

at various concentrations. The apparatus has been improved and all temperature measurements made by a platinum resistance thermometer. A careful study of the possible errors has been made and suitable corrections applied for them.

It has been found that although all the other heats of neutralization studied in this way *decrease* as the concentration of the reagents is diminished, that for acetic acid (which is distinctly less than those of stronger acids) *increases* as the solutions become more dilute. Apparently, however, they tend toward the same value at infinite dilution, about 13.6 Cal. (or 56.8 kilojoules), which would appear to be the most probable value for the heat of the reaction $H^+ + OH^- = H_2O$. A more exact evaluation will be found in a later paper of this series.

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HEATS OF DILUTION AND HEAT CAPACITIES OF HYDROCHLORIC ACID SOLUTIONS¹

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Introduction

Since the publication of preliminary data of the specific heats and heats of dilution of hydrochloric acid solutions by Richards and Rowe,² more accurate methods for the determination of these data have been developed in this Laboratory.³ With the aid of these new methods and apparatus the specific heats of hydrochloric acid solutions at various concentrations have been obtained directly and also indirectly from the heats of dilution at 16 and 20°.⁴

Specific Heats of Hydrochloric Acid Solutions

The specific heats of hydrochloric acid solutions at three concentrations were determined in a manner identical with that previously described.⁵ A variable but small error may have been caused by the action of the hydrochloric acid on the gold-plated heating coil, particularly at the soldered connections. At first a celluloid cement was used to coat these sections. In spite of this precaution the acid solution was able to attack the solder

¹ On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior authors.

² Richards and Rowe, *THIS JOURNAL*, **42**, 1621 (1920).

³ (a) Richards and Gucker, *ibid.*, **47**, 1876 (1925); (b) **51**, 712 (1929).

⁴ The relationship between the temperature coefficient of the heat of dilution and the heat capacity of the factors and products $(\Delta H' - \Delta H)/(T' - T) = \Delta C_p$ generally known as Kirchoff's Law was used for this purpose (ref. 2).

⁵ Richards and Hall, *THIS JOURNAL*, **51**, 707 (1929).

very slowly. A thin coating of paraffin was found to be more effective than the cement. Heat evolved by corrosion must have been slight even in the case of the most concentrated solution and would tend to lower the results to a very small extent.

The water equivalent in all of the determinations with hydrochloric acid was 556.71 g. *in vacuo*. A solution of redistilled hydrochloric acid was titrated against NaOH·25.08H₂O with weight burets and found to be HCl·24.96H₂O and the same value was found by analysis as silver chloride.

WEIGHTS OF HCl·24.96H ₂ O EQUIVALENT TO 556.71 G. OF H ₂ O					
	16.00°		18.00°		20.00°
	g. <i>in vacuo</i>		g. <i>in vacuo</i>		g. <i>in vacuo</i>
	636.42		635.15		634.87
	635.99		635.36		634.62
			635.25		
	636.29		635.24		634.75
Av.	636.23	Av.	635.25	Av.	634.74
Sp. ht.	0.87501	Sp. ht.	0.87636	Sp. ht.	0.87707

When these values for specific heats are corrected to HCl·25.00H₂O by means of the Person-Kirchhoff Law, the following result: at 16°, 0.87518; at 18°, 0.87653; at 20°, 0.87724. These values are subject to a correction of 0.00002 to 0.00004 resulting from differences in evaporation of solution and water.

A solution of redistilled hydrochloric acid was adjusted to about HCl·50H₂O and analyzed by the silver chloride method as HCl·49.99H₂O. Its specific heat at 18° was found to be 0.9337 as the mean of two experiments requiring 596.24 and 596.18 g. *in vacuo* of the acid.

937.01 g. of this acid was diluted with 901.10 g. of water to make a solution of HCl·100H₂O. From three experiments (576.90 g., 576.90 g. and 576.75 g., all *in vacuo*) the specific heat at 18.03° was found to be 0.9651.

Determination of Heats of Dilution

The apparatus and experimental procedure used in these experiments was essentially that described in a recent paper.^{3b} A few minor modifications in apparatus were made. Owing to the solvent action of hydrochloric acid on the gold-plated brass heating coil formerly used to adjust the initial temperature, a simple though adequate heating coil was made from constantan wire (No. 30 B. and S.) enclosed in a thin-walled glass capillary.

One of the most troublesome experimental difficulties encountered was the erratic heating effect arising from the occasional contact of the stirrers with the sides of the calorimeter cans. This difficulty was considerably decreased by bracing the supporting rods of the stirrers and by reducing their width slightly. Further reduction of this heating effect was accomplished by binding the edges of the stirrer in a few places with waxed silk thread.

A new "all copper circuit" galvanometer of high sensitivity was used in conjunction with the platinum resistance thermometer to eliminate thermo-electric currents frequently found in galvanometers of the silver suspension type.

The heat capacity of the apparatus was calculated from the heat capacity of its constituent parts as 76.4 (± 3) mayers. Since the total heat capacity of the system with solution was about 5000 mayers, an error of 3 mayers corresponds to an error in total heat capacity of only 0.06%, which is within the accuracy of the rest of the method.

Hydrochloric acid, doubly distilled, using a quartz condenser, was diluted to approximately HCl·25H₂O. Two solutions were used: the first by analysis as silver chloride was of the concentration HCl·24.95H₂O; the second, HCl·24.98H₂O. The first solution was used for experiments at 20° only, while the second was used one year later at both 16 and 20°, after considerable experience had been gained with the apparatus.

No attempt will be made to present the necessary data for all of the calculations. The same general methods of calculation were used here as described in the previous article in this series.⁶ Two series of dilution experiments were performed with the hydrochloric acid solutions.

The summaries of results are given in Tables I and II.

TABLE I
HEAT CAPACITY PER GRAM OF SOLUTION

Mayers			Solution	Calories			
16°	18°	20°		16°	20°	18°	20°
3.6615	3.6657	3.6673	HCl·25H ₂ O	0.8758	0.8769	0.8772	
3.9017	3.9031	3.9031	HCl·50H ₂ O	.9332	.9336	.9336	
4.0369	4.0367	4.0361	HCl·100H ₂ O	.9656	.9656	.9654	
4.1062	4.1072	4.1082	HCl·200H ₂ O	.9822	.9822	.9822	
4.1452	4.1439	4.1426	HCl·400H ₂ O	.9916	.9912	.9909	
4.1643	4.1628	4.1614	HCl·800H ₂ O	.9961	.9958	.9954	

TABLE II
HEATS OF DILUTION OF HCl·25H₂O

Product	ΔH_{16°		ΔH_{20°		J/°C.	ΔC_p	Cal./°C.
	Joules	Cal.	Joules	Cal.			
HCl·50H ₂ O	-919	-220	-959	-229	-10.0		-2.4
HCl·100H ₂ O	-1427	-341	-1489	-356	-15.6		-3.7
HCl·200H ₂ O	-1739	-416	-1822	-436	-20.5		-4.9
HCl·400H ₂ O	-1942	-464	-2041	-488	-24.5		-5.9
HCl·800H ₂ O	-2080	-497	-2185	-523	-26.3		-6.3
HCl ∞ H ₂ O	[-590]	[-620]

The values for heats of dilution here presented are similar to those found by the earlier method of Richards and Rowe,² although not identical. The differences resulting from the newer method are due primarily to its greater accuracy and also to the use of more dilute solutions, for it is difficult to handle concentrated solutions such as were used in the earlier work. There are few other values in the literature which can be compared, since Thomsen⁷ covered the range from HCl·2H₂O to HCl·300H₂O and Wrewsky and Sawaritzky⁸ almost the same range. If the heat evolved

⁶ The final temperature in these experiments was known within $\pm 0.015^\circ$, as discussed in ref. 3 b, p. 712.

⁷ Thomsen, "Thermochemische Untersuchungen," Leipzig, 1883, Vol. III, p. 72.

⁸ Wrewsky and Sawaritzky, *Z. Physik Chem.*, 112, 90 (1924). See also Tucker, *Trans. Roy. Soc. London*, 215A, 319 (1915).

is plotted against concentration, a smooth curve is obtained, which cannot be easily extrapolated to zero concentration since the curve approaches the axis very obliquely. This shows that thermo-neutrality is reached only with exceedingly dilute solutions.

On the other hand, extrapolation of the curve for specific heats plotted against concentration is more certain and yields the value of 1.000 at zero concentration. Table III compares the values for specific heats determined by different methods.

TABLE III
SPECIFIC HEATS OF HYDROCHLORIC ACID SOLUTIONS (REFERRED TO WATER AT THE SAME TEMPERATURE)

HCl + $\frac{1}{2}$ H ₂ O	Richards, Mair and Hall		Richards and Rowe ^a 18°	Thomsen ^b	Marignac ^c 20-24°	Wrewsky ^d 20.5°
	18°C. Direct	Indirect				
25H ₂ O	0.8766	0.8776	[0.876] ^e	0.8787	[0.875]
50H ₂ O	.9337	0.9333	.9334	.932	.9336	.932
100H ₂ O	.9651	.9653	.9636	.964	.9650	.964
200H ₂ O9821	.9812	.979	.9835	[.981]

^a Ref. 3a. See also Richards and Rowe, *Proc. Am. Acad.*, **49**, 194 (1913).

^b "Thermochemischen Untersuchungen," Vol. I, p. 38.

^c "Oeuvres Complets," Vol. II, p. 624.

^d Wrewsky and Kaigorodoff, *Z. physik. Chem.*, **112**, 83 (1924).

^e Bracketed values were obtained by our interpolations.

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Summary

1. Specific heats of solutions of hydrochloric acid with 25, 50 and 100 moles of water per mole of acid were measured directly by the twin calorimeter method at 18°.

2. Heats of dilution of hydrochloric acid solutions were measured over the range HCl·25H₂O to HCl·800H₂O at 16 and 20°.

3. By the use of the Person-Kirchhoff relation the specific heats of the dilute solutions were calculated.

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