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# CONDENSATION ON IONS

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**Abstract:** The transition of a homogeneous system into a heterogeneous one may occur spontaneously in a labile region of supersaturations; in the metastable region of supersaturations it is realized as an energy barrier-determined process. The limit that separates the labile region from the metastable one is the *boundary supersaturation* $s_b$>>$s_{cr}$, where $s_{cr}$ is the *critical supersaturation*. The Ω-potential thermodynamic formalism, $\Omega = F - G$, where $F$ and $G$ are the Helmholtz and the Gibbs free energies, respectively, allows a straightforward derivation of the formula of Tohmfor and Volmer (1938) for a nucleus formation on an ion. For the case of charged liquid drops, expressions for the capillary pressure, the vapor pressure, the work of formation of equilibrium drops from vapors, and the drop surface tension, are obtained as well. The stability conditions for the charged equilibrium drops are also examined.

**Keywords:** Nucleation, charged drops, critical supersaturation, boundary supersaturation, thermodynamics, Ω- potential
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## 1. Introduction

The theory of phase formation in supersaturated systems is developed by Gibbs [1]. The transition of a homogeneous system into a heterogeneous one may occur spontaneously (in a labile

region); in a metastable (fluctuational) region, it takes place as an energy barrier-determined process. In the latter case, using the well-known Volmer's procedure [2], a *critical supersaturation* $s_{cr}$ can be determined. A *boundary supersaturation* $s_{bn}$ should represent the limit between the metastable and labile regions and, as a rule, $s_{bn} \gg s_{cr}$. The water nucleation on ions, *e.g.*, in the cloud Wilson chamber [3], seems to be a special case when $s_{bn}$ and $s_{cr}$ are relatively close to each other.

Despite of the statement, *e.g.*, in [4,5], that the $\Omega$-potential expressed as

$$\Omega = F - \sum_i \mu_i N_i \qquad (1)$$

($F$ is the Helmholtz free energy, $\mu_i$ and $N_i$ are the chemical potential and mass of the i-th component, respectively) is irrelevant for thermodynamics, this extensive thermodynamic function, rather than the Gibbs free energy $G$, seems to be the most convenient for presenting the results of Gibbs' theory of capillarity (*cf.* [6]). The metastable state of the capillary system includes the nucleus of the new phase. It is a small but macroscopic particle, which is in *unstable equilibrium* with its surroundings. At constant total volume $V$, temperature $T$ and chemical potentials $\mu_i$, $[\Delta\Omega]_{T,V,\mu_i}$ would have a meaning of a reversible work, and this provides a straightforward approach to the determination of the work $W$ of formation of a nucleus in supersaturated systems.

## 2. Work of Drop Formation

The $\Omega$-potential of the homogeneous gas phase $g$ containing an ion with charge $e$ and radius $a$ is

$$\Omega_I = -p^g V + \frac{1}{2}\frac{e^2}{a} \qquad (2)$$

where $p$ stands for pressure while the electrostatic part of $\Omega_I$, *i.e.*, the free energy $\Omega_e$, is calculated by $\Omega_e = \int_V \frac{\varepsilon}{8\pi} E^2 dV$ ; $E = e/r^2$ where $r$ is the radial distance from the ion and the dielectric constant of the vapors $\varepsilon = 1$.

When a liquid drop $l$ is formed around the ion,

$$\Omega_g = -p^g (V - v) - p^l v + \sigma o + \frac{1}{2} e^2 \left(1 - \frac{1}{\varepsilon}\right) \frac{1}{R} + \frac{1}{2} \frac{e^2}{a} \tag{3}$$

with $v = \frac{4}{3}\pi R^3$, $o = 4\pi R^2$, where $R$ is the radius of the spherical liquid drop and $\sigma$ is the surface tension at the drop/gas interface. The free energy $\Omega_e$ is calculated again by $\Omega_e = \int_V \frac{\varepsilon}{8\pi} E^2 dV$ with $E = e / r^2$ for $r>R$ and $E=e/\varepsilon r^2$ for $r<R$ ($\varepsilon$ is the dielectric constant of the liquid drop).

Thus the work of formation of a drop will be

$$\Delta\Omega = -\Delta P v + \sigma o + \frac{1}{2} e^2 \left(1 - \frac{1}{\varepsilon}\right) \frac{1}{R} - \frac{1}{2} e^2 \left(1 - \frac{1}{\varepsilon}\right) \frac{1}{a} \tag{4}$$

with $\Delta P = p^l - p^g$.

## 3. Capillary Pressure of the Drop

By making use of $d\Delta\Omega / dR = 0$, one obtains for the capillary pressure of the drop

$$\Delta P = \frac{2\sigma}{R} - \frac{1}{8\pi} e^2 \left(1 - \frac{1}{\varepsilon}\right) \frac{1}{R^4}. \tag{5}$$

Eq. (5) is a generalization of the Laplace formula for the capillary pressure

$$\Delta P = 2\sigma / R; \tag{6}$$

Eq. (6) follows from Eq. (5) when $e=0$. It is known that the above procedure determines the radius of the dividing surface between the bulk liquid and the gas phase, for which Laplace's law in the form of Eq. (6) is valid; it holds for the *surface of tension* [1]. The expression (5) exhibits an extremum at

$$R_m^3 = \frac{e^2}{4\pi\sigma} \left(1 - \frac{1}{\varepsilon}\right). \tag{7}$$

## 4. Work of Formation of Equilibrium Drops from Vapors

The capillary pressure is the pressure difference between two bulk phases in equilibrium [1]. If Eq. (5) is inserted in Eq. (4), an expression for the work of formation $W$ of an equilibrium drop is readily obtained

$$W = \frac{1}{3}\sigma\omega + \frac{2}{3}e^2\left(1 - \frac{1}{\varepsilon}\right)\frac{1}{R} + const \tag{8}$$

At $e=0$, Eq. (8) gives the well-known Gibbs' result [1]

$$W = \frac{1}{3}\sigma\omega = \frac{1}{2}\Delta P v. \tag{9}$$

## 5. Gibbs-Thomson Equation

Eq (5) determines the difference in the pressures within and outside the equilibrium drop, $p^l$ and and $p^g$, respectively. Obviously, at constant temperature and chemical potentials, both pressures are constant. These pressures can be calculated separately provided that the starting equation is [6]

$$\mu^l(T, p^l) = \mu^g(T, p^g). \tag{10}$$

Therefore,

$$v^l dp^l = v^g dp^g \tag{11}$$

($v^j (j = l, g)$ are molar volumes). As usual $v^l \ll v^g$ and $v^g = \frac{RT}{p^g}$; $R$ is the gas constant, $k$ is the Boltzmann constant, $v_0^l$ is the molecular volume, and, by integrating Eq. (11), using $p^l - p_\infty^l = \Delta P + p^g - p_\infty^g$ (with Eq. (5) for $\Delta P$), and neglecting $v_0^l(p^g - p_\infty^g)$, one obtains

$$KT \ln\frac{p^g}{p_\infty^g} = v_0^l\left[\frac{2\sigma}{R} - \frac{1}{8\pi}\left(1 - \frac{1}{\varepsilon}\right)\frac{1}{R^4}\right] = KT \ln s \tag{12}$$

The dependence of the vapor pressure on $R$ (at $R \to \infty$, $p^g \to p_\infty^g = p_\infty^l$) exhibits an extremum at $R=R_m$. The other charecterics of the Tohmfor and Volmer charged drops are as follow [7]: $T$=265K, $\sigma$=77 dyn/cm, $s_m$= 4.63, $e$=4.8.$10^{-10}$ CGSE, $R_m$= 6.5.$10^{-8}$ cm, $s_{cr}$ = 4.1 (experimental), 3.2 (theoretical); at $s_{cr}$ = 3.2, $R_{cr}$ = 4.8.$10^{-8}$ cm and $R_{max}$= 10.2.$10^{-8}$ cm). The radius $R_m$ is determined by the condition (7). The radius $R_0$ is determined at $s$ = 1. Then, from Eq. (5) at $\Delta P=0$, and together with Eq. (7), it follows that

$$\left(\frac{R_m}{R_0}\right)^3 = 4. \tag{13}$$

**6. Stability Conditions**

At $s<s_m$, two equilibrium drops of different size should exist: a smaller one with a radius $R_m$, and a bigger one with a radius $R_{ma}$; $R_{ma}> R_m$. By using Eqs. (4) and (5), one readily obtains

$$\left(\frac{\partial^2\Omega}{\partial R^2}\right)_{eq} = -8\pi\sigma + 2e^2\left(1-\frac{1}{\varepsilon}\right)\frac{1}{R^3} = 8\pi\sigma\left[\left(\frac{R_m}{R}\right)^3 - 1\right] \tag{14}$$

This implies $\left(\frac{\partial^2\Omega}{\partial R^2}\right)_{eq} > 0$ when $R< R_m$. Thus, at $s< s_m$ the equilibrium drop with radius $R_m$ is in *stable equilibrium* with its surroundings (minimum of the $\Omega$ - potential).

For the other equilibrium drop with $R_{ma} > R_m$, $\left(\frac{\partial^2\Omega}{\partial R^2}\right)_{eq} < 0$. Therefore, this drop is in *unstable equilibrium* with its surroundings (maximum of the $\Omega$ - potential).

At $s \geq s_m$, the condensation does not follow the fluctuational mechanism and nuclei of the new phase do not exist at all. Let us consider the special case of $s = s_m$. It is easily established that the first and the second derivatives of $\Omega$ at $R = R_m$ are both zero. The third derivative is

$$\left(\frac{\partial^3\Omega}{\partial R^3}\right)_{R=R_m} = -24\pi\sigma / R_m < 0 \tag{15}$$

On the other hand,

$$\Omega(R) - \Omega(R_m) = \frac{1}{3!}\left(\frac{\partial^3\Omega}{\partial R^3}\right)_{R=R_m}(R - R_m)^3 \tag{16}$$

*i.e.*, the nonequilibrium drops with $R < R_m$ will grow spontaneously, because $\Omega(R) > \Omega(R_m)$. The same is valid for the nonequilibrium drops with $R > R_m$, since in this case $\Omega(R) < \Omega(R_m)$.

## 7. Work of Nucleus Formation: The Formula of Tohmfor and Volmer

The drop which corresponds to the minimum of the Ω-potential is characterized by the radius $R_m$. Any other nonequilibrium drop, smaller or bigger than the equilibrium one, will spontaneously change its size until the equilibrium radius $R_m$ is reached. Then the work of nucleus formation $W_{TV}$ is obtained by applying Eq. (8):

$$W_{TV} = W_m - W_n = \frac{1}{3}\sigma(o_m - o_n) - \frac{2}{3}e^2\left(1-\frac{1}{\varepsilon}\right)\left(\frac{1}{R_n} - \frac{1}{R_m}\right) \tag{17}$$

This is the formula of Tohmfor and Volmer obtained in 1938 in the framework of the method of Becker and Döring by considering the nucleus formation in a medium containg ions [7] (*cf.* also [2,8]).

## 8. Surface Tension of a Charged Drop

Instead of Eq. (5), one can write $\Delta P = \frac{2\sigma^*}{R}$ where $\sigma^*$ is the surface tension of the charged drop. Then

$$\sigma^* = \sigma - \frac{e^2}{16\pi}\left(1-\frac{1}{\varepsilon}\right)\frac{1}{R^3} \tag{18}$$

The dielectric constant $\varepsilon$ is expected to be $\varepsilon >> 1$ (in the case of water at room temperature $\varepsilon = 80$), and the equation

$$\sigma^* = \sigma - \frac{e^2}{16\pi}\frac{1}{R^3} \tag{19}$$

is valid. As shown by Scheludko [9], the above equation could be obtained by making use of the well-known Lippmann's formula.

At $R=R_m$, the expression (18) leads to $\sigma^* = \frac{3}{4}\sigma$, so that $\Delta P(R = R_m) = \frac{3}{4}\frac{2\sigma}{R_m}$; at $R = R_0$, $\sigma^* = 0$ and $\Delta P(R = R_0) = 0$.

## 9. Conclusion

A new thermodynamic derivation of the formula of Tohmfor and Volmer is presented together the adoption of a teaching strategy that could facilitate the students' conceptual understanding of the process of new phase formation. It seems to be generally accepted that Gibbs' thermodynamic theory of capillarity is difficult for both teaching and learning. A rational reconstruction of this important theory could be realized by making use of the Ω-potential thermodynamic formalism. Only a detail of this new approach [10] is investigated here and a straightforward derivation of the formula of Tohmfor and Volmer for the work of formation of a charged water nucleus is presented. Some special problems such as the formation of nuclei on positive and negative charges as well as the distinction between the surface tension, defined as a *work of stretching* of a surface and the surface tension, reflecting the *work of forming* of a surface, are beyond the present consideration. These problems of the thermodynamic theory of nucleation on charged particles have been examined elsewhere [11].

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