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Shielding of the network from stray pickup together with the absence of harmonics and hum from the oscillator have made it possible to balance the bridge to one or two parts per million using only the two-stage untuned amplifier described. When the bridge is at balance using this amplifier, no sound other than the barely perceptible hiss of the tube noise can be heard in the phones, even though the amplifier is untuned.

## V. Summary

1. The conductivity bridge assembly has been investigated to determine to what extent it is advantageous for chemists to employ recent complicated and expensive developments in communication engineering in such a simple type of alternating current bridge.

2. Several different forms of the oscillator and its power supply, of the bridge network, and of the amplifier, incorporating recent developments in a. c. bridge methods and communication engineering, have been constructed and tested.

3. An adaptation of a new and simple lowdistortion oscillator to conductivity bridge use is described. The oscillator plate supply is of the constant voltage type to reduce a. c. hum and stabilize the regeneration control.

4. Separate detector terminal balance to ground is suggested for conductivity bridges, and its adaptation and use described. The use of 10,000 ohm instead of 1,000 ohm resistors for the ratio-arms and Wagner ground circuit is proposed. Shielding to reduce stray pickup to a minimum is described.

5. A two-stage untuned amplifier with gain sufficient to permit balancing the bridge to one or two parts per million when oscillator harmonics, a. c. hum, and stray pickup have been practically eliminated is suggested for ordinary use of the bridge. A description of a three-stage tuned amplifier is also given.

6. Simplification, ease of construction, and lowered cost have been attained with no loss in precision and with some gain in convenience in the operation of the bridge.

BOSTON, MASS.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF NEW HAMPSHIRE]

# The Magnetic Rotation of Praseodymium, Samarium, and Europium Chlorides in Aqueous Solution at 25°

## BY CHARLES M. MASON, JOSEPH W. HICKEY AND WILFRED K. WILSON

Recently<sup>1</sup> this Laboratory has presented the results of an investigation of the magnetic rotation of lanthanum and neodymium chlorides in aqueous solution. In the present work this method of investigation has been extended to the aqueous solutions of praseodymium, samarium, and europium chlorides. The Verdet constants have been obtained for these solutions over a concentration range from zero (pure water) to 3.5 molal. The dispersion has been studied from 4811 to 6438 Å.

## **Experimental Details**

The rotations were measured with a Franz Schmidt and Haensch model 55 Landolt-Lippich triple-shadow polarimeter with non-magnetic frame. The instrument could be read to one-hundredth degree of arc. The light sources used were a mercury Lab-Arc, sodium Lab-Arc, and a Zeiss electrical spectral lamp fitted with Osram zinc and cadmium-filled bulbs. Monochromatic light was obtained by means of a Winkel-Zeiss monochromator inserted in the optical path between the spectral source and the polarimeter. By this means it was possible to isolate the principal lines of the various spectra with enough intensity left to properly operate the polarimeter.

The solution, the rotation of which was to be measured, was placed in a water-jacketed cell of Pyrex brand glass equipped with optical windows of the same material fused to the ends of the cell. This cell, as placed in the magnet, is shown in Fig. 1. The magnet consisted of 17 layers of approximately 162 turns each of No. 16 B. and S. gage, silk-covered copper wire wound on a bakelite tube 3.5 cm. inside diameter and 24 cm. long. The total number of turns was 2753 and the length of the coil was 23.1 cm. The length of the light path through the solution was 20.08 cm. measured by calibrating the tube with carefully purified sucrose. These data enabled the computation of the field strength, H, of the coil at any point along the axis. The product of the effective field strength times the length of the light path in the cell was determined by integration between limits based on the diameter of the first and last layers of turns to be 11,089.4 gauss. Integration for each layer of turns and summation gave a value of 11,084.6 gauss, a check well within the experimental error of the methods used to measure the angle of rotation. This field strength, when used to compute the Verdet constant of water, gave a value of  $13.11 \times 10^{-3}$  for that constant at 25° and wave length 5893 Å. This com-

<sup>(1)</sup> C. M. Mason, R. D. Gray and G. L. Ernst, THIS JOURNAL, 58, 1600 (1936).

pares very favorably with the value of  $13.07 \times 10^{-3}$  given for water under the same conditions by Rodger and Watson<sup>2</sup> when it is considered that an error of 0.01° in rotation is equivalent to  $0.05 \times 10^{-3}$  in the Verdet constant. The rotation of the end plates was corrected by the determination of their rotation when the cell was empty.

A current of  $4.0 \pm 0.001$  amperes was used, supplied by storage batteries. Current regulation was obtained with a potential divider which was a modification of that described by MacInnes and Longsworth.<sup>3</sup> A potential drop of 0.4 volt was maintained across a standard tenth ohm resistor by controlling the potential divider in the circuit with the magnet so that the galvanometer in the potentiometer circuit showed no deflection during the course of a measurement.

All refractive indices were measured at  $25^{\circ}$  with a standard Pulfrich refractometer. Care was taken to eliminate or correct for any error due to evaporation during the measurement. The temperature was controlled with the same equipment described below for the electromagnet. The refractometer was checked with carefully prepared distilled water using the tables of Tilton and Taylor<sup>4</sup> as a source of standard values.

The temperature in the polarimeter cell was kept constant by circulating water from a thermostat through the jacket of the tube. The temperature of the thermostat was kept so that the temperature in the water jacket of the cell was  $25.00 \pm 0.03^{\circ}$ . A mercury thermoregulator connected through a relay to an electric heater maintained the thermostat at a constant temperature. The actual temperature in the cell was taken as the average of the two thermometers at the ends of the cell, as shown in Fig. 1. All thermometers used were checked against a standard thermometer which had been calibrated by the United States Bureau of Standards.



Fig. 1.—Cell, showing position in magnet.

The rare earth salts had been carefully prepared by repeated recrystallization. The samarium material had been obtained from the Maywood Chemical Co. and the praseodymium material from the estate of the late Charles James. The europium material was very kindly loaned to the department by Dr. Herbert N. McCoy. We wish at this time to thank Dr. McCoy for his generosity in loaning us this material. Its purification and purity is described elsewhere.<sup>6</sup> Since our sample of europium was from the same source, we used the atomic weight, 151.96, recently determined by Baxter and Tuemmler.<sup>6</sup> The chlorides were used as concentrated solutions prepared from the hydrates and analyzed for chloride ion and rare earth ion in the usual way.

The hydrated chlorides were prepared by the following procedure. The oxalate was ignited to the oxide in a muffle furnace at as low a temperature as possible and then dissolved in redistilled arsenic-free hydrochloric acid. It was found best to ignite the oxalate in small batches because it had a tendency to "boil" on decomposition and spatter out of the dish. The oxide was then cooled and added in small portions to the arsenic-free hydrochloric acid in a large beaker. Since some of the oxalate decomposed only to the carbonate, care was taken to prevent the solution from foaming over at this point. It was necessary in some cases to heat the solution for a time on a steam-bath to dissolve the last of the oxide. If, as often was the case, there was carbon remaining from the ignition. it was filtered out at this point. Igniting at high temperatures to remove all of the carbon often makes the oxide difficultly soluble and was to be avoided if possible.

After filtering, the solution was evaporated to a sirup on the steam plate or bath and the chloride shaken out at 0° with hydrogen chloride gas. This hydrated salt was then dried in a current of warm air in a hot-air drier until all of the hydrogen chloride seemed to be removed. The dried salt was then dissolved in a minimum amount of water, one or two drops of concentrated hydrochloric acid added to prevent hydrolysis, and evaporated to a thick sirup. This may be done either over a steam-bath or over a burner. In either case one must be careful to evaporate until just before the sirup begins to crystallize. Not enough evaporation will reduce the yield and too much will cause the whole to set to one solid mass which is of no value and must be dissolved in water and reworked. The sirup was quickly chilled to 0° while stirring very rapidly with a glass stirrer propelled by a motor. This action produced a mass of fine crystals of the hydrate which were easily filtered onto a fritted-glass plate and sucked free of mother liquor. The crystals were then washed with absolute ethanol and dried in a hot-air drier. A good test for the removal of hydrogen chloride was found to be as follows. The hydrate was placed in a glass-stoppered bottle for several days and then examined to see if any odor of the gas had collected in the top of the bottle. Its sharp penetrating odor was very easy to detect.

All of the water used was distilled in an ordinary electrically-heated laboratory still. Only about one-third of the vapor was condensed and collected, the rest being allowed to escape as steam. By employing this procedure, and protecting the water during cooling from the air, it was found that the water so obtained was free of carbon dioxide and other gases. The conductance of the water so obtained was of the order of  $10^{-6}$  reciprocal ohms at  $25^{\circ}$ .

<sup>(2)</sup> J. W. Rodger and W. Watson, Z. physik. Chem., 19, 356 (1896).

<sup>(3)</sup> C. M. Mason and R. D. Gray, Rev. Sci. Instruments, 7, 289 (1936); D. A. Maclunes and L. C. Longsworth, Chem. Rev., 11, 189 (1932).

<sup>(4)</sup> L. W. Tilton and J. K. Taylor, J. Research Natl. Bur. Standards, 20, 419 (1938).

<sup>(5)</sup> H. N. McCoy, This Journal, **57**, 1756 (1935); **58**, 1577, 2278 (1936); **59**, 1131 (1937).

<sup>(6)</sup> G. P. Baxter and F. D. Tuemmler, *ibid.*, **60**, 602 (1938).

Jan., 1940

## Results

The relationship of the magneto-optical rotation to the field strength and length of the light path is expressed by Verdet's law<sup>7</sup>

$$= VHl\cos\alpha \qquad (1)$$

where r is the rotation in minutes, V is the Verdet constant, H is the field strength, l is the length of the light path in cm., and  $\alpha$  is the angle between the path of light and the axis of the magnetic field. For the Faraday effect where the axis of the magnet and the rays of light are parallel, this law reduces to

$$r = VHl \tag{2}$$

When an electromagnet of less than infinite length is used, this becomes

$$r = V \int H \,\mathrm{d}l \tag{3}$$

where H dl is the average field strength over the

#### TABLE I

The Verdet Constants of the Rare Earths in Aqueous Solution in Min./Gauss/Cm.

Praseodymium Chloride, $PrCl_3$ (mol. wt. 247.29)								
Molality <sup>a</sup>	5086	Å. (	5461 Å. î	6362	A. 64	38 Å.		
3.2173	-32.73 -		-26.68	-19.2	23 — 1	-18.75		
3.00	-29	.28 -	-23.78	-17.5	52 - 1	6.66		
2.50	-21	. 53 –	-17.41	-12.5	53 — 1	12.13		
2.00	-13	.71 -	-10.77	- 7.6	66 —	7.50		
1.50	- 5	.84 -	- 4.39	-2.9	95 —	2.89		
1.00	$^{2}$	.25	2.20	1.6	66	1.71		
0.50	10	. 17	8.92	6.4	3	6.32		
.25	14	.03	12.32	8.9	90	8.52		
.00	18	.00	15.50	11.1	.9 1	10.81		
Samarium Chloride, SmCls (mol. wt. 256.80)								
Molali	ty 50	86 Å.	5461 Å.	5893 Å	. 6438	3 Å.		
3.264	4 28	3.02	23.78	20.19	) 16.	82		
3.00	2	7.69	23.52	19.88	B 16.	55		
2.50	20	3.24	22.55	18.90	) 15.	96		
2.00	$2^{\prime}$	4.96	21.37	18.10	) 15.	00		
1.50	23	3.46	20.17	16.96	§ 14.	08		
1.003	2	1.69	18.64	15.75	5 13.	34		
0.50	20	0.25	17.25	14.44	l 12.	43		
.25	18	8.88	16.29	13.82	2 11.	50		
.10	18	3.37	15.86	13.50	) 11.	20		
.00	18	3.00	15.50	13.07	<b>'</b> 10.	82		
Europium Chloride, EuCla (mol. wt. 258.33)								
Molality	4811 Å.	5086 Å.	5461 Å.	5893 Å.	6362 Å.	6438 Å		
2.847	27.16	23.94	20.71	17.73	15.47	15.06		
2.50	26.84	23.73	20.41	17.47	15.32	14.92		
2.00	26.20	22.98	19.77	16.98	14.89	14.35		
1.50	25.06	21.99	18.85	16.07	14.15	13.71		
1.00	23.94	20.73	17.94	15.21	13.45	12.85		
0.50	22.23	19.44	16.82	14.23	12.32	11.62		
.25	21.37	18.73	16.12	13.66	11.78	11.47		
.00	20.57	18.00	15.50	13.07	11.19	10.81		
<sup>a</sup> Moles	of anhy	irous sa	lt per 10	000 g. of	water.			

(7) E. Verdet, Ann. chim. phys., 41, 370 (1854); ibid., 43, 37 (1854); ibid., 52, 129 (1858); ibid., 69, 415 (1863).

light path used. If we choose to calibrate our cell with some pure liquid whose Verdet constant is known, such as water,<sup>2</sup> we find that

$$V = r V_{\rm s} / r_{\rm s} \tag{4}$$

where  $r_s$  and  $V_s$  are the rotation and Verdet constants of the standard liquid used and r and Vare those for the solution being measured. The Verdet constants of the rare earth solutions were obtained by measuring the magnetic rotation of the various solutions and then computed by means of equation (4). The results obtained are given in Table I.

It was also found necessary to determine the densities of the solutions used where they could not be found in the literature. These were determined in a 25-g. Regnault specific gravity bottle in duplicate and are given in Table III as a part of the calculation of the molecular and specific rotation. The refractive indices which were obtained have been expressed in terms of linear equations of the type  $\eta = \eta_0 + am + bm^2$  where  $\eta$  is the refractive index,  $\eta_0$  the refractive index of water, a and b are constants and m is the molality. The values of the constants of these equations are given in Table II, and the refractive indices reproduced by these equations are to within the experimental error, namely,  $\pm 0.0002$ .

#### TABLE II

#### CONSTANTS FOR THE EQUATIONS FOR THE REFRACTIVE INDICES OF RARE EARTH SOLUTIONS

 $\eta = \eta_0 + am + bm^2$ 

Wave length, Å.	<b>7</b> 0	a	ь					
Praseodymium Chloride								
5086	1.33545	0.04658	-0.00261					
5461	1.33386	.04704	00289					
6362	1.33112	.04638	00285					
6438	1.33071	.04644	00287					
	Samari	um Chloride						
5086	1.33545	0.04628	-0.00266					
5461	1.33386	.04614	00269					
5893	1.33238	.04578	00267					
6438	1.33071	.04572	00276					
	Europi	um Chloride						
4811	1.33678	0.04661	-0.00276					
5086	1.33545	.04642	00278					
5461	1.33386	.04586	00269					
5893	1.33238	.04516	00259					
6362	1.33112	.04527	00268					
6438	1.33071	.04538	00272					

#### Discussion

Okazaki<sup>8</sup> has published a series of papers on the

(8) A. Okazaki, Mem. Ryojun Coll. Eng., 6, 181 (1933); ibid., Inouye Commemoration Volume, 209 (1934); 9, 13, 101 (1936);
10, 89, 115 (1937); 12, 33, 45 (1939). Faraday effect in solutions of electrolytes. He has used the following modification of the Schönrock mixture rule

$$(w) = t_1(w_1) + t_2(w_2) \tag{5}$$

where w,  $w_1$  and  $w_2$  are the specific rotations of the

#### TABLE III

THE MOLECULAR ROTATION OF RARE EARTH CHLORIDES IN SOLUTION

Alu		M (m	AICI9)	Neoay	mum		
Molality	5461	Å.	<sup>6</sup> 5893 Å	. <sup>´</sup> Mo	lality	54	61 Å.
2.78	3.9	7	3.08	0	. 50	-'	7.14
2.00	3.6	7	3.14		. 40	-	7.11
1.50	3.6	4	3.20		. 30		6.71
1.00	3.6	5	3.25		. 20		6.82
0.50	3.8	3	3.48		.10	—'	7.17
0.10	• •		3.45	Α	v.		6.99
Av.	3.7	5	3.27				
	:	Lantha: $M(q_{1})$	num Chl	oride (La	.C18)	Min	
Molality	5461 Å	L. 589	93 Å.	Molality	546	1 Å.	5893 Å.
3.40	3.93	3	.31	1.7509	4.	18	3.53
3.10	3.97	3	. 34	1.40	4.	17	3.50
2.80	3.98	3	. 36	0.9967	4.	19	3.48
2.50	4.00	3	. 42	.80	3.	97	3.53
2.20	4.02	3	. 43	.40	4.	05	3.61
				Av.	4.	05	3.45
		Samari	um Chlo	ride (Sm	$C_{1_3}$		
Molality	Densi	ty	5086 Å.	5461 Á	. 589	3 Å.	6438 Å.
3.2644	1.65	58	4.00	3.33	2.	85	2.40
3.00	1.61	15	4.12	3.43	<b>2</b> .	91	2.44
2.50	1.52	31	4.09	3.51	2.	91	2.54
2.00	1.42	91	4.19	3.54	3.	03	2.52
1.50	1.32	98	4.26	3.64	3.	04	2.54
1.003	1.22	50	4.21	3.58	3.	05	2.84
0.50	1.11	38	4.92	3.86	3.	04	3.48
0.25	1.05	63	3.87	3.46	3.	26	2.94
Av.			3.96	3.54	3.	01	2.60
		Europi	um Chlo	ride (Eu $M_{0}$	$(1_3)$		
	<b>D</b>	4811	50,86	5461	์ 5ั่893	6362	6438
Molality	Density	A.	A.	A.	A.	A.	A.
2.847	1.5880	3.18	2.85	2.49	2.20	2.00	1.97
2.50	1.0244	3.34	3.03	2.60	2.30	2.13	2.11
2.00	1.4298	3.58	3.10	2.71	2.45	2.29	2.19
1.50	1.3298	3.68	3.26	2.75	2.44	2.42	2.31
1.00	1.2247	3.91	3.20	2.89	2.52	2.09	2.30
0.50	1.1140	3.81	3.30	3.UI	2.03	2.03	1.8/
0.25	1.0562	3.64	3.30	2.81	2.04	2.00	2.88
AV.	ъ	3.00	3.10 Delation	2.70 1.1	2.40	2.37	2.24
Molality		ee å	546	$M(w_2)$	6362	å	6438 Å
2 0179	y 50	6 0.	- 1/	1 1.	10	1	-0.0
2 00	· - 1	0.9	- 19	t. 1 0	-10.	1 9	-9.9
0.00 0.50	-1	0.0 6 6	- 10	),9 ) Q	- 10.	0	-9.7
2.00	— I _ 1	6.0 6.2	- 10	25	0.	7	-0.4
2.00	1	61	10	2.0 2.4	- J.	5	-0.9
1 00	1	5 7	- 19	2.3	0	5	9_1
0.50	1	5 5	19	2.0 3.0	_ 9.	4	-8.9
0.25	_1	5.7	1 Q	2.5	_ 9.	ō	-9.0
Av.	-1	6.20	-15	3.44	- 9.	- 66	-9.35
	*				~ •		

solution, solvent, and solute, respectively, and  $t_1$  and  $t_2$  are the weight percentages of the solvent and the solute. The molecular rotation, M(w), may be obtained easily by multiplying the specific rotation by the molecular weight. We have used this formula to compute the molecular rotation of the solute,  $M(w_2)$ . The values so computed are included in Table III. We have also included the molecular rotation of aluminum, lanthanum, and neodymium chlorides calculated from data obtained previously.<sup>1,9</sup>

An examination of Table III shows that the mixture rule (equation 5) when applied to the data in Table I holds within limits of experimental error at concentrations below about 3 molal, which represents about 40% anhydrous salt in the solutions. There are some discrepancies in the more dilute solutions but in this region where the rotation is small the errors of measurement are magnified in the computation of the Verdet constant and further magnified in the computations. These results in general confirm and are consistent with the results obtained by Okazaki<sup>8</sup> for many other electrolytes.

Roberts, Wallace and Pierce<sup>10</sup> have calculated for cerium sulfate solutions a quantity  $\Delta/W$  which they call the "specific rotation." This is defined in the equation

$$\Delta = \frac{nV}{(n^2 + 2)^2 d} - \frac{n_w V_w}{(n_w^2 + 2)^2 d_w} (1 - W/100) \quad (6)$$

where *n* is the refractive index of the solution,  $n_w$  that for water, and *W* is the number of grams of salt per 100 g. of solution. *V* is the Verdet constant for the solution and  $V_w$  is that for water. From the theory from which this equation is developed, the quantity  $\Delta/W$  should be independent of the concentration for any given wave length. This constant is independent of the concentration for cerium nitrate<sup>10</sup> and an examination of the data given in Table IV will show if this be true for the salts studied in this investigation.

A study of the data in Table IV shows that the values of  $\Delta/W$  obtained for solutions of praseodymium are constant within limits of error but that in the case of samarium and europium chlorides there seems to be a definite trend to decrease in the more concentrated solutions. It may also be noted that all specific rotations decrease with increasing wave length.

(9) C. M. Mason, THIS JOURNAL, 60, 1644 (1938).

(10) R. W. Roberts, L. A. Wallace and I. T. Pierce, *Phil. Mag.*, (7) **17**, 934 (1934).

Specific	ROTATIONS	s," $\Delta/V$	V, OF	THE .	Rare	Earth	
		Soluti	ONS				
	Praseod	ymium Cl	lloride (H	rC13)			
Molality	50	5461	5461 Å.		6438 Å.		
3.00	_	-5	-5.01		-3.51		
2.50	-	6.01	-5	-5.01		-3.50	
2.00	-	6.00	-4	-4.89		-3.48	
1.50	_	-6.01	-5	-5.02		3.47	
1.00	_	-5.96	-5	-5.04		3.46	
0.50	_	-5	-5.02		3.44		
0.25	_	-4	-4.89		-3.53		
Av.	_	-4	.98	-:	3.48		
	Samar	ium Chlo	ride (Sm	C1 <sub>3</sub> )			
Molality	5086 Å.	5461	$A/W \times A$	105– 5893 Å.	6	438 Å.	
3.2644	1.17	0.9	0.97		(	0.72	
3.0	1.21	1.0	1.01			.74	
2.50	1.22	1.0	1.04			.78	
2.0	1.26	1.0	1.07			.78	
1.50	1.30	1.1	1.11			.80	
1.003	1.30	1.1	1.19			.92	
0.50	1.57	1.2	1.22 .				
0.25	0.80	1.2	1.21 .		• •		
Av.	1.29	1.1	.0	.90		. 79	
	Europ	ium Chlo	ride (Eu	213)			
Molality	4811 Å.	5086 Å.	5461 Å	. 589	3 Å.	6438 Å.	
2.847	0.86	0.78	0.69	0.	60	0.56	
2.50	.91	.85	.73		65	.61	
2.00	1.00	.90	.78		71	.65	
1.50	1.03	.94	.80		72	.69	
1.0	1.14	.95	.85		75	.72	
0.5	1.05	. 98	.90		80	.54	
0.25	0.92	. 99	. 84		81		
Av.	.99	.91	.80		72	.62	

TABLE IV

An interesting anomaly appears in the case of the results for europium chloride. Samarium is definitely less paramagnetic than cerium or praseodymium, as shown by the fact that the Bohr magneton number is about 3.6 for praseodymium and 2.5 for cerium, whereas for samarium it is only about 1.5,<sup>11</sup> and the decidedly less magnetic optical rotatory power of samarium might be explained on this basis. In the case of europium, however, the magneton number given by Van Vleck<sup>11</sup> and since recalculated by Schmidt<sup>12</sup> is about 3.4. Therefore, one might expect that europium would have magnetic optical rotatory powers of the order of those of cerium and praseodymium rather than of the order of magnitude of samarium which it does have. We are not able to offer an explanation of this apparent anomaly.

## Summary

The magnetic rotations of the aqueous solutions of praseodymium, samarium, and europium chlorides have been measured at 25° for the wave lengths  $\lambda$ 4810.5,  $\lambda$ 5085.8,  $\lambda$ 5460.7,  $\lambda$ 5893,  $\lambda$ 6362.4, and  $\lambda$ 6438.47 Å. except in those cases where absorption interfered.

The refractive index of these aqueous solutions has been reported at  $25^{\circ}$ .

The Verdet constants have been calculated, those for samarium and europium solutions being positive and those for praseodymium solutions being negative when referred to water.

The specific and molecular rotations have been calculated and the variation of these properties with concentration noted and discussed.

An interesting anomaly has been observed in the comparison of the Verdet constants with the known magnetic moments of these ions.

(11) These data have been taken from Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, Oxford. 1932, p. 243.

(12) Th. Schmidt, Z. Physik, 108, 408 (1938).

DURHAM, NEW HAMPSHIRE RECEIVED JULY 19, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## Photochemistry of Diiodoacetylene and Tetraiodoethylene

## By John W. Tamblyn and George S. Forbes

The present research represents a further attempt to correlate the mechanisms of photoiodination on either side of the convergence limit of iodine,  $499 \text{ m}\mu$ . Brown<sup>1</sup> states that a continuum in the red, corresponding to production of normal atoms, is not visible below  $50^{\circ}$ . Bonhoeffer and Harteck<sup>2</sup> hold that this mode of dissociation is of minor importance photochemically. The data

(1) Brown, Phys. Rev., 38, 1187 (1931).

(2) Bonhoeffer and Harteck, "Grundlagen der Photochemie," Steinkopff, Dresden, 1933, p. 94. of Rabinowitch and Wood,<sup>3</sup> however, might lead to a contrary conclusion. Dickinson and Nies<sup>4</sup> reevaluated the data of Schumacher and Steiger<sup>5</sup> in terms of the influence of absorbed light intensity. They found the relative efficiencies of quanta corresponding to  $\lambda\lambda$  578, 546 and 436 m $\mu$  to be 0.75, 0.87 and 1.00, respectively. The temperatures were 76.6 and 99°. On the other hand,

- (3) Rabinowitch and Wood, Trans. Faraday Soc., 32, 547 (1936).
- (4) Dickinson and Nies, THIS JOURNAL, 57, 2382 (1935).
- (5) Schumacher and Steiger, Z. physik. Chem., B12, 348 (1931).