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# Hardness of metals from electron transfer reactions at electrode surfaces

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The standard exchange current densities pertaining to electron transfer processes at electrodes are employed to estimate chemical hardness of various metals. This is accomplished by deriving a new parametric relation for hardness in terms of the work function and surface potential of electrons. Hydrogen evolution and ferric/ferrous redox reactions are considered as examples to extract chemical hardness from electrode kinetic data. The surface potential is calculated for a large number of metals using phenomenological thermodynamic considerations. The significance of the methodology is also illustrated by calculating the potential of zero charge of metal/solution interfaces, thus demonstrating that equilibrium as well as kinetic studies in electrochemistry are capable of yielding the hardness of metals. © 2002 American Institute of Physics.

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## I. INTRODUCTION

The concept of chemical hardness plays a central role in the analysis of disproportionation reactions,<sup>1</sup> proton transfer,<sup>2</sup> fragmentation processes,<sup>2</sup> etc. and has immense potentiality in rationalizing the formation of products.<sup>3</sup> This feature is especially useful in the case of isomerization phenomena wherein the mass of the reactants and products becomes equal.<sup>4</sup> Despite extensive investigations on the dependence of hardness upon electronegativity, polarizabilities of atoms/molecules, ionization potentials, etc., its significance in charge-transfer occurring at electrode surfaces has hitherto not been investigated. This limitation is partly attributable to the lack of parametric dependence of hardness upon the properties of metals such as work function, electron density, barrier heights, etc. Since the work function dictates the extent of spillover of the electronic density profile into metal/solution interfaces, its inter-relationship with hardness is crucial in not only comprehending kinetics of electrode processes but also extending density functional theories to interfacial adsorption. Further, it is not surprising that hardness and work function should be intimately related; for the density functional theories which yield energy as a functional of electron-density constitutes *the* starting point for deriving hardness via finite difference approximation<sup>1</sup> as well as the work function of metal/vacuum interfaces after minimization of appropriate trial functions<sup>5</sup> using jellium models with different pseudopotentials.

Among several definitions of hardness ( $\eta$ ), the one given by Pearson<sup>6</sup> is especially convenient wherein  $\eta$  is represented as

$$\eta \approx \frac{\text{IP} - \text{EA}}{2}, \quad (1)$$

where IP and EA denote, respectively, the ionization potential and electron affinity. There has been interesting questions<sup>7</sup> regarding the origin of nonzero values of hardness

for elements. In band theory of metals, the distinction between IP and EA is not made at the Koopman's level of approximation. However, tabular compilations indicate that the IP is larger than the EA, yielding positive values for hardness. An alternate method of interpreting  $\eta$  consists of ascertaining whether the number of electrons in the ground state ( $N_0$ ) and that in the excited state ( $N_1$ ) are unequal. This criterion leads to  $\eta=0$  whenever  $N_0 > N_1$  or  $N_0 < N_1$ . Applying this ansatz to a hypothetical disproportionation reaction<sup>1</sup> such as  $S^* + S^* \rightarrow S^+ + S^{*-}$  one would expect hardness to be zero, if and only if energy of each of the two electrons in  $S^{*-}$  is equal to the energy of the single electron in  $S^*$ . It has been demonstrated that only at the Hückel level of approximation, such a result would emerge. In other cases where more refined methods of incorporating electronic correlations exist, hardness is nonzero in general.<sup>1</sup>

The classical definitions of IP and EA pertain to elements being in their gaseous state to begin with, whereas the concept of hardness defined in terms of EA and IP usually refer to solids. This dichotomy may be resolved by employing two strategies, one assuming the validity of the free-electron gas approximation with different types of local density approximations for metals<sup>5</sup> and the other, which visualizes metals as consisting of large clusters of individual atoms.<sup>8</sup> In free electron models, the ground state energy is represented as a functional of the electron density with exchange and correlation energy terms.<sup>5</sup> Apart from these there have also been attempts to correlate empirically the work function of metals with atomic volume, ionization potential, electronegativity, etc.<sup>9</sup> In the case of cluster approximations, three essential steps are required to derive the EA and IP of these viz. (i) neutral cluster of atoms (ground state), (ii) negative cluster of atoms with an electron being added (anion radical, EA), and (iii) positive cluster of atoms with an electron being removed (cation radical, IP). However, in these methodologies, the convergence of the clusters of atoms to the bulk surface limit will become a crucial issue.

This paper is organized as follows: In Sec. II, a new parametric relation for hardness is derived incorporating the

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surface potential of the metal and work function. The appropriate electron affinity and electronegativity are also computed in a phenomenological manner. Section III deals with the extraction of hardness from electron transfer reactions at electrodes while the potential of zero charge of metal/electrolyte interfaces using this framework is discussed in Sec. IV. Section V concludes with perspectives and summary.

## II. WORK FUNCTION OF METALS AND HARDNESS

In order to obtain  $\eta$  from work functions, we employ the definition of electronegativity. Although different scales of electronegativity exist, the representation due to Mulliken<sup>10</sup> ( $EN_M$ ) is convenient here on account of its direct relationship with IP and EA viz.,

$$EN_M = \frac{IP + EA}{2}. \quad (2)$$

It is imperative to consider here the relative magnitude of the IP and EA so as to ascertain their contribution to  $EN_M$  *vis-a-vis* hardness. The EA of metals ranges from 0.01 eV to 2.4 eV in contrast to IP which varies from  $\approx 4$  eV to 9 eV. Thus it is apparent that the role of EA in dictating the magnitude of hardness is more subdued than the IP. However, its gross neglect *in each case* would yield disagreement with hardness obtained from other methodologies. This is particularly evident in the case of noble metals such as Pt, Pd, Au, Ag having large EA values.

In the case of metals,<sup>11</sup>  $EN_M$  is reported as the negative of the chemical potential ( $-\mu_M$ ). In general,  $\mu_M$  is given as<sup>12</sup>

$$\mu_M = -\Phi_M - \chi_e^M, \quad (3)$$

where  $\Phi_M$  denotes the work function and  $\chi_e^M$  is the surface potential of electrons in metal. Thus we obtain

$$EN_M = \Phi_M + \chi_e^M. \quad (4)$$

Although it is possible to deduce  $\chi_e^M$  from the tabulated  $EN_M$  and  $\Phi_M$  values, we propose an alternate approach whereby  $EN_M$  itself can be computed with the help of Einstein's theory of solids.<sup>13</sup> The chemical potential of metals is represented in this approximation as<sup>13</sup>

$$\mu_M = 3kT \ln \frac{h\nu}{kT} - L_0, \quad (5)$$

where  $k$  and  $h$  denote the Boltzmann constant and Planck constant respectively,  $\nu$  being the vibrational frequency (or equivalently Einstein frequency) while  $L_0$  is the sublimation energy. Equation (5) yields  $EN_M$  as

$$EN_M = L_0 - 3kT \ln \frac{h\nu}{kT}. \quad (6)$$

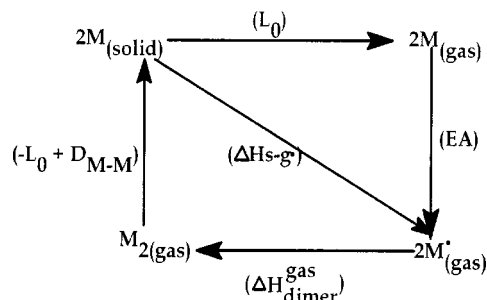
Table I denotes the values of  $EN_M$  calculated using the above equation and an excellent agreement may be noticed with the hitherto available estimates.

In order to compute hardness from Eq. (1), we estimate the EA using a new methodology shown below and subsequently obtain the IP with the help of Eq. (2). The calculation

of the EA of atoms and molecules is a frontier area of research and diverse density functional theories<sup>14</sup> with various basis sets have been proposed to compute adiabatic and vertical EAs for metals, organic compounds, and macromolecules.<sup>15</sup> Here we propose a heuristic approach for obtaining the EA of metal ( $M$ ) and hence a thermochemical cycle depicted in Scheme 1 is constructed which yields

$$L_0 + EA = -L_0 + D_{M-M} + \Delta H_{\text{dimer}}^{\text{gas}}, \quad (7)$$

where  $L_0$ ,  $D_{M-M}$ , and  $\Delta H_{\text{dimer}}^{\text{gas}}$  indicate, respectively, the sublimation,  $M-M$  bond dissociation and dimer gas formation energies.



Computation of EA of metals using a thermochemical cycle.

This implies that

$$EA = -2L_0 + D_{M-M} + \Delta H_{\text{dimer}}^{\text{gas}}. \quad (8)$$

Using Eqs. (4), (6), and (8), the ionization potential IP becomes

$$IP = 2\Phi_M + 2\chi_e^M + 2L_0 - D_{M-M} - \Delta H_{\text{dimer}}^{\text{gas}}. \quad (9)$$

In Table I, the values of the EA and IP deduced using the above equations are shown and a satisfactory agreement is noticed. Equation (1) now yields hardness as

$$\eta = \Phi_M + \chi_e^M + 2L_0 - D_{M-M} - \Delta H_{\text{dimer}}^{\text{gas}}. \quad (10)$$

Equivalently,

$$\eta = \Phi_M + \chi_e^M - EA, \quad (11)$$

which is the desired relation linking chemical hardness with work function of metals. We reiterate here that this strategy of expressing hardness has been necessitated in view of the fact that it is customary to investigate the structure of electrochemical interfaces and rates of electrochemical processes in terms of the work function of metals. Hence, for invoking the concept of chemical hardness, the latter needs to be formulated via work function of metals.

A notable facet of the above analysis is the computation of parameters such as  $EN_M$ , EA, IP, etc. using intuitive considerations coupled with appropriate thermochemical cycle and sublimation energies. The surface potential of electrons in metals becomes

$$\chi_e^M = \Phi_M - 3kT \ln \frac{h\nu}{kT} + L_0 \quad (12)$$

from Eqs. (4) and (6). Table II provides  $\chi_e^M$  estimated using Eq. (12) which involve no adjustable parameters. However,

TABLE I. Electronegativity, ionization potentials, and electron affinities estimated from Eqs. (6), (8), and (9), respectively. (The values of  $\chi_e^M$  are from Table II.)

Metals	EN <sub>M</sub> reported (eV)	EN <sub>M</sub> <sup>calc</sup> (eV) using Eq. (6)	$D_{M-M}$ (eV) <sup>b</sup>	EA <sup>calc</sup> from Eq. (8) (eV)	EA reported <sup>b</sup> (eV)	IP reported <sup>b</sup> (eV)	IP <sup>calc</sup> using Eq. (9) (eV)
Li	3.01	2.90	1.14	0.62	0.62	5.39	5.21
Na	2.85	2.56	0.76	0.52	0.55	5.14	4.60
K	2.42	2.44	0.57	0.47	0.50	4.34	4.41
Rb	2.34	1.96	0.52	0.47	0.49	4.18	4.65
Cs	2.18	2.12	0.46	0.50	0.47	3.89	3.75
Ba	2.40	2.21	1.86	0.16	0.15	5.21	4.26
V	3.60	3.47	2.79	0.55	0.53	6.75	6.39
Nb	4.00	4.06	5.29	0.85	0.89	6.76	7.28
Ta	4.11	4.15	5.50	0.31	0.32	7.55	7.99
Cr	3.72	4.24	1.48	0.71	0.67	6.77	7.77
Re	4.02	3.82	3.66	0.18	0.15	7.83	7.46
Fe	4.06	4.46	0.78	0.22	0.15	7.90	8.70
Ru	4.50	4.77	4.76	1.03	1.05	7.36	8.51
Os	4.90	4.98	5.96	1.06	1.10	8.44	8.90
Ni	4.40	4.65	2.08	1.14	1.16	7.64	8.16
Pd	4.45	4.08	1.04	0.59	0.56	8.34	7.85
Pt	5.60	5.93	3.18	2.18	2.13	8.96	9.68
Cu	4.48	4.59	1.83	1.26	1.24	7.73	7.92
Ag	4.44	4.12	1.66	1.32	1.30	7.58	6.72
Te	5.49	5.62	2.67	2.07	2.02	9.01	9.17
Au	5.77	5.70	2.34	2.32	2.31	9.23	9.08
Se	5.89	5.88	3.45	2.03	1.92	9.85	9.73
Ir	5.40	5.42	5.98	1.34	1.44	8.97	7.22
Al	3.23	3.55	1.38	0.44	0.44	5.99	6.66
Ga	3.20	3.00	1.16	0.31	0.30	5.99	5.69
In	3.10	3.26	3.07	0.30	0.30	5.79	6.22
Tl	3.20	3.10	2.91	0.20	0.20	6.11	6.00
Bi	4.69	4.42	4.19	1.00	0.95	7.29	7.80
Ti	3.45	3.52	3.25	0.07	0.08	6.83	6.84
Zr	3.67	3.63	3.36	0.43	0.43	6.63	6.83
Hf	3.80	3.68	3.41	0.009	0	6.83	6.95
Sc	3.34	3.46	3.19	0.21	0.19	6.56	6.71
Y	3.19	3.11	2.85	0.31	0.31	6.22	5.91
La	3.10	3.08	2.81	0.54	0.52	5.58	5.62
Co	4.30	4.32	4.05	0.58	0.59	7.88	8.06
Rh	4.30	4.98	4.71	1.14	1.13	7.46	8.82
Ge	4.60	4.70	4.39	1.25	1.26	7.90	8.15
Sn	4.30	4.47	4.16	1.02	1.06	7.34	7.92
Sb	4.85	4.78	4.47	1.06	1.11	8.61	8.50

<sup>a</sup>Reference 1.<sup>b</sup>Reference 60.

an early estimate of  $\chi_e^M$  deduced from the dipolar adsorption reports the same as  $-0.4$  eV for *sp* and *d*-metals.

Equation (11) has several interesting features viz. (i) work function and surface potential of electrons in metals dictate the magnitude of hardness. (ii) Since  $\Phi_M$  for metals varies from  $\approx 2$  eV to 5 eV, while the EA and  $\chi_e^M$  are much smaller in magnitude,  $\eta$  is always positive on the basis of Eq. (11). This validates the conjecture that  $\eta$  is  $\geq 0$ , deduced<sup>1</sup> using the convexity assumption of the ground state energy functional. (iii) In view of the fact that work functions pertaining to single crystals can be obtained using a variety of experimental techniques such as photoelectron spectroscopy,<sup>16</sup> thermionic emission,<sup>17,18</sup> etc., hardness for single crystals may also be deduced there from (iv) the well known expression for  $\eta$  as  $(EN_M - EA)$  [Equation (F2) of Parr and Yang<sup>1</sup>] follows from Eqs. (8) and (11). The estimates of  $\eta$  arising from Eq. (11) for a large number of metals reveal

satisfactory agreement with those reported by Pearson<sup>6</sup> (cf. Fig. 1).

### III. ESTIMATION OF HARDNESS FROM ELECTRODE KINETICS

The analysis of electron transfer processes at electrodes has been a subject of various theoretical investigations using molecular dynamics simulation,<sup>19</sup> potential energy surfaces,<sup>20</sup> diverse nature of coupling of the reactant species with electrodes<sup>21–26</sup> etc. The objectives in these methodologies involve extraction of electrode kinetic parameters such as standard exchange current density and symmetry factors and correlation with electronic properties of the metal, in particular its work function. While the hitherto-existing formalisms aid in comprehending the rates and mechanisms of electron transfer reactions, the concepts of density functional theories which provide a first-hand description of any

TABLE II. Surface potential of electrons in metal ( $\chi_e^M$ ) calculated from Eqs. (4) and (6) at 298 K.

Metals	$L_0$ (eV) <sup>a</sup>	$\Delta H_{\text{dimer}}^{\text{gas}}$ (eV) <sup>a</sup>	$\nu$ (cm <sup>-1</sup> ) <sup>b</sup>	$\Phi_M$ (eV) <sup>c</sup>	$\chi_e^M$ (eV) from Eqs. (4) and (6)
Li	2.81	5.10	18666.5	2.93	-0.015
Na	2.47	4.70	18666.5	2.36	0.20
K	2.35	4.60	18666.5	2.29	0.15
Rb	1.87	3.70	18666.5	2.26	0.30
Cs	2.03	4.10	18666.5	1.95	0.17
Ba	2.13	2.56	18666.5	2.52	-0.31
V	3.27	4.30	2833	4.30	-0.83
Nb	3.87	3.30	2833	4.20	-0.14
Ta	3.96	2.73	2833	4.25	-0.10
Cr	4.06	7.35	2075	4.50	-0.26
Re	3.64	3.80	2075	4.32	-0.50
Fe	4.28	8.00	2100	4.75	-0.29
Ru	4.59	5.45	2100	4.71	0.06
Os	4.90	4.90	2100	5.43	-0.45
Ni	4.47	8.00	2666.5	4.85	-0.20
Pd	3.91	7.37	2666.5	5.22	-1.00
Pt	5.75	10.50	2666.5	5.64	0.29
Cu	4.39	8.21	2073	4.93	-0.34
Ag	3.92	7.50	2073	4.30	-0.28
Te	5.30	10.00	1750	4.95	0.67
Au	5.51	11.00	2000	4.78	0.92
Se	5.56	9.70	5178.5	5.90	-0.02
Ir	5.42	6.20	2075	4.85	-0.57
Al	3.35	5.84	2073	4.00	-0.45
Ga	2.80	4.75	2073	3.42	-0.42
In	3.07	5.40	3271	3.69	-0.43
Tl	2.91	5.35	2073	3.54	-0.44
Bi	4.19	7.30	2615	4.34	0.06
Ti	3.25	5.10	2833	4.33	-0.88
Zr	3.36	4.06	2833	4.05	-0.42
Hf	3.41	1.15	2833	3.70	-0.22
Sc	3.19	4.90	2075	3.50	-0.04
Y	2.85	4.36	2075	3.10	0.01
La	2.81	3.60	2075	3.50	-0.42
Co	4.05	6.95	2075	5.00	-0.68
Rh	4.71	7.60	2075	4.98	0
Ge	4.39	7.30	2700	5.00	-0.30
Sn	4.16	7.40	2700	4.42	0.05
Sb	4.47	6.90	2700	4.55	0.23

<sup>a</sup>Reference 61.<sup>b</sup>References 62–64.<sup>c</sup>Reference 60.

$N$ -electron system under varying levels of sophistication,<sup>1</sup> have not yet been exploited in a systematic manner. This limitation can be obviated at least partially, if electrochemical data is represented in terms of parameters derived from density functional theories. Thus, Eq. (11) which relates  $\eta$  with  $\Phi_M$  has far-reaching implications in so far as the metallic characteristic is incorporated via hardness—a central parameter in modern applications of density functional theory to chemical kinetics.<sup>4</sup>

### A. Ferric/ferrous reaction

While any electron transfer process can serve as an illustrative example to obtain hardness of metals, ferric–ferrous redox reaction is regarded as a touchstone in the theory of electron transfer at electrode surfaces in view of its outer sphere nature<sup>26–29</sup> and various simulation procedures are employed for calculating the activation energy barrier, solvent polarization effects, and quantum influences. The

standard exchange current densities have been obtained<sup>28,29</sup> for metals such as Ni, Au, Pd, Pt, Ir, Rh, Ru using Tafel polarization studies while recent thermodynamic considerations<sup>30</sup> yield  $i_0$  as

$$\log i_0 = A + B\Phi_M, \quad (13)$$

where

$$A = \log \left( \frac{FC_{\text{Fe}^{3+}} + k_B T}{S_e h} \right) - \frac{\Delta G_{\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}}}{4.606SN_{\text{Fe}^{3+}} + RT} + \frac{-\Delta G_{\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}}}{4.606SN_{\text{Fe}^{2+}} + RT} - \frac{z_{\text{Fe}^{3+}} F \chi_e^s}{4.606RT} + \frac{z_{\text{Fe}^{2+}} F \chi_e^s}{4.606RT} - \frac{\beta n F E_e}{2.303RT} \quad (14)$$

and

$$B = \frac{F \xi}{2.303RT}. \quad (15)$$

TABLE III. Hardness ( $\eta$ ) calculated from the *experimental* exchange current densities of the ferric/ferrous reaction (Refs. 28, 29) and hydrogen evolution reaction (Ref. 36) at different electrodes. (The surface potential values are from Table II.)

Metals	$\eta_{\text{rep}}$ (eV) <sup>a</sup>	$\eta_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\text{cald}}$ (eV) from Eq. (16)	$\eta_{\text{HER}}^{\text{cald}}$ (eV) from Eqs. (18) and (19)	$-\log i_0^{\text{exp}} (\text{A cm}^{-2})$	
				HER	Fe <sup>3+</sup> /Fe <sup>2+</sup>
Au	3.46	3.35	3.40	6.50	3.60
Bi	3.74	...	3.36	7.80	...
Co	3.60	...	3.41	5.30	...
Fe	3.81	...	4.12	5.60	...
Ir	3.80	3.98	...	...	2.82
Mo	3.10	...	3.16	7.30	...
Ni	3.25	3.47	3.34	5.25	3.44
Nb	3.00	...	3.22	8.40	...
Os	3.80	...	3.34	4.10	...
Pd	3.89	3.65	3.41	3.10	2.22
Pt	3.50	3.21	3.28	3.00	2.60
Re	3.87	...	4.34	3.00	...
Rh	3.16	3.19	...	...	2.77
Ru	3.00	3.12	...	...	3.04
Sb	3.80	...	3.87	5.12	...
Sn	3.05	...	3.33	7.80	...
Ta	3.79	3.66	3.78	8.50	5.54
Ti	3.37	2.78	3.12	8.30	6.54
W	3.58	...	3.96	6.40	...

<sup>a</sup>Reference 6.

In Eqs. (14) and (15),  $A$  and  $B$  include parameters pertaining to ionic species and solvent dipoles viz. the desolvation energies  $\Delta G_{\text{Fe}^{3+}-s}^{\text{3+}}$  and  $\Delta G_{\text{Fe}^{2+}-s}^{\text{2+}}$ , solvation numbers of the species as well as control variables such as bulk concentration of the reactant ( $\text{Fe}^{3+}$ ).  $\chi_e^s$  denotes the surface potential of electrons in solution approximately equal to  $-0.4 \text{ eV}^{31}$ ,  $\xi$  is a dimensionless constant and equals 0.17 for all metals.<sup>30</sup> Substituting Eq. (11) in Eq. (13), we obtain

$$\eta = \frac{\log i_0 - A}{B} + \chi_e^M - EA. \quad (16)$$

The desolvation energies  $\Delta G_{\text{Fe}^{3+}-s}^{\text{3+}}$  and  $\Delta G_{\text{Fe}^{2+}-s}^{\text{2+}}$  as 51.42 eV and 20.55 eV respectively,<sup>32</sup> the solvation numbers<sup>32</sup>  $S_{\text{NFe}}^{\text{3+}}$  and  $S_{\text{NFe}}^{\text{2+}}$  as 11 and 12 and hence  $A$  and  $B$  become  $-17.15$  and  $2.85 \text{ eV}^{-1}$ , respectively (the equilibrium potential  $E_e$  for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is<sup>33</sup> 0.77 V, the symmetry factor  $\beta$  is assumed as 0.5, the charge on  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are 3 and 2, respectively. The bulk concentration<sup>28</sup> of the reactant species  $\text{Fe}^{3+}$  is 0.1 mol, while the area of the electrode  $S_{el}$  is assumed as 0.1  $\text{cm}^2$ ). The validity of Eq. (13) for obtaining standard exchange current densities using the above set of parameters has been demonstrated elsewhere.<sup>30</sup> Table III provides the hardness values deduced from Eq. (16) using the experimental data of  $i_0$  and satisfactory agreement with density functional predictions can be noticed.

We may emphasize here that Eq. (16) constitutes the first phenomenological result in simple electron transfer processes occurring at electrodes which invoke the chemical hardness of metals. Since the standard exchange current density  $i_0$  is customarily estimated from the Tafel polarization,<sup>34</sup> impedance spectroscopy,<sup>35</sup> etc., Eq. (16) provides an “experimental” method for obtaining  $\eta$ .

## B. Hydrogen evolution reaction

While the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  reaction has been investigated only at a few selected metals, the tabulation of  $i_0$  pertaining to the hydrogen evolution reaction (HER) represented as  $\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$  at a large number of  $sp$  and  $d$ -metals is available.<sup>36</sup> The experimental data for  $\log i_0$  exhibit a linear correlation<sup>36</sup> with  $\Phi_M$  as

$$\log i_0 = 6.7\Phi_M - 36.6 \quad \text{and} \quad \log i_0 = 6.7\Phi_M - 39.3 \quad (17)$$

for  $sp$  and  $d$ -metals, respectively. Interestingly, although the slope of  $\log i_0$  vs  $\Phi_M$  is identical for both group of metals, the intercepts are different and arise from the variation in the bulk concentration of the reactant, area of the electrode, etc. Substituting Eq. (11) in Eq. (17), we obtain

$$\eta = \frac{\log i_0 + 36.6}{6.7} + \chi_e^M - EA \quad (18)$$

and

$$\eta = \frac{\log i_0 + 39.3}{6.7} + \chi_e^M - EA \quad (19)$$

for  $sp$  and  $d$ -metals respectively. Equations (18) and (19) enable the calculation of  $\eta$  for a larger number of metals and we reiterate that the experimental data<sup>37</sup> of  $i_0$  has led to the hardness values reported in Table III. While the standard exchange current density ranges from  $10^{-3}$  to  $10^{-11} \text{ A cm}^{-2}$ ,  $\eta$  ranges from 2.4 to 4 eV.

It is of interest to inquire whether any new insights have been obtained by introducing the concept of hardness into the kinetics of electrode processes. For this purpose, let us consider the hydrogen evolution reaction (HER) whose standard exchange current density varies over a much wider

range. The hitherto available mechanistic analysis of the HER on metals indicates the crucial role of the adsorbed hydrogen atom leading to M–H bond formation energies.<sup>38</sup> The present analysis indicates that metals having low  $\eta$  values possess large  $i_0$  and vice versa. Thus it may become possible to interpret the mechanism of electron transfer reactions at electrodes using the principle of hardness.

The free energy of activation  $\Delta G^\ddagger$ , directly obtainable from  $i_0$  is approximately<sup>39</sup> equal to  $\lambda/4$ , where  $\lambda$  denotes the solvent reorganization energy arising in Marcus theory of electron transfer reactions.<sup>40</sup> Consequently, the present methodology of expressing  $i_0$  in terms of hardness leads *inter alia* to the interpretation of solvent reorganization energy using the perspective offered by the hardness concept. Alternatively, the standard exchange current density may also be derived from nonequilibrium statistical thermodynamic considerations as shown by Keizer<sup>41</sup> thus providing an entirely new method of analyzing hardness exploiting the flux-force formalism of Onsager.<sup>42</sup>

#### IV. ELECTRICAL DOUBLE LAYER STUDIES AND HARDNESS

While the foregoing analysis deals with the kinetics of electrochemical reactions for obtaining  $\eta$ , equilibrium properties associated with electrode/electrolyte interfaces may also be employed for the same purpose. One of the simplest parameters characterizing the structure of the electrical double layer is the potential of zero charge<sup>43</sup> ( $E_{pzc}$ ) and its variation with surface coverages is a measure of the extent of ionic or dipolar adsorption.<sup>44</sup> The evaluation of  $E_{pzc}$  with the help of trial functions and pseudopotential approximations within the purview of jellium models<sup>45,46</sup> or surface embedded atom model<sup>47</sup> of electrode surfaces has been a subject of recent investigations. The parametric relation between  $E_{pzc}$  and work function deduced by Trasatti<sup>48</sup> is

$$E_{pzc} = \frac{\Phi_M}{e} - 5.01, \quad (20)$$

where the numerical factor 5.01 eV includes the surface potential difference between the metal and the reference electrode, the dipole potential of water, chemical potential of electrons in solution etc.<sup>48</sup> Using Eq. (11), Eq. (20) can now be written as

$$E_{pzc} = \frac{\eta - \chi_e^M + EA}{e} - 5.01. \quad (21)$$

The values of  $E_{pzc}$  arising from Eq. (21) with the help of hardness deduced from Eq. (11) show satisfactory agreement<sup>49</sup> with the experimental data<sup>48</sup> (Table IV). Hence Eq. (20) may be helpful in interpreting diverse electrosorption processes in terms of hardness, bypassing more laborious computational strategies. Since the potential of zero charge of metals is usually obtained from electrocapillary measurements,<sup>44</sup> the above equation provides a simple method of extracting hardness from experimental data. The correlation of  $E_{pzc}$  with the density of broken bonds has also been attempted for different single crystal faces.<sup>50</sup>

TABLE IV. Potential of zero charge ( $E_{pzc}$ ) for different metal/electrolyte interfaces estimated from Eq. (21). (The surface potential values are from Table II.)

Metals	$\eta_{\text{cald}}$ from Eq. (11)	$E_{pzc}^{\text{cald}}$ from Eq. (21) (V)	$E_{pzc}^{\text{exp}}$ (V) <sup>a</sup>
Li	2.29	-2.08	-1.91
Na	2.04	-2.65	-2.31
K	1.97	-2.72	-2.71
Rb	2.09	-2.75	-2.81
Cs	1.63	-3.06	-3.11
Ag	2.70	-0.71	-0.70
Ga	2.69	-0.60	-0.69
Sn	3.45	-0.49	-0.38
Tl	2.90	-0.74	-0.71

<sup>a</sup>Reference 48.

#### V. PERSPECTIVES AND SUMMARY

The foregoing analysis has provided an interpretation of standard exchange current densities of electron transfer processes at metals and potential of zero charge of electrode/electrolyte interfaces using the principle of chemical hardness. The notion of hardness may become especially useful while rationalizing the electrode dependence of hydrogen evolution reaction—a crucial half-cell reaction in diverse electrochemical energy conversion and storage devices.<sup>51</sup> While work function of metals has long been recognized as an important parameter for studying substrate influences, the availability of an alternate tabulated quantity such as hardness affords a complimentary perspective apart from transcribing results derived elsewhere using the hard–soft acid base (HSAB) principle.<sup>52</sup> In particular, hardness has been found to be an attractive view-point to predict the course of isomerization processes,<sup>52</sup> complexation reactions,<sup>52</sup> etc. It is also worthwhile investigating in the context of heterogeneous electron transfer reactions, the “maximum hardness principle” whose validity is currently being investigated for different acid–base reactions.<sup>53–55</sup> The present approach is a preliminary endeavor in this direction whereby the work function is represented in terms of hardness and surface potential of electrons in metals. Further, the computation of EA, IP, and  $EN_M$  along with  $\chi_e^M$  is also carried out here using a new methodology so as to make the analysis self-consistent. A recent analysis for investigation of electron transfer using the cluster model for Ni(100) through chemisorbed acrylonitrile based upon the equalization of chemical potentials may be noted here.<sup>56</sup>

Apart from the application to electrode kinetic processes, equilibrium properties associated with metal/solution interfaces serve as alternate illustrations for employing chemical hardness. The potential of zero charge ( $E_{pzc}$ ) of electrochemical interfaces has been analyzed using (i) correlation with metallic properties,<sup>57</sup> (ii) surface embedded atom versions,<sup>45</sup> and (iii) jellium models employing different pseudopotentials.<sup>45,58</sup> This formalism affords another method of analyzing  $E_{pzc}$  and its variation with surface coverages. A recent study concerning the influence of the electrode density of states on the current density when monolayers of osmium containing redox couples are formed, deserves mention here.<sup>24</sup> Further, since the second harmonic generation yields

information on electronic density profiles at electrode/solution interfaces<sup>59</sup> and the susceptibilities may be expressed using the  $E_{pzc}$  values, the introduction of hardness is particularly useful in this context.

While the proposed methodology yields some new insights into electrochemical processes, it needs to be further refined in order to investigate in a detailed manner, uncertainties concerning the estimates of surface potentials, work function, electronegativities, etc., as regards their influence on the magnitude of hardness deduced therefrom. Nevertheless, the qualitative insights obtained herein with the help of fundamental metallic properties may still be valid and provide a starting point for diverse applications of hardness concept to electrochemical problems.

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