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With kind regards from
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ON THE TENDENCY OF THE METAL IONS TOWARD COMPLEX FORMATION[1]

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The formation of complex ions in aqueous solution occurs always stepwise, and the stability of the various species MA_n existing in solution is characterized by a series of consecutive mass action constants $k_1, k_2, \cdots k_n$. The data available in the literature show that a certain number N of the ligands A initially taken up by a metal ion M are bound with about the same affinity, and it seems reasonable, therefore, when comparing different systems to use a mean complexity constant $k = \sqrt[N]{k_1 k_2 \cdots k_N}$ as a convenient measure of the tendency to complex formation in a system. In the present review are discussed in some detail the laws which seem to govern the variations in $\log k$ which are brought about as a result of changes (i) in the nature of the ligand and (ii) in the position in the Periodic Table of the metal involved.

Studies of the affinity and heat of formation of solid complex compounds, such as Biltz (9) and his school have carried out on numerous ammoniates, afford very interesting information regarding the energetic phenomena involved in the formation of the molecular compounds from their molecular constituents,— in the examples quoted, metal salts and neutral molecules. By such an approach, however, no direct information can be gained regarding the affinity between the central atom of the compound and the molecules or ions bound to it, although in most cases certain rough estimates can be made. But by quantitative studies of the formation of the complex ions in solution it becomes possible to make a more direct comparison of the tendency of the various metal ions to form complexes under comparable conditions. For lattice forces do not operate in solution and one can almost completely eliminate the influence of the ions which, like the potassium ions in $K_2[Zn(CN)_4]$ and the chloride ions in $[Ni(NH_3)_6]Cl_2$, are only building stones in the crystal lattice without being direct constituents of the complexes themselves. In investigations in solution the mass action constants for the formation of the various complex ions provide a precise measure of their stability, and it is the laws governing these constants which provide the main subject matter of the present review.

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The theoretical basis for an investigation of the stability of complex ions was laid by Arrhenius' dissociation theory and Werner's coördination theory, and the first thorough investigations in this field were initiated by Abegg, Bodländer, and their students (1, 2, 30) at the turn of the century. As a rule, Abegg and

[1] With some minor changes a paper read before the 6th Meeting of Scandinavian chemists held at Lund, Sweden, August, 1947.

Bodländer only determined the overall complexity constant:

$$K_n = \frac{[MA_n]}{[M][A]^n}$$

for the complex MA_n which predominated at high concentrations of the co-ordinated ligand A. In this expression [M] denotes the concentration of the free metal ion and [A] the concentration of the free ligand.

More recent investigations, for a large part carried out by N. Bjerrum and his students, have shown, however, that the formation of complex ions always occurs stepwise, the stability of the various species being characterized by a series of consecutive constants of the form:

$$k_n = \frac{[MA_n]}{[MA_{n-1}][A]} \quad n = 1, 2 \cdots$$

In some cases complexes with more than one metal atom occur; but if one studies the equilibria at very low metal concentrations, the concentration of polynuclear complexes will usually be found to be negligibly small, so that in practice it is still possible to determine the consecutive constants of the system. As yet this has been done only in a relatively small number of cases.

In the mass action expressions given above, concentrations have been used for the sake of simplicity in place of activities.

Generally speaking this is rather a crude approximation, but it is justifiable thermodynamically provided the measurements are carried out with small concentrations of reacting ions in a solution of a highly dissociated neutral salt, e.g., a perchlorate (36). Details of the experimental methods used in investigating equilibria in systems of metal complexes will not be given here, though it is pertinent to emphasize the great importance which attaches to all potentio-metric methods which make it possible to determine either the concentration of free metal ion, or that of the free ligand in the solution under examination. That the concentration of uncoördinated ligand (provided it is a sufficiently strong base) can always be determined with the aid of a glass or hydrogen electrode has proved to be of the greatest practical importance. It should be added that in solutions of systematically varied composition, if only one of the above-mentioned concentration parameters is known, it is relatively easy to carry out a complete calculation of the mass action constants for the whole system (cf. J. Bjerrum (13, 14, 15) and Leden (98)).

Table 1 gives the values of the consecutive constants for a number of systems where it has proved possible to carry out a complete investigation. The immediate practical value of a knowledge of the magnitude of such constants is, of course, that it enables one to calculate the concentration of each individual complex coexisting in a given solution for which the total concentration of metal ion, and of ligand, is known. But even a simple consideration of such constants gives certain additional information. For example, the above expression for the successive constant k_n shows that the numerical value of this constant is equal to the reciprocal of the concentration A of the free ligand when the concentration

of the complexes MA_{n-1} and MA_n are equal. Applying this to the cadmium–cyanide system investigated by Leden (98, 99), one finds that, for example, the concentrations of $Cd(CN)_3^-$ and $Cd(CN)_4^{--}$ are the same when the concentration of free cyanide is only $10^{-3.59}$ mole per liter. On the other hand, the theoretical importance of a knowledge of the consecutive constants is that for each of them we can calculate the corresponding value of $RT \ln k_n$, i.e., the change in the Gibbs free energy at the binding of the nth ligand, and it is especially from this point of view that we shall now review the experimental data.

It will be seen that the consecutive constants for many of the systems are all of the same order of magnitude, whilst in other cases this is true only of some of the ligands first taken up. Thus the mercuric ion binds the first two ligands with a very high affinity and the next two ligands with a far lower affinity; in the same way the cupric and the cadmium ions bind four ammonia molecules uniformly, but beyond that exhibit only a very slight tendency towards further complex formation. In view of these facts the author (13, 17, 19) has considered it expedient to introduce a *characteristic coördination number* determined by the number of the first more firmly and uniformly bound ligands. Figures in table 1, under the column headed by the letter N, denote therefore not the maximum number of the ligands taken up, but only the number of uniformly bound ligands. Should the ligand occupy only one coördinative position, the characteristic coördination number, which is denoted by Z in the table, is numerically equal to N. But if the ligand is bidentate—as, for example, ethylenediamine—Z is equal to $2N$. In consequence of its definition, the characteristic coördination number is frequently smaller than Werner's maximum coördination number, which is mainly determined by the spatial arrangements of ligands around the central ion.

The characteristic coördination number, like Werner's maximum coördination number is, on the whole, a constant for a particular cation and is to be associated with certain specific spatial configurations. The stereochemical configurations corresponding to various characteristic coördination numbers are given in the last column but one of table 1. They have been determined from investigations on the crystal structure, isomerism, magnetic properties, etc. of the solid complex compounds.

As N. Bjerrum (26) was among the first to point out, one should expect, on purely statistical grounds, that the first ligands to be taken up would be bound somewhat more strongly than the subsequent ones. If the ligand is an electrically charged anion, one must reckon in addition with an electrostatic effect, which has the effect of lowering still further the affinity for subsequent ligands. The statistical correction, which can easily be calculated (13), has been introduced in the case of those constants quoted in parentheses in table 1 in such a way that the logarithm of the mean complexity constant defined by

$$\log k = \frac{1}{N} \log K_N = \frac{1}{N} \log k_1 k_2 \cdots k_N$$

has the same value when calculated from the statistically corrected constants as from those determined by direct experiment. It will be seen that in many cases,

TABLE 1

Consecutive complexity constants for a number of selected systems

SYSTEM	LOG k_1	LOG k_2	LOG k_3	LOG k_4	LOG k_5	LOG k_6	N	LOG k	Z	CONFIGURATION	REFERENCES
Ag$^+$ + 2NH$_3$	3.20 (2.90)	3.83 (4.13)					2	3.52	2	Linear	(13)
Ag$^+$ + 2OH$^-$	2.3 (2.0)	1.9 (2.2)					2	2.1	2	Linear	(13, 87)
Hg^{++} + 4NH$_3$	8.8 (8.5)	8.7 (9.0)	1.00	0.78			2	8.75	2	Linear	(13)
Hg^{++} + 4Cl$^-$	7.15 (6.85)	6.9 (7.2)	1.0	0.7			2	7.0	2	Linear	(4, 147)
Zn^{++} + 4NH$_3$	2.37 (1.77)	2.44 (2.26)	2.50 (2.68)	2.15 (2.75)			4	2.37	4	Tetrahedral	(13)
Zn^{++} + 3en	5.92 (5.38)	5.15 (5.69)	1.86				2	5.54	4	Tetrahedral	(17, 45)
Cd^{++} + 6NH$_3$	2.65 (2.05)	2.10 (1.92)	1.44 (1.62)	0.93 (1.53)	-0.4	-0.7	4	1.78	4	Tetrahedral	(13, 98)
Cd^{++} + 4CN$^-$	5.54 (4.94)	5.06 (4.88)	4.65 (4.83)	3.59 (4.19)			4	4.71	4	Tetrahedral	(98, 99)
Cd^{++} + 4I$^-$	2.08 (1.48)	0.77 (0.59)	2.15 (2.33)	1.48 (2.08)			4	1.62	4	Tetrahedral	(97, 98)
Sn^{++} + 4Cl$^-$	1.50 (0.90)	0.74 (0.56)	-0.22 (-0.44)	-0.52 (+0.08)			4	0.38	4	Tetrahedral	(75, 128)

							N	k	Z		
Cu^{++} + 5NH$_3$	4.15 (3.55)	3.50 (3.32)	2.89 (3.07)	2.13 (2.73)	-0.52		4	3.17	4	Planar	(10, 11, 12, 13)
Cu^{++} + 3en	10.72 (10.27)	9.31 (9.76)	-1.0				2	10.02	4	Planar	(19, 45)
Cu^{++} + 4Cl$^-$	-0.2 (-0.8)	-0.7 (-0.9)	-1.5 (-1.3)	-2.2 (-1.6)			4	1.15	4	Planar	(15)
Ni^{++} + 6NH$_3$	2.80 (2.02)	2.24 (1.84)	1.73 (1.60)	1.19 (1.32)	0.75 (1.15)	0.03 (0.81)	6	1.46	6	Octahedral	(13)
Ni^{++} + 3en	7.66 (6.88)	6.40 (6.30)	4.55 (5.43)				3	6.20	6	Octahedral	(13, 45)
Cr^{+++} + 6SCN$^-$	3.1 (2.3)	1.7 (1.3)	1.0 (0.9)	0.3 (0.4)	-0.7 (-0.3)	-1.6 (-0.8)	6	0.63	6	Octahedral	(24, 25)
Al^{+++} + 6F$^-$	6.13 (5.35)	5.02 (4.62)	3.85 (3.72)	2.74 (2.87)	1.63 (2.03)	0.47 (1.25)	6	3.31	6	Octahedral	(38, 41)

N = the number of uniformly bound ligands.

$k = \sqrt[N]{k_1 k_2 \cdots k_N}$.

Z = the characteristic coördination number of the metal ion.

en = NH$_2$CH$_2$CH$_2$NH$_2$.

e.g., the chromic–thiocyanate system, the statistical correction accounts for a large part of the trend in the experimentally determined consecutive constants. Assuming for this system that any effects not accounted for on statistical grounds were due solely to electrostatic causes, N. Bjerrum (26) was able to calculate reasonable values for the dimensions of the complexes. On the other hand in, for example, the cadmium–iodide system, where $\log k_2$ is seen to have an abnormally low value, it is obvious that specific chemical influences must also play a part. In silver and mercury systems where $Z = 2$, it is further worthy of note that the statistically corrected values of k_2 are usually higher than the corresponding values for k_1, regardless of the operation of the electrostatic effect.

Apart from these irregularities remains the fact that a certain number of the ligands initially taken up by a metal are bound with about the same affinity, and it seems reasonable, therefore, when comparing different systems to use k, the average constant defined above, or rather $\log k$, as a convenient measure of their respective tendencies to form complexes.

<div align="center">2</div>

After this brief review of the most important laws pertaining to individual systems of complexes, we shall now proceed to deal with these factors which are responsible for complex formation and to discuss in some detail the laws which seem to govern the variations in $\log k$ which are brought about as a result of changes (*i*) in the nature of the ligand and (*ii*) in the position in the Periodic Table of the metal involved.

According to J. N. Brønsted a base is a molecular species with an affinity for a proton; according to G. N. Lewis it is definable quite generally as a nucleophilic substance. It seems therefore logical to inquire whether the bases with the strongest affinity for hydrogen ion, i.e., the strongest bases in the Brønsted sense of the word, are the best complex builders. Of course, one could scarcely anticipate any universally applicable relationship of this kind, but if one is content to consider a series of closely related ligands it would seem reasonable to expect a certain correlation between the hydrogen-ion affinity of particular ligands and their tendency towards complex formation.

In 1934 Larsson (95) made just such a comparison of the basic strength of various amines and their complex-forming affinity for silver ions and found that a rough proportionality did exist. Larsson only determined the overall complexity constant and his data have since been supplemented by measurements by Carlson, McReynolds, and Verhoek (45) and by Bruehlman and Verhoek (42). Using the glass electrode these investigators followed the procedure introduced by the author (13), and determined both of the consecutive constants. Several measurements of this kind have also been made by Bjerrum, Morsing, Plejl, and Refn (16, 18, 20, 21), who determined in addition the affinity of the mercuric ion for various amines. Table 2 presents the results obtained by Bjerrum and coworkers, together with those of other investigators. Herein k_{H^+} as a measure of the basic strength denotes the reciprocal of the acid dissociation constant of the base cation AH^+

$$k_{H^+} = \frac{[AH^+]}{[A][H^+]}$$

TABLE 2

Comparison of the strengths of various bases, as measured by k_{H^+} with their mean complexity constants with certain metal ions

A. Silver ion

LIGAND	LOG k_{H^+}	LOG k_{Ag^+}	LOG $\frac{k_1}{k_2}$	$\frac{LOG\ k_{Ag^+}}{LOG\ k_{H^+}}$	t °C.	MEDIUM	REFERENCES
p-Nitroaniline	2.0	0.8		0.40	25	Var.*	(95)
m-Nitroaniline	2.5	0.85		0.34	25	Var.*	(95)
β-Naphthylamine	4.28	1.62		0.38	25	Var.*	(95)
Aniline	4.54	1.59		0.35	25	Var.*	(95)
Quinoline	4.98	1.84		0.37	25	Var.*	(95)
Hexamethylenetetramine	5.13	1.79		0.35	20	Dilute	(123)
Pyridine	5.21	2.08	−0.14	0.40	25	0.5 m PyHNO₃	(20)
Pyridine	5.45	2.11	−0.14	0.39	25	Dilute	(159)
α-Picoline	6.20	2.34	−0.14	0.38	25	0.5 m KNO₃	(42)
γ-Picoline	6.26	2.35	−0.22	0.38	25	0.5 m KNO₃	(42)
2,4-Lutidine	6.99	2.59	−0.24	0.37	25	0.5 m KNO₃	(42)
Triethanolamine	7.90	1.82	+1.00	0.23	25	0.4 m KNO₃	(21)
Morpholine	8.70	2.49	−0.42	0.29	25	0.5 m KNO₃	(42)
Diethanolamine	9.00	2.74	−0.10	0.30	25	0.4 m KNO₃	(21)
Ammonia	9.28	3.60	−0.60	0.39	25	0.5 m NH₄NO₃	(13)
β-Methoxyethylamine	9.45	3.17	−0.44	0.34	25	0.5 m KNO₃	(42)
Benzylamine	9.62	3.57	−0.56	0.37	25	0.5 m KNO₃	(42)
Ethanolamine	9.60	3.34	−0.46	0.35	25	0.4 m KNO₃	(21)
Ethanolamine	9.74	3.34	−0.42	0.34	25	0.5 m KNO₃	(42)
Aminoacetate ion	9.76	3.5	+0.4	0.36	20	0.5 m KNO₃	(65)
Ethylenediamine	10.18	3.7	+4.6	0.36	25	1.0 m KNO₃	(16)
Methylamine	10.72	3.34	−0.38	0.31	25	0.5 m NRH₃NO₃	(18)
Ethylamine	10.81	3.65	−0.56	0.34	25	0.5 m KNO₃	(42)
n-Butylamine	10.71	3.74	−0.62	0.35	25	0.5 m NRH₃NO₃	(16)
Isobutylamine	10.72	3.62	−0.48	0.34	25	0.5 m KNO₃	(42)
Triethylamine	10.77	2.4	+0.5	0.22	25	0.4 m NR₃HNO₃	(21)
Diethylamine	10.96	3.10	−0.24	0.28	30	0.5 m KNO₃	(45)
Piperidine	11.12	3.31	−0.29	0.30	25	0.4 m KNO₃	(21)
Piperidine	11.28	3.24	−0.42	0.29	25	0.5 m KNO₃	(42)

* log k_{H^+} in water, log k_{Ag^+} in 50 mole per cent ethanol.

B. Mercuric ion

LIGAND	LOG k_{H^+}	LOG $k_{Hg^{++}}$	LOG $\frac{k_1}{k_2}$	$\frac{LOG\ k_{Hg^{++}}}{LOG\ k_{H^+}}$	t °C.	MEDIUM	REFERENCES
Pyridine	5.21	5.00	+0.2	0.96	25	0.5 m PyHNO₃	(20)
Triethanolamine	7.90	6.56	+0.5	0.83	25	0.4 m KNO₃	(21)
Diethanolamine	9.00	7.83	0.0	0.87	25	0.4 m KNO₃	(21)
Ammonia	9.61	8.75	+0.1	0.91	22	2 m NH₄NO₃	(13)
Ethanolamine	9.60	8.66	−0.3	0.90	25	0.4 m KNO₃	(21)
Aminoacetate ion	9.76	9.6	+1.4	0.98	20	0.5 m KNO₃	(65)
Ethylenediamine	10.18	11.71		1.15	25	1 m KNO₃	(16)
Methylamine	10.72	8.95	−0.7	0.83	25	0.5 m NRH₃NO₃	(20)
n-Butylamine	10.71	9.05	−0.7	0.84	25	0.5 m NRH₃NO₃	(20)
Triethylamine	10.77	7.8	0	0.72	25	0.4 m NR₃HNO₃	(21)
Piperidine	11.12	8.72	+0.04	0.78	25	0.4 m KNO₃	(21)

TABLE 2—*Concluded*

C. *Cupric ion*

LIGAND	$\log k_H^+$	$\log k_{Cu}^{++}$	$\log \frac{k_1}{k_2}$	$\frac{\log k_{Cu}^{++}}{\log k_H^+}$	t	MEDIUM	REFERENCES
					°C.		
$^-OCOCH_2COO^-$	5.67	4.08	+3.05	0.72	25	Dilute	(50)
$^-OCOCOO^-$	4.26	4.2		0.98	18	Dilute	(35)
$^-OCOCH_2NH_2$	9.76	7.60	+1.25	0.78	20	$0.5\,m\,KNO_3$	(65)
$NH_2CH_2CH_2NH_2$	10.18	10.02	+1.41	0.99	25	$1\ \ m\,KNO_3$	(19)
$NH_2CH(CH_3)CH_2NH_2$	9.78	9.83	+1.50	1.00	30	$0.5\,m\,KNO_3$	(45)

D. *Zinc ion*

LIGAND	$\log k_H^+$	$\log k_{Zn}^{++}$	$\log \frac{k_1}{k_2}$	$\frac{\log k_{Zn}^{++}}{\log k_H^+}$	t	MEDIUM	REFERENCES
					°C.		
$^-OCOCOO^-$	4.29	3.68	+2.64	0.86	25	Dilute	(46, 158)
$^-OCOCH_2NH_2$	9.76	4.47	+0.66	0.46	20	$0.5\,m\,KNO_3$	(65)
$NH_2CH_2CH_2NH_2$	10.18	5.53	+0.77	0.54	25	$1\ \ m\,KNO_3$	(17)
$NH_2CH(CH_3)CH_2NH_2$	9.78	5.44	+0.91	0.56	30	$0.5\,m\,KCl$	(45)

while k_M (M = Ag$^+$, Hg^{++}, etc.) denotes the mean complexity constant of the complexes formed in the corresponding metal–amine system.

In those sections of table 2 dealing with silver and mercury complexes the ligands are arranged in order of increasing basic strength, and it will be seen immediately that the tendency to complex formation increases on the whole in the same order. The constancy of the ratios

$$\frac{\log k_{Ag^+}}{\log k_{H^+}} \text{ and } \frac{\log k_{Hg^{++}}}{\log k_{H^+}}$$

shows that there exists even a rough proportionality, although one would actually anticipate only a linear relationship. This becomes quite obvious when it is pointed out how all the k-values are dependent upon the particular units in which the concentration is expressed. If, for example, in place of moles per liter one had used millimoles per liter, all values of $\log k$ listed in tables 1 and 2—regardless of their magnitude—would have been diminished by 3.

A closer scrutiny of the figures shows that the greatest deviations from the average value, 0.36, found for the ratio $\log k_{Ag^+}/\log k_{H^+}$ for primary amines occur with tertiary amines like triethylamine and triethanolamine, but that also the secondary amines investigated, *viz.*, diethylamine, diethanolamine, morpholine, and piperidine show an affinity for the silver ion which is distinctly too small. All the secondary amines studied have

$$\frac{\log k_{Ag^+}}{\log k_{H^+}} \sim 0.29$$

and form a special subgroup in Bruehlman and Verhoek's graphical representation (42). It is, however, noteworthy that the tertiary amines hexamethylenetetramine, pyridine, and its homologs have a relatively high affinity for silver ions and fall into the same group as ammonia and the primary amines. This may undoubtedly be referred in part to the fact that these cyclic tertiary bases have a spatial configuration which is far more favorable to coördination with a metal ion than the more space-requiring configurations of the usual tertiary and secondary amines. If steric factors are indeed the reasons for the far too small tendency of these bases to form complexes, additional evidence would be afforded by k_1 having a relatively high value as compared with k_2; it will be seen that this is, on the whole, the case.
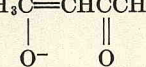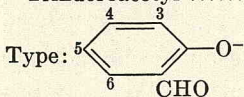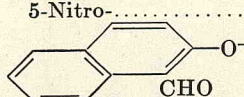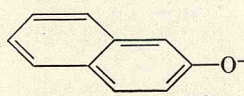
It is also instructive to consider the relative magnitudes of the consecutive constants in the systems with silver and the three chelating ligands, ethanolamine, aminoacetate ion, and ethylenediamine, all of which show a normal value for the ratio $\log k_{Ag^+}/\log k_{H^+}$. It will be seen that ethanolamine behaves toward the silver ion just like an unsubstituted primary amine with $k_1 < k_2$, while the aminoacetate ion has a somewhat greater, and ethylenediamine an abnormally high value for the ratio between the successive constants. This shows directly that the aminoalcohol, and to some extent the aminoacetate ion, are bound only through their amino groups, whilst the ethylenediamine molecule taken up primarily must be assumed to be bound chelately through both of its amino groups, regardless of the fact that the silver ion has linear valencies and thus cannot enter as a constituent of a five-membered ring without some coercion. In coördinating the second molecule of ethylenediamine it must be assumed that the ring is opened—at any rate this assumption explains immediately why even in the case of ethylenediamine a "normal" value is found for the ratio between the mean complexity constant and the basic strength of the amine. On the whole, the mercuric ion systems and those of silver ions with the same amines show great similarities, but it is noteworthy that $\log k_{Hg^{++}}/\log k_{H^+}$ has altogether too high a value in the mercuric–ethylenediamine system. This is undoubtedly because the mercuric ion, as opposed to the silver ion, exhibits a marked tendency to change from a linear to a tetrahedral configuration so that it must be assumed that both ethylenediamine molecules are bound chelately in the mercuric biscomplex.

In the case of those metal ions with characteristic coördination number 4 or 6, not only ethylenediamine but also ligands such as the oxalate, the malonate, and the aminoacetate ions are bound exclusively in the form of chelate rings. Using cupric and zinc ions as typical examples, parts C and D of table 2 present some data which provide certain information regarding the formation of complexes by such chelating ligands. It will be seen, *inter alia*, that the oxalate is more strongly bound to the cupric ion than is the malonate ion, regardless of the fact that the latter is the stronger base. This shows that the five-membered ring as a whole is somewhat more stable than the six-membered ring.

Complex formation between the cupric ion and a large number of chelating ligands of the type of acetylacetone and salicylaldehyde has recently been in-

vestigated by Calvin and Wilson (43) in 50 per cent dioxane–water mixtures, using the glass electrode. Table 3 summarizes their measurements where the chelating ions are the phenoxide ion of the salicylaldehyde (or its derivatives) and the enolate ion of the β-diketones, respectively. Since the anions of the β-diketones exist unquestionably almost exclusively in the enolic form, the
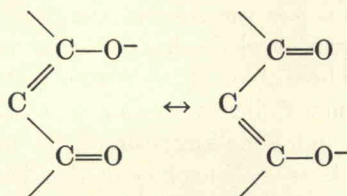
TABLE 3

A summary of Calvin and Wilson's (43) determination of $k_{Cu^{++}}$ and k_{H^+} for some β-diketone and salicylaldehyde systems

LIGAND-ION	LOG $\frac{k_1}{k_2}$	LOG $k_{Cu^{++}}$	LOG k_{H^+}	$\frac{\text{LOG } k_{Cu^{++}}}{\text{LOG } k_{H^+}}$	$\frac{\text{LOG } k_{Ni^{++}}}{\text{LOG } k_{H^+}}$
Type: CH₃C=CHCCH₃ (with O⁻ and O)					
Acetylacetone...................	0.9	8.7	9.7	0.90	0.62*
Furoyl-.......................	0.5	8.4	9.3	0.90	
Benzoyl-......................		9.0	9.8	0.92	
Trifluoroacetyl-................	0.4	6.1	6.7	0.91	
Type: (ring, positions 3,4,5,6) —O⁻ CHO					
Salicylaldehyde.................	1.7	6.6	9.5	0.69	0.48*
3-*n*-Propyl-..................	1.7	7.1	9.6	0.74	
5-Methyl-.....................	1.7	6.7	9.7	0.69	
4,6-Dimethyl-.................	1.6	7.2	10.4	0.69	
3-Fluoro-.....................	1.7	5.7	7.8	0.73	
3-Chloro-.....................	2.0	5.3	7.8	0.68	
5-Chloro-.....................		5.7	8.6	0.66	
3-Nitro-......................	1.5	4.1	6.0	0.68	
4-Nitro-......................	1.4	4.6	7.4	0.62	
5-Nitro-......................	0.7	4.4	5.9	0.75	
(naphthalene) —O⁻ CHO	1.6	7.0	8.4	0.83	
(naphthalene) —O⁻ CHO		5.8	9.9	0.58	

* Mellor (110).

constants measured experimentally are in every case a measure of the affinity of a particular chelating ion for the hydrogen ion and cupric ion, respectively. It will be seen that the ratio log $k_{Cu^{++}}$/log k_{H^+} is surprisingly constant in the diketone systems investigated and shows, on the whole, an equally satisfactory constancy in the salicylaldehyde systems, not least when consideration is given to the great influence of the electronegative substituents on the basic strength of some of the chelating ions. But it should be noted that the two isomers of

o-hydroxynaphthaldehydes behave entirely differently. As Calvin and Wilson pointed out, this is undoubtedly connected with the fact that the double-bond character of the C=C bond in the chelate bridge is far more pronounced in the 1,2- than in the 2,3-compounds. If, following Pauling (122) and taking into account possible mesomeric forms, we express purely schematically the number of bonds in the "double bond" by a number, this will be 2 in the aliphatic compounds, $1\frac{2}{3}$ in the 1,2-naphthalene compound, $1\frac{1}{2}$ in the benzene derivatives, and only $1\frac{1}{3}$ in the 2,3-naphthalene compound. It will be seen that this is the very sequence in which the ratio $\log k_{Cu^{++}}/\log k_{H^{+}}$ falls, and since the effectiveness of the enolate resonance

$$
\begin{array}{ccc}
\diagdown & & \diagdown \\
C\!-\!O^{-} & & C\!=\!O \\
\diagup\!\!\diagup & & \diagup \\
C & \leftrightarrow & C \\
\diagdown & & \diagdown\!\!\diagdown \\
C\!=\!O & & C\!-\!O^{-} \\
\diagup & & \diagup
\end{array}
$$

likewise decreases with the character of the double bond, it is obvious that this resonance augments to a high degree the tendency towards complex formation and is of far greater importance in the formation of a chelate ring with a metal ion than in the simple uptake of a proton.

<div align="center">3</div>

It appears from the foregoing that when due consideration is given to the constitution of the ligand molecules and to steric effects there actually exists in many cases a definite correlation between the basic strength of the different types of ligands and their affinity for metal ions. But this tells us nothing directly concerning the actual nature of the forces of affinity which are responsible for the formation of complexes. When Kossel launched his electrostatic theory in 1916 he was of the opinion that the formation of complexes was determined entirely by the purely electrostatic attraction which existed between metal ions and anions (both regarded as electrically charged spheres) or between metal ions and the dipoles of neutral molecules. This theory, according to which the charge and dimensions of ions determine the stability of complexes, soon proved to be inadequate, and nowadays it is generally assumed that complex compounds are held together by quantum-mechanical electron bonds. That bonds in complexes are to a certain degree directed in space is quite evident from the fact that metal ions with a characteristic coördination number 4 form complexes in some cases with tetrahedral, in other cases with square planar, configuration. It would lead too far to go into details regarding the various theories concerning the chemical bond, theories which are associated with such names as Lewis, Sidgwick, and Pauling, and we shall only remark that according to Sidgwick the typical bond in a complex is effected by the ligand's donating two electrons to the electron system of the metal ion, a polarized electron-pair bond (the "coördinate covalency") being formed.

Abegg and Bodländer (1, 2, 30) found that the position of the metal and the ligand in the electromotive series, or, if one prefers it, their relative electronegativity was of the highest significance in discussing their tendency towards complex formation. This was, in point of fact, at its greatest between the most electronegative metals and the least electronegative ligands, which shows directly that there must be an electron displacement from ligand to metal ion whenever a complex is produced.

The relationship between the radius and electronegativity of the metal ion and its tendency to form complexes is shown for the most important types of ligands in table 4, which provides an extensive compilation of the material available in the literature. For the sake of simplicity the metal ions are not arranged in order of increasing electronegativity or radius but with regard to their position in the Periodic Table. (E^0 = normal potential metal ion–metal in aqueous solution; r = ionic radius according to Goldschmidt, if nothing else is stated.) In tables 1, 2, and 3 the logarithm of the mean complexity constant of the system, i.e., $\log k = 1/N \log k_1 k_2 \cdots k_N$, has been used as a direct measure of the affinity between ligand and metal ion. But what, now, is the actual significance of this quantity? According to modern ideas metal ions become solvated as soon as they are brought into solution and in consequence should themselves be regarded as complex ions. It thus follows that $\log k$ (or more correctly $RT \ln k$) is actually a measure of the change in free energy when a solvent molecule (water molecule) bound coördinatively to the metal ion is replaced by a molecule of some particular ligand. In order to bring out this point more precisely the concentration of water molecules (55 moles per liter) has been introduced into the previous mass action expressions and the quantity

$$\frac{N}{Z} \log k + \log 55$$

has been used in table 4 in place of $\log k$ as a measure of the change in free energy. (In order to express the result in kilocalories one must at 25°C. multiply by the numerical factor 1.362.) The use of this expression has the following advantages: (i) A scale is established such that zero indicates, at least formally, that the ligand under discussion is coördinated with the same affinity as the solvated water molecules. (ii) The value of $\frac{N}{Z} \log k + \log C_{H_2O}$, as opposed to that of $\log k$, is independent of the units in which the concentration terms are expressed. (iii) The expression gives average values per complex-bound group irrespective of the actual coördinative capacity of the ligand.

In order to be able to calculate the quantity thus defined it is sufficient to know the complexity constant K_N for a system, together with the characteristic coördination number of the metal ion. In many cases, however, only a single one or a very few of the consecutive constants are known. In order to make use of this incomplete material, values for the mean complexity constants of such systems have been estimated by applying the general laws to the behavior of the particular system. Values obtained in this way are in most cases rather

uncertain estimates; they are given in parentheses in table 4. On the other hand, values to which a question mark is appended (including the value quoted for the normal potential of the diaquo-aurous ion) are not based on direct experimental measurements but are estimates, pure and simple, made with due regard to empirical regularities.

Table 4 presents data concerning complex formation in a highly condensed form and a number of regularities at once become evident. Thus if we consider the halide ions it is immediately obvious that the mercuric ion and other strongly electronegative cations with 18-electron configurations have the highest affinity for the strongly polarizable iodide ion, whilst small and only slightly deformable ions like Al^{+++} and Fe^{+++} show their maximum affinity towards the fluoride ion, just as H^+ does. This illustrates quite clearly the point that in complex formation the factor of electronegativity is of decisive importance among the more noble metals whilst, in agreement with Kossel's theory, ionic dimensions and ionic charge are the significant features among the more electropositive metals.

The behavior of the cyanide ion is noteworthy. Though in many respects it resembles a halide ion, it shows a high affinity both for ions of the noble metals and for the hydrogen ion and cannot be classified among the halide ions but behaves very much like ammonia. Sidgwick (145) was able to demonstrate this on a purely qualitative basis, but for a number of metal ions of very widely different character the following rule applies quantitatively: "The value of the quantity $\frac{N}{Z} \log k + \log 55$ is in the ratio 1.7:1:0.6 for the ligands CN^-, NH_3, and pyridine." Only the hydrogen ion appears to show a substantial deviation from this rule. A regularity of this kind is very useful, as it makes it possible to make predictions concerning complex formation in systems where measurements either are not available or are difficult to make at all by reason of reaction inertia or side-reactions,—hydrolysis and the like. For example, it is possible to predict an approximate value for association of the cupric ion with the cyanide ion regardless of the fact that the tetracyano–cupric complex is completely unstable in view of the oxidation–reduction reaction:

$$2Cu(CN)_4^{--} \rightarrow 2Cu(CN)_3^{--} + (CN)_2$$

It is also very interesting that the rule cited above enables one to get an idea of the value of the complexity constants of the iron–cyanide complexes. The starting-point here is the affinity of the ferrous ion for pyridine (20). The small value for the relevant quantity $\frac{N}{Z} \log k + \log 55$, taken with the rule mentioned above, leads to the surprising result that the ferrocyanide complex, in spite of its great resistance to attack by other reagents, actually only possesses a relatively small complexity constant. The complexity constant of the somewhat more reactive ferricyanide complex is substantially higher, but this can be directly deduced from the known oxidation–reduction potentials for the aquo–iron and iron–cyanide systems.

Since the cyanide ion falls so well in line with ammonia and pyridine, one may

TABLE 4

Free energy of complex formation

The quantity $\dfrac{N}{Z} \log k + \log 55$ for a large number of complex systems in aqueous solution at room temperature

r (Å)	E^0 (volts)	Z		OH^-	F^-	Cl^-	Br^-	I^-	CN^-	NH_3	Py	½en	SCN^-	$S_2O_3^{2-}$	Ac^-	½Ox^-	½Sal^-	NO_3^-	SO_4^{--}
—	0	1	H^+	17.5	5.3	−4.4	(−6)	(−7)	11.1	10.9	6.9	11.9	<2	3.7	6.5	6.0	11.2	0.4	3.7
0.96*	+0.53	2	Cu^+			4.5	4.7	6.2	(13.2)	7.2	~4?								
1.13	+0.80	2	Ag^+	3.8	<1	4.7	(6.2)	(8.7)	(11.0)	5.3	3.8	4.7	6.6	8.2	2.1			(−0.2)	(1.3)
1.37*	(+2.14?)	2	Au^+			(10.3)			(25.5)	~15?	~9?		(14.2)						
0.83	−0.76	4	Zn^{++}	5.6	~2?	1.5	1.1	(0.4)	6.5	4.1	1.9	4.5	(0.7)	(1.7)	(1.7)	3.6	3.8	<−1	(2.3)
1.03	−0.40	4	Cd^{++}	4.2	1.5	2.3	2.7	3.4	6.4	3.6	2.2	4.3	2.4	3.6	2.2	3.2	3.7	(0.4)	(2.3)
1.12	+0.85	2	Hg^{++}	13.1	<4	8.7	10.6	14.2	(19.2)	10.5	6.7	—	(10.2)					1.7	2.9
0.62	−0.52	6	Ga^{+++}	8.9															
0.92	−0.34	6	In^{+++}		—										(5.5)				
1.05	+0.71	4	Tl^{+++}			5.6	(6.8)	9.3	10.5	~6?	~4?			12.0					
0.44	−0.1	6	Ge^{++++}	—														
0.74		6	Sn^{++++}			(2.6)													
0.84		6	Pb^{++++}																
0.80	+0.35	4	Cu^{++}	5.8		0.6	(0.1)	~0?	~8?	5.0	3.2	6.8			2.6	3.8	5.1	≤0	(2.3)
0.78	−0.24	6 (4)	Ni^{++}			(0.0)	(−0.3)		4.7	3.2	1.7	4.8		(2.0)		(~5)	4.0		(2.4)
0.82	−0.27	6 (4)	Co^{++}			(1.0)	(−0.5)		<4.9	2.6	1.1	4.0				(~4)	3.8		(2.5)
0.83	−0.44	6 (4)	Fe^{++}	(5.0)					~2?	~1?	0.6	3.3	0.8	(2.0)		4.1			
0.91	−1.1	6 (4)	Mn^{++}								(0.1)	2.7				3.0			
	−0.56	6 (4)	Cr^{++}																
0.66	+0.42	6	Co^{+++}	(9.3)					12.4	7.6	~4?	9.9	1.9						
0.67	−0.04	6	Fe^{+++}	(8.0)	4.2	1.5	(0.6)		~7?	~4?	~2?	~6?	2.4			5.5			
0.65	−0.51	6	Cr^{+++}		—	(−1)													
—	+1.40	4	Ag^{++}	5.0		5.0													
—	+0.99	4	Pd^{++}														5.4	(1.5)	

Ionic radius*	n	E°	Ion	OH⁻	F⁻	Cl⁻	Br⁻	I⁻	SCN⁻	S₂O₃²⁻	Ac⁻	Ox²⁻	Sal⁻	NO₃⁻	SO₄²⁻
1.49	4?	−0.34	Tl⁺	<2	(0.7)			~1?	<0.8	0?	3.3	(~0)	(2.0)	(0.3)	(1.3)
—	4	−0.14	Sn⁺⁺	8.2	2.1	1.9	2.7	(4.3)	<0.8		3.5	2.7	3.4	4.0	(1.1)
1.32	4	−0.13	Pb⁺⁺	5.2	2.0	(2.0)	~0.6?		0.9						
1.22	6 (4)		La⁺⁺⁺	(~5)	—										(3.7)
0.57		(−1.7)	Al⁺⁺⁺	(~7.5)	5.1										
0.34	4	−2.0	Be⁺⁺	<7	<0						1.1				
0.78	6 (4)	−2.4	Mg⁺⁺	<3	<0						0.8	(2.9)	3.4		(2.1)
1.06		−2.8	Ca⁺⁺	<2	~1						0.9	(2.7)			(2.3)
1.43		−3.0	Ba⁺⁺	<1			<0					(2.4)			
0.78		−2.96	Li⁺	~0	<−1									(−1.5)	(0.6)
0.98		−2.71	Na⁺		<−1									(−0.6)	(0.7)
1.33		−2.92	K⁺		<−1									(−0.1)	(0.8)

* Ionic radius according to Pauling.

Py = pyridine; en = ethylenediamine; Ac⁻ = acetate ion; Ox⁻⁻ = oxalate ion; Sal⁻ = salicylaldehyde anion.

References to table 4

OH⁻: 13, 96, 87, 72 (Ag⁺, Hg⁺⁺), 55, 131, 103, 127 (Zn⁺⁺, Cd⁺⁺), 66 (Ga⁺⁺⁺), 124, 63, 107 (Cu⁺⁺), 101, 161, 93, 37, 23, 92 (Fe⁺⁺, Fe⁺⁺⁺, Cr⁺⁺⁺, Al⁺⁺⁺), 157 (La⁺⁺⁺), 125, 73, 155, 102 (Pb⁺⁺), 71, 129, 150 (Sn⁺⁺), 130, 74, 51, 88, 53, 47.

F⁻: 3 (Ag⁺), 98 (Cd⁺⁺), 84 (Hg⁺⁺), 38–41, 133.

Cl⁻: 137 (H⁺), 32, 13 (Cu⁺), 60 (Ag⁺), 28, 29 (Au⁺), 148 (Zn⁺⁺), 80, 97, 98 (Cd⁺⁺), 4, 115, 147 (Hg⁺⁺), 15, 152 (Cu⁺⁺), 86 (Co⁺⁺), 120, 121, 134 (Fe⁺⁺, Fe⁺⁺⁺), 22 (Cr⁺⁺⁺), 154 (Pd⁺⁺), 138, 81, 151 (Tl⁺, Tl⁺⁺⁺), 67, 68, 117, 118 (Pb⁺⁺), 128, 75, 149, 132 (Sn⁺⁺, Sn⁺⁺⁺⁺), 136, 106.

Br⁻: 56 (H⁺), 33 (Cu⁺), 59, 31 (Ag⁺), 148 (Zn⁺⁺), 7, 97, 98 (Cd⁺⁺), 115, 4, 147 (Hg⁺⁺), 151 (Tl⁺⁺⁺), 86 (Cu⁺⁺, Ni⁺⁺, Co⁺⁺), 101, 134 (Fe⁺⁺⁺), 67 (Pb⁺⁺), 128 (Sn⁺⁺), 136.

I⁻: 56 (H⁺), 33 (Cu⁺), 59, 31, (Ag⁺), 148 (Zn⁺⁺), 8, 97, 98 (Cd⁺⁺), 115, 4, 147 (Hg⁺⁺), 108 (Tl⁺⁺⁺), 67, 94, 116 (Pb⁺⁺).

CN⁻: 13, 91, 143 (Cu⁺, Hg⁺⁺), 31, 135 (Ag⁺), 30 (Au⁺), 34, 98, 99 (Zn⁺⁺, Cd⁺⁺), 151 (Tl⁺⁺⁺), 109, 140, 77, 89.

NH₃: 10, 11, 12, 13, 85, 152, 98, 160, 54.

Py: 19, 20, 159, 42.

en: 13, 16, 17, 19, 45, 85.

SCN⁻: 31 (Ag⁺), 29 (Au⁺), 97, 98 (Cd⁺⁺), 76, 144 (Hg⁺⁺), 111, 112, 13, 58, 121 (Fe⁺⁺, Fe⁺⁺⁺), 24, 25, 26 (Cr⁺⁺⁺).

S₂O₃⁻⁻: 30, 119 (Ag⁺), 61, 64, 151.

Ac⁻: 104, 105 (Ag⁺), 44 (Zn⁺⁺, Mg⁺⁺, Ca⁺⁺), 98, 83, 57 (Cd⁺⁺, Pb⁺⁺), 126 (Cu⁺⁺), 138, 151 (Tl⁺, Tl⁺⁺⁺).

Ox⁻⁻: 46, 158 (Zn⁺⁺, Cd⁺⁺), 5 (Tl⁺), 90 (Pb⁺⁺), 146 (Be⁺⁺), 35, 141, 113, 114, 139, 142, 152, 156, 102, 48, 44.

Sal⁻: 110, 43.

NO₃⁻: 82 (Hg⁺⁺), 138, 153, 136, 98, 100, 117, 79, 6, 48.

SO₄⁻⁻: 82 (Hg⁺⁺), 136, 48, 52, 98, 113, 49.

be tempted to believe that cyanide complexes are actually isocyanide complexes, but many chemical and roentgenographic data militate strongly against this idea (*cf*. Sidgwick (145)). Thus it is well known that methylisocyanide complexes result from the methylation of cyanide complexes, a result which supports the hypothesis that the complex bond goes from the metal atom to carbon and not to nitrogen.

As emphasized already, the quantity $\frac{N}{Z} \log k + \log 55$ obtained experimentally is only an expression for the mean affinity for the exchange of more or less strongly bound water molecules for a particular ligand and the data in table 4, therefore, reveal nothing directly regarding the stability of the aquo ions themselves. But this does not prevent one from making certain deductions relevant to this problem. In point of fact, a study of table 4 shows that the tendency to form complex bonds to oxygen, or rather to OH^- and the anion of the salicyl-aldehyde (though not to the acetate ion, where the resonance in the carboxylate ion not only reduces the tendency to complex formation but also changes completely the character of the bond) runs parallel to some extent to the tendency to bind on NH_3 and CN^-, whilst the affinity for an ion like, e.g., Cl^-, follows entirely different rules. It seems therefore quite natural to regard OH^-, NH_3, and CN^- as ligands whose complex-forming abilities run parallel to those of the water molecule, and this naturally leads to the conclusion that those metal ions which have an especially high affinity for such "water-like" ligands should also form the most stable aquo ions. Thus an ion like the mercuric ion must be assumed to form a well-defined diaquo ion having a stability resembling that of H_3O^+. On the other hand, an ion like the thallous ion, which has an extremely small affinity for NH_3 and forms compounds with CN^- and OH^- which are known to be highly dissociated electrolytes, cannot be expected to form a well-defined aquo ion.

In the case of ligands like ethylenediamine and the oxalate ion which can form chelate rings the expression $\frac{N}{Z} \log k + \log 55$ represents, as already stated, the average change in free energy for a simple group. A comparison of the values recorded for these ligands with the corresponding ones for ammonia and the acetate ion therefore gives some information concerning the increase of stability which results from chelation. Note further that no ligand can be bound chelately to a hydrogen ion, as in this case the extremely weak and hypothetical hydrogen bond can be ignored. It will be seen that stability is enhanced in every case investigated save the silver–ethylenediamine system where, owing to the tendency of the silver ion to favor a linear configuration, there is a certain amount of strain in the chelate ring (*cf*. page 389).

Among ligands not hitherto mentioned, the thiocyanate and the thiosulfate ions present examples of complex bonds from metal to sulfur. It will be seen that the thiosulfate ion forms the stronger complexes, but that both ions are bound most strongly to the most electronegative elements. In contrast to these ions the acetate ion, and to a still greater degree the nitrate, sulfate, and perchlorate ions, show only a slight tendency to form true complex compounds with definite

stereochemical configurations.[2] But this does not prevent such ions, with their relatively small size, from associating to a considerable extent with ions of an opposite sign by purely Coulombic attraction. Such an ion association is also manifest in solutions of many alkali salts and is especially pronounced in non-aqueous solutions of low dielectric constant. A theory for this purely electro-static "complex formation" was first advanced by N. Bjerrum (27), and this theory was later extended and confirmed for a large number of cases by Fuoss and Kraus (68, 69, 70). The most important feature of the Bjerrum–Fuoss theory is to regard salts whose ionic dimensions exceed a certain critical value as 100 per cent dissociated; conversely, ion-pairs whose mutual distance apart is less than the critical distance are to be regarded as associated. There is, of course, a smooth transition between cases of ion association where the emphasis is on purely physical attraction and the formation of genuine chemical complexes, but it is characteristic that both phenomena can be discussed in terms of the law of mass action. Davies and coworkers (6, 48–53, 106, 113–114, 136, 138) have determined a large number of association constants for so-called strong electrolytes in aqueous solution, using conductivity measurements and taking into account the interionic forces (the Debye–Hückel–Onsager theory). In con-trast to actual complex formation purely ionic association is not characterized by definite coördination numbers, a fact which makes it impossible to compare the two phenomena on a strictly comparable basis. Results from the systems of strong electrolytes are nevertheless included in table 4, log k for the binary association being somewhat arbitrarily identified with log k + log 55. Values for the logarithm of the binary association constant as determined by Davies and his coworkers are arranged in the main in the extreme right-hand columns of table 4 (nitrate and sulfate) and in the lowest rows (the alkali metals and alka-line earths). The figures given for the association of the mercuric ion with nitrate ion and sulfate ion are calculated in the normal way, using the values of k_1 and k_2 determined by Infeldt and Sillén (82). A study of the data shows that the tendency to form ion-pairs is far less specifically variable than the tendency to form complexes. Thus it is very characteristic that the sulfate ion shows pretty much the same tendency to associate with all the divalent ions investigated, a tendency moreover which is even more uniform than one might expect from the known variations in ionic radii. It must be remembered, however, that the behavior during ionic association of the water sheath in hydrated ions has not been clearly established, and it may well be that the variation in the "effective" radius in aqueous solution is considerably smaller than the variation in the crystal radius.

CONCLUSION

It should be clear from this review that on the basis of the available experi-mental data it is possible to establish certain empirical rules regarding the ten-dency of metal ions to form complexes, rules which permit rough calculations of

[2] These observations must be viewed in conjunction with the fact that these oxo-anions are coördinatively saturated and have relatively firmly bound electrons (Fajans and Joos (62)).

the magnitude of the complexity constants in systems not as yet investigated and which provide at the same time some qualitative information concerning the nature of the chemical bonds involved. In order to make further progress it is important not only to investigate new systems but also to increase the accuracy of measurements throughout and to determine, more often than has been the case in the past, the extent to which complex formation is influenced by temperature. Since the complexity constants are really measures of changes in the Gibbs free energy of reaction, if one can also obtain information regarding the change in heat content (the enthalpy) for the same reaction, the change in entropy can be calculated. Thus it would be possible to make yet another substantial advance by purely thermodynamic means and to establish certain fundamental conceptions which, in conjunction with a knowledge of spectra, should lead in the future to a complete understanding of the problems which now lie before us.

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