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A CALORIMETRIC PROCEDURE FOR DETERMINING THE HEATS OF SLOW REACTIONS. II. THE CALORIMETRY OF A SLOW REACTION: THE HEAT OF INVERSION OF SUCROSE BY ACID.

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In the calorimetry of slow processes, the fundamental necessity is the long-continued maintenance of a negligible or precisely measurable heat interchange between the reacting system and its environment. Of the 3 general methods of calorimetric practice, the merodiabatic,[1] the isothermal and the adiabatic, the last alone is adequate in all cases for the establishment of such condition.[2] The complicated corrections for thermal leakage characteristic of merodiabatic calorimetry are not uniformly applicable to evey type of system, and in precise measurement must be

[1] The term merodiabatic, suggested by W. P. White [THIS JOURNAL, 40, 388 (1918)] applies to the customary method, in which measured thermal leakage occurs between the calorimeter and its environment.

[2] The advantages of the adiabatic method for the possible measurement of protracted processes has already been remarked, in a general way, (White, THIS JOURNAL, 40, 1891; Dickinson, Bur. Standards, *Bull.* 11, 207) but has not, in the writer's opinion, been sufficiently emphasized; and the method has not, apparently, been thus applied heretofore.

separately determined. In long-continued operations, their magnitude will be comparable with that of the heat actually measured, and will be affected by comparable errors of observation; while their uncertainty, due to unavoidable differences of manipulation in separate measurements and, in minor degree, to fluctuation in environmental (thermostat) temperature will become increasingly significant with the passage of time. This method, therefore, is inapplicable to the precise measurement of slow reactions. By the isothermal method, on the other hand, a practically constant environment having been established, accidental transfer of heat could be eliminated, or reduced to such magnitude and to such narrow and determinable range of fluctuation that it could be safely corrected for from the results of accessory measurements. With this procedure, furthermore, all kinetic data involved in the analysis of the process examined could be used without correction for the effect of temperature change, and the temperature coefficients of changes in total energy could be left out of consideration. The probable technical difficulties attending its general use, however, are great,[1] and are probably insurmountable in the case of slow reactions which are wholly or in part exothermal.

These considerations are sufficient to justify the choice of the adiabatic method for the calorimetry of any slow process except in special cases. This method makes possible the practical elimination of error in correction for transfer of heat, as does the isothermal method; but unlike the latter, it may easily be adapted to the measurement of thermal changes of whatever character. Its single disadvantage, due to changing temperature, is relatively unimportant, and necessitates merely the application of simple and precisely determinable corrections, of which, in familiar types of slow reaction, only that which affects the kinetic data is measurable.[2]

The following paragraphs describe an adiabatic procedure which, it is believed, will be found generally adequate for the precise calorimetry of slow reactions. For illustrative measurement, the inversion of sucrose by hydrochloric acid, a process which includes both endothermal and exothermal changes, has been chosen. The thermal effects involved in this reaction as experimentally conducted have been analyzed in a previous communication,[3] and the results of this preliminary inspection are here practically applied. The final results leave small doubt that the precision of this sort of measurement is not influenced by errors peculiar to adiabatic procedure beyond the limit set by the errors of precise mercury thermometry, and that in the determination of slow reaction heats, further improvements in accuracy will depend primarily upon a reduc-

[1] See Richards and Rowe, *Proc. Am. Acad.*, 43, 477 (1908).

[2] See the following reference, pp. 1307, 1308.

[3] THIS JOURNAL, 42, 1295 (1920).

tion of the cumulative effect of small sources of uncertainty common to all calorimetry, which though usually insignificant, are exaggerated by the passage of time.

Calorimetric Apparatus: Dimensions and Heat Capacity.—In these measurements an adiabatic calorimeter was used, of the general type devised and subsequently developed by Richards and his co-workers.[1] The accompanying sketch (Fig. 1), drawn particularly so as to show the detail of the instrument as modified for the purpose of the present research, will serve also to recall the general construction, which is now too well known to require further description.

The calorimetric vessel was a cylindrical cup of copper, of a thickness equal to that of the jacket wall, heavily plated with gold and highly burnished. It was supported and held precisely concentric with the polished jacket wall by points of ivory cemented to a closely fitting and rigid frame of boxwood. The widths of the air gaps surrounding it were 40 mm. above, 10 mm. below and 6 mm. laterally. These dimensions do not conform to those calculated by White to be the most effective for general insulation;[2] the calorimetric construction, therefore—which was made in 1913, prior to the appearance of White's important paper—could in this respect probably be improved.[3]

The heat capacity of the whole assembled system, determined by a variety of considerations relative to desirable advantages in experiment, was about 1,000 gram calorie units. This capacity was large enough to make the temperature change from thermal leakage under established conditions very small, and to allow considerable nicety in manipulation; while, with the thermometers employed, it still permitted the detection

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[1] For examples see THIS JOURNAL, 37, 1004–1006; *Proc. Am. Acad.*, 49, 174ff, and references in first citation, p. 994.

[2] W. P. White, THIS JOURNAL, 40, 379 (1918); cf. *Phys. Rev.*, [2] 7, 682 (1916) and *ibid.*, [2] 10, 743 (1917).

[3] White's results indicate that considerably larger basal and lateral spaces might have been used, with corresponding diminution of air conduction. In these determinations, however, transfer of heat by radiation and conduction was relatively unimportant since in the corrections for imperfect adiabaticity, the single assumption was made that the total transfer of heat was proportional to the thermal head (see p. 1923). The really necessary precaution was to reduce transfer by convection as much as possible. The wide upper space necessary for proper manipulation was on this account considered dangerous, but in practice was shown to be not so, in confirmation of White's general conclusions. It is not to be forgotten, however, that in the case of nearly all slow reactions which involve a heat of mixture, sudden changes of temperature are likely to occur at the beginning, which might well make the consistent employment of such very wide air spaces disadvantageous. It will in general be sufficient for experimental purposes to make these spaces no wider than is necessary to prevent undue conduction and thus to avoid the always possible danger of eddying convection currents, excepting in special cases when only gradual temperature changes take place.

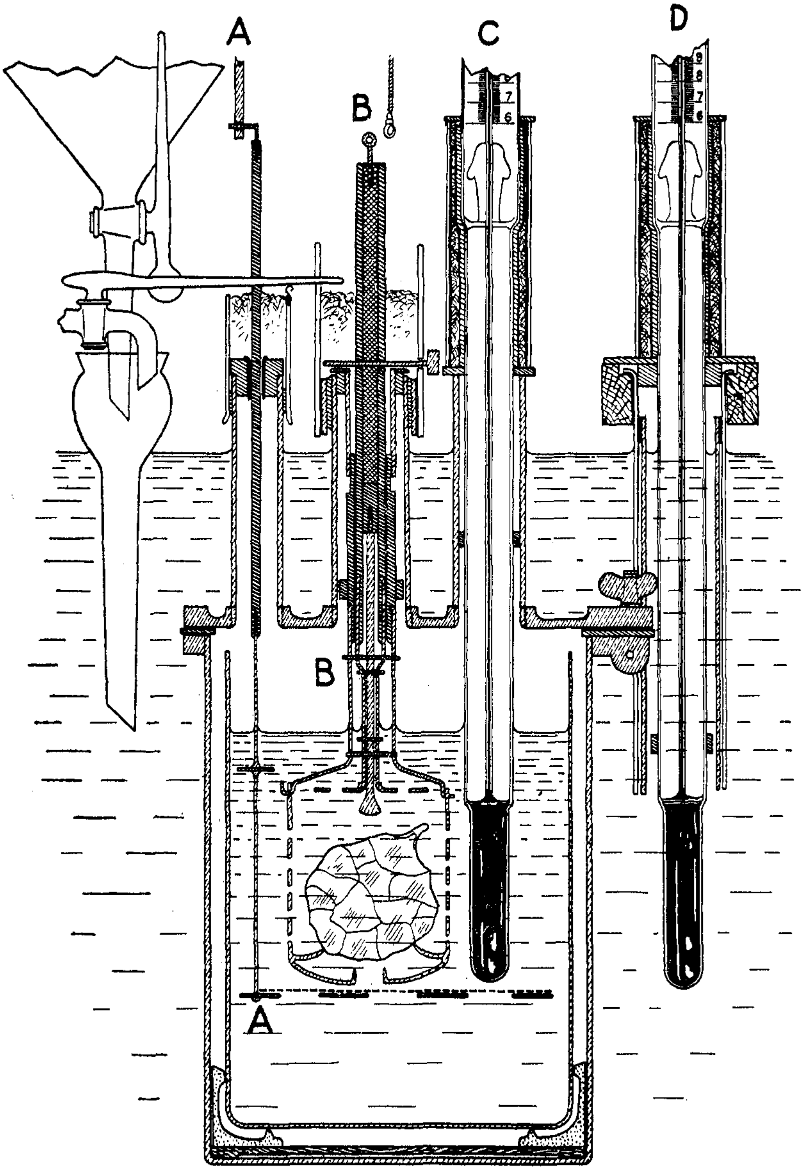

Fig. 1.

In this diagrammatic sketch, mercury, silver mirror surfaces and cement are in heavy black; gold- and nickel-plated copper in broken hatching; lead in cross hatching; vulcanite in heavy single hatching and soft rubber in light single hatching. Ivory, wool and wood will be recognized by characteristic markings. Glass is left unmarked.

Certain liberties have been taken with the section for the sake of clearness; the calorimetric thermometer, for instance, is actually not on the same diameter with the stirrer and mechanism chimneys, though it is here so represented.

of 0.5 calorie of thermal change. It was known in every determination to well within 0.5%, with negligible error of variation.

Constant Temperature Closet.—By the arrangements already described or suggested, the calorimetric system was well insulated from its surrounding bath. The bath in turn protected it as effectively as possible from the environment. There remained, however, unavoidable direct communication and consequent thermal leakage between the calorimeter and the outside air, through the thermometer, the stirrer, and the air in the stirrer chimneys. Such thermal interchange is never wholly eliminated nor made absolutely definable by any method of procedure; and the degree of uncertainty it introduces inevitably increases with the passage of time. As a prerequisite for the successful completion of the measurements under discussion, therefore, a closet had first of all been constructed, so designed that the temperature within it could be maintained for any desired time constant within narrow limits of variation. The essential features of this construction, including the thermostatic mechanism, by means of which its temperature was controlled, may merit future description. In this place it is sufficient to note that within it the temperature in the immediate neighborhood of the calorimeter could be held constant to ±0.1° for any desired interval of time, while that of the whole interior remained uniform and constant to within ±0.3°. By this means, while the bath was held within 0.01° of the reaction temperature, the unavoidable direct leakage was made measurably constant while the calorimeter was stirred, and quite negligible while it was held quiescent. It was sufficient that the temperature of the closet varied no more than 0.5° from the reaction temperature to accomplish this result.

Stirring Mechanism.—The calorimeter contents were agitated by a vertical reciprocating stirrer. This form possesses many advantages in experimental as distinguished from routine procedure over the rotating propeller. The latter is relatively ineffective in preventing thermal stratification unless it is held in a separate chamber so connected with the main calorimeter body that strong currents are made to flow through the connecting orifices;[1] and such a construction, which must be designed with care to ensure with a given arrangement of internal parts sufficient mixing, seems too unadaptable for use as a general laboratory appliance. In the present work, the reciprocating stirrer was in other respects preferable. Besides assuring quick and complete mixing, it made possible a thorough agitation with a minimum of eddying air convection such as would result from surface motion, and thus permitted

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[1] This type of stirrer has been designed and perfected at the Bureau of Standards. For a description of an apparatus which includes it see H. C. Dickinson, *loc. cit.*, Bur. Standards, *Bull.* 11, 210.

the relatively safe use of an open calorimeter vessel; its heating effect was probably smaller than that of an effective rotating stirrer would have been with the system employed; its adequate insulation was quite as certain; and though its motion was no more closely uniform than that of a propeller when the mechanism was in continuous operation, it was more precisely manageable when stirring was intermittent and slight. Finally it assisted so materially in securing a rapid mixture of the reacting ingredients at the beginning of a measurement that on this account alone it could hardly have been dispensed with.[1]

The only obvious disadvantages of this kind of stirrer result either from irregular motion or from actual transfer of air by pumping; both of which effects can be minimized by proper construction. In these measurements, the outer calorimeter stirrer, which was a perforated ring and disk affair of usual design made of gold-plated copper (Fig. 1, AA), was suspended from the outer hanger by long thin rods of polished vulcanite which alone, during movement, entered and left the system. These moved through perforated stoppers at the chimney tops, the holes through which, only slightly larger than the rods, were lined with thin glass and insulated by fine wool held loosely over 20 mm. length above them by large glass tubes which capped the chimneys. The dimensions and adjustment of the stirrer were such that it moved with almost inperceptible lateral displacement, and very smoothly. The ring and disk, always submerged, each traversed a half of the liquid depth, and stirred most effectively the lowest layers where inhomogeneity was most likely. A no time did metal enter the chimneys, or vulcanite come in contact with the calorimeter liquid, the surface of which was only very slightly disturbed. The inner calorimeter stirrer (Fig. 1, BB), was similarly insulated, and was adjusted with similar care.

The external stirring mechanism was a miniature factory construction of steel shafts and crown pulleys easily adjustable to several convenient speeds and lengths of stroke; and was driven by a $^1/_4$ horse-power motor. All transmission was by flat belts 25 mm. wide. The stirring speed was thus made constant within the limits of constancy of the motor speed itself, and varied during a 10 or 12 hours' run no more than 2%. Absolute constancy, such as might have been provided by a synchronous motor, was unnecessary, since during measurement the actual speed could be and was easily measured at half-hour intervals, and corrected for this slight variability with sufficient precision. The mechanism was adjusted, in determination, to a speed of 55.0 to 56.0 strokes per minute over a traversed space of 40 mm., after it had been shown by test that 12 such strokes were sufficient to render a mass of water underlaid with dense, dyed sugar solution, of a volume equal to that which was to be

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[1] The process of mixing is described on p. 1917ff.

measured, apparently homogeneous in refracted light. The speed was invariable throughout a series of measurements; and the length of stroke was made the same in every experiment and invariable in each of these to within a millimeter, by suitable mechanism of adjustment. By a simple device, the inner stirring could be interrupted with ease at any stroke without interference of the bath stirring, which was continuous and always sufficiently rapid to prevent significant lag in the maintenance of thermal homogeneity.

Mechanism for Effecting Solution.—For reasons already discussed,[1] mixture was brought about in these determinations by dissolving dry sucrose in acid. It was obviously advantageous to use as large a mass of sucrose as could be conveniently accommodated by the calorimeter, and at the same time quickly enough dissolved. In order to effect a quick solution, it was necessary that the sucrose be delivered into the acid suddenly from above in such a way that it could not accumulate in any considerable mass at the bottom, and that during this operation the solid be scattered throughout the acid by rapid agitation. Provision against the gradual wetting of the sample while it was being held within the system during the long period in which thermal equilibrium was being established at the desired initial temperature also had to be provided. The final result of several attempts to meet these necessities was the apparatus designated BB in Fig. 1. The sample of very finely pulverized and very dry sucrose, about 35 g. in weight, was held in a fragile bulb of glass, weakened, and in the final determinations put under strain, by having been flattened in the blow-pipe into a roughly polyhedral shape, and sealed at a constricted part of the stem close to the body. Within the calorimeter, this bulb was held in a basket of gold-plated copper, so designed that when immersed in the calorimeter acid, this liquid would have free access to every part inside. The bulb rested on three chisel edges, immediately above a small crown of points which ringed a central orifice at the bottom. The basket hung from a stiff framework of gold-plated copper wire so reinforced that although light and easily detachable it nevertheless held the basket quite rigidly to a large vulcanite tube which supported the whole. This tube extended through the chimney designed to accommodate the mechanism, and was held concentrically within it by a detachable rubber ring, capped with a brass flange at the top, so that when the whole apparatus was assembled, the basket occupied a definite position just submerged beneath the calorimeter acid.

Attached to a smaller and considerably longer vulcanite tube weighted with lead, which could move freely within the larger one that held the basket, a chisel fashioned out of silver rod and heavily plated with gold

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[1] THIS JOURNAL, 42, 1302 (1920).

was held suspended over the bulb by a removable pin which rested on the flange of the larger tube. This chisel was surrounded by a frame of wire, firmly attached to the vulcanite tube into which it was tapped, which carried at a point about 10 mm. above the cutting edge a perforated circular plate, designed to serve as a mixing stirrer within the basket. The entire chisel-stirrer construction could be operated rapidly by hand in such a way as to crush as well as stir the contents of the basket; and could also be attached to the stirrup of the external stirring mechanism by a small chain and pulley arrangement which was so adjusted that when connection was made the basket stirrer moved simultaneously with that in the calorimeter, but in opposition to it.

When it was desired to start the reaction, the chisel was allowed to fall upon the bulb; and this, now broken, was further crushed between the plate of the basket stirrer, operated momentarily by hand, and the sharp edges within the basket upon which it rested. The crown of points at the bottom effectively prevented the retention of sugar by any cup-shaped fragment. The basket stirrer was then attached to the stirring mechanism so that working in conjunction with the calorimeter stirrer, it effectively washed the basket free from all accumulations of solid. The greater bulk of the sugar slush thus formed fell upon the lower plate of the calorimeter stirrer, where it was held by a finely perforated piece of gold foil attached to the plate for this purpose, and was carried up and down through the acid by the motion of the stirrer.

In this way the solution of the sugar was made sufficiently rapid, and by careful routine manipulation, after a little practice, uniformly so.[1]

Thermometry.—The calorimetric thermometers used were closely similar instruments made to specification early in 1913. They were of a type previously found most suitable in work of this character; large bulbed mercury thermometers resembling metastatic instruments of the Beckmann type, which registered, however, the definite temperature range of 15–21° in 0.01° intervals. The length of a degree on each scale was more than 68 mm., so that by the use of a hand lens it was possible to read intervals of 0.0005° with a precision greater than that which is usual in reading 0.001° intervals on similar thermometers of the usual dimensions.

These instruments probably represented the limiting efficiency of mercury-in-glass thermometers. They showed very slight indication of capillary friction either on rising or on falling thread; their registrations

[1] It is clear that the procedure here described or one closely similar may be used for the mixing of any solid sufficiently soluble, or of any liquid sufficiently dense with a reacting liquid, in analagous calorimetric processes. Simple modification would make it generally suitable for the mixing of liquids, excepting in cases where these would react with glass.

were never altered more than 0.0005° by tapping, and usually not at all; their threads were never found broken even after long-continued and violent agitation; and when read with a telescope to 0.0001°, both falling and rising threads showed a strictly continuous motion of the meniscus. If the precision of their standardization and the limit of calorimetric accuracy had justified the procedure, they might have been read accurately to ±0.0001° in this manner. They were very sensitive. The measured coefficient for external pressure, 0.000243° per millimeter for both instruments, was sufficiently large to make the influence of changing barometric pressure a source of possible error in the long-continued measurements. This effect, therefore, was always estimated, though as it happened no correction for it ever had to be applied. The lags of both instruments (determined in a simple manner which, because of its convenience, may merit future remark), were the same, the total lag under conditions of maximum convection being 30 seconds for both instruments, and independent of total temperature change within a range of 0.5°. This lag was insufficient to affect the present measurements excepting during the period of most rapid change, and had to be taken into consideration therefore, only in determining the form of the curves of solution (p. 1926).

The thermometers were standardized by comparison with normal instruments which had been made by Baudin and fully corrected to the hydrogen scale by the Bureau des Poids et Mesures, in 1913. The precision of the comparison, which included 16 registrations between 19.54° and 20.23° was estimated to be consistently within ±0.001°, but was probably closer than this.[1]

In measurement, the corrections for stem exposure were very small, and their well known uncertainty consequently negligible; since the environmental temperature was always roughly constant and within 0.5° of the calorimetric. To maintain this constancy, however, it was found necessary to protect the entire stem of the calorimetric instrument by a mirror, which, in every measurement, was placed between it and the body of the operator.

In order that the calorimeter and bath thermometers should always register definitely comparable temperatures (a matter of the utmost consequence in the maintenance of adiabatic condition) the bath thermometer, which could not be immersed to the level of scale readings, was supported in such wise that the thick thread between scale and bulb was surrounded by a closely fitting cylinder of heavy copper plate, itself protected by a larger cylinder of silvered glass. Since both cylinders were half immersed in the bath, the lower thread of the thermometer was thus held at bath temperature. Both thermometers were further insulated above their points of support by silvered glass tubes packed with wool;

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[1] See the data of Table VI, p. 1938.

and this insulation extended to the same points on the two thermometric scales. By these devices (C and D in Fig. 1), the stem exposures of the two instruments were made identical, and thus negligible in a comparison of their registrations.

A source of thermometric error which seems not to have been observed or at any rate emphasized heretofore was noticed during the calorimetric measurements. At the end of each determination, the final condition, which should have been that of constant temperature, was tested by holding the whole system as closely as possible at equilibrium for an hour. In these tests, under the usual environmental conditions, a rise of 0.00005° per minute was always observed. This rise was very much greater than that due to the very slight stirring, and was the same whether the temperature of the room or that of the bath were above or below that of the calorimeter; but if, either before or after these tests were made, the incandescent tungsten filament lamps of the constant temperature closet were extinguished and the system still kept in equilibrium by flash-light observations and adjustments, there was, after the lapse of 15 minutes, no subsequent measurable temperature change whatever; that is, in the dark the system was constant to ±0.0005°. These observations, confirmed by the results of various modified procedures, seemed to indicate that the registration of encased mercury thermometers is sensibly affected by radiant heat from ordinary artificial illumination. The reason is not far to seek: it is without doubt what may be called, in a word, a "greenhouse" effect; and may be prevented or minimized not only by using light screens with all encased thermometers directly illuminated, but also by opening the shells of such instruments to permit free circulation of air around the thread tubes. The phenomenon is at present being quantitatively investigated.

Bath Adjustment and Control.—In the adiabatic calorimetry of swift reactions it is not impossible to control the bath by hand sufficiently well to reduce the error from thermal leakage to almost negligible magnitude.[1] If accessory devices for automatic regulation be employed, this error may be still further reduced, even beyond the limit of thermometric precision.[2] It is conceivable that similar regulation of the bath during the progress of slow reactions might be made likewise effective; but the precision of adjustment would have to be enormously increased to accomplish such result,[3] and any procedure seemingly adequate for the pur-

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[1] Richards and Barry, THIS JOURNAL, 37, 1010, 1012ff (1915).

[2] Richards and Davis, *ibid.*, 39, 344ff (1917). Note especially the curves on p. 346. See also Richards and Osgood, *ibid.*, 37, 1918 (1915).

[3] The necessary thermal equilibrium could doubtless be indicated with sufficient precision and with least danger from direct conduction leakage, by a multiple thermoelement spanning the space between calorimeter and bath; and the regulation, to be comparably exact, would then have to be automatically controlled by the thermo-

pose would still be open to criticism unless simultaneously with regulation the maintenance of requisite precision were continuously and rigorously tested. For these reasons it was not attempted in this investigation to eliminate thermal leakage; but rather to control it within narrow limits, in such way that on the basis of accessory measurements which defined the relation between actual leakage and thermal head with the system employed, it could be safely corrected for.

The bath was a dilute solution of alkali, the temperature of which could be gradually raised or lowered with equal facility by drips of dil. sulfuric acid and of ice-water.[1] The ice-water was contained in a well insulated bucket high above the calorimeter, flowed through a double-walled tube of glass wrapped in thick felt, only a few centimeters of which, in the region of the attached stopcock, was left exposed, and dripped into the bath at a point diametrically opposite to the bath thermometer. It was determined by test that the insulations provided were sufficient to prevent any significant cooling of the air near the thermometers. The dil. sulfuric acid drip was similarly arranged. Both drips were under fairly constant pressure during any single determination, and their rates of flow were very precisely controlled by long-handled stopcocks lubricated with grease sufficiently viscous to prevent maladjustment from jarring. As essential accessories, and as provision against emergency or accident, an insulated beaker of broken ice and water, a stoppered Dewar cylinder of hot water, and a small buret of conc. sulfuric acid clamped securely above the bath were also kept in readiness.

With this apparatus the bath was controlled during the preperiod, and throughout the long period of slow temperature change which followed solution. Since the air of the closet-thermostat was held at the temperature of reaction, the bath was normally about 2° lower. It was, therefore, continuously heated by the dil. acid drip, so regulated that during 15 minutes its temperature relative to that of the calorimeter

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element itself. It is easy to imagine a workable mechanism of this character which would serve for the measurement of continuously exothermal processes; and its practical adaptation to the measurement of endothermal changes—as by combination with ice-water cooling in the bath, or by introduction of measured energy into the calorimeter—is likewise not inconceivable. Such devices have been more than once suggested, as separately applicable in special cases. But the complete machine constructed so as to follow both types of change in the course of one continuous process (which the present problem would require) seems, surely, a premature conception.

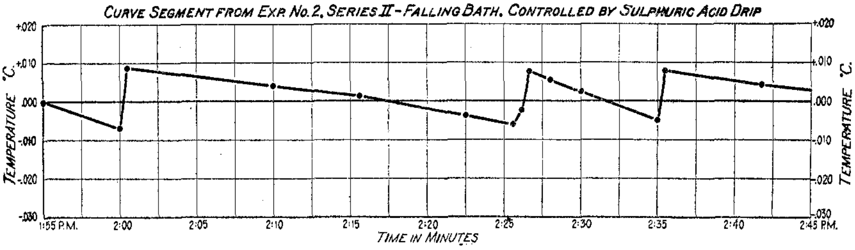
[1] Chemical, in comparison with electrical heating, is disadvantageous only with respect to the danger of possible leakage by corrosion, and of loss of control in long continued operations by accidental exhaustion of reacting material. By electrical heating, the lag in thermal distribution may be reduced, but at the cost of a lessened sensitivity in minute adjustment; and since the distribution lag is less than that of the thermometers, the advantage still remains with the chemical procedure. It is obvious that the ice-water drip is necessary in any case.

would gradually rise or fall to no more than 0.01° of thermal head. This condition was easily and quickly established; and during reaction could be maintained without difficulty by occasional readjustment of the rate of acid flow. When the bath had risen about 0.005° above or had fallen 0.005° below the point of equilibrium, its temperature was readjusted by adding ice-water or conc. acid in such determined quantity that the temperature difference 15 seconds later was the same but in the opposite sense. By this procedure the bath fluctuation, sufficiently defined by frequent thermometric readings, was made roughly periodic about the temperature of reaction, and the mean divergence from equilibrium correspondingly reduced.

In the 2- or 3-minute period which immediately succeeded the breaking of the bulb, the calorimetric temperature fell, and then rose too rapidly to be followed by the drips. By anticipating the first thermometric indication of temperature fall, its approximate rate and its magnitude, it was possible without difficulty to keep the bath during this time within 0.03° or 0.04° of the calorimetric temperature, and at the lowest temperatures reached (at which possible error from thermometric lag was greatest) more closely than this, by successive additions of ice-water and of acid from the accessory supplies. This manipulation, although sufficiently effective, was always hurried, and prevented careful thermometric reading during the first minutes of reaction. In the final determinations, therefore, the temperature fall was followed automatically by use of an ice-water buret. This was a straight glass tube about 3 cm. in diameter, jacketed by 2 larger, concentric glass tubes and thus insulated by 2 narrow dead-air spaces. It was provided with a glass stopcock of large orifice and a set of standardized tips, and was graduated in 0.01° intervals over the maximum range of temperature fall. By reference to the heat of solution measurements, the actual fall for any determination could be roughly estimated in advance from the sample weight; and the approximate lapse of time from initial to minimal temperature determined. In each measurement during the preperiod the buret was chilled by filtered ice-water from the accessory supplies, was then filled with the requisite quantity of the same material, previously held at 0.0° and poured through crushed ice in a Buechner filter; and was stoppered and fitted with a tip which would deliver its contents in the predetermined time. It was then fixed vertically near the drips and kept in readiness for not more than 30 minutes before the breaking of the bulb. It was shown by tests that during this time its contents were not warmed sufficiently either to alter its temperature significantly, or to affect the stem temperatures of the thermometers. A second before the bulb was broken the ice-water buret was opened. It naturally delivered its contents exponentially, so that, while it emptied, the falling temperature of the bath followed that of the calorimeter closely; and since during this time the thermometers could be read with ease at half-minute intervals, the temperature differences between calorimeter and bath were most precisely measured. The minimum bath temperature was never more than 0.02° higher or lower than that of the calorimeter, and was easily and rapidly adjusted to close equilibrium immediately afterward.

The effect of bath fluctuation on the calorimeter temperature was calculated from the results of a series of tests, in which, under different environmental conditions, definite differences of temperature between calorimeter and bath were maintained, with the smallest possible fluctuation, for times varying between 40 and 60 minutes. The results of these tests are tabulated in Table I, A (p. 1924). They show that for differences of less than 0.2° and greater than 0.05° the rate change of calorimeter temperature is proportional to the thermal head maintained, is of the same absolute value for the same thermal head whether the bath is higher than the calorimeter or lower[1] and is not influenced by environmental temperature when this is kept within one degree of the calorimetric. With reference to these data, on the basis of the legitimate assumption that the relations they exhibit will obtain for smaller thermal heads, correction was made in each determination for imperfect adiabaticity. The curve of temperature change within the calorimeter was plotted as a

Curve Segment from Exp. No. 2, Series II - Falling Bath, Controlled by Sulphuric Acid Drip



Curve Segment from Exp. No. 7, Series I—Rising Bath, Controlled by Ice Water Drip

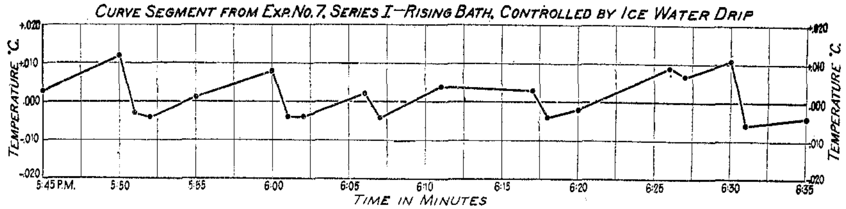


Fig. 2.—Bath temperature fluctuation.

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[1] These results, which, with reference to this calorimeter, appear to be unequivocal, are not in accord with certain observations of Richards and Burgess (This Journal, 32, 449 (1910)) who noticed a much greater rate of change when the bath was lower. This discrepancy is doubtless ascribable to differences in the conditions of experiment in the two cases.

straight line on heavy coördinate paper; and upon this line as axis of reference the curve of bath temperature fluctuation was plotted large by straight line interpolation. Segments of 2 such plots from the records of actual determinations, which show the determined points and very clearly exhibit the general character of the fluctuation, are here included (Fig. 2).[1]

TABLE I.

A.—Influence of Temperature Difference Between Bath and Calorimeter on Rate Change of Calorimetric Temperature.

Temp. of bath relative to temp. of calorimeter.	−0.20°.	−0.10°.	−0.05°.	+0.05°.	+0.10°.	+0.20°.	Environmental temps. ° C.
Rates of change in calorimetric temperature (in degrees per minute).	...	...	...	+0.00024	...	...	19.8
	...	−0.00050	−0.00025	...	+0.00050	...	20.0
	...	−0.00050	...	...	+0.00042	...	20.2
	...	...	...	...	...	...	20.4
	...	...	...	...	...	...	20.6
	...	...	...	+0.00023	...	...	20.8
	...	...	...	...	+0.00047	...	21.0
	...	...	...	...	+0.00050	...	21.2
	−0.00100	−0.00050	...	...	...	+0.00097	21.4
	...	...	...	...	...	...	21.6
	...	...	...	...	...	...	21.8
	−0.00096	...	−0.00025	...	+0.00050	...	22.0

B.—Data on Maintenance of the Adiabatic Condition from Measurements of the Heat of Inversion of Sucrose.

	Expt. No.	Total time of maintenance (in minutes).	Heat interchange between calorimeter and bath (inflow + outflow) (in gram calories).		Heat gained by calorimetric system (inflow — outflow) (in gram calories).		Heat capacity of the system (in gram calorie units).	Temperature correction for imperfect adiabaticity. ° C.
			Total.	Per 100 minutes.	Total.	Per 100 minutes.		
Series I.	1	161	4.5	2.8	−1.7	−1.1	1008°	+0.002
	2	234	6.7	2.8	−2.0	−0.9	1019	+0.002
	3	253	5.7	2.3	−1.0	−0.4	1 18	+0.001
	6	186	3.4	1.8	±0.0	±0.0	1006	±0.000
	7	232	4.2	2.0	+2.0	+0.9	1029	−0.002
Series II.	1	334	9.3	2.8	−1.0	−0.3	1007	+0.001
	2	375	12.3	3.3	+1.0	+0.3	1006	−0.001
	3	398	8.1	2.0	−0.5	−0.1	1007	+0.0005
	4	412	8.6	2.1	+0.9	+0.2	1147	−0.001

The branches of each curve thus drawn having been distinguished as upper or lower by proper designations, the areas between them and the line of reference were cut out as closely as possible, and the upper branch areas weighed against the lower ones. From the data so obtained, the weight of unit area of the paper being determined for each curve, the total temperature change within the calorimeter due to this fluctuation

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[1] The second curve illustrates the control of the bath when the environmental temperature is high, a condition unfavorable to measurement, but not impracticable.

could be readily calculated.[1] It was never greater than 0.002°, the anticipated maximum.

All significant data relative to the actual bath temperature fluctuation in the completed determinations of the heat of inversion of sucrose are collected in Table I, B (p. 1924). These data clearly show that in measurement, error in the correction for imperfect adiabaticity is wholly negligible.

Measurement of Heats of Solution. Accessory Data.

The first measurements carried out with the apparatus and according to the procedures described above were a series of determinations of the heat of solution of sucrose in water; and of anhydrous α-glucose in water, and in hydrochloric acid of the concentration used in the subsequent determinations of inversion heat. The collected results of these experiments served to test the adequacy of the means adopted for insuring quick and a complete solution, to determine the form of the solution curve in the inversion measurements, and to provide data for a comparison of solution heats in water and in acid.

The results of the first dependable measurements made with sucrose are summarized in Table II, A. The corresponding curves appear in Fig. 3 and the data derived from them in Table IV, A. Although these measurements were widely scattered in time, and were carried out under a variety of conditions and by varying procedure without the use of the ice-water buret, and with bulbs of various design only gently flattened, the calorimetric data they yield are fairly satisfactory. The results of the second series of like determinations, in which the ice-water buret was used, and the bulbs put under strain, are, however, more precise. These appear in Table II, B. The corresponding curves are plotted with those of the first series in Fig. 3, and the data derived from them are in Table IV, B. A comparison of corresponding values in the

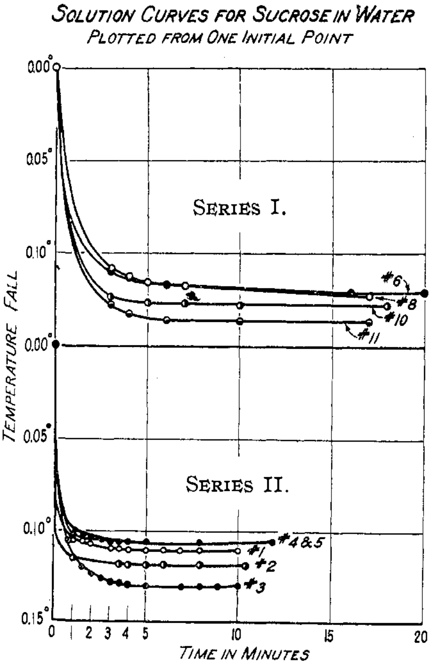

Fig. 3.—Sucrose solution curves.

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[1] The use of the planimeter for integrating curves of this character will have no advantage over the above procedure, a possible gain in time being more than compensated by a loss in precision.

2 series shows clearly the greater precision attained by the use of the ice-water buret, and the greater speed of solution made possible by the use of bulbs under strain.

Of greater present interest are the curves of solution. In Fig. 3, the sucrose curves of the first series have all been plotted through determined points without any smoothing out, and extrapolated to the origin in every case on the assumption that they are exponential; the constant for each curve $\left(p = \frac{1}{t} \log \frac{T_2 - T_1}{T - T_1}\right)$ having been determined from the entire temperature range $(T_0 - T_1)$ and the temperature at the first determined point, marked on the curve by an open circle. The exponential curve thus defined has been plotted across the time interval covered by the determined points and has been found to be very close to the experimental curve in every case, and actually coincident with it in the case of Curve 11. On account of the relatively large error in fixing the times at which solution began, and of the practical impossibility of making accurate readings during the initial period of rapid fall, the plotted initial slopes of these curves are certainly more widely varying, and these plotted curvatures, consequently, less closely exponential than the actual. It appears, therefore, from the general approach to coincidence between the actual and the derived curves that the process of solution is in this case very closely exponential in the sense $pt = \log \frac{T_2 - T_1}{T - T_1}$; and the data (Table IV, A) show that p is the same for all curves within a narrow margin of fluctuation.

In the second series of sucrose measurements, the automatic control of bath temperature by the ice-water buret made it possible to trace the actual curves of temperature fall to points much nearer the origin; so that from them the change in curvature could be determined directly. These curves were found to be of such character that if formulated as $p = \frac{1}{t} \log \frac{T_2 - T_1}{T - T_1}$, p was not a constant for any curve, but decreased with increase in t between similar limits in all cases. This variability is to be attributed for the most part to the greater speed of solution brought about by the use of bulbs under strain. In the first minute of fall, reading error and thermometric lag were on this account relatively large, and the dissolving process, in a mixture still inhomogeneous, was most rapid in the immediate vicinity of the thermometer bulb. All these conditions contributed to make p variable. After two minutes of fall, however, p became nearly constant and practically the same for all curves measured, as in the first series of measurements. Toward the end, p diminished slightly; but this effect was interpreted as due probably to the slow solu-

TABLE II.

Solution of Sucrose in Water: Calorimetric Data.

	Observed temperatures.				Calorimetric corrections:						
Expt. No.	Initial. (Thermometrically corrected.) T_1.	Minimal.	Selected final. T_2.	Observed temperature fall. $T_1 - T_2$.	Corr. for stirring heat.	Corr. for imperfect adiabaticity.	Corrected temperature fall.	Weight of sucrose (grams *in vacuo*).	Temperature fall per gram sucrose.	Heat capacity of system (gram calorie units).	Heat of solution of sucrose in water (gm. cal. per gm.).
A—Series I.											
6	20.033	19.912	19.914	0.119	+0.004	+0.0001	0.123	41.435	0.00297	1152	3.42
8	20.011	19.8865	19.888	0.123	+0.006	+0.0002	0.129	42.531	0.00303	1150	3.49
10	20.149	20.023	20.024	0.125	+0.002	—0.0002	0.127	43.337	0.00293	1150	3.37
11	20.016	19.880	19.880	0.136	—0.001	+0.002	0.137	44.334	0.00309	1152	3.56
										Average,	3.46
							Extreme variation from the average,				2.9%
							Corresponding temperature error,				±0.004°
B—Series II.											
1	19.923	19.8165	19.818	0.105	+0.0049	+0.0006	0.1105	36.699	0.00301	1149	3.46
2	19.985	19.8685	19.8715	0.1135	+0.0041	+0.0002	0.1178	39.180	0.00301	1150	3.46
3	20.071	19.9425	19.945	0.126	+0.0074	+0.0005	0.1339	45.250	0.00296	1152	3.41
4	19.9855	19.882	19.883	0.1025	+0.0060	+0.0002	0.1087	36.565	0.00297	1149	3.41
5	20.0055	19.901	19.904	0.1015	+0.0045	+0.0002	0.1062	35.742	0.00297	1149	3.41
										Average,	3.43
							Extreme variation from the average,				0.87%
							Corresponding temperature error,				±0.001°

TABLE III.

Solution of Anhydrous α-Glucose in Water and in 1.64 Molar Hydrochloric Acid. Calorimetric Data.

	Observed temperatures. (Thermometrically corrected.)				Calorimetric corrections.						
Expt. No.	Initial. T_1	Minimal	Selected final. T_2.	Observed temperature fall. T_1-T_2	Corr. for stirring heat.	Corr. for imperfect adiabaticity.	Corrected temperature fall.	Weight of glucose (gms. *in vacuo*).	Temperature fall per gram glucose.	Heat capacity of the system (gm. cal. units).	Heat of solution (gm. cal. per gm.).
A—Solution in Water.											
1	19.599	19.217	19.226	0.373	+0.013	+0.0003	0.386	31.999	0.01206	1148	13.84
2	20.260	19.898	19.902	0.358	+0.010	—0.0007	0.368	29.854	0.01229	1147	14.11
3	20.120	19.760	19.763	0.357	+0.003	—0.0008	0.359	29.549	0.01215	1147	13.94
										Average,	13.96
							Extreme variation from the average,				1.1%
							Corresponding temperature error,				±0.004°
B—Solution in Acid.											
1	20.252	19.856	19.872	0.380	+0.023	—0.0023	0.401	29.347	0.01366	1005	13.72
3	20.078	19.682	19.687	0.391	+0.008	+0.0014	0.400	28.704	0.0139	1004	14.00
										Average,	13.86
							Extreme variation from the average,				1.0%
							Corresponding temperature error,				±0.004°

TABLE IV.

Data on Kinetics.

Solution of Sucrose in Water, and of Anhydrous α-Glucose in Water and in 1.6 Molar Hydrochloric Acid.

	Expt. No.	Constant of solution p. (in logs$_{10}$).	Time elapsed when solution was		Percentage dissolved		Mean constant of solution.	
			90% complete. (Minutes.)	99% complete. (Minutes.)	in 5 minutes.	in 10 minutes.	(in logs$_{10}$). p_{10}.	(in logs$_e$). p_e.
A—Sucrose in water..................	6	0.17	2.9	13.0	95.4	97.5	..	..
Series I—Bulbs gently flattened........	8	0.16	3.1	14.0	94.7	97.0	..	..
	10	0.24	2.2	7.0	98.4	100	..	..
	11	0.19	2.7	5.0	98.9	100	0.19	0.44
B—Sucrose in water..................	1	0.65	0.7	2.5	100	...	..	..
Series II—Bulbs under strain..........	2	(0.7)	0.4[a]	1.0[a]	100	...	..	..
	3	0.56	1.2	6.0[b]	97.8[b]	100	..	..
	4	0.54	0.7	6.0[b]	98.2[b]	100	..	..
	5	(0.7)	0.5[a]	1.5[a]	100	...	0.6	1.4
C—Glucose in water..................	1	(0.4)	0.8	2.5	100	...	..	..
Bulbs under strain....................	2	(0.5)	1.2	3.5	99.0	100	..	..
	3	(0.6)	1.3	4.0	99.7	100	0.5	1.2
D—Glucose in water..................	1	(0.6)	1.1	2.6	100	...	..	..
Bulbs under strain....................	3	(0.4)	0.8	2.7	100	...	0.5	1.2

Values in parentheses are taken from extrapolated curves.

[a] Bulbs exploded.

[b] Sugar was trapped.

tion of trapped sugar as in Determinations 6 and 8 of the first series. The curves of the second series are doubtless typical; the irregularities they exhibit being common to all such curves, but relatively insignificant excepting when speed of solution is very rapid. The constant p is thus subject to greater variability the larger its value is. Since in the determination of concurrent effect in inversion determinations and the like, it is the ordinate $1/p$ which enters into the calculations,[1] the influence of such variability upon precision of measurement remains small, therefore; and as experiment shows, actually decreases with increase in the speed of solution, so that the maximum speed of solution remains the most advantageous speed, practically as well as theoretically. It is also clear from the theory already developed[2] that the error introduced into a measurement by uncertainty in the value of $1/p$ increases with the slope of the curve of inversion. It is, therefore, disadvantageous to increase the initial speed of reaction beyond a fairly well defined limit of the value k/p, where k is the constant of inversion. In the present measurements this limiting ratio was found to be about $\frac{0.0115}{0.44} = 0.026$. With this ratio, the error introduced by uncertainty in the value of p was ±0.001°; in the determinations actually carried out, with bulbs under strain in 1.64 molar hydrochloric acid to final concentration of 3.5 to 4% solution, the ratio was $\frac{0.0115}{1.4} = 0.008$, and the error negligible. The re-

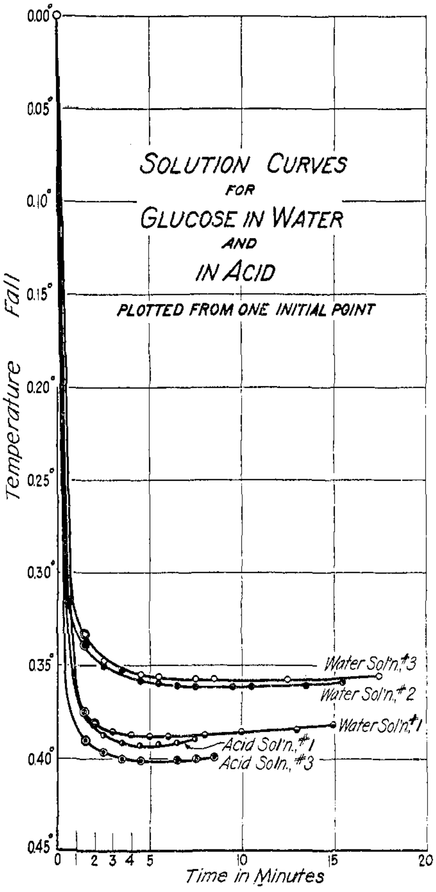

Fig. 4.—Glucose solution curves.

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[1] See THIS JOURNAL, 42, 1301ff (1920).

[2] For the purpose in view, invert sugar would have been the better substance to use. The measurements with α-glucose, however, were of greater interest; and when computed for different time intervals showed that within experimental error, varying speeds of mutarotation did not affect the form of the curve of solution heat.

sults of this series appear in Table II, B; the corresponding curves in Fig. 3, and the data derived from them in Table IV, B.

Three measurements were made of the heat of solution of anhydrous α-glucose in water, and 2 of its heat of solution in 1.6 molar acid. The results of this series are summarized in Table III; the corresponding curves appear in Fig. 4, and the data derived from these in Table IV, C and D. The curves of these measurements show that within the experimental error, no more significant in this case than in that of the sucrose measurements, the constant of solution is the same for water and acid. It follows, by analogy, that the value of p determined for the solution of sucrose in water by an established uniform procedure may be taken without significant error as equal to that for its solution in 1.6 molar acid. Thus the value of p for the inversion measurements was satisfactorily determined. That it may be still more precisely measured without altering in any way the mechanism for effecting solution is evident; but this would probably necessitate the employment of chronographic observations, which would be justifiable only if similar care in observation were justifiable in the inversion measurements; and such would hardly be the case so long as mercury instruments with considerable lag were employed.

For the temperature and acid concentration decided upon as best for the heat of inversion measurements, namely 20° and 1.6 molar concentration, the isothermal constant for the inversion of sucrose by acid $\left(k = \frac{1}{t} \log \frac{a}{a - x}\right)$ had never, apparently, been determined. It was necessary that the exact value of this constant and its isothermal variability under the adopted conditions of measurement be known. The determination of this constant was made at a thermostatic temperature of $20° \pm 0.02°$, according to established procedure and very carefully, by Dr. W. C. Vosburgh, to whom the writer desires to express in this place his great obligation. The data provided by these measurements appear in Table V, A and B. It is clear from this record that sucrose, while being inverted at this temperature by 1.6 molar hydrochloric acid, is not affected by any measureable side reaction; that under these conditions the inversion proceeds in the theoretical manner of monomolecular reaction within observable error; and that the constant of inversion is invariable for a range of sucrose concentration greater than that of the calorimetric work. In another set of measurements Dr. Vosburgh showed that under the same conditions the acid was without perceptible effect upon the products of hydrolysis within a full day after inversion began.[1]

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[1] Compare the experiments of M. M. Harrison (This Journal, 36, 597 (1914)), which, as reported, are inconclusive with respect to the action of acids of greater concentration than 0.7 molar.

TABLE V.

Isothermal Inversion of Sucrose by 1.6 Molar Hydrochloric Acid at 20.0°.

	Time (in minutes). t.	Observed angular rotation (in degrees).	Per cent. inverted. x.	Isothermal constant $k_{10} = \frac{1}{t}\log_{10}\left(\frac{1}{1-x}\right)$
A: Sucrose concentration = 3 g. in 100 g. of the mixture...............	0	(3.46)[a]	0	...
	1.5	3.34	...	...
	6.2	3.12	7.3	0.00531
	15.1	2.69	16.6	0.00522
	35.1	1.84	35.0	0.00533
	75.0	0.70	59.6	0.00525
	135.0	—0.30	81.2	0.00538
	∞	—1.17	100	...
				Average, 0.00530
B: Sucrose concentration = 5 g. in 100 g. of the mixture...............	0	(5.75)[a]	0	...
	1.3	5.57	...	...
	6.0	5.21	7.0	0.00525
	11.6	4.73	13.2	0.00532
	21.4	3.99	22.9	0.00528
	39.4	2.81	38.2	0.00530
	69.5	1.36	57.0	0.00528
	127.4	—0.33	79.0	0.00532
	∞	—1.95	100	...
				Average, 0.00529
C: Sucrose concentration = 5 g. in 100 g. of the mixture...............	0	(6.66)[a]	(0)	...
	1.6	6.29	4.1	...
	13.3	5.15	16.9	(0.00605)
	30.0	3.76	32.4	0.00567
	60.0	1.80	54.4	0.00568
	120.0	—0.42	79.2	0.00571
	180.0	—1.45	90.6	0.00570
	420	—2.24	99.6	...
	510	—2.28	(100.0)	...
	600	—2.28	...	...
	690	—2.26	...	...
	1410	—2.28	...	...
				Average, 0.00569

From A and B: $\left.\begin{matrix} k_{10} = 0.0053 \\ k_e = 0.0122 \end{matrix}\right\}$ for both concentrations.

[a] Extrapolated graphically.

A slight coloration appeared upon neutralization of the samples after 23.5 hours; but no change of rotation was then observable (see Table VI, C).[1]

[1] The higher value of k in the last table is due to a slightly greater concentration of acid. The greater angular rotations are due to the fact that in the first measurements sodium light was used, and in the last, mercury vapor light.

Finally, from these data, the time necessary for measurably complete inversion under the given conditions is discovered to be closely 9 hours. From the data of Nelson and Beegle[1] it is known that long before this time has elapsed the mutarotation of the products of inversion will have been complete, so that the heat of inversion for the full period will include heat of mutarotation.

Measurement of the Heat Inversion.

Of the heat of inversion of sucrose by acid 2 series of determinations were made. The measurements of the first series, though consistent with those of the second, were relatively inexact, and need not be considered here. Those of the second series, more precise, were conducted in the following invariable manner. The calorimetric apparatus having been adjusted and tested, the closet thermostat was heated to 20.0°, and maintained at this temperature for an hour or so, while other preparation was in progress, all necessary precautions being taken against the possibility of excessive partial lag in coming to equilibrium. The bulb containing the sucrose sample, the partial weights of which were already known, having been tested for fracture by immersion in distilled water and dried, was adjusted to proper position in the calorimeter basket, and the whole inner calorimetric mechanism assembled, suspended from the jacket cover. The desired volume of constant boiling acid was then approximately measured out into a graduated cylinder, transferred into the clean calorimeter vessel, and balanced with its container against a fixed tare by pipetting to ±0.01 g., diluted with purest water while balanced against a second tare to within a gram or so of the desired total weight, and finally adjusted by pipetting in such a way as to avoid the removal of more than 2 or 3 drops of liquid to within about ±0.05 g. of equilibrium. The filled vessel, covered with a flat perforated glass plate, was then warmed to a temperature slightly higher than that desired on an electric stove—its temperature being taken by a thermometer previously wetted by acid of approximately the calorimeter acid concentration—readjusted without removal of liquid to within ±0.02 g. of equilibrium, and placed inside the calorimeter jacket. After the insulation had been electrically tested, the whole calorimetric apparatus was assembled and nicely adjusted with the basket immersed, the stirring begun, and the bath brought gradually to exact thermal equilibrium with the calorimeter. The dil. sulfuric acid drip was then adjusted so as to maintain this condition as closely as possible; and thereafter for 30 minutes or more, while the initial stirring correction was being taken and the system examined for possible irregularity of behavior, the bath was regulated in the manner already described.[2] When the stirring correc-

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[1] THIS JOURNAL, 41, 574 (1919).

[2] Page 1921.

tion was found to be constant for a sufficient time, the mirror protecting the calorimeter thermometer was removed, and then in quick succession the ice-water buret was opened, the bulb was broken, its fragments crushed and the contents of the basket rapidly stirred for 15 seconds by hand the inner stirrer, then, was attached to the mechanical stirring arrangement, the mirror replaced, and the fall of calorimetric temperature closely observed by half-minute readings. The whole time occupied by this manipulation was usually much less than a minute. Owing to the rigidity of the construction it was easily carried out in a routine manner, without causing any displacements, such as would involve scraping by the calorimeter stirrer, or any other irregularity of behavior. During the manipulation the temperature of the partially insulated calorimetric thermometer stem rose slightly; but it was shown by blank tests that a degree of warming greater than this did not affect its registration. The previous measurements on the heat of solution of sucrose in water had shown that in its final form the breaking apparatus was so effective that excepting in rare instances no significant amount of sugar was protected from solution by the accidental disposition of bulb fragments. Whenever this had occurred, or whenever any other accident had caused an irregular speed of solution, the thermometer always showed some recognizable indication of the fact. The form of the solution curve plotted at the conclusion of each determination was, therefore, taken as a criterion in judging the dependability of the measurement in this particular. It never showed significant irregularity. At the end of the temperature fall, the thermometer rose after very slight delay. This rise was followed for a few minutes by the addition of conc. sulfuric acid from the accessory buret, to the bath; after it had become uniform, the dilute acid drip was readjusted, and thereafter the bath was controlled as in the preperiod. Continuous stirring was maintained for 30 minutes or more, as a precautionary measure, although in all probability a shorter period would have been quite safe. Thereafter the system was stirred intermittently by a counted number of strokes in groups, immediately following and preceding the thermometric readings, which were taken in pairs. These pairs of readings were always identical within 0.0005°, and showed clearly that the intermittent stirring, although it was so slight as to cause a total rise of only 0.002° or 0.003° in the 6 or more hours during which it was applied, was quite sufficient to maintain a thermal homogeneity measurably constant.

Since for the purpose of estimating the heat of inversion alone by the process of extrapolation discussed in the first section of this paper,[1] it was necessary that the form of the reaction curve be known within the narrowest possible margin of observation error, the thermometric readings

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[1] THIS JOURNAL, 42, 1297ff (1920).

were taken at frequent intervals during the whole course of the change; in the preperiod at intervals of 5 minutes, in the period of rapid change at intervals of one-half and of one minute, and in the period of inversion at intervals of from 2 to 10 minutes. The bath temperatures were simultaneously read, and in the period of slower change more often, so as to ensure as nearly as possible a regularly periodic variation. The temperature change was never rapid enough, considering the thermometric error, to necessitate chronographic observations; the time for each thermometric reading was, therefore, taken with an ordinary but accurately regulated watch. The rate of stirring was taken at intervals of 30 minutes throughout the entire period of measurement, with an accuracy of 0.05%; and barometric observations were made at the beginning and at the end of each determination. The humidity, during the whole series of measurements, was found to be high and not significantly variable, by psychrometric measurements, interpreted by the results of previous observation upon the effects of widely changing humidity at higher temperatures upon the rates of thermal leakage between calorimeter and bath under conditions otherwise fixed. Finally, the illumination was the same at all times.

It was thought unnecessary and probably inadvisable to follow each reaction to full completion, and thus to magnify the possible error from thermal leakage for the sake of actually observing the final few thousandths of a degree of temperature rise. The reactions were, therefore, observed during times which ensured a close approach to completion, and the final temperature computed, by successive approximation from the known minimum temperature as a starting point, by the application of isothermal kinetic equations involving each the mean constant of inversion determined by the corrected curve of observed temperature change. This procedure was legitimate, since the heat of reaction, which was measurably the same for the isothermal and the adiabatic conditions,[1] alone was involved, and since for the minute range extrapolated the error of approximation in the inversion constant used was insignificant. It was determined by calculation that the largest possible error introduced in this process was quite negligible.

At the end of each such measurement the stirring was stopped, but the mechanism of the constant-temperature closet left in operation; and the calorimetric system was allowed to rest for 2 hours or more under the same external conditions. After this interval it was definitely known that the reaction of inversion would have come to an end, and that no consecutive reaction would have occurred (p.)1933. Thereupon, the system was again brought to precise apparent equilibrium, and this condition was maintained with very slight intermittent stirring for an hour or more.

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[1] THIS JOURNAL, 42, 1308 (1920).

The probable effect of radiation upon thermometric registration already described (pp. 1920–1) was thus detected. The calorimeter again under illumination was then continuously stirred for 40 minutes at an observed rate, while very precise adjustment of the bath was still maintained, and the final rate of temperature change due to this effect determined. This rate was always measurably constant, and excepting in the last determination, the same for all. Each complete measurement required from 12 to 14 hours of attention and about 7 + 3 hours of continuous observation.

After the completion of a measurement, the wholly corrected temperature readings were plotted against time observations on coördinate paper sufficiently large to permit the distinction of 0.0005° differences. The correction for imperfect adiabaticity was then determined and the data examined to discover whether or not irregularity in the fluctuation of bath temperature would have effected the form of the curve of observed temperatures (the Experimental Curve in Fig. 5). No such effect was ever discovered. Since it was already known[1] that changes in heat capacity as the reaction progressed would not affect the temperature readings beyond the thermometric error, it remained only to apply a correction for heat of stirring to obtain the true temperature curve of the change. This was done in the following way. The final stirring correction was taken as applicable to the whole period during which it was applied, from the end back to the time at which minimum temperature was reached; on the basis of the assumptions, first, that during this period the concentration was sufficiently constant, and, second, that the viscosities of the sucrose solution and that of the derived glucose solution were nearly enough the same. Accessory measurements of stirring heat in aqueous solutions of sucrose and glucose of corresponding but greater concentration showed that this last assumption, which alone needed confirmation, was justifiable. Significant variations in the stirring speed were corrected for upon the basis of the assumption that the rate change of temperature due to stirring was proportional to the square of the number of strokes the reciprocating stirrer made in unit time. This approximation, in view of the very slight variation of the observed stirring rate, was more than sufficiently close. Correction of this sort was always slight; it hardly affected the form of the derived curve, and introduced a correction never greater than 0.001° in the estimated total heat of stirring. The temperature change due to stirring, thus corrected, was calculated for each 10-minute interval of the reaction period, was graphically subtracted from the corresponding observed temperatures of the experimental curve, and through the new temperatures thus fixed a smooth curve of reaction was drawn. (See Fig. 5.) In every case this curve was very precisely defined by the determined points. In the process of

[1] See THIS JOURNAL, 42, 1299.

"smoothing out" no such point fell more than 0.002° away from the probably correct position, and very few as far out as this. The magnitude of the combined effects of reading, thermometric correction and accidental experimental error on the form of the reaction curve was thus roughly indicated. The temperature toward the end of each measurement was always very nearly constant, although the actual reaction at this time was more than 2 hours short of measurable completion.

From this curve for any reaction it was possible to calculate the empirical constant of inversion for any small temperature range, by using the isothermal equation, which over short segments was strictly applicable. The curves for all determinations were examined in this way; the constant being calculated for 10-minute intervals measured from ordinates 5 minutes apart over 2 hours of the plotted range. The values thus obtained, which at 20.0° were measurably identical with the isothermal values otherwise determined by Dr. Vosburgh (Table V, A) showed with remarkable clearness a continuous increase in the value of the constant with rising temperature. The values shown in Table VI, taken from the curve apparently least affected by experimental error, show the manner and magnitude of this variation, the interpretation of which will be discussed later. At present it is relevant

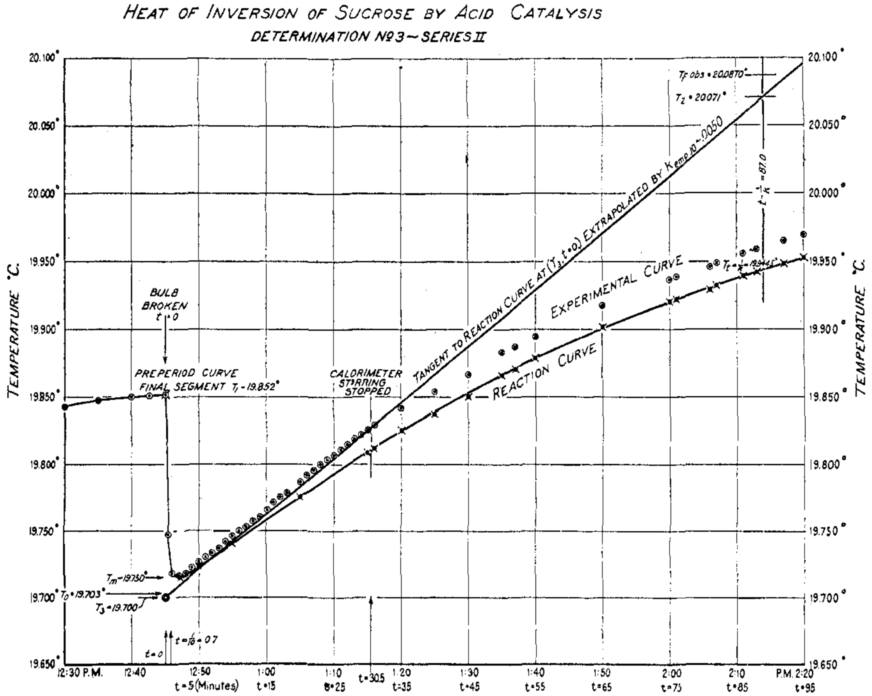

Fig. 5.—Curves of inversion.

TABLE VI.

A—Adiabatic Velocity Coefficients (from the Curve of Determination No. 3).

1. Time interval (t = reaction time elapsed, in minutes).	2. Corresponding observed temperature interval (in degrees).	3. k (in $\log s_{10}$).	4. Observed differences between successive values of k.	5. Mean increments in k for 10-minute intervals. I. Taken from 25 m. intervals.	6. II. Taken from 30 m. intervals.	7. Mean increments in k per degree C. I. Taken from 30 m intervals.	8. II. Taken from 40 m. intervals.	9. Temperature coefficient of k Increment per degree C. Mean values.	10. Observed error in k caused by ±0.001° error in temperature observation.
t = 15 to t = 25	0.035	0.0049	±0.0000						±0.00014
20 to 30	0.033	0.0049	+0.0002	+0.00012		+0.0023		+0.0027	
25 to 35	0.032	0.0051	+0.0001		+0.00013		+0.0031		
30 to 40	0.031	0.0052	+0.0002					+0.0029	
35 to 45	0.030	0.0054	+0.0001	+0.00012		+0.0026			±0.00019
40 to 50	0.029	0.0055	±0.0000					+0.0024	
45 to 55	0.027	0.0055	+0.0001		+0.00010		+0.0022		
50 to 60	0.026	0.0056	+0.0001	+0.00008		+0.0020		+0.0021	
55 to 65	0.025	0.0057	±0.0000						±0.00025
60 to 70	0.023	0.0057	−0.0002						
65 to 75	0.021	0.0055	+0.0001	Calculations hereafter invalidated by experimental error					
70 to 80	0.020	0.0056	+0.0004	(see Column 10.)					
75 to 85	0.020	0.0060	−0.0006						±0.00032
80 to 90	0.017	0.0054	−0.0003						
85 to 95	0.015	0.0051	+0.0007						
90 to 100	0.016	0.0058	±0.0000						
95 to 105	0.015	0.0058	±0.0000						±0.00038
100 to 110	0.014	0.0058	−0.0001						
105 to 115	0.013	0.0057	−0.0001						
110 to 120	0.012	0.0056							

B—Temperature Coefficients of k (Calculated as Above).

Experiment number.	Mean increment in k per degree during first 70 minutes.
2	0.0021
3	0.0025
4	0.0026

to note only that the succession of differences between the constants of adjacent segments could be precisely extrapolated back, from times at which the system was surely homogeneous to the initial time, so that the curve itself could be similarly extended and completed. This was done in every case, and the temperature (T_3 in Fig. 5) at which the extrapolated curve cut the ordinate of initial time ($t = 0$) thus determined. It was then possible by a variety of graphical constructions described in the first section of this paper[1] to determine the temperature (T_0 in Fig. 5) at which the inversion would have begun had solution been instantaneous, and thus to separate the 2 thermal effects of solution and reaction. Among these, the best method was that called the Approximate Tangent Construction.[2] This in practise was found to be as exact as the theoretically preferable Exact Tangent Construction,[3] on account of its greater simplicity and precision. The two yielded in test constructions the same initial temperature. In the measurements of this, the second series, the Approximate Curve Construction[4] also gave identical results, as a consequence of the high speed of solution brought about by the use of bulbs under strain. The Minimum Construction,[5] however, yielded values which varied from the preceding by ±0.002°, as had been anticipated. In drawing the tangent of the accepted construction, advantage was always taken of the fact that, assuming the curve to be of the form $kt = \log \frac{T_2 - T_0}{T_2 - T}$, the tangent would intersect the abscissa of the final temperature (T_2) at $t = 1/k_e$, k_e being the isothermal inversion constant in Naperian logarithms. To eliminate error in the application of this relation to the adiabatic curve, the value k_e was taken as the mean of the corresponding initial and final empirical constants. That this procedure was sufficiently exact is apparent from an inspection of Table VI, which shows that over the interval $t = 0$ to $t = 1/k_e$ the determined temperature coefficient of k was constant within the probable error of measurement.

In this manner 4 consecutive determinations were carried out, the results of which are summarized in Table VII. This table illustrates in detail the preceding observations. The heat of inversion of sucrose is determined to be 10.4 gram calories per gram; and the heat of solution of sucrose in 1.64 molar hydrochloric acid, to 3.6% concentration of sucrose, 4.35 gram calories per gram.[6] The discrepancies between the

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[1] THIS JOURNAL, 42, 1295 (1920).

[2] *Ibid.*, p. 1304.

[3] *Ibid.*, p. 1303.

[4] *Ibid.*, p. 1305.

[5] *Ibid.*, p. 1307.

[6] Among these measurements the first alone was affected by known accidental error. In this case it was found in the routine analysis of calorimeter liquid made after measure-

several results show a variation from the mean which corresponds to a thermometric variation of about ±0.003°, for both heats, and thus confirms the probability that the correction for imperfect adiabaticity involves slight variable error. It is noticeable that the heat of solution of sucrose in acid is distinctly different from its heat of solution in water.

Remarks on Error.

The following results were almost surely unaffected by uncertainty due to concomitant reactions or to change in concentration during measurement. The reacting materials were all of the purity demanded by the most exact procedures of quantitative analysis, and were neither visibly nor measurably affected by storage or manipulation. The various minute precautions taken to ensure this very necessary prerequisite of exact measurement will be discussed in a later communication, but may be omitted here; since the results submitted, though fairly precise, are illustrative rather than final.

In the measurements, the time-reading error was never greater than 10 seconds, and in the periods of rapid change no more than 3 seconds, as was shown by check readings. Error in the record of time intervals and of total time was shown, by standardization of the watch used, to be negligible. It is thus certain that no error in time measurement affected the final results, since thermometric readings taken during the period of rapid change were not used in extrapolation.

The thermometric reading error was ±0.0005°. The calibration error, well fixed not only by the manner of thermometric standardization but by the results obtained in evaluating the temperature coefficient of the constant of inversion (Compare Columns 3 and 10 in Table VI), was probably not greater than ±0.001°. Thermometric error caused by change in external pressure was known to be negligible; that due to possible change in ice point during a determination was assumed to be so, since the thermometers were never subjected to temperature changes exceeding 10° during a whole year. The correction for the effect of change in environmental temperature upon the exposed thermometer stems is negligible so far as the influence of conduction is concerned; but the effect of radiation from the sources of illumination—the possible

ment that copper had been dissolved both from the jacket cover by splashing and from the calorimeter stirrer through an abrasion of the gold plate. The result of this determination is known, therefore, to be too high, but the manner of the accident has prevented the application of a dependable correction. Because the data it provides have a certain value, the determination has been tabulated; but its final results are excluded from the averages.

The accident referred to was caused by the sudden explosion of the bulb, which having been put under too great a strain, was blown into minute fragments and in part pulverized. In the later determinations, the inner surface of the jacket, as well as the abraded area, was protected by paraffin, but no such explosion again occurred.

TABLE VII.

Heat of Inversion of Sucrose by Acid Catalysis.

Summary of Data.

	1. Observed temperatures.	2. Observed temperatures. Calorimetric.	3. Observed temperatures. Calorimetric.	4. Observed temperatures. Calorimetric.	5.	6.	7. Calorimetric corrections (in degrees).	8. Calorimetric corrections (in degrees).	9. Calorimetric corrections (in degrees).	10.	11 Kinetic data.	12. Kinetic data.	13. Kinetic data.
Expt. No.	Environmental. Mean stem temperatures.	Initial, T_1.	Minimal, T_m.	Final, T_f.	Total reaction time observed (in minutes).	Observed final rate change of temperature due to stirring (degrees per min.).	Correction for incomplete reaction.	Correction for stirring heat.	Correction for incomplete adiabaticity.	Corrected final temperature, T_2.	Empirical constant of solution p (in $\log_e$).	Empirical constant of inversion. k (in $\log_e$). Initial.	Empirical constant of inversion. k (in $\log_e$). Final.
1	20.0	19.9450	19.802	20.1855	334	+0.00055	+0.0045	—0.0202	+0.0008	20.1705	1.4	0.0120	0.0128
2	20.0	19.8520	19.716	20.0870	375	+0.00055	+0.0030	—0.0186	—0.0011	20.0705	1.4	0.0115	0.0134
3	20.1	19.8325	19.694	20.0825	398	+0.00055	+0.0020	—0.0272	+0.0005	20.0580	1.4	0.0115	0.0131
4	20.1	19.7805	19.641	20.0400	412	+0.00060	+0.0020	—0.0419	—0.0011	19.9990	1.4	0.0111	0.0124

	14. Derived temperatures.	15. Derived temperatures.	16	7	18	19. (Grams *in vacuo*.)	20. (Grams *in vacuo*.)	21.	22.	23.	24.
Expt. No.	T_3.	T_o.	Observed temperatures at $t = 1/k$.	Value of $\frac{T - T_3}{T_2 - T_3}$ at $t = 1/k$.	Temperature rise caused by inversion, $T_2 - T_o$.	Weight of sucrose.	Weight of acid.	Heat capacity of system (gram calorie units).	Heat of inversion of sucrose (gram calories per gram).	Temperature fall caused by solution, $T_1 - T_o$.	Heat of solution of sucrose in acid (gram calories per gram).
1	19.7855	19.785	20.029	(0.631)	0.382	35.371	1095.2	1006.5	(10.87)	0.157	(4.45)
2	19.700	19.703	19.941	0.649	0.368	35.456	1095.2	1006.4	10.42	0.149	4.24
3	19.667	19.670	19.922	0.657	0.388	38.116	1095.2	1007.3	10.25	0.163	4.32
4	19.635	19.638	19.866	0.635	0.361	39.635	1255.4	1147.0	10.45	0.143	4.14
			Averages,		...	..			10.37	...	4.23
					Extreme variation from the average,				1.2%	...	2.1%
					Corresponding temperature error,				±0.004°	...	±0.003°

"greenhouse effect" already commented upon—is, unless all signs fail, far from insignificant. (See p. 1920.) Since throughout the series the illumination was practically invariable, however, this effect will have introduced a constant error, experimentally measurable. Subject to a correction so determined, the accumulated thermometric errors amount to no more than ±0.002° or 0.5%.

Error in the correction for thermal leakage, insofar as this is caused by radiation, or by air conduction and convection, is negligible, unless the results of the accessory measurements described on p. 1923 are called in question, since the comparative registrations of the calorimetric and bath thermometers, which were twin instruments of equal lag, equally exposed (pp. 1918, 1919) were precisely known, and since the curves of bath temperature fluctuation were rather minutely defined and interpreted with negligible error of approximation. The possible continuous thermal interchange between calorimeter and environment by direct conduction through thermometer and stirrer rods during the 7 or 8 hours of measurement seems also to be very small (p. 1920) but demands further investigation.

The final rate change in temperature due to stirring was subject to an uncertainty not greater than ±0.00003° per minute; and its correction for variation in stirring speeds during measurement (p. 1936) was negligible, since rates of stirring were frequently observed and were known to vary no more than 2%, and regularly. The maximum error in the stirring correction (that of Determination No. 4, in which stirring was unnecessarily continued for 65 minutes) was, therefore, ±0.002°, or 0.5%.

The correction for incomplete reaction, the maximum value of which was +0.0045° (in Determination No. 2) is doubtless unaffected by error in every case (p. 1935).

By a fairly complete examination of the geometrical constructions used in separating the concurrent effects of solution and inversion—an examination based upon estimates of the possible errors involved in the values of p and k, and extended by observations of divergence between the results yielded by different constructions on the same curve, each affected by such error—it has been discovered that the error involved in the practical application of the accepted methods of extrapolation is never necessarily greater than ±0.002°, or 0.5%.

The sum of these several possible errors approximates ±0.006°, or ±1.5%. This value defines the probable extreme discrepancy due to known causes, which is likely to be shown by the results of such a series of measurements. The actual variability for this series is ±1.2%, which indicates that the real precision of measurement was only slightly affected, if at all, by unsuspected factors of uncertainty.

Form of the Reaction Curve.

This inference is confirmed by the form of the determined curves of reaction. These were not only very smooth (see page 1930, and Table VI, A) but they yielded a temperature coefficient of the constant of inversion for the first hour of reaction which was, within thermometric reading error, the same for all dependable measurements (Table VI, B). This result implies directly that the divergence of these empirical curves from the isothermal form is due either to natural cause or to constant error. Since the adiabatic and isothermal heats of reaction are sensibly the same,[1] the only adequate natural cause would seem to be the effect of rising temperature on the value of the inversion constant. To this effect, the Marcelin equation $\frac{d \log k}{dt} = \frac{E}{RT^2}$[2] closely applies, when for this reaction E is taken as 25,000 calories; as Lamble and Lewis have shown.[3] It yields for the absolute temperature and range in these determinations the measurably invariable approximate value $dk/dt = 0.0001$, while the mean of the empirical values tested in Table VI, B is $dk/dt = 0.00025$. The values of $\frac{T_{t=1/k_e} - T_3}{T_2 - T_3}$ in Table VII provide further evidence of the same import. These are more widely variable than the empirical temperature coefficients, since unlike the latter they record direct observations of particular temperatures, and not averages. Their mean is 0.648. The corresponding value for the isothermal curve is 0.632, and that of the adiabatic curves calculated as above, 0.641. The rough agreement thus shown between the empirical results and those of theoretical calculation for the adiabatic condition is close enough to suggest that the original divergence of the exponential curves of reaction from isothermal form may have been due to natural cause alone; for it cannot be assumed that the present measurements embody all of the errors involved in these comparisons. It appears more probable, however, that constant errors, the aggregate effects of which upon reaction speed are of comparable magnitude, affect the present determinations.[4,5] It is the primary pur-

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[1] *Loc. cit.*, THIS JOURNAL, 42, 1308 (1920).

[2] Marcelin, *Compt. rend.*, 158, 116 (1914).

[3] *J. Chem. Soc.*, 107, 233 (1915).

[4] It is believed that the small discrepancies here recorded will soon be more definitely interpreted, in the course of current investigation. This result is desirable for other than calorimetric reasons. If constant error in measurements like those described can be demonstrably eliminated or accurately corrected for, it will become possible to determine any desired variety of adiabatic velocity coefficient and with greater precision their continuous variability over small selected temperature ranges by direct observation of energy changes alone, and thus without dependence on any specific properties of the reacting material. The precision, such measurement if re-

pose of investigations now in progress to trace the causes of such possible residual error. A considerably greater precision of measurement is still possible without abandoning the facile and dependable mercury thermometer. Within a narrower margin of variation, therefore, the known constant errors can be measured. Of these, the effect of radiation on thermometric registration and that of thermal leakage by direct conduction are now being examined; while a check upon the whole procedure, which incidentally provides a means for testing directly the validity of the correction for imperfect adiabaticity and the error of extrapolation, will be provided by the results of a series of measurements now in progress on the heat of hydrolysis of sucrose by invertase.

In conclusion, the writer desires to express his keen sense of personal obligation to the President of Columbia University, and to former colleagues of the Columbia Departments of Physics and Chemistry, by whose generous interest and hospitality the immediate completion of an interrupted work was made possible.

Summary.

1. A procedure is described, whereby the heat of inversion of sucrose by hydrochloric acid,—an exothermal reaction which involves a partially concurrent and endothermal heat of mixture, and which under favorable conditions continues for 9 hours,—is measured with a precision largely determined by the characteristic errors of precise mercury thermometry.

2. The adiabatic method, which alone is applicable in such determination, is thus shown to be generally adequate for the precise calorimetric measurement not only of swift reactions but of any reaction which at ordinary temperature requires less than a day for its completion.

3. A way is thus indicated whereby chemical kinetic and total energy data may in general be directly correlated. The procedure itself illustrates such correlation.

4. Incidently, the procedure suggests a general and uniform method for the precise determination of adiabatic velocity coefficients, and thus of the temperature coefficients of velocity constants, by energy measurement alone.

5. Various modifications of calorimetric practise, necessary for the measurement of slow reaction heats, but generally applicable, are described.

6. Attention is called to a probable source of error in mercury thermometry, due to the effect of radiation on encased thermometer threads.

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sistance thermometers were used, would be at least comparable with that of optical, or other customary procedure.

[5] Incidentally, the fixing of the value $(T_{t=1/k_e} - T_3) \div (T_2 - T_3)$ would make possible the determination of T_2, T_3 having been found by direct extrapolation, without carrying the measurement beyond the time $t = 1/k_e$.

7. The following data are submitted.

Heat of inversion of sucrose by hydrochloric acid at 20° = 10.4 ± 0.06 gram calories per gram.

Heat of solution of sucrose in water at 20° to ca. 4% sucrose concentration = 3.43 ± 0.02 gram calories per gram.

Heat of solution of sucrose in 1.64 molar hydrochloric acid, at 20° to ca. 4% sucrose = 4.23 ± 0.05 gram calories per gram.

Heat of solution, anhydrous α-glucose in water and in 1.64 molar hydrochloric acid, at 20° to ca. 4% glucose = 13.9 ± 0.1 gram calories per gram.

NEW YORK CITY.

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF WARSAW.]

ATOMIC REFRACTION.

BY W. SWIENTOSLAWSKI.

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In 1911, F. Eisenlohr[1] published new calculations of the refractivities of carbon, hydrogen, and other atoms in organic compounds. These calculations do not differ from those used by J. W. Brühl, because both authors assumed that the molecular refractions of the organic compounds are equal to the sums of the refractions of the separate atoms.

$$M_D = \Sigma A_D.$$

According to this supposition, the computation of atomic refraction depends on the average value of the refraction of the CH_2 group and those of certain atoms. If, however, the individual atomic refractions show even small deviations, this method cannot be used.

In order to determine the limits of variations in the refractions caused by carbon and hydrogen atoms in the compounds which contain only the linkings C–C and C–H, I have used the following method of calculation.

1. If we denote by r_C, r_H, and r_{CH_2} the refractions for the D lines of carbon, hydrogen, and the CH_2 group, the molecular refraction, M_D, of the hydrocarbon C_nH_m can be expressed by the following equation,

$$M_D = nr_{CH_2} + (m - 2n)r_H + \Sigma\Delta r_C + \Sigma\Delta r_H, \qquad (1)$$

or

$$M_D = nr_{CH_2} + (m - 2n)r_H + \Sigma\Delta r,$$

where

$$\Sigma\Delta r = \Sigma\Delta r_C + \Sigma\Delta r_H.$$

Equation 1 cannot be solved when the increments $\Sigma\Delta r$ are not known; therefore, we can compute the quantities r_C and r_H only by reference to several chosen compounds, thus obtaining the average values of r_C and r_H on the supposition that $\Sigma\Delta r = 0$.

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[1] *Z. physik. Chem.*, **75**, 605 (1911).