

Thesis.

The Specific Heat of Calcium Chloride
Brines
at Low Temperatures.

Trénée du Pont X '97

Bernard Barrow, X '97.

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In all tests hitherto made on refrigerating plants, one of the chief sources of error has been due to insufficient information concerning the true specific heat of the brine used as the intermediate cooling agent. This is especially true of calcium chloride brines, and as the latter are much used at the present time in preference to ordinary salt brines, the need of suitable investigation of their properties is at once apparent.

The values now in use by most refrigerating companies (those to be found in the "Compend of Mechanical Refrigeration", and which are given in the latter part of this thesis) were determined between temperature limits much higher than those used in practice. Now it is known that the specific heat of calcium chloride solutions changes with the temperature although the character of this variation is not accurately

known. To determine this property of calcium chloride brines at the low temperatures used in practice was the object of this thesis.

The work as laid out included the determination of the specific heat between varying temperature limits of as many strengths of brine as the time should allow. Incidentally the freezing point of these brines was also to be determined.

The first brine experimented upon was of a specific gravity 1.210, made by dissolving ordinary anhydrous calcium chloride in water from the Boston water mains. Brine of this specific gravity is the one most employed by refrigerating companies. An analysis of this brine made by Mr. Root showed the following composition: The CaCl₂ was found to be pure by analysis.

sp. gr.	1.21	22.54%	1.207	22.49	1.206	22.47
	1.205	22.45	1.166	21.73	1.164	21.69

The freezing point of this brine was first taken and found to be -24.8 . A series of tests,

ten in number, was then made in pairs, changing the lower temperature limit by intervals of five degrees, from -20° to 0° , and endeavoring to keep the upper limit approximately constant. The next brine taken up was of the lowest specific gravity used in practice, 1.164, and was examined in the same way, although as the freezing point was naturally much higher (-16°), the number of tests in this series was necessarily fewer than in the first.

The method employed in determining the specific heat was in short the following: - Brine, cooled to the desired temperature was allowed to flow into a vessel ("inner calorimeter" in the diagram) surrounded by warm water contained in a second vessel (the "outer calorimeter") and the temperatures equalized. Then, knowing the weight of water in the "outer calorimeter," the water equivalent of inner and outer calorimeters, the weight of brine let into the inner calorimeter, the corrections to be applied, and assuming the

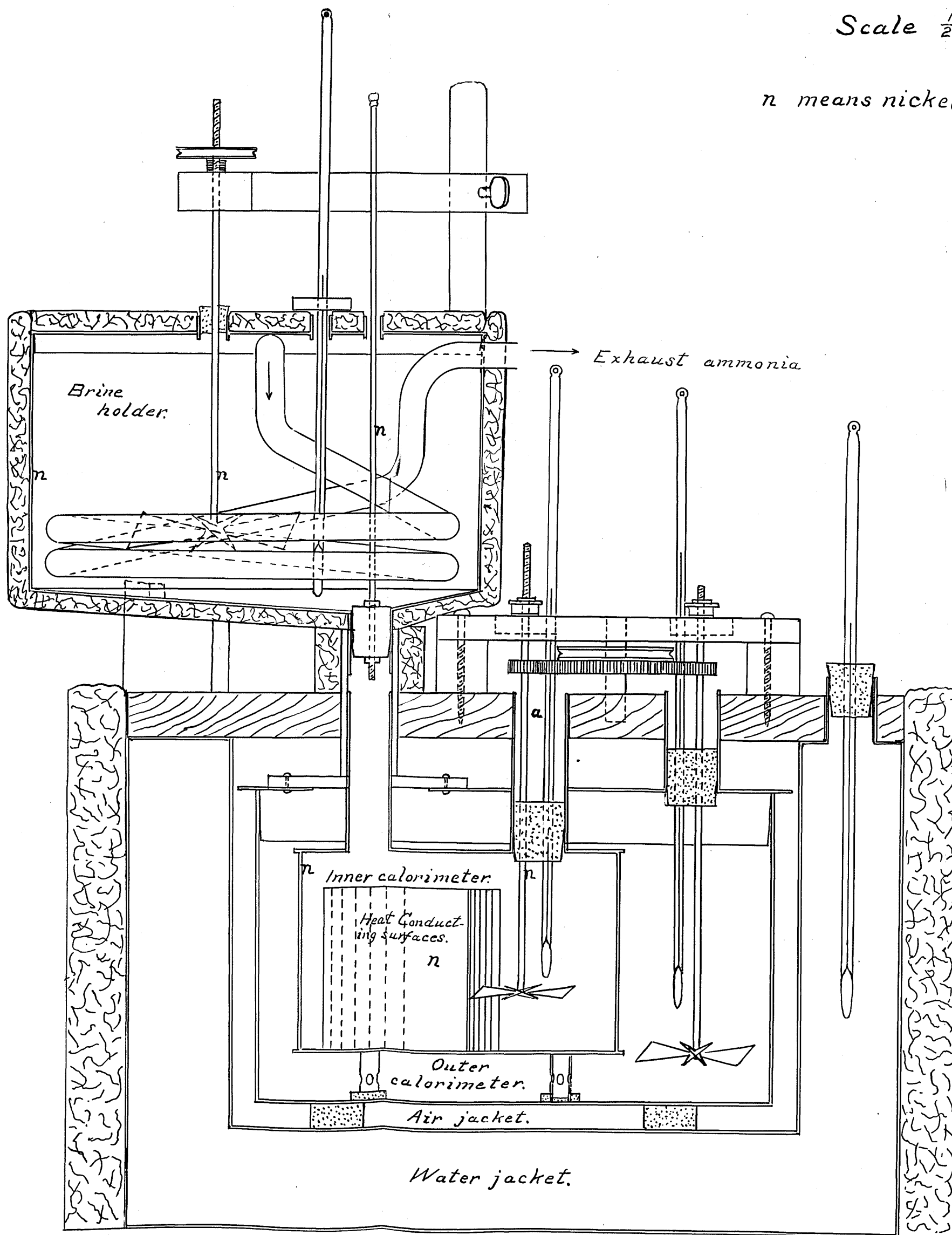
specific heat of water to be that determined by Bartoli and Stracciati (to be found in Landolt and Bornsteins Tables), the mean specific heat of the brine between the observed temperature limits could be calculated.

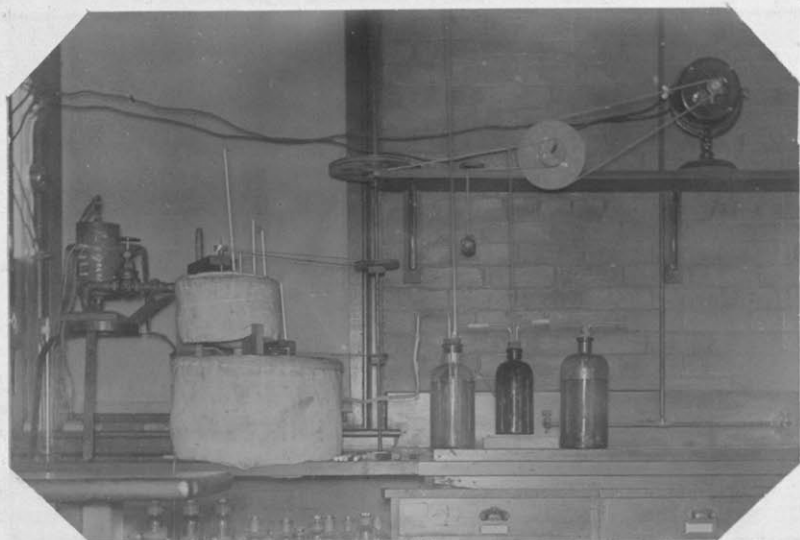
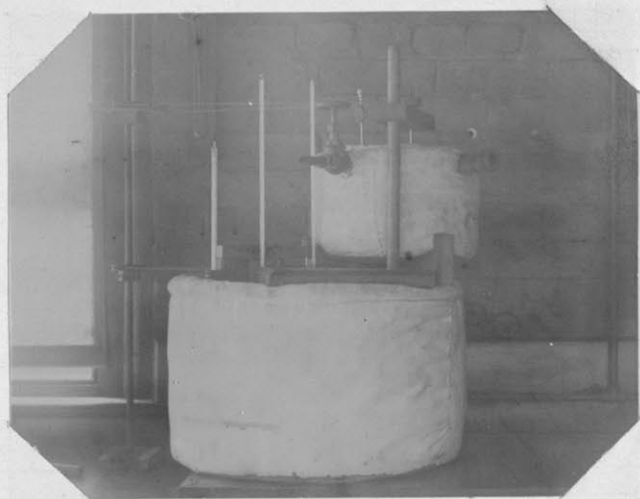
The apparatus employed was that used by Messrs Dorman and Fowle, Course X '93 in their thesis work of that year, with some modifications. Its arrangement may be readily seen from the accompanying section and photographs. It will be evident from the plan that the distance between the cooling vessel for the brine and the calorimeter vessels is comparatively small (about 1 1/2 inches). This change was made to reduce the possible error introduced by gain of heat in passing from one vessel to the other, which was mentioned by the former workers on this subject as being the chief source of inaccuracy. Also profiting from their experience, the system of stirrers was arranged to give a higher rate of speed (about 400 r.p.m). This brought about a

BRINE CALORIMETER

Scale $\frac{1}{2}'' = 1''$

n means nickel-plated brass.





rapid interchange of heat between the two fluids as well as a uniform temperature throughout their masses. It would naturally be supposed that such a rate of speed would cause an appreciable generation of heat due to the violent agitation thus produced, and in fact this was found to be the case in the outer calorimeter. In the inner calorimeter however the blades of the stirrers were placed so nearly horizontal that this heating was less than 0.01 during a fifteen minute test. The truth of these two statements can be verified from the accompanying tests.

The first of these was made Apr. 1, 1897, under the following conditions: Both inner and outer calorimeters were filled with water and the radiation per minute determined, the stirring being done at a slow speed. Then the stirrers were run at their usual speed (400 r.p.m.) and the change in temperature per minute again determined. Finally the power was shut off

and the stirring being done slowly by hand as before, a third set of temperature readings were taken which gave the final radiation per minute. Calling these changes in temperature per minute v_1 , v_2 , and v_3 respectively, it was found that $v_1 = .00125$, $v_2 = .00473$ and $v_3 = 0$.

This would seem to indicate that heat was being generated by one or both of the two stirrers, and it was desired to know whether the one in the inner calorimeter was responsible for any part of it. Accordingly a second test was run under slightly different conditions.

The inner calorimeter was filled with brine but the outer one was left empty and the test made as before. In this case however, $v_1 = .00695$, $v_2 = .00500$ and $v_3 = .00615$, which would seem to point to the fact that no appreciable generation of heat took place in the inner calorimeter.

Since all heat given to the outer calorimeter is taken into account in applying the cooling correction, here there is evidently no source of

error.

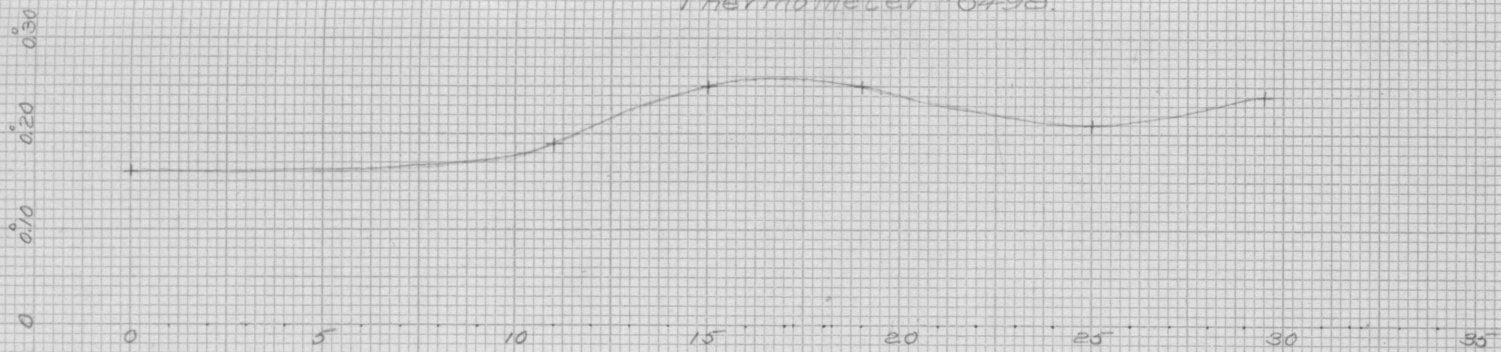
It will be seen from the diagram that an elaborate system of jacketing has been employed consisting of an air jacket, water jacket and hair felt lagging. The purpose of this was to prevent the inner part of the apparatus from being susceptible to outside temperature changes. That this object was attained was shown by the even rate of cooling before and after the different tests.

The evaporation of liquid ammonia served as the means of cooling the brine, the ammonia being recovered by absorption over water. The arrangement of absorption apparatus, ammonia reservoir etc may be seen from the accompanying section and photographs.

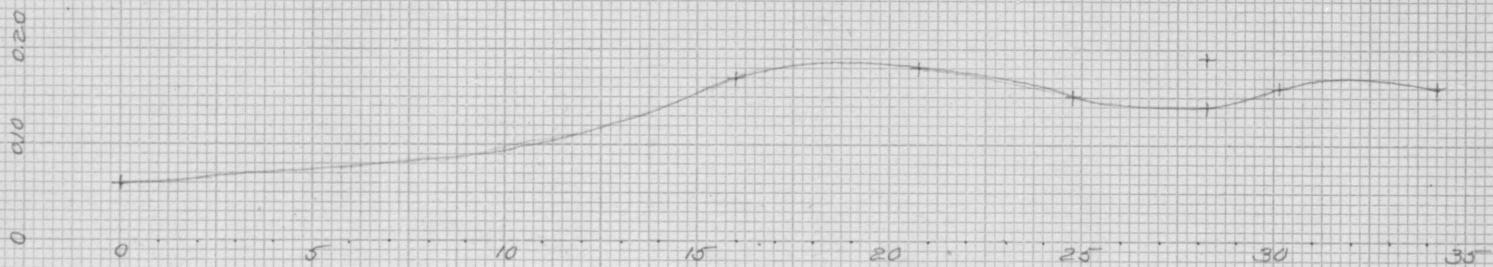
Among the influences which affect the accuracy of specific heat determinations in general, perhaps the most important is that of thermometers. Where the range of temperature is only about five degrees in amount, it is evident that

even a slight inaccuracy in this respect would tend to influence results strongly. Hence careful attention was given this point and all irregularities of bore, lag in reading etc determined as closely as possible with the means at our command. Four thermometers have been used #6498, and #6497, #8794 and #9354. The first two have a range from -5° to $+50^{\circ}$ and are graduated to tenths of degrees. These were compared at intervals of 5° with a standard thermometer kindly loaned by the Physical Department, and curves plotted which are here given. The second two thermometers have a range from -35° to $+50^{\circ}$ and are graduated to fifths of degrees. Of these #8794 was used in the inner calorimeter for temperatures above zero, and so a curve of corrections was made as above between 0° and 35° . Thermometer #9354 was that placed in the brine holder and hence was used for temperatures varying from 0° to -35° . This thermometer could not be

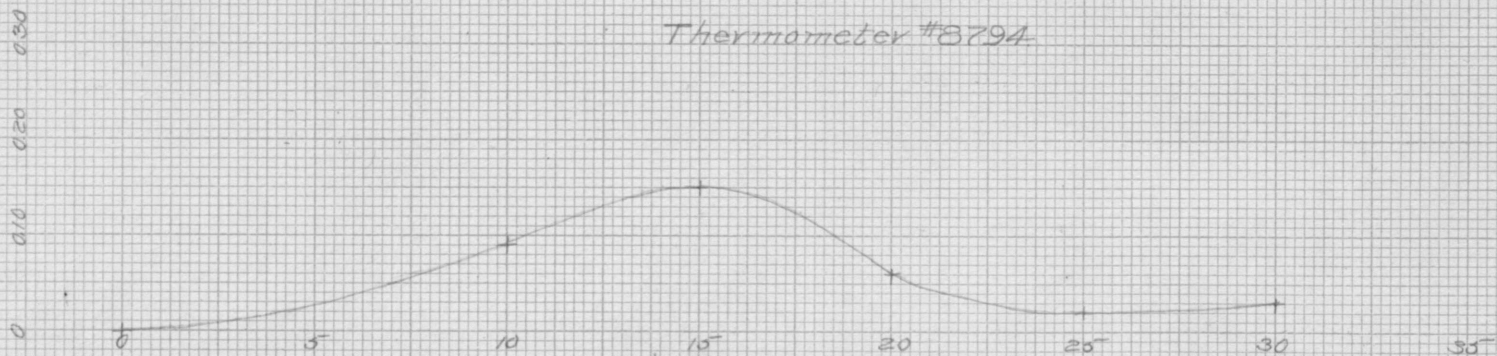
Thermometer #6498.



Thermometer #6497.



Thermometer #8794.



Corrections are subtractive

calibrated by any ordinary means, and we were unable to compare it with a standard at the low temperatures required. As with the others a lag ice reading was taken, and we were forced to be content with this as the only criterion of the accuracy of the thermometer, until an apparently unfortunate combination of circumstances caused its bulb to be broken. By breaking off both ends it was then possible to calibrate the bore of the tube below 0° , and it was found to be without any marked irregularities. The error from this source is therefore slight.

Method of Calculation of Results: The specific heats were calculated from the data of each experiment according to the method used by Prof Holman, of course based on the principle that the gain of heat of the brine let in is equal to the loss of heat of the water in the outer calorimeter, but also making a correction for such heat as is taken from or given to, the outer

calorimeter by external matter.

For convenience the following list of abbreviations used is here given.

t = temperature in outer calorimeter = a variable

t_1 = value of t just before the brine is let in

t_2 = " " " when the temperatures in inner and outer calorimeters have equalized

t_3 = temperature of brine at its entrance.

$t_4 = t_2$ = temperature of brine when the temperatures in inner and outer calorimeters have equalized.

t_j = temperature of the water jacket

s = mean specific heat of water between t_1 and t_2

W_0 = weight of water in outer calorimeter.

W_I = " " brine let in.

W_c = water equivalent of inner calorimeter, outer calorimeter and accompanying stirrers.

$$W = sW_0 + W_c$$

v = rate of cooling at temperature t .

v_1 = rate of cooling in outer calorimeter just before entrance of brine.

v_2 = rate of cooling in outer calorimeter just after temperatures in inner and outer calorimeters have equalized.

θ = value of t when $v = 0$

ρ = mean rate of cooling

$$\tan \alpha = \frac{v_1 - v_2}{t_1 - t_2}$$

T = time required for t_1 to become equal to t_2 .

T = algebraical mean of values of t between t_1 and t_2

Now if there were no interchange of heat between the calorimeters and external matter, the specific heat would be:

$$\text{Sp. Ht} = \frac{W(t_1 - t_2)}{W_1(t_4 - t_3)} \quad \text{but there is a}$$

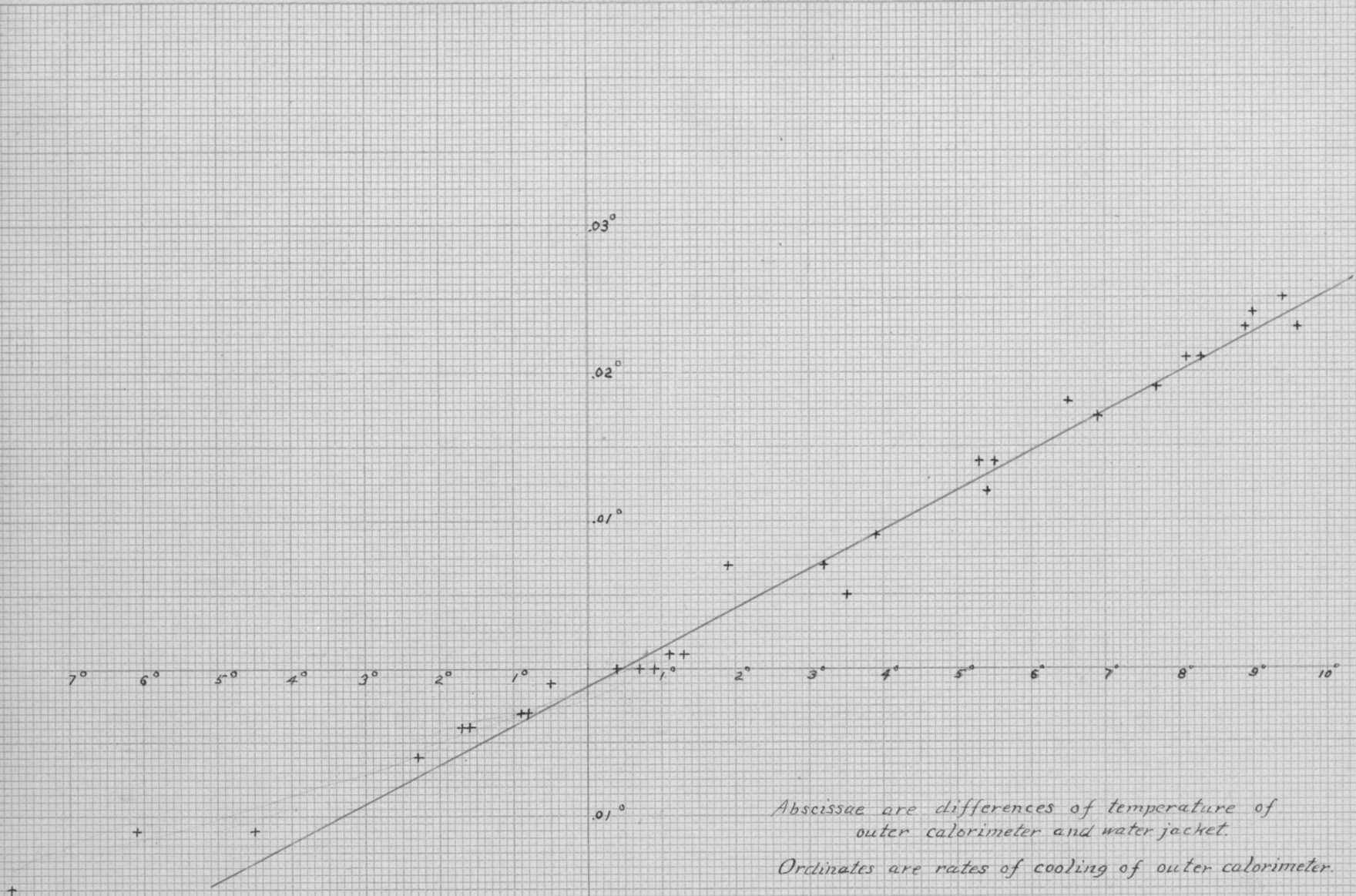
slight change of temperature of the water in the outer calorimeter due to the violent stirring as well as to convection currents in the air jacket, and this change of temperature is called the

cooling correction. This cooling correction may be computed as follows: Since the temperature of water jacket in any one experiment remains practically constant, the assumption is made that the rate of cooling of the water in the outer calorimeter, exclusive of the cooling due to the cold brine in the inner calorimeter, is proportional to the temperature of the outer calorimeter. That the assumption is justified is shown by the accompanying plot in which the abscissae represent differences in temperature of the outer calorimeter and the water jacket, and the ordinates represent the corresponding rates of cooling, obtained respectively from the different values of t_1 , t_2 and t_3 , v_1 and v_2 in the series of experiments.

The points will be seen to lie approximately along a straight line.

Now since v varies with t , and since, when $v_1 = v$, $t = t_1$, and also when $v_1 = v_2$, $t_1 = t_2$ we have

$$\frac{t-t_1}{t_1-t_2} = \frac{v-v_1}{v_1-v_2} \quad \text{or} \quad \frac{t-t_2}{t_2-t_1} = \frac{v-v_2}{v_2-v_1}$$



Abscissae are differences of temperature of outer calorimeter and water jacket.

Ordinates are rates of cooling of outer calorimeter.

and $v = v_1 + (t - t_1) \tan \alpha$ or

$$v = v_2 + (t - t_2) \tan \alpha$$

substituting $v = 0$

$$t = \theta = t_1 - \frac{v_1}{\tan \alpha} \quad \text{or} \quad t = \theta = t_2 - \frac{v_2}{\tan \alpha}$$

Substituting θ for $t_1 - \frac{v_1}{\tan \alpha}$ in $v = v_1 + (t - t_1) \tan \alpha$

$$v = (t - \theta) \tan \alpha$$

$$p = (T - \theta) \tan \alpha$$

and $Ip = \text{cooling correction.}$

T may be found with sufficient accuracy by taking the arithmetical mean of the values of t at two minute intervals throughout the test.

On the following pages the data and results of tests are given in tabulated form. Tests previous to those given were made but it was thought unnecessary to quote them in full, since the results obtained were largely in error.

However, the cause of this inaccuracy might be mentioned. In the first two blank tests the results obtained were much too low, and this was found to be due to leakage past the valve in the holder. The next two blank tests gave results considerably too high (1.007 and 1.011 respectively). This was due to the escape of water in passing from holder to inner calorimeter, along the seam of the neck of the latter. This was not discovered however until four tests on brine had been made which were of course discarded. All the following tests were made after the two above mentioned defects had been remedied.

Blank Test on Water. - May 5, 1897.

Time.	Thermom. #6498.	Thermom. #8794.	Remarks.
2-48-00	33.58		Water jacket = 20.40
-50-	33.50		
51	33.47		
52	33.43		
53	33.38		
54	33.35		
55	33.31		
56	33.27		
57	33.24		Water jacket = 20.50
58	33.20		
59	33.16		
3-00-00	33.13		
01	33.09		
02	33.05		
03	33.02		
04	32.98		
05	32.96		Water jacket = 20.64
-30	31.25		At 3-05-00 - Ice -
06	29.70	10.10	Water let in, temp = 0.16

Time.	Thermom. #6498	Thermom. #8794.	Remarks.
3-06-30	28.40	13.30	
07	27.50	16.60	
30	26.75	18.60	
08	26.20	19.50	
30	25.80	20.70	
09	25.45	21.55	
30	25.21	22.10	
10	25.04	22.70	
30	24.90	23.05	Water jacket = 20.67
11	24.79	23.40	
30	24.71	23.60	
12	24.65	23.74	
30	24.60	23.88	
13	24.56	23.96	
30	24.53	24.04	
14	24.51	24.12	
30	24.49	24.16	
15	24.48	24.18	
30	24.47	24.20	

Time.	Thermom. #6498.	Thermom. #8794.	Remarks.
3-16-00	24.47	24.22	
30	24.46	24.24	
17	24.45	24.24	
30	24.45	24.26	
18	24.44	24.26	
30	24.44	24.26	
19	24.43	24.24	
30	24.43	24.24	Water jacket = 20.72
20	24.43	24.22	
30	24.42	24.22	
21	24.42	24.22	
30	24.41	24.22	
22	24.41	24.22	
30	24.40	24.20	
23	24.40	24.20	Temperatures equalized.
30	24.40	24.20	
24	24.40	24.20	
30	24.40	24.20	
25	24.39	24.20	Water jacket = 20.74

Time.	Thermom. #6498.	Thermom. #8794.	Remarks.
3-25-30	24.39	24.20	
26	24.39	24.20	
30	24.39	24.20	
27	24.39	24.20	
30	24.38	24.20	Water jacket = 20.76
28	24.38	24.20	
30	24.38	24.20	
29	24.38	24.20	
30	24.38	24.18	
30	24.37	24.18	
30	24.37	24.18	
31	24.37	24.18	Water jacket = 20.77
30	24.37	24.18	
32	24.37	24.18	
30	24.37	24.18	
33	24.37	24.18	
30	24.37	24.18	

Blank Test on Water.

May 5, 1897.

$$\underline{W}_0 = 3990 \quad \underline{W}_c = 159 \quad \underline{W} = 4153$$

$$\underline{W}_T = 1439 \quad T = 18$$

$$t_1 = 32.71 \quad t_2 = 24.19 \quad t_1 - t_2 = 8.52$$

$$t_3 = 0.16 \quad t_4 = 24.19 \quad t_5 = 20.70$$

$$S = 1.001$$

$$V_1 = .0365 \quad V_2 = .0050 \quad V_1 - V_2 = .0315$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00372$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 22.90 \quad \theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 22.90$$

Time	t	Time	t	Time	t
3-05	32.71	3-13	24.35	3-21	24.21
-07	27.28	15	24.27	-23	<u>24.19</u>
09	25.24	17	24.24	Mean	25.20 = T
11	24.58	19	24.22		

$$\rho = (T - \theta) \tan \alpha = 0.08556$$

$$\text{Cooling Correction} = T \rho = 0.15$$

$$t_1 - t_2(\text{cor}) = 8.37$$

$$t_4 - t_3(\text{cor}) = 24.18$$

$$\text{Sp. Ht.} = \frac{W(t_1 - t_2)}{W_1(t_4 - t_3)} = 0.999$$

Mean Sp. Ht. between 0.2 and 24.2

$$= 0.999$$

True Value as Determined by Bertoli & Staccioni = 1.002

Blank Test on Water.

May 5, 1897.

$$W_0 = 3995 \text{ gr.} \quad W_c = 159 \text{ grm.} \quad W = 4158 \text{ grm}$$

$$W_1 = 1455 \text{ grm} \quad T = 16 \text{ min.}$$

$$t_1 = 30.60$$

$$t_2 = 22.67$$

$$t_1 - t_2 = 7.93$$

$$t_3 = 0.20$$

$$t_4 = 22.67$$

$$t_3 = 21.38$$

$$S = 1.001$$

$$V_1 = .02500$$

$$V_2 = .00111$$

$$V_1 - V_2 = .02389$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00301$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 22.29$$

$$\theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 22.29$$

Time	t	Time	t
4-35	30.60	4-45	22.70
-37	25.49	-47	22.68
-39	23.62	-49	22.67
-41	22.99	-51	<u>22.67</u>
-43	22.78	Mean =	23.70 = T

$$\rho = (T - \theta) \tan \alpha = .004375$$

$$\text{Cooling Correction} = T\rho = +0.07$$

$$t_1 - t_2 (\text{corr}) = 7.86 \quad t_4 - t_3 (\text{corr}) = 22.54$$

$$\text{Sp. Ht.} = \frac{W(t_1 - t_2) (\text{corr.})}{W_T(t_4 - t_3 (\text{corr.}))} = 0.996$$

Mean Sp. Ht. between 0.2 and 22.7

$$= 0.996$$

True Value as Determined by

$$\text{Bartoli and Stracciati} = 1.002$$

Test on CaCl_2 Brine

$$Sf S = 1.210$$

May 7, 1897.

$$W_0 = 3996 \quad W_c = 159 \quad W = 4155$$

$$W_I = 1658 \quad T = 20 \text{ min.}$$

$$t_1 = 29.36 \quad t_2 = 20.48 \quad t_1 - t_2 = 8.88$$

$$t_3 = -10.70 \quad t_4 = 20.48 \quad t_5 = 20.25$$

$$S = 1.000$$

$$v_1 = .0233 \quad v_2 = 0 \quad v_1 - v_2 = .0233$$

$$\tan \alpha = .00263$$

$$\theta_1 = t_1 - \frac{v_1}{\tan \alpha} = 20.48 \quad \theta_2 = t_2 - \frac{v_2}{\tan \alpha} = 20.48$$

Time	t	Time	t	Time	t
9-27	29.36	9-35	20.61	9-43	20.47
-29	24.19	-37	20.52	9-45	20.97
-31	21.77	-39	20.47	-47	<u>20.48</u>
-33	20.92	-41	20.47	Mean =	21.48 = T

$$\rho = (T - \theta) \tan \alpha = .00263$$

$$\text{Cooling Correction} = T\rho = .05$$

$$t_1 - t_2 \text{ cor} = 8.83$$

$$t_4 - t_3 \text{ cor} = 31.23$$

$$\text{Sp. Ht.} = \frac{W_1 (t_1 - t_2 \text{ cor})}{W_2 (t_4 - t_3 \text{ cor})} = 0.709$$

Mean Sp. Ht between -10.7 and 20.5

$$= 0.709$$

Test on CaCl_2 Brine.

Sp. G. = 1.210

May 10, 1897

$$W_0 = 3996 \quad W_c = 159 \quad W = 4155$$

$$W_T = 1609 \quad T = 14 \text{ min}$$

$$t_1 = 28.46 \quad t_2 = 21.15 \quad t_1 - t_2 = 7.31$$

$$t_3 = -5.20 \quad t_4 = 21.15 \quad t_5 = 20.30$$

$$S = 1.000$$

$$V_1 = .0200 \quad V_2 = 0 \quad V_1 - V_2 = .0200$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00240$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} =$$

$$\theta_2 = t_2 - \frac{V_2}{\tan \alpha} =$$

Time	t	Time	t
2-24-30	28.46	2-34-30	21.17
26-30	23.89	36-30	21.16
28-30	22.05	38-30	<u>21.15</u>
30-30	21.42	Mean =	22.24 = T
32-30	21.23		

$$\rho = (T - \theta) \tan \alpha = .00262$$

$$\text{Cooling Correction} = T\rho = .04$$

$$t_1 - t_2 \text{ cor} = 8.27$$

$$t_4 - t_3 \text{ cor} = 26.39$$

$$\text{Sp. Ht} = \frac{W(t_1 - t_2 \text{ cor})}{W_I(t_4 - t_3 \text{ cor})} = 0.711$$

Mean Sp. Ht between -5.2 and 21.2

$$= 0.711$$

Test on CaCl_2 Brine

Sp. G. = 1.210

May 7, 1897

$$W_0 = 3995 \quad W_c = 159 \quad W = 415$$

$$W_f = 1609 \quad T = 14 \text{ min}$$

$$t_1 = 29.12 \quad t_2 = 20.48 \quad t_1 - t_2 = 8.64$$

$$t_3 = -10.84 \quad t_4 = 20.48 \quad t_7 = 20.63$$

$$S = 1.000$$

$$V_1 = .0243 \quad V_2 = 0 \quad V_1 - V_2 = .0243$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00278$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 20.48$$

$$\theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 20.48$$

Time	t	Time	t
11-09	29.12	11-18	20.50
11	23.69	-21	20.49
13	21.57	-23	<u>20.48</u>
15	20.84	Mean =	21.78 = T
17	20.59		

$$\rho = (T - \theta) \tan \alpha = .00361$$

$$\text{Cooling Correction} = T\rho = .05$$

$$t_1 - t_2 \text{ cor} = 8.59$$

$$t_4 - t_3 \text{ cor} = 31.37$$

$$\text{Sp. Ht} = \frac{W(t_1 - t_2 \text{ cor})}{W_s(t_4 - t_3 \text{ cor})} = 0.707$$

Mean Sp. Ht between -10.8 and 20.5

$$= 0.707$$

Test on Ca Cl₂ Brine

Sp. G. = 1.210

May 6, 1897

$$\bar{W}_0 = 3997 \quad \bar{W}_c = 159 \quad \bar{W} = 4156$$

$$\bar{W}_I = 1700 \quad T = 20 \text{ min.}$$

$$t_1 = 28.42 \quad t_2 = 18.85 \quad t_1 - t_2 = 9.57$$

$$t_3 = -14.54 \quad t_4 = 18.85 \quad t_j = 21.20$$

$$S = 1.000$$

$$v_1 = .01867 \quad v_2 = -.00583 \quad v_1 - v_2 = .02450$$

$$\tan \alpha = \frac{v_1 - v_2}{t_1 - t_2} = .00256$$

$$\theta_1 = t_1 - \frac{v_1}{\tan \alpha} = 21.13 \quad \theta_2 = t_2 - \frac{v_2}{\tan \alpha} = 21.13$$

Time	t	Time	t	Time	t
12-36	26.78	12-44	18.88	12-52	18.82
-38	21.67	-46	18.82	-54	18.83
-40	19.76	-48	18.82	-56	<u>18.85</u>
-42	19.12	-50	18.82	Mean	= 19.64 = T

$$\rho = (T - \theta) / \tan \alpha = -0.00384$$

$$\text{Cooling Correction} = -0.07$$

$$t_1 - t_2 (\text{cor}) = 9.64 \qquad t_4 - t_3 (\text{cor}) = 33.32$$

$$\text{Sp. Ht.} = \frac{W(t_1 - t_2 \text{ cor})}{W_I(t_4 - t_3 \text{ cor})} = 0.707$$

Mean Sp. Ht. between -14.5 and 18.8

$$= 0.707$$

Test on CaCl_2 Brine

Sp. G. = 1.207

May 11, 1897.

$$W_0 = 4000 \quad W_c = 159 \quad W = 4159$$

$$W_T = 1465 \quad T = 14 \text{ min}$$

$$t_1 = 26.68 \quad t_2 = 21.18 \quad t_1 - t_2 = 5.50$$

$$t_3 = -0.52 \quad t_4 = 21.18 \quad t_5 = 20.60$$

$$S = 1.000$$

$$v_1 = .01667 \quad v_2 = .00083 \quad v_1 - v_2 = .01584$$

$$\tan \alpha = \frac{v_1 - v_2}{t_1 - t_2} = .00288$$

$$\theta_1 = t_1 - \frac{v_1}{\tan \alpha} = 20.89 \quad \theta_2 = t_2 - \frac{v_2}{\tan \alpha} = 20.89$$

Time	t	Time	t
9-45	26.68	9-55	21.19
-47	23.18	-57	21.18
-49	21.77	-59	<u>21.18</u>
-51	21.37	Mean =	21.98 = T
-53	21.22		

$$\rho = (T - \theta) \tan \alpha = .00230$$

$$\text{Cooling Correction} = T\rho = .03$$

$$t_1 - t_2 (\text{corr}) = 5.47$$

$$t_4 - t_3 (\text{corr}) = 21.73$$

$$\text{Sp. HT} = \frac{W(t_1 - t_2 \text{ corr})}{W_2(t_4 - t_3 \text{ corr})} = 0.714$$

Mean Sp. HT between .5 and 21.2

$$= .714$$

Test on Calc₂ Brine.

Sp. G. = 1.206

May 11, 1897.

$$W_o = 3999 \quad W_c = 159 \quad W = 4158$$

$$W_I = 1470 \quad T = 14$$

$$t_1 = 25.58 \quad t_2 = 20.29 \quad t_1 - t_2 = 5.29$$

$$t_3 = -.40 \quad t_4 = 20.29 \quad t_j = 20.29$$

$$S = 1.000$$

$$V_1 = .0123 \quad V_2 = 0 \quad V_1 - V_2 = .0123$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .0023$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 20.29 \quad \theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 20.29$$

Time	t	Time	t
11-50	25.58	12-00	20.31
-52	22.28	-02	20.29
-54	20.93	-04	<u>20.29</u>
-56	20.48	Mean	21.08 = T
-58	20.35		

$$\rho = (T - \theta) \tan \alpha = .00182$$

$$\text{Cooling Correction} = T \rho = .03$$

$$t_1 - t_2(\text{cor}) = 5.26$$

$$t_4 - t_3(\text{cor}) = 20.72$$

$$\text{Sp. H.t.} = \frac{W(t_1 - t_2 \text{ cor})}{W_I(t_4 - t_3 \text{ cor})} = 0.718$$

Mean Sp. H.t. between -1.4 and 20.3

$$= 0.718$$

Test on CaCl_2 Brine

Sp. G. = 1.166

May 12, 1897

$$W_0 = 3994 \quad W_c = 159 \quad W = 4157$$

$$W_T = 1433 \quad T = 16$$

$$t_1 = 30.65 \quad t_2 = 22.24 \quad t_1 - t_2 = 8.41$$

$$t_3 = -10.68 \quad t_4 = 22.24 \quad t_5 = 23.2$$

$$S = 1.001$$

$$V_1 = .0210 \quad V_2 = -.0031 \quad V_1 - V_2 = .0241$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00287$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 23.33 \quad \theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 23.32$$

Time	t	Time	t
2-36	30.65	2-46	22.25
2-38	24.79	2-48	22.24
-40	23.03	2-50	22.24
-42	22.47	2-52	22.24
-44	22.30	Mean =	23.22 ± 1

$$\rho = (T - \theta) \tan \alpha = .00316$$

$$\text{Cooling correction} = T\rho = -.05$$

$$t_1 - t_2 (\text{cor}) = 8.46$$

$$t_4 - t_3 (\text{cor}) = 32.87$$

$$\text{Sp. HT} = \frac{W (t_1 - t_2 \text{ cor})}{W_r (t_4 - t_3 \text{ cor})} = 0.747$$

Mean Sp. HT between -10.7 and 22.2

$$= 0.747$$

Test on CaCl_2 Brine.

$$Sf. S. = 1.210$$

May 6, 1897.

$$W_o = 3996 \quad W_c = 159 \quad W = 4155$$

$$W_I = 1744 \quad T = 20 \text{ min.}$$

$$t_1 = 28.89 \quad t_2 = 18.85 \quad t_1 - t_2 = 10.04$$

$$t_3 = -15.12 \quad t_4 = 18.85 \quad t_5 = 20.85$$

$$S = 1.000$$

$$V_1 = .0233 \quad V_2 = -.00571 \quad V_1 - V_2 = .02901$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00289$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 20.83 \quad \theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 20.83$$

Time	t	Time	t	Time	t
10-34	27.77	10-42	18.90	10-50	18.83
36	21.92	-44	18.83	-52	18.84
38	19.86	-46	18.81	-54	<u>18.85</u>
40	19.13	-48	18.82	Mean	= 19.72 = T

$$\rho = (T - \theta) \tan \alpha = 0.321$$

$$\text{Cooling correction} = T\rho = -0.06$$

$$t_1 - t_2 (\text{cor}) = 10.10 \qquad t_4 - t_3 (\text{cor}) = 33.91$$

$$\text{Sp. HT.} = \frac{W(t_1 - t_2 \text{ cor})}{W_r(t_4 - t_3 \text{ cor})} = 0.710$$

Mean Sp. HT. between -15.1° and 18.9°

$$= 0.710$$

Test on CaCl_2 Brine.

Sp. G. = 1.210

May 4, 1897.

$$W_o = 4005 \quad W_c = 159 \quad W = 4164$$

$$W_I = 1835 \quad T = 18.617$$

$$t_1 = 21.70 \quad t_2 = 12.02 \quad t_1 - t_2 = 9.68$$

$$t_3 = -20.16 \quad t_4 = 12.02 \quad t_1 = 19.93$$

$$S = 1.000$$

$$V_1 = .00417 \quad V_2 = -.01500 \quad V_1 - V_2 = .01917$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00196$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 19.66 \quad \theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 19.67$$

Time	t	Time	t	Time	t
1-28	21.70	1-36	12.09	1-44	12.01
-30	15.95	-38	11.99	-46	<u>12.02</u>
-32	13.32	-40	11.99	Mean	= 13.12 = T
-34	12.38	-42	12.00		

$$\rho = (T - \theta) \tan \alpha = -0.1278$$

$$\text{Cooling correction} = T\rho = -0.23$$

$$t_1 - t_2(\text{corr}) = 9.91 \quad t_4 - t_3(\text{corr}) = 31.95$$

$$\text{Sp. Ht.} = \frac{W_2(t_1 - t_2 \text{ corr})}{W_1(t_4 - t_3 \text{ corr})} = 0.704$$

Mean Sp. Ht. between -20.2 and 12.0

$$= 0.704.$$

Test on CaCl_2 Brine

Sp. G = 1.208

May 10, 1897.

$$W_0 = 3998 \quad W_c = 159 \quad W = 4157$$

$$W_T = 1578 \quad T = 14 \text{ min.}$$

$$t_1 = 28.04 \quad t_2 = 20.85 \quad t_1 - t_2 = 7.19$$

$$t_3 = -5.60 \quad t_4 = 20.85 \quad t_5 = 21.65$$

$$S = 1.400$$

$$V_1 = .019 \quad V_2 = 0 \quad V_1 - V_2 = .019$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00264$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 20.85 = \theta_2$$

Time	t	Time	t
3-51	28.04	3-61	20.87
53	23.99	4-03	20.85
55	21.68	4-05	<u>20.85</u>
57	21.12	Mean =	21.91 = T
59	20.93		

$$\rho = (T - \theta) \tan \alpha = .00280$$

$$\text{Cooling Correction} = T\rho = .04$$

$$t_1 - t_2 \text{ cor} = 7.15$$

$$t_4 - t_3 \text{ (cor)} = 26.99$$

$$\text{Sp. Ht} = \frac{W(t_1 - t_2 \text{ cor})}{W_I(t_4 - t_3 \text{ cor})} = 0.711$$

Mean Sp. Ht. between -0.6° and 20.9°

$$= 0.711$$

Test on CaCl_2 Brine

Sp. G. = 1.210

May 4, 1897.

$$W_o = 4006 \quad W_c = 159 \quad W = 4165$$

$$W_I = 1790 \quad T = 16 \text{ min}$$

$$t_1 = 24.00 \quad t_2 = 13.94 \quad t_1 - t_2 = 10.06$$

$$t_3 = -20.08 \quad t_4 = 13.94 \quad t_7 = 20.36$$

$$S = 1.000$$

$$V_1 = .00875 \quad V_2 = -.01133 \quad V_1 - V_2 = .02008$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00200$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 19.62 \quad \theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 19.61$$

Time	t	Time	t
3-39	24.00	3-49	13.96
-41	17.14	-51	13.94
-43	15.05	-53	13.93
-45	14.33	-55	<u>13.94</u>
-47	14.01	Mean =	15.17 = \bar{T}

$$\rho = (T - \theta) \tan \alpha = -0.0890$$

$$\text{Cooling correction} = T\rho = -.14$$

$$t_1 - t_2(\text{cor}) = 10.20$$

$$t_4 - t_3(\text{cor}) = 33.88$$

$$\text{Sp. Ht} = \frac{W(t_1 - t_2 \text{ cor})}{W_I(t_4 - t_3 \text{ cor})} = 0.701$$

Mean Sp. Ht. between -20.1 and 13.9

$$= 0.701$$

Test on CaCl_2 Brine.

Sp. G. = 1.166

May 13, 1897.

$$W_0 = 3995 \quad W_c = 159 \quad W = 4154$$

$$W_I = 1445 \quad T = 20 \text{ min.}$$

$$t_1 = 28.51 \quad t_2 = 22.46 \quad t_1 - t_2 = 6.07$$

$$t_3 = -0.58 \quad t_4 = 22.46 \quad t_7 = 23.4$$

$$S = 1.000$$

$$v_1 = .0140 \quad v_2 = -.00272 \quad v_1 - v_2 = .0167$$

$$\tan \alpha = \frac{v_1 - v_2}{t_1 - t_2} = .00275$$

$$\theta_1 = t_1 - \frac{v_1}{\tan \alpha} = 23.42 \quad \theta_2 = t_2 - \frac{v_2}{\tan \alpha} = 23.44$$

Time	t	Time	t	Time	t
11-37	28.51	11-45	22.58	11-53	22.52
-39	24.65	-47	22.54	-55	22.52
-41	23.23	-49	22.52	-57	<u>22.53</u>
-43	22.73	-51	22.52	Mean	$= 23.13 = \bar{T}$

$$\rho = (T - \theta) \tan \alpha = -0.008$$

$$\text{Cooling correction} = T\rho = -0.01$$

$$t_1 - t_2 (\text{corr}) = 6.08$$

$$t_4 - t_3 (\text{corr}) = 22.03$$

$$\text{Sp. Ht} = \frac{W (t_1 - t_2 \text{ corr})}{W_I (t_4 - t_3 \text{ corr})} = 0.759$$

Mean Sp. Ht between -0.6 and 22.5

$$= 0.759$$

Test on CaCl_2 Brine

Sp. G. = 1.166

May 13, 1897

$$W_0 = 3995 \quad W_c = 10^{-9} \quad W = 4154$$

$$W_T = 1446 \quad T = 10$$

$$t_1 = 29.32 \quad t_2 = 21.11 \quad t_1 - t_2 = 8.21$$

$$t_3 = -10.58 \quad t_4 = 21.11 \quad t_5 = 23.0$$

$$S = 1.000$$

$$r_1 = .0181 \quad r_2 = -.0036 \quad r_1 - r_2 = .0217$$

$$\tan \alpha = \frac{r_1 - r_2}{t_1 - t_2} = .00264$$

$$\theta_1 = t_1 - \frac{r_1}{\tan \alpha} = 22.46 \quad \theta_2 = t_2 - \frac{r_2}{\tan \alpha} = 22.47$$

Time	t	Time	t
9-37	29.32	9-47	21.13
-39	24.29	-49	21.11
-41	22.13	-51	21.11
-43	21.40	-53	21.11
-45	21.18	Mean =	22.20 = T

$$\rho = (T - \theta) \tan \alpha = -0.0007$$

$$\text{Cooling Correction} = T\rho = -0.01$$

$$t_1 - t_2 (\text{cm}) = 8.22$$

$$t_4 - t_3 (\text{cm}) = 31.68$$

$$\text{Sp. Ht} = \frac{W(t_1 - t_2 \text{ cm})}{W_I(t_4 - t_3 \text{ cm})} = 0.745$$

Mean Sp. Ht between -10.6 and 21.1

$$= 0.745$$

Test on CaCl_2 Brine.

Sp. G. = 1.166

May 14, 1897.

$$W_o = 3994 \quad W_c = 159 \quad W = 4157$$

$$W_f = 1344 \quad T = 14 \text{ min}$$

$$t_1 = 31.06 \quad t_2 = 23.94 \quad t_1 - t_2 = 7.12$$

$$t_3 = -4.88 \quad t_4 = 23.94 \quad t_j = 23.8$$

$$S = 1.001$$

$$v_1 = .0207 \quad v_2 = 0 \quad v_1 - v_2 = .0207$$

$$\tan \alpha = \frac{v_1 - v_2}{t_1 - t_2} = .00297$$

$$\theta_1 = t_1 - \frac{v_1}{\tan \alpha} = 23.94 = \theta_2$$

Time	t	Time	t
9-30	31.06	9-40	23.98
32	26.56	42	23.94
34	24.75	44	<u>23.94</u>
36	24.20	Mean =	24.99 = T
38	24.03		

$$\rho = (T - \theta) \tan \alpha = .00312$$

$$\text{Cooling correction} = T\rho = .04$$

$$t_1 - t_2 \text{ cor} = 7.08$$

$$t_4 - t_3 \text{ cor} = 28.83$$

$$\text{Sp. Ht} = \frac{W(t_1 - t_2 \text{ cor})}{W_2(t_4 - t_3 \text{ cor})} = 0.760$$

Mean Sp. Ht. between -4.9 and 23.9

$$= 0.760$$

Test on CaCl_2 Brine

51

Sp. G. = 1.164

May 14, 1897.

$W_o = 3996$ $W_c = 159$ $W = 4159$

$W_I = 1314$ $T = 16 \text{ min.}$

$t_1 = 29.78$ $t_2 = 23.57$ $t_1 - t_2 = 6.21$

$t_3 = -2.06$ $t_4 = 23.57$ $t_5 = 23.8$

$S = 1.001$

$V_1 = .0167$ $V_2 = -.0009$ $V_1 - V_2 = .0176$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00284$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 23.90 \quad \theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 23.89$$

Time	t	Time	t
10-57	29.78	11-07	23.60
59	26.36	09	23.59
11-01	24.50	11	23.58
03	23.89	13	<u>23.57</u>
05	23.66	Mean =	24.48 = T

$$\rho = (T - \theta) \tan \alpha = .00168$$

$$\text{Cooling Correction} = T\rho = 0.03$$

$$t_1 - t_2(\text{cor}) = 6.18$$

$$t_4 - t_3(\text{cor}) = 25.66$$

$$\text{Sp. Ht.} = \frac{W(t_1 - t_2 \text{ cor})}{W_I(t_4 - t_3 \text{ cor})} = 0.762$$

Mean Sp. Ht between -2.1 and 23.6

$$= 0.762$$

Test on CaCl_2 Brine

Sp. G. = 1.164

May 13, 1897.

$$W_0 = 3995 \quad W_c = 159 \quad W = 4154$$

$$W_I = 1412 \quad T = 18 \text{ min.}$$

$$t_1 = 29.53 \quad t_2 = 23.44 \quad t_1 - t_2 = 6.09$$

$$t_3 = -0.18 \quad t_4 = 23.44 \quad t_j = 24.0$$

$$S = 1.000$$

$$V_1 = .0139 \quad V_2 = -.0011 \quad V_1 - V_2 = .0150$$

$$\tan \alpha = \frac{V_1 - V_2}{t_1 - t_2} = .00247$$

$$\theta_1 = t_1 - \frac{V_1}{\tan \alpha} = 23.90 \quad \theta_2 = t_2 - \frac{V_2}{\tan \alpha} = 23.89$$

Time	t	Time	t
2-43	29.53	2-53	23.45
45	25.36	-55	23.44
47	24.15	-57	23.44
49	23.64	-59	23.44
51	23.49	3-01	<u>23.44</u> Mean = 24.10 = \bar{T}

$$\rho = (T - \theta) \tan \alpha = .00052$$

$$\text{Cooling correction} = T\rho = .01$$

$$t_1 - t_2(\text{cor}) = 3.10$$

$$t_4 - t_3(\text{cor}) = 23.61$$

$$\text{Sp. Ht} = \frac{W(t_1 - t_2 \text{ cor})}{W_I(t_4 - t_3 \text{ cor})} = 0.760$$

Mean Sp. Ht. between -0.2 and 23.4

$$= 0.760$$

Discussion of Results:- For convenience the results of tests made have been summarized and are given in the table on the next page.

It is interesting to compare these results with those ordinarily in use. The following table is quoted from the "Compend of Mechanical Refrigeration":

Specific Gravity of Brine.	Specific Heat.	Freezing Point.
1.009	0.966	-0.5
1.043	.964	-2.5
1.087	.896	-5.6
1.134	.860	-9.6
1.166	.840*	-13.5*
1.182	.834	-14.8
1.210	.810*	-18.4*
1.234	.790	-22.1

* interpolated.

It is at once apparent that these values differ widely from the results given on the next page, this difference being anywhere from

Summary of Tests on Brine.

Date of Test.	Sp. G. of Brine.	Temperature Limits		Mean Sp. Heat.
		t_4	t_3	
May 4.	1.210	-20°.2	12°.0	0.704
" "	"	-20°.1	13°.9	0.701
" 6	"	-15°.1	18°.8	0.710
" "	"	-14°.5	18°.8	0.707
" 7	"	-10°.7	20°.5	0.709
" "	"	-10°.8	20°.5	0.707
" 10	"	-5°.2	21°.1	0.711
" "	"	-5°.6	20°.8	0.711
" 11	1.207	-0°.5	21°.2	0.714
" "	1.206	-0°.4	20°.3	0.718
" 12	1.166	-10°.7	22°.2	0.747
" 13	"	-10°.6	21°.1	0.745
" "	"	-0°.6	22°.5	0.759
" "	"	-0°.2	23°.4	0.760
" 14	1.164	-4°.9	23°.9	0.760
" "	"	-2°.1	23°.6	0.762

10 to 15%. This discrepancy can be accounted for either by a diminution of the specific heat at our lower temperatures, or by the presence of impurities in the brines used in determining the ordinarily used values, or by both. The second of these two causes could hardly account for all of this difference, although the high freezing point given in their table would seem to indicate the presence of a not inconsiderable amount of impurities.

It was thought that results of interest might be obtained by calculating from the data at hand the mean specific heat between 0° and -5° , -5° and -10° etc. This has been done and the following are the values obtained for a brine of specific gravity 1.210.

Temp. Limits	Specific Heat.
0 and -5°	.681
-5 " -10	.693
-10 " -15	.715

This would seem to indicate that the value

of the specific heat is a minimum at or near 0° .

In closing, the apparent sources of error might be mentioned. These are first - a gain loss of heat by the brine in passing from holder to calorimeter, second, inaccuracy in temperature readings and thermometers, third, possible conduction of heat through the exposed neck of the inner calorimeter (marked a in section).

From the blank tests quoted it would seem that the constant error of the apparatus is about .4 of 1%, while the mean deviation of results is apparently about 1 of 1%.