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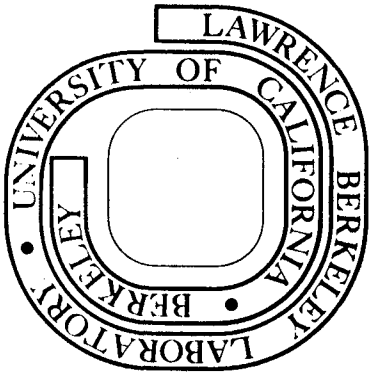

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DISCLAIMER

THE CALCULATION OF HEATS OF FORMATION OF GASEOUS CATIONS FROM CORE ELECTRON BINDING ENERGIES

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ABSTRACT

It is shown that the "core replacement energy" of an atom in a gaseous species is equal to a core binding energy plus the difference between the heats of formation of two isoelectronic species and that it is essentially a constant quantity for the atom, almost independent of the nature of the gaseous species. Core binding energies and heats of formation of gaseous molecules have been combined with the appropriate core replacement energies to calculate the heats of formation of 156 gaseous cations.

INTRODUCTION

The equivalent cores approximation [1-4] may be expressed as follows: The energy of the process in which an electron is transferred from a core level of an atom to the nucleus of the atom is independent of the chemical environment of the atom. Consider, for example, the following specific example of this process, involving the nitrogen atom of the gaseous ammonium ion:

$$NH_4^+ \longrightarrow CH_4^{*+} \tag{1}$$

The asterisk is used to indicate a 1s vacancy. Although reaction 1 is balanced with respect to electrons, protons, and neutrons (assuming the N and C atoms have the same mass numbers), it is not balanced with respect to the elements, as is a normal chemical reaction. The reaction can be converted into a balanced chemical reaction, with its energy changed by a constant amount, by the appropriate addition of the elements nitrogen and carbon in their standard states:

$$C_{graphite} + NH_4^+ \longrightarrow \tfrac{1}{2}N_2 + CH_4^{*+} \tag{2}$$

According to the equivalent cores approximation, all reactions of this type, involving nitrogen-containing cations and the corresponding core-ionized carbon compounds, have the same energy. This energy is called the core replacement energy and is given the symbol Δ_N.

The core ionization of methane has an energy equal to the binding energy of the core electron, $E_B(CH_4)$, and is represented by the following reaction.

$$CH_4 \longrightarrow CH_4^{*+} + e^- \tag{3}$$

By subtracting reaction 3 from reaction 2, we obtain reaction 4, which has the energy $\Delta_N - E_B(CH_4)$.

$$C_{graphite} + NH_4^+ + e^- \longrightarrow \tfrac{1}{2}N_2 + CH_4 \qquad (4)$$

It should be noted that reaction 4 is a normal chemical reaction involving no core-ionized species. The energy of reaction 4 can be equated to the heat of formation of methane minus the heat of formation of the ammonium ion:

$$\Delta_N - E_B(CH_4) = \Delta H_f^\circ(CH_4) - \Delta H_f^\circ(NH_4^+)$$

Thus it has been possible to calculate Δ_N from the core binding energy of methane, measured by X-ray photoelectron spectroscopy, and the heats of formation of CH_4 and NH_4^+ [5]. In essentially the same way, Δ_N has been calculated from 7 other carbon 1s binding energies and the appropriate thermochemical data [5]. The average of all 8 values was 283.68 eV, with a standard deviation of 0.21 eV. This result shows that it should be possible to calculate the heat of formation of any gaseous nitrogen-containing cation with an uncertainty of approximately 0.2 eV if one knows accurate values for the heat of formation and the carbon 1s binding energy of the isoelectronic carbon compound.*

Values of Δ_O have been calculated for oxygen-containing cations from nitrogen 1s binding energies and the heats of formation of the appropriate

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*In ref. [5] it is shown that cations such as NO^+, in which the nitrogen atom has a valence lone pair, have significantly higher Δ_N values. However, such species are fairly rare, and the value 283.68 eV is almost always appropriate.

nitrogen compounds and oxygen-containing cations [5]. It was found that Δ_O = 399.63 eV (std. dev. = 0.29 eV) for ions such as O_2^+, NO^+, and RCO^+, in which the nonbonding valence electrons on the oxygen atoms have relatively high s character, and Δ_O = 399.04 eV (std. dev. = 0.24) for ions such as OH_3^+ and R_2OH^+, in which the nonbonding valence electrons on the oxygen atoms have relatively low s character. Obviously these Δ_O values can be used with appropriate binding energy and thermodynamic data to calculate heats of formation of gaseous oxygen-containing cations.

In this study we have calculated values of Δ_C, Δ_F, Δ_P, Δ_S and Δ_{Cl} from appropriate binding energy and thermodynamic data. These values, as well as the previously determined values of Δ_N and Δ_O, were used with the required binding energy and thermodynamic data to calculate heats of formation of some gaseous cations containing carbon, nitrogen, oxygen, fluorine, sulfur, and chlorine for which reliable heats of formation were previously unknown. We thus hope to bring this relatively unknown method for obtaining thermodynamic data to the attention of scientists concerned with gaseous cations.

RESULTS AND DISCUSSION

Tables 1, 2 and 3 list values of the core replacement energies calculated for cations containing carbon, fluorine, phosphorus, sulfur, and chlorine. The average values of each set of core replacement energies, and the average values previously calculated [5] for nitrogen- and oxygen-containing cations, are given in Table 4 These Δ values are recommended for use in the calculation of the heats of formation of gaseous cations.

Using available core binding energies and heats of formation of gaseous molecules together with the core replacement energies in Table 4, we have

calculated the heats of formation of 156 different gaseous cations. The values are listed in Table 5. The uncertainties in these calculated heats of formation are the combined uncertainties in the core replacement energies (see Table 4), the core binding energies (0.05-0.2 eV), and the heats of formation of the molecules (0.5-30 kcal/mol). Most of the calculated values are believed to have uncertainties of ±8 kcal/mol or less.

The heats of formation of several cations can be calculated by the general method which we have outlined using two or more completely independent sets of data. For example, the heat of formation of NF_4^+ can be calculated either from data for CF_4 or from data for ONF_3. The results of such calculations, summarized in Table 6, serve as an indicator of the general reliability of the method. The average deviation between the independently calculated heats of formation in Table 6 is ±13 kcal/mol.

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TABLE 1

Core replacement energies for carbon-containing cations

Compounds	E_B(B 1s), eV	E_B Ref.	Δ_C, eV	ΔH_f° Ref.
CF_3^+/BF_3	202.8	[6]	186.7	[7,8]
CCl_3^+/BCl_3	200.2	[6,9]	186.7	[7]
$C(OCH_3)_3^+/B(OCH_3)_3$	198.1	[6,9]	185.8	[7,10]
$H_2CH_2BH_2^+/B_2H_6$	196.5	[6,9]	186.2[a]	[7,9]
$C(CH_3)_3^+/B(CH_3)_3$	196.4	[9]	187.8	[7,11,12]
CH_3CO^+/BH_3CO	195.2	[9]	187.5	[7,13]
$N(CH_3)_4^+/BH_3N(CH_3)_3$	193.5[b]	[9,14]	187.2[c]	[9,13]

[a]Because of uncertainty in the estimated heat of formation of $H_2CH_2BH_2^+$, this value was assigned a weight of 0.3 in calculating the average. [b]The value taken from ref. 14 was raised by 0.17 eV because of the use of 248.62 eV as the Ar $2p_{3/2}$ reference. [c]Because of uncertainty in the calculated heat of formation of $N(CH_3)_4^+$, this value was assigned a weight of 0.5 in calculating the average.

TABLE 2

Core replacement energies for fluorine-containing cations

Compounds	E_B(O 1s), eV	E_B Ref.	Δ_F, eV	ΔH_f Ref.
OF^+/O_2	543.75[a]	[15]	529.83	[16]
NF^+/NO	543.5[a]	[17]	529.3	[7]
CF^+/CO	542.57	[18]	529.52	[7,19]
N_2F^+/N_2O	541.4[b]	[17]	528.3	[7]
CF_3^+/COF_2	540.77[c]	[20]	529.88	[7,8]
SO_2F^+/SO_3	540.68	[21]	531.20[d]	[7]
H_2F^+/H_2O	539.88	[22]	529.17	[7, 23]
$CFCl_2^+/COCl_2$	539.72[c]	[20]	529.60[d]	[7]
SOF^+/SO_2	539.70	[21]	530.31[d]	[7]
SF_3^+/SOF_2	539.6[b]	[17]	529.0[e]	[7,24]
CH_2F^+/CH_2O	539.52[b]	[25,26]	529.22	[7]
CH_3FH^+/CH_3OH	539.2[b]	[17]	530.7	[7,27]
CH_3CHF^+/CH_3CHO	538.6[c]	[20,25]	529.7	[7,28]
$(CH_3)_2CF^+/(CH_3)_2CO$	538.00[c]	[20,25]	529.77	[7,28]

[a]Weighted average of spin-split peaks. [b]Based on an O_2 reference E_B of 543.75 eV. [c]Based on an Ar $2p_{3/2}$ reference of 248.62 eV. [d]Because of uncertainty in the heats of formation of the gaseous cations, these values were weighted 0.3 in calculating the average. [e]Because of uncertainty in the heat of formation of SF_3^+, this value was weighted 0.1 in calculating the average.

TABLE 3

Core replacement energies for phosphorus, sulfur, and chlorine-containing cations

Compounds	E_B, eV	Core level	Δ, eV	E_B Ref.	ΔH_f° Ref.
PH_4^+/SiH_4	107.45[a]	Si $2p_{3/2}$	99.29	[29]	[7,30]
SF_5^+/PF_5	145.66[b]	P $2p_{3/2}$	127.17	[31]	[7,13,32]
SF_3^+/PF_3	141.80[c]	P $2p_{3/2}$	126.94	[21]	[7,33]
SH_3^+/PH_3	137.04	P $2p_{3/2}$	128.81	[14]	[13,34,35]
ClO_3^+/SO_3	176.67	S $2p_{3/2}$	159.34	[21]	[7]
ClO_2^+/SO_2	174.64	S $2p_{3/2}$	159.50	[21]	[7]
H_2Cl^+/H_2S	170.4	S $2p_{3/2}$	161.4	[17]	[7,36]

[a]The value differs from that given in Ref. [29] because of a recalibration of the spectrometer. Also see note c. [b]Calcd. assuming a $2p_{3/2}$-$2p_{1/2}$ splitting of 0.84 eV. [c]Based on an Ar $2p_{3/2}$ reference of 248.62 eV.

TABLE 4

Recommended values of core replacement energies

Element in cation	Core level for which E_B required	Δ, eV	Uncertainty in Δ, eV[a]
C	B 1s	186.89	0.73
N	C 1s	283.68	0.21
O (high s density)	N 1s	399.63	0.29
O (low s density)	N 1s	399.04	0.24
F	O 1s	529.60	0.66
P	Si $2p_{3/2}$	99.29	----
S	P $2p_{3/2}$	127.6	1.0
Cl	S $2p_{3/2}$	160.1	1.1

[a]Standard deviation.

TABLE 5

Calculated heats of formation of cations

Cation	ΔH_f°, kcal/mol	Refs.[a]
From boron 1s binding energies:		
$C(C_2H_5)_3^+$	161	[6]
$C(OC_2H_5)_3^+$	6	[6][13]
CBr_3^+	230	[6]
CI_3^+	268	[6]
From carbon 1s binding energies:		
$HCCNH_3^+$	231	[37]
$HCNCH_3^+$	215	[37]
$\overline{CH_2CH_2NH_2}^+$	172	[38]
$CH_3CCNH_3^+$	211	[37]
$CH_3CNCH_3^+$	181	[37]
$C_6H_5NH_3^+$	165	[21]
$C_5H_5NCH_3^+$	165	[21]
$H_3CN_2^+$	225	[21]
H_3NCN^+	225	[21]
$H_2CCHN_2^+$	239	[21]
H_2CNHCN^+	239	[21]
H_2NCHCN^+	239	[21]
$(CH_3)_2NNH_3^+$	169	[14]
$\overline{HNCHCHNHCH}^+$	172	[39]
$\overline{HNNHCHCHCH}^+$	195	[39]

TABLE 5 (contd.)

$C_6H_5N_2^+$	246	[21]
$C_5H_5NCN^+$	222	[21]
NH_2O^+	219	[40]
NH_3OH^+	158	[17,41]
$H(NO)OH^+$	190	[40]
$H(NO)NH_2^+$	199	[20]
$OCCNO^+$	250	[42]
$OCNCO^+$	255	[42]
$\overline{NH_2CH_2O}^+$	195	[38,41]
NH_3CHO	137	[21]
CH_3NHO^+	198	[20]
NH_3COOH^+	79	[17]
CH_3NOOH^+	172	[17]
$NH_3CH_2OH^+$	115	[17]
$CH_3NH_2OH^+$	147	[17]
$CH_3ONH_3^+$	155	[29]
CH_2CHNHO^+	205	[20]
CH_2NHCHO^+	150	[21]
$NH_2{=}CHCHO^+$	150	[21]
$NH_2{=}CHOCH_3^+$	117	[21]
$CH_2NHOCH_3^+$	168	[21]
$CH_2CHONH_3^+$	168	[21]
$(CH_3)_2NO^+$	183	[21]
$NH_3COCH_3^+$	122	[21]
$NH_3(CH_3)NCHO^+$	139	[21]

TABLE 5 (contd.)

$(CH_3)_2NNHO^+$	172	[20]
$\overline{OCHCHNHCH}^+$	144	[39]
$\overline{ONHCHCHCH}$	172	[39]
$C_2H_5(NO)OC_2H_5^+$	141	[17]
$C_6H_5NHO^+$	208	[20]
$C_6H_5(NO)CH_3^+$	194	[20]
$(C_6H_5)_2NO^+$	225	[20]
NH_3F^+	164	[43]
$NH_2F_2^+$	186	[22]
NHF_3^+	191	[20][44,45]
NF_4^+	198	[22,29][45-47]
NOF_2^+	216	[20][13]
CH_2NHF^+	198	[48]
NH_2CHF^+	142	[48]
$CH_2NF_2^+$	207	[48]
$NH_2CF_2^+$	97	[48]
$CHFNF_2^+$	178	[48]
$NHFCF_2^+$	123	[48]
$NF_3CF_3^+$	62	[48]
$\overline{CF_2CF_2CF_2NF_2}^+$	-52	[48][45]
$C_5NF_6^+$	9	[49]
$Si(CH_3)_3NH_3^+$	83	[29,50]
$(CH_3)_2PNH_3^+$	129	[14]
$CH_3SNH_3^+$	164	[21]
ONS^+	236	[51]

TABLE 5 (contd.)

NH_3Cl^+	184	[29]
$NH_2Cl_2^+$	216	[43]
$NHCl_3^+$	241	[43]
NCl_4^+	268	[29]
$NOCl_2^+$	249	[20][13]
$NH_3SiCl_3^+$	40	[21,50]
$N(CH_3)_3Cl^+$	152	[21]
$V(CO)_5NO^+$	39	[52][53]
$C_5H_5V(CO)_3NO^+$	16	[52]
$Cr(CO)_5NO^+$	-20	[21]
$C_5H_5Mn(CO)_2NO^+$	99	[21]
$Mn_2(CO)_9NO^+$	-179	[21][54]
$Ni(CO)_3NO^+$	88	[21]
$Ge(CH_3)_3NH_3^+$	106	[29,50]
$BrNF_3^+$	204	[21]
NH_3Br^+	186	[29]
NBr_4^+	276	[29]
$Mo(CO)_5NO^+$	1	[21]
$Sn(CH_3)_3NH_3^+$	133	[55]
$W(CO)_5NO^+$	10	[21]

<u>From nitrogen 1s binding energies, using Δ_O = 399.04 eV</u>:

$O(CH_3)_3^+$	127	[14]
$(CH_3)_3OBH_3^+$	156	[21][13]
OH_2CHO^+	121	[21]

TABLE 5 (contd.)

$CH_3O_3^+$	285	[48]
$(CH_3)_2OCHO^+$	103	[21]
$C_6H_5O_3^+$	305	[17]
$C_6H_5OH_2^+$	170	[17][56]
$H_2NOH_2^+$	186	[57]
NOO^+	330	[57]
$F_2NOF_2^+$	304	[57]
OOF_3^+	374	[21][58]

From nitrogen 1s binding energies, using Δ_0 = 399.63 eV:

$C_6H_5CO^+$	173	[21]
OF_3^+	304	[57][44,45]
$OOCl^+$	284	[57][13]
SOF_3^+	66	[59][60]

From oxygen 1s binding energies:

$\overline{CH_2CH_2F}^+$	201	[41]
$(CH_3)_2F^+$	163	[29]
$C_2H_5FH^+$	156	[17]
CH_2CHCHF^+	171	[20]
$CH_2CHFCH_3^+$	186	[21]
$\overline{CHCHCHCHF}^+$	230	[48]
$C_6H_5CHF^+$	172	[20]
$C_6H_5(CF)CH_3^+$	151	[20]
$(C_6H_5)_2CF^+$	178	[20]

TABLE 5 (contd.)

NF_4^+	214	[21][61]
NH_2CHF^+	139	[20]
$(CH_3)_2NCHF^+$	116	[20]
OCF^+	179	[22]
$H(CO)FH^+$	163	[25]
$H(CF)OH^+$	125	[25]
$CH_3(CF)OH^+$	141	[17]
$OCCCF^+$	225	[42]
$CH_3(CF)OCH_3^+$	92	[25]
$CH_3(CO)FCH_3^+$	128	[25]
F_3^+	354	[15]
$[(CH_3)_3Si]_2F^+$	-16	[21,50]
PF_4^+	-77	[62][58]
SCF^+	224	[51]
SOF_3^+	70	[62][63]
$ClO_2F_2^+$	262	[62]
$SOFCl_2^+$	142	[62][13]
$SFCl_2^+$	166	[21][13]
$PFCl_3^+$	59	[62]
$VFCl_3^+$	48	[62][53]
$V(CO)_5CF^+$	2	[52][53]
$C_5H_5V(CO)_3CF^+$	30	[52]
$CrOFCl_2^+$	89	[62]
$Cr(CO)_5CF^+$	-8	[21]
$C_5H_5Mn(CO)_2CF^+$	105	[21]

TABLE 5 (contd.)

$Mn_2(CO)_9CF^+$	-172	[21][54]
$Ni(CO)_3CF^+$	98	[21]
$Mo(CO)_5CF^+$	13	[21]
$W(CO)_5CF^+$	21	[21]
<u>From silicon $2p_{3/2}$ binding energies</u>:		
$P(CH_3)_4^+$	100	[29]
PF_4^+	-94	[29]
PCl_4^+	103	[29]
PBr_4^+	145	[29][13]
<u>From phosphorus $2p_{3/2}$ binding energies</u>:		
$S(CH_3)_3^+$	168	[14]
SOF_3^+	67	[21][13]
SCl_3^+	211	[14]
$SOCl_3^+$	175	[14]
$SSCl_3^+$	213	[14][58]
<u>From sulfur $2p_{3/2}$ binding energies</u>:		
$Cl(CH_3)_2^+$	198	[21]
$OCCl^+$	208	[51]
$OClCl_2^+$	282	[21][13]
$O_2ClCl_2^+$	281	[21][13]
ClF_4^+	232	[31]
ClF_6^+	184	[17]

TABLE 5 (contd.)

F_5ClCl^+	195	[59][13]
$ClOF_2^+$	246	[17][24]
$ClO_2F_2^+$	225	[21][63]
PCl_4^+	115	[14][58]
$ClSClCl^+$	263	[59][13]
$SCCl^+$	256	[17]

[a]The first set of references is to the source of the binding energy; the second set of references is to the source of the heat of formation. If only one set of references is given, the references refer to the binding energy, and the heat of formation was taken from ref. 7. Some of the binding energies used in the calculations differ from the literature values because of changes in standard references and because of spectrometer recalibration.

TABLE 6

Heats of formation of cations calculated from more than one core binding energy

Cation	Compound whose E_B and ΔH_f° used to calc ΔH_f°	ΔH_f°, kcal/mol
NF_4^+	$\overset{*}{C}F_4$	198
	$\overset{*}{O}NF_3$	214
NH_2CHF^+	$NH_2C\overset{*}{H}O$	139
	$\overset{*}{C}H_2CHF$	142
PF_4^+	$\overset{*}{S}iF_4$	-94
	$P\overset{*}{O}F_3$	-77
PCl_4^+	$\overset{*}{S}iCl_4$	103
	$P\overset{*}{S}Cl_3$	115
SOF_3^+	$\overset{*}{S}O_2F_2$	70
	$\overset{*}{P}OF_3$	67
	$\overset{*}{N}SF_3$	66
$ClO_2F_2^+$	$\overset{*}{S}O_2F_2$	225
	$Cl\overset{*}{O}_3F$	262

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