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A simple rule of the sequential bond enthalpies in clusters and the possibility of liquid-phase carbon

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ABSTRACT

This letter reports a simple rule on the sequential bond enthalpies $D(B(M)_x-M)$ in clusters $B(M)_{x+1}$, where B is a bonding particle (neutrals, cations, anions, complexes, biochemical particles), M is a neutral material molecule (inorganic and organic) or atom (metal, non-metal and rare gas), x describes the cluster size, and $x=0, 1, 2, 3, \ldots$, etc. Thousands of experimental results for 60 kinds of materials M and 310 kinds of clusters $B(M)_{x+1}$ strongly support the simple rule: the sequential bond enthalpies in clusters regularly drop to an intrinsic value, the vaporization enthalpies of the liquid-phase materials M, i.e., $D(B(M)_x-M$, large $x) \sim \Delta_{vap}H(M)$. Using this simple rule, we have discussed the possibility of liquid-phase carbon.

1. Introduction

The experimental and theoretical studies of cluster energetics have been one of the hot topics in physics, chemistry, and materials science since the 1970s. This is because the studies reveal essential information for catalysis, nano-materials, surface science (like wetting, etching, thin-film growth, adsorption, diffusion and corrosion), combustion, nuclear fusion, bioengineering, space science, clouds, fogs, smog, and environmental science. Kebarle and co-workers measured the thermodynamics in the ion-H_2O clusters [1]. They found that the bond enthalpies $D(H_3O^+(H_2O)_x–H_2O)$ and $D(HO^-(H_2O)_x–H_2O)$ in the large-size clusters are close to the macroscopic vaporization enthalpy of bulk liquid water. This result has been critically re-examined by Castleman, Meot-Ner and many research groups, based on more experiments on the ion-water clusters [2–4]. Armentrout [5] supposed that the sequential bond enthalpies in metal clusters could approach the vaporization enthalpy of fused metals (Ti, V, Cr, Fe, Co, Ni, Nb and Ta).

This letter will take much more experimental BDE data to inspect the sequential bond enthalpies in a variety of clusters. We will discuss the possibility of liquids-phase carbon using information of the bond enthalpies in carbon clusters.

2. Results and discussions

A database of chemical bond enthalpies is available [6]. It allows us to completely search the sequential bond enthalpies $D(B(M)_x-M)$ in clusters $B(M)_{x+1}$, where B is a bonding particle (neutrals, cations, anions, complexes, biochemical particles), M is a neutral materials molecule (inorganic and organic) or atom (metal, non-metal and rare gas), x describes the cluster size, and $x=0, 1, 2, 3,...$, etc. As shown in Table 1, we have tabulated the experimental information for 60 kinds of materials M and 310 kinds of clusters $B(M)_{x+1}$.

For example, the information for 111 kinds of ion-H_2O clusters $B(H_2O)_{x+1}$ is shown in Table 1. For this case, the bonding particle B is a simple positive ion (22 kinds), simple negative ion (4 kinds), positive ion complex (60 kinds), or negative ion complex (25 kinds). From database [6], the $D(B(H_2O)_x-H_2O)$ in clusters $B(H_2O)_{x+1}$ step-by-step decrease and approach a value, 10.5 kcal/mol, i.e., the macroscopic vaporization enthalpy of liquid water at 298 K. All effects of the 111 different ions (positive, negative, simple, complicated, multicharged or biochemical) in Table 1 disappear. This interesting trend is shown in Fig. 1(a). This important fact drives us to carefully re-think about old and essential subjects—solutions, hydration, solvent (water) effect, structure of aqueous solutions, structure and stability of ion-water complexes and water-shared ion-pair complexes, precipitations, as well the phase change between vapor and liquid water.

We have scanned 16 metals M and 27 kinds of metal clusters $B(M)_{x+1}$, as shown in Table 1. Here, the bonding particle B is a neutral atom, atomic dimer, positive ion, or negative ion. The sequential bond

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Table 1
The 60 materials M and 310 clusters $B(M)_{x+1}$ support the simple rule: $D(B(M)_x{-}M$, large $x) \sim \Delta_{vap}H(M)$

No.	Materials (M)	$\Delta_{vap}H(M)$[a], in kcal/mol	Bonding particles (B)	Number of B
1	H_2O	10.5	(a) simple positive ions (22): Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^+, Mg^{2+}, Ca^+, Ca^{2+}, Sr^+, Sr^{2+}, Ba^{2+}, Cr^+, Co^+, Ni^+, Ni^{2+}, Cu^+, Cu^-, Ag^+, Al^+, Pb^+, Bi^+ (b) simple negative ions (4): F^-, Cl^-, Br^-, I^- (c) positive ion complexes (60): $Na^+(NaI)$, CH_5^+, $C_2H_5^+$, $iC_3H_7^+$, $C_6H_6^+$, H_4N^+, $H_4N^+(NH_3)$, $H_4N^+(NH_4I)$, H_3NCHO^+, $CH_3NH_3^+$, CH_3CNH^+, $(CH_3)_2NH_2^+$, $(CH_3CN)_2H^+$, $nC_3H_7NH_2^+$, $nC_3H_7NH_3^+$, $(CH_3)_3NH^+$, $NH_2(CH_2)_2NH_3^+$, $NH_2(CH_2)_3NH_3^+$, (pyridine)H^+, $OH(CH_2)NH_3^+$, (imidozoly)H^+, OH^+, H_3O^+, $OH(H_2SO_4)^+$, H_2COH^+, $OH(H_2SO_4)_2^+$, $OH(H_2SO_4)_3^+$, $CH_3OH_2^+$, $(CH_3OH)_2H^+$, $C_2H_5OH_2^+$, $nC_3H_7OH_2^+$, $iC_3H_7OH_2^+$, CH_3CO^+, t-$C_4H_9OH_2^+$, CH_3CHOH^+, $(CH_3)_2OH^+$, $C_2H_5CO^+$, $(CH_3)_2COH^+$, $((CH_3)_2CO)_2H^+$, $((CH_3)_3CO)_3H^+$, $CH_3COOH_2^+$, $(CH_3COOH)_2H^+$, $(nC_3H_7)_2OH^+$, $(CH_3(OC_2H_4)_3OCH_3)H^+$, (1,2-propanediol)$H^+$, $(CH_3O(CH_2)_2OCH_3)H^+$, $((CH_3CO)_2CH_2)H^+$, $((CH_3CO)_2C_2H_4)H^+$, cyclo-$C_3H_5(CH_3CO)H^+$, (cyclo-$C_3H_5)_2COH^+$, $nC_5H_{11}OH_2^+$, H_3S^+, (hemin)$^+$, (hemin-histidine)$^+$, $GlyH^+$, $TrpH^+$, $TrpGlyH^+$, $GlyNa^+$, $GlnNa^+$, $(AcAlaOCH_3)H^+$ (d) negative ion complexes (25): CH_3^-, cyclo-$C_5H_5^-$, OH^-, CN^-, NO_2^-, NO_3^-, PO_3^-, CO_4^-, $(OH)_2(PO_2)^-$, CH_3CO^-, $HCOO^-$, H_3COO^-, $ClOO^-$, BrO_3^-, IO_3^-, $CH_3COCH_2^-$, $C_6H_5COO^-$, (croconate)$^{2-}$, HS^-, CH_3S^-, SO_2^-, HSO_4^-, $(HSO_4)^-(H_2SO_4)_3$, $(HSO_4)^-(H_2SO_4)_4$, $(HSO_4)^-(H_2SO_4)_5$	111
2	Ti	100.6	Ti^+	1
3	V	109.7	V, V^+	2
4	Nb	163	Nb, Nb^+	2
5	Cr	82.2	Cr, Cr^+	2
6	Fe	83.6	Fe, Fe^+	2
7	Co	90	Co, Co^+	2
8	Ni	88.4	Ni, Ni^+	2
9	Pt	122	Pt^-	1
10	Cu	71.8	Cu, Cu^+, Cu^-	3
11	Ag	59.9	Ag^+, Ag^-	2
12	Au	79.9	Au^+, Au^-	2
13	Hg	14.2	Hg^+	1
14	B	117	B^+	1
15	Al	70.1	Al, Al^+	2
16	Li_2	37.5	Li^+	1
17	Na_2	23.2	Na^+	1
18	K_2	19.1	K^+	1
19	O_2	1.6	O_2^+, HO_2^+, O_2^-, O_3^-, F^-	5
20	CO	1.8	(a) positive ions (7): CH_3^+, SiH_3^+, O_2^+, CO^+, HCO^+, ON^+, Ar^+ (b) negative ions (2): O_4^-, F^-	9
21	CO_2	~5.7	(a) positive ions (4): ON^+, O_2^+, CO_2^+, HCO_2^+ (b) negative ions (7): CO_3^-, O_2^-, NO_2^-, F^-, Cl^-, Br^-, I^-	11
22	CH_4	2.0	(a) positive ions (7): Fe^+, Ni^+, Ag_2^+, CH_5^+, $C_2H_5^+$, $nC_3H_7^+$, $tC_4H_9^+$ (b) negative ions (1): F^-	8
23	C_2H_4	3.2	Ag^+, Ag^{2+}, Cl^-, Br^-, I^-	5
24	C_3H_6	4.0	(a) positive ions (4): Ag^+, Ag_2^+, Ag_3^+, Ag_4^+ (b) negative ions (4): F^-, Cl^-, Br^-, I^-	8
25	C_6H_6	8	$C_6H_6^+$	1
26	CF_4	2.8	CF_3^+, CF_4H^+, CF_3^-	3
27	CH_3Cl	4.8	CH_3^+, CH_2Cl^+, Cl^-	3
28	CH_2Cl_2	6.6	Cl^-	1
29	$CHCl_3$	7.2	Cl^-	1
30	CH_3OH	8.7	(a) positive ions (3): Fe^{2+}(bpy), $CH_3OH_2^+$, $(CH_3OCH_2)_2H^+$ (b) negative ions (4): F^-, Br^-, Cl^-, I^-	7
31	C_2H_5OH	9.7	$C_2H_5OH_2^+$, Cl^-, Br^-	3
32	iC_3H_7OH	10.2	$iC_3H_7OH_2^+$, Cl^-, Br^-, I^-	4
33	nC_3H_7OH	10.6	Cl^-	1
34	tC_4H_9OH	10.8	Cl−, Br^-	2
35	$nC_5H_{11}OH$	~10.6	$nC_5H_{11}OH_2^+$	1
36	CH_3COCH_3	6.5	NH_4^+, Cl^-	2
37	HC(O)OH	~11	$HCOO^-$, Cl^-	2
38	N_2	1.3	(a) positive ions (9): CH_3^+, CF_3^+, ON^+, N_2^+, $Ar(N_2)^+$, N_2H^+, N_3^+, O_2N^+, O_2^+ (b) negative ions (2): O_3^-, O_4^-	11
39	NH_3	4.7	Li^+, Na^+, NH_4^+, NH_4 (radical)	4
40	NO	3.3	ON^+	1
41	N_2O	4.0	(a) positive ions (7): H_3O^+, $C_2H_5^+$, $iC_3H_7^+$, $tC_4H_9^+$, N_2O^+, HON_2^+ (b) negative ions (6): NO^-, O_2^+, O^-, F^-, Cl^-, Br^-, I^-	13
42	HCN	6.0	(a) positive ions (2) H_2CN^+, NH_4^+ (b) negative ions (5): CN^-, CH_3COO^-, Cl^-, Br^-, I^-	7
43	HNO_3	9.3	NO_3^-	1
44	CH_3CN	7.9	(a) positive ions (3): H_2CC^+, ON^+, ON_2^+, (b) negative ions (4): F^-, Cl^-, Br^-, I^-	7
45	CH_3NHCH_3	6	$CH_3NH_2CH_3^+$	1
46	$nC_3H_7NH_2$	7	$nC_3H_7NH_3^+$	1
47	$(CH_3)_3N$	5.3	$NH(CH_3)_3^+$	1
48	Pyridine	8.4	hemin$^+$	1
50	CH_3NO_2	8.6	NO_2^-, $CH_2NO_2^-$, $CH_3NO_3^-$, $CH_3NO_4^-$, Cl^-	5
50	$C_2H_5NO_2$	~10	$C_2H_5NO_2^-$, $C_2H_5NO_4^-$	2
51	H_2S	3.4	H_2S^+, H_3S^+	2
52	OCS	4.4	$C_2H_5^+$, $HOCS^+$, F^-, Br^-	4
53	SO_2	5.7	O_2S^+, Cl^-, I^-	3
54	CS_2	6.4	S_2^+, CS_2^+, F^-, Cl^-	4
55	CH_3SOCH_3	10.3	hemin$^+$, Cl^-, Br^-	3
56	PH_3	3.5	PH_4^+	1
57	Ne	0.4	Ne^+	1
58	Ar	1.5	(a) positive ions (15): H_3^+, D_3^+, CH_3^+, N_2^+, N_2H^+, O_2^+, O_4^+, O_6^+, H_2O^+, Ar^+, $Ar(N_2)^+$, Kr^+, Kr_2^+, Xe^+, Xe_2^+, (b) negative ions (1): NO^-	16
59	Kr	2.1	Kr^+, Xe^+, Xe_2^+	3
60	Xe	3.0	Xe^+, NO^-	2

[a] The data of vaporization enthalpy $\Delta_{vap}H(M)$ are from Refs. 4, 7 and 8.

enthalpies in metal clusters approach the vaporization enthalpy of fused metals.

We have analyzed a large number of available systems. They include metal clusters, non-metal clusters, inorganic clusters, organic cluster, and rare gas clusters. Here, the bonding particle B represents various atoms, ions, neutrals, radicals and biochemical particles. The typical examples are shown in Fig. 1(b) and (c). Bowers and co-workers [9,10] have recently measured the sequential bond enthalpies in clusters $Ag_m^+(C_3H_6)_{x+1}$ in order to elucidate the catalytic properties of metal clusters. Fig. 1(b) illustrates a sum of Bowers' data and the sequential bond enthalpies in cluster $B(C_3H_6)_{x+1}$. For the eight different clusters $B(C_3H_6)_{x+1}$ (here $B=Ag^+$, Ag_2^+, Ag_3^+, Ag_4^+, F^-, Cl^-, Br^-, and I^-), the sequential bond enthalpies drop to ~4 kcal/mol, i.e., the vaporization enthalpies of liquid-phase C_3H_6.

All of the experimental information for 60 kinds of materials M and 310 kinds of clusters $B(M)_{x+1}$ strongly support the simple rule: the sequential bond enthalpies in clusters regularly drop to an intrinsic value, the vaporization enthalpies of the liquid-phase materials M, i.e.,

$$D(B(M)_x{-}M, \text{large } x) \sim \Delta_{vap}H(M) \quad (1)$$

Carbon is one of the most important elements in life. The liquid-phase carbon has never been reported at room temperature. Taking the sequential bond enthalpies $D(B(C)_x\,C)$ in clusters $B(C)_{x+1}$ (here $B=C$, $C^+$and C^-) in the database [6], we have made Fig. 1(d). The three link-lines for $B=C$, $C^+$and C^-show the interesting oscillation around a line of ~170 kcal/mol. Using the relationship (1), we infer the ~170 kcal/mol could be the vaporization enthalpy of the liquid-phase carbon. The ~170 kcal/mol is too close to 171.3 kcal/mol (the

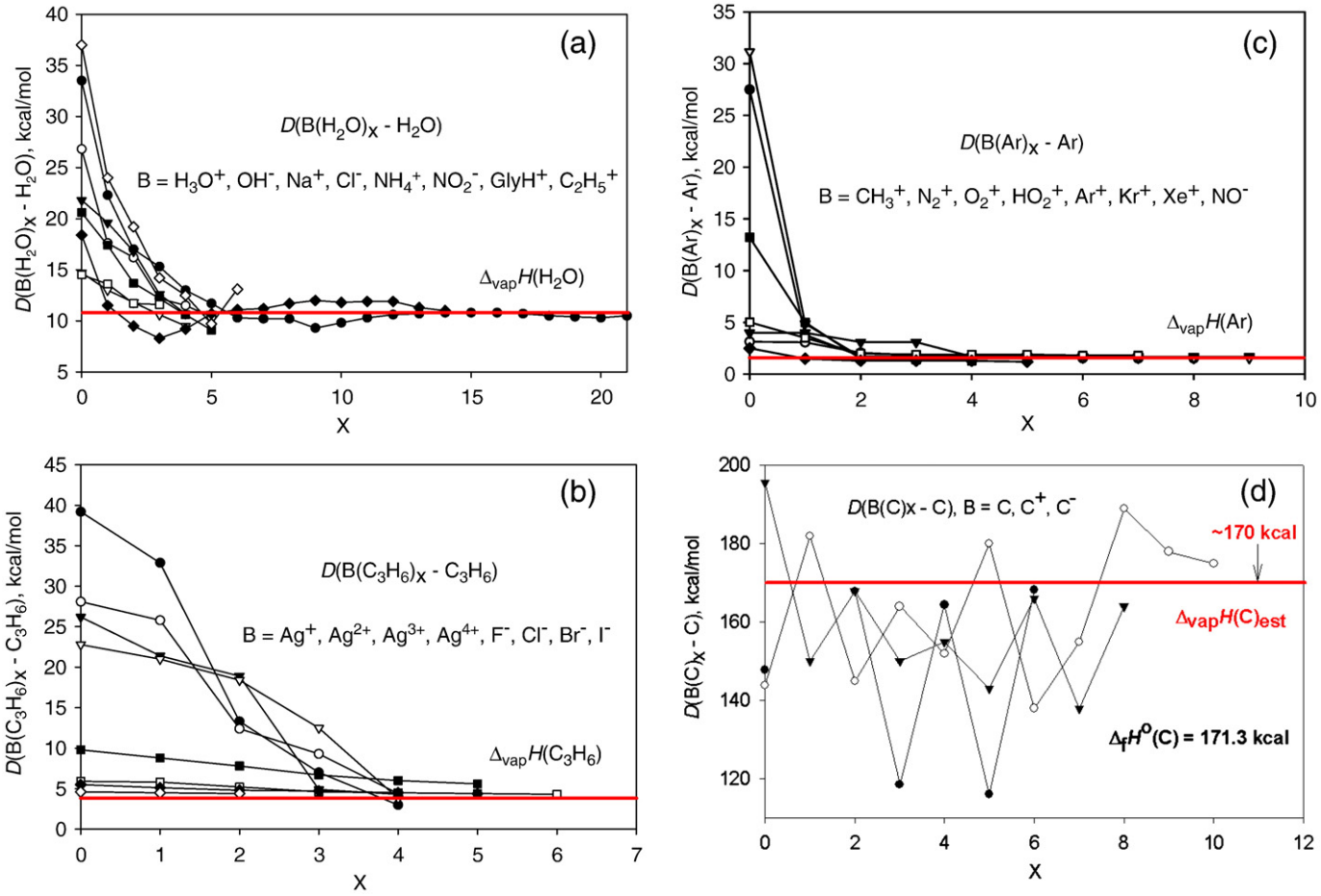

Fig. 1. Relationship between cluster size and sequential bond enthalpies. (a) H_2O, (b) C_3H_6, (c) Ar, and (d) C.

sublimation enthalpy from graphite to gas-phase carbon at 298 K). This means the preparation of the liquid-phase carbon is very difficult.

3. Conclusions

The simple rule by Eq. (1) is drawn from thousands of experimental data. We use it to predict the possibility of liquid-phase carbon.

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