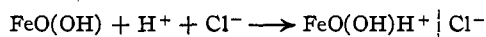


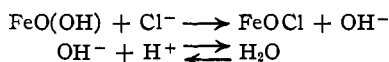
tion the β oxide had been subjected to a drastic perfection process. It may be safely predicted that under equilibrium conditions the ratio Cl:OH in the precipitate will increase with increasing chloride and hydrogen ion concentration in the solution.

$$\left(\frac{\text{Cl}}{\text{OH}}\right)_{\text{precipitate}} = K \left(\frac{\text{Cl}^-}{\text{OH}^-}\right)_{\text{solution}} = K' \{[\text{Cl}^-][\text{H}^+]\}_{\text{solution}}$$

The results show the care that must be exercised in the interpretation of "adsorption" experiments. In all cases mentioned above the "adsorption" of the hydrogen ions was measured, naturally an equivalent amount of anion also disappeared when the adsorbent did not contain adsorbed base.



A similar equivalent removal of hydrogen ions and anions is found when we are dealing with an exchange and subsequent neutralization of the hydroxyl ions sent into solution



The results obtained allow the following conclusions to be drawn: (1) FeOCl and β FeO(OH) (β Fe₂O₃·1H₂O) are isomorphous, and may form mixed crystals over a wide range of Cl:OH ratios. (2) The β oxide is not iron oxide monohydrate, β Fe₂O₃·1H₂O, but has the constitution FeO(OH). (3) The conclusion of Weiser and Milligan⁶ that the yellowish precipitate obtained by slow hydrolysis of ferric chloride solutions contains more or less chloride adsorbed is not warranted. The

precipitate is a mixed crystal of FeOCl and β FeOOH, the composition of which depends upon experimental conditions. Upon washing with ammonia more or less of the chloride in the precipitate is replaced by hydroxyl.

From Table IV it follows that on shaking of the β oxide with hydrobromic acid adsorption equilibrium is attained very quickly, but that no bromide ion enters the lattice of the oxide. Although the bromide ion has about the same size as the chloride ion it apparently does not fit in the lattice of β FeO(OH). This finding is in harmony with the fact discovered by Weiser and Milligan⁶ that upon hydrolysis of ferric bromide not the β but the α oxide is formed. From the results in Tables I and III it is apparent that the β oxide dissolves faster in a solution that is 0.02 *N* in hydrochloric acid and 1 *N* in sodium chloride than in a solution containing corresponding amounts of perchloric acid and sodium perchlorate.

Summary

Upon prolonged shaking of so-called β ferric oxide monohydrate with dilute hydrochloric acid in a sodium chloride solution a continuous decrease of the acid concentration is found. The results indicate that the β oxide is not an oxide monohydrate but has the structure β FeO(OH) which is isomorphous with FeOCl and that these two form mixed crystals.

MINNEAPOLIS, MINN.

RECEIVED FEBRUARY 20, 1936

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

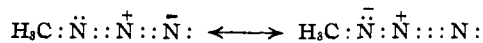
The Configuration of the Azide Ion

BY LUDO K. FREVEL¹

In 1925 it was shown that the azide ion in the azides of sodium and potassium is linear and possesses a center of symmetry.² The collinearity of the azide group in organic compounds, however, was not settled until the electron diffraction work on methyl azide³ and the recent crystal structure determinations of cyanuric triazide^{4,5} revealed definitely that the N₃ group is

linear but not centro-symmetric like the N₃⁻ ion. The symmetry of the azide ion as ascertained from x-ray data was independently supported by Raman spectra of the azide ion in aqueous solution.⁶

This difference between the N₃ group and the N₃⁻ ion can be explained readily. In methyl azide, for example, the following two resonating



structures were found to represent satisfactorily the configuration of the azide group.^{3,4,5}

(6) A. Langseth, J. Rud Nielson and Utoff Sørensen, *Z. physik. Chem.*, **B27**, 100 (1934).

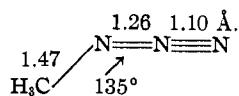
(1) National Research Fellow.

(2) Sterling B. Hendricks and Linus Pauling, *THIS JOURNAL*, **47**, 2904 (1925).

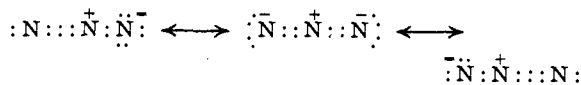
(3) L. O. Brockway and Linus Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933).

(4) E. W. Hughes, *J. Chem. Phys.*, **3**, 1 (1935).

(5) I. E. Knaggs, *Proc. Roy. Soc. (London)*, **A150**, 576 (1935).



To account for the center of symmetry of the N_3^- ion, resonance should occur between the three dominant structures



The static symmetric formulas



doubtless contribute very little to the character of the azide ion, inasmuch as the N-N distance between adjacent nitrogen atoms approaches the triple bond distance in the nitrogen molecule. Moreover, there is no resonance between these latter structures and the above because the two sets of structures differ in the number of unpaired electrons. Also electronic structures like



are ruled out because five orbitals are put about the central nitrogen.

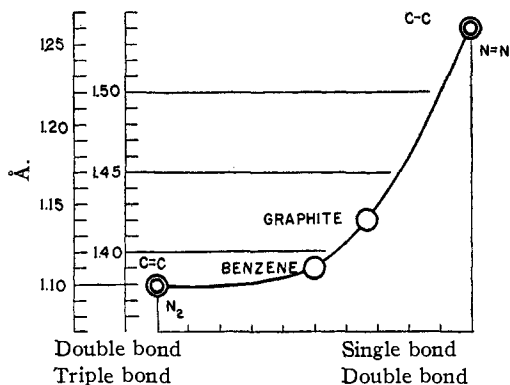


Fig. 1.—A graph of the functional dependence of the covalent interatomic distance on bond character for single bond–double bond resonance⁸ (or double bond–triple bond resonance).

To determine the degree of triple bond character of the nitrogen–nitrogen bond in the azide ion, the author carefully redetermined the N–N distances in the crystals NaN_3 and KN_3 . Table I lists some values for this distance in different azides.

It was shown by Pauling, Brockway and Beach⁸ that the empirical function expressing the

(7) G. Hellman, *Z. Physik*, **82**, 192 (1933).

(8) Linus Pauling, L. O. Brockway and J. Y. Beach, *THIS JOURNAL*, **57**, 2705 (1935).

TABLE I

The approximate value 1.18 Å. was calculated with the aid of Badger's rule,⁹ the force constant for the nitrogen–nitrogen linkage being 14.92×10^6 dynes cm.^{-1} as obtained from the Raman frequency⁴ $\nu_1 = 1348$ cm.^{-1} .

Substance	N–N distance, Å.
NaN_3	1.150 ± 0.016
KN_3	1.145 ± 0.017
NH_4N_3	1.165 ± 0.021
$(\text{N}_3^-)\text{aq.}$	1.18

dependence of carbon–carbon interatomic distance on bond character for single bond–double bond resonance can be applied to bonds other than carbon–carbon linkages. In Fig. 1 the N≡N distance is the internuclear separation in the nitrogen molecule. For the nitrogen–nitrogen double bond distance the value 1.26 Å. was used.¹⁰ It is interesting to note that the increase of 0.16 Å. in going from N≡N to N=N equals the difference between the C–C distance and the C=C distance. Now in view of the applicability of the curve of Fig. 1 to a variety of resonating structures, it appears reasonable to extend the function to the double bond–triple bond resonance in the azide ion. Doing this one finds that a nitrogen–nitrogen distance of 1.15 Å. corresponds to about 30% triple bond character.

It should be pointed out that the somewhat larger distance of 1.165 Å. in ammonium azide¹¹ (corresponding to 24% triple bond character) can be explained by the fact that in a crystal of NH_4N_3 each terminal nitrogen of the azide ion is attached to its two nearest ammonium neighbors by hydrogen bonds. Doubtlessly the double-bond structure $\left(\text{:}\overset{-}{\text{N}}::\overset{+}{\text{N}}::\overset{-}{\text{N}}:\right)$ is partially stabilized by this phenomenon.

Experimental Data

Crystals of sodium azide and potassium azide were prepared by slow crystallization from aqueous solution. In the case of the potassium salt the crystals were clear and showed good face development. Sodium azide, however, gave poor crystals, mostly multiple crystals; and it became expedient to resort to powder data. Filtered MoK radiation from a sealed glass tube operated

(9) Richard M. Badger, *J. Chem. Phys.*, **3**, 710 (1935).

(10) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 224 (1934).

(11) The author recently determined the crystal structure of the orthorhombic crystal ammonium azide and found that each ammonium nitrogen is bridged tetrahedrally by hydrogen bonds to four end-nitrogens of four N_3^- ions and that each terminal nitrogen is attached to two ammonium nitrogens and to the central nitrogen of the linear N_3^- ion. This structure determination will be published in the "Zeitschrift für Kristallographie."

at 20 ma. and 36 kv. was used throughout the x-ray investigation. The visual estimation of intensities of interference maxima was carried out with the aid of a graduated intensity scale ranging in arbitrary units from 1 to 10 and thereafter in units of 5 up to 60. Moreover, the time of exposure for different sets of reflections was varied so that a fairly reliable relationship could be established between strong reflections and weak ones. The intensities from different films were correlated by means of reflections common to two or

TABLE II

INTENSITY DATA FOR POTASSIUM AZIDE

(*hkl*) are the indices referred to the tetragonal unit $a_0 = 6.094 \text{ \AA.}$, $b_0 = 7.056 \text{ \AA.}$ $I_{\text{calcd.}} = 0.00858 \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) F^2$, where F has the values: $4f_{N^-} [\cos 2\pi(h+k)u - \cos 2\pi(h-k)u]$, for l odd and h, k mixed; $4 \left\{ f_{K^+} \cos \frac{\pi l}{2} + f_{N^-} + f_{N^-} [\cos 2\pi(h+k)u + \cos 2\pi(h-k)u] \right\}$, for h, k, l all even; $4 \left\{ f_{K^+} \cos \frac{\pi l}{2} - f_{N^-} - f_{N^-} [\cos 2\pi(h+k)u + \cos 2\pi(h-k)u] \right\}$, for l even and h, k odd. $u = 0.133 \pm 0.002$.

(<i>hkl</i>)	$I_{\text{obsd.}}$	$I_{\text{obsd.}}^{1/2}$	$I_{\text{calcd.}}^{1/2}$
112	200	14.2	21.8
004	100	10.0	14.1
022	50	7.1	7.13
332	45	6.7	7.10
211	40+	6.3+	6.86
024	40	6.3	6.82
312	30	5.5	6.12
224	30-	5.5-	5.78
116	20	4.5	4.86
222	20	4.5	4.67
134	15+	3.9	4.16
424	13	3.6	3.74
123	12	3.5	3.78
532	12	3.5	3.61
444	10	3.2	3.52
336	8+	2.8+	3.13
008	8+	2.8+	3.23
422	7	2.6	2.55
321	7	2.6	2.54
316	6+	2.5	2.37
552	5	2.2	2.26
028	5-	2.2-	2.09
228	4+	2.0+	1.94
226	4+	2.0+	1.92
640	4+	2.0+	1.90
125	3-	1.7-	1.70
323	3-	1.7-	1.70
521	2+	1.4+	1.51
642	2+	1.4+	1.43
550	2	1.4	1.12
334	2	1.4	1.00
118	2-	1.4-	0.95
006	1	1	.40

TABLE III

INTENSITY DATA FOR SODIUM AZIDE

(*hkl*) are the rhombohedral indices referred to the unit $a_0 = 5.481 \text{ \AA.}$, $\alpha = 38^\circ 43'$. $10^4 I_{\text{calcd.}} = 1.672 j \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) F^2$, where F has the values: $f_{Na^+} + f_N + 2f_{N^-} \cos 2\pi(h+k+l)u$, for $h+k+l$ even; $f_{Na^+} - f_N + 2f_{N^-} \cos 2\pi(h+k+l)u$, for $h+k+l$ odd. $u = 0.424_5 \pm 0.001$.

(<i>hkl</i>)	$I_{\text{obsd.}}$	$I_{\text{obsd.}}^{1/2}$	$I_{\text{calcd.}}^{1/2}$
110	18	4.24	4.26
211	3.5	1.87	1.81
221	3.0	1.73	1.74
110	7.2	2.68	2.67
200	2.5	1.58	1.62
433	0.8	0.90	0.95
211	1.7	1.30	1.27

more films. All films were developed for the same effective length of time at a constant temperature of 18° .

In the calculation of intensities the experimental scattering factors for K^+ and Na^+ were used.^{12,13} The f -values for the azide nitrogens ($N^{-1/2}-N^0-N^{-1/2}$) are the Pauling-Sherman values multiplied by a temperature factor $e^{-2(\sin \theta/\lambda)^2}$. Tables II and III show the excellent agreement obtained between calculated intensities and those experimentally observed.

Both for potassium azide and sodium azide the parameter u (see legends to Tables II and III) was located by plotting $I_{\text{calcd.}}^{1/2}$ against u and then finding the value of u within the parameter interval set by intensity inequalities so that a most favorable agreement was had with the experimental data. The variation of ± 0.002 from the most probable value for u is one-half the permissible parameter interval determined by the observed intensities from 15° -oscillation photographs.

The author wishes to thank Professor Pauling for the interest and time he has given this work.

Summary

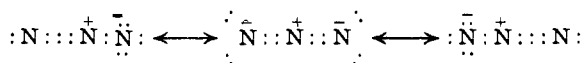
1. The nitrogen-nitrogen distances in the crystals of sodium azide and potassium azide were carefully redetermined in order to ascertain the degree of triple bond character of the N-N bond in the azide ion.

2. The functional dependence of the covalent interatomic distance on bond character for single bond-double bond resonance was extended to the double bond-triple bond resonance in the centro-

(12) R. W. James and G. W. Brindley, *Proc. Roy. Soc. (London)*, **121A**, 155 (1928).

(13) R. W. James and E. M. Firth, *ibid.*, **117A**, 62 (1927).

symmetric azide ion, this configuration of which can be satisfactorily represented by the three structures



PASADENA, CALIF.

RECEIVED MARCH 20, 1936

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Effect of Surface Tension and Electrical Potential on the Stability of Mercury Emulsions

By V. SIVERTZ, W. H. NAYLOR AND H. V. TARTAR

In the preparation of mercury emulsions in water the function of certain ions as emulsifying agents has been attributed largely to the lowering of the interfacial tension between the two liquids.¹

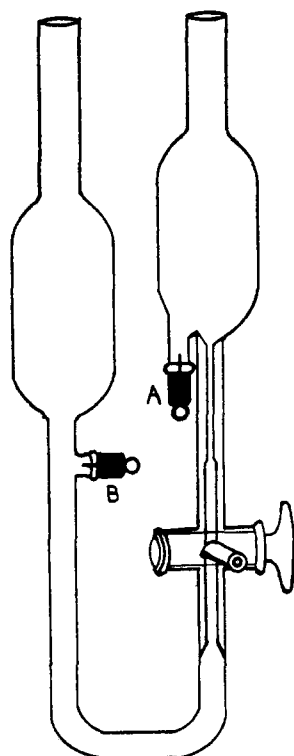


Fig. 1.—The capillimeter.

The work presented in this paper was undertaken to determine the influence of different emulsifying agents on the interfacial tension and electrical potential of a given pair of liquids. For this purpose, mercury emulsions were used because these systems are well adapted for the direct measurements required. It is unnecessary to give here any extensive review of the general literature on mercury emulsions or on the influence of electrolytes on the potential at a mercury-water interface.

Experimental

Purification of Materials.—Distilled water from the laboratory supply was further purified by distillation from alkaline permanganate in an apparatus of Pyrex glass

(1) Svedberg, "Colloid Chemistry," Chemical Catalog Co., 2nd edition, 1928, p. 28.

which had been seasoned by use. The water was received slightly below the boiling temperature in Pyrex bottles to minimize the amount of dissolved gases.

The salts used were of analyzed reagent grade and were tested for purity. Some were first purified by recrystallization. The sodium lauryl sulfonate was prepared by R. M. Reed.²

The mercury was first washed with benzene to remove grease. Then it was shaken with nitric acid (containing a small amount of mercurous nitrate) and air drawn through for several hours. The nitric acid was then removed by thorough washing with distilled water and the mercury dried. This product was further purified by repeated distillation *in vacuo* in a Pyrex still.

Emulsifying Agents.—A number of substances (listed in Table I) were used as emulsifying agents. A concentration of 0.025 *N* was adopted because this concentration gave satisfactory electrical conductivity for e. m. f. measurements. In general, former workers have favored lower concentrations. Nordlund³ considered 0.0025 *N* the optimum concentration. It was found, however, that when a material was an emulsifying agent at the lower concentration, it also functioned when the concentration was increased to 0.025 *N*. Solutions were also used of certain electrolytes which were not emulsifying agents.

Apparatus.—A sketch of the capillimeter used for the interfacial tension measurements is given in Fig. 1. It was made of Pyrex glass with sealed-in tungsten electrodes, A and B, which were protected externally by a metallic sheath of special design. In designing the apparatus, careful adherence was made to specifications of Richards and Coombs⁴ and of Bartell, Case and Brown⁵ for capillary tubes for surface tension measurements. The tubing was tested for uniformity of bore both before and after sealing to the other parts of the apparatus. The radius was $0.03374 \pm 3 \times 10^{-6}$ cm. at 25°.

A special sighting device was made to facilitate the determination with a cathetometer of the height of the wide mercury surface in the capillimeter. A fine platinum wire with a minute bead on the exposed end was sealed into a glass tube. This in turn passed through the hole left by removing the stationary part of a micrometer caliper. The tube was cemented to the moving screw and rotated true. This device was mounted above the mercury

(2) Reed and Tartar, *THIS JOURNAL*, **57**, 570 (1935).

(3) Nordlund, Diss., Upsala, 1918; *J. Chem. Soc.*, **114**, II, 267 (1918).

(4) Richards and Coombs, *THIS JOURNAL*, **37**, 1656 (1915).

(5) Bartell, Case and Brown, *ibid.*, **55**, 2419 (1933).