

Nucleation phenomena in electrochemical systems: thermodynamic concepts

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Abstract Basic thermodynamic concepts related to the initial stages of first-order phase transitions are defined in terms of electrochemical quantities. Theoretical expressions are derived for the nucleation work and for the size of the critical nucleus revealing the supersaturation dependence of these most important physical quantities.

Keywords Electrochemical nucleation · Thermodynamic work · Critical nucleus

List of symbols

a	Ionic activity
e	Elementary electric charge
E	Electrode potential
$E_{0,s}$	Standard state potential
E_{∞}	Equilibrium potential
F	Faraday number
\tilde{G}	Gibbs free energy
$\Delta\tilde{G}$	Thermodynamic work for nucleus formation
k	Boltzmann constant
n_c	Number of atoms in a critical nucleus
T	Absolute temperature
v_M	Molar volume
z	Valence
η	Electrochemical overpotential
μ	Chemical potential
$\tilde{\mu}$	Electrochemical potential

$\Delta\tilde{\mu}$	Thermodynamic supersaturation
$\varphi_{1/2}$	Separation work of a single atom from the half crystal position
φ_i	Separation work of a single atom from the i th site of an n -atomic cluster
$\tilde{\Phi}(n)$	Energy excess of an n -atomic nucleus
ϕ	Galvani potential

Introduction

The formation, growth and dissolution of small clusters of atoms and molecules of different chemical substances are involved in various physical phenomena. Among them adsorption, catalysis, sedimentation, metal plating and corrosion, as well as raining and snowing are certainly of major importance both from a practical and from a scientific point of view.

In two articles I consider the process of electrochemical formation and growth of a new phase when metallic or non-metallic ions from an electrolyte solution discharge on the working electrode, an electronic conductor, playing the role of a substrate for the deposition process. In this special case, the thermodynamic driving force of the phase transition, the supersaturation $\Delta\tilde{\mu}$, can be controlled by controlling the *electrode potential* and the *concentration* of the electrolyte solution, two simple and easily measurable physical quantities.

It is the purpose of the first article to reveal the interrelation between $\Delta\tilde{\mu}$ and two other most important thermodynamic quantities: the work $\Delta\tilde{G}$ for nucleus formation and the size n_c of the critical nucleus, formed in the supersaturated system with a maximal thermodynamic work $\Delta\tilde{G}(n_c)$. However, to make the things clear I find it necessary to consider the conditions for establishment of a stable thermodynamic equilibrium in a real electrochemical system beforehand.

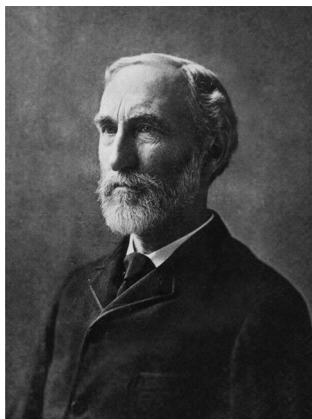
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The state of thermodynamic equilibrium

The state of thermodynamic equilibrium in a multi-component, multi-phase electrochemical system is expressed through the equality of the *electrochemical potentials* $\tilde{\mu}_i^\alpha$ of the coexisting phases, a concept introduced by Gibbs [1] and reintroduced by Guggenheim [2]. Six years later, Lange and Nagel [3] suggested



J. W. Gibbs (1839–1903)

the following general formula for the electrochemical potential $\tilde{\mu}_i^\alpha$ of the i th component of phase α in a multi-component system,

$$\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i e \phi^\alpha \quad (1)$$

In Eq. (1) which is most frequently used nowadays ϕ^α is the inner, Galvani electrical potential of phase α , z_i is the valence of species i , e is the elementary electric charge, and μ_i^α is the chemical potential of phase α given by

$$\mu_i^\alpha = \mu_i^{\alpha,0} + kT \ln a_i^\alpha \quad (2)$$

Here $\mu_i^{\alpha,0}$ is the standard state chemical potential at an activity $a_i^\alpha = 1$ and k is the Boltzmann constant (see also the monograph of the famous German scientist Max Volmer [4]).



Max Volmer (1885–1965)

Consider now three infinitely large phases coexisting at a constant temperature T :

- (i) a solution of metal ions (M^{z+}) with activity a_∞^{sol} and electrochemical potential $\tilde{\mu}_\infty^{\text{sol}}$ given by

$$\tilde{\mu}_\infty^{\text{sol}} = \mu^{\text{sol},0} + kT \ln a_\infty^{\text{sol}} + ze\phi^{\text{sol}} \quad (3)$$

- (ii) a bulk crystal of the same metal (M) with an atomic activity $a_\infty^{\text{M}} = 1$ and electrochemical potential $\tilde{\mu}_\infty^{\text{M}}$ given by

$$\tilde{\mu}_\infty^{\text{M}} = \mu_\infty^{\text{M}} + ze\phi_\infty^{\text{M}} \quad (4)$$

and

- (iii) a layer of metal atoms with activity a_∞^{ad} and electrochemical potential $\tilde{\mu}_\infty^{\text{ad}}$ given by

$$\tilde{\mu}_\infty^{\text{ad}} = \mu_\infty^{\text{ad}} + ze\phi_\infty^{\text{M}} = \mu^{\text{ad},0} + kT \ln a_\infty^{\text{ad}} + ze\phi_\infty^{\text{M}} \quad (5)$$

adsorbed on an inert working electrode.

The state of stable thermodynamic equilibrium in this system is described through the equality of the electrochemical potentials of the coexisting phases:

$$\tilde{\mu}_\infty^{\text{sol}} = \tilde{\mu}_\infty^{\text{M}} = \tilde{\mu}_\infty^{\text{ad}} \quad (6)$$

Thus, the condition $\tilde{\mu}_\infty^{\text{sol}} = \tilde{\mu}_\infty^{\text{M}}$ results in the well-known equation of Nernst:

$$E_\infty = E_{0,s} + \frac{kT}{ze} \ln a_\infty^{\text{sol}} \quad (7)$$

where the difference between the Galvani potentials of the metal crystal and the electrolyte $\phi_\infty^{\text{M}} - \phi^{\text{sol}} = E_\infty$ is the so-called *equilibrium potential* of a bulk metal crystal dipped in a solution of metal ions and $E_{0,s} = (\mu^{\text{sol},0} - \mu_\infty^{\text{M}})/ze$ is the *standard state potential* at ionic activity $a_\infty^{\text{sol}} = 1$.



W. H. Nernst (1864–1941)

In the same way, the condition $\tilde{\mu}_{\infty}^{\text{sol}} = \tilde{\mu}_{\infty}^{\text{M}}$ results in

$$E_{\infty} = E_{0,\text{ad}} + \frac{kT}{ze} \ln \frac{a_{\infty}^{\text{sol}}}{a_{\infty}^{\text{ad}}} \quad (8)$$

which is another theoretical formula for the equilibrium potential E_{∞} now expressed through the ratio between the activities of the electrolyte solution and the metal phase adsorbed on the inert working electrode. Again, $E_{0,\text{ad}}$ is the standard state potential given by $E_{0,\text{ad}} = (\mu^{\text{sol},0} - \mu^{\text{ad},0})/ze$.

Finally, the following general formula for the adatoms' activity a_{∞}^{ad} is obtained combining the two theoretical expressions for the equilibrium potential E_{∞} [Eqs. (7), (8)]:

$$a_{\infty}^{\text{ad}} = \exp \left[\frac{\mu_{\infty}^{\text{M}} - \mu^{\text{ad},0}}{kT} \right] \quad (9)$$

The electrochemical super- and undersaturation

The previous section described the state of stable thermodynamic equilibrium in an electrochemical system at which the process of new phase formation can never take place. It is the purpose of this one to derive theoretical expressions for the thermodynamic super- and undersaturation at which clusters of the new phase either form and grow on the working electrode or dissolve, the building atoms being transformed back to ions in the electrolyte solution.

Most generally, the thermodynamic supersaturation $\Delta\tilde{\mu}$ is defined through the difference between the actual electrochemical potential $\tilde{\mu}^{\text{sol}}$ of the ions in the parent phase, the electrolyte solution, and the equilibrium one $\tilde{\mu}_{\infty}^{\text{sol}}$ ($\tilde{\mu}^{\text{sol}} > \tilde{\mu}_{\infty}^{\text{sol}}$) i.e.,

$$\Delta\tilde{\mu} = \tilde{\mu}^{\text{sol}} - \tilde{\mu}_{\infty}^{\text{sol}} > 0 \quad (10)$$

or, bearing in mind that $\tilde{\mu}_{\infty}^{\text{sol}} = \tilde{\mu}_{\infty}^{\text{M}}$ [Eq. (5)],

$$\Delta\tilde{\mu} = \tilde{\mu}^{\text{sol}} - \tilde{\mu}_{\infty}^{\text{M}} > 0 \quad (10')$$

If, however, the inequality $\tilde{\mu}^{\text{sol}} < \tilde{\mu}_{\infty}^{\text{sol}}$ is fulfilled, then the differences

$$\Delta\tilde{\mu} = \tilde{\mu}^{\text{sol}} - \tilde{\mu}_{\infty}^{\text{sol}} < 0 \quad (11)$$

and

$$\Delta\tilde{\mu} = \tilde{\mu}^{\text{sol}} - \tilde{\mu}_{\infty}^{\text{M}} < 0 \quad (11')$$

define the *electrochemical undersaturation*, which is the thermodynamic driving force for the *dissolution* of the metal phase and this is another case of a first-order phase transition.

Consider now the different ways for applying the supersaturation $\Delta\tilde{\mu}$ to a real electrochemical system consisting, as before, of three different phases: a *solution of metal ions* ($\text{Me}^{\text{z}+}$), a *bulk crystal of the same metal* (Me) and an *inert working electrode* [5].

- (i) The first one is to keep the electrochemical potential $\tilde{\mu}_{\infty}^{\text{sol}}$ of metal ions at its equilibrium value $\tilde{\mu}_{\infty}^{\text{sol}}(a_{\infty}^{\text{sol}})$ but using an external source to polarize the bulk metal crystal to a Galvani potential ϕ more negative than ϕ_{∞}^{M} thus making its actual electrochemical potential $\tilde{\mu}_{\infty}^{\text{M}}(\phi)$ smaller than $\tilde{\mu}_{\infty}^{\text{M}}(\phi_{\infty}^{\text{M}})$ given by Eq. (4). In this case the actual potential $E = \phi - \phi^{\text{sol}}$ of the metal crystal becomes more negative than the equilibrium one $E_{\infty} = \phi_{\infty}^{\text{M}} - \phi^{\text{sol}}$ and it is the difference $E_{\infty} - E = \phi_{\infty}^{\text{M}} - \phi$ which defines the *electrochemical overpotential* (or *electrochemical overvoltage*) η ,

$$\eta = E_{\infty} - E \quad (11)$$

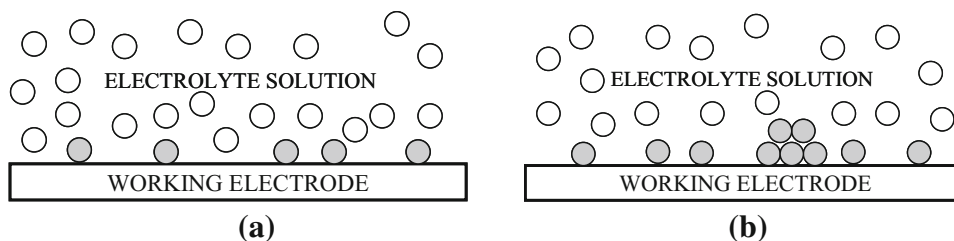
Correspondingly, the thermodynamic supersaturation $\Delta\tilde{\mu}$ is expressed as:

$$\Delta\tilde{\mu} = ze(E_{\infty} - E) = ze\eta \quad (12)$$

Under such conditions, metal ions are able to discharge on the bulk crystal surface and this is what scientists call *electrochemical crystal growth*. If, however, an overpotential $\eta = E_{\infty} - E$ is applied to a *foreign* substrate, say, an inert working electrode then it would be possible to initiate a process of new phase formation and this electrochemical phenomenon will be considered, too. Clearly, Eqs. (11) and (12) imply that in this article the *electrochemical overpotential* η of a cathodic reaction such as reduction of metal ions ($\text{Me}^{\text{z}+}$) to metal atoms (Me) according to $\text{Me}^{\text{z}+} + ze^{-} \rightarrow \text{Me}$ is defined as a positive quantity, $\eta > 0$. Apparently, the same refers to the thermodynamic supersaturation $\Delta\tilde{\mu} > 0$.

- (ii) The second way to supersaturate the parent phase, the electrolyte solution, is to increase its electrochemical potential to a value $\tilde{\mu}^{\text{sol}}$, bigger than the equilibrium one $\tilde{\mu}_{\infty}^{\text{sol}}(a_{\infty}^{\text{sol}})$. This can be done by increasing the activity of the metal ions a^{sol} over the equilibrium activity a_{∞}^{sol} at the same temperature T , i.e., $a^{\text{sol}} > a_{\infty}^{\text{sol}}$, $\tilde{\mu}^{\text{sol}}(a^{\text{sol}}) > \tilde{\mu}_{\infty}^{\text{sol}}(a_{\infty}^{\text{sol}})$. In this case the overpotential η and the supersaturation $\Delta\tilde{\mu}$ are expressed as,

Fig. 1 State of the electrode surface before (a) and after (b) the nucleus formation, the single white and dark circles representing the metal ions and the adsorbed metal atoms, respectively



$$\eta = \frac{kT}{ze} \ln \frac{a^{\text{sol}}}{a_{\infty}^{\text{sol}}} \quad (13)$$

$$\Delta\tilde{\mu} = kT \ln \frac{a^{\text{sol}}}{a_{\infty}^{\text{sol}}} = ze\eta \quad (14)$$

As before, under such conditions metal ions may either deposit on the bulk crystal and make it growing or may form nuclei of the new phase on the inert foreign substrate.

Certainly, a third possibility is to express the electrochemical overpotential η and the supersaturation $\Delta\tilde{\mu}$ through the ratio of the actual, a^{ad} , and the equilibrium, a_{∞}^{ad} , activities of the metal atoms adsorbed on the inert working electrode, i.e.,

$$\eta = \frac{kT}{ze} \ln \frac{a^{\text{ad}}}{a_{\infty}^{\text{ad}}} \quad (15)$$

$$\Delta\tilde{\mu} = kT \ln \frac{a^{\text{ad}}}{a_{\infty}^{\text{ad}}} \quad (16)$$

The last two expressions are most frequently used when the phase formation phenomena take place through adatoms' surface diffusion mechanism [6–13].

The thermodynamic work for nucleus formation

The formation of an n -atomic cluster of the new phase on an inert working electrode polarized to a potential E more negative than the equilibrium potential E_{∞} leads to an initial increase of the Gibbs free energy \tilde{G} of the whole system due to the creation of new phase boundaries. Thus, the Gibbs free energies before (\tilde{G}_1) and after (\tilde{G}_2) the nucleus formation are given by¹

$$\tilde{G}_1 = N\tilde{\mu}_{\infty}^{\text{sol}}(a_{\infty}^{\text{sol}}) + \tilde{G}^* \quad (17)$$

$$\tilde{G}_2 = (N - n)\tilde{\mu}_{\infty}^{\text{sol}}(a_{\infty}^{\text{sol}}) + \tilde{G}^*(n) \quad (18)$$

where N is the total number of ions in the electrolyte solution before the nucleus formation and \tilde{G}^* and $\tilde{G}^*(n)$ account for the energy contribution of the “working electrode-solution” phase boundary before and after the formation of an n -atomic nucleus thereon (Fig. 1) and depend on the actual electrode potential E .

It is namely the difference $\tilde{G}_2 - \tilde{G}_1$, which defines the energy barrier $\Delta\tilde{G}(n)$ for nucleus formation, called *nucleation work* and expressed as

$$\Delta\tilde{G}(n) = \tilde{G}(n) - n\tilde{\mu}_{\infty}^{\text{sol}}(a_{\infty}^{\text{sol}}) \quad (19)$$

where $\tilde{G}(n) = \tilde{G}^*(n) - \tilde{G}^*$ is the Gibbs free energy of the n -atomic cluster of the new phase formed on the inert working electrode.

As seen, the nucleation work $\Delta\tilde{G}(n)$ is expressed through the difference between the Gibbs free energies of n atoms when they are included in a n -atomic cluster of the new phase electrodeposited on the working electrode and when they are part of the parent phase, the electrolyte solution of metal ions. This is probably the most general definition of this fundamental thermodynamic quantity. Certainly, it is important to note that the value of $\tilde{G}(n)$ in Eq. (19) depends strongly on the “nucleus-solution” and the “nucleus-foreign substrate” interactions and this is the reason why the small clusters' structure and their specific physical properties differ significantly from those of the bulk new phase. Nowadays micro- and nano-clusters of atoms and molecules are subject of numerous profound theoretical and experimental investigations.

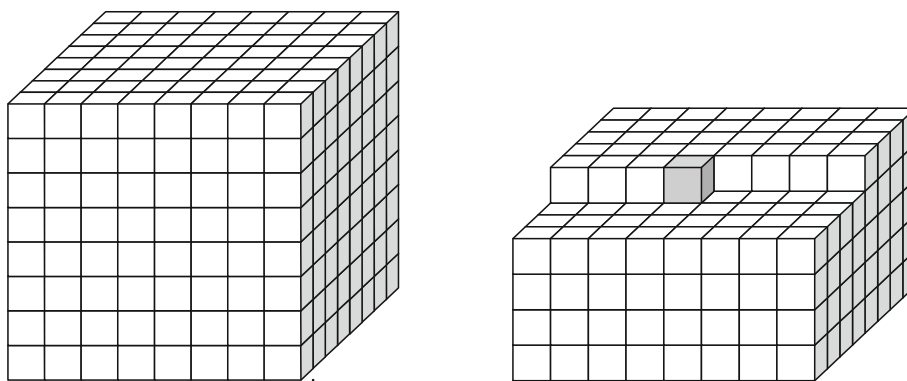
Introducing the supersaturation $\Delta\tilde{\mu} = \tilde{\mu}_{\infty}^{\text{sol}}(a_{\infty}^{\text{sol}}) - \tilde{\mu}_{\infty}^{\text{M}}(\phi)$ in Eq. (19) by adding and subtracting the term $n\tilde{\mu}_{\infty}^{\text{M}}(\phi)$, for the nucleation work $\Delta\tilde{G}(n)$ one obtains [5]:

$$\Delta\tilde{G}(n) = -n\Delta\tilde{\mu} + \tilde{\Phi}(n) \quad (20)$$

Here the quantity $\tilde{\Phi}(n)$ accounts for the *energy excess* of the n -atomic nucleus including the energy contribution of the *nucleus-substrate* and the *nucleus-solution* interface

¹ Strictly speaking, Eq. (18) is valid if the discharge of n ions does not reduce essentially the solution activity a_{∞}^{sol} and its electrochemical potential $\tilde{\mu}_{\infty}^{\text{sol}}(a_{\infty}^{\text{sol}})$ remains constant.

Fig. 2 The Kossel cubic crystal (a) and the atom in the half crystal position (b) [4]

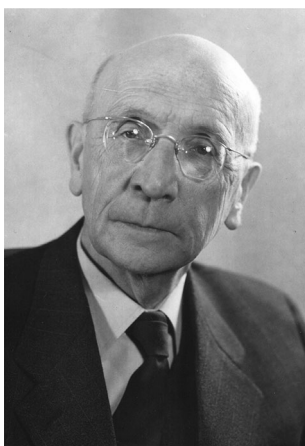


boundaries and is given by [14, 15] (see also Ref. [5] and the references cited therein):

$$\tilde{\Phi}(n) = \tilde{G}(n, E) - n\tilde{\mu}_{\infty}^M(\phi) \approx n\varphi_{1/2} - \sum_1^n \varphi_i \quad (21)$$

The quantities $\varphi_{1/2}$ and φ_i in Eq. (21) stand for the separation works of a single atom from the *half crystal position* (Fig. 2) and from the i th site of an n -atomic cluster, respectively, and are essentially used in the molecular kinetic studies of nucleation and crystal growth phenomena.

In particular, the concept *half crystal position* was defined simultaneously and independently by Walther Kossel [16] and Ivan Stranski [17, 18] in 1927.



W. Kossel (1888–1956)



I. N. Stranski (1897–1979)

Ivan Stranski was the first lecturer in Physical Chemistry at the University of Sofia, Bulgaria within the period 1926–1941. He and his co-workers and later also close friends Rostislav Kaishev, Lubomir Krastanov and Stephan Christov laid the foundations of the Bulgarian Physical Chemistry School. Short biographic remarks for those famous Bulgarian scientists can be found in Refs. [19, 20].

Invited by Walther Kossel, Ivan Stranski left Bulgaria for Germany in 1941 and worked there in various scientific institutions. He was elected foreign member of the Bulgarian Academy of Sciences (BAS) in 1966 when Lubomir Krastanov and Rostislav Kaishev held the positions President and Vice President of BAS.



R. Kaishev, I. Stranski and L. Krastanov, Institute of Physical Chemistry, BAS, 1975

I met Ivan Stranski for the first time during his visit to the Institute of Physical Chemistry in 1975 and had the pleasure to talk personally with him when he visited also my Lab.

article (see also Refs. [5, 24–26] and the references cited therein).



Ivan Stranski's visit to the Institute of Physical Chemistry, BAS, 1975; First row (left to right): G. Bliznakov, D. Nenov, R. Kaishev, I. Stranski, B. Kurtev; Second row (left to right): I. Markov, S. Stoyanov, A. Gittis, S. Neikova, A. Milchev

Back to the purely scientific part of this article, I should say that Eqs. (20) and (21) provide general theoretical expressions for the nucleation work $\Delta\tilde{G}(n)$ and for the energy excess $\tilde{\Phi}(n)$ which reveal the physical significance of these most important physical quantities. To obtain an explicit theoretical formula for $\Delta\tilde{G}(n)$ and to predict its supersaturation dependence is the main task of the *classical nucleation theory* [1, 4, 21–23] described briefly in the next section of this

Classical nucleation theory

If sufficiently large three-dimensional clusters of the new phase² are formed on the electrode surface the nucleus size n can be considered as a continuous variable, the

² Nucleation and growth of two-dimensional clusters of the new phase are not considered in this article. Information on this subject can be found in Refs. [5, 25, 26] (see also the references cited therein).

nucleation work $\Delta\tilde{G}(n)$ as a differentiable function and the condition for a maximum of $\Delta\tilde{G}(n)$ at a certain critical value of the nucleus size, $n = n_c$, $[\text{d}\tilde{G}(n)/\text{d}n]_{n=n_c} = 0$, applied to Eq. (19) results in:

$$\Delta\tilde{\mu} = \left[\frac{\text{d}\tilde{\Phi}(n)}{\text{d}n} \right]_{n=n_c} \quad (22)$$

Equation (22) is a general expression of the famous Gibbs–Thomson equation describing the supersaturation dependence of the size n_c of the *critical nucleus*, formed on the electrode surface with a maximal thermodynamic work $\Delta\tilde{G}(n_c)$. Explicit theoretical formulas obtained in the frameworks of the classical nucleation theory [1, 4, 21–23] and revealing the n_c versus $\Delta\tilde{\mu}$ and the $\Delta\tilde{G}(n_c)$ versus $\Delta\tilde{\mu}$ relationships read [24] (see Fig. 3),

$$n_c = \frac{a^* v_M^2}{\Delta\tilde{\mu}^3} \quad (23)$$

$$\Delta\tilde{G}(n_c) = \frac{1}{2} \frac{a^* v_M^2}{\Delta\tilde{\mu}^2} \quad (24)$$

where v_M is the molar volume of the nucleus substance and the material constant a^* accounts for the *nucleus–solution* and the *nucleus–foreign substrate*-specific free surface and adhesion energies [5].

It is worth noting that combination of Eqs. (23) and (24) yields the following simple relation between the three most important physical quantities in the classical nucleation theory— n_c , $\Delta\tilde{G}(n_c)$ and $\Delta\tilde{\mu}$ [5, 24]:

$$\Delta\tilde{G}(n_c) = \frac{1}{2} n_c \Delta\tilde{\mu} \quad (25)$$

Figure 3 shows schematically the n_c versus $\Delta\tilde{\mu}$ (a) and the $\Delta\tilde{G}(n)$ versus n (b) relationships according to the classical nucleation theory, $n_{c,1}$, $n_{c,2}$ and $n_{c,3}$ being the numbers of atoms in the critical nuclei formed with maximal nucleation works $\Delta\tilde{G}(n_{c,1})$, $\Delta\tilde{G}(n_{c,2})$ and $\Delta\tilde{G}(n_{c,3})$ at the supersaturations $\Delta\tilde{\mu}_1$, $\Delta\tilde{\mu}_2$ and $\Delta\tilde{\mu}_3$, respectively.

Atomistic nucleation theory

The classical nucleation theory operates with macroscopic physical quantities and, therefore, applies to sufficiently large clusters of the new phase for which concepts like *surface* and *volume* do have physical significance. However, detailed experimental studies of electrochemical nucleation of single- and multi-component clusters of the new phase on a foreign substrate unambiguously show that in most cases the size of the critical nuclei does not exceed several atoms. This is what led to the development of the *atomistic theory of electrochemical phase formation* [27–

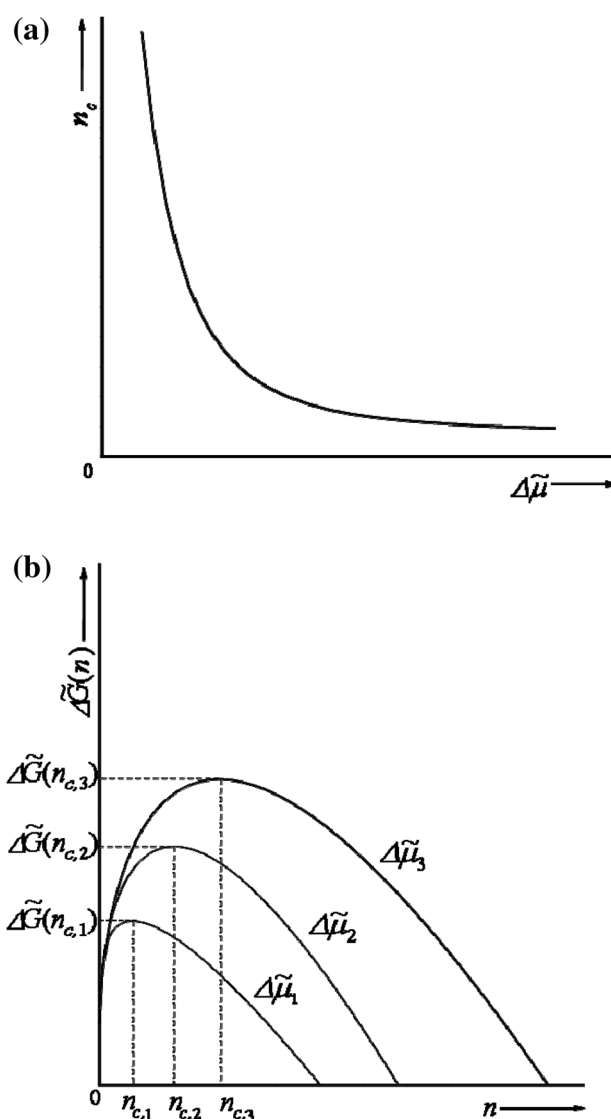


Fig. 3 n_c versus $\Delta\tilde{\mu}$ (a) and $\Delta\tilde{G}(n)$ versus n (b) relationships at different supersaturations $\Delta\tilde{\mu}$ according to the classical nucleation theory; $\Delta\tilde{\mu}_1 > \Delta\tilde{\mu}_2 > \Delta\tilde{\mu}_3$; $n_{c,1} < n_{c,2} < n_{c,3}$; $\Delta\tilde{G}(n_{c,1}) < \Delta\tilde{G}(n_{c,2}) < \Delta\tilde{G}(n_{c,3})$

31], which accounts for the discrete character of the clusters' size alteration at small dimensions (see also Refs. [5, 24] and the references cited therein).³

To make the things clear, let us consider the case of three critical nuclei, which differ only by 1 atom—those consisting of $n_c - 1$, n_c and $n_c + 1$ atoms (Fig. 4) [5]. Three different supersaturations, $\Delta\tilde{\mu}_{n_c-1}$, $\Delta\tilde{\mu}_{n_c}$ and $\Delta\tilde{\mu}_{n_c+1}$, should correspond to these three critical clusters according to the Gibbs–Thomson Eq. (22) and if experiments are

³ Theoretical considerations of nucleation phenomena in case of small clusters of the new phase were performed firstly in case of heterogeneous phase formation from a supersaturated vapour phase [32–37].

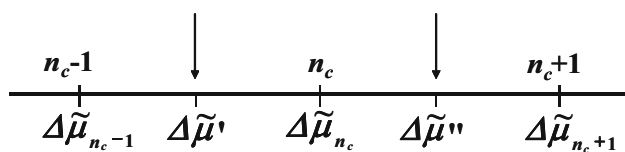


Fig. 4 Supersaturation interval $[\Delta\tilde{\mu}', \Delta\tilde{\mu}'']$ corresponding to the critical nucleus consisting of n_c atoms

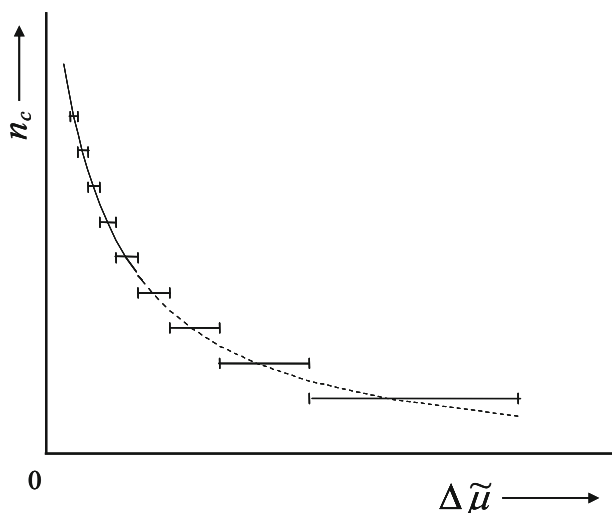


Fig. 5 Supersaturation dependence of the critical nucleus size n_c

performed at these three supersaturations exactly the critical nuclei consisting of $n_c - 1$, n_c and $n_c + 1$ atoms should be determined. What will happen, however, if the experiments are carried out within the supersaturation interval $[\Delta\tilde{\mu}', \Delta\tilde{\mu}'']$ (Fig. 4)?

Apparently there will be no different critical nuclei for all supersaturations from this interval for the simple reason that while supersaturation can be varied by infinitely small amounts, say, varying the overpotential by nanovolts, the size of the nuclei cannot change by less than 1 atom. Therefore, to each critical nucleus should correspond a supersaturation interval and not a fixed supersaturation (Fig. 5). At low supersaturations and large critical nuclei the intervals are short and the Gibbs–Thomson equation (the fluent curve in Fig. 5) describes reasonably well the real n_c versus $\Delta\tilde{\mu}$ relationship. At high supersaturations, however, the size of the critical nuclei strongly diminishes and the intervals become much wider. Then the supersaturation dependence of the critical nucleus size turns into a stepwise relationship and the classical Gibbs–Thomson equation is not valid anymore.

Correspondingly, the nucleation work $\Delta\tilde{G}(n)$ contains several minima and maxima (Fig. 6), the highest maximum giving the work $\Delta\tilde{G}(n_c)$ for nucleus formation of the largest cluster, which plays the role of a critical nucleus at a given supersaturation. As seen the cluster consisting of $n_{c,1}$ atoms

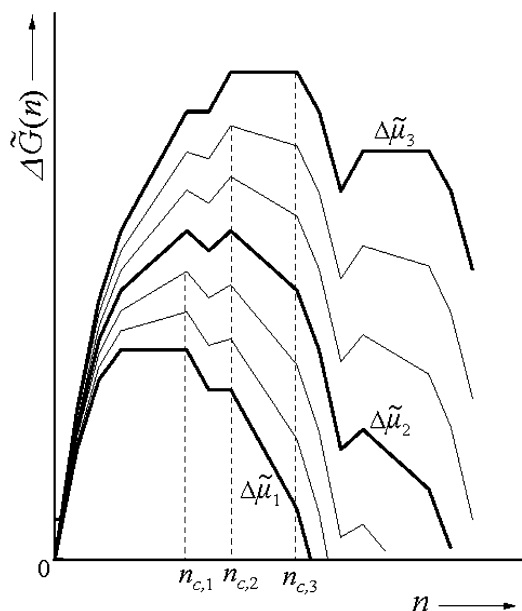


Fig. 6 Dependence of the nucleation work $\Delta\tilde{G}(n)$ on the nucleus size n for different supersaturations, $\Delta\tilde{\mu}_1 > \Delta\tilde{\mu}_2 > \Delta\tilde{\mu}_3$; $n_{c,1} < n_{c,2} < n_{c,3}$; $\Delta\tilde{G}(n_{c,1}) < \Delta\tilde{G}(n_{c,2}) < \Delta\tilde{G}(n_{c,3})$

is a critical nucleus within the supersaturation interval $(\Delta\tilde{\mu}_1, \Delta\tilde{\mu}^* < \Delta\tilde{\mu}_2)$ whereas at the supersaturation $\Delta\tilde{\mu}_2$ the critical nucleus already consists of $n_{c,2}$ atoms. It is the $n_{c,2}$ —atomic cluster which plays the role of a critical nucleus till the supersaturation $\Delta\tilde{\mu}_3$ at which the critical nucleus already consists of $n_{c,3}$ atoms. Thus, the atomistic nucleation theory defines the critical nucleus as *the largest cluster formed with maximal nucleation work*.

Conclusions

In this article I considered the specific properties of electrochemical systems and defined some basic thermodynamic concepts needed for the theoretical description of the first-order electrochemical phase transitions: *the supersaturation $\Delta\tilde{\mu}$, the overpotential η , the nucleation work $\Delta\tilde{G}(n)$ and the size n_c of the critical nucleus*. The next article is devoted to the kinetics of nucleus formation and comments upon another physical quantity, which proves important also from a practical point of view: *the rate of appearance of nuclei* in a supersaturated electrochemical system.

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