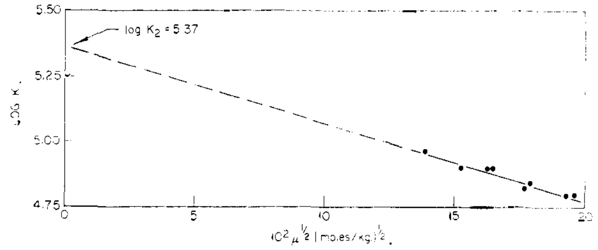

Fig. 1.—Evaluation of the stability constant of the CdCit⁻ ion by extrapolation of equation 4 to infinite dilution.

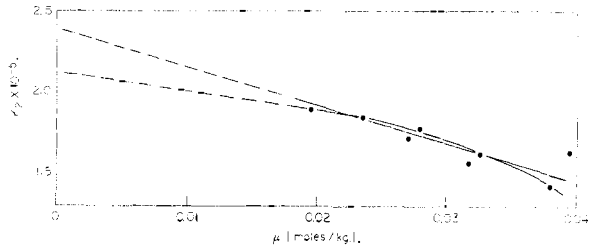

Fig. 2.—Alternate extrapolations to infinite dilution of the values of K_2 calculated from data derived from Cell A-B.

and Ferris[6] for Cell B and those obtained for Cell A during this investigation. Table II also contains the values of K_2 calculated at each selected molality of cadmium chloride. A plot of K_2 *vs.* μ is found in Fig. 2 where a rather systematic decrease in K_2 with increasing ionic strength is observed. This effect may be attributable to errors in the activity coefficients used.[10] Alternate extrapolations to infinite dilution, where activity coefficients are necessarily unity, lead to a value of about 2×10^5 for K_2. This value is obtained by any reasonable extrapolation and is consistent with that obtained by the other method discussed above.

It was unfortunate that reproducible e.m.f. readings could be made only over a narrow range of ionic strength. At ionic strengths less than 0.02 the amount of cadmium in solution was insufficient for satisfactory electrode operation, while at ionic strengths greater than 0.04 a precipitate formed in the solutions. This precipitate was found by chemical analysis to be $Cd_3Cit_2{\cdot}4H_2O$. Calcd. for $Cd_3C_{12}H_{18}O_{18}$: Cd, 42.8; C, 18.3; H, 2.30; O, 36.6. Found: Cd, 43.4; C, 18.0; H, 2.38; O (by difference), 36.2.

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FARGO, NORTH DAKOTA

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, D. I. MENDELEJEV CHEMICAL-TECHNOLOGICAL INSTITUTE]

The Heat Capacities of Sodium Tetraborate on the Basis of the Theory of the Specific Heat of Chain Structures

BY V. V. TARASSOV

RECEIVED MARCH 6, 1958

The heat capacity of anhydrous crystalline sodium tetraborate is analyzed on the basis of the theory of the heat capacity of chain structures earlier advanced by the author. The heat capacity of crystalline $Na_2B_4O_7$ is treated as the sum of contributions from the high-polymer chain anions $(B_4O_7)_\infty$ and the Na^{1+} cations. When the contribution of the Na^{1+} cations is subtracted from the experimental values of the heat capacity of $Na_2B_4O_7$, a strictly linear dependence is obtained, which expresses the limiting law of the heat capacity for a chain structure. The value of the characteristic temperature thus obtained $\theta_{B_4O_7} = 1890°$ coincides exactly with the earlier established value for B_2O_3 and points to the large value of the force constants of binding in the $(B_4O_7)_\infty$ chains.

The theory of the heat capacity of chain and layer structures developed by us (1945–1950)[1] has withstood the test of extensive experimental verification in a number of our papers[1d–j] and in the papers of other authors (De Sorbo,[2] Dworkin, Sasmor, Van Artsdalen, Smith, Brown,[3] Fukuroi and Muto,[4] etc.). In addition, several theoretical investigations, based on a method analogous to that of Born and Karman, have given additional confirmation of our simple laws of distribution of the fundamental frequencies of the lattice in the spectrum of elastic vibrations of chain and layer crystals.

Recently Fukuroi and Muto[4] announced that Yoshimori in analyzing the spectrum of the elastic vibrations of crystalline selenium carried out theoretical calculations which confirm our conception.

Komatsu's paper[5] on the dynamics of the vibrations of the graphite layer lattice is also of considerable interest.

Stockmayer and Hecht considered the spectrum of vibrations of a simple tetragonal lattice composed of high-molecular monoatomic chains. They arrived at results closely approaching ours. The authors mention this circumstance in their paper.[6]

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[1] (a) V. V. Tarassov, *Doklady, Acad. Sci. USSR*, **46**, 22 (1945); (b) **58**, 577 (1947); (c) *Zhurn. Fiz. Khim.*, **24**, 111 (1950); (d) *Doklady, Acad. Sci. USSR*, **84**, 321 (1952); (e) *Zhurn. Fiz. Khim.*, **26**, 1374 (1952); (f) **27**, 744 (1953); (g) *Doklady, Acad. Sci., USSR*, **88**, 1019 (1953); (h) *Trans. Inst. Cryst. Acad. Sci. USSR*, 309 (1954); (i) *Doklady, Acad. Sci. USSR*, **100**, 307 (1955); *Zhurn. Fiz. Khim.*, **29**, 198 (1955); (j) *Doklady, Acad. Sci. USSR*, **107**, 719 (1956).

[2] (a) W. De Sorbo, *J. Chem. Phys.*, **21**, 168 (1953); (b) **21**, 764 (1953); (c) **21**, 1660 (1953); (d) *Acta Metallurgica*, **1**, 503 (1953); (e) *J. Chem. Phys.*, **21**, 1144 (1953); (f) *Acta Metallurgica*, **2**, 274 (1954).

[3] A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, *J. Chem. Phys.*, **22**, 837 (1954); THIS JOURNAL, **77**, 1304 (1955); D. F. Smith, D. Brown, A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, *ibid.*, **78**, 1533 (1956).

[4] T. Fukuroi and Y. Muto, *Sci. Rept. Res. Inst. Tohoku Univ.*, **A8**, No. 3, 213 (1956).

[5] K. Komatsu, *J. Phys. Soc. Japan*, **10**, 346 (1955).

[6] W. H. Stockmayer and C. E. Hecht, *J. Chem. Phys.*, **21**, 1954 (1953).

In similar manner the investigations of Krumhansl and Brooks[7] and Rosenstock[8] confirm the correctness of our law of distribution of frequencies in a layer lattice.

In accordance with the results of our papers the formula of the heat capacity $C_{1(3)}$ for a chain structure has the form

$$C_{1(3)} = 3R\frac{T}{\theta_1}\int_0^{\theta_1/T}\frac{x^2e^x\mathrm{d}x}{(e^x-1)^2} - \frac{\theta_3}{\theta_1}\left[3R\frac{T}{\theta_3}\int_0^{\theta_3/T}\frac{x^2e^x\mathrm{d}x}{(e^x-1)^2} - 9R\left(\frac{T}{\theta_3}\right)^3\int_0^{\theta_3/T}\frac{x^4e^x\mathrm{d}x}{(e^x-1)^2}\right] \equiv$$

$$\equiv 3R\frac{T}{\theta_1}\int_{\theta_3/T}^{\theta_1/T}\left(\frac{x}{2}\right)^2\operatorname{csch}^2\left(\frac{x}{2}\right)\mathrm{d}x + 36R\frac{T^3}{\theta_1\theta_3^{\,2}}\int_0^{\theta_3/T}\left(\frac{x}{2}\right)^4\operatorname{csch}^2\left(\frac{x}{2}\right)\mathrm{d}x \ \ldots . \quad (1)$$

In a number of papers on the low temperature heat capacity of chain crystals the applicability of equation 1 has been proven (selenium and tellurium,[2b,e] Teflon,[9] hydrogen fluoride,[10] etc.

As has been shown,[1b,c] at $\theta_3/\theta_1 \rightarrow 0$ and at $T_3 \rightarrow 0$ the function 1 becomes

$$\lim_{T\rightarrow 0} C_{1(3)} = 3R\frac{T}{\theta_1}\int_0^{\infty}\left(\frac{x}{2}\right)^2\operatorname{csch}^2\left(\frac{x}{2}\right)\mathrm{d}x = \pi^2R\left(\frac{T}{\theta_1}\right)^1 \quad (2)$$

As we have shown in our earlier papers, the heat capacity of some fairly complex chain structures is very well described by equations 1 and 2. In this respect crystal structures fall into two types, differing fundamentally in the *dynamics of the lattice vibrations.*

For the first type of structure (type A) it proved possible to depict the trend of the heat capacity explicitly by equations 1 or 2. For the second type of structure (type B) the heat capacity must be split up into two parts: (1) the heat capacity of the high polymer chain skeleton (the ordinary-chain anion), and (2) the heat capacity of the cation appendages which vibrate like monochromatic Planck–Einstein oscillators.

Hence, for a B-type structure we can write

$$C_{\mathrm{B}} = C_{1(3)} + nC_{\mathrm{Einst.}}$$

where n is the number of gram atoms of the cation appendages. Figure 1 shows an example of the trend of the heat capacity for an A-type structure. It refers to pyroxene ($MgSiO_3$).

From 50 to 300°K. the function 1, taken for five gram atoms in conformity with the formula and structure of the chains $(MgSiO_3)_\infty$, gives an excellent fit to the heat capacity

$$C_{\mathrm{MgSiO_3}} = 5C_{1(3)} \quad (3)$$

The experimental values of the heat capacity of $MgSiO_3$ are taken from the paper of Kelley.[11] The values of the parameters of equation 1 for $MgSiO_3$ were taken equal to $\theta_1 = 1285$ and $\theta_3 = 0.3 \times 1285° = 386°$. These results were published earlier.[12]

As an illustration of a B-type case we can take sodium metasilicate (Na_2SiO_3). As was shown in our above-cited paper,[12] and also in ref 13, the heat capacity of crystalline Na_2SiO_3, according to the data of Kelley,[15] is described by the equation

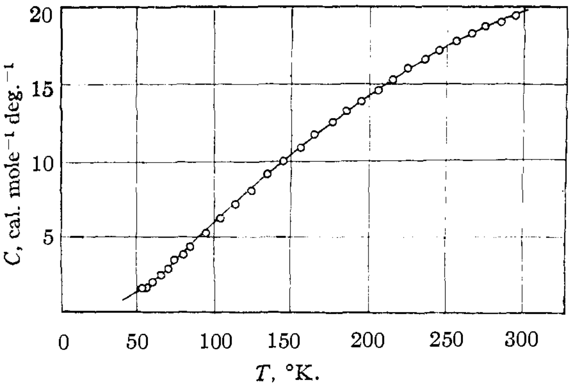

Fig. 1.—Heat capacity of pyroxene ($MgSiO_3$). Experimental values taken from ref. 11. Solid curve computed by eq. 1 for 5 gram atoms for $\theta_1 = 1285°$ and $\theta_3/\theta_1 = 0.3$.

$$C_{\mathrm{Na_2SiO_3}} = 4C_{1(3)} + 2C_{\mathrm{Einst.}} \quad (4)$$

for values of the parameters of equation 1 equal to $\theta_1 = 1323°$, $\theta_2 = 397°$ and $\theta_3 = 256°$.

It will be shown in what follows that the anhydrous salt $Na_2B_4O_7$ is an excellent example of type B, *i.e.*, throughout a wide range of temperatures the heat capacity may be represented as the sum of two terms: (1) the heat capacity of the chain or ribbon high polymer $(B_4O_7)_\infty$ and (2) the heat capacity of the cation monochromatic oscillators 2Na.

However, the case of anhydrous crystalline sodium tetraborate is even more interesting, for here θ_1 is very great, as a result of which almost all the experimental points fall on the linear part of the curve (equation 2) and, hence, the second parameter, *i.e.*, θ_3 becomes superfluous.

In *kernite*,[14] ($Na_2B_4O_7.4H_2O$) as is evident from X-ray data, there are chains of $B_4O_7^{2-}$.

In view of this, it appeared worthwhile to analyze the experimental data on the heat capacity of the anhydrous crystalline salt $Na_2B_4O_7$ on the basis of the conception of the oscillations of chain continuum; this was made possible by the appearance of the paper of Westrum and Grenier[16] containing careful measurements of the heat capacity of anhydrous crystalline and glassy $Na_2B_4O_7$.

As in the case of sodium metasilicate, we regarded the heat capacity of $Na_2B_4O_7$ as consisting of two "independent" parts: the Planck–Einstein contribution of the Na appendages and the contribution of the chain continuum B_4O_7.

Taking this into consideration we attempted to compute the curve of the heat capacity of the B_4O_7 chain skeleton by subtracting the heat capacity contribution of the 2 gram atoms of Na cations from the total heat capacity of $Na_2B_4O_7$. The magnitudes of these contributions were computed using the same characteristic temperature for the vibrations of the Na cations ($\theta_{\mathrm{Na}} = 256°$K.) which

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(7) J. Krumhansl and H. Brooks, *J. Chem. Phys.*, **21**, 1663 (1953).

(8) H. B. Rosenstock, *ibid.*, **21**, 2064 (1953).

(9) V. V. Tarassov, *Doklady, Acad. Sci. USSR*, **100**, 307 (1955); *Trans. D. I. Mendelejev Chem. Techn. Inst. Moscow*, **23**, 157 (1956).

(10) V. V. Tarassov, *Zhurn. Fiz. Khim.*, **26**, 1374 (1952).

(11) K. K. Kelley, THIS JOURNAL, **65**, 339 (1943).

(12) V. V. Tarassov, *Compt. rend. acad. sci. URSS*, **84**, 321 (1952).

(13) V. V. Tarassov and Y. S. Savitskaya, *Zhurn. Fiz. Khim.*, **27**, 744 (1953).

(14) V. P. Portoles, *Estud. Geol. Inst. Mallada*, **5**, 3 (1947); **7**, 21 (1948).

(15) K. K. Kelley, THIS JOURNAL, **61**, 471 (1939).

(16) E. F. Westrum, Jr., and G. Grenier, *ibid.*, **79**, 1799 (1957).

we used earlier in the case of sodium metasilicate.[12] This was based on the assumptions set forth above.

Using Sherman and Ewell's seven-place tables of Einstein's function,[17] we computed the contribution of the Na cations to the heat capacity in 10° intervals from 20 to 300°K. The remarkable result obtained by subtracting the contribution of the heat capacity of 2 Na is demonstrated in Fig. 2. It consists in the following: upon subtraction of the cation contribution 2 Na to the heat capacity curve 1 from the curve depicting the experimental heat capacities of crystalline $Na_2B_4O_7$ according to the Westrum and Grenier curve 2, we obtained points which excellently fit the theoretical straight line 3. This theoretical straight line gives the temperature dependence of the heat capacity of the chain anion lattice of $B_4O_7^{2-}$. The term "theoretical straight line" will be explained below.

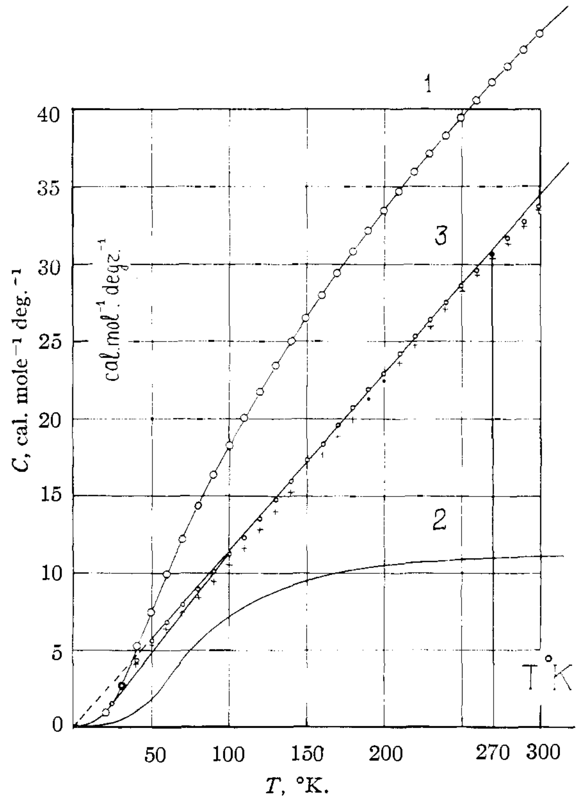

Fig. 2.—Heat capacity of anhydrous sodium tetraborate: 1, from the paper of Westrum and Grenier[16] for crystalline $Na_2B_4O_7$; 2, heat capacity of 2 gram atoms of Na cations computed by Einstein's function for $\theta_{Na} = 256°$; 3, straight line computed by eq. 2 for $\theta_1 = 1890°$; O were obtained by subtracting the ordinates of curve 2 from the ordinates of curve 1; +, the same for glassy tetraborate.

In our earlier papers we explained the trend of the heat capacity of crystalline and glassy boron trioxide B_2O_3 on the basis of the hypothesis of the chain structure of B_2O_3[18,19]: for crystalline B_2O_3 we utilized the measurements of the heat capacity between 17 and 300°K. carried out by Kerr, Herch and Johnston.[20]

The chain model of B_2O_3 makes it possible to interpolate with good results the values of the heat capacity of crystalline and glassy B_2O_3.[19] In addition, the hypothesis of the chain structure of glassy B_2O_3 allows an easy interpretation of the low temperature softening of glassy boron trioxide (~235°) despite the very large energies and strengths of the chemical bonds between the boron and oxygen atoms in the continuous high polymer structure of glassy B_2O_3. According to ref. 18, the mean value of the characteristic temperature for B_2O_3 is $\theta_1^{B_2O_3} = 1890°K$.

Taking this value of the characteristic temperature for the case of the B_4O_7 chains, *i.e.*, assuming that the force constants of these chains do not differ from those of B_2O_3, we can write on the basis of formula 2

$$C_{1(3)} = 11\pi^2 R \left(\frac{T}{1890}\right)^1$$

where the coefficient 11 accounts for the 11 gram atoms per mole of B_4O_7.

We thus utilized the limiting function of the heat capacity of both the B_2O_3 and the B_4O_7 chains with the same characteristic temperature 1890°.

The application of the limiting function in these cases also remains to be explained. Our two-parameter function equation 1 for interacting chains goes over into a one-parameter function both when the *difference* between the two terms in the brackets is small and when the factor θ_3/θ_1 in front of the brackets is close to zero. The latter case ($\theta_3/\theta_1 \rightarrow 0$), however, may be due either to a small value of θ_3, *i.e.*, to a small absolute value of the lateral interaction of the chains, or to a large value of θ_1, *i.e.*, to a large internal elasticity of the chains themselves

In the borates we are undoubtedly dealing with the latter case, since the B–O bond is considerably more elastic than the Si–O bond, approaching the diamond bond.

An additional proof of the validity of our result is the fact that for the chosen value of the characteristic temperature—1890°—the deviation from the linear dependence begins just where it should, on the basis of our assumption. It is well known that the one-dimensional Debye function which we utilized in our investigation of chain structures deviates by 1.56% toward the axis of abscissas from the straight line passing through the origin of coördinates at a value of the temperature equal to $^1/_7\,\theta_1$, which in the given case amounts to 1890/7 = 270°.

It is evident from the graph that this very important detail is also very closely borne out. At sufficiently low temperatures ($T << \theta_1^{1/3}\cdot\theta_3^{2/3}$), the function 1 goes over into the T^3 law

$$C = \frac{12}{5}\,\pi^4 R\,\frac{T^3}{\theta_1^{\,1}\theta_3^{\,2}}$$

whence one can obtain the value of θ_3. For B_4O_7 $\theta_3 = 142°$. In Fig. 2 the curve below 100°K. was plotted on the basis of the two-parameter equation 1 ($\theta_1 = 1890°$, $\theta_3 = 142°$). Above 100°K. (up to $T = 1/7 \times 1890 = 270°K.$) the heat capacities

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(17) Sherman and Ewell, see H. Zeise, "Thermodynamik," Bd. III/1, Tabellen, Verlag S. Hirzel, Leipzig, pp. 208–220.

(18) V. V. Tarassov, *Zhur. Fiz. Khim.. USSR*, **29**, 198 (1955).

(19) V. V. Tarassov and E. F. Stroganov, *Trans. D.I. Mendelejev Chemi. Techn. Inst., Moscow*, **21**, 26 (1956).

(20) E. C. Kerr, H. N. Herch and H. L. Johnston, THIS JOURNAL, **72**, 4738 (1950).

computed according to equation 1 and according to the limiting law 2 practically coincide.

The same method of subtracting the heat capacity contributions of the 2 Na oscillators, when applied to the heat capacity of glassy anhydrous tetraborate according to the data of the same paper by Westrum and Grenier and for the same value of $\theta_{Na} = 256°$, yields points which do not fall on a straight line, as is evident from Fig. 2.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

A Spectrophotometric Study of the Interaction of Bromine with Tetrakis-(*p*-methoxyphenyl)-ethylene[1]

BY ROBERT E. BUCKLES AND W. DALE WOMER

RECEIVED AUGUST 14, 1957

When mixed with bromine in ethylene chloride tetrakis-(*p*-methoxyphenyl)-ethylene (TAE) gave a blue solution immediately. This solution had an absorption peak at 575 mμ which was not characteristic of bromine nor of TAE. Standing produced a new absorbing species (490 mμ). Both of these species acted as if they were complexes in that the bromine was easily removed from each by copper. Less easily removed was bromine held by a third species which was in equilibrium with the complexes. An equilibrium constant (based on concentration) of $(6.8 \pm 0.5)10^2$ l. per mole was measured for the formation of the blue complex in ethylene chloride at 26°. The value for this equilibrium constant increased as the temperature was lowered. No changes in spectra were observed when TAE was mixed with bromine in dilute solutions in carbon tetrachloride. In ethylene chloride other tetraarylethylenes failed to give instantaneous spectral changes when mixed with bromine.

Donor-acceptor complexes[2] have generally come to be accepted as the most useful description of the type of interaction which characterizes the solutions of iodine in the so-called "brown" solvents.[3] Of particular interest has been the interaction of halogens with aromatic compounds.[4] Considerable data have been accumulated in connection with the shifts in the visible and ultraviolet absorption spectra and with the equilibrium constants associated with the formation of the complexes.[5] Also, observations which support the formation of donor–acceptor complexes have been made concerning changes in the infrared spectra[6] and in the dipole moments[7] which accompany solvent interaction with halogens. Consistent with the view that the interaction of halogens with arylethylenes as electron donors gives rise to complexes are the observations reporting the formation of colored solutions,[8] colored, salt-like solids[8e–g] and conducting solutions.[8g]

The present investigation involves the changes in the visible and ultraviolet absorption spectra of tetrakis-(*p*-methoxyphenyl)-ethylene (tetraanisylethylene or TAE) on interaction with bromine.

A solution of TAE in ethylene chloride in the presence of bromine turned blue immediately as had been reported[8a,e] for this interaction. This sort of change is presumed to involve complex formation. As shown in Fig. 1, these blue solutions of TAE with bromine in ethylene chloride also underwent slow changes and the blue color (575 mμ) gradually disappeared as the peak characteristic[9] of the conjugated double bond (330 mμ) also disappeared. At the same time a new peak appeared at 490 mμ. A second complex apparently was formed as a result of a slow but favorable equilibrium with the first complex. Copper powder removed this new peak from the solution. If the copper was kept in contact with the solution for only a short time the resulting solution contained a third absorbing species with a spectrum the same as that of the second complex, within experimental error, except that the peak at 490 mμ was removed. This third species may have been a third complex or the dibromide of TAE. In any event the solution turned yellow on standing. The peak at 490 mμ was again observed in the spectrum but the rest of the spectrum was the same as before the 490 mμ peak returned. Thus, the third complex (or dibromide) was in slow equilibrium with the second complex. Finally all changes could be wiped out and the spectrum of the solution returned to that characteristic of the original ethylene by extended treatment with copper powder. This solution had the spectrum characteristic of the blue complex when mixed with a fresh portion of bromine solution.

This behavior of TAE with bromine to form a blue complex immediately and a yellow complex more slowly is reminiscent of the complexes re-

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(1) From the Ph.D. Thesis of W. Dale Womer. This investigation was sponsored by the Office of Ordnance Research, U. S. Army.

(2) (a) R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); **74**, 811 (1952); (b) *J. Phys. Chem.*, **56**, 801 (1952); (c) *Rec. trav. chim.*, **75**, 845 (1956); (d) C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954); (e) P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1199 (1957).

(3) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).

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(6) W. Haller, G. Jura and G. C. Pimentel, *J. Chem. Phys.*, **22**, 721 (1954); L. D'Or, R. Alewaeters and J. Collin, *Rec. trav. chim.*, **75**, 862 (1956); J. Collin and L. D'Or, *J. Chem. Phys.*, **23**, 397 (1955); R. S. Mulliken, *ibid.*, **23**, 397 (1955); W. B. Person, R. E. Erickson and R. E. Buckles, *ibid.*, **27**, 1211 (1957).

(7) F. Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948).

(8) (a) L. Gattermann, *Ber.*, **22**, 1129 (1889); **28**, 2869 (1895); (b) P. Pfeiffer and P. Schneider, *J. prakt. Chem.*, **129**, 129 (1931); (c) W. Bockemüller and R. Janssen, *Ann.*, **542**, 166 (1939); (d) R. Wizinger, *Z. angew. Chem.*, **39**, 564 (1926); **40**, 503, 675 (1927); (e) R. Wizinger and J. Fontaine, *Ber.*, **60**, 1377 (1927); (f) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 132 (1928); (g) R. E. Buckles and N. A. Meinhardt, THIS JOURNAL, **74**, 1171 (1952).

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