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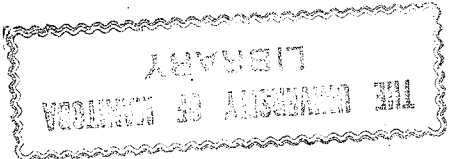
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by

DETERMINING MOLECULAR WEIGHTS.

as a means of

THE BOILING POINT METHOD



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Practical application of the method in the determination of the molecular constant of Tolene.

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EARLY METHODS OF DETERMINING MOLECULAR WEIGHTS.

(1) The Vapor Density Method is one of the more important physical methods used by the early chemists for the purpose of ascertaining the Molecular Weights of substances. The method depends on the fact that if a substance exists in the gaseous state, or can be easily converted into the form of vapor its molecular weight may be approximately determined by weighing a fixed volume of the gas at a known temperature and pressure and calculating the weight in grams which would occupy 22.4 litres at 0°C and 760 m.m. pressure. The best forms of apparatus in use for such determinations are those devised by Dumas, Hofmann, and Victor Meyer¹.

(2) The Vapor Tension Method was first used by Faraday early in the nineteenth century for determining Molecular Weights, but no important advance was made on this qualitative method until 1858 when Wullner found that the lowering of the vapor tension of water by non-volatile dissolved substances is proportional to the amount of the substance present. In 1885 Tamman showed that the molecular lowerings of the vapor pressure produced by salts of similar composition were very nearly the same. He showed too that Wullner's method gives only an approximation as the depression of the vapor tension increases in some cases more rapidly, in others less rapidly than the concentration.

The early investigators worked chiefly with water as solvent and salts as the dissolved substances. Under such conditions it was impossible to attain consistency in the results, as water tends to produce electrolytic dissociation, while salts under dissociation in solution. The idea of using a solvent with little or no dissociating power, and a solute that would not be dissociated occurred first to Raoult who in 1888 used ether as solvent and such organic substances as solutes which would not dissociate in solution. In this way he demonstrated the possibility of obtaining molecular weights of dissolved substances by measuring the lowering of the vapor tension of solutions prepared by them. This method has later been improved by Benzles³, who in 1910 devised an apparatus, by means of which, without any thermometer, molecular weights may be easily determined by static measurements of vapor pressure with an accuracy equal to that obtained by any other method.

(3)

Closely related to the depression of the vapor tension is the Osmotic Pressure and by its measurement the early chemists devised means, which pointed at a later date has more fully developed for molecular weight determinations.

The direct measurement, however, either of the Osmotic Pressure or the Depression of the Vapor Tension is attended with considerable difficulty, and has never found extensive application, partly on this account, but chiefly because a better and more accurate method was discovered.

THE EBULLIOSCOPIC AND THE CRYOSCOPIC METHODS.

When a solute is dissolved in a solvent, besides the lowering of the vapor pressure, there is a lowering of the freezing point, or a rise in the boiling point of the solution and each of these changes provides a means of determining the molecular weight of the dissolved substance. The Freezing Point method, however, is more limited in its application than that based on the measurement of the Boiling Point. It is practicable only when the solvent freezes at a convenient temperature, and applicable only when the solute does not form an isomorphous mixture with the solid solvent.

The method depending on the measurement of the change in boiling point far surpasses all others, both on account of the simplicity in manipulation and the greater accuracy of the results obtained. It was discovered in 1878 by the Physiologist Raoult⁵ who then demonstrated the possibility of obtaining results with it as accurate as with the vapor pressure method, although he preferred the latter up to 1889. It is to the chemist Beckmann⁶ the honor is due of first developing

it into a really practicable method. His apparatus was submitted to the German Society of Scientists on September 21st, 1889; shortly afterwards he published a description of it while at the same time Arrhenius furnished a theoretical basis for the method. With a few modifications which Beckmann made in subsequent years the apparatus remains even to-day the best form used in boiling point determinations. Its chief rivals, however, are worthy of consideration.

DIFFERENT FORMS OF APPARATUS USED IN THE EBULLOSCOPIC METHOD

(1) Sakurai's Method.

Sakurai⁷, a Japanese Chemist, was the first to adopt the method of heating the solution by a stream of vapor issuing from the boiling solvent. The quantity of liquid in the boiling tube is kept constant by passing in a current of vapor from without so that evaporation and condensation balance each other. When the correct temperatures have been obtained the solution is allowed to cool and the percentage composition determined by weighing a measured quantity of the solution, then evaporating it at a gentle heat on a water-bath and weighing the fixed residue.

(2) Landsberger's Method.

This method⁸ is a modification of that formerly devised by Sakurai. The liquid in the boiling tube is heated by the vapor of the solvent passing into it through a

conducting tube from a flask containing the boiling solvent. In this way superheating is prevented. As long as the solution in the boiling tube is under its boiling point some of the vapor condenses, and the latent heat of condensation goes to heat the solution until finally the boiling point is reached. When this happens the vapor passes on through the solution without further condensation, provided no heat is lost to the exterior.

When the experiment is finished, the apparatus is disconnected, the boiling tube allowed to cool, cleaned externally, and weighed, the empty tube being afterwards weighed and the weight of the solvent ascertained by subtraction. A complete determination need not take more than half an hour, and this saving of time, as well as the simplicity of the apparatus, are claimed to be the chief advantages over other forms.

(3) Walker and Lumsden's Method.

In the same year as Landsberger devised his form of apparatus, Walker and Lumsden⁹ modified the method so that several successive readings with the same portion of dissolved substance are made possible. The modification consists in reading the volume of the solution after equilibrium has been established, instead of determining its weight.

In the two methods, different constants are used, the volume constant being equal to the Beckmann constant divided by the density of the solvent at its boiling point.

There are three possible sources of error in using this form of apparatus, these have been pointed out by Meldrum and Turner¹⁰.

(1) Fractionation goes on and should the liquid be impure the boiling point rises. This error can only be avoided by careful purification of the solvent.

(2) The volume of the solution is measured, and taken to be proportional to the solvent, by which it is assumed that the volume change which accompanies the process of solution is negligible. In the weight method if expansion takes place during ^{the} solution it involves a diminution of the concentration of the solution and at the same time presumably a diminution both of the osmotic pressure and of the boiling point elevation, and if the elevation of the boiling point is too small the molecular weight will be too large.

(3) The main source of error is due to the fact that when the solution of the liquid in the vessel is great the pressure at the bottom of the vessel is greater than when the volume is small and consequently the observed boiling point is higher in the first case than in the second. This effect may be so great as to render inoperative the use of certain solvents.

(4) Jones' Method.

This method¹¹ is somewhat similar to that devised by Beckmann. In it the bulb of the thermometer is placed within a platinum cylinder, with platinum tetrahedra underneath. This prevents radiation. The volume of the liquid is so adjusted that it can never boil over the top of the platinum cylinder. As the cooled solvent flows back from the condenser it cannot come into direct contact with the thermometer but must first pass down and then up through the tetrahedra, by which process it is heated to the correct boiling point of the solution. These are the two distinctive features of the apparatus and because of them it is said to give more concordant results than other forms.

(5) Other Methods.

Chief among the other methods that could be considered are those of:

H. B. Hite¹²

F.K.Gameron and W.A.Orndorff¹³

E. B. Ludlam¹⁴

H. N. McCoy¹⁵

W.E.S.Turner and C.T.Pollard¹⁶

(6) Beckmann's Method

In this method¹⁷ the solution is raised to its boiling point by the indirect heat from a burner, and since the boiling point of a solution of a non-volatile substance is t