THE USE OF ELECTRON ACTIVITY CONCEPT IN THE CALCULATION OF OXIDATION REDUCTION EQUILIBRIA*

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The oxidation reduction process of a system can be described by the following general equation:

$$Ox + z\,e \rightleftharpoons Red \qquad (1)$$

where e denotes the electron, z the number of electrons taking part in the reaction. The process can be compared to acid-base reactions, since by uptake of protons an acid, while by liberation of protons a base is formed. Free protons are not present in aqueous solutions of acids and bases neither are free electrons in the solutions of oxidants and reductants.

The equilibrium constant of the oxidation reduction half reaction is

$$K^r = \frac{[Red]}{[Ox]\,[e]^z} \quad (I = const.) \qquad (2)$$

where [Red] and [Ox] are concentrations, while [e] is the electron activity, introduced by Jörgensen [1] and used by Pauling [2], Sillén [3], Johansson [4] etc. Since in dilute solutions the activities depend only on the ionic strength, the value of K^r belonging to a given ionic strength may be considered as constant.

The greater the value of K^r, the greater is the oxidation power of the system.

The negative logarithm of the electron activity, pe can be advantageously used in the description of oxidation reduction equilibria, similarly as the pH in the case of acid-base systems.

$$-\log [e] = pe \qquad (3)$$

From the logarithmic form of Eq. (2) pe can be expressed as:

* Dedicated to Professor L. Erdey on the occasion of his 60th birthday.

$$-\log[e] = pe = \underbrace{\frac{1}{z}\log K^r}_{pe^0} + \frac{1}{z}\log\frac{[\text{Ox}]}{[\text{Red}]} \tag{4}$$

pe is a measure of the reduction power of the medium, very likely to the pH which is a measure of the acidity in the solution. The greater the value of pe, the greater is the oxidation power of the medium.

The first term on the right hand side of Eq. (4) is the standard pe (pe^0) of the system.

The oxidation-reduction potential and pe are in close connection:

$$pe = \frac{E}{2,3\,RT/F} = \frac{E}{0,059} \quad (\text{at } 25\,^\circ\text{C}) \tag{5}$$

E denotes the oxidation-reduction potential in Volts. The standard oxidation-reduction potential of a system is related to the constant K^r as:

$$pe^0 = \frac{E^0}{0,059} = \frac{1}{z}\log K^r \tag{6}$$

It must be stressed, that the equations are to be modified if hydrogen ions also take part in the oxidation-reduction process. Thus

$$\text{Ox} + z\,e + n\,\text{H}^+ \rightleftharpoons \text{Red} + \frac{n}{2}\,\text{H}_2\text{O} \tag{7}$$
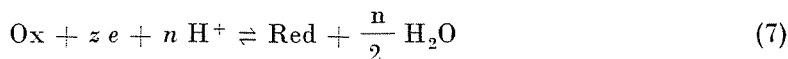
$$K^r = \frac{[\text{Red}]}{[\text{Ox}]\,[e]^z\,[\text{H}^+]^n} \tag{8}$$

$$pe = pe^0 + \frac{1}{z}\log\frac{[\text{Ox}]}{[\text{Red}]} - \frac{n}{z}\,\text{pH} \tag{9}$$

If pH = 0, equation (9) is identical with Eq. (4).

According to definition the value of K^r in the

$$\text{H}^+ + e \rightleftharpoons \frac{1}{2}\,\text{H}_2 \tag{10}$$

reaction is equal to 1. Hence pe^0 of the hydrogen couple is the 0 point of the pe scale.

In an *oxidation reduction titration* a reductant is titrated with an oxidizing agent or vice versa, and the end point of the titration is detected by colour change of an indicator or by potentiometric method.

Let us consider first the case when the titrant is an oxidant and the compound or ion to be determined is oxidized during titration:

$$y\,Ox_t + z\,Red_d \rightarrow y\,Red_t + z\,Ox_d \tag{11}$$
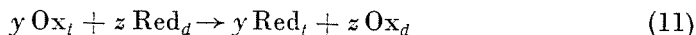
The oxidation reduction equilibria of the two systems involved are:

$$Ox_t + z\,e \rightleftharpoons Red_t \quad \text{(titrant)} \tag{12}$$

$$Ox_d + y\,e \rightleftharpoons Red_d \quad \text{(determined)} \tag{13}$$
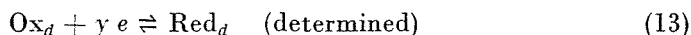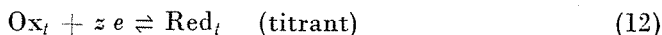
Plotting pe against the volume of titrant during an oxidimetric titration, a curve very similar to those in pH-metric titrations is obtained. The shape of the curve depends on the K^r values of the systems involved and on the number of electrons exchanged.

In the equivalence point

$$y\,[Ox_t]_{eq} + y\,[Red_t]_{eq} = z\,[Ox_d]_{eq} + z\,[Red_d]_{eq} \tag{14}$$

Assuming that the species to be determined was completely in reduced form before titration (which is a fundamental criterion of a quantitative determination), the following equation is also valid:

$$y\,[Red_t] = z\,[Ox_d] \tag{15}$$

Using the equilibrium formulas of the systems:

$$[Ox_t] = \frac{[Red_t]}{K_t^r\,[e]^z} \tag{16}$$

$$[Red_d] = K_d^r\,[Ox_d]\,[e]^y \tag{17}$$

Eq. (14) can be transformed:

$$\frac{1}{K_t^r\,[e]_{eq}^z} = K_d^r\,[e]_{eq}^y \tag{18}$$

From the logarithmic form of Eq. (18) pe of the equivalence point can be expressed as:

$$pe_{eq} = -\log\,[e]_{eq} = \frac{1}{z+y}\,(\log K_t^r + \log_d^r) \tag{19}$$

If pe at the end point of the titration is not the same as at the equivalence point (i.e. $pe_{end} \gtrless pe_{eq}$), titration error arises.

To express the relative titration error in per cent we use the following formula:

$$\triangle \% = 100 \left(\frac{y\,C_t - z\,C_d}{z\,C_d} \right) \tag{20}$$

where C_t and C_d are the total concentrations of the titrant and the substance to be determined, respectively, in the solution at the end point of the titration:

$$C_t = [\mathrm{Ox}_t] + [\mathrm{Red}_t] \tag{21}$$

$$C_d = [\mathrm{Ox}_d] + [\mathrm{Red}_d] \tag{22}$$

Using Eqs (15), (16), (17), (20), (21), (22), we obtain:

$$\triangle \% = 100 \;\; \frac{\dfrac{1}{K_t^r\,[e]^z} - K_d^r\,[e]^y}{1 + K_d^r\,[e]^y} \tag{23}$$

Since in the vicinity of the equivalence point $K_d^r\,[e]^y \ll 1$, the second term in the denominator can be neglected and the formula simplified:

$$\triangle \% \approx 100 \left(\frac{1}{K_t^r\,[e]^z} - K_d^r\,[e]^y \right) \tag{24}$$

On the basis of this equation one can conclude that the error is independent of the concentration of the components at first approximation, and depends only on the K^r values and on the electron activity at the end point. Actually the error is not independent of concentrations, since the constant K^r is dependent on the ionic strength of the solution.

If the titrant is a reductant and an oxidizing agent is titrated, formula (24) can be used, only the signs of the two terms in bracket must be changed.

Using the deduced formula (24) we calculated the titration errors at different pe values in the titration of iron(II)ions with potassium dichromate and in the titration of thallium(III)ions with ascorbic acid standard solution. The logarithmic diagram of the errors calculated can be seen in Fig. 1. Where $\varDelta = 0$, $\log \varDelta = -\infty$, there is the equivalence point. The former titration is "symmetrical", while the latter "unsymmetrical". The values of the constant used are: $\log K_{Tl}^{r} = 21.58$; $\log K_A^{r} = 5.45$ (pH 4); $\log K_{Fe}^{r} = 13.0$; $\log K_{Cr_2O_7}^{r} = 67.5$.

The equations of the straight lines (broken lines) in Fig. 1 are as follows:

$$\log \varDelta' = \log K_d^r + 2 - y\,pe \tag{25}$$

$$\log \Delta'' = z \; pe + 2 - \log K_t^r \tag{26}$$

The pe belonging to the intersection:

$$pe = \frac{1}{z+y} \left(\log K_t^r + \log K_d^r \right) \tag{27}$$

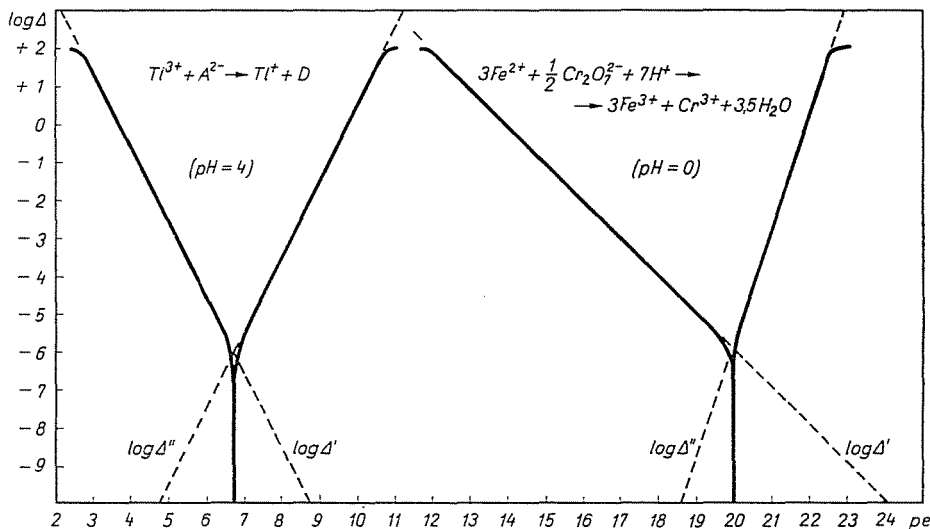gives the equivalence point. (See equation (19).)

Fig. 1. Logarithmic diagram of the titration error in the titration of thallium(III)ions with ascorbic acid and in the titration of iron(II)ions with potassium dichromate standard solution

The *criterion of the quantitative titration* can be deduced if we consider that the species to be determined must be oxidized (or reduced) during the titration to an extent of 99.9%. This means that

$$\log \frac{[Ox_d]}{[Red_d]} > 3 \tag{28}$$

$$pe_{eq} > \frac{1}{y} \log K_d^r + \frac{1}{y} 3 \tag{29}$$

(see Eq. (4)). Using also Eq. (19) we obtain:

$$y \log K_t^r - z \log K_d^r > 3 (z + y) \tag{30}$$

or

$$E_t^0 - E_d^0 > 0{,}18 \; \frac{z+y}{z \cdot y} \qquad \text{Volt} \tag{31}$$

If both the oxidant and reductant in the titration involve the exchange of two electrons per mole (e.g. in the titration of thallium(III)ions with ascorbic acid) the difference between the log K^r values must be greater than 6, i.e. the difference between the standard oxidation reduction potentials greater than 0.18 V, if quantitative determination is required.

By the use of the electron activity concept and "conditional equilibrium constants" it is very convenient to calculate the optimum conditions for titrations also in cases, where the reduced or **oxidized** form of the systems reacts in side reaction with complex forming agents or with protons. The conditional oxidation reduction equilibrium constants can be used similarly to those introduced and used by SCHWARZENBACH [5] and RINGBOM [6] in the chemistry of complexes.

The *conditional oxidation reduction constant* is

$$K^{r_,} = \frac{[\text{Red'}]}{[\text{Ox'}]\,[e]^z} \tag{32}$$

where [Red'] and [Ox'] denote analytical concentrations without any respect to side reactions. The connection between the conditional and real constant:

$$K^{r_,} = K^r \frac{\alpha_{\text{Red}(A)}}{\alpha_{\text{Ox}(B)}} \tag{33}$$

Where $\alpha_{\text{Red}(A)}$ and $\alpha_{\text{Ox}(B)}$ are the side reaction functions:

$$\alpha_{\text{Red}(A)} = 1 + [A]\,\beta_1 + [A]^2\,\beta_2 + \ldots \tag{34}$$

$$\alpha_{\text{Ox}(B)} = 1 + [B]\,\gamma_1 + [B]^2\,\gamma_2 + \ldots \tag{35}$$

[A] and [B] are concentrations of the species reacting with the reduced and oxidized form of the substance resp. β-s and γ-s are complex products or protonization constant products.

Eq. (4) will be modified:

$$pe = \underbrace{pe^0 + \frac{1}{z}\log\frac{\alpha_{\text{Red}(A)}}{\alpha_{\text{Ox}(B)}}}_{pe^{0_,}} + \frac{1}{z}\log\frac{[\text{Ox'}]}{[\text{Red'}]} \tag{36}$$

where $pe^0_,$ is the new "conditional" standard *pe*.

If the criterion of the quantitative determination is not fulfilled, by suitable pH change or by the use of complexing agent — shifting the values of conditional constants — the titration may be realized.

Examples

1. Calculate the *pe* in the transition point of the indicator Variamine Blue in solutions of pH 4, at a concentration of 10^{-4} mole/l; the blue colour of the oxidized form is noticeable if $[Ox'] \sim 10^{-5}$ mole/l.

The indicator redox system and the corresponding equilibrium constant [7] are:

$$V_{Ox} + 2e + 2H^+ \rightleftharpoons V_{Red} \qquad \log K_V^r = 24.8$$
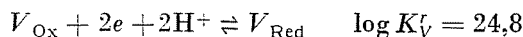
Both the reduced and oxidized form of the indicator take up proton in acidic medium. The protonation constants are: $\log K_{Red} = 5.9$; $\log K_{Ox} = 6.6$ [7]. The indicator in the reduced form is colourless not depending on protonation, while in oxidized form the unprotonated species is yellow, the protonated species blue in solution. The indicator can be used therefore only in solutions of pH < 6.

Answer: In a solution of pH 4, the protonation side reaction functions are:

$$\alpha_{V_{Red}(H)} = 1 + 10^{-4} \cdot 10^{5.9} = 10^{1.9}$$

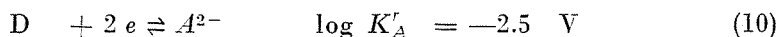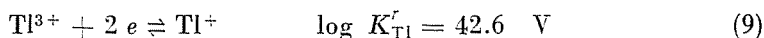$$\alpha_{V_{Ox}(H)} = 1 + 10^{-4} \cdot 10^{6.6} = 10^{2.6}$$

Using Eqs (9) and (36) we have:

$$pe = pe^0 + \frac{1}{2} \log \frac{\alpha_{V_{Red}(H)}}{\alpha_{V_{Ox}(H)}} + \frac{1}{2} \log \frac{[V_{Ox}']}{[V_{Red}']} - pH =$$

$$= 12.4 + \frac{1}{2}(1.9 - 2.6) + \frac{1}{2} \log \frac{10^{-5}}{9 \times 10^{-5}} - 4 = 7.58 \quad (pH = 4)$$

2. Calculate the indicator error in the titration of thallium(III)ions, if as titrant ascorbic acid standard solution, as indicator Variamine Blue is used. According to ERDEY, VIGH and BUZÁS [8] the solution investigated is treated with bromine water and after removing excess bromine with formic acid, the pH of the solution is buffered to pH 4.
The concentration of bromide ions in solution is ca 10^{-1} mole/l.

The equilibrium constants of the two systems are

$$Tl^{3+} + 2e \rightleftharpoons Tl^+ \qquad \log K_{Tl}^r = 42.6 \quad V \tag{9}$$

$$D + 2e \rightleftharpoons A^{2-} \qquad \log K_A^r = -2.5 \quad V \tag{10}$$

The complex products of the bromo-thallium(III) complexes; $\log \beta_1 = 8.3$; $\log \beta_2 = 14.6$; $\log \beta_3 = 19.2$; $\log \beta_4 = 22.3$; $\log \beta_5 = 24.8$; $\log \beta_6 = 26.5$ (11).

Those of hydroxo-thallium complexes: $\log \gamma_1 = 12.9$; $\log \gamma_2 = 25.4$ (12), those of bromo-thallium(I)complexes: $\log \beta_1 = 0.92$; $\log \beta_2 = 0.92$; $\log \beta_3 = 0.40$ (13). The protonation constants of ascorbate ion: $\log K_1 = 11.56$; $\log K_2 = 4.17$ (14). The transition point of the indicator in solution of pH 4 is $pe = 7.58$ (see Example 1).

Answer: We calculate first the side reaction function values, then the conditional constants of the two systems, finally the indicator error [see equations (34), (35), (33) and (24)].

$$\alpha_{Tl\ III(Br)} = 1 + 10^{-1} \cdot 10^{8.3} + 10^{-2} \cdot 10^{14.6} + 10^{-3} \cdot 10^{19.2} + 10^{-4} \cdot 10^{22.3} +$$
$$+ 10^{-5} \cdot 10^{24.8} + 10^{-6} \cdot 10^{26.5} = 10^{21.3}$$

$$\alpha_{Tl\ III(OH)} = 1 + 10^{-10} \cdot 10^{12.9} + 10^{-20} \cdot 10^{25.4} = 10^{5.4}$$

$$\alpha_{Tl\ III} = 10^{21.3} + 10^{5.4} - 1 \sim 10^{21.3}$$

$$\alpha_{Tl\ I(Br)} = 1 + 10^{-1} \cdot 10^{0.92} + 10^{-2} \cdot 10^{0.92} + 10^{-3} \cdot 10^{0.40} = 10^{0.28}$$

$$\alpha_{A(H)} = 1 + 10^{-4} \cdot 10^{11.56} + 10^{-8} \cdot 10^{15.73} = 10^{7.95}$$

The conditional constant of the thallium(III)—thallium(I) and of dehydroascorbic acid—ascorbate couple:

$$\log K_{Tl}^{r} = 42.6 + 0.28 - 21.3 = 21.58$$

$$\log K_{A}^{r} = -2.5 + 7.95 = 5.45$$

The indicator error:

$$= 10^2 \, 10^{5.45} (10^{-7.58})^2 - \frac{1}{10^{21.58} (10^{-7.58})^2} = -3.8 \cdot 10^{-5} \%$$

The indicator used is very suitable to the titration.
The equivalence point according to Eq. (19):

$$pe_{eq} = \frac{1}{4} (21.58 + 5.45) = 6.76$$

Summary

Equations are deduced for calculation of errors and optimum conditions of oxidation reduction titrations using the electron activity concept — first introduced by Jörgensen — and conditional equilibrium constants, which are similar to those used in complex chemistry. Two worked examples are also presented.

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