Influence of Pollutant Particles and Electric Field in Particle Nucleation and Condensation

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Theory of drop growth in presence of external electric field and pollutant particles has been applied to water vapour condensation. In presence of electric field, Helmholtz free energy of formation of water molecule about a critical nucleus is found to be much less than that in absence of the electric field. We see that for vapour just saturated with respect to water, the energy of the nucleus formation rapidly increases with size as r^2_{wc}. *The observations suggests that nucleation rate is extremely sensitive to supersaturation ratio, since the term in the exponent varies as* $S^{-2}_{v,w}$. *Since in presence of ions and electric field a small value of electric field is comparable to very high supersaturation ratio to get a nucleus of given size under similar conditions of temperature.*

Keywords: Nucleation rate, Homogeneous nucleation, Global atmospheric circuit, Precipitation, Electric dipole moment.

1. INTRODUCTION

It is well known fact that there exists an electric field in the atmosphere which is supposed to influence many atmospheric processes. Thunderclouds are known to have strong electric fields. The magnitude of fair weather electric field near the surface of the earth, average over the whole globe, is about 130 V/m. The value in clear atmosphere in countryside is about 60V/m and in highly polluted industrial regions it is as high as 360V/m [1]. The growth of particles in a cloud with the electrical development was used by Levin and Ziv to explain the raingush [2]. In an electrified cloud a sudden growth of precipitation is often observed in association with lightning. Those electrical forces which are responsible to hold the precipitation particles together are weakened drastically and the droplets fall down suddenly in the form of rain, resulting dramatic increase in precipitation rate. Thus the raingush is observed [3].

Wang *et al.* studied about the collection efficiency at atmospheric aerosols or rain drops [4]. The collection of charged aerosols by a conducting sphere in an external electric field and enhancement in the collection efficiency of various shaped aerosol particles by hydrometeors under thunderstorm conditions as compared with fair weather electric field throws light on the importance of the electric fields [5,6]. Jalaluddin *et. al.* reported that the electric field influences the nucleation process [7,8]. Pruppacher found that when charged ions and aerosol particles come in contact with the neutral drops, the nucleation process is enhanced [9].

Loeb and Smith et.al. discussed the disruptive effect of electric field and suggested that the nucleation on the fragments of a drop is responsible for the observed enhancement in nucleation [10,11]. Later, Abbas and Latham gave a possible mechanism for this enhancement [12]. Their results were totally inconsistent with Pruppacher's theory, but did agree with those of Loeb [13,10]. Murino studied theoretically the effect of the electric field on the condensation of water vapour and concluded that under similar conditions of temperature and super saturation the bigger size of the drops can be achieved in a given time than that obtained in absence of electric field [14]. He considered the polarization of water vapour molecules in the electric field of the central dipole alone.

A model of global atmospheric circuit Sapkota *et. al.* has been developed incorporating the pollution due to aerosol particles of anthropogenic and volcanic origin, which shows that ionization is caused by the coronal discharge due to intense electric field beneath thunderclouds in atmospheric layer close to the earth surface [15]. The scavenging of aerosol particles by hydrometeors under external electric field has been discussed by Wang [4,5]. Although, there is a fair weather electric field in a fine day, the field is much larger in thunderstorm situation. Under thunderstorm conditions the electric field effects on scavenging are greatly enhanced.Thus the electric field plays an important role in cloud formation.. Murino has shown that action of a constant and uniform electric field accelerated the condensation of water vapour by a factor depending upon the intensity of electric field [14]. It was shown that a droplet acquires a particular size under very low supersaturation, under an electric field, which would, otherwise, requires very high supersaturation.

In the present paper, we examined, theoretically, the effect of ions and external electric field on water vapour condensation to estimate the Helmholtz free energy of formation of nucleus, nucleation rate and the radius of critically sized nuclei. Comparison has been made with that in ion induced and electric field-free case.

2. THEORITICAL CONSIDERATION OF HOMOGENEOUS NUCLEATION PROCESS

2.1. In Absence of Ions and Electric Field

Our theoretical understanding of the stability of phases has its origins in the classical work of Gibbs on the metastable and unstable states [16]. Consider for simplicity a mean electric field system with a critical point, such as a water vapour transition [17]. Near the ground, ions are produced mainly by ionizing radiations of radioactive substances such as Thoron and Radon. Generally cosmic rays Produce ionization in atmosphere [18].

Dufour and Defay and Abraham have shown that the Helmholtz free energy is the proper thermodynamic potential and Gibb's function is the only approximation of Helmholtz's function [19, 20]. The energy for the formation of nucleus is given by

$$\Delta F = 4\pi\sigma_{W/V}\, r^2_w - 4\,\pi\Delta F_{vol.} r^3_w/3 \qquad (1)$$

where, r_w is the radius of the spherical water nucleus, $\sigma_{W/V}$ is the surface free energy per unit area of water nucleus in water vapour and ΔF_{vol} is the volume free energy of condensate per unit volume per mole.

Here, $\Delta F_{vol} = \rho_w RT \ln S_{v,w} / M_w$

where, ρ_w is the density of water and $\ln S_{v,w}$ is the supersaturation ratio.

Corresponding to the maximum free energy for the critical size of nucleus, we have

$$\partial/\partial r_w(\Delta F) = 0 \quad (2)$$

From equations (1) and (2), the critical radius for the uncharged case is obtained to be

$$r_{wc} = 2\, \sigma_{W/V} / \Delta F_{vol}$$

$$r_{wc} = 2M_w\, \sigma_{W/V} / \rho_w RT \ln S_{v,w} \quad (3)$$

Therefore, critical free energy for uncharged droplet can be written as

$$\Delta F_c = 4\pi\sigma_{W/V}\, r^2_{wc} / 3 \quad (4)$$

When homogeneous nucleation of water from the vapour occurs, the formation of droplets of the clouds takes place. So, we are interested to find the rate at which the droplet appear in the system as a function of saturation ratio. This rate is known as nucleation rate (J) and is measured as the number of droplets appearing per unit volume and per unit time. Rate of nucleation as given by [21]

$$J = \alpha_C / \rho_w[2N^3 M_w\, \sigma_{W/V} / \pi]^{1/2} [e_{sat.w}/RT]^2 S_{v,w} \exp[-\Delta F_c / KT] \quad (5)$$

where, N is the Avogadro number and α_C, is the condensation coefficient. Taking all these critical parameters and calculations have been done in absence of pollutant particles and electric field and values of r_{wc}, ΔF_c, $\ln J$ as the function of temperature and supersaturation ratio at T= 273 K are shown in Table 1.

Table 1: Critical parameters in absence of pollutant particles and Electric field.

$S_{v,w}$	r_{wc} ($\times 10^{-10}$ m.)	ΔF_c ($\times 10^{-15}$ joule)	lnJ
0.6	-	-	-
0.8	-	-	-
1.0	infinite	-	-
1.2	62.61	118.27	-3097.70
1.5	28.51	23.91	-592.83
2.0	16.47	8.18	-175.02
2.5	12.46	4.68	-81.89
3.0	10.39	3.26	-44.02
3.5	9.11	2.50	-23.69
4.0	8.23	2.04	-11.34
4.5	7.59	1.74	-3.26
5.0	7.09	1.52	2.68

2.2. In Presence of Pollutant Particles

In presence of ions the water vapour molecules from cluster with ion as the centre. The condensation takes place at low supersaturations because the necessary energy for germ formation is attained at smaller radii due to addition of electrostatic potential energy. Helmholtz energy expression (1) is modified by [21] as

$$\Delta F' = 4\pi\sigma_{W/V}\, r'^2_w - 4\pi\Delta F'_{vol} r'^3_w /3 + 3(z\, e)^2 / 5\, r'_w \qquad (6)$$

where, the primes indicate the values in the presence of ions. The last term in equation (6) represents the electrostatic energy of the cluster in presence of an ion of charge (ze), 'z' being the charge number and 'e', the electronic charge.

In this case the critical radius can be obtained by setting

$$\partial/\partial r_{w'} (\Delta F') = 0 \qquad (7)$$

The critical super-saturation ratio in the present case can be obtained by

$$\ln S'_{v,w} = 2M_w\, \sigma_{W/V} / \rho_w R T.\, r'_{wc} - 3 M_W Z^2 e^2 / 20\pi\, \rho_w RT.\, r'^4_{wc} \qquad (8)$$

Nucleation rate for charged case is given by

$$J' = \alpha_C / \rho_w [2N^3 M_w\, \sigma_{W/V} / \pi]^{1/2} [e_{sat.w}/RT]^2 S'_{v,w} \exp[-\Delta F'_c / KT] \qquad (9)$$

From equations (8) and (9) the calculated values of r'_{wc}, $\Delta F'_c$, ln J' as the function of temperature and supersaturation ratio at T= 273 K are shown in Table 2.

Table 2: Critical parameters in presence of pollutant particles.

$S_{v,w}$	r_{wc} ($\times 10^{-10}$ m.)	ΔF_c ($\times 10^{-15}$joule)	lnJ
0.6	4.02	5.08	-93.93
0.8	4.16	4.98	-90.99
1.0	4.28	4.89	-88.34
1.2	4.40	4.82	-86.34
1.5	4.52	4.71	-83.19
2.0	4.91	4.57	-79.19
2.5	5.06	4.43	-75.25
3.0	5.50	4.29	-71.36
3.5	6.27	4.13	-66.98
4.0	-	-	-
4.5	-	-	-
5.0	-	-	-

2.3. In Presence of Particles and Electric Field

Eisenberg and Kauzmann reported that water is strongly polarizable medium with electric dipole moment 1.83 × 10^{-21} $C.m^{-1}$ [22]. Application of electric field induces an electric dipole moment on the embryo of water as well as surrounding water vapour molecules. The moment induced on the embryo is

$$P = E\, r^3_w \tag{10}$$

where, r_w is the radius of the water embryo in electric field 'E' and the moment P_1 induced on water vapour molecule is given by

$$P_1 = \alpha\ E_1 \tag{11}$$

where, α is the polarizability of the medium. From the kinetic theory of gases, it is assumed that in a non-uniform electric field, the drift velocity is given by the transformation of potential energy lost in one mean free path in to kinetic energy [23]. Change in potential energy of a molecule in a transition through a distance λ on to the surface of the embryo of radius r''_w is given by $9\,\alpha\,\lambda E^2/2\,r''_w$.

Therefore equation (6) is modified as

$$\Delta F'' = 4\pi\sigma_{W/V}\, r''^2_w - 4\,\pi\Delta F''_{vol} r''^3_w /3 + 3(z\,e)^2/ 5\, r''_w - 9\,\alpha\,\lambda E^2/2\, r''_w \tag{12}$$

where, $\Delta F''_{vol} = \rho_w\, RT\, \ln S''_{v,w} /M_w$.

The critical supersaturation ratio in this case can be written as

$$\ln S'_{v,w} = 2M_w\sigma_{W/V}/\rho_w\, RT.r'_{wc} - 3M_W Z^2 e^2/20\pi\rho_w RT.r'^4_{wc} + 9\,\alpha\,\lambda M_w E^2/8\pi\rho_w\, RT\, r''^4_{w\,c} \tag{13}$$

Further, Nucleation rate is given by

$$J'' = \alpha_C /\rho_w[2N^3\, M_w\, \sigma_{W/V}/\, \pi]^{1/2}\, [e_{sat.w}/RT]^2\, S''_{v,w} \exp\, [-\Delta F''_c / KT] \tag{14}$$

From equations (12), (13) and (14) the calculated values of r''_{wc}, $\Delta F''_c$, ln J'' as the function of temperature and supersaturation ratio and electric field at T= 273 K, are shown in Table 3.

Table 3: Critical parameters in presence of pollutant particles and Electric field.

$S_{v,w}$	r_{wc} ($\times 10^{-10}$ m.)	ΔF_c ($\times 10^{-15}$joule)	lnJ
0.6	3.97	4.94	-90.22
0.8	4.09	4.84	-87.28
1.0	4.19	4.76	-84.93
1.2	4.29	4.69	-82.89
1.5	4.45	4.59	-80.01
2.0	4.70	4.44	-75.75
2.5	4.98	4.31	-72.07
3.0	5.26	4.18	-68.44
3.5	-	-	-
4.0	-	-	-
4.5	-	-	-
5.0	-	-	-

3. RESULTS AND DISCUSSION

In the present calculations the constant values used [21] are :

ρ_w = 1000 kg.m^{-3}, R = 8.314 J.mole^{-1}K^{-1}, $\sigma_{W/V}$ = 72 × 10^{-7} j.Cm^{-2}, α_C = 1.0, N = 6.023 × 10^{23}, k = 1.38 × 10^{-23} J.K^{-1}, e = 1.6 × 10^{-19} C, α = polarizability of the medium = 5 × 10^{-19}, λ = 10^{-6} m., E = 1.5 × 10^{3} V/m, $e_{sat.w}$= saturation vapour pressure over water.

$e_{sat.w} = a_0 + T(a_1 + T(a_2 + T(a_3 + T(a_4 + T(a_5 + a_6)))))$, here T(^{0}C)

a_0 = 6.107799961, a_1 = 4.436518521 × 10^{-1}, a_2 = 1.428945805× 10^{-2}

a_3 = 2.650648471× 10^{-4}, a_4 = 3.031240396 × 10^{-6}, a_5 = 2.034080948 × 10^{-8}

a_6 = 6.136820929 × 10^{-11}

From Table 2 it is clear that condensation takes place at low supersaturation compared to Table 1. While from Table 3, it is clear that condensation takes place at very low supersaturation because of that the necessary energy for germ formation is attained at lower radii due to the addition of electrostatic energy $[3(z\ e)^2/\ 5\ r''_w]$ and also transformation of potential energy in to kinetic energy $[9\alpha\ \lambda E^2/2\ r''_w]$.

For a given temperature, from Table 1 the value of supersaturation varies as r^{-1}_{wc} , while from Table 3, it varies as r''^{-4}_{wc} for smaller radii and r''^{-1}_{wc} for larger radii.

At T = 273K, $S_{v,w}$ = 2.5

r_{wc} = 12.46 A^0, r'_{wc} =5.06 A^0, r''_{wc} = 4.98 A^0 and

At $S_{v,w}$ = 1.0

r_{wc} = infinite, r'_{wc} =4.28 A^0, r''_{wc} = 4.19 A^0

It means that at $S_{v,w} < 1$, (table-1) uncharged water drops cannot exist and in presence of ions and electric field radius of water drops are smaller than in only presence of ions. Hence condensation takes place at smaller radii in presence of ions electric field both (Table 3).

At T = 273K, $S_{v,w}$ = 2.5

$\Delta F = 4.68 \times 10^{-15}$ J, $\Delta F' = 4.43 \times 10^{-15}$ J, $\Delta F'' = 4.31 \times 10^{-15}$ J and

$\ln J = -81.89$, $\ln J' = -75.25$, $\ln J'' = -72.07$

Hence free energy reduces in presence of ions and electric field both (Table 3). i.e. rate of nucleation is increased as compared to ion free and ion induced case (Table 2 and Table 3). Thus we conclude that ions and electric field affect very much the process of condensation and nucleation. Ions supply more energy to the nucleus so that energy necessary and sufficient for phase change is achieved at an early stage at embryo formation and hence there is a remarkable change in nucleation rate in presence of ions and electric field both.

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