

An Empirical Bond Energy Equation

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THERE is no bond-energy equation to predict the correct enthalpy change (ΔH) for a chemical reaction,¹ though Pearson's HSAB principle² may be used to predict the sign of ΔH . Here is suggested a bond-energy equation, which has been developed from experimental data.

A bonding parameter, b , was calculated³ from single-bond dissociation energy (BE) and associated bond distance

(BD) as shown in equation (1), where BE is in ergs/molecule and BD is in cm.:

$$\text{BE/BD} = 10^b \quad (1)$$

Bonding Equation: The b parameter is now related to the radii of the bonded atoms. Figure 1 shows a log-log plot of BE/BD *v.* geometric mean radius of bonded atoms, which

data for the homonuclear diatomics (line 1) are fitted into equation (2). Metallic radii (for CN, 12) are used for the alkali metals and covalent radii for the other elements.

$$BE/BD = nkr^s \quad (2)$$

where BE/BD is in dynes, n is a bonding coefficient and is assigned a value of unity for the "ideal" homonuclear single bond, $k = 1.85 (\pm 0.03) \times 10^{-4}$ dyne/Å, r is atomic radius Å (for a heteronuclear molecule, r is geometric mean radius of the bonded atoms), and $s = -2.62$.

The proportionality constant, k , in equation (2) has the same dimensions as that of a force constant, which is calculated from vibrational spectra and measures the force required to deform a particular bond by a given amount. The two constants are distinguishable in that k is related to atomic radius, while a force constant is involved with bond distance.

Figure 1 shows that BE/BD decreases as the atom radius

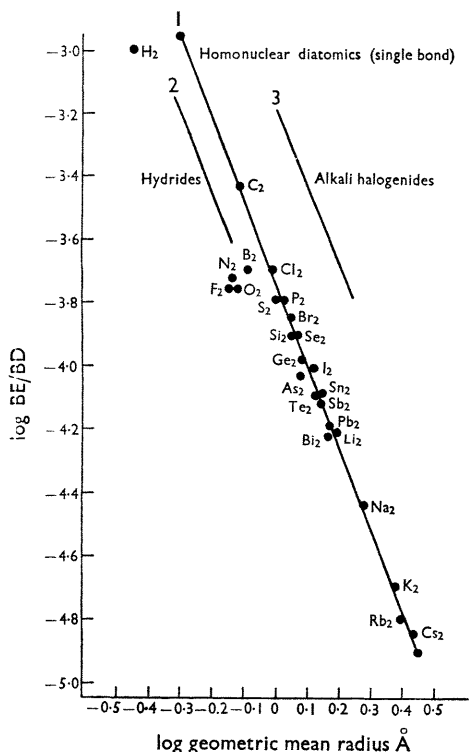


FIGURE. Log-log plot of BE/BD versus geometric mean radius of bonded atoms.

increases in the periodic group (except in group 7 where the value of fluorine is smaller than that of chlorine). The inverse relation between BE/BD and atom radius may be explained by the concepts that the more numerous non-bonding electrons in heavier atoms contribute to the repulsion, and that the overlap of the charge clouds of the bonding electrons in large atoms is less effective.

The n values [determined by equation (2) with BE, BD, r , k , and s] for many of the homonuclear diatomics are close

to unity, while the n values for H_2 , B_2 , N_2 , O_2 , and F_2 are considerably smaller as shown in Table 1.

It is evident in Figure 1 that by shifting the log BE/BD co-ordinate for lines 2 and 3, that these can be made to coincide with line 1. Hence it is possible to retain the constant value of s (slope) in equation (2). In addition a constant value of k is retained. This is done by incorporating the proportionality constant for line 2 or 3 (whichever one may apply) in the n value (determined by equation 2 with BE, BD, r , k , and s) of a heteronuclear bond. Thus the n value of the latter is a comparison with the "ideal" homonuclear single bond (n value of unity).

TABLE 1

n Coefficients of diatomic molecules†

H_2	0.392	HF	1.11	CF	1.49
B_2	0.61	HCl	0.816	CCl	1.18
N_2	0.47	HBr	0.755	CBr	0.82
O_2	0.44	HI	0.66	BF	2.23
F_2	0.41	NaH	0.61	SiF	2.64
Cl ₂	1.05	KH	0.60	PF	2.11
Br ₂	1.06	OH	0.732	AsF	2.04
I ₂	1.06	HO-H	0.835	LiF	3.86
Na ₂	1.0	SH	0.656	LiI	3.25
C ₂	1.0	HS-H	0.755	CsF	4.56
				CsI	4.45

† Calculated by equation (2) from experimental data.

The n values of the heteronuclear bonds are smallest for the hydrides, intermediate for the molecular halides, and largest for the ionic molecules as shown in Table 1.

Bond Energy Equation: Equation (3) is derived from equation (2) and relates the enthalpy change (ΔH) for a reaction to changes (between products and reactants) in three terms: (a) bond distance (ΔBD), (b) geometric mean

TABLE 2

Heats of gas-phase reactions at 25°

	kcal./mole	
	ΔH (exp.)	ΔH (calc.)†
$H_2 + Cl_2 = 2HCl$	-44.12	-43.5
$H_2 + Br_2 = 2HBr$	-17.32	-14.1
$H_2 + I_2 = 2HI$	+12.4	+34
$Na_2 + H_2 = 2NaH$	+26.5	+30
$H_2 + K_2 = 2KH$	+29.4	+23.2
$H_2 + \frac{1}{2}O_2 = H_2O$	-57.8	-57.8
$H_2 + \frac{1}{2}S_2 = H_2S$	-4.8	-5.4
$\frac{1}{2}S_2 + O_2 = SO_2$	-70.96	-71
$\frac{1}{2}F_2 + \frac{1}{2}I_2 = FI$	-13.9	-14.6
$\frac{1}{2}Cl_2 + \frac{1}{2}Br_2 = ClBr$	+3.5	+12.8
$\frac{1}{2}Cl_2 + \frac{1}{2}I_2 = ClI$	+4.1	+5.8
$CS_2 + 2H_2O = CO_2 + 2H_2S$	-16	-16
$CS + PbO = PbS + CO$	-71	-80
$KF + CsI = KI + CsF$	+3.6	+3.4
$LiF + CsI = LiI + CsF$	+17	+16.8

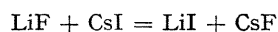
† Calculated by equation (3) from experimental data.

radius of bonded atoms (Δr), and (c) bonding coefficient (Δn).

$$\Delta H = k\Delta n \times \Delta BD \times \Delta r^s / 6.946 \times 10^{-14} \quad (3)$$

where k and s have values as in equation (2) and 1 kcal./mole = 6.946×10^{-14} erg/molecule.

The Δ values in equation (3) are calculated as shown for the following reaction:



$$\Delta n = n(\text{LiI}) + n(\text{CsF}) - n(\text{LiF}) - n(\text{CsI})$$

$$\Delta \text{BD} = [\text{BD}(\text{LiI}) \cdot \text{BD}(\text{CsF})]^{\frac{1}{2}} - [\text{BD}(\text{LiF}) \cdot \text{BD}(\text{CsI})]^{\frac{1}{2}}$$

$$\Delta r = \frac{1}{2} \{ [\gamma(\text{LiI}) \cdot r(\text{CsI})]^{\frac{1}{2}} - [\gamma(\text{CsF}) \cdot r(\text{CsI})]^{\frac{1}{2}} + [\gamma(\text{LiI}) \cdot r(\text{LiF})]^{\frac{1}{2}} + [\gamma(\text{CsF}) \cdot r(\text{LiF})]^{\frac{1}{2}} \}$$

Table 2 shows a number of experimental heats of reaction (ΔH) and the heats calculated by equation (3). The latter ΔH values predict the correct sign for the enthalpy change and are in line with the experimental ΔH values in most of the reactions, which involve either covalent compounds or ionic ones.

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¹ R. G. Pearson, *Chem. Comm.*, 1968, 65.

² R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 643.

³ J. Elson, *J. Chem. Educ.*, 1968, **45**, 564.