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To cite this article: C. Rooth (1957) On a Special Aspect of the Condensation Process and its Importance in the Treatment of Cloud Particle Growth, Tellus, 9:3, 372-377, DOI: [10.3402/tellusa.v9i3.9104](https://doi.org/10.3402/tellusa.v9i3.9104)

To link to this article: <https://doi.org/10.3402/tellusa.v9i3.9104>



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Published online: 15 Dec 2016.



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# On a Special Aspect of the Condensation Process and its Importance in the Treatment of Cloud Particle Growth

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(Manuscript received May 10, 1957)

## *Abstract*

Available data on the rate of exchange of molecules between liquid water and vapour in contact with it are put in relation to atmospheric condensation and evaporation processes. It is shown that this exchange process exerts a quenching action on the rate of growth of small droplets that should contribute to the formation of a broad size spectrum. Surface films may enhance the effect considerably. Experimental data are needed to decide finally the meteorological significance of the effect.

In theoretical treatments of cloud particle growth it is generally assumed that if the chemical composition as well as the size and the surface temperature of a droplet were known, the equilibrium value of water vapour pressure determined by these data can be used as a boundary condition for the diffusion of water vapour to or away from the droplet studied. This is a reasonable assumption as long as the net transport of water vapour is small as compared to the rate of exchange of molecules across the surface of the droplet. It is the purpose of this presentation to show, that this is not always the case, and to indicate some consequences of this fact.

The exchange process at the liquid-vapour boundary may be split into two processes, namely the escape of molecules from the liquid into the vapour phase and the capture of vapour molecules at the liquid surface.

If  $q_e$  denotes the average rate at which water molecules leave the liquid phase, given in g/sec/cm<sup>2</sup>, and if  $q_c$  represents the rate at which molecules from the vapour hit the liquid surface, then at equilibrium:

$$q_e = \alpha q_c \quad (1)$$

where  $\alpha$  is the condensation coefficient that indicates how large a proportion of the molecules hitting the surface are actually caught. According to measurements by ALTY & MACKAY (1935)  $\alpha$  for water has a value of 0.036 at 10° C, decreasing somewhat with rising temperature. Alty also states that for vapours in contact with a crystalline phase of the same substance, the condensation coefficient is near to 1 if the molecules do not have a dipole moment, but it is considerably lower for polar molecules. No value for ice is reported by him.

The magnitude of  $q_e$  can be estimated in the following way:

According to gas kinetic theory (cf KENNARD (1939))

$$q_c = \frac{e}{(2\pi RT)^{1/2}} \quad (2)$$

is the rate at which vapour molecules hit the surface. Here  $e$  is the vapour pressure in dynes/cm<sup>2</sup> immediately at the surface (i.e. at a distance from it approximately equal to the mean free path of the water molecules in the

air.  $R$  is the gas constant per gram of water vapour, and  $T$  is the absolute temperature.

At equilibrium equation (1) will be valid so that

$$q_e = \frac{\alpha e_0}{(2\pi RT)^{1/2}} \quad (3)$$

Now  $q_e$  as well as  $\alpha$  are independent of the state of the vapour phase so that any departure from equilibrium conditions in the exchange of molecules across the surface must be accompanied by a departure of  $q_e$  from the value indicated by (1). This departure is in fact seen to be proportional to the ratio of the actual rate of evaporation or condensation to the exchange rate  $q_e$ .

It is thus clear that when treating the problem of diffusion of water vapour to or from a liquid water surface for which the equilibrium pressure,  $e_0$ , of water vapour is known, one may not apply the boundary condition that.

$$e = e_0 \quad (4)$$

without qualification, but that a term proportional to the rate of evaporation should be included, giving:

$$e = e_0 \left( 1 - \frac{q}{q_e} \right) \quad (5)$$

where  $q$  denotes the rate of evaporation and  $q_e$  is defined above.

Making use of Alty's value for the condensation coefficient one finds that  $q_e$  at  $10^\circ \text{C}$  is equivalent to a rate of evaporation of 180 mm/h, a value so far above what is normally found in nature that the condition (4) can be used safely when treating the evaporation from lakes and other flat surfaces. The significance of the difference between (4) and (5) may, however, be judged more easily by the following argument: If one applies the boundary condition (2) and studies conditions at a small distance  $s$  from the liquid surface under the assumption that the transport of water vapour through the intervening layer takes place only through molecular diffusion, then one arrives at the following expression for the vapour pressure  $e_s$ :

$$e_s = e_0 - \frac{qs}{K} \quad (6)$$

where  $K$  is the appropriate coefficient of diffusion. Comparing (5) and (6) it is clear that the use of the boundary condition (4) in a problem of evaporation or condensation is equivalent to the neglect of an air layer through which the vapour has to pass by molecular diffusion. The thickness  $s$  of that layer is given by the relation

$$s = \frac{Ke_0}{q_e} = \frac{K}{\alpha} (2\pi RT)^{1/2} \quad (7)$$

Again, using the values appropriate at  $10^\circ \text{C}$  and 1,000 mb, we find that  $s = 5.1 \mu$  which can be safely neglected in many meteorological applications. However, in dealing with cloud droplets this is not so.

The growth equation normally used for cloud droplets may be written:

$$\frac{dm}{dt} = 4\pi Kr(e_a - e_0) \quad (8)$$

where  $m$  is the mass of the droplet,  $K$  is the same coefficient of diffusion as was used in (6),  $r$  is the radius of the droplet,  $e_a$  is the ambient partial pressure of water vapour, and  $e_0$  is the equilibrium value determined by the temperature, the radius of curvature, and the chemical composition of the droplet (cf. HOWELL (1949) or SQUIRES (1952)). The actual form of  $e$  is immaterial for this presentation.

According to the reasoning above,  $e_0$  in (8) should be replaced by

$$e_0 \left( 1 - \frac{q}{q_e} \right)$$

with

$$q = -\frac{1}{4\pi r^2} \frac{dm}{dt} \quad (9)$$

the net rate of transport of water vapour per unit area of the droplet surface.

Making use of (7) we finally get:

$$\frac{dm}{dt} = 4\pi Kr(e_a - e_0) \frac{r}{s+r} \quad (10)$$

A comparison between the two expressions for the growth rate is made in fig. 1 where the straight line represents equation (8) and the curved line below it represents equation (10). The value of  $s$  is taken to be  $5 \mu$ , applying

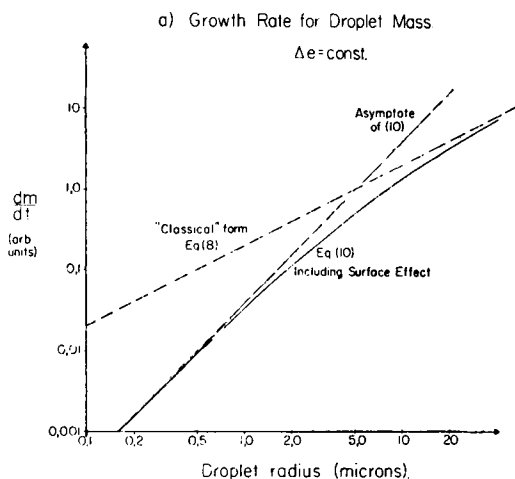
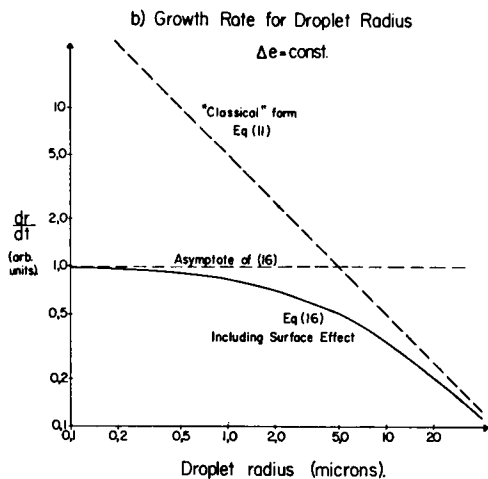


Fig. 1. a) Comparison of theoretical growth rates for a given value of  $e_a - e_0$  according to equations (8) and (10).



b) The same growth rates transformed into rates of change of droplet radius. (Equations (11) and (16)).

at 10° C and 1,000 mb. No conclusions as to the range of  $s$  can be drawn at the present time, since the information regarding the variation of  $\alpha$  is incomplete. If, however,  $\alpha$  were independent of the temperature, then  $s$  according to (7) would increase somewhat with a rise in the temperature.

However spectacular the difference displayed in fig. 1 may be, it is still difficult to judge its significance since the actual values of the excess humidity may vary considerably be-

tween the different members of a cloud droplet spectrum.

In order to elucidate this point one might look upon the development of the particle spectrum in a rising air column below the cloud base level. Hygroscopic particles kept in an environment of constant relative humidity will take on their equilibrium size according to the theory by KÖHLER (1936). Equilibrium curves relating droplet radius to relative humidity for various nucleus sizes are shown in fig. 2. KEITH and ARONS (1954), among others, have shown that the smaller particles follow their equilibrium curves almost perfectly, while the larger ones may lag behind considerably in their growth. Their data were gained by an integration of the usual equation of growth for the individual particles, following them in their motion, and were checked by experiments. The droplets that they used for the measurements of growth rates were however too large to show the effect discussed here.

A simple approximation to the integrated time lag of the particle growth may be reached by the following argument:

Equation (8) can be written as

$$4\pi\varrho r^2 \frac{dr}{dt} = 4\pi kr (e_a - e_0) \quad (8a)$$

where  $\varrho$  is the density of liquid water. Thus

$$\frac{dr}{dt} = \frac{K}{\varrho r} (e_a - e_0) \quad (11)$$

If now  $r_a$  is the equilibrium radius corresponding to the ambient vapour pressure  $e_a$ , then according to the mean value theorem:

$$e_a - e_0 = -(r - r_a) \frac{\partial e_0}{\partial r} \quad (12)$$

where the partial derivative should be determined for a droplet radius lying inbetween  $r$  and  $r_a$ . If the departure from equilibrium is not too great a sufficient approximation is reached by choosing the value  $r$ . Equation (11) may now be rewritten in the form:

$$\frac{d(r - r_a)}{dt} = -\frac{K}{\varrho r} \frac{\partial e_0}{\partial r} (r - r_a) - \frac{dr_a}{dt} \quad (13)$$

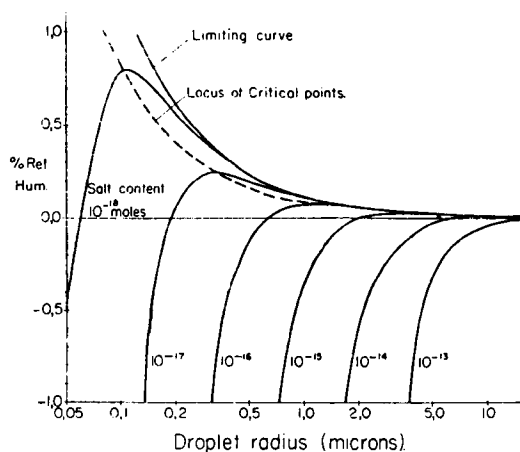


Fig. 2. Equilibrium curves for hygroscopic nuclei. The equilibrium is stable to the left and unstable to the right of the critical point.

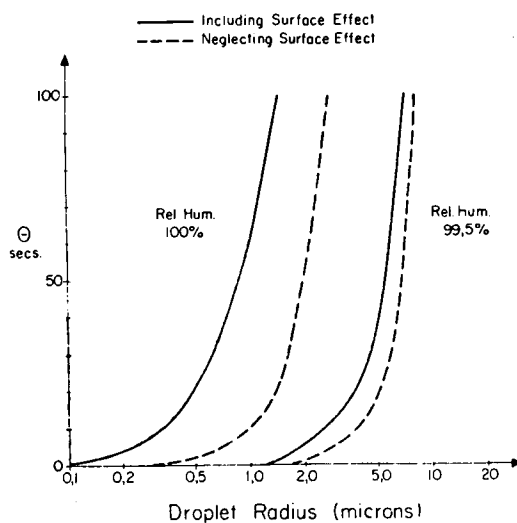


Fig. 3. Comparison of theoretical lag constants for cloud droplets of equilibrium size at 99.5 and 100 % relative humidity. The data apply at a temperature of 10° C.

Denoting the coefficient of  $(r - r_a)$  in the right hand member of (11) by  $\Theta^{-1}$ , so that

$$\Theta = \frac{qr}{K \frac{\partial e_0}{\partial r}} \quad (14)$$

two simple interpretations of equation (13) may be given. If the ambient vapour pressure Tellus IX (1957), 3

is constant, then small deviations from the equilibrium radius will decay exponentially with a time constant equal to  $\Theta$ . If, on the other hand,  $e_a$  undergoes a slow and steady variation, then the two terms in the right hand member of eg (13) will balance approximately. One finds in this case that the actual value of  $r$  will lag behind  $r_a$  so that at each instance it will be approximately equal to the  $r_a$ -value valid  $\Theta$  seconds earlier.

It is easily seen, that the same argument could be developed starting with equation (10), i.e. the modified form of the growth equation, producing the result that

$$\Theta = \frac{q(r+s)}{K \frac{\partial e_0}{\partial r}} \quad (15)$$

These values for the lag  $\Theta$  of the droplet growth should be quite accurate as long as the value of  $\Theta$  does not vary appreciably over time intervals comparable with  $\Theta$  itself.

In fig. 3 two sets of curves are shown, relating droplet radius to lag constant for droplets in equilibrium with an environment of 99.5 % and 100 % relative humidity respectively.

The stippled lines represent the values gained when using the equation in the normal form, while the fully drawn curves indicate the deviations caused by the correction factor  $(1 + s/r)$ . When looking at these curves one should bear in mind that values of  $\Theta$  around 100 seconds or more will not represent actual lags except possibly in cases of extremely slow cooling, and that lag values around 1 second or less have little significance as long as one is not working with very rapid expansions, such as in an Aitken counter. These considerations do, however, still leave room for a considerable influence of the correction factor presented here in the range of particles that have critical radii around a few microns.

An argument similar to that of HOUGHTON (1938) provides still another presentation of the difference between the two versions of the growth equation discussed here. Starting with equation (11)

$$\frac{dr}{dt} = \frac{K}{qr} (e_a - e_0) \quad (11)$$

and the corresponding modified form, which it seen to be

$$\frac{dr}{dt} = \frac{K}{\rho(r+s)} (e_a - e_0) \quad (16)$$

and treating  $s$  as a constant we may integrate the equations to give the following alternative expressions:

$$r_2^2 - r_1^2 = \frac{2K}{\rho} (\overline{e_a - e_0}) (t_2 - t_1) \quad (17)$$

and

$$(r_2 + s)^2 - (r_1 + s)^2 = \frac{2K}{\rho} (\overline{e_a - e_0}) (t_2 - t_1) \quad (18)$$

for the growth of a cloud particle. Here the bar denotes an average over the time interval considered. The only difference between Houghtons reasoning and the present argument is that  $(e_a - e_0)$  here represents the deviation of the ambient vapour pressure from the equilibrium at the surface of the droplet, including the effect of temperature deviations between droplet and environment, while Houghton worked under the simplifying assumption that  $e_0$  could be represented by the saturation vapour pressure at the ambient temperature of the environment. If to begin with,  $\overline{e_a - e_0}$  is prescribed, in analogy again with Houghton, then we see that the ratio  $R$  between the time taken for a droplet to grow from a size  $r_1$  to a size  $r_2$  according to the corrected and the uncorrected formula is

$$R = \frac{r_1 + r_2 + 2s}{r_1 + r_2} \quad (19)$$

For the growth from  $5$  to  $10 \mu$  this ratio is  $5:3$ , again accepting  $s = 5 \mu$ . This change is quite notable as the time scale involved here will generally be tens of seconds up towards a minute. However, in the dynamic development of a cloud the time scale is prescribed rather than the relative humidity, as the latter will increase if the water vapour is not consumed at a rate corresponding to the rate of cooling.

The expected value of the maximum supersaturation attained in the initial cloud formation would under such circumstances be higher according to the modified theory than otherwise. That value is the limiting factor that determines the partition of the particle spectrum

into one part that is growing actively and one inactive part. A higher maximum value of the supersaturation means a smaller limiting size to the nuclei growing actively. This leads to the somewhat surprising conclusion that an effect that slows down the growth of small particles under a given excess humidity may in fact by causing and increase in the relative humidity make it possible for more of the small particles to grow actively in the cloud.

It has thus been shown that the distribution of water vapour in the air in the vicinity of a drop that is evaporating or growing by condensation cannot be determined by considering the diffusion process alone unless the dimensions of the droplet are large compared to a distance  $s$  which is primarily determined by the rate of exchange of molecules between a water surface and the vapour phase under equilibrium conditions. If this distance  $s$  were of the order of  $10 \mu$ , then the results of any investigation regarding the development of cloud particle spectra would be seriously in error, unless the effect of the phase transition on the vapour pressure in the immediate vicinity of the droplets were included. If, on the other hand,  $s$  were around  $1 \mu$  or less, then the practical consequences in cloud physical problems would be very small, as droplets in the submicron range tend to adapt themselves so rapidly to changes in environmental conditions that a change of the time scale by a factor of 10 or even 100 is of little importance in that size range.

Whatever the scale of  $s$  may be, its importance will be greater the more rapid the cooling is in the cloud, as its effect is one of increasing the lag time of the particle growth, leaving the expressions for the equilibrium conditions unchanged.

Now the actual value of  $s = 5 \mu$  used in the present discussion is subject to considerable uncertainty. It is based on the value of  $\alpha = 0.036$  gained by ALTY & MACKAY (1935) by measurements of the rate of evaporation of drops suspended in water vapour of less than equilibrium pressure. The main difficulty in his experiment lies in the determination of the actual surface temperature. According to a discussion by VOLMER (1939) any systematic errors in the determination of  $\alpha$ -values tend to produce results that are too low. The presence of any surface contamination is

particularly serious, but also the problems of heat and vapour diffusion are great when dealing with a substance of relatively high volatility such as water. If the true value of  $\alpha$  were larger, then  $s$  would be proportionally smaller. Its effect would then soon approach the limit of meteorological insignificance. On the other hand, it is known that rain water contains organic matter. If that matter is present already in the cloud droplets, then it may cause the actual  $\alpha$ -values to be much lower than for pure water. Consequently a wider spectrum of droplet sizes could be produced than in a cloud of uncontaminated water droplets. This effect would then greatly favour the onset of droplet growth by coalescence,

especially in cases of relatively strong updraughts. All these conclusions will, however, remain speculations until more and better information regarding the exchange of water molecules across a vapour-liquid interface is made available, as well as data on the possible presence of surface films or cloud droplets.

### Acknowledgements

Thanks are due to members of the International Meteorological Institute for valuable criticism and discussions. The study was made possible through the support given by Statens Tekniska Forskningsråd for work on cloud physics and evaporation problems.

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