A Thermoelectric Method of Measuring Osmotic Pressures

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In 1930 A. V. Hill[1] developed the thermoelectric method of measuring osmotic pressures, using a sensitive thermopile. This method was modified in 1934 by E. J. Baldes[2] who used a single thermocouple. The method so modified and later modifications are the subject of this discussion.

The apparatus consists essentially of a constantan-manganin thermocouple made of wires 0.002 inch in diameter, fashioned into loops (as shown

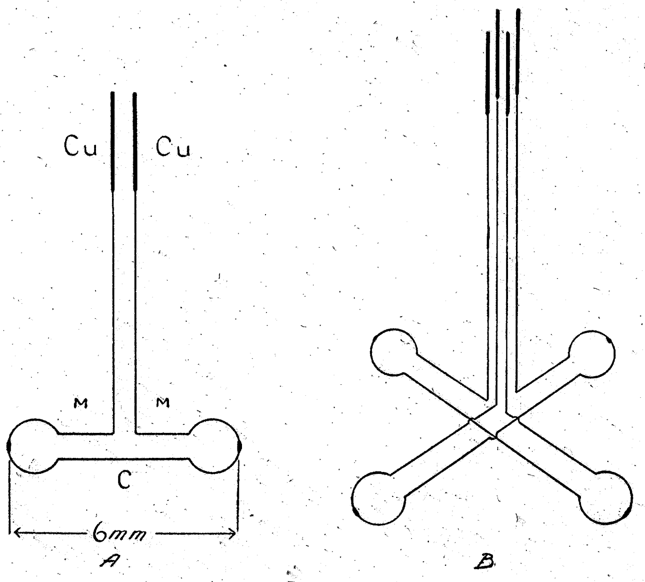

Fig 1

in Fig. 1A) and coated with bakelite varnish. In order to make measurements in duplicate two separate couples are put on one support and enclosed in the same compartment (see Fig. 1B). Either couple may be connected to a galvanometer whose sensitivity is about 10^{-9} ampere.

Small droplets of two solutions whose osmotic pressures are to be compared are placed respectively on the two junctions. The couple is then enclosed in a small water-tight metal chamber the walls of which are covered with filter paper moistened with one of the solutions (see Fig. 2A). The chamber is lowered into a water bath whose temperature is maintained constant to 0.001°C. If, for example, the vapor pressure of one of the droplets is lower than that of the solution on the walls, vapor from the walls will diffuse to the droplet and condense upon it. The latent heat of vaporization which is liberated will raise the temperature of the droplet and consequently the vapor pressure until there is equilibrium with the solution on the walls. This equilibrium is reached in about 20 minutes. A difference of temperature will thus be maintained between the thermojunctions which will cause a current to flow in the galvanometer-thermocouple circuit. This current will be proportional to the original difference in vapor pressure of the two solutions and likewise to the difference in osmotic pressure.

Since this method has been used most often in physiological measurements, the apparatus is calibrated by using 0.9 per cent and 0.8 per cent solutions of NaCl on the loops and 0.9 per cent NaCl on the walls of the chamber. With these solutions a difference in temperature of about 0.006°C. is maintained between the junctions. The sensitivity of the apparatus is

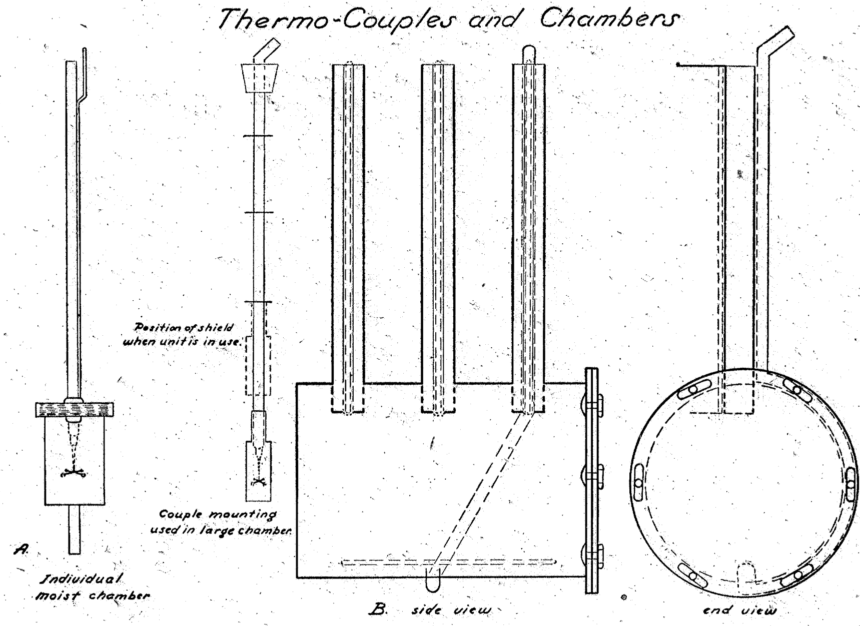

Fig. 2

such that this difference in temperature causes a deflection on the galvanometer scale of at least 50 mm. Thus differences in concentration corresponding to 2 mg of NaCl in 100 gms of water can be detected.

Each thermocouple was found to develop an e.m.f. even when identical solutions were placed upon the two loops. This e.m.f. was usually constant and was allowed for by making two sets of observations in any measurement, the droplets being reversed in the second set. It was found, however, that the above zero e.m.f. is less when the loops are farther removed from the walls. Consequently, the authors had built a large cylindrical brass chamber having a diameter of 6 inches and a length of 12 inches (see Fig. 2B). Three tubes extend from the chamber to a distance of 3 inches above the surface of the water. Three double couples supported by brass rods through which the electrical connections pass are inserted through these tubes into the chamber. The chamber is lined with filter paper moistened with one of the two solutions to be compared and immersed in the water bath. This chamber has proven very satisfactory, giving consistent results.

The zero e.m.f.'s developed in the couples remain nearly constant, the variation of the deflections produced being of the order of 1 mm. The moist filter paper lining remains in good condition, requiring no attention for many days. Three measurements can be made simultaneously and the whole manipulation is simpler than when three individual chambers are used.

Since in the measurement of osmotic pressures of blood it is necessary to make measurements in a mixture of air containing 5 per cent CO_2, tubes are provided in each case for sending such a mixture of gases through the moist chamber.

The accuracy of this method and the possibility of making measurements on small amounts of material at normal physiological temperatures and in an atmosphere of any gas which may be desired, make this method a valuable one in physiological research.[3,4] Since vapor pressure is considered a significant property of solutions, the method may also prove of value in the investigation of the behavior of solutions in general.[5]

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