A New Relation between Dissociation Energy and Molecular Constants of Diatomic Molecules

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An accurate relation, connecting dissociation energy D_0, force constant for infinitesimal amplitude k_e and internuclear equilibrium distance r_e has been deduced from Varshni and Shukla's potential function. It is of the form $D_0 = k_e (A + B r_e^2 + C r_e^4)$, where A, B and C are constants and are the same for groups of similar diatomic molecules. The values of D_0 estimated by this relation are in better agreement with the observed ones than those estimated by Somayajulu, and Tandon et al.

Introduction

The dissociation energies obtained by atomic fluorescence, thermochemical, and spectroscopic methods disagree [1]. To resolve these controversies, various potential functions [2–4] and empirical or semiempirical relations [5–7] connecting the various molecular constants of diatomic molecules, have been suggested. Somayajulu calculated [7] the dissociation energy of diatomic molecules using the relation $(k_e r_e)/D_0 = S$, where k_e is the force constant for infinitesimal amplitude, r_e the internuclear equilibrium distance, D_0 the dissociation energy, and S a constant for a sequence. The results obtained with this relation did not agree with those estimated by Rittner [8], Katti et al. [9] and Varshni [3]. Recently, a relation connecting the dissociation energy with the molecular constants of diatomic molecules in the Sutherland potential function [10], has been given by Tandon and Tandon [11].

In the present communication we suggest a relation between the dissociation energy and the molecular constants for diatomic molecules in the Varshni and Shukla potential function [4]. The new relation yields better results than those estimated by earlier workers [2, 3, 8, 10, 11].

Theoretical

A satisfactory potential function must obey the following conditions:

$$U_{(r_e)} - U_{(\infty)} = -D_0\,,$$

$$(\mathrm{d}U/\mathrm{d}r)_{r=r_e} = 0\,,$$

and

$$(\mathrm{d}^2U/\mathrm{d}r^2)_{r=r_e} = k_e\,. \qquad (1)$$

When these requirements are applied to the Varshni and Shukla's potential function [4]

$$U = -e^2/r + P\,e^{-br^2}\,, \qquad (2)$$

we get

$$D_0/k_e = (2\,b\,r_e^2 - 1)/2\,b\,(2\,b\,r_e^2 - 3)\,, \qquad (3)$$

where P and b are constants for a particular molecular group.

On rearranging (3), we can write

$$D_0 = k_e\,(A + B\,r_e^2 + C\,r_e^4)\,, \qquad (4)$$

where A, B and C are constants for a molecular group and may be assumed to be characteristic for a group of similar molecules. The relation (4) has been applied to about one hundred and fifty diatomic molecules of various groups in the present report.

Data and Procedure

The values of the internuclear equilibrium distance (r_e) are expressed in Å and are taken from the "Tables of interatomic distances and configuration of molecules and ions" (The Chemical Society, London, England 1958), except where indicated. The r_e values in paranthesis are roughly estimated ones.

The values of the force constant for infinitesimal amplitude (k_e), expressed in $m\,d/A$, have been cal-

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Table I. Hydrides of 1 a group. $A=0.8514$, $B=0.7036$, and $C=-0.04269$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated			error %		
				(S)	(T)	(M)	(S)	(T)	(M)
LiH	1.595	1.026	2.429 [a], 2.5 (H)	2.429	2.427	2.428	0	−0.08	0
NaH	1.887	0.781	2.05±0.2 (G), 2.2 (H)	2.187	2.140	2.2	0	0	0
KH	2.244	0.5614	1.86±0.15 (G), 1.86 (H)	1.868	1.859	1.86	0	0	0
RbH	2.376	0.5148	1.70±0.2 (G), 1.9 (H)	1.809	1.837	1.783	0	0	0
CsH	2.494	0.467	1.8 ±0.3 (G), 1.9 (H)	1.728	1.800	1.67	0	0	0
Average error %							0	0.016	0

[a] Ref. 15.

Table II. Hydrides of 1 b group $A=-1.8186$, $B=2.3307$, and $C=-0.4241$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated			error %		
				(S)	(T)	(M)	(S)	(T)	(M)
CuH	1.4631	2.2	2.7±0.3 (G) <2.89 (H)	2.77	2.797	2.797	0	0	0
AgH	1.6174	1.817	2.3±0.1 (G), 2.5 (H)	2.53	2.502	2.502	+1.2	+0.08	0
AuH	0.5237	3.138	4.1 [a], 3.1 (H)	4.14	4.10	4.10	+0.5	0	0
Avervage error %							0.57	0.03	0

[a] The upper state is assumed to be $'\Sigma+$, then it correlates with normal products and gives $D^0=4.1$ eV.

Table III. Hydrides of 2 a group. $A=0.791$, $B=0.02696$, and $C=0.05261$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated			error %		
				(S)	(T)	(M)	(S)	(T)	(M)
BeH	1.343	2.263	2.3±0.3 (G), 2.2 (H)	2.12	2.041	2.279	+4.6	0	0
MgH	1.731	1.275	2.0±0.5 (G), ≦2.49 (H)	1.97	1.704	1.67	0	0	0
CaH	2.002	0.971	1.7 (G), ≦1.70 (H)	1.75	1.70	1.704	+3.0	0	+0.23
SrH	2.1456	0.854	1.65±1 (G), ≦1.68 (H)	1.64	1.702	1.733	0	0	0
BaH	2.232	0.809	1.8 ±0.1 (G), ≦1.82 (H)	1.61	1.745	1.752	−5.3	0	0
Average error %							2.6	0	0.04

Table IV. Hydrides of 3 b group. $A=0.3978$, $B=0.5932$, and $B=-0.04617$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated			error %		
				(S)	(T)	(M)	(S)	(T)	(M)
BH	1.233	2.789	3.0±0.4 (G), <3.51 (H)	3.8	3.4	3.327	11.8	0	0
AlH	1.646	1.62	2.9±0.2 (G), <3.06 (H)	2.72	2.7	2.70	0	0	0
GaH	1.72	1.42 [a]	unknown	2.49	2.088	2.483	—	—	—
InH	1.838	1.28	2.5±0,1 (G), ≦2.48 (H)	2.4	2.4	2.4	0	0	0
TlH	1.87	1.143	≦2.18 (H)	2.18	2.18	2.18	0	0	0
Average error %							3.0	0	0

[a] Ref. 14.

Table V. Hydrides of 4 b group. $A=-0.7194$, $B=1.522$, and $C=-0.2637$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated			error %		
				(S)	(T)	(M)	(S)	(T)	(M)
CH	1.12	4.484	3.47 (G) (H)	3.86	3.47	3.473	+11.2	0	+0.08
SiH	1.521 [a]	2.39 [a]	3.19±0.25 [a]	2.79	2.99	3.324	−5.1	0	0
GeH	(1.66) [b]	1.87	unknown	2.28	2.56	4.567	—	—	—
	(1.591) [c]				2.46				
SnH	1.785	(1.469) [d]	2.13 [e], <3.2 (H)	2.06	2.13	2.136	−3.3	0	0
PbH	1.839	1.445	≦2.04 (H)	2.04	2.14	2.039	0	+4.9	0
Average error %							4.8	1.2	0.01

[a] Ref. 16; [b] Ref. 14; [c] Ref. 7; [d] Ref. 6; [e] assuming predissociation at 3.2 eV occurs into $Sn(^1D)+H(^2S)$.

Table VI. Hydrides of 5 b group. $A=0.1125$, $B=0.4923$ and $C=-0.02429$

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated			error %		
				(S)	(T)	(M)	(S)	(T)	(M)
NH	1.038	6.02	2.7±0.5 (G), 3.8 (H)	4.45	3.70	3.701	+6.0	0	0
PH	1.43	3.26	unknown	3.32	3.63	3.318	—	—	—
AsH	1.58 [a]	2.43 [a]	unknown	2.61	3.15	2.892	—	—	—
SbH	1.76 [a]	2.05 [a]	unknown	2.5	3.10	2.878	—	—	—
BiH	1.809	1.708	2.5±0.3 (G), 2.7 (H)	2.2	2.67	2.50	0	0	0
Average error %							3.0	0	0

[a] Ref. 14.

Table VII. Hydrides of 6 b group. A=0.2061; $B=0.4179, A=0.2061$; $B=0.4179$, and C=−0.0406.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated			error %		
				(S)	(T)	(M)	(S)	(T)	(M)
OH	0.971	7.791	0.393±0.03 [a]	4.519	4.395	4.395	+2.6	0	0
SH	1.34 [b]	4.193 [c]	$4.02 > D_0^0 > 2.88$ [b]	3.59	3.300	3.461	0	0	0
SeH	1.50 [d]	3.18 [a]	unknown	2.99	2.934	2.992	—	—	—
TeH	1.69 [d]	2.53 [c]	unknown	2.70	2.820	2.702	—	—	—
PeH	1.77 [d]	2.1 [d]	unknown	—	2.53	2.344	—	—	—
Average error %							1.3	0	0

[a] Ref. 17; [b] Ref. 18; [c] Ref. 19; [d] Ref. 14.

Table VIII. Hydrides of 7 b group. $A=0.3235$, $B=0.4819$, and $C=-0.0938$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated			error %		
				(S)	(T)	(M)	(S)	(T)	(M)
FH	0.9171	9.655	5.8±0.1 (G), ≦6.40 (H)	5.713	5.81	6.4	0	0	0
ClH	1.275	5.157	4.431 (G), 4.430 (H)	4.242	4.43	4.429	−4.2	0	0
BrH	1.4138	4.116	3.754 (H)	3.754	3.756	3.753	0	+0.05	0
IH	1.604	3.141	3.06±0.01 (G), 3.056 (H)	3.251	2.971	2.960	+5.9	−2.6	−2.9
AtH	1.68 [a]	2.7 [a]	unknown	—	2.539	2.528	—	—	—
Average error %							2.5	0.66	0.72

[a] Ref. 14.

Table IX. 1 a−1 a group. $A=5.0192$, $B=-0.2493$, and $C=0.02101$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated (S)	D_0 calculated (T)	D_0 calculated (M)	error % (S)	error % (T)	error % (M)
LiLi	2.672	0.2552	1.10±0.05 (G), 1.03 (H)	0.98	1.059	1.144	−4.9	0	0
NaNa	3.078	0.1717	0.75±0.03 (G), 0.73 (H)	0.76	0.800	0.7799	0	+2.6	0
KK	3.923	0.0985	0.56±0.04 [a], 0.514 (H)	0.555	0.567	0.6066	0	0	0
RbRb	(4.18) [b]	0.082	0.47±0.05 (G), 0.49 (H)	0.493	0.490	0.5803	0	0	0
CsCs	(4.50) [c]	0.06901	0.45±0.04 (G), 0.45 (H)	0.453	0.449	0.5925	0	0	0
KLi	(3.29) [c]	(0.1487) [d]	unknown	—	0.734	0.7109	—	—	—
RbLi	(3.53) [c]	(0.1294) [d]	unknown	—	0.679	0.6694	—	—	—
CsLi	(3.83) [c]	(0.1094) [d]	unknown	—	0.616	0.6433	—	—	—
KNa	(0.1296) [c]	0.1296	0.62±0.03 (G)	0.65	0.657	0.6499	0	+1.0	0
CsNa	(3.75) [c]	0.108	unknown	0.58	0.597	0.6119	—	—	—
Average error %							0.8	0.6	0

[a] Ref. 20; [b] Ref. 21; [c] Ref. 13; [d] Ref. 6.

Table X. 5 b−5 b group. $A=0.0701$, $B=0.3279$, and $C=-0.02755$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated (S)	D_0 calculated (T)	D_0 calculated (M)	error % (S)	error % (T)	error % (M)
NN	1.0976	22.962	9.756 (H)	11.0	9.753	9.8534	+21.0	−0.3	+0.95
PP	1.8943	5.556	5.03 or 4.12 (H)	4.93	4.938	4.9559	−2.0	−1.8	−1.47
AsAs	2.08	4.069	≦3.96 (H)	3.96	3.96	3.9595	0	0	0
BiBi	2.68	1.836	2.2 or 1.7 (H)	2.3	2.172	1.8433	+4.5	−1.3	+8.4
PN	1.491	10.16	7.1±0.05 [a], (6.3) (H)	7.09	6.86	6.7350	0	−2.5	+6.9
AsN	(1.59) [b]	7.926	5.0±1.0 (G)	5.9	5.795	5.7304	0	0	0
SbN	(1.79) [b]	6.564	5.5 [c]	5.5	5.5	5.5	0	0	0
SbSb	(2.58) [b]	2.193	3.0±2.0 (G), (3.0) (H)	2.65	2.531	2.2633	0	0	0
Average error %							3.43	0.74	2.2

[a] Ref. 22; [b] Ref. 7; [c] Assuming the limit of the upper state to correlate with Sb(^2D) + (^4S).

Table XI. 1 a−7 b group. $A=0.9727$, $B=0.7039$, and $C=-0.03617$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated (S)	D_0 calculated (T)	D_0 calculated (M)	error % (S)	error % (T)	error % (M)
LiF	(1.59) [a]	(2.36) [b]	5.95±0.2 (G), ≦6.6 (H)	5.95	5.95	5.9497	0	0	0
LiCl	(1.97) [c]	1.499 [d]	5.0 ±0.3 (G)	4.8	4.72	4.7363	0	0	0
LiBr	2.17 [e]	1.248 [d]	4.35±0.3 (G)	4.3	4.32	4.3495	0	0	0
LiI	2.392 [e]	0.9727 [f]	3.5 ±0.2 (G)	3.69	3.70	3.7119	0	0	+0.32
NaF	(2.0) [e]	1.465 [b]	4.65±0.2 (G), ≦5.3 (H)	4.65	4.68	4.702	0	0	0
NaCl	2.3606 [e]	1.1 [d]	4.24±0.05 (G)	4.15	4.131	4.1492	+1.0	−1.4	−0.94
NaBr	2.502 [e]	0.959 [d]	3.80±0.1 (G), 3.85 (H)	3.81	3.804	3.7992	0	0	0
NaI	2.7115	0.7631 [d]	3.07±0.1 (G), 3.16 (H)	3.28	3.18	3.1995	+3.5	+0.3	+0.93
KF	2.55 [g]	1205 [a] 1.24 [a]	5.0 ±0.25 (G)	5.0	4.943 5.087	4.9854	0	0	0
KCl	2.667 [e]	1.02 [a]	4.4 ±0.05 (G), 4.42 (H)	4.32	4.30	4.2313	−0.7	−1.1	−2.7
KBr	2.821 [e]	0.83 [a]	3.94±0.05 (G), 3.96 (H)	3.72	3.68	3.5554	−4.4	−5.7	−8.8
KI	3.048 [e]	1.704 [a]	3.32±0.05 (G), 3.33 (H)	3.39	3.35	3.0407	+0.6	0	−5.1
RbF	(2.31) [e]	1.39 [a]	5.35±0.2 (G)	5.1	5.113	5.1413	−1.0	−0.7	0
RbCl	2.787 [h]	1.076	4.50±0.2 (G), >3.96 (H)	4.76	4.718	4.5816	+1.3	+0.4	0
RbBr	2.945 [e]	0.788 [a]	4.0 ±0.25 (G)	3.74	3.63	3.4332	−0.02	−3.2	−8.4
RbI	3.177 [e]	0.633 [a]	3.35±0.1 (G), 3.29 (H)	3.33	3.122	2.7804	0	−3.9	−14.4
CsF	2.345 [e]	1.451	5.5 ±0.2 (G)	5.4	5.38	5.4408	0	0	0
CsCl	2.906 [e]	0.95 [a]	4.6 ±0.2 (G)	4.38	4.4	4.1208	−0.5	0	−6.3
CsBr	3.072 [e]	0.86 [a]	4.1 ±0.25 (G), ≧3.9 (H)	4.19	4.12	3.7766	0	0	−1.9
CsI	3.315 [e]	(0.665) [b]	3.4 ±0.1 (G), 3.3 (H)	3.5	3.40	2.8861	0	0	−12.5
Average error %							0.65	0.83	3.1

[a] Ref. 23; [b] Ref. 7; [c] Ref. 8; [d] Ref. 24; [e] Ref. 25; [f] Ref. 26; [g] Ref. 27; [h] Ref. 28.

Table XII. 1 b−7 b group *. $A=1.7356$, $B=-0.4824$, and $C=0.0684$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated (T)	D_0 calculated (M)	error % (T)	error % (M)
CuF	1.743	3.32	(3.0) (H)	3.0	3.0	0	0
CuCl	(2.24) [a]	2.301	(3.0) (H)	2.4	2.4	−25.0	−25.0
CuBr	(2.42) [a]	2.035	2.7±0.5 (G), (2.5) (H)	2.57	2.57	0	0
CuI	2.40 [b]	1.738	(3.0) (H), 1.9±0.2 (G)	2.14	2.145	+2.0	+2.1
	(2.63) [a]			2.91		−3.0	
AgF	1.998 [c]	(2.619) [d]	unknown	2.26	2.3667	—	—
AgCl	(2.42) [a]	1.832	3.1 (H)	2.31	2.3167	−25.5	−25.2
AgBr	(2.59) [a]	1.637	2.6 (H)	2.60	2.6	0	0
AgI	(2.81) [a]	1.453	2.98 (H)	3.1	3.20	+4.0	+7.5
AuCl	(2.48) [a]	2.564	3.5 (H), 2.8±0.5 (G)	3.50	3.5	0	0
Average error %						6.6	7.4

* D_0 values have not been calculated by Somayajulu (Ref. 7).
[a] Ref. 13; [b] Ref. 21; [c] Ref. 6; [d] Ref. 30, 31.

Table XIII. 2 b−7 b group *. $A=0.7142$, $B=0.04384$, and $C=-0.01078$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated (T)	D_0 calculated (M)	error % (T)	error % (M)
ZnF	(1.59) [a]	(3.441) [b]	unknown	2.496	2.602	—	—
ZnCl	(1.945) [b]	2.046	2.5±1.0 (G)	1.523	1.4852	0	0
ZnBr	(2.136) [b]	(1.661) [c]	unknown	1.165	1.1457	—	—
ZnI	(2.30) [b]	1.25	1.8±0.6 (G)	0.800	0.8056	−33.3	32.8
CdF	(1.723) [b]	(2.74) [b]	unknown	2.045	2.053	—	—
CdCl	(2.094) [b]	1.716	2.2±1.0 (G)	1.225	1.1998	0	0
HgF	(1.74) [a]	2.406	1.8 (H), 1.4±0.5 (G)	1.798	1.799	0	0
HgCl	(2.23) [b]	1.502	1.0 (H)	1.0	0.9998	0	0
HgBr	2.44 [a]	1.180	0.7 (H)	0.7	0.7	0	0
HgI	2.55 [a]	0.7223	0.30±0.05 (G), 0.36 (H)	0.35	0.39	0	+9.0
Average error %						4.2	5.9

* D_0 values have not been calculated by Somayajulu (Ref. 7).
[a] Ref. 21; [b] Ref. 6; [c] Ref. 30, 31.

Table XIV. 2 a−7 b group *. $A=-0.1965$, $B=0.4572$, and $C=-0.01594$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated (T)	D_0 calculated (M)	error % (T)	error % (M)
BeF	1.361	5.768	4.0±1.0 (G)	3.0	3.4354	0	0
BeCl	(1.7) [a]	3.025	3.0 (G)	3.0	3.00	0	0
BeBr	(2.05) [b]	(2.145) [c]	unknown	4.09	3.09	—	—
BeI	(2.33) [b]	(2.612)	unknown	4.69	4.74	—	—
MgF	(1.752) [a]	3.216	3.2±0.7 (G)	3.37	3.39	0	0
MgCl	(2.29) [b]	1.815	3.2 (H)	3.2	3.148	0	0
MgBr	(2.44) [b]	1.514	≦3.35 (H)	2.92	2.96	0	0
MgI	(2.72) [b]	(1.17) [a]	unknown	2.65	2.73	—	—
CaF	(2.02) [a]	2.615	3.15 (H)	3.67	3.67	+16.5	+16.5
CaCl	1.86	1.504	≦2.76 (H)	1.76	1.796	0	0
CaBr	(2.70) [b]	1.274	(2.9) (H)	2.9	2.916	0	+0.54
CaI	(2.98) [b]	1.051	(2.8) (H)	2.7	2.738	−3.6	−2.18
SrF	(2.13) [b]	2.30	2.7±1.0 (G), (3.5) (H)	3.55	3.563	0	0
SrCl	(2.68) [b]	1.345	(3.0) (H), 2.5±1.0 (G)	3.0	3.045	0	0
SrBr	(2.83) [b]	1.146	(2.8) (H)	2.8	2.798	0	0
SrI	(3.11) [b]	0.9231	2.2 (H)	2.5	2.523	+13.6	+14.6
BaF	(2.22) [b]	2.161	(3.8) (H)	3.62	3.607	−4.7	−5.0
BaCl	(2.77) [b]	(1.162) [d]	(2.7) (H)	2.7	2.756	0	+2.1
BaBr	(2.92) [b]	1.109	(2.8) (H)	2.8	2.819	0	0.68
BaI	(3.20) [b]	(0.874) [c]	unknown	2.44	2.458	—	—
Average error %						2.4	2.6

* D_0 values have not been calculated by Somayajulu (Ref. 7).
[a] Ref. 6; [b] Ref. 29; [c] Ref. 30, 31; [d] Ref. 11.

Table XV. 4 b−7 b group *. $A=-0.7087$, $B=0.8361$, and $C=-0.06947$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated (T)	D_0 calculated (M)	error % (T)	error % (M)
CF	1.271 [a]	7.406 [a]	unknown	2.707	3.4119	—	—
CCl	1.73 [b]	3.766	unknown	4.440	4.4114	—	—
CBr	(1.901) [c]	(2.925) [c]	unknown	5.567	4.111	—	—
CI	(2.175) [c]	(2.175) [c]	unknown	3.680	3.6798	—	—
SiF	(1.603) [c]	4.892	4.8 (H)	4.8	4.8	0	0
SiCl	2.00 [b]	2.624	4.0 (H)	4.0	4.0	0	0
SiBr	2.15 [b]	2.213	3.7 (H)	3.7	3.7	0	0
SiI	(2.459) [c]	(1.658) [c]	unknown	3.14	2.9958	—	—
GeF	(1.670) [c]	3.925	(4.9) (H)	4.3	4.25	−10.2	−13.2
GeCl	(2.08) [b]	2.323	(4.0) (H)	3.74	3.736	−6.5	−6.6
GeBr	(2.29) [b]	1.971	(3.0) (H)	3.5	3.47	+16.6	+15.6
GeI	(2.558) [c]	1.523 [c]	unknown	2.94	2.72	—	—
SnF	(1.82) [b]	3.278	3.9 (H)	4.28	4.47	+9.7	+14.6
SnCl	2.32 [b]	1.976	3.6 (H), 3.2±0.5 (G)	3.6	3.515	0	0
SnBr	2.44	1.726	(3.0) (H)	3.247	3.11	+8.2	+3.6
SnI	(2.682) [c]	(1.373) [c]	unknown	2.7	2.39	—	—
PbF	(2.01) [b]	2.630	≤4.5, 3.47 (H)	4.04	4.037	0	0
PbCl	2.43 [b]	1.627	2.6±0.4 (G), 3.1 (H)	3.05	2.938	−1.7	0
PbBr	2.60 [b]	1.449	2.9 (H), 2.2±0.4 (G)	2.82	2.562	−2.7	0
PbI	(2.86) [c]	1.194	2.8 (H)	2.4	1.769	−14.3	−36
Average error %						5.4	6.8

* D_0 values have not been calculated by Somayajulu (Ref. 7).
[a] Ref. 32; [b] Ref. 21; [c] Ref. 6.

Table XVI. 7 b−7 b group. $A=0.1319$, $B=0.1968$, and $C=-0.0099$.

Molecule	r_e	k_e	D_0^0 Observed	D_0 calculated (S)	D_0 calculated (T)	D_0 calculated (M)	error % (S)	error % (T)	error % (M)
FF	1.418	4.453	2.17±0.2 [a], <2.75 (H)	2.313	2.046	2.1699	0	0	0
ClCl	1.988	3.286	2.475 (H), (G)	2.393	2.47	2.4809	−3.3	+0.1	0
BrBr	2.284	2.458	1.9710 (H)	2.056	2.041	2.1854	+4.3	+3.5	+10.8
II	2.667	1.721	1.5417 (H)	1.681	1.457	1.7741	+9.0	−5.5	+15.0
FCl	1.628	4.483 [b]	2.616 or 2.557 (H)	2.719	2.60	2.6176	+4.0	0.6	0
FBr	1.755	4.095 [c]	2.60 or 2.19 (H)	2.637	2.668	2.6375	+2.4	2.6	+1.4
FI	(2.05) [d]	3.64	2.87 (G)	2.73	2.81	2.8541	−4.9	−2.1	−0.55
BrCl	2.138	2.717	2.26 (H)	2.128	2.173	2.2404	−5.8	+3.8	−0.86
ICl	2.321	(2.383) [d]	2.152 (H)	2.026	1.993	2.1597	−5.8	−7.4	0
Average error %							4.27	3.2	3.32

[a] Ref. 33; [b] Ref. 34; [c] Ref. 35; [d] Ref. 7.

culated from molecular data given by Herzberg [12] unless stated otherwise.

The observed values of the dissociation energy D_0^0 referred to 0 K, are expressed in electron volts. The values which are followed by H in paranthesis are taken from Herzberg's molecular data [12]. Similarly G in paranthesis refers to data taken from Gaydon's book [1] or referred by Herzberg as Gaydon's data. D_0^0 values in paranthesis are uncertain ones.

To estimate the values of D_0, the values of the constants A, B and C in Eq. (4) for a molecular group have been calculated using D_0^0, r_e and k_e values for three molecules for which these are known accurately. Having determined A, B and C, mere substitution of k_e and r_e values in Eq. (4) gives D_0 values for other molecules of the group.

Discussion

It is evident from Eq. (4) that the r_e values must be known very accurately, since higher powers of r_e appear in the equation. While accurate k_e values are available for a large number of molecules, ac-

Table XVII. Average percentage errors.

Table No.	Molecular group	S	T	M
I	1 a–H	0	0.016	0
II	1 b–H	0.57	0.03	0
III	2 a–H	2.6	0	0.04
IV	3 b–H	3.0	0	0
V	4 b–H	4.8	1.2	0.01
VI	5 b–H	3.0	0	0
VII	6 b–H	1.3	0	0
VIII	7 b–H	2.5	0.66	0.72
IX	1 a–1 a	0.8	0.6	0
X	5 b–5 b	3.43	0.74	2.2
XI	1 a–7 b	0.65	0.83	3.1
XII	1 b–7 b	—	6.6	7.4
XIII	2 a–7 b	—	2.4	2.6
XIV	2 b–7 b	—	4.2	5.9
XV	4 b–7 b	—	5.4	6.8
XVI	7 b–7 b	4.27	3.2	3.32

curate r_e values are available only for few ones. The r_e values given in paranthesis have been estimated by methods such as Pauling's additivity of atomic radii [5], Schomakev-Stevenson equation [13], Sheline method [14], Varshni's relation [3] or Somayajulu's relation [7]. These estimated values of r_e may produce a large deviation between the observed and the estimated D_0 values. Deviations between the observed and the estimated D_0 values may also be expected in cases where the observed D_0 values are themselves uncertain.

To establish the applicability of the proposed relation, D_0 values along with the percentage errors and observed values estimated by the proposed relation, Somayajulu's relation and Tandon's relation, indicated by M, S & T respectively, have been collected in Tables I – XVI. The percentage errors of different molecular groups have been tabulated in Table XVII.

A close study of these tables reveals that the values of D_0 estimated by this relation are in better agreement with observed ones than those estimated by others [7, 11]. In most of the hydrides under study the percentage error for a molecular group is almost equal to zero (Tables I to VIII), while in halides and other diatomic molecules it lies between 2.6 to 7.4 and 0 – 2.2 respectively. These results establish the validity of the proposed relation for diatomic molecules. The exceptional divergence in a few cases may be attributed to uncertain values of r_e and D_0^0.

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