THE HEAT OF SOLUTION AND SOME PARTIAL MOLAL QUANTITIES

OF THE CONSTITUENTS IN AQUEOUS SOLUTIONS OF THE

DECAHYDRATE OF SODIUM TETRABORATE

BY

JOSEPH R. KANAGY

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INTRODUCTION

For the past few years a study (1) has been made in this laboratory of the hydrates of sodium tetra-borate. A study of the change of the vapor pressure with temperature has permitted certain important thermodynamic calculations. In this investigation the work on sodium tetraborate has been continued by making a study of the aqueous solutions of borax. The heat of solution of the salt and the specific heat of the solutions have been determined at a number of dilutions. From the results several partial molal quantities have been calculated.

REVIEW OF THE LITERATURE

The only value given in the literature for the
heat of solution of sodium tetraborate decahydrate
is one which was obtained by Thomson (2). This is
an integral heat of solution and was determined at a
dilution of 1600 mols of water.

Randall and Bisson (3) have experimented with
aqueous sodium chloride solutions. They measured the
heat of solution at many dilutions and from these
results calculated the partial molal heat content.
Specific heats and heats of dilution were also deter-
mined. All of this work was done at 25°C.

Randall and Rossini (4) studied the aqueous
solutions of several electrolytes including the halides,
nitrates, and sulphates of potassium and sodium at
25°C. The apparent molal heat capacities and partial
molal heat capacities of the solute and solvent were
calculated. These values were shown to be linear
functions of the square root of the molality and
as such could be accurately interpolated to infinite
dilution. The partial molal heat capacities of ions
were shown to be additive at infinite dilution.

Rossini (5,6) has also calculated the partial
molal heat capacities and apparent molal heat capacities
for a great many electrolytes and has shown their rela-

tion to the Debye-Huckel theory of strong electrolytes.

THEORETICAL DISCUSSION

When a mol of sodium tetraborate is dissolved
in enough water to form a given solution the heat
absorbed is called the total or integral heat of solu-
tion. If to a given solution of sodium tetraborate
an additional amount of the solute is added the heat
absorbed per mol is called the partial or differential
heat of solution. The total and partial heats of
solution become identical at infinite dilution.

In order to calculate the free energy of a
reaction at one temperature when the free energy at
another temperature is known it is first necessary
to obtain the value of ΔH, the increase in heat content
accompanying the reaction. This quantity is defined
as the difference between the heat contents of the
substances formed and the heat contents of the sub-
stances disappearing. In case one or more of the
substances involved in the reaction occurs in solution
we must use not the molal heat content, H, of the pure
substance but the heat content of the substance when
in solution at the given concentration. The quantity
$\bar{H}$ is the partial molal heat content and is defined as
the increase in the heat content of a large amount of
the solution at the given concentration when one mol
of the substance is added to it.

It is not possible to determine the absolute
value of H or $\bar{H}$ for any substance but it is possible

to ascertain how much greater or less this is than the
heat content of the same substance in some chosen state.
At any temperature if one is dealing with the partial
molal heat content of water in a solution in which water
is the solvent, pure liquid water may be chosen as the
reference state and designated as $\bar{H}_1^o$. In considering
a solute such as sodium tetraborate, a reference state
must be chosen. In this work the infinitely dilute
solution rather than the solid salt is chosen as the
reference state, and is denoted by $\bar{H}_2^o$. The difference
between the partial molal heat content of any consti-
tuent of a solution and the molal heat content of its
reference state is called the relative heat content
and is designated by L. For solvent and solute, res-
pectively,

$$L_1 = \bar{H}_1 - \bar{H}_1^o \qquad (1)$$
$$L_2 = \bar{H}_2 - \bar{H}_2^o \qquad (2)$$

and at infinite dilution $L_1 = 0$ and $L_2 = 0$.

If to a solution already containing n_1 mols of
water and n_2 mols of salt, dn_2 more mols of salt are
added at constant temperature and pressure and q is
equal to the total increase in heat content, then $\frac{q}{dn_2}$
is equal to the partial heat of solution of the salt
per mol. Representing the molal heat content of the
solid salt by $H_2(s)$, the heat content of the salt used
is $H_2(s)dn_2$. Then,

$$\frac{q}{dn_2} = \bar{H}_2 - H_2(s) = \bar{L}_2 - L_2(s) \qquad (3)$$

where L_2 and $L_2(s)$ are the corresponding relative heat contents. $L_2(s)$ is determined by measuring the heat of solution of the solute in an infinite amount of solvent. In this case $L_2 = 0$, and

$$\frac{q}{dn_2} = -L_2(s) \qquad (4)$$

When $L_2(s)$ is known L_2 may be calculated at any other dilution.

The total heat content of a solution may be represented by the equation,

$$H = n_1 \bar{H}_1 + n_2 \bar{H}_2 \qquad (5)$$

and the total relative heat content,

$$L = H - n_1 \bar{H}_1^O - n_2 \bar{H}_2^O. \qquad (6)$$

Substituting (5) in (6), and then substituting (1) and (2) in the resulting equation,

$$L = n_1 \bar{H}_1 + n_2 \bar{H}_2 - n_1 \bar{H}_1^O - n_2 \bar{H}_2^O$$

$$L = n_1(\bar{H}_1 - \bar{H}_1^O) + n_2(\bar{H}_2 - \bar{H}_2^O)$$

$$L = n_1 \bar{L}_1 + n_2 \bar{L}_2 \qquad (7)$$

By partial differentiation,

$$dL = \bar{L}_1 dn_1 + \bar{L}_2 dn_2 \qquad (8)$$

By general differentiation,

$$dL = d\bar{L}_1 n_1 + dn_1 \bar{L}_1 + dn_2 \bar{L}_2 + d\bar{L}_2 n_2 \qquad (9)$$

Combining (8) and (9) gives,

$$n_1 d\bar{L}_1 + n_2 d\bar{L}_2 = 0 \qquad (10)$$

By transforming and integrating

$$\int d\bar{L}_1 = -\frac{N_2}{N_1} \int d\bar{L}_2 \qquad (11)$$

Thus if $\bar{L}_2$ is known, $\bar{L}_1$ may be calculated by plotting

the mol ratio $\frac{N_2}{N_1}$ against $\overline{L}_2$ and obtaining the area between $\overline{L}_2$ and $\overline{L}_2 = 0$

B. Heat Capacities

When two substances, A and B are mixed together the heat capacities of the mixture will be the sum of the separate substances if the temperature function of the energy state of A and B is the same for the mixture as for each substance separately. Their heat capacities will also be additive if the change in heat capacity of one in going from the pure state into the mixture is exactly negative of the other. If, however, the molecules of one substance exert some influence on the molecules of the other substance, their heat capacities will not be additive.

Thomson (2) says that if an aqueous solution is diluted with water the molecular heat of the solution formed is less than the sum of that of the original solution together with that of the water. This, however, is true only if the solute is a strong electrolyte. This behavior is explained by Randall and Rossini (4) as follows: A system consisting of 1000 g of water has a heat capacity of G calories. If a single molecule of sodium chloride is added to this system so that a new system is formed containing 1000 g of water, one sodium ion and one chloride ion. The heat capacity of this system will be (G-a) calories. Then (-a) is apparently the heat capacity of one sodium ion plus one chloride ion. Since the solution is infinitely dilute, the apparent molal heat capacity and the partial molal

heat capacity for one gram mol of sodium ion plus one gram mol of chloride ion equals -a x 6.06 x 10^{23} calories. The presence of the two ions has so affected the water molecules that their heat capacity has been decreased by an amount equal to (a) calories plus the intrinsic heat capacity of one sodium ion and one chloride ion.

Lewis and Randall (7) give a much more general explanation. Water is made up of a large number of molecular species formed by the aggregation of simple molecules, such as $(H_2O)_3$, $(H_2O)_2$, etc. The larger aggregates are most prevalent near the freezing point. As the temperature is raised these large molecules break up into simpler molecules with the absorption of heat.

It appears that an electrolyte dissolved in water in some way causes these agggegates to break up to a degree which increases with concentration. Thus the large heat capacity of water may be ascribed to the absorption of heat necessary for the dissociation of these aggregates. Since an electrolyte will diminish the number of these aggregates to be broken up, it will in this way lower the heat capacity of the solution.

The methods used by Randall and Rossini (4) of calculating the apparent and partial molal heat capacities will be used in this work. The following symbols will be used: ϕ is the apparent molal heat capacity, m the molality or the number of mols of solute per 1000 g of water, Cp is the heat capacity of that amount of solution of molality m, which contains 1000 g of water plus m mols of solute. $\overline{Cp2}$ is the partial molal

heat capacity of the solute, or $\frac{dCp}{dm}$, and is the change in the heat capacity of a very large amount of solution on the addition of one mol of solute. $\breve{C}p_1^0$ is the heat capacity of one mol of pure water at 25^0 C.

The heat capacity of 1000 g of water may be designated as $55.508\ \breve{C}p_1^0$, and the heat capacity of 1000 g of water plus m mols of salt as Cp. Then ΔCp, the apparent heat capacity of the added salt, is given by the equation,

$$\Delta Cp = Cp - 55.508\ \breve{C}p_1^0 \qquad (12)$$

The apparent heat capacity of the added salt per mol of the added salt is

$$\phi = \frac{\Delta Cp}{m} \qquad (13)$$

Substituting (13) in (12),

$$\phi = \frac{(Cp - 55.508\ \breve{C}p_1^0)}{m} \qquad (14)$$

Differentiating ϕ with respect to $m^{\frac{1}{2}}$,

$$\frac{d\phi}{dm^{\frac{1}{2}}} = \frac{m(\frac{dCp}{dm^{\frac{1}{2}}}) - (Cp - 55.508\ \breve{C}p_1^0)\ 2m^{\frac{1}{2}}}{m^2} \qquad (15)$$

Now $Cp - 55.508\ \breve{C}p_1^0 = m\ \phi$ and $m(\frac{dCp}{dm^{\frac{1}{2}}}) = 2m^{\frac{3}{2}}(\frac{dCp}{dm}) = 2m^{\frac{3}{2}}\overline{C}p_2$

Substituting these values in (15) and multiplying by $m^{\frac{1}{2}}$,

$$\overline{C}p_2 = \phi + \tfrac{1}{2}m^{\frac{1}{2}}(\frac{d\phi}{dm^{\frac{1}{2}}}) \qquad (16)$$

which means that the partial molal heat capacity of the solute is equal to the apparent molal heat capacity plus $\frac{1}{2}$ the product of $m^{\frac{1}{2}}$ times the slope of ϕ plotted against $m^{\frac{1}{2}}$ as in Fig. 8.

When ϕ and $\overline{C}p_2$ are known $\overline{C}p_1$ can be calculated as follows: By definition,

$$Cp = m\overline{C}_{p_2} + 55.508\ \overline{C}_{p_1}\quad (17)$$

and
$$\overline{C}_{p_1} = \frac{(Cp - m\overline{C}_{p_2})}{55.508}\quad (18)$$

Rearranging (14)

$$Cp = m\phi + 55.508\ \overline{C}_{p_1}^{\ o}$$

Substituting (14) in (18),

$$\overline{C}_{p_1}^{\ x} = \frac{(m\phi + 55.508\ \overline{C}_{p_1}^{\ o} - m\overline{C}_{p_2})}{55.508} = \frac{m}{55.508}(\phi - \overline{C}_{p_2}) + \overline{C}_{p_1}^{\ o}\quad (19)$$

APPARATUS AND MATERIALS

The calorimeter used in this work is shown assembled in Fig. 1. A is a Dewar flask with a capacity of about 750 ml. B is a stirrer. C is a glass tube holding the thermocouple wires and junctions, and D is a glass tube about 2.5 cm in diameter to which is fastened a smaller tube of about 3 mm diameter which extends through the cover of the flask. These parts are held in place by means of a cork cover which fits into the flask. The tube D was used as a container for the borax and as a support for the heating coil. The glass rod extending into the tube was used to break the seal on the end of D and force the borax into the water. In making the determinations the calorimeter was immersed to within a half inch of the top in a water thermostat at 25° C.

The water equivalent of the calorimeter and the heat capacities of the solutions were determined by passing a definite quantity of electricity through a coil of wire of known resistance. Fig. 2 is a diagram of the wiring used in measuring accurately a small electric current. A is a potentiometer for measuring the voltage, B a 0.1 ohm standard resistance, C a spill coil, D three lead storage batteries connected in series and E the heating coil.

The potentiometer used to measure the heating current was a Rubicon portable type with a precision of one microvolt. It was used with an external galvano-
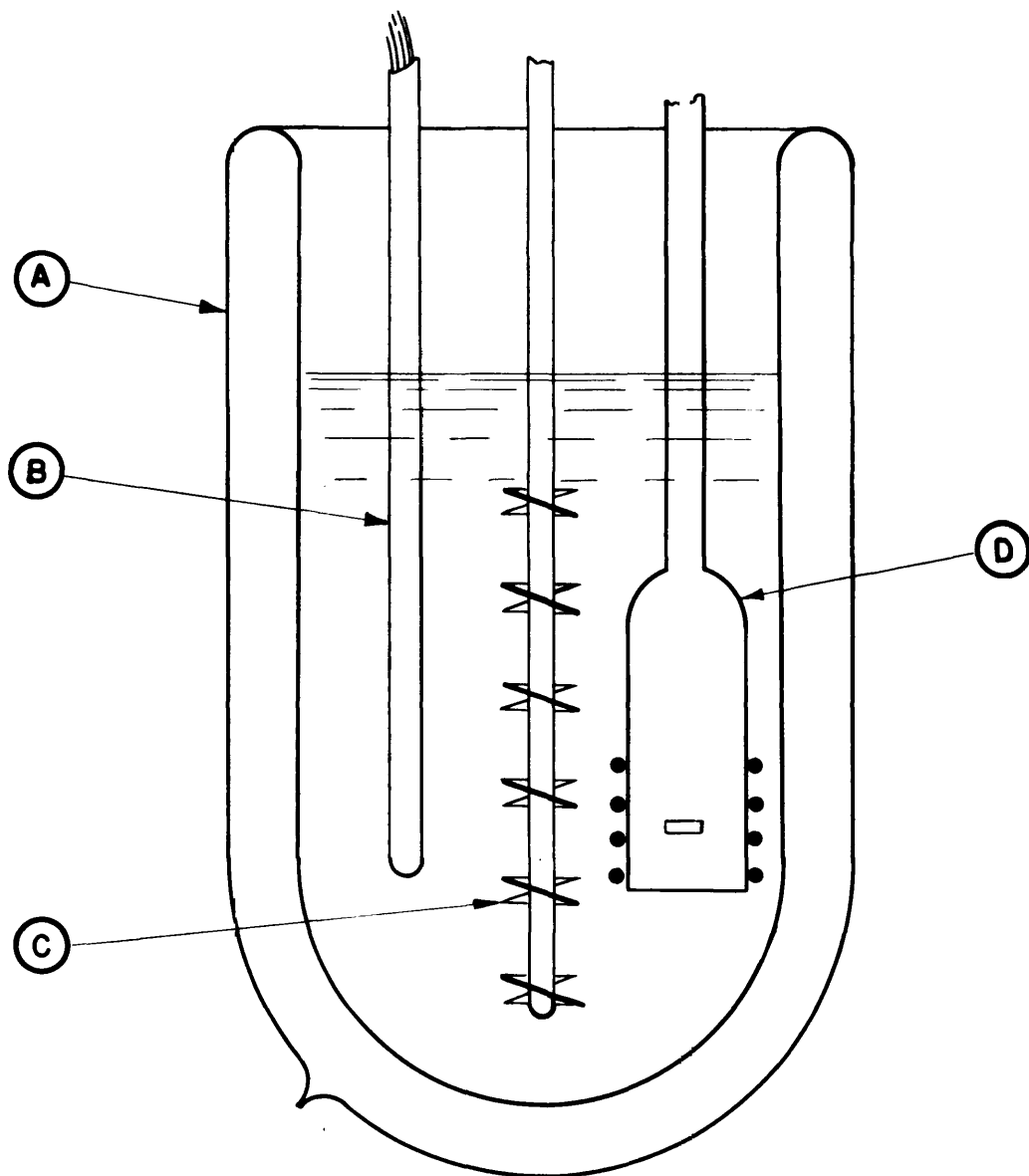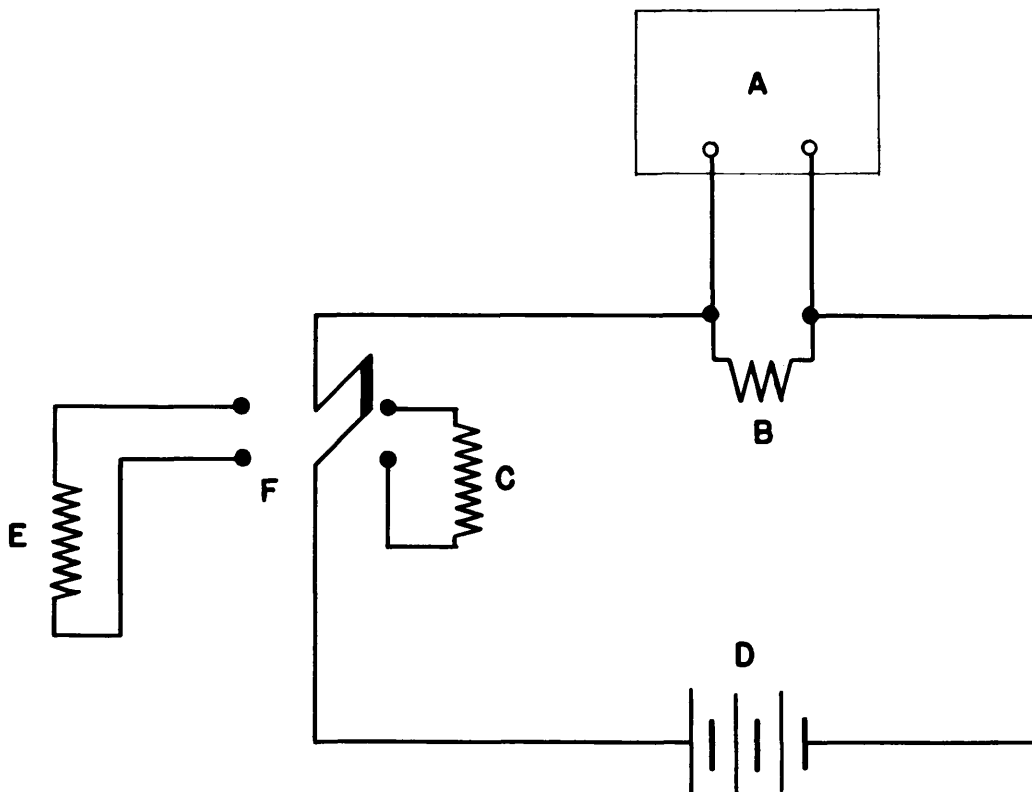
CALORIMETER

(A) — DEWAR FLASK

(B) — THERMOCOUPLES

(C) — STIRRER

(D) — BORAX CONTAINER AND HEATING
WIRE HOLDER.

FIG. 1

WIRING   DIAGRAM   FOR   HEAT   CAPACITY
DETERMINATION

A — POTENTIOMETER

B — 0.1 OHM   STANDARD   RESISTANCE

C — SPILL   COIL

D — STORAGE   BATTERY

E — HEATING   COIL

F — SWITCH

FIG. 2

meter made especially for this potentiometer. This instrument was also used in measuring the temperature changes in the heat of solution determinations.

The purpose of the spill coil is to bring the batteries to a constant voltage before each specific heat determination. It was made to have about the same resistance as the heating coil by winding # 20 constantin wire around a glass tube. The coil was covered with bakelite enamel and hardened in an oven at 110° C. The bakelite coating afforded good insulation.

The lead storage batteries had to be kept almost fully charged in order to obtain a constant E. M. F.

The heating coil was made from #30 constantin wire. The wire was wrapped non-inductively around the lower end of the tube D (Fig. 1) and coated with bakelite enamel. After drying and baking at 110°C. the bakelite made a tough coating which was not attacked by the salt solutions. Copper wire #18 was used for lead wires. The resistance of the heating coil as measured at the National Bureau of Standards was 58.616 ohms.

Before each run the current was first passed through the spill coil for fifteen minutes to allow the batteries to come to a constant voltage. To start a run it was only necessary to throw the double-pole-double-throw switch. A Meylan stop watch calibrated to 0.1 second was used to measure the time. The voltage across the 0.1 ohm standard resistance was measured and from this value the amperage was calculated by means of Ohm's law.

Thermocouples were chosen to measure the temperature changes. Those used were a set of ten junction couples made from #30 copper and constantin wire. The junctions were soldered with silver and insulated with bakelite enamel. The ends of the thermocouples were placed in small glass tubes and imbedded in paraffin. The thermocouples were calibrated by comparing them with a 100° C. thermometer which had been calibrated at the National Bureau of Standards. One junction of the thermocouple was placed in ice at 0° C, and the other was placed with the thermometer in a Dewar flask containing water. The temperature of the water was varied at intervals from 0° to 30° C. and readings taken from the thermometer and thermocouples at each interval. The results are shown in Table I. The E. M. F. change per degree at 25° C. is 373 microvolts.

The borax used in this work was Mallinkrodt's best quality sodium tetraborate decahydrate. The results of an ignition test showed that it contained 9.97 mols of water per mol of borax.

TABLE I

Calibration of the Thermocouples

Temperature	E. M. F. volts	E. M. F. / Temperature
4.65	0.001667	0.0003585
10.04	0.003658	0.0003643
13.23	0.004856	0.0003670
17.33	0.006378	0.0003680
20.58	0.007617	0.0003701
23.29	0.008682	0.0003728
26.72	0.009978	0.0003734
28.68	0.010774	0.0003756

EXPERIMENTAL PROCEDURE

A. Heat Capacity of the Calorimeter

Approximately 650 grams of water adjusted to
about 24.5° C. were added to the Dewar flask. The
flask was put in the thermostat. The end of the glass
tube D was closed with wax paper and sealed with paraf-
fin. This was then put in place on the calorimeter cover
with the thermocouple tube and the stirrer, and the whole
put in place in the calorimeter. The cold junction
of the thermocouple was packed in ice. The stirrer was
started and allowed to run for ten minutes to bring
the system to thermal equilibrium. Readings were then
taken to determine the thermal drift of the calorimeter.
In the meantime the electric current had been passing
through the spill coil and the batteries were giving
a constant E. M. F. The double-pole-double-throw
switch was thrown, the stop watch started, and the
heating continued for ten minutes. A temperature
reading was taken every minute until there was a con-
stant temperature change. The E. M. F. of the heating
current was recorded at the end of the fourth minute of
the ten minute heating period. The water equivalent
of the calorimeter was calculated, using 0.9976 calories
as the specific heat of water at 25° C., and 4.185
joules per calorie as the mechanical equivalent of heat.

TABLE II

Water Equivalent of the Calorimeter

No.	Calories
1	51.1
2	48.6
3	51.3
4	49.6
Average	50.1

At a later stage of the work a new stirrer
and a new tube to hold the borax were used. The water
equivalent of the calorimeter was then found to be
53.2 calories.

B. Heat of Solution Determinations

In the heat of solution experiments, the borax
was ground in a mortar to pass through a 100 mesh
sieve. A charge was then weighed out and placed in
the tube D. The end of the tube was closed with wax
paper sealed on with paraffin. The same preliminary
procedure was used as described above in the heat
capacity determinations. After a constant temperature
change was reached, the glass rod was forced through
the seal and the borax introduced into the solution.
Temperature readings were again taken each minute
until equilibrium was reached. A determination of the
heat capacity of the solution was then made as described
above and this value used in calculating the heat of
solution.

CALCULATIONS

In calorimetric experiments such as those described above it is never possible to obtain an absolutely constant final temperature in the calorimeter, unless this temperature happens to occur so that the heat formed on the inside of the calorimeter, such as the heat of stirring, exactly balances the loss of heat to the surroundings. There will nearly always be a gradual change in temperature of the calorimeter both before and after a run. However an excellent approximation can be made of the actual change in the temperature in the following way: The temperature in the calori-
meter /observed at definite intervals before and after a
      is
run and the temperature readings are plotted against the time. Graphs showing the temperature changes in the calorimeter during the course of a heat of solution and aheat capacity determination are given in Fig. 4, A and B. A sample data sheet, together with a computation sheet showing detailed calculations are given in Tables III and IV.

All of the experiments were divided into three consecutive periods which are classified in order of occurrence as an S-period, an X-period, and a K-period. The S- and K-periods were rating preiods which were for purpose of determining the conduction coefficient, K, and the stirring and evaporation coefficient, W, of the calorimeter. These coefficients varied from day to day,

TEMPERATURE CHANGES
IN CALORIMETER

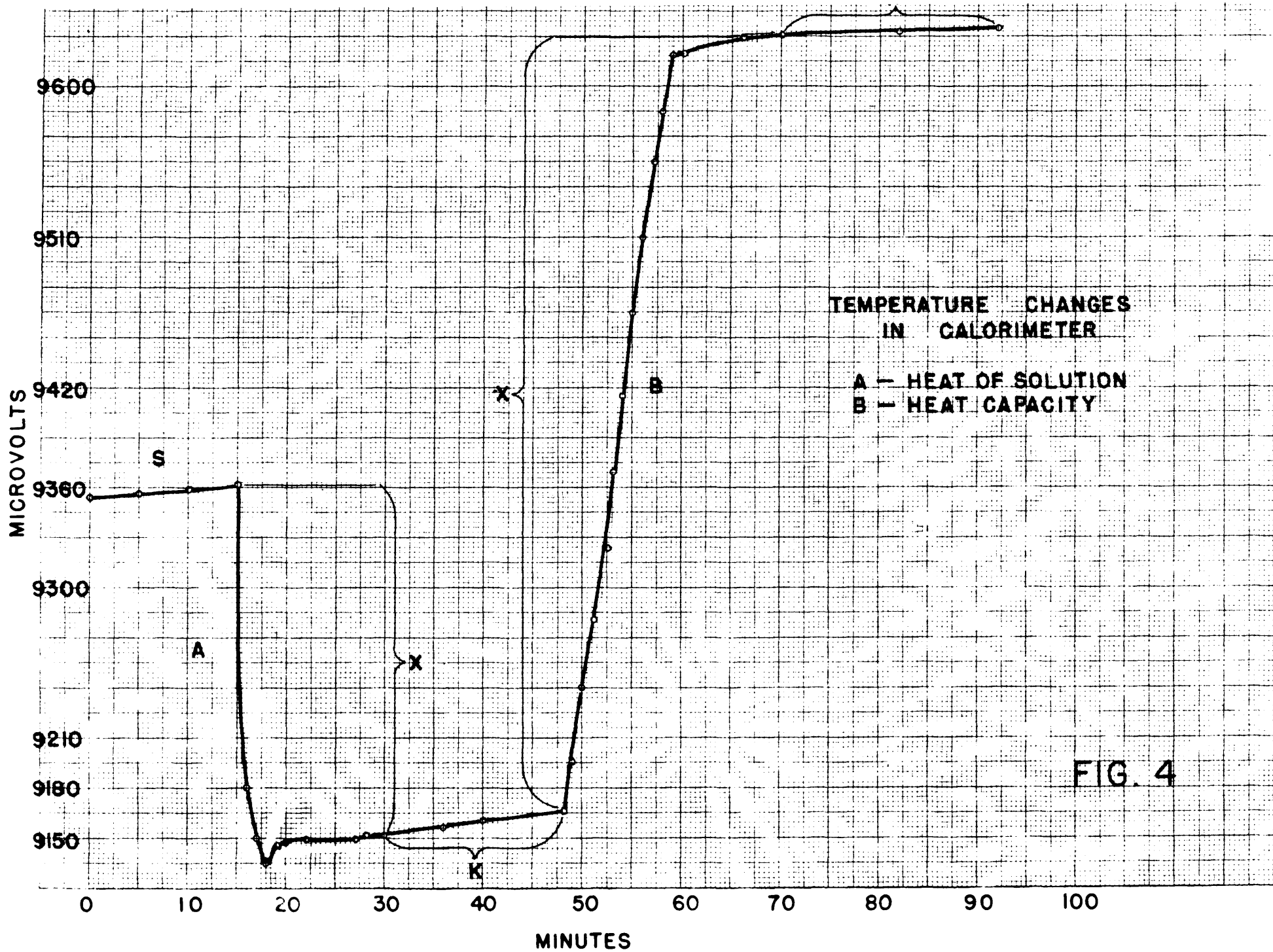A — HEAT OF SOLUTION
B — HEAT CAPACITY

FIG. 4

but were nearly constant for any one test. The X-period
was the experimental period during which the sodium
tetraborate was dissolved in the water or the heating
current passed in.

The S-period was begun after the stirrer had been
running for about fifteen minutes and lasted about fif-
teen minutes. The time-temperature curve for the S-
period is approximately a straight line (see Fig. 4).
The temperature of the water rises because of the heat
of stirring. At the end of the S-period the borax was
introduced and the temperature dropped immediately.
Readings were taken every minute so as to obtain a smooth
curve. When all the borax was dissolved the temperature
began to rise.

The K-period was begun at the point at which con-
stant temperature differentials were obtained. The
temperature was recorded at intervals of two to five
minutes.

Having determined the time-temperature data for the
S-, X-, and K-periods, information was available for
computing the coefficient of conduction, K, the stirring
and evaporation coefficient, W, and the corrected tem-
perature rise or fall during the experimental period.

The observed rate of change of temperature during
the S-period in microvolts per minute, or V_s, is equal
to the observed temperature rise during the S-period
in microvolts divided by the length of the S-period in
minutes, or

$$V_s = \frac{\Delta T_s}{\Delta t_s}$$

Similarly the observed rate of change of temperature during the K-period is:

$$V_k = \frac{\Delta T_k}{\Delta t_k}$$

The mean thermal head during the S-period in degrees or ϕ_s, is equal to the difference between the bath temperature and the mean temperature of the water solution during the S-period, or;

$$\phi_s = (MT)_s - (BT)$$

$$= \frac{T_{s1} + T_{s2}}{2} - (BT)$$

Similarly the mean thermal head during the K-period is:

$$\phi_k = \frac{T_{k1} + T_{k2}}{2} - (BT)$$

The conduction coefficient, K, and the stirring and evaporation coefficient, W, which are assumed to be constant for any one test, are computed from the simultaneous equations:

$$V_s = \phi_s K + W$$

$$V_k = \phi_k K + W$$

After K and W were determined, the net temperature loss, L, during the experimental period due to the effects of conduction, stirring, and evaporation was computed from the formula:

$$L = K\phi_x \Delta T_x + W \Delta t_x$$

ϕ_x is determined by the trapezoidal rule. By this method ϕ_x is determined by taking the sum of one-half

the first ordinate plus one half the last ordinate,
plus the sum of all intervening ordinates, minus the
product of the bath temperature times the time, t_x.
The corrected temperature drop during the experimental
period for a heat of solution determination is equal
to the observed temperature drop plus the net tempera-
ture gain; that is,

$$\Delta T_{x_c} = \Delta T_x + L$$

or for a heat capacity determination it was equal to
the observed temperature rise minus the net temperature
gain, or,

$$\Delta T_{x_c} = \Delta T_x - L$$

TABLE III

Sample Data Sheet

Water
$$\begin{array}{r} 1931.65 \\ \underline{1281.20} \\ 650.45 \end{array}$$

Borax - 6gms.

Heating Current
   Amperage--0.3137
   Time ------10 min. 28.1 sec.

Bath temperature
 in microvolts
   9325

Readings for Heat
  of solution

Resistance of heating
 coil -- 58.616 ohms

Time Minutes	Reading micro volts
0	9355
S 5	9357
10	9359
Borax 15	9362
added 16	9180
17	9160
18	9135
19	9145
20	9147
21	9149
22	9150
X 23	9150
24	9150
25	9150
26	9150
27	9150
28	9152
29	9152
30	9152
36	9157
K 40	9160
43	9162
48	9166

$\phi_s = 33.5$

$V_s = 0.46$

$\phi_k = -166$

$V_k = 0.70$

$\Delta t = 13$

$K = -.0012$

$W = 0.50$

$\Delta T_{uncorr} = 210$ microvolts

$K \phi_x \Delta t_x = 2.5$

$W \Delta T_x = 6.5$

$\Delta T_{corr.} = 219$ microvolts $= \dfrac{219}{373}$

$= 0.538°$ C.

TABLE IV

Computation Sheet

$$\phi_s = \frac{9355 + 9362}{2} - 9325 = 33.5.$$

$$V_s = \frac{9362 - 9355}{15} = 0.46$$

$$\phi_k = \frac{9152 + 9166}{2} - 9325 = -166$$

$$V_k = \frac{9166 - 9152}{20} = 0.70$$

$$V_s = \phi_s K + W = 0.46 = 33.5 \, K + W$$
$$V_k = \phi_k K + W = 0.70 = -166. \, K + W$$

subtracting $-.24 = 199.5 \, K$

$$K = -.0012$$

$W = 0.46 - (33.5 \times -.0012)$
$W = 0.50$

Total correction $L = K\phi_x \Delta t_x + W\Delta t_x$

ϕ_x (by trapezoidal rule) = $\frac{1}{2}$ first ordinate = 4681
$\frac{1}{2}$ last ordinate = 4576
sum intermediate ordinates = 109806
sum   119063

subtract $T_{bath} \times \Delta T_x$
9325 x 13   121225

$$\phi_x \Delta t_x = -2162$$

$K\phi_x \Delta t_x = -.0012 \times -2162 = 2.5$
$W\Delta t_x = 0.50 \times 13 = 6.5$
$L = 9.0$

ΔT_x uncorr = 9362 - 9152 = 210
$L = 9$
ΔT_x corr = 219 microvolts

$$\frac{219}{373} = 0.588°$$

DISCUSSION OF ERRORS

The equation used to calculate the number of calories of heat added to the calorimeter by means of the electric current is

$$H = \frac{I^2 R t}{J}$$

I = amperage

R = resistance of heating coil

t = time

J = constant for converting joules to calories

= 4.185

For a typical run,

I = 0.3137 ± .0002

R = 58.616 ±.003

$t_2 - t_1$ = 628.1

$dt_1 = dt_2 = 0.2$ $\triangle = \sqrt{(.2)^2 + (.2)^2}$ = 0.29

$H = \frac{(.3137)^2 \times 58.616 \times 628.1}{4.185}$ = 865.7

$\triangle H = H \sqrt{(\frac{adI}{I})^2 + (\frac{bdR}{R})^2 + (\frac{cdt}{t})^2}$

$= 865.7 \sqrt{(\frac{2 \times .0002}{.3137})^2 + (\frac{.003}{58.616})^2 + (\frac{.29}{628.1})^2}$

= 865.7 x .0015

= 865.7 ± 1.29 calories

The temperature rise in microvolts may be read to ±1.

$dT_2 = dT_1 = 1$

$\triangle T = \sqrt{(1)^2 + (1)^2}$ = 1.41

$T_2 - T_1$ = 456

Therefore,   T = 456 ± 1.41

Thus there is an error of about 0.30 per cent in reading

the temperature.

The error in determining the amount of heat added
to the calorimeter is negligible in comparison to that
in determining the temperature change. The accuracy in
determining heat capacities can therefore not be expected
to be better than 3 parts in 1000. A better impression
as to their accuracy can be obtained by referring to Fig. 7
where the results are shown compared with similar re-
sults obtained in a calorimeter built at the National
Bureau of Standards which had an accuracy of 1 part in
2000 or 0.05 per cent.

In the heat of solution experiments, the borax and
water were weighed to a milligram and the error here was
negligible. The only appreciable errors in these deter-
minations were those from the temperature readings. Ther-
mal leakage, evaporation, and heat of stirring are corrected
for as described above by determining the actual tempera-
ture drift of the calorimeter before and after a run.
The extent of errors in temperature readings obviously
depended upon the change in temperature, being high for
small changes and low for large changes in temperature.
Thus for 2 grams of borax which gave an E. M. F. change
of only 70 microvolts the error was $\frac{1.4}{70}$ or 2 per cent,
and for 20 grams of the salt which gave an E. M. F.
change of 938 microvolts the error was $\frac{1.4}{938}$ or 0.15 per
cent. The theoretical accuracy however was not reached
for the larger samples of borax due to the fact that a
longer time was required for solution to take place, and
the error in approximating the correct temperature change

became appreciable. The average error throughout
the entire range of heat of solution determinations
is about 0.80 percent.

RESULTS AND DISCUSSION

Heat of solution determinations were made on samples of borax ranging in size from one gram to thirty-five grams. The solubility of the salt prevented the use of more concentrated solutions. Figure 3 is a graph showing the solubility of borax. The results of the heat of solution experiments are given in Table V. The first column gives the number of grams of borax, the second, the molality of the solution, the third, the heat of solution in 1000 grams of water, the fourth, the dilution in mols of water per mol of borax, and the last column gives the heat of solution per mol.

Figure 5 shows the heat of solution per mol plotted against the dilution. The slope of the curve at high dilutions shows that the heat of solution is approaching a constant value at infinite dilution. However, it is difficult to interpolate a curve of this type because it becomes asymptotic; therefore, the results in calories per mol were plotted against the molality in Figure 6. This gives a straight line for the dilute solutions and can be accurately interpolated to infinite dilution, to give a value of 27,370 calories per mol. This value is represented by the symbol L_oS and is the number of calories absorbed when a mol of borax is dissolved in an infinite amount of water. This is the heat of solution of borax.

The results in Table V for the heat of solution

SOLUBILITY OF BORAX $\left(Na_2B_4O_7 \cdot 10H_2O\right)$

FIG. 3

TEMPERATURE °C

CHANGE OF HEAT OF SOLUTION OF
BORAX ($Na_2B_4O_7 \cdot 10H_2O$) WITH DILUTION

FIG. 5

HEAT OF SOLUTION — CALORIES PER MOL

DILUTION — MOLS WATER PER MOL OF BORAX

HEAT OF SOLUTION — CALORIES

MOLALITY

CHANGE OF HEAT OF SOLUTION OF
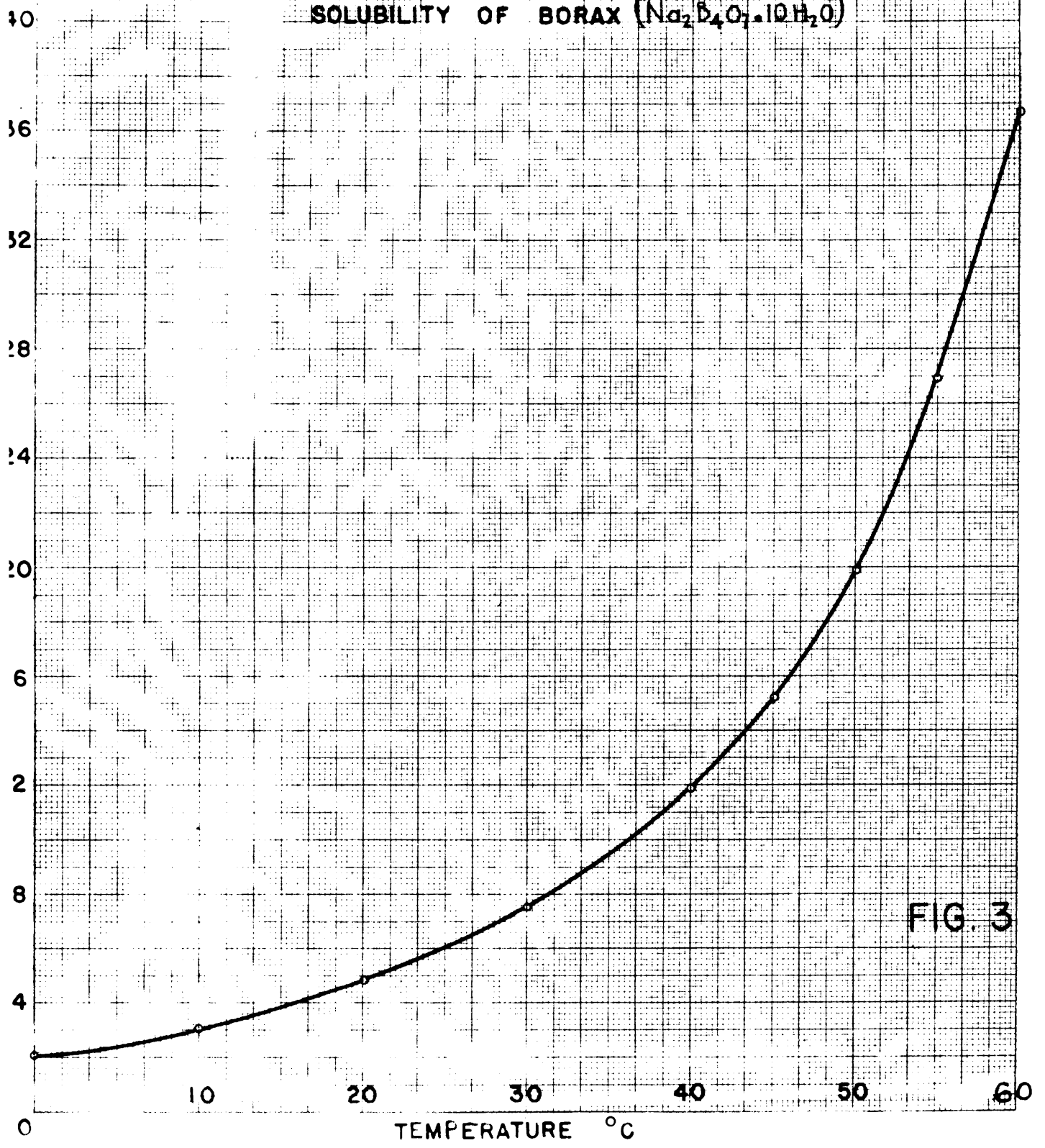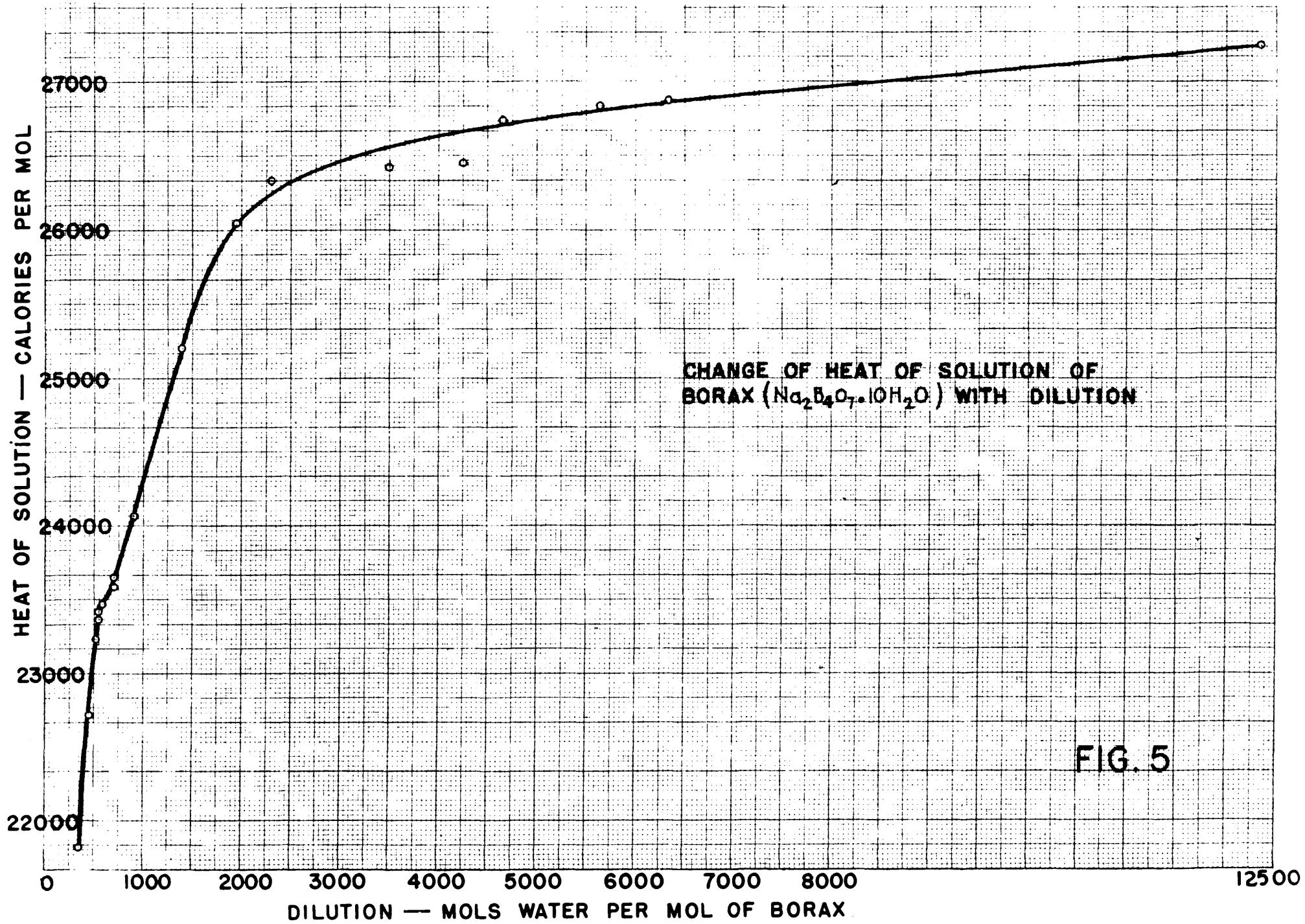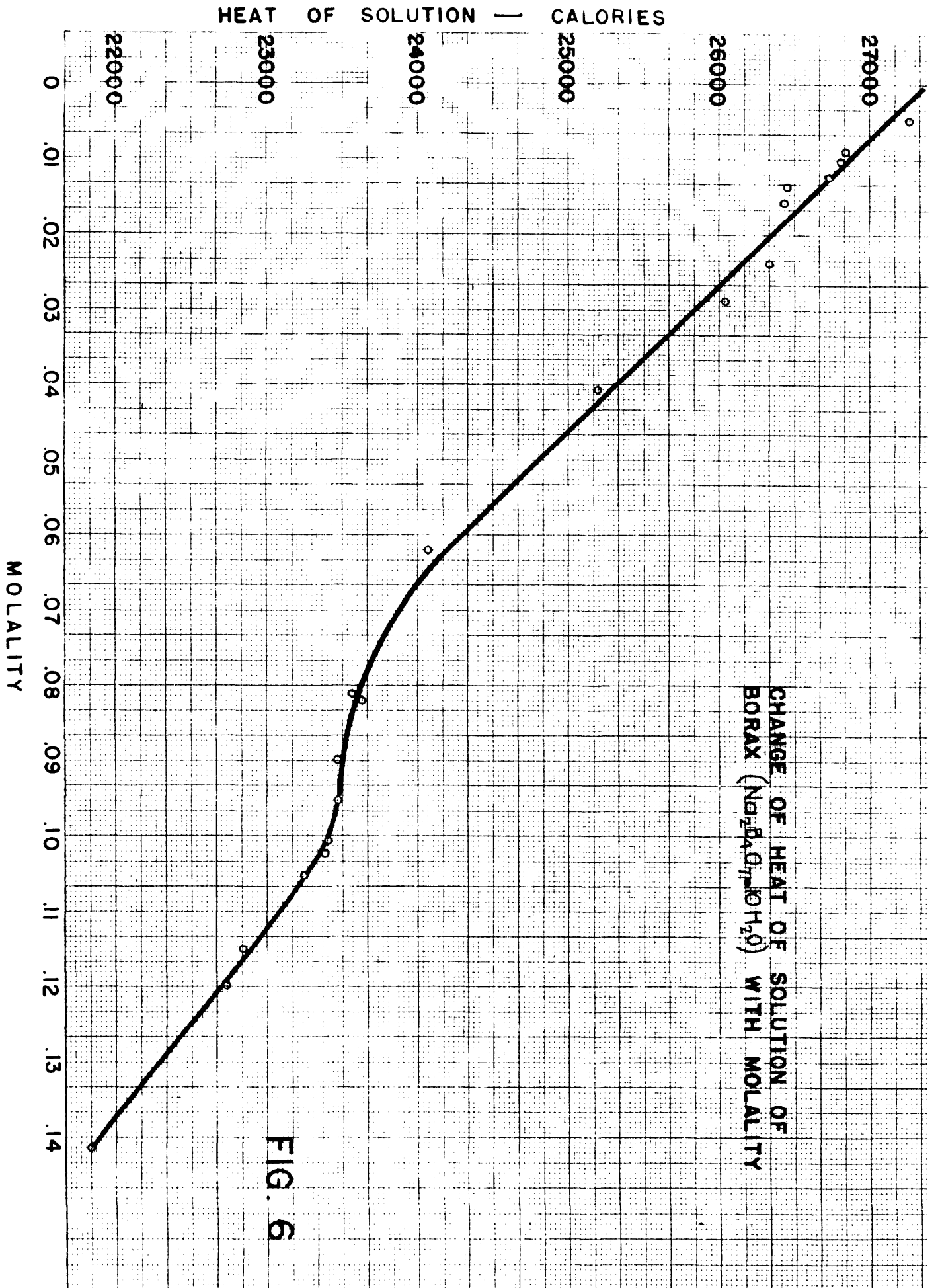BORAX ($Na_2B_4O_7 \cdot 10H_2O$) WITH MOLALITY

FIG. 6

TABLE V

Heats of Solution

Grams borax	Molality	ΔH 1000 gr water calories	Dilution mols water / 1 mol borax	ΔH per mol borax calories
1.04	0.0046	122	12340	27280
2.0	0.0090	235	6310	26630
2.5	0.0101	280	5670	26372
3.0	0.0122	320	4670	26780
3.0	0.0134	347	4240	26440
4.0	0.0155	421	3480	26420
6.0	0.0236	635	2200	26330
7.0	0.0286	731	1980	26040
10.0	0.0408	1010	1390	25210
15.0	0.0622	1471	907	24070
20.0	0.0810	1869	701	23590
20.0	0.0820	1897	692	23650
22.5	0.0899	2062	626	23490
24.0	0.0957	2211	586	23460
25.0	0.1006	2301	556	23400
25.0	0.1024	2382	546	23380
26.0	0.1066	2435	530	23220
28.0	0.1145	2602	487	22840
30.0	0.1201	2712	462	22720
30.0	0.1220	2757	457	22720
35.0	0.1413	3025	393	21820

per 1000 grams of water were plotted against the molality and values dH/dm, or the partial molal heat content of the sodium tetraborate in the solution were obtained by reading off the tangents of the curve at the various concentrations given in the first column of Table VI. By equation (3)

$$\frac{q}{dn_2} = L_2 - L_2 S$$

$$\frac{dH}{dm} = \frac{q}{dn_2}$$

By substituting in this equation the value obtained above for $L_2 S$ and the values for q/dn_2, L_2, the relative partial molal heat content of the sodium tetraborate is obtained. From equation (11)

$$\int dL_1 = \frac{-N_2}{N_1}\int dL_2$$

the relative partial molal heat content of the water may be calculated. This is done by plotting the mol ratio, N_2/N_1, against the values obtained for L_2 and calculating the area cut off by the curve between 0 and the given point. The values obtained for q/dn_2, L_2 and L_1 are given in Table VI.

Two sets of specific heat determinations are given in this report. One set was made at the National Bureau of Standards and the other in this laboratory using the calorimeter in which the heat of solution determinations were made. Since the values obtained at the Bureau of Standards were determined in a calorimeter with an accuracy of about 0.05 per cent, they are

TABLE VI

Partial Molal Quantities
from Heats of Solution

Molality	q/dm_2	$\bar{L}_2$	$\frac{N_2}{N_1} \times 10^{-4}$	$\bar{L}_1$
0	27370	0	0	0
0.0046	26680	-720	0.83	0.05
0.0134	26080	-1380	2.42	0.16
0.0236	24890	-2490	4.25	0.55
0.0285	23450	-385-	5.14	1.20
0.0408	21890	-5480	7.35	2.18
0.0682	21710	-5660	11.21	2.40
0.0820	22210	-5160	14.78	2.02
0.0899	21710	-5660	16.29	2.40
0.0957	21180	-6190	17.22	3.31
0.1006	20590	-6780	18.03	4.??
0.1024	20590	-6780	18.24	6.?9
0.1056	20590	-6780	19.00	4.??
0.1145	18700	-8670	20.65	8.00
0.1201	17530	-9840	21.68	10.47
0.1220	17530	-9840	22.00	10.47
0.1413	15800	-11570	26.35	14.35

used in making all of the calculations given in Table VII.
A comparison of the two sets of results is shown in
Figure 7. The first column in Table VII gives the
molality, the second, the value for the specific heat
obtained at the University of Maryland, the third, the
value obtained at the National Bureau of Standards, the
fourth, the apparent molal heat capacity of borax, the
fifth, the square root of the molality, the sixth, the
partial molal heat capacity of borax and seventh, the
partial molal heat capacity of the water. The apparent
molal heat capacity, the partial molal heat capacity
of the borax and the partial molal heat capacity of the
water were calculated from equations (14), (16) and (19)
respectively.

In Figure 8 the apparent molal heat capacity, ϕ,
and the partial molal heat capacity, $\overline{C}_{p_2}$, are plotted
against the square root of the molality. According to
the Debye-Huckel theory, which is applicable in dilute
solutions, $\overline{C}_{p_2}$, should be a linear function of the square
root of the molality. Four points in the most dilute
region are shown to fall in a straight line. Extrapo-
lation to infinite dilution gives a value of 44.1 for
$C_{p_2}^0$. This value agrees well with that given by Randall
and Rossini (4) for sodium sulfate which is a 2-1 salt
as is borax. The slope of the curve, $\overline{C}_{p_2}$ plotted
against $m^{\frac{1}{2}}$, for borax is 184. This is considerably
higher than the value given by Rossini for potassium

FIG. 7

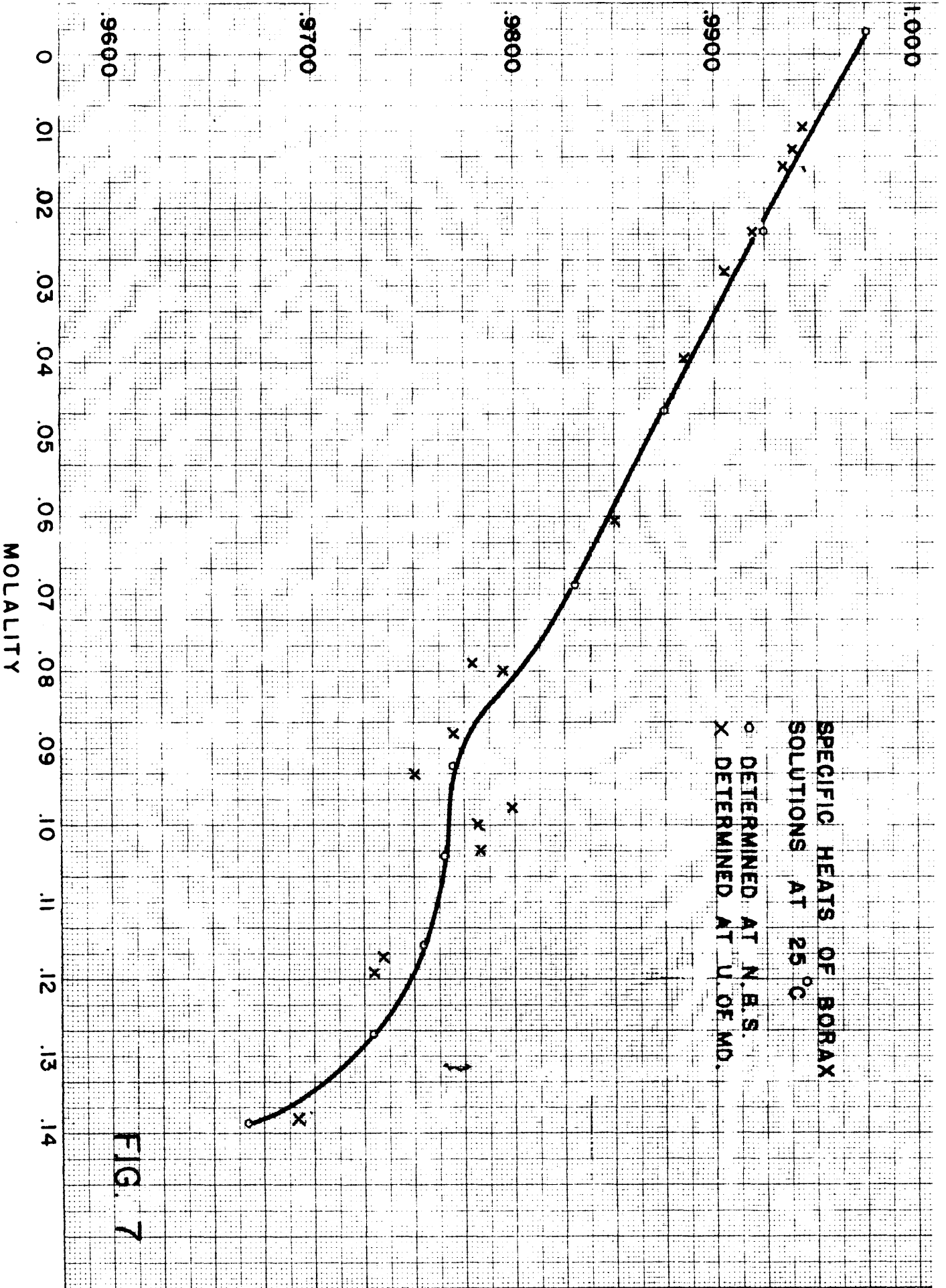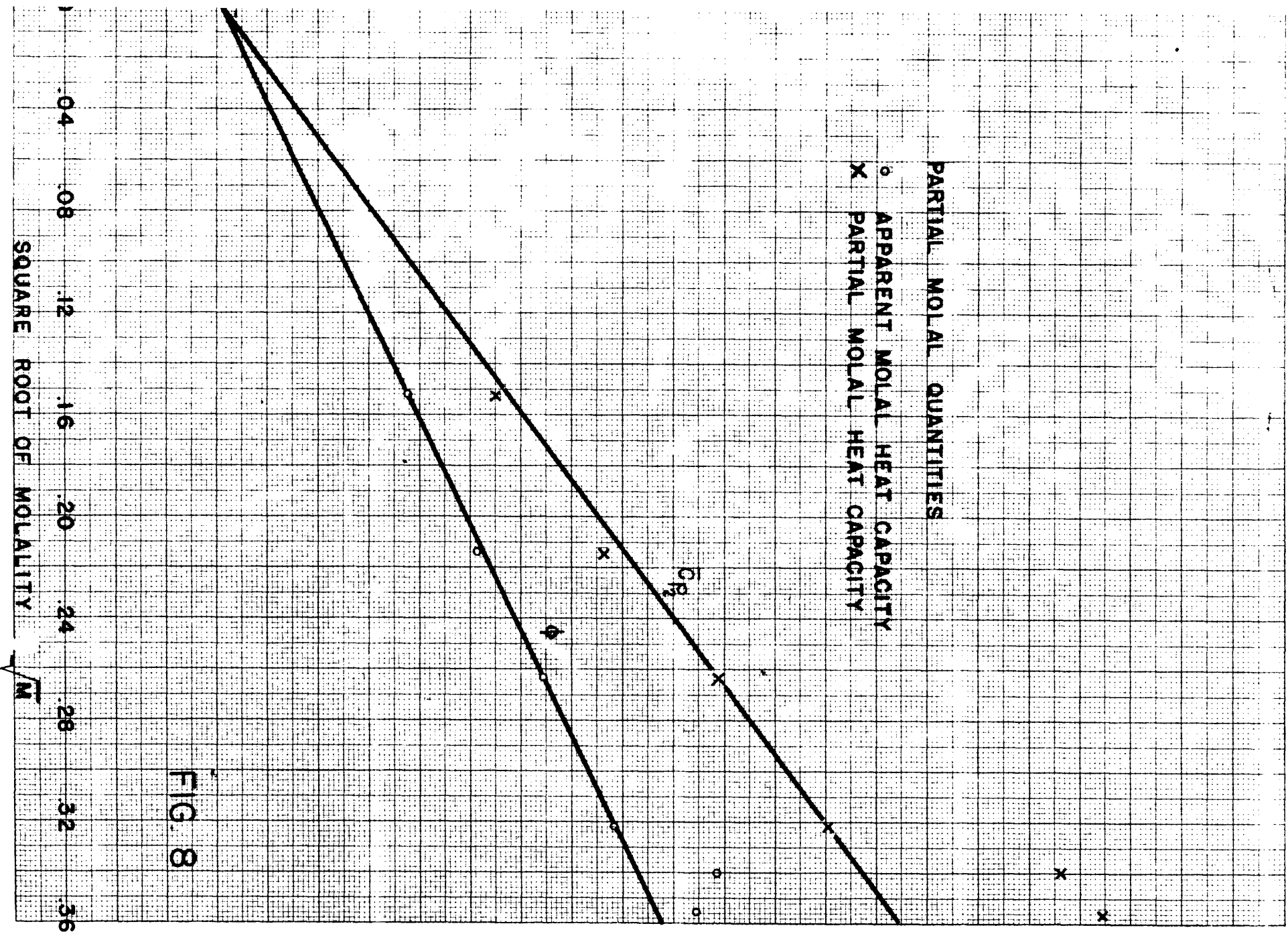SPECIFIC HEATS OF BORAX
SOLUTIONS AT 25 °C

o DETERMINED AT N.B.S.
X DETERMINED AT U. OF MD.

PARTIAL MOLAL QUANTITIES

o   APPARENT MOLAL HEAT CAPACITY
X   PARTIAL MOLAL HEAT CAPACITY

SQUARE ROOT OF MOLALITY

√M̄

FIG. 8

TABLE VII

Heat Capacity Determinations

Molality	Specific Heat U. of Md.	Specific Heat N. B. S.	Apparent Molal Heat Capacity	√m	Partial Molal Heat Capacity Borax	Partial Molal Heat Capacity Water
0	0.9976	----	-44.1	0	●44.1	17.9727
0.0098	0.9943	----	---	---	---	---
0.0119	0.9939	----	---	---	---	---
0.0151	0.9936	----	---	---	---	---
0.0231	0.9919	0.9924	-26.0	0.152	-17.3	17.9691
0.0279	0.9907	----	---	---	---	---
0.0398	0.9984	----	---	---	---	---
0.0462	----	0.9875	-19.4	0.214	-6.8	17.9622
0.0607	0.9851	----	---	---	---	---
0.0693	----	0.9830	-12.9	0.263	4.4	17.9511
0.0800	0.9798	----	---	---	---	---
0.0877	0.9771	----	---	---	---	---
0.0924	----	0.9770	-25.9	0.303	-6.6	17.9406
0.0934	0.9750	----	---	---	---	---
0.0982	0.9801	----	---	---	---	---
0.0999	0.9782	----	---	---	---	---
0.1030	0.9784	----	---	---	---	---
0.1039	----	0.9766	-5.3	0.322	15.4	17.9340
0.1155	----	0.9754	4.3	0.339	38.4	17.9018
0.1172	0.9735	----	---	---	---	---
0.1190	0.9729	----	---	---	---	---
0.1270	----	0.9730	2.4	0.356	42.6	17.8808
0.1380	0.9692	----	---	---	---	---
0.1386	----	0.9668	-27.2	0.372	15.0	17.8674

or sodium sulphate. The rate of increase in $\overline{C}_{p_2}$ for a
polyatomic ion such as $B_4O_7^=$ depends upon configura-
tion, charge and size. This is the reason for the rapid
increase in the value of $\overline{C}_{p_2}$ for borax.

No explanation can be offered for the break in the
heat capacity and heat of solution curves (Figures 6 and
7) at a molality of 0.08 to 0.10. The break is certain
since it is evident at the same molalities in both
curves, and was also observed by an independent worker
at the National Bureau of Standards. The slope of the
curve suggests a phase change. There is also a possibility
of changes in the amount of hydrolysis or ionization
in the aqueous solutions. Such changes, however, usually
take place gradually and an abrupt change in the slope
of the curve would not occur. The results for the
apparent and molal heat capacity in Figure 8 also de-
part abruptly from a straight line showing that some
uncommon change has occured in the solution. This is
not believed to be due to erratic results. The largest
source of error is in the most dilute regions of the
curve. From the equation

$$\phi = \frac{\Delta C_p}{m}$$

it is obvious that for small values of m a given per-
centage error in the calculation of C_p will create a
larger error in ϕ. It can be seen from Figure 8 that
the values of both ϕ and $\overline{C}_{p_2}$ in the dilute solutions
fall on a straight line.

SUMMARY

1. A calorimeter was built which has an accuracy of about 0.3 per cent for temperature changes of one degree.

2. The heat of solution of sodium tetraborate decahydrate was determined at various concentrations ranging from 0 to 0.14 molal.

3. The specific heats of the sodium tetraborate solutions were determined.

4. The differential or true heat of solution of sodium tetraborate was determined by plotting the heats of solution against the molality and interpolating to 0 dilution. It is 27,370 calories per mol.

5. From the values obtained for the heats of solution and specific heats at the various concentrations several important thermodynamic calculations were made.

6. An abrupt change in the slope of the heat of solution and specific heat curves occurred between the concentrations of 0.08 and 0.10 molal.