BINDING ENERGIES OF GASEOUS ALKALI HYDRIDES

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RITTNER has recently proposed a simple procedure for calculating the binding energy of gaseous alkali halide molecules in which the molecule is treated as consisting of ions, each of which is polarized by the electrostatic field of the other. On this basis the following equations give the binding energy \(-W\) and the dipole moment \(\mu\), respectively, at \(0^\circ\text{K}:\)

\[
W = \frac{e^2}{2r} - \frac{e^2}{r}(\alpha_1 + \alpha_2) + 4\pi \varepsilon_0 \alpha_1 \alpha_2 \frac{e^2}{2r^3} - 4\pi \varepsilon_0 \alpha_1 \alpha_2 \frac{e^2}{2r^3},
\]

where

\[
e = \frac{e^2}{r} - \frac{e^2}{r}(\alpha_1 + \alpha_2) + 2\pi \varepsilon_0 \alpha_1 \alpha_2 \frac{e^2}{2r^3},
\]

\(\alpha_1\) and \(\alpha_2\) = polarizabilities of the ions, \(e\) = electronic charge, \(r\) = equilibrium internuclear distance at the potential minimum, \(\rho\) and \(A\) = repulsion constants, and \(C\) = van der Waals' attractive constant. The value for \(\rho\) is obtained by applying the usual requirements for mechanical stability, i.e.,

\[
\frac{dW}{dr}|_{\theta_{eq}} = 0
\]

and

\[
\frac{dW}{dr^2}|_{\theta_{eq}} = P \quad \text{ (force constant)}.
\]

The application of these equations to the entire group of alkali metal halides gave generally good agreement between calculated binding energies and the so-called experimental binding energies given by

\[
-W = D + I - E,
\]

where \(D\) is the dissociation energy of the ionic molecule into neutral atoms, \(I\) is the first ionization potential of the alkali atom, and \(E\) is the electron affinity of the halogen atom.

There are, however, two objections to the conclusion that the agreement obtained by Rittner indicates complete validity of his proposal: (1) The values for the dissociation energies of the alkali metal halides have not been independently determined from spectroscopic data but are most commonly obtained through the application of thermochemical cycles involving the heats of sublimation of the salts, the dissociation energies of the halogen molecules, the electron affinities of the halogen atoms, and other thermochemical data; and (2) Brewer and Mastick have obtained agreement equally as good as Rittner in calculating the alkali metal chlorides, bromides, and iodides as gaseous ionic molecules by making no allowance for either repulsion or polarization effects but merely by using \(\varepsilon^2/r\), the electrostatic attraction, as the energy of separation of the ions. They conclude that "the gaseous state distortion of the positive and negative ions may occur to a great extent whereby increasing the bonding energy which, supplemented by increased dispersion forces, apparently cancels the repulsive force."

It thus seems important to present the results of some calculations concerning the alkali metal hydrides following Rittner's proposed model since (1) the spectra of these molecules have been well analyzed and their dissociation energies are known within a few kcal/mole, and the electron affinity of \(H\) has been calculated very exactly, and (2) the application of the method of Brewer and Mastick does not lead to the proper results for the binding energies of these hydrides. In Table I are listed the data used and in Table II are the results of these computations.

The agreement between the calculated and experimental values of the binding energies is very satisfactory and within the uncertainties of the values for the dissociation energies. The lack of experimental values for the heats of sublimation of these compounds prevents correlation with thermochemical data on the solid compounds and the calculated crystal energies of the solids. It seems definite, however, that the relative effects of polarization and repulsion as computed are very near to those actually existing in gaseous alkali hydrides. The dipole moments have also been calculated but no experimental data are available for comparison.

In view of the excellent agreement obtained both in this work and that of Rittner, it was thought worthwhile to make similar computations for the gaseous alkaline earth oxide molecules. Very poor agreement between the calculated and experimental values was found, the discrepancies amounting to 80--100 kcal/mole. Similarly, an attempt to apply this method for calculation of the binding energies of HF and HCl failed to yield the correct binding energies and gave negative values for the dipole moments.

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6 Values for \(\alpha_1\) and \(\alpha_2\) are from reference 1; \(\alpha_m\) values are from J. Pauling, Proc. Roy. Soc. (London) A114, 181 (1927); \(\alpha_m\) was computed from the data of H. Boie, E. Phys. Chem. 6B, 251 (1930); \(\alpha_m\) values are from L. Brewer, The Chemistry and Metallurgy of Miscellaneous Materials, NNESS IV-19B (McGraw-Hill Book Company, Inc., New York, 1950), p. 165; \(D_{m}\) is from reference 5; and \(D_{m}\) were computed from data in references 3 and 4.

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ERRATUM: Infrared Spectra of \(n\)-Acetylglycine and Diketopiperazine in Polarized Radiation at 23° and at \(-185^\circ\text{C}\)

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THE [101] direction in diketopiperazine crystals was erroneously referred to as [101].

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ERRATUM: Thermodynamic Data and Some Notes on the Nature of Adsorbed Helium

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THE byline of this article appeared as "The Barrett Division, Allied Chemical and Dye Corporation, Philadelphia, Pennsylvania, and it should have been "School of Chemistry and Physics, The Pennsylvania State College, State College, Pennsylvania."

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### Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\times 10^6) cm(^{-1})</th>
<th>(\times 10^6) cm(^{-1})</th>
<th>(\alpha_m) kcal/mole</th>
<th>(B_H) kcal/mole</th>
<th>(D_{m}) kcal/mole</th>
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</thead>
<tbody>
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<td>1035</td>
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<tr>
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<tr>
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<tr>
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<td>244</td>
<td>244</td>
<td>180</td>
<td>890</td>
<td>42</td>
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### Table II

<table>
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<tr>
<th>Compound</th>
<th>(W_{calc}) kcal/mole</th>
<th>(W_{exp}) kcal/mole</th>
<th>(D_{calc}) kcal/mole</th>
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<tr>
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