

A Study of the Absolute Entropy  
of the Chloride Ion in Concentrated Solutions  
as Determined by Thermocell Measurements

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by

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## INTRODUCTION

This research was undertaken as a corollary to the work done by E.S. McKee (1) at Johns Hopkins University in 1950 with the purpose of "determining the entropy of a single aqueous ion. In doing so, we wished to elucidate the theory of aqueous solutions, i.e. hydration and other processes taking place, particularly in concentrated solutions."

Others who have done similar work on aqueous ions, using the thermocell (or thermogalvanic cell), and whose values are used in this thesis, are Goodrich, Goyan, Morse, Preston and Young<sup>(2)</sup>; Bernhardt and Crockford (3); and Crockford and Hall (4). Still others have done work which is less accurate, or less important to this thesis, and are not listed here.

Almost no results have been reported for very concentrated solutions, i.e. 1m to saturation, and that was the specific aim of this research. Processes occurring in concentrated aqueous solutions of ionic compounds are of great importance, particularly solvation of ions, and, with regard to a theoretical or empirical modification of the Debye and Huckel theory, hydration and ion-pair formation. The study of the function of one thermodynamic quantity of a single aqueous ion with respect to concentration and type of cation should prove useful.

## II DISCUSSION

### A. Determination of the Entropy

Other thermodynamic quantities, i.e. heat and free energy, are always given in reference to some arbitrary standard state. Entropy, however, can ordinarily be determined as an absolute value from the third law of thermodynamics. The third law states that the entropy of a pure crystalline compound is zero at the absolute zero of temperature. From the definition of entropy,  $dS = dq/T$ , it is thus possible to determine the absolute entropy of any substance at a given temperature. The entropy of an ionic compound is found, however, only as the total entropy of its ionic species, whether in solution or not. The entropy of a single ion cannot be found by third law measurements alone, so that aqueous ionic entropies are also usually based on an arbitrary standard state.

The use of the thermocell enables us to determine the absolute entropy of a single aqueous ion. Briefly, the thermocell is a galvanic cell, consisting of two identical half cells, and deriving its E.M.F. from the fact that the two half cells are at different temperatures. If one half cell is at temperature  $T$  and the other at  $T + \Delta T$ , then  $\Delta E$ , and, thus,  $\Delta E/\Delta T$ , can be determined for any particular half equation.

From a variation of the Gibbs-Helmholtz equation we have, at constant pressure:

$$-\Delta S = d(\Delta F)/dT.$$

From  $\Delta F = -nFE$  we get,

$$-\Delta S = d(-nFE)/dT$$

or  $S = nF dE/dT.$

If we assume that  $dE/dT = \Delta E/\Delta T$  (this was proven experimentally by McKee and others for differences in temperature up to 10°C), we then have a method for finding the entropy change for a given half equation.

In order to find the entropy of a single ion by this method, a half cell must be used in which only one ion is involved. The particular one used in this research was the calomel cell:



$$\therefore \frac{1}{2}S_{\text{Hg}_2\text{Cl}_2} + S_e - S_{\text{Hg}} - S_{\text{Cl}^-} = nF \Delta E/\Delta T. \quad (1)$$

The entropies of mercury and mercurous chloride are known from third law measurements. The entropy of the electron has been calculated and found to be negligible. Thus, the partial molal entropy of the chloride ion in a particular solution can be determined.

However, there is another term added to equation (1), due to the entropy of transfer of ions across the temperature gradient. McKee treats this as a liquid junction potential and proves it to be negli-

gible, at least within the limits of this work.

#### B. Change of the Entropy

Now that we have a method for determining the absolute entropy of the chloride ion in any aqueous solution at constant temperature, it is important to discuss the factors which may influence the entropy. These factors may be classified as:

(1) the concentration,

(2) the Debye-Huckel contribution (this is the mathematical theory worked out for the entropy term arising from the energy of interaction of an ion with its ion-atmosphere),

(3) the extent of hydration, and

(4) ion-pair formation.

If ions behaved as ideal particles with no interaction among themselves or between them and water molecules, the change in entropy with concentration would simply be:

$$\Delta S = R \ln C_1/C_2.$$

In very dilute solutions this relation should hold true since there should be no change in the other three factors upon further dilution. In the range 0.001 m to 0.1 m the Debye effect becomes appreciable, while for the alkali halides at least, the last two factors would be negligible to 0.1 m (except for lithium). Therefore, this equation would be expected

to hold true in concentrations of 0.1 m or less:

$$\Delta S = R \ln C_1/C_2 + \Delta S_D,$$

where  $\Delta S_D$  is the change in entropy due to ion-ion atmosphere interaction, and can be calculated from the theoretical equation.

In going from concentrated to dilute solutions,  $R \ln C_1/C_2$  is positive and  $\Delta S_D$  is negative (but small at low concentrations), and, thus, the theoretical plot of entropy against log of molality is not quite straight but curves up slightly as the solution gets more concentrated.

At concentrations greater than 0.1 m, the situation is not so simple. No quantitative formula for the change of entropy of an ion with concentration exists, but some qualitative remarks may be made.

Hydration and ion-pair formation become important. In dilute solutions hydration is complete, and the ions are so far apart that the chance of ion-pair formation is negligible, so that neither has any effect on entropy.

In more concentrated solutions, the ions with their waters of hydration begin to crowd each other. It is then possible for one ion to strongly affect the hydration of another ion, distorting the water layer by its own electrical field, or by its own water molecules crowding the waters of hydration around another ion, destroying in part the simple hydration of more dilute solutions. Since entropy is, in a



sense, a measure of the randomness, or disorderliness, of a system, i.e. the greater the disorder, the higher the entropy, this effect might be expected to cause an increase in entropy in more concentrated solutions. However, this interaction of ions on the water molecules of other ions might bring about a sort of quasi-crystalline structure, due to hydrogen bonding, which would then be more orderly and a decrease in entropy might be expected.

I In more concentrated solutions an ion might penetrate the water layer of an oppositely charged ion, and we would have the formation of an ion-pair. This would lead to a decrease in entropy, since this would be the first step in the formation of the orderly crystalline structure of the solid salt. The experimental evidence should indicate which of these factors is most important in a particular solution.

## EXPERIMENTAL PROCEDURE

### A. Apparatus

The tool used to measure  $\Delta E$  was a Leeds and Northrop type K-2 potentiometer which can be read to 0.1 microvolt<sup>on the low range</sup>. This precision was necessary since the potential difference to be measured ranged from 1 to 5 millivolts. The galvanometer used was a Leeds and Northrop 2420 with enclosed lamp and scale and a sensitivity of 0.04 microamperes/mm. The high resistance of dilute solutions made them difficult to measure with this galvanometer sensitivity, but for the concentrated solutions used it was perfectly satisfactory. An unsaturated Weston standard cell, just recently standardized by the National Bureau of Standards, was used. The source of constant E.M.F. was one cell of an automobile battery.

The cells (see Fig. 1) were each constructed of two 20mm by 150mm test tubes connected about 2 inches from the top by a piece of 8 or 10 mm glass tubing. The electrodes(see Fig. 1) by which ~~XXXXXXXX~~<sup>contact</sup> was made with the mercury of the cells were made by sealing a small piece of platinum wire in the end of a piece of glass tubing, which was then partially filled with mercury and the copper lead from the potentiometer inserted into the mercury. This introduced a thermocouple effect which is due to the two mercury-copper contacts at different temperatures.

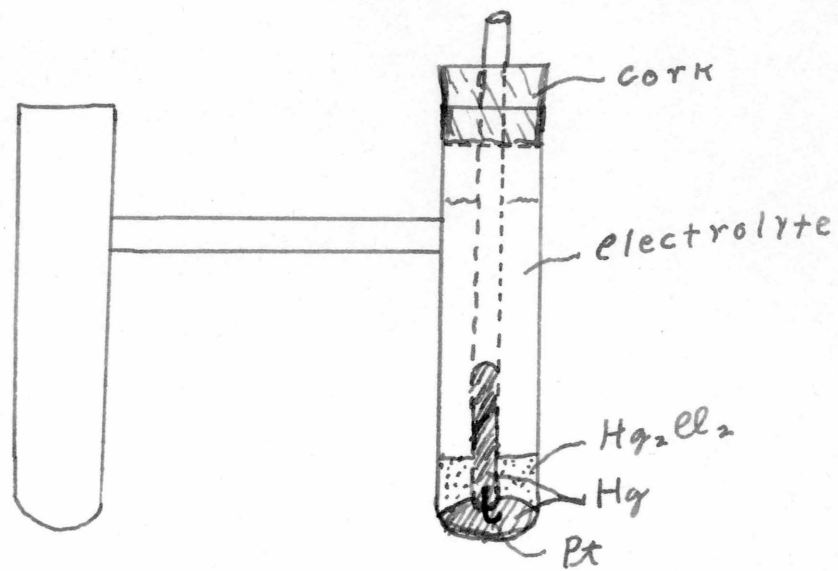


Fig. 1. - A Typical Cell

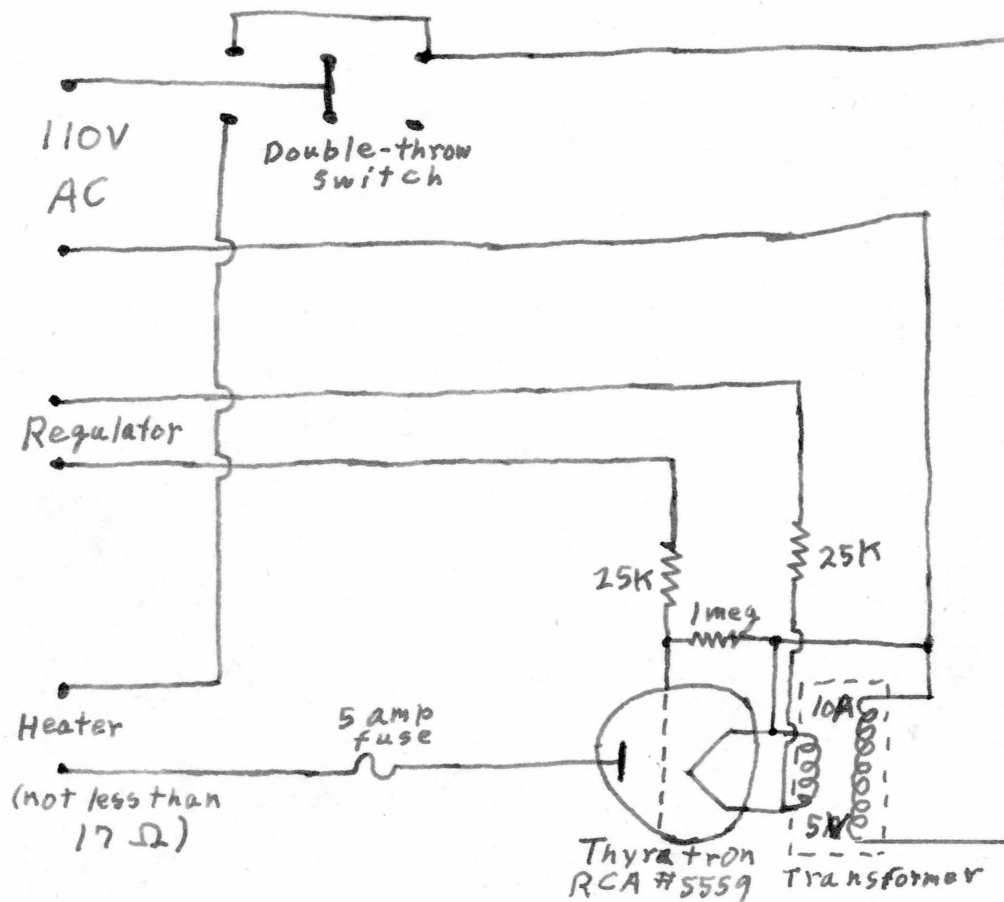


Fig. 2 - The Control Circuit

However, McKee and others have proved this to be negligible, also. The cells were closed, and the electrodes held in place, by means of corks.

The two constant temperature baths were constructed from an insulated rectangular metal box, divided into two compartments by a wooden partition, which had slots cut in it to hold the cells. Water running through copper coils was used for cooling. Mechanical propellor stirrers were used. The heaters were bare coils of nichrome wire wound on ordinary porcelain heater bases. Kerosene was used as the liquid of the baths, in order that the heaters would not have to be insulated, thereby eliminating heat lag.

The temperature of each bath was controlled by means of a Sargent mercury thermoregulator which was connected to the heater through an electronic relay circuit. These circuits (see Fig. 2) were constructed especially for this research, using mercury vapor thyratron tubes.

The temperatures of the baths were measured by differential thermometers, one Beckmann and one Philadelphia. These thermometers were calibrated with each other, and with a Bureau of Standards thermometer.

#### B. Chemicals

Instrument mercury was used for the cells and the electrodes. Baker's C.P. KCl, Merck's reagent grade NaCl, and Mallinkrodt's analytical reagent

grade calomel were used in the cells. The only available LiCl, however, was an ordinary ~~unpurified~~ <sup>of unknown purity</sup> grade.

The solutions were made up by diluting a weighed amount of the dried salt in a volumetric flask with distilled water which had been saturated with calomel.

A cell was prepared (see Fig. 1) by first adding enough mercury to completely cover the platinum electrode lead; adding on top of this a paste made of mercurous chloride, the electrolyte to be used, and a little mercury; and, finally, carefully filling it with the solution. It was not necessary to use oxygen-free cells.

## EXPERIMENTAL RESULTS

In order to get reproducible results, it was necessary to reverse the cells in the two baths and average the values obtained. There was sometimes great deviation between the two values, but the average remained fairly constant, as is shown by the tables on the following pages. The difference was probably due primarily to some peculiarity in the contacts of the platinum-mercury electrodes, the effect of which is cancelled when the cell is reversed and the results averaged. At one point, one cell was failing to give a constant value, but when its electrodes were replaced by a pair of electrodes from a cell which had been giving very good readings, a constant value was obtained immediately.

When first made up, the cells would not generally give good readings, but if allowed to "age" for several days to two weeks, a satisfactory average could usually be obtained.

The actual procedure of measuring was to take a series of readings on each cell, reverse the cells, wait about an hour for equilibrium to be reestablished, and then take another series of readings. The temperature of each bath was determined each time the E.M.F. was being measured. Since there was a slight temperature gradient within the baths, the thermometers were placed next to the cells being read. Approximately

sixty measurements which gave a constant value were made for each cell.

$\Delta T$  ranged from about 5.5°C to 8°C, while the average temperature ranged between 25°C and 26°C. This variation had a negligible effect on entropy, since the change of entropy with temperature is less than 0.1 e.u. per degree, as shown by McKee and others.

The cells actually measured were 4f, 3f, 2f, 1f, 0.1f, 0.01f KCl; 5f, 4f, 3f, 2f, NaCl; and 6f LiCl. The values for the dilute 0.1f and 0.01f KCl solutions check surprisingly well with those of other workers, considering the fact that the resistance of the electrolyte made the reading almost an estimate. For example, the value obtained by other workers for 0.01666 molal KCl is 27.25 e.u. The result from this research is 27.2 e.u. The accuracy of the other results can be seen from the graph (see Fig. 3).

All the measurements made on one cell are included in the following tables in order to illustrate the type of data collected. The values for  $\bar{S}_{Cl^-}$  only are reported for the other cells.

TABLE I

Cell #1

3.000f = 3.314m KCl

#	$\Delta E$ (mv)	T	$T + \Delta T$	$\Delta T$
1	3.45	20.86	28.38	7.52
2	3.45	.61	.34	.73
3	3.47	.64	.40	.76
4	3.51	.89	.31	.42
5	3.54	.81	.38	.57
6	3.55	.73	.33	.60
7	3.55	.73	.30	.57
8	3.55	.67	.38	.71
9	3.55	.65	.34	.69
10	3.55	.59	.38	.79
11	3.56	.60	.35	.75
12	3.66	.74	.36	.62
13	3.65	.95	.38	.43
14	3.64	.80	.46	.66
15	<u>3.60</u>	<u>.79</u>	<u>.38</u>	<u>.59</u>
Av.	3.55	20.74	28.36	7.62

$\Delta S = 11.0$        $\bar{S}_{Cl^-} = 15.9$

Electrodes reversed

16	3.49	21.36	28.90	7.54
17	3.46	.36	.85	.49
18	3.47	.36	.82	.46
19	3.48	.37	.90	.53
20	3.48	.38	.92	.54
21	3.46	.37	.88	.51



TABLE I

(cont'd)

#	$\Delta E(\text{mv})$	$T$	$T + \Delta T$	$\Delta T$
22	3.47	21.38	28.98	7.60
23	3.48	.38	.95	.57
24	3.47	.38	.91	.53
25	3.45	.37	.85	.48
26	3.48	.39	29.03	.64
27	3.48	.39	28.98	.59
28	3.47	.40	.89	.49
29	3.47	.38	.83	.45
30	<u>3.47</u>	<u>.38</u>	<u>.72</u>	<u>.34</u>
Av.	3.47	21.39	28.81	7.42

$$\Delta S = 10.8$$

$$\bar{S}_{Cl^-} = 15.7$$

Electrodes reversed

31	3.44	21.60	28.87	7.27
32	3.48	.62	.99	.37
33	3.49	.61	.96	.35
34	3.50	.60	.90	.30
35	3.48	.60	.78	.18
36	3.45	.58	.75	.17
37	3.47	.60	.90	.30
38	3.47	.61	.84	.23
39	3.47	.58	.77	.19
40	3.44	.56	.73	.17
41	3.45	.61	.93	.32
42	3.48	.62	.90	.28

TABLE I  
(cont'd)

#	<u>ΔE(mv)</u>	<u>T</u>	<u>T + ΔT</u>	<u>ΔT</u>
43	3.47	21.59	28.85	7.26
44	3.45	.58	.75	.17
45	<u>3.42</u>	<u>.58</u>	<u>.77</u>	<u>.19</u>
Av.	3.46	21.60	28.85	7.25

ΔS = 11.0

$\bar{S}_{Cl^-}$  = 15.9

Electrodes reversed

46	3.28	21.63	28.66	7.03
47	3.28	.62	.71	.09
48	3.29	.62	.63	.01
49	3.29	.62	.70	.08
50	3.29	.64	.70	.06
51	3.30	.64	.64	.00
52	3.29	.63	.70	.07
53	3.30	.64	.71	.07
54	3.30	.63	.68	.05
55	3.29	.64	.66	.02
56	3.30	.64	.70	.06
57	3.29	.64	.66	.02
58	3.29	.62	.70	.08
59	3.30	.62	.63	.01
60	<u>3.29</u>	<u>.63</u>	<u>.72</u>	<u>.09</u>
Av.	3.29	21.63	28.68	7.05

ΔS = 10.8

$\bar{S}_{Cl^-}$  = 15.7

Av. ΔS = 10.9

Av.  $\bar{S}_{Cl^-}$  = 15.8

TABLE II

<u><math>\bar{S}_{Cl^-}</math></u>	<u>Reversed</u>	<u>Average</u>
Cell #2 -- 4.000f = 4.582m KCl		
14.7	14.9	14.8
14.5	14.9	14.7
14.6	14.8	14.7
		Av. <u>14.7</u>
Cell #3 -- 1.000f = 1.033m KCl		
19.2	17.8	18.5
18.9	18.3	18.6
		Av. <u>18.55</u>
Cell #4 -- 0.01000f = 0.01000m KCl		
26.1	28.2	<u>27.15</u>
Cell #5 -- 0.1000f = 0.1007m KCl		
22.6	23.9	23.25
21.7	24.7	23.2
		Av. <u>23.2</u>
Cell #6 -- 2.000f = 2.133m KCl		
18.1	15.5	<u>16.8</u>
Cell #7 -- 3.000f = 3.202m NaCl		
15.1	16.4	15.75
14.9	16.4	15.65
14.2	16.7	15.45
14.9	16.1	15.5
		Av. <u>15.6</u>
Cell #8 -- 4.000f = 4.374m NaCl		
14.5	16.0	<u>15.25</u>

TABLE II

(cont'd)

Cell #9 -- 5.000f = 5.610m NaCl

15.1                    14.8                    14.95

15.7                    14.2                    14.95

Av. 14.95

Cell #10 -- 2.000f = 2.087m NaCl

m    16.3                    16.1                    16.2

15.9                    16.5                    16.2

Av. 16.2

Cell #11 -- 6.000f = 6.860m LiCl

12.0                    22.4                    17.2

14.3                    19.8                    17.05

Av. 17.1

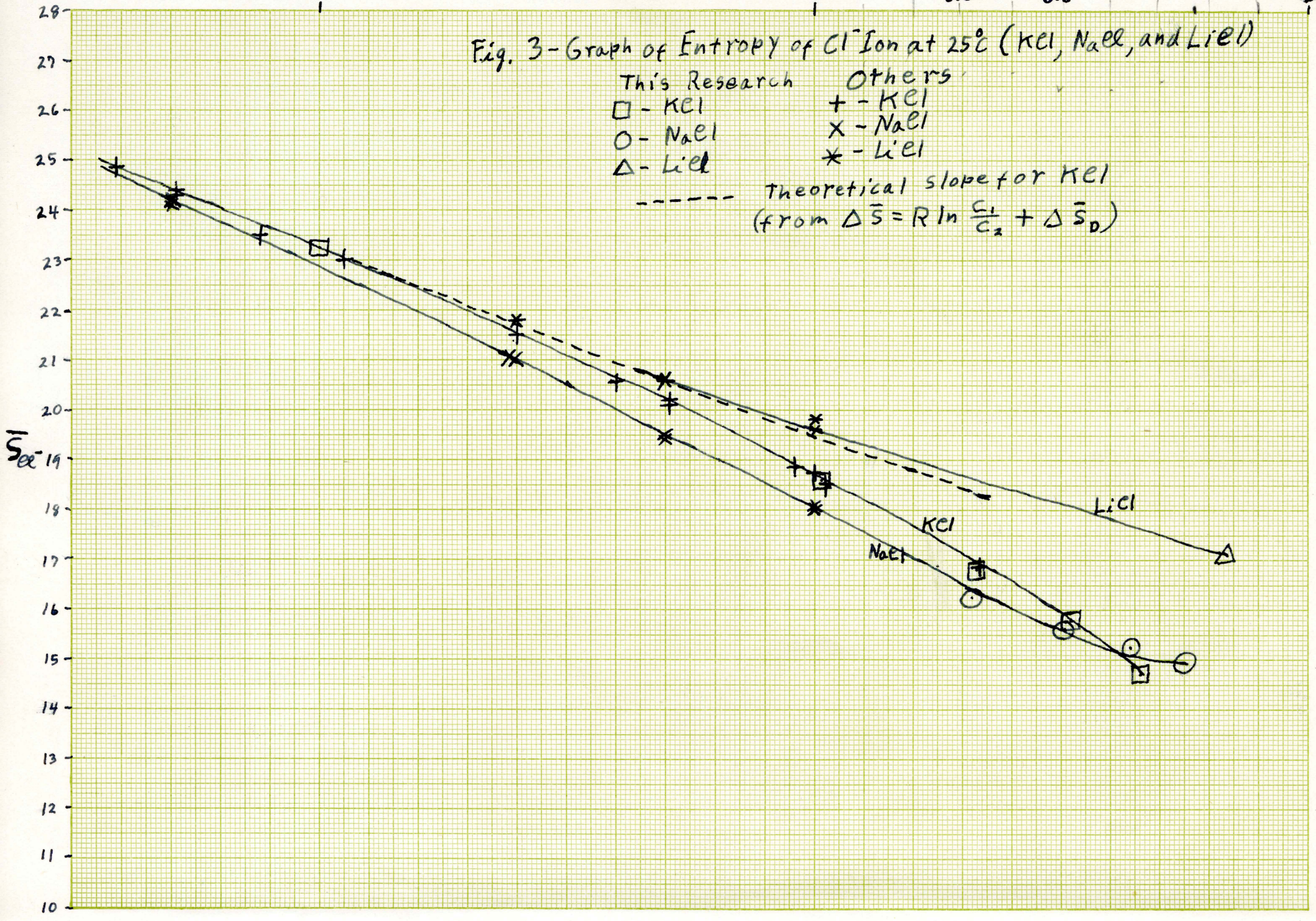
Log m

1m 2m 3m 4m 6m 8m  
0 0.3 0.5

Fig. 3 - Graph of Entropy of Cl<sup>-</sup> Ion at 25°C (KCl, NaCl, and LiCl)

This Research	Others
□ - KCl	+ - KCl
○ - NaCl	x - NaCl
△ - LiCl	* - LiCl

----- Theoretical slope for KCl  
(from  $\Delta \bar{S} = R \ln \frac{c_1}{c_2} + \Delta \bar{S}_D$ )



## CONCLUSIONS

An analysis of the experimental results, as shown in the graph (see Fig. 3), in terms of the entropy factors discussed earlier proves interesting. The tendency of LiCl to rise slightly above the theoretical slope (as calculated from  $S = R \ln C_1/C_2 - S_D$ ) probably excludes the formation of any "quasi-crystalline" hydrogen bond structure, with a corresponding decrease in entropy, since the lithium ion is strongly hydrated and would be expected to form this type bond more readily than any other alkali metal ion. It is easy to see why ion-pair formation is not important in LiCl, since the chloride ion might not be able to penetrate the strongly held water layer around the lithium ion. It is predicted that the entropy of the chloride ion will rise above the theoretical in concentrated solutions of the alkaline earth chlorides since the cations are all strongly hydrated.

If we exclude the possibility of hydrogen-bond formation, the downward trend of KCl is obviously due to ion-pair formation. Hydration effects seem to be unimportant in this solution. It is predicted that the entropy in cesium and rubidium chlorides will drop below the theoretical in concentrated solutions, but not as sharply as in KCl.

The case of NaCl is puzzling, and proves diffi-

cult to interpret. It is obvious that at least two factors, opposing each other, have an effect. Since we have eliminated hydrogen bonding, the early downward trend, stronger than in KCl, must be due to ion-pair formation. This is reasonable, since the sodium ion does not form a stable aquo-complex (although more strongly hydrated than the potassium ion) and therefore would be expected to form bonds with chloride ions more easily than a potassium ion. The upward trend at almost the saturation point is possibly due to the other hydration effect, but it is difficult to see why this should become important after ion-pair formation has occurred.

The main conclusion which can validly be drawn is that more work needs being done. The entropy of the chloride ion needs to be comprehensively studied in solutions of all its alkali and alkaline earth chlorides, hydrochloric acid, and other metallic chlorides, before a clear cut qualitative pattern could possibly be discerned. It is regretted that more work could not be done this year, but the apparatus was bought and constructed with an eye to future senior research students.

## SUMMARY

1. The theory of the thermocell and the method for determining the entropy of a single aqueous ion are discussed. Absolute and standard entropy are contrasted. The factors which affect the entropy in solution are listed and discussed.
2. The construction and use of the apparatus and chemicals for measuring the entropy of the chloride ion is explained in detail.
3. The experimental results obtained are reported in tabular and graphic form and compared with the values of other workers. Limitations and peculiarities of measuring are explained.
4. The experimental results are analyzed qualitatively in the light of the factors which affect the entropy of an aqueous ion, and the need for further research is emphasized.



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