CCCCXXIII.—*The Heat of Solution of Sodium Car-
bonate and the Specific Heats of its Solutions.*

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IN connexion with technical calculations involving thermal pro-
perties of sodium carbonate solutions, it was necessary to construct
a suitable calorimeter in which specific heats of solutions or solids
and heats of solution or dilution could be determined with moderate
rapidity and an over-all accuracy of 0·5%.

Most of the accurate work on the specific heats of inorganic salts and heats of solution has been carried out at about 20°, but in technical practice data are often required at or above 120°. As these cannot be obtained from the published results at the lower temperatures, practical determinations are necessary.

Many high-precision calorimeters of the adiabatic type have been used with dilute solutions of inorganic salts, and the aim of the present work was to employ the adiabatic principles in devising a conveniently manipulated calorimeter which could be operated with greater speed, at higher concentrations of solution, and at temperatures at which evaporation had to be avoided. The calorimeter to be described, therefore, represents a compromise between high accuracy and convenience of operation. As well as being convenient in use and readily adaptable, it gave results accurate to within 0·5%, which was sufficient for the purposes required ; and much thermochemical work has been carried out with it between 10° and 500° but mainly below 120°.

The results obtained with sodium carbonate solutions are given as an extension of the temperature range over which such data exist, and as illustrating the working of the calorimeter. Although these results are less accurate than those which have been obtained at lower temperatures and greater dilutions by the use of calorimeters of high precision, they provide new data over a range of concentrations and temperatures in which the published results for well-known salt solutions are extremely meagre.

<center>E X P E R I M E N T A L.</center>

Since the data required of the calorimeter were to include the variation of specific heat of substances with temperature, it was necessary to adopt a method by which a trustworthy result might be obtained from only a small temperature interval. Many specific-heat data have been obtained by the cooling-curve and the mixture method, and, as these can only give a mean specific heat over a considerable temperature range, the variation with temperature is largely obscured. Further, as it was desired to work with solutions of high vapour pressure, it was essential that the surroundings of the liquid under investigation should never be at a lower temperature than that of the liquid itself, for otherwise the vapour would condense on the cooler parts of the apparatus and the heat thus lost by evaporation from the liquid would cause a large error in the calculation of the specific heat.

It was necessary, therefore, to use some form of the adiabatic method, in which the calorimeter containing the solution is entirely surrounded by, but thermally insulated from, a jacket which,

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throughout an experiment, can be kept at the same temperature as the solution. In this way all heat interchange between the calorimeter and its surroundings is reduced to a minimum, and the inaccuracies of calculation of the heat losses such as occur in the older methods are avoided.

Many workers, particularly Richards and Rowe (*J. Amer. Chem. Soc.*, 1925, **47**, 1876), Williams and Daniels (*ibid.*, 1924, **46**, 907), and Cohen and Moesveld (*Z. physikal. Chem.*, 1920, **95**, 305), have used various forms of adiabatic calorimeters and high accuracies have been obtained. Although most of such work has been confined to temperatures of the order of 20°, yet the method is readily applicable to work at higher temperatures, and the calorimeter used in the present work has been designed on lines developed by the above workers, with modifications which increase the temperature range and speed of working whilst still giving sufficient accuracy for all practical purposes.

During the progress of the work the calorimeter has been modified in various respects, but a brief outline of its original form is given before its final form is described.

Original Apparatus.—The first series of determinations consisted of an investigation of the change of specific heat of sodium carbonate solutions with temperature, and the apparatus was closely similar to that described by Cohen and Moesveld, embodying adiabatic control, electric heating, and the use of calibrated Beckmann thermometers.

In order to avoid attack by corrosive liquids, for which specific-heat data were required, all the internal parts of the calorimeter were of carefully gilded silver, manufactured by Messrs. Johnson, Matthey and Co., Ltd.

The inner calorimeter was contained in, and thermally insulated by an air gap from, an enclosing cylinder, the top of which was fitted with openings and vertical tubes so placed as to receive the thermometer, stirrer, heater, etc. This cylinder was immersed in a larger tank of oil, which constituted the adiabatic bath and could be heated and its temperature controlled by means of a Cressall resistance heater immersed in the oil and connected to the supply mains through an adjustable resistance. Efficient stirring of the oil was obtained by means of an Archimedes screw stirrer, and the whole was insulated from the air by means of an outer jacket containing loosely packed asbestos.

The stirrer in the inner calorimeter consisted of a glass shaft carrying three propeller blades, its upper portion being cemented into a brass tube which passed through a small pressure gland attached to the top of the enclosing cylinder. The type of heater

originally used consisted of a rectangular piece of mica on which was wound the nichrome resistance wire. This was encased in a rectangular sheath of gilded silver which was filled with sperm oil so as to reduce the lag.

The temperatures of the inner calorimeter and of the outer bath were observed by means of two Beckmann thermometers which had been calibrated by the National Physical Laboratory to within 0·005°, the corrections varying from about 0·5% at 20° to 5·0% at 90°. Although this arrangement gave satisfactory results, the necessity for setting the thermometer for each experiment and the application of the thermometer corrections were troublesome, and it was realised that a platinum resistance thermometer would be much more suited to calorimetric work, particularly at temperatures over 100°.

Later Apparatus.—In designing the second calorimeter, attention was paid to the possibility of working on substances other than sodium carbonate at temperatures up to 500°, at which the apparatus has proved to be quite satisfactory. This calorimeter, which has given numerous results accurate to within 0·5%, combines the essential features of the above-mentioned high-precision calorimeters with rapidity and ease of working.

The chief modifications were intended to increase the range of the apparatus, and included the replacement of the two Beckmann thermometers by a resistance thermometer and a differential thermocouple; the heater was replaced by one of another type, and a smaller and more easily handled outer tank was used.

The apparatus is shown in Fig. 1. The solution under investigation was contained in a silver beaker, *A*, 7·0 cm. in diameter and 20·0 cm. high, supported by a small Pyrex-glass tripod, *B*, from the base of the enclosing steel cylinder. Three wedges of asbestos or bakelite served to hold the upper portion of the beaker rigidly in the centre of the cylinder. The size of the outer cylinder was such that the beaker was separated from it at all points by an air gap 1·5 cm. in width. The rim of the outer cylinder was provided with a carefully machined flange, *C*, to which the top of the cylinder could be attached by means of six steel bolts, *D*. This top was fitted with vertical steel tubes, *E*, 13·5 cm. high, so placed that the glass tubes supporting the heater, thermometer, thermocouples, etc., passing through them, were suitably disposed in the inner calorimeter. The outer cylinder was immersed in a mild-steel tank, *F*, 28·5 cm. in diameter and 50·0 cm. high, containing the adiabatic liquid which was chosen according to the temperature range of the experiment. For temperatures up to 150°, oil was used, and above this temperature an equimolecular mixture of potassium nitrate and sodium

nitrate was found very satisfactory. The depth of immersion of the calorimeter in the tank was such that its top was 10·5 cm. below the

FIG. 1.
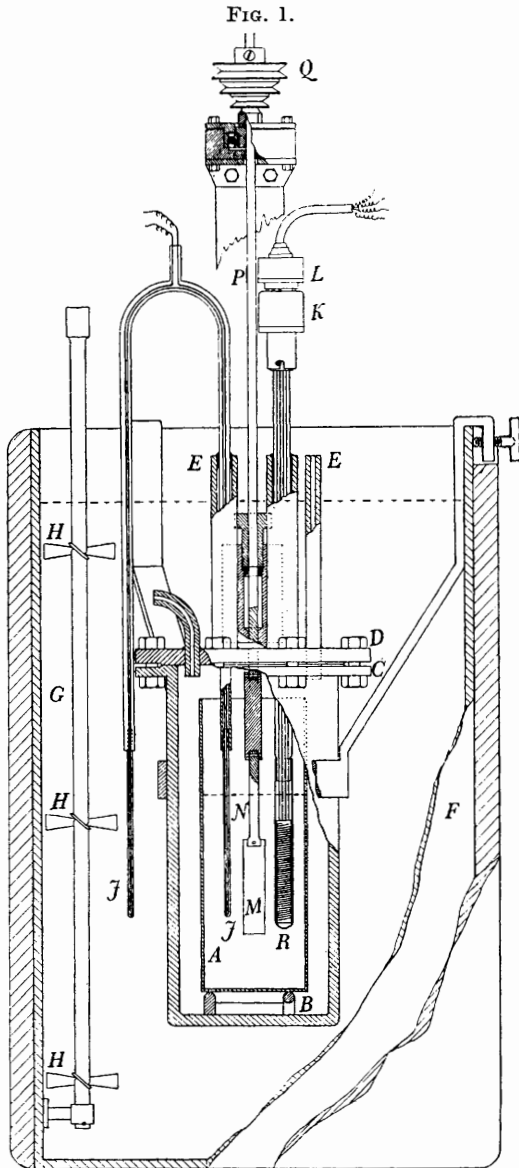
liquid surface, the vertical steel tubes thus projecting by 3·0 cm. Electric heating was provided by winding the outer curved surface

of the tank with nichrome ribbon, and this was well lagged by means of a thick covering of a hard-baked paste composed of powdered asbestos, kieselguhr, and sodium silicate solution. Gas heating was also provided, the tank being supported at a convenient height by a large tripod welded to the tank and to a heavy iron base-plate.

Efficient stirring of the liquid in the tank was obtained by means of a shaft, G, fitted with three pairs of blades, H. The temperature of the bath when working in the neighbourhood of 30° did not vary from point to point by more than 0·03°. The stirrer revolved in a cycle-hub bearing attached to the rim of the outer tank by means of a welded support, and was driven through a spring belt from the motor used to operate the stirrer in the inner calorimeter.

The main features of the apparatus are described in the following sections.

(1) *Adiabatic control.* Equality of temperature of the inner calorimeter and of the liquid in the tank was indicated by means of a single differential thermocouple, JJ, instead of by the observation of the two temperatures, as in the original apparatus. The couple was of 26 S.W.G. copper–constantan, one element being placed in the inner calorimeter and the other in the outer tank. The free ends of the couple were connected to flexible copper wire, the connexion being kept at 0° by immersion in oil-filled test-tubes embedded in powdered ice contained in a Dewar vessel. The flexible wire was connected to a galvanometer of the D'Arsonval type mounted in a suitable position together with a lamp and scale. This arrangement gave sufficiently sensitive control, a deflexion of 0·5 mm. corresponding to a temperature difference of 0·004°. This deflexion could be observed and corrected by the adjustment of one of the gas burners under the calorimeter tank.

For work at low temperatures (below 50°), the lag of the couples was minimised by the use of thin silver sheaths 0·35 cm. in external diameter and 12·8 cm. long. The couple was insulated with double windings of silk, and fitted into the sheath with very little clearance. The space between the sheath and the couple was then filled with oil.

The element in the inner calorimeter passed through a glass tube which was cemented into one of the vertical pipes attached to the lid of the cylinder. The glass tube was of such internal diameter as to receive the open end of the silver sheath which was held in this position by cement, and its height was adjusted so that 3·0 cm. of the sheath projected from the liquid when filled to a fixed point in the calorimeter. As the distance between the surface of the liquid and the top of the enclosing cylinder was 9·5 cm., there was a length of 4·5 cm. of glass tube which gave efficient thermal insulation between the liquid and its surroundings.

(2) *Temperature measurement.* Having secured satisfactory adiabatic control, it was necessary only to measure the temperature of either the inner calorimeter or the adiabatic bath, and of these the former was preferable. For this purpose a platinum resistance thermometer of 60 ohms resistance, made by the Cambridge Instrument Co., was used. The thermometer was provided with a Pyrex sheath which passed through one of the tubes in the top of the enclosing vessel of the calorimeter, and was cemented in this at such a height that the windings of the thermometer were below the surface level of the liquid in the inner calorimeter. When corrosive liquids were used, the lower portion of the sheath was protected by a silver sleeve.

In order to avoid confusion and to facilitate connexion of the thermometer to the measuring circuit, the base of an ordinary four-pin wireless valve, K, was permanently attached to the upper end of the Pyrex sheath and the four leads of the thermometer were connected to the bases of the pins. Four-ply insulated wire was used to connect the thermometer with the measuring apparatus, which was suitably placed at some distance from the thermometer, and a valve socket, L, was attached to the end of this wire so that the thermometer could be quickly and correctly coupled without risk of reversal of the connexions.

The thermometer was used in conjunction with a differential galvanometer made by Hartmann and Braun of Frankfurt. The overlapping-shunt method of measuring the resistance of the thermometer by the use of a differential galvanometer is fully described by Jaeger (*Z. Inst.*, 1904, R. 24, 288), and the principle of this method of elimination of inequality of lead resistance is given by Glazebrook ("Dictionary of Applied Physics," Vol. II, 1922, p. 724). It possesses advantages over the potential method in that only a very small current (0·002 amp.) flows through the thermometer, and it is more convenient and much less expensive than a bridge method for the same accuracy.

The apparatus includes a precision resistance box, a variable resistance and shunts, and two damping resistances of 1000 ohms. The circuit is reversed by means of a six-pole mercury commutator, and the time required to take the five readings necessary for the calculation of the resistance is of the order of 30 secs. It is, therefore, convenient for calorimetric work in obtaining the initial and final temperatures in an experiment, and approach towards constancy of temperature is shown by observing the slow movement of the spot of light on the scale.

The resistance of each coil of the galvanometer was 60 ohms, and

its sensitivity 6.75×10^{-9} amp. per 1 mm. deflexion at a distance of 100 cm.

The thermometer was calibrated in the laboratory from time to time by the determination of the ice, steam, and sulphur points in the manner described by Griffiths ("Methods of Measuring Temperature," 1918, p. 51).

Though the method is not the most accurate, it possesses great advantages and is sensitive to $0.01°$ over the range 0—500°. This was sufficiently accurate for the required specific-heat work so long as the temperature range of the experiment was greater than 5°.

(3) *Calorimeter stirrer and heater.* The stirrer of the inner calorimeter consisted of a rectangular silver plate, M, $6.5 \times 1.5 \times 0.2$ cm., fitted with a silver tubular shaft, N, 6·0 cm. in length. The stirrer was rotated by means of a vertical steel shaft, P, passing through a small pressure gland attached to the top of the enclosing vessel and through a bearing above which a small brass pulley, Q, was attached to the shaft. The stirrer was driven from that in the outer bath by means of a spring belt. Connexion between the end of the steel rod, which projected 1 cm. below the top of the enclosing vessel, and the silver stirrer was made by means of a glass rod 6·0 cm. in length, and in this way the silver stirrer was thermally insulated from the surroundings of the calorimeter. The metal-to-glass joint was made by means of a pin passing through a diametrical hole in the metal and glass, and the height of the stirrer was such that the liquid surface in the calorimeter was cut by the silver shaft so as to avoid splashing.

Heat was supplied to the inner calorimeter by means of an electrical heater, R, consisting of nichrome wire wound on to a cylindrical porcelain former 7·0 cm. long and 1·1 cm. in diameter and having spiral grooves which received the wire. This fitted into a silver sheath 11·5 cm. long, and was insulated from it by means of a thin lining of mica. The heater was supported at the proper height by means of a Pyrex tube, which fitted tightly into the open end of the silver sheath. This tube passed through, and was cemented into, a steel tube fitted to the lid of the enclosing vessel. Two insulated copper leads were attached to each end of the nichrome wire and passed through the Pyrex tube, at the upper end of which they could be connected to the external circuit by means of a valve socket and base, as in the case of the thermometer.

The heater had a resistance of 7·10 ohms, had a small lag, and was very satisfactory in continued use. Ten 2-volt secondary batteries of large capacity supplied the current to the heater, and the energy so supplied was determined in the usual manner by the measurement

of the fall in potential across the heater and across a standard resistance in series with it. This measurement was made by means of a multi-range potentiometer, and the period during which the current flowed through the heater was noted by means of a Venner time switch reading to 0·01 sec.

By means of a reversing switch, it was possible to pass the current through a dummy heater of the same resistance as the actual heater, and this was done for a period of about an hour before commencing an experiment. The switch was then quickly reversed, and the current through the heater found to be very steady. Readings of the potential drop across the heater and across the standard resistance were taken at intervals of one minute during an experiment so that the energy supplied was fully recorded, and this was probably the most accurate of the measurements involved in an experiment.

The four current and potential copper leads from the heater constituted the most important source of thermal leakage between the calorimeter and its surroundings, but as the length of the wires between the surface level of the liquid in the calorimeter and the top of the enclosing vessel was 9·5 cm., and as the adiabatic control was sensitive to 0·01°, the leak was always small.

The heater was used in all experiments with the same length of the silver sheath projecting above the liquid, although trials have shown that this length may be varied considerably without significant alteration of the water equivalent.

(4) *Method of introduction of liquids and solids into the calorimeter.* In the determination of heats of dilution, the concentrated solution was contained in the inner calorimeter, and the water in a glass flask 25·0 cm. long and 5·5 cm. in diameter, which was submerged in the outer bath. This flask was provided with an internal central tube which emerged at the top and through which the water could be forced by means of compressed air through a second tube. The outer end of the first of these tubes was connected by a short piece of tube to a pipe in the lid of the enclosing vessel. A glass tube was attached to the lower end of this pipe 1 cm. below the top of the vessel, and served to lead the water to the bottom of the solution in the calorimeter. As the heat of dilution of sodium carbonate solutions was carried out at 30°, it was unnecessary to work with a completely enclosed calorimeter, and an opening was provided by means of which excess air pressure in the calorimeter was avoided on forcing the water over.

A triple differential thermocouple was used in these experiments, one element being placed in the calorimeter, the second in the outer bath, and the third in the flask containing the water. In this manner equality of the three temperatures was established before the

dilution was carried out. By the measurement of the rise or fall of temperature, and from a knowledge of the specific heat of the diluted solution, the heat of dilution at the datum temperature was obtained. The amount of water introduced was checked by analysis of the final solution.

In the measurements of heats of solution, the method adopted consisted in placing the solvent in the inner calorimeter at the datum temperature and introducing the solid also at that temperature. The method of introduction varied with the temperature at which the determination was required. At low temperatures, *e.g.*, in the measurement of the heat of solution of sodium carbonate in water at 30°, the necessary amount of the pure dry salt was contained in a silver beaker which was lowered into the outer bath of the calorimeter. When the temperature of the solid, as shown by a thermocouple, was uniform and equal to that of the inner calorimeter to within 0·1°, the beaker was removed from the adiabatic bath and its contents quickly poured into the calorimeter through the steel tube which ordinarily supported the electric heater. With substances such as sodium carbonate, the necessary correction involved in this procedure was small, the heat conductivity being low and the time of exposure to the air very short.

The introduction of the carbonate into the water was preferable, for it avoided the caking which, as is well known, occurs with the reverse order of mixing.

In the measurement of heats of solution at high temperatures, the heater was removed from its steel tube in the top of the enclosing vessel, and the tube fitted with a small steel cone which closed its lower end and was supported by means of a thin central rod held in position by a small spring. The tube was filled with the solid to within 1 cm. below the level of the liquid in the outer bath, and when the temperature of the solid, as shown by a small thermocouple, was uniform and approximated closely to that of the inner calorimeter, the spring was depressed and the solid allowed to fall into the water contained in the calorimeter.

Experimental Procedure.—In order to illustrate the procedure adopted, the case of a specific-heat determination may be considered. The solution in question was heated in the silver calorimeter to a temperature slightly higher than that at which the determination was required. The calorimeter was then assembled and immersed in the outer bath, which had been heated to approximately the datum temperature.

When the temperature of the solution was sufficiently near to the datum temperature, that of the outer bath was carefully adjusted so that the temperature of the solution remained constant over a

period of 10 minutes. The mean deflexion (d), during this time, of the galvanometer in the differential thermocouple circuit was observed, and was maintained as constant as possible throughout the experiment. This small deflexion was made up of those corresponding to (i) the slight differences between the calibration curves of the two thermo-junctions and (ii) the thermal head necessary to compensate for heat conduction from the inner calorimeter. In all experiments the latter was very small, the rate of cooling of the inner calorimeter when the inner and the outer temperature were identical being scarcely perceptible. This was partly due to the compensation of heat losses by the generation of heat by the inner stirrer, which was rotated at a constant speed in clear solutions of 100 r.p.m.

After maintaining the constant temperature for 10 minutes, the temperature of the inner calorimeter was determined carefully by means of the resistance thermometer, the current from the secondary battery switched over from the dummy to the actual heater, and the time switch started. While minute readings of the potential fall across the heater and the standard shunt were being taken, the temperature of the outer bath was controlled so as to maintain as closely as possible the deflexion (d) of the galvanometer.

When the rise of temperature was sufficient to give the desired accuracy on the two thermometer readings, the heater was switched off and the calorimeter allowed to attain a steady final temperature, which was determined by the resistance thermometer. The temperature usually rose slowly for a period of about 90 secs. after switching off, and then became constant. During the experiment the outer bath was alternately slightly hotter and colder than the inner calorimeter, but it was possible to keep the differences small $(0.07°)$ except in heat of solution experiments, in which the change in temperature was very rapid. The galvanometer deflexion (D) was noted at one-minute intervals, and values of $(D - d)$ recorded. At the end of the experiment these values were summed algebraically, and with practice it was possible to keep this net thermal head $(\Sigma[D - d])$ very small.

The adiabatic correction to be applied in the calculation of the result was obtained by multiplying the net thermal head by the "radiation constant," which was found by observing the rate of rise in temperature of the inner calorimeter when the thermal head was maintained at 1°. This constant, then, includes all heat conduction along the heater leads, etc., as well as true radiation across the air gap, and at 30° had the value $0.008°$ per degree per min. In view of the good adiabatic control, the correction to be applied was generally quite negligible.

Water equivalent. The water equivalent of the calorimeter was

determined by the use of an 11·5% solution of sodium chloride of specific heat of 0·8779 at 18°, as determined by Richards (Landolt–Börnstein "Tabellen"), and a 10·03% solution of ammonium nitrate, of which the specific heat at 32·3° is given as 0·9250 by Cohen and Moesveld (*Proc. K. Akad. Wetensch. Amsterdam,* 1924, **27**, 567).

Several determinations were made during the progress of the work, and the values obtained were within 1·5 cals. of the mean, *viz.*, 53·0 cals. per degree. This corresponds to an error of 0·3% in a specific-heat determination. In the case of the original apparatus, with which the specific heat of sodium carbonate solutions was investigated, the agreement between the water equivalent determinations was within 8 cals., which again corresponds to an error in the specific-heat values of 0·3%, the capacity of the calorimeter being considerably greater than that of the final apparatus.

The results obtained in a determination of the water equivalent are given below, as being typical of all the experiments in this work :

Initial temp. $(T_1) = 14 \cdot 382°$; final temp. $(T_2) = 22 \cdot 903°$
Temperature rise $= 8 \cdot 521°$
Net thermal head $= + 1 \cdot 3 \times 0 \cdot 07°$
∴ Adiabatic correction (to be subtracted $= 1 \cdot 3 \times 0 \cdot 07 \times 0 \cdot 008°$
    from observed rise) $= 0 \cdot 00073°$
∴ True temperature rise $= 8 \cdot 520°$
Mean potentiometer readings during experiment :
  Across standard shunt (0·2 ohm) $= 0 \cdot 3224$ volt
    ,,   heater $= 0 \cdot 3817 \times 30$ volts
  Against standard cell $= 0 \cdot 9909$ volt
  Voltage of standard cell at 20° $= 1 \cdot 0183$ volts

  ∴ Current through heater (C) $= \dfrac{0 \cdot 3224 \times 1 \cdot 0183}{0 \cdot 2 \times 0 \cdot 9909}$ amp.
$= 1 \cdot 6567$ amp.

  Voltage across heater (V) $= \dfrac{0 \cdot 3817 \times 1 \cdot 0183 \times 30}{0 \cdot 9909}$ volts
$= 11 \cdot 768$ volts

  Heat input (Q) $= CVt \times 0 \cdot 2389$ cals.
  Time of flow of current (t) $= 960$ secs.
  ∴ Q $= 4471 \cdot 3$ cals.
  Weight of 11·5% NaCl solution $= 538 \cdot 7$ g.
  Specific heat $= 0 \cdot 8779$
  ∴ Heat input to solution (Q_1) $= 4029 \cdot 6$ cals.
  ∴ Water equivalent $= (Q - Q_1)/(T_2 - T_1)$
$= 51 \cdot 8$ cals. per degree.

Results.

The specific heat of solutions of sodium carbonate has been measured at four temperatures, and the heat of solution–concentration curve determined at 30°. Very little work appears to have been done on the specific heat of these solutions with the exception of that of Thomsen (*Ann. Physik,* 1871, **142**, 337) and of Marignac ("International Critical Tables," Vol. V, p. 124) at 18°. Thomsen gives values for solutions containing 50, 100, and 200 mols. of water per mol. of sodium carbonate.

In the case of the heat of solution also, the results given in the literature are almost completely confined to the work of Thomsen at 18°

Specific Heat of Solutions of Sodium Carbonate.—The specific heat–concentration curves of sodium carbonate solutions were determined at temperatures of 17·6°, 30·0°, and 76·6°, and one measurement was made at 98·0° by means of the first calorimeter.   In all the work the sodium carbonate was A.R. material supplied by British Drug Houses, Ltd., and was heated to constant weight before being used to make up the solutions.

FIG. 2.

Solid, % by weight.
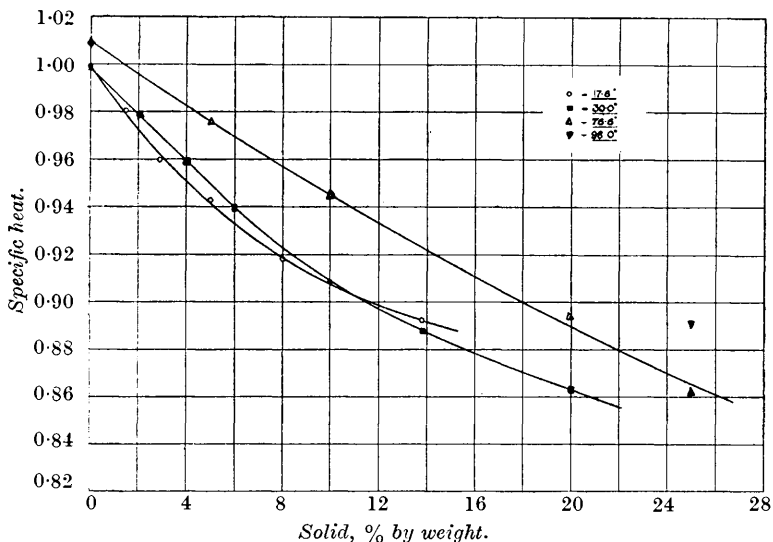
The temperature range covered in each experiment was about 4°, and the accuracy of the determinations is in general within 0·5%, and rather higher (0·3%) at the lower temperatures.   The results are given in Table I and shown graphically in Fig. 2.

It is seen that the curve for 17·6° cuts that for 30° at a concentration of 11%.   It is unlikely that this is actually the case, and the intersection is most probably due to the fact that the last point on the former curve is fairly near to the saturation concentration at that temperature.   It is possible, therefore, that a small amount of solid had crystallised out before the commencement of the experiment, in which case the heat of solution of even a very minute quantity of the decahydrate would be sufficient to give as a result a high apparent specific heat.   Although the intersection is improbable, a definite decision on the point is rather beyond the limitations of the

TABLE I.

Na₂CO₃, % by wt.	Temperature.			
	17·6°.	30·0°.	76·6°.	98·0°.
0·000	0·9992	0·9986	1·0098	1·0084
1·498	0·9807			
2·000		0·9786		
2·901	0·9597			
4·000		0·9594		
5·000	0·9428		0·9761	
6·000		0·9392		
8·000	0·9183			
10·000	0·9086		0·9452	
13·790	0·8924			
13·840		0·8881		
20·000		0·8631	0·8936	
25·000			0·8615	0·8911

apparatus, since allowance for an experimental error of 0·5% would enable the curves to be drawn without intersection.

The following equation to the experimentally determined curve at 30° was obtained :

$$S_{30°} = 0·9986 - 0·01123\, X + 0·000223\, X^2$$

where $S_{30°}$ = specific heat at 30°, and X = concentration of solution in g. per 100 g. The observed and calculated values are compared in Table II. The agreement is satisfactory, and the equation may be considered to represent the data at 30° with fair accuracy.

TABLE II.

| Conc., g./100 g. ...	0·0	2·0	4·0	6·0	13·84	20·0
Spec. heat, calc. ...	0·9986	0·9770	0·9573	0·9392	0·8859	0·8632
,, obs. ...	0·9986	0·9786	0·9594	0·9392	0·8881	0·8631
Diff. × 10⁴	0	−16	−21	0	−22	−1

The three specific heat values given by Thomsen may be compared with the 17·6° curve shown in Fig. 2. These values refer to 18° and are 0·985, 0·933, and 0·896 for solutions of concentration 2·9, 5·57, and 10·55% respectively. They are about 0·5% below those obtained at 17·6°, although the agreement would be closer if the doubtful point on the 17·6° curve were rejected.

The Heat of Solution of Sodium Carbonate and the Heat of Dilution of its Solutions at 30°.—The results of this work may be expressed in the form of a heat of solution–concentration curve, and this was determined by the measurement of a series of heats of dilution and of the heat of solution to one concentration. The sodium carbonate used was prepared as before. In all cases the weighings of the contents of the calorimeter were checked by analysis.

Two determinations of the heat of solution were carried out in which pure dry carbonate at 30° was introduced into water contained in the calorimeter at 30° in sufficient quantity to give a

solution of concentration 5·13%. The results obtained were 6·479 and 6·501 kg.-cals. per g.-mol. of sodium carbonate. They agree to within 0·3%, the mean value being 6·490 kg.-cals. per 1 g.-mol. This agreement is of the same order as that to which the specific

FIG. 3.

Concentration, g. of Na₂CO₃ per 100 g. of solution.
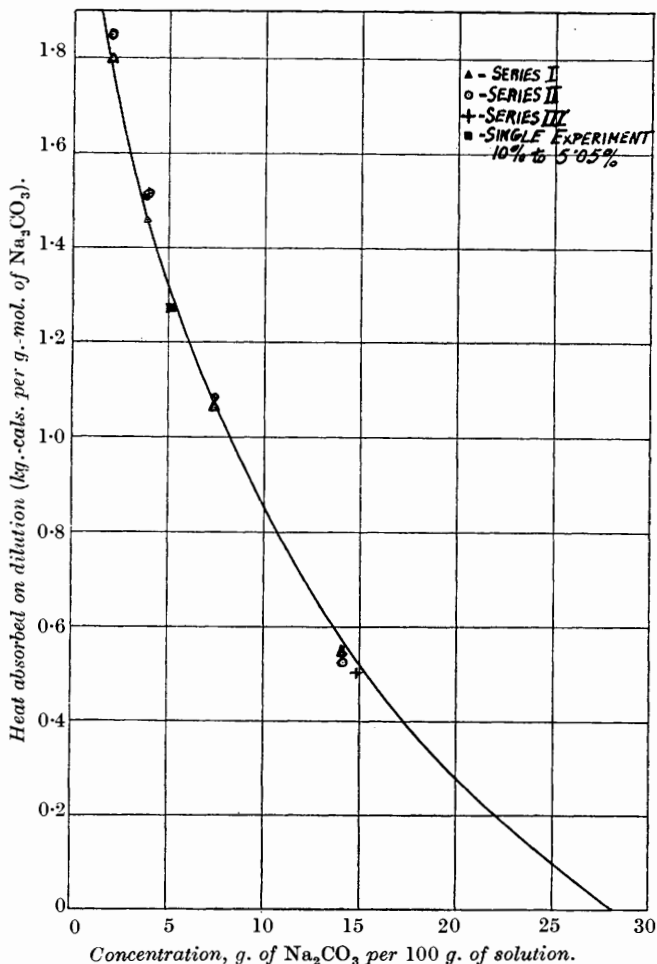
heat data were determined, and the result may be taken as being accurate to within these limits.

In the work on the heat of dilution, the fall in temperature on effecting the dilution varied within wide limits, so that the error introduced by the limitations of the thermometer, which, as previously stated, was sensitive to a change of temperature of 0·01°,

gave rise to an error in the final result which varied according to the concentration range of the experiment. The over-all accuracy of the heat of dilution curve over the complete range of concentrations, viz., 1—28·4%, is of the order of 3%. In the heat of solution curve, constructed from the dilution figures together with the experimentally determined heat of solution, this error is, of course, considerably reduced.

In the calculation of the heats of dilution at 30° from the observed fall in temperature from the datum temperature of 30°, the specific heat values used were those given for that temperature in the preceding section.

The experimental results in the heat of dilution series are given in Table III and those of the three series are embodied in Fig. 3.

TABLE III.

Initial conc., %.	Dilution range, %.	Heat of dilution, kg.-cals. per g.-mol.	
		over dilution range.	from initial to final conc.
28·24	28·24—14·04	0·5436	0·5436
	14·04— 7·43	0·5181	1·0617
	7·43— 3·87	0·3997	1·4614
	3·87— 1·97	0·3428	1·8042
28·24	28·24—14·13	0·5250	0·5250
	14·13— 7·52	0·5829	1·1079
	7·52— 3·86	0·4015	1·5094
	3·86— 1·95	0·3462	1·8556
28·40	28·40—14·96	0·5011	0·5011
	14·96— 7·53	0·5837	1·0848
	7·53— 3·82	0·4264	1·5112
10·00	10·00— 5·05	0·4260	0·4260

Discussion.

Heat of Dilution.—The experimental results plotted in Fig. 3 give the heat of dilution from 28·24% to various concentrations. From this curve the heats of dilution to various percentages have been taken, and the dilution is expressed in Table IV as g.-mols. of water added to the 28·24% solution per g.-mol. of sodium carbonate.

An equation to the heat of dilution curve has been obtained, viz.,

$$Q = -2·066\,Y/(Y + 54·8)$$

where Q = heat of dilution per g.-mol. of sodium carbonate, and Y = number of mols. of water added in diluting the 28·24% solution per g.-mol. of sodium carbonate. In cols. 4 and 5 the heats of dilution read off from the experimentally determined curve are compared with those given by the equation. The agreement is seen to be as good as the accuracy of the experimental work over the range covered.

TABLE IV.

Final conc., %.	Mols. H$_2$O per mol. Na$_2$CO$_3$.	Mols. H$_2$O added.	Heat evolved, Q.		
			Found.	Calc.	Diff., %.
28·24	14·94	0	0	0	—
25·0	17·67	2·73	−0·101	−0·098	3·0
20·0	23·56	8·62	−0·280	−0·280	0
15·0	33·38	18·44	−0·519	−0·521	0·4
10·0	53·00	38·06	−0·850	−0·848	0·25
5·13	108·9	93·96	−1·306	−1·306	0
5·0	112·0	97·06	−1·321	−1·320	0·1
2·5	229·8	214·9	−1·692	−1·648	2·5

In the above relation when $Y = \infty$, $Q = -2 \cdot 066$, *i.e.*, the heat of dilution of sodium carbonate solutions from 28·24% to infinite dilution is 2·066 kg.-cals. per g.-mol. of sodium carbonate.

FIG. 4.
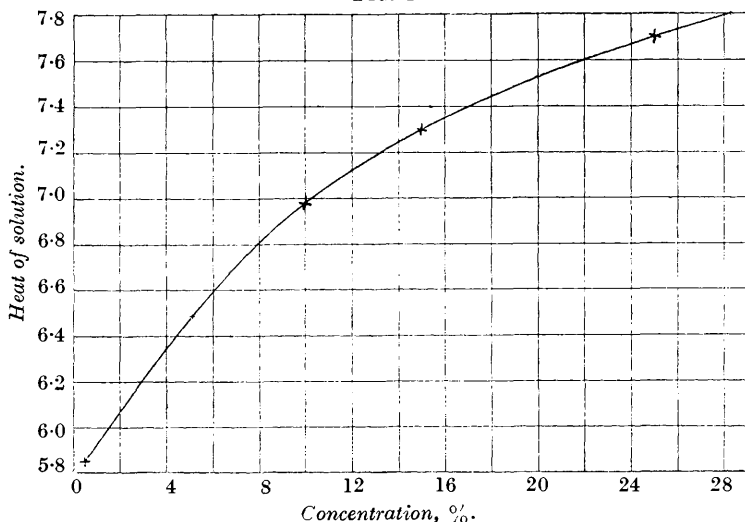
Heat of Solution to Various Concentrations.—From the heat of solution experiments, we have

Heat of solution of Na$_2$CO$_3$ to 5·13% solution = 6·49 kg.-cals. per
g.-mol. of Na$_2$CO$_3$

and from the previous table

Heat of dilution from 28·24 to 5·13%   = −1·306   ,,   ,,
Hence, heat of solution to 28·24%   = (6·49 + 1·306) ,, ,,
= 7·796   ,,   ,,

The heat of solution to any concentration below 28·24% is given by $Q = 7 \cdot 796 - 2 \cdot 066 Y/(Y + 54 \cdot 8)$ or, if Z is put equal to the number of mols. of water per mol. of carbonate in the final solution, $Q = 7 \cdot 796 - 2 \cdot 066(Z - 14 \cdot 94)/(Z + 39 \cdot 9)$.

The curve (Fig. 4) giving the heat of solution to various concentrations has been constructed by the addition to the experimentally determined heat of solution to a 5·13% solution, of the measured heats of dilution to this concentration.   In the following table these experimental values are compared with those given by the heat of

Solution, %	0·5	5·13	10	15	20	25	28·24
Heat evolved :							
Found..................	6·11	6·49	6·95	7·28	7·51	7·70	7·80
Calc.	6·15	6·49	6·95	7·27	7·52	7·70	7·80
Diff., %	0·7	0	0	0·1	0·1	0	0

solution equation; for practical purposes, therefore, the heat of solution to concentrations below 30% at 30° may be taken from the equation.

In addition to the experiments described above, a considerable amount of other thermochemical work has been carried out with this apparatus, and it is hoped to include further results concerning sodium carbonate in a subsequent publication.