Open Access Library Journal
2025, Volume 12, e13274
ISSN Online: 2333-9721
ISSN Print: 2333-9705

Mathematical Model of the Functional Interrelation between Electrode Potential and Electrode Affinity

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How to cite this paper: Avtor, G.G. (2025) Mathematical Model of the Functional Interrelation between Electrode Potential and Electrode Affinity. *Open Access Library Journal*, **12**: e13274.
https://doi.org/10.4236/oalib.1113274

Received: March 15, 2025
Accepted: July 19, 2025
Published: July 22, 2025

Abstract

The question concerns the determination of the ratio and interrelation between two important quantities (electrode potential, reduction potential **(Reduction potentials)**, and electron affinity) in most elements of the periodic table of Mendeleev; I have derived a general formula describing this interrelation:

$$0.04 \cdot K_0^m \cdot n_e^n \cdot E_e = \varphi^0$$

where the formula takes into account both the number of external valence electrons (n_e) And the ordinal number in the periodic table of Mendeleyev. With this arrangement, the internal periodicity of the electrode potentials is revealed by the ordinal number. It is clear from the table that the theoretical results are in good agreement with the experiment. The experimental results are given in the table. I also showed in the corresponding formula that the rate constant of a chemical reaction and the constant of chemical equilibrium depend on such an important quantity as the electron affinity. I have provided relevant literature sources and studies describing the interrelation between the above-mentioned quantities (reduction potential and electron affinity) in such widely studied substances as fullerenes, aromatic hydrocarbons and metal complexes.

Subject Areas

Physical Chemistry

Keywords

Electrode Potential, Periodic System, Activation Energy, Electron Affinity, Chemical Reaction Rate

1. Introduction

The interrelation between two physical quantities (electrode potential - reduction potential and electron affinity) has been experimentally measured and studied in such widely studied substances as fullerenes, aromatic hydrocarbons and metal complexes, about which many scientific papers have been written [1], so its study is relevant. The discovery and isolation of fullerenes launched a whole new area of research into the properties of this third form of carbon.' The molecule belongs to a well-studied class of compounds — aromatic hydrocarbons. Therefore, it is important to compare the data accumulated on aromatic hydrocarbons with the data obtained on fullerenes. Two particularly important properties are: the half-wave recovery potential and the acceleration of $E_{1/2}$ and gas-phase electrons, E_{As}. The gas-phase electron ablation of several fullerenes is quite large, e.g. 2.65 eV for C60, 3.05 eV for C84, and 4.06 eV for C60 F48, which are among the largest values for an organic molecule obtained to date. The first recovery of the half-wave potential of a given molecule is associated with its electrons in the gas phase, and these two indices can be used to determine the energy difference between a neutral molecule and a negative ion in the gas phase and in solution $-\Delta\Delta G_{sol}$. Alternatively, if this energy difference can be estimated for a given molecule, then the gas-phase electron acceleration can be determined in terms of the reversible recovery potential or vice versa.

Determining this procedure is the ultimate goal of this paper.

The interrelation between E_A and $E_{1/2}$ is usually given as shown in Equation 1.

$$E_{1/2} = E_A - \Delta\Delta G_{sol} + E_{ref} \tag{1}$$

where $E_{1/2}$ and E_A are the experimental values of the reduction potential and electron affinity for the given molecule, and E_{ref} is the reference potential expressed in volts. For example, $E_{ref} = -4.71\ \text{V}$ if the potential is specified in SCE. [1]

2. Results and Discussion

Tables 1-3 summarize the experimental data for fullerenes, aromatic hydrocarbons, and metal complexes. The $-\Delta\Delta G_{sol}$ values given in **Tables 1-3** were calculated using Equation 1 and the corresponding $E_{1/2}$ and E_A values. The errors in -$\Delta\Delta G_{sol}$ were calculated from both the E_A and $E_{1/2}$ errors.

Table 1. Electron affinites (E_A's), reduction potentials ($E_{1/2}$'s), and solvation energy difference from gas paths to solution between the natural molecule and its alnon (−ΔΔGsal) for fullerenes.

species	E_A (eV)	E_{red} (V)	$-\Delta\Delta G_{vol}$ (eV)	ref	
				E_A	$E_{1/2}$
C60F41	4.06 ± 0.25	1.04 ± 0.06	1.69 ± 0.25	6	19
C36	3.14 ± 0.06	0.27 ± 0.06	1.84 ± 0.09	5a	18
C34	3.07 ± 0.06	0.12 ± 0.06	1.76 ± 0.09	5a	18
C78	3.05 ± 0.06	0.02 ± 0.06	1.68 ± 0.09	5a	18

Continued

C76	2.86 ± 0.05	−0.15 ± 0.06	1.70 ± 0.08	5a	18
C70	2.72 ± 0.05	−0.26 ± 0.06	1.73 ± 0.08	5a	18
C60	2.65 ± 0.05	−0.26 ± 0.06	1.80 ± 0.05	4	18
		av:	1.76 ± 0.06		

Table 2. Electron Affinites (E_S's), Resuction Potentials (E_{red}'s), and Solvation Energy Differences from Gas Phase to Solution between the Natural Molecule and Its Anion ($-\Delta\Delta G_{sol}$'s) for Aromatic.

Hydrocarbons (Group A)				ref	
species	E_A (eV)	E_{red} (V)	$-\Delta\Delta G_{sal}$ (eV)	E_A	E_{red}
benzo(a)pyrene	0.83 ± 0.12	−1.99 ± 0.05	1.89 ± 0.13	tw, 8	15
benzanthracenc	0.70 ± 0.05	−2.06 ± 0.05	1.95 ± 0.07	tw, 8	15
dibenz(a,j)antracence	0.69 ± 0.16	−2.07 ± 0.05	1.95 ± 0.17	tw, 8	15
dibenz(a,j)antracence	0.68 ± 0.12	−2.05 ± 0.05	1.98 ± 0.13	tw, 8	15
pyrene	0.56 ± 0.03	−2.10 ± 0.05	2.05 ± 0.08	tw,	15
anthracence	0.66 ± 0.01	−1.96 ± 0.05	2.09 ± 0.09	tw, 8	15
benzo(c)phenanthracene	0.54 ± 0.04	−2.24 ± 0.05	1.93 ± 0.06	tw, 8	15
benzo(e)payrene	0.49 ± 0.16	−2.17 ± 0.05	2.05 ± 0.17	tw, 8	15
chrysene	0.42 ± 0.04	−2.31 ± 0.05	1.98 ± 0.06	tw, 8	15
phenanthrene	0.31 ± 0.02	−2.46 ± 0.05	1.94 ± 0.05	tw, 8	15
thipenylene	0.29 ± 0.02	−2.46 ± 0.05	1.96 ± 0.05	tw, 8	15
naphthalene	0.15 ± 0.05	−2.51 ± 0.05	2.05 ± 0.07	tw, 8	15
penracene	1.35 ± 0.05	−1.30 ± 0.05	2.06 ± 0.07	14	15
tetracene	1.07 ± 0.05	−1.64 ± 0.05	2.00 ± 0.07	14	15
perylene	0.97 ± 0.05	−1.67 ± 0.05	2.07 ± 0.07	14	15
benzo(a)pyrene	0.75 ± 0.05	−1.99 ± 0.05	1.97 ± 0.07	14	15
1.1-diphenylethyline	0.40 ± 0.06	−2.32 ± 0.05	1.99 ± 0.08	29	15
stillbene	0.35 ± 0.05	−2.21 ± 0.05	2.15 ± 0.07	29	15
styrene	0.15 ± 0.06	−2.65 ± 0.05	2.07 ± 0.07	29	15
biphenil	0.13 ± 0.06	−2.60 ± 0.05	1.91 ± 0.08	29	15
benzenc	−0.72	−3.42 ± 0.10	1.98 ± 0.08	tw	33
			av:1.99 ± 0.05		

Main Part

I tried to theoretically study the interrelation between the above physical quantities (electrode potential and electron affinity) and generalize it to most elements of the periodic table of Mendeleev, as a result of which I wrote a theoretical general formula for this interrelation, which looks like this.

Table 3. Electron affinites (E_A's), reduction potentials (E_{red}'s), and solvation energy differencec from gas paths to solution between the natural molecule and its Alnon ($-\Delta\Delta G_{sal}$) from metal complexes.

					ref	
species	E_A (eV)	E_{red} (V)		$-\Delta\Delta G_{vol}$ (eV)	E_A	E_{red}
((TTP)FxBCle)FeCl	3.35 ± 0.20	0.45 ± 0.05		1.81 ± 0.21	26	ref in 26
((TTP)FxCl	3.14 ± 0.20	0.25 ± 0.05		1.82 ± 0.21	26	ref in 26
(TPPo-Cl_2ßCl_2)leCl	2.82 ± 0.11	0.27 ± 0.05		2.16 ± 0.12	26	ref in 26
(TPP-piv)Fe	2.07 ± 0.11	−0.65 ± 0.05		1.99 ± 0.12	26	ref in 26
(TPPo-Cl_2)Fe	1.86 ± 0.11	−0.88 ± 0.05		1.97 ± 0.12	26	ref in 26
(TPP)Fe	1.87 ± 0.11	−0.83 ± 0.05		2.01 ± 0.12	26	ref in 26
((TPP)CHO)Ni	1.74 ± 0.11	−0.99 ± 0.05		1.98 ± 0.12	26	ref in 26
(TPP)H_2	1.69 ± 0.11	−1.10 ± 0.05		1.92 ± 0.12	26	ref in 26
(TPP)Ni	1.51 ± 0.11	−1.19 ± 0.05		2.01 ± 0.12	26	ref in 26
			av:	1.99 ± 0.12	26	ref in 26
Min$(acac)_3$	2.57 ± 0.22	−0.09 ± 0.05		2.05 ± 0.23	27	ref in 27
Co$(acac)_3$	2.05 ± 0.18	−0.34 ± 0.05		2.32 ± 0.19	27	ref in 27
Fe$(acac)_3$	1.87 ± 0.10	−0.67 ± 0.05		2.17 ± 0.11	27	ref in 27
Ru$(acac)_3$	1.68 ± 0.10	−0.70 ± 0.05		2.33 ± 0.11	27	ref in 27
V$(acac)_3$	1.08 ± 0.10	−1.48 ± 0.05		2.15 ± 0.11	27	ref in 27
Cv$(acac)_3$	0.87 ± 0.10	−1.83 ± 0.05		2.01 ± 0.11	27	ref in 27
			av:	2.19 ± 0.14	27	ref in 27
				Rouff at al.		

$$K_0^m \cdot n_e^n \cdot 0.04 \cdot E_e = \varphi^0$$ Figure N1

where E_e is the electron affinity; φ^0 - Is the corresponding standard electrode potential.

K_0 is a constant value for elements with a given atomic number in the periodic table; 0.04 is a constant value for any element.

n_e - corresponds to the atomic (group) number of the element in the periodic table, which is numerically equal to the sum of electrons in the outer valence shell of the given element.

Let us arrange the electrode potentials for the elements in a row (group) by their ordinal numbers, where in the table, on the left side of the equation, the values are indicated: E_e - Electron affinity, also K_0 -; n_e - quantity; And on the right side of the equation is the theoretically calculated electrode potential modulus - $|\varphi^0|$ და And in the parentheses next to it is written the corresponding experimentally measured quantity - the modulus of the electrode potential. $|\varphi_{ex}^0|$ in this place there should be positive meanings , for exmaple , for H.

$$K_0 = 1.25; E_e = 72.8; n_e = 1; \varphi^0 = 2.32; \varphi_{ex}^0 = 2.25$$

Table 4. Groups of electrode potentials.

I GROUP	II GROUP	III GROUP
$K_0 = 1.25; n_e = 1$	$K_0 = 1.5; n_e = 2$	$K_0 = 1.25; n_e = 3$
$\underline{E_e}\ \ \underline{\lvert\varphi^0\rvert}\ \ \underline{\lvert\varphi^0_{\exp}\rvert}$	$\text{Be} - 1.5 \times 2^0 \times 0.04 \times 48 = 2.88(2.64)$	$\text{B} - 1.5 \times 3^0 \times 27 \times 0.04 = 1.62(1.79)$
$\text{H} - \frac{1}{1.25} \times 0.04 \times 72.8 = 2.32(2.25\exp)$	$\text{Mg} - 1.5 \times 2^0 \times 0.04 \times 40 = 2.40(2.37)$	$\text{Al} - 1.5 \times 3^0 \times 0.04 \times 41.76 = 1.67(1.66)$
$\text{Li} - 1.25 \times 0.04 \times 59.8 = 2.99(3.05)$	$\text{Zn} - \frac{1}{1.5 \times 2} \times 0.04 \times 58 = 0.77(0.76)$	$\text{Sc} - 3 \times 0.04 \times 17.307 = 2.07(2.07)$
$\text{Na} - 1.25 \times 0.04 \times 52.7 = 2.63(2.71)$	$\text{Cd} - \frac{1}{1.5 \times 2^2} \times 0.04 \times 68 = 0.44(0.44)$	$\text{Ga} - \frac{1.5}{3} \times 0.04 \times 30 = 0.60(0.53)$
$\text{K} - 1.25^2 \times 0.04 \times 48.4 = 3.02(2.92)$	$\text{Ba} - 1.5 \times 2^2 \times 0.04 \times 14 = 3.36(2.99)$	$\text{Y} - \frac{3}{1.5} \times 0.04 \times 29.6 = 2.368(2.372)$
$\text{Rb} - 1.25^2 \times 0.04 \times 47 = 2.93(2.92)$	$\text{Hg} - \frac{1.5}{2^2} \times 0.04 \times 48 = 0.72(0.79)$	$\text{In} - \frac{1.5}{3^2} \times 0.04 \times 37.04 = 0.24(0.34)$
$\text{Cs} - 1.25^2 \times 0.04 \times 45.5 = 2.85(3.0)$	$\text{Ra} - 1.5 \times 2^2 \times 0.04 \times 9.64 = 2.31(2.80)$	$\text{Ac} - \frac{1.5}{3} \times 0.04 \times 33.77 = 0.67(0.70)$

IV GROUP	V GROUP	VI GROUP
$K_0 = 1.5; \frac{1}{3} n_e = 4$	$K_0 = 2; n_e = 5$	$K_0 = 1.5; 2n_e = 6$
$\text{Si} - \frac{1}{1.5 \times 4} \times 0.04 \times 133 = 0.88(0.9)$	$\text{P} - \frac{1}{5} \times 0.04 \times 71.7 = 0.50(0.49)$	$\text{O} - \frac{1.5}{6} \times 0.04 \times 141 = 1.20(1.22)$
$\text{Ge} - \frac{1}{3 \times 4} \times 0.04 \times 119 = 0.39(0.37)$	$\text{P} - \frac{1}{2 \times 5} \times 0.04 \times 71.7 = 0.28(0.276)$	$\text{S} - \frac{2}{6} \times 0.04 \times 200 = 0.60(0.50)$
$\text{C} - \frac{1}{3 \times 4} \times 0.04 \times 122 = 0.40(0.43)(1)$	$\text{N} - \frac{1}{2 \times 5} \times 0.04 \times 699 = 2.80(3.0)$	$\text{Se} - \frac{1.5}{6} \times 0.04 \times 195 = 0.80(0.74)$
$\text{C} - \frac{1}{1.5 \times 4} \times 0.04 \times 122 = 0.81(0.70)(2)$	$\text{N} - \frac{1}{4 \times 5} \times 0.04 \times 699 = 1.39(1.42)$	$\text{Mo} - \frac{1}{6} \times 0.04 \times 72.10 = 0.48(0.43)$
$\text{Ti} - 2 \times 0.04 \times 20 = 1.60(1.63)$	$\text{V} - \frac{1}{5} \times 0.04 \times 50 = 0.40(0.34)$	$\text{Cr} - \frac{1}{6} \times 0.04 \times 64 = 0.42(0.46)$
$\text{Sn} - \frac{1}{1.5 \times 4^2} \times 0.04 \times 107 = 0.17(0.15)$	$\text{V} - \frac{1}{2 \times 5} \times 0.04 \times 50 = 0.20(0.26)$	$\text{Cr} - \frac{1}{3} \times 0.04 \times 64 = 0.85(0.74)$
$\text{Hf} - 4 \times 0.04 \times 17.18 = 2.72(2.5)$	$\text{V} - \frac{1}{2} \times 0.04 \times 50 = 1(1)$	
$\text{Pb} - \frac{1}{4} \times 0.04 \times 34.4189 = 0.344(0.35)(1)$	$\text{As} - \frac{1}{2 \times 5} \times 0.04 \times 78 = 0.30(0.23)$	
$\text{Pb} - \frac{1}{2 \times 4} \times 0.04 \times 34.4189 = 0.086(0.126)(2)$	$\text{Nb} - \frac{1}{3} \times 0.04 \times 88.516 = 1.18(1.0)$	
$\text{Pb} - \frac{1}{2} \times 0.04 \times 34.4189 = 0.68(0.58)$	$\text{Sb} - \frac{1}{2 \times 5} \times 0.04 \times 103 = 0.4(0.2)$	
	$\text{Ta} - \frac{1}{2} \times 0.04 \times 31 = 0.62(0.75)$	

VII GROUP	
$K_0 = 1.5; n_e = 7$	For the parts of lantanoid and actinoid is $K_0 = 1.60$
$F_2 - \frac{1.5}{7} \times 0.04 \times 327.9 = 2.80$	$\text{Tm} - \frac{1}{1.60} \times 0.04 \times 99 = 2.47(2.40\exp)$
$Cl_2 - \frac{1}{1.5 \times 7} \times 0.04 \times 348.8 = 1.32$	$\text{Fm} - 1.60 \times 0.04 \times 33.96 = 2.173(2.30)$
$Br_2 - \frac{1}{1.5 \times 7} \times 0.04 \times 325 = 1.23$	$\text{Pu} - \frac{1}{1.60} \times 0.04 \times 48.33 = 1.20(1.25)$
$I_2 - \frac{1}{3 \times 7} \times 0.04 \times 295 = 0.56$	

Continued

$Mn-\frac{3}{7}\times 0.04\times 50=0.85(0.90)$	$Md-\frac{1}{1.60}\times 0.04\times 93.91=2.34(2.40)$
$At-\frac{1}{1.5\times 7}\times 0.04\times 233=0.88(1.0)$	$Dy-1.60\times 0.04\times 34=2.176(2.29)$
General formula of electrode potential is the following:	$Lr-1.60\times 0.04\times 30.04=1.92(1.96)$
$\varphi^0=0.04\times K_0^m\times n_e^n\times E_e-1$	$Ho-1.60\times 0.04\times 32.64=2.1(2.1)$
where $n=1;-1;-2;0$	$Bk-\frac{1}{1.60^2}\times 0.04\times 165.24=2.60(2.80)$
$ln=1;-1;2$;	$Yb-\sqrt{1.60}\times 0.04\times 50=2.60(2.76)$
	$Bs-1.60\times 0.04\times 28.60=1.83$

For B_e $E_e=48; n_e=2; K_0=1.5; \varphi^0=2.88; \varphi^0_{ex}=2.64$ And so on.

$0.04\cdot K_0^m\cdot n_e^n\cdot E_e=\varphi^0$ The latter formula includes both positive and negative values of electrode potential (in the case of negative potential $0.04\cdot K_0^m\cdot n_e^n\cdot E_e$ is multiplied by -1). In the table H means $2H^-$ Cd means Cd^{2+}; Zn means Zn^{2+} And so on for all elements. Not specified for simplicity.

With this arrangement of electrode potentials in **Table 4**, internal periodicity by ordinal number is revealed. The experimental data [2] [3] meet well the theoretical data, which means that the theory is correct.

The value of the so-called second radiation constant is:

$$C_2=hc/k_B=1.4387752\times 10^{-2}\ \text{m}\cdot\text{K}$$

where h is Planck's constant, c – speed of light k_B - Boltzmann's constant, it is approximately 0.04 : $C_2\approx 0.04$

Taking it into account in Formula 1 gives us the following:

$$\frac{ch}{k_B}\cdot k_o^m\cdot n_e^n E_e=\varphi^o \quad (1)$$

For reactions occurring under standard conditions, the interrelation between the change in Gibbs energy (ΔG) and the electrode potential (φ^o standart) is expressed by the equation: [4]

$$\Delta G=nF\varphi^o \quad (2)$$

where F- Faraday number n- The number of electrons participating in an oxidation-reduction process, in moles.

1) And the interrelation between the equilibrium constant (K) and the standard Gibbs energy (ΔG^O) has the following form:

$$\Delta G^O=-RT\ln K \quad (3)$$

where R is the universal gas constant, T is the temperature (in Kelvin)

Combining formulas 2 and 3 gives us:

$$-nF\varphi=-RT\ln K$$

2) And taking into account equation 1a in this last equation gives us:

$$-\frac{nFhcK_o^m n_e^n E_e}{K_B}=-RT\ln K$$

From which the logarithm of the equilibrium constant $\ln K$ will be as follows:

$$-\frac{nFhcK_o^m n_e^n E_e}{K_B RT} = -\ln K \tag{4}$$

Let's express the logarithms ($\ln k_1; \ln k_2$) of the rate constants of a chemical reaction concerning temperature T_1 და T_2 using the Arrhenius equation:

$$\ln k_1 = -\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \ln A; \quad \ln k_2 = -\frac{E_a}{R}\left(\frac{1}{T_2}\right) + \ln A;$$

Let's express the equilibrium constant as the difference of these two equations:

$$\ln K = \ln k_2 - \ln k_1 = -\frac{E_a}{R}\left(\frac{1}{T_2}\right) + \ln A - \left(-\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \ln A\right)$$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}\right) + \ln A + \frac{E_a}{R}\left(\frac{1}{T_1}\right) - \ln A$$

Finally, we get: $\ln K = \ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

And taking into account 3a in the latter, gives us:

$$\frac{nFhcK_o^m n_e^n E_e}{K_B RT} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = (\ln k - \ln A)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)T \tag{5}$$

From the latter, we can derive the rate constant (k) of a chemical reaction.

Van't Hoff's isochore: $\mathrm{d}\ln K/\mathrm{d}T = -Q/RT^2$

Taking into account 3A, it is expressed as follows:

$$\frac{nFhcK_o^m n_e^n}{k_B RT}\frac{\mathrm{d}E_e}{\mathrm{d}T} = -Q/RT^2$$

Ultimately, we can say that I have expressed the constant of chemical equilibrium by the electron affinity, and I have also expressed the rate constant of a chemical reaction, Van't Hoff's isochore, by the electron affinity.

3. Conclusion

My approach is that when determining the electrode potential, not only the electron affinity takes part, but also the number of external valence electrons, the ordinal number of chemical elements in the periodic system is taken into account, thus internal periodicity manifests itself. In addition, I was able to depict the chemical equilibrium constant in a new way, the chemical reaction rate constant, the Van't Hoff's isochore in a new way.

Conflicts of Interest

The author declares no conflicts of interest.

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