SOME NEW HYPOTHESES AS TO DIFFERENT STATES OF MATTER

BY N. T. BACON

My mind has never been satisfied with the current reason given to explain why molecules condense from a vessel filled with saturated vapor when the temperature is reduced, for this same reduction should cause a reduction of pressure, even without condensation.

We have as a point of departure in considering this matter several assumptions which seem fairly enough based to be made the foundation for further reasoning. First among these is the consideration of matter in the solid state. Bragg's hypothesis seems to meet with general approval. This is practically that in the solid condition molecules are made up of atoms having their constituent electrons arranged according to a specific plan, so that they are virtually minute crystals continuously combined. This would preclude rotation of the molecules as such. From direct experiment it is evident that in the solid condition matter is generally almost incompressible. Moreover, in this state, these molecules cannot be displaced with reference to each other. We are, therefore, justified in assuming that they lie much as bricks in a wall, possibly not in absolute contact, though, if not, with almost absolutely constant spaces separating them, which would be represented by the mortar between the bricks in a wall; and that they are in three dimensional contact, that is to say, they touch each other up and down, north and south and east and west, so that their spheres of influence (which include the interstitial spaces), to use the word in a geographical sense as distinguished from a geometrical sense, are in contact on all sides.

In the liquid state much of this appears likewise to be true. There is generally no material difference in volume at the point of fusion, though, with the exception of ice, practically all solids are a little heavier than the liquid form of the same substance, so that practically in this state the molecules are again in three dimensional contact as in the solid condition, although the distance between the centers of their spheres of influence probably averages somewhat greater than in the solid condition. The distinction between these two states is sharp, however, in that the liquid molecules can be displaced readily from each other and probably the molecules are rotating around their axes or in orbits or both. The liquid state seems to be almost as incompressible as the solid, and this characteristic of incompressibility follows far up the temperature scale, although in the liquid condition expansion by heat averages greater than in the solid. It would, therefore, appear that in both of these states the expansion is probably due to increase in the diameter of the spheres of influence of the molecules. Bridgman's experiments on the fusion curve of ice VI show that the relative incompressibility of ice VI and water must remain very nearly the same, as from 8000 atmospheres up the curve is virtually a straight line.

Although the liquid condition expands materially as it approaches the critical point, nevertheless we have no reason to consider that there is any change from three dimensional contact of the molecules as they approach this point, although there comes into contemplation the possibility that the rapid increase in volume may be due to molecules in the vapor state dissolved as vapor by other molecules of the same kind in the liquid state. This is analogous to Richards' explanation of the action of water between 0° C and 4° C as due to solution of ice molecules as such, and like S_μ in S_λ.

The data with reference to critical points are insufficient, this point being extremely difficult to work over for most gases, on account of the combination necessary of immense pressure with high temperature. But from such data as we have, we assume that at this point the volume in the gaseous condition is the same as in the liquid condition.

We have seen that in the liquid condition, in spite of the rapidly advancing pressure necessary to maintain simultaneously the liquid and gaseous states, the volume of the liquid, and therefore, probably the volume of the molecule in the liquid condition, or at least the volume of the sphere of influence of the liquid molecule, was increasing rapidly. It appears, however, from the experiments of Andrews and others, that in spite of increasing temperature at least the sphere of influence of the gaseous molecule can be reduced by advancing pressure in spite of advancing temperature when above the critical point.

As we can have present there both liquid and gaseous phases, but beyond this only the gaseous phase, it is evident that the critical point marks the limit at which the substance can exist in the form of saturated vapor and, therefore, that at this point when both phases are in equilibrium the gaseous phase must be saturated. We find, therefore, that at this point the volume of the saturated vapor is the same as that of the liquid and also the specific gravities are the same, so that it seems almost certain that as the spheres of influence completely fill the space occupied by the liquid so that the liquid is immobilized, in like manner the spheres of action of the gaseous molecules must be in three dimensional contact so that for lack of a free path no translatory motion of the individual molecule is possible any more than in the liquid condition, though this motion is characteristic of gases and unsaturated vapors.

Summarizing, so far we seem to have demonstrated that in the solid and liquid conditions we have matter virtually incompressible, though under very high pressure, but constantly increasing in volume with increasing temperature, and for the liquid state with this condition continuing all the way to the critical point, except that near the critical point the apparent compressibility of the liquid phase may be increased by solution of molecules in their vapor condition, so that the inference seems justified that in these conditions the molecule is constantly increasing the diameter of its sphere of influence as temperature increases up to this same point. At this same point we find again the sphere of influence of the molecule in the gaseous condition to be of the same size as in the liquid condition since it occupies the same space and has the same specific gravity. We find also that at the critical point the volatile form is at the dividing line between a saturated vapor and a true gas, and moreover that at this dividing line the vapor cannot act as a true gas because the spheres of influence of its molecules are in three dimensional contact, precluding translatory motion. We find, however, that although the molecules in the liquid condition continue to increase the dimensions of their spheres of influence with advancing temperature in spite of advancing pressure, nevertheless gaseous molecules can be compressed materially so as to occupy a smaller volume than at the critical point even at temperatures well above the critical point. Is it not a fair inference, in view of these things, that in the condition of a true gas the spheres of influence of molecules decrease with advancing temperature so as to allow a free path and thus cause them to follow Boyle's Law?

Considering again the probability that in the gaseous condition the diameter of the sphere of influence of the molecule is an inverse function of the temperature, we should find a probability that in the vapor condition at temperatures below the critical the molecule would continue to expand. If this is true we should have a direct explanation of the separation of condensate whenever a saturated vapor is cooled under constant volume. There would no longer be room in their gaseous state for all the expanding molecules, so that some of them would be obliged to go into the less bulky liquid form. There is no latent heat at the critical point, so that the gradual increase in latent heat set free with descending temperature would be explained by the gradually increasing work of compressing the vapor molecules into the liquid form.

Of course in the condition of saturated vapor the spheres of influence of the molecules cannot represent a plenum, for we recognize that the quantity of water vapor to saturate any volume is nearly, if not absolutely, independent of whether any other gas is present of which the liquid phase at the temperature in question would not form a solution with water. I have seen statistics showing slightly greater amounts for saturation in the presence of air. If correct, these would indicate that air has a solvent power for aqueous vapor, but this difference falls within the margin of probable error, and may have been due to adsorption films on the walls or to infinitesimal liquid drops not observed or to errors in weighing. It seems unlikely that a greater amount could be present except chemically combined as a constituent of other molecules. Perhaps the delimitation of the spheres of influence is due to the shortening of the orbits of the outlying electrons, causing them to fall in towards the central nucleus and thus liquefy whenever they are checked in their flight by contact with, or even close approach to electrons charged with electricity of equal wave length, while immune to electrons of inharmonic charges.

Interesting information as to the size of the absolute spheres of influence should be obtainable by the study of the compressibility of vapors and gases near their critical points, and especially with mixtures where both are near this point. If the rapid increase in volume of the liquid approaching this point is due to solution as such of vapor molecules, we should find a different (and greater) specific volume for the liquid brought to this temperature in the presence of vapor than if carried up continuously under a pressure greater than the critical pressure; just as we find different densities for S_λ according to whether it has or has not S_μ dissolved in it.

A further development of this conception has grown out of consideration of saturated solutions of $BaSO_4$. We are so familiar with the idea of dilute solutions that until a few weeks ago it never occurred to me to ask how it could be that (according to Calvert's determination) one single ion of Ba, in the presence of a corresponding ion of SO_4, could so far affect simultaneously 10,000,000 molecules of water as to deprive everyone of them of the power to dissolve any more $BaSO_4$. It is bad enough to try to imagine how the conductivity is so much increased by any salt at such immense dilution, and all parts of such a solution must have like properties before passage of the current, as it will pass equally well up or down, East or West, or North or South. I cannot explain the increase in conductivity of water to many times its value in the pure state by addition of one molecule of $BaSO_4$ in 10,000,000 of water on the theory that the $BaSO_4$ breaks up into only two parts. I cannot see how in this case that the resulting ions should do more than act as at best metallic conductors bridging between the few water molecules with which they were in immediate contact, but leaving unaltered the conductivity through the vast mass of others, and thus changing the conductivity of the whole by an amount barely perceptible by the most delicate instruments. When it comes to showing why, after absorbing freely up to this point, the solution can thereafter take up no more, I find the easiest explanation in assuming a virtual expansion of the molecules of the solute so as practically to occupy all the inter-molecular space of the solvent, in much the same way in which I have supposed molecules in the volatile conditions to increase the diameter of the spheres of influence of their molecules as temperature falls.

It first struck me that $BaSO_4$ could not dissociate much, for we know from $CaSO_4$ that the solubility of the SO_4 ion is relatively high, and I thought that the solubility of $BaCl_2$ showed that of Ba to be high till it came over me that this alkaline ion was probably $BaCl +$. This led me to consider whether the Ba ion as such might not be totally insoluble (which now I do not think), but that led in turn to consideration of solubility of the metals at large.

It occurred to me that I had stumbled on a new characteristic of the metals as such. The metals are (except perhaps carbon, which is as insoluble) practically the only things which carry the electric current by what we call metallic conduction. I have, I believe, successfully refuted Findlay's argument for the solubility of mercury in bromonaphthalene, and Nernst's for the existence of theoretical vapor tensions of all substances at all temperatures above the absolute zero, postulating instead of this last, a critical point for each substance below which the expanding spheres of influence grow so great as to become wabbly and lose coherent structure, and cease to rebound on contacts, so that they adsorb or condense completely on limiting surfaces, making for the volatile phase a lower limit corresponding to the critical point at the upper limit for liquids.

Assuming that my explanation of the action of mercury is correct, I believe that we can postulate a general characteristic of the metals hitherto undescribed. Together with carbon they seem to be more or less soluble in each other, but otherwise totally insoluble except as they go into chemical combination. I know of no aqueous solution from which a metal can be separated as such by mere boiling or evaporation at lower temperature, or by change of temperature or pressure. In fact the only cases that I know of where metals separate as such from solutions are where the alkaline metals are left by evaporation of anhydrous ammonia, and there I believe that the remarkable changes of color point to the formation of chemical combinations in the solutions.

From my standpoint the so-called colloidal solutions are merely individual molecules held in suspension and carry a current only mechanically through a menstruum which does *not* dissolve them. They take a charge by metallic conduction and thus are repelled from one pole and attracted to the other so as to carry the current rather as a multitude of boats rather then as a bridge.

I find it hard to believe that the solvent power for $BaSO_4$ of a molecule of water can be destroyed by contact of whatever kind with $BaSO_4$ of a molecule of water separated from the former by sixty-five ($= {}^1/_2 \sqrt[3]{10{,}000{,}000}$) intervening molecules of water not in contact with $BaSO_4$ so that by way of explanation I find myself reduced to the conception of the $BaSO_4$ breaking up into an enormous number of electrons, or emanations of which electrons are built, each having the characteristic periodicity of $BaSO_4$ (and not solely of any constituent thereof) and that these so permeate the solvent that each molecule of this is in some way in contact, periodic at least, with such particles, so as to maintain an equilibrium relation.

It seems to me that hydrolysis represents a condition where the complicated periodicity of the salt becomes too extended, so that part of the solute loses coherence and the fractions revert to their simpler (though related) periodicity, each in its own condition, as if the other were not present. I believe these conditions to be quite different from those of electrolysis. In this I imagine the ions to exist as atoms combined with charges of electricity (instead of complementary atoms) to make virtual molecules suspended in the menstruum much as are the metallic molecules in colloidal solutions and very different from the clouds of diffused electrons or emanations filling intermolecular spaces which by my theory make a continuity of the particles of the solute roughly answering to that of Bragg for matter in crystalline form.

This involves recognizing inherent differences between solvent and solute. I have been led by other arguments to believe that while in many cases substances are mutually soluble, so that each acts both (or either) as solvent and (or) solute; in other cases one has a distinctly different type of action from the other. I have been able to prove false at least one of the arguments on which Findlay bases his assertion that solvent and solute are indistinguishable.

I appreciate that my idea is difficult to grasp, but it seems to me mechanically easier to imagine than the customary hypothesis that one Ba ion existing as a concentrated unit can simultaneously neutralize the capacity for Ba, in the presence of equivalent SO_4, of 10,000,000 molecules of water with which it is not in contact at all, and is only connected to by a chain of many other aqueous molecules, all equally out of contact with Ba.

Some of my friends have tried to explain this action by an effect radiating from the Ba ion, by adsorption, or by consecutive contacts with all the water molecules. Any radiant effect should diminish as the square of the distance increases, so that at say fifty times the diameter of an aqueous molecule the effect should be infinitesimal compared with that in contact with the Ba. If, therefore, another molecule of $BaSO_4$ should be mechanically introduced into the solution at this point, we should get there the relatively high effect near a nucleus, so that in a mud of precipitated $BaSO_4$ we should get a multiplicity of such local supersaturations, with reduction of the relatively great subsaturated volumes and thus a high average supersaturation under just the circumstances of contact with the solid phase, which we recognize as most destructive of supersaturation.

I cannot see how adsorption can act through a layer fifty molecules thick of homogeneous water, nor, especially in view of the very slow net progress of particles shifting by the Brownian movements, can I think it possible for the heavy Ba ion to strike consecutively each of 10,000,000 water molecules with sufficient frequency to prevent them from showing additional effect from additional $BaSO_4$ molecules in suspension.

It has been objected also that this involves an enormous amount of latent heat to overcome the centripetal forces of the atom. I am not at all sure that in cases of high dilution we do not have the latent heat of volatilization to add to the latent heat of fusion, which would signify that some of the dissolved molecules were dissolved in volatile form, as I supposed some to be in liquids approaching the critical temperature. This would perhaps indicate the existence of the vapor of the solute in the intermolecular spaces of the solvent.

We know almost nothing of the inter-molecular centripetal forces and why in the solid form they hold things together. Why might it not be the characteristic of solvents to cause these forces to attract the particles held in check by them toward molecules of the solvent instead of toward a common center?

Peace Dale, R. I.
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