The activity of a salt of hemoglobin has been investigated by experiment in order to determine the degree of accuracy in the assumptions that have been made in the thermodynamical treatment of a salt of variable composition in a system of many components.

CAMBRIDGE, ENGLAND

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

SPECIFIC HEATS OF SODIUM AND POTASSIUM HYDROXIDE SOLUTIONS[1]

BY THEODORE W. RICHARDS AND LAWRENCE P. HALL

RECEIVED SEPTEMBER 18, 1928 PUBLISHED MARCH 6, 1929

In a previous publication[2] from this Laboratory it was pointed out that a serious discrepancy existed between the value then found for the specific heat of $NaOH \cdot 25H_2O$ and earlier values. Since this datum was to be made the basis for the specific heats of other solutions, heats of dilution, heats of neutralization, etc., the new and higher value demanded confirmation.[3]

Hence part of the work was repeated with even greater care, especially studying possible sources of error and inaugurating a few slight modifications and improvements in procedure. The outcome was in general essentially in accord with the work of Richards and Gucker, as will be shown.[4]

Procedure with Modifications

The twin calorimeter system used previously was rebuilt in essentially the same form as described on pp. 1878–1881 of ref. 2. Standardization of new thermocouples showed a sensitivity of 0.000340° per mm. of scale reading for the larger thermocouple and 0.000527° per mm. for the smaller ones. Slight changes in the apparatus made it necessary to redetermine the water equivalent. Later it was found advisable to use a smaller amount of liquid in each can to avoid errors from splashing or spilling in assembling and handling the apparatus.

The chief causes of minor variations were found in maintenance of adiabatic conditions at all times and in trouble from unequal evaporation from the calorimeter cans, one containing water and the other solutions. The former difficulty was in part eliminated by trying out and adjusting

---

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

[2] Richards and Gucker, THIS JOURNAL, 47, 1876 (1925).

[3] Earlier records present a bewildering variety of specific heat values for sodium hydroxide solutions, particularly for the more concentrated ones. Richards and Rowe, [THIS JOURNAL, 43, 770 (1921)] took 0.855 for $NaOH \cdot 10H_2O$—choosing from among old values ranging all the way from 0.84 to 0.89. It will be shown that this choice, although perhaps the best possible at the time, was much too low in value.

[4] Ref. 2 and the following paper in this series.

the heaters before the experiment, and for this purpose the solutions were put in at a temperature below that at which the experiment proper was to begin. The calorimetric system was then warmed to nearly 16° and during this period of heating the controls were so adjusted that conditions could be kept continuously adiabatic during the measured rise in temperature from 16 to 20°. The fore and after drifts were measured as before.

Some variation in adiabatic conditions arose because the small thermels in the outer bath were sensitive to the radiations from the heating lamps. The use of the two 40-watt lamps was discontinued. Also, the thermocouples were placed so that they were shielded from direct radiation of the carbon lamps.

The errors from evaporation have been discussed[5] and likewise methods for their prevention and control. Paper collars were again used. However, from careful observation it appeared that closed calorimeter cans, with the minimum of air space above the solution and water, would be necessary to prevent this source of error.[6]

With conditions exactly adiabatic, unequal evaporation occurred in the two calorimeter cans, due in part to an adsorption effect on the inner surface of the submarine covers. Also it was found on exploration with sensitive thermometers that the surface of the outer bath, on account of evaporation into the room, could become slightly cooler than the bulk of the bath, thereby cooling the submarine lids and encouraging condensation. Since it was not practicable to cover this bath, as has often been done in this Laboratory, the amount of water was increased and the stirrer adjusted so that it drew water more rapidly from below.

Evaporation difficulties were further diminished by keeping the temperature of the outer bath slightly higher than formerly. At 16° with a thermal head of +0.005 to +0.007° very little change in the temperature of the calorimetric system itself occurred in the fore period, during which the drift was found to be smaller and more regular. Similar benefits resulted from gradually increasing the thermal head during the course of the heating to a final value of +0.007°. Such a positive head would not appreciably influence the temperature of either calorimeter. It was found that when the temperature of either or both of the calorimeters was above that of the bath, peculiar and erratic drifts were obtained. For this reason another slight change in procedure was made when it so happened that a difference in temperature between the water and solution resulted during the heating period. Instead of holding the outside bath at the average temperature of the two cans, it was kept at least as warm as the warmer can. In this way the drifts were made more uniform without introducing any serious error from thermal leakage.

[5] Ref. 2, p. 1882.

[6] *Cf.* Gucker, THIS JOURNAL, 50, 1005 (1928).

Purification of Sodium Hydroxide

Except for these minor modifications, the experiments were performed in much the same way as described by Richards and Gucker.[2] The sodium hydroxide solutions were prepared as before, except that after crystallization of the hydroxide in platinum and separation of the insoluble sodium carbonate, a small amount of barium hydroxide solution, freshly prepared from recrystallized material, was carefully added to remove the last trace of carbonate. Any excess of barium was not desired. However, on some occasions when a slight trace was found, it was removed with a trace of sulfuric acid.[7]

The solutions thus prepared were apparently free from sulfate, barium, carbonate and chloride. It was later found that a slight amount of potassium was present, amounting (in the case of the solution used in the present work for the specific heat of $NaOH\cdot25H_2O$) to between 0.1 and 0.2% of potassium (compared with the sodium present). This result was attained by difference through analysis as sulfate and hydroxide, and by direct comparison with similar amounts of precipitate produced with sodium cobalti-nitrite with known standards of similar composition.

In commercially "pure" samples of sodium hydroxide similar to that used for crystallization, sometimes as much as 0.3% of potassium was found; this impurity was reduced to about 0.1% by one crystallization. After a second recrystallization (as in the case of the solution $NaOH\cdot101H_2O$) no test for potassium could be obtained.[8]

In the first experiments the $NaOH\cdot25H_2O$ solution was analyzed for caustic alkali, exactly as had been done before, by determining the weight of dried sodium chloride made from it. However, it was found that this method, as it had been carried out in the earlier work,[9] did not give the exact concentration of the solution, in spite of the agreement of the analyses. For this reason the first values obtained in confirmation of the new specific heat were discarded. The solution finally used for $NaOH\cdot25H_2O$ was standardized not only by sodium chloride and sodium sulfate residues but also by titration with weight burets against hydrochloric acid standardized by silver chloride determinations.[10]

[7] *Cf.* Richards and Rowe, *Proc. Am. Acad.*, **49**, 183 (1913).

[8] The manufacturers reported that the potassium content varies from lot to lot and falls between 0.3 and 0.5% for the "c. p." material.

[9] *Cf.* ref. 2, p. 1883.

[10] The method of determining sodium as a chloride residue was investigated to find the error introduced by the retention of water. Some time ago attention was called to the difficulty of obtaining dry salts, especially anhydrous crystals [T. W. Richards, *Proc. Am. Phil. Soc.*, **42**, 28 (1903)]. Sodium chloride crystals are notorious for their decrepitation on drying, a phenomenon depending on the bursting forth of included mother liquor.

In order to follow its behavior, a really anhydrous salt was prepared as the starting point. Pure sodium chloride, previously pulverized and dried in an oven, was fused in a covered platinum dish. The material thus obtained was neutral to phenolphthalein, methyl orange and methyl red. Weighed samples of this fused salt were dissolved and the solution evaporated in flasks in an oven at 100°, exactly as in the earlier analysis of sodium hydroxide by sodium chloride residue. Crystals about one cubic millimeter were formed. These gave an apparently constant weight after a few hours' heating at 150°. However, the salt thus dried without fusion was found to weigh 0.66 to 0.80% more than the really anhydrous substance (average 0.73%). The following modification

Analysis of $NaOH\cdot 25H_2O$ by evaporation as chloride showed the water content per mole to be 25.03 H_2O (the average of two analyses); by evaporation and fusion as sulfate, 25.06, 25.08, 25.07, average 25.07 H_2O; by titration with standard acid 25.08, 25.08, 25.09, average 25.08 H_2O.

The calorimetric experiment consisted in finding the weight of solution which showed exactly the same temperature rise as a given weight of water, when precisely the same quantity of heat was added.[11] A new "water equivalent" or weight of water fitting the conditions was determined as 556.42 g. of water at 18.00°, which corrected to vacuum was 557.01 g. *in vacuo*, as the average of six experiments. The "balancing weight," or thermally equivalent weight of $NaOH\cdot 25.08H_2O$ was 610.21 g. *in vacuo*, the average of five experiments (609.61, 609.61, 609.49, 609.72 and 609.67 g. in air) at the average temperature of 18.02°. By use of the temperature coefficient determined by Richards and Gucker, the specific heat at 18.00° is calculated as 0.91280 for $NaOH\cdot 25.08H_2O$. This value may be accurately corrected to $NaOH\cdot 25.00H_2O$ by determining the value for the temperature coefficient for a dilution by a single molecule of water and by using the proper fraction of this value in Kirchhoff's Law.[12]

The specific heat of $NaOH\cdot 25.00H_2O$ then appears as 0.91262, to which should be added 0.00002 as the correction for cooling due to difference in evaporation of $NaOH\cdot 25H_2O$ solution and water, yielding 0.91264. One further small correction, that for the difference in heat capacity due to the trace of potassium, may be approximated by taking 0.15% (the approximate potassium content) of the difference in specific heats of sodium and potassium hydroxide solutions at this dilution (0 00007). The value 0.91271 is, therefore, the final value for $NaOH\cdot 25.00H_2O$ at 18.00°.

Besides this determination, a direct determination of the specific heat of $NaOH\cdot 101H_2O$ was made. This determination provided a corroboration of the specific heat values determined indirectly from heats of dilution. Analysis as sodium chloride residue, using the method of evaporation in an oven at 150–160°, showed the concentration of this solution to be $NaOH\cdot 101.08H_2O$.[13]

---

of the sodium chloride method was found to reduce to 0.05% or less the error of the result; it is not to be commended except for its rapidity. Indeed, the good result may be partly due to a compensation of errors. Nothing short of fusion will yield perfectly dry salt. If the sample solution of sodium chloride in a 125-cc. Erlenmeyer flask with anti-spattering bulb (such as is used in evaporating filtrates in flasks) is evaporated in an oven maintained at 150–160°, the salt is left as a powder which can be dried almost completely at 300–310°. As there is danger from spattering, the flask and bulb must be weighed together.

[11] Ref. 2, p. 1888.

[12] *Cf.* later paper for details of this correction.

[13] After this specific heat had been determined, it was found, as discussed in a previous footnote, that this method might produce an error of +0.05% in analysis which would correspond to +0.005% error in specific heat.

In this case the "water equivalent" of 596.01 g. *in vacuo* (average of four experiments) was found to be thermally equivalent to 614.84 g. *in vacuo* of solution (average of four determinations), the specific heat of which was, therefore, 0.96939 at 18.00°. Correcting this to $NaOH \cdot 100H_2O$, we obtain 0.96904.

A rough measurement of the specific heat of a solution $NaOH \cdot 50.0H_2O$ also was made. This solution was adequately analyzed both by titration with acid and by evaporating the resulting salt in an oven at 160°, which process gave essentially identical results. The value obtained for the specific heat was 0.946 (507.7 g. of water being equivalent to 536.7 g. of solution). Minor temporary defects in the apparatus, chiefly tending to make the result too low, were experienced but the outcome could hardly be far from the truth.

These values are all essentially consistent with one another and with the heats of dilution found by Richards and Rowe. They are, however, all consistently higher than the final values calculated by these latter experimenters, who unfortunately had based their whole series on an erroneous value for $NaOH \cdot 10H_2O$, taken from older work[14] of others. The recent values are unquestionably far more trustworthy.

Since earlier values for the specific heat of sodium hydroxide solutions had been found to be in error, the question arose as to the correctness of specific heats of other hydroxide solutions. Accordingly, a solution of potassium hydroxide was prepared in a way similar to that used for the sodium hydroxide solutions.

This solution by titration against standardized hydrochloric acid was found to be $KOH \cdot 100H_2O$; by residue as KCl, $KOH \cdot 99.96H_2O$. The unimportant difference between these two results was doubtless chiefly due to water retained by the potassium chloride after rapid evaporation at 160°. Two more standardizations for the "water equivalent" (performed immediately after the $KOH \cdot 100H_2O$ solution had been examined) confirmed the value (found in the similar preceding experiments with $NaOH \cdot 101H_2O$) of 596.01 g. *in vacuo.* As the average of four experiments, 622.97 g. *in vacuo* of $KOH \cdot 100H_2O$ was found to be thermally equivalent. The specific heat of this solution, then, is 0.9567—a value which confirms exactly the early value for this dilute solution found by Richards and Rowe,[15] as well as their value found from heats of dilution.[16] Hence, evidently, the older results for potassium hydroxide were very nearly correct.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

---

[14] See Richards and Rowe, THIS JOURNAL, **43**, 781 (1921).

[15] Richards and Rowe, *Proc. Am. Acad.*, **49**, 197 (1913).

[16] Richards and Rowe, THIS JOURNAL, **44**, 694 (footnote 27) (1922).

Summary

1. Several modifications and improvements made in the differential method for the determination of specific heats are presented.

2. The following values were found for specific heats at 18.00°. NaOH·$25H_2O$, 0.9127, thus confirming the recent high value found by Richards and Gucker; NaOH·$50H_2O$, 0.946; NaOH·$100H_2O$, 0.9690 and KOH·$100H_2O$, 0.9567.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE HEATS OF DILUTION OF SODIUM HYDROXIDE, ACETIC ACID AND SODIUM ACETATE, AND THEIR BEARING ON HEAT CAPACITIES AND HEAT OF NEUTRALIZATION[1]

BY THEODORE W. RICHARDS AND FRANK T. GUCKER, JR.

RECEIVED SEPTEMBER 18, 1928 PUBLISHED MARCH 6, 1929

Introduction

The most convenient and accurate way of studying heats of neutralization at successive concentrations is to determine the heat of neutralization at one concentration and the successive heats of dilution of the factors and products. In previous researches this method has been applied to several strong acids and bases, of which the heat of neutralization was found to *decrease* as the concentration decreased.[2] The present publication presents the first detailed study of an opposite case (acetic acid), in which the heat of neutralization was found to *increase* as the concentration decreased.

Method and Apparatus for Determining Heats of Dilution.—The principles involved in this research are essentially those of the previous dilution experiments.[3] Some differences in experimental detail, however, were applied and the calorimeter was greatly improved. The changes are fully described in the present paper.

The Calorimeter Proper

Figure 1 gives a general idea of the calorimetric apparatus. Two concentric platinum cans were used, the inner, C_2, having half the volume of the outer, C_1. (This assembly was designated Aa by Richards and Rowe.) The inner can always contained the solution and the outer can pure water. The liquids were agitated by two reciprocating stirrers, one, S_2, for the inner can and the other, S_1, for the annular space between the two. A somewhat elaborate mechanism was devised to keep the stirrers rigid (thus

---

[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 author under the general direction of Dr. Lawrence P. Hall.

[2] Richards and Rowe, THIS JOURNAL, **44**, 704 (1922).

[3] Richards and Rowe, *ibid.*, **42**, 1621 (1920); **43**, 770 (1921).