[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Influence of Water upon the Photolysis of Ozone at λλ 280, 254 and 210 mμ

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This paper deals with the photolysis of ozone at λλ 280, 254 and 210 mμ in the presence of liquid water and its saturated vapor at approximately 2 and 20°. Warburg[1] photolyzed ozonized oxygen saturated at room temperature with water vapor and observed that the quantum yield, ϕ (ozone molecules decomposed per quantum absorbed by ozone), was noticeably higher than in the dry gas, but that oxygen, nitrogen and helium mixed with dry ozone acted as inhibitors. Later investigations[2] have fully confirmed the inhibiting effect of these and other gases, but the influence of water has not received further attention. In this investigation we have varied the partial pressure of ozone, p_{O_3}, from a few millimeters as in Warburg's experiments, up to one atmosphere.

Experimental

The source and purification of materials, the trapezoidal reaction cell, and the apparatus for following the rate of decomposition by the use of a spiral quartz manometer have been described,[3,4] as well as the somewhat elaborate experimental procedure. Stopcocks were completely eliminated, and other precautions to exclude impurities, particularly vapors of organic substances and of mercury, were not relaxed.

Our light source embodied the principle worked out by Forbes and Brackett,[5] but resembled more nearly that of Wiig and Kistiakowsky,[6] owing to our need for compactness and portability. The electrical "hook-up" has already been described.[5] It was found, by trial, that optimum intensity and constancy of radiation were not obtainable from disk electrodes of zinc less than 85 mm. in diameter and 12 mm. in thickness, with a period of rotation greater than fifty minutes. Our disks were cast 120 mm. in diameter and 12 mm. thick in mill-steel molds warmed to 250°. The rim of each disk was turned in a lathe to produce a double beveled edge (the included angle was 120°), the faces of which were of equal width. To avoid wobbling, each disk was mounted flush against a fixed aluminum washer, 60 mm. in diameter, by means of a much smaller washer and nut. The spark, 2 mm. in length,

was stabilized by a blast of air through an 8-mm. glass tube at right angles to the axis of the collimating lens. Fumes were sucked away through a 24-mm. glass tube, and the blast was thereby made more effective. The electrode supports were countersunk in an 18-mm. bakelite slab which could be raised and lowered on a slotted steel upright. This upright could be turned to permit quick replacement of the disks. After each complete revolution with the spark running, the worn edges were machined again. The spark gap was centered by turning the upright until the slab met a suitable stop.

The monochromator employed crystal quartz lenses[5] and a Cornu prism[5] mounted on a 6-mm. bakelite slab which was pivoted[3] under the light source. The collimating slit,[7] 1 mm. wide, had jaws cut from fine-grained gray talc (from the Ward Instrument Co., Rochester, N. Y.) which formed a V pointing toward the spark. The edges, beveled on the sides next the spark, were 10 mm. from it. To avoid short circuits and decline in available light intensity, the jaws, lenses and prism were often freed from accumulated dust. Our monochromatic light was then as intense and constant as that described by Forbes and Brackett.[5]

Small residual fluctuations in intensity were followed, every five minutes during a photolysis, by swinging the whole monochromator around its pivot; so as to bring its exit slit exactly in line with the slit of a linear thermopile[5] and noting the galvanometer[5] deflection. We verified the previous observation that the deflection, under these circumstances, was proportional to total light flux as determined by the method of integration behind the exit slit.[5] Careful electrical screening of thermopile and leads proved essential. A space of 8 mm. was provided between exit slit and thermopile slit for mounting the rectangular quartz cell (all seams fused) 40 x 87 x 5.65 mm. (inside measurements). The actinometer solution in this cell, well stirred with a spiral of platinum ribbon, was 0.001 M in uranyl sulfate and 0.005 M in oxalic acid. Its quantum yield had been carefully compared with that of the more concentrated solution previously standardized in this Laboratory.[8,9] The photolyzed solution was compared with "dark" solution using 0.01 N permanganate. The front window of the gas cell[4] (40 cc. including connections) and that of the actinometer cell were cut from the same piece of clear quartz plate, 0.85 mm. thick. As the depth of the gas cell was 50 mm. and p_{O_3} never below 10 mm., absorption of light was "complete" in all our experiments. To photolyze the ozone, the monochromator was swung around its pivot so as to bring its exit slit into line with the center of this front window. Other details of the photolysis and of the actinometric procedure, including the necessary corrections, have been given.[4] The "dark"

(1) Warburg, *Sitzb. preuss. Akad. Wiss.*, 644 (1913).

(2) For summaries of the literature see (a) Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems," Longmans, Green and Co., New York, 1929; (b) Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., New York, 1932; (c) Schumacher, *Z. physik. Chem.*, **17B**, 405 (1932); (d) Beretta and Schumacher, *ibid.*, **17B**, 417 (1932).

(3) Forbes, Kistiakowsky and Heidt, THIS JOURNAL, **54**, 3246 (1932).

(4) Heidt, Kistiakowsky and Forbes, *ibid.*, **55**, 223 (1933).

(5) Forbes and Brackett, *ibid.*, **53**, 3973 (1931).

(6) Wiig and Kistiakowsky, *ibid.*, **54**, 1806 (1932).

(7) F. P. Brackett, doctoral thesis, 1932, Widener Library, Cambridge, Mass.

(8) W. G. Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

(9) Forbes and Brackett, *ibid.*, **55**, 4459 (1933).

reaction of ozone was followed before and after each photolysis, and found to be negligible over the time of any photolysis.

Three separate fillings of the gas cell, identified by the first serial numbers in the tables, were made. After each filling, the water was frozen in the reaction cell with carbon dioxide snow, and the cell connected with the diffusion pump until no pressure was observed in the McLeod gage. Thereupon, ozone freshly purified by fractionation was introduced—for the first filling a first fraction, for the second filling a middle fraction and so on. The second serial number refers to a series of experiments under conditions approximately identical, and a small letter refers to an individual experiment. In the second column appears, with the average wave length, the number of spectral lines in the close group used for photolysis. All pressures were recalculated to $0°$, in terms of mm. of mercury at $0°$. P is the total pressure in the cell during a photolysis (including p_{H_2O}), ΔP the increase in P, and p_{O_3}, p_{O_2}, p_{H_2O} partial pressures. An average is denoted by a bar over the symbol in question.

Results of the investigation are summarized in Table I. It is evident from the magnitude of ϕ that the reaction has chain characteristics in view of which the difficulty of reproducing ϕ with exactness is not surprising. Figure 1 shows

$\log_{10} \phi$ plotted at each of several wave lengths against $\log E$, where E is average light flux in quanta per minute absorbed by ozone. In all such experiments p_{O_3} and p_{O_2} were large compared with Δp_{O_3} and Δp_{O_2}, while p_{H_2O} was fixed by holding temperature constant. It will be noted that the slopes average -0.37 at $\lambda\ 210\ m\mu$ (irrespective of partial and total pressures) and -0.24 at $\lambda\lambda\ 254$ and $280\ m\mu$, thus showing that ϕ is inversely proportional to the corresponding powers of light intensity. In the course of similar experiments on dry ozone now in progress we have noted a more definite tendency for these lines to become less steep as λ increases. Obviously this relationship would have been obscured if we had used polychromatic light, like many other investigators. Since the radiation is absorbed only by ozone, this means that ϕ is inversely proportional to the corresponding power of $[O_3^*]$, the concentration of ozone molecules which are activated by light. Before studying the kinetics of the reaction at a fixed wave length, it is therefore necessary to recalculate ϕ to the same

TABLE I

Serial number	λ in mμ	$\bar{P}$ mm.	$\bar{p}_{O_3}$	$\bar{p}_{O_2}$	Cell temp., t_0	p_{H_2O}	Quanta absorbed per min. $E \times 10^{-16}$	Time of photolysis min.-sec.	ΔP	ϕ	$\dfrac{\bar{\phi}_E}{E = 7.5} \times 10^{16}$
1–1a	210–4	1114	604	495	18.0	15.48	16	19–30	24.22	22	
b		1141	550	575	18.3	15.77	17	19– 0	23.77	22	27
c		1168	498	654	18.4	15.87	16	23–30	26.61	20	
1–2a	254–2	1183	468	699	17.7	15.19	8.7	15– 0	3.76	8.2	
b		1192	448	728	18.0	15.48	8.6	21–15	4.83	7.5	7.5
c		1197	438	743	18.2	15.67	8.2	24– 7	4.18	6.0	
1–3a	254–2	1200	410	784	2.8	5.6	5.5	22–10	2.75	6.4	
b		1205	400	800	1.4	5.1	6.0	23–15	3.32	6.8	5.4
c		1212	388	819	1.6	5.14	6.0	21–10	2.60	5.8	
d		1214	382	827	1.6	5.14	5.5	20– 7	1.83	4.7	
1–4a	210–4	1221	368	848	1.4	5.07	9.0	21– 9	9.36	14	
b		1233	344	884	2.4	5.45	5.6	15–13	4.79	16	15
2–1a	280–2	640	356	264	21.9	19.64	7.3	18–21	20.97	45	
b		663	310	334	21.4	18.94	6.1	11– 0	10.57	45	43
2–2a	254–2	687	258	411	20.0	17.54	5.1	21–30	7.37	19	
b		694	244	432	20.1	17.70	5.5	21–20	6.00	15	15
2–3a	210–4	710	212	481	19.4	16.89	5.5	13–33	16.59	63	
b		727	178	531	20.0	17.54	5.5	12– 9	14.83	63	54
c		741	150	573	20.1	17.64	5.5	9–39	10.29	55	
2–4a	210–4	747	114	628	1.3	5.03	3.7	19–39	11.12	43	
b		758	92	661	1.8	5.22	3.6	21–35	11.91	43	34
2–5a	254–2	769	70	694	1.4	5.07	5.1	23–15	2.19	5.2	
b		770	68	697	1.6	5.14	4.9	24–28	2.23	5.3	4.6
2–6a	280–2	774	61	708	1.4	5.07	2.6	15– 6	1.29	9.3	
b		776	58	713	1.4	5.07	3.1	20–37	3.38	15	8.7
2–7a	280–2	791	56	715	21.3	19.00	7.1	23–50	10.13	17	
b		800	36	745	21.2	18.88	6.1	21–21	8.36	18	17

TABLE I (Concluded)

Serial number	λ in mμ	$\bar{P}$ mm.	$\bar{p}_{O_3}$	$\bar{p}_{O_2}$	Cell temp., t_c	p_{H_2O}	Quanta absorbed per min. $E \times 10^{-16}$	Time of photolysis min.–sec.	ΔP	ϕ	$\bar{\phi}_E$ $E = 7.5 \times 10^{16}$
2-8a	254-2	805	26	760	20.9	18.54	12	24-27	3.76	3.8	
b		809	18	773	20.8	18.42	11	23-18	3.53	4.0	4.5
2-9a	210-4	812	14	779	21.5	19.23	10	28-52	1.88	1.7	
b		813	11	783	21.5	19.23	10	31- 8	1.82	1.6	1.8
3-1a	254-2	923	729	189	1.8	5.22	12	18-23	6.23	8.3	
b		931	717	209	1.4	5.07	12	19- 0	7.49	9.6	10.5
3-2a	254-2	939	705	215	20.9	18.54	12	16- 0	9.98	15	
b		961	681	262	20.7	18.31	12	19- 5	11.83	15	17.5
3-3a	280-2	987	627	342	20.0	17.54	9.0	15-45	15.42	31	
b		1022	549	455	19.9	17.43	6.0	15-59	12.26	36	33
3-4a	280-2	994	589	400	1.7	5.18	8.6	16-11	6.16	13	
b		1008	569	434	1.8	5.20	9.6	20- 0	10.03	15	15
3-5a	210-4	1062	471	574	20.0	17.48	15	17- 6	30.52	34	
b		1119	361	741	19.8	17.32	12	10-22	17.06	38	44
3-6a	210-4	1078	419	654	1.5	5.11	14	10-25	8.54	17	
b		1091	395	691	1.4	5.05	14	11-50	11.65	20	22
c		1102	369	728	1.4	5.07	14	11- 0	9.18	17	
3-7a	210-4	1132	337	777	20.0	17.54	0.7	22-57	7.09	120	
b		1139	321	800	20.2	17.75	.7	28-54	6.31	90	49
c		1145	311	816	20.2	17.75	.3	29- 0	3.94	130	
3-8a	210-4	1166	267	881	20.1	17.64	9.9	10- 2	14.11	40	
b		1184	231	935	20.3	17.86	12	10-48	18.08	39	45
3-9a	280-2	1200	201	981	20.4	17.97	1.5	33- 5	4.77	27	
b		1204	191	995	20.25	17.81	1.4	29-57	3.73	25	15
3-10a	280-2	1211	179	1014	20.5	18.09	13	10-10	7.95	17	
b		1212	176	1018	20.2	17.75	5.1	12-13	4.01	18	19
3-11a	254-2	1217	167	1032	20.4	17.97	1.7	28-58	2.14	12	
b		1218	164	1036	20.0	17.54	1.8	25-47	1.92	12	7.4
3-12a	254-2	1222	157	1047	20.5	18.09	9.6	15-14	4.17	8.2	
b		1227	146	1063	20.3	17.86	9.3	22-15	5.72	7.8	8.6
3-13a	210-4	1253	95	1140	20.4	17.97	1.4	26- 0	7.01	55	
b		1260	83	1159	20.4	17.97	0.9	24-30	4.62	60	31
3-14a	210-4	1267	69	1180	20.2	17.75	7.4	9-22	7.40	30	
b		1273	57	1198	20.5	18.09	7.2	11-21	7.52	26	27
3-15a	210-4	1278	45	1215	20.5	18.09	1.2	15-43	2.42	38	21
b		1282	37	1227	20.6	18.20	1.0	22-15	2.69	33	17
3-16a	210-4	1285	31	1236	20.6	18.20	5.8	12- 2	4.53	18	16
b		1289	23	1250	20.9	18.60	4.7	11-19	3.06	16	14
Warburg[1]	210-4	760	50	691	Room	19 ± 3	7.4	4- 0		10	9.0
Warburg[1]	254-2	760	56	685	Room	19 ± 3	9.0	4- 0		6	5.8
Warburg[1]	287-1	760	53	688	Room	19 ± 3	24.0	4- 0		5	6.7

value of E, arbitrarily taken as 7.5×10^{16} quanta per minute (the average of Table I, column 8). In a study of the photochemical oxidation of quinine and its derivatives by chromic acid[10] we likewise plotted log ϕ_q (based upon light absorbed by alkaloid only) against log E absorbed by the alkaloid at each of several wave lengths. Parallel straight lines resulted just as in the present research. No such regularity would have come to

light in the diagram for the alkaloids if total light intensity had been taken. We therefore maintain that *the concentration of activated molecules is fundamental in the interpretation of quantum yields, no matter whether the system is liquid or gaseous.*

As a further consequence of the linear character of the plots of log ϕ against log E in the liquid and in the gaseous systems, it can be inferred that the collision number of activated molecules in the liquid phase differs only by a

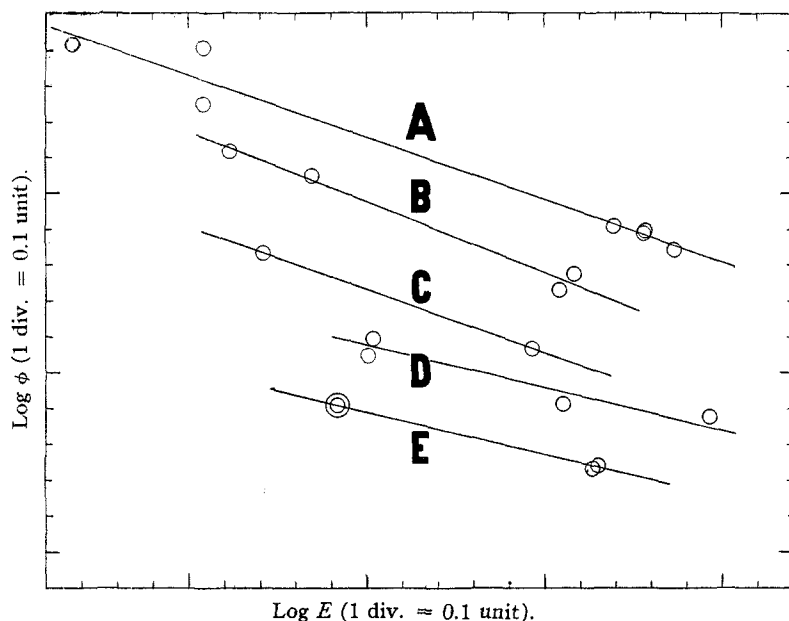(10) Forbes and Heidt, THIS JOURNAL, **55**, 2407 (1933).

Log E (1 div. $=$ 0.1 unit).

Fig. 1.

Curve	λ in mμ	Serial number	$\bar{P}$	$\bar{p}_{O_3}$	$\bar{p}_{O_2}$	p_{H_2O}	$E \times 10^{-16}$	Log₁₀E	ϕ	Log ϕ	Slope
A	210-4	3-5a	1062	471	574	17.5	15	17.26	34	1.54	
		b	1119	361	741	17.3	12	17.08	38	1.59	
		3-7a	1132	337	777	17.5	0.7	15.08	120	2.10	
		b	1139	321	800	17.8	0.7	15.08	90	1.95	
		c	1145	311	816	17.8	0.3	15.47	130	2.11	
		3-8a	1166	267	881	17.6	10	16.99	40	1.61	
		b	1184	231	935	17.9	12	17.08	39	1.59	-0.36
B	210-4	3-13a	1253	95	1140	18.0	1.4	16.14	55	1.74	
		b	1260	83	1159	18.0	0.8	15.91	63	1.81	
		3-14a	1267	69	1180	17.8	7.4	16.88	30	1.47	
		b	1273	57	1198	18.1	7.2	16.84	26	1.43	-0.40
C	210-4	3-15b	1282	37	1227	18.2	1.0	16.00	33	1.53	
		3-16a	1285	31	1236	18.2	5.8	16.76	18	1.27	-0.35
D	280-2	3-9a	1200	201	981	18.0	1.5	16.18	28	1.43	
		b	1204	191	995	17.8	1.5	16.15	24	1.40	
		3-10a	1211	179	1014	18.1	13	17.11	17	1.23	
		b	1212	176	1018	17.8	5.1	16.71	18	1.25	-0.24
E	254-2	3-11a	1217	167	1032	18.0	1.8	16.24	12	1.08	
		b	1218	164	1036	17.5	1.8	16.24	12	1.08	
		3-12a	1222	157	1047	18.1	9.6	16.98	8.2	0.91	
		b	1227	146	1063	17.9	9.3	16.97	7.8	0.90	-0.24

constant factor from that in the gas phase (other variables fixed) in agreement with our assumption, in an earlier paper,[11] concerning the combination of the equations for the number of bimolecular collisions in the gas phase with the displacement equations of Einstein and von Schumolukowski.

The influence of wave length upon ϕ_E can be studied only after eliminating the effect upon $[O_3^*]$ of corresponding changes in the extinction coefficient, K. It will then be possible to decide whether ϕ, and in consequence the reaction mechanism, changes with λ. In this connection a redetermination of K at each of the wave lengths involved appears desirable, in view of lack

(11) Forbes, Heidt and Brackett, THIS JOURNAL, 55, 595 (1933).

of agreement among existing data. In any case, this phase of the problem could better be discussed after completion of experiments on dry ozone now in progress.

The role of water vapor in the reaction is shown in Table II, which includes all measurements of changes of ϕ with temperature under conditions approximately identical. Ten degree temperature coefficients (last column) appear to be independent of λ, of P, of p_{O_3} and of p_{O_2}. They are, however, equal to the ten-degree temperature coefficient of $\sqrt{p_{H_2O}}$. In other words, ϕ over the temperature interval considered, is proportional to $\sqrt{[H_2O]}$, which suggests that thermal heats of activation involved in the reaction are negligible, as well as the ten degree temperature coefficient of the collision number, as is to be expected from the kinetic theory. This recalls the square root relationship noted by Semenoff[12] in his study of gas explosions, likewise involving oxygen atoms and correlated by him with his theory of branching chains.

Influences of the Partial Pressures.—Some tendency may be noted in Table I for ϕ to

TABLE II

Serial number	λ in mμ	$\bar{P}$	$\bar{p}_{O_3}$	$\bar{p}_{O_2}$	$\bar{T}$	$\bar{p}_{H_2O}$	$\bar{\phi}_E$	$\delta_{100}\phi$
1-1	210-4	1151	527	575	18.2	15.7	27	
1-4		1227	356	866	1.9	5.3	15	1.44
2-3		726	180	528	19.8	17.4	54	
2-4		753	103	645	1.6	5.1	34	1.30
3-5		1090	416	658	19.9	17.4	44	
3-6		1090	394	691	1.4	5.1	22	1.45
3-8		1175	250	903	20.2	17.8	45	1.47
1-2	254-2	1190	450	720	18.0	15.5	7.5	
1-3		1208	400	803	1.8	5.2	5.4	1.21
3-2		950	693	238	20.8	18.4	18	
3-1		927	723	199	1.6	5.1	11	1.34
2-7	280-2	795	46	730	21.3	19.0	17	
2-6		775	60	711	1.4	5.1	8.7	1.41
3-3		1005	588	399	20.0	17.5	33	
3-4		1001	579	417	1.7	5.2	15	1.57
δ_{100} $\sqrt{p_{H_2O}}$	= 1.4						Average	1.4

(12) Semenoff, Physik. Z. der Sowjetunion, 4, 709 (1933).

increase with p_{O_3} and to decrease as p_{O_2} increases. More evident, however, is the tendency for ϕ to decrease as P increases, suggesting that a three-body collision involving regeneration of ozone from oxygen molecules and oxygen atoms is important.

Summary

Carefully purified ozone was photolyzed at $\lambda\lambda$ 280, 254 and 210 mμ in the presence of saturated water vapor at 2 and 20°. Partial pressures of ozone ranged from 10 mm. to one atmosphere. The observed quantum yields, ϕ, determined with numerous precautions, ranged from

1.6 to 130, indicating a chain mechanism. Increase in p_{O_3} raised ϕ rather noticeably while increase in total pressure or in p_{O_2} depressed it.

At any given wave length, ϕ was found to be inversely proportional to a fixed power of light intensity. This power was 0.37 at λ 210 mμ independent of partial pressures, and 0.24 at both $\lambda\lambda$ 254 and 280 mμ in spite of marked differences in absorption coefficients.

Over the temperature interval 2 to 20°, ϕ, adjusted as above, was found proportional to the square root of the concentration of water molecules. The implications of this fact are suggested.

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The Thermodynamics of Aqueous Barium Chloride Solutions from Electromotive Force Measurements[1]

BY EMERSON A. TIPPETTS AND ROY F. NEWTON

The thermodynamic properties of aqueous barium chloride solutions have been determined from e. m. f. measurements on cells of the type Ba (two-phase amalgam) | BaCl$_2$ (m) | Hg$_2$Cl$_2$ | Hg, at 0, 15, 25, 35 and 45°. The activity coefficients calculated by Pearce and Gelbach[2] from e. m. f. data at 25°, and those calculated by Hepburn[3] from vapor pressure measurements at 25°, show large deviations in the more concentrated regions from the accepted values of Lucasse[4] calculated from e. m. f. data at the same temperature. Furthermore, preliminary measurements[5] indicated that the activity coefficient, as a function of temperature for given molality, passes through a maximum at about 20°. These factors all indicated the desirability of a comprehensive study of the thermodynamic behavior of barium chloride in aqueous solution at various temperatures.

Materials and Apparatus

The materials used in this investigation were purified with utmost care. The water used for making the barium chloride solutions was prepared by successive distillation of laboratory distilled water from alkaline permanganate, barium hydroxide and finally from a silica still from which the water was collected in a silica receiver.

The barium chloride was purified by three recrystallizations from water purified as described. A concentrated stock solution was made from this salt, and solutions for the cells were made by diluting this stock solution. These solutions were analyzed by evaporating weighed portions to dryness in a weighing bottle at about 100° and subsequent heating to about 150° for several hours. This is a very satisfactory method for analysis as the salt has no tendency to creep out of the vessel during the evaporation process. The residue is anhydrous and is allowed to cool in the closed weighing bottle in a desiccator before weighing.

The mercury used in making the barium amalgam and calomel was purified by washing with nitric acid and distilling three times under reduced pressure in a current of air.

The calomel was prepared by electrolysis of redistilled hydrochloric acid. Calomel thus prepared was washed, shaken with mercury and allowed to stand for several days before being used.

The barium amalgam was prepared by electrolysis of a saturated solution of barium chloride. Electrolysis was continued until two phases were present, at which time the solution was drawn off and the amalgam washed repeatedly with 95% ethyl alcohol and finally with anhydrous ether until dry. The amalgam was then covered with a layer of light mineral oil and kept in glass-stoppered weighing bottles until used. This layer of oil prevented excessive reaction with oxygen or carbon dioxide of the air. The oil was previously saturated with beeswax, since beeswax was used to coat the amalgam compartment of the cell to prevent creeping of the liquid around the amalgam. It was important that the oil adhering to the amalgam should not dissolve this film of beeswax.

The constant temperature baths were controlled within ±0.01° at 15, 25 and 35°, and within ±0.02° at 0 and

(1) Based upon a thesis submitted by Emerson A. Tippetts to the Faculty of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

(2) Pearce and Gelbach. J. Phys. Chem., 29, 1023 (1925).

(3) Hepburn, J. Chem. Soc., 1284 (1932).

(4) Lucasse, THIS JOURNAL, 47, 743 (1925).

(5) Newton and Tippetts, ibid., 54, 3779 (1932).