THE RELATIVE ENTHALPIES
FOR PERCHLORIC ACID

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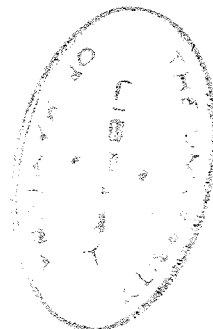

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ABSTRACT

THE RELATIVE ENTHALPIES FOR PERCHLORIC ACID

The apparent relative enthalpies for perchloric acid were determined for correlation with existing data on ionic association. Since the required auxillary data was available, the approach was made through the heats of neutralization for the system, perchloric acid - sodium hydroxide. The reactions were carried out in a bomb calorimeter of the isothermal type over the concentration range from one to twenty four molal. By interpolation, the values for the heat of neutralization were obtained at integral values of the reactant molality. The minimum accuracy of these results is estimated to be .1 per cent.

The calculated apparent relative enthalpies for perchloric acid which are considered to be accurate to at least forty calories differ greatly from the only other reported values. These are due to Berthelot but because of their early date cannot be regarded as reliable.

The correlation with the Raman spectra data for association indicated that dilutions change from exothermic to endothermic reactions at the same concentration about which dissociation is effectively complete. This is consistent with the postulate that the hydration of ionic species is exothermic; and when ions are no longer formed hydration effectively ceases. The remaining endothermic process of separating charged particles then predominates with further dilution.

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INTRODUCTION

Until the development of the Debye-Hückel theory
some thirty years ago, very little was attempted experiment-
ally toward the strong electrolyte solution. Since then,
intensive research has been directed toward the strong
electrolyte but principally in the very dilute regions where
the above theory is applicable, with the result that a large
portion of the concentration range has remained virtually
untouched. The working postulate of the above theory is
that only interionic effects are of importance and in view of
the success about which the theory can boast, it is reason-
able to assume that in the very dilute regions interionic
attraction is the principal factor.

This particular project does not attempt to solve
the problem of the strong electrolytic solution, but it
does postulate conditions which may well apply and it does
attempt to justify these postulates.

One of the first postulates which is held in general
by many at the present, is that three basic phenomena can
be considered in a strong electrolyte solution, interionic
attraction, ionic hydration and ionic association. This in
no way excludes any additional factors.

In view of ionic hydration, postulated to account
for observed deviations from ideality, Stokes and Robinson (1)
offered the consideration that the water involved in hydration
of ions is unavailable as a solvent and concentrations must

be correspondingly evaluated with regard to this decrease in solvent. A factor n, the hydration parameter, appears in the mathematical formulation bearing the significance of the number of water molecules associated with each hydrated solute ion. This approach has offered an extention of the region, though still dilute, in which a theory is applicable. This accomplishment is regarded as an indication of the validity of the approach.

The third factor, that of association, is assumed to be non-existent in the Debye-Hückel treatment, however this is now known not to be the case for many "strong electrolytes" of the 2:1 type and for the strong acids. Rao (2) and Redlich and Bigeleisen (3) have determined, through Raman spectra, the degree of association for nitric acid showing that in solutions as dilute as one molal the acid is only 95 per cent dissociated.

Thus, it is seen that at least three phenomena are responsible for the behaviour of the strong electrolyte solution, and the extent to which any one of these factors contributes to solution properties is a requirement for the development of a suitable theory.

In opposition to hydration of the "molecule" or ion pair, it is postulated here that hydration occurs for the single ion and therefore is dependent on dissociation. Should this be the case, then dilution beyond the concentration at which an electrolyte is effectively totally dissociated

would not involve further hydration. Furthermore, since hydration is the only factor which can be considered exothermic in the dilution process, it is expected that dilution beyond this critical concentration will not be exothermic. The test for this proposal will thus require apparent relative enthalpy, which is the negative of the heat of dilution, and association data for a strong electrolyte.

The degree of association for perchloric acid has been determined by Redlich, Holt, and Bigeleisen (4) and this suggested correlation with the corresponding heats of dilution. This latter data has been determined by Berthelot, (5). However, thermochemical work of this era evokes considerable doubt with regard to accuracy.

The experimental undertaking of this present work was thus to accurately determine the relative enthalpies for perchloric acid in view of correlation with the optical data for association.

At the time, sufficient auxillary data was available to enable the calculations of relative enthalpies from heats of neutralization for the system; perchloric acid - sodium hydroxide. Therefore, since the calorimetric apparatus was available the approach was made through this reaction. Apart from intrinsic interest, heats of neutralization were convenient since the reaction is rapid and well defined.

The calorimeter used was designed specifically for neutralization determinations up to high concentrations.

The magnitudes of the heats of these reactions necessitate the use of a sealed reaction bomb, since quantities of steam are produced which if not confined would lead to indeterminable heat exchanges with the surroundings. This excluded any possibility of an open system as used by Richards and Rowe (6), Sturtevant (7) and Pitzer (8). Furthermore, the rapid evolution of heat encountered in a neutralization rendered an adiabatic system quite impractical with the result that an isothermal jacket was required.

THE CALORIMETER

THE REACTION BOMB

The various components of the reaction vessel are shown in Figure 1. The bomb was a two piece cylinder, six inches in length and three inches in diameter, which was joined by bolting the flanged halves to a Teflon gasket. In general, the calorimeter was similar to that designed by Biermann(9). The casing, fabricated from mild steel, was protected from the reactants by liners constructed of gold laid on a silver base. Within this assembly the gasket supported a gold cup and a small Teflon hammer. The main body of the bomb contained the reacting base while the suspended cup held the acid. These reactants were combined and mixed by a 10 R.P.M. end over end rotation of the cylinder about a horizontal axis. The acid cup was sealed by a sandwich of silicone stopcock grease between two layers of gold foil, which was in turn sealed to the cup lip with a thin film of the grease. On rotation the hammer swung against this seal, ruptured it and so allowed the reactants to mix. To insure complete rinsing and mixing of all the contents, the cup was offset to one side of the bomb so that the liquid would, in part, wash back into the cup with each rotation.

THE CALORIMETER INNER CAN

To obtain a system in which temperature could be conveniently measured and thermal equilibrium maintained,

FIGURE 1. The reaction vessel components

the reaction bomb was immersed in a container holding a fluid which was rapidly stirred. The general design of this system is similar to that employed by Dickinson (10).

The two side columns of the inner can (Figure 2) each contained a screw stirrer running in a bearing assembly; also contained in the left column was a cylindrical calibration heater through which the calorimeter fluid was driven by the stirrer. In the centre of this can was a bearing-mounted ring assembly in which the reaction vessel was mounted. A gear system within this ring assembly transmitted torque from a vertical shaft to the horizontal axis of the ring. All connections with the exterior, for applying mechanical power, were made through the use of lucite drive shafts because of their low heat conduction.

With all components assembled, the required volume of the calorimeter fluid was about four litres.

THE CALORIMETER JACKET

For thermal isolation, the inner structure was placed in a well of similar shape but larger dimensions (Figure 3). In turn, this jacket was immersed in an isothermal bath controlled by the conventional mercury regulator and vacuum tube relay. To conform with the requirements of Newton's cooling law, as they are set forth by White (11), the air gap between the can and jacket was about $1\frac{1}{2}$ centimeters and the surfaces were nickel-plated to minimize radiation.

The external connections for mechanical and electrical
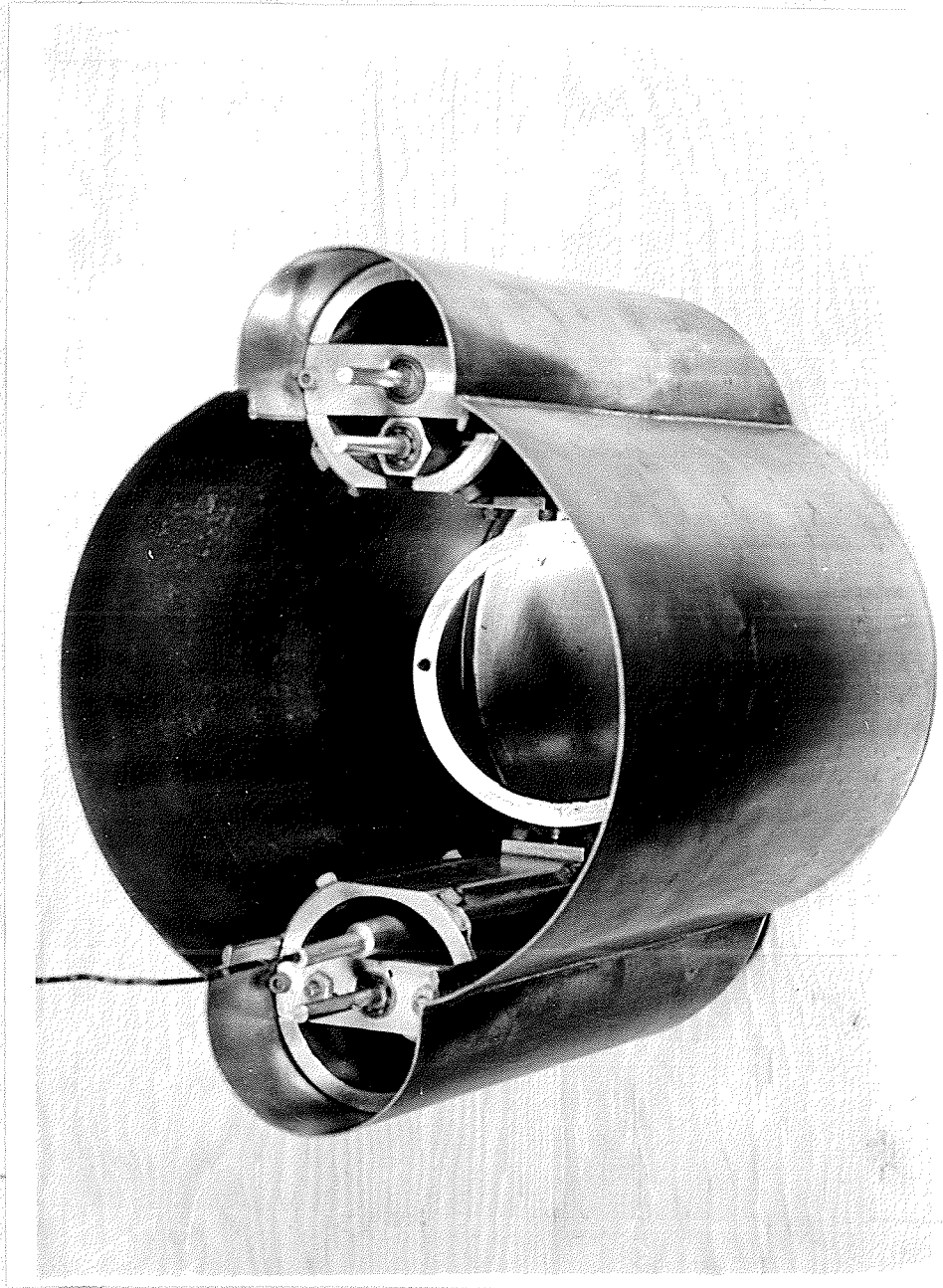
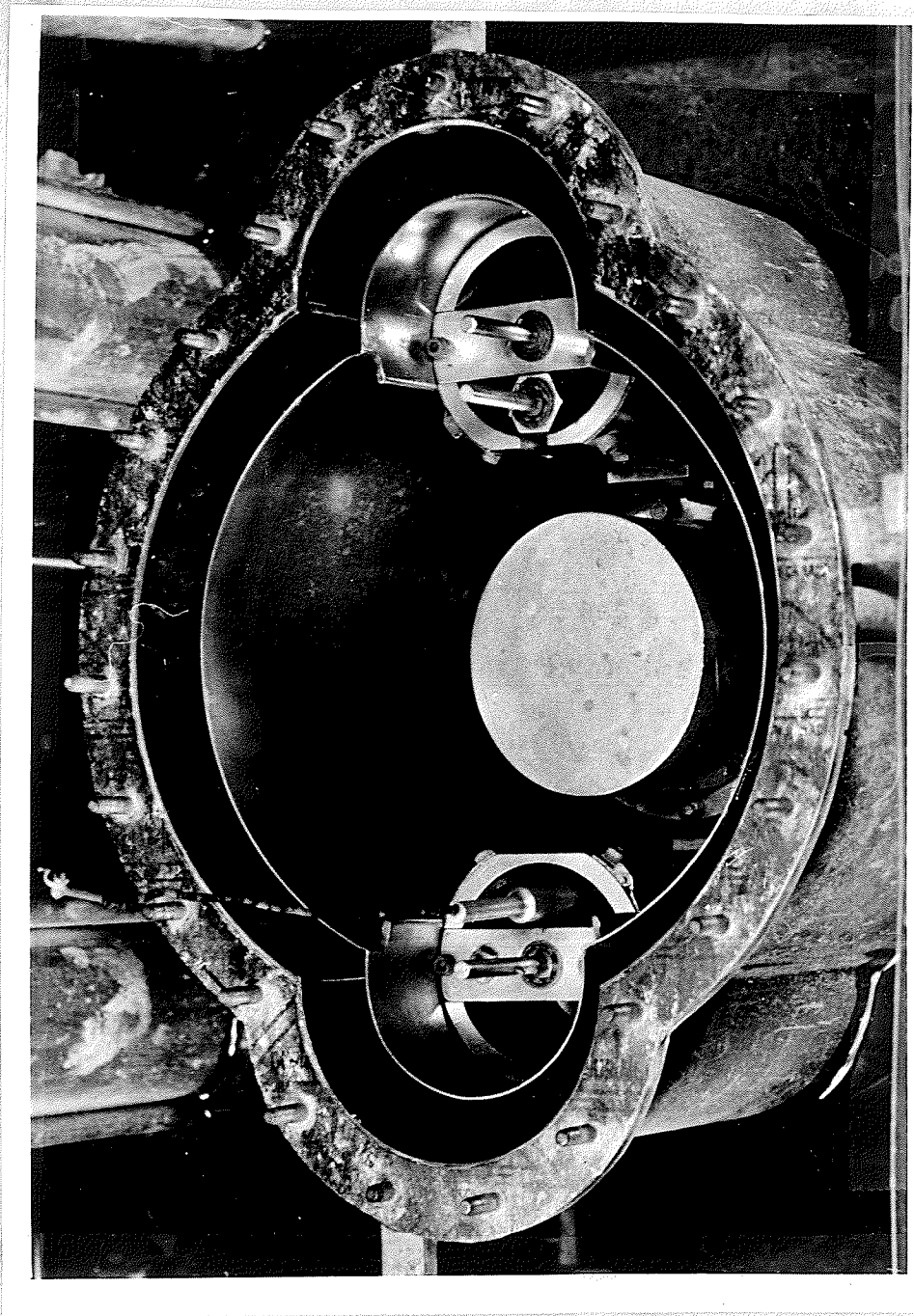FIGURE 2. The calorimeter inner can

FIGURE 3. The calorimeter jacket

requirements were brought through openings in the jacket top which was bolted against a fibre gasket for a water-tight seal. Complete immersion was effected by raising the water level through gravity flow from a reservoir. The action of two larger stirrers in this thermostat offered a turbulent circulation of water about the jacket. A Variac in the heater circuit enabled voltage regulation for a minimum temperature hunt.

Three motors for stirring and rotation, in addition to electrical connections, were mounted on a brass plate which spanned the thermostat (Figure 4).

TEMPERATURE MEASUREMENT

Temperature was measured by the immersion of a Leeds and Northrup type 8160 platinum resistance thermometer in the calorimeter fluid. The thermometer had been calibrated by the manufacturer and as a further check was compared to a glass-sheathed platinum thermometer, made and calibrated by the National Research Council of Canada. The coil resistance of the thermometer was measured with a Mueller bridge, made by the Rubicon Company and calibrated for internal consistency against a standard resistor.

The ice point for the thermometer was taken twice over an eight-month period and gave a variation of .0001 ohm, which is totally negligible in this work.

TIME MEASUREMENT

The time interval during which electrical energy was supplied to the calibration heater was measured by means
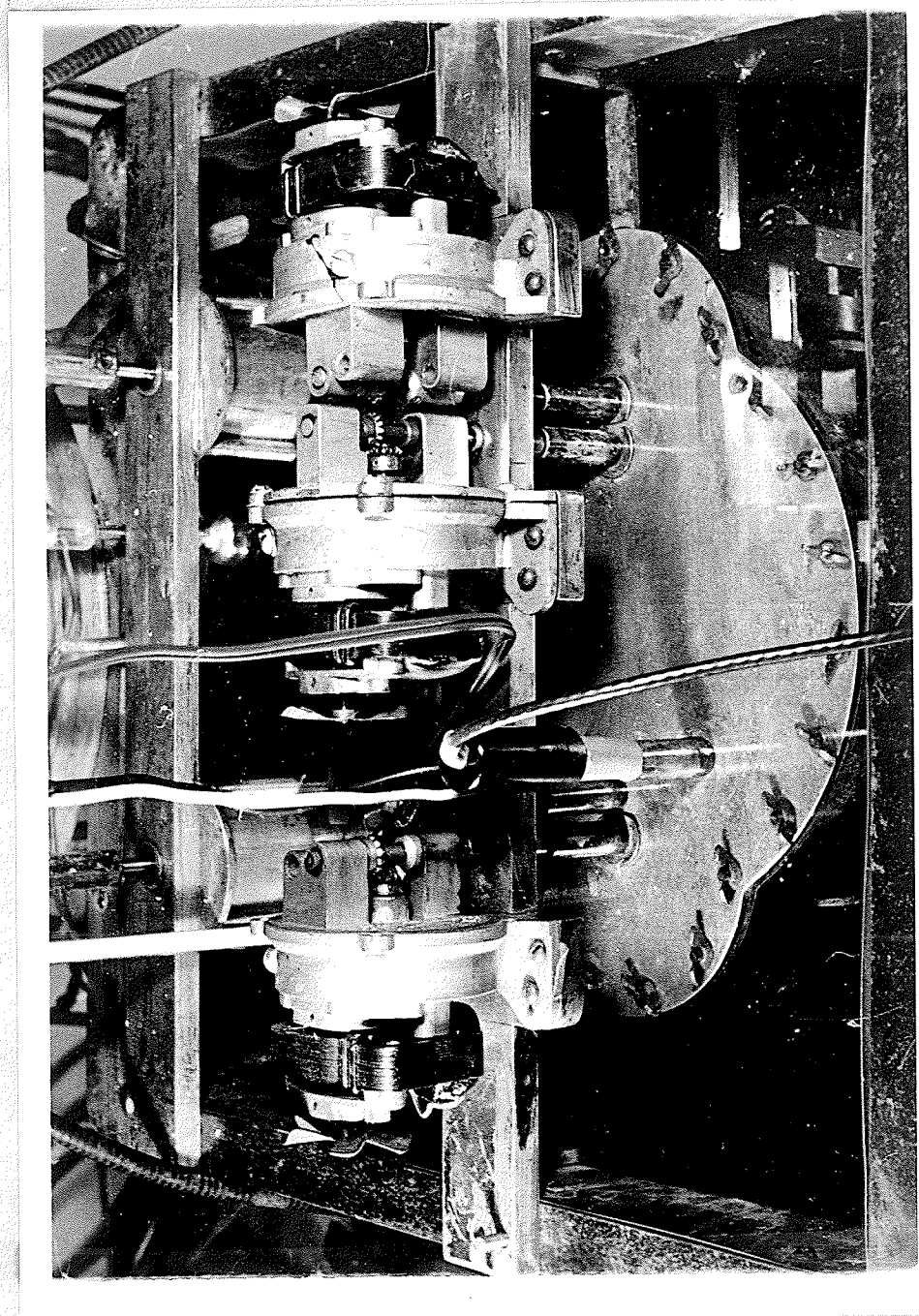
FIGURE 4. The assembled calorimeter

of an electric timer manufactured by the Standard Electric
Time Company. The synchronous timer motor was coupled to
the dial by a clutch which was activated over the heating
period by one pole of a double pole double throw relay,
the other pole of which switched the power supply from a
dummy load to the heater. A toggle switch in series with
the relay coil controlled the above simultaneous action.

A second synchronous motor-driven timer, a Cenco
"Time-it" stop watch, was also required since the calcu-
lation of the corrected temperature rise depended on the
variation of the calorimeter temperature with time. During
reactions, this variation was too rapid to enable manual
recording and so a semi-automatic method was employed.
When the temperature reached a pre-set value and a bridge
balance was obtained, the dial settings and timer were
simultaneously photographed with a 35 m.m. Robot II camera.
About 25 photographs were required for each calibration and
neutralization run.

CALCULATION OF THE CORRECTED TEMPERATURE RISE

All methods of calculating the temperature rise
due to the calorimeter reaction alone begin by assuming the
applicability of Newton's law which offers a means of cal-
culating the temperature change due to conduction. Of the
three possible modes of heat transfer, only conduction
need be considered since convection has been sufficiently
reduced by the gap dimensions between the inner can and
jacket and radiation by the nickel-plated surfaces. Accord-
ing to Newton's law, the variation of temperature with time
is proportional to the thermal gradient between the calori-
meter and jacket, with a small additive term, W, representing
the heat introduced by mechanical action, ie., stirring and
bomb rotation. This can be expressed as:

$$R = \frac{dT}{dt} = K(T-T_j) + W$$

On integration, the value of the temperature change due to
heat exchange between calorimeter and jacket and due to
mechanical action will be obtained. This temperature change
is a correction term which is to be applied to an observed
temperature change.

The method of evaluating the above integral was a
graphical one due to Dickinson (10) with modifications by
Biermann (9); the general method is well described by
Sturtevant (12).

ELECTRICAL CALIBRATION

A full wave mercury rectifier with an electronic voltage regulation section was used to supply a constant voltage to the heater. This unit similar in design to that described by Biermann (9), had a dummy load of equal resistance to the heater. With this arrangement, long warm-up periods for regulation of the supply were available without a load change in switching to the calibration heater. This heater was wound with 80 ohms of 26 gauge Advance wire on a threaded bakelite cylinder. The brass enclosing jacket served as one lead for the electrical input while the other lead was brought through a Teflon sleeve to the top of the calorimeter.

In addition to temperature, the basic measurements in the calibration were those of heater voltage and current, calorimeter fluid mass, and time which was taken directly from the synchronized timer.

The water used as the calorimeter fluid was weighed in a five litre flask on a large solution balance which was accurate to 10 milligrams.

The voltage drop across the heater was obtained from a measurement of the potential across a volt box in parallel with the heater. The ratio used was that designated as 100:1, which gave the ratio 100.02:1 on calibration. This ratio enabled the heating voltages, which were about 80 volts, to be measured with a Rubicon type B potentiometer.

The accompanying standard Weston cells were certified by the National Research Council.

The measurement of the potential drop across a standard 1/10 ohm resistor, calibrated by the manufacturer, the Rubicon Company, placed in series with the heater gave the required current measurement.

In the electrical calibration every effort was made to duplicate the conditions of a neutralization run. The differences were the application of electrical power and the weighing into the reaction vessel of distilled water in place of reactants.

During the calibrations two observers were required, one to record time-temperature data and the second to record current and potential readings. In general, the water weighed into the calorimeter can was below the standard reaction temperature and consequently had to be brought to 25°C. This was done with the calibration heater and offered a means of checking the relay operation immediately before the actual calibration. The thermostat was regulated at 26.5°C, the mid-point in a three-degree temperature rise, to give the minimum thermal gradient. There was thus a small temperature rise due to this gradient which after the heating was reversed to produce a temperature drop. For this foreperiod the temperature rise was followed for 400 seconds, after which the power was switched to the heater and a three-degree rise followed. The after-period involved a temperature decrease

which was followed for about 800 seconds. The average rate of temperature change with time for the fore and after periods was about a hundredth of a degree in 500 seconds.

THE HEAT OF NEUTRALIZATION MEASUREMENT

SODIUM HYDROXIDE - - PREPARATION AND ANALYSIS

A saturated solution was prepared from Fischer
Analytic Reagent sodium hydroxide which was then placed in
a large alkali-etched flask where sodium carbonate was
allowed to settle. After a month, this stock solution was
filtered through glass wool, where the sodium carbonate was
removed and the solution was stored in polyethylene bottles.
The solution was analyzed and portions of it were quantita-
tively diluted to the required concentrations where a second
analysis was made.

The analysis for sodium hydroxide was an indirect
one in which an excess of reagent grade hydrochloric acid
was added to a weighed sample of the base solution. Over-
night, this was evaporated to dryness on a hot plate at
$200^{\circ}C$ during which the excess hydrochloric acid was removed
by evaporation. The residual halide was dissolved and
precipitated with an excess of silver nitrate. After stand-
ing in darkness for at least six hours, the precipitate was
gathered in a sintered glass crucible of medium porosity
and dried in an oven at $160^{\circ}C$ overnight. Seven samples
were run for each analysis with a resultant accuracy to
.05 per cent or better. The accuracy of the quantitative
dilutions not only gave the required concentrations but also
offered a means of evaluating the consistency of the analysis.

All weighings were made with weights calibrated by

the National Research Council and proper buoyancy correct-
ions to vacuum conditions were employed.

PERCHLORIC ACID -- PREPARATION AND ANALYSIS

Baker Reagent Grade perchloric acid was used with
redistilled water in the preparation of the required
solutions. The 70 -72 per cent stock concentration was
analyzed and quantitatively diluted to within one part in
one thousand of the sodium hydroxide molality. This pro-
cedure eliminated further complications due to concentration
differences in the calculation of the heat of neutralization.
The analysis of perchloric acid was acidimetric using a .1
molal solution of sodium hydroxide which had been standard-
ized against potassium acid phthalate. The large quantity
of dilute base gave an accuracy of .04 per cent in a weight
titration. The indicator used was brom-thymol blue which
gave a sharp color transition from yellow to deep blue with
an intermediate green showing neutrality. Seven samples
were taken for each acid analysis.

GENERAL METHOD

To minimize the exposure of the reactant to the
atmosphere, a systematized procedure was followed for load-
ing the bomb. Preliminary weighings were made for the base
containing buret and the water flask to allow rapid weighing
during the assembly. The acid was then weighed into the
inner cup which was immediately sealed with a previously
prepared "sandwich". From the weight of acid used, the

exact weight of sodium hydroxide solution required for the neutralization was calculated, and, this amount was then weighed into the base of the bomb which was quickly sealed. Since it was impossible to weigh into the bomb the exact equivalent of base, the difference was kept such that the acid was in slight excess. This difference never exceeded .1 per cent of the equivalent value and its presence tended to reduce the error introduced by any carbonate present in the base.

After placement of the bomb in the well, about four litres of water were weighed into the can. The remainder of the calorimeter was quickly assembled and while the bath level was brought above the jacket top the inner temperature was brought to $25^{\circ}C$ by the heater. Readings were taken for the fore and after periods as in the calibration, but the temperature rise was now effected by the mixing of the reactants through bomb rotation. In general, the reaction period was shorter for the neutralization than for the calibration due to a more rapid energy release.

THE CALIBRATION

The heater current was found by dividing the
potential drop across the standard resistor by its calib-
rated value. However, a correction had to be included to
account for the current that flowed through the volt box
in parallel with the heater. The volt box resistance was
measured as 15,140 ohms and its corresponding current ob-
tained by dividing this resistance into the observed poten-
tial. The current flowing through the heater was thus the
observed current minus the current flowing through the volt
box. The determined quantities of potential, current, and
time enabled the calculation of the energy input in absolute
joules. Division of this quantity by the corrected temp-
erature rise then gave the total heat capacity of the system
in absolute joules per degree Celsius, which was reduced to
defined calories per degree Celsius by the factor 4.1840.

The heat capacity of calorimeter water was calculated
from the specific heat data of Osborne, Stimson, and
Ginnings (13), while the pertinent temperature was taken as
the mean value of the temperature interval. The subtraction
of this heat capacity from the total yielded the heat capacity
for the calorimeter.

The mean value of this quantity from fourteen trials
was 590.4 ± 1.8 defined calories per degree Celsius. The
variation is compatible with the power line fluctuation
appearing in the input timer.

THE HEAT OF NEUTRALIZATION

The calculation of the heat of neutralization for sodium hydroxide and perchloric acid was simplied by the extreme solubility of sodium perchlorate and therefore the absence of precipitation.

The heat liberated in each neutralization was the product of the temperature rise and the total heat capacity of the system. This last quantity involved the heat capacities of the calorimeter, the calorimeter fluid, and the neutralization products. The first of these terms was assumed to remain constant after calibration, while that for the calorimeter water was obtained directly from mass and specific heat (13). Harned and others (14) have shown that for sodium chloride solutions containing a slight amount of hydrochloric acid, specific heats are essentially the same as sodium chloride solutions of corresponding ionic strength. Therefore, while the product solution actually contained the excess perchloric acid, no detectable error will result if the approximation is made that the mass and specific heat of the solution can be calculated on the basis that the number of moles of sodium perchlorate finally present is equal to the number of moles of perchloric acid used and that the amount of water finally present is equal to the amount of water initially present plus the water produced in the reaction. The specific heat data for sodium perchlorate is that of Colomina and Nicolas (15).

The heat evolved per mole was calculated in terms of the base which was the limiting reactant.

The lack of specific heat data for perchloric acid rendered the calculation of a temperature coefficient for this neutralization system impossible. This condition necessitated that all reaction temperatures deviate from 25°C by not more than .1 degree, while in general this deviation was found to be less than .03 degrees. Rossini (16) has calculated the temperature coefficient for neutralization in the infinitely dilute solution as 50 calories per degree and further calculations by Biermann (9) for the systems hydrochloric acid - potassium hydroxide and hydrobromic acid - sodium hydroxide give the same approximate value of 50 calories per degree Celsius. The application of this co-efficient, assumed to apply to this system, gives an average correction of about six calories, which is well below the anticipated experimental error. The experimental values for the heat of neutralization of perchloric acid with sodium hydroxide are given in Table 1 and plotted in Figure 5.

TABLE 1

EXPERIMENTAL DATA FOR PERCHLORIC ACID AND SODIUM HYDROXIDE

| m(HClO$_4$)	m(NaOH)	m	$-\Delta H_N$(cals.)
24.299	24.291	24.29	24,086 24,089
20.081	20.099	20.09	21,822 21,851
16.083	16.090	16.09	19,474 19,476
13.411	13.410	13.41	17,824 17,834 17,837
11.233	11.221	11.23	16,626 16,627
9.193	9.195	9.194	15,633 15,628
7.860	7.856	7.858	14,980 14,982
6.080	6.103	6.092	14,317 14,301
5.008	5.018	5.013	14,032 14,034
4.020	4.014	4.017	13,673 13,684
2.524	2.538	2.531	13,478 13,485 13,470
1.012	1.011	1.012	13,381 13,383 13,401
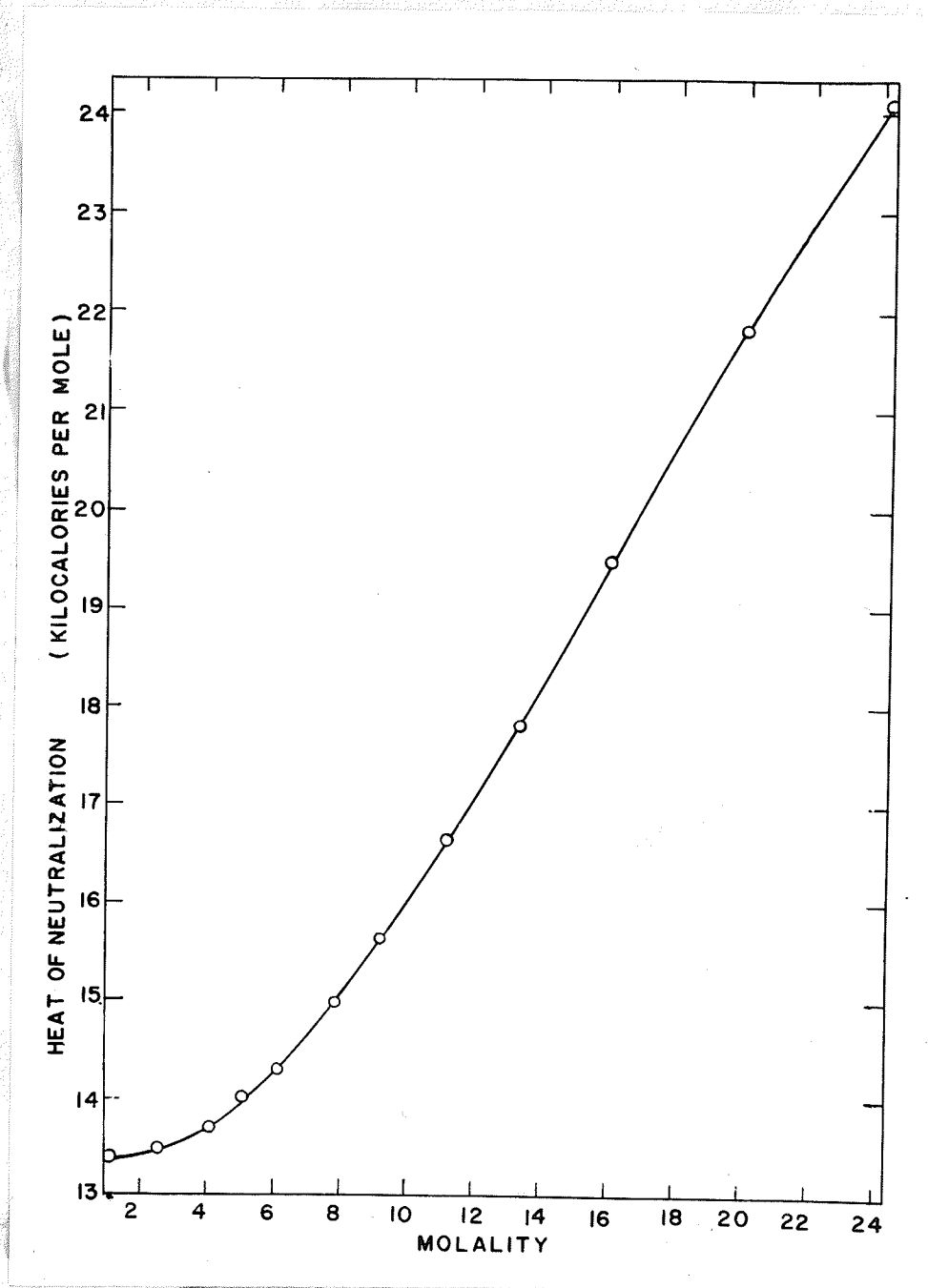
FIGURE 5. Heat of neutralization for the system
sodium hydroxide - perchloric acid

DISCUSSION OF EXPERIMENTAL ERRORS

CALIBRATION ERRORS

The sources of error encountered in the calibration arise from the evaluation of the energy input, the temperature rise and the heat capacity of the water employed.

Any error in the heat capacity of the water is totally negligible since the mass is known to better than .001 per cent and the specific heat to better than .005 per cent. In addition, any error in the specific heat data for water would tend to cancel out because of use in both calibration and neutralization since the quantity of water used never deviated from 4050 grams by more than 50 grams.

The average deviations of the voltage delivered by the power supply were in general less than .1 per cent. Furthermore, this deviation is a linear drift rather than a random fluctuation so that the average of the voltage readings for any one calibration would have an uncertainty well below .1 per cent. The maximum error in the energy input due to both current and voltage drifts was therefore estimated as .06 per cent.

The potentiometer was warrented by the manufacturer to a minimum accuracy of .01 per cent, however, internal calibration revealed no measurable error. Therefore errors in the volt box ratio and resistance due to calibration against the potentiometer are less than .01 per cent. The standard cell and standard resistor are known to .005 and

.01 percentages respectively.

The maximum possible error in the calibration energy can then be considered as .07 per cent.

The consistency of points along the time - temperature curves indicates that the reproducibility of temperature differences was about .00001 ohm. However, in the bridge calibration this same sensitivity was the limiting quantity and we can thus know temperature differences to about .0004°C, exclusive of errors in correction for heat exchange with the surroundings. This is equivalent to a maximum uncertainty of .02 per cent in a two degree temperature rise. Since this rise is corrected in the same manner, for both calibration and neutralization, small errors inherent in the method will tend to cancel.

An uncertainty of not more than three calories is thus expected in the total heat capacity of about 4700 calories.

NEUTRALIZATION ERRORS

The precision obtained in the standard methods used for analysis was better than .05 per cent at all times. The error in analysis of the base appears directly in the heat of neutralization as calculated per mole. Data from National Bureau of Standards, Circular 500, indicate that the heat of neutralization of an alkali carbonate is about half that of the hydroxide per equivalent. The carbonate present in the hydroxide solutions is estimated to be less

than .08 mole per cent, which will introduce an error of .03 per cent into the measured heat.

The error in the specific heat data for sodium perchlorate solutions is about .1 per cent. Since the average resultant solution had a heat capacity of about 100 calories, this error amounts to .1 calorie which is completely insignificant in comparison to the total heat capacity of about 4700 calories.

The maximum estimated error is .15% and the real error is probably well below this value.

DISCUSSION OF EXPERIMENTAL RESULTS

For convenience in future utilization, the interpolation of the experimental results to integral values of molality is desirable. This is accomplished by approximating the data with the analytical function

$$\Delta H_N = 13,031 + 175.75m + 13.12m^2$$

The heats of neutralization were then calculated from this equation for the experimental concentrations and the deviations from the experimental values were plotted against the molality (Figure 6). The smoothness of this curve is indicative of the self consistency of the experimental results. From the general equation and the corresponding deviation corrections the heats of reaction at integral molalities were tabulated (Table 2).

The interpolations of auxilliary data to integral values of molality are tabulated in Table 2. The apparent relative enthalpies of sodium perchlorate, $\phi_L(NaClO_4)$, are those determined by Nicolas and Colomina (15) while the same properties for sodium hydroxide are principly due to Bertetti and McCabe (17). The Bertetti and McCabe data required conversion from the English system of units and the temperature conversion involved the specific heat data also reported by these investigators. A further correction of twenty-seven calories was added to all their values of the molar heat of dilution to infinite dilution to bring them into agreement with the data of Sturtevant (18). The
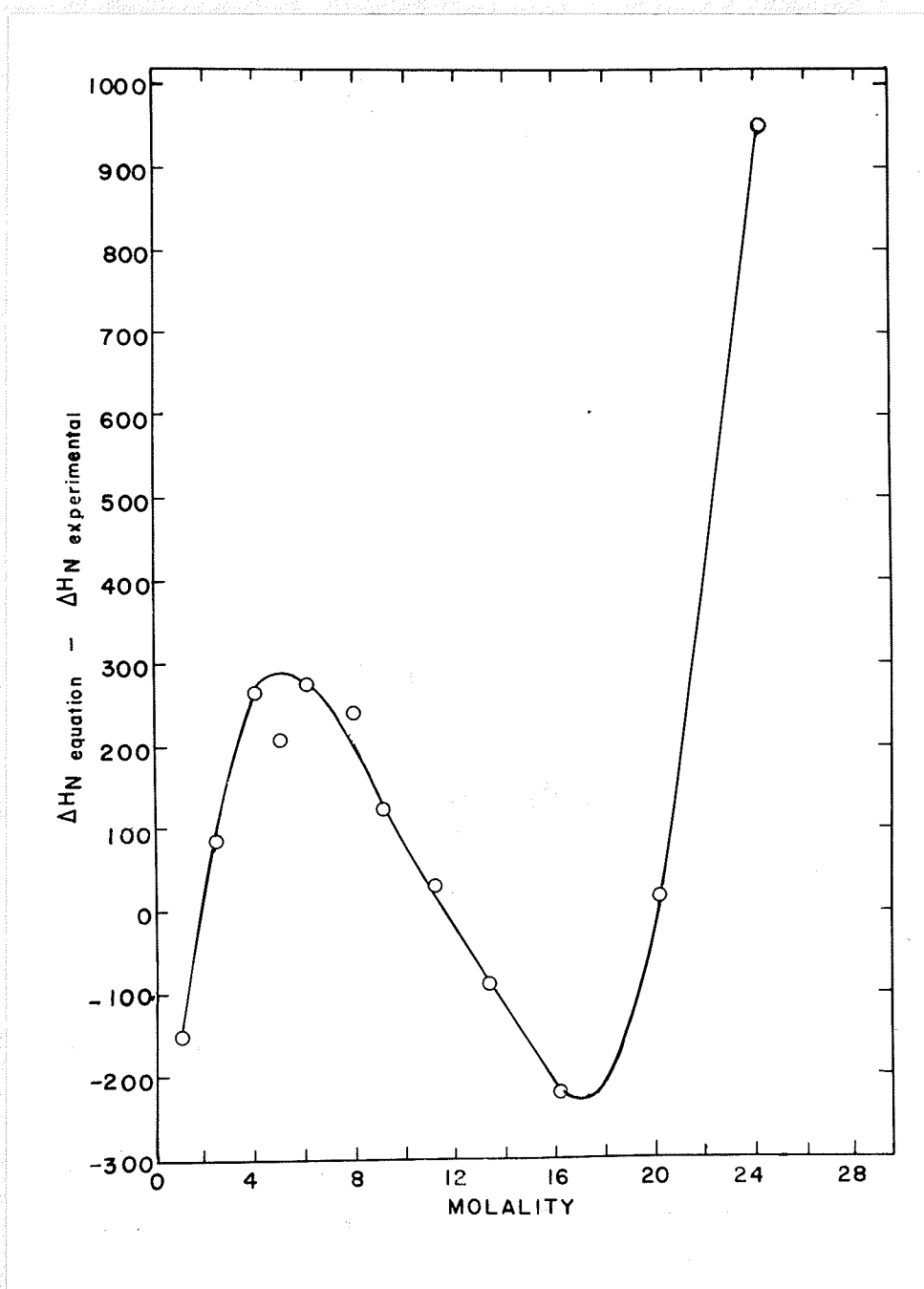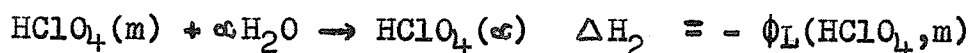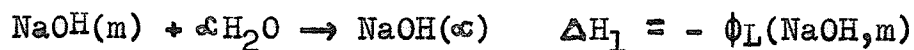
FIGURE 6. The deviation curve

TABLE 2

DATA FOR THE APPARENT RELATIVE ENTHALPY OF PERCHLORIC ACID

m	m'	$-\Delta H_N$	$\phi_L(NaOH)m$	$-\phi_L(NaClO_4)m'$
1	.4955	13,378	82	271
2	.9823	13,439	8	481
3	1.460	13,509	-21	664
4	1.930	13,673	4	836
5	2.392	13,953	69	985
6	2.846	14,279	167	1115
7	3.293	14,663	303	1217
8	3.731	15,087	474	1316
9	4.163	15,537	677	1412
10	4.587	16,012	906	1491
11	5.004	16,514	1162	1558
12	5.415	17,041	1435	1617
13	5.819	17,596	1729	1673
14	6.217	18,178	2019	1725
15	6.608	18,785	2319	1774
16	6.993	19,417	2615	1820
17	7.372	20,017	2909	1862
18	7.745	20,605	3194	1902
19	8.113	21,201	3476	1936
20	8.475	21,786	3741	1967
21	8.831	22,288	3995	1995
22	9.182	22,804	4239	2020
23	9.528	23,347	4475	2044
24	9.868	23,921	4696	2062

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need for this correction arises because Bertetti and McCabe measured heats of dilution only above 13.59 per cent using the value given by Richards and Gucker (19) for the molar heat of sodium hydroxide from 13.59 per cent to infinite dilution, and thus introduced into their data the error incurred in the parabolic extrapolation to infinite dilution. The heat of neutralization at infinite dilution, ΔH_N^o, is that due to Bender and Biermann (20) and has the numerical value of $13,321 \pm 20$ calories per mole at $25^\circ C$. The apparent relative enthalpies for perchloric acid are calculated through the expression for the heat of neutralization which can be realized from the following Hess Law procedure.

The initial conditions are sodium hydroxide at the molality m and perchloric acid at the same molality. Neutralization then produces sodium perchlorate at the molality m', where from mole to mole considerations $NaClO_4(m')$ will be a mole of sodium perchlorate in $(\frac{55.51}{m} + \frac{55.51}{m} + 1)$ moles of water. First consider the dilution of the reactants to infinite dilution;

$$NaOH(m) + \infty H_2O \rightarrow NaOH(\infty) \quad \Delta H_1 = - \phi_L(NaOH,m)$$

$$HClO_4(m) + \infty H_2O \rightarrow HClO_4(\infty) \quad \Delta H_2 = - \phi_L(HClO_4,m)$$

Now consider the neutralization occuring at this infinite dilution;

$$HClO_4(\infty) + NaOH(\infty) \rightarrow NaClO_4(\infty) \quad \Delta H_3 = \Delta H_N^o$$
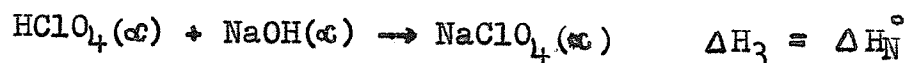
and finally the concentration of the sodium perchlorate
to the required solution;

$$NaClO_4(c) \longrightarrow NaClO_4(m') + H_2O \qquad \Delta H_4 = \phi_L(NaClO_4, m')$$
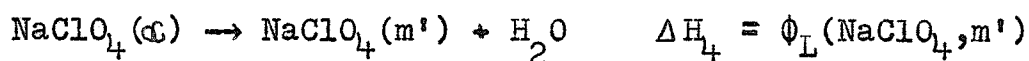
The overall heat of the reaction will be the sum of the
above heat effects;

$$\Delta H_N = \Delta H_N^\circ + \phi_L(NaClO_4, m') - \phi_L(HClO_4, m) - \phi_L(NaOH, m)$$

The values for the apparent relative enthalpy of perchloric
acid are tested in Table 3 and plotted against molality in
Figure 7.

Since the experimental errors of four different
experimenting groups are combined here, there results a
maximum possible error of about forty calories. In con-
sideration of this uncertainty, the smoothness of the ϕ_L
versus molality curve for perchloric acid leaves little to
be desired.

For the calculation of the relative partial molar
enthalpy, $\bar{L}_2(HClO_4)$, portions of the above curves were
fitted to analytical expressions containing four constants.
Differentiation of these equations with respect to molality
and the evaluation of the slopes for integral molality
values gave the required form for direct substitution into
the conventional thermodynamic expression for the partial
molar property in terms of the associated apparent quantity

$$\bar{L}_2 = \phi_L + m\frac{d\phi_L}{dm}$$

The values of $\bar{L}_2$ for perchloric acid are listed in Table 3.

TABLE 3

RELATIVE ENTHALPIES OF PERCHLORIC ACID

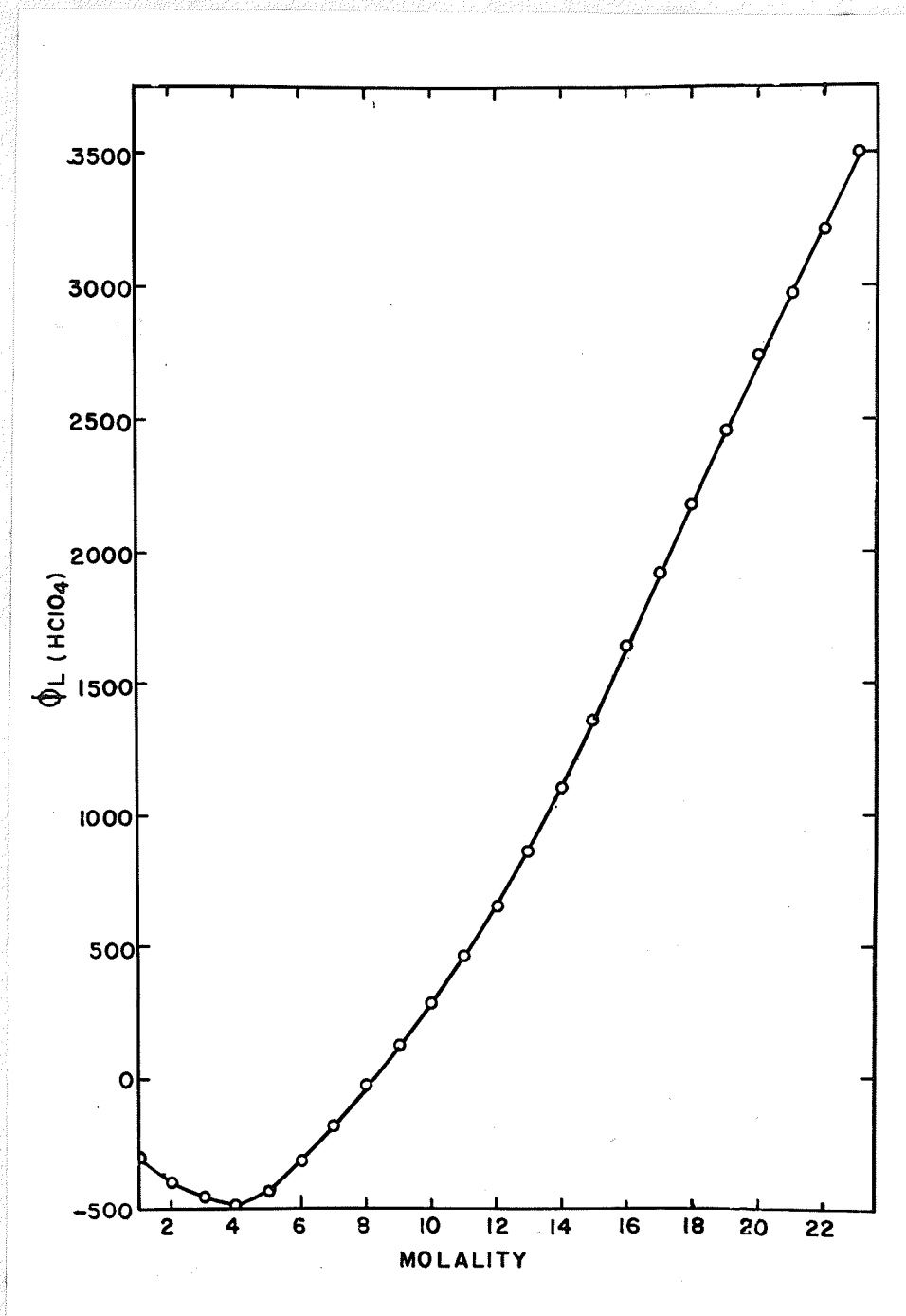| m	$\Phi_L(HClO_4)m$	$\bar{L}_2(HClO_4)m$
1	-296	-392
2	-381	-540
3	-455	-642
4	-498	-498
5	-422	147
6	-324	418
7	-178	765
8	-24	1151
9	127	1568
10	294	2040
11	473	2564
12	668	3149
13	873	3792
14	1113	4521
15	1371	5323
16	1661	6216
17	1925	7008
18	2188	7084
19	2468	7560
20	2757	8037
21	2977	8437
22	3224	8856
23	3507	9303
24	3842	9794

FIGURE 7. The apparent relative enthalpies for perchloric acid

The alternative enthalpy data for perchloric acid
is that due to Berthelot (5) and a few of his interpolated
values are listed below for purposes of comparison with the
corresponding values obtained in this work.

m	ϕ_L (Berthelot)	ϕ_L (this work)
2	-20	-381
3	-10	-455
4	5	-498
8	220	- 24
9	305	127
15	880	1371

The observed discrepancies cannot be realized in terms of
experimental errors of such large magnitudes in this
present work and therefore must be considered to exist in
the earlier work.   This can perhaps be attributed to the
methods of calorimeter calibration then available, which
exclude electronic equipment.   Furthermore, it is reasonable
to doubt the purity and analysis of the acid used by Berthelot
since in 1882 perchloric acid was a chemical curiosity and
relatively little was known about its structure and analysis.

Correlation of the values of ϕ_L obtained in this
work with the association data observed by Redlich, Holt,
and Bigeleisen (4) leads to a surprising consistency.   The
above data indicates that about eight molal, perchloric acid
is effectively totally dissociated.   From Table 3 it is
seen that at the concentration of eight molal the sign of

the apparent relative enthalpy changes from plus to minus
indicating that heat is absorbed on the dilution of solutions
below this molality. The indication is that exothermic pro-
cesses no longer occur, or at least are no longer prominent
when dissociation is complete. This is in close harmony
with the introductory postulate that hydration is effectively
complete when ionic species are no longer produced. How-
ever, the possibility of hydration of the undissociated ion
pairs cannot be dismissed, though the accompanying heat
effect must be very small in comparison to that for the ion.

Further significance can be offered by a consideration
of the apparent relative enthalpies for a number of strong
electrolytes. The following is a portion of a table from
Harned and Owen (14);

m	LiCl	LiBr	NaCl[X]	NaBr[X]	KF	KCl[X]	KBr[X]	HNO$_3$	HClO$_4$[X]
1	334	322	-23	-37	190	-26	-104	140	-29
3.5	683	652	-355	-424	260	-355	-557	200	-475

The values for HClO$_4$ are from this work and those for HNO$_3$
are from the National Bureau of Standards Circular 500.
The solutes in the above table which are commonly considered
as the strongest electrolytes[X], and therefore highly dis-
sociated all show negative values for ϕ_L at low concentrations.
This indicates that the dilution of these solutions is
accompanied by an absorption of heat and hydration as an
exothermic process does not predominate. The principal
effect here can be considered as the separation of ionic

charges. The magnitude of this effect is shown rather consistently in the above table.

This is not so for the weaker "strong electrolytes" which continue to exhibit an evolution of heat on dilution at low concentrations, indicating that the addition of water favours the formation of a "structure" having a lower energy. By previous reasoning, the process can be considered as the solvation of the dissociation products. It is to be noted, that this in no way implies that all of the ion types formed are hydrated.

The above results and reasoning appear to offer a reasonable description of the strong electrolyte in general, rather than just the strong acid. The main conclusion which one might attempt to draw is that hydration and dissociation are the principal contributors to the relative enthalpies of strong electrolytes. Only at more dilute regions where dissociation is complete does interionic energy become predominant.

Redlich and others (3) (4) have estimated the heat of dissociation for nitric acid from the temperature dependence of association. Thus, since the overall effect is known and the contribution of interionic energy approximated, it is possible in theory to be able to calculate the heat of hydration.

Before the same quantitative correlation can be applied to nitric, as has been done for perchloric acid,

accurate redeterminations of the relative enthalpies will be required. The existing data for the more concentrated regions principally stems from the same source as the early perchloric data. In the meanwhile, it is qualitatively seen that nitric acid continues to evolve heat on dilution below one molal indicating by the here-contained proposal that hydration and therefore dissociation processes are still occuring. In consistency with the perchloric acid results, nitric acid is reported by Redlich and Bigeleisen, (3), to be only 95 per cent dissociated at one molal.

An additional strong acid of current interest to which this approach could be undertaken is trifluoro acetic acid. However, both thermochemical and optical data are lacking. The determinations of these quantities may offer additional support for this present picture of the strong electrolyte solution.

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SUMMARY

The heats of neutralization for the system, per-chloric acid and sodium hydroxide, were determined at 25°C over the concentration range from one to twenty four molal in a bomb type isothermal jacket calorimeter. The heats of neutralization were interpolated to integral values of molality from which the apparent relative enthalpies and the relative partial molar enthalpies were calculated for perchloric acid. These values surplant the earlier relative enthalpy data for perchloric acid.

A comparison was made between the degree of ionization obtained from Raman spectra and the apparent relative enthalpy for perchloric acid, with the result that a satisfactory picture was obtained for the strong acid solution.