Fig. 2. Excess molar Gibbs energy of mixing in the system KBF_4—KF—KCl. The isoenergy values are in J mol^{-1}.

borate anions as well as the extent of the reaction (*A*) may be determined only by means of other methods.

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Generalizing View on Reduction of Some Cu(II) Complexes

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Dedicated to Professor V. Gutmann, in honour of his 70th birthday

A general expression describing certain redox processes, in which Cu(II) complexes with the ligands having a reducing and stabilizing influence on the central atom take part, has been derived. The obtained results qualitatively describe the redox processes and enable to obtain by means of some known data also their quantitative evaluation.

It is known that the copper(II) complexes in the presence of some ligands undergo the redox processes in which the central atom is reduced to Cu(I). However, in the presence of the other ligands, central atom is not reduced. This phenomenon was mainly observed at the preparation of Cu(I), Cu(II), and Cu(I)—Cu(II) complexes [1], when the Cu(II) complexes with certain types of ligands could be prepared only under some conditions [2].

On the basis of the experimental results, the ligands in the redox processes of the Cu(II) complexes can be approximately divided [3] into two groups: The ligands which cause the reduction of the central atom (Lr) and the ligands which do not exert this influence on Cu(II) and it can be stated that they stabilize the oxidation state of copper(II) (Ls). As an example of the Lr ligands the following ones can be given: Cl^- [4—7], Br^- [8, 9], I^- [10, 11], NC^- [12, 13], NCS^- [14, 15],
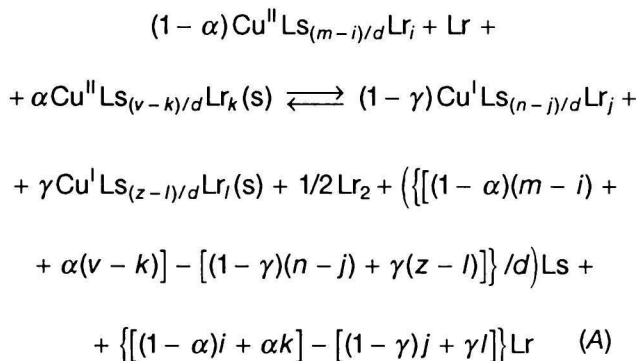
and S-donor ligands with C=S [16, 17] and thiolate [18, 19] groups.

For instance, in the role of Ls ligands can be some molecules of solvents as water [20], acetonitrile [6, 7], dimethyl sulfoxide [21], acetone [4, 22], and also bi- or polydentate ligands with nitrogen, oxygen, or sulfur donor atoms which form relatively stable complexes with Cu(II) [23—25]. These ligands can be in the coordination sphere of Cu(II) together with the Lr ligands without the observed reduction of the central atom [23—30].

The aim of this work is to give by means of thermodynamics an unifying view on the feasibility of the processes with the Cu(II) compounds in which the reduction of the Cu(II) atom can or need not occur.

THEORETICAL

The course of some observed redox processes involving the Cu(II) complexes may be generally described by the chemical equation

$$(1 - \alpha)Cu^{II}Ls_{(m-i)/d}Lr_i + Lr +$$

$$+ \alpha Cu^{II}Ls_{(v-k)/d}Lr_k(s) \rightleftharpoons (1 - \gamma)Cu^ILs_{(n-j)/d}Lr_j +$$

$$+ \gamma Cu^ILs_{(z-l)/d}Lr_l(s) + 1/2 Lr_2 + (\{[(1 - \alpha)(m - i) +$$

$$+ \alpha(v - k)] - [(1 - \gamma)(n - j) + \gamma(z - l)]\}/d)Ls +$$

$$+ \{[(1 - \alpha)i + \alpha k] - [(1 - \gamma)j + \gamma l]\}Lr \quad (A)$$

where $i \in <0, m>$, $j \in <0, n>$, m and n are the maximal coordination numbers of the central atoms, d is the donicity of the Lr ligand (the Lr ligands are always considered as monodentate), α, $\gamma \in \{0, 1\}$ that implies the possibility of the reaction of an insoluble (slightly soluble; $\alpha = 1$) or soluble ($\alpha = 0$) copper(II) compound to yield an insoluble ($\gamma = 1$) or soluble ($\gamma = 0$) copper(I) compound, $k \in <1, m>$, $v \in <k, m>$, $l \in <1, n>$, $z \in <l, n>$. The charge of particles in eqn (A) is not considered and it will not be taken into account in the following chemical equations, either.

The chemical reaction (A) is regarded as algebraical combination of the subsequent processes with the corresponding standard-state Gibbs energy change $\Delta G°$:
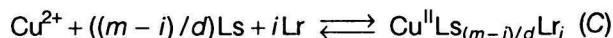
1. Redox process

$$Cu^{2+} + Lr \rightleftharpoons Cu^+ + 1/2 Lr_2 \quad (B)$$
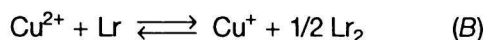
$$\Delta G_r° = -nF\Delta E° = -RT \ln K_r \quad (1)$$

$$\Delta E° = E°(Cu^{2+}/Cu^+) - E°(Lr_2/Lr) \quad (2)$$

2. Formation of the Cu(II) and Cu(I) complexes with the Ls and Lr ligands

Cu(II) complexes

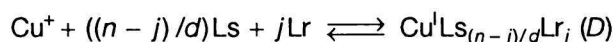$$Cu^{2+} + ((m - i)/d)Ls + iLr \rightleftharpoons Cu^{II}Ls_{(m-i)/d}Lr_i \quad (C)$$

$$\Delta G_c^{o\,II} = -RT \ln \beta_{(m-i)/d,\,i}^{(II)Ls,\,Lr} \quad (3)$$

where $\beta_{(m-i)/d,\,i}^{(II)Ls,\,Lr}$ is overall stability constant of the Cu(II) ion with $(m - i)/d$ Ls and i Lr ligands.
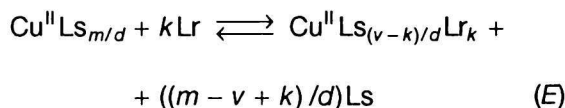
Cu(I) complexes

$$Cu^+ + ((n - j)/d)Ls + jLr \rightleftharpoons Cu^ILs_{(n-j)/d}Lr_j \quad (D)$$

$$\Delta G_c^{o\,I} = -RT \ln \beta_{(n-j)/d,\,j}^{(I)Ls,\,Lr} \quad (4)$$

where $\beta_{(n-j)/d,\,j}^{(I)Ls,\,Lr}$ is overall stability constant of the Cu(I) ion with $(n - j)/d$ Ls and j Lr ligands.

3. Formation of the insoluble Cu(II) and Cu(I) compounds

Insoluble Cu(II) compound

$$Cu^{II}Ls_{m/d} + kLr \rightleftharpoons Cu^{II}Ls_{(v-k)/d}Lr_k +$$

$$+ ((m - v + k)/d)Ls \quad (E)$$

$$\Delta G_p^{o\,II} = RT[\ln S(Cu^{II}Ls_{(v-k)/d}Lr_k) + \ln \beta_{m/d}^{(II)Ls}] \quad (5)$$

where $S(Cu^{II}Ls_{(v-k)/d}Lr_k)$ is solubility product constant of the insoluble Cu(II) compound and $\beta_{m/d}^{(II)Ls}$ is overall stability constant of the Cu(II) ion with m/d Ls ligands.

Insoluble Cu(I) compound

$$Cu^ILs_{n/d} + lLr \rightleftharpoons Cu^ILs_{(z-l)/d}Lr_l +$$

$$+ ((n - z + l)/d)Ls \quad (F)$$
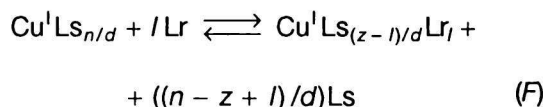
$$\Delta G_p^{o\,I} = RT[\ln S(Cu^ILs_{(z-l)/d}Lr_l) + \ln \beta_{n/d}^{(I)Ls}] \quad (6)$$

where $S(Cu^ILs_{(z-l)/d}Lr_l)$ is the solubility product constant of the insoluble Cu(I) compound and $\beta_{n/d}^{(I)Ls}$ is overall stability constant of the Cu(I) ion with n/d Ls ligands.

The equilibrium constant of the chemical reaction (A) $K_{j,i}$, can be considered as an extent of the feasibility of the reaction. The logarithm of the constant is

$$\ln K_{j,i} = \ln K_r + (1 - \gamma) \ln \beta_{(n-j)/d, j}^{(I)Ls, Lr} -$$

$$- \gamma \left[\ln S(Cu^I Ls_{(z-j)/d} Lr_j) + \ln \beta_{n/d}^{(I)Ls} \right] -$$

$$- (1 - \alpha) \ln \beta_{(m-i)/d, i}^{(II)Ls, Lr} +$$

$$+ \alpha \left[\ln S(Cu^I Ls_{(v-k)/d} Lr_k + \ln \beta_{m/d}^{(II)Ls} \right] \quad (7)$$

where the indices j and i express the number of the Lr ligands in the Cu(I) and Cu(II) compounds of the considered redox reaction.

From eqn (7) it follows that the feasibility of the chemical reaction (A) depends on: the redox properties of the system Lr_2/Lr characterized by the standard electrode potential; the stability of the Cu(II) and Cu(I) complexes with the Ls and Lr ligands characterized by the overall stability constant; the solubility of the Cu(II) and Cu(I) compounds characterized by the solubility product constant.

It means that the feasibility of any redox reaction (A) is positively influenced with the redox system Lr_2/Lr with the small value of the standard electrode potential, great value of the overall stability constant of the Cu(I) complexes, and small value of the solubility product constant of the insoluble Cu(I) compounds. The feasibility of the reaction (A) is negatively influenced with great stability of the Cu(II) complexes and small solubility of the slightly soluble (insoluble) Cu(I) compounds.

The reduction of the Cu(II) complex, where Ls = H_2O, $d = 1$, $\alpha = 0$, and Lr = Cl^-, Br^-, NCS^- I^- CN^-, respectively, in which the insoluble Cu(I) compound CuLr ($\gamma = 1$, $l = z = 1$) is formed, can be according to the chemical equation (A) written

$$Cu^{II} Ls_{(m-i)} Lr_i + Lr \rightleftharpoons Cu^I Lr(s) + 1/2 Lr_2 +$$

$$+ (m - i)Ls + (i - 1)Lr \quad (G)$$
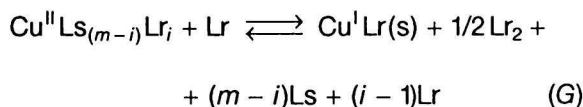
The logarithm of the equilibrium constant according to eqn (7) is

$$\log K_{1,i}^{p,c} = \log K_r - \log S(CuLr) - \log \beta_i^{(II)Lr} \quad (8)$$

where indices in the upper part of the constant express the type of the Cu(I) and Cu(II) compounds in the redox process (p — precipitation, c — complex). From the $\log K_{1,i}^{p,c}$ values summarized in Table 1 it is possible to consider the feasibility of the reactions (G) quantitatively.

The reduction of the Cu(II) complex, where Ls = H_2O, $d = 1$, $\alpha = 0$ and Lr = Cl^- Br^-, NCS^-, I^-, thiourea (tu) , CN^-, respectively, in which the $CuLr_j$ complex ($\gamma = 0$) is formed, is expressed by the chemical equation

Table 1. The log $K_{1,j}^{p,c}$ Values of the Reaction (G) for Ls = H_2O

Lr	log $K_{1,0}^{p,c}$	log $K_{1,1}^{p,c}$	log $K_{1,2}^{p,c}$	log $K_{1,3}^{p,c}$	log $K_{1,4}^{p,c}$
Cl^-	− 12.9	− 13.0	− 13.6	− 13.1	− 12.8
Br^-	− 6.4	− 5.9	–	–	–
NCS^-	4.4	2.6	1.6	–	–
I^-	6.3	–	–	–	–
CN^-	25.4	–	–	–	–

The log $K_{1,j}^{p,c}$ values were calculated with the standard electrode potentials [31], solubility product constant [32], and Cu(II) complex stability constants [33—35].

$$Cu^{II} Ls_{(m-i)} Lr_i + Lr \rightleftharpoons CuLr_j + 1/2 Lr_2 +$$

$$+ (m - i)Ls + (i - j)Lr \quad (H)$$
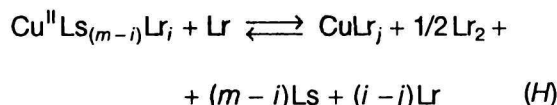
The logarithm of the equilibrium constant is

$$\log K_{j,i}^{c,c} = \log K_r + \log \beta_j^{(I)Lr} - \log \beta_i^{(II)Lr} \quad (9)$$

The log $K_{j,i}^{c,c}$ values summarized in Table 2 give the possibility to consider the feasibility of the reactions (H) quantitatively.

By the substitution of the first two members in eqn (9) for $\log K_{j,0}^{c,c}$ we get

$$\log K_{j,i}^{c,c} = \log K_{j,0}^{c,c} - \log \beta_i^{(II)Lr} \quad (10)$$

A plot of $\log K_{j,0}^{c,c}$ vs. $\log \beta_i^{(II)Lr}$ for Lr = Cl^-, Br^-, NCS^- I^- tu, CN^-, respectively, Ls = H_2O and $j = 2$ shows the influence of the Cu(II) complex stability (with the Lr ligand) on the feasibility of the reactions (H) (Fig. 1).

The log $K_{j,i}^{c,c}$ values of the reaction (H), when Ls = acetonitrile (AN) or dimethyl sulfoxide (DMSO), and Lr = Cl^-, Br^-, NCS^- I^-, respectively, are summarized in Tables 3 and 4. It was observed

Table 2. The log $K_{j,i}^{c,c}$ Values of the Reaction (H) for Ls = H_2O

Lr	i	log $K_{1,i}^{c,c}$	log $K_{2,i}^{c,c}$	log $K_{3,i}^{c,c}$	log $K_{4,i}^{c,c}$
Cl^-	0	–	− 14.24	− 14.31	–
	1	–	− 14.30	− 14.37	–
	2	–	− 14.91	− 14.88	–
	3	–	− 14.44	− 14.51	–
	4	–	− 13.47	− 13.54	–
Br^-	0	–	− 9.02	− 7.85	–
	1	–	− 8.25	− 7.30	–
NCS^-	0	–	0.60	1.20	1.63
	1	–	− 2.34	− 0.54	− 0.11
	2	–	− 3.34	− 1.54	− 1.11
I^-	0	–	2.30	4.03	3.00
tu	0	5.80	8.60	11.50	13.70
CN^-	0	–	27.60	32.70	33.80

The log $K_{j,i}^{c,c}$ values were calculated with the standard electrode potentials [31], Cu(I) complexes stability constants [32, 36—38], and Cu(II) complex stability constants [33—35].
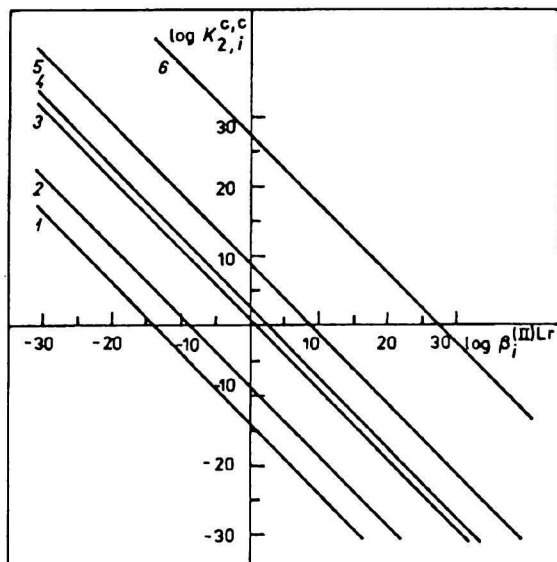
Fig. 1. The dependence of log $K_{2,j}^{c,c}$ (reaction (H)) vs. log $\beta_j^{(II)Lr}$ (eqn (10)) for Ls = H_2O and Lr = Cl^- (1), Br^- (2), NCS^- (3), I^- (4), tu (5), CN^- (6).

Table 3. The log $K_{j,i}^{c,c}$ Values of the Reaction (H) for Ls = AN

Lr	i	log $K_{1,j}^{c,c}$	log $K_{2,j}^{c,c}$
Cl^-	0	− 3.3	2.7
	1	− 13.0	− 7.0
	2	− 20.9	− 14.9
	3	− 28.7	− 22.0
	4	− 31.7	− 25.7
Br^-	0	− 7.58	− 3.66
NCS^-	0	− 3.38	0.22
	2	− 10.98	− 7.38
I^-	0	− 1.86	1.34

The log $K_{j,i}^{c,c}$ values were calculated by means of the standard electrode potentials of Cu^{2+}/Cu^+ and Cl_2/Cl^- [39], Br_2/Br^- and I_2/I^- [40], $(NCS)_2/NCS^-$ (it was calculated from ΔG_f°) [41], Cu(I) complex stability constants [42, 43], and Cu(II) complex stability constants [44, 45].

Table 4. The log $K_{j,i}^{c,c}$ Values of the Reaction (H) for Ls = DMSO

Lr	i	log $K_{1,j}^{c,c}$	log $K_{2,j}^{c,c}$	log $K_{3,j}^{c,c}$
Cl^-	0	− 5.34	− 0.84	− 0.25
	1	− 8.77	− 4.27	− 3.67
	2	− 11.47	− 6.97	− 6.38
	3	− 13.73	− 9.23	− 8.64
	4	− 15.53	− 11.03	− 10.44
Br^-	0	− 2.98	0.77	−
	1	− 6.38	− 2.63	−
	2	− 7.28	− 3.53	−
NCS^-	0	− 0.94	4.06	−
	1	− 4.14	0.86	−
	2	− 6.24	− 1.24	−
I^-	0	4.43	7.13	−

The log $K_{j,i}^{c,c}$ values were calculated by means of the standard electrode potentials of Cu^{2+}/Cu^+ [40] and the other redox systems calculated from ΔG_f° [41], Cu(I) complex stability constants [46, 47], and Cu(II) complex stability constants [48, 49].

that the chlorocopper(II) complexes are reduced in acetonitrile at certain conditions [6, 7], but their reduction was not observed in dimethyl sulfoxide [21]. The reduction of Cu(II) with iodide ion was also observed in acetonitrile [11].

CONCLUSION

The generalization of the experimental data, considering the reduction or stabilization of some Cu(II) complexes with the reducing ligands in coordination sphere, has shown that the course of the redox processes may be qualitatively described by means of the thermodynamic quantities of the individual reactants and products. In the case when necessary data are accessible the characterization of the redox processes involving Cu(II) compounds can be also expressed quantitatively.

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Determination of Trace Lead in Human Urine Using Hanging Mercury Drop Semimicroelectrode Influence of Matrix Effect and Its Elimination

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Trace amounts of Pb were determined in human urine by anodic stripping voltammetry on hanging mercury drop electrode. Two types of electrodes were used: electrode of conventional dimension ($r = 440$ μm) and semimicroelectrode ($r = 40$ μm). Described is the possibility of simplification of the experiment and minimization of the sample volume and of time-consuming irradiation and deaeration by using the semimicroelectrode. Good precision and accuracy were obtained when using the simplified short procedure.

Determination of trace and ultratrace amount of metals in the human body and liquids is now assuming increasing importance in clinical analysis. In all of the analytical methods for metals determination it is necessary to consider the influence of matrix, which in the case of urine is formed largely by organic species. It can have a substantial influence on accuracy of determination. Some authors use mineralization with acids for decomposition of organic species in human urine samples which can lead to a contamination of the sample [1, 2]. A suitable procedure avoiding such a contamination is the method of *Batley* and *Farrar* [3] using low-energy UV or high-energy γ irradiations for decomposition of organic matter.

Anodic stripping voltammetry (ASV) belongs to the most suitable methods for determination of low concentrations of metals. *Copeland* and co-