Chemical Hardness of Metal Ions in the Gas Phase: a Thermochemical Approach†

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The heterolytic dissociative version of Pauling's bond-energy equation, proposed earlier for an AB molecule, has now been generalised for molecules of type AB_n in order to rank a number of multivalent cations in terms of their gas-phase chemical hardnesses. The chemical hardness of a cation is found to be related to its charge and size, and Klopman's frontier-orbital energy. The results are used to systematise the gas-phase affinity displayed between a monovalent anionic ligand (specifically, a halide) and a metal ion.

In co-ordination chemistry the need to rank various metal ions in terms of a certain physicochemical parameter in order to understand the stability and reactivity of their complexes has been felt for a very long time. The Irving–Williams series proposed in 1948,[1] which indicates that for a given ligand the stability of its complexes with some bivalent metal ions in aqueous media follows the trend $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, can be said to be the first step towards it. However, soon it was discovered that in aqueous media the halides of some metal ions (*e.g.* Li^+, Zn^{2+}, Fe^{3+}) follow the stability order $F^- > Cl^- > Br^- > I^-$, while for others (*e.g.* Ag^+, Hg^{2+}, Au^{3+}) the order is reversed. Metal ions of the former type were denoted class (a) and the latter class (b) by Ahrland *et al.*[2] in 1958. While ranking of the metal ions of a particular Periodic Group was possible in terms of the class (a) or (b) character, to do this for all types of metal ions proved difficult. Hence their work was restricted only to the qualitative classification of the metal ions in terms of (a) and (b). Thus far the stability constant, a thermodynamic quantity, had been used for ranking or classifying the metal ions. In 1963 Pearson[3] first used polarisability, a property of the metal ion, for this purpose and called class (a) 'hard' and class (b) 'soft'. He also introduced another category, 'borderline'. The hardness of a chemical species increases as its polarisability decreases. However, this concept, being qualitative, was no better than the (a), (b) classification. Later several workers attempted to sort metal ions using functions of their radii, charges and ionisation potentials, but the lines of demarcation were drawn in an arbitrary manner.[4,5] In 1983 Parr and Pearson[6] gave a quantitative definition of hardness (η) of a chemical species in terms of its ionisation potential E_i and electron affinity E_{ea} [equation (1)]. This was used to rank a number of metal ions.[7]

$$\eta = (E_i - E_{ea})/2 \qquad (1)$$

Since equation (1) applies to a free ion or an isolated chemical species only, to describe the hardness of an ion in a molecule, Pearson[8] later introduced another concept, 'chemical hardness'. However, for the lack of an appropriate measure, the desired ranking of the metal ions in terms of chemical hardness is yet to be achieved. We attempt to do this here by using a novel thermochemical method.

Earlier bond-energy data were used by Pearson[8] to rank various metal ions. Elsewhere, we have discussed the problems inherent in this approach,[9] and recently developed an ionic version of Pauling's bond-energy equation for AB molecules to derive a new parameter γ characteristic of an ion in a molecule. The equation is generalised here for molecules of type AB_n [equation (2)], *n* is the valency of the cation, $D(A^{n+}B^-{}_n)$ the energy required for dissociating the molecule into the cation A^{n+} and *n* B^- ions and $D(A^+A^-)$ and $D(B^+B^-)$ the heterolytic bond-dissociation energies of molecules A_2 and B_2 respectively.

$$D(A^{n+}B^-{}_n)/n = \tfrac{1}{2}[D(A^+A^-) + D(B^+B^-)] + 2(\gamma_{A^{n+}} - \gamma_{B^-})^2 \qquad (2)$$

The various bond energies are expressed in kcal mol^{-1}. Using the $D(A^{n+}B^-{}_n)$ values for some polyhalides, we have evaluated the γ parameter for a number of multivalent cations with *n* up to 4 (Tables 1 and 2). Some of the $D(A^{n+}B^-{}_n)$ values have been estimated from the heat of formation (ΔH_f°) data[11a] of the various species involved in equation (3). Other values of

$$AB_n \longrightarrow A^{n+} + nB^- \qquad (3)$$

$D(A^{n+}B^-{}_n)$ used in Table 1 are taken from ref. 10. The $D(A^+A^-)$ or $D(B^+B^-)$ values were estimated as earlier[9] from the homolytic bond-dissociation energy[11b] and appropriate E_i and E_{ea} data.[7] Equation (2) actually gives $|\Delta\gamma| = |\gamma_{A^{n+}} - \gamma_{B^-}|$ (Table 1). The individual γ values were assigned as earlier with γ_{F^-} set to 0.0 as the reference.[9] The individual γ values of the various cations studied here are given in Table 2. The γ scale essentially helps us rank the metal ions considered. Some non-metals also have been included for comparison.

In 1968 Klopman[12] derived a 'frontier orbital energy' ($E^‡$) from the E_i and E_{ea} values of an ion and proposed it as a quantitative measure of Pearson's concept of hardness. Apparently not much attention has been paid to this definition. Recently we have shown it to be very useful in assessing the hardness of a chemical group as well, even in the solution phase.[13] The quantity $E^‡$ for a cationic acceptor M^{n+} is calculated from the ionisation potential $E_{i(n-1)}$ and electron affinity $E_{ea(n-1)}$ of the corresponding $M^{(n-1)+}$ ion [equation (4)]. In equation (4), which gives only the gas-phase value of $E^‡$, the

$$-E^‡ = E_{i(n-1)} - 0.25[E_{i(n-1)} - E_{ea(n-1)}] \qquad (4)$$

factor 0.25 is somewhat arbitrary. For anionic donors the relevant equation takes a slightly different form. In our earlier work[14] although for monovalent anions we observed an excellent linear correspondence between $E^‡$ and our γ values, for monoatomic monovalent cations the correspondence was rather poor. Here we have found that a very good linear correlation exists between $E^‡$ and γ for some 27 monoatomic

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† *Non-SI units employed:* cal = 4.184 J; eV ≈ 1.60×10^{-19} J.

Table 1 Calculation of $|\Delta\gamma|$ for some AB_n molecules ($n \leqslant 4$)[a]

$A^{n+}B^{-}{}_{n}$	$D(A^{n+}B^{-}{}_{n})/n$	$D_{\frac{1}{2}}$	δ	$\lvert\Delta\gamma\rvert$	$\lvert\delta - \delta_{calc}\rvert$ (%)
$F^{+}F^{-}$	360.29				
$Cl^{+}Cl^{-}$	273.81				
$Br^{+}Br^{-}$	240.99				
$I^{+}I^{-}$	206.01				
$Be^{+}Be^{-}$	219.23				
$Be^{2+}F^{-}{}_{2}$	387.5	289.76	97.74	5.5	9.61
$Be^{2+}Cl^{-}{}_{2}$	342.5	246.52	95.98	6.5	3.35
$Be^{2+}Br^{-}{}_{2}$	331	230.11	100.89	7.0	0.87
$Be^{2+}I^{-}{}_{2}$	318	212.62	105.38	7.5	2.24
$Mg^{+}Mg^{-}$	181.91				
$Mg^{2+}F^{-}{}_{2}$	308.5	271.10	37.40	3.5	4.18
$Mg^{2+}Cl^{-}{}_{2}$	272.5	227.86	44.64	4.5	1.52
$Mg^{2+}Br^{-}{}_{2}$	261.75[b]	211.45	50.30	5.0	0.11
$Mg^{2+}I^{-}{}_{2}$	254.15[b]	193.96	60.19	5.5	0.12
$Ca^{+}Ca^{-}$	193.17				
$Ca^{2+}F^{-}{}_{2}$	258.84[b]	276.73	−17.89	0.5[c]	7.10
$Ca^{2+}Cl^{-}{}_{2}$	227.69[b]	233.49	−5.80	1.5[c]	4.52
$Ca^{2+}Br^{-}{}_{2}$	221.84[b]	217.08	4.76	2.0	1.46
$Ca^{2+}I^{-}{}_{2}$	215.64[b]	199.59	16.05	2.5	1.65
$Sr^{+}Sr^{-}$	174.34				
$Sr^{2+}F^{-}{}_{2}$	240.63[b]	267.31	−26.68	*c*	
$Sr^{2+}Cl^{-}{}_{2}$	219	224.07	−5.07	*c*	
$Sr^{2+}Br^{-}{}_{2}$	207.08[b]	207.66	−0.58	*c*	
$Sr^{2+}I^{-}{}_{2}$	199	190.17	8.82	—	
$Ti^{+}Ti^{-}$	189.22				
$Ti^{2+}F^{-}{}_{2}$	287.5	274.75	12.75	3.0	1.83
$Ti^{2+}Cl^{-}{}_{2}$	264.5	231.51	32.99	4.0	0.37
$Ti^{2+}Br^{-}{}_{2}$	253.5	215.10	38.40	4.5	0.83
$Ti^{2+}I^{-}{}_{2}$	245	197.61	47.39	5.0	1.06
$V^{+}V^{-}$	200.87				
$V^{2+}F^{-}{}_{2}$	295	280.58	14.42	3.0	1.21
$V^{2+}Cl^{-}{}_{2}$	274.5	237.34	37.16	4.0	1.88
$V^{2+}Br^{-}{}_{2}$	263.5	220.93	42.57	4.5	0.78
$V^{2+}I^{-}{}_{2}$	256	203.44	52.56	5.0	1.00
$Cr^{+}Cr^{-}$	177.90				
$Cr^{2+}F^{-}{}_{2}$	301.9	269.09	32.80	4.0	0.26
$Cr^{2+}Cl^{-}{}_{2}$	273.65	225.85	47.79	5.0	0.81
$Cr^{2+}Br^{-}{}_{2}$	269.7	209.44	60.25	5.5	0.09
$Cr^{2+}I^{-}{}_{2}$	258.1	191.95	66.14	6.0	2.27
$Mn^{+}Mn^{-}$	177.77				
$Mn^{2+}F^{-}{}_{2}$	296	269.03	26.97	3.5	0.83
$Mn^{2+}Cl^{-}{}_{2}$	273	225.79	47.21	4.5	2.46
$Mn^{2+}Br^{-}{}_{2}$	264.5	209.38	55.12	5.0	1.93
$Mn^{2+}I^{-}{}_{2}$	256	191.89	64.11	5.5	1.41
$Fe^{+}Fe^{-}$	199.72				
$Fe^{2+}F^{-}{}_{2}$	312.5	280.00	32.5	4.0	0.16
$Fe^{2+}Cl^{-}{}_{2}$	285	236.76	48.24	5.0	0.62
$Fe^{2+}Br^{-}{}_{2}$	278.5	220.35	58.15	5.5	0.85
$Fe^{2+}I^{-}{}_{2}$	270	202.86	67.14	6.0	1.80
$Co^{+}Co^{-}$	203.73				
$Co^{2+}F^{-}{}_{2}$	319	282.01	36.99	4.0	1.56
$Co^{2+}Cl^{-}{}_{2}$	291.5	238.77	52.73	5.0	0.94
$Co^{2+}Br^{-}{}_{2}$	284	222.36	61.64	5.5	0.40
$Co^{2+}I^{-}{}_{2}$	275.5	204.87	70.63	6.0	0.50
$Ni^{+}Ni^{-}$	198.24				
$Ni^{2+}F^{-}{}_{2}$	327.5	279.26	48.24	4.5	2.36
$Ni^{2+}Cl^{-}{}_{2}$	299	236.02	62.98	5.5	0.83
$Ni^{2+}Br^{-}{}_{2}$	292.5	219.61	72.89	6.0	0.30
$Ni^{2+}I^{-}{}_{2}$	284.5	202.12	82.38	6.5	0.74
$Cu^{+}Cu^{-}$	192.08				
$Cu^{2+}F^{-}{}_{2}$	333	276.18	56.82	5.0	2.05
$Cu^{2+}Cl^{-}{}_{2}$	307.5	232.94	74.56	6.0	0.83
$Cu^{2+}Br^{-}{}_{2}$	303.5	216.53	86.97	6.5	0.81
$Cu^{2+}I^{-}{}_{2}$	294.5	199.04	95.46	7.0	0.86
$Zn^{+}Zn^{-}$	234.83				
$Zn^{2+}F^{-}{}_{2}$	327.5	297.56	29.94	4.0	0.63
$Zn^{2+}Cl^{-}{}_{2}$	308.0	254.32	53.68	5.0	1.19
$Zn^{2+}Br^{-}{}_{2}$	300.5	237.91	62.59	5.5	0.69
$Zn^{2+}I^{-}{}_{2}$	291.5	220.42	71.08	6.0	0.31
$Cd^{+}Cd^{-}$	216.68				
$Cd^{2+}F^{-}{}_{2}$	295.5	288.48	7.01	3.0	3.72
$Cd^{2+}Cl^{-}{}_{2}$	280.0	245.24	34.75	4.0	0.98
$Cd^{2+}Br^{-}{}_{2}$	276.0	228.83	47.16	4.5	2.41

Table 1 (*continued*)

$A^{n+}B^{-}_{n}$	$D(A^{n+}B^{-}_{n})/n$	$D_{\frac{1}{2}}$	δ	$\lvert\Delta\gamma\rvert$	$\lvert\delta - \delta_{calc}\rvert$ (%)
$Cd^{2+}I^{-}_{2}$	270.0	211.34	58.65	5.0	3.20
$Hg^{+}Hg^{-}$	257.27				
$Hg^{2+}F^{-}_{2}$	318.5	308.78	9.72	3.5	4.64
$Hg^{2+}Cl^{-}_{2}$	303.5	265.54	37.96	4.5	0.95
$Hg^{2+}Br^{-}_{2}$	300	249.13	50.87	5.0	0.29
$Hg^{2+}I^{-}_{2}$	297	231.64	65.36	5.5	1.64
$Sn^{+}Sn^{-}$	187.13				
$Sn^{2+}F^{-}_{2}$	282.5	273.71	8.79	2.5	1.31
$Sn^{2+}Cl^{-}_{2}$	257.0	230.47	26.53	3.5	0.79
$Sn^{2+}Br^{-}_{2}$	249.5	214.06	35.44	4.0	1.38
$Sn^{2+}I^{-}_{2}$	240.0	196.57	43.43	4.5	1.22
$Pb^{+}Pb^{-}$	183.27				
$Pb^{2+}F^{-}_{2}$	271.5	271.78	−0.28	2.0[c]	3.04
$Pb^{2+}Cl^{-}_{2}$	246.5	228.54	17.96	3.0	0.02
$Pb^{2+}Br^{-}_{2}$	240.0	212.13	27.87	3.5	1.40
$Pb^{2+}I^{-}_{2}$	235.0	194.64	40.36	4.0	3.55
$Al^{+}Al^{-}$	172.02				
$Al^{3+}F^{-}_{3}$	468.17[b]	266.15	202.01	8.5	12.28
$Al^{3+}Cl^{-}_{3}$	424.57[b]	222.91	201.65	9.5	4.98
$Al^{3+}Br^{-}_{3}$	414.87[b]	206.50	208.36	10.0	2.01
$Al^{3+}I^{-}_{3}$	406.43[b]	189.01	217.41	10.5	0.76
$Ga^{+}Ga^{-}$	164.44				
$Ga^{3+}Cl^{-}_{3}$	440.2[b]	219.12	221.07	10.0	4.78
$Ga^{3+}I^{-}_{3}$	427.67[b]	185.22	242.44	11.0	0.10
$In^{+}In^{-}$	150.83				
$In^{3+}Br^{-}_{3}$	392.42[b]	195.91	196.51	10.0	0.89
$In^{3+}I^{-}_{3}$	388.45[b]	178.42	210.03	10.5	2.69
$Sb^{+}Sb^{-}$	246.52				
$Sb^{3+}Cl^{-}_{3}$	376.73[b]	260.16	116.56	7.5	1.08
$Sb^{3+}Br^{-}_{3}$	370.13[b]	243.75	126.37	8.0	0.44
$Ti^{+}Ti^{-}$	189.22				
$Ti^{4+}Br^{-}_{4}$	532.02[b]	215.10	316.91	12.50	0.83
$Ti^{4+}I^{-}_{4}$	524.7[b]	197.61	327.08	13.00	2.08
$Si^{+}Si^{-}$	233.98				
$Si^{4+}F^{-}_{4}$	654.91[b]	297.13	357.77	12.00	10.65
$Si^{4+}Cl^{-}_{4}$	603.57[b]	253.89	349.67	13.00	1.93
$Si^{4+}Br^{-}_{4}$	592.04[b]	237.48	354.55	13.50	1.68

[a] Meanings of the symbols: $D_{\frac{1}{2}} = [D(A^{+}A^{-}) + D(B^{+}B^{-})]/2$; $\delta = [D(A^{n+}B^{-}_{n})/n] - D_{\frac{1}{2}}$; $\delta_{calc} = 2(\lvert\Delta\gamma\rvert \text{ value assigned})^{2}$; $\lvert\delta - \delta_{calc}\rvert = 100\lvert\delta - \delta_{calc}\rvert/[D(A^{n+}B^{-}_{n})/n]$ %; others as in the text. The various bond-energy data are given in kcal mol^{-1}; $D(A^{n+}B^{-}_{n})$ values taken from ref. 10 unless otherwise specified. [b] Calculated as mentioned in the text. [c] $(\delta/2)^{\frac{1}{2}}$ becomes imaginary.

cations with n values up to 3 (for data see Table 2; correlation coefficient 0.943). The relevant $E_{i(n-1)}$ and $E_{ea(n-1)}$ data for calculating $E^{\ddagger}$ are taken from ref. 10(*c*). (Inclusion of tetravalent cations leads to a non-linear relation.) Thus we feel that the γ parameters can be identified with the chemical hardness of an ion.

In general the hardness of a cation in the gas phase increases as the γ value increases, *e.g.* Table 2 shows that in the gas phase Ti^{4+} is much harder than H^{+} which is harder than Li^{+}. The various gas-phase hardness orders obtained are probably in line with those expected chemically. Examples are $Si^{4+} > Al^{3+} > Mg^{2+} > Na^{+}$ and $Be^{2+} > Mg^{2+} > Ca^{2+}$. The observations that Ti^{4+} is harder than Ti^{2+} and Cu^{2+} is harder than Cu^{+} support the general notion that the hardness of a metal ion increases with increase in its oxidation state.

It is generally believed that the hardness of an ion is related to its size and charge,[15] but the nature of the relation is not known clearly. Here we have observed that, for some 17 monoatomic cations with charge z, our γ values are non-linearly related to z^{2}/r where r is the radius of a cation[16] (for data see Table 2). The result is that as z^{2}/r increases, the hardness increases.

As revealed by Table 1, for a particular halide the thermochemical stability of its metal complex in the gas phase increases as the γ value of the metal ion increases. The Irving–Williams effect on the γ values also can be discerned (Table 2). In fact, across the series Ca^{2+} to Zn^{2+}, the trend in the γ values essentially runs parallel to the recognised[10] stability order of the corresponding halides. In terms of η [equation (1)], the hardness trend of the metal ions in question is found to be $Fe^{2+} < Co^{2+} \approx Cu^{2+} < Ni^{2+} < Mn^{2+} < Zn^{2+} < Ca^{2+} < Mg^{2+}$.[7] This is probably because, as mentioned earlier, equation (1) does not characterise the binding site(s) of a chemical species. However, for a given metal ion, the relation between the γ parameter and the thermochemical stability of its halides is slightly complicated. It is found that there are two types of metal ions: (1) those for which the gas-phase thermochemical stability of the halides decreases as $\lvert\Delta\gamma\rvert$ decreases, *e.g.* for Li^{+} $\lvert\Delta\gamma\rvert$ follows the order $F^{-} > Cl^{-} > Br^{-} > I^{-}$ and its gas-phase affinity for the halides also decreases in the same order; (2) those for which the gas-phase thermochemical stability of the halides decreases as $\lvert\Delta\gamma\rvert$ increases, *e.g.* for Be^{2+} $\lvert\Delta\gamma\rvert$ follows the order $F^{-} < Cl^{-} < Br^{-} < I^{-}$ and its gas-phase affinity for the halides decreases in the reverse order.

Though introduction of further classifications of the metal ions in co-ordination chemistry is unwarranted, here we use the classification in terms of (1) and (2) only to systematise the gas-phase affinity of a particular metal ion towards the halides. The monovalent metal ions are found to fall in class (1) and the higher-valent ones in (2). It is possible that some metal ions may fall in between.

We now examine Pearson's hard–soft acid–base (HSAB) principle in terms of the γ parameter. The principle states that a hard acid prefers to co-ordinate to a hard base and a soft acid to a soft base.[3,6–8] This apparently simple statement can explain

Table 2 The γ parameter, Klopman's frontier-orbital energy and z^2/r for some mono-, bi-, tri- and tetra-valent cations[a]

M^{n+}	γ	$-E^{\ddagger}$	z^2/r
H^+	−2.0	10.39	
Li^+	−6.0	4.20	1.667
Na^+	−6.5	3.99	1.053
K^+	−7.0	3.38	0.752
Rb^+	−7.0	3.26	0.676
Cs^+	−7.0	3.03	0.592
Cu^+	−6.5	6.10	1.042
Be^{2+}	5.5	15.99	12.903
Mg^{2+}	3.5	13.19	6.154
Ca^{2+}	0.5	10.43	4.040
Ti^{2+}	3.0	11.89	
V^{2+}	3.0	12.67	
Cr^{2+}	4.0	14.07	
Mn^{2+}	3.5	13.59	5.000
Fe^{2+}	4.0	14.10	5.263
Co^{2+}	4.0	14.76	5.405
Ni^{2+}	4.5	15.53	5.797
Cu^{2+}	5.0	17.15	5.556[b]
Zn^{2+}	4.0	15.82	5.405
Cd^{2+}	3.0	14.93	4.124
Hg^{2+}	3.5	16.68	3.636
Sn^{2+}	2.5	12.81	
Pb^{2+}	2.0	13.13	3.306
Al^{3+}	8.5	26.04	18.000
Ga^{3+}	9.0	28.16	14.516
In^{3+}	8.5	25.74	11.111
Sb^{3+}	6.5	23.11	
Si^{4+}	12.0	42.23	39.024
Ti^{4+}	11.0	39.32	23.529

[a] Meanings of the symbols as in the text. Units used: γ, Datta–Singh's unit $kcal^{\frac{1}{2}}\ mol^{-\frac{1}{2}}$ [as derived from equation (2)]; $E^{\ddagger}$, eV; r, Å (Pauling's ionic radius unless otherwise stated). [b] Goldschmidt's radius.

the selective interactions between acids and bases displayed in exchange or metathetical reactions. For example, in the gas-phase reaction (5) Al^{3+} which is a harder acid than Cr^{2+} prefers

$$\begin{array}{lcccccccl} & 3CrF_2 & + & 2AlBr_3 & \longrightarrow & 3CrBr_2 & + & 2AlF_3 & (5) \\ \Delta\gamma & 4.0 & & 10.0 & & 5.5 & & 8.5 & \end{array}$$

to bind F^-, the harder of the two bases F^- and Br^-, leading to an exothermic reaction [$\Delta H^0 = -126.6$ kcal mol^{-1} (calculated)]. Earlier we have shown that[9,14] an exchange reaction proceeds in a direction so as to minimise $|\Delta\Delta\gamma|$. This observation is quite general, as metathetical reactions also follow this trend. Reaction (5) is used again to illustrate this point. For this reaction, which thermochemically proceeds from left to right, $|\Delta\Delta\gamma|$ on the left-hand side is 6.0 while $|\Delta\Delta\gamma|$ on the right is 3.0. Of a number of metathetical reactions examined, there are few exceptions. For reactions between the halides of multivalent cations with those of monovalent ones, $|\Delta\Delta\gamma|_{left}$ is found to be uniformly equal to $|\Delta\Delta\gamma|_{right}$; consequently such reactions are predicted to proceed thermochemically in any direction. An example of such cases is the gas-phase reaction (6) [ΔH^0 =

$$\begin{array}{lcccccccl} & CaF_2 & + & 2CsI & \longrightarrow & CaI_2 & + & 2CsF & (6) \\ \Delta\gamma & 0.5 & & 5.0 & & 2.5 & & 7.0 & \end{array}$$

+22.8 kcal mol^{-1} (calculated)].

Thus here we have shown that the ionic version of Pauling's bond-energy equation yields a parameter with which the metal ions can be ranked in terms of their gas-phase chemical hardnesses. We feel that the various results obtained for the halides can be extended to other monovalent anionic ligands.

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