مجلة جامعة بابل / العلوم الصرفة والتطبيقية / العدد (4) / المجلد (17) : 2009

More Results On Ions

Samah Abd Alhadi
Babylon University
College of Science For Women
Dept. Of Computer

Moyad Abbas Salman
Ministry of industry and Minerals
State Company for Leather Industries

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* $s_m >> s_{cr}$, 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.

الخلاصة

انتقال النظام المتجانس إلى نظام متنافر قد يحدث تلقائيا في المنطقة المتغيرة من التشبع الزائد في المنطقة الثابتة من التشبع الزائد يلاحظ عملية تحديد معرقل للطاقة الحد الذي يفصل المنطقة المتغيرة من شبه هي التشبع الزائد الحرج, ألتشكيله الاليه الحرارية, s_{cr}) حيث ($s_m >> s_{cr}$, الثابتة هي حدود التشبع الزائد هي طاقة هلمهولتز وطاقة جيبس الحرة G,F حيث $\Omega = F - G$ الكاملة

تقوم بالسماح للاشتقاق المباشر من صيغة توهمفوز وفولمر(1938) للتركيبة النوويه على الايون بالنسبة إلى حالة قطرات السائل المشحونة والتحولات في الضغط الشعري وضغط البخار فان شكل القطرات المتوازنه من البخار وتوتر سطح القطرة يتم استحصالها .ظروف الثابتة للقطرات المتوازنة المشحونة هي مفحوصة ايضا

1. Introduction

The theory of phase formation in supersaturated systems is developed by Gibbs [Gibbs ,19961]. 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 [Rothman,Lichter, Nevitte .R,.N 2005, Volmer M.1939], a *critical supersaturation* s_{cr} can be determined. A *boundary supersaturation* s_m should represent the limit between the metastable and labile regions and, as a rule, $s_m >> s_{cr}$. The water nucleation on ions, *e.g.*, in the cloud Wilson chamber [Wilson. 1954], seems to be a special case when s_m and s_{cr} are relatively close to each other.

Despite of the statement, *e.g.*, in [Münster. A 1990, Ter Haar. D, Wergeland .H 1967], that the **Ω**-potential expressed as

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

(F is the Helmholtz free energy, μ_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 ([Landau. & Lifshitz, 1980; Rusanov & Kuni, 1984]). 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 μ_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 Ω-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 Ω_I, *i.e.*, the free energy Ω_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 ε = 1.

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

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

with $v = \frac{4}{3}\pi R^3$, $o = 4\pi R^2$, where *R* is the radius of the spherical liquid drop and σ is the surface tension at the drop/gas interface. The free energy Ω_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* (ε is the dielectric constant of the liquid drop).

Thus the work of formation of a drop will be

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

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

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* [Gibbs , 1961, Stern, 2007]. 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 [Gibbs , 1961]. If Eq. (5) is inserted in Eq. (4), an expression for the work of formation W of an equilibrium drop is readily obtained

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

At e=0, Eq. (8) gives the well-known Gibbs' result [Gibbs .J.W 19961]

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

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 [Landau. L.D. , Lifshitz. E.M. 1980, Toshev. B.V., . *Disp. J1997*]

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

Therefore,

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

($v^j (j=l,g$) are molar volumes). As usual v^l « v^g and $v^g = RT/P^g$; R is the gas constant, k is the

Boltzmann constant, v^l_0 is the molecular volume, and, by integrating Eq. (11), using P^l-$P_\infty{}^l$ $=\triangle P+P^g$-$P_\infty{}^g$(with Eq. (5) for ΔP), and neglecting v^l_0 (P^g-$P_\infty{}^g$), one obtains

$$kT\ln\frac{p^g}{p^g_\infty}=v^l_0\left[\frac{2\sigma}{R}-\frac{1}{8\pi}\left(1-\frac{1}{\varepsilon}\right)\frac{1}{R^4}\right]=kT\ln s \qquad (12)$$

The dependence of the vapor pressure on R (at $R\infty\rightarrow$, $P^g\rightarrow P_\infty{}^l$) exhibits an extremum at $R=R_m$. The other charecterics of the Tohmfor and Volmer charged drops are as follow [Tohmfor &Volmer 1938; Schustr ,Finkelstein , 2006]: T=265K, σ =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_{st}= 4.8.10^{-8} cm and R_{un}= 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 ΔP=0, and together with Eq. (7), it follows that

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

.

6. Stability Conditions

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

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

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_{st} is in *stable equilibrium* with its surroundings (minimum of the **Ω** - potential).

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

At $s\leq s_m$, 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 **Ω** at $R = R_m$ are both zero. The third derivative is

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

On the other hand,

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

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 . $\Omega(R) < \Omega(R_m)$

References

Gibbs .J.W., (1961) *The Scientific Papers of J. Willard Gibbs. In Two Volumes. Vol. I. Thermodynamics,* Dover: New York. pp 219-331.

Landau. L.D. , Lifshitz. E.M. (1980). *Statistical Physics. Part I,* Pergamon: Oxford.

Münster. A, (1990) *Chemische Thermodynamik,* Akademie Verlag: Berlin**.**

Rothman, Lichter, Nevitte .R,.N, (2005). Politics and PROFESSIONAL Advancement Among College Faculty,The Forum,Vol3,Aryicle2

Rusanov. A.I., Kuni. F.M.,(1984) *Colloid. J Interface Sci., 100,*264

Scheludko. A, (1984).*Kolloidnaya khimiya* [Colloid Chemistry], Mir: Moskwa**.**

Schustr.S.J ,Finkelstein .M ,TheAmerican Faculty (2006). :The Restructuring of Academic Work and Carees .Baltimore :Johvs Hopkins University, Press,460

Stern, N., (2007) The economics of climate change: the stren review, HM Treasury, viwed

Ter Haar. D, (1967).Wergeland .H., *Elements of the Thermodynamics,* Addison-Wesley: London, 1967**.**

Tohmfor G. Volmer, M. (1938) *Ann. Phys.* p*33*-109.

Tohmfor. J.P, Pound. G.M, (1963). *Condensation and Evaporation. Nucleation and Growth Kinetics,* Pergamon: Oxford.

Toshev. B.V.,(1997). . *Disp. J, Sci. Technol.* 1997,Vol *18*, p 801.

Volmer M., (1939). *Kinetik der Phasenbildung,* Steinkopff: Leipzig.

Wilson. G,(1954). *Kamera Wilsona* [Wilson Chamber], Gostehizdat:Moskwa.