Studies on the Thermo-chemistry of Certain Carbohydrates in Alkaline Solution

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INTRODUCTION

This paper presents the results from a series of experiments on the thermal effects produced when carbohydrates are introduced into alkali solutions. These experiments consisted in measuring the heats of reaction produced. Such data has been sought by a number of investigators in carbohydrate chemistry. It was hoped that a study of these effects might yield information helpful in the interpretation of the mechanism involved in such reactions. The alkali used was sodium hydroxide and the temperature 25° C.

The apparatus chosen for the experimental part of the study was an adiabatic calorimeter previously described.[1] Certain modifications of this instrument are mentioned later. Careful attention to the factors considered by W. P. White[2] as essential for the requirements of an apparatus for precise work was given to the modified construction of this calorimetric instrument.

Incidental to the main study, a carefully checked determination of the heat capacity of the calorimeter vessel was made; specific heats of various concentrations of sodium hydroxide solutions of 25° C. were measured since such data was not available in the literature and the heats of solutions for a number of sugars not found elsewhere were determined.

Reasons for the sugars selected in this study are given later.

PART I

APPARATUS

The experimental apparatus used in this work consists, in general, of three principal parts: (1) the calorimeter flask, (2) the constant temperature bath or jacket, and (3) the constant temperature air closet.

Calorimeter Flask: The calorimeter flask is a cylindrical silvered [3] DeWar vacuum tube (marked O, Fig. 1) of 334 m.m. depth and 71 m.m. inside diameter and of slightly more than 1300 c.c. capacity. It is fitted with a rubber [4] stopper,[4a] Z, Figure 1, through which passes the connecting rod of the vertical reciprocating stirring apparatus P, the thermometer X, and a glass rod M to the sample cup B (or the heating unit for specific heat determinations). The flask was tested and shows no measurable temperature change during a period of one hour when a thermal head of 0.024° C. is existent between the bath and the calorimeter. This is adequate since a thermal head of 0.01° C. or less is not difficult of maintenance and all determinations were of a period of one hour or less.

The stirrer P and chimney N have been described previously.[1] The stirrer is driven by an induction motor described later. The most satisfactory speed of the stirrer in the DeWar flask was found to be twenty-two strokes per minute. Greater speed produced a measurable heat of stirring during a period of one hour for water solutions in the DeWar. Slower stirring did not give uniform temperatures throughout the calorimeter solution.

The calorimeter Beckmann thermometer X, previously described [1b] was calibrated by the U. S. Bureau of Standards (B.S. No. 35605). It was set with its 2° reading closely equivalent to 25° C. The author cannot agree with Barry[5] that 0.0005° can be easily read on such a thermometer. The interval between degrees on the thermometer here used is the same distance as that on the thermometer used by Barry. He makes no mention of the aid of a telescope which was used in the present work.

Sticking of the mercury sometimes occurs with these fine bore Beckmann thermometers. A tapping device for the calorimeter's thermometer was constructed to prevent this. It consisted of an ordinary doorbell, a small transformer, a doorbell push button, a thin flexible metal strip with a soft rubber tip on one end, and the necessary wire.

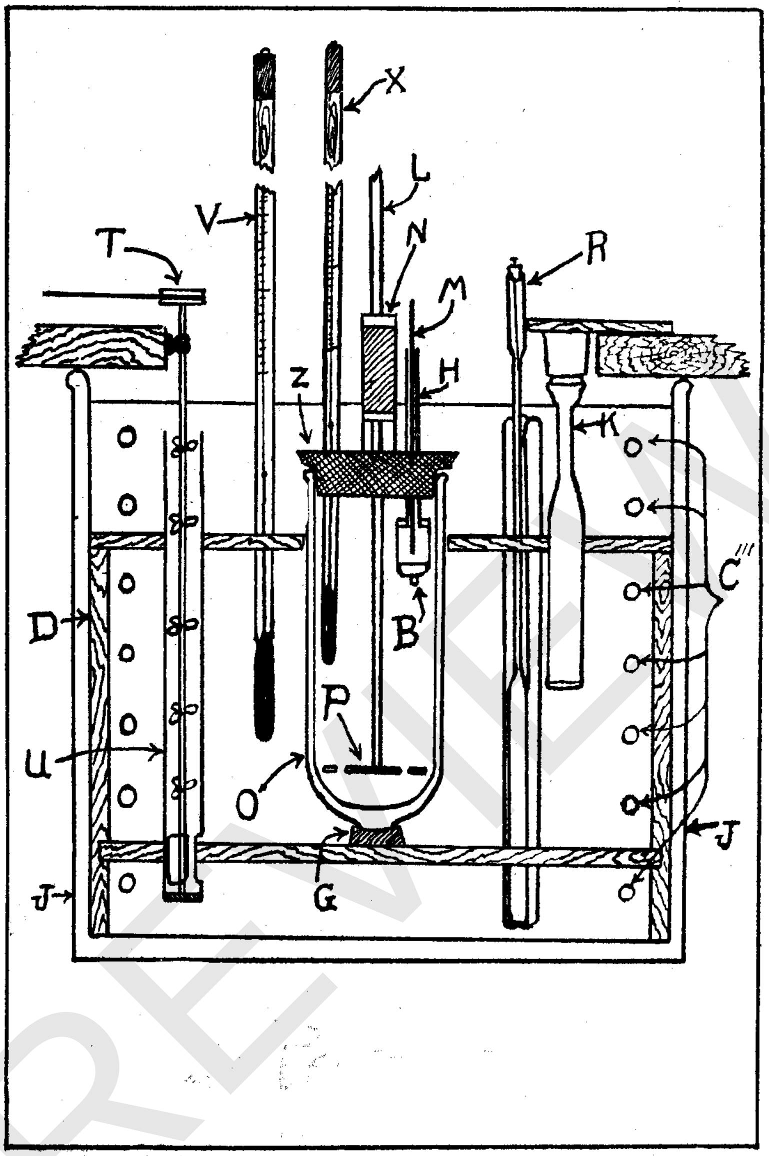


Figure 1

Stem corrections for the calorimeter's thermometer were negligible as calculated for the maximum rise in temperature even when the thermal head between the air closet and the calorimeter was a maximum of 0.1° C. The constant temperature closet tends to minimize such errors since the temperatures of the air closet, bath and calorimeter were always very nearly equivalent.

The dilution cup, used in heat measurements of sugars, is an improvement over that previously described. It was constructed from a 60 m.m. by 30 m.m. ground glass stoppered weighing bottle, and has a total heat capacity of approximately 4.32 calories. The heat capacity of the dilution cup is in remarkably good agreement with the heat capacity of the heating unit which is 4.33 calories, so that substitution of one for the other produces an error of less than .008% in the total heat capacity of the chamber.

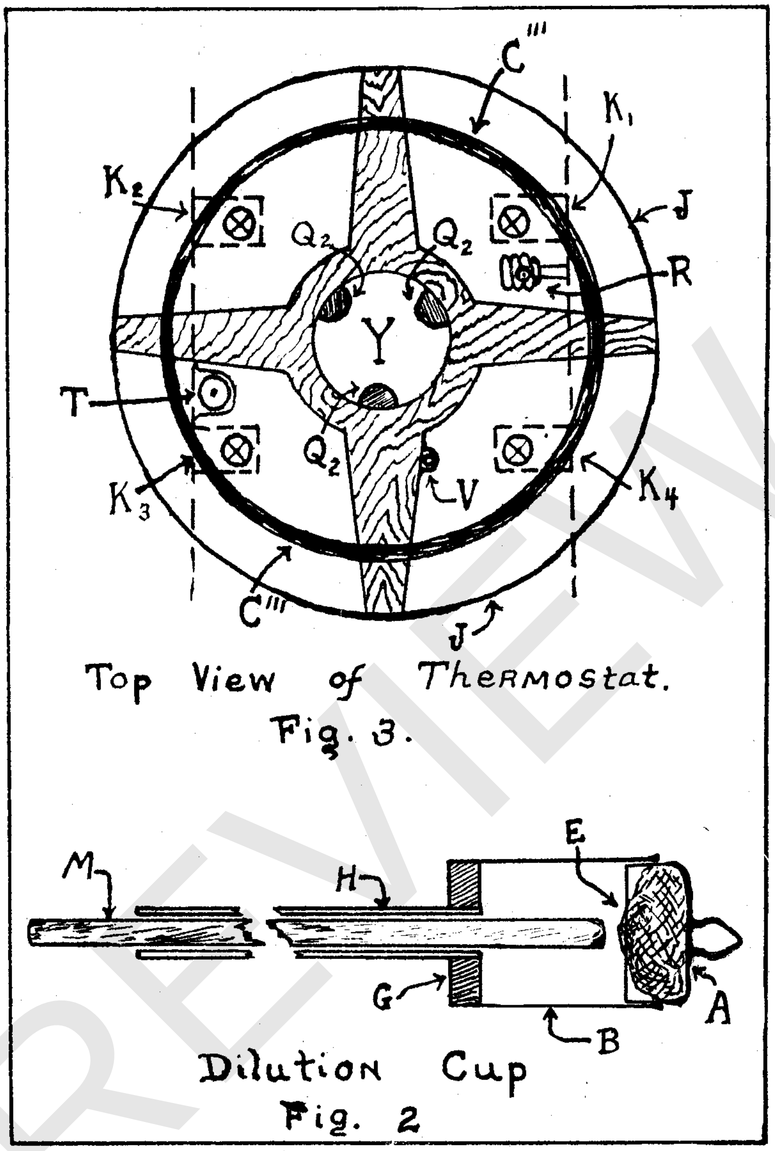
The dilution cup is shown in Figure 2. G is a rubber stopper with a glass tube H in the center. M is the dropping rod which releases the sugar sample contained in the hollow cap A of the weighing tube. Pieces of rubber tubing around the glass rod M and the tube H regulate the position of the dilution cup in the calorimeter solution. The stopper A swings back against the side of the calorimeter on a nickle wire support when pushed out, so that it does not interfere with the stirring.

Although most of the dilution cup rests in the alkali solution, capillary elevation of the alkali up into the sugar sample is highly improbable. Such action, and its introduction of error, was possible with the older type of cup previously reported.[1]

An electro-magnet arrangement is successfully used in dumping the sugar sample into the calorimeter's solution. This arrangement made it unnecessary to open the constant temperature cabinet to release the sugar sample.

The calorimeter heating unit, used in specific heat determinations, is a compact coil of 125 c.m. of No. 30 platinum wire enclosed in a pyrex glass tube and is provided with heavy number ten copper leads. Its resistance was measured under the same conditions as when in use and found to be 4.785± 0.001 ohms.

Thermostatic Bath or *Calorimeter Jacket:* The calorimeter is enclosed in a thermo-regulated water bath J, Figure 1. It is an improved one over that reported [1] and has been increased in volume from 80 liters to 120 liters capacity. The bath is kept at a constant temperature, if desired, by a mercury-toluene thermo-regulator in series with a polarized relay.



Figures 2 and 3