resonance stabilization of the benzene molecule.

5. The available data on dehydrogenation of these ring systems can be accounted for satisfactorily on the basis of probable equilibria.

6. The Balandin multiplet hypothesis thereby loses its principal support.

7. The Balandin hypothesis is invalidated by the observation of catalytic hydrogenation of unsaturated cyclopentenes and cycloheptenes on catalysts configurationally unsuitable on the basis of the multiplet hypothesis.

PRINCETON, N. J. RECEIVED FEBRUARY 4, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

Studies on Phosphorescent Zinc Sulfide[1]

BY WILLIAM H. BYLER

Introduction

The purpose of this work was to develop a controlled method of preparation of phosphorescent zinc sulfide so that a defined group of preparations could be studied for correlation of certain luminous properties among themselves and with the composition and method of preparation of the phosphors. Efforts to correlate the results of different investigators have sometimes been futile because radical differences in luminous properties may result from very slight differences in composition or method of preparation of the materials. By this approach, it was hoped that new light might be thrown on the problems of the necessary conditions for phosphorescence and the nature of the mechanisms of luminescence processes. A simple, objective method of measurement of luminosity was developed in order to facilitate the study.

Preparation of Phosphorescent Zinc Sulfide.—The method employed in this work involved heat treatment of sulfide which was precipitated from ammoniacal solution, washed, filtered, dried at 105°, ground and passed through 200-mesh silk. The calcined material was soaked in water, dried, and passed through 200-mesh silk. Copper solution was added before the precipitation and flux in the dry state was mixed into the wet sulfide.

The difficulty of obtaining a uniform product is due to the effect of variable composition resulting from slight differences in method of preparation, to the marked effect of mere traces of certain metals, and to the important influence of physical state on luminous properties. Using constant heat treatment, the effects of the last two of these factors are usually not revealed except by measurement of luminosity but the first effect sometimes may be recognized by casual examination of color or tendency of the lumpy product to separate into individual crystals.

It is known that the color may be varied widely by variation of composition and heat treatment, but these factors may be held constant within the limits of control and the color still vary somewhat. Guntz[2] demonstrated the important role of zinc oxide in color determination and variations observed in the preliminary stages of this work may be explained on that basis. The amount of zinc oxide in the finished material may be influenced by (1) the character of the atmosphere in the furnace, (2) the reaction of zinc sulfide with water which is present in the dried material in a hydrate, (3) the reaction of the retained ammonium chloride with zinc oxide, and (4) the reaction of zinc oxide with zinc sulfide. The atmosphere in the gas furnace was kept slightly oxidizing and lids were placed loosely on the crucibles. Uniform washing conditions and timing of the filtration process were depended upon to regulate the amount of foreign salts retained by the sulfide.

Ease of disintegration of the lumps in water is significant because the amount of handling required to get the product into powder form is reflected in the quality. There is some evidence that intergrowth of crystals is promoted by a large excess of ammonium chloride. This may be due to reaction of the ammonium chloride with zinc sulfide or oxide to produce zinc chloride. This salt adsorbed on the surface of zinc sulfide crystals would promote cementing.

Metals of the iron group are particularly active as poisons. It is important to use pure starting material and to be on guard against contamination at every step. Any cobalt and nickel present in the electrolytic zinc was plated out almost completely on the zinc during the solution process. Any iron remaining was removed by precipitation as ferric hydroxide.

The physical state of the finished zinc sulfide crystals is largely controllable through regulation of the heat treatment. Calcination temperature could be controlled to within less than 5°. But the physical condition of the dried zinc sulfide is subject to significant variation. When a large excess of hydrogen sulfide is used, the washed precipitate filters quite slowly and shrinks to a brittle, green-yellow mass when dried. When the excess of hydrogen sulfide is small, the filtration is much faster, the shrinkage on drying is not so great, and the dried lumps are snow-white. Difference in color can be explained on the basis of difference in sulfur content. Differences in speed of filtration and density are probably due to difference in particle size or extent of aggregation of particles

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[1] From a thesis submitted to the faculty of the Graduate School in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] A. A. Guntz, *Ann. chim.*, **5**, 157 (1926).

which is traceable to the aging process. In the light of Kolthoff's[3] theory, difference in extent of aging may be pictured as due to a lower solubility of zinc sulfide in the solution containing a larger excess of hydrogen sulfide. Uniformity in this factor was attempted by measuring the hydrogen sulfide, using the same proportion of water for washing the precipitate, and allowing the same time for aging.

With these more incidental variables under reasonable control, a group of samples was prepared in which composition and heat treatment were varied. Coustal[4] lists copper, manganese, iron, cobalt, and nickel as hyperactive in their effects on phosphorescent zinc sulfide. Copper was used throughout as activator and nickel was chosen to demonstrate the effect of a poison. Sodium chloride was used as flux at a concentration of 2% for all samples. Blende samples were calcined at 950° and wurtzite samples at 1060°.

Decay of Phosphorescence

Method of Measurement.—A diagram of the central part of the set-up used in measuring luminous intensity of the samples during decay of phosphorescence is shown in Fig. 1. A is a brass plate with attached strips of brass extending into a beaker of water, C. B is the phosphorescent material held in a 1.6-mm. depression, 4 cm. in diameter and spread out level with the surface of the brass. D is an electric heater and E a thermometer. The temperature could be controlled to within a small fraction of 1°. F represents glass plates insulated from the brass with wool cloth. G and J are shutters. H is a 2.5 v. lamp which was standardized with a MacBeth illuminometer. I is a copper oxide photocell connected direct to a galvanometer through a universal shunt. The galvanometer sensitivity was 3.7×10^{-10} amp./mm. at 1 meter and resistance 509 ohms. K is a track along which the arc lamp and the box holding the photocell could be moved. L is a thermometer. M is an Eveready carbon arc lamp fitted with "c" carbons and No. 587 Corning filter. N is a lever and weight system for moving cell and lamp. When a catch on the frame was released at the end of an excitation period, the lamp was quickly removed and the cell was placed directly above the sample with cell surface 1 cm. from sample surface.

Since the short-circuit current is proportional to the amount of incident light flux, the galvanometer deflection may be taken, to a first approximation, as a measure of relative light intensity. Two scales at different distances from the galvanometer were used to promote accuracy of measurements when the decay was rapid and when the deflection was small. All results are given in terms of deflections on the scale 291 cm. from the coil. Multiplication of deflections in centimeters by 1.72 gives the brightness in μL. Slowly changing characteristics of the cell necessitate standardization before each measurement. A temperature–response curve was constructed so that temperature corrections could be made readily. Sufficient constancy of light from the arc was obtained by filing the carbon ends flat before each exposure, cleaning the filter free of soot each time, control of voltage across the arc at 100 v., and control of arc burning time. Timing was done with a metronome and significant readings were obtained within eight to twelve seconds after excitation. The effect of electromagnetic damping was not negligible and corrections were determined from drift curves with the cell not illuminated. Samples were extinguished completely by ten-minute exposures to infrared light before each measurement.

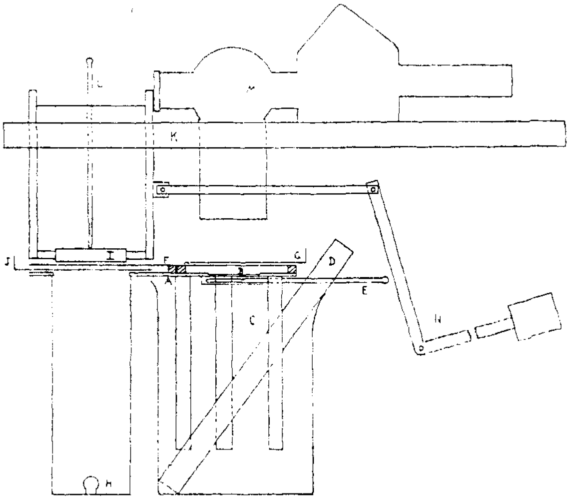

Fig. 1.—Apparatus for measurement of phosphorescence.

Law of Decay.—Guntz[5] and Coustal[6] have reviewed the various types of equations which have been proposed to represent the law of decay. Most discussion has centered around the question of whether the decay can be expressed by a hyperbolic equation or whether a sum of exponential equations must be employed. If the decay is so complex as to require a number of separate equations, not much information can be gained from this approach. Furthermore, the more general form of the hyperbolic law, which has been found to fit the experimental data in a number of cases, is difficult to interpret. Antonov-Romanovskij[7] has stated the law as follows

$$I = I_0 a^\alpha/(a + t)^\alpha \qquad (1)$$

where I is intensity of light at time, t; I_0 is initial intensity; a and α are constants. When α is not equal to 2, one cannot picture a simple mechanism for the decay process, but with α having this value, the equation may be put into the form

$$I^{-0.5} = I_0^{-0.5} + k't \qquad (2)$$

This is the equation which was used by Nichols and Merritt,[8] which later was found to apply in

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(3) I. M. Kolthoff, *Science*, **84**, 376 (1936).

(4) R. Coustal. *J. chim. phys.*. **28**, 277 (1931).

(5) A. A. Guntz, *Ann. chim.*, **6**, 5 (1926).

(6) R. Coustal, *J. chim. phys.*, **28**, 345 (1931).

(7) V. Antonov-Romanovskij, *Compt. rend. acad. sci. U. R. S. S.*, [N. S.] **2**, 108 (1935).

(8) E. L. Nichols and E. Merritt, "Studies in Luminescence," Carnegie Inst. of Wash., 1912.

the case of a single crystal of zinc sulfide by Antonov-Romanovskij,[9] and which has been found applicable to the preparations studied in this work. As suggested by Guntz,[5] this form of the law may be interpreted as resulting from a second-order reaction in the decay process.

Starting with the differential equation which characterizes second-order reactions and assuming the intensity of phosphorescence to be proportional to the rate of change, whatever its nature, the following equation may be derived

$$\mathrm{d}c/\mathrm{d}t = kc^2;\ 1/c = (1/c_0) + kt$$
$$I = kc^2;\ c = I^{0.5}/k^{0.5}$$
$$k^{0.5}/I^{0.5} = k^{0.5}/I_0^{0.5} + kt$$
$$I^{-0.5} = I_0^{-0.5} + k^{0.5}t \qquad (3)$$

where k is the specific reaction rate. Therefore, k', which is the slope of the straight line resulting from a plot of $I^{-0.5}$ against t, is the square root of the specific reaction rate. The values obtained in this way are only relative specific rates.

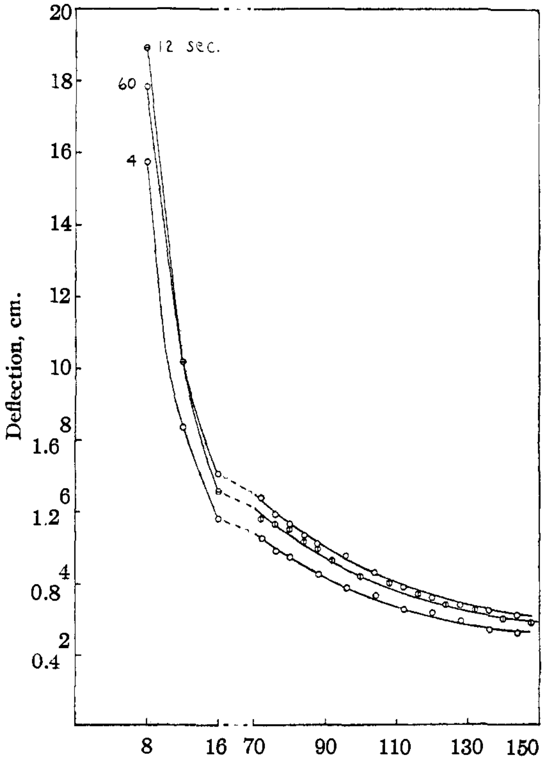

Fig. 2.—Effect of period of excitation on the decay of phosphorescence.

By extrapolating as shown in Fig. 3, the initial intensity, I_0, may be obtained. However, this is the true initial intensity for this band only if the same law of decay and the same k' hold from the beginning. Using a special method for getting readings a few seconds after beginning of decay, it was found that at least one of these conditions does not obtain. It was not until six seconds after excitation that the points fell on the line corresponding to the initial lines of Fig. 3, the earlier readings being far too high. Extrapolation gave an absurd value for initial intensity. Since Antonov-Romanovskij[9] found equation (2) to hold over the range from six-tenths to three seconds for a single crystal, it appears that different crystals of a given sample do not decay uniformly during the first few seconds. The important fact from the point of view of this discussion is that there is another process in the series of processes of decay which precedes those represented by the curves of Fig. 3 and which is much more rapid. When initial intensity is discussed later, unless otherwise specified, it is the hypothetical intensity corresponding to the first line of the decay processes which is meant.

The separate lines corresponding to a single decay curve are interpreted as representing separate processes with characteristic rates. A given process cannot start until the preceding one is practically completed.

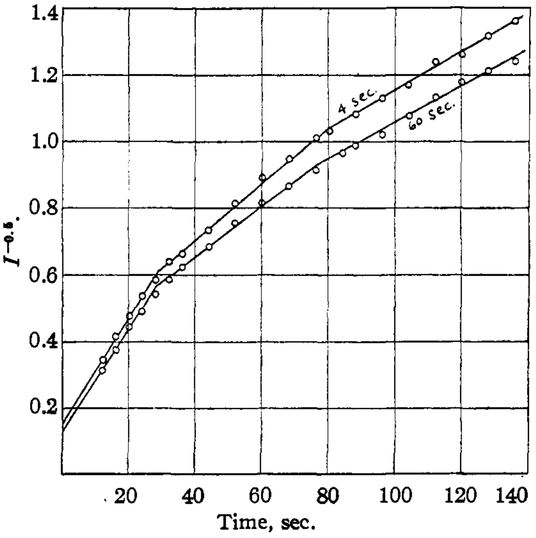

Fig. 3.—Effect of period of excitation on the decay of phosphorescence.

Effect of Period of Excitation.—In attempting to fix the proper period of excitation, it was discovered that an intermediate exposure caused a higher peak deflection than either a shorter or longer exposure but that the intensity over the

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[9] V. Antonov-Romanovskij, *Compt. rend. acad. sci. U. R. S. S.*, [N. S.] **2**, 97 (1936).

latter part of the decay period increased in a regular manner with increase of exposure. The effect is illustrated by Fig. 2 in which the intermediate portions of the curves are omitted. The $I^{-0.5}$–t curves for the four- and sixty-second exposures are given in Fig. 3. These measurements were made on a sample of blende; similar results were obtained for wurtzite.

The principal conclusion drawn from these observations is that the process of excitation is complex rather than a simple one-stage process. It is evident from the curves of Fig. 3 that the rates of excitation of the states corresponding to the different decay processes are different and that the process with slowest decay is also excited most slowly. The specific reaction rates of corresponding processes appear to be independent of the time of excitation.

The relatively high total initial intensity resulting from intermediate exposure time may be particularly significant. This may be explained by assuming a definite relation between the processes whereby excitation of the later stages cannot take place until some of the excited phase of the initial process has been produced. This reaction reaches completion much more quickly than the others, after which the concentration of the product decreases as it is used up or stabilized by formation of other excited phases.

The period of excitation for all subsequent work was twenty seconds.

Effect of Temperature.—Decay curves were obtained both at 30 and 45° for all samples for which the heat treatment had been varied. Curves for a sample of blende and for a sample of wurtzite are shown in Fig. 4. For this particular sample of wurtzite, increased temperature causes slight increases in specific reaction rates for the first two measured processes and hardly any increase for the third. On the other hand, the blende shows decreased rates for all processes. Substituting in the Arrhenius equation the values of the specific reaction rates obtained by squaring the slopes of the lines, activation energies were calculated. The results are given in Table I.

TABLE I

ACTIVATION ENERGY

Sample	Heat treatment Temp., °C.	Heat treatment Period, hrs.	Activation energy, cal. A_1	Activation energy, cal. A_2	Activation energy, cal. A_3
1	950	1	3730	−3780	−20,870
2	950	2	1155	4320	− 8,050
3	950	3	−2090	−5770	−19,550
4	1060	1	5420	320	−10,390
5	1060	2	3310	3092	0

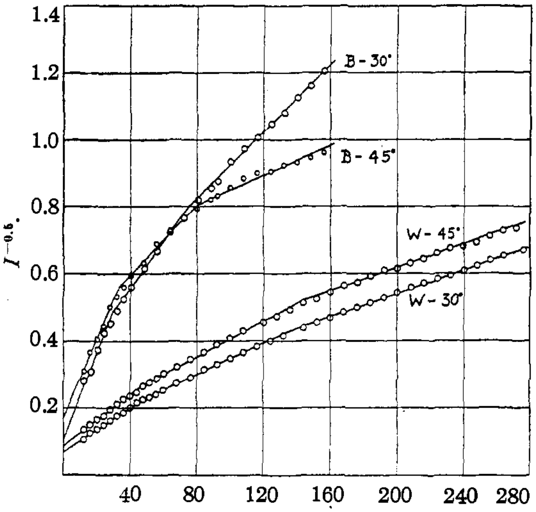

Fig. 4.—Effect of temperature on the decay of phosphorescence of blende and wurtzite.

With the exception of A_2 for sample 2, the activation energies decrease from first to third processes. Increased heat treatment tends to decrease A_1 and increase A_3. These facts further emphasize the reality of separate processes in decay and reveal an important connection between the mechanisms and the physical state of the crystals.

Since it is difficult to conceive of a simple process having negative energy of activation, the negative signs indicate that the changes taking place during decay are complex. A possible explanation may be derived from thermodynamic considerations. Considering the actual light-giving change as a simple process independent of any other, it must proceed at increased rate with rise in temperature. But we may picture an auxiliary reaction which is reversible during decay and is exothermic in the direction of decay. Such a system may be represented as follows

$$\mathrm{W} + \mathrm{X} \rightleftarrows \mathrm{Y} + \text{heat} \ldots\ldots\ldots\ldots\ldots (1)$$

$$\mathrm{Y} + \mathrm{Z} \longrightarrow \text{light} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Reaction (1) must precede reaction (2) but, in cases of negative activation energy, the latter must be the slower reaction. Otherwise Y would be used up so fast that the actual rate-controlling change would be the activation of W and X which would be faster at higher temperature. Using the thermodynamic approach, we have implied nothing concerning the nature of the reactants or reactions. However, the same essential processes may be involved in all cases whether the over-all activation energies are negative or positive.

Effect of Composition.—Decay curves obtained for a group of samples with varied copper content were all similar to those already shown. A strikingly different type of decay was found for samples having a nickel content above a very low minimum. Curves for the three nickel samples studied along with one for a sample with no nickel are given in Fig. 5. This is an example of the vanishing type of phosphorescence discussed by Nichols and Howes.[10] When this type of decay is described as having increasing rate, it should be kept in mind that it is the specific rate of change of the metastable state which is increasing. The rate of decay of the phosphorescent light is decreasing in these samples.

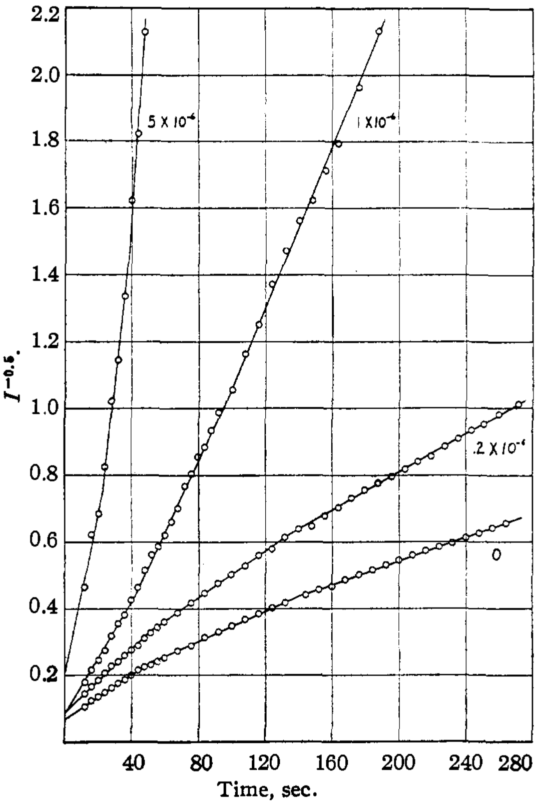

Fig. 5.—Effect of nickel on the decay of phosphorescence. Nickel concentrations are stated in grams per gram of zinc sulfide.

Correlation of Luminous Properties, Composition, and Heat Treatment

Experimental.—Other luminous properties studied were fluorescence, fluorescence growth rate, and α-particle response. Little change is needed in the set-up of Fig. 1 for these measurements. For the α-particle source, a year-old sample of mesothorium measuring about 5.5 mg. radium equivalent was spread on a glass plate which could be substituted for the regular plate of Fig. 1. When in position, the source was 3 mm. above the sample, and the light coming through the film of mesothorium and glass plate was measured ten minutes after start of exposure.

On account of the unsteadiness of the arc light, a 2-watt argon glow lamp was used as source of excitation for measurement of fluorescence. The cell box was placed in the frame so that the cell surface made an angle of 70° with the horizontal and was 6 cm. from the edge of the sample. Correction for reflected light was determined by making a measurement with sulfur in the sample position. The factor required to convert readings with the cell in this position to those comparable to decay and α-response measurements was determined by placing diffusing white paper over the opening above the standard lamp and taking readings with the cell in the two positions. The ratio of response to the arc to response to the glow lamp was found to be about 27.4. With these corrections, the results are comparable to other measurements. They are only approximately correct but the relative results are accurate to within 5% or less.

Crystal size was measured with an optical micrometer. The microscope also was used to distinguish wurtzite from blende on the basis of birefringence.

The data are collected in Tables II and III. All samples of Table II contain 0.25×10^{-4} gram of copper per gram of zinc sulfide. The heat treatment was the same for all samples of Table III, namely, two hours at 1060°. Luminosities are stated in terms of centimeters deflection on the scale 291 cm. from the galvanometer. The sample temperature was 30° for all of these measurements. Rate of growth of fluorescence is given indirectly by the time required to reach one-half the maximum. The k's represent specific reaction rates for the separate decay processes.

Discussion of Results.—The results show that the preparation of materials was not controlled perfectly but that the control was sufficient to allow study of the effects of factors which were deliberately varied. Sample 8 shows the effect of uncontrolled variables most clearly. However, the cause of its peculiarities was traced to a slight difference in state of the material before calcination although it had the brittleness and yellow color of other samples. A sample having the white color before calcining was studied and found to exhibit the same type differences from normal material as are shown by sample 8 but to a much greater extent.

Although 950° is 70° below the transition point

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[10] E. L. Nichols and H. L. Howes, *Nat. Acad. Sci. Proc.*, **4**, 305 (1918.)

TABLE II

HEAT TREATMENT AND LUMINOUS PROPERTIES

Sample	Heat treatment Temp., °C.	Heat treatment Period, hrs.	Av. cryst. diam., μ	Fluorescence, cm.	α-Response, cm.	$^1/_2$ Fluor. growth time, sec.	I_0, cm.	$k_1 \times 10^5$	$k_2 \times 10^5$	$k_3 \times 10^1$
1	950	1	4.96	17,540	25.9	8.8	34.3	21.32	11.88	5.63
2	950	2	5.72	18,060	25.6	7.2	49.8	23.41	7.92	4.87
3	950	3	7.20	17,560	26.8	9.8	87.0	17.42	6.12	2.60
4	1060	1	6.04	16,880	24.9	9.3	74.4	3.11	1.68	0.77
5	1060	2	8.72	16,590	22.9	11.7	207.5	1.08	0.54	.31

TABLE III

COMPOSITION AND LUMINOUS PROPERTIES

Sample	(Cu/ZnS) $\times 10^{-4}$	(Ni/ZnS) $\times 10^{-6}$	Fluorescence. cm.	α-Response. cm.	$^1/_2$ Fluor. growth time, sec.	I_0, cm.	$k_1 \times 10^5$	$k_2 \times 10^5$	$k_3 \times 10^5$
6	0.125	0	14,000	19.1	12.5	258.0	1.18	0.50	0.29
5	.25	0	16,590	22.9	11.7	207.5	1.08	.54	.31
7	.5	0	17,670	23.9	10.7	145.5	1.28	.47	.35
8	1.0	0	13,450	20.0	12.8	197.3	1.06	.62	.59
9	2.0	0	14,990	19.9	10.3	100.0	2.97	2.33	1.54
10	0.25	0.2	16,250	21.5	11.6	123.5	2.23	1.20	0.89
11	.25	1.0	11,110	18.1	13.7	138.0	6.86	11.24	15.27
12	.25	5.0	4,770	9.8	15.8	29.2	66.56	192.7	398.2

between pure blende and wurtzite,[11] it was found that samples 1, 2, and 3 contained small amounts of wurtzite, the amount increasing with period of heating to about 20% in sample 3. Almost 100% of the crystals of sample 4 are birefringent. While it is obvious that this fundamental difference in lattice structure is responsible for marked differences in properties, the overlapping of some of the properties indicates that this is not the only important change resulting from heat treatment. Since crystal size is a function of amount of heat treatment, it was necessary to examine the effect of this variable independently of others by separation of a sample into two average size groups. It was found that variations in particle size are not sufficient to account for observed differences in properties. Other possible effects which may accompany increased heat treatment are increased opportunity for diffusion of the foreign metal and for progress of any chemical reaction which may take place with possible attending alteration of crystal forces. Since the significant factors in general appear to exert their influences in a continuous fashion, it is concluded that the most important structural feature is physical rather than chemical in nature; that is, the crystal structure and slight variations in crystal forces are the factors which largely determine the luminous properties.[12,13]

As heat treatment is increased, initial intensity increases but fluorescence rises to a maximum then decreases. The importance of an intermediate condition for fluorescence is also shown by the effect of copper content. There is also an optimum copper concentration for phosphorescence which falls below the range studied here, and the results of Coustal[4] show that there is an optimum heat treatment for a given copper content. If the copper is only in the interstices as suggested by Tiede and Weisz,[14] the principal effect of heat treatment so far as copper is concerned is probably to increase its rate of diffusion. This causes increased distortion of the lattice. The peak of the favorable effect of lattice distortion may be passed by excessive heat treatment with a given copper content or by excess copper with a given heat treatment.

Optimum conditions are not identical for fluorescence and phosphorescence and there is a great difference between fluorescence intensity and initial phosphorescence, but the two appear to be not entirely unrelated for, other things being equal, decreased fluorescence follows increased initial phosphorescence. The total fluorescence emission seems to be made up of a part which is independent of phosphorescence and another part which is conditioned by the mechanism involved in phosphorescence.

Excluding two nickel samples, there is good correlation between initial phosphorescence and

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(11) E. T. Allen and J. L. Crenshaw, *Am. J. Sci.*, **184**, ser. 4. 341 (1917).

(12) A. Schleede, *Naturwissenschaften*, **14**, 586 (1926).

(13) A. Schloemer, *J. prakt. Chem.*, **137**, 40 (1933).

(14) E. Tiede and E. Weisz, *Ber.*, **65**, 364 (1932).

growth rate of fluorescence; samples with high initial phosphorescence respond more slowly. This shows the influence of the phosphorescence mechanism upon fluorescence. If a part of the total fluorescence is due to operation of the phosphorescence process during excitation, a sample with high initial phosphorescence should be expected to reach its maximum more slowly because a larger proportion of the total light would depend upon a comparatively slow process. The exceptions in the cases of the nickel samples may be due to an effect on the rate of the main fluorescence process. Any change in crystal conditions may be expected to exert an effect on all processes but it is also probable that a certain degree of specificity obtains.

In all cases, for different samples, as initial phosphorescence increases, the specific reaction rates decrease. This is in accord with Perrin's[15] theory on fluorescence of solutions which assumes a protective effect of critical molecules upon one another which increases with their concentration. But it was found by variation of excitation time that the concentration of excited phase in a given sample could be varied without affecting the specific reaction rate. It is concluded, therefore, that the structural conditions which favor a large maximum concentration of excited phase also favor the stability of that phase, once formed.

At certain concentrations, the effects of copper and nickel appear to be similar.

A Suggested Theory

The strictly chemical theories of phosphorescence conflict with established relations between phosphorescence and electrical phenomena. A large proportion of recent investigators in the field of phosphorescence have interpreted observed phenomena in terms of the essential ideas of Lenard's photoelectron theory. But the results of Coustal[4] have thrown doubt on the idea of phosphorogen atoms forming the nuclei of active centers, and other features of the theory require amplification.

The relations observed in this work together with certain results of other workers suggest a theory which is different in certain essentials from others which have been advanced. The central assumption of the theory is that the actual light-giving mechanism is identical for fluorescence and all of the various decay processes of phosphorescence. This is based on the similarity of the spectra; it has been found that the phosphorescence spectrum is the same throughout the measurable period of decay.[8] The radiation is due to fall of electrons from excited levels to their normal levels, previous excitation having caused the reverse transfer.

$$\begin{tikzcd}
 & e \arrow[d, shift left, "1"] & \\
D \arrow[r, shift left, "4"] & A \arrow[u, shift left] \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & B \arrow[l, shift left, "2"] \\
 & C \arrow[u, shift left, "3"] &
\end{tikzcd}$$

The new distribution of charge resulting from the excitation shifts allows a slight change in orientation of atoms which is the source of stability of the first excited state. Thermal agitation is responsible for the shift back to normal and the change is so slight that the decay period is extremely short.

But there are other changes represented by reactions 2, 3, and 4, which take place during excitation and have the effect of increasing the stability of the first excited state. That there is a definite relation between the changed conditions represented by B, C, and D is shown by the separation of the processes of decay. No reverse change from the C condition can take place until the B change is practically completed and no D change can occur until the C change is in turn nearly completed. There may be other changes of similar nature either following D or preceding B. Each reverse change has its characteristic specific reaction rate and is so related to the emission process proper, reaction 1, that the latter can take place only as the slower change proceeds. Reactions 2, 3, and 4 have the nature of second order reactions as shown by the law of decay. They must each be directly related to reaction 1 as controls on the rate because in the nickel samples the latter processes have higher rates. This excludes the possibility of a stepwise series of changes from D through C and B to A.

Maximum phosphorescence corresponds to extension of the changes throughout the crystal. The forward as well as reverse changes vary in speed as shown by the effect of excitation period. Reaction 2 is reversible at all times since there is no change of comparable nature preceding it so that there is a certain part of the fluorescence which is controlled by this change. A much larger part of the total fluorescent light depends on reaction 1 independently of the phosphorescence

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(15) J. Perrin, *Compt. rend.*, **177**, 612 (1923).

mechanisms. But this reaction is so fast that its effect on phosphorescence is observable only during the first few seconds. In some substances there are no changes corresponding to the auxiliary reactions and they may exhibit fluorescence but no persistent phosphorescence.

The high total initial phosphorescence resulting from intermediate excitation time may well be explained in terms of the connection between the main reaction and the stabilizing changes.

The behavior of the materials at very low temperature is accounted for by the theory. When a sample was irradiated at room temperature and plunged into liquid air, the glow was gone by the time liquid air temperature was reached. It reappeared on warming. But when irradiated at liquid air temperature, the phosphorescence was quite persistent. After irradiation at room temperature, the part of reaction 1 which is independent of B, C, and D proceeds rapidly to completion and is practically finished when the low temperature is reached. The stabilizing shifts are completely frozen but may be caused to proceed again by warming. After irradiation at liquid air temperature, a glow is maintained for some time because reaction 1 is much slower at this temperature.

The available information does not allow specification of the nature of the auxiliary changes. Perhaps all of the properties studied in this work may be rationalized by assuming that the changes are shifts in relative positions or orientations of atoms. Some of them fit into the picture of additional electron shifts.

The theory is in accord with various results of other investigators. However, it is not offered as a finished theory for some of its main premises have not been tested adequately and, without further amplification, it does not account for all of the established facts.

Acknowledgment.—This work was suggested by Dr. Herman Schlundt. I am deeply indebted to him for his invaluable advice and encouragement.

I wish to express appreciation of the helpful suggestions given by Dr. H. E. Bent, Dr. L. B. Thomas, and Dr. A. E. Stearn, all of the Department of Chemistry.

I am also glad to acknowledge my indebtedness to the Department of Physics for the use of the illuminometer and to Dr. A. C. Krueger for the use of some of his apparatus.

Summary

A method of preparation of phosphorescent zinc sulfide has been developed by which samples with properties reasonably free of the influence of incidental variables may be prepared. Simple, objective methods for measurement of phosphorescence decay rate, fluorescence, fluorescence growth rate, and α-particle response have been developed.

A group of samples in which certain significant factors were varied has been prepared and studied. The decay of phosphorescence after the first few seconds was found to correspond to a series of second order reactions. The total initial phosphorescence intensity was found to be greater after an intermediate period of excitation than after either shorter or longer periods. The effect of temperature on rate of decay was studied and activation energies for the several processes of decay were calculated. Some of these were found to be negative. Two samples containing nickel were shown to exhibit the vanishing type of phosphorescence. Certain relations between luminous properties, composition, and heat treatment with bearing on the theory were observed and discussed. A theory of phosphorescence has been outlined.

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