The Raman Spectrum of Orthophosphoric Acid

Myron A. Jeppesen and Raymond M. Bell

LETTERS TO THE EDITOR

The Raman Spectrum of Orthophosphoric Acid

The Raman spectrum of orthophosphoric acid has been investigated by Nisi.[1] He found frequency differences of 356, 498 and 911 cm^{-1} for 84 percent (by weight?); 512 and 906 for 50 percent; and 505 and 898 for 25 percent. The writers have made a study of H_3PO_4 at concentrations ranging from 50 mole percent (the highest available) to 10 percent. The results agree with those of Nisi.

One strong line appears at all concentrations. Measurements of it are as follows (with the excitation by 4358A accurate to about 2 cm^{-1}):

Mole percent		Excited by 4358	Excited by 4047
50	22,029	909	
	23,798		907
40	22,033	905	
	23,801		904
30	22,037	901	
	23,807		898
20	22,042	896	
	23,807		898
10	22,043	895	
	23,812		893

When the product of exposure time and mole percent is made constant, this line appears to have the same intensity at all concentrations. A shift in frequency of about 14 cm^{-1} is clearly indicated.

Other lines which appear at 50 percent are: 22,448 (490), 22,579 (359), 23,607 (909), and 24,212 (493). 490 and 359 cm^{-1} are broad and weak. The 23,607 line is probably excited by 4078A. These weak lines could not be measured at lower concentrations, except 23,624 (892) at 10 percent.

MYRON A. JEPPESEN
RAYMOND M. BELL

Department of Physics,
Pennsylvania State College,
April 22, 1935.

[1] Nisi, Jap. J. Phys. **5**, 119 (1929).

The Vitreous State

In a recent article,[1] Zachariasen has commented my paper on the vitreous state, published in the January number of this Journal.[2] In the following, the comments of Zachariasen are briefly discussed.

My statement that Zachariasen's viewpoint is only adaptable to cases in which the oxygen polyhedra form three-dimensional networks, is based on the fact, that Zachariasen only treats this case. The requirement of a three-dimensional network is the fourth of his rules which he thinks must be fulfilled if an oxide is to form a glass. Later, this rule is also generally applied to oxides, without considering the possibility that the corresponding crystal structure could be characterized by a network of oxygen polyhedra, extended in less than three dimensions. Also in his summary, Zachariasen speaks only of three-dimensional networks.

Zachariasen further says that it is "no real progress to present a theory for the structure of glass in terms of the equally unknown structure of the liquids." I think, in contrary, that this is the most logical way of attacking the glass problem. We know from several analogies that the liquid and vitreous states must be closely connected and we then make use of conceptions of the liquid state which are so general and obvious that they are very likely to be true. I do not think this is more dangerous than direct comparisons between the vitreous and the crystalline state.

The fact that I have not given any detailed description of the structure of the fragments, possible in a glass, is caused by the multitude of structures existing in different glasses and by the variation which can be expected for the different fragments in one definite glass. I have pointed out the importance of definite coordinations within the fragments and I think a consideration of this fact is sufficient for making clear the general structure of a fragment.

It is a matter of course, that a glass, built according to my theory, must be optically clear as the constituting fragments or groups are small compared to the wavelength of light.

It is my opinion that it is the tendency of certain atoms to attain a certain oxygen coordination and the strength with which oxygen is bound to these atoms which is the main cause of the glass forming tendency of vitreous oxides. As Zachariasen remarks, I added in the summary that "the glass forming tendency . . . seems to be especially large when the corresponding crystals contain radicals or molecules unlimited in one or more dimensions" but I do not admit that this statement is too general when it is read in connection with the preceding sentence which implies that these groups must be contained in the melt and kept together with strong (probably in many cases homopolar) forces. In this way I explained why SiO_2 can form glass and

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 $(PO_4)^{-3}$ to exist in the melt but I did not discuss the question whether these groups are formed by polymerization of $(PO_4)^{-3}$ 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.

<div align="right">GUNNAR HÄGG</div>

Institute of General and Inorganic Chemistry,
University of Stockholm,
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 $Fe(C_{12}H_8N_2)_3^{+++}$. 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 $[Fe(C_{12}H_8N_2)_2(H_2O)(OH)]Cl_2$, 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.

<div align="right">GEORGE H. WALDEN
LOUIS P. HAMMETT
ALLISON GAINES, JR.</div>

Department of Chemistry,
Columbia University,
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 titration[1] and by gas analysis. None or a very small amount of hydrogen is produced, the decomposition proceeding essentially according to: $2H_2O_2 = 2H_2O + O_2$. 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
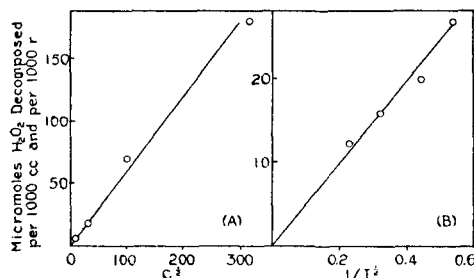

FIG. 1. Decomposition of hydrogen peroxide as a function of: (A) Square root of concentration (C in micromoles per 1000 cc) for an intensity of 9.5 r/sec. (B) Inverse square root of intensity (I in r/sec.) for a concentration of 1.0 millimole H_2O_2 per 1000 cc.

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 results[2-8] 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-