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# The Thermal Dissociation of Barium Hydride

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THE THERMAL DISSOCIATION OF

BARIUM HYDRIDE

THE THERMAL DISSOCIATION OF  
BARIUM HYDRIDE

A thesis, presented to the Department  
of Chemistry of Union College, in partial ful-  
fillment of the requirements for the degree of  
Bachelor of Science in Chemistry

By Edward R. Kane

Approved by Charles B. Sturd

May 21, 1940



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## INTRODUCTION

For the past fifteen years rather extensive investigations have been carried on in this laboratory concerning the thermal dissociation of the hydrides of the alkaline earth metals. During this period considerable time has been spent in devising suitable apparatus for the work and improved methods of procedure. Each successive worker on the problem in this laboratory has contributed materially to some phase of the investigations, or at least suggested from his experience improvements to be made in existing methods. It is, however, unfortunate that, because of the nature of the course in which these investigations have been undertaken, time for research has in each case been limited to one academic year. As a period of apprenticeship in working with a vacuum system is advisable if not necessary, and unforeseen difficulties have arisen in the past even after the system had been placed in good working order, this time limit has in several instances curtailed work which at the time gave promise of success.

The hydride problem had not been a subject of research for several years, and parts of the glass system and much of the auxiliary equipment had been broken or needed cleaning and reassembling. It has been the chief task of the writer to restore the system to its former state so that it will be available for the completion of the work on barium hydride and also for the commencement of the research contemplated on strontium hydride. The system is now completely set up and in readiness for actual measurements to be made. The work is being continued by the present writer in the hope of obtaining the desired dissociation data for barium hydride.



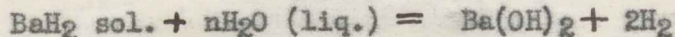
## HISTORICAL

Barium hydride has been prepared by numerous different methods, a few of which will be mentioned briefly. In most cases, however, the resulting product is of doubtful purity.

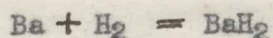
Winkler<sup>1</sup> succeeded in preparing the hydride of barium by heating red hot a baryte-magnesium mixture.

Guntz<sup>2</sup> placed some barium amalgam in a small iron boat and heated it in a current of hydrogen up to 1200° at which temperature the hydride and amalgam separated into layers. Upon raising the temperature up to nearly 1400° he obtained some molten, grayish barium hydride. The hydride volatilized slowly at 1400°, and its vapors attacked strongly the porcelain tube.

Guntz<sup>3</sup> also calculated the heat of formation of the hydride of barium calorimetrically from an experimental determination of the heat of reaction of



which he found to be +55.0 cal., and other calorimetric data on reactions of barium. The value he obtained in this manner for



was +37.5 cal.

Gautier<sup>4</sup> studied the absorption of hydrogen by a barium-cadmium alloy (about 55% barium) with rising temperature. He found that hydrogen began to be absorbed at 350°. As the temperature was slowly raised hydrogen was liberated from a certain point on. Then a new absorption resulted at about 570°, when the cadmium began to distill quite rapidly. Finally at 675° he observed that the hydride of barium began to dissociate.

The above mentioned investigators studied the hydride without previously having prepared the metal. However, Dafert and Micklaus<sup>5</sup> used metallic



barium, prepared by the classical method of Guntz<sup>6</sup>, which had been redistilled several times. They observed that if the barium were finely divided the reaction with hydrogen began to take place at 120° and was vigorous at any rate at 170-180°.

Ephraim and Michel<sup>7</sup> have given 732-800° as the range of temperature at which dissociation commences, depending upon the sample of metal used.

More recently, Remy-Gennete<sup>8</sup> has investigated the problem of absorption of hydrogen by barium at ordinary temperatures. In one experiment he found that at room temperature the pressure of hydrogen over a sample of barium dropped from 639 mm. to about 1 mm. over a period of some 76 days. He also has discovered what he thinks may be the dissociation pressure of the hydride at room temperature. The value he obtained is 1.5 mm. at 19° C. However, the barium he used had been in contact with air and this fact should be considered in evaluating his results.

Conlon<sup>9</sup> has concluded that barium will unite with hydrogen to form the hydride at about 400° and that the hydride dissociates extensively above a temperature of 500°. Huttig<sup>10</sup>, however, has collected a mass of information on the metallic hydrides in general and has given a portion of the dissociation curve for barium hydride which indicates that the dissociation begins in the neighborhood of 450°.

Thus the investigations concerning the hydride of barium have not yet attained anywhere near the degree of development and agreement that has now apparently been secured for calcium hydride in the work of Remy-Gennete<sup>11</sup>, Hurd and Walker<sup>12</sup>, and Johnson, Stubbs, Sidwell, Pechukas<sup>13</sup>.



## APPARATUS AND PLAN OF PROCEDURE

The glass system used to measure the thermal dissociation of barium hydride is a reconstructed and repaired version of the one first set up by Conlon<sup>9</sup>. Drawings of the vacuum system, hydrogen storage and purification system, and hydrogen supply system are presented in Figs. 1, 2, and 3. Full descriptions of this apparatus are given by Conlon<sup>9</sup>. The only variation from this is that in the present investigation it is planned to use ordinary tank hydrogen and not a KOH cell source. It is believed that the tank hydrogen will be sufficiently pure after diffusion through the heated platinum filter in the purification system (Fig. 2).

The part of the system in which the dissociation of the hydride actually takes place is shown in Fig. 4. The furnace T is a nichrome wire resistance type, thermally insulated with gray alundum cement and asbestos. The thermocouple U of the chromel-alumel type will be obtained from the General Electric Company and calibrated at the freezing points of lead, aluminum, and zinc. The cold junction will be at 0° in an ice and distilled water mixture in a Dewar flask, while the other end will be as indicated on the quartz tube. The e.m.f. measurements will be made with a type K Leeds and Northrup potentiometer. The tube V is of clear quartz, 14 mm. in diameter and 56 cm. long. The de Khotinsky joint W is built up over the glass to prevent the softening of the seal and the sucking in of air, since the thermal radiation from the hot end of the tube is transmitted readily by the quartz at high temperatures as pointed out by Hurd and Walker<sup>12</sup>. The barium will be placed in the nickel cylinder X and the dissociation measurements made in much the same way as described by Hurd and Walker<sup>12</sup>.

The electrical circuit which controls the current through the furnace is shown in Fig. 5 and has been described in detail by Moore<sup>14</sup>. In

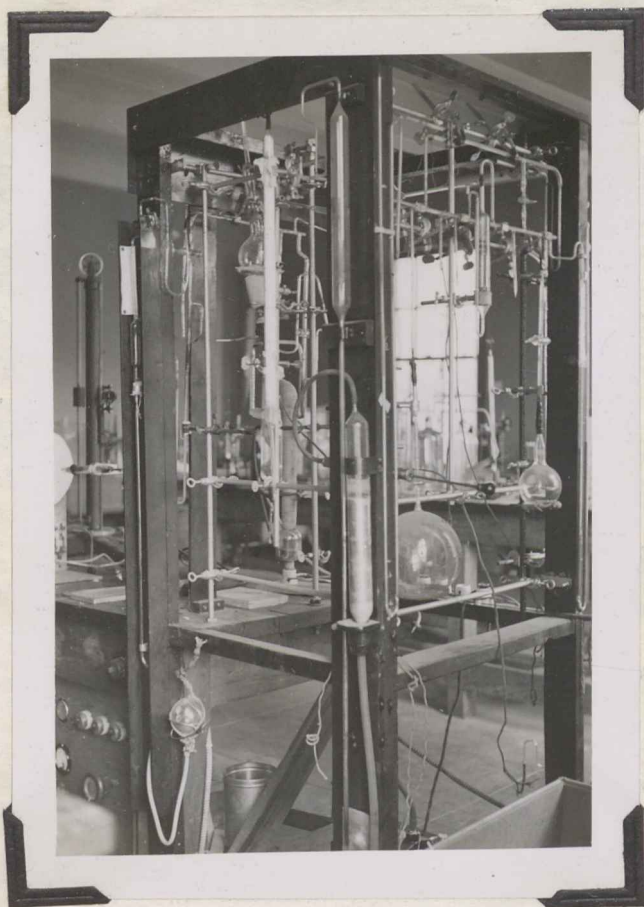


PLATE I. General View of System

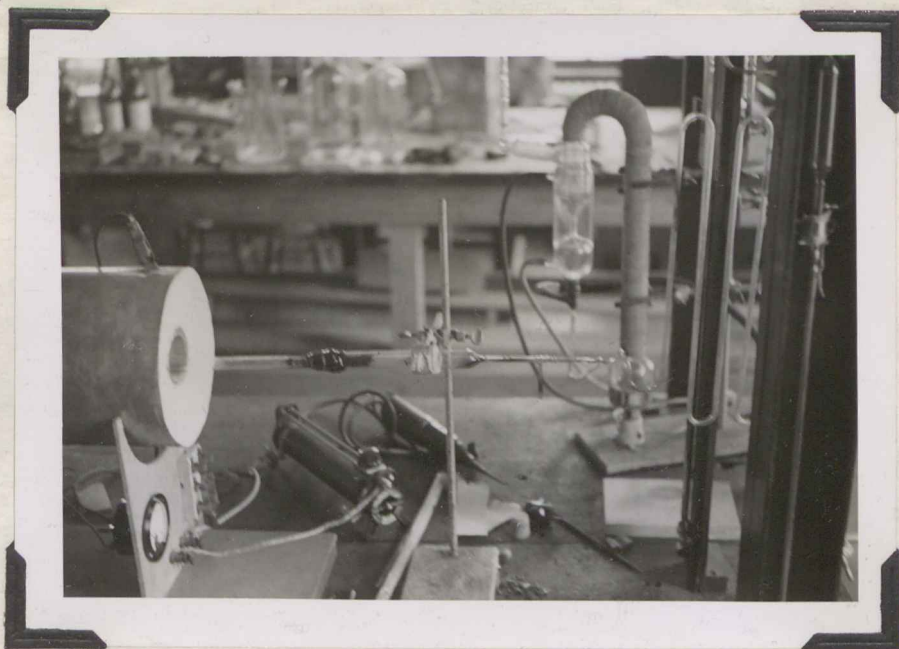
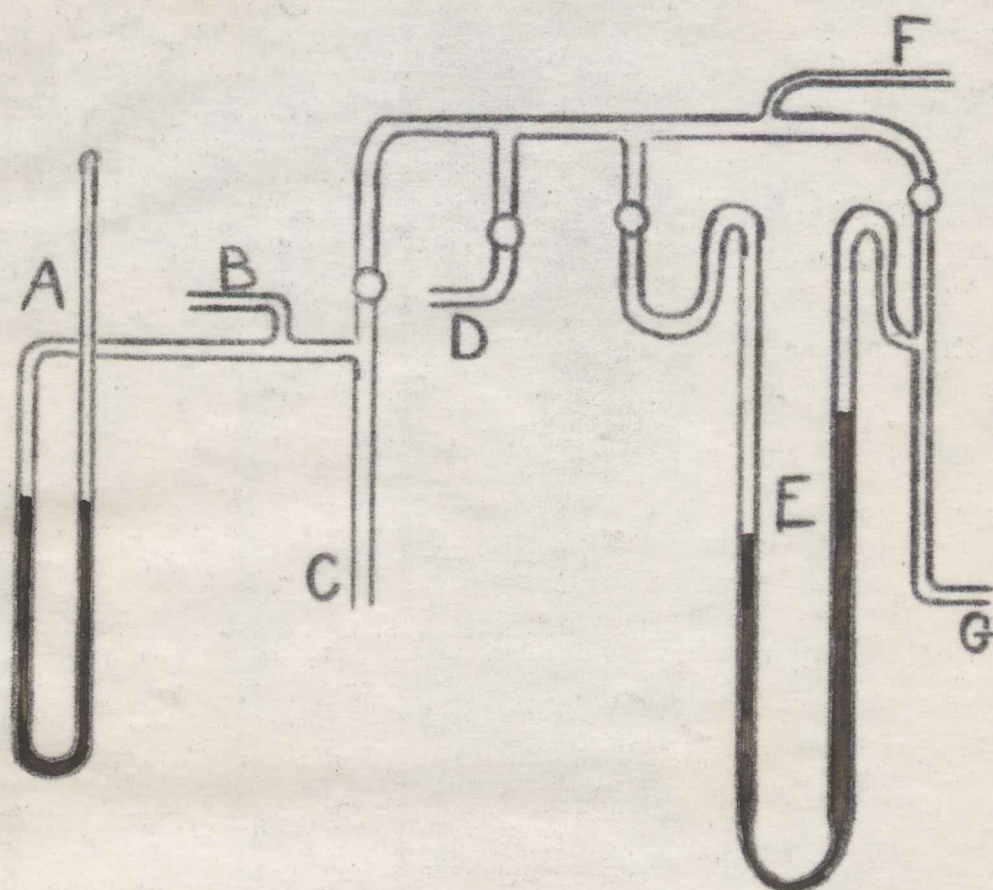


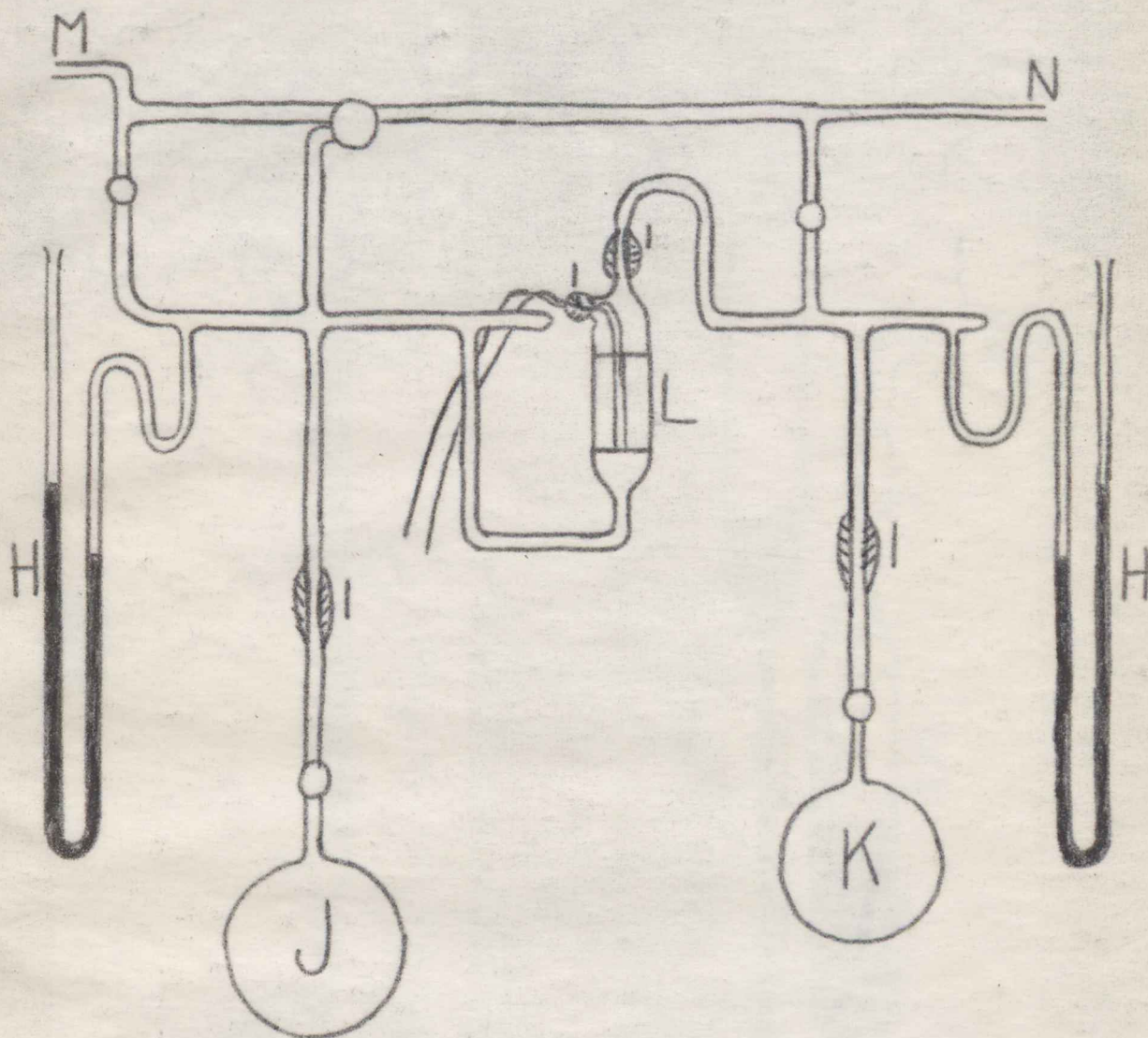
PLATE II. View of Dissociation Tube





- A. Manometer
- B. Lead to mercury still
- C. Lead to mercury and oil pumps
- D. Lead to hydrogen system
- E. Manometer for measuring dissociation pressure
- F. Lead to McLeod gauge
- G. Lead to dissociation tube

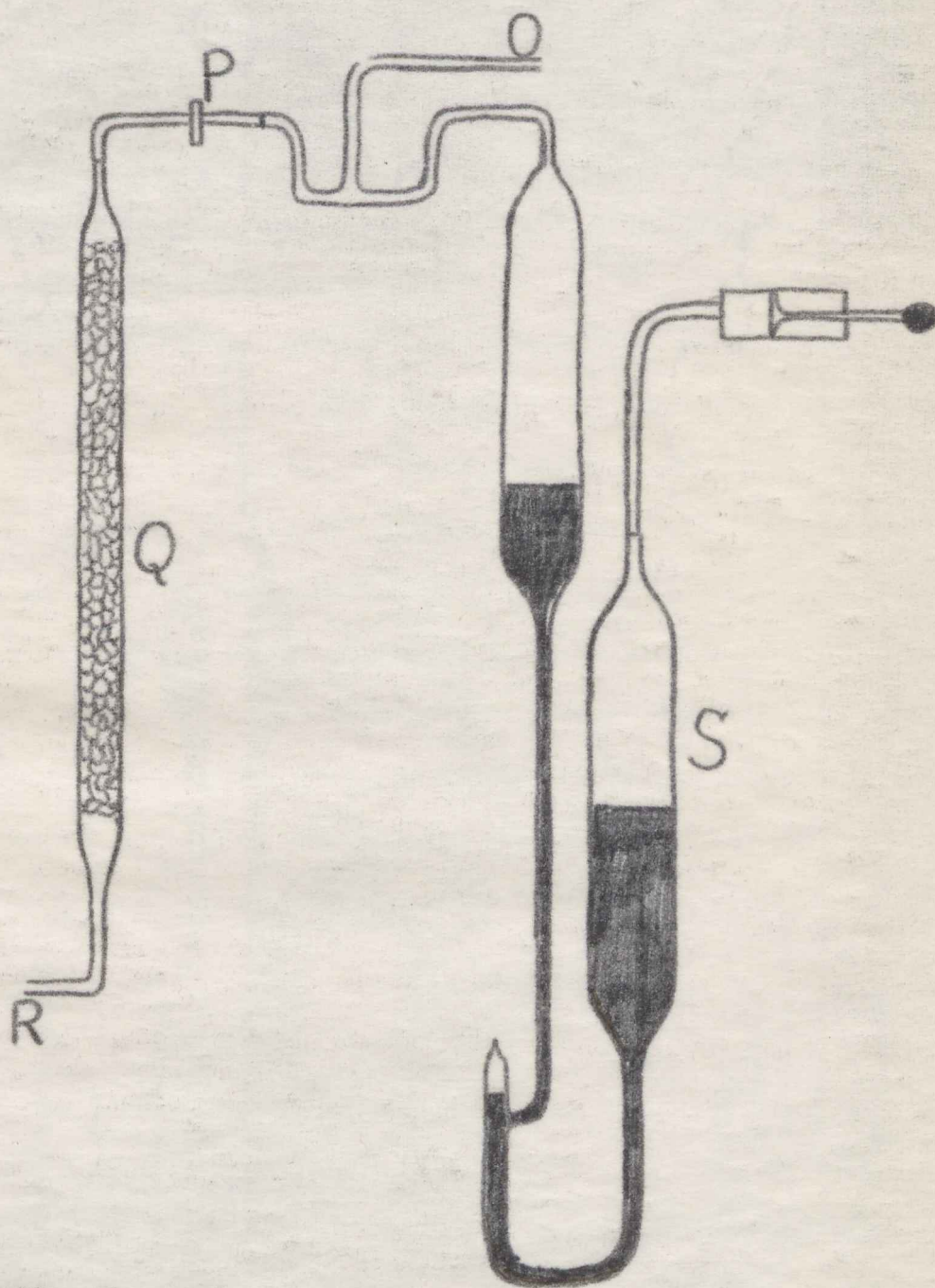
FIGURE 1. Vacuum System



- H. Manometers
- I. DeKhotinsky seals
- J. Impure hydrogen bulb
- K. Pure hydrogen bulb
- L. Platinum filtering unit
- M. Lead to hydrogen source
- N. Lead to vacuum system

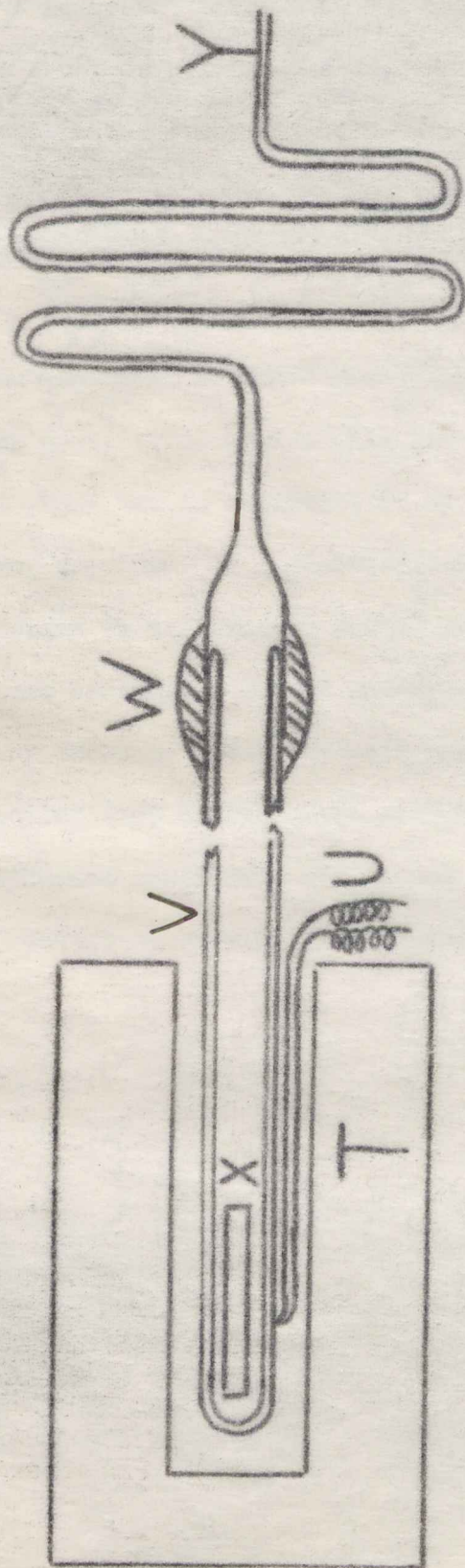
FIGURE 2. Hydrogen Storage and Purification System





- O. Lead to purification system
- P. Clamp regulator
- Q. Calcium chloride tube
- R. Lead to hydrogen tank
- S. Mercury piston pump

FIGURE 3. Hydrogen Supply System



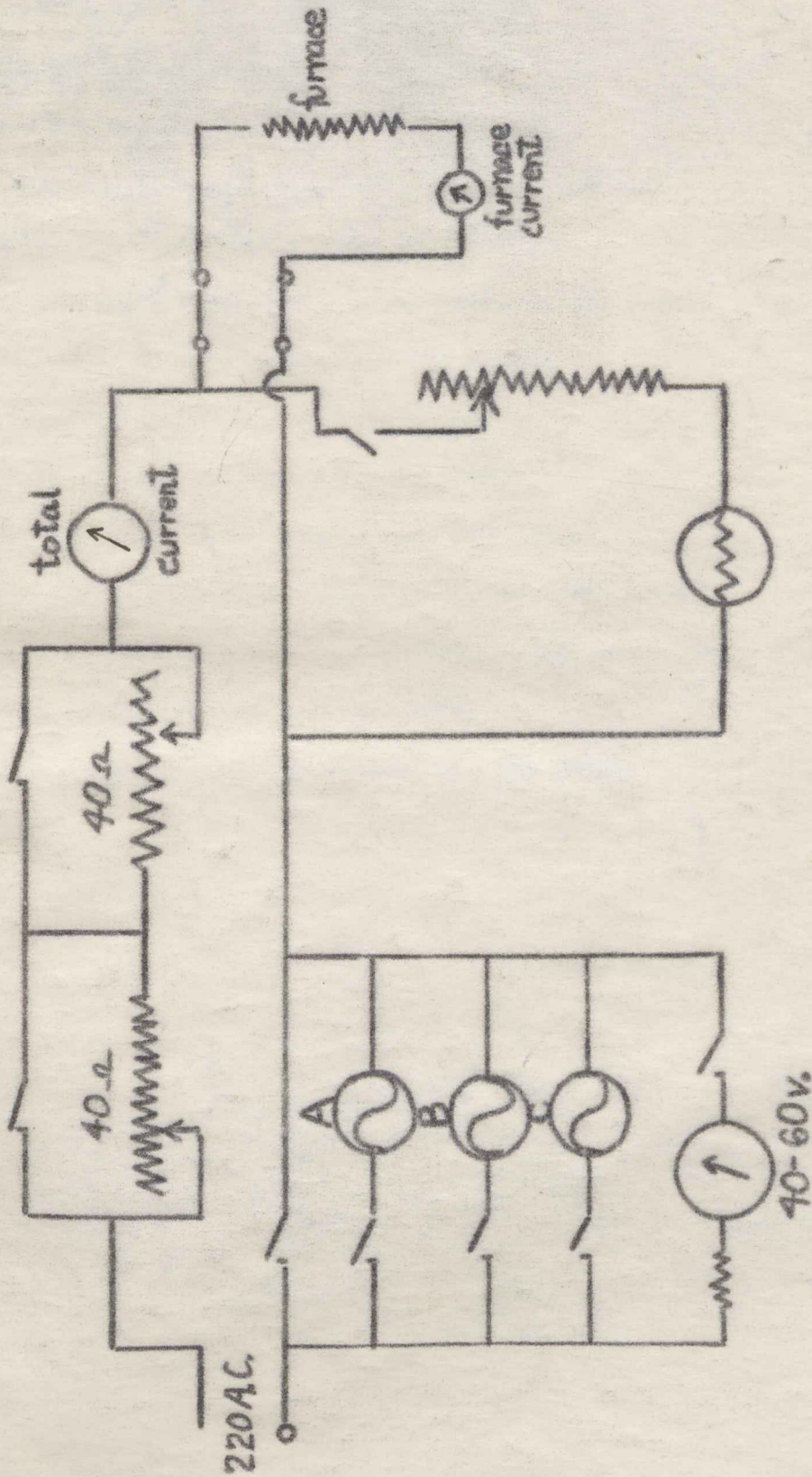
- T. Furnace  
 U. Thermocouple  
 V. Clear quartz tube  
 W. De Khotinsky seal  
 X. Nickel cylinder  
 Y. Lead to vacuum system

**FIGURE 4.** Dissociation Tube System



Fig. 5, A, B, C represent three U.V. 876 ballast tubes<sup>15</sup> which pass a maximum of 1.7 amperes each, or 5.1 amperes together, and serve to keep the furnace current constant (and thereby maintain constant temperature during runs taken over a period of time) in spite of line voltage fluctuations. The variable resistance shunted across the furnace permits any furnace current desired to be obtained.

Barium has been obtained from King Laboratories, Syracuse, New York, which is 97-98% pure. This barium will have to be purified before it can be used. Present plans are to redistill it by a procedure analogous to that used by Johnson<sup>13</sup> for calcium. If redistillation is not successful, it may be necessary to return to the amalgam method of Conlon<sup>9</sup>, or to seek a new method of preparing pure barium. A method suggested by W. A. Ruggles of the General Electric Company seems to offer the most promise of producing the pure metal. It involves heating pure barium oxide with finely divided tantalum filings in vacuo in a molybdenum container, and is not a simple method; but would necessitate the construction of considerable apparatus to carry it out.



**FIGURE 5.** Electrical Circuit for Controlling Furnace Current



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