And so let me conclude my remarks on the outlook for chemistry in America by emphasizing that we have a goodly heritage of success both in our great industries and in our great universities, which will form the safe basis of a brilliant future, if we will but approach the problems of the moment and of the immediate future in characteristically American fashion with a spirit wisely combining altruistic principles with practical, worldly common sense. This means the "square deal" in industrial life for the product of the brains of the research chemist, combined with wise laws to insure to capital a fair and tolerably safe return for investment in chemical industries, needed to make our country chemically independent. And it means too the placing of chemistry in our universities on a plane with the other great professions, law and medicine, in order to hold in this great science, so important for the welfare of the nation, the needed numbers of men of brilliant minds and energetic ambitions—combined with the devotion on their part to the search for the truth, to the establishment of the great laws of our science, for the sake of that truth, that science, alone!

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS, No. 27.]

HEATS OF DILUTION: I. A CALORIMETER FOR MEASURING HEATS OF DILUTION. II. THE HEAT OF DILUTION OF THREE NORMAL ETHYL ALCOHOL.

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A number of years ago E. W. Washburn suggested to one of the authors that a promising method of attack on problems connected with aqueous solutions lies in the accurate determination of heats of dilution. With the aid of such measurements, and the freezing points, the vapor-pressure lowerings of the solutions can be calculated thermodynamically. Aqueous solutions of alcohols constitute an important class of solutions since, due to the similarity of methyl and ethyl alcohol to water, the "thermodynamic environment" will change but slightly with the concentration. A knowledge of the vapor pressures of such solutions is evidently desirable, as it represents the behavior of aqueous solutions when the effect of changes of the medium or "thermodynamic environment" is at a minimum. Direct-pressure measurements by any of the present methods are not possible with such solutions as the constituents of the solutions are both volatile.

This article describes the calorimeter used in measuring the small amounts of heat evolved during the addition of water to aqueous solutions of alcohol. The results of a series of determinations of the heat of dilution of three normal alcohol, with varying amounts of water, are also included. The authors wish to take this opportunity to thank E. W. Washburn for his interest and assistance during this investigation. Acknowledgment should also be made to I. R. Ruby, E. N. Chapman, H. J. Krase and E. K. Strachan for assistance at different stages of the research.

1. The Calorimetric Method.

The calorimeter operates on a principle which is a modification of that used in the adiabatic calorimeter of T. W. Richards and collaborators.[1] In the Richards apparatus the bath surrounding the calorimeter is kept, throughout a determination, at the same temperature as the calorimeter vessel in which the heat is being evolved. This arrangement eliminates the radiation and conduction of heat from the calorimeter. A correction must, however, be made for a heat effect due to stirring. In the calorimeter about to be described it has been found desirable to keep the temperature of the environment slightly lower (about 0.15°) than that of the calorimeter. A difference of temperature is found by trial at which a thermometer inserted in the calorimeter remains constant indefinitely. When this condition is realized the effects of radiation, conduction of heat, and vaporization exactly balance the heat effect due to stirring. This experimentally determined difference is maintained throughout a determination. This can readily be accomplished by the use of a differential thermometer in the form of a series of thermojunctions to measure the temperature difference, and an electrical heater in the bath surrounding the calorimeter. This modification of the adiabatic method makes the use of platinum resistance thermometers reading to 0.0001° practical and convenient. Due to the nature of the electrical measurements these instruments are not suitable for use with rapidly changing temperatures.

With no difference of temperature between the calorimeter vessel and "surroundings" the temperature of the calorimeter rose from 0.0007° to 0.0010° in intervals of two minutes. This change is too rapid for accurate determinations of the temperature at any instant due to galvanometer lag, etc. With the surroundings about 0.07° lower in temperature the change was reduced to 0.0004° or 0.0005°, which could be determined with more certainty. The change was completely stopped when the calorimeter had a temperature roughly 0.15° higher than the surroundings and the temperature of the calorimeter could then be measured with the greatest exactness.

In order to eliminate errors due to lack of sufficiently accurate specific heat data for the solutions and for the other materials of which the calorimeter is constructed, and uncertainties arising from the calibration of the thermometer, a carefully measured amount of electrical energy is converted into heat in the calorimeter, after each determination of a heat

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[1] Richards, THIS JOURNAL, **31**, 1275 (1909); Richards and Burgess, *Ibid.*, **32**, 431 (1910); Richards and Rowe, *Proc. Am. Acad. Arts Sci.*, **49**, 173; Richards and Barry, THIS JOURNAL, **37**, 993 (1915), etc.

effect from a dilution, and the corresponding rise of temperature measured. The heat effect due to the dilution H_D (in joules) can then be found by the simple proportion

$$H_D : EIt = R_D : R_E.$$

E is the electromotive force, I the current and t the time in seconds during which the current is passed into the calorimeter. R_D and R_E are the changes in temperature, in resistance units, due to the dilution and the electrical heating, respectively. This assumes, of course, that the relation between the resistance of the thermometer and its temperature is linear. The relation between the resistance change and the temperature change on the hydrogen scale is not, as is well known, a simple proportion. The small correction involved will be discussed in a later paragraph.

With the method as outlined, all heat radiation, heat conduction, vaporization, and stirring corrections are eliminated.

In order to reduce radiation and convection effects to a relatively small value a large calorimeter was constructed (the calorimeter vessel contains 10 liters) since a large vessel exposes a smaller surface per unit of volume than a smaller one. It is probable, however, that with the excellent control of the heat losses obtained in our later work a smaller instrument would have worked about as well.

2. The Calorimeter.

The calorimeter, exclusive of the external stirring mechanism and the electrical measuring instruments, is outlined in cross section in Fig. 2, and a view from the top is shown in Fig. 1. The calorimeter vessel A-A is 21 cm. deep and is separated on the sides and bottom by a 6 mm. air space from the surrounding vessel B-B. Both of these vessels are made of heavy copper, and nickel plated. Separation of the two vessels is provided by the gasket *a*, made of rubber tubing, and by the supporting ring of hard rubber, *o*. The seams of both these vessels are brazed as it has been found that solder is soon attacked when kept under water. Vessel B-B is supported on three brass legs, *b*, that fit snugly into holes in a wooden false bottom in the larger vessel C. The vessel B-B carries the cover M-M, of 3 mm. brass, which can be clamped onto the 2 cm. flange of the surrounding vessel B-B. A rubber gasket, *e-e*, is interposed between the cover and flange. Screwed into the cover are a number of tubes, each two inches long, through which pass the platinum resistance thermometer P, the leads from the heater H, the arms from the stirrers S-S and S′, the wire supports *g-g* of the dilution cup *g*, one leg of the thermojunction J, and the rod X. The tube *l* is for the purpose of filling the dilution cup.

The sides of the dilution cup G are made of thin sheet copper fastened to a brass ring at the top and to a sheet brass bottom. A brass cover 3 mm. thick carries the tubes *l′* and *q*. This cover makes a water-tight connection with the ring at the top of the cup, by means of the rubber gasket and screws as shown. The tube l' fits under the tube l and is used for filling the cup. The stirrer S′ passes through tube q. In a vertical line under a tube in the calorimeter cover M-M two holes, y and z, are bored in the cover and bottom of the dilution cup. The hole y is close by a rubber stopper fastened to the brass rod x, and the hole z is also closed by a rubber stopper. By pushing down the rod x the holes y and z can be opened in turn. The reasons for this design of the dilution cup will be considered later. The cup is held in place by means of wires fastened into tubes in the cover M-M.

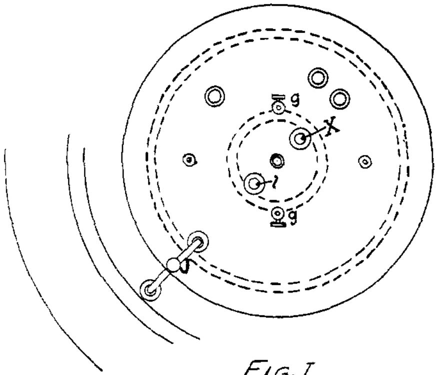

FIG. I

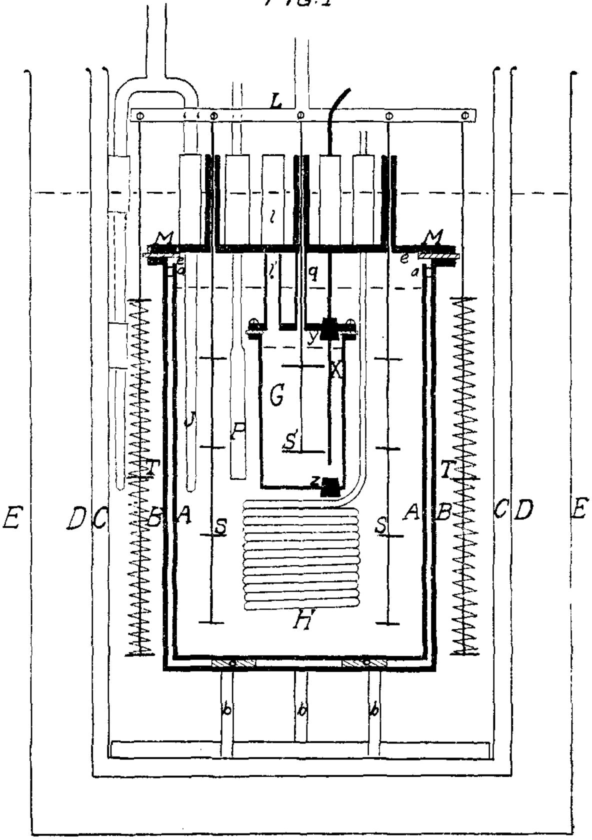

FIG. 2

The stirrer S-S consists of four brass disks, 18 cm. outside and 12.7 cm. inside diameter, each with ten 16 mm. holes punched at intervals.

Water is poured between the vessels B and C, and to a depth of about 3.8 cm. over the cover M-M. The space occupied by this water will be referred to, for convenience, as the "surroundings." In the annular space between the vessels B and C is placed a stirrer, T-T, consisting of three galvanized iron disks of 24 cm. internal and 32 cm. external diameter, each disk containing eight holes. This stirrer carries four coils, each containing 8 meters of No. 18 nichrome wire. The coils pass through the stirrer disks on wooden insulators and are arranged diagonally to the direction of motion of the stirrer. These coils are connected in series through a key to a source of 110-volt alternating current. By means of this arrangement the temperature of the "surroundings" can be raised at any time.

It has occurred to Richards and others that the "surroundings" can be heated electrically. From the recommendation of oil as the surrounding bath or a careful insulation of the heating coils, it would appear that these workers feared that stray currents would pass through the calorimeter and the resulting heating effects would be a source of error. As the calorimeter vessel A is thoroughly insulated from the surrounding vessel except at the top, the only way stray currents can pass through the calorimeter is by the shunting down through the stirrer S-S of currents flowing across the cover M-M. This would, obviously, only take place if there were, during the operation, a difference of potential between the rods of the stirrer. To test this a 110-volt direct current was passed through the heating coils of the "surroundings," and a sensitive galvanometer was connected to the rods of the stirrer S-S. As no deflection was observed, no error can arise from this cause.

The stirrers S-S, S′, and T-T are all connected to the yoke L, which is given an up and down motion of 5 cm. sixty times per minute by means of a crank operated, through a system of pulleys, by a $^1/_6$ H. P. electric motor. Experiments have shown that this system of motor stirring is very efficient, and that heat generated at any point in the calorimeter is spread through it in one or two seconds. Observations of the deflections of the galvanometer connected with the thermojunctions show that the stirring of the "surroundings" is also very efficient. Introduction of heat through the heating coils is accompanied by immediate response in the thermojunction system.

The vessels C, D and E are of heavy galvanized iron. Vessel D is separated from vessel C by an air space. The space between the vessels D and E was originally designed to give a very rough regulation of the radiation from the "surroundings." It was found, however, that closer regulation of the temperature of the water in this space made the regulation of the "surroundings" very much easier. Accordingly, a stirrer was constructed of light metal rods. This stirrer carries heating coils similar to those on the stirrer in the "surroundings." It is connected to the yoke which operates the other stirrers but is not shown in this drawing.

3. The Platinum Resistance Thermometers.

A number of platinum resistance thermometers, of three quite different types, have been worked with. These include one of the Heraeus type, several of our own manufacture, and three of the Leeds and Northrup "calorimeter bulbs."

The Heraeus type thermometer consists of a coil of very fine platinum wire fused into quartz. The resistance of this instrument has been found to vary greatly with changes of the current passed through it. This is probably due to the fact that the temperature of the thermometer is higher, when measurements are being made, than that of the liquid in which it is immersed. This excess of temperature (and resistance) will depend upon the rate at which heat is conducted from the thermometer. The excess temperature will obviously be greater in a short, fine wire, which has a small surface, and in which the current density is high, than in a longer, coarser wire of the same resistance. Successful calorimetric determinations have, however, been carried out with this type of thermometer since, due to the method used in this investigation, the conditions affecting the temperature measurements need be constant only for one complete determination. The main disqualification of the "sealed in" form of thermometer is, however, its sensitiveness to accidental jars.

A rather annoying peculiarity of this kind of instrument is the large "throw" of the galvanometer when the battery circuit of the Wheatstone bridge is closed. Due to heating effect, a bridge which is in balance when the current is on is not in balance when the current is off, so that the galvanometer will shift while the thermometer is heating up.

All the difficulties with the thermometer described above were encountered with the thermometers of our own manufacture, so that they will not be described further than to say that they consisted of fine platinum wire sealed into glass or passed through capillary tubing.

We have also made use of several of the platinum resistance thermometers designed by Dickinson and Mueller,[1] to whose articles the reader is referred for details not given below.

The first two thermometers were of the type described in the earlier paper by these authors. In the construction of these instruments 0.02 mm. platinum wire was wound on mica strips and insulated by other mica strips from the silver sheath. The sheath was fastened to a glass tube through which passed the leads, and at the upper end of which was a bulb containing P_2O_5. These thermometers were satisfactory for short periods only, as the initial high insulation soon broke down and the measuring system of the thermometer was affected by stray currents in the calorimeter. These difficulties may have been caused by the fact that,

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[1] Bur. Standards, *Bull.* 3, 641 (1907), Reprint No. 68 and 9, 483 (1913), Reprint No. 200.

due to their fragility, they were always somewhat damaged in shipment.

The later paper by Dickinson and Mueller describes a thermometer[1] with which we have had much more success. Wire 0.1 mm. is used in the coils, so that the resistance of the thermometer is practically independent of small changes in the measuring current. A number of improvements have been made in the drying bulb, and the instrument throughout is of more robust construction. The resistance of the thermometer is approximately 25 ohms at 0°. The platinum wire coil is remarkably compact, the external width of the silver sheath being 10 mm. and the thickness 1 mm. The thermometer lag has been found to be negligible.

4. The Resistance Measurements.

The resistance of the thermometer is measured by means of a Wheatstone bridge, specially designed for this work by H. C. Dickinson and E. F. Mueller, of the U. S. Bureau of Standards, to whom we are glad to take this opportunity of acknowledging our great indebtedness. The bridge was manufactured by the Leeds and Northrup Company. A diagram of the connections of this bridge is shown in the upper right hand corner of Fig. 3. R_1 and R_2 represent the ratio coils of the bridge. 100 and 1000

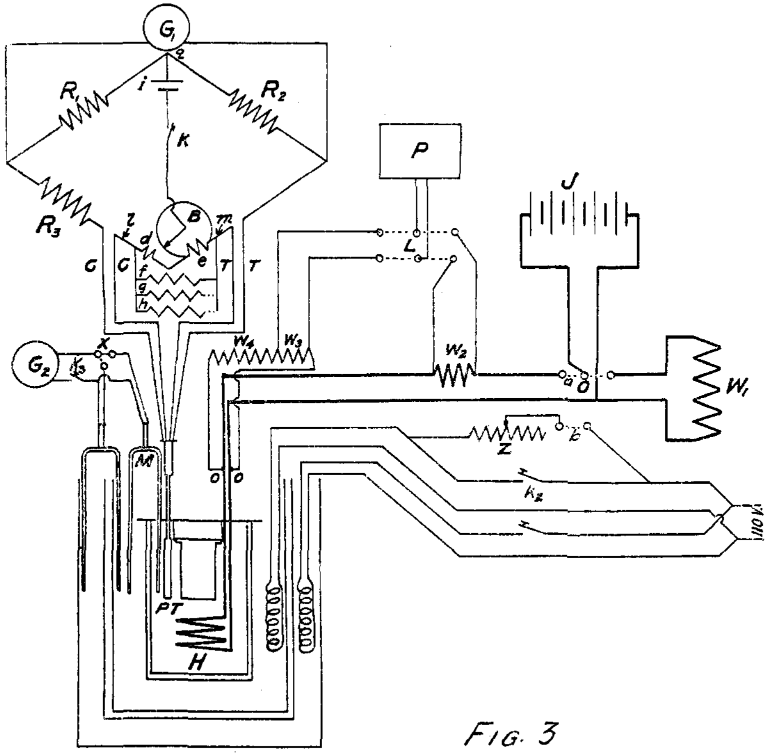

FIG. 3

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[1] Made by Leeds and Northrup, Philadelphia.

ohm ratio coils are provided but only the 100 ohm coils have been used. R_3 is an adjustable resistance of 100 ohms, the lowest coils being 0.01 ohm. The compensative leads *c-c* of the thermometer are placed in series in this arm of the bridge. In the remaining arm the main leads T-T of the thermometer PT are connected. In this arm is also placed the bridge wire B, shunted by a resistance, *e*. This wire is wound on a marble drum 15 cm. in diameter, and consists of eleven turns of No. 13 B & S Manganin Wire. *d* is a resistance equal to that of the shunted bridge wire, 0.55 ohm. The shunts *f*, *g* and *h* are so arranged that the resistance between the points *l* and *m* can be adjusted to 0.11, 0.22 or 0.55 ohm, equal, respectively, to the increase of resistance when the temperature of a 25 ohm thermometer is increased roughly 1.1°, 2.2° or 5.5°. The shunt which gives a change of resistance corresponding to 1.1° is the only one that has been used so far. As each turn of the bridge wire is graduated in 200 divisions which can be readily estimated to fifths, temperature changes corresponding to 0.0001° can be read with ease. The bridge, including the bridge wire, was calibrated, when new, by the Bureau of Standards. The examination of the bridge wire showed it to be remarkably uniform. The separate turns of the wire have been repeatedly compared against the 0.01 ohm coils in the adjustable resistance R_3.[1] These comparisons show clearly that no error of over 0.0001° can arise from a lack of uniformity of the bridge wire, and that the wire has not been worn by the sliding contact while in use.

A dry cell *i* is connected through a key, *k*, between the junction of the ratio coils *q* and the sliding contact on the bridge wire *d*.

A very important part of the equipment is the galvanometer G, which is connected, as shown, to the terminals of the ratio coils. The instrument used early in this investigation was of the Broca suspended magnet type. This had not quite the required sensitivity, and its zero constantly shifted due to changing magnetic conditions, even when surrounded on all sides by a screen of 6 mm. soft iron. The instrument now in use is a Leeds and Northrup "high sensitivity" galvanometer of the D'Arsonval design. It has a sensitivity of about 2 mm. per micro-volt at a scale distance of one meter, which is ample for our requirements. The resistance of the galvanometer is 13.5 ohms.

5. The Calorimeter Heater and Connections.

As has been stated, the heat capacity of the calorimeter is obtained, as a part of each determination of a heat of dilution, by observing the tem-

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[1] It is interesting to note, in connection with a paper by J. J. Manley [*Phil. Mag.*, **33**, 211 (1917)] on "Lubrication of Resistance Box Plugs," that we were able to shift and replace plugs, lubricated with transformer oil, without the appearance of variations of more than 0.00001 ohm. This agrees substantially with Manley's results with vaseline as lubricant.

perature rise accompanying the introduction of a carefully measured amount of heat produced by the passage of an electric current through a heating coil in the calorimeter. The electrical connections, which resemble in many particulars those used in a calorimeter designed by Jaeger and von Steinwehr,[1] are shown in the right side of Fig. 3. The source of the current for heating J, consists of a large capacity storage battery arranged to deliver ten volts. This battery is connected to the double throw switch O. From here the current can be made to pass through the heater H in the calorimeter or through W_1, a resistance equal to that of the heater and leads. By sending current through this resistance the cells are given a preliminary polarization, and a steady current is obtained when the cells are connected to the heater.

In series with the heater is the resistance W_2, of 0.6419 ohm. This is made of four strips of constantan ribbon, in parallel, wound on four glass spools, which are immersed in an oil bath. The resistance W_2 has heavy brass terminals carrying mercury cups, from which leads are run to the double throw switch L and from there to the potentiometer P. From the voltage obtained by the potentiometer and the resistance of W_2, the current passing through the heater can, of course, be calculated. W_2 is designed to carry the current (about three amperes) without changing its resistance. As the result of careful measurements, no appreciable variation of the resistance was found when the temperature of the oil bath was changed from 20° to 25°.

The resistances W_3 and W_4 in series are shunted across the terminals O-O of the heater H. W_4 is a resistance of 10,000 ohms, and W_3 is fixed at a value such that the voltage at its terminals is approximately equal to the potential drop through W_2. By adjustment of the double throw switch L the E. M. F. drop in W_3 can be read upon the potentiometer P. From this reading and a knowledge of the resistances W_3 and W_4 the voltage drop through the heater can be calculated. A small correction is necessary to take account of the current passing through the shunt W_3-W_4.

The potentiometer is fitted with a suitable galvanometer, and is adjusted against a Weston standard cell, which has been repeatedly compared with a similar cell calibrated by the Bureau of Standards. The time during which current is passed into the heater is determined by an accurate clock which is arranged to operate a telegraph sounder once every second.

Several types of heater, all of which had resistance of about 3.5 ohms, have been experimented with. The most satisfactory form consists of about ten feet of manganin wire soldered to No. 16 copper wire leads. The wire and leads are insulated with asbestos and passed through copper tubing. This tubing is wound into a helix.

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[1] *Ann. Phys.*, [4] **21**, 23 (1906).

The introduction of heat into the "surroundings" must take place simultaneously with the heating of the solution of the calorimeter vessel. This is greatly facilitated by the simple device indicated at O. When the current from the storage battery is shifted from the polarizing resistance W_1 to the heater H, the alternating current is sent through the coils in the "surroundings" at the same instant, as the connectors *a* and *b* work together. In series with the alternating current is the rheostat *z*. A position of the sliding contact of the rheostat can readily be found by trial, such that the difference of temperature between the calorimeter and "surroundings" (measured by the throw of the galvanometer G_2) can be kept constant with but little attention from the operator, leaving him free to take potentiometer readings. The final adjustments can be made by shifting the sliding contact on *z*, or by sending the whole strength of the alternating current through the coils of the "surroundings" closing key K_2. A similar arrangement for heating the external bath simultaneously with the calorimeter is in use but is not shown on the diagram.

6. The Differential Temperature Indicators.

A differential thermometer (M in Fig. 3) consisting of a set of sixteen copper-constantan thermojunctions is employed to measure the constant temperature difference that must be maintained between the calorimeter and "surroundings" during a determination. In the construction of the thermojunctions a number of White's[1] suggestions were followed. The junctions are enclosed in glass tubing and connected directly to a sensitive galvanometer, G_2, which gives deflections proportional, on an arbitrary scale, to the temperature difference. Since indications of 0.001° are ample for this purpose many of the precautions mentioned by White are unnecessary in the construction of the thermojunctions.

With the galvanometer used, a temperature difference of 0.15° gives a deflection of 40 mm. at a scale distance of one meter. A key, K_3, is placed in series with the galvanometer, so that the circuit can be reopened at any time and correction made for the shift, if any, of the zero of the galvanometer. Another less sensitive set of thermojunctions is placed between the "surroundings" and the external bath (Vessels D and E of Fig. 2). By means of the switch X (Fig. 3) galvanometer G_2 can be used with either set of thermojunctions.

7. The Design of the Dilution Cup.

In the earlier work the dilution cup was of the design shown in Fig. 4; with this arrangement the water in the cup and the solution in the calorimeter could be mixed by first pushing the stopper *z* out of the bottom by means of the rod *x* and then lowering the whole cup by means of the wires *g*-*g* passing through tubes in the cover. The brass ring *h* was normally

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[1] THIS JOURNAL, 36, 2292 (1914).

pressed against the cover of the calorimeter. It was, obviously, important to know whether the water in this cup was at the same temperature as the solution in the calorimeter; accordingly, the experiment was tried of "diluting" water with water, in order to observe possible temperature changes. The results of this experiment are given in some detail as they illustrate the excellent thermal regulation obtained, as well as give the data on which is based the final design of the dilution cup. Table I contains the figures obtained in this experiment. The first column gives the time, Col. 2 the reading of the differential thermometer, and Col. 3 the corresponding resistance of the thermometer. It will be recalled that a change of resistance of 0.00001 ohm is very nearly equal to 0.0001° so that the last figure in Col. 3 represents 0.0001°. At the beginning of the experiment the "surroundings" of the calorimeter were 8.2 units lower (about 0.17°) than the calorimeter. This was slightly too large a difference as the temperature slowly decreased. A similar decrease, but much slower, is noted when the difference was changed to 7.5. A slight increase is seen with a difference of 7.3, and the correct value is found at 7.4, the platinum resistance thermometer showing no detectable change within 0.0001° for eight minutes. At this point the stopper z was forced out and a slight drop of temperature (0.0002°) observed. This drop is, in all probability, due to heat conducted along the sides of the cup

TABLE I.

Time.		Differential thermometer reading.	Resistance of thermometer.	Time		Differential thermometer reading.	Resistance of thermometer.
Hrs.	Mins.			Hrs.	Mins.		
			27.710+				
2	35	8.2	0.01075		09	Lowered cup	...
	42	8.2	0.01070		10	7.4	1056
	45	8.2	0.01069		13	7.4	1055
	49	8.0	67		19	7.4	57
	54	8.0	64		25	7.4	60
	58	8.0	62		34	7.4	64
3	07	7.5	60		..	Raised cup to original position	
	10	7.5	60—				
	14	7.5	59		36	7.4	1065
	19	7.5	58		40	7.4	65
	26	7.5	57		46	7.4	65
	31	7.5	57			Lowered cup	
	37	7.3	57		48	7.4	0.01063
	44	7.3	58		53	7.4	65
	48	7.4	59		58	7.5	68
	55	7.4	59	4	59	Raised cup	
	58	7.4	59	5	01	7.4	1069
4	04	7.4	59	5	06	7.4	69
	06	Forced stopper out			10	7.4	69
	07	7.4	1057		15	7.4	69
	08	7.4	57				

to the cover of the calorimeter with which the cup is in contact. That this heat conduction takes place is clearly shown by the readings taken after the cup was lowered into the calorimeter liquid. The initial drop of one unit is partially due to the immersion of the upper part of the cup which has been chilled by contact with the cover. This is followed by a slow rise of temperature, due to the fact that the difference (7.4 units) is not enough to offset the stirring effect when heat is not being carried out of the calorimeter by the contact of the dilution cup with the cover. When raised to its original position the balance of conduction, radiation, etc., was again obtained and the thermometer showed no change in ten minutes. To prove that these effects were not the result of accident the cup was lowered and raised again, with, as will be observed, identical results.

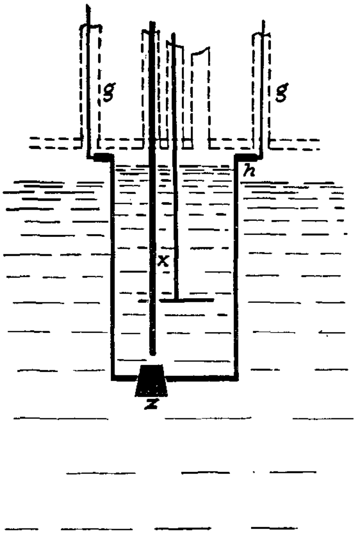

Fig. 4

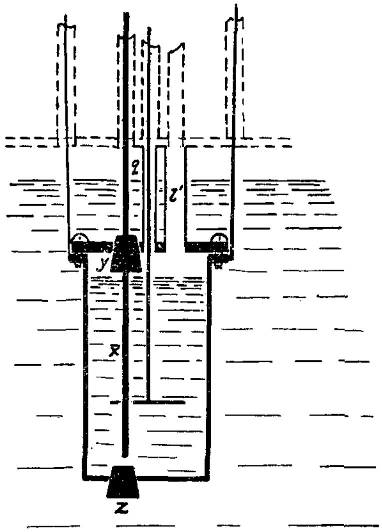

Fig. 5

It is evident from this experiment that no large portion of the dilution cup should come into contact with the cover of the calorimeter, and that the rate with which heat is conducted to the cover should not change during a determination. Both these conditions are met by the design of dilution cup indicated in Fig. 5. In this arrangement the cup is provided with its own cover fastened on with screws and a rubber gasket. The cover is provided with tubes fitting directly under similar tubes in the calorimeter cover. Through one of these tubes the cup can be filled, and through the other the rod of the stirrer passes. Holes y and z are placed in a vertical line under a tube in the calorimeter cover. These can be closed with rubber stoppers, one of which is fastened to the rod *x*. The entire cup is submerged in the liquid in the calorimeter. To operate, the rod *x* is pushed down carrying the stopper in hole *y* with it. The solution then rushes into the free space in the cup. The stopper in *z* is next displaced and the circulation through the cup soon causes thorough mixing.

A disadvantage of the older type of cup was that solution would rush into it when the stopper was pushed out, unless the level of the water in the cup was higher than that of the surrounding solution. If this took place, the temperature of the cup would be greater, temporarily, than the rest of the calorimeter, and radiation from this point to the cover would occur more rapidly than elsewhere. This probably accounts for some of the irregularities in our earlier work. An advantage of the new type of cup is that, almost up to its capacity, it can be used for any amount of water.[1]

With this improved design of cup the "dilution" of water with water is unaccompanied by any heat effect, showing that the heat flow from the calorimeter is unchanged during a dilution, and that the water in the dilution cup is at the same temperature as the liquid surrounding it. The figures obtained in a trial of the cup are as follows:

Time.	Differential thermometer reading.	Resistance of thermometer. R+.
8 : 44	8.1	0.01061
8 : 50	8.1	0.01061
8 : 56	8.1	0.01061
9 : 03	8.1	0.01061
9 : 05	Upper stopper out	...
9 : 06	8.1	0.01061
9 : 08	Lower stopper out	...
9 : 09	8.1	0.01061
9 : 12	8.1	0.01061

8. The "Water Equivalent" of the Calorimeter.

The best test that can be made of the thermometer and electrical heating systems is a study of the effect of introducing different amounts of electrical energy into the calorimeter. Such data can be used for the determination of the "water equivalent" of the calorimeter if a known amount of water is in the instrument. This "water equivalent" is, of course, the difference between the heat necessary to raise the whole calorimeter system one degree and the heat necessary to raise the water in the calorimeter through the same temperature interval. A knowledge of this constant is necessary for the calculation of the specific heats of the solutions, although not needed for the determination of heats of dilution.

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[1] It is advisable to use a cup of such dimensions that the level of the liquid in the calorimeter is not greatly changed on dilution.

A summary of the results of several determinations of the "water equivalent" is given in Table II. The columns contain, in order, the mean temperatures of the determination T, the number of grams of water in the calorimeter W, the electromotive force E, the current I, the time in seconds, S, the change of resistance of the thermometer ΔR, and Δt (the relation between ΔR and Δt is discussed below) and the "water equivalent." In calculating the latter 4:184 was used as the relation between the joule and the calorie, and 0.9993[1] as the specific heat of water in the range covered.

Table II.

No.	Mean T.	W.	E.	I.	S.	ΔR.	Δt.	"Water equivalent."
1.........	24.91	9712	6.9750	2.4317	600.5	0.02395	0.2395	456.6
2.........	25.03	9712	6.9740	2.4312	299.6	0.01194	0.1194	458.8
3.........	24.94	9862	6.9749	2.4313	599.6	0.02358	0.2358	451.6
4.........	25.14	9862	6.9740	2.4313	359.6	0.01414	0.1414	451.2
5.........	25.14	10012	6.9726	2.4307	599.5	0.02321	0.2321	457.6
6.........	25.29	10012	6.9713	2.4301	299.5	0.01160	0.1160	448.9

The results are interesting as examples of the performance of the calorimeter. As will be observed, the quantity of water and the amount of heat introduced were both varied. The water equivalent, however, agrees within 10 calories in the different determinations. A simple calculation shows that an error of 0.0001° in the measurement of the temperature leads to an error of 4 calories in the case of determination No. 1, and of 8.8 calories in the case of No. 6. Furthermore, the "water equivalent" is only about 4.5% of the total heat capacity.

The relation between the difference of temperature on the hydrogen scale, Δt, and the change of resistance, ΔR, of a platinum resistance thermometer is given by the formula

$$\Delta t = \frac{100}{(R_{100} - R_o)\left(1 + \frac{\delta}{100} - \frac{2\delta T}{100^2}\right)} \Delta R,$$

in which R_{100} is the resistance of the thermometer in steam at 760 mm. pressure, R_o is the resistance of the thermometer in melting ice, and δ is an empirical constant. This formula is a rearrangement of the Callendar formulas, made by Dickinson and Mueller.[2] Of the three constants R_{100} and R_o were carefully determined in this laboratory and a value of δ (1.47) recommended[3] by the Bureau of Standards was used.

9. Outline of a Calorimetric Determination.

An outline of a complete determination of a heat of dilution is given in the following: About 30 liters of the solution were prepared and kept

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[1] Bur. Standards, *Bull.* **12**, 47 (1915).

[2] *Ibid.*, 9, 490 (1913), Reprint No. 200.

[3] Private communication.

in a carboy. From this a portion of about 9.5 liters was poured into a 10-liter bottle and weighed to 1 g. on an accurate balance. This gave more than the necessary accuracy (0.01%). The calorimeter was then assembled, with the calorimeter vessel A (Figs. 2 and 3) and the dilution cup G both empty, and the stoppers *y* and *z* in place. The 9.5 liters of solution were then brought to the desired temperature, and siphoned through the tube that later held the thermometer. After draining, the bottle was again weighed. The dilution water was then run into the vessel G through the tubes *l* and *l'*. The "surroundings" were next filled with water, which was then brought to a temperature slightly lower than that of the solution in the calorimeter. The platinum resistance thermometer was next inserted, and stirring was commenced. Readings of the temperature of the calorimeter, and of the temperature difference between the calorimeter vessel and "surroundings" were now taken. This difference was next adjusted by trial as described on page 2120. Table III, which gives all the figures obtained in a typical determination, illustrates the regulation obtained. A difference was readily found at which the temperature of the calorimeter remained constant to 0.0001° for 14 minutes. After diluting, and allowing sufficient time for thorough mixing, constant temperatures were again obtained for three successive readings. Current was next passed through the heater for ten minutes, following which the measurements indicated that a constant temperature was again established. The columns headed "volts" and "amperes" are potentiometer readings. The actual values of these quantities are calculated from these readings and the values of the resistances W_2, W_3 and W_4, (Fig. 3).

TABLE III.

Dilution of 4 *N* Ethyl Alcohol at 25°. Weight of Solution 9612 g. Weight of Water 99.94 g.

Time. Hrs. Mins.	Differential thermometer reading.	Platinum thermometer resistance.	Time. Hrs. Mins.	Differential thermometer reading.	Platinum thermometer resistance.	Amperes.	Volts.	Dilution.
1 : 00	2.2	27.85717	1 : 33	2.1	0.85830	..	..	
1 : 04	2.2	85717	1 : 36	2.1	0.85922	..	..	
1 : 07	2.2	85716	1 : 38	2.1	924	..	..	
1 : 12	2.2	716	1 : 40	2.1	924	..	..	
1 : 17	2.2	715	1 : 43	2.1	924	..	..	
1 : 17	2.1	....	1 : 46	2.1	...	1.5545	1.5549	
1 : 24	2.1	715	1 : 49	2.1	...	44	48	Current passed through heater for 10 minutes
1 : 29	2.1	715	1 : 51	2.1	...	43	47	
1 : 31	2.1	715	1 : 53	2.1	...	42	46	
			1 : 55	2.1	...	41	45	
			1 : 58	2.1	27.88197	..	..	
			2 : 00	...	0.88196	..	..	
			2 : 03	...	0.88196	..	..	

10. Analysis of the Alcohol Solutions.

The analyses of the alcohol solutions have, in most cases, been carried out by means of determinations of the density of the solutions. The pycnometers were of the Ostwald-Sprengel type, with capacities of about 26 cc. Check determinations of the density agreed to 0.002%, giving an accuracy of 0.01% on the concentration of the alcohol when interpolations were made from the data of Osborne, McKelvy and Bearce.[1] The pycnometers were calibrated with distilled water saturated with air, and the solutions were also thoroughly saturated with air. The measurements were made at 25° in a Freas thermostat. Fluctuations of temperature were not over 0.02°.

The results of the density measurements were repeatedly compared with analyses made with the help of a Zeiss interferometer. The instrument was used differentially as described by Adams.[2] The comparison solutions were made up by weight from carefully purified alcohol and water. An accuracy of 0.01% can readily be attained by this method.

11. The Heat of Dilution of 3 *N* Ethyl Alcohol Solutions.

The "partial" or "reversible" heat of dilution is the quantity desired in most thermodynamic calculations. This may be defined as the heat

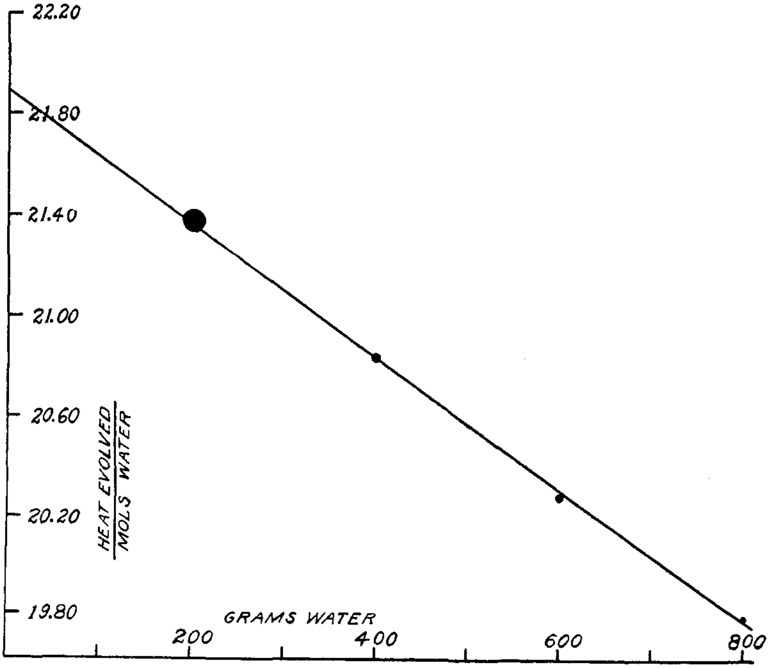

FIG 6

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[1] Bur. Standards, *Bull.* 9, 424 (1913).

[2] THIS JOURNAL, 37, 1181 (1915).

evolved or absorbed on the addition of one mol of solvent to an infinite amount of solution. This quantity can, obviously, not be measured directly. A knowledge of this reversible heat of dilution can, however, usually be obtained by studying the effect of adding varying amounts of solvent to the solution. On dividing the values of the resulting heat effects, by the corresponding number of mols of solvent added, a series of molal heats of dilution is obtained. If these molal heats of dilution are plotted as ordinates against the corresponding amounts of solvent as abcissae a straight line is usually obtained which, when extended to the zero ordinate, gives the quantity sought.

The results of a series of measurements of the dilution of 3 *N* ethyl alcohol solutions are given in Table IV, and plotted in Fig. 6. The circles around the points in the figure represent the error that would be produced by an error of 0.0001° in the temperature measurement. This represents but a small portion of the data in hand. A forthcoming article will give further data and a theoretical discussion of the results.

TABLE IV.

Heats of Dilution of 3 *N* Ethyl Alcohol Solutions.

Wt. of solutions. G.	Wt. of water. G.	Heat of diln. Calories.	$\frac{\text{Heat of diln.}}{\text{Mols. water}}$.
9611	801.24	881.1	19.81
9612	800.96	881.2	19.82
9612	600.91	676.8	20.30
9611	600.39	676.3	20.30
9611	400.48	463.3	20.84
9610	400.95	463.8	20.84
9611	200.61	237.4	21.32
9612	200.11	237.4	21.37
		"Reversible" heat of dilution,	21.80

Summary.

A calorimeter designed for the accurate measurement of heats of dilution, based on a modification of the adiabatic principle, is described. The data obtained in a series of determinations of the heats of dilution of 3 *N* ethyl alcohol solutions are given and the "reversible" heat of dilution of this solution is calculated.

URBANA, ILLINOIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

A STUDY OF THE SYSTEM ANILINE-HEXANE.

BY DONALD B. KEYES AND JOEL H. HILDEBRAND.

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A successful method for accounting for the deviation from Raoult's law is of extreme importance to nearly all questions involving the theory of solutions. Two radically different methods for doing this have been