

A Bond Energy Relation for Multiple Bonds

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A Bond Energy Relation for Multiple Bonds

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MAKING use of the notion of preserved tetrahedral angles and circularly bent single bonds constituting multiple bonds,¹ the following energy relation is obtained, viz.,

$$E = E_1(1+p) \left[1 - c \left(\frac{R_1}{R} \right)^2 \left(\frac{R_1 - R}{R_1} \right) \right] \quad (1)$$

where p is the bond order and equal to 0, 1, 2 for single, double, and triple bonds, respectively; E_1 is the single bond energy, R_1 is the single bond distance, and c is a constant.

Using Pauling's² values for the multiple bond energies of the CC and CN bonds, the observed and calculated values of the double bond energies and of the CC bond energy in benzene are compared.

	Single bond	Double bond	Triple bond	Benzene
CC cal. (Obs.)†	58.6	100	123	86
CC cal. (calc. from (1))	58.6*	99	123*	87.2*
R in Å	1.55	1.33	1.21	1.39
CN cal. (Obs.)	48.6	94	144	
CN cal. (calc. from (1))	48.6*	96.5	144*	
R in Å	1.47	1.27	1.15	

† Bond energies and bond distances from Pauling, reference 2.

* These more reliable values were used to calculate the constant of Eq. (1).

The bond order for benzene was taken as $p = 2/3$; the calculated bond order from Eq. (1) and the value 86 cal. is 0.64 which is intermediate to the values .667 and .623 given by Coulson, Proc. Roy. Soc. 169, 413 (1939) and Penney, Proc. Roy. Soc. A158, 306 (1937), respectively.

Equation (1) which involves two constants reproduces the data to within ± 2.5 percent in the worst cases and with better accuracy in the single to double bond range. Until more reliable bond energies are known it is probably just as accurate and certainly more expedient to use this expression rather than one involving more constants.³

Where a bond distance or a bond order is known the order or distance may be calculated from the relation $R = R_1[2/3 + 1/3(1/3)^{p/2}]$ for first row atoms¹ and the corresponding bond energies evaluated from Eq. (1).

¹ H. J. Bernstein, J. Chem. Phys. 15, 284 (1947), see appendix.

² L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939).

³ J. L. Kavanau, J. Chem. Phys. 15, 77 (1947). In this paper a three constant expression for the bond energy as a function of bond order is

given in the form $E = E_0 \left[1 - \left(1 - \frac{1+p}{A} \right)^B \right]$ where E_0 , A , B are constants and p is the bond order.

Errata: "Vibrational Frequencies of the Isotopic Water Molecules; Equilibria with the Isotopic Hydrogens"

[J. Chem. Phys. 11, 101 (1943)]

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IN applying their elegantly simplified method¹ for calculating isotopic equilibria to the water-hydrogen equilibria, Drs. Goepfert-Mayer and Bigeleisen discovered certain discrepancies in the above paper. The errors were arithmetical.

Table XI, *Frequencies and anharmonicities of hydrogen molecules*:

Multiply all anharmonicities by two.

Table XII, H_0^0 values:

Change values for hydrogen molecules to 6208, 5389, 4411, 4030, 3610, 5084 in the order given previously.

Table XIII, $(F - H_0^0)/T$ values:

HDO, DTO, T₂O up by 0.05, 0.11, and 0.29, respectively, at all temperatures (e.g., for HDO at 25°C change -39.80 to -39.75).

Table XIV, *Moments of inertia*:

Change value for HDO from 16.6 to 16.2.

These changes cause up to 5 percent correction on three of the nine equilibrium constants. The corrected values are:

TABLE XV. Equilibrium constants.

	Equilibrium	20°C	100°C	200°C	300°C	400°C	500°C
(5)	$\frac{(HDO)}{(H_2O)(D_2O)}$	3.89	3.96	3.97	3.97	3.97	4.00
(8)	$\frac{(HTO)^2}{(H_2O)(T_2O)}$	3.44	3.63	3.83	3.86	3.95	4.00
(9)	$\frac{(DTO)^2}{(D_2O)(T_2O)}$	3.59	3.69	3.74	3.78	3.83	3.86

The equilibria (1) and (2), (3), (4), (6), and (7) for the partition of the hydrogen isotopes between the water and hydrogen molecules are unchanged.

¹ J. Bigeleisen and M. G. Mayer, J. Chem. Phys. 15, 261 (1947).