MASTER

LBL-9690
CONF-8001144--1

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED BY TIC SEP 10 1980

Presented at the Faraday Symposia of the Chemical Society No. 14, "Diatomic Metals and Metallic Clusters", Manchester, England, January 1980

MODELS FOR CALCULATION OF DISSOCIATION ENERGIES OF HOMONUCLEAR DIATOMIC MOLECULES

Leo Brewer and John S. Winn

August 1979

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

LBL-9690

Models for Calculation of Dissociation Energies of Homonuclear Diatomic Molecules

Leo Brewer and John S. Winn

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and the Department of Chemistry, University of California, Berkeley, CA 94720, U.S.A.

Address for Proofs:

Professor Leo Brewer
Department of Chemistry
University of California
Berkeley, CA 94720 U.S.A.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

There are no illustrations.

Short title:
Dissociation Energy Model

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Abstract

The variation of known dissociation energies of the transition metal diatomics across the Periodic Table is rather irregular in a manner similar to the irregular variation of the enthalpies of sublimation of the bulk metals. This has suggested that the valence-bond model used for bulk metallic systems might be applicable to the gaseous diatomic molecules as well as to the various clusters intermediate between the bulk and the diatomic molecules. The available dissociation energies were converted to valence-state bonding energies considering various degrees of promotion to optimize the bonding. It was found that the model used for the bulk metals was applicable to the diatomic molecules. The degree of promotion of electrons to increase the number of bonding electrons is smaller than for the bulk, but the trends in bonding energy parallel the behavior found for the bulk metals. Thus using the established trends in bonding energies for the bulk elements, it was possible to calculate all unknown

dissociation energies to provide a complete table of dissociation energies for all M_2 molecules from H_2 to Lr_2. The details of the calculations and final values will be presented.

For solids such as Mg, Al, Si and most of the transition metals, large promotion energies are offset by strong bonding between the valence state atoms. The main question is whether bonding in the diatomics is adequate to sustain extensive promotion. The most extreme example for which a considerable difference would be expected between the bulk and the diatomics would be that of the Group IIA and IIB metals. The first section of this paper which deals with the alkaline earths Mg and Ca will demonstrate a significant influence of the excited valence state even for these elements. The next section will then expand the treatment to transition metals.

THE ALKALINE EARTHS

While most of the diatomics metals have at least one unpaired electron per atom to contribute towards bonding, the

Group IIA dnd IIB metals do not. With ground state configurations ns^2 and $(n-1)d^{10}ns^2$, respectively, the diatomics of these metals should be van der Waals molecules, analogous to the rare gas diatomics, with very small dissociation energies. However, the first excited states of the rare gases involve excitation to a shell of the next higher principal quantum number, but the Group IIA and IIB atoms have nsnp and ns(n-1)d excited configurations available at considerably lower energy. These low-lying configurations are certainly of importance in the bulk metal bonding. In this section, we show how these low-lying states influence even the weakly bound diatomics, and how spectroscopic data on weakly bound species may be treated to yield accurate estimates of the dissociation energy.

We restrict the spectroscopic analysis to Mg_2 and Ca_2, the only two diatomics of these groups for which detailed spectral constants of the ground electronic state have been measured. The approach is to invert spectroscopic constants

(ω_e, $\omega_e x_e$, B_e, α_e, *etc.*) to the parameters of a potential function expansion. We use the expansion

$$V(R) = e_o\lambda^2[1 + \sum_{n=1} e_n\lambda^n] \tag{1}$$

where

$$\lambda = 1 - (R_e/R)^p.$$

This potential function has been applied to several weakly bound diatomics with very good success.[1-4] The parameters are e_o (with units of energy), the correction coefficients e_n, the equilibrium bond length R_e, and the parameter p, which need not be integral. Note, however, if p=6, and e_n=0, n=1,2,3..., then eqn(1) is the familiar Lennard-Jones (6-12) potential. The expressions relating these parameters to spectroscopic constants have appeared in the literature.[3,5]

For Mg_2, we have used the constants obtained by Vidal and Scheingraber[6] in their analysis of the spectrum reported by Balfour and Douglas.[7] For Ca_2, we used the constants by Balfour and Whitlock.[8] The parameters one obtains for the potential functions of the $^1\Sigma_g^+$ ground states are given in table 1. Dissociation energies are obtained by setting λ = 1

Table 1. Parameters of eqn(1) for $X'\Sigma_g^+$ ground states of Mg_2 and Ca_2.

Mg_2		Ca_2	
e_o	= 785.94K	e_o	= 2570.8K
p	= 3.59	p	= 3.57
e_1^a	= 0	e_1^a	= 0
e_2	= 0.05899	e_2	= -0.2317
e_3	= 0.07966	e_3	= -0.1200
e_4	= -0.1229	e_4	= 0.0597
e_5	= -0.147		
e_6	= 0.108		
R_e	= 3.890 Å	R_e	= 4.2774 Å

[a]The constant e_1 is identically zero by our choice for determining p, as discussed in ref.(1-5).

in eqn(1). The predictions are dissociation energies of 768K for Mg_2 and 1820K for Ca_2. These values are 20 and 15%, respectively, larger than spectroscopic estimates[6,8] of the dissociation energy and are in all likelihood truly in error by these amounts.

The source of this error can be traced to the very informative parameter, p. Note from table 1 that $p \sim 3.6$ for Mg_2 and Ca_2, which means eqn(1) approaches the separated atom limit at large R like $R^{-3.6}$. In contrast, one knows that the proper large R behavior should be R^{-6}, in accordance with dispersion theory. Thus eqn(1) rises toward the dissociation plateau too slowly and thereby overestimates the dissociation limit.

The parameter p (as well as the others) is evaluated from equilibrium properties of the diatomic and perhaps should not be expected to give the proper long-range behavior to the full potential. Yet, in many cases[1,2,4] as diverse as Ar_2, NaAr and $BeAr^+$, the value of p is large enough to give the proper long-range behavior. (Actually, theoretical arguments predict[3]

that p will be closer to the value n-1 than to n where n is the expected long-range exponent. This prediction is observed in the previously reported molecules). Therefore, the small value of p for Mg_2 and Ca_2 is informative. For most chemically bound diatomics, p is in the range 0.4 to 2.5 (and parenthetically eqn(1) does not converge at all well for these molecules). Thus, the alkaline earth diatomics have potential functions with a shape near R_e which is intermediate to that of truly non-bonded diatomics such as Ar_2 and NaAr and that of ordinary chemically bound diatomics. Perturbation theory expressions[5] for p indicate the role of excited state mixing in determining the value of p. It is clear that one is observing the effects of this mixing in the alkaline earth ground states, even though the bonding remains very weak.

Transition Metal Diatomics

The alkaline earth example illustrates that promotion from the ground atomic state plays a small but definite role in the bonding of even the weakly bound Group II element diatomics.

Most atoms have a filled valence s orbital in the ground state, and promotion of an s electron to provide two bonding electrons is important for the bulk metals. In addition promotion of inner shell d or f electrons can play an important role. The lanthanide elements provide a clear illustration of the role of promotion of 4f electrons in the homonuclear diatomic gases. Kant and Lin[9] noted that the dissociation energies of the diatomic lanthanides decreased steadily from cerium to europium with a large increase for gadolinium with again a steady decrease to ytterbium. They pointed out that the trends were parallel to those for the enthalpies of sublimation of the bulk metals and that the trends were due to the increasing difficulty of promotion of 4f electrons with increasing nuclear charge. Examination of the experimental values tabulated in table 2 indicates similar parallel trends for the 3d transition metals.[10,11] However, the quantitative analysis of the data to be illustrated below shows that there are substantial differences between the bonding in the M_2 gas and in the bulk solid for many elements.

Table 2. Valence State Bonding Enthalpies of Diatomics.

Element	$\Delta H_0^\circ/R$, kK		Reference	Valence State	Valence Bonding in kK per electron d	sp
H	51.967	±0.001	(12)	1s		52.
He	0.		(13)			
Li	12.16	±0.1	(14)	2s		12.
Be	(<0.3)					
B	35.	±3	(13)	2p		33.
C	72.	±1	(13)	$2p^2$		36.
N	113.25	±0.1	(12)	$2p^3$		38.
O	59.36	±0.02	(12)	$2p^4$		29.7
F	18.59	±0.07	(13)	$2p^5$		18.6
Ne	0.025	±0.004	(18)			
Na	8.36	±0.1	(13)	3s		8.
Mg	0.5814	±0.002	(18)			
Al	20.	±2	(15,16,17)	3p		20.
Si	37.3	±1	(13,17)	$3p^2$		19.
P	58.41	±0.03	(12)	$3p^3$		19.5
S	50.704	±0.03	(12,13)	$3p^4$		25.
Cl	28.774	±0.001	(12)	$3p^5$		29.
Ar	0.122	±0.002	(13,18)			
K	6.0	±0.1	(13)	4s		6.
Ca	1.5	±0.2	(18)			
Sc	19.1	±3.	(15)	$3d^2 4s$	17.	18.
Ti	16	±3	(15)	$3d^{2.5}4s4p^{0.5}$	8.	19.
V	28.6	±2.	(15)	$3d^{3.5}4s4p^{0.5}$	7.2	20.
Cr	18.	±3.	(15)	$3d^{4.5}4s4p^{0.5}$	2.5	21.
Mn	5.	±3.	(15)			
Fe	14.6	±2.5	(15)	$3d^{6.5}4s4p^{0.5}$	5.5	22.
Co	20.	±3.	(15)	$3d^{7.5}4s4p^{0.5}$	10.	22.5
Ni	26.	±2.5	(19)	$3d^{8.5}4s4p^{0.5}$	19.5	23.
Cu	23.5	±2	(13,15,20)	4s		23.5
Zn	2.	±0.5	(21)			
Ga	16.6	±1	(15)	4p		16.6
Ge	32.6	±1.5	(15,20)	$4p^2$		16.3
As	45.95	±0.01	(13)	$4p^3$		15.3
Se	39.58	±0.03	(13,22)	$4p^4$		19.8
Br	22.873	±0.001	(12)	$4p^5$		22.9
Kr	0.182	±0.002	(13,18)			

cont'd.

Table 2, cont'd.

Element	$\Delta H_0^\circ/R$, kK		References	Valence State	Valence Bonding in kK per electron d	sp
Rb	5.7	±0.5	(13)	5s		5.7
Sr	(1.7)					
Y	18.8	±3	(15)	$4d^2 5s$	18.7	13
Zr	(40)			$4d^3 5s$	13.3	14
Nb	56	±5	(23)	$4d^4 5s$	10.3	15
Mo	44.	±5	(23,24)	$4d^5 5s$	5.6	16
Tc	(34)			$4d^6 5s$	6.1	17
Ru	(37)			$4d^7 5s$	6.3	18
Rh	32.8	±3	(25,26)	$4d^8 5s$	7.2	18.5
Pd	12.6	±2.5	(15)	$4d^9 5s$	12.5	19
Ag	19.3	±0.8	(13,15,20)	5s		19.3
Cd	1.1	±0.2	(13,21)			
In	12.	±1	(15)	5p		12.
Sn	23.	±2	(15)	$5p^2$		12.5
Sb	35.9	±0.5	(13)	$5p^3$		12.
Te	31.07	±0.1	(22)	$5p^4$		15.5
I	17.899	±0.001	(12)	$5p^5$		18.
Xe	0.266	±0.003	(18)			
Cs	4.57	±0.1	(13)	6s		4.6
Ba	(3)	±2		5d6s	14	15
La	29.	±3	(15)	$5d^2 6s$	10	17
Ce	29.	±3	(9,15)	$4f5d^2 6s$	9	18
Pr	18	±3.5	(9)	$4f^2 5d^2 6s$	8.5	19
Nd	10	±3.5	(9)	$4f^3 5d^2 6s$	8.5	20
Pm	(8.5)			$4f^4 5d^2 6s$	8	21
Sm	7	±3	(9)	$4f^6 5d^{0.5} 6s 6p^{0.5}$	19	22
Eu	4	±2	(9)	$4f^7 5d^{0.5} 6s 6p^{0.5}$	17	23
Gd	20.5	±4	(9)	$4f^7 5d^2 6s$	7	24
Tb	15	±3	(9,27)	$4f^8 5d^2 6s$	7	25
Dy	8	±4	(9)	$4f^{10} 6s 6p$		26
Ho	8	±3	(9,28)	$4f^{11} 6s 6p$		27
Er	8	±3	(9)	$4f^{12} 6s 6p$		27
Tm	6	±2	(9)	$4f^{13} 6s 6p$		27
Yb	2	±2	(9,29)	$4f^{14} 6s 6p$		26
Lu	(20)		(15)	$5d 6s 6p$	18	26
Hf	(40)	±6		$5d^2 6s 6p$	14	26
Ta	(42)	±6		$5d^4 6s$	11	26
W	(58)	±8		$5d^5 6s$	8	26
Re	(38)	±10		$5d^5 6s 6p$	8	26
Os	(44)	±6		$5d^7 6s$	11	26
Ir	(42)	±6		$5d^8 6s$	12	26
Pt	40	±5	(30)	$5d^9 6s$	13.5	26.5
Au	26.7	±1	(13)	6s		26.7
Hg	0.9	±0.15	(13,21)			
Tl	(7)	±3	(31)	6p		7
Pb	9.5	±3	(13)	$6p^2$		5
Bi	23.6	±1	(15)	$6p^3$		8
Po	18	±3	(32)	$6p^4$		9
At	(10)			$6p^5$		10
Rn	(0.3)					

cont'd.

Table 2, cont'd.

Element	ΔH_0^o/ R, kK		References	Valence State	Valence Bonding in kK per electron d	sp
Fr	(4)	±1		7s		4
Ra	(2)	±1				
Ac	(12)	±7		$6d^2 7s$	11	16
Th	34	±4	(15,33)	$6d^3 7s$	11	17
Pa	(29)			$5f6d^3 7s$	10.5	17.5
U	20	±6	(34)	$5f^3 6d^2 7s$	10	18
Np	(17)	±7		$5f^4 6d^2 7s$	10	19
Pu	(3)	±3				
Am	(3)					
Cm	(13)	±7		$5f^7 6d^2 7s$	10	22
Bk	(2)	±2				
Cf	(2)					
Es	(2)					
Fm	(2)					
Md	(2)					
No	(2)					
Lr	(20)	±10		$7s^2 7p$		20

The second column of table 2 presents values of $\Delta H_0^o/R$ for $M_2(g) = 2M(g)$. Calculated or estimated values are given in parentheses. Uncertainties are listed for all experimental values based on a critical evaluation of the literature. When a review paper adequately covers the literature and arrives at a value considered acceptable, only a reference to the review paper is given. Otherwise, references are given to the original papers. As the experimental values were used to calibrate the variation of bonding with nuclear charge across the Periodic Table, the calculated values obtained by interpolation of bonding values have uncertainties close to those of adjoining elements but generally larger by about 1 kilokelvin. Thus uncertainties are not indicated as they can be obtained from the uncertainties given for neighboring experimental values. However, where extrapolations are necessary or if there is reason to suspect the accuracy of the bonding trends, uncertainties are also indicated for the calculated values. The fourth column of table 2 gives the electronic configuration

of the atomic valence state selected as illustrated below. No configuration is shown for van der Waals molecules. The trends in bonding are shown in the last column where $\Delta H_0^o/R$ for dissociation of $M_2(g)$, in its ground state, to the atoms in the indicated valence state has been divided by the number of bonding electrons per atom with a separation into bonding per d- or per sp-electron for the transition elements.

The method of determining the effective electronic configuration in the valence state is quite straightforward for most elements. The enthalpy of dissociation of $M_2(g)$ to two $M(g)$ in their ground state is given by $\Delta H_0^o/R = (n-1)E_d/R + E_s/R - 2P$ for a transition metal with ground state $d^{n-2}s^2$ and a valence state $d^{n-1}s$. The promotion of a ground state atom to the valence state requires P kilokelvin for one atom or 2P for two atoms. E_d is the bonding energy (more strictly enthalpy, but at 0K they are essentially identical), per d electron and E_s is the bonding energy per s electron.

The promotion energies to levels of each electronic configuration for elements other than the lanthanides and actinides are tabulated by Moore (35). Due to lack of data for the lanthanides and actinides, a model for prediction of promotion energies had previously been developed (36). The recent review (37) of values for the lanthanides has confirmed the reliability of the model, and where experimental data are still lacking, the predictions of the model can be confidently used. As noted earlier (10), the energy corresponding to the lowest state of each configuration can be accurately used in place of a weighted mean of all the levels of a configuration if the valence state bonding energies are obtained from experimental data using the same basis for the promotion energies. For the transition metals, there are often two configurations, *e.g.*, $4d^{n-1}5s$ or $4d^{n-2}5s5p$, that might contribute significantly. One can differentiate the energy equation (10) to obtain the optimum mix, but the data are not accurate enough to specify

more closely than one-half electron as in $3d^{2.5}4s4p^{0.5}$ for Ti. Table 3 gives the promotion energies for those transition-metals, lanthanides, and actinides where one might have to consider the contribution of two configurations.

With the various promotions energies available, the procedure for calculation of unknown dissociation energies involves the combination of the promotion energy for a given valence state with the interpolated bonding energies. For some elements with no unpaired electrons in the ground atomic state, one calculates that no reasonable bonding energies could offset the promotion to even the lowest excited state and the cohesion of the atoms must be due primarily to van der Waals interactions. The noble gases, the Group II elements Zn to Hg, Be to Sr, and Ra, and the actinides Bk to No and probably Pu and Am fall into the van der Waals class. Most of these actinides have unpaired 5f electrons, but the 5f electrons are so localized, particularily for the second half or the series,

Table 3. Promotion energies to valence states.

Element	Ground State	$d^{n-1}s$ Promotion Energy kKelvin	$d^{n-2}sp$ Promotion Energy kKelvin
Sc	$3d4s^2$	16.575	22.550
Ti	$3d^24s^2$	9.434	22.844
V	$3d^34s^2$	3.039	23.541
Cr	$3d^54s$	0.	35.929
Fe	$3d^64s^2$	9.968	27.842
Co	$3d^74s^2$	5.011	33.973
Ni	$3d^84s^2$	0.295	37.054
Y	$4d5s^2$	15.737	21.509
Zr	$4d^25s^2$	7.008	21.270
Nb	$4d^45s$	0.	23.988
Mo	$4d^55s$	0.	40.094
Tc	$4d^55s^2$	3.702	23.638
Ru	$4d^75s$	0.	36.278
Rh	$4d^85s$	0.	(48.)
Pd	$4d^{10}$	9.444	<73.
Ba	$6s^2$	12.998	17.648
		$f^{n-3}d^2s$	$f^{n-3}dsp$
La	$5d6s^2$	3.867	19.078
Ce	$4f5d6s^2$	3.409	19.444
Pr	$4f^36s^2$	9.660	26.080
Nd	$4f^46s^2$	12.661	29.167
Pm	$4f^56s^2$	(14.4)	(31.)
		$f^{n-3}d^2s$	$f^{n-3}dsp$
Sm	$4f^66s^2$	15.540	19.850
Eu	$4f^76s^2$	18.595	20.241
		$f^{n-2}d\ s$	$f^{n-2}sp$
Gd	$4f^75d6s^2$	9.177	20.195
Tb	$4f^96s^2$	11.784	21.6
		$f^{n-2}ds$	$f^{n-2}sp$
Dy	$4f^{10}6s^2$	25.201	22.396
Ho	$4f^{11}6s^2$	27.146	22.812
Er	$4f^{12}6s^2$	27.858	23.483
Tm	$4f^{13}6s^2$	29.362	24.088
Yb	$4f^{14}6s^2$	35.235	24.875
		$d^{n-1}s$	$d^{n-2}sp$
Lu	$5d6s^2$	27.123	25.074
Hf	$5d^26s^2$	20.276	20.169
Ta	$5d^36s^2$	14.041	25.013
W	$5d^46s^2$	4.246	27.897
Re	$5d^56s^2$	16.912	27.265
Os	$5d^66s^2$	7.401	33.758
Ir	$5d^76s^2$	4.079	37.851
Pt	$5d^96s$	0.	43.390

cont'd.

Table 3. cont'd.

Element	Ground State	$d^{n-1}s$ Promotion Energy kKelvin		$d^{n-2}sp$ Promotion Energy kKelvin	
Ac	$6d7s^2$	13.261		19.730	
Th	$6d^27s^2$	8.004		20.812	
Pa	$5f^26d7s^2$	(10.)	$[fd^3s]$	(23.)	$[fd^2sp]$
U	$5f^36d7s^2$	8.991	$[f^3d^2s]$	21.070	$[f^3dsp]$
Np	$5f^46d7s^2$	(10.8)	$[f^4d^2s]$	(21.)	$[f^4dsp]$
Pu	$5f^67s^2$	21.455	$[f^5d^2s]$	22.300	$[f^6sp]$
Am	$5f^77s^2$	(21.)	$[f^7ds]$	22.457	$[f^7sp]$
Cm	$5f^76d7s^2$	14.597	$[f^7d^2s]$	21.045	$[f^7dsp]$

that they contribute insignificantly to the bonding. Ba is an exception among the Group II elements in that the 5d6s configuration is close enough to the ground $6s^2$ configuration to allow substantial contribution although the net contribution to $\Delta H_0^o/R$ is still only 3 ±2 kK. For Eu and Yb, likewise, the calculations indicate that they are not van der Waals molecules.

For transition-metals of groups III-VI, the valence state configurations are essentially the same for the diatomic and the solids in consisting of a mixing of the $d^{n-1}s$ and $d^{n-2}sp$ configurations with less p contribution for diatomic Zr, Ta, W and group III and more p contribution for diatomic Hf than for the solid. A much more dramatic difference is found for Fe to Cu which can promote to a $d^{n-2.5}sp^{1.5}$ valence state in the solid but can only achieve $d^{n-1.5}sp^{0.5}$ for Fe, Co and Ni diatomics and no substantial promotion for Cu which uses the ground $d^{10}s$ configuration. For the 4d and 5d groups VII-XI, all use the $d^{n-1}s$ valence state for the diatomic with the exception of Re which is able to promote to d^5sp.

Examination of the bonding energies given in table 2 show that the irregular behavior of the dissociation energies of the diatomic is due to three contributions that change in different ways with variation of position in the Periodic Table. There is first the contribution from promotion energies which are known quite accurately for most elements. Secondly, there is the increase of the s,p bonding with increasing nuclear charge for a given period with a reduction in bonding per electron for multiple bonding and a reduction in p bonding when the core includes the closed s subshell of the outer shell. Thirdly, there is the reduction in d bonding with nuclear charge for a given period up to the d^5 configuration and an increase in bonding per d electron beyond the d^5 configuration as the most localized orbitals are used by non-bonding electrons and the most extended orbitals are used by bonding electrons. The contribution of d bonding is greatly increased from 3d to 4d to 5d due

to the contraction of the ns^2np^6 subshell, with increasing nuclear charge, relative to the nd orbital. These same trends are found for the bulk metals, and the simple smooth trends found for each of these factors makes the prediction of bonding energies and, therefore, dissociation energies quite straightforward and reasonably accurate.

ACKNOWLEDGMENT: We thank J. H. Cobble for his help in the analysis of the Mg_2 and Ca_2 potential functions. J. S. Winn acknowledges partial support from an Alfred P. Sloan Research Fellowship.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciencies, U. S. Department of Energy under contract No. W-7405-Eng-48.

References

1. J. H. Goble, D. C. Hartman and J. S. Winn, *J. Chem. Phys.*, 1977, 67, 4206.

2. J. H. Goble and J. S. Winn, *J. Chem. Phys.*, 1979, 70, 2051.

3. J. H. Goble and J. S. Winn, *J. Chem. Phys.*, 1979, 70, 2058.

4. J. H. Goble, S. M. Walsh and J. S. Winn, to be published.

5. A. J. Thakkar, *J. Chem. Phys.*, 1975, 62, 1693.

6. C. R. Vidal and H. Scheingraber, *J. Mol. Spectr.*, 1977, 65, 46.

7. W. J. Balfour and A. E. Douglas, *Canad. J. Phys.*, 1970, 48, 901; W. C. Stwalley, *Chem. Phys. Letters*, 1970, 7, 600.

8. W. J. Balfour and R. F. Whitlock, *Canad. J. Phys.*, 1975, 53, 472.

9. A. Kant and S. S. Lin, *Monatsh.*, 1972, 103, 757-763.

10. L. Brewer, *"Viewpoints of Stability of Metallic Structures"* in book, *Phase Stability in Metals and Alloys*, ed. P. Rudman, J. Stringer, and R. L. Jaffee, (McGraw-Hill, New York, 1967). pp. 39-61, 241-9, 344-6, 560-8.

11. L. Brewer, *Science*, 1968, 161, 115-122.

12. The Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions has

12. cont'd.

critically evaluated the D_0 and ΔH of formation values for atomic and diatomic states of H, N, P, O, S, Cl, Br, and I. The Br_2 and I_2 values were slightly revised to correspond to the recent values reported by Barrow *et al.* (R. F. Barrow, D. F. Broyd, L. B. Pederson, and K. K. Yee, *Chem. Phys. Lett.* 1973, 18, 357-8). The S_2 value was changed in acknowledgment of the objection raised by Huber and Herzberg[13] to the use of a D_0 value that does not relate to the actual lowest rotational level of S_2. The D_0 values in cm^{-1} given in CODATA Report Part I, Bulletin 5 (Dec.1971) and Part 7 (Sept.1975) were multiplied by hc/k = 1.4388 cmK to obtain the values in kelvin. Br_2 and Cl_2 differ from the others in not having a predominant isotope thus resulting in a small difference between D_0 and ΔH_0^o of dissociation of the dimer. The ΔH values reported by CODATA in *J. Chem. Therm.*, 1976, 8, 603-5 were converted to ΔH_0^o and divided by $R = 8.31433\ J\ K^{-1}$, but the uncertainties are those of the original D_0^o values.

13. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecule.* Van Nostrand Reinhold Co. (1979).

14. D. D. Konowalow and M. L. Olson, *J. Chem. Phys.*, 1979, 71, 450-57.

15. K. A. Gingerich, *J. Crystl. Growth*, 1971, 9, 31-45.

16. C. A. Stearns and F. J. Kohl, *High Temp. Sci.*, 1973, 5, 113-127.

17. C. Chatillon, A. Michel and A. Pattoret, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 1975, 280(25), 1505-8.

18. W. J. Balfour, *J. Chem. Educ.*, 1979, 56, 452-3.

19. A. Kant, *J. Chem. Phys.*, 1964, 41, 1872-6 and 1968, 49, 5144-6. E. Rutner and G. L. Haury, *J. Chem. Eng. Data*, 1974, 19, 19-27 obtained a different value upon repeating Kant's Third-Law calculations, but they used the atomic weight of nickel rather than twice the atomic weight of nickel for the molecular weight of Ni_2.

20. A. Neckel and G. Sodeck, *Monatsh.*, 1972, 103, 367-82.

21. K. D. Carlson and K. R. Kushnir, *J. Phys. Chem.*, 1964, 68, 1566-7.

22. J. Drowart and S. Smoes, *J. C. S. Faraday Trans. II*, 1977, 73, 1755-67.

23. S. K. Gupta and K. A. Gingerich, *Inorg. Chem.*, 1978, 17, 321-3 and *J. Chem. Phys.*, 1979, 70, 5350-3, report values of $D(Nb_2)$ and $D(Mo_2)$ from Third-Law calculations which include no electronic contributions in the calculation of $-(G^o-H^o_{298})/RT$. Brewer and Lamoreaux (24) have pointed out that, even with a $^1\Sigma$ ground state, low-lying electronic states of higher multiplicity are expected to be populated at the temperature range of measurements and electronic terms must be included. The value given for Nb_2 has been corrected in a manner similar to the correction for Mo_2(24).

24. L. Brewer and R. H. Lamoreaux (1979), Part I, Atomic Energy Review, Molybdenum: Physiocochemical Properties of Its Compounds and Alloys, International Atomic Energy Agency, Vienna.

25. D. L. Cocke and K. A. Gingerich, *J. Chem. Phys.*, 1974, 60,1953-65.

26. V. Piacente, G. Balduici, G. Bari, *J.Less-Common Metals*, 1974,37, 123-7.

27. J. Kordis, K. A. Gingerich and R. J. Seyse, *J. Chem. Phys.*, 1974, 61, 5114-21.

28. D. L. Cocke and K. A. Gingerich, *J. Phys. Chem.*, 75, 3264-70 (1971)

29. M. Guido and G. Balducci, *J. Chem. Phys.*, 1972, 57, 5611-2.

30. G. D. Blue, R. S. Carbonara, and C. A. Alexander, *Proc. 18th Annual Conf. on Mass Spectrometry and Allied Topics*, San Francisco, June 1970 and private communication reporting upper limit of 90 kcal/mole for $D(Pt_2)$.

31. J. Drowart and R. E. Honig, *J. Phys. Chem.*, 1957, 61, 980-5.

32. D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements, Advances in Chem. Ser.*, 1956, No. 18.

33. K. A. Gingerich, *High Temperature Sci.*, 1969, 1, 258-67.

34. R. Stern and N. Lang, Lawrence Livermore Laboratory, San Francisco Bay Area Conference on High-Temperature Science & Technology, 08 March 1979 report an upper limit of 15 kilo kelvin for $D(U_2)$ compared to 20±5kK reported by K. A. Gingerich and G. D. Blue, *J.Chem.Phys.*,1967,47,5447-49 and 26±3kK reported by L. N. Gorokhov, A. M. Emel'yanov, Yu. S. Khodeev, High Temperature, 1974, 12, 1156-8.

35. C. E. Moore, Atomic Energy Levels, Vols. 1-3, U. S. Government Printing Office, Washington, D.C., 1949, 1952, 1958.

36. L. Brewer, *J. Opt. Soc. Am.*, 1971, 61, 1101-1111.

37. W. C. Martin, R. Zalubas, and L. Hagan, Atomic Energy Levels - The Rare-Earth Elements, NSRDS-NBS 60, U. S. Government Printing Office, Washington, D.C., 1978.