

On the enhancement of probability of ion induced nucleation on partially wettable, water insoluble planar substrate

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The nucleating behaviour of partially wettable, water insoluble planar substrate has been studied. The rate and probability of nucleation were found to be enhanced in ion induced nucleation. It is found that there exists a threshold for angle of contact above which the effect of ions is dominant. The effect of ions is more pronounced at low supersaturation ratios and low temperatures for the material of large angle of contact w.r.t. water.

1 Introduction

The supersaturations necessary for the formation of water drop nucleus about the foreign particles, such as dust particles, ions etc. (heterogeneous nucleation) are much less than those required for pure water vapour (homogeneous nucleation). Supersaturations as high as several hundred per cent, which would be necessary for drop formation via homogeneous nucleation, do not occur in nature, but that typically supersaturations remain below 10% and most often even below 1%. This indicates that drop formation in the atmosphere occurs via heterogeneous nucleation involving aerosol particles (AP). The AP which are capable of initiating drop formation at the observed low supersaturations are called cloud condensation nuclei (CCN).

Also, cloud glaciation generally begins at temperatures much warmer than required for the homogeneous freezing of water. Mossop *et al.*¹ observed ice crystals in a long lived cumulus cloud whose top was probably never colder than -4°C , and which was not seeded with ice particles from clouds at higher altitudes. Such behaviour indicates that some fraction of local AP also can serve as ice forming nuclei (IN).

Classical water drop nucleation theory was applied by Fletcher² to planar as well as spherically convex surfaces of various sizes and discussed the effect of size. Mc Donald³ explained the dependence of critical supersaturation ratio on the radius

of the spherical insoluble substrates. Fletcher⁴ considered various shapes of AP for the production of a crystalline phase. Mahata and Alofs⁵ modified the heterogeneous nucleation theory of Fletcher^{2,4} to consider nucleation on a water insoluble, partially wettable, spherically concave substrate. The distribution of water insoluble aerosol particles with diameters in the range 3-60 μm has been studied by Rosinski *et al.*⁶ as a function of hailstone radius for a collection of large hailstones ingested by a storm, indicating an active role of AP, in the development of the embryos.

Further, Mason⁷ has mentioned the water condensation on ions. Varshneya⁸, in an attempt to detect the ionizing radiation through supercooled liquids, demonstrated that really the ice nucleus formation on ions was possible. Later he gave the theory of homogeneous condensation and ice nucleation on ions⁹. The ions are produced in the lower atmosphere by radioactivity and galactic cosmic rays. The effect of ions in water condensation and ice nucleation had been studied^{10,11} to show that ion induced nucleation takes place at much lower supersaturations than those required for homogeneous ion-free nucleation.

In the present paper we consider the nucleation on a charged aerosol particle and examine the enhancement in the probability of nucleation on partially wettable, water insoluble AP. Unfortunately, little is known about the contact angle of

Table 1 – Contact angle of water on selected solid surfaces in air¹⁸

Substrate	Angle of contact deg
Cadmium iodide	0
Silver iodide	9-17
Platinum	40
Quartz, beach sand	43-52
Polyvinyl formal	50
Silver chloride	50-55
Lead iodide	64-80
Surface soil	65.2-68.9
Gold	65.5
Polyethylene terephthalate	70
Silver	79.5
Polymethylmetacrylate	80
Polyethylene	94
Teflon	100-117

water on insoluble AP, except for some experiments of water against certain silicates (Table 1).

2 Theoretical considerations

2.1 Water vapour condensation

The cases of homogeneous nucleation and the heterogeneous nucleation on water soluble hygroscopic salt particles have been treated in detail by many workers¹²⁻¹⁵. Intermediate between these two opposite cases are the insoluble particles which can nucleate at moderate supersaturations depending on their size and extents to which their surfaces are hydrophobic or hydrophilic, non-wettable or wettable. Ions are also known to enhance the process of nucleation.

In nucleation process taking place on partially wettable, water insoluble aerosol particles, water embryo assumes the shape of a cap. In this case the angle of contact is the main controlling factor. Angle of contact depends on the relative nature between the substrate and water. It differs from one pair to another. Joany and Gennes¹⁶ discussed the contact angle hysteresis and obtained formulae for 'advancing' and 'receding' contact angles in terms of the distribution of chemical defect strength and defect sharpness in case of chemically heterogeneous planar substrate. The substrates are known to have a variety of shapes⁴. Although no direct observations of the shape of water nucleus are available, some experimental justification for the spherical cap assumption has been provided¹⁷. In the classical models of drop formation the Gibbs' function has been taken into

consideration. However, it has been shown that the Helmholtz free energy is the proper thermodynamic potential and the Gibbs' function is only its approximation^{12,13}. For practical purposes, the resulting difference turns out to be negligible. The Helmholtz free energy of the system is given by¹⁸.

$$\Delta F_p = [-(4\pi\Delta f_{vol}r_p^3/3) + 4\pi\sigma_{w/v}r_p^2]f(m_{w/v}) \quad \dots (1)$$

where,

$$f(m_{w/v}) = (2 + m_{w/v})(1 - m_{w/v})^2/4$$

$$\Delta f_{vol} = (\rho_w RT \ln S_{v,w})/M_w, \text{ the Helmholtz free energy per unit volume of condensate}$$

$$m_{w/v} = \cos \theta.$$

Here suffix 'p' stands for planar substrate; ρ_w is the density of condensate (water), R the universal gas constant, T the temperature of the system in K, $S_{v,w}$ the supersaturation ratio, M_w the molecular weight of water, and θ the contact angle of drop surface with the surface of aerosol particles, r_p the radius of embryo about planar substrate and $\sigma_{w/v}$ the surface tension of water-vapour interface.

If the aerosol particle is charged, it provides additional electrostatic energy. The electrostatic energy term ΔF_{pE} has been given⁹ to be

$$\Delta F_{pE} = 3Q^2/5r_p' \\ = 3(Ze)^2/5r_p' \quad \dots (2)$$

where $Q = Ze$, the charge on the ion, Z the charge number and e the electronic charge.

In the above expression the dielectric constant of water has not been included, because it is believed that the embryos have already been formed with their structural configuration of the condensed phase. Its inclusion, however, does not lead to more refinement in the calculations. The presence of ions thus modifies the Helmholtz free energy of formation of the nucleus. The modified expression is given by

$$\Delta F_p' = [-(4\pi\Delta f_{vol}r_p'^3/3) + 4\pi\sigma_{w/v}r_p'^2 \\ + 3(Ze)^2/5r_p']f(m_{w/v}) \quad \dots (3)$$

where r_p' is the new radius of the drop.

Eq. (3) can be written as

$$\Delta F_p' = [-Ar_p'^3 + Br_p'^2 + C/r_p']f(m_{w/v}) \quad \dots (4)$$

where A , B and C are arbitrary constants with

$$A = 4\pi\Delta f_{vol}/3 \\ = (4\pi\rho_w RT \ln S_{v,w})/3M_w, \text{ constant for a given temperature and supersaturation ratio}$$

$$B = 4\pi\sigma_{w/v}$$

$$C = 3(Ze)^2/5$$

The curve of $\Delta F_p'$ peaks for a particular value

of r_p . If the size of the condensed drop is more than the above value of r_p , the drop increases in size, otherwise it evaporates. This critical size of drop is obtained by setting $\partial(\Delta F_p)/\partial r_p$ equal to zero. Thus the critical size of uncharged drop (r_p^*) for cloud nucleation is given by

$$r_p^* = 2 \sigma_w / \Delta f_{vol} \quad \dots (5)$$

However, the critical sizes of the charged drops ($r_p'^*$) could not be obtained directly. It has been obtained numerically. Setting $\partial(\Delta F_p^*)/\partial r_p' = 0$, Eq. (4) reduces to

$$-3A r_p'^*{}^2 + 2B r_p'^* - (C/r_p'^*{}^2) = 0 \quad \dots (6)$$

or,
$$-3A r_p'^*{}^4 + 2B r_p'^*{}^3 - C = 0, [\because r_p'^* \neq 0] \quad \dots (7)$$

The resulting equation [Eq. (7)] is a fourth order equation. It gives at least two real roots, $r_{1p}'^*$ and $r_{2p}'^*$. Figs 1 and 2 represent the variation of $\Delta F_p'/f(m_w/v)$ with the radius of the embryo as the function of supersaturation ratio and temperature, respectively.

In the case of charged particles, the free energy curve usually features a minimum and a maximum. The minimum corresponds to the most stable state with the largest percentage of pre-nucleation embryos. The maximum corresponds to the unstable equilibrium, or critical state, and once a charged ion-substrate cluster passes this maximum, it grows to a droplet size. Radii $r_{1p}'^*$ and $r_{2p}'^*$ correspond to the minimum and maximum free energy, respectively. The corresponding free energy barriers are $\Delta F_{1p}'^*$ and $\Delta F_{2p}'^*$. The energy barrier for controlling nucleation is represented by the difference $\Delta F_p'^* (= \Delta F_{2p}'^* - \Delta F_{1p}'^*)$,

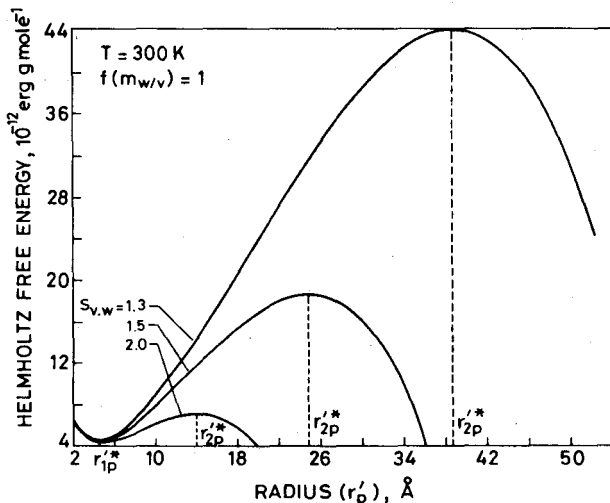


Fig. 1 - Variation of the Helmholtz free energy with radius of an embryo about charged planar substrate at $T = 300K$ as the function of supersaturation ratio

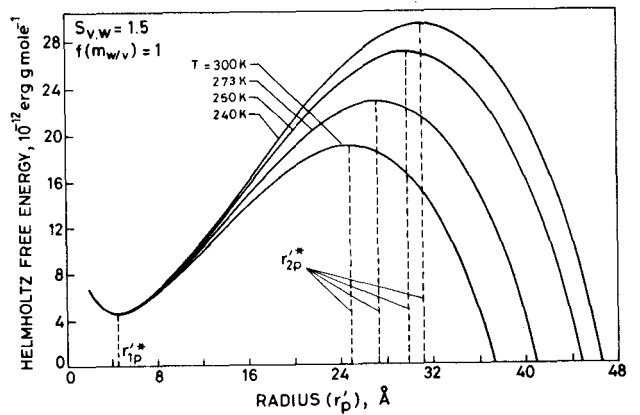


Fig. 2 - Same as in Fig. 1 except that $S_{v,w} = 1.5$ as the function of temperature

between most stable and the critical state. The higher the supersaturation ratio, the lower will be the nucleation energy barrier (Fig. 1) with $r_{1p}'^*$ increasing and $r_{2p}'^*$ decreasing, while r_p^* (without charge) is also found to decrease (not shown in figure). At a supersaturation ratio of about 3.5 at 300K, $r_{1p}'^*$ and $r_{2p}'^*$ become approximately equal and the free energy barrier to nucleation of charged planar substrate vanishes, and all the charged particles are nucleated. Similarly, Fig. 2 exhibits the variation of Helmholtz free energy of formation of nucleus with radius as a function of temperature. The higher the temperature, the lower will be the nucleation energy barrier with $r_{2p}'^*$ decreasing.

Substituting the radius of a critical drop from Eq. (5) in Eq. (1), one gets the Helmholtz free energy of drop formation as follows.

$$\Delta F_p^* = [16 \pi M_w^2 \sigma_w^3 / 3 (\rho_w RT \ln S_{v,w})^2] f(m_w/v) \quad \dots (8)$$

For the charged droplets, the free energy minimum at $r_p = r_{1p}'^*$ is

$$\Delta F_{1p}'^* = [-(4 \pi \Delta f_{vol} r_{1p}'^*{}^3 / 3) + 4 \pi \sigma_w / r_{1p}'^* + 3(Ze)^2 / (5 r_{1p}'^*)] f(m_w/v) \quad \dots (9)$$

and the free energy maximum at $r_p = r_{2p}'^*$ is

$$\Delta F_{2p}'^* = [-(4 \pi \Delta f_{vol} r_{2p}'^*{}^3 / 3) + 4 \pi \sigma_w / r_{2p}'^* + 3(Ze)^2 / (5 r_{2p}'^*)] f(m_w/v) \quad \dots (10)$$

the free energy barrier between the most stable and critical state is, therefore, obtained as

$$\Delta F_p'^* = \Delta F_{2p}'^* - \Delta F_{1p}'^* \quad \dots (11)$$

The corresponding rate of surface nucleation of uncharged water drop is

$$J_p = [\pi Z_s e_{sat} r_p'^*{}^2 / (2 \pi m_w k T)]^{1/2} \times C_{1,s} \exp[-\Delta F_p^* / kT] \quad \dots (12)$$

and for charged drops is

$$J'_p = [\pi Z_s e_{\text{sat}\cdot w} r_{2p}^{*2} / (2 \pi m_w kT)^{1/2}] \times C_{1\cdot s} \exp[-\Delta F_p^*/kT] \quad \dots (13)$$

where k is Boltzmann constant, Z_s the Zeldovich factor for surface nucleation which is a function of ΔF_p and the temperature, $C_{1\cdot s}$, the concentration of single water molecules adsorbed on the surface, $e_{\text{sat}\cdot w}$, the saturated vapour pressure of water and m_w , the mass of a water molecule. Fletcher² estimated the prefactor to the exponential term in Eq. (12) to be of the order of 10^{24} - $10^{27} \text{ cm}^{-2} \text{ s}^{-1}$ at 0°C . However, for our purpose we divide Eq. (13) by Eq. (12) to obtain the ratio

$$R_p = J'_p/J_p = (r_{2p}^*/r_p^*)^2 \exp[(\Delta F_p^* - \Delta F_p'^*)/kT] \quad \dots (14)$$

Though the Zeldovich factor Z_s is a function of $(\Delta F_p^*)^{1/2}$, we have not considered its variation with the state of ionization. For all practical purposes the influence of Zeldovich factor on the value of R_p is negligible.

Table 2 shows the variation of R_p with the contact angle for different typical values of supersaturation ratio $S_{v\cdot w}$. It is evident from Table 2 that the rate of nucleation of charged drops is very high for low supersaturation ratios. At a given angle of contact and temperature, as the supersaturation ratio increases, the value of R_p decreases. For example, at $\theta=30^\circ$ and $T=273\text{K}$, the value of $\ln R_p$ decreases from 1.50 to 0.72 for an increase in supersaturation ratio ($S_{v\cdot w}$) from 1.3 to 3.0. Similarly at a given $S_{v\cdot w}$ and θ , increasing temperature decreases the value of $\ln R_p$. For ex-

ample, at $\theta=30^\circ$ and $S_{v\cdot w}=1.3$, $\ln R_p$ decreases from 1.65 to 1.50 for a temperature increase from 250K to 273K. Also, at a temperature 300K and supersaturation ratio of 3.0, $\ln R_p$ is positive only above a contact angle of 26° . Thus one may assume that at $S_{v\cdot w}=3.0$, the nucleation of charged drops is ineffective compared to the uncharged drops. However, above about $S_{v\cdot w}=3.5$, the value of R_p remains always less than 1 and the nucleation on uncharged drops is dominant. The supersaturation ratio¹⁹ in a cloud is typically around 1. Thus one may conclude that the nucleation in a cloud is dominant on ions and charged aerosol particles.

The critical angle θ_c above which the value of $\ln R_p$ is positive (i.e. above which the nucleation of charged drops is dominant) increases with increasing supersaturation ratio. The value of θ_c decreases with decreasing temperature. This shows that the nucleation of charged drops is more effective at lower temperatures. Table 3 gives the critical angles of contact at some arbitrary values of temperature and supersaturation ratios.

Strayer and Donnelly²⁰ experimentally determined the probability of nucleation by an ion for a Vortex ring in He-II. The probability of nucleation on an uncharged insoluble planar substrate is the exponential part of Eq. (12). i.e.,

$$P_p = \exp[-\Delta F_p^*/kT] \quad \dots (15)$$

and, in the case of charged drops [Eq. (13)], it is

$$P'_p = \exp[-\Delta F_p'^*/kT] \quad \dots (16)$$

Thus, the ratio of the probabilities of nucleation

Table 2 – Natural logarithm of the factor of enhancement of nucleation rate ($\ln R_p$) about charged to uncharged planar substrate at 250 K and 273 K as a function of supersaturation ratio ($S_{v\cdot w}$) and angle of contact (θ)

$S_{v\cdot w}$	$\ln R_p$ at an angle of contact (in deg)							
	10	20	30	40	50	60	70	80
At temp 250 K								
1.3	0.018	0.340	1.65	4.87	10.84	20.10	32.60	47.13
1.5	0.015	0.321	1.57	4.62	10.29	19.08	30.96	45.33
2.0	-0.015	0.256	1.36	4.07	9.10	16.90	27.44	40.18
2.5	-0.065	0.177	1.17	3.59	8.09	15.07	24.50	35.90
3.0	-0.142	0.075	0.96	3.12	7.15	13.39	21.81	32.00
At temp 273 K								
1.3	0.015	0.307	1.50	4.41	9.84	18.23	29.58	43.30
1.5	0.007	0.282	1.40	4.16	9.27	17.19	27.90	40.84
2.0	-0.023	0.218	1.20	3.61	8.08	15.02	24.39	35.71
2.5	-0.106	0.105	0.97	3.08	7.01	13.09	21.32	31.26
3.0	-0.218	-0.034	0.72	2.55	5.97	11.27	18.42	27.07

Table 3 – Critical angle of contact (θ_c) above which $R_p \geq 1$ at 250, 273 and 300K as a function of supersaturation ratio ($S_{v,w}$)

Temperature °K	θ_c at supersaturation ratio				
	1.3	1.5	2.0	2.5	3.0
250	6.5	7.5	12.0	15.0	18.5
273	7.0	8.0	12.5	17.5	21.0
300	7.5	8.5	15.0	19.0	26.0

of drops on charged to uncharged planar substrate is given by

$$S_p = (P'_p/P_p) = \exp[(\Delta F_p^* - \Delta F'_p^*)/kT] \dots (17)$$

Figs 3-5 show the variation of $\ln S_p$ with different parameters such as angle of contact, temperature, supersaturation ratio etc. From Figs 3-5 it is clear that the probability of nucleation of charged drops is very high for low supersaturation ratios. As the supersaturation ratio increases, the value of S_p decreases in the same fashion as R_p does. The variations of S_p have been discussed in detail in Sec. 3.

As it is evident from the preceding paragraphs, the parameters R_p and S_p are highly dependent on the angle of contact, θ . The contact angle depends upon the material of the particle on which the nucleation takes place. The value of θ ranges from 0° for cadmium iodide to $100-117^\circ$ for teflon (Table 1). For good nucleating substances like platinum, AgI, AgCl, quartz and beach sand it ranges from 9 to 50° .

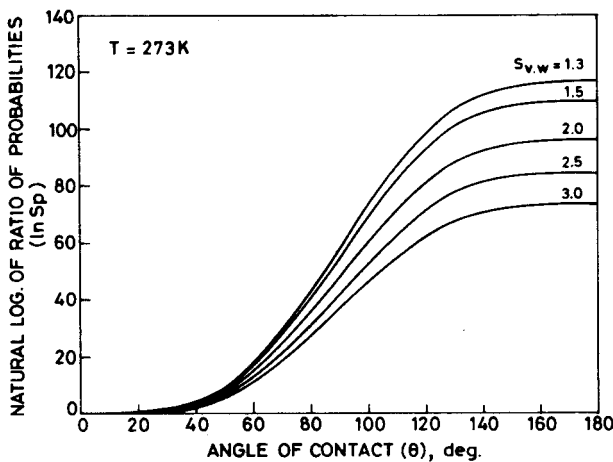


Fig. 3 – Natural logarithm of the ratio of probabilities of nucleation about a charged to uncharged planar substrate varying with the angle of contact at $T=273K$ as the function of supersaturation ratio

2.2 Freezing of supercooled water following water condensation

We now consider the heterogeneous ice deposition. Assuming the spherical cap model for ice nucleation and following the procedure presented in Sec. 2.1, one can write the Helmholtz free energy for critical size of uncharged ice crystal nucleus as

$$\Delta F_{gp}^* = [-(4\pi\Delta f_{vol}r_{gp}^{*3}/3) + 4\pi\sigma_{g/v}r_{gp}^{*2}]f(m_{g/v}) \dots (18)$$

and, for stable charged ice nuclei, at $r=r_{1gp}^*$ as

$$\Delta F_{1gp}^* = [-(4\pi\Delta f_{vol}r_{1gp}^{*3}/3) + 4\pi\sigma_{g/v}r_{1gp}^{*2} + 3(Ze)^2/(5r_{1gp}^*)]f(m_{g/v}) \dots (19)$$

For unstable charged critical nuclei, at $r=r_{2gp}^*$, we have

$$\Delta F_{2gp}^* = [-(4\pi\Delta f_{vol}r_{2gp}^{*3}/3) + 4\pi\sigma_{g/v}r_{2gp}^{*2} + 3(Ze)^2/(5r_{2gp}^*)]f(m_{g/v}) \dots (20)$$

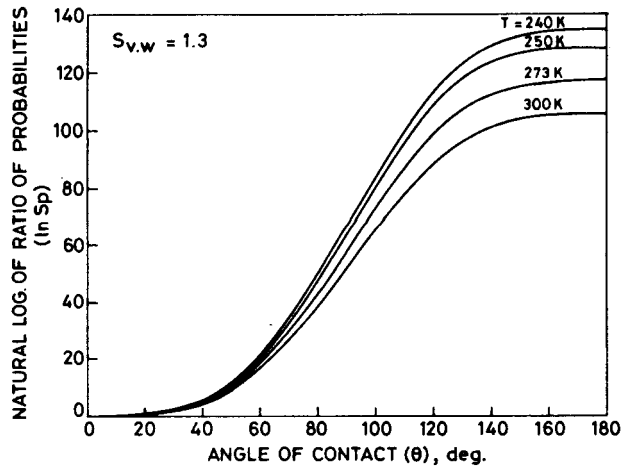


Fig. 4 – Same as in Fig. 3 except at $S_{v,w}=1.3$ as the function of temperature

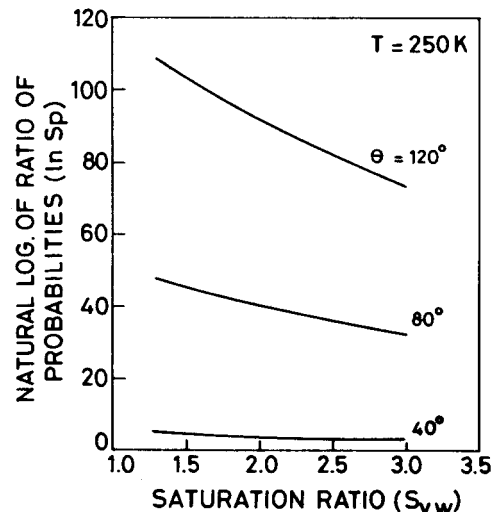


Fig. 5 – Same as in Fig. 3 except as varying with supersaturation ratio at $T=250K$ as the function of the angle of contact

Here r_{1gp}^* and r_{2gp}^* correspond, respectively, to the minimum and maximum free energy. Suffix gp represents the case of ice nucleus formation about the insoluble planar substrate. Hence, the free energy barrier for nucleation between the most stable and the critical (unstable) state is

$$\Delta F_{gp}^* = \Delta F_{2gp}^* - \Delta F_{1gp}^* \quad \dots (21)$$

In the present case, Δf_{vol} is given by

$$\Delta f_{vol} = (L\rho_g/M_w)(T\Delta T/T_0^2) \quad \dots (22)$$

where ρ_g is the density of ice, L the latent heat of freezing, T the temperature at which nucleation takes place, T_0 the thermodynamic freezing temperature and ΔT the amount of supercooling. The value of $\sigma_{g/v}$ is taken to be $100 \text{ erg}\cdot\text{cm}^{-2}$. The compatibility parameter $m_{g/v}$ is now not only the cosine of the contact angle, but it depends upon the surface energy of the substrate against vapour ($\sigma_{n/v}$) and ice ($\sigma_{n/g}$) and on the interfacial surface energy $\sigma_{g/v}$ of nucleating particles¹⁸ as given by

$$m_{g/v} = (\sigma_{n/v} - \sigma_{n/g})/\sigma_{g/v} \quad \dots (23)$$

The value of $\sigma_{n/v}$ varies considerably depending upon the kind of substrate. It ranges from 21 to $43 \text{ erg}\cdot\text{cm}^{-2}$ for soil and sand to $190 \text{ erg}\cdot\text{cm}^{-2}$ for AgI. It is found experimentally that in the central portion of a snow crystal the clay minerals are the maximum. Therefore, for any fruitful computation the lower values of $\sigma_{n/v}$ will be preferred. The value of $\sigma_{n/g}$ may approximately be taken equal to $20 \text{ erg}\cdot\text{cm}^{-2}$.

Adopting the procedure described in Sec. 2.1, the ratio of the rate of nucleus formation of charged to uncharged ice crystals is given by

$$R_{gp} = (r_{2gp}^*/r_{1gp}^*)^2 \exp[(\Delta F_{gp}^* - \Delta F_{gp}^*)/kT] \quad \dots (24)$$

In the case of heterogeneous ice nucleation in supercooled water one must add the activation energy ($\Delta F_{g/w}^*$) for water molecules to cross the water/ice boundary, to the Helmholtz free energy for the critical size of the nuclei. The total energy of the nucleus formation about the uncharged insoluble planar substrate is given by

$$\Delta F_{Tp}^* = \Delta F_{gp}^* + \Delta F_{g/w}^*, \quad \dots (25)$$

for charged stable nuclei at $r = r_{1gp}^*$ by

$$\Delta F_{1Tp}^* = \Delta F_{1gp}^* + \Delta F_{g/w}^* \quad \dots (26)$$

and, for charged critical nuclei at $r = r_{2gp}^*$ by

$$\Delta F_{2Tp}^* = \Delta F_{2gp}^* + \Delta F_{g/w}^* \quad \dots (27)$$

The expressions for ΔF_{gp}^* and ΔF_{gp}^* are written analogous to the Eqs (18)-(20).

The rate of nucleation in this case for uncharged nuclei is given by

$$J_{gp} = (kT/h)Z_s N\Omega_{gp} C_s \exp[-(\Delta F_{gp}^* + \Delta F_{g/w}^*)/kT] \quad \dots (28)$$

Similar expression can be written for the case of charged nuclei from Eqs (25)-(27). Here $N\Omega_{gp}$ is the number of water molecules contained in the ice nucleus, N being Avogadro's number. The term, $Z_s N\Omega_{gp}$ is approximately of the order of unity. Now the ratio of the rate of nucleation can be readily obtained as

$$R'_{gp} = \exp[(\Delta F_{gp}^* - \Delta F_{gp}^*)/kT] \quad \dots (29)$$

where,

$$\Delta F_{gp}^* = \Delta F_{2gp}^* - \Delta F_{1gp}^*$$

It is evident from the computed values of the ratio of R_{gp} and R'_{gp} that the ice formation on charged substrate is dominant over the uncharged substrates. Thus, one may argue that practically the atmospheric ice formation takes place on ions. The atmospheric ions are in abundance ($\sim 10^9 \text{ m}^{-3}$) near the ground surface and the number density increases with increasing altitude (maximum at about 15 km).

For a given value of $m_{g/v}$, the efficiency of ice formation decreases for decreasing temperature. With increasing value of $m_{g/v}$, the value of $\ln R'_{gp}$ decreases. It has really been found that the ice formation on some substrates like sand and soil with small values of $m_{g/v}$ is more pronounced compared to others like AgI with high values of $m_{g/v}$.

The value of $\sigma_{g/v}$ is taken to be $20 \text{ erg}\cdot\text{cm}^{-2}$. The nature of variation of R_{gp}' is the same as that for R_{gp} , but the values are about two orders of magnitude less. For $m_{g/w} = 1.00$, J_{gp}' becomes less than J_{gp} showing that at this point the charges become completely ineffective in ice formation. This value of $m_{g/w}$ corresponds to the substrates with high value of surface energy (say AgI and AgCl) against water. The substrates with low surface energy (say sand and soil) correspond to the minimum value of $m_{g/w}$. In fact it has experimentally been found¹⁸ that the surface soil has the strong nucleability. Clays such as kaolinite often exhibited varying ice nucleating ability. The wind tunnel experiments have also exhibited the same results.

3 Results and discussion

From Figs 1 and 2, it is evident that in the case of charged particles the critical size of nuclei (r_{2p}^*) decreases, while radii of stable nuclei (r_{1p}^*) increase with increasing supersaturation ratios. The radii of stable nuclei are almost constant but the critical radii r_{2p}^* decrease with increasing temperature.

The critical sizes of the charged nuclei about planar substrate are given by setting $\partial(\Delta F_p^*)/\partial r_p^* = 0$. This results in Eq. (6) which can further be written as

$$-3A r_p^{*2} + 2B r_p^* = C/r_p^{*2} \quad \dots (30)$$

The L.H.S. and R.H.S. of Eq. (30) have been plotted in Fig. 6(b). The points of intersection of these two curves are the two real roots of Eq. (6), shown in Fig. 6(a). The two roots r_{1p}^* and r_{2p}^* correspond to the minimum and maximum in the Helmholtz free energy variation with radius. The energy barrier to nucleation is given by Eq. (11) as

$$\Delta F_p^* = \Delta F_{2p}^* - \Delta F_{1p}^*$$

The energy decreases with increasing supersaturation ratio in both charged and uncharged cases. Also, it decreases with increasing temperature. Above the supersaturation ratio of about 3.5 at $T=300K$, the critical sizes r_{1p}^* and r_{2p}^* become approximately equal and the free energy barrier to nucleation of charged planar substrate vanishes and all the charged particles are nucleated. In homogeneous ion induced nucleation at $T=300K$ such threshold supersaturation ratios are 4.7 for positive ion and 4.1 for negative ion²¹, and 3.0 for both the ions²², whereas experimental values are 4.87 for positive ions and 4.14 for negative ions²³.

The factor of enhancement R_p of nucleation rate as the function of temperature, supersaturation ratio and angle of contact, exhibits that at a given temperature and angle of contact, the ratio decreases with increasing supersaturation ratio. But it increases with increasing angle of contact at a given temperature and supersaturation ratio. For example, at $T=273K$ and $S_{v,w}=1.5$, we have $\ln R_p = 1.40$ at $\theta = 30^\circ$ and 17.19 at $\theta = 60^\circ$.

The probability of nucleation on a partially wettable, water insoluble planar substrate has been discussed for charged and uncharged cases. The comparisons have also been made with the pure water nucleation (homogeneous). It is evident from the following discussion that ions enhance the nucleability of water insoluble planar substrates. Fig. 3 shows the enhancement, in the nucleation probability varying with the angle of contact as the function of supersaturation ratio, of ion induced water insoluble planar substrate as compared to that of uncharged planar. From Fig. 3 it is clear that the ratio of the probabilities of nucleation increases with increasing angle of contact at a given temperature and supersaturation ratio. The increase is moderate and linear between the angles 60° and 110° . For lower values of θ , the increase is fast and for higher values of $\theta (>130^\circ)$ the ratio is approximately constant (and highest). At $T=273K$ and $S_{v,w}=1.5$, $\ln S_p$ increases from 1.42 to 4.12 (190.14%) for θ changing from 30 to 40° , and from 100.8 to 105.9 (5.06%) for θ changing from 130 to 140° . Also, the enhancement in the ratio of probabilities at a constant supersaturation ratio decreases with increase in temperature (Fig. 4). For θ increasing from 60 to 110° , the value of $\ln S_p$ increases from 21.00 to 100.3 at $T=240K$ and $S_{v,w}=1.3$, while it increases from 16.43 to 78.51 for the same increase in θ at $T=300$ and $S_{v,w}=1.3$. This indicates that at higher values of θ , the ions play an appreciable role in nucleation. Its more elaboration, varying with supersaturation ratio as the function of angle of contact, has been shown in Fig. 5 which suggests that at a given temperature the ratio of probabilities decreases with increase in supersaturation ratio. From Fig. 5 it is also clear that for lower values of θ , the variation of $\ln S_p$ is less steep than that for higher values of θ . At temperature 250K, the value of $\ln S_p$ decreases from 4.87 to 3.28 ($\tan^{-1} 0.93$) for $\theta=40^\circ$, and from 108.5 to 73.13 ($\tan^{-1} 20.8$) for $\theta=120^\circ$ for the same increase in $S_{v,w}$ (from 1.3 to 3.0).

Fig. 7 represents the ratio of the probabilities of nucleation of charged to uncharged planar substrate and also the comparison with that of

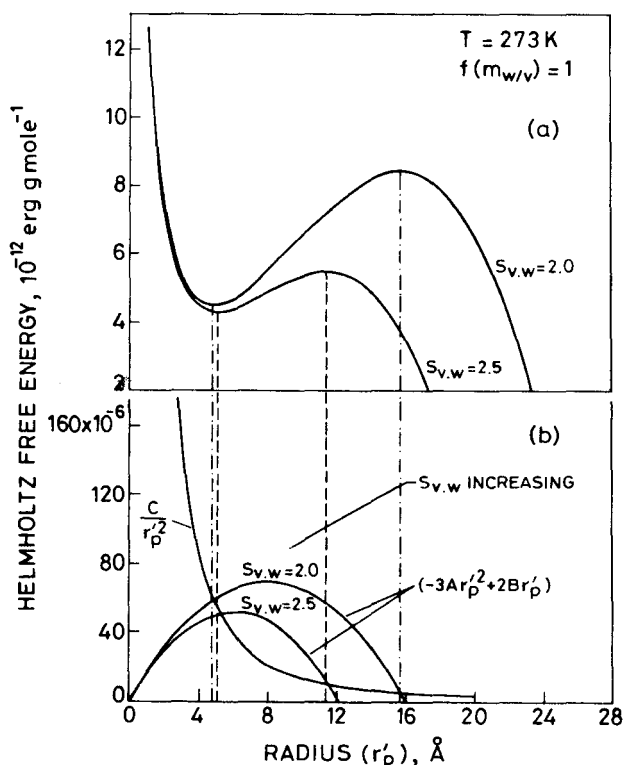


Fig. 6 - Graphical solution of Eq. (6) at $T=273K$ as the function of supersaturation ratio

charged planar substrate to uncharged pure water, and charged to uncharged water nucleus, varying with the angle of contact at $T=273\text{K}$ for supersaturation ratios 1.5 and 2.5. From Fig. 7 it is evident that for higher values of θ , the ratios converge to the value of ratio of charged water nucleus to uncharged one (independent of θ). For smaller values of θ , the ratio of charged insoluble planar substrate to uncharged water is much higher than the ratio of charged to uncharged water nucleus, while the ratio of charged to uncharged water insoluble planar substrate is lower. The difference decreases with the increase of θ .

It would be worthwhile at this point to compare the theoretically obtained results in Sec. 2 with experimental observations. From studies of ice nucleation on ions we can conclude that the presence of negative ions decreases the supersaturation ratio required for drop nucleation below the value required under homogeneous conditions. However, positive ions raised the critical supersaturation ratio. A qualitative explanation to this effect was given in terms of the structural arrangement of pseudo-crystalline water molecules²⁴. Singh *et al.*¹⁰ explained this behaviour of

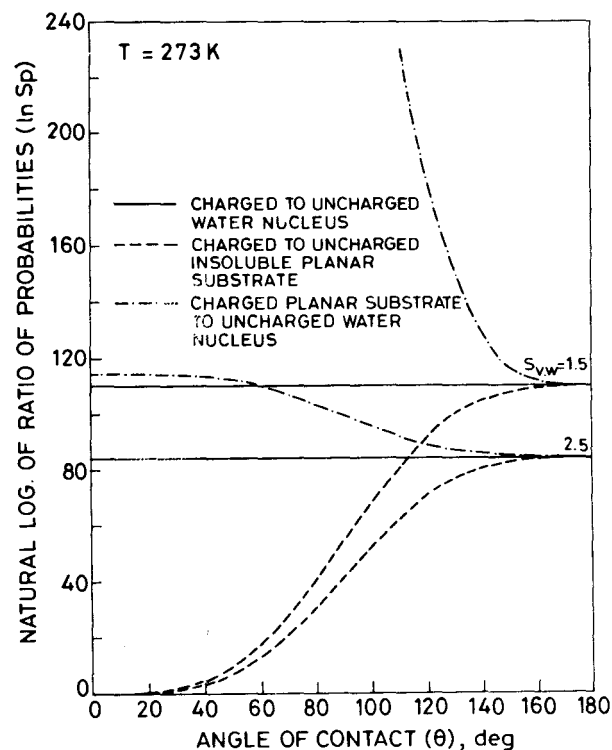


Fig. 7 – Same as in Fig. 3 except also for the ratio of probabilities of nucleation about charged planar substrate to uncharged water nucleus, and that of charged to uncharged water nucleus

ions in the case of water condensation and ice deposition.

The most significant effect of ions has been on ice formation. The supercooled water drops containing particles of quartz or naphthalene were nucleated to ice at significantly warmer temperatures when the particles carried a net negative charge than when they were neutral²⁵. Direct evidence of ice formation on charged particles was provided by Varshneya⁸, where he detected the cosmic ray radiation through the supercooled water. Abbas and Latham²⁶ observed that the charged nuclei produced during corona discharges or sparks promoted ice formation from the supercooled drops. In a wind tunnel study it has been found that the freely suspended supercooled charged drops froze at higher temperature as compared to the uncharged drops²⁷. Thus the ions affect the ice formation and drop nucleation considerably.

The presence, on insoluble planar substrate, of a foreign ion (chemical inhomogeneity on the surface) which is hydrophilic relative to the rest of the solid surface, creates active site for preferred adsorption of water molecules from the vapour, and hence preferred water drop formation. Chemical inhomogeneities attract water molecules to the substrate surface by means of electric forces which develop between the dipole moment of the water molecule and the net dipole or charge on the foreign ion. Growth of water cluster at such a site is also aided by the relatively higher mobility of molecules on the substrate surface surrounding the hydrophilic site.

4 Conclusion

From the above theoretical considerations one may conclude that in the formation of atmospheric clouds the aerosol particles play a significant role. The ions when attached to these AP enhance the nucleability by several orders. The enhancement in the rate of nucleation, and the probability of nucleation of water drops and ice crystals about charged insoluble planar substrate are by several orders. The nucleability of the charged substrate decreases with increasing contact angle depending upon the nature of material.

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