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of Saturday March 31, 1900.

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The following papers were read:

**Chemistry.** — Prof. H. W. BAKHUIS ROOZEBOOM presents an article by Dr. A. SMITS entitled: "*Determination of the decrease in the vapour tension of solutions by means of the determination of the increase in the boiling point.*"

(Read January 27, 1900.)

*Introduction.*

The peculiar result obtained with the micromanometer<sup>1)</sup> induced me to try and determine the decrease in vapour tension by another

<sup>1)</sup> Verslag Kon. Academie Jan. 2, 1897, Nov. 27 1897, Sept. 30 1899 and Proceedings Sept. 30, 1899.

method. It seemed to me there would be no particular difficulty in comparing the vapour tensions of pure water and solutions at a temperature different from  $0^{\circ}$ . I tried to gain my object by determining the difference in pressure required to equalise the boiling points of pure water and saline solutions.

In an article entitled: „An apparatus to keep the vapour tension of a boiling liquid constant,”<sup>1)</sup> the apparatus is described which I will briefly call „manostat”. This manostat enables me to reduce the pressure in a certain space to any desired extent, within definite limits, and then to keep it constant within 0.5 m. m. of water. By regulating the pressure of this apparatus it is therefore possible to make all solutions show the same boiling point. To be able to accurately read off the diminution in pressure, pure water is boiled under the same condition as the solution and from its decrease in temperature may be calculated the decrease in pressure corresponding with the decrease in vapour tension of the solution.

### *Preliminary Experiments.*

I experienced great difficulties in my preliminary work when using the apparatus of BECKMANN<sup>2)</sup>. Firstly, because the indication of the thermometer was dependent on the degree of heating; this is chiefly due to the wrong manner in which the condensed solvent runs back into the boiling mass.

Secondly, because the actual boiling vessel was not sufficiently screened to prevent radiation, which was shown by the fact, that mild air-currents had a perceptible influence on the indication of the thermometer.

A third drawback experienced in my preliminary trials, but which was not caused by any defect in BECKMANN's apparatus was as follows:

The indication of the thermometer appeared to be dependent on the place occupied by the mercury reservoir in the column of liquid. As far as I am aware, nobody has, as yet, called attention to this fact but as will be shown presently, it is a factor which under special circumstances is to be reckoned with. On account of this, a number of published results are undoubtedly faulty.

It is plain that this phenomenon may be accounted for by the difference in pressure between the different layers of liquid, but that it should be noticed so decidedly in boiling water or in boiling

<sup>1)</sup> Verslag Kon. Acad. Nov. 27 1897.

<sup>2)</sup> Zeitschr. f. physik. Chem. 1891.

solutions astonished me somewhat as during the boiling a certain amount of mixing takes place by the rising of the vapour bubbles. The difference in temperature between two aqueous layers of a boiling watercolumn at a distance of 1 c. m. of each other ought, theoretically, to amount to  $\pm 0.036^\circ$ . My actual experiments gave values laying between  $0.015$  and  $0.030^\circ$ . A change in the position of the thermometer had a smaller influence, when the instrument was deeply immersed in the liquid than when it was nearer the surface. This is only natural if we remember, that the vapour bubbles ascending from the bottom layers are larger in size than those of the top layers so that the mixing process in the former is less imperfect.

In any case it was shown that the "mixing" during the boiling was by no means sufficient to quite neutralize the difference in temperature between the different layers of liquid. As however the difference in temperature is partly neutralized, we are dealing here with a state of labile equilibrium.

After having tried BECKMANN's process, I applied the method proposed by S. SAKURAI<sup>1)</sup>, because the results, obtained by W. LANDSBERGER<sup>2)</sup>, who used this process in a slightly simplified form for the determination of molecular weights, inspired me with confidence. On further investigation however, it appeared to me that no very accurate results are obtainable by this method. As was to be expected, the boiling point of the water or of the solution depended on the temperature of the steam which was blown into it. Unless the evaporation keeps perfectly equal pace with the condensation, the pressure in the steam-generating flask is liable to constant variation and as this affects the temperature of the steam we cannot be certain of a constant boiling point. For this reason I abandoned the method.

All this induced me to have a new boiling apparatus constructed with the object of avoiding the first two sources of error arising from the use of BECKMANN's apparatus, although convinced that the third objection would still remain.

As we know by experience that a liquid boils more readily in a metallic vessel with a rough interior surface than in a glass one, in other words that, even without special precautions, the danger of overheating is smaller when using a metallic vessel instead of a glass one, a metallic vessel seemed to me preferable to one made of glass and I, therefore, decided to determine the boiling points in vessels

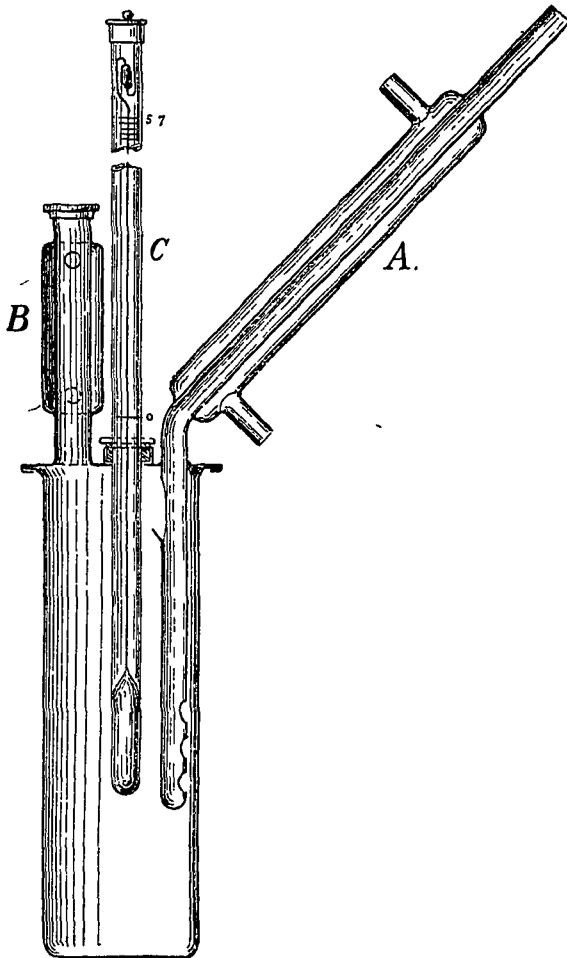
<sup>1)</sup> Journ. of the chemical Society 63. 495.

<sup>2)</sup> Zeitschr. f. Anorg. Chem. 17. 423.

made of silver, which had also the advantage that they could be readily made in any desired shape. The construction of the apparatus, presently to be fully described, was entrusted on the recommendation of Prof. H. C. DIBBITS, to Mr. BEGGER of Utrecht, who has performed his task with great skill and ability.

*Description of the Apparatus.*

The actual boiling vessels consist of cylindrical silver vessels closed at one end. They have a height of 20 cm. and a diameter of 6 cm. The



*Fig. 1.*

bottom and sides walls consist of one piece. As will be seen from the accompanying drawing (Fig. I) the top of the silver cylinder is closed with a lid through which pass the glass condensing tube *A* and the thermometer *C*. This tube, shown in the drawing on a reduced scale, has a diameter of 1 cm. and reaches inside the cylinder to a distance of 2 cm. from the bottom. The tube is sealed at the bottom, but at its side turned away from the thermometer it is provided with three openings of 1 cm. diam. Just underneath the lid, the tube has another oval opening 2.5 cm. long and turned towards the thermometer.

The holes below serve to allow the condensed vapour to mix with the boiling liquid, whilst the oval hole at the top serves to carry off the watervapour. The thermometer which is provided with an india-rubber ring may be connected airtight with the lid by means of a screw. The second small silver condenser *B* is 1.5 cm. wide and

may also be closed at the top by means of a screw. Through this tube, salts are introduced into the apparatus. Two of these instruments are placed in a copper waterbath with two cylindrical openings from the bottom to the lid. The edges of the lids of the silver cylinders rest on the lid of the copper waterbath which is 22 cm. in height. The bottom of the silver cylinders, therefore, do not fall within the plane of the bottom of the copper waterbath. The waterbath has a diameter of 24 cm. and has besides the two cylindrical openings already mentioned, two other holes in the lid; through one of these passes a thermometer and through the other the tube of a large condenser. The arrangement is shown in Fig. II.

Both the condensing tubes  $A$  and  $A'$  are connected by means of the india-rubber tubes  $a$  and  $a'$  with the Tpiece  $T$ , whilst the latter may be connected with the manostat by means of the tube  $m$ . The heating of the waterbath takes place by means of two small luminous flames of two Bunsen burners, whilst underneath each silver cylinder a Bunsen-burner was placed, the flame of which was so regulated that it just touched the bottom of the cylinder.

As regards the arrangement of the manostat I still have to mention that I have replaced the aspirator by a water-suction air pump. To be able to regulate the diminution in pressure in the suction-pipes, I connected it with the following arrangement consisting of a glass cylinder closed by a doubly perforated cork. Through the one hole passes one of the tubes of a Tpiece which stops just underneath the cork. Through the other hole is introduced a long glass tube which may be moved up and down with a little friction. The glass cylinder is almost filled with water. If now, the Tpiece is linked to the suctionpipe of the pump, the suction may be easily regulated by pushing the long tube more or less down into the water. This arrangement works very regularly and easily and for my purpose it is preferable to an aspirator.

The second boiling vessel filled with water serves to keep the operator well informed about the action of the manostat. A change of pressure in the apparatus of 1 mm. of water causes a change in the boiling point of  $\pm 0.003^\circ$ .

#### *Preliminary observations with the new Apparatus.*

It was first of all necessary to ascertain what kind of nucleus ought to be put into the silver cylinders to prevent overheating.

My first trials were made with "shot" but the result was not satisfactory as overheating could not be entirely prevented in this manner and it seemed to me desirable to choose a substance of a

lower specific gravity. The choice fell on enamel grains with some silver (tetrahaedra) and experiments made with these gave very satisfactory results. With a constant pressure, the boiling point of water remained constant to  $0.002^{\circ}$ ; introduction of more enamel grains had no influence on the boiling point. Secondly, it had to be ascertained in how far the indication of the thermometer depended on the height of the column of liquid above the bulb. Experiments showed that a displacement of the thermometer of 1 cm. causes a difference of  $0.010$ — $0.030^{\circ}$  in its indications. On adding water in such quantity as to increase the depth above the bulb by 1 cm. a change of temperature was noticed which was always larger than that caused by a 1 cm. displacement of the thermometer, but the change of temperature was always smaller than  $0.030^{\circ}$ . This phenomenon may be explained by the fact that in the latter experiment the mercury bulb remains in the same liquid layer, whilst in the first experiment it was transferred to a layer of a different "mixing".

It is not a matter of astonishment that, even, when, using these boiling vessels, a change in the position of the thermometer causes a change in its indication and about to the same extent as I noticed with glass vessels, if we consider that the vessels have a diameter of 6 cm. At a very small distance from the side, the influence

READINGS OF THE THERMOMETERS.

Left Thermometer.	Right Thermometer.
1.610	2.100
1.598 1 c.m. higher	2.100
1.610 " " lower	2.099
1.598 " " higher	2.100
1.578 2 " "	2.100
1.553 3 " "	2.099
1.550 4 " "	2.100
1.550 5 " "	2.100
1.550 4 " "	2.099
1.552 3 " "	2.099
1 576 2 " "	2.099
1.598 1 " "	2.099
1.610 0 " "	2.099

A. SMITS. Determination of the decrease in the vapour tension of solutions by means of the determination of the increase in the boiling point.

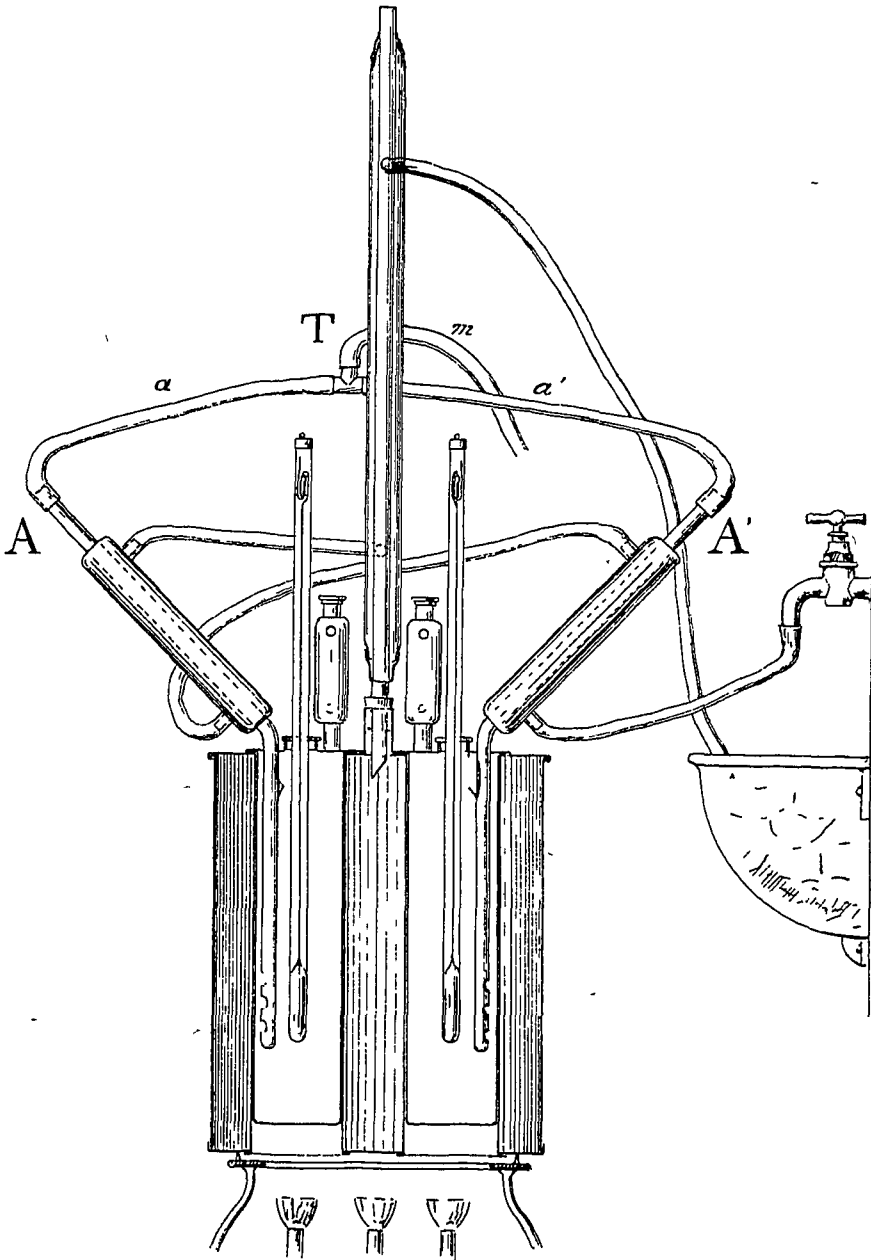


Fig. II.

of the conductivity of the silver may be perceptible, but it is not astonishing that this influence is no longer noticeable at a distance of 3cm.

In using these vessels, I again noticed that the lower down the thermometers are placed in the liquid, the smaller becomes the difference in temperature between the different liquid layers. In the following table, the thermometer on the left is displaced each time 1 cm. whilst the position of the one on the right was left unchanged.

It will be noticed from this table that, when the thermometer was raised by 3 c. m., the mercury reservoir was surrounded by vapour. It is plain, that, if we want to get different concentrations by adding salt to the water or to the solution, we must determine beforehand what will be the influence at that position of the thermometer, of a definite increase of the depth of liquid above its mercury reservoir, so as to be able to make a correction if necessary. If still more concentrated solutions are to be examined, it is desirable to avoid the correction by successively introducing into the apparatus equal quantities of solution and taking care not to alter the position of the thermometer. I next made the following experiment to compare the two BECKMANN thermometers.

Distilled water was introduced into both boiling vessels and the boiling point read off, the pressure being kept constant by means of the manostat. The pressure was then changed to such an extent, that the thermometers fell about  $0.5^{\circ}$ . After some time the thermometers were again carefully read off. This experiment was repeated at different tensions.

I herewith communicate some of the results.

Thermometer I	Thermometer II	Difference in the Readings.
1.457	1.195	0.262
I 0.884	0.622	0.262
2.658	2.076	0.582
II 2.058	1.474	0.584
2.090	1.508	0.582
III 1.614	1.030	0.584
1.610	2.100	0.490
IV 1.285	1.775	0.490
	eto.	



The result was very satisfactory as the readings of the boiling points only showed a difference of at most  $0.003^\circ$  when the temperature was lowered to the extent of  $\pm 0.5^\circ$ . Finally it was ascertained what influence was exercised on the boiling point by the method of heating. An experiment showed that the turning of the flames either up or down, did not affect the boiling point as long as, the liquid was kept actively boiling.

#### *Way of Experimenting.*

The experiment may now be made as follows: — First of all distilled water is introduced into both boiling vessels, and also grains of enamel and silver tetrahaedra, whilst the quantity of water, intended for the vessel in which salt is afterwards to be dissolved, is being weighed. The four burners are next lit, water being allowed to flow through the large condensers A and A'. When the water boils both in the copper waterbath and the silver cylinders, the flames under the waterbath are turned low and those under the silver vessels are regulated. By means of the rubber tube *m*. the silver cylinders are connected with the manostat and the latter is set in action. To know the pressure which exists in the apparatus during this first experiment, the barometer and the watermanometer of the manostat are read off.

After a quarter of an hour, both the thermometers are read off by means of a magnifying glass and the correction with the manostat is interrupted. The burner underneath the vessel intended for the salt is removed and water is passed through the small condenser. The stopper of the small condenser may then be removed without fear of any loss of watervapour. A weighed quantity of salt is now introduced and the stopper reinserted. The burner is now replaced underneath the boiling vessel, while the water is allowed to pass for some time through the small condenser to rinse down small particles of solid matter adhering to the inside of the condenser by means of the condensed steam. After a while, the boiling vessels are again connected with the manostat and the latter is so arranged that the boiling point of the salt solution is *the same* as that of the water; the thermometers are read off at intervals. The fall observed in the thermometer which is placed in the boiling water, corresponds with the decrease in vapour tension of the solution at the temperature of the salt solutions, which is the same for every concentration.

The results of my investigation will be communicated after the close of another investigation, which I have started with Mr. PH. KOHNSTAMM

as to the question whether generally speaking the temperature of the vapour of any boiling liquid or of a solution is the same as that of the liquid.

I may mention here that H. B. HITE<sup>1)</sup> and H. C. JONES<sup>2)</sup> have succeeded in constructing an apparatus, which gives very satisfactory results with certain solvents. Both have remembered, that in the first place care must be taken that the condensing liquid shall not come in direct contact with the thermometer. The method of JONES is much preferable to HITE's method on account of its simplicity and also because it gives better results when using solvents of a high boiling point. When however I tried the process, using water as solvent, I found that the results were then not very accurate. Although in JONES' method, a displacement of the thermometer exercises little influence on the boiling point as the mercury reservoir is entirely surrounded by metal, the boiling point is sensibly influenced by the method of heating. I further found that the method of S. L. BIGELOW<sup>3)</sup> (heating by electricity) may give very good results in the case of non-electrolytes, if the platinum wire is not twisted into a spiral but left straight. If the wire is then passed through a small Utube the vapour bubbles do not come into contact with the mercury reservoir of the thermometer, but they ascend at both sides of the thermometer. Operating in this manner the boiling point is constant when using the same number of ampères. This method is not at all applicable in the case of electrolytes on account of electrolysis setting in. An attempt which I made, to get a constant boiling point by heating with a boiling liquid instead of a flame, ended in failure. I used liquids of different boiling points varying from 105° to 183° but did not obtain a constant boiling point in this manner.

The result of my investigation is, therefore, as follows :

The apparatus used till now for the determination of the increase in boiling point of aqueous solutions give very satisfactory results in the determination of molecularweights but they are not sufficiently delicate to study the decrease of vapour tensions. For this purpose metallic boiling vessels seem to be desirable, also an arrangement which enables us to regulate with great accuracy the pressure above the boiling solutions and to keep the same constant.

*Amsterdam, Jan. 1900. Univ. Chem. Labor.*

<sup>1)</sup> Amer. Chem. J. 17, 502.

<sup>2)</sup> Zeit. Phys. Chem. 21 114.

<sup>3)</sup> Amer. Chem. J. 22 280.