299. *The Thermochemistry of Solutions. Part I. A Calorimeter for Use with Non-aqueous Solvents.*

By F. A. Askew, N. S. Jackson, O. Gatty, and J. H. Wolfenden.

This part describes two types of calorimeter appropriate to the study of the thermochemistry of non-aqueous electrolyte solutions and sufficiently sensitive for use at the low concentrations where theoretical interpretation is least difficult.

The experimental difficulties peculiar to the thermochemistry of non-aqueous solutions are attributable to the following factors: (1) the high volatility of most non-aqueous solvents, and the serious thermal effects caused by evaporation; (2) the hygroscopic nature of the solvents and of those salts which have an appreciable solubility therein; (3) the low solubility of salts in solvents other than water; (4) the inconvenience of preparing pure solvents on anything but a small scale; (5) the solvent effect of non-aqueous solvents on thermal and electrical insulators, varnishes, greases, etc.

The first two factors make it imperative that the calorimeter shall be completely sealed, and necessitate a special technique for the introduction of the salt; the third factor precludes measurements except at high dilutions, and the fourth and fifth factors together prevent the use of Lange's extremely precise differential technique.

Both the calorimeters described below are adapted from the rotating calorimeter of Lipsett, Johnson, and Maass (*J. Amer. Chem. Soc.*, 1927, **49**, 935, 1940), the notable advantages of which are that the calorimeter is completely sealed, and that a high degree of adiabatic control is so easily achieved that a calorimeter of small capacity may be used without a disproportionate increase in thermal leakage due to the increased surface/volume ratio. The principles of their calorimeter are all embodied in our own. Modifications have been made in certain details, but it is only in the design of the calorimeter for heats of solution that any essentially novel feature has been introduced. Since the difference between this calorimeter and that for heats of solution is confined to the construction of the innermost silver vessel (the calorimeter proper), these two vessels are described first, the remaining apparatus and procedure being, for the most part, common to both types of measurement.

Calorimeter for Heats of Dilution.—The calorimeter (Fig. 1) is of pure silver and has an effective capacity of about 80 c.c. The detachable end *A* has a flat ground surface which screws up flush to another flat surface on the end of the calorimeter. Two silver plugs *B*, *B*, fitting into ground sockets permit the introduction of pipettes into inner and outer compartments of the calorimeter. The plugs and the screw-end of the calorimeter are lubricated with carefully purified vaselin; sealed in this way, the calorimeter is completely liquid-tight to water, the alcohols, nitrobenzene, nitromethane, and benzonitrile, but not to acetone and benzene.

An inner vessel, *C*, also of pure silver, is mounted inside the calorimeter on two horizontal rails and serves to contain the solution to be diluted. Two alternative inner vessels are used, of capacities 30 c.c. and 10 c.c. The inner vessel can be closed by a lid, which is of pure silver for the larger vessel, and of gold for the smaller. It is designed so as to catch in the clips, *I*, *I*, after falling off during the first rotation of the calorimeter, and is held there during the remainder of the experiment.

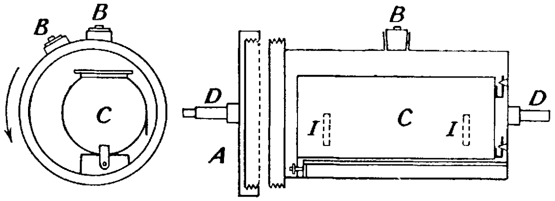
The two axles, *D*, *D*, bearing the calorimeter consist of insulating fibre; the one rests in a **U**-shaped brass bearing, and the other screws into the steel driving shaft by means of which the calorimeter is rotated.

Calorimeter for Heats of Solution.—In this calorimeter (Fig. 2) the detachable screw-in axles contain an insulating section of fibre, and the inner vessel and plugs are replaced by the valve *A*, constructed so as to enable a glass bulb *B* containing the dry weighed salt to be broken by percussion transmitted through a thin silver diaphragm *E*, 0·1 mm. thick. This bulb is held in the perforated silver cup *C* (2·8 cm. long), screwing on to the valve proper *D* (also 2·8 cm. long), which is hollow and is closed at its lower end by *E*. The cup is screwed on to the valve until the glass bulb presses against the diaphragm. A silver rod *F* rests loosely in *D* and is pressed gently against the diaphragm by a spring, held down by the nut *G*. When the bulb is in position and the calorimeter has been filled with the solvent, the valve and cup are screwed down into a valve-seating *H*, which is silver-soldered to the wall of the calorimeter. The valve screws into this seating until the ground conical head of the valve presses tightly against the sharp edge of the seating, making an unlubricated gas-tight contact of the type often used in gas-cylinders. A small hole bored through the seating allows equalisation of pressure to be maintained until the final cone-and-edge contact is established.

At the appropriate moment, a brass plunger, which normally hangs in one of the brass outlet tubes of the submarine, is allowed to fall about 8 cm. on to the projecting end of the rod *F*; the shock, transmitted through the diaphragm, breaks the bulb, and dissolution of the salt begins. The brass plunger is tipped with ebonite so as to prevent conduction of the heat to or from the calorimeter during the few seconds of contact. The heat developed by the impact is negligible.

The glass bulbs were cylindrical with flat ends, being about 1 cm. long and 0·4 cm. in diameter They were drawn out from test-tube glass; care was needed in their construction in order to obtain the requisite degree of fragility, for they must be thin enough to break under the impact of the plunger but stout enough to be screwed in tightly without breaking. Unless they are flat-bottomed, they tend to slip diagonally, without breaking, when struck by the plunger. The final drying of the salt to constant weight took place in the bulb itself, which was then sealed off.

FIG. 1.



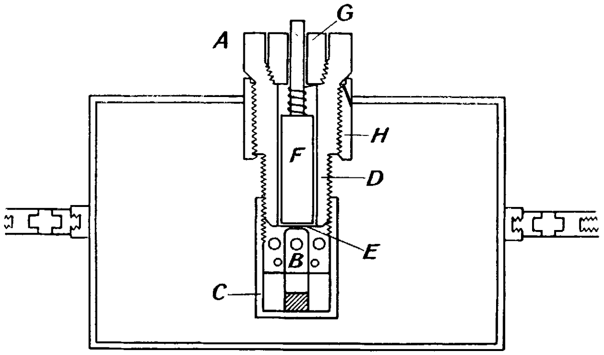


FIG. 2.

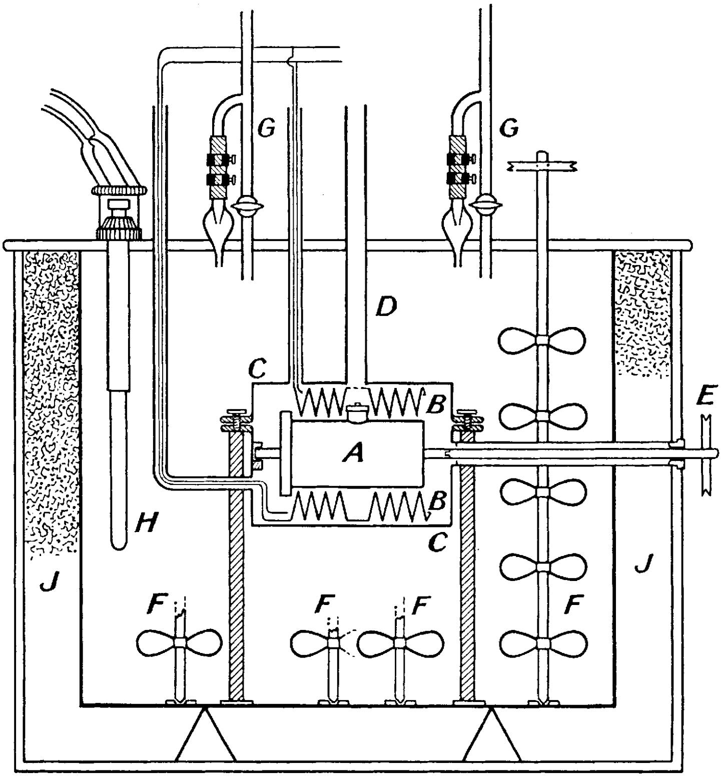
With the aid of this valve, it was possible to make satisfactory measurements of heats of solution of highly hygroscopic salts.

Auxiliary Apparatus (Fig. 3).—*The "submarine."* This consists of a copper cylinder, 11·5 cm. long and 8 cm. in diameter, divided into two flanged portions across a horizontal plane just above the axis of the cylinder. The lower portion stands on brass legs fixed to the earthenware bottom of the water-bath. The upper portion may be screwed down to this by means of screws through the wide brass flange common to both halves; this flange smeared with vaselin yields an absolutely water-tight joint. Three copper tubes soldered into the submarine carry the leads to the thermel and the plunger. A fourth tube is horizontal and carries the axle and bearings by which the calorimeter is rotated.

Rotation of the calorimeter. The calorimeter is rotated by means of a steel spindle screwed into one of its axles; the spindle is carried on bearings inside a hollow tube from the interior of the submarine to the exterior of the wooden box containing the water-bath. The outside end of the spindle bears a pulley wheel connected by means of a waxed cord to the rotation motor. Early experiments showed that with non-synchronous motors the variation of the speed of rotation of the calorimeter and the consequent variations in the heat of stirring could constitute a serious source of error. The rotation was therefore effected by a three-phase synchronous motor. A system of reducing worm gears and of pulleys ensured a constant rate of rotation of 8 r.p.m.

Water-bath. The water-bath is contained in a cylindrical earthenware vessel about 1 ft. deep and 1 ft. in diameter; this vessel is surrounded by a wooden box packed with insulating slag-wool and covered with uralite sheets, perforated to admit stirrers, drips, etc. The bath is very vigorously stirred by four stirrers, each bearing eight propellor blades. Two cans supply hot water and ice-water respectively; each supply may be delivered to the bath by a wide tube or a narrow drip so that the temperature of the bath may be maintained constant to within 0·0005° for a long period or changed by 2° or 3° in a few minutes. This degree of temperature control is only possible if the uralite cover is carefully arranged so as to reduce evaporation from the bath to a minimum.

FIG. 3.



A. Calorimeter.
BB. Thermels.
C. "Submarine."
D. Tube for plunger.
E. Pulley to synchronous motor.
FF. Bath stirrers.
GG. Water drips (hot and cold).
H. Platinum resistance thermometer.
JJ. Insulating space filled with slag wool.

The "thermel." Two thermels were installed at different times and are now used in series together. The first, consisting of eleven pairs of copper–constantan junctions, was made, as described by Lipsett, Johnson, and Maass, by soldering together alternate lengths of copper and constantan wire of 0·02 mm. diameter and rolling out the composite wire until it formed a ribbon 0·8 mm. wide and 0·03 mm. thick. This ribbon was wound in the form of a helix so that one set of junctions was about 1 mm. from the calorimeter and the other was fixed by means of shellac and de Khotinsky cement to a very thin strip of mica attached to the lower half of the submarine.

A second thermel was constructed later as described by Keefer (*Physikal. Z.*, 1928, **29**, 682); this contained 26 pairs of copper–constantan junctions made from rolled-out wire of the same dimensions as above, and was mounted in the upper half of the submarine with the aid of thin glass rods which provided the necessary rigidity. In both thermels the junctions which faced the calorimeter were coated with a mixture of platinum-black and lamp-black to increase their absorptive power.

The thermel was connected to a sensitive short-period galvanometer contained in a draught-proof box; a system of switches made it possible to place thermel and galvanometer directly in series, or alternatively, to put a resistance of 1000 ohms in series with the galvanometer and a 130-ohm damping resistance in parallel. The latter arrangement is used in the initial adjustments of bath temperature, when differences greater than 1° are to be recorded. With the former arrangement, corresponding to maximum sensitivity, 1 mm. deflexion on the galvanometer scale was found to correspond to a temperature difference of 0·0008°. Since the galvanometer spot was reflected into a reading microscope carrying a scale graduated in 0·1 mm., it was thus possible to measure temperature differences between calorimeter and submarine with a precision of 0·0001°.

Precautions against electrical leakages. Elaborate precautions were necessary to eliminate electrical leaks and stray potentials due to thermo-electric effects, more particularly in the thermel circuit. At the suggestion of Dr. Maass, the leads from the thermel and thermometer were carried on an " equipotential railway " consisting of two earthed parallel copper wires, along which transverse glass rods were fixed at intervals. On these rods, which were coated with a film of mixed paraffin wax and rubber, were laid the leads, which were all of insulated single-strand copper wire encased in rubber tubing. Soldered joints, when used to join the thermel to the leads, were arranged in pairs and carefully protected from draughts. All metal parts of the apparatus, together with a leaden sheet covering the table which bore the calorimeter and difference bridge, were connected to the same earth as the wires of the " equipotential railway." It was even found necessary for the operator to stand on an earthed shield owing to potential differences between floor and walls of the room. The switches used at first for making and breaking the galvanometer circuits were of the anti-thermo-electric " clothes-pin " type (White, *J. Amer. Chem. Soc.*, 1914, **36**, 1862). These were suspected of giving bad contacts and were replaced by spirals of copper wire, amalgamated at their tips, dipping into mercury cups drilled in an ebonite sheet. It was not until all these precautions had been developed that the galvanometer readings became completely unaffected by draughts, the switching on and off of the electric motors, etc.

Resistance thermometer and bridge. The thermometer had a resistance of 25·579 ohms, and the ratio of its resistance at 100° to that at 0° was 1·39115. It was enclosed in a silver sheath of thin blade-like form; this design has a very low thermal lag of the order of 1 sec. The resistance of the thermometer was measured on a Smith difference bridge with a precision of 0·00001 ohm, corresponding to 0·0001°. Both thermometer and bridge were standardised by the N.P.L. The bridge balance was determined by reversing the direction of the current from the bridge through a galvanometer contained in the same draught-proof box that contained the thermel galvanometer. This reversal method doubles the galvanometer deflexion if the bridge is not exactly balanced. The difference in time-lag of the thermometer and the thermel for a sudden small change in temperature of the bath is about 2 secs., the thermometer reaching equilibrium again first.

Procedure.—For heats of dilution, the inner vessel is fixed inside the calorimeter and filled from a weight-pipette with the solution to be diluted. The lid is then placed on the inner vessel, and the open end of the calorimeter screwed up. The sealed calorimeter is placed in the submarine, and the steel axle connected to the rotation motor screwed into position. The outer portion of the calorimeter is then filled with a weighed portion of pure solvent through the appropriate plug-hole, and both plugs, lightly smeared with vaselin, are inserted firmly into their sockets. The upper half of the submarine is now screwed into position, the wide flange being heavily greased.

The bath is filled with water, the calorimeter brought to 20° ± 0·1°, and the bath brought to within 0·001° of the calorimeter temperature and maintained at this for at least 20 mins. The calorimeter may now be assumed to be at a uniform temperature, and the first accurate temperature determination is made, simultaneous readings of the thermel and resistance thermometer being taken at 1-min. intervals for at least 6 mins.

The rotation of the calorimeter is then begun and maintained for 4 mins. The temperature of the bath is continuously adjusted to that of the calorimeter throughout the dilution. The rotation is then stopped, and another series of thermel–thermometer readings serves to establish the final temperature of the calorimeter after dilution. The rotation is then resumed for a second period of 4 mins., and a third series of temperature readings is made. The first temperature change corresponds to the heat of dilution, the second to the heat of stirring; from the two the corrected temperature difference due to the dilution process alone is found. Before and after the experiment the bridge-centre of the difference bridge is measured, as well as the zero reading of the thermel galvanometer.

The procedure during the measurement of a heat of solution is identical in all essential respects, except that the weighed bulb of salt and the percussion valve replace the inner vessel and its solution. The process of solution is much slower than of dilution, so longer rotation (rarely exceeding 15 mins.) is necessary to ensure complete solution.

The following example illustrates the experimental procedure for the heat of dilution of sodium perchlorate in methyl alcohol.

Wt. of $NaClO_4$ (in vac.) = 0·3774 g. = 0·003082 mol.
Wt. of initial solvent (in vac.) = 16·944 g.; initial concn. of soln. = 0·1430 mol./l.
Wt. of added solvent (in vac.) = 19·270 g.; final „ „ = 0·0666 „

Time, mins.
0 Calorimeter filled, and sealed. Temp. adjusted to *ca.* 20°.
95 Bath adjusted to within 0·001° of above temp.
135 Temp. readings begun. Below are tabulated bridge readings, each of which corresponds to two commutations of the difference bridge and is corrected for the temperature difference between bath and calorimeter registered by the thermel galvanometer.
138 27·59869 ohms 142 27·59869 ohms
140 27·59866 „ 144 27·59868 „ } Initial temp. = 19·9451°.
145 Rotation of calorimeter begun; dilution takes place.
151 Rotation stopped.
155 27·60166 ohms 159 27·60163 ohms
157 27·60164 „ 161 27·60195 „ } Temp. after diln. = 19·9744°.
162 Rotation started to determine heat of stirring.
168 Rotation stopped.
172 27·60190 ohms 176 27·60190 ohms
174 27·60189 „ 178 27·60190 „ } Temp. after stirring = 19·9769°.
185 Bridge centre = 0·80335.

Temp. change uncorr. for heat of stirring = 0·0293°.
„ „ corr. „ „ „ = 0·0268°.
Heat capacity of calorimeter and air-gap = 14·59 cals./degree.
Heat capacity of initial solution = 10·22 „
Heat capacity of added solvent = 11·55 „
Total heat capacity = 38·36 „
Heat evolved during dilution = 1·19 cals.
Heat of dilution per mol. of sodium perchlorate = 0·316 kg.-cals.

Calibration of the Calorimeters.—Heat capacity of the dilution calorimeter. The design of this calorimeter enables its heat capacity to be calculated from the masses and specific heats of the component parts. This involved measurements of the approximate specific heat of silver solder and of the fibre contained in the axles. It was assumed that one-half of each axle contributed to the effective heat capacity of the calorimeter. A further correction term was added for the heat capacity of the air in the calorimeter and in the gap between this and the submarine; it was assumed that the fraction of the air gap contributing to this heat capacity was in the ratio of the surface areas of calorimeter and submarine (*i.e.*, *ca.* 1 : 3).

The details of the heat capacity of the calorimeter, with the larger inner vessel *G*, are as follows :

Material.	Mass, g.	Sp. heat.	Heat capacity, cals./degree.
Silver	241·74	0·0559	13·515
Silver solder	1·6	0·0826	0·116
Fibre axles	0·45	0·34	0·155
Vaselin	0·11	0·6	0·06
Air			0·04
Total			13·89

If the smaller inner vessel, *H*, was used, the value was 13·41 cals./degree.

In order to check these calculations and to test the accuracy of the apparatus, the heat capacity of the calorimeter was determined experimentally by carrying out the neutralisation of sodium hydroxide by hydrochloric acid. Richards and Rowe (*J. Amer. Chem. Soc.*, 1922, **44**, 699) found the heat evolved during the reaction $NaOH + 100H_2O + HCl + 100H_2O = NaCl + 201H_2O$ to be 13,895 cals./mol. at 20°. Solutions of acid and alkali, purified and made up according to their specifications, were neutralised in the dilution calorimeter, with vessel *G*; 8 measurements, using different equivalent amounts of acid and alkali, gave 13·86 cals./degree for the heat capacity of the calorimeter. The concordance between this and the foregoing calculated value constitutes a valuable test of the precision of which the apparatus is capable.

Heat capacity of the solution calorimeter. This value, calculated in a manner similar to that described above, is 10·52 cals./degree; whereas when the calorimeter was used to measure the heat of solution of sodium chloride in water at a concentration of about $N/60$, the value obtained was 10·48 cals./degree, if the data of Lipsett, Johnson, and Maass (*loc. cit.*, p. 940) are taken as correct.

The leakage coefficient of the calorimeters. Since the temperature equality of calorimeter and submarine can never be perfectly maintained, especially during rapid temperature changes, it is important to know the thermal leakage across the 18-mm. air gap between the two. The average value of this quantity from a series of measurements was 1·12 cals./min. per degree of temperature difference between calorimeter and submarine. Such a leakage coefficient indicates virtually perfect adiabaticity during all our experiments, since the worst cases of temperature inequality (recorded during the heat of neutralisation experiments) would have produced an error of less than 0·1% in the temperature change measured. For the usual temperature changes (0·01° or less) the correction is negligible.

Tests of temperature homogeneity and completeness of mixing. Experiments were carried out to test whether the time elapsing between the assembly of the calorimeter and the dilution process was sufficient to allow the calorimeter and its contents to come to an absolutely uniform temperature. This was done by assembling the dilution calorimeter with the same liquid in both the inner and the outer vessel, and carrying out the procedure of a heat of dilution as usual. Repeated experiments with water and benzonitrile showed no sensible temperature change.

Another series of experiments was carried out with the dilution calorimeter to prove that the 4 mins.' rotation normally allowed for the dilution process sufficed for complete mixing. For this purpose, a concentrated aqueous solution of potassium nitrate, which absorbs considerable heat on dilution, was diluted in the calorimeter; if mixing were incomplete to the extent of as little as 0·5%, the positive heat of stirring during the second period of rotation would have been annulled by the heat absorbed in the completion of the process of dilution. The experiments showed that complete mixing was certainly brought about during the 4 mins.; *e.g.*, in one experiment, the temperature change on dilution was — 0·1461°; a second and a third period of rotation, also of 4 mins.' duration, after the dilution process, showed temperature rises of 0·0004° in each case.

The degree of accuracy attainable with the calorimeters. In attempting to assess this factor, it is convenient to divide the sources of error into three categories : (i) in temperature measurement; (ii) in the heat capacity of the calorimeter and its contents; (iii) miscellaneous.

(i) The Smith difference bridge is capable of reading (relative) temperatures to 0·0001°. The readings of the thermel, with which those of the resistance thermometer must be combined to establish the temperature of the calorimeter, are susceptible to greater error, principally owing to vibration in the galvanometer : any single reading might be in error by 0·0002°. Whenever the thermel readings showed vibration, at least 6 pairs of readings of thermometer and thermel were made. Statistical analysis of the standard deviations of our temperature readings suggests that the error in the mean adopted is not likely to exceed 0·0001° and is probably not greater than 0·00005°.

Any errors due to variations in the heat of stirring are minimised, in so far as the *rate* of stirring is concerned, by the use of the synchronous motor. On the other hand, in the measurement of heats of dilution an element of uncertainty is introduced by the possibility that the lid of the inner vessel may escape from the hooks designed to hold it; this difficulty rarely occurred and was always accompanied by an obviously abnormal heat of stirring, and variations in the rate of development of heat by rotation of the calorimeter rarely exceeded the errors of thermometry.

(ii) By far the greatest uncertainty in the heat capacity of the calorimeter system is that in the specific heats of the solvents, which were taken to be inappreciably different from those of the dilute solutions used. The recorded values for the specific heat of many common liquids are remarkably discordant and the accepted values cannot be trusted to less than about 2%. Since the solution constitutes three-quarters of the heat capacity of the system, this introduces an uncertainty of about 1·5% in the results in some solvents. It is unlikely that the calculated heat capacity of the calorimeter itself, confirmed as it is by experimental measurements, is in error by more than 0·1 cal./degree, *i.e.*, 0·2% of the total heat capacity. It is therefore unlikely that the absolute values of heats of solution and dilution adopted are in error from this source by more than 2%.

(iii) In the measurement of heats of solution by the glass-bulb technique, the only possibility of error owing to premature absorption of water arises during the very short exposure to the air between the final weighing and the sealing of the bulb. Trial experiments suggest that the amount of water thus absorbed cannot have exceeded 0·0003 g. even for the most hygroscopic salts. Assuming that the heat change involved in this absorption is of the order of magnitude of the heat of formation of salt hydrates, it can be estimated that the consequent error in the heat of solution of the salt measured cannot have exceeded, even in the unfavourable circumstances postulated, more than 25 cals./mol.

In the earlier stages of the work the heats of solution of a number of non-hygroscopic salts were determined in the " dilution " calorimeter, using the smaller inner vessel, according to the method of Lipsett, Johnson, and Maass for sodium chloride dissolving in water. It was found, in spite of numerous trials, that no liquid thinly smeared between inner vessel and lid was adequate to protect hygroscopic salts from attack by the solvents. Even heavy medicinal paraffin was unable to protect sodium iodide or lithium bromide from the vapour of water or the alcohols. The dilution calorimeter was therefore only used for the heat of solution of those non-hygroscopic salts which trial had shown to absorb no more than insignificant quantities of solvent vapour during several hours' exposure in the calorimeter. Duplicate experiments made later with the sealed-bulb technique on the same salts showed that no serious errors had been introduced in this way.

Summary Estimate of Errors. It is difficult to summarise in general terms the degree of precision of which the two calorimeters are capable. This is not only because temperature errors are independent of the total heat change measured while heat capacity errors are not, but also because details such as the molecular weight of the salt and the specific heat of the solvent are sometimes of considerable moment in determining the effect of a given error in the final result; *e.g.*, in measuring the heat of solution of 0·05 g. of silver perchlorate ($M = 208$) in 40 g. of water (sp. heat = 0·999), an error of 0·0002° in the temperature change leads to an error of 42 cals./mol. in the heat of solution, but an exactly similar temperature error in the corresponding measurement for lithium chloride ($M = 42$) in ethyl alcohol (sp. heat = 0·57) leads to an error of only 4 cals./mol.

In general, it may be stated that (*a*) in heats of dilution, the error of an individual determination is unlikely to exceed 100 cals./mol. for concentrations near 0·01N (this error is inversely proportional to the concentration measured); (*b*) in heats of solution, the error of an individual determination in the most unfavourable circumstances is not likely to exceed 200 cals./mol. at the concentrations usually measured (0·1—0·01N); (*c*) the absolute value of all the heat changes measured in non-aqueous solvents is subject to an uncertainty of 1½% or thereabouts (see p. 1367).

It will be seen from Part II that the concordance of all but the earlier measurements is consistent with at least this degree of accuracy. From the observations recorded there, it may be shown that the root mean square deviation of the individual values for the heat of solution at infinite dilution from their respective means is 150 cals./mol. when estimated from all the 107 cases where the necessary data are available, this including many of the earliest measurements.

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PHYSICAL CHEMISTRY LABORATORY, BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.
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