

less except at the lower end of the scale. Similarly, in the list of fixed points given at the foot of Table II, the magnitude of the uncertainty in the temperature scale is such that the temperatures above 1000° may be rounded off to the nearest degree.

The reference curves given in Tables I and II are intended for use in conjunction with the appropriate deviation curve. This correction curve is determined for each element by calibration at several of the fixed points—preferably three or more—given at the foot of each table; whence it is simply constructed by plotting¹ ΔE as ordinate ($\Delta E = E$ observed — E standard) against E_{obs} as abscissa, and joining up the various points. Then in order to obtain the temperatures corresponding to the electromotive force reading indicated by the element, the appropriate value of ΔE (as obtained from its deviation curve by inspection) is subtracted algebraically from the observed value of E before the latter is converted into degrees by means of the table. There need be no apprehension of error in the use of this method even with deviations of as much as 100 microvolts; especially if sufficient calibration points be taken within the specific temperature range, and if the deviation curve so obtained does not depart too far from a straight line.

It should be borne in mind that neither of these tables has an *absolute* significance; it represents merely an arbitrary reference curve which is substantially the mean of the three elements (E, F, G) used by Day and Sosman as standards; for the curve does not differ from the average reading of these elements by more than 1 microvolt, except at the somewhat less certain nickel point, where the divergence amounts to 5 microvolts.

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NOTE.

An Electrical Contact Vapor-Pressure Thermoregulator.—The change in the pressure of a saturated vapor with change in temperature has been made use of by various investigators as a means of automatic temperature control. Andreae² devised a thermoregulator in which a small quantity of some volatile liquid, such as ether, alcohol, or water, was utilized to increase the change of pressure per degree of a suitably enclosed volume of air or other gas. Lothar Meyer³ made use of the same principle. Benoit⁴ described a thermoregulator similar to the foregoing, with certain mechanical improvements. Kahlbaum⁵

¹ It is obvious that the required accuracy is secured by plotting on a small scale; a sheet of coordinate paper 20×20 cm. is ample.

² *Wied. Annalen*, 4, 614.

³ *Ber.*, 16, 1088 (1883).

⁴ *Wied. Beibl.*, 4, 296.

⁵ *Ber.*, 19, 2860 (1886).

first devised a regulator depending only upon the vapor pressure of a saturated vapor, without the additional pressure of air or other gas. In all of the above devices the change of vapor pressure, or combined air and vapor pressure, regulated the rate of flow of the gas used in heating the air or water bath.

Recently Esclangon¹ has described a saturated vapor thermoregulator in which the increase in vapor pressure with temperature rise causes a movement of mercury in a circular tube, pivoted so as to rotate about its center. This movement of mercury destroys the equilibrium of the balanced system by displacing its center of gravity, causing the tube to rotate sufficiently to make and break an external electrical contact. This apparatus is obviously unsuited for the temperature control of a water bath in which the water is being vigorously stirred.

The form of vapor-pressure thermoregulator herein described is essentially an upright U-tube closed at both extremities. One side of the tube contains a volatile liquid whose boiling point lies near the desired temperature of the bath. Above the liquid is its saturated vapor with or without admixture of air or other gas. The pressure exerted by the vapor, or the vapor and gas, supports a mercury column, which makes and breaks an electrical contact on the other side of the U-tube. This contact is made in an atmosphere of carbon dioxide.

The use of air, in addition to the saturated vapor, influences the accuracy of the thermoregulator in several ways. (1) It augments by approximately one-tenth the pressure-increase per degree rise in temperature, when the air has atmospheric density. (2) It decreases the rate of evaporation of the liquid due to a temperature rise. (3) It increases both the specific heat and the thermal conductivity, two effects which tend to neutralize each other. The author has not attempted to investigate those conditions which correspond to a maximum pressure-increase per degree change in the temperature of the bath per second. However, it is probable that the use of a gas in addition to the saturated vapor increases slightly the sensitiveness of the apparatus.

An electrical contact thermoregulator, utilizing the pressure of saturated ether vapor, has been in use for some time in this laboratory. It has kept the temperature of a water bath of 350 liters capacity at 30° with an accuracy of from 0.01° to 0.005° for several days at a time, the room temperature being subject to the usual variations of the average laboratory. The bath is made of galvanized sheet iron, surrounded by 1-inch pine boards. During the warm weather no cover was used for the bath. During the colder weather, a cover of plate glass, in three pieces for convenience in handling, has been used. The heat is supplied by ordinary carbon filament incandescent lamps, and the bath is stirred by a 1/30

¹ *Compt. rend.*, 156, 1667-70 (1913).

horse-power motor. The resistance in series with the motor consists of two 100 watt lamps in parallel, and these are dipped into the bath. Thus this source of heat is utilized. Two dry batteries operate the heating circuit through the thermoregulator and a 150 ohm relay. The inside dimensions of the bath are: depth, 70 cm.; width, 70 cm.; length, 80 cm.

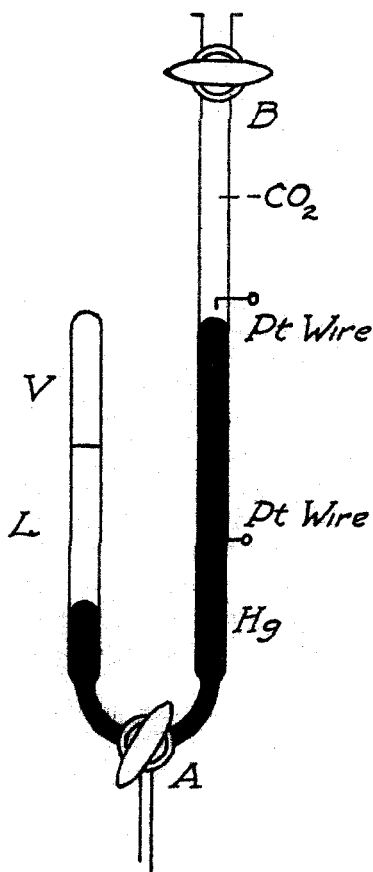
In all cases where there has been a noticeable variation of temperature beyond the limits above mentioned, it has been due to failure of the relay to operate, caused by the contacts partially fusing together, or else to an insufficient heat supply, following a sudden drop in external temperature.

As is usually the custom, a certain number of lamps are shunted around the

relay so as to provide a constant amount of heat sufficient to keep the water bath near to the desired temperature. The remainder of the lamps operate through the relay and provide a variable amount of heat, depending on the external fluctuations of temperature.

When no cover is used, and when the room temperature varied between 27° and 30° , one 60 watt lamp has been found to furnish sufficient heat, in addition to the lamps used as resistance for the motor. When a cover is used, and when the room temperature varies between 18° and 23° , one 100 watt lamp and one 60 watt lamp are necessary, besides the motor-resistance lamps. In the latter case, the 100 watt lamp can be shunted around the relay. These specifications are only approximate, but will serve to give some idea of the heat requirement of the bath described above.¹

The thermoregulator, as actually constructed, is shown in the accompanying figure. L is the liquid, above which is the saturated vapor; A is a three-way stopcock; B is a stopcock. As can be seen at once, air is here used in addition to the saturated ether vapor, the partial pressure of the former amounting to about



Scale 1:3

¹The author, since the preparation of this article, has reduced the heat requirement about 50% by the use of double-walls for the bath. The 1-inch space between the walls is filled with sawdust.

28 cm. of mercury at 30°. The pressure of the saturated ether vapor at 30° amounts to 63.6 cm. The carbon dioxide present in the other arm of the apparatus is at approximately atmospheric pressure.

To prepare for operation, the apparatus is first carefully cleaned and dried. It is then inverted, and pure, dry ether, or other liquid, is poured, by means of the lower outlet tube, into the proper arm until it contains several cc. Air is expelled at this time, if so desired, by gently warming the liquid. A is then turned until connection is made with the other arm of the U-tube; B is closed. Mercury, carefully freed from all impurities, including moisture, is poured into this side of the U-tube until nearly full. A is then turned so as to close both arms of the apparatus, which is then placed upright, as in the figure. B is opened. Connection is made between the two sides of the thermoregulator, after which B is again closed, preparatory to immersion in the water bath. Before it is placed in the bath, however, both stopcocks are protected by an application of buret wax, to guard against entrance of water vapor. In addition, the tube above B is closed by a rubber stopper, while the lower outlet tube is closed by a rubber tube and pinchcock.

The thermoregulator is now placed in the water bath, which is at the desired temperature. If the mercury column stands above the upper platinum contact, it is drawn off by means of the lower outlet tube. If it falls below this point, more mercury is added from the top. By such manipulation, the column of mercury can be easily adjusted so as to make and break contact at the desired temperature. Finally, the air above the platinum contact is replaced by dry carbon dioxide, a mercury seal placed above B, and the thermoregulator securely fixed in the water bath.

The vapor-pressure thermoregulator is surpassed in ultimate sensitiveness by the well-known toluene thermoregulator. That is, by using a large volume of toluene and causing it to expand in a tube of small diameter, we can theoretically increase the sensitiveness to any desired degree. It is impractical, however, to use a tube of a diameter much less than 2 mm., since in a smaller tube the mercury is apt to stick to the sides. An increase in the amount of toluene used causes the temperature of the toluene to lag considerably behind the temperature of the bath, especially where this is subjected to the influence of a considerable change of external temperature. This difficulty has been overcome, in part, by various workers by enclosing the toluene in long cylindrical tubes, placed around the walls of the thermostat.

The author has not actually compared the sensitiveness of the vapor pressure thermoregulator with that of the toluene thermoregulator, but one experiment will illustrate the rapidity with which the former can adapt itself to the changing temperature of a water bath.

The thermoregulator, adjusted to 30°, was removed from the bath

and allowed to attain the room temperature of 25° . The water bath was then heated to 30.1° . The regulator, which had a temperature of 25° , was then immersed in the bath. In 30 seconds from the time of immersion, the thermoregulator automatically operated the relay and cut off the heating current. It is this rapidity of accommodation which makes the vapor-pressure thermoregulator especially suited for temperature control in those cases where no great care is taken to prevent any sudden change of external temperature and where the amount of heat, supplied under the control of the relay and thermoregulator, is in considerable excess of the exact amount required to maintain the bath at the desired temperature.

A gas thermoregulator so constructed as to be independent of atmospheric pressure would have, at room temperature, a maximum sensitiveness of approximately one-tenth that of the saturated ether vapor thermoregulator. This is true when the gas used exerts a pressure of 760 mm. at 0° . Of course, if it were possible to construct a thermoregulator containing a gas under high pressure, a degree of sensitiveness heretofore unattained could be secured. Referring to the PV isothermals of a gas, we see that the vertical distance between two consecutive isothermals, which represents the increase in pressure per degree at constant volume, can be made as large as desired by choosing high pressures and small volumes. The difficulty here, however, and it seems insurmountable, would be to devise a means of confining the gas at such high pressure without the use of a mercury column of huge dimensions.

Summary.

1. The author has devised a form of vapor-pressure thermoregulator unaffected by changes in atmospheric pressure, and utilizing an electrical contact in dry carbon dioxide gas.
2. The thermoregulator is light and easily adjusted, is adapted for use in fluid baths, and is unaffected by motion of the fluid.
3. The rapidity, with which it adjusts itself to changes in the temperature of the bath, makes it especially suitable for the accurate temperature control of the average thermostat.
4. It has an observed sensitiveness of 0.01° to 0.005° .

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The third session of the Council of the International Association of Chemical Societies was held at the Institute Solvay, Brussels, September 19-23, 1913. The meeting was held in Brussels instead of London in acknowledgment of Monsieur Solvay's munificent, unconditioned gift of