

## Crystals of Luminescent ZnF<sub>2</sub>: Mn

Peter D. Johnson and Ferd E. Williams

Citation: *The Journal of Chemical Physics* **17**, 583 (1949); doi: 10.1063/1.1747332

View online: <http://dx.doi.org/10.1063/1.1747332>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/17/6?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[Theoretical study of the predissociation of the A<sup>2</sup>Π state of ZnF including quasi-diabatisation of the spin-orbit coupling](#)

*J. Chem. Phys.* **137**, 164318 (2012); 10.1063/1.4762444

[Crystal Structure of Luminescent ZnSiP<sub>2</sub>](#)

*J. Chem. Phys.* **52**, 5607 (1970); 10.1063/1.1672831

[Modification in Technique for Growing Single Crystals of ZnF<sub>2</sub>:Mn](#)

*J. Appl. Phys.* **31**, 2063 (1960); 10.1063/1.1735498

[Mechanism of Luminescence in the ZnF<sub>2</sub> : Mn Phosphor](#)

*J. Chem. Phys.* **27**, 600 (1957); 10.1063/1.1743789

[Energy States and Luminescent Processes in the ZnF<sub>2</sub>: Mn Phosphor](#)

*J. Chem. Phys.* **26**, 612 (1957); 10.1063/1.1743356

---



TABLE I.\* The viscosity of 50 mole percent liquid mixtures obtained using a Cannon-Fenske-Ostwald viscometer.

Mixtures	T°K	tsec.	$\frac{10^4\eta}{\rho^2}$	$\frac{10^2\eta}{\rho}$	$\rho$	$10^2\eta$
Ph-n-C <sub>7</sub>	298.0	203.2	0.2724	0.5534	0.753	0.4167
	318.0	170.7	0.2719	0.4642	0.734	0.3407
	335.8	146.4	0.2715	0.3975	0.717	0.2850
Ph-n-C <sub>10</sub>	298.0	318.3	0.2724	0.8672	0.774	0.6712
	318.0	255.6	0.2719	0.6951	0.757	0.5262
	335.8	212.1	0.2715	0.5758	0.742	0.4272
Ph-n-C <sub>12</sub>	298.0	374.5	0.3099	1.1607	0.780	0.9053
	318.0	293.0	0.3088	0.9049	0.763	0.6904
	335.8	237.8	0.3089	0.7345	0.748	0.5494
Ph-n-C <sub>14</sub>	298.0	506.3	0.3099	1.5689	0.790	1.2394
	318.0	385.1	0.3088	1.1893	0.775	0.9217
	335.8	305.6	0.3089	0.9439	0.760	0.7175
Ph-n-C <sub>18</sub>	298.0	762.6	0.2724	2.0783	0.794	1.6502
	318.0	562.0	0.2729	1.5281	0.780	1.1919
	335.8	437.2	0.2715	1.1870	0.765	0.9081
	298.0	671.2	0.3099	2.0799	0.794	1.6515
	318.0	495.2	0.3088	1.5292	0.780	1.1928
	335.8	385.1	0.3089	1.1897	0.765	0.9100
Ph-n-C <sub>18</sub>	298.0	975.3	0.2724	2.6416	0.799	2.1226
	318.0	702.4	0.2719	1.9099	0.786	1.5012
	335.8	538.4	0.2715	1.4617	0.772	1.1284
n-C <sub>7</sub> -n-C <sub>12</sub>	298.0	402.0	0.2724	1.0950	0.719	0.7873
	318.0	317.4	0.2719	0.8630	0.702	0.6058
	335.8	260.1	0.2715	0.7062	0.688	0.4859
	298.0	353.1	0.3099	1.0943	0.719	0.7868
	318.0	279.3	0.3088	0.8624	0.702	0.6054
	335.8	228.1	0.3089	0.7047	0.688	0.4849
n-C <sub>7</sub> -n-C <sub>14</sub>	298.0	517.3	0.2724	1.4091	0.732	1.0314
	318.0	398.3	0.2719	1.0830	0.716	0.7754
	335.8	322.6	0.2715	0.8759	0.702	0.6149
n-C <sub>7</sub> -n-C <sub>16</sub>	298.0	600.3	0.3099	1.8603	0.740	1.3766
	318.0	448.7	0.3088	1.3856	0.725	1.0046
	335.8	353.1	0.3089	1.0906	0.712	0.7765
n-C <sub>7</sub> -n-C <sub>18</sub>	298.0	746.3	0.3099	2.3128	0.748	1.7300
	318.0	546.9	0.3088	1.6888	0.735	1.2412
	335.8	422.2	0.3089	1.3042	0.722	0.9416
i-C <sub>7</sub> -n-C <sub>12</sub>	298.0	338.0	0.3099	1.0474	0.715	0.7489
	318.0	269.1	0.3088	0.8310	0.699	0.5809
	335.8	221.6	0.3089	0.6845	0.684	0.4682
i-C <sub>7</sub> -n-C <sub>16</sub>	298.0	574.7	0.3099	1.7810	0.738	1.3144
	318.0	432.0	0.3088	1.3340	0.722	0.9631
	335.8	342.9	0.3089	1.0592	0.709	0.7510
Ph-i-C <sub>7</sub>	298.0	188.0	0.2724	0.5121	0.747	0.3825
	318.0	158.4	0.2719	0.4307	0.729	0.3140
	335.8	136.6	0.2715	0.3709	0.712	0.2641
i-C <sub>7</sub>	298.0	185.5	0.2724	0.5054	0.671	0.3391
	318.0	158.1	0.2719	0.4298	0.654	0.2811
	335.8	137.0	0.2715	0.3720	0.639	0.2377

\* Note: T = temperature °K;  $\rho$  = density g/cc; t = time, sec.;  $\eta$  = viscosity poises.

An empirical equation, the form of which was suggested by Roegiers and Roegiers,<sup>2</sup> best correlates the present viscosity data.

$$\eta = \eta_2 \left( \frac{\eta_1}{\eta_2} \right)^{c_1 \epsilon / (c_1 \epsilon + c_2)} \quad (1)$$

For a value of the parameter  $\epsilon = 1.45$  and for 50 mole percent mixtures, (1) takes the form

$$\eta = \eta_2 \left( \frac{\eta_1}{\eta_2} \right)^{0.592} \quad (2)$$

Use of (2) to calculate the viscosity of mixtures in the n-C<sub>7</sub>-n-C<sub>x</sub> and Ph-n-C<sub>x</sub> series at 25°, 45°, and 63°C yielded values subject to an average error of about 5 percent and a maximum error of 14 percent.

Figure 1 shows typical results for the two series at a temperature of 25°C. As well as calculated and experimental values of the viscosity for 50 mole percent mixtures the viscosity of the pure compounds is also indicated.

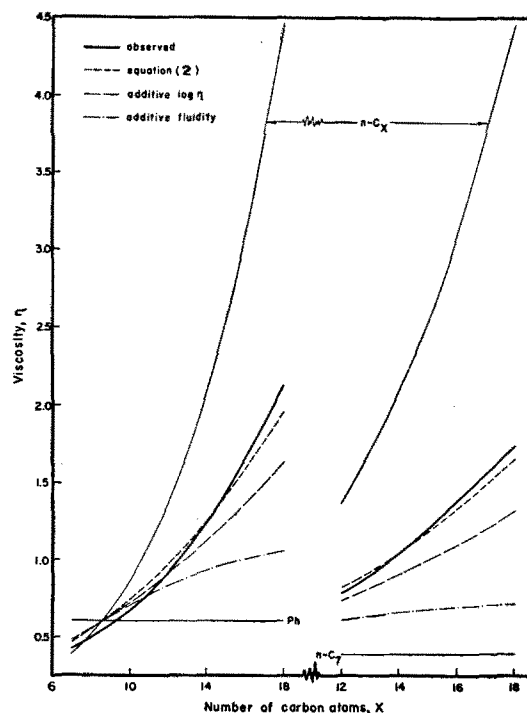


Fig. 1. A comparison of experimental and calculated values for the viscosity of liquid mixtures in the series: Ph-n-C<sub>x</sub> and n-C<sub>7</sub>-n-C<sub>x</sub> at 25°C.

Viscosities were also calculated using the equation suggested by Eyring, *et al.*<sup>3</sup> for liquid mixtures. The results are not shown on the graph, but coincide quite closely with the results predicted from additive fluidities.

<sup>1</sup> Giller and Drickamer, *Ind. Eng. Chem.* (to be published).

<sup>2</sup> M. Roegiers, and L. Roegiers, *The Viscosities of "Normal" Fluids* (Société des Huiles de Cavel et Roegiers (Electron Oil Works) Coupure 197, Ghent, 1945).

<sup>3</sup> Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 516.

### Crystals of Luminescent ZnF<sub>2</sub>:Mn\*

PETER D. JOHNSON AND FERD E. WILLIAMS  
Chemistry Department, University of North Carolina,  
Chapel Hill, North Carolina

April 18, 1949

IN the course of a fundamental study of ZnF<sub>2</sub>:Mn<sup>1</sup> it has been found possible to prepare clear transparent crystals of this phosphor, efficiently excited by cathode rays and 2537Å radiation, of dimensions 1×1×2 mm.

Preliminary unsuccessful attempts to grow large crystals of ZnF<sub>2</sub>:Mn involved slow cooling both under pressure and in vacuum, evaporating in vacuum, and lifting a platinum rod slowly from a melt. A modification of the simple method of Tamman and Veszi<sup>2</sup> was successful and has yielded the best results to date. The components of the phosphor mixed with a small amount of NH<sub>4</sub>F were fused at atmospheric pressure in a platinum crucible, with a tightly fitting cover, over a Bunsen burner. The gas supply to the burner was gradually decreased over a period of one hour. By means of platinum vs. platinum-rhodium thermocouples at various points in the melt, it was found that the crystallization occurred over a period of 15 minutes. The clear transparent crystals formed near the upper outside edge of the melt, where the temperature gradient was estimated to be 3°C/mm. The method, in addition, invariably yielded larger opaque fragments with definite parallel and perpendicular cleavage planes.

Effort was made to prepare clear crystals of diverse activator content. 4.0 mole percent  $\text{MnF}_2$  was found to be the maximum activator content for which evidence of clear crystal formation was encountered. A lower limit of 0.5 mole percent  $\text{MnF}_2$  also was evident. Apparently, the activator inhibits the reduction of  $\text{Zn}^{++}$  on fusing  $\text{ZnF}_2$ . Chemical analysis of the transparent crystals obtained from a melt originally containing 2.2 mole percent  $\text{MnF}_2$  indicated an activator concentration of 1.4 mole percent.

Examination of the crystals under a polarizing microscope revealed considerable strain and some twinning. Laue x-ray photographs indicated that the crystals consist of a number of crystallites oriented to within a few degrees of each other.\*\* Conchoidal fracture of the crystals was common.

Fundamental measurements of the significant luminescent properties of the clear transparent crystals of  $\text{ZnF}_2\cdot\text{Mn}$  are in progress, and effort is being made to prepare even larger transparent crystals of the phosphor.

\* Supported by the ONR under Contract N7onr-284, T.O. 1.

<sup>1</sup> F. E. Williams, J. Opt. Soc. Am. 37, 302 (1947).

<sup>2</sup> Tamman and Veszi, Z. Anorg. Allgem. Chem. 150, 355 (1925).

\*\* The authors are indebted to Mr. E. Fullam and Mr. E. Asp of the Research Laboratory of the General Electric Company for making, respectively, the microscopic and x-ray examinations.

## Mass Spectrum of Hydrogen Deuteride (HD)

R. A. FRIEDEL AND A. G. SHARKEY, JR.

Bureau of Mines, Synthetic Liquid Fuels, Research and Development  
Branch, Bruceton, Pennsylvania  
April 1, 1949

THE direct chemical preparation of hydrogen deuteride, 99± percent pure, has been reported by Wender, Friedel, and Orchin.<sup>1</sup> The fragmentation pattern under electron impact of this compound is of theoretical importance for comparison with the fragmentation patterns of  $\text{H}_2$  and  $\text{D}_2$ , and is of analytical importance for determination of hydrogen-deuterium mixtures, as in the calculation of equilibrium constants for the reaction  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ . The unknown production of  $\text{D}^+$ , mass 2, from fragmentation of HD interferes with the analysis of  $\text{H}_2$ . This interference has been supposed slight, as is the unknown interference of  $\text{D}^+$  from  $\text{D}_2$ ,<sup>2</sup> but if neglected, these can produce errors of several percent in calculation of equilibrium constants.

The relative abundance of  $\text{D}^+$  from HD cannot be determined directly because of the interference of unknown  $\text{H}_2$

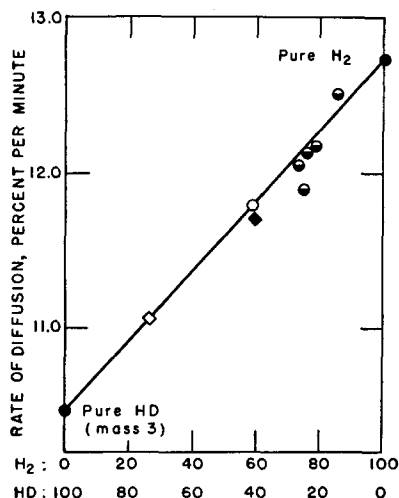


FIG. 1. Rate of diffusion curve for determination of  $\text{H}_2$  impurity and relative abundance of  $\text{D}^+$  from HD. Straight line drawn between values for pure  $\text{H}_2$  and HD (mass 3). Rates of diffusion measured at mass 2: ○ = HD Sample 1; ● = Synthetic blend of  $\text{H}_2$  and HD Sample 1; ◇ = HD Sample 2 (highest purity); ◇ = Synthetic blend of  $\text{H}_2$  and HD Sample 2.

TABLE I. Mass spectra of  $\text{H}_2$ , HD, and  $\text{D}_2$ ; 70-electron volts.

Mass	Ions	$\text{H}_2$	HD	$\text{D}_2$
1	$\text{H}^+$	2.01 <sup>a</sup>	0.82	
2	$\text{H}_2^+$ or $\text{D}^+$	100.0	1.13	1.06 <sup>b</sup>
3	$\text{HD}^+$		100.0	
4	$\text{D}_2^+$			100.0
Sensitivity coefficients (ionization per unit pressure)		25.4	25.5	25.6
$\text{H}^+$ from $\text{H}_2/\text{D}^+$ from $\text{D}_2$		1.9 <sup>c</sup>		

<sup>a,b,c</sup> Corresponding values from Bauer and Beach, J. Chem. Phys. 15, 150 (1947), are: (a) 2.52, (b) 1.32, and (c) 1.9.

impurity. This difficulty was circumvented by measurements of rates of diffusion through the leak system of the mass spectrometer (Consolidated Model 21-102). Relative rates for  $\text{H}_2$ , measured at mass 2, and for HD, measured at mass 3, were found to be 12.72 and 10.46 percent per minute, respectively. These two values were plotted *versus*  $\text{H}_2$  and HD percentages, and a straight line was drawn between them (Fig. 1). Then, measurements were made at mass 2 for two samples of HD with unknown  $\text{H}_2$  impurity; thus, the rates of diffusion were due to mixtures of HD and  $\text{H}_2$ .<sup>\*</sup> The rate values were applied to the straight-line plot and the percentages of  $\text{D}^+$  and  $\text{H}_2^+$  which comprised the mass 2-ion peak were read from the abscissa. From these values the percentages of  $\text{H}_2$  impurity and the relative abundance of  $\text{D}^+$ ,  $1.13 \pm 0.05$ , were determined. Composition of the HD sample of higher purity was found to be 98.8 percent HD, 0.4 percent  $\text{H}_2$ , plus 0.8 percent  $\text{D}_2$  determined by direct analysis. Linearity of the relationship, rate of diffusion *versus* concentration, was checked by measuring the rates for six synthetic blends of HD plus small amounts of  $\text{H}_2$ . The resulting points fit the straight line within experimental error of the measurements (Fig. 1).

The relative abundances of all ions from HD,  $\text{H}_2$  (100 percent), and  $\text{D}_2$  (99.2 percent  $\text{D}_2$ , 0.8 percent HD) are given in Table I. Data were obtained with 70-volt electrons and magnetic scanning. It will be noted that the total monatomic ions from  $\text{H}_2$  and HD are practically equal and are twice the amount of monatomic ions obtained from  $\text{D}_2$ . The values for  $\text{H}^+$  and  $\text{D}^+$  from  $\text{H}_2$  and  $\text{D}_2$ , obtained by Bauer and Beach<sup>2</sup> with 70-volt electrons, are included in the table. Absolute values of the two sets of data are not expected to compare; but the ratios,  $\text{H}^+$  from  $\text{H}_2/\text{D}^+$  from  $\text{D}_2$ , compare exactly with each other and quite well with Stevenson's<sup>3</sup> calculated value. The relative sensitivity coefficients (ionization of the parent molecule per unit pressure) from four sets of data for  $\text{H}_2$ , HD, and  $\text{D}_2$  are essentially equal, as expected.<sup>4</sup>

Equilibrium constants at 500°C for  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  have been calculated, using the calibration data in Table I, for three samples<sup>5</sup> equilibrated over an iron catalyst. The corrected average  $K_{500^\circ\text{C}}$  in Table II is  $3.87 \pm 0.02$ , as compared to the theoretical value of 3.83.<sup>6</sup> If mass 2 values are not corrected for  $\text{D}^+$  ions from HD, in these samples of low  $\text{H}_2$  content, the average  $K_{500^\circ\text{C}}$  is low,  $3.70 \pm 0.02$ . This correction was not

TABLE II. Calculation of equilibrium constants at 500°C for  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  from mass spectrometer analyses.

Sample	Mass 2 corrected for $\text{D}^+$ from HD	Mass 2 corrected for $\text{D}^+$ from HD	Mass 2 corrected for $\text{D}^+$ from HD	No HD correction	Theory
	$\text{D}_2$	HD Percent	$\text{H}_2$	$K_{500^\circ\text{C}}$	$K_{500^\circ\text{C}}$
A	39.1	46.5	14.4	3.84	3.71
A	38.8	46.6	14.6	3.84	3.71
B	41.6	45.5	12.9	3.86	3.71
B	41.6	45.5	12.9	3.86	3.72
C	55.1	38.1	6.8	3.90	3.68
C	55.2	38.1	6.7	3.90	3.68

Average  $3.87 \pm 0.02$   $3.70 \pm 0.02$  3.83

Rittenberg, Bleakney, and Urey,  $K_{468^\circ\text{C}} = 3.75 \pm 0.07$   
Theoretical,  $K_{468^\circ\text{C}} = 3.82$