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THE STABILITY OF MIXED COMPLEXES IN SOLUTION

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CONTENTS

ABBREVIATIONS

aht – 2-acetyl-3-hydroxythiophene ($d = 3$)
alan – alanine (A^-, $d = 2$)
aspg – asparagine (A^-, $d = 3$)
aspt – aspartate (A^{2-}, $d = 3$)
chromotropate – 1,8-dihydroxynaphthalene-3,6-disulfonate (A^{4-}, $d = 2$)
cdta – cyclohexane – 1,2-diamine-*N,N,N′,N′*–tetraacetate (A^{4-}, $d = 6$)
dien – diethylenetriamine ($d = 3$)
dmg – dimethylglyoxime (A^-, $d = 2$)
edda – ethylenediamine-*N,N′*-diacetate (A^{2-}, $d = 4$)
edta – ethylenediamine-*N,N,N′,N′*-tetraacetate (A^{4-}, $d = 6$)
en – ethylenediamine ($d = 2$)
gl – glycinate (A^-, $d = 2$)
glgl – glycylglycinate (A^-, $d = 3$)
glut – glutamate (A^{2-}, $d = 3$
hedta – *N*-hydroxyethyl ethylenediamine-*N,N′,N′*-triacetate (A^{3-}, $d = 6$)
himda – *N*-hydroxyethyl iminodiacetate (A^{2-}, $d = 4$)
imda – iminodiacetate (A^{2-}, $d = 3$)
maps – methyl-α-picolyl sulfide ($d = 2$)
nta – nitrilotriacetate (A^{3-}, $d = 4$)
pn – propylene-1,2-diamine ($d = 2$)
tetren – tetraethylene pentamine ($d = 5$)
tironate – 1,2-dihydroxybenzene-3,5-disulfonate (A^{4-}, $d = 2$)

A. INTRODUCTION

(i) Definitions and scope

It is now generally agreed that in a solution containing metal ions and two different suitable ligands, mixed-ligand complexes will be formed. The key word in this statement is *suitable*, since instances have been found where mixed-ligand complexes cannot be formed because of certain properties of the ligands. In the case of monodentate ligands having the same type of bonding to the central ions, however, there is no question that mixed-ligand complexes are formed, and are relatively stable. This view has been recognized for only about a decade and a half. To quote early workers: "the chief point to note is that the mixed ions are formed as readily (or very nearly so) as those derived from only two simple ions. This is perhaps slightly unexpected, but it is difficult to think of any reason why this should not be so"[1]. Systematic investigations of mixed complex formation were rare up to that date. In most cases, where a determination of the stability of a mixed complex was made, this was done to explain deviations from expectation in a study of binary complex formation.

Since then, many studies have been directed towards a better understanding of the formation of mixed complexes in solution. Most authors recognized the importance of statistical factors in determining the stability of the mixed complexes, although other factors, such as repulsion between unlike ligands, geometric factors, dipole interactions with the solvent, the type of bonds formed, and outer *versus* inner-orbital coordination, have also been discussed (section E). In order to draw general conclusions, it is important to have an overall picture of the data available. Fridman and coworkers[2], and Kida[3], published tables comparing the stabilities of several mixed complexes, and another table is included in a general compilation of stability constants[4]. A comprehensive table, however, is presented here for the first time.

Solid double salts, in particular double halides, have been well known for a long time, but this class of compound, illustrated by PbClF, lead chlorofluoride, the well known analytical precipitate for fluoride[5], will not be further dealt with in this review. Mixed halides exist also in the vapor phase, and indeed most theories for the stability of mixed complexes pertain implicitly to isolated complexes in the vapor phase, rather than to condensed systems with solvent present. However, only few instances of measurements on the stability of mixed species in the vapor phase could be found. The formation of lead bromochloride in the vapor is, perhaps, the most clear-cut recent example[6]. The standard free energy change for the reaction

$$PbCl_2(g)+PbBr_2(g) \rightleftharpoons 2\ PbClBr(g) \tag{1}$$

is +0.94 kcal at 700° per mole of PbClBr. The authors hope that further work in this direction will be done, since the information obtained can be related to theoretical treatments more clearly than can stabilities in solution.

The information reviewed here is restricted to solutions, where the solvent may be water, an organic solvent, an aqueous-organic solvent mixture, or a molten salt. Since solvent molecules (or ions, in the case of molten salts) are also ligands, all binary complexes which are not coordinatively saturated with a given ligand are, strictly speaking, mixed-ligand complexes. The aquation reactions of, say, platinum metal halogeno-complexes are indeed substitution reactions of one ligand by another, leading to mixed aquo-halogeno species. A consideration of systems where one of the ligands is the solvent, or derives directly from the solvent by hydrolysis, such as the following:

$$trans\ Ir(H_2O)_2Cl_4^{2-}(aq)+H_2O \rightleftharpoons Ir(H_2O)_3Cl_3^{-}(aq)+Cl^{-}(aq)^7 \tag{2}$$

$$ThY+H_2O \rightleftharpoons ThYOH^{-}+H^{+}\ (Y^{4-} = \text{ethylenediamine tetraacetate})^8 \tag{3}$$

$$\begin{aligned}&Hg(NO_3)Cl_3^{2-}\ (\text{in (K, Li)}NO_3\ \text{melt})+Cl^{-}\ (\text{in (K, Li)}NO_3\ \text{melt}) \rightleftharpoons\\ &HgCl_4^{2-}(\text{in (K, Li)}NO_3\ \text{melt})+\text{solvent}^9\end{aligned} \tag{4}$$

is outside the scope of this review, except for certain hydroxide systems with monodentate ligands. Mixed complexes with more than two ligands, are excluded from the present review, whilst solution systems with two distinct ligands not deriving from the solvent are included. The *ternary* species, or mixed complexes, are made up of the central ion and of ligands of two kinds, in addition to solvent molecules required to make up the coordination sphere. The *binary* species, or the parent complexes, contain only one kind of ligand.

The mixed complex formation systems considered here can be regarded as falling into three categories. The first includes the many systems for which it is possible to compare the ternary with the binary complex stabilities. Such systems are discussed in detail. For others this has been impossible, either because of lack of data, or because of fundamental difficulties such as the nonformation of certain species. Whatever quantitative data pertaining to the stability of the mixed complexes of this category are available, are reported here, but not discussed. Finally, there is a large group of mixed complexes, identified qualitatively in solution, for which no stability constants have been reported, and which are therefore merely listed in this work without detailed comment or review.

The literature survey on which this review is based covers the period up to and including 1967.

(ii) Mixed complex formation constants

The stability of a mixed complex is best measured by the overall formation equilibrium constant (stability constant) β_{ij}, according to the reaction

$$\mathrm{M}+i\mathrm{A}+j\mathrm{B} \rightleftarrows \mathrm{MA}_i\mathrm{N}_j \tag{5}$$

Here M is the central ion (with charge omitted), forming mononuclear complexes, and A and B are ligands, either or both of them being anions or uncharged. The sum of the indices $n = i+j \leq N$, cannot exceed the coordination number N, and will be termed the level of coordination[10] if both ligands are monodentate. A total of $N-n$ coordination sites will then be occupied by the solvent.

The mixed complex and equilibrium constants relating to its formation will henceforth be designated by the subscript $_{ij}$. Often it is not the constant β_{ij} which is reported, but the equilibrium constant of a substitution reaction:

$$\mathrm{MA}_{i+1}\mathrm{B}_{j-1}+\mathrm{B} \rightleftarrows \mathrm{MA}_i\mathrm{B}_j+\mathrm{A} \tag{6}$$

The equilibrium constant will be denoted $K(+\mathrm{B}-\mathrm{A})_{ij}$, and similarly for multiple substitutions

$$\mathrm{MA}_{i+q}\mathrm{B}_{j-p}+pB \rightleftarrows \mathrm{MA}_i\mathrm{B}_j+q\mathrm{A} \tag{7}$$

The overall equilibrium constant will be $K(+p\mathrm{B}-q\mathrm{A})_{ij}$, where p need not equal q. Another general type of reaction often used in mixed-complex formation studies is that of addition:

$$\mathrm{MA}_i\mathrm{B}_{j-1}+\mathrm{B} \rightleftarrows \mathrm{MA}_i\mathrm{B}_j \tag{8}$$

with an equilibrium constant $K(+\mathrm{B})_{ij}$, and similarly for the addition of pB ligands, $K(+p\mathrm{B})_{ij}$.

The practice of reporting different equilibrium constants for the formation of a given mixed complex is dictated by experimental expedience. In order to compare the stability of the ternary complex with the stabilities of the parent binary complexes, additional information is required, If β_{ij} has been reported, it is necessary also to know β_{n0} and β_{0n} for MA_n and MB_n respectively, or the equilibrium constant for the complete sequence of substitution reactions of types (6) and (7), *i.e.* $K(+n\mathrm{B}-n\mathrm{A})_{0n}$ for

$$\mathrm{MA}_n+n\mathrm{B} \rightleftarrows \mathrm{MB}_n+n\mathrm{A} \tag{9}$$

The comparison can, of course, be made only at a constant coordination level n. This has been defined above for monodentate ligands, but can be enlarged to include ligands of any denticities d_A and d_B, and in that case $id_\mathrm{A}+jd_\mathrm{B} \leq N$ must remain constant for a comparison to be meaningful. Still, unless the denticity of all the ligands is the same, difficulties with units and dimensions may be encountered, complicating the comparison of numerical values of the stability constants[11].

(iii) Mixed complex stabilization constants

When the stabilities of ternary and binary complexes are compared, it is convenient to consider the dimensionless *mixing constant* $K_{\mathrm{M}(ij)}$ for the formation of a mole of mixed complex:

$$i/n\ \mathrm{MA}_n+j/n\ \mathrm{MB}_n \rightleftarrows \mathrm{MA}_i\mathrm{B}_j \tag{10}$$

This is the constant sometimes directly measured experimentally (*e.g.*[10]), and often reported by the authors themselves, after calculation from other constants, for reactions such as (5)–(9):

$$K_{\mathrm{M}(ij)} = \beta_{ij}/\beta_{n0}{}^{i/n}\beta_{0n}{}^{j/n} \tag{11}$$

$$= \beta(+j\mathrm{B}-j\mathrm{A})_{ij}/\beta(+n\mathrm{B}-n\mathrm{A})_{0n}{}^{j/n} \tag{12}$$

It is obvious that a major contribution to $K_{\mathrm{M}(ij)}$ will arise from statistical arguments alone. It is therefore convenient to define a *stabilization constant* K_S[12], which for ligands of equal denticity d will be given by

$$\log K_\mathrm{S} = \log K_\mathrm{M}-\log (n/i) \tag{13}$$

where (n/i) is the binominal coefficient. The justification for this definition will be discussed further below. The stabilization constant then measures extra stability (sometimes instability) of the ternary complex, due to electrostatic forces, geometric factors, solvent effect, etc., in addition to the statistical factor.

A large body of data exists on a type of mixed chelate complex which cannot be analysed in terms of mixing constants. These complexes involve a highly multidentate ligand such as ethylenediamine tetraacetate, together with a monodentate or bidentate ligand. In such systems it is customary to compare the two reactions (with charges omitted):

$$\mathrm{MA(H_2O)}_{N-d_\mathrm{A}}+\mathrm{B} \rightleftarrows \mathrm{MAB(H_2O)}_{N-d_\mathrm{A}-d_\mathrm{B}}+d_\mathrm{B}\mathrm{H_2O} \tag{14}$$

$$\mathrm{M(H_2O)}_N+\mathrm{B} \rightleftarrows \mathrm{MB(H_2O)}_{N-d_\mathrm{B}}+d_\mathrm{B}\mathrm{H_2O} \tag{15}$$

where d_A and d_B are the denticities of the ligands, and $d_A > d_B$. The ratio of the equilibrium constants, K_Δ, is a dimensionless parameter denoting the stabilization of the mixed complex. The difference, $\log K_\Delta$, between the logarithms of the equilibrium constants of reactions (14) and (15) is the same if the roles of A and B in these reactions are interchanged[13]. Moreover, $\log K$ is also the value of the equilibrium constant for the disproportionation reaction (16)[13,14], where, for the sake of clarity, the coordinated solvent and the charges are omitted:

$$MA + MB \rightleftarrows MAB + M \tag{16}$$

This shows that $\log K_\Delta$ can be calculated from the stability constants of the binary and ternary complexes $\log K_\Delta = \log \beta_{11} - \log \beta_{10} - \log \beta_{01}$. This approach can now be generalized to any mixed complex MA_iB_j:

$$\log K_{\Delta(ij)} = \log \beta_{ij} - \log \beta_{i0} - \log \beta_{0j} \tag{17}$$

The greatest utility of this approach is, however, for the simpler case discussed above.

(iv) Predominance area diagrams

The stability constants β_{ij} are a direct measure of the stability of the mixed complexes, and the mixing constants K_M are a good measure of their relative stabilities. It is, however, also useful to have a graphical representation of the formation of the binary and ternary species, but three dimensions are required: concentration of free A, concentration of free B, and % formation. It is possible to make a series of cuts at, say, constant [A], and present the per cent formation

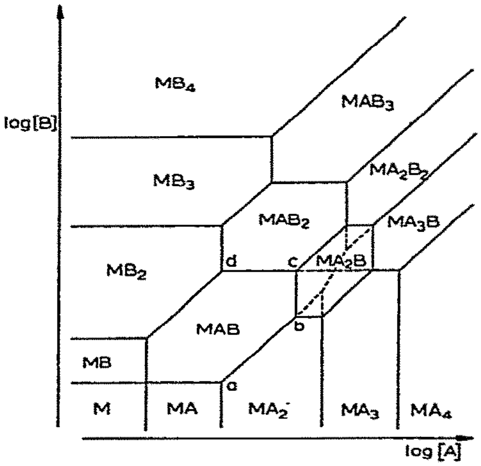

Fig. 1. A predominance area diagram for a hypothetical system of ternary complexes MA_iB_j at coordination levels up to $i+j = 4$.

of the species as a function of varying [B]. A convenient way of obtaining an overall picture is to use a predominance-area diagram[15]. A schematic diagram for a hypothetical system M–A–B is shown in Fig. 1. The ordinates are log [A] and log [B], and areas are marked with the predominating species MA_iB_j at the corresponding concentrations. Lines are then the loci of points where the concentrations of the two adjacent species are equal, and at triple points the concentrations of three complexes are equal.

The vertical line ending at *a* has the formula log [A] $= \log \beta_{10} - \log \beta_{20}$. For the horizontal line *c*–*d* the formula is log [B] $= \log \beta_{11} - \log \beta_{12}$. For the oblique line *a*–*b* the formula is log [B] $= \log \beta_{20} - \log \beta_{11} + \log$ [A]. For the point *c* the coordinates are log [A] $= \log \beta_{11} - \log \beta_{21}$ and log [B] $= \log \beta_{11} - \log \beta_{12}$. For this hypothetical case, all the binary and ternary complexes that can be formed up to a coordination level $n = 4$ are formed. One can easily perceive the (free) ligand concentration ranges within which a given coordination level is held. One also sees that for this hypothetical system MA_2B is less "important" than the other mixed species. Indeed, if it did not exist, then the areas of the surrounding species would meet at the dotted lines.

To illustrate real cases where in fact certain species are highly destabilized, ($K_S \ll 1$), whereas others are strongly stabilized, ($K_S \gg 1$), Figs. 2 and 3 have been prepared from the data for the Hg–Cl–Br and Hg–Cl–*I* systems, respectively, in molten potassium-lithium nitrate eutectic at 150 °C. The shaded area in each diagram corresponds to a region of ligand concentrations where no single species predominates. Note for the former system that neither $HgCl_3^-$ nor $HgBr_3^-$ are important binary species, and that HgClBr is strongly stabilized. The latter system

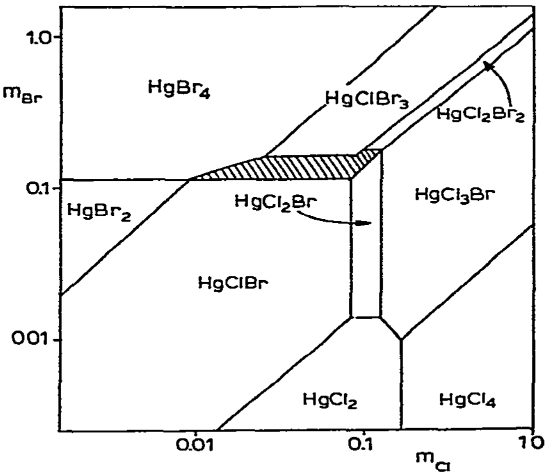

Fig. 2. Predominance area diagram for $HgCl_iBr_j$ ternary complexes in potassium-lithium nitrate eutectic at 150°, calculated from data in Ref. 16. In the shaded area several complexes coexist, with none predominating.

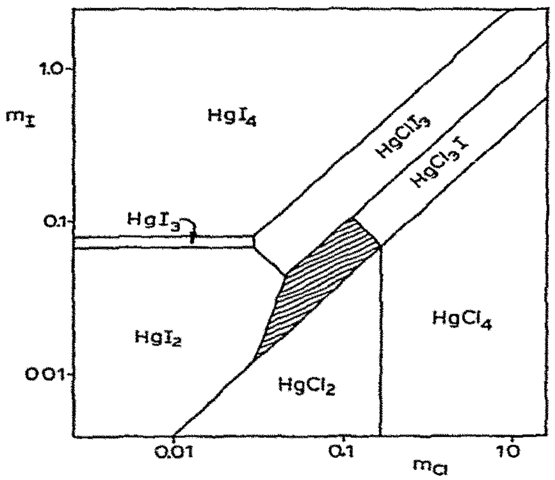

Fig. 3. Predominance area diagram as in Fig. 2 but for $HgCl_iI_j$.

shows that HgI_3^- does predominate in a narrow region, but that of the coordinatively unsaturated mixed species, none is particularly stable, and of the saturated ones, only the unsymmetrical ones are important. This information is, of course, implicit in the values of K_M (see Table 1 below), but its implications are clarified by the diagrams.

B. RELATIVE STABILITY OF MIXED COMPLEXES WITH MONODENTATE LIGANDS

This section contains a compilation of those systems where it has been possible to calculate mixing constants K_M or ratios of ligand addition constants K_A with reasonable reliability. The purpose is not to examine each item in the compilation critically, but to present the factual background against which certain generalizations can be proposed in a later section. When, however, gross inconsistencies occur in the data, these are pointed out and traced to their origins if possible.

(i) Mixed halide complexes

The heavier halide ions, chloride, bromide and iodide, tend in solution to form fairly stable complexes with "B"-type or "soft" metal ions. Mixed complex formation has therefore been observed for some transition-metal and many post-transition-metal ions. The halides, being spherical monatomic anions acting as monodentate ligands, present the least difficulties for theoretical interpretation of the magnitude of the K_S values observed. Furthermore, in most cases the reports on the mixed complexes either give the mixing constants K_M themselves, or provide all the data required for calculating them. There is thus no problem of incompatible data pertaining to different experimental conditions for the binary and ternary complexes.

The data available are shown in Table 1. For some complexes there are separate entries for values reported by different authors or pertaining to different media. These include aqueous solutions, with composition reported according to the usage in *Stability Constants*[4], organic solutions and a molten potassium-lithium nitrate eutectic. For the latter the temperature is also recorded, whereas for the other media room temperature is implied, usually 25°. The equilibrium constant reported originally by the author (equations 5–10) is also mentioned, but in every case K_M and K_S have been calculated and are shown.

TABLE 1

RELATIVE STABILITY OF MIXED HALIDE COMPLEXES

Complex	*Ref.*	*Constant*	*Conditions*	*log K_M*	*log K_S*
$MoOCl_4Br^{2-}$	17	$K(+Br, -Cl)$	8.2M H(Cl, Br)	0.34	−0.36
$MoOCl_3Br_2^{2-}$	17	$K(+Br, -Cl)$	8.2M H(Cl, Br)	1.02	0.02
$MoOCl_2Br_3^{2-}$	17	$K(+Br, -Cl)$	8.2M H(Cl, Br)	0.88	−0.12
$PdCl_2Br_2^{2-}$	18	$K(+2Br, -2Cl)$	$\mu = 1.1$	0.97	0.19
$PdCl_3Br^{2-}$	19	K_M	4.0M Li$^+$, 2.0M ClO$_4^-$ 2.0M halide	0.52	−0.08
$PdCl_2Br_2^{2-}$	19	K_M	4.0M Li$^+$, 2.0M ClO$_4^-$ 2.0M halide	0.57	−0.21
$PdClBr_3^{2-}$	19	K_M	4.0M Li$^+$, 2.0M ClO$_4^-$ 2.0M halide	0.49	−0.11
$PdBr_3I^{2-}$	20	K_M	4.0M Li$^+$, 2.0M ClO$_4^-$ 2.0M halide	0.69	0.09
$PdBr_2I_2^{2-}$	20	K_M	4.0M Li$^+$, 2.0M ClO$_4^-$ 2.0M halide	1.62	0.84
$PdBrI_3^{2-}$	20	K_M	4.0M Li$^+$, 2.0M ClO$_4^-$ 2.0M halide	1.26	0.66
$PtCl_3Br^{2-}$	21	$K(+Br, -Cl)$	0.3M NaClO$_4$	0.47	−0.13
$PtCl_2Br_2^{2-}$	21	$K(+Br, -Cl)$	0.3M NaClO$_4$	0.78	0.00
$PtClBr_3^{2-}$	21	$K(+Br, -Cl)$	0.3M NaClO$_4$	0.53	−0.07
$CuClI^-$	22	β_{11}	nitrate, var.	2.22	1.92
$CuBrI^-$	22	β_{11}	nitrate, var.	1.30	1.00
$AgCl_3Br^{3-}$	23	β_{31}	halide, var.	1.85	1.25
$AgClBr_3^{3-}$	23	β_{13}	halide, var.	1.47	0.87
$AgCl_3Br^{3-}$	24	K_M	7M NaClO$_4$	1.22	0.62
$AgClBr_3^{3-}$	24	K_M	7M NaClO$_4$	1.25	0.65
$AgCl_2I^{2-}$	24	K_M	7M NaClO$_4$	−0.72	−1.20
$AgBr_2I^{2-}$	24	K_M	7M NaClO$_4$	1.68	1.20
$AgBrI_2^{2-}$	24	K_M	7M NaClO$_4$	1.11	0.63
$AgBrI_3^{3-}$	24	K_M	7M NaClO$_4$	0.85	0.25
$AuCl_3Br^-$	25	$K(+Br, -Cl)$	$\mu = 0.1M$	0.58	−0.02
$AuCl_2Br_2^-$	25	$K(+Br, -Cl)$	$\mu = 0.1M$	0.68	−0.10
$AuClBr_3^-$	25	$K(+Br, -Cl)$	$\mu = 0.1M$	0.43	−0.17
ZnClBr	26, 27	K_M	(Li, K)NO$_3$ eutectic, 180°	0.21	−0.09
	26	K_M	polyphenyl eutectic, 180°	0.47	0.17
	28	K_M	aqu. soln.	0.33	0.03
$ZnCl_2Br^-$	27	K_M	(Li, K)NO$_3$ eutectic, 180°	0.00	−0.48
$ZnClBr_2^-$	27	K_M	(Li, K)NO$_3$ eutectic, 180°	0.20	−0.28

[continued]

TABLE 1 – *(continued)*

Complex	*Ref.*	*Constant*	*Conditions*	*log K_M*	*log K_S*
ZnClI	26, 27	K_M	(Li, K)NO_3 eutectic, 180°	0.19	−0.11
	26	K_M	polyphenyl eutectic, 180°	0.35	0.05
ZnBrI	26, 27	K_M	(Li, K)NO_3 eutectic, 180°	0.10	−0.20
	26	K_M	polyphenyl eutectic, 180°	0.26	−0.04
CdClBr	29	K_M	(Li, K)NO_3 or polyphenyl eutectics 150–200°	0.7	0.4
CdClI	29	K_M	(Li, K)NO_3 or polyphenyl eutectics 150–200°	0.7	0.4
CdBrI	29	K_M	(Li, K)NO_3 or polyphenyl eutectics 150–200°	0.7	0.4
$CdCl_2Br^-$	2	β_{21}	halide, var.	0.14	−0.34
$CdClBr_2^-$	2	β_{12}	halide, var.	0.48	0.00
$CdCl_2I^-$	2	β_{21}	halide, var.	0.59	0.11
$CdCl_2I_2^{2-}$	2	β_{22}	6M $NaClO_4$	0.59	−0.19
$CdClI_3^{2-}$	2	β_{13}	6M $NaClO_4$	0.20	−0.40
CdBrI	30	K_M	2M $NaClO_4$	0.49	0.19
$CdBr_2I^-$	30	K_M	2M $NaClO_4$	0.46	−0.02
$CdBrI_2^-$	30	K_M	2M $NaClO_4$	0.71	0.23
$CdBr_3I^{2-}$	2	β_{31}	6M $NaClO_4$	0.30	−0.30
	30	K_M	2M $NaClO_4$	0.42	−0.18
$CdBr_2I_2^{2-}$	2	β_{22}	6M $NaClO_4$	0.48	−0.30
	30	K_M	2M $NaClO_4$	0.85	0.07
$CdBrI_3^{2-}$	2	β_{13}	6M $NaClO_4$	0.35	−0.25
	30	K_M	2M $NaClO_4$	0.64	0.04
HgClBr	12, 31	K_M	0.5M $NaClO_4$	0.60	0.30
	10	K_M	dil.	0.57	0.27
	16, 32	K_M	(Li, K)NO_3 eutectic 150°	0.93	0.63
	32	K_M	polyphenyl eutectic 150°	0.85	0.55
	33	K_M	benzene	0.58	0.28
HgClI	31	K_M	0.5M $NaClO_4$	0.88	0.58
	10	K_M	dil.	0.68	0.38
	16, 32	K_M	(Li, K)NO_3 eutectic, 180°	0.21	−0.09
	32	K_M	polyphenyl eutectic, 180°	0.83	0.53
HgClI	33	K_M	benzene	0.75	0.45
HgBrI	31	K_M	0.5M $NaClO_4$	0.55	0.25
	10	K_M	dil	0.54	0.24
	16, 32	K_M	(Li, K)NO_3 eutectic 150°	−0.50	−0.80
	32	K_M	polyphenyl eutectic 150°	0.79	0.49
	33	K_M	benzene	0.38	0.08
$HgCl_2Br^-$	16	K_M	(Li, K)NO_3 eutectic 150°	1.22	0.74
$HgClBr_2^-$	16	K_M	(Li, K)NO_3 eutectic 150°	0.82	0.34
$HgCl_3Br^{2-}$	16	K_M	(Li, K)NO_3 eutectic 150°	1.23	0.63
$HgCl_2Br_2^{2-}$	16	K_M	(Li, K)NO_3 eutectic 150°	1.06	0.28
$HgClBr_3^{3-}$	16	K_M	(Li, K)NO_3 eutectic 150°	0.81	0.21
$HgCl_2I^-$	16	K_M	(Li, K)NO_3 eutectic 150°	0.27	−0.21
$HgClI_2^-$	16	K_M	(Li, K)NO_3 eutectic 150°	−0.27	−0.75
$HgCl_3I^{2-}$	16	K_M	(Li, K)NO_3 eutectic 150°	1.49	0.89
$HgCl_2I_2^{2-}$	16	K_M	(Li, K)NO_3 eutectic 150°	0.21	−0.57
$HgClI_3^{2-}$	16	K_M	(Li, K)NO_3 eutectic 150°	0.42	−0.18
$HgBrI_2^-$	34	K_M	1 M Li NO_3	0.68	0.20
	34	K_M	1 M (Na or K) NO_3	0.98	0.50
	34	K_M	1 M $M+_4NO_3$	1.29	0.71

TABLE 1 – *(continued)*

Complex	*Ref.*	*Constant*	*Conditions*	*log K_M*	*log K_S*
$HgBr_2I_2^{2-}$	34	K_M	1M Li NO_3	2.20	1.42
	34	K_M	1M (Na or K) NO_3	2.28	1.50
$HgBr_2I_2^{2-}$	34	K_M	1M NH_4NO_3	2.30	1.52
$HgBr_2I^-$	15	$K(+I)$	0.5M $NaClO_4$	0.81	0.33
	16	K_M	(Li, K)NO_3eutectic, 150°	0.07	−0.41
$HgBrI_2^-$	15	$K(+I)$	0.5M $NaClO_4$	0.99	0.51
	35	K_M	0.5M $NaClO_4$	0.98	0.50
	16	K_M	(Li, K)NO_3 eutectic, 150°	−0.32	−0.80
$HgBr_3I^{2-}$	16	K_M	(Li, K)NO_3 eutectic, 150°	0.29	−0.31
	15	$K(+I)$	0.5M $NaClO_4$	1.10	0.50
	36	$K(+I, -Br)$	1M bromide	0.83	0.23
$HgBr_2I_2^{2-}$	16	K_M	(Li, K)NO_3 eutectic, 150°	−0.08	−0.86
	15	$K(+I)$	0.5M $NaClO_3$	1.80	1.02
	35	K_M	0.5M $NaClO_3$	2.27	1.49
	36	$K(+2I, -2Br)$	1M bromide	1.11	0.33
$HgBrI_3^{2-}$	16	K_M	(Li, K)NO_3 eutectic, 150°	0.11	−0.49
	15, 33	$K(+I)$	0.5M $NaClO_4$	0.97	0.37
	35			1.37	0.77
	36	$K(+3I, -3Br)$	1M bromide	1.01	0.41
$InClBr^+$	37	β_{11}	Na halide, var.	0.48	0.18
$InCl_2Br$	37, 37b	β_{21}	Na halide, var.		
			(37 b) 4M $NaNO_3$	−0.33	−0.81
$TlClBr^-$	37, 37a	β_{11}	K halide var; (37a)	0.19	−0.11
$TlClBr_2^{2-}$	37, 37a	β_{21}	0 corr	0.86	0.38
$TlBrI^-$	37	β_{11}	K halide, var.	0.77	0.47
$TlBrI_2^2$	37	β_{12}	K halide var,	0.90	0.42
$PbCl_3Br^{2-}$	2	β_{31}	6M $NaClO_4$	0.37	−0.23
$PbCl_2Br_2^{2-}$	2	β_{22}	6M $NaClO_4$	0.69	−0.09
$PbClBr_3^{2-}$	2	β_{13}	6M $NaClO_4$	0.60	0.00
$PbBr_3I^{2-}$	2	β_{31}	6M $NaClO_4$	0.33	−0.27
$PbBr_2I_2^{2-}$	2	β_{22}	6M $NaClO_4$	0.40	−0.38
$PbBrI_3^{2-}$	2	β_{13}	6M $NaClO_4$	0.45	−0.15
$BiCl_4Br^{2-*}$	38	$K(+Br, -Cl)$	4M halide	0.61	−0.09
$BiCl_3Br_2^{2-*}$	38	$K(+Br, -Cl)$	4M halide	1.48	0.48
$BiCl_2Br_3^{2-*}$	38	$K(+Br, -Cl)$	4M halide	1.30	0.30
$BiClBr_4^{2-*}$	38	$K(+Br, -Cl)$	4M halide	0.88	0.18
$BiCl_2I$	39	K_M	dioxane	0.10	−0.38
$BiClI_2$	39	K_M	dioxane	−0.36	−0.84

* A referee has pointed out that the coordination level in 4M halide solutions is in dispute and may be six instead of five. This would change the numerical values of K_M and K_S but not the conclusion that mixed complexes are formed, with significant stabilization of the middle members.

As can be seen from the Table, the values of log K_S are usually small, falling between the limits -0.5 to $+1.0$, with positive values predominating. This means that statistical behavior is a fair first approximation, and some stabilization effects, which should also allow for destabilization, should be accounted for in a better approximation.

Some entries are definitely out of line. These are the values for $CuClI^-$; $AgCl_2I^{2-}$; HgBrI, $HgBrI_2^-$ and $HgClI_2^-$ in the nitrate melt; $InCl_2Br$; and $BiClI_2$

in dioxane. In the case of $InCl_2Br$, K_M had to be calculated from data pertaining to different media, and the values for the binary complexes themselves are not in good agreement. For $CuClI^-$ the results may be in error, since in the solubility equation used for the calculations, the formation of higher complexes such as $CuCl_2I^{2-}$ has been ignored (it has been included for the bromide case). For the other cases, especially the molten salt media, the complex species shown are coordinatively unsaturated, and thus contain solvent molecules or anions, in addition to the bulky iodide ion, possibly causing especially large steric effects.

In general, the results obtained for aqueous solutions, organic solvents and the molten nitrate eutectic medium do not show marked differences, although there are some outstanding cases of a strong solvent effect. In addition to the cases pointed out above, the mercury chloride–iodide and bromide–iodide systems are destabilized in the molten salt, although "normal" in aqueous and organic solutions. The strong temperature dependence and the mutually contrasting behavior of the zinc and cadmium systems[16,26,27,29,32] need to be taken into account when these systems are discussed.

In general in a study of mixed halide complexes, as well as of other mixed complexes where the ligands have the same charge, the values of K_M should not depend strongly on the ionic medium employed (but see section E). In particular when the complexes are coordinatively saturated, when the coordination level n equals the coordination number N, the activity coefficient quotient in dilute solutions is a product of ratios of activity coefficients of ions of the same charge and nearly the same size, so it should approximate closely to unity:

$$K_M{}^{T^n} = \frac{{}^a\mathrm{MA}_i\mathrm{B}_j{}^n}{{}^a\mathrm{MA}_n{}^i\,{}^a\mathrm{MB}_n{}^j} = \frac{[\mathrm{MA}_i\mathrm{B}_j]^n}{[\mathrm{MA}_n]^i[M\mathrm{B}_n]^j} \cdot \frac{{}^y\mathrm{MA}_i\mathrm{B}_j{}^i\,{}^y\mathrm{MA}_i\mathrm{B}_j{}^j}{{}^y\mathrm{MA}_n{}^i\,{}^y\mathrm{MB}_n{}^j} \simeq \frac{\beta_{ij^n}}{\beta_{n0}{}^i\beta_{0n}{}^j} \tag{18}$$

Therefore the concentration quotient, which is the quotient of the β's usually given as K_M, should closely approximate to the invariant thermodynamic $K_M{}^T$, and be independent of the medium. The results for mixed mercury bromide–iodide complexes in aqueous alkali metal nitrate media of ionic strength 1.0[34] support this prediction. For $HgBr_2I_2{}^{2-}$ log K_M varies only slightly, from 2.20 for $LiNO_3$, 2.27 for $NaNO_3$, 2.28 for KNO_3, 2.30 for NH_4NO_3 to 2.33 for $RbNO_3$, while for the coordinatively unsaturated $HgBrI_2{}^-$, where a molecule of solvent, or possibly a nitrate anion, occupies the fourth coordination site, the variation is much more pronounced: from 0.68 for $LiNO_3$ to 1.46 for a $RbNO_3$ medium.

Although hydrogen dihalide anions and the trihalide anions are not metal complexes, they can be treated formally as if they were. Vibrational spectra of mixed dihalides[40] and trihalides[41] are known, but the stabilities of the former have not been measured in solution. The latter, however, are well documented, and values of the equilibrium constants of

$$X_2 + Y^- \rightleftarrows X_2Y^- \qquad K(+Y)_{21} \tag{19}$$

have been reported by many authors. The constants for

$$X_2+X^- \rightleftarrows X_3^- \qquad K(+X)_{30} \tag{20}$$

are also well known. Unfortunately, there are only a few determinations of constants starting from the binary interhalogen

$$XY+Y^- \rightleftarrows XY_2^- \qquad K(+Y)_{12} \tag{21}$$

If X is the heavier of the two halogens, X_2Y^- can be considered as a mixed complex with X^+ (formally) the central ion and X^- and Y^- the ligands. Thus the mixing constant K_M is defined by the equilibrium

$$\tfrac{1}{2}X_3^- + \tfrac{1}{2}XY_2^- \rightleftarrows X_2Y^- \qquad K_M \tag{22}$$

and can be calculated from the above equilibria and

$$X_2+Y^- \rightleftarrows XY+X^- \qquad K(+Y-X)_{11} \tag{23}$$

as

$$K_M = K_{21}(K_{11}K_{12}K_{30})^{-\frac{1}{2}} \tag{24}$$

TABLE 2

RELATIVE STABILITIES OF "MIXED" TRIHALIDE ANIONS

Complex	*Ref.*	*Constant*	*Conditions*	*Ref.*	*log K_M*	*log K_S*
$BrClBr^-$	42	$K(+Cl)$	var.	(47, 48)	0.53	0.23
	43	$K(+Cl)$	HCl var.	(47, 48)	0.54	0.24
	44	$K(+Cl)$	var. 16°	(47, 48)	1.11	0.71
	45	$K(+Cl)$	var.	(47, 48)	0.47	0.17
	46	$K(+Cl)$	0 corr.	(47, 48)	0.53	0.23
	47	$K(+Cl)$	0 corr.	(48)	0.45	0.15
	48	$K(+Cl)$	var.	(47)	0.56	0.26
$IClBr^-$	49	$K(+Cl)$	1M HCl	(49a)	1.08	0.78
	50	K_M	dil.		0.61	0.31
$IClI^-$	42	$K(+Cl)$	var.	(49a)	1.80	1.50
	43	$K(+Cl)$	HCl var.	(49a)	1.65	1.35
	44	$K(+Cl)$	var. 16°	(49a)	1.99	1.69
	49	$K(+Cl)$	var.	(49a)	1.65	1.35
	51	$K(+Cl)$	0 corr.	(49a)	1.53	1.23
	45	$K(+Cl)$	var.	(49a)	1.98	1.69
	48	$K(+Cl)$	KCl, var.	(49a)	1.68	1.38
	52	$K(+Cl, -I)$	dil.	(49a)	1.52	1.22
$IBrI^-$	42	$K(+Br)$	var.	(50, 54)	1.14	0.84
	43	$K(+Br)$	HBr var.	(50, 54)	1.19	0.89
	44	$K(+Br)$	var. 16°	(50, 54)	1.30	1.00
$IBrI^-$	53	$K(+Br)$	HBr var.	(50. 54)	1.11	0.81
	45	$K(+Br)$	var.	(50, 54)	1.13	0.83
	47	$K(+Br)$	dil.	(50, 54)	1.20	0.90
	54	$K(+Br)$	0.02M $HClO_4$		1.05	0.75
	50	K_M	dil.		1.22	0.92
$AtClI^-$	50	K_M	dil.		0.68	0.38
$AtBrI^-$	50	K_M	dil.		1.37	1.07
$I\,I\,CN^-$	55	K_M	phosphate buffer		3.07	2.77

The values of K_M calculated in this manner, and values of K_S derived from eq. (13), are shown in Table 2. Unlike Table 1, the necessary data for the "binary complexes" have been obtained from sources other than those giving the data for the "ternary complexes", and the sources used are indicated under the heading "Conditions".

The results for the mixed trihalide ions fall into the pattern set by the mixed halide complexes of metals. The only entry grossly out of line is that pertaining to I_2CN^-, which admittedly is not a trihalide, and perhaps should not be compared with I_3^- and $I(CN)_2^-$ as "binary" complexes, since it may not contain iodine as the "central atom", but rather cyanide. In that case, however, the species $(CN)_3^-$ is not available for comparison.

(ii) Mixed complexes involving non-halide anionic ligands

The pseudohalide anions too, cyanide and thiocyanate, have been studied by several authors as ligands of mixed complexes, the other ligand usually being a halide anion. The cyanide ion, however, is not necessarily "compatible" with halide ions, because of the strong π-bonding character of the former (see section E). With the other anions studied, mainly oxy-anions such as thiosulfate, sulfate, nitrate, etc., there may be some doubt as to whether they are monodentate, and therefore "compatible" with monodentate ligands such as the halides. Furthermore, seldom have the constants for the binary complexes been measured by the authors who also published the ternary constants, and under the same conditions. This will make the entries for K_M and K_S more liable to error than those shown in Table 1.

The available data have been collected in Tables 3 and 4, arranged in the same order as Table 1. Table 3 contains mixed pseudohalide-halide complexes, and Table 4 other mixed complexes with anions as ligands.

TABLE 3

RELATIVE STABILITIES OF MIXED PSEUDOHALIDE-HALIDE COMPLEXES

Complex	*Ref.*	*Constant*	*Conditions*	*log K_M*	*log K_S*
$FeF(SCN)^+$	56	K_M	0.5M $HClO_4$	−0.15	−0.45
$FeCl(SCN)^+$	57	β_{11}	1.2M $NaClO_4$	0.37	0.07
$FeCl_2(SCN)$	57	β_{21}	1.2M $NaClO_4$	1.2	0.7
$FeBr(SCN)^+$	57	β_{11}	1.2M $NaClO_4$ (1,57a)	0.0	0.3
$PdCl_3(SCN)^{2-}$	58	$K(+SCN, -Cl)$	1.1M NaCl	1.64	1.04
$PdCl_2(SCN)_2^{2-}$	58	$K(+SCN, -Cl)$	1.1M NaCl	2.15	1.37
$PdCl(SCN)_3^{2-}$	58	$K(+SCN, -Cl)$	1.1M NaCl	1.35	0.75
$PdCl(SCN)_3^{2-}$	18	$K(+SCN, -Cl)$	1.1M NaCl	1.26	0.66
$PdBr_3(SCN)^{2-}$	18	$K(+SCN, -Br)$	1.1M NaBr	1.42	0.82
$PdBr_2(SCN)_2^{2-}$	18	$K(+SCN, -Br)$	1.1M NaBr	1.61	0.83
$PdBr(SCN)_3^{2-}$	18	$K(+SCN, -Br)$	1.1M NaBr	1.30	0.70
$CuCl(SCN)^-$	59	β_{11}	4.0M $NaNO_3$	−0.9	−1.2
$CuBr(SCN)^-$	59	β_{11}	2.0M $NaNO_3$	−0.7	−1.0

TABLE 3 – *(continued)*

Complex	*Ref.*	*Constant*	*Conditions*	*log K_M*	*log K_S*
$CuI(SCN)^-$	22	K_M	nitrate, var.	1.40	1.10
$CuI_2(SCN)^{2-}$	22	β_{21}	nitrate, var.	0.52	0.04
$CuI(SCN)_2^{2-}$	22	β_{12}	nitrate, var.	0.38	−0.10
$CuI_3(SCN)^{3-}$	22	β_{31}	nitrate, var.	0.53	−0.07
$CuI_2(SCN)_2^{3-}$	22	β_{22}	nitrate, var.	0.84	0.06
$CuI(SCN)_3^{3-}$	22	β_{13}	nitrate, var	1.11	0.51
$AgI(SCN)^-$	60	β_{11}	nitrate, var. (60a, b)	0.5	0.2
$AgI(SeCN)_2^{2-}$	61	β_{12}	2M KNO_3	1.62	1.14
$Ag(SeCN)(SCN)_2^{2-}$	61	β_{12}	2M KNO_3	3.06	2.58
$AgCl(SCN)_3^{3-}$	62	K_M	dil KSCN	0.74	0.14
$AgBr(SCN)_3^{3-}$	62	K_M	dil KSCN	0.80	0.20
$AgI(SCN)_3^{3-}$	62	K_M	dil KSCN	2.64	2.04
$HgCl(CN)$	63	K_M	0 corr	0.46	0.16
	63	K_M	dioxane	0.54	0.24
$HgBr(CN)$	63	K_M	0 corr	0.15	−0.15
	63	K_M	dioxane	0.13	−0.17
$HgI(CN)$	63	K_M	0 corr	−0.48	−0.78
	63	K_M	dioxane	−0.35	−0.65
$HgCl(CN)_2^-$	64	$K(+Cl)$	4M $NaNO_3$ (64a)	3.6	3.1
$HgCl(SCN)$	65	β_{11}	nitrate, var. (64a)	0.73	0.33
$HgCl(SCN)_2^-$	68	$K(+Cl)$	0.5M $NaNO_3$ (64a, 68a)	1.15	0.67
$HgBr(SCN)$	65	β_{11}	nitrate, var. (64a)	0.40	0.10
$HgBr(SCN)_2^-$	68	$K(+Br)$	0.5M $NaNO_3$ (64a, 68a)	0.31	−0.17
$HgCl(CN)_3^{2-}$	64	$K(+Cl)$	2M $NaNO_3$ (64a)	3.5	2.9
$HgBr(CN)_3^{2-}$	64	$K(+Br)$	2M $NaNO_3$ (64a)	2.8	2.2
$Hg(SCN)(CN)_3^{2-}$	64	$K(+SCN)$	2M $NaNO_3$ (64a)	2.9	2.3
$HgI_2(SCN)_2^{2-}$	35	K_M	?	2.55	1.77
$HgI_3(SCN)^{2-}$	35	K_M	?	2.04	1.44
$HgI_2(SeCN)^-$	35, 66	K_M	1M $NaClO_4$	0.76	0.28
$HgI_2(SeCN)_2^{2-}$	35, 66	K_M	1M $NaClO_4$	−0.01	−0.79
$HgI_3(SeCN)^{2-}$	35, 66	K_M	1M $NaClO_4$	0.38	−0.22
$BiCl(SCN)^+$	67	β_{11}	2M(ClO_4^-), 1M H^+	1.43	1.13
$BiCl(SCN)_2$	67	β_{12}	2M(ClO_4^-), 1M H^+ (67a)	0.80	0.50
$BiBr(SCN)^+$	67	β_{11}	2M(ClO_4^-), 1M H^+	1.87	1.39
$BiBr(SCN)_2$	67	β_{12}	2M(ClO_4^-), 1M H^+ (67a)	1.41	0.93

TABLE 4

RELATIVE STABILITIES OF MIXED COMPLEXES WITH OXY-ANION LIGANDS

Complex	*Ref.*	*Constant*	*Conditions*	*log K_M*	*log K_S*
$YCl(CH_3CO_2)^+$	69	K_M		−0.07	−0.37
$LaCl(CH_3CO_2)^+$	69	K_M		−0.25	−0.55
$HfCl(SO_4)^+$	70	β_{11}	2M H^+	0.57	0.27
$Hf(NO_3)(SO_4)^+$	70	β_{11}	2M H^+	1.00	0.70
$ThF(NO_3)^{2+}$	71	β_{11}	0.5M $NaClO_4$ (71a)	0.48	0.18
$ThF_2(NO_3)^+$	71	β_{21}	0.5M $NaClO_4$ (71b, 72)	1.26	0.78
$Th(NO_3)(SO_4)^+$	72	β_{11}	?	1.03	0.73
$Th(NO_3)_2(SO_4)$	72	β_{21}	? (72a)	1.23	0.75
$UO_2(CH_3CO_2)(SO_4)^-$	73	β_{11}	1M $NaClO_4$	0.33	0.03

[continued]

TABLE 4 – *(continued)*

Complex	*Ref.*	*Constant*	*Conditions*		*log K_M*	*log K_S*
$UO_2(CH_3CO_2)(SO_4)_2^{3-}$	73	β_{12}	1M $NaClO_4$		0.22	−0.26
$Fe(SCN)(SO_4)$	74	β_{11}	1.2M $NaClO_4$	(57)	0.32	−0.02
$Fe(SCN)(SO_4)_2^{2-}$	74	β_{12}	1.2M $NaClO_4$	(57)	1.8	1.3
$Ni(CH_3CO_2)(SO_4)^-$	75	β_{11}	1M $NaClO_4$	(75a)	−1.34	−1.64
$CuI(S_2O_3)^{2-}$*	76	β_{11}	var. (76a)		0.21	−0.09
$Cu(SCN)(S_2O_3)^{2-}$	76	β_{11}	var. (76b)		2.57	2.37
$Cu(CH_3CO_2)(SO_4)^-$	77	β_{11}	1 M $NaClO_4$		0.38	0.08
$AgCl(S_2O_3)^{2-}$	60	β_{11}	?	(60b, c)	0.8	0.5
$AgBr(S_2O_3)^{2-}$	60	β_{11}	?	(60b, c)	1.8	1.5
$AgI(S_2O_3)^{2-}$	60	β_{11}	?	(60b, c)	0.0	−0.3
$AgCl(S_2O_3)_2^{4-}$	78	β_{12}	var.	(78a)	0.51	0.03
$AgBr(S_2O_3)_2^{4-}$	78	β_{12}	var.	(78a)	0.62	0.14
$AgBr_2(S_2O_3)^{3-}$	78	β_{21}	var.	(78a)	1.25	0.77
$AgI(S_2O_3)_2^{4-}$	78	β_{12}	var.	(78a)	0.17	0.31
$AgI_2(S_2O_3)^{3-}$	78	β_{21}	var.	(78a)	0.20	−0.28
$AgCl(S_2O_3)_2^{4-}$	78	β_{12}	var.	(78b)	0.21	−0.27
$CdCl_2(S_2O_3)_2^{4-}$	62	K_M			0.53	−0.25
$CdBr_2(S_2O_3)_2^{4-}$	62	K_M			0.7	−0.08
$Cd(SCN)_2(S_2O_3)_2^{4-}$	62	K_M			0.75	−0.03
$Hg(CH_3CO_2)(CN)$	79	$K(+CH_3CO_2, -CN)$	var.	(64, 79a)	1.9	1.6
$HgI_2(S_2O_3)^{2-}$	80	K_M	$S_2O_3^{2-}$ var.		−0.21	−0.69
$HgI_3(S_2O_3)^{3-}$	35	K_M	$\mu = 3$M		−0.76	−1.36
$HgI_2(SO_3)^{2-}$	34, 35	K_M	SO_3^{2-} var.		2.29	1.81
$HgI_3(SO_3)^-$	35	K_M	$\mu = 3$M		2.1	1.5
$PbCl_2(NO_2)^-$	81	β_{21}	KNO_2 var.		1.46	0.98
$PbBr_2(NO_2)^-$	81	β_{21}			2.08	1.60
$Pb(SCN)_2(NO_2)^-$	81	β_{21}			6.87	6.4

* A referee has pointed out that unpublished work in his laboratory throws doubt on the formation of $CuI(S_2O_3)^{2-}$ when CuI is dissolved in thiosulfate solutions, the only species observed by him being $Cu(S_2O_3)_2^{3-}$.

Several entries in these Tables are rather dubious. Thus the very high value log $K_M = 3.06$ for the quite similar ligands thiocyanate and selenocyanate in $Ag(SeCN)(SCN)_2^{2-}$ is rather unlikely, as is also the value log $K_M = 6.87$ calculated for $Pb(SCN)_2(NO_2)^-$. On the other hand, the value log $K_M = -1.34$ for $Ni(CH_3CO_2)(SO_4)^-$ is too low, in view of the "normal" value 0.38 observed for the otherwise similar $Cu(CH_3CO_2)(SO_4)^-$. On the whole, however, the general trend of $-0.5 < \log K_S < +1.0$ is observed for the cases shown in Tables 3 and 4 too.

As mentioned in the introduction, the review does not consider mixed complexes which involve the solvent, either directly, or through hydrolysis.

Indeed, hydrolysed chelates containing a poly-dentate ligand and a hydrox-

TABLE 5

RELATIVE STABILITIES OF MIXED COMPLEXES INVOLVING THE HYDROXIDE ION

Complex	*Ref.*	*Constant*	*Conditions*	*log* K_M	*log* K_S
$B(OH)_2F_2^-$	82	$K(+OH, -F)$	var. (83a, b)	2.48	1.70
$B(OH)F_3^-$	83	$K(+OH, -F)$	var. (83a, b)	0.99	0.39
$Th(OH)(IO_3)^{2+}$	84	β_{11}	0.5M $LiNO_3$ (84a)	2.2	1.9
$Fe(OH)(SCN)^+$	57	β_{11}	1.2M $NaClO_4$ (57b)	−2.12	−2.42
$Pt(OH)_3Cl^{2-}$	85	$K(+H^+Cl^-, -H_2O)$	1M NaCl	0.82	0.22
$Pt(OH)_2Cl_2^{2-}$	85	$K(+H^+Cl^-, -H_2O)$	1M NaCl	1.35	0.57
$Pt(OH)Cl_3^{2-}$	85	$K(+H^+Cl^-, -H_2O)$	1M NaCl	0.93	0.33
$Pt(OH)_3Br^{2-}$	86	$K(+OH, -Br)$	0.1M KBr	1.1	0.5
$Pt(OH)_2Br_2^{2-}$	86	$K(+OH, -Br)$	0.1M KBr	1.8	1.0
$Pt(OH)Br_3^{2-}$	86	$K(+OH, -Br)$	0.1M KBr	1.8	1.2
$Ag(OH)CN^-$	87	β_{11}	hydroxide, var. (87a)	1.46	1.16
$Au(OH)_3Cl^-$	88	$K(+H^+Cl^-, -H_2O)$	0 corr	1.33	0.73
$Au(OH)_3Cl^-$	89	$K(+H^+Cl^-, -H_2O)$	0 corr	1.50	0.90
$Au(OH)_2Cl_2^-$	88	$K(+H^+Cl^-, -H_2O)$	0 corr	1.75	0.97
	89	$K(+H^+Cl^-, -H_2O)$	0 corr	2.05	1.27
$Au(OH)Cl_3^-$	88	$K(+H^+Cl^-, -H_2O$	0 corr	1.09	0.49
	89	$K(+H^+Cl^-, -H_2O$	0 corr	1.60	1.00
$Cd(OH)Cl$	90	$K(+OH^-, -Cl)$	0 corr (76a, b)	0.35	0.05
$Cd(OH)I$	91	β_{11}	3M $NaClO_4$ (91a)	3.6	3.3
$Hg(OH)(CN)$	92	β_{11}	2M $NaNO_3$ (38)	1.22	0.92
$Hg(OH)(CN)_2^-$	79	$K(+OH^-)$	var. (38, 79b)	1.7	1.2
$As(OH)_2Cl$	93	$K(+H^+Cl, -H_2O)$	0 corr.	1.84	1.36
$As(OH)Cl_2$	93	$K(+H^+Cl, -H_2O)$	0 corr.	1.28	0.80

ide ion are common. These cannot be discussed on the same basis as the mixed complexes considered hitherto, but if the second ligand is a simple monodentate anion, and the hydrolysis products of the metal are mononuclear, a comparison of the ternary and binary complexes can be made, much as above.

(iii) Mixed complexes involving monodentate neutral ligands

As discussed above (p. 286), mixing constants K_M for complexes having two anionic ligands of equal charge should be insensitive to the medium employed, and therefore better comparable with theoretical calculations (but see section E). The same should be true for two monodentate uncharged ligands, such as ammonia and pyridine. In two papers[94,95], Fridman and coworkers have reported on mixed complexes with these two ligands for cobalt, nickel, copper, zinc and cadmium (Table 6). The same medium (1.0M NH_4NO_3) has been used throughout, and in every case K_M has been calculated by the authors themselves.

Several systems where one of the ligands is ammonia and the other a monodentate anion have also been studied. Here, of course, the charge of the mixed complex is different from both the ammine complexed cation and the anionic complex, and furthermore, signs of "incompatibility" are observed, *e.g.* in the fact

TABLE 6

RELATIVE STABILITIES OF MIXED AMMONIA-PYRIDINE COMPLEXES

Complex	*Ref.*	*log K_M*	*log K_S*	*Complex*	*Ref.*	*log K_M*	*log K_S*
$Co(NH_3)py^{2+}$	94	0.26	−0.04	$Cu(NH_3)py^{2+}$	94	0.63	0.33
$Co(NH_3)_2py^{2+}$	94	0.06	−0.42	$Cu(NH_3)_2py^{2+}$	94	0.94	0.46
$Co(NH_3)py_2{}^{2+}$	94	0.31	−0.17	$Cu(NH_3)py_2{}^{2+}$	94	0.80	0.32
$Co(NH_3)_3py^{2+}$	94	0.23	−0.37	$Cu(NH_3)_3py^{2+}$	94	0.47	−0.13
$Co(NH_3)_2py_2{}^{2+}$	94	0.34	−0.43	$Cu(NH_3)_2py_2{}^{2+}$	94	1.2	0.4
	95	0.33	−0.44		95	1.2	0.4
$Co(NH_3)py_3{}^{2+}$	94	0.59	−0.01	$Cu(NH_3)py_3{}^{2+}$	94	1.0	0.4
$Co(NH_3)_3py_2{}^{2+}$	94	1.9	0.9	$Zn(NH_3)py^{2+}$	95	0.66	0.36
$Co(NH_3)_2py_3{}^{2+}$	94	1.5	0.5	$Zn(NH_3)_2py^{2+}$	95	0.46	−0.02
$Co(NH_3)py_4{}^{2+}$	94	0.8	0.1	$Zn(NH_3)_2py_2{}^{2+}$	95	0.48	0.00
$Co(NH_3)_3py_3{}^{2+}$	94	2.6	1.3	$Zn(NH_3)_3py^{2+}$	95	0.0	−0.6
$Co(NH_3)_2py_4{}^{2+}$	94	2.0	0.8	$Zn(NH_3)_2py_2{}^{2+}$	95	0.43	−0.35
$Ni(NH_3)py^{2+}$	94	0.44	0.14	$Zn(NH_3)py_3{}^{2+}$	95	0.16	−0.44
$Ni(NH_3)_2py^{2+}$	94	0.96	0.48	$Cd(NH_3)py^{2+}$	95	−0.28	−0.58
$Ni(NH_3)py_2{}^{2+}$	94	0.85	0.37	$Cd(NH_3)_2py^{2+}$	95	0.80	0.32
$Ni(NH_3)_3py^{2+}$	94	0.47	−0.13	$Cd(NH_3)py_2{}^{2+}$	95	0.44	−0.04
$Ni(NH_3)_2py_2{}^{2+}$	94	0.59	−0.19	$Cd(NH_3)_3py^{2+}$	95	0.78	0.18
	95	0.59	−0.19	$Cd(NH_3)_2py_2{}^{2+}$	95	1.23	0.45
$Ni(NH_3)py_3{}^{2+}$	94	0.57	0.03	$Cd(NH_3)py_3{}^{2+}$	95	0.44	−0.16
$Ni(NH_3)_3py_2{}^{2+}$	94	0.7	0.3				

TABLE 7

RELATIVE STABILITY OF AMMINE-ANIONIC LIGAND MIXED COMPLEXES

Complex	*Ref.*	*Constant*	*Conditions*		*log K_M*	*log K_S*
$Pt(NH_3)_3Cl^+$	96	β_{31}	$\mu = 1$M	(96a)	2.2	1.6
cis $Pt(NH_3)_2Cl_2$	96	β_{22}	$\mu = 1$M		3.5	2.7
trans $Pt(NH_3)_2Cl_2$	96	β_{22}	$\mu = 1$M		2.4	1.6
$Pt(NH_3)Cl_3{}^-$	96	β_{13}	$\mu = 1$M		2.8	2.2
trans $Pt(NH_3)_2I_2$	97	β_{22}	$\mu = 1$M		0.2	−0.6
$Cu(NH_3)NO_2{}^+$	98	β_{11}	1M $NaClO_4$	(98a)	0.49	0.19
$Cu(NH_3)(NO_2)_2$	98	β_{12}	1M $NaClO_4$	(98a)	0.9	0.4
$Ag(NH_3)Cl$	99	β_{11}	1M NH_4ClO_4		0.1	−0.2
$Ag(NH_3)Br$	99	β_{11}	1M NH_4ClO_4		0.30	0.00
$Ag(NH_3)(SCN)$	100	$K(+SCN)$	dil	(98a, 100)	2.68	2.38
$Ag(NH_3)(CN)$	101	K_M	dil	(101a, b)	0.82	0.52
$Ag(NH_3)(NO_2)_2$	102	β_{11}	dil	(98a)	0.65	0.35
$Zn(NH_3)_3Cl^+$	103	$K(+NH_3, -Cl)$	10% NH_4Cl		0.45	−0.15
$Zn(NH_3)_2Cl_2$	103	$K(+NH_3, -Cl)$	10% NH_4Cl		0.60	−0.18
$Zn(NH_3)Cl_3{}^-$	103	$K(+NH_3, -Cl)$	10% NH_4Cl		0.43	−0.17
$Zn(NH_3)(OH)^+$	104	β_{11}	0.1M $NaClO_4$	(104a)	0.48	0.18
$Zn(NH_3)_2(OH)^+$	104	β_{21}	0.1M $NaClO_4$	(104a)	1.59	1.11
$Zn(NH_3)(OH)_2$	104	β_{12}	0.1M $NaClO_4$	(104a)	1.60	1.12
$Zn(NH_3)_3(OH)^+$	104	β_{31}	0.1M $NaClO_4$	(104a)	1.32	0.72
$Zn(NH_3)_2(OH)_2$	104	β_{22}	0.1M $NaClO_4$	(104a)	0.63	0.03
$Zn(NH_3)(OH)_3{}^-$	104	β_{13}	0.1M $NaClO_4$	(104a)	1.38	0.78
$Cd(NH_3)_3I^+$	105	β_{31}	3M $NaClO_4$		0.21	−0.39
$Cd(NH_3)_2I_2$	105	β_{22}	3M $NaClO_4$		0.52	−0.26
$Cd(NH_3)I_3{}^-$	105	β_{13}	3N $NaClO_4$		0.45	−0.15

that the maximum coordination number for ammonia is often different from that for the anion (*e.g.*, lower for silver, $Ag(NH_3)_2^+$ *vs.* $AgCl_4^{3-}$, and higher for cadmium, $Cd(NH_3)_6^{2+}$ *vs.* CdI_4^{2-}). This difference is also due to a change in coordination configuration, *e.g.* octahedral for the ammine complexes and tetrahedral for the halide complexes. It is therefore impossible to draw general conclusions from the data compiled in Table 7, and the meaning of the values of K_M and K_S, which have been calculated formally, is not clear.

Two neutral ligands are involved in cases of mixed solvate formation. Of the many cases where this undoubtedly occurs, *i.e.* where solutes are dissolved in, or extracted by, a mixture of solvents, only very few have been analysed in terms of equilibrium constants. The only case found[106] where a mixing constant could be calculated, is that of the extraction of nitric acid with mixtures of methyl isobutyl ketone and of cyclohexanone, where $HNO_3(CH_3COC_4H_9)(cyc\text{-}C_6H_{10}O)$ is formed in benzene solutions of the extractants with $\log K_M = 0.42$ and $\log K_S = 0.12$.

C. RELATIVE STABILITY OF MIXED COMPLEXES WITH MULTIDENTATE LIGANDS

(i) Mixed complexes with equi-dentate chelating ligands

A large number of systems of mixed complexes where one or both of the ligands is multidentate have been studied. In relatively few of these systems is the coordination level kept constant on mixing, as is ensured when the denticity of the two ligands is the same. Only in such cases is it meaningful to compare the ternary with the binary complexes, and calculate mixing constants. In some such cases, it is possible to compare very similar ligands with only minor differences, such as d- and l-aspartic acid, or as acetylacetone and trifluoroacetylacetone. In other cases, where quite different ligands are used, such as ethylenediamine and oxalate, the mixed complex is similar to a bis (bifunctional) complex, in this case the bisglycinate. The mixing constants calculated for systems where the coordination level is kept constant are shown in Table 8.

TABLE 8

RELATIVE STABILITIES OF MIXED CHELATE COMPLEXES

Complex	*Ref.*	*Ligand A*	*Ligand B*	*Conditions*	*log K_M*	*log K_S*
ZrA_3B	107	acetylacetone	trifluoro acetyl acetone	benzene	1.26	0.66
ZrA_2B_2	107	acetylacetone	trifluoro acetyl acetone	benzene	1.72	0.94
$ZrAB_3$	107	acetylacetone	trifluoro acetyl acetone	benzene	1.38	0.78
HfA_3B	107	acetylacetone	trifluoro acetyl acetone	benzene	1.18	0.58
HfA_2B_2	107	acetylacetone	trifluoro acetyl acetone	benzene	1.61	0.83
$HfAB_3$	107	acetylacetone	trifluoro acetyl acetone	benzene	1.28	0.68

[continued]

TABLE 8 – *(continued)*

Complex	*Ref.*	*Ligand A*	*Ligand B*	*Conditions*	*log K_M*	*log K_S*
NiAB	108	ethylenediamine	oxalate	1M KNO_3	0.78	0.48
	109	ethylenediamine	oxalate	dil. en	0.35	0.05
NiA_2B	108	ethylenediamine	oxalate	1M KNO_3	1.25	0.77
$NiAB_2$	108	ethylenediamine	oxalate	1M KNO_3	1.13	0.65
CuAB	109	ethylenediamine	oxalate	dil. en	0.57	0.27
	110	ethylenediamine	oxalate	1M KNO_3	0.70	0.40
	111	ethylenediamine	oxalate	1M $NaNO_3$(111)	0.22	−0.08
CuAB	112	ethylenediamine	oxalate	0.25M $NaNO_3$	0.55	0.25
$CuAB^{2-}$	113	ethylenediamine	pyrophosphate		1.2	0.9
$CuAB^{+}$	112	ethylenediamine	acetylacetone	75% dioxane-aq.	0.21	−0.09
$CuAB^{2+}$	114	ethylenediamine	histamine	0.15M KNO_3	0.76	0.46
$CuAB^{+}$	114	ethylenediamine	serine anion	0.15M KNO_3	0.38	0.08
CuAB	114	ethylenediamine	salicylate dianion	0.15M KNO_3	0.70	0.40
$CuAB^{+}$	114	histamine	serine anion	0.15 MKNO_3	1.47	1.17
CuAB	115	acetylacetone	oxine	H_2O	1.10	0.80
	115	acetylacetone	oxine	CCl_4	1.01	0.71
	115	acetylacetone	oxine	3-methyl butanol	0.99	0.69
	115	acetylacetone	oxine	acetone	0.85	0.55
	115	acetylacetone	oxine	benzene	0.58	0.28
	115	acetylacetone	oxine	chloroform	0.47	0.17
CuAB	117	glycinate	ethylenediamine	90% acetone	0.14	−0.16
	117	glycinate	ethylenediamine	60% acetone	0.30	0.0
	117	glycinate	ethylenediamine	20% acetone	0.52	0.22
CuAB	112	acetylacetone	dimethylglyoxime	50% dioxane in EtOH	−0.02	−0.32
CuAB	116	glycinate	glycollate	1M $NaClO_4$	0.75	0.45
CuAB	117	glycinate	5-sulfosalicylate	1M $NaClO_4$	0.51	0.21
CuAB	118	glycinate	alaninate	0.05M $NaClO_4$	0.17	−0.13
	118	glycinate	alaninate	0.15M $NaClO_4$	0.17	−0.13
CuAB	118	glycinate	alaninate	0.35M $NaClO_4$	0.15	−0.15
	118	glycinate	alaninate	0.65M $NaClO_4$	0.19	−0.11
	118	glycinate	alaninate	1.00M $NaClO_4$	0.42	0.12
	118	glycinate	alaninate	2.00M $NaClO_4$	0.69	0.39
	119	glycinate	alaninate	1M $NaClO_4$	0.32	0.02
CuAB	119	glycinate	l-tyrosinate	1M $NaClO_4$	0.49	0.19
CuAB	119	glycinate	5-sulfosalicylate	1M $NaClO_4$	0.51	0.21
CuAB	119	alaninate	5-sulfosalicylate	1M $NaClO_4$	0.77	0.47
CuAB	119	alaninate	l-tyrosinate	1M $NaClO_4$	0.80	0.50
CuAB	120	l-aspartate	d-aspartate	dil. aq.	−0.33	−0.63
CuAB	121	5-sulfo-salicylate	1,2-diaminopropane	0 corr.	1.97	1.67
	121	5-sulfo-salicylate	1,2-diaminopropane	0.1M $NaClO_4$	0.92	0.62
	121	5-sulfo-salicylate	1,2-diaminopropane	1.0M $NaClO_4$	0.05	−0.25
	121	5-sulfo-salicylate	1,2-diaminopropane	2.0M $NaClO_4$	−0.13	−0.43
CuAB	114	salicylate dianion	histamine	0.15M KNO_3	1.33	1.03
$CuAB^{-}$	114	salicylate dianion	serinate	0.15M KNO_3	0.12	−0.18
$CuAB_2^{-}$	122	salicylate dianion	oxalate	0.06M $K_2C_2O_4$ (122)	4.41	4.31
CuAB	123	dipyridyl	catecholate	0.1M KNO_3 (123a, b)	1.42	1.12
CuAB	123	dipyridyl	salicylate	0.1M KNO_3 (123a, b)	2.88	2.58
$CuAB^{-}$	123	dipyridyl	5-sulfosalicylate	0.1M KNO_3 (123a, b)	2.91	2.61

TABLE 8 – *(continued)*

Complex	*Ref.*	*Ligand A*	*Ligand B*	*Conditions*	*log K_M*	*log K_S*
CuAB	124	2-thenoyl-trifluoro acetonate	isopropyltropolonate	CCl_4	0.86	0.56
CuAB	124	2-thenoyl-trifluoro acetonate	isopropyltropolonate	chloroform	0.73	0.43
	124	2-thenoyl-trifluoro acetonate	isopropyltropolonate	hexone	0.48	0.18
ZnAB	124	2-thenoyl-trifluoro acetonate	isopropxltropolonate	CCl_4	0.8	0.5
	124	2-thenoyl-trifluoro acetonate	isopropyltropolonate	chloroform	0.50	0.20
	124	2-thenoyl-trifluoro acetonate	isopropyltropolonate	hexone	0.15	−0.15
ZnAB	125	ethylenediamine	oxalate	1M (KNO_3)	0.54	0.24
ZnA_2B	125	ethylenediamine	oxalate	1M (KNO_3)	1.46	0.98
$ZnAB_2$	125	ethylenediamine	oxalate	1M (KNO_3)	1.72	1.24
CdAB	109	ethylenediamine	oxalate	dil.en	0.60	0.30
	125	ethylenediamine	oxalate	1M KNO_3(111b)	0.35	0.05
	111	ethylenediamine	oxalate	1M $NaNO_3$(111)	0.15	−0.15
CdA_2B	111	ethylenediamine	oxalate	1M $NaNO_3$(111)	1.2	0.7
CdA_2B	125	ethylenediamine	oxalate	1M KNO_3	1.25	0.77
$CdAB_2$	111	ethylenediamine	oxalate	1M $NaNO_3$	0.8	0.3
	125	ethylenediamine	oxalate	1M KNO_3	1.72	1.24

(ii) Mixed complexes formed at a varying coordination level

Where the level of coordination is not kept constant, when the ligands differ in denticity, it is possible to compare the mixed complex with the binary complexes through the parameter K (eq.17), since, according to the definition, $d_A > d_B$, ligand A may occupy so many of the coordination positions that there is no possibility of adding ligand B without releasing some of the coordinating groups of A. In such a case, when $d_A + d_B > N$, destabilization occurs, and $\log K_\Delta < 0$. Otherwise, it is often found that $\log K_\Delta > 0$, and the ternary complex is relatively stabilized, the equilibrium (16) then lying to the right. The systems for which comparative data were found, so that K_Δ could be calculated, are shown in Tables 9 and 10.

TABLE 9

THE RELATIVE STABILITY OF RARE EARTH HEDTA-IMDA AND HEDTA-HIMDA TERNARY AND BINARY COMPLEXES AT 25° IN A 0.1M (KNO_3) MEDIUM[126]

M	$-\log K_\Delta$		M	$-\log K_\Delta$		M	$-\log K_\Delta$	
	imda	*himda*		*imda*	*himda*		*imda*	*himda*
Y	1.68	4.83	Sm	2.07	4.61	Ho	1.60	4.42
La	2.66	3.96	Eu	1.96	4.49	Er	1.69	4.62
Ce	2.68	4.39	Gd	1.72	4.44	Tm	2.27	5.09
Pr	2.60	4.44	Tb	1.60	4.35	Yb	2.68	5.33
Nd	2.43	4.57	Dy	1.55	4.27	Lu	3.10	5.62

TABLE 10

THE RELATIVE STABILITIES OF TERNARY AND BINARY COMPLEXES WITH LIGANDS OF DIFFERENT DENTICITIES

Complex of ligand A	*Ligand B*	*Ref.*	*Conditions*	*log K_A*
Th edta	oxine-5-sulfonate	127	0.1M KCl	−2.53
cdta				−2.82
Mn^{II} gl	pyruvate	14	0.1M	+1.5
gl_2				+1.1
Fe^{II} dmg_2	SCN^-	128	var. KSCN	−0.60
	2 SCN^-			+1.23
Fe^{III}nta	$CH_3CO_2^-$	129	0.1M	−1.4
	tironate			−5.4
	chromotropate			−19.9
Co^{II}en	SO_4^{2-}	130	2.72M $NaClO_4$	−2.3
en_2				−2.1
en_3				−3.6
Co^{II}dipy	γ picolinate	131	50% aq. dioxane, 0.1M	−0.2
	maps			0.0
	aht			0.0
$Co^{II}$$dmg_2$	2 Cl^-	128	var. KCl	+1.7
	SCN^-		var. KSCN	+1.9
	2 SCN^-			+4.8
Co^{II}edta	en	132		−4.2
Ni^{II}dien	glycinate	133	0.5M NaCl	−0.64
	oxalate		0.5M KNO_3	−0.81
Ni^{II}tetren	NH_3		0.5M $NaClO_4$	−1.91
		134	0.4M $NaNO_3$	−1.34
Ni^{II}dipy	γ picolinate	131	50% aq. dioxane, 0.1M	−0.2
	maps			−0.3
	aht			0.0
Ni^{II}gl	pyruvate	135	0.5M KCl	+1.27
gl_2				+1.77
Ni^{II}glgl	imidazole	131		−0.1
Ni^{II}nta	salicylate	136		−0.75
	NH_3	133	0.5M $NaClO_4$	−0.20
		134	0.25M $NaNO_3$	−0.5
	en	133	0.5M $NaClO_4$	−0.40
	gl		0.5M NaCl	−0.88
		136	0.5M $NaNO_3$	−1.37
	oxalate	133	0.5M KNO_3	−3.13
Ni^{II}edta	NH_3		0.5M KCl	−1.39
		134	0.4M $NaNO_3$	−1.38
Ni^{II}edda	NH_3	133	0.5M $NaClO_4$	−0.74
hedta	NH_3		0.5M $NaClO_4$	−0.74
		134	0.25M $NaNO_3$	−1.18
$Cu^{I}$$en_2$	$S_2O_3^{2-}$	137	1M $Na_2S_2O_3$	−8.1
	SO_3^{2-}		1M Na_2SO_4	−6.5
Cu^{II}en	$P_3O_{10}^{3-}$	141	1M $NaNO_3$	−0.47
en_2				−5.34
en	imda	138	dil.	−1.20
	2 pyridine	139	dil.	−1.88
Cu^{II}pn	2 pyridine			−1.91
Cu^{II}dipy	γ picolinate	131	50% aq. dioxane, 0.1M	−0.6

TABLE 10 – *(continued)*

Complex of ligand A	*Ligand B*	*Ref.*	*Conditions*	$\log K_\Delta$
	maps			−1.0
	aht			+0.5
	pyrocatecholate	140	0.1M KNO_3	+0.4
	tiron			+0.9
	salicylate			+0.3
	5-sulfosalicylate			+0.3
Cu^{II}phen	oxine 5-sulfonate	142	dil.	0.0
Cu^{II}pyrophosphate	NH_3	143	1M NH_4NO_3	−1.7
	$2NH_3$			−2.64
Cu^{II}gl	en	139	dil.	−1.58
	pn			−1.61
	2 pyridine			−1.97
Cu^{II}gl	NH_3	144	dil.	−1.86
	2 NH_3			−0.99
Cu^{II}glgl	imidazole	131		−0.35
Cu^{II}nta	picolinate	145		+0.15
	en	146		−3.61
	salicylate	136		−5.28
Cu^{II}edta	en	146		−9.25
		132		−7.4
Ag^{I}en	oxalate	109		+0.10
Zn^{II}dipy	γ picolinate	131	50% aq. dioxane, 0.1M	−0.2
	maps			0.0
	aht			0.0
Zn^{II}gl	pyruvate	14	0.1M	+1.4
gl_2				+1.7
$Cd^{II}gl_2$	$4NH_3$	147	dil.	−5.95
$alan_2$				−5.51
β-$alan_2$				−4.21
$aspg_2$	$2NH_3$			−2.29
$aspt_2$				−2.24
$glut_2$				−3.12
glgl	imidazole	131		0.0

D. NON-COMPARATIVE DATA ON MIXED COMPLEX STABILITIES

An attempt has been made at a comprehensive presentation of the comparative data available on ternary complex stability as related to the stabilities of the parent binary complexes. In addition to this material, given in sections B and C, there is a very large quantity of information on the stabilities of mixed compleves which cannot be related to the binary data. Since this material cannot be dealt with completely in this review, only examples will be given. Non-comparative data can arise for several reasons.

A trivial reason, though often encountered, is that the stabilities of the binary complexes have not been determined, although expected to be readily measurable.

An example may be the bismuth–chloride–cyanide system[67], where $BiCl(CN)^+$ is formed, but whereas the stability of $BiCl_2{}^+$ is known, that of $Bi(CN)_2{}^+$ is not.

In some cases, however, lack of data for one of the parent binary complexes is due to non-formation of such a species, as when two binary complex systems have different coordination configurations, as encountered for example with halide and ammine complexes. Thus in the silver ammonia-halide system, the linear complex $Ag(NH_3)_2{}^+$ adds on bromide ions[99] to form $Ag(NH_3)_2Br$ and $Ag(NH_3)_2Br_2{}^-$, but whereas a (presumably tetrahedral) $AgBr_4{}^{3-}$ species exists, the addition of ammonia molecules to $Ag(NH_3)_2{}^+$ cannot apparently take place.

In other cases, it is not the species with the higher coordination number that are unstable but the intermediate species, in a system where complexes are apparently not formed in a stepwise manner, *e.g.* the iron(III) phenanthroline cyanide system[148]. The following constants have been reported for the species $Fe(phen)_i(CN)_j{}^{3-j}$: $\log \beta_{14} = 21.3$, $\log \beta_{22} = 26.3$ and $\log \beta_{30} = 21.3$. However, there is no sense in calculating K_M, since the ligands differ in denticity, and it is impossible to calculate K_Δ, since the species with $i = 0$ and $j = 2$ or 4 are not formed.

The, again, many replacement reactions have been studied where the complete conversion of MA_n to MB_n has not been attained, while there are no appropriate β_{n0} and β_{0n} data. A possible example may be the uranium(IV) chloride-bromide system in nitromethane[149], where the values of $\log K_{51}$ (+Br−Cl) and $\log K_{42}$(+Br–Cl) have been reported, but the stabilities of neither $YCl_6{}^{2-}$ nor $UBr_6{}^{2-}$ in nitromethane are known.

In the case of mixed hydroxo complexes, the binary metal ion-hydroxide ion system seldom forms mononuclear complexes, so that it is again impossible to compare the stability of the ternary species with proper binary ones. In the presence of an anionic ligand, the effective charge on the metal ion is reduced, so that it is a weaker acid than the "binary" aquo ion $M(H_2O)_N{}^{m+}$, and its tendency to polymerize into polynuclear species diminishes. Thus, for the system [150] $Cu(OH)_j$ (pyridine), with $j = 1,2$ or 3, there is no good evidence that mononuclear species $Cu(OH)_n{}^{2-n}$ with $n = 2,3$ or 4 are formed[4].

There are thus many types of mixed complexes where no comparative data for ternary and binary species can be presented. Such systems involving multidentate ligands are too numerous to list, but for purposes of reference, systems with simple monodentate ligands are listed in Table 11.

TABLE 11

STABILITY DATA FOR SOME MIXED COMPLEXES WITH MONODENTATE LIGANDS

Complex	*Ref.*	*Constant*	*log Constant*
$ScCl(SCN)_2$	151	$K_{12}(+2SCN)$	2.57
$NdF(CO_3)_3{}^{4-}$	152	$K_{13}(+F, -CO_3)$	−0.36
$NdF_2(CO_3)_2{}^{3-}$		$K_{22}(+F, -2CO_3)$	−0.95
$ErF_2(CO_3)_2{}^{3-}$		$K_{22}(+F, -2CO_3)$	0.89
$Hf(NO_3)(SO_4)_2{}^-$	70	β_{12}	5.73

TABLE 11 – *(continued)*

Complex	*Ref.*	*Constant*	*log Constant*
UCl_5Br^{2-}	149	K_{51}(+Br, −Cl)	−0.52
$UCl_4Br_2^{2-}$		K_{42}(+Br, −Cl)	−1.30
$Fe(OH)(HSCH_2CO_2)$	153	β_{11}	12.37
$Ni(CH_3CO_2)(SO_4)_2^{3-}$	75	β_{12}	0.48
$Ni(CN)_5Cl^{4-}$	154	K_{51}(+Cl)	−0.66
$Pd(OH)Cl_3^{2-}$	155	K_{13}(+OH, −Cl)	5.7
$Pd(OH)Br_3^{2}$		K_{13}(+OH, −Br)	4.23
$Pd(N_3)_2Cl_2^{2-}$	156	K_{22}(+2N$_3$, −2Cl)	−9.22
$Pt(NH_2OH)_4(OH)_2^{2+}$	157	K_{42}(+2OH)	19.04
$PtCl(NH_3)_3$	158	β_{13}	4.72
cis$PtCl_4(NH_3)_2$		K_{42}(+2NH$_3$)	1.64
trans $PtCl_4(NH_3)_2$		K_{42}(+2NH$_3$)	1.80
$Cu(CH_3CO_2)(SO_4)^-$	159	β_{11}	1.6
$Cu(CH_3CO_2)(SO_4)_2^{3-}$		β_{12}	1.85
$Cu(OH)P_2O_7^{3-}$	160	β_{11}	15.73
$Cu(OH)(C_5H_5N)^+$	150	β_{11}	8.68
$Cu(OH)(C_5H_5N)_2^+$		β_{12}	10.27
$Cu(OH)(C_5H_5N)_3^+$		β_{13}	11.67
$AgI_3(SeCN)^{3-}$	61	β_{31}	14.66
$AgI(SeCN)_3^{3-}$		β_{13}	14.72
$Ag(SCN)(SeCN)_3^{3-}$		β_{13}	13.4
$Ag(NH_3)_2BrO_3$	161	β_{21}	−4.5
$Ag(NH_3)_2IO_3$		β_{21}	−4.5
$Ag(NH_3)_2Cl_2^-$		β_{22}	−4.5
$Ag(NH_3)Cl_2^-$	99	β_{12}	6.46
$Ag(NH_3)_2Cl$		β_{21}	7.0
$Ag(NH_3)Br_2^-$		β_{12}	7.77
$Ag(NH_3)_2Br$		β_{21}	7.55
$Ag(NH_3)Br_3^{2-}$		β_{13}	8.2
$Ag(NH_3)_2Br_2^-$		β_{22}	7.6
$AgI_3(S_2O_3)^4$	78	β_{31}	13.52
$AgBr_3(S_2O_3)^{4-}$		β_{31}	9.99
$Ag(CN)_2(S_2O_3)_2^{5-}$		β_{22}	18.15
$Ag(CN)_3(S_2O_3)^{4-}$		β_{31}	21.28
$Au(OH)Cl_3^-$	162	K_{13}(+H$_2$O–H, Cl)	−6.22
$Au(OH)_2Cl_2^-$		K_{22}(+H$_2$O–H, Cl)	−7.04
$Au(OH)Cl_3^-$	163	K_{13}(+H$_2$O–H, Cl)	−5.63
$Au(OH)Cl_2$		K_{12}(+H$_2$O–H, Cl)	−5.40
$ZnCl_3Br^2$	27	K_{31}(+Cl, +Br)	1.30
$ZnCl_2Br_2^{2-}$		K_{22}(+2Br)	1.54
$ZnClBr_3^{2-}$		K_{13}(+Br, −Cl)	0.60
$ZnCl_2I^-$		K_{21}(+I)	0.38
$ZnClI_2^-$		K_{12}(+2I, −Cl)	0.08
$ZnCl_3I^{2-}$		K_{31}(+Cl, +I)	0.90
$ZnCl_2I_2^{2-}$		K_{22}(+2I)	0.50
$ZnBr_2I^-$		K_{21}(I)	0.11
$Hg_2(OH)P_2O_7^{3-}$	164	β_{11}	16.11
$HgI_2(SC(NH_2)_2)_2$	165	K_M	2.11
$Hg(CN)_2NO_3^-$	79	β_{12}	33.5
$Hg(CN)_2Cl^-$	166	K_{21}(+Cl)	−0.11
$Hg(CN)_2Br^-$		K_{21}(+Br)	0.06
$InCl_3Br^-$	37	β_{31}	2.90
$BiClCN^+$	67	β_{11}	4.71

In addition to the information given in Table 11, reference should also be made to the cases of addition of halide ions to noble metal-ammine complexes, listed in ref. 4. Constants K_{ij} ($+j$Cl), with i referring to ammonia ligands, are given for palladium and platinum, and the magnitude of the constants is good evidence that inner-sphere complexes are formed. The formation of outer-sphere complexes, such as $Co(NH_3)_6{}^{3+}Cl^-$ or $Pten_3{}^{4+}Cl^-$ is also listed there, but these should obviously not be termed mixed complexes.

A further important class of ternary complexes for which comparative data cannot be obtained is that occurring in systems of synergistic solvent extraction involving adduct formation in the organic phase[167]. Calling the chelating extractant HX and the synergistic solvating extractant S, the extraction equilibrium can be written as

$$M^{m+}+m\overline{HX}+(N-dm)\,\overline{S}\rightleftharpoons\overline{MX_mS_{N-dm}}+mH^+ \tag{25}$$

where a bar over a symbol denotes the organic phase, and d is the denticity of the chelating agent. Usually, for extraction to occur, $d = 2$ and $N = 2m$. If, however, N-$dm > 0$, water molecules occupy the remaining coordination sites, and the resulting complex $MX_m(H_2O)_{N-dm}$ is strongly hydrogen-bonded to the water in

TABLE 12

REFERENCES FOR TERNARY ADDUCT STABILITIES IN EXTRACTION EQUILIBRIA

I. HX = THENOYLTRIFLUOROACETONE(HTTA)

S	*References*
Tributylphosphate (TBP)	168–179
Dibutyl butylphosphonate (DBBP)	172, 180
Tributylphosphine oxide (TBPO)	181
Dibutylsulfoxide (DBSO)	169
Triphenyl phosphate (TPP)	171, 172, 178
Triphenylphosphine oxide (TPPO)	172, 178
Trioctylphosphine oxide (TOPO)	169–172, 178, 182, 183
Tributoxyethyl phosphate (TBEP)	179
Diethylhexyl ethylhexylphosphonate (DEHEHP)	180
N-Butylacetanilide	171
2-Ethylhexyl alcohol	171
Methyl isobutylketone	169, 176, 177
Quinoline	169

II. OTHER CHELATING AGENTS

HX	*S*	*References*
Isopropyltropolone	TBP	169, 176, 177
Acetylacetone	pyridine, 3-acetylpyridine, 4-benzoyl pyridine, 3-picoline, 4-picoline	184
	quinoline, isoquinoline	185
Dimethylglyoxime	pyridine, butylamine, dibutylamine, triethylamine, aniline, dimethylaniline	176
	dodecylamine, quinoline	176, 177

the aqueous phase, and shows little extractability. Replacement of the coordinated water by the solvating S, therefore, strongly enhances the extractability.

The mixed complex MX_mS_{N-dm} can also be formed from the coordinatively unsaturated MX_m in the organic phase, by addition of synergist molecules S. Equilibrium constants for such homogeneous reactions, designated K_{111} in ref. 167, as well as those for the heterogeneous equilibrium (25), designated K_{121} there, have been determined for a considerable number of systems with HX being thenoyltrifluoroacetone (HTTA). The synergist S is typically tributyl phosphate (TBP) or trioctylphosphine oxide (TOPO).

However, complexes involving M^{m+} and S only, without the participation of an anion, whether X^- or any other, are not formed in either phase, so that one of the parent binary species for the ternary adduct is missing. Since the data have recently been compiled in tables[167], they will not be repeated here. Table 12 lists the works in which the equilibrium constants of the ternary adducts are reported.

E. FACTORS GOVERNING MIXED COMPLEX FORMATION

It is obvious that all the factors affecting the formation of binary complexes will also apply to mixed complexes. However, these will not be enumerated as the purpose here is to dwell on factors which cause *differences* between the mixed complexes and pure complexes. The basic difference is, of course, the fact that mixed complexes contain different ligands and all other changes in behaviour can be inferred as conclusions from this. The inferences that can be drawn are of two kinds: (a) qualitative rules which by their nature are somewhat imprecise but have the advantage that they are widely applicable to predict the behaviour of many kinds of systems and (b) quantitative treatments which allow more complete and exact information to be obtained, but have the disadvantage that their practical applicability is limited to few systems only, because of the difficulties inherent in the calculations.

(i) Qualitative approaches

There are two main changes that could be expected when we go from binary to mixed complexes of the same coordination level: (1) structural changes (*i.e.* changes in the geometry of the molecule) which have rarely been discussed[33,186,187], (2) energy changes (*i.e.* mostly changes in bond energy and of course in mutual interaction of the ligands). Changes in energy always occur and it is on these that most discussions on mixed complexes have centered. In particular, interest has been greatest in the comparative stability of mixed and "parent" binary complexes, *i.e.* are mixed complexes stabilized or destabilized relative to the appropriate binary complexes. Qualitatively the question is one of the formation of complexes.

Will mixed complexes tend to form from the parent complexes or will they, on the contrary, tend to disproportionate into the parent complexes. Quantitatively, as we shall see in the next section, this means calculation of the mixing constant (or the disproportionation constant) but this is rather difficult, and so, qualitative rules and correlations have been sought, (whether theoretical, semi-empirical or empirical) to indicate if and when mixed complexes will or will not be formed.

Before proceeding with the qualitative discussion, we will categorize and enumerate the stabilizing-destabilizing effects recognized today. These fall into two categories: Extra-molecular (*i.e.* involving the environment of the complex) and intra-molecular (not involving the environment). The extra-molecular effects are the solvent effect and the ionic-strength effect. The intramolecular effects are the statistical effect, the change in bond strengths and the ligand interactions. There is some connection between the two groups (*e.g.* solvent effects can influence bond strengths). Nevertheless, it is convenient to treat them separately because the intramolecular effects have been treated quantitatively while the extramolecular effects have not.

Let us start with the qualitative interpretation of the intramolecular effects. The statistical effect does not lend itself very well to qualitative treatment except for the generalization that entropy factors should be different for different coordination numbers and levels and for ligands having a different number of coordination positions, and several years ago a fairly thorough quantitative treatment was published[12]. Nevertheless, as recently as two years ago we still find statements in the literature such as a "suggestion" that "the entropy component should result in a mixed triplet (*i.e.* MXY) being approximately twice as stable as the mean value for the 'pure' species".[188]

The main question which is worthwhile asking qualitatively, is what are the rules for mixed complex formation, *i.e.* can we divide ligands and central ions into categories which form mixed complexes and categories which do not. And indeed we find several approaches in this direction. Some of them are formulated as brief rules such as[111]: Mixed complexes should be preferred over simple complexes whenever the concentration of the ligands involved is such that $\beta_{\mathrm{MAi}}[\mathrm{A}]^{i} = \beta_{\mathrm{MB}j}[\mathrm{B}]^{j}$ the mixed complex being $\mathrm{MA}_i\mathrm{B}_j$.

A more fundamental approach starts from the premise (usually correct) that

$$K(+\mathrm{B}-\mathrm{A})_{ij} > K(+\mathrm{B}-\mathrm{A})_{(i-1)\,(j+1)} \tag{26}$$

Assuming that this holds, mixed complex formation will be detectable. But if

$$K(+\mathrm{B}-\mathrm{A})_{0n} \gg K(+\mathrm{B}-\mathrm{A})_{i\, \doteq\, 0\, j} \tag{27}$$

no mixed complex formation can be observed.

Inequality (27) means that the stability (formation energy) of MB_n is much larger than that of the $\mathrm{MA}_i\mathrm{B}_j$ complex. When this may occur can be shown by means of a "stabilization diagram" of "stabilization energy", E (*i.e.* complex formation energy), *vs.* ligand field strength, F (due to the surrounding ligands).

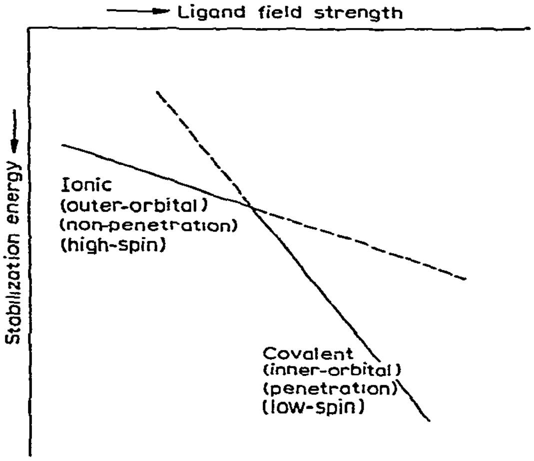

Fig. 4. Diagram of binding energy of ligands as a function of their ligand field strength.

According to this, there will be a sudden large selective increase in stability when passing from ligands tending to form high-spin complexes to ligands tending to form low-spin complexes. This large increase, leading to inequality (27), will prevent appreciable formation of the mixed complexes. This leads to the conclusion that any pair of ligands which form only high-spin, or only low-spin, complexes with a certain central ion can form mixed complexes with it. However, it will be difficult to obtain a mixed complex of a d^4 to d^7 metal containing both high-spin-complex- and low-spin-complex-forming ligands with regard to this metal, because then the mixed complex will tend to disproportionate into one-type ligand metal complexes. A change from high-spin to a low-spin complex is observable by the sudden decrease in the magnetic moment due to reduction in the number of unpaired electrons in the complex[191,192].

A somewhat similar theory has been put forward with respect to covalent complexes[3]. According to this, formation of mixed complexes depends on the type of bond formed between the metal and the ligand—whether σ or π. σ-Bond effects in coordination compounds are assumed to work in the same direction as electrostatic effects in ionic complexes, *i.e.* they promote mixed complex formation because the destabilization caused by ligand (electrostatic) repulsion is smaller in a mixed complex than in the parent complexes. On the other hand, π-bonding ligands which allow back donation from the central ion into the unsaturated ligand π-orbitals lower the electron concentration near the central ion and thus their effect is opposite to σ-bonding ligands. Thus if both ligands are σ- or π-bonding, mixed complexes are formed, but π -bonding ligands tend to exclude non-π bonding ligands and such mixed complexes should be unstable.

To the above energetic considerations, geometric considerations should be added. Thus no mixed complex should be formed if the parents differ in steric configuration (*i.e.* one tetrahedral and one planar).

There can also be specific reasons in special cases for the non-formation of mixed complexes, such as conjugation effects[193] stabilizing one of the parent complexes, or chelate formation[194].

After having discussed the formation of mixed complexes, let us turn to their stabilization relative to the parent complex. The statistical effect has provided a plausible explanation for this stabilization but already in the first theoretical treatments of mixed complexes and ion association it was found that "the mixtures are making a better than statistical use of their additional opportunities... and are... generating a more than statistical proportion of mixed ions"[195]. In other words, the number of complexes for which the experimental value of K_M is found identical with that calculated from statistical considerations is rather small. Usually K_M is found to be larger although there are also cases in which K_M is smaller than statistically expected (see Tables 1–8). This "enhancement" (or "de-enhancement" as the case may be) as it was first called has been attributed qualitatively to a variety of factors some of them intramolecular, such as bonding between ligands of different type[108] or assymetry of the ligand field[109]. However, the extramolecular effects are also of considerable importance. Thus, when the formation of a mixed complex involves neutralization of charge, *i.e.* when the mixed species is neutral while the binary species are charged, the extra stabilization is considerably larger than when no such neutralization occurs[11,138]. This "charge neutralization" effect is probably due to the favorable entropy change in the desolvation of the charged species, *i.e.* the neutralization of charge of the parent complexes would be expected to be accompanied by a positive entropy change due to a decreased orientation of the solvent molecules.

On the other hand, if both binary and ternary species are neutral, stabilization of the mixed complex could be the result of polar-solvent effects. One would expect a sufficiently polar medium (such as water) to stabilize the polar mixed ligand complex relative to the non-polar binary complexes,[10,39,196] unless entropy effects are larger than the solvation energy effect. Exactly what this polar-solvent effect consists of is not clear. Attempts to correlate K_M with the dielectric constant or dipole moment of the solvents have failed. Some correlation has been found with the ionization potential of the solvent molecules[115] and therefore it has been suggested that the effect observed is a dispersion effect. The redistribution of electron density on mixed complex formation (due to a strengthening of the bond formed by the ligand which is a better σ-donor and π-acceptor, and a weakening of the other ligand) leads to a change in the polarity of the bonds and a corresponding change in the energy of the intermolecular interaction of the complex with the solvent, possibly reflected in the degree of solvation of the complex.

The stabilization of mixed anion complexes in solution has also been found to be considerably affected by the ionic strength[118,121] and could also be influenced by the concentration and type of cations present[128,197]. This could be due either to some electrostatic-polarization effect of the cations or again, indirectly, to a solvent effect. The formation of the mixed complexes may involve displacing water molecules from the coordination shell of the central ion. The cations reduce the water activity to varying degrees while the stability of the mixed complex could depend on the water activity, as at low water activity the coordinated water molecules are more readily exchanged by the ligand thus stabilizing the mixed complex. Also, decreased water activity would involve the decrease of the hydration of the ligand which facilitates its coordination, again stabilizing the complex. There is probably a difference between the hydration of the mixed complex and the parent complexes. However, there is no real experimental confirmation of the above possibilities[128,197].

Having dealt with environmental effects we shall conclude the section with a few more qualitative observations on intramolecular factors which will serve as a prelude to the more quantitative treatments introduced in the following section.

The stabilization of a mixed complex is dependent on the level of coordination. It has been experimentally confirmed[110,111] in several cases that the unsaturated mixed complex, ($n < N$) shows greater deviations (stabilization) than the saturated ($n = N$) complex.

The stabilization or mixing constant is also dependent on the stability constants of the parent complexes. For some series of compounds[63,198,199] the relation $\log K_M = \Delta \log \beta_n$ has been observed, *i.e.* K_M increases with increasing difference between the stability constants of the binary complexes.

The stability (not stabilization) constant of mixed complexes is dependent on the redox potentials of both the central ion and the ligands. For various series of compounds[200,201] β_{ij} is found to increase with increase in the redox potential of the central ion and decrease in the potential of the ligands if the metal–ligand bond is of predominantly covalent character. If ionic bonds are predominant then β_{ij} increases with increase in the potential of the ligand.

There seems to be a general concensus that if the ligands are sufficiently "different" the mixed complex is unstable. This has been given its most modern expression in HSAB[202,203] (hard-soft–acid–base theory) language as follows: Soft bases tend to group together on a given central atom and hard ligands tend to group together. A special term has even been coined to describe this mutual stabilizing effect- symbiosis[204]. However, again in HSAB language, the factor of intrinsic strength will counterbalance the symbiosis and will favour the mixed species if X and Y differ markedly in base strength.

Finally, it should be mentioned that empirical equations including most of the factors mentioned above have been fitted by computer to stability constants in order to determine the relative weight of the various effects[133].

(ii) Quantitative treatments

There seem to be only two distinct attempts to put the stabilization problem on a quantitative basis. One is rather formal and leans to thermodynamics. The other is more conceptual and leans to molecular dynamics.

The first approach[22,105,205,206] is based on a comparison between the free energies of a central ion N and two ligands A, B when they are in solution at infinite dilution (G°_M, G°_A, G°_B) and when they are at distances equal to the length of the coordinate bonds (G'_M, G'_A, G'_B). We can then write for the energy of formation of MA_iB_j:

$$RT \ln \beta_{ij} = -\Delta G = (G_m - G'_m + i\,(G^\circ_A - G'_A) + j(G^\circ_B - G'_B) \tag{28}$$

and also

$$G^\circ_m - G'_m = i(G^\circ_A - G'_A) + j(G^\circ_B - G'_B) \tag{29}$$

as the change in the free energy of formation of M when the ligands are coordinated to it is accompanied by an equivalent change in the energies of formation of the latter. From the differential

$$\mathrm{d}G'_M = \left(\frac{\partial G'_M}{\partial i}\right)_j \mathrm{d}i + \left(\frac{\partial G'_M}{\partial i}\right)_i \mathrm{d}j \tag{30}$$

we can obtain

$$G^\circ_A - G'_A = \left(\frac{\partial G'_M}{\partial i}\right)_j + i\left(\frac{\partial G'_A}{\partial i}\right)_j + j\left(\frac{\partial G'_B}{\partial i}\right)_j \tag{31}$$

$$G^\circ_B - G'_B = \left(\frac{\partial G'_M}{\partial j}\right)_i + i\left(\frac{\partial G'_A}{\partial j}\right)_i + j\left(\frac{\partial G'_B}{\partial j}\right)_i \tag{32}$$

($G^\circ_A - G'_A$) and ($G^\circ_B - G'_B$) are thus a measure of the strength of the individual coordinate bonds while the derivatives of G'_A and G'_B are a measure of the influence of the intramolecular environment on these bonds.

If we assume that the change in the strength of the bonds with change in the numbers of ligands in the complex is due to mutual screening of A and B, i.e. the bond strength decreases as the number of ligands increases, we can write:

$$G^\circ_A - G'_B = \Delta G'_{A(1)} - (i-1)\left(\frac{\partial G'_A}{\partial i}\right)_j - j\left(\frac{\partial G'_A}{\partial j}\right)_i \tag{33}$$

$$G^\circ_B - G'_B = \Delta G'_{B(1)} - i\left(\frac{\partial G'_B}{\partial i}\right)_j - (j-1)\left(\frac{\partial G'_B}{\partial j}\right)_i \tag{34}$$

where $\Delta G_{A(1)}$ and $\Delta G_{B(1)}$ are the changes in the free energies of A and B during the formation of MA and MB. *i.e.* of a single metal–ligand bond. Substituting (29), (33) and (34) into (28), we obtain

$$RT \ln \beta_{ij} = -2\left[i\Delta G_{A(1)} - i(i-1)\left(\frac{\partial G'_A}{\partial i}\right)_j - ij\left(\frac{\partial G'_A}{\partial j}\right)_i + \right.$$

$$+ i\Delta G_{B}(1) - j(j-1)\left(\frac{\partial G'_{B}}{\partial j}\right)_{i} - ij\left(\frac{\partial G'_{B}}{\partial i}\right)_{j}\Bigg] \tag{35}$$

If we assume the derivatives of G'_A and G'_B are independent of the number of ligands, and remembering that $\Delta F_{X(1)} = -RT\ln \beta_{10}$ etc., we obtain

$$\ln \beta_{ij} = \frac{i}{n} \ln \beta_{n0} + \frac{j}{n} \ln \beta_{0n} + \frac{2ij}{RT}\left[\left(\frac{\partial G'_{A}}{\partial i}\right)_{j} - \left(\frac{\partial G'_{A}}{\partial j}\right)_{i} + \right.$$

$$\left. + \left(\frac{\partial G'_{B}}{\partial j}\right)_{i} - \left(\frac{\partial G'_{B}}{\partial :}\right)_{j}\right] \tag{36}$$

or

$$RT \ln K_M = 2ij \left[\left(\frac{\partial G'_{A}}{\partial i}\right)_{j} - \left(\frac{\partial G'_{A}}{\partial j}\right)_{i} + \left(\frac{\partial G'_{B}}{\partial j}\right)_{i} - \left(\frac{\partial G'_{B}}{\partial i}\right)_{j}\right] \tag{37}$$

Therefore $\mathrm{d}\ln K_M/\mathrm{d}i = 0$ when $i = n/2$ *i.e.* K_M is maximal when $i = j$.
Also $\ln K_M > 0$ if:

$$\text{(a)} \left(\frac{\partial G'_{A}}{\partial i}\right)_{j} > \left(\frac{\partial G'_{A}}{\partial j}\right)_{i} \quad \text{and} \quad \left(\frac{\partial G'_{B}}{\partial j}\right)_{i} > \left(\frac{\partial G'_{B}}{\partial i}\right)_{j} \tag{38}$$

In this case, A weakens M-A more than B and B weakens M-B more than A, *i.e.* the bonds in MA_iB_j are stronger than in MA_n and MB_n

$$\text{(b)} \left(\frac{\partial G'_{A}}{\partial i}\right)_{j} > \left(\frac{\partial G'_{A}}{\partial j}\right)_{i} \quad \text{and} \quad \left(\frac{\partial G'_{B}}{\partial i}\right)_{j} > \left(\frac{\partial G'_{B}}{\partial j}\right)_{i}$$

but

$$\left(\frac{\partial G'_{A}}{\partial j}\right)_{i} - \left(\frac{\partial G'_{A}}{\partial i}\right)_{j} < \left(\frac{\partial G'_{B}}{\partial j}\right)_{i} - \left(\frac{\partial G'_{B}}{\partial i}\right)_{j} \tag{39}$$

In this case, M-A becomes stronger and M-B weaker during formation of the ternary from the binary complexes but the M-B weakening is less than the M-A strengthening. If the opposite is true then $\ln K_M < 0$. This also happens if both M-A and M-B weaken, and, obviously if the roles of A and B are interchanged.

To find out in practice which of the above cases holds in a certain system, G'_A is calculated from experimental data using

$$G'_A = G^{\circ}_A - \frac{RT}{4_j} \ln \frac{\beta_{ij}\beta_{10}}{\beta_{0j}} \qquad \text{for } MA_iB_j \tag{40}$$

$$G'_A = G^{\circ}_A - \frac{RT}{2n} \ln \beta_{n0} \qquad \text{for } MA_n \tag{41}$$

and analogously for G'_B. The difference $G'_A\,(MA_iB_j) - G'_A\,(MA_n)$ gives the change in bond energy on going from MA_n to MA_iB_j.

Calculations on various experimental systems show no case in which both bonds become weaker. Cases *are* observed in which both bonds become stronger. This usually occurs when the different ligands interact weakly with one another. The effect tends to disappear with increase in the number of ligands, in the difference between them, and with decrease in the size of the central ion.

In most cases, one bond becomes stronger and the other weaker, and two types of behaviour are distinguished. In one the changes in bond strengths depend chiefly on the electrostatic potentials, as all ions involved are "hard". The strength of the bond formed by the coordinated particle with greater charge and smaller size, *i.e.* the harder one, is increased at the expense of the other. Here both ligands and/or central ions are only slightly polarised. In the second group the opposite is the case and the bond with the softer, *i.e.*, less electronegative ligand (small charge, large size) is strengthened. Here the tendency to covalent bonding and competition for the valence orbitals of the central ion determine the bond strength. In all these cases log K_{M} can be either positive or negative. To determine its sign the following equation has been derived[206]:

$$\frac{RT}{2mF}\ln K_{\mathrm{M}} = k(E^{\circ}{}_{\mathrm{M}}-\bar{E}_{\mathrm{L}}-\varphi^{\circ}{}_{\mathrm{M}}+\varphi^{\circ}{}_{\mathrm{L}})+C\Delta\varphi \qquad (42)$$

where k and c are constants, m is the number of electrons transferred in the reaction and F is the Faraday constant.

$\varphi^{\circ}{}_{\mathrm{M}}$ and $\varphi^{\circ}{}_{\mathrm{L}}$ are the potentials corresponding to the energies of the metal ion and ligands (ligands with similar properties, such as halides, are assumed to have the same potential, and this has been shown to be a good approximation for the case of the halides[207]). $\Delta\varphi$ is a correction to allow for changes in the energies of the valence states due to interaction between the different coordinated particles. $\bar{E}_{\mathrm{L}}$ is given by $\bar{E}_{\mathrm{L}} = i/n\ E^{\circ}{}_{\mathrm{A}}+j/n\ E^{\circ}{}_{\mathrm{B}}$ where $E^{\circ}{}_{\mathrm{M}}$, $E^{\circ}{}_{\mathrm{A}}$ and $E^{\circ}{}_{\mathrm{B}}$ are the standard redox potentials.

Since for a given central ion all terms on the right hand side of (42) except $\bar{E}_{\mathrm{L}}$ are constant we find that log K_{M} is linearly dependent on the overall potential of the redox systems for the ligands. A similar linear dependence on $\bar{E}_{\mathrm{L}}$ can be derived also for β_{ij}. In Fig. 5 the continuous line describes log β_{ij} as a function of $\bar{E}_{\mathrm{L}}$ while the broken line describes i/n log $\beta_{n0}+j/n$ log β_{0n}. as a function of $\bar{E}_{\mathrm{L}}$. The vertical distance between the two lines represents log K_{M} at this $\bar{E}_{\mathrm{L}}$. When the broken line is below the continuous line log $K_{\mathrm{M}} > 0$ and vice versa.

It is clear from Fig. 5 that β_{n0} and β_{0n} change in the same direction as β_{ij} but this is not true for K_{M}. For complexes of metal ions which are weakly polarized in the field of the ligands this constant decreases with increase in the β's.

Thus the increased stability of mixed complexes in solution is assumed to be due to the combined reducing action of the ligands on the central atom. The mutual influence of the ligands depends on the magnitude of the reducing action which they exert on the cation. A sufficiently great difference in the reduction

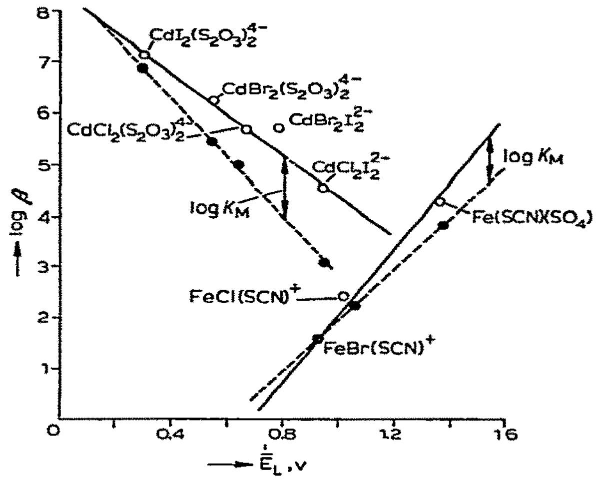

Fig. 5. The overall stability constants of ternary complexes as a function of the average redox potential of the ligands. The continuous lines give the experimental log β_{ij}, while the broken lines give the weighted average between β_{n0} and β_{0n}.

potentials of A and B leads to their incompatibility in the same complex. They become less compatible as the oxidation potential of the central ion decreases.

The above treatment is useful in correlating a large amount of data and predicting the behaviour of a system if several other similar systems have been measured. However, it leans heavily on experimental determination of the very quantities it calculates and so its usefulness to predict is limited. Also, as it does not use a model but relies only on formal calculation it does not lend itself to picturization.

The second treatment[3,12,33,199] is based on a model[208,209] which we shall call the "polarized-ion model" but which has been called by various other names and is rather well known. It has been used for calculations of force constants, energies, equilibria etc[210–221]. It is thus quite useful although somewhat contro-

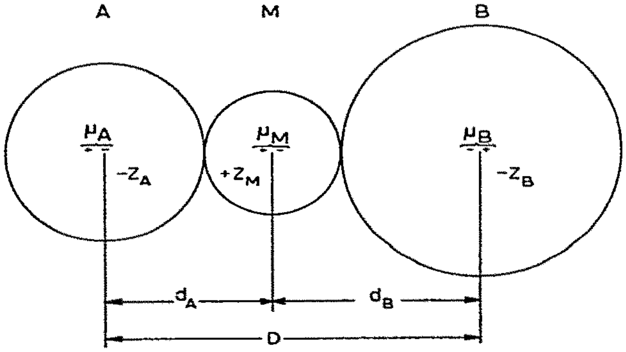

Fig. 6. A diagram of the polarized ion model for the linear ternary complex MAB.

versial. It is described in Fig. 6 for the case of a linear MAB molecule. In order to apply it to the stability of mixed complexes Bjerrum's classification[222] has been accepted according to which the factors influencing mixed complex formation are divided into a "statistical effect" and a "ligand effect".

The statistical effect is evaluated by showing that the number of molecules $MA_iB_jS_{N-n}$ is proportional to

$$\frac{a^i b^j (1-a-b)^{N-n} N!}{i!j!(N-n)!} \tag{43}$$

where N is the coordination number, n is the coordination level[14], S is a solvent molecule and a or b are the probabilities, assumed independent, of ligand A or B to be found at a coordination position. If similar expressions are written for MA_n and MB_n and if we assume that K_M is due to the statistical effect only we obtain that $K_M = n/i$ and is independent of the coordination number, the occupation of coordination positions by solvent molecules and the affinity of the ligands for the central metal ion.

Thus the principal problem is the calculation of the "ligand effect", which is expressed as K_S (p. 5), and it is calculated on the basis of the polarized-ion model. This treats the complex as a system of polarized spheres in contact held together by purely electrostatic forces. The first attempts at calculation on this basis took account of the charges only, neglecting the polarizability of the spheres[3]. It was found that for all cases treated (linear, square planar, tetrahedral and octahedral) $E_{\text{mixed}}\text{-}E_{\text{binary average}} = K(z_A - z_B)^2/r$ where E is the electrostatic energy of the complex, z_A and z_B are the charges of A and B respectively, r is the ligand–metal internuclear distance and K is a constant dependent on the geometry. The above expression is always positive, thus predicting stabilization of the mixed complex in every case. This, as we know is not always true. Also, neglect of polarization assumes purely ionic bonds, which, again, is unlikely in most cases. Finally, the agreement with experiment is not very good.

The next step was the introduction of polarization effects. This was done[12,33] by means of point dipoles assumed at the centers of the spheres and given by αF where F is the electric field at the center of a sphere and α is the appropriate polarizability of the ion. Thus, *e.g.*, for an MAB complex the following expression is deduced, where d_A is the internuclear distance M-A, and similarly for d_B, D_A is the internuclear distance A-B, and μ are the moments of the point dipoles:

$$\begin{aligned} E(\mathrm{MAB}) = & -\frac{z_A z_M}{d_A} - \frac{z_B z_M}{d_B} + \frac{z_A z_B}{D} - \frac{z_M \mu_A}{d_A^2} - \frac{z_M \mu_B}{d_B^2} \\ & - \frac{z_A \mu_M}{d_A^2} + \frac{z_A \mu_B}{D^2} + \frac{z_B \mu_M}{d_B^2} + \frac{z_B \mu_A}{D^2} - \frac{2\mu_M \mu_A}{d_A^3} \\ & + \frac{2\mu_M \mu_B}{d_B^3} + \frac{2\mu_A \mu_B}{D^3} + \frac{\mu_A^2}{2\alpha_A} + \frac{\mu_M^2}{2\alpha_M} + \frac{\mu_B^2}{2\alpha_B} \end{aligned} \tag{44}$$

This, of course, is not a complete expression but includes all interactions up to quadrupoles. When similar expressions are written for MA_n and MB_n and the equations for the various F's are solved it is possible to derive an expression for E_{mixed}-$E_{\text{average binary}}$ containing both stabilizing and destabilizing terms. Moreover the comparison of K_M's calculated in this way with experimental values is fairly satisfactory, but more than that: comparison of K_S (ligand effect) with experimental values of ΔH also showed reasonable agreement. (Table 13).

TABLE 13

COMPARISON OF CALCULATED MIXING AND STABILIZATION CONSTANTS WITH EXPERIMENTAL VALUES

Complex	*log* K_M[33] *calculated*	*log* K_M[10] *experimental*	$\Delta H \left(\frac{Kcal}{mole}\right)$[33] *calculated*	$\Delta H \left(\frac{Kcal}{mole}\right)$[33] *experimental*
Hg Cl Br	0.51	0.60	−0.41	−0.5
Hg Cl I	0.92	0.88	−0.79	−0.7
Hg Br I	0.53	0.55	−0.34	−0.4

Similar calculations were carried out very recently on ion association in low dielectric constant solvents[188,223,224] and also in the gaseous phase[225], and similar conclusions were reached.

This treatment has the advantage over the previous one that it is much more *ab initio* and does not require any measurements of stability constants. It lends itself easily to picturization and is more obviously related to the relevant physical quantities and stability factors. However it does have some serious drawbacks: Although polarization in effect allows for some degree of covalency it is not clear whether this is adequate. Solvent effects are not included except very indirectly. Polarizability values have to be known and these are not reliable as yet. A dielectric constant $\varepsilon = 1$ has been used in all cases except the treatment of ion association in solution where the dielectric constant of the solvent ($\varepsilon \leq 7$) was used. Neither value is quite satisfactory, but criteria for deciding the issue are not available.

It would seem that a combination of both the above treatments would be most useful until quantum-mechanical calculations come within reach.

F. METHODS FOR DETERMINING THE STABILITY OF MIXED COMPLEXES

(i) General

Most of the methods useful for the determination of the stability of mononuclear binary complexes may also be used for ternary complexes. The book by Rossotti and Rossotti[226] contains a chapter mainly devoted to this problem, as does a more recent book by Beck[227]. In applying such methods, it must be borne in mind that considerably higher precision is necessary in the study of ternary than in the study of binary systems, since usually only second-order effects are involved, and more parameters are used to describe the systems. This also necessitates very strict adherence to the condition that activity coefficients should be kept constant when using ionic media if concentrations are to replace activities in mass-action-law expressions. The observance of this condition is assumed in the following.

There are two general approaches to the determination of the stability constants of mixed complexes. In one, the two ligands are added independently, over a wide concentration range of each, and data are obtained as a function of the two variables, the free ligand concentrations. The constants β_{ij} then relate the concentrations of the complexes to those of the free metal ion and the free ligands. In the other approach, the ligand concentration level is selected so that the coordination level is constant at a value $n = i+j$, and the replacement reactions (6) and (7) are studied as a function of the ratio of free ligand concentrations $R = [\mathrm{B}]/[\mathrm{A}]$. Different experimental methods may be appropriate for the two approaches, and the general equations used are stated below.

If the ligand concentrations are varied independently, the total central ion concentration is given as follows, with charges on species omitted for the sake of clarity:

$$C_{\mathrm{M}} = [\mathrm{M}] \sum_{i=0}^{N-j} \sum_{j=0}^{N-i} \beta_{ij}[\mathrm{A}]^i[\mathrm{B}]^j \tag{45}$$

Methods such as potentiometry or polarography, as well as some others, often determine the ratio $[\mathrm{M}]/C_{\mathrm{M}}$ at C_{M} concentrations low in comparison with C_{A} and C_{B}, so that the approximations $[\mathrm{A}] \simeq C_{\mathrm{A}}$ and $[\mathrm{B}] \simeq C_{\mathrm{B}}$ are valid. It is then possible to hold the concentration of one of the ligands, say A, constant, and measure $[\mathrm{M}]/C_{\mathrm{M}}$ as a function of the other. For any given j value, then, the sum

$$C_{\mathrm{A}j} = \sum_{i=0}^{N-j} \beta_{ij} C_{\mathrm{A}}{}^{i} = \text{constant} \tag{46}$$

and may be inserted in eqn. (101) to give

$$C_{\mathrm{M}} = [\mathrm{M}] \sum_{j=0}^{N} C_{\mathrm{A}j} C_{\mathrm{B}}{}^{j} \tag{46a}$$

This can now be solved for the $C_{\mathrm{A}j}$ parameters by the calculation methods appropriate for binary complexes. Finally, the $C_{\mathrm{A}j}$ values for a series of C_{A} values are analysed in terms of eqn. (46), to obtain the individual β_{ij} values. The same procedure, possibly even with the same data, should now be followed with the roles of A and B exchanged. That is, cuts are first made at constant B concentrations, to obtain the parameters $C_{\mathrm{B}i}$, and these are then analysed again in terms of the β_{ij} constants, which should, of course, agree with the previous set.

If the sum of the concentrations of the (free) ligands is held constant at

C_{A+B} and their ratio R is varied, it is possible to eliminate the individual ligand concentrations from (45), and write

$$C_M = [M] \sum_{i=0}^{N-j} \sum_{j=0}^{N-i} \beta_{ij} C_{A+B}^{i+j} R^j (1+R)^{-(i+j)} = [M] \sum_{k=0}^{n} C' R^k (1+R)^{k-n} \quad (47)$$

The last equality holds when the coordination level $n = i+j$ remains constant, C' then being a constant parameter.

When this last condition prevails (usually when $n = N$ the coordination number, at sufficiently high ligand concentrations), it is preferable to proceed in terms of displacement reactions. With such reactions, at a constant coordination level n, it is useful to remember that the average ligand numbers for the two ligands are simply related as

$$\bar{n}_A + \bar{n}_B = n \quad (48)$$

Writing for convenience $\beta(+jB-jA)_{ij}$ (as defined for eqn. (7)) $= \beta_{nj}{}^R$, one can express the total central ion concentration as

$$C_M = [MA_n] \sum_{j=0}^{n} \beta_{nj}{}^R [B]^j [A]^{-j} = [MA_n] \sum_{j=0}^{n} \beta_{nj}{}^R R^j \quad (49)$$

The fraction of the central ion in the form of the kth mixed complex $MA_{n-k}B_k$ is given as

$$\alpha_k = \beta_{nk}{}^R R^k / \sum_{j=0}^{n} \beta_{nj}{}^R R^j \quad (50)$$

If this is differentiated, the kth mixed complex will be at a maximal concentration at a ligand ratio $R_{k\ \mathrm{max}}$ which may sometimes be experimentally determined. It has been shown[228] that in this case

$$\sum (k-j) \beta_{nj}{}^R R_{k\mathrm{max}}{}^j = 0 \quad (51)$$

and if the values of $R_{k\ \mathrm{max}}$ are known for $k = 1,2 \ldots n$, the set of equations (50) can be solved for the n values of $\beta_{nj}{}^R$, without requiring knowledge of the concentrations of the mixed species themselves.

A special sub-case occurs when there is no excess free ligand present, and both ligands are bound very strongly to the central group. This is the case, for instance, in low-dielectric-constant solvents where the uncharged species MA_n and MB_n interact to form the MA_iB_j species. The ratio R then gives the ratio of the total concentrations C_B/C_A, of ligands bound in the various species. It should be noted that the fraction of each species MA_iB_j is maximal at $R = i/j$, the value being independent of the equilibrium constant[228].

(ii) Electrometric methods

Electrometric methods (potentiometry with metal or redox electrodes, pH-metric titrations and polarography) are relatively simple, hence useful, methods for the determination of mixed complex stabilities, since they need no parameters in addition to the stability constants and data available from a parallel study of the binary systems.

With a suitable metal electrode, the ratio $C_M/[M]$ given in eqn. (45) can be determined directly. Hence, by using a series of measurements at, say, constant C_A, the parameters C_{Aj} (eqn. 46a) can be determined, and then, *via* eqn. (46), the values of β_{ij}. This method has been used by some of the earlier workers in this field[129,229].

The polarographic method is similar, in principle. The equation used is

$$E_{\frac{1}{2}} - E^\circ_{\frac{1}{2}} = (RT/nF)\,(\bar{I}/I^\circ) + (RT/nF)\ln \sum \beta_{ij} C_A{}^i C_B{}^j \tag{52}$$

where $E_{\frac{1}{2}}$ is the half-wave potential in a solution containing the ligands, $E^\circ_{\frac{1}{2}}$ is that in a similar solution which does not, $\bar{I}$ is the weighted average diffusion coefficient of the complexes and I° that of the metal cation. However, in order to avoid complications arising from the introduction of additional parameters, the diffusion coefficients of the various complexes, a non-verifiable assumption is made. In the present case, even more than with polarographic investigations of binary complexes, the assumption that the first term on the right hand side can be neglected is necessary. If this is done, the evaluation of the β_{ij} values from eqn. (52) via eqns. (46) and (46a) is straightforward[111].

A method widely used with ligands, which can add hydrogen ions in aqueous solutions, is the pH titration method[73,98,230], best applied when one ligand is appreciably more basic than the other. The basic ligand is titrated first alone, then in the presence of the metal ion, and finally in the presence of both the metal ion and the less basic ligand. The more basic ligand, B, must form strong complexes, and its concentration must be comparable to the metal ion ($C_B \leq N\,C_M$), so that $\bar{n}_B$ can be obtained from the titration. In solutions containing A also, $\bar{n}_B$ will be smaller by the amount of $\Delta\bar{n}_B$. Then, by the integration[230]

$$\ln C_{Aj} = \int_0^{[B]\max} (\Delta\bar{n}_B/[B])\mathrm{d}[B] \tag{53}$$

where $[B]_{\max}$ is the value above which $\Delta\bar{n}_B$ equals zero within the experimental error, and by solving eqn. (46), the β_{ij} values are obtainable. This method is best applied for species MA_iB, *i.e.* for $j = 1$, *e.g.* when B is a strong chelating ligand. Instead of the integration (53), the values of $\bar{n}_B$ obtained from the pH titration and those of $\bar{n}_A$ obtained from eqn. (48) can be used under conditions where replacement reactions occur exclusively, employing for instance the half-integral-$\bar{n}$ method[108,110].

(iii) Spectrophotometric methods

The spectrophotometric methods are based on solutions of the general equation

$$\bar{\varepsilon} = \sum_{i=0}^{N-j} \sum_{j=0}^{N-i} \alpha_{ij}\varepsilon_{ij} \tag{54}$$

where $\bar{\varepsilon}$ is the absorbance of the solution containing both ligands, per cm path length and per mol/l of central ion, α_{ij} are the fractions of the central ion in the form of MA_iB_j, and ε_{ij} the molar absorptivities of these species. Each species is thus characterized by two parameters, β_{ij} and ε_{ij}, the latter being dependent on the wavelength. Solutions of this equation were offered by Watters and coworkers[110, 113,143] in the early days of studies of mixed complexes. Their method is based on the principle that where an isosbestic point exists, there are only two absorbing species in equilibrium. Thus, for a replacement system (see p. 311) with $n = 2$, at the wavelength of an isosbestic point, where, say, $\varepsilon_{11} = \varepsilon_{20} \neq \varepsilon_{02}$, the fraction $\alpha_{02} = (\varepsilon_{20}-\bar{\varepsilon})\,(\varepsilon_{20}-\varepsilon_{02})$ is obtained for solutions where the absorption curve no longer passes through the isosbestic point. The constant $K_M = 4\,(\alpha_{02}-R/(1+R))^2/\alpha_{02}(\alpha_{02}+\,(1-R)/(1+R))$ can then be calculated.

Spectrophotometric methods are most appropriate for conditions where replacement reactions prevail, and Newman and Hume have published very general (and complicated) equations for such systems[231]. They have shown that in the case of the coexistence in solution of only three species such as MA_n, MA_iB_j and MA_pB_q (or MB_n and two mixed species), where p and q need not necessarily differ by unity from i and j, but $i+j = p+q = n$, linear relationships are applicable as solutions for eqn. (52). In the most complicated case treated, all three species absorb light, and the resulting equation is

$$\begin{aligned}\bar{\varepsilon} &= (\beta_{pq}{}^{\mathrm{R}}/\beta_{ij}{}^{\mathrm{R}})\{[\beta_{ij}{}^{\mathrm{R}}(\varepsilon_n-\bar{\varepsilon})\,(C_{\mathrm{A}}{}^{n-i}/C_{\mathrm{B}}{}^{j})-\bar{\varepsilon}+\varepsilon_{ij}]\\ &\times(C_{\mathrm{A}}{}^{i-p}/C_{\mathrm{B}}{}^{q-j})\}+\varepsilon_{pq}\end{aligned} \tag{55}$$

Sets of values of i and j are assumed, until a pair is found, such that a straight line results from a plot of $\bar{\varepsilon}$ *vs.* the expression in the braces. Since the latter, however, contains several unknown parameters, this is clearly impractical. Various simpler cases are treated, until the simplest is reached, where there are only two species, and only the binary one absorbs light at a particular wavelength. Then

$$\log\,(\bar{\varepsilon}/(\varepsilon_n-\bar{\varepsilon})) = \log\,(\mathrm{C}_{\mathrm{A}}{}^{n-i}/C_{\mathrm{B}}{}^{j})+\log\beta_{ij}{}^{\mathrm{R}} \tag{56}$$

Linear relationships have possibly become less important by the advent of electronic computers. In any case, simpler equations have been proposed for replacement reactions[10,19,39,63].

The equations are simplest for the case $n = 2$,where only one mixed complex exists. The method of continuous variation[226] gives qualitative information on the formation of the mixed complex, and helps to select the wavelength where the difference

$$\Delta = \bar{\varepsilon}-(x\varepsilon_{20}+(1-x)\,\varepsilon_{02}) \tag{57}$$

is largest. In one method[232] the value of $\alpha_n(x_i)/\alpha_{11}(0.5)$ is plotted against K_M, where $K_M = \alpha^2_{11}/[(x-\frac{1}{2}\alpha_{11})(1-x-\frac{1}{2}\alpha_{11})]$. Since $\Delta(x_i)$ is proportional to $\alpha_{11}(x_i)$ for any concentration (fraction) x_i, the value of K_M can be read from the plot at the experimental $\Delta(x_i)/\Delta(0.5)$. Alternatively[10], the value of α_{11} is obtained from

$$\alpha_{11} = \Delta/(\varepsilon_{11}-\tfrac{1}{2}(\varepsilon_{20}+\varepsilon_{02})) \tag{58}$$

and ε_{11} is obtained at low, and high, R values from

$$\begin{aligned}\varepsilon_{11} &= [\bar{\varepsilon}(1+R)-\varepsilon_{20}(1-R)]/2R \text{ (at low } R) \\ &= [\bar{\varepsilon}(1+R)-\varepsilon_{02}(R-1)]/2 \text{ (at high } R)\end{aligned} \tag{59}$$

and finally K_M is calculated from

$$K_M = 4\alpha_{11}{}^2 \Big/ \left[(1-\alpha_{11})^2 - \frac{(1-R)^2}{(1+R)^2}\right] \tag{60}$$

Since the values of α_{11} are not very sensitive to K_M, the precision of the methods depending on the determination of α_{11} is not high[10,31].

The spectrophotometric methods usually employ light absorption measurements in the ultraviolet or visible region. Raman scattering data can also be used, and indeed very early work by Delwaulle demonstrated the existence of mixed complexes in solution by Raman spectroscopy[233]. The photographic plate technique used in the early days was not suitable for the quantitative evaluation of the data. Present-day photomultiplier measurements and improved Raman techniques should be able to supply definitive quantitative information[234,235].

(iv) Two-phase distribution methods

The solubility of a sparingly soluble solid MA_m in a solution containing the ligand B is usually a good indication of the formation of complexes, either binary MB_n, or mixed MA_iB_j. A distinction between these cases can be made when the dependence on the concentrations of B or of A is measured[76]. Fridman and Sarbaev[22] have shown that the solubility of MA_m (expressed as the concentration of M: $s = C_M$ (saturated)) is given as

$$s/K_sC_A{}^{i-m} = \beta_{i0}+\beta_{i1}C_B+\ldots\beta_{i,N-i}\,C_B{}^{N-i} \tag{61}$$

provided that $(\partial \log s/\partial \log C_A)_{C_B} = i-m = constant$. In eqn. (61) K_s is the solubility product $[M][A]^m$, and the equality $[A] = C_A$ is assumed. It is readily seen that, from (61)

$$(\partial \log s/\partial \log C_B)_{C_A} = \bar{n}_B \tag{62}$$

which can then be used to calculate the constants β_{ij}, at the constant value i. A recent review[236] summarizes the techniques and calculation methods used in such solubility measurements.

Liquid-liquid distribution has been employed for suitable systems, yielding stability constants for both phases. The simplest application, again, is for replacement reactions with $n = 2$, such as the mercury halides[31]. The distribution constants for the three species are designated as D_{20}, D_{11} and D_{02}, the volume ratio of the phases (or the mass ratios of the solvents, if the molal scale is used, as is the practice for molten salts) is designated as q, which for extraction from aqueous solutions is usually unity, so that the parameters $P_{20} = q+D_{20}$, etc., can be defined[32]. This is necessary since the total concentration of the central ion is now distributed between the two phases, so that in terms of the species in one phase, the total concentration ratio becomes:

$$R = (2[\mathrm{MB_2}]P_{02}+[\mathrm{MAB}]P_{11})/(2[\mathrm{MA_2}]P_{20}+[\mathrm{MAB}]P_{11}) \tag{63}$$

In a similar way, in principle, to that used in the spectrophotometric method (eqn. (59)) the unknown P_{11} is obtained:

$$\begin{aligned} P_{11} &= 2\,R\,P\,P_{20}/[2\,R\,P_{20}-(1-R)\,(P-P_{20})] \text{ for small } R \\ &= 2\,P\,P_{02}/[2\,P_{02}+(R-1)\,(P_{02}{}^{-}\,P)] \text{ for large } R \end{aligned} \tag{64}$$

Here $P = q+D$, where D is the observed distribution ratio. For $R = 1$, the value of K_{M} is obtained as

$$K_{\mathrm{M}} = [P_{20}\,(P_{02}-P)-P_{02}\,(P-P_{20})]^2/[(P-P_{11})\,{}^2P_{20}P_{02}] \tag{65}$$

or the whole set of data near $R = 1$ can be used, with a more complicated equation. This treatment is valid if $P_{20} < P > P_{02}$ for the whole range of R. If, however, an extremum occurs, which is the case when the mixed complex is destabilized in one or the other of the phases, this treatment is inapplicable. The alternative is[32] to use the values $R_{\max}$ and $D_{\max}$ at the extremum, where $\mathrm{d}P/dR = 0$, provided that $D_{20} < D_{11} > D_{02}$, obtaining

$$K_{\mathrm{M}} = 4[R_{\max}(D_{\max}-D_{02})-(D_{\max}-D_{20})]^2/[(R_{\max}-1)\,(D_{\max}-D_{20})\,(D_{\max}-D_{02})] \tag{66}$$

The distribution method has also been used in cases where addition reactions (eqn. (8)) and a non-constant coordination level occur.[15] For the mercury halides with excess halide and tracer mercury concentration, where species with $n = 2$ only occur in the organic phase, all the concentrations can be related to C_{A} and the species $\mathrm{MA_2}$ in the aqueous phase. For instance, $[\overline{\mathrm{MAB}}] = [\mathrm{MA_2}]D_{11}\,\beta_{11}{}^{\mathrm{R}}R$ and $[\mathrm{MA_2B_2}] = [\mathrm{MA_2}]\,\beta\,(+2\mathrm{B})_{22}R^2C_{\mathrm{A}}{}^2$. The distribution ratio can be written as

$$D = \sum^{2} D_{ij}\beta((i-2)\mathrm{A}, j\mathrm{B})_{ij}R^j \,/ \sum^{4} \beta((\mathrm{i}-2)\mathrm{A}, j\mathrm{B})_{ij}C_{\mathrm{A}}{}^{i+j-2}R^j \tag{67}$$

This has been solved by using cuts at constant C_{A} or at constant R. Equations to be used when the distribution of the ligand is measured have also been derived[15].

Ion exchange methods are widely used for the determination of the stability of binary complexes[167], and should, in principle, be applicable also for mixed complexes. They have, however, not been used for this purpose.

(v) Sources of error

Many of the stability constants for ternary complexes listed in the tables of sections B and C have been obtained under carefully controlled conditions, and with suitable experimental and computational methods. Although, unfortunately, some reported values have not been obtained under optimal conditions, it will be assumed in the following discussion that such parameters as temperature, nature and concentration of the ionic medium, purity of reagents, etc., are effectively controlled. It is further assumed that the best methods, as recommended in standard works, *e.g.* ref. 226, are employed. What, then, are the remaining sources of error?

In electrometric methods, it seems that the requirement that one free ligand concentration is kept constant while the other is varied may be a major source of error when the condition $C_M \ll [A], [B]$ cannot be obeyed. The recommendation that C_M be extrapolated to zero may introduce uncertainties in the measured values of $C_M/[M]$ because of electrode instability, effect of impurities, etc. Keeping C_A constant while varying C_B, in the anticipation that [A] will remain constant, may thus not be a sufficiently good approximation, and iterations aimed at a constant [A] will be necessary. The advantage of some electrometric methods is that each species has associated with it only one parameter and that the relationship between the measured concentration variables $C_M/[M]$, [A] and [B] is through a simple power series with the β_{ij} as coefficients. When, however, a secondary variable such as $\bar{n}$ is used, the calculation (eqn. (53)) depends on differences $\Delta\bar{n}_B$ and a subsequent integration, and the precision is expected to be low.

Spectrophotometric and distribution methods usually depend on differences between the measured property of the solution and that expected if no ternary complexes were formed. The methods also depend on intensive properties of the species, which are generally unknown, and must be considered as additional parameters to be determined from the data. The precision attainable depends to a large extent on the difference between the actual value of the intensive property of the ternary complex on the one hand, and the weighted average of the properties of the binary complexes on the other. As has been pointed out above for replacement reactions at a constant coordination level, the fraction α_{ij} is maximal at $R = i/j$, without regard to the stability of the species. Thus, in eqn. (57), the quantity $\Delta/\bar{\varepsilon}$ should be an appreciable fraction.

Even if the fractions α_{ij} can be determined with reasonable confidence, small errors are magnified when the constants K_M are calculated. It has been shown[31] that when only MAB is formed

$$dK_M/K_M = (1 - \tfrac{1}{2}K_M)\, d\alpha_{11}/\alpha_{11} \tag{68}$$

so that errors in α_{11} are magnified by the factor $(1 + \tfrac{1}{2}K_M)$, which is of the order of three or so for many systems. When more species are formed, such errors are compounded.

In two-phase distibution methods, a major source of error is the possibility that mixed species will be present in both phases. In liquid–liquid distribution of uncharged species, this has been taken into account (eqns. 63–67), but detracts from the attainable precision. In other extraction systems, *e.g.* of chelates, this is not always properly considered, and the same is true of solubility measurements. This possibility must be examined, and either dismissed on the basis of experimental findings, or taken into account in the calculations. If one of the phases is free from ternary complexes, the number of intensive properties of the species is considerably reduced, and the attainable precision should thereby be considerably improved.

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