

CCCXVIII.—*The Influence of Intensive Drying on Inner Equilibria. Part III.*

By ANDREAS SMITS.

THE author's theory of allotropy (*Chem. Weekblad*, 1910, 7, 79, 155; *Versl. Akad. Wetensch. Amsterdam*, 1910, 18, 808; *Z. physikal. Chem.*, 1911, 76, 421) is based on a hypothesis consisting of two parts. The first part states that every phase, and therefore also every crystalline phase, of an allotropic substance is a state which in certain circumstances can behave as a poly-component phase. The second part states that this behaviour must be attributed to complexity, *i.e.*, to the existence of different molecular species; when these are in inner equilibrium, however, the behaviour of the system is unary, *i.e.*, it behaves as a one-component system.

When this theory was published, it was pointed out that such a single substance would be expected to behave as a poly-component phase under two conditions, *viz.*, during rapid working or by use of a negative catalyst.

In 1912 (J., 101, 2339) H. B. Baker and Mrs. Baker showed that intensive drying had the effect of raising the boiling points of nitrogen trioxide and nitrogen tetroxide by  $44^{\circ}$  and  $47^{\circ}$  respectively. These results, which were unknown to me until 1921, seemed to indicate that in the moist liquid an inner equilibrium exists between different species of molecules (simple and complex molecules), and that either this inner equilibrium was fixed or the inner transformations were retarded by intensive drying.

In these experiments it seemed therefore that we had a very distinct confirmation of the theory of allotropy, and that intensive drying was an excellent method of proving the complexity of a so-called single substance (*Z. physikal. Chem.*, 1922, 100, 477). The results published by Baker (J., 1922, 121, 568), showing a great elevation of boiling point in ten liquids that had been intensively dried for several years, supplied a further confirmation of the theory, since several of these liquids were regarded as quite normal, single substances. This increase in boiling point might possibly have been ascribed to great superheating (rendered possible in some unknown way by intensive drying, see p. 2407), had not Baker found exactly parallel effects in the surface tension and vapour density, the latter being 2—3 times that found with moist liquids (this vol., p. 1051).

These results seemed to point to an inner equilibrium between different species of molecules in the moist liquid, as postulated by the theory. To explain the behaviour of the intensively dried substances as a whole, the author assumed that intensive drying causes first a retardation of the velocity of the establishment of, and possibly also a displacement of, the inner equilibrium, and finally a fixation of it ("The Theory of Allotropy," 1922, p. 310; J., 1924, 125, 1068).

Although this hypothesis was very probable, it still lacked a direct proof. The author therefore studied the influence of intensive drying on the vapour pressure. If the establishment of inner equilibrium is retarded, it will be manifested by a retarded change of the vapour pressure with temperature and by a temporary decrease of the vapour pressure after partial distillation.

A displacement of the inner equilibrium, however, will be revealed by a change of the vapour pressure at constant temperature, whilst a fixation of the inner equilibrium, as the final state of the process of intensive drying, should enable us to separate completely the different molecular species of the so-called single substance.

I wish to state emphatically that these studies can give us a proof of the explanation of the intensive drying which I have advanced. These considerations explain the behaviour of dried substances without making any special assumptions about the "mechanism"

of the action of the water molecules, as indeed every thermodynamical consideration does. A theory about that "mechanism" will undoubtedly be advanced before very long; it will not displace the present theory, however, but will complete it. It is necessary to emphasise this point because it seems that some confusion still exists on the matter.

(1) *Discussion of Vapour-density and Vapour-pressure Determinations.*

In an earlier paper we showed that intensively dried hexane in rapid evaporation behaved as a mixture, and we will shortly publish a detailed confirmation of this fact. Also, changes of vapour pressure at constant temperature, and without distillation, have been found in some cases, but even after several years' drying these changes are relatively small. On the other hand, Baker's experiments on the abnormally high vapour densities (*loc. cit.*) seem to contradict these results.

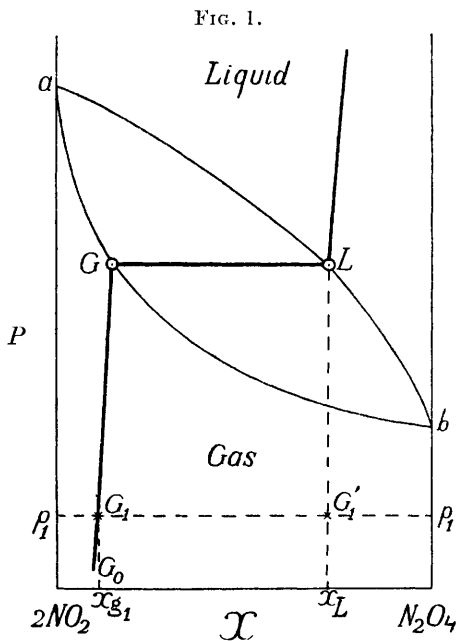
It was most unlikely that our carefully purified liquids, dried in either small or large apparatus for 2—5 years with a relative very large quantity of purest distilled phosphorus pentoxide, would be less completely dried than those of Baker; and it was therefore probable that there was some simple explanation of this apparent contradiction. Since studies of "velocity" phenomena, such as rapid distillation and rapid heating, showed rather large effects, whilst "equilibrium" phenomena, such as the vapour pressure, revealed little or no effect, it was obvious that the anomaly would disappear if the properties studied by Baker were actually velocity phenomena.

In reviewing Baker's experiments, we will discuss first his determination of the vapour density by the method of Victor Meyer, taking a simple example, such as nitrogen tetroxide; the  $P$ - $x$  diagram of the pseudo-system at the temperature at which the experiment is carried out is given in Fig. 1 (see *op. cit.*, p. 24, Fig. 32).<sup>\*</sup> Supposing now that, if in inner equilibrium at the given temperature, the coexisting phases are  $L$  and  $G$ , these phases will be present if the little bulb, used in Victor Meyer's method, is filled with moist nitrogen tetroxide. Further, we will suppose that the horizontal line  $p_1 p_1$  corresponds with a pressure of 1 atmosphere. If the bulb is broken, the liquid evaporates, but that evaporation is accompanied by a chemical transformation, namely,  $N_2O_4 \rightarrow 2NO_2$ , and the unsaturated vapour formed is given by the point  $G_1$ , lying on the vapour curve  $GG_0$  of the unary figure, so that the composition

\* The only difference is that the temperature corresponding with Fig. 32 is above the critical temperature of the pseudo-component  $a$ .

of the vapour formed is not  $x_L$  but  $x_{G_1}$ , and it is to this composition that the vapour density found corresponds.

If, however, the nitrogen tetroxide is so intensely dried that, although the inner equilibrium is not yet fixed, the inner transformations are distinctly retarded, the result of the vapour-density determination will now be quite different. This time, when the little bulb is broken, the liquid will to some extent behave as a mixture. Let us suppose, on the one hand, that the liquid behaves as a real mixture; in this case the reaction  $N_2O_4 \rightarrow 2NO_2$  will not take place, and if all the liquid is evaporated, a gas phase  $G_1'$  will be



formed, the composition of which is equal to the composition of the liquid before the bulb was broken. Consequently, the vapour density found will then correspond with the composition  $x_L$ . On the other hand, it is now evident that, if the inner equilibrium is not yet fixed but the inner transformations are only retarded, the composition of the gas phase, at the moment of the reading, will be given by a point between  $G_1$  and  $G_1'$ ; consequently in this case the vapour density will show an abnormally high value, notwithstanding that the inner transformations are not yet stopped,

but only retarded. If it had been possible to wait until the slow substance had reached inner equilibrium before the readings were taken, the ordinary vapour density would have been found, but in this method readings had to be taken quickly, so as to avoid errors due to the diffusion of the vapour into the air column.

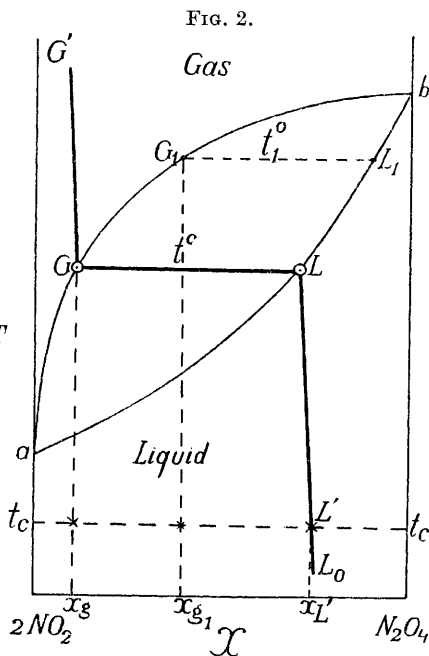
Hence, we see that vapour density, as determined by the Victor Meyer method, gives a value corresponding to a velocity phenomenon and that this method makes it possible to obtain large changes of the vapour density, since it enables us to find *temporary changes* which disappear if one waits until inner equilibrium in the gas phase is established. Similar results would be obtained by Dumas' method.

The vapour pressure of the same dried liquid, at constant temperature, however, is an equilibrium phenomenon, and is still completely unchanged.

It is evident that the determination of the latent heat of vaporisation or condensation is the determination of the effect of a velocity phenomenon, and, indeed, it seems one of the best methods for finding whether a retardation of the inner transformation has already occurred. Considering a  $T$ - $x$  diagram for constant pressure, say 1 atm. (Fig. 2; see also *op. cit.*, p. 27, upper part of Fig. 38), we see that in the pseudo-diagram the unary figure is given by the curves  $L_0L$  and  $GG'$  and the horizontal line  $GL$ ; consequently  $L$  and  $G$  are the coexisting liquid and gas phases at the boiling point.

Suppose now that we determine the heat of condensation, and the temperature of the calorimeter corresponds with the horizontal line  $t_c$ , we have to consider two cases. (1) If the substance behaves in a unary manner, the vapour phase  $G$  will be transformed into the liquid phase  $L'$ , lying on the curve  $LL_0$ , and the heat of condensation therefore contains an exothermic heat of reaction corresponding with the change of composition from  $x_g$  to  $x_{L'}$ . (2) If, however,

the substance has become slow, by intensive drying, and therefore behaves to some extent as a mixture, the point representing the boiling liquid will move along the curve  $Lb$  and that of the vapour phase along the curve  $Gb$  in such a way that the coexisting phases always lie on the same horizontal line—if the boiling point is increased, for instance, from  $t^\circ$  to  $t_1^\circ$ , the coexisting phases are  $L_1$  and  $G_1$ . Now it is evident that the condensation of the vapour phase  $G_1$  in the calorimeter will give rise to a smaller heat of condensation, since the composition of this vapour phase  $x_{g_1}$  is nearer to  $x_{L'}$ , than is  $x_g$ , so that, although the composition of the condensed vapours lies between  $x_g$  and  $x_{g_1}$ , the exothermal chemical reaction is smaller than



in the first case, in which the substance was assumed to behave in a unary manner.

The following observations may be made on the enormous increase in the boiling points of intensively dried liquids observed by Baker. The apparatus contained two distilling flasks, each with two side tubes, and to one of these tubes was sealed the side piece of the other. In the determination of the boiling point, the liquid was distilled by heating the containing flask in an oil-bath, the other flask being cooled in water or in ice. When sufficient liquid had collected in the second flask, this was heated in the oil-bath while the first was cooled. That, after ten years' drying, the inner equilibrium was not yet fixed and the liquid behaved, on evaporation, as a mixture, follows from a remarkable fact mentioned by Baker himself (J., 1922, **121**, 568), namely, that when the condensed liquid from the distillation was again heated, it did not enter into a state of ebullition until the abnormally high temperature had been reached. Further, speaking of his result obtained with benzene, he says (*loc. cit.*), "The liquid boiled at 106° quite steadily. Some of the liquid was distilled from the apparatus into a distilling flask and left for a day exposed to moist air. Its boiling point was found to be 105°." The boiling point of the distillate was consequently the same as that of the residue and was still unchanged after a day in contact with moist air. If the inner equilibrium had been fixed, a distillate with abnormally low boiling point would have been formed, whereas both experiments indicate that just the opposite occurred, thus proving that the inner transformations had been merely retarded, so that the liquid on distillation behaves as a mixture. But since the transformations are not stopped, the inner equilibrium will after some time be re-established in the distillate, which will then show the same behaviour as the initial liquid. The second experiment proves that, notwithstanding the contact with moist air, the liquid was still slow.

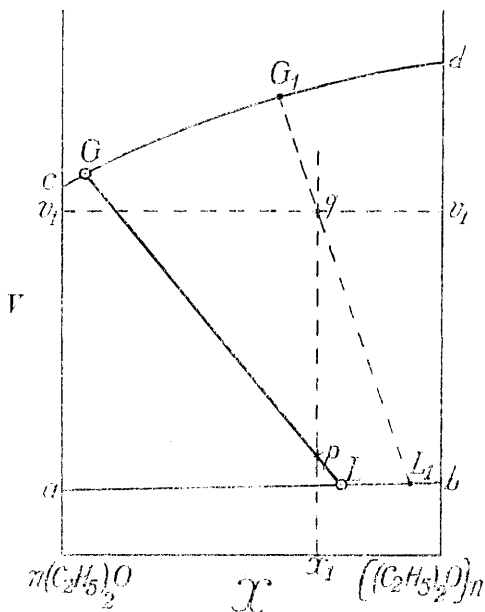
The following experiment indicates the same thing.

I wrote to Prof. Baker that I was very anxious to know what the vapour pressures of his dried liquids were, and he kindly determined that of dried ether, using a dried barometer tube of mercury, surrounded by a water jacket. On being admitted to the tube, the ether gave at 20° a vapour pressure of 374 mm. Hg instead of 442 mm., but this value rose slowly. This also is completely in agreement with a slow establishment of the inner equilibrium, which can be understood most easily by using a diagram (Fig. 3) in which the molecular volume  $V$  is plotted against the composition  $x$  (expressed, for instance, as mols. %). The temperature considered is that at which the vapour-pressure determination is carried out.

At this temperature,  $a$  is the volume of  $n$  g.-mols. of pure liquid

$(C_2H_5)_2O$ , *i.e.*, liquid consisting only of the first pseudo-component [the single molecules  $(C_2H_5)_2O$ ], or the completely dissociated second pseudo-component, under its own vapour pressure, and  $c$  is the volume of  $n$  g.-mols. of gaseous  $(C_2H_5)_2O$  in equilibrium with this liquid phase. The points  $b$  and  $d$  have the same significance with respect to 1 g.-mol. of the second pseudo-component,  $[(C_2H_5)_2O]_n$ . The vapour pressure of pure liquid  $(C_2H_5)_2O$  will be much larger than that of pure liquid  $[(C_2H_5)_2O]_n$ , and the molecular volume of the coexisting vapour is therefore much smaller than that of the vapour coexisting with  $[(C_2H_5)_2O]_n$ . In Fig. 3 it is supposed that the difference is so large (which is quite possible) that  $n$  times the molecular volume of the vapour coexisting with liquid  $(C_2H_5)_2O$  is even smaller than the molecular volume of the vapour coexisting with liquid  $[(C_2H_5)_2O]_n$ , but this is not essential. The line  $ab$ , the binodal for the liquids, gives the molecular volumes of the liquid mixtures, whilst  $cd$ , the binodal for the vapours, gives the molecular volumes of the gaseous mixtures of the pseudo-system. If the system of all these liquids and vapours behaves in a

FIG. 3.



unary manner only one liquid and one vapour coexist, namely those given by the points  $L$  and  $G$ . From the situation of these coexisting phases we see that the liquid phase is rich in the polymeric or complex molecules, whilst the vapour phase is rich in the single molecules. This coexistence corresponds to a definite pressure, the vapour pressure of the liquid in inner equilibrium.

Suppose now that the bulb with dried ether was nearly completely filled, *i.e.*, the volume of vapour was relatively very small. Drawing the nodal line  $LG$ , we can conclude from this that the state of the mixture must be represented by a point on this line and quite near to  $L$ , so that the total composition corresponds with  $x_1$ , for in this

case the quantities of the phases  $L$  and  $G$ , which together form the system are in the ratio  $G_p/L_p$ . After the bulb is broken, the system attains a relatively large volume, given, say, by the horizontal line  $v_1v_1$ ; then we see that, if in the first moments the substance behaves as a mixture, owing to its sluggishness caused by intensive drying, the point  $q$  can tell us what the state of the coexisting phases will be during the first moments. For the state of a mixture of composition  $x_1$  at a volume  $v_1$  is given by the point  $q$  on the nodal line  $L_1G_1$ , and from the position of this point we see that the quantities of the coexisting phases are largely changed and the ratio has now become  $G_1q/L_1q$ . This nodal line is situated in the region of lower pressures, so that the vapour pressure will be abnormally low. But as the inner equilibrium is not yet fixed, the inner transformations, which are only strongly retarded, are taking place in the direction of the inner equilibrium, which will be reached after some time, *i.e.*, the vapour pressure will increase.

In the experiments of Prof. and Mrs. Baker on nitrogen trioxide and nitrogen tetroxide a similar phenomenon took place. Directly after the bulb is broken the liquid must evaporate strongly, changing the composition of the coexisting phases in the direction of lower vapour pressure, *i.e.*, higher boiling points, and as the boiling liquid slowly distils, the behaviour as a mixture is continued.

## (2) *Discussion of Surface-tension Determinations.*

We have now to deal with the determination of the surface tension; it is true that this is not a velocity phenomenon but this property is not trustworthy in this case for the following reasons. Baker (this vol., p. 1055) describes experiments in which a tube of 1 cm. diameter was prepared with two platinum plates 7 cm. long fixed facing each other at the lower end of the tube, and having a thermometer placed between them. Benzene was introduced just to cover the plates, which were connected with a 400-volt battery for some hours, and its boiling point was thus raised to 91°. This effect was not destroyed when the apparatus stood for a few days with the plates disconnected from the battery—the boiling point was 88° and the boiling was steady, not violent. While the boiling was proceeding, the voltage was again applied and within 2 minutes the evolution of bubbles was stopped. Measurements of the surface tension of the liquid indicated a 2—3-fold increase in molecular weight.

I had previously carried out sparking experiments and had been impressed by the efficiency of strong electric fields in drying dielectrics, but had delayed their application in this direction. I therefore repeated Baker's experiment (in collaboration with my



assistant Mr. Bruin), using an apparatus of exactly the same dimensions. Before the platinum plates were connected with the 400-volt battery, the boiling point of the benzene was  $80.5^{\circ}$ , and after the current had passed for 4 hours the boiling point had risen to  $95^{\circ}$  but then sank to  $88^{\circ}$  under steady boiling, even if the platinum plates were disconnected from the battery. The electrodes were now connected together, and after 2 days the boiling point was again determined, without applying an electrical field: it was still high (*viz.*,  $93^{\circ}$ ), but sank again to  $88^{\circ}$  under steady boiling. The bubbles originated from a small part of the platinum wire, fixed to one of the plates.

Now it is known that the most favourable condition for superheating is to heat in a bath, and the best way to prevent superheating is to heat with a small flame applied at a point on the bulb containing the liquid. When heating was effected in the latter way, with application of the electrical field, the benzene boiled at  $80.5^{\circ}$  and the phenomenon mentioned by Baker had disappeared completely, thus showing that his high boiling points may be affected to an unknown degree by superheating.

At the same time we determined the influence of an electrical field on the vapour pressure, since if such a field had any influence on the position of the inner equilibrium, it would also change the vapour pressure. A similar tube with platinum plates was connected to a glass-spring indicator and to a little bulb containing phosphoric oxide. Benzene was introduced in the tube so as just to cover the plates. The apparatus was highly evacuated, and, without application of an electrical field, the vapour pressure was determined over the range  $40-90^{\circ}$ . The experiment was then repeated, applying an electrical field, first of 400 volts and then of 800 volts. The result was that the vapour-pressure lines coincided *completely*. From this we may conclude that the electrical field does not effect any change in the inner equilibrium, and that the increase in boiling point is most probably due to the removal of electrically charged dust particles by the field, in which case superheating occurs more easily when heating is carried out in a bath. Hence we must infer that, had Baker heated the liquid with a very small flame (micro-burner), instead of in a bath, he would have found a normal boiling point for his dust-free liquid.

From his surface tension measurements, Baker calculated that the molecular weight was 2—3 times the normal, but the vapour-pressure determination, and, we may now add, also the boiling-point measurements, showed that the inner state of the liquid is not changed at all. Therefore it seems most probable that, if a liquid by long standing in a sealed tube has become free from dust particles,

the surface tension may be changed, and is therefore no longer a trustworthy criterion as to the state of the inner equilibrium.

### *Conclusions.*

Consequently, my conclusions are : (1) That as yet neither Baker nor I have stopped the inner transformations in the *liquid* phase of a single substance but we have succeeded, as shown especially by Baker's determination of vapour density and latent heat, in retarding the velocity of the inner transformations by intensive drying of liquids, so that the substance behaves as a mixture with regard to what we have termed velocity phenomena. (2) Moreover, we have realised a fixation of the inner equilibrium in the *solid* phase and in the coexisting gas phase of a single substance by intensively drying sulphur trioxide, and our continued investigation of phosphoric oxide points to the same result. (3) With regard to the *gas* phase of a single substance, it is most probable that Baker, using small quantities, has realised a fixation.

In answer to the question whether intensive drying can effect a displacement of the inner equilibrium, we can say that in some cases relatively small displacements are found with liquids, that Baker most probably has realised a very strong displacement with gases, and that we have found a very distinct change in the case of ammonium chloride (preliminary paper, *Rec. trav. chim.*, 1927, **46**, 445).

### *Summary.*

The present state of our knowledge of intensive drying is discussed. It is pointed out that intensively dried hexane in rapid distillation behaves as a mixture, but that the changes of vapour pressure at constant temperature, without distillation, are relatively small even after several years' drying. This appears to be in conflict with experiments in which Baker obtained abnormally high vapour densities for perfectly dry liquids. In seeking an explanation of this anomaly, it is seen that rapid evaporation and distillation are "velocity" phenomena, whereas vapour pressure is an "equilibrium" phenomenon, and that large effects are to be expected in the former case and negligible or zero effects in the latter. The two types of result are therefore reconciled.

Baker's surface-tension experiments alone appeared to present a difficulty, but it has now been shown that this property is not a trustworthy criterion for internal equilibrium, for it may be altered by removal of dust particles from a liquid during long standing.

Further, it has been demonstrated experimentally that an electric field has no influence on the vapour pressure of benzene or on its

boiling point, provided that, during the determination of the latter, superheating be avoided by the use of a small flame instead of a bath.

Our recent results will be published shortly.

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