DFT Method Estimation of Standard Redox Potential of Metals

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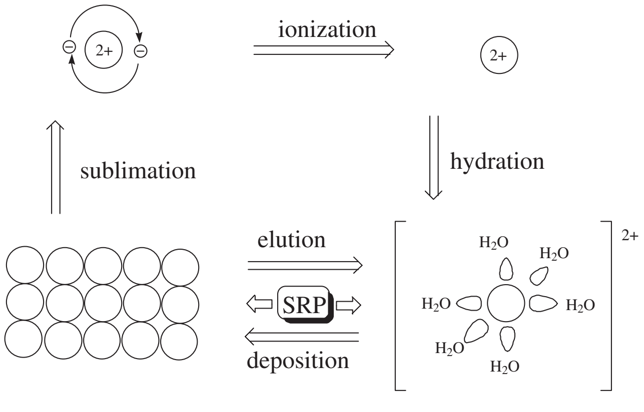
The DFT method calculation was carried out to evaluate standard redox potential for metal/metal cation systems. With the Born–Haber cycle, standard redox potential is composed of the cohesive energy, ionization energy, and hydration energy. Utilizing experimental values of the cohesive energy of metals, the root-mean-square deviation of calculated and experimental values was 0.29 V for 17 ions.

As for the standard redox potential (SRP) E^0 indicating the equilibrium of ions and metals, computational chemistry approach has not yet been done although it is the most fundamental quantity in electrochemistry. The SRP corresponds to a process in which a metal ion begins to be deposited and reduced on the solid metal electrode soaking in acid solution. However, it is easily anticipated that many factors relating adsorption and coordination of solvent molecules to metal surfaces and metal ions influence the process in complicated manner. In recent years, quantum chemical methodology for solution chemistry has developed. The techniques managing solvent as continuum models have been established, and incorporated in many MO and DFT method programs. It means that new approaches on electrochemistry become possible. In this study, we try to evaluate the SRP based on the DFT calculations.

To get an image of change of states easily, we consider the opposite direction of the process, i.e., the process from solid metal to a hydrated metal ion. This process is partitioned into the three processes utilizing the Born–Haber cycle, as shown in Scheme 1: (a) sublimation or cohesion to atoms from solid, (b) ionization of atom, and (c) formation of hydrated complex from the bare ion and water molecules. The SRP is estimated as the sum of the energy changes in three processes.



Scheme 1. Born–Haber cycle and SRP process.

The energy change derived for the change of state from solid metal to a hydrated metal ion is expressed in Eq 1.

$$\Delta\mathcal{E} = \mathcal{E}_{\mathrm{cohe}}^{\mathrm{expt}} + \mathcal{E}_{\mathrm{ion}} + \mathcal{E}_{\mathrm{hydra}} \qquad (1)$$

The first term of the right-hand side $\mathcal{E}_{\mathrm{cohe}}^{\mathrm{expt}}$ is the energy of sublimation from solid to gas. This quantity is equal to the cohesive energy, which could be evaluated as an energy difference between the bulk solid and an isolated atom if the band calculations are carried out. Since the other processes are able to be evaluated by molecular models, and the purpose of present letter is not to report precise evaluation of the cohesive energy, so experimental values of the cohesive energy are employed in this study.[1] The 2nd term $\mathcal{E}_{\mathrm{ion}}$ and the 3rd term $\mathcal{E}_{\mathrm{hydra}}$ of the right-hand side are the ionization energy and hydration energy, respectively. The ionization energies are estimated as the energy difference between a neutral atom and a cation, as in Eq 2.

$$\mathcal{E}_{\mathrm{ion}} = \mathcal{E}[\mathrm{M}]^{n+} - \mathcal{E}[\mathrm{M}]^0 \qquad (2)$$

The hydration energy is expressed as in Eq 3.

$$\mathcal{E}_{\mathrm{hydra}} = \mathcal{E}[\mathrm{M(OH_2)_6}^{n+}] - \mathcal{E}[\mathrm{M}^{n+}] - \mathcal{E}[\mathrm{H_{12}O_6}] \qquad (3)$$

In the present calculation, six water molecules are assigned to around the metal cation, and the hydration energy is a difference between the energy of an aqueous complex and the sum of energies of a bare cation and an aqueous cluster composed of six water molecules. Three types of coordination modes of aqueous complexes are considered: (a) six coordination octahedral structure, (b) four coordination tetrahedral structure with two water molecules in the second coordination shell, and (c) two coordination linear structure with four water molecules in the second coordination shell. As for the aqueous cluster, the structure of $H_{12}O_6$ is optimized.

In this letter, we only report the results with solvent effects, and the total energy changes are expressed in Eq 4, where the energy of metal cation appears twice in the opposite sign, and they are offset.

$$\begin{aligned}\Delta\mathcal{E} &= \mathcal{E}_{\mathrm{cohe}}^{\mathrm{expt}} + \mathcal{E}_{\mathrm{ion}} + \mathcal{E}_{\mathrm{hydra}} \\ &= \mathcal{E}_{\mathrm{cohe}}^{\mathrm{expt}} - \mathcal{E}[\mathrm{M}]^0 + \mathcal{E}[\mathrm{M(OH_2)_6}^{n+}] - \mathcal{E}[\mathrm{H_{12}O_6}]\end{aligned} \qquad (4)$$

Considering that the SRP is relative quantity against the standard hydrogen electrode potential, the relation between the energy difference $\Delta\mathcal{E}$ in Eq 1 and the SRP is expressed in Eq 5, where ν is the number of electrons transferred from atom to cation. The absolute potential value for hydrogen electrode is taken from the paper by Reiss and Heller.[2]

$$E^0 = \frac{\Delta\mathcal{E}}{\nu|e|} - 4.43 \qquad (5)$$

All the calculation is carried out with Gaussian 98 program package.[3] The Becke three-parameter Lee–Yang–Parr hybrid functionals are employed.[4–7] The Los Alamos model core potential basis sets are used.[8,9] The solvent effect is accounted by the self-consistent reaction field method, and the calculation is carried out at the level of polarized continuum model (PCM)[10] The entropy term was evaluated by the harmonic frequency analysis beneath the PCM simultaneously. The metal ions investigated are K^+, Ca^{2+}, Ti^{2+}, Mn^{2+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Cu^+, Ag^+, Pd^{2+}, Pt^{2+}, Au^{3+}, and Au^+ in the increasing order of experimental SRP values.[11]

For all the metal ions examined, three types of aqueous complex are optimized. The hydration energy is evaluated using the structure of the most stable aqueous complex, and therefrom the SRP is estimated. Table 1 shows the cohesive, ionization, hydration free energies, and calculated and experimental SRP values. Figure 1 shows comparison between the both SRP's. Maximum deviation is found to be 0.61 V for K^+, and followed by −0.44, −0.40, −0.38, −0.38 V, respectively, for Zn^{2+}, Co^{2+}, Ag^+, Au^{3+}. However the root-mean-square deviation of calculated and experimental values was 0.29 V for the seventeen ions.

Table 1. Calculated and experimental values for SRP and its compoments

Ion	cohe.	ioniza.	hydra.	SRP	SRP(exp)
K^+	0.934	4.46	−3.28	−2.32	−2.93
Ca^{2+}	1.84	18.21	−16.23	−2.52	−2.84
Ti^{2+}	4.85	20.56	−19.78	−1.62	−1.63
Mn^{2+}	2.92	23.18	−19.97	−1.36	−1.18
Zn^{2+}	1.35	26.38	−21.28	−1.21	−0.76
Cr^{3+}	4.1	58.82	−51.61	−0.66	−0.74
Fe^{2+}	4.28	24.90	−21.55	−0.61	−0.44
Co^{2+}	4.39	25.11	−22.00	−0.68	−0.28
Ni^{2+}	4.44	26.36	−22.51	−0.29	−0.26
Fe^{3+}	4.28	56.63	−47.96	−0.11	−0.04
Cu^{2+}	3.49	28.62	−22.56	0.35	0.34
Cu^+	3.49	7.84	−6.55	0.35	0.52
Ag^+	2.95	7.77	−5.11	1.18	0.80
Pd^{2+}	3.89	30.85	−23.53	1.17	0.92
Pt^{2+}	5.84	29.82	−24.19	1.31	1.19
Au^{3+}	3.81	66.05	−50.87	1.90	1.52
Au^+	3.81	9.44	−6.64	2.18	1.83

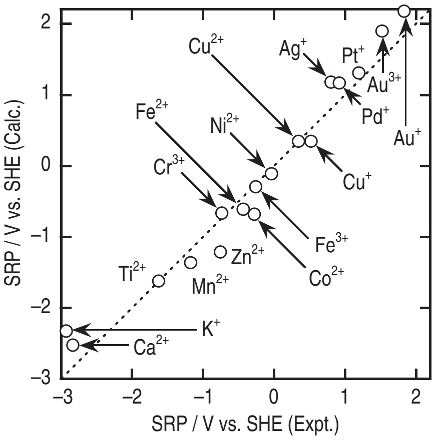


Figure 1. Comparison of calculated and experimental SRPs.

It is a kind of surprise that we have reproduced the SRP by the DFT calculation based on a very simple idea. We did not refer in this letter that the results without the PCM calculation. The calculations using aqueous complex in vacuum lead to the results far from the experimental values.

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