

On the Solid Condensation Nucleus which is not Soluble in Water (Studies on the Formation of Cloud and Rain III)

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$$= 2\pi\rho_2 \int_s^{s+2R} df \int_f^{r_0} r\phi_{12}(r)dr,$$

where ρ_2 is the molecular density of the nucleus (number of molecules per unit volume) and indices 1 and 2 denote the water and the nucleus respectively.

In the case of most substance the mutual potential energy of two molecules depends on the VAN DER WAALS attractive force and in this case $\phi_{12}(r)$ will be expressed as $\phi_{12}(r) = -\frac{c_{12}}{r^6}$, then

$$U_{12}(R, x) = -\frac{\pi\rho_2c_{12}}{12} \left\{ \frac{3}{R+x} \left(\frac{1}{x^2} - \frac{1}{(2R+x)^2} \right) + 2 \left(\frac{1}{(2R+x)^3} - \frac{1}{x^3} \right) \right\} \dots\dots (1)$$

Therefore when the solid nucleus is covered with water film the potential energy of the water molecule at P can be expressed as

$$U(R, x) = U_{11}(R+x, \delta_{11}) - U_{11}(R, x) + U_{12}(R, x), \dots\dots\dots (2)$$

where δ_{11} is the distance between two neighbouring water molecules.

The stability or instability of the equilibrium between the water film and the surrounding water vapour can be inferred from the fact that the thermodynamic potential ϕ of the system constituted by them, considered as a function of the thickness of the film h , for a fixed value of the total number of molecules in two phases has a minimum in the former case and a maximum in the latter (just as in the case of the equilibrium between a liquid drop and its supersaturated vapour).

The potential ϕ can be calculated as follows. When the film is a part of a large mass of water its evaporation energy is equal to $\frac{4}{3}\pi\{(R+h)^3 - R^3\}\rho_1 U_\infty$, where U_∞ is the evaporation energy of a large mass of water referred to one molecule. The difference between this energy and the energy of the film

is the correction to the normal value of the evaporation energy due to the small thickness and the spherical shell shape of the film. Thus

$$W(R, h) = \frac{4}{3}\pi\rho_1 U_\infty \{(R+h)^3 - R^3\} - \int_0^h 4\pi\rho_1(R+x)^2 U(R, x) dx \dots (3)$$

can be defined as the corresponding correction to the potential energy of the film. In the above formula the integrand of the second term of the right-hand side is as follows. For the term corresponding to the first term of the formula (2) which enters in the integration of the second term of (3) it is from 0 to h , for the second term from δ_{11} to h , and the third term from δ_{12} to h .

Denoting the total number of molecules of water and water vapour by N (fixed) we thus obtain the following expression for ϕ as a function of h ,

$$\phi = [N - \frac{4}{3}\pi\rho_1\{(R+h)^3 - R^3\}]\phi_A + \frac{4}{3}\pi\rho_1 \times \{(R+h)^3 - R^3\}\phi_B + W(R, h), \dots\dots\dots (4)$$

where ϕ_A and ϕ_B are the chemical potential referred to one molecule of the water vapour and that of the liquid water respectively. The thermodynamic equilibrium of the system under consideration is determined by the condition $\delta\phi = 0$, which, in connection with $N = \text{const.}$, leads to the equation

$$\phi_B - \phi_A + U_\infty - U(R, h) = 0. \dots\dots\dots (5)$$

Now we shall calculate the potential $U(R, h)$.

$$U_{11}(R+h, \delta_{11}) = -\frac{4}{3} \frac{\pi\rho_1c_{11}(R+h)^3}{\delta_{11}^3(2R+2h+\delta_{11})^3} \\ = -\frac{\pi\rho_1c_{11}}{6\delta_{11}^3} \left(1 - \frac{3\delta_{11}}{2(R+h)} \right), \\ U_{11}(R, h) = -\frac{4\pi\rho_1c_{11}R^3}{3h^3(2R+h)^3}, \\ U_{12}(R, h) = -\frac{4\pi\rho_2c_{12}R^3}{3h^3(2R+h)^3}.$$

However as $U_{11}(\infty, \delta_{11}) \left(= -\frac{\pi\rho_1c_{11}}{6\delta_{11}^3} \right)$ is the

potential energy of a large mass of water referred to one molecule, it is nothing but the evaporation energy referred to one molecule or U_∞ . Again, $U_{12}(R, h)/U_{11}(R, h)$ ($=\rho_2c_{12}/\rho_1c_{11}$) is the ratio between the adhesive force of water to the solid nucleus and the cohesive force of water, and we shall denote it by ϵ .

Moreover, the product of the surface area of one molecule S and the surface energy of water U_s is approximately equal to the half of the evaporation energy referred to one molecule U_∞ . Thus we have $SU_s = \frac{1}{2} U_\infty$. If we denote the volume which one water molecule occupies by v_B , then we have $v_B = \frac{4}{3} \pi \times \left(\frac{\delta_{11}}{2}\right)^3$, $v_B \rho_1 = 1$ and $S = 4\pi \left(\frac{\delta_{11}}{2}\right)^2 = \frac{2}{3} \frac{v_B}{\delta_{11}}$. Therefore we get $U_\infty = \frac{4}{3} \frac{v_B}{\delta_{11}} U_s$ and $\frac{3}{2} \frac{\delta_{11}}{R+h} = \frac{2v_B U_s}{(R+h)U_\infty}$. As the surface energy U_s is nearly equal to the surface tension σ , we obtain the following expression for $U(R, h)$.

$$U(R, h) = U_\infty \left(1 - \frac{2v_B \sigma}{(R+h)U_\infty} \right) + 8(\epsilon - 1)U_\infty \frac{R^3}{h^3(2R+h)^3}.$$

Then equation (5) reduces to

$$\phi_B - \phi_A + \frac{2v_B \sigma}{R+h} - 8(\epsilon - 1)U_\infty \frac{R^3 \delta_{11}^3}{h^3(2R+h)^3} = 0. \tag{6}$$

If we denote the maximum water vapour pressure on the film by $P_{R,h}$ and that on the plane water surface at the same temperature T by P_∞ , then

$$\phi_B - \phi_A = -kT \log \frac{P_{R,h}}{P_\infty} \tag{7}$$

where k is the BOLTZMANN's constant. Putting (7) into (6) we have

$$kT \log \frac{P_{R,h}}{P_\infty} = \frac{2\sigma v_B}{R+h} - 8(\epsilon - 1)U_\infty \frac{R^3 \delta_{11}^3}{h^3(2R+h)^3}. \tag{8}$$

This is the formula which gives the maximum water vapour pressure on the water film which is formed on the solid nucleus.

§ 3. Role of the Solid Nucleus in Condensation Processes.

In the above equation if we put $\epsilon = 1$ and $h = 0$, we have the formula which gives the maximum water vapour pressure on the water drop with a radius R , namely

$$kT \log \frac{P_R}{P_\infty} = \frac{2\sigma v_B}{R},$$

and this is nothing but THOMSON's formula.

Again if we put $R = \infty$, the maximum water vapour pressure on the water film which covers the plane solid body will be obtained⁽⁴⁾ as

$$kT \log \frac{P_h}{P_\infty} = -(\epsilon - 1)U_\infty \frac{\delta_{11}^3}{h^3}.$$

From these special cases the physical meaning of the equation (8) will be easily understood. When the nucleus is wetted fairly well by water then $\epsilon \geq 1$ and the contact angle between them is zero, when $0 < \epsilon < 1$ the nucleus is poorly wetted and the contact angle is $0^\circ \sim 180^\circ$, and when $\epsilon = 0$ it is not wetted at all and the contact angle is 180° . Therefore when the solid nucleus is wetted fairly well the water vapour pressure on it will be lowered than that on the water drop of the same size by the second term of the right-hand side of the equation (8). However when it is poorly wetted the vapour pressure on it is higher than that on the water drop, so it is difficult to act as a condensation nucleus.

In Fig. 2 the relation between the relative humidity ($P_{R,h}/P_\infty$) and the thickness of the film h was illustrated. In order to compare with the water drop, relative humidity required for condensation on it was also illustrated (Curve I in Fig. 2-a), its radius being

taken on abscissa instead of the thickness of the film.

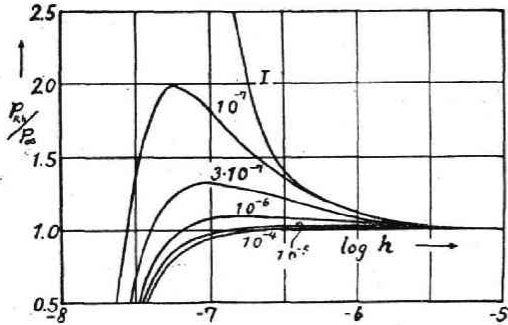


Fig. 2 (a)

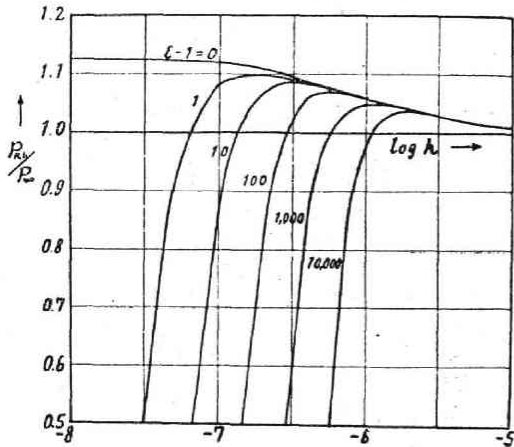


Fig. 2 (b)

Relative Humidity over Water Films on Solid Nuclei, (a) in relation to their Radii R and (b) to $\epsilon-1$.

Curve I in (a) illustrates the relative humidity over water drop, the abscissa of which denotes its radius instead of the thickness of the film.

When $\epsilon > 1$ each curve has a maximum and the thickness of the film corresponding to it h^* is given in Table 1 for the case $\epsilon-1=1$ and $T=273$.

Table 1

R (cm)	10^{-4}	10^{-5}	10^{-6}	10^{-7}
h^*/R	0.018	0.054	0.17	0.56
h^* (cm)	1.8×10^{-6}	5.4×10^{-7}	1.7×10^{-7}	5.6×10^{-8}

When the nucleus is not too small h^* can be given approximately by the following expression

$$h^* = \left\{ \frac{3(\epsilon-1)U_\infty \theta_{11}^3 R^3}{2\sigma v_B} \right\}^{\frac{1}{4}}$$

Fig. 2 is extremely valuable as it illustrates the changes in the thickness of the film or the size of the nucleus as the relative humidity changes, and its explanation will be given quite similarly with the case of the condensation on the hygroscopic nucleus⁽¹⁾. In Fig. 3 which is reproduced from Fig. 2, if we start

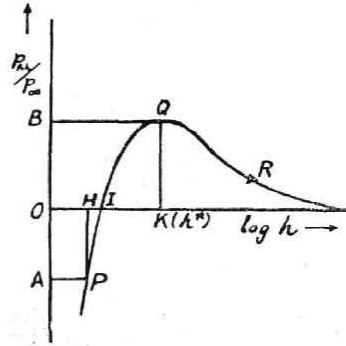


Fig. 3

with the relative humidity represented by the point A, water film with a thickness represented by H will be formed on the nucleus. If the relative humidity increases the drop will grow by condensation, the change in the thickness of the film with change in humidity being represented by the curve in the figure. If the relative humidity is further increased rising over saturation so that supersaturation sets in, the drop does not grow indefinitely but increases in size, remaining in equilibrium with the supersaturated atmosphere at each point on the curve until Q is reached. For thickness greater than h^* the equilibrium relative humidity decreases as the drop grows bigger. This is an unstable state, for the larger the drop grows the smaller in the relative humidity with which it is in equilibrium. Thus, if the relative humidity is maintained or increased the drop will grow indefinitely and will form a cloud particle.

From the above consideration it is easily

understood that the role of the solid nucleus in condensation process depends upon the relative humidity which corresponds to the critical thickness h^* . The relative humidity referred above was tabulated below.

Table 2

$R(\text{cm})$ $\epsilon-1$	10^{-4}	10^{-5}	10^{-6}	10^{-7}
0	100.12	101.2	113.0	330
1	100.12	101.1	110.4	200
10	100.11	101.1	108.7	166
100	100.11	101.0	107.1	141
1,000	100.11	100.9	105.1	126
10,000	100.10	100.7	103.5	116

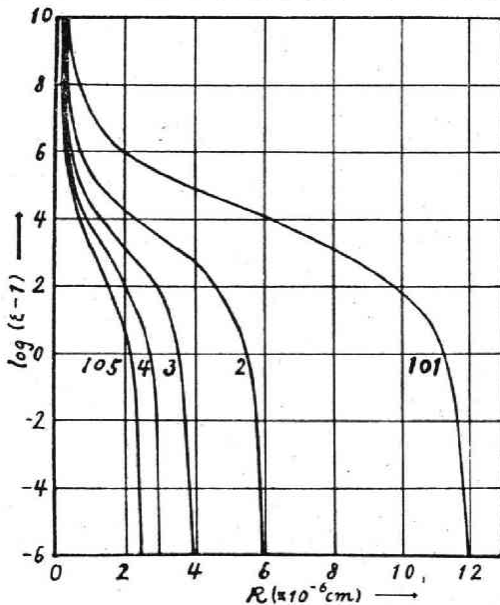


Fig. 4 Relative Humidity which is Required to Condensation on the Solid Nuclei in Relation to their Radii R and $\log(\epsilon-1)$.

The relative humidity corresponding to h^* depends both on ϵ and R , so the relation between them was illustrated in Fig. 4 for the humidity from 101 to 105 % for every 1%.

From the above table and Fig. 4 we can see that the solid nucleus which is wetted by water lowers considerably the maximum water vapour pressure on it and can act as a condensation nucleus in the atmosphere.

It is our regret, however, that the value of ϵ has been measured for no substances, therefore we cannot decide what kind of substance is most effective in condensation. As most solid nuclei contain small cracks and fissures it is easily presumed that they can act as condensation nuclei in the atmosphere even when the value of ϵ is not so large. For instance, with rapidly ascending air, as in cumulo-nimbus or in thunderstorms, supersaturation of over 5% may occur and in these cases the solid nuclei will be able to act as condensation nuclei.

Finally solid nucleus for which ϵ is less than 1 it is poorly wetted or is not wetted at all by water and the water vapour pressure on such a nucleus is higher than that on the water drop of the same size, therefore it is clear that such particle cannot act as a condensation nucleus at all.

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