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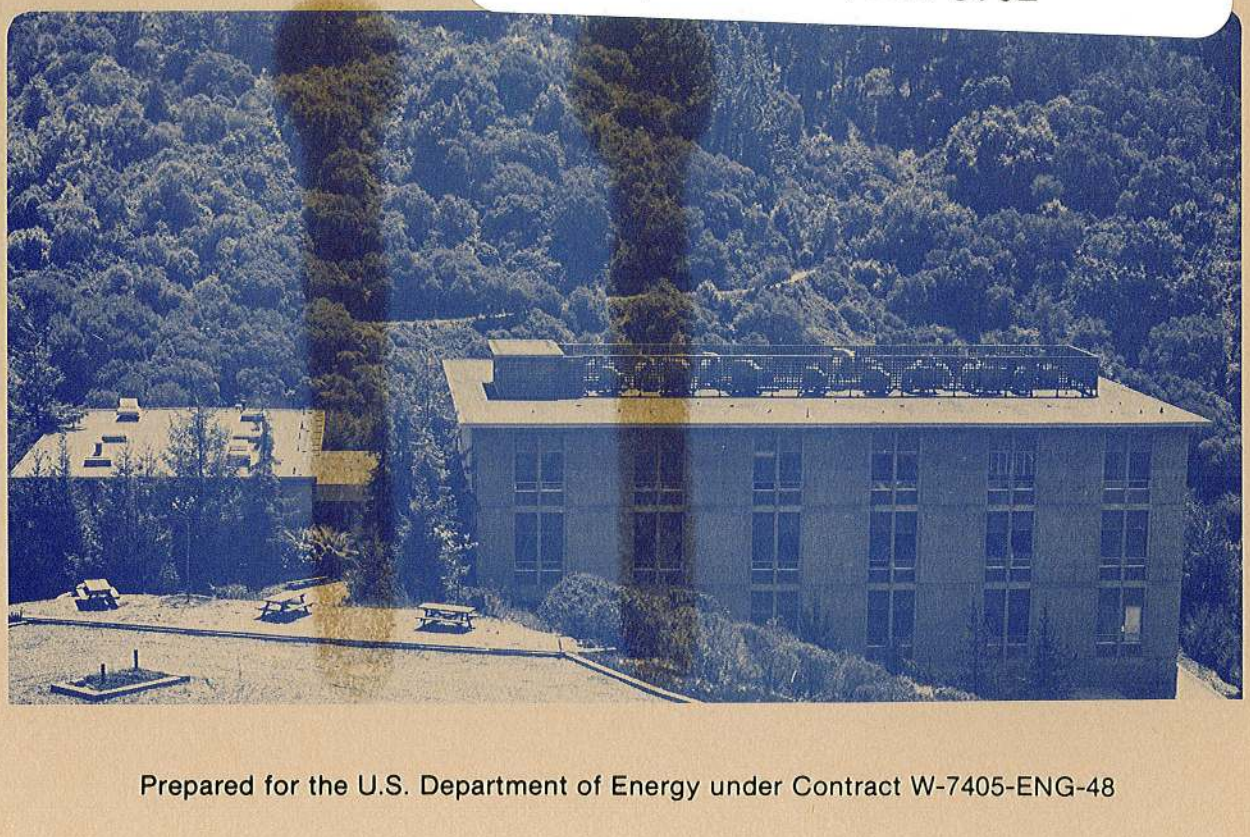

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ON THE ELECTROCHEMICAL PROPERTIES OF SMALL CLUSTERS OF METAL ATOMS AND THEIR ROLE IN THE SURFACE ENHANCED RAMAN SCATTERING

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ABSTRACT

Starting with equations for the shift of the reversible redox potential of small metal particles with size, the electrochemical properties of these particles are discussed. Approximate equations are given for the relationship between the particle size and the surface charge, the potential of zero charge, the surface potential, work function and quantities related to this function. The influence of these properties on redox reactions, electrosorption and chemisorption are discussed. The results are used to explain experimental observation in connection with the surface enhanced Raman effect.

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I. INTRODUCTION

It is well known that small particles have properties quite different from the properties of the bulk materials.[1] Recently, it was found by Henglein[2] that small metal particles possess unusual catalytic properties in radiolysis and this was explained qualitatively by a shift in the redox potential. In a series of papers Henglein et al.[2] investigated the catalyzed reduction of several organic molecules, the catalysts being metal clusters of silver, gold and copper. Another series of experiments, demonstrating the unusual electrochemical properties of small metal particles, was carried out by Ross.[9] He deposited platinum on graphite supports and compared the electrochemical properties of the electrodes with the known behavior of bulk platinum.

A deviation from the electrochemical properties of the bulk material was also found for silver nuclei[10-12] formed as latent image in photographic layers.[10] This deviation was explained more quanitatively by use of Kelvin's equation.[11,12] Among the various theories explaining the surface-enhanced Raman scattering is the idea that the surface enhancement is caused by the unusual optical properties of small metal particles. Results of experiments suggesting such a mechanism were carried out with solutions of colloidal gold and silver by Greighton, Blatchford and Albrecht.[4] A similar experiment by Wetzerl and Gerischer[5] mainly confirmed the earlier results. Explanations were given by Hexter and Albrecht[6] and by Moskovits.[7] The cluster explanation suggests that one has to look not only on the

optical properties of the small particles, but also on their electrochemical behavior. Considering the deviations of the general electrochemistry of these particles from that of the bulk, one might be able to understand the electrochemical procedures of activation and deactivation of electrodes encountered in Raman studies.

For these reasons, we have tried to find a more general description of the electrochemical properties of small metal particles. Starting with equations for the shift of the reversible potential with dispersion, we will discuss various other electrochemical properties such as surface charge, the potential of zero charge, the surface potential, the work function and related quantities. The approximate relations between these functions and the size will enable us to explain the electrochemical behavior of dispersed metals in more detail.

II. THE REDOX POTENTIAL OF METAL CLUSTERS

What is the redox-potential of metals in a dispersed state? It was recognized that it is different from the bulk metal and for the special case of a single silver atom in equilibrium with silver ions Henglein[2] calculated the dramatic value of -1.8 V for the standard potential, which has to be compared with the standard potential of bulk silver of +0.799 V vs the NHE.

In the attempt to derive the equation for the potential of clusters of more then just one atom, we construct an electrochemical cell consisting of two half cells. One contains a metal in its bulk

state, Me_b, the other in the dispersed state, Me_d. The cell reaction is described by the following equations

$$Me_b \rightarrow Me^{z+}_{solv} + z\ e^- \tag{1a}$$

$$Me^{+}_{solv} + z\ e^- \rightarrow Me_d \tag{1b}$$

$$Me_b \rightarrow Me_d \quad . \tag{1c}$$

The overall electrode reaction is the transference of one mole bulk metal into the dispersed form. The voltage of this electrochemical cell can be calculated from the free energy of the dispersion process

$$\Delta G_D = G_d - G_b \tag{2}$$

$$\Delta \epsilon_D = \epsilon_d - \epsilon_b = -\frac{\Delta G_D}{zF} \quad . \tag{3}$$

One way to find ΔG_D is to look for the change of free energy associated with the change in surface area. In a first approximation one can consider a small particle of a sphere of radius r. The change of free energy with surface area A it is given by

$$dG = \gamma\ dA \tag{4}$$

where γ is the surface tension. We substitute

$$dA = 8\pi\ r\ dr \tag{5}$$

$$dr = \frac{v_M}{4\pi r^2}\ dn \quad , \tag{6}$$

where v_M is the molar volume, n the number of moles. Integrating between n = 0 and n = 1, we get the free surface energy of one mole of particles of radius r. The free surface energy of the bulk can be neglected and we obtain

$$\Delta G_D = \frac{2\gamma\ v_M}{r} \quad , \tag{7}$$

This is an analogous expression to the Kelvin equation.

If, in addition, we take the crystallography of the particles into account, we have to apply Wulf's law, substituting γ by γ_i/r_i. For crystallites in their crystallographic equilibrium γ_i/r_i should be constant. So while Eq. (7) is not changed in principle, separation into γ and r would give mean values γ and r. For growing nuclei, of course, the condition of equilibrium will rarely be satisfied and in general we have to expect nonequilibrium values of γ and r. But in all these cases Eq. (7) will be a good approximation as long as the size of the particles is not less than 100 atoms, equal to approximately 10Å of radius.

For a long period of time, Eq. (7) was considered as too simple a model to be applied for the sophisticated photographic process. But

recently the validity of Eq. (7) was demonstrated for silver clusters deposited on bromide layers.[11,12]

Inserting Eq. (7) into Eq. (6) we obtain the following relationship for the potential difference $\Delta\varepsilon_D$:

$$\Delta\varepsilon_D = -\frac{2\gamma\ v_M}{zF}\ \frac{1}{r} \tag{8}$$

Thus, the deviation of the redox potential of small metal particles from the redox potential of the bulk is proportional to the ratio γ/z and to the reciprocal radius $1/r$.

Some values of γ obtained for a number of metals mainly by the zero-creep method are listed in Table I. These values refer to vacuum and will be different in an electrolyte, depending on the properties of the double layer. One can therefore use only approximate values for γ/r in calculations of $\Delta\varepsilon_D$. The result of one such calculation is shown in Figs. 1a and 1b. The data show that the shift of the redox potential is significant for particles with radius as large as 100Å.

While Eq. (8) will describe the potential shift for particle sizes above 10Å with sufficient accuracy it becomes inaccurate for the interesting small particles consisting of only a few atoms (Fig. 2). A more general way to obtain ΔG_D is therefore described using the following circular process (Fig. 2). In vacuum ΔG_D must be equal to the value of the sum of the free energy of sublimation ΔG_{sub}, of the free energy associated with the clustering of single metal atoms

ΔG_{Cl} and in a solution, with the energy of the interaction of the surface atoms with the solvent molecules ΔG_{solv}. Thus, one obtains

$$\Delta G_D = \Delta G_{sub} + \Delta G_{Cl} + \Delta G_{solv}. \tag{9}$$

This equation allows one to obtain ΔG_D from quantum chemical first principle calculations, taking ΔG_{sub} from experiments and neglecting ΔG_{solv}. Calculations for the clustering energy have recently been carried out for Ag clusters,[8a] for Cu clusters[16,8b] and others.[8b] These calculations show an oscillating behavior of the energy with the number of atoms. The possibility to test this result with electrochemical methods is a great challenge for this discipline.

III. SMALL METAL CLUSTERS ON SURFACES

Metal clusters formed on surfaces can have two dimensional shape. In this case, instead of taking γ, the boundary free energy has to be used.[10,17] Then the differential free energy change is given by the equation

$$dG = \delta \, dl \quad , \tag{10}$$

where l is the boundary length of the two dimensional clusters. If we assume discs as the approximate form of the two dimensional nuclei, dl is related to dn, the differential of the mole number, by the relation

$$dl = \frac{A_M}{r}\, dr \quad . \tag{11}$$

Here, A_M is the molar area of the cluster forming atoms and r is the mean radius of the discs. Substituting Eqs. (11) and (10) and integrating for one mole gives one the change of free energy for the transformation of one mole of clusters into bulk metal,

$$\Delta\varepsilon = \varepsilon_d - \varepsilon_b = -\frac{\delta\, A_M}{zF}\,\frac{1}{r} \quad , \tag{13}$$

where r is now the radius of the cluster disc on the surface.

The energy δ will depend considerably on the structure of the surface of the supporting material.

IV. THE CHARGE OF THE PARTICLES AND THE POTENTIAL OF ZERO CHARGE

In this chapter we will discuss the behavior of the surface charge in the dispersion process. The free energy of the cell reaction $Me_b \rightarrow Me_d$ was calculated without any consideration for the charge. Therefore, changes in the charge can only occur in a way that does not influence ΔG_D. We will discuss the influence of this argument by carrying out the circular process illustrated in Fig. 3.

First we have to discharge the bulk metal. The work to discharge a compact sphere of one mole of metal atoms (radius R) is given by the equation

$$W_b = -\frac{q_b^2}{4\pi\varepsilon_o\varepsilon R} \quad , \tag{14a}$$

where $\varepsilon_o = 8.859 \times 10^{-14}$ (coul $V^{-1}cm^{-1}$, the dielectric constant of the vacuum in the SI system). After dispersion into particles of radius r of the now uncharged bulk metal we have to recharge these particles. The work for this process is

$$W_d = +\frac{q_d^2}{4\pi\varepsilon_o\varepsilon r} \quad . \tag{14b}$$

It follows (Fig. 3) that

$$\Delta G_{D,q} = W_b + \Delta G_D + W_d \ . \tag{15}$$

The values for ΔG are equal if

$$W_b = -W_d \ . \tag{16a}$$

Extending Eq. (14) by $3M/4\pi R^3\delta = 1$ and rearranging we obtain a condition for the change of the charge during the dispersion process,

$$\frac{q_b}{4\pi r^2} = \frac{q_b}{4\pi R^2} \quad . \tag{16b}$$

This relation shows that the surface charge density has to be constant, while the net charge of the particles decreases with particle size: $q_d \sim r^2$.

While the dispersed metal has the same surface charge density as the bulk metal the equilibrium redox potential is much more negative. This has the consequence that the potential of zero charge has to be shifted by the same amount as the redox potential,

$$\epsilon_{pzc,d} - \epsilon_{pzc,b} = \Delta\epsilon_D \ , \tag{17}$$

which is a different expression of the equality $\Delta G_{D,q} = \Delta G_D$.

V. THE SURFACE POTENTIAL

With the properties so far derived we can look at more specific properties of the double layer of the small particles. The potential across the double layer is separated into two contributions. The surface potential χ and the Volta potential ψ. The Volta potential is determined by the charge on the surface and was already discussed in the foregoing chapter.

The surface potential χ represents the dipole structure of the surface, and is mainly dependent on the dipole density $N \cdot \mu$,

$$\chi = f(N\ \mu) \ . \tag{18}$$

The dipole layer between the metal atoms and the electrolyte will in general be a closely packed layer of solvent molecules and their images in the metal. It is postulated that this layer is, as a first

approximation, independent of the particle size. To illustrate this reasoning we will form the ratio between the number of metal atoms N_M (surface area per atom A_M) and the number of dipole molecules N_D (surface area per molecule A_D). The ratio is given by

$$\frac{N_D}{N_M} = \frac{A_M}{A_D} \frac{(r + a)^2}{r^2} \simeq \frac{A_M}{A_D}\left(1 + 2\frac{a}{r}\right) . \tag{19}$$

As r increases, this ratio very soon becomes approximately constant. For clusters $r \geq 10Å$ the dipole density $N = A_D^{-1}$ will be approximately constant, regardless of the size of the particles. Thus χ will become independent on r. It follows,

$$\chi_d - \chi_b \simeq 0 . \tag{20}$$

VI. THE WORK FUNCTION AND THE CHEMICAL POTENTIAL OF ELECTRONS

Changes of the potential of zero charge can, according to the literature,[14] be related to changes in the work function. We can write for the differences between dispersed and bulk metal

$$W_d - W_b = F(\varepsilon_{pzc,d} - \varepsilon_{pzc,b}) . \tag{21}$$

It follows using Eq. (10)

$$W_d - W_b = F\Delta\varepsilon_D < 0 . \tag{22}$$

The work function is defined by the equation $W = -\mu + F$. The μ is the chemical potential of the electrons. According to the foregoing chapter $\chi_d - \chi_b \simeq 0$ (at least for particles above a limiting radius of ca 10Å). With Eq. (25) we obtain

$$\mu_d - \mu_b \simeq -F\Delta\varepsilon_D > 0 \tag{23}$$

The chemical potential of electrons in dispersed metals is higher than in the bulk metal.

The chemical potential of electrons in a metal is also related to the concept of electronegativity. We can deduce from Eq. (23) that the electronegativity is increased with decreasing particle size.

VI. CONCLUSIONS FOR THE ELECTROCHEMICAL BEHAVIOR

The result of the foregoing discussion can be summarized in three points which, as we have tried to show, have one common origin: Metal atoms in a small array are in energetically less favorable positions compared to bulk positions.

a) Cathodic shift of the equilibrium potential: This point determines the equilibrium properties as well as the ability for reduction or oxidation. The results by Hanglein[3] can be explained qualitatively by these properties. The experiments with silver clusters on silver bromide of Malinowski et al.,[11,12] gave quantitative evidence for the prediction that a particle in a special redox environment will grow or decrease in size depending on the equilibrium condition. The stabilization of the latent image in photographic

layers with a particle size between 4 and 40 silver atoms[15] is another example.

b) Cathodic shift of the potential of zero charge ε_{pzc}. Electrosorption on a surface depends on the position of the potential with regard to the potential of zero charge ε_{pzc}. Because of the shift of this potential for small particles we expect a change in the electrosorption properties. An experimental confirmation for this prediction is given by the experimental results by Ross.[9] A cathodic shift of -150 mV was measured for the formation of the oxide electrosorption layer on graphite-supported platinum clusters if compared to bulk platinum. The particle size was approximately 20Å. The shift would predict a ratio γ/z between 1500 and 2000 erg cm^{-1} in agreement with the values for the energy of platinum in Table I.

c) The decrease of the work function W. The decrease of the work function can be considered as a reduced electron affinity of small particles. With regard to the electron donor properties of metals this means a stronger ability to form charge transfer complexes. In a preliminary search we have not been able to find examples for this property which explicitely demonstrate the dependence on particle size. Otherwise, the complex formation between silver and pyridine and its importance for the surface enhanced Raman spectroscopy may become an example, if one accepts the cluster explanation for this phenomenon.

VII. THE ELECTROCHEMICAL PROPERTIES OF SMALL METAL PARTICLES AND THE SURFACE ENHANCED RAMON EFFECT

In the observation of the so called surface enhanced Raman effect (SERS) some of the most fundamental experimental results have not yet found reasonable explanations. This includes the following points

- Why is the oxidation reduction cycle so important.
- Why does silver deposition at moderate cathodic potentials result in no enhancement but deposition at high cathodic potentials[18] does.
- Why does the enhancement effect irreversibly disappear after the polarization is increased above a limiting cathodic potential.[19]

The answers to these questions may be found by considering the outstanding electrochemical properties of microparticles especially of smallest size (e.g., 4-40Å for Ag[15]). The explanations described are a further support for the idea that these particles are also responsible for the optical process of enhancement.[6,7]

- The formation of clusters and microcrystallytes on surfaces in metal deposition is favored (especially for silver) by rather crude electrochemical conditions with regard to the electrode potential as well as with regard to diffusion limitations. Special deposition forms (whisker, powder deposition) are obtained under very similar conditions as necessary to activate an electrode for enhanced Raman scattering.

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Table I. Values of surface energy, valence state, molar volume and bulk equilibrium potentials for some common electrode materials.

Metal	γ erg cm^{-2}	T °C	$\gamma_{25°C}$ [1] erg cm^{-2}	Z [2]	V_M cm^3 mole^{-1}	ε_B [3] V
Ag	1140	930	1590	1	10,28	0.80
Au	1370	1040	1880	1	10,21	1.68
Cu	1750	900	2190	1	7,12	0.52
	1710	1000				
Pt	2300	1310	3240	2	9,10	1.2
Fe_γ	2170	1380	2930	2	7,11	-0.41
Fe_δ	2320	1410				
Co	1970	1350	2640	2	6,62	-0.28
Ni	1860	1220	2460	2	6,60	-0.23
Cr	2200	1550	2960	(2)	7,22	-0.41
Ti	1700	1600	2490	(2)	10,64	-1.63

1) Calculated with $-\partial\gamma/\partial T = 0.5$ erg cm^{-2} Grad^{-1}.
2) Lowest valence state
3) For the lowest valence state.

FIGURE CAPTIONS

Fig. 1. Cathodic shift of the reversible redox potential of a metal electrode with decreasing particle radius (after Eq. (7)), for three selected values of surface energy a) for particle size up to 250Å, b) for very small particle size.

Fig. 2. Circular process to relate the free energy for dispersion ΔG_D to the calculated free energy of cluster formation ΔG_{Cl}. ΔCr_{sub}, ΔG_{solv} free energy of sublimination and solvation, respectively.

Fig. 3. Circular process to find the conditions for the behavior of the surface charge during the dispersion process.

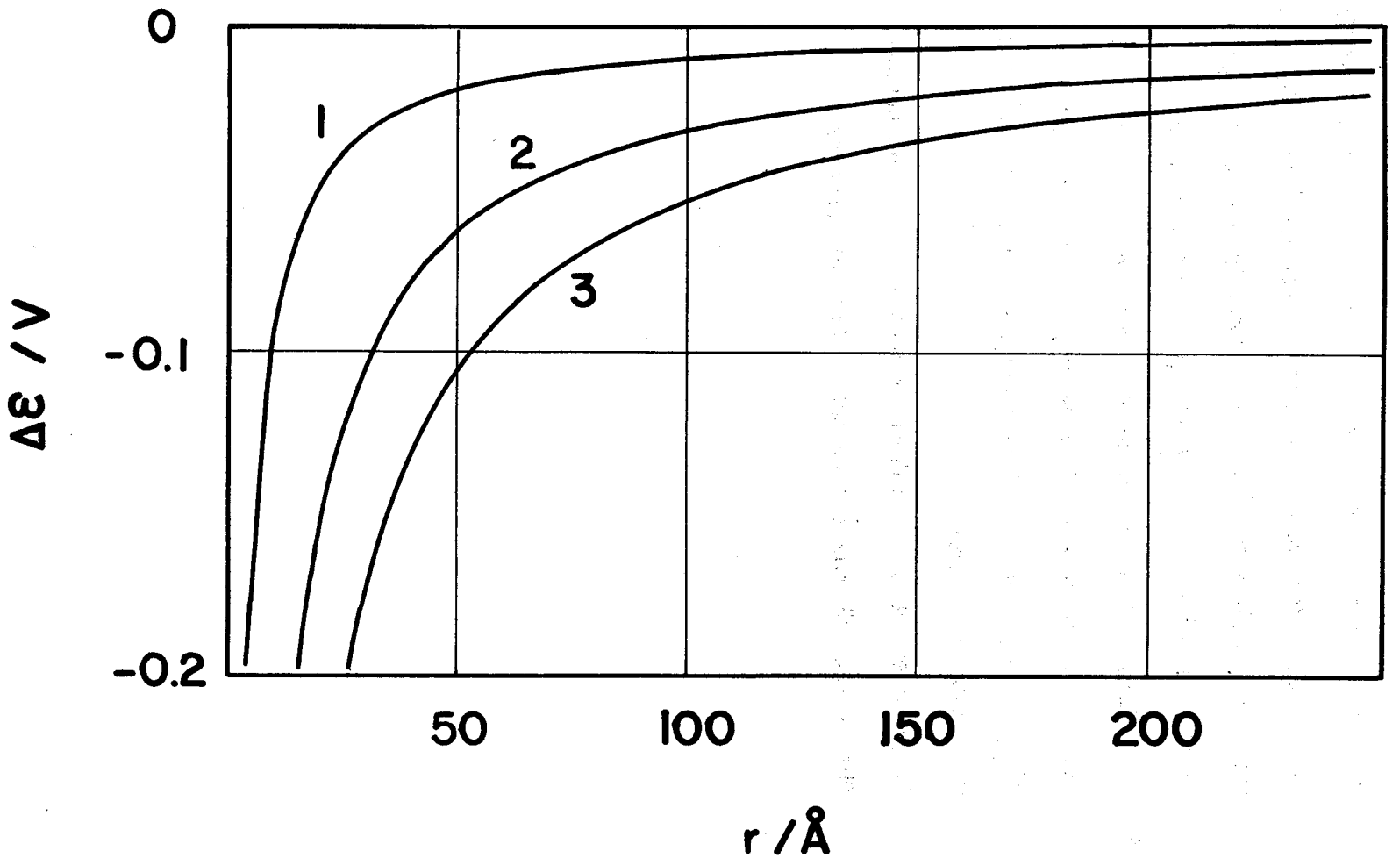

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Figure 1 a

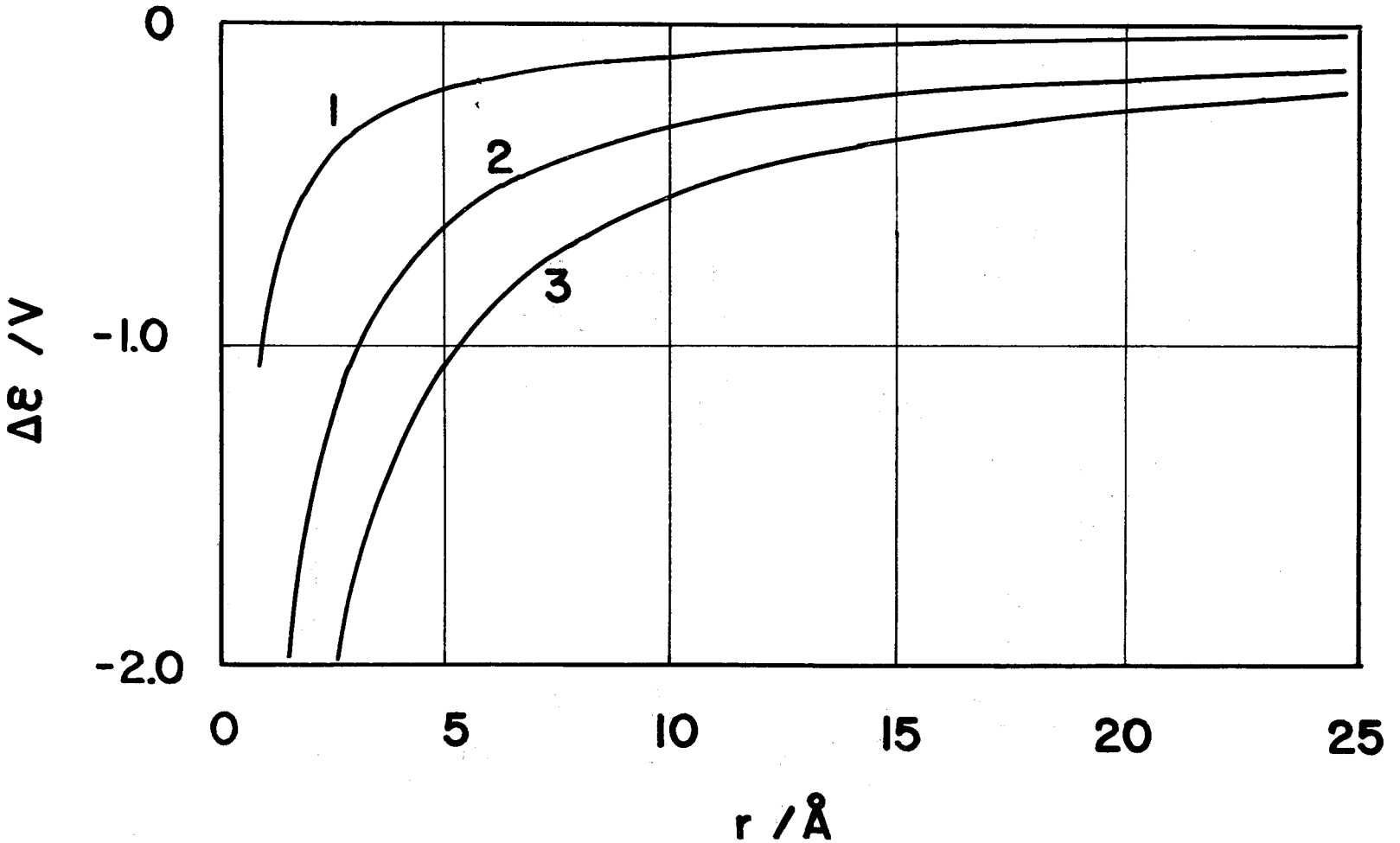

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Figure 1 b

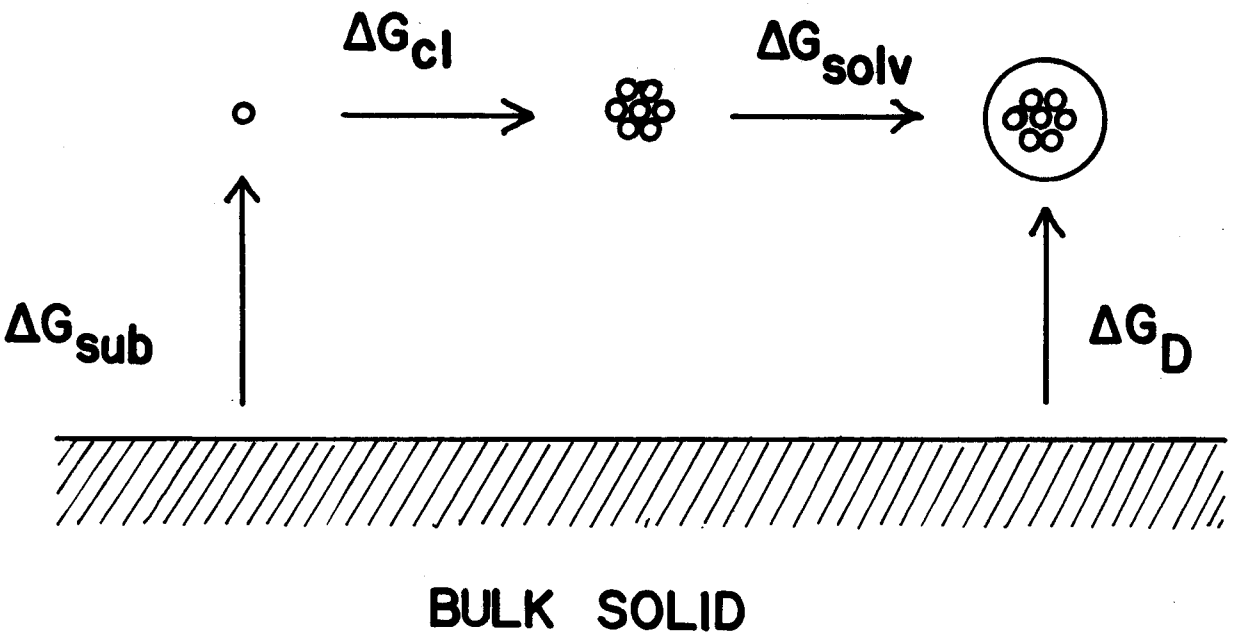

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Figure 2

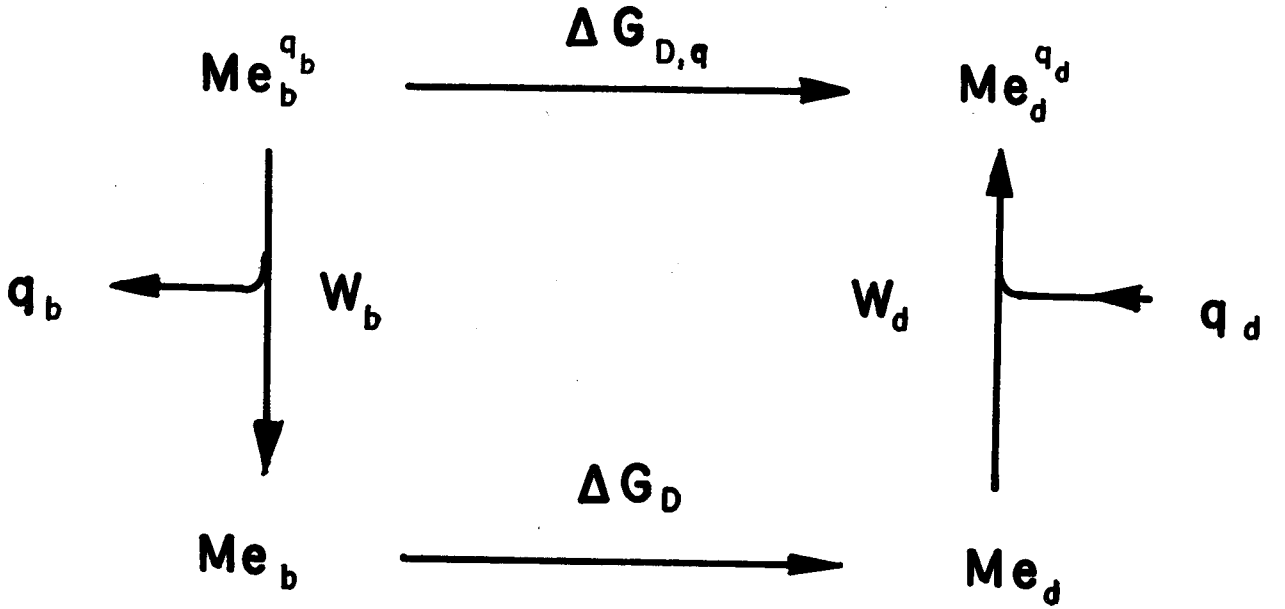

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Figure 3