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Heats of Dilution of Concentrated Solutions

Wm. S. Tucker

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XI. *Heats of Dilution of Concentrated Solutions.*

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Communicated by Prof. H. L. CALLENDAR, *F.R.S.*

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(1) REVIEW OF PREVIOUS WORK ON HEATS OF DILUTION.

HEATS of dilution have been exhaustively studied by Prof. JULIUS THOMSEN for a very large number of aqueous solutions.* His method chiefly consisted in taking some concentrated solution and diluting it considerably. The total amount of heat generated or absorbed in this process was thus found and quoted against the final concentration expressed in molecules of water to one molecule of solute. It is to be noted that during the process of dilution most of the thermal change occurs in the early stages, and that after the first ten molecules of water are added the total heat generated or absorbed increases but slightly.

The probable reason for this procedure is, that the experimenter finishes the operation with a dilute solution, so that starting with various initial concentrations, he may need only a few specific heats of certain dilute solutions. It must be

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remembered that only the final specific heat of the solution need be known in order to measure the heat generated.

This process of largely diluting a solution, *i.e.*, in all cases using a larger bulk of solvent than solution, has been employed also by BERTHELOT,[*] STEINWEHR,[†] and BISHOP.[‡]

Very few experimenters quote results sufficiently numerous to establish any relation between heat of dilution and concentration. THOMSEN, from results on solutions of nitric acid and sulphuric acid, deduces a hyperbolic relation between the total heat of dilution and the final concentration N in molecules of water per molecule of solute. It is of the form $Q = \frac{aN}{N + b}$ where a and b are arbitrary constants. The equations admit of no simple interpretation.

For hydrochloric acid solutions, he employs the different type of equation $Q = a - \frac{b}{N}$.

THOMSEN obtained a large number of readings for sodium hydroxide solutions. At low concentrations the heat of dilution changes sign, and no attempt was made to give a relation between Q and N.

Acetic acid also changes the sign of its heat of dilution. It is negative for strong solutions and positive for weak ones. A great number of results were published by THOMSEN for many salts, but not sufficient in any one case for the purpose of deducing a Q and N relation.

RÜMELIN[§] has more recently found heats of dilution for phosphoric acid solutions, but only for four concentrations. LEMOINE[||] also examined lithium chloride solutions, but quoted results in which no high order of accuracy was suggested. These methods differ from those previously quoted, for here the diluting was done in stages.

Summing up all the results and the conclusions derived from them by the various authors, there seems to be no simple law which can be applied to all satisfactorily.

The author in previous work with concentrated solutions[¶] has obtained evidence in certain cases of those solutions being simpler in character than weaker ones. The present paper deals almost entirely with the thermal effects in what may be called concentrated solutions, and a sufficient number of observations are taken to get a good concentration relation with heat of dilution. Heats of dilution were found for

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[*] 'Annales de Chimie et de Physique,' vol. IV., p. 468, 1875.

[†] 'Zeitschr. für Phys. Chem.,' vol. 38, p. 185, 1901.

[‡] 'Physical Review,' vol. 26, p. 169, 1908.

[§] 'Zeitschr. für Phys. Chem.,' vol. 58, p. 458, 1907.

[||] 'Comptes Rendus,' vol. 125, p. 604, 1907.

[¶] 'Proceedings of the Physical Society,' vol. XXV., Part II., p. 111.

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the concentrated solutions without making them dilute in the process; thus about 20 gr. of water were added to 300 gr. of solution. The heat generated or absorbed in this case divided by the number of gr. molecules of water added, gives the differential heat of dilution sufficiently accurately for a concentration which is the mean of the initial and final concentrations.

The differential heat of dilution $d\,Q/dN$ may be defined as the quantity of heat liberated or absorbed per molecule of water added to an infinite quantity of solution, whose concentration will thereby be unaffected. This condition can only be approximated to, but the error in the above estimate will be small.

THOMSEN added large quantities of water and so obtained a total heat $Q = \int_{N_2}^{N_1} \frac{dQ}{dN} \, . \, \delta N$. This involved a large thermal equivalent and a small rise in temperature.

By the method here described the thermal capacity is kept sufficiently low to give a fair rise in temperature on dilution, and the relatively small quantity of water employed can be placed in a vessel completely immersed in the solution. Temperatures can thus be well equalised before dilution takes place.

The following record describes work extending from October, 1912, to December, 1914. The accurate determination of heat of dilution is necessarily a tedious business, owing to the fact that only one observation can be taken in an ordinary working day of six hours.

(2) DESCRIPTION OF APPARATUS. (Diagram I.)

Measurement of Temperature.

In most of the previous researches on heat of dilution a mercury thermometer was employed. Here temperature changes were measured with certainty by a platinum thermometer with fundamental interval of 12·8 ohms—mounted in a very thin-walled cylindrical bulb, whose length is not far short of the depth of the solution. Long experience with the working of this thermometer in other researches and careful application of all the corrections peculiar to it, enable the author to guarantee its readings. (Diagram I., T.)

Importance of Stirring.

One of the most important features of the experiment is the stirrer. Different types were tested, and the most efficient one was found to be of the screw propeller type turned by a high speed motor. The process of mixing was rapidly performed even with some of the very viscous solutions employed, and a careful experiment was performed to see if any appreciable temperature rise was indicated during the process. After long periods, less than $\frac{1}{100}$° C. rise was noticeable. (Diagram I., S.)

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The Choice of a Calorimeter.

Radiation is another factor which becomes important when very small temperature changes are produced. A very well made Dewar cylinder was employed. (Diagram I., AA.) Its walls were well silvered, and during the experiments its contents, together with stirrer thermometer and other adjuncts, were shut in by a well-fitting cork stopper, which again was covered with a layer of cotton wool.

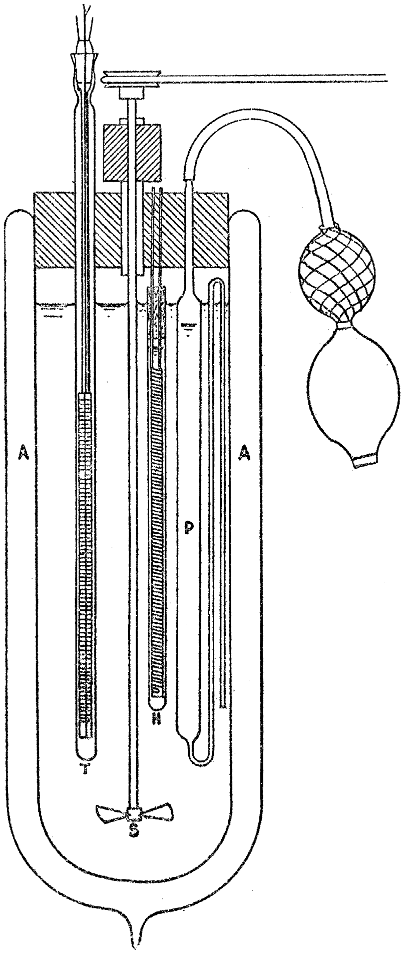

Diagram I.

Curves were plotted when the contents had varying thermal capacities, and these were found to be perfectly smooth and enabled one to estimate with certainty the rate of cooling at any temperature. The cubical capacity of the vessel was about 400 c.c., and in no case did it contain more than 300 c.c. of solution. For 20 degrees excess of temperature in the contents over that of the room, a rate of cooling of about 0·038° C. occurred per minute.

Each series of observations was accompanied by its own radiation experiment and complete consistency was given throughout.

The Mixing Pipette.

It is highly important that the water added should have the same temperature as the solution. A thin walled glass pipette was employed of the form shown in the diagram. (I., P.) Its bulb passes throughout the length of the cylindrical mass of solution, and parallel to the bulb of the thermometer. Two such pipettes were employed—one with a capacity of about 25 c.c., the other about 45 c.c. The water was weighed out in these, the former being used when the solutions were strong, the latter when weak. The walls were of thin glass, and the syphon tube was of such length as to introduce the water at the bottom of the vessel containing the solution. The water, being of course less dense than the solution, would rise, and the process of mixing would be assisted in consequence.

Before mixing, the glass bulb with its contents was left immersed in the solution for some hours, and the stirrer was worked continuously. In this way error due to temperature difference was brought to a minimum. The upper end of the pipette is then connected by a thin rubber tube with the rubber ball, such as is used for a scent

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spray, and the water is projected out. (Diagram I., P.) The process of mixing is then carried out, and after a sufficient time the temperature change is noted. Some estimate is made of the water in the pipette which has not been driven out, viz., that wetting the walls of the tube. For this purpose, the tube being removed, dried externally and weighed, allowance is now made in the amount of water quoted.

Thermal Capacity of Vessel and its Contents.

The thermal capacity of the vessel and its contents must be very carefully determined, a process which is always difficult. When a glass mixing vessel is employed special care has to be taken in the determination, as glass has a high specific heat. Moreover, its low conducting power involves the temperature not being so nearly equal throughout its mass. Thus it was found that the thermal capacity differed with the amount of solution taken. In all cases quantities of solution taken were of either 250, 275 or 300 c.c., the amounts being measured by standardised measuring vessels.

Thermal capacities were found for the vessel and its contents also, when the mixing pipettes were present or absent. To ensure accuracy experiments were repeated. Consistent values were obtained. Roughly speaking the thermal capacity was of the order of one-tenth that of the total thermal capacity.

Mode of Heating.

The method of determining the thermal capacity of the vessel under the varying conditions, was that of heating by a known electric current a weighed quantity of water contained in the vessel. Some difficulty was experienced in the construction of a satisfactory heating coil. The difficulty was solved by selecting a piece of glass tubing of very thin walls, and elliptical in section. (Diagram I., H.) Manganin wire was wound upon a flat strip of mica and inserted into the tube, one end of which was sealed. Good thermal contact between the coil and the walls of this tube was ensured by filling up the tube with the best lubricating oil, and the upper end was lightly close with glass wool. The coil so made was thus perfectly insulated, and yet presented a large heating surface. There was found to be very little lag in the taking up of the heat by the solution. The length of the coil was so taken as to extend throughout the depth of the solution.

The heat generated was measured by the products $\frac{\mathrm{CE}t}{4{\cdot}185}$ where C is the current, E the volts, t the time in seconds, and 4·185 the mean value of JOULE's equivalent. A Weston ammeter and a Weston voltmeter were employed having ranges from 0 to 5 in both cases. It was found possible to read to 0·005 ampere or volt with fair accuracy. Both instruments were calibrated against standards and the observations quoted are those observed, to which the requisite correction is applied. The

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instruments employed showed an accuracy to within 0·02 of a volt or ampere almost throughout their whole scale. The heating coil was of about 0·9 ohm resistance, and such a current was employed as to give readings nearly at the middle of the scales in each instrument. The steadiness of the current was determined by the condition of the secondary cells employed. Such variations as there were, however, were eliminated by readings of each instrument during each minute of heating.

To find the Thermal Capacity of the Apparatus.

One typical set of observations may be quoted.

May 8, 1913.

250 gr. of water were heated for 940 seconds, and the following readings of voltmeter and ammeter were taken alternately—at minute intervals.

Corrected Readings.

Ammeter.	Voltmeter.	Ammeter.	Voltmeter.
2·945	2·595	2·910	2·570
2·935	2·590	2·910	2·570
2·930	2·590	2·910	2·570
2·930	2·590	2·905	2·560
2·940	2·595	2·920	2·580
2·940	2·600	2·925	2·580
2·940	2·595	2·925	2·585
2·920	2·570	2·915	2·575

The mean value of the current is 2·925 amperes and of the P.D. 2·582 volts. The heat supplied is 1696·4 calories. Initial temperature 15·37° C. Final temperature 21·22° C.

The mean radiation at the final temperature is 0·0072° C. per minute, and the correction for the whole period 0·06° C.

Hence, the corrected temperature rise is 5·91° C., and the water absorbs 1477·5 calories. The heat absorbed by the apparatus is thus 218·9 calories, giving a water equivalent of 37·0 gr.

For 275 gr. of water, the water equivalent was found to be 42·5 gr. When the mixing pipettes were employed, values of 44·75 and 45·6 gr. were obtained respectively.

(3) DETAILED OBSERVATIONS FOR HYDROCHLORIC ACID SOLUTIONS.

1. *Experiments at Air Temperature.*

Four typical strong solutions were studied :—Hydrochloric acid, lithium chloride, sodium hydroxide, and calcium chloride.

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TABLE I.—Observations in the Determinations of Specific Heats of Hydrogen Chloride Solutions.

No.	Density at 17° C.	Concentration.	Mass.	Initial temperature.	Final temperature.	Radiation.	Rise in temperature.	Mean current.	Mean P.D.	Calories supplied.	Calories absorbed by vessel.	Calories available.	Mean temperature.	Specific heat.
				° C.	° C.	°	° C.						° C.	
I.	1·1588	22·80	318·7	6·54	11·54	0·34	5·00	2·991	2·681	1149·8	212·5	937·3	9·00	0·588
II.	1·1472	20·23	315·4	7·25	12·26	0·35	5·01	3·000	2·695	1159·5	213·9	945·6	9·75	0·599
III.	1·1336	17·80	311·6	6·79	11·70	0·25	4·91	2·995	2·692	1156·3	208·6	947·7	9·29	0·619
IV.	1·1100	13·80	305·2	7·59	12·77	0·25	5·18	2·991	2·687	1267·0	220·1	1046·9	10·18	0·662
V.	1·0908	10·95	299·9	7·89	13·23	0·22	5·34	2·957	2·657	1351·3	227·0	1124·3	10·56	0·702
VI.	1·0664	7·70	293·3	7·09	12·23	0·22	5·14	2·965	2·672	1362·9	218·5	1154·4	9·66	0·766
VII.	1·0454	5·40	288·2	8·16	12·97	0·22	4·81	2·913	2·664	1335·0	204·4	1130·6	10·56	0·815
VIII.	1·0372	4·06	285·2	8·09	12·81	0·22	4·72	2·953	2·660	1351·3	200·6	1150·7	10·45	0·855

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In order to obtain their values of heat of dilution a series of specific heat values must be found for varying concentrations. As all the experiments were to be performed at air temperatures, varying from 15° C. to 20° C., the method of heating was adopted as described above.

Only a short range of temperature rise was permitted as the specific heat may change rapidly with temperature. For this reason, such heat was supplied as to keep this rise of temperature to about 5° or 6° C. The time chosen for the heating process was 1000 seconds, for some solutions, but in the case of hydrochloric acid solutions which have a low specific heat at high concentrations, periods of 10, 11, and 12 minutes were employed.

In order to show the manner in which the observations were taken the full details for hydrochloric acid solutions are given. Eight solutions are taken and are distinguished by numbers, the strongest being solution 1. The acid employed was the purest obtainable, and the more dilute solutions were obtained from the stock solution by adding distilled water. Observations of specific heat determinations were taken from May 15 to June 6, 1913, and are quoted in Tables I. and II.

Some preliminary experiments with concentrated solutions showed that the gas was driven off to an appreciable extent when the temperature exceeded air temperature. For this reason the solutions were cooled about 8° below air temperature, so that their mean temperature is about 5° below that of the air. Later experiments show that the specific heat alters very little with temperature for these solutions, hence no appreciable error is introduced into the heats of dilution as calculated from these specific heats.

Table I., p. 325, shows the relation between the specific heat and the concentration, expressed as molecules per 100 molecules of water, the molecular weight being taken as 36·5.

The concentration was obtained from density tables supplied by LUNGE and MARCHLEWSKI. The final temperature is corrected for radiation, and the mean temperature of these is nearly that of the solution for the given determination.

275 c.c. of the acid were employed throughout, and the water equivalent is 42·5 gr. The first three solutions were heated for 600 seconds, the fourth for 660 seconds, and the remainder for 720 seconds.

For the purpose of interpolation many attempts were made to get an equation connecting specific heat and concentration. No simple equation appears to satisfy the condition for dilute as well as strong solutions. The author's interest, however, is chiefly in the concentrated solutions, and for solutions whose strengths lie between the limits of 7·7 and 22·8 molecules of the solute to 100 molecules of water it was found that an equation of the type $sn^a = b$ was suitable, where s and n are specific heat and concentration respectively, while a and b are constants.

In the case of hydrogen chloride the equation takes the simple form

$$sn^{1/4} = 1 \cdot 277.$$

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Table II. shows the degree of accuracy obtained.

TABLE II.

Concentration (n).	Specific heat (s).	Specific heat by calculation.
22·8	0·588	0·584
20·23	0·599	0·602
17·80	0·619	0·622
13·80	0·662	0·662
10·95	0·702	0·702
7·70	0·766	0·767
5·40	0·815	0·838

The last value in this table shows the failure of the relation for dilute solutions, but since heats of dilution at this concentration are so small, very little relative error is introduced by interpolating graphically.

The value of the constant b changes with the temperature.

Heat of Dilution.

All the observations were taken with the initial temperature of the solution and the water that of the air. No radiation correction need be applied, since the process of mixing was very rapid. In the first six experiments the smaller pipette was employed, and the water equivalent 44·75 gr.; for the next two experiments, the larger pipette was used with water equivalent 45·6 gr. The last two experiments were performed by a pipette which was not immersed in the solution. The solution and distilled water were brought to the same temperature (that of the air) by enclosing the latter in a vessel immersed in the former. Quantities of each were measured out in turn—in experiment (IX.), 200 c.c. of solution to 100 of water, and in (X.), 150 c.c. of each. The mixing process was performed in the same vessel, and the water equivalent was 46·0 gr.

As a check on the concentration the densities of the solutions were obtained before and after mixing, and the new value of concentration after the process of mixing was found by application of the expression

$$C' = \frac{1800\,Qcd}{(1800+cm)\,(Qd+x) - Q\,dcm}$$

where c is the initial concentration in molecules of acid per 100 molecules of water,

Q the volume of solution taken in c.c.,
d its density at the temperature employed (gr./c.c.)
m the molecular weight—here 36·5,
x the number of gr. of water added.

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TABLE III.

No. of solution.	Density at 15° C.	Concentration molecules per 100 molecules.	Density after dilution (15° C.).	Final concentration.	Mean concentration.	Mass of solution.	Mass of water added.	Initial temperature.	Final temperature.	Temperature rise.	Total mass of solution and water.	Specific heat after mixing.	Water equivalent.	No. of calories.	Mean temperature.	Heat of dilution calories per molecule.	THOMSEN'S values.
I.	1·1635	23·50	1·1505	20·85	22·17	290·9	22·71	° C. 18·27	° C. 21·72	° C. 3·45	313·6	0·598	232·25	801·3	° C. 19·99	635	589·8
II.	1·1505	20·85	1·1375	18·50	19·62	287·6	22·5	18·60	21·40	2·80	310·1	0·615	235·45	659·3	20·00	527·5	462
III.	1·1375	18·50	1·1252	16·30	17·40	284·48	23·1	17·82	20·15	2·34	308·0	0·636	240·95	563·8	18·98	439·3	363·4
IV.	1·1252	16·30	1·1138	14·45	15·37	281·3	23·4	17·78	19·67	1·89	304·7	0·656	244·6	459·9	18·72	353·8	283·6
V.	1·1138	14·45	1·1048	13·00	13·72	278·45	23·02	17·39	18·88	1·49	301·5	0·675	248·25	369·9	18·13	289·2	225·8
VI.	1·0975	11·95	1·0900	10·83	11·39	274·4	23·91	17·03	18·00	0·97	298·3	0·707	255·65	247·9	17·51	186·2	155·8
VII.	1·0900	10·83	1·0770	9·15	9·99	272·5	41·7	17·013	18·085	1·072	314·2	0·737	277·2	297·1	17·55	128·3	119·8
VIII.	1·0770	9·15	1·0665	7·76	8·45	269·25	41·76	18·350	19·173	0·823	311·0	0·763	282·9	232·8	18·76	100·4	85·7
IX.	1·0665	7·76	1·0448	4·98	6·37	213·3	100	18·105	19·165	0·960	313·3	0·828	305·3	293·1	18·63	52·8	48·7
X.	1·0448	4·98	1·0223	2·42	3·70	156·7	150	17·835	18·316	0·481	306·7	0·900	322·9	154·9	18·07	18·54	16·44

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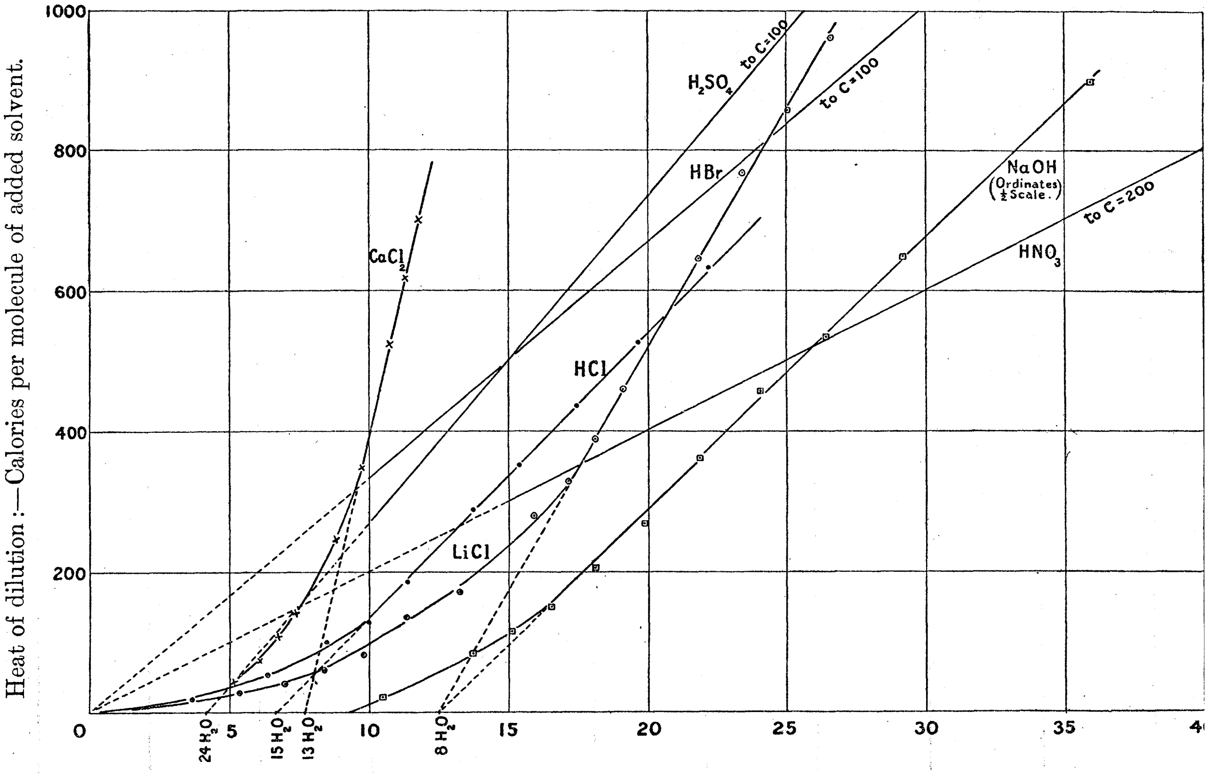
Table (III.) contains all the observations; the strongest solution is placed first in the series.

Note.—In obtaining the specific heats of the solutions, a slight correction is made for the change of specific heat with temperature. A later series of experiments were performed in which the change was found for different concentrations.



Concentration :- -Molecules per 100 molecules of water.

Diagram II.

Diagram II. includes the curve showing the relation between heat of dilution and concentration for hydrogen chloride.

(4) Study of the Results Obtained.

In the above table a column gives Thomsen's values and the results are calculated out from the relation,

$$\frac{Q}{n} = 17{,}340 - 12{,}000\,\frac{n}{N}$$

where Q is the heat generated per n gr. molecules of solute dissolved in N molecules of solvent.

The heat of dilution is given by

$$\frac{dQ}{dN} = 12{,}000\left(\frac{n}{N}\right)^2.$$

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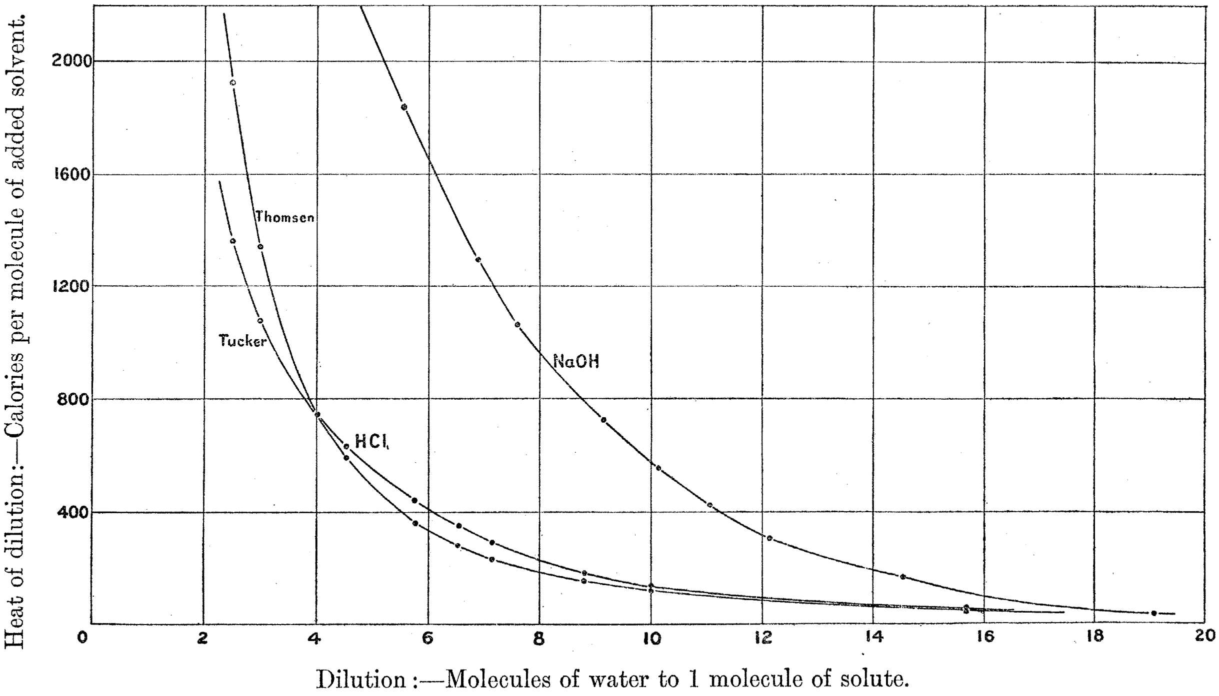
It will be seen that the results derived from his equation lie considerably below those obtained by experiment.

The discrepancy between THOMSEN'S values and those here obtained does not appear from the value of total heat of dilution quite so obviously. Thus on diluting a solution from $HCl . 2·6H_2O$ to $HCl . 10H_2O$, nearly the same quantity of heat appears to be generated. The reason for this is that THOMSEN'S dQ/dN exceeds the values here obtained for solutions of strength exceeding $HCl . 4H_2O$.

In order to obtain a measure of the total heat generated, values of dQ/dN can be plotted against number of molecules of water per molecule of solute, *i.e.*, the abscissæ would read "dilution" instead of concentration. (See Diagram III.)



Dilution:—Molecules of water to 1 molecule of solute.

Diagram III.

The area intercepted between two ordinates separated δN would be $\frac{dQ}{dN}\,\delta N$, and between limits of concentration N_1 and N_2.

$$\int_{N_2}^{N_1} \frac{dQ}{dN}\,dN.$$

It will be seen that the curves cross at $N = 4$, and that the total areas from the two curves are nearly equal.

The curve connecting heat of dilution and concentration for hydrochloric acid, should, by THOMSEN'S theory, be parabolic. The results of the above experiments show that with concentrations exceeding $HCl . 10H_2O$ the values lie very nearly on a straight line, which however, for lower concentrations, bends round and approaches the origin. If the straight portion be produced it cuts the axis of concentration at

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6·66 molecules per 100 molecules, which is $HCl.15H_2O$. For concentrations above 10 therefore—when all concentrations are reduced in such a manner as to assume $HCl.15H_2O$ as the solvent—a proportional relation is obtained between heat of dilution and concentration.

This may be best expressed by the equation

$$\frac{dQ}{dN} = a\left(\frac{n}{N} - c\right).$$

If c is expressed in gramme-molecules of solute per molecule of solvent, and a is the tangent of the angle of slope of the portion referred to (4082), taking N as 1,

$$\frac{dQ}{dN} = a\,(n - 0{\cdot}0666).$$

If expressed in terms of dilution

$$n = \frac{1}{N}, \qquad \text{and} \qquad \frac{dQ}{dN} = \frac{a}{N} - 0{\cdot}0666a,$$

and the total heat generated, when one molecule of solute combined with N_1 molecules of solvent is diluted till combined with N_2 molecules, is expressed by

$$Q_0 = \int_{N_1}^{N_2} \frac{dQ}{dN} = \Big[a \log_e N\Big]_{N_1}^{N_2} - \Big[0{\cdot}0666aN\Big]_{N_1}^{N_2}.$$

Giving N_1 the value 2·6, which is about THOMSEN's maximum concentration, and N_2 the value 10, THOMSEN's values give 3415 calories, while those obtained above give 3427 calories. For concentrations below 10 molecules of water the two curves nearly coincide, so that the total heat obtained by diluting very largely would be nearly the same.

The following results (Table IV.) show the degree of accuracy with which the equation

$$\frac{dQ}{dN} = 4082\left(\frac{n}{N} - 0{\cdot}0666\right),$$

fits the results for concentrations above 10 molecules per 100 molecules.

TABLE IV.

Concentration molecule per 100 molecules.	Results of experiment.	Results by calculation.	Percentage error.
22·17	635	632·9	−0·33
19·62	527·5	528·7	+0·23
17·40	439·3	438·2	−0·25
15·37	353·8	355·3	+0·43
13·72	289·2	287·9	−0·45
11·39	186·2	192·8	+3·01
9·99	128·3	135·7	+5·81

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TABLE V.

No. of solution.	Density.	Concentration molecules per 100 molecules of H_2O.	Mass.	Heating current.	P.D.	Initial temperature.	Final temperature.	Mean temperature.	Rise in temperature.	Heat supplied.	Heat used by apparatus.	Heat used by solution.	Specific heat.
			gr.	amperes.	volts.	° C.	° C.	° C.	° C.	calories.			
1	1·2604	29·43	378·1	3·143	2·858	14·78	22·35	18·56	7·57	2146	321·7	1824·3	0·637
2	1·2156	22·76	334·4	2·902	2·805	14·30	21·61	17·45	7·31	1945	290·6	1654·4	0·677
3	1·1592	15·48	318·8	2·825	2·732	16·04	22·76	19·40	6·72	1844	267·1	1576·9	0·736
4	1·1280	12·13	310·1	2·805	2·712	16·45	23·03	19·74	6·58	1818	261·5	1556·5	0·763
5	1·0988	8·97	302·2	2·952	2·854	16·61	23·65	20·13	7·04	2013	279·8	1733·2	0·815
6	1·0716	6·15	294·7	2·935	2·842	14·29	21·05	17·67	6·76	1993	268·7	1724·3	0·857
7	1·0540	4·54	289·8	3·112	2·852	14·72	21·78	18·25	7·06	2121	280·6	1840·4	0·883

For the range of strong solutions from 29·43 to 8·97 molecules per 100 molecules, the equation for interpolation can be written

$$SN^{1/5} = 1 \cdot 268.$$

This equation is of the same type as that employed for hydrochloric acid.

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TABLE VI.

No. of solution.	Initial concentration.	Final concentration.	Mean concentration.	Mass of solution.	Mass of water added.	Total mass.	Specific heat after dilution.	Water equivalent of apparatus.	Initial temperature.	Final temperature.	Mean temperature.	Rise in temperature.	No. of calories.	Heat of solution calories per molecule.
				gr.	gr.	gr.			° C.	° C.	° C.	° C.		
1	27·30	25·90	26·60	343·2	14·46	357·7	0·657	44·75	16·14	18·90	17·52	2·76	774·3	960·7
2	25·90	24·19	25·05	340·5	14·22	354·7	0·668	44·75	13·02	15·43	14·41	2·41	651·3	858·6
3	24·19	22·62	23·40	337·0	14·18	351·2	0·678	44·75	14·65	16·79	15·92	2·14	609·5	767·6
4	22·62	21·10	21·86	334·2	14·05	348·2	0·689	44·75	14·38	16·15	15·96	1·77	508·2	644·8
5	21·10	19·70	20·40	331·1	14·01	345·1	0·700	44·75	14·49	16·00	15·24	1·51	435·4	554·9
6	19·70	18·50	19·10	328·4	14·39	342·8	0·709	44·75	13·82	15·09	14·45	1·27	370·6	460·5
7	18·50	17·68	18·09	325·8	14·19	340·0	0·717	44·75	14·16	15·23	14·74	1·07	309·4	391·5
8	17·68	16·46	17·07	323·6	14·56	338·2	0·728	44·75	15·39	16·31	15·85	0·92	267·7	330·9
9	16·46	15·42	15·93	321·2	14·31	335·5	0·736	44·75	15·27	16·04	15·65	0·77	224·55	282·4
10	14·32	12·10	13·21	316·0	33·50	349·5	0·763	45·6	15·55	16·58	16·11	1·03	303·2	172·8
11	12·10	10·62	11·36	310·1	31·24	341·3	0·782	45·6	16·05	16·81	16·43	0·76	237·5	136·8
12	10·62	8·97	9·80	306·7	50·00	356·7	0·803	42·5	17·155	17·85	17·50	0·70	228·6	82·3
13	8·97	7·80	8·38	302·2	50·00	352·2	0·825	42·5	14·18	14·695	14·42	0·515	171·5	61·7
14	7·80	6·15	6·97	299·3	50·00	349·3	0·856	42·5	14·30	14·606	14·45	0·306	111·6	40·2
15	6·15	4·54	5·31	294·7	50·00	344·7	0·890	42·5	13·815	14·063	13·93	0·248	86·6	31·1
16	4·54	3·28	3·91	289·9	50·00	339·9	0·916	42·5	14·10	14·270	14·18	0·170	60·2	21·6

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(5) Lithium Chloride. (Molecular weight 42·5.)

The solutions of lithium chloride were treated in precisely the same way as those of hydrogen chloride. The solutions when concentrated, possessed a much greater viscosity and greater care had to be taken in stirring. Also the solutions were very hygroscopic and the experiments were performed, as far as possible, in an air-tight vessel.

The following tables (Tables V. and VI.) summarise the observations. As the same mixing vessel was used and the same quantities of solution, the same water equivalents were employed. In the specific heat determinations the current and voltage employed are the mean of sixteen observations for each solution. The specific heats were obtained for nearly the same range of temperature as that employed for the heat of dilution determinations, hence no temperature correction for specific heat need be applied. Seven specific heats were found and 300 c.c. of each solution were taken.

The curve connecting heat of dilution and concentration shows a more gradual increase of the former with increase of the latter. The same peculiar property, however, is shown for concentrations exceeding $LiCl . 6H_2O$ above this value to concentration $LiCl . 3H_2O$, the truest representation for this portion is a straight line which cuts the concentration curve at $LiCl . 8H_2O$. (Diagram II.)

For this range the equation may be written

$$\frac{dQ}{dN} = 6927\left(\frac{n}{N} - 0{\cdot}125\right).$$

A few experiments have been performed by Dunnington and Hoggard with lithium chloride ('American Chemical Journal,' vol. 22, p. 210, 1899). Their method was only approximate, as they did not attempt high accuracy. The following few results show good agreement with those obtained above :—

Mean concentration.	Results by interpolation.	By Dunnington and Hoggard.
22·22	672·9	678
18·33	403·8	422
13·39	180	183

Lemoine* has determined heats of dilution for some concentrations of lithium chloride, but his results are not expressed to give a high degree of accuracy sufficient to compare with the above results.

(6) Sodium Hydroxide. (Molecular weight 40.)

With solutions of sodium hydroxide the same processes were employed. It was found more convenient to take 250 c.c. of the solutions for the specific heat determinations.

'Comptes Rendus,' vol. 125, 1897, p. 603.

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The gilded brass stirrer with its glass insulated shaft was replaced by a glass one, the shaft and the propeller blades being fused together. Some slight modification of the water equivalent was made to suit the new conditions. The strong solutions were very viscous and the rate of stirring was increased.

Some slight change in the heating coil due to a short circuit of a few turns altered the resistance of the heating coil—but errors were eliminated by taking readings of both ammeter and voltmeter each minute. The heating occupied a thousand seconds in all cases.

Table VII. gives the data from which the variation of specific heat with concentration was obtained.

Table VIII. gives the data for the heats of dilution of the solutions at various concentrations, and at the temperature of the air.

One of the curves in Diagram II. shows the nature of the relation between heat of dilution and concentration. The points do not lie so evenly on the curve as in the case of hydrochloric acid, and this is doubtless due to the greater difficulty of experimenting with a highly viscous solution. It is, however, interesting to note that the points for higher concentrations lie most nearly on a straight line, which passes through the axis of concentration at 12·5 molecules per 100 molecules of water. This would correspond to a concentration of $NaOH . 8H_2O$.

The equation most nearly expressing this part of the curve is

$$\frac{dQ}{dN} = 7840\left(\frac{n}{N} - 0{\cdot}125\right)$$

and this may be considered to hold while the concentration changes from $NaOH . 6H_2O$ to $NaOH . 3H_2O$; within the same range the heat of dilution changes to five times its value at the lower concentration.

A curve (fig. 7) may be plotted connecting heat of dilution and the inverse of concentration, and from it the total heat of dilution as found by THOMSEN can be estimated from the relation

$$\int_{N_2}^{N_1} \frac{dQ}{dN}\, dN.$$

The relation between Q and N for concentrations below $NaOH . 6H_2O$ is very uncertain. Both THOMSEN and BERTHELOT found the heat of dilution to become negative for high dilutions, and this also was observed in the above experiment for concentrations below those recorded above. The effect, however, was very small.

THOMSEN gives the number of calories evolved in changing the composition of the solution from $NaOH . 3H_2O$ to $NaOH . 5H_2O$ as 2131 calories. Integrating the above equation between these limits we get $Q = 7840 \log_e \frac{5}{3} - 7840 \times 0{\cdot}125 \times 2$, which gives 2083 calories. Thus although a quite different interpretation of the experimental results is given, the results are in good agreement.

By reference to the curve it is seen that a further dilution of four molecules of

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TABLE VII.

No. of solution.	Density.	Concen-tration.	Mass.	Heating current.	P.D.	Initial tempera-ture.	Final tempera-ture.	Mean tempera-ture.	Rise in tempera-ture.	Heat supplied.	Heat used by apparatus.	Heat used by solution.	Specific heat.
			gr.	amperes.	volts.	° C.	° C.	° C.	° C.	calories.			
1	1·5028	40·61	375·7	3·053	2·725	18·57	24·58	21·57	6·01	1990	222·3	1767·7	0·783
2	1·4624	34·87	365·6	2·987	2·734	16·93	22·96	19·94	6·03	1951	223·1	1727·9	0·784
3	1·4344	30·34	358·6	2·954	2·668	15·91	21·82	18·86	5·91	1883	218·6	1664·4	0·785
4	1·3848	24·57	346·2	2·944	2·635	21·01	26·98	23·99	5·97	1853	223·1	1629·9	0·790
5	1·3100	17·66	327·5	2·927	2·571	19·54	24·50	22·52	5·96	1798	220·5	1577·5	0·807
6	1·1460	8·872	286·5	2·801	2·553	16·21	22·34	19·27	6·13	1709	226·8	1472·2	0·844

Radiation corrections were made and are included in the final temperature above quoted. Other specific heat determinations were made with more dilute solutions, but as they do not come within the range of the heat of dilution experiments, they are not quoted.

The initial temperature was always the air temperature, thus simplifying radiation corrections.

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TABLE VIII.

No. of solution.	Initial concentration.	Final concentration.	Mean concentration.	Mass of solution.	Mass of water added.	Total mass.	Specific heat after dilution.	Initial temperature.	Final temperature.	Mean temperature.	Rise in temperature.	No. of calories.	Heat of solution calories per gramme.	Heat of solution calories per molecule.
1	37·93	33·97	35·95	gr. 373·2	gr. 21·8	gr. 395·0	0·784	° C. 18·86	° C. 25·19	° C. 22·02	° C. 6·33	2225	102·1	1838
2	30·66	27·70	29·18	358·5	22·78	381·3	0·786	17·27	22·08	19·67	4·81	1644	72·15	1299
3	27·70	25·14	26·42	352·8	22·2	375·0	0·789	18·18	22·08	20·13	3·90	1318	59·35	1069
4	25·14	22·95	24·04	347·8	21·26	369·1	0·793	17·91	21·15	19·53	3·24	1084	51·06	919·1
5	22·95	20·84	21·89	342·2	22·83	365·0	0·798	20·16	22·93	21·54	2·77	923·2	40·41	727·4
6	20·84	18·97	19·90	336·2	22·68	358·9	0·802	19·35	21·41	20·38	2·06	679·5	29·95	539·2
7	18·97	17·28	18·12	331·0	23·05	354·0	0·808	18·17	20·79	18·98	1·62	531·4	23·05	414·9
8	17·28	15·72	16·50	326·2	22·25	348·4	0·814	21·66	22·81	22·23	1·15	374·4	16·83	303·0
9	15·72	14·41	15·06	321·2	22·6	343·8	0·818	16·93	17·82	17·38	0·91	294·1	13·01	234·2
10	14·41	13·14	13·78	316·0	23·3	339·3	0·823	17·74	18·31	18·07	0·67	219·2	9·40	169·2
11	11·30	9·66	10·48	303·7	41·2	344·9	0·839	19·42	19·68	19·55	0·26	86·7	2·10	37·8

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water, *i.e.*, from $NaOH.5H_2O$ to $NaOH.9H_2O$, 979·2 calories are produced. For the same range THOMSEN gives 962. This agreement is as good as the difficult nature of the experiment will allow, under the conditions chosen.

(7) HEAT OF DILUTION OF CALCIUM CHLORIDE SOLUTIONS.

All the above solutions yield two ions to the molecule. A fourth solution, that of calcium chloride, was chosen, not only because of its existence in a high condition of concentration, but also because it yielded three ions to the molecule. The concentrations were obtained from the density table given by PICKERING, and the molecular weight is taken as 111.

Tables IX. and X. give the data obtained in experiments in which the procedure was very much the same as in the above solutions.

The curve for calcium chloride is of a different character. A small change of slope occurs for all concentrations. For a limited distance at high concentrations the curve appears to be nearly a straight line which would cut the axis of concentration, if produced at about 7·69 molecules per 100 molecules. This would make a limiting concentration of $CaCl_2.13H_2O$.

Many attempts were made to get an equation connecting dQ/dN and n/N, but without satisfactory result. The total heat of dilution can, however, be obtained graphically by plotting dQ/dN and N/n, as in the case of hydrochloric acid, when the total heat is measured by area.

The recorded temperature changes on dilution were smaller than in the above solutions, and the degree of accuracy was consequently not so high.

(8) VARIATION OF HEAT OF DILUTON WITH TEMPERATURE.

The above heats of dilution were determined under nearly isothermal conditions and at air temperatures.

Very little work has been done to determine the variation of heat of dilution with temperature. COLSON* has obtained a so-called "dead point" for various solutions. He found certain temperatures at which the heat of dilution vanishes for certain solutions. Taking one of these solutions he found the dead point the same for all concentrations. Later on, however, when experimenting with sodium sulphate, he found the dead point to vary with varying concentration. He concluded that those solutions giving a constant dead point contain solutes in which the state of aggregation is independent of the concentration, and cited sodium sulphate as a substance whose composition varies with concentration.

MAGIE† found a change in heat of dilution for barium chloride from positive to negative, giving a zero effect at temperatures which decrease as the dilution increases.

* 'Comptes Rendus,' vol. 134, pp. 1496–1497, 1902.

† 'Amer. Phil. Soc. Proc.,' vol. 51, 1912.

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TABLE IX.

No. of solution.	Density, gramme per cubic centimetre.	Concentration.	Mass.	Heating current.	P.D.	Initial temperature.	Final temperature.	Mean temperature.	Rise in temperature.	Heat supplied.	Heat absorbed by apparatus.	Heat absorbed by solution.	Specific heat.
			gr.	ampere.	volts.	° C.	° C.	° C.	° C.	calories.			
1	1·409	11·36	493·6	2·23	2·95	15·00	19·60	17·30	4·60	1572	178·9	1393	0·613
2	1·390	10·52	486·2	2·19	2·93	15·10	19·62	17·36	4·52	1540	175·8	1364	0·621
3	1·347	9·02	471·1	2·16	2·94	15·50	19·95	17·72	4·45	1517	173·1	1344	0·641
4	1·325	8·27	463·3	2·16	2·93	16·01	20·45	18·23	4·44	1513	172·7	1340	0·651
5	1·239	5·69	495·6	2·16	2·94	16·19	20·35	18·27	4·16	1609	161·8	1447	0·701
6	1·174	4·00	410·4	2·12	2·94	16·14	20·40	18·27	4·26	1489	165·7	1313	0·757
7	1·091	1·98	381·3	2·11	2·94	17·74	21·86	19·80	4·12	1482	160·3	1322	0·841

In the above determinations 350 c.c. of solution were taken except in experiment (5) where 400 c.c. is taken, and the current is run for 1060 seconds instead of 1000 seconds in the other determinations.

The results give good agreement with the determinations of DICKINSON, MUELLER, and GEORGE ('Bureau of Standards, Bull.,' 6, pp. 379–408, February, 1910).

By interpolation their result for experiment (5) would be 0·696, and for experiment (6) 0·753.

For the purposes of interpolation the relation $SN^{1/5} = 0{\cdot}9952$ was found to hold with remarkable accuracy between the concentrations 11·36 and 4 molecules to 100 molecules of water.

This equation is very similar to that for lithium chloride.

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TABLE X.

No. of solution.	Initial concentration.	Final concentration.	Mean concentration.	Mass of solution. gr.	Mass of water added. gr.	Total mass. gr.	Specific heat after dilution.	Initial temperature. ° C.	Final temperature. ° C.	Mean temperature. ° C.	Rise in temperature. ° C.	No. of calories.	Heat of dilution calories per molecule.
1	12·06	11·56	11·82	496·0	12·29	508·3	0·612	17·29	18·68	17·98	1·39	479·8	702·9
2	11·56	11·00	11·28	493·0	14·82	507·8	0·614	17·33	18·79	18·06	1·46	510·6	614·9
3	11·00	10·48	10·74	490·0	14·63	504·6	0·622	17·91	19·15	18·53	1·24	432·5	532·3
4	10·01	9·516	9·76	481·3	15·00	496·3	0·634	17·70	18·54	18·12	0·84	293·9	351·0
5	9·066	8·66	8·86	472·3	14·27	486·6	0·644	17·83	18·44	18·13	0·61	213·6	269·1
6	8·267	7·919	8·09	463·7	14·39	478·1	0·655	17·78	18·21	17·99	0·43	149·7	187·2
7	7·919	7·567	7·74	460·2	14·31	474·5	0·660	17·55	17·92	17·73	0·37	128·8	162·0
8	7·567	7·226	7·39	456·3	14·63	470·9	0·666	17·72	18·05	17·88	0·33	115·2	141·7
9	6·906	6·603	6·75	449·5	14·55	464·0	0·678	17·05	17·30	17·17	0·25	87·4	108·2
10	6·603	5·560	6·08	381·9	50·00	431·9	0·703	15·870	16·465	16·161	0·585	201·8	72·7
11	5·560	4·650	5·11	370·5	50·00	420·5	0·712	16·030	16·365	16·20	0·335	115·0	41·4
12	4·650	3·82	4·25	360	50·00	410·0	0·760	16·02	16·265	16·14	0·245	85·2	30·6
13	3·82	3·20	3·51	350·1	50·00	400·1	0·784	14·81	14·94	14·87	0·13	46·1	16·2

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No record is given of a systematic study of the variation in heat of dilution by either of these investigators.

In order to obtain numerical results, the manner in which the specific heat varies with temperature must first be found.

The temperature effect on the heats of dilution of hydrogen chloride and lithium chloride were investigated.

The experiments were more difficult to carry out owing to radiation corrections which now become a greater consideration. Also the range of temperatures for which the heat of dilution experiments were possible is limited. With concentrated hydrochloric acid no temperature above 20° C. could be attempted, and below 0° C. the water employed would, of course, freeze.

With lithium chloride solutions the maximum concentration employed at air temperatures could not be employed at 0° C. owing to the much smaller solubility of the salt. Since, therefore, only moderately strong solutions could be taken much smaller temperature changes were observed on dilution. Attempts were made to get the heat dilution of these solutions at temperatures above 30° C., but without success, owing to the small heating effect and the large radiation.

To eliminate the radiation loss the heating coil employed for the specific heat experiments was tried, but it was found impossible to regulate the temperature of the coil with sufficient delicacy. Observations were made, but failed to give consistent results on repetition.

In each specific heat and heat of dilution experiment, separate radiation-loss experiments were made, and these were checked in the following manner.

The quantity of solution to be experimented with was introduced into the vessel and its temperature raised from about −10° C. (to which it had been previously cooled), by means of the heating coil, by steps of about 5° C. to about 50° or 60° C. The rate of cooling was then plotted against temperature, and gave a curve which closely approximated to a straight line, within the range 10° C. on either side of air temperatures. The points all lay perfectly on the curve, and the curve cut the axis of temperature at a point which was found to coincide exactly with air temperature.

The regularity of this effect, and the certainty with which it could be measured, made experiments with a relatively large radiation loss quite satisfactory. Thus, in the specific heat determination of lithium chloride solution at a temperature of about 70° C., a rise in temperature by heating of 10·21° C. is observed, while the radiation loss is about 2° C.

For lithium chloride only one concentration of solution was attempted, as the results only showed a small change in heat of dilution; and moreover with the concentrations less than that employed the heating effect is so small, since in both solutions it falls off very rapidly as the concentration is diminished.

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The following specific heats were obtained for hydrochloric acid :—

Concentration molecule per 100 molecules.	Temperature.	Specific heat.
	° C.	
23·75	− 3·87	0·589
	11·94	0·583
	17·05	0·585
14·9	− 4·03	0·657
	1·30	0·647
	16·25	0·651
10·44	− 3·92	0·722
	5·89	0·715
	19·78	0·718
	24·01	0·732
	28·07	0·751

The above table shows that at about air temperatures very little change occurs in the specific heat of concentrated hydrochloric acid solutions.

Even allowing for possible errors of experiment there is evidence of a minimum value whose position lies between 5° C. and 15° C.

The above results are consistent with those previously obtained at an average temperature of 9·92° C. Thus for concentration 23·75 the specific heat by interpolation is 0·583; for concentration 14·9 the value is 0·648; and for concentration 10·44 it is 0·711.

The values employed in the subjoined table of heats of dilution were derived from the above tabulated values by interpolation.

The process of equalisation of temperatures before mixing water with the solution was performed as nearly as possible before the pipette was immersed in the solution. After immersion the pipette was left for some hours and the solution was continuously stirred by the propeller stirrer, driven at a high speed.

The process of mixing of water and solution was allowed five minutes to complete, and during this interval the radiation correction was applied. It was always found that after that period the temperature changes were always those which would be foretold by the previous radiation experiments.

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The following values of heat of dilution were obtained for hydrochloric acid :—

Concentration.	Temperature.	Heat of dilution per molecule of water added.
	° C.	
22·23	2·12	510·5
	9·61	551·6
	20·00	581·3
18·85	3·57	455·9
	20·00	498·7

In both cases, therefore, the heat of dilution rises with temperature, and the mean coefficient of increase with temperature is greater for the concentrated solution than for the dilute one, between the extreme ranges of temperature.

Lithium Chloride.

The specific heats of a solution of lithium chloride were found in the same manner as those of hydrogen chloride. It is possible, however, to employ higher temperatures than in the above case. On the other hand, the strongest solutions could not be used at the low temperatures owing to the solution becoming saturated.

At the highest temperatures radiation becomes far more prominent, and larger heating currents were employed. The solutions were heated for 1000 seconds.

The following table gives the specific heats of a solution of lithium chloride (concentration 18·8) at various temperatures :—

Temperature.	Specific heat.
° C.	
− 0·99	0·688
12·65	0·718
21·67	0·739
35·79	0·780
41·19	0·792

The specific heat increases rapidly with temperature, the relation between them being nearly a linear one. Heats of dilution for a solution of concentration 14·2 molecule per 100 molecules are here quoted.

Temperature.	Specific heat.	Heat of dilution.
° C.		
2·13	0·734	221·6
5·98	0·742	218·5
22·04	0·800	221·5

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It is evident that although the thermal capacity of the solution may change rapidly with temperature the heat of dilution suffers very little change.

(9) Examination of Thomsen's Results.*

In most of Thomsen's experiments the ranges of concentration are not such as make the results comparable with those quoted above.

There are, however, a few substances such as sulphuric acid, nitric acid, and hydrobromic acid, other than the above substances, in which a series of results are obtained at high concentrations.

Thomsen finds a hyperbolic relation between total heats of dilution and concentration. With the first two acids named this relation is of the form

$$Q = \frac{aN}{N+b}$$

where a and b are constants and N = number of molecules of water to one molecule of acid.

The heat of dilution at any given concentration then becomes

$$\frac{dQ}{dN} = \frac{ab}{(N+b)^2}.$$

This form of relation cannot be applied to other substances such as hydrochloric acid and sodium hydroxide. In the latter case the heat of dilution changes sign when the solution is very dilute. The varying thermal changes observed at higher dilutions for several substances, suggests that these solutions are more complex than the stronger ones.

Moreover experimental difficulties prevent the measurement of these quantities with sufficient accuracy to warrant their use for deriving a general equation to represent the thermal changes for all concentrations.

An attempt is therefore made to analyse the results for stronger solutions only, and it will be found that the relation $Q = a \log_e N + bN + c$ holds well under these conditions.

(1) *Sulphuric Acid.*

From Thomsen's values of Q for N = 1, N = 2 and N = 5 respectively, the equation is

$$Q = 4666 \log_e N - 196\ N + 6595.$$

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* 'Thermochemische Untersuchungen.'

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The accuracy with which this can be applied is comparable with that of **Thomsen's** formula—in fact the accuracy is greater if the most dilute solution is ignored.

Concentration molecules of water to 1 molecule of acid (N).	Results by experiment. (Q).	By calculation.	
		Thomsen's equation.	New equation.
1	6,379	6,383	6,379
2	9,418	9,428	9,418
3	11,137	11,108	11,114
5	13,108	12,840	13,108
9	14,952	14,883	15,061
19	16,256	16,315	16,587
49	16,684	17,270	14,931

The equation for heat of dilution now becomes

$$\frac{dQ}{dN} = \frac{4666}{N} - 196.$$

Plotting dQ/dN and $1/N$ thus gives a straight line which cuts the axis at $N = 23{\cdot}8$, which is nearly $H_2SO_4 . 24H_2O$. (Diagram II.) The suggestion might be made, therefore, that accepting the linear relation between Q and $1/N$, the heats generated were such as if the true solvent were $H_2SO_4 . 24H_2O$ instead of pure water.

(2) *Nitric Acid.*

Thomsen gives six results for Q with solutions diluted down to five molecules of water.

Taking three of the values

$$N = \tfrac{1}{2}, \qquad N = 2{\cdot}5, \qquad \text{and} \qquad N = 5,$$

the equation derived is

$$Q = 2099 \log_e N - 18\, N + 3437.$$

By reference to the preceding equations the low value of the coefficient of N corresponds to $\frac{2099}{18}$ molecules of water in the limiting case where dQ/dN vanishes. A further equation derived from $N = \frac{1}{2}$, and $N = 5$, which assumes the coefficient of N to vanish, gives quite as satisfactory a relation, if allowance for experimental errors is made.

Here

$$Q = 2020 \log_e N + 3406.$$

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Values of Q derived from these two equations are shown in the table (columns 3 and 4). THOMSEN's results derived from the relation

$$\frac{N \times 8974}{N + 1{\cdot}737}$$

are shown in column (5).

Concentration molecule of water to 1 molecule of acid (N). (1)	Values of Q.			
	By experiment. (2)	By calculation.		
		New equation (1). (3)	New equation (2). (4)	THOMSEN'S equation. (5)
0·5	2005	2005	2005	2008
1·0	3285	3419	3406	3285
1·5	4160	4153	4225	4160
2·5	5276	5276	5258	5301
3·0	5690	5641	5625	5710
5·0	6655	6655	6655	6668

THOMSEN quotes results for concentration below $HNO_3 . 10H_2O$, but for them neither of the above formulæ holds. Referring to the simpler equation here adopted good agreement is obtained except for N = 1 where an error of about 3·5 per cent is shown.

The heat of dilution at any given concentration is now given by

$$\frac{dQ}{dN} = \frac{2020}{N},$$

i.e., with slight error the heat of dilution is proportional to the concentration. (Diagram II.)

Developing a similar argument to that employed for sulphuric acid, there will be no limiting hydrate formed.

(3) *Hydrobromic Acid.*

THOMSEN gives six values for total heat of dilution for various concentrations of hydrobromic acid. The last of the series is for a weak solution, and is ignored. The equation is derived from the concentrations N = 3 and N = 6, is

$$Q = 3356 \log_e N + 12{,}222.$$

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The following table shows the good agreement obtained :—

Concentration molecules of water to 1 molecule of acid.	Values of Q.	
	By calculation.	By experiment.
2	13,817	13,860
3	15,910	15,910
5	17,622	17,620
6	18,250	18,250
10	19,949	19,100
100	—	19,910

Thomsen does not quote an expression for this acid. It is seen as before that the above type of equation gives good agreement over those ranges in which heat is most generated, and therefore most accurately measured. As with nitric acid, no limiting hydrate appears to be formed since

$$\frac{dQ}{dN} = \frac{3356}{N}.$$

The graph for this relation is shown in Diagram II.

(4) *Acetic Acid.*

This solution differs from all the others since the heat of dilution for the highest concentrations is negative, acquires a minimum value, rises to zero and for dilute solutions becomes positive.

The results do not lend themselves to either of the forms of equation used by Thomsen. Results are quoted for concentrations between $CH_3 . COOH . \frac{1}{2}H_2O$ and $CH_3 . COOH . 8H_2O$. The greatest measurable thermal changes occur in this range.

An equation is developed by the method of least squares, and found to be

$$Q = -63{\cdot}49 \log_e N + 40{\cdot}84\, N - 194{\cdot}09,$$

and the table here given shows the order of agreement between experimental results and those calculated.

Concentration molecules of water to 1 molecule of acid (N).	Values of Q.	
	By calculation.	By experiment.
0·5	−129·7	−130
1·0	−153·1	−152
1·5	−158·6	−165
2·0	−156·4	−156
4·0	−118·6	−111
8·0	+ 0·37	− 2

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THOMSEN must have experienced great difficulty in measuring accurately such small quantities of heat, and the variation of the calculated from the experimental values are well within the limits of his possible experimental errors.

The limiting concentration is in this case well within the range over which the linear relation holds. Thus the heat of dilution

$$\frac{dQ}{dN} = -63{\cdot}49\left(\frac{n}{N} - \frac{40{\cdot}84}{63{\cdot}49}\right).$$

The second term within the brackets has very nearly the value $\frac{2}{3}$ and corresponds to

$$2CH_3 . COOH . 3H_2O, \qquad \text{or} \qquad CH_3 . COOH . 1{\cdot}5H_2O.$$

Values of dQ/dN are obtained from concentration $0{\cdot}5H_2O$ to $8H_2O$. The negative values are obtained while there is excess of acid added to the critical hydrate $2CH_3 . COOH . 3H_2O$, and the positive values when there is excess of water.

DUNNINGTON AND HOGGARD'S RESULTS.*

A series of determinations of heats of dilution for different strong solutions, were made by the above investigators. They made saturated solutions of various salts, and then added water until some whole number of molecules of water was associated with each molecule of the salt. Then one or two molecules of water were further added, and the heat generated or absorbed quoted.

A solution of ammonium acetate was taken in three molecules of water. Heat was generated throughout the process of dilution. The results quoted show a distinct break in continuity between solutions containing from six to eight molecules of water.

Lithium chloride is the only other solution which generates heat to any extent on dilution. These results have already been compared with those obtained above.

One solution only is given with values extending over a range of concentrated solutions, in which heat is absorbed. This is ammonium nitrate solution. The initial and final concentrations are quoted in columns I. and II. in the subjoined table, expressed in molecules of water (N) to one molecule of solution. The heat generated was quoted as in column III., using the same type of relation as that previously adopted for this heat.

$$Q = a \log_e \frac{N_2}{N_1} + b\,(N_2 - N_1).$$

Values of a and b are thus formed for the range of solutions between $N = 3$ and $N = 12$. They are

$$a = -1172 \qquad b = +48{\cdot}77.$$

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* 'Amer. Chem. Journal,' vol. 22, p. 211.

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Column IV. shows the calculated value, which it may be noted compares most favourably with Column III.

I. Initial concentration. N_1.	II. Final concentration. N_2.	III. Experimental values. Q.	IV. Calculated values.
3	4	− 290	− 288·9
3	5	− 495	− 502·4
3	6	− 667	− 668·9
3	8	− 911	− 914
3	10	− 1105	− 1075·4
3	12	− 1241	− 1201

The equation for heat of dilution is

$$\frac{dQ}{dN} = -\frac{1172}{N} + 48{\cdot}77$$

and applies most accurately for concentrations from $NH_4NO_3 . 3H_2O$ and $NH_4NO_3 . 10H_20$, after which it shows a similar divergence to that exhibited by the other concentrated solutions.

Here we have a case of a solution giving negative heats of dilution ; yet the same relation may still be applied. The extrapolated value of dQ/dN vanishes when $N = 24{\cdot}01$, suggesting a solution of limiting concentration $NH_4NO_3 . 24H_2O$. This may be interpreted in a similar manner suggesting that the first effect of adding water is to produce this solution, and that we are really diluting solutions, with another weak solution, not water, of strength $NH_4NO_3 . 24H_2O$.

(10) Conclusion and Summary.

To sum up, the following equations can be quoted for heats of dilution for strong solutions.

(1) Hydrochloric acid ($N < 10$)

$$\frac{dQ}{dN} = \frac{4082}{N} - 272{\cdot}1.$$

(2) Nitric acid (Thomsen) ($N < 6$)

$$\frac{dQ}{dN} = \frac{2020}{N}.$$

(3) Sulphuric acid (Thomsen) ($N < 15$)

$$\frac{dQ}{dN} = \frac{4666}{N} - 196.$$

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(4) Hydrobromic acid (THOMSEN) ($N < 10$)

$$\frac{dQ}{dN} = \frac{3356}{N}.$$

(5) Acetic acid (THOMSEN) ($N < 10$)

$$\frac{dQ}{dN} = -\frac{63{\cdot}49}{N} + 40{\cdot}84.$$

(6) Sodium hydroxide ($N < 6$)

$$\frac{dQ}{dN} = -\frac{7840}{N} - 980.$$

(7) Lithium chloride ($N < 6$)

$$\frac{dQ}{dN} = \frac{6968}{N} - 871.$$

(8) Ammonium nitrate ($N < 10$)

$$\frac{dQ}{dN} = -\frac{1172}{N} + 48{\cdot}77.$$

The following table of heats of dilution can thus be drawn up:—

Molecules of water to 1 molecule of acid. N.	Values of $\frac{dQ}{dN}$.				
	HCl.	H_2SO_4.	HNO_3.	HBr.	$CH_3 . COOH$.
1	—	4470	2020	(3356)	− 22·7
2	—	2137	1010	1678	+ 9·1
3	(1089)	1359	673	1118	19·6
4	749	970	505	839	25·0
5	544	737	404	671	27·1
6	408	581	(336)	559	30·2
7	311	470	—	479	31·8
8	238	387	—	419	32·9
9	182	322	—	373	—
10	—	271	—	336	—

The quantities within the brackets are extrapolation values.

The following general conclusions may be drawn from the above facts:—

(1) That, in spite of the varying thermal effects obtained on diluting different solutions, these effects may be expressed in a simple manner for the range over which the solutions may be considered concentrated;

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(2) That when the solutions become more dilute they, at the same time, become more complex;

(3) That those thermal changes occur in strong aqueous solutions, which suggest that the solute is dissolved, not in water, but in some definite hydrate of the solute, in general containing a large number of molecules of water.

In special cases, however, such as that of acetic acid, the water molecules may be few in number, while with nitric and hydrobromic acids the solvent becomes pure water.

(4) That calcium chloride does not show the effect in so marked a degree, probably because it is impossible to work with solutions of the same relative strength.

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