HEATS OF NEUTRALIZATION AT CONSTANT CONCENTRATION AND THE HEAT OF IONIZATION OF WATER[1]

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In an extensive series of investigations Richards and his collaborators have studied the heats of neutralization[2] of a number of pairs of acids and bases, and the heats of dilution[2b,3] of these and of their salts. Unfortunately, from the point of view of those who prefer things simple, the effect of further dilution was in most cases perceptible in the case of each neutralization, the heats of reactions leading to the formation of various salts differed perceptibly even in the most dilute solutions, and the conclusion of a previous generation—that the heats of neutralization of all strong bases and acids are the same, and are equal to the heat of the formation of water from its ions—was shown to be but a rough approximation.

Richards and Rowe[2a] discussed at length the difficulties involved in the extrapolation of the heats of neutralization to infinite dilution in order to find the heat of ionization. As pointed out by Richards and Hall,[2b] their new values for sodium salts improve the extrapolation considerably. Richards and Mair[2c] plot the heats of neutralization for the cases of sodium chloride, sodium nitrate and sodium acetate and estimate the heat of ionization at $20°$ as 13,650 $20°$-calories. They also[3e] find the heats of neutralization in the case of the sodium citrates to be much smaller than for the strong inorganic acids, and note that they do not approach the value to which these stronger acids tend at infinite dilution. They note also that citric acid and the acid citrates "are only slightly ionized even in the most dilute solutions investigated, so that it is probable that heat effects due to their ionization continue into solutions infinitely dilute."

Experiments with the continuous-flow calorimeter have confirmed[4] the heats for sodium and potassium chloride in the dilute region at $20°$, though measurements at higher temperatures do not appear consistent with the existing temperature coefficients.

Lange and Messner[5] have observed with a 1000-junction thermocouple

[1] Original manuscript received June 7, 1930.

[2] (a) Richards and Rowe, THIS JOURNAL, **44**, 684 (1922); (b) Richards and Hall ibid., **51**, 731 (1929); (c) Richards and Mair, ibid., **51**, 737 (1929).

[3] (a) Richards and Rowe, ibid., **42**, 1621 (1920); (b) ibid., **43**, 770 (1921); (c) Richards and Gucker, ibid., **51**, 712 (1929); (d) Richards, Mair and Hall, ibid., **51**, 726 (1929); (e) Richards and Mair, ibid., **51**, 740 (1929).

[4] (a) Keyes, Gillespie and Mitsukuri, ibid., **44**, 707 (1922); (b) Gillespie, Lambert and Gibson, ibid., **52**, 3806 (1930).

[5] Lange and Messner, Naturwissenschaften, **15**, 521 (1927).

significant heats on the further dilution of solutions of univalent salts as weak as 0.01 normal.

Object and Scope of the Work.—At the time of the appearance of the paper of Richards and Rowe we were working with the continuous-flow calorimeter on heats of neutralization. We were much impressed with the difficulties emphasized by them in the extrapolation of the data for various salts to the same point at infinite dilution in order to find the heat of ionization. The suggestion occurred that there is a dilution involved in any experiment on neutralization, a dilution attended by a heat effect which varies from salt to salt. If a systematic "correction" were made for this dilution, the results for various products of neutralization reactions ought to be more consistent. Application of the idea to the results of Richards and Rowe bore out the expectation: the picture was very clear, provided we assumed an error of about 25 calories in their result for sodium chloride in the dilute region. This assumption has since been shown true by the data of Richards and Hall[2b] and Gillespie, Lambert and Gibson.[4b] Since our first calculations, the available data have been greatly extended in the publications to which reference has been made above, and we have taken the new data into consideration.

We hoped that the application of our method (1) might give a clearer picture of the relations for various acids and bases, and that better extrapolated results might be obtained for (2) the heat of ionization and (3) its temperature coefficient. To anticipate, we think that our hopes have been justified with reference to points (1) and (3). As to the heat of ionization, we have not found it expedient to seek to improve by curve-plotting the recent estimation by Richards and Hall[2b] of the limiting value for the heat of neutralization for sodium chloride, based on especially accurate data, but are content to point out that their value gives directly the limiting value of the heat of neutralization at constant concentration and hence the heat of ionization, and to show by a new plot that the data for six inorganic salts appear consistent with their limiting value.

The objects of this paper are (1) to define the heat of neutralization at constant concentration; (2) to give an improved definition of the heat of ionization, in terms of the heat of neutralization at constant concentration; (3) to examine by curve plotting the extrapolation to infinite dilution of heats of neutralization at constant concentration for various acids and bases; and (4) to derive a value for the temperature coefficient of the heat of ionization.

The Heat of Neutralization at Constant Concentration and the Heat of Ionization.—When a mole of a (monobasic) acid, dissolved in x moles of water, is neutralized with a mole of a (monoacid) base, dissolved in x moles of water, the change of state may be written

$$[MOH \cdot xH_2O] + [HB \cdot xH_2O] = [MB \cdot (2x + 1)H_2O] \tag{1}$$
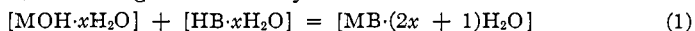
Supposing complete ionization it may also be written in the ionic form

$$[M^+ (c_1) + OH^- (c_1)] + [H^+ (c_1) + B^- (c_1)] = [M^+ (c_2) + B^- (c_2)] \qquad (2)$$
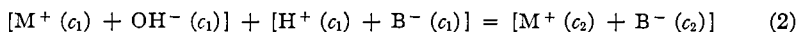
where c_1 in the first solution is the concentration of M^+ and of OH^- in gram ions per liter in the solution of MOH, and there is a similar meaning of c_1 and c_2 for the other two solutions. In all cases the substances whose formulas are represented within brackets are supposed to be mixed, and substances whose formulas, not within the same bracket, are separated by plus or equality signs are supposed to be physically separated.

Since the salt solution contains all the water present in the original solutions (plus one mole), and there is little volume change on mixing the solutions, the concentration c_2 of the ions of the salt is about one-half of c_1. It is therefore clear from equation (2) that in the neutralization experiment there occurs not only a disappearance of OH^- and H^+, but also a dilution of the ions M^+ and B^-. It is generally supposed at present that strong acids, bases and salts are completely ionized at any reasonable dilution. The fact observed and emphasized by Richards and Rowe that the heat attending reaction (1) varies with the nature of the salt formed and with the dilution points therefore to the possible importance of the heat effects attending the dilution of these ions.

Muller[6] obtained nearly the same heats of neutralization at infinite dilution for potassium chloride and sulfate, by subtracting the heat effect for the acid in question on dilution from a molal solution to infinite dilution, from the extrapolated value of the heat of neutralization—a method of finding the heat of ionization not wholly clear, as remarked by Richards and Rowe.
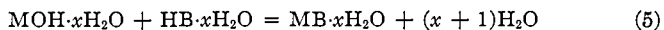
We wish to obtain the heat effect of the reaction

$$H^+ \, aq + OH^- \, aq = HOH \, aq \qquad (3)$$
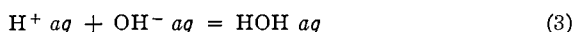
Now it is not clear that equation (3) defines sufficiently a change of state, even if definite values are assigned to the symbol aq (and, of course, the temperature and pressure are fixed). For the equation does not represent the effect of the other ions necessarily present, and we dare not assume that an extrapolation to infinite dilution, when it is conducted without reference to these other ions, will necessarily give a correct or even a definite result.

If we subtract, from the heat effect H_1 of reaction (1), the heat effect H_4 of the reaction
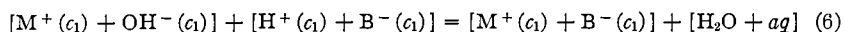
$$MB \cdot xH_2O + (x + 1)H_2O = MB \cdot (2x + 1)H_2O \qquad (4)$$

we obtain the heat effect H_5 of the reaction

$$MOH \cdot xH_2O + HB \cdot xH_2O = MB \cdot xH_2O + (x + 1)H_2O \qquad (5)$$

Such a reaction will be termed a neutralization at constant concentration. If this is written in the ionic form we have

$$[M^+ (c_1) + OH^- (c_1)] + [H^+ (c_1) + B^- (c_1)] = [M^+ (c_1) + B^- (c_1)] + [H_2O + aq] \quad (6)$$

6 Muller, *Bull. soc. chim.*, [4] **23**, 8 (1918).

This change of state (5) is worth attention. When the ionization is supposed complete, equation (6) shows a disappearance of OH^- and H^+ to form a mole of water, and a bringing together in the same solution of the other ions M^+ and B^-. So far as these ions are concerned, they experience no change of concentration, and are, in fact, associated with the same number of moles of water and the same number of ions of opposite sign after the change of state, as before. At infinite dilution there should be no heat effect involved in replacing an ion A with an ion B of the same sign and charge at the same distance from an ion C of opposite sign. Consequently the limiting value of the heat effect of reaction (5), provided all the electrolytes are strong, may be taken as the heat of formation of water from its ions.

$$\text{Limit } H_5 \text{ (strong electrolytes)} = \text{heat of formation of } H_2O \text{ from its ions} \qquad (7)$$
$$1/x = 0$$

Equations (5) and (7) define completely the heat of ionization of water.

The limiting value of H_1 also will be the heat of ionization according to the above definition, provided that the value of H_4 approaches zero at infinite dilution, or provided that the heat effect of the following reaction becomes zero as x becomes infinite

$$MB \cdot xH_2O + xH_2O = MB \cdot 2xH_2O \qquad (8)$$
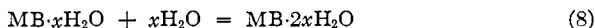
We cannot immediately state that the limiting value of H_8 for this reaction is zero simply because the limiting value is zero for the reaction

$$MB \cdot xH_2O + H_2O = MB \cdot (x + 1)H_2O \qquad (9)$$
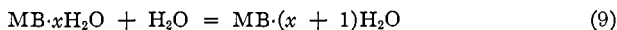
Nor do the recent data on heats of dilution establish zero as the limit of H_8, though the only cases in which values other than zero are rather definitely suggested by the plots are for lithium nitrate,[3b] citric acid[3e] and sodium acetate.[3c] Yet *a priori* notions suggest the value zero, and in our hands plots of H_1 and of H_5 do not lead to different values for the heat of ionization.

The advantage of the heat of neutralization at constant concentration for finding the heat of ionization by curve-plotting does not depend on a difference in the limits, but lies in the manner in which the limit is approached. The disturbing effect of the dilution, which finally disappears at infinite dilution, is present at the dilutions at which measurements are made.

The method outlined above for finding the heat of ionization of water implies that the electrolytes are strong. In the case of the weak acids, the ionization is but slight at the greatest dilutions in question, and we can hardly expect that the course of the curve in the infinitely dilute region will be definitely established by the available data. Consequently, one may expect to be limited, in any method of extrapolation, to the case of strong electrolytes.

Plots of the Heat of Neutralization

Richards and Hall[2b] combined one value for the heat of neutralization (for sodium chloride) at a finite dilution with three heats of dilution, each extrapolated to infinite dilution, though from rather high dilutions. If the addition of the thermochemical equations is carried out, it is found that their value for the heat of neutralization in the case of sodium chloride at infinite dilution, 13,653 20°-calories at 20°, is for the reaction

$$NaOH \cdot \infty H_2O + HCl \cdot \infty H_2O = NaCl \cdot \infty H_2O + (\infty + 1)H_2O \qquad (10)$$
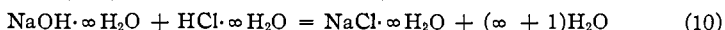
which is strictly of the type of a neutralization at constant concentration. When the measured heats of neutralization, which extend to value of 400
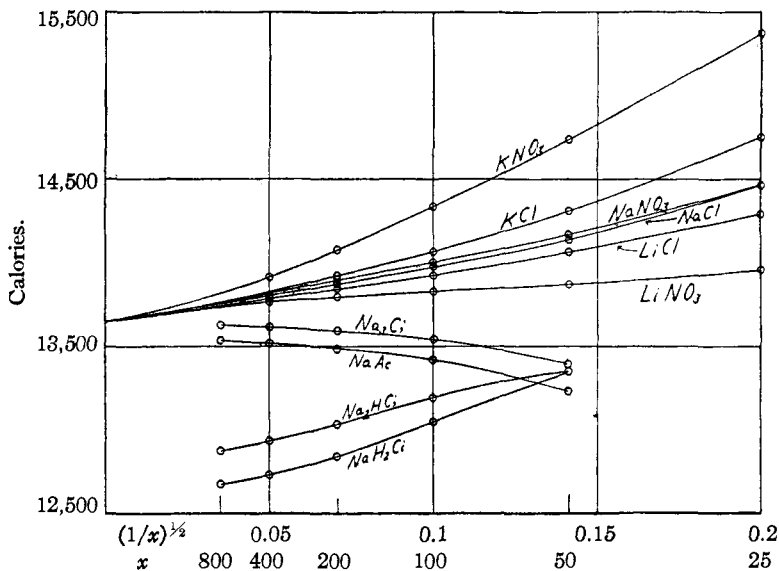

Fig. 1.—Heats of neutralization at constant concentration at 20° in 20°-calories.

for x of equation (1), are plotted against $1/x$, the course of the curves obtained (reference 2c, Fig. 1) for sodium chloride and nitrate does not suggest so low a value, and Richards and Mair[2c] introduce a bending downward of the curves for these salts, and a bending upward for the curve for sodium acetate, which brings the extrapolated values to 13,650. When the heats at constant concentration are plotted over the same range of values of x, the bending for sodium chloride and nitrate is already in evidence, and the use of a different variable as abscissa is indicated.

The square root of $1/x$ has been used as abscissa for the plots of heat of neutralization at constant concentration shown in Fig. 1, where x and the heat effect are defined by equation (5). Lange[7] has recently published

[7] Principally in Z. Elektrochem. and Z. physik. Chem.

many heats of dilutions of salt solutions, but heats at 20° would have to be determined by interpolation at other temperatures, which interpolation is in some cases uncertain. The results for strong electrolytes at $x = 400$ were obtained by combining the heat at $x = 200$ with the heats of dilution of acid and base from 200 to 400 and the estimated heat of dilution of the salt from 400 to 401.

The value 13,650 was found to be an excellent compromise point for the strong electrolytes. No curves intersect below about the concentration $1/x = 0.02$, which is not true of the plots of the ordinary heats of neutralization. At $x = 400$ four of the six points for inorganic salts lie exactly on the curves; the points for potassium chloride and sodium nitrate are a little lower (10–20 cal.) than indicated by the smooth curves. The plot shows that the value 13,650, given by Richards and Hall for the heat of neutralization at 20° of hydrochloric acid and sodium hydroxide at infinite dilution, is supported by the curves for the six inorganic salts and may be taken therefore as the heat of ionization of water. The curves for the organic salts, with the exception of trisodium citrate, do not point to this value, but this appears to be of little consequence.

The Temperature Coefficient of the Heat of Ionization

The temperature coefficient of the heat of neutralization at constant concentration, dH_5/dt, is evidently equal to the difference, $dH_1/dt - dH_4/dt$. The limiting value at zero concentration should be equal to the temperature coefficient of the heat of the formation of water from its ions, and one may expect an easier extrapolation than in the case of the ordinary temperature coefficient, dH_1/dt.

From the data of Richards and his collaborators both temperature coefficients were computed, using besides the necessary heats of dilution the molal heat capacities given by Richards and Rowe, except when new specific heat values were available, as in the cases of hydrochloric acid[3d] and sodium hydroxide.[3c] In the computations the same atomic weights were used as by Richards, and the new specific heats at 18° in 20°-calories were converted into values at 18° in 18°-calories by multiplication with the factor 0.999737, which was obtained by interpolation from the paper of Osborne, Stimson and Fiock.[8] All the intermediate calculations were referred to 18°-calories at 18°, as consistency is necessary when dealing with the large numbers involved. The results, being small numbers obtained by taking differences, may equally well refer to 20°-calories, and in view of their uncertainty may be taken to refer to the temperature of 20°.

Table I gives the temperature coefficients corresponding to the value of x. A denotes the ordinary coefficient and B the coefficient at constant con-

[8] Osborne, Stimson and Fiock, *Mech. Eng.*, **51**, 125 (1929), Table III.

centration. The average values for the six salts are also given for each value of x.

TABLE I

TEMPERATURE COEFFICIENTS OF HEATS OF NEUTRALIZATION

x	KCl A	KCl B	NaCl A	NaCl B	LiCl A	LiCl B	KNO_3 A	KNO_3 B	$NaNO_3$ A	$NaNO_3$ B	$LiNO_3$ A	$LiNO_3$ B	Average A	Average B
25	36.2	41.5	33.6	40.6	29.0	31.2	36.0	46.8	33.6	42.0	25.5	29.6	32.3	38.6
50	40.8	44.5	39.3	43.6	34.9	37.7	39.8	47.0	39.9	46.7	34.7	37.4	38.2	42.8
100	45.1	47.0	45.0	47.0	38.7	41.4	45.3	48.0	46.5	49.7	40.4	43.5	43.5	46.1
200	46.1	49.5	46.3	51.4	41.1	42.3	47.2	49.8	50.6	52.8	41.8	43.4	45.5	48.2

When the values for each salt were plotted against the concentration, a confused picture resulted. The extrapolation in any particular case usually appeared uncertain, and it seemed out of the question to find a compromise intercept on the axis of zero concentration, to which a family of curves might be drawn. This was true for the ordinary temperature coefficient, as well as for the one at constant concentration. Such plots are a very severe test of the precision of data on heat capacity.

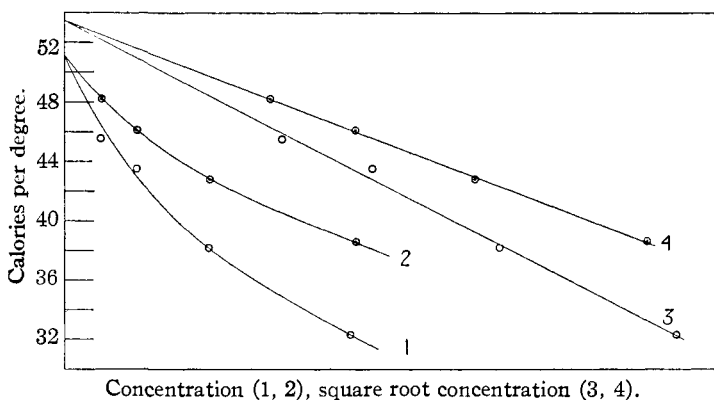Concentration (1, 2), square root concentration (3, 4).

Fig. 2.—Temperature coefficients of heats of neutralization.

The data should furnish, however, a means of obtaining a better value for the temperature coefficient of the heat of ionization than has previously been obtained. The average coefficients were therefore plotted, in spite of the large departures from the average shown by the various salts. Figure 2 shows the plot obtained. Curve 1 shows the ordinary temperature coefficient, and curve 2 that at constant concentration, plotted against the final concentration, $1/(2x + 1)$ and $1/x$, respectively. The curves bend sharply upward, curve 2 being the better defined. The straight lines 3 and 4 show the ordinary coefficient and that at constant concentration, respectively, when plotted against the square root of the final concentration. The square root plots help to estimate the degree of bending necessary near the axis of zero concentration in the case of the first two curves. The scales of abscissas are not the same, but are uniform for each curve.

The introduction of a slight curvature in lines 3 and 4 would permit an excellent compromise point for all four lines at 52 calories per degree, which is therefore accepted as the result for $d\,\Delta H/dt$ for the heat absorption ΔH for the formation of water from its ions. The indirect computations of Noyes, Kato and Sosman[9] give about 49.4.

Summary

The heat of neutralization at constant concentration is defined to be the heat effect $(-\,\Delta H)$ of the reaction: $MOH \cdot xH_2O + HB \cdot xH_2O = MB \cdot xH_2O + (x + 1)H_2O$. It was found possible, using the recent precise heats of neutralization and of dilution of Richards and Rowe, Hall, Gucker and Mair, to extrapolate satisfactorily such heats of neutralization to the same point at infinite dilution for six inorganic salts (K, Na, Li; chlorides and nitrates). The square root of $1/x$ was taken as abscissa. The value 13,650 $20°$-gram calories (or 57.07 kilojoules) found by Richards and Hall for the heat of neutralization at $20°$ at infinite dilution in the case of sodium chloride was found to be an excellent extrapolated value for the family of six curves, and it may be taken as the heat $(-\,\Delta H)$ of the formation of water from its ions at $20°$. This is in agreement with the conclusion of Richards and Mair, who introduced, however, bending in the plots in the region of extrapolation and gave considerable weight to the heats for sodium acetate, neither of which has been done in the present case.

For the temperature coefficient of the heats, individual extrapolations for the various salts could not be made. On plotting the average values for the six inorganic salts, the temperature coefficients at constant concentration were distinctly a smoother function of the concentration or of its square root. The temperature coefficient of the heat of formation of water from its ions $(-d\,\Delta H/dt)$ was estimated to be -52 calories, or -217 joules, per degree in the neighborhood of $20°$.

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[9] Noyes, Kato and Sosman, THIS JOURNAL, **32**, 159 (1910).