2. The standard potential of the Ag | AgCl | Cl^- electrode has been determined from the cells containing acid and salt, and excellent agreement obtained with the values recently recorded by Harned and Ehlers.

3. The dissociation constant of water has been determined by using both a method depending on E_0, and a method depending on the electromotive forces of the acid and hydroxide–salt cell. The values of K agree within the estimated limit of accuracy (± 0.04 millivolt) with those determined simultaneously by Harned and Hamer.

4. The activity coefficient of hydrochloric acid in the lithium chloride solutions has been computed.

5. The ionic activity coefficient and dissociation of water in lithium chloride solutions have been computed.

6. The partial molal heat content of hydrochloric acid in lithium chloride solutions has been calculated.

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A Calorimetric Method for Determining the Rates of Interdiffusion of Reacting Liquids

BY FREDERICK BARRY AND ALLAN KAY SMITH

The calorimetric study described in this paper was suggested by Professor H. A. Fales,[1] who called our attention to the fact that physicochemical determinations which necessitate the measurement of electrode potentials are limited at present in both accuracy and scope because we have no means of measuring directly the values of the liquid potentials which are established whenever dissimilar solutions are placed in juxtaposition, as for instance in the salt bridges of primary cells.[2] Such potentials are always associated with the interdiffusion of electrolytes, and are generally assumed to be caused by the oppositely directed movements of ions across a liquid interface. If this assumption is valid, it should be possible to calculate their values from the rates of ionic interdiffusion, if these can be

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[1] Our indebtedness to Professor Fales for this suggestion which has led to the recognition of several new possibilities in adiabatic calorimetry, is increased by his further criticisms and interpretations of various findings, in the light of their bearing upon general theoretical considerations not here discussed.

[2] In the absence of definite knowledge in this matter, many formulas have been deduced from theoretical premises for calculating liquid junction potentials, among which the best known are those of Nernst, *Z. physik. Chem.*, **2**, 613 (1888); **4**, 129 (1889); Planck, *Wied. Ann.*, **39**, 161 (1889); **40**, 561 (1890); Henderson, *Z. physik. Chem.*, **59**, 118 (1906); Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909); MacInnes, *ibid.*, **37**, 2391 (1915). These are either based on diverse and incompletely verified assumptions, or are applicable only to particular combinations of electrolytes. They are, consequently, of questionable dependability in precise experimental work, excepting in special cases, and the desirability of actual measurements with which to test the assumptions upon which they severally rest is correspondingly clear.

precisely determined, without the aid of any additional hypotheses.[3] It was suggested that the precise adiabatic control of protracted processes which had been developed in this Laboratory[4] could be utilized for the measurement of the rate of development of heat during the slow interdiffusion of such electrolytes; whence, from known heats of reaction, their diffusion rates could be calculated.

This paper describes a first attempt to measure in this way the rate of one such interdiffusion. The liquids used were sodium hydroxide and hydrochloric acid solutions in equivalent concentrations—these having been chosen because their heat of reaction is conveniently large, and because in neutralization the boundary conditions of all thermally effective diffusion are definable with precision. It will be evident from the implications of the following discussion that the methods found necessary for the solution of the diffusion problem in this simple case are capable of further development and are likely to prove useful for other sorts of calorimetric measurement in which the use of thermally inhomogeneous systems is unavoidable.

Preliminary Tests.—Before an actual calorimetric measurement of the chosen diffusion could be attempted it was, clearly, necessary first to know whether or not the solutions could be brought into juxtaposition with initial turbulence slight enough not to affect the regularity of the diffusion process itself after a lapse of time conveniently short, and maintained thereafter under conditions no more favorable than those of measurement sufficiently quiescent to make this diffusion fairly reproducible in measurements conducted under like environmental conditions in vessels of different configuration. For calorimetric purposes it was also important to determine the curvature of the interface in the same circumstances.[5] To secure this knowledge, preliminary tests were made with apparatus not dissimilar to that which had been tentatively designed for the calorimetric measurements.

Upon an immovable pillar in a closet the temperature of which was purposely allowed to fluctuate slowly and irregularly within the anticipated maximal range of a calorimetric measurement (*ca.* ±0.5°) cylindrical glass vessels were placed, the diameters of which were between 4 and 14 cm.—that of the largest being greater than the diameter of the calorimeter vessel. In the first series of tests these cylinders were partly filled with 0.500 ± 0.001 molar sodium hydroxide; and above them, rigidly clamped in place, separatory funnels filled with equimolar hydrochloric acid were so placed that they would deliver acid upon the surface of the alkali, turbulence being minimized by very shallow glass dishes about 2 cm. in diameter attached to their extremities, which

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[3] Very few attempts at such determination have thus far been made. Besides the early work of Lord Kelvin and of Graham, practically all we have are some incomplete experiments by Osborn and Jackson, *Biochem. J.*, **8**, 246 (1914), in which it was attempted to measure by an analytical method the diffusion of salts in the presence of other salts, and the repetition and interpretation of this work by Walpole, *ibid.*, **9**, 132 (1915).

[4] THIS JOURNAL, **42**, 1911 (1920); **44**, 899 (1922).

[5] See below, p. 2218.

caught the falling stream of liquid and redirected it horizontally across their edges. In the second series of tests the cylinders held acid, and the tubes of the funnels delivered alkali directly upon the bottom of the vessel, turbulence being reduced in this case by a flat collar fixed horizontally at the extremity of the tube. The acid was thus by both arrangements superposed upon the alkali, which in equivalent concentration is more dense. The surface of contact was made visible by phenolphthalein which, when it was present in both solutions, exhibited the region of precise neutrality as the flat surface of a vividly red liquid, and when it was originally present in the acid alone, produced an equally persistent appearance more favorable to observation, like that of a very delicate red membrane between two colorless liquids. With the indicator thus disposed, therefore, observations were made. When the liquids were brought into juxtaposition by either procedure the initial turbulence, though observable, was very slight, and after a minute or so, undetectable. The neutral interface was apparently plane even at its outer and inner peripheries, where it was in contact with the vessel wall and the funnel tube and was not broken by moderate jarring and rocking. After all such disturbance it quickly regained its original quiescence without perceptible change of contour; and during diffusion it moved steadily with negative acceleration toward the alkali, without perceptible distortion. To check these observations with precision, several diffusions in vessels of different diameters were observed, during three hours or more, with a cathetometer telescope: thus vertical distortions of the interface of a few hundredths of a millimeter could certainly be measured and smaller distortions detected; but in all cases the surface remained plane within this limit of variation. The speed of its movement for systems of the same concentrations at the same temperature in vessels of different dimensions was, after the first hour or less (during which time the variable effects on initial turbulence appeared to persist), the same at equal intervals of time after mixture to within 1.6 mm. in a total mean advance of 40 mm. during four and one-half hours; which indicated that the phenomenon was reproducible under conditions less favorable than those of calorimetric measurement (since temperature was not so well controlled) and for the anticipated extreme duration of such measurement, to about 4%. The two curves of speed from which these data are derived (selected for precision of measurement) are shown in Fig. 1; the magnitude of the effect of difference in the amount of initial turbulence which they exhibit is typical.

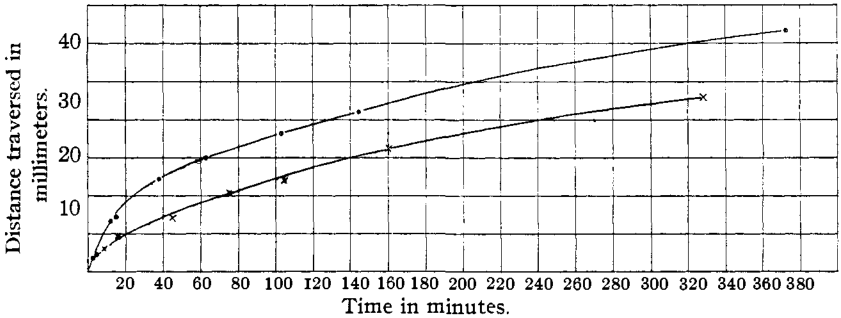

Fig. 1.—Movement of neutral boundary plane.

From the results of these tests it was judged that, for the purposes of a methodical research, the stability of diffusing systems arranged in the manner described, the efficacy of the technique of superposition and the reproducibility of the process were satisfactory. It was also inferred from the fact that the neutral interface (at which the preponderating heat of the process would be developed) always remained precisely plane, that any horizontal zone of a system of this type would remain, when undisturbed, thermally homogeneous within narrow limits, and that the problem of measuring the mean temperature of any such system would resolve itself, consequently, into that of determining the average temperature of a vertical column throughout its depth, correction being subsequently made for such disturbance of thermal symmetry about the axis as might be caused by the conducting walls and tubes of the calorimetric apparatus, were this significant. These matters decided, the more serious experimental difficulty remained, that, namely, of measuring with precision the heat developed at a slowly moving central plane in a quiescent liquid, and its rate of evolution, during several hours. The calorimetric problem thus presented was of a wholly novel character, for though the control and continuous measurement of protracted processes of longer duration had been already accomplished,[4] a necessary condition of such determination was that the reacting system should be thermally homogeneous; and in a diffusion, obviously, it cannot be so.

Apparatus, Preparations and Procedure

The installation used in this work was an adiabatic calorimeter similar to those previously used in this Laboratory for the study of slow reactions,[4] which, however, included certain improvements of design. Its special internal construction is shown in Fig. 2. The cylindrical calorimeter vessel, of the usual dimensions and weight,[6] had been die-pressed without visible shear from a single sheet of copper, and was heavily plated with gold. A cup (C) similarly made of about a third its capacity and of slightly smaller diameter was fitted in close metallic contact with its upper zone, and held flush with the rim by external pins (P), which rested without projecting in slits cut through the wall. The bottom of this cup, which was a shallow eccentric cone, bore at its pierced apex a brass collar into which either of two delivery tubes (D_1, D_2) could be screwed; one of these, by which acid was delivered upon the surface of alkali in the calorimeter vessel, traversed the middle third of its height; the other, by which alkali was delivered underneath acid in the calorimeter vessel, being of such length that it reached nearly to the bottom. The shorter tube was pierced close to its lower end by horizontal lateral slits, and closed across this end by a shallow dish 14 mm. in diameter; the lower end of the longer was open and fitted with a flat collar of the same diameter—these constructions being intended to minimize turbulence during delivery. The rate of delivery was regulated by a conical valve (V) closely fitting the collar which bore the delivery tubes, and was moved vertically by a brass rod (R) which bore a threaded block (VS) held rigidly directly above the valve by a heavy horizontal brass bar (B) through which it moved, the bar itself being soldered diametrically across the cup flush with its rim. All of these parts were heavily plated with gold, excepting the valve-cone and the threaded block on the valve-rod, which were solid gold.[7] The valve-rod at a point slightly above its threaded block was interrupted by a rod of vulcanite (I) attached by cemented screws (SS), which traversed the insulating air gap and the upper levels of the enclosing bath through telescoped chimneys of vulcanite

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[6] Height 153 mm., diameter 104 mm., thickness of wall 0.5 mm.

[7] The mixed calorimeter contents (neutral) showed no contamination by copper after any accepted determination.

on the calorimeter and jacket chimneys, constructed and insulated much as in other adiabatic assemblages previously used and tested. At a convenient point above the bath, the upper metal part of the valve-rod passed through accurately machined bearings in the metal case (B_1B_2) and at its extremity bore a large graduated mushroom head, which by its position with respect to a fixed scale (M) indicated (with reference to previous tests) the actual rate of flow during delivery, and made possible its precise duplication or variation in successive measurements. The whole apparatus worked very well if the necessary precaution was taken to exclude air from the delivery tube by filling it with solution before assemblage; otherwise delivery was incomplete. The two methods of delivery yielded concordant results; but that by which the alkali was delivered beneath the acid showed much less initial mixing, and in certain cases such mixing was not detectable, the form of the curve for the rate of evolution of heat being definable by the same empirical formulation for its initial as well as for its final segments.[8]

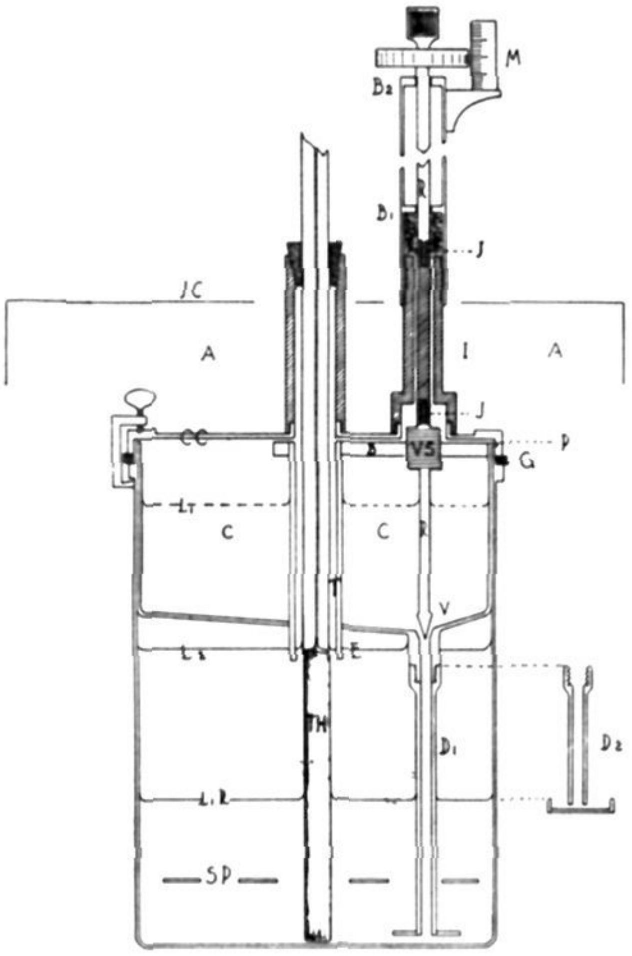

Fig. 2.—Diffusion calorimeter. A vertical diametrical section reduced to $^1/_3$ actual size: metal left blank, vulcanite single-hatched, soft rubber double-hatched, cement black. The cup and delivery mechanism are explained in the text. Other labeled parts are: CC, calorimeter cover; G, gasket; A, insulating air gap; JC, jacket cover; TH, thermometer; T, cylindrical tube through cup to accommodate thermometer; E, its extension to facilitate conduction from liquid to upper parts; SP, stirrer plate; its rods pass through chimneys on the diameter perpendicular to that of the section.

Preparations.—The hydrochloric acid used was prepared from a commercial concentrated acid of highest purity, half diluted and redistilled through silica. The middle half of the constant-boiling portion of this distillate was diluted with close approximation to the desired concentrations of 0.500, 0.250 and 0.125 normal, analyzed while still fresh by precipitation with silver nitrate, and finally adjusted to these normalities precisely to ±0.0003 normal; and was stored in "non-sol" glass. The sodium hydroxide solutions were made from comparably pure material, freed from carbonate by precipitation with barium hydroxide, the excess of which was removed by an exactly adjusted amount of sodium sulfate solution. Having been standardized against the hydrochloric acid, and precisely adjusted to the same normalities, it was kept in paraffin lined bottles, and properly protected from contamination by carbonate.

Assemblage.—Closely equal volumes of these solutions within 0.1° of the desired initial temperature of measurement were placed, respectively, in the calorimeter vessel and in its cup—disposed according to the intended method of delivery; and the whole

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(8) As in determination No. 27, Table III, p. 2226.

partial assemblage brought within one part in ten thousand (within 0.01 g.) to the fixed weight of a prepared tare by small additions of acid. Complete closure was then immediately effected, assemblage completed, and the system left under thermostatic control at the desired initial temperature.

Thermometry.—The calorimetric thermometer was one of a pair of twin mercury instruments, made to precise specification for this work. These were solid stem thermometers of the standard normal type, but of limited ranges of from *ca.* 19 to 25°, graduated in 0.01° intervals, the length of a degree being 70 mm. Their bulbs were of such length that they would completely traverse the intended invariable depth of the interdiffusing liquids, and were exactly cylindrical within less than 0.02 mm., their ends having been made as nearly flat as seemed advisable in consideration of the necessity of avoiding excessive strain. In practice, therefore, they almost exactly traversed the entire solution after mixture, and thus determined the mean temperature at its axis. The one thermometer used in this work as a calorimetric instrument was calibrated by an electrical method recently described[9] precisely to ±0.0002°; and was read with a telescope, at stationary temperatures micrometrically to ±0.0002° or less, and on a moving thread by estimation to ±0.0005° or less. The comparative registrations of its twin, which was used as a bath thermometer, were determined at 0.01° intervals on a slowly rising thread in an adiabatic system, by estimation to ±0.001°, and read with the same precision. Neither of these instruments, though both were new, showed any inconsistencies of registration as great at 0.001°, and their ice-points, determined by adiabatic comparison with a Baudin standard (Bureau Internat. No. 18,537) showed no change within its limit, a satisfactory indication that strain had been avoided in their construction, despite their peculiar form.

Adiabatic Control.—The calorimeter was insulated by an enveloping air gap 40 mm. thick,[10] and kept as closely as possible adiabatic during the period of diffusion—adequately so, it proved—by manual control of a fluctuating bath temperature with reference to the mean head indicated by the corrected registrations of the twin thermometers equally immersed and exposed, according to former practice.[11] During the isothermal pre-periods it was left for several hours under the thermostatic control of a system of the Beaver[12] type, and thus kept constant to ±0.002°, until during the last hour, by accessory hand manipulation, this usually adequate constancy could be improved. In all pre-periods the temperature of the system was so nearly constant (or, occasionally, drifting so nearly linearly below the permissible rate of 0.001° per hour) that measurements were unaffected by temperature drift beyond a desired limit of 0.0005°; and during measurement the bath fluctuation was invariably so slight and regular that no correction for imperfect adiabaticity ever had to be applied, and leakage by direct conduction was utterly negligible.

This very satisfactory control, which was not only more consistently precise but more facile than that of former measurements, was due in great measure to the installation of an air thermostat of small dimensions (60 × 30 × 120 cm.) which completely enclosed the calorimetric system. This device has been elsewhere described.[13] By its use the temperature of the immediate environment during pre-periods was kept constant to ±0.03°, not infrequently for ten hours or more. During measurements, in which the change of temperature usually exceeded 0.1°, its temperature was adjusted at intervals of thirty minutes or more to constancy at successive temperature levels, which seldom differed by more than 0.05° from that of the calorimeter, by a simple mechanism

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(9) THIS JOURNAL, **54**, 3785 (1932).

(10) *Ibid.*, **44**, 902 ff (1922).

(11) Ref. 4, above.

(12) Beaver and Beaver, *J. Ind. Eng. Chem.*, **15**, 359 (1923).

(13) THIS JOURNAL, **54**, 3785 (1932).

which turned the contact-bearing screw of its bimetallic regulator through measurable and pre-evaluated distances.[14]

Determination of Thermal Inhomogeneity.—Experimental procedure having been determined, the necessary investigation of irregularity in thermal distribution within the reacting liquids was undertaken, prior to measurement of the heat of diffusion itself. On account of the symmetry of the system, this investigation was reduced to the solution of two problems. First, since the determination of the average temperature by an integrating thermometer placed at the axis of the calorimeter rested upon the presupposition that the temperature gradients on all vertical sections of the liquid was the same—a condition which obtained when all of its horizontal levels were isothermal—it was necessary to discover whether or not the actual anticipated approximation to this condition was close enough to justify the assumption; and by such means that, if it were not, the consequent error could be determined with adequate precision. Second, since the adiabatic control was based upon the further suppositions that the mean temperature of the calorimeter surface was, closely enough, that indicated by the central thermometer, and that the highly conducting wall of the vessel would diminish its vertical temperature gradients sufficiently to eliminate significant convection in the gap (although it was known that the upper levels of liquid must, on account of internal vertical convection, be warmer than those below and that this diminution must be slight if horizontal levels were to remain sensibly isothermal), it was necessary to measure and integrate the actual vertical temperature gradients adjacent to the wall, and to estimate their effect upon leakage.

To determine these thermal gradients, local temperatures within the body of a diffusing system were observed with thermoelements. The calorimeter was provided with a special cup traversed by open partitions so placed that they permitted the mechanical adjustment of two sets of thermels—the one at any desired levels, the other at any desired distances from the axis on three radii at right angles to each other, between points a millimeter away from thermometer and periphery, respectively. By small racks and pinions attached to the calorimeter cover the thermels were precisely placed and moved, their positions being indicated by graduated screw-heads on the attached operating rods which moved against stationary pointers outside the system. Since the heat capacity of the special cup was not significantly greater than that of the one which it replaced, and was otherwise precisely like it, since the solutions used were of the same mass and concentration as those of the diffusion measure-

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(14) The possible precision of this simple accessory (which is, of course, only a conveniently controllable modification of a device frequently used) was considerably greater than that here indicated, which was adequate in these measurements. Its efficacy in preventing significant direct conduction leakage, in rendering the bath fluctuation slower, more regular and hence more easily controlled, and in eliminating all corrections for stem-exposure in thermometry will fully justify in any precise calorimetry the small trouble incident to its construction.

ments, and were similarly manipulated, and since the calorimeter with its attached thermoelement mechanism was effectively insulated and kept under an adiabatic control as precise as that of the determinations of diffusion rate, there is no doubt that the gradients observed in the accessory measurements were closely the same in both magnitude and location as those that characterized the measurements of diffusion. It remains to be said that the thermels themselves were carefully made of calibrated wire, precisely standardized with reference to the indications of the calorimeter thermometer, and read with all necessary precaution.

Radial Gradients.—The results of a large number of measurements of radial inhomogeneity at different levels in the reacting system showed that these were never greater than a few ten-thousandths of a degree, since they were quite undetectable, the few deflections of the galvanometer which were observed when the thermel branches were in the same horizontal plane being always ascribable to parasitic electromotive forces which were detected directly before and after measurement. From this negative result it was inferred that the long-bulbed thermometer measured the mean temperature of the whole system precisely to 0.001°.

The only part of the liquid that might have been at a lower mean temperature than the rest was a cylindrical shell outside the peripheral thermel certainly not more than 2 mm. thick, and therefore of less than 0.075 the total heat capacity of the liquid. To lower the mean temperature of the system 0.001°, its own mean temperature must have been 0.013° lower than that indicated by the thermometer. But the maximum total vertical gradient in the liquid itself during the period of measurement was only 0.013°.

Furthermore, the heat capacity of that part of the calorimeter which was not in immediate contact with the liquid was 0.055 of the whole. The difference between its thermal content at the temperature of the upper levels of liquid (in closest contact with it) and at the mean temperature of the liquid as indicated by the thermometer, under the condition of maximal vertical difference of temperature during measurement, would be 0.0007 that of the whole, and would represent a maximal uncertainty of 0.0007° in the determination of the mean temperature of the whole system, at the initial stage. After an hour this would be reduced to 0.0001° (Table I).

Vertical Gradients.—Determinations of vertical temperature gradients were, in this research, confined to an initial series of measurements which defined the total differences of temperature between the neutral zone and the surface and bottom of the liquid, respectively, at different times during the process of diffusion, the data they yielded being sufficient to demonstrate the negligibility of error in the estimation of leakage by the means adopted, and the consequent adequacy of adiabatic control. A typical example of several consistent sets is shown in Table I.

It will be noted that these gradients were not those of the vessel wall itself, but of liquid a millimeter or more distant from it, and must, therefore, have been considerably greater than the surface gradients; so that any inferences derived from them respecting the influence of surface in-

TABLE I

Thermel No.	Sensitivity in degrees	Elapsed time, minutes	Observed galvanometer deflections, mm.	Total vertical gradients, peripheral, degrees Below neutral zone	Total vertical gradients, peripheral, degrees Above neutral zone
4	±0.0002	17	5.0	0.013	
4		19	3.2	.0087	
4		22	2.2	.0057	
4		25	2.0	.0052	
4		30	1.6	.0042	
4		55	1.0	.0026	
2	± .0003	40	0.3		0.0018
2		65	.2		.0012
1	± .0001 –	66	.1		.0008

homogeneity on leakage would necessarily lead to excessive estimates, which, if they pointed to its negligibility, would be conclusive. The most evident of these demonstrated the insignificance of convections thus occasioned, for, by extrapolation of the tabulated data, the largest total gradient in the solution during the first fifteen minutes of diffusion was found to be 0.04°, and it was known that vertical temperature heads of this magnitude produce, under conditions much more favorable, no significant increase, by convection, of the leakage due to conduction and radiation in systems of this type.[15] There remained to be estimated, therefore, only the error occasioned by this largest gradient in the estimation of conduction and radiation leakage, which under calorimetric conditions are sensibly proportional to thermal head. To determine roughly an upper limit to the possible value of this error, it was assumed that the 0.04° gradient did actually exist in that zone of the vertical wall which was in contact with the liquid, and—with even more unfavorable approximation—that all other calorimeter surfaces were at the temperature of the lowest liquid levels. According to these suppositions, the mercury thermometer at the calorimeter axis indicated precisely the mean superficial temperature of the designated zone, the gradients in which were thus eliminated from consideration, so that the problem reduced itself to a determination of the uncompensated effect of the lower temperature assumed as that of the rest of the calorimeter surface. This was easily calculated, for short successive intervals of time and for the whole duration of the process, from the leakage modulus of the whole (isothermal) surface previously determined, the proportional area of the surface considered, and its temperature defect, assumed as initially 0.02° (half the maximum gradient) and as thereafter diminishing with the observed decrease of the gradient.[16] The final result of this estimate was that if the

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(15) THIS JOURNAL, **44**, 925, Table VI (1922).

(16) The whole superficial area of the calorimeter was 674 sq. cm.; that of the lateral zone at the thermometric temperature 336 sq. cm.; the remaining area was therefore 338 sq. cm. or almost exactly half of the whole. The leakage modulus for the whole surface at 0.01° head was 0.000011°

temperature indicated by the thermometer were taken as that of the whole calorimeter surface in the estimation of conduction and radiation leakage (and therefore of total leakage) the consequent error would be quite negligible.

Measurement of the Heat of Diffusion.—With the apparatus and by the procedure already described,[17] several continuous calorimetric measurements of the interdiffusion of hydrochloric acid and sodium hydroxide solutions were made, of which all but three of a continuous series of seventeen were judged upon their completion to be dependable.[18] Of these nine were made with 0.250 molar solutions (Expts. 18 to 22 inclusive, 25, 32, 33 and 34); three with 0.125 molar solutions (Expts. 24, 27 and 29); and two with 0.500 molar solutions (Expts. 30 and 31). All were carried out at the same initial temperature, 20.00 ± 0.03°, excepting the last two (Expts. 33 and 34), which were made at 25.00° for the purpose of determining, if it were possible within this range, a temperature coefficient of the process. In duration, all exceeded four hours. The adiabatic control was invariably sufficiently precise to make corrections for leakage less than 0.0002°, that is to say negligible, for any interval of time; and it was judged from the regularity of the graphs of change of temperature with time (which were plotted without smoothing off through all finally determined points), that no thermometric error was greater than 0.001°. The adequacy of the other experimental precautions was likewise confirmed by the results of measurement. Excepting with respect to the amount of initial turbulence, all determinations were found—by procedures of intercomparison yet to be described—to be consistently representative of a single type of process within a limit of divergence comparable to the thermometric error. Because of this consistency, it is unnecessary to present and discuss here the whole bulk of data. In Table II will be found the final results of all the more dependable determinations (those, namely, in which alkali was delivered underneath the acid) which were made with 0.125 molar solutions. In addition, four were made with 0.250 molar and two with 0.500 molar solutions, with comparable precision. In Table III, data of measurements made with solutions of each of these concentrations are arranged to make their several divergences from a single empirical formulation apparent. The curves of all these determinations,

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per minute [THIS JOURNAL, **44**, 919 Table V (1922), confirmed for the present system], and the same for half the surface at its initial head of 0.02°. The limiting error of a correction for leakage based upon the acceptance of the thermometric temperature as that of the calorimetric surface as a whole would therefore be for the first fifteen minutes 0.000011° × 15, or closely 0.0002°; for the next fifteen minutes (with reference to the data of Table 1) about 0.0001°, for the next hour 0.0001° and thereafter less than 0.0001° per hour. The maximal total error from this source for a determination lasting $4^1/_2$ hours—the longest duration in this group of measurements—would therefore be less than 0.0006°, which is approximately the error of observation.

(17) See p. 2218.

(18) The rejected determinations showed incomplete delivery and excessive initial turbulence. The experiments numbered 1 to 17 were either preliminary trials or measurements of inhomogeneity. Original experiment numbers are here retained.

together with two of determinations in which acid was delivered on the surface of the alkali, are shown in Fig. 3.

TABLE II

CHANGE OF TEMPERATURE DURING DIFFUSION

A: 0.125 Molar Solutions

Detn. No. 27 $T = 0.05\ Ct^{0.584}$		Detn. No. 29				Detn. No. 24			
Elapsed time, minutes	Temp. rise, millidegrees A	Elapsed time, minutes	Temp. rise, millidegrees B	Δ B-A	d	Elapsed time, minutes	Temp. rise, millidegrees C	Δ C-A	d
Period of initial turbulence not here recorded									
11	26	(10)	(44)	18	0	7	169	143	+6
		11	45						
15	32	(14)	(51)	19	+1	11	173	141	+4
(17)	(35)	16	55	20	+2				
18	37	(17)	(56)	19	+1				
22	41	21	62	19	+1	18	183	142	+5
27	46	26	64	18	0				
32	50	31	70	20	+2	28	191	141	+
37	54	36	75	21	+3	33	193	139	+
47	62	46	82	20	+2	43	197	135	−
57	70	56	88	18	0	53	202	132	−
67	75	66	95	20	+2	63	209	134	−
77	81	76	101	20	+2	73	214	133	−5
87	86	86	106	20	+2	83	222	136	−1
97	91	96	110	19	+1	93	226	134	−3
107	96	106	116	19	+1	103	232	136	−1
117	102	116	120	18	0	113	237	135	−2
127	107	126	125	18	0	123	242	135	−2
137	111	136	129	18	0	133	247	136	−1
147	116	146	134	18	0	143	252	136	−1
157	120	156	138	18	0	153	256	136	−1
167	124	166	142	18	0	163	261	137	0
177	128	176	145	17	−1	173	266	138	+1
187	132	186	148	16	−2	183	271	139	+2
197	136	196	152	16	−2	193	274	138	+1
207	140	206	156	16	−2	203	278	138	+1
217	144	216	158	14	−4	213	282	138	+1
227	148	226	162	14	−4	223	286	138	+1
237	151	236	165	14	−4	233	290	139	+2
247	154	246	168	14	−4	243	293	139	+2

Average Δ = 17.9 a. d. = 0.8

Average Δ = 137.2 a. d. = 1.1

Mean a. d. = 0.6

For convenience, comparisons are made here between observed rather than interpolated temperatures, and hence between those read not at the same times, but in Detn. No. 29 at times 1 minute earlier and in Detn. No. 24 at times 4 minutes earlier than the times of Detn. No. 27.

Δ is difference between temperatures thus selected for comparison, d is deviation from the average of all the differences Δ. Values in parentheses are interpolated. Development of heat in the initial periods is shown by the curves of Fig. 3.

TABLE III

COMPARISON OF OBSERVED CHANGES OF TEMPERATURE WITH THOSE CALCULATED BY THE FORMULA $T = 0.05\ Ct^{0.584}$

Detn. No. 27; $C = 0.125\ M$				Detn. No. 33; $C = 0.250\ M$				Detn. No. 30; $C = 0.500\ M$			
Time, t, minutes	Temperature, T Obs. millidegrees	Temperature, T Calcd. millidegrees	Δ	Time, t, minutes	Temperature, T Obs. millidegrees	Temperature, T Calcd. millidegrees	Δ	Time, t, minutes	Temperature, T Obs. millidegrees	Temperature, T Calcd. millidegrees	Δ
5	14	16	+2								
10	24	24	0	10	56	48	− 8				
15	32	30	−2	15	84	61	−23	15	179	122	− 57
18	37	36	−1								
								25	234	164	− 70
32	50	47	−3								
37	54	52	−2	39	127	106	−21	39	288	212	− 76
47	62	59	−3	49	144	122	−22				
57	70	67	−3	59	158	135	−23	60	357	273	− 84
67	75	73	−2	69	173	148	−25	69	383	296	− 87
77	81	79	−2	79	184	160	−24	79	407	321	− 86
87	86	85	−1	89	196	172	−24	89	432	342	− 90
97	91	90	−1	99	209	183	−26	99	456	366	− 90
107	96	96	0	109	221	194	−27	109	479	387	− 92
117	102	100	−2	119	232	204	−28	119	500	408	− 92
127	107	106	−1	129	241	213	−28	129	521	427	− 94
137	111	111	0	139	252	223	−29	139	543	446	− 97
147	116	115	−1	149	261	232	−29	144	551	455	− 96
157	120	120	0	159	270	242	−28	154	570	474	− 96
167	124	124	0	169	279	250	−29	164	589	482	− 97
177	128	128	0	179	287	256	−31	174	607	509	− 98
187	132	133	+1	189	294	267	−27	184	625	526	− 99
197	136	137	+1	199	303	275	−28	194	642	542	−100
207	140	141	+1	209	311	283	−28	204	657	559	− 98
217	144	145	+1	219	319	291	−28	214	673	574	− 99
227	148	149	+1	229	326	299	−27	224	688	588	−100
237	151	152	+1	239	334	306	−28	234	705	604	−101
247	154	156	+2	249	341	314	−27	244	719	620	− 99
				259	349	321	−28	254	734	634	−100
a. d. = 0.4				a. d. after 100 minutes = 0.9				a. d. after 120 minutes = 1.5 after 170 minutes = 0.8			

The curves show most clearly the only significant experimental irregularities, which are those of initial turbulence. These effects were most noticeable when acid was delivered upon the surface of the alkali. The curves of determinations thus conducted (*e. g.*, Nos. 18 and 22 in Fig. 3) show sharp maxima in the initial segments, followed by depressions and subsequent short elevations of greater slope than those determined by backward extrapolation. The curves of those determinations in which alkali was introduced below the acid show no apparent irregularities of this sort, though they do indicate—by the fact that those which represent the diffusion of solutions of the same concentration are not superposed but lie one above another, as do corresponding curves in the other group—that considerable and unequal heats of mixture were developed by both methods of delivery. This heat, however, was evidently much smaller when alkali was introduced below the acid, and in one determination (Expt. 27) it appears to have been negligible, since in this case the heat initially developed is least of all, and a single empirical formulation fits the curve, not only over the long segment which appears to represent the diffusion after the period of mixture was past—which is the usual case—but over its whole length.

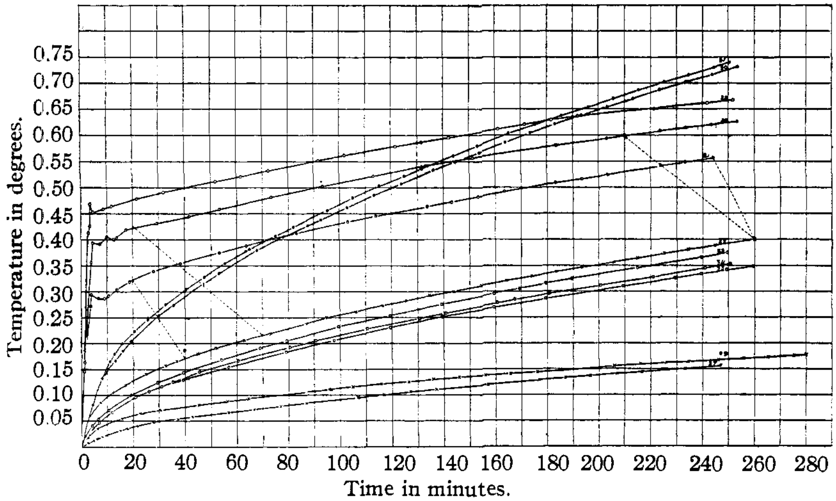

Fig. 3.—Experimental curves showing rates of change in temperature during diffusions and the superimposed effects of initial turbulence. The curves bear the experiment numbers. The determined points of curves for 0.500 *M* solutions are marked with black disks; those of 0.250 and 0.125 *M* solutions with circles and with crosses, respectively. Curves 20, 21 and 22 are those of determinations in which acid was delivered on the surface of alkali; the others, of determinations in which alkali was delivered beneath acid.

This formulation is $T = 0.05\ Ct^{0.584}$, where T is the temperature rise in degrees centigrade, C the equivalent concentration, and t the time in minutes. To prove that it does actually define the rate of temperature change in an undisturbed diffusion—that it does not represent the combined effect of diffusion and persistent though diminishing intermixture by turbulence—it is sufficient to show that it is applicable to the curves of other like determinations in which initial mixture was greater in different degrees, since in such cases the effect of mixture must have been variable. The close approach to parallelism of the curves of determinations made with solutions of the same concentration (Table II) indicates though it does not prove the absence of such variable effects after the lapse of an hour or less; but it is evident that—since initial mixture in different determinations diminished to a different extent the reaction concentrations of the solutions at the indeterminate times when its effect seemingly vanished and undisturbed diffusion began—the diffusing systems cannot have been in exactly corresponding states after the lapse of the same intervals of time, despite their close approach to parallelism. To determine these corresponding states in order to effect more minute comparisons, it is necessary only to identify on the several curves examined near the time ordinate where they seem to become parallel—or more safely at ordinates which represent times later than this by some constant interval—points at which the slopes are equal, for since the speed of reaction (and consequently the heat evolved, and the rise of temperature in systems of identical capacity) will be proportional to concentration, such points will represent times at which the concentrations are the same, and the segments beyond them will correspond. Such corresponding segments are shown by the transverse dotted lines in Fig. 3.[19]

In a similar manner the curves of determinations made with solutions of different concentration may be compared; for since the rate at which heat is developed will be, *ceteris paribus*, proportional to concentration, all that is necessary is to multiply the ordinates of such curves by factors which are the reciprocals of their relative concentrations to reduce these rates to comparable magnitude, and then to compare segments of equal initial slope as in the former case.

The curves of all fourteen dependable determinations have been thus variously transposed, or reduced and transposed, and their corresponding segments superposed by a second transposition through the ordinate distances between their initial points. This comparison (which it is unnecessary to describe at length) showed that the results of determinations made with solutions of any one concentration were consistent, after the first half hour or less of diffusion, within thermometric error ($\pm 0.001°$); but that those made with solutions of different concentrations remained divergent for much longer times. From the unadjusted data of Table III, however, it is clear that after the lapse of three hours the rates at which heat was developed by diffusion were the same for solutions of all concentrations. This is shown by the consistency of the differences, Δ, which indicates parallelism of the corresponding curves, after two hours in the case of 0.250 normal solutions, and after three hours in the case of 0.500 normal solutions. It is to be inferred, therefore, that the observed discrepancies of the rates of heat development in solutions of different concentrations are

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(19) If the initial points of these segments represent times at which the curves compared are first observed to be strictly parallel, then their abcissas measure the durations of the effects of turbulence, with a precision equal to the error of temperature measurement divided by the slope of the curve at the point; and the intercepts on the ordinate axis determined by the backward extrapolation of their corresponding segments measure the total heats of mixture, differences between these heats in different determinations being measured by the ordinate distances between the points. It is evident from the slopes of the transversals that though the persistence of a greater heat of mixture is longer, there is no proportionality between thermal effect and duration.

due, not to a variability of rate with concentration, but merely to the very slowly diminishing effects of initial turbulence which ultimately become negligible. All determinations illustrate, therefore, a uniform process masked in varying degrees by the superimposed effects of initial turbulence, which process is defined for all concentrations up to half-normal by the formulation $T = 0.05\ Ct^{0.584}$.

The precision of measurement, determined from the data of the later periods of diffusion and extrapolated to the origin by formulation, approximates a mean of ±0.65% for 0.125 normal solutions, which diminishes proportionally with increase of concentration. This precision of measurement is not inferior to that which was sought, and is, in this sense, satisfactory. It is, however, insufficient to determine a temperature coefficient for the process; the two measurements carried out at 25° gave results which were so closely consistent with the rest that they justify nothing more than the statement that the temperature coefficient is not greater than 0.3% within a range of 5°, and that, therefore, it is negligibly variable for the half-degree range of the experimental process.

Heat Capacity of the System.—To effect the necessary conversion of temperatures thus determined into quantities of energy, the heat capacity of the calorimetric system holding a tared quantity of water at 20° was determined by an electrical method[20] with a precision of about 2.4 mayers;[21] and those of the acid-alkali systems actually used were derived from this by substitution of the calculated heat capacities of the solutions for that of the water. This was done because the weights of the solutions were not precisely the same in the several determinations,[22] and was permissible since all portions of acid and alkali had been weighed accurately to the nearest 0.01 g., and since the very precise data of Richards and Rowe on their specific heats under comparable conditions were available.[23] The average heat capacities thus determined, and the mean deviations of single values from this average were: for concentrations 0.250 *N*, and 0.125 *N*,

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(20) The heat capacity of the standardization calorimeter was determined at 20–21° by the very exactly measured electrical heat necessary to raise its temperature through two overlapping standardized intervals on the thermometer used in the diffusion measurements; first when it held its usual tared mass of water, and second when it held in addition a small accessory heating coil (quiescent) designed for use with the diffusion calorimeter.

(21) Joules ÷ degrees centigrade (see T. W. Richards, *Proc. Am. Acad.*, **36**, 327 (1900)). This precision—about ±0.58 gram-calorie units, which corresponds to a thermometric precision of ±0.0007° in the diffusion measurements—was determined by that of the measurements made with the accessory coil. Those made with the standardization apparatus, twelve in all, showed an average mean deviation from the mean of ±0.31 gram-calorie units, corresponding to ±0.0003° with that system. The lower final precision, however, being adequate, was not improved.

(22) This variability, obviously, cannot have affected the form of the curves representing the rate of temperature change, but will have affected the estimation of heat of mixture from these curves. From the temperature rise due to mixture as determined by the temperature–time curves (footnotes 49 and 51) the heat of mixture can be found to 0.1% by using the two mean heat capacities here given; but it may also be found by using, in place of data provided by the curves, the total rise in temperature in a given interval, less that caused by diffusion alone according to the formula. Cross checks are thus provided upon precision of estimation.

(23) THIS JOURNAL, **42**, 1621 (1920); **43**, 770 (1921).

3550.1 ± 2.1 mayers (848.7 ± 0.5 g. c. u.); and for the concentration 0.500 *N*, 3465.6 ± 1.2 mayers (828.5 ± 0.3 g. c. u.).

Speed of Diffusion.—From the relation $T = 0.05\ Ct^{0.584}$ the speed of diffusion at the plane of contact (the neutral plane) may be simply calculated as follows. The total heat developed in *t* minutes is *HT*, where *H* is the heat capacity of the system. If *Q*, in comparable units, is the heat of neutralization of a gram-equivalent under the conditions, then during *t* minutes of diffusion *HT/Q* gram-equivalents of both hydrochloric acid and sodium hydroxide have crossed the plane of contact; and if *A* is the area of this plane in square centimeters, *HT/QA* gram-equivalents have crossed each square centimeter of it in the same time. Therefore, since $T = 0.05\ Ct^{0.584}$, the speed of diffusion for both hydrochloric acid and sodium hydroxide at the contact plane, in gram-equivalents per minute through a square centimeter, is

$$\frac{H(0.05C)}{QA}\frac{\mathrm{d}}{\mathrm{d}t}t^{0.584} = \frac{H(0.05C)}{QA}\ 0.584\ t^{-0.416}$$

In these determinations, *A* was invariably 85.0 sq. cm. *C* had three values: 0.500, 0.250 and 0.125-gram equivalents per liter. *H* had two values: for the concentration $C = 0.500$, 828.5 ± 0.3, and for the concentrations $C = 0.250$ and 0.125, 848.7 ± 0.5 gram calorie units. The three corresponding values of *Q* are 13,880, 13,810 and 13,760 calories, respectively, per gram-equivalent neutralized.[24]

From these data the speeds of diffusion at the plane of contact will be, during four hours, at 20–25°

For solutions 0.125 *N* $(2.64 \times 10^{-6})t^{-0.416}$
For solutions 0.250 *N* $(5.27 \times 10^{-6})t^{-0.416}$
For solutions 0.500 *N* $(10.25 \times 10^{-6})t^{-0.416}$

These results fulfil the immediate purpose of the investigation.

Summary

1. This paper presents the first of a series of studies on the possibilities of the calorimetric control of protracted processes in thermally inhomogeneous systems. A method is described whereby it is possible to measure, with a precision somewhat better than 1 gram-calorie, the heat generated during four hours or more in an unstirred mass of liquid which develops a maximal vertical inhomogeneity of temperature (due to thermal stratification) of about 0.015°.

2. By this method the rates of interdiffusion of equimolar solutions of HCl·Aq and NaOH·Aq have been determined, the plane of contact being at 20–25°.

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[24] Data from Richards and Rowe, THIS JOURNAL, **44**, 702, 703 (1922).