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The lattice energies of the alkaline earth oxides and the affinity of oxygen for two electrons.

By M. F. C. LADD and W. H. LEE, *Chemistry Department, Battersea College of Technology, London, S. W. 11, England*

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The lattice energies of the oxides MgO, CaO and BaO have been calculated using an equation previously developed. From the results the electron affinity, $E(O^{2-})$, was deduced and hence the lattice energies of the remaining alkaline earth oxides.

1. Introduction

It seems probable that the energy change for the reaction, $O(\text{gas}) + 2e \rightarrow O^{2-}(\text{gas})$, can be estimated only indirectly from a consideration of lattice energies. On the other hand, for the process, $O(\text{gas}) + e \rightarrow O^-(\text{gas})$, as with the corresponding reactions of the halogens, several experimental determinations have been made (Ta-You, 1955; Schuler & Bingel, 1955; Senftleben, 1926; Lozier, 1934; Vier & Mayer, 1944; Briegleb, 1942; Metlay & Kimball, 1948; Moiseiwitsch, 1954; Branscomb & Smith, 1955).

Calculations of the lattice energies of the alkaline earth oxides have been carried out previously (Sherman, 1932; van Arkel & de Boer, 1931; Mayer & Maltbie, 1932; de Boer & Verwey, 1936; Kapustinskii, 1943; Fowler, 1936; Kapustinskii & Yatsimirskii, 1956; Huggins & Sakamoto, 1957; Morris, 1957; Pritchard, 1953). The results are summarized in Table 1 together with the derived electron affinity, $E(O^{2-})$; for comparison, the present work is included.

The values from Pritchard (1953) represent only the average of the results of earlier work (Sherman, 1932; van Arkel & de Boer, 1931; Mayer & Maltbie, 1932; de Boer & Verwey, 1936; Kapustinskii, 1943) and thus these data together with the derived electron affinity are not of great significance.

2. Calculations

In order to obtain an estimate of the electron affinity $E(O^{2-})$ the lattice energies of MgO, CaO and BaO were calculated using an equation previously developed and applied successfully (Ladd & Lee, 1958, 1959, 1960a, 1960b). These three compounds were chosen since it was considered that for them reliable structural data were available (Table 2).

The interatomic distances, r_0 , were taken from the latest data in the A.S.T.M. Index with the exception of BaO (Zollweg, 1955). The compressibilities, β , were obtained by extrapolation of the data of Weir (1956) to unit pressure and are different from the values he deduced by averaging the volume decrements, assuming a linear relationship between volume change and applied pressure. The values of the constants C and D are those evaluated by Huggins & Sakamoto (1957). The zero-point energy term is represented in these oxides by $\frac{3}{2}h\nu_{\text{max}}$, ν_{max} is the maximum infrared lattice frequency (Born & Mayer, 1932); the following values were obtained.

	$10^{12}\nu_{\text{max}}$ (sec. ⁻¹)	$\frac{3}{2}h\nu_{\text{max}}$ (kg.cal./mole)	Lattice energy, $U(r_0)$, kg.cal./mole
MgO	17.1*	3.7	-942
CaO	11.1†	2.4	-865
BaO	5.7†	1.2	-756

* Willmott (1950). † Parodi (1934).

Of the more recent evaluations of these lattice energies in Table 17-9, we have considered in earlier work (1959, 1960b) a number of objections to the methods used and these remarks apply equally to the oxides.

Table 1. *Lattice energies of the alkaline earth oxides and the affinity of oxygen for two electrons*

	References										Present work	
	1	2	3	4	5	6	7	8		9		10
BeO	—	1080	1030	—	—	—	—	1026	1082	—	1055	1097 ± 10
MgO	940	936	920	939	914	976	934	907	938	—	930	942 ± 10
CaO	824	830	825	831	826	876	845	816	841	—	831	853 ± 10
SrO	791	784	780	766	769	829	789	769	792	—	778	806 ± 10
BaO	747	740	735	727	731	780	751	724	746	741	736	766 ± 10
RaO	—	—	—	—	—	—	—	—	—	—	—	751 ± 10
$E(O^{2-})$	168	173	—	150	—	—	—	162 (176)*		160	156	179 ± 8
	1 Sherman, 1932.			5 Kapustinskii, 1943.			8 Huggins & Sakamoto, 1957.					
	2 van Arkel & de Boer, 1931.			6 Fowler, 1936.			9 Morris, 1957.					
	3 Mayer & Maltbie, 1932.			7 Kapustinskii & Yatsimirskii, 1956.			10 Pritchard, 1953.					
	4 de Boer & Verwey, 1936.						* Huggins & Sakamoto, 1957, p. 250.					

Table 2. *Structural parameters for magnesium, calcium and barium oxides*

	r_0 (Å)	$10^{12}\beta$ (barye ⁻¹)	$10^{60}C$ erg cm. ⁸ /molecule	$10^{76}D$ erg cm. ⁸ /molecule
MgO	2.106(5)	0.44	47	17
CaO	2.405(3)	0.49	135	83
BaO	2.769(6)	0.82	394	477

In particular, the two sets of values quoted by Huggins & Sakamoto (1957) were derived using two differing and arbitrarily selected (Huggins, 1956) values for the repulsion exponent ρ . We have found not only different values for ρ but also that each compound has its own characteristic value for the exponent.

	ρ (Huggins & Sakamoto)	ρ (present work)
MgO	0.400	0.333
CaO	0.400	0.333
BaO	0.400	0.333

We have further calculated the lattice energy of barium oxide by an equation similar to that of Born & Landé (1918) but employing an exponential form for the repulsion term (Pauling, 1928) and using the values of r_0 and β from Table 2. This leads to the result $U(r_0) = -753$ kg.cal./mole, very similar to that obtained with this equation using the inverse r^n repulsion expression (Morris, 1957).

It has been our experience that any modification of the Born-Landé equation (Ladd & Lee, 1958; Born & Mayer, 1932) so as to include the attractive potential energy terms represented by C/r^6 and D/r^8 always leads to a lower (more negative) value for the lattice energy. It seems unlikely then that this quantity for barium oxide can be greater than about -753 kg.cal./mole.

Applying the Born-Haber cycle in the form,

$$\Delta H_f(\text{cryst.}) - \Delta H_f(\text{M}^{2+}\text{gas}) - \frac{1}{2}\text{D}(\text{O}_2) - \text{E}(\text{O}^{2-}) + 1.2 - U(r_0) = 0,$$

to the oxides of magnesium, calcium and barium we arrive at the value of 179 ± 8 kg.cal./g.atom for the electron affinity, $\text{E}(\text{O}^{2-})$, taking the thermodynamic data from the compilation of Rossini *et al.* (1952). To complete the series of lattice energies of the alkaline earth oxides we have used data from the same source together with the mean value for $\text{E}(\text{O}^{2-})$ just derived; these results are listed in Table 1.

The uncertainty in the calculated values of the lattice energies of MgO, CaO and BaO lies in the low accuracy with which their compressibilities have been measured (Weir, 1956; Bridgman, 1949). More reliable data would undoubtedly lead to a further refinement of these values.

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A simple method for the determination of $\partial^2\rho/\partial x^2$ at atomic positions. By H. W. EHRLICH, *Chemistry Department, The University, Edinburgh, 9, Scotland*

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The value of $\partial^2\rho/\partial x^2$ at atomic positions is required when assessing the accuracy of a structure determination or when determining the magnitude of a shift indicated by an ($F_o - F_c$) map. In principle, the most reliable method

of deriving this quantity is from an F_o synthesis, but many refinements are now carried out by techniques not requiring such a summation. Furthermore, for a reliable determination of $\partial^2\rho/\partial x^2$, the Fourier synthesis must be