Summary

A simple apparatus and method for obtaining solubilities of gases in water and similar liquids has been described.

The solubilities of nitrogen in water at 50, 75 and 100° from 25 to 1000 atmospheres were measured.

The absorption coefficient showed a distinct minimum at about 70° which became more pronounced with increase in pressure.

It has been shown that at present it is not possible to predict the solubility of nitrogen in water at high pressures from low pressure data with any degree of certainty.

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Luminescence and Crystalline Structure[1]

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Many inorganic solids exhibit luminescence which may appear as fluorescence, phosphorescence or thermoluminescence. Small quantities of dissolved inorganic materials may confer upon these solids the ability to gather energy which may be emitted as luminescence. Such dissolved substances are termed activators. Lenard[2] has proposed the hypothesis that the absorbing and re-emitting center in luminescent solids consists of an atom or molecule of the activator linked with a definite number of solvent molecules. This investigator attributed each luminescence band to a different type of center. In recent years the hypothesis of Lenard has been transposed into a modified form in which it is stated that the manner of linkage of an atom of the activator with a definite number of solvent atoms occurs by substitution of the activator atom for one of the solvent atoms in a definite crystalline lattice.

Tiede and his co-workers[3] have presented some experimental evidence for the crystalline structure theory of luminescence. These workers find that the property of luminescence appears coincident with the occurrence of marked crystalline structure both in the case of calcium tungstate and boron nitride phosphors. On the other hand, Lenard and his students[4] stated that the Lenard phosphors (alkaline earth sulfides oxides or selenides) appear to be hardened glass-like materials. In view of the contradictory statements and the somewhat indirect evidence, information

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(1) Presented in part before the Physical and Inorganic Division at the 84th Meeting of the American Chemical Society, Denver, Colo., August 22 to 26, 1932.

(2) Lenard, *Sitz. Heidelb. Akad.*, 1917, 1918.

(3) Tiede and Schleede, *Z. Elektrochem.*, **29**, 305 (1923); Tiede and Tomaschek, *ibid.*, **29**, 303 (1923); Schleede, *Z. Physik*, **18**, 109 (1923).

(4) Pringsheim, "Fluorescenz und Phosphorescenz," Julius Springer, Berlin, 1928, p. 263.

which will furnish a more definite answer to the question should be of value.

The Relation of the Optimum Concentration to Crystalline Structure.—It has been found by numerous workers in the past that whenever an activator is responsible for luminescence there is found a certain concentration of activator at which the luminescence is of greatest intensity. This concentration is termed the optimum concentration. The optimum concentration is related to the number of atoms which constitute a single lattice group in the crystal theory of luminescence. Late in 1930 Ewles[5] developed a mathematical relation between concentration and intensity of luminescence based upon the substituted activator atom crystal lattice theory. He found that to a first degree of approximation the intensity for a single luminescence band would be given by the expression

$$F = ACe^{-nC}$$

where F is the intensity, A a constant, C the concentration of activator, and n the number of solvent atoms in one crystal group. Ewles pointed out that differentiation of this function indicates that the maximum value of the intensity will be found at the concentration $C = 1/n$. Therefore, the determination of the optimum concentration gives the value of n, the number of solvent atoms associated with each activator atom in the crystal lattice. Without recourse to any formal mathematics it seems evident that if the luminescence is to be conditioned only by the assumption that an atom of activator is linked with a definite number of solvent atoms, the optimum concentration will be the one at which this particular ratio exists. Conversely, if at the optimum concentration the ratio of the number of activator atoms to solvent atoms is $1/S$ then the inference may be drawn that one activator atom would be associated with S solvent atoms in each Lenard center. Moreover, this would be true whether or not the group was a crystalline unit.

Nyswander and Cohn[6] have observed that zinc borate glasses which contain manganese as an activator exhibit thermoluminescence when exposed to ultraviolet light. The relation of the intensity of luminescence to the concentration of manganese has been measured accurately by Cohn and Harkins.[7] The optimum concentration of manganese in the case of thermoluminescence is close to 0.2% manganese. The optimum concentration is not changed when the exciting light is passed through a Corex A blue-purple filter (thickness 4.26 mm.), although the intensity of thermoluminescence is markedly reduced. This indicates that the optimum concentration for thermoluminescence does not vary with the wave length of exciting light in the region examined.

It has been found that zinc borate glasses which contain manganese ex-

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(5) Ewles, *Proc. Roy. Soc.* (London), **129**, 509 (1930).

(6) Nyswander and Cohn, *J. Optical Soc. Am.*, **20**, 131 (1930).

(7) Cohn and Harkins, THIS JOURNAL, **52**, 5146 (1930).

hibit fluorescence when exposed to ultraviolet light. The relation of fluorescence intensity to concentration of manganese is represented by the curves of Fig. 1. Curve A represents the relative intensities of fluorescence obtained when the exciting ultraviolet light passed through a Corex A blue-purple filter of thickness 4.26 mm. whose transmission limit was about 2350 Å. Curve B represents the relative values of fluorescence when the exciting ultraviolet light was transmitted through a Corex A red-purple filter of thickness 4.22 mm. whose transmission limit was about 2480 Å. It will be noted that the optimum concentration is approximately 1.75% manganese in both cases, although the efficiency of excitation of fluorescence is greater for the shorter wave lengths. This signifies that the optimum concentration for fluorescence is independent of the wave length of exciting light in the region of the spectrum in which thermoluminescence may also be excited.

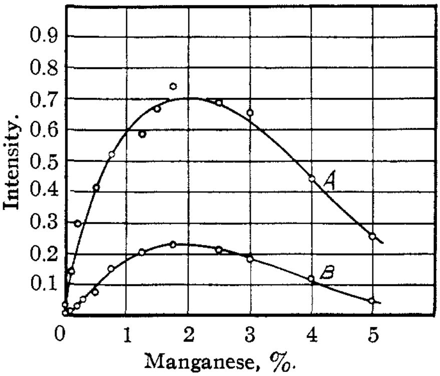

Fig. 1.—The intensity of fluorescence of zinc borate glasses which contain manganese. Curve A represents intensities when excited through a filter of transmission limit 2350 Å.; Curve B, 2480 Å.

The values of the intensity of fluorescence were obtained with the aid of a fluorescence camera whose construction is indicated in Fig. 2. A represents a quartz mercury arc, V a Corex A filter which passed the exciting ultraviolet light, but not the visible of wave length longer than about 4500 Å. S is the glass sample which is 6 mm. square and 2.6 mm. thick, with polished faces and ground upon the edges with emery flour. F indicates a second filter which transmitted red light of wave lengths greater than 5900 Å. L is the lens which passed the fluorescent light from the sample S to the photographic plate. The latter is carried by a rack and pinion upon the back of the camera B. The exciting light passed through the filter to the sample S and a fluorescent comparison sample S′ in the same plane as S but not shown in the diagram. The fluorescent light emerged from the edge of the sample S and the comparison sample S′ and was photographed. By this means a photographic record of intensities of a series of samples

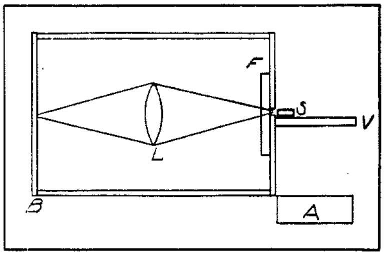

Fig. 2.—Simplified section through fluorescence camera: A, quartz mercury arc; V, filter for ultraviolet light; S, glass specimen; F, filter transparent to fluorescent light; L, lens.

each having the intensity of the comparison alongside was obtained upon a single photographic plate. The density of the deposit upon the photographic plate was determined with the aid of a photoelectric densitometer. The latter consisted of a lamp operated at constant voltage with the aid of a Delta regulating transformer; a small half circle opening over which the images of the plate could be placed; a Weston photronic cell; and a galvanometer. The fluorescent intensities represented in Fig. 1 were graphed in terms of the density of the photographic image obtained after a three-minute exposure to the fluorescence excited by a mercury arc in fused quartz ("Lab-Arc") operating upon 2 amperes, alternating current.

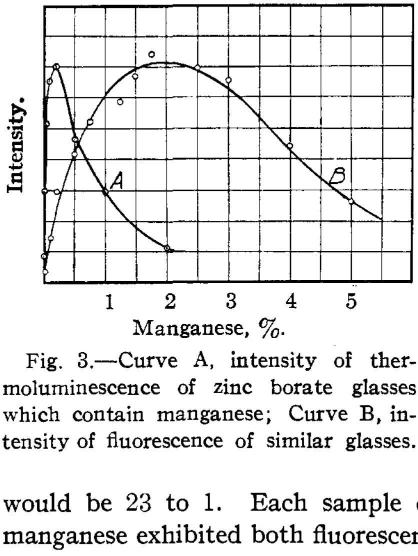

Fig. 3.—Curve A, intensity of thermoluminescence of zinc borate glasses which contain manganese; Curve B, intensity of fluorescence of similar glasses.

In Fig. 3 Curve A represents the intensity of thermoluminescence and Curve B, the intensity of fluorescence as affected by the concentration of the manganese which served as the activator. The intensity coördinates are not equal for the two curves. Inasmuch as the zinc borate glass solvent which composed the specimens had a composition equivalent to $Zn(BO_2)_2 \cdot {}^1/_4ZnO$, the ratio of the number of zinc atoms to manganese atoms in each of the lattices suggested by the data from the optimum was readily computed. In thermoluminescence the ratio of zinc to manganese atoms in a lattice group would be 200 to 1, whereas in the case of fluorescence the ratio of zinc to manganese atoms would be 23 to 1. Each sample of zinc borate glass which contained manganese exhibited both fluorescence and thermoluminescence and therefore would contain both lattice groups. At this stage of presentation of experimental evidence, therefore, two different crystalline lattices would be indicated as being present in each specimen on the basis of the crystal lattice theory.

The Relation of the Emission Spectrum to Crystalline Structure.—If the luminescence of an inorganic solid is to be attributed to a unit lattice grouping, the spectrum of the luminescence is also to be assigned to this unit. This is postulated by both the Lenard and the crystal lattice theories. It is therefore pertinent to our problem to investigate the comparative spectra of fluorescence and thermoluminescence.

The emission spectrum of fluorescence was secured. This spectrum is a band extending from about 5670 to 6750 Å. The maximum intensity is about 6100 Å. The photographic exposure was made upon a panchromatic plate. The exposure time was two hours. An "extreme red" sensitive plate showed no detectable darkening in the region 7200 to 7600 Å. after a ten-hour exposure, which indicates that the panchromatic plate is sensitive in the spectral region occupied by the fluorescence band. The experimental arrangement was similar to that which is used to obtain Raman spectra. The emission spectrum of thermoluminescence was next obtained. Efforts to accomplish this were unsuccessful until an improvised spectrograph of large light gathering power was constructed in which the thermoluminescence sample served as its own slit. The thermoluminescence emission spectrum, photographed upon a panchromatic plate, was found to be a band in the same region of the spectrum as that of fluorescence. The maximum intensity was 6050 ±50 Å.

The evidence indicates that the emission spectra of fluorescence and thermoluminescence are alike, within experimental error. The luminescence therefore should be occasioned by a single lattice group. The conclusion given by evidence from the condition of the optimum was that two crystalline groups were present in each specimen of the zinc borate glass which contained manganese. The conclusion presented by the evidence from emission spectra is in direct conflict with that obtained from the conditions of the optimum as based upon the substituted crystal lattice theory. Therefore, the results indicate that the crystalline structure theory does not account for the luminescence of zinc borate glasses which contain manganese as the activator.

In order to correlate this evidence with x-ray crystal analysis data, powder photographs of zinc borate glasses which contained manganese were taken. The specimens were exposed for the long period of two hundred and forty hours in a Hull powder x-ray diffraction apparatus. The resulting films presented no lines which would indicate the occurrence of crystal planes.

Summary

1. Zinc borate glasses which contain manganese have been found to exhibit fluorescence when exposed to ultraviolet light.
2. The relation of intensity of fluorescence to concentration of manganese has been determined.
3. The emission spectrum of fluorescence has been obtained and is a band extending from about 5670 to 6750 Å. with its maximum in the region of 6100 Å.
4. The thermoluminescence emission spectrum has been obtained and has been found to be a band with a maximum at 6050 ± 50 Å.
5. Results obtained have been interpreted in the light of the substituted crystalline lattice theory. It is concluded from these results that this theory does not account for luminescence in zinc borate glasses.

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