

Dielectric Behavior of Some Bentonites

Sabita Ghosh

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reactive nature of HF (g) on glass. A mixture of HCl and H₂ of known composition gave $P_{H_2}/P_{HCl} = 2.1[I_{H_2^+}/I_{HCl^+}]$ for 75 V ionizing electrons. For P_{H_2}/P_{HF} we use $1.5[I_{H_2^+}/I_{HF^+}]$, anticipating that HF should have a cross section between that for HCl and H₂. Values of K₂ and K₃ were insensitive to electron

TABLE II. Thermochemical data for reactions involving gaseous boroxine and its fluoro derivatives.

Reaction	Temp. (range) °K	K_{eq} (range)	ΔS° (entropy units)	ΔH° (kcal/mole) (range)
1	1246-1326	4.2×10^{-2} - 2.3×10^{-2}	9 ± 3	24.9 - 21.8
2	1246-1326	0.62-0.46	-2.2 ± 2.0	-1.5 - -0.8
3	1246-1326	1.0 - 0.63	-2.2 ± 2.0	-2.8 - -1.6

* Entropies for H₂ and HF from reference 4; $S^\circ(B_3O_3F_3) - S^\circ(B_3O_3FH)$ estimated.

^b Assume ΔS° due mainly to change in symmetry.

energies between 20 and 75 V and to reaction temperature. Increase in P_{H_2}/P_{BF_3} had little effect on K values although the $B_3O_3H_2^+/B_2O_3F_3^+$ ratio increased, as expected, with shift in equilibrium toward the more hydrogenated species.

Thermochemical data are summarized in Table II. These data when combined with a heat of formation for $B_3O_3F_3(g)$ of -567 kcal/mole⁵ at 298°K give heats of formation for $B_3O_3F_2H(g)$, $B_3O_3FH_2(g)$ and $B_3O_3H_3(g)$ of -479 ± 5 , -392 ± 6 , and -307 ± 8 kcal/mole, respectively. These data indicate a fairly high stability for $B_3O_3H_3(g)$ which is assumed to have a six-membered ring structure.

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† Alfred P. Sloan Fellow.

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⁵ This value calculated from data in references 2 and 4.

Dielectric Behavior of Some Bentonites

SABITA GHOSH

Khaira Laboratory of Physics, University College of Science, Calcutta

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PREVIOUS workers^{1,2} determined the absorption (loss tangent) of specific clay minerals at different frequencies and at different temperatures. In the present communication are given the results of the experiments on the dielectric properties of some Ben-

tonites at various frequencies. These experiments were carried out to find out the relationship between the dielectric properties of these clay minerals and their basal spacings as revealed by x-ray diffraction studies. The measurements included the determination of the dielectric constant ϵ' , the loss tangent ($\tan \delta$), within the range of frequencies from 100 kc/sec to 4 Mc/sec, and the relaxation time τ for the different samples. The minerals which were used originated from Hannover (Germany) and England, and from Kashmir, Assam, and Rajasthan in India. The powdered minerals were sieved through 200-mesh screen, and these were then transferred to a container fitted with two brass electrodes. This served as the experimental condenser.

The instrument used for the measurement of the dielectric constant and the loss tangent as functions of frequency was a precision type of Q meter. With this instrument the dielectric constant and the loss tangent of the different samples were measured in the usual way. The results are shown graphically in Figs. 1 and 2. From Fig. 1, it is clear that the observed dielectric constant of the different samples of Bentonites decreases with the increase of frequency tending to a limiting value at about 3 Mc/sec. The variations of $\tan \delta$ with the frequency for different samples are shown in Fig. 2. The $\tan \delta$ curves show definite maxima at frequencies which are not the same for all the samples. The values of the relaxation time τ were obtained from $\tau = 1/2\pi f_{max}$, where f_{max} is the frequency for minimum absorption. The values of the frequencies for maximum absorption for the Bentonites from Hannover (Germany), England, Assam, Kashmir (pink variety), Rajasthan, Kashmir (grey variety) were found to be 240, 167, 240, 240, 300, and 167 kc/sec, respectively. The corresponding relaxation times are 6.6×10^{-7} , 9.5×10^{-7} , 6.6×10^{-7} , 6.6×10^{-7} , 5.3×10^{-7} , and 9.5×10^{-7} sec.

Further measurements are in progress with other groups of clay minerals of different sources. Investigations are also in progress on different complexes of

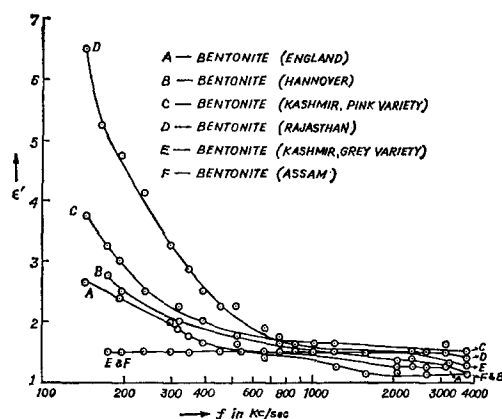


FIG. 1. Variation of dielectric constant with frequency.

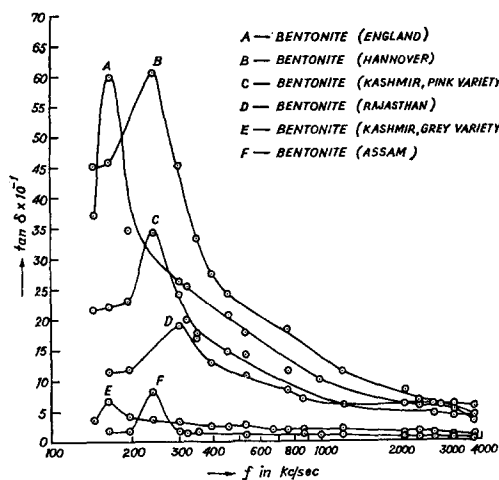


FIG. 2. Variation of loss tangent with frequency.

clay minerals, brought about by cation exchange process, in order to see how their dielectric properties vary with the nature of the cation present and their basal spacings.

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Gaussian Orbitals for Many-Electron Molecular Wave Functions

LELAND C. ALLEN

Department of Chemistry, Princeton University
Princeton, New Jersey

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THE Gaussian basis orbitals proposed by S. F. Boys¹ in 1950 have the form $x^l y^m z^n \exp(-ar_A^2)$, where r_A^2 is equal to $(x-A_x)^2 + (y-A_y)^2 + (z-A_z)^2$. In terms of spherical harmonics, $Y_l^{lm}(\theta, \phi)$; about a given center the Gaussians may be expressed as $r_p^q \exp(-ar^2 Y_l^{lm}(\theta, \phi))$, where $a > 0$; p is integral, equal to or greater than l , and restricted to even values for even l , odd values for odd l . This may be contrasted with the more frequently used and familiar exponential form, $r^q \exp(-br) Y_l^{lm}(\theta, \phi)$, where $b > 0$ and q has any integral value.² Since Boys' proposal, numerous discouraging calculations using Gaussians have been carried out. For example, in several one- and two-electron systems McWeeny³ found the choice of Gaussians both critical and difficult. Meckler⁴ obtained approximately one-half of the experimental energy for his

O₂ wavefunction. Calculations by Kimball and Neumark⁵ on H₂, He, and H⁻ gave total energy errors varying from 14% to 33%. In these examples each atomic orbital was represented by a single Gaussian. On the other hand, use of a single exponential basis function for each atomic shell in an atomic or molecular problem leads to total energy errors of approximately 1%. It is thus clear that the substitution of a single Gaussian for a single exponential is very poor indeed. A somewhat more encouraging calculation utilizing Gaussian basis functions has been done by Nesbet⁶ on CH₄. Nesbet's single-determinant free-atom carbon wave function employed several *s* and *p* basis orbitals and gave a total energy error of 2.1%. In general, however, Gaussians have not been extensively explored for use in atomic and molecular calculations, and this is a direct consequence of the results obtainable with *single* exponential basis orbitals in contrast to those obtainable with *single* Gaussian orbitals.

In the last few years two circumstances have arisen which requires a re-evaluation. The first of these is the continuing computational difficulty generally experienced in the evaluation of three- and four-center-two-electron integrals with exponential basis orbitals. The second is the need to employ a more adequate basis set than those made from single exponential orbitals. All molecular calculations made so far⁷ indicate that significantly improved results are obtainable with Hartree-Fock atomic basis orbitals. Solutions with this type of basis function yield approximately 99.5% of the total energy. This is only approximately 0.5% greater than that found for single exponential orbitals, but it must be remembered that 0.5% of the total energy is roughly

TABLE I. Comparison of Gaussian and exponential basis functions for the analytic approximation of Hartree-Fock orbitals.

Atom	Number of Gaussian terms	Number of exponential terms (Löwdin) ^a	Fitting parameters (<i>p</i> 's; <i>a</i> 's)	Maximum fitting error
Li, 1s	4	2	1, 1, 1, 1; 0.66, 2.4, 10, 60.	0.010
2s	4	3	1, 3, 1, 1; 0.033, 0.18, 2.2, 22.	0.017
F, 1s	5	2	1, 1, 1, 1, 1; 5.0, 15.5, 55, 250, 1800.	0.012
2s	5	3	1, 1, 1, 1, 1; 0.4, 1.35, 13, 67, 556.	0.027
N, 2p	4	3	2, 2, 2, 2; 0.14, 0.44, 1.55, 7.5.	0.020
Ge, 4s	6	5	1, 5, 1; 0.12, 0.70, 2.2, 1, 1, 1; 18.5, 230, 1500.	0.020
4p	5	5	2, 2, 2, 2, 2; 0.045, 0.17, 3.0, 44.4, 220.	0.017

^a P. O. Löwdin, *Phys. Rev.* **103**, 1746 (1956).