THE BOILING POINT METHOD

as a means of

DETERMINING MOLECULAR WEIGHTS.

by

David Allison, B. A.

Being a Thesis presented to the Department of
Chemistry of the University of Manitoba, in partial
fulfilment of the requirements for the degree of
Master of Arts.

University of Manitoba,

April, 1919.

THE BOILING POINT METHOD

as a means of

DETERMINING MOLECULAR WEIGHTS.

. . . .

C O N T E N T S.

REFERENCES.

1.   J. Walker, Intro. to Phys. Chem., 197 (1913)

2.   J.C.S., Abs. 1145(1888)

3.   J.A.C.S., 1615-1624 (1910)

4.   J.C.S., Abs. 11. 1071, (1911).

5.   J.C.S., Abs. 1145, (1888)

6.   J.C.S., Abs. 933, (1889)

7.   J.C.S., Trans. 989, (1892)

8.   J.C.S., Abs. 11. 283, (1898)

9.   J.C.S., Trans. 502, (1898)

10. J.C.S., Trans. 876, (1908)

11. Amer. Chem.J., 581-597, (1897)

12. Amer.Chem.J., 507-517, (1895).

13. Amer. Chem. J., 517-531, (1895)

14. J.C.S., Trans. 1193, (1902).

15. Amer. Chem. J., 353-360, (1900)

16. Chem. News. (109) 34, (1914).

17. J.C.S., Abs., 933, (1889)

REFERENCES (Cont).

18.   J.C.S., Trans. 11. 1751-1776, (1914).

19.   J.C.S., Trans. 777-783, (1902).

20.   Bigelow, Theor. and Phys. Chem., 313, (1914).
        Walker, Intro. to Phys. Chem. 194, (1913).

21.   J.C.S., Abs. 11. 236, (1898).

22.   J. Amer. Chem. Soc., 997, (1915).

23.   J.C.S., Abs., 412, (1890).

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 0.0 and 760 m.m. pressure. The best forms of apparatus in use for such determinations are those devised by Dumas, Hofmann, and Victor Meyer[1].

(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[2] 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 produced by them. This method has later been improved by Menzies[3], 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 Fouard[4] 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
Physicist Raoult[5] who then demonstrated the possibility of
obtaining results with it as accurate as with the vapor press-
ure method, although he preferred the latter up to 1889. It
is to the chemist Beckmann[6] the honor is due of first developing

it into a really practicable method. His apparatus was submitt-
ed 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.

Sakurai[7], 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 method[8] 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 Lumsden[9] 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 Turner[10].

(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 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 method[11] 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:

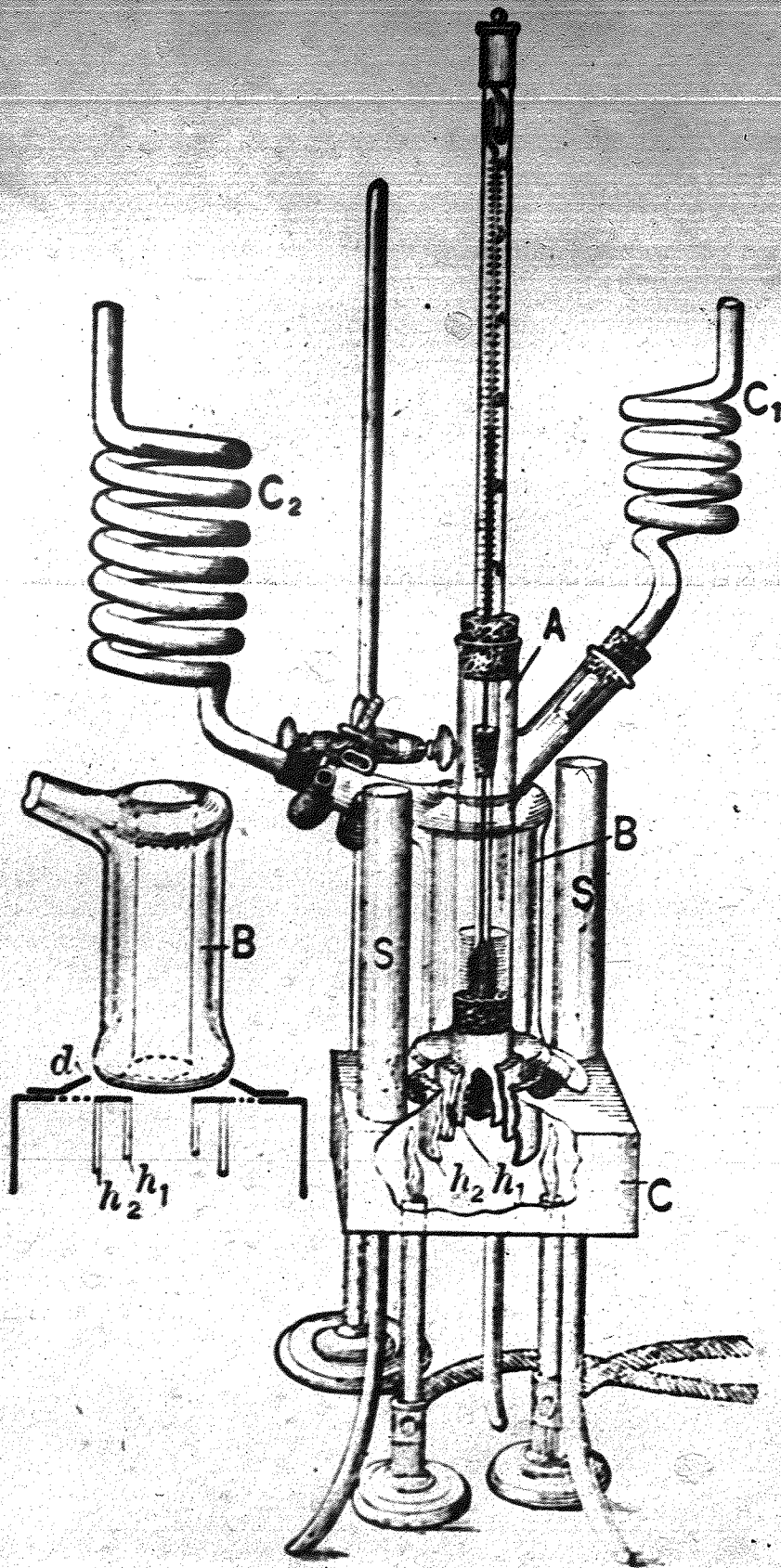H. B. Hite[12]

F.K.Cameron and W.R.Orndorff[13]

E. B. Ludlam.[14]

H. N. McCoy[15].

W.E.S.Turner and C.T.Pollard[16].

(6) Beckmann's Method

In this method[17] 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

C_2

C_1

A

B

S

B

S

B

d

h_2 h_1

h_2 h_1

C

the temperature at which the solution is in equilibrium with
the vapor of the boiling solvent, the bulb of the thermometer
must be placed in the solution itself and not in the vapor
issuing from it. If the thermometer were placed in the vapor
only it would register approximately the temperature of the
solvent and not that of equilibrium. Since the Mercury bulb
is placed directly in the liquid the utmost precautions must
be taken to prevent superheating. This is done in the follow-
ing manner:

The boiling tube A Fig.1. is about 2.5 cm. in diameter,
it has a thick platinum wire fused through the bottom and is
filled for about 4 cm. with glass beads or aluminium or platin-
um tetrahedra. The object of the platinum wire is to conduct
the external heat into the solution so that the bubbles of
vapor will form chiefly at one place and thus prevent super-
heating. The glass beads or tetrahedra are used to split up
the large bubbles of vapor into smaller ones so that more
intimate mixing of the solution and the vapor of the solvent
may be secured.

A standard Beckmann thermometer must be used. In it
the scale is divided into 1/100 of a degree, and by using a
lens or magnifying glass can be read to 1/1000. The bulb of
the thermometer is placed just above the beads or tetrahedra
and completely covered by the solvent.

Radiation to the surrounding media is reduced to a minimum, by encircling the boiling tube with a vapor jacket B containing about 20 cc. of the boiling solvent. In this way the risk of superheating is greatly reduced. Both vessels are provided with reflux water or air condensers C_1 and C_2. The asbestos heating chamber C contains two asbestos rings h_1 and h_2 to protect the boiling vessel from the direct heat of the flame, and two asbestos funnels S and S to carry away the products of combustion. The heat of the burners reaches the liquid in the vapor jacket through the ring of wire gauze visible at d

(d)   METHOD OF CARRYING OUT A DETERMINATION WITH BECKMANN'S

BOILING POINT APPARATUS.

To perform the experiment the boiling tube is first weighed, then about 20 grams of the solvent are put into it. The apparatus is then connected up, placed in position, and the heating begun. The flame is so regulated that the condensed solvent drops back only very slowly from the condenser. The boiling is never hastened by using a large flame. When the thermometer becomes steady, which usually takes more than half an hour, it is read off. The flame is then removed and a weighed quantity of the solute added through the condenser, either in the form of a pastile if a solid, or from a specially shaped pipette if a liquid. If air condensers are used the

liquid should be allowed to cool considerably before the
condenser is removed and the solute added. This necessitates
a loss of time and possibly a loss of vapor from the solvent,
so that the water condensers should be used if possible, as
these need not be removed from the tube in adding the solute.
As soon as this operation is finished the heat is again applied
and the boiling point determined. It is found to have raised;
and the difference between the first and second readings of
the thermometer is the rise in boiling point due to the
presence of the dissolved substance. The same process is again
gone through when more solute is added to the solution and the
rise in boiling point determined. The operation is repeated
until several successive readings have been taken.

(e)   PRECAUTIONS TO BE TAKEN AND CONDITIONS NECESSARY TO
                    ENSURE ACCURATE RESULTS.

In determining the boiling point of a solution of a non-
volatile substance, elaborate precautions should be taken to
secure accurate results and the closest attention must be paid
to the following points:

(1)   The vapor and the solution must be intimately
mixed in order that a proper equilibrium may be established.

(2)   Regular boiling must be ensured.

(3) The heat exchange with the surroundings must be reduced to a minimum, otherwise the temperature observed is not the temperature of equilibrium.

(4) Since both the boiling point and the heat of vaporization vary with the pressure at which ebullition takes place, there is no definite molecular elevation for any one solvent unless the pressure is specified.

(5) An essential condition for the success of the boiling point is that the dissolved substance should not itself give off an appreciable amount of vapor at the boiling point of the solvent. It is only applicable therefore to substances of comparatively high boiling point and cannot be employed with success for volatile substances such as alcohol or benzene.

(6) The dissolved substance must not associate in solution, that is, two or more molecules must not combine to form a larger one. If association takes place this gives too great a value for the molecular weight. (Association becomes apparent as a rule in solvents of dielectric constant less than 18.0, and the higher the dielectric constant of the solvent the smaller is the degree of association of the solute)[18].

Dissociation on the other hand gives a value much smaller than the true molecular weight. This is found to be the

case in almost every instance when acids, bases, or salts
are used.

(7) A certain fraction usually 0.2 or 0.3 gram is
deducted from the weight of solvent used, because this quantity
is in the form of vapor or just condensed during the experiment
The exact amount to be deducted can readily be determined for
each solvent by calculating the weight of vapor filling the
tube and part of the condenser during the experiment.

(8) The barometic pressure should be taken at the
beginning and at the end of the experiment and a correction
made if necessary, as a small variation in the barometric
height may have considerable influence on the accuracy of the
result. If too great a variation has occurred, it is much
better to neglect the results and to repeat the experiment at
a more favourable time. If however it is desired to correct
from observed to normal pressure Δt is to be added where

$$\Delta t = (760-p)(273+t)c.[19]$$

(9) Irregular boiling and bumping must be avoided.

(10) Substances used must be easily purified.

(11) The theory on which the calculation for molecular
weights by the boiling point method is based holds good for
dilute solutions only.

(12) A standard Beckmann thermometer must be used in the determination, and a necessary precaution is to tap the thermometer before taking a reading. The height of the mercury is read by the use of a lens or magnifying glass. Before using the thermometer it should be properly set, that is the amount 4° f mercury in the bulb must be so regulated that at the particular temperature of the experiment the end of the mercury thread is on the scale.

(13) If a hygroscopic solvent is used the condensers attached to the boiling tubes must be protected with a drying agent such as calcium chloride.

(14) Corks or rubber must not be acted upon by the solvent .

POSSIBLE ERRORS.

Errors of various kinds may occur in the determination of the value of the molecular weight by the boiling point method, so that only an approximate value of the true one may be obtained. The two chief kinds of errors are:

(1) Constant Errors

(2) Accidental Errors.

(1) Constant errors may be due to some error in the apparatus, or to the neglect of certain factors which influence the results. If a constant error occurs exercising an

appreciable effect all in one direction, the values
obtained may differ considerably from the true value.
Such errors may be caused by the heating of the glass, or
the barometer or the thermometer may be out.

(2) Accidental errors on the other hand may have either a
positive or a negative effect. They may be due to a too hasty
observation, or to a change in the barometric pressure during
the determination.

THE PRINCIPLE ON WHICH THE METHOD DEPENDS.

The possibilities which form the foundation for the
boiling point method were not at first recognized, but were
gradually evolved from observations of the vapor pressure of
solutions and solvents by such investigators as Wullner, Ostwald
and Raoult. These men early observed the approximate pro-
portionality between the diminution of the vapor pressure and
the elevation of the boiling point, and from these observations
established the three following fundamental facts.

(1). A solute when dissolved in a solvent always
produces an appreciable rise in the boiling point of
the solution.

(2). The rise in boiling point is proportional to the
amount of substance dissolved.

(3). Grammolecular quantities of different solutes,
or equimolecular solutes in the same solvent give the
same rise in boiling point, provided the necessary pre-
cautions are taken to select undissociating or unassoc-
iating substances.

A thorough study of the effect of the dissolved
substance on the boiling point of a liquid has shown that
the rise in boiling point of the solvent produced by
dissolving in it a non-ionized solute is proportional to the
weight of the substance dissolved, and inversely proportional
to the weight of the solvent, and to the molecular weight of
the dissolved substance. These facts can be expressed by the
formula:

$$\Delta t = C \frac{S}{S_1 \times M}$$

where

Δt = the rise in boiling point.

S = the weight of the solute.

S_1 = the weight of the solvent.

M = the molecular weight of the solute.

C = a constant [20].

The value of C can be found for any solvent by
determining the rise in boiling point produced by dissolving
a definite weight of some suitable solute in a known quantity
of the solvent. For example, it has been found that when 0.5
gram of a substance having a molecular weight of 133 is
dissolved in 18.5 grams of benzene the boiling point of the
solvent is raised 0.555° C. We can now substitute these values

in the formula

$$\Delta t = C \frac{S}{S_1 \times M}$$

$$.555 = C \frac{.5}{18.5 \times 133}$$

$$C = \frac{.555 \times 18.5 \times 133}{.5} = 2730.$$

From this we find that C = 2730 which is the value
of the constant when the solvent used is benzene. In a
similar way constants for other solvents may be found.

If the above equation is written in the form:

$$M = \frac{C \times S}{S_1 \times \Delta t}$$

and if the constant for the solvent is known, it is quite
evident that an unknown molecular weight can be determined by
observing the rise in boiling point of the solvent produced
by dissolving in it a known weight of the solute. For
example, the rise in boiling point of benzene was $0.40°$ C
when 0.464 gram of a certain substance was dissolved in 20
grams of the solvent, and by substituting these values in the
formula we get 158.34 grams as the molecular weight of the
substance.

$$M = \frac{2730 \times 0.464}{20 \times 0.40} = 158.34$$

From theoretical considerations it has been found
possible to calculate an approximate value for the constant C.
According to the Law of Trouton[21]

$$C = 0.0096 \ T \ M$$

where

T = the absolute boiling temperature

M = the molecular weight of the solvent.

Again if we adopt the method first worked out by Ostwald, and later modified by Jones, we have

$$C = \frac{2 \ T^2}{100 \ L}$$

where

T = the absolute boiling temperature

L = the latent heat of vaporization of the solvent.

or let

T = the absolute boiling temperature

W = the latent heat of vaporization

then

$$C = \frac{0.0198 \ T^2}{W}$$

If the heat of vaporization of a substance is not known it can be determined by observing the rise in boiling point produced by dissolving in it another substance of known molecular weight.

The constant C remains in each case the same and is valid for all suitable solutes in a given solvent.
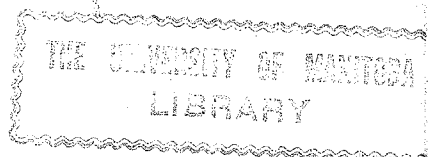
PRACTICAL APPLICATION OF BECKMANN'S BOILING

POINT METHOD IN DETERMINING THE MOLECULAR

CONSTANT OF TOLUENE.

The purpose for which this experimental work was
undertaken was to determine the molecular constant of Toluene
by Beckmann's Method. All the substances used were first
purified and every precaution taken to ensure accuracy in the
results. It was of course necessary to run several determin-
ations for practice and to observe closely the behaviour of
the boiling point in a very dilute solution and a more concent-
rated one. The best agreeing results were obtained by using
the quantities of solute and solvent recorded. No attempt
has been made to give all the results obtained and the practice
determinations are discarded. Results from the four following
substances are given:

(1) Diphenylamine $(C_6 H_5)_2 NH$.

(2) Phenanthrene $C_{14} H_{10}$

(3) Diphenyl $C_{12} H_{10}$

(4) Diphenylmethene $CH_2 (C_6 H_5)_2$

The formula $\Delta t = C \dfrac{g}{S_1 \times M}$ was applicable.

PURIFICATION OF SUBSTANCES.

The toluene was obtained from Mallinckrodt's N.Y., and
special attention was given to its purification. The method

adopted was nearly similar to that used by Richards and
Barry[22]. The toluene was first shaken with successive
portions of sulphuric acid until the acid remained colorless
after four successive agitations. The last traces of acid
were removed by means of a solution of sodium hydroxide, and
this in turn by repeated washing with water. The toluene was
again shaken with successive portions of clean Mercury until
the Mercury remained colorless after three successive agitat-
ions. It was again washed with water and dried with carefully
prepared sodium which had been freshly cut and washed for a
long time with purified toluene, again cut and washed and
pressed into a thin wire through a press which had been
previously washed with toluene. The first and last portions
of the wire were discarded. The toluene was now dried at 100°
over sodium and kept over sodium for some time. It was then
decanted off and distilled from an ordinary distilling flask
containing some boiling tubes. The fraction distilling over
first at a constant temperature was carefully preserved in
a glass stoppered bottle and used as solvent.

The substances used as solutes were obtained from
Kahlbauns and were labelled as pure. The sample of diphenyl-
methane however had a faint yellowish appearance so it was
redistilled, and the pure fraction distilling over at a

constant temperature was taken and the melting point determined. It was sharp at 26.5°

The original diphenylamine was pure. It had no unpleasant odor, contained no oil, and the color was not affected on exposure to light. It had a sharp melting point at 53°.

Both the diphenyl and the phenanthrene were pure. Their melting points were sharp at 70.5° and 100.3° respectively.

In calculating the results all the data of the experiment are not given. For example, the following formula was used

$$C = \frac{M \times \Delta t \times S_1}{S}$$

where

C = the constant to be found

M = the molecular weight of the solute

Δt = the rise in boiling point

S_1 = the corrected weight of solvent

S = the weight of solute added.

In the first result obtained using phenanthrene as solute, the molecular weight is 178.15 grams and the rise in boiling-point produced by adding 0.4181 grams of the substance to 19.11 grams of toluene was 0.39°. Substituting these

values in the formula gives

$$c = \frac{178.15 \times .39 \times 19.11}{.4181} = 3176$$

Again 0.204 grams of solute were added to the solution and the rise in boiling point produced was $0.19°$. These quantities are added to the first ones and the formula becomes

$$c = \frac{178.15 \times .58 \times 19.11}{.6221} = 3174.$$

More solute was added to the solution until sufficient readings were obtained.

The volume of the tube filled with the vapor of the solvent at the temperature of the experiment was estimated at 80 cc. This gives a correction of 0.23 grams which was subtracted from the weight of toluene in the boiling tube.

The glass beads were used in the first experimental work but were soon discarded, as much better results were obtained by using aluminium tetrahedra.

The boiling tubes were protected from the outside moisture with calcium chloride tubes.

USING PHENANTHRENE.

Weight of toluene (corrected solvent)   = 19.11 grams.

1. $C = \dfrac{178.15 \times .39 \times 19.11}{.4181}$ = 3176

2. $C = \dfrac{178.15 \times .58 \times 19.11}{.6221}$ = 3174

3. $C = \dfrac{178.15 \times .825 \times 19.11}{.8843}$ = 3176

4. $C = \dfrac{178.15 \times 1.113 \times 19.11}{1.1907}$ = 3182

Mean of 1, 2, 3, 4   = 3177

USING PHENANTHRENE

Weight of toluene (corrected solvent)   = 20.00 grams.

1. $C = \dfrac{178.15 \times .34 \times 20.0}{.3813}$ = 3177

2. $C = \dfrac{178.15 \times .512 \times 20.0}{.5955}$ = 3183

3. $C = \dfrac{178.15 \times .781 \times 20.0}{.8745}$ = 3182

4. $C = \dfrac{178.15 \times .935 \times 20.0}{1.0479}$ = 3179

Mean of 1, 2, 3, 4,   = 3180

USING DIPHENYL.

Weight of toluene (corrected solvent = 20.25 grams.

1. C $= \dfrac{154.14 \times .42 \times 20.25}{.4129}$ = 3175

2. C $= \dfrac{154.14 \times .58 \times 20.25}{.5705}$ = 3173

3. C $= \dfrac{154.14 \times .832 \times 20.25}{.8163}$ = 3181

4. C $= \dfrac{154.14 \times 1.063 \times 20.25}{1.0417}$ = 3185

Mean of 1, 2, 3, 4 = 3178

USING DIPHENYL.

Weight of toluene (corrected solvent) = 19.55 grams.

1. C $= \dfrac{154.14 \times .45 \times 19.55}{.4262}$ = 3181

2. C $= \dfrac{154.14 \times .702 \times 19.55}{.6652}$ = 3180

3. C $= \dfrac{154.14 \times .972 \times 19.55}{.9199}$ = 3184

4. C $= \dfrac{154.14 \times 1.23 \times 19.55}{1.1619}$ = 3190

Mean of 1, 2, 3, 4, = 3184.

USING DIPHENYLMETHANE.

Weight of Toluene (corrected solvent) = 19.31 grams.

1. $C = \dfrac{168.16 \times .37 \times 19.31}{.3771}$ = 3186

2. $C = \dfrac{168.16 \times .526 \times 19.31}{.5356}$ = 3188

3. $C = \dfrac{168.16 \times .866 \times 19.31}{.8828}$ = 3185

4. $C = \dfrac{168.16 \times 1.152 \times 19.31}{1.170}$ = 3197

Mean of 1, 2, 3, 4 = 3189.

USING DIPHENYLMETHANE.

Weight of Toluene (corrected solvent) = 19.82 grams

1. $C = \dfrac{168.16 \times .432 \times 19.82}{.4516}$ = 3188

2. $C = \dfrac{168.16 \times .653 \times 19.82}{.6816}$ = 3193

3. $C = \dfrac{168.16 \times .948 \times 19.82}{.9892}$ = 3194

4. $C = \dfrac{168.16 \times 1.260 \times 19.82}{1.3127}$ = 3199

Mean of 1, 2, 3, 4 = 3193.

USING DIPHENYLAMINE

Weight of Toluene (corrected solvent) = 20.10 grams.

1. $C = \dfrac{169.16 \times .42 \times 20.1}{.4478}$ = 3189

2. $C = \dfrac{169.16 \times .615 \times 20.1}{.6555}$ = 3190

3. $C = \dfrac{169.16 \times .932 \times 20.1}{.9905}$ = 3199

4. $C = \dfrac{169.16 \times 1.17 \times 20.1}{1.2435}$ = 3199

Mean of 1, 2, 3, 4, = 3194

USING DIPHENYLAMINE

Weight of Toluene (corrected solvent) = 18.20 gr.

1. $C = \dfrac{169.16 \times .36 \times 18.20}{.3466}$ = 3187

2. $C = \dfrac{169.16 \times .582 \times 18.20}{.5610}$ = 3193

3. $C = \dfrac{169.16 \times .92 \times 18.20}{.8810}$ = 3204

4. $C = \dfrac{169.16 \times 1.21 \times 18.20}{1.1773}$ = 3206

5. $C = \dfrac{169.16 \times 1.43 \times 18.20}{1.3664}$ = 3211

Mean of 1, 2, 3, 4, 5 = 3200.

THE RESULTS.

The mean value of the molecular constant of toluene as obtained from these results is 3187 so that if we wish to find the molecular weight of a substance by Beckmann's boiling point apparatus using toluene as solvent the above constant must be employed. The value obtained by experiment is considerably higher than the one calculated from the theoretical considerations in the formula $C = \dfrac{0.0198T^2}{W}$ which gives the approximate value at infinite dilution. When the absolute boiling temperature rises and the heat of vaporisation is diminished the value obtained for C is higher. In the experimental results there is on the whole a rise in the value of the constant C for a rise in boiling point but this need not necessarily be expected[23]. The values obtained are fairly constant at the concentrations and for the substances used. The mean barometric pressure was 754.2 m.m. In using pure naphthalene as solute it was found that the value obtained for the constant was nearly 300 too low. This no doubt indicates that the naphthalene was somewhat volatile in the vapor of the boiling solvent. The results obtained are not recorded, and no attempt is made to give data of the first experimental work in which smaller and greater quantities of the solutes were used. If an error has occurred and the value of the constant C is too high the cause may be due to the use of a non-standardized thermometer.

B I B L I O G R A P H Y.

1. Bigelow. Theoretical and Physical Chemistry (1914)

2. Biltz (trans. Jones and King) Practical Methods for
   determining Molecular Weights, (1899)

3. Findlay. Practical Physical Chemistry, (1906)

4. Jones. Elements of Physical Chemistry, (1902)

5. Jones. Nature of Solutions, (1917)

6. Nernst W. Theoretical Chemistry, (1904)

7. Ostwald (trans.J.Walker) Physico Chemical Measurements (1894

8. Ostwald (trans. M.M.P.Muir) Solutions, (1891)

9. Philips, J.C. Physical Chemistry (1910)

10. Walker, J. Introduction to Physical Chemistry, (1913)

11. Washburn, Principles of Physical Chemistry (1915)