9. Summary.

1. By transference experiments in the presence of raffinose as a reference substance, the true transference number of caesium ion in 1.2 *M* caesium chloride solution at 25° has been found to be 0.491 and the water transference 0.33 ± 0.06 formula weights of H_2O per faraday, from anode to cathode. Caesium ion is thus the least hydrated of the alkali ions. It carries on the average 0.65 mol less H_2O than potassium ion.
2. Similar experiments with potassium nitrate solutions showed that the water transference was from anode to cathode with this salt also.
3. The effect of caesium chloride upon the specific rotatory power of raffinose is the same as that of potassium chloride. It increases $[\alpha]_E$, 0.09° per mol of salt added to a liter of the 0.1 *M* raffinose solution.
4. Contrary to a statement in the literature, caesium chloride is not appreciably volatile with steam.

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THE HEAT OF NEUTRALIZATION OF HYDROXYLAMINE AND TETRAMETHYLAMMONIUM HYDROXIDE.

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Recent thermochemical measurements by Richards and his co-workers, using the adiabatic calorimeter, have shown conclusively that many of the thermochemical data in the literature are of very questionable accuracy. The adiabatic calorimeter permits a degree of accuracy heretofore unattainable in thermochemical measurements and for the first time puts these measurements on a par with the measurements of other physicochemical constants. Since considerable of the thermochemical data in the literature have been determined by but two investigators (Berthelot and Thomsen), and as the data are often the results of single measurements, by methods which at best could give only approximate values, it has seemed highly desirable that these measurements be repeated, using the methods for precise calorimetry now available.

This paper deals with the measurement of the heat of neutralization of hydroxylamine and tetramethylammonium hydroxide when neutralized with hydrochloric, sulfuric, and trichloroacetic acids in aqueous solutions, using an adiabatic calorimeter. The method followed was practically the same as that used by Richards and Rowe,[1] and the adiabatic bath employed was similar to the one designed by Richards and Burgess[2] and by Richards and Jesse.[3]

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[1] *Z. physik. Chem.*, 64, 187 (1908); *Proc. Am. Acad.*, 43, 475 (1908).

[2] THIS JOURNAL, 32, 431 (1910).

[3] *Ibid.*, 32, 268 (1910).

Materials.

Trichloroacetic Acid.—A well-known manufacturer's purest trichloroacetic acid was used. The sample taken for the experiments showed but the slightest trace of hydrochloric acid.

Tetramethylammonium Hydroxide.—This base was prepared from recrystallized tetramethylammonium iodide by dissolving the latter in pure water and agitating the solution for several hours at about 45°, with an excess of freshly precipitated silver oxide, avoiding contact with air as much as possible. The warm solution was filtered quickly by powerful suction, through a layer of several filter papers, directly into the container designed for the base. The hydroxide was then carefully standardized by titration with a standard solution of sulfuric acid, using methyl orange as indicator.[1] The strength of the sulfuric acid solution had previously been determined by careful gravimetric analyses.

Hydroxylamine.—Freshly prepared hydroxylamine was used exclusively. The base was made from dry hydroxylamine phosphate $[(NH_2OH)_3.H_3PO_4]$ by distilling the latter at a low pressure, according to the method of Uhlenhuth.[2] In this distillation 20 g. of the salt were heated in a fractionating bulb at about 20–30 mm. pressure. The salt decomposed into phosphoric acid and hydroxylamine, the base passing over into the ice-cooled receiver where it solidified. The fraction distilling between 90° and 130° at about 25 mm. pressure was used.

Since hydroxylamine is explosive at higher temperatures, it is necessary to take proper precautions during the distillation.

Strength of Solutions.

Generally the solutions were made up to a concentration approximating, in some cases, to the ratio of one mol of the reagent to fifty of water, and, in other instances, to the ratio of one to two hundred.

Trichloroacetic Acid.—The acid was dissolved in pure, distilled water and the solutions were made up to the desired strength, guided by titration against a standard solution of sodium hydroxide, using methyl orange as indicator.

Hydroxylamine.—The crystalline hydroxylamine, obtained from the decomposition of hydroxylamine phosphate $[(NH_2OH)_3.H_3PO_4]$, was dissolved in pure, cold water immediately upon the completion of the distillation. The solutions were then made up to the required strength, as indicated by titration against a gravimetrically standardized solution of sulfuric acid, using methyl orange as indicator. The solutions were kept in ice because the base decomposes slowly at the ordinary room

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[1] The base exhibited no apparent change of strength on standing for a considerable time, as was indicated by its titration, in the same manner, five months after the experiments herein described were performed.

[2] *Ann.*, 311, 117 (1900).

temperature. The calorimetric measurements were, therefore, made as soon as possible after standardization of the solutions.

Tetramethylammonium Hydroxide.—The strength of the solution of this base was obtained by titration as previously stated, and the hydroxide was kept in a receptacle adapted to prevent atmospheric carbon dioxide from coming in contact with it.

Method and Apparatus.

The thermal data were obtained in exactly the same manner as described by Mathews[1] in his experiments on the adiabatic measurements of heats of reaction in nonaqueous solutions. The accompanying diagram represents in cross-section the essential parts of the apparatus. The adiabatic bath D and the necessary fixtures were adjusted in identically the same way as were the corresponding parts of the apparatus used by Mathews.

A weighed quantity (of a known volume) of the solution of the base to be neutralized was placed in the platinum bottle A, which was suspended in a known weight of water contained in the platinum calorimeter B. The quantity of acid required to exactly neutralize the alkali (plus a predetermined amount necessary to compensate for the wetting of the walls and for loss on drainage) was placed in the jacketed, cylindrical compartment C, from which it could be run into A through a stopcock. The acid in C and the base in A were stirred, the former by means of a heavy platinum spiral surrounding the thermometer J, and the latter by a platinum stirrer, P. The water in B was stirred by a silver stirrer, H, attached to two hard-rubber rods. A standardized Beckmann thermometer, I, which could easily be read to 0.001° by the aid of a sliding telescopic lens, was placed in B to register the rise in temperature of the water in the calorimeter. In order that the acid and alkali might be at the same temperature at the time of mixing, the pump E was used to force a strong current of the alkali solution in D through the jacket, L. As the Beckmann thermometer J had previously been carefully compared with the standardized thermometer I, it was possible to determine when the temperatures of the acid and the base were precisely the same, by referring to the table of comparison. The Beckmann thermometer I had been standardized very accurately, in the adiabatic calorimeter, against a thermometer standardized by the Bureau of Standards.

When the acid and the alkali had reached exactly the same temperature, they were quickly mixed by allowing the acid in C to run into the alkali in A, the last drop in the delivery tube of C being forced out by a quick compression of the rubber bulb M. As the temperature in B began to rise, the temperature of the bath D was made to rise by running

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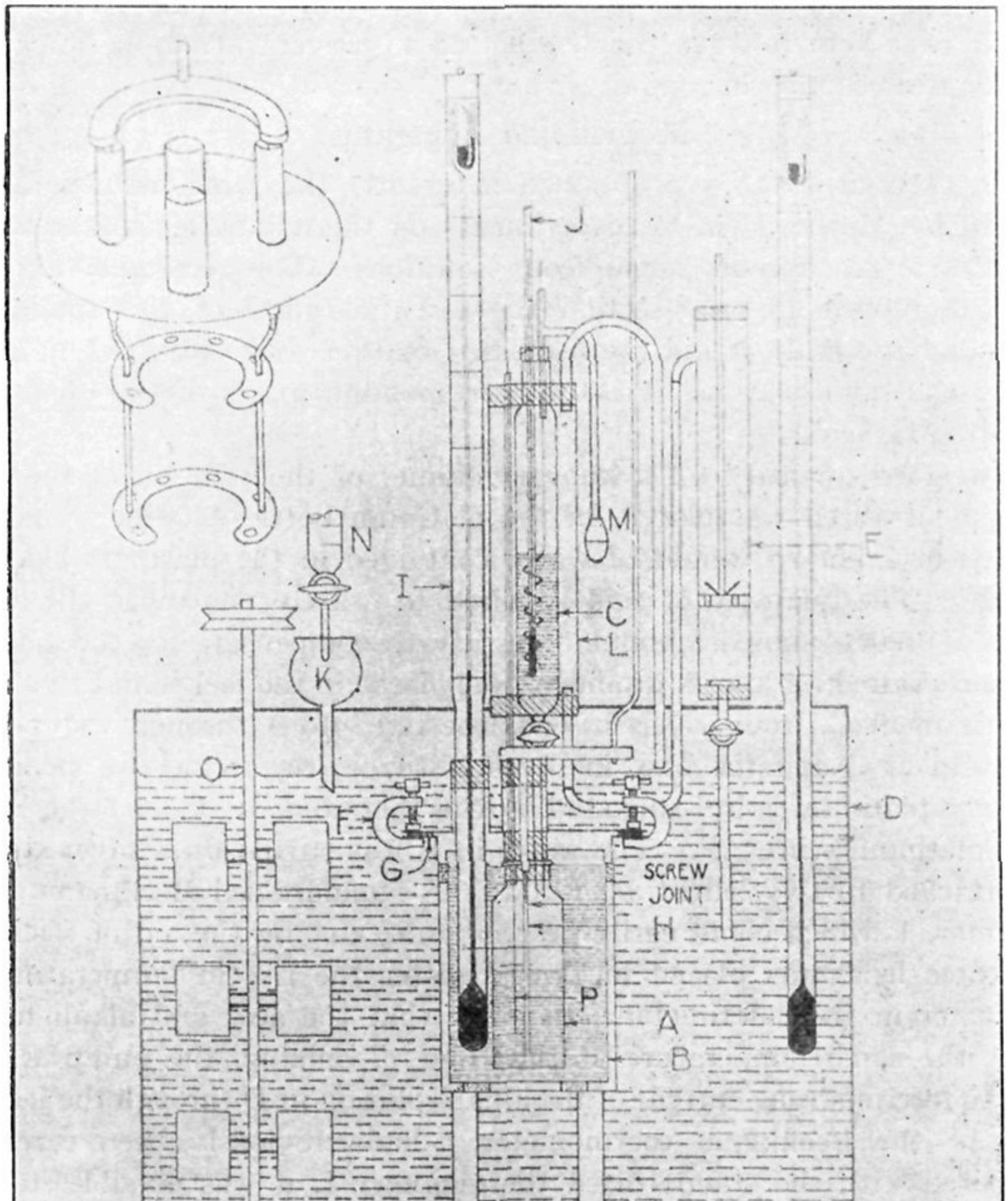
[1] THIS JOURNAL, 33, 1291 (1911).

concentrated sulfuric acid from the buret N into the alkali. The flow was so controlled that the temperature in D, as indicated by its thermometer, was always equal to that in B, as shown by the thermometer I.



The solution in D was stirred very thoroughly by a powerful stirrer, O. The stirrers and pump were run by an electric motor at a definite speed throughout all the experiments. The platinum calorimeter B was supported within a closed copper vessel by means of dry cork points, thus avoiding direct contact with the surrounding bath.

In order to calculate the water equivalent of the salt solution resulting from the reaction, the bottle A, with its contents, was weighed after each experiment to ascertain the exact weight of the salt solution. The water equivalent of the solution was then computed from its weight and specific heat, the latter value having been obtained previously by adiabatic measurements.

In every experiment the amount of acid required for the exact neutralization, plus a certain excess to make up for the loss of liquid adhering to the walls of compartment, C, was determined before the actual measurement was made.

TABLE I.

Heat evolved by the neutralization of 40.77 g. of 1.354 *N* hydrochloric acid (gravimetrically standardized) by 2.71 *N* sodium hydroxide.

Initial temp. (cor.) of the NaOH in C and of the HCl in A (of the calorimeter)			18.159°
Final temp. of the calorimeter (cor.)			19.606°
Rise in temperature			1.447°
Water in the calorimeter			450.00 g.
Wt. of the platinum calorimeter	B	100.73 g.	
Water equivalent of calorimeter	B =	100.73 × 0.0324 =	3.264 g.
Wt. of the platinum bottle	A	52.436 g.	
Water equivalent of bottle	A =	52.436 × 0.0324 =	1.699 g.
Wt. of the silver stirrer	H	23.876 g.	
Water equivalent of stirrer	H =	23.876 × 0.055 =	1.313 g.
Wt. of the platinum stirrer	P	7.831 g.	
Water equivalent of stirrer	P =	7.831 × 0.0324 =	0.254 g.
Water equivalent of thermometer	I =		2.163 g.
Total water equivalent of the calorimeter and fittings			8.693 g.
Water equivalent of the 63.02 g. of NaCl solution formed, sp. ht. being 0.95[1]			59.87 g.
Total water equivalent =		(450 + 98.693 + 59.87) =	518.563 g.
Total heat evolved by the reaction = 518.56 × 1.447 =			750.35 cals.

The results given in Table II are taken from four experiments conducted to determine the heat liberated as shown in Table I.

TABLE II.

Total water equivalent.	Initial temp. of acid and base (cor.).	Rise in temp. (cor.).	Total heat liberated.
518.56	18.159°	1.447°	750.35 cals.
518.59	19.521°	1.446°	749.88 cals.
518.61	20.203°	1.446°	749.91 cals.
518.54	18.462°	1.447°	750.32 cals.
		Average,	750.12 cals.

Hence, by exactly neutralizing 40.77 g. of 1.354 *N* hydrochloric acid by 2.71 *N* sodium hydroxide 750.12 calories of heat are evolved.

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[1] Thomsen's value for the specific heat.

TABLE III.

The specific heat of hydroxylamine sulfate $[(NH_2OH)_2.H_2SO_4]$ solution formed by the neutralization of 30.22 g. of 1.0578 *N* hydroxylamine by 1.0607 *N* sulfuric acid. (The approximate molecular ratio of the base or acid to water was 1 : 50.)

Wt. of 1.354 *N* hydrochloric acid	40.77 g.
Excess of NaOH solution taken	0.07 cc.
Wt. of the hydroxylamine sulfate solution placed in the calorimeter	450.00 g.
Initial temp. (cor.) of the NaOH in C and of HCl in A (of the calorimeter)	18.535°
Final temp. of the calorimeter (cor.)	20.049°
Rise in temperature	1.514°
Water equivalent of the 62.96 g. of NaCl solution formed (sp. ht. 0.95)[1]	59.81 g.
Water equivalent of the calorimeter and fittings (Table I)	8.69 g.
Total water equivalent	68.50 g.
Total heat absorbed exclusive of the hydroxylamine sulfate solution = 68.50 × 1.514	103.71 cals.
Heat liberated by the neutralization of 40.77 g. of 1.354 *N* hydrochloric acid (Table II)	750.12 cals.
Therefore, the total heat taken up by the hydroxylamine sulfate solution = 750.12 — 103.71 = 646.41 cals.	
Specific heat of the solution = 646.41 ÷ (450 × 1.514) = 0.9488	

TABLE IV.

Heat evolved by the neutralization of 30.22 g. of 1.0578 *N* hydroxylamine by 1.0607 *N* sulfuric acid. (The molecular ratio of base or acid to water was approximately 1 : 50.)

Wt. of hydroxylamine taken	30.22 g.
Wt. of sulfuric acid used	30.98 g.
Initial temp. (cor.) of the sulfuric acid in C and of the hydroxylamine in A (of the calorimeter)	18.464°
Final temp. of the calorimeter (cor.)	19.169°
Rise in temperature	0.705°
Water in the calorimeter	450.00 g.
Water equivalent of the 61.21 g. of hydroxylamine sulfate solution formed, sp. ht. 0.9488 (Table III)	58.08 g.
Water equivalent of the calorimeter and fittings	8.69 g.
Total water equivalent	516.77 g.
Heat evolved by the reaction = 516.77 × 0.705 =	364.32 cals.
Since the 30.22 g. of hydroxylamine solution measured 30.08 cc. (at 20°), this amount of heat was liberated by neutralizing 30.08/1000 × 1.0578 × 33 or 1.05 g. of the base in the given concentration. The heat evolved by the neutralization of 1 g. molecule of hydroxylamine will, therefore, be 364.32 × 33/1.05 = 364.32 × 31.43 = 11450.5 cals.	

The calorimetric procedure consisted in first finding the amount of heat evolved in the neutralization of a definite weight of a certain hydrochloric acid solution by a certain sodium hydroxide solution, the strength

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[1] Thomsen's value.

of both being known, using a known weight of water in the calorimeter. This identical reaction was repeated, quantitatively, whenever it was desired to use it as a source of a definite, known amount of heat in measuring the specific heat of the salt solution which was formed in the process of any given neutralization. The water equivalent of the calorimeter and fittings was calculated from the heat capacities of the several parts. The water equivalent of the sodium chloride solution resulting from the neutralization was computed, using Thomsen's value for the specific heat of sodium chloride solution at the given concentration and temperature.

TABLE V.

Results of the measurements of the specific heat of the salt solution formed in the bottle A during the various neutralizations. In each of these determinations 450 g. of the salt solution in question were placed in the calorimeter.

Salt solution.	Approx. mol. ratio of acid or base to water.	Initial temp. of acid and alkali.	Rise in temperature.	Water equivalent.	Specific heat.
$NH_2OH.HCl$	1:50	18.854°	1.510°	68.54	0.9516
		18.712°	1.510°	68.54	0.9516
		18.638°	1.508°	68.54	0.9530
				Mean,	0.9521
$NH_2OH.HCl$	1:200	18.649°	1.477°	68.45	0.9765
		18.664°	1.478°	68.50	0.9757
				Mean,	0.9761
$(NH_2OH)_2.H_2SO_4$	1:50	18.535°	1.514°	68.50	0.9488
		18.762°	1.513°	68.50	0.9495
				Mean,	0.9491
$(NH_2OH)_2.H_2SO_4$	1:200	18.588°	1.476°	68.61	0.9769
		18.657°	1.477°	68.60	0.9763
		18.596°	1.475°	68.55	0.9777
				Mean,	0.9770
$NH_2OH.CCl_3COOH$	1:100	18.694°	1.506°	68.53	0.9545
		18.726°	1.507°	68.59	0.9537
		18.582°	1.505°	68.50	0.9553
				Mean,	0.9545
$NH_2OH.CCl_3COOH$	1:200	18.684°	1.479°	68.50	0.9748
		18.708°	1.480°	68.51	0.9741
				Mean,	0.9744
$(CH_3)_4NOH.HCl$	1:200	18.726°	1.482°	68.50	0.9726
		18.750°	1.482°	68.59	0.9724
				Mean,	0.9725
$[(CH_3)_4NOH]_2.H_2SO_4$	1:200	18.756°	1.479°	68.54	0.9748
		18.715°	1.479°	68.52	0.9748
				Mean,	0.9748
$(CH_3)_4NOH.CCl_3COOH$	1:200	18.705°	1.485°	68.59	0.9701
		18.657°	1.487°	68.60	0.9684
		18.683°	1.486°	68.62	0.9693
				Mean,	0.9693

TABLE VI.

Base and acid and their approx. mol. ratio to water.		Wt. and vol. of solution of base taken.	Wt. of salt solution formed and its sp. ht.	Initial temp. of acid and base.	Rise in temperature.	Total water equivalent.	Heat from the reaction.	Heat liberated by one mol.
NH_2OH	1.0564 *N*	30.139 g.	60.79 g.	18.021°	0.581°	516.57	300.13	9475 cals.
HCl	1.0559 *N*	30.00 cc.	60.72	18.485°	0.582°	516.50	300.60	9490 cals.
Mol. ratio	1:50		60.77	18.079°	0.581°	516.54	300.11	9474 cals.
			60.76	18.681°	0.582°	516.54	300.62	9491 cals.
			sp. ht. 0.9521				Mean,	9483 cals.
NH_2OH	0.2642 *N*	30.0385 g.	60.21 g.	18.641°	0.142°	517.46	73.48	9271 cals.
HCl	0.2639 *N*	30.00 cc.	60.19	18.597°	0.143°	517.44	73.99	9335 cals.
Mol. ratio	1:200		60.15	18.528°	0.142°	517.40	73.48	9271 cals.
			sp. ht. 0.9761				Mean,	9292 cals.
NH_2OH	1.0578 *N*	30.220 g.	61.21 g.	18.464°	0.705°	516.78	364.32	11450 cals.
H_2SO_4	1.0607 *N*	30.08 cc.	61.18	18.694°	0.705°	516.76	364.31	11450 cals.
Mol. ratio	1:50		61.20	18.607°	0.704°	516.78	363.81	11435 cals.
			sp. ht. 0.9491				Mean,	11445 cals.
NH_2OH	0.2670 *N*	30.035 g.	60.38 g.	18.729°	0.171°	517.68	88.52	11070 cals.
H_2SO_4	0.2657 *N*	29.95 cc.	60.47	18.792°	0.171°	517.77	88.54	11072 cals.
Mol. ratio	1:200		60.40	18.577°	0.171°	517.70	88.53	11071 cals.
			sp. ht. 0.9770				Mean,	11071 cals.

NH_2OH	0.5266 *N*	30.0735 g.	61.21 g.	18.565°	0.296°	517.11	153.06	9670 cals.
CCl_3COOH	0.5243 *N*	30.05 cc.	61.16	18.644°	0.296°	517.07	153.05	9670 cals.
Mol. ratio	1:100		61.18	18.678°	0.297°	517.09	153.57	9702 cals.
			sp. ht. 0.9545				Mean,	9681 cals.
NH_2OH	0.2642 *N*	30.0385 g.	60.84 g.	18.598°	0.142°	517.97	73.55	9280 cals.
CCl_3COOH	0.2621 *N*	30.00 cc.	60.90	18.649°	0.142°	518.03	73.56	9281 cals.
Mol. ratio	1:200		60.85	18.619°	0.142°	517.97	73.55	9280 cals.
			sp. ht. 0.9744				Mean,	9280 cals.
$(CH_3)_4NOH$	0.2660 *N*	30.027 g.	60.64 g.	18.726°	0.194°	517.66	100.43	12594 cals.
HCl	0.2639 *N*	29.98 cc.	60.70	18.781°	0.195°	517.72	100.95	12659 cals.
Mol. ratio	1:200		60.68	18.694°	0.195°	517.70	100.95	12659 cals.
			sp. ht. 0.9725				Mean,	12637 cals.
$(CH_3)_4NOH$	0.2660 *N*	30.027 g.	60.46 g.	18.729°	0.222°	517.63	114.91	14410 cals.
H_2SO_4	0.2651 *N*	29.98 cc.	60.42	18.761°	0.223°	517.59	115.42	14474 cals.
Mol. ratio	1:200		60.42	18.712°	0.222°	517.59	114.90	14408 cals.
			sp. ht. 0.9748				Mean,	14431 cals.
$(CH_3)_4NOH$	0.2660 *N*	30.027 g.	61.92 g.	18.700°	0.194°	518.71	100.63	12619 cals.
CCl_3COOH	0.2621 *N*	29.98 cc.	61.81	18.678°	0.194°	518.60	100.61	12616 cals.
Mol. ratio	1:200		61.84	18.774°	0.194°	518.63	100.62	12617 cals.
			sp. ht. 0.9693				Mean,	12617 cals.

The second step concerned itself with the measurement of the heat liberated when neutralizing a definite weight of a given base by a certain acid, the exact strength of each solution being known, and the same amount of water being placed in the calorimeter as before. Since a knowledge of the water equivalent of the salt solution formed in any neutralization was indispensible, it became necessary to measure the specific heat of such solution.

Hence the third step consisted in measuring the specific heat of the salt solutions formed. This value was obtained by substituting, in the calorimeter, an equal weight of the salt solution in question for the water originally used in it, and then repeating the neutralization of the hydrochloric acid with the sodium hydroxide to liberate an exact, known amount of heat as described above.

The preceding results are given to illustrate the method and calculation involved (Tables I, III, IV).

The final data for the heat liberated by the neutralization of solutions of hydroxylamine and tetramethyl ammonium hydroxide by solutions of hydrochloric, sulfuric, and trichloroacetic acids are tabulated in Table VI.

It will be noticed, in Table VI, that the heat of neutralization of a given base decreases considerably with the increase in the dilution of the solutions. Thus, the heat evolved when hydroxylamine acted on hydrochloric acid, in a molar concentration of 1 to 50, was 191 calories higher than when the reaction took place in a concentration of 1 to 200. Similarly, when the same base acted on sulfuric acid, in a concentration of 1 to 50, 374 calories more were liberated than when the reaction occurred in a concentration of 1 to 200. Again, when this base was neutralized by trichloroacetic acid, in the ratio of 1 to 100, 401 calories more were given off than when the neutralization took place in the ratio of 1 to 200. The table also shows that the heats of neutralization of trichloroacetic and hydrochloric acids with a given base were approximately the same for the dilution of 1 to 200. For convenience in comparing these results Table VII is given. The corresponding values obtained by Thomsen are given in brackets.

TABLE VII.

$NH_2OH + HCl$.		$NH_2OH + CCl_3COOH$.		$NH_2OH + {}^1/_2H_2SO_4$.	
Conc.	Heat liberated.	Conc.	Heat liberated.	Conc.	Heat liberated.
1:50	9483 cals.	1:100	9681 cals.	1:50	11445 cals.
1:200	9292 cals.	1:200	9280 cals.	1:200	11071 cals.
	[9260]				[10790]
$(CH_3)_4NOH + HCl$.		$(CH_3)_4NOH + CCl_3COOH$.		$(CH_3)_4NOH + {}^1/_2H_2SO_4$.	
1:200	12637 cals.	1:200	12617 cals.	1:200	14431 cals.
	[13745]				[15515]

The thermal effect due to a definite amount of dilution in the sulfate was nearly twice that produced in the chloride by the same amount of dilution, whereas the thermal change in the trichloroacetate, caused by a dilution only half as great, was considerably larger than that brought about in the sulfate.

The values for the heats of neutralization of hydroxylamine are approximately the same as Thomsen's, our figures ranging from 0.3% to 2.6% higher. In the case of tetramethylammonium hydroxide, however, the values obtained are about 7.5% lower than Thomsen's. No data on the heats of neutralization of the two bases with trichloroacetic acid have been found in the literature for comparison.

The results recorded in this paper are believed to possess an unusually high degree of precision, and yet, such results are to be expected from the exact method of calorimetry employed.

Summary.

1. The heats of neutralization of hydroxylamine and tetramethylammonium hydroxide when neutralized by hydrochloric, sulfuric, and trichloroacetic acids, in aqueous solutions, have been measured adiabatically.

2. The results obtained for hydroxylamine are from 0.3% to 2.6% higher and for tetramethylammonium hydroxide about 7.5% lower than Thomsen's values for the same bases (Table VII).

3. The heats of neutralization of hydroxylamine and tetramethylammonium hydroxide with trichloroacetic acid have been measured for the first time, as far as we are aware.

In conclusion the writer wishes to express his obligation to Professor J. H. Mathews for helpful suggestions as well as for aid in obtaining the apparatus used.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE.]

A CRITICISM OF THE ELECTRON CONCEPTION OF VALENCE.

BY ROGER F. BRUNEL.

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Physical investigations of recent years have convinced most chemists that atoms of all elements contain, if they are not made up of, negative electrons, held in position by a positive charge. The attractive force between atoms is thus electrical in origin. This view is shared by the author.

In 1909, Nelson, Beans, and Falk[1] published an article developing the idea that "every chemical bond formed between two atoms involves the transfer of a corpuscle from one atom to the other,"[2] a conception for which

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[1] *School Mines Quart.*, 30, 179 (1909).

[2] THIS JOURNAL, 35, 1810 (1913).