INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON EQUILIBRIUM DATA*

Critical Evaluation of Equilibrium Constants in Solution
Part B: Equilibrium Constants of Liquid-Liquid Distribution Systems

CRITICAL EVALUATION OF EQUILIBRIUM CONSTANTS INVOLVING ACETYLACETONE AND ITS METAL CHELATES

Prepared for publication by
J. STARÝ
Technical University, Prague, Czechoslovakia
and
J. O. LILJENZIN
Chalmers University of Technology, Goteborg, Sweden

CRITICAL EVALUATION OF EQUILIBRIUM CONSTANTS INVOLVING

ACETYLACETONE AND ITS METAL CHELATES

Acetylacetone(2,4-pentanedione, MW 100.12), the simplest of the beta-diketones, is among the most versatile and most used chelating agents in solvent extraction. Acetylacetone is known to form neutral chelates with about 60 metals; most of them exhibit low solubility in the aqueous phase but dissolve readily in organic solvents, used as diluents in solvent extraction processes.

The aim of the present communication is to compile, discuss and critically evaluate the published data on the dissociation, solubility and liquid-liquid distribution of acetylacetone and its metal chelates. When the data of several authors are compared, all reliable constants obtained under the same conditions are averaged, weighted inversely to their standard deviations and the error quoted as the standard deviation of this average. The thermodynamic constants were recalculated by the present authors from the original data using the least-squares method with a 95% confidence interval (68L).

1. Dissociation of acetylacetone

In aqueous solutions, acetylacetone (HA) is in equilibrium with hydrogen ions (H^+) and with acetylacetonate (enolate) ions (A^-). The concentration dissociation constant of the acid HA is defined as

$$K_a = [H^+][A^-]/[HA] \tag{1}$$

where the square brackets denote the molar concentration of the species. For practical purposes the "mixed" (Brønsted) dissociation constants are sometimes determined

$$K'_a = (H^+)' [A^-]/[HA] \tag{2}$$

where $(H^+)'$ denotes the hydrogen ion operational activity. The thermodynamic dissociation constant is defined as follows

$$K^o_a = (H^+)(A^-)/(HA) = K_a \, y_{H^+} \, y_{A^-}/y_{HA} \tag{3}$$

where y denotes the molar activity coefficient of the species. Several reviews of the published values of dissociation constants of acetylacetone under various conditions are available (64 S, 71 Sa, 78 S). Table 1 shows the dependence of K_a (mol dm^{-3}) on the temperature for I = 0 and I = 1.0

mol dm^{-3}.

Table 1   Dissociation constants K_a°/mol dm^{-3} and K_a/mol dm^{-3} at different temperatures and ionic strength I/mol dm^{-3}

Temp. °C	pK$_a^\circ$ I → 0 (54 I, 55 Ib)	pK$_a^\circ$ I → 0 (61 L)	pK$_a$ I = 1.0 (69 L)	pK$_a$ I = 1.0 (72 K)
10	9.10	9.11 $\pm$0.02	(9.180)[a]	9.25
15		9.09 $\pm$0.02	9.118	
20	9.02		(9.057)[a]	9.09
25	(8.99)	9.03 $^{+}$0.03	8.994	(9.02)
30	8.95		(8.934)[a]	8.96
35		8.97 $\pm$0.05	8.876	
40	8.86		(8.812)[a]	
45		8.91 $\pm$0.02	8.750	
ΔH°/kJ mol^{-1}	11.8	10.9 $\pm$0.3		
	(13$\pm$2)[b]	(10.0 $\pm$0.7)[b]	(21.4 $\pm$0.6)[b]	(24 $\pm$8)[b]
ΔS°/J mol^{-1}K^{-1}				
	-134	-202 $\pm$8[c]		
	(-127 $\pm$6)[b]	(-139 $\pm$2)[b]	(-100 $\pm$2)[b]	(-93 $\pm$28)[b]

[a] pK$_a$ = (9.3027 $\pm$0.0003) - (0.01228 $\pm$0.00028)t, where 10 < t/°C < 45 (69 L)

[b] data recalculated by the present authors using least-squares method

[c] misprint in the original paper

Taking into account also the other published data for pK$_a^\circ$ at 25°C and I → 0 : 8.94 (40 S), 8.93 (45 E) and 9.03 (63 G), the recommended value for pK$_a^\circ$ is 8.99 $\pm$0.04 at 25°C and I → 0.

Very good agreement has been obtained in the determination of the pK$_a$-value at 25°C and I = 1 M (Na$^+$, H$^+$)ClO$_4^-$ by three independent groups of authors: 8.994 (69 L), 8.99 (71 S, 73 S) and 9.05 $\pm$0.03 (77 B). The value of pK$_a$ determined by (65 S) is lower (8.878 $\pm$0.007); in this case, however, 1 M (K$^+$, H$^+$)Cl$^-$ has been used for adjusting the ionic strength which can influence the enol-keto equilibrium. Even lower values have been obtained for the mixed dissociation constant at 25°C and I = 1 M (Na$^+$, H$^+$)ClO$_4^-$:

pK_a' = 8.71 (63 G) and 8.76 (61 P) (from this paper it is not evident whether concentration or mixed constants were determined). Taking into consideration data obtained for 1M $(Na^+, H^+)ClO_4^-$ the recommended value of pK_a will be 9.00 $\pm$0.03 at 25°C.

It is of interest to note that the recommended values for the dissocia-tion constants of acetylacetone are the same for I → 0 and I = 1 M $(Na^+, H^+)ClO_4^-$. This surprising fact has been explained in terms of a shift in the enol-keto equilibrium towards the keto form, as evidenced from NMR and spectrophotometric measurements (69 L).

The values of pK_a = 8.82 (53 R, 68 G) and 8.85 (79 S), determined at 25°C and I = 0.1 M $(Na^+, H^+)ClO_4^-$, are in a good agreement with the calcula-ted value. Other published pK_a values under similar conditions are 8.88 (65 O) and 8.81 $\pm$0.04 (8.84 $\pm$0.04 at 20°C)(70 K). It should be noted, how-ever, that it is not evident whether concentration or mixed constants were determined. The constants pK_a = 8.62 and 8.67 (71 S, 73 S) are appreciably lower and they were not taken into consideration for the recommendation of the most reliable value.

pK_a values determined at other ionic strengths at 25°C are: 8.98 (68 Ga) at I = 0.017 mol dm^{-3}, 8.88 (71 R) at I = 0.02 mol dm^{-3}, 8.81 (51 C) and 8.97 (77 Sc) at I = 0.2 mol dm^{-3}.

The values of $\Delta H^°$, given in Table 1, differ from the value $\Delta H^°$ = 14.7 $\pm$0.2 kJ mol^{-1} (78 P) determined by direct calorimetric measurements at I = 0.05 -1.5 M $(Na^+, H^+)NO_3^-$, $(Na^+, H^+)Cl^-$ or $(K^+, H^+)NO_3^-$ in the temperature range from 15 to 55°C.

Table 2   Recommended values of dissociation constants K_a /mol dm^{-3} of acetylacetone at 25°C

	I → 0	I = 0.1 M NaClO$_4$	I = 1 M NaClO$_4$
pK_a	8.99 $\pm$0.04	8.83 $\pm$0.02	9.00 $\pm$0.03

2. Solubility of acetylacetone

Acetylacetone is miscible with a variety of organic solvents; its solu-bility in neutral aqueous solution is 1.72 mol dm^{-3} at 20°C (58 R) and 1.92 mol dm^{-3} at 25°C (69 J). The solubility increases with increasing ionic strength and acidity (see Table 3), due probably to a shift of the enol-keto

equilibrium (69 J). In earlier papers (54 S, 58 R), the increase of the

solubility has been explained by the formation of species of the type H_2A^+.

Table 3   Solubility of acetylacetone (mol dm^{-3}) at 25°C (69 J)

Concentration of electrolyte (mol dm^{-3})	0	1.0	2.5	5.0
$NaClO_4$		1.92	3.56	5.5	∞
$HClO_4$		1.92	4.88	∞	∞

3. Distribution of acetylacetone

The distribution of acetylacetone between an organic solvent and an

aqueous phase can be described as

$$D_{HA} = [\overline{HA}]/[HA] + [A^-] = K_{D(HA)}/(1 + K_a[H^+]^{-1}) \qquad (4)$$

where

$$K_{D(HA)} = [\overline{HA}]/[HA] \qquad (5)$$

and the bar ($[^-]$) indicates the organic phase species.

Experimentally determined $K_{D(HA)}$ values for 18 organic solvents have

been summarized in a previous communication (78 S). The very good agree-

ment found between data determined by different authors (64 W, 72 K, 73 K,

73 S, 74 K, 77 B, 78 S) enables us to recommend the most reliable constants

for 9 commonly used organic solvents (Table 4).

Distribution constants decrease with increase of the ionic strength and

the acidity of the aqueous phase. This is in line with the increasing solu-

bility of acetylacetone in aqueous electrolyte solutions.

Table 4   Recommended values of distribution constants, log $K_{D(HA)}$, between
           water and various organic solvents, 25°C. (Total concentration of
           acetylacetone, $c_{HA} \leq 0.1$ mol dm^{-3}).

Solvent	I/mol dm^{-3}		
	0.001	0.1	1.0
n-Hexane	-0.02 ± 0.01		-0.06 ± 0.04
Cyclohexane	0.00 ± 0.01		-0.04 ± 0.04
Benzene	0.77 ± 0.01	0.74 ± 0.02	0.64 ± 0.02
Toluene	0.66 ± 0.01	0.62 ± 0.01	0.55 ± 0.02
Xylene	0.57 ± 0.01		0.52 ± 0.01

Table 4 (Continuation)

| Solvent | I/mol dm^{-3} | | |
	0.001	0.1	1.0
Dichloromethane	1.41 $\pm$0.02	1.32 $\pm$0.02	
Trichloromethane (chloroform)	1.38 $\pm$0.02	1.37 $\pm$0.01	1.25 $\pm$0.03
Tetrachloromethane (carbon tetrachloride)	0.52 $\pm$0.01	0.51 $\pm$0.01	0.42 $\pm$0.02
3-Methyl butanol			0.54 $\pm$0.02

$K_{D(HA)}$ values also depend on the total concentration of acetylacetone, c_{HA}. Log $K_{D(HA)}$ of pure acetylacetone, calculated from its solubility in water is 0.76 at 20°C and 0.72 at 25°C. Using benzene as an organic solvent, $K_{D(HA)}$ does not depend on c_{HA} but decreases in trichloromethand, and increases in tetrachloromethane are observed with increasing c_{HA}. This effect becomes especially pronounced at c_{HA} higher than 0.5 mol dm^{-3}.

The distribution constant also depends on the temperature: for trichloromethane as the organic solvent, ΔH^O = -11 $\pm$1 kJ mol^{-1} and ΔS^O = -12.3 $\pm$0.8 J mol K^{-1} at temperatures between 10 and 35°C (69 J). $K_{D(HA)}$ for dichloromethane has been also found to be temperature dependent, though to a lesser extent than for trichloromethane. No temperature dependence has been found for tetrachloromethane (69 J).

4. Stability and liquid-liquid distribution of metal acetylacetonates

General

Overall concentration stability constants, β_n, or thermodynamic stability constants, β_n^O,

$$\beta_n = [MA_n^{(m-n)+}]/[M^{m+}][A^-]^n \tag{6}$$

$$\beta_n^O = (MA_n^{(m-n)+})/(M^{m+})(A^-)^n = \beta_n \; {}^{y_{MA_n}}/{}^{y_M} \; y_A{}^n \tag{7}$$

are used to characterize the formation of complexes in the aqueous phase. When these data are not available, the corresponding stepwise stability constants K_n or K_n^O

$$K_n = [MA_n^{(m-n)+}]/[MA_{n-1}^{(m-n-1)+}][A^-] \tag{8}$$

$$K_n^o = (MA_n^{(m-n)+})/(MA_{n-1}^{(m-n-1)})(A^-) = K_n \, {}^yMA_n / {}^yMA_{n-1} {}^yA \tag{9}$$

are included in the present compilation (y denotes the molar activity coeffi-
cient of the species).

Eqs. (7) and (9) can be used for recalculation of the stability con-
stants of metal acetylacetonates for $I = 0 - 0.1$ mol dm^{-3}. Experimentally
found values of stability constants at $I = 1$ mol dm^{-3} are usually higher
than those at 0.1 mol dm^{-3}, which is probably connected with the fact that
pK$_a$ at $I = 0.1$ mol dm^{-3} is lower than those at $I = 0$ and 1.0 mol dm^{-3}.

The stability constants can be also calculated from thermodynamic data
according to

$$\Delta G_n^o = \Delta H_n^o - T \Delta S_n^o = -RT \ln \beta_n^o \tag{10}$$

from which

$$\log \beta_n^o = [\Delta S_n^o - \Delta H_n^o/T]/2.303R \tag{11}$$

In some publications the complex formation of the metal with hydroxide
ion, e.e. hydrolysis, was not taken into consideration. This can lead to
large errors in the determination of stability constants. Additionally,
the presence of acetic acid impurity in acetylacetone(the commercial pro-
duct usually contains several percent of the acid) may also cause errors in
the determination of stability constants, especially when using potentio-
metric methods.

The overall extraction constant K_{ex}, involving the metal chelate forma-
tion and its distribution in liquid-liquid system can be expressed as

$$K_{ex} = [\overline{MA_m}] [H^+]^m / [M^{m+}] [\overline{HA}]^m = K_{D(MA_m)} \, \beta_m \, K_a^m / K_{D(HA)}^m \tag{12}$$

where

$$K_{D(MA_m)} = [\overline{MA_m}]/[MA_m] \tag{13}$$

Expressing the hydrogen ion term as an activity, the extraction constant
is denoted as K'_{ex}.

Distribution constants of metal acetylacetonates $K_{D(MA_m)}$ are generally
not too large, and for this reason they can be experimentally determined
with a sufficient precision; however, the possible formation of hydroxo-
complexes has to be considered.

The heterogeneous overall stability constant $\overline{\beta}_m$ of the chelate MA_m

$$\overline{\beta}_m = [MA_m]/[M^{m+}][A^-]^m = \beta_m K_{D(MA_m)} \qquad (14)$$

can be calculated from know K_{ex}, K_a and $K_{D(HA)}$ values according to eq. (12).
The β_m value can be calculated from the $\overline{\beta}_m$ value using eq. (14) when $K_{D(MA_m)}$
is known.

Beryllium acetylacetonate

The stability constants of beryllium complexes with acetylacetone at
various T and I are summarized in Tables 5 and 6.

Table 5   Stability constants of beryllium acetylacetonate β_n at different
          temperatures (55 I, 55 Ib, 72 K)

Temp. °C	log β_1 I → O	log β_2 I → O	log β_2 I = 1 mol dm^{-3}
10	7.93	14.89	16.32 ?
20	7.88	14.63	15.40 ?
30	7.83	14.54	14.32
40	7.67	14.11	
ΔH_n^O (kJ mol^{-1})	-8.4	-37	
	$(-16 \pm 20)^a$	$(-41 \pm 35)^a$	$(-164 \pm 139)^a$
ΔS_n^O (J mol^{-1}K^{-1})	121	154	
	$(96 \pm 68)^a$	$(141 \pm 118)^a$	$(266 \pm 474)^a$

[a] Recalculated by the present authors using least-squares method

Table 6   Survey of stability constants of beryllium acetylacetonate, 25°C

| log β_1	log β_2	I/mol dm^{-3}	Method	Ref.
7.85[a]	14.58[a]	0	potent.	55 Ib
7.96	14.67	<0.02	potent.	63 G
8.17	14.54	low	distr.	59 K
7.53[a]	14.10[a]	0.1	potent.	55 Ib
7.44 ±0.08	14.06 ±0.06	0.1	potent.	79 S
7.55	14.35	1.0	potent.	63 G
7.27	14.26	1.0	distr.	68 R

[a] Recalculated data using eq. (7).

The general agreement of data obtained by different authors at 25°C enables us to recommend the most reliable constants at different I (Table 7). On the other hand, the values of ΔH_n^o and ΔS_n^o determined by the potentiometric method (55 I, 55 Ib) are not in agreement with experimental data obtained by the liquid-liquid distribution method (72 K) even taking into account the different experimental conditions.

At higher values of pH, the following reactions were found to take place (63 G):

$$BeA^+ = BeA(OH) + H^+$$

with an equilibrium constant log K = -6.4 at 25°C and I → 0, and

$$BeA(OH) = BeA(OH)_2^- + H^+$$
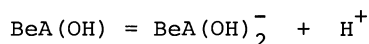
with an equilibrium constant log K = -9.8 at 25°C and I → 0.

The distribution constant of BeA_2 using trichloromethane as solvent (log $K_{D(BeA_2)}$ = 2.15, 2.45 and 3.05 at 10°C, 20°C and 30°C, respectively; I = 1.0 mol dm^{-3} (72 K)) is higher than those using pure acetylacetone (log $K_{D(BeA_2)}$ = 1.61 at 25°C and low I (59 K)).

The extraction constant log K'_{ex} = -2.79 at 25°C and I = 0.1 M (Na^+, H^+) ClO_4^- (63 S) for benzene as organic solvent is in agreement with the value log K'_{ex} = -2.6 at 20°C and I = 1 mol dm^{-3} for trichloromethane (68 R).

Table 7   Recommended values of stability constants of beryllium acetylacetonate, 25°C

I/mol dm^3	0	0.1	1.0
log β_1	7.9 $\pm$0.1	7.48 $\pm$0.06	
log β_2	14.62 $\pm$0.06	14.08 $\pm$0.04	14.30 $\pm$0.05

Magnesium acetylacetonate

The stability constants of magnesium acetylacetonate have been determined by a potentiometric method at different I from which β_n^o values were calculated for I → 0 (55 I, 55 Ib) (Table 8).

At 25°C and I = 0.1 M (Na^+, H^+)ClO_4^- the following values of stability constants were obtained (79 S): log β_1 = 3.36 $\pm$0.02 and log β_2 = 5.93 $\pm$0.09. These data are in a good agreement with Izatt's values obtained by the recalculation for the above conditions: log β_1 = 3.33 and log β_2 = 5.8 which allows to recommend the most reliable data of stability constants of magnesium acetylacetonate (Table 9).

Table 8   Stability constants of magnesium acetylacetonate

β_n at I → O (55 I, 55 Ib)

Temp. °C	$\log \beta_1$	$\log \beta_2$
10	3.75	6.50
20	3.67	6.38
30	3.63	6.17
40	3.65	6.09
ΔH_n^o /kJ mol^{-1}	-7.5 (-6 $\pm$11)[a]	-26 (-24 $\pm$12)[a]
ΔS_n^o /J mol^{-1}K^{-1}	46 (51 $\pm$37)[a]	35[b] (38 $\pm$39)[a]

[a] Recalculated by the present authors using least-squares method.

[b] The value 57 J mol^{-1}K^{-1} given in the original paper is evidentaly a misprint.

Table 9   Recommended values of stability constants of magnesium

acetylacetonate β_n, 25°C

I/mol dm^3	0	0.1
$\log \beta_1$	3.65 $\pm$0.05	3.34 $\pm$0.03
$\log \beta_2$	6.28 $\pm$0.10	5.86 $\pm$0.08

Scandium acetylacetonate

The first stability constant of scandium acetylacetonate $\log \beta_1 = 8.4$ $\pm$0.1 at 20°C and I = 0.01 mol dm^{-3} (66 Ka) determined spectrophotometrically, and $\log \beta_1 = 8.3$ at 25°C and I = 0.1 mol dm^3 (66 S), determined from distribution data are in a good agreement. However, the potentiometric method gives, at 30°C and I → O (calculated from data obtained at different I), the following results: $\log \beta_1^o = 8.0$ $\pm$0.1 and $\log \beta_2 = 15.2$ $\pm$0.2 (55 Ia); for I = 0.1 mol dm^3 we obtain much lower values: $\log \beta_1 = 7.5$ $\pm$0.1 and $\log \beta_2$ = 14.3 $\pm$0.2.

The value of $\log \beta_3$ has not been determined because of the low solubility of scandium acetylacetonate in aqueous solutions. From the heterogeneous stability constant $\log \overline{\beta}_3 = 22.89$ at 20°C and I = 0.1 M (Na$^+$, H$^+$)

ClO_4^- (63 S) and 23.1^a at 25°C and I = 0.1 M (Na^+, H^+)ClO_4^- (64 O) it can be expected (see eq. (14)) that $\log \beta_3 \lesssim 21.3$ because $\log K_{D(ScA_3)} \gtrsim 1.7$ for benzene as organic solvent (63 S).

The extraction constants using benzene as solvent $\log K'_{ex}$ = -5.83 at 20°C and I = 0.1 M (Na^+, H^+)ClO_4^- (63 S); -5.9^a at 25°C and I = 0.1M (Na^+,H^+) ClO_4^- (64 O) and -5.5^a at 25°C and I = 0.5 M (Na^+, H^+)ClO_4^- (67 F). For tri-chloromethane a greater disagreement has been found: $\log K_{ex}$ = -7.1^a at 25°C and I = 0.1 M (Na^+, H^+)ClO_4^- (64 O) and -6.35 in the same conditions (66 S).

Yttrium and rare earth acetylacetonates

The stability constants of yttrium and rare earth acetylacetonates determined by the potentiometric (54 I, 55 Ia, 60 G, 64 Y) and ion-exchange (64 P) methods at different experimental conditions are summarized in Table 10. It is of interest to note that in the plot $\log \beta_1$ as a function of atomic number, only the first part of the curve increases linearly (from La to Eu), whereas in the second part (from Gd to Lu) $\log \beta_1$ value is nearly constant. The difference between consecutive elements in the first part is about 0.15, but the total variation from Tb to Lu is only 0.2

A survey of thermodynamic constants determined by the direct calori-metric measurements is given in Table 11.

Distribution constants of rare earth acetylacetonates increase with increasing atomic number: $\log K_{D(MA_3)}$ are -0.39; -0.30; -0.16; -0.03; 0.04; 0.19; 0.33 and 0.8 for Nd, Sm, Gd, Tb, Dy, Ho, Er and Lu, respectively for pure acetylacetone used as a solvent at 25°C and low I (60 B). Acetylace-tonates lighter than Sm have a very limited solubility in acetylacetone, while those heavier than Sm have a greatly increased solubility. Distribu-tion constant of cerium(IV) acetylacetone $\log K_{D(CeA_4)}$ > 2 for benzene as a solvent (62 Sa) (for n-hexane ΔH_D^o = 40 kJ mol^{-1} and ΔS_D^o = 108 J $mol^{-1}K^{-1}$ (77 A)).

Although extraction constants were not determined, their approximate values can be calculated according to eq. (12) using the values of β_3 and $K_{D(MA_3)}$.

---

[a] These constants have been calculated by the present authors from experi-mental data given in original papers.

Table 10   Stability constants of yttrium and rare earth acetylacetonates β_n

Metal	Temp °C	I mol dm^3	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Ref.
Y	30	0	6.40 ±0.10	11.10 ±0.15	13.9 ±0.2	55 Ia
	30	0.1	5.87 ±0.02	10.85 ±0.08	14.10 ±0.12	60 G
	25	2.0	5.57 ±0.05	10.16 ±0.15		54 Y
La	30	0	5.10 ±0.10	8.95 ±0.15	11.85 ±0.20	55 Ia
	30	0.1	4.96 ±0.03	8.41 ±0.08	10.91 ±0.20	60 G
	25	2.0	4.71 ±0.05	8.16 ±0.15		64 Y
Ce	30	0	5.28 ±0.11	9.26 ±0.20		54 I
	30	0.1	4.8 ±0.1	8.5 ±0.2		54 I
	30	0.1	5.09 ±0.04	8.4 ±0.1	11.3 ±0.2	60 G
Pr	30	0	5.43 ±0.13	9.56 ±0.23	12.52 ±0.36	54 I
	30	0.1	4.9 ±0.1	8.7 ±0.2	11.5 ±0.2	54 I
	30	0.1	5.27 ±0.03	9.20 ±0.08	12.4 ±0.1	60 G
	25	2.0	5.01 ±0.05	8.84 ±0.15		64 Y
Nd	30	0	5.60 ±0.10	9.90 ±0.15	13.1 ±0.2	55 Ia
	30	0.1	5.30 ±0.04	9.40 ±0.07	12.6 ±0.1	60 G
Sm	30	0	5.9 ±0.1	10.4 ±0.15	13.6 ±0.2	55 Ia
	30	0.1	5.59 ±0.02	10.05 ±0.03	12.95 ±0.04	60 G
	25	2.0	5.32 ±0.05	9.72 ±0.15		64 Y
Eu	30	0	6.05 ±0.10	10.60 ±0.15	14.05 ±0.20	55 Ia
	30	0.1	5.87 ±0.03	10.35 ±0.06	13.64 ±0.08	60 G
	25	2.0	5.41 ±0.05	9.71 ±0.15		64 Y
Gd	30	0.1	5.90 ±0.03	10.38 ±0.08	13.79 ±0.09	60 G
	25	2.0	5.42 ±0.05	9.81 ±0.15		64 Y
Tb	30	0.1	6.02 ±0.01	10.63 ±0.05	14.04 ±0.06	60 G
Dy	30	0.1	6.03 ±0.01	10.70 ±0.03	14.04 ±0.07	60 G
	25	2.0	5.74 ±0.05	10.22 ±0.15		64 Y
Ho	30	0.1	6.05 ±0.01	10.73 ±0.02	14.13 ±0.12	60 G
	30	0.1	5.65	10.41		64 P
Er	30	0.1	5.99 ±0.01	10.67 ±0.04	14.05 ±0.05	60 G
	25	2.0	5.70 ±0.05	10.08 ±0.15		64 Y

Table 10 (continuation)

Metal	Temp °C	I mol dm^{-3}	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Reg.
Tm	30	0.1	6.09 ± 0.01	10.85 ± 0.03	14.33 ± 0.05	60 G
	25	2.0	6.03 ± 0.05	10.75 ± 0.15		64 Y
Yb	30	0.1	6.18 ± 0.01	11.04 ± 0.03	14.64 ± 0.05	60 G
	30	0.1	5.7	10.15		64 P
Lu	30	0.1	6.23 ± 0.04	11.00 ± 0.11	14.63 ± 0.18	60 G
	25	2.0	5.98 ± 0.05	10.78 ± 0.15		64 Y

Table 11   Thermodynamic constants ΔH_n^o /kJ mol^{-1} and ΔS_n^o / J mol^{-1}K^{-1} at 25°C and I = 0.05 mol dm^{-3} (78 P)

Metal	ΔH_1^o	ΔH_2^o	ΔH_3^o	ΔS_1^o	ΔS_2^o	ΔS_3^o
La	-1.3 ± 0.1	-2.7 ± 0.2	-5.9 ± 1.7	88 ± 2	147 ± 3	184 ± 4
Pr	-1.6 ± 0.4	-5.9 ± 1.2	-16 ± 6	92 ± 3	173 ± 5	205 ± 25
Nd	-2.4 ± 0.4	-5.7 ± 0.8	-18 ± 5	90 ± 3	156 ± 4	176 ± 20
Sm	-3.2 ± 0.5	-11.8 ± 0.8	-19 ± 7	93 ± 3	148 ± 4	180 ± 25
Gd	-4.4 ± 0.6	-13.4 ± 1.5	-25 ± 8	95 ± 3	149 ± 5	176 ± 30
Tb	-5.2 ± 0.5	-13.2 ± 1.0	-28 ± 5	94 ± 3	154 ± 4	167 ± 20
Dy	-5.2 ± 0.8	-14.9 ± 2.0	-31 ± 8	95 ± 4	150 ± 7	159 ± 25
Ho	-4.7 ± 0.6	-14.1 ± 1.8	-31 ± 10	97 ± 3	153 ± 6	159 ± 33
Er	-4.5 ± 0.7	-14.6 ± 2.1	-30 ± 8	97 ± 3	151 ± 8	163 ± 28
Yb	-4.2 ± 0.6	-13.0 ± 1.3	-31 ± 10	101 ± 3	163 ± 5	197 ± 33
Lu	-3.6 ± 0.4	-10.5 ± 1.8	-22 ± 8	104 ± 3	170 ± 6	201 ± 28

Titanium acetylacetonate

The stability constants of titanium(III) complexes with acetylacetone were determined at 25°C and I = 1.0 mol dm^{-3} by means of spectrophotometric method: $\log \beta_1$ = 10.43, $\log \beta_2$ = 18.82 and $\log \beta_3$ = 24.9 (66 V).

Zirconium acetylacetonate

The stability of zirconium acetylacetonate has been determined from the distribution of zirconium between pure acetylacetone and an aqueous phase at 25°C and low I: $\log \beta_1$ = 8.38, $\log \beta_2$ = 15.96, $\log \beta_3$ = 23.22 and

log β_4 = 30.08 (59 K). The distribution constant determined under these conditions is log $K_{D(ZrA_4)}$ = 0.40 (59 K). The hydrolysis of zirconium ions has not been considered and for this reason the above data should be regarded as the lowest values of stability constants. The spectrophotometric method gives a substantially higher value for log β_1 = 11.25 $\pm$0.10 at 18-20°C in 1 M HCl (66 K).

Hafnium acetylacetonate

The formation of hafnium acetylacetonate has been investigated by two independent groups of authors (59 K, 61 P) both utilizing the liquid-liquid distribution method. The values of stability constants determined at 25°C and low I are: log β_1 = 8.73, log β_2 = 15.37, log β_3 = 21.75 and log β_4 = 28.10 (59 K). At 25°C and I = 1 M (Na$^+$, H$^+$)ClO$_4^-$, the following constants were determined (61 P): log β_1 = 7.4, log β_2 = 14.7, log β_3 = 21.4 and log β_4 = 28.1. Although the disagreement between the data obtained is not very large (considering the difference in I), it should be noted that the hydrolysis of hafnium ions has not been considered in any of the publications. The values of experimentally determined distribution constants for pure acetylacetone (log $K_{D(HfA_4)}$ = 0.82 at 25°C and low I (59 K)) and for benzene solution of this reagent (log $K_{D(HfA_4)}$ = 1.0 at 25°C and I = 1 M (Na$^+$, H$^+$) ClO$_4^-$ (61 P)) seem to be too low for such a coordinatively saturated chelate. This suggests that mixed hydroxo-complexes are also formed in the aqueous phase. The data should thus be considered as the lowest possible values of the respective equilibrium constants.

Thorium acetylacetonate

Stability constants of thorium acetylacetonate determined by the potentimetric (55 Ia) and by the liquid-liquid distribution methods (50 R, 53 Ra, 53 Rb, 58 P, 61 R) are summarized in Table 12.

The distribution constant log $K_{D(ThA_4)}$ = 2.50 $\pm$0.05 at 25°C and I = 0.1M (Na$^+$, H$^+$)ClO$_4^-$ for benzene as the organic solvent has been determined independently by (50 R) and (58 P). Using trichloromethane as solvent log $K_{D(ThA_4)}$ = 2.55 $\pm$0.05 at 25°C and I = 0.1 M (Na$^+$, H$^+$)ClO$_4^-$ (53 Rb) and using n-hexane log $K_{D(ThA_4)}$ = 0.64 (ΔH_D^0 = 68 kJ mol^{-1}, ΔS_D^0 = 245 J mol^{-1}K^{-1}) at 25°C and I = 1 M (Na$^+$, H$^+$)ClO$_4^-$ (77 A).

Table 12   Stability constants of thorium acetylacetonates β_n

T/°C	30	25	25	25
I/mol dm^{-3}	0	0.01	0.1	0.1
Ref.	55 Ia	50 R, 61 R	53 Ra, 61 R	58 P
log β_1	8.8	7.82 $\pm$0.16[a]	8.00 $\pm$0.17	7.75
log β_2	16.2	15.57 $\pm$0.08[b]	15.48 $\pm$0.31	15.34
log β_3	22.5	21.72 $\pm$0.12[b]	21.48 $\pm$0.42	22.23
log β_4	26.7	26.86 $\pm$0.19[b]	26.78 $\pm$0.47	27.01

[a] Calculated using limiting value method. [b] Calculated using least-squares method

The value of the extraction constant can be calculated from the tenta-
tive values of β_4 and $K_{D(ThA_4)}$ (see Table 13) using eq. (12):   log K_{ex} =
-9.0 and -11.4 at 25°C and I = 0.1 M (Na$^+$, H$^+$)ClO$_4^-$ for benzene and trichloro-
methane, respectively.   The value of log K'_{ex} = -12.16 at 20°C and I = 0.1 M
(Na$^+$, H$^+$)ClO$_4^-$ is in error because the stepwise formation of thorium complex
has not been taken into account.

Table 13   Tentative values of equilibrium constants of thorium acetyl-
         acetonate at 25°C and I = 0.1 mol dm^{-3}

|	
log β_1	= 7.8 $\pm$0.1
log β_2	= 14.4 $\pm$0.2
log β_3	= 21.8 $\pm$0.3
log β_4	= 26.8 $\pm$0.2
log $K_{D(ThA_4)}$	= 2.50 $\pm$0.05 for benzene
log K_{ex}	= -9.0 $\pm$0.1 for benzene

Vanadium acetylacetonate

Vanadium(II) forms mono, bis and tris acetylacetonate complexes (65 Sb).
The stability constants at 25°C and 1 M (K$^+$, H$^+$)Cl$^-$ are: log β_1 = 5.383
$\pm$0.012, log β_2 = 10.189 $\pm$0.028 and log β_3 = 14.704 $\pm$0.014 (65 Sb).

Vanadium (IV) forms complexes of type VOA$^+$ (log β_1 = 8.68 at 25°C) and
VOA$_2$ (log β_2 = 15.79 at 25°C; I not given) (56 B).

Protactinium acetylacetonate

Protactinium(IV) forms mono and bis acetylacetonate complexes of type $PaOA^+$ and $PaOA_2$ (74 L). However, in a large excess of sulfate ions the presence of the tris-acetylacetonate complex $Pa(OH)A_3$ has been observed (74 La). Distribution data for Pa(IV) between acetylacetone solution in benzene and $1\ M(Na^+, H^+)ClO_4^-$ in the temperature range from 5° to 45°C have been used for the determination of stability constants and the corresponding ΔH_n^o and ΔS_n^o values (74 L). Using least-squares method the following values have been obtained for 25°C: $\log \beta_1 = 6.1 \pm 0.1$, $\log \beta_2 = 13.15 \pm 0.13$ and $\log K_{D(PaOA_2)} = 2.07 \pm 0.10$.

The extraction constant $\log K_{ex} = -4.13 \pm 0.05$ at 25°C and 1M (Na^+, H^+) ClO_4^-, and from its variation with temperature, $\Delta H^o = 30 \pm 2$ kJ mol^{-1} and $\Delta S^o = 22 \pm 8$ J $mol^{-1}K^{-1}$ (74 L). On the other hand, from distribution data for acetylacetone solution in benzene and $(1-x)\ M\ (Na^+, H^+)ClO_4^- + xM\ Na_2SO_4$ in the temperature range from 3° to 48°C the extraction constant of the reaction

$$Pa(OH)SO_4^+ + 3\ \overline{HA} = \overline{Pa(OH)A_3} + 3H^+ + SO_4^{2-}$$
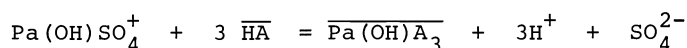
was found to be $\log K_{ex} = -8.17 \pm 0.06$ at 25°C and from its temperature dependence, $\Delta H^o = 14 \pm 3$ kJ mol^{-1} and $\Delta S^o = -110 \pm 11$ J $mol^{-1}K^{-1}$ (74 La).

Protactinium(V) forms mono, bis- and tris-acetylacetonates of the type $PaOA^{2+}$, PaO_2A, $PaO_2A_2^-$ and $PaOA_3$ and an adduct with acetylacetone of the type $PaOA_3 \cdot 2HA$ (70 La). Distribution data for Pa(V) between HA solutions in xylene and $3\ M\ (Na^+, H^+)ClO_4^-$ have been used for the determination of stability constants for the following type of reactions

$$PaO^{3+} + x\ HA = PaO(HA)_x(H)_{-y}^{(3-y)+} + y\ H^+$$
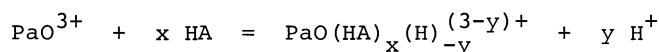
The values of $\log \beta_{xy}$ obtained from a least-squares fit to the distribution data are $\log \beta_{11} = 1.00 \pm 0.17$, $\log \beta_{13} = -2.10 \pm 0.15$, $\log \beta_{24} = -7.77 \pm 0.16$, $\log \beta_{33} = 0.38 \pm 0.11$ and $\log (\beta_{53}K_{D53}) = 0.73 \pm 0.18$ at 25°C (70 La). The following distribution constants were also obtained: $\log K_{D13} = 0.02 \pm 0.12$ and $\log K_{D33} = 0.06 \pm 0.30$. The model for the formation of protactinium (V) acetylacetonate is partly supported by an earlier investigation (68 D) of the distribution of Pa(V) between HA in benzene and $1\ M\ (Na^+, H^+)ClO_4^-$ at 25°C.

Assuming the extraction reaction

$$Pa(OH)_3^{2+} + 4\overline{HA} = \overline{Pa(OH)_3A_2 \cdot 2HA} + 2 H^+$$
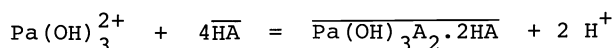
the extraction constant is log $K_{ex} = 2.5$.

The complicated aqueous chemistry of Pa and the paucity of data makes the selection of recommended values impossible at the present time.
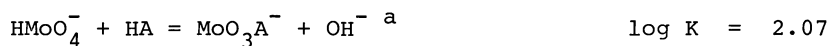
Chromium acetylacetonate

Stability constants of chromium(II) acetylacetonate have been determined potentiometrically at 25°C and 1 M $(K^+, H^+)Cl^-$: log $\beta_1 = 5.96 \pm 0.02$ and log $\beta_2 = 11.70 \pm 0.03$ using $pK_a = 8.878$ (65 Sa).

Molybdenum acetylacetonate

From the distribution of molybdenum(V) ($c_{Mo} = 0.001$ mol dm^{-3}) between acetylacetone solution in trichloromethane and hydrochloric acid (or ammonium chloride) of different concentration the following equilibrium constants have been calculated at 20°C: log $\beta_1 = 10.37$, log $\beta_2 = 20.36$ and log $K_{D(MoO(OH)A_2)} = -0.29$ (68 A).

The distribution of molybdenum(VI) ($c_{Mo} = 0.05$ mol dm^{-3}) under the above conditions has been described by the following reactions (68 A):

$$MoO_2^{2+} + A^- = MoO_2A^+ \qquad\qquad \log\ _1 = 10.57$$

$$MoO_2^{2+} + 2A^- = MoO_2A_2 \qquad\qquad \log\ _2 = 20.49$$

$$MoO_2A_2 = \overline{MoO_2A_2} \qquad\qquad \log K_D =\ 1.69$$

$$MoO_2A_2 + OH^- = MoO_3A^- + HA \qquad\qquad \log K =\ 10.61$$

$$HMoO_4^- + HA = MoO_3A^- + OH^-\ ^a \qquad\qquad \log K =\ 2.07$$

It should be noted that the formation of polymeric species has been neglected in the calculations, the values thus should be regarded as tentative.

Uranium acetylacetonate

Distribution data of uranium(IV) between acetylacetone solutions in benzene and 0.1 M $(Na^+, H^+)ClO_4^-$ have been used for the determination of stability constants (55 R, 61 R). Using the two-parameter method the following values were obtained:

log $\beta_1 = 9.05 \pm 0.16$; log $\beta_2 = 17.02 \pm 0.34$; log $\beta_3 = 23.92 \pm 0.52$ and log $\beta_4 = 29.76 \pm 0.63$. A least-squares analysis (61 R) gives: log $\beta_1 = 9.02$

---

[a] Evidently misprint in the original paper.

± 0.29, log $\beta_2 = 17.28\pm0.44$, log $\beta_3 = 23.80\pm0.50$ and log $\beta_4 = 29.78\pm0.62$.

The distribution constant of uranium(IV) acetylacetonate at 25°C for benzene as organic solvent is log $K_{D(UA_4)} = 2.63\pm0.03$ at 0.1 M $(Na^+, H^+)ClO_4^-$ (61 R) and for n-hexane log $K_{D(UA_4)} = 0.66$ at I M $(Na^+, H^+)ClO_4^-$ $(\Delta H^0 = 65$ kJ mol^{-1}, $\Delta S^0 = 230$ J $mol^{-1}K^{-1})$ (77 A).

The extraction constant calculated from eq. (12) is log $K_{ex} = -5.9$ at 25°C and I = 0.1 mol dm^{-3} for benzene as solvent.
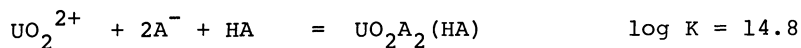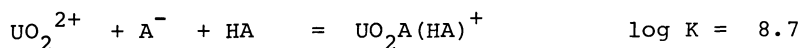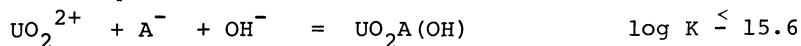
Stability constants of uranium(VI) acetylacetonate are summarized in Table 14. The results are rather scattered thus only tentative values are included in Table 15.

Table 14   Survey of stability constants of uranium(VI) acetylacetonate

log β_1	log β_2	I/mol dm^{-3}	T/°C	Method	Ref.
7.94	14.47	0	10	potent.	55 Ib
7.66	14.15	0	20	potent.	55 Ib
7.73	14.11	0	30	potent.	55 I
7.42	13.68	0	40	potent.	55 Ib
8.87	14.13	low	25	distr.	59 K
7.4[a]	13.6[a]	0.1	25	potent.	55 Ib
6.8	13.1	0.1	25	distr.	55 R
7.0$\pm$0.1	13.5$\pm$0.1	0.1	25	potent.	79 S
7.5	12.3	1	25	polarog.	63 J

[a] Data recalculated using eqs. (7) and (11).

Using the distribution method (55 R), the formation of mixed complexes of the type $UO_2A(OH)$, $UO_2A(HA)^+$ and $UO_2A_2(HA)$ has been detected and the respective equilibrium constants K have been determined at 25°C and I = 0.1M $(Na^+, H^+)ClO_4^-$:

$$UO_2^{2+} + A^- + OH^- = UO_2A(OH) \qquad \log K \leq 15.6$$

$$UO_2^{2+} + A^- + HA = UO_2A(HA)^+ \qquad \log K = 8.7$$

$$UO_2^{2+} + 2A^- + HA = UO_2A_2(HA) \qquad \log K = 14.8$$

It should be noted, however, that the potentiometric method (79 S) did not prove the formation of the complex $UO_2A(HA)^+$.

Distribution constants of uranium(VI) acetylacetonate at 25°C and I = 0.1 M $(Na^+, H^+)ClO_4^-$ are: log $K_{D(UO_2A_2)} = 0.25$ and log $K_{D(UO_2A_2HA))} = 1.52$ using benzene as organic solvent (55 R).

The value of the extraction constants calculated from the above data: $\log K_{ex}$ = -5.5 and -3.6 for the extraction of UO_2A_2 and $UO_2A_2(HA)$, respectively. By the direct determination, the following data were obtained: $\log K_{ex}$ = -5.85 (67 B) and -6.1 at 30°C and I = 2 M(Li^+, H^+)ClO_4^- (67 N); solvent benzene. The formation of mixed complexes, however, was not taken into account.

Table 15.   Tentative values of stability constants of uranium(VI) acetylacetonates 25°C

I/mol dm^{-3}	0	0.1
$\log \beta_1$	7.7 ±0.2	7.1 ±0.2
$\log \beta_2$	14.1 ±0.2	13.4 ±0.2

Neptunium acetylacetonate

The investigation of the distribution of neptinium(IV) between different organic solvents containing acetylacetone and 1 M (Na^+, H^+)ClO_4^- has been used for the determination of stability constants: $\log \beta_1$ = 8.58 ±0.07, $\log \beta_2$ = 17.23 ±0.12, $\log \beta_3$ = 23.94 ±0.14 and $\log \beta_4$ = 30.22 ±0.16 (70 L).

The distribution constants, $\log K_{D(NpA_4)}$, increase in the order: 0.537±0.008 for n-hexane (ΔH_D^0 = 72±2 kJ mol^{-1}, ΔS_D^0 = 251.3±0.2 J $mol^{-1}K^{-1}$), 0.812±0.007 for cyclohexane (ΔH_D^0 = 64.9±0.4 kJ mol^{-1}, ΔS_D^0 = 233.5±0.1 J mol^{-1} K^{-1}), 1.23±0.01 for 4-methyl-2-pentanone(hexone), 2.68±0.02 for tetrachloromethane, and 3.45±0.04 for benzene at 25°C and I = 1 M (Na^+, H^+)ClO_4^- (70 L).

The values of the extraction constants calculated from eq. (12) using data included in (70 L) are: $\log K_{ex}$ = -5.13 for n-hexane, -4.96 for cyclohexane and benzene or tetrachloromethane.

A spectrophotometric titration of pentavalent neptunium with acetylacetone shows the formation of 1:1 and 1:2 chelates with stability constants $\log \beta_1$ = 4.08±0.01 and $\log \beta_2$ = 7.00±0.02 at 25°C and I = 0.1 M (Na^+, H^+) ClO_4^-; $\log \beta_1$ = 4.08±0.02 and $\log \beta_2$ = 7.07±0.02 at 25°C and I = 1 M (Na^+, H^+) ClO_4^- (72 G).

Plutonium acetylacetonate

The stability constants of plutonium(IV) acetylacetonate have been determined by the liquid-liquid distribution method at 25°C and I = 0.1 M (Na^+, H^+)ClO_4^- (55 R, 60 R, 61 R). Using the ligand number method, the

following values were obtained: $\log \beta_1 = 10.0 \pm 1.0$, $\log \beta_2 = 19.1 \pm 1.2$,
$\log \beta_3 = 27.6 \pm 1.5$ and $\log \beta_4 = 33.5 \pm 1.8$; two-parameter analysis gives $\log \beta_1$
$= 10.5 \pm 1.0$, $\log \beta_2 = 19.7 \pm 1.5$, $\log \beta_3 = 23.1 \pm 2$ and $\log \beta_4 = 34.0 \pm 2.1$ (55 Rb,
70 L). The least-squares method allows the determination of only $\log K_2 K_3 =$
17.77 ± 0.12 and $\log K_4 = 5.91 \pm 0.09$ (61 R).

The distribution constant is $\log K_{D(PuA_4)} = 2.54 \pm 0.07$ and 2.6 ± 0.3 at
25°C and $I = 0.1$ M $(Na^+, H^+)ClO_4^-$ for benzene and trichloromethane, respec-
tively (55 Rb, 60 R).

Manganese acetylacetonate

Stability constants of manganese(II) acetylacetonate determined at
different T and I are summarized in Tables 16 and 17.

Table 16   Stability constants of manganese(II) acetylacetonate at $I \to 0$

$T/°C$	$\log \beta_1$	$\log \beta_2$
10	4.28	7.53
20	4.24	7.35
30	4.18	7.25
40	4.11	7.07
$\Delta H_n^o / kJ\ mol^{-1}$	-10.5	-30
	$(-9.6 \pm 4.5)^a$	$(-25 \pm 8)^a$
	5.4 ± 1.0^b	-18.5 ± 1.1^b
	6.3^c	
$\Delta S_n^o / J\ mol^{-1}K^{-1}$	46	39
	$(48 \pm 15)^a$	$(55 \pm 28)^a$
	56.1 ± 3.8^b	68 ± 4^b
	59^c	

[a] Recalculated by the present authors using least-squares method.
[b] Obtained by calorimetric measurements at $I = 0.05$ mol dm^{-3} (78 P).
[c] Obtained by liquid-liquid distribution method at $I = 0.1$ mol dm^{-3} (68 G).

Table 17 Survey of stability constants of manganese(II) acetylacetonate, 25°C

$\log \beta_1$	$\log \beta_2$	$I/mol\ dm^{-3}$	Method	Ref.
4.21^a	7.30^a	0	potent.	55 I, 55 Ib
3.88^b	6.81^b	0.05		78 P
3.89^a	6.82^a	0.1	potent.	55 I, 55 Ib
4.07		0.1	distr.	68 G
3.79 ± 0.06	6.81 ± 0.10	0.1	potent.	79 S
4.09	6.98	1	distr.	77 Sb

[a] Recalculated using eqs. (7) and (11).   [b] Calculated using eq. (11).

The general agreement in stability constants determined using various methods allows us to recommend the most reliable values (Table 18).

The distribution constant log $K_{D(MnA_2)}$ = -1.23 at 25°C and I = 1M (Na$^+$, H$^+$)ClO$_4^-$ for tetrachloromethane as organic solvent; log K_{ex} = -11.8 under the same conditions (77 Sb).

Table 18   Recommended values of stability constants of manganese(II) acetylacetonate, 25°C

I/mol dm^{-3}	0	0.1
log β_1	4.21$\pm$0.05	3.91$\pm$0.11
log β_2	7.3 $\pm$0.1	6.82$\pm$0.02

Iron acetylacetonate

Stability constants of iron(II) acetylacetonate have been determined only by a single group of authors using reliable potentiometric method: log β_1 = 5.07 and log β_2 = 8.67 at 30°C and I → O (55 I).

A survey of equilibrium constants of iron(III) acetylacetonates is given in Table 19.

Table 19   Equilibrium constants of iron(III) acetylacetonates

T/°C	I/mol dm^{-3}	log β_1	log β_2	log β_3	log K_{ex}	Ref.
25	0	11.4 (?)	22.1 (?)	26.7		51 B
30	0	9.8$\pm$0.3	18.8$\pm$0.6	26.2$\pm$0.9		55 Ia
25	low	9.27	17.98	23.87		59 K
30	0.1	9.3$\pm$0.3[a]	18.0$\pm$0.6[a]	25.3$\pm$0.9[a]		55 Ia
20	0.1				-1.39[b]	63 S
20	0.1	9.17	18.34		-0.98[b]	71 K
(?)	0.4	10.6	19.7			76 F
25	1.0	10.5				71 F

[a] Recalculated using eqs. (7) and (11). [b] Benzene was used as the organic solvent.

From the data in Table 19 it is evident that the differences between reported values are too large as to be explained only by the changes of T and I, thus, only tentative constants at· I = 0.1 mol dm^{-3} can be given (Table 20). The polarographic method allows only the determination of stepwise stability constants: log K_2 = 8.4 and log K_3 = 6.5 at 25°C and I = 0.1 mol dm^{-3} (63 P). Using the tentative values of log β_1 = 9.25, then log β_2 = 17.65 and log β_3 = 24.15.

From the heterogeneous stability constants log $\overline{\beta}_3$ = 27.42 (63 S) and

27.49 (71 K) at 20°C and I = 0.1 M $(Na^+, H^+)ClO_4^-$ it follows that $\log \beta_3 =$

24.5 for the distribution constant $\log K_{D(FeA_3)} = 3$ (59 K) using benzene as

organic solvent ($\log K_{D(FeA_3)} = 2.95$ and 1.45 at 25°C and I = 1 M (Na^+, H^+)

ClO_4^- for benzene and 4-methyl-2-pentanone, respectively (68 L).

Table 20   Tentative equilibrium constants of iron(III) acetylacetonate
at I = 0.1 mol dm^{-3} and T = 20-30°C

$\log \beta_1 = 9.25 \pm 0.10$	$\log \beta_3 = 24.5 \pm 0.3$	
$\log \beta_2 = 18.0 \pm 0.2$	$\log K_{ex} = -1.1 \pm 0.2$ for benzene as organic solvent	

Cobalt acetylacetonate

The stability constants of cobalt(II) acetylacetonate determined at
various T and I are summarized in Tables 21 and 22. The general agreement
between values obtained by different authors allows us to recommend the most
reliable data.

Table 21   Stability constants of cobalt acetylacetonate at I → 0 (55 I, 55 Ib)

Temp/°C	$\log \beta_1$	$\log \beta_2$
10	5.58	9.92
20	5.40	9.57
30	5.40	9.51
40	5.34	9.30
ΔH_n^o / kJ mol^{-1}	-5.0	-26
	$(-12 \pm 18)^a$	$(-33 \pm 26)^a$
	-11.8 ± 1.4^b	-33.7 ± 1.8^b
ΔS_n^o/J $mol^{-1}K^{-1}$	88	98
	$(62 \pm 60)^a$	$(73 \pm 88)^a$
	57 ± 5^b	60 ± 6^b

[a] Recalculated by the present authors using least-squares method.
[b] Determined by calorimetric measurements at I = 0.05 mol dm^{-3} (78 P)

Table 22   Survey of stability constants of cobalt(II) acetylacetonates, 25°C

I/mol dm^{-3}	$\log \beta_1$	$\log \beta_2$	Method	Ref.
0	5.40^a	9.54^a	potent.	55 I, 55 Ib
0.017	5.51	9.74	potent.	68 Ga
0.05	5.07^b	9.05^b		78 P
0.1	5.08^a	9.06^a	potent.	55 I, 55 Ib
0.1	5.18	9.42 (?)	potent.	69 Sa
0.1	5.09 ± 0.04	9.08 ± 0.04	potent.	79 S

[a] Recalculated using eqs. (7) and (11).   [b] Recalculated using eq. (11).

Cobalt(II) acetylacetonate is extracted into tetrachloromethane only slightly: $\log K_{D(CoA_2)}$ = -0.94 at 25°C and I = 1 M(Na$^+$, H$^+$)ClO$_4^-$ (74 S).

Table 23   Recommended values of stability constants of cobalt(II) acetylacetonate, 25°C

I/mol dm^{-3}	0	0.1
$\log \beta_1$	5.4$\pm$0.1	5.10$\pm$0.06
$\log \beta_2$	9.5$\pm$0.1	9.08$\pm$0.04

Nickel acetylacetonate

A survey of stability constants of nickel acetylacetonate is given in Tables 24 and 25.

Table 24   Stability constants of nickel acetylacetonate at I = 0 (55 I,55 Ib)

Temp./°C	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
10	6.16	11.00	13.51
20	6.06	10.77	13.09
30	5.92$\pm$0.05	10.38$\pm$0.16	12.49
40	5.86	10.26	12.16
ΔH_n^o / kJ mol^{-1}	-28[a]	-54[a]	-82[a]
	(-17.7$\pm$6.7)[b]	(-44$\pm$24)[b]	(-79$\pm$23)[b]
	-17[c]	-41[c]	
	-17.7$\pm$1.1[d]	-38$\pm$1[d]	
	-14[e]	-32[e]	
ΔS_n^o / J mol^{-1}K^{-1}	50	50	
	(55$\pm$23)[b]	(54$\pm$80)[b]	
	46[c]	59[c]	
	53$\pm$4[d]	66$\pm$5[d]	
	63[e]	80[e]	

[a] Evidently an error in the original paper: ΔH_n^o should be -17, -44 and -72 kJ mol^{-1} for $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$, respectively.

[b] Recalculated by the present authors using least-squares method.

[c] Determined potentiometrically at I = 0.02 mol dm^{-3} (71 R).

[d] Determined by calorimetric measurements at I = 0.05 mol dm^{-3} (78 P).

[e] Determined at I = 0.1 mol dm^{-3} (68 G).

Table 25   Survey of stability constants of nickel acetylacetonate, 25°C

$I/\text{mol dm}^{-3}$	$\log \beta_1$	$\log \beta_2$	Method	Ref.
0	5.92	10.49	potent.	49 M
0	5.99[a]	10.58[a]	potent.	55 I, 55 Ib
0.017	6.05	10.66	potent.	68 Ga
0.02	5.69	10.16	potent.	71 R
0.05	5.66[b]	10.8[b]		78 P
0.1	5.67[a]	10.10[a]	potent.	55 I, 55 Ib
0.1	5.72	9.66 (?)	distr.	68 G
0.1	$5.74^{\pm}0.03$	$10.23^{\pm}0.04$	potent.	79 S

[a] Recalculated data using eqs. (7) and (11).

[b] Data calculated using eq. (11).

The value $\log \beta_2$ = 9.66 (68 G) is too low in comparison to other pub-
lished data - thus not taken into consideration for the evaluation of the
most reliable data (Table 26).

The distribution constant of nickel acetylacetonate between tetrachloro-
methane and 1 M $(\text{Na}^+, \text{H}^+)\text{ClO}_4^-$ at 25°C is very low: $\log K_{D(\text{NiA}_2)}$ = -2 ∿-2.5
(77 S).

Table 26   Recommended values of stability constants of nickel
           acetylacetonate, 25 °C

$I/\text{mol dm}^{-3}$	0	0.1
$\log \beta_1$	$5.96^{\pm}0.05$	$5.71^{\pm}0.04$
$\log \beta_2$	$10.54^{\pm}0.05$	$10.16^{\pm}0.09$

Palladium acetylacetonate

The reaction between palladium(II) chloride and acetylacetone has been
investigated spectrophotometrically and potentiometrically in order to deter-
mine the stability constants of palladium acetylacetonate (57 D). By extra-

polation to zero chloride concentration the following stability constants

have been determined: $\log \beta_1 = 16.7\pm0.2$, 16.2 and 15.4 at 20°, 30° and 40°C,

respectively ($\Delta H_1^0 = -75\pm17$ kJ mol^{-1}, $\Delta S_1^0 = 59\pm54$ J mol^{-1}K^{-1}); $\log \beta_2 = 27.1$

±0.4 and 25.9 ± 0.4 at 30° and 40°C, respectively ($\Delta H_2^0 = -150\pm34$ kJ mol^{-1}).

Copper acetylacetonate

Stability constants of copper acetylacetonate determined by the poten-

tiometric method (55 I, 55 Ib) and from liquid-liquid distribution data

(69 La) at various temperatures are summarized in Table 27. A survey of sta-

bility, distribution and extraction constants of copper acetylacetonate is

given in Table 28.

For the calculation of β_1 and β_2 at $I = 0.1$ mol dm^{-3}, a pK_a value of

8.62 (71 S) has been used instead of 8.83 which leads to the lower value of

the stability constants (by recalculation we obtained $\log \beta_1 = 7.95$ and

Table 27   Stability and distribution constants of copper acetylacetone
            at different temperatures

Temp./°C	$\log \beta_1$ $I = 0$ (55 I, 55 Ib)	$\log \beta_1$ $I = 1$ mol dm^{-3} (69 La)	$\log \beta_1$ $I = 0$ (55 I, 55 Ib)	$\log \beta_1$ $I = 1$ mol dm^{-3} (69 La)	$\log K_{D(CuA_2)}$
10	8.38 ± 0.02		15.44 ± 0.05		
20	8.31 ± 0.02	8.14 ± 0.10	15.16 ± 0.07	14.94 ± 0.10	1.01^a
25		8.05 ± 0.08		14.75 ± 0.10	1.10^a
30	8.22 ± 0.02	7.96 ± 0.07	14.95	14.57 ± 0.08	1.18^a
35		7.88 ± 0.06		14.42 ± 0.07	1.24^a
40	7.76 ± 0.02	7.80 ± 0.05	14.36	14.26 ± 0.05	1.28^a
ΔH_n^0/ kJ mol^{-1}	-19.7 $(-33\pm51)^b$ -30^c -18.9 ± 0.5^d -20.1^e	-28.9 ± 2.5	-47.3 $(-58\pm47)^b$ -62^c -44.4 ± 1.1^d -42.2^e	-60 ± 6	23 ± 2
ΔS_n^0/ J mol^{-1}K^{-1}	92 $(46\pm172)^b$ 59^c 88 ± 2^d 88^e	56.7 ± 0.03	130 $(91\pm159)^b$ 79^c 122 ± 4^d 142^e	82	98.9 ± 0.2

[a] Benzene was used as the organic solvent.
[b] Data recalculated by the present authors using least-squares method.
[c] $I = 0.02$ mol dm^{-3} (61 R). [d] $I = 0.05$ mol dm^{-3} (78 P). [e] $I = 0.1$ mol dm^{-3} (68 G)

log β_2 = 14.7). No explanation has been found for the high values of the
stability constants obtained by the liquid-liquid distribution method (59 K,
69 I); these data were not considered for the recommendation of the most
reliable values (Table 29).

   The log $K_{D(CuA_2)}$ values determined at 25°C and 1 M (Na^+, H^+)ClO_4^- are:
-0.04 for cyclohexane, 1.04 for benzene, 0.85 for toluene, 0.80 for xylene,
2.54 for trichloromethane and 0.85 for tetrachloromethane (75 A). The value
log $K_{D(CuA_2)}$ = 1.80$\pm$0.10 (77 B) determined under the same conditions for
trichloromethane as organic solvent seems to be too low in view of the high
solubility of copper chelate in this solvent. The distribution constants can
be compared with the solubility data of copper acetylacetonate determined at
20°C (76 K, 77 K): 7.08 x 10^{-5} mol dm^{-3} in cyclohexane, 3.48 x 10^{-3} mol dm^{-3}

Table 28   Survey of equilibrium constants of copper acetylacetonate

T/°C	I/ mol dm^{-3}	log β_1	log β_2	log $K_{D(CuA_2)}$	log K_{ex}	Ref.
25	0	8.26[a]	15.05[a]			55 I, 55 I
25	low	8.96(?)	15.8 (?)			55 K
25	0.02	8.29	14.99			71 R
25	0.05	7.92[b]	14.18[b] (?)			78 P
25	0.1	7.94[a]	14.57[a]			55 I, 55 I
25	0.1	8.16	14.76			68 G
20	0.1				-3.93[c]	63 S
25	0.1				-3.76[c]	69 H
20	0.1	8.41	14.82	0.85[c]	-3.60[c]	71 K, 77
25	0.1	7.74	14.28 (?)	0.70[d]	-3.47[d]	71 S
25	0.1	7.98$\pm$0.11	14.80$\pm$0.08			79 S
20	0.18	8.70	15.24 (?)	0.80[c]	-3.3[c]	65 I
25	1.0	8.05$\pm$0.08	14.75$\pm$0.10	1.10[c]	-3.5[c]	69 La
20	1.0	8.28	14.56			71 K
25	1.0	7.81	14.22 (?)	0.83[d]	-3.73[d]	71 S
25	1.0	8.42$\pm$0.10	15.47 (?)			77 B
25	3.0	8.41	15.42			71 S

[a] Data recalculated using eqs. (7) and (11).
[b] Data recalculated using eq. (11).
[c] Benzene was used as the organic solvent.
[d] Tetrachloromethane was used as the organic solvent.

Table 29   Recommended values of equilibrium constants of copper
            acetylacetonate, 25°C

$I/mol\ dm^{-3}$	0	0.1	1.0
$\log\ \beta_1$	8.25 ± 0.05	8.0 ± 0.1	8.1 ± 0.2
$\log\ \beta_2$	15.05 ± 0.10	14.8 ± 0.1	~ 14.7
$\log\ K_{D(CuA_2)}$		0.85 ± 0.05[a]	1.07 ± 0.03[a]
$\log\ K_{ex}$		-3.75 ± 0.10[a]	-3.6 ± 0.1[a]

[a] Benzene was used as the organic solvent

in benzene, $1.65 \times 10^{-3}\ mol\ dm^{-3}$ in toluene, $2.27 \times 10^{-1}\ mol\ dm^{-3}$ in tri-
chloromethane, $1.99 \times 10^{-3}\ mol\ dm^{-3}$ in tetrachloromethane, and 3.80×10^{-4}
$mol\ dm^{-3}$ in neutral aqueous solutions.

    The extraction constants for benzene as the organic solvent are in
general agreement (Table 28); the value of $\log\ K_{ex}$ = -4.32 and -4.56 (67 N)
for 2 M $(Li^+, H^+)Cl^-$ were determined only from two experimental points (at
pH = 2.2 and 2.7) and were thus not taken into consideration for the
recommendation of the most reliable constants.
    The extraction constant for tetrachloromethane $\log\ K_{ex}$ = -3.41 at 20°C
and I = 0.1 $mol\ dm^{-3}$ (73 K) and -3.47 at 25°C and I = 0.1 $mol\ dm^{-3}$ (71 S);
the agreement between the values is very good. For trichloromethane $\log\ K_{ex}$ =
-2.98 at 20°C and I = 0.1 $mol\ dm^{-3}$ and for toluene $\log\ K_{ex}$ = -3.73 under the
same conditions (73 K).

Zinc acetylacetonate

    The stability constants of zinc acetylacetonate, determined by the
potentiometric method (54 I, 55 Ib) and by the liquid-liquid distribution
method (69 La) at various temperatures, are summarized in Table 30. A survey
of stability, distribution and extraction constants of zinc acetylacetonate
at 25°C is given in Table 31, and the most reliable equilibrium constants
in Table 32.

    It has been found that at higher acetylacetonate ion concentrations
anionic complexes of the type ZnA_3^- are formed (71 S, 74 S, 76 S) with log
K_3 = 1.50 at 20°C and I = 0.1 M $(Na^+, H^+)ClO_4^-$ (76 S).
    The $\log\ K_{D(ZnA_2)}$ values at 25°C and I = 1 M$(Na^+, H^+)ClO_4^-$ are (75 A):
-1.57 for n-hexane, -1.16 for cyclohexane, -0.27 for benzene, -0.37 for
toluene, -0.47 for xylene, 0.83 for trichloromethane and -0.39 for tetra-
chloromethane.

Table 30   Stability and distribution constants of zinc acetylacetonate at different temperatures and ionic strengths I (mol dm^{-3})

Temp./°C	$\log \beta_1$ I → 0 (54 I, 55 Ib)	$\log \beta_1$ I = 1 (69 La)	$\log \beta_2$ I → 0 (54 I, 55 Ib)	$\log \beta_2$ I = 1 (69 La)	$\log K_{D(ZnA_2)}$ [a] I = 1 (69 La)
10	5.14	4.63 ± 0.06[b]	9.16	8.75 ± 0.05[b]	-0.57 ± 0.02[b]
20	5.07		9.02		
25		4.63 ± 0.05		8.60 ± 0.04	-0.19 ± 0.01
30	4.98	4.64 ± 0.05[c]	8.81	8.50 ± 0.03[c]	0.00 ± 0.01
40	5.00	4.65 ± 0.04	8.88	8.42 ± 0.04	0.21 ± 0.01
ΔH^{o}_{n}/ kJ mol^{-1}	-8.0 (-9 ± 11)[d] -7.4 ± 0.2[e] -6.3[f]	1.3 ± 1.7	$-$ (-18 ± 29)[d] -20 ± 1[e] -14.2[f]	-20.0 ± 3.8	47 ± 3
ΔS^{o}_{n}/ J mol^{-1}K^{-1}	71 (67 ± 39)[d] 64.9 ± 1.3[e] 67[f]	92.8 ± 0.2	$-$ (111 ± 97)[d] 86 ± 4[e] 100[f]	98.0 ± 0.5	153.8 ± 0.1

[a] Benzene was used as the organic solvent.   [b] At 12°C   [c] At 32°C
[d] Recalculated data by the present authors using least-squares method.
[e] At I = 0.05 mol dm^{-3} (78 P).   [f] At I = 0.1 mol dm^{-3} (68 G).

Table 31 Stability, distribution and extraction constants of zinc acetylacetonate at 25°C and different ionic strengths I (mol dm^{-3})

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log K_{D(ZnA_2)}$	$\log K_{ex}$	I	Ref.
5.03 ± 0.05[a]	8.9 ± 0.1[a]				0	54 I, 55 Ib
5.06	8.72				low	59 K
4.68[b]	8.07[b]				0.05	78 P
4.71[a]	8.3[a]				0.1	54 I, 55 Ib
4.68	7.92(?)				0.1	68 G
4.85	8.22	9.43	-0.65[c]	-10.69[c]	0.1	71 S
4.60 ± 0.05	8.34 ± 0.05				0.1	79 S
4.63 ± 0.05	8.60 ± 0.04		-0.19 ± 0.01[d]	-11.0[d]	1	69 La
4.58	7.76	9.16	-0.38[c]	-11.4[c]	1	71 S, 74 S

[a] Recalculated data using eqs.(7) and (11).   [b] Calculated from eqs.(10) and (11).
[c] Tetrachloromethane as organic solvent.   [d] Benzene as organic solvent.

Table 32 Recommended values of equilibrium constants of zinc acetylacetonate, 25°C

I/mol dm^{-3}	0	0.1	1.0
log β_1	5.03$\pm$0.05	4.70$\pm$0.08	4.60$\pm$0.04
log β_2	8.8 $\pm$0.1	8.3 $\pm$0.1	
log K_{ex}			-11.0[a]

[a] Benzene was used as the organic solvent.

Cadmium acetylacetonate

Stability constants of cadmium complexes with acetylacetone at various temperatures and $I \to 0$ (55 I, 55 Ib) are given in Table 33

Table 33   Stability constants of cadmium acetylacetonate at $I \to 0$

T/°C	log β_1	log β_2
10	3.88	6.78
20	3.84	6.72
30	3.83	6.59
40	3.77	6.24
ΔH^o_n/ kJ mol^{-1}	-5.4 (-5.7$\pm$5.0)[a]	- (-29$\pm$37)[a]
ΔS^o_n/ J mol^{-1}K^{-1}	54 (54$\pm$17)[a]	- (27$\pm$124)[a]

[a] Recalculated by the present authors using least-squares method.

Stability constants determined by the potentiometric method at 25°C and I = 0.1 mol dm^{-3} (79 S): log β_1 = 3.48$\pm$0.02 and log β_2 = 6.26$\pm$0.08 are in good agreement with the values, log β_1 = 3.51 and log β_2 = 6.2, obtained by recalculation of Izatt's data (55 I, 55 Ib) using eqs. (7) and (11). The polarographic method gives for log β_2 the value 6.12 at 30°C and 0.7M (K^+,H^+) NO_3^- (62 S). Data obtained at 25°C and I = 1M (Na^+, H^+)ClO_4^- by the liquid-liquid distribution method are (77 Sa): log β_1 = 3.94 and log β_2 = 6.68.

The distribution constant of the chelate is very low: log $K_{D(CdA_2)}$ = -2.4 at 25°C and I = 1 M (Na^+, H^+)ClO_4^- using tetrachloromethane as organic solvent (77 Sa): log K_{ex} = -14.3 under these conditions (77 Sa).

Table 34 Recommended values of stability constants of cadmium acetylacetonate, 25°C

I/mol dm^{-3}	0	0.1
log β_1	3.83$\pm$0.05	3.48$\pm$0.03
log β_2	6.6 $\pm$0.1	6.26$\pm$0.08

Mercury acetylacetonate

The stability constants of mercury(II) acetylacetonate determined at 30°C and I = 0.5 mol dm^{-3}:   log β_2 = 21.56 (at I = 1 mol dm^{-3} log β_2 = 21.37) (55 I) are in a good agreement with the value of log β_1 = 12.9 and log β_2 = 20.1 at 25°C and I = 0.1 mol dm^{-3} (75 V) taking into account the different experimental conditions. In both publications the influence of the formation of mercury(II) complexes with chloride ions has been considered.

Aluminium acetylacetonate

Stability constants of aluminium acetylacetonate were determined potentiometrically at 30°C and I → 0 (55 Ia): log β_1 = 8.6$^{\pm}$0.2, log β_2 = 16.5$^{\pm}$0.3 and log β_3 = 22.3$^{\pm}$0.4. By recalculation using eq. (7) we obtain for I = 0.1 mol dm^{-3}: log β_1 = 8.1$^{\pm}$0.2, log β_2 = 15.7$^{\pm}$0.3 and log β_3 = 21.4$^{\pm}$0.4; these data are in a good agreement with log β_1 = 8.25, log β_2 = 15.6 and log β_3 = 21.5 determined by the distribution method at 25°C and low I (59 K).

The heterogeneous stability constant log $\bar{\beta}_3$ = 22.32 at 20°C and I = 0.1 (Na$^+$, H$^+$)ClO$_4^-$ using benzene as the organic solvent (63 S); log $K_{D(AlA_3)}$ = 1.0 under these conditions (63 S) and log β_3 = 21.3 from eq. (14).

The extraction constant log K'_{ex} = 6.48 at 20°C and I = 0.1 mol dm^{-3} using benzene as organic solvent (63 S).

Table 35 Tentative equilibrium constants of aluminium acetylacetonate at 20-30°C

I/mol dm^{-3}	0	0.1
log β_1	8.6$^{\pm}$0.2	8.2$^{\pm}$0.2
log β_2	16.5$^{\pm}$0.3	15.7$^{\pm}$0.2
log β_3	22.3$^{\pm}$0.4	21.4$^{\pm}$0.2
log K_{ex}		-6.5$^{\pm}$0.2[a]

[a]   Benzene was used as the organic solvent.

Gallium acetylacetonate

The potentiometric method gives for the stability constants of gallium acetylacetonate at 30°C and I → O the following values: log β_1 = 9.4$^{\pm}$0.2, log β_2 = 17.75$^{\pm}$0.30 and log β_3 = 23.65$^{\pm}$0.40 (55 Ia). The distribution method gives at 25°C and low I much lower values of stability constants (59 K): log β_1 = 7.79, log β_2 = 15.27 and log β_3 = 21.56, whereas at I = 1M (Na$^+$, H$^+$)ClO$_4^-$ the following values have been obtained: log β_1 = 9.29$^{\pm}$0.07, log β_2 = 17.27$^{\pm}$0.12 and log β_3 = 23.65$^{\pm}$0.08 (72 L). Because of the great differences in the data published, the values of stability constants at I → O (55 Ia) and I = 1 mol dm^{-3} (72 L) should be considered only as tentative.

The value of $\log K_{D(GaA_3)}$ reported for benzene at 25°C and I = 1 mol dm^{-3} is 2.43$\pm$0.03 (72 L), whereas it is only 1.4 for pure acetylacetone at low I (59 K).

The extraction constant is $\log K'_{ex}$ = -5.51 at 20°C and I = 0.1 mol dm^{-3} in benzene as the organic solvent (63 S). From the experimental data of (59 K) we obtain $\log K_{ex}$ = -6.0 at 25°C and low I using pure acetylacetone as organic solvent.

Indium acetylacetonate

Stability constants of indium acetylacetonate have been determined by the potentiometric (55 Ia, 77 Sc), liquid-liquid distribution (58 R) and polarographic methods (66 C) (Table 36). The value of β_3 cannot be determined by the potentiometric method because of the low solubility of the indium chelate of the type InA$_3$ in aqueous solutions. The stability constants determined by the polarographic method are considerably larger than those determined by other methods and were thus not taken into consideration for the evaluation of the tentative constant for indium complexes. (Table 37).

Table 36   Stability constants of indium acetylacetonate at different temperatures and ionic strengths I (mol dm^{-3})

T	I	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Ref.
30	0	8.0$\pm$0.2	15.1$\pm$0.3		55 Ia
30	0.1	(7.5$\pm$0.2)[a]	(14.3$\pm$0.3)[a]		55 Ia
20	0.1	8.08$\pm$0.05	14.3$\pm$0.1	18.6$\pm$0.1	58 R
25	0.2	7.71	14.52		77 Sc
35	0.2	7.61	14.30		77 Sc
45	0.2	7.51	14.08		77 Sc
25	0.5	8.80$\pm$0.05	16.2$\pm$0.1	22.2$\pm$0.1	66 C

[a] Data recalculated according to eq. (7).

The heterogeneous stability constant was found to be $\log \overline{\beta}_3$ = 21.6 at 20°C and I = 0.1 (Na$^+$, H$^+$)ClO$_4^-$ using benzene as organic solvent (63 S) and the distribution constant $\log K_{D(InA_3)}$ = 3.23 under these conditions (58 R); from eq. (14), $\log \beta_3$ = 18.4.

The distribution constant $\log K_{D(InA_3)}$ = 3.23 at 20°C and I = 0.1 mol dm^{-3} using benzene or trichloromethane as the organic solvents; for tetrachloromethane $\log K_{D(InA_3)}$ = 2.63 under these conditions.

The extraction constant is $\log K'_{ex}$ = -7.2 at 20°C and I = 0.1 mol dm^{-3} in benzene and tetrachloromethane; for trichloromethane, $\log K'_{ex}$ = -9.1 (58 R, 63 S).

Table 37   Tentative stability constants of indium acetylacetonate
             at 20-30°C

I/mol dm^{-3}	0	0.1
log β_1	$8.0^{\pm}0.2$	$7.8^{\pm}0.3$
log β_2	$15.1^{\pm}0.3$	$14.4^{\pm}0.2$
log β_3		$18.5^{\pm}0.2$

Thallium acetylacetonate

The stability constants of thallium(III) complexes with acetylacetone
have been determined only by a single group of authors (69 B) using the liquid
liquid distribution method (69 B).   At $20^{\pm}2$°C and I = 0.1 M (Na$^+$, H$^+$)ClO$_4^-$
the following constants have been determined: log β_1 = 8.78, log β_2 = 16.78
and log β_3 = 24.60.   In this paper the hydrolysis of thallium(III) ions has
been neglected.   The relatively low value of the distribution constant
log $K_{D(InA_3)}$ = 1.07 in benzene as the organic solvent suggests the formation
of hydroxocomplexes in the aqueous phase.   These values thus should be con-
sidered as the lowest values of stability constants of indium acetylacetonate
(from the experimental results given in (63 S) it follows that the hetero-
geneous stability constant log β_3 is about 28 and according to eq. (14),
log β_3 $\overset{<}{=}$ 27).

Lead acetylacetonate

The following stability constants were determined by the liquid-liquid
distribution method at 25°C and low I (59 K):   log β_1 = 4.51 and log β_2= 7.00.
The data agree with the stability constants determined by the potentiometric
method at 25°C and I = 0.1 mol dm^{-3} (79 S):   log β_1 = $4.57^{\pm}0.04$ and log β_2 =
$7.28^{\pm}0.09$ which allows to recommend the tentative data for lead complexes
(Table 38).   The polarographic method gives for 30°C and I = 0.7 mol dm^{-3} a
much lower value for log β_2 = 6.3 (62 S).

The extraction constant log K'_{ex} = -10.15 at 20°C and I = 0.1 mol dm^{-3}
(63 S).

Table 38   Tentative stability constants of lead acetylacetonate at 25°C
             and ionic strength I = 0.1 mol dm^{-3}

log β_1	=	$4.5^{\pm}0.1$
log β_2	=	$7.2^{\pm}0.2$

References

40 S Schwarzenbach G., Lutz K., Helv. Chim. Acta, 23, 1147 (1940)

45 E Eidinoff M. L., J. Amer. Chem. Soc., 67, 2072 (1945)

49 M Maley L. E., Mellor D. P., Austr. J. Sci. Res., 2A, 92 (1949)

50 R Rydberg J., Acta Chem. Scand., 4, 1503 (1950)

51 C Cartledge G. H., J. Amer. Chem. Soc., 73, 4416 (1951)

53 B Badoz-Lambling J., Ann. Chim. (France) 8, 586 (1953)

53 R Rydberg J., Svensk Kem. Tidskr., 65, 37 (1953)

53 Ra Rydberg J., Arkiv Kemi, 5, 517 (1953)

53 Rb Rydberg J., Arkiv Kemi, 5, 413 (1953)

54 I Izatt R. M., Haas Ch. G., Block B. P., Fernelius W. C.,

      J. Phys. Chem., 58, 1133 (1954)

54 S Steinbach J. F., Freiser H., Anal. Chem., 26, 375 (1954)

55 I Izatt R. M., Fernelius W. C., Block B. P., J. Phys. Chem.,

      59, 80 (1955)

55 Ia Izatt R. M., Fernelius W. C., Haas Ch. G., Block B. P.,

      J. Phys. Chem., 59, 170 (1955)

55 Ib Izatt R. M., Fernelius W. C., Block B. P., J. Phys. Chem.,

      59, 235 (1955)

55 R Rydberg J., Svensk Kem. Tidskr., 67, 499 (1955)

55 Ra Rydberg J., Arkiv. Kemi, 8, 113 (1955)

55 Rb Rydberg J., Arkiv. Kemi, 8, 101 (1955)

56 B Brito R., Tryjillo R., Anales Real Soc. Espan., Fiz. Quim.,

      52 B, 407 (1956)

56 R Rydberg J., Arkiv. Kemi, 9, 109 (1956)

57 D Droll H. A., Block B. P., Fernelius W. C., J. Phys. Chem.,

      61, 1000 (1957)

58 P Peshkova V. M., Zozulya A. P., Nauch. Dokl. Vysshey Shkoly,

      Khim. Khim. Tekhnol., 1, 470 (1958)

58 R Rudenko N. P., Starý J., Trudy Komm. Anal. Khim., 9, 28 (1958)

59 K Krishen A., Freiser H., Anal. Chem., 31, 923 (1959)

60 B Brown W. B., Steinbach J. F., Wagner W. F., J. Inorg. Nucl. Chem.,

      13, 119 (1960)

60 G Grenthe I., Fernelius W. C., J. Amer. Chem. Soc., 82, 6258 (1960)

60 R   Rydberg J., Acta Chem. Scand., 14, 157 (1960)

61 L   Laloi L., Rumpf P., Bull Soc. Chim. France, 1645 (1961)

61 P   Peshkova V. M., Pen-An, Zh. Neorg. Khim., 6, 2082 (1961)

61 R   Rydberg J., Acta Chem. Scand., 15, 1723 (1961)

62 S   Saraiya S. C., Srinivasan V. S., Sundaran A. K., Current Sci.

        (India) 31, 187 (1962

63 J   Jeftic L., Branica M., Croat. Chem. Acta, 35, 203 (1963)

63 G   Green R. W., Alexander P. W., J. Phys. Chem., 67, 905 (1963)

63 P   Petek M., Branica M., J. Polarog. Soc., 9, 1 (1963)

63 S   Starý J., Hladký E., Anal. Chim. Acta, 28, 227 (1963)

64 O   Omori T., Wakahayashi T., Oki S., Suzuki N., J. Inorg. Nucl. Chem.,

        26, 2265 (1964)

64 P   Prášilová J., J. Inorg. Nucl. Chem., 26, 661 (1964)

64 S   Sillén L. G., Martell A. E., Stability Constants of Metal-Ion

        Complexes, The Chemical Society, London 1964

64 W   Wakahayashi T., Oki S., Omori T., Suzuki N., J. Inorg. Nucl. Chem.,

        26, 2255 (1964)

64 Y   Yoneda H., Choppin G. R., Bear J. L., Quagliano J. V.,

        Inorg. Chem., 3, 1642 (1964)

65 I   Irving H.M.N.H., Al-Niami N. S., J. Inorg. Nucl. Chem.,

        27, 419 (1965)

65 Ia   Irving H.M.N.H., Al-Niami N. S., J. Inorg. Nucl. Chem.,

        27, 1671 (1965)

65 O   Oki S., Bull. Chem. Soc. Japan, 38, 522 (1965)

65 S   Schaefer W. P., Mathisen M. E., Inorg. Chem., 4, 431 (1965)

65 Sa   Schaefer W. P., Inorg. Chem., 4, 642 (1965)

66 C   Cosovic B., Branica M., J. Polarog. Soc., 12, 5 (1966)

66 K   Korenman I. M., Sheyanova F. R., Guryeva Z. M., Zh. Neorg. Khim.,

        11, 2761 (1966)

66 Ka   Korenman I. M., Zaglyadimova N. V., Zh. Neorg. Khim.,

        11, 2774 (1966)

66 S   Sekine T., Koizumi A., Sakairi M., Bull. Chem. Soc. Japan,

        39, 2681 (1966)

66 V   Van der Linden W. E., Den Boef G., Anal. Chim. Acta, 37, 179 (1966)

67 B   Batzar K., Goldberg D. E., Newman L., J. Inorg. Nucl. Chem.,
        29, 1511 (1967)

67 F   Fadeeva V. I., Abder Rakhmid Abbad, Vestnik Moskov. Univ.,
        Ser. Khim., 22, No. 6, 52 (1967)

67 N   Newman L., Klotz P., Solvent Extraction Chemistry (Eds. Dyrssen D.,
        Liljenzin J. O., Rydberg J.) 128, North-Holland, Amsterdam 1967

68 A   Afanas´ev O. P., Bantysh A. H., Knyazev D. A., Zh. Neorg. Khim.,
        13, 352 (1968)

68 D   Dyachkova R. A., Khlebnikov V. P., Spitzin V. I., Radiokhimiya,
        10, 21 (1968)

68 G   Gutnikov G., Freiser H., Anal. Chem., 40, 39 (1968)

68 Ga   Gentile·P. S., Dagnar A., J. Chem. Eng. Data, 13, 236 (1968)

68 L   Lark P. D., Craven B. R., Bosworth R.C.L., The Handling of Chemical
        Data, Pergamon Press, Oxford 1968

68 R   Rudenko N. P., Sevastyanov A. I., Lanskaya N. G., Zh. Neorg.
        Khim., 13, 1566 (1968)

69 B   Busev A. I., Filip V. Z., Vestnik Moskov. Univ., Ser. Khim.,
        No. 4, 92 (1969)

69 H   Hasegawa Y., Bull. Chem. Soc. Japan, 42, 3425 (1969)

69 J   Johansson H., Rydberg J., Acta Chem. Scand., 23, 2797 (1969)

69 L   Liljenzin J. O., Acta Chem. Scand., 23, 3592 (1969)

69 La   Liljenzin J. O., Starý J., Rydberg J., Solvent Extraction Research
        (Eds. Kertes A. S., Marcus Y.) p. 21, Wiley, New York 1969

70 K   Koshimura H., Okubo T., Anal. Chim. Acta, 49, 67 (1970)

70 L   Liljenzin J. O., Starý J., J. Inorg. Nucl. Chem., 32, 1357 (1970)

70 La   Liljenzin J. O., Acta Chem. Scand., 24, 1655 (1970)

71 F   Fay D. P., Nichols A. R., Sutin N., Inorg. Chem., 10, 2906 (1971)

71 K   Koshimura H., Okubo T., Anal. Chim. Acta, 55, 163 (1971)

71 R   Rao B., Mathur H. B., J. Inorg. Nucl. Chem., 33, 2919 (1971)

71 S   Sekine T., Ihara N., Bull. Chem. Soc. Japan, 44, 2942 (1971)

71 Sa   Sillén L. G., Martell A. E., Stability Constants of Metal-Ion
        Complexes, The Chemical Society, London 1971

72 G   Gross J., Keller C., J. Inorg. Nucl. Chem., 34, 725 (1972)

72 K   Kuznetsov A. F., Sevastyanov A. I., Rudenko N. P., Khimiya
        Protsessov Ekstraktsii (Eds. Zolotov Yu. A., Spivakov B. Ya.,
        254 Nauka, Moscow 1972

72 L   Liljenzin J. O., Vadashi K., Rydberg J., Trans. Royal Inst.
        Technol., No. 280, 408 Stockholm 1972

73 K   Koshimura H., Okubo T., Anal. Chim. Acta, _67_, 331 (1973)

73 S   Sekine T., Hasegawa Y., Ihara N., J. Inorg. Nucl. Chem.,
        _35_, 3968 (1973)

74 K   Korenman I. M., Gryaznova M. I., Zh. Anal. Khim., _29_, 964 (1974)

74 L   Lundquist R., Acta Chem. Scand., A 28, 243 (1974)

74 La   Lundquist R., Rydberg J., Acta Chem. Scand., A 28, 399 (1974)

74 S   Sekine T., Murai R., Niitsu M., Ihara N., J. Inorg. Nucl. Chem.,
        _36_, 2569 (1974)

75 A   Allard B., The Coordination of Tetravalent Actinide Chelate Complexes
        with Beta-Diketones, Chalmers University of Technology,
        Göteborg 1975

75 V   Van der Linden W. E., Beers C., Talanta, _22_, 89 (1975)

76 F   Fomin V. V., Averbach L. I., Leman G. A., Konovalova S. A.,
        Zh. Neorg. Khim., 21, 1008 (1976)

76 K   Koshimura H., J. Inorg. Nucl. Chem., _38_, 1705 (1976)

76 S   Studnicková M., Smola J., Pololáník L., Coll. Czechos. Chem.
        Comm., _41_, 1312 (1976)

77 A   Allard B., J. Inorg. Nucl. Chem., _39_, 694 (1977)

77 B   Bottari E., Montali R., Monatsh. Chem., _108_, 1033 (1977)

77 K   Koshimura H., J. Inorg. Nucl. Chem., _39_, 148 (1977)

77 S   Sekine T., Iwahori S., Murai R., J. Inorg. Nucl. Chem.,
        _39_, 363 (1977)

77 Sa   Sekine T., Iwahori S., Johnsson S., Murai R., J. Inorg. Nucl. Chem.,
        _39_, 1092 (1977)

77 Sb   Sekine T., Murai R., Takahashi K., Iwahori S., Bull. Chem. Soc.
        Japan, _50_, 3415 (1977)

77 Sc   Sarin R., Munshi K. N., J. Indian Chem. Soc., _54_, 659 (1977)

78 P   Prik G. A., Kozer B. E., Metal Beta-Diketonates, 47, Nauka,
        Moscow 1978

78 S   Starý J., Freiser H., Equilibrium Constant of Liquid-Liquid
        Distribution Reactions, Part IV. Chelating Extractants,
        Pergamon Press, Oxford 1978

79 S   Starý J., Kratzer K., Stability Constants of Metal Beta-
        Diketonates, Czech Technical University, Prague 1979