

# The Noble Gas Configuration— Not the Driving Force but the Rule of the Game in Chemistry

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The seminal tool that the chemist uses to systematize elemental relationships is the periodic table. It serves as a framework, as an outline of organization, for the vast and widely diversified information of chemistry. In the discussion of the fundamental basis of periodic laws, however, it is often not easy to distinguish between cause and effect. A case in point is the traditional statement that the driving force of chemical reactions among elements is rooted in the propensity of the elements to attain the noble gas configuration. This scheme has emerged from the specific pattern found for the changes of the oxidation numbers across the periodic table in the context of the fact that the noble gases are the only elements that are stable as monatomic species under ambient conditions. The other atoms gain or lose electrons (ionic compounds) or share electrons (covalent compounds) to make a filled or empty outer layer. The noble gas configuration is said to impart a desirable level of stability into a system. Once noble-gas-configured ions are formed, the oppositely charged ions attract each other in an ionic bond.

It should be emphasized, however, that the formation of the noble-gas-configured ions is always—the only exception being the halogens—an energetically demanding process. The formation of any cation in the gas phase is endothermic, requiring ionization energy. For anions, at most only one electron can be added to a free atom in the gas phase (1). Doubly charged anions such as  $O^{2-}$  and  $S^{2-}$ , though noble-gas-configured ions, are more bookkeeping quantities than chemical entities, not amenable to direct observation. For example, the first and second electron affinities (2, 3) of the oxygen atom are +141 and about  $-745 \text{ kJ mol}^{-1}$ , respectively, and so a free oxide ion  $O^{2-}$  would lose an electron to produce the monoanion  $O^-$ . Other multiply charged monatomic anions would behave similarly (Table 1).

It is worthwhile to note that in spite of the greater electronegativity of oxygen, it is much more difficult to form  $O^{2-}$  than  $S^{2-}$  or  $Se^{2-}$ . This results from the stronger interelectronic repulsions owing to the small size of the oxide ion. Similar remarks apply to  $N^{3-}$  compared to  $P^{3-}$  and  $As^{3-}$ . In other words, O and N have a small charge capacity.

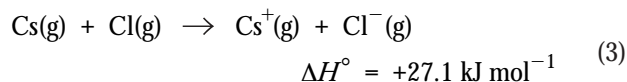
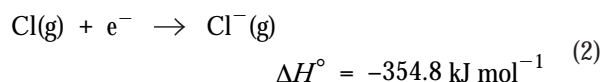
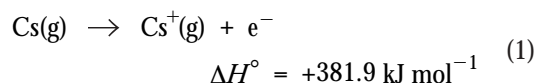
Table 1. Electron Affinities ( $\text{kJ mol}^{-1}$ )  
of Nonmetallic Elements

Electron Affinity	O	S	Se	N	P	As
$EA_1^a$	141.0	200.4	194.9	7.1 <sup>b</sup>	72.0	78.1
$EA_2^b$	-745	-456	-410	-674	-469	-435
$EA_3^b$				-1071	-887	-803

<sup>a</sup>Experimental.

<sup>b</sup>Data taken from ref 3.

Even the most favorable electron transfer between two neutral elements to obtain the noble-gas-configured ions, given by the reaction between cesium and chlorine, is an endothermic process:



In eqs 1 and 2, the ionization potential, IP, of cesium and the electron affinity, EA, of chlorine, which are both internal energy changes at absolute zero, have been transformed to enthalpies at 298 K. This is done by noting that each mole of ideal gas increases the enthalpy by  $(5/2)RT$ , which contains  $(3/2)RT$  as the thermal energy of one mole of an ideal monatomic gas and the remaining  $RT$  is the volume work associated with the formation of one mole of gas,

$$\Delta H_{\text{IP}} = \text{IP} + z^{5/2} RT \quad (4a)$$

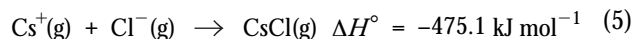
$$\Delta H_{\text{EA}} = -\text{EA} - z^{5/2} RT \quad (4b)$$

where  $z$  is the change in the oxidation state. By convention the atom, ion, and electron are all taken to be ideal gases in their standard states. Although the standard state of the electron is arbitrary (4), this assumption does not change the final analysis since the electrons produced in one step are consumed in the other. Notwithstanding this, the same standard state must be used throughout.

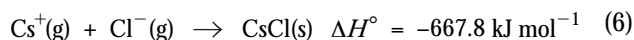
At this point a brief comment on the sign convention for electron affinity is in order. A detailed account of this confusing topic has been given recently (5). Accordingly I use the original, and still appropriate, convention that a positive electron affinity corresponds to a positive electron detachment energy or equivalently the energy of ionization of the negative ion. This convention is appealing for at least two reasons. First, it is in keeping with the term's other uses such as proton affinity, which is positive if the addition of a proton to the target species is exothermic, and the binding affinity. Second, the treatment of electron affinity and ionization energies remains under the umbrella of one treatment with EA featuring the "zeroth ionization energy" (6).

However, in order to make the bookkeeping in Born–Haber cycles somewhat easier, one may use the alternative quantity  $\Delta H_{\text{EA}}$  according to eq 4b.

The stabilization of ions is not performed without the action of Coulombic forces of attraction between the oppositely charged species, which more than offsets the unfavorableness of noble-gas-configured-ion formation. The formation of a gaseous ion pair is highly exothermic,



and more exothermic if the crystalline salt is formed,



### Formation of Ion Pairs

The ion-pair-formation enthalpy of eq 5 is the negative of the sum ( $\text{BDE} + \Delta H_{\text{IP}} + \Delta H_{\text{EA}}$ ), where BDE is the gas-

phase bond dissociation enthalpy of the molecule into neutral atoms (Figure 1). The value of  $475 \text{ kJ mol}^{-1}$  is very close to  $478 \text{ kJ mol}^{-1}$  calculated from Coulomb's law ( $R_0$  is in Å)

$$E_{\text{cou}} = \frac{1389 Z_1 Z_2}{R_0} \text{ kJ mol}^{-1} \quad (7)$$

with  $R_0 = 2.906 \text{ Å}$ , the experimental internuclear distance in the  $\text{Cs}^+\text{Cl}^-$  ion pair. The simple point-charge model works well because of sizeable cancellations of polarizability and repulsive effects. This is shown in more detail for the whole series of the alkali halide gas-phase molecules based on the truncated Rittner model or simply the T-Rittner model (7). According to this model the total binding energy of the molecule is

$$E = -\frac{e^2}{R_0} - \frac{e^2(\alpha_1 + \alpha_2)}{2R_0^4} - \frac{C_6}{R_0^6} + E_{\text{rep}} \quad (8)$$

**Table 2. Polarizabilities in Different Environments, Lattice Energies, and Internuclear Distances for the Alkali Halides**

Alkali Halide	Free Ion <sup>a</sup> / Å	Crystal <sup>b</sup> / Å	Diatomic <sup>c</sup> / Å	$\Delta H_{\text{diff}}^{\text{d}}$ / (kJ mol <sup>-1</sup> )	$\Delta R_0^{\text{e}}$ / Å
LiF	2.84	0.92	0.63	277	0.45
LiCl	4.40	2.97	2.23	220	0.55
LiBr	5.59	4.16	3.14	203	0.58
LiI	8.31	6.22	4.85	191	0.61
NaF	2.96	1.16	0.87	241	0.38
NaCl	4.52	3.29	2.75	228	0.45
NaBr	5.71	4.42	3.81	213	0.48
NaI	8.43	6.54	5.84	198	0.52
KF	3.60	2.01	1.85	238	0.51
KCl	5.16	4.17	3.82	214	0.47
KBr	6.35	5.35	4.88	215	0.47
KI	9.07	7.47	6.94	199	0.49
RbF	4.16	2.58	2.57	229	0.55
RbCl	5.71	4.80	4.70	216	0.49
RbBr	6.91	6.01	5.93	212	0.49
RbI	9.63	8.15	7.94	208	0.48
CsF	5.16	3.61	3.91	199	0.67
CsCl	6.71	5.89	6.33	193	0.56
CsBr	7.90	7.00	7.74	209	0.55
CsI	10.63	9.15	8.75	192	0.51

<sup>a</sup>Taken from ref 1. <sup>b</sup>Values from ref 10. <sup>c</sup>From eq 10.

<sup>d</sup>Differences between the lattice enthalpies,  $\Delta H_{\text{L}}^\circ$ , and the ion pair formation enthalpies,  $\Delta H_{\text{G}}^\circ$ :  $\Delta H_{\text{diff}} = \Delta H_{\text{L}}^\circ - \Delta H_{\text{G}}^\circ$ .

<sup>e</sup>Differences in internuclear distances in the lattice and the gaseous ion pair.

**Table 3. Calculated and Experimental MX Binding Energies<sup>a</sup>**

Alkali Halide	$-E_{\text{cou}}$	$-E_{\text{pol}}$	$-E_{\text{vdW}}$	$E_{\text{rep}}$	$-\Delta H_{\text{G}}^{\text{ob}}$ (calc)	$-\Delta H_{\text{G}}^\circ$ (exp)
LiF	888	73	7.0	219	752	769
LiCl	687	93	3.8	162	625	641
LiBr	640	98	3.5	157	588	614
LiI	581	103	2.9	147	541	570
NaF	721	44	13.3	142	639	687
NaCl	588	61	9.7	116	546	559
NaBr	555	68	9.4	113	521	539
NaI	512	75	8.6	109	489	505
KF	639	58	27.8	157	570	588
KCl	521	52	20.5	112	485	503
KBr	492	54	20.7	107	462	474
KI	456	56	19.1	100	433	449
RbF	612	67	33.5	165	550	563
RbCl	498	54	24.9	113	467	476
RbBr	472	55	25.3	108	446	453
RbI	437	54	23.6	99	418	421
CsF	592	90	45.5	197	533	566
CsCl	478	62	32.2	122	452	475
CsBr	452	60	32.5	112	435	440
CsI	419	50	30.4	105	398	418

<sup>a</sup>Coulomb force:  $E_{\text{cou}}$ , polarization energy:  $E_{\text{pol}}$ , van der Waals energy:  $E_{\text{vdW}}$ , repulsion energy:  $E_{\text{rep}}$ , and binding enthalpy:  $\Delta H_{\text{G}}^\circ$ . All energies are in kJ mol<sup>-1</sup>.

<sup>b</sup> $\Delta H_{\text{G}}^\circ = \sum E - 2.5 \text{ kJ mol}^{-1}$ , since one mole gas is consumed in ion pair formation.

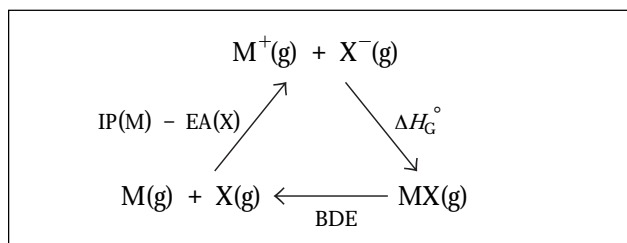


Figure 1. Thermodynamic cycle for determination of the ion pair formation enthalpy  $\Delta H_G^\circ$ . Note that  $IP(M) - EA(X)$  is identical to  $\Delta H_{ip} + \Delta H_{EA}$ , see eqs 4a and 4b.

where the first term on the right-hand side of the equation represents the Coulomb electrostatic interaction energy, the second term arises from the mutual polarization of ions, the third term represents the van der Waals dipole–dipole energy, and the last term is the overlap repulsive energy of the closed electron shells, mainly a consequence of the Pauli exclusion principle.

The Coulomb energy is calculated from eq 7. The assessment of the polarization energy needs the electronic polarizabilities of the constituent ions. The sum of the polarizabilities,  $\sum\alpha$ , as derived by comparing the experimental dipole moment with that calculated from the bond distance if the ions were spherical is used (8)

$$\mu = eR_0 - \frac{e\sum\alpha}{R_0^2} \quad (9)$$

When  $\alpha$  is in  $\text{\AA}^3$  and the dipole moment in Debye, we have (for a diatomic molecule)

$$\sum\alpha = R_0^2 (R_0 - 0.2082\mu_{\text{exp}}) \quad (10)$$

With  $\sum\alpha$  given, the polarization energy, the second term in eq 8, is

$$E_{\text{pol}} = -\frac{694.5\sum\alpha}{R_0^4} \text{ kJ mol}^{-1} \quad (11)$$

It may be noted that there is no unique method by which the sum of the polarizabilities can be separated into  $\alpha_1$  and

$\alpha_2$ . Furthermore, the free ion polarizabilities may not be used, since the extent of polarization varies with the environment. The damping is typically greater in the diatomic molecules than in the crystal, since in the latter the overlap effect is spherically symmetric, whereas in the diatomic molecules the effect is directed along the internuclear axis (9). However, some irregularities are encountered for the heavier alkali metals. Table 2 compares the sums of polarizabilities obtained (a) by adding the free ion values, (b) from eq 10 for diatomics, and (c) from the crystal (10) as derived from the refractive index, whose square is the optical dielectric constant, according to

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{\sum\alpha}{V} \quad (12)$$

where  $V$  is the volume per ion pair. The other two contributions in eq 8, namely the van der Waals energy and the repulsive energy, are taken from the literature (11). Table 3 summarizes the various contributions to the MX binding energies.

The agreement between theory and experiment is satisfactory though not perfect (Table 3). Unfortunately the values of neither the repulsive energy nor the van der Waals energy are particularly reliable. For the former, the distance dependence of the repulsive potential is not well established (12), and for the latter, several divergent formulas for estimating the coefficient  $C_6$  have been suggested (11). Notwithstanding this, the theory and experiment discrepancies may further be reduced by allowing for contributions from quadrupolar polarizabilities,  $\beta$ ,

$$E_{\text{quad}} = -\frac{694.5\sum\beta}{R_0^6} \text{ kJ mol}^{-1} \quad (13)$$

which may well be as important as the van der Waals interaction (13). However, although rough estimates of free state quadrupole polarizabilities are available (14) it is still unknown to which extent they are diminished in a molecular environment.

Notwithstanding these challenges, the purpose of the present analysis is to show that polarizability plus van der Waals forces largely compensate the repulsive forces. This is ultimately the reason why the binding energy in the alkali

Table 4. Bond Lengths of Diatomic Gas-Phase Alkali Halide Molecules

Atom	Li		Na		K		Rb		Cs
F	1.564	(0.37)	1.926	(0.24)	2.172	(0.10)	2.27	(0.07)	2.345
	(0.46)		(0.43)		(0.50)		(0.52)		(0.57)
Cl	2.021	(0.34)	2.361	(0.31)	2.666	(0.12)	2.787	(0.12)	2.906
	(0.15)		(0.14)		(0.15)		(0.15)		(0.16)
Br	2.17	(0.33)	2.502	(0.32)	2.821	(0.12)	2.945	(0.13)	3.072
	(0.22)		(0.21)		(0.23)		(0.24)		(0.24)
I	2.392	(0.32)	2.711	(0.34)	3.048	(0.13)	3.177	(0.13)	3.315

Note: Numbers in parentheses are the differences between the bond lengths of the diatomic molecules. All values are in  $\text{\AA}$ .

halide gas molecules can be reasonably well described in simple Coulombic terms. Note, however, that this is least adequate for the fluorides for which the repulsive contributions are exceptionally high (Table 3). This effect is reflected by the bond lengths (Table 4) in that the fluorides deteriorate the approximate additivity of ionic radii in the alkali halide molecules, whereas there is a fairly constant difference in radii between iodide and bromide as well as bromide and chloride. The difference between fluoride and chloride varies notably in going from lithium to cesium.

We are now in a position to make some statements about the most stable oxidation states in an ionic compound MX. For this purpose we chose arbitrarily two pairs of isoelectronic ions, namely KCl and MgO. According to Figure 1, the ion pair is stable if the difference of  $IP(M) - EA(X)$  and the Coulomb energy is negative. The electron affinity of  $Cl^{2-}$  may well be higher than -700 and that of  $O^{3-}$  higher than -1000  $\text{kJ mol}^{-1}$  (see Table 1). It should be mentioned that the omission of the electron affinities, because they are much lower than the ionization potentials, does not change the substance of the conclusions. Further, it may be loosely assumed, in the spirit of Bragg's radii (15), that the bond length, 2.67 Å for KCl(g) and 1.75 Å for MgO(g), is invariant with the charge type; that is, the decrease in radius of the cation on increase in positive charge is counterbalanced by a similar increase of the anionic radius on increase in negative charge.

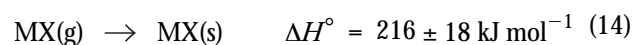
The values in Table 5 clearly show that the release of energy is greatest for the combination of the noble-gas-configured ions. This is the result of two phenomena: (a) the atomic shell structure and (b) increase in ionization energy (and hence electronegativity) in the periodic table from left-to-right. Although the second ionization energy for a metal is always larger than the first, and the third larger than the

second, the increase is moderate except when the noble gas configuration is broken. When this happens the ionization energy rises markedly because the electron is being removed from the next-inner shell.

The result that the ion-pair-formation energy is largely dominated by the Coulomb forces allows the ionic states of endothermic "exotic" gas-phase molecules such as BO to be assessed. For this entity both the BDE ( $808.8 \pm 20.9 \text{ kJ mol}^{-1}$ ) and the bond length (1.204 Å) are known (16). Since maximum ionic charges are sought, the composition might be envisaged as  $B^{2+}O^{2-}$ . In the framework of the approximate relationship shown in Table 6, it is seen that BDE calculated for  $B^{2+}O^{2-}$  is much closer to the experimental value than that of  $B^+O^-$ . The same analysis is also successful in describing the gas-phase molecule AlO.

### Ionic Lattice Formation

When the gaseous ion pair solidifies into the crystalline salt,



there is further energy release that, remarkably, is fairly invariant with the alkali halide salt. This is seen in Table 2 where the differences in enthalpy,  $\Delta H_{\text{diff}}$ , are calculated with the lattice enthalpies  $\Delta H_L^\circ$  derived from a Born-Fajans-Haber cycle (17). Again, the fluorides are discrepant. For these, the strong repulsive forces in the ion pair are particularly mitigated through bond lengthening in the ionic lattice. After all, the relative constancy of the quantity  $\Delta H_{\text{diff}}$  is obviously intimately mirrored by a fairly constant increase in the internuclear distance by  $0.51 \pm 0.05 \text{ Å}$  in going from the gas-phase molecules to the lattice (Table 2).

To get a better understanding, a consideration of theoretical calculations of the lattice energy, which is the lattice enthalpy at  $T = 0$ , is pertinent. At first it may be mentioned that the extra stabilization in an ionic lattice is due to the greatly increased number of interacting particles relative to a simple ion pair. This is the reason why the highest possible coordination number is adopted. This many-body problem was first treated by summing the pairwise Coulomb interactions in terms of a crystal-structure-specific factor termed the geometric Madelung constant. Later on Kapustinskii recognized that the quotient of the Madelung constant and the sum of the ions in the formula unit is fairly invariant with crystal structure. The repulsive forces were treated in a similar manner. When further van der Waals forces are included by the term  $C/R_0^6$  and the zero-point energy by  $D$ , a generalized equation for the lattice energy is (18, 19)

$$U_0 = \frac{A \sum n_i z_i^2}{R_0} \left( 1 - \frac{B}{R_0} \right) + \frac{C}{R_0^6} + D \quad (15)$$

Here  $n$  is the number and  $z$  is the charge of each ion in the formula. For instance,  $\sum n z^2$  is 2 for NaCl, 6 for  $\text{Na}_2\text{O}$ , and 30 for  $\text{Al}_2\text{O}_3$ . The parameter  $A$  represents the Coulomb forces. Since Kapustinskii chose the rock salt structure as the representative,  $A = 1214 \text{ kJ mol}^{-1} \text{ Å}$  given by the product of 1389.3 (from eq 7) and 1.7476 (the Madelung constant for

Table 5. Various Ionic Combinations<sup>a</sup>

Ionic Cpd	$IP(M) - EA(X)^b$	$E_{\text{cou}}$	$\Delta$
$K^+Cl^-$	1203	521	682
$K^+Cl^-$	70	521	-451
$K^{2+}Cl^{2-}$	3471 + (> 700)	2083	> 2100
$Mg^-O^+$	1333	794	539
$Mg^+O^-$	597	794	-197
$Mg^{2+}O^{2-}$	2790	3177	-387
$Mg^{3+}O^{3-}$	9921 + (> 1000)	7147	> 3800

<sup>a</sup>All values are in  $\text{kJ mol}^{-1}$ .

<sup>b</sup>Or  $IP(X) - EA(M)$ .

Table 6. Ion-Pair-Formation Energy for BO

Ionic Cpd	$E_{\text{cou}}$	$-IP(M)$	$+EA(X)$	$\approx \text{BDE}$
$B^{2+}O^{2-}$	4613	3228	-604	781
$B^+O^-$	1153	801	141	493

NOTE: All values in  $\text{kJ mol}^{-1}$ . The bond dissociation energy, BDE, is calculated from the following equation:  $E_{\text{cou}} - IP(M) + EA(X) \approx \text{BDE}$ .

the rock salt structure) and 0.5 (in order to compensate for the introduced factor  $n$ ). Further the softness parameter  $B$  is 0.345 Å, which is a representative value for the alkali metal NaCl-type structures.

It may be mentioned that polarization energies (featured by the second term in eq 8) are absent in a highly symmetric lattice because of mutual cancellations. Consequently non-Coulombic forces are much less important in a cubic lattice compared to the diatomic state. The component terms in the lattice energies as taken from the work by Cubicciotti (20) are listed in Table 7 with the zero-point energies recalculated from recent values of the Debye temperature (21).

On inspecting Tables 3 and 7 one finds the reason for the near constancy of the differences ( $\Delta H_L^\circ - \Delta H_C^\circ$ ): At first, for both the ion pair and the lattice, the Coulomb term has the largest contribution. Now in going from the ion pair to the lattice, the increase in the factor  $A$  (the Madelung constant, which is unity for the ion pair) is compensated by a relatively constant increase in the internuclear distance reducing the repulsive forces. Whereas in the ion pair the repulsion term is calculated to be on average 23.6% of the attractive term, in the lattice it is just 12.0%.

In a recent paper, Carter (18) has treated the constants  $A$ ,  $B$ ,  $C$ , and  $D$  in eq 15 as adjustable parameters and fitted this equation to the Born–Haber cycle lattice energies of the group I and II (except for beryllium) halides, oxides, and sulfides, which resulted in

$$U_0 = \frac{1249.3 \sum n_i z_i^2}{R_0} \left(1 - \frac{0.462}{R_0}\right) + \frac{5794.6}{R_0^6} + 34.1 \quad (16)$$

Although the physical significance of the individual parameters may not be taken too seriously, this equation appears to be at present the most expedient formula for estimating lattice energies from just internuclear distance (or the cation–anion radius sum). Pertinent values for the alkali halides are included in Table 7.

### Covalent Bonding

It is remarkable that even many senior students do not have a clear understanding of the origin of covalent bonding. Analogously to ionic bonding, the picture often presented conveys the idea that electron sharing across a bond is due to the striving for the noble gas configuration. In fact, the octet rule in the framework of the Lewis symbol emphasizes this configuration as a stable state. The traditional interpretation in electrostatic terms claims that the bond forms because an electron between two nuclei can attract both nuclei, leading to a decrease in the energy. However, it has been repeatedly argued that this point of view is based on a fallacious application of the virial theorem (22, 23). Rather, the stabilization of a molecule is mainly due to the delocalization of the electronic motion over two or more atoms joined by chemical bonds. Strictly, though, covalent bonding should be considered as a superposition phenomenon, with chemistry featuring the “quantum science” (24); put crudely, it is a kinetic effect. This was first suggested by Hellmann in 1933 (25). Since the bond region is larger in size compared to the

atomic orbital, the electron is free to move in a larger space. This lowers the kinetic energy of the electron as a consequence of the uncertainty principle. Thus the increase of density in the bonding region is an *effect* due to the bond rather than the *cause* of the bond (26). But despite the justified criticism of the electrostatic picture of covalent bonding there are even recent papers adhering to it (27, 28).

It may be worthwhile to examine the energies necessary for charge transfer in the typically covalent molecules dihydrogen and the dihalogens using the above scheme. With the experimental bond lengths of the gas-phase molecules (0.74, 1.41, 1.99, 2.28, 2.67 Å, in the order quoted below) the following values are obtained and shown in Table 8. The positive values of  $\Delta$  reveal that at the bond lengths considered the Coulomb forces do not overcome the energy needed for charge transfer. The interatomic distances depend primarily on the sizes of the constituent atoms and secondarily on the forces acting on them. In fact, the cation–anion distance in an ion pair differs just by a few tenths of an angstrom from the sum of the corresponding atomic radii: an example, the bond length in NaCl(g) is 2.36 Å versus the sum of the atomic radii of 2.53 Å. (For a recent compilation of atomic radii see ref 29.) Because of it the ionization potential (in other words, electronegativity) is the critical factor for determining the nature of bonding. Thus, NaCl(g) is ionic and

Table 7. Calculated and Experimental MX Lattice Energies<sup>a</sup>

Alkali Halide	$-E_{\text{cou}}$	$-E_{\text{vdW}}^b$	$E_{\text{rep}}$	Zero-point <sup>c</sup>	$\Delta H_L^\circ$ calc <sup>d</sup>	$\Delta H_L^\circ$ (eq16) <sup>d</sup>	$\Delta H_L^\circ$ (exp)
LiF	1205	19	178	8.2	1036	1077	1046
LiCl	945	27	117	5.5	847	849	861
LiBr	882	29	105	3.7	801	801	817
LiI	809	34	96	3.9	742	744	761
NaF	1048	20	143	6.6	916	935	928
NaCl	861	24	104	4.4	775	786	787
NaBr	812	26	94	3.6	738	748	751
NaI	750	28	82	3.2	691	700	703
KF	908	31	119	5.2	813	819	826
KCl	771	31	89	3.9	707	716	717
KBr	736	32	84	3.1	679	689	689
KI	687	32	75	2.7	639	648	648
RbF	862	38	116	4.3	778	784	792
RbCl	738	37	85	3.2	684	691	692
RbBr	705	36	79	2.4	657	665	665
RbI	661	37	73	2.0	621	630	629
CsF	807	46	101	3.0	746	742	756
CsCl	686	50	82	2.7	650	659	668
CsBr	658	53	77	2.0	631	636	649
CsI	619	52	68	1.7	600	607	610

<sup>a</sup>All energies are in  $\text{kJ mol}^{-1}$ : coulomb energy (Madelung,  $E_{\text{cou}}$ ), van der Waals energy ( $E_{\text{vdW}}$ ), repulsion energy ( $E_{\text{rep}}$ ), zero-point energy, and lattice enthalpies at 298 K.

<sup>b</sup>Including both dipole–dipole and dipole–quadrupole energies.

<sup>c</sup>Recalculated from recent Debye temperatures (21).

<sup>d</sup> $\Delta H_L^\circ = \sum E (= U_0) - RT$ .

Cl<sub>2</sub> is covalent because of the different ionization potentials of sodium (496 kJ mol<sup>-1</sup>) and chlorine (1251 kJ mol<sup>-1</sup>). On average, there is a factor of three increase in the ionization potential across a period.

An exception to the rule is hydrogen. According to the negative value of  $\Delta$  (Table 8) the two hydrogen atoms should charge to each other. The particular situation of this element is rooted in the fact that upon addition of an electron to form the hydride anion the number of electrons is doubled. This leads to strong screening of the nucleus with concomitant tremendous increase in the radius (1.48–1.73 Å, depending on the counter-atom; ref 18, 30) on the basis of the relationship  $R = (n^2/Z_{\text{eff}})a_0$ , where  $n$  is the value of the valence level,  $Z_{\text{eff}}$  is the effective nuclear charge on the valence level electron, and the term  $a_0$  is a constant that represents the selection of units for the radius. Because of the closely associated high polarizability, the hydride radius is variable but is always more than twice as large as the bond length of the H<sub>2</sub> molecule. In this context, a deeper description of the stability of the ionic bond in terms of quantum restrictions for orbitals is relevant. Actually without quantized energy levels cations and anions could not coexist as neighbors; that is, the ions would discharge each other (31). This would be the case when a proton and a hydride ion are brought closely together. Incidentally, if the pressure is increased further, say to 200 GPa, a conversion of molecular to metallic hydrogen would take place (32).

### Absolute and Relative Stabilities

Clearly, in the free state the great majority of noble-gas-configured ions are thermodynamically unstable entities. Regardless, the stability of an individual electron configuration is often analyzed in relative terms by looking for trends in the framework of the periodic table. Along these lines it has long been recognized that atoms with completely filled shells or subshells possess extra stability (or more strictly lesser instability) in comparison to their open-shell neighbors. This is evidenced by various physical properties such as ionization energies, electron affinities, atomic polarizabilities, hardness, and electronegativities (33), with many of these parameters being interrelated. A less known example is the approximate relation between polarizability and ionization potential (1).

The physical basis of the relative stabilities of half-filled subshells is interelectron repulsions, which may be further dissected into Coulomb and exchange (parallel spin avoidance) contributions (34). It is interesting to note that this feature is reflected even by some bulk physical properties,

which show a sharp discontinuity in the middle of a period. For instance, the melting point and the electrical resistivity of the 3d metals show a sharp minimum and maximum, respectively, for manganese, which has, in the gas phase, the s<sup>2</sup>d<sup>5</sup> electron configuration. Similarly, europium (f<sup>7</sup>s<sup>2</sup>) and ytterbium (f<sup>14</sup>s<sup>2</sup>) have anomalously low melting points in the series of the lanthanide metals. Furthermore, the remarkable stability of the Eu<sup>2+</sup> and Yb<sup>2+</sup> cations may also be the result of the half-filled and filled f shells (35).

### Conclusion

Although the bonding behavior of the main-group elements can typically be considered as the result of gaining, losing, or sharing valence electrons to achieve the same configuration as the nearest noble gas, the driving force of neither ionic nor covalent bonding derives from it.

In introducing the driving forces for forming chemical compounds, I would like to start with superordinate matters by sketching the basic forces of nature that play central roles making the Universe what it is. In this way the features of chemistry are more fully appreciated. It is currently held that four fundamental forces within all atoms dictate interactions between individual particles and the large-scale behavior of all matter throughout the Universe. These are, in increasing order of strength, (a) gravity, (b) the weak nuclear force, (c) electromagnetism, and (d) the strong nuclear force. Apart from omnipresent gravity the other three forces are easy to derive from the atomic structure.

The whole of chemistry is the manifestation of varieties of just one force—the electromagnetic. This force acting between charges holds atoms and molecules together. Covalent bonding goes back to the binding energy between negatively charged electrons and the positively charged nucleus of an atom. The superposition of electron waves brings about a delocalization of the electronic motion over two or more atoms with lowered kinetic energy of the electron as a consequence of the uncertainty principle. Ionic bonding occurs since the attraction between a cation and an anion releases more energy than that needed for electron transfer to produce the ions. The combination of both interaction mechanisms would result in polar covalent bonding. There are also other effects of the electromagnetic force such as the emission and absorption of light and other forms of electromagnetic radiation.

The striving for bonding, covalent or ionic, is subject to certain limitations. In case of covalent bonding it is the number of orbitals, that is one-electron wave functions, and the Pauli principle imposing the important quantum restriction that no more than one electron of given spin may occupy a given orbital. In case of ionic bonding there is a notable fine tuning between the numerical value of the constant in Coulomb's law and the variation of the ionization energy with the energy level according to the formula  $E = 1312 (Z_{\text{eff}}^2/n_{\text{eff}}^2)$  kJ mol<sup>-1</sup>. As a result, only the electrons of the outermost shell, termed valence shell, are directly associated to the chemical behavior of the atoms. It is the sum of all of these features that make the noble gas configuration the preferred configuration for the arrangement of electrons in all atoms within a chemical compound. The preference of this arrangement, however, may not be mistaken as the driving force for chemi-

Table 8. Energies of Ionic H<sub>2</sub> and X<sub>2</sub>

Ionic Cpd	IP – EA	$E_{\text{Coul}}$	$\Delta$
H <sup>+</sup> H <sup>-</sup>	1239	1874	-634
F <sup>+</sup> F <sup>-</sup>	1353	984	368
Cl <sup>+</sup> Cl <sup>-</sup>	903	699	204
Br <sup>+</sup> Br <sup>-</sup>	815	609	206
I <sup>+</sup> I <sup>-</sup>	713	521	192

NOTE: All values in kJ mol<sup>-1</sup>.

cal interactions. Rather, the noble gas configuration should be considered the outcome of the game by which chemical elements combine with each other. The rules of the game are the various factors identified in this paper.

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