Pearson's Chemical Hardness, Heterolytic Dissociative Version of Pauling's Bond-energy Equation and A Novel Approach towards Understanding Pearson's Hard–Soft Acid–Base Principle‡

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The empirical chemical hardness parameters developed recently by Pearson have been examined critically. It was found that these parameters normally characterise a group but not the corresponding ion as postulated. Equation (i) has been found quite successful when the heterolytic dissociation of

$$D(A^+B^-) - \tfrac{1}{2}[D(A^+A^-) + D(B^+B^-)] = 2|\Delta\gamma|^2 \quad \text{(i)}$$

AB into $A^+ + B^-$ follows the general notion of electronegativity (*i.e.* the more electronegative part of AB dissociates as the anion), where $D(A^+B^-)$ is the energy required to dissociate the AB bond into $A^+ + B^-$ and $D(A^+A^-)$ and $D(B^+B^-)$ are the heterolytic bond-dissociation energies of the molecules AA and BB respectively. Equation (i) has been used to define a new parameter γ, where $|\Delta\gamma| = |\gamma_{A^+} - \gamma_{B^-}|$. The γ parameters characterise the ions, and have been used to rank various monovalent anions and cations in a unified way to explain the hard–soft acid–base principle of Pearson. It was found that a reaction of type (ii) proceeds from left to right in the gas phase if the

$$AB + CD \longrightarrow AC + BD \quad \text{(ii)}$$

$|\Delta\Delta\gamma|$ value of the right-hand side is greater than that of the left. Out of some 282 gas-phase reactions considered, there are few exceptions. Emphasis has been placed on explaining the course of inorganic reactions. It is felt that the γ parameter can be identified with the chemical hardness of an ion.

The classification of acceptors and donors in inorganic reactions is a very old and important problem.[1–6] The earliest meaningful classification was done by Ahrland *et al.*[3] in 1958. They divided the metal ions into two classes, (a) and (b). Class (a) metal ions form halides whose stability in water is of the order $MF_n > MCl_n > MBr_n > MI_n$. Class (b) metal ions form halides whose stability is in the opposite order. The various thermodynamic and bond-energetic aspects of these two types of behaviour were critically examined later by Williams and Hale[4] in 1966. To quantify the notion to the extent possible, they used[4] a plot of $(\Sigma\text{i.p.})/z^2$, where i.p. = ionisation potential and z = charge of the cation, against the Pauling ionic radius (r) of various cations to separate the metal ions of class (a) from those of class (b). The curve of demarkation was drawn, however, in a somewhat arbitrary manner.

Earlier in 1963, the ΔH values for gaseous displacement reactions of the type $MX(g) + Y^-(g) \longrightarrow MY(g) + X^-(g)$, where X^- and Y^- are halide, were used by Pearson[5] as a measure of class (b) character. He then grouped a variety of metal ions and Lewis acids into three categories: class (a), class (b) and borderline. From polarisability considerations Pearson chose to call class (a) 'hard' and class (b) 'soft'. (Simply stated, polarisability, as understood now, is the ease with which the electron cloud in a chemical species can be deformed. A less-polarisable chemical species is 'hard' and a more polarisable one 'soft'.) This parallelism was questioned by Williams and Hale[4] who felt that 'it cannot be convincingly shown that class (a) and class (b) is related to polarisability. Furthermore it is not clear that such definitions as 'soft' and 'hard' really refer to the same physical properties in neutral acceptors as in ions.' Their conclusion was[4] that 'it is not just good enough to confuse a simple classification into (a) and (b) types for although (a) and (b) have no meaning 'soft' and 'hard' have clear descriptive significance in English.' Such controversy is justified since (a) and (b) refer to the classification of the metal ions in the aqueous medium and Pearson's classification applies in the gas phase; the solvation of the ions plays an important role. That Pearson's hard–soft classification was gaining in popularity was clear from the attempt of Hudson[7] in 1966 to correlate the concept of hard and soft acids and bases (HSAB) with nucleophilic displacement reactions. The main advantages of Pearson's classification are its wider applicability and its ability to generalise certain chemical phenomena.[5,6,8] The generalisation is now known as Pearson's HSAB principle which states that 'hard acids prefer to co-ordinate to hard bases and soft acids prefer to co-ordinate to soft bases'.[8] An explanatory example of this principle is reaction (1) in the gas phase where Li^+ is a hard acid, F^- a hard base, Cs^+ a soft acid and I^- a soft base.

$$\underset{\text{h s}}{LiI} + \underset{\text{s h}}{CsF} \longrightarrow \underset{\text{h h}}{LiF} + \underset{\text{s s}}{CsI} \qquad \Delta H^\circ = -14 \text{ kcal mol}^{-1} \quad (1)$$

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Non-SI units employed: cal = 4.184 J, eV $\approx 1.60 \times 10^{-19}$ J.

Hard–hard (h–h) and soft-soft (s–s) interactions are preferred over hard–soft (h–s) interactions.

Pearson's hard–soft classification remained qualitative for a very long time. In 1980, Jensen [9] used a plot of second i.p. *vs.* z/r to classify the divalent metal ions into three broad categories; hard, borderline and soft. The curves drawn for this purpose were again somewhat arbitrary. Nevertheless, it was an attempt to quantify the basic idea. Interestingly, this graphical classification was later accepted and used by Williams [10] also. The quantitative definition, equation (2), of the absolute

$$\eta = (\text{i.p.} - \text{e.a.})/2 \quad (2)$$

hardness (η) of a chemical species was given by Parr and Pearson [11] in 1983, where e.a. is the electron affinity. The higher the value of η the harder is the chemical species. As shown later by Pearson,[12] equation (2) can be used to rank the acids and bases; however, in the case of anions the relevant data become inaccessible. Moreover, equation (2) indicates the global value of η. It has been shown by Parr and co-workers [13,14] that η may not be the same at all points in a chemical species. To apply the HSAB principle to a chemical reaction of type (1), one needs to know the hardness of the reacting species at the reaction sites, which is termed as 'chemical hardness'. Recently Pearson [15] has evolved a method to rank the various monovalent cationic acids and monovalent anionic bases according to their 'chemical hardness' derived from homolytic bond-dissociation energy data.

In this article we shall examine the nature of Pearson's chemical hardness [16] for various monovalent ions. As we do so, we shall feel the need for a unified scale for cations and anions. To formulate this, a heterolytic dissociative version of Pauling's bond-energy equation is developed empirically. Before we go on to our own work, it is imperative to discuss further Pearson's chemical hardness.

Pearson's Chemical Hardness and Homolytic Bond-dissociation Energy.—A general acid–base reaction is (3)

$$A + :B \longrightarrow A:B \quad (3)$$

where A is a Lewis acid and B a Lewis base. The nature of the A–B bond is related to the hardness of A and B. 'Soft acids and bases form covalent bonds, which are further stabilised by mutual polarisation, including hyperconjugation. Hard acids and bases form ionic bonds.'[16] According to the HSAB principle a correct matching of the hardness/softness between A and B gives rise to an extra stability of the A–B bond. It should be remembered that this principle actually applies to heterolytic bond dissociation.[15,16] However, Pearson proposed that the difference $\Delta_{A^+} = D(\text{A–F}) - D(\text{A–I})$, where A^+ is a Lewis acid and the D values are homolytic bond-dissociation energies of the molecules (corresponding fluoride and iodide) given within the parentheses, can be used for ordering the acids: the larger the value of Δ_{A^+} the harder is the acid A^+. Some examples are given in Table 1. Similarly $\Delta_{B^-} = D(\text{H–B}) - D(\text{CH}_3\text{–B})$ (Table 2), or $\Delta'_{B^-} = D(\text{CH}_3\text{CO–B}) - D(\text{CH}_3\text{–B})$ (Table 2) can be used to rank the bases, B^-. It should be mentioned that a similar approach was adopted much earlier by Williams and Hale [4] to rank various anionic (mono- and di-valent) bases of which, apparently, Pearson did not take any notice. Instead of organic cations, they used [4] metal ions as references. From Tables 1 and 2 one can visualise how bond strength is affected by Δ, Pearson's chemical hardness. An example of the effect of proper matching of soft–soft or hard–hard combinations on bond strength is the gas-phase reaction (4).

$$SiH_3I + HOF \longrightarrow SiH_3F + HOI \qquad \Delta H^\circ = -68 \text{ kcal mol}^{-1} \quad (4)$$

Table 1 Pearson's empirical hardness parameters (Δ_{A^+}) for some cationic Lewis acids (A^+) and the electronegativities of the corresponding groups (A)[a]

Acid A^+	D(A–F)	D(A–I)	Δ_{A^+}	χ_A[b]
SiH_3^+	148[c]	72[c]	76	1.76
CF_3^+	130[d]	55[d]	75 ± 6	2.58
HCO^+	122[c]	52[c]	70	2.44
CH_3CO^+	120[c]	50[c]	70	2.42
H^+	135	70	65 ± 1	2.1[e]
tert-C_4H_9	108[c]	50[c]	58	2.65
$C_2H_5^+$	108[d]	53[d]	55 ± 2	2.59
Li^+	137	83	54 ± 8	1.0[e]
CH_3^+	110[d]	57[d]	53 ± 1.5	2.68
iso-$C_3H_7^+$	106[d]	53[d]	53 ± 3	2.54
Cu^+	87	34	53 ± 9	1.9[e]
Na^+	114	73	41	0.9[e]
Cs^+	120	80	40 ± 15	0.7[e]
K^+	117	78	39 ± 8	0.8[e]
Tl^+	105	67	38 ± 10	1.8[e]
Rb^+	117	79	38 ± 8	0.8[e]
I^+	66	36	30 ± 1	2.5[e]
Ag^+	83	61	22	1.9[e]
Au^+	73	55	18	2.4[e]
OH^+	56[c]	48	6	3.46

[a] For the meanings of the symbols, see text. The bond-energy data, given in kcal mol^{-1}, are taken from the Table E.1 of ref. 17 unless otherwise mentioned. [b] In Pauling's unit; from ref. 16 unless otherwise specified. [c] From ref. 15. [d] From ref. 18. [e] From ref. 19.

Results and Discussion

The Nature of Pearson's Chemical Hardness and the Relation with Pauling's Group Electronegativity.—Recently we have evaluated [16,20] the electronegativities of a number of groups with reference to H using Pauling's thermochemical method. These group electronegativities are called Pauling's group electronegativities which we now want to correlate with Pearson's chemical hardness (Δ).

The Δ parameters can be calculated from Pauling's bond-energy equation [19] [equation (5)] where χ_A and χ_B are the

$$D(\text{A–B}) = \tfrac{1}{2}[D(\text{A–A}) + D(\text{B–B})] + 23(\chi_A - \chi_B)^2 \quad (5)$$

electronegativities of the atoms A and B. We have shown [16,20] that such an equation can be applied even when A and B are two groups. Using equation (5) we can write expression (6)* which

$$\Delta_{B^-} = \tfrac{1}{2}[D(\text{H–H}) - D(\text{CH}_3\text{–CH}_3)] + 23(\chi_H^2 - \chi_{CH_3}^2) - 46\chi_B(\chi_H - \chi_{CH_3}) \quad (6)$$

shows that Δ_{B^-} should vary linearly with χ_B, *i.e.* the electronegativity of the group B corresponding to the anionic base B^-. It also shows that the slope will be positive if $\chi_H < \chi_{CH_3}$ and the intercept can be calculated beforehand. In Fig. 1 we have plotted the χ_B values (Table 2) *versus* Δ_{B^-} for some 17 groups/atoms. Quite satisfactory linearity ($r = 0.873$) is observed. The slope is found to be 12.81 against the calculated value of 26.68 and the intercept is -21.92 kcal mol^{-1} (calculated value = -57.34 kcal mol^{-1}).

* This equation is a simplified version. The value of the constant in equation (5) which is 23 for diatomic molecules will depend on the nature of the reference group when applied to polyatomic molecules.[20] If for H–B molecules the constant is K, for CH_3–B molecules it will be K' Actually in refs. 16 and 20 we used a different form of Pauling's bond-energy equation involving the geometric instead of the arithmatic mean. However from our work it is clear that $K' > K$. Thus the actual equation will be different. Since K and K' will be comparable to the value of 23, we have an advantage in using the value of the constant as 23 uniformly.

Table 2 Pearson's empirical hardness parameter Δ_{B^-} and Δ_{B^-}' (using acetyl cation as one of the references) for some anionic bases (B^-) and the electronegativities of the corresponding groups (B)[a]

Base B^-	D(H–B)[b]	D(CH_3–B)[b]	Δ_{B^-}	D(CH_3CO–B)[b]	Δ_{B^-}'	χ_B[c]
OH^-	119	92	27 ± 2	109	17	3.46
F^-	135[d]	110	25 ± 2	120	10	4.0[e]
$CH_3CO_2^-$	106	83[f]	23	84	1	3.51
NH_2^-	107	85	22 ± 2.5	95	10	3.10
CH_3O^-	104	83	21 ± 2	98	15	3.40
Cl^-	102[d]	85	17 ± 0.5	84	−1	3.0[e]
SH^-	91	74	17 ± 3	74	0	2.65
NO_2^-	78	61	17			3.38
Br^-	87[d]	71	16 ± 1	65	−6	2.8[e]
n-$C_3H_7S^-$	87[f]	72[f]	15			2.54
CH_3^-	105	90	15 ± 1	85	−5	2.68
CH_3S^-	91	77	14 ± 3			2.54
I^-	70[d]	57	13 ± 0.5	51	−6	2.5[e]
NC^-[g]	110[f]	98[f]	12			
CF_3^-	107	102	5 ± 4			2.58
HCO^-	87	82	5 ± 2.5			2.44
CH_3CO^-	86	81	5 ± 2			2.42
GeH_3^-	87[f]	83[f]	4			
SiH_3^-	90	88	2			1.76
CN^-[h]	124[f]	122[f]	2			
H^-	103[d]	105	−2 ± 0.5	89	−16	2.1[e]
$C_2H_5S^-$		72		76	4	2.54

[a] For the meanings of the symbols, see text. [b] In kcal mol^{-1}; from ref. 18 unless otherwise specified. [c] In Pauling's unit; from ref. 16 unless otherwise mentioned. [d] From Table E.1 in ref. 17. [e] From ref. 19. [f] From ref. 15. [g] N-Binding. [h] C-Binding.

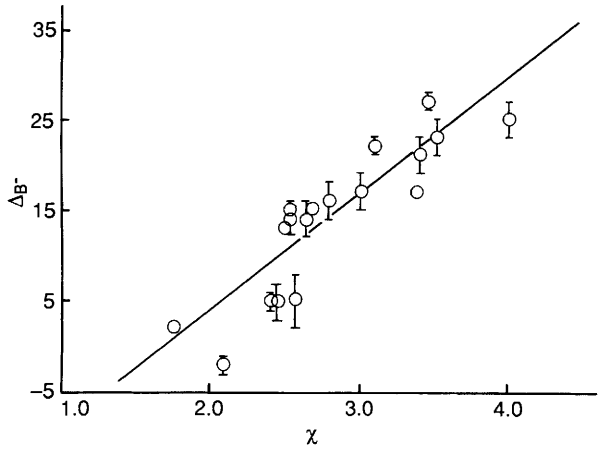

Fig. 1 Variation of Pearson's empirical chemical hardness Δ_{B^-} of an anionic base B^- with χ_B, the electronegativity of the corresponding group B; for data, see Table 2

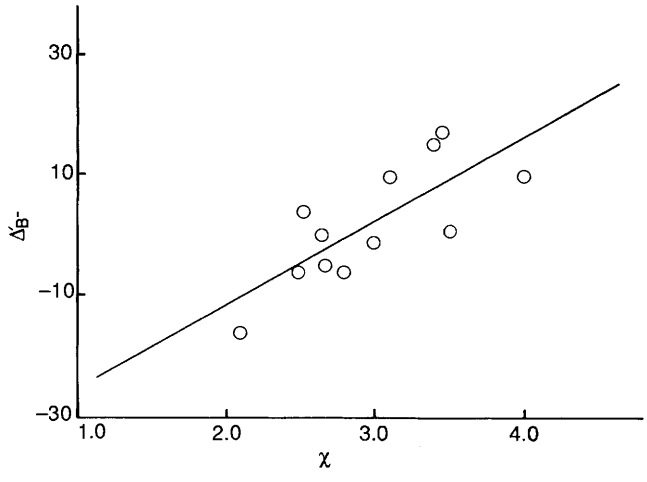

Fig. 2 The variation of Pearson's hardness parameter Δ'_{B^-} of an anion B^- with χ_B, the electronegativity of the group B; for the data, see Table 2

Similarly, we can write expression (7), where again a positive

$$\Delta_{B^-}' = \tfrac{1}{2}[D(CH_3CO\text{–}CH_3CO) - D(CH_3)] + 23(\chi_{CH_3CO}^2 - \chi_{CH_3}^2) - 46\chi_B(\chi_{CH_3CO} - \chi_{CH_3}) \quad (7)$$

slope is indicated if $\chi_{CH_3CO} < \chi_{CH_3}$. When Δ_{B^-}' is plotted against the χ_B values in Fig. 2, for some 12 groups/atoms, a somewhat poor (r = 0.769) straight line with a positive slope, as expected, is obtained. However, the slope (13.92) and the intercept (−39.55) match very well with the calculated slope (11.96) and the intercept (−42.00). One of the reasons for the poor fits obtained in the Figs. 1 and 2 is probably the oversimplification of equations (6) and (7) as indicated in the footnote.

Thus we find that Δ_{B^-} or Δ_{B^-}' is essentially related to χ_B. A significant observation[21–24] is that the electronegativity of a neutral species χ = (i.p. + e.a.)/2 is proportional to its hardness, *i.e.* $2\eta = \rho\chi$. The proportionality constant ρ takes the same value,[23] 1.6 ± 0.25, for atoms and molecules. In Table 3 we have shown that for some 25 radicals the value remains more or less unchanged, 1.58 ± 0.37. It has been proposed recently that for groups also the proportionality holds and the proportionality constant remains the same (1.6), using this a reasonable scale for group electronegativity has been devised from *ab initio* group charge calculations.[25] The proportionality between χ and η for groups means that Δ_{B^-} or Δ_{B^-}' actually indicates the hardness of a group B. It should be noted that a group, which is a fragment of a molecule, and the corresponding radical may be structurally quite different. When a group is allowed to relax structurally it yields the geometry of the corresponding radical. For this reason almost no correlation is found[20] between the experimental electronegativity of a radical and that calculated for the corresponding group. Hence the hardness trend observed for radicals may not be the same as found from studies of the Δ parameters. This is evident from the following comparisons. From Tables 3 and 4, the order of hardness for radicals is found to be F > H > OH > CH_3O ≈ NH_2 > HO_2 > CN > HCO ≈ CH_3 > Cl > NO > C_6H_5 > C_2H_5 > PH_2 > Br > C_2H_3 ≈ SH > *iso*-C_3H_7 > CH_3CO > SeH > I ≈ NO_2 > *tert*-C_4H_9 > CCl_3 > SiH_3 > C_6H_5O >

Table 3 The constancy of $2\eta/\chi$ for some radicals[a]

Radical	i.p.	e.a.	χ	η	$2\eta/\chi$
OH	13.17	1.83	7.50	5.67	1.51
NH_2	11.40	0.74	6.07	5.33	1.76
CH_3	9.82	0.08	4.95	4.87	1.97
SH	10.41	2.30	6.40	4.10	1.28
PH_2	9.83	1.25	5.54	4.29	1.55
SiH_3	8.14	1.41	4.78	3.37	1.41
SeH	9.80	2.20	6.00	3.80	1.27
HO_2	11.53	1.19	6.36	5.17	1.63
CN	14.02	3.82	8.92	5.10	1.14
C_6H_5S	8.63	2.47	5.55	3.08	1.11
C_6H_5O	8.85	2.35	5.60	3.25	1.16
C_2H_5	8.38	−0.39	4.00	4.39	2.20
iso-C_3H_7	7.57	−0.48	3.55	4.03	2.27
tert-C_4H_9	6.93	−0.30	3.31	3.62	2.19
C_6H_5	8.95	0.10	4.52	4.43	1.96
C_2H_3	8.93	0.74	4.85	4.11	1.70
HCO	9.90	0.17	5.04	4.87	1.93
CH_3CO	8.05	0.30	4.18	3.88	1.86
CCl_3	8.78	1.90	5.34	3.44	1.29
$SiCl_3$	7.92	2.50	5.21	2.71	1.04
NO	9.25	0.02	4.63	4.62	2.00
$Mn(CO)_5$	8.44	2.00	5.22	3.22	1.23
NO_2	9.78[b]	2.38[b]	6.08	3.70	1.22
CH_3O	12.30[b]	1.58[b]	6.94	5.36	1.54
CH_3S	8.06[c]	1.90[c]	4.98	3.08	1.24
				average	1.58 ± 0.37

[a] For the meanings of the symbols, see text. The i.p. and e.a. values given in eV are taken from ref. 15 unless otherwise specified. [b] From Tables 2.4B and 2.6 in ref. 17. [c] From ref. 12.

Table 4 Experimental ionisation potentials and electron affinities of the various atoms and radicals used in the present study[a]

Atom/radical	i.p.	e.a.	η
H	13.60	0.75	6.43
Li	5.39	0.62	2.39
F	17.42	3.40	7.01
Na	5.14	0.55	2.30
Cl	13.01	3.62	4.70
K	4.34	0.50	1.92
Cu	7.73	1.23	3.25
Br	11.84	3.36	4.24
Rb	4.18	0.49	1.85
I	10.45	3.06	3.70
Cs	3.89	0.47	1.71
OH	13.17	1.83	5.67
NH_2	11.40	0.74	5.33
CH_3	9.82	0.08	4.87
SH	10.41	2.30	4.10
SiH_3	8.14	1.41	3.37
CH_3S	8.06	1.90	3.10
C_2H_5	8.38	−0.39	4.39
iso-C_3H_7	7.57	−0.48	4.03
tert-C_4H_9	6.93	−0.30	3.62
NO_2	9.78[b]	2.38[b]	3.70
CH_3O	12.30[b]	1.58[b]	5.36

[a] For the meanings of the symbols, see text; the i.p. and e.a. values given in eV are taken from refs. 12 and 15 unless otherwise specified. [b] From Tables 2.4B and 2.6 in ref. 17.

$CH_3S \approx C_6H_5S$, while the experimental η for F is 7.01 eV and that for C_6H_5S is 3.08 eV. From Table 2 we find that $OH^- \approx F^- > CH_3CO_2^- > NH_2^- \approx CH_3O^- > Cl^- \approx SH^- \approx NO_2^- > Br^- > n\text{-}C_3H_7S^- \approx CH_3^- > CH_3S^- > NC^- \approx I^- \gg CF_3^- \approx HCO^- \approx CH_3CO^- > SiH_3^- \approx CN^- > H^-$. There are several discrepancies, H being the most prominent. Though η_{OH} (= 5.67 eV) is much lower than η_F (= 7.01 eV), the chemical hardness of the OH group is comparable to that of F. The position of CN in the radicals does not fit with its position in the groups as –CN or –NC. As a radical, SH which is much softer than Cl, as a group becomes equally as hard as Cl. The CH_3S radical is almost the softest but becomes harder than I as a group. As a group, SiH_3 is one of the most soft though as a radical it is harder than CH_3S. The position of CH_3CO also differs in the two trends.

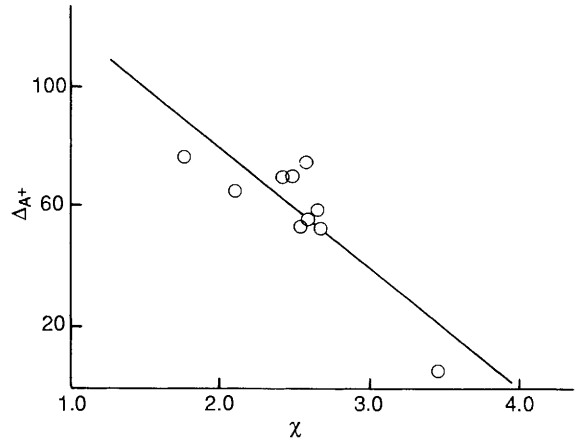

Fig. 3 The variation Pearson's empirical hardness parameter Δ_{A^+} of a cationic acid A^+ with χ_A, the electronegativity of the corresponding group A; for the data, see Table 1

From Table 2 the order of the anionic bases based on Δ_{B^-}' is found to be $OH^- > CH_3O^- > NH_2^- \approx F^- > C_2H_5S^- > CH_3CO_2^- > SH^- > Cl^- > CH_3^- > Br^- \approx I^- \gg H^-$. Obviously this ordering differs not only from the trend observed in the radicals but also from that found from Δ_{B^-}. This is not unexpected. In the case of group electronegativity we have seen[16,20] that χ_B values depend on the reference chosen. For the HB molecules χ_B is evaluated with respect to H[16] which does not give scope for multiple bonding between H and B. However in molecules like CH_3–B or CH_3CO–B, where the reference becomes CH_3 or CH_3CO, hyperconjugation or a similar small amount of multiple bonding exists between B and the reference group which will affect the nature of χ_B. Similarly we realise that the chemical hardness of a group may depend on the nature of the reference groups. That the trend in the polarisability of various chemical species is affected by the reference chosen was observed earlier also by Hudson[7] and Williams and Hale.[4]

When Δ_{A^+} is plotted against χ_A values (Table 1) in Fig. 3 for some 10 organic cations (OH^+ included) we get a reasonably good straight line (r = 0.851). The slope is found to be −39.73 (calculated −69.00) and the intercept as 158.30 (calculated 224.95). However, if we plot $-\Delta_{A^+}$ *vs.* χ_A, the trend of the group hardness is similar to that found from Table 2: $OH \gg CH_3 \approx$ *iso*-$C_3H_7 \approx C_2H_5 >$ *tert*-$C_4H_9 \gg H > CH_3CO \approx HCO > CF_3 \approx SiH_3$. Thus we find that Δ_{A^+}, like Δ_{B^-} or Δ_{B^-}', essentially describes group hardness. However the metals are out of line which is not yet understood.

A similar analysis based on Pauling's bond-energy equation was attempted by Pearson[15] himself. The results were negative because of the lack of proper group electronegativity data, especially for CH_3 and CH_3CO. We have shown that[16] Pauling's thermochemical method yields $\chi_{CH_3CO} < \chi_{CH_3}$. The group electronegativity scale developed by Datta[25] also shows that the CH_3 group is more electronegative than CH_3CO.

The Need for a Unified Hardness Scale for Ions.—In deriving the chemical hardness parameters (Tables 1 and 2) Pearson[15] assumes that, for example, for the two series AF and AI considered, the difference D(A–F) − D(A–I) describes the hardness of A^+ while all other bond-determining factors are constant. A serious problem is encountered when comparing FOH and IOH: FOH can be considered as F^-OH^+ but IOH,

since $\chi_{OH} > \chi_I$, is definitely I^+OH^-. Thus it is not clear what will be described by the difference D(F–OH) − D(I–OH). Similar problems are likely to arise in the case of various groups depending on the electronegativity differences. For example, D(H–SiH_3) − D(CH_3–SiH_3) should describe the hardness of SiH_3^+ but not of SiH_3^- as postulated by Pearson, since $\chi_{CH_3} > \chi_H > \chi_{SiH_3}$.[16,25] However all such inconsistencies do not appear if we accept that the various bond-energy differences (the Δ values) only characterise the groups, as we have shown in the previous section. Thus it follows that a scale for the chemical hardness of the ions does not exist. In order to apply the HSAB principle one needs such a scale. Though for cations we have the experimental η scale, for anions we may not have such an experimental scale as pointed out in an earlier section. Moreover the experimental gas-phase η scale for isolated ions may not describe the chemical hardness which characterises the binding site(s). In Tables 1 and 2 Pearson[15] attempted to categorise the monovalent ions on two different scales, one for the cations and another for the anions, not on a uniform scale for both types of ions. Now we try to develop an approach to rank the monovalent ions (of both types) on a unified scale to explain the HSAB principle of Pearson.

The γ Parameters and the Heterolytic Dissociative Version of Pauling's Bond-energy Equation.—As noted earlier the HSAB principle actually refers to the heterolytic bond dissociation. When it says that perfect matching of local (at the reaction sites) hardness between A^+ and B^- leads to an extra amount of stability of the A–B bond, it means the heterolytic dissociation $AB \rightarrow A^+ + B^-$. On the same lines, we have empirically formulated equation (8) where $D(A^+B^-)$ is the energy for

$$D(A^+B^-) - \tfrac{1}{2}[D(A^+A^-) + D(B^+B^-)] = \delta = 2|\Delta\gamma|^2 \quad (8)$$

heterolytic dissociation of the A–B into A^+ and B^-, $D(A^+A^-)$ and $D(B^+B^-)$ represent the heterolytic dissociation of A–A and B–B, and $|\Delta\gamma| = |\gamma_{A^+} - \gamma_{B^-}|$. If the difference between γ_{A^+} and γ_{B^-} is large, δ will be large. The meaning of the γ parameters will be clear later on. At this stage we note that equation (8) probably is a heterolytic dissociative version of Pauling's bond-energy equation (5). In Table 5 the $|\Delta\gamma|$ values for various monovalent cations and anions are given. The heterolytic bond-dissociation energy for an A–B bond is calculated by equation (9) from the corresponding homolytic

$$D(A^+B^-) = (A\text{–}B) + \text{i.p.}(A) - \text{e.a.}(B) \quad (9)$$

bond-dissociation energy D(A–B) with the knowledge of the ionisation potential of the atom/radical A and the electron affinity of the atom/radical B (Table 4). It should be remembered that in equation (9) the i.p. and e.a. are expressed in kcal mol^{-1}. Equation (8) only gives the magnitude of Δγ. The assignment of the γ values follows the same method adopted by Pauling[19] to assign the electronegativities of the atoms. We have set $\gamma_{F^-} = 0.0$. With this reference a γ scale for several monovalent ions has been constructed and is displayed in Fig. 4. Assignments of the γ values to the halides and to the cations Li^+ and Na^+ are discussed as examples. From Table 5, we find that $|\gamma_{Li^+} - \gamma_{F^-}| = 6.0$. With $\gamma_{F^-} = 0$, γ_{Li^+} is −6.0 (note that the negative sign is arbitrary) and in Fig. 4 Li^+ is placed six arbitrary units away from F^-. Since $|\gamma_{Li^+} - \gamma_{Cl^-}| = 5.0$ (Table 5), Cl^- is five units away from Li^+ but one unit away from F^-, *i.e.* γ_{Cl^-} is −1.0 (Fig. 4). Similarly, $\gamma_{Br^-} = -1.5$ ($|\gamma_{Li^+} - \gamma_{Br^-}| = 4.5$) and $\gamma_{I^-} = -2.0$ ($|\gamma_{Li^+} - \gamma_{I^-}| = 4.0$). Now since $|\gamma_{Na^+} \gamma_{F^-}| = 6.5$ (Table 5), $|\gamma_{Li^+} \gamma_{Na^+}| = |(\gamma_{Li^+} - \gamma_{F^-}) - (\gamma_{Na^+} - \gamma_{F^-})| = 0.5$ and since $|\gamma_{Na^+} - \gamma_{Cl^-}| = 5.5$, $|\gamma_{Li^+} - \gamma_{Na^+}| = 0.5$ (Fig. 4) and so on.

It should be noted that the Δγ values assigned differ from $(\delta/2)^{\frac{1}{2}}$ slightly due to rounding off and to match the whole pattern (Table 5). However the error incorporated in this way is small. Our statistical calculations show that out of the 86 dissociation processes considered, for 76 processes (88%) which do not lead to an imaginary value of Δγ, ($\delta - \delta_{calc}$) lies within the narrow range of 20.29 to −19.71 kcal mol^{-1} introducing the maximum error of ±10% in the average $D(A^+B^-)$ values.

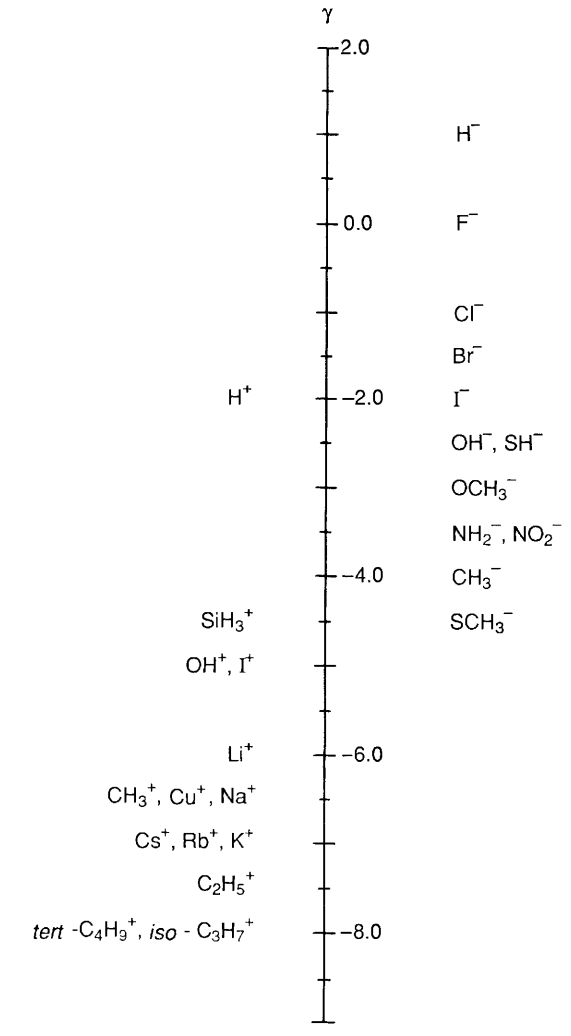

Fig. 4 The γ-scale (see Table 5)

Equation (8) fails when the dissociation process considered is not in keeping with the general notion of electronegativity. For example, if for LiF the dissociation $Li^+ + F^-$ (contrary to the notion of electronegativity) is considered, Δγ is found to be imaginary. However when the electronegativity difference between A and B becomes comparable then one of the processes $A^+ + B^-$ or $A^- + B^+$ gives a real value of Δγ. For the HX species (X = halogen/any group of atoms), the $H^+ + X^-$ type of dissociation has always led to an imaginary value of Δγ except for HF and HCl. The reason is not clear at present. However we have fixed the position of H^+ with respect to F^- and Cl^-. It should be clear that a mimimum of two references are needed to assign the γ value of an ion.

Application of the γ Scale to explain the HSAB *Principle.*—The HSAB principle can be applied to any reaction of type (10)

$$AB + CD \longrightarrow AC + BD \quad (10)$$

in the gas phase provided the acids (cations) and the bases (anions) are identified correctly. Usually the concept of electronegativity is used for this purpose. For example, a more electronegative part of AB or CD is considered to be the anion (base). When the two parts of AB or CD have comparable electronegativity, depending on the reaction, any of them can be

Table 5 The γ-parameters[a]

A^+B^-	D(A–B)[b]	$D(A^+B^-)$	$D_{\ddagger}$[c]	δ	$(\delta/2)^{\ddagger}$	|Δγ| value assigned	δ_{calc}[d]	$\delta - \delta_{calc}$
F^+F^-	37.00	360.29						
Cl^+Cl^-	57.29	273.81						
Br^+Br^-	45.45	240.99						
I^+I^-	35.60	206.01	206.01	00.00		3.00	18.00	−18.00
Li^+Li^-	25	134.99						
Li^+F^-	137	182.89	247.64	64.75	5.69	6.0	72.00	−7.25
Li^+Cl^-	111	151.81	204.40	52.59	5.13	5.0	50.00	2.59
Li^+Br^-	100	146.81	187.99	41.18	4.54	4.5	40.50	0.68
Li^+I^-	83	136.73	170.50	33.77	4.11	4.0	32.00	1.77
Na^+Na^-	17.3	123.14						
Na^+F^-	114	154.12	241.71	87.59	6.62	6.5	84.50	3.09
Na^+Cl^-	97.5	132.55	198.47	65.92	5.74	5.5	60.50	5.42
Na^+Br^-	86.7	127.75	182.06	54.31	5.21	5.0	50.00	4.31
Na^+I^-	72.7	120.66	164.57	43.91	4.68	4.5	40.50	3.41
K^+K^-	11.8	100.35						
K^+F^-	117	138.67	230.32	91.65	6.77	7.0	98.00	−6.35
K^+Cl^-	101	117.60	187.08	69.48	5.89	6.0	72.00	−2.52
K^+Br^-	90.5	113.10	170.67	57.57	5.36	5.5	60.50	−2.93
K^+I^-	78	107.51	153.18	45.67	4.78	5.0	50.00	−4.33
Rb^+Rb^-	10.8	95.89						
Rb^+F^-	117	134.99	228.09	93.10	6.82	7.0	98.00	−4.90
Rb^+Cl^-	106	118.91	184.85	65.94	5.74	6.0	72.00	−6.06
Rb^+Br^-	92	110.91	168.44	57.53	5.36	5.5	60.50	−2.97
Rb^+I^-	79	104.83	150.95	46.12	4.80	5.0	50.00	−3.88
Cs^+Cs^-	10.4	89.26						
Cs^+F^-	120	131.30	224.77	93.47	6.84	7.0	98.00	−4.53
Cs^+Cl^-	104	110.22	181.53	71.31	5.97	6.0	72.00	−0.69
Cs^+Br^-	99.5	111.72	165.12	53.40	5.17	5.5	60.50	−7.10
Cs^+I^-	80	99.14	147.63	48.49	4.92	5.0	50.00	−1.51
Cu^+Cu^-	60.9	210.78						
Cu^+F^-	87.2	187.04	285.53	98.49	7.02	6.5	84.50	13.99
Cu^+Cl^-	86.2	180.97	242.29	61.32	5.54	5.5	60.50	0.82
Cu^+Br^-	78.9	179.67	225.88	46.21	4.81	5.0	50.00	−3.79
Cu^+I^-	34	141.68	208.39	66.71	5.77	4.5	40.50	26.21
$CH_3^+CH_3^-$	90.4	314.99	314.99	00.00		2.5	12.50	−12.50
$CH_3^+F^-$	109.9	257.94	337.64	79.70	6.31	6.5	84.50	−4.80
$CH_3^+Cl^-$	84.6	227.56	294.40	66.84	5.78	5.5	60.50	6.34
$CH_3^+Br^-$	70.9	219.86	277.99	58.13	5.39	5.0	50.00	8.13
$CH_3^+I^-$	57.2	213.08	260.50	47.42	4.87	4.5	40.50	6.92
$I^+CH_3^-$	57.2	296.32	260.50	−35.82	*e*	1.0	2.00	−37.82
H^+H^-	103.25	399.56	399.56	00.00		3.0	18.00	−18.00
H^+F^-	135	370.20	379.92	9.72	2.20	2.0	8.00	1.72
H^+Cl^-	102.3	332.43	336.68	4.25	1.46	1.0	2.00	2.25
H^+Br^-	86.6	322.72	320.27	−2.45	*e*	0.5	0.50	−2.95
H^+I^-	70.4	313.44	302.78	−10.66	*e*	0.0	0.00	−10.66
$H^+CH_3^-$	105.1	416.86	357.27	−59.59	*e*	2.0	8.00	−67.59
Li^+H^-	58	164.99	267.27	102.28	7.15	7.0	98.00	4.28
Na^+H^-	47	148.23	261.35	113.12	7.52	7.5	112.50	0.62
K^+H^-	43	125.78	249.95	124.17	7.88	8.0	128.00	−3.83
Rb^+H^-	39	118.09	247.72	129.63	8.05	8.0	128.00	1.63
Cs^+H^-	42	114.40	244.41	130.01	8.06	8.0	128.00	2.01
Cu^+H^-	66	226.95	305.17	78.22	6.25	7.5	112.50	−34.28
$Li^+CH_3^-$	61	183.44	224.99	41.55	4.56	2.0	8.00	33.55
OH^+OH^-	51	312.49	312.49	00.00		2.5	12.50	−12.50
H^+OH^-	119	390.40	356.02	−34.38	*e*	0.5	0.50	−34.88
OH^+F^-	56[f]	281.29	336.39	55.10	5.25	5.0	50.00	5.10
OH^+Cl^-	52.1	272.31	293.15	20.84	3.23	4.0	32.00	−11.16
I^+OH^-	48	246.77	259.25	12.48	2.50	2.5	12.50	−0.02
$CH_3^+OH^-$	92.3	276.54	313.74	37.20	4.31	4.0	32.00	5.20
I^+F^-	66.4	228.96	283.15	54.19	5.20	5.0	50.00	4.19
I^+Cl^-	49.7	207.19	239.91	32.72	4.04	4.0	32.00	0.72
I^+Br^-	41.9	205.39	223.50	18.11	3.01	3.5	24.50	−6.39
$C_2H_5^+C_2H_5^-$	82.2	284.43						
$C_2H_5^+F^-$	107.7	222.53	322.36	99.83	7.06	7.5	112.50	−12.67
$C_2H_5^+Cl^-$	79.9	189.66	279.12	89.46	6.69	6.5	84.50	4.96
$C_2H_5^+Br^-$	67.8	183.56	262.71	79.15	6.29	6.0	72.00	7.15
$C_2H_5^+I^-$	53.4	176.07	245.22	69.15	5.88	5.5	60.50	8.65
iso-$C_3H_7^+$*iso*-$C_3H_7^-$	79.0	264.62						
iso-$C_3H_7^+F^-$	106.5	202.66	312.45	109.79	7.41	8.0	128.00	−18.21
iso-$C_3H_7^+Cl^-$	80.7	171.78	269.21	97.43	6.98	7.0	98.00	−0.57
iso-$C_3H_7^+Br^-$	68.4	165.48	252.80	87.32	6.61	6.5	84.50	2.82
iso-$C_3H_7^+I^-$	53.5	157.50	235.31	77.81	6.24	6.0	72.00	5.81
$C_2H_5^+OH^-$	91.5	242.54	298.46	55.92	5.29	5.0	50.00	5.92
iso-$C_3H_7^+OH^-$	92.7	225.06	288.55	63.49	5.63	5.5	60.50	2.99

Table 5 (*continued*)

A^+B^-	D(A–B)[b]	$D(A^+B^-)$	$D_{\frac{1}{2}}$[c]	δ	$(\delta/2)^{\frac{1}{2}}$	|Δγ| value assigned	δ_{calc}[d]	$\delta - \delta_{calc}$
tert-$C_4H_9^+$ *tert*-$C_4H_9^-$	71.2	237.92						
tert-$C_4H_9^+OH^-$	92.8	210.40	275.20	64.80	5.69	5.5	60.50	4.30
$CH_3O^+CH_3O^-$	37.6	284.79						
$H^+CH_3O^-$	104.4	381.57	342.17	−39.40	*e*	1.0	2.00	−41.40
$CH_3^+CH_3O^-$	83.3	273.31	299.89	26.58	3.64	3.5	24.50	2.08
$C_2H_5^+CH_3O^-$	81.8	238.60	284.61	46.01	4.80	4.5	40.50	5.51
$NO_2^+NO_2^-$	13.6	184.24						
$H^+NO_2^-$	78.3	337.02	291.90	−45.12	*e*	1.5	4.50	−49.62
$CH_3^+NO_2^-$	60.8	232.36	249.61	17.25	2.94	3.0	18.00	−0.75
iso-$C_3H_7^+NO_2^-$	59.0	178.68	224.43	45.75	4.78	4.5	40.50	5.25
$NH_2^+NH_2^-$	65.8	311.61						
$H^+NH_2^-$	107.4	403.94	355.58	−48.36	*e*	1.5	4.50	−52.86
$CH_3^+NH_2^-$	84.9	294.27	313.30	19.03	3.08	3.0	18.00	1.03
$C_2H_5^+NH_2^-$	81.6	257.77	298.02	40.25	4.49	4.0	32.00	8.25
SH^+SH^-	66	253.01						
$CH_3^+SH^-$	74.0	247.40	284.00	36.60	4.28	4.0	32.00	4.60
$C_2H_5^+SH^-$	70.5	210.70	268.72	58.02	5.39	5.0	50.00	8.02
tert-$C_4H_9^+SH^-$	68.4	175.16	245.46	70.30	5.93	5.5	60.50	9.80
H^+SH^-	91.1	351.67	326.28	−25.39	*e*	0.5	0.50	−25.89
$CH_3S^+CH_3S^-$	72	214.04						
$CH_3^+CH_3S^-$	77.2	259.83	264.51	4.68	1.53	2.0	8.00	−3.32
$C_2H_5^+CH_3S^-$	73.3	222.72	249.23	26.51	3.64	3.0	18.00	8.51
$SiH_3^+SiH_3^-$	74	229.19						
$SiH_3^+CH_3^-$	88.2	274.05	272.09	−1.96	*e*	0.5	0.50	−2.46
$SiH_3^+F^-$	148[f]	257.30	294.74	37.44	4.33	4.5	40.50	−3.06
$SiH_3^+I^-$	72[f]	189.14	217.60	28.46	3.77	2.5	12.50	15.96
$SiH_3^+H^-$	90.3	260.71	314.37	−53.66	5.18	5.5	60.50	−6.84
$H^+SiH_3^-$	90.3	371.39	314.37	−57.02	*e*			
$CH_3^+SiH_3^-$	88.2	282.13	272.09	−10.04	*e*			
$I^+SiH_3^-$	72[f]	280.45	217.60	−62.85	*e*			
$C_2H_5^+CH_3^-$	85.8	277.19	299.71	22.52	3.35	3.5	24.50	−1.98
$CH_3^+C_2H_5^-$	85.8	321.23	299.71	−21.52	*e*			
iso-$C_3H_7^+CH_3^-$	85.7	258.41	289.80	31.39	3.96	4.0	32.00	−0.61
tert-$C_4H_9^+CH_3^-$	84.1	242.05	276.45	34.40	4.15	4.0	32.00	2.40

[a] Meanings of the symbols as in the text. All bond-energy data are given in kcal mol^{-1}. [b] Either from ref. 18 or from Table E.1 in ref. 17 unless otherwise mentioned. [c] $D_{\frac{1}{2}} = \frac{1}{2}[D(A^+A^-) + D(B^+B^-)]$. [d] $\delta_{calc} = 2(|\Delta\gamma| \text{ value assigned})^2$. [e] Δγ found to be imaginary. [f] From ref. 15.

considered as an acid or a base. Pearson[15] has discussed this aspect in some detail.

Whether the reaction (10) will take place in the gas phase can be predicted by the HSAB principle. An example has been given earlier, reaction (1). In terms of our γ parameters it is found that the reaction is driven in that direction where the magnitude of the difference in the Δγ values of the products is minimised. In other words, if $|\Delta\gamma_{AB} - \Delta\gamma_{CD}| > |\Delta\gamma_{AC} - \Delta\gamma_{BD}|$, reaction (10) will proceed in the gas phase as shown. Otherwise the reverse reaction will take place in gas phase. [We have checked whether a gas-phase reaction is feasible thermochemically, see SUP 56822. However, when $\Delta H^\circ \leqslant -10$ kcal mol^{-1} or $\geqslant 10$ kcal mol^{-1}, we can confidently say that thermochemical considerations lead to the same conclusions as reached from the thermodynamic point of view, since in Table 6 we find that for a reaction of type (10), where two bonds are broken and two new bonds are created, the $T\Delta S^\circ$ values usually lie in between ±2 kcal mol^{-1} (at 298 K)]. Examples in gas phase are as follows. In example (i) $|\Delta\Delta\gamma|$ on the left-hand side is 3.0 while on the right it is 1.0. Hence the forward reaction will take place. In (ii) $|\Delta\Delta\gamma|$ on the left is 0.5 and on the right is 2.0. Hence the forward reaction cannot take place. In (iii) $|\Delta\Delta\gamma|_{left} >$

$$\begin{array}{lccccc} & Li^+I^- & + & Cs^+F^- & \longrightarrow & Li^+F^- + Cs^+I^- \\ \Delta\gamma: & 4.0 & & 7.0 & & 6.0 \quad 5.0 \end{array}$$
$$\Delta H^\circ = -14 \text{ kcal mol}^{-1} \quad \text{(i)}$$

$$\begin{array}{lccccc} & Cu^+Cl^- & + & I^+F^- & \longrightarrow & Cu^+F^- + I^+Cl^- \\ \Delta\gamma: & 5.5 & & 5.0 & & 6.5 \quad 4.5 \end{array}$$

$$\begin{array}{lccccc} & Cs^+F^- & + & H^+I^- & \longrightarrow & Cs^+I^- + H^+F^- \\ \Delta\gamma: & 7.0 & & 0.0 & & 5.0 \quad 2.0 \end{array}$$
$$\Delta H^\circ = -24.6 \text{ kcal mol}^{-1} \quad \text{(iii)}$$

$$\begin{array}{lccccc} & CH_3^-I^+ & + & H^+F^- & \longrightarrow & CH_3^-H^+ + I^+F^- \\ \Delta\gamma: & 1.0 & & 2.0 & & 2.0 \quad 5.0 \end{array}$$
$$\Delta H^\circ = 20.7 \text{ kcal mol}^{-1} \quad \text{(iv)}$$
$$|\Delta\Delta\gamma|_{left} < |\Delta\Delta\gamma|_{right}$$

$$\begin{array}{lccccc} & Cu^+Br^- & + & Rb^+H^- & \longrightarrow & Cu^+H^- + Rb^+Br^- \\ \Delta\gamma: & 5.0 & & 8.0 & & 7.5 \quad 5.5 \end{array}$$
$$\Delta H^\circ = -40.1 \text{ kcal mol}^{-1} \quad \text{(v)}$$
$$|\Delta\Delta\gamma|_{left} > |\Delta\Delta\gamma|_{right}$$

$$\begin{array}{lccccc} & H^+F^- & + & Na^+H^- & \longrightarrow & Na^+F^- + H^+H^- \\ \Delta\gamma: & 2.0 & & 7.5 & & 6.5 \quad 3.0 \end{array}$$
$$\Delta H^\circ = -35.25 \text{ kcal mol}^{-1} \quad \text{(vi)}$$
$$|\Delta\Delta\gamma|_{left} > |\Delta\Delta\gamma|_{right}$$

$$\begin{array}{lccccc} & H^+I^- & + & Li^+F^- & \longrightarrow & H^+F^- + Li^+I^- \\ \Delta\gamma: & 0.0 & & 6.0 & & 2.0 \quad 4.0 \end{array}$$
$$\Delta H^\circ = -10.6 \text{ kcal mol}^{-1} \quad \text{(vii)}$$
$$|\Delta\Delta\gamma|_{left} > |\Delta\Delta\gamma|_{right}$$

$$\begin{array}{lccccc} & SiH_3^+Cl^- & + & CH_3^+F^- & \longrightarrow & SiH_3^+F^- + CH_3^+Cl^- \\ \Delta\gamma: & 3.5 & & 6.5 & & 4.5 \quad 3.0 \end{array}$$
$$\Delta H^\circ = -20 \text{ kcal mol}^{-1} \quad \text{(viii)}$$

Table 6 Some reactions of type (10) and their $T\Delta S°$ values at 298 K *

Reactions	$T\Delta S°$
$H_2 + F_2 \longrightarrow 2HF$	1.0
$H_2 + Cl_2 \longrightarrow 2HCl$	1.4
$H_2 + I_2 \longrightarrow 2HI$	1.4
$HCl + HF \longrightarrow H_2 + FCl$	−0.9
$HCl + HI \longrightarrow H_2 + ICl$	−1.1
$CH_4 + HCl \longrightarrow CH_3Cl + H_2$	−0.5
$CH_3NH_2 + HF \longrightarrow CH_3F + NH_3$	−0.1
$CH_3NH_2 + HI \longrightarrow CH_3I + NH_3$	−0.2
$C_2H_5NH_2 + HI \longrightarrow C_2H_5I + NH_3$	−0.2
$CH_3OH + HI \longrightarrow CH_3I + H_2O$	−0.2

* The $T\Delta S°$ values given in kcal mol^{-1} are calculated from the gas-phase $S°$ data in Tables 6 and 7 in ref. 26.

$$\begin{array}{lccccc} & SiH_3^+I^- & + OH^+F^- & \longrightarrow & SiH_3^+F^- & + OH^+I^- \\ \Delta\gamma: & 2.5 & 5.0 & & 4.5 & 3.0 \end{array}$$
$$\Delta H° = -68 \text{ kcal mol}^{-1} \quad (ix)$$
$$|\Delta\Delta\gamma|_{left} > |\Delta\Delta|_{right}$$

$|\Delta\Delta\gamma|_{right}$ hence the forward reaction will occur. In example (x) since $|\Delta\Delta\gamma|_{left} < |\Delta\Delta\gamma|_{right}$ the forward reaction cannot occur.

$$\begin{array}{lcccccc} & CH_3^+OH^- & + Li^+F^- & \longrightarrow & CH_3^+F^- & + Li^+OH^- & \\ \Delta\gamma: & 4.0 & 6.0 & & 6.5 & 3.5 & (x) \end{array}$$

More examples can be found in SUP 56822. There are reactions for which our γ parameters fail. Such exceptions, which are not many, are of two types. The obvious one is, as in example (xi) even though $|\Delta\Delta\gamma|_{left} < |\Delta\Delta\gamma|_{right}$, the reaction

$$\begin{array}{lccccc} & Li^+H^- & + \textit{iso}\text{-}C_3H_7^+I^- & \longrightarrow & Li^+I^- & + \textit{iso}\text{-}C_3H_7^+H^- \\ \Delta\gamma: & 7.0 & 6.0 & & 4.0 & 9.0 \end{array}$$
$$\Delta H° = -66.6 \text{ kcal mol}^{-1} \quad (xi)$$

takes place from left to right. However such reactions can be generalised. The reactions involving unsubstituted alkanes, H_2 and I_2 are found to be in this class. Incidentally many such reactions cannot be explained by the HSAB principle also. Examples are shown in equations (xii)–(xiv). Another type of

$$\begin{array}{lccccc} & Li^+H^- & + CH_3^+I^- & \longrightarrow & Li^+I^- & + CH_3^+H^- \\ & h\ s & h\ s & & h\ s & h\ s \end{array}$$
$$\Delta H° = -72.9 \text{ kcal mol}^{-1} \quad (xii)$$

$$\begin{array}{lccccc} & CH_3^+H^- & + H^+NO_2^- & \longrightarrow & CH_3^+NO_2^- & + H^+H^- \\ & h\ s & h\ h(s) & & h\ h(s) & h\ s \end{array}$$
$$\Delta H° = 19.35 \text{ kcal mol}^{-1} \quad (xiii)$$

$$\begin{array}{lccccc} & Cs^+H^- & + C_2H_5^+I^- & \longrightarrow & Cs^+I^- & + C_2H_5^+H^- \\ & s\ s & h\ s & & s\ s & h\ s \end{array}$$
$$\Delta H° = -82.8 \text{ kcal mol}^{-1} \quad (xiv)$$

exception comprises the cases where $|\Delta\Delta\gamma|_{left} = |\Delta\Delta\gamma|_{right}$ so that reaction in any direction is predicted. Ideally for such reactions $\Delta H°$ should be 0. Examples are shown in equations (xv)–(xvii). More examples can be found in SUP 56822.

$$\begin{array}{lccccc} & Cs^+F^- & + Rb^+H^- & \longrightarrow & Cs^+H^- & + Rb^+F^- \\ \Delta\gamma: & 7.0 & 8.0 & & 8.0 & 7.0 \end{array}$$
$$\Delta H° = 0.0 \text{ kcal mol}^{-1} \quad (xv)$$

$$\begin{array}{lccccc} & OH^+F^- & + OH^-I^+ & \longrightarrow & OH^+OH^- & + I^+F^- \\ \Delta\gamma & 5.0 & 2.5 & & 2.5 & 5.0 \end{array}$$
$$\Delta H° = -13.4 \text{ kcal mol}^{-1} \quad (xvi)$$

$$\begin{array}{lccccc} & \textit{iso}\text{-}C_3H_7^+I^- & + H^+NO_2^- & \longrightarrow & \textit{iso}\text{-}C_3H_7^+NO_2^- & + H^+I^- \\ \Delta\gamma: & 6.0 & 1.5 & & 4.5 & 0.0 \end{array}$$
$$\Delta H° = 2.4 \text{ kcal mol}^{-1} \quad (xvii)$$

Interestingly the $\Delta H°$ values for most of these reactions are within the range of ± 8 kcal mol^{-1}. The $\Delta H°$ values are calculated from the homolytic bond-dissociation energies. An average error of ± 2 kcal mol^{-1} per bond-energy determination leads to a maximum error of ± 8 kcal mol^{-1} for the whole reaction.

The Nature of the γ *Parameters.*—The various relative orders of the γ parameters in Fig. 4 are as follows: $F^- > Cl^- > Br^- > I^-$; $F^- > OH^- > NH_2^- > CH_3^-$; $OH^- > CH_3O^-$; $SH^- > CH_3S^-$; and $H^+ > Li^+ > Na^+ > K^+ \approx Rb^+ \approx Cs^+$; $SiH_3^+ > CH_3^+ > C_2H_5^+ > \textit{iso}\text{-}C_3H_7^+ \approx \textit{tert}\text{-}C_4H_9^+$. These are also the trends expected from the general notion of hardness introduced by Pearson.[12] Thus it is tempting to identify the γ parameters as the hardness of the ions. However there are several differences between the trends of the γ parameters and Pearson's hardness. The most important is the position of H^-: this ion is known to be chemically very soft, however the γ parameter for H^- is the highest.

Since the γ parameters are derived using the ionisation potential and electron affinity of the appropriate radicals, an attempt can be made to examine the relation between these quantities. By using equations (9) and (5) it can be shown that equation (8) yields (see Appendix) (11). In equation (11)

$$|\Delta\gamma|^2 = 34.17(\chi_A - \chi_B) + 11.50(\Delta\chi_G)^2 \quad (11)$$

$\chi_A - \chi_B$ ($=\Delta\chi_R$) is the electronegativity difference between the radicals corresponding to the groups A and B (in Pauling's unit) and $\Delta\chi_G$ the difference in the group electronegativities (in Pauling's unit). If A and B are two atoms, $\Delta\chi_R$ and $\Delta\chi_G$ are the same quantity as discussed in an earlier section. Quantitative evaluation of $|\Delta\gamma|$ by equation (11) cannot be recommended at all since large errors are introduced through Pauling's bond-energy equation (which is only approximate) and through the conversion of Mulliken's definition into Pauling's one necessary to arrive at the form of equation (11) (see Appendix). However the equation is useful in showing that because of the proportionality between electronegativity and hardness of a neutral species as mentioned earlier, $|\Delta\gamma|$ which characterises the ions is a non-linear function of the appropriate hardness differences of the neutral species.

The major defect of Pearson's concept of hardness is that it fails to enumerate the bonding in molecules which can be divided into two identical parts, *e.g.* H_2, H_2O_2, C_2H_6, *etc.* Since according to Pearson H^- is very soft and H^+ very hard, their interaction in H_2 should lead to a very weak bond, which is not true. Similar problems do not appear in the γ scale. The $|\Delta\gamma|$ values in such cases lie within 3 (*e.g.* $\Delta\gamma_{H^+,H^-} = 3.0$, $\Delta\gamma_{OH^+,OH^-} = 2.5$, $\Delta\gamma_{I^+,I^-} = 3.0$, *etc.*), the anionic part being harder than the cationic part. According to Pearson, if an anion is very hard its corresponding cation is very soft and *vice versa*. A reason for the γ parameter of an anion being greater than that of the corresponding cation may be the closed-shell nature of the anions.

We have seen in the last section that a reaction of type (10) in the gas phase is driven in that direction where the $\Delta\gamma$ parameters tend to equalise, *i.e.* $|\Delta\Delta\gamma|$ is minimised. This is reminiscent of Datta's geometric mean principle of hardness equalisation,[24] which states that equalisation of the hardness parameters is a driving force in molecule formation.

Conclusion

We have shown that Pearson's empirical chemical hardness parameters[15] do not characterise the ions but characterise the corresponding groups. We have developed a new set of parameters, γ, to rank the monovalent anions and cations in a

unified way to explain the HSAB principle. For a particular reaction of type (10) to occur from left to right in the gas phase, it is found that $|\Delta\Delta\gamma|$ on the right has to be smaller than $|\Delta\Delta\gamma|$ on the left. The γ scale has been successfully applied to some 282 reactions with few exceptions. Emphasis has been given to inorganic rather than organic reactions, the main reason being that for most organic reactions examined by us the ΔH° values are very small (SUP 56822). For deriving the γ parameters we have developed empirically a heterolytic dissociative version of Pauling's bond-energy equation. (Incidentally Pauling's bond-energy equation also cannot be derived; it is based on intuition.) Equation (8) is quite successful in cases where the dissociation process considered abides by the general notion of electronegativity. Incidentally, when the homolytic dissociative version of Pauling's bond-energy equation, *i.e.* equation (5), is applied to exchange reactions of type (10) it is known[27] to give rise to a sign for ΔH° exactly opposite to that observed experimentally. In conclusion we feel that the γ parameter can be identified with the chemical hardness of an ion.

Appendix

Derivation of Equation (11).—By using equation (9), equation (8) can be rewritten as (A1), where i.p. and e.a. are in eV. The

$$2|\Delta\gamma|^2 = D(\text{A–B}) - \tfrac{1}{2}[D(\text{A–A}) + D(\text{B–B})] + 23.06[\text{i.p.(A)} + \text{e.a.(A)}]/2 - 23.06[\text{i.p.(B)} + \text{e.a.(B)}]/2 \quad \text{(A1)}$$

factor 23.06 is to convert eV into kcal mol^{-1}. Now (i.p. + e.a.)/2 is Mulliken's definition of electronegativity expressed in eV. The relation between Mulliken's electronegativity (χ^M) and Pauling's electronegativity (χ) is given[25] by equation (A2) from

$$\chi = 0.336(\chi^M - 0.615) \quad \text{(A2)}$$

which and equation (A1) we can write expression (A3) where χ_A

$$2|\Delta\gamma|^2 = D(\text{A–B}) - \tfrac{1}{2}[D(\text{A–A}) + D(\text{B–B})] + 68.63(\chi_A - \chi_B) \quad \text{(A3)}$$

and χ_B are the electronegativities of the radicals A and B in Pauling's unit. By Pauling's bond-energy equation (5) it follows that equation (A3) takes the form (A4) where χ_G is the

$$2|\Delta\gamma|^2 = 23(\Delta\chi_G)^2 + 68.63(\chi_A - \chi_B) \quad \text{(A4)}$$

electronegativity difference of the groups corresponding to radicals A and B in Pauling's unit. Equation (11) follows directly from equation (A4) by diving both sides by 2.

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