Chemistry. — *"Saline solutions with two boiling points and phenomena connected therewith."* By Prof. H. W. Bakhuis Roozeboom.

(Communicated in the meeting of December 28, 1901.)

The present communication is connected with my researches on the vapour pressure curves of saturated solutions which were completed as far back as 1889. These researches related to systems in which gases and water, water and salts, or ammonia and salts were the components. They led to the result that in all cases the vapour pressure curves of saturated solutions, that is of solutions which are in contact with a solid phase, have a similar course, it being immaterial whether the solid phase is one of the two components or a combination of them. In the case of water and salt we start at lower temperatures with less concentrated solutions. Generally the concentration of the saturated solution increases on raising the temperature, so that in the ideal case we finally arrive at the melting point of the salt which forms the solid phase, which may be either a hydrated or anhydrous salt. In all cases in which that melting point is attainable, the vapour pressure curve shows the form indicated in the annexed figure *A B C*, from which it
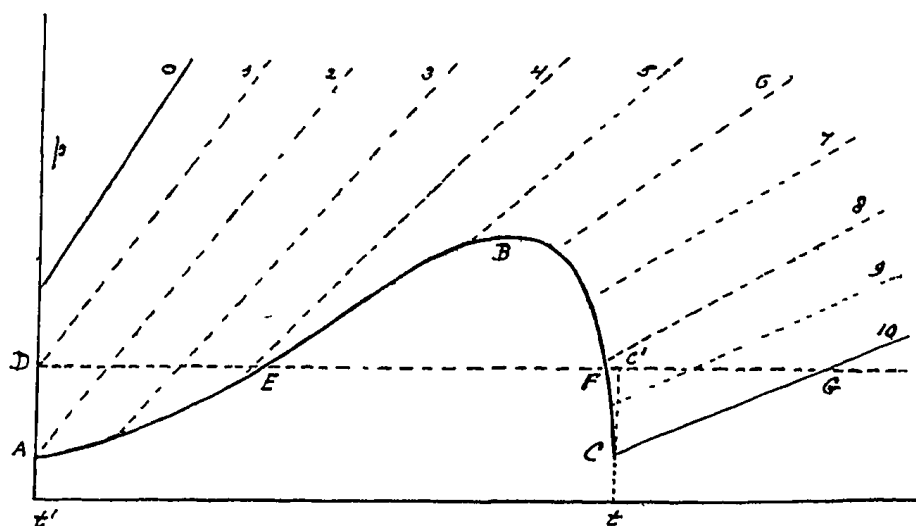
is seen that the vapour pressure of the saturated solution increases first from *A* to *B*, reaches a maximum in *B* and then decreases from *B* to the melting point, *C*, of the salt.

In order to indicate the increasing concentration of the solution

the lines 0—10 have also been drawn, these lines representing the vapour pressures of water and of solutions containing 10, 20...100 mol. per cent of salt, so that 10 represents the vapour pressure of the fused salt.

On the line AB, the evaporation of the saturated solution takes place when heat is supplied. If we disregard the small quantity of salt in the vapour the following process takes place:

Saturated solution → solid salt + water vapour.

As long as the solution is very rich in water, the evaporation of the water absorbs more heat than is yielded by the solidification of the salt dissolved therein. Consequently the vapour pressure increases with the elevation of the temperature. With the elevation of the temperature, however, the concentration of the solution is increased and a point B will be reached where these two quantities of heat become equal; here the thermic effect becomes *nil* and this point is the maximum.

At still higher temperatures and still more concentrated solutions on the part BC of the curve, the evaporation of the small quantity of water would on the other hand absorb less heat than that yielded by the crystallisation of the large amount of salt dissolved therein, consequently the evaporation of the saturated solution would evolve heat; therefore the vapour pressure now decreases.

If the evaporation of the salt is disregarded the line BC ought to end vertically in C [1]).

Up to now this peculiar course of the line ABC was only observed by me in the case of solutions saturated with $Ca\ Cl_2 . 6\ H_2O$ [2]). Although quantitative agreement was found with the course calculated from the quantities of heat, the pressures were here so small that the example was little suited to bring out the great significance of the matter.

As other phenomena outside the region of salts with water could only find their explanation in the course indicated by the vapour curve, I thought it desirable to further examine this curve and the phenomena connected with it by means of other examples.

Dr. Smits, to whom I wish to express here my thanks, at my request took charge of the experiments. Our choice fell on some

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[1]) Van 't Hoff. Vorlesungen I. 35 (1898).

[2]) Recueil trav. Chim. Pays-Bas. 8. 100 (1889).

anhydrous salts. Among these many are known whose curve of solubility may be continued up to their melting point C. If this melting point is situated far enough above 100°, the solubility at this temperature is still small enough that the saturated solutions belong to the part AB of the vapour pressure curve. If we now draw a line $DEFG$ parallel to the temperature axis at a height of $p = 1$ atm. this will intersect the vapour pressure curve first in a point E which is situated above 100° and indicates the temperature at which the saturated solution has a vapour pressure of 1 atm.

If, therefore, we start with a saturated solution at a lower temperature, the vapour pressure will rise from A to E owing to the continuous solution of solid salt caused by the heating, but in an open vessel it will not be able to get above that point, for, on further heating, the solution will evaporate to dryness while the temperature remains constant. For we have got here three phases, solid salt, solution and vapour at a constant pressure of 1 atm.

The same result is obtained in a still more striking manner when we start with a dilute solution boiling at t'. Owing to the boiling its concentration will increase and so we travel along all the points of the line DE until the saturation point E is reached. The boiling point does not rise any further because in proportion as the water evaporates solid salt is deposited and the concentration remains unchanged.

This state of affairs has been repeatedly observed by different investigators. We were satisfied with convincing ourselves that the temperature in E remains very constant if the regularity of the boiling is promoted by passing steam, and the source of heat is an oilbath and not a naked flame. We will call the point E the first boiling point.

As soon as the solution is quite evaporated, the temperature may rise and so we further proceed along the line EF while the salt remains exposed to water vapour of 1 atm. This line EF now intersects the vapour pressure curve of the saturated solution for the second time at F. As soon as this point was exceeded we should arrive, along FG, in the region of the unsaturated solutions. Consequently a new solution must form in F.

In F, therefore, a solution is formed from solid salt and aqueous vapour of 1 atm. pressure, which being just the reverse of the evaporating of the saturated solution on branch BC, will absorb heat. Consequently, on supplying heat the temperature in F remains again constant until all the salt has been solved for which generally but very little water is required.

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From here we proceed with continued heating and constant loss of water along the line FG to solutions gradually getting 'poorer in water, until we should have reached in G the boiling point of the salt itself.

I will now call the point F the second boiling point of the saturated solution. This solution, however; will not show the phenomenon of boiling on heating but on cooling. We may for that object proceed along the reverse way, melt the salt, bring it in contact with water vapour which would yield the solution corresponding with C and cool the same. If we continue passing H_2O over or through the liquid this will absorb more of it as t decreases until the point F is reached. On further cooling, solid salt would crystallise and the pressure consequently increase along FB; this not being possible at 1 atm. pressure the liquid in F boils to dryness on cooling — the temperature remaining again constant.

It is a very remarkable sight to see the boiling start as soon as the hot liquid commences to deposit solid salt and the phenomenon may be accelerated by taking the vessel out of the oilbath in which the melting of the salt and its saturation with aqueous vapour took place. The quicker the vessel cools the more rapid the boiling takes place. On continuing to cool, absorption of aqueous vapour ought of course, to take place again at E.

The following table contains the observations collected by Dr. Smits.

Salt.	1st boiling point	2nd Boiling point	Melting point
K NO₃	115	331	334
Na NO₃	120	310	313
Na Cl O₃	126	255	261
Ag NO₃	133	191	208
Tl NO₃	105	196	205

From this list it appears that the second boiling points are generally situated close to the melting points. This follows from the small value of the temperature interval which will generally exist in systems containing salts and water between the points B and C on account of the great heat of evaporation of the water, causing the point B, and even more so F, to correspond to solutions containing very little water.

For salts with low melting points the 1st boiling point will generally be situated at higher temperatures (Tl NO$_3$ does not conform to this rule) because the solubility at lower temperatures is generally greater than with salts having a high melting point. In such a case the distance from E to C and therefore also from E to F becomes smaller. This will as a rule be coupled with the fact that the maximum pressure at B is lower. Of the examples cited, Ag NO$_3$ has been more closely investigated.

Drs. Cohen and Smits, in a preliminary experiment, found the following vapour pressures of the saturated solution.

t	p		t	p	
133°	760	mM.	170°	1010	mM.
135°	800	»	185°	900	»
150°	960	»	191°	760	»
160°	1000	»			

From this we derive a maximum at 167° and 1015 m.m. The lower the maximum point of the curve, the greater is the chance that the points F and C will lie at widely different temperatures because the part of the curve BC must now bend round more suddenly in order to end vertically in C. The greatest difference between the second boiling point and the melting point has been found in the case of Ag NO$_3$. If we take salts with a still lower melting point, the maximum pressure may then fall below 1 atm. and the line $DEFG$ will, therefore, lie entirely in the region of the unsaturated solutions above the curve.

Such salts will therefore, completely liquefy, at lower temperatures, in aqueous vapour of 1 atm. pressure and this solution will never deposit solid salt when the temperature is raised.

Such a case occurs for instance with NH$_4$ NO$_3$ (m. p. 164°) and of course always with salts melting below 100° as was shown in the case of ammonium acetate (m. p. 89°).

In the case of such salts the two boiling points of the saturated solutions can only appear at a lower pressure or they may appear at 1 atm. if a more volatile solvent is taken which boils below the melting point and in which the solubility of the salt at lower temperatures is not too large. Dr. Smits succesfully used alcohol in the case of NH$_4$ NO$_3$. The alcohol boiled at 78°.4, the first boiling point of the saturated solution was situated at 83°, the second at 161°, therefore 3° below the melting point.

Consequently there can be no doubt about the generality of the

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phenomenon. A single remark may show its importance in explaining several widely varying chemical processes. First of all, attention may be called to the occurrence of water in plutonic rocks. BUNSEN [1] when carrying on his investigations on the Icelandic rocks suggested that liquefied rocks might have absorbed water. Since GAUTIER has lately demonstrated the presence of 1 to 2 per cent of water in all kinds of igneous rocks, this possibility has well nigh become a certainty. BUNSEN, however, could only account for the absorption by assuming the existence of enormous pressures. The investigations and views now communicated lead to the belief that the absorption may possibly take place at a very low pressure [2]; and it is not even precluded that afterwards on cooling and solidification, the dissolved aqueous vapour did not escape owing to supersaturation phenomena assisted perhaps by rapid congealing, or because, on cooling, hydrated silicates are deposited first. Owing to our complete ignorance as to the situation of the vapour pressure curves of solutions of anhydrous and hydrated silicates when close to their melting points, it is not possible to form a decided opinion.

But we have already got a better insight in a totally different sphere of phenomena, namely the oxidation of melted metals. The system water $+$ salt is indeed quite comparable with the system oxygen $+$ metal and therefore a hydrated salt with an oxide. Of late it has been abundantly proved that all kinds of melted metals dissolve the gases of the air, oxygen in particular. Whether we must consider this to be a simple solution or a solution of the oxide makes no difference for in either case the quantity of oxygen dissolved is dependent on p and t. The melting point of the metals is lowered thereby even much more than was formerly believed, for instance 20° for silver and 16° for copper. With a free supply of air the absorption therefore takes place at $^1/_5$ atm. oxygen pressure.

A line similar to $AEBFC$ necessarily exists for the oxygen containing liquids saturated with solid metal. If now a horizontal line drawn for $^1/_5$ atm. intersects this line below the maximum it means that on cooling to the point F the metal will crystallise and all the dissolved oxygen will be expelled. This phenomenon is shown for instance by silver; it is known under the name of spitting.

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[1] Lieb. Ann 61. 271. (1847).

Pogg. Ann. 83. 237. 240. (1851)

[2] It is no objection that the melting temperatures are situated very far above the critical temperature of water, as we are dealing here with solutions containing very little water whose critical temperature is therefore considerably raised.

This spitting therefore takes place at the point called above the second boiling point. A similar phenomenon is shown by lead oxide which on melting also absorbs excess of oxygen but releases it on cooling.

On the other hand it is not shown by copper, either because the line CFB cannot be continued up to the maximum, or because this maximum is situated below $\frac{1}{5}$ atm. so that in the presence of air the absorption of oxygen will cause the formation of Cu_2O.

In all these cases, a point corresponding with the first boiling point of salt solutions does not appear to exist because before that time other vapour pressure lines appear in connection with the fact that at lower temperatures the lower or higher oxides are stable. As to the exact conditions of their formation much might be deduced from existing investigations, which I must, however, pass over here.

The foregoing may also be applied to the absorption and loss of H_2, CO_2 and other gases, and to the formation of chemical compounds with those gases.

Chemistry. — "*The Enantiotropy of Tin.*" (VII). By Prof. ERNST COHEN. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of December 28, 1901)

1. Through the kindness of Prof. PAUL of Tübingen who informed me that a very striking case of *tin plague* had occured at Ohlau in Silesie, I am in a position to communicate some particulars about this case.

The case owes its importance to the dimensions of the corrosion. At my request Dr. HAMBERGER of Ohlau gave me some further information about the matter.

The catholic church in the said village possesses an organ which was repaired in the year 1833. While of the newly fitted pipes no less then 28 became corroded in a very high degree, the old pipes were not affected. The phenomenon was again noticed for the first time 18 years ago (1883). The two accompanying illustrations taken from photographs show to what extent the pipes have been attacked. According to Dr. HAMBERGER the corrosion is still going on.

It is worthy of notice that the wooden roof of the church is situated immediately above the pipes, causing the church to be very warm in summer but very cold in winter time.

The average winter temperature at Ohlau is — $1°,64$ C., the average yearly temperature + $7°,97$ C.