Allotropy.

By Prof. A. SMITS, University of Amsterdam.

THE liquid state of aggregation or phase of an element under its own vapour pressure is always stable over a certain temperature range, that is to say, from the critical point to the solidifying or melting-point. Below this point the liquid is not stable, for in this case it has gone beyond its range and should have crystallised, but seems to be too indolent or has forgotten to do it.

All liquids can be cooled more or less below the solidifying point without freezing, or, in other words, can be supercooled. This supercooled state is metastable, since although it is not stable it can be realised. But what about the crystallised aggregation? If only one solid state exists the case is very simple, for then we can say, from the solidifying point to lower temperatures the solid state is stable. It is generally found, however, that the same element can exist in two or more crystalline states, or modifications, differing in physical and chemical properties. This phenomenon is called *allotropy*, or better *phase-allotropy*, as the intention is to indicate the appearance of two or more similar *phases*. If at any time two liquid states of an element are found, one may also speak of phase-allotropy. It should be observed that though we have referred here to elements, the same holds for compounds, if the different phases have the same composition.

Two cases must now be distinguished. It is possible that what is said above holds only for one of the solid states, whilst the other modifications are always metastable. This phenomenon is called *monotropy*. The peculiarity of such metastable states is, that contact with the stable state or with a solution, etc., can effect the transformation into the stable state. When such a metastable state can be heated to the melting-point, then it appears that the melting temperature is lower than that of the stable state. Sometimes these melting-points are very close and sometimes they are a great way apart. For example, the stable violet phosphorus melts at 589.5°C ., whilst the metastable black modification melts at 588° , and the metastable white modification at 44.1° . It appears also that the stability is transferred from one modification to the other. For example, over a certain temperature range *A* is stable and *B* metastable, and above a given temperature the position is reversed; *B* becomes stable and *A* metastable, and at this given temperature both of the two modifications can exist stable, side by side, and be in equilibrium. This temperature is called the transition temperature and is completely comparable with the melting temperature, at which the solid and the liquid aggregation are in equilibrium. This phenomenon is called *enantiotropy*. A good example is mercury iodide: below 127° the red tetragonal modification is stable and above this temperature the yellow rhombic modification is the stable one. At 127° , the transition temperature, both forms are stable. It must be remembered here that we have considered liquid and solid phases, being under vapour pressure. It is necessary to mention here that it happens frequently, that whilst under vapour pressure only one crystalline

phase is stable; under higher pressures the transition phenomenon occurs.

Though, consequently, two modifications only can be stable, side by side, at the transition temperature, it happens frequently, owing to retardation, that a stable and a metastable modification exist side by side over a large range of temperature. In this case, consequently, the substance is a *conglomerate* of two modifications, one only of which is stable. This behaviour, as it is only a consequence of retardation phenomena, might have been expected, and has no connexion at all with those to be described below.

Until fifteen years ago it was considered that the so-called single substances were completely understood, and that no new aspects remained for investigation. The connexion between the different aggregations of a single substance was indicated simply by a diagram on which the vapour pressure curves and melting-point curves were drawn, or in other words, by indicating how the vapour pressure changes with temperature and how the melting-point changes with pressure. Such a diagram shows that the vapour pressure of the liquid or of the solid state, at a certain temperature, has a constant value, and the same holds for the melting-point at a definite pressure. As, however, in some cases it was found that the vapour pressure could be changed without altering the temperature, and that the melting-point could be altered without changing the pressure, and that in certain cases the transition temperature could be shifted, it was clear that something was lacking in our knowledge of the states of aggregation.

Some of these phenomena to which I refer are described below. It was found that by partial distillation of most carefully purified crystalline violet phosphorus at 360° , a residue was obtained showing a much lower vapour pressure than the original substance. The original violet phosphorus at 460° had a vapour pressure of 3 atmospheres, whilst the vapour pressure of the residue at the same temperature was 1 atmosphere (*Zeitsch. f. phys. chem.*, 91, 249, 1916; "The Theory of Allotropy," p. 214). Further, it was found that the melting-point of violet phosphorus was considerably lower when the substance was slowly heated, than that observed when the heating was carried out quickly. The maximum difference observed was about 20° , and the melting did not take place at a constant temperature, but over a range of temperature (*Zeitsch. f. phys. chem.*, 91, 249, 1916; "The Theory of Allotropy," p. 195).

In the same way, according to the previous history of the substance, the fat trilaurine could be caused to melt, arbitrarily, at any temperature between 18° and 46° . Rhombic sulphur showed similar results, but on a small scale. As regards the transition phenomenon mentioned above, it was found that according to the rate of cooling the transition temperature of mercury iodide could be raised some degrees ("The Theory of Allotropy," pp. 188, 193, 201, 206), and the same holds for the transformation of β -cristobalite into α -cristobalite, where the effect is more marked. Two crystalline modifications of silica pre-

pared at 1600° showed that the transformation $\beta \rightarrow \alpha$ had already taken place about 18° above the temperature at which the change in material prepared at 1000° occurs.

It is evident that a change of the vapour-pressure of the liquid state causes a change in the boiling-point; consequently a change of the boiling-point indicates that the vapour-pressure of the liquid is altered. A change of the vapour-pressure of the liquid causes also a change of the melting-point, unless the new vapour tension of the solid state has accidentally such a value that the new vapour tension lines of liquid and solid meet at the ordinary melting temperature.

As regards changes of the boiling-point, most interesting results were obtained by H. B. Baker and Mrs. Baker (*Trans. Chem. Soc.*, 51, 2339, 1912). They found that while pure, not intensively dried nitrogen trioxide boils under atmospheric pressure at -2°, the intensively dried liquid, freed from the last traces of water by phosphorus pentoxide, boiled at +43°, that is, 45° higher. With nitrogen tetroxide they obtained a similar result, the boiling-point of the intensively dried liquid having risen more than 47°.

These investigations were the beginning of a series of still more important experiments, carried out by Baker (*Trans. Chem. Soc.*, 121, 568, 1922) on the intensive drying of ten liquids and some solid substances of very different character. The examination of these substances, being postponed by the War much longer than was intended, was delayed eight or nine years. The result was that all the liquids showed a great rise of boiling-point. For example, the boiling-point of benzene had risen from 80° to 109°, that of ethyl alcohol from 78.5° to 138°, that of ethyl ether from 35° to 83°, that of hexane from 68.4° to 82°, that of bromine from 63° to 118°, and that of mercury from 358° to 420°.

Further, it was found that if these intensively dried liquids were allowed to take up a trace of water-vapour, for which purpose contact with ordinary dried air (air which had been passed first through concentrated sulphuric acid and then over phosphorus pentoxide) was sufficient, the liquids regained their original state with the normal boiling-points. In some cases, as with alcohol, the normal state was reached in twenty-four hours, but with benzene it required a month.

At first sight it might be thought that this phenomenon is a simple superheating of the liquid. Indeed it is well known that if a liquid and the wall of the vessel containing the liquid are freed from gases, it is possible to heat the liquid some degrees above the normal boiling-point before boiling occurs. Now if intensive drying facilitates this phenomenon, Baker's results might be described to superheating. For those who are not familiar with the phenomenon of superheating, it may be mentioned that should anyone succeed in heating water in an open vessel, for example, up to 130°, it would be most necessary for the experimenter to place it under cover, since that at any moment an intense and explosive boiling might take place (explosion of boilers). Taking now into consideration the fact that boiling-points up to 60° above the normal boiling-points were observed by Baker and that the boiling took place very quietly, then it is clear that considerable superheating was altogether out of the

question. Corresponding to this, Baker found that at the same temperature intensively dried ether showed a lower vapour-pressure than the moist liquid. The vapour-pressure is a quantity which can be accurately measured, and since a decrease of vapour-pressure corresponds to a rise of the boiling-point, it was proved that the phenomenon observed by Baker was the result of a change of the state of the substance involving a change of the vapour-pressure. That the state of the substance is really changed by intensive drying followed from the results obtained by determining the mean size of the molecules in the intensively dried liquids, for which values were found 2 to 2.5 times as large as in the moist liquids. Consequently, association or polymerisation had taken place.

These results, being completely unsuspected and lying far beyond the horizon of current conceptions, were at the time not generally accepted. It was not possible to say how Baker could have erred, but one could simply not believe that the properties of a substance could change so much.

Though chemists and physicists in general were sceptical, in the chemical laboratory of the University of Amsterdam the results obtained by Baker were received with great enthusiasm, since there in 1911 a theory had been put forward by means of which such results could be easily explained. Baker's results were, indeed, a valuable confirmation of the new theory ("The Theory of Allotropy," 1922).

This theory assumes that every state of aggregation, even of the most simple substance, in reality is complex, that is to say, it is built up of molecules of different kinds. Taking, for example, benzene, it is assumed that in each state of aggregation, namely, gaseous, liquid, and solid, it consists of different kinds of molecules. For simplicity only two different kinds of molecules are assumed, indicated by the indices α and β , thus $C_6H_6\alpha$ and $C_6H_6\beta$. In general, we cannot say beforehand in what way these kinds of molecules will differ. First, it is possible that these molecules are equal in size but different in structure, and these differences may be very small. Secondly, the molecules may be of different size. With benzene it is probable that the different kinds of molecules differ in size, and for simplicity we shall assume here that one kind is a simple molecule, C_6H_6 , and the other kind is an associated molecule $(C_6H_6)_n$, formed by combination of n simple molecules to form a new large molecule. Let us consider now pure benzene. This liquid boils at 80°. Supposing we had a liquid consisting only of simple molecules C_6H_6 , then this liquid would be more volatile, would have a higher vapour-pressure and a lower boiling-point than ordinary benzene, let us say 70°. If we had, on the other hand, a liquid containing only the larger molecules $(C_6H_6)_n$, this liquid would be much less volatile, and would have a much higher boiling temperature, let us say 150°. Ordinary benzene boils at 80°, since in this liquid, molecules of the liquid boiling at 70° and molecules of the liquid boiling at 150° are present side by side.

It is natural then to ask: Is benzene a mixture? Certainly it is, for that is exactly what these considerations indicate. Benzene vapour and benzene liquid are gaseous and liquid mixtures, and crystallised benzene, that is to say, every crystal of the solid

state, is also a mixture, namely, a mixed crystal, but, as we shall see, they are not ordinary mixtures.

By adding water to alcohol we obtain an ordinary mixture, and the properties of that mixture depend on the proportion in which the substances are mixed. A certain mixture begins to boil at a definite temperature, begins to solidify at a definite temperature, and shows a definite vapour-pressure at a certain temperature. The property by which a liquid is known as a mixture is this, that by distilling off a portion, or by solidifying a part, we obtain a liquid of different composition and therefore different boiling-point, different vapour-pressure, and different solidifying point. The easiest manipulation is partial distillation. Applying this method, for example, to a mixture of equal quantities of water and alcohol, then a vapour escapes which is richer in alcohol than the liquid, and the remaining liquid has become poorer in alcohol, effecting a decrease of the vapour tension and an increase of the boiling-point.

This decrease of the vapour-pressure and increase of the boiling-point by partial distillation is a characteristic property of a mixture. If a solidifying mixture gives mixed crystals—*i.e.* crystals in which all the substances we have mixed are present, just as every drop of a liquid mixture contains each part present (a mixture of chlorine and bromine is a very good example)—then for these mixed crystals this rule holds just as for liquid mixtures, namely, by partial distillation the vapour tension is decreased.

It is mentioned above, however, that pure benzene is a mixture. Yet if benzene is submitted to partial distillation the properties of the liquid are not changed at all. Vapour-pressure, boiling-point, melting-point are exactly the same as before. What is, then, the explanation of this behaviour, which is characteristic of a true simple substance, whilst benzene is not simple? It seems indeed a contradiction, but it is not so. Although benzene is composed of different kinds of molecules, it behaves as a single substance, on account of the great velocity with which these kinds of molecules are transformed in each other. These mutual transformations are indicated in the following way:

These two very rapid opposite reactions lead to a so-called equilibrium, in which the proportion between the single and the associated molecules, or the composition, has a definite value at constant temperature and pressure. If we have to do with ordinary dried benzene, we have no means of changing this composition, temperature and pressure remaining constant. Let us assume we had an instrument which enabled us, just as a stork catching fish from the water, to catch up and carry off the large molecules in liquid benzene. Still we should not succeed in making the remaining liquid poorer in big molecules, for so soon as the number of large molecules is decreased the small molecules will be associated to form large molecules, until that proportion between small and large molecules is reached which corresponds with the inner equilibrium.

By distilling benzene as rapidly as possible a similar process occurs; the smaller molecules are more rapid than the large ones, and in consequence of this the

smaller molecules will leave the liquid surface in greater numbers per second than the large molecules. Notwithstanding this the liquid does not get poorer in small molecules, since the larger molecules dissociate until the proportion of the different kinds of molecules, corresponding with the inner equilibrium, is reached.

According to these considerations, a so-called simple substance is in reality a mixture, not an ordinary one, but a mixture with an inner equilibrium. Now it is evident that if we were able, for example, in the case of benzene to withdraw the big molecules with a velocity greater than the velocity with which they are formed again, the properties of benzene would change. But in most substances these inner transformations are so rapid that an artificial change of the composition is impossible.

We can say, consequently, that it is the rapid establishment of the equilibrium between the different kinds of molecules of the same substance (inner equilibrium) which makes a substance such as ordinary pure benzene, behave as a true single substance.

Considering the results of Baker's experiments from this point of view, it is not difficult to give an explanation of them. Only one very probable supposition is to be made, namely, that the process of intensive drying effects a decrease of the velocity of the transformation between the different kinds of molecules, and that finally the transformation is stopped completely.

In benzene, not intensively dried, the two opposite rapid transformations,

are taking place, but in intensely dried benzene these transformations take place no longer, and the arrows have no longer any signification; the two kinds of molecules have become strangers to each other; *i.e.* intensively dried benzene has become an ordinary mixture.

What can we say now of this mixture? We have already mentioned above that a liquid consisting exclusively of the small simple molecules, C_6H_6 , would be more volatile and would boil perhaps at 70° , whilst a liquid containing only the big, associated, molecules $(\text{C}_6\text{H}_6)_n$ would be much less volatile and would boil perhaps at 150° . From this it follows that when, by intensive drying, benzene has become an ordinary mixture, it is a mixture of two substances differing greatly in volatility. Heating this mixture in an open vessel, then, as in most cases, principally the more volatile part will escape, by which the remaining liquid becomes richer in the less volatile part, and when the boiling-point is reached the liquid, considerably enriched in the less volatile and higher boiling part, will begin to boil at a temperature higher than the boiling-point of moist benzene.

This explanation has been tested and confirmed (*Jour. Chem. Soc.*, 125, 1068, 1924), but in addition another supposition has been confirmed, namely, that the process of intensive drying effects more or less a change in the proportion between the different kinds of molecules at the drying temperature; *i.e.* it effects a change of the inner equilibrium (*Jour. Chem. Soc.*, 128, 2655 and 2657, 1926). It seems that with the progress of the drying process the molecular proportion mentioned above changes gradually more or less; this is accom-

panied by a decrease of the velocity of the two opposite transformations, until finally *they are stopped completely*. Now it will be clear that the theory is also capable of explaining the phenomenon noted already in the solid state of some substances, for the theory states that every state of aggregation, consequently also the crystalline state of a so-called single substance, is built up of different kinds of molecules. The crystalline state of a single substance is consequently a mixed crystal, not an ordinary one, but a mixed crystal in inner equilibrium.

As I have observed already, the velocity with which the inner equilibrium between the different kinds of molecules is established in the different states of aggregation, seems to be a very characteristic property of substances, so that we can speak of rapid and slow substances. Rapid substances can undergo rapid changes without coming out of inner equilibrium, but slow ones can be disturbed. In the light of these new considerations, the results obtained with violet phosphorus can be explained easily. Violet phosphorus is a slow crystalline substance; it is a slow mixed crystal, and therefore evaporation at relatively low temperatures will cause the remaining mixed crystal to become poorer in the most volatile molecular species, thereby decreasing its vapour tension.

Another phenomenon, mentioned already, showing that the melting-point and transition-point depend on the previous history, can also be predicted by the theory. If the pressure is kept constant and the temperature is changed, it will of course depend on the velocity with which inner equilibrium is established and the rate of change of the temperature, whether for practical purpose inner equilibrium always exists. If the temperature changes so rapidly that the inner equilibrium cannot adjust itself to it, inner equilibrium is not realised, but disturbed conditions are obtained, which are naturally metastable, and the properties of these states, such as specific gravity, solubility, transition-point, melting-point, boiling-point, etc., will deviate from those of the inner equilibrium state. In connexion with this it is clear that it is very difficult or impossible to show complexity with rapid substances. It is easily understood, therefore, that complexity is apparent only in rather slow substances, and as most substances are rapid, the complexity was only proved in a relative small number of cases.

It will be evident now how valuable it is to have a means by which it is possible to change a rapid substance into a slow substance, and finally to bring all inner molecular transformations to rest. A substance to which this has been applied with great success is sulphur trioxide (*Jour. Chem. Soc.*, 125, 2554, 1924; 128, 1108, 1603, 1926). The intensely dried crystalline state has been studied in detail and the phenomenon already found with violet phosphorus was observed here in a marked degree. It was found that sulphur trioxide, dried for one month or longer in a certain way with freshly distilled, purest, very fine phosphorus pentoxide, becomes so exceedingly slow that it behaves distinctly as a mixture. Since the range of temperature and pressure within which that behaviour reveals itself is much more easily approached than in the case of phosphorus, it could be studied more closely. Thus we could obtain by partial distillation substances of nearly

every lower vapour-pressure and, within wide limits, of varying melting-points. The vapour-pressure could at 50° be reduced to 1/15 of its normal value, whilst the melting-point could be raised from 62° to 95°, an increase of no less than 33°. The melting process in such a crystalline state, which has been much changed by partial distillation, is rather dangerous, since in the liquid formed, notwithstanding the intensive drying, in consequence of the higher temperature, inner transformations take place very rapidly. This causes a rapid increase of vapour-pressure, so that the chances are that the apparatus will burst.

The influence of X-rays on such markedly changed crystalline states is also noteworthy. We found that X-rays affect not only the establishment of the inner equilibrium, but also the transformation of the metastable forms into the stable modifications. I have referred here to the phenomena, observed with phosphorus and sulphur trioxide, but recently we have found analogous phenomena with a number of other substances such as phosphorus pentoxide, nitrogen tetroxide, hexane, benzene, etc.

All these phenomena show the complexity of the so-called simple substances, and we may expect that other substances in the intensely dried state will also show complexity, for there is little doubt that complexity is a general phenomenon. Whilst the old ideas of allotropy are completely powerless to explain these phenomena, they give strong confirmation to the principles on which the theory of allotropy is built, while the new phenomena can be explained completely by this theory. The new theory of allotropy shows among other things that in the most simple case the vapour-pressure lines and the melting-point line of a so-called single substance belong to a pressure-temperature-composition model in three dimensions, in which the two different kinds of molecules are the components. These lines take up a particular place in this space model, since they indicate the phases which are in inner equilibrium. But the whole space model refers to the field of the so-called single substance. When the substance is indeed completely dry and inner transformations are stopped, the whole domain of the substance can be studied. So long, however, as the intensive drying is not complete and the inner transformations are only strongly retarded, the same space model shows which phenomena may be expected. As to the different kinds of molecules, I have pointed out that the reason for the existence of these different kinds of molecules must probably often be sought in the existence of different kinds of atoms (*Ber. Sachs. Akad. Leipzig*, 75, 58, 1923), and in connexion with this it is interesting that recently, from the side of physicists, the same assumption has been made on quite different grounds (de Haas, *Kon. Akad. Amsterdam*, 1926).

Finally, to prevent confusion it is necessary to direct attention to the following points. Recently, papers have been published referring to experiments on the influence of 'traces' of water on different properties of substances, as for example solubility, etc. It will be sufficient to state here that these experiments deal with substances containing 'traces' of water *many thousand times* larger than in our cases of intensive drying and are consequently in quite a different field.

From the preceding considerations it follows that

whilst for several years the so-called single substances were considered to have been completely investigated, and it was believed that new points of view could only be obtained by the study of more complicated systems, the close study of these single substances has recently become extremely interesting. From the new point of view already reached, the phenomenon of allotropy with all the various phenomena associated with it and the influence of intensive drying can be surveyed.

In conclusion, one among several interesting questions may be put forward here. Consider for a moment a substance such as benzene, which has become an ordinary mixture by intensive dryings. Benzene is one among the large number of substances for which, after drying in the ordinary way, various physical constants, such as critical-point, melting-point, vapour-tension, specific weight, etc., are determined. Now it cannot be said that these constants have no value; on the contrary, they are very valuable, but they are not physical constants of the pure substance but of impure benzene, contaminated by an extremely small trace of

water. Before the phenomena to which I have referred above were known, one would have attached little value to this observation, and one would have answered, that such an extremely small contamination cannot have any perceptible influence and can therefore be neglected. This is quite true, speaking of contamination in general, but now we know that water is a very special contamination, for on removing it completely, benzene becomes an ordinary mixture and our physical constants are no longer suitable. Thus the new theory opens up another field for investigations, on which many generations of scientific workers may carry out important research. In future the so-called single substances will be really purified, which means they will also be dried intensively. From the mixtures obtained in this way the components will be separated and studied carefully. Thus the components of a so-called simple substance will be discovered, and no doubt will often cause great surprise, since big and noteworthy differences may exist between the different kinds of molecules.

Sea-birds: Their Relation to the Fisheries and Agriculture.

By Dr. WALTER E. COLLINGE.

UNDER the above title in *NATURE* of April 8, 1920 (pp. 172-173), I gave a brief résumé of an investigation on the economic status of the commoner species of sea-birds of Great Britain then being carried out under the auspices of the Carnegie Trust for the Universities of Scotland. In that investigation, large series of each species from various localities during each month of the year were examined, and the food content of the stomach was estimated by the volumetric method. The investigation has now been completed, and a final résumé of the more important results may not be without interest. In all, nineteen species were examined, embracing 2309 specimens.

One of the most striking facts shown by this work is the very small percentage of fish consumed by the common gull, the herring gull, the black-headed gull, the common tern, the little auk, and the puffin. Hitherto, it has been generally assumed that all sea-birds feed upon fish, and that this item of their diet constituted the bulk, but such is far from the case. Of the total bulk of food consumed in a year, fish constitutes only 5.16 per cent. in the common gull, 18.20 per cent. in the herring gull, 3.73 per cent. in the black-headed gull, 18.01 per cent. in the common tern, 1.17 per cent. in the little auk, and 22.22 per cent. in the puffin. In the first three species, much of this small percentage of fish is obtained from shore refuse.

The case of the black-headed gull is most striking and significant. As a destroyer of injurious insects it is a most valuable bird, 24.70 per cent. of its food being of this nature, which is more than that consumed by either the rook or the blackbird. It also takes 4.38 per cent. of neutral insects and 0.19 per cent. of beneficial ones. The nature of the insect food is of considerable interest, both on account of the enormous amount that is consumed, and the particular species. Of these latter, it must here suffice to state that upwards of sixty different species were identified.

Respecting the bulk of food, accepting Newstead's

computation that each bird feeding upon crane-flies will consume some 4000 per day or 28,000 per week, the total quantity destroyed must be enormous. On the Fife-shire coast we have estimated in passing from field to field that at least 5000 birds were present on the land ten miles south of St. Andrews. Such flocks would consume 140,000,000 insects in a week. This, however, is only on a small area. All along the coast and farther inland the same thing is taking place, so that the amount of insect life consumed must be prodigious. Moreover, it must be borne in mind that the percentage of cereals destroyed by this species is only 0.37 per cent. A similar striking record can be shown for the other five species mentioned.

Of the fish consumed, 27 species were identified. The highest percentage consumed of any one species was 9 per cent. in the case of the greater sand eel, 8 per cent. of the lesser sand eel, 6.5 per cent. of the gurnard, and 6 per cent. each of cod and herring; haddock follows with 5.5 per cent., and then gunnel and sprat each 3.5 per cent.; of flat fishes (all species), only 2.5 per cent. was present. Practically the whole of the food of the cormorant, shag, gannet, goosander, red-breasted merganser, and great skua consists of fish, whilst 50 per cent. of the same item forms the food of the guillemot and the black-throated and great northern divers.

The bulk of the fish-food consumed by the nineteen species of birds investigated consists of species that are exceedingly common and also plentiful. There is no scarcity of these fishes, and were they still more plentiful they would in all probability only form additional food for predaceous fishes, and thereby add to the increase of a factor over which man has little or no control.

Of the 2309 stomachs examined, 422 were empty or nearly so. It would seem that if there is any scarcity or lack of food, the female bird is the one to suffer, for of 97 partly filled stomachs of the herring gull,