21599

(continued)

Table 2.1 (continued)

Cations	z_I	M_I /kg·mol^{-1}
Phosphate, PO_4^{3-}	−3	0.09497
Hexacyanoferrate(III), $Fe(CN)_6^{3-}$	−3	0.21195
Hexacyanocobaltate(III), $Co(CN)_6^{3-}$	−3	0.21611
Hexacyanoferrate(II), $Fe(CN)_6^{4-}$	−4	0.21195

multiplied by the appropriate stoichiometric coefficients v_I, to make up the molar mass of the ionic liquid (molten salt).

Thermodynamic quantities that pertain to isolated ions in the ideal gas state (designated as 'ig') and to their formation from the elements in their standard states are well defined. The standard molar entropy and constant-pressure heat capacity, $S°(I^{z\pm},ig)$ and $C_P°(I^{z\pm},ig)$, of isolated ions are recoded in Table 2.2 in J·K^{-1}·mol^{-1} for the standard temperature $T° = 298.15$ K and pressure $P° = 0.1$ MPa. The standard molar Gibbs energy and the enthalpy of formation, $\Delta_f G°(I^{z\pm},ig)$ and $\Delta_f H°(I^{z\pm},ig)$, in kJ·mol^{-1} of many ions are also recorded in Table 2.2, The values of the Gibbs energies having been obtained from the enthalpies and entropies: $\Delta_f G°\left(I^{z\pm}, \text{ig}\right) = \Delta_f H°\left(I^{z\pm}, \text{ig}\right) - T°\left[S°\left(I^{z\pm}, \text{ig}\right) - \Sigma S°(\text{elements}, \text{ig})\right]$ in a manner that is thermodynamically consistent.

The standard molar entropy of isolated monatomic ions with no unpaired electrons reflects the translational entropy alone and depends only on the mass of the ion. At $T° = 298.15$ K and $P° = 0.1$ MPa the standard molar entropy is then $S°\left(I^{z\pm}, \text{ig}\right) = 108.85 + {}^{3}\!/_{2}\ln(M/M°)\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, where $M/M°$ is the relative molar mass ($M° = 1$ kg·mol^{-1}). The standard molar heat capacity of monatomic ions with no unpaired electrons depends on the translational degrees of freedom alone, hence is common to all the monatomic ions: $C_P°\left(I^{z\pm}, \text{ig}\right) = {}^{5}\!/_{2}R = 20.79\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, where $R = 8.31451$ J·K^{-1}·mol^{-1} is the gas constant. Monatomic ions with unpaired electrons have a contribution from electronic spin to the heat capacity and entropy and polyatomic ions have contributions from their rotational and vibrational modes.

The standard molar volume of an isolated ion is a trivial quantity, being the same for all ions: $V°\left(I^{z\pm}, \text{ig}\right) = RT°/P° = 0.02479\ \text{m}^3 \cdot \text{mol}^{-1}$.

Values are provided for some ions not to be found in molten salts (e.g., H^+) and for a few cations relevant to low-melting salts and RTILs, but for most of the latter no data could be found, nor for most of the polyatomic anions relevant to the RTILs.

The shape of isolated monatomic ions is spherical, but ions that consist of several atoms may have any shape. The common ones are planar (NO_3^-, CO_3^{2-}), tetrahedral (NH_4^+, BF_4^-), octahedral (PF_6^{4-}), elongated (SCN^-), or more irregular, as they are for the ions constituting RTILs that generally have low symmetry (otherwise higher melting salts result). Tetrahedral and octahedral ions approximate spherical shape for many purposes and are termed globular. The size of an isolated ion cannot be specified readily, because its outer electron shell extends indefinitely around the inner ones and the nucleus. The sizes of ions in condensed liquid phases

Table 2.2 The standard molar entropy $S^{o}(\mathrm{I}^{z\pm},\mathrm{ig})$ [1] and constant-pressure molar heat capacity $C_{P}^{o}(\mathrm{I}^{z\pm},\mathrm{ig})$ [2] and the standard molar enthalpy $\Delta_{f}H^{o}(\mathrm{I}^{z\pm},\mathrm{ig})$ and Gibbs energy $\Delta_{f}G^{o}(\mathrm{I}^{z\pm},\mathrm{ig})$ of formation [3] of isolated ions at the standard temperature $T^{o} = 298.15$ K and pressure $P^{o} = 0.1$ MPa

Ion	$S^{\circ}(\mathrm{I}^{z\pm},\mathrm{ig})$/ $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$	$C_{P}^{\circ}(\mathrm{I}^{z\pm},\mathrm{ig})$/ $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$	$\Delta_{f}H^{\circ}(\mathrm{I}^{z\pm},\mathrm{ig})$/ $\mathrm{kJ{\cdot}mol^{-1}}$	$\Delta_{f}G^{\circ}(\mathrm{I}^{z\pm},\mathrm{ig})$/ $\mathrm{kJ{\cdot}mol^{-1}}$
H^{+}	108.9	20.8	1536.2	1523.2
Li^{+}	133.0	20.8	685.78	654.8
Na^{+}	148.0	20.8	609.36	580.5
K^{+}	154.6	20.8	514.26	487.3
Rb^{+}	164.4	20.8	490.1	464
Cs^{+}	169.9	20.8	457.96	432.7
Cu^{+}	161.1	20.8	1089.99	1051.9
Ag^{+}	167.4	20.8	1021.73	984.5
Tl^{+}	175.3	20.8	772.2	739
Be^{2+}	136.3	20.8	2993.23	2955.4
Mg^{2+}	148.7	20.8	2348.5	2300.3
Ca^{2+}	154.9	20.8	1925.9	1892.1
Sr^{2+}	164.7	20.8	1790.54	1757
Ba^{2+}	170.4	20.8	1660.38	1628.3
Ra^{2+}	176.6	20.8	1659.79	
V^{2+}	182.1	29.6	2590.86	2545.2
Cr^{2+}	181.7	31.2	2655.71	2592
Mn^{2+}	173.8	20.8	2519.69	2477.4
Fe^{2+}	180.3	25.9	2749.93	2689.6
Co^{2+}	179.5	22.9	2844.2	2785.7
Ni^{2+}	178.1	21.7	2931.39	2873.4
Cu^{2+}	176.0	20.8	3054.07	3011.5
Zn^{2+}	161.1	20.8	2782.78	2747.2
Cd^{2+}	167.8	20.8	2623.54	2588.9
Sn^{2+}	168.5	20.8	2434.8	2399.9
Pb^{2+}	175.5	20.8	2373.33	2328.6
Al^{3+}	150.2	20.8	5483.17	5446.9
Sc^{3+}	156.4	20.8	4652.31	4616
V^{3+}	177.8	20.8	5424.6	5380.2
Cr^{3+}	179.0	20.8	5648.4	5602.1
Fe^{3+}	174.0	20.8	5712.8	5669.1
Ga^{3+}	161.9	20.8	5816.6	5780.5
Y^{3+}	164.9	20.8	4199.86	4163.9
In^{3+}	168.1	20.8	5322	5289.1
Sb^{3+}	169.0	20.8	5151	5114
La^{3+}	170.5	20.8	3904.9	3871
Ce^{3+}	185.5	20.8	3970.6	3936.8
Pr^{3+}	188.9	20.8	4005.8	3971.3

(continued)

Table 2.2 (continued)

Ion	$S^\circ(I^{z\pm},ig)/$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$	$C_P^\circ(I^{z\pm},ig)/$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$	$\Delta_f H^\circ(I^{z\pm},ig)/$ $kJ{\cdot}mol^{-1}$	$\Delta_f G^\circ(I^{z\pm},ig)/$ $kJ{\cdot}mol^{-1}$
Nd^{3+}	191.6	20.8	4050	4014.6
Pm^{3+}	191.0	20.8	4079 [4]	4044
Sm^{3+}	189.0	20.8	4100	4065.1
Eu^{3+}	181.0	20.8	4230	4199.4
Gd^{3+}	189.3	20.8	4163	4126.9
Tb3+	193.5	20.8	41967	41614.1
Dy^{3+}	195.5	20.8	4205	4169
Ho^{3+}	196.2	20.8	4243	4207
Er^{3+}	195.9	20.8	4268	4231.4
Tm^{3+}	194.3	20.8	4297	4261.2
Yb^{3+}	190.5	20.8	4367.3	4328.3
Lu^{3+}	173.4	20.8	4350	4293.5
Tl^{3+}	175.3	20.8	5639.2	5606.1
Bi^{3+}	175.9	20.8	5004	4968.1
U^{3+}	195.5	20.8	4176 [5]	4132.4
Zr^{4+}	165.2	20.8	8261 [4]	8223.4
Sn^{4+}	168.5	20.8	9320.7	9285.8
Ce^{4+}	170.6	20.8	7523	7493.6
Hf^{4+}	173.6	20.8	8192	8153.2
Th^{4+}	176.9	20.8	7021	6984.2
U^{4+}	186.4	20.8	7327 [5]	7286.4
H_3O^+	192.8	34.9	570.7 [6]	602.2
NH_4^+	186.3	34.9	630 [4]	681
$C(NH_2)_3^+$	264.5 [8]	77.9 [7]	462 [7]	
Me_4N^+	331.9 [2]	109.6	537 [9]	73.4
Et_4N^+	483	201 [10]	411 [7]	712
Pr_4N^+	641	294 [10]	307 [7]	
Bu_4N^+		386 [10]	221 [7]	
Ph_4P^+	651.0 [2]	366.3		
Ph_4As^+	650.0 [2]	368.6		
$Etmim^+$			243 [11]	
$Bumim^+$			195 [11]	
F^-	145.6	20.8	−255.39	−268.6
Cl^-	154.4	20.8	−233.13	−241.4
Br^-	163.6	20.8	−219.07	−245.1
I^-	169.4	20.8	−197	−230.2
OH^-	172.3	29.1	−143.5	−144.8
SH^-	186.2	29.1	−120 [12]	−146.6
CN^-	196.7	29.1	36 [12]	−59.2

(continued)

Table 2.2 (continued)

Ion	$S°(I^{z\pm},ig)$/ $J·K^{-1}·mol^{-1}$	$C_P°(I^{z\pm},ig)$/ $J·K^{-1}·mol^{-1}$	$\Delta_f H°(I^{z\pm},ig)$/ $kJ·mol^{-1}$	$\Delta_f G°(I^{z\pm},ig)$/ $kJ·mol^{-1}$
NCO^-	218.9	38.0	−192 [4]	−196.4
SCN^-	232.5	43.2	−49	
N_3^-	212.25	37.9	180.7	203.1
HF_2^-	211.3	34.0	−683 [4]	−666
I_3^-	334.7	61.7	−482 [4]	−529.9
BO_2^-	215.8	38.4	−667 [3]	−668
NO_2^-	236.2	37.1	−202 [12]	−182.7
NO_3^-	245.2	44.7	−320 [12]	−272.8
ClO_3^-	264.3	57.6	−200 [12]	−153.8
BrO_3^-	278.7	60.4	−145 [12]	−113.7
IO_3^-	288.2	62.0	−208 [12]	−184.9
ClO_4^-	263.0	62.0	−344 [12]	−266.8
MnO_4^-	277.8	72.4	−723.8	−674.8
ReO_4^-	284.1	74.7	−976 [2]	−930.4
BF_4^-	267.9	67.8	−1687 [4]	−1644.2
HCO_2^-	238.2	38.8	−460 [13]	−452.7
$CH_3CO_2^-$	278.2	61.4	−504.2 [13]	−464.1
$PhCO_2^-$	338.0 [8]	117.9	−400.4 [13]	−330.6
$CF_3CO_2^-$	331.0 [2]	89.3	−1194 [4]	−1138
$CF_3SO_3^-$	346.0 [2]	107.6		
BPh_4^-	656.0 [2]	363.7 [2]		
HSO_4^-	283.0	70.9	−953 [4]	−886.1
PF_6^-	299.6 [8]	104.7	−2109.9 [4]	−2005.6
SbF_6^-	345.5 [8]	124.0	−1993 [4]	−1901
$AlCl_4^-$		205 [14]	−1159 [15]	
$N(CN)_2^-$			161.5 [11][a]	
$N(CF_3SO_2)_2^-$			−2020.5 [11][a]	
O^{2-}	143.3	20.8	950 [4]	939.7
S^{2-}	152.1	20.8		
CO_3^{2-}	246.1	44.4	−321 [12]	−300.9
SiO_3^{2-}		57.6 [14]		
$Si_2O_5^{2-}$		101.9 [14]		
SO_3^{2-}	264.3	52.6		−1035.5
SO_4^{2-}	263.6	62.4	−758 [12]	−704.8
SeO_4^{2-}	281.2	73.5		
CrO_4^{2-}	281.4	74.8	−705 [12]	−659.5
MoO_4^{2-}	291.1	77.0		
WO_4^{2-}	296.6	76.6		
$S_2O_3^{2-}$	291.1	71.0		
SiF_6^{2-}	309.9	113.1	−2161 [4]	−2183.4
$Cr_2O_7^{2-}$	379.7	140.8		

(continued)

Table 2.2 (continued)

Ion	$S°(I^{z±},ig)$/ $J·K^{-1}·mol^{-1}$	$C_P°(I^{z±},ig)$/ $J·K^{-1}·mol^{-1}$	$\Delta_fH°(I^{z±},ig)$/ $kJ·mol^{-1}$	$\Delta_fG°(I^{z±},ig)$/ $kJ·mol^{-1}$
PO_4^{3-}	266.4	65.4		
$Fe(CN)_6^{3-}$	491.6 [2]	217.1		
$Co(CN)_6^{3-}$	464.8	210.2		
$Fe(CN)_6^{4-}$	469.8	210.6		

References are provided for data not found in those given in this caption

[a] When the value for $\Delta_fH°(Cl^-,ig)$ in this Table is used as a reference, but when the value for $\Delta_fH°(NO_3^-,ig)$ is used it yields values 31 kJ mol^{-1} more negative for anions, more positive for cations)

(molten salts and RTILs), however, are generally taken as being the same as those in crystals, in which they may be determined by x-ray or neutron diffraction methods. These sizes, expressed as ionic radii or ionic volumes, are dealt with below and in the following chapters.

Some other properties of isolated ions have been determined: the magnetic susceptibility, the polarizability, and the softness/hardness. These properties of isolated ions are portable and additive. This means that these properties of ions are not appreciably sensitive to the environment of the ions, whether they are isolated, in crystalline compounds, or in molten salts. The property of a compound is the sum of the stoichiometrically weighted properties of its constituting cations and anions. These values for many ions were critically selected and reported by Marcus [4].

The molar magnetic susceptibilities, χ_{Im}, are rather insensitive to the environment in which the ions are situated, whether isolated or in a condensed phase. Ions are diamagnetic, that is, they are repulsed out from a magnetic field, unless they have one or more unpaired electrons in their electronic shells. The consequence is that most RTILs are diamagnetic, and only a few RTILs have been prepared with paramagnetic anions, such as $FeCl_4^-$. The χ_{Im} values of diamagnetic ions have the dimension of a molar volume and are negative, ranging from a few to several tens of the unit -10^{-12} $m^3·mol^{-1}$. Ions that have n unpaired electrons in their electronic shells are paramagnetic, are attracted into a magnetic field, and have positive molar susceptibilities. A paramagnetic ion with n unpaired electrons has $\chi_{\mathrm{Im}} = +1.676n(n+2) \times 10^{-9} m^3 ·mol^{-1}$ at $T° = 298.15$ K. The values of χ_{Im} for many ions are shown in Table 2.3.

The polarizibility, α_{I}, of an ion is obtained indirectly from the molar refractivity, but the molar refractivity can be obtained experimentally only for neutral species (salts), either in crystals or in dilute solutions. The molar refractivity R_{D} of a salt is generally determined from the refractive index at the sodium D line (589 nm), n_{D}, according to the Lorenz-Lorentz expression: $R_{\mathrm{D}} = V\left(n_D^2 - 1\right)/\left(n_D^2 + 2\right)$, where $V = (M/\rho)$ is the molar volume and M and ρ are the molar mass and the density. The molar refractivity of a salt is not very sensitive to the environment of the ions, so that it may be ascribed to the neutral combinations of the bare cations and anions. It must then be split appropriately between the cations and the anions, but no

Table 2.3 The magnetic susceptibility, χ_{Im}, the molar refraction at the sodium D line, R_D (normalized to the value for Na^+), the polarizability α and the softness parameter σ of isolated ions

Cation	$\chi_{\mathrm{Im}}\ 10^{-12}\ \mathrm{m^3 \cdot mol^{-1}}$	$R_D\ 10^{-6}\ \mathrm{m^3 \cdot mol^{-1}}$	$\alpha\ 10^{-3}\ \mathrm{nm^3}$	σ
H^+	−6.6[a]	−0.3	−0.12	−0.30
Li^+	−3[a]	0.08	0.03	−1.32
Na^+	−2.3[a]	0.65	0.26	−0.90
K^+	−11.2[a]	2.71	1.07	−0.88
Rb^+	−20.1[a]	4.1	1.63	−0.83
Cs^+	−34[a]	6.89	2.73	−0.84
Cu^+	−12	3.1	1.23	−0.52
Ag^+	−24	5.1	2.02	−0.12
Tl^+	−34	11.5	4.56	−0.10
Be^{2+}	−6			−0.93
Mg^{2+}	−5 [17]	−0.7	−0.28	−0.71
Ca^{2+}	−8 [17]	1.59	0.63	−0.96
Sr^{2+}	−9[a]	2.65	1.05	−0.94
Ba^{2+}	−21.5[a]	5.17	2.05	−0.96
Mn^{2+}	20.7	2.2	0.87	−0.45
Fe^{2+}	19.6	2.1	0.83	−0.46
Co^{2+}	18.5	2.05	0.81	−0.41
Ni^{2+}	17.5	1.6	0.63	−0.41
Cu^{2+}	16.4	1.3	0.52	+0.08
Zn^{2+}	−10	1.39	0.55	+0.05
Cd^{2+}	−22.5	3.22	1.28	+0.28
Sn^{2+}	−20			−0.01
Pb^{2+}	−28	11.9	4.72	+0.11
Al^{3+}	−3.1	−1.18	−0.47	−0.61
Sc^{3+}	−6 [18]	1.6	0.63	−0.92
V^{3+}	10 [18]	3.5[d]	1.39	−0.59
Cr^{3+}	16			−0.40
Fe^{3+}	15.6	3.2	1.27	+0.03
Ga^{3+}	−8	5 [17]	2	−0.01
Y^{3+}	−12 [18]	2.4	0.95	−0.99
In^{3+}	−19	1.7 [17]	0.67	+0.18
Sb^{3+}	−14 [18]	8.8[d]	3.49	+0.33
La^{3+}	−20 [18]	2.74	1.09	−1.05
Ce^{3+}	20 [18]	3.4 [17]	1.35	−1.02
Pr^{3+}	20 [18]	3.3 [17]	1.31	−0.93
Nd^{3+}	20 [18]	3.1 [17]	1.23	−0.88
Sm^{3+}	20 [18]	2.9 [17]	1.15	−0.66
Eu^{3+}	20 [18]	2.7 [17]	1.07	−0.49
Gd^{3+}	20 [18]	2.6 [17]	1.03	−0.96
Tb^{3+}	19 [18]	2.5 [17]	0.99	−0.94
Dy^{3+}	19 [18]	2.4 [17]	0.95	−0.80

(continued)

Table 2.3 (continued)

Cation	χ_{Im} 10^{-12} $\mathrm{m^3{\cdot}mol^{-1}}$	R_{D} 10^{-6} $\mathrm{m^3{\cdot}mol^{-1}}$	α 10^{-3} $\mathrm{nm^3}$	σ
$\mathrm{Ho^{3+}}$	19 [18]	2.2 [17]	0.87	−0.83
$\mathrm{Er^{3+}}$	18 [18]	2.1 [17]	0.83	−0.87
$\mathrm{Tm^{3+}}$	18 [18]	2.0 [17]	0.79	−0.73
$\mathrm{Yb^{3+}}$	18 [18]	2.0 [17]	0.79	−0.57
$\mathrm{Lu^{3+}}$	−17 [18]			−0.84
$\mathrm{Tl^{3+}}$	−31	2.2 [17]	0.87	+0.77
$\mathrm{Bi^{3+}}$	−25	8.1	3.21	+0.52
$\mathrm{Zr^{4+}}$	−12.5	1.0 [17]	0.40	−0.73
$\mathrm{Sn^{4+}}$	−16	1.3 [17]	0.52	+0.26
$\mathrm{Ce^{4+}}$	−21	1.9 [17]	0.75	−0.40
$\mathrm{Hf^{4+}}$	−16 [18]	4.3 [19]	1.70	−0.91
$\mathrm{Th^{4+}}$	−31.2	6.8 [19]	2.70	−0.97
$\mathrm{U^{4+}}$	−35 [25]			−0.46
NH4+	−11.5	4.7	1.86	−0.90
$\mathrm{C(NH_2)_3}$+		11.21 [7]	4.44	
$\mathrm{Me_4N}$+	−65	22.9	9.08	+0.11
$\mathrm{Et_4N}$+		43	17	
$\mathrm{Pr_4N}$+		61	24	
$\mathrm{Bu_4N}$+		79	31	
$\mathrm{Ph_4As}$+	−229	115.3	45.7	+6.61
$\mathrm{C_1mim^+}$ [b]			10.98 [20][b]	
$\mathrm{C}_n\mathrm{mim^+}$		$21.6+4.7n$[c]		
$\mathrm{C_nPy^+}$		$19.9+5.0n$[c]		
$\mathrm{RR'_3N^+}$		$4.90n_{\mathrm{C\ total}}$[c]		
$\mathrm{TdHx_3P^+}$		158.2[c]		

Anion	χ_{Im} 10^{-12} $\mathrm{m^3{\cdot}mol^{-1}}$	R_{D} 10^{-6} $\mathrm{m^3{\cdot}mol^{-1}}$	$\alpha(\mathrm{I^{z\pm}},\mathrm{ig})$ 10^{-3} $\mathrm{nm^3}$	σ
$\mathrm{F^-}$	−13[a]	2.21	0.88	−0.36
$\mathrm{Cl^-}$	−28[a]	8.63	3.42	+0.21
$\mathrm{Br^-}$	−39[a]	12.24	4.85	+0.47
$\mathrm{I^-}$	−56.7[a]	18.95	7.51	+0.80
$\mathrm{OH^-}$	−12[a]	4.65	1.84	+0.30
$\mathrm{SH^-}$		12.8	5.07	+0.95
$\mathrm{CN^-}$	−18	7.9	3.13	+0.71
$\mathrm{NCO^-}$	−21			+1.01
$\mathrm{SCN^-}$	−35	17	6.7	+1.15
$\mathrm{N_3{}^-}$		11	4.4	+1.06
$\mathrm{HF_2{}^-}$				−1.54
$\mathrm{BO_2{}^-}$				−0.64
$\mathrm{NO_2{}^-}$	−15[a]	8.7	3.45	+0.45
$\mathrm{NO_3{}^-}$	−23[a]	10.43	4.13	+0.33
$\mathrm{ClO_3{}^-}$	−32	12.1	4.80	+0.33
$\mathrm{BrO_3{}^-}$	−40	15.2	6.03	

(continued)

Table 2.3 (continued)

Anion	χ_{Im} 10^{-12} $\mathrm{m^3 \cdot mol^{-1}}$	R_D 10^{-6} $\mathrm{m^3 \cdot mol^{-1}}$	$\alpha(\mathrm{I}^{z\pm},\mathrm{ig})$ 10^{-3} $\mathrm{nm^3}$	σ
IO_3^-	−50	18.85	7.47	
ClO_4^-	−34	12.77	5.06	0.00
MnO_4^-				+0.16
ReO_4^-	−60 [18]			−0.10
BF_4^-	−39	7.5[c]	2.80 [20]	0.00
PF_6^-		11.0[c]	4.18	
HCO_2^-	−21	9.43 [17]	3.74	−0.03
$CH_3CO_2^-$	−32.4	13.87	5.50	+0.08
$CF_3CO_2^-$	−50		5.23 [20]	
$CH_3SO_3^-$			6.30 [20]	
$CF_3SO_3^-$		17.7[c]	6.88 [20]	
$MePhSO_3^-$			15.55 [20]	
$N(CN)_2^-$		17.5[c]	6.11 [20]	
$B(CN)_4^-$		27.5[c]		
NTF_2^- [d]		34.8[c]	13.59 [20]	
$MeSO_4^-$ [c]			6.94[c] [20]	
BPh_4^-	−215	108.7	43.1	+7.16
HSO_4^-	−37 [17]			
O^{2-}	−12			
S^{2-}	−38			+1.39
CO_3^{2-}	−34[a]	11.45	4.54	−0.20
SO_3^{2-}	−38	12.9	5.11	−0.04
SO_4^{2-}	−40	13.79	5.47	−0.08
SeO_4^{2-}	−51	16.4	6.50	
CrO_4^{2-}	−51	27.5 [19]	10.90	
MoO_4^{2-}	−55	25.2 [19]	9.99	
WO_4^{2-}	−61	23.2 [19]	9.20	
$S_2O_3^{2-}$	−49	23.2	9.20	
SiF_6^{2-}		11.01 [19]	4.36	
SO_3^{2-}	−38	12.9	5.11	−0.04
SO_4^{2-}	−40	13.79	5.47	−0.08
SeO_4^{2-}	−51	16.4	6.50	
CrO_4^{2-}	−51	27.5 [19]	10.90	
PO_4^{3-}	−50	15.1	5.99	−0.48
$Fe(CN)_6^{3-}$		50.7 [19]	20.1	+3.52
$Co(CN)_6^{3-}$		46.7 [19]	18.5	
$Fe(CN)_6^{4-}$				+3.93

References are shown for data not selected in [4]

[a] In aqueous solutions

[b] Also for other $C_n$mim$^+$ (1-alkyl-3-methylimidazolium) cations $9.20 + 1.78n$

[c] Also for other $C_nSO_4^-$ anions $5.15 + 1.79n$

[d] bis(trifluoromethylsulfonyl)amide

[c] From values for room temperature ionic liquids, Table 6.10

theoretically valid way to do this is known. Therefore, an empirical expedient has to be resorted to, assuming the additivity of the stoichiometrically weighted values for the cations and anions, $R_D = \Sigma \nu_I R_{DI}$. The establishment of an ionic scale of polarizabilities has been made on the basis of the empirical value $R_D(Na^+) = 0.65\ cm^3 \cdot mol^{-1}$ at 25 °C. The polarizability of an isolated ion is then: $\alpha\left(I^{z\pm}, ig\right) = 3R_{ID}/4\pi N_A = R_{ID}/2.5227 \times 10^{30}$ (for R_{DI} in $cm^3 \cdot mol^{-1}$), yielding values of the order of $10^{-3}\ nm^3 \cdot particle^{-1}$. The temperature coefficient of R_D is rather small, approximately $+0.01\ cm^3 \cdot mol^{-1} \cdot K^{-1}$. Values of R_{ID} and α are shown in Table 2.3 for many ions. Negative values of α and R_{ID} for very small ions (H^+, Mg^{2+}, and Al^{3+}) should be understood only in connection with their effects on the overall polarizability of compounds containing them.

A property of 'softness' or 'hardness' can be ascribed to an ion and is loosely related to its polarizability. The originally [16] softness parameters σ_I were based on the arbitrary assignment of zero to the hydrogen ion for cations and to the hydroxide ion for anions. A common scale for ions of both charge signs is produced when $0.3z_I$ units are subtracted/added from/to the original cation/anion values. Positive values of the softness parameter denote 'soft' ions and negative values denote 'hard' ions. The σ_I values of many ions are recorded in Table 2.3.

2.2 The Sizes of Ions in Condensed Phases

The sizes of isolated ions are ill-defined, as mentioned above, but due to the strong repulsion of the contagious electronic shells of ions in condensed phases the ions can be assigned definite sizes. The inter-ionic distances in crystals can be measured by x-ray and neutron diffraction with an uncertainty of a fraction of a pm. An early discussion of the application of diffraction methods to molten salts is that of Levy and Danford [21], a more recent review of this subject (concerning neutron diffraction) is that of Neilson and Adya [22] and still more recently also applications to RTILs have been added by Neilson et al. [23]. Diffraction measurements yield the pair distribution function, the peaks in the curves denoting the distances between pairs of atoms, as dealt with in detail in Chap. 3. However, only for monatomic and globular ions may individual ionic radii be assigned unequivocally, provided the additivity of ionic radii is assured and the radius of a key ion is assigned. These individual ionic radii, r_I, do depend on the coordination numbers of the ions and a set for the characteristic coordination in salt crystals has been established by Shannon and Prewitt [24, 25]. These radii, as selected in [4] and annotated there, are listed in Table 2.4.

In molten salts (typically, alkali metal halides) the cation-anion distances are ~5 % shorter and the anion-anion distances are ~5 % longer than in salt crystals at the melting point, but are very near the distances in the crystals at room temperature, the coordination numbers being 10 % lower in the molten salts than in the

Table 2.4 Ionic radii, r_I [4], thermochemical ionic radii, r_{Ith} [26], and ionic volumes v_I [27], from these references except where otherwise noted

Ion	r_I/pm	r_{Ith}/pm	v_I/ nm^3
Li^+	69		0.00199
Na^+	102		0.00394
K^+	138		0.00986
Rb^+	149		0.01386
Cs^+	170		0.01882
Cu^+	96		
Ag^+	115		
Tl^+	150		
Be^{2+}	35		0.0002 [29]
Mg^{2+}	72		0.00199
Ca^{2+}	100		0.00499
Sr^{2+}	113		0.00858
Ba^{2+}	136		0.01225
V^{2+}	79		0.0016 [29]
Cr^{2+}	82		0.0024 [29]
Mn^{2+}	83		0.0032 [29]
Fe^{2+}	78		0.0022 [29]
Co^{2+}	75		0.0022 [29]
Ni^{2+}	69		0.0020 [29]
Cu^{2+}	73		
Zn^{2+}	75		0.0024 [29]
Cd^{2+}	95		0.0046 [29]
Sn^{2+}	93		
Pb^{2+}	118		0.0069 [29]
Al^{3+}	53		0.0008 [29]
Sc^{3+}	75		0.0024 [29]
V^{3+}	64		0.0012 [29]
Cr^{3+}	62		0.0011 [29]
Fe^{3+}	65		0.0013 [29]
Co^{3+}	65		0.0011 [29]
Ga^{3+}	62		0.0010 [29]
Y^{3+}	90		0.0031 [29]
In^{3+}	79		0.0021 [29]
Sb^{3+}	77		0.0019 [29]
La^{3+}	105		0.0076 [29]
Ce^{3+}	101		0.0069 [29]
Pr^{3+}	100		0.0065 [29]
Nd^{3+}	99		0.0064 [29]
Pm^{3+}	97		
Sm^{3+}	96		0.0060 [29]
Eu^{3+}	95		0.0060 [29]
Gd^{3+}	94		0.0057 [29]

(continued)

Table 2.4 (continued)

Ion	r_I/pm	r_{Ith}/pm	v_I/ nm^3
Tb^{3+}	93		0.0054 [29]
Dy^{3+}	91		0.0051 [29]
Ho^{3+}	90		0.0049 [29]
Er^{3+}	89		0.0047 [29]
Tm^{3+}	88		0.0047 [29]
Yb^{3+}	87		0.0042 [29]
Lu^{3+}	86		0.0041 [29]
Tl^{3+}	88		0.0048 [29]
Bi^{3+}	102		
U^{3+}	104		
Zr^{4+}	72		0.0028 [29]
Sn^{4+}	69		0.0017 [29]
Ce^{4+}	80		0.0045 [29]
Hf^{4+}	71		0.0025 [29]
Th^{4+}	100		0.0056 [29]
U^{4+}	97		0.0049 [29]
NH_4^+	148		0.021
$C(NH_2)_3^+$	210 [7]		
Me_4N^+	280	234	0.113
Et_4N^+	337		0.199
Pr_4N^+	379		
Bu_4N^+	413		
Pe_4N^+	443		
Ph_4P^+	424		
Ph_4As^+	425		
F^-	133	126	0.025
Cl^-	181	168	0.047
Br^-	196	190	0.056
I^-	220	211	0.072
OH^-	133	152	0.032
SH^-	207	191	0.057
CN^-	191	187	0.050
NCO^-	203	193	0.054
SCN^-	213	209	0.071
N_3^-	195	180	0.058
HF_2^-	172	172	0.047
I_3^-	470	272	0.180 [29]
BO_2^-	240		
NO_2^-	192	187	0.055
NO_3^-	200	200	0.064
ClO_3^-	200	208	0.073
BrO_3^-	191	214	0.072

(continued)

Table 2.4 (continued)

Ion	r_I/pm	r_{Ith}/pm	v_I/ nm^3
IO_3^-	181	218	0.075
ClO_4^-	240	225	0.082
MnO_4^-	240	220	0.088
ReO_4^-	260	227	0.098 [29]
BF_4^-	230	205	0.073
HCO_2^-	204	200	0.056
$CH_3CO_2^-$	232	194	
BPh_4^-	421		
HSO_4^-	190	221	0.087 [29]
PF_6^-	245	242	0.109
SbF_6^-	282	252	0.121
O^{2-}	140	141	0.043
S^{2-}	184	189	0.067
CO_3^{2-}	178	189	0.061
SO_3^{2-}	200	204	0.071
SO_4^{2-}	230	218	0.091
SeO_4^{2-}	243	229	0.103
CrO_4^{2-}	240	229	0.097
MoO_4^{2-}	254	231	0.088
WO_4^{2-}	270	237	0.088
$S_2O_3^{2-}$	250	251	0.104
SiF_6^{2-}	259	248	0.112
$Cr_2O_7^{2-}$	320	292	0.167
PO_4^{3-}	238	230	0.090
AsO_4^{3-}	248	237	0.088
$Fe(CN)_6^{3-}$	440	347	0.265
$Co(CN)_6^{3-}$	430	349	0.263
$Fe(CN)_6^{4-}$	450		

crystals. Therefore the concept of an ionic radius in molten salts, equating it to that in crystals, should be used with due caution.

The ionic radius has a much more vague meaning for non-spherical ions. An approximate value of r_I is the cube root of (3/4π) times the volumes of their ellipsoids of rotation with axes a and b. For elongated rod-like ions, $a > b$ and their radii are $r_I \approx (4\pi a^2 b/3)^{1/3}$, examples being SCN^- and I_3^-. For planar ions, $a < b$ and their radii are $r_I \approx (4\pi ab^2/3)^{1/3}$, examples being NO_3^- and CO_3^{2-}. The sizes of polyatomic (non-globular) ions in crystals are also expressed by their thermochemical radii r_{Ith} according to Jenkins and co-workers [26]. The uncertainties of these radii, listed in Table 2.4, are ±20 pm for uni- and divalent anions increasing to twice this amount for trivalent ones. These values are based on the Goldschmidt radii for the alkali metal counter-ions, r_+^G, rather than the Shannon-Prewitt ones [24, 25].

A different approach to the sizes of ions is to consider their volumes rather than their radii [27]. The volume of a formula unit of the salt M_pX_q, obtained from the unit cell volume from x-ray diffraction of crystals of the salt, is assumed to be additive in the individual ionic volumes: $v\left(M_pX_q\right) = pv_+ + qv_-$. The Goldschmidt radii of the alkali metal cations were used to define $v_+ = (4\pi/3){r_+}^{G\ 3}$, obtaining the anion volumes by difference. Individual ionic volumes calculated on this basis by Glasser and Jenkins are also shown in Table 2.4 [28]. They differ considerably from previously reported values [17, 27] by the same authors. Protonated anions, such as HSO_4^-, are smaller than their non-protonated parent anions, such as SO_4^{2-}, because the lowered negative charge diminishes the repulsion between, the electrons, causing shrinkage of the anionic volume, whereas the added proton does not contribute appreciably to the volume.

The relationship between the ionic radii r_I and the ionic volumes v_I leads directly to $v_I = (4\pi/3)(r_I)^3$ and a set of such volumes, denoted as v_M is reported in [17]. The ionic volumes obtained from the formula unit volumes in crystals [28], denoted as v_J, is also shown in [17], with $v_J = (1.258 \pm 0.016)v_M$ having been established with a correlation coefficient of 0.995 for 55 cations. The larger size of v_J takes into account the void spaces between the (more or less spherical) ions. Another way to express this, based on the suggestion of Mukerjee [29] regarding such ions in solution, is to use the factor $k = 1.213$ multiplying the radius of univalent monatomic ions: $v_I = (4\pi/3)(kr_I)^3$. This factor is near the value, 1.159, that is geometrically required for close-packed spheres of arbitrary but comparable sizes.

The ionic volumes of the constituents of room temperature ionic liquids are derived from the densities, hence molar volumes, of these RTILs, using the ionic volumes of anions that were established for crystals [28]. These ionic volumes are presented and discussed in Chap. 6 in relationship with the densities of the RTILs [30].

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