

The Magnetic Properties of the Phenanthroline Ferric Complexes

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BeO not. The fact that TiO_2 is not known in the vitreous state is also explained by the more basic character of this oxide, which is connected with weaker bonds between Ti and O.

Concerning H_3PO_4 , I explained its glass forming tendency by assuming larger groups than $(\text{PO}_4)^{-3}$ to exist in the melt but I did not discuss the question whether these groups are formed by polymerization of $(\text{PO}_4)^{-3}$ radicals only or if hydrogen was necessary at the construction.

I consider the glasses as supercooled liquids in which the supercooling tendency is caused by groups in the melt which can be added with difficulty directly to the lattice and within which the atoms are kept together by so strong forces as to make their separation difficult. My theory of the structure of glasses is based on this assumption and the problem of the glass forming tendency of a substance is brought back to the question whether such groups are to be expected in the melt. Zachariasen, on the contrary, has assumed a certain type of structure, characterizing the vitreous state. Starting from the corresponding crystal structures, he then discusses the possibility of constructing the vitreous structure.

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April 2, 1935.

¹ W. H. Zachariasen, *J. Chem. Phys.* 3, 162 (1935).

² G. Hägg, *J. Chem. Phys.* 3, 42 (1935).

The Magnetic Properties of the Phenanthroline Ferric Complexes

We have investigated the magnetic susceptibilities of the complex ions formed by the base ortho-phenanthroline with ferric ion. Blau, who discovered some forty years ago the extraordinary stability of the complex metallic ions formed by this base, reported that two ferric complexes are formed, which are not directly interconvertible. One of these is intensely blue in color; can be obtained only by oxidation of the ferrous complex; and has, as the analysis of several solid salts demonstrate, the formula $\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3^{+++}$. The other is brown, and is formed by the direct reaction of ferric salts with phenanthroline. We have obtained a solid brown salt whose analysis corresponds to the formula $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}_2$, but other compounds are undoubtedly also present in the solutions obtained by addition of phenanthroline to solutions of ferric salts. As is indeed to be expected of complexes as stable as these, their formation from ferric ion is accompanied by a very considerable decrease in magnetic susceptibility. According to the theories of Lewis and Pauling the linkages concerned are therefore to be considered as of the shared electron rather than of the ion-dipole type. From measurements in aqueous solution the atomic susceptibility of the iron atom in the blue complex is 2446×10^{-6} which is practically identical with the value observed with ferricyanide ion and generally accepted as

the normal one for coordinatively bound ferric ion. The corresponding value for the brown complex is, however, only 826×10^{-6} . The low value for the magnetic moment, 1.4 Bohr magnetons, to which this leads is perhaps to be attributed to the existence in a single molecular grouping of two or more iron atoms so oriented that their moments partially neutralize each other. There are indeed other indications, now under investigation, that the brown complex has a higher molecular weight than would correspond to a single iron atom per molecule.

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May 6, 1935.

The Decomposition of Hydrogen Peroxide by the Irradiation of Its Aqueous Solution with X-Rays*

Gas-free (unbuffered) solutions of hydrogen peroxide were irradiated with x-rays and the resulting decomposition determined by electrometric titration¹ and by gas analysis. None or a very small amount of hydrogen is produced, the decomposition proceeding essentially according to: $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$. Over the range of concentrations (0.0001 to 0.1 moles H_2O_2 /1000 cc) and x-ray intensities (3 to 15 r/sec.) used, the number of moles of hydrogen peroxide decomposed per unit of dosage increases as the square root of the concentration and decreases as the square root of the x-ray intensity. (Fig. 1.) For a special set of conditions, the

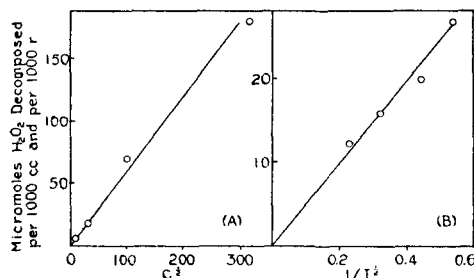


FIG. 1. Decomposition of hydrogen peroxide as a function of: (A) Square root of concentration (C in micromoles per 1000 cc) for an intensity of 9.5 r/sec. (B) Inverse square root of intensity (I in r/sec.) for a concentration of 1.0 millimole H_2O_2 per 1000 cc.

dependence of the decomposition** on the temperature was determined between 0° and 50°C . (Fig. 2.) The temperature coefficient shows a remarkable rise with the temperature; its value, between 15°C and 25°C is 1.18.[†]

A comparison with results²⁻⁸ obtained for the decomposition of hydrogen peroxide with light is of interest. The evidence is not wholly clear, but the increase of the quantum efficiency with the square root of the concentra-

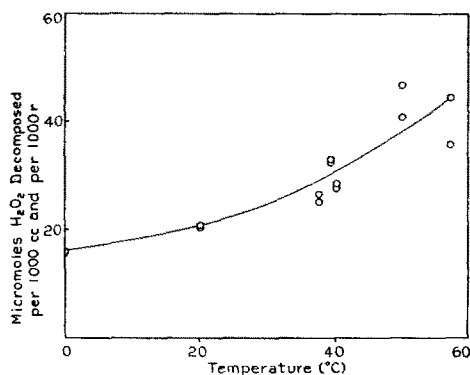


FIG. 2. Decomposition of hydrogen peroxide as a function of the temperature for an x-ray intensity of 3.0 r/sec. and a concentration of 1.0 millimole H_2O_2 per 1000 cc.

tion (except when the concentration is very large)^{2, 8} and with the inverse square root of the intensity, appears consistent with the experimental data. This would be in agreement with the present results if we assume that the decomposition in the case of x-rays is not due to the direct activation of the hydrogen peroxide molecules by the x-ray electrons, but that the primary process is the activation of water molecules^{1, 9-13} followed by the transfer of energy from these activated molecules to the hydrogen peroxide.^{††} On this assumption, the quantum efficiency (in the case of light) should be compared to the number of moles of hydrogen peroxide decomposed per unit of x-ray dosage. It should also be noted that if the decomposition were due to the direct activation of the hydrogen peroxide molecules by the x-ray electrons, in the extreme case as many as 10,000 molecules of hydrogen peroxide would be decomposed for each hydrogen peroxide molecule activated, an unlikely number in view of the relatively short chains observed in the case of light.

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March 30, 1935.

* I am indebted to Dr. E. R. Brownscombe for assisting with these measurements.

** The decomposition of nonirradiated blanks was corrected for, and amounted, at 50°C, to a few percent of that produced during irradiation.

† For the decomposition by light, Allmand and Style, reference 2, found the temperature coefficient (at room temperature) to be: 1.42 for $\lambda = 3650\text{\AA}$, and 1.38 for $\lambda = 2750\text{\AA}$.

†† On this assumption, in our experiments the number of molecules of hydrogen peroxide activated would be expected^{1, 9-13} to be of the order of 10^{10} /cc/sec. With light, intensities producing from 10^{10} to 10^{16} activations/cc/sec. have been used.

¹ Fricke, J. Chem. Phys. 2, 556 (1934).

² Allmand and Style, J. Chem. Soc. (1930), 596, 606.

³ Tian, Comptes rendus 151, 1040 (1910); 156, 1601, 1758, 1879 (1913).

⁴ Henri and Wurmser, Comptes rendus 156, 1012 (1913); 157, 126 (1913).

⁵ Kornfeld, Zeits. f. wiss. Phot. 21, 66 (1921).

⁶ Wither, Trans. Faraday Soc. 21, 459 (1925).

⁷ Heide, J. Am. Chem. Soc. 54, 2840 (1932).

⁸ Qureshi and Rahman, Zeits. f. physik. Chemie 36, 664 (1932).

⁹ Fricke and Morse, Phil. Mag. 7, 129 (1929).

¹⁰ Fricke and Brownscombe, J. Am. Chem. Soc. 55, 2358 (1933).

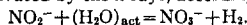
¹¹ Fricke and Brownscombe, Phys. Rev. 44, 240 (1933).

¹² Fricke and Hart, J. Chem. Phys. 2, 824 (1934).

¹³ Fricke and Hart, J. Chem. Phys. 3, 60 (1935).

The Oxidation of the Nitrite to the Nitrate Ion by the Irradiation of Its Aqueous Solutions with X-Rays

Gas-free solutions containing the nitrite ion were irradiated with x-rays and were analyzed for hydrogen and oxygen; and for nitrite by electrometric titration with potassium permanganate. The nitrite ion is oxidized to the nitrate ion and hydrogen liberated in the equivalent amount. The amount of nitrite oxidized is independent of the concentration of the nitrite ion from 0.05 to 100.0 millimoles/1000 cc and of the hydrogen ion concentration from pH = 2.0 to 11.0 and equals 0.55 micromole/1000 r/1000 cc. It is concluded that the transformation is due to water molecules activated by the x-rays, according to:



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The Far Ultraviolet Absorption Spectra and Ionization Potentials of the Ethyl Halides

The absorption spectrum of ethyl iodide is essentially similar to that of methyl iodide¹ and starts at about the same wavelength. Two electronic series containing a large number of terms appear. The upper members can be extrapolated in the form of Rydberg series to ionization potentials of 9.295 ± 0.005 and 9.885 ± 0.005 volts. Thus a difference of about 0.6 volt is maintained in going from methyl to ethyl iodide though the ionization potentials of the latter are diminished by 0.2 volt relative to the corresponding ones in methyl iodide.

The first resonance bands of ethyl bromide start around 1770Å and thus suffer a short wavelength shift of 15Å relative to the corresponding bands in methyl bromide. They are much more diffuse but two series limits can still be observed. These can be extrapolated to the ionization potentials 10.24 ± 0.01 and 10.56 ± 0.01 volts corresponding to a diminution of 0.25 volt relative to the values obtained for methyl bromide.² Part of the difficulty of observing these limits is a background of continuous absorption arising from excitation in the CC bond.

In the case of ethyl chloride only the first few bands are sharp. These are shifted to long wavelengths by about 0.36 volt relative to the analogous bands in methyl chloride. The electronic difference of 0.08 volt is maintained and it is estimated that the ionization potentials of ethyl chloride are about 0.38 volt less than those given for methyl chloride.

The above data provide considerable support for the suggestion put forward by the author³ that the dipoles of methyl and ethyl groups have a strong influence in reducing the ionization potentials of electrons in adjacent bonds. R. S. Mulliken⁴ has shown that the spectra of the