FACTORS DETERMINING STABILITY OF CERTAIN TYPES OF COMPLEX COMPOUNDS IN AQUEOUS SOLUTIONS

K. B. Yatsimirksy

There has accumulated during the last few years quite a significant amount of material on the stability of complex compounds in aqueous solutions. Instability constants have been determined for 700-800 complex ions. The existence of such a tremendous mass of factual material makes it possible to pose the question of elucidation of factors determining stability of the groups of complex compounds which have received the most study. Those complex compounds are considered whose central atoms can form stable hydrated ions (complex compounds of silver, copper, aluminum and other metals). Complex compounds of platinum, gold antimony, tetravalent lead, and some of the platinum group metals, on dissociation in aqueous solutions, do not form hydrated ions and are not considered in this paper.

For complex compounds forming hydrated ions upon dissociation, the chemical bond approximates the ionic type, the central atom preserving the properties of the ions to a considerable extent, and in such cases central atoms can be mentioned as well as central ions.

The stability of complex compounds with some additives, for the cases investigated, is determined by such characteristics of the central ions as charge, radius, and its polarizability (ability to deform the electronic shell of the additive atoms, with tendency to covalent bond formation). To clarify the role of various factors, it was expedient to investigate a group of complex ions with the same additives in which only one characteristic of the central ions is changing (charge, radius or polarizing action), and two others of approximately the same stability.*

In order to elucidate the effect of charge upon the stability of complex compounds, three sets of cations of approximately the same dimensions were chosen: 1) Na^+, Ca^{2+}, Y^{3+}, Th^{4+} (cation radius $r_c = 1.04 \pm 0.06$ A), 2) K^+, Sr^{2+}, La^{3+} ($r_c = 1.27 \pm 0.06$ A) and 3) Ag^+, Hg^{2+}, Tl^{3+} ($r_c = 1.09 \pm 0.04$ A).

In the first two sets, the cations possess a complete shell of eight electrons and low oxidizing potential, and in the third set the cations possess a shell of eighteen electrons, with approximately the same oxidizing potential (about 0.8 v.). It can be assumed that in a related series the polarizing action of the cations is approximately the same.

In Table 1 are given values for the indices of instability constants ($pK = -\log K_{instab.}$) for the three series of ions. In almost all cases, pK increases with increase in charge. Particularly noticeable is the increase in pK with low or highly charged additives. The stability of complexes with large amounts of additives of low charge changes but little with a change in charge of the central ion (complex iodides, bromides, nitrates, and others).

The change in pK with change in charge proceeds so regularly that in some cases interpolation is possible. Thus, for example, values for the instability constant indices of nitrate and iodate complexes of yttrium can be evaluated: For YNO_3^{2+} $pK = 0.45 \pm 0.07$, for YIO_3^{2+} $pK = 1.9 \pm 0.3$.

To clarify the effects of other factors upon the stability of complex compounds, we might examine a little more closely the function which the author, together with Grinberg, developed [4]. It was demonstrated that the thermal effect of MA_n complex formation in aqueous solutions of a central ion, M, and additive, A, can be represented by the following equation:

$$\Delta H = W_{aq} - W_c + \text{const}_1, \qquad (1)$$

where W_{aq} and W_c = respectively, the energy of addition of nH_2O molecules and n particles of A to the central ion. It was indicated earlier [5] that the energy of addition can be presented as a sum of two factors: the energy of electrostatic attraction (W^i) and the polarization energy (P). Equation (1) can therefore be modified in the following manner:

$$\Delta H = W^i_{aq} - W^i_c + P_{aq} - P_c, + \text{const}_1. \qquad (2)$$

* Values for instability constants are taken from the author's review article [1] and other reviews [2,3].

TABLE 1

Indices of Instability Constants for a Series of Ions with Alternating Charge

Types of complex ions	pK for the charge of the central ions (Z)			
	+1	+2	+3	+4
	K^+ Sr^{2+} La^{3+}			
ROH^{Z-1}	(−0.7)	1.0	3.3	-
$RS_2O_3^{Z-2}$	0.1	2.0	-	-
$RP_3O_9^{Z-3}$	1.2	3.4	5.7	-
$RFe(CN)_6^{Z-3}$	1.2	2.8	3.7	-
	Na^+, Ca^{2+}, Y^{3+}, Th^{4+}			
RIO_3^{Z-1}	-	0.9	-	2.9
RNO_3^{Z-1}	-	0.3	-	0.6
RSO_4^{Z-2}	0.7	2.3	3.5	4.1
$RC_2O_4^{Z-2}$	-	3.0	7.3	-
$REdta^{Z-4}$*	-	11.1	18.0	-
	Ag^+, Hg^{2+}, Ti^{3+}			
ROH^{Z-1}	2.3	10.3	14.8	-
RNH_3^{Z}	3.2	8.8	-	-
RCl^{Z-1}	2.7	5.3	8.1	-
RBr^{Z-1}	9	9.1	9.7	-

The polarization energy is calculated by means of an empirical equation of the type

$$P = n\beta\alpha\rho \qquad (3)$$

where α = polarizability of the additives, ρ = polarizing action of the cation, β = a coefficient, being determined by the additive dimensions and those of the central ion. Whereupon,

$$P_c - P_{aq} = n(\beta_c \alpha_A - \beta_{aq} \alpha_{H_2O})\rho, \qquad (4)$$

The value in parentheses is related to the relative polarizability of additive A, and will be symbolized as b'. The b' value depends not only upon the ratio between the polarizabilities of the additive and of the water (α_A and α_{H_2O}), but also depends upon the dimensions of the central ions and of the additives.

For acid complexes, we then have

$$\Delta H = \frac{A}{(r + r_W)^2} - \frac{B}{r + r_A} - nb''\rho + const_1, \qquad (5)$$

where r, r_A and r_W = the radii, respectively, of the central ion, the anion-additive and a water molecule, and A and B = constants, determined by the charges (or by the dipole moments) of the reacting particles and by the spatial configuration of the complex.

In the case of monotypical complexes, entropy change for the reaction in question fluctuates within a comparatively small range [6], and therefore a simple function exists between the instability constant and ΔH

$$RT \ln K_{inst.} \approx \Delta H + const_2. \qquad (6)$$

If a series of complexes is selected with an approximately constant polarization energy, then the effect of radius upon the ΔH value can be revealed, and as a consequence of which, the stability of the complexes. For this purpose, Equation (5) can be differentiated

$$\frac{\partial \Delta H}{\partial r} = \frac{B}{(r + r_A)^2} - \frac{2A}{(r + r_W)^3}. \qquad (7)$$

* Edta = ethylenediaminetetracetate.

It follows from Equation (7) that with an increase in cation radius, the stability of the complexes may increase (if the first member of the first part of the equation is smaller than the second), decrease, and pass through a maximum. An increase in stability of the complexes with increase in cation radius should be observed in the case of anion-additives of high radius values (r_A), and, contrariwise, for the case of small anions, the stability of complexes should decrease with an increase in cation radius.

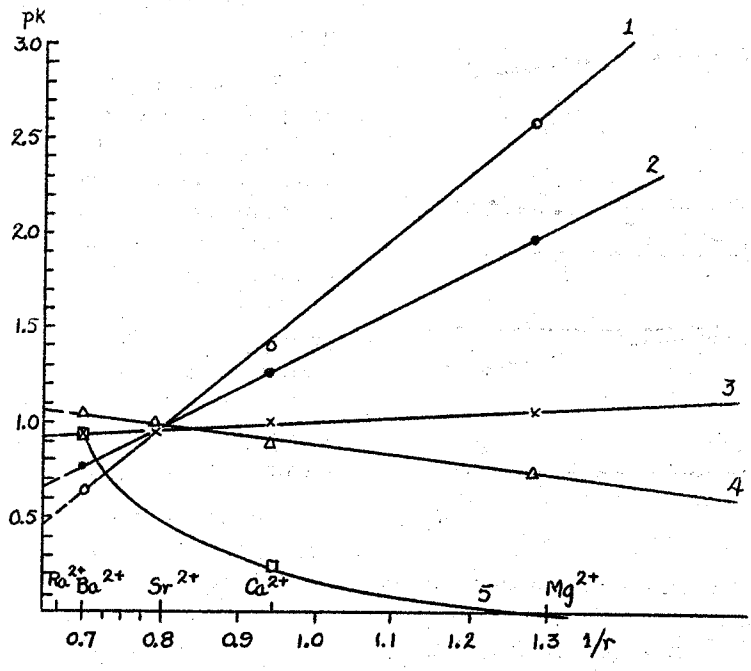

Fig. 1. Instability constant indices for a series of doubly-charged ions of varying radius.
1) MOH^+ (r_A = 1.40), 2) MAlan$^+$, 3) $MCH_3CO_2^+$ (r_A = 1.59), 4) MIO_3^+ (r_A = 1.82), 5) RNO_3^+ (r_A = 1.89).

These views are confirmed by extensive experimental material. In Figs. 1 and 2 there is shown the change in stability of complex ions formed from elements of the second main group of the Mendeleev periodic system. In the case of small singly-charged ions (r_A < 1.6 A) and α-aminoacids, the stability of the complexes changes continuously from Mg^{++} to Ba^{++}. If the radius of the anion-additive exceeds 1.6 A (nitrates, iodates) then the stability of the complex compound changes in reverse order. Apparently the same rules are observed also by doubly-charged anion-additives; stability of the oxalate complexes increases with decrease in radius, stability of succinate complexes being almost independent of the cation radius value, and finally, stability of thiosulfate complexes increasing with increase in radius. Indices for the instability constant of complexes with triply- and quadruply-charged anion-additives either do not change with change in radius, or pass through a maximum.

The mechanisms found here can be utilized to control data on stability of complex compounds, the values for certain constants being found by interpolation, and possibly by extrapolation. Such extrapolation is quite permissible according to data indicated by Shubert and other investigators[7,8].

Sulfate complexes of magnesium and calcium have approximately the same stability (pK = 2.3 ± 0.1). The sulfate ion radius = 2.30 A. Utilizing the mechanisms developed here, the author has assumed that barium and strontium also form sulfate complexes with instability constants equal to 2.3 ± 0.2 for $BaSO_4$ and $SrSO_4$. From this point of view the dissolution of $BaSO_4$ in concentrated H_2SO_4 can be explained not only by formation of an acid salt, but also by formation of a complex of the type $Ba(SO_4)_2^{2-}$.

There are no data in the literature pertaining to calcium pyrophosphate complexes, but the existance of magnesium pyrophosphate complexes has been proved [9]. Since the pyrophosphate ion charge is high, and its dimensions considerable, the existence of such complexes can be demonstrated by direct qualitative experiment: the precipitate of calcium pyrophosphate dissolved readily in excess sodium pyrophosphate.

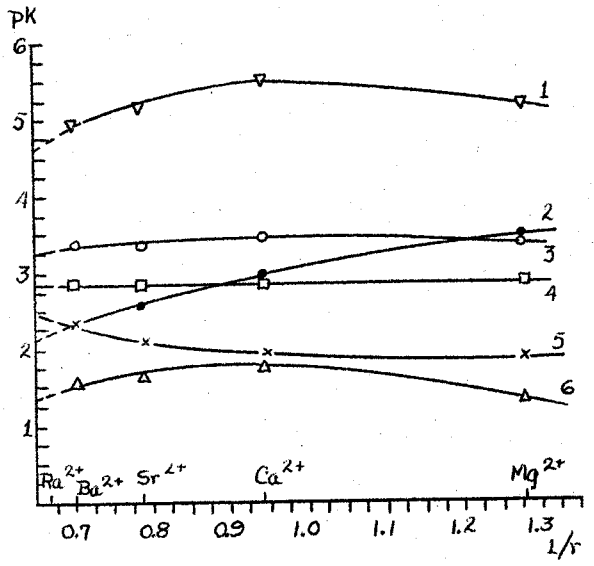

Fig. 2. Indices for instability constants for a series of doubly-charged ions with varying radii.

1) $MP_4O_{12}^{2-}$, 2) $MP_3O_9^-$, 3) MC_2O_4, 4) $MFe(CN)_6^-$, 5) MS_2O_3, 6) $MC_4H_4O_4$.

For monotypical complex compounds, formed from ions of the same charge and of approximately the same volume, the following relationship is derived from Equations (5) and (6):

$$pK = a' + nb\rho, \qquad (8)$$

where a' = a constant, including many values which do not change for a series of isochoric ions, and b = b'/RT, signifying the relative polarizability of the additive.

The following can be given as examples of the group of isochoric ions: Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}. There is preserved in this series a constant change in complex stability with any of the additives. This observation has been made by a number of investigators [4,10,11]; copius material confirming this rule has been given by Irving and Williams [3]. Upon filling one or two coordination positions in the internal sphere, stability of the complexes in this series increases in the following order: Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}. With a large number of monomial additives, the order indicated may be slightly out of line.

Continuity in change of stability for various complexes in a series of isochoric ions is explainable by the fact that only one characteristic is changed (polarizing action of the cation), the remaining being constant. For complexes with a given group of additives, there can be observed a change in stability of a determined order among ions of various radii [1,6]. However, with other additives of the series indicated, transpositions can be observed in similar fashion when an attempt is made to put into the investigated series non-isochoric ions (for example Pb^{2+} and Cd^{2+}).

Equation (8) can be utilized with that data on hand with respect to relative polarizability of additives (b), and polarizing action of the cations (ρ). A number of investigators have related the polarizing action of ions with ionization potential values [5,6,10,11]. Such dependence of course exists, but is observed only approximately, and only for isochoric ions. This dependence can be utilized only for qualitative comparisons of stability change in the series quoted.

For development of quantitative relations, the author will utilize conditional values for relative polarizability of additives, taking the polarizability of alaninate (α-aminopropionate) as equal to unity. The course of subsequent deliberations will not be altered if alaninate polarizability be taken as equal to any other constant value, or if some other additive is selected as a standard of polarizability. Choice of alaninate as the standard of polarizability was motivated by the fact that agreement in values for alaninate instability constants were independently arrived at by several investigators [12,13]. From Equation (8) one obtains

$$\rho = pK_1^0 - a', \qquad (9)$$

where pK_1^0 = index for instability of complexes of the type $MCH_3CHNH_2COO^+$ (abbreviated further to $MAlan^+$). By means of these values, as can be seen, the polarizing action for cations of the series investigated can be expressed. The pK_1^0 values are given as follows: Mg^{2+} 2.0, Mn^{2+} 3.0, Fe^{2+} 4.0,* Co^{2+} 4.8, Zn^{2+} 5.2, Ni^{2+} 6.0, Cu^{2+} 8.5.

From Equations (8) and (9) one obtains

$$pK = a + nb\, pK_1^0, \qquad (10)$$

where $a = a'(1 - nb)$.

* Interpolated value

Equation (10) is used for complex compounds of the type MA and MA_2 for the cases of ammoniates, alaninates, glycinates and glycylglycinates. Upon adding one particle of additive, Equation (10) is used for complexes with ethylenediamine, propylenediamine, diethylenetriamine, acetate, oxalate, malonate, succinate, hydroxyl, salicylic and sulfosalicylic aldehydes, thiosulfate, trimetaphosphate, tetrametaphosphate, iminodiacetate, iminodipropionate, iminopropionoacetate, hydroxy-ethyliminoacetate, oxyquinolate and dioxydiethylglycinate. Thus, Equation (10) has been checked on 27 series of complex compounds, certain examples being given in Figs. 3 and 4. Average deviations in pK values amount to ± 0.15.

In the cases investigated, all instability constant indices for a series of isochoric ions are related to each other by a direct linear function.

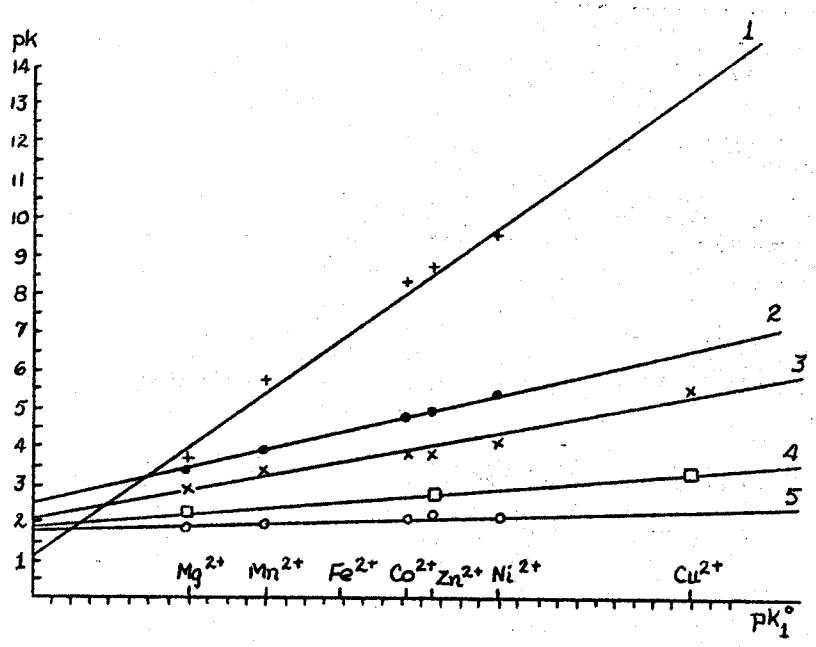

Fig. 3. Indices for instability constants in a series of isochoric ions.
1) $M[HOC_2H_4N(CH_2CO_2)_2]$, 2) MC_2O_4, 3) $MCH_2(CO_2)_2$, 4) $M(CH_2CO_2)_2$, 5) MS_2O_3.

Equation (10) is not observed, however, if more than two nitrogen or oxygen atoms enter into the internal sphere. Deviations in linear function are observed in the case of ammoniacal complexes containing more than two ammonia molecules, ethylenediamine complexes with two or more molecules of ethylenediamine, as well as with complexes of ethylenediaminotetraacetate, nitrilotriacetate and other similar additives; nevertheless, there exists in these cases a linear relationship between the indices for instability constants within a related group of complex compounds.

Constants for Equation (10) for various groups of complexes are given in Table 2; relative polarizability of additives has been calculated through a tangent of the angle of slope for the straight line, $pK - pK_1^0$.

Relative polarizability of additives is determined by the nature of the atoms, by which there is obtained a relationship between the central atoms (the lowest values for b are for additives bound to oxygen; average value – for amino acids (bound through O and N); highest b values are characteristic of additives bound to the central atom through nitrogen).

The linear functions revealed between indices for instability constants can be used as control for data at hand. For examples, we might quote data for $CoOH^+$, published in the same year and same journal. According to Gayer and Woontner [14], the pK = 1.8, and according to Chaberek Courtney and Martell [15], the pK for $CoOH^+$ is 5.1. According to Equation (10), utilizing the constants given in Table 2, the pK is 4.4.

The linear function found can also be utilized to calculate an unknown instability constant by interpolation or extrapolation. In Table 2 there are given constants of Equation 10 for 27 series of complex compounds calc., from 128 values for instability constants. Instability constant values are not known for 61 complexes, but can be evaluated to an

accuracy of ± 0.3, the constants being given in Table. 2

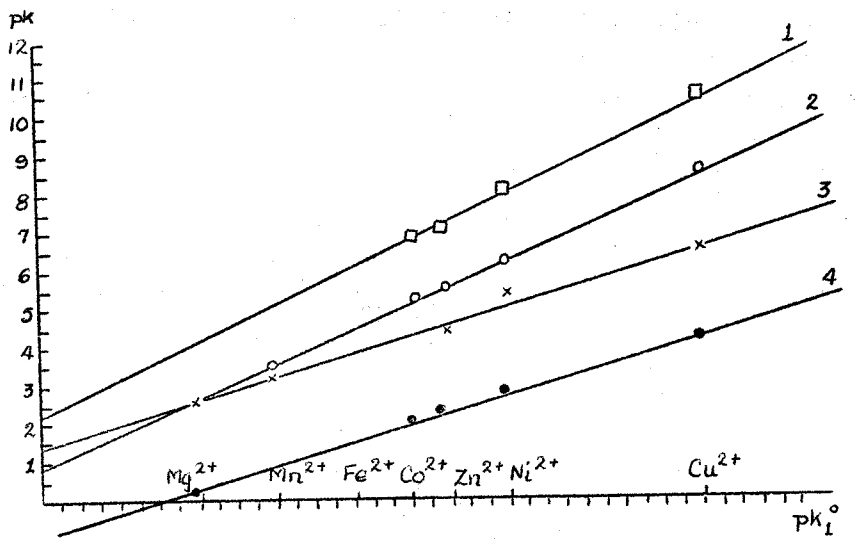

Fig. 4. Indices for instability constants in a series of isochoric ions.
1) $MP_4O_{12}^{2-}$, 2) $MP_2O_9^-$, 3) MC_2O_4, 4) $MFe(CN)_6^-$, 5) MS_2O_3, 6) $MC_4H_4O_6$.

TABLE 2
Equation (10) constant for complexes with doubly-charged isochoric ions (radius 0.8-0.9 A)

Additive	No. of additives	a	Relative polarizability	Additive	No of additives	a	Relative polarizability
SO_4^{2-}	1	2.35	0.00	o-oxyquinolate	1	5.0	0.96
$P_3O_9^{3-}$	1	3.4	0.00	$(OHC_2H_4)_2NCH_2CO_2^-$	1	0.4	0.96
$P_4O_{12}^{4-}$	1	5.2	0.00	$H_2NCH_2CO_2^-$	1	0.9	0.90
$S_2O_3^{2-}$	1	1.8	0.06	$H_2NCH_2CO_2^-$	2	0.4	0.90
$CH_3CO_2^-$	1	0.7	0.18	$CH_3CHNH_2CO_2^-$	2	−1.0	1.00
$(CH_2CO_2)_2^{2-}$	1	1.8	0.18	$HN(CH_2CO_2^-)(C_2H_4CO_2^-)$	1	0.5	1.12
$CH_2(CO_2)_2^{2-}$	1	2.0	0.41				
$C_2O_4^{2-}$	1	2.5	0.47	$HN(C_2H_4CO_2)_2^{2-}$	1	−0.8	1.19
$C_6H_3(CHO)(SO_3^-)(O^-)$	1	0.0	0.62	$HN(CH_2CO_2)_2^{2-}$	1	2.2	0.97
				$HOC_2H_4N(CH_2CO_2)_2^{2-}$	1	1.1	1.44
				NH_3	1	−1.0	0.61
$C_6H_4(CHO)(O^-)$	1	1.5	0.67	NH_3	2	−2.2	0.59
				$C_2H_4(NH_2)_2$	1	−1.7	1.44
OH^-	1	1.4	0.62	$CH_3C_2H_3(NH_2)_2$	1	−1.7	1.44
$NH_2CH_2COHNCH_2COO^-$ (glycyl-glycinate)	1	−0.2	0.76	diethylenetriamine	1	−3.0	2.3
$NH_2CH_2CONHCH_2COO^-$	2	−2.0	0.80				

Some examples of such an evaluation of instability constants for ammoniacal, ethylenediamine, sulfate, thiosulfate, acetate and oxalate complexes are given in Table 3. Instability constants can be evaluated in a number of other cases by similar procedure.

The linear function for pK, as revealed by the author, can be used to predict the possibility of existence of new complexes and for evaluation of their stability. If a complex compound of given type is found in solution for magnes-

ium, copper, and one other intermediate member of the series, and in such case the presence of a linear function between the pK's has been established, then there should also exist for the four remaining ions a complex compound of the type in question, and instability constant values for them can be determined by interpolation.

TABLE 3
Calculated instability constant values for certain complexes

Complex ion	pK	Complex ion	pK
$MnNH_3^{2+}$	0.8	$FeOH^+$	3.9
$Mn(NH_3)_2^{2+}$	1.3	$CoOH^+$	4.4
$FeNH_3^{2+}$	1.4	$MnCH_3COO^+$	1.2
$Fe(NH_3)_2^{2+}$	2.2	$FeCH_3CO_2^+$	1.4
$FeSO_4$	2.3	$NiCH_3CO_2^+$	1.8
FeS_2O_3	2.0	CuC_2O_4	6.5
FeC_2O_4	4.4	$MgC_2H_4(NH_2)_2^{2+}$	1.2

The question of the nature of additive effect upon stability of the complex compounds is found to be somewhat more complicated. The value of the additive charge (stabilization of the complex with increase in additive charge), its dimensions and polarizability play an important role, determined in first approximation by the nature of the atoms entering into the internal sphere. The entropy factor plays a considerable role in this case, since the entropy change fluctuates within a wide range, depending upon the nature and number of additives.

SUMMARY

1. The stability of complexes in aqueous solution increases with an increase in charge of the central ion. This effect is especially strong in the case of anion-additives with small radii or large charges.

2. The stability of complexes with large additives increases with increase in radius of the central ion, the stability of complexes with small additives and of amino acids decreasing with an increase in radius of the cationic complex.

3. The polarizing action of isochoric ions Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} can be characterized by means of its instability constant values for complexes of the metals enumerated with alanine (pK_1^0). Instability constant values for monotypical complexes in a series of isochoric ions are related to each other by a simple linear function.

The linear function which has been revealed can be utilized to evaluate instability constants for a series of complexes.

LITERATURE CITED

[1] K. B. Yatsimirsky, Prog. Chem. 22, 410 (1953).

[2] R. J. P. Williams, J. Chem. Soc., 1952, 3770.

[3] H. Irving, R. J. Williams, J. Chem. Soc., 1953, 3192.

[4] A. A. Grinberg and K. B. Yatsimirksy, Bull. Acad. Sci. USSR, Div. Chem. Sci. 2, 211 (1952).

[5] K. B. Yatsimirksy, Thermochemistry of Complex Compounds, Moscow, Acad. Sci. USSR Press (1951).

[6] ibid. J. Phys. Chem. 25, 221 (1951).

[7] J. Shubert, E. R. Russel, L. S. Myers, J. Biol. Chem., 185, 387 (1950).

[8] R. F. Lumb, A. E. Martell, J. phys. Chem., 57, 690 (1953).

[9] L. B. Rogers, C. A. Reynolds, J. Am. Chem. Soc., 71, 2081 (1949).

[10] H. Irving, R. J. P. Williams, Nature, 162, 746 (1948).

[11] M. Calvin, N. C. Melchior, J. Am. Chem. Soc., 70, 3270 (1948).

[12] L. E. Maley, D P. Mellor, Nature 165, 453 (1950).

[13] C. B. Monk, Trans. Far. Soc., 47, 285 297 (1951).

[14] K. H. Gayer, L. Woontmer, J. Am. Chem. Soc., 74, 1436 (1952).

[15] S. Chaberek, R. C. Courtney, A. E. Martell, J. Am. Chem. Soc., 74, 5059 (1952).

Received March 25, 1954

Ivanovo Institute of Chemical Technology