

perfected form of it, should make it possible to correlate completely all of the intermetallic systems.

Summary

1. Various means of estimating the relative internal pressures of metals are discussed and tables are given.
2. Data are given showing the correlation between these tables and the behavior of binary metallic solutions.

BERKELEY, CALIFORNIA

EXTREMELY DRY LIQUIDS

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RECEIVED AUGUST 13, 1923

The very important discoveries of Baker¹ concerning the boiling points and other properties of highly desiccated liquids have opened a large and most promising field of physicochemical investigation. The startling results which have already been obtained have aroused some degree of skepticism, because of a suspicion that they were irreconcilable with fundamental thermodynamic principles; but I am convinced that no essential conflict exists, and that the chief observations which have so far been made not only may be interpreted thermodynamically, but also permit, with the aid of thermodynamics, some valuable predictions.

At first the experiments seemed to indicate that the removal of the smallest traces of water produced profound changes in the static properties of a liquid, such as might be explained by a large shift of inner equilibrium through the formation of a larger number of complex molecules from simple molecules. Smits² believes that such a change in equilibrium is thermodynamically possible and that it is in fact the explanation of the facts observed by Baker.

With this conclusion I can by no means agree. It is not absolutely prohibited by the laws of thermodynamics alone, but any one who will read the chapter on dilute solutions in the recent treatise on thermodynamics by Professor Randall and myself will see how little is required, besides the laws of thermodynamics, to prove Raoult's law for the infinitely dilute solution. For solutions of moderate concentration its approximate validity has been attested by hundreds of observations of the most varied sorts. The only marked exceptions occur when the solute dissociates, and then the activity of the solvent is diminished two, three, or more times as much as Raoult's law predicts, according as the solute molecule dissociates into two, three, or more molecules. Smits' hypothesis seems

¹ Baker, *Phil. Trans.*, 79A, 583 (1888); *J. Chem. Soc.*, 65, 611 (1893); 81, 400 (1902); 91, 1862 (1907); 101, 2339 (1912); 121, 568 (1922).

² Smits, *Proc. acad. Sci. Amsterdam*, 26, No. 3 (1923).

to imply changes in the activity of the solvent which are thousands or millions times as great as those given by Raoult's law.

Therefore, I think we must conclude that the mere removal of the last traces of water from a liquid could not appreciably change the existing equilibrium between the several molecular species, which might be assumed to exist. If water acts as a catalyst for the process of interchange between one molecular species and another, its removal could only serve to "freeze" the already existing state of equilibrium, by inhibiting further interchange between the various forms.

Such a behavior is well known in the case of liquid sulfur which contains two distinct molecular species known as S_8 and S_6 , which probably have the formulas S_8 and S_6 . When the liquid sulfur contains a trace of a substance very similar to water, namely ammonia, there is rapid interchange between the two species, so that equilibrium follows rapidly upon any change of condition, and the substance behaves like an ordinary pure liquid. But if the trace of ammonia is removed, the change from one species to the other is inhibited, and the sulfur behaves like a mixture. For example, it does not freeze at a fixed temperature, but the temperature changes during the process of freezing.

Let us consider, as a simple case, a hypothetical liquid consisting solely of simple molecules A and complex molecules of a single molecular species B; and let us assume that in the presence of moisture complete equilibrium is instantly established between A and B. Also in the vapor phase we may assume the same equilibrium to exist, although here the proportion of complex molecules might be negligibly small. Essentially, therefore, we may postulate a liquid consisting of a mixture of molecules A and B, and a vapor consisting merely of molecules A, all in equilibrium with one another.

Let us now imagine the removal of the last traces of water, or other catalyst, so as to inhibit the reaction $A \rightleftharpoons B$, in either direction. If this should be done at constant temperature, the vapor pressure will be the same as before, as well as the proportions of A and B in the liquid. But, if the liquid is now heated, more of the A molecules will escape into the vapor phase, and eventually the liquid will consist almost entirely of molecules B. In order to boil this liquid, a temperature must be attained at which either the B molecules themselves vaporize, or the rate of formation of A from B, in spite of the absence of catalyst, is rendered appreciable by the increase of temperature. Both of these processes might occur simultaneously.

This view of the phenomenon is in complete accordance with the latest experiments of Professor Baker,³ carried out in coöperation with Professor Smits. It was found that a sample of carefully dried benzene, similar

³ Baker, *J. Chem. Soc.*, **121**, 568 (1922).

to those which had already shown abnormally high boiling points, could be fractionally distilled, like a mixture of two independent components, the temperature of a thermometer placed above the boiling liquid rising steadily throughout the course of the distillation.

It is conceivable that in some cases the process of fractionation might not be observable and the dried liquid might almost immediately exhibit a constant high boiling point. If in the equilibrium mixture the proportion of A molecules were very small, their distillation from the dried mixture might not be noticeable, and the liquid could be heated directly to the new boiling point at which the vapor pressure of the B molecules would be equal to the atmospheric pressure, or at which the transition from B molecules to A molecules would be sufficiently rapid to give in the vapor phase a mixture of the two species, such that their total pressure would be equal to the atmospheric.

All these considerations lead to the interesting prediction that we shall find liquids with abnormally low boiling points as well as those with abnormally high boiling points. For thermodynamics teaches us that anything which inhibits the reaction $A \rightleftharpoons B$ in one direction must also inhibit it in the other direction, and if, therefore, we could obtain a liquid containing only A molecules, it might have a much lower boiling point than the normal liquid. Thus if the normal vapor consists almost entirely of A molecules we should be able, by passing the vapor through phosphorus pentoxide and then condensing it, to obtain a liquid of very high vapor pressure and correspondingly low boiling point.

It seems likely that experiments with dried liquids and vapor may be conducted without exorbitant expenditure of time. In Baker's experiments the liquids employed had been dried over phosphorus pentoxide through a period of years, but it is to be observed that he depended in the main upon a process of diffusion, or accidental convection, to bring the moisture to the surface of the phosphorus pentoxide, and it probably was necessary to remove the moisture not only from the liquid and vapor but also from the surface of his glass vessel. By employing specially treated glass or some less hygroscopic material for the vessel, and by providing a circulating system which would rapidly carry the material to be dried through the phosphorus pentoxide, it should be possible to lessen very greatly the time required for drying. If such experiments prove to be successful, it should be possible to obtain results more quantitative than any so far secured. Such quantitative results would then be amenable to the same sort of precise thermodynamic treatment which has already been accorded to the case of liquid sulfur.⁴

While I have assumed for the sake of simplicity that the absence of water

⁴ See Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

inhibits a single reaction between a simple molecular species A and a more complex molecular species B, we may anticipate that the actual facts will often prove to be far more complicated than this. There is nothing in the chemical properties of some of the liquids investigated by Baker to lead us to expect any one complex molecule to show exceptional stability. Rather we should expect the formation of double, triple, quadruple molecules, and so on, to be evidence of a tendency in the condensed liquid phase toward the formation of indefinite aggregates, perhaps not entirely dissimilar to those which are produced in the process of crystallization, or at least due to forces similar to crystalline forces in that they operate only between molecules which are brought into close proximity. These, however, are questions which it is hardly worth while to discuss until further experimental information is at hand.

While at present the above explanation of the peculiar properties of dried liquids is the only one consistent with thermodynamics that seems at all plausible, it must be confessed that some of the results obtained by Baker still seem a little mysterious. According to this explanation, the static properties of a liquid, when it is freed from the last trace of water at a fixed temperature, should remain essentially the same. By a static property I mean such a one as the volume, and indeed Baker has found that the density of liquids is the same after thorough drying.

Whether surface tension is to be regarded as a static property would depend upon its method of measurement. If the liquid is allowed to rise in a capillary, a process occurs which is analogous to the formation of a new phase, and the surface tension so measured need not be the same in the dried and the undried liquid. In fact, the results indicate that the surface tension so measured is higher in the dried than in the undried liquids but further experiments in this direction should be undertaken.

Baker has found that the color of liquid nitrogen trioxide changes when the last trace of moisture is removed. This might of course be explained by attributing a very high coloring power to the water itself, but it is conceivable that color itself is not a static property, and that the absorption of light is accompanied by a chemical process which does not occur in the absence of a catalyst.

Perhaps the most puzzling observations made so far are those concerning the freezing points of the dried liquids. In every case the freezing points of the dried liquids have proved to be higher than those of the undried. We know little regarding the mechanism of crystallization. It might have been expected that complex molecular species would crystallize more readily than the simple molecular species, but on the other hand the liquid complex may not be of the sort that would fit into the crystal structure, and if so it would be the simple molecules which would most readily take part in the process of crystallization. This appears

to be the case. If a liquid is dried at a certain temperature to the extent of inhibiting the interchange between simple and complex molecules, and the temperature is then lowered, there will be a larger proportion of simple molecules than there would be in the equilibrium liquid at this lower temperature. The simple species would therefore have a higher activity in the dried liquid, and if it is this species that crystallizes, freezing will begin at a higher temperature than in the case of the normal liquid. However, as the simple molecules crystallize the freezing point should drop, and indeed fall ultimately below that of the undried liquid.

Finally, it is to be remarked that if it is found by experiment that circulation of a liquid through phosphorus pentoxide does not give the same results that are obtained when the liquid stands over phosphorus pentoxide; and if at the same time it is found that the static properties of the dried liquid do differ materially from those of the undried, we should be forced to an explanation which at present seems rather unlikely. It would be necessary to assume that a liquid in the ordinary state is not in the condition of highest stability, but tends to go over on quiet standing to another condition, just as a finely divided precipitate tends to form a single perfect crystal, or as a drawn wire tends to assume a coarsely crystalline condition. If the liquid on standing over phosphorus pentoxide really assumes a more stable state, then the original state could not be restored merely by the addition of a trace of water, but some agitation of the liquid would also be required in order to furnish the necessary energy for the conversion of the liquid into its normal, less stable, state. However, there seems to be nothing in the present stage of the experiments which would indicate the need for adopting so bizarre a conclusion.

Summary

The remarkable effects produced by removing the last traces of water from liquids promise to furnish information of great value concerning the liquid state. The only plausible explanation of these effects that seems consistent with thermodynamics rests on the assumption that water is a catalyst for processes between various molecular states, and that its removal merely inhibits such processes. If this explanation is correct the process of drying only "freezes" an existing equilibrium and (at constant temperature) cannot alter the static properties of the liquid. This leads to interesting predictions, for example, that liquids will be found that exhibit abnormally low, as well as abnormally high boiling points.

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