

THE VAPOR TENSIONS OF LIQUID MIXTURES. BY W. LASH MILLER, PH.D.,
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Much of the recent remarkable progress in physico-chemical work is due to experimental and theoretical investigations on the vapor tensions of solutions, and Professor Van 't Hoff's paper showing the relations between the tensions, freezing-points, boiling-points, osmotic pressures and compositions of solutions marks a new epoch in the science. In his celebrated monograph "On equilibrium in heterogeneous systems" Prof. Willard Gibbs has deduced an equation (1) from which may be obtained a relation between the alterations produced in the vapor tensions of the components of a liquid mixture by altering the composition of the mixture. A close examination of this result of Gibbs and of the method by which it was obtained, shows that his equation contains as special cases many of the results of Van 't Hoff referred to above; it is consequently very desirable to subject the equation in its most general form to a direct comparison with experimental results. Such a control would be afforded by a set of measurements of the tensions and compositions of the vapors given off at any constant temperature by mixtures of two liquids in different proportions, but curiously enough no complete set of measurements of the nature referred to seems as yet to have been published. We have undertaken to supply the requisite data by an investigation of the case of mixtures of alcohol and water; the present paper contains a short description of the apparatus employed, the results of the measurements, and their comparison with the theory will form the subject of a subsequent communication.

The apparatus, as finally constructed, consists of a cylindrical vessel to hold five litres, made of tinned copper, and provided with five openings. Of these, the first is fitted with a thermometer, the second with a means of filling and emptying the vessel, the third with means of electrical communication to a heating coil suspended in the liquid; while through the fourth passes a glass tube to convey the vapors to a condenser, from which the condensed liquid drops back through the fifth opening into the apparatus. When desired, small quantities of the condensed vapor may be removed and their composition ascertained; these analyses, together with a knowledge of the composition of the contents of the copper vessel and measurements of the temperature and pressure, give all the data necessary for testing the accuracy of the equation of Gibbs referred to above.

In order to protect the vapor from partial condensation (and consequent fractionation) on the way to the condenser, the tube through which it passes is wound with insulated wire and may thus be kept hot, electrically; errors due to splashing of the boiling liquid have been provided against by a special construction at the bottom of the tube; condensation on the walls of the copper vessel itself is prevented by surrounding the latter with a tin cylinder wound with wire and kept at the temperature desired by means of an adjustable electrical current, while the absence of super-heating, and a thorough equilibrium between vapor and liquid, are secured by the use of perforated copper plates (under the surface of the liquid) through which the vapor must find its way.

As it is desirable that the boiling points of the mixtures should be varied at

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