

## REPORT DOCUMENTATION

AD-A257 057

-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing the collection of information, gathering the data needed, and completing and reviewing the collection of information, including suggestions for reducing this burden, to Washington, D.C. Highway, Suite 1204, Arlington, VA 22202-4302 and to the Office of Management.

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1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

OCTOBER, 1992

4. TITLE AND SUBTITLE

MOLECULAR CAPACITANCE: SEQUENTIAL ELECTRON-TRANSFER  
ENERGETICS FOR SOLUTION-PHASE METALLIC CLUSTERS IN  
RELATION TO GAS-PHASE CLUSTERS AND ANALOGOUS INTERFACES

5. FUNDING NUMBERS

CONTRACT NO.  
N00014-91-J-1409

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION  
REPORT NUMBER

TECHNICAL REPORT  
NO. 134

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

DIVISION OF SPONSORED PROGRAMS  
PURDUE RESEARCH FOUNDATION  
PURDUE UNIVERSITY  
WEST LAFAYETTE, IN 47907

10. SPONSORING / MONITORING  
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

DTIC  
SELECTE  
NOV 02 1992  
S B

12a. DISTRIBUTION / AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE AND SALE; ITS DISTRIBUTION  
IS UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

A simple electrostatic treatment of the energetics of sequential solution-phase electron transfers involving metallic clusters and other large solutes is outlined and related to the conventional description for charging of gas-phase clusters with the objective of linking these phenomena and assessing phenomenologically the role of solvation in the former class of systems. The common occurrence of electron transfer sequences for solution-phase solutes suggests the concept of "molecular capacitance," denoting the dependence of the surface charge density upon the electrode potential; the present treatment is related to conventional descriptions of the capacitance of metal electrode-solution interfaces. The notion of the "potential of zero charge,"  $E_{pzc}$ , for cluster solutes, which also emerges from the electrostatic treatment, is related to the corresponding quantities for both metal-solution and metal-vacuum interfaces. The analysis therefore provides an instructive link between the charging energetics of spherical clusters and planar surfaces in solution- versus gas-phase environments. Illustrative

14. SUBJECT TERMS

SOULTION-PHASE ELECTRON TRANSFERS, GAS-PHASE CLUSTERS,  
MOLECULAR CAPACITANCE, POTENTIAL OF ZERO CHARGE

15. NUMBER OF PAGES

30

16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION  
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION  
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

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13. ABSTRACT (continued)

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Contract No. N00014-91-J-1409

Technical Report No. 134

Molecular Capacitance:

Sequential Electron-Transfer Energetics for  
Solution-Phase Metallic Clusters in Relation to  
Gas-Phase Clusters and Analogous Interfaces

by

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Prepared for Publication

in

Journal of Physical Chemistry

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October 1992

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## **ABSTRACT**

A simple electrostatic treatment of the energetics of sequential solution-phase electron transfers involving metallic clusters and other large solutes is outlined and related to the conventional description for charging of gas-phase clusters with the objective of linking these phenomena and assessing phenomenologically the role of solvation in the former class of systems. The common occurrence of electron transfer sequences for solution-phase solutes suggests the concept of "molecular capacitance," denoting the dependence of the surface charge density upon the electrode potential; the present treatment is related to conventional descriptions of the capacitance of metal electrode-solution interfaces. The notion of the "potential of zero charge,"  $E_{pzc}$ , for cluster solutes, which also emerges from the electrostatic treatment, is related to the corresponding quantities for both metal-solution and metal-vacuum interfaces. The analysis therefore provides an instructive link between the charging energetics of spherical clusters and planar surfaces in solution- versus gas-phase environments. Illustrative applications of this treatment are outlined for the cathodic charging of buckminsterfullerene and high-nuclearity platinum carbonyl clusters. The applicability of the dielectric-continuum description of solvent-dependent cluster charging is examined. While only of semiquantitative validity, the analysis can prove useful for separating classical electrostatic and quantum (molecular-orbital) contributions to the cluster capacitance. The approximate correspondence between  $E_{pzc}$  for the platinum carbonyl clusters and for analogous platinum-solution and -vacuum interfaces is also noted.

## Introduction

Interest in the physical and chemical behavior of metal clusters and related systems has been heightened recently by developments in diverse research areas. The evolution of supersonic beams sources has led to a broadening exploration of the electronic and other spectroscopic properties of gas-phase clusters, especially metal systems.<sup>1</sup> The recent discovery of a simple preparative route for producing  $C_{60}$  and other fullerenes has triggered intense efforts to characterize their physics and chemistry.<sup>2</sup> These remarkable molecules constitute a new category of metallic clusters that can be examined in solution and in the solid state as well as in the gas phase. This feature is shared by a variety of large ligand-stabilized transition-metal clusters that have been synthesized extensively in recent years.<sup>3,4</sup>

Important properties of all metallic clusters are their propensity towards electron capture or loss; i.e. reduction or oxidation. These processes for gas-phase clusters, as probed by electron affinity (EA) or ionization potential (IP) measurements, respectively, exhibit well-documented trends with cluster size and electronic structure.<sup>1a,5-8</sup> Metallic clusters in solution can readily also undergo reversible oxidation and especially reduction. A significant difference from gas-phase systems, however, is that *sequencies* of reversible electron-transfer steps can be observed for solution-phase clusters, reflecting in large part the stabilization afforded to the charged species by the solvating medium. For example,  $C_{60}$  can be electroreduced in five sequential one-electron steps to  $C_{60}^{5-}$  in benzene,<sup>9</sup> and the high-nuclearity platinum carbonyl cluster  $[Pt_{24}(CO)_{30}]^n$  can be transformed electrochemically through seven redox states ( $n = 0$  to  $-6$ ) in dichloromethane.<sup>10</sup>

Given the occurrence of such rich electron-transfer (ET) chemistry for some solution-phase cluster systems, it is of fundamental interest to both understand

the factors determining the sequential ET energetics and relate them to the corresponding behavior of the gas-phase systems. As discussed recently for small inorganic and organic redox couples,<sup>11,12</sup> comparisons between the redox potentials in solution and gas-phase environments can provide basic insight into the role of solvation upon the ET energetics. In addition, a focus of attention for gas-phase metallic clusters is the relationship of their electronic properties to those of analogous metal-vacuum interfaces.<sup>1,3a</sup> Solution-phase clusters can be perceived along these lines as being analogous to metallic-solution (i.e. electrochemical) interfaces (the "ionizable metal cluster-electrode surface" analogy<sup>10</sup>). These considerations together prompt the more general issue of the manner in which solvation factors can influence the electron-charging energetics of metallic clusters in relation to metal surfaces. Despite their intriguing nature and broadbased interdisciplinary significance, discussions of the relationships between, and commonalities in, the physical properties of such solution-/gas-phase cluster/surface systems are conspicuous by their absence in the literature.

In the present article we utilize illustrative experimental data for fullerenes and high-nuclearity platinum carbonyls in exploring how solvation factors can influence the sequential ET energetics for metallic clusters and related systems. A phenomenological treatment of dielectric solvation effects upon such cluster charging is developed, and examined for these systems in the light of the recently documented success of the Born model in describing the solvent-dependent consecutive ET energetics for simple organometallic solutes.<sup>13</sup> The similarity between ionizable metallic clusters and electrode surfaces is that both can be charged progressively by altering the electrode potential<sup>10b</sup> This suggests the notion of "molecular capacitance", describing the relation between the charge state of electroactive metallic clusters and the electrode potential

in analogous fashion to the familiar capacitive (i.e. charge-potential) behavior of electrode-solution interfaces. We explore herein the major factors that are anticipated to determine the molecular capacitance of spherical metallic clusters in relation to electrode surfaces, again with illustrative reference to the fullerene and platinum carbonyl systems; the latter species also invite interesting comparisons with platinum electrodes. These concepts are also discussed in comparison with the oft-explored relationships between the ET properties (IP and EA values) of gas-phase clusters and the corresponding metal-vacuum interfaces.<sup>1a,5-8</sup>

### Electrostatic Analysis

We consider primarily here neutral metallic clusters, MC, that can form a series of anionic species, MC<sup>n</sup> (n is negative) via sequential reversible one-electron transfers depicted generally as:



where n = 0, -1, -2, etc., with formal (or standard) electrode potentials for the first and subsequent ET steps denoted here as E<sub>n</sub><sup>f</sup>. The simplest treatment of such processes considers the electroactive solute to be a conducting sphere with the energetics of electron addition determined by classical electrostatics. This problem has been discussed in some detail for electron addition or loss in gas-phase clusters, for which the following formula has been derived<sup>14</sup>

$$\Phi_r = \Phi_{WF} + (n - 0.5)e^2/r \quad (2)$$

Here e is the electronic charge, r is the radius of the conducting sphere,  $\Phi_r$ (eV) is either an ionization potential or electron affinity (for n > 0 and n ≤ 0, respectively), and  $\Phi_{WF}$ (eV) is the work function of the corresponding metal-vacuum interface. Such gas-phase formulae are usually written for the special case

where  $n = 1$  or  $0$ , i.e., to describe the formation of singly charged cations or anions (IP or EA), although multicharged ionizations have occasionally been considered in this manner.<sup>15</sup> The work function refers to the limiting case of an infinitely large cluster composed of the same metal (and surface packing density), for which  $IP = EA$ . For finite cluster radii, Eq. (2) predicts that the IP and EA values should be divergent, the former increasing and the latter decreasing as  $r$  diminishes. This reflects the increasing energy cost of electron loss or addition arising from electrostatic repulsion involving the net positive or negative charge density formed around the conducting sphere under these conditions.

Equation (2) differs significantly from EA- or IP-work function expressions quoted earlier in the literature in that the coefficients  $5/8$  and  $3/8$  are commonly contained in the latter EA and IP formulae, rather than the symmetric value of  $1/2$  appearing in Eq. (2).<sup>1a,8</sup> However, even though the former IP formula yields IP-cluster size variations in reasonable accord with experiment, the  $3/8$  term (and the  $5/8$  coefficient in the EA expression) have been shown to be incorrect on the basis of both classical and quantum electrodynamics, arising from an inappropriate choice of image potentials.<sup>14</sup> (The apparent success of the earlier IP formula for small clusters probably arises from the fortuitous influence of additional "quantum-size" effects in the experimental data, which are however beyond the realm of such classical electrostatic treatments.<sup>8,14a</sup>) The symmetric form of Eq. (2), along with the coefficient  $1/2$ , is strongly reminiscent of formulae resulting from the Born model of ionic solvation. Indeed, Eq. (2) can be derived by invoking the requirement of consistency between the Born charging energy and the image potential cut-off in the electrostatic charging process.<sup>14a</sup>

Corresponding relationships applicable directly to electrochemical systems

can also be derived readily from Eq. (2) by utilizing the Born model of solvation. According to the Born Model,<sup>16</sup> the difference in solvation free energy between the two components of the redox couple in Eq. (1),  $MC^{n-1}$  and  $MC^n$ , is

$$(\Delta G_{n-1} - \Delta G_n) = [(n-1)^2 e^2 / 2r - n^2 e^2 / 2r](1 - \epsilon_s^{-1}) = -[(n-0.5)e^2 / r](1 - \epsilon_s^{-1}) \quad (3)$$

This formula predicts the shift in the energetics in a redox couple of charge type  $(n/n-1)$  resulting from the couple being present in a solvating medium of dielectric constant  $\epsilon_s$  rather than in vacuum (for which  $\epsilon_s = 1$ ). Combining Eqs. (2) and (3) yields

$$\Phi_r = \Phi_{WF} + (n - 0.5)e^2 / \epsilon_s r \quad (4)$$

Reexpressing Eq. (4) in terms of electrode potentials rather than energies yields

$$E_n^f = E(r \rightarrow \infty) + (n - 0.5)e / \epsilon_s r \quad (5)$$

where  $E_n^f$  is the electrode potential (either formal or standard potential) of the redox couple having a charge type  $(n/n-1)$  in a solvent of dielectric constant  $\epsilon_s$ . The quantity  $E(r \rightarrow \infty)$ , which corresponds to  $\Phi_{WF}$ , refers to the electrode potential of an infinitely large cluster (i.e. a surface) of the same uncharged metal contacting the solvating medium. Equation (5) as well as Eq. (3) applies to oxidized as well as reduced clusters, i.e. where  $n > 0$  as well as where  $n \leq 0$ .

A simple alternative derivation of Eq. (5) can be made by considering electron transfer between a macroscopically large piece of metal and a microscopic spherical cluster of the same material, having radius  $r$ , both present in a medium of dielectric constant  $\epsilon_s$ . From the Born model, the free energy required to charge the cluster with  $n$  electrons in this fashion is

$$\Delta G = n^2 e^2 / 2\epsilon_s r \quad (6)$$

Consider a portion of this process involving the transfer of  $y$  electrons to a cluster charged previously with  $n$  electrons, that is, electron transfer involving a redox couple of charge type  $(n/n-y)$ . The difference in free energies required to form  $MC^{n-y}$  and  $MC^n$  from the neutral cluster  $MC$  will therefore be [cf Eq. (3)]

$$\Delta G_{n-y} - \Delta G_n = -(n - 0.5y)e^2/\epsilon_s r \quad (7)$$

Again converting to electrode potentials yields

$$E_n^f = E(r \rightarrow \infty) + (n - 0.5y)e/\epsilon_s r \quad (8)$$

Equation (8) is a more general form of Eq. (5), being applicable also to multielectron transfers, i.e. to  $y > 1$ .

Two modifications to the simple Born-like form of Eq. (8) are nevertheless worth noting for the present purposes. Firstly, it is desirable to add a term  $\delta$  to the "hard-sphere" cluster radius  $r$  in order to account for the "electron spillover beyond the atomic cores", yielding the larger radius  $(r + \delta)$ .<sup>14,17</sup> Secondly, Eqs. (5) and (8) do not consider the effect of the electrolyte ionic atmosphere in modifying the cluster charge-dependent solvation energy. This latter factor can be accounted for approximately by recasting Eq. (8) in the more general form (cf ref. 14a):

$$E_n^f = E(r \rightarrow \infty) + (n - 0.5y)(e/\epsilon_s r)[1 + (r/d_s)]^{-1} \quad (9)$$

The bracketed term contains the Debye screening length  $d_s$  which denotes the distance over which the charge on the central (cluster) ion is screened effectively by the surrounding electrolyte ions. Since for moderate or large clusters in electrolyte solutions one anticipates that  $r$  (or  $r + \delta$ )  $\sim d_s$ , this factor can exert a significant influence on the spacing between sequential  $E_n^f$  values. Additionally, however, more marked deviations from the predictions of

Eqs. (8) or (9) may well arise from the occurrence of "dielectric saturation" effects, whereby the effective solvent dielectric constant in the vicinity of the solute falls below the "bulk-phase" value  $\epsilon_s$  (vide infra).<sup>18</sup>

The close relationship between the corresponding gas- and solution-phase formulae, Eqs. (2) and (5), is worthy of further comment. Given the form of Eq. (2), the  $E(r \rightarrow \infty)$  term in Eq. (5) [and Eqs. (8) and (9)] refers clearly to the potential of an uncharged metal surface in a given solution composed of the same material (and structure) as the metallic cluster under consideration in the appropriate solvent. This quantity is well known in electrochemistry as the "potential of zero charge",  $E_{pzc}$ ; it can be considered to constitute the "electrochemical work function".<sup>19</sup> Indeed, the close relationship between  $E_{pzc}$  and  $\Phi_{WF}$  for metal surfaces has been explored in detail.<sup>19</sup>

Given the present objective of relating the electron-transfer energetics involving metallic clusters in gas- and solution-phase systems, it is necessary to establish a connection between the potential scales relevant to these two types of environment, appearing in Eqs. (2) and (5), respectively. While in solution-phase electrochemical systems the electrode potentials are normally referred to a reference electrode in the same solvent, the reference employed for gas-phase systems is usually the electron in vacuum.<sup>20</sup> This difference inevitably raises the oft-discussed (and vexing!) question of the "absolute" electrode potential, more specifically the relation between the reference electrode and vacuum scales. Most discussion has concerned the aqueous normal hydrogen electrode (NHE), for which the "absolute" potential  $E_x(\text{ref})$  has been estimated to lie between 4.45 and 4.8 V.<sup>21-24</sup> Another complication is that little consideration has been given in the literature to the establishment of such "absolute" potential scales for convenient reference electrodes in nonaqueous solvents, such as those of interest here.

Finally, as introduced above, the charge-potential relationships for metallic clusters may usefully be expressed in terms of a "molecular capacitance" in formally the same manner as for electrode surfaces. (This notion is valid despite the occurrence of electrostatic charging of the cluster solutes by *faradaic* means, i.e. involving electrochemical electron transfer, rather than the *non-faradaic* charging to which the capacitance of metal electrode-solution interfaces inherently refers). The capacitance is expressed generally (in integral form) as

$$C_s = \sigma / (E - E_{pzc}) \quad (10)$$

where  $\sigma$  is the surface charge density (i.e. charge per unit area) for either a planar or spherical (cluster) interface. As noted above,  $E_{pzc}$  can be identified for cluster systems with  $E(r \rightarrow \infty)$  as defined in Eq. (4). For planar surfaces,  $E$  is the applied electrode potential corresponding to a given  $\sigma$  value. The  $E_n^f$  values measured for cluster solutes refer instead to the "transition potential" where the two adjacent charge states forming the redox couple are in equilibrium. Consequently, then, the effective cluster charge density  $\delta$  associated with each sequential  $E_n^f$  value can be taken as the average of those for the oxidized and reduced forms of the redox couple. [Indeed, this is the physical reason that the "average redox charge"  $(n - 0.5y)$  appears in Eq. (8), rather than  $n$  or  $(n - y)$ .] Given that the effective surface area of a spherical cluster is simply  $4\pi r^2$  [or  $4\pi(r + \delta)^2$ ], the cluster capacitance can therefore be expressed on the basis of Eq. (8) as

$$C_s = \epsilon_s / 4\pi r \quad (11)$$

or from Eq. (9) as

$$C_s = [1 + (r/d_s)] \epsilon_s / 4\pi r \quad (12a)$$

$$= (r + d_s) \epsilon_s / 4\pi r d_s \quad (12b)$$

The form of Eq. (12b) emphasizes the interesting geometric relationship anticipated on this basis between the electrostatic capacitance of spherical metallic clusters and planar electrode surfaces. In the limit where  $r \gg d_s$ :

$$C_s = \epsilon_s / 4\pi d_s \quad (13)$$

This is the usual continuum formula for a parallel-plate capacitor, describing formally the so-called inner-layer electrode capacitance, where  $d_s$  is now the inner-layer thickness determined by the closest approach of the diffuse-layer ions that constitute the "ionic atmosphere" of the electrochemical interface.<sup>25</sup> In the opposite limit, where  $r \ll d_s$ , Eq. (12) reduces to the Born-like expression Eq. (11). Equation (12b) therefore provides an instructive, if perhaps only formal, means of relating the capacitances of metallic cluster and planar interfacial systems anticipated from classical electrostatics.

The dependence of  $E_n^f$  upon  $(\epsilon_s r)^{-1}$  expected for one-electron transfers on the basis of Eq. (9) (in the limit where  $r \ll d_s$ ) is shown schematically for various cluster charges ( $n = 3$  to  $-2$ ) in Fig. 1. The right-hand axis refers to the vacuum limit (i.e. where  $\epsilon_s = 1$ ), and the left-hand axis to the (hypothetical) limit where  $\epsilon_s = \infty$ , corresponding to the situation where coulombic interactions are screened perfectly by the surrounding dielectric medium. Of more practical interest is the vertical displacement between successive redox transitions (i.e.  $E_n^f$  values) for various  $\epsilon_s$  or  $r$  values. Figure 1 illustrates that the electrode potential spacing between these transitions (and hence  $C_s^{-1}$ ) should increase as the dielectric constant decreases. A useful expression for the potential spacing between successive one-electron transfers,  $\Delta E_1$ , anticipated on the basis of Eq. (9) is

$$\begin{aligned}\Delta E_1 &= (e/\epsilon_s r)[1 + (r/d_s)]^{-1} \\ &= (14.4 \text{ V}/\epsilon_s r)[1 + (r/d_s)]^{-1}\end{aligned}\quad (14)$$

where  $r$  and  $d_s$  are given in Å. This prediction is considered further below.

It should be borne in mind, of course, that the practical usefulness of the foregoing relationships depends somewhat on the applicability of continuum electrostatics to such systems. The failures of the simple Born model for describing the solvation energetics of small ionic solutes are well known.<sup>16</sup> This treatment nevertheless appears to be remarkably effective in describing the solvation of some larger monocharged solutes, such as metallocene ions.<sup>13</sup> Moreover, its limitations can insightfully be described in terms of semi-macroscopic models which account for shorter-range solvation effects, including the anticipated spatial variations in the effective solvent dielectric constant already mentioned.<sup>18</sup>

It also should be noted that this classical electrostatic analysis necessarily does not consider quantum effects arising from the microscopic nature of the metallic clusters. Thus while large clusters are anticipated to have electronic band structures approaching those of bulk metals, the energetics of sequential electron transfer in smaller systems are expected to be affected by HOMO-LUMO separation, spin-pairing and related quantum effects. These factors might be expected to enlarge the spacing between successive formal potentials and hence yield smaller  $C_s$  values which will be proportionately less sensitive to variations in  $\epsilon_s$ . These effects can formally be accounted for by rewriting Eq. (9) as

$$E_n^f = E(r \rightarrow \infty) + Q[f(n)] + (n - 0.5y)(e/\epsilon_s r)[1 + r/d_s]^{-1} \quad (15)$$

The additional "quantum" term  $Q$  is generally expected to be a function of  $n$ .

Nevertheless, it is anticipated that  $Q$  will be essentially independent of the dielectric medium, so that the *solvent-dependent* displacements of the consecutive  $E_n^f$  values, and hence the variations in  $C_n^{-1}$  with the effective medium dielectric constant, should be largely unaffected.

Despite these limitations, then, the above electrostatic analysis should provide a useful unifying framework for examining the ionization of solution-phase clusters in relation to the conventional treatments of both gas-phase cluster and interfacial analogs. In the following section, we explore the behavior of some experimental cluster systems in the light of these considerations.

#### Application to Experimental Cluster Systems: Molecular Capacitance

On the basis of the foregoing, it is clearly of interest to examine the dependence of the formal potentials for sequential electron transfers involving cluster solutes upon the ionic charge. Figure 2 displays such a plot of  $E_n^f$  versus  $(n - 0.5y)$ , where  $n$  is the charge number of the oxidized form and  $y$  is the number of electrons transferred in each step, for  $C_{60}$  (filled symbols) and platinum carbonyl clusters (open symbols). The former data, taken from ref. 9, refer to benzene, tetrahydrofuran (THF), benzonitrile and dimethylformamide (DMF). (These solvents, of varying polarity, were selected from a larger data set in ref. 9c.) The latter data, from ref. 10b, are for  $Pt_{24}(CO)_{30}$ ,  $Pt_{38}(CO)_{44}$ , and  $Pt_{26}(CO)_{32}$  in dichloromethane and acetonitrile. (See the figure caption for symbol legends; the reference electrode in each case is ferrocenium-ferrocene,  $Cp_2Fe^{+/0}$ , in the same solvent, and the supporting electrolyte is tetrabutylammonium perchlorate in most cases.) While the first two platinum clusters exhibit uniformly one-electron transfers, as for  $C_{60}$  reduction, several of the  $[Pt_{26}(CO)_{32}]^n$  steps involve two-electron steps between adjacent even-charged redox states. This behavior reflects a relative instability of the odd-

charged redox states, as manifested also in the generally narrower potential ranges over which these species are stable in  $[\text{Pt}_{24}(\text{CO})_{30}]^n$  and  $[\text{Pt}_{38}(\text{CO})_{44}]^n$  compared with the even-charged states.<sup>10</sup> While such alterations in stability with Pt cluster charge are readily evident in the  $E_n^f - (n - 0.5y)$  dependencies, the plots are nevertheless roughly linear. Such charge-alternation effects are absent for  $\text{C}_{60}^n$ ; while the plots are closer to linearity than for the Pt clusters, the slopes tend to increase towards more negative charges (Fig. 2).

The comparison of the observed  $E_n^f - (n - 0.5y)$  dependencies with Eqs. (9) and (12) is of particular interest here. The near-linearity of the  $E_n^f - (n - 0.5y)$  plots for  $\text{C}_{60}^n$  suggests that the local dielectric constant of the solvating medium coupled with the effective Debye screening length do not depend markedly on the cluster charge. Assuming for the moment that Eqs. (9) and (12) are applicable and that  $d_s \gg r$ , since the effective radius of  $\text{C}_{60}$  is about  $4.7 \text{ \AA}$ <sup>26</sup> the average  $E_n^f - n$  slope shown in Fig. 2 for  $\text{C}_{60}^n$  (0.53 V) yields an effective "molecular capacitance"  $C_s$  equal to ca  $11 \mu\text{F cm}^{-2}$  and a  $\epsilon_s$  value of 6.0.

Since the dielectric constants for the four solvents included for  $\text{C}_{60}$  in Fig. 2 vary considerably, from 2.3 (benzene, squares) to 36.7 (DMF, upright triangles), this observed insensitivity of the molecular capacitance (i.e. the inverse  $E_n^f - n$  slope) to the solvating medium is unexpected, at least on the basis of Eq. (11). However, a complication is that most of the solvent media in which the  $\text{C}_{60}^n$  data were obtained are relatively nonpolar (say  $\epsilon_s \leq 20$ ), so that the stability of the  $\text{C}_{60}^n$  anions, and hence the  $\Delta E_1$  spacings, can be affected substantially by ion pairing with the supporting electrolyte cations, especially given the high (0.1M) concentrations employed in ref. 9c. This effect, which can formally be accounted for by smaller  $d_s$  values in Eqs. (9) and (14), will tend to decrease  $\Delta E_1$  (and hence increase  $C_s$ ), thereby offsetting the effects of smaller  $\epsilon_s$ . Ion pairing is undoubtedly very extensive in benzene, yielding

effectively  $d_s < r$  and enlarging  $C_s$  above the low value anticipated on the basis of the very small solvent dielectric constant. The high electrostatic fields surrounding the charged cluster may also cause dielectric saturation, especially as  $-n$  increases, yielding marked decreases in the effective  $\epsilon_s$  values in the vicinity of the ion.<sup>18</sup> These effects should therefore combine to "buffer" the capacitance values, yielding smaller variations with the solvent than predicted on the basis of the continuum electrostatic picture, in harmony with the observed solvent-insensitive  $\Delta E_1$  values for  $C_{60}^0$  (Fig. 2). These coupled effects should be less important in more polar media, such as DMF and benzonitrile ( $\epsilon_s = 36.5$  and 25, respectively) for which  $C_{60}$  data are included in Fig. 2. Indeed, the  $\Delta E_1$  values in the former solvent tend to be significantly (ca 0.05 V) smaller than in the latter, roughly consistent with the ca 0.04 V difference predicted from Eq. (14) if  $d_s \gg r$ .

Evidence that the solvent-dependent behavior predicted by Eq. (14) is fulfilled quantitatively in some cases is provided by a recent study of the consecutive two-electron reductions of  $Cp_2Co^+$  ( $Cp$  = cyclopentadienyl) and  $Cb_2Ni$  ( $Cb$  = o-dicarbollide).<sup>13</sup> The difference in  $E_n^f$  values,  $\Delta E_1$ , between the  $Cp_2Co^{+/0}$  and  $Cp_2Co^{0/-}$  redox transitions, for example, increases with increasing  $\epsilon_s^{-1}$  for a number of polar solvents having  $\epsilon_s$  values in the range of 20–65, with a slope essentially equal to the value,  $(e/\epsilon_s r)$ , anticipated from Eq. (12) when  $r$  is taken as the crystallographic radius of  $Cp_2Co$  (ca 3.8 Å) and  $d_s \gg r$ . The effects of electrolyte ion pairing upon  $\Delta E_1$  were deduced to be small or negligible except in acetone ( $\epsilon_s = 20.5$ ).<sup>13</sup>

Given that the ferrocenium-ferrocene ( $Cp_2Fe^{+/0}$ ) couple employed as the reference electrode (Fig. 2) should be solvated in near-identical fashion to  $Cp_2Co^{+/0}$ , one might anticipate that the  $E_n^f$  values for  $C_{60}^{0/-}$  and consecutive  $C_{60}^{n/n-1}$  redox couples when measured versus  $Cp_2Fe^{+/0}$  would exhibit a similar dependence on

the solvent. This expectation, however, is not entirely fulfilled. Thus the ordering of the  $E_n^f$  values for  $C_{60}^{0/-}$ , in the sequence DMF > benzene > THF > benzonitrile (Fig. 2), differs from that anticipated from the  $\epsilon_s$  values (DMF > benzonitrile > THF > benzene). Moreover, the displacement between these solvent-dependent  $E_n^f$  values for successive electron transfers does not expand entirely in proportion to  $(n - 0.5)$ , as predicted by Eq. (9). As above, these deviations from the predictions of the dielectric continuum treatment for the solvation of  $C_{60}^n$  are probably due in part to the use of relatively nonpolar solvents, obliged by solubility constraints, augmented by the multiple anionic cluster charges produced by successive electron transfers. As already noted, these circumstances will favor the occurrence of complications from ion pairing and dielectric saturation.

A significant issue is the possibility that such solvent-dependent  $E_n^f - n$  data could be used to provide at least rough estimates of the "quantum" contribution,  $Q[f(n)]$  in Eq. (15), to the energetics of successive electron transfer. For  $Cp_2Co^{+/0/-}$ , for example,  $Q$  can be deduced from the y-intercept of the  $\Delta E_1$  versus  $\epsilon^{-1}$  plot<sup>13a</sup> to be large, 0.85 V. This is unsurprising since spin pairing, orbital relaxation, and related quantum effects should abound in influencing the successive ET energetics of such mononuclear organometallic redox systems. It is tempting to extract in similar fashion  $Q[f(n)]$  values for  $C_{60}^n$ . Utilizing  $E_n^f - n$  data in polar solvents such as DMF for this purpose (Fig. 2), thereby minimizing complications from ion pairing, yields  $Q \approx 0.4$  V from Eq. (15), roughly independent of  $n$ . The validity of such estimates, however, are unfortunately dependent on the presumption that the  $\epsilon_s$  values for the bulk-phase solvent can be employed in Eq. (15). The occurrence of dielectric saturation, by which  $\epsilon_s$  falls well below the bulk-phase value, would diminish the resulting  $Q$  estimates. The deduction that  $Q \approx 0$  V using Eq. (15), i.e. that quantum effects

are essentially absent, requires nonetheless that  $\epsilon_s \sim 8$ . While this degree of dielectric saturation (in DMF) may be unlikely, the electrostatic analysis also requires that the added electrons are delocalized uniformly around the near-spherical  $C_{60}$  cage. Theoretical evidence that the situation is rather more complicated, involving electron pair-binding, has been presented.<sup>29a</sup> On the other hand, successive electron additions (up to six) into  $C_{60}$  involve a triply degenerate  $t_{1u}$  orbital (having  $I_h$  symmetry), and the spin-pairing energies have been calculated to be small (0.04 eV).<sup>29b</sup>

The alternating "even-odd"  $E_n^f$  spacing noted above for the platinum carbonyl clusters (Fig. 2) is a clear manifestation of the energetic importance of quantum effects for these systems. While detailed electronic structural calculations are lacking for such complex high-nuclearity clusters, the relative instability of the odd- relative to even-electron redox states is qualitatively consistent with the sequential spin-paired filling of orbitals having successively increasing energies. As for  $C_{60}^n$ , the Pt clusters exhibit a relative insensitivity of the molecular capacitance to the solvent.<sup>10b</sup> As an illustration, data are included in Fig. 2 for  $[Pt_{24}(CO)_{30}]^n$  and  $[Pt_{26}(CO)_{32}]^n$  in two solvents, acetonitrile and dichloromethane, having  $\epsilon_s$  values of 36 and 9, respectively. Despite these large differences in dielectric properties, the  $E_n^f \sim n$  slopes are again similar (values within ca 20% in these two solvents).<sup>30</sup> The  $E_n^f$  values are also insensitive to the nature and concentration of the supporting electrolyte in a given solvent.<sup>10b</sup>

As discussed briefly in Ref. 10b, the platinum carbonyl systems provide an interesting opportunity to compare the capacitive properties of metal clusters with these of analogous planar metal-solution interfaces. Both  $Pt_{24}(CO)_{30}$  and  $Pt_{26}(CO)_{32}$  offer an effective surface area of about  $3 \times 10^{-14} \text{ cm}^2$ ,<sup>10b</sup> yielding a  $C_s$  estimate of approximately  $15 \mu\text{F cm}^{-2}$  from the data in Fig. 1. This quantity can be compared with the value of  $C_s$  observed in CO-saturated Pt(111) and Pt(110)

surfaces in acetonitrile,  $6 \pm 1 \mu\text{F cm}^{-2}$ .<sup>10b</sup> The roughly twofold-larger capacitance values thereby deduced for the Pt clusters compared with analogous electrode-solution interfaces may be rationalized straightforwardly by referring to Eqs. (11)-(13). Presuming that  $\epsilon_s$  and  $d_s$  is similar for the cluster and planar interfacial systems, the capacitance ratio in the former versus the latter environment according to Eqs. (12) and (13) is given simply by  $(r + d_s)/r$ . The ca twofold larger capacitance observed for the cluster versus the planar interface can therefore be understood on this basis if, as might be anticipated,  $r \sim d_s$ .

This simple analysis necessarily ignores several additional factors which might be expected to influence significantly the capacitance of the metal clusters in comparison with metal surfaces. The sequential filling of discrete molecular orbitals as noted above for the Pt clusters, which should tend to diminish the cluster capacitance, will essentially be absent for metal surfaces since the latter feature continuous electronic energy bands. Nevertheless, modern theoretical treatments of metal electrode-solution interfaces emphasize that the electronic properties of the metal as well as the solvent dielectric can exert important influences upon the electrode capacitance and other equilibrium properties.<sup>31</sup> One important factor is the "electron spillover" from the metal surface ion cores, yielding an "electronic dipolar" contribution to the surface potential. This effect is expected to be significantly charge-dependent, and is therefore predicted to enhance the surface capacitance.<sup>31</sup> An analogous phenomenon (noted above as the  $\delta$  term in the effective cluster radius) may contribute to the capacitance properties of metal clusters, but appropriate theoretical treatments have yet to be developed.

In principle, the same charge-dependent analysis as considered in this section for metallic clusters (and surfaces) in solution could also be applied

to clusters in gas-phase and vacuum environments. A simplification is that the dielectric-continuum description of the solute charge-screening properties of a vacuum, with  $\epsilon_s = 1$ , is more reliable than in molecular solvents! However, a practical limitation is that information on sequential charging energetics, especially for electron affinities, is rare for gas-phase metal clusters, so that the notion of "molecular capacitance" is less useful in this environment. Instead, the usual approach for testing electrostatic analyses such as Eq. (2) for gas-phase systems is to alter the charge density by varying the cluster radius (via alterations in the number of metal atoms) rather than the number of electrons added or subtracted. While the experimental data are indeed roughly describable in terms of the continuum-electrostatic model, interesting deviations occur such as "even-odd" (or "magic-number") electronic effects;<sup>1a,8</sup> these are apparently related to the effects noted here for the sequential charging of platinum carbonyl clusters.

#### Comparison Between Electron Affinities of Solution-Phase Clusters and Related Gas-Phase and Electrode Surface Data

As alluded to above, formal potential-cluster charge data such as presented in Fig. 2 also provide interesting opportunities for comparing the electron-transfer energetics for solution-phase clusters with both metal surfaces and gas-phase clusters. The former type of comparison can be pursued readily by examining the intercepts of  $E_n^f - (n - 0.5y)$  plots. This intercept, labelled  $E(r \rightarrow \infty)$  in Eq. (9), can be viewed as the thermodynamic potential at which infinitesimal amounts of electronic charge (much smaller than  $e$ ) can be added (or removed) from the uncharged cluster solute. Consequently, as already mentioned,  $E(r \rightarrow \infty)$  can be considered to be the effective potential of zero charge (or "electrochemical work function") of the cluster solvent system.

The  $E_n^f - (n - 0.5y)$  plot for the platinum carbonyl clusters in Fig. 2

yields an intercept  $E(r \rightarrow \infty)$ , of about 0.6 V versus  $\text{Fc}^{+/0}$ . This value is compatible with corresponding  $E_{\text{pzc}}$  values for CO-saturated Pt(111) and (110) in acetonitrile and other nonaqueous media, 0.7 and 0.5 ( $\pm 0.05$ ) V versus  $\text{Cp}_2\text{Fe}^{+/0}$ , respectively,<sup>32</sup> as extracted from an infrared spectroscopic analysis.<sup>33</sup> These  $E_{\text{pzc}}$  values have been shown in turn to be closely compatible with the surface potentials of the corresponding CO-saturated Pt(111)- and (110)-uhv interfaces as determined from work-function data.<sup>33,34</sup> Given that the platinum clusters consist of small Pt(111) facets bordered by terrace edges resembling (110) atomic rows,<sup>10b</sup> the observed  $E(r \rightarrow \infty)$  value is close to that expected if the electronic properties of the uncharged clusters indeed match those of the planar surfaces.

The corresponding comparison for  $\text{C}_{60}$  is less meaningful: the cluster is actually a hollow sphere so that its electronic properties should necessarily differ from bulk-phase carbon. The latter behaves as a semi-metal, having a surface space-charge region on the basis of capacitance-potential data for basal-plane graphite interfaces.<sup>35</sup> Nevertheless, the  $E(r \rightarrow \infty)$  value deduced for  $\text{C}_{60}$  from Fig. 2, ca -0.6 V versus  $\text{Cp}_2\text{Fe}^{+/0}$ , is not greatly different from  $E_{\text{pzc}}$  values for basal-plane graphite, -0.4 V versus  $\text{Cp}_2\text{Fe}^{+/0}$ .<sup>36,37</sup>

As mentioned above, related comparisons have commonly been undertaken between the EA and IP values for gas-phase metal clusters and the work function of corresponding metal surfaces in vacuum.<sup>1,5-8</sup> A difference with the solution-phase clusters, however, is that the extrapolation to infinitesimally small cluster charge densities, so to yield  $E(r \rightarrow \infty)$  [or  $\Phi(r \rightarrow \infty)$ ] is usually achieved from plots of EA (or IP) versus  $r^{-1}$ , rather than  $\Phi_r$  versus  $(n - 0.5)$  [Eq. (2)]. This situation reflects the relative ease by which metal clusters of varying size can be prepared by means of supersonic jet expansion, together with the paucity of data for sequential electron transfers in gas-phase systems.

Another type of comparison, which can be undertaken instructively for  $\text{C}_{60}$ ,

involves matching the electron affinity of the solution cluster with the measured EA for the gas-phase species. The latter value for  $C_{60}$  is  $2.65 (\pm 0.05) \text{ eV}$ .<sup>38</sup> The difference between this EA value and the gas-phase IP for  $Cp_2Fe^{+/0}$ ,  $6.7 \text{ eV}$ ,<sup>11</sup> can be viewed as the "gas-phase" formal potential,  $E_{gas}^f$ , of  $C_{60}^{0/-}$  with respect to  $Cp_2Fe^{+/0}$ . This  $E_{gas}^f$  value is related to the solution-phase formal potential of  $C_{60}^{0/-}$  versus  $Cp_2Fe^{+/0}$ ,  $E_{sol}^f$ , according to the Born model [cf Eqs. (3), (6)] by

$$F(E_{gas}^f - E_{sol}^f) = \Delta G_{solv}(C_{60}^{0/-}) - \Delta G_{solv}(Cp_2Fe^{+/0}) = -0.5e^2(1-\epsilon_s^{-1})(r_c^{-1} + r_f^{-1}) \quad (16)$$

where  $F$  is the Faraday,  $\Delta G_{solv}$  are the solvation energies of the redox couples, and  $r_c$  and  $r_f$  are the effective radii of the fullerene and ferrocene species. [Note that the solvation energies for  $C_{60}^{0/-}$  and  $Cp_2Fe^{+/0}$  appear here with the reversed sign due to the opposite redox-couple charge type, yielding the positive sign in the last term in Eq. (16).] Inserting the  $E_{gas}^f$  and  $E_{sol}^f$  values,  $-4.05 \text{ V}$  and  $-0.9 \text{ V}$  (the latter obtained in benzonitrile),<sup>9</sup> into Eq. (15) along with  $r_c = 4.7 \text{ \AA}$  and  $r_f = 3.8 \text{ \AA}$ <sup>11</sup> yields an estimate of the dielectric term  $(1-\epsilon_s^{-1})$  of  $0.92$ , yielding roughly  $\epsilon_s = 10$ . The large ( $4.05 \text{ V}$ ) separation in "gas-phase"  $E_n^f$  values between  $Cp_2Fe^{+/0}$  and  $C_{60}^{0/-}$  is diminished substantially (by  $3.15 \text{ V}$ ) in benzonitrile, reflecting the sum of solvation energies of the two redox couples involved. The extent of the stabilization in benzonitrile is approximately consistent with the dielectric-continuum estimate,  $3.30 \text{ V}$ , obtained from Eq. (16), given the likely uncertainties ( $\pm 0.05 \text{ V}$ ) in the gas-phase potentials. Similar results are obtained from the data in ref. 9c for other polar solvents.

The extraction of solvation energies for individual redox couples, such as  $C_{60}^{0/-}$ , is necessarily subject to greater uncertainty since this requires making an assumption regarding the relationship between the vacuum and electrochemical reference electrode scales or, equivalently, the absolute solvation energy of the reference-electrode couple (vide supra). Nevertheless, persuasive evidence has

been presented recently that the solvation energy of  $\text{Cp}_2\text{Fe}^{+/0}$ , as for  $\text{Cp}_2\text{Co}^{+/0/-}$ , is described approximately by the Born formula,<sup>13a</sup> yielding  $\Delta G_{\text{solv}}(\text{Cp}_2\text{Fe}^{+/0}) = 1.83\text{eV}$  in benzonitrile, for example. From the electrode-potential data noted above, we deduce in this manner that  $\Delta G_{\text{solv}}(\text{C}_{60}^{0/-}) = -(3.15 - 1.83) = -1.32\text{eV}$  in benzonitrile. This "experimental" value is slightly less negative than the corresponding Born prediction,  $-1.47\text{eV}$ . The source of the residual disparity,  $0.15\text{eV}$ , may of course lie partly in the  $\text{Cp}_2\text{Fe}^{+/0}$  rather than the  $\text{C}_{60}^{0/-}$  solvation component. Nevertheless, this analysis indicates that the simple Born model is effective in predicting approximately the stabilization of  $\text{C}_{60}^-$  afforded by polar solvation. Corresponding analyses for multicharged fullerenes are, largely, precluded by the paucity of the required electron-affinity data. The dianion  $\text{C}_{60}^{2-}$  has been prepared in the gas phase, indicating that the second electron affinity is positive, although probably close to zero.<sup>39</sup> The substantial (ca 2–2.5eV) separation between the first and second EA values is roughly consistent with the value, 3.0 V, extracted from Eq. (14) for  $r = 4.7\text{\AA}$ ,  $d_s \gg r$ , and  $\epsilon_s = 1$ .

### Concluding Remarks

While the quantitative applicability of the treatment described herein is restricted inevitably by the limitations of the dielectric-continuum model, we believe that the foregoing discussion testifies to the conceptual value of interrelating the charging energetics of metallic clusters and surfaces in solution- and gas-phase environments. In particular, examining the solvent-dependent electrode potentials for sequential electron transfer in clusters and other suitably large electroactive solutes (the "molecular capacitance") can allow an approximate delineation to be achieved between the chemical electrostatic and molecular-orbital (i.e. quantum) components of the cluster-charging energetics. Moreover, comparisons between the capacitance of ionizable clusters and corresponding electrochemical surfaces, and also between the

effective potentials of zero charge, can provide fundamental insight into the similarities and differences in the electronic properties of these related yet distinct states of matter.

One pertinent issue is the degree to which the Born model can describe the charge-dependent solvation energetics of cluster and related solutes. The recently documented success of this treatment for metallocene and related redox couples in polar solvents<sup>13</sup> is not entirely mirrored by the behavior of the  $C_{60}^{0/-}$  couple under these conditions. Not surprisingly, however, the Born model appears less effective in weakly polar media and/or for multicharged solutes as encountered with the  $C_{60}^n$  system. The examination of more sophisticated solvation treatments in this context would probably be worthwhile.

The recent emergence of the fullerenes as bona fide chemical species characterized in liquid- and solid-state, as well as gas-phase, environments provides a rich and potentially even diverse new class of clusters with which the relationships between solution- and gas-phase ET energetics can be explored in detail. The further exploration of ionizable metal clusters along these lines, however, would be of particular interest since they also can forge insightful links with the behavior of metal surfaces in solution and vacuum environments. Establishing such behavioral relationships is indeed an emerging objective in electrochemical surface science.<sup>24</sup>

#### Acknowledgments

Professor Karl Kadish kindly shared his comprehensive formal-potential data for buckminsterfullerene (ref. 9c) prior to publication. The hospitality of Profs. A. M. Bradshaw and H. Gerischer towards M.J.W. at the Fritz-Haber Institut, Berlin, where this paper was written, is gratefully acknowledged, as is the Humboldt Stiftung for providing a Senior Scientist Award to M.J.W. This work is also supported by the Office of Naval Research.

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## Figure Captions

### Figure 1

Schematic dependence of formal potential for sequential electron addition  $MC^n + e^- = MC^{n-1}$  to metal cluster MC as a function of  $(\epsilon_s r)^{-1}$ , where  $\epsilon_s$  is the medium dielectric constant and  $r$  is the cluster radius, for various cluster charges,  $n$ , (as indicated), as predicted from Eq. (5).

### Figure 2

Plot of formal potentials for sequential electron transfer involving  $C_{60}$  (filled symbols) and Pt carbonyl clusters (open symbols) in selected solvents as a function of  $(n - 0.5y)$ , where  $n$  is the charge number of the oxidized cluster form, and  $y$  is the number of electrons transferred in each step ( $y = 1$ , except for  $[Pt_{26}(CO)_{32}]^n$ ). Key to cluster/solvent media: filled upright triangles,  $C_{60}$  in dimethylformamide with 0.1M tetrabutylammonium perchlorate (TBAP); filled squares,  $C_{60}$  in benzonitrile with 0.1M TBAP (or tetrapropylammonium salt); filled inverted triangles,  $C_{60}$  in tetrahydrofuran with 0.1M TBAP; filled circles,  $C_{60}$  in benzene with 1.2M tetraheptylammonium perchlorate (at 40°C). All  $C_{60}$  data from ref. 9, especially ref. 9c.

Open upright triangles,  $[Pt_{24}(CO)_{30}]^n$  in dichloromethane with 0.3M TBAP; open inverted triangles,  $[Pt_{24}(CO)_{30}]^n$  in acetonitrile with 0.15M TBAP; open squares,  $[Pt_{26}(CO)_{30}]^n$  in dichloromethane with 0.15M TBAP; open diamonds,  $[Pt_{26}(CO)_{30}]^n$  in acetonitrile with 0.15M TBAP; open circles,  $[Pt_{38}(CO)_{44}]^n$  in dichloromethane with 0.15M TBAP. All platinum carbonyl data are from ref. 10b. The straight lines shown are approximate "guides to the eye" through the experimental points.

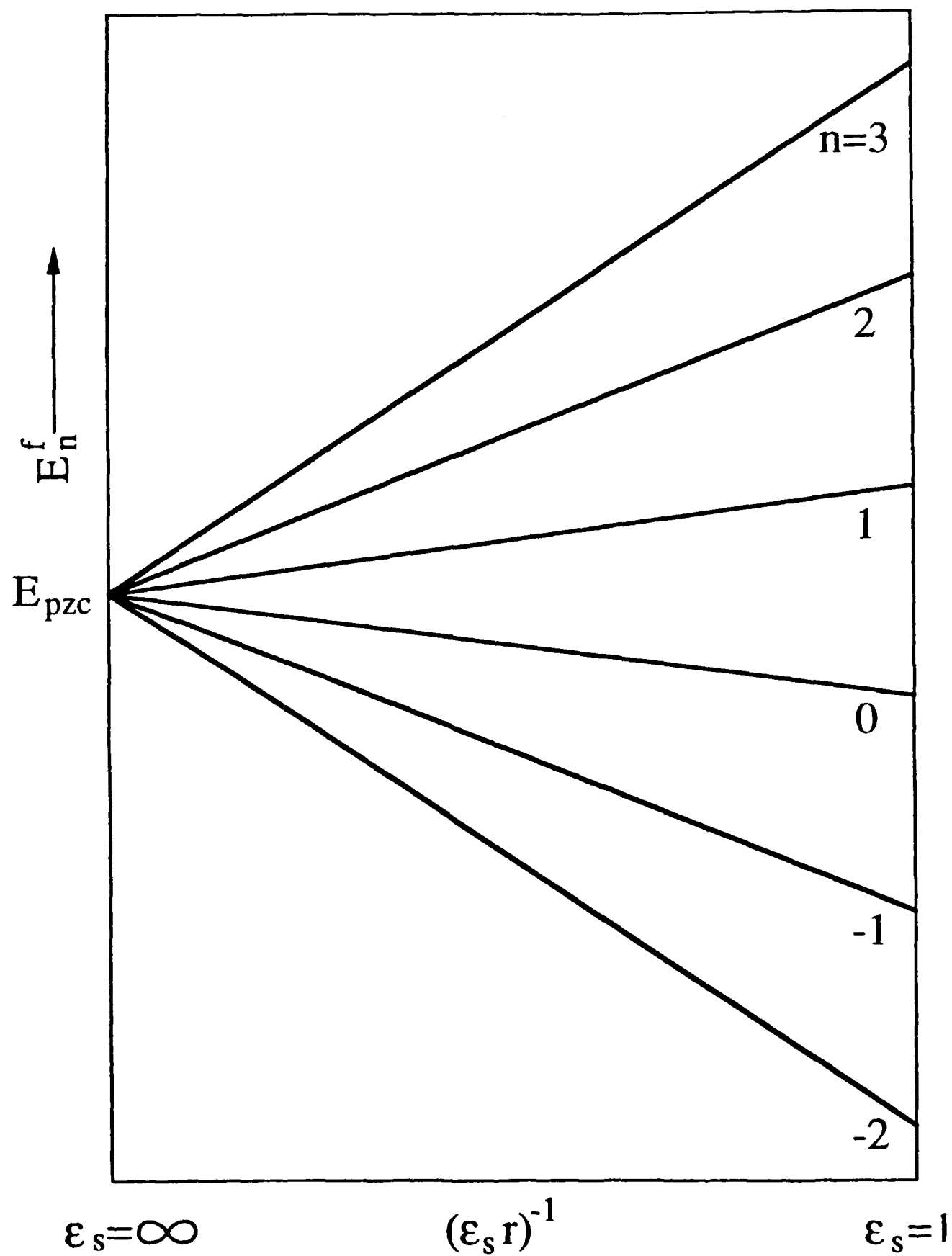
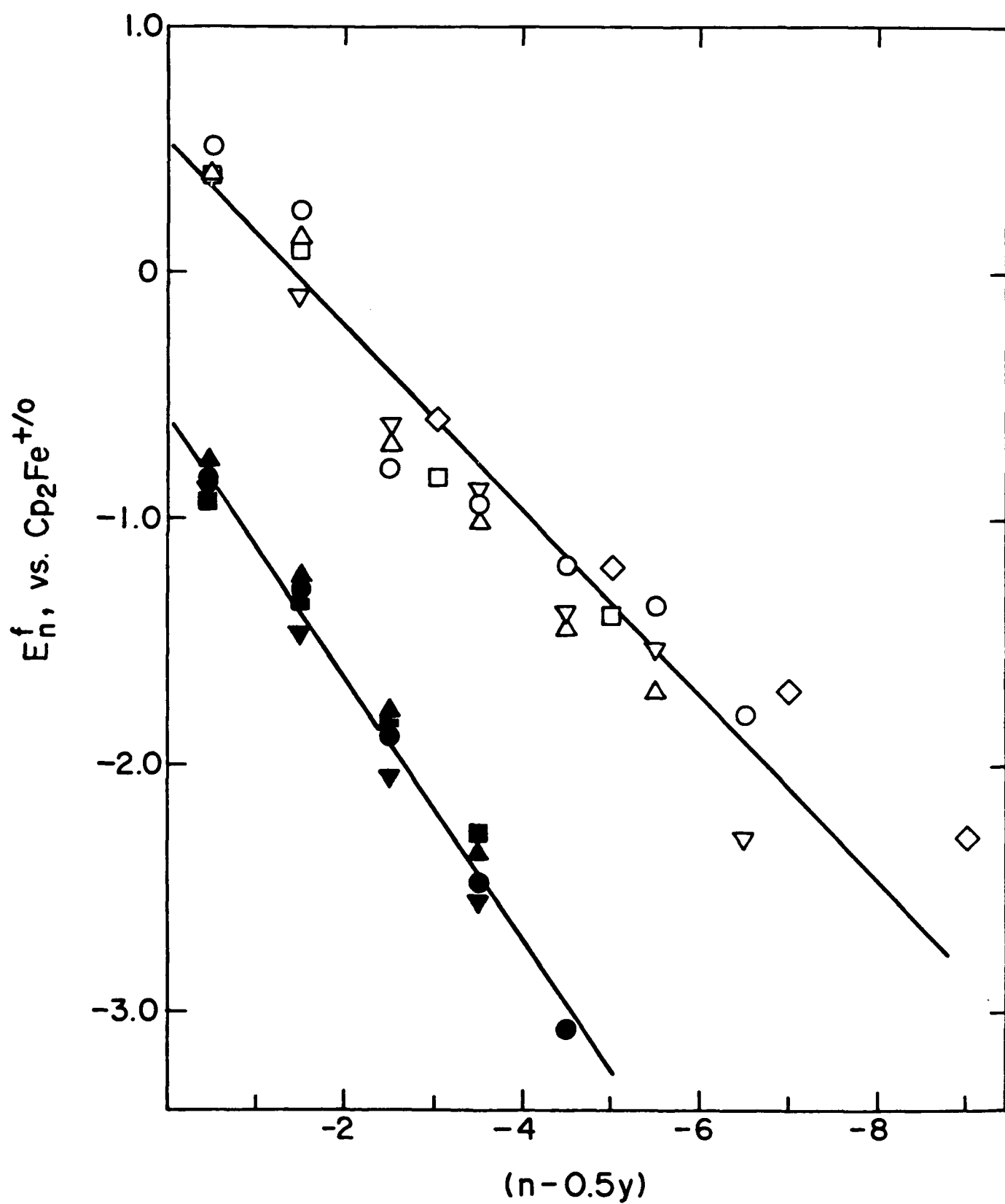


FIG 1



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