the range -10.6 to -8.9, which is exhibited by the first transition series, Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}.

A number of the early results have been reviewed by Sweeton and Baes (II.44), and the stability of $FeOH^+$ appears to be best defined by the work of Hedström (II.45), Morozumi and Posey (II.46), Sweeton and Baes (II.44), and Mesmer (II.47). Since oxidation of Fe^{2+} and most protolytic impurities would liberate acid, one would expect that the smaller values reported for Q_{11} reflect studies in which those two factors were minimal. Sweeton and Baes studied the solubility of Fe_3O_4 over wide ranges of solution composition (10^{-4} m HCl to 4×10^{-4} m NaOH) between 50°C and 300°C at 1 atm of hydrogen:

$$1/3\,Fe_3O_4(c) + (2-y)H^+ + 1/3\,H_2(g) \rightleftharpoons Fe(OH)_y^{(2-y)+} + (4/3-y)H_2O \qquad \text{[II.66]}$$
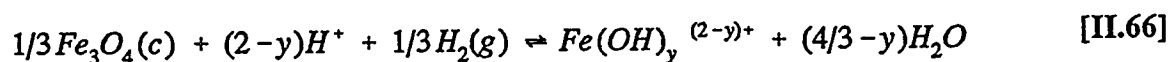
Magnetite is the stable solid phase, and equilibrium constants derived from the solubility behavior expressed in terms of the homogeneous equilibria

$$Fe^{2+} + yH_2O \rightleftharpoons Fe(OH)_y^{(2-y)+} + yH^+ \qquad \text{[II.67]}$$
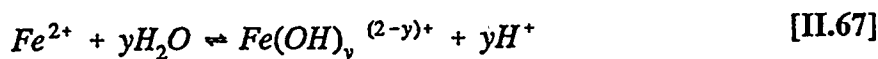
are given in Table II.2. These data give a vale of -9.3 for log K_{11} at 25° with an estimated uncertainty of $\pm$ 0.5 log unit. Hedström (II.45) obtained a value of -9.5 $\pm$ 0.2 in 1 M $NaClO_4$ at 25°C from titration experiments with a glass electrode in a cell similar to that of Forsling et al. (II.48). His experiments were conducted on 0.008 M to 0.050 M Fe(II) solutions, and the maximum hydroxyl number obtained in the more dilute solutions was 0.006. Similar results were obtained by Mesmer (II.47), also using

II.50

Table II.2

Fe^{2+} Hydrolysis Equilibria as a Function of Temperature, 298° - 573°K

From Sweeton and Baes (II.24)

$$Fe^{2+} + yH_2O \rightleftharpoons Fe(OH)_y^{(2-y)+} + yH+$$
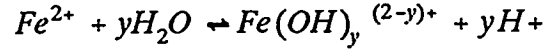
$$Log K_{1y} = \frac{1}{2.303R} \left[\frac{-A}{T} + B(\ln T - 1) + D \right]$$

Species	A (cal/mole)	B ($cal\ mole^{-1}{}^oK^{-1}$)	D ($cal\ mole^{-1}{}^oK^{-1}$)	Log K_{1y}(298°K)
FeOH$^+$	15143	-6.46	38.49	-9.3 $\pm$ 0.5
Fe(OH)$_2$	31491	-9.81	57.64	-20.5 $\pm$ 1.0
Fe(OH)$_3^-$	35921	-9.81	31.84	-29.4 $\pm$ 1.2

Species	ΔH_{1y} ^{a} (kcal/mole)	ΔS_{1y} ^{a} ($cal\ mole^{-1}{}^oK^{-1}$)
FeOH$^+$	13.2 $\pm$ 1.6	1.7 $\pm$ 4
Fe(OH)$_2$(aq)	28.6 $\pm$ 2.9	1.7 $\pm$ 6
Fe(OH)$_3^-$	30.3 $\pm$ 3.6	-14.2 $\pm$ 7

a 298°C

a titration procedure, with a hydrogen electrode for measurement of acidity. This work in dilute FeCl$_2$ solutions gave a value of log Q_{11} of -9.58 $\pm$ 0.08 and a value of -9.49 $\pm$ 0.08 for log K_{11}. This result is in good agreement with that of Morozumi and Posey (II.46), who generated both the Fe^{2+} and the H$^+$ coulometrically (see Table II.3).

II.51

Table II.3

Observed Values of Q_{11} for Fe^{2+} at 25°C

Medium	Log Q_{11}	Source
Very dilute	-9.3	II.44
0.003 M FeCl$_2$	-9.58	II.47
1 M NaClO$_4$	-9.5	II.45
Very dilute	-9.5	II.46

The first hydrolysis constant at 25°C is:

$$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+, \log K_{11} = -9.5 \pm 0.1 \qquad \text{[II.68]}$$
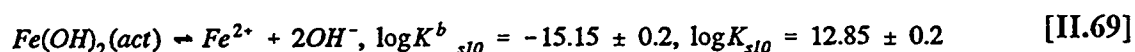
There are no estimates for stabilities of polynuclear species in the ferrous system.

Ehrenfreund and Leibenguth (II.49) reported additional determinations of log Q_{11} in 2 M $(NH_4)_2SO_4$ and in 2 M $NaClO_4$ using a spectrophotometric method in the ultraviolet region. They assigned a strong absorption occurring in the region 240 to 440 nm to the $FeOH^+$ species and measured pH with a glass electrode. The Fe(II) concentration was 5×10^{-5} to 10^{-4} M, and they obtained surprisingly close agreement for log Q_{11} in the two media [-8.1 in 2 M $NaClO_4$ and -8.3 in 2 M $(NH_4)_2SO_4$] in view of the fact that one would expect considerable complexing by NH_3 and SO_4^{2-} in a 2 M $(NH_4)_2SO_4$ solution. These authors pointed out that the presence of ferric ion could lead to strong interference, but precautions were taken to minimize this factor. Baes and Mesmer question these results since lower values for log Q_{11} would be more
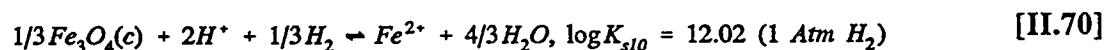
consistent with the data of Table II.3 and the data for the other divalent transition metal ions.

II.G.2. Ferrous Hydroxide.

The solubility of metastable $Fe(OH)_2$ in a relatively active form has been reported along with a review of the other determinations by Leussing and Kolthoff (II.50). The solubility product for $Fe(OH)_2$ is:

$$Fe(OH)_2(act) \rightharpoonup Fe^{2+} + 2OH^-, \log K^b{}_{s10} = -15.15 \pm 0.2, \log K_{s10} = 12.85 \pm 0.2 \qquad [\text{II.69}]$$

This result compared with log K_{s10} (1 atm H_2) for magnetite from Sweeton and Baes (II.44):

$$1/3 Fe_3O_4(c) + 2H^+ + 1/3 H_2 \rightharpoonup Fe^{2+} + 4/3 H_2O, \log K_{s10} = 12.02 \ (1 \ Atm \ H_2) \qquad [\text{II.70}]$$

shows (in agreement with thermodynamic data) that magnetite is the stable phase in the presence of hydrogen.

Gayer and Woontner (II.51) carried out solubility studies in dilute base, where the principal reaction is:

$$Fe(OH)_2(act) + OH^- \rightharpoonup Fe(OH)_3^-, \log K^b{}_{s13} = -5.08 \pm 0.05 \qquad [\text{II.71}]$$

By combining results from $Fe(OH)_2$ solubilities Baes and Mesmer can estimate log K_{13} as -31.9, which is considerably lower than the value of Sweeton and Baes in Table II.2 (-29.4). The solid phases possibly were not identical in the two studies of Leussing and Kolthoff (II.50) and Gayer and Woontner (II.51). Alternatively, the value of Sweeton and Baes (II.44) may be high because of neglect of the $Fe(OH)_4^{2-}$:

II.53

$$Fe(OH)_2(c) + 2OH^- \rightleftharpoons Fe(OH)_4{}^{2-}, \quad \log K^b{}_{s14} = -5.5 \pm 0.1 \qquad [\text{II.72}]$$
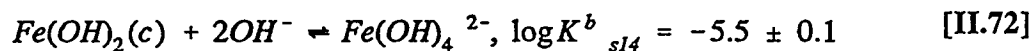
Again, estimation of $\log K_{14}$ (-46) by combination of these data with the solubility

product of Leussing and Kolthoff (II.50) has the uncertainty regarding the solid phase.

II.G.3. Fe^{3+} Hydrolysis in Solution

The hydrolysis of Fe^{3+} was examined by Hedström (II.52) at 25°C in 3 M

$NaClO_4$ using a calomel electrode in combination with glass and Fe^{3+}/Fe^{2+} electrodes.

He observed the formation of a gelatinous precipitate with the addition of sodium

hydroxide, which dissolved slowly. However, by use of sodium hydrogen carbonate

solutions as the titrant, this difficulty was averted, enabling attainment of hydroxyl

numbers as high as 0.5 to 0.7 before precipitation occurred. Biedermann and

Schindler (II.53) subsequently demonstrated that in a portion of these experiments the

solutions were supersaturated with the solid phase, believed to be FeO(OH). This fact

does not, however, affect the conclusions made regarding equilibria in solution.
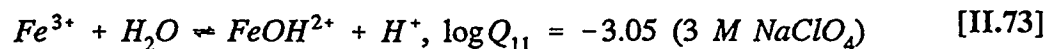
This is one of the rare instances in which the hydrogen ion concentration and

the metal ion concentration were both observed experimentally, enhancing the

reliability of the conclusions. Hedström's data do show greater scatter than is usually

observed in such studies, possibly resulting from precipitation in the experiments. The

results of this study have been widely quoted and have been confirmed at least in part

by several other workers. The species $FeOH^{2+}$, $Fe(OH)_2{}^+$, and $Fe_2(OH)_2{}^{4+}$ were

identified by Hedström, and their formation quotients are given in Table II.4 along with

the results of other primarily spectrophotometric studies in different media. The results

of this extensive work are in good agreement on the value for $\log Q_{11}$, with expected

Table II.4
Hydrolysis Products of Fe^{3+}

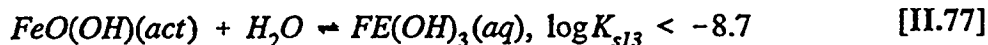| Medium	Temperature (°C)	Log Q_{xy}				Source
		$FeOH^{2+}$	$Fe(OH)_2^+$	$Fe_2(OH)_2^{4+}$	$Fe_3(OH)_4^{5+}$	
0.15 M $NaClO_4$	18.2	-2.73				II.54
0.08 M $NaClO_4$	20.0	-2.68				
0.15 M $NaClO_4$	35.5	-2.32				
0.0117 M $NaClO_4$	18.0	-2.55				II.56
	25.0	-2.37				
	32.0	-2.19				
0.0217 M $NaClO_4$	18.0	-2.60				II.56
	25.0	-2.42				
	32.0	-2.25				
0.0317 M $NaClO_4$	18.0	-2.63				II.56
	25.0	-2.45				
	32.0	-2.28				
1.00 M $NaClO_4$	18.0	-2.96		-2.92		II.56
	25.0	-2.79		-2.72		
	32.0	-2.61		-2.51		
1 M $NaClO_4$[a]	20.0	-2.64	-5.85	-2.65		II.57
0.5 M $NaClO_4$	25.0	-2.72				II.58
0.25 M $NaClO_4$	25.0	-2.66		-2.75		II.59
3.0 M $NaClO_4$	25.0	-3.05	-6.3	-2.91		II.52
3.0 M $NaClO_4$	25.0	-3.05	-6.31	-2.96	-5.77	II.54
0.15 M $NaClO_4$[a]	20.0	-2.73				II.60

a. Corrected for g_{H+}.

variations due to the medium. Biedermann has repeated the measurements of Hedström, giving an additional minor species, $Fe_3(OH)_4^{5+}$, along with those given by Hedström - $FeOH^{2+}$, $Fe(OH)_2^+$, and $Fe_2(OH)_2^{4+}$ (results quoted by Schlyter, II.54):

II.55

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+, \quad \log Q_{11} = -3.05 \quad (3 \; M \; NaClO_4) \qquad \text{[II.73]}$$

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+, \quad \log Q_{12} = -6.31 \quad (3 \; M \; NaClO_4) \qquad \text{[II.74]}$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} \; 2H^+, \quad \log Q_{22} = -2.96 \quad (3 \; M \; NaClO_4) \qquad \text{[II.75]}$$

$$3Fe^{3+} + 4H_2O \rightleftharpoons Fe_3(OH)_4^{5+} + 4H^+, \quad \log Q_{34} = -5.77 \quad (3 \; M \; NaClO_4) \qquad \text{[II.76]}$$
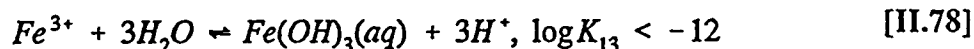
Absorption spectroscopy has been employed very extensively in the study of the hydrolysis behavior of ferric ion. The more important of these studies have indicated essential agreement with the potentiometric results on the hydrolysis mechanism. The spectra of the two species $Fe(H_2O)_6{}^{3+}$ and $Fe(H_2O)_5OH^{2+}$ (Turner and Miles, II.61) along with the spectrum of the dimer (Milburn and Vosburgh, II.62), presumably $Fe_2(H_2O)_8(OH)_2{}^{4+}$. Over a very short span of wavelength are shown in Figure II.31. These absorptions are undoubtedly of the charge-transfer type, based on the region of occurrence and the magnitude of the extinction coefficients. Although there is some disagreement among investigators on the magnitudes of the extinction coefficients, the more recent work is consistent with Figure II.31. [Mulay and Selwood (II.63) mistakenly assigned the absorption at 340 nm exclusively to the dimeric species.] It is apparent that the dimer does have a relatively strong absorption in that region. Olson and Simonson (II.64), Siddall and Vosburgh (II.65), and Milburn and Vosburgh (II.62) have observed an isosbestic point in dilute Fe(III) solutions at about 273 nm due presumably to Fe^{3+} and $FeOH^{2+}$. The disappearance of the isosbestic

point at higher concentration is consistent with the appearance of the third species $Fe_2(OH)_2^{4+}$.

By ultracentrifugation of saturated solutions, Lengweiler et al. (II.66) were able to place a limit on the value of log K_{s13}:

$$FeO(OH)(act) + H_2O \rightleftharpoons FE(OH)_3(aq), \quad \log K_{s13} < -8.7 \qquad [\text{II.77}]$$

from which Baes and Mesmer estimate log K_{13} using K_{s10} for α-FeO(OH):

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3(aq) + 3H^+, \quad \log K_{13} < -12 \qquad [\text{II.78}]$$

Baes and Mesmer estimate log K_{14} from the value of log Q_{s10} by Biedermann and
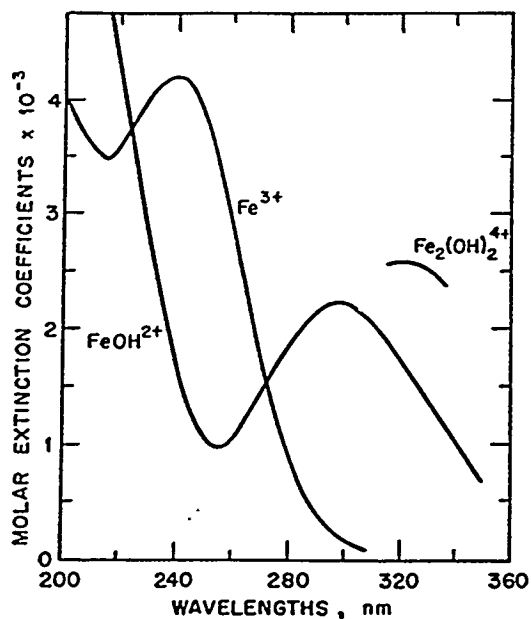

Figure II.31. Absorption spectra of Fe(III) species. From data of Turner and Miles (II.61) and Milburn and Vosburgh (II.62) (from reference II.24).

Schindler (II.54), log $Q^{b'}_{s14}$ of Lengweiler et al. (II.67), log Q'_w, and the ionic strength effect (Table II.5):

II.57

Table II.5

Summary of Fe^{2+} and Fe^{3+} Hydrolysis at 25°C (from reference II.24)

$$Log\,Q_{xy} = log K_{xy} + aI^{1/2}/(1 + I^{1/2}) + bm_x$$

Species or Phase	Log K_{xy}	a	b $m_X = 0.1$	$m_X = 1.0$	$m_X = 3.0$	$\sigma(log\,Q_{xy})$
			Fe^{2+}			
$FeOH^+$	-9.5	-1.022	0.4	0.2	0.1	± 0.1
$Fe(OH)_2$	-20.6	-1.022	0.30	0.05	-0.04	± 1.0
$Fe(OH)_3^-$	-31	0	-0.05	-0.21	-0.26	± 1.5
$Fe(OH)_4^{2-}$	-46	2.044	-0.34	-0.34	-0.34	± 0.3
$Fe(OH)_2(act)$ (log Q_{s10})	12.85	1.022	-0.30	-0.05	-0.04	± 0.2
			Fe^{3+}			
$FeOH^{2+}$	-2.19	-2.044	1.18	0.44	0.18	± 0.02
$Fe(OH)_2^+$	-5.67	-3.066	2.02	0.78	0.25	± 0.1
$Fe(OH)_3$	< -12	-3.066	2.40	0.86	0.34	
$Fe(OH)_4^-$	-21.6	-2.044	2.08	0.67	0.13	± 0.2
$Fe_2(OH)_2^{4+}$	-2.95	0	1.07	0.32	0.06	± 0.05
$Fe_3(OH)_4^{5+}$	-6.3	1.022		(0)		± 0.1
α-FeO(OH) (log Q_{s10})	0.5	3.066	-2.40	-0.86	-0.34	± 0.8
FeO(OH)(am)	2.5					± 0.1

$$Fe^{3+} + 4H_2O \rightleftharpoons Fe(OH)_4^- + 4H^+, \quad log K_{14} = -21.6 \pm 0.2 \qquad [II.79]$$
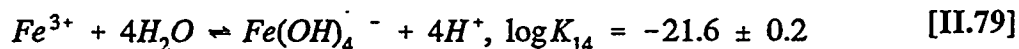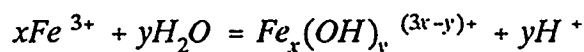
Table II.6 summarizes the thermodynamic data of Milburn (II.56) from

temperature coefficient measurements and of Arnek and Schlyter (II.68) from

calorimetric measurements in $NaClO_4$ media. The main hydrolysis species in the

Table II.6

Enthalpy and Entropy of Fe^{3+} Hydrolysis
Equilibria in $NaClO_4$ Media at 25°C (from reference II.24)

$$xFe^{3+} + yH_2O = Fe_x(OH)_y^{(3x-y)+} + yH^+$$

Ionic strength of medium	Species	ΔH_{xy} (kcal/mole)	ΔS_{xy} $(cal\ mole^{-1}{}^{\circ}K^{-1})$	Source
0	$FeOH^{2+}$	10.4 ± 0.2	25.0 ± 0.7	II.56
0	$Fe_2(OH)_2^{4+}$	13.5 ± 1.0	32 ± 4	II.56
1	$FeOH^{2+}$	10.2 ± 0.3	21 ± 1	II.56
1	$Fe_2(OH)_2^{4+}$	12.2 ± 1.2	28 ± 5	II.56
3	$FeOH^{2+}$	11.0 ± 1.8	23 ± 6	II.68
3	$Fe_2(OH)_2^{4+}$	10.0 ± 0.4	20 ± 1.3	II.68
3	$Fe_3(OH)_4^{5+}$	14.3 ± 2.1	22 ± 7	II.68

range of solution composition examined by Arnek and Schlyter is the dinuclear

species, $Fe_2(OH)_2^{4+}$. The species $FeOH^{2+}$, $Fe(OH)^{2+}$, and $Fe_3(OH)_4^{5+}$ represent only

a small fraction of the total ferric iron; the species $Fe(OH)_2$ was in fact neglected in the

interpretation of the calorimetric data.

II.G.4.   Magnetic Moments and Kinetics

Mulay and Selwood (II.63) reported interesting but somewhat controversial

evidence for diamagnetism of the dimer $Fe_2(OH)_2^{4+}$ in contrast to the strong

paramagnetism arising from the five unpaired electrons of Fe^{3+}. Schugar et al. (II.69)

have reinterpreted the magnetic susceptibility data in terms of a paramagnetic species

II.59

with three unpaired electrons per iron atom. The analogous complex $(FeHEDTA)_2O^{2-}$ (HEDTA is the trivalent anion of N-hydroxyethylethylenediaminetriacetic acid) has only two unpaired electrons and is considered to have an Fe-O-Fe bridge. The authors suggest that the higher magnetic moment of the aquohydroxy dimer may indicate a dihydroxy bridge.

Wendt (II.70) studied the kinetics of the hydroxo-iron(III) monomer-dimer equilibrium using pressure-jump relaxation techniques. Several years later the work was repeated using a stopped-flow apparatus while following the concentration of dimeric species spectrophotometrically. Conocchioli et al. (II.71) and also Sommer and Margerum (II.72) in similar work obtained values for the rate constants for the disappearance of the dimer in the following reaction:

$$Fe_2(OH)_2{}^{4+} \rightleftharpoons 2FeOH^{2+} \qquad \text{[II.80]}$$

All of these investigations agree on the rate law for the disappearance of $Fe_2(OH)_2{}^{4+}$:

$$\frac{-d[Fe_2(OH)_2{}^{4+}]}{dt} = (k_1 + k_2[H^+])[Fe_2(OH)_2{}^{4+}] \qquad \text{[II.81]}$$

with the rate constants tabulated in Table II.7.

II.G.5. Ferric Hydroxides

The equilibrium solid phases formed from ferric solutions are fairly well established. Some information is available on the solubilities of several of the phases in different media. The solid phases which have been reported are α-, β-, and γ-FeO(OH), α-Fe$_2$O$_3$ [the most stable form for Fe(III)], and the active and inactive forms of amorphous Fe(OH)$_3$ with unknown hydroxide and oxide content.

Table II.7

Rate Constants for the Decomposition of
$Fe_2(OH)_2^{4+}$ in 3 M $NaClO_4$ at Various Temperatures (from reference II.24)

$$-d[Fe_2(OH)_2{}^{4+}]/dt = (k_1 + k_2[H^+])[Fe_2(OH)_2{}^{4+}]$$

Temperature (°C)	k_1 (sec^{-1})	k_2 (M^{-1} sec^{-1})	Source
14.3	0.1 ± 0.1	2.4 ± 0.1	II.72
15.0	0.15 ± 0.05	1.75 ± 0.2	II.73
25.0	0.4 ± 0.2	3.1 ± 0.1	II.72
25.0	0.4 ± 0.1	3.1 ± 0.2	II.73
25.0	0.35	3.5	II.71
32.0	1.0 ± 0.1	4.6 ± 0.3	II.73
34.8	1.0 ± 0.5	5.4 ± 0.3	II.72

The β form of FeO(OH) precipitates from chloride media, and this highly active substance often contains interstitial anions such as Cl$^-$ or F$^-$ (Dasgupta and Mackay, (II.74); Biedermann and Chow (II.75)). Nitrate and sulfate solutions, however, give α-FeO(OH) on heating in alkaline solutions or $FeSO_4$ solutions (Van Oosterhout, (II.76)). Feitknecht and Michaelis (II.77) have shown that upon addition of base to ferric perchlorate solutions, α-FeO(OH) and amorphous $Fe(OH)_3$ are produced. The amorphous $(Fe(OH)_3$ slowly transforms to α-FeO(OH) and α-Fe_2O_3. In their experiments, no stable state was reached even after several years, but if a small amount of ferrous ions is present, complete crystallization of the amorphous hydroxide to α-FeO(OH) takes place. Some of the other conditions affecting the rate of crystallization of α-FeO(OH) were also examined by Schwertmann and Fischer (II.78).

The solubility product of "β-FeO(OH)" containing chloride ions was examined by Biedermann and Chow in 0.5 M NaCl at 25°. The emf data obtained under a steady-state condition after more than two months were explained in terms of the equilibrium:

$$Fe(OH)_{2.7}Cl_{0.3}(c) + 2.7H^+ \rightleftharpoons Fe^{3+} + 2.7H_2O + 0.3CL^-, \log Q = 3.04 \pm 0.05 \qquad \text{[II.82]}$$
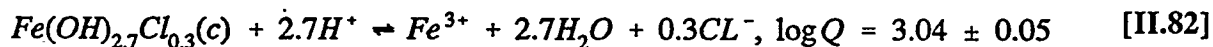
The quantity $[Fe^{3+}]$ in the equilibrium expression was taken as the total Fe(III) present, although in the NaCl medium, Fe^{3+} is complexed by chloride. The solid phase gave the same X-ray pattern as reported by several others for β-FeO(OH).

Schindler et al. (II.79) have reported data on aged amorphous FeO(OH) and α-FeO(OH), both aged for several years:

$$FeO(OH)(am) + 3H^+ + H_2O \rightleftharpoons Fe^{3+} + 3H_2O, \log Q_{s10} = 3.55 \pm 0.1 \ (3 \ M \ NaClO_4) \qquad \text{[II.83]}$$

$$FeO(OH)(\alpha) + 3H^+ + H_2O \rightleftharpoons Fe^{3+} + 3H_2O, \log Q_{s10} = 1.4 \pm 0.8 \ (3 \ M \ NaClO_4) \qquad \text{[II.84]}$$

Also, Biedermann and Schindler (II.53) have studied the steady state reached after 200 hr with amorphous ferric hydroxide [believed to be FeO(OH)] in 3 M $NaClO_4$ at 25°. Their value for log Q_{s10} is 3.96 $\pm$ 0.10. They have also reviewed the earlier work by other authors.

However, the free energy data of the NBS compilation indicate that Fe_2O_3 is the most stable phase in this system, with log K_{s10} of -1.88.

II.G.6.   Summary of Chemistry of Iron

Ferrous ion hydrolyzes to produce the array of mononuclear species $FeOH^+$ to $Fe(OH)_4^{2-}$ between pH 7 and 14, but their stabilities are known with less precision than is generally possible. Magnetite is the stable solid phase in equilibrium with the

ferrous ion. Polynuclear species of ferrous ion which may exist at high concentrations

of Fe(II) have not been reported. The distribution of species and the solubility of

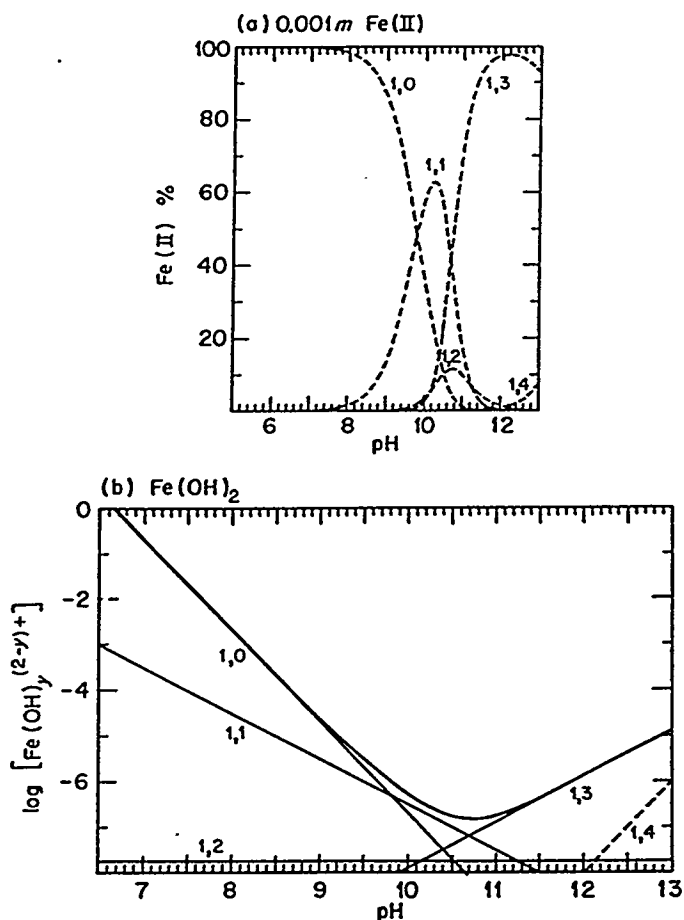$Fe(OH)_2$ are shown in Figure II.32. Ferric ion hydrolyzes much more readily than

Figure II.32. Distribution of hydrolysis products (x,y) at I = 1m and 25° in (a) 10^{-3} Fe(II) and (b) solutions saturated with $Fe(OH)_2$. The dashed curves in a denote regions supersaturated with respect to $Fe(OH)_2$; the heavy curve in b is the total concentration of Fe(II) (reference II.24).

ferrous ion, beginning at about pH 1. A dinuclear species, $Fe_2(OH)_2^{4+}$, and two

mononuclear species, $FeOH^{2+}$ and $Fe(OH)_2^+$, are formed in acidic solutions, while

$Fe(OH)_3(aq)$ and $Fe(OH)_4^-$ appear in neutral and basic media. There is evidence for

the formation of a small amount of $Fe_3(OH)_4^{5+}$ before precipitation occurs. The stable

form of precipitated ferric hydroxide is α-FeO(OH), but attainment of equilibrium and interconversion of various other phases are very slow in this system, requiring several years at 25°C. The distribution of Fe(III) species and the solubility of α-FeO(OH) are shown in Figure II.33.
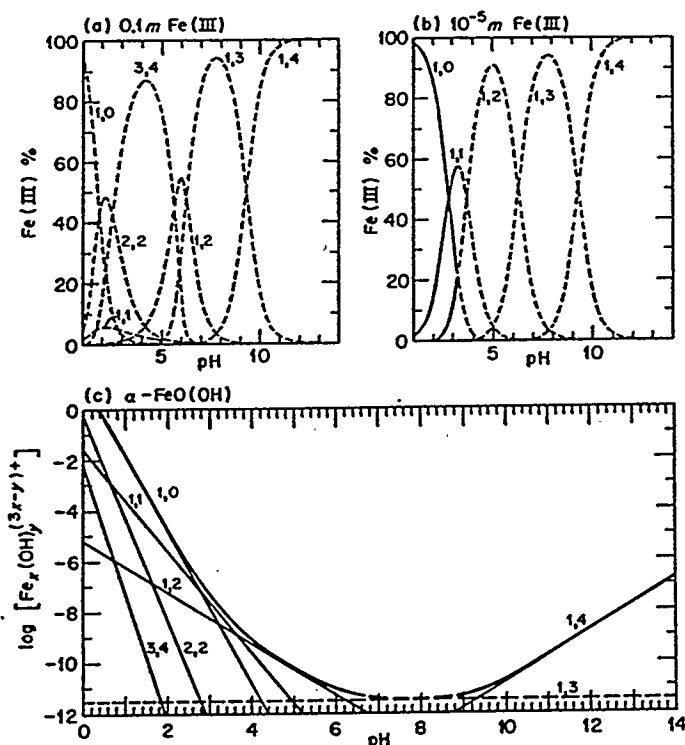

Figure II.33. **Distribution of hydrolysis products (x,y) at I = 1m and 25° in (a) 0.1m Fe(III), (b) 10^{-5}m Fe(III), and (c) solutions saturated with α-FeO(OH). The dashed curves in a and b denote regions supersaturated with respect to α-FeO(OH); the heavy curve in c is the total concentration of Fe(III) (reference II.24).**

As stated above, the aqueous chemistry of iron(III) is complicated (II.80, II.81, II.82). Weiser (II.83) summarized the older literature and states that, owing to the extremely low solubility of hydrated iron oxide, the nucleation proceeds much more rapidly than the growth. As a result a large number of very small particles are generated flocculating to a gelatinous precipitate when alkali is added to a iron(III)

solution. The precipitate does not display an X-ray pattern nor one or more well defined hydrates. At 350 to 550°C, depending on the heating rate and the preparation conditions, the precipitate exhibits a glow phenomenon, which has been demonstrated to be due to sintering. The glow phenomenon hence is brought about by the lattice energy rapidly set free during the sintering of the extremely small iron oxide particles. The onset of the sintering may be ascribed to the loss of water covering the iron oxide particles and thus stabilizing the small particles. However, small water-free hematite particles display also the glow phenomenon, which indicates that it is not necessarily related to the loss of water. As iron oxide and chromium oxide are exhibiting the glow phenomenon in contrast to finely divided (hydrated) alumina, the onset of rapid sintering may be related to the oxides becoming non-stoichiometric. As a result mobile vacancies are created that lead to rapid sintering and thus to the rapid evolution of the heat of crystallization.

Van der Giessen (II.84) studied the chemical and physical properties of iron(III) oxide hydrate; he noted two divergent views of precipitation. One group of authors holds the opinion that with increasing pH levels, Fe(III) ions form charged species $Fe(OH)_n^{n+}$ and these charged species gradually polymerize with the addition of alkali (II.85, II.86). Other authors feel that addition of hdyroxyl ions immediately leads to the formation of a small hydrated iron oxide particles of a larger molecular weight (II.87, II.88). According to the later authors, the added hydroxyl ions are not distributed evenly over the Fe(III) ions, but are concentrated in a limited number of hydrated oxide particles. Van der Giessen experimentally investigated the effect of addition of

II.65

alkali to iron(III) solutions at 25°C. The added hydroxyl ions are consumed at a pH level of about 2 without formation of a visible precipitate. The color of the solution becomes darker brown, indicating that a reaction is nevertheless proceeding. At a pH of 2.4 the pH raises more rapidly on addition of alkali and the viscosity of the solution increases. Van der Giessen assumed that EDTA reacts rapidly only with monomeric $Fe(H_2O)_6$ and not with polymeric Fe(III) species. Measuring the consumption of EDTA, he concluded that above a pH level of about 2 monomeric Fe(III) species are no longer present in the solution.

Van der Giessen argued that his results indicated that addition of hydroxyl ions initially leads to formation of a colloidal dispersion of small hydrated iron oxide particle. When the reaction to produce hydrated iron oxide is completed, the pH increases which leads to flocculation of the particles and to an increase of the viscosity. He characterized the hydrated iron oxide particles by magnetic measurements, Mössbauer experiments, X-ray diffraction, infrared spectroscopy and electron microscopy. To obtain an X-ray pattern Mo radiation had to be utilized. The diffraction pattern thus measured does not correspond to any known (hydrated) iron oxide and resembles that of δ-FeOOH. The Mössbauer results indicated all the iron was present in one state, while magnetic measurements and electron-microscopy pointed to particles of a fairly uniform size of 3 nm.

Later Dousma and de Bruyn (II.89-II.91) and Dousma (II.92) studied the precipitation of Fe(III) also at higher temperatures and at much lower concentrations. They, moreover, used special techniques to maintain homogeneous solutions and to

II.66

avoid local elevated concentrations. From the optical density changes during the pH increase of the solutions, these authors concluded that initially hydrolysis of monomers and formation of hydrolysed dimers proceeds. Subsequently there is a rapid reversible growth of small polymers followed by an irreversible reaction to small polymers. Finally a precipitate results. The particles first formed were found to exhibit dimensions of about 4 nm; during the flocculation the particles conglomerate to clusters of 20 to 50 nm.

Van der Woude (II.93) especially studied the crystallization of precipitated hydrated iron(III) oxide. In agreement with the above authors he observed formation of particles of 3 to 5 nm at pH levels above about 2 at temperatures below 55°C. The amorphous particles were extremely stable in a pH range from 4 to 9; reaction to the more stable goethite, α-FeOOH, proceeds very slowly. Above 55°C the precipitate also reacts to hematite, α-Fe$_2$O$_3$, while above 85°C hematite is formed exclusively. The size of the hematite particles is 50 to 60 nm. Rapid addition of alkali leads to smaller particles of 15 nm.

Rapid precipitation from a homogeneous solution generally leads to the crystallization to large particles of α-FeOH or α-Fe$_2$O$_3$. Holding an amorphous hydrated oxide species for a prolonged period at a pH level below 4, where recyrstallization can proceed fairly rapidly results in the formation of large particles of FeOOH (below 55°C) or Fe$_2$O$_3$ (above 85°C). Recrystallization of the amorphous hydrated iron(III) oxide in the pH range of 4 to 9 is slow. When the iron solution is

prepared using Fe(III) chloride it is nearly impossible to prevent the formation of β-FeOOH (II.91).

Precipitation of Fe(III) appears to be rather complicated and difficult to control so that precipitation of Fe(II) may be preferred for the preparation of iron(III) oxide. With Fe(II), however, the preparation of iron(III) and prevention of uncontrolled oxidation of the iron(III) have to be envisioned. Dissolution of metallic iron into hydrochloric acid using an excess of the metal leads to an Fe(II) solution. To prevent oxidation of Fe(II) to Fe(III), this can be done by keeping the suspension at about 95°C under nitrogen and subsequently cooling.

Since in the pH range 2 to 6 the solubility of Fe(III) is much lower than that of Fe(II), oxidation of Fe(II) in this pH range can be used to effect precipitation. Better results are obtained when the oxidation is carried out by a dissolved oxidizing agent, such as nitrate ions. With a homogeneous oxidation Fe_3O_4 results, the Fe(III) ions react with Fe(II) to produce magnetite of a low solubility. Since hydrolysis of the Fe(III) formed by the oxidation causes H^+-ions to be set free, the pH has to be kept constant. The degree of hydration of magnetite is smaller than that of either hydrated amorphous Fe(III) oxide or Fe(II) hydroxide. The small magnetite particles may rapidly oxidize on exposure to atmospheric air and in the presence of water the resulting Fe(III) oxide particles take up the usual large amounts of water. However, when oxygen is excluded during separation from the liquid and during drying of the material, the extent of hydration of the iron species may remain low even after complete oxidation to Fe(III).

REFERENCES - Section II

II.1.   J. Garside, *Chem. & Ind.*, **1983**, 509.

II.2.   R. W. Rousseau, *Chemtech*, **10**, 566 (1980).

II.3.   J. Garside, L. Brecevic, and J. W. Mullin, *J. Crystal Growth*, **57**, 233 (1982).

II.4.   A. T. Bell, *Catal. Rev. - Sci. Eng.*, **23** 203 (1981).

II.5.   P. Juzasek and R. J. Davey, *AIChEJ*, **24**, 460 (1977).

II.6.   L.-M. Tau, H. Dabbagh, S.-Q Bao, and B. H. Davis, *Catal. Lett.*, **7**, 127 (1990).

II.7.   G. Tammann, "Kristallisieren und Schmelzen", J. A. Barth, Leipzig, 1903.

II.8.   W. Ostwald, "Die wissenschaftlichen Grundlagen der analytischen Chemie",

W. Engelmann, Leipzig, 1897.

II.9.   M. Volmer, "Kinetik der Phasenbildung", Th. Steinkopff, Dresden, 1939.

II.10.   A. E. Nielsen, "Kinetics of Precipitation", Pergamon Press, Oxford, 1964.

II.11.   K. H. Lieser, *Angew. Chem. Internat. Edit.*, **8**, 189 (1969).

II.12.   J. W. Gibbs, "Scientific Papers", Yale University Press, New Haven, 1957, pg.
258; W. Thomson, *Proc. Roy. Soc. Edinburgh*, **7**, 63 (1870).

II.13.   M. Volmer and A. Weber, *Z. physik. Chem.*, **Abt. A119**, 277 (1926).

II.14.   R. Becker and W. Döring, *Ann. Physik.*, **24**, 719 (1935).

II.15.   M. Kahlweit, *Z. physik. Chem.*, **N.F. 25**, 1 (1960).

II.16.   W. Kossel, *Nachr. Ges. Wiss. Göttingen, math.-physik. Kl.*, 135 (1927); *Ann.
Physik.*, **21**, 455 (1934); **33**, 651 (1938).

II.17.   I. N. Stranski, *Z. physik. Chem.*, **Abt. A136**, 259 (1928).

II.18.   F. C. Frank, *Discuss. Faraday Soc.*, **5**, 48 (1949).

II.19.   K. Neumann, "Kinetik der Phasenbildung", Th. Steinkopff, Dresden, pg. 209,

1939.

II.20.   R. Marc, *Z. physik. Chem.*, **Abt. A61**, 385 (1908).

II.21.   J. Kolthoff, *Chem. Weekbl.*, **29**, 362 (1931); *Proc. Kon. nederl. Adak. Wetensch.*,

Ser. **40**, 82 (1937).

II.22.   Ph. Gütlich and K. H. Lieser, *Z. physik. Chem.*, **N.F. 26**, 257 (1965).

II.23.   A. Fabrikanos and K. H. Lieser, *Z. physik. Chem.*, **N.F. 51**, 130 (1966).

II.24.   C. F. Baes, Jr. and R. E. Mesmer, "The Hydrolysis of Cations", John Wiley &

Sons, New York, NY, 1976.

II.25.   N. Bjerrum, "Studies over Basiska Kromiforbindeiser", thesis, Copenhagen,

1908.

II.26.   A. Werner, *Ber.*, **40**, 272 (1907).

II.27.   P. Pfeiffer, *Ber.*, **40**, 4036 (1907).

II.28.   L. G. Sillén, *Quart. Rev.*, **13**, 146 (1959).

II.29.   J. D. F. Ramsay, *Chem. Soc. Rev.*, **15**, 335 (1986).

II.30.   W. Stumm and J. J. Morgan, "Aquatic Chemistry", Wiley Interscience, New

York, 1981.

II.31.   R. Zsigmondy and E. Hückel, *Z. Physik. Chem.*, **116**, 291 (1925).

II.32.   V. K. La Mer and M. D. Barnes, *J. Colloid Sci.*, **1**, 71 (1946).

II.33.   D. Sinclair and V. K. La Mer, *Chem. Rev.*, **44**, 245 (1949).

II.34.   V. K. La Mer and R. H. Dinegar, *J. Am. Chem. Soc.*, **72**, 4847 (1950).

II.35.   R. K. Iler, "The Chemistry of Silica", Wiley and Sons, New York, 1979.

II.36. J. D. F. Ramsay, S. R. Daish and C. J. Wright, *Faraday Discuss. Chem. Soc.*, **65**, 65 (1978).

II.37. E. Matijevic, *Chem. Revs.*, **14**, 22 (1981).

II.38. J. H. L. Watson, W.Heller and W. Wejtowicz, *J. Phys. Chem.*, **16**, 997 (1948).

II.39. J. H. L. Watson, R. R. Cardell, Jr. and W. Heller, *J. Phys. Chem.*, **66**, 1757 (1962).

II.40. V. K. LaMer, *Ind. Eng. Chem.*, **44**, 1270 (1952).

II.41   E. Matijevic, *Acc. Chem. Res.*, **14**, 22 (1981).

II.42. R. L. Rowell, J. P. Kratohvil, and M. Kerker, *J. Colloid Interface Sci.*, **27**, 501 (1968).

II.43. F. A. Cotton and G. Wilkinson, *Adv. Inorg. Chem.*, 3rd ed., Interscience Publishers, New York, 1972.

II.44. F. H. Sweeton and C. F. Baes, Jr., *J. Chem. Thermodyn.*, **2**, 479 (1970).

II.45. B. O. A. Hedström, *Ark. Kemi.*, **5**, 457 (1953a).

II.46. T. Morozumi and F. A. Posey, *Denki Kagaku*, **35**, 633 (1967).

II.47. R. E. Mesmer, *Inorg. Chem.*, **10**, 857 (1971).

II.48. W. Forsling, S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

II.49. M. Ehrenfreund and J. L. Leibenguth, *Bull. Soc. Chim. France*, 2492, 2498 (1970).

II.50. D. L. Leussing and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **75**, 2476 (1953).

II.51. K. H. Gayer and L. Woontner, *J. Phys. Chem.*, **60**, 1569 (1956).

II.52. B. O. A. Hedström, *Ark. Kemi.*, **6**, 1 (1953b).

II.53.   G. Biedermann and P. Schindler, *Acta Chem. Scand.*, **11**, 731 (1957).

II.54.   K. Schlyter, *Trans. Roy. Inst. Technol., Stockholm*, **No. 195** (1962).

II.55.   D. H. Richards and K. W. Sykes, *J. Chem. Soc.*, 3626 (1962).

II.56.   R. M. Milburn, *J. Amer. Chem. Soc.*, **79**, 537 (1957).

II.57.   D. D. Perrin, *J. Chem. Soc.*, 1710 (1959).

II.58.   M. S. Tsao, thesis, University of California, Brkeley, 1952.

II.59.   B. Behar and G. Stein, *Isr. J. Chem.*, **7**, 827 (1969).

II.60.   Fordham, A. W., *Aust. J. Chem.*, **22**, 1111 (1969).

II.61.   R. C. Turner and K. E.Miles, *Can. J. Chem.*, **35**, 1002 (1957).

II.62.   R. M. Milburn and W. C. Vosburgh, *J. Amer. Chem. Soc.*, **77**, 1352 (1955).

II.63.   L. N. Mulay and P. W. Selwood, *J. Amer.Chem. Soc.*, **77**, 2693 (1955).

II.64.   A. R. Olson and T. R. Simonson, *J. Chem. PHys.*, **17**, 1322 (1949).

II.65.   T. H. Siddall, III, and W. C. Vosburgh, *J. Amer. Chem. Soc.*, **73**, 4270 (1951).

II.66.   H. Lengweiler, W. Feitknecht and W. Buser, *Helv. Chim. Acta*, **44**, 796 (1961a).

II.67.   H. Lengweiler, W. Buser and W. Feitknecht, *Helv. Chim. Acta*, **44**, 805 (1961b).

II.68.   R. Arnek and K. Schlyter, *Acta Chem. Scand.*, **22**, 1327 (1968a).

II.69.   H. Schugar, C. Walling, R. B. Jones and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3712 (1967).

II.70.   H. Wendt, *Z. Elektrochem.*, **66**, 235 (1962).

II.72

II.71.   T. J. Conocchioli, E. J. Hamilton,Jr., and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965).

II.72.   B. A. Sommer and D. W. Margerum, *Inorg. Chem.*, **9**, 2517 (1970).

II.73.   B. Lutz and H. Wendt, *Ber. Bunsenges Phys. Chem.*, **74**, 372 (1970).

II.74.   D. R. Dasgupta and A. L. Mackay, *J. Phys. Chem. Soc. Japan*, **14**, 932 (1959).

II.75.   G. Biedermann and J. T. Chow, *Acta Chem. Scand.*, **20**, 1376 (1966).

II.76.   G. W. Van Oosterhout, *J. Inorg. Nucl. Chem.*, **29**, 1235 (1967).

II.77.   W. Feitknecht and W. Michaelis, *Helv. Chim. Acta*, **45**, 212 (1962).

II.78.   U. Schwertmann and W. R. Fischer, *Z. Anorg. Allgem. Chem.*, **346**, 137 (1966).

II.79.   P. Schindler, W. Michaelis and W. Feitknecht, *Helv. Chim. Acta*, **46**, 444 (1963).

II.80.   J. W. Geus, *Appl. Catal.*, **25**, 313 (1986).

II.81.   R. N. Sylva, *Rev. Pure Appl. Chem.*, **22**, 115 (1972).

II.82.   R. J. Atkinson, A. M. Posner and J. P. Quirk, *Clays and Clay Min.*, **25**, 49 (1977).

II.83.   H. B. Weiser, "Inorganic Colloid Chemistry", Vol II, Chapter II, p. 27, John Wiley & Sons, New York, NY (1935).

II.84.   A. A. van der Giessen, *Philips Res. Repts.*, **12** (1968).

II.85.   Th. H. Siddall and W. C. Vosburgh, *J. Am. Chem. Soc.*, **73**, 427 (1951).

II.86.   L. N. Mulay and P. W. Selwood, *J. Am. Chem. Soc.*, **76**, 6207 (1954).

II.87.   G. Jander and A. Winkel, *Z. anorg. allgem. Chem.*, **193**, 1 (1930).

II.88.   G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils and P. Saltman, *J. Am. Chem. Soc.*, **88**, 2721 (1966).

II.89.   J. Dousma and P. L. de Bruyn, *J. Colloid Interface Sci.*, **56**, 527 (1976).

II.90.   J. Dousma and P. L. de Bruyn, *J. Colloid Interface Sci.*, **64**, 154 (1978).

II.91.   J. Dousma and P. L. de Bruyn, *J. Colloid Interface Sci.*, **72**, 314 (1979).

II.92.   J. Dousma, "A Colloidal Chemical Study of the Formation of Iron Oxyhydroxide", Thesis, University of Utrecht (1979).

II.93.   J. H. A. van der Woude, "The Formation of Colloidal Iron(III) Oxyhydroxide", Thesis, University of Utrecht (1983).