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Studies of the Hydration of Metal Acetylacetonates[1]

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The distribution constants of metal acetylacetonates and other β-diketonates between water and n-C_7H_{16}, C_6H_6, CCl_4, and $CHCl_3$ were determined as a function of temperature. The thermodynamic functions associated with this process were obtained and interpreted in terms of the hydration of the complexes in water. The order of decreasing hydration of the trivalent acetylacetonates is Al > Co > Cr > Rh. The results with $CHCl_3$ indicate much stronger interaction between this solvent and the complexes than was found for the other organic solvents. The lower hydration of cobalt(III) propionylacetonate than chromium(III) 3-methylacetylacetonate supports the idea that hydration takes place through the octahedral faces. Polarographic diffusion coefficients support the lower hydration of $Cr(acac)_3$ than $Co(acac)_3$.

Introduction

An area of considerable interest in inorganic chemistry is that of the hydration of ions. While some success has been achieved in the determination of the number of water molecules in the primary coordination sphere for certain transition metal ions,[2] no evidence has been obtained concerning the hydration of complexes in which the primary coordination sphere is already filled with ligands other than water.

Evidence for secondary coordination involving ligands other than water has been obtained using several different experimental procedures. Werner[3] and Larsson[4] have found that the molecular rotation of optically active $[Co(en)_3]^{3+}$ depends on the anion and Larsson was able to show that $S_2O_3^{2-}$ forms a stronger complex than SO_4^{2-}. Larsson and Tobiason[5] verified the above stability order using anion-exchange studies with $Co(NH_3)_6]^{3+}$ and also obtained the stability order $Br^- > Cl^- > F^-$, with indications that up to four ligands were attached in the second coordination sphere. The opposite stability order for the halides was found by Evans and Nancollas[6] in a spectrophotometric investigation. Earlier spectral evidence was obtained by Linhard[7] and by Yoneda[8] using SCN^-, SO_3^{2-}, CO_3^{2-}, and $S_2O_3^{2-}$ with the complex ammines and ethylenediamines of Co(III) and Cr(III).

Erdman[9] has interpreted kinetic data to mean that $[Cr(en)_3]^{3+}$ is more highly hydrated than $[Co(en)_3]^{3+}$, but as yet there has been no concrete evidence concerning the hydration of complex ions. The present work is directed toward obtaining thermodynamic evidence for the secondary coordination of water to certain metal complexes. The distribution constants (K_D) for the distribution between water and organic solvents have been determined for several metal acetylacetonates and other substituted diketonates.

Experimental

Reagents.—Cobalt(III) acetylacetonate[10] and chromium(III) acetylacetonate[11] were prepared by standard procedures. Aluminum acetylacetonate was prepared by the method of Steinbach[12] in which an aqueous solution of Al(III) of pH ~0.5 saturated with acetylacetone is made basic after extraction with excess acetylacetone to remove iron impurities in the aluminum sulfate starting material. Rhodium(III) acetylacetonate was prepared according to the method of Dwyer and Sargeson[13] using $Rh(NO_3)_3$ prepared by a procedure described by Fay and Piper.[14] [Trivalent metal acetylacetonates will be abbreviated as $M(acac)_3$.]

Propionylacetone (2,4-hexanedione) was prepared by the method of Adams and Hauser[15] and cobalt(III) propionylacetonate $[Co(prac)_3]$ was prepared in a yield of about 25% by a method analogous to that used for the preparation of the acetylacetonate.[11] The melting point was found to be 87° after recrystallization from methanol–water.

Cobalt(III) methylacetylacetonate $[Co(meac)_3]$ was prepared by a method used by Bauer and Drinkard[16] for $Co(acac)_3$. The compound rapidly underwent autoxidation with the evolution of biacetyl[17] and could not be isolated in a pure state. The ligand, 3-methylacetylacetone (3-methyl-2,4-pentanedione), was prepared by the method of Kelso, Greenlee, Derfer, and Boord.[18]

Chromium(III) methylacetylacetonate $[Cr(meac)_3]$ was prepared using a procedure analogous to that used for the preparation of the acetylacetonate.[11] A 57% yield was obtained. After recrystallization from ethanol–water the large needles, which were maroon in sunlight and green-brown in incandescent light, melted at 238°. The compound was analyzed for Cr by decomposition with nitric acid and roasting to Cr_2O_3. *Anal.* Calcd. for $Cr(C_6H_9O_2)_3$: Cr, 13.29. Found: Cr, 13.17.

Doubly distilled water was used throughout. Fisher A.C.S. reagent grade CCl_4 was used without purification since distillation did not affect the values of K_D obtained and gave values of K_D lower than technical grade CCl_4 distilled twice through a 7.5-plate column. Twice distilled benzene (thiophene-free) yielded the same values of K_D as Fisher A.C.S. reagent grade benzene and was used throughout. Fisher Spectranalyzed n-C_7H_{16} was used without further purification. Fisher A.C.S.

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[1] Taken in part from a thesis submitted by P. D. Hopkins to the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, 1963. Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

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[9] W. C. Erdman, Ph.D. Thesis, University of Pittsburgh, 1959, p. 107.

[10] B. E. Bryant and W. C. Fernelius, *Inorg. Syn.*, **5**, 188 (1957).

[11] W. C. Fernelius and J. E. Blanch, *ibid.*, **5**, 130 (1957).

[12] J. F. Steinbach, Ph.D. Thesis, University of Pittsburgh, 1953, p. 14.

[13] F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953).

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[17] E. M. Arnett, H. Freiser, and M. A. Mendelsohn, *ibid.*, **84**, 2482 (1962).

[18] R. G. Kelso, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **77**, 1751 (1955).

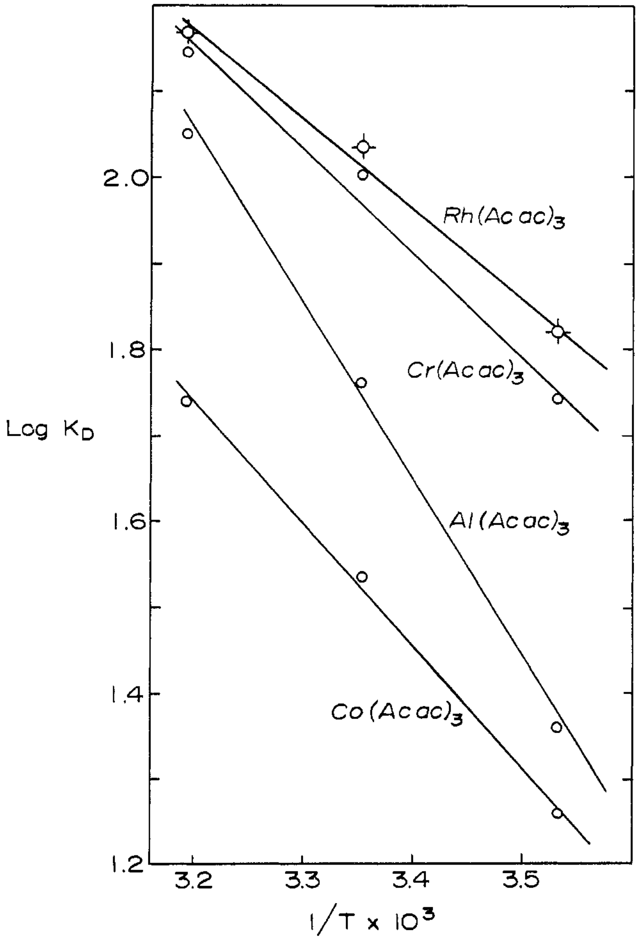

Fig. 1.—Plot of K_D *vs.* $1/T$ for the distribution of metal acetylacetonates between water and CCl_4.

reagent grade $CHCl_3$ was used as is when removal of the ethanol stabilizer both by the sulfuric acid[19] and alumina chromatography[20] methods gave the same values of K_D as the original solvent.

Procedure.—The distribution equilibrium was attained by adding a measured volume of doubly distilled water to a measured volume of a solution of the complex in the organic solvent made up by dissolving an accurately weighed sample of the complex. The two phases were then equilibrated by means of a Vibro-mixer which effected intimate mixing of the phases. A water bath thermostated to within ±0.05° was used in all experiments. Analysis revealed that equilibrium was reached in less than 30 min., but the time of mixing was usually 1 hr. to ensure that equilibrium was reached. The aqueous phase was analyzed spectrophotometrically, either in the visible or ultraviolet region depending upon the concentration. The concentration of the nonaqueous phase was calculated from the original concentration and the aqueous phase analysis. In cases where the concentration of the nonaqueous phase was determined independently by evaporation and weighing, excellent mass balances were obtained. The molar absorptivities in water are given in Table I.

Because of the very low solubility of $Co(acac)_3$ in *n*-heptane the above procedure was modified in this case. A nearly saturated solution of $Co(acac)_3$ in water was made and after equilibration the concentrations of the two phases were calculated from the initial and final absorbances of the aqueous phase.

It was necessary to adopt a different procedure for obtaining the distribution constants for $Al(acac)_3$ between H_2O and CCl_4 because of the lability of $Al(acac)_3$ in contrast to the inertness of the other compounds studied. The dissociation and resultant hydrolysis of the Al^{3+} and $acac^-$ ions and the extraction of the molecular Hacac into the CCl_4 not only made analysis difficult but also yielded an aqueous phase with considerable ionic strength and a changed CCl_4 layer, both of which were found in the case of $Co(acac)_2$ to shift the equilibrium toward the CCl_4 phase. After determining the minimum time to reach equilibrium [using $Co(acac)_3$ in H_2O and CCl_4] by hand shaking a flask containing the system (~5 sec. at 40°, ~10 sec. at 25°, and ~15 sec. at 10°), the system $Al(acac)_3$–H_2O–CCl_4 was shaken several times for these minimum time intervals and the total Al in the H_2O phase was measured as a function of time, using a standard procedure.[21] The $Al(acac)_3$ concentration was then determined by extrapolation, a procedure possible because the rate of equilibration was found to be much faster (at least 8 times) than the rate of decomposition.

Table I

Optical Absorption Data

Compound	λ_{max}, mμ	ϵ_{max}
$Co(acac)_3$	590	132
$Co(acac)_3$	255	32,400
$Cr(acac)_3$	256	11,740
$Rh(acac)_3$	316	11,000
$Co(prac)_3$	257	33,000
$Cr(meac)_3$	350	13,700
$Cr(meac)_3$	271	11,200

In most cases K_D was determined at 10.0, 25.0, and 40.0°. The thermodynamic quantities $\Delta F°$, $\Delta H°$, and $\Delta S°$ for the standard state of 1 *M* at 25° were calculated by the usual procedure. The slopes of the lines of log K_D *vs.* $1/T$ were determined using the least squares method.

Diffusion Coefficients.—Polarographic studies were conducted using a Sargent Model XV recording polarograph, standard H-cell, Sargent S-30490 saturated calomel electrode (s.c.e.), and a dropping mercury electrode (d.m.e.). The supporting electrolyte was 10^{-2} *M* $(C_2H_5)_4NBr$ and ~0.005% Triton X-100 was used as a maximum suppressor.

Solubilities.—Solubilities in H_2O were determined using the same apparatus as in the distribution studies. Solubilities in CCl_4 were determined by cooling a hot saturated solution of the chelate to the desired temperature in a 10 × 250 mm. test tube, withdrawing a given volume in a pipet fitted with a Pyrex glass wool plug, evaporating the solvent in a wide mouth weighing bottle, and weighing the residue.

Results and Discussion

For the distribution of a metal complex between two immiscible liquid phases (an organic liquid and water) the distribution constant (K_D) may be defined as

$$K_D = [\text{complex}]_{\text{org}}/[\text{complex}]_{\text{aq}}$$

where the concentrations are the thermodynamic concentrations or activities. The distribution constant for $Co(acac)_3$ between H_2O and CCl_4 was studied as a function of concentration at 25°. The value of K_D was found to be independent of concentration over the range 0.3–28 mg. of complex/ml. of CCl_4.

In order to be certain that distribution constants were not determined in a region where solubility limits were approached, solubilities of $Co(acac)_3$ and $Cr(acac)_3$ were determined and are tabulated in Table II.

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[19] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1957, p. 176.

[20] K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Co., New York, N. Y., 1960, p. 250.

[21] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. IIa, D. Van Nostrand and Co., Princeton, N. J., 1959, p. 181.

TABLE II

SOLUBILITIES OF Co(III) AND Cr(III) ACETYLACETONATES

Compound	T, °C.	H_2O, g./l.	CCl_4, g./100 ml.
$Co(acac)_3$	10	2.0	3.8
$Co(acac)_3$	25	1.3	4.4
$Co(acac)_3$	40	1.1	5.8
$Cr(acac)_3$	25	0.9	9.3

The distribution constants for $Co(acac)_3$ between H_2O and CCl_4 were found to increase from 34.2 for H_2O to 37.3 for 0.1 M KNO_3 to 72.0 for 1.0 M KNO_3 as expected for a salt effect. The effects of acetic acid–sodium acetate and ammonia–ammonium nitrate buffers were no greater than expected for their ionic strengths. It can be concluded that K_D is independent of any pH effects and ionization of the 3-hydrogen of the acetylacetonate ring does not occur.

TABLE III

DISTRIBUTION CONSTANTS (K_D = $[\text{complex}]_{\text{org}}/[\text{complex}]_{\text{aq}}$) AND THERMODYNAMIC FUNCTIONS FOR THE REACTION $(\text{complex})_{\text{org}} \rightarrow (\text{complex})_{\text{aq}}$

		$K_D{}^a$			T = 25.0°		
Complex	Organic solvent	10.0°	25.0°	40.0°	$\Delta H°$, kcal.	$\Delta F°$, kcal.	$\Delta S°$, e.u.
$Al(acac)_3$	CCl_4	23	57	112	−9.3	2.4	−39
$Co(acac)_3$	CCl_4	18.1	34.2	54.7	−6.5	2.09	−29
$Cr(acac)_3$	CCl_4	55.1	99.8	140.2	−5.5	2.72	−28
$Rh(acac)_3$	CCl_4	66.1	108.0	146.7	−4.7	2.76	−25
$Co(acac)_3$	C_6H_6	57.7	109.2	166.6	−6.3	2.77	−30
$Co(acac)_3$	n-C_7H_{16}	(0.028)	0.092	0.232	−9.6	−1.5	−27
$Co(acac)_3$	$CHCl_3$	4860	4390	(1240)	$+1^b$	~5	. . .
$Co(prac)_3$	CCl_4	. . .	(1490)	(1960)	. . .	4.3	. . .
$Cr(meac)_3$	CCl_4	. . .	812	. . .	. . .	4.0	. . .

[a] Values enclosed in parentheses are of doubtful accuracy (see text), all others are good to within ±2%. [b] Calculated from 10 and 25° data only.

The distribution constants for the systems studied and the thermodynamic properties which were determined from them are given in Table III. The value of K_D for $Co(acac)_3$ in $CHCl_3$–H_2O at 40° is in doubt because of a lack of precision, possibly because of some reaction of $Co(acac)_3$ with $CHCl_3$ at the higher temperature. The value of K_D for $Co(acac)_3$ in n-C_7H_{16}–H_2O at 10° may be in error because of the small differences in the initial and final absorbances of the aqueous layer, although the approach to a straight line for the three points in the log K_D $vs.$ $1/T$ relation is good. The reason for the lack of precision in determining K_D for the system $Co(prac)_3$–CCl_4–H_2O cannot be definitely located. However, small amounts of impurities could cause a large percentage shift in K_D since the value of K_D is large and the concentrations in the aqueous phases were very small ($ca.$ 5×10^{-5} M).

The $\Delta H°$ for the distribution of $Co(acac)_3$ is nearly the same for C_6H_6 or CCl_4 as the organic solvent, and is similar but somewhat more negative for n-C_7H_{16}. The change in sign of $\Delta H°$ when $CHCl_3$ is the organic solvent indicates a much stronger complex–solvent interaction than with the other organic solvents. This is not surprising since the $CHCl_3$ molecule has a permanent dipole moment and the ability to hydrogen bond. Hydrogen bonding between $Co(acac)_3$ and $CHCl_3$ would be expected to involve the carbonyl oxygens of the ligands. However, Jones, *et al.*,[22] found solutions of $Cr(acac)_3$ in $CHCl_3$ and several other organic solvents to be regular, indicating no specific interactions between solute and solvent. The $\Delta H°$ and $\Delta S°$ for the dissolution of $Cr(acac)_3(s)$ in $CHCl_3$ are appreciably higher than for C_6H_6 or CCl_4, but the values for $C_6H_5CH_3$ are much higher than those for $CHCl_3$. These observations suggest that hydrogen bonding between $M(acac)_3$ and $CHCl_3$ is of little importance. A reasonable interpretation of the large negative entropy changes in going from the organic solvents to water would be that they are the result of extensive "structure-making"[23] in the aqueous layer.

The curvatures in the log K_D $vs.$ $1/T$ lines (Fig. 1) are very slight so that the value of $\Delta H°$ found (by least-squares method) should be reasonably accurate (within $ca.$ 5%). Even if the curvature is real, the least-squares line should be a good approximation to the tangent at the midpoint of the arc.

The enthalpy change in going from CCl_4 to H_2O varies when the central metal ion in the acetylacetonate complex is changed, although the ionic radii of the M^{3+} ions are similar (0.57 to 0.69 Å.), and the sizes of the molecules (diameter about 12 Å.) should be nearly identical. All four metals have electronic configurations for which regular octahedral complexes are expected. Under these conditions the molecules should behave almost identically in the various organic solvents. In the absence of specific interactions with the organic solvents, any differences in the thermodynamics of the distributions would reflect differences in the aqueous phase. With this assumption, the order of hydration of the acetylacetonates is Al > Co > Cr > Rh.

Because most of the exterior of an octahedral metal acetylacetonate complex is hydrocarbon in nature, one might expect solvent molecules to approach through the relatively open octahedral faces. These are the regions of approach to the positive metal ions but they are also the regions of maximum density of the nonbonding (t_{2g}) d-orbitals. Since Al has no d-electrons,

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[22] M. M. Jones, A. T. Davila, J. E. Hix, Jr., and R. V. Dilts, *J. Inorg. Nucl. Chem.*, **25**, 369 (1963).

[23] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

it is not surprising that Al(acac)$_3$ is most highly hydrated. Also as expected Rh(acac)$_3$ with the greatest number of electrons is least hydrated. The ionic radii of Co^{3+} and Cr^{3+} are the same (0.65 Å.), so that the complexes differ only in atomic number and the number of d-electrons. Since Co(acac)$_3$ (d^6) has twice as many outer shell electrons as Cr(acac)$_3$ (d^3) in the octahedral faces, it might be expected that Co(acac)$_3$ would be hydrated to a lesser extent than Cr(acac)$_3$. However, the $\Delta H°$ values indicate that the opposite order of hydration is true. That Co(acac)$_3$ should be hydrated more than Cr(acac)$_3$ can be explained by reference to the molar electron polarizations ($_{E}P$) of metal acetylacetonates.[24] Although Fe(acac)$_3$ contains thirteen more electrons than Al(acac)$_3$, the molar electron polarizations are nearly identical (91.5 and 91.1 cm.^{3}, respectively). The 3d^5-electrons of Fe(acac)$_3$ have spherical symmetry and are not concentrated in the octahedral faces. The added polarization of Co(acac)$_3$ (99.4 cm.^{3}) or Cr(acac)$_3$ (95.3 cm.^{3}) might be attributed to the nonspherically symmetric d-electrons. As a water molecule approaches an octahedral face of the complex, these d-electrons are displaced, reducing the screening of the cation. Since the molar electron polarization of Co(acac)$_3$ is greater than that for Cr(acac)$_3$ and the nuclear charge of Co is higher, the Co(acac)$_3$ becomes more highly hydrated than Cr(acac)$_3$.

The data for the distributions of Co(prac)$_3$ and Cr(meac)$_3$ support the assumption that hydration occurs through the octahedral faces. Addition of a methyl group to the 3-carbon of the acetylacetonate ion [as in Cr(meac)$_3$] causes a shift in the free energy, $\Delta F°$, of 1.3 kcal./mole toward the CCl$_4$ layer, while addition of the methyl group to the end of the chain [Co(prac)$_3$] causes a shift of 2.2 kcal./mole. The addition of the methyl group to the end of the acetylacetonate ion increases the shielding of the octahedral face so that hydration is less favorable. Addition to the 3-carbon would not affect hydration since this methyl group would not shield the central ion at all; it points directly away from the central ion.

The diffusion coefficients, which were calculated from the Ilkovic equation using polarographic data, were found to be 6.2×10^{-6} cm.^{2} sec.$^{-1}$ for Co(acac)$_3$ and 7.0×10^{-6} cm.^{2} sec.$^{-1}$ for Cr(acac)$_3$. The $E_{1/2}$ values (-0.1 and -1.45 v., respectively) are only approximate because of irreversibility. The value of n (number of electrons involved in the reduction) was determined by noting that there was a second wave for Co(acac)$_3$ at about -1.4 v. which was twice as high as the first one, indicating one and two electron reductions. These two molecules, which are identical in size, have slightly different values of D, indicating that the effective radii in solution are different. The more highly hydrated Co(acac)$_3$ would be expected to diffuse more slowly.

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[24] A. E. Finn, G. C. Hampson, and L. E. Sutton, *J. Chem. Soc.*, 1254 (1938).

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The Kinetics of Formation of the Nickel Monooxalate Complex in Solution[1]

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The rate of formation of the monooxalate complex of nickel(II) both in neutral and in acid solution has been studied by the use of a flow technique. The results are interpreted in terms of the reactions $Ni^{2+} + A^{2-} \underset{k_{1d}}{\overset{k_{1f}}{\rightleftharpoons}} NiA$ and $Ni^{2+} + HA^- \underset{k_{2d}}{\overset{k_{2f}}{\rightleftharpoons}} NiA + H^+$ where A^{2-} represents the oxalate ion. At 25.0° and ionic strength 0.10 M, $k_{1f} = 7.5 \times 10^4$ M^{-1} sec.$^{-1}$, $k_{2f} = 5 \times 10^3$ M^{-1} sec.$^{-1}$, $k_{1d} = 3.6$ sec.$^{-1}$, and $k_{2d} = 1.5 \times 10^3$ M^{-1} sec.$^{-1}$. Studies at various temperatures between 5 and 35° give $\Delta H_{1f}^* = 14$ kcal. mole^{-1}, $\Delta H_{2f}^* = 14$ kcal. mole^{-1}, $\Delta S_{1f}^* = 12$ cal. deg.$^{-1}$ mole^{-1}, and $\Delta S_{2f}^* = 7$ cal. deg. mole^{-1}. The results are consistent with a model in which the rate-determining step is the elimination of a water molecule from the inner hydration shell of the nickel ion.

The question of complex and ion pair formation in electrolyte solutions has been much discussed. In cases such as the bivalent metal sulfates where the association is only moderately strong, conductance and other data give definite indication of ion pair formation. It has been suggested that the derived association constants are merely artifacts arising from the breakdown of the Debye–Hückel theory.[3] Such arguments, however, disregard the strong kinetic evidence in

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Visiting Scientist from the Chemistry Department, The University, Glasgow, W. 2, Scotland.

[3] E. A. Guggenheim, *Discussions Faraday Soc.*, **24**, 53 (1957).