

Electrode Potentials and Chemical Kinetics

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

$$K_o^m \cdot n_e^n \cdot 0,04 \cdot E_e = \varphi^0 \text{ figure N1}$$

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

K_o 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.

I Group	II Group	III Group
$K_o = 1,25 \cdot n_e = 1$ $E_e \cdot \varphi^0 \cdot \varphi_{exp}^0 $ $H - \frac{1}{1,25} \cdot 0,04 \cdot 72,8 = 2,32 \text{ (2.25 exp)}$ $Li - 1,25 \cdot 0,04 \cdot 59,8 = 2,99 \text{ (3.05)}$ $Na - 1,25 \cdot 0,04 \cdot 52,7 = 2,63 \text{ (2.71)}$ $K - 1,25^2 \cdot 0,04 \cdot 48,4 = 3,02 \text{ (2.92)}$ $Rb - 1,25^2 \cdot 0,04 \cdot 47 = 2,93 \text{ (2.92)}$ $Cs - 1,25^2 \cdot 0,04 \cdot 45,5 = 2,85 \text{ (3.0)}$	$K_o = 1,5 \cdot n_e = 2$ $Be - 1,5 \cdot 2^0 \cdot 0,04 \cdot 48 = 2,88 \text{ (2.64)}$ $Mg - 1,5 \cdot 2^0 \cdot 0,04 \cdot 40 = 2,40 \text{ (2.37)}$ $Zn - \frac{1}{1,5 \cdot 2} \cdot 0,04 \cdot 58 = 0,77 \text{ (0.76)}$ $Cd - \frac{1}{1,5 \cdot 2^2} \cdot 0,04 \cdot 68 = 0,44 \text{ (0.44)}$ $Ba - 1,5 \cdot 2^2 \cdot 0,04 \cdot 14 = 3,36 \text{ (2.99)}$ $Hg - \frac{1,5}{2^2} \cdot 0,04 \cdot 48 = 0,72 \text{ (0.79)}$ $Ra - 1,5 \cdot 2^2 \cdot 0,04 \cdot 9,64 = 2,31 \text{ (2.80)}$	$K_o = 1,25 \cdot n_e = 3$ $B - 1,5 \cdot 3^0 \cdot 27 \cdot 0,04 = 1,62 \text{ (1.79)}$ $Al - 1,5 \cdot 3^0 \cdot 0,04 \cdot 41,76 = 1,67 \text{ (1.66)}$ $Sc - 3 \cdot 0,04 \cdot 17,307 = 2,07 \text{ (2.07)}$ $Ga - \frac{1,5}{3} \cdot 0,04 \cdot 30 = 0,60 \text{ (0.53)}$ $Y - \frac{3}{1,5} \cdot 0,04 \cdot 29,6 = 2,368 \text{ (2.372)}$ $In - \frac{1,5}{3^2} \cdot 0,04 \cdot 37,04 = 0,24 \text{ (0.34)}$ $Ac - \frac{1,5}{3} \cdot 0,04 \cdot 33,77 = 0,67 \text{ (0.70)}$
IV Group	V Group	VI Group
$K_o = 1,5; \frac{1}{3} \cdot n_e = 4$ $Si - \frac{1}{1,5 \cdot 4} \cdot 0,04 \cdot 133 = 0,88 \text{ (0.9)}$ $Ge - \frac{1}{3 \cdot 4} \cdot 0,04 \cdot 119 = 0,39 \text{ (0.37)}$ $C - \frac{1}{3 \cdot 4} \cdot 0,04 \cdot 122 = 0,40 \text{ (0.43) (1)}$ $C - \frac{1}{1,5 \cdot 4} \cdot 0,04 \cdot 122 = 0,81 \text{ (0.70) (2)}$ $Ti - 2 \cdot 0,04 \cdot 20 = 1,60 \text{ (1.63)}$ $Sn - \frac{1}{1,5 \cdot 4^2} \cdot 0,04 \cdot 107 = 0,17 \text{ (0.15)}$	$K_o = 2; n_e = 5$ $P - \frac{1}{5} \cdot 0,04 \cdot 71,7 = 0,50 \text{ (0.49)}$ $P - \frac{1}{2 \cdot 5} \cdot 0,04 \cdot 71,7 = 0,28 \text{ (0.276)}$ $N - \frac{1}{2 \cdot 5} \cdot 0,04 \cdot 699 = 2,80 \text{ (3.0)}$ $N - \frac{1}{4 \cdot 5} \cdot 0,04 \cdot 699 = 1,39 \text{ (1.42)}$ $V - \frac{1}{5} \cdot 0,04 \cdot 50 = 0,40 \text{ (0.34)}$ $V - \frac{1}{2 \cdot 5} \cdot 0,04 \cdot 50 = 0,20 \text{ (0.26)}$	$K_o = 1,5; 2 \cdot n_e = 6$ $O - \frac{1,5}{6} \cdot 0,04 \cdot 141 = 1,20 \text{ (1.22)}$ $S - \frac{2}{6} \cdot 0,04 \cdot 200 = 0,60 \text{ (0.50)}$ $Se - \frac{1,5}{6} \cdot 0,04 \cdot 195 = 0,80 \text{ (0.74)}$ $Mo - \frac{1}{6} \cdot 0,04 \cdot 72,10 = 0,48 \text{ (0.43)}$ $Cr - \frac{1}{6} \cdot 0,04 \cdot 64 = 0,42 \text{ (0.46)}$ $Cr - \frac{1}{3} \cdot 0,04 \cdot 64 = 0,85 \text{ (0.74)}$

$\text{Hf} - 4 \cdot 0.04 \cdot 17.18 = 2.72 \text{ (2.5)}$ $\text{Pb} - \frac{1}{4} \cdot 0.04 \cdot 34.4189 = 0.344 \text{ (0.35)(1)}$ $\text{Pb} - \frac{1}{2 \cdot 4} \cdot 0.04 \cdot 34.4189 = 0.086 \text{ (0.126)(2)}$ $\text{Pb} - \frac{1}{2} \cdot 0.04 \cdot 34.4189 = 0.68 \text{ (0.58)}$	$\text{V} - \frac{1}{2} \cdot 0.04 \cdot 50 = 1 \text{ (1)}$ $\text{AS} - \frac{1}{2 \cdot 5} \cdot 0.04 \cdot 78 = 0.30 \text{ (0.23)}$ $\text{Nb} - \frac{1}{3} \cdot 0.04 \cdot 88.516 = 1.18 \text{ (1.0)}$ $\text{SB} - \frac{1}{2 \cdot 5} \cdot 0.04 \cdot 103 = 0.4 \text{ (0.2)}$ $\text{Ta} - \frac{1}{2} \cdot 0.04 \cdot 31 = 0.62 \text{ (0.75)}$	
VII Group		
$K_0 = 1.5; n_e = 7$ $\text{F}_2 - \frac{1.5}{7} \cdot 0.04 \cdot 327.9 = 2.80$ $\text{Cl}_2 - \frac{1}{1.5 \cdot 7} \cdot 0.04 \cdot 348.8 = 1.32$ $\text{Br}_2 - \frac{1}{1.5 \cdot 7} \cdot 0.04 \cdot 325 = 1.23$ $\text{I}_2 - \frac{1}{3 \cdot 7} \cdot 0.04 \cdot 295 = 0.56$ $\text{Mn} - \frac{3}{7} \cdot 0.04 \cdot 50 = 0.85 \text{ (0.90)}$ $\text{At} - \frac{1}{1.5 \cdot 7} \cdot 0.04 \cdot 233 = 0.88 \text{ (1.0)}$ General formula of electrode potential is the following: $\varphi^0 = 0.04 \cdot K_0^m \cdot n_e^n \cdot E_e - 1$ where $n = 1; -1; -2; 0$ $\ln = 1; -1; 2;$	For the parts of lantanoid and actinoid is $K_0 = 1.60$ $\text{Tm} - \frac{1}{1.60} \cdot 0.04 \cdot 99 = 2.47 \text{ (2.40 exp)}$ $\text{Fm} - 1.60 \cdot 0.04 \cdot 33.96 = 2.173 \text{ (2.30)}$ $\text{Pu} - \frac{1}{1.60} \cdot 0.04 \cdot 48.33 = 1.20 \text{ (1.25)}$ $\text{Md} - \frac{1}{1.60} \cdot 0.04 \cdot 93.91 = 2.34 \text{ (2.40)}$ $\text{DY} - 1.60 \cdot 0.04 \cdot 34 = 2.176 \text{ (2.29)}$ $\text{Lr} - 1.60 \cdot 0.04 \cdot 30.04 = 1.92 \text{ (1.96)}$ $\text{Ho} - 1.60 \cdot 0.04 \cdot 32.64 = 2.1 \text{ (2.1)}$ $\text{BK} - \frac{1}{1.60^2} \cdot 0.04 \cdot 165.24 = 2.60 \text{ (2.80)}$ $\text{Yb} - \sqrt{1.60} \cdot 0.04 \cdot 50 = 2.60 \text{ (2.76)}$ $\text{Bs} - 1.60 \cdot 0.04 \cdot 28.60 = 1.83$	

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 $|\varphi^0|$. And in the parentheses next to it is written the corresponding experimentally measured quantity - the modulus of the electrode potential. $|\varphi_{ex}^0|$ Positive values; for example for H

$$K_0 = 1.25 \ E_e = 72,8 \ n_e = 1 \ \varphi^0 = 2,32 \ \varphi_{ex}^0 = 2,25$$

$$\text{For } B_e \ E_e = 48; \ n_e = 2; \ K_0 = 1,5; \ \varphi^0 = 2,88; \ \varphi_{ex}^0 = 2,64 \text{ And so on.}$$

$0,04 \cdot K_0^m \cdot n_e^n \cdot E_e = \varphi^0$ 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 the table, internal periodicity by ordinal number is revealed. The experimental data [1,2] meet well the theoretical data, which means that the theory is correct.

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

$$C_2 = hc/k_B = 1,4387752 \cdot 10^{-2} m \cdot k$$

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:

$$\frac{ch}{k_B} \cdot K_0^m \cdot n_e^n E_e = \varphi^0$$

For reactions occurring under standard conditions, the interrelation between the change in Gibbs energy (ΔG) and the electrode potential (φ^0 standart) is expressed by the equation: [3] - $\Delta G = nF\varphi^0$

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

And the interrelation between the equilibrium constant (K) and the standard Gibbs energy (ΔG^0) has the following form: $\Delta G^0 = -RT \ln K$ figure - (3)

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

Combining formulas 2 and 3 gives us:

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

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

$$-\frac{nFhcK_0^m n_e^n E_e}{K_B} = -RT \ln K$$

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

$$-\frac{nFhcK_0^m n_e^n E_e}{K_B RT} = -\ln K \text{ figure - (3a)}$$

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

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

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

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

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

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

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

$$\frac{nFhcK_0^m n_e^n E_e}{K_B RT} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = (\ln k - \ln A) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \text{ figure - (4)}$$

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

Van't Hoff's isochore: $d \ln K / dT = -Q / RT^2$

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

$$\frac{nFhcK_0^m n_e^n}{K_B RT} \frac{dE_e}{dT} = -Q / RT^2$$

The equilibrium constant for $AB + e(-) = AB(-)$

$$\ln K_{eq} T^{3/2} = \ln [Qan] + \ln [S] + 12,43 + \frac{Ea}{RT}$$

Inserting (4) in this latter gives the equality:

$$\left(\frac{0,04nFhcK_0^m n_e^n E_e}{RT} \right) T^{3/2} = \ln (Qan) + \ln (S) + 12,43 + \frac{Ea}{RT}$$

In which $\frac{hc}{K_B} \approx 0,04$

This equation shows that the electron affinity (E_e) and the activation energy (Ea) are proportional to each other.

The Qan is the ratio of the anion to neutral partition function and

S is the ratio of the spin partition function.

The 12.43 is from fundamental constants.

The table below shows the proportional relationship between activation energy and electron affinity:

Table 1: Relative Bond Orders, Electron Affinities, and Activation Energies (in eV)

	E_e (eV) ($n = 0$)	E_e (eV) ($n = 0$)	E_e (eV) literature	RBO literature	E_e (eV) ($n = 1$)	E_e (eV) ($n = 1$)	E_e (eV) literature	RBO literature
	2.60(10)	0.65(2)	2.45	0.65	2.60(10)	0.65(2)	2.45	0.65
	2.45(3)	0.65(2)	2.45	0.64	2.20	0.63(2)	2.20	0.60
	2.00(3)	0.56(2)	2.00	0.64	1.80	0.43(2)	1.80	0.60
	1.60(3)	0.20(2)	1.55	0.69	1.40	0.20(2)	1.26	0.65
	twa	tw	[8,22,26]	tw	tw	tw	[8,22,26]	tw
	1.03(3)	0.15(1)	1.06	0.31	0.80(3)	0.13(1)	0.72	0.25
	0.65(3)	0.10(1)	0.65	0.30	0.45(3)	0.05(1)	0.45	0.27
	0.25(3)	0.03(1)	0.15	0.37	0.10(3)	0.03(1)	0.10	0.33
	0.10(5)	0.08(1)	0.05	0.06	0.08(5)	0.01(1)	0.05	0.06
	Tw	tw	[6-8,22]	tw	tw	tw	[6-8,22]	tw

^aThis work

Above mentioned table and equality are given from the following scientific work:

Electron affinities and activation energies for reactions with thermal electrons: SF_6 and SF_5

Similar results are received from the following substances: O_2 , CS_2 , $C_6 S_6$ the nucleic acids, anthracene and c and others.

Let us give the following equality:

$$K = \frac{aK_B T}{h} K_c^\# = \frac{aK_B T}{h} \exp \left[-\frac{\Delta(G_0^\#)}{RT} \right]$$

In this equality, we receive the following equality considering (3) and (4) equalities:

$$K = \frac{aK_B T}{h} K_c^\# = \frac{aK_B T}{h} \exp \left[-\frac{0,04 \cdot n \cdot F \cdot K_0^m \cdot n_e^n E_e}{RT} \right] \quad (6)$$

And in the equality: $\ln K = \ln \frac{aK_B T}{h} K_c^\# = \ln K_0^s + Z_A Z_B \sqrt{\mu}$

Considering (6), provides connection between electron affinity and ionic strength (μ). With the following form:

$$\ln K = \ln \frac{aK_B T}{h} \exp \left[-\frac{0,04 \cdot n \cdot F \cdot K_0^m \cdot n_e^n E_e}{RT} \right] = \ln K_0^s + Z_A Z_B \sqrt{\mu}$$

Here it is $\frac{hc}{K_B} \approx 0,04$ too

In the following equality:

$$\ln K_c = \sum_j V_j; \ln C_j$$

Considering (4) provides connection between electron affinity and concentration (C):

$$\ln K_c = \frac{0,04 \cdot n \cdot F \cdot K_0^m \cdot n_e^n E_e}{RT} = \sum_j V_j; \ln C_j$$

Where K_c is the equilibrium constant.

The diffusion coefficient is expressed as follows:

$$D_j = \frac{a^2 K_0 T}{2h} \exp \left[-\frac{\Delta G_0^\#}{RT} \right]$$

And the relationship between the diffusion coefficient and the electron affinity is expressed as follows:

$$D_j = \frac{a^2 K_0 T}{2h} \exp \left[-\frac{[0,04 \cdot n \cdot F \cdot K_0^m \cdot n_e^a Ee]}{RT} \right]$$

The flux of plane I will be

$$J_j = -D_j \left[\frac{\partial [M]_j}{\partial x} \right]_j$$

As we know, the differential form of the Arrhenius equation is as follows:

$$\frac{d \ln K}{dT} = \frac{E}{RT^2} \quad (7)$$

but: $\frac{d \ln K}{dT} = \frac{d \ln K^*}{dT}$ that's why we receive that

$$\frac{d \ln K^*}{dT} = \frac{E}{RT^2} \quad (7a)$$

When the activation E heat is constant with respect to temperature, then, considering and integrating (7) and (7a) equations, we accept:

$$\ln K = \ln K^* = \frac{E}{R} \int (dT/t)^2 + const = -\frac{E}{RT} + const \quad (7b)$$

Let's insert (4) – equation in (7b) and we receive:

$$\ln K = \ln K^* = \frac{0,04 \cdot n \cdot F \cdot K_0^m \cdot n_e^a Ee}{RT} = const - \frac{E}{RT}$$

Where K – is chemical rate constant and K* - is equilibrium constant.

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.

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 [4,5].

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