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Electrode Potencials and Chemical Kinetics

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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 · K0 m • ne n • Ee = φ0

0 φ where E is the electron affinity; - Is the corresponding standard electrode potential. e K, 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- corresponds to the atomic (group) number of the element in the periodic e table, which is numerically equal to the sum of electrons in the outer valence shell of the given element.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 ha.

Keywords: Electrode Potential, Electron Affinity, Chemical Reaction Rate.

Introduction

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:

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

where E_e is the electron affinity; φo - 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
$K = 1,25\ n = 1\ o\ e\ 0\|\ 0\ \ \|E\|\varphi\|\varphi\ e\|$ $exp\|$ $H -^{1}\ \cdot 0.04\cdot 72.8 = 2.32\ (2.25\ exp)$ 1.25 $Li - 1.25\cdot 0.04\cdot 59.8 = 2.99\ (3.05)$ $Na - 1.25\cdot 0.04\cdot 52.7 = 2.63\ (2.71)\ 2$ $K - 1.25\ \cdot 0.04\cdot 48.4 = 3.02\ (2.92)\ 2$ $RB - 1.25\ \cdot 0.04\cdot 47 = 2.93\ (2.92)\ 2$ $C - 1.25\ \cdot 0.04\cdot 45.5 = 2.85\ (3.0)\ S$	$K = 1,5\ n = 2\ o\ e\ 0$ $Be - 1.5\cdot 2\ \cdot 0.04\cdot 48 = 2.88\ (2.64)\ 0$ $Mg - 1.5\cdot 2\ \cdot 0.04\cdot 40 = 2.40\ (2.37)$ $Zn -^{1}\ \cdot 0.04\cdot 58 = 0.77\ (0.76)\ 1.5\cdot 2$ $Cd -^{1}\ \cdot 0.04\cdot 68 = 0.44\ (0.44)\ 2\ 1.5\cdot 2$ 2 $Ba - 1.5\cdot 2\ \cdot 0.04\cdot 14 = 3.36\ (2.99)$ $Hg -^{1.5} \cdot 0.04\cdot 48 = 0.72\ (0.79)\ 2\ 2\ 2$ $Ra - 1.5\cdot 2\ \cdot 0.04\cdot 9.64 = 2.31\ (2.80)$	$K = 1,25\ n = 3\ o\ e\ 0$ $B - 1.5\cdot 3\ \cdot 27\cdot 0.04 = 1.62\ (1.79)\ 0$ $Al - 1.5\cdot 3\ \cdot 0.04\cdot 41.76 = 1.67\ (1.66)$ $SC - 3\cdot 0.04\cdot 17.307 = 2.07\ (2.07)$ $Ga -^{1.5} \cdot 0.04\cdot 30 = 0.60\ (0.53)\ 3$ $Y -^{3} \cdot 0.04\cdot 29.6 = 2.368\ (2.372)\ 1.5$ $In -^{1.5} \cdot 0.04\cdot 37.04 = 0.24\ (0.34)\ 2\ 3$ $AC -^{1.5} \cdot 0.04\cdot 33.77 = 0.67\ (0.70)\ 3$
IV GROUP	V GROUP	VI GROUP
$K = 1,5;\ ^{1}\ n = 4\ o\ 3\ \ e$ $Si -^{1}\ \cdot 0.04\cdot 133 = 0.88\ (0.9)\ 1.5\cdot 4$ $Ge -^{1}\ \cdot 0.04\cdot 119 = 0.39\ (0.37)\ 3\cdot 4$ $C -^{1}\ \cdot 0.04\cdot 122 = 0.40\ (0.43)\ (1)3\cdot 4$ $C -^{1}\ \cdot 0.04\cdot 122 = 0.81\ (0.70)\ (2)\ 1.5\cdot 4$ $Ti - 2\cdot 0.04\cdot 20 = 1.60\ (1.63)$ $Sn -^{1}\ \cdot 0.04\cdot 107 = 0.17\ (0.15)\ 2\ 1.5\cdot 4$ $Hf - 4\cdot 0.04\cdot 17.18 = 2.72\ (2.5)$ $Pb -^{1} \cdot 0.04\cdot 34.4189 = 0.344\ (0.35(1)$ 4 $Pb -^{1}\ \cdot 0.04\cdot 34.4189 = 0.086\ (0.$ 126)(2) 2·4 $Pb -^{1} \cdot 0.04\cdot 34.4189 = 0.68\ (0.58)\ 2$	$K = 2;\ n = 5\ o\ e$ $P -^{1} \cdot 0.04\cdot 71.7 = 0.50\ (0.49)\ 5$ $P -^{1}\ \cdot 0.04\cdot 71.7 = 0.28\ (0.276)\ 2\cdot 5$ $N -^{1}\ \cdot 0.04\cdot 699 = 2.80\ (3.0)\ 2\cdot 5$ $N -^{1}\ \cdot 0.04\cdot 699 = 1.39\ (1.42)\ 4\cdot 5$ $V -^{1} \cdot 0.04\cdot 50 = 0.40\ (0.34)\ 5$ $V -^{1}\ \cdot 0.04\cdot 50 = 0.20\ (0.26)\ 2\cdot 5$ $V -^{1} \cdot 0.04\cdot 50 = 1\ (1)\ 2$ $AS -^{1}\ \cdot 0.04\cdot 78 = 0.30\ (0.23)\ 2\cdot 5$ $Nb -^{1} \cdot 0.04\cdot 88.516 = 1.18\ (1.0)\ 3$ $SB -^{1}\ \cdot 0.04\cdot 103 = 0.4\ (0.2)\ 2\cdot 5$ $Ta -^{1} \cdot 0.04\cdot 31 = 0.62\ (0.75)\ 2$	$K = 1,5;2\ n = 6\ o\ e$ $O -^{1.5} \cdot 0.04\cdot 141 = 1.20\ (1.22)\ 6$ $S -^{2} \cdot 0.04\cdot 200 = 0.60\ (0.50)\ 6$ $Se -^{1.5} \cdot 0.04\cdot 195 = 0.80\ (0.74)\ 6$ $Mo -^{1} \cdot 0.04\cdot 72.10 = 0.48\ (0.43)\ 6$ $Cr -^{1} \cdot 0.04\cdot 64 = 0.42\ (0.46)\ 6$ $Cr -^{1} \cdot 0.04\cdot 64 = 0.85\ (0.74)\ 3$
VII GROUP		
$K = 1,5;\ n = 7\ o\ e$ $F -^{1.5} \cdot 0.04\cdot 327.9 = 2.80\ 2\ 7$ $Cl -^{1}\ \cdot 0.04\cdot 348.8 = 1.32\ 2\ \ \ 1.5\cdot 7$ $Br -^{1}\ \cdot 0.04\cdot 325 = 1.23\ 2\ \ \ 1.5\cdot 7$ $I -^{1} \cdot 0.04\cdot 295 = 0.56\ 2\ \ \ 3\cdot 7$ $Mn -^{3} \cdot 0.04\cdot 50 = 0.85\ (0.90)\ 7$ $At -^{1}\ \cdot 0.04\cdot 233 = 0.88\ (1.0)\ 1.5\cdot 7$ General formula of electrode potential is the following: $0\ \ \ \ m\ \ \ \ n$ $\varphi = 0.04\cdot K\ \bullet n\ \bullet E - 1\ 0\ e\ e$ where n = 1; –1; –2; 0 ln = 1; –1; 2;	For the parts of lantanoid and actinoid is $K = 1.60\ 0$ $Tm -^{1}\ \cdot 0.04\cdot 99 = 2.47\ (2.40\ exp)$ 1.60 $Fm - 1.60\cdot 0.04\cdot 33.96 = 2.173\ (2.30)$ $Pu -^{1}\ \cdot 0.04\cdot 48.33 = 1.20\ (1.25)$ 1.60 $Md -^{1}\ \cdot 0.04\cdot 93.91 = 2.34\ (2.40)$ 1.60 $DY - 1.60\cdot 0.04\cdot 34 = 2.176\ (2.29)$ $Lr - 1.60\cdot 0.04\cdot 30.04 = 1.92\ (1.96)$ $Ho - 1.60\cdot 0.04\cdot 32.64 = 2.1\ (2.1)$ $BK -^{1}\ \cdot 0.04\cdot 165.24 = 2.60\ (2.80)2$ 1.60 $Yb - 1.60\ \cdot 0.04\cdot 50 = 2.60\ (2.76)$ $BS - 1.60\cdot 0.04\cdot 28.60 = 1.83$	

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 - Electron affinity, also K –; n - quantity; And on the right side of

e 0 e

the equation is the theoretically calculated electrode potential modulus --^{0} და And in the parentheses next to it is written the corresponding experimentally measured quantity - the modulus of the electrode potential. $\varphi_{ex}{}^{0}$ დადებითი მნიშვნელობები ;

მაგალითად H-სთვის

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

For Be $Ee = 48$; $ne = 2$; $K0 = 1{,}5$; $\varphi 0 = 2{,}88$; $\varphi ex\ 0 = 2{,}64$ And so on.

ve $0{,}04 \cdot K0\ m{\bullet}ne\ n \bullet E\ e = \varphi 0$ The latter formula includes both positive and negative values of electrode potential (in the case of negative potential $K_0^m \cdot n_e^n \cdot E_e$ multiplied by -1). In the table H means 2 − means 2+ 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 [2,3] meet well the theoretical data, which means that the theory is correct.

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

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

Where h is Planck's constant, approximately 0.04 : $C \approx 0.\ 04.\ 04$ 2

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

$$\frac{ch}{k_B} \cdot K_0^m \cdot n_e^n E_e = \varphi^0 \quad \text{figure - (1a)}$$

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: [4] - ΔG=$nF\varphi^0$ figure -(2)

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: figure - (3) where R is the universal gas constant, T is the temperature (in Kelvin) Combining formulas 2 and 3 gives us:

$$-\ nF\varphi = -\ RTlnK$$

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

$$-\ \frac{nFhcK_0^m n_e^n Ee}{K_B} = -\ RTlnK$$

From which the logarithm of the equilibrium constant LnK will be as follows:

$$-\ \frac{nFhcK_0^m n_e^n Ee}{K_B RT} = -\ lnK \qquad \text{figure - (3a)}$$

Let's express the logarithms (lnk_1; lnk_2) of the rate constants of a chemical reaction concerning temperature T_1 T_2 using the Arrhenius equation:

$$lnk_1 = -\frac{E_a}{R}\left(\frac{1}{T_1}\right) + lnA; \quad lnk_2 = -\frac{E_a}{R}\left(\frac{1}{T_2}\right) + lnA;$$

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

$$lnK = lnk_2 - lnk_1 = -\frac{E_a}{R}\left(\frac{1}{T_2}\right) + lnA - \left(-\frac{E_a}{R}\left(\frac{1}{T_1}\right) + lnA\right)$$

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

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

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

$$\frac{nFhcK_0^m n_e^n E_e}{K_B RT} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = (lnk - lnA)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)T \qquad \text{figure - (4)}$$

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

Van’t Hoff’s isochore: $dLnK/dT = -Q/RT^2$

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 equilibrum constant for AB+e(-)=AB(-)

$$LnKeqT^{3/2} = Ln[Qan] + Ln[S] + 12{,}43 + \frac{Ea}{RT}$$

Inserting (4) in this latter gives the equality:

$$\left(\frac{0{,}04nFK_0^m n_e^n Ee}{RT}\right)T^{3/2} = Ln(Qan) + Ln(S) + 12{,}43 + \frac{Ea}{RT} \quad \text{In which } \frac{hc}{k_B}\ 0{,}04$$

This equation shows that the electron affinity (Ee) 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

Table 1: Relative Bond Orders, Electron Affinities, and Activation Energies (In Ev)

	E (eV) (n = 0)	E (eV) (n = 0)	E (eV) literatur e	RBO literatur e	E (eV) (n = 1)	E (eV) (n = 1)	E (eV), literatur e	RBO literatur e
OXO	2.60(10)	0.65(2)	2.45	0.65	2.60(10)	0.65(2)	2.45	0.65
0-b-n	2.45(3)	0.65(2)	2.45	0.64	2.20	0.63(2)	2.20	0.60
1-b-n	2.00(3)	0.56(2)	2.00	0.64	1.80	0.43(2)	1.80	0.60

2b-n	1.60(3)	0.20(2)	1.55	0.69	1.40	0.20(2)	1.26	0.65
Referenc	twa	tw	[8,22,26]	tw	tw	tw	[8,22,26]	tw
es	1.03(3)	0.15(1)	1.06	0.31	0.80(3)	0.13(1)	0.72	0.25
0-a-n	0.65(3)	0.10(1)	0.65	0.30	0.45(3)	0.05(1)	0.45	0.27
1-a-n	0.25(3)	0.03(1)	0.15	0.37	0.10(3)	0.03(1)	0.10	0.33
2-a-n	0.10(5)	0.08(1)	0.05	0.06	0.08(5)	0.01(1)	0.05	0.06
0-C-n								
Referenc	tw	tw	[6-8,22]	tw	tw	tw	[6-8,22]	tw
es								
aThis work								

Above mentioned table and equality are given from the following scientific work: Electron affinities and activation energies for reactions with therminal electrons:

SF_5 *and* SF_6 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:

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

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

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

And in the equality: $LnK = Ln\frac{\alpha K_g T}{h} K_0^{\#} = LnK_0^{*} + Z_A Z_B\sqrt{\mu}$

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

$$LnK = Ln\frac{\alpha K_g T}{h} exp\left[-\frac{0{,}04 \cdot n \cdot F \cdot K_0^{m} \cdot n_s^{n} Ee}{RT}\right] = LnK_0^{s} + Z_A Z_B\sqrt{\mu}$$

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

In the following equality:

$$LnK_c = \sum_i V_i LnC_i$$

Considering (4) provides connection between electron affinity and concentration

(C) :

$$LnK_c = \frac{0{,}04 \cdot n \cdot F \cdot K_0^{m} \cdot n_s^{n} Ee}{RT} = \sum_i V_i LnC_i$$

Where K is the equilibrium constant.

The diffusion coefficient is expressed as follows:

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

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

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

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

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

$$\frac{dLnK}{dT} = \frac{E}{RT^2} \quad (7)$$

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

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

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

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

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

$$LnK = LnK^{*} = \frac{0{,}04 \cdot n \cdot F \cdot K_0^{m} \cdot n_s^{n} Ee}{RT} = const - \frac{E}{RT}$$

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 [1-5].

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