

in order to determine the influence of the many important factors which would affect the results and it, therefore, is undesirable to draw any final conclusions as to the magnitude or the importance of the separation of the gases by distillation within a magnetic field either upon a small or a large scale.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

A SYNThERMAL REGULATOR, A DEVICE FOR AUTOMATICALLY MAINTAINING AN ADIABATIC CONDITION IN CALORIMETRY.

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The method of adiabatic calorimetry, as recently developed in the Harvard Chemical Laboratories, demands that the bath surrounding the calorimeter should be changed in temperature at the same rate as the calorimeter itself, so that no heat should be lost or gained during the calorimetric determination. The outside bath has therefore, been heated or cooled either by a suitable chemical reaction, or by hot or cold water, or by electricity,¹ so as to keep pace with the inside. Heretofore this quantitative identity of temperature has usually been established from moment to moment by the experimenter, who has observed both temperatures, and acted accordingly. That this technique is feasible and accurate has been abundantly proved; but, nevertheless, with quick reactions the method makes considerable demands upon the operator; accordingly, it seemed worth while to arrange an automatic device for relieving him of strain. Such a device might be called a "synthermal regulator."

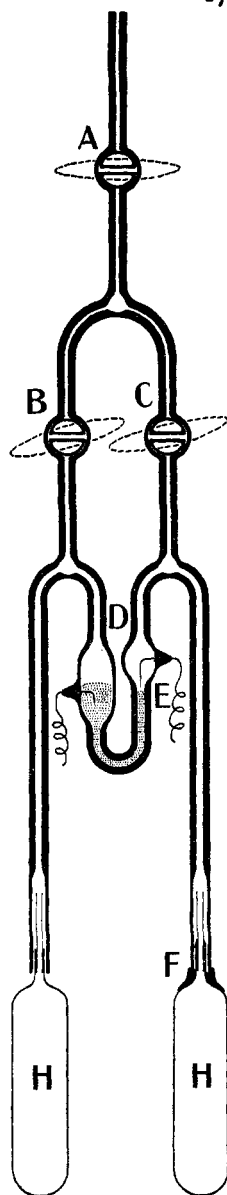
Obvious methods for accomplishing this end will occur to any one familiar with this kind of problem. A multiple thermocouple or a pair of resistance thermometers might be connected with a delicate galvanometer in such a fashion that any inequality in the temperature of the two baths would cause a deflection in a galvanometer, and thus through a relay operate a mechanism for equalizing the temperature, but it would be difficult to provide an adequate relay. A differential mercury-, or, better, a differential gas-thermometer might be used to attain the object sought, and this seemed much more promising. Because the relay seemed to be the

¹ Richards, *THIS JOURNAL*, 31, 1280 (1909); see also Benedict and Higgins, *Ibid.*, 32, 462 (1910).

crucial part of the contrivance, and because the last-named method requires a less sensitive relay than the others, it was tested first, and is described herewith. With a differential gas thermometer, in which contact is made between a very fine platinum point and a small meniscus, a fairly strong electric current may be sharply made and broken; and this, through a common long-distance telegraph relay, can govern a powerful current capable either of directly heating the outside bath or of operating any desired mechanism for this purpose.

The differential thermometer took the form illustrated in Fig. 1. Two rounded copper or silver cylinders, holding each about 28 cc., were attached by de Khotinsky cement or sealing wax (afterwards covered with paraffin to protect from caustic liquids) to a very narrow glass U tube (1.5 mm. diameter) with bulbs of familiar form. Suitable stopcocks were provided above so that the whole contrivance could be filled with hydrogen (chosen because of its great conductivity) and conveniently adjusted. A finely pointed platinum wire, containing 8% of iridium, was sealed into one of the bulbs so as to make contact with mercury at the widening of the capillary U-tube. This differential thermometer is highly sensitive, quickly making and breaking contact within $1/100^{\circ}$. It should be set up with the platinum wire outward, so as to make the current when the inner vessel is the warmer. The electromotive force of the current employed should be moderately low, to diminish sparking; and the hydrogen must be pure to avoid combustion, because the removal of hydrogen in this way may cause changes in the setting. The current thus made and broken is sent through a good relay as already indicated.

With a regulating current thus made and broken, it is possible, as stated, to operate a variety of mechanisms for regulating the temperature of the outer bath of the calorimeter. In our first experiments we used the strong current for turning on and off the flow of sulfuric acid into the outer



SYNThERMAI, REGULATOR.
(About $1/3$ actual size.)

- A, B, C—Glass stopcocks for filling and regulation.
D—U-tube with bulbs containing mercury.
E—Very finely pointed platinum wire sealed in to make mercury contact.
F—Cement joint attaching HH, metal bulbs.

bath, which contained alkali; the current was led through an electromagnet which operated a plunger-valve in the delivering vessel. For cooling reactions, ice-water could obviously be delivered in a similar way. Unless the size of the jet is rather carefully proportioned to its task, this device was found at times to admit too much liquid at once, overstepping the mark; we overcame this difficulty, with a constant jet, by cutting off the current every few seconds with the help of a constantly rotating circular key.

With apparatus thus constituted, it was found that equality in temperature between the inside and outside vessels could be usually maintained within 0.02° , or at most 0.03° , even when the rise in temperature in the baths was rapid. With slow temperature changes the adjustment is even better. Thus it is capable of rendering real service in adiabatic calorimetry, and might also be useful in regulating a bath around apparatus for determining freezing points, or in other similar exigencies.

This apparatus was devised in the autumn of 1912. More recently, one of us, with the collaboration of Dr. S. Tamaru, has used it in a different way: the stronger current of electricity from the relay was employed directly for heating the outside bath. Although not so suitable for very rapid reactions as the method of adding sulfuric acid to alkali, this method is very convenient for moderately slow ones; and we found that the regulator worked sufficiently well for many purposes when used in this way. In the course of this later work the importance of equality of pressure in the two metal bulbs at the moment of electrical contact became evident. This is easily adjusted by the stopcocks and slight tilting of the apparatus. Otherwise, of course, the quantity $\Delta p/\Delta t$ may be perceptibly different on the two sides, and, therefore, a progressing deviation of the two temperatures may occur.

The chief difficulty with very rapid reactions seems to be the lack of equable distribution of the heat, especially in the inner calorimeter vessel. If the different parts of this vessel are unequal in temperature, of course the action of the differential thermometer will be irregular. Evidently very efficient stirring is necessary in both the inner and the outer vessel.

We are indebted to the Carnegie Institution of Washington for much of the apparatus used in these experiments.

Summary.

In brief, a delicate differential hydrogen thermometer with a sensitive mercury contact was devised. This, with the help of a relay, enabled a stronger current to operate a heating or cooling mechanism for causing one bath to follow the temperature of another within 0.03° . The apparatus which may be called a "synthermal regulator," is of service in adiabatic calorimetry, or in other cases where identical but changing temperatures are desired in two contiguous vessels.