medium effect of acetic acid has been directly determined, and full details of the calculations are included.

3.   A simple extrapolation function has been derived, and applied to a determination of the primary medium effect of acetic acid and to the data of Åkerlöf.[14]

4.   It has been demonstrated experimentally that the primary, secondary, and total medium effects of acetic acid are closely proportional to the mole fraction of acetic acid in the solvent when the concentration of the electrolyte is expressed as molarity.

5.   Equations relating the primary medium effects in different concentration units were derived and applied to a comparison of the primary medium effect obtained in this paper, with that calculated by Harned and Owen[2] from data on sodium chloride solutions containing acetic acid.

6.   Two useful approximate equations were derived which interrelated the primary medium effects of a particular medium upon two similar electrolytes.   The importance of these equations, in the calculation of approximate medium effects from very limited data, has been pointed out, and the magnitude of the approximations involved has been estimated from Åkerlöf's data.

NEW HAVEN, CONNECTICUT

THE SPEED OF DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF HYDROCHLORIC ACID

BY E. A. BUDGE

The decomposition of hydrogen peroxide into oxygen and water in the presence of hydrochloric acid has been studied recently by Livingston and Bray,[1] who measured the concentration of peroxide after various time intervals by titration with permanganate, and also by Maass and Hiebert,[2] who followed the reaction by measuring the rate of evolution of oxygen. Both pairs of investigators worked mainly at 25° and found the reaction to be unimolecular with respect to the hydrogen peroxide.   Maass and Hiebert, however, obtained velocity coefficients which differed from those of Livingston and Bray for (presumably) identical conditions and they also found a well-marked period of acceleration for the more concentrated solutions.   In Fig. 1 some of the values obtained by these workers are shown in the one graph, values of log k being plotted as ordinates and the concentration of hydrochloric acid (in g. moles per liter) as abscissas. Curve I shows some of Livingston and Bray's results and Curve II some

[1] R. S. Livingston and W. C. Bray, THIS JOURNAL, 47, 2069 (1925).

[2] O. Maass and P. G. Hiebert, ibid., 46, 290 (1924).

of those of Maass and Hiebert, both at 25°. The other curves will be referred to later.

The present author was prompted to study the same reaction since the inconsistency in these results seemed to be in accord with certain mathematical investigations carried out by him,[3] in which it is shown that in the case of consecutive reactions it is possible for experimental reaction velocity coefficients to have different values according as they are based on measurements of reactants or of resultants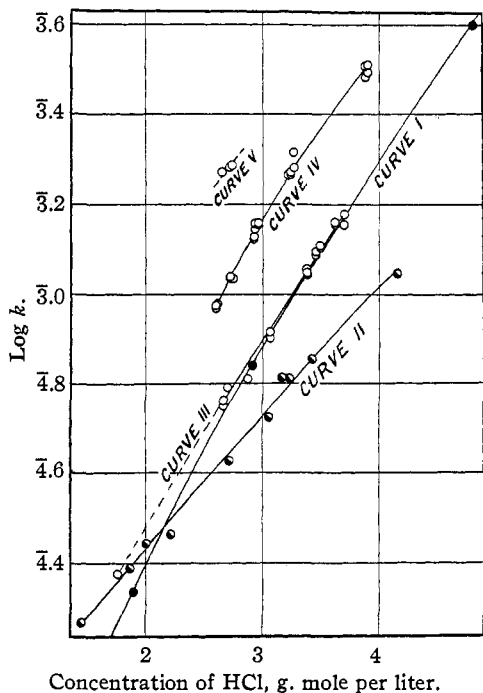. The coefficient by resultant may show an initial acceleration, whereas that by reactant shows no disturbance whatever. Certain types of catalysis, supersaturation of solution with respect to gaseous resultant, and initial changes of temperature due to heat effects on mixing may also cause similar initial disturbances.

Fig. 1.—Variation of k with temperature and concentration of hydrochloric acid.

Accordingly, experiments were carried out using methods practically the same as those used by Livingston and Bray and by Maass and Hiebert. The two methods were made as comparable as possible by preparing the reaction mixture, bringing it rapidly to the temperature of the bath and dividing it between the two reaction vessels, which were placed side by side in the same bath. In preparing these mixtures commercial 3% hydrogen peroxide and c. p. hydrochloric acid were used. The hydrochloric acid was freed from a trace of impurity (probably iron chloride) by letting it stand for some hours with hydrogen peroxide and then twice distilling, the constant-boiling fraction alone being used. Since the methods were directly compared and the values obtained agreed well with those of Livingston and Bray, further purification of materials was considered unnecessary.

The gas evolution apparatus used by Maass and Hiebert was modified by omitting the tubes of concentrated sulfuric acid and potassium iodide solution and a simpler method of calculating the velocity coefficients was employed. "Instantaneous" values of the unimolecular velocity coefficient were obtained by dividing the rate of evolution of oxygen (in cc. per minute) by the total volume of oxygen (in cc.) yet to be evolved from the instant of the measurement until complete decomposition of the peroxide. This

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[3] E. A. Budge, "Reports of the Australasian Association for the Advancement of Science," Hobart Meeting, January, 1928, XIX, 147.

necessitated continuing the reaction to near completion and then estimating the residual peroxide. This was done either by heating the reaction mixture to near boiling until the peroxide was decomposed or by titration of an aliquot part of the reaction mixture by permanganate. To render the measurements involved in this method less tedious, an automatic bubble counter[4] was developed and used. From the readings of this instrument the rate of evolution of oxygen (in bubbles per minute) and also the total volume of oxygen (in bubbles) up to the instant of measurement were easily obtainable.

Throughout the investigation the concentration of hydrochloric acid in the reaction mixtures was measured by the Iceland spar method.[5] In some cases this was checked by precipitation of silver chloride with concordant results.

The results obtained by the titration method showed a very constant unimolecular coefficient which agreed well with those given by Livingston and Bray for corresponding conditions. The results obtained by the gas evolution method showed a well-marked period of acceleration (lasting from forty to eighty minutes) and thereafter a constant unimolecular coefficient, which was practically identical with that given by the titration method. This period of acceleration has since been shown to be due (at least in part) to supersaturation of the reaction mixture with oxygen.[6]

Accordingly, a new apparatus for the gas evolution method was installed with the object of testing whether there were any irregularity other than that due to supersaturation. A diagram of this apparatus is shown in Fig. 2.

In this apparatus a wide-mouthed bottle A was used as reaction vessel. The mouth of this was closed by a trebly-bored rubber stopper B, which was firmly clamped in position (the clamps are not shown in the diagram) and had its lower surface covered with vaseline. The reagents were added to the bottle through tube C, which was closed by a well-fitting rubber stopper.

Fig. 2.—Apparatus for measurement of speed of gas evolution (not to scale).

The middle hole of the rubber stopper carried a mercury seal D and allowed the entrance of the stirrer, which was directly coupled to the shaft of a small motor E. For most of its length the stirrer was of solid glass rod, but, about 5 cm. from the bottom, a T-shaped piece of glass tubing was sealed on and this was provided with a small hole at F. This stirrer, which was rotated at about 1000 r. p. m., proved very efficient in overcoming supersaturation. On account of centrifugal action, gas from the top of the bottle entered
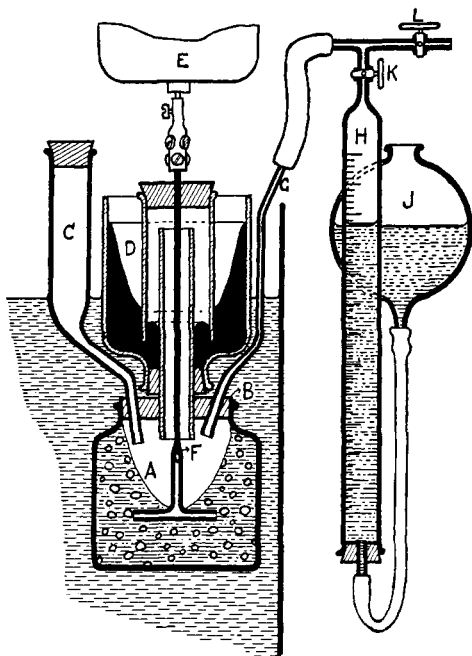
⁴ E. A. Budge, THIS JOURNAL, 53, 2451 (1931).

⁵ D. O. Masson, Chem. News, 81, 73 (1900).

⁶ The author is much indebted to Professor Bray and Mr. B. Makower for suggesting this possibility.

at the hole F and was discharged in a constant stream of bubbles through the open arms of the T-piece. Thus not only was the liquid violently agitated but also it was continually charged with a multitude of small gas bubbles. The third hole in the rubber stopper B carried a tube G leading to the gas buret H, which was filled with water and connected to the counterpoised leveling bulb J. The stopcocks K and L facilitated the manipulation of this part of the apparatus.

The apparatus was used as follows. The charge of peroxide was placed in the vessel A after the stirrer had been adjusted to run steadily without vibration and the apparatus had been placed in position in the bath and proved free from leakage. When this peroxide had reached the temperature of the bath and while the stirrer was running at full speed, the necessary hydrochloric acid was added as rapidly as possible by means of the tube C, which was at once stoppered. On account of the heat of dilution of the acid, it was necessary to determine by previous trial what its temperature must be before addition in order that the temperature of the mixture in the bottle should be the same as that of the bath immediately after the addition. The zero time for the reaction was taken as the instant when half of the acid had been added and measurements of the rate of evolution of oxygen were begun as soon as possible. To make one of these measurements, the stopcocks K and L were opened and J raised until the level of the water was near the top of the buret. After noting the reading of the buret, the stopcock L was closed at a noted instant. As the oxygen accumulated in H, J was lowered to keep the pressure of the gas roughly that of the air outside. When a suitable volume of gas had been collected, K was closed at a noted instant and when the two water menisci were on the same level and the volume of gas was read off. If the readings are taken quickly, several measurements of the rate of gas evolution can be made in quick succession without expelling the gas from the buret. While both K and L are closed, the pressure in the rest of the apparatus rises slightly, but, on opening K again and lowering J, this excess pressure is relieved and a second reading can be taken. The volume of gas collected was corrected for pressure and temperature and divided by the time during which the gas had been collected. This furnished the rate of evolution of oxygen in cc. per minute; this rate of evolution was considered to measure the speed of the reaction at the instant midway between the instants of closing stopcocks L and K. Where several repetitions (usually overlapping one another) were made as described above, the average of the rates was used for further computation. By opening K and L and raising J, the gas collected in the buret was expelled and the apparatus made ready for further rate measurements.

From the values of the speed of reaction at various times thus obtained the unimolecular reaction velocity coefficient was obtained by plotting the logarithm of the speed (in cc. per minute) against the time (in minutes) from the zero of the reaction. The points plotted should lie on a straight line if the reaction is truly unimolecular. The velocity coefficient is obtained by multiplying the slope of the line by -2.303. This method is especially convenient for studying the early stages of the reaction as it does not necessitate continuing the experiment after sufficient readings have been made to determine the straight line with sufficient accuracy. Also, the method is not affected by what happens to the reaction mixture between readings, provided that its temperature remains constant and that the stirrer has been running for a sufficiently long time before making the reading to overcome supersaturation. This method was subsequently used to recalculate the results of the

previous gas evolution experiments; the results agreed well with those of the former method.

The period of acceleration was now very much shorter (from three to fifteen minutes) and, since it was very variable in duplicate experiments and was reduced by higher speed of stirring, it is considered to be almost entirely, if not entirely, due to supersaturation. In any case, it is too short to enable sufficiently accurate rate measurements to be made to permit its use in determining the mechanism of the reaction. Table I gives the condensed results of one experiment by this method. The number of the reading is given in column 1, the time in minutes from the zero of the reaction

TABLE I

Run G47. June 8, 1931. Temperature of bath, 25.00°. Reaction mixture: 181 cc. of hydrogen peroxide (3%) at 25.0° to which was added 196 cc. of HCl (dilute) at 15.8°, giving a mixture containing 3.282 g. mole of HCl per 1000 g. and 0.44 g. mole of H_2O_2 per liter at 25.0°.

Reading number	Time, minutes	Time of collection, minutes	Oxygen, cc.	Speed of reaction in cc. of O_2 per minute
1	1.5	0.83	1.01	1.22
2	2.3	2.45	3.04	1.24
3	2.7	3.32	5.16	1.55
4	3.4	4.55	8.78	1.93
5	3.7	5.25	10.73	2.05
6	4.1	6.08	13.21	2.18
7	4.6	6.92	15.57	2.25
8	5.1	8.00	18.08	2.26
9	5.4	8.58	20.26	2.36
10	5.7	9.25	22.00	2.38
11	6.2	10.22	24.70	2.41
12	6.8	11.43	28.02	2.45
13	7.2	12.18	30.08	2.47
14	7.6	12.97	32.20	2.48
15	8.0	13.80	34.52	2.50
16	20.0	4.50	12.49	2.78
		5.70	15.93	
		6.75	18.79	
17	31.2	1.58	4.36	2.71
		3.03	8.12	
		4.12	11.12	
18	38.3	4.08	10.96	2.70
		5.17	13.97	
		6.17	16.55	
		7.00	19.07	
19	51.6	4.08	10.55	2.60
		5.13	13.37	
		7.42	19.28	
20	104.1	4.67	11.28	2.41
		6.17	14.91	
		8.83	21.07	

TABLE I　(*Concluded*)

Reading number	Time, minutes	Time of collection, minutes	Oxygen, cc.	Speed of reaction in cc. of O₂ per minute
		4.95	11.02	
21	148.5	5.97	13.28	2.22
		7.57	16.74	
		5.33	11.43	
22	169.7	6.47	13.98	2.15
		7.60	16.33	
		7.47	15.43	
23	202.7	8.83	18.27	2.07
		10.00	20.79	
		6.30	12.58	
24	221.4	8.50	16.86	2.00
		9.75	19.56	
		5.60	10.48	
25	259.3	7.25	13.71	1.88
		10.33	19.30	

to the middle of the collection period in column 2, the duration in minutes of the collection period in column 3, the volume of the collected oxygen (in cc., corrected for pressure and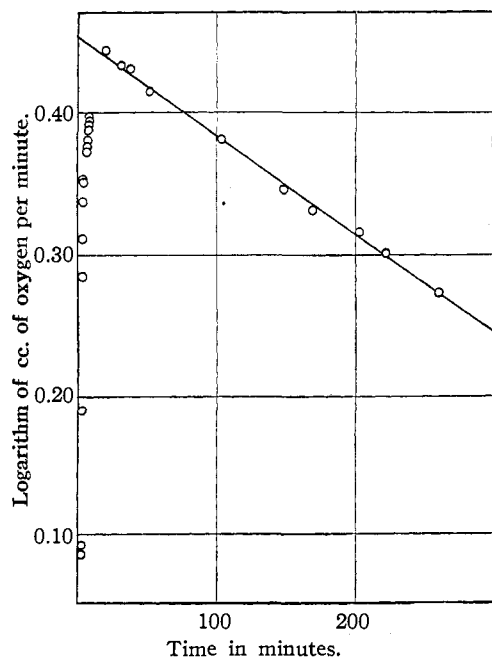 temperature) in column 4 and the rate of evolution of oxygen (in cc. per minute) in the last column. The horizontal lines show when the gas was discharged from the buret. At the beginning of this experiment the stirrer was run at low speed; just before reading number 17 it was speeded up; before 19 it was slowed again; before 22 speeded up; before 24 slowed down again and between 24 and 25 it was stopped altogether for seventeen minutes and then run at full speed. This was to test the efficiency of the stirrer in overcoming supersaturation. The plot of these measurements is shown in Fig. 3, the logarithm of the rate of evolution of gas being plotted as ordinate and the time from zero as abscissa.

Fig. 3.—Graphical evaluation of k from measured speed of gas evolution.

The constancy of the velocity coefficient by reactant in the early stages of the reaction was also investigated by a titration method. A measured weight of hydrogen peroxide solution of known titer was placed in a weighing bottle and hung in the bath. At zero time a suitable volume of hydrochloric acid of known concentration was added to the weighing bottle and the weight of acid added was determined by weighing its containing vessel (a stoppered U-tube) before and after the addition of acid. The temperature of the acid was so adjusted before addition that the heat of dilution of the acid just brought the temperature of the mixture to that of the bath. Meanwhile a large beakerful of dilute sulfuric acid had been tinted to a suitable end-point by permanganate. Half of this was reserved for comparison to define the end-point of the titration and to the other half there was added from a weighed weight buret standard permanganate in quantity slightly less than that needed to react with the peroxide in the weighing bottle. At the expiration of the desired reaction period, the weighing bottle was removed from the bath and rapidly washed on the outside with distilled water. The stopper was then removed, the bottle and contents were added to the beaker containing the permanganate solution and the titration then finished so that the tint of the solution matched the blank. From the weight of permanganate solution required and the known titer of the peroxide before addition of acid, the fraction of the peroxide remaining undecomposed could be calculated. Also the concentration of hydrochloric acid in the mixture was calculated. By this means a number of results were obtained for the one reaction period and slightly differing concentrations of acid. The fraction of the peroxide undecomposed at the end of the reaction period was then interpolated graphically for some chosen acid concentration. By a repetition of this process for other reaction periods, ranging from two to forty-five minutes, values were obtained for the fraction of the peroxide undecomposed for a series of times and all for the one acid concentration. The method was very tedious but as far as could be seen the results were exact. On plotting the logarithm of the fraction of peroxide undecomposed against the reaction time, a straight line was obtained in each series of experiments. Hence no measurable irregularity was found in the velocity coefficient as determined by titration of the peroxide, even in the early stages of the reaction.

Table II contains in condensed form the results of all the present experiments in which there are no known sources of gross inaccuracy. In this table the distinguishing number of the experiment is given in column 1. Experiments in which the peroxide was determined by titration are distinguished by T, those in which the rate of evolution of oxygen was measured by G, those in which the rate of evolution of oxygen was measured by bubble counter by B, and two series in which weight titration by permanganate was used are distinguished by W. The concentration of hydrochloric acid in gram molecules per 1000 g. of reaction mixture is given in column 2. The approximate initial concentration of hydrogen peroxide in gram molecules per liter is given in column 3. The total duration of the experiment is given in column 4 and the value of the unimolecular velocity coefficient (k) is given in column 5.

In Fig. 1 these results are shown graphed along with those results of Livingston and Bray[1] and of Maass and Hiebert[2] which fall within the limits of the graph. In this figure, values of log k are plotted as ordinates and concentration of hydrochloric acid as abscissas. Curve I shows Livingston and Bray's results at 25°; Curve II shows Maass and Hiebert's

TABLE II

COLLECTED RESULTS OF EXPERIMENTS ON THE SPEED OF DECOMPOSITION OF HYDROGEN
PEROXIDE IN THE PRESENCE OF HYDROCHLORIC ACID

Expt.	Concn. of HCl	Concn. of peroxide	Duration of expt.	$k \times 10^4$
		Experiments at 25°		
G53	1.714	2.62	210 min.	3
T20	2.566	0.93	25 hours	7.2
G20	2.566	.93	26 hours	7.1
G36	2.598	.64	220 min.	7.8
W2	2.75		7 min.	8.1
T21	2.908	.81	24 hours	10.43
B21	2.908	.81	22 hours	10.4
G41	2.911	.56	150 min.	10
T18	3.212	.83	22 hours	14.4
B18	3.212	.83	22 hours	14.1
T19	3.213	.86	27 hours	14.4
B19	3.213	.86	27 hours	14.0
G49	3.28	.43	135 min.	15.6
G47	3.282	.44	260 min.	15.5
T17	3.282	.89	17 hours	15.7
B17	3.282	.89	18 hours	15.5
T16	3.308	.91	20 hours	16.1
B16	3.308	.91	20 hours	16.0
T15	3.425	.91	18 hours	18.2
B15	3.425	.91	16 hours	18.0
W1	3.50	.	45 min.	18
		Experiments at 30°		
			Hours	
T10	2.494	0.90	25	11.9
G10	2.494	.90	25	11.7
T11	2.500	.89	27	12.0
G11	2.500	.89	27	11.8
T9	2.607	.59	25	13.8
G9	2.607	.59	26	13.7
T8	2.626	.56	25	13.6
G8	2.626	.56	25	13.7
T5	2.801	.92	25	16.9
G5	2.801	.92	22	16.8
T3	2.810	.93	15	17.55
G3	2.810	.93	19	18
T4	2.828	.94	18	17.95
G4	2.828	.94	18	18
T6	3.045	1.20	22	23.0
T2	3.082	1.28	25	23.5
G2	3.082	1.28	25	23.2
T1	3.102	1.28	26	26
G1	3.102	1.28	21	24
T13	3.651	0.66	9	40.4
G13	3.651	.66	19	38
T12	3.667	.68	19	40.5
G12	3.667	.68	19	39

TABLE II   (*Concluded*)

Expt.	Concn. of HCl	Concn. of peroxide	Duration of expt.	$k \times 10^4$
		Experiments at 35°		
G46	2.549	0.31	260 min.	23.5
G44	2.602	.27	330 min.	24.0
G45	2.617	.31	315 min.	24.2

results at 25°; the results of the present investigation are shown in Curves III (25°), IV (30°) and V (35°). It will be seen that the present results are in good agreement with those of Livingston and Bray and quite discordant with those of Maass and Hiebert.

The Temperature Coefficient

Livingston and Bray[1] state that the temperature coefficient of the reaction is 3.60 for a rise of temperature of 10°. This value is based on their measurements at 25 and 40°. The method of calculation used by them appears, however, to be incorrect, in that they have assumed the ratio of velocity coefficients for two temperatures 10° apart to be two-thirds of the ratio of coefficients for temperatures 15° apart. A preferable procedure would seem to be based on the well-known Arrhenius formula

$$\log (k_2/k_1) = A(1/T_1 - 1/T_2)$$

Calculation of the constant A in this expression from Livingston and Bray's data leads to $A = 4500$ and the ratio $k_{35°} : k_{25°}$ derived from this is about 3.1. The results of the present investigation also permit of the calculation of a temperature coefficient. That derived from measurements at 25° and 30° is 3.1, A being 4550. The measurements at 35° are fewer and less reliable than the others but the value of the temperature coefficient derived directly from the measurements at 25 and 35° is 3.25, which leads to $A = 4700$. The value (3.60) given by Livingston and Bray is therefore certainly too high and the true value is in the neighborhood of 3.1.

The author desires to express his sincere thanks to Professor E. J. Hartung for the generous manner in which he has made available facilities for carrying on this work and for his very helpful criticism and advice.

Summary

The decomposition of hydrogen peroxide in the presence of hydrochloric acid has been studied over a moderate range of concentrations at temperatures of 25, 30 and 35°, by methods which have involved measurements of both the residual peroxide and of the rate of evolution of oxygen.

1.   The velocity coefficients obtained agree closely with those of Livingston and Bray and disagree with those of Maass and Hiebert.

2.   When the concentration of the residual peroxide is measured, the reaction is strictly unimolecular from the first within the limits of measurement.

3. When the rate of evolution of oxygen is measured, the reaction is strictly unimolecular after a very short period of acceleration which is ascribed to supersaturation.

4. The temperature coefficient of the reaction is about 3.1.

5. A method of weight titration of hydrogen peroxide by permanganate is described which enabled reaction velocity measurements to be carried out in the very early stages of the reaction.

6. A graphical method is described which enables unimolecular velocity coefficients to be calculated from measurements of the rate of evolution of gas without any knowledge of the total volume of gas evolved or the exact concentration of the peroxide.

It is believed that both these methods are new.

MELBOURNE, VICTORIA, AUSTRALIA

ABSORPTION SPECTRA AT HIGH PRESSURES AND AT LOW TEMPERATURES. THE TRANSPARENCY OF ARGON AND METHANE[1]

BY B. J. EISEMAN, JR.

The purpose of this investigation was to study the absorption spectra of a number of substances whose pressure, volume, and temperature relations suggested the possibility of molecular aggregation as a factor in the attempt to account for the physical properties at high concentration and at low temperature. Since it was not possible to predict the spectral region of the absorption of the supposed associated or aggregated molecular species, the spectral region selected was the visible and the quartz ultra-violet, where absorption may be most readily studied. In this paper we shall describe the design of apparatus found satisfactory for the purpose and the results of the studies with argon and methane.

Method.—The light absorption was determined by the method of photographic spectrophotometry. The relative blackening of the photographic plate served as a measure of the light transmission through the empty absorption tube and through the tube filled with fluid.

An Adam Hilger E 1 spectrograph with glass and quartz optical system was used for photographing the spectra. Exposures were twenty minutes to one hour for slit widths of 0.01 to 0.02 millimeter.

An under-water spark served as a source of continuous light. However, the usual aluminum and copper electrodes were replaced advantageously by magnesium electrodes for the shorter wave lengths. In later work we have used the hydrogen discharge tube as

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[1] The results presented here are to be found in greater detail in the Ph.D. Thesis of B. J. Eiseman, Jr., Massachusetts Institute of Technology, 1927.