Inorganica Chimica Acta, 24 (1977) 149–157
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Bond Energy Terms in Oxides and Oxo-anions

C. GLIDEWELL
Chemistry Department, University of St. Andrews, Fife, KY16 9ST, Scotland, U.K.

Received December 30, 1976

Experimental ΔH^{ϕ}_f *values are employed to calculate mean bond dissociation energies for homogeneous neutral gaseous oxides* MO_p, $\bar{D}_1$ *for dissociation into neutral atoms, and* $\bar{D}_2$ *for dissociation into oxide ions and cations* M^{+2p}*: similarly, sums of bond energy terms* ΣB_1 *and* ΣB_2 *are calculated for heterogeneous neutral oxides. By use of* ΔH^{ϕ}_f *values for simple salts,* $\bar{D}_2$ *values are calculated for the oxo-anions,* CO_3^{-2}, NO_3^-, NO_2^-, SO_4^{-2}, SO_3^{-2}, SeO_4^{-2}, SeO_3^{-2}, TeO_3^{-2}, ClO_4^-, ClO_3^-, ClO_2^-, BrO_4^-, BrO_3^-, IO_4^-, IO_3^-, CrO_4^{-2}, MnO_4^-, MnO_4^{-2}, TcO_4^- *and* ReO_4^-.

Introduction

In previous papers [1, 2], metal–ligand coordinate bond energy terms have been calculated for metal-ion complexes containing water, ammonia and 1,2-diaminoethane as ligands, together with data for a few examples of complexes containing fluoride and cyanide. In this paper, mean bond dissociation energies are calculated for the dissociation of homogeneous neutral oxo compounds MO_p into both neutral atoms ($\bar{D}_1$) and ions (O^{-2} and M^{+2p}) ($\bar{D}_2$), and for the dissociation of homogeneous oxo-anions MO_q^{-x} into ions. A few data for heterogeneous neutral oxo compounds and homogeneous neutral thio compounds are also included.

Results

For a neutral gaseous oxo compound MO_p whose enthalpy of formation is ΔH^{ϕ}_f, we may write

$$p\bar{D}_1(M\text{–}O) = \Delta H^{\phi}_{sub}(M) + p/2D(O_2) - \Delta H^{\phi}_f$$

for its dissociation into neutral atoms and

$$p\bar{D}_2(M\text{–}O) = p\bar{D}_1(M\text{–}O) + \sum_{1}^{2p} I(M) - p[E_1(O) + E_2(O)]$$

for its dissociation into ions, where $\sum_{1}^{2p} I(M)$ represents the sum of the successive ionisation energies of M, and $[E_1(O) + E_2(O)]$ the electron affinities of oxygen.

Values of $\Delta H^{\phi}_{f(g)}$ were taken largely from the JANAF tables [3], and otherwise as specifically cited. In Table I are presented the calculated values of $\bar{D}_1$ and $\bar{D}_2$ for neutral oxides: in the calculation of $\bar{D}_2$, ionisation energies were taken from the compilation of Lakatos, Bohus and Medgyesi [4]. Also included in Table I are a number of values derived [5] from spectroscopic rather than thermochemical data. For heterogeneous oxo compounds containing bonds of more than one type, only a sum of bond energy terms can be derived from ΔH^{ϕ}_f: in Table II are presented values of ΣB_1 for dissociation to neutral atoms and ΣB_2 for dissociation into ions, $(M^{+2p} + O^{-2})$.

For the species in Table I, $\bar{D}_2$ refers to their ionisation to oxide ions and cationic M, except in the examples of HO, FO, ClO, and BrO. For HO → $H^+ + O^-$, ΔH^{ϕ} is +1417 kJ mol^{-1}, whereas for HO → $H^- + O^+$, ΔH^{ϕ} is only +900 kJ mol^{-1}: similarly for FO, ClO and BrO dissociating to $X^+ + O^-$, the enthalpies are respectively +1753, +1382, and +1214 kJ mol^{-1}, greater than the enthalpies for dissociation to $X^- + O^+$ by 558, 148, and 12 kJ mol^{-1} respectively. For IO the dissociation to $I^- + O^+$ has ΔH^{ϕ} of +1203 kJ mol^{-1}, 152 kJ mol^{-1}, greater than that for the dissociation to $I^+ + O^-$. Values of $\bar{D}_2$ for actinoid oxides cannot be calculated because the required ionisation energy data are unavailable. Temperature corrections were not applied since in many cases these are smaller than the experimental uncertainties.

For an ionic compound $(M^{+n})_m[XO_p]^{-nm}$ whose enthalpy of formation as a crystalline solid is ΔH^{ϕ}_f, and whose lattice energy is U, we may write

$$m[\Delta H^{\phi}_{sub}(M)] + \Delta H^{\phi}_{sub}(X) + p/2D(O_2) + m\,\Sigma\, I(M) + \Sigma\, I(X) + p[E_1(O) + E_2(O)] - U - \Delta H^{\phi}_f = p\bar{D}_2$$

where the terms ΔH^{ϕ}_{sub} represent atomisation enthalpies of M and X, and $\bar{D}_2$ represents the mean dissociation energy of the anion into cations of X in the oxidation state (2p–nm) and oxide ions; for example $\bar{D}_2$ for SO_4^{-2} represents one-quarter of ΔH^{ϕ} for the

TABLE I. Bond Dissociation Energies in Neutral, Homogeneous Oxo-compounds.

Compound	$\Delta H^{\phi}_{f(g)}$/kJ mol^{-1}	$\bar{D}_1$/kJ mol^{-1}	$\bar{D}_2$/kJ mol^{-1}	Comments
(i) Hydrogen				
HO	+39.5	427	900[n]	See text
H_2O	−241.8	463	1928[o]	
(ii) Group I				
LiO	+84.1	326	704	
Li_2O	−166.9	369	1216	C_{2v}
Li_2O_2	−242.7	266	455	D_{2h}
NaO	+83.7	275	629	
KO	+71.1	268	544	
(iii) Group II				
BeO	+129.7	452	3761	
Be_2O	−62.8	488	1714	$D_{\infty h}$
Be_2O_2	−410.0	393	2048	D_{2h}
Be_3O_3	−1054	466	2121	D_{3h}
Be_4O_4	−1590	489	2144	D_{4h}
Be_5O_5	−2113	502	2157	D_{5h}
Be_6O_6	−2661	512	2167	D_{6h}
MgO	+4.2	391	3232	
CaO	a	431	2819	
SrO	a	464	2730	
BaO	a	527	2648	
(iv) Group III				
BO	+25.1	795	4675	
B_2O	+96.2	647	1774	C_{2v}
BO_2	−284.5	677	–	$D_{\infty h}$
AlO	+90.4	480	3527	
Al_2O	−131.4	578	1481	C_{2v}
AlO_2	+16.7	401	–	
GaO	a	243	3454	
Ga_2O	−87.9[b]	311	1217	
InO	a	105	3137	
Tl_2O	+5.0[c]	212	1128	
(v) Group IV				
CO	−110.5	1037	5164	
CO_2	−393.5	802	8595	
SiO	−99.6	799	3815	
SiO_2	−305.4	627	6253	
GeO	−45.2[d]	588	3540	
SnO	a	552	3325	
PbO	+48.0	397	3216	
(vi) Group V				
NO	+90.4	631	5542	
NO_2	+33.5	468	9275	
NO_3	+71.1	383	–	D_{3h}
PO	−6.1	589	4156	
PO_2	−297.1	564	6607	
P_4O_6	−1648.2	373	2641	T_d
AsO	a	477	3875	
As_4O_6	−1209.2	321	2225	T_d
SbO	a	310	3591	
Sb_4O_6	−1233[e]	315	2141	T_d
BiO	a	385	3351	

Compound	$\Delta H^{\phi}_{f(g)}$/kJ mol^{-1}	$\bar{D}_1$/kJ mol^{-1}	$\bar{D}_2$/kJ mol^{-1}	Comments
(vii) Group VI				
O_2	0.0	497	–	
O_3	+34.1	356	–	
SO	+6.1	481	4386	
SO_2	−296.8	516	6756	
SO_3	−395.7	460	10001	D_{3h}
SeO	+39.7[f]	416	4085	
SeO_2	−109.6[g]	407	6393	
SeO_3	−92.0[h]	348	9536	D_{3h}
TeO	+179.9[i]	261	3095	
TeO_2	−78.5[i]	384	5237	
(viii) Group VII				
FO	+113.4	214	1195[p]	See text
F_2O	−18.4	213	2220[q]	
ClO	+101.2	269	1234[r]	See text
Cl_2O	+87.9	201	1784[s]	
ClO_2	+104.6	257	7178	
ClO_3	+154.8[b]	237	10360	
BrO	a	213	1202[t]	See text
IO	a	184	1051[u]	See text
(ix) Group VIII				
XeO_3	+527.3[j]	73	8300	
XeO_4	+642.3[j]	88	11391	
(x) Sc Triad				
ScO	a	577	3096	
YO	a	674	3123	
LaO	a	674	2972	
(xi) Ti Triad				
TiO	+15.7	702	3323	
TiO_2	−259.4	613	5661	
ZrO	+58.6	802	3381	
ZrO_2	−286.2	698	5079	
(xii) V Triad				
VO	a	527	3245	
VO_2	a	623	6061	
TaO_2	a	734	5206	
(xiii) Cr Triad				
CrO	a	519	3416	
MoO	+387.0	526	3422	
MoO_2	−13.0	587	5909	
MoO_3	−360.7	590	8512	D_{3h}
WO	+425.1	673	3804	
WO_2	+76.6	635	5374	
WO_3	−292.9	629	7513	D_{3h}
(xiv) Mn Triad				
MnO	a	385	3264	
(xv) Fe Triad				
FeO	+236.8	410	3384	
RuO	+355.6[k]	533	3514	
RuO_2	+118.8[k]	509	5967	
RuO_3	−71.1[k]	486	8974	
RuO_4	−185.8[l]	455	12268	

Compound	$\Delta H^{\phi}_{f(g)}$/kJ mol^{-1}	$\bar{D}_1$/kJ mol^{-1}	$\bar{D}_2$/kJ mol^{-1}	Comments
OsO_2	−251.0[l]	770	5801	
OsO_3	−104.6[l]	549	8043	
OsO_4	−342.3[l]	532	10709	
(xvi) Co Triad				
RhO	+380.7[k]	426	3542	
RhO_2	+175.7[k]	439	6041	
IrO_2	+207.9[k]	477	5575	
IrO_3	+25.9[k]	464	8230	
	+8.4[m]	475	8240	
(xvii) Ni Triad				
NiO	a	<414	<3550	
PdO	+334.7	293	3625	
PtO	+428.0	385	3694	
PtO_2	+158.2	456	5815	
(xviii) Cu Triad				
CuO	+240.6	345	3701	
AgO	a	134	3591	
(xix) Zn Triad				
ZnO	+191.5[b]	187	3479	
CdO	a	<368	<3520	
HgO	+41.8	268	3738	
(xx) Lanthanoids				
LaO	a	674	2972	
CeO	a	623	3004	
PrO	a	594	2791	
GdO	a	481	2886	
LuO	a	414	3011	
(xxi) Actinoids				
ThO_2	a	774		See text
UO	a	828		
UO_2	a	741		
UO_3	a	708		

[a] Ref. 5. [b] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, N. B. S. Technical Note 270-3, Washington, D.C. (1968). [c] D. Cubicciotti, *High Temp. Sci.*, *1*, 11 (1969). [d] W. L. Jolly and W. M. Latimer, *J. Am. Chem. Soc.*, *74*, 5757 (1952). [e] Ref. 6. [f] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions", Prentice-Hall, Englewood Cliffs, N.J. (1952). [g] A. Glassner, USAEC Report ANL-5750 (1958). [h] S. M. Gadzhiev, R. B. Dobrotin, and A. V. Suvorov, *Zhur. Neorg. Khim.*, *11*, 2155 (1966). Vapour consists of monomer–tetramer mixture, F. C. Mijlhoff, *Rec. Trav. Chim.*, *84*, 74 (1965). [i] W. A. Dutton and W. C. Cooper, *Chem. Revs.*, *66*, 657 (1966). [j] S. R. Gunn, *J. Am. Chem. Soc.*, *87*, 2290 (1965). [k] J. H. Norman, H. G. Staley and W. E. Bell, *Advan. Chem. Ser.*, *72*, 101 (1968). [l] A. B. Nikol'skii and A. N. Ryabov, *Russ. J. Inorg. Chem.*, *10*, 1 (1966). [m] H. Schäfer and H. J. Heitland, *Z. Anorg. Allg. Chem.*, *304*, 249 (1960). [n] D_2 for $HO \rightarrow H^- + O^+$. For $HO \rightarrow H^+ + O^-$, D_2 is 1417 kJ mol^{-1}. [o] $\bar{D}_2$ for $H_2O \rightarrow 2H^- + O^{+2}$ is 1993 kJ mol^{-1}. [p] For $FO \rightarrow F^- + O^+$. For $FO \rightarrow F^+ + O^-$, D_2 is 1753 kJ mol^{-1}. [q] For $F_2O \rightarrow 2F^+ + O^{-2}$. For $F_2O \rightarrow 2F^- + O^{+2}$, $\bar{D}_2$ is 2231 kJ mol^{-1}. [r] For $ClO \rightarrow Cl^- + O^+$. For $ClO \rightarrow Cl^+ + O^-$, D_2 is 1382 kJ mol^{-1}. [s] For $Cl_2O \rightarrow 2Cl^+ + O^{-2}$. For $Cl_2O \rightarrow 2Cl^- + O^{+2}$, $\bar{D}_2$ is 2204 kJ mol^{-1}. [t] For $BrO \rightarrow Br^- + O^+$. For $BrO \rightarrow Br^+ + O^-$, D_2 is 1214 kJ mol^{-1}. [u] For $IO \rightarrow I^+ + O^-$. For $IO \rightarrow I^- + O^+$, D_2 is 1203 kJ mol^{-1}.

process: $SO^{-2}_{4(g)} \rightarrow S^{+6}_{(g)} + 4O^{-2}_{(g)}$. In Table IV are set out values of $\bar{D}_2$ for a number of anions: atomisation energies are from Kubaschewski, Evans and Alcock [6], and lattice energies are from Yatsimirskii [7]. Enthalpies of formation are available for many more salts of some of these anions, such as sulphate(VI), nitrate(V) and carbonate: however, wherever possible, data employed have been restricted to Group IA metal ions, since these exhibit the least covalence in their salts [8]. Where this is not possible, because of lack of ΔH^{ϕ}_f data, as in the examples of sulphate(IV) and selenate(IV), the variation of $\bar{D}_2$

TABLE II. Bond Energy Term Sums in Neutral Heterogeneous Oxo-Compounds.

Compound	$\Delta H^{\phi}_{f(g)}$/kJ mol^{-1}	ΣB_1/kJ mol^{-1}	ΣB_2/MJ mol^{-1}	
HO_2	+20.9	694	–	C_s
H_2O_2	−136.1	1069	2.02[g]	C_2
B_2O_2	−456.1	2096	9.86[h]	D_{2h}
B_2O_3	−833.2	2721	18.45	C_{2v}
Al_2O_2	−405.8	1547	7.46[i]	C_{2h}
C_2O	+286.6	1389	–	C_{2v}
C_3O_2	−93.6	2731	–	D_{2h}
N_2O	+82.0	1112	–	C_{2v}
N_2O_3	+82.8	1609	21.24	C_s
N_2O_4	+9.1	1931	34.38	D_{2h}
N_2O_5	+11.3	2178	56.95	C_{2v}
P_4O_{10}	−2834.2[a]	6657	81.40	Td
S_2O	−56.5	781	–	C_s
FO_2	+12.6	564	–	C_s
$ClOClO_3$	+209.9[b]	1027	–	C_s
Cl_2O_7	+306.6[c]	1674	85.12	C_{2v}
V_2O_5	d	3033	38.02	C_{2v}
Mn_2O_7	+589.4[e]	2892	82.99	?D_{3d}
Tc_2O_7	+975.7[f]	3917	68.21	?D_{3d}
Re_2O_7	+1098.3[f]	4396	63.68	C_{2v}

[a]Ref. 6. [b]C. J. Schack and D. Pilipovich, *Inorg. Chem.*, *9*, 1387 (1970). [c]$\Delta H^{\phi}_{f(l)}$, +272.0 kJ mol^{-1}, NBS Technical Note 270-3, Washington, D.C., (1968); ΔH^{ϕ}_{vap}, +34.6 kJ mol^{-1}, C. F. Goodeve and J. Powney, *J. Chem. Soc.*, 2078 (1932). [d]Ref. 5. [e]$\Delta H^{\phi}_{f(s)}$, −728.4 kJ mol^{-1}, O. Glemser and H. Schröder, *Z. Anorg. Allg. Chem.*, *271*, 293 (1953): ΔH^{ϕ}_{sub} taken as +139 kJ mol^{-1}, those for Tc_2O_7 and Re_2O_7 being +137.7 kJ mol^{-1} and +139.7 kJ mol^{-1} respectively[a]. [f]$\Delta H^{\phi}_{f(s)}$, −1113.4 kJ mol^{-1} for Tc_2O_7 and −1238.0 kJ mol^{-1} for Re_2O_7, J. W. Cobble, W. T. Smith, Jr. and G. E. Boyd, *J. Am. Chem. Soc.*, *75*, 5773 (1953) *et seq.* [g]For $H_2O_2 \rightarrow 2H^- + 2O^+$: for $H_2O_2 \rightarrow 2H^+ + 2O^-$, ΣB_2 = 3.41 MJ mol^{-1}. [h]$2B^{+2} + 2O^{-2}$. [i]$2Al^{+2} + 2O^{-2}$.

TABLE III. Bond Dissociation Energies in Sulphur Compounds.

Compound	$\Delta H^{\phi}_{f(g)}$/kJ mol^{-1}	$\bar{D}_1$/kJ mol^{-1}	$\bar{D}_2$/kJ mol^{-1} [d]
HS	+133.9	322	481[e]
H_2S	−20.6	347	1132[f]
MgS	+138.9	246	2769
BS	+334.8	474	4037
AlS	+200.8	359	3088
CS	+230.1	721	4495
CS_2	+117.1	536	8011
SiS	+70.8	618	3316
GeS	+79.7[a]	542	3176
NS	+263.6	447	4113[g]
PS	+156.1	416	3666
Sb_4S_6	−124.7[a]	217	2075
OS	+6.1	481	4386[h]
S_2	+129.0	347	–
S_4	+132.8[b]	205	–
S_6	+114.9[b]	219	–
S_8	+102.3	225	–
Cl_2S	−19.7	250	1673[i]
ZnS	+63.1[c]	304	3279
HgS	+12.6[c]	287	3438

[a]Ref. 6. [b]H. Braune, S. Peter and V. Neveling, *Z. Naturforsch.*, *6a*, 32 (1951). [c]NBS Technical Note 270-3, Washington, D.C. (1968). [d]For ionisation to S^{-2} or S^- unless noted otherwise. [e]For $HS \rightarrow H^- + S^+$: D_2 for $HS \rightarrow H^+ + S^-$ is 1435 kJ mol^{-1}. [f]for $H_2S \rightarrow 2H^- + S^{+2}$: $\bar{D}_2$ for $H_2S \rightarrow 2H^+ + S^{-2}$ is 1827 kJ mol^{-1}. [g]For $NS \rightarrow N^{-2} + S^{+2}$: D_2 for $NS \rightarrow N^{+2} + S^{-2}$ is 5040 kJ mol^{-1}. [h]For $OS \rightarrow O^{-2} + S^{+2}$: D_2 for $OS \rightarrow O^{+2} + S^{-2}$ is 5517 kJ mol^{-1}. [i]For $Cl_2S \rightarrow 2Cl^+ + S^{-2}$: $\bar{D}_2$ for $Cl_2S \rightarrow 2Cl^- + S^{+2}$ is 2224 kJ mol^{-1}.

TABLE IV. Bond Dissociation Energies in Oxo-anions.

Anion	Compound	$-\Delta H_f^\phi$/kJ mol^{-1}		$\bar{D}_2$/kJ mol^{-1}
(i) Carbonate				
	Na_2CO_3	1130.9[a]		5913
	K_2CO_3	1150.2[a]		5927
	Rb_2CO_3	1128.0[b]		5936
	Cs_2CO_3	1160.6[b]		5949
			mean	5931
(ii) Nitrate(V)				
	$NaNO_3$	466.5[b]		9748
	KNO_3	492.9[b]		9748
	$RbNO_3$	489.5[b]		9750
	$CsNO_3$	494.1[b]		9749
			mean	9749
(iii) Nitrate(III)				
	$NaNO_2$	359.4[b]		5618
	KNO_2	370.3[b]		5616
			mean	5617
(iv) Sulphate(VI)				
	Na_2SO_4	1384.5[b]		7769
	K_2SO_4	1433.9[b]		7774
	Rb_2SO_4	1424.7[b]		7780
	Cs_2SO_4	1420.0[b]		7777
			mean	7775
(v) Sulphate(IV)				
	Cs_2SO_3	1102.9[c]		4741
	$SrSO_3$	1169.0[d]		4758
	$PbSO_3$	656.9[d]		4803
	Ag_2SO_3	478.6[d]		4845
	$CdSO_3$	690.4[c]		4827
			mean	4795
(vi) Selenate(VI)				
	Na_2SeO_4	1093.3[e]		7443
	K_2SeO_4	1110.0[f]		7437
	$MgSeO_4$	983.2[g]		7475
	Tl_2SeO_4	639.3[h]		7464
			mean	7455
(vii) Selenate(IV)				
	Na_2SeO_3	963.6[i]		4432
	$SrSeO_3$	1048.5[j]		4511
	$PbSeO_3$	533.0[k]		4556
	$MnSeO_3$	694.1[l]		4520
	$CdSeO_3$	579.9[m]		4580
			mean	4520
(viii) Tellurate(IV)				
	Na_2TeO_3	997.0[n]		3837
	K_2TeO_3	1012.9[n]		3855

Anion	Compound	$-\Delta H_f^\ominus$/kJ mol^{-1}		$\bar{D}_2$/kJ mol^{-1}
	Rb_2TeO_3	999.6[n]		3869
	Cs_2TeO_3	983.7[n]		3870
	$CaTeO_3$	1060.2[o]		3849
			mean	3856
(ix) Chlorate(VII)				
	$NaClO_4$	385.8[b]		10942
	$KClO_4$	431.8[p]		10946
	$RbClO_4$	434.7[b]		10950
	$CsClO_4$	434.7[b]		10946
			mean	10946
(x) Chlorate(V)				
	$NaClO_3$	358.6[b]		7348
	$KClO_3$	397.9[p]		7357
	$RbClO_3$	391.2[b]		7360
			mean	7355
(xi) Chlorate(III)				
	$NaClO_2$	304.2[b]		4636
(xii) Bromate(VII)				
	$KBrO_4$	287.4[p]		9915
(xiii) Bromate(V)				
	$KBrO_3$	359.8[p]		6746
(xiv) Iodate(VII)				
	KIO_4	460.7[p]		8767
(xv) Iodate(V)				
	KIO_3	500.0[p]		5984
(xvi) Chromate(VI)				
	Na_2CrO_4	1333.0[q]		7848
	K_2CrO_4	1388.7[r]		7852
			mean	7850
(xvii) Manganate(VII)				
	$KMnO_4$	839.3[s]		10894
(xviii) Manganate(VI)				
	Na_2MnO_4	1146.4[t]		7979
	K_2MnO_4	1184.1[t]		7991
	$BaMnO_4$	1225.9[s]		8025
			mean	7998
(xix) Technetate(VII)				
	$KTcO_4$	1014.8[u]		9101
(xx) Rhenate(VII)				
	$KReO_4$	1100.4[v]		8188

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[a] Ref. 3. [b] NBS Circular 500, Washington, D.C. (1952). [c] A. A. Shidlovskii and A. A. Voskresenskii, *Zhur. Fiz. Khim.*, *41*, 1246 (1967). [d] A. A. Shidlovskii and A. A. Voskresenskii, *Zhur. Fiz. Khim.*, *37*, 2062 (1963). [e] N. M. Selivanova and T. A. Sazykina, *Zhur. Prikl. Khim.*, *37*, 514 (1964). *Chem. Abs.*, *60*, 15215g (1964). [f] N. M. Selivanova, G. A. Zubova, I. I. Abramov, A. V. Kalinkina, and T. A. Sazykina, *Tr. Mosk. Khim-Technol. Inst.*, *38*, 21 (1962); *Chem. Abs.*, *60*, 1181f (1964). [g] N. M. Seli-

vanova, V. A. Schneider, and R. I. Ryabova, *Zhur. Neorg. Khim.*, *6*, 27 (1961). [h]N. M. Selivanova, *Zhur. Fiz. Khim.*, *32*, 1277 (1958). [i]T. V. Klushina, N. M. Selivanova and S. S. Titov, *Tr. Mosk. Khim-Tekhnol. Inst.*, *49*, 28 (1965); *Chem. Abs.*, *65*, 4733g (1966). [j]N. M. Selivanova and Z. L. Leshchinskaya, *Zhur. Neorg. Khim.*, *8*, 563 (1963). [k]N. M. Selivanova and Z. L. Leshchinskaya, *Tr. Mosk. Khim-Technol. Inst.*, *38*, 37 (1962); *Chem. Abs.*, *60*, 1181a (1964). [l]Z. L. Leshchinskaya and N. M. Selivanova, *Izv. Vyssh. Ucheb. Zaved. Khim. Khim-Tekhnol.*, *9*, 523 (1966); *Chem. Abs.*, *66*, 108978b (1967). [m]S. S. Bakeeva, E. A. Buketov and A. S. Pashinkin, *Zhur. Neorg. Khim.*, *13*, 1779 (1968). [n]T. A. Khachaturyan, K. K. Samplavskaya, and M. Kh. Karapet'yants, *Zhur. Neorg. Khim.*, *14*, 1151 (1969). [o]E. A. Ivankova, K. K. Samplavskaya, and M. Kh. Karapet'yants, *Tr. Mosk. Khim-Tekhnol. Inst.*, *54*, 5 (1967); *Chem. Abs.*, *69*, 22641m (1968). [p]G. K. Johnson, P. N. Smith, E. H. Appelman and W. N. Hubbard, *Inorg. Chem.*, *9*, 119 (1970). [q]T. Nelson, C. Moss and L. G. Hepler, *J. Phys. Chem.*, *64*, 376 (1960). [r]C. N. Muldrow, Jr., and J. G. Hepler, *J. Am. Chem. Soc.*, *79*, 4045 (1957). [s]T. A. Zordon and L. G. Hepler, *Chem. Revs.*, *68*, 737 (1968). [t]R. A. W. Hill and J. F. Williamson, *J. Chem. Soc.*, 2417 (1957). [u]J. W. Cobble, W. T. Smith Jr., and G. E. Boyd, *J. Am. Chem. Soc.*, *75*, 5777 (1953). [v]G. E. Boyd, J. W. Cobble, and W. T. Smith Jr., *J. Am. Chem. Soc.*, *75*, 5783 (1953).

TABLE V. Bond Dissociation Energies in Miscellaneous Oxo-ions.

Ion	Fragment Ions	$-\Delta H^{\phi}_{f(g)}$/kJ mol^{-1} [a]	$\bar{D}_2$/kJ mol^{-1}
HO^+	$H^+ + O$	−1317.1	462
HO^-	$H^+ + O^{-2}$	143.9	2576
H_3O^+	$3H^+ + O^{-2}$	−581.2	1637
LiO^-	$Li^+ + O^{-2}$	66.9	1650
NaO^-	$Na^+ + O^{-2}$	121.3	1629
KO^-	$K^+ + O^{-2}$	138.1	1429
BO_2^-	$B^{+3} + 2O^{-2}$	497.9	4880
AlO^+	$Al^{+3} + O^{-2}$	−1004.2	5358
AlO_2^-	$Al^{+3} + 2O^{-2}$	175.7	3720
CO_2^-	$C^{+3} + 2O^{-2}$	441.4	5508
NO^+	$N^{+3} + O^{-2}$	−990.4	9219
NO_2^+	$N^{+5} + 2O^{-2}$	−1160.6	13434
NO_2^-	$N^{+3} + 2O^{-2}$	359.4	5735

[a]All ΔH^{ϕ}_f data from JANAF tables, ref 3, except NO_2^+: NBS Technical Note 270-3, Washington, D.C. (1968).

with cation is substantially greater, probably because of covalence between cation and anion. $\bar{D}_2$ values for the ionic dissociation of a number of miscellaneous gaseous ions are set out in Table V: the values derived for nitrate(III) from the vapour-phase ΔH^{ϕ}_f and from the ΔH^{ϕ}_f values for $NaNO_2$ and KNO_2 are within 2% of one another.

Discussion

Inspection of the $\bar{D}_1$ data presented in Table I reveals a number of general trends. Firstly, and as expected, $\bar{D}$ generally decreases in species MO, M_2O or MO_2 as M becomes heavier within any group: this is a general finding for mean bond dissociation energies. Secondly when M = H, Li, Be, Al, Ga, but not B, F or Cl, $\bar{D}_1(MO) < \bar{D}_2(M_2O)$. Thirdly, for oxides MO in which M has principle quantum number n = 2 or 3, D_1 passes through a maximum at CO and SiO: this is in accord with simple concepts of bond order in these species, being 1.5 in LiO, NaO, FO and ClO and 3.0 in CO and SiO. When n = 4 or 5, D_1 decreases monotonically from GeO to BrO and from SnO to IO: amongst the d-metal oxides MO there appear to be few horizontal regularities. Similarly $\bar{D}_1$ in the oxides MO_2 exhibits a maximum at CO_2 and SiO_2, when n = 2 and 3 respectively. Fourthly, $\bar{D}_1$ generally decreases as the formal oxidation state of M increases: molybdenum is the most obvious exception but others are tellurium, xenon and vanadium. The extent to which these exceptions are real, rather than a reflection of inaccurate data cannot be judged in the absence of further experimental data.

For heterogeneous oxides only sums of bond energy terms can be deduced from experimental data, the partitioning of the atomisation enthalpy into individual bond contribution being achieved only by making the assumption that values of $\bar{D}$ can be transferred between similar molecules. Transfering data from NO and NO_2 gives B(N–N) in N_2O_3 and N_2O_4 of 46 kJ mol^{-1} and 59 kJ mol^{-1} respectively: similarly ΣB_1 for P_4O_{10} and $\bar{D}_1$ for P_4O_6 give B(P=O) in P_4O_{10} of 545 kJ mol^{-1}. In the examples of HO_2 and H_2O_2, transfer of bond energy terms implies $\bar{B}$(H–O) = 375 kJ mol^{-1} and $\bar{B}$(O–O) = 319 kJ mol^{-1} in these species.

Amongst the sulphides (Table III), the same general trends as observed for oxides appear to be manifested by the few data available. For gaseous

TABLE VI. Enthalpies of Gas-Phase Ionic Reactions.

	Reaction (gas-phase)	ΔH^{ϕ}/kJ mol^{-1}
1.	$H_2O \rightarrow H^+ + OH^-$	+1280
2.	$H_2O + H^+ \rightarrow H_3O^+$	−1055
3.	$CO_2 + O^{-2} \rightarrow CO_3^{-2}$	−603
4.	$NO^+ + O^{-2} \rightarrow NO_2^-$	−2015
5.	$NO_2^+ + O^{-2} \rightarrow NO_3^-$	−2379
6.	$N_2O_3 \rightarrow NO^+ + NO_2^-$	+783
7.	$N_2O_4 \rightarrow NO_2^+ + NO_2^-$	−1748
8.	$N_2O_5 \rightarrow NO_2^+ + NO_3^-$	+836
9.	$SO_2 + O^{-2} \rightarrow SO_3^{-2}$	−873[a]
10.	$SO_3 + O^{-2} \rightarrow SO_4^{-2}$	−1097
11.	$SeO_2 + O^{-2} \rightarrow SeO_3^{-2}$	−774[a]
12.	$SeO_3 + O^{-2} \rightarrow SeO_4^{-2}$	−1212
13.	$TeO_2 + O^{-2} \rightarrow TeO_3^{-2}$	−1094
14.	$2ClO_2 + O^{-2} \rightarrow ClO_2^- + ClO_3^-$	−1240
15.	$2ClO_3 + O^{-2} \rightarrow ClO_3^- + ClO_4^-$	−1993
16.	$Cl_2O_7 + O^{-2} \rightarrow 2ClO_4^-$	−2454
17.	$Mn_2O_7 + O^{-2} \rightarrow 2MnO_4^-$	−4157
18.	$Tc_2O_7 + O^{-2} \rightarrow 2TcO_4^-$	−4603
19.	$Re_2O_7 + O^{-2} \rightarrow 2ReO_4^-$	−1823

[a] See text.

carbonyl sulphide OCS, ΔH_f^{ϕ} is [3] −138.4 kJ mol^{-1}, so that ΣB_1 = 1339 kJ mol^{-1} almost identical with $\bar{D}_1(CO_2) + \bar{D}_1(CS_2)$ = 1338 kJ mol^{-1}: however, for gaseous OS_2, ΔH_f^{ϕ} is [3] −56.4 kJ mol^{-1}, so that ΣB_1 = 782 kJ mol^{-1}: this is not reproduced by transfering bond energy terms for analogous molecules, since $\bar{D}_1(SO_2) + D_1(S_2)$ = 863 kJ mol^{-1} and $D_1(SO) + D_1(S_2)$ = 828 kJ mol^{-1}. For a number of sulphides, MS_p, $\bar{D}_2$ is smaller for the dissociation into M^{-2p} and S^{+2} than for the reverse dissociation into M^{+2p} and S^{-2} *e.g.* when M = H, N, O but not Cl. The oxides exhibit this behaviour when M = H, but not N and when M = F, Cl, Br but not I; for halogen oxo-species MO, the difference between the D_2 values, $D_2(M^+, O^-) - D_2(M^-, O^+)$ becomes less positive as M becomes heavier, and is negative when M = I, doubtless reflecting the increasing metallic character of the heavier halogens.

The data in Tables I–III indicate that, without exception $\bar{D}_1 < \bar{D}_2$ and $\Sigma B_1 < \Sigma B_2$, even for such highly ionic compounds as $KO_{(g)}$: this generalisation is probably more a reflection of the work expended in charge separation than of the charge distribution in the undissociated molecules.

In oxoanions, $\bar{D}_1$ for the dissociation into neutral atoms cannot be defined, and for comparison of bond dissociation energies in a neutral oxide MO_p and the oxoanion containing M in the same oxidation state such as MO_{p+1}^{-2}, $\bar{D}_2$ must be employed. Values for common anions are in Table IV: as with all such values, the $\bar{D}_2$ values in the Table are dominated by $\Sigma I(M)$. By combining data from Tables I, II, IV and V, enthalpies of gas-phase ionic reactions can be calculated, and a number of these are set out in Table VI. Of these enthalpies, those for reactions 9 and 11 are unlikely to be very accurate since the $\bar{D}_2$ values in SO_3^{-2} and SeO_3^{-2} are themselves not likely to be very accurate, as discussed earlier. If values of $\bar{D}_2$ are taken only from Cs_2SO_3 and Na_2SeO_3 respectively, the ΔH^{ϕ} values for reactions 9 and 11 become −711 kJ mol^{-1} and −510 kJ mol^{-1} respectively.

References

1 C. Glidewell, *Inorg. Chim. Acta, 15,* 85 (1975).
2 C. Glidewell, *J. Coordination Chem., 6,* 189 (1977).
3 "JANAF Thermochemical Tables", Dow Chemical Co., Midland, Michigan, 1965 *et seq.*
4 B. Lakatos, J. Bohus and G. Medgyesi, *Acta Chim. Hung., 20,* 1 (1959).
5 L. Brewer, *Chem. Revs., 52,* 1 (1953).
6 O. Kubaschewski, E. Ll. Evans and C. B. Alcock, "Metallurgical Thermochemistry", Pergamon, Oxford (1967).
7 K. B. Yatsimirskii, "Thermochemistry of Complex Compounds", Moscow (1951).
8 E. Mooser and W. B. Pearson, *Acta Cryst., 12,* 1015 (1959).