THE BOILING-POINTS OF MIXTURES OF CHLORAL AND WATER

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In May, 1899, I did some work at the suggestion of Dr. W. D. Bancroft on the boiling-points of mixtures of chloral and water. The results were rather unsatisfactory owing to the difficulty of obtaining concordant readings on the thermometer. The results are shown in plot No. 1 (curves 1 and 2 are from different settings of the Beckmann).

The difficulty mentioned, led to the adoption of a modification of the apparatus described by Bigelow in the American Chemical Journal of October, 1899. Fig. 1 shows the apparatus used in 1899; Fig. 2 that by which the accompanying results were obtained.

In practice, the current was usually kept at about 2.25 amp., but it was frequently increased during the experiment to 2.5 amp., or even more, without any change in the reading of the thermometer.

The following tables show the effect of varying the current and also the amount of liquid.

35 cc. water			50 cc. water		
Barom.	Temp.	Current	Barom.	Temp.	Current
755.0	5.17°	2.25	755.0	4.96°	2.25
755.0	5.18	2.25	755.0	4.98	2.25
755.0	5.20	2.25	755.0	4.95	2.25
755.0	5.22	2.25	755.0	4.87	2.25
755.0	5.24	2.25	755.0	5.18	2.50
755.0	5.25	2.25	755.0	5.23	2.50
755.0	5.25	2.25	755.0	5.25	2.50
755.0	5.25	2.50	755.0	5.26	2.50
755.0	5.26	2.50	755.0	5.25	2.50
755.0	5.25	2.50	755.0	5.26	2.75
755.0	5.25	2.50	755.0	5.25	2.75

¹ Does not boil.

Fig. 1

Fig. 2

A is a bath of brine.

B is a burette.

C, C, are condensers.

D is an open tube communicating with the air.

E is an asbestos jacket.

F, F, are terminals of the spiral.

S is a platinum spiral of about 15 ohms resistance, connecting with the power circuit.

H is a small watch-glass supported by a platinum wire sealed into it. It protects the thermometer from superheated vapor.

T is a Beckmann thermometer.

N is a test-tube $1\frac{1}{4}$ by 8 in.

The temperature in this, as in all the work, was taken every five minutes. This table shows that the apparatus is all that could be desired. The only disadvantage was that it would not work with over 60 cc liquid.

The break between curves No. 1 and No. 2, plot 2, is due probably to the impurity noted at this point. Curve No. 2, plot 1, probably represents the true conditions at this point. The drop in curve No. 3, plot 2, I am unable to explain. This curve was plotted from Table VII.

TABLE I

Started with 53.4 grams pure chloral and added water from burette.

C = 2.5 amp.

	Barometer	Observed temp.	Temp. cor. to barom. = 755	Burette	Vol. water	Pct. water
*1	758.70	2.18		3.85	0	0
2		2.10		"	0	0
3		2.09		"	0	0
4	758.80	2.06		"	0	0
5		2.05		"	0	0
6		2.05	1.90°	"	0	0
7	758.90	1.44		4.00	0.15	0.28
8		1.50		"	"	"
9		1.48	1.34	"	"	"
10	759.00	1.23		4.10	0.25	0.46
11		1.26	1.10	4.10	"	"
12		1.10		4.20	0.35	0.65
*13	759.00	1.10	0.97	"	"	"
14		1.13		"	"	"
15		0.92		4.30	0.45	0.84
16	758.85	0.98	0.83	"	"	"
17		0.98		"	"	"
18		0.79		4.40	0.55	1.02
19	758.80	0.85	0.70	"	"	"
20		0.85		"	"	"
21	754.00	0.90		4.7	0.55	1.02
22		0.74		"	"	"
23		0.73	0.77	"	"	"
24		0.72		"	"	"
25		0.62		4.8	0.65	1.20
26	754.30	0.67	0.70	"	"	"
27	754.30	0.68		"	"	"
28	754.3	0.50		4.9	0.75	1.39
29	754.35	0.62	0.64	"	"	"
30		0.63		"	"	"
31		0.56		5.0	0.85	1.57
32	754.40	0.35	0.37	"	"	"
33		0.36		"	"	"
34		0.18	0.22	5.2	1.05	1.93
35		0.22		"	"	"

¹ Crystals began to separate on the sides of tube and on stem of the thermometer.² Next day ; melted down crystals and started again.

TABLE I—(Continued.)

	Barometer	Observed temp.	Temp. cor. to barom. = 755	Burette	Vol. water	Pct. water
36	754.60	0.12	0.21	5.4	1.25	2.28
37		0.17		"	"	"
38		0.18		"	"	"
39		0.22		"	"	"
40	754.70	0.12	0.19	5.6	1.45	2.64
41		0.17		"	"	"
42		0.17		"	"	"
*43		0.09		5.8	1.65	3.00
44		0.10	0.12	"	"	"

TABLE II

Started with 55.0 grams $C.Cl_3COH.H_2O$; current = 2.25 amp.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Total vol. water	Pct. water
45	748.0	1.97	2.26°	7.50	5.98	10.87 ¹
*46		2.00		"	"	"
47		2.02		"	"	"
48		2.06		7.7	6.18	11.01
49	748.20	2.06	2.31	"	"	"
50		2.13		7.9	6.38	11.52 ²
51		2.15		"	"	"
52		2.25		8.2	6.68	12.21
53	748.30	2.25	2.50	"	"	" ²
54		2.26		8.5	6.98	12.46
55		2.26		"	"	"
56		2.36		8.8	7.28	12.93
57	748.50	2.38	2.70	"	"	"
58		2.46		9.1	7.58	13.40
59		2.47		"	"	"
60		2.55		9.5	7.98	14.00 ²
61	748.70	2.56	2.80	"	"	"
*62		2.71		10.00	8.48	14.92
63		2.71		"	"	"
64		2.83		10.50	8.98	15.50
65	748.70	2.75	3.00	"	"	"
66		2.77		"	"	"
67		2.90		11.00	9.48	16.20
68		2.89		"	"	"

¹ Crystals separate abundantly.

² Melted crystals.

TABLE II—(Continued).

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Total vol. water	Pot. water
69	748.70	2.98	3.15 (?)	11.55	10.03	16.98
70		2.88		"	"	" ¹
71		2.90		"	"	"
72		2.90		"	"	"
73	748.70	2.97	3.20	12.00	10.48	17.61 ¹
74		2.98		"	"	"
75		3.07	3.30	12.50	10.98	18.30 ²
76		3.07		"	"	"
77	748.80	3.11	3.34	13.00	11.58	19.14
78		3.11		"	"	"
79		3.18	3.40	13.55	12.13	19.87
80		3.18		"	"	"
81	752.70	3.37	3.45	13.55	12.13	19.87 ³
82		3.37		"	"	"
83		3.36		"	"	"
84	752.70	3.41	3.50	14.00	12.58	20.45
85		3.42		"	"	"
86	752.70	3.45	3.52	14.50	13.08	21.07
87		3.44		"	"	"
88		3.47	3.54	15.00	13.58	21.74
89		3.45		"	"	"
*90		3.47	3.54	15.50	14.08	22.35
91		3.45		"	"	"
92	752.70	3.45	3.53	16.00	14.58	22.96
93		3.45		"	"	"
94		3.46	3.54	16.50	15.08	23.56
95		3.46		"	"	"
96		3.45	3.52	17.00	15.58	24.03
97	753.80	3.43		"	"	"
98		3.41	3.46	1.90	"	" ³
99		3.40		"	"	"
*100		3.44	3.49	3.00	16.58	25.27 ⁴
101		3.50	3.54	4.00	17.58	26.40
102	753.80	3.52	3.56	5.00	18.58	27.50
103		3.54	3.58	6.00	19.58	28.54
*104		3.56	3.60	7.00	20.58	29.57

¹ Melted crystals.² Fewer crystals.³ Next day.⁴ No crystals separate.

At this point the liquid was slightly colored (yellow), due partly to the reaction of the chloral hydrate on the rubber stopper. Work was stopped as soon as the color was noticed. There was also too much liquid in the apparatus to continue.

TABLE III

Made up of a solution containing 28.7 pct. water and started again.

C = 2.25 amp.

	Barometer	Observed temp.	Temp. cor. to barom. = 755	Burette	Vol. water	Pct. water
*105	750.70	3.78	3.86°		14.35	28.70
106		3.72			"	"
107		3.71			"	"
108		3.70		7.00	"	"
109	750.70	3.71	3.86	7.50	14.85	29.40
110		3.70	3.85	8.00	15.35	30.10
111		3.71	3.86	8.50	15.85	30.77
112	751.00	3.68	3.83	9.00	16.35	31.44
113		3.70	3.85	9.50	16.85	32.10
114		3.73	3.88	10.00	17.35	32.74
115	751.00	3.79	3.93	10.50	17.85	33.36
116		3.77	"	"	"	"
117		3.80	3.95	11.00	18.35	33.98
118		3.72	3.88	11.50	18.85	34.59
119		3.74	3.88	"	"	"
120		3.78	3.93	12.00	19.35	35.20
121		3.79	3.94	12.50	19.85	35.76
122		3.78	3.93	13.00	20.35	36.74
123	751.00	3.71	3.92	13.50	20.85	36.90
124		3.77	3.92	14.00	21.35	37.45
125		3.76	3.91	14.50	21.85	38.00
126		3.74	3.88	15.00	22.35	38.53
127		3.72	3.86	16.00	22.85	39.06
128		3.70	3.86	16.00	23.35	39.58
*129		3.69	3.84	16.50	23.85	40.08
130	751.00	3.68	3.83	17.00	24.35	40.58
131	751.00	3.68	3.83	17.50	24.85	41.07
132		3.67	3.82	18.00	25.35	41.56
133		3.68	3.83	18.50	25.85	42.03
134		3.67	3.82	19.00	26.35	42.50
135	751.00	3.67	3.82	20.00	27.35	43.41
136		3.67	3.82	"	"	"
137		3.67	3.82	21.00	28.35	44.29
138		3.68	3.83	22.05	29.40	45.23
139		3.69	3.84	23.00	30.35	45.99

¹ The liquid commenced to foam and did so until about 75 pct. water had been added.

TABLE IV

Continued with 48.5 grams of the liquid left at the end of last experiment. (45.99 pct. water) ; C = 2.25 amp.

	Barometer	Observed temp.	Temp. cor. to barom. = 755	Burette	Vól. water	Pct. water
140	751.20	3.70	3.85°	7.1	22.30	45.99
141		3.71		"	"	"
142		3.72	3.87	7.50	22.70	46.42
143		3.72	3.87	8.00	23.20	46.96
144	752.40	3.71	3.85	"	"	" ¹
145		3.76		"	"	"
146		3.76		"	"	"
147		3.76		8.50	23.7	47.50
148	752.40	3.77	3.86	9.00	24.2	48.01
149		3.77	3.86	9.50	24.7	48.52
150		3.77	3.86	10.00	25.2	49.02
151		3.78	3.87	10.50	25.70	49.52
*152	752.40	3.79	3.88	11.00	26.20	50.00
153		3.79	3.88	11.50	26.70	50.47
154		3.80	3.89	12.00	27.2	51.13
155		3.80	3.89	13.00	28.2	52.03
156	752.5	3.80	3.89	14.00	29.2	52.90
157		3.84	3.93	15.00	30.2	53.63
158		3.83	3.92	16.00	31.2	54.54
159		3.82	3.91	17.00	32.2	55.33
160	752.6	3.83	3.92	18.00	33.2	56.08
161		3.85	3.94	19.00	34.2	56.81
162		3.85	3.94	20.00	35.2	57.52

¹ Stood over until next day.

TABLE V

Continued 42.7 grams liquid left from last experiment (57.52 pct.).
C = 2.25 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. water	Pct. water
163	752.70	3.95 }	4.02°	0		57.52
164		3.95 }	"	2.6		"
165		3.96	4.03	3.50	25.46	58.25
166		3.98	4.05	4.50	26.46	59.33
*167		3.99	4.06	5.50	27.46	60.22
168	752.70	4.00	4.07	6.50	28.46	61.07
169		4.02	4.09	7.50	29.46	61.90
170		4.03	4.09	8.50	30.46	62.67
171		4.03	4.09	9.50	31.46	63.43
172		4.05	4.11	10.50	32.46	64.15
173	752.60	4.06	4.12	12.00	33.96	65.18
174		4.06 }	4.13	13.50	35.46	66.16
175		4.06 }	4.13	"	"	66.16
176		4.08	4.15	15.50	37.46	67.37
177		4.09	4.16	17.50	39.46	68.51
178	752.50	4.09	4.16	19.50	41.46	69.56
179		4.09 }	4.16	21.50	43.46	70.55
180		4.10 }	4.17	"	"	"

TABLE VI

Continued with 35.35 grams of the liquid from last experiment.

C = 2.25 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. water	Pct. water
181	752.50	4.10	4.17°			70.55
182		4.11		3.00		"
183		4.11	4.18	4.00	25.94	71.36
184		4.15	4.22	5.00	26.94	72.13
185		4.15	"	"	"	"
186	752.80	4.15	4.22	6.00	27.94	72.86
187		3.95		7.00	28.94	73.54
188		4.15		"	"	"
189		4.01	4.10	"	"	"
190		4.05		"	"	"
191	752.70	4.05		"	"	"
192		4.02	4.12	8.00	29.94	74.20
193		4.03		"	"	"
194		4.04	4.12	9.00	30.94	74.84
195		4.06		"	"	"
196	752.70	4.08	4.15	10.00	31.94	75.42
197		4.08		"	"	"
198		4.09	4.17	11.00	32.94	75.98
199		4.11		"	"	"
200		4.30	4.37	12.00	33.94	76.53
201	752.70	4.31		"	"	"
202		4.33	4.40	13.00	34.94	77.05
203		4.33	4.40	13.00	34.94	77.05 ¹

¹ Liquid still foams, but not so badly.

TABLE VII

Started again with 35 grams distilled water and added from burette
a solution of chloral hydrate in water (48.50 pct. chloral).

Sp. gr. 1.3. C = 2.25 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. chloral	Pct. water
*204	756.70	5.32	5.25°			100.0
205		5.32	"			"
206		5.33	5.26			"
207		5.33	"	7.55		"
208		5.28	5.22	7.80	0.16	99.55
209	757.00	5.29	"	"	"	"
210		5.23	5.16	8.50	0.59	98.37
211		5.19	5.12	9.00	0.92	97.50
212		5.11	5.04	9.50	1.32	96.48
*213		5.09	5.00	10.50	1.85	95.20
214		5.04	4.97	11.50	2.60	93.57
*215	757.00	3.96	3.90	12.50	3.10	92.53
216		3.96	"	"	"	"
217		3.89	3.82	13.50	3.75	91.24
218		3.84	3.77	14.50	4.38	90.07
219		3.76	3.70	16.00	5.33	88.40
220		3.68	3.60	18.00	6.56	86.50
221	757.00	3.67	"	"	"	"
222		3.62	3.55	20.00	7.81	84.75
*223		3.62	"	"	"	"

¹ Liquid began to foam at this point and foaming increased with addition of chloral.

TABLE VIII

Started with 32.4 grams water, and added pure chloral from a burette. Sp. gr. chloral 1.51 at 20° C. C = 2.5 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. chloral	Pct. water
*224	757.25	5.35	5.27°	17.55	0	100
225	"	5.36		"	0	100
226	"	5.33	5.22	17.75	0.302	99.08
227	757.25	5.33		"	"	"
228	"	5.29	5.21	18.00	0.68	97.95
229	757.25	5.29		"	"	"
230	"	5.24	5.17	18.20	0.98	97.06
231	"	5.25		"	"	"
232	"	5.22		"	"	"
233	757.25	5.24		18.20	"	"
234	"	5.25	5.17	"	"	"
235	"	5.25		"	"	"
236	"	5.22	5.14	18.40	1.283	96.19
237	757.25	5.22		"	"	"
238	"	5.17	5.10	18.60	1.58	95.34
239	"	5.17		"	"	"
240	757.20	5.10	5.02	18.90	2.04	94.60
241	"	5.09		"	"	"
242	"	5.04	4.97	19.20	2.50	92.76
243	757.10	5.04		"	"	"
244	"	4.96	4.89	19.50	2.90	91.77
245	"	4.96		"	"	"
*246	"	4.87	4.80	20.00	3.70	89.75
247	757.0	4.87		"	"	"
248	"	4.77	4.70	20.50	4.45	87.92
249	"	4.78		"	"	"
250	"	4.96	4.62	21.00	5.21	86.15
251	"	4.96		"	"	"
252	"	4.63	4.56	21.50	5.96	84.46
253	756.90	4.63		"	"	"
254	"	4.55	4.49	22.00	6.72	82.83
255	"	4.53		22.00	"	"
256	756.70	4.45	4.40	22.50	7.47	81.25
257	"	4.46		"	"	"
*258	"	4.39	4.32	23.00	8.23	79.75
259	756.50	4.35		"	"	"

TABLE IX

Started with 30 cc. water + 5 cc. pure chloral (20.11 pct. chloral),
and added pure chloral from a burette. C = 2.50 amperes.

	Barometer	Temp. observed	Temp. cor. to barom. = 755	Burette	Wt. chloral	Pct. water
260	754.5	4.33	4.39°	13.40	7.55	79.89
261		4.35		"	"	79.89
262		4.37		"	"	"
263		4.37		"	"	"
264	754.70	4.37	4.28	"	"	"
265		4.26		14.40	9.06	76.81
266		4.28		"	"	"
267		4.23		14.90	9.81	75.35
268	754.80	4.24	4.23	"	"	"
269		4.22		15.40	10.57	73.95
270		4.22		"	"	"
271		4.19		15.90	11.31	72.60
272	754.80	4.19	4.20	15.90	11.31	72.60
273		4.19		16.40	12.08	71.29
274		4.19		"	"	"
275		4.17		16.90	12.83	70.03
276	755.0	4.18	4.18	"	"	"

Note. — Only the readings marked with a star (*) are plotted, the individual determinations falling too close together to be well represented on this scale.