

# NUCLEI IN EVAPORATION AND CONDENSATION<sup>1</sup>

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The condition of dissolved non-polar gases in water solution is entirely a matter of speculation. There is evidence that bubbles small enough to escape observation are very persistent and that the properties of water are affected noticeably by their presence.

The supersaturation of vapors in the absence of nuclei is subject to thermodynamic treatment. The Thomson equation is no longer valid when the single drop ceases to determine a liquid phase. The drop ceases to constitute a liquid phase when the number of molecules becomes small enough so that the share of each molecule in the (colligative) entropy of the drop becomes considerable. The drop now becomes a molecular aggregate in a homogeneous equilibrium and a definite limit to supersaturation is established. Experimental data are in general agreement with the conclusions of this theory.

The nuclei of evaporation and condensation become bubbles or drops. The bubble and the drop are the opposite faces of the coin, so to speak, of which the liquid-vapor interface is the coin disk itself. The low entropy of surface formation of water indicates a high degree of structure in the surface, just as in the body of the liquid. One can hardly avoid the conclusion that water is a unique liquid which always must be discussed as a special case.

That the density of the liquid is greater than the density of ice is a bizarre fact which raises many questions. It seems to be clearly established that ice is a four-coördinated structure with hydrogen bonds maintaining a distance of 2.76 Å. between the oxygen atoms. Since the hydrogen bond is a very weak bond, these linkages can not be considered as fully established except at the lowest temperatures. For the same reason water does not form a glass; the shift to a crystalline structure takes place too readily. As a matter of fact, Pauling considers that ice is only imperfectly crystalline and is to a small degree tautomeric with a glass. If the hydrogen bonds were stronger, one might expect water to form a glass of the same density and coördination number as ice. In liquid water (4) the average distance between oxygen atoms is increased to about 3.0 Å. The increased density is accounted for by the fact that the coördination number is on the average greater than 4.0, perhaps as much as 4.5. Since the hydrogen bonds are constantly breaking and re-forming, this is only an average figure. The increased density is easily understood, even though the average distance between molecules is greater. Likewise the heat of fusion is easily accounted for by the fact that both the hydrogen-bond energy and the van der

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Waals energy will be considerably decreased by an increase in interatomic distances.

Not all of the properties of liquid water are so easily accounted for, however. For example, consider the solubility of gases, such as oxygen or methane, which are a long way above their critical temperatures. It is easily understood that, although ice has an open structure, the small tolerances of the lattice do not allow the inclusion of foreign molecules. How then can the liquid phase, which is denser, make room for the dissolved gas?

If one assumes that the gas molecules are simply entrapped in the mesh of the liquid water, then the solubility should increase with temperature. It does in some cases but usually not. For example, the heat of solution of methane is negative.

Finally there is the strange group of hydrates formed by the gases such as chlorine, methane, and argon. These hydrates are believed to contain eight molecules of water per molecule of gas. Since the unit of structure in hexagonal ice is a group of eight water molecules, it has been suggested by some that the hydrates are made up by enclosing one molecule of gas in one of the ice units, but this idea is untenable because there is no room for a gas molecule in such a cluster.

#### FOREIGN NUCLEI

It might be supposed that the theory of fluctuations would account for the initiation of all types of processes in the liquid state in which a new phase appears, but it is an interesting fact that most of the investigators who have studied processes of this type in water solution have been led to postulate the presence of foreign substances in some form of dispersion or solution. Among the phenomena which have been studied are the coagulation of sols (3), the tensile strength and superheating of water (2; see also 6), and the effect of centrifuging on the E.M.F. of a galvanic cell. One may conclude in every case that they are due to the presence of impurities and note that treatment of the water by such drastic processes as ultrafiltration, ultrasonic radiation, or high pressure often causes these effects to disappear. Without generalizing in any way as to how these effects are produced, one may assume that in some cases at least the homogeneous structure of water vapor is disturbed by the presence of dissolved gases in various states of dispersion.

We shall consider, therefore, what the behavior of a dissolved gas such as oxygen might be. If the gas is not molecularly dispersed, the bubbles to escape detection must be less than  $10^{-7}$  cm. in radius. Such a bubble at 1 atm. would not contain more than one molecule, but at the high internal pressure existing in water the density might well be greater than that of liquid oxygen at the critical temperature. If one wonders how a bubble at such a pressure can exist in equilibrium with the external atmospheric pressure, it is only necessary to remember that this pressure is largely an internal pressure due to forces acting throughout the liquid. The only pressure acting on the bubble tending to cause it to disappear is the pressure due to interfacial tension. The interfacial tension

between oxygen and water on a flat surface is large. For limited surfaces of high convexity it might be small. The very large partial molal volume of these gases in water solution lends some support to the hypothesis of a low interfacial tension at the surface of small bubbles. If the bubble were under a very high pressure, the partial molal volume could scarcely be so great.

It is not surprising that the solubility of oxygen in water is small, but it is paradoxical that the temperature coefficient of solubility is negative. This implies that the heat of solution is negative; in other words, that the attraction of water molecules for oxygen molecules is greater than the mutual attraction between water molecules. But if this is the case, the solubility should be greater in the first place.

We shall have to try for another explanation. The small solubility means a negative entropy of solution. This negative entropy of solution could be due to a very definite orientation of water molecules in the interface. The energy liberated by this orientation would account for the negative heat of solution without assuming strong attraction between oxygen and water molecules.

This resembles the "iceberg" theory (1), so-called, but there can be no resemblance to an ice structure. The ease with which water supercools argues against any structure resembling hexagonal ice forming in the liquid state. The reason for this is obvious of course: the high internal pressure makes the ice structure unstable because of its low bulk density. A pentagonal dodecahedron would form a somewhat larger unit (thirty molecules) than the hexagonal unit of eight molecules and there would be room on the inside for a gas molecule. It seems probable, however, that the most stable configuration would be a bubble containing a number of gas molecules. The water molecules in the surface of this bubble would be oriented in such a way as to form at least three hydrogen bonds per molecule. The fourth hydrogen would project on the inner surface of the bubble in such a way as to be attracted strongly to gas molecules by polarization forces. This arrangement would give a low or zero interfacial tension and a negative heat and entropy of solution.

There will be a size of bubble for which the heat of solution and entropy will be a maximum (negative) but the distribution will be statistical. It may be that equilibrium can be established only at the gas-liquid surface, so that the distribution of size may be far from that which would be predicted. There may be more bubbles containing only one molecule than of any other size, but these may represent only a small percentage of the total gas dissolved.

#### CONDENSATION OF WATER VAPOR

In discussing the condensation of vapor we shall treat only the case in which foreign nuclei such as ions and dust particles are assumed to be absent. In the vapor of a hydrocarbon oil there may be a few large molecules which serve as nuclei for condensation. In water vapor in a pure state the nuclei must be aggregates of water molecules which grow by accretion, starting with the association of two water molecules to form a bimolecular complex. We shall refer to these aggregates as clusters until they become large enough to form drops. We

shall define the terms "cluster" and "drop" somewhat arbitrarily by applying a distinguishing criterion of thermodynamics. If the aggregate contains enough molecules so that its behavior in the presence of vapor at a given temperature and pressure is uniquely determined, independently of the number of such aggregates present in a given volume, then it constitutes a liquid phase and we shall call it a drop. On the other hand, if the aggregate contains a small number of molecules so that its behavior is statistical and depends upon the concentration, we shall call it a cluster. There is of course a gradual transition from cluster to drop which must occur somewhere between 100 and 1000 molecules per aggregate, i.e., in the range of radius  $10^{-7}$  to  $2 \times 10^{-7}$ . As we shall see later, a drop will determine an equilibrium saturation pressure and hence can no longer be considered as a nucleus.

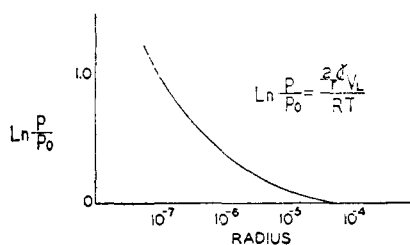


FIG. 1 Plot of Thomson equation

#### THE THOMSON EQUATION

The Thomson equation

$$\ln \frac{p}{p_0} = \frac{2\gamma}{rV}$$

cannot be assumed to hold below a radius of  $10^{-7}$  (133 molecules) for two reasons: (1) As the number of molecules decreases, the concept of a flat surface under uniform tension must fail. (2) It is obviously impossible to speak of a saturation pressure when the equilibrium pressure depends upon the concentration of clusters present, as it obviously does in the limit when only bimolecular clusters are present. So long as the saturation pressure is fixed by the presence of a single drop we are dealing with vapor-liquid equilibrium, but when the aggregates become small enough so that their concentration is significant in determining equilibrium we have a homogeneous instead of a heterogeneous equilibrium. Accordingly we have drawn the curve for  $\ln p/p_0$  (figure 1) down to  $r = 10^{-7}$  ( $\ln p/p_0 = 1$ ). The curve is extended beyond the point as a broken line. This broken line indicates not only that the Thomson equation cannot hold but that *no saturation pressure exists for this region* ( $< 10^{-7}$ ).

#### THERMODYNAMIC EQUATIONS

The equilibrium between vapor and liquid drops or molecular clusters may be

conveniently expressed by the equation:

$$S_v - S_L = \frac{4H\gamma}{T}$$

Here  $S_v$ , the entropy per mole of vapor, is given by the equation

$$S_v = S^0 - R \ln P$$

where  $S^0$  is the standard entropy at unit pressure.  $S_c$ , the entropy per mole of the liquid drop of molecular cluster, is represented by

$$S_c = S_L + \frac{1}{n} (S^0)_{col} - \frac{2\gamma V}{T}$$

Here  $S_L$  is the entropy per mole of liquid in the mass;  $(S^0)_{col}$  is the contribution of translational, rotational, and concentration terms to the entropy of aggreg-

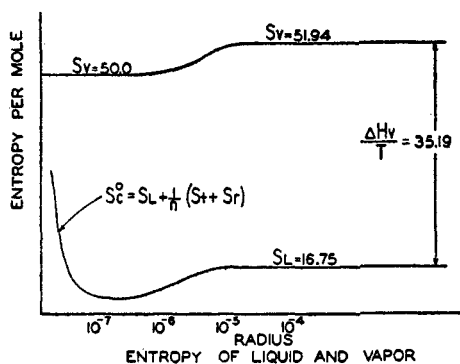


FIG. 2. Plot of entropy curves for liquid and vapor as a function of radius

gates composed of  $n$  molecules each and treated as a gaseous phase. The effect of surface tension in reducing the entropy of the liquid comes directly out of the Thomson equation, and we shall assume  $\Delta H_v$ , the heat of vaporization, to be constant so long as the Thomson equation holds. The entropy curves for liquid and vapor are plotted in figure 2 as a function of radius.

THE MINIMUM ENTROPY FOR SMALL DROPS

The entropy curve for the liquid shows a minimum in the neighborhood of radius  $10^{-7}$ . This minimum marks the transition from cluster to drop, in other words, the limit of the saturation curve corresponding to a liquid-vapor equilibrium. The existence and approximate location of this minimum require justification, and this justification can be given both from theoretical considerations and from the behavior of supersaturated vapor as reported by investigations.

The maximum decrease in entropy due to surface tension is about two units. Beyond this point a new effect becomes important, *viz.*, the colligative entropy. Because the aggregates representing the liquid phase are in suspension, they may

be treated as large molecules forming a part of the homogeneous vapor phase and possessing translational, rotational, and volume concentration entropy. The share of this entropy per molecule is only  $1/n$  times the total, where  $n$  is the number of water molecules per aggregate. When the number of molecules per aggregate is less than 100, this contribution will more than offset the decrease in entropy due to surface tension and hence a minimum in the entropy of the liquid phase must occur at or near this radius ( $10^{-7}$ ).

One can calculate the entropy of the drop and estimate the entropy of the bimolecular cluster. (The heat of dissociation of the bimolecular cluster is estimated at 5000 cal. and entropy of dissociation at 20 E.S.U.) The entropy of cluster of intermediate size is obtained by an interpolation made on the assumption that the decrease in heat of vaporization is offset by an increase in vibrational entropy. This last assumption is a variation of the Trouton rule and quite reliable. Hence one locates the minimum entropy as occurring at or near a radius of  $10^{-7}$ .

This estimate based on theoretical calculations receives a very satisfactory confirmation from the experimentally reported behavior. It is, of course, not easy to reconcile all of the facts as reported in the literature.<sup>2</sup> One cannot be sure of the absence of foreign nuclei in all cases. Supersaturation in cloud chambers is complicated by the presence of air and condensation on the walls. The most reliable experiments are those in which superheated steam is expanded through a nozzle.

The following conclusions seem to be established on a fairly reliable basis for pure water vapor: (1) A threefold saturation ( $\ln p/p_0 \sim 1$ ) does not result in rapid condensation. (2) If the saturation is increased to four- or fivefold ( $\ln p/p_0 = 1.5$ ) condensation will take place in 20–40 microsec. with a drop concentration of  $10^6$ – $10^8$  per cubic centimeter.

#### THE SUPERSATURATION REGION

It does not affect the conclusions of this paper seriously if the above limits are not strictly accurate. One can be certain that certain limits of supersaturation exist such that at the lower limit condensation does not occur and at the upper limit it occurs very rapidly. These limits are separated by a difference in the pressure of the vapor that corresponds to about one entropy unit. In figure 3 the equilibrium concentrations of clusters are shown for the lower and upper limiting pressures. The ratio of the concentrations between the two curves is given by the relation

$$R \ln C = n\Delta S$$

where  $\Delta S$  is taken as one entropy unit.

#### THE BOTTLENECK FOR GROWTH OF NUCLEI

The lower curve in figure 3 is for  $\ln p/p_0 = 1$  and shows a minimum in the neighborhood of  $r = 10^{-7}$  corresponding to the minimum entropy for the con-

<sup>2</sup> Ruedy (5) has summarized the experimental data on supersaturation in the literature.

densing phase. At this minimum the probable concentration of aggregates is vanishingly small. Since condensation must take place by the growth of clusters with drops, and since this growth cannot take place unless a large concentration of clusters is present at equilibrium, no condensation will occur. If the probability of the existence of a cluster is small, the cluster will not grow but will diminish in size.

If, however, the supersaturation is increased to  $\ln p/p_0 = 1.5$ , we have the upper curve with a minimum somewhat below  $r = 10^{-7}$  but at concentrations high enough to permit a rapid growth of clusters into drops. There is no point in trying to draw the concentration curve beyond the minimum, because it represents a concentration that will never be realized since supersaturation of the vapor is no longer possible in this region.

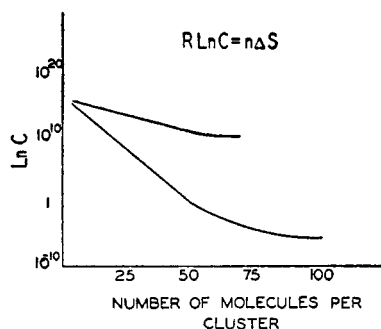


FIG. 3. Equilibrium concentrations of clusters for the lower and upper limiting pressures

#### MECHANISM OF GROWTH OF NUCLEI

Bimolecular complexes must be formed by triple collisions. There are some  $10^{24}$  triple collisions per second at the threefold saturation; hence a concentration of  $10^{16}$  bimolecular complexes can be formed in a matter of microseconds. A cluster grows by individual accretion. The collisions are inelastic but, of course, for each molecule condensing another must evaporate, otherwise the temperature of the cluster would rise without limit. Actually, the temperature of the cluster will rise until the rate of evaporation is equal to the rate of condensation from the supersaturated vapor. For a threefold saturation this would amount to 15 or 20°. About 150 cal. per mole will be lost on each exchange of molecules, so that perhaps one molecule will adhere permanently for each hundred exchanged. The rate of growth may be calculated by the kinetic theory to be  $4.65 \times 10^{21} \times r^2$  for threefold saturation at 25°C. A cluster would grow to a radius of  $10^{-7}$  cm. in a few microseconds.

#### GROWTH BY AGGLOMERATION

If the clusters are small so that the Brownian motion is rapid and the concentration high ( $> 10^{10}$ ), then collisions between clusters will be numerous and will result in a rapid growth by agglomeration with a corresponding reduction in the total number present. This accounts for the fact that in a rapid conden-

sation the number of droplets per cubic centimeter will not exceed  $10^8$ . However, if the clusters are small the heat liberated is so great that many molecules must be evaporated and little gain in size will result from the collision. The reason for this is that the heat of condensation increases rapidly with increasing size of the cluster and levels off when it becomes a drop of  $10^{-7}$  radius. For example, let us suppose the heat of condensation per mole (including surface energy) in a cluster of 50 molecules to be 5000 cal. and in a cluster of 100 molecules to be 7500 cal. The heat of agglomeration would be so great as to require the evaporation of nearly one-third of the molecules contained in the two drops.

In this paper no attempt has been made to calculate the over-all rate of growth of clusters of sizes and hence the absolute rate of condensation. Such a calculation undoubtedly is possible but laborious.

It is not immediately obvious that the considerations of this paper apply to the condensation of water vapor in the atmosphere because foreign nuclei are usually present and hence the supersaturation is small. It is conceivable, however, that under extreme conditions a high degree of supersaturation may be reached.

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