tained from calculations using the critical amplitudes of specific heat (4 systems: $\overline{X}^* = 2.1$).[1]

The experimental data available at the present time are not accurate enough to answer the question definitely whether X^* (or X) has a material independent value for binary critical mixtures, However, the larger part of the data compiled in Table I of Ref. 1 and in Table I of this study seem to indicate a material independence of X^* for binary critical mixtures.

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Theoretical studies of molecular ions: Be₂⁻

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The ground state of the diatomic molecule Be_2 is bound by less than 1 kcal/mole, if it is bound at all.[1] This is not surprising in view of the fact that the two closed-shell $1s^2 2s^2$ Be atoms combine to give a ground electronic state whose wavefunction is dominated by the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2$ configuration, which contains an equal number of bonding and antibonding electrons. Our second-order perturbation theory calculations,[2] as well as the earlier work of Bender and Davidson,[3] indicate that the ground $^1\Sigma_g$ potential curve of Be_2 is indeed repulsive. Of course the ground states of analogous diatomics (Mg_2, Hg_2, Cd_2) are bound[1] due to the much larger dispersion interactions which occur in these more polarizable species. Thus, in this series of diatomics whose constituent atoms have the $ns^2 np^0$ configuration, Be_2 is somewhat exceptional.

If one were to remove an electron from the antibonding $2\sigma_u$ orbital of Be_2 to form Be_2^+ ($^2\Sigma_u$), one would expect the resulting state of the cation to be bound. As Fraga and Ransil[4] have shown, and as our calculations demonstrate, the lowest $^2\Sigma_u$ state of Be_2^+ is bound with an equilibrium bond length of approximately 4.56 a.u.

Analogously, if one were to add an electron to the $3\sigma_g$ orbital of Be_2, one might expect to increase the bonding characteristics of the system. Because of the near de-

generacy of the $2s$ and $2p$ orbitals of Be, and because the $2p_\sigma$ atomic orbitals will interact more strongly than the $2p_\pi$ orbitals over the range of internuclear distances considered here, one expects that the $3\sigma_g$ molecular orbital, which contains a large component of atomic $2p_\sigma$ character, would be the energetically most likely orbital to consider when adding an electron to Be_2 to form Be_2^-. The results of the calculations which are discussed in this Letter indicate that the lowest $^2\Sigma_g$ of Be_2^- is indeed stable with respect to electron detachment and dissociation. We predict an equilibrium bond length of 4.62 a.u.

TABLE I. Slater-type orbital basis for Be_2.

Orbital	Exponent
$1s$	2.950
$2s$	1.150
$2p_\sigma$	1.500
$1s'$	5.750
$2s'$	1.724
$2s''$	0.550
$2p_\sigma'$	0.500
$2p_\sigma''$	1.046
$2p_\pi$	0.500

TABLE II. Energies of Be_2, Be_2^+, Be_2^- (in a.u.)[a].

R (a.u.)	$-E_{Be_2}$	$-E_{Be_2^+}$	$-E_{Be_2^-}$
3.10	0.0964	−0.1582	0.1140
3.50	0.1452	−0.1094	0.1615
3.70	0.1590	−0.0905	0.1746
4.10	0.1745	−0.0811	0.1884
4.33	0.1790	−0.0778	0.1916
4.45	0.1805	−0.0770	0.1918
4.60	0.1820	−0.0767	0.1928
4.80	0.1833	−0.0775	0.1925
5.00	0.1841	−0.0791	0.1916
5.20	0.1847	−0.0813	0.1903
5.40	0.1852	−0.0839	0.1887
5.60	0.1855	−0.0869	0.1871
5.80	0.1858	−0.0899	0.1854

[a]29.000 a.u. has been added to each energy.

and a vibrational frequency[5] of approximately 620 cm^{-1} for this anion. Our results show that the $^2\Sigma_g$ Be_2^- and $^1\Sigma_g$ Be_2 potential curves cross at 5.8 a.u., which is near the $v = 3$ outer turning point of Be_2^-. For larger internuclear distances the negative ion is unstable with respect to the neutral plus an electron infinitely far away. The vertical electron detachment energy of Be_2^- at $R_e = 4.62$ a.u. is 0.29 eV. We also find that for R < 4.7 a.u., the $^2\pi_u$ state of Be_2^- lies below the repulsive $^1\Sigma_g$ state of the neutral; this excited state of Be_2^- does not appear to be bound with respect to dissociation.

The Slater-type orbital basis set used in this work is shown in Table I. The orbital exponents of the diffuse $2s$, $2p_\sigma$, and $2p_\pi$ functions were varied (at $R = 4.33$ a.u.) to maximize the electron affinity of Be_2 without adversely affecting the energy (SCF plus correlation) of the neutral parent molecule. The SCF plus second-order correlation energy of Be_2, together with the energies of Be_2^- and Be_2^+ obtained by combining our computed electron affinities (E.A.) and ionization potentials (I.P.) with the correlated Be_2 energies given for a range of internuclear distances in Table II. The E.A.'s and I.P.'s were calculated within the framework of the third-order electron propagator theory described in Refs.[6-8] We

found it essential to adequately treat the effects of orbital relaxation and electron correlation in calculating the E.A. of Be_2. The difference between the Koopmans' theorem approximation to the E.A. and our computed E.A. is of the order of 0.6 eV over the entire range of internuclear distances studied. Because the E.A. of Be_2 varies from 0.6 eV to 0.0 eV over this same range of internuclear distances, it is obvious that a Koopmans' theorem level description of the E.A. is inadequate. It is our belief that similar conclusions regarding correlation and relaxation effects can be made for diatomics of the homologous ns^2np^0 atoms. We expect that Mg_2, Zn_2, Cd_2, and Hg_2, whose atoms all have slightly negative electron affinities,[9] will also possess stable $^2\Sigma$ negative ions with vertical detachment energies greater than that for Be_2.

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