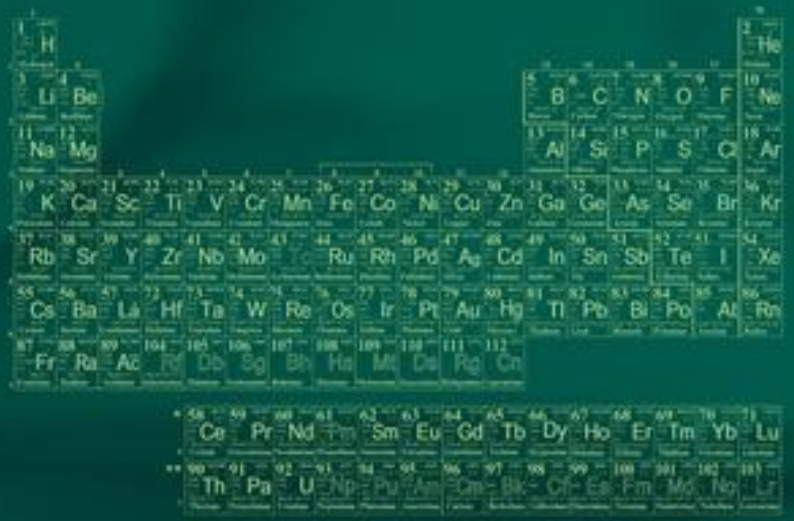
Nataliya Turova

Inorganic Chemistry in Tables



Springer

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ISBN 978-3-642-20486-9 e-ISBN 978-3-642-20487-6
DOI 10.1007/978-3-642-20487-6
Springer Heidelberg Dordrecht London New York

Library of Congress Control Number: 2011932247

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INTRODUCTION

The present review of Inorganic Chemistry course is developed in the form of reference schemes, presenting the information on one or several related elements derivatives and their mutual transformations. The compounds are placed from left to right in an order corresponding to the increase in the formal oxidation number of the element considered (the numbers being noted in the upper part of each page) so that peroxide derivatives usually finish this sequence. For each distinct oxidation state the upper position in the column is occupied by an oxide, its hydrated forms, followed then by basic (and oxo) salts, normal salts of oxoacids (such as halogenates, sulfates, nitrates, phosphates, carbonates, acetates, oxalates etc.). Below are placed binary derivatives (in an order corresponding to the decrease in the second element group number) - halides, sulfides etc. and the most prominent representatives of complex derivatives. Cationic forms are placed on the left side of this column and the anionic - on the right one. Thus a special coordinate system is built where the position of each compound in this scheme is unambiguously determined by the central atom oxidation number (in the horizontal direction) and the nature of ligand (in the vertical one). The search mode for necessary information is then considerably simplified.

The mutual transformations are displayed by arrows. In its proximity the reagents or other factors responsible for the reaction pathway such as catalysts, solvents (their composition is given in brackets), temperature, pressure, irradiation by visual ($h\nu$-Vis) or ultraviolet ($h\nu$-UV) light are noted. Reaction byproducts are given in brackets and supplied with the "-" sign. The reactions proceeding without an oxidation number change are shown by the black arrow, oxidation processes by the red one and reduction processes by the green one.

Only the most important reactions, i.e. those of synthesis or the most characteristic of the given compound are present in the schemes.

The compounds are usually characterized by following data: chemical formula, in some cases the name, appearance, density, melting and boiling points or sublimation temperature, the temperature attributed to the beginning of thermal decomposition, the standard formation enthalpy ($\Delta H=\Delta H^0_{298}$, kJ/mole), air sensitivity, solubility in different solvents (the insoluble compounds are shown as sediments, for example, AgCl↓), acidity and basicity constants, instability constants for the complexes (the precision in the latter case being equal to the order of magnitude). In some special cases are described the magnetic and electric properties and are given the values of effective magnetic moment (μ_{eff}, μB), dielectric constant (ε), dipole moment (μ, D) and is provided a short description of crystalline and molecular structure: the lattice type (for the structural type representatives), unit cell parameters (for pure elements polymorphs only), coordination number and coordination polyhedron of the central atom, interatomic

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_1, © Springer-Verlag Berlin Heidelberg 2011

distances (Å) and bond angles (°) and hybridization types. The composition of the coordination polyhedron is described in the following manner: in the rectangular brackets are given the central atom, terminal and bridging ligands, the index of the latter being given as a fraction, the numerator of which shows the number of such ligands and the denominator - the number of bonds in which they participate. For example, in the $[Cu(H_2O)_2Cl_{4/2}]$ octahedra, present in the structure of $CuCl_2{\cdot}2H_2O$ the water molecules are terminal ligands, while all the four chlorine atoms there are bidentate bridging ones. For the most important groups the vibration frequencies are given in IR (ν, cm^{-1}).

Some distinct schemes show also the formula of the most important ions present in water solutions and their mutual transformations. The half-life periods for isotopes are placed below their symbols. The names of minerals and customary names of chemicals are indicated in parentheses.

At least the reader will find here a table highlighting stereochemistry of inorganic compounds. Its starting point is the idea of the correspondence between the coordination polyhedron and the hybridization state of the central atom, given by the valence bonding approach. In spite of all the restrictions laid upon the applicability of this approach, it seems to be helpful for systematization of the experimental data in inorganic chemistry.

The present "Tables" can be used as a compressed reference book, where the main types of compounds characteristic for an element are presented and demonstrated in a single scheme. The adopted order of presentation permits to visualize the RedOx transitions as well as the reactions proceeding without changes in the oxidation state.

Regarding modern training strategies with their requirement to master huge amount of data such a handbook as the present "Tables" should serve as a useful addition to textbooks and lectures, which helps to arrange the delivered information in a system.

Following textbooks and monographs were used in the "Tables":

F.A.Cotton, G.Wilkinson, C.A.Murilo, M.Bochmann, Advanced Inorganic Chemistry, 6th Ed., John Wiley & Sons, 1999.

N.N.Greenwood, A.Earnshaw, Chemistry of the Elements, Elsevier Ltd, 1984, 1997.

D.F.Shriver, P.W.Atkins, Inorganic Chemistry, W.H.Freeman and Co., N-Y, 1999.

B.V.Nekrasov, The Principles of General Chemistry, "Khimiya", 1973.

H.Remy, Lehrbuch der anorganischen Chemie, 1971.

A.F.Wells, Structural Inorganic Chemistry, Clarendon Press, Oxford, 1986.

Handbuch der Präparativen Anorganischen Chemie/ Herausgegeben von G.Brauer, III Aufl., F. Enke Verlag, Stuttgart, 1981.

I.Kostov, Mineralogy, Oliver and Boyd, Edinburg, London, 1968.

M.Kh.Karapetyants, M.L.Karapetyants, Main Thermodynamic Constants of Inorganic and Organic Substances, "Khimiya", 1968.

R.J.Gillespie, I.Hargittai, The VSEPR Model of Molecular Geometry, Allyn and Bacon, 1991.
Yu.Yu.Lurie, Handbook of Analytical Chemistry, "Khimiya", 1989.

In some cases the data from *Gmelin Handbuch der anorganischen Chemie* as well as from original publications have been used.

The present edition is a revised and completed version of the reference- and schoolbook «Неорганическая химия в таблицах» which is regularly republished in Russia and appeared in Japan in 1981 (by Kodansha Ltd.).
During the last years the material of the "Tables" has been significantly expanded with new data derived from monographs, reviews and original publications. In sum the list of references includes about 6000 items and can be found at the end of the book.

Some changes and improvements have also been entered considering the teaching experience obtained at the universities of Russia and Japan as well as at general education chemistry schools where the "Tables" are applied. Its original references provide an opportunity to overlook the published information on distinct derivatives or classes of compounds.

Acknowledgments.
The author is deeply grateful to her teachers, Professor Dr. A. V. Novoselova and Docent Dr. N. S. Tamm. Due to their constant interest and support the book came to existence and is hopefully worthy of their memory. Assistance and advice were received from specialists in chemistry of certain elements and classes of compounds, the author's colleagues from the Department of Inorganic Chemistry, Faculty of Chemistry, Moscow State University. The author is indebted to the reviewers of the Russian edition - Professor Dr. G. G. Devyatykh, Professor Dr. Yu. A. Buslaev, Professor Dr. M. Kh. Karapetyants and Professor Dr. S. I. Drakin and also to Professor Dr. Kozo Sone, translator and editor of the Japanese edition. The author is also indebted to Dr. I. V. Svitan'ko, Vice-Chairman of the Board of the Higher College of Chemistry of Russian Academy of Sciences, on whose initiative this edition found its way to publication. An especial acknowledgement is made to A. V. Bobkov, N. A. Sviridova, K. V. Mikhailov, G. V. Varvanina and M. Ya. Kats for their efficiency in computer type-setting. Special thanks to D. E. Tcheboukov, E. I. Ivannikova, M. S. Votchal, E. A. Zheligovskaya and Yu. N. Torkhov for their efforts towards arranging the English edition.

Send your comments and offers to the author under the address: M. V. Lomonosov Moscow State University, Chemistry Department. Moscow 119899, Russia. E-mail: *turova.natalie@gmail.com*

ABBREVIATION

abs.	absence
ac.	acid
act.	active
admix.	admixture
alc.	alcohol
alk.	alkali
Am	amine
amorph.	amorphous
an.	anode
anal.	analogous
aq.	aqua
at.	atom
atm.	atmosphere
ax.	axial
b.p.	boiling point
bas.	base, -ic
bipyr.	bipyramidal
bl.	blue
blk.	black
br.	bridging
brn.	brown
bz.	benzene
cat.	catalyst
cath.	cathode
cl. pack.	close packing
CN	coord. number
coef.	coefficient
coll.	colloidal
colrl.	colourlless
comp.	compound
compl.	complex
conc.	concentrate,~tion
conduct.	conductor
cool.	cooling
cr.	crystalline, ~zation
cub.	cubical
cubooct.	cubooctahedron
d.	day
d	density
dec.	decomposition
defic.	deficiency
distil.	distillation
diamagn.	diamagnetic
diff.	different
dil.	diluted
Diox	dioxan
Dipy	2,2'dipyridil
disord.	disorder
diss.	dissociating
dist.	distorted
dodecah.	dodecahedron
EN	electronegativity, $(NH_2CH_2\text{-})_2$
el.	electron
electrol.	electrolysis
equ.	equatorial
ex.	exists
exp.	explosive
ext.	extent
extr.	extraction
ferromagn.	ferromagnetic
form.	formation
gen.	general
gr.	group
grn.	green
h.	hour
Hal	Halogen
hex.	hexagonal
homol.	homologous
hydr.	hydrolysis
hyg.	hygroscopic
icosah.	icosahedron
immed.	immediate
incul.	inculation
infl.	inflame
isostr.	isostructural
L	ligand
liq.	liquid
m.p.	melting point
met.	metal
min.	minute
mol.	molecule
monocl.	monoclinic
oct.	octahedron
org.	organic
Ox	oxide, ~ant, ~ation, ~dize
paramagn.	paramagnetic
passiv.	passivity, ~ation
pentag.	pentagonal
Phen	phenanthroline
powd.	powder
prec.	precipitate, ~ation
prop.	property
purp.	purple
Py	pyridine
pyram.	pyramid
react.	reaction, ~ive
Red	reduction, ~ant
rh.	rhombic
s.	second; solution
sld.	solid
slow.	slowly
sol.	soluble, -ility
solv.	solvent
SP	solubility product
stab.	stable, -ility
stoich.	stoichiometry
str.	structure (cr.)
subl	sublimate, ~ ion
subst.	substance
surp.	surplus
sym.	symmetrical
term.	terminal
tetr.	tetragonal
tetrah.	tetrahedron
tricl.	triclinic
trig.	trigonal
unpair.	unpaired (el.)
unstab.	unstable
v.	very
vac.	vacuum
visc.	viscous
vlt.	violet
vol.	volumenous
volat.	volatile
wh.	white
y.	year
yel.	yellow

ε	dielectric constant
μ	dipole moment
$\mu_{eff.}$	effective magnetic moment (M.B.)
μ–at.	br. at.
hν (vis)	visible
hν (UV)	ultraviolet
hν (IR)	infrared
ψ-	polyhedron, where one or several vertices occupied by an el. pair

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HALOGENS, ASTATINE

1 – | **1 +** | **EN**

	2s	2p	3d	EN
Fluorine F^0	↓↑	↓↑ ↓↑ ↓		4.1
Chlorin Cl^0	3s ↓↑	3p ↓↑ ↓↑ ↓	3d	3.0
Bromin Br^0	4s ↓↑	4p ↓↑ ↓↑ ↓	4d	2.8
Iodine I^0	5s ↓↑	5p ↓↑ ↓↑ ↓	5d	2.2
Astatine At^0	6s ↓↑	6p ↓↑ ↓↑ ↓	6d	1.9

an. ox. (+KF)

OF_2
gas, colrl., toxic, with smell of O_3
m.p. −224
b.p. −145
dec. 200
ΔH +24
sol. in H_2O 6.5 %
$+H_2O \xrightarrow[\text{exp.}]{t} HF + O$
v. strong Ox
HOF, liq., colrl., m.p. −117

Halogen hydrides, HHal

	$(HF)_n$	HCl	HBr	HI
	gas, colrl., with a sharp smell			
d	0.92	1.64	3.64	5.79
m.p.	−83	−112	−84	−51
b.p.	19.5	−84	−67	−35 (p)
degree of diss. by 1000°	10^{-13}	10^{-2}	0.5	33
ΔH	−271	−92	−34	+26
H—Hal	1.00	1.27	1.41	1.62
μ (gas)	1.91	1.08	0.79	0.42
ε (liq)	84 (0°)	4.6	6.3 (−80°)	—
sol. in H_2O	40 hydrofluoric	35 -chloric	55 -bromic	70 mass. % -iodic ac.
degree of diss. 0.1 N s.,%	9	93	93	95
$\cdot n H_2O$, n =	0.25; 0.5 (=$[H_3O]^+[HF_2]^-$); 1(=$[H_3O]^+F^-$)	1; 2; 3; 6 (=$[H_{14}O_6]^{2+}Cl_2^-$) 52)	2; 3; 4	2; 3; 4
	chem. act. only in the presence of H_2O			

H_2SO_4

Halides, $MHal_n$

		$M[HF_2]$, M = Na, K [F—H . . . F]$^-$	$[NR_4][HCl_2]$, hydr.	$[NR_4][HBr_2]$, unstab.	$[NR_4][HI_2]$
		MF · HF			
Resist. to hydr.	**ionic**	m.p. **LiF**↓ 870 **NaF** 997, · **HF** **KF** 857, · **2 H_2O** **NH_4F** subl. **CaF_2** 1419 **AlF_3** 1040	m.p. **NaCl** 801 **KCl** 776 **NH_4Cl** 335, subl. **$CaCl_2$** 782	m.p. **NaBr** 755 **KBr** 735 **$CaBr_2$** 760, · **$n H_2O$**, n = 3, 6	m.p. **NaI** 662 **KI** 686
	polymer	**UF_3** 1495 **UF_4**↓ 1036	**$MgCl_2$** 714 **$AlCl_3$** 180 **VCl_2** 1350	**$MgBr_2$** 710 **$NbBr_2$** (dec.) 710 **$NbBr_4$** 300, subl.	**CaI_2** 783 **MgI_2** 633, (dec.) **SnI_2** 320
S. in org. solv; + H_2O → HHal + E(OH)$_n$	**molecular**	**UF_6** 56 (subl.) **XeF_6** 49 (subl.) **MoF_6** 17.5 (liq.) **PF_3** −152 (gas) **SeF_6** −47 (subl.)	**VCl_4** < −20 **$GeCl_4$** −50 **PCl_3** −94 **BCl_3** −107, gas b.p. 13	**$MgBr_2$** 710 **$NbBr_5$** 268 **$(AlBr_3)_2$** 98 **PBr_3** −40, (liq.)	**SnI_4** 145, (subl.) **$(AlI_3)_2$** 191 **PI_3** 61
Examples of insol. salts		**BaF_2**↓ 1353 **PbF_2**↓ 855	**AgCl**↓ 457 **CuCl**↓ 501 **$PbCl_2$** 450	**AgBr**↓, yel., 434 **CuBr**↓, grn., 504 **$PbBr_2$**, wh., 373	**AgI**↓, yel., 560 **CuI**↓, wh., 605 **PbI_2**↓, yel., 412

SbF_5 — K_2MnF_6 29)

H_2 (Pt); H_2 ($h\nu$,-vis); MnO_2; $KMnO_4$; O_2 (−H_2O, < 600°); H_2(expl.); H_2 (Pt); Cl_2; H_2SO_4; (−$C_{10}H_8Br_4$); P; $h\nu$-vis (−H_2); Cl_2; H_2SO_4; O_2 ($h\nu$-vis); $P(H_2O$ −H_3PO_3); H_2S

F_2	Cl_2	Br_2	I_2	At
gas, light-yel.	gas, yel.-grn.	liq., red	cr., blk.	met., volat. < I_2
	with a sharp smell			
d (20°) 1.69 g/l	3.21 g/l	3.21 g/cm^3	4.94 g/cm^3	—
m.p. −219	−101	−7	113.7	337
b.p. −188	−34	60	183	302
ΔH_{dis} = 158	243	192	150 $3I_2(liq) \rightleftarrows I_3^+ + I_3^-$	
sol. in H_2O, (⟶ O_2 + HF)	0.68	3.5	0.03 mass. %	
			sol. in RH, RГ, CS_2, CCl_4	
In str. – Hal_2 mol.; CN Hal = 1 (= 8 – 7)				
Hal–Hal 1.42 (gas)	1.99	2.28	2.67	

Cl_2 — HgO (−Hg_2OCl_2↓); Bi_2O_3 (−BiOCl↓)

Cl_2O
gas, yel.-orange, with a smell of Cl_2
m.p. −121, b.p. 3.8
liq, exp., brn.
$\xrightarrow{20°}$ Cl_2 + ClO_2
ΔH = +80
sol. in H_2O (99 vol. %), CCl_4
μ = 1,7; angular mol.
· **2 H_2O** m.p. −36 53)

Br_2O 39)
liq., brn., m.p. −17, dec. −40

H_2O | $-H_2O$ | H_2O | $[TeF_5](O\ r)$

HOCl hypochlorous	**HOBr** -bromous	**HOI** -iodous ac.
conc. in saturated s. of Hal_2 10^{-2}	10^{-3}	$10^{-5}M$
max. conc. 20%, v. strong Ox.,	30%	—
distil. in vac. 30°		unstab.
$K_{ac.} = 10^{-8}$ angular mol., v. strong Ox	10^{-9}	10^{-11} $K_{bas} = 10^{-10}$

MOH | H_2CO_3 ($K_1 = 10^{-7}$)

MOH (−HCl)

MOHal, hypohalites, v. strong Ox.

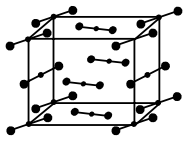
NaOCl, exp. 70°, **KOCl**, m.p. 2,5 **$Ca(OCl)_2$**, · **3 H_2O**, (m.p. 86) ·**1/3 $Ca(OH)_2$** · **$x H_2O$**, "lime chloride" ($\xrightarrow{t}$ O_2 + $CaCl_2$)	**NaOBr** · **$n H_2O$**, n=5, 7 **KOBr** · **3 H_2O** light yel. $\xrightarrow{t}$ MBr + $MBrO_3$ (other salts are not known)	**MOI**, known only in s.

an. ox. KF · nHF (in melt); MCl (in s.)

Cl_2 · 5.75 H_2O (8 : 46) m.p. 9.6

Br_2 · 7^2/$_3$ H_2O (6 : 46) 5 with dec.

Clathrates in the ice str.



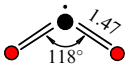
Hal_2 str.

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3+ 4+ 5+ «6+» 7+

$h\nu$(UV) ($-Cl_2$); O_3

ClO_2 [53]
gas, yel.-brn.
$d = 1.64$,
m.p. –59,
liq., red,
$\Delta H = +104$
exp.,
dimer in CCl_4 & str., $\mu = 0.78$,
readily sol. in H_2O,
paramagn.



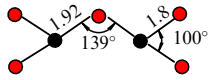
Br_2O_4 [2)]
cr.,
light.-yel.,
40 (dec.)

I_2O_4 =
$[I^{III}O]^+[I^{V}O_3]^-$
cr., yel.
130° → I_2 + I_2O_5

[6, 37)]
$(IO_2)_n$, cr.

Hal_2 —(O_3, (freon, –50°)→ **ClO_2**
Br_2O_3, sld., yel. ← t — **ClO_2**

Br_2O_5 [45)]
I_2O_5 cr., colrl.,
dec. $h\nu$(vis) → darken,
180 → I_2 + O_2
$\Delta H = -184$



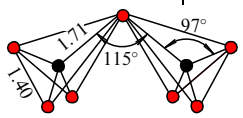
H_2O / $-H_2O$ (240°)

HI_3O_8; MI_3O_8

ClO_3, liq., red, [39, 51)]
smoky, m.p. 3.5,
b.p. 203, $\Delta H = +156$,
exp., $\xrightarrow{20°}$ ClO_2 + O_2,
in liq. and s. in CCl_4 – dimer, in str. – $[ClO_2]^+[ClO_4]^-$
Cl—O 1.41–1.47

$t(-O_2)$

Cl_2O_7, oil, colrl.,
m.p. –90, b.p. 87,
exp. 120, $d = 1.86$,
(stab. > ClO_3, ClO_2),
$\Delta H = +275$, sol. in CCl_4, $\mu = 0.72$,
middle Ox. [52)]



V VII
I_2O_6 = $[IO_2][IO_4]$
cr., light yel.
dec. > 100°
+ H_2O ⟶
⟶ HIO_3 + H_5IO_6 [56)]

H_2O (slow) / $-H_2O$ [1)] (P_2O_5; oleum)

Hal
O
H
•• Located el. pair

$[IO]^+X^-$, [6)]
X = HSO_4, NO_3, BF_4,
"salts of iodyl",
yel., paramagn. (p^2) [6)]

H_2O ($h\nu$-vis.)

H_2O (exp.)

$HClO_3$ chloric
$HBrO_3$ bromic
$(HIO_3)_n$ iodic ac.,
cr., colrl.,
$d = 4.63$, m.p. 110 with dec., $K = 10^{-1}$,
in s. $n = 2 - 3$,

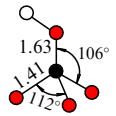


ex. only in s.
max. conc. 40%
40° exp.
50%
strong ac.
v. strong Ox
$\xrightarrow{-H_2O}$ $ClO_2 + Cl_2O_7$

HNO_3
I_2

$HClO_4$
perchloric
liq., colrl., $d = 1.77$,
m.p. –101,
b.p. 16/18 mm,
$3HClO_4 \rightleftarrows Cl_2O_7 + H_3O[ClO_4]$
100% (exp.), m.p. 50,
$K = 38$, Ox in conc. s. or when heated,
azeotrop – 72% $HClO_4$;
oil, b.p. 111/20,
· **nH_2O**, n = 1–3, 5 [52)]

$HBrO_4 \cdot 2H_2O$ [55)]
perbromic
v. strong Ox,
max. conc. 83%,
stab. < 55%, volat.
Ox > $HClO_4$



$HIO_4 \cdot nH_2O$ [56)]
periodic ac.,
cr., colrl.
HIO_4,
↑ 100°
$H_4I_2O_9$, **$H_7I_3O_{14}$**
↑ 80°
H_5IO_6,
m.p. 122 with dec.,
$K_1 = 10^{-2}$, $K_2 = 10^{-8}$,
$K_3 = 10^{-15}$,
mol. — trig. antiprism

$HClO_2$, chlorous ac.,
rapidly dec. in dil. s.
(→ HCl + $HClO_3$ + ClO_2)
$K = 10^{-2}$, v. strong Ox

H_2SO_4

H_2SO_4 (–$BaSO_4$↓)

H_2SO_4

M_2IO_4 [57)]
MI_3O_8; [23)]
paramagn. (s^1)

t

$M_2O_n \cdot mHal_2O_7$

perchlorates [4)]	perbromates [43)]	periodates [5)]
m.p.		
$LiClO_4$ 247	**$MBrO_4$**,	**$NaH_4IO_6 \cdot H_2O$**, dec. 175
$NaClO_4$ 482 (dec.)	M = Li–Cs,	= $Na(H_3O)[I(OH)_3O_3]$
$KClO_4$ 610 (dec.)	sol. Li > Cs,	**$Na_2H_3IO_6$**
$Ba(ClO_4)_2$ 505	stab. Li < Cs,	**$M_3H_2IO_6$**, M = Na↓, Ba/2
$AgClO_4$, dec. 486	$\xrightarrow{t}$ $MBrO_3$ +	Na_2O_2 ↓↑ H_2O
strong Ox	+ O_2	**Na_5IO_6**, dec. 800
only in melt	weak Ox,	**$K_4H_2I_2O_{10}$**; **$Ca_2I_2O_9$**↓ – dimeso-
	stab. < $MClO_4$ and MIO_4	**KIO_4**↓; **$NaIO_4$** – meta-
		MO_2 ↓↑ H_2O
		$M_3IO_5 \cdot nH_2O$ – mesoperiodates

ortho-

$[HalO_4]^-$ – tetrah. (sp^3), $[IO_6]^{3-}$ – oct. (sp^3d^2);
$[IO_5]^{3-}$ – tetr. pyram. (sp^3d), in str. **MIO_5** – net of oct.
$[I_2O_{10}]^{6-}$ – 2 oct. with common edge

Chlorites [38)]
$NaClO_2$, · 3 H_2O
$Ca(ClO_2)_2 \cdot 4H_2O$
$Ba(ClO_2)_2$
$AgClO_2$↓, **$Pb(ClO_2)_2$**↓,
yel., not oxidants;
$\xrightarrow{t}$ MCl + $MClO_3$,
exp.,
angular $[:\ddot{Cl}O_2]^-$
anions

Bromites [47)]
$LiBrO_2$, · H_2O
$Ba(BrO_2)_2$,
wh. powders,
$\xrightarrow{t}$ $MBr_n + O_2$,
+ $H_2O \rightarrow MBr_n +$
+ $M(BrO_3)_n$,
anion ψ-tetrah.

$t(-O_2)$

$MHalO_3$,

Chlorates	Bromates	Iodates
m.p.	m.p.	
$NaClO_3$ 262 (dec.)	**$NaBrO_3$** 381	**$NaIO_3$** (in "saltpetre")
$KClO_3$ 368, dec. 400	**$KBrO_3$** 343 with dec.	**KIO_3** (str. anal. of MNO_3)
"Berthollet's salt"	**$AgBrO_3$** dec.	**$MIO_3 \cdot nHIO_3$**
$Ca(ClO_3)_2$, · 2 H_2O	**$Ba(BrO_3)_2$** 260 with dec.,	**(KHI_2O_6, $NaH_2I_3O_9$)**
$Ba(ClO_3)_2$ 414, · H_2O	· H_2O	**$AgIO_3$**↓, wh.
poison		**$Ba(IO_3)_2$** ⟶ $Ba_5(IO_6)_2$ +
		+ I_2 + O_2
Ox – only in melt		
$[:HalO_3]$ – ψ-tetrah. (sp^3)		
Hal—O 1.45–1.50	1.78	1.78–1.82
∠ OHalO 106	112	97 or dist oct.

$t(-O_2)$

an. Ox; F_2

MOH
Hal_2 (t, –MHal)

INTERHALOGEN COMPOUNDS

1/n− **1/n+** **1+** **3+**

$M^+[Hal_n]^-$, polyhalides [30]

M^+ = NH_4, K–Cs, $[R_4N]$, $[Ph_4As]$, $[PBr_4]$, [Ln (caprolactam)$_6$] /3

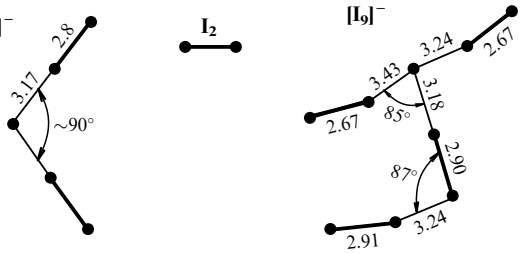
$[Me_4N]Cl_3$	**$KI_3 \cdot H_2O$**, cr., brn., m.p. 38, dec. 225
$RbBr_3$, dec. 140	**CsI_3**, m.p. 207
$CsBr_3$, m.p. 180	**$KI_5 \cdot 2C_6H_6$**
	$RbI_7 \cdot 4C_6H_6$
$CsBr_5$, cr., red	**$RbI_9 \cdot 4C_6H_6$**
	Cs_2I_8, cr., vlt.
	$[Et_4N][I(I_2)_n]$, $n = 2, 3, 4$
	$[H(theobromine)]_4^+[I_{16}]^{4-}$, anion $(I_3^- — I_2 — I_3^-)_2$

$[Hal_3]^-$, linear (ψ-trig. bipyr.)

Br — Br 2.4–2.9;	I — I 2.9–3.1

Cs[I(IBr)] is used to purify Cs (salts of K and Rb do not ex.). Stab. of $MHalHal'_n$ increases and sol. in H_2O decreases in [Li – Cs – R_4N] series; CCl_4, Et_2O, bz. accelerate the dec. $MHalHal'_n \rightarrow MHal' + HalHal'$ (extr. with Et_2O).

$[I_5]^-$ **I_2** **$[I_9]^-$**



ClI_3	**BrI_3** [57]
Mol. — ψ-trig. bipyr.	
Cl — I 1.58, 1.70	Br — I 1.73, 1.81

MHal

Hal_2

F_2

(270°)

(10°)

$SbF_5 + ClF$; BrF_5; IF_5; AsF_5; $S_2O_6F_2$; PF_5;

ClF, gas, colrl.	**BrF**, liq., red	**IF**, cr., red
m.p. −156	−33	—
b.p. −100	20	—
ΔH −50	−42	−89
μ 0.65	1.29	—
	20° ⟶ Br_2 + BrF_3	−14° ⟶ I_2 + IF_5

+ $H_2O \longrightarrow Hal_2 + O_2 + HF$

F_2(t)

ClF_3	**BrF_3**	**IF_3**
gas, colrl.	liq., colrl.	cr., yel.
m.p. −76	9	–
b.p. 12	127	dec. −28 ($\longrightarrow I_2 + IF_5$)
ΔH −163	−255	−496
μ 0.55	1.19	
in gas — $(ClF_3)_2$		

2 $HalF_3$(liq.) ⇄ $HalF_2^+ + HalF_4^-$
T-shaped mol. (ψ-trig. bipyr.)
+ $E_2O_n \longrightarrow EF_n + Hal_2 + O_2$ (method for determination of O); + Ir, Os, SiO_2 inflam.

MF

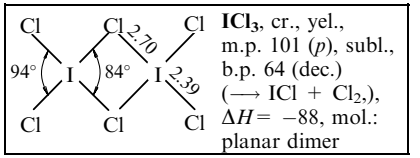
$M[ClF_2]$, $M[BrF_2]$, $M[IF_2]$, M = K–Cs, dec. 230, linear anions [64]

$[ClF_2]^+X^-$, $[BrF_2]^+X^-$ [11], **$[BrCl_2]^+X^-$, $[ClBr_2]^+X^-$, $[IF_2]^+X^-$**, X = AuF_4, PF_6, BF_4, AsF_6, SbF_6, BiF_6, PtF_6, Stab.: Sb > As > P, ψ-tetrah cations. (sp^3)

$M[ClF_4]$, $M[BrF_4]$, $M[IF_4]$, M = K–Cs, [NO], cr., colrl., squares anions (ψ-oct., sp^3d^2) **$RbBr_2F_7$** [3]

BrCl (⇄ $Br_2 + Cl_2$)	**ICl**, needle, red (α), brn. (β)
dis. 40% (20°), gas, yel.	27 (α), 14 (β)
m.p. −54	97 (dec.)
b.p. 5 with dec.	−33
$\Delta H_{dis.}$ = +15	0.65
μ = 0.57	2 ICl(liq.) ⇄ $I^+ + ICl_2^-$
	2.32, str.: zigzag chains; Cl- and I-agents in org. synthesis

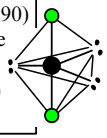
$[Cl_3]^+X^-$
$[Br_n]^+X^-$, n = 2, 3, 5; red
$[I_n]^+X^-$, n = 2–5, bl.
$[I_2Cl]^+X^-$, blue or red
$[Br_2Cl]^+X^-$,
$[I_3Cl_2]^+X^-$,
X = $AlCl_4$, HSO_4, SO_3F, Sb_2F_{11}, SbF_6, Sb_3F_{16}, IF_6
I_3^+, I_4^{2+}, Br_2^+, polycations,
$[I_3]^+$ — angular
$[I_4]^{2+}$ — rectangular [7, 36]



ICl_3, cr., yel., m.p. 101 (p), subl., b.p. 64 (dec.) ($\longrightarrow$ ICl + Cl_2,), ΔH = −88, mol.: planar dimer

Cs[$BrCl_2$], cr., yel., m.p. 205, dec. 150	**H[ICl_2]**, $K = 10^{-3}$
	M[ICl_2], M = K (dec. 215), Rb, Cs (m.p. 238, dec. 290)
	[PyH], [PCl_4], cr., orange

anions [:$\ddot{I}$$\ddot{H}$$\ddot{a}$$\ddot{l}$$Cl_2$] linear ($\psi$-trig. bipyr.) ($sp^3d$), I — Cl 2.55 [9]



$[ICl_2]^+X^-$, cr., red, cation: ψ-tetrah.
$[IBr_2]^+X^-$, X = Sb_2F_{11}, $SbCl_6$, $AlCl_4$ [8, 12]

I_2 — $SbCl_5 + Cl_2$

IBr ⇄ $I_2 + Br_2$, dis. 8% (20°), cr., red, m.p. 42, b.p. 119 (dec.), ΔH = −10, μ = 1.21, I — Br 2.52; **2IBr · Dipy**, [33]

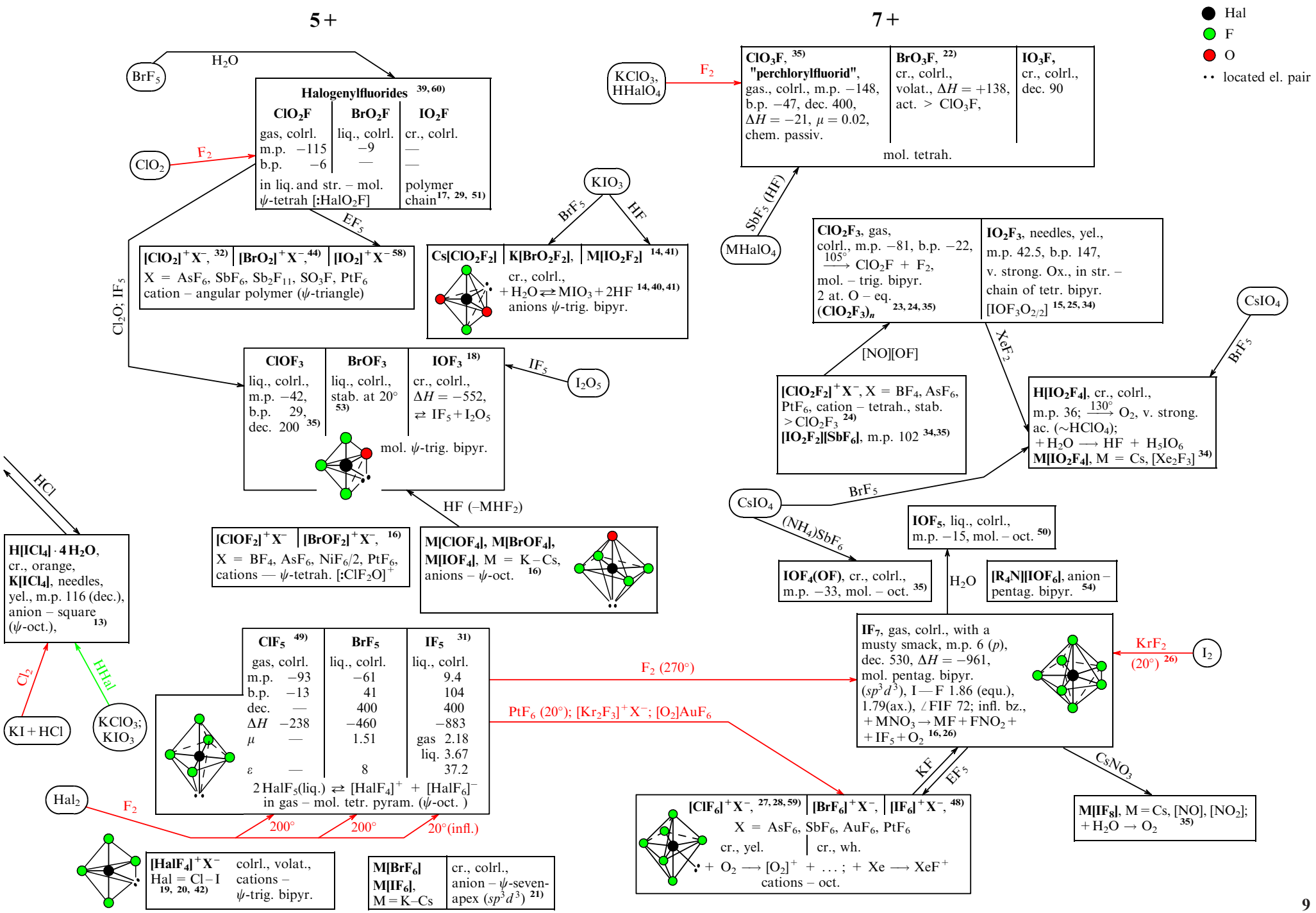
IN_3 — $[R_4P][NbBr_6]$

$[Ph_4P]Br$

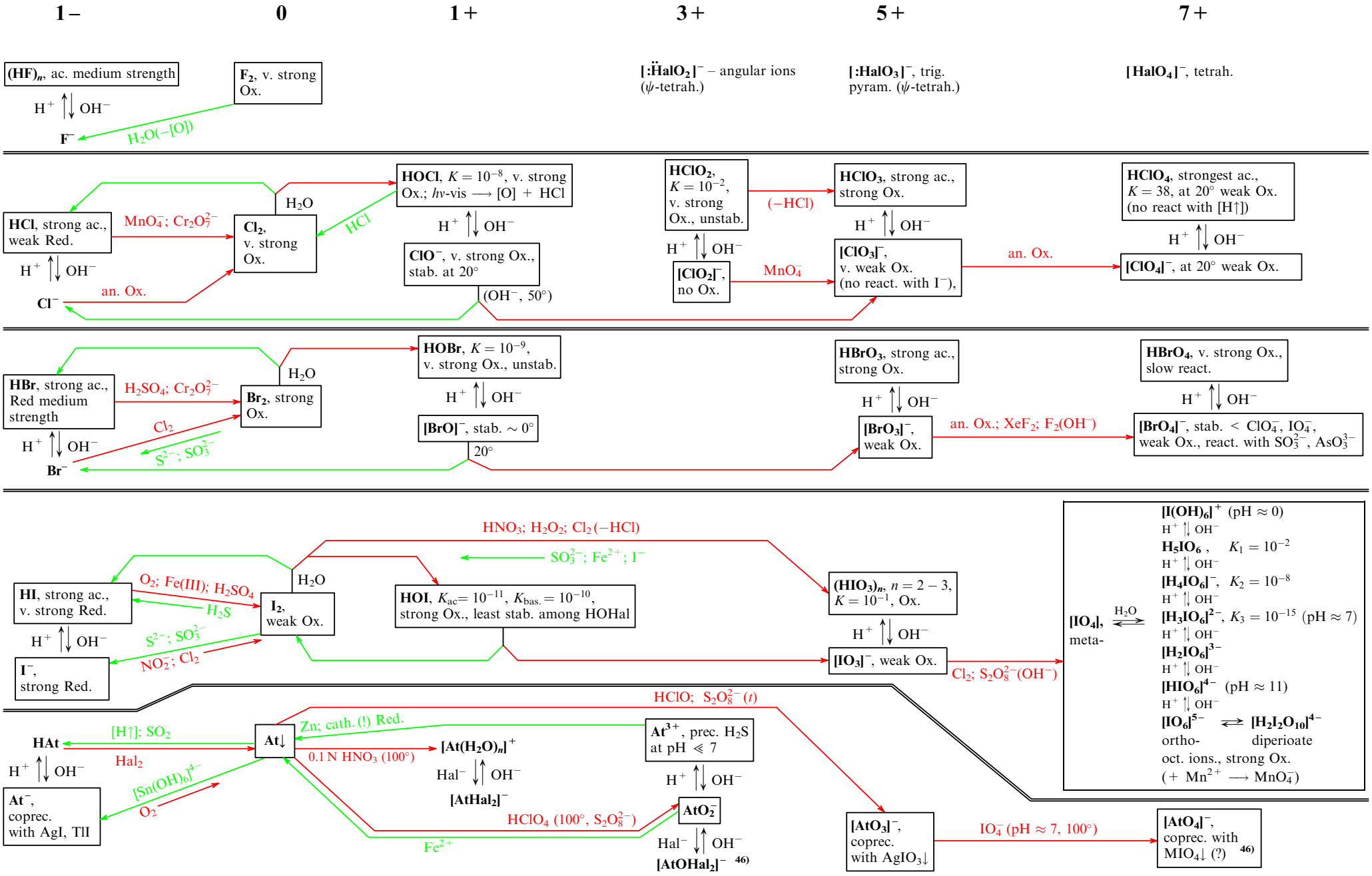
MI — Br_2

H[IBr_2], $K = 10^{-3}$
M[IBr_2], M = K (m.p. 58, dec. 180); Cs (m.p. 243, dec. 320); [Ph_4P], cr., red., linear anion [10]

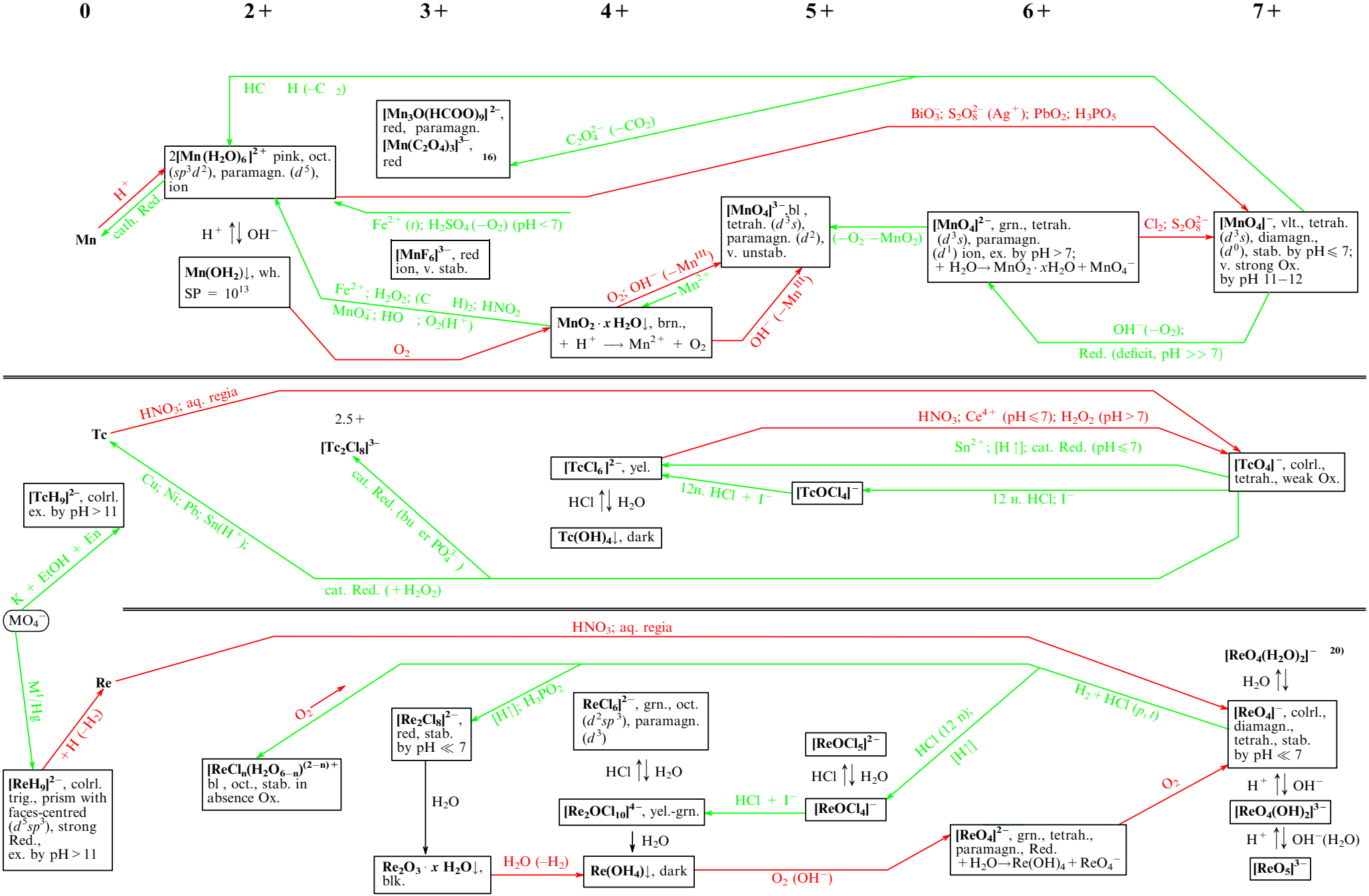
$HalF_n$ – v. strong F-agents and Ox., used for the synthesys of comp. with the highest degrees of Ox; hyg., diamagn.; react. decreases in the $ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF$ series.
Act. of $HalF_n$ decreases with increasing n; at the same n falls in Cl > Br > I series.


5+
7+
Hal
F
O
•• located el. pair
BrF5
H2O
Halogenylfluorides 39, 60)
ClO2F | BrO2F | IO2F
gas, colrl. | liq., colrl. | cr., colrl.
m.p. −115 | −9 | —
b.p. −6 | — | —
in liq. and str. – mol. ψ-tetrah [:HalO2F] | polymer chain 17, 29, 51)
ClO2
F2
EF5
Cl2O; IF5
[ClO2]+X−, 32) | [BrO2]+X−, 44) | [IO2]+X− 58)
X = AsF6, SbF6, Sb2F11, SO3F, PtF6
cation – angular polymer (ψ-triangle)
KIO3
BrF5
HF
Cs[ClO2F2] | K[BrO2F2], | M[IO2F2] 14, 41)
cr., colrl.,
+H2O ⇄ MIO3 + 2HF 14, 40, 41)
anions ψ-trig. bipyr.
KClO3, HHalO4
F2
ClO3F, 35) "perchlorylfluorid", gas., colrl., m.p. −148, b.p. −47, dec. 400, ΔH = −21, μ = 0.02, chem. passiv.
BrO3F, 22) cr., colrl., volat., ΔH = +138, act. > ClO3F,
IO3F, cr., colrl., dec. 90
mol. tetrah.
SbF5 (HF)
MHalO4
ClO2F3, gas, colrl., m.p. −81, b.p. −22, 105° → ClO2F + F2, mol. – trig. bipyr. 2 at. O – eq. (ClO2F3)n 23, 24, 35)
IO2F3, needles, yel., m.p. 42.5, b.p. 147, v. strong. Ox., in str. – chain of tetr. bipyr. [IOF3O2/2] 15, 25, 34)
CsIO4
BrF5
XeF2
[NO][OF]
[ClO2F2]+X−, X = BF4, AsF6, PtF6, cation – tetrah., stab. > ClO2F3 24)
[IO2F2][SbF6], m.p. 102 34,35)
H[IO2F4], cr., colrl., m.p. 36; 130° → O2, v. strong. ac. (~HClO4); +H2O → HF + H5IO6
M[IO2F4], M = Cs, [Xe2F3] 34)
ClOF3 | BrOF3 | IOF3 18)
liq., colrl., m.p. −42, b.p. 29, dec. 200 35) | liq., colrl., stab. at 20° 53) | cr., colrl., ΔH = −552, ⇄ IF5 + I2O5
mol. ψ-trig. bipyr.
IF5
I2O5
HF (–MHF2)
[ClOF2]+X− | [BrOF2]+X−, 16)
X = BF4, AsF6, NiF6/2, PtF6, cations — ψ-tetrah. [:ClF2O]+
M[ClOF4], M[BrOF4], M[IOF4], M = K–Cs, anions – ψ-oct. 16)
HCl
H[ICl4]·4H2O, cr., orange, K[ICl4], needles, yel., m.p. 116 (dec.), anion – square (ψ-oct.), 13)
Cl2
HHal
KI + HCl
KClO3; KIO3
CsIO4
BrF5
(NH4)SbF6
IOF5, liq., colrl., m.p. −15, mol. – oct. 50)
IOF4(OF), cr., colrl., m.p. −33, mol. – oct. 35)
H2O
[R4N][IOF6], anion – pentag. bipyr. 54)
ClF5 49) | BrF5 | IF5 31)
gas, colrl. | liq., colrl. | liq., colrl.
m.p. −93 | −61 | 9.4
b.p. −13 | 41 | 104
dec. — | 400 | 400
ΔH −238 | −460 | −883
μ — | 1.51 | gas 2.18, liq. 3.67
ε — | 8 | 37.2
2 HalF5(liq.) ⇄ [HalF4]+ + [HalF6]−
in gas – mol. tetr. pyram. (ψ-oct.)
F2 (270°)
PtF6 (20°); [Kr2F3]+X−; [O2]AuF6
IF7, gas, colrl., with a musty smack, m.p. 6 (p), dec. 530, ΔH = −961, mol. pentag. bipyr. (sp3d3), I—F 1.86 (equ.), 1.79(ax.), ∠FIF 72; infl. bz., +MNO3 → MF + FNO2 + +IF5 + O2 16, 26)
KrF2 (20°) 26)
I2
Hal2
F2
200°
200°
20°(infl.)
[HalF4]+X− Hal = Cl–I 19, 20, 42) colrl., volat., cations – ψ-trig. bipyr.
M[BrF6] M[IF6], M = K–Cs | cr., colrl., anion – ψ-seven-apex (sp3d3) 21)
KF
EF5
CsNO3
[ClF6]+X−, 27, 28, 59) | [BrF6]+X−, | [IF6]+X−, 48)
X = AsF6, SbF6, AuF6, PtF6
cr., yel. | cr., wh.
+ O2 → [O2]+ + ... ; + Xe → XeF+
cations – oct.
M[IF8], M = Cs, [NO], [NO2]; +H2O → O2 35)

HALOGEN AND ASTATINE IONS IN AQUEOUS SOLUTIONS



MANGANESE, TECHNETIUM AND RHENIUM IONS IN AQUEOUS SOLUTIONS



MANGANESE

Mn^0 3*d* ↓ | | | | ↓ ; 4*s* ↓↑ ; 4*p* | | | ; 4*d* | | | ; **EN** 1.6

2+ (d^5) **3+ (d^4)**

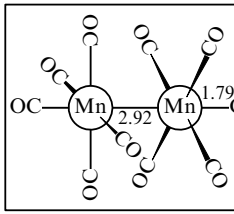
Mn, met., silvery, hard, brittle,
m. p. 1245, b. p. 2080, sol. in dil. ac., H_2O (*t*),
$E_0 Mn^{2+}/Mn_{sld.} = -1.19$, paramagn.
α-, cub. (α-Fe str. type), *d* = 7.43, *a* = 8.91
↓ 727°
β-, cub. cl. pack (α-Cu str. type), *d* = 7.29,
a = 6.30, Mn — Mn 2.6
↓ 1079°
γ-, cub. (dist. cl. pack), *d* = 6.37, *a* = 3.86
↓ 1143°
δ-, cub. (α-Fe str. type), *d* = 6.28, *a* = 3.08

O_2(*t*)
H_2(*t*), Al
H_2SO_4
cath. Red. (H_2O)
C(−CO)
H_2SO_4(−O_2)
MnO_2
HCl(−Cl_2)
CO + Mg(−Cl_2); Na

MnO_2 + Fe_2O_3

Ferromanganese: ⩾70 % Mn, ~ 20 % Fe,
6–7 % C, < 2 % Si, > 0.35 % P, 0.03 % Si
Mirror cast iron: contain 15–20 % Mn
Manganese steel: 12–15 % Mn,
1–2 % C, wear-resisting alloy
Mn-bronze: 95 % Cu + 5 % Mn

0 (d^7)



[Mn(CO)$_5$]$_2$, cr., gold-yel.,
m. p. 154 (*p*), subl. 50/10^{-2},
sol. in org. solv.,
dist. with steam,
mol. – cluster, μ = 0.98
Mn$_4$(CO)$_{16}$ [17]
MnTc(CO)$_{14}$

HMn(CO)$_5$, liq., colrl., m. p. −25, stab. at 25°,
weak ac., $K = 10^{-2}$, oct. mol. [1]
(H$_3$Mn$_3$(CO)$_{12}$)
MMn(CO)$_5$, M = M^I, $SnCl_3$, R_3Sn
diamagn., ∑e = 18, anion – trig. bipyr.
[(OC:)$_4$Mn(:NO)], cr., red, m. p. −1, diamagn. [2]
[Mn(PPh$_3$)$_5$]$_2$, cr., colrl., volat., sol. in org. solv.

Mn$_{1.0–1.13}$O, grey-grn., m. p. 1780,
$\Delta H = -384$, sol. in ac., melt KCl,
semiconduct., NaCl str. type, Mn — O 2.22

H_2(> 1200°)

Mn$_3$O$_4$ = $Mn^{III}_2[Mn^{II}O_4]$,
blk.-brn., m.p. 1705,
$\Delta H = -1385$, "hausmannite"

O_2 (> 500°)
940°; H_2 (230°)

Mn$_2$O$_3$, brn., $\Delta H = -959$,
cub. str., oct. [MnO_6]

250°, vac.

Mn(OH)$_2$↓, wh., stoich. copmos.,
$K_{bas.\,2} = 10^{-4}$, $K_{ac.\,1} = 10^{-19}$, SP = 10^{-13},
sol. in presence of NH_4^+; CdI_2 str. type,
Mn — O 2.22, "pyrochroite"

in air (OH^-) (immed.)

100°
MnO(OH) ⟵ **Mn$_2$O$_3$ · *x* H$_2$O**↓, brn.
"manganite", "groutit"

MOH (conc.)
H_2O (N_2)

OH^- (pH ~ 9)

Mn(ClO$_4$)$_2$, $\xleftarrow{>60°}$ **· 2 H$_2$O**, **· 6 H$_2$O** [23]
MnSO$_4$, colrl., m. p. 700, dec. 650, [21]
· *n* H$_2$O, *n* = 7, 6 − 1, pink
MnSO$_3$ · *n* H$_2$O, *n* = 1, 3; **MnS$_2$O$_6$ · 6 H$_2$O**,
Mn(NO$_3$)$_2$, · 6 H$_2$O, (m.p. 26), **3 H$_2$O**
Mn$_3$(PO$_4$)$_2$ · *n* H$_2$O, *n* = 4, 7;
MnHPO$_4$ · 3 H$_2$O, **Mn(H$_2$PO$_4$)$_2$ · 2 H$_2$O**, [12]
NH$_4$MnPO$_4$ · H$_2$O↓ $\xrightarrow{t}$ **Mn$_2$P$_2$O$_7$**, m. p. 1196
MnHPO$_3$ · 3.6H$_2$O; Mn(H$_2$PO$_3$)$_2$; **Cs$_2$Mn(PO$_3$)$_4$** [12]
MnCO$_3$↓, wh., $\xrightarrow{>100°}$ MnO + CO_2; **Mn$_3$(AsO$_3$)$_2$**↓
SP = 10^{-10}, "rhodochrosite"
Mn(HCOO)$_2$ · 2 H$_2$O; **Mn(CH$_3$COO)$_2$**; **· *n* H$_2$O**, [20]
MnC$_2$O$_4$ · *n* H$_2$O ↓, *n* = 2, 3
Mn$_2$[SiO$_4$], "tefroit"; **MnSiO$_3$**, "rhodonite",
Mn[SiF$_6$] · 6 H$_2$O, readily sol. in H_2O

Manganates (II) [24]
Na$_4$[Mn(OH)$_6$],
Na$_2$Mn(OH)$_4$, red
M$_2$Mn$_2$O$_3$; **BaMnO$_2$**
Mn — O 2.08–2.11

MnSO$_4$
H_2O_2 + NH_3

Mn$_2$(SO$_4$)$_3$, powd.,
grn., amorph., dec. 300
↑ *t*
· H$_2$SO$_4$ · 4 H$_2$O, red
· Cs$_2$SO$_4$ · 24 H$_2$O,
alum, red [26]
MnPO$_4$ · H$_2$O; **MnHP$_2$O$_7$** [22]

Manganates (III) [15]
Ca$_3$[Mn(OH)$_6$]$_2$
Na$_5$[MnO$_4$];
Na$_4$Mn$_2$O$_5$; **MMnO$_2$**,
red, anions –
tetrah. or oct.
Mn — O 1.86–1.95

H_2SO_4 (conc., $-O_2$)

M^I[Mn(ClO$_4$)$_3$] [19]
[NO$_2$][Mn(ClO$_4$)$_3$]
[Ph$_4$As]$_2$[Mn(NO$_3$)$_4$] [13]
[NO][Mn(NO$_3$)$_3$], yel.
NaMnPO$_4$,
Cs$_2$Mn(PO$_3$)$_4$; **Ba$_2$[Mn(AsO$_4$)$_2$]** [13]

KMnO$_4$

K$_2$[Mn(C$_2$O$_4$)$_2$] · 2 H$_2$O [5]

[Mn$_3$O(OAc)$_7$(H$_2$O)$_6$] [6]
[Mn$_3$O$_2$(OAc)$_5$(AcOH)$_{1.5}$]
Mn$_2$(C$_2$O$_4$)$_3$ · 2 H$_2$O

M$_3$[Mn(C$_2$O$_4$)$_3$] · 3 H$_2$O
red [16]

[22]	m. p.	b. p.	Δ*H*	· *n*H$_2$O
MnF$_2$,	930	1640	−847	4
MnCl$_2$,	650	1231	−481	2, 4
MnBr$_2$,	698	–	−377	4
MnI$_2$,	638	–	−306	4

MnHal$_2$ – cr., pink
In gas – linear mol., MnF_2 – rutile struct.;
$MnBr_2$, MnI_2 – CdI_2 str. type

F$_2$ (250°); XeF$_2$

600°

KMnF$_3$, **M$_2$MnF$_4$**, grn.,
anion – tetrah. (sp^3)
NaMnCl$_3$; **M$_2$MnCl$_4$**
Rb$_3$Mn$_2$Cl$_7$; **Na$_2$Mn$_3$Cl$_8$**
K$_4$MnCl$_6$; **MMn$_4$Cl$_9$** [4]
anions – oct.
Cs$_3$MnBr$_5$; **Rb$_2$MnBr$_4$** [9]

MnF$_3$, red, $\Delta H = -996$,
in str. – layers of oct.;
· 2 H$_2$O;
+ H_2O ⟶ MnO_2 +
+ Mn^{2+} + HF
MnCl$_3$, cr., brn., dec. −40,
sol in abs. alc.,
· Dipy, red [28]

MMnF$_4$, **· H$_2$O**
M$_2$MnF$_5$, **· H$_2$O**
M$_3$MnF$_6$, M = K–Cs,
M^{II}/2, red, v. stab.,
anions – oct.
NaMn$_3$F$_{10}$
M$_2$[MnCl$_5$], red
M$_3$MnCl$_6$
Rb[MnCl$_4$ · (H$_2$O)$_2$] [28]

Mn(CN)$_2$↓
Mn(NCS)$_2$, cr., yel., **· 4 H$_2$O**, grn.

CN$^-$

K$_4$[Mn(CN)$_6$] · 3 H$_2$O, bl.,
anion – oct., (d^2sp^3, 1 unpair el.),
only low-spin compl. Mn(II)
M$_4$[Mn(NCS)$_6$] [25]

Ba$_2$MnS$_3$, chain of oct.

MnS · *x* H$_2$O↓, amorph., flesh-colored, SP = 10^{-15}, sol. in HCl;
+ O_2 ⟶ $MnO_2 \cdot n H_2O$ + S (slow.)
↓ −H$_2$O (τ, *t*)
MnS, cr., grn., m. p. 1615, $\Delta H = -205$, NaCl str. type,
"manganesian blende" (alabandite).

300°

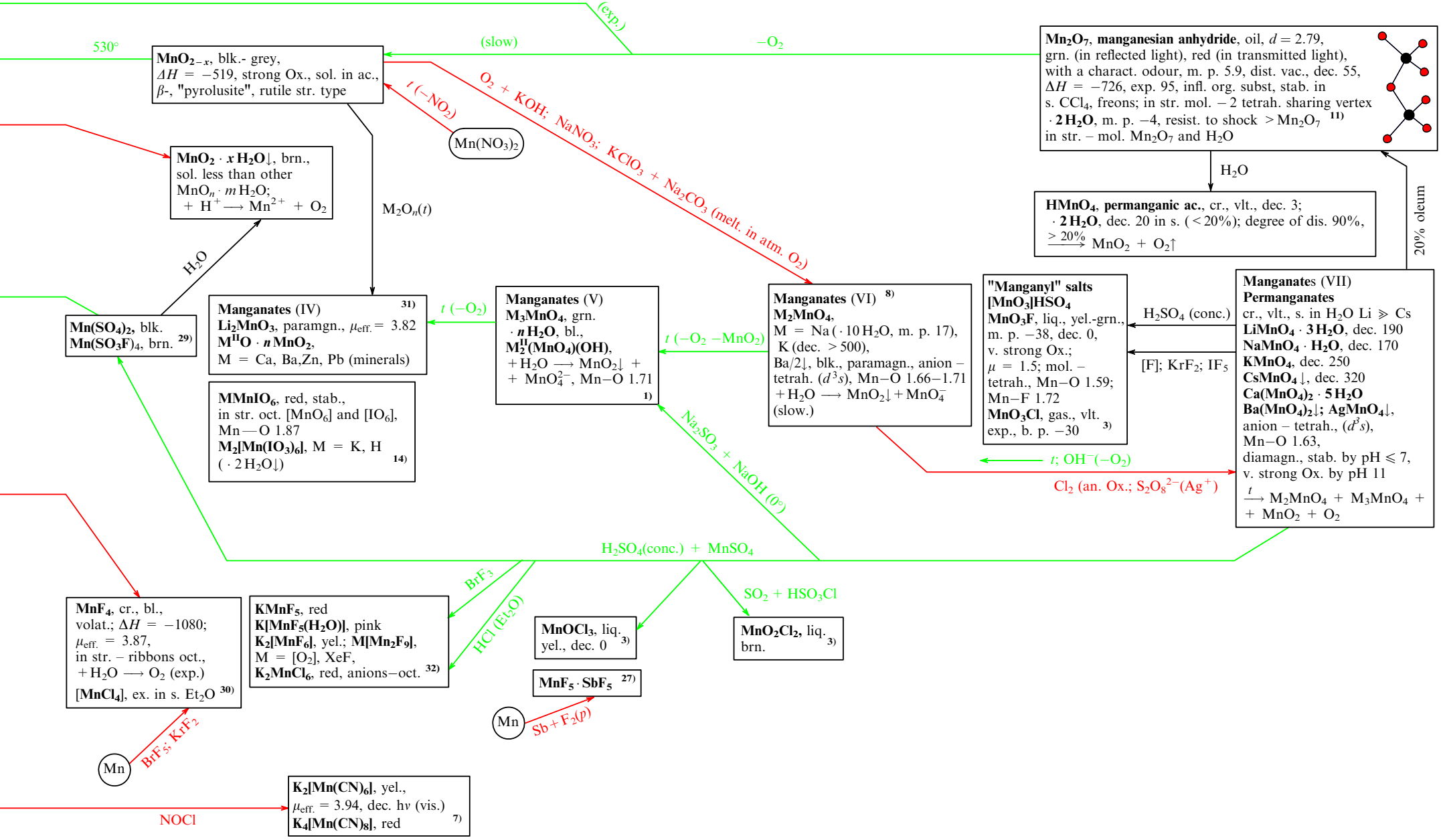
MnS$_2$, blk., "mangankiese"
MnSe, **MnSe$_2$**, **MnTe$_2$**, FeS_2 str. type

Mn$_4$N; **Mn$_2$N**; **Mn$_3$N$_2$**; **Mn$_7$C$_3$**, [18]
Mn$_3$C, m. p. 1520, **MnSi**; **Mn$_2$P**; **MnP**

M$_3$[Mn(CN)$_6$], brn.,
· 6 H$_2$O, red
oct. anion, paramagn.
(d^2sp^3, 2 unpair el.),
isostr. to M$_3$[Fe(CN)$_6$] [10],
only low-spin compl. Mn(III)
K$_3$[Mn(CN)$_5$(H$_2$O)] · KCN [6]

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4 + (d^3) **5 + (d^2)** **6 + (d^1)** **7 + (d^0)**



TECHNETIUM, RHENIUM

	4*d*	5*s*	5*p*	5*d*	EN
Tc^0	↓ ↓ ↓ ↓ ↓	↓↑			1.4
	5*d*	**6*s***	**6*p***	**6*d***	
Re^0	↓ ↓ ↓ ↓ ↓	↓↑			1.5

2+ (d^5)

3+ (d^4)

4+ (d^3)

TcO$_2$ cr. blk., sol. in conc. HHal, HNO$_3$, H$_2$O$_2$ subl. 1000, $\Delta H = -435$, monocl., dist. TiO$_2$ str. type

ReO$_2$ [26] cr. blk., sol. in conc. HHal, HNO$_3$, H$_2$O$_2$ $\xrightarrow{>850°}$ Re + Re$_2$O$_7$, $\Delta H = -446$, α-, TiO$_2$ str. type; β-, rh., chains of oct. with common edge, Re—Re 2.61 [4]

NH$_4$MO$_4$ —*t* (−N$_2$−H$_2$O)→ TcO$_2$ / ReO$_2$

TcO$_2$ —(NH$_4$)$_2$MCl$_6$; NH$_4$MO$_4$, H$_2$ (−N$_2$)→ Tc

ReO$_2$ —H$_2$ (300°)→ Re

Re$_2$O$_7$ —H$_2$ (300°)→ ReO$_2$

Re$_2$O$_3$ · *n* H$_2$O↓, blk., sol. in HHal (*t*); + O$_2$ ⟶ HReO$_4$

M(OH)$_4$↓, brn.-blk., sol. in ac., alk.

Re$_2$O$_7$ —H$_2$O (−H$_2$)→ M(OH)$_4$↓

M(OH)$_4$↓ —OH$^-$ (−N$_2$)→ Re$_2$O$_3$ · *n* H$_2$O↓

M(OH)$_4$↓ —NaOH(*t*)→ Renates (IV)

M(OH)$_4$↓ —H$_2$O→ TcCl$_4$

Cs$_2$[Re$_2$(HPO$_4$)$_4$(H$_3$PO$_4$)$_2$], Re≡Re 2.24 [37]

[ReCl(CH$_3$COO)$_2$]$_2$, [ReCl$_2$(CH$_3$COO)(H$_2$O)], [ReHal$_2$(CH$_3$COO)]$_2$ [24]

3.5+ [Re$_2$OCl$_3$(EtCOO)$_2$(PPh$_3$)$_2$] – 2 [ReO$_{2/2}$ClCl$_{1/2}$P], Re≡Re 2.51

TcCl$_4$, cr. red., paramagn., in str. linear chains of oct. with common edge Tc—Tc 3.62

Renates (IV) Na$_2$ReO$_3$; Ca$_2$ReO$_4$ Ca$_3$ReO$_5$, brn.

K$_4$[ReO$_2$(CN)$_4$], blk., easily Ox.

M$_4$[Re$_2$OCl$_{10}$], yel.-grn., paramagn., [Cl$_5$Re—O—ReCl$_5$]$^{4-}$ 2 oct. with common vertex, ∠ReORe 180

K$_2$MF$_6$, M = Tc, Re, grn., anion stab. even at pH > 7 **K$_2$MCl$_6$**, yel.-grn. **K$_2$MBr$_6$**, red., **K$_2$MI$_6$** [25]

K$_2$[MH$_9$], cr. colrl. stab. by pH ≫ 7 **Na$_2$[ReH$_9$]**, dec. 245 **Ba[ReH$_9$]**, anion trig. prism with centreted faces (d^5sp^3)

KTcO$_4$ —K + En + alc.→ **K$_2$[MH$_9$]**

KReO$_4$ —K/Hg→ **K$_2$[MH$_9$]**

	Tc	Re
	met. silver-wh., darken in the air	
d	11.5	21.0
m. p.	~2200	3190
b. p.	~4600	~5900
sol. in	HNO$_3$, aq. regia	H$_2$SO$_4$ (*t*), HNO$_3$, (H$_2$O$_2$ + NH$_4$OH)
E_0 MO$_4^-$/M$_{sld.}$	+0.47	+0.37
	hex. cl. pack.	
a	2.73	2.76
c	4.40	4.46
M—M	2.73	2.76

2.5+ [Tc$_2$(CH$_3$COO)$_4$Hal], Hal = Cl, Br, Tc=Tc 2.12 [13]

M$_3$[Tc$_2$Cl$_8$], M = K, NH$_4$, blk., str. anal. of [Re$_2$Cl$_8$]$^{2-}$, (1 unpair. el) [22]

ReOCl, + H$_2$O ⟶ H$_2$ + Re(II); $\xrightarrow{500°}$ Re + ReCl$_3$ + ReO$_3$Cl [24]

H[Re(CO)$_5$], ↑H$_2$O **Na[M(CO)$_5$]**, **Na$_3$Re(CO)$_4$** [20]

H[Re(CO)$_5$] —*t* (−H$_2$)→ Tc

0 (d^7)

	[Tc(CO)$_5$]$_2$	[Re(CO)$_5$]$_2$
	cr. colrl., poorly. sol. in. org. solv., stab.in air	
subl.	50/10^{-2}	difficult volat.,
m.p.	160 (*p*)	m. p. 177 (*p*), dec. 250, μ = 1.18
isostruct.	[Mn(CO)$_5$]$_2$, M—M 3.02	
M—C	1.90(ax.) 2.00(equ.)	2.01
C—O	1.20 (ax.),	1.12 (equ.)

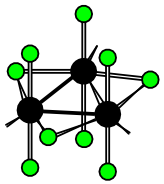
Tc —I$_2$ (110°)→ **ReCl$_2$ · 4H$_2$O**, bl. **· 2HCl · 2H$_2$O**, grn. **[≡ReBr$_2$(PR$_3$)$_2$]$_2$** [23] **ReI$_2$**, blk., diamagn. cluster [23]

Tc —F$_2$ (500°)→ **ReOF$_3$** [37]

Tc$_2$Cl$_4$(PR$_3$)$_4$ [40]

ReCl$_3$, cr. vlt., m. p. 257, b. p. 327, sol. in alc., Diox, $\Delta H = -264$, in str. and gas – cluster [Re$_3$Cl$_9$], Re=Re 2.48, $\xrightarrow{450°}$ Re + ReCl$_5$

Re —Cl$_2$, 600°→ ReCl$_3$

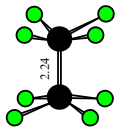


[Re$_3$Cl$_9$(H$_2$O)$_3$]·*n* H$_2$O · 2CH$_3$COOH

ReBr$_3$, cr. red-brn., $\Delta H = -163$, chains of clusters [Re$_3$Br$_9$]

ReI$_3$, blk., in str. – chains of triangles [(Re$_3$I$_3$)I$_4$I$_{4/2}$] [38]

M$_3$[Re$_3$Hal$_{12}$], M = Rb, Cs, anion – [Re$_3$Hal$_9$]$^-$ + 3Hal$^-$ (term). **M$_2$[Re$_3$Hal$_{11}$]**, M = Cs, [R$_4$As], **M$_2$[Re$_3$Cl$_{10}$]**, anion [Re$_3$Hal$_9$] + nHal$^-$ **M$_2$[Re$_2$Hal$_8$]**, Hal = Cl, Br, diamagn. cluster – 2 tetr. pyr. [ReHal$_4$Re]



ReF$_6$ —H$_2$ (200°), (70°)→ **ReF$_4$**

ReCl$_5$ —H$_2$ (200°), (70°)→ **ReF$_4$**

ReF$_4$, cr. yel.-grn., m. p.. 125, b. p. ≈ 735, subl. 300 **ReCl$_4$**, cr. blk.-brn., stab. in atm. N$_2$, sol. in ac., Thf, $\xrightarrow{t}$ ReCl$_3$ + ReCl$_5$; in str. – chains of pairs of oct. (with common faces), linked by vertices – [Re$_2$Cl$_7$Cl$_{2/2}$], Re—Re 2.73 **ReBr$_4$**, cr. dark red. **ReI$_4$**, cr. blk.; $\xrightarrow{550°}$ ReI$_3$ + I$_2$

[ReCl$_4$(PR$_3$)$_3$] —t→ **K$_2$MF$_6$**

3.25+ M$_2$[Re$_4$Br$_{15}$] = = M$_2$[Re$^{III}_3$ Br$_9$][Re^{IV}Br$_6$]

[Tc(CO)$_4$]$_2$, cr. brn.

Re$_2$(CO)$_n$(PR$_3$)$_{10-n}$ [19]

[Re(PF$_3$)$_5$]$_2$, cr. colrl., m. p. 182, volat., sol. in org. solv., alk. ⟶ dec. **[Tc(PF$_3$)$_5$]$_2$**, unstab., **{Re[P(OR)$_3$]$_5$}$_2$** [21]

MRe(PF$_3$)$_5$ H$_5$Re(PR$_3$)$_3$, mol. – dodecah. [16]

HRe$_3$(CO)$_{14}$ [16,20] **H$_3$Re$_3$(CO)$_{12}$, M$_2$[HRe$_3$(CO)$_{12}$] M$_2$[H$_3$Re$_3$(CO)$_{10}$] M[H$_4$Re$_3$(CO)$_{10}$]**, cluster-triangle **M$_2$Re$_4$(CO)$_{16}$ M$_2$[H$_2$Re$_4$(CO)$_{12}$]**

Tc —CO (*p*, *t*)→ M$_2$O$_7$; KMO$_4$ —HCl + H$_2$ (300°, *p*)→ [Re(CO)$_5$]$_2$

Re(NO)$_2$(PR$_3$)I$_2$ [19] **M(CO)$_5$Hal** [1,3] **[Re(CO)$_3$ClPy$_2$]** [14]

K$_4$[Re(CN)$_6$] · 3H$_2$O, M$_3$[Re(CN)$_5$(H$_2$O)]

K$_5$[Re(CN)$_6$], Re(N$_2$)Cl(CO)$_4$ [2] **[MI(CO)$_5$]** [1,14]

ReF$_3$(CO)$_3$ [ReCl$_3$(PEt$_3$)]$_2$, mol. cluster 2 crossing tetr. pyr. [ReCl$_3$PRe], Re—Re 2.22

Re —O$_2$ + MBr→ ReHal$_5$ —t→ Re

K$_3$[Re(CN)$_6$] · 3H$_2$O, grn. **K$_4$[M(CN)$_7$] · H$_2$O**, yel., diamagn., anion – pentag. bipyr. [17]

K$_2$[Tc(CN)$_6$], red. —KBH$_4$→ **K$_3$[Re(CN)$_6$] · 3H$_2$O**

Synthesis of Tc:
$^{92}_{42}$Mo ($^2_1$D$^+$, 2*n*) $^{92}_{43}$**Tc**; $^{92}_{42}$Mo ($^2_1$D, *n*) $^{92}_{43}$**Tc**
4.5 m. 2.7h.
(Perrier, Segre, 1937)
$^{235}_{92}$U ⟶ $^{99}_{43}$**Tc*** —γ→ $^{99}_{43}$**Tc** (in nature)
$2 \cdot 10^5$y.

● Re ● Hal ● O

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5+ (d^2)

6+ (d^1)

7+ (d^0)

Re_2O_5 (?), cr. bl., dec. 200;
+ H_2O ⟶ ReO_2↓ + $HReO_4$

Re (t)

cath. Red

$MReO_4$

TcO_3 | **ReO_3** [26]
cr. red with met. lustre (grn. in thin layers), sol. in conc. alk.

m. p. 160,
$\Delta H = -602$, $\xrightarrow{>400°}$ ReO_2 + Re_2O_7;
+ NaOH ⟶ ReO_2 + $NaReO_4$,
frame of oct.

H_2O (t)

$ReO_3 \cdot En$ = $[Re^{V}O_2En_2][Re^{VII}O_4]$

$[Re^{V}O_2][Re^{VII}O_4]$, "blue"

CO; M

Re (200°)

O_2 (160°)

O_2 (Ox. baking)

ReS_2 (in "molybdenite")

HNO_3

Tc_2O_7 [30]
yel., volat., hyg. not Ox. org. subst. (see Mn_2O_7 !), sol. in H_2O, alc., Et_2O, ac., Py
m. p. 120,
b. p. 311,
dec. 260,
$\Delta H = -1127$,
weak paramagn.

Re_2O_7 [26, 30)
m. p. 301, b. p. 362, dec. 600,
$\Delta H = -1234$,
colrl. $\underset{-80°}{\rightleftharpoons}$ yel. $\overset{t}{\rightleftarrows}$ dark
layers of tetrah. and oct. with common vertex. In gas – mol. –
2 tetrah. with common vertex, · **3 Py**.

H_2O (+Q)

160°

ReO_2F [37)

$[MO_2Py_4]X \cdot 2H_2O$
X = Cl, ClO_4 [28)

Rhenates (V)
$NaReO_3$, meta-, light yel.
$M_4Re_2O_7$, pyro-, M_3ReO_4, ortho-,
+ H_2O ⟶ $Re(OH)_4$↓ + $MReO_4$

$[R_4N][ReBr_4O(H_2O)]$, $(NH_4)_2[TcOCl_5]$

$TcOCl_3$, cr. brn., subl. 900
$TcOBr_3$, cr. brn., subl. 400.

5.85+,
$H_{0.15}ReO_3$↓, cr. golden, sol. in HNO_3, semiconduct.
$\xrightarrow{t}$ H_2O + ReO_{3-x} [26)

$[ReO_2(RCOO)_2]_2$

$BaTcO_4$, | **Rhenates (VI)**
Li_4ReO_5, Li_6ReO_6, M_2ReO_4, M = Na, K, Ba/2↓, cr. grn.;
+ H_2O ⟶ $Re(OH)_4$↓ + $MReO_4$

$HTcO_4$,
cr. red,
s. fade at dil.

$H_4Re_2O_9$ =
$[O_3Re{-}O{-}ReO_3(H_2O)_2]$,
cr. colrl., mol. – tetrah. and oct. with common vertex, ∠ReORe 179
strong ac., extr. $C_5H_{11}OH$
$H_2Re_2O_8 \cdot 3$ Diox, m.p. 110 [31)

HNO_3

M; ReO_2

$M^{I}O_2$ (t)

$HClO_4$; H_2SO_4

Pertechnates
$M[TcO_4]$,
KMO_4, m. p. 540, b. p. 1000

Perrhenates [10)
$Li_5[ReO_6]$, anioin – oct.,
$Ca_5Re_2O_{12}$, $M[ReO_4]$, colrl., sol. in H_2O < $MTcO_4$
m. p. 555, b. p. 1370
anions – tetrah.
M_3ReO_5, "mesoperrhenates", orange, anion – tetr. pyram. [33)

$TcOF_4$, m. p. 134, mol. – cycle $[TcOF_3F_{2/2}]_3$, Tc=O 1.66, Tc—F ≈ 1.8
$TcOCl_4$, m. p. ~ 35, $\xrightarrow{>-78°}$ Cl_2 + $TcOCl_3$

	m. p.	b. p.
$ReOF_4$, cr. bl. [27)]	108	172
$ReOCl_4$, cr. grn.-brn.	30	228
$ReOBr_4$, cr. bl.	dec.	>80

+ H_2O ⟶ $Re(OH)_4$↓ + $HReO_4$;
$\xrightarrow{t}$ Re + ReO_3Hal + Hal_2;
chains of oct. $[ReOF_3F_{2/2}]$-*cis*,
Re=O 1.65, in gas–mol., Re=O 1.66

$M[ReOF_5]$, [29)]
M = K–Cs,
cr. bl., grn.,
sol. in Et_2O, acet.
$M_2[ReOCl_6]$,
M = Rb, Cs;
+ H_2O ⟶
$M_2[Re^{IV}Cl_6]$ + $MReO_4$

H_2O

$K[ReOX_4]$, X = Cl, I, SCN, anion tetr. pyr.,
O – at the vertex, Re≡O 1.72
$M_2[ReOCl_5]$, M = NH_4, K–Cs, cr., yel-grn.,
anion oct., Re=O 2.09,
μ_{eff} = 0.4 [5)]

$ReOF_3$, cr. bk., unvolat.
$ReOCl_3$
$[ReOCl(RCOO)_2]_2$,
$[ReOCl_3(PPh_3)_2]$
$ReOX_3Dipy$,
X = Cl (grn., vlt.), Br (grn.), ClO_4 (bl.) [15)]

O_2; Bi_2O_3

	11,36)]	m. p.	b. p.
TcO_3F, liq. yel.		18	100
TcO_3Cl, liq. colrl.		–	25
ReO_3F, cr. yel.		147	164
ReO_3Cl, liq. colrl.		5	132
ReO_3Br, cr. colrl		40	163

mol. – tetrah., Re—O 1.70
ReO_3X, X = SO_3F, NO_3, RCOO

$M_2ReO_3F_3$, [32)] anion – oct.
$M_2ReO_3Cl_3$, M = K, Cs, $[R_4N]$,
$M[ReO_3Cl_2]$, **$M_2[ReO_3N]$**

	m.p.	b.p.
TcF_5, m. p. 50		
ReF_5, cr. yel.-grn., $\xrightarrow{t}$ MF_4 + MF_6	48	221
$ReCl_5$, cr. brn., $\xrightarrow{190°}$ $ReCl_3$ + Cl_2;	260 subl. 150	360

mol. – 2 oct., with common edge.
$ReBr_5$, cr. bl.-grn.; t⟶ $ReBr_3$ + Br_2;
M^{IV} + MO_4^- (H_2O)

$MTcF_6$
$MReF_6$,
cr. colrl., paramagn.

$PHal_3$ (−$PHal_5$, 20°)

TcF_6, cr. golden, m. p. 37, b. p. 55
$TcCl_6$, cr. grn., $\xrightarrow{20°}$ $TcCl_4$ + Cl_2

ReF_6, cr. yel., m. p. 19, b. p. 48, strong F–agent
$ReCl_6$, cr. grn., m. p. 22, stab. only in gas

v. react.
+ H_2O ⟶ $M(OH)_4$ + HMO_4 + HHal;
mol. – oct.

$ReNCl_3$, blk., nonvolat, μ_{eff} = 1.75 [28)]

$M_2[ReF_8]$, pink., anion – antiprism
$M[ReF_7]$, cr. yel., unstab.

H_2O

O_2

$S_2O_6F_2$

Re

TcO_2F_3, cr. yel., m. p. ~ 200, in str. chains $[TcO_2F_2F_{2/2}]$
ReO_2F_3, cr. yel., m. p. 90, b. p. 185
$ReO_2(SO_3F)_3$, cr. colrl.
$ReO_2(OTeF_5)_3$, mol. – trig. bipyr. [12), 13)]

$[R_4N][ReO_2(OTeF_5)_4]$-*cis* [12)]
$M[ReO_2F_4]$

$K_3[MO_2(CN)_4]$, *trans*-, orange, diamagn. (d^2!), anion – oct. (d^2sp^3) [6, 17)]
$M_2[ReO(OH)(CN)_4]$, vlt. [7)]

$K_2[Re(CN)_8]$, purp.

H_2O (−H_2)

O_2

$K_2[TcO(CN)_5] \cdot 4H_2O$ – yel. [17)]

$[N{\equiv}ReF_2(PR_3)_2]$, CN Re 5,
$[N{\equiv}ReCl_2(PR_3)_3]$, oct.

N_2H_4 + HHal + PR_3

N_2H_4 + KCN

$K_3[Re(CN)_8] \cdot H_2O$, brn., diamagn., anion – dodecah. (d^4sp^3) [8)]
$K_2[N{\equiv}Re(-NC\text{-}i)_4] \cdot H_2O$, pink, chains of tetr. pyr. $[Re(NC)_4N_{2/2}]$

Re_2O_7

$Cs[Re(NCS)_6]$

ReS; ReS_2 blk., subl. 1000, part of MoS_2 "molybdenite";
ReS_3 $\xrightarrow{H_2}$ **Re_2S_7**, blk., sol. in HNO_3, (H_2O_2 + MOH);
$M_2^{I}S_7$↓, pH sediment. Tc_2S_7 > Re_2S_7;
$\xrightarrow{t}$ MS_2 + S; **Re_2P, ReP, ReP_2, ReP_3**
TcC, TcC_2, $ReSi_2$

$ReOF_5$, cr. colrl., m. p. 41, b. p. 73, $\Delta H = -1229$, mol. – oct. [34)]

$[ReOF_4]^+X^-$ [18)]

ReF_7, cr. yel., m. p. 48, b. p. 72, $\Delta H = -1432$, mol. – pentag. bipyr.

$[ReF_6]^+X^-$, X = SbF_6, Sb_2F_{11} [35)]

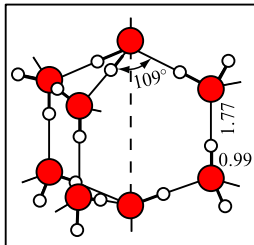
$M[ReOF_6]$, M = Cs, [NO], cr. grn. [12)]

$M[ReF_8]$, M = K, [NO], $[NO_2]$, cr. yel., anion Archimedes antiprism (d^5sp^2) [12)]

$K_2[Re(CN)_8(OH)]$

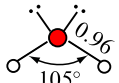
OXYGEN

2 – 1 – 1/2 – 1/3 –



“Ice mol.” $(H_2O)_8$

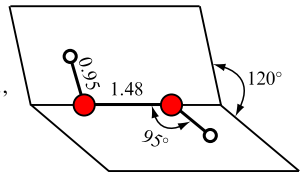
H_2O, water, liq., colrl., d^0 0.9999, d^{20} 0.9982, m.p. 0, b.p. 100, dec. 2000, $\Delta H = -286$, $\varepsilon = 81$, $\mu = 1.86$, $H_2O \rightleftarrows H^+ + OH^-$, $K = 10^{-16}$, $K_W = [H^+][OH^-] = 0.86 \cdot 10^{-14}$ (20°), pH = $-\lg[H^+]$; in gas — angular mol. (ψ-tetrah.), d^4 10000 > d^0 — ice. In str. of ice — O at. in site of hex. celle ZnS (wurtzite) type, dist. tetrah. $[OH_4]$ — form “ice mol.”



radiolysis ($-H_2$ $-O_2$)

PbS↓; I^- HNO_2; Fe^{2+}

H_2O_2, hydrogen peroxide, liq., bl., visc., d^{20} 1.450, m.p. –0.43 (prone to superfusion), b.p. 150 (vac.,) $\Delta H = -188$, $\varepsilon = 73$, $\mu = 2.1$, diamagn., in liq. — associates, extr. Et_2O, $H_2O_2 \rightleftarrows H^+ + HO_2^-$; $K = 10^{-12}$; $H_2O_2 \longrightarrow H_2O + O_2$ (quicly at pH > 7). H_2O_2 high purity stab. in conc. s. Inhibitors dec.: H_2SO_4, H_3PO_4, $Na_4P_2O_7$, cat. dec.: OH^-, M^{n+}, Pt, Cu, enzyme catalase. Strong Ox. **$Na_2CO_3 \cdot 1.5\,H_2O_2$, $Li_2O_2 \cdot H_2O_2 \cdot 2\,H_2O$** [13]



Mol. 2 intersecting ψ-tetrah.

an Ox; *hν* (UV); rectification of air

H_2 (500°, exp.; 20°, Pt)

H_2O_4, glass, diamagn., $\Delta H = -117$, dec. 30 [1]

anthraquinol (–anthraquinone); [H↑]; H_2 (in s.)

H_2 (Pd)

M (K – Cs) (pO_2)

E_2O_n M_2O_n M = Li–Cs, Ca–Ba (20°), Mg, Zn, Fe (*t*)

Comp. of hydroxonium [9)]
$[H_3O]^+X^-$, stab., X = AsF_6, SbF_6 (dec. 193 and 357), PtF_6, cation ψ-tetrah.
$[(H_3O) \cdot n\,H_2O]^+X^-$, n = 1 ($[H_5O_2]^+$), 2 ($[H_7O_3]^+$); $[H_{14}O_6]^{2+}$), 3 ($[H_9O_4]^+$ – pyram. $[O(H\cdots OH_2)_3]$)

$EO_m(OH)_n$, ac.

	–p*K*
m = 0, H_3BO_3,	10
weak ac.	
m = 1, HNO_3,	4
ac. middle parce	
m = 2, HPO_3,	2
strong. ac.	
m = 3, $HClO_4$	*K*=38

$M_2O_n \cdot xH_2O$, amphoteric
M = Al, Cr, Fe(III), V(V)

$M(OH)_n$, bases
M = K, (K = 3) Li (0.5), Ba (0.25), Mg (0.02), La (10^{-3})
In str. **$[Me_4N]OH \cdot H_2O$** – $[H_6O_4]^{2-}$ [11)]

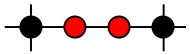
an Ox (–20°)

H_2O ($-H_nEO_m$)

$[M_{O_m}]^{n+} + OH^-$ $H^+ \longrightarrow$

H^+ OH^-

$H_x[E(O_2)_nO_m]$, peroxiacides
HNO_4, H_3PO_5, H_2SO_5, $H_2S_2O_8$, $H_4P_2O_8$,



Peroxides
$M_2^+[O_2]^{2-}$, M = Li–Cs, Mg–Ba/2, cr. colrl., diamagn., O—O 1.50 (1σ-bond.) **$\cdot 8\,H_2O$**, M = Na, Mg–Ba/2; + H_2O (surp.) $\longrightarrow$ H_2O_2 + MOH; strong. Ox (in melt.) + Fe $\longrightarrow$ M_2FeO_4

O_2 (p, t)

Superoxides
$M^+[O_2]^-$, M = Na–Cs, $[R_4N]$, Mg – Ba/2, cr., yel.-brn., paramagn., dec. 675(Na), –30(Mg), FeS_2 str. type (Na), CaC_2 (K – Cs); O—O 1.33, (1.5-bond.), v. strong Ox. + H_2O $\longrightarrow$ H_2O_2 + + O_2 + $M(OH)_n$

O_3 $-O_2$

Ozonides [2)]
M[O_3], M = Na–Cs, Sr, Ba/2, cr., red., sol. in H_2O (stab. at pH > 7), liq. NH_3; paramagn. in str. — layers of $[O_3]^-$, O—O 1.34–1.42, $+H_2O \xrightarrow{(H^+)} O_2 + MOH$

O_3 (freon)

MOH ($-H_2O$ $-O_2$)

O_3

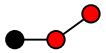
Peroxosalts [12)]
$K_2[Ti(O_2)(SO_4)_2]$;
$K_3[Nb(O_2)_4]$;
$K_2[Mo(O_2)_4]$,
$K_4[Zr(O_2)_4]$; $K_3[Cr^V(O_2)_4]$



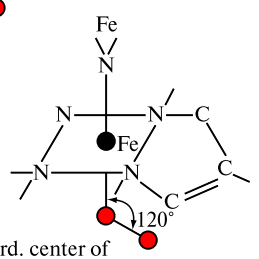
Oxygenyl compl. contain bidentate gr. $[O_2]$
O_2 attached irreversible **$[Pt(PPh_3)_2(O_2)] \cdot 1.5C_6H_6$**, O—O > 1.45
O_2 attached reversible **$[IrCl(CO)(PPh_3)_2(O_2)]$**, O—O ≤ 1.45
(“Waska compl.”) [5, 6, 9)]



Compl. whith monodentate gr.

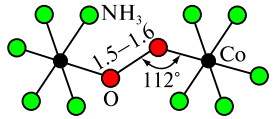


Hemoglobin, vitamin B_{12} (cobalomin), chlorophyll contain porphyrine cycle (with at Fe, Co, Mg respectively). In hemoglobin $[FeN_5]$ tetr. pyram., at the base 4 N at. of porphyrin cycle, at the vertex — N of histidine, the VI — vertex attached O_2 reversibly. [3, 10)]



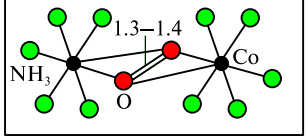
Coord. center of oxihemoglobin str. (by Pauling)

$\{[(NH_3)_5Co^{III}]_2(O_2)^{2-}\}^{4+}X_4$, peroxides, cr. brn., diamagn. [3, 10)]



HNO_3↓

$\{[(NH_3)_5Co^{III}]_2(O_2)^-\}^{5+}X_5$, superoxides, grn., paramagn.



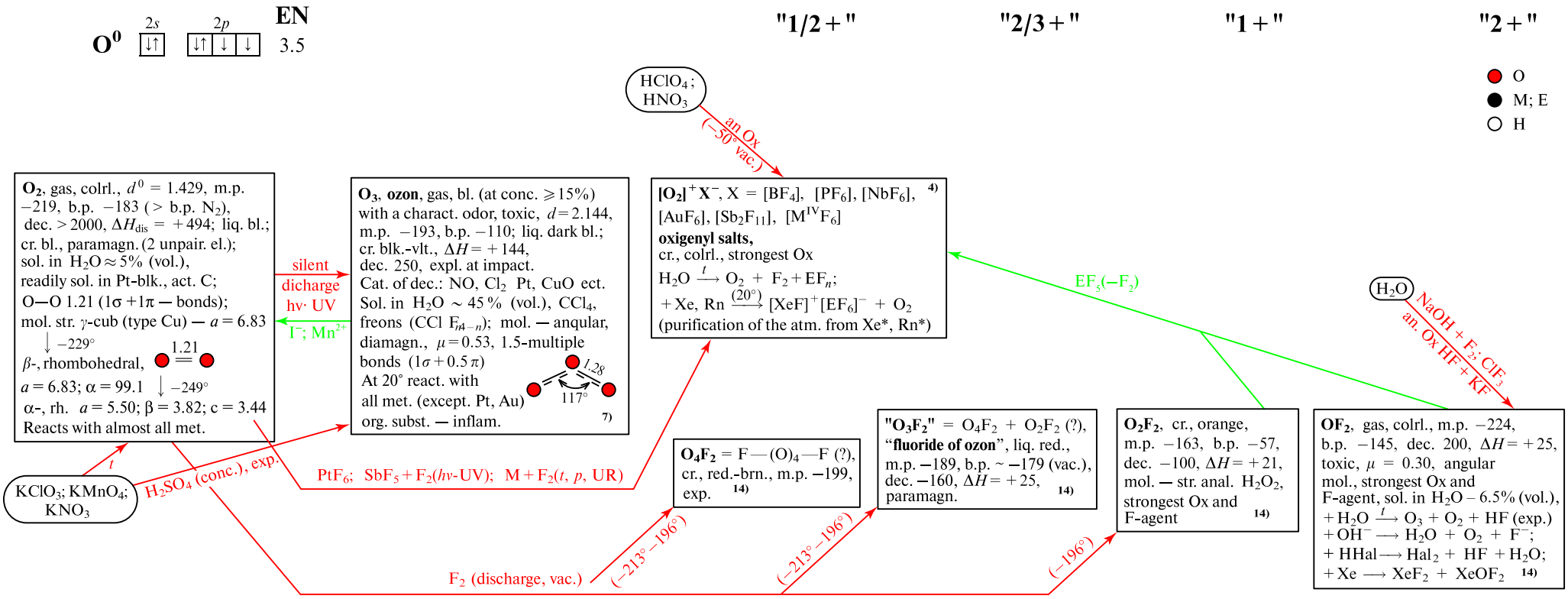
O_2

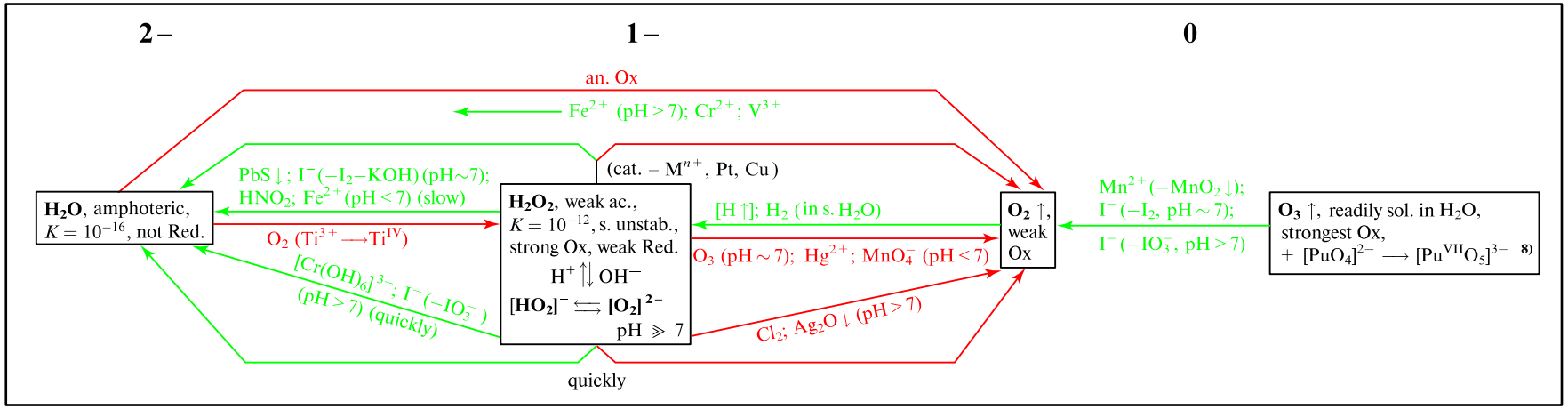
$[Co(NH_3)_6]^{2+}$

Oxides M_2O_n

		m.p.	b.p.
Ionic	+H_2O ⟶ $M(OH)_n$		
		Li_2O	1570	
		K_2O	740	
		anti-CaF_2 str. type		
		CaO	2614	
		BaO	1923	
		NaCl str. type		
Molecular	+H_2O ⟶ $E_2O_n \cdot x\,H_2O$			
		Cl_2O_7	–90	87
		Mn_2O_7	5.9	dec.
		mol. — 2 tetrah. whith common vertex		
		P_2O_3	24	175
		in str. — P_4O_6		
Polymer	not react with H_2O			
		BeO	2580	4260
		ZnO	1969 (*p*)	
		ZnS — wurtzite str. type		
		Al_2O_3	2072	~3500
		corundum str. type		
		FeO	1368,	NaCl
		TiO_2	1870	~3500
Met.-like				
		$MnO_{(1.0-1.13)}$		m.p. 1780
		NbO_2		2080

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_6, © Springer-Verlag Berlin Heidelberg 2011


O⁰
2s
2p
EN
3.5
"1/2+"
"2/3+"
"1+"
"2+"
O
M; E
H
O₂, gas, colrl., d⁰ = 1.429, m.p. −219, b.p. −183 (> b.p. N₂), dec. > 2000, ΔH_dis = +494; liq. bl.; cr. bl., paramagn. (2 unpair. el.); sol. in H₂O ≈ 5% (vol.), readily sol. in Pt-blk., act. C; O—O 1.21 (1σ +1π — bonds); mol. str. γ-cub (type Cu) — a = 6.83
↓ −229°
β-, rhombohedral, a = 6.83; α = 99.1
↓ −249°
α-, rh. a = 5.50; β = 3.82; c = 3.44
Reacts with almost all met.
1.21
silent discharge
hν· UV
I⁻; Mn²⁺
O₃, ozon, gas, bl. (at conc. ⩾15%) with a charact. odor, toxic, d = 2.144, m.p. −193, b.p. −110; liq. dark bl.; cr. blk.-vlt., ΔH = +144, dec. 250, expl. at impact. Cat. of dec.: NO, Cl₂ Pt, CuO ect. Sol. in H₂O ~ 45 % (vol.), CCl₄, freons (CCl F_{4−n}); mol. — angular, diamagn., μ = 0.53, 1.5-multiple bonds (1σ + 0.5 π) At 20° react. with all met. (except. Pt, Au) org. subst. — inflam. 7)
1.28
117°
HClO₄; HNO₃
an. Ox (−50°, vac.)
[O₂]⁺X⁻, X = [BF₄], [PF₆], [NbF₆], [AuF₆], [Sb₂F₁₁], [M^IVF₆] 4)
oxigenyl salts, cr., colrl., strongest Ox
H₂O —t→ O₂ + F₂ + EF_n;
+Xe, Rn —(20°)→ [XeF]⁺[EF₆]⁻ + O₂
(purification of the atm. from Xe*, Rn*)
EF₅(−F₂)
H₂O
NaOH + F₂; ClF₃
an. Ox HF + KF
KClO₃; KMnO₄; KNO₃
t
H₂SO₄ (conc.), exp.
PtF₆; SbF₅ + F₂(hν-UV); M + F₂(t, p, UR)
O₄F₂ = F—(O)₄—F (?), cr., red.-brn., m.p. −199, exp. 14)
"O₃F₂" = O₄F₂ + O₂F₂ (?), "fluoride of ozon", liq. red., m.p. −189, b.p. ~ −179 (vac.), dec. −160, ΔH = +25, paramagn. 14)
O₂F₂, cr., orange, m.p. −163, b.p. −57, dec. −100, ΔH = +21, mol. — str. anal. H₂O₂, strongest Ox and F-agent 14)
OF₂, gas, colrl., m.p. −224, b.p. −145, dec. 200, ΔH = +25, toxic, μ = 0.30, angular mol., strongest Ox and F-agent, sol. in H₂O – 6.5% (vol.),
+H₂O —t→ O₃ + O₂ + HF (exp.)
+OH⁻ ⟶ H₂O + O₂ + F⁻;
+HHal ⟶ Hal₂ + HF + H₂O;
+Xe ⟶ XeF₂ + XeOF₂ 14)
F₂ (discharge, vac.)
(−213° −196°)
(−213° −196°)
(−196°)


2−
1−
0
an. Ox
Fe²⁺ (pH > 7); Cr²⁺; V³⁺
PbS↓; I⁻(−I₂−KOH)(pH~7); HNO₂; Fe²⁺(pH < 7) (slow)
(cat. – M^{n+}, Pt, Cu)
H₂O, amphoteric, K = 10⁻¹⁶, not Red.
H₂O₂, weak ac., K = 10⁻¹², s. unstab., strong Ox, weak Red.
H⁺ ⇅ OH⁻
[HO₂]⁻ ⇌ [O₂]²⁻
pH ⩾ 7
O₂ ↑, weak Ox
Mn²⁺(−MnO₂↓); I⁻(−I₂, pH ~ 7); I⁻(−IO₃⁻, pH > 7)
O₃ ↑, readily sol. in H₂O, strongest Ox, + [PuO₄]²⁻ ⟶ [Pu^VIIO₅]³⁻ 8)
O₂ (Ti³⁺ ⟶ Ti^IV)
[H↑]; H₂ (in s. H₂O)
O₃ (pH ~ 7); Hg²⁺; MnO₄⁻ (pH < 7)
[Cr(OH)₆]³⁻; I⁻(−IO₃⁻) (pH > 7) (quickly)
Cl₂; Ag₂O↓ (pH > 7)
quickly

SULPHUR

2− | 2/n− | 1+ | 2+ | 3+

H_2 (pumice, 600°); HI (gas); C_nH_{2n+2}

O_2 (300°)

O_2 (−5% SO_3); H_2SO_4; HNO_3(*t*)

CO from blast gases (Al_2O_3)

H_2S, hydrogen sulphide, gas, colrl., toxic, with characteristic odour, m.p. −86, b.p. −60, dec. 300, $\Delta H = -20$, $\mu = 0.93$, $\varepsilon = 6$, solv. for org. subst.; $2H_2S$ (liq.) ⇄ $[H_3S^+] + [HS^-]$, $[H_3S^+][HS^-] = 10^{-33}$; angular mol., S—H 1.33, ∠HSH 92 (p^2), sol. in H_2O 75% (vol.), weak ac., $K_1 = 10^{-7}$, $K_2 = 10^{-14}$

S_nCl_2 (−HCl)

H_2S_n, $n \leqslant 35$, **polysulphanes**, oils, yel., ex. at pH ≪ 7, and in Et_2O, bz. s., visc. growing with *n*, m.p. −88 – −50 ($n = 2-5$) **H_2S_2** – str. anal. of H_2O_2, $\mu = 1.17$, S—S 2.05. $K_1 = 10^{-4}$, $K_2 = 10^{-6}$ [44]

H_2O

S_nCl_2

MOH | HCl (conc.)

MOEt (alc.)

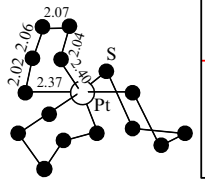
SbF_5 + HF

MCl_n; M_2O_n (*t*)

Hydrosulphides, cr., colrl., sol. readily in H_2O, alc., salt out from Et_2O s. **LiHS**, dec. 50 **NaHS**, m.p. 350, · ***n*** H_2O, $n = 2, 3$ (m.p. 22) **KHS**, m.p. 455 **$Ca(HS)_2 \cdot 6H_2O$**, dec. 15 **$Ba(HS)_2 \cdot 4H_2O$**

$[H_3S]^+[SbF_6]^-$, dec. 90, ψ-tetrah. cation [31]

M_2S_n, $n \leqslant 9$ [1, 10] **polysulphides**, cr., with icreases *n* colour: yel. → red. and stab. decreases; sol. in H_2O, alc. **$M_3[Cu(S_4)_n]$**, $n = 2, 3$ **$M_2[Pt(S_5)_3]$** **$M_2[Ag_2(S_6)_2)]$**



Fe[S_2], "pyrite"; [32] **Mn[S_2]**, "Mangankiese"

Sulphides M_2S_x

		m.p.	· ***n*** H_2O
Ionic	**Li_2S**	950	· ***n***
	Na_2S	1180	· **9**
	K_2S	840	· **5**
	Cu_2S↓	1130	
	Ag_2S↓	842	
Covalent + H_2O→$M(OH)_n$ + H_2S		m.p.	b.p.
	SiS_2↓	1090	1130
	Sb_2S_3↓	548	990
	Bi_2S_3↓	685(dec.)	—
	P_4S_5	288	514
	Al_2S_3	1120 (*p*)	—
	ZnS↓	1900 (*p*)	
	CdS↓	1475	
Metal-like	**TiS** **TiS_2** **TiS_3** **$Fe_{1-x}S$** **$CrS_{0.95-1.5}$**	Stab. in air, sol. in ac., conduct. (MS) or semiconduct. (MS_2, MS_3)	

$M_2S_n + O_2 \xrightarrow{t} M_2SO_4 \xrightarrow{t} M_2O_n + SO_2 + O_2$; $+ C \xrightarrow{t} M + CS_2\uparrow$

M; E; M_2O_n (*t*)

K (20°); Na (liq. NH_3)

H_2; C (*t*)

M_2SO_4

S, cr., yel., $d = 2.1$, m.p. 119, b.p. 445, readily sol. in CS_2, turpentine, sol. in bz., CN S 2 [11]

α-, rhomb., $d = 2.07$, m.p. 113, $a = 10.46$, $b = 12.86$, $c = 24.49$, str.: crown mol. S_8, S—S 2.06, ∠SSS 108.



slow

95°

β-, monocl., $d = 1.96$, m.p. 119, $a = 10.90$, $b = 10.96$, $c = 11.02$, $\beta = 83$, str.: mol. S_8

Amorph. (plastic)

λ	+	**μ**
yel., over-cooled liq., sol. in CS_2		brn., polymer (chain of S_n), insol. in CS_2

119°

λ-, liq., yel., transparent, > 159° – brn., max. visc. at 200°, $S_8 \rightleftarrows S_7 \rightleftarrows S_6 \rightleftarrows S_4$

rapid cooling

−80°

Purple, str.: paramagn. mol. S_2 (el. anal. of O_2)

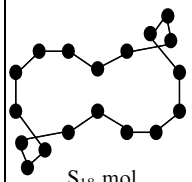
−180° (rapidly)

445°

Vapour

$S_8 \rightleftarrows S_7 \rightleftarrows S_6 \overset{650°}{\rightleftarrows} S_4 \overset{900°}{\rightleftarrows} S_2 \overset{1500°}{\rightleftarrows} S$

orange red yel.



Cycles S_n, cr., orange (S_6) — yel. (S_{20}), $d = 2.02-2.09$, m.p. 39 (S_7), 50 (S_9), 148 (S_{12}), 128 (S_{18}), 124 (S_{20}); S_{10} dec. ~60, str.: nonplanar cycles [33]

S_{18} mol.

$S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

$S_2O_6F_2$; AsF_5; $SO_3 + H_2SO_4$

S_nO, $n = 6-10$, yel., sol. in CS_2, −20° ↓ (*hν*-vis) SO_2 + S; chains of S_n cycles



2)

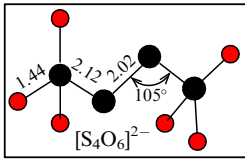
$SOCl_2$ | H_2S_n

(1.7–3.3) + **$H_2S_nO_6$**, $n = 20-13, 6, 5, 4, 3$, **polythionic ac.**, strong, ex. only in s., *n* and stab. increases with [H_2S]:[SO_2]

20° ⟶ S↓ + SO_2 + H_2SO_4 (slow.) [24]

H_2S + H_2O (many)

$HClO_4$ (−$KClO_4$↓)



$M_2S_nO_6$, polythionates, cr., colrl., stab. in s., decreases with increasing *n*; anion: 2 [SO_3S] tetrah., linked zigzag $(S)_{n-4}$ chain [24]

$K_2S_6O_6$ $K_2S_5O_6$ $K_2S_4O_6$ $K_2S_3O_6$

S_2Cl_2 | SCl_2 | I_2 | SO_2; H_2O_2

S_2O (∼"SO"), gas, colrl., stab., < −196° – cr., orange, $\Delta H = -96$, $\mu = 1.47$, does not react with O_2, angular mol. [27]

SO_2 Glow discharge

H_2O

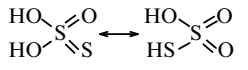
$H_2S_2O_2$, thiosulphorous ac., > 20° ⟶ H_2S + S + + SO_2

SO_2

H_2S

HSO_3Cl

$H_2S_2O_3$, thiosulphuric ac., $K_2 = 10^{-2}$, liq., oily, −78° ⟶ $H_2S + H_2S_3O_6$ ⟶ ⟶ S↓(orange) + H_2SO_3 + + H_2SO_4



$H_2S_2O_4$, ditionous ac., ex. in s., $K_1 = 0.5$, $K_2 = 10^{-3}$; ⟶ S↓ + H_2SO_3

O_2

HCl

Thiosulphates **$Na_2S_2O_3$**, 100° ← · **$5H_2O$** (m.p. 48); 200° ⟶ Na_2S_5 + Na_2SO_4 **$K_2S_2O_3$**, dec. 430, · ***n*** H_2O, $n = 0.5$; 1.67(−H_2O, 180°) **$BaS_2O_3 \cdot H_2O$**↓ **$M_3[Ag(S_2O_3)_2]$**, $[SO_3S]^{2-}$ tetrah.

Dithionites **$Na_2S_2O_4 \cdot 2H_2O$** **ZnS_2O_4**; **CoS_2O_4**, anion $[O_2S—SO_2]^{2-}$: 2 intersecting [SO_2S] ψ-tetrah. , $[S_2O_4]^{2-}$ ⇄ $2SO_2^-$, strong Red.

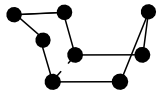
$NaHCO_3$ (−Na_2SO_3−CO_2)

H_2SO_2, sulphoxylic ac.,

$S(OH)_2 \rightleftarrows HO—S(=O)H$

$CoSO_2 \cdot 3H_2O$, **$NaHSO_2 \cdot HCHO \cdot 2H_2O$**, m.p. 63, "rongalit", Red.

$[S_n]^{2+}(AsF_6)_2^-$, $n = 16, 19$, cr., red, cation $[(cyclo\text{-}S_7)_2S_5]^{2+}$ **$[S_8]^{2+}X_2^-$**, X = HS_2O_7, $AlCl_4$, AsF_6, Sb_2F_{11} **$[S_8][HS_3O_{10}]_2$** (∼"S_2O_3"), cr., bl., sol. in oleum; −15° ⟶ S + SO_2 + SO_3; + H_2O ⟶ S + $H_2S_nO_6$ + + H_2SO_4; [3]



$[S_8]^{2+}$

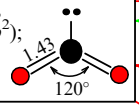
↓ O_2 (immed.)

$[S_4]^{2+}X_2^-$, cr., yel., square cation

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_7, © Springer-Verlag Berlin Heidelberg 2011

4+

SO_2, gas, colorl., with a pungent odour, m.p. −75, [37] b.p. −10, dec. 2500, $\Delta H = -297$, sol. in H_2O 98% (vol.), ε = 13; liq. SO_2 sol. N_2, $MHal_n$, org. subst., μ = 1.63, angular mol. (ψ-triangle [:SO_2], sp^2); strong Red., weak Ox: + H (Pd) ⟶ H_2S; · **7⅔ H_2O** (6 : 46) – clathrate



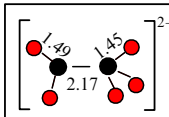
O_2 (t; Pt, V_2O_5, Ag_3VO_4); O_3

> 400° (−O_2)

O_2 (−Fe_2O_3)

FeS_2

NaHSO₃ (dry)



$M_2S_2O_5$, pyrosulphites ("metabisulphites"), M = Na–Cs, $\xrightarrow{20°}$ SO_2 + M_2SO_3 [4] **$Na_2S_2O_5 \cdot H_2O \rightleftarrows 2\,NaHSO_3$**

NO_2 + H_2O (−NO)

S; Cu(*t*); HI; H_2S

Sulphurous ac. ("H_2SO_3")

$SO_2 + H_2O \rightleftarrows SO_2 \cdot n\,H_2O \rightleftarrows H^+ + HSO_3^- \rightleftarrows 2\,H^+ + SO_3^{2-}$,

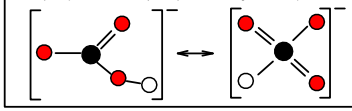
$K_1 = \dfrac{[H^+][HSO_3^-]}{[SO_2]_{eq.}} = 10^{-2}$, $K_2 = 10^{-7}$; Red.

$[SO_2]_{eq.} = [SO_2]_{gen.} - [HSO_3^-] - [SO_3^{2-}]$; $\xrightarrow{150°}$ S↓ + H_2SO_4

Hg; Zn

M_2CO_3 (0°)

$MHSO_3$, hydrosulphites, M = Na, K, Cs (cr.); Li, Ca/2 (ex. only in s.)



t

MnO_2

$H_2S_2O_6$, dithionic. ac., strong, ex. in s., stab. to Ox.

H_2SO_4

Ditionates $M_2S_2O_6 \cdot 2\,H_2O$, M = Li, Na **$K_2S_2O_6$** **$M^{II}S_2O_6 \cdot n\,H_2O$**, M^{II} = Ca, Sr (n = 4), Ba (n = 2), Mn, all salts sol. in H_2O, anion – $[O_3S—SO_3]^{2-}$ – 2 intersecting tetrah. [58]

O_2

Sulphites

Li_2SO_3, dec. 455

Na_2SO_3 $\xleftarrow{33°}$ **$\cdot 7\,H_2O$; $K_2SO_3 \cdot 2\,H_2O$**

$CaSO_3 \cdot 2\,H_2O$↓; **$BaSO_3$**↓

$\xrightarrow{600°}$ M_2S + M_2SO_4, readily sol. in H_2O

$[:SO_3]^{2-}$ – ψ-tetrah., strong Red.

$HSO_2F \rightleftarrows$ HF (liq.) + SO_2 (liq.), fluorsulphine ac., m. p. −84

POHal₃

SO_2 MF

MSO_2F, M = Na–Cs, $\xrightleftharpoons{20°}$ MF + SO_2↑, soft F-agents: + $(PNCl_2)_3$⟶ ⟶ $(PNF_2)_3$ + MCl + SO_2

Thionilhalides	m.p.	b.p.	ΔH	μ
SOF_2, gas, colrl.	−129	−44	−711	1.62
SOFCl, gas, colrl.	−137	+12	—	—
$SOCl_2$, liq., colrl.	−100	+76	−247	1.44
$SOBr_2$, liq., orange	−52	138 dec.	−75	1.47

$\xrightarrow{t}$ SO_2 + S_2Hal_2 + Hal_2; mol. [:$SOHal_2$] – ψ-tetrah. [54]

PHal₅ (−POHal₃)

F_2 (Pt); Cl_2 (camphora)

SO_2

	m.p.	b.p.
$S_2O_5F_2$, liq., colrl.	−48	51
$S_2O_5Cl_2$, liq., colrl.	−37	–

Sulphurilhalides, colrl. [38]

	m.p.	b.p.	dec.	ΔH	μ
SO_2F_2, gas	−137	−51	400	−856	1.11
SO_2FCl, gas	−125	+7	—	—	—
SO_2Cl_2, liq.	−54	69	300	−393	1.80
SO_2FBr, liq.	−86	40	—	—	—

SOF_4, gas, colrl., m.p. −100, b.p. −49, mol. – trig. bipyr., 300°⟶$SF_6 + SO_2F_2$ [7]

$[SOF_3]^+[AsF_6]^-$ [8]

$Cs^+[SOF_5]^-$, $\xrightarrow{210°}$ SF_6 + O_2 + …

H_2O

KHF_2; CH_2Cl_2 [36]

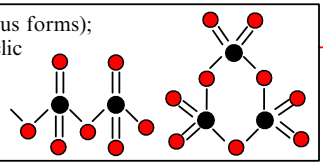
H_2O (−HHal)

HHal

SO_3 MHal (*t*)

6+

SO_3, cr., wh., silky, m.p. 17–145 (various forms); ΔH = −395 (gas); −462 (β). In str. – cyclic trimers or chains of tetrah. [SO_4] (sp^3). In gas – SO_3 – triangle, S=O 1.41, ∠OSO 120 (sp^2); strong Ox.



O_3

S_2O_7, m.p. 0, subl. 10

3° (−O_2)

SO_4, m.p. 3 (dec.), + H_2O ⟶ [O]; + Mn^{2+} ⟶ $HMnO_4$

SO_2 O_2 (glow discharge)

$Na_2S_2O_7$; $Fe_2(SO_4)_3$ *t*

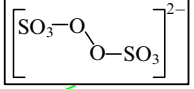
H_2SO_4

$M_2S_3O_{10}$, trisulphates, M = M^I, $M^{II}/2$, [ClO_2], [S_8]/2, [NO_2]

$H_2S_2O_7$, di(pyro)sulphuric ac., cr., colrl., hyg. m.p. 35

an. Ox.

$H_2S_2O_8$, persulphuric ac., cr., m.p. 65 (dec.), strong ac., Ox.



an. Ox.; H_2O_2 (100%)

H_2SO_5, Caro ac., cr., colrl., hyg., m.p. 7 (dec.), in s. stab. > $H_2S_2O_8$, $K_2 = 10^{-10}$, sol. in Et_2O, + H_2O ⟶ H_2SO_4 + + H_2O_2, v. strong. Ox, + bz. ⟶ exp.

H_2O SO_3

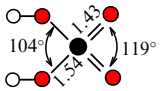
Pyrosulphates, $M_2S_2O_7$, M = Na, K, anion – 2 tetrah. with a common vertex

H_2SO_4, ulp c ac., oil, colrl., v. hyg., ("monohydrate"), m.p. 10, b.p. 340 (dec.),

$2\,H_2SO_4$ (100%) $\rightleftarrows [H_3SO_4]^+ + [HSO_4]^- \rightleftarrows [H_3O]^+ + [HS_2O_7]^-$;

$K = 10^{-4}$ $K = 10^{-5}$

ε = 100 (25°), solv. $M_2(SO_4)_n$, strong Ox., in gas – mol. – dist. tetrah. (sp^3); **· H_2O**, n = 1 – 4, 6, 5 (m.p. −84), 8 (−110°); b.p. of azeotrope (98% H_2SO_4) 337;



H_2SO_4 $\xrightleftharpoons{H_2O}$ $[H_3O]^+ + [HSO_4]^- \rightleftarrows 2\,[H_3O]^+ + [SO_4]^{2-}$, (< 100%) strong ac., $K_2 = 10^{-2}$ [34]

H_2O

$M_2S_4O_{14}$, $[O_3S—OSO_2—O—]_2^{2-}$

SO_3

$M_2S_2O_8$, persulphates, M = K, NH_4, Ba/2 (· 4 H_2O), $\xrightarrow{100°}$ $M_2S_2O_7 + O_2$ $[O_3S–O–O–SO_3]^{2-}$

$MHSO_5$, ↓ H_2O O_2 + $MHSO_4$, [39] $[SO_4—OH]^-$ (1.46)

an. Ox

Hydrosulphates [25]

$NaHSO_4$ (m. p. 186); **· H_2O** = Na[H_3O][SO_4]

$KHSO_4$ (m.p. 210, "mercallit");

[H_3O] HSO_4] = "$H_2SO_4 \cdot H_2O$";

[NO] HSO_4], "nitrososulphuric ac."

H_2SO_4 MOH

Sulphates

Na_2SO_4, m. p. 884, b. p. 1430; **· 10 H_2O**, "Glauber salt"

K_2SO_4, m. p. 1076, b. p. > 2000; **$BaSO_4$**↓, m. p. 1580

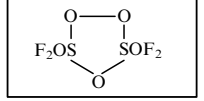
$MgSO_4$, dec. 1155; **· 7 H_2O**, "Epsom salt"

$CaSO_4$↓, m. p. 1450; **· 2 H_2O**, "plaster stone";

$CuSO_4$, dec. 650; **· 5 H_2O** ("vitriol");

$[SO_4]^{2-}$ – regular tetrah. (sp^3); S—O 1.48, not Ox, mol. M_2SO_4 (M = K–Cs) ex. in gas.

$S_2O_5F_2$, liq., colrl., m.p. −95, b.p. 35



SO_3F_2 = $(FO)SO_2F$ [39]

SO_4F_2, yel. g., b.p. 0, dec. 50, [FSO_2OOF]

Halogensulphonic. ac., HSO_3Hal,

Hal = F, Cl, Br; liq., colrl. (F, Cl); yel. (Br); m.p. −87, b.p. 169 (F); m.p. −80, b.p. 152 (Cl); m.p. −7(dec.) (Br)

HSO_3F – strongest ac., stab., F-agent

MSO_3F, M = Li, K, XeF^+, $[Sb_4]^{2+}$ **$Ba(SO_3F)_2$**, **$Cs[M(SO_3F)_n]$**, **MSO_3Cl**, unstab.; **$M^{II}(SO_3Cl)_2$** [12] **$H[SbF_2(SO_3F)_4]$**, most strong ac.

$S_2O_6F_2$, liq., colrl., m.p. −55, b.p. 67, $(FSO_2—O—)_2$, strong F-agent

120° ↓↑

SO_3F, brn., dec. 200 [23]

F_2, XeF_2

SO_3

SF_5Cl

$S_2O_2F_{10}$, liq., colrl., m.p. −95, b.p. 49, dec. 200, $(F_5—S—O–)_2$

O_2 $h\nu$(vis)

SULPHUR HALIDES

1+ 2+ 3+ 4+

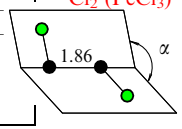
$S_n\Gamma_2$, Hal = Cl – I,[40] $n \leqslant 100$, **halogensulfanes**, oils or sld., orange

H_2; H_2S_n ⟷ 20° (–S)

	m.p.	b.p.	ΔH
S_2F_2, gas, colrl.	–133	–15	–227
S_2Cl_2, liq., colrl.	–80	138	–58
S_2Br_2, liq., red, d = 2.63	–40	57/0.2	–17
	dec. 90	—	—
S_2I_2, cr., brn.	dec. 30	—	—

Str. anal. of H_2O_2, strong. Hal-agents; S_2Cl_2 solv. of S, I_2, $MHal_n$, org. subst; + $H_2O \longrightarrow H_2S_2O_3$; $S_2Cl_2 \cdot n\,AlCl_3$

20° (slow., $-Cl_2$) ⟷ Cl_2 ($FeCl_3$)

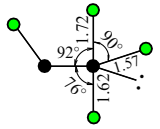


$[S_7I]^+AsF_6^-$, cr., orange, in cation cycle S_7 [35]

$[I_2]AsF_6$ ⟷ AgF; Cl_2 (defic.); Br_2 (surp.)

S

	m.p.	b.p.
$(SF_2)_2$, liq., bl.	–98	39
SCl_2, liq., red	–125	60 (dec.)

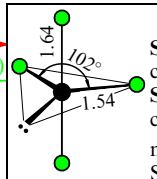


[43]

$[S_2I_4]^{2+}(AsF_6)_2^-$, cation – trig. prism. [35]

Cl_2 (liq.) ⟷ HF (gas) > –30°

$I_2 + AsF_5$ (liq. SO_2); F_2(–190°); $Cl_2 + NaF$; $Hal_2 + EHal_n$



	m.p.	b.p.	ΔH
SF_4, gas, colrl., toxic	–121	–37	–769
SCl_4, cr., colrl.	–34 (dec.)	—	–54

mol. – ψ-trig. bipyr.; $SF_4 + M_2O_n \longrightarrow MF_n$; + $H_2O \longrightarrow SO_2$ + HHal;

$EHal_n$ ⟷ MF

$[SF_3]^+[BF_4]^-$
$[SCl_3]^+[AlCl_4]^-$
$[SBr_3]^+[SbHal_6]^-$, yel., cations – ψ-tetrah., [5, 22, 45]

$M^+[SF_5]^-$, [6] M = Cs, $[R_4N]$, anion – ψ-oct.

SULPHUR NITRIDES

2+

0.28+ $Na^+[S_7N]^-$, cr., grn.

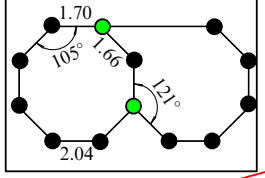
Na (–H_2)

(0.25–0.66)+ $S_n(CN)_2$, n = 3 – 8, **cyansulfanes**, m.p. 93 (n = 3), 39 (n = 6), str. anal. S_nHal_2

0.57+ [41] $[S_7N]^+[HSO_3]^-$, cr., red

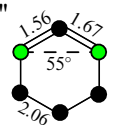
(0.31–0.4)+ $(S_7N)_2S_n$, m.p. 137 (n = 1), 98 (dec.) (n = 2), 97 (n = 3), 16 (n = 5), sol. in CS_2, not hydr., mol. 2 cycles connected of chain S_n

0.54+ $S_{11}N_2$, m.p. 150 (dec.), sol. in CS_2, (α, β) [14]



S_nCl_2(–2 HCl)

1.5+ [13] S_4N_2 (earlier "S_5N_2"), cr., red, m.p. 23 (–80° light-yel.), distil. in vac., sol. in org. solv., 100° – exp., μ = 1.74, mol. – "half-chair"



CS_2 + NH_3

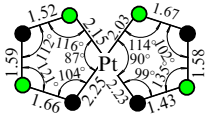
S_2Cl_2

2+ $[S_2N]^+[ЭГ_6]^-$, cr., yel., gr. [S—N—S] – linear, [17]

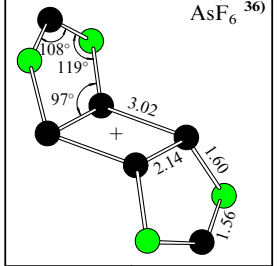
[SN][AsF_6] ⟷ S

NaR (–RH) ⟷ $Na_4^+[S_4N_4]^{4-}$ **LiAl**$[S_4N_4]$

$M^{II}[S_2N_2H]_2$, M^{II} = Ni, Co, Pt, Pd stab. in air, $\mu_{eff.}$ = 1.9 (Co), 0 (Ni) mol. is planar



2.3+ $[S_6N_4]^{2+}X_2^-$, X = $FeCl_4$, SO_3F, AsF_6 [36]



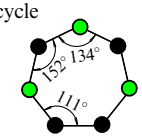
HSO_3Cl

$[S_3N_2]X$, X = Cl, AsF_6, [15] cation planar

$M^{II}[S_2N_2]$, M^{II} = Cu, Pb, Fe, Co, Ni, cr., with intensive colour, sol. in org. solv., paramagn. (M^{II} = Fe, Co (2 and 1 unpair. el. [16]

2.66+ $S_3N_2Cl_2$

2.5+ $[S_4N_3]^+X^-$, X = Cl (cr., yel., dec. 170), Br, I, NO_3, SCN, HSO_4, cation planar 7-member cycle



2.67+ $M^+[S_3N_3]^-$, M = K–Cs, exp., anion. – 6-member planar cycle [30]

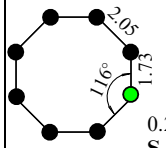
2.75+ $M^+[S_4N_4]^-$, stab. < –25°, anion paramagn.

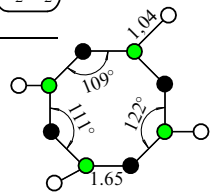
cath. Red., K + THF

S_2Cl_2; HHal ⟷ NH_3 + SCl_2

S_4N_4

Imides $S_n(NH)_{8-n}$





0.28+ S_7NH, m.p. 113	0.66+ $S_6(NH)_2$, 3 isomers: (1, 3), (1, 4) and (1, 5), S—S 2.05, S—N 1.67–1.72 [19]	1.2+ $S_5(NH)_3$ 2 isomers: (1, 3, 5) and (1, 3, 6)

2+ $S_4(NH)_4$,

$S_n(NH)_{8-n}$, mol. – 8-members rings – "crowns" (4 at. in parallel planes, look S_8!), cr., colrl., at. H easily substit.

0.5+ **M**$[S_4N]$, cr., purp., stab. in air, anion – chain of $[S_2NS_2]$ [42]

0.66+ **M**$[Cu(S_3N)_2]$, in anion – 5-member ring $[CuS_3N]$

NH_3 (liq.)

S, S_2Cl_2

$SnCl_2$

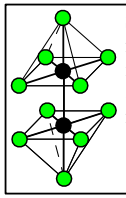
$M(CO)_m$–MCl_2

$Fe(CO)_5$

$Fe^{II}[S_4N_4]$, cr., blk., dec. 100, solv. in Py, ↓ + H_2O $Fe(OH)_3$

● S
● N, Hal
○ H

5+



S_2F_{10}, liq., colrl., v. toxic, m.p. −53, b.p. 29, $\Delta H = -2134$, inert at 20°, not react. with H_2O, alk., strong F-agent (*t*), mol. – 2 tetr. pyram., S—S 2.2

H_2 (*hv*-vis) ⟵ ⟶ HaI_2

6+

	m.p.	b.p.	dec.	ΔH	μ
SF_6, gas, colrl.	−50 (*p*)	−64 (subl.)	800	−1226	0
SF_5Cl, gas, colrl.	−64	−19	—	—	1.58
SF_5Br	—	−116	—	—	—

mol. – oct. (sp^3d^2), passiv., not react. with O_2, ac., alk.; + HI (gas) ⟶ HF + H_2S + I_2;
$SF_6 \cdot 17\,H_2O$, clathrate [21]

SF_5OOX, X = H, SO_2F, COF, CF_3, SF_4OSF_5 [20]

F_2(20°)
Cl_2 + CsF (−CsCl)
OF_2

S
SF_4

$(SF_5)_2O$, liq., colrl., m.p. −155, b.p. 31, mol. – 2 oct. with common vertex
$[SF_5]^+X^-$, X = OF ("SOF_6", m.p. −86, b.p. −35); OCl, CF_3, $SO_4/2$ [9]

H_2O (−80°) ⟶

$H[OSF_5]$, cr., subl. – 65
$M[OSF_5]$, M = Cs, Xe/6, W/6 [46]

[x] Ox-state of S calculated on the assumption of formal Ox-states of N 3− and H 1+

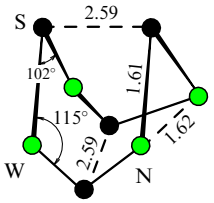
● S
● F, N

3+

$(SN)_x$, **polythiasyl**, golden fibres (bl. in thin layers), exp. ~ 240°, subl. vac. 135, insol. in H_2O and org. solv., dec. of alk., str.: zigzag chains, S—N 1.59 и 1.63; ∠SNS 119.9, ∠NSN 106.2; paramagn., conduct. (delocalization of π-el. along of chain) [28]
· ***n*** **HaI_2** (*n* = 0.04 – 0.4) – canal comp. inclusion, conduct.

124–139°

S_4N_4↓, **cyclotetrathiazyl**, **thiazen**, cr., golden, (−100° colrl., >100° red), *d* = 2.2, m.p. ~ 180, subl. 130/0.1, exp. 130°, ΔH = + 460, sol. in bz., CCl_4, μ = 0.72; in mol. – square [N_4], over and under – at 2 at. S, they form dist. tetrah.
+ $H_2O \xrightarrow{t} NH_3 + S_3O_6^{2-} + S_2O_3^{2-}$; + HI ⟶ H_2S + + NH_3 + I_2; · ***m*** **$EHal_n$**, E = B, Sn, Sb, S, Se, Ti, Nb, W



(300° ⟶ −80° vac., AgF_2)

S_2N_2, cr., colrl., volat.; sol. in Et_2O.; exp. 30°; 20° ⟶ S_4N_4 + $(SN)_x$, mol. – square [29]
· **$SbCl_5$**

NH_3(−CCl_4)
S_2Cl_2

2.67+ **$K[S_3N_3]$** anion – plane cycle [29]

$M^I_3[S_2N_3]$, cr., yel., exp.
$Na[H_2S_2N_3]$, cr., brn.

MNH₂

$S_2N_3H_3$, HN=S=N—S—NH_2, amidoimidonitride, sld., red, in liq. NH_3 – monobasic ac., + Pb^{2+} ⟶ PbN_2S_2 + $S(NH_2)_2$

3.6+ **S_5N_6**, cr., yel., exp., subl. 45/10^{-2}; mol. – basket [55]

3.2+ **$[S_5N_5]^+X^-$**, 3.5+ **$[S_4N_4]^{2+}X_2^-$** **thiazile salts**; cations – plane 10- or 8-membered rings [50]

3.5+ **$M[S_4N_5]$**, cr., yel., exp., N – in middles of edges of tetrah. [S_4], [52]

$[S_4N_5]^+X^-$ [56]

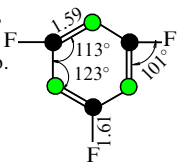
AgF_2 (CCl_4)
Cl_2
HgF_2 (CCl_4); Br_2

$S(NSiMe_3)_2$

AgF_2

$(NSF)_4$, needles, colrl., m.p. 153, mol. – 8-membered rings

	m.p.	b.p.
$(NSF)_3$, cr., colrl.	74	93
$(NSCl)_3$, yel.	163	—
$(NSBr)_3$, red	—	—
$[N_3S_3F_2]^+X^-$		[18]



NSF_3, gas, colrl., b.p. −73, passiv., not hydrol.; + $H_2O \xrightarrow{t}$ HF + HSO_3NH_2; μ = 1.91, mol. – tetrah., S≡N 1.42

4+

Thiasylhalides
NSF, gas, colrl., hygr., m.p. −79, b.p. 5; + H_2O ⟶ NH_4F + SO_2 (immed.), μ = 1.90
NSCl, gas, yel.-grn., v. unstab. (semiproduct in synthesis of S_4N_4), angular mol.
$[Co(NSF)^0_6][AsF_6]_2$ [53]
NSBr



Cl_2 + CsCl

NH_4Cl (−S)
S_2Cl_2

cyclo-(−NH−S=NH)$_3$, diimide

	m.p.	b.p.
N≡SF_2Cl	—	—
$F_2N—SF_5$	−110	−16
$F_2N—OSF_5$	−139	−10
$F_2N—OSO_2F$	−129	−2
$F_2N—SO_2F$	−111	−18
$Cl_2N—SF_5$	—	80
ClFN—SF_4	—	25
HN(F)—SF_5	−71	25
FN=$(SOF_2)_2$	−80	−61
FN=SF_4	−99	−13

[47]

Oxonitrides

2.66+	3.33+	4+ [51]	5.33+ [54]
S_3N_2O, liq., red, O=S=(N=S)$_2$	**$S_3N_2O_2$**, cr., yel., m.p. 101, S=(N=S=O)$_2$	**$S_4N_4O_2$**, mol. – cycle	**$S_3N_2O_5$**, cr., colrl., subl., in mol. – 6-membered cycle O[S(O)$_2$N]$_2$S

$SOCl_2$
NH_3
NaN_3
S_4N_4
SO_3

Sulfanurhalides, [−N=S(OCl)]$_3$

		m.p.	b.p.	μ
$(NSOF)_3$, liq., colrl.	α-	17	138	—
	β-	13	130	—
$(NSOCl)_3$ cr., colrl.	α-	145	—	3.9
	β-	48	—	1.9

mol. – 6-membered cycles (α-"armchair", β-"bath") [49]

4+ **K[NSO]**, thionitrite (tiasat), cr., colrl., exp., m.p. 190

3.3+ **$M[S_3N_3O]$**, **$M[S_3N_3O_2]$**, bl.-vlt.
$M[S_4N_5O]$, anions – cycles
$M_3[ON(SO_3)_2]$, nitrosodisulphonate [57]

$Hg[NSOF_2]_2$ [48]
$Ag_4[SO_2N_2]$, sulphamide, anion – [N—S(O)$_2$—N]$^{4-}$

SELENIUM, TELLURIUM, POLONIUM

"2/*n*; 2+"

4+

Formation of Po in the nuclear decay

$^{238}_{92}U \xrightarrow{\alpha} \ldots {}^{218}_{84}Po \xrightarrow[3.05\ m.]{\beta,\gamma} {}^{214}_{83}Bi \xrightarrow{\beta,\gamma} {}^{214}_{84}Po$ 1.45 · 10⁻⁴ s.

$^{210}_{83}Bi \xrightarrow{\beta,\gamma} {}^{210}_{84}Po$ 7 · 10⁻⁹ % in U–are 138.4 d.

$^{235}_{92}U \xrightarrow{\alpha} \ldots {}^{215}_{84}Po \xrightarrow[1.8\cdot10^{-3}\ s.]{} \ldots {}^{211}_{84}Po \xrightarrow[5\cdot10^{-3}\ s.]{} \ldots$

$^{232}_{90}Th \xrightarrow{\alpha} \ldots {}^{216}_{84}Po \xrightarrow[0.158\ s.]{\alpha} \ldots {}^{212}_{83}Bi \xrightarrow{\beta,\gamma} {}^{212}_{84}Po$ 3 · 10⁻⁷ s.

Synthesis:

$^{209}_{83}Bi(n,\gamma)\ ^{210}_{83}Bi \xrightarrow{\beta} \ldots\ ^{210}_{84}$ **Po**, distil. vac 138.4 d.

	4*s*	4*p*	4*d*	EN
Se⁰	↓↑	↓↑ ↓ ↓		2.4
Te⁰	5*s* ↓↑	5*p* ↓↑ ↓ ↓	5*d*	2.1
Po⁰	6*s* ↓↑	6*p* ↓↑ ↓ ↓	6*d*	1.8

2–

H_2Se	H_2Te	H_2Po
gas, colrl., toxic with unpleasure odour		output ⩽ 0.1%
m. p. −65	−49	−36
b. p. −42	−2	+35
ΔH = +84	+100	v. unstab.
dec. 280	>0	
sol. in H_2O 75	50%(vol.)	
$K_1 = 10^{-4}$	10^{-3}	
$K_2 = 10^{-11}$	10^{-5}	
angular mol.		
E—H 1.46	1.66	
∠HEH 90.6	90.2	

H_2; C_nH_{2n+2}; Mg + HCl

HF + SbF_5

$[H_3Se]^+[SbF_6]^-$ dec. −180 [41]

M^{n+} H^+

M (l); Na (NH_3 liq.)

Selenides	Tellurides	Polonides
M^IHSe, cr. colrl., hig.	**$Na_2Te_n \cdot 9H_2O$** cr. colrl.	**M_2Po**, M = Na–Cs, CaF_2 str. type
M_2Se,	**Al_2Te_3**	**MPo**, M = Be–Ra, Zn–Hg, Ni, Pb; NaCl, str. type, blk., volat.
	Ag_2Te, "hessite"	
Cu_2Se, "berzelianite"	**$AuTe_2$**, "calaverite"	
HgSe, "timanite"		
Hg(Se,S) "onofrite"	**HgTe**, "coloradoite"	
PbSe	**PbTe**, "altaite"	
	$Bi_2Te_{22}S$ "tetradymite"	

ME, M = Ge–Pb, Zn–Hg, As, Mn, Bi; E = Se, Te, semiconduct., photoresistive mater., lasers

Polyselenides, -tellurides
M_2Se_n, *n* = 2–6
Rb_2Se_3, **RbSe**, **$Rb_{11}Se_8$**, **$RbSe_2$**, **$RbSe_3$**, red
Na_2Te_n, *n* = 2–6; blk. [25]

$Na_4[SnSe_4] \cdot 16H_2O$, [26]

Se_2C; $(SeN)_4$
$SePa$; **Se_3P_2**; **Se_5P_2**
TeC; **Te_3N_4**; **Te_3P_2**
$Se_3N_2Cl_2$ ("Se_4N_2") = $= [Se_3N_2]^{2+}Cl_2^-$, cation cycle [42]

Se_4S_4, red., m. p. 113
Se_2S_6, orange, m. p. 122
Se_nS_{8-n}; **TeS_7**, mol. cycles
$[E_nS_{8-n}]$ [30]

PoS↓, blk.

$PoHal_2$, Hal = Cl(red), Br(brn.)

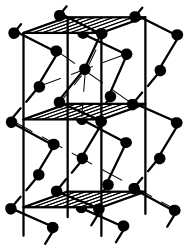
$PoSO_3$, red

EO_2 $PoCl_4$ C; H_2 H_2

Se
powd., amorph., red. (106° → blk.) or glass, *d* = 4.3; in str. – tangled chains
↓CS_2
s. orange with grn. tint
↓ < 72°
α-, cr. red., *d* = 4.5, monocl., *a* = 9.05, *b* = 9.07, *c* = 11.61, β = 90°46′, in str. – cicles Se_8; Se—Se 2.35, ∠SeSeSe 102;
β-, cr. red., *d* = 4.4; m. p. 180 (rapid heating) monocl., *a* = 12.85, *b* = 8.04, *c* = 9.31, β = 93°8′, in str. – Se_8 "crown"
↓ 130°
"grey" Se (thermodinamically stab.), *d* = 4.81, m. p. 217, b. p. 685
sol. in H_2SO_4, HNO_3, aq. regia., (alk. + H_2O_2)
Metal – like conduct.
has photoconduct.
a 4.36, *c* 4.96
in str. – spiral chains, CN 6
E—E 2.37
∠EEE 105
$Se_8 \underset{red.}{\rightleftarrows} Se_6 \rightleftarrows Se_4 \rightleftarrows Se_2$
E_2 – el. anal. of O_2, paramagn.
E—E 2.19

Te
"amorph", powd., brn., in str. – chains, Te—Te 2.86, ∠TeTeTe 102
110° *t*
silvery - gray, *d* = 6.24, m. p. 450, b. p. 990
fragile (plaint at high *t*)
hex. cr.
a 4.45, *c* 5.93
E—E 2.82
∠EEE 102
in gas – mol.
Te_2, yel.

Po
met., silvery-wh., glows in the dark, *d* = 9.4, m. p. 254, b. p. 962, sol. in HCl, conc. HNO_3, melt. alk., $E_0Po^{4+}/Po_{sld.}$ = +0.765
α-, cub. *a* = 3.34, ∠MMM 90, CN 6
18° ↑↓ 54°
β-, rhombohedral, CN 6. Ex. at 20° due to heat during braking of α-particles


Se, Te hex. str.

EF; ECl_4 + $AlCl_3$
Br_2; SeO_2 + HCl

Se_2Hal_2 [27]
Hal = Cl, Br, oils, red, m.p. – 85; 5 b.p. 127; 225 t⟶Se + $SeHal_4$

$TeHal_2$, Hal = Cl (grn.), Br (brn.) m.p. 208; 280 b.p. 328; 340. mol. ψ-tetrah. [29]

TeI [2]
I, I, Te—Te—I, Te—Te, I

Hal₂

PoS↓, blk.

$PoHal_2$, Hal = Cl(red), Br(brn.)

$PoSO_3$, red

t PoCl₄

Na_2SeO_3; Na_2Se_3 S; Se

$Na_2[SeSO_3]$, [3, 21, 25]
$M_2[Se(SO_3)_2]$
$M_2[Se_nS_{2m}(SO_3)_2]$
$K_2[TeS_2(SO_3)_2]$

$[E_n]^{2+}X_2$
X = $AlCl_4$, HS_2O_7
E = Se, Te, n = 4
n = (yel., red), squares; n = 6, "bath" [1]

[SeO]SO_4
$SeO(SO_3F)_2$
$[Se(OH)_3]^+[ClO_4]^-$, cr. colrl., m.p. 33, cation – ψ-tetrah.

Selenylhalides [29, 31]

	m. p.	b. p.	μ
$SeOF_2$, liq. colrl.	14.5	125	2.84
$SeOCl_2$, liq. yel., p. S, Se, Br_2, I_2, ε = 46	11	179 (dec.)	2.62
$SeOBr_2$, cr. orange	42	217 (dec)	—

mol. ψ-tetrah. [:$SeOI_2$], Se = O 1.60,

t (−Br_2)

	m. p.	b. p.	ΔH
SeF_4, liq. colrl., μ = 1.78, mol. – ψ-trig. bipyr.	−10	108	−849
$SeCl_4$, cr. colrl., $\overset{t}{\rightleftarrows}$ Cl_2 + $SeCl_2$(gas) in gas – mol. – tetrah.(!), in str. – tetramers	305 (*p*)	196	−184
$SeBr_4$, cr. yel.	—	—	75
SeI_4 (?)	—	—	—

[29]

$[:SeF_3]^+[Nb_2F_{11}]^-$, ∠FSeF 94 [22]
$[:SeCl_3]^+X^-$, X = $AlCl_4$, AsF_6, cation – ψ-tetrah
$[:SeBr_3]^+[AsF_6]^-$, in str. – frame of oct.
$[:SeI_3]^+[AsHal_6]^-$

SeO_2, needles, hyg., colrl., *d* = 3.95, subl. 337, m. p. ~ 350(*p*), ΔH = −239, sol. in H_2O 69% (25°), alc., acet., CH_3COOH; "selenolit", in str. – chains; in gas (toxic, with smell of rotten radishes), mol. – monomer
Se—O 1.61, ∠OSeO 113, μ = 2.7

70° H_2O

O_2(+NO_2, bl. flame) HNO_3 Se

H_2SeO_3, selenious ac., cr. colrl., hyg., m. p. 70, ΔH = −527; $K_1 = 10^{-3}$, $K_2 = 10^{-9}$; Red.; in str. – net of ψ-tetrah. [:SeO_3], Se—OH 1.74, Se=O 1.64 [4]

Se + Hal_2; HCl
SO_3 (*t*)
$HClO_4$ MOH

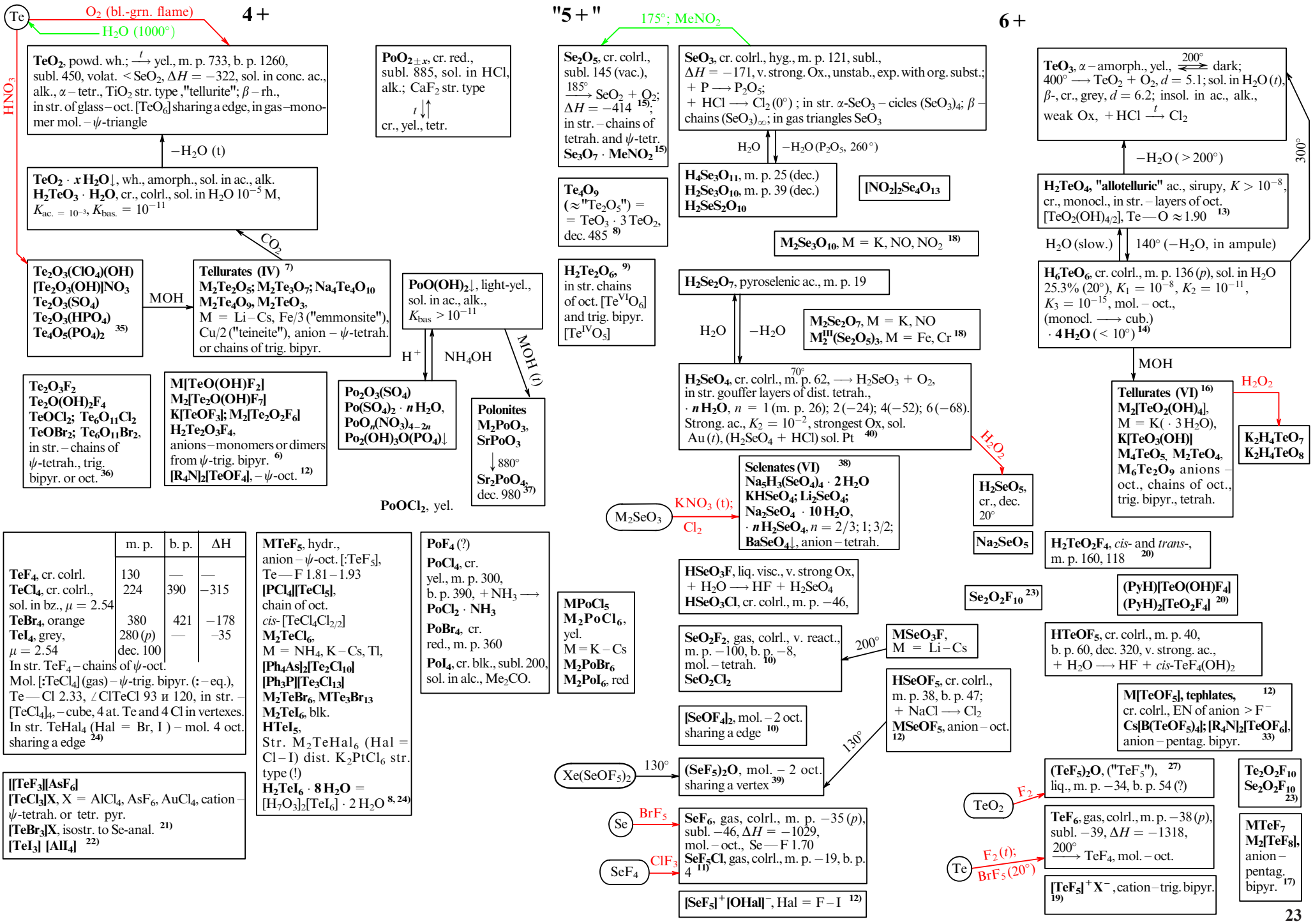
Selenates (IV) $NaH_7[SeO_3]_4$
$MH_3(SeO_3)_2$, M = Li–Cs
$Na_2SeO_3 \cdot 5H_2O$; **Ag_2SeO_3**↓, SP = 10^{-15}; **$M^{II}SeO_3 \cdot nH_2O$**, *n* = 2, M = Cu ("holkomenite"), Pb ("kerstenite"), *n* = 1, M = Mn, Co, Ni, Zn, Cd, $[:SeO_3]^{2-}$ – ψ-tetrah. [7]

M[SeO_2F], cr. colrl., [43]
Zn[SeO_2F_2] · 6H_2O
$H_2SeO_2Cl_2$, liq. yel., b. p. 170 (dec.)

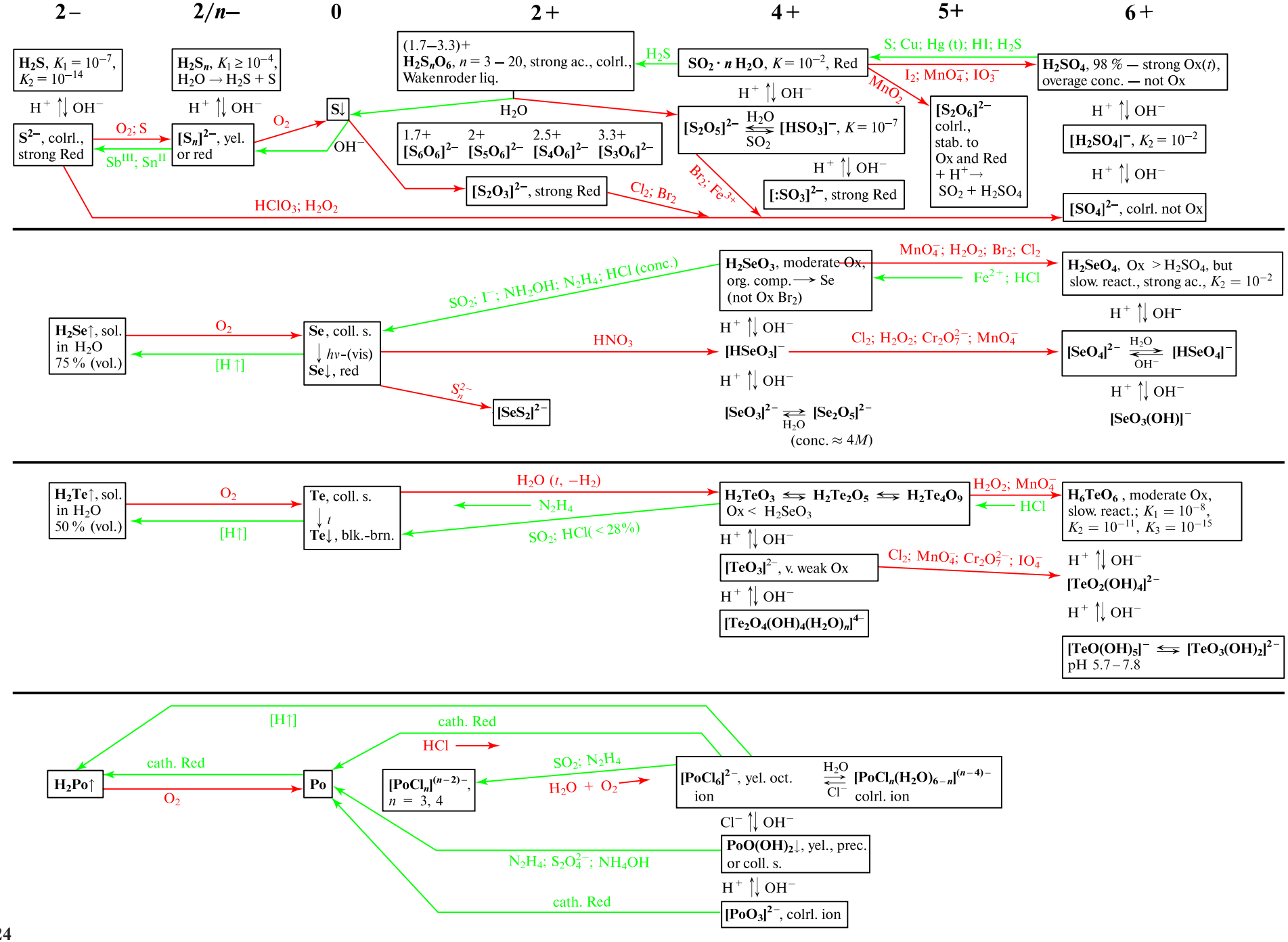
$[R_4N]_2[SeOCl_4]$, yel. [32]
M[$SeOHal_3$]
M[$SeO(OMe)_3$], needles, anion – ψ-trig. bipyr.

$CsSeF_5$, anion – ψ-oct. [5]
M_2SeF_6
M_2SeCl_6, M = NH_4, K–Cs, yel.
Me_2SeBr_6, **H_2SeBr_6**, **· 8H_2O**
$M_2Se_2Br_{10}$ [32]
Cs_2SeI_6
Str. K_2PtCl_6, type, anion – regular oct.

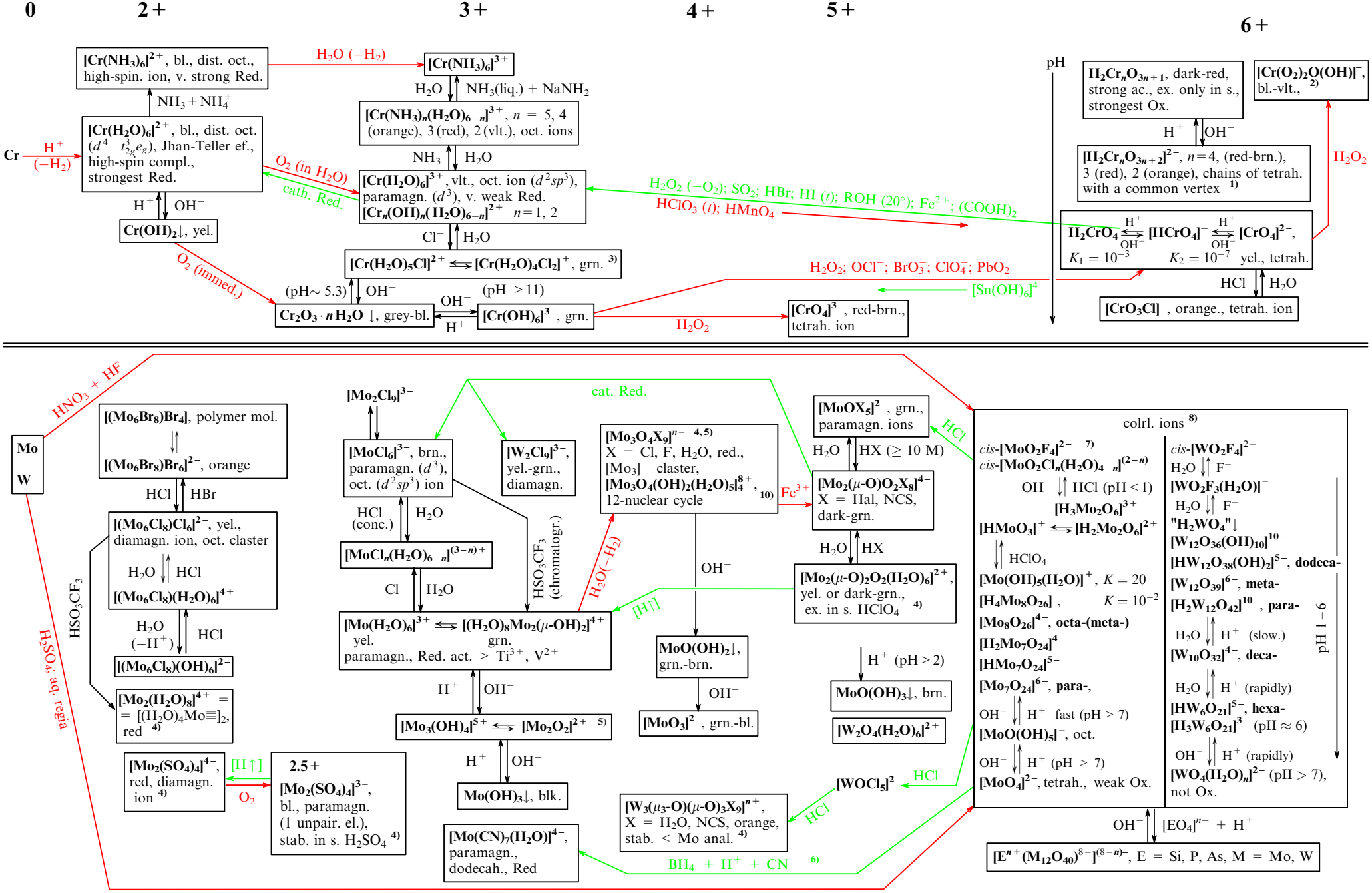
N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_8, © Springer-Verlag Berlin Heidelberg 2011


4+
"5+"
6+
Te
O2 (bl.-grn. flame)
H2O (1000°)
HNO3
TeO2, powd. wh.; t → yel., m. p. 733, b. p. 1260, subl. 450, volat. < SeO2, ΔH = −322, sol. in conc. ac., alk., α – tetr., TiO2 str. type ,"tellurite"; β – rh., in str. of glass – oct. [TeO6] sharing a edge, in gas – monomer mol. – ψ-triangle
PoO2±x, cr. red., subl. 885, sol. in HCl, alk.; CaF2 str. type
t ↓↑
cr., yel., tetr.
−H2O (t)
TeO2 · x H2O↓, wh., amorph., sol. in ac., alk.
H2TeO3 · H2O, cr., colrl., sol. in H2O 10−5 M, Kac. = 10−3, Kbas. = 10−11
CO2
Te2O3(ClO4)(OH)
[Te2O3(OH)]NO3
Te2O3(SO4)
Te2O3(HPO4)
Te4O5(PO4)2 35)
MOH
Tellurates (IV) 7)
M2Te2O5; M2Te3O7; Na4Te4O10
M2Te4O9, M2TeO3,
M = Li – Cs, Fe/3 ("emmonsite"), Cu/2 ("teineite"), anion – ψ-tetrah. or chains of trig. bipyr.
PoO(OH)2↓, light-yel., sol. in ac., alk., Kbas > 10−11
H+
NH4OH
MOH (t)
Te2O3F2
Te2O(OH)2F4
TeOCl2; Te6O11Cl2
TeOBr2; Te6O11Br2,
in str. – chains of ψ-tetrah., trig. bipyr. or oct. 36)
M[TeO(OH)F2]
M2[Te2O(OH)F7]
K[TeOF3]; M2[Te2O2F6]
H2Te2O3F4,
anions – monomers or dimers from ψ-trig. bipyr. 6)
[R4N]2[TeOF4], – ψ-oct. 12)
Po2O3(SO4)
Po(SO4)2 · n H2O,
PoOn(NO3)4−2n
Po2(OH)3O(PO4)↓
Polonites
M2PoO3,
SrPoO3
↓ 880°
Sr2PoO4,
dec. 980 37)
PoOCl2, yel.
m. p. b. p. ΔH
TeF4, cr. colrl. 130 — —
TeCl4, cr. colrl., sol. in bz., μ = 2.54 224 390 −315
TeBr4, orange 380 421 −178
TeI4, grey, μ = 2.54 280 (p) dec. 100 — −35
In str. TeF4 – chains of ψ-oct.
Mol. [:TeCl4] (gas) – ψ-trig. bipyr. (: – eq.), Te — Cl 2.33, ∠ClTeCl 93 и 120, in str. – [TeCl4]4, – cube, 4 at. Te and 4 Cl in vertexes.
In str. TeHal4 (Hal = Br, I) – mol. 4 oct. sharing a edge 24)
[TeF3][AsF6]
[TeCl3]X, X = AlCl4, AsF6, AuCl4, cation – ψ-tetrah. or tetr. pyr.
[TeBr3]X, isostr. to Se-anal. 21)
[TeI3] [AlI4] 22)
MTeF5, hydr., anion – ψ-oct. [:TeF5], Te — F 1.81 – 1.93
[PCl4][TeCl5], chain of oct. cis-[TeCl4Cl2/2]
M2TeCl6, M = NH4, K – Cs, Tl,
[Ph4As]2[Te2Cl10]
[Ph3P][Te3Cl13]
M2TeBr6, MTe3Br13
M2TeI6, blk.
HTeI5,
Str. M2TeHal6 (Hal = Cl – I) dist. K2PtCl6 str. type (!)
H2TeI6 · 8 H2O = [H7O3]2[TeI6] · 2 H2O 8, 24)
PoF4 (?)
PoCl4, cr. yel., m. p. 300, b. p. 390, + NH3 → PoCl2 · NH3
PoBr4, cr. red., m. p. 360
PoI4, cr. blk., subl. 200, sol. in alc., Me2CO.
MPoCl5
M2PoCl6, yel.
M = K – Cs
M2PoBr6
M2PoI6, red
175°; MeNO2
Se2O5, cr. colrl., subl. 145 (vac.), 185° → SeO2 + O2; ΔH = −414 15); in str. – chains of tetrah. and ψ-tetr.
Se3O7 · MeNO2 15)
SeO3, cr. colrl., hyg., m. p. 121, subl., ΔH = −171, v. strong. Ox., unstab., exp. with org. subst.; + P → P2O5; + HCl → Cl2 (0°); in str. α-SeO3 – cicles (SeO3)4; β – chains (SeO3)∞; in gas triangles SeO3
H2O
−H2O (P2O5, 260°)
H4Se3O11, m. p. 25 (dec.)
H2Se3O10, m. p. 39 (dec.)
H2SeS2O10
[NO2]2Se4O13
Te4O9 (≈"Te2O5") = = TeO3 · 3 TeO2, dec. 485 8)
M2Se3O10, M = K, NO, NO2 18)
H2Te2O6, 9) in str. chains of oct. [TeVIO6] and trig. bipyr. [TeIVO5]
H2Se2O7, pyroselenic ac., m. p. 19
H2O
−H2O
M2Se2O7, M = K, NO
MII2(Se2O5)3, M = Fe, Cr 18)
H2SeO4, cr. colrl., m. p. 62, 70° → H2SeO3 + O2, in str. gouffer layers of dist. tetrah., · n H2O, n = 1 (m. p. 26); 2 (−24); 4 (−52); 6 (−68). Strong. ac., K2 = 10−2, strongest Ox, sol. Au (t), (H2SeO4 + HCl) sol. Pt 40)
M2SeO3
KNO3 (t); Cl2
Selenates (VI) 38)
Na5H3(SeO4)4 · 2 H2O
KHSeO4; Li2SeO4;
Na2SeO4 · 10 H2O,
· n H2SeO4, n = 2/3; 1; 3/2;
BaSeO4↓, anion – tetrah.
HSeO3F, liq. visc., v. strong Ox, + H2O → HF + H2SeO4
HSeO3Cl, cr. colrl., m. p. −46,
SeO2F2, gas, colrl., v. react., m. p. −100, b. p. −8, mol. – tetrah. 10)
SeO2Cl2
200°
MSeO3F, M = Li – Cs
[SeOF4]2, mol. – 2 oct. sharing a edge 10)
HSeOF5, cr. colrl., m. p. 38, b. p. 47; + NaCl → Cl2
MSeOF5, anion – oct. 12)
130°
Xe(SeOF5)2
130°
(SeF5)2O, mol. – 2 oct. sharing a vertex 39)
Se
BrF5
SeF6, gas, colrl., m. p. −35 (p), subl. −46, ΔH = −1029, mol. – oct., Se — F 1.70
SeF4
ClF3
SeF5Cl, gas, colrl., m. p. −19, b. p. 4 11)
[SeF5]+[OHal]−, Hal = F – I 12)
H2O2
H2SeO5, cr., dec. 20°
Na2SeO5
Se2O2F10 23)
TeO3, α – amorph., yel., 200° ⇌ dark; 400° → TeO2 + O2, d = 5.1; sol. in H2O (t), β-, cr., grey, d = 6.2; insol. in ac., alk., weak Ox, + HCl → Cl2
300°
−H2O (> 200°)
H2TeO4, "allotelluric" ac., sirupy, K > 10−8, cr., monocl., in str. – layers of oct. [TeO2(OH)4/2], Te — O ≈ 1.90 13)
H2O (slow.)
140° (−H2O, in ampule)
H6TeO6, cr. colrl., m. p. 136 (p), sol. in H2O 25.3% (20°), K1 = 10−8, K2 = 10−11, K3 = 10−15, mol. – oct., (monocl. → cub.) · 4 H2O (< 10°) 14)
MOH
Tellurates (VI) 16)
M2[TeO2(OH)4], M = K(· 3 H2O),
K[TeO3(OH)]
M4TeO5, M2TeO4,
M6Te2O9 anions – oct., chains of oct., trig. bipyr., tetrah.
H2O2
K2H4TeO7
K2H4TeO8
H2TeO2F4, cis- and trans-, m. p. 160, 118 20)
(PyH)[TeO(OH)F4]
(PyH)2[TeO2F4] 20)
HTeOF5, cr. colrl., m. p. 40, b. p. 60, dec. 320, v. strong. ac., + H2O → HF + cis-TeF4(OH)2
M[TeOF5], tephlates, 12) cr. colrl., EN of anion > F−
Cs[B(TeOF5)4]; [R4N]2[TeOF6], anion – pentag. bipyr. 33)
TeO2
F2
(TeF5)2O, ("TeF5"), 27) liq., m. p. −34, b. p. 54 (?)
Te2O2F10
Se2O2F10 23)
TeF6, gas, colrl., m. p. −38 (p), subl. −39, ΔH = −1318,
200° → TeF4, mol. – oct.
MTeF7
M2[TeF8], anion – pentag. bipyr. 17)
Te
F2 (t); BrF5 (20°)
[TeF5]+X−, cation – trig. bipyr. 19)

SULPHUR, SELENIUM, TELLURIUM AND POLONIUM IONS IN AQUEOUS SOLUTIONS



CHROMIUM, MOLYBDENUM [9] AND TUNGSTEN IONS IN AQUEOUS SOLUTIONS



CHROMIUM

Cr^0 3*d* ↓↓↓↓↓ 4*s* ↓ 4*p* □□□ **EN** 1.6

2 + (d^4) **3 + (d^3)**

Cr, met., iron-grey, plastic (later on vac. distil.), chem. passiv. (v. thin layer Cr_2O_3 on surface), $d = 7.2$, m. p. 1890, b. p. 2680, sol. in HCl, dil. H_2SO_4, passiv. HNO_3;
$E_0Cr^{2+}/Cr_{sld.} = -0.91$, $E_0Cr^{3+}/Cr_{sld} = -0.74$, cub. (α-Fe type), $a = 2.88$, Cr—Cr 2.54

O_2(Hg)

CrO, cr., blk., chem. inert, $\xrightarrow{700°}$ Cr + Cr_2O_3

$Cr(OH)_2$↓, yel., sol. in ac., $K_1 \cdot K_{2bas=10^{-17}}$

O_2 (*t*)

Cr_2O_3, grn., m. p. 2340 (*p*), $\Delta H = -1134$, insol. in ac., interfuse whith alk., $M_2S_2O_7$, sol. in $NaBrO_3 + H_2O$ (⟶ $Na_2Cr_2O_7 + H_2Cr_2O_7 + Br_2$), Al_2O_3 – korund str. type, "eskolaite"

430° ($-H_2O$)

CrO(OH), grn., CdI_2 str. type [36]
$Cr(OH)_3$↓, isostr. to $Al(OH)_3$, "hydrargillite"
↑ $-H_2O$ (slow.)
$Cr_2O_3 \cdot n\,H_2O$↓, gel, grey-bl., $K_1 \cdot K_2 \cdot K_{3bas} = 10^{-30}$; $K_к = 10^{-16}$, sol. in ac., alk., poorly in NH_4OH, peptizate of $CrCl_3$

Al (*t*)

$(NH_4)_2Cr_2O_7$ 280° ($-N_2-H_2O$)

Hal$_2$

H^+ ⇕ OH^-

$Cr_2(SO_4)_3$, pink., sol. in H_2O in presence Cr^{2+}
$\cdot n\,H_2O$ (n = 18, 15), $[Cr(H_2O)_6]_2(SO_4)_3 \cdot (n-12)\,H_2O]$,
$\cdot M^I_2SO_4 \cdot 24\,H_2O$ = $[M(H_2O)_6]^+[Cr(H_2O)_6]^{3+}(SO_4)_2$, M = Na–Cs, vlt. alum,
$\cdot n\,H_2SO_4 \cdot m\,H_2O$ (n, m = 1, 14; 2, 18) [34]
$Cr(NO_3)_3$, grn., dec. 60, **$\cdot n\,H_2O$**, n = 9, 7.5 red, m. p. 37 and 100
$CrPO_4 \cdot n\,H_2O$↓, n = 6 (vlt.), 4 (grn.), 2 (vlt.)
$CrHP_2O_7 \cdot 7\,H_2O$; **$Cr(PO_3)_3$** [35]
$Cr(CH_3COO)_3 \cdot 6\,H_2O$, bl.-vlt. needle.
$[Cr_3O^*(RCOO)_6(H_2O)_3]^+X^- \cdot n\,H_2O$, grn., in cation [$O^*Cr_3$] – triangle, [$CrO^*O_4(OH_2)$] – oct. [4]
$Cr_2(C_2O_4)_3 \cdot n\,H_2O$↓, vlt., unstab. **CrOCl**

$-H_2O$

$Cr(CO)_6$ N_2O_5

Ferrochrome, 60–85% Cr, rest – Fe. In system Fe–Cr ex. sld. s. subtracting and **FeCr** (m. p. 930)
Steel chromous, 0.7–1.6 % Cr, 0.1–1 % C;
Cr-Ni, 0.6–1.5 % Cr, 1–4 % Ni, 0.1–0.4 % C, v. hard, plastic, noncorrosive; rustless, ⩾12 %; instrumental 12 % Cr, 0.8–1.5 % C [contain $(CrFe)_7C_3$]; heat resistant – 15 % Cr + + 1 % Si (stab. < 800°), 25 %Cr (< 950°)
Cermets, heat-fast mat., such as 72 % Cr, 28 % Al_2O_3 or 83 % Cr_2O_3, 15 % Ni, 2 % WC

C; Al(*t*)

FeO · Cr_2O_3

$Cr(ClO_4)_2 \cdot 6\,H_2O$
$CrSO_4 \cdot n\,H_2O$, n = 7 ("bl. vitriol"), 5, 4, 3, 1 (colrl.) **$\cdot M_2SO_4 \cdot 6\,H_2O$**
$CrHPO_3 \cdot 2\,H_2O$↓ [37]
$Cr_2(CH_3COO)_4$, yel., Cr—Cr 2.29
$[Cr(CH_3COO)_2(H_2O)]_2$↓, red, stab. to O_2, diamagn.
$[Cr_2(HCOO)_4(H_2O)_2]_3 \cdot 10\,H_2O$ [33]

$CrCl_3$

CO + Na
$LiAlH_4$

0 (d^0)

$Na_2[Cr(CO)_5]$
$M[HCr(CO)_5]$
$Na_2[Cr_2(CO)_{10}]$
$M[HCr_2(CO)_{10}]$
$K_2[Cr_3(CO)_{14}]$ [32]

MeOH

MOH

$Cr(CO)_6$, cr., colrl., subl.147, $\Delta H = -983$, stab. to conc. ac. and alk., air Ox., diamagn., mol. – oct. [20]

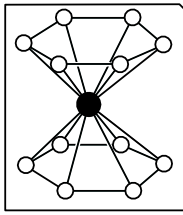
NO($h\nu$ – uv)

$Cr(NO)_4$, cr., blk.-brn., volat., dec. in air., diamagn., mol. – tetrah. [1, 23]

$Cr(PF_3)_6$, cr., colrl., m. p. 193, subl. vac. 20, sol. in org. solv., dec. alk.

$[CrDipy_3]$, cr., blk., v. unstab., mol. – oct. [22]

PF_3



$Cr(C_6H_6)_2$, dibenzolchromium, cr., brn., m. p. 284, sol. in org. solv., diamagn., mol. – hex. prism

$M_6[Cr(CN)_6]$

	m. p.	ΔH	**$\cdot n\,H_2O$**, n =
CrF_2↓, grey	894	−761	–
$CrCl_2$, colrl., needle, hyg.	824	−397	6; **4** (bl.-grn.) 3 (bl.) [2]
$CrBr_2$, colrl.	842	−318	**6**
CrI_2, red	795	−158	–

Str. CrF_2 and $CrCl_2$ – dist. TiO_2 type, CrI_2 – chain of oct., in gas – Cr_2Cl_4 [33]

$t(-I_2)$

MCrF$_3$
MCrCl$_3$
M_2CrCl_4; M_3CrCl_5
$M_2[CrBr_4]$; $MCrBr_3$
$M_2[CrBr_4(H_2O)_2]$
$CsCrI_3$; anions $[CrHal_3]^-$ – chains of oct.
μ_{eff} = 4.9 (sp^3d^2) [3]

	subl.	μ_{eff}	ΔH	**$\cdot n\,H_2O$**, n =
CrF_3, grn.,	1200	—	−1113	**3, 3.5, 4, 5, 6, 9** [31]
$CrCl_3$↓, vlt., + Cr^{2+}, sol. in H_2O;	1150	3.69	−510	**10** (< 6°), **6** sol. in H_2O, alc., ex. 3 isomers
$CrBr_3$↓, blk.,	600 m. p.	3.94	−402	**6** (grn. and vlt.)
CrI_3, blk.,	—	4.03	−201	**9** (blk.-vlt.)

+ Cr^{2+} – sol. in H_2O
In str. CrF_3 – net of oct., $CrCl_3$, $CrBr_3$ – layers of oct.

MCl + HCl

$H_2O(+Cr^{2+})$

$[Cr(H_2O)_6]Cl_3$, grey-bl., insol in acet.
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, light-grn., sol. in acet.
cis-**$[Cr(H_2O)_4Cl_2]Cl \cdot 2\,H_2O$**, dark-grn.
$[Cr(H_2O)_4Br_2]Br \cdot 2\,H_2O$, grn.
$[Cr(H_2O)_6]Br_3$, vlt. [31]

$[CrDipy_3]X_2$, X = ClO_4, Br, blk., low-spin, instant Ox.
$[CrDipy_2(H_2O)_2]Cl_2$, high-spin [22]

$Cr(CN)_2 \cdot 2\,H_2O$ μ_{eff} = 2.73 [23]

CN^-

$K_4[Cr(CN)_6] \cdot 2\,H_2O$, bl., anion oct. ($d^2sp^3$), – 2 unpair. el., μ_{eff} = 3.2
$K_3[Cr(CN)_5(NO)]$, light grn.

$Cr(C_5H_5)_2$, chromocene, cr., red, m. p. 173, in air Ox., low-spin (2 unpair. el.), str. anal. $Fe(C_5H_5)_n$ [28]

$K_4[Cr(NCS)_6]$
$Na_3[Cr(NCS)_5(H_2O)] \cdot 8\,H_2O$, bl., μ_{eff} = 4.5
$[AmH][Cr(NCS)_4]$, red, [22]

Cr_2S_3↓, blk., sol. in ac.-Ox.; **CrS**↓
Cr_2N, m. p. 1650, **CrN**, m. p. 1500
$Cr_{23}C_6$(~"Cr_4C"), m. p., dec. 1900, **Cr_3C_2**, m. p. 1520
Cr_7C_3, m.p. 1680, **CrC**, v. hard, resist. to Ox. and ac.

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_9, © Springer-Verlag Berlin Heidelberg 2011

4 + (d^2)

5 + (d^1)

6 + (d^0)

$HClO_4$, HIO_3; O_2 (< 400°, *p*)

$Cr(NO_3)_3 \cdot 9\,H_2O$ — *t* (−NO_2 −, . . .)

CrO_2, blk., dec. 450, $\Delta H = -594$, conduct., ferromagn., TiO_2 str. type [7]

$Cr_2O_5 \approx Cr^{III}_2[Cr^{VI}_2O_7]_3$, 500° → Cr_2O_3

280° / 220°

Cr_3O_8

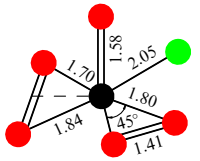
H_2O_2

CrO_3, needles, red, toxic, m.p. 197, subl., $\Delta H = -577$, sol. in H_2O 62% (15°), in str. – chains of tetrah., $\cdot n\,H_2O$, $n = 1 - 4$, v. strong Ox. + $C_2H_5OH \longrightarrow CH_3COOH + Cr^{3+}$

H_2O_2 (0°) (−CrO_5)

H_2SO_4

[$Cr(O_2)_2OL$], L = Me_2O (exp. 30°), Py (stab.), cr., bl., sol. in Et_2O, bz., diamagn., mol. – pentag. pyram.

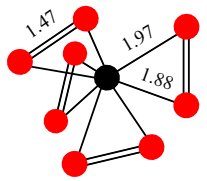


[$Cr(O_2)_2(NH_3)_3$], cr., brn., paramagn. (2 unpair. el.), mol. – pentag. bipyr.

MOH

Peroxochromates **$M[Cr(O_2)_2O(OH)] \cdot H_2O$**, bl.-vlt., exp. (*t*), diamagn. [17]

$M_3[Cr(O_2)_4]$, cr., red-brn., exp. > 170°, readily sol. in H_2O (Na) paramagn. (1 unpair. el.),



anion – dodecah.

Tetrachromates, $M_2Cr_4O_{13}$, brn.-red
M = K– Cs; 210° → $K_2Cr_2O_7 + CrO_3$ [12]

Trichromates, $M_2Cr_3O_{10}$, red
M = Na (·H_2O), K – Cs
$K_2Cr_3O_{10}$ 243° → $K_2Cr_2O_7 + CrO_3$ [13]

H_2SO_4 (conc.)

Bichromates, orange

	m. p.	dec.	sol. in H_2O, %
$Na_2Cr_2O_7$	320	400	62 · **2 H_2O**
$K_2Cr_2O_7$	398	> 500	13 —

$(NH_4)_2Cr_2O_7$ $\xrightarrow[\text{burn}]{200°}$ $Cr_2O_3 + N_2 + H_2O$

$M^{II}Cr_2O_7$, M^{II} = Ca, Ba (· 2 H_2O), Pb ("crocoite"), sol. in H_2O, v. strong Ox.; + HCl $\xrightarrow{t}$ $Cl_2 + CrCl_3$, anion – chain 2 dist. tetrah. sharing vertex

Chromates, yel.

	m. p.	sol. in H_2O
Li_2CrO_4 · **2 H_2O**	—	60
Na_2CrO_4	792	46
· **10 H_2O**	20	—
K_2CrO_4	968 – 980	39 (20°)
$(NH_4)_2CrO_4$	dec. 200	—

$CaCrO_4$, "chromatite"; · **2 H_2O**, **$BaCrO_4$**↓; **$PbCrO_4 \cdot H_2O$**↓, "iranite"; **Ag_2CrO_4**↓, anion – tetrah. (d^3s), Cr — O 1.60 – 1.67 [14]

$Na_4CrO_5 \cdot 13\,H_2O$, orthochromate, yel. + $OH^- \longrightarrow NaCrO_4$

H_2O_2, (30%)

anion – tetrah.

HHal

$M[CrO_3F]$, M = Li (· 2 H_2O), Na (· 2 H_2O), K – Cs [18]
$K[CrO_3Cl]$, orange., stab. at pH ≪ 7
$K[CrO_3Br]$, brn., **$K[CrO_3I]$**, red,
+ $H_2O \rightleftarrows K_2Cr_2O_7 + HHal$ [16]

$M_2[CrO_2F_4]$, M = K, Cs, Ca, Mg [11]
$M[CrO_2F_3]$, M = [NO_2], [NO]

[NO][$CrOF_5$], pink [9]

Sr_3CrN_3 [20]

$M[CrI^VO_6]_n \cdot m\,H_2O$, $\xrightarrow{t}$ $M^I_2Cr_2O_7 + I_2O_5$↑ [15]

Cr
O
N
CH

M_2CO_3

Chromates (III) [21]
$M_3[Cr(OH)_6]$ M = M^I, Ba/2
$MCrO_2$, M = Li –Cs, grn.
$Cr_2O_3 \cdot M^{II}O$,
M^{II} = Mg ("magnesiochromite"), Fe ("chromite"), spinel

Chromates (IV) [19]
Na_4CrO_4, grn., μ_{eff} = 2.8
$M^{II}CrO_3$, **$M^{II}_2CrO_4$**,
blk., stab. in air, tetrah.
Ba_3CrO_5, grn.
$M^{II}_4CrO_6$, M^{II} = Sr, Ba;
+ $H_2O \longrightarrow$ Cr(III) + Cr(VI)

Chromates (V) [27]
$M^I_3CrO_4$, grn., paramagn., μ_{eff} = 1.60
$M^{II}_3(CrO_4)_2$
blk., anion – tetrah.
$MCr_3O_8 = MCr^{III}[Cr^{IV}O_4]_2$

MOH (t, $-O_2$, $-H_2O$); NaN_3 [31]

"$Cr_2(SO_4)_3 \cdot n\,H_2O$", [34]
$= H_m[Cr_z(SO_4)_{1.5n}(OH)_x(H_2O)_y]$,
$n \leqslant 6$, "grn. sulfates" (do not give react. on Cr^{3+} and SO_4^{2-})

$Na_2CO_3 + O_2$ (1200°, $-Fe_2O_3$, $-CO_2$); $KNO_3 + Na_2CO_3$

Na_2O (600°)

Cr

F_2 (350°)

F_2 (*t*, *p*)

$M_3[Cr(C_2O_4)_3] \cdot n\,H_2O$, cr. with pleochroism – red-bl.-grn., anion oct. [30]

$M^I_3[CrF_6]$, **Rb_2CrF_5**, **$M[CrF_4]_n$**, in str. – isolated. or condensed oct.; [25]
$M_3[CrCl_6]$, **$M_3[Cr_2Cl_9]$**, red, paramagn., μ_{eff} = 3.77, anion – 2 oct. with a common face
$M_2[CrCl_5(H_2O)]$,
$M_2[CrCl_2(H_2O)_4]Cl_3$, grn.
$Cs_3[Cr_2Br_9]$, μ_{eff} = 3.81
$M_2[CrBr_5(H_2O)]$, vlt.
$M_2[CrBr_2(H_2O)_4]Br_3$, grn. [29]

CrF_4, grn., subl., m. p. 200, $\Delta H = -1196$, react with the glass, $\mu_{eff} \sim 3$, insol. in org. solv.
$CrCl_4$, **$CrBr_4$** } in gas

$M[CrF_5]$, pink, μ_{eff} = 3.1
$M_2[CrF_6]$, M = K – Cs, paramagn., oct. compl.

$Cr(OC_4H_9\text{-}t)_4$, cr., bl., volat., $\Delta H = -1276$, strong Ox., paramagn., mol. – tetrah. (d^3s) [8]

$K_3[Cr(CN)_6]$, yel., dec. 150, (d^3, 3 unpair. el.) high-spin, oct.

$K_3[Cr(NCS)_6] \cdot 4\,H_2O$, vlt., v. stab. [24]
$M[Cr(NCS)_4(NH_3)_2]$-*trans*, M = NH_4 ("Reineke salt"), Cu/2↓, Hg/2↓, H, red

$NaCrS_2$, red, sol. in H_2O
$K_2[Cr_4S_7]$, **$Fe[CrS_2]_2$**,
MCr_5S_8, M = K – Cs [6]

$CrOF_3$, in str. – oct. $[CrOFF_{4/2}]$, μ_{eff} = 1.82
$CrOCl_3$, red, cr., dec. > 0°, subl., $+H_2O \rightarrow Cr^{3+} +$ + Cr(VI) [9]

$M[CrOF_4]$, purp.
$M[CrOCl_4]$, **$M_2[CrOCl_5]$**, μ_{eff} = 1.7 [26]

MCl + BrF_3; MCl + HCl

MCrF$_6$

CrO_3

F_2 (> 250°, $-O_2$)

PHal$_5$ HHal

CrO_2X_2, X = ClO_4, CH_3COO, SO_3F, NO_3, OR, Sb_2F_{11}, SbF_6 [11]

HX; ClO_3 ($-ClO_2$ $-Cl_2$)

ClF, WF_6

CrF_5, cr., crimson colour, hyg., m. p. 30, in str. – chains of oct., in gas – trig. bipyr.; $+SO_3 \rightarrow S_2O_6F_2 +$ + $Cr(SO_3F)_3$ [9]

SbF$_5$

$[CrF_4]^+[Sb_2F_{11}]^-$, liq., red-brn., −23° – glass, b. p. 377 [9]

Chromylhalides [9, 10]

	m. p.	b. p.
CrO_2F_2, cr., vlt.	30	subl.
CrO_2Cl_2, liq., red	−97	117
CrO_2Br_2, cr.	–	–

sol. in CCl_4, v. strong Ox., + org. mol. exp., mol. – dist. tetrah.

SiO_2 (20°) $SO_3(SO_2Cl_2)$

$CrO(SO_4)_2$
$CrOF_4$, cr., red, m. p. 55; · **KrF_2** [9]
CrF_6, cr., citrine > −100 → CrF_5 [9]

MOLYBDENUM, TUNGSTEN

	4d	5d	5s	6s	5p	6p	EN
Mo^0	↓ ↓ ↓ ↓ ↓		↓				1.3
W^0	↓ ↓ ↓ ↓		↓↑				1.4

	Mo	W
	met., greyish-wh.	
d	10.2	19.3
m.p.	2620	3420
b.p.	~4630	5680
sol. in	H_2SO_4 (conc.)	($HF + HNO_3$)
passiv.	HNO_3	v. poorly sol. in aq. regia
	readily sol. in the melt ($KNO_3 + NaOH$)	
$E_0 M^{3+}/M_{sld.}$	−0.20	−0.15
$E_0 [MO_4]^{2-}/M_{sld.}$	−1.05	−1.05
	cub. (α-Fe str. type)	
a	3.14	3.16
M — M	2.80	2.80

Ferromolibdenum ⩾ 55 % Mo, 1–2 % Si, ⩽ 0.1–0.2 % C, 0.1–0.2 % P, S, rest — Fe.

-tungsten 65–80 % W, 0.4–1 % Si, 0.2–0.7 % Mn, 0.3 % Cu, 0.5 % C, 0.1 % S and P, rest — Fe.

In the systems M—Fe — ex. sld. s. subtraction and **Mo_6Fe_7**, **Mo_2Fe_3**, **W_6Fe_7**, **WFe_2** (m.p. 1540, 1480, 1640, 1046)

Instrumental steels — and Cr, V, C, Mn, Si "**Pobedit**" 80–87 % W, 6–15 % Co, 5–7 % C

2+ (d^4)

Met.-like phases
(inclusion E in str. M);
in systems Mo(W) — B(C, N, S) — phases
v. hard, refractory, inert.
Mo_2C (m.p. 2690), WC (2600 dec.)
W_2C (2800), *d* = 17.3; **MoC** (2700) [42]
M_2B; MB; MB_2; M_2B_5
M_2N; MN; MP_4
M_3Si; M_3Si_2; M_5Si_3; MSi_2

$[Mo_2^{II}Cl_8]^{4-}$ —K_2SO_4→ **$K_4[Mo_2(SO_4)_4]$**, · **2 H_2O**, pink —O_2 (trace)→ 2.5+ **$K_3[Mo_2(SO_4)_4]$** · **2.5 H_2O**, bl., μ_{eff} = 1.69 [3]; + H_2O ⟶ $[Mo_2]^{4+}$ + Mo(III)

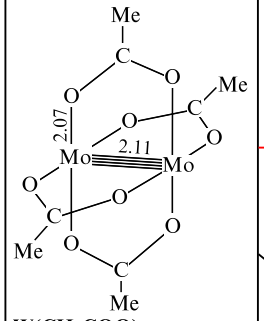
$[Mo_2^{II}Cl_8]^{4-}$ —$O_2 + H_3PO_4$→ **$Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$**, purp., stab. in air, Mo≡Mo 2.22 [45]

$M_3[Mo_2(HPO_4)_4]Cl$

$Mo(OH)_3$ ↓, blk., poorly sol. in ac.

$Mo_2(SO_3F)_4$ [71]

$[Mo(RCOO)_2]_2$, yel., subl. 300, diamagn.



$W(CH_3COO)_2$
MoW(RCOO)$_4$
MoCr(RCOO)$_4$ [32]

I_2 → 2.5+ **$[Mo_2(RCOO)_4]^+[I_3]^-$** **$[MoW(RCOO)_4]I$**, cr., brn., μ_{eff} = 1.67 [43]

KCN → **$K_5[Mo(CN)_7]$**, diamagn., anion pentag. bipyr. **$K_4[M(CN)_6]$** **$K_6[M(CN)_8]$** [7]

NOCl → **$K_2[Mo(CN)_5]$**, red, strong. Red **$K_4[Mo(CN)_7]$** · **2 H_2O**, blk., μ_{eff} = 1.75, pentag. bipyr. **$K_4[Mo(CN)_7(H_2O)]$**, in s. dodecah. **$K_5[Mo(CN)_8]$** [7]

$K_2[W(CN)_5(H_2O)]$

$K_3[M(NCS)_6]$ · ***n*** **H_2O**, paramagn., $\mu_{eff} \approx 3.8$, stab. to Ox, not hydr.

1+ **$K_4[Mo(CN)_5(NO)^0]$** [45], cr., vlt.

0 (d^0)

$WH_6 \cdot 2\,PMe_2Et$

$[R_4N][HM_2(CO)_{10}]$
$Na_2[M_2(CO)_{10}]$
$Na_2[Mo_3(CO)_{14}]$ [33]

RCOOH → **$M(CO)_6$** , cr. colrl., subl. vac. 30–50 b.p. 156 (Mo), 175 (W), dec. ≈ 120, ΔH = −979 (Mo), 961 (W) [22], sol. in org. solv., insol. in ac., alk., mol. oct.

CO + Na; Zn → **$M(PF_3)_6$**, cr. colrl., subl. vac. 40, m.p. 196 (Mo), 214 (p, W); **$W[P(OMe)_3]_6$**

$MoCl_5$; WCl_6 —Cu + PF_3 (*p*, *t*)→ **$[M(N_2)_2(PR_3)_4]$**-*cis* [2]
$[M(N_2)_2[(R_2P—CH_2—)_2]_2$, *cis*-, *trans*-
cr. orange, stab. by air, mol. — oct.
+ EtOH + KOH ⟶ NH_3 + … [1]
+ *i*-PrOH ⟶ N_2H_4 + …

$MoCl_4(PR_3)_2$ —Na + N_2 (Thf)→ **$[M(N_2)_2(PR_3)_4]$**-*cis* [2]

$Mo_{12}S_{14}$; Mo_9S_{11}
Mo_6S_8, in str. colomnes from triangle $[Mo_3]$

3+ (d^3)

Mo —H_2O (800°)→ **MoO_2** | **WO_2**
cr. brn., diamagn.
subl. 1000 | m.p. ≈ 1270
↓ | b.p. ≈ 1700
Mo + MoO_3 | > 1050
ΔH = −586 | −590
sol. in ac.-Ox, conc. alk., dist. rutile str. type

$MoO(OH)_2$↓ = = $H_2Mo_5O_7(OH)_8$, olive-grn., poorly sol. in alk. (⟶$[MoO_3]^{2-}$, grn.-bl. s.) [26]

$Mg_2Mo_3O_8$ [20]

$Mo(O_2)(SO_3F)_4$ [71]

Mo —$S_2O_6F_2$→ **$Mo(O_2)(SO_3F)_4$** [71]

Mo —$Na_2MoO_4 + MoO_3 + P_2O_5$→ **$Na[Mo_2P_3O_{12}]$**, frame of oct. $[MoO_6]$
$Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]$ · **4 H_2O** · · **0.5 $H_2C_2O_4$**, in anion cluster triangle $[OMo_3]$
$[R_4N]_4[Mo_3O_4(NCS)_8(H_2O)]$ [46]

$K_4[MO_2(CN)_4]$-*trans*, diamagn., oct., Mo = O 1.83, Mo — C 2.20
$K_3[MO(OH)(CN)_4]$ · ***n*** **H_2O**
$K_6[M_2O_3(CN)_8]$ · ***n*** **H_2O** [47]

$K[Mo(CN)_5]$, diamagn., anion tetr. pyr. (d^4s)
$H_4[M(CN)_8]$ · **6 H_2O**
$K_4[M(CN)_8]$ · **2 H_2O**, yel., anion dodecah. (d^4sp^3) in str., antiprism in s. (d^5sp^2)

$K_2[Mo(NCS)_6]$
$M_5[W_3O_4(NCS)_9]$ · ***n*** **H_2O**

S (*t*) → **MoS_2**↓, "molybdenit", m.p. ≈ 2100, [72] ΔH = −248, sol. in aq. regia
WS_2↓, "tungstenit", sol. in (HNO_3 + HF), melt alk.; semiconduct., graphite str. type, —*t*→ str. anal. C_{60}

$(NH_4)_2[Mo_3S(S_2)_6]$ · **0.5 H_2O** [48]

4+ (d^2)

NH_3; H_2 → **MoO_2** | **WO_2**
cr. brn., diamagn.
subl. 1000 | m.p. ≈ 1270
↓ | b.p. ≈ 1700
Mo + MoO_3 | > 1050
ΔH = −586 | −590
sol. in ac.-Ox, conc. alk., dist. rutile str. type

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_10, © Springer-Verlag Berlin Heidelberg 2011

5+ (d^1)

		5.5+	5.6+	5.75+	5.78+		
Mo_2O_5, cr., blk.-vlt., sol. in ac. (*t*)	5.44+ **$W_{18}O_{49}$**, in str. layers of cluster $[W_6]$ [20]	**Mo_4O_{11}**, bl.-vlt. | **$Mo_{17}O_{47}$** [20]	**Mo_5O_{14}**	**Mo_8O_{23}** bl.	**Mo_9O_{26}** blk.	5.80+ **$W_{20}O_{58}$**, bl.-vlt.	5.9+ **$W_{50}O_{148}$**, **$W_{40}O_{118}$**, red-vlt.

$\xrightarrow{t}$ $MO_2 + MO_3$

$-H_2O$

Coll. s. of hydrated oxide, $MoO_{3-n}(OH)_n$, $n = 2 - 0$ (4–6)+

4.4+ **$Mo_5O_7(OH)_8$**	**$MoO(OH)_3\downarrow$** brn., sol. in ac.	$n = 1 - 0$, "**molybdenum blue**" **$Mo_4O_{10}(OH)_2$** | **$Mo_4O_{11} \cdot x\,H_2O$** | 5.67+ **$Mo_6O_{17} \cdot H_2O$** | 5.75+ **$Mo_8O_{23} \cdot 8\,H_2O$** cr., bl., not react. with alk. and NH_4OH, weak Red

5+ **$M^{II}(MoO_3)_2$**, M^{II} = Mg–Ba

(5.5–5.9)+ **$WO_{3-n}(OH)_n$**, $n = 0.5 - 0.1$, "tungstig. bl.", v. strong Red

H_2S; SO_2 / Sn^{2+}; HI

M (*t*)

M O_2(*t*)

6+ (d^0)

$(NH_4)_2MO_4$ — 500° (O_2), ($-NH_3-H_2O$)

MoO_3, needle, light grn. ($t \rightarrow$ yel.), $d = 4.69$	**WO_3**, cr. yel. $\rightleftarrows$ orange
volat. with steam	
m.p. 795, b.p. 1155, subl. 650, $\Delta H = -753$,	m.p. 1473 (*p*), subl. 850, $\Delta H = -841$, d ~7.2
sol. in alk., NH_4OH, HF; in gas cyclic trimere	
Chains of tetrah. [Mo—O 1.67 (term.), 1.95 (br.)]; some more 2 bonds form net of oct. "molibdite" · **1/3 NH_3**, in cavities of chains MoO_3 [68]	In all forms (tetr., rh., monocl., tricl.) dist. ReO_3 str. type, frame of oct. $[WO_6]$, W—O 1.72–2.16

$t(-H_2O)$

$MoO_3 \cdot 1/3\,H_2O$, molybdic. ac. [13] **$MoO_3 \cdot H_2O\downarrow$**, needle, colrl., from hot s., dec. 115, in str. α-tricl. — chains of oct. $[MoO_{4/2}(H_2O)]$, Mo=O 1.69–2.28, Mo—OH_2 2.35 yel., monocl.	**$WO_3 \cdot 1/3\,H_2O$, tungstic ac.** **$H_2WO_4\downarrow$**, cr., yel., insol. in H_2O, ac., dec. 100, "tungstite", in str. — chains of oct. $[WO_{4/2}(H_2O)]$, W=O 1.69, W—OH_2 2.34 [51]
$-H_2O$ (H^+, *t*)	$-H_2O$ (H^+, *t*)
$MoO_3 \cdot 2\,H_2O\downarrow$, cr., yel., dec. 70, str. anal. $MoO_3 \cdot H_2O$, II mol. H_2O — in cavities str. In str. — chains of oct. $[MoO_6]$ and $[H_3O]^+$ [14]	**$WO_4 \cdot H_2O\downarrow$**, wh., "hydrotungstite" [52]

H_2; Na; W; Zn(*t*)

H^+ ↕ OH^-

Bronzes — tungstates and molybdates of M^I and M^{II}

(5.67–5.74)+ **K_nMoO_3**, cr., $n = 0.33$ (red), 0.30 (bl.), 0.26 (red), semiconduct. [50]	(5.1–5.7)+ **Na_nWO_3**, ($0.3 \leqslant n \leqslant 0.9$), cr. with met. luster and conduct., yel. ($n = 0\ 9$), red (0.6), bl.-vlt. (0.3); cub. str. $CaTiO_3$, type, net of oct. $[WO_6]$ (at. W^{IV} and W^V equivalent)

Isopolymolybdates [17]

$Na_2[H_{18}Mo_{10}O_{40}]$; $M_6[Mo_{10}O_{33}]$
$M_2[Mo_{10}O_{31}] \cdot n\,H_2O$
$M_8[Mo_{10}O_{34}] \cdot nH_2O$
$M_4[Mo_8O_{26}] \cdot n\,H_2O\downarrow$

$M_6[Mo_7O_{24}] \cdot 4\,H_2O$
M = NH_4, K, Rb
$Cs_2[Mo_7O_{22}]$

meta- para-

anions — blocks of oct. with common edges, M—O ≈ 1 7 (term.) 1.9–2.4 (μ-)

$M_2[Mo_6O_{19}]$; **$Cs_2[Mo_5O_{16}]$**; **$M_2[Mo_4O_{13}] \cdot n\,H_2O$**,
$M_2[Mo_3O_{10}]$; **$M_2[Mo_2O_7]$**, sol. in H_2O
$M_2[MoO_4]$, M = Na (m.p. 687), K (919), colrl., readily sol. in H_2O, Ag↓ (yel.), tetrah., Mo—O 1.77
$M^{II}MoO_4\downarrow$, M^{II} = Mg, Ca ("povellite"), Sr, Ba, Pb ("wulfenite") Cd, Mn–Zn; **$M^{II}_3[MoO_6]$**, M^{II} = Mg–Ba, oct.
$K_4[MoO_5]$, anion — trig. bipyr.

-tungstates [17]

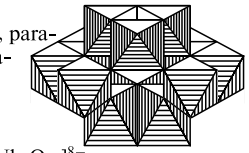
$M_{10}[W_{12}O_{36}(OH)_{10}] \cdot n\,H_2O$, para-
$M_6[H_2W_{12}O_{40}] \cdot n\,H_2O$, meta-
$Na_{10}[W_{12}O_{41}] \cdot 28\,H_2O$,
anion 4 triples of oct. with common vertices
$[R_4N]_2[W_6O_{19}]$, str. anal. of $[Nb_6O_{19}]^{8-}$
$M_8W_4O_{16}$
$K_2W_3O_{10}$, frame of oct. with common edges

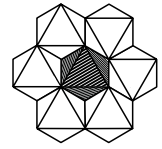
$M_2[W_2O_7]$, chains of tetrah. or oct. with common vertices
$M_2[WO_4]$, M = Na (m.p. 692), K (921); $\cdot 2\,H_2O$, colrl., v. readily sol. in H_2O; $M^{II}/2\downarrow$ = Ca ("scheelite") Sr—Ra, Pb ("stolzite"), tetrah., W—O 1.79
$M^{II}(WO_4)_n$, M = Mg, Mn, Fe–Zn, (Mn, Fe) — ("wolframite"), Cd, Pb } oct.
$M_6[WO_6]$, M = Li, Mg–Ba/2

H_mEO_4 ↕ MOH

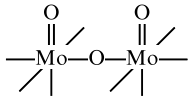
Heteropolymolybdates and -tungstates [20]

I. **$[E^{n+}(M_{12}O_{40})]^{(8-n)}$** = X; E = B, Si, Ge, Ti, Zr, P, As
$H_{8-n}X$, strong ac., readily sol. in H_2O, Et_2O; **$H_4[Si(Mo_{12}O_{40})] \cdot 13\,H_2O$**; **$H_3[P(Mo_{12}O_{40})] \cdot 30\,H_2O$**
$M_{8-n}X$, M = Li–Na, Mg/2, $[R_4N]\downarrow$, Cs↓, Rb↓, Ag↓, Ba/2↓, NH_4, K; in anion cubooct. $[M_{12}]$ (from 12 oct.) in the center — tetrah. $[EO_4]$. About each from 4 at. O — tetrah. $[OEM_3^{VI}]$ (Keggin, str.)
$(NH_4)_3[P(Mo_{12}O_{40})] \cdot n\,H_2O\downarrow$; **$K_4[Si(W_{12}O_{40})]$**;
II. **$(NH_4)_2H_6[Ce^{IV}(Mo_{12}O_{42})] \cdot 12\,H_2O$**, in anion 6 gr. $[Mo_2O_9]$ (2 oct. with common edges) about icosah. $[CeO_{12}]$
III. **$Na_3H_6[Cr^{III}(Mo_6O_{24})]$**, oct. $[CrO_6]$ – in the centre of plane ring from 6 oct. $[MoO_6]$, with common edges





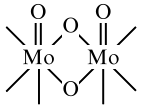
$MoOPO_4 \cdot 2\,H_2O$ [73]



α-, β-$K_2Mo_2O_4P_2O_7$
α-$K_2Mo_2O_3(PO_4)_2$;
$KCsMo_2O_3(PO_4)_2$
$K_3(MoO)_4(PO_4)_5$,
$K_3[WO_2(C_2O_4)_2]$

Ce^{IV}; MnO_4^-

$H_3[M(CN)_8] \cdot 6\,H_2O$
$K_3[M(CN)_8] \cdot n\,H_2O$, n = 0, 2 (yel.), Mo (bl.) anion twocap. trig. prism., μ_{eff} = 1.61 [24]



$M_4[Mo_2O_4(NCS)_6]$
$K_4[Mo_2O_3(NCS)_8] \cdot 4\,H_2O$
$K_2[MoO(NCS)_5]$ [49]

$Mo(NCS)_5 \cdot 2\,Me_2CO$

$Mo_2S_5 \cdot n\,H_2O\downarrow$

$(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2] \cdot 2\,H_2O$ [52]

$MoO_2(ClO_4)_2$ **$Cs[MoO_2(ClO_4)_3]$**;
$MoO_2(SO_4)$ **$Cs_2[MoO_2(ClO_4)_4]$** [69]
$MoO(SO_4)_2$ **$K_4[MoO_4(SO_4)]$**;
$MoO(SO_3F)_4$
$WO(ClO_4)_4$ [69] **$K_2[Mo_2O_6(SO_4)]$**
$WO(SO_4)_2$

$SO_3(SO_2Cl_2)$

MoO_2Cl_2; WCl_6

$W(NCS)_6 \cdot 2\,Me_2CO$

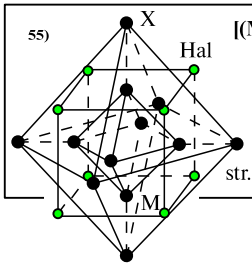
$MS_3 \cdot n\,H_2O\downarrow \underset{H^+}{\overset{S^{2-}}{\rightleftharpoons}} (NH_4)_2[MS_4]$ [54]

5.3+
$M_2W_3S_9$
$M_2W_3OS_8 \cdot 2\,H_2O$ [53]

MOLYBDENUM AND TUNGSTEN HALIDES AND OXOHALIDES

2+ (d^4)

$Mo_3Cl_4(OH)_2 \cdot 7\,H_2O$ =
= $[(Mo_6Cl_8)(OH)_4(H_2O)_2]\cdot 12\,H_2O$, cr. yel.
$Mo_3Cl_5(OH) \cdot H_2O$ =
= $[(Mo_6Cl_8)Cl_2(OH)_2(H_2O)_2]$



$[(M_6Hal_8)X_6]$, X = Hal, OH, H_2O, cluster — oct. $[M_6]$ in the center of the cube $[Hal_8]$. Outside "big" oct. $[X_6]$, M — M 2.62–2.65, M — Hal 2.4–2.5 (Cl), 2.6 (Br), 2.8 (I); stab. $(W_6Hal_8) \ll (Mo_6Hal_8)$. str. of $[(M_6Hal_8)X_6]$

$MoOHal \cdot 4\,H_2O$, Hal = F–Br
WOCl, blk., insol. in ac.
$\xrightarrow{450^\circ}$ W + WO_2Cl_2 [58]

Sb_2O_3

$K_2[MoCl_5(H_2O)]$, red

Mo —($MoHal_5$)→ ; Mo —(Hal_2)→

	ΔH	μ_{eff}	
MoF_3, cr. yel.	−910	—	**WCl_3**, cr. brn., insol. in ac.,
$MoCl_3\downarrow$, red, dec. 500	−393	0.7	$\xrightarrow{550^\circ}$ WCl_2 + WCl_5
$MoBr_3\downarrow$, blk.-grn.	—	1.24	**WBr_3**
MoI_3, fibre, blk., $\xrightarrow{430^\circ}$ MoI_2 + I_2 m.p. 900(?)	−113	1.4	**WI_3**

$MoHal_3$ — nonvolat., light Ox; $t \rightarrow Mo_6Hal_{12} + MoHal_4\uparrow$ · **3 L**, L = NH_3, Phen, Dipy, not Ox, $\mu_{eff} \approx 3.7$. MoF_3 isostr. to ReO_3 (abs. M—M). Str. α-$MoCl_3$ like $AlCl_3$, but Mo — Mo 2.76 and 3.71; β — isostr. to $FeCl_3$. In str. $MoBr_3$, MoI_3 — chains of oct. with common face [59]

In str. WCl_3 and WBr_3 — mol. $[(W_6Hal_{12})Hal_6]$. $[W_6]$ oct. is inscribed in $[Cl_{12}]$ cubooct. 6 at. Cl are over centers of squares faces — form outer oct. (see $[Nb_6Cl_{12}]^+$) [59]

W —($WHal_4$, t)→ ; Mo —($MoHal_5$)→ ; Mo —(Hal_2)→

$MoI_{2.67}$ (≈ "Mo_3I_8")
$MoI_{2.87}$ (≈ "Mo_8I_{23}"), semiconduct. [57]

2.5+ **$Mo_2Cl_5En_4$** [20]

$MoCl_2\downarrow(\alpha,\beta)$, cr., yel., sol. in ac., NH_4OH, alc., Et_2O, $\xrightarrow{700^\circ}$ Mo + $MoCl_5$ · **$n\,H_2O$**, n = 8, 4/3

$MoBr_2\downarrow$, cr. orange, · **1/3 H_2O**, sol. in alk.

MoI_2, blk., subl. 227, $\xrightarrow{800^\circ}$ Mo + …

WCl_2, amorph powd., gray, unstab. + $H_2O \longrightarrow H_2\uparrow$

WBr_2, cr. bl.-blk., dec. 400, + $H_2O \longrightarrow H_2\uparrow$

$WI_2\downarrow$, orange, dec. H_2O (*t*)

In str. diamagn. $MHal_2$ — layers of "big" oct. $[(M_6Hal_8)Hal_2Hal_{4/2}]$ [21]

$MoHal_2 \cdot 1/3\,L$ = $[(Mo_6Hal_8)Hal_4L_2]$; L = H_2O, Py, Dipy, En; **$[\equiv MoBr_2(PR_3)_2]_2$**; [23] **$WCl_2 \cdot 2\,Thf$**

2.33+ **W_6Br_{14}** = $=[(W_6Br_8)Br_6]$ **W_6I_{14}** 2.5+ **W_6I_{15}** [57]	2.67+ **W_6Br_{16}** = $=[(W_6Br_8)Br_6]Br_2$,

Mo —($COCl_2$, H_2)→

2.25+ **$(R_4N)_2[Mo_4I_{11}]$**, anion — cluster "butterfly" $[Mo_4]$ [57]

$M_2(OAc)_4$ —($KHal$)→

$K_4[M_2Hal_8] \cdot 2\,H_2O$, Hal = Cl, Br, anion — str. anal. $[Re_2Cl_8]^{2-}$, Mo ≡ Mo 2.14, W ≡ W 2.26,
$(NH_4)_5[Mo_2Cl_9] \cdot H_2O$
$M^IMo_3Hal_7 \cdot n\,H_2O$ =
= $M^I_2[(Mo_6Hal_8)Hal_6] \cdot n\,H_2O$,
M^I = H, NH_4, $[R_4N]$;
Hal = Cl, Br
$[PyH]_3[\equiv MoBr_3(H_2O)]_2Br$
$H_2[(W_6Cl_8)Cl_6] \cdot 8\,H_2O$ [56]

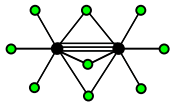
$Na_2[(Mo_6Cl_8)(OR)_6]$ [6]

$[M^I(CO)_4I]_2$, diamagn., M—M 3.16 [25]

MCl_5 —($Al + NaHal + AlHal_3$; [5] $Mo + MCl$)→

$K_3[MoF_6]$, brn., [40]
m.p. 734, paramagn., anion — oct.
$K_3[MoCl_6]$, red, grn.-bl. s. — unstab., $\mu_{eff} \approx 3.8$, oct. (d^2sp^3),
$M_2[MoCl_5(H_2O)]$
$K_3[MoBr_6]$
$K_3[Mo_2Hal_9]$, Hal = F–Br, $\mu_{eff} \approx 0.6 - 0.8$, str. anal. $K_3[W_2Cl_9]$, Mo—Mo 2.65 (Cl), 2.82 (Br)
$M_3[Mo_2Cl_8H]$, M = Rb, Cs in anion — gr. [Mo — H — Mo]

$K_5[W_3Cl_{14}]$, grn., (s. — red)
$K_3[W_2Hal_9]$, Hal = Cl, Br, μ_{eff} = 0.47/1 at. W, anion — cluster



$[M_2Hal_9]^{3-}$ str.

$Mo_2(OBu^+)_6$, cr., yel.-grn., diamagn., attached CO_2 reversible [34]

3+ (d^3)

WOHal_4 —($SnHal_2$)→

$MoOF_2$
$MoOCl_2$, brn., in str. — chains of oct. $[MoO_{2/2}Cl_{4/2}]$ -*trans*

$WOF_2\downarrow$, grey, insol. in aq. regia
$WOCl_2$, golden, subl. 500, ΔH = −832
$WOBr_2$
WOI_2 [9]

$K_2[MoOF_4] \cdot H_2O$
$(NH_4)_5[Mo_3O_4F_9] \cdot n\,H_2O$ [60]
$K_4[W_2OCl_{10}]$, gr. [WOW]-line [31]

WCl_2 —(WCl_n (n = 4 – 6)→

MoF_5 —(Si)→

WBr_5 —(H_2 (400°)→

Mo —(Cl_2 (1000°)→

[10]	ΔH	
MoF_4, cr. grn., nonvolat.	−1138	**WF_4**, cr. red, nonhydr., ΔH = −1210
$MoCl_4$, red-brn., subl., dec. 130, insol. in org. solv.	− 479	**WCl_4**, grey-brn., hyg., diamagn., ΔH = −506; $\xrightarrow{500^\circ}$ $WCl_2 + WCl_5$
$MoBr_4$, cr. blk., unstab. μ_{eff} = 1.28	−310	**WBr_4**, diamagn., nonvolat.
MoI_4, cr. blk., m.p. ≈ 400, unstab.	—	**WI_4**, blk.

$MoHal_4$ — strong Red, hydr., + $H_2O \longrightarrow Mo^{III} + Mo^V$
$MoCl_4$, $MoBr_4$ in gas — tetrah. (d^3s), $MoBr_4$, WCl_4, WBr_4 — isostr. to $NbCl_4$; **· 2 Py**, paramagn.; **· 2 MeCN**

M_2MoF_6, brn., not hydr.

M_2MoCl_6, grn.
M_2WCl_6, red
} M = K – Cs, K_2PtCl_6 str. type

M_2WBr_6, olive-grn., weak paramagn. [11]
+ $H_2O \longrightarrow MoOCl_5^{2-}$ + …

3.5+ **$(R_4N)_2[W_2Br_9]$** [43]

$[Mo(NO)_2Cl_2(PPh_3)_2]$ [8]

4+ (d^2)

5 + (d^1)

6 + (d^0)

Mo_2F_9, ↓ 150° $MoF_4 + MoF_6$

MoO_2Cl
$[MoO_2ClDipy]_2$
$[Mo_2O_3Cl_4Dipy_2]$

$MoO(OH)_3$ —MF + HF→ $(NH_4)_2[Mo_2O_4F_4(H_2O)_2]$, $K_3[Mo_2O_4F_5]$, $(NH_4)_4[Mo_2O_4F_6]$, $M_2[Mo_2O_4Cl_4(H_2O)_2] \cdot n\,H_2O$, diamagn., 2 oct. with common edges [O_2], Mo = Mo 2.57, Mo — O 1.68–2.04 [61]

MoF_6 (20°) ← $Mo(CO)_6$

$SnCl_2$

Mo —HNO_3 + HF→ $M_3[Mo_4O_{12}F_3]$ [18]

$K[MO_3F]$, chains of oct. with common edges $[MO_2O_{2/2}F_2]$
$Cs_2[MO_3F_2]$,
$(NH_4)_3[MO_3F_3]$, oct., 3 at. O *cis*-, ferroel.
$H_2MoO_3F_2 \cdot H_2O$; $Cs_3[Mo_2O_6F_3]$
$[Ph_4P]\,[MoO_3Cl]$ [29]

$NH_4[MoO_2F_3]$, zigzag. chain of oct. $[MoO_2F_2F_{2/2}]$
$K_2[MO_2F_4]$-*cis*, oct.
$K_3[WO_2F_5]$; $K_3[W_2O_4F_7]$;
$K_6[W_2O_5F_8]$
$K_2[MO_2Cl_4]$, K_2PtCl_6 str. type (O and Cl — in statistics) $\cdot\,2H_2O$ [5]

$K[MOF_5]$, anion — dis. oct.
$NH_4[MoOCl_5]$
$NH_4[MoOBr_5]$ [28]

WO_3 —WCl_6→

MoO_2F_2, colrl., subl. 270, $\Delta H = -1089$ MoO_2Cl_2, yel., m.p. 170, subl. 161; $\cdot H_2O$, in str. — chains of oct. *trans*-$[MoOCl_2(H_2O)O_{2/2}]$ $[MoO_2X_2(OPPh_3)_2]$, X = Cl, NO_3 [27] $Mo_2(OR)_2$; *n* Am [15]	WO_2F_2 (?), cr., colrl., $\cdot$ L, L = = Dipy, Phen WO_2Cl_2, yel., m.p. 497 (dec.) WO_2Br_2, cr., red, $\Delta H = -719$ WO_2I_2 $\Delta H = -607$ $\xrightarrow{t}$ WO_3 + $WOHal_4$; slow. hydr.
In gas — mol. MoO_2Cl_2, tetrah.; MO_2Hal_2 (Hal = Cl – I) layers of chains oct. $[MO_{4/2}Hal_2]$ [35]	

M —$O_2 + F_2$→ MoO_3 —$SOCl_2$→

		m.p.	b.p.	ΔH
$MoOF_4$, cr., colrl., m.p. 97, b.p. 186	WOF_4, colrl.	110	186	−1489
$MoOCl_4$, grn., subl. 104, v. hyg., strong Ox	$WOCl_4$, red, volat. > WO_2Cl_2	211	233	−740
$MoO(OTeF_5)_4$ [41]	$WOBr_4$, blk.	277	327	−582
In str. — chains of oct. $[MoOF_3F_{2/2}]$ and cycles from 4 oct. $[WO_{2/2}F_4]$, $[MOCl_4]_2$ — 2 oct. with common edge $[Cl_2]$. In gas — tetr. pyram. $MOHal_4$. In str. $MOHal_4$ — linear chains of oct. $[WO_{2/2}Hal_4]$. [16]				

$MoOCl_3$, cr. blk.-brn. >200° → $MoCl_3 + MoO_2Cl_2$; $\cdot\,2\,OPR_3$, grn.; $\cdot$ Dipy; $\cdot$ *n* ROH, grn.
$MoOBr_3$

$WOCl_3$, grn.
$WOBr_3$

In tetr. str. α-$MOHal_3$ (Hal = Cl, Br) — chains of oct. $[MHal_2Hal_{2/2}O_{2/2}]$ with common edges $[Hal_2]$; in monocl. β-$MOHal_3$ chains of oct. $[MHalHal_{4/2}O]$, at. O — term.

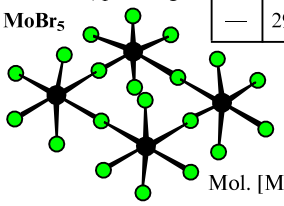
$K_2[MoOF_5]$, $\cdot H_2O$, oct.
H_2MoOCl_5, grn.
$K_2[MOHal_5]$, grn., μ_{eff} = 1.67
$Rb[MOCl_4]$, tetr. pyram., μ_{eff} = 1.76—1.86
$K[MOHal_4(H_2O)]$, Hal = Cl, Br [65]

liq. SO_2(−$SOCl_2$) ↑

O_2 (*t*) →

	m.p.	b.p.	μ_{eff}
MoF_5 [10], cr., yel.	67	214	—
$MoCl_5$, cr. blk., hyg. sol. in bz., paramagn.	194	268	1.67
$MoBr_5$	—	296	1.12

	m.p.	b.p.	ΔH
WF_5; 60° → $WF_4 + WF_6$	—	—	—
WCl_5, cr., blk.-grn. μ_{eff} = 1.67	253	288	−569
WBr_5, cr., brn.	276	333	−364



In str. MF_5 — cycles from 4 oct., linear gr. [M—F—M], in gas — $(MoF_5)_2$. In str. MCl_5 — dimers — 2 oct. with common edges, in gas — monomers — tetr. pyram., dimers and cyclic trimers.
Mol. $[MoF_5]_4$

MCl (−Cl_2) →

$Na[MF_6]$, anion oct. (d^2sp^3), Mo — F 1.74
$K_3[MF_8]$
$KWCl_6$, grn., + H_2O ⟶ blue; $\xrightarrow{t}$ $K_2WCl_6 + WCl_6$; anion — dist. oct.
K_2WCl_7
$KWBr_6$, grn. [66]

		m.p.	b.p.	ΔH
MoF_6, liq., colrl., d = 2.55, [64] m.p. 18, b.p. 35, $\Delta H = -1636$	WF_6, gas, colrl.	2	17	−1761
	WF_5Cl, gas, colrl.	−30	—	—
	WCl_6↓, cr., blk.-vlt.	281	348	−681
	350° → WCl_5; sol. in ROH, Et_2O			
	WBr_6↓, cr., bl.-blk., dec. H_2O (*t*); $\cdot$ 3 Am	—	—	−385
v. hyg., react., sol. in org. solv., HF (liq.); MoF_6 — strong. F — agent; in gas and str. $MHal_6$ — mol. oct. [70]				

$M^I[MF_7]$, M^I = Rb, Cs, [NO], $[NO_2]$, Tl, $[Cu(MeCN)_5]$ [30]
$K_2[MF_8]$

$K1 + IF_5$ → $M(CO)_6$

Mo —Cl_2; MoF_6→

H_2; Si (HF liq.) →

M —Hal_2; XeF_2→

$MoF(OMo)_5$ [37]

$W(OR)_6$ [36, 38]
$W(OEF_5)_6$, E = S, Se, Te [41]

$[R_4N][M(OR)Cl_5]$ [12]
$[R_4N][M(OR)_2Hal_4]$

$MoCl_n(OR)_{5-n}$ [67]

$[WSHal_4]_2$, Hal = Cl, Br, mol. — 2 oct. with common edges $[Hal_2]$
$WSeCl_4$, W = Se 2.20, W — Cl 2.28 [63]

IN_3 ↓

$MoNBr_2$, cr. brn., hyg., dec. 420, μ_{eff} = 0.65, $\cdot\,H_2O$ [62]; Mo_2NCl_7

200° ←

$[MoNCl_3]_4 \cdot 4\,R_2O$, [39] in mol. — square $[N_4]$, 4 oct. Mo — in middles of sides
$MoNBr_3$, brn., polymer, $\cdot\,POCl_3$

$WNBr_3$, cr., blk., hyg.

$[Ph_4As][MoNCl_4]$, anion — tetr. pyram.
$[Ph_4P][WNBr_4]$ [39]

● M
● O
● Hal

URANIUM

U^0 5f: ↓ ↓ ↓ | 6d: | 7s: ↓↑

EN 1.2

U, met., silver-wh., v. hard, ductile, yel. in air, then blk., finely desintegrated is pyrophoric, m.p. 1134, b.p. ~ 4200, sol. in ac., (MOH + H_2O_2), passiv. conc. HNO_3
$E_0U^{3+}/U_{sld} = -1.80$, $E_0U^{4+}/U_{sld} = -1.17$
α-, rh. (dist. hex. cl. pack), $d = 19.12$, CN 4 + 8
$a = 2.85$, $b = 5.86$, $c = 4.95$
↓ 662°
β-, tetr. layered str., $d = 18.11$, brittle
$a = 10.59$, $c = 5.63$
↓ 772°
γ-, cub. (α-Fe type), stab. at 20° by fusing with Cr, Mo, $d = 18.06$, plastic,
$a = 3.52$, U—U 3.05

Ca → UCl_4; UF_3
Ba; cath. Red → UF_4; KUF_5
H_2O (−H_2 −UH_3) →

air; S; N_2; H_2 →

U(Dipy)$_n$, $n = 3, 4$, dark grn., Ox in air, needle [19]

U(O,N,C) (before "UO_2"), oxocarbonitride, sld. s., metal-like phase, ex. on the surface of the met.

UOS

US_2, blk., m.p. 1850, sol. in ac. $\gamma \xrightarrow{425°} \beta \xrightarrow{1350°} \alpha$

US_3, blk., sol. in conc. HNO_3 **U_2S_3; U_3S_5**

US, yel., m.p. 2460, sol. in ac., $\Delta H = -377$, NaCl str. type

USe_2 [23]

UN, powd., grey, Ox in air, m.p. 2850 (*p*), dec. > 1900
$\Delta H = -288$, insol. in ac., NaCl str. type **U_3N_4**; **U_2N_3**

UN_2, blk., CaF_2 str. type

UP, m.p. 2850; **U_3P_4**, **U_2P_3**, **UP_2**, blk.

UC, vlt., m.p. 2400, NaCl str. type, $\Delta H = -88$
U_2C_3, $\Delta H = -205$
UC_2, red, hydr., m.p. 2350, $\Delta H = -163$, CaC_2 str. type
USi_2, m.p. 1700; **U_3Si_2**, m.p. 1665
UH_{3-x}, blk., brittle, dec. 330, $\Delta H = -125$, conduct., inflam. in air, dec. ac.,
$+H_2O \xrightarrow{350°} UO_2 + H_2$;
β-, $d = 10.9$, cub., tetrah. and icosah.
$[UH_{12}] \xrightarrow{< -100°}$ α-, cub., ferromagn., $d = 11.11$; 350°⟶U

Radioactive series of U—Ra (A = 4n + 2)
$^{238}_{92}U \xrightarrow{\alpha} {}^{234}_{90}Th \xrightarrow{\beta^-,\gamma} {}^{234}_{91}Pa \xrightarrow{\beta^-,\gamma} {}^{234}_{92}U \xrightarrow{\alpha} {}^{230}_{90}Th$
$4.51 \cdot 10^9$ y. $2.48 \cdot 10^5$ y.
99.27 % in minerals 0.0056 %
Series of Ac (A = 4n + 3)
$^{235}_{92}U$ ("AcU") $\xrightarrow{\alpha}$ $^{231}_{90}Th$ ...
$7 \cdot 10^8$ y., 0.72 % in minerals
Nuclear fuel

3+ (f^3 or f^2d^1)

UO_{2+x}, blk.-brn., sometimes pyrophoric, m.p. 2850, subl. 1400, $\Delta H = -1083$, sol. in ac., chem. inert., "uraninite", CaF_2 str. type, U—O 2.37 (+ThO_2, "breggerite", +Ln_2O_3, "cleveite")

O_2 → 4.5^+ **U_4O_9**, blk.

1125° → 4.66^+ **U_3O_7**, α, β-metastab. phase → UO_2

H_2 (900°); CO (750°) →

−H_2O ↓

$U(OH)_4$↓, light-grn., sol. in ac., Red

$U(OH)_2SO_4$
$UO(RCOO)_2 \cdot n H_2O$, grn. [26]

Uranates (IV)
$M^{II}UO_3$, blk.-brn.
M^{II} = Ca – Ba

H_2 (500°) ← $M^{II}_3UO_6$

$U(IO_3)_4$
$U(SO_4)_2 \cdot n H_2O$, $n = 4, 8$, grn., in str. — $[UO_4(H_2O)_4]$ — Archimedes antiprism
$U(NO_3)_4$, **$U(PO_3)_4$** [26]
$U(HCOO)_4$, $\mu_{eff} = 3.27$ [1]
$U(CH_3COO)_4$, threads, grn., chains of twocap antiprism (CN = 10)
$U(C_2O_4)_2 \cdot 6H_2O$; **$USiO_4$**, "coffinite"

$M[U(SO_4)_2] \cdot n H_2O$, brn., CN U 9 [24]

cath. Red (H_2SO_4, 0°) ↑

UOCl, $\Delta H = -834$
UOBr, $\mu_{eff} = 3.4–3.7$
UOI
$U_2(SO_4)_3 \cdot 9H_2O$
UPO_4, brn.
$U(HCOO)_3$, grn. [22]

UO_2Cl_2 → $(COOH)_2$ → *hν*-vis

$Cs_2[U(NO_3)_6]$
$K_4[U(C_2O_4)_4] \cdot 4H_2O$, grn., CN U 10
$Ba_2[U(C_2O_4)_4] \cdot 8H_2O$, red-vlt. [29]

O_2 →

$UOF_2 \cdot H_2O$
$UOCl_2$, $\Delta H = -1069$, CN U = 7, 8, 9
$\mu_{eff} = 2.73$
$UOBr_2$, yel. $\overset{t}{\rightleftarrows} O_2 + UHal_4$ [1]
UOI_2

UO_3 → C + CCl_2F_2 (freon-12) →

$U_2O_2Cl_5$ [30]

UF_3, cr., vlt., m.p. 1495, b.p. 2300, $\Delta H = -1444$
UCl_3, needles, grn. or red, hyg.
$\overset{t}{\longrightarrow} UCl_2 + UCl_4 + UCl_5$; in hex. str. — dist. cl. pack. Cl, CN U 9;
m.p. 835, b.p. 1780, $\Delta H = -891$
UBr_3, red, UCl_3 str. type, m.p. 730, $\Delta H = -761$
UI_3, blk., $PuBr_3$, str. type
blk., m.p. 680, b.p. ~1750, $\Delta H = -573$
· **4 L**, L = Thf, Py, mol. pentag. bipyr. [17]

Al; H_2 (*t*) ←

$MUCl_4 \cdot 4H_2O$, M = K, NH_4
CN U 9 or 8
K_2UCl_5 [25]
K_3UCl_6, vlt.
KU_2Cl_7, brn., $+H_2O \longrightarrow U^{IV}$;
$\mu_{eff} = 3.7$ [24]

[15, 27)	m.p.	b.p.	ΔH
UF_4↓, cr. grn., SP = 10^{-22}, ZrF_4, str. type; · **H_2O**	1036	1450 (subl.)	−1897 / −1910
UCl_4, cr. grn., sol. in org. solv., in tetr. str. — 2 crossing tetrah. $[UCl_4]$, CN U = 4 + 4	590	792	−1023
UBr_4, brn., in str. — chains of pentag. bipyr. $[UBrBr_{6/2}]$,	519	766 (dec.)	−899
UI_4, blk., chains of oct.	520 (dec.)	—	−527

$(NH_4)U_3F_{13}$, CN U 9 (threecap prism)
KU_2F_9, **$(NH_4)_4[UF_8]$**, antiprism
$M_3[UF_7]$, grn., anion pentag. bipyr.
$M_2[UF_6]$, chains of dodecah. or trig. antiprism
$Ba_2[UCl_8]$; **$M_2[UCl_6]$**, oct. [2]
$M_2[UBr_6]$, **$[R_4N]_2[UI_6]$**

4.25^+ **U_4F_{17}**, 4.5^+ **U_2F_9**, blk.

NaU_2Cl_6 [34]

$U(BH_4)_4$, dark-grn., subl., · **R_2O** [28]

4+ (f^2 or f^1d^1)

Aqueous solution

0	3+	4+	5+	6+

Na; Zn/Hg

$[U(H_2O)_8]^{3+}$, red-brn. ⇄ H_2O; $O_2(H+)$ / [H↑] ⇄ **$[U(H_2O)_8]^{4+}$**, grn.

$[UF_6]^-$, bl., resist. to Ox ← F⁻ ← cath. Red ← **$[UO_2(H_2O)_6]^{2+}$**, yel., diamagn., hex. bipyr., $[UO_2]$ – dumb-bell (*sf*)

$H^+ \uparrow\downarrow OH^-$ → **$[U(H_2O)_7(OH)]^{3+}$**, brn. (pH ≈ 2)

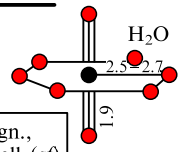
$H^+ \uparrow\downarrow H_2O$ → **$[(UO_2)_2(OH)_2]^{2+} \rightleftarrows [(UO_2)_3(OH)_5]^+$** [16]
$K = 10^{-6}$ $K = 10^{-16}$

$[UO_2]^+$, v. unstab., ex. at pH 2–4 ← H_2O

U↓ → H^+ (−H_2) → $H^+ \uparrow\downarrow OH^-$ → **$U(OH)_4$**↓, light-grn.

$H^+ \uparrow\downarrow OH^-$ → **$UO_2(OH)_2 \cdot H_2O$**↓, yel.

O_2; I_2; Fe^{3+} / O_2 →



N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_11, © Springer-Verlag Berlin Heidelberg 2011

$5+(f^1$ or $d^1)$

$6+(f^0d^0)$

O_2 ($>200°$) →

5.1+ **$U_{13}O_{34}$**, **$U_{11}O_{29}$**, stab. phasen

5.2+ **$UO_{2.6}$**, meta-stab., para-magn.

5.33+ **U_3O_8**, blk.-grn. $d = 8.3$, dec. 1450, $\Delta H = -3584$,
↓HNO_3
$U^{4+} + [UO_2]^{2+}$,
α-, chains of pentag. bipyr.
↓1350°
β-, 2 at. U CN 7, 1 at. — oct.

$>450°$

5.8+ **$UO_{2.9}$**, metastab. phase

UO_3, orange, 7 cr. forms, 1 amorph., $\Delta H = -1230$.
α-UO_3 layers $[(UO_2)O_6]$ are linked by chains U—O—U– [32]

$UO_2(NO_3)_2$
$(NH_4)_2U_2O_7$
t

400° ↑ | H_2O ↓

$H_2U_2O_7$, cr., light grn.
$UO_2(OH)_2$↓, **uranic. ac.**, cr. yel. or amorph. prec.
SP = 10^{-22}; sol. in ac., α-, layered str. U≡O 1.71, U—OH 2.5;
β-, layers of oct., $[UO_2(OH)_4]$ with common edges $(OH)_2$
↑ 100°
· **H_2O**, "shopit", "masyuit"; · **2/3 H_2O** , "becquerelite"

$UO_2(NO_3)_2$
(pH ~ 3)

$UO_2(O_2)\cdot n\,H_2O$↓, yel., $n = 2, 4$ [33]

H_2O_2 (pH ≫ 7)

$H_2O + MOH$

Peroxouranates
$Na_4[UO_2(O_2)_3]\cdot 9\,H_2O$
$K_4UO_6\cdot 6\,H_2O$
$M_4U_2O_{10}\cdot n\,H_2O$,
$Na_2U_2O_9\cdot 7\,H_2O$↓
$M_4[UO_2(O_2)(CO_3)_2]$

O_2 (inflam) U

t

H_2

Uranates (V)
Li_7UO_6, grn.
Li_3UO_4, yel.
$LiUO_3$, vlt.

$Cs_2U_4O_{12}$ [6]
$Cs_2U_9O_{27}$

Uranates (VI), $M_2O_n\cdot m\,UO_3$↓ [6]
$M^{II}_3UO_6$, orange, **Li_6UO_6**, anion — oct., U—O 2.09
Na_4UO_5, **$M^{II}_2UO_5$**, red, "mesouranate"; **M_2UO_4**; **$MgUO_4$**, yel., chains of oct., $[(UO_2)O_{4/2}]$, U=O 1.92, U—O 2.50
$Na_2U_2O_7$, "clarkeit", orange; **$(NH_4)_2U_2O_7$**, yel.
$K_2U_4O_{13}$; **$PbU_4O_{13}\cdot 5\,H_2O$**, **$Cs_2U_5O_{16}$**, **$K_4U_5O_{17}$**; **$M_2U_6O_{19}\cdot 11\,H_2O$**
$M_2U_7O_{22}$, **$Pb_3U_8O_{27}\cdot 4\,H_2O$**, "curite", **$Cs_2U_{15}O_{46}$**; **$Cs_2U_{16}O_{49}$**

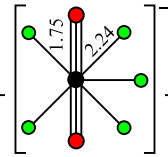
H_2O_2

Uranyl salts $[O=U=O]^{2+}$, cr., yel., fluoresce, U=O 1.61–1.93, U—O 2.3–2.4

UO_2 + HNO_3
U + N_2O_4

$UO_2(ClO_4)_2$ $\xleftarrow{270°}$ **$\cdot 6\,H_2O$**, m.p. 185 $\xleftarrow{150°}$ **$[NO_2][UO_2(ClO_4)_3]$** [12]
$UO_2(SO_4)$ $\xleftarrow{175°}$ **$\cdot n\,H_2O$**, $n = 2.5, 3.5$
$M_2[UO_2(SO_4)_2(H_2O)_2]$; **$M_4[UO_2(SO_4)_3]$**;
$M[UO_2(NO_3)_3]$; **$Cs_2[UO_2(NO_3)_4]$** [20]
$UO_2(SeO_4)\cdot 4\,H_2O$ [14]
$M[UO_2(PO_4)_m]\cdot n\,H_2O$, M = H, Li–K, Ca, Cu, Pb, Mg ("autunite")
$UO_2(NO_3)_2\cdot 6\,H_2O$, m.p. 60, sol. in alc., Et_2O
$M[UO_2(AsO_4)_n]\cdot m\,H_2O$;
$M_2[(UO_2)_2(VO_4)_2]\cdot n\,H_2O$, M = K ("carnotite"); Ca/2 ("tuyamunite")
$(NH_4)_4[X]\cdot 2\,H_2O$; **$Ca_2[X]\cdot 10\,H_2O$**, ("uranothallite"), X = $[UO_2(CO_3)_3]$, hex. bipyr. [7];
NaX′, X = **$[UO_2(CH_3COO)_3]$**
$NaMgX_3'\cdot 9\,H_2O$↓; **$MZnX_3'\cdot 6\,H_2O$**↓
$Na_2[UO_2(C_2O_4)_2]\cdot 2\,H_2O$, **$(NH_4)_4[UO_2(C_2O_4)_3]$** anion pentag. and hex. bipyr.
$(H_3O)_2[Ca(UO_2)_2(SiO_4)_2]\cdot 2\,H_2O$, "uranophan" [7]
$UO_2(CH_3COO)_2$, dec. 300 $\xleftarrow{110°}$ **$\cdot 2\,H_2O$**
$UO_2(C_2O_4)\cdot 3\,H_2O$↓

UO_2F_2, m.p. 1303, hex. bipyr. $[UO_2F_6]$;
$K_1 = 10^{-4}$, $K_2 = 10^{-5}$, $\Delta H = -1636$
$\xrightarrow[700°]{}$ $UF_6 + U_3O_8 + O_2$ [34]
UO_2Cl_2, m.p. 578; $\Delta H = 1255$; **$\cdot n\,H_2O$**, $n = 3, 1$;
UO_2Br_2, $\Delta H = -1159$ [34]
$M_3[(UO_2)_2F_7]$; **$M_4[(UO_2)_2F_8]$**; **$K_5[(UO_2)_2F_9]$**
$Cs_2[(UO_2)_2F_6(H_2O)_2]$, [8] **$Cs_2[UO_2F_4]$**; **$K_3[UO_2F_5]$**
$Cs[(UO_2)_2Cl_5]$, **$M_2[UO_2Cl_4]$**, tetrag. and pentag. bipyr.
$M_2[UO_2Br_4]$, M = Cs, $[R_4N]$, oblate oct. [9, 12]



$U_5O_{12}Cl$ [3]
UO_2F
UO_2Cl, $\mu_{eff} = 1.36$, $\xrightarrow{t}$ $UOCl_2 + Cl_2$
UO_2Br, in str. layers of pentag. bipyr. [3]

	ΔH
$UOCl_3$, brn.	−1188
$UOBr_3$, red-brn.	−988
UOI_3	−853

NH_3 + ROH

$[R_4N]_2[UOF_5]$
$[PyH]_2[UOCl_5]$
$[R_4N]_2[UOBr_5]$ [13]

[5]	m.p.	ΔH
UF_5↓, colrl. $\xrightarrow{>150°}$ $UF_6 + U_2F_9 + U_4F_{17}$, + $H_2O \longrightarrow UF_4 + UO_2F_2$;		
α-, linear chains of oct. with common vertex	287 (*p*)	−2030
β-, net of 8-vertex, b.p. 530	348	—
UCl_5, needle, red-brn., hyg. $\xrightarrow{120°}$ $UCl_4 + UCl_6$; + $H_2O \longrightarrow$ $\longrightarrow UCl_4 + UO_2Cl_2$;	320 (*p*)	−1041
$[U_2Cl_{10}]$ 2 oct. with common edges		
UBr_5, blk.-brn., $\xrightarrow{80°}$ $UBr_4 + Br_2$ mol. $[U_2Br_{10}]$	—	−858

$M_3[UF_8]$; **$M_2[UF_7]$**
Cs$[UF_6]$, bl., oct.

$HUF_6\cdot n\,H_2O$, $n = 2.5, 1.25$, grn., resist. to Ox
+ $H_2O \longrightarrow UF_4$↓ + UO_2F_2
$[R_4N]_3[UCl_8]$
M$[UCl_6]$, M = NO, $[PCl_4]$ [4]

$[U^VF_4][U^{VI}OF_5]$
$(UO_2)_2Cl_3$ [31]

$[UF_4]^+[SbF_6]^-$, cation dodecah. [5]

hv (UV); 150°(−Cl_2)

UF_4 — $F_2 + Cl_2$; O_2; XeF_n

UOF$_4$, orange $\xrightarrow{150°}$ $UF_6 + UO_2F_2$;
+ $H_2O \longrightarrow UO_2F_2$ [10]
$\xrightarrow[MF\ (SO_2)]{}$ **M$[UOF_5]$**, M = NH_4, K — Cs,

UF_6, colrl., sol. in $C_2H_4Cl_2$, Et_2O, m.p. 64 (*p*), subl. 57, $\Delta H = -2180$, mol. dist. oct.,
Ox; + HBr $\longrightarrow$ $Br_2 + UF_4 + HF$ [14]
UCl_6, cr., dark grn., sol. in CCl_4, m.p. 177 (dec.), $\Delta H = -1068$, hex. cl. pack [11]

$(NH_4)_4[UF_{10}]$, **$Na_3[UF_9]$**, yel., dec. 300
$M_2[UF_8]$, dist. $[UF_8]$
M$[UF_7]$, M = Na, $[NO]^+$, $[NO_2]^+$, anion pentag. bipyr. [18]

TRANSURANIUM ELEMENTS (An)

		5*f*	6*d*	7*s*	EN [41]
Neptunium	$_{93}Np^0$	↓ ↓ ↓ ↓ ↓		↓↑	1.3
Plutonium	$_{94}Pu^0$	↓ ↓ ↓ ↓ ↓ ↓		↓↑	1.2
Americium	$_{95}Am^0$	↓ ↓ ↓ ↓ ↓ ↓ ↓		↓↑	1.3
Curium	$_{96}Cm^0$	↓ ↓ ↓ ↓ ↓ ↓ ↓	↓	↓↑	1.2
Berkelium	$_{97}Bk^0$	↓↑ ↓ ↓ ↓ ↓ ↓ ↓	↓	↓↑	1.2
Californium	$_{98}Cf^0$	↓↑ ↓↑ ↓↑ ↓ ↓ ↓	↓	↓↑	1.2
Einsteinium	$_{99}Es^0$	↓↑ ↓↑ ↓↑ ↓↑ ↓ ↓	↓	↓↑	1.2
Fermium	$_{100}Fm^0$	↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓		↓↑	1.2
Mendelevium	$_{101}Md^0$	↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓		↓↑	1.2
Nobelium	$_{102}No^0$	↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑		↓↑	
Lawrencium	$_{103}Lr^0$	↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑	↓	↓↑	

Rutherfordium	$_{104}Rf$	**Meitnerium**	$_{109}Mt$
Dubnium	$_{105}Db$	**Darmstadtium**	$_{110}Ds$
Seaborgium	$_{106}Sg$	**Röntgenium**	$_{111}Rg$
Bohrium	$_{107}Bh$	**Copernicium**	$_{112}Cn$ [24]
Hassium	$_{108}Hs$		

***) Authors:**
Seaborg (S.)
Ghiorsso (G.)
Armbruster (A.)
Münzenberg (M.)
Flerov (F.)
Oganesian (O.)

Discovery *)	Synthesys [30]
$^{238}_{92}U\ (n,\gamma)\ ^{239}_{92}U \xrightarrow[\beta^-]{} {}^{239}_{93}\mathbf{Np}$ 2.3 d. (McMillan, Abelson, 1940)	In a nucl. reactor $^{238}_{92}U\ (n,2n)\ ^{237}_{92}U \xrightarrow{\beta^-} {}^{237}_{93}\mathbf{Np}$ (A = 4n + 1) 2.14 · 10⁶ y.
$^{238}_{92}U\ (^2_1d,2n)\ ^{238}_{93}Np \xrightarrow[\beta^-]{} {}^{238}_{94}\mathbf{Pu}$ (S., 1941) 86.4 y.	$^{239}_{93}Np \xrightarrow[2.35\ d.]{\beta^-} {}^{239}_{94}\mathbf{Pu}$ (A = 4n + 3) 24390 y.
$^{241}_{94}Pu \xrightarrow[13\ y.]{\beta^-} {}^{241}_{95}\mathbf{Am}$ (S., G., 1944) 436 y.	$^{242}_{94}Pu\ (n,\beta)\ ^{243}_{95}\mathbf{Am}$ 7370 y.
$^{239}_{94}Pu\ (\alpha,n)\ ^{242}_{96}\mathbf{Cm}$ (S., G., 1944) 163 d.	$^{239}_{94}Pu\ (n,\gamma) \ldots {}^{244}_{95}Am \xrightarrow[\beta^-]{} {}^{244}_{96}\mathbf{Cm}$ 19 d.
$^{241}_{95}Am\ (\alpha,2n)\ ^{243}_{97}\mathbf{Bk}$ (G., S., 1944) 4.5 h.	$^{244}_{96}Cm\ (\alpha,p)\ ^{247}_{97}\mathbf{Bk}$ (in accelerator) 1380 y.
$^{242}_{96}Cm\ (\alpha,n)\ ^{245}_{98}\mathbf{Cf}$ (G., S.,1950) 44 min.	$^{244}_{96}Cm \ldots {}^{250}_{97}Bk \xrightarrow[\beta^-]{} {}^{250}_{98}\mathbf{Cf}(n,\gamma)$ 12 y.
$^{238}_{92}U(\leqslant 15n, 6\beta)\ ^{253}_{98}Cf \xrightarrow[\beta^-]{} {}^{253}_{99}\mathbf{Es}$ (S., 1952) 20.03 d.	$^{252}_{98}Cf(n,\gamma)\ ^{253}_{98}Cf \xrightarrow[\beta^-]{} {}^{253}_{99}\mathbf{Es}\ (n,\gamma)\ ^{254}_{99}\mathbf{Es}$ 20 d. > 2 y.
$^{253}_{99}Es - {}^{255}_{100}\mathbf{Fm}$ (G., 1952 г.) 22 h.	$^{238}_{92}U\ (^{16}_{8}O,\ 4n)\ ^{250}_{100}\mathbf{Fm}$ 30 min.
$^{253}_{99}Es\ (\alpha,n)\ ^{256}_{101}\mathbf{Md}$ (G., S., 1955) 77 min.	$^{254}_{99}Es\ (^4_2He)\ ^{258}_{101}\mathbf{Md}$ 60 d.
$^{241}_{94}Pu\ (^{16}_{8}O,\ 4n)\ ^{253}_{102}\mathbf{No}$ (F., 1958) 95 s.	$^{241}_{94}Pu\ (^{18}_{8}O,\ 4n)\ ^{255}_{102}\mathbf{No}$ 3 min.
$^{246}_{96}Cm\ (^{12}_{6}C,\ 4n)\ ^{254}_{102}\mathbf{No}$ (G., S., 1958) 3 s.	$^{238}_{92}U\ (^{22}_{10}Ne,\ 4n)\ ^{259}_{102}\mathbf{No}$ 58 min.
$^{252}_{98}Cf\ (^{10}_{5}B,\ 5n)\ ^{257}_{103}\mathbf{Lr}$ (G., 1961) 8 s.	
$^{243}_{95}Am\ (^{18}_{8}O,\ 5n)\ ^{256}_{103}\mathbf{Lr}$ (F., 1965) 35 s.	
$^{242}_{94}Pu\ (^{22}_{10}Ne,\ 4n)\ ^{260}_{104}\mathbf{Rf}$ (F., 1964) 0.3 s.	
$^{249}_{97}Bk\ (^{15}_{7}N,\ 3n)\ ^{261}_{104}\mathbf{Rf}$ (G., 1969) 70 s.	
$^{243}_{95}Am\ (^{22}_{10}Ne,\ 4n)\ ^{261}_{105}\mathbf{Db}$ (F., 1971) 1.8 s.	
$^{249}_{98}Cf\ (^{15}_{7}N,\ 4n)\ ^{260}_{105}\mathbf{Db}$ (G., 1970) 9 s.	
$^{249}_{98}Cf\ (^{18}_{8}O,\ 4n)\ ^{263}_{106}\mathbf{Sg}$ (G., 1974) 0.8 s.	
$^{208}_{82}Pb\ (^{54}_{24}Cr,\ 2n)\ ^{260}_{106}\mathbf{Sg}$ (F., O., 1974) 3.6 ms.	
$^{209}_{83}Bi\ (^{54}_{24}Cr,\ n)\ ^{262}_{107}\mathbf{Bh}$ (A., M., 1981) 102 ms.	
$^{208}_{82}Pb\ (^{58}_{26}Fe,\ n)\ ^{265}_{108}\mathbf{Hs}$ (A., M.; O., 1984) $1.8 \cdot 10^{-3}$ s.	
$^{209}_{83}Bi\ (^{58}_{26}Fe,\ n)\ ^{266}_{109}\mathbf{Mt}$ (M., 1982) $5 \cdot 10^{-3}$ s.	
$^{208}_{82}Pb\ (^{62}_{28}Ni,\ n)\ ^{269}_{110}\mathbf{Ds}$ (A., M., 1994) 0.17 ms.	
$^{209}_{83}Bi\ (^{64}_{28}Ni,\ n)\ ^{272}_{111}\mathbf{Rg}$ (A., M., 1994) 2.04 ms.	
$^{208}_{82}Pb\ (^{70}_{30}Zn,\ n)\ ^{277}_{112}\mathbf{Cn}$ (A., M., 2010) 280 ms.	

Np	**Pu**	**Am**	**Cm**	**Bk** [17]	**Cf** [17]	**Es**
Met. silver-wh., mild, sol. in HCl, insol. in conc. HNO_3, H_2SO_4, ox. in air						
d 20.4 m.p. 637 b.p. 4082 $E_0M^{3+}/M_{sld.} = -1.79$	19.8 640 3352 −1.58	11.7 1176 2880 −2.07	13.5 1345 3110 −2.06	14.8 1050 subl. −2.01	— 900±30 subl. −1.93	— 860 — −2.00
α-, rh. (dist. α-Fe str. type), CN 4 (disphenoid), *a* = 4.72, *b* = 4.88, *c* = 6.66	α-, monocl., *a* = 6.18, *b* = 4.82, *c* = 10.96, *β* = 101.79	α-, hex. four-layered cl. pack.				
↓ 280°	↓ 122°					
β-, tetr., *d* = 19.4, *a* = 4.89, *c* = 3.38	*β*-, monocl., *d* = 17.8, *a* = 9.28, *b* = 10.46, *c* = 7.86, *β* = 92.13	*a* = 3.47 *c* = 11.24	3.49 11.33	3.42 11.07	3.38 11.04 (I form) *a* = 4.00 *c* = 12.80 (II form)	
↓ 576°	↓ 207°	↓ *p*				
γ-, cub. (α-Fe str. type) *d* = 18.0, *a* = 3.43	*γ*-, rh., *d* = 17.2, *a* = 3.16, *b* = 5.76, *c* = 10.16, CN 12	cub. (α-Fe type) *d* = 13.1 *a* = 4.89			↓ 600°	
	↓ 315°	↓ *p*				
	δ-, cub. cl. pack., *d* = 15.9, *a* = 4.6	rh. (α-U str. type) *a* = 3.06 *b* = 5.97 *c* = 5.17	↓ *p*			
	↓ 457°					
	δ′-, tetr., *d* = 16.0, *a* = 3.31, *c* = 4.48		*β*-, cub. cl. pack.			
	↓ 472°		*d* = 13.25		—	
	ε-, cub. (α-Fe type), *d* = 16.5,	*a* = 3.63	*a* = 4.93 [1]		*a* = 5.06	

2+

AnO, films, powd., blk., conduct., insertion phases of at. O in cub. cl. pack. of met., NaCl str. type

3+

An_2O_3, An = Np, Pu, Am, Cm, Cf, Es; La_2O_3 str. type (Pu), Mn_2O_3 str. type (Cf) [19, 22]

$An(OH)_3\downarrow$, [20] An = Np (red), Pu (bl.), Am (pink), Cm (wh.), isostr. hex. $La(OH)_3$

O_2

NH_4OH

$An(ClO_4)_3$, An = Np, Pu [5]
$An(IO_3)_3\downarrow$, Pu, Cm
$An_2(SO_4)_3$, Pu(· 7 H_2O), Am, Cm, Bk
$An(NO_3)_3$, Am, Cm
$AnPO_4$, Pu(· 9 H_2O), Cm(· *x* H_2O)
$CmAsO_4$, $CmVO_4$
$An_2(C_2O_4)_3$, Pu, Am(· 10 H_2O), Cm↓
$An(HCOO)_3$, Pu, Am, Cm [5]

$LiAmO_2$ [20]

AnOCl, isostr. to PbClF [31]

$K_5An(SO_4)_4$
An = Np, Pu
$M[Pu(SO_4)_2] \cdot n H_2O$

An → HaI_2

H_2 (?)

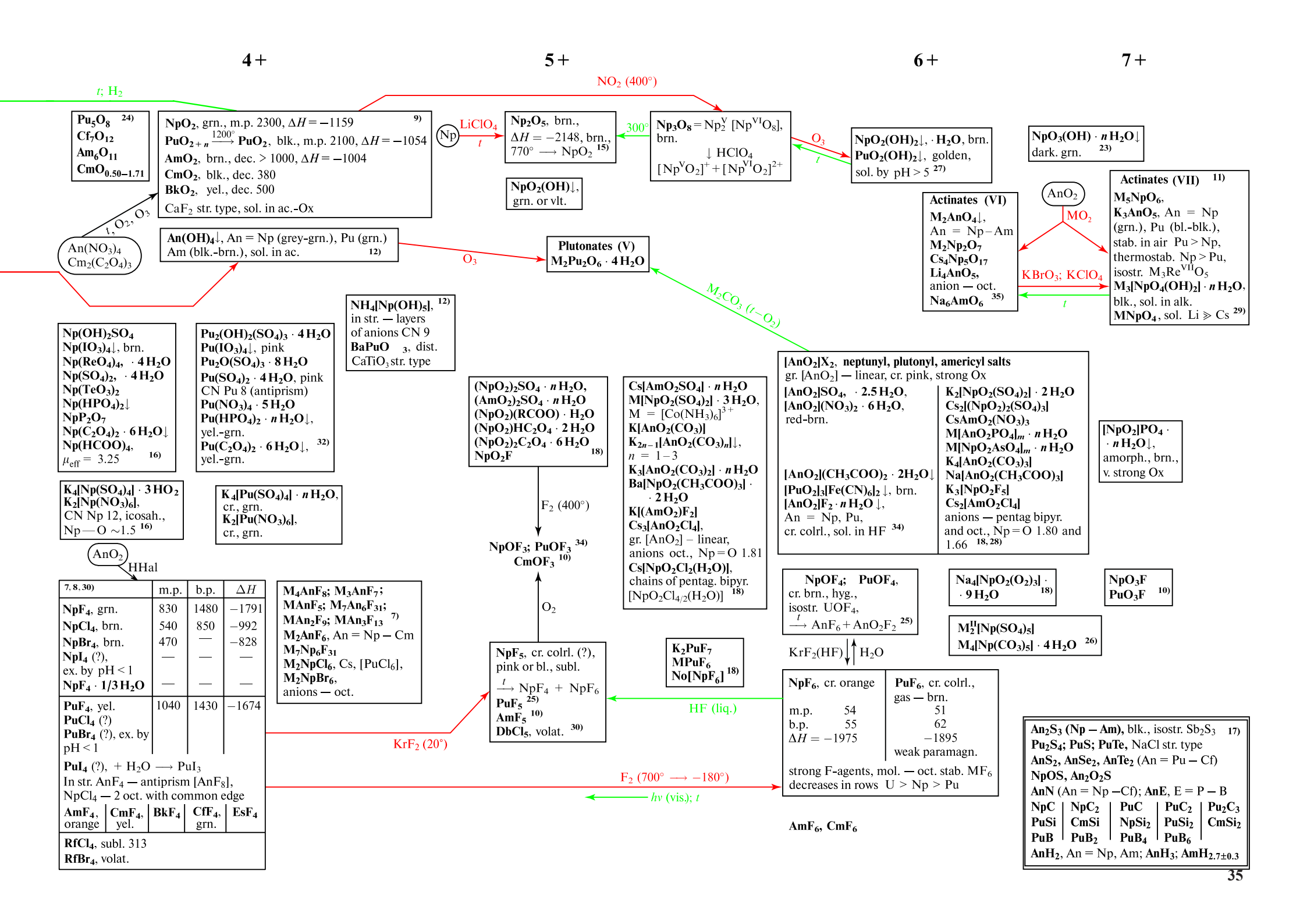
$AmCl_2$
$BkCl_2$
$CfBr_2$
$EsCl_2$ [3]

	m.p.	b.p.	ΔH
NpF_3, purp.	1380	2200	−1506
$NpCl_3$, colorl.	802	1500	−904
$NpBr_3$, grn.	750	—	−774
NpI_3, brn.	767	—	−594
PuF_3, purp.	1426	2300	−1569
$PuCl_3$, grn. · *n* H_2O, *n* = 1; 3; 6	760	1770	−963
$PuBr_3$, grn. · 6 H_2O	—	—	−832
PuI_3, grn. · 4L	780	—	−556
$AmF_3\downarrow$, pink	1430	2070	−1648
$AmCl_3$, pink	850	1750	−1041
$AmBr_3$, colrl.	680	—	−912
AmI_3, yel.	—	—	—
$CmF_3\downarrow$ **CfF_3**	—	—	—
$CmCl_3$ **$CfCl_3$**	545	**$BkCl_3$**	**EsF_3**
$CmBr_3$ **$CfBr_3$**	700	**$BkBr_3$**	**$EsCl_3$**
— **CfI_3**	700	—	**$EsBr_3$** [6] **EsI_3**

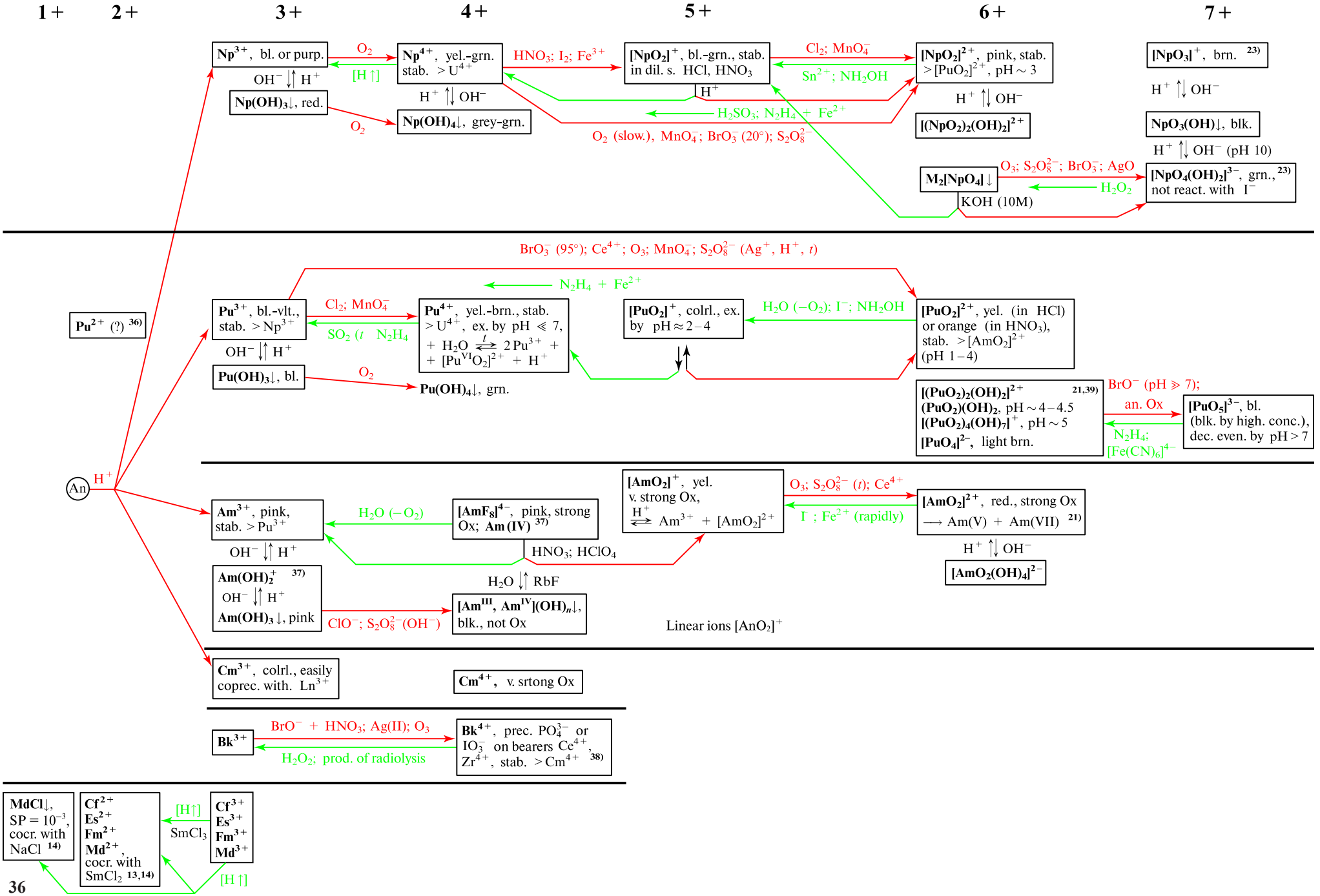
Str. AnF_3 – LaF_3 type (CN 11), $AnCl_3$ – UCl_3 type (CN 9); $AnBr_3$ and AnI_3 – CN 8.

$MAnF_4$,
M_2AnF_5,
M_3AnF_6,
MAn_2F_7,
An = Pu, Am
$Cs_2Na[AnCl_6]$,
An = Np, Pu, Am,Cm,Bk [2,4]

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_12, © Springer-Verlag Berlin Heidelberg 2011


4+
5+
6+
7+
t; H2
NO2 (400°)
Pu5O8 24)
Cf7O12
Am6O11
CmO0.50–1.71
NpO2, grn., m.p. 2300, ΔH = –1159 9)
PuO2+n 1200° PuO2, blk., m.p. 2100, ΔH = –1054
AmO2, brn., dec. > 1000, ΔH = –1004
CmO2, blk., dec. 380
BkO2, yel., dec. 500
CaF2 str. type, sol. in ac.-Ox
Np
LiClO4
t
Np2O5, brn., ΔH = –2148, brn., 770° → NpO2 15)
300°
Np3O8 = Np2V [NpVIO8], brn.
↓ HClO4
[NpVO2]+ + [NpVIO2]2+
O3
t
NpO2(OH)2↓, · H2O, brn.
PuO2(OH)2↓, golden, sol. by pH > 5 27)
NpO2(OH)↓, grn. or vlt.
NpO3(OH) · n H2O↓ dark. grn. 23)
t; O2; O3
An(NO3)4
Cm2(C2O4)3
An(OH)4↓, An = Np (grey-grn.), Pu (grn.) Am (blk.-brn.), sol. in ac. 12)
O3
Plutonates (V) M2Pu2O6 · 4 H2O
M2CO3 (t – O2)
Actinates (VI) M2AnO4↓, An = Np – Am M2Np2O7 Cs4Np5O17 Li4AnO5, anion — oct. Na6AmO6 35)
AnO2
MO2
KBrO3; KClO4
t
Actinates (VII) 11) M5NpO6, K3AnO5, An = Np (grn.), Pu (bl.-blk.), stab. in air Pu > Np, thermostab. Np > Pu, isostr. M3ReVIIO5 M3[NpO4(OH)2] · n H2O, blk., sol. in alk. MNpO4, sol. Li ≫ Cs 29)
NH4[Np(OH)5], 12) in str. — layers of anions CN 9 BaPuO3, dist. CaTiO3 str. type
Np(OH)2SO4
Np(IO3)4↓, brn.
Np(ReO4)4, · 4 H2O
Np(SO4)2, · 4 H2O
Np(TeO3)2
Np(HPO4)2↓
NpP2O7
Np(C2O4)2 · 6 H2O↓
Np(HCOO)4, μeff = 3.25 16)
Pu2(OH)2(SO4)3 · 4 H2O
Pu(IO3)4↓, pink
Pu2O(SO4)3 · 8 H2O
Pu(SO4)2 · 4 H2O, pink CN Pu 8 (antiprism)
Pu(NO3)4 · 5 H2O
Pu(HPO4)2 · n H2O↓, yel.-grn.
Pu(C2O4)2 · 6 H2O↓, 32) yel.-grn.
(NpO2)2SO4 · n H2O, (AmO2)2SO4 · n H2O
(NpO2)(RCOO) · H2O
(NpO2)HC2O4 · 2 H2O
(NpO2)2C2O4 · 6 H2O
NpO2F 18)
F2 (400°)
NpOF3; PuOF3 34)
CmOF3 10)
O2
Cs[AmO2SO4] · n H2O
M[NpO2(SO4)2] · 3 H2O, M = [Co(NH3)6]3+
K[AnO2(CO3)]
K2n–1[AnO2(CO3)n]↓, n = 1–3
K3[AnO2(CO3)2] · n H2O
Ba[NpO2(CH3COO)3] · · 2 H2O
K[(AmO2)F2]
Cs3[AnO2Cl4], gr. [AnO2] – linear, anions oct., Np = O 1.81
Cs[NpO2Cl2(H2O)], chains of pentag. bipyr. [NpO2Cl4/2(H2O)] 18)
[AnO2]X2, neptunyl, plutonyl, americyl salts
gr. [AnO2] — linear, cr. pink, strong Ox
[AnO2]SO4, · 2.5 H2O, [AnO2](NO3)2 · 6 H2O, red-brn.
[AnO2](CH3COO)2 · 2H2O↓
[PuO2]3[Fe(CN)6]2↓, brn.
[AnO2]F2 · n H2O↓, An = Np, Pu, cr. colrl., sol. in HF 34)
K2[NpO2(SO4)2] · 2 H2O
Cs2[(NpO2)2(SO4)3]
CsAmO2(NO3)3
M[AnO2PO4]m · n H2O
M[NpO2AsO4]m · n H2O
K4[AnO2(CO3)3]
Na[AnO2(CH3COO)3]
K3[NpO2F5]
Cs2[AmO2Cl4]
anions — pentag bipyr. and oct., Np = O 1.80 and 1.66 18, 28)
[NpO2]PO4 · · n H2O↓, amorph., brn., v. strong Ox
K4[Np(SO4)4] · 3 HO2
K2[Np(NO3)6], CN Np 12, icosah., Np — O ~1.5 16)
K4[Pu(SO4)4] · n H2O, cr., grn.
K2[Pu(NO3)6], cr., grn.
AnO2
HHal
7, 8, 30)
m.p.
b.p.
ΔH
NpF4, grn. 830 1480 –1791
NpCl4, brn. 540 850 –992
NpBr4, brn. 470 — –828
NpI4 (?), ex. by pH < 1 — — —
NpF4 · 1/3 H2O — — —
PuF4, yel. 1040 1430 –1674
PuCl4 (?)
PuBr4 (?), ex. by pH < 1
PuI4 (?), + H2O → PuI3
In str. AnF4 — antiprism [AnF8], NpCl4 — 2 oct. with common edge
AmF4, orange
CmF4, yel.
BkF4
CfF4, grn.
EsF4
RfCl4, subl. 313
RfBr4, volat.
M4AnF8; M3AnF7; MAnF5; M7An6F31; MAn2F9; MAn3F13 7)
M2AnF6, An = Np – Cm
M7Np6F31
M2NpCl6, Cs, [PuCl6],
M2NpBr6, anions — oct.
KrF2 (20°)
NpF5, cr. colrl. (?), pink or bl., subl. t → NpF4 + NpF6
PuF5 25)
AmF5 10)
DbCl5, volat. 30)
K2PuF7
MPuF6
No[NpF6] 18)
HF (liq.)
NpOF4; PuOF4, cr. brn., hyg., isostr. UOF4, t → AnF6 + AnO2F2 25)
KrF2(HF) ↕ H2O
Na4[NpO2(O2)3] · · 9 H2O 18)
M2II[Np(SO4)5]
M4[Np(CO3)5] · 4 H2O 26)
NpO3F
PuO3F 10)
NpF6, cr. orange
m.p. 54
b.p. 55
ΔH = –1975
PuF6, cr. colrl., gas — brn.
51
62
–1895
weak paramagn.
strong F-agents, mol. — oct. stab. MF6 decreases in rows U > Np > Pu
F2 (700° → –180°)
hv (vis.); t
AmF6, CmF6
An2S3 (Np – Am), blk., isostr. Sb2S3 17)
Pu2S4; PuS; PuTe, NaCl str. type
An2S3, An2Se3, An2Te3 (An = Pu – Cf)
NpOS, An2O2S
AnN (An = Np – Cf); AnE, E = P – B
NpC PuSi PuB
NpC2 CmSi PuB2
PuC NpSi2 PuB4
PuC2 PuSi2 PuB6
Pu2C3 CmSi2
AnH2, An = Np, Am; AnH3; AmH2.7±0.3

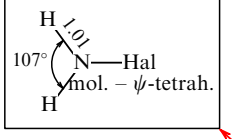
TRANSURANIC ELEMENTS IONS IN AQUEOUS SOLUTIONS



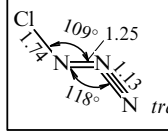
NITROGEN HALIDES AND OXOHALIDES

«3–» 1– 1/3 + 1 + 2 + 3 + 5 +

NH_2F, F–amine
NH_2Cl, Cl–amine



Halogenazides	m. p.	b. p.
FN_3, gas yel.	–139	–30
$\xrightarrow{t}$ N_2 + N_2F_2		
ClN_3, gas colrl.	–100	–15
BrN_3, liq. red	–45	—
IN_3, cr. yel.	—	— [20]



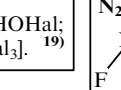
HN_3 — F_2 (–NH_4F, –N_2) → Halogenazides
Halogenazides — I_2 (–AgI) → AgN_3

NCl_3, "nitrogen chloride", oil, yel., with a pungent smell, m. p. –27, b.p. 71, exp. 90°, ΔH = +230, sol. in H_2O
NBr_3, cr. red, exp., stab. s. in CH_2Cl_2;
+ NH_3 ⟶ NH_2Br [12,19]
↓ I_2
NBr_2I, cr. brn., dec. –20
NI_3↓, cr. dark red, dec. 78, subl., exp.
· ***n*** NH_3↓, cr., brn., exp. 20°
n = 1, red needles,
n = 3, stab.
+ H_2O ⟶ NH_3 + HOHal;
Mol. – ψ-tetrah [:$NHal_3$]. [19]

NH_4Cl — Hal_2 → NCl_3
NH_3 — Hal_2 → NCl_3
NH_3 — Cl_2 (pH 4.5) → NH_2Cl

NHF_2, difluoramide, gas colrl., m. p. –116, b. p. –23, dec. 200, exp., ΔH = –67, μ = 1.93, mol. – ψ-tetrah.

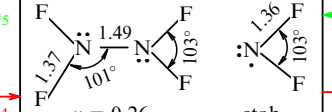
NH_3 — F_2 → NHF_2
NHF_2 — KF (–KHF_2) → **N_2F_2**, [21] **difluorodiazine**



	m. p.	b. p.	ΔH
cis-	–196	–106	+67
trans-	–172	–111	+79

slow $\xrightarrow{20°}$ $N_2 + F_2$ $\xrightarrow{100°}$ NF_3

N_2F_2, tetrafluorhydrazine, gas, m. p. –162, b. p. –74, ΔH = –8,
$N_2F_4 \rightleftarrows 2\,NF_2^{\bullet}$



μ = 0.26, strongest F–agent
stab. radical

F_2 — Hg; C; $Fe(CO)_5$ → N_2F_2
N_2F_2 — $KMnO_4$ → N_2F_4
F_2 — Cu; Fe; Hg; C; OF_2; F_2; ClF_3; → **NF_3, nitrogen fluoride**, gas. colrl., toxic, m. p. –209, b. p. –129, dec. 600, ΔH = –125, chem. inert. even at high *t*, μ = 0.21. Mol. – ψ-tetrah.,
+ H_2O $\xrightarrow[\text{spark}]{t}$ HF + NO + NO_2 [12]

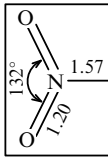
N_2F_4 — EF_n → **$[N_2F_3]^+X^-$**, $X = Sb_2F_{11}$, EF_6 (E = As, Sb, Sn); strongest F–agents (+ Rn ⟶ RnF_n) [4]

$[N_2F]^+X^-$, X = BF_4, SbF_6, AsF_6, dec. –5, 100, 200 [2]

N_2O_4 — CoF_3; F_2 → **Nitril halides**
HNO_3 — HSO_3Cl → **Nitril halides**

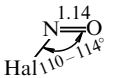
Nitril halides	m. p.	b. p.	dec.	ΔH	μ
NO_2F, gas colrl.	–166	–72	300	–79	0.47
NO_2Cl, gas colrl.	–145	–14	—	—	0.42

[14] mol. – triangle; **[NO_2][OHal]** = "Hal(NO_3)"



NO_2CF_3, gas colrl., b. p. –31
NO_2CCl_3, "chlorpikrin", liq., colrl., m. p. –64, b. p. 112;
C—Hal 1.33 (F), 1.73 (Cl)

NO — Hal_2 (act. C) → **Nitrozylhalides** [14]
$NaNO_2$ — $POCl_3$ (*t*) → **Nitrozylhalides** [14]
Nitrozylhalides [14] — O_3; *t* (–O_2) → N_2O_4
N_2O_4 → **Nitrozylhalides** [14]



	m. p.	b. p.	dec.	ΔH
NOF, gas colrl.	–133	–60	—	–63
· ***n*HF** = $[NO]^+[F(HF)_n]^-$, *n* = 3, 4; · ***n*** H_2O, clathrate				
NOCl, gas yel.	–60	–6	> 100	+50
NOBr, gas brn.	–55	–2	~ 20	+79
NON_3, liq. yel.	–57	—	–50	—
$NOCF_3$, gas bl.	–197	–87	chem. inert	

Hal – agents: NOF + Si ⟶ SiF_4 + NO

Nitrozylhalides [14] — F_2 → NO → **NOF_3, "nitrogen trifluoride oxide"**, gas colrl., m. p. –160, b. p. –80, dec. 300, ΔH = –134, μ = 0.04, mol. – tetrah., strong F-agent,
+ N_2O_4 $\xrightarrow{t}$ NOF + NO_2F;
+ Cl_2 ⟶ ClF + NOF;
not react. with SiO_2, и H_2O [5]

NOF_3, "nitrogen trifluoride oxide" — EF_n → **$[NOF_2]^+[EF_6]^-$**, E = As, Sb, v. act. Ox., cation – triangle
$[NOCl_2]^+[SbCl_6]^-$, dec. 145. [22]

O_2NOOCF_3 [15]

OF_2; POF_3 → **NF_3, nitrogen fluoride**

$[NF_2]^+X^-$, X = SF_5, SO_2F, SO_3F, gas, colrl, unstab.;
NF_2CF_3, m. p. –122, b. p. –77

$[NF_4]^+X^-$, perfluorammonium salts, [6]
X = HF_2, BF_4, $HalO_4$, EF_6/n (E = Si–Ti, As–Nb, Mn, Ni), dec. 100–300, cation – tetrah.
+ H_2O ⟶ $NF_3 + O_2 + HF + H_nEO_4$

NF_3, nitrogen fluoride — an. Ox. → NH_4HF_2
NH_4HF_2 — $[K_2F]^+X^-$ → **$[NF_4]^+X^-$, perfluorammonium salts**

NF_2Cl, nitrogen chloride difluoride, m. p. –190, b. p. –67, dec. 100 (→ NF_3), ΔH = +17, mol. – ψ-tetrah.

N_2F_4 — Cl_2 (*hν*-B); NO; Hg → **NF_2Cl**, nitrogen chloride difluoride

NHF_2 — $Cl_2 + KF$ → **NF_2Cl**, nitrogen chloride difluoride

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_13, © Springer-Verlag Berlin Heidelberg 2011

NITROGEN

EN 3,1

N^0 2s ↑↓ 2p ↓ ↓ ↓

3– 2– 1/3– 0 1+ 2+

NH_3, ammonia, gas colrl., pungent odour, $d = 0.77$, m. p. –78, b. p. –33, $\Delta H = -46$, $(NH_3)_n$ – associated by H-bonds, mol. – ψ-tetrah. [:NH_3], sp^3), $\mu = 1.46$, $\varepsilon = 22$ (–34°), solv. for M^I, M^{II}, $MHal_n$, S, MNO_3, MNH_2;
$Na + NH_3(liq.) \leftrightarrows Na^+ + e \cdot NH_3^-$ (bl.); $2\,NH_3(liq.) \leftrightarrows NH_4^+ + NH_2^-$, $[NH_4^+][NH_2^-] = 10^{-33}$ (–50°); sol. in H_2O 34%(wt.) = 99% (vol.), pH = 11.8

$NH_3 + H_2O \overset{K=0.2}{\rightleftharpoons}$ **$NH_3 \cdot H_2O$** (= H_3N...HOH) $\overset{K=10^{-5}}{\rightleftharpoons} NH_4^+ + OH^-$,
"ammonium hydroxide", "NH_4OH"
$+ O_2$; Cl_2; $CuO(t) \longrightarrow N_2$ $\quad K = \dfrac{[NH_4^+][OH^-]}{[NH_3 \cdot H_2O]} = 10^{-5}$

n $NH_3 \cdot H_2O$, n = 2[$(NH_4)_2O$, m. p. 78, dec.], 1 = "NH_4OH" [23]
(m. p. –77, in str.–chains $(H_2O)_n$, connected mol. NH_3);
1/2 (m. p. –97, in str.–mol. H_2O – disordered)
$MX_n \cdot y\,NH_3$

HX ↑ OH⁻

Ammonium salts
NH_4Hal $\overset{t}{\rightleftarrows} NH_3 + HHal$, stab. $NH_4I > NH_4F$
$(NH_4)_2SO_4$, dec. 357
NH_4HSO_4, m. p. 251, b. p. 490
NH_4HCO_3, dec. 40
NH_4X, X = NO_2, ClO_4, $Cr_2O_7/2$, $\overset{t}{\longrightarrow} N_2 + H_2O + E_2O_n$
NH_4NO_3 $\overset{210°}{\longrightarrow} N_2O + H_2O$ (slow); $\longrightarrow N_2 + H_2O + O_2$ (exp.)
cation – tetrah. (sp^3), N – H 1.03
$[R_4N]^+X^-$ – tetraalkylammonium salts

H₂O ↑ Na (–H_2; 350°)

Amides
$NaNH_2$, cr. colrl., m. p. 210, b. p. 400, K (338), Rb (309); sol. in NH_3 liq.
$Ba(NH_2)_2$, m. p. 280; **$Cr(NH_2)_3$**, dec. 100, $+ H_2O \longrightarrow NH_3 + M(OH)_n$
$O=C(NH_2)_2$, carbamide (urea),
$Ca(CN)_2$, cyanamide, subl. 1200, $+ H_2O \overset{t}{\longrightarrow} CaCO_3 + NH_3$,
anion $[N=C=N]^{2-}$ linear

t (–NH_3) ↓

Imidies
Li_2NH, **$S_n(NH)_{8-n}$**, – rings

M ↓

Nitrides, M_3N_x

Salt-like $H_2O \longrightarrow NH_3$	**M_3N**, cr. red., Li (m. p. 814); v. act. Na (dec. 200); K – Cs (exp.) **M_2N**, M = Ca – Ba, *anti*-$CdCl_2$ str. **Mg_3N_2**, dec. 1500 } stab. in air **Ca_3N_2**, m. p. 1195 } Mn_2O_3 str. **Zn_3N_2**, dec. 700 } type [3] **Be_3N_2**, m. p. 2200 (dec.) **Cu_3N**, dec. 450, *anti*-RO_3 str. type
Covalent	**BN**, wh., dec. 2500, m. p. 3000 ($p\,N_2$) **AlN**, wh., dec. 2200 } wurtzite **GaN**, yel. } str. type **InN**, blk. **Si_3N_4**, wh., subl. 1900 NaCl str. type, dielectric or semyconduct., stab. therm., to Ox, M-melts, ac. resist. (t)
Metal-like	**TiN**, m. p. 3200 **CrN**, m. p. 1500 **ZrN**, m. p. 2980 **AnN**, An = Th, U, Pu **VN**, NaCl str. type **Nb_2N**, **Cr_2N**, **Fe_4N**, **Co_3N**, **Co_2N**, **Ni_3N**, **Ni_4N**, N intercalation phase in M-str., refractory, v. hard, brittle, with met. thermal and elect. conduct., chem. inert

Ca_2NHal [24]

t (–NH_3) ↓

NO_2 [H↑]; Pt/C
MNO_3 SO_2; cath. Red.
CaC_2 (1000°, –C, cyanamid. method of binding N_2)

NH_2OH, hydroxylamine, cr. colrl., m. p. 33, b. p. 58/22 mm, exp. 100°, $\Delta H = -113$;
$+ H_2O \leftrightarrows NH_3OH^+ + OH^-$; $K_{bas.} = 10^{-8}$; (conc. s.);
↓ (OH^-, Pt)
$N_2 + NH_3 + N_2O$;
strong. Red, mol. – ψ-tetrah.

$[NH_3OH]^+X^-$, hydroxylammonium salts, X = Cl (m. p. 151), ClO_4, $SO_4/2$, NO_3, $PO_4/3$, cr., stab., dist. tetrah. cation, N — H 0.99, N — O 1.41 [9]

N_2 ↑

Li (20°); Mg – Ba; Al; Ti – Mn; Ln; Mo; W(t); MH; $TiO_2 + C$

N_2H_4, hydrazine (diamide), liq. colrl., fumed, m. p. 2, b. p. 114, $\overset{t}{\longrightarrow} NH_3 + N_2$,
$\Delta H = +52$ (liq.), $+95$ (gas), $\mu = 1.83$, $\varepsilon = 52$
$+ H_2O \leftrightarrows N_2H_5^+ + OH^-$, $K_1 = 10^{-6}$;
$N_2H_5^+ + H_2O \leftrightarrows N_2H_6^{2+} + OH^-$,
$K_2 = 10^{-16}$, strong Red.

NaOCl (0.2% gelatine)

HX ↓ Na ↓ NH₃ (liq.) ↑

N_2H_5OH hydrazine hydrate,, liq., colrl., m. p. –52, b. p. 119, $K_{bas.} = 10^{-6}$, $\Delta H = -243$

$Na[N_2H_3]$, cr. yel., exp.

N_4H_4, tetrazene, [17]
trans-$H_2N-N=N-N=N-NH_2$,
cr. colrl., subl. vac. –15,
$\overset{t}{\longrightarrow} N_2 + N_2H_4 + NH_4$ [N_3]

O_2 (t); Cl_2; CuO

HNO_2

NOCl
NH_3

NH_2Cl, chloramine, oil colrl., m. p. –60, vac. distil.;
$+ H_2O \leftrightarrows NH_3 + HOCl$;
Ox; mol. – ψ-tetrah. (sp^3)

HN_3, hydrazoic ac., liq. colrl., toxic, pungent. m. p. –80, b. p. 37, $d = 1.13$, exp. 300°, $\Delta H = +293$,
stab. in dil. soln., [20]
$K = 10^{-5}$, $\mu = 0.83$, strong Ox (react. with Cu; HN_3 + HCl sol. Pt)

HNO_2 > 300° (exp.)

M (–N_2–NH_3) ↓

EF₅ ↓

$[H_2N_3]^+[EF_6]^-$, aminodiazonium salts, cr. colrl., stab. at 20°, cation: $[H_2\dot{N}-N=N]^+$ [22]

$M(N_3)_n$, azides [25]
NaN_3, colrl., dec. 275; ΔH +21
KN_3, m. p. 350, dec. 355 without exp.
M^{II} = Hg, Pb, Ba ($\cdot H_2O\downarrow$), $[SO_2]$, $[CrO_2]$; [SO], detonators, linear anion $[:\bar{N}=\overset{+}{N}=\bar{N}:]^-$,
N — N 1.17 [25]

t (–M)

Hydrasonium salts [11]
$[N_2H_5]Hal$, Hal = F, Cl
↑ H_2O
$[N_2H_6]X_2$, X = Hal, $SO_4/2$
$TiF_6/2$, cation-*trans*

H^+ ↔ MCl_n

NH_3
N_2H_4

N_2, gas colrl., $d^0 = 1.25$, m. p. –210, b. p. –196, degree of diss. = 0.1% (3000°), $\Delta H_{dis.} = 945$, sol. in H_2O 2% (vol.) (0°), v. chem. inert., N — N 1.095, ($1\sigma + 2\pi$ bonds), $\nu_{N\equiv N}$ 2331 cm^{-1}, mol. str. α- cub. cl. pack., $a = 5.66$; > –238° ⟶ β-, hex. cl. pack., $a = 4.04$; $c = 6.67$ (mol. rotation imitates spheric sym.

H_2; NH_3 (t, exp.) > 500°

$OsCl_3 + PR_3 + Zn/Hg$;
$Ti(C_5H_5)_2$;
$Ni(ac\text{–}ac)_2 + PPh_3 + eth.$
$VCl_3(Thf)_3 + Na + PR_3$

Dinitrogen complexes [7]
$[M(N_2)(NH_3)_5]Cl_2$,
M^{II} = Ru, Os, cr., yel., diamagn., stab. to the act. of H_2O and O_2
$[M(N_2)(PR_3)_3]$, M^0 = Co, Ni
$[Os(N_2)(PR_3)_3Cl_2]$;
$[Ti(N_2)(C_5H_5)_2]_2$,
$+ RMgHal \rightarrow NH_3 + ...$;
$[W(N_2)_2(PR_3)_4]$,
linear [N≡N: → M] gr.,
N — N 1.12 – 1.6, ∠MNN 177 – 179
$[(NH_3)_5RuN\equiv]_2X_4$, N—N (br.) 1.25
$K[Co(N_2)(PR_3)_3]$, **$(PR_3)_3Fe(N_2)H_2$**
$[Na(Thf)][V(N_2)_2(PR_3)_2]$

HI; HCl + Pt(–N_2)
HI; H_2SO_3; Fe^{2+}
HNO_3

$[NH_4]^+$, $H^+ \uparrow\downarrow OH^-$:NH_3, weak Red

[H↑]; Sn^{2+}
OCl^-

$[N_2H_5]^+$ $H^+ \uparrow\downarrow OH^-$:N_2H_4, strong Red

NH_3
OCl^-

:NH_2Cl $\overset{H_2O}{\rightleftharpoons} NH_3 + HOCl$, Ox

(pH < 12)
(pH > 14)

$[NH_3OH]^+$, Ox $H^+ \uparrow\downarrow OH^-$:NH_2OH, strong Red

OCl^-; IO_3^-; VO_3^-

HN_3, v. strong. Ox, $K = 10^{-5}$ $H^+ \uparrow\downarrow OH^-$ $[N_3]^-$

HNO_2

N_2↑, H_2O-sol. 2 vol. %

H_2SO_3 slowly

N_2O↑ sol. in H_2O 56 vol. %

H_2SO_3

NO↑ sol. in H_2O – 6 vol. % ↓ OH^-
$N_2 + N_2O + NO_2$

Fe^{2+}

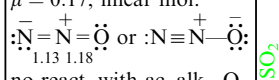
$[Fe^I(NO)^+(H_2O)_5]^{2+}$ brn. s.

Ti^{3+}; Mo^{3+} (t)
Ti^{3+}
Cr^{2+} (pH ~ 7); [H↑]

$V(OH)_2 + Mg(OH)_2$; $Cr(OH)_2$

1 +

N_2O, nitrogen (I) oxide (laughing gas), colrl., m. p. −91, b. p. −88, $d = 1.98$, $\Delta H = +81$, sol. in H_2O 56 vol.% (0°), $\mu = 0.17$, linear mol.



no react. with ac.,alk., O_2, but supports burn

· **5.75 H_2O** (8:46), clathrate

$-H_2O$

$H_2N_2O_2$, hyponitrous ac., cr. colrl., exp., sol. in H_2O, alc. $K_1 = 10^{-7}$, $K_2 = 10^{-12}$, v. weak Ox and Red., [3]

+ MnO_4^- ⟶ NO_3^-;

+ [H↑] ⟶ $[NH_3OH]^+$

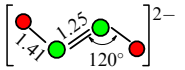
H_2; H_2S

O_2 (4000°, arch);

$M_2N_2O_2$, hyponitrites, [3] M = Na (dec. 335),

$\xrightarrow{t}$ $Na_2O + NaNO_2 + N_2$,

Ag↓ (yel.), Ba/2



cis- and *trans*-

$K_3[N(SO_3)_2]\cdot H_2O$, nitridosulfonate, anion: $[O_3S—N—SO_3]^{3-}$, ∠ONO 121, N—S 1.61, S=O 1.47

$M_2[HN(SO_3)_2]$, imidosulfonates [26]

$HN(SO_2Hal)_2$, Hal = Cl, F, imidosulfuryl halides [27]

2 +

NO, nitrogen (II) oxyde, gas, colrl., toxic. m. p. −164, b. p. −151, $d = 1.34$, $\Delta H = +90$, paramagn., $\mu = 0.16$, N=O 1.15, ($\sigma + 1.5\pi$), $\nu_{N=O}$ 1876, in liq. and cr. *cis*-N_2O_2 — trapezium, (N—N 2.18, O—O 2.62), diamagn., sol in H_2O, ac., not support burning; (:NO) – donor of 3 el., forms dative bond M→(NO)$^+$.

1) Gr. [M—(N≡O)$^+$] linear, $\nu_{N—O}$ 1580–1940

[Fe(:NO)$_2$(:CO)$_2$]; Cr(:NO)$_4$; [Mn(:NO)$_3$(:CO)], diamagn., $\Sigma e = 18$

2) Gr. [M—(N=O)$^-$] angular, ∠MNO 120, $\nu_{N—O}$ 1200–1040

$K_3[Co^{III}(NO)(CN)_5]$; $[Co^{III}(NO)(NH_3)_5]X_2$ [7]

SO_2

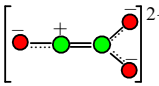
O_2 (Pt, Rh)

NH_3

NH_2OH; Na/Hg

MNO_2

$M_2N_2O_3$, hyponitrates [3] (salt of hyponitric ac. which does not ex.), M = Li–Cs, Ca–Ba/2, Na(·H_2O) "Angeli salt", stab. at pH ≈ 7; dec. 290–370; planar anion

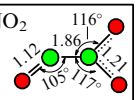


N=N 1.26, N—O 1.31–1.35

$Na_4N_2O_4$↓, salt of hydronitrous ac., powd. yel., exp. >100° or + H_2O

3 +

N_2O_3 ⇆ NO + NO_2 (100% at 100°, 90% at 25°)



nitrogen (III), oxide (nitrous anhydrid); gas, red-brn., toxic, $d = 1.45$, m. p. −101, $\Delta H = +84$, bl. in liq. and cr., sol. in H_2O with delamination, planar mol. in gas. $\mu = 2.12$; in str. – $[NO]^+[NO_2]^-$, N—O 1.12 (in cation), 1.21 (in anion) [12]

O_2 (immed.); NO_2

O_2 (immed.); NO

Cu; SO_2

HNO_3 33%

H_2O

HNO_2, nitrous ac., v. strong Ox



HO—N=O ⇄ H—N(=O)=O

Only in s. (conc. – bl.) and gas, planar mol. (*trans*-) are known

$H_2O + NO^+ \rightleftarrows HNO_2 \rightleftarrows H^+ + NO_2^-$

$K_{bas.} = 10^{-7}$, $K_{ac.} = 10^{-3}$;

$+ H^+ \longrightarrow NO + HNO_3 + H_2O$

HNO_3 90% H_2O

SO_2

Nitrosonium salts (nitrosyls), [8, 10, 16] cr. colrl., v. hyg.

[NO]HSO$_4$, m. p. 73;

[NO]$_2$S$_2$O$_7$, m. p. 233, b. p. 360

[NO]XF$_4$, X = B, Br

[NO]$_2$[MCl$_6$], M = Sn, Ti–Hf, Th, V

[NO]AlCl$_4$; [NO]Mo^{V}F$_6$; [NO]$_2$XeF$_4$

[NO][M(NO$_3$)$_3$], M = Cu, Mn

$[NO]_m[M(NO_3)_4] = "M(NO_3)_m \cdot nN_2O_4"$

Bond order $[:N\equiv O:]^+ = 3(\sigma + 2\pi)$,

N—O 1.06; $\nu = 1860 - 2400\ cm^{-1}$

H_2SO_4

Nitrites, cr., colrl. or light.-yel., volat. (500°, vak.)

	m.p.	m.dec.
$LiNO_2$	220 · **H_2O**	
$NaNO_2$	284	900
KNO_2	438	350
$RbNO_2$	422	–
$CsNO_2$	398	–
$Ba(NO_2)_2$	– · **H_2O**	200
Ag–NO_2↓	–	140

$\xrightarrow{t}$ $NO_2 + NO + N_2 + O_2 + ...$;

$[:NO_2]^-$ – ψ-triangle (sp^2), N—O 1.1–1.2; ∠ONO 113–132, strong Ox in melts

↓M_2O (300°)

M_3NO_3 = $[M_3O][NO_2]$, M = Na–Rb, instant. hydr., in cavities of str. – $[Na_3O]$ (*anti*-ReO_3 type) – gr. $[NO_2]$ [28]

Na (NH_3 liq.)

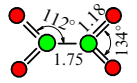
$NONH_2$, cr. orange, dec. −30 (⟶ N_2 + NH_4NO_2)

4 +

Nitrogen (IV) oxide

N_2O_4 ⇆ 2 NO_2 −58 кDg

tetroxide, colrl. 99.8% (21°)	dioxide, brn. 100% (140°)
$\Delta H = +10$	$\Delta H = +34$
diamagn., $\mu = 0$	paramagn., $\mu = 0.29$



gas, brn., toxic, m. p. –11, b. p. 21, liq. brn., cr. colrl., el. conduct. 10^3 times > liq.,

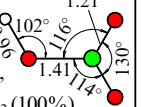
N_2O_4 (liq.) ⇆ $NO^+ + NO_3^-$.

RCN, RCOOH, HNO_3 and other el. donors intensity diss. (⟶ [D:NO]$^+$);

+ M→$M(NO_3)_n \cdot m N_2O_4$ + NO,

M = Na, Cu, Fe, Mn etc. [32]

H_2O

HNO_3, nitric ac., colrl. liq., 

($\xrightarrow{h\nu\text{-(vis.)}}$ $NO_2\uparrow + H_2O + O_2\uparrow$),

brn., m. p. −41, b. p. 84 (extrapol.),

$H_3O^+ + NO_3^- + N_2O_5 \rightleftarrows 3\,HNO_3$ (100%)

⇄ $H_3O^+ + NO_2^+ + 2\,NO^-$, mol. – plane, 3% v. weak. Ox., 5% + Mg ⟶ H_2 (at the begin of react.); 30% Ox., 60% – v. strong Ox. (+3 HCl + Au ⟶ H[$AuCl_4$] + NO + H_2O)

$\mu = 2.16$; Al, Cr, Fe – are passiv., Au, Pt, Rh, Ir – do not react · ***n*** **H_2O**, $n = 3$ (= $[H_7O_3]^+[NO_3]^-$); 1 (= $[H_3O]^+[NO_3]^-$); [18] b. p. of azeotrope with H_2O (68% HNO_3) 122, $d = 1.40$ $K \geqslant 20$ (conc. s.), strong ac.

As_2O_3; starch $(C_6H_{10}O_5)_x$; $H_2(Pd)$

H_2O_2

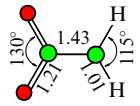
HX

H_2O

$[NO_2]^+X^-$, nitronium salts [8] (nitriles), X = PF_6, AsF_6, VF_6, HSO_4, HS_2O_7, MoF_7, ClO_4, cr., colrl., v. hyg., v. strong Ox, linear cation $[O=N=O]^+$; N—O 1.15, $\nu_{[NO_2]^+} = 2350 - 2320,\ 1400\ cm^{-1}$

$t\,(-O_2)$; C; Fe

NO_2NH_2, nitroamide, cr. colrl., m. p. 75 (dec) sol. in H_2O, alc., Et_2O, $K_{ac.} = 10^{-7}$, $\mu = 3.6$, + OH^- ⟶ H_2O + N_2, stab. in MeCN



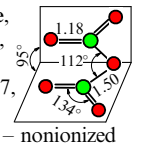
dihedral angle ∠52 [29]

N_2O_4

MCl_n; M(−NO)

5 +

N_2O_5, nitric anhydride, cr. colrl., volat., toxic, m. p. 41 (*p*), subl. 32, b. p. 45, exp., $d = 2.17$, $\Delta H = -42$, in str. – $[NO_2]^+[NO_3]^-$, in gas – nonionized mol., $\mu = 1.39$ [12,13]



$Pb(NO_3)_2$

t (−PbO−O_2)

O_3(−78→ −25°)

20° (−O_2)

Cu (*t*)

HI

H_2O

$-H_2O(P_2O_5)$

$AgNO_3$

Cl_2

O_3 (liq.)

NO_3, nitrogen peroxide, wh., unstab., sol. in Et_2O



H_2O

$HNO_3 + HNO_2 + O_2$

H_2O_2 (100%)

HNO_4, pernitric ac., [30] exp., 1.5 M s. ex. ~30 min.,

+ H_2O ⟶

⟶ $HNO_2 + O_2$

H_2O_2

H_2O

$O_3 + H_2$ (−190°)

N_2

NH_4OOH (CCl_4)

$M[NO_3(HNO_3)_2]$, M = K–Cs [18]

$M[H(NO_3)_2]$, M = K–Cs

NH_4NO_4, pernitrate, dec. 5 [30]

H_2SO_4(−NaHSO$_4$) Glauber's method

Nitrates [31]

cr. colrl.	m. p.	
$LiNO_3$	261 (dec.)	· **3 H_2O**
$NaNO_3$	308	dec. 380
"Chile salpetre"		
KNO_3	334	dec. 400
$Ca(NO_3)_2$	561	· **4 H_2O**
$Ba(NO_3)_2$	592	
$Pb(NO_3)_2$	208 (dec.)	
$AgNO_3$	210	dec. 300

sol. in liq. NH_3; planar triangle anion, ∠ONO 120 (sp^2), N—O 1.18–1.25; Ox only in melt., in gas – mol. M^INO_3 — str. anal. of HNO_3;

$M(NO_3)_n \cdot x\,H_2O \xrightarrow{t} M_2O_n + H_2O + NO_2 + O_2$;

M^INO_3, $M^{II}(NO_3)_2$, M = Li–Cs, Ca–Ba, Ni

$\xrightarrow{t}$ $M(NO_2)_n + O_2 + NO + NO_2$

$M(NO_3)_n$, M = Be, Al, Mg, Fe, Co, Ni, Ti, Sn^{IV},

↓M^I_2O (300°)

$M^I_3[NO_4]$, ortonitrates, anion tetrah., N—O 1.38 [16]

[H↑] 3 + 4 + 5 +

HMnO$_4$; HOCl

HBr(*t*); HI; Fe^{2+}

HNO_2, v. strong Ox (in dil. s.), $K = 10^{-3}$, $H^+ \uparrow\downarrow OH^-$, **$[:NO_2]^-$**, Red agent

$H_2O_2(H^+)$

[HOONO], $K_{ac.} > 10^{-6}$

HNO_3, strong. ac., strong Ox $H^+ \uparrow\downarrow OH^-$ **$[NO_3]^-$**, v. veak Ox (in s.)

Cu; Hg; HI(−HIO_3)

NO_2 ↓ H_2O → $HNO_2 + HNO_3$, Ox

O_2 (immed.) [H↑]

O_2

[H↑] (Al; Zn + OH^-)

N

O

H

•• Located el. pair

PHOSPHORUS

3– 2– P^0 3s 3p 3d EN 2.1 1+ 2+

PH_3, phosphine, gas, colrl., toxic, with odour of rotten fish, m. p. −134, b. p −88, infl. 150°, $\Delta H = +5$, v. strong Red., sol. in H_2O 20% (vol.), μ = 0.58; mol. – trig. pyr., P—H 1.42, ∠HPH 93 (p^3);

$PH_4^+ + H_2O \overset{H^+}{\underset{K=10^{-29}}{\rightleftharpoons}} PH_3 + H_2O \underset{K=10^{-29}}{\rightleftharpoons} H_3O^+ + PH_2^-$

v. weak donor; **$[Ni(PH_3)_4]$, $[CoN_2(PR_3)_3]$**

$t(-H_2)$ → ; H_2(300°, p); HCl(−PCl_3); MOH(−MH_2PO_2)

P_2H_4, diphosphine, liq., colrl., m. p. −99, b. p 63, str. analog N_2H_4, inflam. at 20° (admix. PH_3), not react. with ac., >0 ⟶ $PH_3 + (PH)_n$; · ***n*** **(H_2O)** [15]

$(PH)_n$, yel., not react with ac., alc.

$Ca_3(PO_4)_2$; C(−CO); C + SiO_2 (1500° −$CaSiO_3$ −CO↑)

P_2O_5; $S_2O_6F_2$; $H_2S_2O_7$

$[P_8]^{2+}(HSO_3F)_2^-$
$[P_4]^{2+}(HSO_4)_2^-$,
(ex. only in s.)
$[P_8]^{2+}$, bl.,
$[P_4]^{2+}$, colrl., diamagn. [3]

$(PO)_n$

P_2I_4; H_2O

$H_4P_2O_4 = H_2[H_2P_2O_4]$

$H[OPH(O)—PH_2]$ [23]

$[R_4N][Ru_4(CO)_{12}(\mu_3\text{-}PO)$ [38]

HX; OH⁻

Phosphonium salts $[PH_4]X$, cr., colrl.
$[PH_4]ClO_4$, exp.
PH_4Hal ⇄ PH_3 + HHal (gas) t. subl.
PH_4Cl −28
PH_4Br 38
PH_4I 18 (m. p.), 80 (b. p.),
v. strong Red.;
$+H_2O$ ⟶ PH_3 + HHal;
cation – tetrah. (sp^3)

(H↑); H_3PO_3

H_2O; M (liq. NH_3); H_2O; Ca_3P_2

MPH_2, dihydrophosphides, cr., colrl., infl.
↓ 100° vac. (−PH_3)
Na_2PH; $MAl(PH_2)_4$ [15]

M; M_2O_n; $MHal_n$(gas); HCl

Ca_2PI; Ca_3PI_3 [12); Ca + I_2 (t)

Phosphides M_3P_x

Salt - like + H_2O ⟶ PH_3

Li_3P; Na_3P; Na_2P_5 (m. p. 650) [1)
K_2P_5; $Ba[P_5]_2$; $Rb_4[P_6]$, in str. – plane cycles $[P_5]$ and $[P_6]$
K_4P_3; K_5P_4
Mg_3P_2; Ca_3P_2; **Zn_3P_2; Cd_3P_2** } + O_2 – infl., + H_2O ⟶ PH_3 + ...
Cu_3P↓; **CuP_2**↓, insol. in HNO_3 (t)

Covalent

BP↓, dec. >2000, insol. in ac. and alk., str. diamond type
AlP, dec. 2000, + H_2O ⟶ PH_3
InP↓, dec. 1070
GaP↓, m. p. 1467
AsP↓, dec. 750
} str. sphalerite (ZnS) type; Semiconduct. [22]

Metal-like

	m. p.	
Ti_3P	—	
TiP	1580	Conduct. (TiP) or semiconduct.
Cr_3P	—	(CrP), chem. passiv.
CrP	1600	(act. increases with decreasing
Fe_3P	1200	content P); sol. in Na_2O_2 melt
Fe_2P	1356	
FeP	ferromagn.	
FeP_2		

M(t); Cu^{2+}; Ag^+ (+H_2O −H_3PO_3)

P_4, wh., soft, waxlike, toxic, (yel. – admix. $P_{red.}$ and As), m. p. 44, b. p., 257, sol. in CS_2, NH_3, SO_2, infl. 40°, d = 1.83. In cube str. (Cu type), mol. P_4 – tetrah., P—P 2.21, ∠PPP 60, CN P 3. Strain in tetrah. causes chem. act. [34)]

44° cool; subl.; 250°, $p > 5 \cdot 10^7$ Pa (I_2; Na; $h\nu$-UV, X-rays)

Liq. P_4

~600° (p); cool 280°

Gas $P_4 \overset{1000°}{\rightleftharpoons} P_2 \overset{2000°}{\rightleftharpoons} P$ [P≡P], P—P 1.90, el. anal. to N_2

P_n, red, insol. in CS_2, not toxic, infl. 240°, subl. 429, d = 2.2–2.4, mol. – chains of diff. lengths P—P 2.24, ∠PPP 102

550°

P_n, blk., subl. 453, m. p. ~1000° (p), d = 2.69, thermodinamically stab., non-react., infl. 400°, str. – gauffer layers of trig. bypyr., graphite similar semiconduct.
↓ $83000 \cdot 10^5$ Pa
P, met., rhombohedral, As str. type P—P 2.38, d = 3.56

2.21; 2.18

CN P = 3 in all forms

(25°, $35 \cdot 10^8$ Pa; Hg, 370°)

O_2 (20, chain react. → PO· luminescence)

$Ba[H_2P_2O_5]$↓

$H_3PO_2 = H[H_2PO_2]$
hypophosphorous ac.
cr., colrl., hyg., m. p. 27
$K = 10^{-1}$, sol. in alc., Et_2O
50° ⟶ $PH_3 + H_3PO_4$
v. strong Red. (in conc. s., t) [19)]

PCl_3(−P); Hg^{2+}; Cu^{2+}

H^+(cationite); H_2SO_4

M[H_2PO_2]$_n$, hypophosphites
$NaH_2PO_2 \cdot H_2O$ [19)]
MH_2PO_2; $NH_4H_2PO_2$
$Mg(H_2PO_2)_2 \cdot 6H_2O$
$Ba(H_2PO_2)_2 \cdot H_2O$
$Ca(H_2PO_2)_2$,
readily sol. in H_2O, anion – dist. tetrah., P — O 1.52

$Ba(OH)_2$ (−PH_3↑)

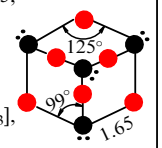
$[MCl(P_4)_2(PR_3)_2]$
M = Rh, Ir [2)]

$Ca_3(PO_4)_2$; C + SiO_2 (1500° −$CaSiO_3$ −CO↑); C(−CO); P_2O_5

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_14, © Springer-Verlag Berlin Heidelberg 2011

3+ 4+ 5+

P_2O_3, phosphorous oxide (III) cr., wh., m. p. 24, b. p 175, $\Delta H = -1640$ (for P_4O_6), sol. in org. solv. In gas, s., one modif. – dimers P_4O_6. In mol. – 4 ψ-tetrah. [:PO_3], with sharing vertex form. the "big tetrah." [P_4]. In sld.– polymers from tetrah. [PO_4].



P_4O_8 [21]
P_4O_9
$H_4P_2O_6$

$Na_3HP_2O_6 \cdot 4H_2O$
$Na_2H_2P_2O_6$

$M_6P_6O_{12} \cdot nH_2O$, M = Rb, Cs, Ba/2, **hexametaphosphites** [31]

$Mn_3H_6P_4O_{12} \cdot 1.5H_2O$ [16]

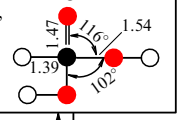
H_2O (slow.)

$H_4P_2O_5$ = $H_2[H_2P_2O_5]$, di(pyro)phosphorous ac. needles, colrl., m. p. 38, dec. 130

PCl_3 ⇕ H_2O

$M_2[H_2P_2O_5]$, pyrophosphites
$Na_2H_2P_2O_5$; **$ZnH_2P_2O_5$** [11]

H_3PO_3 = $H_2[HPO_3]$, **phosphorous ac.**, cr., colrl., hyg., m. p. 74, dec. 200, $K_1 = 10^{-2}$, $K_2 = 10^{-7}$, sol. in H_2O, alc.; mol. – dist. tetrah.;
H_3PO_3 (cr.) $\xrightarrow{t}$ $PH_3 + H_3PO_4$; strong Red., by 20° not react. with HNO_3,
$H_2[HPO_3] \rightleftarrows P(OH)_3$



H^+ ⇕ OH^-

MH[HPO_3], hydrophosphites
NaH_2PO_3, **$\cdot 2.5H_2O$**, m. p. 42, dec. 100
KH_2PO_3; **$Zn(H_2PO_3)_2$**,
anion – dist. tetrah., P—O 1.51 [11]

$H_2SO_4(-SO_2)$

H_2O (OH^-, H_2↑)

$M_2[HPO_3]$, phosphites [31]
$Na_2HPO_3 \cdot 5H_2O$,
m. p. 53, dec. 120
K_2HPO_3; **$MgHPO_3 \cdot 6H_2O$**
Ag_2HPO_3↓, wh.; **$CaHPO_3$**↓;
$CrHPO_3 \cdot 2H_2O$,
$\xrightarrow{t}$ $M_3PO_4 + PH_3 + P + \ldots$
$[HPO_3]^{2-}$ – dist. tetrah.

$P_{wh.}$

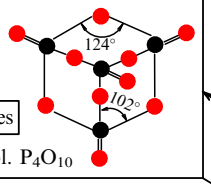
$HClO_4$; HNO_3; H_2O (700°, Pt, Cu)

P_{red}

P_2O_5, phosphoric anhydride, wh., v. hyg. (mixture of amorph. and hex.), rapidly react. with H_2O; v. strong dehydrating agent. In gas and hex. str. – P_4O_{10}, in mol.– tetrah. [P_4], on the edges – 6 br. at O; at each at. P – 1 term. at. O, P = O 1.40–1.49 and 3 br. P—O 1.56–1.65

α-, hex. (rhombohedral) mol. str., d = 2.3, m. p. 422 (p), subl. 359 (volat. < P_2O_5), $\Delta H = -2988$ (for P_4O_{10}), v. react.

422° ⇕ t → liq., volat., fluent (mol. P_4O_{10}) → t → liq., nonvolat., visc. (polymeric mol.) → cool → glasses



mol. P_4O_{10}

P_4O_{11}

SiO_2 ($-CaSiO_3$, t)

$M_2O_n(t)$

H_2O (a lack, 0°)

$(HPO_3)_n$, n = 3, 4, 6, **"metaphosphoric ac."**, glass paste, colrl., hyg., m. p. ≈40, subl., sol. in H_2O, alc; strong. ac., $K_3 = 10^{-2}$, $K_4 = 10^{-3}$, only one P-ac. coagulated protein (large charge of the anion), in str. – disord. arrangment of cyclic mol. $(HPO_3)_4$ and others

MOH

$[P(OH)_4]^+X^-$, phosphoryl salts [35]

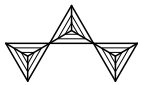
$-H_2O$ (300°)

H_2O (H^+, t)

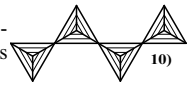
Polymetaphosphates
$M^I_n[P_nO_{3n-1}(OH)_2]$, n = 20–70, form from s.; well, but slow. sol. in H_2O (with fractional oligomerization)

M_2HPO_4 ($-H_2O$)

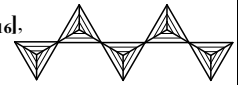
$M_5[P_3O_{10}]$, triphosphates
$NaZn_2[P_3O_{10}] \cdot 9.5H_2O$
$(NH_4)_5[P_3O_{10}] \cdot H_2O$ [10]



$M_6[P_4O_{13}]$ – tetra-
$Na_6[P_4O_{13}]$ – glass [10]



$M_7[P_5O_{16}]$, penta-



MH_2PO_4 t ($-H_2O$)

Cyclometaphosphates [32, 37]
$[M(PO_3)_m]_n$, n = 3–6, 8, 10, 12, in str. – nonplanar cyclic anions $[PO_3]^{n-}_n$ from tetrah. [PO_4], P—O 1.6–1.7 (br.), 1.4–1.5 (term.), ∠OPO 100–119, ∠POP 103–139

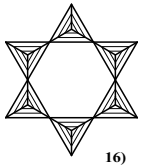
trimeta-, "chair",
$Li_3[P_3O_9] \cdot 3H_2O$
$Na_3[P_3O_9] \cdot nH_2O$,



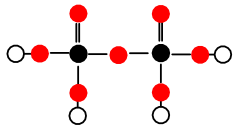
tetrameta-, "chair" and "bath" [4]
$Li_4[P_4O_{12}] \cdot 6H_2O$
$Na_4[P_4O_{12}]$, **$\cdot 4H_2O$**



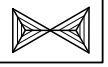
hexameta-,
$Li_6[P_6O_{18}] \cdot 5H_2O$
$Na_6[P_6O_{18}] \cdot 6H_2O$ [16]



$H_4P_2O_7$, **di(pyro)phosphoric ac.**, glass or cr., colrl., m. p. 61, $K_1 = 10^{-2}$, $K_2 = 10^{-3}$, $K_3 = 10^{-7}$, $K_4 = 10^{-10}$, sol. in H_2O, alc., Et_2O

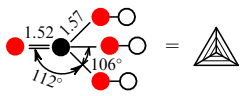


Di(pyro)phosphates
$Na_2H_2P_2O_7$, dec. 220, **$\cdot 6H_2O$**; **$Na_4P_2O_7$**, m. p. 988, **$\cdot 10H_2O$**; **$Ag_4P_2O_7$**↓, wh.; **$K_4P_2O_7 \cdot 3H_2O$**, ($\xrightarrow{300°}$ H_2O,);
$M^{II}_2P_2O_7$↓, M^{II} = Mg–Ba, Zn, $\xrightarrow{t}$ $M^{II}_3(PO_4)_2 + P_2O_5$↑, anion – 2 tetrah. whith a common vertex, ∠POP 130–157



43°

H_3PO_4, **orthophosphoric ac.**, cr., colrl., hyg., non toxic, m. p. 42, $K_1 = 10^{-2}$, $K_2 = 10^{-7}$, $K_3 = 10^{-12}$, sol. in alc., ε = 61 (25°), 2 $H_3PO_4 \rightleftarrows [H_4PO_4]^+ + [H_2PO_4]^-$, mol. – dist. tetrah, weak Ox. (>350°), react. with M, SiO_2;
$\cdot 1/2H_2O$, m. p. 30 (80% s. H_3PO_4, – visc. liq.); commercial preparation ≈ 85%



t ($-H_2O$)

H_2SO_4

$Ca_3(PO_4)_2$

Mono(ortho)phosphates

Monobasic (primary)
$M[H_2PO_4]_n$, sol. in H_2O (any M)
NaH_2PO_4, dec. 200; **KH_2PO_4**,
m. p. 253 (dec.); **$(NH_4)H_2PO_4$**, m. p. 190
$Ca(H_2PO_4)_2$, "duble superphosphate"
$Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4$↓, "simple"
$\xrightarrow{t}$ $M(PO_3)_n + H_2O$.
In str. – chains of anions whith H-bonds

Dibasic (secondary) [35]
$M_2[HPO_4]_n$, sol. in H_2O only if M^I
Na_2HPO_4, (dec. 300),
$\cdot nH_2O$ n=12 (dec. 35), 7 (48), 2 (95);
$NaNH_4HPO_4$, "phosphoric salt",
$\xrightarrow{t}$ $NaPO_3 + NH_3 + H_2O$;
$CaHPO_4$, **$\cdot 2H_2O$** ↓, "brushite"
SP = 10^{-6}, "precipitate", $\xrightarrow{t}$ $M_4P_2O_7 + H_2O$

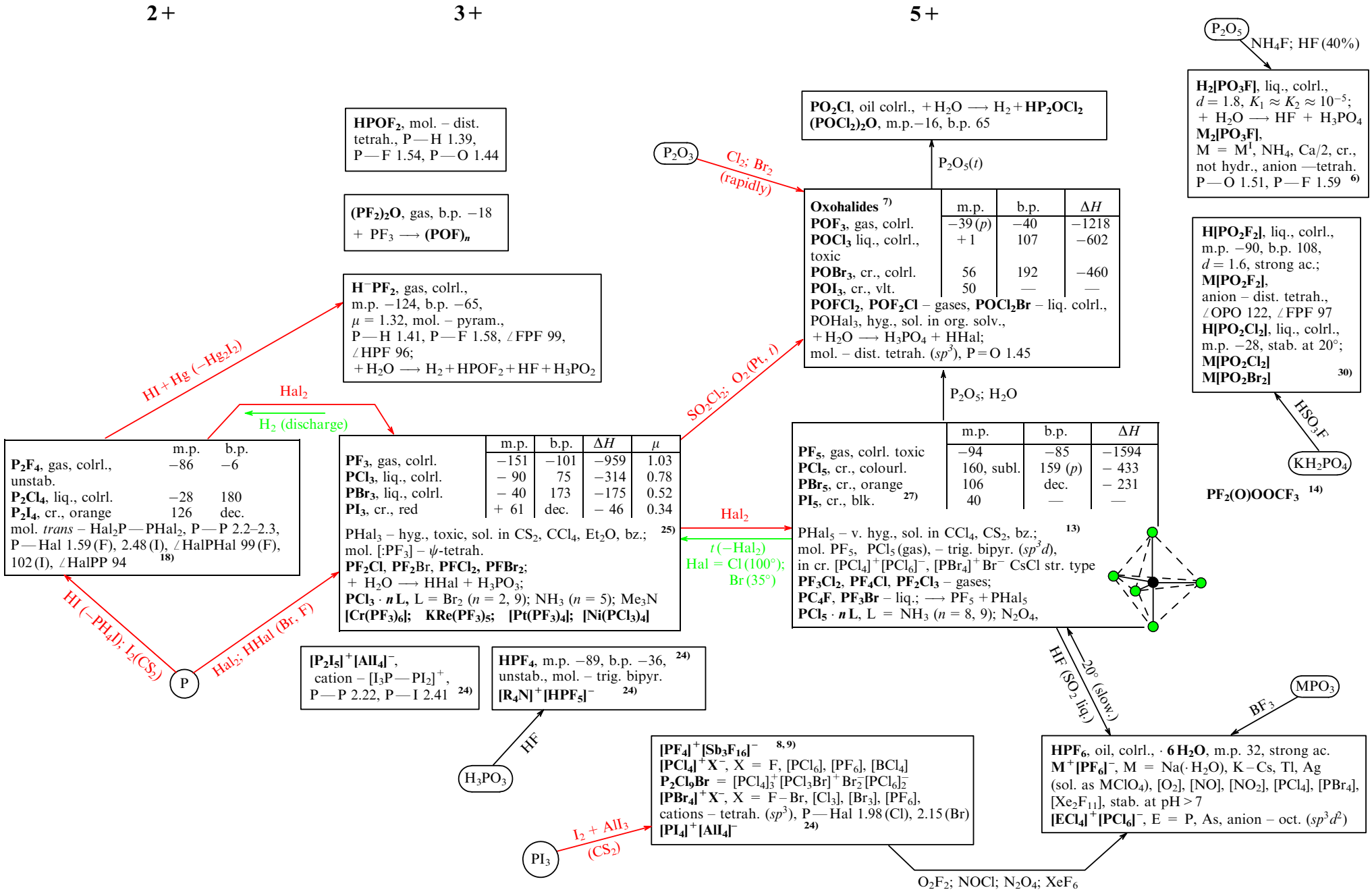
Threebasic (tertiary), **$M_3[PO_4]_n$**,
sol. in H_2O only at M = Na–Cs, NH_4;
Na_3PO_4, m. p. 1340, **$\cdot nH_2O$** n = 10, 12
$Ca_3(PO_4)_2$↓, m. p. 1670, SP = 10^{-25};
$Ca_5(PO_4)_3(F, Cl, OH)$, "fluor-", "chlor-", "hydroxylapatites";
anion – regular tetrah. (sp^3)

$H_4P_2O_8$
$K_4P_2O_8$

H_3PO_5 [5]
H_3PO_6 [5]

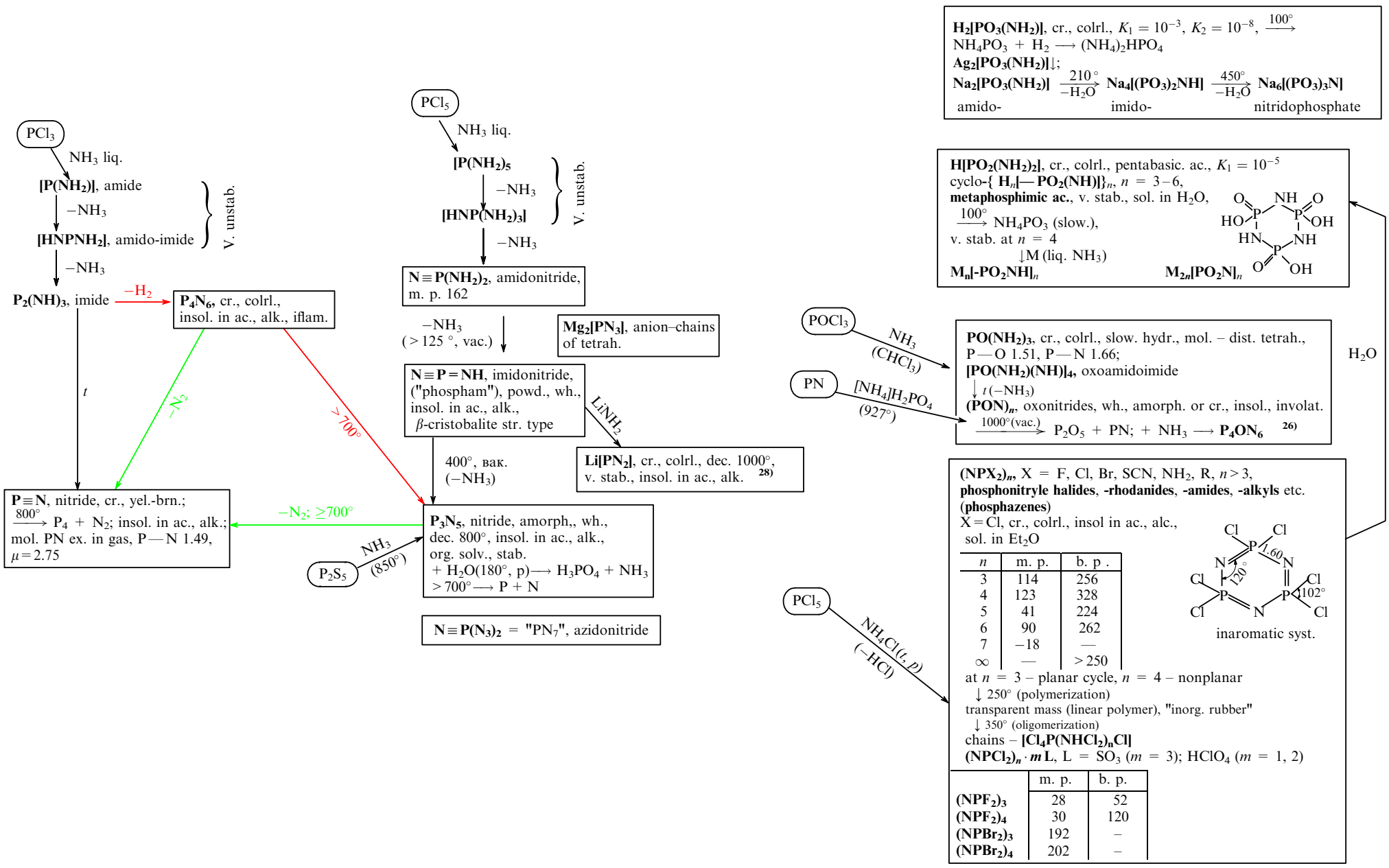
P
O
H

PHOSPHORUS HALIDES AND OXOHALIDES

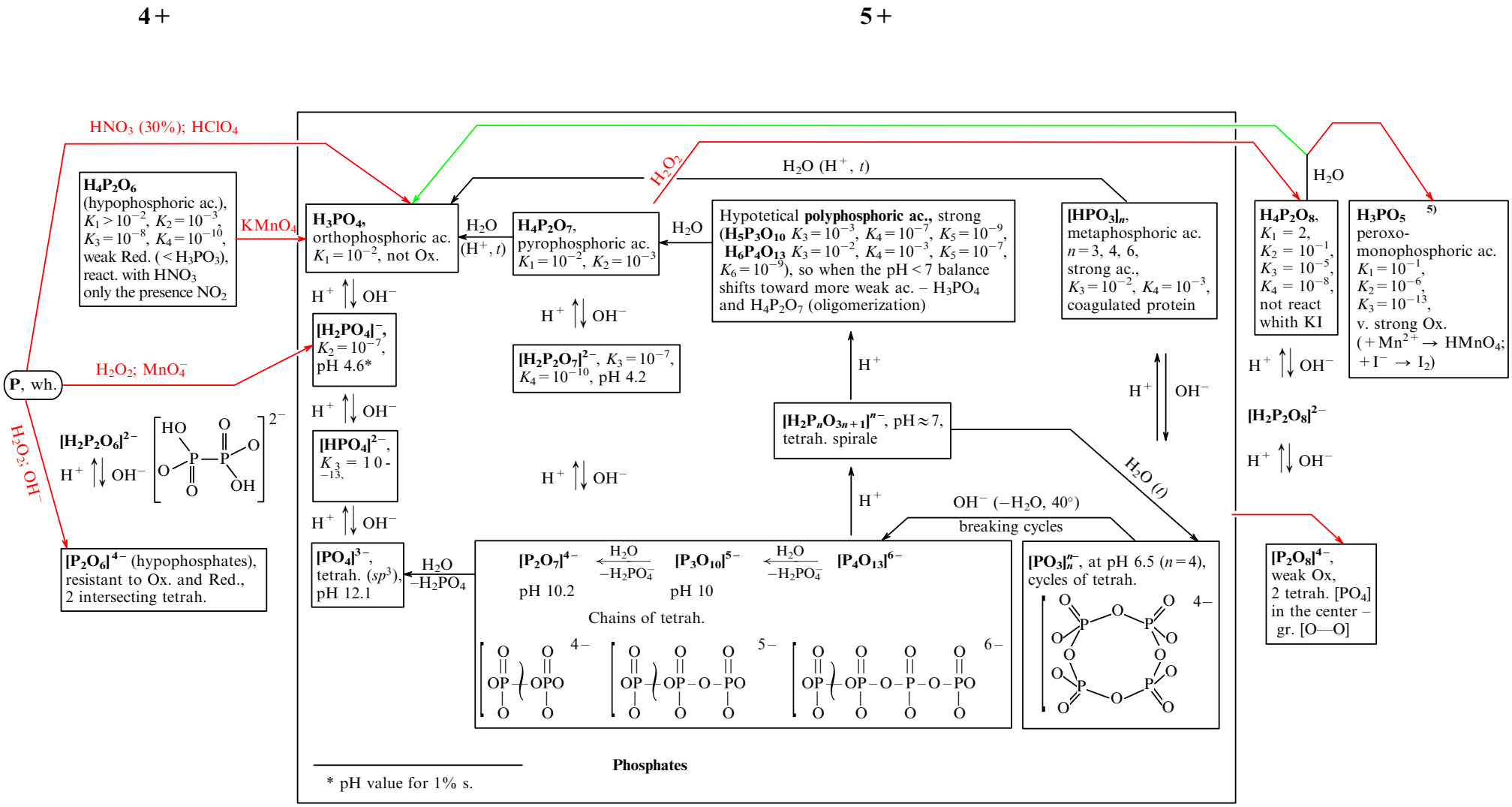


3+

5+


PCl3
NH3 liq.
[P(NH2)], amide
−NH3
[HNPNH2], amido-imide
−NH3
P2(NH)3, imide
V. unstab.
−H2
P4N6, cr., colrl., insol. in ac., alk., iflam.
t
−N2
>700°
PCl5
NH3 liq.
[P(NH2)5
−NH3
[HNP(NH2)3]
−NH3
V. unstab.
N≡P(NH2)2, amidonitride, m. p. 162
−NH3 (>125 °, vac.)
Mg2[PN3], anion–chains of tetrah.
N≡P=NH, imidonitride, ("phospham"), powd., wh., insol. in ac., alk., β-cristobalite str. type
LiNH2
Li[PN2], cr., colrl., dec. 1000°, v. stab., insol. in ac., alk. 28)
400°, вак. (−NH3)
P3N5, nitride, amorph,, wh., dec. 800°, insol. in ac., alk., org. solv., stab.
+ H2O(180°, p)⟶ H3PO4 + NH3
>700°⟶ P + N
−N2; ≥700°
P2S5
NH3 (850°)
P≡N, nitride, cr., yel.-brn.;
800°⟶ P4 + N2; insol. in ac., alk.;
mol. PN ex. in gas, P—N 1.49,
μ=2.75
N≡P(N3)2 = "PN7", azidonitride
H2[PO3(NH2)], cr., colrl., K1 = 10−3, K2 = 10−8, 100°⟶
NH4PO3 + H2 ⟶ (NH4)2HPO4
Ag2[PO3(NH2)]↓;
Na2[PO3(NH2)] 210°/−H2O Na4[(PO3)2NH] 450°/−H2O Na6[(PO3)3N]
amido-
imido-
nitridophosphate
H[PO2(NH2)2], cr., colrl., pentabasic. ac., K1 = 10−5
cyclo-{ Hn[— PO2(NH)]}n, n = 3–6,
metaphosphimic ac., v. stab., sol. in H2O,
100°⟶ NH4PO3 (slow.),
v. stab. at n = 4
↓M (liq. NH3)
Mn[-PO2NH]n
M2n[PO2N]n
POCl3
NH3 (CHCl3)
PN
[NH4]H2PO4 (927°)
PO(NH2)3, cr., colrl., slow. hydr., mol. – dist. tetrah.,
P—O 1.51, P—N 1.66;
[PO(NH2)(NH)]4, oxoamidoimide
↓t(−NH3)
(PON)n, oxonitrides, wh., amorph. or cr., insol., involat.
1000°(vac.)⟶ P2O5 + PN; + NH3 ⟶ P4ON6 26)
H2O
(NPX2)n, X = F, Cl, Br, SCN, NH2, R, n>3,
phosphonitryle halides, -rhodanides, -amides, -alkyls etc.
(phosphazenes)
X=Cl, cr., colrl., insol in ac., alc., sol. in Et2O
n | m. p. | b. p.
3 | 114 | 256
4 | 123 | 328
5 | 41 | 224
6 | 90 | 262
7 | −18 | —
∞ | — | >250
at n = 3 – planar cycle, n = 4 – nonplanar
↓250° (polymerization)
transparent mass (linear polymer), "inorg. rubber"
↓350° (oligomerization)
chains – [Cl4P(NHCl2)nCl]
(NPCl2)n·mL, L = SO3 (m = 3); HClO4 (m = 1, 2)
inaromatic syst.
PCl5
NH4Cl(t, p) (−HCl)
m. p. | b. p.
(NPF2)3 | 28 | 52
(NPF2)4 | 30 | 120
(NPBr2)3 | 192 | –
(NPBr2)4 | 202 | –

PHOSPHORUS IONS IN AQUEOUS SOLUTIONS



SULPHUR-CONTAINING DERIVATIVES OF PHOSPHORUS [29]

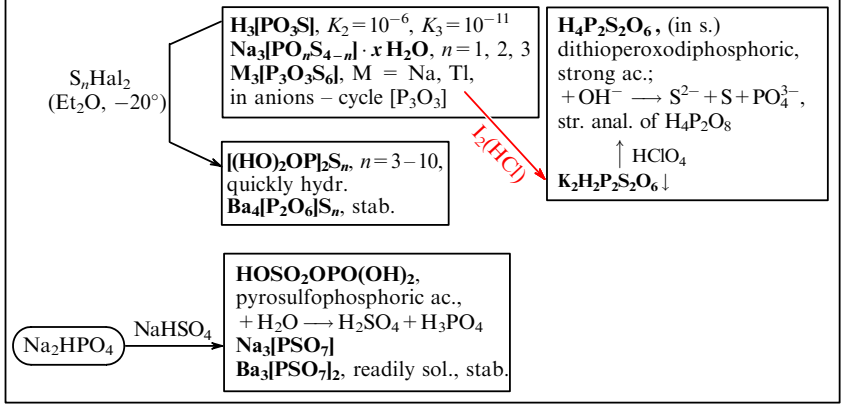
Thiohalides [20]	m. p.	b. p.	μ
PSF_3, gas, colrl., inflam.	−149	−52	0.63
$PSCl_3$, liq.	−36	125	1.41
$PSBr_3$, cr.	37	206	—
PSFClBr	—	98	—
PSI_3, cr.	47	—	—

In tetramer. mol. – tetrah. [P_4], P—P 2.20, P—S 1.86–2.19, P—Hal 2.19 (Br), 2.48 (I), in gas – monomer. mol. $PSHal_3$ – dist. tetrah.
$P_4S_3I_2$, cr., orang., m. p. 121, 3 at. S-br.– along the edges
$PS(NCS)_3$, liq.

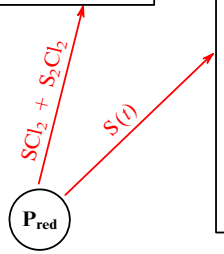
$PS(NH_2)_3$, cr., colorl., slow hydrol.
$(SPN)_n$

Oxosulfides [12]
3.5+ **$P_4O_4S_3$**; **4+** **P_4O_7S**; **5+** **$P_4O_4S_6$**, **$P_4O_6S_4$**, m. p. 102, b. p. 295, **$P_4O_tS_3$**

Oxothiophosphoric ac. and oxothiophosphates



Polysulfides
$(PS)_n$; **$(P_2S_{11})_n$**; **$(P_2S_{14})_n$**, yel. subst., sol in alk., dec. 200



Sulfides [17]
cr., yel., volat, sol. in CS_2, bz., naphthalene (melt.), inflam. (*t*), hyg. (except P_4S_3)

	P_4S_2	**P_4S_3**	**P_4S_4** **$(PS)_n$**	**P_4S_5**	**P_4S_n** $n = 5.5–6.7$	**P_4S_7**	**P_4S_9**	**P_4S_{10}**
m. p.	46	174	—	162 dec.	232 dec.	308	250 dec.	288 514
b. p.	—	408 most stab.	—	—	—	523	—	

In mol. all P_4S_n – tetrah. [P_4], P—P 2.2, S (br.) – on the edges of tetrah., at $n > 6$ at. S – term., P—S 2.1 (br.), 1.9 (term.); P_4S_6 and P_4S_{10} – str. anal. of P_4O_6 и P_4O_{10}

P_4Se_3, cr., orang. m. p. 247 [16]

Thiophosphates [23]

3+	**4+**		**5+**
$M_3[PS_3]$ **$M_4[P_4S_8]$**, not hydr., in anions – square [P_4]	**$[R_4N]_2[H_2P_2S_6]$** **$M^{II}_2[P_2S_6]$**, M = Cd, Hg, Sn, Fe anion – 2 crossing tetrah.	**$Zn_4[P_2S_6]_3$ = $= Zn_4[P^{IV}_2S_6] \cdot [P^{V}_2S_6]_2$**	**$H_3[PS_4]$** **$M_3[PS_4]$**, $+H_2O \longrightarrow H_2S + M_3[PS_nO_{4-n}]$, n = 0–3, anion – tetrah. **$Ag_7[PS_6]$** **$Ag_4[P_2S_7]$**, anion isostr. to $[P_2O_7]^{4-}$

In all anions P—S 1.99–2.12, P—P 2.28

ARSENIC, ANTIMONY, BISMUTH

3 – * 2 – 2/n + 3 +

	4s	4p	4d	EN
As⁰	↓↑	↓ ↓ ↓		2.2
Sb⁰	↓↑	↓ ↓ ↓		1.9
Bi⁰	↓↑	↓ ↓ ↓		1.7

	As	Sb	Bi
	met. grey, brittle		met. silver-wh.
d	5.72	6.62	9.80
m.p.	817/36 · 10^5 Pa	630	271
b.p.	615, subl.	1634	1564
	sol. in ac.-Ox.		
	sol. in alk. (t)		
$E_0 E^{3+}/E_{sld}$	+0.30	+0.24	+0.23
	met. conductivity (increases from As to Bi)		
	α- hex. (rhombohedral), blk. P str. – like		
a	4.12	4.50	4.75
α	54.1	57.1	57.2
	CN 3 (= 8 – 5)		
E — E	2.78	3.18	3.64
between layers	3.33	3.36	3.53
	↕ subl. in atm. H_2↑	↑ 270 (As)	
	β-, powd., blk. amorph. or mirror		
	stab. in air		
d	4.7 – 5.1	5.3	
		> –80° (–SbH₃)	
	γ-, cr., yel., wax-like,		
	d = 1.97, dec. 358, sol. in CS_2, volat. with H_2O vapour, v. react. (oxidised in air),		
	In str. As_4 mol., tetrah., As — As 2.44	contains ≈10% SbH_3	

hν-Vis.

AsH_3, arsine | SbH_3, stibine | BiH_3, bismuthine

	AsH_3	SbH_3	BiH_3
	gas colrl., v. toxic, with odour of garlic	of H_2S [18]	v. unstab.
m.p.	–117	–94	—
b.p.	–62	–18	—
dec.	300	150, exp. 20	slowly ⩾ 20
ΔH	+67	+147	+231

sol. in H_2O ≈ 17 vol. %; sol. in CS_2 ≈ 99 vol. %; μ 0.22 | 0.12; mol. – trig. pyram.; no donor act., strong Red · **5.75 H_2O** (8 : 46), clathrate

As_2H_4 –100° → **$(AsH)_n$**, red, polymer, sol. in HNO_3

$SnCl_4(Et_2O)$; $SnCl_2$; $AsCl_3$; M (liq. NH_3); $HgCl_2$; [H↑] Marsh test; E^{III}, E^V; HCl; t (–H_2) (preparation of high-purity E) [19]

M^IAsH_2, M = Li – K, cr. yel., dec. 0 (Li), 10 (Na), 80°(K) (⟶ H_2 + MAs^I); **$HAs(HgCl)_2$**↓, cr. yel.; **$KSbH_2$**, stab. < $KAsH_2$

M_3E_n [20]

	Arsenides	Antimonides (stibides)	Bismuthides
Salt-like		**CsSb; M_2Sb; Li_3Sb_2**	**M_2Bi_4; MBi**
	M_3As, M = Li – K	**M_3Sb**, M = Li – K	**M_3Bi**, bl.-vlt.
	M_3As_{11}	**M_4Sb_7; M_2Sb_4; $LiSb_2$,**	
	$SrAs_3$; Sr_3As_4; $Ba_3[As_7]_2$	+ H_2O ⟶ MOH + EH_3↑	
	Ca_3As_2; CaAs₂	**Mg_3Sb_2; BaSb₃; $Ca_{16}Sb_{11}$**	**$Ca_{11}Bi_{10}$**
	Mg_3As_2; Cu_3As_2	**$Ca_{11}Sb_{10}$; $Ba_3[Sb_7]_2$;**	**Mg_3Bi_2**
	Zn_3As_2; ZnAs₂	**ZnSb; CdSb**	
	+ HCl ⟶ EH_3↑ + MCl; in str. [E_7] clusters, rings, chains		
Covalent	**AlAs**, m.p. 1740	**AlSb**	**LnBi**
	GaAs; InAs, m.p. 1238,	**GaSb**	
	943, sphalerite str. type,	**InSb**	
	semiconduct.; **LnAs;**	**LnSb**	
	+ H_2O ⟶ AsH_3↑ + …	**$CsSnSb_3$**, ex. in gas	
	Ba[Zn_2As_2], layers of [$ZnAs_{4/4}$] tetrah.	**$Ca_{14}AlSb_{11}$** [30]	
Metal-like	**TiAs; ZrAs; NiAs,** NiAs str. type, "red Ni pyrite"	**Ti_4Sb**	Ag, Zn, Cd, Pb, Sn, Fe – Ni do not form bismuthides **U_3Bi_4, $PtBi_2$, Au_2Bi** – intermet. comp.
	FeAs; CoAs	**TiSb; CoSb; NiSb** ("breithauptite"), NiAs str. type.	
	VAs; CrAs, MnP str. type;	**$TiSb_2$; $CoSb_2$; $NiSb_2$,**	
	V_5As_3; **$FeAs_2$**, "löllingite"	**NiSbS**, "ullmannite"	
	FeAsS, "arsenopyrite" ("mispickel")	**Cu_3Sb, Cu_2Sb**	
	Cu_3As_2↓		
	As(HgCl)₃↓, brn. ↓ $HgCl_2$		
	Hg_3As_2↓, blk.		
	$Ag_3E \cdot 3AgNO_3$ = $[EAg_6]^{3+}(NO_3)_3^-$, cr., yel.		

Cu^{2+}; $HgCl_2$; $AgNO_3$; EH_3; M

SbH_3; O_2(–90°); rapid cool.

Fusible alloys of Bi (eutonics)

m.p.	Alloy compos., %			
	Bi	Pb	Sn	
60.5 (Fild's met.)	32.5	–	16.5	51.5 - In
71 (Wood's met.)	50	25	12.5	12.5 - Cd
92	50	30	20	—
48	36	28	6	30-Hg
melts under friction	29	57	—	14-Hg
Type-metal alloy	—	60	15	25-Sb

Zintl polyanions
$[Na_2L_4]Bi_4$
$[Na_3L_4]Sb_7$
$[Na_3L_n]As_{11}$,
L = En, cryptand [30]

Na + L; $BiHal_3$; $NaM(CO)_n$

$Bi[Co(CO)_4]_3$
$BiIr_3(CO)_9$, clusters tetrah. [4]

O_2(t); E_2S_3; O_2; H_2O (t); H_2; C; KCN

As_2O_3, glass or cr. cub., colrl. | **Sb_2O_3**↓

	As_2O_3	Sb_2O_3
	m.p. 278, ΔH = –665, sol. in H_2O (≈2%), "arsenolite", d = 3.87	ΔH = –707, sol. in HCl, HNO_3, alk.; "senarmontite", d = 5.58
	mol. E_4O_6 in site of diamond [str. anal. of P_4O_6;]	
	↓ 221°	E CN = 3 + 3 570° ↕ 360° (pO_2)
	monocl., "claudetite", d = 4.29	rh., "valentinite", d = 5.75
	m.p. 315, b.p. 465	m. p. 656, subl. 1570
	gauffer layers of ψ-tetrah. [:$EO_{3/2}$]	

in gas – mol. E_4O_6 1800° ⟶ E_2O_3 [26]

H_2O; 20° (–H_2O)

$HAsO_2 + H_2O$ ⇄ H_3AsO_3, known in s. only, $K_{ac1} = 10^{-9}$, $K_{bas} = 10^{-14}$, pH ≈ 5

$Sb_2O_3 \cdot n H_2O$↓, wh., sol. in ac. and alk. **SbO(OH)**

H_2SO_4 (conc.); HNO_3 (conc.); MOH; MOH (–H_2); H_2SO_4 (conc.); oleum; $As(OH)SO_4$; $As(HSO_4)_3$

Arsenates [III]
NaH_2AsO_3;
K_3AsO_3
Ag_3AsO_3↓, yel., SP = 10^{-17}
CuHAsO₃↓, yel., [:AsO_3] – ψ-tetrah.
$KH(AsO_2)_2 \cdot H_2O$
$MAsO_2$,
$Pb(AsO_2)_2$↓, yel., chains of ψ-tetrah. [:$AsOO_{2/2}$]

$(SbO)_nX$, oxosalts [19]
$Sb_4O_5(OH)ClO_4 \cdot 1.5 H_2O$
$[Sb(OH)SO_4(H_2O)]_2$
$Sb_4O_4(OH)_2(SO_4)$,
"klebelsbergite"
$Sb_2O(SO_4)_2$; $Sb_6O_7(SO_4)_2$
$[H_5O_2]^+Sb_4O_2(OH)(SO_4)_4$
$[(SbO)_2(OH)(NO_3)]_2$,
disphenoid [:SbO_4],
ψ-tetrah. [:SbO_3] and oct.,
$SbO(H_2PO_4) \cdot H_2O$

H_2SO_4 (conc.); H_2O (surplus)

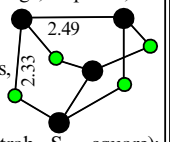
$H_2S_2O_7$; $BiCl_3 + AlCl_3$; $K_2S_2O_8 + S_2O_6F_2$; HSO_3F

$[As_8]^{2+}$, $[As_4]^{2+}$, $[Sb_4]^{4+}$, ex. in s., colrl., diamagn. (bl. due to $[S_8]^{2+}$ impurity)
$[Bi_5]^{3+}[AlCl_4]^-_3$, m.p. 253
$[Bi_8]^{2+}[AlCl_4]^-_2$
$[Bi_9]^{5+}Bi^+[HfCl_6]^{2-}_3$, cations – $[Bi_n]^{m+}$, n = 3 (triangle), n = 5 (trig. bipyr.), n = 8 (square antiprism) and n = 9 (three-cap trig. prism), Bi — Bi 3.1 – 3.9 [1]

$Sb(ClO_4)_3$,
210° ⟶ **$SbO(ClO_4)$** [2]
$Sb_2(SO_4)_3$, needles, colrl., **$\cdot H_2O$**
$Sb(NO_3)_3$; $Sb_2(HPO_3)_3$
$SbPO_4$, stab. at 1200°
$SbMO_4$, M = Ta, Nb, "stibiotantalite", "columbite"

$AgNO_3$ (acetone); $SbCl_3$

As_4S_4, glass or cr., orange, m.p. 320, b.p. 565, sol. in M_2S and $NaHCO_3$;
As_4S_4 – in str. and gas, anal. of S_4N_4 (but S and E at. exchanged their places: As_4 – tetrah., S_4 – square); "realgar";
+ KOH ⟶ As↓ + $KAsO_2$ + K_3AsS_3
100° ⟶ **As_4S_3, AsS_2** [1] **Bi_4S_4**



As_2S_3↓, yel., SP = 10^{-29}, cr., golden, m. p. 310, b. p. 723, ΔH = –96, sol. in $(NH_4)_2CO_3$, HNO_3;
+ OH^- ⟶ $[ES_nO_{3-n}]^{3-}$; + S^{2-} ⟶ $[ES_3]^{3-}$; + S_n^{2-} ⟶ $[E^VS_4]^{3-}$
"orpiment", monocl.
bands of ψ-tetrah. [:ES_3]
in gas As_4S_6 mol., str. anal. of P_4O_6,

Sb_2S_3↓, orange, SP = 10^{-30}, cr., grey, m. p. 560, b. p. 1160, ΔH = –158, sol. in conc. HCl (t);
"antimonite", rh.

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_15, © Springer-Verlag Berlin Heidelberg 2011

$KClO_3$

Bi_2O_3, cr. yel., $\overset{t}{\rightleftarrows}$ brn., "bismite", d = 8.2–8.9, m.p. 824 (rh.), 860 (tetr.), b.p. 1890, $\Delta H = -577$, sol. in ac.; Bi_2O_3 melt dissolv. Pt; α-, monocl. $\xrightarrow{729°}$ δ-, cube, m.p. 824; cool. $\longrightarrow$ β-, tetr. + γ-, cube — metastab.; for all forms frame of oct. [43]

150°

BiO(OH) $\xrightarrow[100°]{}$ **$Bi(OH)_3$**↓, wh., sol. in ac. and conc. alk.
$[Bi_2O(OH)_2](OH)_2$, str. anal. of sulfate

$E_2O_4 = E^{III}E^{V}O_4$,
AsO_2 [24]
SbO_2↓, colrl. $\xrightarrow{t}$ yel., dec. 1060,
Sb_6O_{13}
BiO_2, brn., m.p. 305 (dec.)
Bi_4O_7, **$SbAsO_4$**
$BiSbO_4$ [27]
$M_2Sb_2O_5$ = $M_2[Sb^{III}O][Sb^{V}O_4]$
$BaBi^{III}Bi^{V}O_5$, perovskite str.

As_2O_5, glass colrl., hyg., dec. 400, $\Delta H = -928$; rh. $\overset{225°}{\rightleftarrows}$ tetr., in str. frame of tetrah. and oct. [35]

H_2O 120° ($-H_2O$)

$H_3AsO_4 \cdot 0.5\,H_2O$, cr. hyg., colrl., m.p. 35, dec. 160, readily sol. in H_2O, $K_1 = 10^{-2}$, $K_2 = 10^{-7}$, $K_3 = 10^{-12}$
$H_5As_3O_{10}$, chains of oct. and tetrah. with common vertices; **$H_3AsO_4 \cdot 2\,H_2O$**

Sb_2O_5↓, cr. yel., frame of oct. with common edges and vertices,
$\xrightarrow{600°}$ **Sb_6O_{13}** $\xrightarrow{940°}$ **SbO_2**, $\Delta H = -1008$,
sol. in alk., conc. HCl, M_2CO_3, M_2S [35,36]

420°

$H[Sb(OH)_6]$ $\underset{H_2O}{\rightleftharpoons}$ **$Sb_2O_5 \cdot n\,H_2O$**↓
(in s.) n = 3.9–0.45 (< 290°) [36]

$Bi_2O_n \cdot x\,H_2O$↓, n = 4–5, from yel. to blk., easily evolves O_2
$Bi_2O_{4.7} \cdot 3\,H_2O$ [37]

MOH HNO₃

Bismuthates (V) [38]
$NaBiO_3$↓, cr. yel.
$KBiO_3$, red-vlt.
$Ba(BiO_3)_2 \cdot 4\,H_2O$, orange
$AgBiO_3$↓, blk.
M_3BiO_4; **Li_5BiO_5**, anions oct.
Li_7BiO_6, ionic conduct., [BiO_6] oct.

$M_2O_2 + O_2(t)$

Bi_2O_3

MOH

Antimonates (III) [21]
$M_3[Sb(OH)_6]$,
$M[Sb(OH)_4]$,
anion tetrah.
$NaSbO_2 \cdot 3\,H_2O$↓
$BaSb_3O_5(OH)$
Na_3SbO_3; **$NaSb_5O_8$**
$M_2Sb_6O_{10}$; **$M_2Sb_4O_7$**,
in str. ψ-tetrah. and ψ-trig. bipyr.,
$M^{II}[Sb_2O_4]$,
M^{II} = Mg, Zn, Mn–Ni, str. anal. of Pb_3O_4

$BiO(ClO_4)$, sol. in H_2O [23, 28]
$[Bi_6O_4(OH)_4](ClO_4)_6 \cdot 7\,H_2O$
$[Bi_2O(OH)_2]SO_4$, cation chain of oct. and pentagons
$Bi_2O(SO_4)_2$, Bi CN 7 and 8,
$[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4\,H_2O$
$[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3\,H_2O$
$[Bi_6O_4(OH)_4(NO_3)(H_2O)](NO_3)_5$,
cation – [Bi_6]-oct., μ_3-O and μ_3-OH – over centras of faces,
Bi — Bi ~ 3.6, [:BiO_4] – disphenoid
$Bi_2O_2CO_3$, 400° ⟶ Bi_2O_3

Bismuthates (III)
$M_3[BiO_3]$, light-yel.,
$CsBiO_2$, ψ-tetrah. or chains of $[BiO_{4/2}]_\infty$ [21]
$Ba_2Bi_2O_5$

O_2 t

E_2O_3 E_2O_5

Arsenates (V), cr. colrl. [39]
ortho-
$NaH_2AsO_4 \cdot n\,H_2O$, n = 1, 4
KH_2AsO_4, m.p. 288
$M_2HAsO_4 \cdot n\,H_2O$,
$M_2^{II}AsO_4(OH)$,
M = Cu ("olivinite"), Zn
$CaHAsO_4 \cdot 2\,H_2O$,
"pharmacolite"; **M_3AsO_4**,
$M_3^{II}[AsO_4]_2 \cdot 8\,H_2O$, M = Zn ("koettigite"), Co ("erythrite")
$Ca_2Mg(AsO_4)_2 \cdot 2\,H_2O$,
"belovite"
Ag_3AsO_4↓, brn., SP = 10^{-20}
NH_4MgAsO_4↓
di (pyro-)
$Na_2H_2As_2O_7$; **$Ba(H_3As_2O_7)_2$**
$Mg_2As_2O_7$

tri-
$Na_3H_2As_3O_{10}$, **$K_5As_3O_{10}$**

meta-
$NaAsO_3$; **$Ba(AsO_3)_2$**↓, chains or rings of tetrah.
$M^{II}(AsO_3)_2$, M^{II} = Ca, Cd, Pb, frame oct. of [AsO_6]
$Na_3H_5As_4O_{14}$, frame [AsO_6] oct., and [AsO_4] tetrah.
$BaH_6As_4O_{14}$

90° (−H_2O)
135° (−H_2O)
230° (−H_2O)

HNO₃ (conc.) aq.regia

E

$MClO_3$; MNO_3

Antimonates (V) [13]
$M[Sb(OH)_6]$, M = Li, Rb, Cs, Na↓, K↓, NH_4↓, Ag↓, $[Mg(H_2O)_6]/2$↓, NaCl str. type anion oct.
$M_2Sb_2O_5(OH)_2 \cdot n\,H_2O$,
M = Na (n = 1)↓, K (n = 4)
$MSbO_3$↓; **$K_2Sb_4O_{11}$**; **MSb_5O_{13}**
$K_3Sb_5O_{14}$; **$M_4[Sb_8O_{12}(OH)_{20}]$**
$M^{II}Sb_2O_6$↓; **$M_2^{II}Sb_2O_7$**↓;
$M_7^{II}Sb_2O_{12}$; **$M^{III}SbO_4$**↓,
M_5SbO_5, condensed oct. [13,38]

$M_2[Bi(ClO_4)_5]$; **$MBi(ClO_4)_4$**
$K[Bi(SO_4)_2]$
$K_3[Bi(SO_4)_3]$
$M_3[Bi(S_2O_3)_3]$, M = Na, K↓, NH_4↓, Sr/2↓, Ba/2↓, cr., yel.
$M_3^{II}[Bi(NO_3)_6]_2 \cdot 24\,H_2O$
$K_2[Bi(HCOO)_5]$, Bi CN 10,
$Rb[Bi(SCN_4)]$ [5]

$Bi(ClO_4)_3 \cdot 5\,H_2O$ **$Bi(IO_3)_3$**↓
$Bi_2(SO_4)_3$, needles, m.p. 710 (*p*)
$Bi(NO_3)_3 \cdot 5\,H_2O$, dec. 80, sol. in eth., ac., Bi CN 10,
$BiPO_4$↓, sol. in HCl
$Bi[VO_4]$, "pucherite"
$Bi[AsO_4]$, "rooseveltite", isostr. to "monazite"
$Bi_2(C_2O_4)_3$↓; **$Bi(HCOO)_3$**
$Bi(OCOCH_3)_3$, Bi CN 9
$Bi_4(SiO_4)_3$, "eulytine" [33]

H_2O

$M_2S_n + S$ (*t*)

H_2SO_4 (conc.) N_2O_4 HNO_3 (conc.)

Bi

$[H_6As_4O_{14}]^{2-}$

Bi_2O_2S, blk., frame of antiprisms [$Bi_4O_4S_4$]
Bi_2O_2Se [33]

Bi_2S_3↓, dark-brn., SP = 10^{-72}, "bismuthinite" ("bismuth glance"), cr., blk., m.p. 685 with dec., $\Delta H = -156$, sol. only in conc. HNO_3, isostr. to Sb_2S_3, Bi CN 7
Bi_2Se_3, cr. blk., m.p. 710, b.p. 1007
Bi_2Te_3, m.p. 580, b.p. 1172, $\Delta H = -79$
$PbBi_2S_4$, "bismutitoplagionite" } double sulfides
$CuBiS_2$, "emplectite" } (not sulfosalts)

Sulfosalts [6]
M_3AsS_3, light-yel., hyg.
Ag_3AsS_3, "proustite"
Cu_3AsS_4, "enargite"
$TlAsS_2$, "lorandite"
$PbAs_2S_4$, "sartorite"
$Cs_2Sb_8S_{13}$;
$RbSb_3S_5 \cdot H_2O$
$NaSbS_2$; **$K_2Sb_4S_7 \cdot H_2O$**
M_3SbS_3; **$AsSbS_3$**, "getchellite"
$Ag_{24}Sb_2S_{15}$, "polyargyrite"
$CuSbS_2$, "chalcostibite:
$PbSb_2S_4$, "zinkenite"
In str. tetrah. and ψ-tetrah.

As_2S_3 S_n^{2-}; $S + OH^-$

H_2S (H^+)

$MBiS_2$, NaCl str. type with statistical distribution of M
$K_8Bi_2S_7$
KBi_3S_5, semiconduct., units of oct. with common edges
$K_2Bi_4S_7$ [34]

As_2S_5↓, yel.
$\xrightarrow{500°}$ As_3S_3 + S, $\Delta H = -146$, in gas – As_4S_{10} mol., str. anal. of P_4O_{10}

$M_3[AsO_3S]$; **$M_3[AsOS_3]$**; [10]
$Na_3[AsO_2S_2] \cdot 11\,H_2O$
M_3AsS_4, M = Na, NH_4, Cu/2 ("luzonite"), colrl., anion tetrah.

H_2S (H^+, $-Sb_2S_3$↓ $-S$↓)

Sb_2S_5 (?)↓, orange cr., dec. 170 [12]

S^{2-} / H^+

$M_3[SbS_4]$, M = Na (· 9 H_2O, Schlippe salt), K (· 4.5 H_2O), cr. vlt., anion – tetrah.

$SbO(NO_3)_3$, cr. yel.
$SbO(PO_4)$, str. frame of [SbO_6] oct. and [PO_4] tetrah.
$\xrightarrow{945°}$ $SbPO_4$ [41]

550°

$HSb(PO_4)_2 \cdot 4\,H_2O$
$M[Sb(PO_4)_2]$,
M = Li–Cs [41]

$M_2[AsO_3(OOH)]$
$M_2[As_2O_4(O_2)F_2]$ [40]

Sulfosalts [6]
M_3AsS_3, light-yel., hyg.
Ag_3AsS_3, "proustite"
Cu_3AsS_4, "enargite"
$TlAsS_2$, "lorandite"
$PbAs_2S_4$, "sartorite"
$Cs_2Sb_8S_{13}$;
$RbSb_3S_5 \cdot H_2O$
$NaSbS_2$; **$K_2Sb_4S_7 \cdot H_2O$**
M_3SbS_3; **$AsSbS_3$**, "getchellite"
$Ag_{24}Sb_2S_{15}$, "polyargyrite"
$CuSbS_2$, "chalcostibite:
$PbSb_2S_4$, "zinkenite"
In str. tetrah. and ψ-tetrah.

$M[Sb(ClO_4)_4]$ [21]
$M[Sb(SO_4)_2]$
$[H_3O]_2[Sb_2(SO_4)_4]$
$Ca[Sb_4O_4(OH)_2(SO_4)_2]$, "peretaite"
$Na_3Sb(PO_4)_2$, in str. chains of [SbO_6] – oct.
$K_2[Sb_2(C_4H_2O_6)_2]$ **$\cdot 3\,H_2O$**, tartaric emetic., cr. colrl., readily sol. in H_2O, ex. as 2 optical isomers, [:SbO_4]–disphenoid

ARSENIC, ANTIMONY AND BISMUTH HALIDES AND OXOHALIDES

3+

	m.p.	b.p.	ΔH	μ
AsF_3, liq. colrl.	−6	63	−858 [22]	2.81
$AsCl_3$, liq. colrl.	−16	130	−336	1.97
$AsBr_3$, cr. colrl.	33	221	−201	—
AsI_3, cr. red	146	403	−67	—

H_2

As_2I_4, cr. dark red, m.p. 136 (dec.), $\downarrow H_2O$ $As + AsI_3$

MHal

M[AsF_4], M = K−Cs, [SCl_3], ψ-trig. bipyr., **KAs_2F_7** = K[AsF_4][AsF_3], [22] **[SCl_3]$^+$[AsF_3Cl]$^-$** **$KAsCl_4$**

[AsF_2]$^+$[SbF_6]$^-$ **[$AsCl_2$]$^+$[$SbCl_6$]$^-$**

$AsHal_3$ and $SbHal_3$ hyg., sol. in Et_2O, $AsCl_3$ (ε = 13) dissolv. S, P; melthed $SbHal_3$ readily dissolv. $MHal_n$; $AsHal_3 + H_2O \rightleftarrows As(OH)_3 + HHal$ (rate of hydr. F ≫ Cl > Br > I); $SbHal_3 + H_2O \rightleftarrows Sb(OH)_nHal_{3-n} + HHal \xrightarrow{H_2O} SbOHal\downarrow$; $SbCl_3$ sol. in H_2O ~80%; in str. and gas: [:$EHal_3$] mol. ψ-tetrah., EI_3 – layered polymers, isostruct. to $FeCl_3$

$As_2O_3 + F_2$; O_3 (−78°); Cl_2 (−105°, UV)

AsO_2Cl, cr. colrl., insol. in org. solvs.
$AsOF_3$, g. colrl., m.p. −68, b.p. −26
$(AsOF_3)_n$, powd., wh., hyg.
$AsOCl_3$, cr. colrl., dec. −25 → $(As_2O_3Cl_4)_n$ [32]

AsF_5, g. colrl., v. hyg., m.p. −80, b.p. −53 ΔH = −1066, mol. trig. bipyr. (sp^3d), strong F- acceptor
$AsCl_5$, ex. in Cl_2 s. at $t \leqslant -50°$ [15]

M_2AsO_3F; **$MAsO_2F_2$**
$MAsOF_4$, M = K−Cs, anion $[As_2O_2F_8]$: 2 oct. with common edge $[O_2]$ [9]
$M_2[(AsF_5)_2O]$, **M[AsF_5(OH)]**, anion oct.

M[AsF_6], M = M^I, [NF_4], [$AsCl_4$], [SCl_3], [ClF_4], [ClO_2], [IO_2], [IF_6], [XeF], [Xe_2F_3], anion oct., resist to hydr.
M_2AsF_7
M[$AsCl_6$], M = [PCl_4], [Et_4N], cr., orange

[AsF_4]$^+$[PtF_6]$^-$ [42]
[$AsCl_4$]$^+X^-$, X = PCl_6, $AlCl_4$, AsF_6, SbF_6
[$AsBr_4$]$^+X^-$; **[AsI_4]$^+X^-$**, unstab.

E Hal_2

$Sb_3O_2F_5$; **SbOF** **Sb_3O_4F** [25]
SbOCl↓; **$Sb_4O_5Cl_2$↓**; **$Sb_8O_{11}Hal_2$**, **$Sb_4O_5Br_2$↓**; Hal = Cl−I
Sb_3O_4I; **Sb_5O_7I**
ψ-tetrah., trig. bipyr. and Hal^-,
SbEHal, E = S−Te, Hal = Cl−I, semiconduct.

$SbCl_n$, $n \leqslant 3$, exp. Sb, graphite-like mass, exp. at friction, d = 5.8, in str. – at. Sb, $[SbCl]^{2+}$, $[SbCl_2]^+$, Cl^-

cath. Red (≪ 0°)

	m.p.	b.p.	ΔH
SbF_3, cr. colrl.	292	319, subl.	−916
$SbCl_3$, cr. colrl.	73	233	−382
$SbBr_3$, cr. colrl.	97	289	−260
SbI_3, cr. red	171	401	−100

$SbHal_3$ (Hal = F−Br) isostr. to YF_3; SbI_3 isostr. to PI_3. $SbHal_3$ sol. in ROH, bz., Diox; · ***n*** **L**, L = Dipy, C_6H_6, $C_{10}H_8$ – π-compl.

MHal

M[SbF_4]; **Na_2SbF_5**; **KSb_2F_7**; **$Li_3Sb_2F_9$**; **$NaSb_3F_{10}$**; **K[F(:SbF_3)$_4$]**; **$K_3Sb_4F_{15}$**; **$Na_3Sb_5F_{18}$**; anion − ψ-trig. bipyr. (disphenoid) or oct.
$M_4Sb_4F_{16}$, anion [:$SbF_3F_{2/2}$] ring
M[$SbCl_4$]; **$M_2[SbCl_5]$**; **$M_3[SbCl_6]$**; **Cs_4SbCl_7**; **Cs_5SbCl_8**; **$M_3Sb_2Cl_9$**; **$Cs_5Sb_2Cl_{11}$**; **$M_7Sb_3Cl_{16}$**
$Tl_2Sb_3Cl_{11}$, anion oct., ψ-oct.
$RbSbBr_4$; **$K_2Sb_2Br_9$**; **M_3SbBr_6**, oct.

SbF_4 = $[Sb^{III}_2F_4]^{2+}[Sb^VF_6]^-_2$
$Sb_{11}F_{43}$ = $[Sb^{III}_6F_{13}]^{5+}[Sb^VF_6]^-_5$, cation chain of 2 completed and 3 [:SbF_3] ψ-tetrah.
$M_2[Sb^VF_6][(Sb^{III}F_2)(Sb^VF_6)_2]$ [8]
$Sb_2F_4Cl_5$
[$SbCl_4$], brn. s.

$(SbOF_3)_n$; **SbO_2F**
SbO_2Cl; **$SbOCl_3$**↓, yel., hyg., insol. in org. solvs.; + H_2O ⟶ $Sb_2O_5 \cdot n\,H_2O$↓

H_2O

	m.p.	b.p.
$(SbF_5)_n$, oil colrl., visc., weakly hyg.	8.3	149
$SbCl_5$, liq. colrl.	3	102/vac.
$SbBr_5$ (?)	—	—

ΔH SbF_5 = −439, dissolv. S, Se, Te; v. strong F^- - acceptor; $SbCl_5$ – strong Cl - agent. In liq. $(SbF_5)_n$ (n = 5 − 10) chains of [$SbF_4F_{2/2}$] oct., in str. tetramers of *cis*-[$SbF_4F_{2/2}$] oct., [11] in gas [$SbF_3F_{2/2}$]$_3$ cycles.
$SbHal_5 \xrightarrow{t}$:$SbHal_3$ + Hal_2; equ. ax.
+ H_2O ⟶ $SbOHal_3$ + 2 HHal; equ. ax.
$SbCl_5 \cdot$ L, L = NOCl, $POCl_3$, SO_2, mol. oct.

M[SbF_6]; **M[Sb_2F_{11}]**, M = M^I, [NF_4], [$AsCl_4$], [S_{16}]/2, [SF_3], [H_2F], [Cl_3], [$HalF_2$], [$HalF_4$], [XeF_3], [XeF_5], [$XeOF_3$], [Xe_2F_{11}], anions oct. or 2 oct. with common vertex [17]
M[Sb_3F_{16}], M = [PF_4], [Br_2], anion chain of 3 oct., [$SbF_4F_{2/2}$]-*trans* in the centre
$M_2[SbF_7]$; **$H_3[SbF_8]$**, Sb CN 7 and 8
$[BrF_4]^+[Sb_7F_{36}]^-$
$HSbCl_6 \cdot 3\,H_2O$, cr. grn., hyg.; **$[H_{14}O_6][SbCl_6]_2$**
M[$SbCl_6$], M = M^I, [SCl_3], [NO], [ICl_2], [PyH]
M[$(SbCl_5)_2X$], X = F, CN, N_3
H[$SbBr_6$] · 3 H_2O; **M[$SbBr_6$]**, oct.
Cs[SbI_6] [14,16]

$MSbOF_4M_2Sb_2OF_{10}$, **M[SbF_5(OH)]**, [16]
Na[SbF_4(OH)$_2$], **H[$SbF_{6-n}(SO_3F)_n$]**, n = 0−3

E Hal_2; BrF_5

HCl (conc.)

Sb_2S_3

BiOF; **$Bi_7O_9F_3$**; **Bi_3O_4F**; **$Bi_{13}O_{19}F$**
BiOCl; **$Bi_4O_5Cl_2$**; **Bi_3O_4Cl**; **$Bi_{12}O_{17}Cl_2$**; **$Bi_{24}O_{31}Cl_{10}$**
BiOBr; **$Bi_{12}O_{15}Br_6$**; **Bi_3O_4Br**; **$Bi_{12}O_{17}Br_2$**; **$Bi_{24}O_{31}Br_{10}$**
BiOI; **Bi_5O_7I**, str. $[Bi_{10}O_{14}]^{2n+}_n$ columns, Bi CN 7, 8 and 9. Str. of other oxohalides: HalBiOBiHal... layers (in BiOHal) or $[Bi_{12}O_{15}]^{6+}$ of ψ-oct. [29]
BiSHal, **BiSeHal**, Hal = Cl−I, Bi CN 8

$MBi_3O_4Cl_2$
$LiBi_2O_3Cl$
$BaBiO_2Cl$

M_2SbCl_6, M = Rb, Cs, blk., diamagn.; + H_2O ⟶ $M_3[SbCl_6]$ + + $M[SbCl_6]$
M_2SbBr_6, blk., diamagn., isostr. to K_2PtCl_6, $[Sb^{III}Hal_6]$ and $[Sb^VHal_6]$

Bi

$BiHal_3$; Hg_2Cl_2

aq.regia

H^+ ↑ H_2O

	m.p.	b.p.	ΔH
BiF_3↓, cr. grey [31]	727	900	−899
$BiCl_3$, cr. wh., darkening in light	234	447	−379
$BiBr_3$, cr. yel.	219	461	−260
BiI_3↓, cr. brn., sol. in I^-, $S_2O_3^{2-}$, AsO_3^{3-} presence.	408	439	−109

In gas [:$BiHal_3$] ψ-tetrah., in ion str. BiF_3 and $BiCl_3$ (YF_3 type) Bi CN 8+1, in $BiBr_3$ (α- and β-): dist. oct.; BiI_3 isostr. to $FeCl_3$,
$BiCl_3 \cdot n$ L, L = NO, NO_2, NOCl

MBiF$_4$, struct. [BiF_9] grs. [7]
K_2BiF_5; **K_3BiF_6**; **KBi_2F_7**; **KBi_3F_{10}**
MBiCl$_4$; **$M_2[BiCl_5]$**; **M_3BiCl_6**;
Cs_4BiCl_7; **$Rb_3Bi_2Cl_9$**; **$Rb_7Bi_3Cl_{16}$**;
$M_2Bi_2Cl_8$, anion 2 ψ-oct. with common edge
M_2BiBr_5; **M_3BiBr_6**; **$Cs_3Bi_2Br_9$**
$M_4[Bi_2Br_{10}] \cdot 4\,H_2O$;
$M_7[BiBr_6][Bi_2Br_{10}]$, anions – oct. or ψ-oct.
$KBiI_4$; **$HBiI_4 \cdot 4\,H_2O$**; **$M_3[Bi_2I_9]$**
$Rb_5I(I_3)[BiI_6]$

$Bi_{24}Cl_{28}$ (≈ "BiCl") = **$[Bi_9]^{5+}_2[Bi^{III}Cl_5]^{2-}_4[Bi^{III}_2Cl_8]^{2-}$**
cr. brn., hyg.,
m.p. 163; $\xrightarrow{300°}$ Bi + $BiCl_3$;
Bi_6Cl_7; **$Bi_2[GaHal_4]_2$**;
$Bi_{24}Br_{28}$, semiconduct.
BiI, m.p. 318 with dec.
Bi_7I_2; **Bi_9I_2**
$Bi_{10}I_3$, m.p. 295 [1]

[SbF_4]$^+$[SO_3F]$^-$; **[$SbCl_4$]$^+X^-$**, X = SbF_6, $SO_4/2$, Hal
Sb(OTeF$_5$)$_6$ [44]

$SbF(NO_3)_4$; **$SbF_3(NO_3)_2$**

K[$BiOF_4$]
$BaBiO_2Cl$
$LiBi_2O_3Cl$
$MBi_3O_4Cl_2$

MF + BrF_3

E_2O_3

BrF_3

Bi

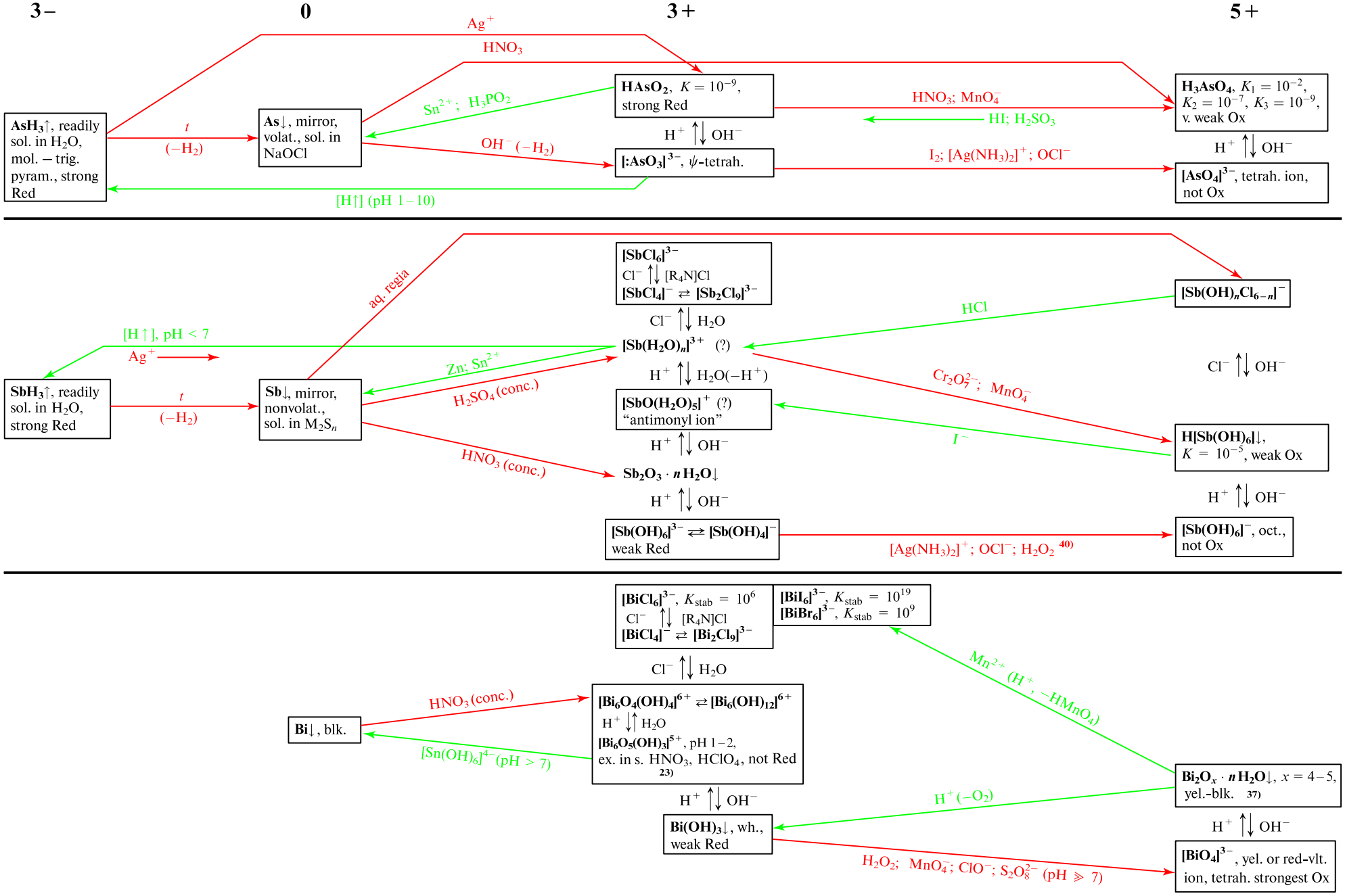
F_2 (500°); ClF_3 (350°)

BiF_5, needles, colrl., m.p. 151, b.p. 230, v. strong F-agent, in α-UF_5 str. – chains of *trans*-[$BiF_4F_{2/2}$] oct. [17]

MF + F_2 (p); [NH_4]BF_4

M[BiF_6], M = Li−Cs, Mg−Ba/2, [BrF_2], [O_2], [H_3O], [XeF_3], NF_4 [17]
+ H_2O ⟶ $O_2 + H_2O_2 + \ldots$

ARSENIC, ANTIMONY AND BISMUTH IONS IN AQUEOUS SOLUTIONS



VANADIUM

V^0 3d: ↓ ↓ ↓ | 4s: ↓↑ | 4p:

EN 1.5

2+ (d^3)

3+ (d^2)

0 (d^5)

V_8O;
V_4O;
$V_2O_{1\pm x}$ [41]

$VO_{1\pm n}$, n = 0.25, cr., blk. with met. lustrous, m.p. 1830, ΔH = −412, sol. in ac., conduct. (at high t — semiconduct.), NaCl str. type, V—O 2.05, V—V 2.89 [5]

V_2O_3, cr. blk., m.p. 1970, ΔH = −1239, sol. in ac. "karelianite", corundum (Al_2O_3) str. type V—O 2.00

VO(OH), "montroseite", str. anal. AlOOH

$V(OH)_3\downarrow$, brn.-grn., sol. in ac., strong Red

$V(OH)_2\downarrow$, brn., sol. in ac.

2.8+ $M^{II}V_{10}O_{15}$, struct. — net. of V^{II}, V^{III}-oct. [39]

MVO_2, M = Li–K, blk., isostruct. to $KFeO_2$ [7]

V_2O_5

V, met., wh., hard, d = 6.1, m.p. 1920, b.p. 3450, $E_0V^{2+}/V_{sld.}$ = −1.17; $E_0V^{3+}/V_{sld.}$ = −0.86; sol. in HF, aq. reg. (20°), HNO_3, H_2SO_4 – conc. (t); α-Fe type cub. struct., a = 3.03, V—V 2.68

M

Ferrovanadium 30–80% V; 3.5% Si; >2% Al; 1% C; 0.1–0.2% P and S; 70–10% Fe. Sld. s. and **VFe** (m.p. 1234) occur in the Fe–V system. **Vanadium steels** (0.2 % V) ductile, tensile, high abrasion resist. and rupture strength. **Al–V alloys** corrosion-resist.

$V_2O_5 + Fe_2O_3$

C; Si; Al

$V(ClO_4)_2 \cdot 6H_2O$, needles, red-vlt.

$VSO_4 \cdot nH_2O$, n = 7 (vlt. vitriol, isostruct. $FeSO_4 \cdot 7H_2O$), 6, 4, 1, $\cdot M_2SO_4 \cdot 6H_2O$, Tutton salts

$[V(H_2O)_6](CF_3SO_3)_2$ [3]

V_3S, $VS_{1+n}\downarrow$, n = 0.17–0.53, NiAs str. type

V_3S_4, V_2S_3 [43], V_5S_8, $Li[VS_2]$ [11]

VN, V_3N, Li_7VN_4

VP, VP_2, V_3P_2, V_2P, V_3P

VC_2, + $H_2O \rightarrow C_2H_4 + C_2H_2$

VC, V_2C, V_3Si; met.-like incul. phases in the str. of V

V_2O_5

$H_2SO_4 + S$

H_3PO_4

NH_4F (−N_2)

V(OH)(SO4) [2]

$V_2(SO_4)_3\downarrow$, cr. orange (monocl.) grn. (hex.), 400° → SO_2 + $VOSO_4$ ↑ −H_2O $\cdot nH_2O$, n = 2, 4, 10 $\cdot M_2SO_4 \cdot 24H_2O$, vlt. alum, stab. in air [2]

$V(H_2PO_3)_3\downarrow$, yel.-grn. [26]

VPO_4, brn.

$[V(PO_3)_3]_n$, n = 4, ∞; yel.-grn., chains of [VO_6] oct. and [PO_4] tetrah.

$V_4(P_2O_7)_3$, str. pairs of [V_2O_9] oct.

$V(CH_3COO)_3$

$[V_3O(CH_2ClCOO)_6(H_2O)_3]^+X^- \cdot 3H_2O$, str. anal. of Cr (III) acetate [2]

230°

$H[V(SO_4)_2] \cdot nH_2O$, n = 4, 6, grn. [8]

$M[V(SO_4)_2]$, cr., grn., $\cdot 6H_2O$, vlt., [VO_6], oct.

$Na_3V(SO_4)_3$, grn.

$Cs[VHP_3O_{10}]$, $Rb[V(HPO_4)_2]$ (α, β)

$Cs[V_2P_5O_{16}]$, in str. — chains of [PO_4], tetrah. with [VO_6] oct.

$M_3[V(C_2O_4)_3]$, anion — oct. [26]

V + H_3PO_4; SO_2 ($NaHSO_4$)

V_2O_5

VOF; VOCl, powd. brn.

VOBr, vlt., dec. 480

VOI, stab. < VOBr < VOCl [37]

$M_3[VOCl_4]$, M = K–Cs [9]

VCl_3

CO + Mg/Zn (Py, t, p)

$HV(CO)_6$, unstab. [1]

↑ H^+

$M[V(CO)_6]$, M = Na, K, NH_4, [R_4N], cr., yel., stab., diamagn., anion — oct., Σe = 18

$M_3V(CO)_5$

$V(CO)_6$, cr., bl.-grn., subl. 40–50 vac., dec. 60, Ox in air, orange, s. in org. s., v. unstab.; paramagn. (Σe = 17!), mol. — dist. oct., V—C 2.01, C—O 1.14 [35]

$V(:CO)_5(:NO)$, stab. > > $V(CO)_6$, (Σe = 18)

$(R_3P)Au–V(CO)_6$

PR_3 ($h\nu$-UV)

$M[V(CO)_4(PR_3)_2]$

$[R_4N][V(CO)_5(PR_3)]$

$[V(CO)_5(PR_3)]$, cr., grn. m.p. 104 [35]

$V[(—CH_2—PR_2)_2]_3$

Hal2

(I2) (ex.) (defic.)

[3]	ΔH
VF_2, cr. light-grn., $\cdot 4H_2O$, bl.	—
VCl_2, cr. light-grn., m.p. 1350, subl. 1000 $\cdot 4H_2O$	−451
VBr_2, cr. brn., $\cdot 6H_2O$	−348
VI_2, α-, cr. blk., β-, red, subl. 800, >1400° → V + I_2	−264

HF

Str. VF_2 — CaF_2 type, $VHal_2$ (Hal = Cl, Br, I) — CdI_2 type

$VHal_2 \cdot nNH_3$; $VHal_2 \cdot nL$ L = Thf, Dme, C_6H_5OH,

$[V(\mu\text{-}Cl)_3Thf_6]^+X^-$ [45]

$V(C_5H_5)_2$, vanadicen [36]

MVF3, M = Na–Rb

$MVCl_3$, M = K m.p. (946), NH_4, Tl

K_2VCl_4

$Cs_2VCl_4 \cdot 2H_2O$

$MVBr_3$, pink-brn. [4]

$KVBr_3 \cdot 6H_2O$, vlt.

t (−Hal_2); H_2 (t)

	ΔH
VF_3, cr. grn., subl. 800, $\cdot 3H_2O$	−1335
VCl_3, cr. vlt., nonvolat.	−782
500° → VCl_2 + VCl_4, $\cdot 6H_2O$	
VBr_3, blk.-grn.	−452
280° → VBr_2 + Br_2	
VI_3, blk., μ_{eff} = 2.92 [3]	−280
280° → VI_2 + I_2	

$VHal_3$ (Hal = F, Cl, Br) isostr. to $FeCl_3$

VF_3 — isostr. to BiI_3; [18]

$VHal_3$ weakly hyg., poorly sol. in H_2O, better sol. in alc.; in str. $VCl_3 \cdot 6H_2O$ cation $[VCl_2(H_2O)_4]^+$

trans-$[VCl_3(SMe_2)_2]$, mol. trig. bipyr.

K_3VF_6, m.p. 1020, V—F 1.93 [25]

$(NH_4)_3VF_6\downarrow$, m.p. 1400, yel.-grn.

$M_2[VF_5(H_2O)]$, cr., grn.

$M[VF_4(H_2O)_2]$

$M[VCl_4]$, tetrah., $\cdot nH_2O$, M = K–Cs, n = 0 (vlt.), 1 (red), 4 (grn.)

$Cs_2[VCl_2(H_2O)_4]Cl_3$ -*trans*;

$Cs_3[VCl_2(H_2O)_4]Cl_4$

M_2VCl_5, M_3VCl_6, $M_3[V_2Cl_9]$, anions — trig. bipyr., oct., pairs of oct. with common face

$M[VBr_4]$, $Cs_2[VBr_2(H_2O)_4]Br_3$-*trans*

$K_3[V(CN)_6] \cdot 3H_2O$, cr., red

$K_4[V(CN)_7] \cdot 2H_2O$, vlt., pentag. bipyr. [10]

$M_3[V(NCS)_6]$, M = Na (·12 H_2O), K

$K_4[V(CN)_6] \cdot 3H_2O$, yel., anion — oct.

μ_{eff} = 3.83

$K_4[V(CN)_6(NO)]$, diamagn.

$M_4[V(NCS)_6] \cdot nH_2O$, μ_{eff} = 3.8 [40]

$[V(NH_2)(NH_3)_5]Hal_2$, red

$V(NH_2)Cl_2$ 300° → V(NH)Cl $\xrightarrow{t}$ VN [6]

$Li[VDipy_3] \cdot 4Thf$

$[VDipy_3]$, oct.

$[V(C_6H_4F_2-1.4)_2]$, mol. — sandwich

$V(C_6H_6)_2$

$[VDipy_3]^+X^-$, cation — oct.

$K_5[V(CN)_5(NO)^+]$

$K_5[V(CN)_5]$, cr. pink.

(I2)

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_16, © Springer-Verlag Berlin Heidelberg 2011

$(3.5-3.75)+$ V_nO_{2n-1} V_3O_5 [42]

VO_2, cr., hyg., m.p. 1545, b.p. ~ 2700, $\Delta H = -720$, sol. in ac. and alk., rutile type "paramontrosite"; · **2/3 H_2O**, "doloresite" [34]

$(COOH)_2$; $V_2O_3(t)$; H_2 — 750° — 4.33+ **V_6O_{13}**, cr., bl.-blk., dec. 650, in str. oct. **V_4O_9; V_3O_7** = $V^{IV}[V^V_2O_7]$ [34]

t (N_2) — NH_4VO_3

3.5 + **$V_2O_2(OH)_3$**, "haeggite"

$VO(OH)_2$↓, yel., sol. in ac. and alk. "duttonite" [12]

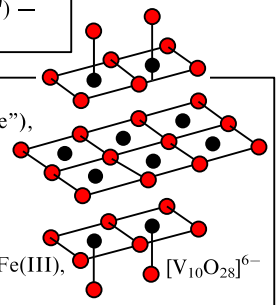
4.66+ **$V_3O_7 \cdot H_2O$**; 4.8+ **$V_2O_{4.8} \cdot n H_2O$**, $n = 0.5, 3.5$, blk., "corvusite" [30]

V_2O_5, cr., orange, m.p. 680, dec. 700, $\Delta H = -1573$, sol. in $H_2O \approx 0.04\%$, sol. in ac. and alk., volat. with H_2O vapour (⇆ $H_4V_2O_7$ gas), V_2O_5 (liq.) ⇆ $VO_2^+ + VO_3^-$ (conduct.), double chains of [VO_5] tetrag. pyram., V=O 1.58, V–O 1.78–2.0 (4 bonds); · **$n H_2O$**, $n = 1$ ("HVO_3", "navajoite"), 2 ("$H_4V_2O_7$"), 3 ("H_3VO_4") — fibrous cr. [28]

NH_4VO_3 (t, $-NH_3$, $-H_2O$)

O_2 — V — M_2O_2 + MOH

Vanadates (V) [24]
$M_6V_{10}O_{28} \cdot n H_2O$, M = Na ($n = 18$), Ca/2 ($n = 17$ "pascoite"), cr., orange, anion of 10 dist. oct. [VO_6] with common edges, V—O 1.68, 1.80, 1.90, V—V 3.04–3.32
$K_3V_5O_{14}$; $[R_4N]_3HV_4O_{12}$; $K_5V_3O_{10}$; MV_3O_8
$M_4V_2O_7$, M = Na (· H_2O), K (·2 H_2O), Ag↓
MVO_3, condenced tetrah., trig. bipyrs., tetr. pyram. or oct.
$M_3[VO_4]_n$, tetrah., M = Na, Ag↓, Sr, Ba, Al, Sc, Ln, Bi, Fe(III),
$Pb_5[VO_4]_3Cl$, "vanadinite", yel.-red, isostr. to apatites [29]
$K(UO_2)[VO_4] \cdot 1.5 H_2O$, "carnotite"



Vanadyl (IV) salts, O = VX_2
$VO(ClO_4)_2 \cdot 5 H_2O$ [31, 46]
$VOSO_4$↓, cr., grn.
· **$n H_2O$**, $n = 1-3, 5$ (= $[VO(H_2O)_5]SO_4(H_2O)$), 6 (bl., readily sol. in H_2O, alc.); · **0.5 H_2SO_4**;
· **$n M_2SO_4$**, n = 1, 2, bl.
$VOSeO_3$, light-grn.
$(VO)_3(PO_4)_2 \cdot 9 H_2O$
$VO(HPO_4) \cdot n H_2O$
$VO(H_2PO_4)_2$, bl.
$(VO)_2P_2O_7$ [46]
$VO(C_2O_4) \cdot n H_2O$, n = 2, 4
$VO(RCOO)_2$ [39]

MOH / HX

Vanadates (IV) [44]
cr., yel. or brn.
$Na(VO)_2(OH)_5$; $K_2V_3O_7 \cdot 2.66 H_2O$
$M^I_4VO_4$ (ortho-)
$M^{II}_3VO_5$; $M^{II}_2VO_4$; $M^I_2VO_3$ (meta-)
$M^I_2V_2O_5$, (pyro-), from melts.
$M_2V_4O_9 \cdot 7 H_2O$ (tetra-), cr., formed from s.
$CaV_4O_9 \cdot 5 H_2O$, "simplotite"
$H_8[Mo_3V_3O_{19}]$; $M_3[Mo_2V_4O_{19}H_7]$, bl.

$M_xV_2O_5$, M = Li–Cs, NH_4, Cu, Ag, $0 < x < 1$, **bronzes**, in str. at. of V(IV) and V(V), CN 5 [18]
$M_5[V_{15}O_{36}]$, $M_8[V_{19}O_{41}(OH)_9]$, clusters, sphere and ellipse

VO_2; M

Ba[VO(PO$_4$)]$_2$ · 4 H_2O
$K_2[VO(P_2O_7)]$, anion — tetr. pyram.
$Sr[VO(AsO_4)]_2$, str. chains of oct.
$Na_{14}[V_{18}O_{42}(CO_3)] \cdot 28 H_2O$
$(NH_4)_2[VO(C_2O_4)_2] \cdot 2 H_2O$, cr., bl.

V — N_2O_4 — **$[VO_2]^+X$**, X = NO_3, ClO_4, Cl, cr., red, strong Ox agent, ex. at pH < 1
$[VO_2(RCOO)]_4$ [19]

O_3; ClO_3

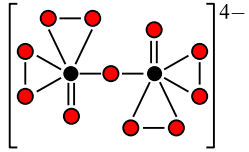
$V_2O_3(SO_4)_2 \cdot 2 H_2O$, in str. oct. and [$SO_4$] tetrah. [47]

O_3; ClO_3

$M[VO_2(SO_4)]$ [21]
$M_3[VO_2(C_2O_4)_2]$-*cis*, oct.
$M_3[VO_2F_4]$, linear gr. [O = V = O] [22]
$M_2[VO_2F_3]$, **$Cs_3[(VO_2)_2F_5]$**
$M[VO_2Cl_2]$, M = K–Cs

$(NH_4)_4[V_2O_3(SO_4)_4]$ [22]
$K[VO(SO_4)_2]$

$M[VO_2(O_2)] \cdot 0.5 H_2O$
$M_2[V_2O_2(O_2)_4(H_2O)]$
$(NH_4)_4[V_2O_{11}]$, yel., anion —



$K_3[VO_2(O_2)_2(H_2O)]$↓, yel.
$K_3[VO(O_2)_3]$;
$K_2[V(OH)(O_2)_3]$ [27]
$M_3[V(O_2)_4] \cdot n H_2O$↓, M = K (bl.-vlt.), NH_4 (colrl.)

VOX$_3$, yel., hyg.	m.p.	b.p.	ΔH
$VO(ClO_4)_3$, liq.	22	33.5	—
$VO(NO_3)_3$, liq.	2	68	—
$VO(PO_4) \cdot 2 H_2O$, cr. *)	—	—	— [21]
$VO(SO_3F)_3$, cr., red	120	dec. 190	—
VOF_3, cr.	300	480	−1251
		subl. > 110	
$VOCl_3$, liq., d = 1.829	−77	128	−740
$VOBr_3$, liq.		130/vac. dec. 180	—

VOF$_3$ str. network of [$VOF_{4/2}$] oct.; VOHal$_3$ (Hal = Cl–Br) in str. and gas — tetrah. mol. [20]

ClO_3 — V_2O_5 — $SOCl_2$; C + Cl_2; HCl + P_2O_5; N_2O_5 — V_2O_5

Hal_2 — V_2O_3 — SO$_3$

$V_2O(SO_4)_4$, yel., unstab.

VOF_2, yel.
$VOCl_2$, grn., subl., dec. 300; · **2.5 H_2O**
$VOBr_2$, yel., dec. 180
$VOI_2 \cdot 2.5 H_2O$, cr., brn.
VOHal$_2$, hyg., readily sol. in H_2O, alc. [13]

$M_3[VOF_5]$; $Cs_3[V_2O_2F_7]$; $Cs[VOF_3]$
$M_2[VOF_4]$; $K_2[VOF_4(H_2O)]$, bl.
$M_2[VOCl_4]$; $Cs_3[VOCl_5]$, anion — chains of oct.
$K_3[VO(CN)_5]$, anion oct.
$M_2[VO(NCS)_4]$ [15]

$M[VOF_4]$, cr., yel.-grn., str. — chains of oct. [$VF_5O_{ax.}$], V shifted to O by 0.31 from equ. plane V=O 1.57, V—F 1.79 (equ.), 2.33 (ax.) [23]
$M_2[VOF_5]$; **$Cs_3(VO)_2F_9$**
$[PyH][VOCl_4]$; **$M_2[VOCl_5]$**, grn. [32]

$[VO_3]^+X^-$, peroxo vanadyl salts, cr., red-brn.

KCl + ICl

	ΔH
VF_4, cr., hyg., yel.-brn.	−1412
300° ⟶ $VF_3 + VF_5$↑, in str. oct. layers	
VCl_4, liq., red, v. hyg., m.p. ⩽ −20, b.p. 154, slow. dec. 20 (⟶ $VCl_3 + Cl_2$↑)	−694
VBr_4, cr., red (is formed on cooling the gas (550° ⟶ −78°), dec. −23 (⟶ $VBr_3 + Br_2$), mol. tetrah. [46]	−393

M_2VF_6, anion — oct. [16]
M_2VCl_6, M = K (brn.), Rb (pink) Cs (vlt.)
$M[VCl_5]$, M = [PCl_4], (previously "VCl_5", brn., m.p. 260 [17]), [SCl_3] (cr., blk., m.p. 32)

VF_5, cr., colrl., v. hyg., m.p. 19, b.p. 48, $\Delta H = 1473$, liq. ⇆ $VF_4^+ + VF_6^-$; in gas — mol., trig. bipyr., + H_2O ⟶ V_2O_5↓ + HF (violently); **$[VF_4]^+[SbF_6]^-$** [38]

$M[VF_6]$, M = NH_4, K (dec. 300), Ag, [NO], [NO_2], [Xe_2F_{11}], colrl. H_2O ⟶ **Ag[$VF_4(OH)_2$]**-*trans* [33]

Cl_2(200°) — V — F_2; BrF_3

Cl_2(130°) — VN — **$Cl_3V = NCl$**, m.p. 132, subl., in gas, monomers [14] in str. — dimers with 2 Cl-br.
$Cl_3V = NHal$, Hal = Br, I, mol. — trig. pyr.

MVF$_4$ — XeF_2 — VCl$_3$ — MCl + BrF_3

$M_2[V(CN)_7]$, CN V = 7

(VO)$^{2+}$ — $OH^- + S^{2-}$

Thiovanadates (IV), sol. in H_2O, $+H^+$ ⟶ VS↓ + S + ...
$BaVS_3$, in str. — linear chains of [VS_4] tetrah., V—V 2.81, conduct.

$VCl(NH_2)_3$, brn.-grn.; **$VCl_4(NO)$**
$V_2Cl_7(NO)$, **$V_2Cl_8(NO)_5$**, cr., subl.
$VO(NH_2)_2$, blk., $\xrightarrow{t}$ **VO(NH)** $\xrightarrow{t}$ **$(VO)_3N_2$** ⟶ **VON**

V_2S_5↓, powd., brn., sol. in alk., M_2S, dil. HNO_3, is readily Ox in air, $\xrightarrow{t}$ $V(S_2)_2 + V_2S_3$ + ...

M_2S / 60° (N_2)

$M[VO_2S] \cdot H_2O$; **$Na[VOS_2] \cdot 2 H_2O$**
$(NH_4)_3[VS_4]$, vlt., (s. — red), anion — tetrah.

$(NH_4)_2S$ — NH_4VO_3

● V
● O

NIOBIUM, TANTALUM, PROTACTINIUM

3+ (d^2) 4+ (d^2)

EN

Nb^0 4d 5s 5p 5d 1.2

Ta^0 5d 6s 6p 6d 1.3

Pa^0 6d 5f 7s 1.1

or $5f^2 6d^1 7s^2$

K_2NbOF_5 + Nb_2O_5; K_2TaF_7 + Ta_2O_5

Na; cath. Red

M_2O_5

$-O_2$ (2000°); MC; SiO; Ca

MCl_5

t; H_2

Nb	Ta	Pa
met. grey, hard, ductile and tensile, paramagn.		met. lustrous, ductile, tarnish in air
d 8.6	16.6	15.4
m.p. 2468	3010	≈1570
b.p. 4927	5425	4500
sol. in (HF + HNO_3) and alk. melt		sol. in ac., $E_0 Pa^{5+}/Pa_{sld}$ = −1.0, str.-tetr. body-centered (different from other M)
insol. in ac.-Ox and aq. reg., cub. (α-Fe type)		
a = 3.29	3.29	*a* = 3.92, *c* = 3.24, Pa—Pa 3.12 (8 at.) and 3.24 (2 at.) ("cub. Pa" – oxonitride) [2]
M—M 2.92	2.92	

O_2 (20°)

NbO$_n$, *n* = 0.94–1.04, grey, with met. lustre and conduct., m.p. 1945, ΔH = −406, NaCl str. type, [Nb_6] oct., Nb—Nb 2.80 and 3.20; **NbON** [28]

PaO, film at the met. surface, NaCl str. type, Pa—O 2.48

Nb; H_2 (*t*)

O_2 (*t*)

NbO$_2$, cr. bl.-blk., m.p. 2080, ΔH = −808, Ox in air, diamagn., semiconduct., sol. in conc. alk. (*t*), dist. rutile str., cluster

(500°)

(1550°)

PaO$_{2\pm n}$, cr. bl., sol. only in HF, CaF_2 str. type, ΔH = −1029, ↓ *t*, cr., red, tetr.

2.5+ [32] **Nb_4O_5**, [NbO_4] squares

Ta(OH)$_3$↓, grn.; + H_2O ⟶ H_2↑

$NaNb_{16}O_{18}$ [32]
$Ba_3Nb_{16}O_{23}$

MNbO$_2$, M = Li, Na, cr. bl.-blk., [18]

M_2O + NbO

TaO$_2$ (?), cr., blk.-brn.

3.5+ **$NaNb_{10}O_{18}$**, [Nb_6O_{12}] clusters and [$Nb^{V}O_6$] oct. [18]

NbOCl$_2$, **NbOI$_2$**, cr. blk., dec. 500, chains of oct., diamagn.

Nb_2O_5 + $NbCl_5$

Nb

3.3+ **$NaNb_3O_5F$** [29]

MC, cr. grey, with met. lustre, subl. >3000, m.p. 3500 (Nb), 3900 (Ta), NaCl str. type, Ox >800°

−H_2

H_2

NbH$_{1-x}$, *x* = 0–0.3; **TaH$_{0.9}$**, sld. s. inculcat., dec. >600°, sphalerite str. type, met.-like substs., insol. in aq. regia. Sld. s. of the limit comp. **PaH_3**, cr. blk., cube.

3.7+ **$K_4[H_5O_2][Nb_3O_2(SO_4)_6(H_2O)_3] \cdot 5H_2O$**, [$Nb_3$] cluster – triangle

HCl (800°)

HF + H_2

	subl.
NbF$_4$, cr. blk., + H_2O ⟶ NbO_2F; ⟶ NbF_5 + Nb_2F_5; dist. str. perovskite, **NbCl$_4$**, needles, blk.-vlt., ΔH = −694; >300° ⟶ $NbCl_3$ + $NbCl_5$; + H_2O ⟶ bl. s. **NbBr$_4$**, cr. brn. **NbI$_4$**, cr. grey	—
In $NbHal_4$ str. chains of dist. oct., diamagn. [27]	275
	502
	264

$M^{II}NbF_6$, μ_{eff} = 1.15
K_3NbF_7, m.p. 840, isostr. to K_3NbOF_6, anion pentag. bipyr. [16]
M_2NbCl_6, [6,22]
$M_4[Nb(CN)_8]$

Nb

MHal$_5$

Py (−$PyHal_2$)

[MHal$_4$Py$_2$], Hal = Cl–I, cr. grn. or red (2 forms), paramagn.

PaO$_2$

HF+H_2; M_2PaF_6

CCl_4(500°)

PaF$_4$↓, cr. brn., m.p. 1030, b.p. 1630, insol. in (HNO_3 + HF), ΔH = −1996
$PaCl_4$, cr. yel.-grn., subl. >400, m.p. 680, b.p. 850, UCl_4 str. type, ΔH = −1045 [22]
$PaBr_4$, ΔH = −863

TaOCl$_2$, TaOBr$_2$ TaOI$_2$, blk. cr., graphite-like [30]

M_2TaCl_6, vlt.

PaOHal$_2$, [31] Hal = Cl–I

TaCl$_4$, cr. blk.-grn., hyg., subl. 300, [4]
300°/210° $TaCl_3$ + $TaCl_5$; ΔH = −707; + $NbCl_5$
320° ⟶ $TaCl_5$ + $NbCl_4$
TaBr$_4$, ΔH = −52.5
TaI$_4$, cr. blk., m.p. 398, isostr. NbI_4
$TaCl_2I_2$, chains of [$TaI_{4/2}Cl_2$] oct.

Na$_3$[Ta(CO)$_5$]
M[Ta(CO)$_5$(NH$_3$)]
M^I[M(CO)$_6$]
TaH(CO)$_2$
[(R_2P—CH_2–)$_2$]$_2$, [12]
CN Ta 7
(single-cap oct.)

Nb$_{21}$S$_8$; NbS$_{1-x}$; Ta$_6$S; Ta$_2$S; Nb$_3$S$_4$, phase with met. conduct.
M$_{1+x}$S$_3$; MS$_2$; M$_2$Se$_3$; MSe$_2$; MTe$_2$ [3], powd., blk., insol. in ac. and alk.; $CdCl_2$ or CdI_2 str. types
$BaTaS_3$, semiconduct., Ta—Ta 2.87
NbN, m.p. 2300; **Nb_2N**, m.p. 2420; **Nb_3N_4; Nb_3N_5; Nb_5N_6; Nb_4N_5; TaN**, m.p. 3090; **Ta_2N; Ta_3N_5; PaN_2**, met.-like phases, v. hard, hot. resist., + O_2 (*t*) ⟶ M_2O_5 [3]
MP, MP_2, dark grey, sol. in conc. H_2SO_4, HNO_3

Ferroniobium, 23–75% Nb and Ta; 10–11.5% Si; 7% Ti; 7% Al; 0.15% P; <0.5% S; 0.12% C; rest Fe; in the systems M – Fe ex. sld. s. subtraction, **Nb_2Fe_3** (m.p. 1660) and **$TaFe_3$**

Fe

PaCl$_5$ PaI$_5$

(*t*, vac.)

Ba (1500°)

PaF_4

2.7+ **$[Ta_6Cl_{12}(OH)_4(H_2O)_9] \cdot 10H_2O$**

NbBr$_2$ NbI$_2$, blk.

2.33+ **M_6Hal_{14}** = $=[M_6Hal_{10}Hal_{2/2}]Hal_3$, M = Nb, Ta, Hal = Cl–I, cr. dark brn., stab. in air; ⟶ M + $MHal_4$, **$[M_6Hal_{12}]X_2 \cdot 8H_2O$**, X = Hal (cr., grn.), OH (blk.), stab. in air, diamagn. [4]

2.5+ **Nb_2F_5** = $=[Nb_6F_{12}]F_3$, ReO_3 str. type **Ta_2Hal_5**↓, Hal = Cl, Br, cr., blk.

2.67+ **Nb_3Cl_8**, blk-grn. **Nb_3Br_8**, blk., hydr., subl. 400 **$NbHal_{3.13}$**; **Nb_3I_8** **$TaBr_{2.83}$** [4]

NbF$_3$↓, [5] bl.-blk., **$NbF_{3.13}$** **$Nb_2Cl_6 \cdot nL$**, L = Me_2S, PR_3 **NbI$_3$**, blk.

TaF$_3$↓, **$TaCl_{3\pm x}$**, grn., strong. Red ↓ >440° $TaCl_5$ + Ta_6Cl_{14} **$TaBr_{3\pm x}$**, grey-grn. [4] **TaI$_3$**

t (−NbI_5)

Nb; Pb; Cd (*t*)

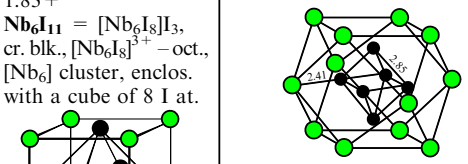
Ta

Al; H_2

MHal$_5$

M$_2$TaCl$_5$, M = K–Cs, red

1.83+ **Nb_6I_{11}** = $[Nb_6I_8]I_3$, cr. blk., $[Nb_6I_8]^{3+}$ – oct., [Nb_6] cluster, enclos. with a cube of 8 I at.



$[Nb_6Cl_{12}]^{n+}$, oct. [Nb_6] – cluster is surrounded by cubooct. of 12 Cl at., M—M 2.85 (Nb), 2.88 (Ta), M—Cl 2.41 (Nb), 2.44 (Ta)

(2.33–2.67)+ **$K_n[(Nb_6Hal_{12})Hal_6]$**, *n* = 2, 3, 4, Nb—Nb 2.97–3.02
M[(Ta_6Cl_{12})(H_2O)$_6$]Hal$_4$ [4]
(Me_4N)$_2$[Ta_6Cl_{12}(OH)$_6$] · 21 H_2O [5]

Nb(C_5H_5)$_2$, ex. in s. [1]

● Nb
● Hal

Formation of Pa in the nuclear decay

$^{235}_{92}U \xrightarrow{\alpha} {}^{231}_{90}Th \xrightarrow{\beta^-} {}^{231}_{91}Pa \xrightarrow{\alpha} {}^{227}_{89}Ac \longrightarrow \cdots$

3.28·10^4 y.

$^{238}_{92}U \xrightarrow{\alpha} {}^{234}_{90}Th \xrightarrow{\beta^-,\gamma} {}^{234}_{91}Pa^{*} \xrightarrow{\beta^-,\gamma} {}^{234}_{92}U \longrightarrow \cdots$

1.18 m., 6.75 h.

Synthesis of Pa

$^{230}_{90}Th(n,\gamma)^{231}_{90}Th \xrightarrow{\beta^-} {}^{231}_{91}Pa \longrightarrow \ldots$

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_17, © Springer-Verlag Berlin Heidelberg 2011

5 + (d^0)

M → O_2 → Nb_2O_{5-n} $n \le 0.54$ [26] | Ta_2O_5 [7] | Pa_2O_5

cr. colrl., diamagn., sol. in conc. HF

not Red with M | not Red with H_2

$\Delta H = -1903$ | -2055 | -2092

α-, rh., Ta CN 7 (pentag. bipyr.)

↓ 830° | ↓ 1320° | t ↓

β-monocl., m.p. 1490, oct. and tetrah., Nb—O 1.98 and 1.83 | β-monocl., m.p. 1872, oct. and pentag. bipyr. layers, Ta—O 1.71–2.38 | cube, 1800

H_2

M_2CO_3

$-H_2O$ | 500°

H_2SO_4 (t, p) | 100°

$Nb_2O_5 \cdot n H_2O\downarrow$ wh., gelatinous, sol. in conc. HF and alk. $K_{ac\,1} = 10^{-8}$ and $K_{bas\,1} = 10^{-15}$

HNb_3O_8, isostr. to Nb_3O_7F

$HNbO_3 = [H_3O]Nb_3O_8$

$Ta_2O_5 \cdot n H_2O\downarrow$ HF and alk. 10^{-10} and 10^{-13}

HTa_3O_8

$HTaO_3$ [9]

$Pa(OH)_5\downarrow$, not reacts. with alk., M_2CO_3

MOH (20°)

+ HNO₃ (ion exchange)

Niobates, tantalates (V) [13]

$[R_4N]_8H_4Nb_{12}O_{36} \cdot 28 H_2O$

$Na_{14}Nb_{12}O_{37}$, sol. in H_2O (pH≈5!)

$[R_4N]_6[Nb_{10}O_{28}] \cdot n H_2O$, isostr. to $[V_{10}O_{28}]^{6-}$

$Rb_4Ta_{10}O_{27}$; $K_3Nb_7O_{19}$

$M_8[M_6O_{19}] \cdot n H_2O$, M = K ($n$ = 12–16), Li↓, Na↓, v. strongly hydr., not oligomerised.

$Rb_4M_6O_{17}$; $K_7[M_5O_{16}] \cdot n H_2O$, n = 10–32; $Cs_3Ta_5O_{14}$; KTa_5O_{13}

$CaTa_4O_{11}$; KM_3O_8; $NaNb_3O_8 \cdot H_2O$; $Ca_2Ta_2O_7$

$Sn(Nb,Ta)_2O_7$, "thoreaulite", $(Y,U)(Nb,Ti)_2O_6$, "euxenite"

KMO_3 (*meta*-), perovskite type str., ferroelectrics

$(Fe^{II},Mn^{II})[MO_3]_2$, "columbite" (M = Nb), "tantalite" (M = Ta)

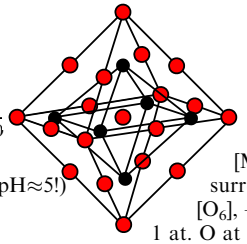
$(Na,Ce,Ca,Sr)[(Nb,Ti)O_3]$, "loparite" [Ta : Nb = 1 : (12–20)]

$CaNa(MO_3)_2F$, M = Nb ("pyrochlore"), Ta ("microlite")

K_3MO_4 (*ortho*-)

$M^{III}TaO_4$, M^{III} = Y ("formanite"), Sb ("stibiotantalite"), Bi ("bismutotantalite"), Al ("simpsonite"); K_5MO_5; Li_7NbO_6

Niobate and tantalate struct. – condenced tetrag. pyram., oct., dodecah. or pentag. bipyr. [14]



$[M_6O_{19}]^{8-}$ [M_6] oct. is surrounded by [O_6], – oct. with 1 at. O at centre and 12 at. at the middles of edges

H_2O_2 (–O_2; t)

$H[MO_4] \cdot n H_2O$, cr., yel. (Nb) colrl. (Ta), dec. > 100; + H_2SO_4 (t) ⟶ $M_2O_5 \cdot n H_2O\downarrow$

H_2SO_4 (dil.)

$K_3[M^V(O_2)_4] \cdot n H_2O$, dist. dodecah. (at. Nb displaced from equ. plane) CN 7 (pentag. bipyr.)

$(NH_4)_3[M(O_2)_2F_4]$, anion – oct. [11]

$MPa(NO_3)_6$, M = M^I, H, colrl., unstab.

$H[PaO_2(SO_4)]$

$H[PaO(SO_4)_2]$

↑ 400°

$H_3[PaO(SO_4)_3]$

$H_3[PaO(SeO_4)_3]$

$PaO(NO_3)_3 \cdot n H_2O$, n = 1–4

$PaOCl_3$, cr., colrl.

$PaOBr_3$, Pa CN 7 (pentag. bipyr.), Pa—Br 2.91 (equ.), 2.6 (ax.), Pa—O 2.14–2.27 [21]

$Pa_2OF_8 = (F_4Pa)_2O$, colrl., isostr. U_2F_9, Pa CN 9

$K_2Ta_4O_9F_4$ [23]

$K_3Ta_4O_8F_7$

$KTaO_2F_2$

$M_2Ta_2O_3F_6$

$(\approx 2\,K_2TaF_7 \cdot Ta_2O_5)$, Marignac salt

M_2TaOF_5; $BaTaOF_9$

$K_3[TaOF_6]$, anion – single-cap oct. (d^5sp)

HF (45%)

HF | H_2O

$MTaF_6$, M = K, $[O_2]$, $[XeF_5]$, $[Xe_2F_{11}]$, $H(\cdot n H_2O)$ [9]

$M_2[TaF_7]\downarrow$, M = H, K–Cs

$K_3[TaF_8]$, m.p. 780, anion – antiprism

$MTaCl_6$, M = Na–Cs, anion – oct.

$TaO(ClO_4)_3$; $TaO(NO_3)_3$; $TaO(PO_4)$

$CsTaO(ClO_4)_4$

$Ta(ClO_4)_5$; $Ta_2(SO_4)_5$; $Ta(SO_3F)_5$; $Ta(TeOF_5)_5$; $Ta_3(PO_4)_5\downarrow$ [20]

$Cs_2Ta(ClO_4)_7$; $CsTa(ClO_4)_6$; $CsTa(PO_4)_2$; $KTa(PO_3)_2(P_2O_7)$

Ta_3O_7Hal, Hal = F, Cl [20, 30]

TaO_2X, X = F–I, ClO_4

$TaOF_3$, $\Delta H = -1297$

$TaOCl_3$, amorph., wh., v. hyg., $\Delta H = -891$, 327° ⟶ Ta_2O_5 + $TaCl_5$

$TaOBr_3$, cr., yel., $\Delta H = -853$

$TaOI_3$, $\Delta H = -723$

Ta_2O_5 — $C + Cl_2$; $SOCl_2$; $AlCl_3$

	m.p.	b.p.	ΔH
TaF_5, colrl.	97	230	–1903
$TaCl_4F$	214	—	—
$TaCl_5$, colrl.	217	239	–858
$TaBr_5$, yel.	266	349	–598
TaI_5, blk.	496	543 subl.	–489

Nb_2O_5 — N_2O_5; $HClO_4$; Cl_2O_7

$Nb_2O(SO_4)_4$

$NbO(NO_3)_3$

$NbO(PO_4) = NbPO_5$, str. units of 2 [NbO_6] oct. and [PO_4] tetrah. [25]

$Nb(ClO_4)_5$; $Nb_3(PO_4)_5$

Nb_2O_5 — $SOCl_2$; CBr_4; $Nb + I_2$

$NbOF_3$

$NbOCl_3$, cr. colrl., subl. 335; 350° ⟶ $NbCl_5 + Nb_2O_5$; chains of coupled $[NbCl_2Cl_{2/2}O_{2/2}]$ oct. with common edge

$NbOBr_3$, yel., subl., isostr. to $NbOCl_3$,

$NbOI_3$, ruby-red, 150° ⟶ $NbOI_2 + I_2$

$CaNaNb_2O_6F$, "pyrochlore"

$K_5(NbO_3)_4F$; $NaNbO_2F_2$

$M_3[NbOF_6]$

$M_2[NbOF_5] \cdot n H_2O$, M = K (sol. in H_2O is 11 times > than that of $K_2Ta_2O_3F_6$) method of separation Nb – Ta according to Marignac, anion dist. oct. [24]

$M[NbOF_4]$, chains of *trans*-$[NbO_{2/2}F_4]$ oct., Nb at. displaced from equ. plane at 0.23

$M_2[NbOCl_5]$; $M[NbOCl_4]$, anion tetr. pyram.

$Rb[NbO(SO_4)_2]$, layers of $[O=Nb(SO_4)_5]$ oct., Nb=O 1.73, Nb—O 1.96–2.26

$M[Nb_2(OH)_2(PO_4)_3] \cdot n H_2O$

$M_3[NbO(C_2O_4)_3]$;

$Cs[NbO(P_2O_7)]$ [17]

$Cs[Nb(ClO_4)_6]$

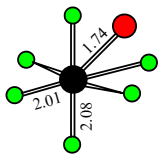
$NbO_2(ClO_4)$ $NbO(ClO_4)_3$

$Nb_2O_4(SO_4)$; $Nb_2O_3(SO_4)_2$ [4]

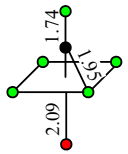
$Nb_5O_{11}Cl_3$

Nb_3O_7Cl, cr., bl.

NbO_2Hal, Hal = F–I (Cl – yel., I – red)



$[NbOF_6]^{3-}$



$[NbOF_5]^{2-}$

$Nb_{12}O_{29}$ $Nb_{22}O_{54}$ $Nb_{25}O_{62}$, stab. phases

(4–5) + M_xNbO_3, bronzes, M = Na–Ba

Ba_xTaO_3

	m.p.	b.p.	ΔH
NbF_5, cr. colrl.,	80	23	–1812
$NbCl_4F$, yel.	—	—	
$NbCl_5$, colrl. cr.,	205	254	–797
183° ⟶ yel.			
$NbBr_5$, red	268	362	–556
NbI_5, bronze	320 dec.	—	–426

M; H_2

$MNbF_6$, M = H, K–Cs, $[BrF_2]$, $[O_2]$ $[SeF_3]^+[Nb_2F_{11}]^-$, anion 2 oct. with common vertex, Nb—F 1.8–2.0

$M_2NbF_7\downarrow$, anion single-cap trig. prism (d^5sp), Nb—F 1.8

K_3NbF_8; $MNbCl_6$ [4]

$K[M(OR)_6]$ [33, 34]

$[NbF_4]^+[SbF_6]^-$, cr. subl. 40, zigzag chains of $[NbF_{2/2}F_4]$ oct. and separate $[SbF_6]$ oct. [8]

$MHal_5$, cr., volat., hyg., sol. in Et_2O, $POCl_3$, liq. NH_3; + H_2O ⟶ $M_2O_5 \cdot x H_2O$ [19]

MF_5 – str. anal. of $(MoF_5)_4$; str. of other $MHal_5$ – dimers (2 oct. with common edge), in g. – $(MF_5)_3$ – planar cycle of oct., $MHal_5$ – trig. bipyr. (d^3sp)

$MHal_5 \cdot L$, L = NH_3, Et_2O, $POCl_3$, NOCl, NO

	m.p.	subl. t	ΔH [15]
PaF_5, colrl. $\cdot 2H_2O\downarrow$,	—	500	–2190
$PaCl_5$, yel.-grn.	301	160	–1143
$PaBr_5$, orange	317	—	–863
PaI_5, blk.	300	—	

$PaCl_5$ – chains of pentag. bipyr.

$KPaF_6$, Pa CN 8 [10]

$K_2PaF_7\downarrow$, insol. in 5% HF, in str. chains of $[PaF_9]$ gr.

M_3PaF_8, anion cube

$M_4[PaF_9]$, Pa CN 9

$MPaCl_6$, yel.

M_3PaCl_8,

M = [NO], $[R_4N]$

$NbO(NCS)_3$

$NbO(NH_2)_3$

$[M(NCS)_5]_2$, red-brn.

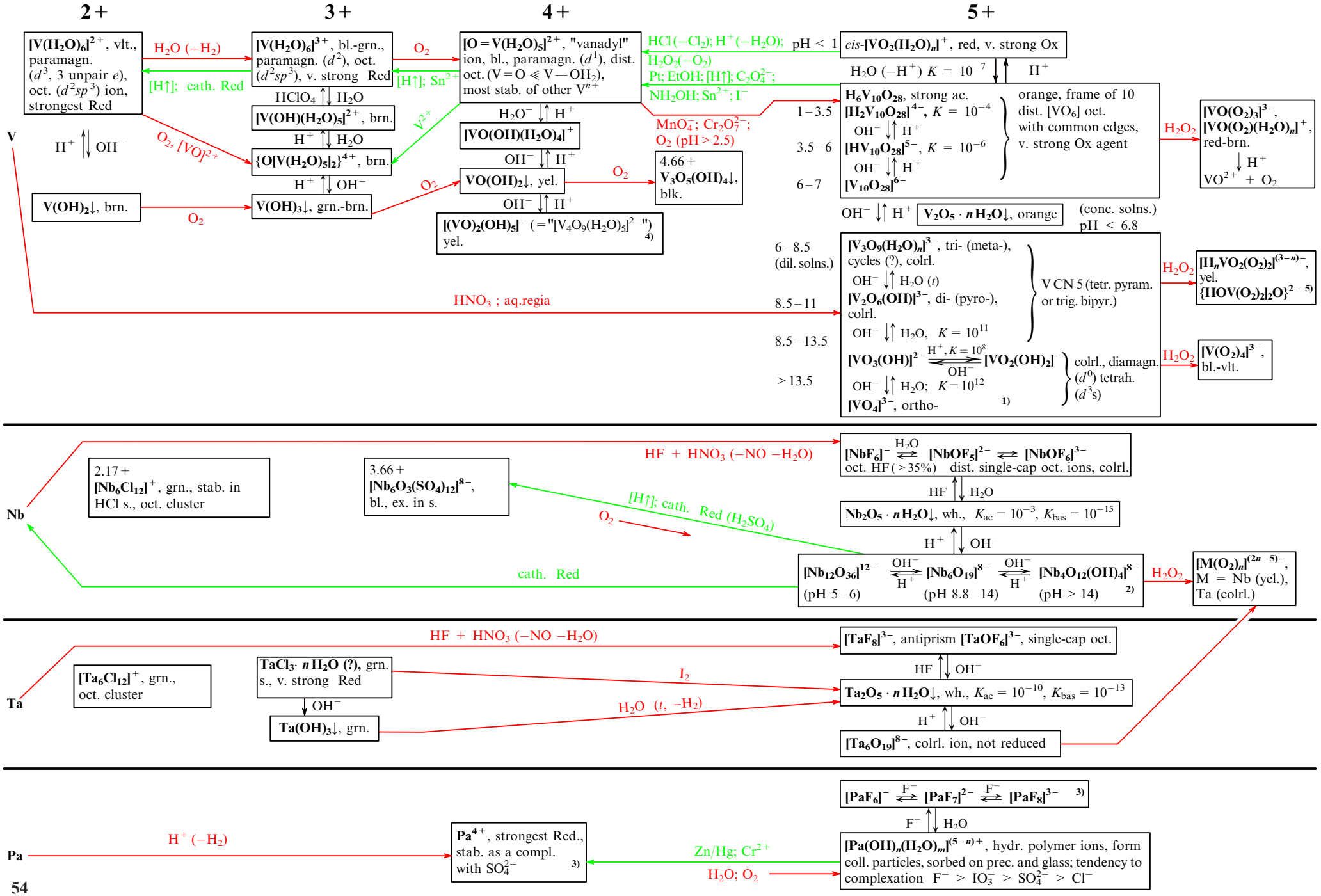
$K[M(NCS)_6]$, dark-bl. (Nb), orange (Ta)

M

O

Hal

VANADIUM, NIOBIUM, TANTALUM AND PROTACTINIUM IONS IN AQUEOUS SOLUTIONS



CARBON HALIDES

1+

Acetylenedihalides Hal—C≡C—Hal	m. p.	b. p.
C_2F_2, gas	—	−76
C_2Cl_2, liq., exp.	−64	32
C_2Br_2, liq., $+O_2 \rightarrow$ exp.	−23	76
C_2I_2, cr., colrl.	82 (dec.)	—

Na_2C_2, Hal_2

Phenylhexahalides	m. p.	b. p.
C_6F_6,liq.. colrl.	−11	82
C_6Cl_6, cr., colrl.	231	322
C_6Br_6, cr., colrl.	316	subl.
C_6I_6, cr., red-brn.	350 (dec.)	—

KF; NO (−NOX); $[O_2]$ $[EF_6]$ (WF_6, $-O_2$)

$[C_6F_6]^+X^-$, X = SbF_6, Sb_2F_{11}, AsF_6 (cr., orange, m.p. 61, dec., sol. in liq. HF, μ_{eff} = 1.3) [4]

2/n+

Ethylenetetrahalides

Hal, Hal; C=C; Hal, Hal

	m.p.	b.p.
C_2F_4, gas, colrl., insol. in H_2O, org. solv.	−142	−76
600° ↓		
$(C_2F_4)_n$, "teflon", dec. 450, does not react. with Na, org. solv.	—	—
C_2Cl_4, liq., colrl.	−22	121
C_2I_4, cr., yel.	187	subl.

Zn; Cl_2 (p, t); Hal_2

Ethanehexahalides $Hal_3C—CHal_3$	m.p.	b.p.
C_2F_6, gas, colrl.	−101	−78
C_2Cl_6, cr., colrl.	189(p)	186
C_2Br_6, cr., colrl.	148	210

C_nH_m; HHal (−H_2)

4+

CO_2; Cl_2 (act. C)

Carbonylhalides	m.p.	b.p.	μ	C—Hal
COF_2, gas, colrl.	−114	−83	0.95	1.32
$COCl_2$, "phosgene", gas, colrl., toxic	−128	+ 8	1.17	1.74
$COBr_2$, liq., colrl.,	—	65 (dec)	—	1.92

Hyg.; $+ H_2O \longrightarrow H_2CO_3 + HHal$ (speed F ⋙ Cl > Br), mol. – triangles (sp^2).
$+ M_2O_n \longrightarrow MO_xBr_{n-2x}$, (M = V, Mo, U, Re) [30]

SiC; F_2; F_2; BrF_5; C amorph.

	m.p.	b.p.	ΔH	C—Hal
CF_4, gas, colrl.	−184	−128	−223	1.32
CF_2Cl_2, gas, colrl., "freon-12"	−155	− 30	—	1.34 / 1.74
CCl_4, liq., toxic	− 23	77	− 32	1.77
CBr_4, cr., yel.	94	189	+ 20	1.94
CI_4, cr., red.	171	90	+ 73 (subl.)	2.12

$CF_{4-n}Cl_n$, "freons", solv. O_3, fats, pitch; not hydr., passiv., not burn., mol. – tetrah. (sp^3), stab. CF_4 ⋙ CCl_4 > CBr_4 > CI_4

X_2; $Hg(CF_3)_2$

Compounds of CF_3 [13]

$[CF_3]X$, X = I (b. p. −22)*, ClO (+47), FO (−95), SF_5 (−20), NO_2 (−31), NO (−87, bl.), NF_2 (−77), PI_2, PH_2; O/2 (−61), S/2 (−22), O_2/2 (−37), N/3 (−70), gas, colrl., passiv. (except $FOCH_3$). In mol. – v. stab. gr. CF_3, strongest acceptor el.,

$CF_3I + KOH \xrightarrow{(alc.)} KOI + CHF_3$

$H_2E^{III}O_2CF_3$, $H_2E^{V}O_3CF_3$, E = P, As, v. strong ac.

HSO_3CF_3, $F_3C—OS(=O)OH$, the most strong ac.

CF_3COOH, liq., colrl., m. p. −15, b. p. 72, K = 1, ε = 8.5
CF_3COOM, toxic

*) Indicated in parentheses b.p.

$[Ph_4P]^+[CBr_5]^-$, in str. – chains of tetrah. $[CBr_4]$ and Br^-, C—Br ≈ 1.96, Br—Br 3.19 [23]

CF_3OOX, X = H, Cl, $-CF_2OOCF_3$;
$(CF_3)_2C(OH)(OOH)$ [16]

CARBON IONS IN AQUEOUS SOLUTIONS

2+ **3+** **4+**

Pd^{2+} (−Pd); Ag^+; MnO_4^- (Ag^+); $Cr_2O_7^{2-}$ (Hg^{2+}); ClO_3^- (Os^{VIII})

CO↑, poorly sol. in H_2O

$-H_2O$ | H_2O (p, t)

HCOOH, strong Red., $K = 10^{-4}$

H^+ | OH^-

$[HCOO]^-$, weak. Red., ion – triangle

$HgCl_2$($-Hg_2Cl_2$↓); Ag^+

$[—COOH]_2$, $K_1 = 10^{-1}$, $K_2 = 10^{-5}$, Red.

MnO_4^-

H^+ | OH^-

$[-COO]_2^{2-}$, ion – 2 triangles

CO_2↑
↑↓ H_2O (slow., pH < 8)
H_2CO_3, $K_1 = 10^{-7}$
↑↓ CO_3^{2-} + H_2O
$[HCO_3]^-$, $K_2 = 10^{-11}$; pH ≈ 8
H^+↑↓ OH^- (immed.)
$[CO_3]^{2-}$, triangle, pH > 8

OH^- (slow)

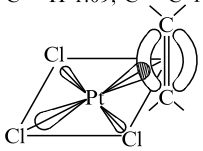
CARBON

C^0 2s ↓↑ 2p ↓ ↓ ☐ EN 2.5

$(2+2/n)-$ $2-$ $1-$

Hydrocarbons (homologous series)

C_nH_{2n+2} alkanes	C_nH_{2n} alkenes	C_nH_{2n-2} alkynes	C_nH_{2n-6} aromatic comp.
CH_4, methane, gas, colrl., m.p. −184, b.p. −161, $\Delta H = -75$ **C_2H_6**, ethane, gas, colrl., m.p. −183, b.p. −89, $\Delta H = 84.8$, inert, mol. — tetrah. and 2 tetrah. with a common vertex (sp^3), C—H 1.09, C—C 1.54	**$CH_2=CH_2$**, ethylene, gas, m.p. −169, b.p. −104, $\Delta H = +55$, ∠HCC = ∠HCH = 120 (sp^2), C—H 1.09, C—C 1.43	**$CH\equiv CH$**, acetylene gas m.p. −81.8 (*p*), subl. −83.6, $\Delta H = +227$, sol. and liq. exp. ∠HCC = 180 (*sp*), C—H 1.06, C—C 1.32	**C_6H_6**, benzene, m.p. 5.5, b.p. 80, $\Delta H = +49$, ∠CCC = ∠HCC = 120 (sp^2), C—H 1.08, C—C 1.35–1.43



$K[PtCl_3(C_2H_4)]$ — **π-compl.** Multiple bonds — donors of π-el. Dative bonds are formed by procrastination el. from invaded *d*-orbitals M of on the π*-orbitals of L; M=Ag, Hg (II), Co, Pt, Pd (II)

$Co_2(CO)_6(RC\equiv CR)$ **$[Pt(PR_3)_2(PhC\equiv)_2]$** **$Cr(C_6H_6)_2$**, **$AgClO_4 \cdot C_6H_6$**

H_2O H_2O H_2O

Carbides

	Derivates of methane, ethane	Derivates of ethylene and allene	Derivates of acetylene
Salt-like (stoichiometric)	**Al_4C_3**, m.p. >2800, insolated anions $[C]^{4-}$; + $H_2O \xrightarrow{t} CH_4\uparrow$ **Pu_2C_3**, gr. $[C_2]$, C—C 1.54 (C_2H_6!)	**ThC_2**, m.p. 2655, yel. **UC_2**, m.p. 2350, + $H_2O \rightarrow C_2H_4 + H_2 +$ + CH_4 + C_nH_m, in dist. CaC_2 str. — ions $[C\equiv C]^{4-}$, C—C 1.34	**M_2C_2**, M = Li – K, NaCl str. type **CaC_2**, m.p. 2300 } str. anal. **BaC_2** » >1780 } CaC_2, in str. — ions $[C\equiv C]^{2-}$ **$Al_2[C_2]_3$**, C—C 1.24, + $H_2O \longrightarrow C_2H_2$ + ... (exp.) v. act., inflam. in atm. CO_2
Cova-lent	**SiC**, "carborundum", colrl., dec. > 2200, ZnS str. type **$B_4C = B_{12}[C_3]$**, cr. blk., m.p. 2450, b.p. > 3500, in NaCl str. type — icosah. $[B_{12}]$ and linear gr. $[C_3]$, v. hard, inert, hot resistant., ac.-proof		
Metal-like (nonstoichiometric)	m.p. **Cr_3C_2** (dec.) 1900 **Cr_7C_3** 1680 **$Cr_{23}C_6$** (≈"Cr_4C") 1520 **CrC** — v. hard, inert, ac. proof, stab. to Ox < 1000°	m.p. **Fe_3C**, "cementite" 1650 **Mn_3C** 1520 cr. grey or blk., **$(Fe, Cr)_3C$**, **$(Fe, Mo)_3C$** v. hard, give hardness of steels; + $H^+ \rightarrow$ H_2 + CH_4 + C_nH_m	m.p. **HfC** 3890 } NaCl **VC** 2830 } str. type **NbC** 3500 **Hf_2C** — } hex. **V_2C** — } cl. pack. **Nb_2C** — Comp. whith met. bond, conduct., v. hard (9–10), brittle and hot resist., sol. only in (HF + HNO_3) (*t*) and melt. (alk. + O_2)

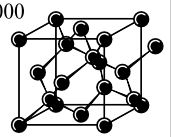
Trig. prism. $[CM_6]$ form chains C_∞ in dist. str. M, C—C ≈ 1.65

O_2 (defic.)

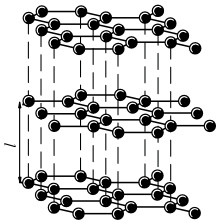
M; M_2O_n

1200–1800°, 6.7 GPa (Ni, graphite) [1]

Diamond, cr., oct. or cube, colrl., m.p. >4000 ($125 \cdot 10^2$ Pa), $d = 3.51$, hard 10, fragile, dielectric, chem. stab., in str. — cubes, $a = 3.56$, face-centred cube whith 4 at. in the centra of 4 from 8 small cubes, tetrah. (sp^3), C—C 1.54, CN 4



> 1200° ↕ *p*, *t* (Fe, Cr, Pt)

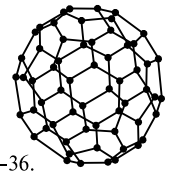


Graphite, cr., blk., $d = 2.22$, sld. 1–5, subl. 3700, two-laeyr hex. str., $a = 2.46$; $c = 6.69$; C—C 1.41, CN 3 ∠CCC 120 (sp^2). Interlayer C—C 3.34 (*l*), conduct. along the layer is associated with delocalization π-bonds. In the minerale ex. rhombo-hedral graphite a three-layer str.

Amorph C (soot, wood and animal coal), fein-cr. form of graphite with defects in str., $d = 1.8–2.1$, most act., adsorbent of liq. and gas.

arc (exstr. $C_6H_5CH_3$)

Fullerenes, C_n, $n = 60$ ("buckminster-fullerene"), 70, ...,dark powd, subl. vac. >400, sol. in bz., spherical mol. **C_{60}**, mol. "football", consis. of 12 five- and 20 six-membered cycles C—C 1.45 and 1.39, dec. >1000, semiconduct. **$C_{60}X_n$**, X = Hal, H, n = 1–36. **M_nC_{60}**, M = K (n = 3, superconduct. Rb (n = 3, 4, 6), Eu (n = 1 – 6)



[1]

> 3500°

Graphene, transparent monocryst. films, conduct. and semiconduct., graphite layer thickness of 1 at., C—C 1.42 (Nobel Prize, 2010) [3]

C_2H_2 Cu^{2+}, $+FeCl_3$

Carbyne, blk. powd., semiconduct., $d = 1.9–2.0$, in str. linear chains $(-C\equiv C-C\equiv)_\infty$; **polycumulen** $(=C=C=)_\infty$

Gas **C_2** at 3100°, C—C 1.31

M (liq., gas) $MHal_m$ (gas) $MCl_m + Cl_2$ an Ox + H_2SO_4 Br_2

Compounds of graphite (*l* — distance between of layers

"Graphitides" MC_n, $n \leqslant 60$ [1,14]	Inclusion comp. [2]	Salts of graphite [2]	
LiC_6, **BaC_6** [1,14] **$M_{1-x}C_8$**, M = K–Cs, cr., red, infl. in air, conduct. > graphite + $H_2O \longrightarrow H_2$ + MOH + graphite **In monolayer str.** *l* = 3.7 (Li), 5.4 (K), 5.6 (Rb), 5.9 (Cs), CN M 12 (hex. prism) **MC_{16}**, M = K–Cs; **K_6C_{60}**, dielectric **M^0C_n**, M = Mo, W, Mn–Ni, *l* = 5.6	**$C_n \cdot L$**, L = $AlHal_3$, SbF_5, AsF_5, $GaBr_3$, $FeCl_3$, $LnCl_3$, $CrCl_3$, FeS_2, MoO_3, XeF_6, **$C_{21}CrCl_3$**, *l* = 12.80 **$C_{22-29}CrCl_3$**, *l* = 16.57 **$C_{6.3}(Au_2Cl_6)$**, *l* = 6.80 **$C_{33}AlBr_3$**, *l* = 20.10 **$C_{8.5}IF_5$**; **$C_{38}UBr_5$**; **$C_{13}UF_6$** conduct. > graphite	**$C_n^+ Cl^- \cdot MC_m$**, M = Be, Al, Ga, Fe, Au, W, U; *l* = 9–13 [2] **$C_n^+X^-$**, X = NO_3, ClO_4, SO_3F, AsF_6, cr., bl., *l* ≈ 8 ↑ HX **$C_{24}^+[HSO_4] \cdot 2H_2SO_4$**, bl., *l* ≈ 8	**$C_8^+Br^-$**, *l* = 7.05, anions $[Br_2]^-$, Br—Br 2.1–2.2

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_18, © Springer-Verlag Berlin Heidelberg 2011

CO_2 (> 600°, "gasification of firing");
H_2O (1000°, $-H_2$, "water-gas")

C_3O_2, suboxide, gas, colrl., whith sharp odour, m.p. −107, b.p. 7, $\Delta H = -96$, ↓20° sld. red polymer, + C + CO_2; v. react., mol. linear O=C=C=C=O

H_2O / $-H_2O$

Malonic ac. $CH_2(COOH)_2$, cr. colrl., m.p 135 dec. $K_1 = 10^{-3}$, $K_2 = 10^{-6}$

CO, carbon monoxide, gas, colrl., toxic, m.p. −205, b.p. −191, $\Delta H = -110$, sol. in H_2O 3% (vol.) (0°), insol. in ac., alk., inert, strong Red (*t*); $+I_2O_5 \xrightarrow{140°} I_2 + CO_2$, C≡O 1.13, el. anal. N_2, $\mu = 0.12$

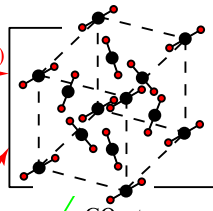
O_2 [700°; $MnO_2 + CuO$, 20°]; M_2O_n(*t*, −M); H_2O ($-H_2$, 500)

C (> 1000°)

M (*p*) / *t* (−M)

$M^0(:CO)_n$, M = V–Ni, Mo–Pd, W–Pt, carbonyls, cr. or liq., toxic, volat., insol. in H_2O, sol. in org. solv., $\Sigma e = 18$ [exept $V(CO)_6$] gr. [M—C—O (term.)] — linear (∠MCO 171–178); C—O (term.) 1.12–1.29

H_2O (*p*, *t*) / $-H_2O$



CO_2, carbon dioxide, gas, colrl., subl. −78, b.p. 20/58 · 10^5 Pa, $\Delta H = -393$, sol. in $H_2O \approx 50$ % (vol.), in face-centered cube — mol. CO_2 in 3 non-intersecting direction, C—O 1.16, ∠OCO 180 (*sp*)
Donor π-el., in **[Rh(CO)(PR$_3$)$_2$(OH)(CO$_2$)]**
CO_2 attached reversible [12]

H_2O

Carbonic ac. [5]

$CO_2 + H_2O \overset{slow.}{\rightleftharpoons} [H_2CO_3] \overset{immed.}{\rightleftharpoons} H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$

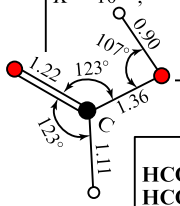
$K_1 = \frac{[H^+][HCO_3^-]}{[H_2O][CO_2]} = 10^{-7}$; $K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-4}$; $K_2 = 10^{-11}$;

pH ≈ 3.7 Mol. H_2CO_3 ex. in gas

"$H_2CO_3 \cdot R_2O$" = $[R_2OH]^+[HCO_3]^-$, cr., colrl.
R = Me (m.p. −47), Et (dec. −10)

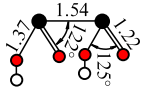
conc. H_2SO_4 (−H_2O) / H_2 (*t*)

HCOOH, formylic ac., liq., with strong odour, *d* = 1.23, m.p. 8, b.p. 100, readily sol. in H_2O, $\mu = 1.35$, $\varepsilon = 56$, mol. — planar, strong Red, azeatrope — 77 %, b.p. 107, $K = 10^{-4}$;



t (Al$_2$O$_3$) → $H_2O + CO_2$; *t* (ZnO) → $CO_2 + H_2$

(—COOH)$_2$, oxalic ac., cr., colrl., m.p. 189 (dec.), subl. 158, toxic, sol. in H_2O, alc. $K_1 = 10^{-1}$, $K_2 = 10^{-5}$, mol. — planar -*trans* ↑30° · **2 H_2O**, m.p. 10



H_2S (−ZnS)

Formiates [18]
HCOOLi · H_2O
HCOONa, m.p. 225; dec. 300
$(HCOO)_2Ca$↓; $(HCOO)_2Cu \cdot H_2O$↓
$(HCOO)_2Zn$; HCOOAg↓
→ $H_2O + M_2O_n + CO$

H_2SO_4

Oxalates
$LiHC_2O_4 \cdot H_2O$
$NaHC_2O_4 \cdot H_2O$
$Li_2C_2O_4$, $Na_2C_2O_4$
$K_2C_2O_4 \cdot H_2O$
BaC_2O_4↓, CaC_2O_4
$(NH_4)_2C_2O_4 \cdot H_2O$
$FeC_2O_4 \cdot 2H_2O$↓
$M_2[Fe(C_2O_4)_2] \cdot n H_2O$
anion — 2 crossing triangles

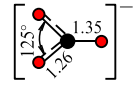
M(*t*)

$NH_3 + NaCl$ (−NH_4Cl) (Solvay process)

HCl (R_2O, −35°)

M_2O_2; H_2O_2 + MOH

Bicarbonates
LiHCO$_3$
NaHCO$_3$, (baking soda), dec. 160, (60° — in s.), poorly sol. in H_2O;
· $Na_2CO_3 \cdot 2H_2O$, "trona"
KHCO$_3$, dec. 100, readily sol. in H_2O
NH_4HCO_3, dec. 36, poorly sol. in H_2O
$Ca(HCO_3)_2$, ex. in natural waters, anion — dist. triangle



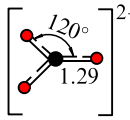
an. Ox; H_2O_2

MHCO$_4$
M_2CO_4, anion $[O_2COO]^{2-}$
M_2CO_5 [8]

$K_4[H_2(CO_3)_3] \cdot 1.5\ H_2O$ [8]

t (−H_2O −CO_2)

Carbonates
Sol. only in the case M^I (except Li)
Na_2CO_3, "soda ash.", m.p. 854
$n H_2O$, *n* = 1, 7, 10 ("soda cr.", "natron")
K_2CO_3, m.p. 901 ("potash"), **· $n H_2O_2$**
$\cdot n H_2O$, *n* = 2, 1.5
$(NH_4)_2CO_3$, dec. 58, v. readily sol. in H_2O
$M^{II}CO_3$↓, M^{II} = Mg ("magnesite"), Ca ("calcite", "aragonite"), Sr ("strontianite"), Ba ("witherite"), Fe ("siderite"), Mn ("rhodochrosite"), Pb ("cerussite"), $[UO_2]$ ("rutherfordine")
$CaMg(CO_3)_2$, "dolomite"
$Cu_2(CO_3)(OH)_2$, "malachite"
$[BiO]_2CO_3$, "bismuthite"
$M_2(CO_3)_n \xrightarrow{t} M_2O_n + CO_2$,
$[CO_3]^{2-}$ — correct triangle (sp^2)



an. Ox / H_2O

Peroxocarbonates [7]
$M_2C_2O_6$, cr., colrl., hyg., stab.
↓H_2O
$MHCO_3 + H_2O_2$; anion — $[O_2COOCO_2]^{2-}$ 2 triangles, $+ I^- \longrightarrow I_2$

CH$_3$COOH, acetic ac., oil (100 % — icy), colrl., m.p. 17, b.p. 118, $[CH_3COOH_2^+][CH_3COO^-] = 10^{-12}$, solv. SO_2, M Hal$_n$, M(NO$_3$)$_n$, $\varepsilon = 6$, in gas — dimers, in s. H_2O – weak ac., $K = 10^{-5}$, not Red; not react. with MnO_4^-, $Cr_2O_7^{2-}$, an. Ox ⟶ $CO_2 + C_2H_6$

H^+ / OH^-

Acetates

	m.p.	
$CH_3COOLi \cdot 2H_2O$	70	
CH_3COONa,	324,	**$\cdot 3H_2O$** (m.p. 58)
CH_3COOK,	292,	**$\cdot CH_3COOH$**
CH_3COONH_4,	114,	**$\cdot CH_3COOH$**
$M(CH_3COO)_n$	M = Zn–Hg, poorly diss.	

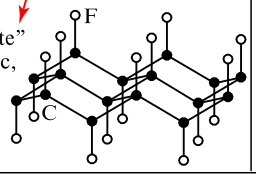
$M(CH_3COO)_n \xrightarrow{t} M_2O_n + CO_2 + H_2O$
$M^{II}_2(CH_3COO)_4 \cdot 2H_2O$, M^{II} = Cr, Mo, Rh, Cu, mol. — clusters
$M^{II}_4O^*(CH_3COO)_6$, M^{II} = Be, Zn, in mol. — tetrah. $[O^*M_4]$ and $[MO^*O_3]^-$
$[M^{III}_3O^*(CH_3COO)_6]^+X^-$, M^{III} = Cr, Fe, Al, Ru, Rh, in cat. $[O^*M_3]$ — triangle and $[MO^*O_5]$ — oct., CH_3COO^- bidentate

1+
MOC≡COM
M = Na–Cs, cr., colrl., hyg., pyrophoric, CaC_2 str. type [19]

$HNO_3 + H_2SO_4 + KClO_3$
$KMnO_4$

F_2 + HF / [H$^+$] / F_2 (*t*) / *t* (−CO_2)

	"Oxides and ac."
$C^+_4F^-$, cr., blk., dec. 100, in mono-layer str. *l* = 5.4 **CF_n**, $n \leqslant 1.12$, "fluorid of graphite" cr., colrl., dec. 800, inert, dielectric, in str. — **gauffer** layers, *l* = 5–8 thermostab. grease, resist. to Ox $+ F_2 \xrightarrow[\text{(inflame)}]{630} CF_4^\circ + C$ [3]	**C_nO**, $n \geqslant 2$, cr., colrl. or yel.-brn., dielectrics in str. — gauffer layers CN 4, *l* ≈ 7, later turgidity in liq. *l* ⩽ 19 **$C_n(HS_2O_8)$** [4]



● C
● O
○ H

NITROGEN DERIVATIVES OF CARBON

2+ **3+** **4+**

CO → NH_3 ($-H_2O$, ThO_2, 500°)

1.06 1.13 / 1.01 1.17
H—C≡N ⇄ (t) **H—N=C,**
prussic ac. **hidrocyanic ac.**
(ammonocarbonous), liq., colrl., v. toxic, mol. linear *iso*-form — with odour of almond, volat., associates, $d = 0.697$; m.p. −13, b.p. 26, (by 20° — 0.5 % *iso*-form), $K = 10^{-9}$, $\mu = 2.96$, $\varepsilon = 107$ (25°), $\xrightarrow{h\nu\text{-vis}}$ NH_3 + $HCOOH$ + $(COOH)_2$ + …, burn vlt. flame

$(HCN)_3$, "triazine", 6-member ring
m.p. 86, inclined to hydr.

$(HCN)_4$, (unstab.) $\underset{-H_2O}{\overset{H_2O}{\rightleftharpoons}}$ $HCOONH_4$ [27]

H^+; KHS (*t*)

NH_3 (*t*); $K_2CO_3 + NH_3$; C

Cyanides (prussiates)
NaCN, m.p. 564, b.p. 1497, NaCl str. type; $\cdot 2H_2O$
KCN, m.p. 634
NH_4CN, dec. 36
$Ca(CN)_2$, $Hg(CN)_2$, readily sol. in H_2O, not diss., toxic — only strong dis. salts
AgCN↓, wh. $\xrightarrow{MCN}$ **$M[Ag(CN)_2]$**
$Fe(CN)_2$↓ $\xrightarrow{KCN}$ **$K_4[Fe(CN)_6]$**
$M_6[Cr^0(CN)_6]$
$M_3O(CN)$, M = Na, K, *anti*-$CaTiO_3$ str. type [27]; strong Red,
+ $OCl^- \longrightarrow HCO_3^- + N_2 + Cl_2$

0.6+ **C_5N**, [9] cr. graphite str.

[R—C≡N:], nitriles
$MHal_n \cdot m\,RCN$
[R—N≡C:], isonitriles
$[Fe(CNR)_6]^{2+}$
$Ni^0(CNR)_4$

$S(CN)_2$ (*t*, $-CS_2$)

C_6N_4, amorph., yel., insol. in H_2O, org. solv., adsorb. H_2O, $\xrightarrow{\approx 700°}$ $(CN)_2 + N_2$

$HC(CN)_3$, cyanoform
$M[C(CN)_3]_n$, M = K, Ag, UO_2

Cl_2 (zeolites)

O_2 (Ag, *t*); Cl_2; NO_2

$(—CN)_2$, dicyanogen (nitril of oxalic ac.), gas, colrl., toxic, m.p. −28, b.p. −21, $\Delta H = +293$, mol. N≡C—C≡N linear, C—N 1.13, C—C 1.37; chem. anal. of Hal_2; + NaOH ⟶ NaCN + NaOCN; + $O_2 \longrightarrow CO_2 + N_2$; $H_2SO_4 \longrightarrow CO + CO_2 + (NH_4)_2SO_4$ ($t \leqslant 4500°$, red flame), $\xrightarrow{>1000°}$ 2 CN· (C—N 1.17), stab. by v. hight *t*

hv (vis.) (slow) ⇅ 860°; Pt

$(CN)_6$, hexacyane, cr., colrl., m.p. 119, b.p. 262, mol. cycle $[-N=C(CN)-]_3$;
+ $4H_2O \rightleftharpoons (NH_4)_2C_2O_4$

$HgCl_2$; $CuSO_4$

350° (−Ag)

$Hal_2(H_2O)$

O_2 (Ni, *t*); PbO (*t*); MnO_4^-

H_2O

Cyan halides		m.p.	b.p.	μ
FCN	gas, colrl.	−82	−46	1.68
ClCN	»	−7	13	—
BrCN	cr.	51	61	2.9
ICN	cr.	146 (*p*)	140	3.7

$(N_3)CN$; $X(CN)_2$, (X = S–Te, N_2, CO);
$P(CN)_3$, v. toxic, subl., sol. in H_2O (⟶ HCN + HHalO), [15]
mol. linear, **$[Fe(—NCBr)_6]X_2$**
t ↑ time

$(HalCN)_3$, cyanur halides, mol. — cycles [6]
$(FCN)_3$, m.p. −38, b.p. 74
$(ClCN)_3$, m.p. 146, b.p. 190
$\left[-N=\underset{\displaystyle Hal}{\underset{|}{C}}-\right]_3$

$HN(CN)_2$, dicyanamide, strong ac.

H_2CN_2, diazarine [26]

MNH_2; Na_2CN_2

$M[N(CN)_2]_n$, [25]
M = M^I, Tl, Ag, Hg, $[N\equiv C—N—C\equiv N]^-$ (1.15, 1.28)

$COCl_2$ → NH_3

$CO(NH_2)_2$, carbamide (urea), cr., colrl., m.p. 133, subl. vac., readily sol. in H_2O, alc., liq. NH_3, SO_2;
$\underset{}{\overset{H_2O}{\rightleftharpoons}}$ $[CO(NH_2)(NH_3)]^+ + [CO(NH_2)(NH)]^-$, $K_{bas.} = 10^{-14}$; + $H_2O \longrightarrow (NH_4)_2CO_3$ (in ground)
+ HX ⟶ **$[CO(NH_2)(NH_3)]^+X^-$**↓, X = NO_3, H_2PO_4,
+ $H_2S_2O_7 \longrightarrow NH_2SO_3H + CO_2$; weak Red (stab. to MnO_4^-, H_2O_2); + $OCl^- \longrightarrow N_2$,
mol. — plain

t (−NH_3)

H(0.99)**N≡C(1.21)=O(1.17)** ⇄ (*t*) **N≡C—OH**
isocyanic **cyanic ac.**
liq., colrl., with odour of acetic ac. v. unstab., m.p. −87, b.p. 25; by 20° ⩾ 98% *iso*-form; in conc. s. — trimers, $K = 10^{-4}$;
+ $H_2O \longrightarrow CO_2 + NH_3 \longrightarrow CO(NH_2)_2$

OH⁻ ⇄ H⁺

NH_2CN, cyanamide, cr., colrl., hyg., m.p. 46, sol. in H_2O, alc., Et_2O, $\mu = 4.24$,
+ H_2O $\xrightarrow{(H^+,\,OH^-)}$ $CO(NH_2)_2$;
in org. solv. ⇄ HN=C=NH, carbodiimide

H_2SO_4 ⇄ MOR

Cyanamides [17]
$NaHCN_2$, K_2CN_2, $\xrightarrow{400°}$ KCN + K + N_2;
MCN_2, M = Mg–Ba
$CaCN_2$, subl. ≈ 1200, $\xrightarrow[>1000°]{}$ $Ca(CN)_2$ +
+ Ca + N_2 + CaC_2; $\cdot n\,H_2O$, $n = 1-3$;
+ $H_2O \longrightarrow CaCO_3 + NH_3$ (fertilizer);
Ag_2CN_2↓, yel., SP = 10^{-10}, anion — linear, isoel. of CO_2
$[\cdot\ddot{N}^{1.23}=C=\ddot{N}\cdot]^{-2}$ and $[H^{0.90}-\ddot{N}^{1.28}\equiv C^{1.18}-\ddot{N}\cdot]^-$

NH₃

M + NH₃; N_2 ($CaCl_2$) — C; CaC_2

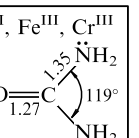
Na — $CO(NH_2)_2$

$(NH_2)_2CNH$, guanidine, cr., m.p. 50 (dec.), strong bas.
$\underset{}{\overset{H_2O}{\rightleftharpoons}}$ $[(NH_2)_3C]^+ + [(NH_2)C(NH)_2]^-$;
+ H_2O $\xrightarrow{(OH^-)}$ $CO(NH_2)_2 + NH_3$

$NH_4[NH_2CO_2]$, carbamate
+ $H_2O \rightleftharpoons 2NH_4^+ + CO_3^{2-}$

H_2O

$MCl_n \cdot 2[:OC(NH_2)_2]$, M = Zn, Cu^{II}, Fe^{III}, Cr^{III}
$MCl_2 \cdot 2(:NH_2)_2CO$, M = Pd, Pt;
$L \cdot [:OC(NH_2)_2]$, L = H_2O_2, MeOH
$CO(NH_2)(NHNH_2)$, semicarbazide, cr., colrl., m.p. 96, sol. in alc. H_2O



$(HNCO)_3$, cyanuric ac.
mol. — plane cycle, poorly sol. in H_2O, $K_1 = 10^{-7}$, $K_2 = 10^{-12}$, $K_3 = 10^{-15}$

$(HNCO)_n$, [20]
cyamelide
$K_3(NCO)_3$
cyanurate

M_2CO_3 ($-CO_2 - NH_3 - H_2O$)

Cyanates
NaOCN, m.p. 50; **KOCN**, $\xrightarrow{700°}$ KCN + K_2CO_3 + N_2 + CO; **NH_4OCN**, $\xrightarrow{60°}$ $CO(NH_2)_2$ (Wöhler, 1824); **AgOCN**↓, SP = 10^{-7},
+ $H_2O \longrightarrow MHCO_3 + NH_3$; **$K_2[M(NCO)_4]$**, M = Mn–Zn, $[N\equiv C—O]^-$ — linear, (unknowh — on any at. — N or O banded with M), not toxic
$Si(—NCO)_4$, m.p. 26, b.p. 186
$Si(—ONC)_4$, m.p. 35, b.p. 245

$P(—NCO)_3$, R—NCO, isocyanates
$M_3[Mo(—OCN)_6]$, cyanates

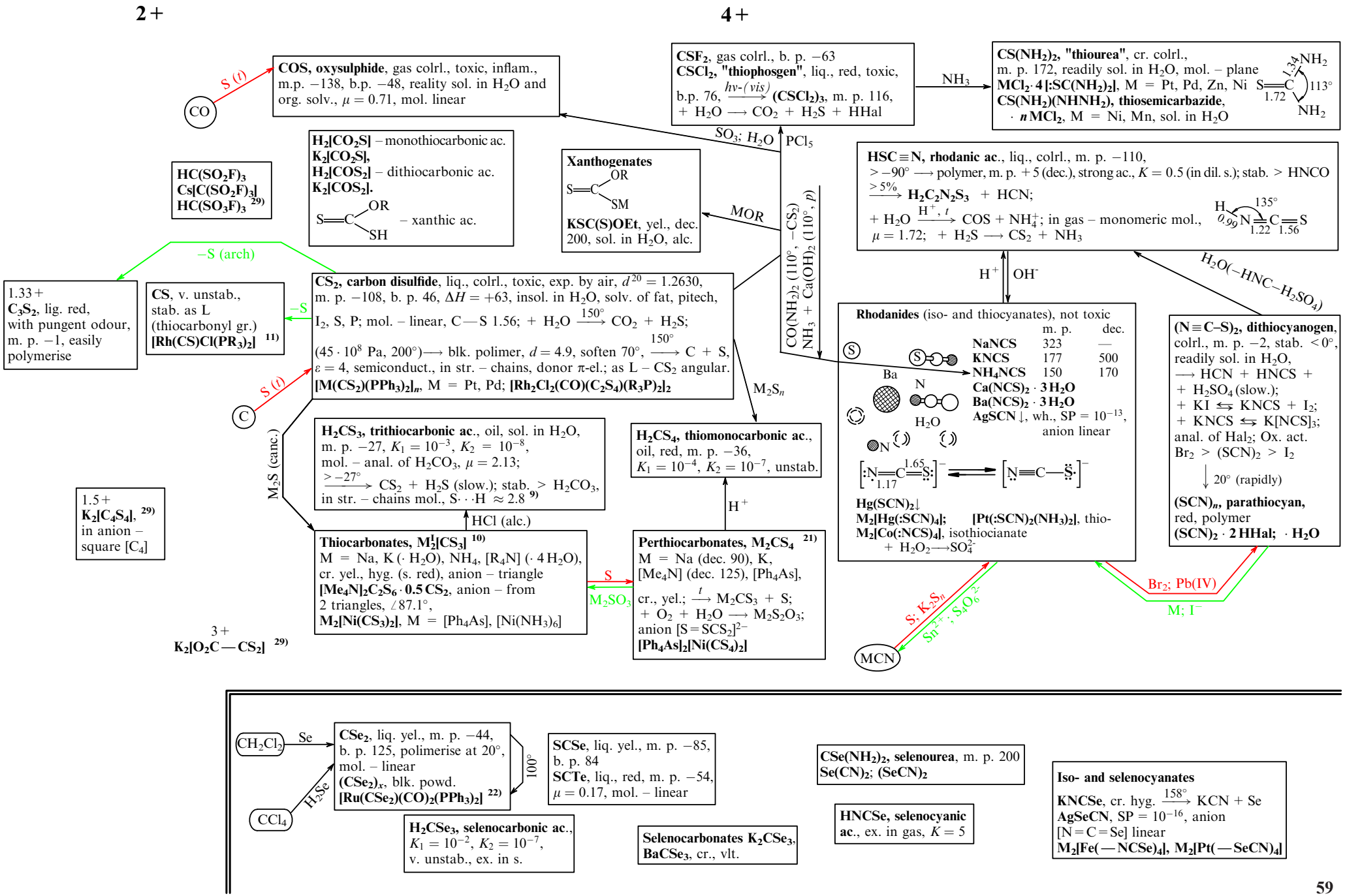
H—O—N=C,
fulminic ac.
$\mu = 3.06$

Melamine
$(NH_2CN)_3$, strong bas., mol. — plane cycle

Fulminates
Ag(ON=C)↓; **$Hg(ON=C)_2$**↓, exp. ⟶ Hg + CO + N_2 (detonator); **$M[Au(ONC)_2]$**

$[(NH_2)_3C]^+X^-$, [24]
guanidinium salts

SULPHUR AND SELEN DERIVATIVES OF CARBON



SILICON

4– 2– 1– Si^0 3s ↓↑ 3p ↓ ↓ 3d EN 1.8 1+ 2+ 3+

Silanes Si_nH_{2n+2}
gas or liq., toxic, with a characteristic odor, infl. in air, stab. decreases in homol. series, sol. in org solv., insol. in aq., hydr. at pH > 7, str. anal. to C_nH_{2n}+2, Si—H 1.48, Si— Si 2.32
ΔH SiH_4 = +33; strong Red.; $+Hal_2 \rightarrow Si_nH_{2n+2-x}Hal_x$ (exp.)

4–	3–	2.67–	2.5–	2.25–
SiH_4 mono-	**Si_2H_6** di-	**Si_3H_8** tri-	**Si_4H_{10}** tetra-	**Si_8H_{18}** octasilane
d 0.68 (−185°)	0.68 (−25°)	0.743 (0°)	0.825 (0°)	
m.p. −185	−132	−117	−84	
b.p. −112	−14	+53	+107	

$(SiH_2)_n$, polysilen, cr., brn., inflam. by air, dec. 380

Si_5H_{10}, Si_6H_{12}, cicle, liq. colrl., inflam. [1)]

$(SiH)_n$, siline, yel., amorph.

Si, single-cr., grey, powd. brn. ("amorphous Si"), *d* = 2.3, m.p. 1415, b.p. ~3250, insol. in ac., sol. in alk. $E_{0\,SiO_4^{4-}/Si_{sld.}}$ = −1.86, semiconduct. (< 150°), (*d* and conduct. inerease at m.p.), diamond str. type, *a* = 5.42, Si — Si 2.35.
Si high pure, powd. wh., + H_2O ⟶ H_2↑
↓ 2 · 10^{10} Pa
Si met., str. anal. of "wh. Sn", *d* = 2.55, Si — Si 2.30, 2.39 in distr. tetrah.
Si -hex., *a* = 4.04, *c* = 6.60, wurtzite str. type [4)]

780° (−H_2)

Mg; Al; CaC_2; C

Si; C (1300°)

SiO_2

$(SiO)_n$, powd., brn., stab. in gas > 1000°, ΔH = 769, slow. Ox
$\xrightarrow{t}$ Si + SiO_2 (subl.);
+H_2O + MOH ⟶
⟶ M_2SiO_3 + H_2

$(SiOOH)_n$↓, silicooxalic ac., powd. exp. if friction
+NaOH ⟶
H_2 + Na_2SiO_3

$(SiS)_n$

Na; Zn

$SiCl_4$

$(Si_nH_{2n+1})_2O$, silocsanes, gas or liq., dec. alk.

H_2 (1, p)
$LiAlH_4$
$H_2(AlCl_3)$

SiO_2
$SiCl_4$
$SiHHal_3$

HCl

Na (−NaHal)

KH

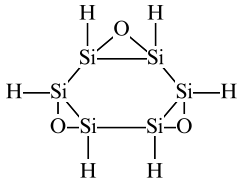
H_2O (−H_2 −SiO_2 · *n* H_2O − M_2SiO_3)

[SiH_3]X — derivates of "silil", colrl., hyg., inflam. in air, mol. — tetrah. X = Hal, SH, CN, NCS, N_3, Me, PH_2, O/2, S/2, Se/2, CN_2/2, N/3, CH/3, P/3

	m.p.	b.p.	*d*	**K[SiH_3]**, cr. colrl., NaCl str. type, dec. 200
$(SiH_3)_2O$	−144	−15 (dec. 600)	0.88 (−80°)	
↑ H_2O				
SiH_3F	—	−88	—	
SiH_3Cl	−118	−30	1.15 (−113°)	
SiH_3Br	−94	+2	1.53 (0°)	
SiH_3I	−57	45	2.03 (15°)	

SiH_3Hal $\xrightarrow{20°}$ SiH_2Hal_2 + SiH_4

$(H_6Si_6O_3)_n$, siloxene



cr. colrl., strong Red,
+ Br_2 ⟶ $H_3Si_6O_3Br_3$;
+ HBr ⟶ $H_5Si_6O_3Br$
+ I_2 ⟶ $H_5Si_6O_3I$

H_2O

$H_6Si_6O_6$, cr. vlt.

M; M_2O

Cl_2, $SbCl_3$($CaCl_2$)

HCl + EtOH (−H_2)

$(H_2Si_2O_3)_n$, *n* = 4 – 7 **polysiloxanes**, cr. wh., sensetive to light,
$\xrightarrow{500°}$ H_2 + Si_2O_3 (?)
$H_{10}Si_{10}O_{15}$, mol. — cycle [14)]

H_2O

H_2O(−HHal)

HHal

	m.p.	b.p.	ΔH
$SiHF_3$, gas, colrl.	−110	−80	−1184
$SiHCl_3$, liq., colrl.	−126	33	−519
$SiHBr_3$, liq., colrl.	−60	112	−327
$SiHI_3$, liq., red.	+8	220	–

	m.p.	b.p.	*d*
SiH_2F_2	−122	−78	—
SiH_2Cl_2	−122	8	1.42 (−122°)
SiH_2Br_2	−70	66	2.17 (0°)
SiH_2I_2	−1	150	2.73 (20°)

2200°

C (2000°)

$SiCl_4$

M_xSi_y, silicides

Salt-like

inflam. in air, strong Red	in str.:
M_2Si, M = Mg, Ca	isolate at. Si, *anti*-CaF_2 str.
MSi, M = Ca – Ba	gauffer laeyrs Si_∞
MSi, M = Na – Cs	tetrah. $[Si_4]^{4-}$; +H_2O ⟶ exp.
MSi_2, M = Ca – Ba	laeyrs Si_∞

Metal-like

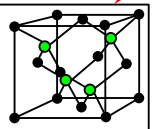
ac. resist., sol. in alk., thermostab., paramagn.

V_2Si	isolat. at. Si
$FeSi_2$	gr. $[Si_2]$
MSi_2, M = Cr, Mo, Ti	layers Si_∞
Mn_5Si_3, Fe_5Si_3	chains Si_∞
MSi, M = Ti, Zr, Mn, Fe	three-dimensional net Si_∞

"Ferrosilicium" contain 9–15, 43–50 or 72–95 % Si — low-, middle-, high silicon

M_2O_n (−CO_2)

SiC, carborundum, cr. colrl., dec. 2830, diamond str. type, semiconduct. <1000°, v. hard, sol. only in (HF + HNO_3);
+ NaOH + O_2 $\xrightarrow{t}$ Na_2CO_3 + Na_2SiO_3;
+H_2O $\xrightarrow{1300°}$ SiO_2 + CH_4; + Cl_2 $\xrightarrow{>600°}$ $SiCl_4$ + C



Si(Dipy)$_3$, cr. blk.

SiO_2 + FeO

C (1, −CO↑)

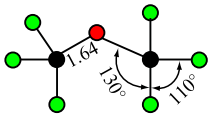
$SiHal_n$, *n* = 1–3 [2,5,6)]
$(SiHal)_\infty$, BN str. type, **$Si_{10}Cl_{18}$**, oil
$(SiHal_2)_n$ ⇆ Si + $SiHal_4$; + H_2O ⟶ $[Si(OH)_2]_n$ in gas — monomers.
Si_nHal_{2n+2}, liq. or cr. colrl., str. anal. of C_nH_{2n+2}; Si—Si 2.34
$Si_{25}Cl_{52}$ (2.08+); **$Si_{10}Cl_{22}$** (2.2+), liq., visc.
Si_6Cl_{14} (2.33+), m.p. 318; **Si_5Hal_{12}** (2.4+);
Si_4F_{10} (2.5+), m.p. 67, b.p. 85;
Si_3F_8 (2.67+), m.p. −1, b.p. 42; **Si_2Hal_6** (3+), m.p. −19 (F); 3 (Cl); 90 (Br); b.p. 147 (Cl); 265 (Br) inflam. in air

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_19, © Springer-Verlag Berlin Heidelberg 2011

O_2 (> 1000°); M_2O_n (silicothermic Red. of M)

	m.p.	b.p.
Si_2OF_6	−47	−23
Si_2OCl_6	—	137
Si_2OBr_6		unstab.

+ $H_2O \longrightarrow SiO_2$ + HHal [7]



SiX_4, X = CH_3COO (m.p. 110), NCS, NCO, NO_3 (· 2 Py), N_3 (exp.), PO_4/3↓, ClO_4 (· 2 MeCN) cr., colrl., sol. in org. solv., mol. tetrah.
SiP_2O_7, m.p. 1290, in str. — framework $[P_2O_7]$ and oct. $[SiO_6]$ [3]

ClF$_5$; XeF$_4$ — O$_2$; B$_2$O$_3$(*t*) — $K_2[Si(CH_3COO)_6]$ [10]

Hal$_2$ + C; Al_2O_3

	m.p.	b.p.	d^{20}	ΔH
SiF_4, gas, toxic	−77 (*p*)	−95	—	−1615
$SiCl_4$, liq.	−68	57	1.48	−685
$SiBr_4$, liq.	5	153	2.81	−460
SiI_4, cr.	122	290	—	−210

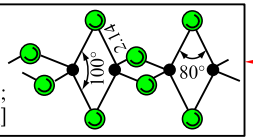
gas inflam., $\xrightarrow{t}$ Si + I_2;
SiF_nCl_{4-n}, $SiCl_nBr_{4-n}$, $SiBr_2F_2$, colrl., hyg.

H$_2$O

H_2SiF_6, silicofluoric ac., v. strong, ex. only in s. (conc. ≤ 61 %), toxic, volat.
· **2 H_2O**, m.p. 19;
· **4 H_2O** (= $[H_5O_2]_2SiF_6$);
· **6 H_2O** (= $[H_5O_2]_2SiF_6 \cdot 2\,H_2O$);
azeotrope with H_2O 13.3%.
Silicofluoride
M_2SiF_6↓M = Na, K, Rb, Ba/2, M = Li, NH_4, Cs, Mg/2, Zn/2, Al/3, sol. in H_2O; $\xrightarrow{400°}$ MF + SiF_4↑;
K_2PtCl_6 str. type, anion — oct.,
$MSiF_5$, M = Cs, $[R_4N]$, $[AsPh_4]$
K_3SiF_7 [11]

Hal$_2$; HF

SiS_2, needle, colrl., hyg. m.p. 1090, b.p. 1130, subl., $\Delta H = -205$, $H_2O \longrightarrow SiO_2 \cdot x\,H_2O + H_2S$; in str. chains of tetrah. $[SiS_{4/2}]$



S; H_2S(*t*) — Si

N$_2$ (1500°)

M_2SiS_3, Ca_2SiS_4
$Na_4[Si_4S_{10}]$ [9]

Si_3N_4, powd., wh., inert, subl. 1900, semiconduct., $\Delta H = -749$; + NaOH (*t*) $\longrightarrow Na_4SiO_4 + NH_3$; + HF $\longrightarrow (NH_4)_2SiF_6 + SiF_4$; in str. — framework tetrah. $[SiN_4]$ and triangle $[NSi_3]$ [8]

t(−H_2−NH_3)

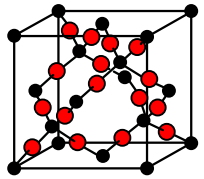
$(Si_2NCl_5)_n$; **$(SiCl_3)_3N$**; **$O(SiN)_2$**; **$Si(NH_2)_4$** $\xrightarrow{t}$ **$[Si(NH)_2]_n$**;
$Si_2(NH)_3$ $\xrightarrow{t}$ **SiN**; **Si_2P** $\xrightarrow{600°}$ **SiP**; **SiAs**; **$SiAs_2$**

LiOSiN [9]
$K_4[Si(NH)_4]$
$K_2[Si(NH)_3]$
$Ca(SiN)_2$, **$CaSiN_2$**,
K_2SiAs_2 [8]

SiO_2, cr., or glass, colrl., refractory, sol. in HF and alk., $\Delta H = -879$ (α-quartz), in str. — tetrah. $[SiO_4]$, linked all vertex. [12]

"β-quartz", *d* = 2.65, hex., optically act. —573°→ "α-quartz", m.p. 1550, hex., piezoelectric —867°→ "α-tridymite", *d* = 2.28–2.33, hex. —1470°, *t*, *p*→ "α-cristobalite", *d* = 2.32, m.p. 1728, b.p. 2950, cub. → "coesite", *d* = 3.01, monocl., framework of tetrah. "stishovite", *d* = 4.28, tetr., TiO_2 str. type (CN Si 6), Si—O 1.75–1.81, insol. in HF

"α-tridymite" —141–163°→ "β-tridymite" rh.
"α-cristobalite" —270°→ "β-cristobalite" tetr.
"γ-tridymite" ←115°— "β-tridymite"


α-cristobalite str.

Fibrous SiO_2 isostr. SiS_2 (form from gas). In quartz glass — unregulated arrangement of tetrah. $[SiO_4]$, *d* = 2.20

MOH; M_2CO_3 (*t*)

−H_2O(*t*)

$[SiO_2 \cdot x\,H_2O]_n$, *x* < 2, form sole and gele
H_4SiO_4, ex. in true s., $K_1 = 10^{-10}$, $K_2 = K_3 = 10^{-12}$

H_2O — Si(OR)$_4$

H_2CO_3 ↕ MHal; M_2SO_4 (*t*)

$M_2O_n \cdot m\,SiO_2 \cdot x\,H_2O$, silicates, — tetrah. $[SiO_4]$, Si—O ≈ 1.57 (term.), 1.68 (br.)
In str. of silicates $[SiO_4]$ are connected only to vertex

Insular

$[SiO_4]^{4-}$, ortho-
$Be_2[SiO_4]$, "phenacit"
$Mg_3Al_2[SiO_4]_3$, "garnets"

$[Si_2O_7]^{6-}$, diortho-
$Sc_2[Si_2O_7]$, "thortveitite"

$[Si_3O_9]^{6-}$, trimeta-
$BaTi[Si_3O_9]$, "benitoite"

$[Si_4O_{12}]^{8-}$, tetrameta-
$Ca_2Fe^{II}Al_2(BO_3)(OH)[Si_4O_{12}]$, "axinite"

$[Si_6O_{18}]^{12-}$, hexameta-
$Be_3Al_2[Si_6O_{18}]$, "beryl"

Chains, pyroxenes **$[SiO_3]^{2-}_{\infty}$**, polymeta-
$Cu[SiO_3]$
$Mg_2[SiO_3]_2$, "enstatite"
$Ca_3[SiO_3]_3$, "vollastonite"

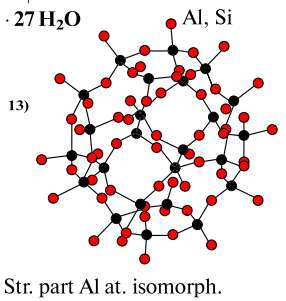
Bands, amphiboles **$[Si_4O_{11}]^{6-}_{\infty}$**
$Ca_2Mg_5(Si_4O_{11})_2(OH)_2$, "tremolite"

Plates
$[Si_2O_5]^{2-}_{\infty}$, dimeta-
$Mg_3[Si_2O_5]_2(OH)_2$, "talcum"
$KAl_2[(Si_3Al)O_{10}](OH)_2$, "muscovite" (mica)

In aq. s. of silicates (they ascribed to the composition M_2SiO_3) ex eq. of association

$n\,[SiO_4]^{4-}$ $\overset{2H^+(-H_2O)}{\rightleftharpoons}$ $n/2\,[Si_2O_7]^{6-}$ $\overset{n\,H^+(-n/2\,H_2O)}{\rightleftharpoons}$ $[Si_nO_{3n}]^{2n-}$
OH$^-$ ↕ 3 H$^+$ OH$^-$ ↕ 4 H$^+$ OH$^-$ ↕ *n* H$^+$
$n\,[H_3SiO_4]^-$ ⇌ $n/2\,[H_4Si_2O_7]^{2-}$ ⇌ $[H_nSi_nO_{3n}]^{n-}$
orto- diorto- *n* = 3–6, meta (cicles)

Frame of alumosilicates, in str. — tridimensional net of tetrah. $[(Si,Al)O_4]$
$K[(AlO_2)(SiO_2)_3]$, "feldspar"
$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$, zeolites
↑ 350°
· **27 H_2O**

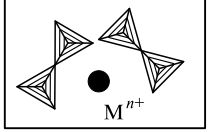


[13]

Str. part Al at. isomorph. substitute Si at. in tetrah., part forms $[AlO_6]$ oct. — ex. cavities in form of cubooct., D = 11.4 with openings 4.2 and 2.0 Å ("mol. sieves")

$Ba_7[Si_7O_{21}] \cdot 10\,BaCl_2$ [13]
cycle of tetrah.

Glass
$Na_2O \cdot CaO \cdot 6\,SiO_2$, in str. — $[SiO_4]$ and M — dispos. unregular



● Si
● O
● C, S

GERMANIUM, TIN, LEAD

4 – **2 +**

Ge_nH_{2n+2}, germanes		
colrl.	m.p.	b.p.
GeH_4 dec. 220, $\Delta H = +92$	−166	−88
Ge_2H_6	−109	31
Ge_3H_8	−106	111
Ge_4H_{10}	—	177
Ge_5H_{12}	—	234
Ge_9H_{20}		

+ HCl ⟶ GeH_nCl_{4-n}; + HI ⟶ GeI_2 + H_2; str. anal. C_nH_{2n+2}; Ge—H 1.53, Ge—Ge 2.41 [18]

SnH_4, stannan — m.p. −146, b.p. −52, dec. 20, $\Delta H = +163$, mol. tetrah., Sn—H 1.70
Sn_2H_6

PbH_4 plumban, gas, colrl., v. unstab., $\Delta H = +251$

Polygermanes, sld. **$(GeH_2)_n$**; yel., v. react. **$(GeH)_n$**; wh., stab. only in NH_3 liq.

	4*s*	4*p*	4*d*	EN
Ge^0	↓↑	↓ ↓		2.0
	5*s*	5*p*	5*d*	
Sn^0	↓↑	↓ ↓		1.8
	6*s*	6*p*	6*d*	
Pb^0	↓↑	↓ ↓		1.5

$GeOCl_2$ —*t* (−Cl_2)→ **GeO** (?), powd., grey, subl. 700, $\Delta H = -255$, poorly sol. in ac., alk. ↑ 650° yel. form

350° (N_2) ↑ **$Ge(OH)_2$**↓, wh., yel., or red, sol. in ac. $K_{ac.} < K_{ac.}(CH_3COOH)$, + alk. → brn. sol

SnO, dark bl. (red form — metastab.) m.p. 1040, b.p. 1425, $\Delta H = -284$, Ox in air; α-PbO str. type; sld. SnO —*t*→ Sn + SnO_2, but stab. in liq. and gas

120°(N_2) ↑ **$SnO \cdot n\,H_2O$**↓, wh., sol. in ac., alk. **$Sn_6O_4(OH)_4$** ("6 SnO · 2 H_2O"), mol. — cluster [Sn_6], over the centre of faces — 4 OH and 4 O-gr. [21]

[H↑] ← PbMg; LiAlH$_4$; NaBH$_4$ ← MCl_4

GeO_2 —H_2 (1000°)→ **Ge**

SnO —*C* (*t*)→ **Sn**

CO_2(−CO) ← **Pb** ← PbS —H_2 (600°); PbO; $PbSO_4$→

Ge	Sn	Pb
met. grey, v. hard, brittle, >550°, plient, semicon-duct., transparent for IR-rays	α-, "grey", $d = 5.75$, diamond str. type $a = 6.49$, Sn−Sn 2.81, semiconduct.	mild, bl.-wh., does not transmit γ - and XR-emission
d 5.32	>13.2° ↓ β-, "wh.", met. ductil. 7.31	11.3
m.p. 937	—	327
b.p. 2850	—	1751
sol. in alk., HNO_3 (slow.), H_2SO_4, aq. regia	sol. in conc. ac. and alk.	sol. in HNO_3 (dil.), H_2SO_4 (>80%), ($CH_3COOH + O_2$)
$E_0 M^{2+}/M_{sld.} \approx 0$	−0.136	−0.126
cub. diamond str. a = 5.66, Ge—Ge 2.45	tetr. (dist. diamond type), $a = 5.82$, $c = 3.17$ Sn—Sn 3.17 and 3.02	cub. cl. pack. $a = 4.94$, Pb—Pb 3.50
125° ↑↓ $12 \cdot 10^9$ Pa wh. Sn, str. type $d = 8.47$; $a = 4.88$, $c = 2.58$	↓ 161° γ-, rh., brittle, $d = 6.6$, m.p. 232, b.p. 2620	

[GeH_3]X, "germyle" comp.
GeH_3F
GeH_3Cl, liq., colrl., m.p. −52, b.p. 28, $\mu = 2$ 13
GeH_3Br
GeH_3I
Mol. — tetrah., ∠HGeH 111, Ge—H 1.52, Ge—Hal 1.73 (F), 2.15 (Cl), 2.31 (Br), in str. — chains, Ge—Hal . . . Ge
H_3GeSiH_3, m.p. −120, b.p. +7
GeH_3PH_2
$(GeH_3)_3P$

SiH$_4$; $(SiH_3)_3P$; I_2(−HI)

Na(NH_3 liq.)

$NaMH_3$, M = Ge, Sn, cr., colrl. (NH_3 liq.) ⇌ $Na^+ + [GeH_3]^-$; stab. Ge ≫ Sn, > −33° ⟶ NaGe + $3H_2$

SnH_3Br

M (*t*) →

Germanides [8]
MGe, M = Na–Cs, cr., dark, in str. — tetrah. [Ge_4], Ge—Ge 2.58, ≈ 400° ⟶ Na + Ge
MGe_4, M = K–Cs
M_4Ge_{17} = $M_4[Ge_4]_2[Ge_9]$

Zintle polyanions salt [19]
$Na_n[E_9]$, **E** = Ge, Sn, n = 2, 3, 4;
$Na_2[Sn_4]$; $Na_2[Pb_5]$; $NaPb_3$ [8]
$Na_5[TlSn_3]$, $Na[GaSn_5]$
$Na_8[SnSb_4]$, in str. — dist. cubes [$SnSb_4Na_4$]
$Sr[Sn_3Sb_4]$, anion — 30 at. cycle
−L ↑↓ L (NH_3, En, cryptands)
$[Na_4En_5][Ge_9]$
$[Na_4En_7][Sn_9]$
$[Na(NH_3)_9]_4[Pb_9]$
$[K Crypt]_3[Sn_9]$ anions — trig. threecap. prism

M ↓

Alloys
Bronzes, Cu + Sn
Babbits (for bearings), Pb + Sb + Cu
Typographical, 5–30% Sn, 10–20% Sb, 50–80% Pb
Soft solder, 30–70% Sn, rest — Pb, m.p. 181 (65% Sn)

$Ge[Fe(CO)_4]_4$, mol. tetrah.
$\{HSn[Mn(CO)_5]_2\}_2$, cluster, [$SnHMn_2Sn$] – tetrah., Sn—Sn 2.89, Sn—Mn 2.73 [1]

GeH_2Cl_2, **GeH_2Br_2**, mol. tetrah.

GeS_2 —H_2 (500°)→ **GeS**↓, cr., grey, with. met. lustre m.p. 615, subl. 800, $\Delta H = -105$, sol. in $(NH_4)_2S_n$, in str. layers of oct. [GeS_6]
$Cu_3(Fe,Ge)S_4$, "germanite"; + HNO_3 + H_2SO_4 → GeO_2↓ [22]

$Ge(CN)_2$, **$Ge(NCS)_2$**

NaOH (*t*, −H_2) ←
HCl + H_2SO_4 ←
HNO_3(−NH_4^+) ←

$[Sn_3O(OH)_2]SO_4$
$[Sn_3O(OH)]PO_4$, in cation — triangle [Sn_3], [:SnO_3] ψ-tetrah.
$Sn_2O(NO_3)_2$, [2]
$[Sn_3(OH)_4](NO_3)_2$
dec. 100

Stannates (II) [20]
$M_4[Sn(OH)_6]$, oct.
$Na[Sn(OH)_3]$
$Na_2[Sn_2O(OH)_4]$
$Na_4[Sn_4O(OH)_{10}]$
$Ba[SnO(OH)_2]$
$M^I_4SnO_3$; $K_2Sn_2O_3$
K_2SnO_2, in str. ψ-tetrah. [:SnO_3], light yel.

$SnSO_4$, cr., colrl., dec. 360, in str. — ψ-tetrah. [:SnO_3]; **· 2 H_2O**
$Sn(NO_3)_2 \cdot 20\,H_2O$, v. unstab.
$Sn_3(PO_4)_2$, in str. [:SnO_3] — ψ-tetrah. and oct. [SnO_6] [2]
$SnC_2O_4 \cdot H_2O$ poorly sol. in H_2O

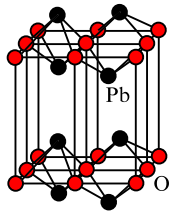
$Na_2Sn(C_2O_4)_2$, [:SnO_4] — ψ-tetr. pyr. [23]

Pb —HNO_3→ —$H_2O + CO_2$→ —$CH_3COOH + O_2$→

SnS↓, brn., SP = 10^{-28}, m.p. 800, b.p. 1230, $\Delta H = -105$, sol. in ac.-Ox, conc. HCl, $(NH_4)_2S_n$

$M_2Sn_2S_8$; $M_2Sn_2S_5$
$Cs_5Sn_2S_6$; Cs_2SnS_{14} [10]

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_20, © Springer-Verlag Berlin Heidelberg 2011



Pb —O_2 (t)→ **PbO**, α-, red, "litharge", tetr., in str. — layers of tetr. pyram. [:PbO_4], d = 9.36, sol. in H_2O 2 times > "massicot" —489°→ β-, yel., "massicot", rh., m.p. 886, b.p. 1580, d = 9.66; ΔH = −217, sol. in ac.

C; PbS

H_2O (t); pH ~1.3 / 9

PbO · $x\,H_2O$↓, wh., sol. in ac., alk., $K_{ac.1} = 10^{-12}$, $K_{bas.1} = 10^{-3}$, $K_{bas.2} = 10^{-8}$; +NaOH (t, p) ⟶ **$Pb_6O_4(OH)_4$**, **$Pb_{13}O_7(OH)_{12}$** [21,26]

−H_2O

PbO —O_2 (t), > 550°→ **Pb_3O_4** = $Pb_2^{II}Pb^{IV}O_4$, red, "saturnine", dec. 500, chains of [:$Pb^{II}O_3$] and [$Pb^{IV}O_6$]; ↓HNO_3 → PbO_2↓ + 2 $Pb(NO_3)_2$

PbO_2 —400°→ **Pb_3O_4**

Pb_2O_3 (?) = $Pb^{II}[Pb^{IV}O_3]$, orange, dec. 360 ↓HNO_3 (dil.) → PbO_2↓ + $Pb(NO_3)_2$

−H_2O

$Pb_2O_3 \cdot 3\,H_2O$↓

Ge —O_2 (t); HNO_3→ **GeO_2**, wh., α-, hex., α-quartz str. type (CN Ge 4), d = 4.70, m.p. 1116, b.p. 1200, ΔH = −536−582 (diff. forms), sol. in H_2O 0.4%, readily — in alk., β-, tetr., TiO_2 str. type (CN Ge 6), d = 6.24, m.p. 1086, poorly sol. in alk.; melt —cool→ glass

H_2 (1000°)

$GeO_2 \cdot x\,H_2O$↓, wh., form true s. in H_2O **H_2GeO_3**, $K_{ac.1} = 10^{-9}$, $K_{ac.2} = 10^{-13}$

Sn —O_2(t)→ **SnO_2**, cr. colrl., m.p. 1630, subl. 1800, ΔH = −577, "cassiterite" ("tin ore"), sol. in H_2SO_4 (t), TiO_2 str. type, —t, p→ CaF_2 str. type (CN 8)

C; H_2

HNO_3 (conc.)

$Pb(NO_3)_2$ / $Pb(CH_3COO)_2$ —$CaCl(OCl) + H_2O$→ **PbO_2**↓, powd., blk.-brn., dec. 300, d = 9.5, ΔH = −276, sol. in conc. ac., alk., inflam. S, P, "plattnerite", TiO_2 str. type; + H_2SO_4 ⟶ O_2 [27]

Pb_3O_4 —HNO_3→

β-$SnO_2 \cdot x\,H_2O$↓ ($x \leqslant 1$), insol. in ac., alk., peptizate, **· 1.5 H_2O** [29]

↑−H_2O (t, OH^-, time)

α-$SnO_2 \cdot x\,H_2O$↓ (x = 1−2), gel, sol. in ac., alk., $K_{ac} = 10^{-10}$

−H_2O

$PbO_2 \cdot x\,H_2O$↓(?)

H_2O

MOH; M_2O; CaO (t)

CO_2

Stannates (IV) [17]
$M_2[Sn(OH)_6]$ = **"$M_2SnO_3 \cdot 3\,H_2O$"**
Li_8SnO_6, oct.
K_2SnO_3 —t→ **$K_2Sn_3O_7$**
$M_4[SnO_4]$, tetrah.
$CoSnO_3$
$M_4[Sn(Mo_{12}O_{40})]$

Plumbanates (IV)
$M_2[Pb(OH)_6]$
Li_8PbO_6, oct.
$Na_6[PbO_5]$, tetr. pyram.; **$K_2Pb_3O_7$**
M_2PbO_3, chains of tetr. pyram.
$M_4[PbO_4]$, tetrah.
$Cu_6^{II}PbO_8$ [15]

NH_4OH

Germanates (IV)
$M_2[Ge(OH)_6]$
$Na_2[GeO_2(OH)_2] \cdot 6\,H_2O$
M_4GeO_4; **M_2GeO_3**
$Li_2Ge_7O_{15}$; **$M_6Ge_2O_7$**
$Tl_8Ge_5O_{14}$; **$K_2Ge_8O_{17}$** [14]
isolate and condensed tetrah.

(—GeOOH)$_2$, wh., nonvolat. str. anal. of (−COOH)$_2$

H$_2$O

Ge_2Cl_6

Plumbates (II) [25]
$Na_2[Pb(OH)_4]$
Ba_3PbO_4; **$M_4[PbO_3]$**
$M_4[Pb_2O_4]$; **$M_2Pb_2O_3$**, ψ-tetrah. [:PbO_3]

Plumbates (II, IV) [32]
$KPbO_2$, **$Rb_2Pb_4O_7$**
$M_7Pb_2O_7$, in str. Pb^{II} − oct. or [:$Pb^{IV}O_3$], − ψ-tetrah.

$Pb(ClO_4)_2 \cdot 3\,H_2O$; **$[Pb_4(OH)_4](ClO_4)_4 \cdot 2\,H_2O$**
$Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$; **$Pb(ClO_2)_2$**, exp. 126
$Pb(ClO_3)_2 \cdot H_2O$, dec. 110
$Pb(BrO_3)_2 \cdot H_2O$, dec. 180
$Pb(IO_3)_2$↓, dec. 300; **$PbHIO_5$**↓, dec. 130, **· H_2O**
$PbSO_4$↓, m.p. 1170, SP = 10^{-8}, K_{dis} = 10^{-4}, sol. in conc. ac. "anglesite", CN Pb 12;
· PbO, "lanarkite"; **· 4 PbO** [5]
$Pb(HSO_4)_2 \cdot H_2O$↓; **$PbSO_3$**↓; **$PbS_2O_8 \cdot 3\,H_2O$**; **$PbS_2O_6 \cdot 4\,H_2O$**,
$PbCrO_4$↓, "chrome yel.", m.p. 844, SP = 10^{-14}, sol. in conc. HNO_3, alk.
$Pb_2Cr_2O_7$, red; + H_2O ⟶ $PbCrO_4$↓
$Pb(NO_3)_2$, dec. 470, insol. in conc. HNO_3; alk.; **· H_2O**, CN Pb 9; 10 [28]
$Pb(OH)_n(NO_3)_{2-n}$, n = 1, 1.45, 1.5, 1.7
$Pb_3(PO_4)_2$↓, m.p. 1014; **$Pb_5(PO_4)_3Cl$**
$Pb_2P_2O_7$; **· H_2O**↓; **$PbHAsO_4$**↓;
$PbH_4(AsO_4)_2$↓, dec. 140; **$Pb_5(AsO_4)_3Cl$**
$Pb(HCO_3)_2$, **$PbCO_3$**↓, "cerussite", dec. 300
CN Pb 9; **$Pb_3(CO_3)_2(OH)_2$**↓, "hydrocerussite"; "wh. lead" [11]
$Pb(CH_3COO)_2$, m.p. 280, ←75°· **· 3 H_2O**
("lead sugar"); **· 10 H_2O**, m.p. 22
$PbSiO_3$, "alamosite"
Pb_2SiO_4, in str. (contain Ba) ψ -oct. [:PbO_5] [5]
$Pb_3Si_2O_7$, "barysilite"
PbZn[SiO_4], "larsenite "

Pb —H_2SO_4→ **$H_2[Pb(SO_4)_2]$** —H_2O→ **$M_2[Pb(SO_4)_2]$**

2.3 + **$Sn_7(OH)_{12}(SO_4)_2$** [33]

$K_2[Pb(NO_3)(NO_2)_3] \cdot H_2O$, [30] orange, CN Pb 9 (8 O + 1 N)
$K[Pb_4(PO_4)_3]$, in str. [:PbO_6] and [PbO_9]

$Sn_2(CH_3COO)_6$, dec. 300

$Na[Pb(CH_3COO)_3] \cdot 3\,H_2O$

Sn_2S_3, chains of oct. Sn (II), Sn (IV)

PbS↓, blk., m.p. 1120, b.p. 1281, ΔH = −92, SP = 10^{-29}, sol. in dil. HNO_3, insol. in $(NH_4)_2S_n$ (unlike GeS, SnS), in alk., "lead glance", NaCl str. type, semiconduct.
Pb[S_2], dec. ~20; + HCl ⟶ H_2S_2

$M_2[Pb(SCN)_4]$

$Pb(CN)_2$↓, sol. in KCN

GeCl$_4$ —SO_3→ **$Ge(SO_4)_2$**
$GeCl_n(ClO_4)_{4-n}$, n = 2, 3 [43]
$Ge(CH_3COO)_4$, m.p. 156

$SnCl_4$ —N_2O_5; $ClNO_3$→

$M_2[Ge(ClO_4)_6]$, M = Cs, ClO_2
$M[GeIO_6]$ [28]
$K_2[Ge(C_2O_4)_3] \cdot H_2O$
$K_2Ge(CH_3COO)_6$

$Sn(SO_3F)_4$
$Sn(SO_4)_2 \cdot 2\,H_2O$, dec. 50, $K_{dis.}$ = 10^{-3}
$Sn(NO_3)_4$, m.p. 91 subl., sol. in CCl_4, hydr., CN 8
$Sn(CH_3COO)_4$, m.p. 253

$SnCl_2(ClO_4)_2$ [24]

$M_2[Sn(ClO_4)_6]$, M = Cs, ClO_2
$Cs_2[Sn(NO_3)_6]$
$KSnOPO_4$
$K_2[Sn(OCOCH_3)_6]$
$[R_4N][Sn(OCOCH_3)_5]$, anion — pentag. pyram. [28]

Pb_3O_4 —$CH_3COOH + Cl_2$→
$Pb(OH)_2SO_4$
$Pb(SO_4)_2$, yel.
$Pb(CH_3COO)_4$, m.p. 175

M[$PbIO_6$] [28]
$K_2[Pb(SO_4)_3]$, yel., + H_2O → PbO_2
$K_2[Pb(CH_3COO)_6]$

GeS_2↓, wh., m.p. 800, SP = 10^{-9}, sol. in $(NH_4)_2S$, net of tetrah. [GeS_4]

S^{2-} / H^+

M_2GeS_3 [31]
$M_2Ge_2S_5$
$M_6Ge_2O_7 \cdot n\,H_2O$
$Cu_2^ICu^{II}[GeS_4]$, "germanite"
Ag_8GeS_6, "argyrodite"
$Ag_8(Sn,Ge)S_6$
$M_6[Ge_2Se_7]$
· 9 H_2O

SnS_2, scales, "leaf-gold" —>500°→ **Sn_2S_3** + S
ΔH = −167; CdI_2 str. type; **· 2 H_2O**, brn., sol. in alk., M_2S; + HCl ⟶ $HSnCl_3$ + + H_2S + S↓

$Sn(C_5H_5)_4$ [16]

S^{2-} / H^+

Thiostannates
$Na_4SnS_4 \cdot 14\,H_2O$, tetrah. **M_2SnS_3**, chains of oct.
$Na_4Sn_3S_8$, chains of tetrah. and trig. bipyr. [9,13]
$Na_6Sn_2S_7$, 2 tetrah. with common vertex [9,13]
Cu_2FeSnS_4, "tin pyrite", "stannite"

$Ge(CN)_4$ —MCN→ **$M_2[Ge(CN)_6]$**
$Ge(NCS)_4$ **$M_2[Ge(NCS)_6]$**

GERMANIUM, TIN AND LEAD HALIDES

2+

"3+"

4+

1000° (−Cl_2)

Ge

$GeCl_{0.9}$, cr., yel. 360°↓ Ge + $GeCl_4$

GeF_2, cr. colrl., m.p. 111, $\Delta H = +473$, in str. ψ-tetrah. [:GeF_3]
$GeCl_2$↓, powd., wh., $\xrightarrow{75°}$ Ge + $GeCl_4$
$GeBr_2$, condens. oct.
GeI_2, yel., m.p. 460; $\Delta H = -113$,
$\xrightarrow{t}$ Ge + GeI_4; CdI_2 str. type.
In gas angular mol. [:$GeHal_2$] [12]

HCl (40°)

$MGeF_3$, + O_2 ⟶ M_2GeF_6
$MGeCl_3$, M = Rb, Cs, ψ-tetrah. [37]
$HGeCl_3$, Ge-chloroform, liq. colrl., m.p. −71, b.p. 75; + H_2O ⟶ $Ge(OH)_2$↓; mol. — tetrah., Ge—H 1.55, Ge—Cl 2.11, ∠ClGeCl 108
$HGeBr_3$, $\xrightarrow{>10°}$ $GeBr_2$ + HBr
$HGeI_3$

Ge_2F_6, [6] $\Delta H = -1632$
Ge_2Cl_6, colrl., m.p. 41, $\Delta H = -565$ volat.

Ge (430°)

$GeOF_2$ [6]
$GeOCl_2$ (?), oil, colrl., m.p. −56;
t ⟶ GeO (yel.) + Cl_2; + H_2O ⟶ $Ge(OH)_2$ + O_2 (?)

[42]	m.p.	b.p.	ΔH
GeF_4, gas, colrl., odour garlic, · **3 H_2O**	−15 (*p*)	−37 (subl.)	−1188
GeF_3Cl	−66	−20	—
GeF_2Cl_2	−52	−4	—
$GeFCl_3$	−50	37	—
$GeCl_4$, liq. colrl., insol. in HCl, sol. in org. solv.	−50	86	−540
$GeBr_4$, liq. colrl.	26	187	−348
$GeCl_3I$	—	—	—
GeI_4, cr. orange	146	377 (dec.)	−142
$GeHal_4 \cdot 2L$, oct.			

M[GeF_5], M = [O_2], XeF_5, NO_2, CN Ge 5 or 6
K_2GeF_6, m.p. 730, b.p. 835, readily sol. in H_2O, K_2PtCl_6 str. type
M_3GeF_7
M_2GeCl_6 [34]

HF (*p*, 200°)

Ge

[Sn_2F_3]Hal; [Sn_3F_5]Hal; [Sn_5F_n]Hal_{10-n}, Hal = Cl–I [40]

I_2 (−HI)

Ge

aq. regia (−NO)

F_2 (HF liq.); SnF_4

[3]	m.p.	b.p.	ΔH
SnF_2, colrl.	215	—	−648
$SnCl_2$, colrl.	247	652	−352
· **2 H_2O**,	38	—	—
80° ⟶ · **H_2O**	—	—	—
$SnBr_2$, yel.	232	638	−254
SnI_2, red., weak dis. in s.	320	720	−152

$SnCl_2$, $\xrightleftharpoons{H_2O}$ **$Sn_4(OH)_6Cl_2$**↓; $SnHal_2$ sol. in org. solv. In str. SnF_2 cicles [:$SnFF_{2/2}]_4$, $SnCl_2$ — chains of ψ-tetrah. [:$SnClCl_{2/2}$]; SnI_2 — 1/3 at. Sn form chains of oct., 2/3 — gr. [SnI_7]. In gas — angular mol. [:$SnHal_2$]. In str. $SnCl_2 \cdot n\,H_2O$ — ψ-tetrah. [:$SnCl_n(H_2O)_{3-n}$]

$KSnF_3 \cdot 0.5\,H_2O$, anion chains of ψ-tetrah. [4]
$NaSn_2F_5$, anion [F_2=Sn—F—Sn=F_2]$^-$,
MSn_3F_7
$HSnCl_3 \cdot 3\,H_2O$, m.p. −27
[H_9O_4]$_2$[$SnCl_6$] · 2 H_2O
M[$SnCl_3$] · H_2O, anion [:$SnCl_3$]
[R_4N]$_3$[$Cr(SnHal_3)_6$]
MSn_2Br_5, **[R_4N][$SnBr_3$]**
$MSnI_3$, **MSn_2I_5**, **M_3SnI_5**
Stab. of [$SnHal_4$]$^{2-}$ decreases in the series F > Cl > Br > I

Sn_7F_{16} = [7]
$[Sn^{II}_6F_{10}]^{2+}[Sn^{IV}F_6]^{2-}$
Sn_3F_8↓ =
$[Sn^{II}F_{4/2}]_2[Sn^{IV}F_2F_{4/2}]$
Sn_2F_6
Sn_2Cl_6, $\xrightarrow{65°}$ Sn + $SnCl_4$

$SnOF_2$, $\xrightarrow{t}$ SnO + SnF_4

[36]	m.p.	b.p.	ΔH
SnF_4, cr. colrl.	—	705 (subl.)	—
$SnCl_4$, liq. colrl.	−34	114	—
· **5 H_2O**	56	—	—
$SnCl_3Br$, liq. colrl.	−1	50	—
$SnClBr_3$, liq. yel.	1	73	—
$SnBr_4$, cr. colrl.	31	205	−93
· **4 H_2O**	—	—	—
SnI_4, cr. yel.	145 (subl.)	344	−215

In str. SnF_4 – layers of $[SnF_2F_{4/2}]_\infty$, $SnHal_4$ (Hal = Cl–I) — tetrah.
$SnHal_4 \cdot 2L$ – oct.

Hal$_2$

Sn

[NF_4][SnF_5], anion — *cis*-$[SnF_4F_{2/2}]_\infty$
$M_2[SnF_6]$, · H_2O, anion oct.
$(NH_4)_3[SnF_6]F$
M_3HSnF_8 = $M_3[HF_2][SnF_6]$
$H_2SnCl_6 \cdot 6\,H_2O$, m.p. 19
M_2SnCl_6, K_2PtCl_6 str. type
$MSnCl_5$, anion — trig. bipyr.
H_2SnBr_6, · **8 H_2O**
M_2SnBr_6
M_2SnI_6 [35]

HCl

Sn

Zn, Mg, Al (t)

n **$PbCl_2 \cdot Pb(OH)_2$**↓, *n* = 1 ("laurionite") square antiprism [PbO_3Cl_5]; 2 ("fidlerite"); 3 ("penfieldite")
$PbCl_2 \cdot n\,PbO$, *n* = 2 ("mendipide"); 3 ("blikside"); 6
$Pb_3O_2Br_2$, chain of tetrah. [PbO_4], CN Pb 6
$PbI_2 \cdot 2\,PbO$, CN Pb 6–8 [5]

[39]	SP	m.p.	b.p.	ΔH
PbF_2↓, colrl.	10^{-8}	855	1292	−677
PbClF↓, » "matlockite"	10^{-9}	—	—	—
$PbCl_2$↓, » "cotunnite"	10^{-5}	501	954	−360
$PbBr_2$↓, » (melt — red)	10^{-6}	373	916	−276
PbI_2↓, golden	10^{-9}	412	954	−175

Str. PbF_2, $PbCl_2$ type CaF_2; $PbBr_2$ rh., CN Pb 9 (threecap. prism.); PbI_2 — CdI_2 str. type; in layered str. PbClF — CN Pb 9; in gas angular mol. $PbHal_2$

Hal$_2$

Pb^{2+}

Hal$_2$

MPb_2Cl_5; **$M^{III}[Pb_4Cl_{11}]$**
$MPbCl_3$; **M_2PbCl_4**
Tl_3PbCl_5
MPb_2Br_5; **M_2PbBr_4**
Tl_3PbBr_5
$HPbI_3 \cdot 3\,H_2O$
$MPbI_3$; **Tl_3PbI_5**
Tl_4PbI_6, colrl., anions oct. or single-cap trig. prism [:$PbHal_7$]. Stab. [$PbHal_4$]$^{2-}$ increase in the series F < Cl < Br < I [38]

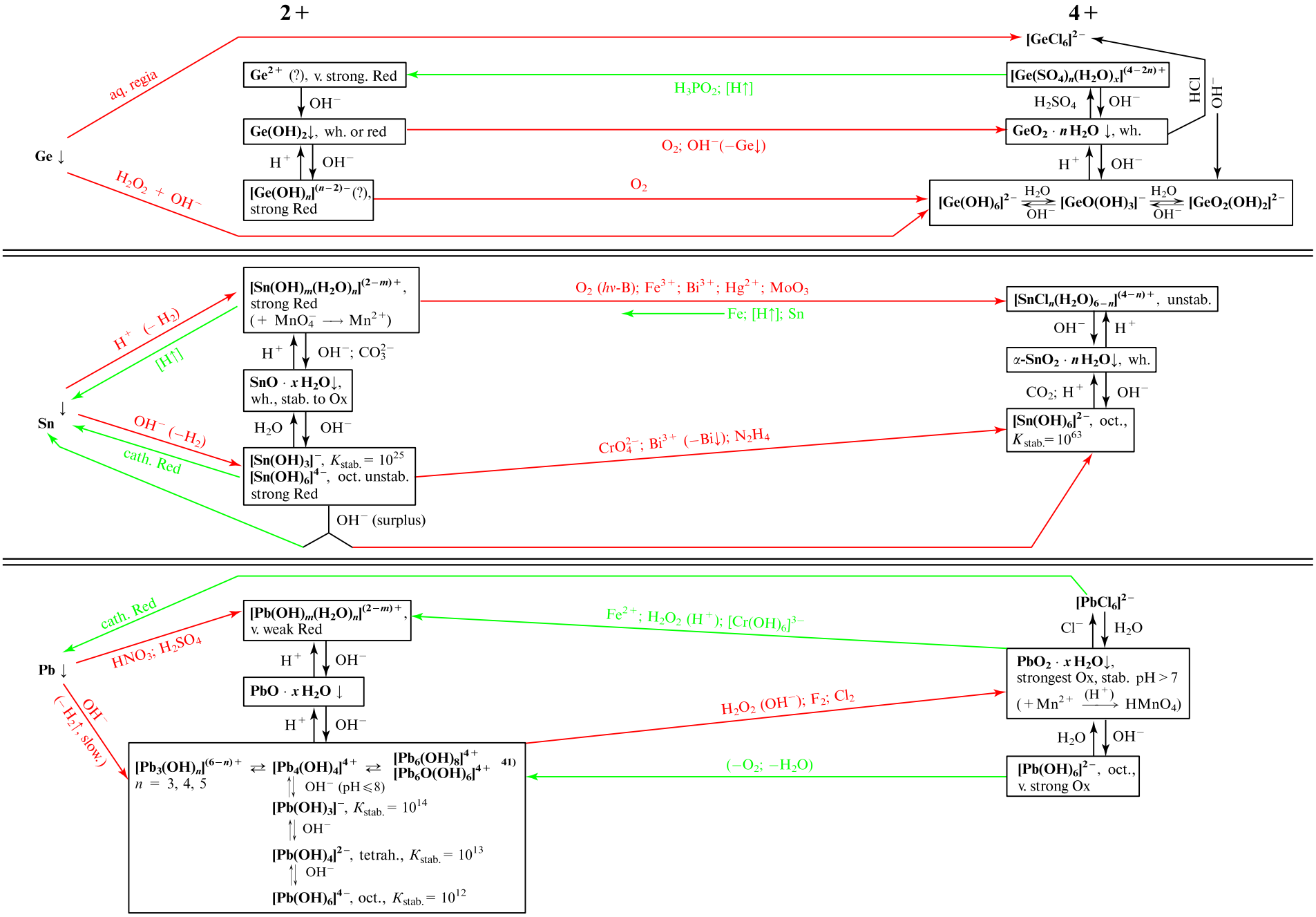
H_2O (−Hal_2)

$PbOCl_2$, cr., vlt.

PbF_4, needle, colrl., hyg., m.p. 600
$\Delta H = -941$; in str. — layers of oct.
$PbCl_4$, liq. yel., fumed, [36] m.p. −15, exp. 105, $\Delta H = -331$, in str. tetrah.,
+ H_2O ⟶ $PbHal_2$↓ + Hal_2

$M_3[HPbF_8]$
M_2PbF_6, oct.
$SrPbF_6$ = $Sr[PbF_4F_{2/2}]F$
M_2PbCl_6, cr., yel., K_2PtCl_6 str. type Pb—Cl 2.50
↓ Br_2
M_2PbBr_6
M_2PbI_6

GERMANIUM, TIN AND LEAD IONS IN AQUEOUS SOLUTIONS



TITANIUM, ZIRCONIUM, HAFNIUM

	3d	4d	5d	4s	5s	6s	4p	5p	6p	EN
Ti^0	↓ ↓			↓↑						1.5
Zr^0		↓ ↓			↓↑					1.4
Hf^0			↓ ↓			↓↑				1.3

MCl_4 (melt) — Mg; Na; cath. Red

MI_4 — t, vac. ($-I_2$)

O_2 (i)

Ti_6O, Ti_3O, Ti_2O, Zr_3O

Ti	Zr	Hf
met., silver-wh., ductile (brittle in presence of trace O, N, C, H), stab. in air		
d 4.5	6.5	13.1
m. p. 1668	1855	2230
b. p. 3260	~4340	5197
$E_0Ti^{2+}/Ti_{sld.} = -1.63$	$E_0M^{4+}/M_{sld.} = -1.43$	−1.57
$E_0Ti^{3+}/Ti_{sld.} = -1.21$		
sol. in HF, HCl, conc. H_2SO_4 alk.; passiv. HNO_3	ac. resist., sol. in (HF + HNO_3), aq. regia	
α-, hex. cl. pack.		
a = 2.95	3.22	3.20
c = 4.68	5.13	5.08
↓ 882°	↓ 862°	↓ 1760°
β-, cub., α-Fe str. type		
a = 3.32	3.61	3.54

$MHal_4$

MCl, M = Zr, Hf, powd., blk., graphite-like. str. MMClClM . . . **ZrCl**, $\Delta H = -286$ **$HfCl_n$**, $n = 0.92-0.99$ $\Delta H = -289$ **ZrBr**, $\Delta H = -193$ **HfBr**, $\Delta H = -204$ **$ZrI_{1.0-1.3}$**, $\Delta H = -142$; $t \longrightarrow M + MCl_4$

Ferroalloys, hard, visc., corrosion resist. **"Ferrotitanium"**, 15–25 or 40–50% Ti, 3–6% Si, 5–8% Al, 3% Cu, ≈ 0.1% C, S, P; in system Fe–Ti ex. sld. s. subtraction, **Ti_2Fe**, **TiFe**, **$TiFe_2$**, and **$TiFe_3$** **"Ferrozirconium"**, deoxidant in steels; in system Fe–Zr ex. sld. s. and **Zr_2Fe_3** (m. p. 1640)

C; Al

$TiO_2 + Fe_2O_3$ (ore)

$0(d^4)$

$M_2[Zr(CO)_6]$, [15] **$Li_2[TiDipy_3] \cdot 6\,Thf$**

Li(Thf)

MCl_4

$[MDipy_3]$, cr. vlt., sol. in bz., mol. – oct. **$Ti(C_6H_6)_2$** **$K_4Ti(CN)_4$**, $\mu_{eff.} = 2.17$ **$K_5Zr(CN)_5$**, $\mu_{eff.} = 2.69$ [14]

$2+(d^2)$

Ti (1700°)

$TiO_{1\pm x}$, powd. golden, m. p. 1750, $\Delta H = -519$, sol. in dil. ac. ($\longrightarrow H_2\uparrow$), NaCl str. type

$Ti(OH)_2\downarrow$ blk., immed. Ox in air

H_2SO_4 (dil.)

$Ti_2(SO_4)_3\downarrow$, grn., sol. in ac. **$\cdot M_2SO_4 \cdot 24\,H_2O$**, M = Rb,Cs, red, alum **$3\,Ti_2(SO_4)_3 \cdot H_2SO_4 \cdot 25\,H_2O$**, vlt.

TiOCl; **TiOBr** [30]

$TiCl_4$

M: AlR_3

M_2TiCl_4 **$CsTiCl_3$**, blk., chains of oct. **$Na_2Ti_3Cl_8$**, in str. cluster $[Ti_3]^{6+}$ [18]

TiF_2, dec. 354, CaF_2 str. type [29] 2.29 + **Ti_7Hal_{16}**, Hal = Cl–I, blk., inflam. in air, $\Delta H = -514$ (Cl), −389 (Br), −268 (I); sol. in H_2O, alc., liq. NH_3; in str. – at. Ti(II), Ti(IV), Ti — Ti 2.95 **$Ti(AlCl_4)_2$**, in str. oct. $[TiCl_6]$

H_2; t

ZrF_2, **Zr_6Cl_{15}** [14] **$ZrBr_2$**, stab. in air **$[ZrI_2]_6$**; **$ZrI_{2.4}$**, clusters, Zr — Zr 3.20, $t \longrightarrow ZrCl + ZrCl_4$; $t \longrightarrow Zr + ZrI_4$; $\Delta H = -963$ (F), −522 (Cl), −260 (I)

$HfCl_{1.92-1.98}$ [17] **$HfBr_2$**, $t \longrightarrow HfHal + HfHal_4$

$CsZr_6I_{14}$

$3+(d^1)$

Ti_2O_3, powd. vlt., m. p. 1830, $\Delta H = -1518$, sol. in ac.-Ox; $\xrightarrow{t}$ TiO + TiO_2; α- Al_2O_3 (corundum) str. type

H_2 (1000°)

Ti_3O_5, bl., $\Delta H = -2456$ **Ti_4O_7** [2]

2000°

$Ti(OH)_3\downarrow$, vlt., sol. in ac., strong Red, + $NO_3^- \longrightarrow NH_3$

OH^-

O_2 conjugate react.: $H_2O + O_2 \longrightarrow H_2O_2$

$MTiO_2$, titanates (III), M = Li, Na, Mg/2

$M[Ti(SO_4)_2] \cdot 12\,H_2O$, M = Rb, Cs, H (· $4\,H_2O$) **$M[Ti_3(SO_4)_5] \cdot n\,H_2O$**

Bronzes [2] **Na_xTiO_2**, $x = 0.2-0.5$, blk., layers of oct. **$Na_{1.7}Ti_6O_{11}$**; **$NaTi_2O_4$**

TiF_3, purp. or vlt., $\Delta H = -1490$ [3] $\xrightarrow{950°}$ **Ti + TiF_4** **$TiCl_3$**, subl. 400, $\Delta H = -719$, α-, vlt., isostr. $FeCl_3$, β-, chains of oct., brn., **$\cdot 6\,H_2O$**, vlt. or grn. **$TiBr_3$**, blk., $\Delta H = -548$, **$\cdot 6\,H_2O$**, vlt. **TiI_3**, needle, blk., $\Delta H = -339$ In str. $MHal_3$ (Hal = Cl–I) – mol. – 2 oct. with common faces; $t \longrightarrow M(II) + M(IV)$;

$MTiF_4$, M = Na—Cs, pink, layers of oct. **M_3TiF_6**, vlt., bl., **$Na_5Ti_3F_{14}$** **K_3TiCl_6**; **$CsTi_2Cl_7$** **$Cs_3Ti_2Cl_9$**, $\mu_{eff.} = 1.3$, **$K_2[TiCl_5(H_2O)]$** **$Cs_2[TiCl_2(H_2O)_4]Cl_3$-*trans***, cr. with dichroism (colrl.–vlt.) **K_3TiBr_6**; **$K_3Ti_2Br_9$** [3] [6] **$K_5[Ti(CN)_8]$**

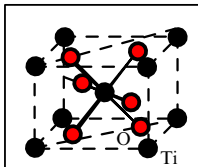
[17]	ΔH	
$ZrCl_3\downarrow$, blk.–grn., in str. – chains	−755	**$HfCl_{2.8-2.9}$**, 420° ⟶ $HfCl_2$, $\Delta H = -758$ **HfI_3**, blk. $\Delta H = -473$; stab. > ZrI_3
$ZrBr_3\downarrow$, blk.	−727	
$ZrI_{2.64-3.4}$, blk.–vlt.	−536	
$ZrHal_3$ – v. strong Red + $H_2O \longrightarrow H_2$ (immed.) + $Ti^{IV} \longrightarrow Ti^{2+}$; + K^+ (liq. NH_3) ⟶ K		

Ti_2S; Zr_2S; Hf_2S; TiE; Ti_2E_3; TiE_2; Zr_2E_3; ZrE_2, Hf_2E_3; HfS_2; TiS_3; HfE_3; ZrE_3; E = S–Te conduct., semiconduct., dielectr., stab. in air, sol. in conc. H_2SO_4, HNO_3 **$M_2^ITiS_3$**; **$BaMS_3$**, M = Ti–Hf. **Zr_4N**, **Zr_3N_4**, **MN**, v. hard, m. p. ≈3000, sol. in alk. (*t*), (HF + $KMnO_4$), el. conduct. MN > M; **Li_5TiN_3**; **$BaZrN_2$** **Zr_2ON_2**; **ZrO_8N_4**; **$Zr_7O_{9.5}N_3$** **ZrB_{12}** **$TiH_{1.5-2.0}$**, **$ZrH_{1.3-2.0}$** [10]

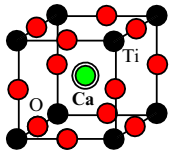
0	2+	3+	4+
Ti	**$[Ti(H_2O)_6]^{2+}$**, colrl. (?), paramagn. (d^2), oct. (d^2sp^3)	[H ↑] ⟷ $H_2O(-H_2)$ **$[Ti(H_2O)_6]^{3+}$**, vlt., paramagn. (d^1), oct. (d^2sp^3) ion	[H ↑] ⟷ O_2; H_2O(Pt) **$[Ti(OH)_n(H_2O)_{6-n}]^{(4-n)+}$**, $n \leqslant 4$ **$[Ti(OH)_nHal_{6-n}]^{2-}$**, **$[(TiO)_8(OH)_{12}]^{4+}$** [16] diamagn. oct. ions, colrl.
Zr	H^+	**$[Zr(H_2O)_6]^{3+}$**, orange, oct. $H_2O(-H_2)$	**$[Zr_4(OH)_8(H_2O)_{16}]^{8+}$** ⇄ **$[Zr(OH)_5(H_2O)_n]^-$** ⇄ **$[Zr(OH)_6]^{2-}$** $\xrightarrow{SO_4^{2-}}$ **$[Zr_{18}O_{10}(OH)_{26}(SO_4)_{13}]^0$** [16] CN Zr8
	aq. regia.; HF + HNO_3		

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_21, © Springer-Verlag Berlin Heidelberg 2011

4 + (d^0)



TiO_2, colrl., d = 3.6–4.3, m. p. 1870, b. p. ≈3000, slow. sol. in ac.– Ox, fused with alk., $NaHSO_4$, ΔH = −941, in tetr. str. "rutile" – net of oct. $[TiO_6]$ with common vertex and triangles $[OTi_3]$. In str. "brucite" and "anatase" – dist. oct.; "anatase" $\xrightarrow{850°}$ "rutile" $\xrightarrow{t,\,p}$ cube, CaF_2 str. type [28]



$CaTiO_3$ str.

$-H_2O$ (t, time)

O_2 (> 600°)

Ca (700°)

Ti

HNO_3 (t)

$TiO(OH)_2 \cdot n\,H_2O\downarrow$, wh., amorph, n < 1, "β-titanic ac.", sol. in HF, conc. HNO_3 (t); X–ray lines of anatase ↑ $-H_2O$ (t, time) n = 1–2, "α-titanic ac.", freshly precipitated, sol. in ac., conc. alk. [11]

MOH (conc.) ($-H_2$)

Titanates [13]
$K_6Ti_2O_7$; $M_2^{II}Ti_2O_5$; $Na_2Ti_3O_7$; $K_2Ti_4O_9$; $Na_4Ti_5O_{12}$
$K_2Ti_6O_{13}$, (fibrous);
$Na_2Ti_7O_{15}$; $Na_2Ti_9O_{19}$
$M_2^{I}TiO_3$, $M^{II}TiO_3$ — meta-, M^{II} = Ca ("perovskite"), Mg ("geikielite"), Fe ("ilmenite"), in str. – chains of oct.
$BaTiO_3$, ferroelectric;
$M_4[TiO_4]$, $Ba_2[TiO_4]$, orto-

MO_2, powd. wh., sol. in HF, melt. alk.
ZrO_2, m. p. = 2850; d = 5.73; ΔH = −1101, α-, monocl. ("baddeleite"),
α- $\underset{1000°}{\overset{1150°}{\rightleftarrows}}$ β-, tetr. $\xrightarrow{2300°}$ γ-, cub., CN Zr 8
HfO_2, m. p. = 2900; d = 9.68; ΔH = −1130 inregular. str. CN M 7, CaF_2, str. type, stab. at 20° with introduction of Y_2O_3, $M^{II}O$

O_2 (4500°)

M

1000°

β-$MO(OH)_2$, wh., sol. in ac. $\xleftarrow{140°}$ **α-$MO_2 \cdot n\,H_2O\downarrow$**, yel., sol. in ac., peptizate, alk.

Zirconates, Hafnates [20]
$Na_2[Hf(OH)_6]$; $K_3Hf_2O_3(OH)_5$; $K_2Hf_2O_4(OH)_2$; $Na_2Hf_4O_9 \cdot 5\,H_2O$; Li_8HfO_6
K_2MO_3; $CaMO_3$; $PbMO_3$, ferroelectrics
$M_6Zr_2O_7$; $K_4Zr_5O_{12}$, oct.
Cs_4ZrO_4, anion tetrah., 300° ⟶ **Cs_2ZrO_3**
$CaTi[Zr_3O_9]$, "calcirtite"
$M_4[Zr(Mo_{12}O_{40})] \cdot n\,H_2O$

NH_4OH; $(NH_4)_2S$; M_2CO_3

an. Ox.

$HOOM(OH)_3\downarrow$, gels, brn. (Ti), wh. (Zr, Hf); + $I^- \longrightarrow I_2$; stab. Ti < Zr, Hf < Th

$Zr_2(O_2)_3SO_4 \cdot n\,H_2O$, [21] n = 8–10

$[Ti(O_2)_2(H_2O)_n]$

H_2O_2 + OH^-

$K_4TiO_4 \cdot 4\,H_2O_2 \cdot 2\,H_2O$, **$K_4M(O_2)_4 \cdot 6\,H_2O$**, M = Zr, Hf, colrl.

H_2O_2 + OH^-

H_2O_2

$K_2[M(O_2)(SO_4)_2] \cdot 3\,H_2O$, red (Ti), colrl. (Zr, Hf)

$M_3[TiF_5(O_2)] \cdot nH_2O$
$K_4[Ti_2F_8(O_2)_2]$. anions – pentag. bipyr. or 2 pyram. with common edge [21]

$K_3[Zr_2(O_2)_2F_7]$, **$\cdot H_2O$** [21]
$K_3[Zr_3F_6(OH)(O_2)_4] \cdot 3\,H_2O$

Cl_2O_7 + $HClO_4$

$ZrCl_4$

$ZrO(ClO_4)_2 \cdot 8\,H_2O$, m. p. 145 [7,23]
$M(ClO_4)_4$, volat., m. p. 96 (Zr), 105 (Hf), in mol. CN M 8
$M(IO_3)_4\downarrow$, insol. in HNO_3, anion – antiprism
$M(OH)_2SO_4$; **$\cdot 4\,H_2O$**
$M_2O_3(NO_3)_2 \cdot 5\,H_2O$,
$MO(NO_3)_2 \cdot n\,H_2O$, n = 3.5–4.5, in str. – $[M(OH)_2(NO_3)_2(H_2O)_4]$
$ZrO(OH)(NO_3) \cdot n\,H_2O$, n = 2, 6
$M(NO_3)_4$, in str. $[M(OH)_2(NO_3)_2(H_2O)_4]$
subl. $\overset{t}{\longleftarrow}$ **$\cdot x\,N_2O_5$**; **$Zr(NO_2)_4$**
$M(HPO_4)_2 \cdot n\,H_2O\downarrow$, variable composit, unlike other M^{n+} expect Pa (pH ≪ 7); s. in H_2SO_4 + H_2O ⟶ $Hf(HPO_4)_2\downarrow$ + Zr^{IV} (in s.)
$MO(C_2O_4) \cdot n\,H_2O\downarrow$, sol. in $H_2C_2O_4$, HCl
$Zr(RCOO)_4$; **$ZrO(CH_3COO)_2$**
$ZrSiO_4\downarrow$, "zirkon", contain >1% HfO_2

$Cs_2[M(ClO_4)_6]$; **$Cs[M(ClO_4)_5]$**; [4,7,33]
$Cs_3[Zr(ClO_4)_7]$
"$Zr(SO_4)_2 \cdot n\,H_2O$", n = 4, 5, 7, contain ions $[Zr(SO_4)_4(H_2O)_4]^{4-}$, $[Zr_2(SO_4)_6(H_2O)_4]^{4-}$, antiprism $[MO_8]$
$K_2[M_2(OH)_4(SO_4)_3(H_2O)_n]$
$Na_6[M_2(OH)_4(SO_4)_5]$;
$Na_{12}[M_2O(SO_4)_9(H_2O)_n]$
$Na_6[M(SO_4)_5(H_2O)_n]$
$[R_4N]_2[M(NO_3)_6]$; **$[NO]_2[Zr(NO_3)_4]$**, [32]
$[(NO_2)(NO)_3]^{4+}[Zr(NO_3)_5]^-$, CN Zr 9
$KZrH(PO_4)_2$; **$Na_2Zr(PO_4)_2 \cdot n\,H_2O$**
$Na_5Zr(PO_4)_3$, **$LiHf_2(PO_4)_3$** [19]
$H_4[MO(C_2O_4)_3] \cdot 7\,H_2O$
$Na_4[M(C_2O_4)_4] \cdot 3\,H_2O$
$M_2Zr[Si_2O_5]_3$, M = Na ("elpidite"),
$M_2Zr[Si_3O_9]$, M = K ("vadeite"),
$Na_5Zr_2[Si_6O_{18}]Cl \cdot 2\,H_2O$, "eudialyte"

$HClO_4$ (100%)

SO_3

N_2O_5

$Ti(ClO_4)_4$, colrl., m. p. 85, subl. 70, dec. 110, CN Ti 8 (dodecah.) [7]
$TiO(ClO_4)_2 \cdot 6\,H_2O$, poorly sol. in H_2O
$TiOSO_4$, dec. 500; **$\cdot H_2O$** [26]
$Ti(SO_4)_2$, **$Ti(OTeF_5)_4$**
$TiO(NO_3)_2 \cdot n\,H_2O$,
$Ti(NO_3)_4$, m. p. 58, subl. 40, inflam. org. subst., CN Ti 8 (dodecah. $[TiO_4N_4]$)
$Ti(HPO_4)_2 \cdot n\,H_2O$, n = 1, 2; **TiP_2O_7**, **$(TiO)_2(P_2O_7)_2$**; **$Ti(HAsO_4)_2 \cdot H_2O$**
$Ba_2Ti[SiO_4]_2$, "fresnoite"
$BaTi[SiO_3]_3$, "benitoite"
$M_2Ti_2[SiO_4]_2O$, M = Na ("ramsayite"), Ca/2 ("sphene", "titanite")

H_2SO_4 (475°)

H_2O

$Cs_2[Ti(ClO_4)_6]$ [7]
$M_2[Ti(IO_3)_6]$ [8]
$H_4[Ti(SO_4)O_3]$ = "$TiOSO_4 \cdot 2\,H_2O$"↓, "titanylsulfat"
$K_2[Ti(SO_4)_3]$; **$K_2[TiO(SO_2)_2]$**
$Na_5Ti(PO_4)_3$
$MTiOPO_4$; **$MTi_2(PO_4)_3$**;
$K_2[TiO(C_2O_4)_2] \cdot n\,H_2O$
$Na_2[TiO(SiO_4)]$, CN Ti 5
$K_3H[Ti_4O_4(SiO_4)_3] \cdot 4\,H_2O$

As_2O_3

H_2O

HF

$TiOHal_2$, Hal = F, Cl (yel.), I (brn.)

$[Ti_8O_{12}(H_2O)_{24}]Cl_8 \cdot HCl \cdot 7\,H_2O$ [27]

[5]	m. p.	b. p.	ΔH
TiF_4, cr. colrl.	—	283	−1644
$\cdot 2\,H_2O$		subl.	
TiF_3Cl, powd. yel.,	—	—	—
$\xrightarrow{125°}$ TiF_4 + $TiCl_4$			
$TiCl_4$, liq. colrl.	−23	136	−803
$TiBr_4$, cr. yel.	40	231	−619
$TiCl_nI_{4-n}$, n = 1, 2, 3	—	—	—
TiI_4, cr. brn., $\overset{t}{\rightleftarrows}$ Ti + I_2	155	377	−510

$TiHal_4 + H_2O \longrightarrow TiO_2 \cdot n\,H_2O\downarrow$ (pH ⩾ 1.5); in str. and gas – mol. $TiHal_4$ — tetrah. (d^3s), in str. α-TiI_4 – chains of oct.
$\cdot$ L, L = $POCl_3$, SCl_4;
$\cdot 2$ L, L = NOCl, R_2O, R_2S, RCN

Ti

HNO_3 + HF

H_2O

K_3HTiF_8 = $K_3[HF_2][TiF_6]$
H_2TiF_6, **$M_2TiF_6 \cdot H_2O\downarrow$**,
$[O_2][TiF_5]$
K_2TiCl_6, yel., K_2PtCl_6 str. type
$MTiCl_5$, M = $[R_4N]$, $[R_4As]$
$M[Ti_2Cl_9]$, M = $[SCl_3]$, $[PCl_4]$,
$[R_4N][TiBr_5]$,
K_2TiBr_6, red
M_2TiI_6, dark-red [1,12]

$M_2[Ti(NCS)_6]$ [9]
$BaTiO(OPr\text{-}i)_4 \cdot PrOH$ [31]

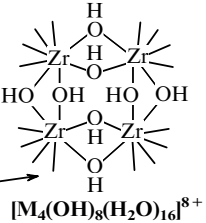
$Zr_3F_8O_2$; **Zr_2F_6O**, **$M_2O_3Cl_2 \cdot 5\,H_2O\downarrow$**; **$MOCl_2$** [24]

[25]	subl.	m. p. (p)	ΔH		subl.	m. p. (p)	ΔH
$ZrF_4\downarrow$	903	912	−1911	$HfF_4\downarrow$	974	1025	−1929
$ZrCl_4$	331	437	−979	$HfCl_4$	317	432	−988
$ZrBr_4$	357	450	−761	$HfBr_4$	322	420	−837
ZrI_4	431	499	−485	HfI_4	392	—	−586

+ $H_2O \longrightarrow MOHal_2$
In monocl. str. MF_4 – antiprism $[MF_8]$. In str. $ZrF_4 \cdot H_2O$ – frame of dodecah., $MF_4 \cdot 3\,H_2O$ – $[(H_2O)_3F_3Zr]_2F_2$ and chains – Hf — F — Hf . . ., CN M 8. In str. $MHal_4$ (Hal = Cl – I) – chains of oct. $[MHal_2Hal_{4/2}]$, in gas – mol. tetrah.

Pb_5ZrF_{14}; **Pb_3ZrF_{10}**; [22]
$Li_4[MF_8]$, **$M_2[Zr_2F_{10}(H_2O)_2]$**
dodecah. or antiprism
$M_3^IMF_7$, pentag. bipyr. or single-cap. trig. prism
$M_2^IMF_6\downarrow$, dodecah. (4 μ-F), antiprism, 2 single-cap. trig. prism (CN 7), 2 gr. $[MF_5F_{3/2}]$ or oct.
$H_2ZrF_6 \cdot H_2O$; **M^IZrF_5**, chains of oct. **$[H_3O]ZrF_5 \cdot H_2O$**
$M_2^IMCl_6$, **MZr_2Cl_9**; **K_3ZrCl_7**
$Rb_2[HfBr_6]$, oct.

In str. of salts of "titanyl", "zirconyl", "hafnyl" — polymer chains — M — O — M — O — linked polydentate anions. In oct. $[TiO_6]$ and gr. $[HfO_8]$ (antiprism or dodecah.) includet at. of anions and H_2O. Ions $[M = O]^{2+}$ dont ex. in the str. and s. In str. of $MOCl_2 \cdot 8\,H_2O$ (Zr, Hf) – cations



$[M_4(OH)_8(H_2O)_{16}]^{8+}$

THORIUM

Th^0 5f° | 6d: ↓ ↓ | 7s: ↓↑ | 7p: | **EN** 1.1

2 + (d^2) **3 + (d^1)** **4 + (d^0)**

Th, met., silver-wh., pliant, $d = 11.7$, m.p. 1750, b.p. 4200, tarnish in air; powd. pyrophoric sol. in (conc. HCl + F$^-$), aq. regia, passiv. conc. HNO_3, $E_0Th^{4+}/Th_{sld} = -1.87$, α-, cub. cl. pack $a = 5.08$, Th—Th 3.59 ↓ 1365° β-, α-Fe str. type, $a = 4.11$

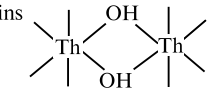
O_2; Ca (Ar, 1100°); H_2O (steam)

ThO_2, powd., wh., $d = 9.87$, m.p. 3220, b.p. 4400, sol. in conc. H_2SO_4 (*t*), (HF + HNO_3), bright light in flame (in the presence 1% Ce_2O_3), $\Delta H = -1225$, CaF_2 str. type (CN Th 8), "thorianite" (+ UO_2)

$Th(C_2O_4)_2$ —600°, (−CO_2−CO)→ **ThO_2**

t

$Th(OH)_4$↓, gel wh., SP = 10^{-35}, sol. in ac., M_2CO_3 (unlike La $(OH)_3$↓), absorb, CO_2, peptizate alk., in str. — chains



NH_4OH; $(NH_4)_2S$; M_2CO_3

$Th_2O_7 \cdot 4H_2O$ [13] = $2ThO_2 \cdot 3H_2O_2 \cdot H_2O$
$Th(O_2)^{2-}_{1.6}O_{0.15}X_{0.5} \cdot nH_2O$

$[Th(HSO_4)(SO_4)]^+$ [8]

$[ThCl_n]^{(4-n)+}$; $[Th(NO_3)]^{3+}$

aq. regia; $H^+ + F^-$

$[ThF_n(H_2O)_m]^{(n-4)-}$

F^- ↑↓

$[Th(H_2O)_n]^{4+}$

Th — $HClO_4$ ↑↓ H_2O (pH > 3)

$[Th(OH)_n(H_2O)_m]^{(4-n)+}$, $n = 1-3$

H^+ ↑↓ H_2O

$[Th_2(OH)_6(H_2O)_n]^{2+}$ ...

H^+ ↑↓ OH^-

$[Th_6(OH)_{15}(H_2O)_n]^{9+}$ ↓ **$[Th_4(OH)_{12}]^{4+}$** in polymeric ions — OH-br.

H^+ ↑↓ OH^-

$Th(OH)_4$↓, wh.

S; H_2S; H_2; N_2

cath. Red: Ca; Ba; Mg; *t*

Th Hal_4

ThS; Th_2S_3; Th_4S_7; ThS_2
Th_2S_5, CN Th 10 [9]
Th_3N_4, ("Th_2N_3"), **ThN**
Th_2N_2O
ThC, **ThC_2**, + $H_2O \longrightarrow CH_4 + C_nH_{2n} + \ldots$
ThSi; **$ThSi_2$**; **Th_3Si_2**
ThB_4, **ThB_6**
ThH_2, **Th_4H_{15}**

$Th(IO_3)_4$↓, insol. in 50% HNO_3 [unlike $Ln(IO_3)_3$]
$Th(OH)_2SO_4$ [10]
$Th(SO_4)_2$, colrl., hyg., $\cdot nH_2O$, n = 2, 4, 6, 8, 9, in str. — $[Th_6O_4(OH)_4]^{12+}$
$Th(OH)_2CrO_4 \cdot H_2O$
$Th(NO_3)_4$, $\xleftarrow{N_2O_5}$ $\cdot 5H_2O$, in s. hydr. readily sol. in alc. R_2O, acet. (unlike $Ln(NO_3)_3$), in str. — $[ThO_8(H_2O)_3]$
$Th(PO_3)_4$↓, cr., from melt., hydr., sol. in ac.; **(Zn, Th)PO_4**, "monazite"
$Th(HAsO_4)_2 \cdot nH_2O$, n = 1–4 [11]
$ThO(CO_3) \cdot 8H_2O$↓
$Th(HCOO)_4$ [5]; **$[Th(HCOO)_4(H_2O)_2] \cdot H_2O$**, CN Th 10
$Th(C_2O_4)_2 \cdot 6H_2O$↓, insol. in ac. (unlike Zr)
$ThSiO_4$, "orangite", "thorite" (blk.)

$K[Th_4(IO_3)_{17}] \cdot 18H_2O$↓ [6]
$H_2[Th_2(SO_4)_5] \cdot 2H_2O$; **$M_8[Th(SO_4)_6]$**
$M_2[Th(SO_4)_3]$, $\cdot nH_2O$, CN Th 9
$M_4[Th(SO_4)_4] \cdot 2H_2O$, CN Th 9 (trig. prism. with centered faces)
$M[Th(NO_3)_5]$; **$M_2[Th(NO_3)_6]$**, M = M^I, H
$Mg[Th(NO_3)_6] \cdot 8H_2O$, CN Th 12 (icosah.)

$Na_6[Th(CO_3)_5] \cdot 12H_2O$, CN Th 10; [6]
$M_2Th(CO_3)_3 \cdot nH_2O$; **$Na_4Th(CO_3)_4 \cdot 7H_2O$**
$(NH_4)_2[Th_2(C_2O_4)_5]$↓
$M_4[Th(C_2O_4)_4]$, M = K, NH_4, anion — twocap square antiprism [7]

$Th(O_2)SO_4 \cdot 3H_2O$
$H_2[Th(O_2)(SO_4)_2]$

ThOHal$_2$, Hal = F – I, in str. — chains Th—O—Th—

3, 4)	m.p.	b.p.	ΔH	$\cdot nH_2O$, n =
ThF_4↓, SP = 10^{-26}, insol. in ac.	1100	1680	−2096	1/6, 2, 4
$ThCl_4$, colrl.	770	922	−1192	2–12, **8**
$ThBr_4$, »	678 [4]	880	−1012	4, 7, 8, 10, 12
ThI_4, yel.	566	837	−673	10

In str. ThF_4 (ZrF_4 str. type) — antiprism $[MF_8]$; $ThCl_4$, $ThBr_4$ (UCl_4 str. type) — 2 crossing tetrah. (CN = 4 + 4).
$ThF_4 \cdot 1/6\,H_2O$, trig. twocap. prism and tetr. antiprism

$ThCl_2$ (?) [1]
$ThBr_2$
ThI_2 = $Th^{4+}(I^-)_2e_2$ (?), cr. golden, conduct., m.p. 566, CdI_2 str. type, 880° ⟶ Th + ThI_4↑

$ThCl_3$ (?) [1]
$ThBr_3$
ThI_3, α-, β-, CN Th 8 (cube and square antiprism), Th—Th 3.46

Th

K_5ThF_9 (CN Th 8) [2]
Na_4ThF_8; **M_3ThF_7**, CN Th 9 (tetr. single-cap prism)
Th—F 2.36–2.40
M_2ThF_6; **$MThF_5$**; **$RbTh_3F_{13}$**
M_2ThCl_6; **$[PyH]_2[ThCl_6]$**
M_2ThBr_6
K_2ThI_6; **Li_3ThI_7**, in str. — tetr. single-cap. prism $[ThI_9]$

$[R_4N]_4[Th(NCS)_8]$, anion — cube [14]

$(NH_4)_3[ThF_5(O_2)]$

$Th(CH_3COCHCOCH_3)_4$, subl. 160; in mol. — dodecah. $[ThO_8]$ [12]
$Th(BH_4)_4$, sol. in Et_2O, m.p. 204, subl. 40 (vac.)

Th — HCl conc. (output 25 %) → **$H_{1.3}ThO_{1.3}Cl_{0.7}$**↓, (before "ThO"), blk.

Use of Th:

$^{232}_{90}Th\ (n, \gamma)\ ^{233}_{90}Th \xrightarrow{\beta^-} {}^{233}_{91}Pa \xrightarrow{\beta^-} {}^{233}_{92}U$ nuclear fuel

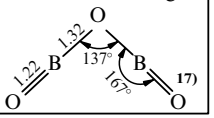
N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_22, © Springer-Verlag Berlin Heidelberg 2011

BORON OXYGENOUS COMPOUNDS

B_2O_3, cr., colrl., $d = 2.56$, m. p., 450, b. p. 2250, $\Delta H = -1276$, str. contain flat chains of triangles $[B_2O_3]$, (all O-at. br.), B—O 1.33–1.40

↑ H_2O (5–10%, *p*, *t*)

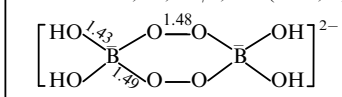
Glass, hyg., soften at ≈200°, $\Delta H = -1256$, readily sol. in H_2O, str. contain random arrangment of triangles $[BO_3]$ (sp^2); in gas – angular mol.



17)

$B_2O_3 \cdot E_2O_5$, E = P, As, cristobalite str. (Si ⟶ B, E), cr., not hyg., sol. in alk.

"Perborates" 18)
$LiBO_3 \cdot H_2O$
$M_2[B_2(O_2)_2(OH)_4] \cdot n\,H_2O$ = "$MBO_3 \cdot n\,H_2O$", M = Li–Cs; Sr, Ba/2, Na (n = 0, 2, 4, 6),

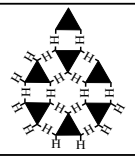


cycle of the chair type, do not react with KI

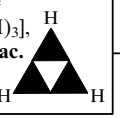
acids

Boric acid $B_2O_3 \cdot n\,H_2O$ and borates $M_2O_n \cdot m\,B_2O_3 \cdot x\,H_2O$ 8,20)
in $[BO_3]$ triangle B—O 1.32–1.52, in $[BO_4]$ tetrah. 1.43–1.54

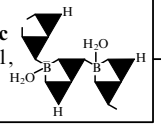
H_3BO_3, orthoboric ac., "sassolin", cr., colrl., plate, $d = 1.43$, m. p. 171, grn. flame, sol. in H_2O 4.3% (20°), layered str.



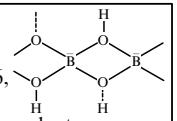
70° (−H_2O) → **α-$[HBO_2]_3$** = $[B_3O_3(OH)_3]$, **trimetaboric ac.** m. p. 176, rh. str.



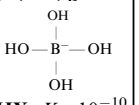
130° → **β-$[HBO_2]_\infty$**, **polymetaboric** ac., m. p. 201, monocl., chain str.



140° → **γ-$[HBO_2]_\infty$**, **polymetaboric** ac., m. p. 236, v. slow. sol. in H_2O, framework str.



$[B(OH)_4]^- = X$



HX, $K = 10^{-10}$

$H_2O + H^+$ ⇄ M $(OH)_n$

$[B_3O_3(OH)_4]^- = X$ 30)
HX – strong ac.
KX · $n\,H_2O$

MOH ⇄ $H_2O + H^+$

$[B_4O_5(OH)_4]^{2-} = X$
in anion: 2 nonplanar cycles $[B_3O_3]$
$Na_2X \cdot 8\,H_2O$ = "$Na_2B_4O_7 \cdot 10\,H_2O$", "borax", m. p. 75
↓ 62°
$Na_2X \cdot 3\,H_2O$ = "$Na_2B_4O_7 \cdot 5\,H_2O$", "tinkalkonite" (jewelry drill)
$(NH_4)_2X \cdot 2\,H_2O$
$K_2X \cdot n\,H_2O$, n = 2, 3; **$Cs_2X \cdot 3\,H_2O$**

$[B_5O_6(OH)_4]^- = X$, 2 plain cycles in perpendicular plane
MX · 3 H_2O, "$MB_5O_8 \cdot 5\,H_2O$", M = Li, Na ("sborgit")
$MX \cdot 2\,H_2O = MB_5O_8 \cdot 4\,H_2O$
M = K–Cs, NH_4, Tl

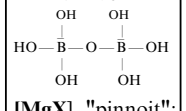
H_2O_2 → B(OMe)$_3$ + M^IOR → H_2O_2 (30%)

$[B_6O_7(OH)_6]^{2-}$
$MgX \cdot n\,H_2O$, n = 2–4 15)
$CaX \cdot H_2O$ (?)
$Na_6MgX_4 \cdot 10\,H_2O$ 16)

island "hydrates" and ions in sol.

LiX · 6 H_2O
NaX, · 2 H_2O,
α-CsX · 2 H_2O
$M^{II}X_2$, · 2 H_2O,
M^{II} = Ca–Ba
CuClX, "bandylite" 9)

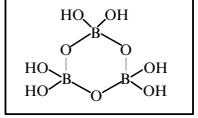
$[B_2O(OH)_6]^{2-} = X$



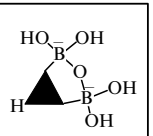
[MgX], "pinnoit"; **$Na_2X \cdot 5\,H_2O$**

$[B_2O_4(OH)]^{3-}$ 25)
$Mg_2X(OH)$, "asharit"
$Ca_2X(OH)$, "sibirskit"

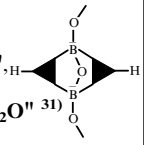
$[B_3O_3(OH)_6]^{3-} = X$
$Ca_3X_2 \cdot 2\,H_2O$ 30)



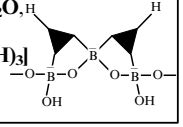
$[B_3O_3(OH)_5]^{2-} = X$
MgX, · $n\,H_2O$, n = 3, 5 ("inderite", "kurnakovit")
CaX · $n\,H_2O$, n = 1; 2; 4
$CaMgX_2 \cdot 6\,H_2O$;
ZnX · H_2O 10)



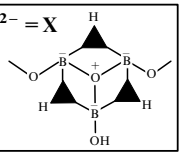
$[B_4O_6(OH)_2]^{2-} = X$
$Na_2X \cdot 3\,H_2O$ = = "$Na_2B_4O_7 \cdot 4\,H_2O$", "kernite"
Na_2X = "$Na_2B_4O_7 \cdot H_2O$" 31)
$K_2X \cdot 3\,H_2O$



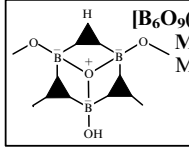
$[B_5O_7(OH)_4]^{3-} = X$
NaCaX · 3 H_2O, "probertit"
$Na_2[B_5O_7(OH)_3] \cdot 2\,H_2O$, "eskurusit"



$[B_6O_8(OH)_4]^{2-} = X$
$CaX_2 \cdot 3\,H_2O$

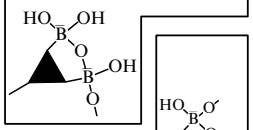


$[B_6O_9(OH)_2]^{2-} = X$
$M^{II}X \cdot 3\,H_2O$,
M^{II} = Ca–Ba 15)

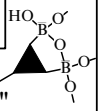


3-dimensional polyborates

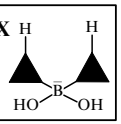
$[B_3O_4(OH)_3]^{2-}$
CaX · H_2O, "colemanit"
$CaMgX_2 \cdot 3\,H_2O$, "hydroborazite"



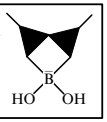
$[B_3O_5(OH)]^{2-}$
CaX, "fabianit"



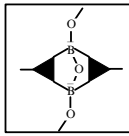
$[B_3O_4(OH)_4]^{3-} = X$
$K_3X \cdot 2\,H_2O$ 11)

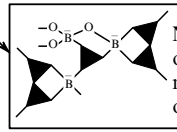


$[B_3O_4(OH)_2]^- = X$
TlX · 0.5 H_2O 11)



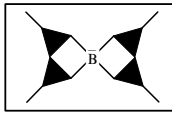
$[B_4O_7]^{2-} = X$
M_2X_n, M = Li, Mg, Zn, Cd 13)



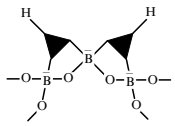


$Na_2B_4O_7$, m. p. 741 or 711, slow. cr. from melt or by annealing of the glass 14)

MB_5O_8, M = K, Rb



$[B_5O_8(OH)_2]^{3-} = X$



Li_3X, **$Na_3X \cdot H_2O$** 32)

$NaCa_2[B_9O_{14}(OH)_4] \cdot 2\,H_2O$
$Na_8[B_{12}O_{20}(OH)_4]$
$Ag_6[B_{12}O_{18}(OH)_6] \cdot 3\,H_2O$,
str.: chains or layers of triangles and tetrah. 27)

MgAl[BO_4], "singalite", $[BO_4]$ tetrah. and $[MO_6]$ oct.

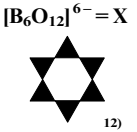
Island

$[BO_3]^{3-} = X$ orthoborates
M_3X_n, M = Li, Na, Mg, Ba, Cd, In, Sc, Ln, Mn, Ni, Co 28)

$[B_2O_5]^{4-} = X$ pyro-
M^{II}_2X, M^{II} = Fe, Co, Mn 29)

$[B_3O_6]^{3-} = X$ trimeta-
M = Na, K, Ca–Ba/2

$[B_6O_{12}]^{6-} = X$

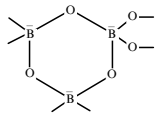

12)

Chain



$[M(BO_2)_n]_\infty$, polymeta-
M = Li, Mg–Ba, Pb, Cu, Mn, Fe, $[B_2O_4]_\infty$ chains

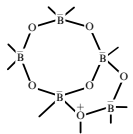
Framework



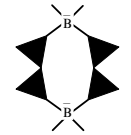
β-$LiBO_2$, **$Cu(BO_2)_2$** 12)



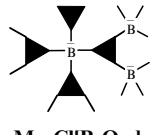
MB_3O_5, 11)
M = Li, Cs



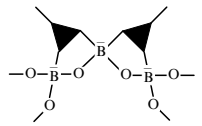
$M^{II}B_4O_7$,
M = Sr, Pb



$M_5[B_5O_{10}]$ 12)



$Mg_3Cl[B_7O_{13}]$, "boracite"



$Na_3[B_5O_9] \cdot H_2O$ 32)

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_23, © Springer-Verlag Berlin Heidelberg 2011

BOREON

B_2O_3 + H_2 (Al + $AlCl_3$);
BCl_3 + H_2 (discharge, in vac.);
BF_3 + LiH (−$LiBF_4$);
alloy (MgB_2 + Mg) + H_3PO_4
(Stock method)

BH_3 [:L]

L	m. p.	b. p.
Me_2O	dec. −80	—
Me_2S	−83	38
MeCN	—	—
SiH_3CN	—	—
CO	−137	−64
NH_3, → **$[H_3NBH_2NH_3]^+(BH_4)^-$**		
NMe_3, "borazan"	94	171
N_2H_4	61 (dec.)	
PH_3	—	—
PMe_3	103	—
PF_3	−116	−62
$P(NH_2)_3$	—	—
$AsMe_3$	74	dec. 120
$P(NMe_2)_3$↓	—	—

Mol. – tetrah.,
B—H 1.19–1.21, ∠HBH 114,
B—L 1.54 (C), 1.56 (N), 1.84 (P)

L

B_2H_6 → LiH, NaH [$B(OMe)_3$]

alloy MgB_2 + Mg → H_3PO_4 (Stock)

Boranes, gases, liq. or cr. with disgusting odour, separate by distil.; + H_2O ⟶ H_3BO_3 + H_2, do not react. with conc. H_2SO_4, act. lowering in homolog. series, ΔH of burning is v. great (−485 B_2H_6). Mol. consists of triangles [B_3], [B_2H], [BH_2], μ- B–at. (CN 4) and H (CN 2), B—B 1.68–1.95, B—H 1.10–1.36 (term., μ); el.– defic. mol. with multicentr. bonds

Homolog. series	3–	1.8–	1.67–	1.5–	1.4–	1.25–	1.22–
B_nH_{n+4}	**B_2H_6** diborane, gas	**B_5H_9** penta-9	**B_6H_{10}** hexa-10	**B_8H_{12}** octa-12	**$B_{10}H_{14}$** deka-14	**$B_{16}H_{20}$** cr.	**$B_{18}H_{22}$** cr.
m. p.	−165	−46	−62	−20	100	99	180 (*n*)
b. p.	−92	60	108	—	213	—	129 (*iso*)
dec.	>25	150 (slow)	25 (slow)	−20	250	—	—
ΔH	+35	+114	+84	—	−39	—	—
μ	0	3.37 (liq.)	—	—	3.62 (bzl.)	—	—
in air + H_2O	inflam. dec. immed.	inflam. hydr. (*t*)	stab. hydr. (*t*)	?	v. stab. ⇄ H_3O^+ + + $B_{10}H_{13}^-$	—	strong ac., $K_2 = 10^{-8}$
	mol. – two fragments of icosah. with common edge B—B						

200°

Homolog. series	2.5–	2.2–	2.0–	1.7–	1.6–	1.3–
B_nH_{n+6}	**B_4H_{10}** tetra-	**B_5H_{11}** penta-11	**B_6H_{12}** hexa-12	**B_9H_{15}** ennea-15	**$B_{10}H_{16}$** deca-16	**$B_{20}H_{26}$** 2,2′-Bi(nido)-deca
m. p.	−120	−122	−82	3	cr.	mol. – 2 basket [$B_{10}H_{14}$] with bond B—B [34]
b. p.	18 (dec.)	63	80–90	—		
dec.	25	25 (⟶$B_{10}H_{14}$)	25	75		
ΔH	+68	+92	—	—		
μ	0.56 (bz.)	—	—	—		
in air + H_2O	stab. slow. hydr.	inflam. rapid hydr.	stab. ⟶ B_4H_{10} + H_3BO_3 + H_2	stab.		

60° *t* (urotropine)

I_2 (−HI)

−H_2 (350°, vac.)

0.8–
$B_{20}H_{16}$, icosoboran-16, cr., colrl., hyg., m. p. 197, stab. in air, sol. in org. solv., + H_2O ⇄ $H[B_{20}H_{16}(OH)_2]$; mol. – 2 [$B_{10}H_{14}$] with common faces

B_5H_9 → C_2H_2 (discharge)

$B_nC_2H_{n+2}$, carboranes [1]
(isoel. of boranes)
$B_3H_3C_2H_2$, ($\Sigma e = 22 = \Sigma e$ B_4H_{10}),
m. p. −126, b. p. −4
$B_{10}H_{10}C_2H_2$, "carborane"
($\Sigma e = 50 = \Sigma e$ $[B_{12}H_{12}]^{2-}$),
cr. colrl., sol. in org. solv., insol. in ac., alk.
Mol. – icosah.

HC—CH
$B_{10}H_{10}$

Isomers: *orto*-, (C, C-1.2), m. p. 320, μ = 4.53
↓ 475°
meta (*neo*)-(C, C-1.3), m. p. 263, μ = 2.85,
↓ 615°
para (*iso*)- (C, C-1.4), m. p. 261, μ = 0

B_2O_3 → C

B_4C, carbide, blk., v. hard, d = 2.5, m. p. 2450, b. p. > 3500, ΔH = −71, NaCl str. type, ([B_{12}] = Na^+, linear gr., [C=C=C] = Cl^-)
↑ 1200° (–C)
BC_3, film, str. anal. of graphite
$B_{13}C_2$, B_2Si, B_4Si [26]

Borohydrides

MOH (−H_2−M_3BO_3)

		dec.	
Salt-like	**$LiBH_4$**, colrl.	278	nonvolat., + H_2O → H_2↑, (Li ≫ Na > K), strong Red., NaCl str. type, $[BH_4]^-$ – tetrah.
	$NaBH_4$	400	
	KBH_4	500	
	$Mg(BH_4)_2$	280	
	$Ca(BH_4)_2$	320	
	$MBH_4 \cdot n H_2O$	—	
Polymer	**$CuBH_4$**	−12	unstab.
	$Zn(BH_4)_2$, **$Cd(BH_4)_2$**, colrl.	85, 25	insol. in org. solv., hyg.
Covalent	**$Be(BH_4)_2$**, **$Al(BH_4)_3$**, colrl.	91, −65 (m. p.) 45 (b. p.)	volat., sol. in Et_2O, C_nH_m, immed. hydr., in mol. – μ- H
	$Sn(BH_4)_4$, yel.	−65	
	$Ti(BH_4)_4$, grn.	25	
	$Zr(BH_4)_4$, **$Hf(BH_4)_4$**, colrl.	29 (m. p.) 128 (b. p.), 29 (m. p.) 118 (b. p.)	
	$U(BH_4)_4$, grn.	70	

3–	2.3–	2–	1.4–	1.33–	1.2–	1.1–	0.9–	0.8–	0.75–	0.67–
$Na[B_2H_7]$, anion $[H_3B\cdots H\text{-}\cdots BH_3]$	**$Na[B_3H_8]$**, stab. to hydr.	**$M_2[B_2H_6]$**, [24]	**$M[B_5H_8]$**, **$M[B_9H_{14}]$**, **$M[B_{10}H_{15}]$**	**$M[B_6H_9]$**, **$M[B_{11}H_{14}]$**	**$M[B_9H_{12}]$**, unstab. **$M[B_{10}H_{13}]$**, **$M_2[B_{10}H_{14}]$**, stab. to hydr., mol. basket	**$M[B_{11}H_{13}]$**, stab. at pH ≫ 7	**$M[B_9H_9]$**	**$M_2[B_{10}H_{10}]$**, stab. to ac., alk. + MnO_4^- ⟶ $[B(OH)_4]^-$ **$(H_3O)_2[B_{10}H_{10}]$**, v. strong ac., anion two-cap antiprism ↓ **$M_2[B_{12}H_{12}]$**, **$H_2[B_{12}H_{12}] \cdot n H_2O$**, v. strong ac. [24] **$Na_2[B_{20}H_{18}]$**, **$M_3[B_{20}H_{19}]$** [21]	**$M_2[B_8H_8]$**, **$K_4[B_{20}H_{18}] \cdot 2H_2O$**; + H_2O ⟶ $B_{18}H_{22}$	**$M_2[B_6H_6]$** oct.

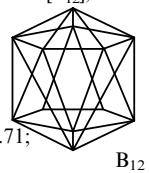
$B_{10}H_{14}$ (+ H_2O) H^+ OH^- MnO_4^-; $Cr_2O_7^{2-}$

M = Li – Cs, $[R_4N]$, $[R_4P]$, sol. in Et_2O

B⁰ 2s ↓↑ 2p ↓ | EN 2.0

1+ 2+ 3+

B, powd. amorph., colrl. (brn. – ture) or cr. blk., m. p. ≈2075, b. p. ~3700, hard ≈ diamond, sol. in HNO_3, H_2SO_4, insol. in alk.; monocr. – semiconduct.; α-, tetr., d=2.37, a=8.73, c = 5.03, in str. – icosah. [B_{12}], B—B 1.60–1.80, CN B 5 (=8–3); β-, rhombohedral, d=2.46, a = 10.92, c = 23.81, cub. cl. pack. [B_{12}], B—B 1.71; vitriform B [36]



BBr_3 (t, $-Br_2$) | BCl_3 H_2(1200°) | BI_3 1000° ($-I_2$)

B_2O | B_2O_3 + Zn | ZnO (1500°) | B_2O_3 + H_2O

B_2O [2]
B_6O
B_7O
$B_{13}O_2$

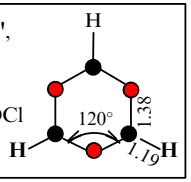
B_2O_3 (> 1000°)

$(BO)_x$, powd. wh., amorph., subl. 1500, v. react.; + H_2O ⟶ $B_2(OH)_4$ + H_3BO_3 in gas – linear mol. O=B—B=O

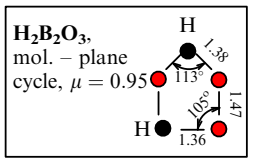
$-H_2O$ (250°, vac.)

$B_2(OH)_4$, hipoboric ac., cr. colrl., sol. in H_2O, alk., strong Red.; + O_2 + OH^- ⟶ $[B(OH)_4]^-$; + H_2O $\xrightarrow{90°}$ H_2 + H_3BO_3

$B_3O_3H_3$, "boroksin", mol.: plane cycle; $\xrightarrow{t}$ B_2H_6 + B_2O_3; + HCl ⟶ H_2 + BOCl



$H_2B_2O_3$, mol. – plane cycle, μ = 0.95



BX_3, cr. colrl., v. hyg.
$B(ClO_4)_3$, dec. –5;
$B(HSO_4)_3$
$B(OTeF_5)_3$
$B(NO_3)_3$, dec. 0;
BPO_4 m. p. 1600
$BAsO_4$
$B(CH_3COO)_3$, m. p. 149 [19]
$B_2O(CH_3COO)_4$

M_2SO_4

$M[B(ClO_4)_4]$ [5,19]
$M[B(HSO_4)_4]$
$M[B(SO_4)_2]$
$K[B(SO_3Hal)_4]$
$M[B(NO_3)_4]$
$M[B(CH_3COO)_4]$
$Na[B_2O(CH_3COO)_5]$
M = K–Cs, [R_4N] Anions tetrah.

H_3BO_3 | KF

K[BF(OH)$_3$]
H[BF_2(OH)$_2$], K[BF_2(OH)$_2$]
↑ H_2O(–HF)
H[BF_3(OH)] = "$BF_3 \cdot H_2O$", cr. colrl., m. p. 10, strong ac.
$[H_3O]^+[BF_3(OH)]^-$ = "$BF_3 \cdot 2H_2O$", m. p. 6, b. p. 60/133 Pa, anion tetrah.

HF | H_2O $K_{hydr.} = 10^{-3}$ | **M[BF_3(OH)]** [7] **Ba[BF_3O]**

HBF_4, ex. only in s., strong ac., toxic
M[BF_4], M = Na (m. p. 384, "ferrucite"), K (m. p. 570), NH_4 (subl. 350), Cs↓ ("avogadrite"), [R_4N]↓, [NO], [NO_2], [ClF_2] (m. p. 30), [ClO_2], [NF_4] (dec. 240; + H_2O ⟶ O_2), [XeF_5], [O_2] (stab. < 0), M^{n+} – readily sol. in H_2O; anion – tetrah., B—F 1.39–1.41
M[BCl_4], M = NH_4, K–Cs, [R_4N], [PyH], [PCl_4], cr. colrl. ([NO] – orange.), rapidly hydr.
M[$BHal_3X$], Hal = F, Cl, X = Cl, ClO_4, NO_3 [22]

BN, nitrid, **"wh. graphite"**, d = 2.34, m. p. 3000 (p N_2), subl., dec. 1000, ΔH = –256, chem. inert, sol. in melt alk., slow. hydr., hex. str. of graphite B—N 1.45, ∠NBN 120 (sp^2)

↓ 1800°, $6 \cdot 10^9$ Pa

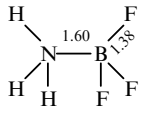
"borazon", cr. yel.-blk., m. p. > 3200 (p), v. hard, cube, diamond str. type, dec. 2000, B—N 1.57 (sp^3) [6]

F₂ (20°); Cl₂ (400°); Br₂ (700°); I₂ (900°)

$BF_2(OH)$, mol. – triangle ↑$B_2O_3(t)$ [4]

	m. p.	b. p.	ΔH
BF_3, gas colrl.	–127	–100	–1138
BCl_3, gas colrl.	–107	13	–404
BBr_3, liq. colrl.	–46	90	–243
BI_3, cr. colrl.	50	210 (dec)	–38

In cr. and gas – triangles BCl_3 (sp^2); BF_3 + H_2O ⇄ HBF_4 + H_3BO_3; $BHal_3$ + H_2O ⟶ H_3BO_3 + HHal (Hal = Cl–I); $BHal_3$ – v. strong Lewise ac.
[$BHal_3$(:L)], L = NR_3, PR_3, AsR_3, R_2O, R_2S, R_2CO,
[$BF_3(NH_3)$], m. p. 162(p), $\xrightarrow{125°}$ BN + NH_4BF_4,
+ H_2O ⟶ $[NH_4]^+$ + $[BF_3OH]^-$ readily sol. in H_2O;
Mol: 2 cross tetrah.
[$BCl_3(NH_3)$] [33]

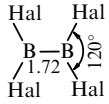


⇄ H_2O ⟶ > 20°

NH_4Cl (t)

$B_3O_3X_3$, boroxols, stab. decreases in the series: R > NR_2 > OR > Hal > H

B_2F_4, gas colrl. m. p. –56, ΔH —
B_2Cl_4, liq. colrl. m. p. –93, ΔH –491
B_2Br_4, liq. colrl. m. p. +1, ΔH —
B_2I_4, cr. yel. m. p. —, ΔH —
+ H_2O ⟶ $BHal_3$ + B_2H_6;
+ NH_3 ⟶ NH_4Cl + $B_2(NH)_2$;
+ [R_4N]Cl ⟶ [R_4N]$_2$[B_2Cl_6];
0° (slow.) ⟶ $(BHal)_n$ + $BHal_3$.
In str. – mol. B_2Hal_4

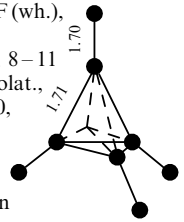


[37]

(BO)$_x$ | Hg

discharge (–Hal$_2$)

$(BHal)_n$, Hal = F (wh.), Cl (yel.), Br (red), I (blk.), n = 4, 7, 8–11
B_4Cl_4, cr., yel., volat., m. p. 95, dec. 200, inflam. in air., mol. – tetrah. (4 el. pairs at. B dispensed between 6 B—B bonds).
B_8Cl_8, cr., red., mol. – antiprism [B_8]
B_8Br_8, brn., subl.
B_9Cl_9; B_9Br_9, mol. three-cap. trig. prism
B_9I_9, brn., b. p. 200
$B_{10}Cl_{10}$, orange.; **$B_{10}Cl_{11}$** [3, 37]



[R_4N]$_2$$B_9Hal_9$, Hal = Cl, I
$M_2[B_{10}Cl_{10}]$, M = Na—Cs, dec. > 100°
$Cs_2B_{12}Cl_{12}$, sol. in unpolar. solv., colour, stab. in air [23]

$M^I_3BO_3$ + M_2O_n

M(t): M_2O_n + C (t)

cath. Red

Borides

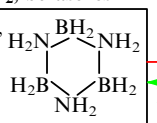
M_4B, M_3B, M_2B		M_3B_2	MB	M_3B_4	MB_2	MB_6	MB_{12}
Mn, V, Cr	Cr, Mo, W, Nb, Ta, Mn, Fe, Co, Ni, Be	V, Nb	Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni	Nb, Ta, Cr, Mn	Mg, Al, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, U, Fe	Ca, Sr, Ba, Ln, As, Th	Al, U, Zr
Isolate at. B	*anti* – CaF str. type	gr. [B_2]	NaCl str. type or chains B_∞	Flat ribbons of 6-member cycles	Layers graphite type	Framework CsCl str. type, oct. ([B_6] = Cs, M = Cl)	NaCl str. type, cubooct. ([B_{12}] = Na, M = Cl)

Borides of transit. M nonstoich. comp. (especially MB_2) – v. hard, heat-resist. (m. p. TiB_2 > Ti 1000°), ac. resist. (TaB_2 insolv. in aq. regia), B—M bond – met. (conduct. ZrB_2 about 10 time > Zr),
"Ferroboron" (1.2% B, 3–5% Al, 3–4% Si, 0.1% C, 0.02% S, ≈80% Fe) – desoxidant.

3– 2– 1+ 3+

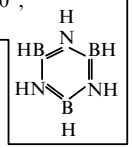
$H_2B=NX_2$, borasenes

$B_3N_3H_{12}$, cr., dec., 150, sol. in NH_3, org. solv.



t | MBH$_4$

$(HBNH)_3$, borazol, "inorg. bz.", m. p. –56, b. p. 55, ΔH = –548, stab. at 500°, μ = 0.5



HCl | MBH$_4$

$(BClNH)_3$, cr., subl. 80/15 mm, mol. nonplanar cycle

$(–BCl_2—NH_2)_3$, mol. chair [35]

2–	m. p.	b. p.
B_2H_5Cl, gas	–142	–11
B_2H_5Br, gas	–104	+10
B_2H_5I, liq.	–110	–

+ Na/Hg ⟶ B_4H_{10}

B_2H_6 | HHal | Hal_2 | MOH

3– M[BH_3(OH)], hypoborates

H_2O (–H_2)

1– M[$H_2B(OH)_2$] Na[H_2BF_2]

H_2O

M[HB(OH)$_3$]

HBHal$_2$, Hal = F–Br

$B_4N_6H_8$; $B_4N_8H_6$; $B_{24}N_{36}$, str. anal. of fullerene [35]

BERYLLIUM, ALUMINIUM

	2s	2p	3s	3p	3d	EN
Be^0	↓↑					1.5
Al^0			↓↑	↓		1.5

$BeCl_2$ + NaCl, m.p. 224 — cath. Red

BeF_2 — Mg (1300°)

HBr, O_2, Na_3AlF_6 — cath. Red (in melt)

Be	Al
met. wh., lustrous (covered with finest film of oxides), light	
hard, brittle, transparent to X-ray	mild, ductile
d 1.85	2.70
m.p. 1287	660
b.p. 2507	≈2500
$E_0 M^{n+}/M_{sld}$ = −1.85	−1.70
$E_0 [M(OH)_4]^{n-}/M_{sld}$ = −2.52	−2.34
sol. in dil. ac., alk., passiv. HNO_3	
sol. in HF, NH_4F	insol. in HF, H_3PO_4, CH_3COOH; met. higt purity sol. in $(HCl + Cu^{2+} + H_2O_2)$
hex. cl. pack.	cub. cl. pack.
a = 2.28, c = 3.58	a = 4.04
M — M 2.28	M — M 2.86

"Be-bronze": Cu + ⩽6% Be, alloys wiht hight hardness, mechanical strength, corrosion resistant

Steels Cr—Mo—Al. Al increases resist. to corrosion, wear and abrasion.
Alloys for magnets, 12–15 % Al
Duralumin, hard alloy, 93–95 % Al, 2.2–5.5 % Cu, 0.5–2.0 % Mg, 0.5–1.2 % Mn, 0.2–1.0 % Si
Silumin, 10–14 % Si, 0.1 % Na, rest — Al

$[Be(Dipy)_2]$, paramagn., $\mu_{eff.}$ = 2.1 (2 unpair. el.) sp^3 – ?) [18]	**$[Al(Dipy)_3]$**, $\mu_{eff.}$ = 2.32

$[AlHal(NB_3)]_4$, Hal = Br, I, in mol. — cicle $[Al_4]$ ↓ $AlBr_3$
$Al_2Br_4 \cdot 2L$, dec. 100 [29]

BeO	Al_2O_3
powd., inert. after calcination, fused with alk., $K_2S_2O_7$	
m.p. 2580 (cool. ⟶ glass), b.p. 4260, ΔH = −611 [1], in gas—mol. and $(BeO)_n$ – cycles	m.p. 2072, b.p. ~3500, ΔH = −1670 (α); d = 3.96; liq. (in melt Na_3AlF_6) ⇄ $[AlO]^+ + [AlO_2]^-$; α-, rhombohedral, pass., "corundum", "ruby" (+ Cr^{III}, red.), "sapphire" (+ Ti, Fe^{II}, bl.), v. hard, in str. — hex.
↓ subl.; $NaBO_2$ + melt	cl. pack. at. O, β-, hex. (~ $Na_2O \cdot 10\,Al_2O_3$), sld. electrolyte ←^{t} γ-, cube
cr., wurtzite str. type, CN Be 4	**($Al_{2.67}O_4$)**, spinel str. type, chem., act.; + H_2O ⟶ $Al(OH)_3$
"bromellite", Be—O 1.64; volat. in current of O_2	

AlO(OH), β-"diaspore" ←$^{350°}_{NaOH}$ γ-"boehmite" (in "bauxites"), dec. 360, layers of oct.

↑180 – 200°

$NaOH + H_2O$

$NaBeF_3$ Na_2BeF_4

$Be(OH)_2$	$Al(OH)_3$
cr., poorly sol. in alk., subl. 1200, isostr. ε-$Zn(OH)_2$	α-"gibbsite", "hydrargillite", monocl. (stab.); β-"bayerite", hex.; γ-"nordstrandite", tricl., sol. in conc. alk.
↑ time, OH^-	
$BeO \cdot nH_2O$↓	**$Al_2O_3 \cdot nH_2O$**↓
	wh., gel, sol. in ac., alk., insol. in NH_3 and NH_4X
sol. in $(NH_4)_2CO_3$	sol. in $EtNH_2$
$Be^{2+} + 2\,OH^- \rightleftarrows Be(OH)_2\downarrow \overset{H_2O}{\rightleftarrows} 2\,H^+ + [Be(OH)_4]^{2-}$	$Al^{3+} + 3\,OH^- \rightleftarrows Al(OH)_3\downarrow \overset{H_2O}{\rightleftarrows} H^+ + [Al(OH)_4]^-$
$K_{bas.} = 10^{-15} - 10^{-22}$, $K_{ac.} = 10^{-25}$	$K_{bas.} = 10^{-33}$, $K_{ac.} = 10^{-8}$

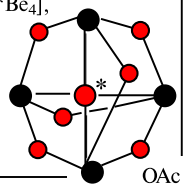
NH_4OH NH_4OH

$(MeO)_2SO_2$ (180°)

$[-(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O\downarrow]$

stages: 1) 1600°; 2) $+H_2SO_4(-SiO_2\downarrow)$; 3) $+(NH_4)_2SO_4$

$Be(ClO_4)_2$ [10], **$4\,H_2O$** ⟶$^{250°}$ **$Be_4O(ClO_4)_6$**, m.p. 165, subl. 100
$Be(IO_4)_2 \cdot 8\,H_2O$; $Be_3(IO_5)_2 \cdot 12\,H_2O$; $Be(IO_3)_2 \cdot 4\,H_2O$
$BeSO_4$, hyg. m.p. 540, dec. 580;
$\cdot 2\,H_2O$, ←$^{89°}$ **$\cdot 4\,H_2O$**; **$\cdot M_2SO_4 \cdot 2\,H_2O$**, M = K, NH_4 [10]
$BeSeO_4$, ←$^{213°}$ **$\cdot 2\,H_2O$** ←$^{75°}$ **$\cdot 4\,H_2O$**; **Be_4TeO_7**
$Be(NO_3)_2$, ←$^{50°}$ **$\cdot 2\,N_2O_4$**, yel., sol. in alc., **$\cdot nH_2O$** n = 2, 4, 6, 7; subl. ⟶ **$Be_4O(NO_3)_6$**, colrl., volat., insol. in org. solv.
$Be(H_2PO_4)_2 \cdot H_2O$; $BeHPO_4 \cdot H_2O$↓; **$Be_3(PO_4)_2 \cdot 6\,H_2O$**↓, SP = 10^{-38}, hydr.
$Be(NH_4)PO_4 \cdot H_2O$↓, SP = 10^{-20}; ⟶$^{700°}$ **$Be_2P_2O_7$**; **$Be_2[PO_4](OH) \cdot 4\,H_2O$**
$NaBe[PO_4]$, **$Be(PO_3)_2$**↓, in str. — net of tetrah. $[PO_4]$ and $[BeO_4]$ [2]
$Be(NH_4)AsO_4 \cdot 1.5\,H_2O$↓, ⟶$^{400°}$ **$Be_2As_2O_7$** + **$Be_3(AsO_4)_2$**
$BeCO_3 \cdot 4\,H_2O$↓, dec. 100, $\overset{MHCO_3\,(t)}{CO_2\,(p)}$⟶ **$Be(CO_3)_n(OH)_{2-2n}$**↓, sol. in M_2CO_3
$[Be(HCOO)_2]_n$↓, **$[Be(OCOCH_3)_2]_n$**↓— polymers, insol. in org. solv.
$Be_4O(OCOCH_3)_6$, cr. cub. (diamond str. type), m.p. 285, subl. > 220, b.p. 331, readily sol. in $CHCl_3$, poorly in bz.; in centre mol. tetrah. [O*Be_4], connect. 4 tetrah. [BeO*O_3]; CH_3COO — bidentate [2, 3]
$BeC_2O_4 \cdot 3\,H_2O$, readily sol. in H_2O



$Be_2[SiO_4]$, "phenacite"; **$Be_3Al_2[Si_6O_{18}]$**, "beryl"; (transparent — "emerald", + Cr^{III} — "aquamarin")
$Be_4[Si_2O_7](OH)_2$, "bertrandite"; **$BeAl[SiO_4](OH)$**"euclase"

$Al(ClO_4)_3$, volat., [10] **$\cdot nH_2O$**, n = 15, 12, 9, 6; **$Al(ClO_3)_3 \cdot nH_2O$**, n = 9, 6
$Al(BrO_3)_3 \cdot 9\,H_2O$, m.p. 62, dec. 100; **$Al(IO_3)_3 \cdot nH_2O$**, n = 6, 8
$Al_2(SO_4)_3$, dec. 500, **$\cdot 9\,H_2O$**, ←$^{86°}$ **$\cdot 18\,H_2O$** ("alunogen");
$\cdot M_2SO_4 \cdot 24\,H_2O$, M = NH_4, K – Cs, alum.
ΔH sol. ⩽ 0, in cub. str. — oct. $[M(H_2O)_6]^+$, $[Al(H_2O)_6]^{3+}$, tetrah. $[SO_4]^{2-}$
$\cdot M^{II}SO_4 \cdot 22\,H_2O$, M^{II} = Mg, Fe^{II}; **$Al_2(SO_4)(OH)_4 \cdot 7\,H_2O$** [8]
$Al_{13}(SO_4)_3(OH)_{33} \cdot 46\,H_2O$, Keggin str.; **$Al_{13}(CrO_4)_{14}(OH)_{11} \cdot nH_2O$** [8]
$Al(NO_3)_3$, subl. vac. [22] ←^{N_2O_5} **$\cdot 9\,H_2O$**, m.p.73, dec. 134
$Al_6(PO_4)_4(OH)_6 \cdot 5\,H_2O$; **$KAlP_2O_7$**; **$NaAl_3(PO_4)_2(OH)_4$**
$AlPO_4$↓, m.p. ≈1400, insol. in ac., quartz str. type, does not form glasses; **$\cdot 2\,H_2O$**, "variscite"; **$Al(H_2PO_4)_3$**,
$AlAsO_4$↓, quartz str. type ⟶$^{t,\,p}$ TiO_2— type; **$\cdot 2\,H_2O$**
$KAl_4(AsO_4)_3(OH)_4 \cdot 8\,H_2O$, **$Al_5(CO_3)(OH)_{13} \cdot 5\,H_2O$**, "scarborite" [19]
$Mg_6Al_2(CO_3)(OH)_{16} \cdot 4\,H_2O$, "hydrotaleite"
$Al(CH_3COO)_3$; + H_2O (trace) ⟶ **$[Al_3O(CH_3COO)_6]^+X^-$**, str. anal of Cr^{III} and Fe^{III} — acetates, non volat. [22]
$Al_2(C_2O_4)_3 \cdot 4\,H_2O$, sol. in H_2O
$Al_2[Si_2O_5](OH)_4$, "kaolinite"; **$Al[Si_2O_5](OH) \cdot nH_2O$**, "montmorillonite"
Al_2SiO_5, "andalusite", "sillimanite", m.p. 1860, **$Al_2[SiO_4](F,OH)_2$**, "topaz"

$ClNO_2$ — $AlCl_3$

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_24, © Springer-Verlag Berlin Heidelberg 2011

BeO

$C + Cl_2$; $CHal_4$ (t)

$(NH_4)_2BeF_4$ (t)

$Be_3Al_2Si_6O_{18}$ — Na_2SiF_6 (700°; $-Na_3AlF_6\downarrow$, $-SiO_2\downarrow$, "Kopo-process")

Be(OH)Cl · 2 H₂O [24]

$Al(OH)_2Cl \cdot 4H_2O$, **AlOHal**

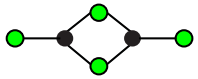
$Al_2O_3 x \cdot H_2O$

$HF + Na_2CO_3$

Beryllates [5]
$Na_2Be(OH)_2O$; $M_2[Be(OH)_4]$; $Na[Be(OH)_3]$
Na_2BeO_2; $M_2Be_2O_3$; $K_4Be_3O_5$; M_4BeO_3;
str. chains of tetrah. and triangles;
$Al_2[BeO_4]$

[1, 16]	m.p.	b.p.	ΔH	$\cdot n H_2O$
BeF_2	820	> 800 (subl.)	−1025	—
$BeCl_2$	425	520 (subl.)	−494	**4** (m.p. 96)
$BeBr_2$	509	540	−369	**4**
BeI_2	480	530	−167	**4**

$BeHal_2$ — cr. colrl. (BeF_2 — glass), str. frame (Hal = F) or chains of tetrah. (Hal = Cl—I), str. anal. of SiO_2. In gas linear mol. $BeHal_2$(*sp*) or Be_2Hal_4



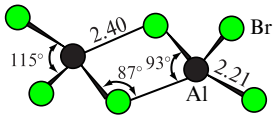
(sp^2)

$BeHal_2$, sol. in H_2O, ROH, Et_2O, **$\cdot n$ ROH**, n = 3, 4; **$\cdot 2Et_2O$**; **$\cdot n NH_3$**, n = 12, 6, **4**, 2 (Cl); 13, 6 и 4 (I); **$\cdot L_2$**, L = RCHO, R_2CO, RNO_2, RCN, Py, R_3N, H_2S, R_2O, Thf; mol. tetrah. **$\cdot L$**, L = Dipy, Diox; **$BeCl_2 \cdot 3 POCl_3$**

$MBeF_3$, chain of $[BeF_2F_{2/2}]$, tetrah.
$M_2[BeF_4]$, tetrah.
MBe_2F_5, **$M_3Be_2F_7$**, 2 tetrah. with common vertex
$M_2[BeCl_4]$, M = Li–Cs, Tl, Ba/2;
$CsBeCl_3$
$HBeCl_3 \cdot 2 Py$, **MBe_2Cl_5**, [4]
M = NH_4, K–Cs

[14]	m.p.	b.p.	ΔH	$\cdot n H_2O$
$AlF_3\downarrow$	1040	1279	−1510	**1**, 3, 5↓
$AlCl_3$	193(*p*)	180 (subl.)	−704	**6**
$AlBr_3$	98	255	−514	**6**
AlI_3	191	386	−310	**6**

$AlHal_3$ — cr. colrl., hyg., sol. in ROH, Et_2O (Hal = Cl—I), bz., CS_2 (Br, I). Str. AlF_3 ReO_3 type, $[AlF_6]$ — trig. antiprizm; $AlCl_3$ — isotruct. $FeCl_3$; $AlHal_3$ (Hal = Cl—I) in s. and gas dimers (2 tetrah. sharing edge)



$AlCl_3 \cdot 6 L = [AlL_6]Cl_3$, L = H_2O (dec. 200), NH_3 (dec. 180), cation — oct.
[$AlHal_3L$], L = R_2O, R_2CO, Py, R_3N, NH_3, H_2S, NO, PH_3, PCl_3 [14], $SbBr_3$, $POCl_3$, HCN mol. dist. tetrah., in s. monomers

$MAlF_4\downarrow$, tetrah. or layers of $[AlF_{4/2}F_2]_\infty$ oct.
$[XeF_5]^+[Al_2F_7]^-$, dec. 130
$M_2AlF_5\downarrow$, chains of oct. $[AlF_4F_{2/2}]_\infty$
$(H_3O)_2AlF_5 \cdot 3 H_2O$
$Na_3AlF_6\downarrow$, m.p. 1012, "cryolite", liq. $\rightleftarrows 3 Na^+ + AlF_4^- + 2 F^-$
Ca_2AlF_7, in str. $[AlF_6]^{3-} F^-$ [12]
M[$AlCl_4$], M = Na (m.p. 185), K (256), Cs (377), $[SCl_3]$, $[SeCl_3]$ (164), $[TeCl_3]$ (149), [NO] (180), $[PCl_4]$, $[BeCl(Et_2O)_3]$ (55),
$M^{II}/2$ (V–Ni), $[Bi_n]/3$ (n = 3, 5),
$[Te_4][Al_2Cl_7]_2$
$HAlCl_4 \cdot Diox$; [11]
M[$AlBr_4$], **MAl_2Br_7**,
M[AlI_4]; **$Li[Al_2I_7]$** [13]

Aluminates [6]
$Na_{10}[Al(OH)_6]_2(OH)_4$; **$Na_9[Al(OH)_6]_2(OH)_3 \cdot 6 H_2O$**;
$M^{II}_3[Al(OH)_6]_2$; **$Ba_2[Al_2(OH)_{10}]$**; **$Ba_2[Al_4(OH)_{16}]$**;
$Ba[AlO(OH)_2]_2$; **Na_3AlO_3**; **Li_5AlO_4**; **$Na_{17}[Al_5O_{16}]$**;
$Na_{14}[Al_4O_{13}]$; **$KLi_4[AlO_4]$**, anions — oct. and condensed tetrah.
$M^{II}O \cdot Al_2O_3$, M = Mg (spinel), Zn ("Zn-spinel"), Fe ("hercynite"), cub. str., oct. $[AlO_6]$, tetrah. $[M^{II}O_4]$, $[OM^{II}Al_3]$, cl. pack. at. O

BeS, powd., grey, not hydr., $\Delta H = -235$, sphalerite str. type

$M_2[Be(NO_3)_4]$, M = $[R_4N]$, [NO] [20]
$M_2[Be(CO_3)_2]$
$[Co(NH_3)_6]_2[Be_4O(CO_3)_6] \cdot 10 H_2O\downarrow$, orange
$M_2[Be(C_2O_4)_2]$, M = Na($\cdot H_2O$), K, PyH, $[Co(NH_3)_6]/3$ [7]

Be_3N_2, **AlN**, salt-like, cr. colrl., v. hard, subl., m.p. ~2200 (*p*) (dec.), ΔH = −192 (Be), −318 (Al), ac.-resist. (*t*); powd. — act., $+ H_2O \longrightarrow M(OH)_n + NH_3$; str. *anti*- Mn_2O_3 (Be), wurtzite (Al)
$Be(N_3)_2$, wh., insol. in org. solv., not exp.; **$Al[N_3]_3$**

Be_2C_3, **Al_4C_3**, "methanides", cr. yel. or brn., (admix C), dec. > 2000, $+ H_2O \longrightarrow CH_4\uparrow + M(OH)_n$, str. *anti*- CaF_2, ΔH = −91 (Be), −208 (Al)
BeC_2, **$Al_2[C_2]_3$**, **acetylides**, $+ H_2O \longrightarrow C_2H_2\uparrow + M(OH)_n$

$LiAl(NH_2)_4$ [27]

Al_2S_3, needles, m.p. 1120, ΔH = −651, hydr., [26]
random. str. sphalerite type (α-, β-) or corrundum (γ-)
Al_2Se_3, yel.; **Al_2Te_3**, brn. (ΔH = −567 and −326)
AlP, **AlAs**, orange, sphalerite str. type

$ZnAl_2S_4$, spinel str. type
$MAlSe_2$, yel.; **$MAlTe_2$** red.
Li_3AlP_2; **Li_3AlAs_2**, **Li_3AlN_2**
Li[Al(EH_2)$_4$], **E** = P, As

$MAl(ClO_4)_4$, M = K–Cs, $[ClO_2]$
$Li_2[Al(ClO_4)_5]$ [10]; **$(NH_4)_3[Al(ClO_4)_6]$**
$HAl(SO_4)_2 \cdot 4 H_2O$
$Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_4 \cdot n H_2O$
$M[Al(NO_3)_4]$, M = $[NO_2]$, Rb, Cs
$M_2[Al(NO_3)_5]$, **$M_3[Al(NO_3)_6]$** [9], M = K–Cs
$[H_3O][Al_3(H_2PO_4)_6(HPO_4)_2] \cdot 4 H_2O$ [19]
$KAlP_2O_7$, $[AlO_6]$ — oct.
$NH_4[Al_2(OH)(H_2O)(PO_4)_2] \cdot n H_2O$, [17]
$M_3[Al(C_2O_4)_3] \cdot n H_2O$, M = Na, Mg/2
Na[AlSiO$_4$] ("nepheline"), in str. — net of tetrah. $[SiO_4]$ and $[AlO_4]$
K[$(AlO_2)(SiO_2)_3$], "orthoclase", zeolites (see "Si")

Be_3P_2, **BeP_2**, red, semiconduct. [23]
$BeAs_2$

$Be(NCS)_2$, **$Be(CN)_2$**, **$\cdot 0.5 Et_2O$**,
$Al(NCS)_3 \cdot 2 Et_2O$ [25]
$Al(CN)_3 \cdot Et_2O$

$M_2[Be(NCS)_4] \cdot 2 L$
$M[Be(NCS)_3] \cdot n L$,
$Li[Al(NCS)_4]$
$Li[Al(CN)_4]$

$AlCl_3$ — $LiH\downarrow$ (Et_2O–$LiCl\downarrow$)

$LiAlH_4$, cr. dec. 125, sol. in Et_2O
$\cdot n Et_2O$, n = 1, 2, 2.5, 3,
$\cdot n$ Thf, n = 1, 2, 3, 5.
$+ H_2O \longrightarrow H_2$, mild Red.
$+ R_2C{=}O \longrightarrow R_2CHOH$;
$+ MH \longrightarrow$ **$M[AlH_4]_n$**
M = Na, K (stab. > $LiAlH_4$), Sn^{II}, Sn^{IV}, Ti, Nb, stab. < 0°, anion tetrah.
$M_3[AlH_6]$, M = Li (dec. 210), Na (m.p. 260, insol. in Thf)

$AlCl_3$

$(AlH_3)_n \cdot x Et_2O$, wh. hid. polymer
AlH_3, monomer, dec. 105, frame of oct., dec. 105
$\cdot NH_3 \xrightarrow[>-30°]{-H_2} H_2N{-}AlH_2 \xrightarrow[20°]{-H_2}$
$\cdot NMe_3$, m.p. 76, $\cdot 2 NMe_3$, m.p. 95, subl. 40 (vac.), mol. — trig. bipyr.
AlH_nHal_{3-n}, volat., sol. in Et_2O
AlH_2I, m.p. 35; **AlH_2I**, m.p. 80
Al[BH_4]$_3$, cr., subl. > 0, infl.

1) BeR_2 + $LiAlH_4$; 2) $BeCl_2$ + $LiH\downarrow$; 3) BeR_2 (t, $-C_nH_{2n}$)

$(BeH_2)_n$, wh. polymer, nonvolat., dec. 100 (method 1), 240 (method 3), ΔH = +125; $+ H_2 \longrightarrow$ cr. hex., in str. frame of tetr.
$Be(BH_4)_2$, subl. 91, dec. 123, in polym. str. gr. $[BeH_6]$ [11]

$LiBeH_3$
Li_2BeH_4 [11]

$Be(OR)_2$ [15, 21]
$Al(OR)_3$
M[$Al(OR)_4$]
cat. Red. C=O and polymerization

M
Hal
O

M + Al + H_2 — C_6H_{14} (t, p)

GALLIUM, INDIUM, THALLIUM

	4s	4p	4d	EN
Ga^0	↓↑	↓		1.6
	5s	5p	5d	
In^0	↓↑	↓		1.7
	6s	6p	6d	
Tl^0	↓↑	↓		1.8

1 +

2+, "2+"

Ga^{3+} (mother sol. after prec. of Al) — cath. Red Zn; Al

M_2O_3 MCl_3 — H_2 (l)

In^{3+}; Tl^+ — Zn; Al; cath. Red

Ga	In	Tl
met., silver-wh., v. mild		
stab. in air		Ox in air
d 5.9	7.3	11.9
$d_{liq.}$ 6.1 (!)	—	—
m.p. 29.8	157	304
(supercool. −40°)		
b.p. 2403	2024	1475
sol. in NH_4OH, ac., alk.	sol. in ac.	sol. in ac.-Ox
poorly sol. in HNO_3		and (H_2O + O_2)
E_0M^{3+}/M_{sld} = −0.56	−0.34	E_0Tl^+/Tl_{sld} = −0.34
α-, graphite-like		α-, hex. cl. pack.
rh. str., a = 4.52,		a = 3.45, c = 5.51
b = 7.65, c = 4.51,		↓ 235°
in str. and melt — mol.		β-, cub. cl. pack.
Ga_2, Ga — Ga 2.48		a = 3.87, Tl — Tl 3.35
↓ 170°		↓ 115°
β-, face-centered tetr. str. (γ-Mn str. type)		↓ 37 · 10^8 Pa
a = 2.81, c = 4.45,	a = 4.60,	γ-, cub. (α-Fe str. type)
d = 6.6; CN 4 + 8,	c = 4.94,	a = 4.85, m.p. 650
Ga — Ga 2.81, 2.99,	In — In	(9 · 10^9 Pa)
γ-, cub., a = 5.95,	3.24; 3.37	
d = 6.59, CN 8,		
Ga — Ga 2.78 [4]		

M^I_{23} $[Tl_5]^{7-}_2$ $[Tl_9]^{9-}$ [33]

$M[Co(CO)_4]_3$ [3]

Alloys

Low-melting: 82% Ga + 12% Sn + 6% Zn, m.p. 17; 24% In + 76% Ga, m.p. 16

Ac.-resist.: 70% Pb + 20% Sn + 10% Tl, insol. in H_2SO_4, HCl, HNO_3

Ga_2O, cr., brn., subl. 500; 700° → Ga + Ga_2O_3; ΔH = −343; + H_2SO_4 → H_2S + Ga^{3+}

In_2O (?), cr. blk., subl. 700. sol. in HCl

Tl_2O, powd. blk. or yel., hyg., m.p. 303, subl. 400, b.p. ≈1100; ΔH = −175, dist. [13] *anti*-CdI_2 str. type

H_2 (175°) / O_2 — Tl_2O_3

↓ H_2O

TlOH, · **2 H_2O**, yel., sol. in H_2O, alc., strong bas., $K_{bas.}$ = 0.33; ΔH = −239

MTlO, M = K–Cs, red, str. like Tl_2O

Na_3TlO_2, in str. — triangle $[MO_3]$, + O_2 → $NaTlO_2$; + H_2O → TlOH + NaOH [28]

Ga_2O_3; SiO_2; CO_2 — In_2O_3 — r; H_2

CO_2 (−CO, 850°) — O_2 (l) — H_2O + O_2

$Ba(OH)_2$

$TlClO_4$, cr., colrl., m.p. 501; **$TlClO_3$**

$TlIO_3$, CN Tl 3, Tl — O 3.02–3.48 [29]

Tl_2SO_4, m.p. 645, chem. pesticide

· **$M^{III}_2(SO_4)_3$ · 24 H_2O**, alum; · ***n*** **H_2SO_4**, n = 1/6, 1, 2

Tl_2SO_3, yel.; **$NaTl_3(SO_3)_2$; $Tl_2S_2O_3$; $NaTlS_2O_3$ · H_2O**

Tl_2SeO_4, m.p. > 400; **$TlH_3(SeO_3)_2$; Tl_6TeO_6**, orange

Tl_2CrO_4↓, yel., m.p. 633, SP = 10^{-9}

$Tl_2Cr_2O_7$↓, orange, m.p. 360

$TlNO_3$, m.p. 206 (β), 334 (α), b.p. 438

$TlNO_2$↓, yel. (compare Ag !)

Tl_3PO_4↓, colrl., sol. in ac., CN Tl 3 — H_3PO_4 → **TlH_2PO_4**

$TlH_5(PO_4)_2$, in str. — oct. [29]

$Tl_4P_2O_7$, dec. 120, readily sol. in H_2O

Tl_2CO_3, m.p. 273, dec. 300; readily sol. in H_2O, CO_2 → **TlHCO₃**↓

$TlCH_3COO$, needle, m.p. 131, sol. in alc.

TlHCOO, m.p. 104, sol. in H_2O ≈85%, d s. 3.3–4.7

Tl_2SiF_6 · 2 H_2O, readily sol. in H_2O

$Tl^I_3[Tl^{III}O_3]$ [26]

$GaCl_3$ — Hal_2 — hν(vis)(−Hal_2) — $InCl_2$

GaCl · 2 Diox
GaBr
GaI,
m.p. 271 (dec.)

$HGaCl_2$, cr. colrl., m.p. 29, sol. in bz. 150° → H_2 + Ga_2Cl_4

Ga[$AlCl_4$] [27]

[1]	m.p.	b.p.	ΔH
InCl, α-, yel., cube	225	653	−186
β-, red, rh.			
InBr, orange, rh.	285	662	−175
InI, red-brn.	360	743	−117

In str. α-InCl (NaCl str. type) tetrah. [In_4]; β-InCl, InBr and InI — isostr. yel. TlI.

M[Co(CO)]

$(InH)_n$, dec. 340, insol. in org. solv., + H_2O → In + $In(OH)_3$ + H_2↑

	SP	m.p.	b.p.	ΔH
TlF, readily sol. in H_2O	—	327	840	−310
TlCl↓, wh.	10^{-4}	431	818	−205
TlBr↓, light yel.	10^{-6}	461	816	−171
TlI↓, yel.	10^{-8}	442	825	−125
↓ 168° red				

"**TlI_3**↓" = $Tl^+[I_3]^-$, blk., isostr. to RbI_3; in s.: $Tl^+ + I^-_3 \rightleftarrows Tl^{3+} + 3I^-$. TlHal sol. in conc. H_2SO_4, HNO_3; str. TlF — rh., dist. NaCl str. type; TlCl, TlBr, TlI (red) — CsCl type; TlI (yel.) — rh., layered str. (CN 7); [35] in gas — TlHal and Tl_2F_2

$CsTlBr_2$; Cs_2TlBr_3; $TlAlCl_4$, m.p. 308

TlCN; TlSCN, m.p. 234

$[Tl_6I_6]$ · M^+_2 $[I_4]^{2-}$, M = Ag, Au, Tl, Pb/2 [30]

[TlOMe]$_4$, cuban [14]

Tl_2S↓, bl.-blk., m.p. 448, subl. > 360, b.p. 1367, ΔH = −42; + O_2 → Tl_2O + $Tl_2S_2O_3$, *anti*-CdI_2 str. **$TlCu^I_3S_2$**, "chalkotahlite"; **$TlFeS_2$**, "raguinit"; **$M_4Tl_2S_3$** [30]

Ga_2S blk. 1000° → Ga + Ga_2S_2
Ga_4S_5, dec. 1200
Ga_2S_2, yel., m.p. 970

In_2S, blk. [13]
In_2Se, red
In_5S_4, In_6S_7

Ga_2Cl_5

[9] **Ga_4Hal_6** = $Ga^I_2[Ga^{II}_2Hal_6]$, Hal = Br, I

1.4 +
In_5Br_7 = $In^I_3[In^{II}_2Br_6]Br$, anion — cluster, In — In ~2.70
1.5 +
In_2Hal_3 = $In^I_2[In^{II}_2Hal_6]$
In_2Cl_3, m.p. 323, b.p. 641
In_2Br_3, m.p. 232
1.75 +
In_4Cl_7, m.p. 260, b.p. 710
In_4Br_7, m.p. 201
1.8 +
[31] **In_5Cl_9** = $In^I_3[In^{III}_2Cl_9]$

Ga; H_2 — MHal₃

M_2Hal_4 = $M^I[M^{III}Hal_4]$, anions — tetrah., Ga^I — three-cap. trig. prism, In^I — dodecah.

GaHal₂	**InHal₂**
F —	unstab.
Cl m.p. 176	240
b.p. 535	655
μ = 8.9	ΔH = −402
200° → Ga + $GaCl_3$ + H_2O → H_2 + Ga↓ + + **GaCl(OH) · 0.5 H_2O**↓, orange + H_2O → In + $InHal_3$	
Br m.p. 153 (α)	198
165 (β)	—
b.p. —	638
colrl.	ΔH = −113
I m.p. 211	225
yel.	brn. [9,31]

$[R_4N]_2[Ga_2Hal_6]$, Hal = Cl, Br, anion — cluster, Ga · Ga ~ 2.4 [9]

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_25, © Springer-Verlag Berlin Heidelberg 2011

$Tl^{I}_{3}[Tl^{III}O_3]$ [26]

3+

In —O_2 (t, bl.-vlt. flame)→ In_2O_3, yel., $\xrightarrow{t}$ brn., m.p. 1910 (*p*), b.p. ~3300°, $\Delta H = -920$, Mn_2O_3 str. type, semiconduct.
In_2O_3 ←H_2; C (800°)— In_2O_3

Ga_2O_3, wh., m.p. 1795, $\Delta H = -1089$ (*β*), α-, rh., isostr. to corundum, oct.; *β*-,monocl., tetrah. and oct.; γ-, Mn_2O_3 str. type; only α-form
sol. in ac. and alk.

↑ 300°

GaOOH, isostr. AlOOH [2]
$Ga_2O_3 \cdot x\,H_2O\downarrow$, wh., sol. in ac., alk., conc. NH_4OH
$K_{2\,ac.} = K_{2\,bas.} = 10^{-11}$, $K_{3\,ac.} = K_{3\,bas.} = 10^{-12}$
$Ga(OH)_3$

↑ 340°

$In(OH)_3\downarrow$, wh., sol. in ac., poorly in conc. alk.
str. like ReO_3
InO(OH), isostr. CrO(OH) [24]

$H_2O \uparrow\downarrow$ 15 н. MOH

Indates [22]
$M_3[In(OH)_6] \cdot 2\,H_2O$
$Rb_2[In(OH)_5(H_2O)]$
$Ba_3[In_2(OH)_{12}]$, oct.
$Na_5[InO_4]$, $Cs_6[In_2O_6]$
Li_3InO_3; $MInO_2$
$Rb_2In_4O_7$

Tl —O_3; O_2 (−Tl_2O)→ Tl_2O_3, brn., m.p. 716 (*p*), $\Delta H = -390$,
$\xrightarrow{500°}$ O_2, strong Ox; + S ⟶ exp., Mn_2O_3 str. type
$(Tl,Fe)_2O_3$, "avicennit"

↑ 100°

$Tl_2O_3 \cdot x\,H_2O\downarrow$, brn., sol. in ac., peptiz. alk., prez. at pH ⩾ 1, strong. Ox

↘ M_2O (+O_2)

Tallates [13]
$Na_3[Tl(OH)_6]$; $Na_8Tl_2O_7 \cdot 3\,H_2O$
$M_5[TlO_4]$, yel., tetrah.
$\xrightarrow{t}$ M_3TlO_3 $\xrightarrow{t}$ **$MTlO_2$; $CaTl_2O_4$;**
$M^{II}_2Tl_2O_5$, frame of oct.

Gallates [35]
$Na_{10}[Ga(OH)_6]_2(OH)_4$; $Ca_3[Ga(OH)_6]_2$;
$K_2[Ga_2O(OH)_6]$; $M[Ga(OH)_4]$; $MGaO_2$;
M_3GaO_3; M_5GaO_4; $M_8Ga_2O_7$;
$CaGa_4O_7$; $LiGa_5O_8$; $M_2Ga_{12}O_{19}$,
anions — isolate or condensed
tetrah. or oct. Ga—O 1.78—1.90 or 2.00

GaCl₃ —Cl_2O_6→

$Ga(ClO_4)_3 \cdot 6\,H_2O$
$Ga_5(IO_6)_3 \cdot 3\,H_2O$
$Ga_2(SO_4)_3 \cdot 18\,H_2O$
$\cdot M^{I}_2SO_4 \cdot 24\,H_2O$,
M = K–Cs, alum
$Ga(NO_3)_3$, subl. 140, **$\cdot 8\,H_2O$**
$GaPO_4$, m.p. 1670, **$\cdot 2\,H_2O\downarrow$**
$Ga(H_2PO_4)_3$ $\xrightarrow{t}$ **$Ga(PO_3)_3$**
$GaAsO_4$, frame of tetrah. [15]

M[Ga(ClO₄)₄] [15]
$Li_7[Ga(IO_6)_2] \cdot 4\,H_2O$
$HGa(SO_4)_2 \cdot 4\,H_2O$
$M[Ga(NO_3)_4]$
$Rb[Ga_4(HPO_4)(PO_4)_4] \cdot 0.5\,H_2O$,
CN Ga 4, 5 and 6
$Cs_2[Ga(H_2PO_4)(HPO_4)]$
$\cdot H_3PO_4 \cdot 0.5\,H_2O$
$(NH_4)_3[Ga(C_2O_4)_3] \cdot 2\,H_2O$

$In(ClO_4)_3 \cdot 8\,H_2O$ [25]
$In(IO_3)_3\downarrow$
$In(OH)SO_4 \cdot 2\,H_2O$
$In_2(SO_4)_3$, dec. 600,
$\cdot M^{I}_2SO_4 \cdot 24\,H_2O$
$In_2(SeO_3)_3 \cdot 5\,H_2O$ [7]
$[InNO_3(H_2O)_5](NO_3)_2$
$InPO_4 \cdot 2\,H_2O\downarrow$
$InAsO_4 \cdot H_2O\downarrow$
$[In_2(C_2O_4)_3(H_2O)_4]$,
$\cdot 2\,H_2O$, anion
pentag. bipyr.

$MIn(SO_4)_2 \cdot 4H_2O$,
in str. — layers of oct.
$[InO_4(H_2O)_2]$-*trans*
$M_3[In(SO_4)_3]$ [11]
$Na[In(SeO_4)_2] \cdot 6\,H_2O$
$(NH_4)_2[In(NO_3)_5]$
$K[In(C_2O_4)_2] \cdot n\,H_2O$

Tl(OH)SO₄ · 2 H₂O, pesticide
$Tl_2(SeO_4)_3$; $\xrightarrow{t}$ Tl_2SeO_4
Tl_6TeO_{12}
$Tl(NO_3)_3 \cdot 3\,H_2O$, CN Tl 9
$TlPO_4$, **$\cdot 2\,H_2O$**
$Tl(CH_3COO)_3$, chains of
$[TlO_4O_{4/2}]$ [20]

$HTl(SO_4)_2 \cdot 4\,H_2O$
$MTl(SO_4)_2 \cdot n\,H_2O$,
$M_3[Tl(SO_4)_3]$, chains
of oct.
$(NH_4)[Tl(CH_3COO)_4]$
$H[Tl(C_2O_4)_2] \cdot 3\,H_2O$
$M[Tl(C_2O_4)_2]$
$M_3[Tl(C_2O_4)_3]$ [7]

TlOF↓, grn.
TlOBr [21]

$TlSO_4 = Tl^{I}[Tl^{III}(SO_4)_2]$
1.67 +
$Tl_3(NO_3)_5$ =
$Tl^{I}_2[Tl^{III}(NO_3)_5]$,
m.p. 150, + H_2O (air)
⟶ dark
$Tl^{I}[Tl^{III}(CH_3COO)_4]$,
anion — dodecah. [17]

TlF_2, isostr. CaF_2
$Tl_2Hal_4 = Tl^{I}[Tl^{III}Hal_4]$,
Hal = Cl, Br, colrl.,
anion — tetrah., CN Tl^{I} 8,
+ H_2O ⟶ $Tl_4Br_6 + TlBr_3$
$Tl_2Cl_2Br_2$ [10]

1.33 +
Tl_6I_8 =
= $Tl^{I}_5[Tl^{III}I_8]$

Tl_2F_3 [17]
$Tl_4Hal_6\downarrow = Tl^{I}_3[Tl^{III}Hal_6]$,
Hal = Cl (yel.), Br (red),
(CN Tl^{I} 7, 8, 9)
$Tl_4Cl_4Br_2$, + H_2O ⟶
$TlBr\downarrow + TlBr_3 + \cdots$

$Tl_4S_3 = Tl^{I}_3[Tl^{III}S_3]$
TlS

GaF_3, colrl., volat.
m.p. > 1000 (*p*), subl.
950, $\Delta H = -1019$,
$\cdot 3\,H_2O$
$GaCl_3$, needles, colrl.
m.p. 78, b.p. 201,
$\Delta H = -523$
$GaBr_3$, colrl., m.p. 122,
b.p. 279, $\Delta H = -385$
GaI_3, yel., m.p. 212,
b.p. 346, $\Delta H = -213$
In gas Ga_2Hal_6, and
$GaHal_3$ triangles;
·L, L = H_2O, ROH,
R_2O, NH_3, NR_3, PCl_3

$(GaH_3)_n$; $Ga[AlH_4]_3$ [32]

Ga_2S_3, yel., m.p. 1250,
$\Delta H = -510$, hydr.; dist.
ZnS str. type

t ← **$(NH_4)_3GaF_6$;**
$[R_4N][GaF_4] \cdot H_2O$
$M_2[GaF_5(H_2O)]$
$M[GaCl_4]$, tetrah. [5, 13, 34]
$HGaCl_4$, extr. MeCOOBu
from 6 N s. HCl
KGa_2Cl_7
MGa_3Br_{10}; $K[GaI_4]$ [16]

In str. $GaHal_3$ and $InHal_3$
(Hal = Br, I) — dimers,
anal. Al_2Hal_6; *t* → triangles
$MHal_3$; MF_3 — isostr. to ReO_3
$InCl_3$ — isostr. to $AlCl_3$.
In str. $InF_3 \cdot H_2O$ chains of
oct. $[InF_{2/2}(H_2O,F)_4]$

M[Ga(NCS)₄] [8]
$M_3[Ga(NCS)_6]$

MGaS₂, in str. — layers
of tetrah.
$CuGaS_2$, "gallit" [19]

InF_3, colrl., m.p. 1172,
b.p. > 1200, $\Delta H =$
-1029, **$\cdot n\,H_2O$**
$InCl_3$, m.p. 586 (*p*)
b.p. 617 (subl. 498),
$\Delta H = -537$; **$\cdot 4\,H_2O$**
$InBr_3$, colrl. (brn.
melt.), m.p. 420 (*p*),
subl. 409, $\Delta H = -418$
InI_3, m.p. 225, b.p. 447
β-yel. $\underset{57°}{\overset{5°}{\rightleftarrows}}$ α-red
d = 4.72 | 5.32
$\Delta H = -224$ | -229
(+ $CHCl_3$) ⟶
⟶ In↓ + I_2 [18]
$[InCl_3(PPh_3)_2]$, trig.
bipyr.

$In_3S_3\downarrow$, α-, cub. yel.
β-, vlt., subl. 800,
m.p. 1050, $\Delta H = -426$,
semiconduct.

t ← **$(NH_4)_3InF_6\downarrow$**
$[R_4N]_2[InF_5] \cdot n\,H_2O$,
square pyram.
$Ba_3In_2F_{12}$; $Rb_2In_3F_{11}$
MIn_2F_7, oct. and
pentag. bipyr.
$M_4[InCl_6]Cl$; $M_3[InCl_6]$
$Rb_2[InCl_5(H_2O)]$
$(R_4N)_2InCl_5$; $KInCl_4$
$HInCl_4$, unstab.
M_3InBr_6; $[R_4N]_2[InBr_5]$
$[R_4N][InBr_4]$, tetrah.
$M_4[InBr_6]Br$
$MInI_4$, **$HInI_4$** [6, 12, 16]
$[R_4N]_3[In(NCS)_6]$ [23]

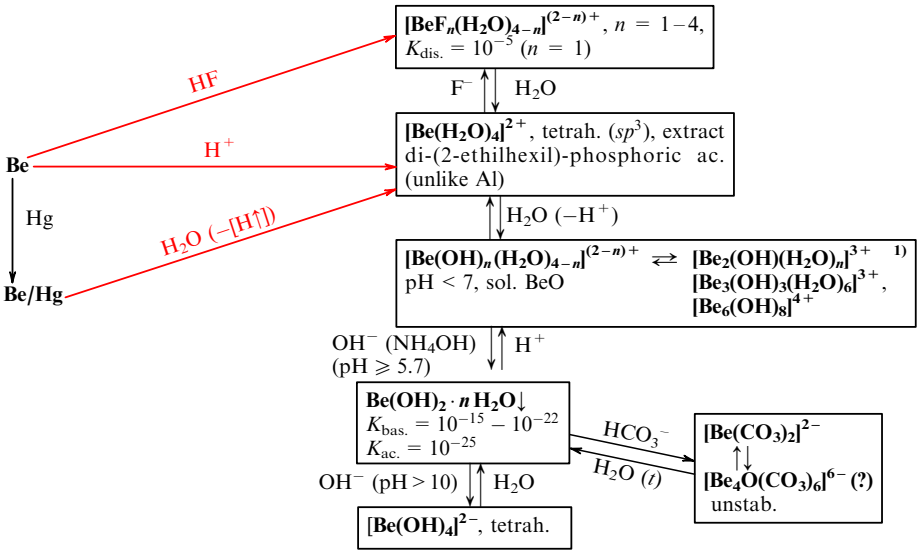
MInS₂, M = Na (yel.)
K (pink), Cu/2 ("roquesite")
Fe/2 ("indite")

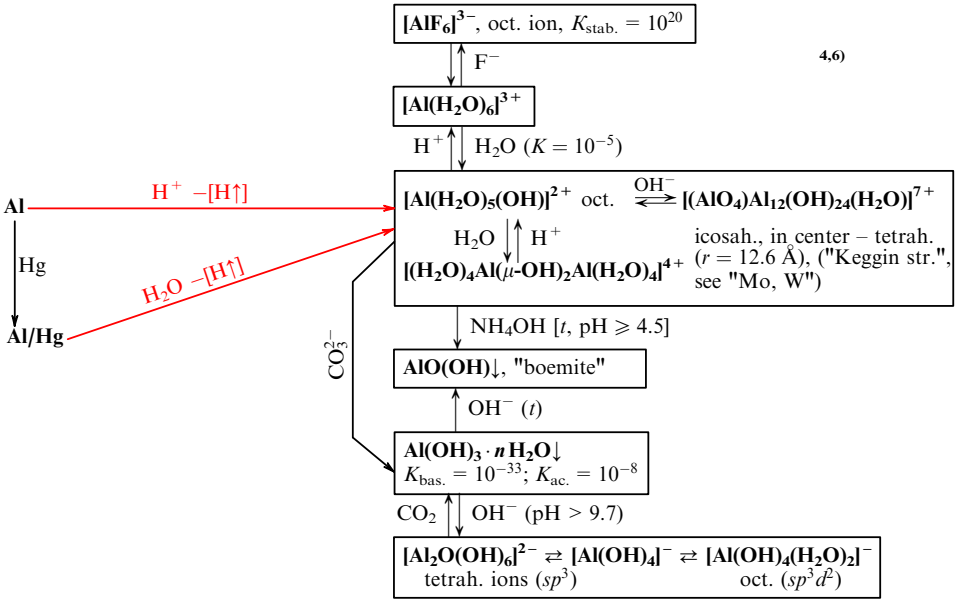
TlF_3, light grn., m.p. 550
(dec.), $\Delta H = -573$,
YF_3 str. type
$TlCl_3$, colrl., dec. 40,
sol. in alc., isostr. $AlCl_3$,
$\Delta H = -352$
$TlBr_3$, yel., unstab.
$Tl\,Hal_3 \cdot 4\,H_2O$ =
= $[Tl\,Hal_3(H_2O)_2](H_2O)_2$,
mol. — trig. bipyr.
$TlBr_3 \cdot n\,Py$, *n* = 2 (trig.
bipyr.), 3 (oct.)
$[TlClBrIL_2]$, trig. bipyr.

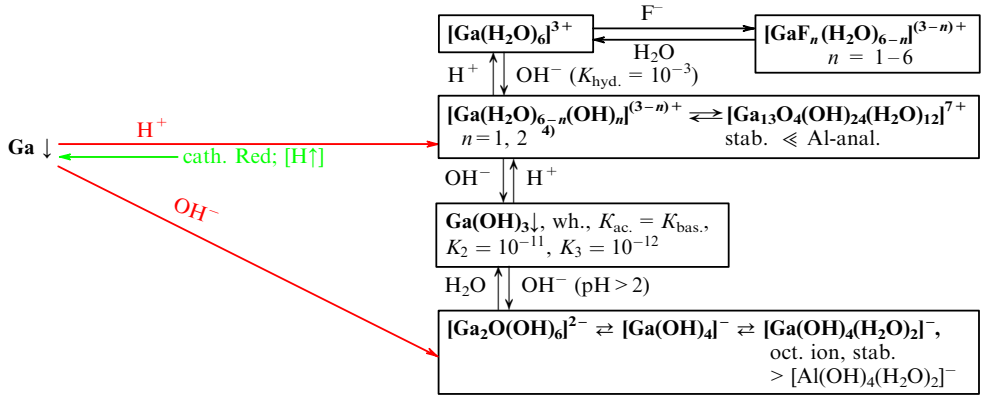
$M[TlF_4]$, **MTl_2F_7** [12]
M_3TlF_6, **Ba_2TlF_7**
$HTlCl_4 \cdot 3\,H_2O$; $KTlCl_4$
$(R_4N)_2TlCl_5$, $K_{stab.} = 10^{18}$
$M_2[TlCl_5(H_2O)]$
$M_3[TlCl_6] \cdot 2\,H_2O$
$M_3[Tl_2Cl_9]$, **$K[TlCl_4]$**
$M[TlBr_4(H_2O)_2]$
$M[TlBr_4]$, $K_{stab.} = 10^{24}$
Cs_2TlBr_5; **$Cs_3Tl_2Br_9$**,
$Rb_3TlBr_6 \cdot 8/7\,H_2O$
$M[TlI_4]$, dark red, $K_{stab.} = 10^{32}$

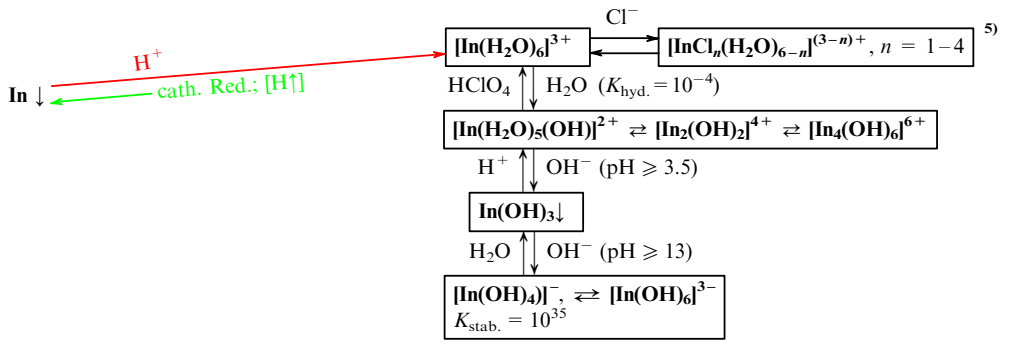
TlCl —+Br + L→
TlHal —Hal_2; $Hal_2 + H_2O$→

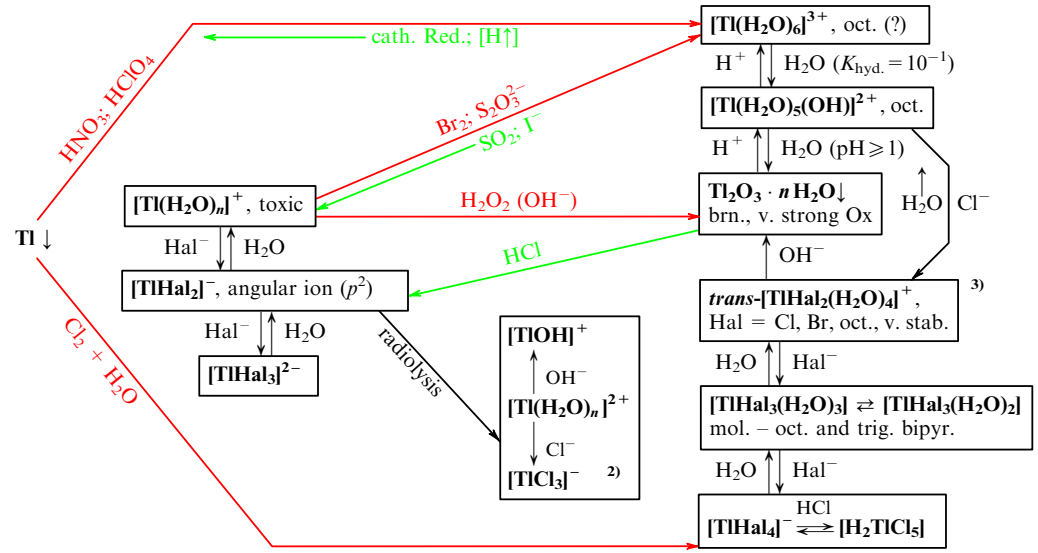
Tl_2S_3, blk., m.p. 260, sol.
in HNO_3, $\Delta H = -116$
Tl_2S_5, red and blk.


Be
Hg
Be/Hg
HF
H+
H2O (–[H↑])
[BeFn(H2O)4–n](2–n)+, n = 1–4, Kdis. = 10–5 (n = 1)
F– H2O
[Be(H2O)4]2+, tetrah. (sp3), extract di-(2-ethilhexil)-phosphoric ac. (unlike Al)
H2O (–H+)
[Be(OH)n(H2O)4–n](2–n)+ ⇄ [Be2(OH)(H2O)n]3+ 1)
[Be3(OH)3(H2O)6]3+,
[Be6(OH)8]4+
pH < 7, sol. BeO
OH– (NH4OH) (pH ⩾ 5.7)
H+
Be(OH)2 · n H2O↓
Kbas. = 10–15 – 10–22
Kac. = 10–25
HCO3–
H2O (t)
[Be(CO3)2]2–
[Be4O(CO3)6]6– (?)
unstab.
OH– (pH > 10)
H2O
[Be(OH)4]2–, tetrah.


Al
Hg
Al/Hg
H+ –[H↑]
H2O –[H↑]
[AlF6]3–, oct. ion, Kstab. = 1020
F–
4,6)
[Al(H2O)6]3+
H+ H2O (K = 10–5)
[Al(H2O)5(OH)]2+ oct. OH– ⇄ [(AlO4)Al12(OH)24(H2O)]7+
H2O H+
[(H2O)4Al(μ-OH)2Al(H2O)4]4+
icosah., in center – tetrah. (r = 12.6 Å), ("Keggin str.", see "Mo, W")
NH4OH [t, pH ⩾ 4.5]
CO32–
AlO(OH)↓, "boemite"
OH– (t)
Al(OH)3 · n H2O↓
Kbas. = 10–33; Kac. = 10–8
CO2 OH– (pH > 9.7)
[Al2O(OH)6]2– ⇄ [Al(OH)4]– ⇄ [Al(OH)4(H2O)2]–
tetrah. ions (sp3)
oct. (sp3d2)


Ga ↓
H+
cath. Red; [H↑]
OH–
[Ga(H2O)6]3+
F–
H2O
[GaFn(H2O)6–n](3–n)+
n = 1–6
H+ OH– (Khyd. = 10–3)
[Ga(H2O)6–n(OH)n](3–n)+ ⇄ [Ga13O4(OH)24(H2O)12]7+
n = 1, 2 4)
stab. ≪ Al-anal.
OH– H+
Ga(OH)3↓, wh., Kac. = Kbas., K2 = 10–11, K3 = 10–12
H2O OH– (pH > 2)
[Ga2O(OH)6]2– ⇄ [Ga(OH)4]– ⇄ [Ga(OH)4(H2O)2]–,
oct. ion, stab.
> [Al(OH)4(H2O)2]–


In ↓
H+
cath. Red.; [H↑]
Cl–
[In(H2O)6]3+
[InCln(H2O)6–n](3–n)+, n = 1–4
5)
HClO4 H2O (Khyd. = 10–4)
[In(H2O)5(OH)]2+ ⇄ [In2(OH)2]4+ ⇄ [In4(OH)6]6+
H+ OH– (pH ⩾ 3.5)
In(OH)3↓
H2O OH– (pH ⩾ 13)
[In(OH)4)]– ⇄ [In(OH)6]3–
Kstab. = 1035


Tl ↓
HNO3; HClO4
Cl2 + H2O
cath. Red.; [H↑]
Br2; S2O32–
SO2; I–
[Tl(H2O)n]+, toxic
Hal– H2O
[TlHal2]–, angular ion (p2)
Hal– H2O
[TlHal3]2–
H2O2 (OH–)
HCl
radiolysis
[TlOH]+
OH–
[Tl(H2O)n]2+
Cl–
[TlCl3]– 2)
[Tl(H2O)6]3+, oct. (?)
H+ H2O (Khyd. = 10–1)
[Tl(H2O)5(OH)]2+, oct.
H+ H2O (pH ⩾ 1)
Tl2O3 · n H2O↓
brn., v. strong Ox
H2O Cl–
OH–
trans-[TlHal2(H2O)4]+,
Hal = Cl, Br, oct., v. stab.
3)
H2O Hal–
[TlHal3(H2O)3] ⇄ [TlHal3(H2O)2]
mol. – oct. and trig. bipyr.
H2O Hal–
HCl
[TlHal4]– ⇄ [H2TlCl5]

SCANDIUM, ACTINIUM

$3+(d^0)$

	3d	4s	4p	EN
Sc^0	↓	↓↑		1.2
	6d	7s	7p	
Ac^0	↓	↓↑		1.0

ScF_3, $ScCl_3$ —Ca; cat. Red→ **Sc** ← Th (t)— Ac_2O_3

	Sc	Ac [5]
	met. silver-wh., mild with yel. reflection	shine in darkness
d	3.02	10.1
m.p.	1541	1050
b.p.	~2850	3390
sol. in H_2O slow.		v. react.
passiv. ($HF + HNO_3$)		
$E_0 M^{3+}/M_{sld}$	−2.08	−2.6
α-, hex. cl. pack.		—
a = 3.31, c = 5.27 ↓ 1335°		
β-, cub. cl. pack.		
a	4.53	5.31
M—M (ex. by 20°)	3.26	3.76

$Sc(Dipy)_3$

$[ScCl_n]^{(3-n)+}$, n = 1, 2 unstab. — **$[Sc(SO_4)_n]^{(2n-3)-}$**, n = 2, 3

$Cl^- \uparrow\downarrow H_2O$ — $SO_4^{2-} \uparrow\downarrow H_2O$ [7]

$[Sc(H_2O)_6]^{3+} \underset{H^+}{\overset{H_2O}{\rightleftharpoons}} [Sc(OH)]^{2+} \rightleftarrows [Sc_2(OH)_2]^{4+} \rightleftarrows [Sc_3(OH)_5]^{4+}$

oct. ion, hydr. and polimerize increases with pH

$[Ac(H_2O)_n]^{3+}$, hydr. $< Ln^{3+}$, extr. TBP $< Ln^{3+}$, wash out of the cationite after Ln^{3+}

H_2O; H^+ / H_2O / M

ScCl, [6] **Sc_7Cl_{10}**, **Sc_5Cl_8**, **Sc_7Cl_{12}**, chains of oct. [Sc_6] with common edges Sc—Sc 3.15–3.41, μ_{eff} = 1.04

Sc (t)

O_2 (250°)

Sc_2O_3, powd., wh., d = 2.75, m.p. 2489, sol. in conc. ac. (t), ΔH = −1907, Mn_2O_3 str. type

↑ 460°

ScO(OH), str. anal. of AlO(OH)

↑ 250°

$Sc_2O_3 \cdot n H_2O\downarrow$, gel, sol. in conc. ac., alk. (t) —OH^- (160°)→ **$Sc(OH)_3\downarrow$**, cube str. like ReO_3, ∠ScOSc 143

$K_{bas.}$ $Al(OH)_3 < Sc(OH)_3 < Ln(OH)_3$

NaOH (conc.)

Scandates [4]

$M_3[Sc(OH)_6]$, $\cdot n H_2O$, Sc—O 2.12; **$M^{II}_3Sc_2(OH)_{12}$**

$Na[Sc(OH)_4]$ —300°→ **$Na(ScO_2)_n$**, frame of oct.

Ac_2O_3, wh. powd., ΔH = −2047, La_2O_3 str. type

$Ac(OH)_3\downarrow$, wh., sol. in ac. $K_{bas.} > Ln(OH)_3$

$Sc(ClO_4)_3$ [1]
$Sc(IO_3)_3$, $\cdot 2 H_2O$, [1]
$Sc_2(SO_4)_3$, $\cdot n H_2O$, n = 5, 6;
$\cdot K_2SO_4 \cdot n H_2O$
$\cdot Cs_2SO_4 \cdot 24 H_2O$, alum (0°)
$Sc_2(SeO_4)_3$, $\cdot 5 H_2O$ [2]
$Sc_2(TeO_4)_3 \cdot 3 H_2O$ [1]
$Sc_2(CrO_4)_3 \cdot 6 H_2O$, orange
$Sc(NO_3)_3$; $\cdot n H_2O$, n = 2, 3, 4, $\cdot 2$ Dipy
$Sc(OH)(NO_3)_2 \cdot 3 H_2O$
$ScHP_2O_7 \cdot 3 H_2O\downarrow$; **$ScPO_4 \cdot 2 H_2O$**
$Sc(H_2PO_4)_3$; **$Sc(PO_3)_3$** [9]
$Sc_4(OH)_{12-n}(CO_3)_n \cdot x H_2O\downarrow$
$Sc(RCOO)_3$, chains of oct. [11]
$Sc_2(C_2O_4)_3 \cdot 5 H_2O\downarrow$, insol. in ac.
$(Sc,Y)_2Si_2O_7$, "thortveitite";
$Sc_2Si_2O_7$, "befanamite";
$ScBO_3$, oct. [ScO_6] and triangle [BO_3]
$[Sc(\mu\text{-}OH)(H_2O)_5]_2Hal_4 \cdot 2 H_2O$, CN Sc 7 [14]
ScOF, ZrO_2 str. type, CN Sc 7

$M[Sc(ClO_4)_4]$
$MSc_3(OH)_6(SO_4)_2 \cdot 4 H_2O$ [8]
$M[Sc(SO_4)_2]$, M = Li, K–Cs [8]
$M_3[Sc(SO_4)_3]$, M = H, Na–Cs

$M[Sc(CrO_4)_2] \cdot n H_2O$, M = Na–Cs
$M_2[Sc(NO_3)_5]$, M = K–Cs, [NO] (= "$Sc(NO_3)_3 \cdot 2 N_2O_4$"), CN Sc 9 [10]
$M_3Sc_2(PO_4)_3$, M = Li, Na [9]
$M_5[Sc(CO_3)_4] \cdot n H_2O$; **$M[Sc(CO_3)_2] \cdot n H_2O$**, M = Na–Cs, NH_4
$M[Sc(C_2O_4)_2]$; **$M_3[Sc(C_2O_4)_3] \cdot 5 H_2O$**

$Ac(NO_3)_3$
$AcPO_4$, $\cdot 0.5 H_2O\downarrow$
$Ac_2(C_2O_4)_3\downarrow$

AcOHal, Hal = Cl, Br
AcOF, CaF_2 str. type
↑ H_2O (1000°)
$AcF_3\downarrow$, LaF_3 str. type
$AcCl_3$, UCl_3 str. type
$AcBr_3$, UCl_3 str. type
AcI_3, —

[13]	m.p.	subl.	ΔH	$\cdot n H_2O$ n =
$ScF_3\downarrow$, colrl.	1530	—	−1548	—
$ScCl_3$, colrl. hyg.	940 (p)	965	−941	6
$ScBr_3$, colrl.	960 (p)	929	−752	6
ScI_3, colrl.	945 (p)	910	−552	6

In str. ScF_3 — frame of oct. with common vertex, $ScHal_3$ — isostr. $FeCl_3$, in gas — triangles (d^2s)

$MScF_4$, M_2ScF_5, M_3ScF_6, KSc_2F_7, chains of pentag. bipyr.
Sr_2ScF_7 [12]
K_3ScCl_6; **Na_3ScBr_6**, ionic conduct.

$Sc(OH)(NCS)_2 \cdot 11 H_2O$, yel.
$Sc(NCS)_3 \cdot 2$ Dipy

$M[Sc(NCS)_4] \cdot n H_2O$
$M_3[Sc(NCS)_6] \cdot n H_2O$, M = M^I, [DipyH]

Sc_2S_3, yel., hydr., semiconduct., blk. — conduct.
ScN, insol. in ac., alk., NaCl — str. type
ScC; **Sc_4C_3**; **ScH_2** — CaF_2 str. type

Ac_2S_3,
AcH, **AcH_3**,

$ScHal_3$ —N_2O_5→ **$Sc(NO_3)_3$**
Sc^{3+} —CO_3^{2-} + CO_2→ **$Sc(OH)(NO_3)_2$**
N_2O_5 → **$ScBO_3$**

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_26, © Springer-Verlag Berlin Heidelberg 2011

YTTRIUM, LANTHANUM, LANTHANIDES (Ln)

2+

Cerium group

		4f	5d	6s	EN
Lanthanum	La^0		↓	↓↑	1.08
Cerium	Ce^{0*}	↓		↓↑	1.08
Praseodymium	Pr^0	↓ ↓		↓↑	1.07
Neodimium	Nd^0	↓ ↓ ↓		↓↑	1.07
Promethium	Pm^0	↓ ↓ ↓ ↓		↓↑	1.07
Samarium	Sm^0	↓ ↓ ↓ ↓ ↓		↓↑	1.07
Europium	Eu^0	↓ ↓ ↓ ↓ ↓ ↓		↓↑	1.01

Yttrium group

		4f	5d	6s	EN
Gadolinium	Gd^0	↓ ↓ ↓ ↓ ↓ ↓ ↓	↓	↓↑	1.11
Terbium	Tb^{0**}	↓↑ ↓ ↓ ↓ ↓ ↓ ↓		↓↑	1.10
Dysprosium	Dy^0	↓↑ ↓↑ ↓ ↓ ↓ ↓ ↓		↓↑	1.10
Holmium	Ho^0	↓↑ ↓↑ ↓↑ ↓ ↓ ↓ ↓		↓↑	1.10
Erbium	Er^0	↓↑ ↓↑ ↓↑ ↓↑ ↓ ↓ ↓		↓↑	1.11
Thulium	Tm^0	↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓ ↓		↓↑	1.11
Ytterbium	Yb^0	↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑		↓↑	1.06
Lutetium	Lu^0	↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑ ↓↑	↓	↓↑	1.14

		4d	5s	EN
Yttrium	Y^0	↓	↓↑	1.11

*) or $4f^1 5d^1 6s^2$
**) or $4f^8 5d^1 6s^2$

Synthesis of Pm:
$^{144}_{60}Nd\ (^2_1D,\ n)\ ^{145}_{61}Pm$ (18 y.)
$^{235}_{92}U\ (n)\ ^{147}_{61}Pm$ + Pu + ··· (in reactor) (2.62 y.)

$LnCl_3$ (La–Gd) —Ca; cath. Red→ Ln

Ln —Ca; cath. Red→ LnF_3 (Tb–Y)

	La	Ce△△	Pr	Nd	Pm	Sm	Eu*	Gd**	Tb	Dy**	Ho**	Er	Tm	Yb*	Lu	Y
	Met. silver-wh., pliant, tarnish. in moist air, dec. H_2O (*t*); sol. in ac. (except. HF and H_3PO_4), paramagn.															
d	6.17	7.3	6.8	7.0	7.26	7.5	5.3	7.9	8.3	8.5	8.8	9.0	9.3	7.0	9.8	4.58
m.p.	920	804	935	1024	1180	1072	826	1312	1356	1407	1470	1522	1545	821	1663	1528
b.p.	3450	3450	3510	3080	~3000	1800	1440	3272	3073	2587	2707	2857	1947	1211	3412	3322
$E_0 M^{3+}/M_{sld.}$	−2.38	−2.34	−2.35	−2.32	−2.29	−2.30	−1.99	−2.28	−2.31	−2.29	−2.32	−2.32	−2.32	−2.22	−2.30	−2.37
$E_0 M^{2+}/M_{sld.}$	—	—	—	—	—	−2.67	−2.80	−2.64	—	−2.20	—	—	−2.3	−2.8	—	—
	α-, hex. cl. pack.					rhombo-hedral	α-, hex. cl. pack.							cub. cl. p.	α-, hex. cl. pack.	
a	3.77	3.68	3.67	3.66	3.65	*a* = 9.00		3.63	3.60	3.59	3.57	3.56	3.54	5.48	3.51	3.65
c	12.16	11.92	11.83	11.80	11.65	α = 23°13′		5.78	5.69	5.65	5.62	5.59	5.56		5.55	5.73
	γ-, cub. cl. pack.															
a	5.03	5.16	↓ 798°	↓ 862°	1)	↓ 917°		↓ 1264°	↓ 1317°		↓ 1400°	↓ 1367°		↓ 798°		↓ 1480°
	↓ 868°	↓ 725°														
	β-, cub. (α-Fe — str. type)															
a	4.26	4.12	4.13	4.13		4.07	4.58	4.06	4.02		3.96	3.94		4.44	3.90	4.11

*) Sol. in liq. NH_3. **) Ferromagn. △△) Pyrophoric.

Colour $[Ln(H_2O)_8]^{3+}$

$\Sigma fe = 7-n$		n		$\Sigma fe = 7+n$
La, colrl.	(f^0)	**7**	(f^{14})	colrl. **Lu**
Ce, »	(f^1)	**6**	(f^{13})	» **Yb**
Pr, yel.-grn.	(f^2)	**5**	(f^{12})	light-grn. **Tm**
Nd, pink	(f^3)	**4**	(f^{11})	pink **Er**
Pm »	(f^4)	**3**	(f^{10})	light-yel. **Ho**
Sm, yel.	(f^5)	**2**	(f^9)	light-grn. **Dy**
Eu, light-yel.	(f^6)	**1**	(f^8)	light-pink **Tb**
Gd colrl.	(f^7)	**0**		

$[Ln(H_2O)_8]^{3+} + H_2O \rightleftarrows [Ln(H_2O)_7(OH)]^{2+} + H^+$,
cub. ions $[Ln(H_2O)_8]^{3+}$; degree of hydr. La → Lu

stab. $Sm^{2+} < Yb^{2+} < Eu^{2+}$

$[Sm(H_2O)_n]^{2+}$, red, strong Red —Na/Hg→ $[Sm(H_2O)_8]^{3+}$, yel., cube
$[Sm(H_2O)_8]^{3+}$ —O_2→ $[Sm(H_2O)_n]^{2+}$

$[Eu(H_2O)_n]^{2+}$, colrl., mild Red —[H ↑]→ $[Eu(H_2O)_8]^{3+}$, yel., cube
$[Eu(H_2O)_8]^{3+}$ —O_2→ $[Eu(H_2O)_n]^{2+}$

$[Yb(H_2O)_n]^{2+}$, grn., strong Red —[H ↑]→ $[Yb(H_2O)_8]^{3+}$, colrl.
$[Yb(H_2O)_8]^{3+}$ —H_2O→ $[Yb(H_2O)_n]^{2+}$

$[Ce(H_2O)_8]^{3+}$, colrl. —$S_2O_8^{2-}$; BiO_3^-→ $[Ce_6(OH)_n(H_2O)_m]^{(24-n)+}$, orange, strong Ox, polymers even by pH ≪ 7
$[Ce_6(OH)_n(H_2O)_m]^{(24-n)+}$ —HCl→ $[Ce(H_2O)_8]^{3+}$, colrl.

$H^+ \uparrow\downarrow OH^-$

$Ce(OH)_3\downarrow$, wh. —O_2; Ag^+→ $Ce(OH)\downarrow_4$ yel brn
$Ce(OH)\downarrow_4$ yel brn —$H_2O_2 + H^+$→ $[Ce(H_2O)_8]^{3+}$, colrl.

$H^+ \uparrow\downarrow H_2O$

14)

Ln²⁺: Nd^{2+} (f^4), Sm^{2+} (f^6), Eu^{2+} (f^7), Ho^{2+} (f^{11}), Tm^{2+} (f^{13}), Yb^{2+} (f^{14})

EuO, red., m.p. 1700, distil. in vac. + H_2O ⟶ $H_2\uparrow$ (slow.), NaCl str. type ["SmO" = **Sm_2ON**; "YbO" = **Yb_2OC**; "LnO", Ln = La–Sm, Yb, cr., golden, with met. lustre, unstab. in air, conduct., contain Ln^{3+} 8)

Eu_3O_4 = $Eu^{II}Eu^{III}_2O_4$

graphite (*t*) → Ln_2O_3

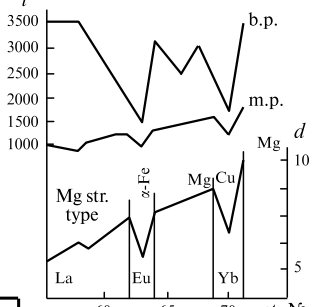
$Eu(OH)_2$, · **H_2O**, sol. in H_2O (comp. Sr— Ba!), used for the separation of Ln; isostr. $M(OH)_2 \cdot H_2O$ (M = Sr, Ba) 8)

Ca → $LnHal_3$

Y_2Hal_3, 23) Hal = Cl, Br
Gd_2Cl_3
Tb_6Br_7
Ln_7I_{12}, Ln = Tb, Er, Lu
Er_7I_{10}, Er_4I_5 in str. — chains of oct., cluster $[Ln_6Hal_{12}]$

$LnF_2\downarrow$	Ln = La–Eu, Yb, red, CaF_2 str. type					
13)	**$NdCl_2$**	**$SmCl_2$**	**$EuCl_2$**	**$HoCl_2$**	**$TmCl_2$**	**$YbCl_2$**
	grn.	brn.	colrl.	yel.	grn.	yel.
m.p.	841	859	738	527	720	723
ΔH	−707	−798	−833	—	−712	−709

$PbCl_2$ str. type; $\xrightarrow{t}$ Ln + $LnCl_3$
$LnBr_2$, Ln = Sm, Eu, Tm, Dy, Yb, blk.
LnI_2, Ln = Nd, Sm, Eu, Tm; CdI_2 str. type
"LnI_2" = $Ln^{3+}I^-_2e^-$, Ln = La, Ce, Pr, Gd, Dy, met. conduct., in str. clusters $[Pr_4]$ and $[I_4]$, Pr — Pr 3.87 2, 38, 43)



Periodicity of changes in the physical property and str. Ln

$CsLnCl_3$, Ln = Sm, Eu, Tm, Yb; $CaTiO_3$ str. type
MLn_2Cl_5, chains of single-cap antiprism $[LnCl_7]$ and $[LnCl_8]$,
$NaEu_2Cl_6$ 22, 25)

La_2Br_5, blk. 24)
Pr_2Hal_5
Nd_3Cl_7; **Eu_4Cl_9**
Sm_6Br_{11}; **Yb_4F_9**

$Eu(ClO_4)_2$
$LnSO_4\downarrow$, Ln = Sm (orange), Eu (colrl.), Yb (yel.-grn.); + H^+ ⟶ H_2 + ...
$SmCO_3$
$KEu(CH_3COO)_3$, CN Eu 8 and 9
$Eu_3(BO_3)_2$; **EuB_2O_4**; **$Eu_2B_2O_5$**; **EuB_4O_7**
Ln_4OCl_6, Ln = Sm, Yb, at. O in center of $[Ln_4]$ tetrah., CN Ln 9 + 1
Er_3OBr_4 22)

$KEu(NH_2)_3$; **$Na_2Eu_3(NH_2)_8$** 26)

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_27, © Springer-Verlag Berlin Heidelberg 2011

3+ **4+**

O_2 (t, p)

Ln_2O_3, refractory, m.p. ⩾2000, b.p. ≈4300, colour corresp. Ln^{3+}, $\Delta H = -1791$ (Pm) – 1883 (Er); hex. layered str. La_2O_3 type, CN 7 (single-cap oct.) (La—Pm); monocl. β-Sm_2O_3 type, CN Sm 6 or 7 (Sm—Gd); cub. Mn_2O_3 type, CN 6(Pm—Lu, Y) [3]

H_2 (> 1000°)

Ce_7O_{12} **Ce_4O_7**, bl. **Tb_7O_{12}** **Tb_4O_7**, **$Tb_{11}O_{20}$**, brn. **Pr_7O_{12-x}** **Pr_9O_{16+x}**; **Pr_6O_{11}**, **$Pr_{10}O_{18}$** **$Pr_{12}O_{22}$**, blk.-brn., CaF_2, str. type [18]

H^+ ($-Ln^{3+}$)

H_2 (t)

CeO_2, powd., wh. ($\xrightarrow{t}$ yel.), m.p. 2700 (p), $\Delta H = -1087$, sol. only in conc. H_2SO_4 (t); + H^+ + H_2O_2 ⟶ Ce^{3+}; **(Ce, Th)O_2**, "cerianit", **PrO_2**, blk.-brn., dec. 400 (p O_2 = 1 atm); $\Delta H = -1004$; **TbO_2**, brn., dec. 400, str. LnO_2-CaF_2 type

Ce(f^0), Pr(f^1), Nd(f^2), Tb(f^7), Dy(f^8)

Superoxyde [12] **$Ln(O_2)_3$**, Ln = La, Pr, Nd, Dy **$Nd_2O_2(O_2)$**, in str. oct. $[NdO_4(O_2)_{2/2}]$

O_2

Ln

H_2O + O_2

LnO(OH), ionic str., CN 7 (single-cap trig. prism.)

$-H_2O$ (Nd 600, Sm 500, Ho 300, Lu 100°)

H_2O (+ Q)

$Ln_2O_3 \cdot x\,H_2O\downarrow$, gels, colour corresp. Ln^{3+}; $\xrightarrow{(MOH,\ t,\ p)}$ **$Ln(OH)_3\downarrow$**, UCl_3 str. type (CN 9); **$Lu(OH)_3$** — dist. ReO_3 str. type (CN 6), sol. in ac., strong bas., absorb. CO_2; $K_{bas.}$, t. dec., SP low La→Lu

O_2

$Ce_2^{III}(Ce^{IV}O_3)_3 \cdot x\,H_2O\downarrow$, cr., bl.-vlt.

Ln

$CeO_2 \cdot nH_2O\downarrow$, gel, yel.-brn. SP = 10^{-50}

$M^I_2O_n$(t)

M_2LnO_3, **$Li_8[LnO_6]$**, Ln = Ce, Pr, Tb **$Li_6Tb_2O_7$**, **$M_{16}Tb_3O_{14}$**, in str. — chains of tetr. pyram. **$BaLnO_3$**, $BaTiO_3$ str. type, + H^+ ⟶ Ln^{3+} + $O_2\uparrow$ [27]

$Ln(OH)_3 \cdot n\,H_2O_2 \cdot x\,H_2O$, Ln = La, Sm, Eu, Lu, stab. La > Lu [7]

$Ce(OH)_3(OOH)$, cr. red-orange (qualit. react.)

↓ H_2O_2

$Ce(OOH)_4$, orange

Ln^{3+} $H_2O_2+OH^-$

$K_5Ce_2(SO_4)_6 \cdot H_2O$ [29]

Ce(OH)CO_3

O_2 + H_2O glucose

Lantanates Na[Nd(OH)$_4$], $MLnO_2$ [4]
$Na_4Ln(OH)_7 \cdot n\,H_2O$, Ln = Yb, Lu

$Ce(ClO_4)_3$, $\xleftarrow{t}$ **$\cdot 8\,H_2O$** [31]; **$Ln(ClO_3)_3 \cdot n\,H_2O$**, Ln = La, Yb; n = 1, 3 CN 9, 8 **$[Ln(H_2O)_9][BrO_3)_3$**; **$Ln(IO_3)_3\downarrow$** (Ce–Lu), CN Ln 8 min sol. Gd
$HLa_3(IO_3)_{10} \cdot 7\,H_2O$; **$HPr(IO_3)_4$**; **$LnH_2IO_6 \cdot 3\,H_2O$**; $\xrightarrow{t}$ **$LnIO_5$**, **$\cdot 4\,H_2O$**
$Ln_2(SO_4)_3$, dec. 780 (La), 630 (Ce), readily sol. in H_2O (0°); **$\cdot 8\,H_2O\downarrow$**; [33] sol. decreases with t, $K_{dis}[Ln(SO_4)]^+ = 10^{-4}$; **$\cdot 9\,H_2O$** (La, Ce), CN 12, **$\cdot 14\,H_2O$** (Ce); **$Pr_2O_2(SO_4)$**, **$Ln_2(SO_3)_3 \cdot 6\,H_2O$** [33]; **$La_2(SeO_4)_3 \cdot 5\,H_2O$**
$Ln(NO_3)_3 \cdot n\,H_2O$, n = 6 (Pr–Nd), CN 10; (La, Ce), CN Ln 11; n = 5, (Y, Eu, Er); n = 4 (Tm–Lu); n = 3 (= $[Yb(NO_3)_3(H_2O)_3]$, n = 3.5 (= $[Y(H_2O)_5(NO_3)_2][Y(H_2O)_2(NO_3)_4]$); n = 1–6 (Tb); [38]
$\xrightarrow{t}$ **$LnO(NO_3)$**, t dec. decreases Ce → Lu; **$La(OH)_2(NO_3)$**;
$LnPO_4\downarrow$ (Er–Yb), [22] **(Ce,La,Y,Th)PO_4**, "monazite"; **YPO_4**, "xenotime"; **$YAsO_4$**, "chernovite"; **(Y,U)[Nb,Ti]$_2O_6$**, "euxenite"; **(Na,Ca,Ln)$_2$[Ti,Nb,Ta)$_2O_6$]**, "loparite"; **$Ln_2(CO_3)_3 \cdot n\,H_2O\downarrow$**, SP ≈ 10^{-20}; **$La_2(CO_3)_3 \cdot 8\,H_2O$**, "lanthanite"; **$Ce(OH)CO_3$**; **(Ce,La . . .)$FCO_3$**, "bastnasite"; **$Ln(C_2O_4)_3 \cdot 10\,H_2O\downarrow$** insol. in dil. ac. and $(NH_4)_2C_2O_4$ (unlike Y, Th) Ln gr. Ce sol. < gr. Y, dec. (500–600), grow Ce→Lu
$La(CH_3COO)_3$ $\xrightarrow{NH_4OH}$ **$La(OH)_n(CH_3COO)_{3-n}\downarrow$**, gel, + I_2 →, bl.
$Be_2Y_2Fe[Si_2O_{10}]$, "gadolinite", "ytterbite" contain Sc, Eu–Lu
$Y_2[Si_2O_7]$, "thalenite" [10, 22, 31–33, 43]

$Cs[Ce(ClO_4)_4]$, **$Cs_2[Ce(ClO_4)_5]$**, **$Cs_3[Ce(ClO_4)_6]$** [31]
$M_3[Ln(SO_4)_3]$, (Y, La); **$M_5[Ln(SO_4)_4]$**, (La, Pr); **$M_4[Y_2(SO_4)_5]$**; **$K_8[Y_2(SO_4)_7]$**;
$K[Ln(SO_4)_2] \cdot H_2O$, (La–Sm) poorly sol. in H_2O; (Eu –Dy) middle; (Tb – Lu, Y) readily; **$K_6[Y_4(SO_4)_9]$** [34]
$M[Ln(SO_4)_2(H_2O)_3](H_2O)$, (Pr, Sm)
$M_2[Ln(NO_3)_5]$, M = M^I, [NO], CN Ln 10;
$Li_3[Ln(NO_3)_5]NO_3$:
$M_3[Ce(NO_3)_6]$; **$M_3[Nd_2(NO_3)_9]$**;
$M_2[Ln(NO_3)_5(H_2O)_2] \cdot 2\,H_2O$, (La–Sm), CN Ln 12, sol. La → Gd
$Mg_3[Ln_2(NO_3)_{12}] \cdot 24\,H_2O$;
$M_2[Ln(NO_3)_5] \cdot H_2O$; [17] **$K_3Ce_2(NO_3)_9$**
$Cs[Ln(NO_3)_4(H_2O)_2]$ (Nd–Tm); [17]
$M_5[Nd_2(NO_3)_{11}] \cdot H_2O$;
$K_3[Ln(NO_2)_6]$ [35]
$M_3Ln(PO_4)_2$; **$M^ILn[P_4O_{12}]$**, **$K_2Nd[P_5O_{15}]$**;
$KLa_2(PO_3)_7 \cdot 10\,H_2O$; **$CsLn(PO_3)_4$**, CN 8
$M[Ln(CO_3)_2] \cdot n\,H_2O$; **$M_5Ln(CO_3)_4 \cdot n\,H_2O$**
$M_3[Ln(CO_3)_3] \cdot 6\,H_2O$;
$[MLn(H_2O)_n](C_2O_4)_2 \cdot H_2O$
$K_3[Y(C_2O_4)_3] \cdot 9\,H_2O$ [37]

$Ce(ClO_4)_4$; **$CeHIO_6 \cdot 3\,H_2O$** [10]
$Ce(SO_4)_2$, powd., yel. dec. 350, poorly sol. in H_2O, insol. in conc. H_2SO_4; **$\cdot n\,H_2O$**, n = 12, 8, 4; orange, in str. — Archimedes antiprism
$CeOSO_4 \cdot H_2O$
$Ce_2(OH)_2(H_2O)_4(SO_4)_3$ [28]
$Ce(OH)(NO_3)_3 \cdot 3\,H_2O$, red (s. yel.) [6]
$[CePhen_4](NO_3)_4$
$Ce(HPO_4)_2\downarrow$, insol. in 4 n HNO_3
CeP_2O_7; **$Ce(HAsO_4)_2 \cdot 2\,H_2O$**
$Ce_2(CO_3)_3(OH)_2\downarrow$, red
$Ce(CH_3COO)_4$, red
$Ce_6O_4(OH)_4(CH_3COO)_{12}$ [30]

HNO_3

Na_2CO_3

$K_8[Ce_2(SO_4)_8] \cdot 4\,H_2O\downarrow$, orange
$(NH_4)_6[Ce(SO_4)_5] \cdot 2\,H_2O$, red
$M_2[Ce(NO_3)_6]$, M = M^I, $M^{II}/2$ ($\cdot 8\,H_2O$, red)
H (extr. from s. in HNO_3 — TBP, by Et_2O(degree of extr. La → Lu)
$K_2Ce(PO_4)_2 \cdot H_2O$
$Na_6[Ce(CO_3)_5]$, **$\cdot 12\,H_2O$**, CN Ce 10, all $[CO_3]$ bidentate [15]

$Ce_2(CO_3)_2(O_2)\downarrow$, dark-red [19]

$M_8[(CO_3)_3Ce]_2(O_2)_2 \cdot n\,H_2O$, M = Na ($n$ = 18, 30), K (12), orange CN Ce 8 [19]

LnO Hal$\downarrow$, CaF_2 or PbFCl str. type; **$LnCl(OH)_2$**, in str. — CN 8 [39]

La_2Br_5
Pr_2Hal_8
Nd_3Cl_7
Nd_4Br_9
Eu_4Cl_9
Sm_6Br_{13}
Sm_5Br_{11}
$Sm_{11}Br_{24}$
Yb_4F_9

[21]	m.p. La	m.p. Lu	b.p. La	b.p. Lu	$-\Delta H$ [40] La	$-\Delta H$ [40] Lu	$\cdot n\,H_2O$
$LnF_3\downarrow$	1430	1184	2330	2230	1727	1702	4; 1↓
$LnCl_3$	862	925	1750	1480	1070	954	6; 7; 8; 9; 15
$LnBr_3$	786	960	1780	1410	997	795	6 (Sm, Gd); 7 (La)
LnI_3	779	1048	1580	1210	700	556	9 (La–Ho); 8 (Er –Lu) 6 (La–Lu)

(Ca,Y,Ce)F_n, n = 2–3, "yttrofluorite";
$LnCl_3 \cdot n\,H_2O$, n = 6, 7 [21], **$LnI_3 \cdot (I_2)_n \cdot 6\,L\downarrow$** [9]
Ln Hal_3, cr. hyg., sol. in alc. (Cl – I); str. LnF_3 (La–Ho) LaF_3 type ("tysonite"), hex. layered, CN 11; (Sm – Lu) – YF_3 type, CN 9, (3-cap. prism); form anom. sld. s. with CaF_2; $LnCl_3$ (La–Gd) and $LnBr_3$ (La–Pr), CN 9; La Cl_3 (Dy–Lu, Y) — CN 6; $LnBr_3$ (Nd, Sm), LnI_3 (La–Nd), CN 8; (Sm –Lu), $LnBr_3$(Dy–Ho) —CN 6.
$LnHal_3$ — in gas triangles or pyram.

F_2; KrF_2

H_2 (t); t ($-F_2$)

$Tb^{III}(Tb^{IV}F_5)_3$

		dec.	ΔH
$CeF_4\downarrow$	colrl.	800	−1962
PrF_4	colrl.	250	−1705
TbF_4	yel.	550	—

ZrF_4 str. type, in gas — tetrah.; $LnF_4\downarrow + H_2O \xrightarrow{t}$ $LnF_3 + HF + O_2$ [11]

M_2LnF_5, CN Ln 7 [5]
M_3LnF_6, oct. (stab. Lu > La)
$MLnF_4$, Ln = La–Tb, CaF_2 str. type
$RbLn_2F_7$; **$BaLn_2F_8$**, **MLn_3F_{10}**
$M_3Ln_2F_9$, **$(NH_4)_3Ln_2F_9 \cdot H_2O$**
K_3LnCl_6; **$Cs_3LaCl_6 \cdot 4\,H_2O$**,
$Cs_3Ln_2Cl_9$, **$BaPrCl_5$**
Li_3CeBr_6, **M_3TmBr_6**, **$M_3Tm_2Br_9$**

F_2(p); XeF_2

$LiCeF_5$, **Li_4CeF_8**, **M_2LnF_6**, **$M_7Ln_6F_{31}$**, M = Na–Cs, Ln = Ce–Nd, Tb–Dy, Tm, colrl., CN Ln = 7–9
Cs_3LnF_7, Ln = Nd, Tb, Dy;
+ H_2O $\xrightarrow{90°}$ O_2 + . . .
M_2CeCl_6, M = Rb, Cs, $[R_4N]$ orange, anion — oct. Ce—Cl 2.59–2.62;
+ H_2O ⟶ Ce(III) + $O_2\uparrow$ . . .
$H_2CeCl_6 \cdot 4$ Diox, orange

LnS$\downarrow$, Ln = Sm, Eu, Yb; **LaS, CeS** = $Ln^{3+}S^{2-}e^-$, yel., conduct.
Ln_3S_4(Ce,Sm); **$Ln_2S_3\downarrow$**, CN (Lu – Yb) 6; (Dy – Tm) 6 and 7; (La – Sm, Gd – Dy) 7 and 8; Ce – 8 (dodecah.)
Ln_2S_4; **Ln_2O_2S**; **La[S_2]**; **LnSe, LnTe** semiconduct.; **Ln_3Se_4** [16]
LnN, LnP, blk., conduct. [26]
LnE, E = As, Sb, Bi, resist. to hydr.; **Ln_2C_3** (La–Ho); **Ln_3C** (Sm–Lu)
LnC_2, yel., conduct.; + H_2O ⟶ C_2H_2 + H_2 + . . .

MAGNESIUM, ALKALI-EARTH METALS, RADIUM

		3s	3p	3d	EN
Magnesium	Mg^0	↓↑			1.2
		4s	4p	4d	
Calcium	Ca^0	↓↑			1.0
		5s	5p	5d	
Strontium	Sr^0	↓↑			1.0
		6s	6p	6d	
Barium	Ba^0	↓↑			0.9
		7s	7p	7d	
Radium	Ra^0	↓↑			0.9

MgO + CaO from "dolomite" → Si (1200°) → Mg

MgO → C (> 2000°) → Alkaline earth metals

MO → Al [1200°] → Alkaline earth metals

MCO_3 → t → MgO, CaO, SrO, BaO, RaO

O_2 (t, Mg – wh. flash); Ca – orang.; Sr, Ra – red.; Ba – yel.-grn. flame → Alkaline earth metals

	MgO	CaO	SrO	BaO	RaO
	cr. colrl., hyg.				
	"periclase"	"lime"			
m. p.	2850	2614	2430	1923	—
b. p.	3600	2850	—	≈2000	—
ΔH	−598	−636	−590	−556	−544

NaCl str. type, in gas – mol. MO; MgO – inert after calcination; **$Ba_{1\pm x}O$**, red

O_2; (Ba < 600°, H_2O); (Sr, p) → **$M[O_2]$, peroxide**, cr. colrl., diamagn., CaC_2 str. type, O—O 1.49, strong Ox.

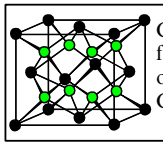
> 600° ←

	MgO_2↓(?)	CaO_2 [25]	SrO_2	BaO_2
	dec. 20	380 (exp. 275)	480	750 (m. p. 450)
ΔH	= −623	−652	−640	−632
		· **8 H_2O**↓	· **8 H_2O**↓ dec. ≈100	· **8 H_2O**
	· **n H_2O_2**	n = 0.5, 2	n = 1, 2	n = 1, 2

H_2O_2 / H_2O ↔ $Mg(OH)_2$↓, $Ca(OH)_2$↓, $Sr(OH)_2$↓, $Ba(OH)_2$ [$Ra(OH)_2$]

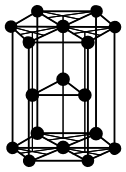
	$Mg(OH)_2$↓ "brucite"	$Ca(OH)_2$↓ "portlandite"	$Sr(OH)_2$↓	$Ba(OH)_2$ [$Ra(OH)_2$]
m. p.	—	—	450	408 (dec.)
dec.	350	580	710 (?)	—
SP	10^{-11}	10^{-5}	10^{-4}	sol. in H_2O
	CdI_2 str. type	· **n H_2O**	in str. CN = 7	
$K_{bas.2}$	10^{-3}	10^{-2}	10^{-1}	10^{-1}
	$Na_2[Mg(OH)_4]$ [4]		in str. $M(OH)_2 \cdot n H_2O$ CN M = 8 (antiprism)	n = 8, 1–3

$M[O_2]_2$ and $M[O_3]_2$ see tab. "Oxygen" [3,11]



CaF_2 str.; Ca-at. at the sites of face-centered cube, F – centers of 8 small cubes; CN Ca 8 (cube), F 4 (tetrah.)

	Mg	Ca	Sr	Ba	Ra
		Alkaline earth metals			
	met., lustrous			soft	
	wh.	wh.	light yel.	wh.	wh.
	on the surface of the finest film MgO	oxidized in air. Ra ≫ Mg			glows in the dark
	diamagn.				paramagn.
d	1.74	1.54	2.69	3.6	≈6
m. p.	651	851	1000 [10]	727	969
b. p.	1107	1482	1390	1860	1536
$E_0 M^{2+}/M_{Sld.}$	−2.34	−2.84	−2.89	−2.90	−2.92
	sol. in dil. ac. (except HF)	react. with H_2O, alk., sol. in liq. NH_3 (< M^I)			
		α-, cl. cub. pack.			
	+ NH_4X (→ H_2 + NH_3); + RHal(→RMgHal)	a = 5.56	6.05		
		M—M 3.94	4.30		
		464° ↓	↓ 250°		
	Hex. cl. pack. (Mg str. type), CN 12, at.– in sites of cell and in centers of 3 from 6 trig. prism;				
		β-			
a = 3.20		3.98	4.31		
c = 5.20		6.52	7.05		
			↓ 605°		
			γ-, cub. (α-Fe str.type)		
			a = 4.84	5.02	5.15



Mg(OH)Hal

	m. p.	b. p.	ΔH	
MgF_2↓, "sallaite", TiO_2 str. type	1396	2260	−1121	SP = 10^{-9}, sol. in HNO_3
$MgCl_2$ "chloromagnesite", $CdCl_2$ str. type	714	1418	− 644	· **6 H_2O** "bischofite"
$MgBr_2$, CdI_2 str. type	710	1430	−519	· **6 H_2O**
MgI_2, CdI_2 str. type	633 (dec.)	1014	−360	· **8 H_2O**

$MgHal_2 \cdot n$L, L = NR_3, R_2O, $R_2C{=}O$; n = 2, 6

$NaMgF_3$, [8] "neighborit" **K_2MgF_4** **$M_4Mg_3F_{10}$**, **$MMgCl_3$**, **$M_2[MgCl_4]$**, [9] **Na_6MgCl_8**

$[Mg(H_2O)_6][CaCl_6]$ "tahihydrat" [23]

$Ca(OH)Hal \cdot 0.5\,H_2O$; $CaCl_2 \cdot 3\,Ca(OH)_2 \cdot 12\,H_2O$

	m. p.	b. p.	ΔH	
CaF_2↓, "fluorite"	1419	≈2500	−1222	SP = 10^{-11}
$CaCl_2$, dist., TiO_2 str. type	782	≈2000	− 799	· **n H_2O** n = 1, 2, 6
$CaBr_2$, dist., TiO_2 str.type	760	1830	−685	· **n H_2O** n = 3, 6
CaI_2, CdI_2 str. type	784	1760	−536	· **6 H_2O**

$Sr(OH)Cl \cdot 4\,H_2O$ [21]

	m. p.	b. p.	ΔH	
SrF_2↓, CaF_2 str. type	1473	2460	−1222	SP = 10^{-9}
$SrCl_2$ CaF_2 str. type	873	2030	− 799	· **n H_2O** n = 1, 2, 6
$SrBr_2$, dist. $PbCl_2$ str., CN 7 [12]	643	—	−685	· **n H_2O** n = 1, 2, 6
SrI_2, $PbCl_2$ str. type	515	—	−536	· **n H_2O** n = 2, 6

$Ba(OH)Cl \cdot 2\,H_2O$ [20]

	m. p.	b. p.	ΔH	
BaF_2↓, CaF_2 str. type	1353	2260	−1196	SP = 10^{-6}
$BaCl_2$ $PbCl_2$ str. type	962	1830	− 858	· **n H_2O** n = 1, 2
$BaBr_2$, $PbCl_2$ str.type	853	—	−757	· **n H_2O** n = 1, 2
BaI_2, $PbCl_2$ str. type	740	—	−607	· **n H_2O** n = 2, 6

	m. p.	[5]
RaF_2↓,	—	—
$RaCl_2$	≈ 900	· **2 H_2O**
$RaBr_2$*	728	· **n H_2O**
	900	**n** = 2, 6
RaI_2	—	—

* rapidly yel.

In gas –linear mol. $MgHal_2$, $CaHal_2$ (Cl–I), $SrHal_2$ (Br, I), angular – CaF_2, $SrHal_2$ (F, Cl) and $BaCl_2$ [21]

Mg light alloys: [Mg + Al (⩽10%) + Zn (⩽4%) + Mn (⩽1.7%)] – "electron"; [5–30% Mg + Al] – "magnaly", hardness > Al

Formation of Ra in nuclear decay; $^{232}_{90}Th \xrightarrow{\alpha} {}^{228}_{88}Ra \longrightarrow {}^{228}_{90}Th \xrightarrow{\alpha,\gamma} {}^{224}_{88}Ra \longrightarrow$ 3.64 d.; $^{238}_{92}U \xrightarrow{\alpha} \cdots {}^{230}_{90}Th \xrightarrow{\alpha,\gamma} {}^{226}_{88}Ra \longrightarrow \cdots$; $^{235}_{92}U \xrightarrow{\alpha} \cdots {}^{227}_{90}Th \xrightarrow{\alpha,\gamma} {}^{223}_{88}Ra \longrightarrow \cdots$ 1617 y. 11.3 d. (series U–Ra and Ac)

Isolation of ^{226}Ra from U-ore (≈10^{-5}%): 1) coprecipit. with $BaSO_4$↓; 2) dissolution in complexone; 3) chromatographic

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_28, © Springer-Verlag Berlin Heidelberg 2011

$Mg(ClO_4)_2$, "anhydrone", m. p. 246, dec. 382., readily sol. in alc., $\cdot\ 6H_2O$, m. p. 147; $M^I[Mg(ClO_4)_3]$ [15]
$M(ClO_4)_2$, M = Ca, Sr ($\cdot\ H_2O$), Ba (dec. 505), $\cdot\ nH_2O$, desiccators
$M(ClO_3)_2$, dec. 120 (Sr),m. p. 414 (Ba); $\cdot\ nH_2O$, n = 6 (Mg), 2 (Ca), 8 (Sr), 1 (Ba), readily sol. in H_2O
$Ca(ClO)_2$; $\cdot\ 3H_2O$; $\cdot\ 1/3\,Ca(OH)_2 \cdot x\,H_2O$, "lime chloride"
$Ba(ClO_2)_2$, dec. 235
$M(BrO_3)_2 \cdot nH_2O$, n = 6 (Mg), 1 (Ca, Sr sol.; Ba↓), dec. > 200
$Mg(IO_3)_2$, $\cdot\ nH_2O$, n = 4, 1, dec. 210, readily sol. in H_2O;
$M(IO_3)_2$↓, SP = 10^{-6} (Ca), 10^{-13} (Sr), 10^{-9} (Ba), 10^{-14} (Ra)
$Ba_5(IO_6)_2$; $M_2I_2O_9 \cdot nH_2O$↓, M = Ca (n = 8); Ba (n = 3) [14]

$M(HCO_3)_2$, sol. in H_2O (M = Mg, Ca, – cause "temporary hardness" H_2O)
t ↓↑ CO_2
$MgCO_3$↓, "magnesite", dec. 350; $\cdot\ nH_2O$, n = 2, 3, 5
$\cdot\ M^I_2CO_3$, M^I = K, NH_4, Ca/2 ("dolomite")
$CaCO_3$↓, "calcite", m. p. 1340 (p), "aragonite", dec. 825, SP = 10^{-9}; $\cdot\ nH_2O$↓, n = 6, 3, 1, 0.65
$SrCO_3$↓, "strontianite", dec. 1350, m . p. 1497 (p), SP = 10^{-9}
$BaCO_3$↓, "witherite", dec. 1450, m. p. 1740 (p), SP = 10^{-9}
$RaCO_3$↓
"Magnesite" and "dolomite" are isostr. to "calcite", "strontianite", "witherite" and $RaCO_3$ – to "aragonite"

Hydrides
$(MgH_2)_n$, 1) powd. wh., dec. ≈300, inflam. in air, rapidly react. with H_2O;
2) inact. form., α- stab. in air, slow. react. with H_2O,
ΔH = –71, TiO_2 str. type; $\xrightarrow{p,\ 300^\circ}$ β-, γ- dec. 390°, in str. – CN Mg 6 and 8 [2]
MH_2, M = Ca–Ba, $d > d$ M, dec. ≈600, stab. Ca > Sr > Ba, insol. in liq. NH_3; $PbCl_2$ str. type (CN 9); ΔH = –188 (Ca); –176 (Sr); –170 (Ba); d = 1.90 (Ca); 3.27 (Sr); 4.21 (Ba)
+ H_2O ⟶ H_2 (exp. react.);
+ E_2O_n ⟶ E + MO + H_2 (E = Al, Ti, Nb, W);
+ BCl_3 ⟶ B_2H_6 + MCl_2; MH_2 + H_2 ⇄ MH_n, $n \leqslant 4$,
M = Sr, Ba

175°; $LiAlH_4$ ← R_2Mg
MH →
$KMgH_3$ [17]
K_2MgH_4
$Li[MH_3]$, M = Ca – Ba
Cs_2CaH_4,
K_2NiF_4 str. type

$MgSO_4$, m. p. 1185 (dec.) ("arcanite"), $\xleftarrow{200^\circ}$ $\cdot\ nH_2O$, n = 1, 2, 4 – 7 ("epsomite", "bitter salt");
$\cdot\ K_2SO_4 \cdot nH_2O$, n = 6 ("scheonite"), 4 ("leonite")
$CaSO_4$↓, m.p. 1450, "anhidrite" $\underset{}{\overset{163^\circ}{\rightleftarrows}}$ $\cdot\ 0.5H_2O$ $\underset{H_2O}{\overset{100^\circ}{\rightleftarrows}}$ $\cdot\ 2H_2O$↓ "gyps",
SP = 10^{-5}, K = 10^{-3}; $\cdot\ M_2SO_4$, M = H, K, NH_4, Na.
MSO_4↓, M = Sr (m. p. 1500 (p), dec. 1580, SP = 10^{-7}), Ba (m. p. 1580, dec.), SP = 10^{-10}, "baryta"; Ra, SP = 10^{-12}, sol. in EDTA [16]
$MSO_3 \cdot nH_2O$↓, n = 6 (Mg), 2, 4 (Ca), 0 (Sr, Ba)
$MS_2O_3 \cdot nH_2O$, n = 6 and 3 (Mg, Ca); 5, 1 (Sr,), 1, 2 (Ba↓)
$MS_2O_6 \cdot nH_2O$, n = 4 (Ca, Sr), 2 (Ba), readily sol. in H_2O
$MSeO_4 \cdot nH_2O$, n = 6 (Mg, readily sol. in H_2O), 2 (Ca, sol.), 0 (Sr↓, SP = 10^{-5}; Ba↓; Ra↓) $MCrO_4 \cdot nH_2O$, yel., n = 7 (Mg, readily sol.), 2 (Ca, sol.), 0 (Sr↓, SP = 10^{-5}; Ba↓; Ra↓, SP = 10^{-10}),
$MCr_2O_7 \cdot nH_2O$, n = 3 (Sr), 2 (Ba), red, readily sol. in H_2O

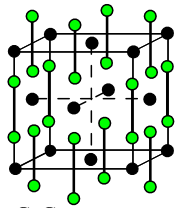
$M(CH_3COO)_2$, M = Mg (m. p. 323, dec.), 450 (Ba), $\cdot\ nH_2O$, n = 4 (Mg), 1, 2 (Ca), 0.5 (Sr), 3 and 1 (Ba)
$M(HCOO)_2$, $\cdot\ 2H_2O$, M = Mg — Sr, $K_{dis.} = 10^{-3}$
$MC_2O_4 \cdot nH_2O$↓, n = 2 (Mg), 3, 2 , 1 (Ca), 1 (Sr), 0 (Ba); SP = 10^{-4} (Mg), 10^{-9} (Ca), $6 \cdot 10^{-8}$ (Sr), 10^{-7} (Ba)

$M(CN)_2$, M = Mg, Ca, Ba, Sr ($\cdot\ 4H_2O$), linear mol., in str. – polymer chains with bonds M — C, M — N
$CaCN_2$, cyanamide, subl. 1200°; + H_2O ⟶ NH_3↑
$M(NCS)_2$, $\cdot\ nH_2O$, cr. hyg., readilty sol. in H_2O, alc., in str.-oct. $[MgN_2(H_2O)_4]$, Mg — N 2.10, Mg — O 2.09 [22]

$M(NH_2)_2$ "amides", M = Mg (infl.), Ba (m. p . 290), wh., insol. in liq. NH_3; in str. – tetrah. $[MgN_{4/2}]$ [12]
↓ 400° (–NH_3) **$M^I_2[Mg(NH_2)_4]$** [18]
MNH, imides, cr., yel. **$KM^{II}(NH_2)_3$**, (M^{II} = Ca, Sr)
t ↓↑ H_2 (–MH_2)
M_3N_2, "nitrides", M = Mg (dec. 1500, ΔH = –477), Ca (m. p. 1195, ΔH = –439), Sr (> 1000, –389), Ba (1000, –364), cr. colrl.,
+ H_2O ⟶ $M(OH)_n$ + NH_3↑;
+ CO ⟶ MO + N_2 + C (M = Ca, Sr);
N_2 ↓↑ t ↓ 500° (vac. –N_2)
BaN_2, M_3N_4, blk.-brn. **M_4N_8**, M = Sr, Ba, blk.
+ H^+ ⇄ N_2 + NH_3 + $M(OH)_2$
$M(N_3)_2$, azides
powd., gray or red
M_2NHal **$K_2[Ca(N_3)_4(H_2O)_4]$** [19]

$M(NO_3)_2$, dec. > 300, $\xleftarrow{t}$ $\cdot\ N_2O_4$; $\cdot\ nH_2O$, n = 6.2
$M(NO_3)_2$, m. p. 561 (dec.) (Ca), 570 (Sr), 592 (Ba),
$\xrightarrow{t}$ $M(NO_2)_2$ + O_2 ⟶ NO_2 + MO;
$\cdot\ nH_2O$, n = 3, 4 (Ca, Sr), 2 (Ba), 1 (Ca – Ba) dec. ~ 100
$M(NO_2)_2$, dec. 240 (Sr), 217 (Ba); Ra
$\cdot\ nH_2O$, n = 4 (Ca), 1 (Ca – Ba,); $K_2Na(NO)_2)_4$ [5]
$MN_2O_2 \cdot nH_2O$↓, n = 5 (Sr), 4 (Ba)

N_2



$Ba(C{\equiv}CH)_2 \cdot 4NH_3$,
$M[C_2]$, carbides (acetylides),
M = Ca (m. p. 2300, ΔH = –58), Sr, Ba (1780, –50); dec. ~ 2000, CaC_2 str. type, tetr., dist. NaCl str. ($[C_2]^{2-}$ = Cl^-);
+ H_2O ⟶ $M(OH)_2$ + C_2H_2↑ (BaC_2 – inflam.);
+ N_2 ⟶ **MCN_2**
MgC_2 $\xrightarrow{600^\circ}$ $Mg_2[C{=}C{=}C]$; ΔH = +88;
+ H_2O ⟶ $CH_3C{\equiv}CH$ + $CH_2{=}C{=}CH_2$

C (in electric stove) ←
M; MO

Silicates
Mg_2SiO_4, ("forsterite"); **$(Mg,Fe)_2SiO_4$**, ("olivine");
$Mg_2Si_2O_6$, ("enstatite"); **$Mg_3Si_4O_{10}(OH)_2$**, ("talc");
$CaMg(SiO_3)_2$, ("diopside"); **Ca_2SiO_4**, $\cdot\ nH_2O$, ("hillebrandite");
$CaSiO_3$ $\cdot\ nH_2O$ "solanite"; **$Ca_3[Si_2O_7]$**, ("rankinite");
$Ca_3[Si_3O_9]$, ("wollastonite"); **$BaSiO_3$**, $\cdot\ 6H_2O$; [5]
$RaSi_2O_5$

$M_3(PO_4)_2$↓, amorph., m. p. 1357 (Mg), 1670 (Ca), 1727 (Ba); $\cdot\ nH_2O$ (Mg, n = 22, 8, 4; Ca, n = 4, 5); SP = 10^{-24} (Mg), 10^{-26} (Ca), 10^{-28} (Sr), 10^{-23} (Ba);
$M(NH_4)PO_4$, $\cdot\ nH_2O$, n = 6 (Mg), 7 (Ca);
$Ca_5[PO_4]_3(F, Cl, OH)$, "apatite"; **$Ca_8H_2(PO_4)_6 \cdot 5H_2O$**
$MHPO_4 \cdot nH_2O$↓, n = 3, 7 (Mg,); 2 (Ca, SP = 10^{-6}); 0 (Sr, 10^{-6}; Ba, 10^{-7});
$M(H_2PO_4)_2$, $\cdot\ nH_2O$, n = 6, 2 (Mg), 1 (Ca, Ba), 0 (Ca, Ba)
$M_2P_2O_7$↓, m. p. 1383 (Mg), 1230 (Ca),
$\cdot\ nH_2O$, n = 6, 3 (Mg), 5 (Ca)

$[M(OR)_2]$, aloxides, cr., v. hyg., insol. in ROH, liq. NH_3, $Mg(OH)_2$ str. type
$Mg(OMe)_2 \cdot 3.5\,MeOH$; **$Ba(OR)_2$** $\cdot\ nROH$, n = 1,4, R = Me, Et, sol. in ROH, liq. NH_3 [6]
$Mg(C_5H_5)_2$. isostr. $Fe(C_5H_5)_2$ [13]

$M_3(AsO_4)_2 \cdot nH_2O$, n = 8 (Mg, "hernesite"); 3 (Ca); 0 (Ba↓, amorph., m .p. 1605)
$M(NH_4)AsO_4 \cdot 6H_2O$↓, M = Mg, Ca
$MHAsO_4 \cdot nH_2O$, n = 7 (Mg, "rosslerite"); 1↓ (Sr, Ba)
$M(AsO_3)_2$↓, n = 4 (Sr), 0 (Ba, dec. 500)
$M_2As_2O_7$, M = Sr, Ba (dec. 800) [7]

C (1, $-CO_2$) → $CaSO_4$

$M(HS)_2 \cdot nH_2O$, n = 6 (Ca), 0 (Sr), 4 (Ba), readily sol. in H_2O
MS↓, m. p. ~2000° (dec.)
ΔH = –352 (Mg), –460 (Ca), –452 (Sr), –443 (Ba); NaCl str. type
+ H_2O ⇄ $M(HS)_2$ + $M(OH)_2$;
MgS_4; MgS_5
$SrS_4 \cdot nH_2O$, n = 6, 4; **SrS_5**, yel.
BaS_2, m. p. 925
BaS_3, grn., m. p. 554; **BaS_4**, red, readily sol. in H_2O, dec. 300; $\cdot\ 2H_2O$

H_2 ↗ M ↘ N_2 (t)

0 **2+**

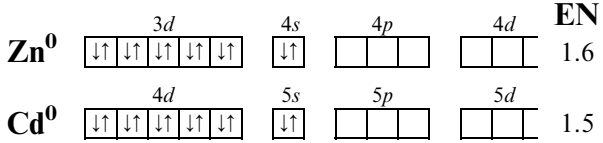
$Mg \xrightarrow[(-H_2\uparrow)]{H^+;\ H_2O+NH_4^+} [Mg(H_2O)_6]^{2+}$, oct. ion

$M \xrightarrow{H_2O\ (-H_2)} [M(H_2O)_n]^{2+}$, stab. Ba < Sr < Ca < Mg,

EDTA ↓

$M[EDTA]^{2-}$, $K_{stab.}$ = 10^9 (Mg), 10^{11} (Ca), 10^9 (Sr), 10^8 (Ba)
EDTA = $[-CH_2N(CH_2COO)_2]_2]^{4-}$

ZINC, CADMIUM



	Zn	Cd
met. wh., mild, lustrous		
d	7.14	8.65
brittle		ductile
> 150° – tough		
> 200° – frail		
m. p.	419	321
b. p.	913	766
el. conduct.		
	16 times	13 > Hg
sol. in dil. ac., alk., NH_4OH		in dil. ac.
$E_0 M^{2+}/M_{sld.}$	−0.76	−0.40
dist. hex. cl. pack.		
a = 2.66		2.97
c = 4.94		5.61
M — M	2.66	2.97

M

Alloys
Zn + Cu – brass;
Zn + Fe – in non-corrosive coating;
Zn + 4% Al + 3% C + + 0.1% Mg – high mechanical strength (printing alloys).
Fusible alloys based on Cd

$1+$ $[Zn_2]^{2+}[ZnCl_4]^{2-}$ (ex. in melt Zn + $ZnCl_2$) [20]

$Cd(I)$

$CdCl_2$

$Cd^ICl \cdot n\,CdCl_2$, red-blk. melt
↓ $AlCl_3$
$Cd^I_2[AlCl_4]_2$, cr. yel., sol. in bz.
↓ H_2O
Cd + Cd^{2+}, $[Cd_2]^{2+}$ diamagn., stab. ≪ $[Hg_2]^{2+}$ [3]

C; CO; H_2

O_2 (bl. flame – Zn; red – Cd)

HX (H_2O)

cath. Red

N_2O_4

ZnO, wh. ($\overset{500°}{\rightleftarrows}$ yel.), m. p. 1969 (*p*), subl. 1725 (dec.), $\Delta H = -348$, "zincite", wurtzite str. type, framework of tetrah.

250° (– H_2O)

$Zn(OH)_2$↓, wh., sol. in ac., alk., NH_4X, $K_{bas.2} = 10^{-5}$, $K_{ac_1} = 10^{-12}$, $K_{ac_2} = 10^{-13}$, aging prec. α-, $Mg(OH)_2$ str. type, (oct. ZnO_6) ⟶ β- ⟶ γ- ⟶ . . . ε- (tetrah. $[ZnO_4]$).

$-NH_3$

$[Zn(NH_3)_4(H_2O)_2](H_2O)_2$

CdO, brn.; $\xrightarrow{t(O_2)}$ red.; subl. ~900 (partial dec.) ($\xrightarrow{900°}$ Cd + O_2), $\Delta H = -260$, sol. in NH_4X, ac., NaCl str. type, Cd — O 2.35.

200° (– H_2O)

$Cd(OH)_2$↓, wh., SP = 10^{-14}, sol. in ac., NH_4OH ($K_{bas.2} = 10^{-3}$), in conc. alk. v. slow.; α-, β- – CdI_2, str. type, γ- – in str. – pair oct. with common faces. [27]

MOH (conc. *r*)

Zincates, cadmates [1,6]
$Na_2[M(OH)_4] \cdot 2\,H_2O$; $Na[Zn(OH)_3]$
$Ba_2[M(OH)_6]$, anion – oct.
$Ba[Zn_2(OH)_6] \cdot 5\,H_2O$,
K_4ZnO_3, anion – triangle
$M_2(Zn/Cd)O_2$↓, chains of tetrah.
$Na_6[MO_4]$, $K_2Cd_2O_3$, $K_2Zn_6O_7$

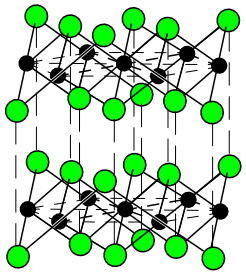
$Li[Cd(ClO_4)_3]$; $Na[Cd_2(ClO_4)_5]$
$K_2[M(S_2O_3)_2] \cdot H_2O$, $K_{stab} = 10^5$(Zn) [12]
$M_2[Zn(NO_3)_4]$, M = NO, R_4N
$[NO][Zn(NO_3)_3]$; $M_2[Zn(NO_2)_4]$
$M_2[Cd(NO_2)_4]$, stab. > Zn-compl.,
$KZn_2H(PO_4)_2$; $MZnPO_4$, cycles of tetrah. $[PO_4]$ и $[ZnO_4]$,
$Na[Cd(HCOO)_3]$, anion – layers of oct.
$Na_2[M(C_2O_4)_2]$ [10]

$M(ClO_4)_2$,	**$\cdot n\,H_2O$**, n = 2, 4, 6 [23]	n = 2,6
$M(ClO_3)_2 \cdot 4\,H_2O$		n = 2
$M(ClO_2)_2 \cdot 2\,H_2O$		n = 2
$M(BrO_3)_2 \cdot 6\,H_2O$, m. p. 100, $[Zn(H_2O)_6]^{2+}$		n = 2, CN Cd 7 [32]
$M(IO_3)_2 \cdot 2\,H_2O$↓, framework oct. [4]		n = 1, 6; CN Cd 7
$M(MnO_4)_2 \cdot 6\,H_2O$, blk., readily sol. in H_2O		n = 6, vet.,
MSO_4, dec. 620, oct. ("zinkosit")		m. p. 1135
	$\cdot n\,H_2O$, n = 7, 6, 1; t ⟶ **$Zn_3O(SO_4)_2$** [8]	n = 7, 4, 2.67; in str. – oct.
	$\cdot (NH_4)_2SO_4 \cdot 6\,H_2O$, Tutton salts	**$Cd_2(OH)_2SO_4$**
$MSO_3 \cdot 2.5\,H_2O$		n = 2
$MS_2O_3 \cdot 6\,H_2O$, readily sol. in H_2O		$K_{dis.} = 10^{-4}$
$MS_2O_6 \cdot 6\,H_2O$		n = 6
$MSeO_4 \cdot 5\,H_2O$		n = 1, oct. $[CdO_6]$ [15]
$M(NO_3)_2$, volat. $\overset{100°}{\longleftarrow}$	**$\cdot 2\,N_2O_4$**; [24]	m. p. 353 [33]
	$\cdot n\,H_2O$; n = 2.3, 6, 9;	n = 2, 4 (in str.
	$\cdot n\,Zn(OH)_2 \cdot m\,H_2O$↓, n = 1– 4, m = 0–2. [11]	dodecah., CN M 8)
$M_3(PO_4)_2$↓, m. p. 1060,	**$\cdot 4\,H_2O$**	m. p. 1500 [31]
$M(H_2PO_4)_2 \cdot n\,H_2O$, n = 1, 2		—
$M_2P_2O_7$↓, m. p. 1017		**$\cdot 2\,H_2O$**
$M(PO_3)_2$↓, m. p. 872		
$M_3(AsO_4)_2 \cdot 8\,H_2O$↓, "kottigite"; **$Zn_3(AsO_3)_2$**		**$CdHAsO_4 \cdot 2\,H_2O$**
MCO_3↓, dec. 200, "smithsonit"		dec. 300; $\overset{CO_3^{2-}}{\longleftarrow}$ **$\cdot Cd(OH)_2$**,
$\xrightarrow{H_2O}$ **$\cdot n\,Zn(OH)_2 \cdot m\,H_2O$**↓		
$M(CH_3COO)_2$, m. p. 242; framework of tetrah.;		m. p. 256; $\overset{130°}{\longleftarrow}$ **$\cdot 2\,H_2O$**
$\cdot 2\,H_2O$, dec. 100. oct. $[ZnO_6]$, $K_{dis.} = 10^{-2}$ [22]	↓ 250°	
↓ 250°		↓ 262°
$M_4O^*(CH_3COO)_6$, m. p. 272, subl., sol. in $CHCl_3$,		non volat.
		isostr. Be- anal.
$M(HCOO)_4$,	**$\cdot 2\,H_2O$**↓	n = 1, CN Cd 7 [29]
MC_2O_4, SP = 10^{-9}, $K_{dis.} = 10^{-5}$;	**$\cdot 2\,H_2O$**↓	dec. 340; n = 3, $K_{dis.} = 10^{-4}$
$M_2[SiO_4]$, m. p. 1509, "villemite"		m. p. 1252
$MSiO_3$, m. p. 1437		m. p. 1242
$Zn_4O(BO_2)_6$, m. p. 980, str. anal. of $Zn_4O(CH_3COO)_6$;		—
$Zn(BO_2)_2$		—

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$MO_2 \cdot n\,H_2O\downarrow$, M = Zn, Cd, powd. wh. or yel., exp. > 200° [26]

M^{2+} — $OH^- + H_2O_2$



CdI_2 str.

$ZnHal_2 \cdot n\,Zn(OH)_2 \cdot m\,H_2O\downarrow$, Hal = Cl–I, n = 1, 4, layers of tetrah. and oct. **$Zn_5(OH)_8Cl_2 \cdot H_2O$** [25]

$M(OH)Hal\downarrow$, **$CdHal_2 \cdot 3Cd(OH)_2\downarrow$**, layers of oct. [30]

[21]	m. p.	b. p.	ΔH	str. type	$\cdot n\,H_2O$, n =
$ZnF_2\downarrow$	875	1502	−765	TiO_2	4
$ZnCl_2$	326 (β)	733	−414	—	4, 3, 2.5,
	315 (α)				1.5, 1
$ZnBr_2$	394	670	−327	$CdCl_2$	3, 2
ZnI_2	446	624 (dec.)	−209	CdI_2, $CdCl_2$	2

	m. p.	b. p.	ΔH	str. type	$\cdot n\,H_2O$, n =
$CdF_2\downarrow$	1072	1753	-698	CaF_2	2
$CdCl_2$	568	964	−389	$CdCl_2$	1–4
$CdBr_2$	567	863	−314	$CdCl_2$	2, 4
CdI_2	388	754	−201	CdI_2	—

cr. colrl., hyg., $ZnHal_2$ sol. in H_2O > $CdHal_2$, readily sol. in alc. Et_2O, weak electrolytes, prone to autocomplexing, in s.: $Cd^{2+} + 2\,[CdHal_3]^- \rightleftarrows 3\,CdHal_2 \rightleftarrows 3\,[CdHal]^+ + 3\,Hal^-$; $2\,CdHal_2 \rightleftarrows Cd^{2+} + [CdHal_4]^{2-}$, in gas – linear mol. $MHal_2$. In str. $ZnCl_2$ (α-, β-) – net of dist. tetrah., in str. $ZnBr_2$, ZnI_2 – framework of tetrah.; in layered str. CdI_2 – hex. cl. pack [ICdI], in rhombohedral str. $CdCl_2$ – [ClCdClClCd]
$[ZnHal_2L_2]$, L = NH_3, Py (mol. tetrah.), N_2H_4; **$[CdHal_2L_2]$**, L = NH_3, Py (chains of oct.) $[CdHal_{4/2}N_2]$ – *trans*, **$CdI_2 \cdot 10\,NH_3$** [5,28]

$RbMF_3$; **M_2ZnF_4**,; **$K_3Zn_2F_7$**, **$Sr_4Zn_3F_{14}$**
$K_2[MCl_4]$, M = Zn (anion tetrah.); Cd (layers of oct., stab. ≫ $[ZnCl_4]^{2-}$
KZn_2Cl_5; **$KMCl_3 \cdot n\,H_2O$**.
$M_4[CdCl_6]$, anion – oct.
$N_3ZnCl_5 = N_3[ZnCl_4]Cl$
Na_6CdCl_8
$RbMBr_3$; **Rb_2MBr_4**, tetrah.
Rb_4CdBr_6 oct.
$KMI_3 \cdot n\,H_2O$; chain of tetrah.
$Li_2[MI_4]$ [2,13]

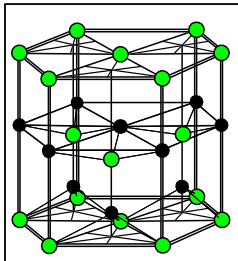
$Zn(CN)_2\downarrow$, wh., dec. 800
$Cd(CN)_2\downarrow$, colrl., dec. 200
$[Cd(CN)_2]_n \cdot m\,H_2O \cdot m\,R_2O$, ($n$ = 3, 8) [17]
$Cd(CN)_2 \cdot L$, L = DMPA, DMSO, in str. linear canals

$M_2[Zn(CN)_4]$, anion – tetrah., $K_{stab.} = 10^{20}$
$K[Zn(CN)_3] \cdot 2.5\,H_2O = K_2Zn[Zn(CN)_6] \cdot 5\,H_2O$, in str. – oct. $[ZnC_6]$ and tetrah. $[ZnN_4]$
$M_2[Cd(CN)_4]$, $K_{stab.} = 10^{18}$; **$M[Cd(CN)_3]$**

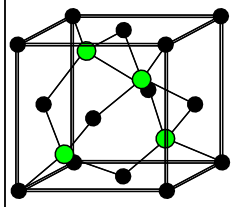
$Zn(NCS)_2\downarrow$, colrl., in str. – layers of tetrah. [19]
$[Zn(NCS)_2(N_2H_4)_2]$, mol. – oct.
$Cd(SCN)_2$, colrl., in str. – oct. $[CdS_4N_2]$ [17]
$[Cd(SCN)_2(N_2H_4)_2]$, mol. – oct.

$K_2[Zn(–NCS)_4] \cdot 3H_2O$, tetrah. $[ZnN_4]$, $K_{stab.} = 10^3$
$M_2[Cd(—SCN)_4]$, anion – dist. oct. $[CdN_2S_{4/2}]$, $K_{stab.} = 10^3$
$M[Cd(SCN)_3]$, M = Rb, Cs, chains of alternate oct. $[CdS_2N_4]$ — $[CdS_4N_2]$ (M = Rb), $[CdS_6]$ — $[CdN_6]$ (M = Cs)
$Ba_2[Cd(—SCN)_6] \cdot 7\,H_2O$ [7]

$ZnSO_4$ — BaS



ZnS↓, wh., amorph., SP = 10^{-24}, sol. in HCl,
↓ H_2S (dry)
β-**ZnS**, "wurtzite", m. p. 1900 (p), subl. 1185, ΔH = −192, hex. cl. pack., $[ZnS_4]$ and $[SZn_4]$ – tetrah.
↑ 1020°



α-**ZnS**, "sphalerite"
ΔH = −205, diamond cub. str., tetrah. **Na_2ZnS_2** [16]
$[ZnS_4]$ and $[SZn_4]$

CdS↓, yel. $\xrightarrow{t,\,H^+}$ red., m. p. 1475(p)
ΔH = −150, SP = 10^{-27}, sol. in conc. HCl,
α-, "greenockite", semiconduct., wurtzite str. type
β-, sphalerite str. type

Zn/Hg — KNH_2 (NH_3, liq.)

	m. p.	ΔH		m. p.	ΔH
ZnSe↓, yel.	1575	−130	**CdSe**↓, red	1250 (p)	−105
ZnTe↓, red	1239	−121	**CdTe**↓, brn.	1090	−100
semiconduct.					
Zn_3N_2, blk.	700 (dec.)	−21	**$Cd(N_3)_2$**, yel.	−21	+163
$Zn(N_3)_2$, colrl., exp. · **$2.5\,H_2O$**	—	[9]	**Cd_3N_2**, blk.	—	—
$Zn(NH_2)_2$, wh.	—	—	**$Cd(NH_2)_2$**, wh.	—	—
Zn_3P_2	420	—	**Cd_3P_2**, grey ⟵ **CdP_2**, orange		
Zn_3As_2	1015	—	**Cd_3As_2**	721	—
ZnC_2, wh.	—	—	**$CdC_2\downarrow$**, +HCl → $C_2H_2\uparrow$		
$(ZnH_2)_n$ (?), wh., insol. in Et_2O	dec. 90	— [9]	**CdH_2**, wh., insol. in Et_2O	dec. −20	—

C_2H_4 (t) — M

$K_2[Zn(NH_2)_4]$; **LiZnN**
$M_2[Zn(N_3)_4]$, M = K, Cs
$Cs_3[Zn_2(N_3)_7]$; **$Cs[Zn_2(N_3)_5]$**
$K[Zn_3(N_3)_7]$ [14]

$K_2[Cd(NH_2)_4]$
$K[Cd(N_3)_3] \cdot H_2O$
$K_2[Cd(N_3)_4]$
$Tl_8Cd_3(N_3)_{14}$, [18]

● Zn, Cd
● I, S

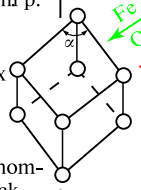
MERCURY

"1+"

Hg^0 5d ↓↑↓↑↓↑↓↑↓↑ 6s ↓↑ 6p ☐☐☐ 6d ☐☐☐

EN 1.4

Hg, liq. silver-wh., $d = 13.55$, m p. −38.86, b.p. 357, emulsionize conc. s. $FeCl_3$, in HI ($\longrightarrow H_2 + [HgI_4]^{2-}$) and ac.-Ox
$E_0[Hg]_2^{2+}/2Hg_{liq.} = +0.79$,
$E_0 Hg^{2+}/Hg_{liq.} = +0.85$,
$E_0 2Hg^{2+}/[Hg]_2^{2+} = +0.91$, in rhombohedral srt. — dist. cub. cl. pack. $a = 3.00$, $\alpha = 70°32'$, CN 6 (=8− 2), Hg—Hg 3.00



O_2 (350°, slow.)
> 400° ($-O_2$)

Fe ($-FeS$)
O_2 ($-SO_2$)

HgS

H_2SO_4 (*t*)
HNO_3 (1:1, *t*)

AsF_5 (liq. SO_2)

M

Amalgams

Hg form comp. with elements with filled *d*-orbitals — M^I, M^{II}, Cu, Ag, Au.
In system Na–Hg ex. comp. **Na_3Hg, Na_3Hg_2, NaHg** (m.p. 212), **Na_7Hg_8** (222), **$NaHg_2$** (354), **$NaHg_4$** (156).
Sol. in Hg: Cd, Zn, Pb; insol. Al, Ti, Zr, Bi, Nb, Ta, Mo, W, Re, Fe, Ni
Rb_5Hg_{16}, m.p. 157.
In str. — squares $[Hg_4]$ and cubes $[Hg_8]$ [17]

$[Hg_4]^{2+}[AsF_6]_2^-$, cation — $[Hg_{\overline{2.57}}Hg_{\overline{2.70}}Hg — Hg]^{2+}$
$[Hg_3]^{2+}X_2^-$, X = $AlCl_4$, PF_6, $[AsF_6]$, $[Sb_2F_{11}]$, yel. cation — linear, diamagn. $[Hg_{\overline{2.62}}Hg_{\overline{2.59}}Hg]^{2+}$; [1]
$[Hg_3]^{2+} \rightarrow Hg + [Hg_2]^{2+}$

$Hg_2SO_4 \cdot Hg_2(OH)_2\downarrow$ [19]
$Hg_4(OH)(NO_3)_3$, **$Hg_{10}(OH)_4(NO_3)_6$**
$Hg_4O(NO_3)_2 \cdot HNO_3$

H_2O

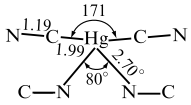
$Hg_2(ClO_4)_2$, dec. 230; **$\cdot 4H_2O$**, **$Hg_2(ClO_3)_2$**, dec. 250
$Hg_2(BrO_3)_2$, colrl., **$Hg_2(IO_3)_2\downarrow$**, yel. [14]
$Hg_2SO_4\downarrow$, SP = 10^{-7}
$Hg_2(NO_3)_2 \cdot 2H_2O$, m.p. 70 (dec.), **$\cdot N_2H_4$**
$[Hg_2]_3(PO_4)_2\downarrow$, sol. in HNO_3; **$M_6[Hg_2(P_2O_7)_2]$**
$Hg_2HAsO_4\downarrow$, yel., **$Hg_2CO_3\downarrow$**, wh., SP = 10^{-16}, grow dark ($\longrightarrow Hg\downarrow + HgO\downarrow + CO_2$)
$Hg_2(CH_3COO)_2$; **$Hg_2(HCOO)_2\downarrow$**; **$Hg_2C_2O_4\downarrow$**
$Hg_2[SiF_6] \cdot 2H_2O$, in str. — linear gr. $[H_2O — Hg–]_2^{2+}$

$Hg_4O_2(NO_3)_2$ = $= [Hg_2^I](OHg^{II})_2(NO_3)_2$
$Hg_2Cl_2 \cdot n HgO$, $n = 1$, "eglestonite"
$n = 2$, "terlinguaite"

[14]	SP	m.p.	ΔH	Hg—Hal
Hg_2F_2, yel.; $+H_2O \longrightarrow$ Hg + HgO↓ + HHal	—	570	−485	2.14
$Hg_2Cl_2\downarrow$, "calomel", colrl., sol. in HNO_3	10^{-18}	400 (dec.)	−265	2.43
$Hg_2Br_2\downarrow$, colrl.	10^{-23}	340 (subl.)	−205	2.71
$Hg_2I_2\downarrow$, yel.-grn. unstab.	10^{-28}	290	−96	2.69

In str. — linear mol. Hal—Hg—Hg—Hal, Hg—Hg 2.5–2.7

$Hg_2(SCN)_2\downarrow$, colrl., v. unstab., $\longrightarrow$ Hg + $Hg(SCN)_2\downarrow$
$Hg_2(N_3)_2\downarrow$, wh., photosensitive, exp.



Ammino-, amido-, nitridocomplexes [6]

$[Hg(NH_3)_4]X_2$, X = ClO_4, $SO_4/2$
$[Hg(NH_3)_2Cl_2]\downarrow$, "fusible wh. prec.", m.p. 300, mol. tetrah.
$[HgNH_2]Cl\downarrow$, "infusible wh. prec."; $\xrightarrow{t}$ $Hg_2Cl_2 + NH_3 + N_2$;
sol. in dil. ac., cation zigzag chain, CN Hg 2

$HgCl_2$ (conc. s.) + NH_4^+
$H_2O \longrightarrow$
$HgCl_2$ (dil. s)
NH_4OH
HgO (yel.)
$M_2[HgI_4]$

↓ H_2O

$[Hg_2N]OH \cdot n H_2O$, n = 2, 1, 0, "Millon base", yel., in str. — net of tetrah. $[NHg_{4/2}]$, gr. [N—Hg—N] — linear (*sp*), H_2O and OH^- in cavity

↓ HX

$[Hg_2N]X \cdot n H_2O\downarrow$, X = Cl ("mosesite"), CN, NO_3, $SO_4/2$, $CO_3/2$, yel.
I ($\cdot H_2O$), brn., m.p. ≈130, exp.

$Hg(NO_3)_2$ (400°, $-NO_2$ $-O_2$)

2+

HgO↓, yel. or red $\overset{t}{\rightleftarrows}$ blk. (different of size particle), volat., dec. 400, $\Delta H = -92$, p. в к.; + MHal $\xrightarrow{(H_2O)}$ $HgHal_2$ + MOH, in rh. str. — plane zigzag chain, ∠OHgO 179 (*sp*), "montroydite"
↑↓ H_2O
$Hg(OH)_2$ (?), SP = 10^{-16}, $K_{bas.\,1,2} = 10^{-22}$

HgX_2

$Hg_2O(OH)ClO_4$; **$Hg_3O_2(ClO_4)_2$**; **$HgSO_4 \cdot 2H_2O\downarrow$** = $[Hg(OHg)_2]^{2+}(SO_4)^{2-}$;
$Hg_3O_2(NO_3)_2$; **$HgCO_3 \cdot n HgO\downarrow$**, n = 2, 3; **HgF(OH)**, chains of oct.
$HgCl_2 \cdot n HgO$, n = 1/2 ($[(OHgCl)_3]Cl^-$, cation — triangle, ∠HgOHg = 118°; ∠OHgCl = 175°, colrl.); 1; 2 = $[Hg_2(OHg)_4Cl]Cl_3$), blk.; 3 (yel.); 4 (red and blk.) [14]
$Hg(CN)_2 \cdot HgO\downarrow$, colrl.; in str. — mol. O[HgCN]$_2$

OH^-

$Hg(ClO_4)_2$, m.p. 170, $\overset{HClO_4}{\longleftarrow}$ **$\cdot n H_2O$**, n = 2, 6, oct. $[Hg(H_2O)_6]^{2+}$ [2]
$Hg(ClO_3)_2$, colrl.; **$Hg(ClO_2)_2\downarrow$**, red; **$Hg(BrO_3)_2 \cdot 2H_2O\downarrow$**, colrl.; **$Hg_2HIO_6$**, brn.;
$Hg_3(H_2IO_6)_2$, yel.; **HgH_3IO_6**, colrl.; **$Hg_3(IO_5)_2$**, blk.; **$Hg_5(IO_6)_2$**; **$Hg(IO_3)_2\downarrow$**, colrl. [10]
$HgSO_4$, colrl. ($\xrightarrow{t}$ yel.; red) $\xrightarrow{500°}$ Hg + SO_2 + O_2; in str. oct. $[HgO_6]$; **$\cdot H_2O$** ; **$\cdot 2H_2O$**
$HgSO_3\downarrow$; **$Hg_2(SeO_3)_2 \cdot H_2O$**, CN Hg 5 and 7; **$HgSeO_4 \cdot H_2O$**
$Hg(NO_3)_2$, **$\cdot N_2O_4$**; **$\cdot n H_2O$**, n = 1, 0.5, readily sol. in H_2O, hydr.; **$Hg(NO_2)_2$** [10]
$Hg_3(PO_4)_2\downarrow$, wh., sol. in ac., in str. gr. [O—Hg—O], ∠Hg = 166; [3] **$Hg_3(AsO_4)_2\downarrow$**, yel.
$Hg(CH_3COO)_2$, colrl., dec. 180, $K_{dis.} = 10^{-9}$, chains of squares $[HgO_4]$;
$HgC_2O_4\downarrow$ [10]

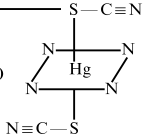
Hg
N_2O_4
Hal_2; HI

[5]	m.p.	b.p.	ΔH	Hg—Hal
$HgF_2\downarrow$, colrl., + $H_2O \longrightarrow$ hydr., **$\cdot 2H_2O$**	645	650	−397	2.43
$HgCl_2$, "corrosive subl.", sol. in H_2O, alc., Et_2O	280	304	−231	2.29
$HgBr_2$, colrl., poorly sol. in H_2O	238	322	−175	2.48
$HgI_2\downarrow$, red, SP = 10^{-12} (tetr.), sol. in bz., Et_2O, $CHCl_3$; $\xrightarrow{131°}$ yel., rh.	259	354	−105	—

Str. HgF_2 — CaF_2 type (CN 8); in str. $HgHal_2$ (Hal = Cl – I) linear mol. HgI_2 (red) layer of tetrah. $[HgI_{4/2}]$; in str. $HgF_2 \cdot H_2O$ – layers of antiprisms $[HgO_4F_4]$.
In melt $2HgHal_2 \rightleftarrows HgHal^+ + HgHal_3^-$
$[HgHal_2 \cdot L]_2$; **$HgHal_2 \cdot 2L$**, L = R_2S, R_3P, R_3As

Hg
HNO_3 + EtOH
S (20°)

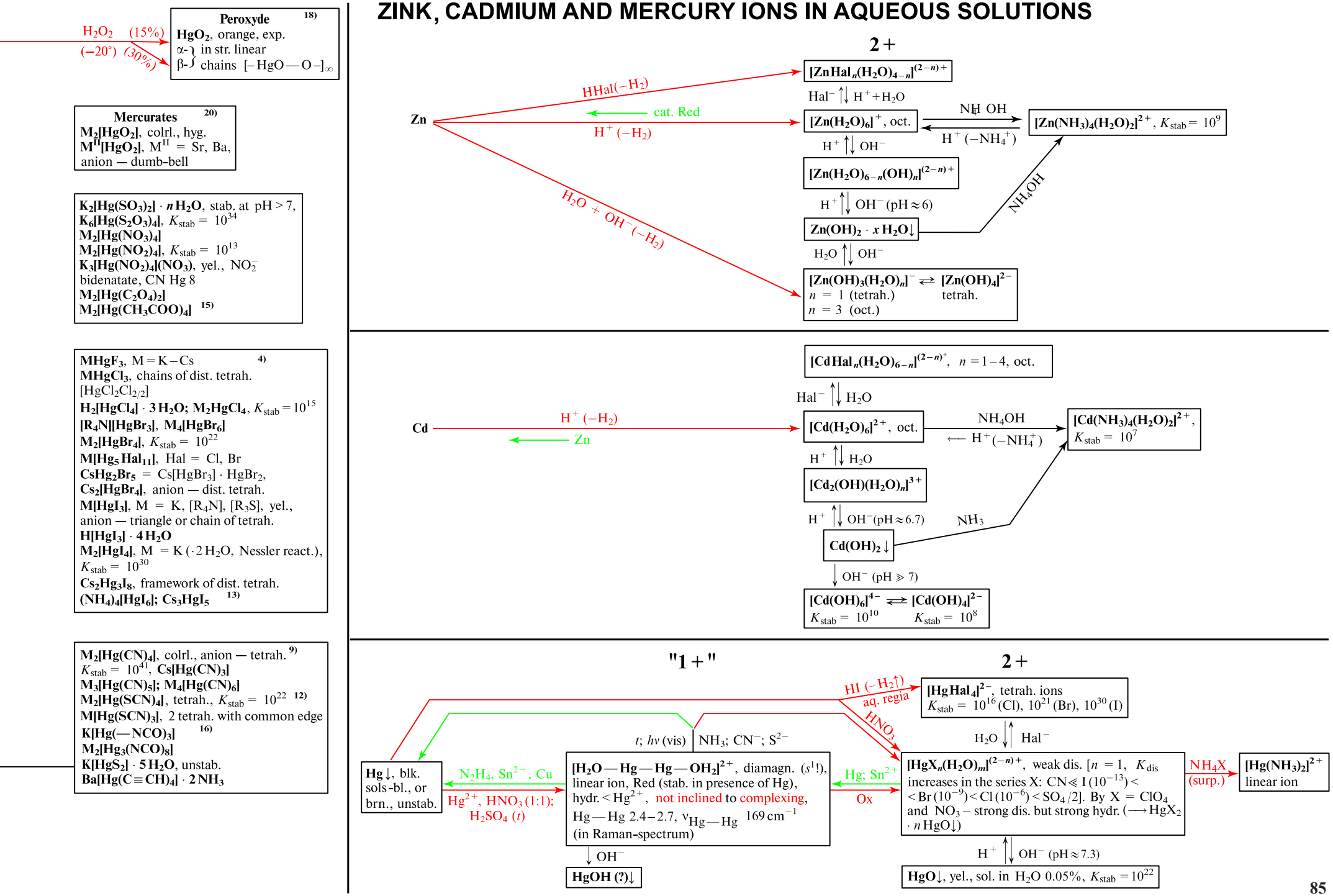
$Hg(CN)_2$, colrl., dec. 320, sol in H_2O 100 g/l, not dis.
$[HgCN]^+X^-$, X = NO_3, $[MF_6]/2$ (M = Ti, Zr, Sn) [5]
$Hg(SCN)_2\downarrow$, needle, colrl., dec. 165 with bulbing, in str. — dist. oct. [7]
Hg(SCN)Hal; Hal = Cl, Br, in str. — dist. oct. $[HgHal_3SN_2]$
$Hg(ONC)_2 \cdot 1/2 H_2O$, fulminate (detonator)



HgS↓, cr. or amorph. powd., β-cub., blk. ("metacinnabarite"), $d = 7.7$, m.p. 820 (*p*)
$\Delta H = -58$; sphalerite str. type, in str. — chains, sol. in HI, ac. regia
S_n^{2-} ↓↑ 344°
α-hex., red, "zinnober" ("zinnabarite"), $d = 8.1$, subl. 559, in str. — spirals
Hg—S—Hg, ∠Hg = 172 [11]
$[Hg(SHg)_2]X_2$, X = $SO_4/2$, F, Cl (wh.), Br (yel.), I (orange), NO_3, BF_4, SiF_6, TiF_6
$\xrightarrow{h\nu\,(vis)}$ blk.
Hg[S]$_2$, colrl., dec. 390 ($\longrightarrow$ HgS + S); **HgSe** blk., m.p. 799, $\Delta H = -46$, "timmanite"
HgTe, blk., m.p. 667, $\Delta H = -13$, "coradoite"; $p \longrightarrow$ Hg + Te
$Hg(N_3)_2\downarrow$, colrl., exp.; **$HgC_2\downarrow$**, acetylide, exp., CaC_2 str. type;
$+H_2O + HCl \longrightarrow HgCl_2 + CH_3CHO$ (Kucherov react.)
$[(HOHg–)(OHg_2=)C–]_2$, "K.A. Hofmann base" [8]

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_30, © Springer-Verlag Berlin Heidelberg 2011

ZINK, CADMIUM AND MERCURY IONS IN AQUEOUS SOLUTIONS



ALKALI METALS, FRANCIUM

		2s	3s	3p	3d	4s	4p	4d	5s	5p	5d	6s	6p	6d	EN
Lithium	**Li^0**	↓													1.0
Sodium	**Na^0**		↓												1.0
Potassium	**K^0**					↓									0.9
Rubidium	**Rb^0**								↓						0.8
Caesium	**Cs^0**											↓			0.8

Cs_4O [9]
Cs_7O
$Cs_{11}O_3$

LiCl + KCl — Cath. Red

NaCl + 60% $CaCl_2$ (m. p. 580) — Cath. Red

MCl — Na (gas); Ca (800°, vac.)

	Li	Na	K	Rb	Cs	Fr [1]
	met. silver-wh.				golden	—
Solidity (diamand – 10)	0.6	0.4	0.5	0.3	0.2	—
	Ox in air with infl.					
d	0.54	0.97	0.86	1.52	1.90	2.46
m. p.	180	97.8	64	39	28.7	23
b. p.	1337	886	776	696	705	669
$E_0 M^+/M_{sld.}$	−3.04	−2.71	−2.92	−2.92	−2.92	—
	$+H_2O \longrightarrow$ [H↑]; sol. in NH_3 liq. (bl. s.), $[M(NH_3)_6] \rightleftarrows [M(NH_3)_6]^+ + [e(NH_3)_n]^-$("polaron"); $\longrightarrow MNH_2 + H_2$					
	α-Fe str. type (cub.)					
a = 3.50		4.28	5.33	5.62	6.08	
M — M	3.10	3.80	4.70	4.96	5.34	—
	↑ > 195° cub. cl. pack					
a = 4.41		5.34	—	—	—	—
	in gas – mol. M and M_2 (< 5%)					
M — M	2.67	3.08	3.93	4.32	4.55	—
		red.	vlt.	orange		
ΔH M_2	−107	−72	−49	−45	−44	—

Hg (+Q)

Amalgams
Sld. or pasty subst., strong Red; in M – Hg syst. ex. the comp. in the following ranges of relations:
(6:1) – (1:3) – Li, (3:1) – (1:4) – Na; (1:1) – (1:9) – K; (7:8) – (1:9) – Rb; (1:2) – (1:10) – Cs

[Li(NH$_3$)$_4$]
[LiDipy]; [MDipy] · 2.6 Thf, dark-red (Na), vlt. (K). Ox by air **[NaPy$_2$],** dark-grn.

Formation Fr in nuclear decay: $^{227}_{89}Ac \xrightarrow[21.8\ y.]{\alpha} {}^{223}_{87}Fr \xrightarrow[21.8\ m.]{\beta^-} {}^{229}_{88}Ra \xrightarrow[10^{-22}\%\ in\ crust]{} \ldots$

O_2 (Na – yel. flame)

O_2 (Li – red flame)

Oxides, cr., hyg., subl. vac. (10^{-5}mm), *anti*-CaF_2 str. type (CN M 4); str. Cs_2O – *anti*-$CdCl_2$ type (CN Cs 3)

	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
	colrl.	colrl.	yel.	yel.	orange
m. p.	1570	—	740	—	495
b. p.	2600	—	—	—	—
dec.	> 1000	400	—	400	300
ΔH	−594	−418	−340	−331	−318

$\xrightarrow{t}$ colour increase; $\xrightarrow{t}$ M_2O_2 + M; in gas – mol. linear [12]

O_2 (*t*)

M

Peroxydes, cr. colrl., hyg. (yel. at admix MO_2), diamagn., O — O 1.50 – 1.54 [2]

	Li_2O_2	Na_2O_2	K_2O_2	Rb_2O_2	Cs_2O_2
m. p.	—	596	—	567	597
dec.	342	675	—	1010	650
ΔH	−636	−510	−494	−422	−402
· n H_2O_2, n = 2		4	4	4	4
· n H_2O, n = 1, 2		8	—	—	—

strong Ox.: + Fe $\xrightarrow{t}$ M_2FeO_4;
$[M_2O_2 + CaCl(OCl)]$ ("oxylit") + $CO_2 \longrightarrow O_2 + M_2CO_3$

H_2O

O_2 (K, Rb — vlt., Cs — bl. flame)

Superoxides and ozonides see. tabl. "O" [4,8]

M_3N

(*t*, vac., $-N_2$)

H_2O ($-H_2$)

Alkali, cr. colrl., subl. ≈400, sol. in H_2O, alc. (CsOH ≫ LiOH), liq. NH_3. Melt react. with glass, (Pt + O_2); insol. Ag, Ni, Fe, volat. (expect LiOH) [13]

	LiOH	NaOH	KOH	RbOH	CsOH
m. p.	473	321	405	382	339
b. p.	925	1390	1320	—	—
dec.	600	> 2000	> 2000	—	—
ΔH	−487	−428	−427	−414	−407
· n H_2O n = 1	1; 2; 3.5; 4; 7	1; 2; 4	1; 2	0.5; 1; 2; 3	
$K_{dis.}$	1.5	3.4	5.1	—	—

MCl — H_2O, electrol. ($-H_2-Cl_2$)

$Ba(OH)_2$ ($-BaSO_4$↓)

$MClO_4$, M = Li (m. p. 247, dec. 500), readily sol. in alc., Et_2O; · **3 H_2O**; Na (482 m. p., dec.) · **H_2O**; K (610 m. p., dec), Rb↓, Cs↓ (~ 700 m. p., dec.), Fr↓
$MClO_3$, M = Li (m. p. 129, dec. 270), · **0.5 H_2O**; Na (262); K ("berthollet salt"), (m. p. 368, dec. 400), sol. in H_2O Li ≫ Cs
$MBrO_3$, M = Na (m. p. 381), K (434, m. p., dec.); Rb (430); Cs (420), sol. in H_2O Na ≫ K – Cs,
MIO_3, M = Li – K (m. p. 560), Rb↓, Cs↓ **$MIO_3 \cdot n\,HIO_3$**
MIO_4, M = Na, dec. 300 (· **3 H_2O**), K↓ (m. p. 582), Rb↓, Cs↓
See Tabl. "Hal"

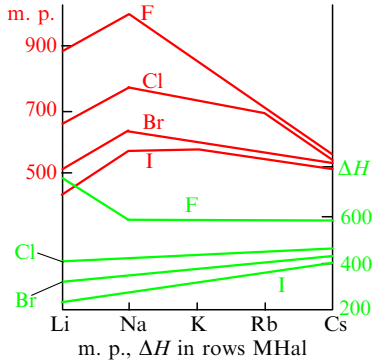
MNO_3, M = Li (m. p. 261, dec. 475; · **3 H_2O**), Na (308, dec. 380, "Chilean nitrate"), K (334, "potassium salpeter"), Rb (313; · **n HNO_3**, n = 1; 2), Cs (414, dec. 585; · **n HNO_3**, n = 1 и 2),
mol. str. anal. HNO_3; $\xrightarrow{t}$ $MNO_2 + O_2$
MNO_2 See Tabl. "N"

$MHSO_4$, M = Li (m. p. 170), Na (186, · **H_2O**), K (210), Cs; · **0.5 H_2SO_4**
· **n H_2SO_4**, (n = 1, 2, 3) M = Na – Cs [14]
Li_2SO_4, m. p. 860; · **H_2O**, v. readily sol. in H_2O
· **M_2SO_4,** M = Na, K, NH_4; · **2 M_2SO_4 · 9 H_2O**, M = Na, K
Na_2SO_4, m. p. 884, b. p. 1430, ("tehnardit") $\Delta H_{sol.} < 0$
· **n H_2O**, n = 7, 10 ("glauber salt"), $\Delta H_{sol.} < 0$, dec. 32.4
M_2SO_4, M = K (m. p. 1076, b. p. > 2000), Rb (1066), Cs (1019, subl. 900); volat. Li > Na < K < Rb < Cs, in gas – mol. M_2SO_4 (M = K – Cs)
· **$M^{III}_2(SO_4)_3 \cdot 24\,H_2O$** = $[M^I(H_2O)_6] \cdot [M^{III}(H_2O)_6](SO_4)_2]$, M^{III} = Al, V – Co etc., "alum", cr. cub. (See Tabl. "S")

M_3PO_4, M = Li↓ (m. p. 837; · **n H_2O**, n = 1/2, 12↓), Na (1340; · **n H_2O**, n = 10, 12), K (1340)
MH_2PO_4, M = Li (dec. 100), Na (dec. 200; · **n H_2O**, n = 1, 2), K (m. p. 253, dec.);
$MH_5(PO_4)_2$, M = K – Cs [11]
M_2HPO_4, M = Li (dec. 100), Na (· **n H_2O**, n = 2, 7, 12), K
MPO_3; MH_2PO_2; M_2HPO_3; $M_4P_2O_7$, $Rb_2H_2P_2O_7 \cdot 1/2H_2O$ [15]
See Tabl. "P"

$MHCO_3$, M = Li (dec. ~ 0), Na (dec. 160), K (dec. 100), Rb (· **H_2O**), Cs (dec. 175), sol. in H_2O Cs ≫ Na
Na_2CO_3, m. p. 854 ("soda ash"),
· **n H_2O**, n = 1, 7, 10 ("soda cr."),
· **1.5 H_2O_2 · H_2O**
M_2CO_3, cr., hyg., M = Li↓ (m. p. 735), K ("potash", · **n H_2O**, n = 2, 1.5), Rb (873, dec. 900, · **H_2O**), Cs (dec. 610), sol. in H_2O Cs ≫ Li
RCOOM, $M_2C_2O_4$ [10]
See Tabl. "C"

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_31, © Springer-Verlag Berlin Heidelberg 2011

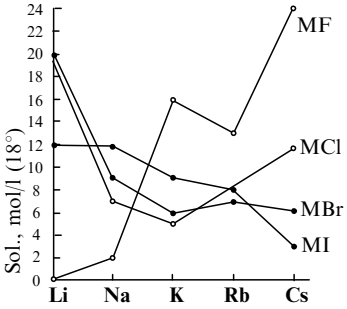


m. p., ΔH in rows MHal

	m. p.	b. p.	ΔH
LiF↓, sol. in HF	870	1724	−611
LiCl,	614	1397	−406
· H_2O	—	—	—
LiBr,	550	1310	−352
· 2 H_2O	44	—	—
LiI,	469	1190	−272
· 3 H_2O	73	—	—

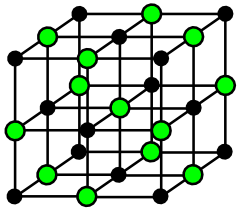
	m. p.	b. p.	ΔH
KF, "carobbiite"	857	1502	−565
· 2 H_2O	41	—	—
KHF_2	239	—	—
KCl, "sylvite"	776	1430	−434
KBr	735	1383	−393
KI	686	1330	−327
$K[I_3]$, bl.	45	dec. 225	—

	m. p.	b. p.
RbF,	798	1430
· *n* H_2O, *n* = 3, 3/2,	—	—
· *n* HF, *n* = 1, 2, 3	—	—
RbCl	726	1395
RbBr	692	1352
RbI	656	1327
$Rb[I_n]$, n = 7, 9, brn.	—	—
$Rb_2(OH)I$ [16]		

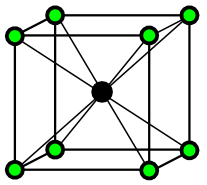


Solubility of MHal in H_2O

	m. p.	b. p.	ΔH
NaF	997	1785	−569
$NaHF_2$	—	—	—
NaCl, "halite"	801	1465	−410
· 2 H_2O	< 0°	—	—
NaBr	755	1392	−360
· 2 H_2O	—	—	—
NaI	662	1304	—
· 2 H_2O	—	—	—
Na_3OCl [16]			


NaCl str.

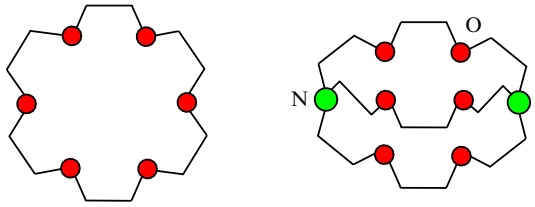
	m. p.	b. p.	ΔH
CsF,	684	1302	−531
· *n* H_2O, *n* = 2/3, 1/5	—	—	—
· HF	—	—	—
CsCl	646	1295	−431
CsBr	638	1297	−410
CsI	622	1280	—


CsCl str.

Halides, cr. colrl., hyg.
MHal (Li – Rb) and CsF – NaCl str. type
CsHal (Cl – I) – CsCl str. type (CN = 8)
in gas M_2Hal_2 mol. – flat rh.,
∠HalMHal = 108 (Cl) – 116 (I);
ΔH sol. MCl in $H_2O \approx O$; KHal sol. in liq. NH_3;
LiBr, LiI – sol. in Et_2O

MN_3, azides, cr. colrl., $\xrightarrow{t}$ M (high purity) + N_2 (without exp.);
ΔH = +21 (Na), −1 (K), −10 (Cs), readily sol. in H_2O, alc.
+ CS_2 ⟶ $KS(CSN_3)$; + I_2 ⟶ KI + N_2
↓ (*t*, vac., $-N_2$)
M_3N, nitrides, cr. ruby-red., M = Li (m. p. 845, ΔH = −47), Na (dec. 200), K – Cs (exp.); + H_2O ⟶ NH_3 + MOH
↓ H_2
Li_2NH, imides, cr. colrl., *anti*-CaF_2 str. type
↓ H_2
MNH_2, amides, cr. colrl. or light grn.; m. p. 390 (Li), 210 (Na), 338 (K), 309 (Rb), 261 (Cs); subl. ≈400; sol. in liq. NH_3;
liq. ⇄ $M^+ + [NH_2]^-$; + $H_2O \rightarrow$ MOH + NH_3;
chem. act. $CsNH_2 \gg LiNH_2$ (See Tabl. "N")

Compl. M^+ with macrocycles (L)



crown-ether (18 – crown – 6) cryptand –222

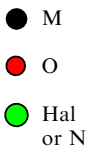
Stab. compl. are form. by M^+ when diametr corresponds to the cavity size an L mol. So Li^+ and Na^+ (r = 0.6 – 1.0) form stab. cryptates with 211 and 221 cryptandes, K^+ (*r* = 1.38) with 18-cr.-6 and 222 – cryptande. The stab. series is K > Rb > Cs ≈ Na > Li. This allows one to selectively bind various M. [17]

Hydrides, cr. colrl., insol. in NH_3 liq., org. sol., NaCl str. type

	LiH	NaH	KH	RbH	CsH
m. p.	691	≈800	≈400	≈400	≈400 (*p* H_2, Na – Cs)
ΔH	−91	−56	−57	−54	−56
M — H	2.04	2.44	2.85	3.02	3.19

melt. ⇄ $M^+ + H^-$, in gas – mol. MH (Li — H 1.60), μ_{LiH} = 5.88, v. strong Red;
+ H_2O ⟶ H_2 + MOH; + CO_2 ⟶ HCOOM; chem. act. CsH ⩾ LiH

Used for separation of M^I and the allocation of Rb and Cs: [5]
$MBiI_4$, M = K – Cs↓
$MBiCl_4$; M_2BiCl_5; M_3BiCl_6; $Rb_3Bi_2Cl_9$; Cs_4BiCl_7,
$M[Sb(OH)_6]$, M = Li, Na↓, K
M_3SbHal_6, Hal = Cl, Br, M = Li, Na, K – Cs↓
$MHC_4H_4O_6$, hydrotartrates, M = Li, Na (sol. in. H_2O), NH_4, K – Fr↓ (sol. in. ac., alk.)
$M_2[SiF_6]$, M = Li (· 2 H_2O, dec. 100, readily sol. in H_2O, alc.), Na↓ ("mallardite"), K↓ ("hieratite"), Rb↓, NH_4, Cs (v. readily sol. in H_2O); $\xrightarrow{t}$ MF + SiF_4
$M_2[SnCl_6]$, M = Li, Na (sol. in H_2O), K – Cs↓
$M[BF_4]$, M = Na (m. p. 384, readily sol. in H_2O), K↓ (m. p. 530),
$M[BPh_4]$, M = Li, Na (sol. in H_2O), K – Cs↓
$M_3[Co(NO_2)_6]$, cr. yel., M = Li, Na (sol. in H_2O), NH_4↓, K – Fr↓
$M_2[PtCl_6]$, cr. yel., M = Li, Na (sol. in H_2O), NH_4, K – Fr (poorly sol. in H_2O, insol. in alc.)
$MZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$, M = Li↓, Na↓
$M_3P(Mo_{12}O_{40})$, M = Li – Na (sol. in H_2O), K – Fr↓
$M_4[Si(W_{12}O_{40})]$, M = K – Fr↓



M_2S, cr. colrl., hyg., readily sol. in H_2O, alc.
+ O_2 + H_2O ⟶ $M_2S_2O_3$ + MOH

	Li_2S	Na_2S	K_2S	Rb_2S	Cs_2S
m. p.	950	1180	840 (?)	—	—
ΔH	−448	−373	−426 (?)	−348	−339
		· 9 H_2O	· 5 H_2O	· 4 H_2O	· 4 H_2O
		m. p. 50	60	dec. 200	—
		anti-CaF_2 – str. type [6]			

MHS, **M_2S_n** (see Tabl. "S")

MOR, alkoxides, cr., v. hyg., sol. in ROH (LiOR-*t* – sol. in Et_2O, bz., C_nH_m), in s. – diss.
+ H_2O ⇄ MOH + ROH; str. anal. of LiOH (M = Li, Na, R = Me, CN 4) or α-KOH (K – Cs, Me, CN 5).
· *n* ROH, *n* = 2 (Li, Me, Et), 5, 4, 3 (Na, Me), 3, 2 (Na, Et, *n*-, *i*-Pr, *n*-, *i*-Bu); 5, 3, 1 (K, Me); 1 (K, Et), 7, 5, 2, 1 (Rb, Cs, Me), 1 (Cs, Et, Pr) [3,7]
$[MOBu\text{-}t]_4$, M = K – Cs – cubane-like tetramers, CN 3; cat. react. polymerization, condensation, Red. C = O gr.
"MCO" = $(MOC{\equiv})_2$, **acetylendiolates**, pyrophoric, CaC_2 str. type

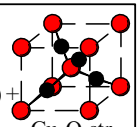
COPPER

Cu^0 3d ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ | 4s ↓ | 4p | 4d

EN 1.8

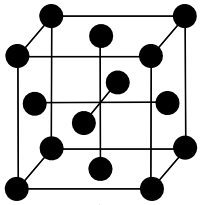
1+ (d^{10})

Cu_2O↓, "red oxyde", m.p. 1236, dec. 1800, $\Delta H = -167$, CN Cu 2 (*sp*), dumb-bell; $[CuO_2]$, $[OCu_4]$ – tetrah., SP = 10^{-15}, sol. in NH_4OH, HHal (conc.) + + H_2SO_4 (dil.) ⟶ Cu↓ + $CuSO_4$



Cu_2O str.

Cu, met. yel-red., ductile, high electro- and heat conduct., $d = 8.9$, m.p. 1085, b.p. 2540, sol. in ac.-Ox., NH_4OH, KCN, Ox in air.
$E_0 Cu^{2+}/Cu_{sld.} = +0.34$
$E_0 Cu^{+}/Cu_{sld.} = +0.52$
diamagn., in str. – facecentred cube, $a = 3.61$ (cub. cl. pack., Cu str. type)



CN 12 (cubooct.), Cu — Cu 2.56

electrolytic rafining in s. $CuSO_4$

Zn; Fe; cath. Red — $CuCl_2$

M; H_2; CO (250°); C — O_2 (> 200°)

H_2SO_4 (200°)

$(CH_3)_2SO_4$ (160°)

M_2O_2 (*t*), M_2O (*t*)

Cuprates (I), [14]
MCuO, M = Li – K, chains of squares $[Cu_4O_4]^{4-}$
$M_3[CuO_2]$, yel., + H_2O ⟶ Cu↓ + Cu^{II}

Cu_2SO_4, grey, m.p. ~400; + H_2O ⟶ Cu↓ + $CuSO_4$; strong Red, damb-bell $[CuO_2]$; · **$2NH_3$** [25]
$Cu_2SO_3 \cdot H_2O$↓, wh.;
$CuCH_3COO$↓, needles, colrl., chains of 8-member cycles [1]

$M[CuSO_3]$; **$M_3[Cu(SO_3)_2]$**;
$K_{stab} = 10^8$ 10^9

CCl_4 (C, 700°); $CuHal_2 + H^+$

Zn; Fe; cath. Red.

$O_2 + SiO_2$ (– $FeSiO_3$ – SO_2↑) ↓ in production of H_2SO_4

Alloys
90% Cu + 10% Sn – bronze;
90% Cu + 10% Zn – tombak;
60% Cu + 40% Zn – brass;
50% Cu + 45% Al + 5% Zn – Dewar alloy;
95% Cu + 4% Sn + 1% Zn – mint alloy

[26]	m.p.	b.p.	ΔH	SP	Cu — Hal
CuCl↓	450	1212	−136	10^{-7}	2.16
CuBr↓	504	1345	−105	10^{-9}	—
CuI↓	605	1336	−68	10^{-12}	2.44

CuHal, wh., sol. in surp. NH_3, MCN, $M_2S_2O_3$. Str. CuHal sphalerite type, CN Cu 4 (sp^3), in gas –trimer cycles.

HCl / H_2O

$HCuCl_2$, $KCuCl_2$; K_2CuCl_3
MCu_2Cl_3, anions – chains of tetrah.
M_2CuBr_3; **$[R_4N]_3[Cu_2Br_4]$** chains of triangels or tetrah.
$M_2[CuI_3]$, $Cs_3Cu_2I_5$,
$M[Cu_2I_3]$, $[PyH]_2[Cu_5HaI_7]$,
Hal = Br,I $[NO]^+[CuX_2]^-$,
X = Hal,CN,SEN,blk., sol. in ROH [2]

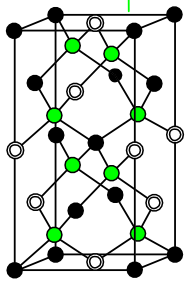
$[CuHal(PR_3)]_4$, in mol.– cub – $[Cu\text{-}eHal]_4$
$[CuI(C_5H_{11}N)]_4$, in mol.– tetrah. $[Cu_4]$ [27]

CuH↓, cr., red-brn., dec. 20, $\Delta H = +21$, wurtzite str. type

H_3PO_2; $NaBH_4$

$CuSO_4$

Cu Fe S



$CuFeS_2$ str.

CuCN↓, colrl., m.p.. 473, SP = 10^{-20}
$Cu_{2-x}S$↓, grey, SP = 10^{-50}, "copper glance", m.p. 1130; $\Delta H = -79$
$Cu^IFe^{III}S_2$, "cooper pyrites", "chalcopyrite", in str. – tetrah. $[Cu^IS_4]$, $[Fe^{III}S_4]$, $[SCu_2Fe_2]$, sphalerite str. type
Cu_2Se, bl., m.p. 1112; **Cu_2Te**, blk., m.p. 855
Cu_3N, grn., dec. 300, $\Delta H = +75$
CuN_3; $\xrightarrow{h\nu}$ Cu + N_2
Cu_3P, m.p. 1022; **Cu_3As; Cu_3Sb; Cu_2Sb**
Cu_2C_2, acetylide, red-brn., · **H_2O**

$M[Cu(CN)_2]$, colrl., $K_{stab} = 10^{24}$
$K_3[Cu_2(CN)_4] \cdot H_2O$,
CN Cu = 3: anion – tetrah., $K_{stab.} = 10^{24}$
$M_3[Cu(CN)_4]$
$Cs[Cu(SCN)_2]$, $K_{stab.} = 10^{12}$ [16]
$K_2[Cu(SCN)_3]$; $Na_3[Cu(SCN)_4] \cdot 4H_2O$
KCuS, anion – zigzag chain
KCu_4S_3, bl., semiconduct., layer of tetrah. $[CuS_4]$

2+ (d^9)

$Cu_4O_3 = Cu_2^I[Cu_2^{II}O_3]$, "paramelaconit" [22]

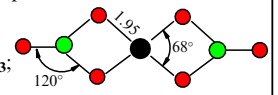
CuO, "blk. oxyde", m.p. 1335 (p O_2), dec. 1026, $\Delta H = -1565$, in str. – squares $[CuO_4]$ (dsp^2)

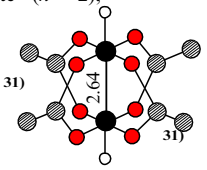
t (under s.) [5]

$Cu(OH)_2$↓, bl., sol. in ac., NH_4OH, in str. layers of oct.; + MOH (conc.) ⟶ vlt. coll. s. [30]

$[NO]ClO_4$ (200°)

$Cu(ClO_4)_2$, yel.-grn., dec. 130, volat., · ***n*** **H_2O**, n = 6, 2
$Cu(ClO_3)_2 \cdot 6H_2O$; **$Cu(BrO_3)_2 \cdot nH_2O$**, n = 6, 2 (bl.), [7]
$Cu(IO_3)_2$; $\xrightarrow{290°}$ CuO + I_2 + O_2; · ***n*** **H_2O**, n = 1, 2/3, [3]
Cu_2HIO_6↓, · ***n*** **H_2O**↓, n = 1, 2
$CuSO_4$, colrl., dec. 550, $\xleftarrow{258°}$ · ***n*** **H_2O**, n = 1, 3, 5 ("vitriol"), bl., 7 [3]
$Cu(NO_3)_2$, bl., subl. 200, m.p. 226, in gas – planar mol. · ***n*** **H_2O**, n = 9; 6; 2.5; 1 [23]
$Cu(NO_2)_2$, m.p. 147
$Cu_3(PO_4)_2 \cdot nH_2O$↓, n = 1, 3; **$Cu_4H(PO_4)_3$**; [24]
$CuHPO_4 \cdot nH_2O$; **$Cu(H_2PO_4)_2$**
n **$CuCO_3 \cdot Cu(OH)_2$**↓, "malachite" (n = 1), "azurite" (n = 2), in str. oct. $[CuO_6]$; + CO_2 (p, t) ⟶ **$CuCO_3$**↓
$Cu(CH_3COO)_2$, grn., sol. in H_2O and org. solv.
t (–H_2O)
$[Cu(CH_3COO)_2(H_2O)]_2$, grn., cluster, diamagn. [31]
$CuC_2O_4 \cdot H_2O$↓, bl.; $\xrightarrow{t(N_2)}$ Cu + CO_2 + H_2O
$Cu_6[Si_6O_{18}] \cdot 6H_2O$, "dioptase" [12]





H_2SO_4 (conc.) / HNO_3

$CH_3COOH + O_2$

Hal_2; HHal + O_2; aq. regia

Cu O N C X, H_20

$CuHal_2 \cdot 3Cu(OH)_2$, CdI_2 str. type; **Cu_2OCl_2, $Cu(OH)Cl$,** in str. – layers of elongated oct.

	m.p.	dec.	ΔH	Cu — Hal ax.	Cu — Hal equ.	· ***n*** **H_2O**, n =
CuF_2, colrl.,	950	—	−536	2.27	1.93	**2**, bl.
$CuCl_2$, yel.	596	1000	−216	2.95	2.30	**2**, bl.
$CuBr_2$, blk.	—	290	−134	3.18	2.40	**2**, brn.

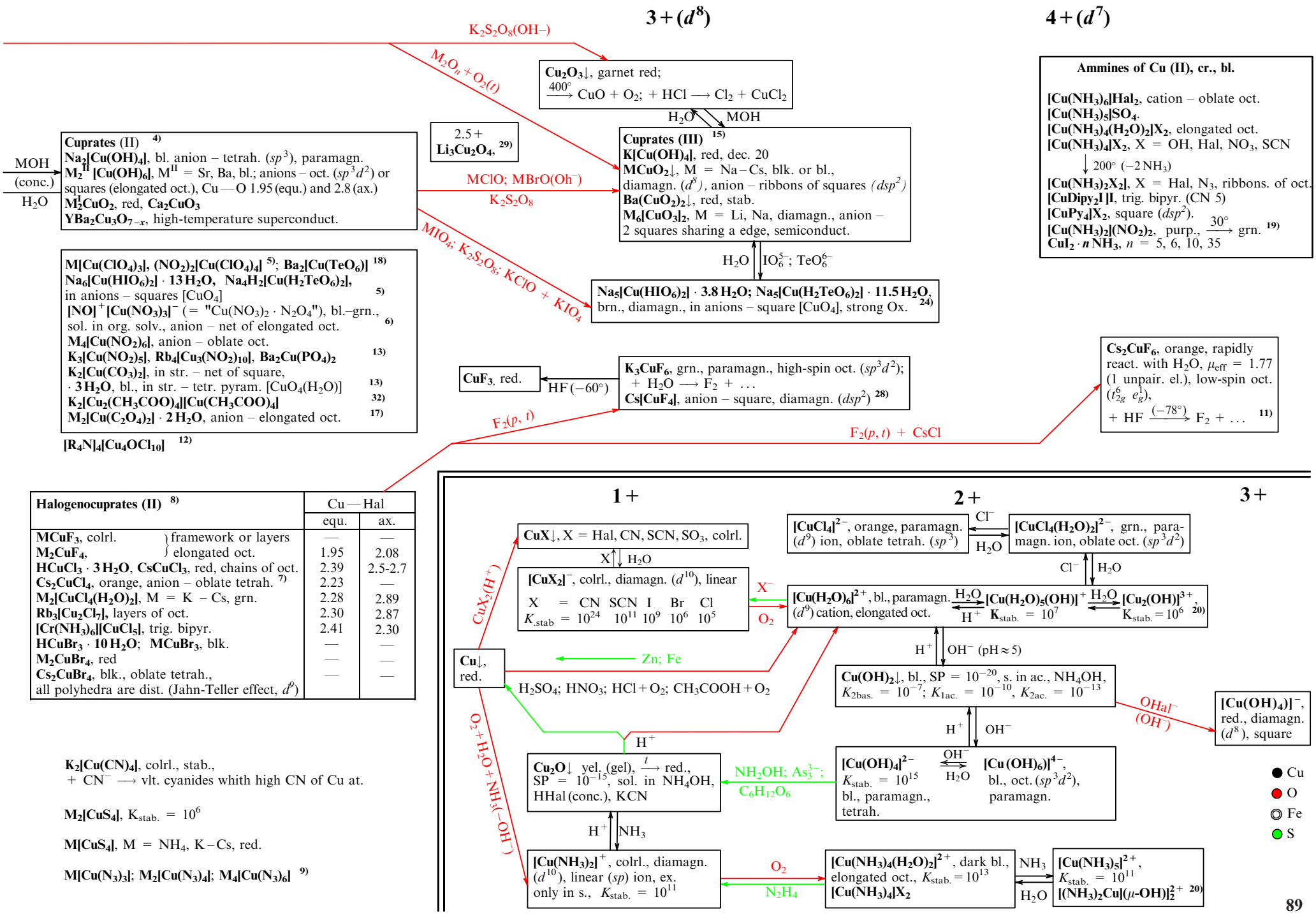
$CuHal_2$ (Hal = Cl,Br), sol. in H_2O, ROH, Py, ac.; str. CuF_2 – dist. rutile type, in str. $CuCl_2$, $CuBr_2$ – ribbon of squares.
$[CuHal_2(NO)]_2$ [21]

$Cu(CN)_2$↓, powd., yell.-brn.
$\xrightarrow{20°}$ CuCN + $(CN)_2$↑; + H_2O ⟶ CuCN↓ + O_2 (slow.)

CuS↓, blk., dec. 220, SP = 10^{-38}, sol. in ac.-Ox, M_2S_n, "covellite", $\Delta H = -53$, conduct. $\xrightarrow{200°}$ Cu_2S + S
CuS_3; Cu_2S_5; CuSe; $CuSe_2$
$Cu(N_3)_2$↓, cr., brn., exp.
CuC_2↓, acetylide

Cu^{2+} / $H_2S + H^+$

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_32, © Springer-Verlag Berlin Heidelberg 2011


3+ (d^8)
4+ (d^7)
$K_2S_2O_8$(OH–)
$M_2O_n + O_2(t)$
Cu_2O_3↓, garnet red;
400° → CuO + O_2; + HCl ⟶ Cl_2 + $CuCl_2$
H_2O MOH
2.5+
$Li_3Cu_2O_4$, 29)
MOH
(conc.)
H_2O
Cuprates (II) 4)
$Na_2[Cu(OH)_4]$, bl. anion – tetrah. (sp^3), paramagn.
$M^{II}_2[Cu(OH)_6]$, M^{II} = Sr, Ba, bl.; anions – oct. (sp^3d^2) or squares (elongated oct.), Cu—O 1.95 (equ.) and 2.8 (ax.)
$M^I_2CuO_2$, red, Ca_2CuO_3
$YBa_2Cu_3O_{7-x}$, high-temperature superconduct.
MClO; MBrO(Oh^-)
$K_2S_2O_8$
MIO_4; $K_2S_2O_8$; KClO + KIO_4
Cuprates (III) 15)
$K[Cu(OH)_4]$, red, dec. 20
$MCuO_2$↓, M = Na–Cs, blk. or bl., diamagn. (d^8), anion – ribbons of squares (dsp^2)
$Ba(CuO_2)_2$↓, red, stab.
$M_6[CuO_3]_2$, M = Li, Na, diamagn., anion – 2 squares sharing a edge, semiconduct.
H_2O IO_6^{5-}; TeO_6^{6-}
$Na_5[Cu(HIO_6)_2] \cdot 3.8\,H_2O$; $Na_5[Cu(H_2TeO_6)_2] \cdot 11.5\,H_2O$, 24)
brn., diamagn., in anions – square $[CuO_4]$, strong Ox.
Ammines of Cu (II), cr., bl.
$[Cu(NH_3)_6]Hal_2$, cation – oblate oct.
$[Cu(NH_3)_5]SO_4$.
$[Cu(NH_3)_4(H_2O)_2]X_2$, elongated oct.
$[Cu(NH_3)_4]X_2$, X = OH, Hal, NO_3, SCN
↓ 200° (–2 NH_3)
$[Cu(NH_3)_2X_2]$, X = Hal, N_3, ribbons. of oct.
$[CuDipy_2]I$, trig. bipyr. (CN 5)
$[CuPy_4]X_2$, square (dsp^2).
$[Cu(NH_3)_2](NO_2)_2$, purp., 30° → grn. 19)
$CuI_2 \cdot n\,NH_3$, n = 5, 6, 10, 35
$M[Cu(ClO_4)_3]$, $(NO_2)_2[Cu(ClO_4)_4]$ 5); $Ba_2[Cu(TeO_6)]$ 18)
$Na_6[Cu(HIO_6)_2] \cdot 13\,H_2O$, $Na_4H_2[Cu(H_2TeO_6)_2]$,
in anions – squares $[CuO_4]$ 5)
$[NO]^+[Cu(NO_3)_3]^-$ (= "$Cu(NO_3)_2 \cdot N_2O_4$"), bl.–grn., sol. in org. solv., anion – net of elongated oct. 6)
$M_4[Cu(NO_2)_6]$, anion – oblate oct.
$K_3[Cu(NO_2)_5]$, $Rb_4[Cu_3(NO_2)_{10}]$, $Ba_2Cu(PO_4)_2$ 13)
$K_2[Cu(CO_3)_2]$, in str. – net of square, $\cdot 3\,H_2O$, bl., in str. – tetr. pyram. $[CuO_4(H_2O)]$ 13)
$K_2[Cu_2(CH_3COO)_4][Cu(CH_3COO)_4]$ 32)
$M_2[Cu(C_2O_4)_2] \cdot 2\,H_2O$, anion – elongated oct. 17)
$[R_4N]_4[Cu_4OCl_{10}]$ 12)
CuF_3, red.
HF (–60°)
K_3CuF_6, grn., paramagn., high-spin oct. (sp^3d^2); + H_2O ⟶ F_2 + …
$Cs[CuF_4]$, anion – square, diamagn. (dsp^2) 28)
$F_2(p, t)$
$F_2(p, t)$ + CsCl
Cs_2CuF_6, orange, rapidly react. with H_2O, μ_{eff} = 1.77 (1 unpair. el.), low-spin oct. ($t_{2g}^6\ e_g^1$),
+ HF (–78°) → F_2 + … 11)
Halogenocuprates (II) 8)
Cu—Hal
equ. | ax.
$MCuF_3$, colrl. } framework or layers — | —
M_2CuF_4, } elongated oct. 1.95 | 2.08
$HCuCl_3 \cdot 3\,H_2O$, $CsCuCl_3$, red, chains of oct. 2.39 | 2.5-2.7
Cs_2CuCl_4, orange, anion – oblate tetrah. 7) 2.23 | —
$M_2[CuCl_4(H_2O)_2]$, M = K – Cs, grn. 2.28 | 2.89
$Rb_3[Cu_2Cl_7]$, layers of oct. 2.30 | 2.87
$[Cr(NH_3)_6][CuCl_5]$, trig. bipyr. 2.41 | 2.30
$HCuBr_3 \cdot 10\,H_2O$; $MCuBr_3$, blk. — | —
M_2CuBr_4, red — | —
Cs_2CuBr_4, blk., oblate tetrah., all polyhedra are dist. (Jahn-Teller effect, d^9) — | —
$K_2[Cu(CN)_4]$, colrl., stab.,
+ CN^- ⟶ vlt. cyanides whith high CN of Cu at.
$M_2[CuS_4]$, $K_{stab.}$ = 10^6
$M[CuS_4]$, M = NH_4, K–Cs, red.
$M[Cu(N_3)_3]$; $M_2[Cu(N_3)_4]$; $M_4[Cu(N_3)_6]$ 9)
1+
2+
3+
$[CuCl_4]^{2-}$, orange, paramagn. (d^9) ion, oblate tetrah. (sp^3)
Cl^-
H_2O
$[CuCl_4(H_2O)_2]^{2-}$, grn., paramagn. ion, oblate oct. (sp^3d^2)
Cl^- H_2O
CuX↓, X = Hal, CN, SCN, SO_3, colrl.
X H_2O
$[CuX_2]^-$, colrl., diamagn. (d^{10}), linear
X = CN SCN I Br Cl
K_{stab} = 10^{24} 10^{11} 10^9 10^6 10^5
$CuX_2(H^+)$
X^-
O_2
$[Cu(H_2O)_6]^{2+}$, bl., paramagn. (d^9) cation, elongated oct.
H_2O H^+ K_{stab} = 10^7
$[Cu(H_2O)_5(OH)]^+$
H_2O K_{stab} = 10^6 20)
$[Cu_2(OH)]^{3+}$,
Cu↓, red.
Zn; Fe
H_2SO_4; HNO_3; HCl + O_2; $CH_3COOH + O_2$
H^+ OH^- (pH ≈ 5)
$Cu(OH)_2$↓, bl., SP = 10^{-20}, s. in ac., NH_4OH, $K_{2bas.}$ = 10^{-7}; $K_{1ac.}$ = 10^{-10}, $K_{2ac.}$ = 10^{-13}
$OHal^-$ (OH^-)
$[Cu(OH)_4]^-$, red., diamagn. (d^8), square
H^+ OH^-
$O_2 + H_2O + NH_3(-OH^-)$
H^+
Cu_2O↓ yel. (gel), $\xrightarrow{t}$ red., SP = 10^{-15}, sol. in NH_4OH, HHal (conc.), KCN
NH_2OH; As_3^{3-}; $C_6H_{12}O_6$
$[Cu(OH)_4]^{2-}$ K_{stab} = 10^{15} bl., paramagn., tetrah.
OH^- H_2O
$[Cu(OH)_6]^{4-}$, bl., oct. (sp^3d^2), paramagn.
H^+ NH_3
$[Cu(NH_3)_2]^+$, colrl., diamagn. (d^{10}), linear (sp) ion, ex. only in s., K_{stab} = 10^{11}
O_2
N_2H_4
$[Cu(NH_3)_4(H_2O)_2]^{2+}$, dark bl., elongated oct., K_{stab} = 10^{13}
$[Cu(NH_3)_4]X_2$
NH_3 H_2O
$[Cu(NH_3)_5]^{2+}$, K_{stab} = 10^{11}
$[(NH_3)_2Cu](\mu\text{-}OH)]_2^{2+}$ 20)
Cu
O
Fe
S

SILVER

Ag⁰ 4d ↓↑ ↓↑ ↓↑ ↓↑ ↓↑ | 5s ↓ | 5p | 5d | EN 1.4

1+ (d^{10}) **2+ (d^9) or "2+"** **3+ (d^8)** **"4+" 5+ (d^6)**

Ag, met., wh., ductile, with high thermal and electrical conduct., $d = 10.5$, m.p. 962, b.p. 2210, sol. in ac.-Ox., ($KCN + O_2$), $E_0 Ag^+/Ag_{sol.} = 0.80$; cub. cl. pack., $a = 4.08$, Ag — Ag 2.88
Coll. Ag, grn. or blk. leaves with met. lustre ("collargol"), powd. yel.-brn. ("protargol"), have sterillizing effect.

Ag_3O, [19] conduct., in str. – oct. $[Ag_6]$

Ag_2O, brn., dec. 300, $\Delta H = -29$, SP $= 10^{-8}$, sol. in ac., NH_4OH, KCN; $+H_2O \rightleftarrows Ag^+ + OH^-$ (pH > 7), $K = 10^{-4}$; cub., isostr. to Cu_2O (CN Ag 2, *sp*)

AgOH

AgO↓ = $Ag^I Ag^{III} O_2$, blk., cub., dec. 100 (α), 178 (β); $\Delta H = -13$, sol. in HNO_3, $HClO_4$; $+ H_2SO_4 \longrightarrow Ag_2SO_4 + O_2$↑; v. Ox., semiconduct., diamagn., in str. α-form dumb-bells $[Ag^I O_2]$ and squares $[Ag^{III} O_4]$, in str. β-form – tetrah. $[Ag^{I,III} O_4]$ [8,17)]

Ag_3O_4 = $Ag_2^{III} Ag^{II} O_4$, blk. [17)] — 20°

Ag_2O_3, blk., dec. −20, isostr. to Au_2O_3 [13, 17)] — $O_3(H^+)$; an. Ox.

Argentates [7)]
$K[Ag(OH)_2]$, ex. in s. pH ≫ 7
$M_4[Ag_4O_4]$, M = Li–Cs, yel., anion – square
$M_3[AgO_2]$, dumb-bell (*sp*),
$Na_4Ag_2O_3$; **$Na_2Ag_4O_3$**
MAg_3O_2; $+H_2O \rightarrow Ag + O_2 + ...$

Ag_7O_8X, X = HF_2, ClO_4, HSO_4, NO_3, blk., with met. lustre, conduct. [2)]
$+ H_2O \xrightarrow{t} AgO\downarrow + O_2 + AgNO_3$, in str. – cubes $[Ag^I O_8]$ and squares $[Ag^{III} O_4]$

$M_5[Ag(HIO_6)_2] \cdot n\,H_2O$
$Na_5[Ag(H_2TeO_6)_2] \cdot 12.5\,H_2O$
light yel., diamagn. (d^8), anion – square (dsp^2) [15)]

$Ag(SO_3F)_2$, dec. 210; $+ H_2O \longrightarrow O_2 + ...$,
$[AgPy_4]X_2$, X = NO_3, $S_2O_8/2$, orange., v. strong Ox., cation – square $[AgN_4]$ [14)]
$Ag_3(PO_4)_2$, **$AgCrO_4$**

$Cs[Ag(SO_3F)_3]$, **$K_2[Ag(SO_3F)_4]$**

Alloys
90% Ag + 10% Cu – silver-,
90% Au + 10% Ag – gold, monetary alloys
Amalgams, is easily formed, containes **Ag_4Hg_3**, **Ag_5Hg_8** (m.p. 276 and 127). In system Ag–Zn–Pb – delamination, Ag sol. in Zn-layer (over)

"Rough Pb"

AgClO₄, colrl., dec. 486, readily sol. in H_2O, org. solv.
$AgClO_3$, colrl., m.p. 230, dec. 270; $+ H^+ \longrightarrow AgCl\downarrow + O_2$
$AgBrO_3$, poorly sol. in H_2O, stab. in $H^+ > AgClO_3$
$AgIO_3$↓, SP $= 10^{-10}$, insol. in ac. (*t*)
$Ag_2H_3IO_6$↓, yel.; **Ag_5IO_6**↓, blk.

Ag_2SO_4↓, cr., colrl., m.p. 660; $\xrightarrow{1000°} Ag + SO_2 + O_2$;
SP $= 10^{-4}$, in str. CN Ag 6; $+H_2SO_4 \longrightarrow$ **$AgHSO_4$**
$Ag_2S_2O_3$↓, wh., $+ H_2O \longrightarrow Ag_2S\downarrow + H_2SO_4$
Ag_2CrO_4↓, red-brn.; **$Ag_2Cr_2O_7$**↓, dark-red
$AgNO_3$↓, cr., colrl., m.p. 212, dec. 444, sol. in H_2O, alc., Py, MeCN, liq. NH_3, coagulated protein
$AgNO_2$↓, [= AgONO + Ag—NO_2], light yel., dec. 140, SP $= 10^{-3}$; **$\cdot NH_3$** = $[Ag(NH_3)_2]^+[Ag(NO_2)_2]^-$
$AgPO_3$↓, colrl., m.p. 482, sol. in dil. ac.
$Ag_4P_2O_7$↓, colrl., m.p. 585
Ag_3PO_4↓, yel., m.p. 849, SP $= 10^{-19}$
Ag_3AsO_4↓, red; **Ag_3AsO_3**↓, yel.
Ag_2CO_3↓, light yel., dec. 100; SP $= 10^{-12}$, in str. – tetrah. $[AgO_4]$
$AgCH_3COO$, sol. in H_2O ~1%, $K_{dis} = 0.2$ [21)]
Ag[BF_4]; **Ag[$\ni F_6$]**, E = P, As, Sb, Nb, Ta
Ag_3BO_3, in str. – chains of dumb-bells $[AgO_2]$ [22)]
Ag[EH_4], E = B (wh.), Al (yel.), Ga (orange), dec. −30, −50, −75; **$\cdot n\,PR_3$**, stab. > 100°
$[Ag_3Hal](NO_3)_2$, Hal = Cl–I, CN, SCN [11)]

	m.p.	b.p.	ΔH	SP	Solv.
AgF, colrl., stab. to *hv*-vis **$\cdot n\,H_2O$**, *n* = 1, 2, 4, **$\cdot n\,HF$**, *n* = 1, 3	435	—	−201	—	$H_2O \approx 65\%$
AgCl↓, colrl., "chlorargyrite" (melt. – orange), **$\cdot n\,NH_3$**, *n* = 1–3	457	1554	−127	10^{-10}	NH_4OH, KCN, $M_2S_2O_3$
AgBr↓, wh. or yel.-grn. "bromargyrite"	434	700	−99	10^{-13}	NH_4OH, $M_2S_2O_3$, $K_{dis} = 10^{-4}$
AgI↓, light yel. "iodargyrite"	560 dec.	—	−62	10^{-16}	KCN, $M_2S_2O_3$, NH_4OH

Stab. to *hv*-vis AgBr > AgCl > AgI. Str. AgHal (Hal = F–Br)
NaCl type (CN Ag 6), AgI – sphalerite or wurtzite types. [10)]

Ag_2F = $Ag_2^+ F^- e^-$, cr., bronze-grn., $\Delta H = -50$, conduct., stab. to *hv*-vis.
$+H_2O \xrightarrow{t} Ag + AgF$; *anti*-$CdI_2$ str. type, Ag—F 2.46, Ag—Ag 2.86

$M^{II}AgF_3$, [1)]
$M[AgCl_2]$, anion – tetrah., $K_{stab} = 10^6$
$M[AgBr_2]$, $K_{stab} = 10^6$
$MAgI_2$, **M_2AgI_3**, in str. – chain of tetrah.
$KAg_3I_4 \cdot 8\,H_2O$;
$[R_4N]_2Ag_{13}I_{15}$, **$RbAg_4I_5$** ionic conduct., in str. – channels from tetrah. $[I_4]$; Ag^+ can migrate along the channels
$(PyH)_5Ag_{18}I_{23}$
$[AgHal_2]^-$, $K_{stab} = 10^5$ (Cl), $8 \cdot 10^7$ (Br), 10^{12} (I)

AgF_2, cr., colrl., m.p. 690, $\Delta H = -347$, paramagn. (< −110°), ferromagn., strongest F-agent; $+ H_2O \longrightarrow Ag_2O + O_3 + HF$, in str. – squares $[AgF_4]$
Ag[$M^{IV}F_6$], M^{IV} = Ge–Pb, Ti–Hf, Rh, Pt, Pd, stab. < 600°, $\mu_{eff} = 2.0$ [3, 4)]

$MAgF_3$, M = K–Cs
M_2AgF_4, M = = K–Cs, Ca–Ba/2, Cd/2, Hg/2, anion – square [5)]
Ba_2AgF_6

AgF_3↓, [6)] red-brn., diamagn., 200° → $AgF_2 + F_2$

$Cs_2[AgF_6]$, K_2PtCl_6 str. type, oct. $[Ag^{III}F_6]$, $d^8 (t_{2g}^6 e_g^2)$ and $[Ag^V F_6]$ [16)]

M[AgF_4], M = K–Cs, $[O_2]$, yel., v. hyg., diamgn., anion – square, **Ba[AgF_5]** [6)]

AgF — $CsF + F_2$ (*p*)
MAgO — F_2

$Ag_2SO_4 + M^{II}CO_3$ — F_2

$MF + F_2$; ClF_3

MNO_2

K_2CO_3

$Na_3[Ag(S_2O_3)_2]$, $K_{stab} = 10^{14}$
$K[Ag(NO_2)_2]$, $K_{stab} = 10^3$
$Cs_3Ba[Ag(NO_2)_6] \cdot 2\,H_2O$
$K[Ag(CO_3)]$, in str. – chain of tetrah. $[AgO_4]$

an. Ox. (Pt); +Py

an. Ox. (OH^-); $K_2S_2O_8$ (90°); O_3 (OH^-); MOH (conc.); M_2O_2; M_2O; Ag; H_2O (*t*) ⇕ HX (dil.); HX; O_2 (200°); (> 300°); $H_2NC_2H_4OH$ (pH 9) [12)]; $-H_2O$ (> −50°); $-Zn\uparrow$ (1250°); Zn (*t*); Hal_2; $KIO_4 + KOH$ (an. Ox.; $K_2S_2O_8$); O_2 (–SO_2, baking); *hv* ($-F_2$)

1+

Ag^+, colrl., stab. to hydr., antibakterial

An. Ox. ⇕ H_2O ($-O_2$)

Ag^{2+} (?), brn. s., v. strong Ox.

0

Ag↓, coll. s.

HNO_3; H_2SO_4; $C_{12}H_{22}O_{11}$; [H⁺]

H^+ ⇕ OH^- pH > 7

$[Ag(OH)_2]^-$, colrl. linear, $K_{stab} = 10^4$, strong bas.

$[Ag(NH_3)_2]^+$, linear, $K_{stab} = 10^7$

$[AgAm_4]^{2+}$, square
$[AgAm_6]^{2+}$, oct., brn. or orange, paramagn. (d^9), v. strong Ox.

$O_2 + KCN$; Zn; Ag

M[$Ag(CN)_2$], linear ion, $K_{stab} = 10^{21}$
$M_n[Ag(SCN)_{n+1}]$, $n = 1-5$, $K_{stab} = 10^8$ [9, 18)]

$AgNO_3$ conc. s. — H_2S; NH_3

Ag_2S↓, blk., m.p. 827, sol. in HNO_3 (*t*), KCN; SP $= 10^{-50}$, in Ag–Pb ores [18)]
$AgCN$↓, wh., stab. to *hv*-vis, SP $= 10^{-14}$, in str. – linear chains
$AgSCN$↓, wh., SP $= 10^{-12}$
Ag_3N↓, nitride, exp., brn., $\Delta H = +225$, SP $= 10^{-9}$ [20)]
AgN_3↓, azide, m.p. 252, exp. 300°, —Ag—N=N^+=N^-— [20)]
AgONC, fulminate, exp., detonator; **AgOCN**, cyanat
$CuAg_3S_2$, "jalpaite"; **Ag_8GeS_6**, "argirodite"

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GOLD

$1+(d^{10})$ "2+" $3+(d^8)$ $5+(d^6)$ $7+(d^4)$

Au^0 5d ↓↑ ↓↑ ↓↑ ↓↑ ↓↑ | 6s ↓ | 6p | 6d | EN 1.4

AuO = $Au^I[Au^{III}O_2]$, powd., grn.

Au_2O_3, powd., brn., $\Delta H = -3$, net of squares [5]

> 260°; H_2; CO (100°)

100°

AuO(OH)

$-H_2O(P_2O_5)$

$Au_2O \cdot x\,H_2O$↓, dark-vlt.; + MOH ⟶ bl. sol.

MOH

$Au_2O_3 \cdot 2\,H_2O$↓, "auric ac.", yel.-brn., sol. in ac., alk., $K_{ac} = 10^{-12}$ (I), 10^{-14} (II), 10^{-16} (III) > $K_{bas.}$

OH^- H^+ (pH ≈ 7)

Au, met. yel., d = 19.32, m. p. 1064.4; b. p. 2947, volat. > 1000°, does not react. with O_2, N_2, C, S; sol. in aq. regia, (Cl_2 + HCl), (H_2SO_4 + HNO_3), (H_2SO_4 + $HMnO_4$), H_2SeO_4 (t), (KCN + O_2); $E_0 Au^+/Au_{sld.}$ = 1.68, $E_0 Au^{3+}/Au_{sld.}$ = 1.50 Cub. cl. pack. (Cu str. type), a = 4.08, Au — Au 2.88

electrolytic – refining in s. $HAuCl_4$

Aurates (I), **Cs[AuO]**, in str. – anions $[Au_4O_4]^{4-}$ [6] **Na_3AuO_2**,

$Zn[-M_2Zn(CN)_4]$ K[Au(CN)$_4$]

$NaNO_3$ (–NO)

H_2O

Aurates (III), $K[Au(OH)_4] \cdot H_2O$, yel. **$M^{II}[Au(OH)_4]_2$**, M = Ca – Ba (**$\cdot 5\,H_2O$**, grn.), anion – square (dsp^2) **$NaAuO_2$, $M_6[Au_2O_6]$**, anion – 2 squares sharing a edge [12]

$M_3[Au(S_2O_3)_2] \cdot H_2O$, colrl., anion – linear [S – Au – S] [9]

$[Au(SO_3F)_3]_2$ **$Au_2(SeO_4)_3$**, yel. **$Au(TeOF_5)_3$** [14]

$Na_5[Au(HIO_6)_2] \cdot 3.5\,H_2O$ [13] **$M[Au(SO_3F)_4]$**; **$M[Au(SO_4)_2]$**, yel.; **$K_5[Au(SO_3)_4]$**, colrl. **$M[Au(NO_3)_4]$**, yel. **$H[Au(NO_3)_4] \cdot 3\,H_2O$**, yel. **$K_2H[Au(NO_3)_6]$**, **$M[Au(CH_3COO)_4]$**, anion – square

Cl_2(350°); Br_2 (70°); I_2 (50 – 100°)

H_2SeO_4; HSO_3F; an. Ox

F_2(350°); Cl_2 (200°); Br_2 (20°)

AuOCl↓, red, sol. in conc. HCl; 290° ⟶ Au + Cl_2 + O_2; [8]

"Coll. gold" (negativ), is formed in v. dil. s., with increasing particle size color changes as follows: red ("Cassius purple"), bl., vlt., blk.

electro-dispergating

[1,17]	ΔH
AuF, ex. only in gas	—
AuCl↓, cr., light yel., unstab.	−33
AuBr↓, cr., yel.	−18
AuI↓, cr., light-yel.	+1

In str.– chains Hal: Au

$AuHal \xrightarrow{t} Au + Hal_2$;

$+ H_2O \xrightarrow{t,\,h\nu(vis)} Au + [AuHal_4]^-$ stab. AuI > AuCl;

$\cdot n\,NH_3$ (n = 1–12); **$\cdot n\,PH_3$** (n = 1, 2); **$\cdot$ CO**; **$\cdot PR_3$** **AuCl(CO)**, mol. dumb-bell

M[$AuCl_2$], $K_{stab.} = 10^9$, **M[$AuBr_2$]**, $K_{stab.} = 10^{13}$ **M[AuI_2]**, anions diamagn., linear (sp), + H_2O ⟶ ⟶ Au + [$AuHal_4$]$^-$

$AuCl_2$, red, diamagn., $[Au^{III}Au^{I}Cl_4]^0$, $[Au^{III}Cl_2Cl_{2/2}]^0$, $[Au^{I}Cl_{2/2}]^0$ – chair, square, dumb-bell [16]

$M_2Au_2Hal_6$, in str. – dumb-bell $[Au^{I}Hal_2]^-$ and squares $[Au^{III}Hal_4]^-$ [16]

	dec.	ΔH
AuF_3, orange	500	−348
$AuCl_3$, red., m. p. 288 (p)	150	−117
$AuBr_3$, brn.	100	−54
AuI_3↓, grn.	20	—

$AuHal_3 \xrightarrow{t} AuHal + Hal_2$. In str. AuF_3 – spirals from squares. In str. and gas – Au_2Hal_6 (Hal = Cl – I) – flat dimeres [7,8]

M[AuF_4]$_n$, light-yel., anion – elong. oct. **$MAuCl_4$**, M = Na ("Au-salt"), K ($\cdot H_2O$), Cs↓, yel., diamagn. **$HAuCl_4 \cdot 4\,H_2O$**, "Au-chloride", light-yel., hyg., needles, $K_{stab.} = 10^{22}$ $\xrightarrow{120°}$ $AuCl_3 + H_2O + HCl$ **$KAuBr_4 \cdot 2\,H_2O$**, purp., anion – square, $K_{stab.} = 10^{31}$ **K_3AuBr_6**, yel., anion – dist. oct. **KAuI$_4$**, blk., strong Ox. **HAuI$_4$**, unstab. [2]

AuF_5, red-brn., m. p. 75, diamagn., $\Delta H = -473$, in str. – cycle $[AuF_5]_4$, in gas $[AuF_5]_2$ [3]

[F] 100°

AuF_7, cr. yel., volat. ↓ H_2O $Au_2O_3 + Au$ [4]

60°

M[AuF_6]$_n$, yel., diamagn., anion – oct. (d^2sp^3) [3]

KrF_2 KrF_2 + MF (liq. HF)

Cl_2 + HCl Br_2 + KBr + H_2O KCN + O_2 + H_2O ("cyanidation")

Alloys
Amalgam contain **$AuHg_2$, $AuHg_3$, Au_3Hg** (m. p. 124, 310, 421)
In the system Cu — Au - continuous series of sld. s., < 400° in sld. phase form **$Cu_3Au_{1\pm n}$** and **$CuAu_{1\pm n}$** ("superstr.")

AuCN↓, yel., isostr. to AgCN **AuSCN**↓, dec. 140; + H_2O ⟶ $Au(SCN)_3$ + H_2

HCl

M[$Au(CN)_2$], colrl., anion – linear, $K_{stab.} = 10^{39}$ **M[$Au(SCN)_2$]**, $K_{stab.} = 10^{23}$

Hal_2 + CN^-

H[$Au(CN)_4$]·3H_2O, sol. in alc., Et_2O **K[$Au(CN)_4$]**, $\xleftarrow{200°}$ **$\cdot H_2O$**, colrl., anion – square, $K_{stab.} = 10^{56}$ **K[$Au(SCN)_4$]**, orange, $K_{stab.} = 10^{42}$

$Au(CN)_3 \cdot 3\,H_2O$↓, colrl. **$Au(SCN)_3$**↓, red, v. unstab.

Au_2S↓, grey or brn. powd., sol. in aq. regia; $\xrightarrow{240°}$ Au + S **Au_2S_2**↓, blk.-brn. **Au_3N**, nitride, exp.; **$\cdot NH_3$** **AuN_3**, azide, colrl., sol. in H_2O, ΔH = +280, exp. even in s. **Au_2C_2**, yel., exp. [18] **$[Au(NH_3)_2]^+$**, colrl., linear cation, $K_{stab.} = 10^{27}$ **$[Au(H_2O)_2]^+$**

$M_3[AuS_2]$, colrl., anion dumb-bell **MAuS** [10]

K[$Au(C\equiv CH)_2$]

Au_2S_3, blk., hydr.; $\xrightarrow{200°}$ Au + S

$NaAuS_2 \cdot 4\,H_2O$, colrl., dec. 30

H_2S gas ($\leqslant 10°$)

$[Au_2O_3 \cdot x\,NH_3 + Au(NH_2)_nX_m(NH)_p]$↓, "fulminic gold", yel.-brn., exp., sol. in KCN

NH_4NO_3 (surp.) + NH_3

HAuCl$_4$

$[Au(NH_3)_4]X_3$↓, X = NO_3, CrO_4/2, insol. in conc. ac.

NH_4Cl (surp.) + NH_3

$[Au(NH_3)_4]^{3+}$, colrl. ion, $K_{stab.} = 10^{30}$

$[Au(H_2O)_4]^{3+}$

Au

$1-(s^2)$ **$0\ (d^{10}s^1)$**
M^+Au^-, M = K – Cs
M_3OAu [19]

$[Au_4L_4(\mu\text{-}I_2)]$; $[Au_6L_8]X_2$;
$Au_5L_4Cl = [Au^I(Au^0L)_4]^+Cl^-$;
$[Au_8L_7]X_2 = [Au^I(Au^0L)_7]X_2$;
$[Au_9L_8]X_3$; $[Au_{11}L_7X_3]$;
L = PR_3; clusters – $[Au_n]$, n = 4 (tetrah.), 6 (oct.), etc. [11]

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IRON

Fe^0 3*d* ↓↑ ↓ ↓ ↓ ↓ | 4*s* ↓↑ | 4*p* | 4*d* — **EN** 1.6

2+ (d^6)

Fe$_{1-x}$O, cr., blk., m.p. 1368, ΔH = −268, pyrophoric, $\xrightarrow{570°}$ Fe + Fe_3O_4; NaCl str. type, Fe—O 2.15, "wustite"

$-H_2O$ ↑ 200°

Fe(OH)$_2$↓, wh., SP = 10^{-16}, $K_{bas.}$ = 10^{-2}, CdI_2 str. type, Fe—OH 2.23
(Fe,Mg)(OH)$_2$, "amakinit"

H^+ ⇄ OH^-

Fe, met., wh., d = 7.9, m.p. 1539, b.p. ≈ 3200, inclined to corrosion, sol. in dil. ac. (→ Fe^{2+}) and conc. alk. (*t*) (→ $[Fe(OH)_6]^{4-}$), passiv. in cold with ac.-Ox., $E_0 Fe^{2+}/Fe_{sld}$ = −0.44, $E_0 Fe^{3+}/Fe_{sld}$ = −0.036,

1.3 · 10^9 Па

α-Fe, body-centered cube, CN 8 (cube), a = 2.86, ferromagn.
↓ 769° (Curie point)
β-, isostr. to α-Fe, a = 2.90
↓ 911°
γ-, cub. cl. pac., a = 3.56, Fe—Fe 2.58
↓ 1390°
δ-, isostr. to α-Fe, a = 2.94
ε-, hex. cl. pac., d = 9.1
"Carbonyl iron", pyrophoric

} paramagn.

H_2; CO(*t*); C (in blast-furnace)

HEO_n (dil.)

HF; HCl; Br_2; I_2

Fe(ClO$_4$)$_2$ · 6 H$_2$O, colrl. [26]

FeSO$_4$, cr., colrl.; $\xrightarrow{700°}$ Fe_2O_3 + SO_2 + SO_3
↑ (*t*, H_2)
· ***n*** **H$_2$O**, n = 7 (grn., vitriol), "melanterite", 6–4, 1
(NH$_4$)$_2$SO$_4$ · 6 H$_2$O, Mohr salt; · **H$_2$SO$_4$ · 3 H$_2$O**; **FeSO$_3$ · 3 H$_2$O**
Fe(NO$_3$)$_2$ · 6 H$_2$O, m.p. 60.5 (dec.)
Fe$_3$(PO$_4$)$_2$ · *n* H$_2$O↓, n = 8; 4; 2 ("vivianite", "ludlamite", "strengite")
FeHPO$_4$ · 2 H$_2$O↓; **Fe$_4$O(PO$_4$)$_2$**
Fe(H$_2$PO$_4$)$_2$ · 2 H$_2$O, in str. – layers of oct. [26]
Fe$_3$(AsO$_4$)$_2$ · 8 H$_2$O, "symplesite" (tricl.), "parasymplesite" (monocl.)
FeCO$_3$↓, "siderite"; $\xrightarrow{400°}$ Fe_3O_4 + CO + CO_2 ; $CO_2 + H_2O$ ⇄
Fe(HCO$_3$)$_2$, in natural waters, + O_2 ⟶ $Fe_2O_3 \cdot n H_2O$↓ + CO_2
Fe(CH$_3$COO)$_2$, · **4 H$_2$O**; **Fe(HCOO)$_2$ · 2 H$_2$O**;
FeC$_2$O$_4$ · H$_2$O, n = 2; 5, yel., "gumboldin"; $\xrightarrow{160°}$ FeO + CO + CO_2
Fe$_3$Al$_2$[SiO$_4$]$_3$, "garnet"; **Fe$_2$SiO$_4$**, "fayalite"; **FeSiO$_3$**, "klinoferrosilite"

< 0.3% C – mild steels, ⩽2 – **steels**, ⩽4 – **cast irons**
Fe$_3$C, carbide (cementit), stab. > 1100°, m.p. 1650, ΔH = +25; + H^+ ⟶ H_2 + C_nH_{2n+2};
ferromagn. (> 214°), in str. – trig. prism $[FeC_6]$, CN Fe 2
Ferroalloys – with high content of E (E = B, Si, P, Cr, Mo, W, Mn, Ti, Zr, Nb), intermediate materials in production of steels

CO (200°, 10^7 Pa) > 130° ⟶

[1, 27]	m.p.	b.p.	ΔH	str. type	Fe—Hal (gas)	· ***n*** **H$_2$O**, n =
FeF$_2$, colrl.	1100	—	−661	TiO_2	1.77	**8**, **4**
FeCl$_2$, colrl.	674	1026	−343	CdI_2	2.16	**4**, **2**
FeBr$_2$, grn.	684 (*p*)	927	−247	CdI_2	2.31	**6**, **4**
FeI$_2$, brn.	592	827	−125	CdI_2	—	**4**

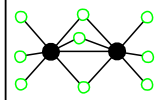
0 (d^8)

H$_2$Fe(CO)$_4$, gas, colrl., m.p. −70, dec. −10, infl., sol. in H_2O, K_1 = 10^{-5}, diamagn., Σ*e* = 18
M$_2$[Fe(CO)$_4$], M = Na (infl.), NH_4

> −10° (−H_2)

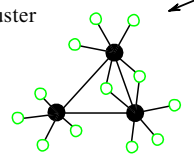
Fe(CO)$_5$, pentacarbonyl, liq., yel. (colrl. < −196°), d = 1.46, m.p. −20, b.p. 103, ΔH = −733, insol. in H_2O, sol. in bz., Et_2O, liq. NH_3; + H^+ → Fe^{2+} + CO + H_2; toxic, diamagn., Σ*e* = 8 + (2 × 5) = 18; mol. – trig. bipyr. (dsp^3)

↓ *hν*-vis (−CO)



Fe$_2$(CO)$_9$, enneacarbonyl, cr., yel., hyg., nonvolat., sol. in Py, acet.; diamagn.; mol. – 2 oct. with common faces, cluster

Fe$_3$(CO)$_{12}$↓, tetracarbonyl, cr., blk.-grn., subl. 60 (vac.), dec. 140, Ox. in air, does not react. with ac., alk., diamagn., in mol. – cluster $[Fe_3]$ [5, 14]



t ⟶ *hν*-vis (−CO)

H$_2$Fe$_2$(CO)$_8$, cr., red
M$_2$[Fe$_2$(CO)$_8$], cr., brn., diamagn.

M$_2$[Fe$_3$(CO)$_{11}$], M = H (liq., red), K, R_4N, $[Ni(NH_3)_6]/2$, cr., red-brn., diamagn.
M$_2$[Fe$_4$(CO)$_{13}$], M = $[Co^{III}(C_5H_5)_2]$, [FePy]/2, in anion – tetrah. $[Fe_4]$

[Fe(:NO)$_4$], tetranitrosyl, needles, blk., v. act.; + H^+ ⟶ $[Fe(NO)(H_2O)_5]^+$ [13]

[Fe(:PX$_3$)$_5$], X = F (cr., yel., m.p. 45); OMe (subl. vac. 80); R, volat., diamagn. (Σ*e* = 18)

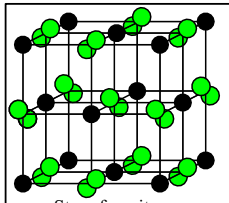
[FeDipy$_3$], cr., blk.; + H_2O ⟶ $[FeDipy_3]^{2+}$ + H_2↑ [11]

M$_2$Fe(PF$_3$)$_4$, M = H (colrl., m.p. −80), K

Na[FeDipy$_3$], cr., blk.

"Fe(CN)$_2$"↓ = $Fe_2[Fe(CN)_6]$, wh. (prec. brn.), dec. 500
Fe(NCS)$_2$ · 3 H$_2$O, cr., grn.

CN^-; KOH [$-Fe(OH)_2$↓]



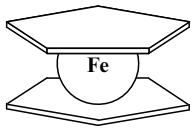
Str. of pyrite

Fe$_{1-x}$S↓, cr., brn., m.p. 1193, ΔH = −96, SP = 10^{-19}, sol. in ac.; + O_2 ⟶ $FeSO_4$; "pyrrotine", NiAs str. type

S (500°) ↓↑ > 700°(−S)

Fe[S$_2$], "pyrite", "marcasite", cr., golden, m.p. 1171, ΔH = −175, NaCl str. type, $([S_2]^{-2}$ = $Cl^-)$, Fe—S 2.26, S—S 2.17 **Fe$_3$S$_4$**, "greigite"; **FeAsS**, "arsenopyrite"

NaC_5H_5



Fe(C$_5$H$_5$)$_2$, ferrocene, cr., orange, m.p. 173, subl. 100, distil. with steam, stab. in air, diamagn., mol. – trig. antiprism, Fe—C 2.05

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3 + (d^5)

4 + (d^4)
5 + (d^3)
6 + (d^2)

Fe — H_2O (−H_2, < 570°); O_2 (*t*) → **Fe_3O_4** = $Fe^{III}(Fe^{II}, Fe^{III})O_4$, blk. with met. lustre, ferromagn., m.p. 1538 (dec.), $\Delta H = -1116$, insol. in ac., semiconduct., "magnetite", in str. inverse spinel — tetrah. [$Fe^{III}O_4$], oct. — [Fe^{II}, $Fe^{III}O_6$]

O_2 (*t*) / H_2 (> 750°)

air (*t*) → **Fe_2O_3**, red, $\xrightarrow{t}$ grey, $\Delta H = -820$, α-, hex., m.p. 1562 (dec.), paramagn., semiconduct., "red hematite", corund str. type; γ-, brn., ferromagn., "maghemite", cub. str. of spinel with partial filling of vacancies of Fe

> 1400°

FeO(OH), α-, β-, γ-, "ironstone" ("limonite"), ("lapidokrokit" + + "goethite"), AlO(OH) str. type – "boehmite", ferromagn. [10]

$-H_2O$

Fe — $K_2O_2 + KOH$; $KNO_3 + KOH$; an. Ox. → **Ferrates** [7, 4]
(IV) Li_2FeO_3; Na_4FeO_4; $M^{II}_2FeO_4$; Ba_3FeO_5 blk. > 0° → Fe^{III} + Fe^{V}
(V) K_3FeO_4, blk., paramagn., $\mu_{eff.} = 3.88$, anion – tetrah.
(VI) K_2FeO_4, red-vlt., isostr. to K_2CrO_4, dec. 200
$BaFeO_4$, dec. 120, · **H_2O**↓, red, paramagn., $\mu_{eff.} = 3$, anion – tetrah. (d^3s); + H_2O → → $Fe_2O_3 \cdot n H_2O$ + O_2

O_2 (immed.) / MOH (conc.) / H_2O → **$FeO \cdot n Fe_2O_3 \cdot x H_2O$**, dark-grn. → O_2 → **$Fe_2O_3 \cdot n H_2O$**↓, brn., sol. in ac. and conc. alk.; $K_{1ac.} = 10^{-13}$; $K_{1bas.} = 10^{-10}$, n = 4, 6, 2.5, **$Fe(OH)_3$**, "bernal", $CaTiO_3$ str. type

Ferrates (II) [7]
$Na_2[Fe(OH)_4] \cdot 2H_2O$, grn.
$Ba_2[Fe(OH)_6]$↓,
$Na_4[FeO_3]$; **$Cs_2K_4[Fe_2O_5]$**, red, in anions — 1 and 2 triangle, CN Fe 3 (d^2s)

$NaFe_2O_3$
$Li_xFe_3O_4$; $Li_xFe_2O_3$ [28]

Fe + $NaFeO_2$ (1000°) → **$Fe_2O_3 \cdot n H_2O$**↓

OH^-, CO_3^{2-} → **Ferrates (III)** [18]
$Na_4[Fe(OH)_7] \cdot 2H_2O$; $Na_5[Fe(OH)_8] \cdot 5H_2O$, **$M_5FeO_4$**; **$K_6[Fe_2O_6]$**; **$M_4Fe_2O_5$**; **$K_{14}[Fe_4O_{13}]$**; anions – tetrah., str. anal. of silicates
$MFeO_2$, red, NaCl str. type
$M^{II}(FeO_2)_2$ = $M^{II}Fe^{III}[Fe^{III}O_4]$, semiconduct., str. — converted spinel

H_2O / MOH (conc.) → **Ferrates (III)**

KClO + KOH → *t* (−O_2) → **Ferrates**

$Fe(ClO_4)_3$, colrl., **· 10 H_2O**, cr., pink [9]
$Fe_2(SO_4)_3$, colrl., dec. ≈500;
· $n H_2O$, n = 10, 9, 7, 6
· M_2SO_4 · 24 H_2O, alum, colrl.
(vlt. due to Mn^{3+} traces)
$Fe(SO_4)(OH) \cdot n H_2O$, n = 1.5, 2, 5
$Fe_2(SeO_3)_3 \cdot n H_2O$
$Fe(NO_3)_3$, [6] **· 9 H_2O**, dec. 50; **· 6 H_2O** (m.p. 40)
$Fe(H_3O)(HPO_4)_2$; [3] **$Fe_4(PO_4)_3(OH)_3$** [9];
$Fe_3(H_3O)(HPO_4)_2(H_2PO_4)_6 \cdot 4H_2O$ [9]
$Fe(H_2PO_4)_3$, **· $n H_2O$**, n = 1, 0.5; **$FePO_4$**↓, yel.
$[Fe_3O^*(RCOO)_6]^+X^-$, red, in the centre – triangle [Fe_3O^*], **$Fe_{11}O_6(OH)_6(RCOO)_{15}$**
$Fe_4O_2(RCOO)_8(H_2O)_6$,
$Fe_2(C_2O_4)_3 \cdot 5H_2O$, yel.; **$NaFe(SiO_3)_2$**, "aegirin"

$[ClO_2][Fe(ClO_4)_4]$, **$M_2[Fe(IO_6)]$**, **$M_3[Fe(SO_4)_3]$**, [3, 6, 15]
$M[Fe(NO_3)_4]$, M = Cs, [R4N], [NO] (= "$Fe(NO_3)_3 \cdot N_2O_4$"), $[(NO_3)^-(NO)_3^+]^{2+}$ (= "$Fe(NO_3)_3 \cdot 1.5\,N_2O_4$"), anion – dodecah., CN Fe 8 (sp^3d^4), **$(NO)[Fe(NO_2)_4]$**
$M[Fe_3(H_2PO_4)_6(HPO_4)_2] \cdot 4H_2O$; **$(NH_4)Fe(HPO_4)_2$**
$Li_3Fe_2(PO_4)_3$; **$K_3Fe_3(PO_4)_4 \cdot H_2O$**; **$M_2[Fe_4O(PO_4)_4]$** [3]
$M_3[Fe(C_2O_4)_3]$, **$RbFe(SeO_4)_2$** [16]

$[Ph_4As]_2[Fe(NO_3)_4]$ [15]
$M_4[Fe(NO_2)_6]$; **$[NO][Fe(NO_3)_4]$**
$K_2[Fe(C_2O_4)_2] \cdot 6H_2O$, cr., yel., sol. in H_2O (unlike the Co- & Ni-comp.)

N_2O_5 → Fe → Hal_2

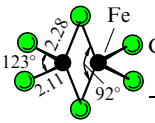
$Fe_2F_5 \cdot n H_2O$,
n = 2 (red), 7 (yel.)
(= $[Fe^{II}(H_2O)_6][Fe^{III}F_5(H_2O)]$;
$Fe_3F_8 \cdot 2H_2O$ = 2 $[Fe^{III}F_{6/2}] \times$ $\times [Fe^{II}F_{4/2}(H_2O)_2]$
brozes — **K_xFeF_3**, $x < 1$,
Fe_3I_8 = 2 $FeI_3 \cdot FeI_2$ [17]

$MFeF_3$, M = K–Cs
$M_2[FeF_4]$; **$Ba_2[Fe_3F_{10}]$**; **$Cs_7Fe_4F_{15}$**
$MFeCl_3$, M = Rb, Cs, in str. – oct.
$M_2[FeCl_4]$, M = Li, K (· 2 H_2O), colrl., high-spin (4 unpaired el.)
M_3FeCl_5, M = NH_4, Tl; **Na_6FeCl_8**
Cs_3FeBr_5 [8]

$H_4[Fe(CN)_6]$, "ferrocyanic ac.", cr., colrl., strong ac., $K_3 = 10^{-2}$, $K_4 = 10^{-4}$; **· n X**, X = H_2SO_4, Et_2O
$K_4[Fe(CN)_6] \cdot 3H_2O$, "yel. prussiate of potash", dec. 87, diamagn., anion – oct. (d^2sp^3), $K_{stab.} = 10^{37}$, non toxic
$Ba_2[Fe(CN)_6]$ [2]

Fe^{3+} → **"Berlin bl."**, **"prussian bl."**, **"Turnbul's bl."**, coll. s.
$MFe^{II}Fe^{III}(CN)_6$,
M = Na–Rb, dec. alk.,
in cub. str. – CN on edges of oct. [$Fe^{II}C_6$] and [$Fe^{III}N_6$]
Fe^{III}_4 $[Fe^{II}(CN)_6]_3 \cdot 14–16 H_2O$↓, cr., bl., in str. – oct. [$Fe^{II}C_6$], [$Fe^{III}N_6$], [$Fe^{III}N_2O_4$], ferromagn. [24]

	ΔH	· $n H_2O$, n =
FeF_3, light grn., subl. > 1000, m.p. 1027, b.p. 1327	−994	**4.5**, **3**, colrl. or pink, sol. in HF [20]
$FeCl_3$, brn., m.p. 308, b.p. 317, in str. – layers of oct., in gas. – dimers	−396	**6**, cr., yel.-brn., m.p. 37, = $[FeCl_2(H_2O)_4]Cl(H_2O)_2$, **2.5**
$FeBr_3$, brn., subl.; 100° → $FeBr_2 + Br_2$, isostr. to $FeCl_3$	−264	**6**, red
FeI_3↓ ⇄ $FeI_2 + I_2$		



$Fe(OR)_3$↓, R = Me, Et; **$Fe_{10}O_4(OEt)_{22}$** [4]

$M[FeF_4]$, M = Rb, Cs, colrl., [21, 25]
$\mu_{eff.} = 5.85$, in str. – layers of oct.
M_2FeF_5, in str. – chains of oct.
$M_3[FeF_6]$; **$H_3[FeF_6] \cdot 3H_2O$**, **$M_2[FeF_5(H_2O)]$**,
$M[FeCl_4]$, M = M^I, $[PCl_4]$, anion – tetrah.
$M_2[FeCl_5]$; **$K_2[FeCl_5(H_2O)]$**, **$M_3[FeCl_6]$**, **$Cs_3[Fe_2Cl_9]$**, anions – oct. (sp^3d^2)
$M[FeBr_4]$, M = Li–Cs, Tl, Ag; anion – oct. **$CsFeI_4$**

$[NO][FeOCl_2]$, **$M_2[Fe_2OCl_6]$** [21]

Fe — $E + F_2$ (*p*) → **$FeF_5 \cdot EF_5$**, E = Sb, Pt
Cs_2FeF_6 [22]

Fe — $I_2 + CsI$ (*t*, *p*)

FeOF, blk.; **FeOCl**, red., [20]

Fe^{2+}

$H_3[Fe(CN)_6]$, ferricianic ac., brn., strong ac., unstab.
$M_3[Fe(CN)_6]$, M = K ("red prussiate of potash"), Na(· 6 H_2O), yel.-brn., low-spin (1 unpared. el.), anion – dist. oct. (t_{2g}^5; d^2sp^3), toxic
$M_n[Fe^{III}(CN)_5X]$, X = CO, NO, Py, NH_3, H_2O, NO_2^-, **"prussides"**, low-spin compl.

"$Fe(CN)_3$"↓ = $Fe[Fe(CN)_6]$, brn.

Fe — Fe^{3+} — S^{2-} (0°; N_2) → **Fe_2S_3**, yel.-grn., + H_2O ⟶ FeS↓ + S↓ + $Fe_2O_3 \cdot n H_2O$↓

Fe — S (*t*) →

$Fe(NCS)_3 \cdot 3H_2O$, red, sol. in alc., Et_2O

$K_3[Fe(NCS)_6] \cdot 2H_2O$, red, unstab. + H_2O ⟶ $[Fe(NCS)_n(H_2O)_{6-n}]^{(n-3)-}$, $K_{1-3} = 10^{-4.6}$; $K_{1-6} = 10^{-3}$ [29]

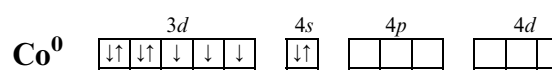
$M_2[Fe(NCS)_4]$; **$M_4[Fe(NCS)_6]$**, $K_{stab.} = 10^2$

KFe_2S_3, in str. – chains $[FeS_{4/2}]_\infty$, [19]
$Na_3Fe_2S_4$

K_2S (*t*) → **$M[FeS_2]$**, bl., · $n H_2O$, cr., red-vlt., anion – $[FeS_{4/2}]_\infty$, **Na_3FeS_3**, **$Ba_{1+x}Fe_2S_4$** [23]

● Fe
● Hal, S
○ CO

COBALT



Co, met., wh., sld., fragile > Fe, act. < Fe, d = 8.9, m.p. 1495, b.p. 2960, sol. in dil. ac. (20°), passivated at b.p. and ac.-Ox., $E_{0\,Co^{2+}/Co_{sld.}}$ = −0.277, ferromagn. (< 1300°), fines – pyrophoric, α-, hex. cl. pack, a = 2.51; c = 4.07, Co—Co 2.50
↓ 430°
β-, cub. pl. pack, Mg str. type, a = 3.55, stab. at 20° in atm. H_2

$[Co(NH_3)_x(H_2O)_{6-x}]^{n+}$, products of hydro-metallurgical technol. ← H_2 (p)

O_2 (≳ 300°)

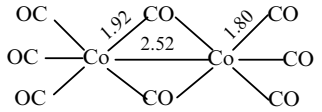
H_2 (500°), C, Al

t (−CO)

CO (200°, p)

0 (d^9)

$Co_2(CO)_8$, cr., orange, m.p. 51, dec. 60, Ox. by air, sol. in org. solv., insol. in ac., dec. alk.; diamagn., mol. – 2 trig. bipyr. with sharing edge:



in s. – mol. $[Co(CO)_4]$
$Co_2(CO)_6L_2$, L = PR_3, RC≡CR, without bridge CO, Co—Co 2.67
$Co_4(CO)_{12}$, cr., blk.;
60° → Co + CO; mol. – tetrah. cluster $[Co_4]$, Co—Co 2.49, in vertex – gr. $[Co(CO)_3]$, in base – 3 tetrah. $[Co(CO)_2(CO)_{2/2}]$ with sharing vertex
$Co_6(CO)_{16}$, cr., blk. [4]

H_2 (p) / Na/Hg

$HCo(CO)_4$, gas, colrl., m.p. −26, b.p. 10, in s. H_2O – strong ac., mol. – trig. bipyr., H—Co 1.2, Co—C 1.8
$M[Co(CO)_4]$, M = Li, K, Ag, Zn/2, Pb/2, Tl, Hg/2, $[Ni(NH_3)_6]/2$, $SiCl_3$, SiH_3 [22]

M

$M[Co_3(CO)_{10}]$, M = Li–K, cr., red
$K_2[Co_6(CO)_{15}]$, oct. cluster, Co—Co 2.51, 9 CO-term., 3 μ_2-, 3 μ_3-CO, Co—C 1.74, 1.90, 2.00
$M[HCo_6(CO)_{15}]$, H – in center of oct. $[Co_6]$, Co—H 1.82
$K_4[Co_6(CO)_{14}]$, cr., red
$K[Co_6N(CO)_{15}]$, **$M[Co_6P(CO)_{16}]$** [20]

$Li_4CoPh_3 \cdot 5\,Thf$ [23]

50° (−CO)

NO (−CO) (*hv*-Vis)

$Co(NO)_3$, cr., blk., dec. 100, Ox. in air, diamagn.
$[CoDipy_3]$, cr., bl., Ox. O_2

$[Co(PF_3)_4]_n$, cr., vlt. [24]
$[Co(N_2)(PPh_3)_3]$, cr., yel., sol. in bzl., Et_2O., stab. to hydr.
$Co[P(OR)_3]_4$, · **L**, L = NO, CS_2, SO_2, O_2 [19]

$HCo[P(OPh)_3]_4$, in mol. – linear gr. $[CoN—]_2$, Co—N 1.22, N—N 1.12 [4]
$HCo(PF_3)_4$, liq., grn., m.p. −51, b.p. 80, dec. 250, in s. H_2O – strong ac.
$H_3Co(PPh_3)_3$, hydrogenation cat. [11]
$HCo(PR_3)_3(N_2)$, in mol. – dist. trig. pyram. $[CoP_3N]$, gr. [CoN≡N] – linear [28]
$K[Co(PR_3)_3(N_2)]$, anion – tetrah., Co—N 1.70, N≡N 1.17 [11]

H_2+CO (t, p)

$Co_3N \xleftarrow{200°} Co_2N \xleftarrow{150°} CoN$
Co_3C; **Co_2C**

$Co(CO)_3(PPh_3)Hal$, Hal = Cl–I, cr., Ox. in air, sol. in bzl., diamagn. ($\sum e = 18$)
$Co(NO)_2Hal$, cr., blk., in liq. and gas – dimers with 2 μ-Hal
$(NO)_2Co(PPh_2)_2Co(NO)_2$
$\{Co[P(OR)_3]_5\}^+X^-$ [11]

$[Co(PR_3)_3Hal]$, Hal = Cl–I, mol. – tetrah., μ_{eff} = 3.12, (2 unpair. el.)

$Co_3(CO)_9S$, paramagn., $[Co_3S]$ – tetrah. [18]

$[(C_5H_5)CoL]$, L = NO, C_5H_6 [15]

$K_3[Co(CN)_4]$, cr., yel., > 20° → red-brn., Ox. in air, anion – square
$K_2[Co(CN)_3(CO)]$

$[CoDipy_3]ClO_4$

$Co(PF_3)_4I$, cr., brn.

$[Co(MeCN)_5]Hal$, v. stab.

2 + (d^7)

$Co_{1-x}O$, cr., grn.-blk., m.p. 1935, dec. 2800, ΔH = −239, sol. in ac., conc. alk., antiferromagn., NaCl str. type, Co—O 2.15

−O_2 (< 500°)
> 900°

170° (−H_2O) (N_2)

$Co(OH)_2$↓, pink, SP = 10^{-16}, sol. in ac., alk., NH_4OH, K_{bas} = 10^{-4}, CdI_2 str. type

MOH (conc.)
H_2O

OH^- H^+

$Co(OH)_nX_{2-n} \cdot m\,H_2O$↓, bl., bas. salts

OH^- H^+

H^+

$Co(ClO_4)_2$, dec. 210; **$\cdot n\,H_2O$**, n = 4, 6, red [25]
$CoSO_4$, pink, dec. 650; **$\cdot n\,H_2O$**, n = 7 ("red vitriol", "biberite"), 6 ("marcasite"), 4 ("aplovite"), 1
· **$M_2SO_4 \cdot 6\,H_2O$**, Tutton salts [9]
· **$1.5\,Co(OH)_2 \cdot 2.5\,H_2O$**↓, vlt.;
$CoSO_3 \cdot n\,H_2O$↓, red, n = 5, 3, 2.5, 2 [7]
$Co(NO_3)_2$, purp.; **$\cdot 6\,H_2O$**, red
$Co_3(PO_4)_2$, red, CN Co 5;
$\cdot n\,H_2O$↓, n = 2, 8, s. in H_3PO_4, NH_4OH; [6]
$Co_5(PO_4)_2(OH)_4$; **$Co(H_2PO_4)_2 \cdot 3\,H_3PO_4$**;
$CoHPO_4 \cdot 3\,H_2O$ [12]
$Co_3(AsO_4)_2 \cdot 8\,H_2O$↓, "erythrite",
$CoCO_3$, red, "spherokobaltite", isostr. to $CaCO_3$;
$\cdot 6\,H_2O$↓, formed in surplus CO_2;
$Co(CH_3COO)_2$; **$\cdot 4\,H_2O$**, red, irreversible attached O_2 [6]
$Co_3(CH_3COO)_4O$; **$Co(HCOO)_2 \cdot 2\,H_2O$** [6]
$CoC_2O_4 \cdot 2\,H_2O$↓, pink; $\xrightarrow{t\,(N_2)}$ Co + 2 CO_2

t (−N_2O_4)

[NO][Co(NO$_3$)$_3$]

270°

$CoHal_2 \cdot 9\,Co(OH)_2 \cdot 8\,H_2O$↓, Hal = Cl, Br, "grn. bas. halides", in two-layer str. – layers of oct. $[Co(OH)_6]$ and $[Co(OH)Hal(H_2O)_4]$
$CoHal_2 \cdot 3\,Co(OH)_2 \cdot H_2O$↓, "pink bas. chloride", "red bas. bromide", CdI_2 str. type; **Co(OH)Cl** [21]

Co → Hal_2 (20°) (Hal = Cl–I)

OH^-

	m.p.	b.p.	ΔH	· $n\,H_2O$, n =
CoF_2↓, pink	1200	~1740	−661	**4, 2**
$CoCl_2$, bl.	740	1049	−318	**6, 4, 2, 1**
$CoBr_2$, grn.	678	927	−213	**6, 2**
CoI_2, blk.	520	570 subl.	−88	**6** pink-vlt.

str. CoF_2 – TiO_2 type, $CoHal_2$ (Hal = Cl–I) – CdI_2 type; in gas – linear mol. [1]

$Co(CN)_2$, cr., bl., dec. 450; **$\cdot 2.3\,H_2O$**↓ = $Co_2[Co(CN)_6] \cdot 7\,H_2O$
$Co(NCS)_2 \cdot 3\,H_2O$, red-vlt.

CoS↓, blk., m.p. 1116, α-, amorph., sol. in CH_3COOH, SP = 10^{-23}, β-, insol. in ac., form colloid. s., SP = 10^{-27}, NiAs str. type
CoS_2↓, blk., FeS_2 str. type
Co_3S_4, "linnaeite", spinel
CoAsS, "cobalt glance"; **$CoAs_2$**, "wh. cobalt"
$CoAs_3$, "scutterudite"; + O_2 ⟶ Co_3O_4

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_36, © Springer-Verlag Berlin Heidelberg 2011

3+ (d^6)

4+ (d^5)

$-O_2$ (< 500°)

> 900°

Co_3O_4 = $Co_2^{III}[Co^{II}O_4]$, blk., ΔH = −904, normal spinel str.

$-O_2$ (> 250°)

$H_2O_2(OH^-)$; NaOCl; O_2 (slow.)

CoO(OH), "stanierit", 150° ↑ **$Co_2O_3 \cdot n\,H_2O$**↓, brn., sol. in NH_4OH, insol. in alk.

$H_2O_2(OH^-)$; OCl^-

$CoO_2 \cdot nH_2O$↓, blk.

Kobaltates (II) [10]
$Na_2[Co(OH)_4]$; **$Ba_2[Co(OH)_6]$**
$Li_6[CoO_4]$, **Na_4CoO_3**, red-vlt.
$CoO \cdot M_2O_3$, spinels

O_2

H_2SO_4

Kobaltates (III)
$K_3[Co(OH)_6]$, grn.
Na_5CoO_4, vlt., anion – tetrah.
$M^{II}Co_2O_4$, spinels (M^{II} = Zn, "Rinman green"), in str. – layers of tetr. pyram.

(3.3–3.5)+
K_xCoO_2, x = 0.5–0.67, "bronze" [14]

Kobaltates (IV) [3]
Li_8CoO_6; **$K_6Co_2O_7$**
M_4CoO_4, M = Li–Cs
Ba_2CoO_4; **$BaCoO_3$**,
red-brn., anions – tetrah. or chains of oct.

K_3CoF_7; **Cs_2CoF_6**,
yel.-brn., anion – oct.
K_2PtCl_6 str. type

Co

N_2O_4

$(NO_2)_2[Co(ClO_4)_4]$; **$NH_4[Co(ClO_4)_3]$**; [25]
$K_2[Co_3(OH)_2(SO_4)_3] \cdot 2\,H_2O$ [17]
$K_2[Co(SO_3)_2]$, red;
$M[Co(NO_3)_3]$, M = NO (="$Co(NO_3)_2 \cdot N_2O_4$") [27]
$M_2[Co(NO_3)_4]$,
M = R_4N, NO
anion – dodecah. [CoO_8]
$K_2[Co(NO_2)_4]$, cr., yel.
$K_4[Co(NO_2)_6]$, low-spin oct.
(1 unpair. el.), μ_{eff} = 1.85
$(NH_4)_2[Co(CO_3)_2]$↓, cr., red
$K_2[Co(CO_3)_2(H_2O)_4]$-*trans* [19]
$K_4[Co(HCOO)_6]$; **$Cs[Co(HCOO)_3]$**,
$K_2[Co(C_2O_4)_2] \cdot 6\,H_2O$, red-brn. [19]

$Co_2(SO_4)_3 \cdot 18\,H_2O$,
bl.-grn., dec. 30
$\cdot M_2^I SO_4 \cdot 24\,H_2O$,
dark-bl., alum, v. unstab., diamagn.
$Co(CH_3COO)_3$, blk-grn., dec. 100
$[Co_3O(HCOO)_6]^+X^-$ [18]

$M_3[Co(NO_2)_6]$↓, yel.
CN Co 12 (icosah.)
$Na_3[Co(CO_3)_3] \cdot 3\,H_2O$↓, grn.
$(NH_4)_3[Co(C_2O_4)_3] \cdot 3\,H_2O$

O_2

CoF_2

XeF_2

$[XeF_5]CoF_4$, cr., bl., dec. 80, μ = 5.5, anion – layers of oct.
M_3CoF_6, M = Li–Cs, bl., high-spin, μ_{eff} = 4.3, (sp^3d^2), 4 unpair. el. [16]

M_2CoF_4; **M_4CoF_6**, pink, high-spin (3 unpair. el.), oct. ion
$MCoCl_3$, bl., in str. – chain of oct.
M_2CoCl_4, bl., paramagn. (3 unpair. el.), anion – tetrah.
M_2CoBr_4, tetrah., (sp^3)
$Cs_2[CoI_4]$
Cs_3CoI_5 = $Cs_3[CoI_4]I$, grn., [8,9]

CoF_3, brn., subl., dec. 350, ΔH = −774, strong Ox.,
+ E ⟶ EF_n (E = As, P, C, Si),
$\cdot 3.5\,H_2O$, grn., paramagn. (4 unpair. el.); [10,11]
+ H_2O ⟶ $Co(OH)_3$↓ + HF
$CoCl_3$, grn., unstab., ΔH = −268, $h\nu$-vis → dec.

H_2O ($-H_2$)

$[R_4N]_3[Co(CN)_5]$, yel., anion – tetr. pyram., $K_{stab} = 10^{19}$
$K_6[Co_2(CN)_{10}] \cdot 6\,H_2O$, red, diamagn.
$M_2[Co(—NCS)_4] \cdot n\,H_2O$, high-spin, $K_{stab} = 10^2$
$M_3[Co(NCS)_5]$; **$M_4[Co(NCS)_6]$** [2]
$M_2[Co(CNO)_4]$, $K_{stab} = 10^5$

$Co(CN)_3$, bl.; **$\cdot 2\,H_2O$**, red [26]

120°

$M[Co(CN)_4]$ $\xleftarrow{t}$ **$M[Co(CN)_4(H_2O)_2]$**,
M = H, M^1, red
$H_3[Co(CN)_6] \cdot H_2O$, cr., colrl., strong tribasic ac.

H_2S ↑ $\quad\xleftarrow{Cu^{2+}}\quad$ ↑ H_2SO_4

$Cu_3[Co(CN)_6]_2$↓ **$K_3[Co(CN)_6]$**,
yel., anion – oct. (d^2sp^3),
Co—C 1.90, $K_{stab} = 10^{64}$ [5]

Amminocomplexes of Co [14]

2+

$[Co(NH_3)_6]^{2+}$, yel., oct., high-spin (sp^3d^2), μ_{eff} = 5.04, $K_{stab} = 10^4$
Red.

O_2

$\{[(NH_3)_5Co^{III}]_2(O_2)^{2-}\}X_4$, **peroxides**, brn.,
O—O 1.47–1.65;
$\nu_{O—O}$ 850–860 cm^{-1}
diamagn.

t; HNO_3

$\{[(NH_3)_5Co^{III}]_2(O_2)^{-}\}X_5$, **superoxides**, grn., paramagn. (1 unpair. el.),
O—O 1.31–1.45;
$\nu_{O—O}$ 870–890 cm^{-1} [5,13]

(see Tab. "O")

$[Co(NH_3)_4]^{2+}$, $K_{stab} = 10^5$

$[Co(NH_3)_2Hal_2]$,
α-, mol. – tetrah.
β-, chain of oct.

Act. coal

O_2

3+

Hexammines
$[Co(NH_3)_6](OH)_3$, yel., strong bas., $K_3 = 10^{-2}$
$[Co(NH_3)_6]^{3+}$, "luteosalts" (yel.) diamagn., $K_{stab} = 10^{36}$

Pentammines
$[Co(NH_3)_5X]^{2+}$, X = Hal, NO_3, "purpureosalts"
$[Co(NH_3)_5(H_2O)]^{3+}$, "roseo-"

Tetrammines
$[Co(NH_3)_4Cl_2]^+$,
trans-, "praseo-" (grn.),
cis-, "violeo-" (vlt.)
$[Co(NH_3)_4(NO_2)_2]^+$,
trans-, "croceo-" (yel.),
cis-, "flavo-" (brn.)

Triammines
fas-**$[Co(NH_3)_3(NO_2)_3]$**, (yel.-brn.)

Diammines
trans-**$[Co(NH_3)_2(NO_2)_4]^-$**,

Monoammines
$[Co(NH_3)(CN)_5]^{2-}$

NICKEL

Ni^0 3d ↓↑ ↓↑ ↓↑ ↓ ↓ | 4s ↓↑ | 4p | 4d

EN 1.8

1 + (d^9)

2 + (d^8)

$Ni_{1-x}O$, cr. blk-grn., m. p. 1990, ΔH = −239, sol. in ac., "bunsenite", dist. NaCl str. type

↑ 250°

$Ni(OH)_2$↓, apple-grn., sol. in ac., NH_4OH; insol. in conc. alk., SP = 10^{-17}, CdI_2 str. type

O_2(l)

H_2 (400°); C

Ni, met., lustrous, wh., d = 8.9, m. p. 1455, b. p. ~2900, act. < Fe and Co; sol. in ac. (passiv. conc. HNO_3) and [NH_4OH + $(NH_4)_2CO_3$]; $E_0Ni^{2+}/Ni_{sld.}$ = −0.234; ferromagn. (< 358°); α-, hex. cl. pack., a = 2.65, c = 4.32, Ni—Ni 2.48

↓ 250°

β-, cube cl. pack., a = 3.52 (stab. at 20°)

"Ni Raney Sceletal", powd. (400–800 nm), blk., infl. in air, contain sol. H_2 (⩽300 at.%), hydrogenation cat.

Cath. Red

H^+

↑ conc. NaOH [−$NaAl(OH)_4$]

Alloy Ni–Al

Ni-alloys: content 4–5% Ni increases corrosion resist. of steels; (36% Ni + 0.2% C + 64% Fe), "invar", min. coeff. of linear expansion; "magnetic alloy" 11–14% Al, 22–34% Ni, rest – Fe

CO (50–80°) 180°

N_2O_4 (MeCN)

$Ni(ClO_4)_2$, · **n H_2O**, n = 4, 6, bl-grn., m. p. 149; · **6 NH_3** [23]

$Ni(ClO_3)_2$ · **6 H_2O**, grn., dec. 80

$Ni(IO_3)_2$↓, yel. needles; · **4 H_2O; NiH_3IO_6** · **6 H_2O** [23]

$NiSO_4$, yel., dec. 640 [3]; · **7 H_2O**, "grn. vitriol", · **6 H_2O**, bl. or grn., "retgersite", · **M_2SO_4** · **6 H_2O** (Tutton salt)[7]

NiS_2O_3 · **6 H_2O** [7]

$Ni(NO_3)_2$, light grn., dec. 220 (vac.); · **6 H_2O**, m. p. 57, dec. 105

$Ni(NO_2)_2$, light grn., dec. 220

$NiHPO_4$ · **n H_2O**, n = 3, 3/2; **$Ni_3(HP_2O_7)_2$** · **10 H_2O;**

$Ni(H_3P_2O_7)_2$ · **2 H_2O;** [25]

$Ni_3(PO_4)_2$ · **7 H_2O**↓, grn.; **$Ni_2P_2O_7$** · **6 H_2O**↓, grn.;

$Ni(H_2PO_2)_2$ · **6 H_2O;** **$Ni_3(AsO_4)_2$** ↓, yel., · **8 H_2O**, "annabergite"

$NiCO_3$↓, yel. or grn., isostr. to $CaCO_3$ ←CO_2 (p) · **6 H_2O**↓

↑ HCO_3^-

3 $Ni(OH)_2$ · **2 $NiCO_3$** · **4 H_2O**↓

$Ni(CH_3COO)_2$; · **4 H_2O**, grn., hydr., K_2 = 10^{-3} [26]

NiC_2O_4 · **2 H_2O**↓, $\xrightarrow{t}$ Ni + 2 CO_2; **$Ni(HCOO)_2$** · **2 H_2O**

$NiSiF_6$ · **6 H_2O**, grn., sol. in H_2O

Cs[Ni(ClO$_4$)$_3$]

$(NO_2)_2[Ni(ClO_4)_4]$

[NO][$Ni_2(NO_3)_5$] = = $Ni(NO_3)_2$ · 0.5 N_2O_4

$M_2[Ni(NO_3)_4]$; **M[$Ni(NO_3)_3$]**

$M_4[Ni(NO_2)_6]$, · **H_2O**;

$NaNi_4(PO_4)_3$

$M_2[Ni(CO_3)_2(H_2O)_4]$ [23]

$Na_2[Ni_8(CO_3)_6(OH)_6]$ · **6 H_2O**

$K_2[Ni(CH_3COO)_4(H_2O)_2](H_2O)_2$

$M_2[Ni(C_2O_4)_2]$

$HNi(N_2)(PR_3)_2$

$H_2Ni(CO)_6$, · **NH_3**

$M_2[Ni_2(CO)_6]$

0 (d^{10})

Ni(CO)$_4$, liq., colrl., toxic, m.p. −19, b.p. 43, dec. 180, ΔH = −146, exp. in air, sol. in org. solv., insol. in ac., alk., diamagn., mol. – tetrah. (sp^3)

M/Hg

$H_2[Ni_3(CO)_8]$, cr. dark red

$Li_2[Ni_3(CO)_8]$

$M_2[Ni_3(CO)_8]_2$, M = K, NH_4, [4]

anion – trig. antiprism

$[Ni(CO)_n(PPh_3)_{4-n}]$, cr. light yel., mol. – tetrah. [6]

$[Ni(CO)_n(PF_3)_{4-n}]$

Ni_2H [13]

Zn + NO

$[Ni(NO)(NO_2)]$↓,

$[Ni(NO)(PPh_2)]_4$

$[Ni(NO)Hal]_4$,

$[Ni(NO)(PR_3)I]_2$,

$[NiHal(PPh_3)_2]_2$,

$[Ni(PR_3)_4][BPh_4]$,

NiX · **n Am**, X = BH_4, BF_4, Am = Dipy, Phen

$[Ni(\mu\text{-}PR_2)(CO)_2]_2$ [14]

Ni(OH)Cl, CdI_2 str. type; **$NiHal_2$** · **3 $Ni(OH)_2$**

	m.p.	m. subl.	ΔH	· **n H_2O**, n =
NiF_2↓, yel.	1160	1474	−657	**3, 4, 6**
$NiCl_2$, yel.	1001	970	−305	**4, 6**
$NiBr_2$, brn.	963	919	−211	**6**
NiI_2, blk.-grn.	797	970	−96	**6**

NiF_2 – TiO_2 str. type; $NiHal_2$ (Hal = Cl–I) – $CdCl_2$ type,[16] in gas – NiF_2 – linear mol., · **PR_3** [8]

M[NiF_3], perovskite str. type

$M_2[NiF_4]$, in str. – layers [NiF_6]

$M_2[NiCl_4]$; **$Cs_3[NiCl_5]$**; **$KNiCl_3$**, anions – chains of oct.

$M_2[NiBr_4]$, anion – tetrah.

Cs[$NiBr_3$], in str. – net of oct. [24]

$H_2[Ni_4(CO)_9]$, cr. blk.-vlt. $K_2 = 10^{-10}$

$M_2[Ni_4(CO)_9]$, M = Na, K, Mg/2, Cd/2, [$Ni(NH_3)_2$]/2

anion – tetrah.

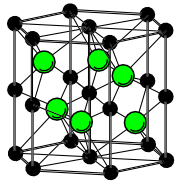
$[Ni(PX_3)_4]$, X = F (liq. colrl., m. p. −55, b. p. 71), H, Cl, R, OR, OCN, mol. – tetrah.

$[Ni(PR_3)_3(N_2)]$

$[Ni(PPh_3)_2(O_2)]$; + $H_2O \longrightarrow H_2O_2$ + ... [1]

NiS↓, cr., blk., m. p. 797, "fibrous pyrite" ("millerite"), α-, NiAs str. type, sol. in ac., SP = 10^{-21} $\xrightarrow{(O_2)}$ β-, insol. in ac., form coll. s., SP = 10^{-26}; **Ni_3S_4**; **Ni_3S_2**; **NiS_2**, "vaesite", FeS_2 str. type

NiAs, "copper-Ni" ("nickeline"), m. p. 968, in str. – at. Ni in site of "two-story" hex. cell, at. As – in centra of trig. prism, oct. [$NiAs_6$] and [$AsNi_6$]



$[NiPy_3(SO_2)^0]$, dec. 150, not Ox. [12]

$[NiDipy_2]$, cr. bl., pyrophoric

$Ni(C_5H_6)_2$; **$[(PR_3)_2Ni(N_2)Ni(PR_3)_2]$**

$M_2[Ni(S_4)_2]$

$Ni(C_5H_5)_2$, nickelecen [17]

$M_2Ni_5(CO)_{12}$; **$M_2Ni_6(CO)_{12}$**

$M_2Ni_9(CO)_{18}$; **$M_2[Ni_8(CO)_{16}C]$** [11]

$M_nH_{4-n}Ni_{12}(CO)_{21}$, n = 2, 3 [10]

$K_4[Ni(CN)_4]$, anion – tetrah. (sp^3); + $H_2O \longrightarrow K_4[Ni_2(CN)_6] + H_2$ + + KCN + KOH;

$M_4[Ni_2(CN)_6]$ [2]

$K_3[Ni(CN)_4]$

$K_4[Ni_2(CN)_6(CO)_2]$

$K_4[Ni_2(CN)_6(NO)_2]$

K

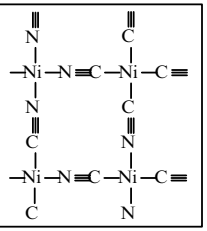
(NH_3)

$Ni(CN)_2$, cr. yel., 420° ⟶ Ni + N_2 + C (exp.), in str. – plane layers of oct.

↑ 200°

· **4 H_2O**↓, grn.

· **NH_3** · **C_6H_6**,- clathrate



$[Ni(ER_3)_4]$, E = As, Sb; **$[Ni(PR_3)]_2(\mu\text{-}CS_2)_2$** [4]

$Ni(OR)_2$↓, grn. (R = Me), vlt. (Et–*i*-Pr) [28]

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_37, © Springer-Verlag Berlin Heidelberg 2011

$Cl_2(OH^-)$; BrO_3^-, an. Ox.;
$Fe(OH)_2(-Fe\downarrow)$
(in alk. Edison battery)

2.66+
Ni_3O_4, in str. – oct. Ni(II) and tetrah. Ni(IV) [21]

$-H_2O$

$Ni_3O_4 \cdot 6H_2O$; $Ni_2O_2(OH)$ [21]

$-O_2$

$Ni_2O_3 \cdot nH_2O\downarrow$, blk., v. strong Ox. [15]

MO_2; $KClO_3 + O_2$ (t)

$NiO_2 \cdot nH_2O\downarrow$, blk.

M_2O_n (t)

Nickelates (II) [20]
$Na_2[Ni(OH)_4]$
M_2NiO_2, from yel.-grn. to red, anion – chains of squares $[NiO_{4/2}]$ (M = Na)
or dumb-bell $[NiO_2]$
(K); $+H_2O \rightarrow Ni(OH)_2$

2.5+ [21]
$K_9Ni_2O_7$, red. (I)
$K_3Ni_2O_4$, blk. (II),
in str. I – ribbons of squares,
II – tetrah. $[Ni^{III}O_4]$ and triangle $[Ni^{II}O_3]$, Ni—O 1.80–1.96

Nickelates (III) [15]
$MNiO_2$, M = Li, Na
$Ba_2Ni_2O_5$, blk.,
m. p. 1200 (in atm. O_2)
Na_5NiO_4, anion – tetrah., paramagn.,
$+H_2SO_4 \rightarrow O_2$

t ($-O_2$)

Nickelates (IV) [18]
M_2NiO_3, M = K, Ba/2,
blk., paramagn. (μ_{eff} = 2.1),
in str. – columns of oct. with common face,
$+ H_2O \longrightarrow O_2 + Ni(OH)_2$

$[NiHal_3L_2]$, Hal = Cl, Br, L = AsR_3, PR_3, En, cr., bl., μ_{eff} = 1.89, mol. – trig. bipyr. or tetr. pyram.,
Ni—Br 2.35–2.42, Ni—P 2.23
$NiClEn_2(ClO_4)_2$ =
= $[Ni^{II}Cl_2En_2][Ni^{IV}En_2][ClO_4]_4$, [19]

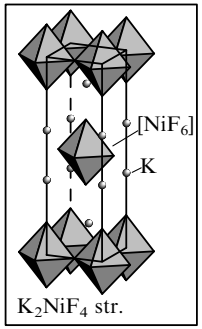
$NiSO_4$
$M_2Ni(OH)_4$

$M_2S_2O_8 + M_3H_2IO_6$

$M[NiIO_6] \cdot nH_2O$,
M = Na, K, purp.,
in str. – oct. $[NiO_6]$ and $[IO_6]$,
semiconduct.
$Li_2[Ni(HTeO_4)_6] \cdot 2H_2O$ [18]

F_2

550° ($-F_2$)



K_2NiF_4 str.

Complexes Ni (II) with nitrogencontaining ligands

$[NiAm_6]X_2$, Am = NH_3, Py, En/2
$[Ni(NH_3)_6](OH)_2 \cdot 8H_2O$, vlt., v. unstab.
$[Ni(NH_3)_6]X_2$, X = $ClO_4\downarrow$, $[I_9]$, Cl
$[NiEn_2]X_2$, cation – square
***trans*-$[NiPy_4Hal_2]$**, mol. – oct.
$NiPy_2Hal_2$, in str. – chains of oct.
$[Ni(MeCN)_6](ClO_4)_2$, red
$[Ni(MeCN)_4(ClO_4)_2]$, bl.
$[Ni(MeCN)_2(ClO_4)_2]$, light grn.
$[Ni(NO)^+(OH)_3]$, bl., mol. – tetrah. (sp^3), 2 unpair el.

M_3NiF_6, M = Li–K, cr., vlt., stab. in air., hydr.,
μ_{eff} = 2.5, anion – oct.;
$+ HF_{(liq.)} \longrightarrow M_2NiF_6 + NiF_2$ [9]

$NiF_4\downarrow$,
cr., brn.,
0° $\longrightarrow NiF_3$ [5]

BF_3;
AsF_5

M_2NiF_6, M = Na–Cs, Ba/2, $[O_2]$, $[XeF_5]$, [NO], red., diamagn., K_2PtCl_6 str. type, anion – oct. (d^2sp^3), strong F-agents
($+Xe \xrightarrow{(ClF_3)} XeF_2 + M_3NiF_6$) [5]

F_2

300–500° ($-NiF_2-F_2$)

NiF_2

F_2; ClF_3; ($KrF_2 + XeF_6$)

$Na_3[Ni(CH_2{=}NO)_6]$, cr., brn.

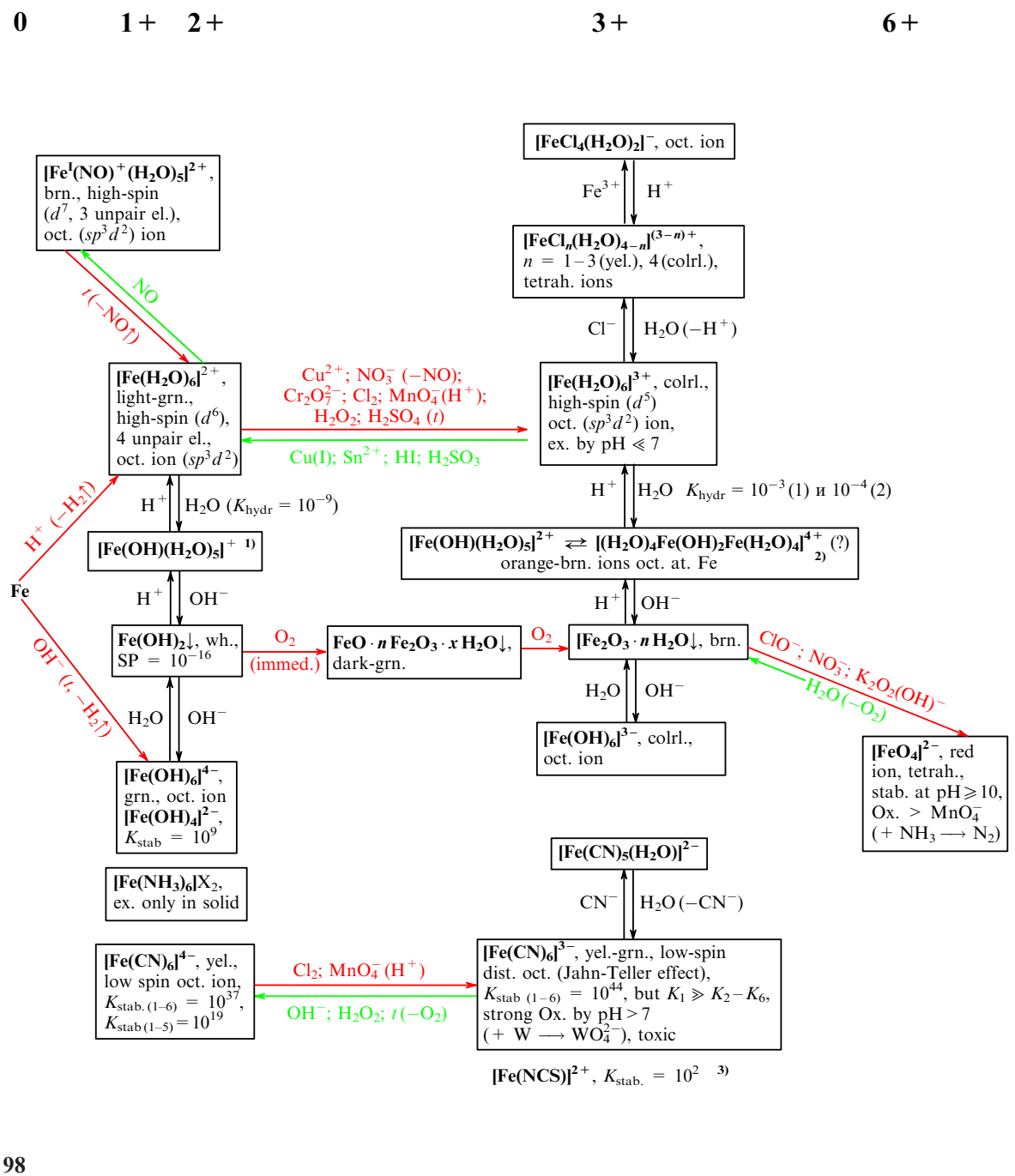
O_2

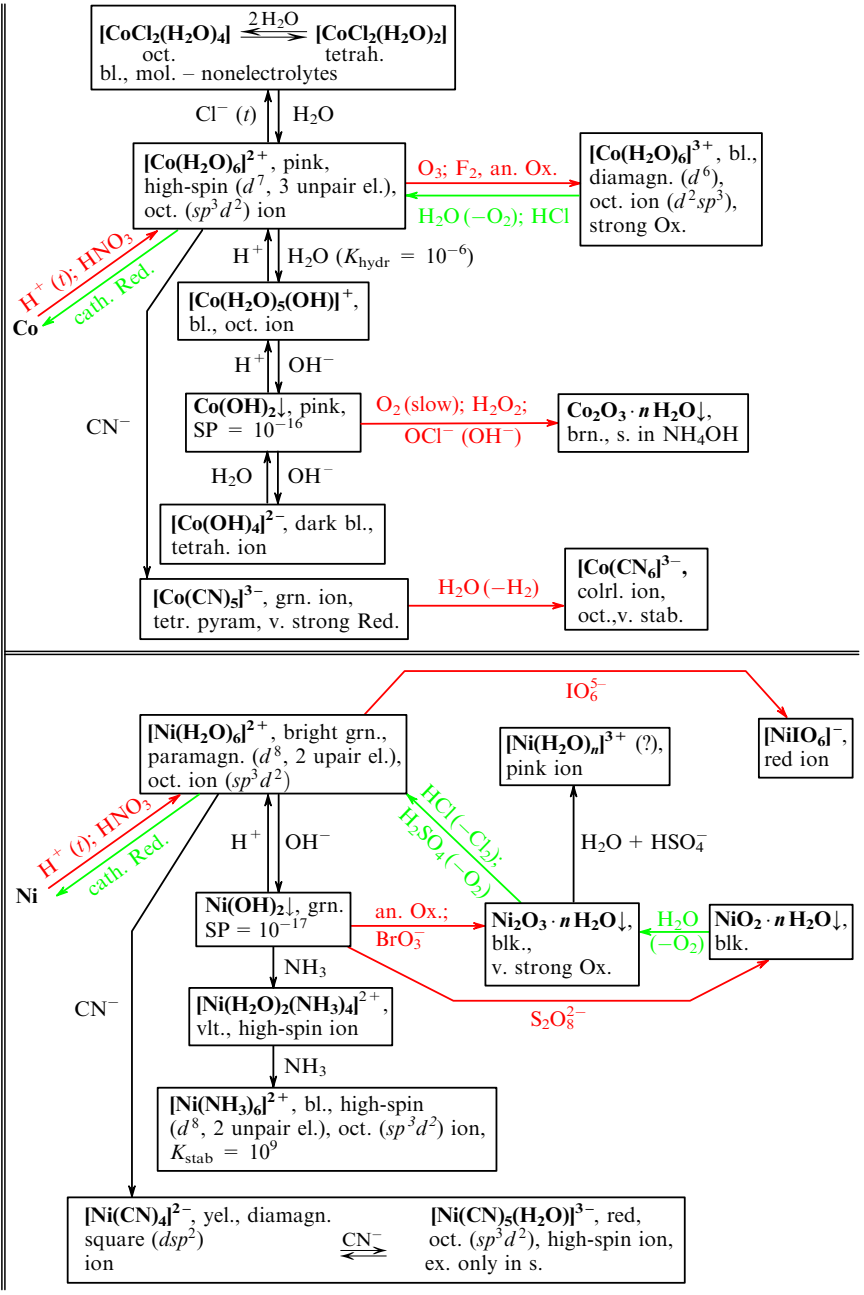
$Na_2[Ni(CH_2{=}NO)_6]$, m. p. 230, readily sol. in H_2O, insol. in org. solv., diamagn.

$M_2[Ni(CN)_4]$, M = Na (yel.), K (orange), cr., diamagn., $K_{stab} = 10^{31}$, in str. – columns of squares (dsp^2),
$M_3[Ni(CN)_5]$
$M_4[Ni(NCS)_6]$, $K_{stab} = 10^2$
$M_2[Ni(NCO)_4]$, $K_{stab} = 10^6$
$M_2[Ni(S_4)_2]$, anion – square
$Cs_2[Ni(N_3)_4] \cdot nH_2O$
$K_4[Ni(N_3)_6] \cdot 3H_2O$, anion – oct. [22]

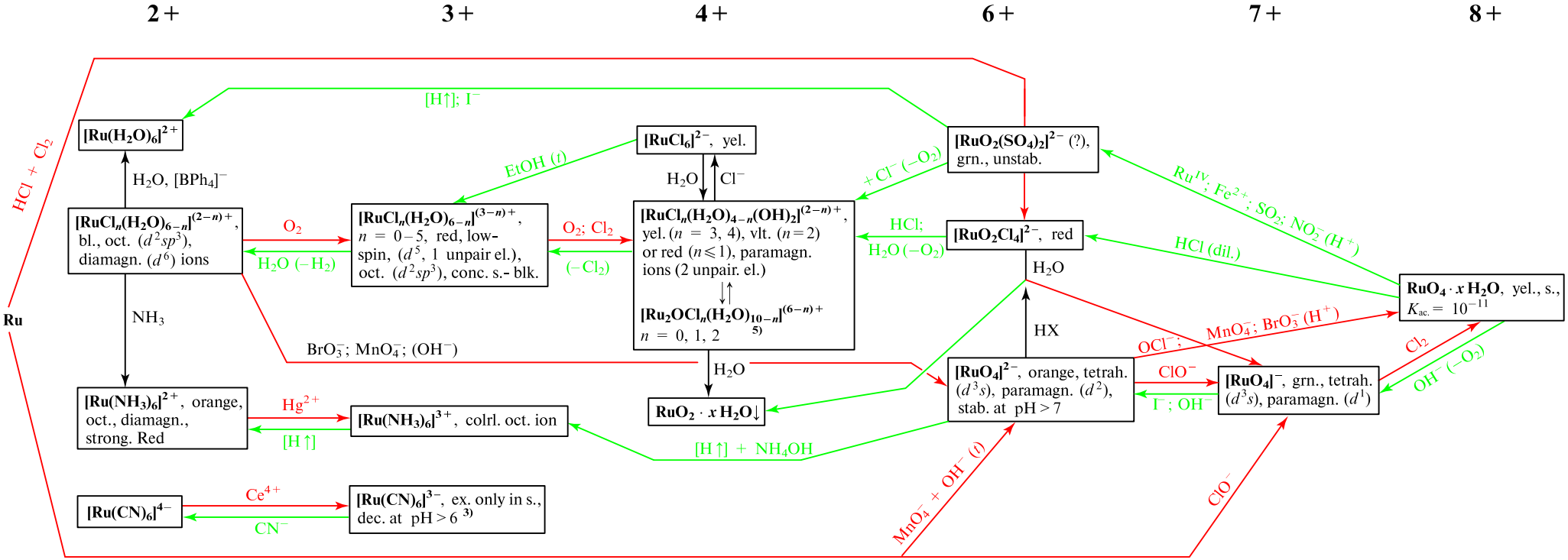
$[Ni(C_5H_5)_2]^+X^-$, salts of nickelocinium, cr. orange, paramagn. (1 unpair el.), stab. > $Ni(C_5H_5)_2$

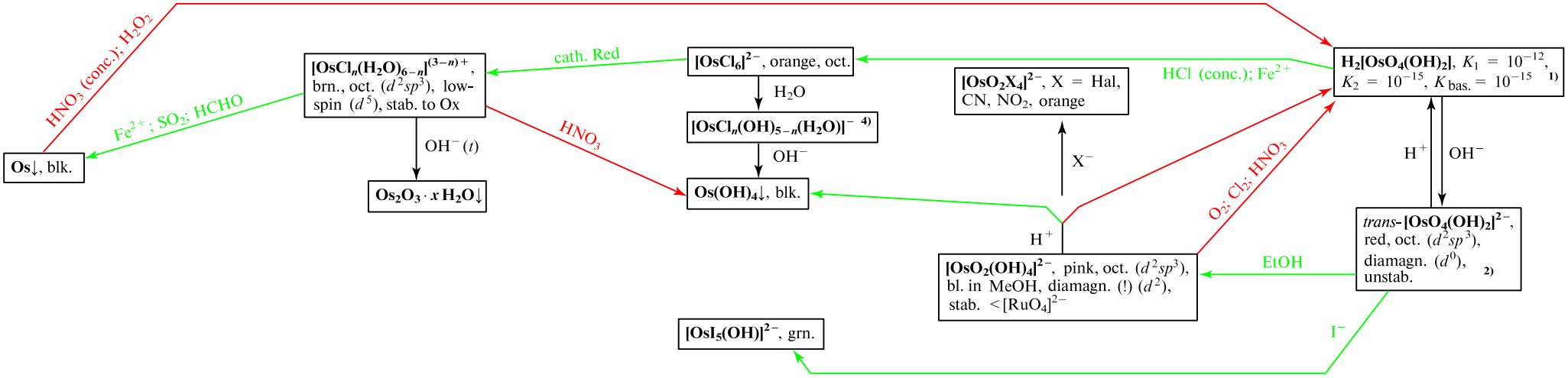
● Ni
● As


0
1+
2+
3+
6+
Fe
[Fe^I(NO)^+(H2O)5]^2+, brn., high-spin (d^7, 3 unpair el.), oct. (sp^3d^2) ion
NO
t (−NO↑)
[Fe(H2O)6]^2+, light-grn., high-spin (d^6), 4 unpair el., oct. ion (sp^3d^2)
Cu^2+; NO3^− (−NO); Cr2O7^2−; Cl2; MnO4^− (H^+); H2O2; H2SO4 (t)
Cu(I); Sn^2+; HI; H2SO3
[Fe(H2O)6]^3+, colrl., high-spin (d^5) oct. (sp^3d^2) ion, ex. by pH ≪ 7
[FeCl4(H2O)2]^−, oct. ion
Fe^3+
H^+
[FeCln(H2O)4−n]^(3−n)+, n = 1−3 (yel.), 4 (colrl.), tetrah. ions
Cl^−
H2O (−H^+)
H^+ (−H2↑)
H^+
H2O (Khydr = 10^−9)
[Fe(OH)(H2O)5]^+ 1)
H2O Khydr = 10^−3 (1) и 10^−4 (2)
[Fe(OH)(H2O)5]^2+ ⇄ [(H2O)4Fe(OH)2Fe(H2O)4]^4+ (?) 2)
orange-brn. ions oct. at. Fe
H^+
OH^−
Fe(OH)2↓, wh., SP = 10^−16
O2 (immed.)
FeO · n Fe2O3 · x H2O↓, dark-grn.
O2
[Fe2O3 · n H2O↓, brn.
ClO^−; NO3^−; K2O2(OH)^−
H2O (−O2)
[FeO4]^2−, red ion, tetrah., stab. at pH ⩾ 10, Ox. > MnO4^− (+ NH3 ⟶ N2)
OH^− (t, −H2↑)
H2O
OH^−
[Fe(OH)6]^4−, grn., oct. ion
[Fe(OH)4]^2−, Kstab = 10^9
[Fe(OH)6]^3−, colrl., oct. ion
[Fe(NH3)6]X2, ex. only in solid
[Fe(CN)5(H2O)]^2−
CN^−
H2O (−CN^−)
[Fe(CN)6]^4−, yel., low spin oct. ion, Kstab.(1−6) = 10^37, Kstab(1−5) = 10^19
Cl2; MnO4^− (H^+)
OH^−; H2O2; t (−O2)
[Fe(CN)6]^3−, yel.-grn., low-spin dist. oct. (Jahn-Teller effect), Kstab (1−6) = 10^44, but K1 ⩾ K2 − K6, strong Ox. by pH > 7 (+ W ⟶ WO4^2−), toxic
[Fe(NCS)]^2+, Kstab. = 10^2 3)


0
2+
3+
4+
[CoCl2(H2O)4] ⇄ [CoCl2(H2O)2] + 2H2O
oct. tetrah.
bl., mol. – nonelectrolytes
Cl^− (t)
H2O
[Co(H2O)6]^2+, pink, high-spin (d^7, 3 unpair el.), oct. (sp^3d^2) ion
O3; F2, an. Ox.
H2O (−O2); HCl
[Co(H2O)6]^3+, bl., diamagn. (d^6), oct. ion (d^2sp^3), strong Ox.
Co
H^+ (t); HNO3
cath. Red.
H^+
H2O (Khydr = 10^−6)
[Co(H2O)5(OH)]^+, bl., oct. ion
OH^−
CN^−
Co(OH)2↓, pink, SP = 10^−16
O2 (slow); H2O2; OCl^− (OH^−)
Co2O3 · n H2O↓, brn., s. in NH4OH
[Co(OH)4]^2−, dark bl., tetrah. ion
[Co(CN)5]^3−, grn. ion, tetr. pyram, v. strong Red.
H2O (−H2)
[Co(CN6]^3−, colrl. ion, oct.,v. stab.
IO6^5−
[Ni(H2O)6]^2+, bright grn., paramagn. (d^8, 2 upair el.), oct. ion (sp^3d^2)
[Ni(H2O)n]^3+ (?), pink ion
[NiIO6]^−, red ion
H^+ (t); HNO3
cath. Red.
Ni
HCl (−Cl2); H2SO4 (−O2)
H2O + HSO4^−
Ni(OH)2↓, grn. SP = 10^−17
an. Ox.; BrO3^−
Ni2O3 · n H2O↓, blk., v. strong Ox.
H2O (−O2)
NiO2 · n H2O↓, blk.
NH3
CN^−
S2O8^2−
[Ni(H2O)2(NH3)4]^2+, vlt., high-spin ion
[Ni(NH3)6]^2+, bl., high-spin (d^8, 2 unpair el.), oct. (sp^3d^2) ion, Kstab = 10^9
[Ni(CN)4]^2−, yel., diamagn. square (dsp^2) ion
CN^−
[Ni(CN)5(H2O)]^3−, red, oct. (sp^3d^2), high-spin ion, ex. only in s.

RUTHENIUM AND OSMIUM IONS IN AQUEOUS SOLUTIONS





RUTHENIUM

Ru^0 4d ↓↑ ↓↑ ↓ ↓ ↓ | 5s ↓ | 5p | 5d | EN 1.4

1+ (d^7) **2+ (d^6)** **3+ (d^5)**

Ru, met., silver-wh., hard, d = 12.6, m.p. 2607, b.p. 4900, non-corrosive, sol. in (HCl + O_2), (MOH + MNO_3), M_2O_2 (t); hex. cl. pack, a = 2.70, c = 4.28, Ru—Ru 2.67 ↑ Recristal. from Sn-melt. blk. amorph. powd., sol. in (H_2SO_4 + $MBrO_3$)

H_2; O_2 (t); $NaIO_4 + H_2SO_4 + NH_4^+$

0(d^8)

CO (180°, 2 · 10^7 Pa)

$Ru(CO)_5$, liq. colrl., m.p. −22, sol. in org. solv., mol. trig. bipyr. (dsp^3); $\triangle H$ = −1054 [4]

CO; RuS_2; $RuI_3 + Ag$

$H_2Ru(CO)(PR_3)_2$ [2]
$H_2Ru(N_2)(PPh_3)_3$
$H_2Ru(PPh_3)_4$

Ru(CO)Br

50°; $h\nu$ (vis)

CO + ROH (+R_3N)

$[Ru_3(CO)_{12}$, needles orange, $(CO)_4Ru(\mu)_2Ru(CO)_4$, $Ru(CO)_4$ subl. (dec.) 150, mol. — [1] triangle, Ru—Ru 2.85

150°

$Ru_3C(CO)_{12}$ [5]
$[Ru_5C(CO)_{15}]$, str. anal. of $[Fe_5C(CO)_{15}]$ [22]

M

$M_2[Ru_3(CO)_{11}]$
$MHRu_3(CO)_{11}$
$HRu_3(CO)_{10}(NO)$ [36]

$M_2Ru_4(CO)_{12}$ [2]
$M_6Ru_4(CO)_{11}$
$M_4Ru_4(CO)_{12}$
$M_2Ru_4(CO)_{13}$, tetrah. cluster $[Ru_4]$, Ru—Ru ~2.8

$h\nu$ (vis)

$[Ru(CO)_4]_\infty$, in str. — [1] chains of plane mol.

H_2

$Ru(CO)_4(PR_3)_3$ [2, 16]
$[Ru(CO)_n(PR_3)_{5-n}]$
$[Ru(O_2)(CO)_2(PR_3)_2]$
$[Ru_3(CO)_n(PR_3)_{12-n}]$

$M_6Ru_6(CO)_{16}$ [37]
$M_4Ru_6(CO)_{17}$
$MHRu_6(CO)_{18}$
$H_2Ru_6(CO)_{18}$, oct. cluster $[Ru_6]$, Ru—Ru 2.87

$[Ru(NO)_5]$, cr., red
$[Ru(NO)_2(PR_3)_2]$
$Ru(NO)^+Cl(PR_3)_2$ [1]

$M_2[Ru_{10}H_2(CO)_{25}]$
$M_3[Ru_{11}H(CO)_{27}]$

$[RuDipy_3]$ [1]

$Ru_6C^*(CO)_{17}$, [22]
$H_2Ru_6C(CO)_{16}$
$M_2[Ru_6C(CO)_{16}]$, cr. red, oct., cluster, Ru—Ru 2.90, Ru—C* 2.05, CN Ru 8

O_2(l)

$Ru(OH)_2$↓, brn. — H_2O (−H_2) → **$Ru(OH)_3 \cdot x\,H_2O$**↓, 100° ⟶ Ru + RuO_2 + H_2O; [32] + O_2 ⟶ $RuO_2 \cdot x\,H_2O$↓

OH⁻

$Ru(NO_3)_3 \cdot 6\,H_2O$, **$[Ru_3O(CH_3COO)_6]^+X^-$**, X = Cl, CH_3COO [17, 23]

$Ru(NO)^+(OH)_3 \cdot 2\,H_2O$↓, brn. [35]

HX ↓↑ OH⁻

$[Ru(NO)^+X_n(H_2O)_{5-n}]^{(n-3)-}$, X = Cl, NO_3, n = 0–5
$[Ru(NO)^+(NH_3)_5]Cl_3 \cdot H_2O$
$[Ru(NO)^+(NH_3)_4X]$
$[Ru(NO)^+(NH_3)_2Cl_3]$-*cis*
$[Ru(NO)^+Cl_3(PPh_3)_2]$
$K_2[Ru(NO)^+X_5]$, X = F–I, CN
$K_2[Ru(NO)^+Cl_{5-2n}(C_2O_4)_n]$
***trans*-$M_2[Ru(NO)^+(OH)(NO_2)_4]$**
$M_2[Ru(NO)^+F_5] \cdot H_2O$
red-orange, diamagn., oct., v. stab., gr. [Ru=N⁺=Ö] — linear, Ru—N 1.7–1.8, N—O 1.15, $\nu_{[N=O]^+}$ 1800–1935 см$^{-1}$

$RuCl_n$; RuO_2 — HCl + HNO_3; NO

$(NH_4)_2Ru(SO_4)_2 \cdot 6\,H_2O$ [23]
$Na_4[Ru(NH_3)_2(SO_3)_2(HSO_3)_2]$
$M_4[Ru(NO_2)_6]$, anion — oct. $[RuN_6]$ [19]

$[Ru(SO_4)(SO_2)^0(PR_3)_2]_2 \cdot PhMe$, mol. — oct.

$Ru_2(RCOO)_4$; **$[Ru(RCOO)_2(CO)(PR_3)_2]$** [23]

$RuCl_2$↓, brn., insol. in ac., alk., $CdCl_2$ str. type
· **2.5 PR_3** = $[Ru_2Cl_4(PR_3)_5]$, diamagn., mol. — 2 oct. $[RuP_3Cl_{3/2}]$
· **3 PPh_3** = $[RuCl_2(PPh_3)_3]$-*trans*, mol. — tetr. pyr. [6]
· **4 PPh_3** = $[RuCl_2(PR_3)_4]$, oct.
· **3 PEt_2Ph** = $[Ru_2Cl_3(PR_3)_6]^+[RuCl_3(PR_3)_3]^-$
$RuClH(PPh_3)_3$ — homogenous catalyst of hydrogenation
$RuCl_2(AsPh_3)_3$; + O_2 ⟶ $[RuCl_2(AsPh_3)_3(O_2)]$, m.p. 300 (dec.), paramagn., ν_{O-O} 880 cm^{-1}
$[Ru(CO)Cl_2(PR_3)_3]$
$Ru(CO)_2Hal_2$, Hal = Cl (yel.), Br (orange, subl. 220) I (orange, subl. 200)
$[Ru(CO)_3Cl_2]_2$ [39]
$[Ru(CO)_2Cl_2(PR_3)_2]$, *cis*- and *trans*-
$[Ru(CO)_2I_2Py_2]$, orange, diamagn.
$[Ru(CO)_3Br_2]_2$, mol. — 2 oct. $[Ru(CO)_3BrBr_{2/2}]$,
cis-**$[Ru(CO)_4I_2]$**

CO; PR_3; ROH; CO (250°)

$Cs_2[RuHal_4(O_2)]$ [15]

$(R_4N)_2(H_7O_3)_2[Ru_3Cl_{12}]$, [20] grn., anion — chain of 3 oct., with common faces
$K_2[Ru(CO)_2I_2(CN)_2]$
$Ru_2^{II,III}Cl_5(PBu_3)_4$, paramagn. (1 unpair el.), mol. — 2 oct. with common face

Ru; Hal_2; I_2 (200°); RuF_5; RuO_4; HI

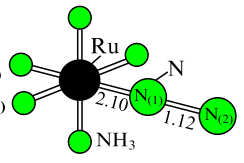
	ΔH
RuF_3↓, brn., hyg., ReO_3 str. type	—
$RuCl_3$, α-, brn., insol. in H_2O, alc., $FeCl_3$ str. type ↑ 450° (Cl_2)	−204
β-, brn., sol. in alc., Ox in air, chains of oct. with common edges · **H_2O**	—
$RuBr_3$, dark grn., chains of oct. $[RuBr_{6/2}]$	−180
RuI_3↓, blk., dec. 300	−158

$Ru(BF_4)_2 \cdot 6\,H_2O$ —N_2 (10^5 Pa)→ **$\{[(H_2O)_5Ru]_2N_2\}(BF_4)_4$** [13]
RuS_2, $RuSe_2$, $RuTe_2$

K_2RuO_4; KCN + H_2O (100°)

$H_4[Ru(CN)_6]$
$M_4[Ru(CN)_6] \cdot n\,H_2O$
$Fe_4^{III}[Ru(CN)_6]_3$, semicond. [12]

$[Ru(NH_3)_6]Cl_2$, orange
$[RuDipy_3]Cl_2$, red, inert
$[Ru(NH_3)_5(N_2)]X_2$, X = Cl–I, BF_4 [7]
$[(NH_3)_5Ru—(N=N)—Ru(NH_3)_5]BF_4$ [3]
trans-**$[Ru(NH_3)_4(L_2)]Cl_2$**, L = N_2, O_2 [15]
trans-**$[Ru(NH_3)_4(:SO_2)^0L]X_n$** L = H_2O
↓↑ $H_2O(-H^+)$
$[Ru(NH_3)_4(HSO_3)(H_2O)]^+$ ⇄ (H^+) *trans*-**$[Ru(NH_3)_4(SO_3)(H_2O)]$** [18]



NO + HCl; N_2H_4; Mg; [H↑]; $RNHNH_2$

$[Ru(NH_3)_6]Hal_3$ } colrl.
$[Ru(NH_3)_5X]Hal_n$, } or yel.
$[Ru(NH_3)_4Hal_2]Hal$
$[Ru(NH_3)_3Hal_3]$
$[Ru(Dipy)_3]X_3$
$[Ru(Dipy)_2Cl_2]Cl$
$[RuHal_3(PR_3)_3]$ [23]

NaHSO₃

$[Ru_3^{II,III}O(CH_3COO)_6(H_2O)_3]_n$
$[Ru_2(RCOO)_4]^+Hal^-$, paramagn., chains of dimer mol., μ-Hal [17]
$[(NH_3)_5Ru^{III}(S_2)^-Ru^{II}(NH_3)_5]X_4$ [33]
$[(NH_3)_5Ru^{III}—L—Ru^{II}(NH_3)_5]X_5$

$[RuPR_3)_2(O_2)^0(NO)X_2]$, X = Cl, OH, CN, NCS, cath. Ox PR_3 [14]

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$Ru(OH)_3$, $RuCl_3$, RuS_2 —O_2→ **RuO_2**, powd. blk., non volat., insol. in ac., alc. —1300°→ $Ru + RuO_4$; ↓ 960° (vac.); cr., bl., d = 6.97, $\Delta H = -302$, rutile str. type, Ru—O 1.94–1.98

$(NH_4)_2RuO_4$ —t→ **RuO_2**

RuO_2 —$-O_2$, exp. (108°, $h\nu$-vis)→ **RuO_4**, cr., toxic, with O_3 odor, stab. > 1000°, $\Delta H = -239$, readily sol. in H_2O, CCl_4, exp. with org. subst. (kept adsorb. on Al_2O_3), dimagn., α-, yel., m.p. 25, subl. 27, d = 3.29; 35°(p) ↓↑ 40° [26]; β-, brn., m.p. 27, subl., tetrah.

RuO_2 —$Na_2RuO_4 + Ru$, K_2O→ (3.75–3.97)+ **$Na_{3-x}Ru_4O_9$**, $0 \leqslant x \leqslant 0.9$, "bronze", cr. with bl. met. lustrous, in str. — frame of oct. $[RuO_6]$, Ru—Ru 2.83; **KRu_4O_8**, blk., dec. 1100, insol. in aq. regia [11]

RuO_2 —$Na_2CO_3(t)$→ **$Na_{14}Ru_7O_{24+x}$**, blk., in str. — clusters $[Ru_7O_{24}]^{13-}$ [27]

RuO_2 —Na_2O_2 (O_2, t)→ **Ruthenates (V)** [8] **Na_3RuO_4**, powd. bl., sol. in H_2O, anion — 4 oct. with common edges **$Na_4Ru_2O_7$**, column of oct. with common faces **$Sr_4Ru_2O_9$**

$RuO_2 \cdot x\,H_2O$↓, blk., sol. in ac.

—H_2O, HCl (+ Cl_2)→ **RuF_4**, yel., hyg. + SiO_2 —>280°→ SiF_4 **"$Ru(OH)Cl_3$"**, red- brn. (contain $RuCl_3$, $[Ru_n^{III,IV}(OH)_m(H_2O)_xCl_y]$) ↑ H_2O **$RuCl_4 \cdot 5\,H_2O$**, red, hyg., dec. 100

Ruthenates (IV) **M_2RuO_3**, chains of oct. $[RuO_{6/2}]$ **Na_4RuO_4** **$Na_2Ru_4O_9$** **$Na_4Ru_3O_8$** [27]

$K_2[Ru(C_2O_4)_3]$, blk.

$K_4[(Cl_5Ru)_2O] \cdot H_2O$, brn., diamagn. ∠RuORu 180 **$Cs_4[Ru_2OBr_{10}]$**

$Cs_2[Ru_2(SO_4)_4(H_2O)_2]$ [32] **$M^{II}[Ru_2O(OCOCH_3)_6(H_2O)_3]$** **$K_3[Ru(C_2O_4)_3] \cdot 4.5\,H_2O$** **$H[Ru(C_2O_4)_2] \cdot 2.5\,H_2O$**, grn., anion — oct. [31]

$K_3[RuF_6]$ [28] **$M_4[RuCl_7]$**, **$M_3[RuCl_6]$** **$M_2[RuCl_5]$** ***cis*-$M_2[RuCl_4(H_2O)_2] \cdot H_2O$** **$M_2[RuCl_5(H_2O)]$**, dark red **$M_2[RuBr_5(H_2O)]$**; **$M_3Ru_2Br_9$**

EtOH

$M_2[RuF_6]$, yel. or pink (M = Ba/2, bl.), low-spin anion **$M_2[RuCl_6]$**, red-brn., s.-yel. **$M_3[RuCl_7]$** CN Ru 7 **$M_2[RuBr_6]$**, blk.

RuF_5, brn., hyg. > P_2O_5, m.p. 86, b.p. 227 (subl.), $\Delta H = -891$, sol. in BrF_3, in gas — cycles trimer, in str. — tetramer [21]

$K[RuF_6]$, bl. or pink ↑ $KF(t)$ **$[BrF_2]^+[RuF_6]^-$**, oct. (d^2sp^3), paramagn. (d^3) **$M[RuF_6]$**, M = $[O_2]$, $[H_3O]$, [KrF], $[ClF_2]$, Ru—F ~1.84 **[KrF][Ru_2F_{11}]** [9]

120°

RuF_6, red-brn., m.p. 54, —$h\nu$-vis→ $RuF_5 + F_2$; + H_2O → RuO_4 + + RuO_2 + O_2 + … [38]

$[R_4(C_5H_5)_2I]I_3$ [10]

M_2RuF_8 (?), cr. colrl.

RuF_8 (?) [24]

$[Ph_4As][RuNCl_4]$, anion — tetr. pyr., Ru≡N 1.57, Ru—Cl 2.31, ∠NRuCl 104.6, ∠ClRuCl 86.4 and 150.8 **$Cs_2[NRuHal_5]$**, Hal = Cl, Br [15]

RuO_4 —Ru, O_2 (700°); O_3 (20°); NO_2, H_2→ **Perrutenates** **$K[RuO_4]$** **$Na[RuO_4] \cdot H_2O$**, blk. (s. — grn.), poorly sol. in H_2O; —200°→ $O_2 + K_2RuO_4$ anion — tetrah.

RuO_4 —MOCl, $KMnO_4$, MOH(—O_2)→ **Perrutenates**

Ruthenates (VI) [25] **$M_2[RuO_3(OH)_2]$**, grn. (red in thin layers, orange — in s.), anion trig. bipyr. or tetrah.

Perrutenates —OCl^-→ **Ruthenates (VI)**; —200°→ **Perrutenates**

$RuO_4 \cdot NH_3$, dec. −20° **$RuO_4 \cdot 2\,Py$**, stab. at 20° ***n*$RuO_4 \cdot PF_3$**, n = 1, 2 **$RuO_4 \cdot 2\,NO$**

RuO_4 —HCl→ **$H_2[RuO_2Cl_4] \cdot 3\,H_2O$** **$M_2[RuO_2Cl_4]$**, M = Rb, Cs, purp., + H_2O → RuO_4 + RuO_2

RuO_4 —MNO_3; $KMnO_4$ + MOH (t)→ **Ruthenates (VI)**

$RuO(SO_4)_2$, brn. dec. 150; + H_2O → RuO_2 + …

***trans*-$M_6[RuO_2(HIO_6)_2]$**, anion oct., Ru=O 1.73, Ru—O 2.01 **$M_6[RuO_2(H_2TeO_6)_2]$** [30]

RuO_4 —$Cl_2(H_2O)$ + HCl→ **$H_2[RuO_2Cl_4] \cdot 3\,H_2O$**

RuO_4 —$BrF_3 + SiO_2$ (20°)→ **$RuOF_4$**, cr., colrl., m.p. 115 [38]

RuO_4 —F_2 (—700°→ −196°); TbF_4 (t)→ **RuF_6**

RuO_4 —$HCl + Cl_2(H_2O)$, $KClO_3 + KCl$ (t), F_2 (300°)→ **RuF_4**

RuO_4 —BrF_3 (20°)→ **$K[RuF_6]$**

RuO_4 —I (—Kr)→ **RuF_6**

RuO_4 —KCl + F_2 (300°)→ RuCl₃

RuF_5 —I_2 (—IF_5)→ **RuF_4**

RuF_4 —NH_3→ **$K_3[Ru_2NCl_8(H_2O)_2]$**, anion — oct. *trans*-$[RuCl_4(H_2O)N_{1/2}]$

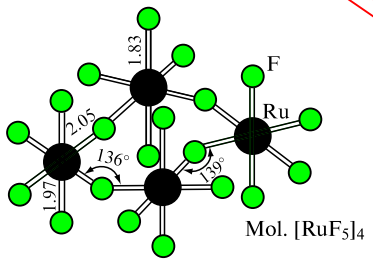
$RuCl_3$ —$NH_4Cl + NH_3$ (t)→ **$(R_4N)_3[Ru(—NCS)_6]$** **$K_3[Ru(NCS)_n(—SCN)_{6-n}]$** n = 1–4 [29]

$[(NH_3)_5Ru^{IV}—O—Ru^{III}(NH_3)_4—O—Ru^{IV}(NH_3)_5]X_7$, X = NO_3, $SO_4/2$, cr., brn., paramagn. (1 unpair. el., in cation — linear gr. $[Ru_3O_2]$ **$\{[(Dipy)_2(OH)Ru^{III,IV}]_2O\}X_3$** [34]

$[(NH_3)_5Ru^{III}—O—Ru^{IV}(NH_3)_4—O—Ru^{III}(NH_3)_5]Cl_6 \cdot 3\,H_2O$, "rutenic red" (paint), diamagn., 150° → H_2O, sol. in NH_4OH

$\{[(NH_3)_5Ru^{III}]_2(\mu\text{-}O)\}X_4$ —Br_2→ **$\{[(NH_3)_5Ru^{III,IV}]_2(\mu\text{-}O)\}X_5$** [34]

an. Ox → **$[(Dipy)_2(O)Ru^{IV}—O—Ru^{V}(O)(Dipy)_2]X_3$** [34]



Mol. $[RuF_5]_4$

OSMIUM

Os^0 5d ↑↓ ↓ ↓ ↓ ↓ | 6s ↑↓ | 6p | 6d | EN 1.5

Os, met., wh.-bl., hard, brittle, the most heavy, d = 22.6, m.p. 3027, b.p. ~5000, Ox in air, sol. in HNO_3, hex. cl. pack., a = 2.73, c = 4.32, Os—Os 2.70

O_2 (20°) → **OsO**, blk., s. in ac.

O_2; NO (defic.) → **OsO_2**, blk.-brn., $\xrightarrow{>500°}$ Os + OsO_4; ΔH = −260, pyrophoric (⟶ OsO_4,), sol. in ac., rutile str. type

H_2

↑ $-H_2O$ (N_2)

$Os(OH)_4$↓, blk.

$Os_2O_3 \cdot x\,H_2O$↓

Osmates (IV), $M^{II}[Os(OH)_6]$, $M^{II}OsO_3$, M = Ca–Ba, Pb, $CaTiO_3$ str. type
$\xrightarrow[(N_2)]{t}$ MO + Os + O_2 [6]

$K_8[Os_2O_2(SO_4)_6]$, diamagn., Os—Os 2.45 [33]
$M_8[Os(SO_3)_6]$, colrl.
$M_6[Os(SO_3)_5(H_2O)]$, colrl.
$M_6[Os(SO_3)_4X_2]$, X = Cl (yel.), OH (vlt.)
$M_4[(Hal_5Os)_2O] \cdot H_2O$, Hal = Cl, Br [33]
$(NH_4)_2[Os(OH)Cl_5]$, brn.

KNO_2 (surp.)

$Os(SO_3F)_3$, grn. α-, β-, m.p. 30, 140
$[OsCl(CH_3COO)_2]_2$ [28]

$M_4[Os(SO_3)_3]$
$M_2[Os(NO)^+(OH)(NO_2)_4]$
$K_2[Os(NO)^+F_5] \cdot H_2O$
$(NO)_2[Os(NO)^+Cl_5]$
$(PR_4)[Os(NO)^+Cl_4]$

$OsSO_3$↓
$[Os(RCOO)_2(CO)(PR_3)_2]$ [17]

$[Os_2(CO)_8Hal_2]$
$Os_2(CO)_6(\mu\text{-}I)_2$

***cis*-$[Os(NO)(NH_3)_2 \times$**
$\times Br_2(OH)]$ [29]

OsO_4

CO (p, t) → **$Os(CO)_5$**, liq. colrl., m.p. −15, mol. — trig. bipyr., ΔH = −1033 [5]

$H_2Os(CO)_4$, cr. colrl., m.p. 149
$Na_2Os(CO)_4$, stab. in air [1]
$H_2Os(CO)(PR_3)_3$

$H_2Os_2(CO)_8$, oil, colrl. [1]

$Os_2(CO)_9$, cr. orange, m.p. 64, dec. 20, triangle $[Os_2(CO)]$

hν-UV(−40°)

$H_2Os_3(CO)_{10}$, **$\cdot L$** [2]
$H_2Os_3(CO)_{12}$
$M_2Os_3(CO)_{11}$

K; H_2

$Os_3(CO)_{12}$, cr. yel., m.p. 224, subl. 130, mol. — cluster $[Os_3]$
$Os_3(CO)_{11}$ Py

$Os_3(CO)_{12}Hal_2$

$H_4Os_4(CO)_{12}$ [2,18]
$M_2H_2Os_4(CO)_{12}$
$MHOs_4(CO)_{13}$, anion tetrah. cluster

H_2

200°

$Os_5(CO)_n$, cr. pink, n = 16–19

CO (t, p)

$M_2[Os_5(CO)_{14}C]$
$Os_5(CO)_{15}C_4$ [16]
$[Os_5(CO)_{15}C]$
$Os_6(\mu_3\text{-}O)(CO)_{19}$ [4]

$H_2Os_5(CO)_{15}$
$M_2[Os_5(CO)_{15}]$, anion trig. bipyr.

KOH + MeOH

$Os_6(CO)_{18}$, cr. brn., mol. — twocap. tetrah. $[Os_6]$
$Os_6(CO)_{20}$ [4]

$H_2Os_6(CO)_{18}$
$M_2[Os_6(CO)_{18}]$
oct. cluster [30]

RCN

$Os_7(CO)_{21}$, cr. orange, $[Os_7]$ – singl-cap. oct., all CO — term.
$Os_8(CO)_{23}$, orange [3]

$M_2Os_7(CO)_{20}$
$M_2Os_8(CO)_{22}$ [31]

$M_2[Os_{10}C(CO)_{24}]$, fourcap. oct.

$Os(CO)_2(PR_3)_3$
$[Os(CO)_3(PPh_3)_2]$
O_2↓
$Os(CO)_2(PR_3)_2(O_2)$ [5]
***cis*-$[Os(PR_3)_3H(CO)Hal]$**
$Os(PF_3)_5$
$[Os(NH_3)_6]$
$[Os(NH_3)_5(C_6H_6)]$ [5]
$[OsDipy_3]$

$OsFBr$ $\xrightarrow{20°}$
$OsF_2 + OsBr_2$ [8]
$OsCl_2$↓, brn., s. in alc., Et_2O; $CdCl_2$ str. type
$OsBr_2$
OsI_2 (?), blk.

$M_2[OsHal_4(CO)_2]$
$M[OsCl_3(CO)_3]$

560° (−$OsCl_4$↑)

Os (surp.)

Cl_2 (< 500°)

$OsCl_3$, brn., subl. 350, sol. in H_2O, alc., **$\cdot 3\,H_2O$**, grn.
OsI_3 $\xrightarrow{325°}$ [28] Os + I_2

$M[Os(NO)^+F_5]$ [33]

$(NH_4)_2[OsCl_5]$
$K_3[OsCl_6] \cdot 3\,H_2O$
red
$Cs_3Os_2Br_9$
$M_3[OsBr_6]$
$M_2[Os_2Br_8]$, Os ≡ Os in anion
$M_2[Os_4I_{14}]$, 2 gr. $[Os_2I_8]$ with common edge

Os_2OCl_6
Os_2OBr_6

Br_2 (330°)

OsF_4, yel. m.p. 230, subl., **$\cdot 2\,PF_3$**
$OsCl_4$, needle, subl. 650, sol. in ac.-Ox, $\xrightarrow{t}$ $OsCl_3$
$OsBr_4$↓, blk. chain of oct. $\xrightarrow{t}$ $OsBr_{4-n}$ [27]

$M_2[OsF_6]$, colrl., not hydr.
$M_2[OsCl_6]$, M = H, Na (· 2 H_2O), K↓, NH_4↓, orange or brn., (s. — orange or grn.), low-spin., oct., $K_2[PtCl_6]$ str. type
$(R_4N)_2[Os_2Cl_{10}]$, anion — 2 oct. sharing a edge [24]
$M_2[OsBr_6]$, M = H, K, brn. (s. — purp.)
$H_2[OsI_6] \cdot 2\,H_2O$; **$M_2[OsI_6]$**, blk., $\xrightarrow{t}$ $OsI_3 + I_2 + H_2O$

Nitrogenyl compl. [12]
$[Os(NH_3)_5(N_2)]Hal_2$, yel., diamagn., stab. to Ox, gr. [Os—N≡N] linear
↓ HNO_2
***cis*-$[Os(NH_3)_4(N_2)_2]Hal_2$**
$[Os(NH_3)_4(N_2)Hal]Hal$
$[Os(PR_3)_3(N_2)Hal_2]$, colrl.

$[OsDipy_3]Cl_2 \cdot n\,H_2O$
$Os(CO)_nHal_2$ [34]

CO (220°)

$H_4[Os(CN)_6]$
$K_4[Os(CN)_6] \cdot 3\,H_2O$, colrl., diamagn.
$Fe_4^{III}[Os(CN)_6]_3$, semiconduct. [11]

KCN

M_2OsO_4

H_2S

OsS_2↓, $OsSe_2$, $OsTe_2$, blk., FeS_2, str. type

***mer*-$[OsCl_3Py_3]$**
$[OsDipy_3]Cl_3$
$[Os(NH_3)_6]Hal_3$, colrl.
$[Os(NH_3)_5Br]Br_2$, pink
$[Os(NH_3)_3(PR_3)_2Cl_3]$

$Os(CO)_2Br_3$
$[Os(PR_3)Hal_3]$

K[$OsNCl_5$]

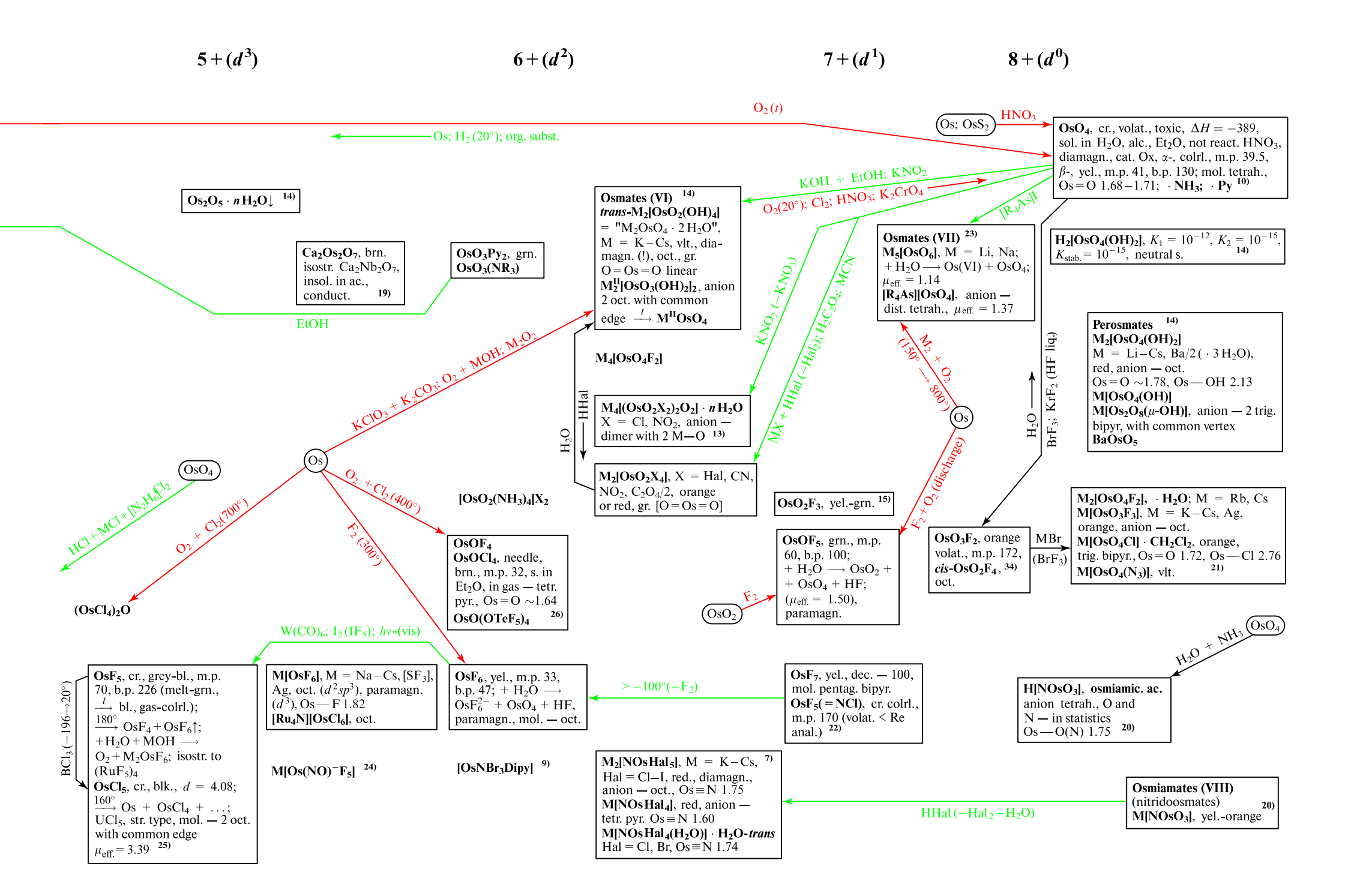
$SnCl_2$

$M_2[Os(NH_3)Cl_5]$

$K_2[Os(CO)Cl_5] \cdot H_2O$ [11]

$[R_4As]_2[OsCl_5(NCS)]$
$[R_4As]_2[OsCl_5(SCN)]$,
$[R_4As]_2[OsCl_2(NCS)_2(SCN)_2]$
$[R_4As]_2[OsICl_3(NCS)_2]$ [35]

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_39, © Springer-Verlag Berlin Heidelberg 2011


5 + (d^3)
6 + (d^2)
7 + (d^1)
8 + (d^0)
O_2 (t)
Os; OsS_2
HNO_3
OsO_4, cr., volat., toxic, $\Delta H = -389$, sol. in H_2O, alc., Et_2O, not react. HNO_3, diamagn., cat. Ox, α-, colrl., m.p. 39.5, β-, yel., m.p. 41, b.p. 130; mol. tetrah., Os = O 1.68–1.71; · NH_3; · Py [10]
Os; H_2 (20°); org. subst.
KOH + EtOH; KNO_2
O_2(20°); Cl_2; HNO_3; K_2CrO_4
[R_4As]
$Os_2O_5 \cdot n H_2O\downarrow$ [14]
Osmates (VI) [14]
trans-$M_2^{II}[OsO_2(OH)_4]$ = "$M_2OsO_4 \cdot 2H_2O$", M = K–Cs, vlt., diamagn. (!), oct., gr. O = Os = O linear
$M_2^{II}[OsO_3(OH)_2]_2$, anion 2 oct. with common edge $\xrightarrow{t}$ $M^{II}OsO_4$
Osmates (VII) [23]
$M_5[OsO_6]$, M = Li, Na; $+H_2O \longrightarrow$ Os(VI) + OsO_4; $\mu_{eff.} = 1.14$
$[R_4As][OsO_4]$, anion — dist. tetrah., $\mu_{eff.} = 1.37$
$H_2[OsO_4(OH)_2]$, $K_1 = 10^{-12}$, $K_2 = 10^{-15}$, $K_{stab.} = 10^{-15}$, neutral s. [14]
$Ca_2Os_2O_7$, brn. isostr. $Ca_2Nb_2O_7$, insol. in ac., conduct. [19]
OsO_3Py_2, grn. $OsO_3(NR_3)$
EtOH
KNO_2 (–KNO_3)
$MX + HHal$ (–$HHal_2$); $H_2C_2O_4$; MCN
M_2 + O_2 (150° → 800°)
BrF_3; KrF_2 (HF liq.)
Perosmates [14]
$M_2[OsO_4(OH)_2]$
M = Li–Cs, Ba/2 (· $3H_2O$), red, anion — oct.
Os = O ~1.78, Os — OH 2.13
$M[OsO_4(OH)]$
$M[Os_2O_8(\mu\text{-}OH)]$, anion — 2 trig. bipyr, with common vertex
$BaOsO_5$
$KClO_3 + K_2CO_3$; O_2 + MOH; M_2O_2
$M_4[OsO_4F_2]$
H_2O — HHal
$M_4[(OsO_2X_2)_2O_2] \cdot n H_2O$
X = Cl, NO_2, anion — dimer with 2 M—O [13]
$M_2[OsO_2X_4]$, X = Hal, CN, NO_2, $C_2O_4/2$, orange or red, gr. [O = Os = O]
H_2O — HHal
Os
OsO_4
$HCl + MCl + [N_2H_6]Cl_2$
$O_2 + Cl_2$(700°)
$O_2 + Cl_2$ (400°)
F_2 (300°)
$[OsO_2(NH_3)_4]X_2$
OsO_2F_3, yel.-grn. [15]
$F_2 + O_2$ (discharge)
OsO_3F_2, orange volat., m.p. 172, cis-OsO_2F_4, [34] oct.
MBr
(BrF_3)
$M_2[OsO_4F_2]$, · H_2O; M = Rb, Cs
$M[OsO_3F_3]$, M = K–Cs, Ag, orange, anion — oct.
$M[OsO_4Cl] \cdot CH_2Cl_2$, orange, trig. bipyr., Os = O 1.72, Os — Cl 2.76
$M[OsO_4(N_3)]$, vlt. [21]
OsF_4
$OsOCl_4$, needle, brn., m.p. 32, s. in Et_2O, in gas — tetr. pyr., Os = O ~1.64
$OsO(OTeF_5)_4$ [26]
OsO_5, grn., m.p. 60, b.p. 100; + $H_2O \longrightarrow$ OsO_2 + + OsO_4 + HF; ($\mu_{eff.} = 1.50$), paramagn.
F_2
OsO_2
$(OsCl_4)_2O$
$W(CO)_6$; $I_2(IF_5)$; hv-(vis)
OsF_5, cr., grey-bl., m.p. 70, b.p. 226 (melt-grn., $\xrightarrow{t}$ bl., gas-colrl.); $\xrightarrow{180°}$ $OsF_4 + OsF_6\uparrow$; $+H_2O + MOH \longrightarrow$ $O_2 + M_2OsF_6$; isostr. to $(RuF_5)_4$
$OsCl_5$, cr., blk., d = 4.08; $\xrightarrow{160°}$ Os + $OsCl_4$ + …; UCl_5, str. type, mol. — 2 oct. with common edge
$\mu_{eff.} = 3.39$ [25]
BCl_3 (–196→20°)
$M[OsF_6]$, M = Na–Cs, [SF_3], Ag, oct. (d^2sp^3), paramagn. (d^3), Os — F 1.82
$[Ru_4N][OsCl_6]$, oct.
OsF_6, yel., m.p. 33, b.p. 47; + $H_2O \longrightarrow$ OsF_6^{2-} + OsO_4 + HF, paramagn., mol. — oct.
> –100° (–F_2)
OsF_7, yel., dec. — 100, mol. pentag. bipyr.
OsF_5(=NCl), cr. colrl., m.p. 170 (volat. < Re anal.) [22]
$H_2O + NH_3$
OsO_4
H[$NOsO_3$], osmiamic. ac. anion tetrah., O and N — in statistics
Os — O(N) 1.75 [20]
$M[Os(NO)^-F_5]$ [24]
[$OsNBr_3Dipy$] [9]
$M_2[NOsHal_5]$, M = K–Cs, Hal = Cl–I, red., diamagn., anion — oct., Os≡N 1.75
$M[NOsHal_4]$, red, anion — tetr. pyr. Os≡N 1.60
$M[NOsHal_4(H_2O)] \cdot H_2O$-trans Hal = Cl, Br, Os≡N 1.74
HHal (–Hal_2 –H_2O)
Osmiamates (VIII) (nitridoosmates) [20]
$M[NOsO_3]$, yel.-orange

RHODIUM

Rh^0 4d ↑↓ ↑↓ ↑↓ ↓ ↓ | 5s ↓ | 5p | 5d

EN 1.5

1 + (d^8) **2 + (d^7)**

O_2 (800°)

Rh_2SO_4 [19], $\cdot n H_2O$, n = 4, 12, 15

> 1100°; H_2

$Rh(OH)_2$↓ bl., strong Red

$M_4[Sn(OH)_6]$

$[Rh(NH_3)_3Cl_3]$; $[Rh(NH_3)_5Cl]Cl_2$

t

Rh, met. wh., ductile, d = 12.44, m.p. 1963, b.p. ~3700, corrosion-resist. > Pt, slow dissolv. in conc. H_2SO_4, (HBr + NaClO) (*t*), insol. in aq. regia; paramagn. Cub. cl. pack., a = 3.79, Rh—Rh 2.68

↓ pulverizing

Rh black, sol. in ac.- Ox, most act. hydrogenation cat.

> 964°

$[Rh(NH_3)(PPh_3)_3]ClO_4$
$[RhX(PPh_3)_3]$, X = Cl, NO_3 [29]
$[RhDipy_2]X$, X = NO_3 (paramagn. monomer), ClO_4 (diamagn. dimer)

RhCl

958° ($p\ Cl_2 = 10^5$ Pa)

$RhCl_3$

H_2 + CO (*t*, *p*)

M[Rh(CO)$_4$]
HRh(CO)$_4$, cr., light yel., m.p. −10 (dec.), tetrah.
M[Rh_5(CO)$_{15}$], trig. bipyr. [1]
M[Rh_6(CO)$_{15}$]
$M_2[Rh_6(CO)_{15}]$
$M_4[Rh_6(CO)_{14}]$ [2]
$[Me_4N]_3[Rh_7(CO)_{16}]$, cluster $[Rh_7]$ – single-cap oct.
$M_3Rh_9(CO)_{13}$ [8]
$M_3[Rh_{11}(CO)_{23}]$ [8]
$M_2[Rh_{12}(CO)_{30}]$
↓ t
$M_2[H_3Rh_{13}(CO)_{24}]$
$M_4[Rh_{14}(CO)_n]$, n = 25, 26
$M_3[Rh_{15}(CO)_{27}]$
$M_3[Rh_{17}(CO)_{30}]$
$[R_4N]_4[Rh_{22}(CO)_{37}]$ [2, 23]

M[Rh(CO)$_4$]

KOH

0 (d^9) CO

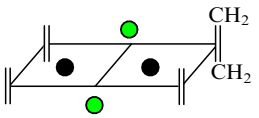
$Rh_2(CO)_8$, cr. orange, hyg., m.p. 76 (dec.) [12]
↓ t
$Rh_4(CO)_{12}$, cr., red, dec. 150, does not react with H_2O [12]

$Rh_6(CO)_{16}$ (previously "$Rh_4(CO)_{11}$"), cr. blk., dec. 220, does not react with H_2O, sol. in org. solv.; mol. – oct. cluster $[Rh_6]$ (Rh–Rh 2.78), cat. for P–C bond cleavage in PR_3 (⟶ RCHO + RCH_2OH) [2]

t ⟶ CO (Ag)

L ($p = 10^5$ Pa)

$[RhX(CO)_2]_2$, X = Hal, NO_3, SCN, $SO_4/2$, RCOO, C_5H_5, cr., Hal = Cl (orange, m.p. 123); Br (brn., 118); I (ruby red, 114), sol. in org. solv., diamagn., mol. – 2 squares with common Hal—Hal side, Rh—Rh 3.12
$[RhCl(CO)L_2]$, L = Py, PR_3, AsR_3, mol. – square (dsp^2), hydrogen. ation cat.
$[RhCl(CO)L]_2$, L = C_2H_4, PR_3, CO [9]
$[RhX(CO)(PR_3)_2]$, X = OH, HCO_3, reversible adds CO_2 [15]
$[RhCl(CS)(PPh_3)_2]$, square [14]
$[RhCl(NO)(AsR_3)_2]$
$[RHal(NO)_2]_n$↓, Hal = Cl, Br, I, cr., dark brn.
$[RhHal_2(NO)(PR_3)_2]$
$RhHal(PR_3)_2$, cr. red
$[RhCl(PR_3)_3]$, cr. red, hydrogenation cat. of C≡C and C=C bonds aldehyde synthesis from C_nH_{2n}, H_2 and CO
$[RhCl(CH_2=CH_2)_2]_2$



RCHO + PR_3

EtOH + PR_3

CO (*t*)

$M_2[Rh_2Hal_4(CO)_2]$, ex. in H_2O s. [13]
$H[RhCl_2(CO)(PR_3)]$
$[R_4N][RhHal_2(CO)_2]$-*cis*, cr., yel., diamagn., square

$[Rh_2(\mu\text{-}SO_4)_2Py_6] \cdot n H_2O$
$[Rh_2(\mu\text{-}H_2PO_4)_4(H_2O)_2]$, Rh—Rh 2.5–2.6 [17]
$[Rh(NO_3)(PPh_3)_3]ClO_4$ [29]
$[Rh(RCOO)_2]_2$ cr. grn., diamagn., isostr. to Cu^{II} and Cr^{II} acetates, cluster, Rh CN 5
$[Rh(CH_3COO)_2L]_2$, L = H_2O, ROH, PR_3, NH_3, Py, cr. grn. or bl., diamagn. cluster, isostruct. to $[Cu(CH_3COO)_2L]_2$

$M_4[Rh_2(SO_4)_4(H_2O)_2] \cdot n H_2O$, M = Na–Cs, $[H_3O]$, grn.,
$Na_2[Rh(SO_3)_2] \cdot 2H_2O$
$M_4[Rh_2(CO_3)_4] \cdot n H_2O$, M = Na, K ($n$ = 2.5), Cs (n = 6.3; 7.5); NH_4 (n = 4.5), Ba/2, diamagn. clusters [16]

$M_2[Rh_2(CH_3COO)_4Hal_2]$, Hal = Cl, Br, Rh—Rh 2.47, Rh—O 2.07, Rh—Hal 2.06 (Cl), 2.53 (Br) [27]

2.5 +
$[Rh_2(CH_3COO)_5]$
$[Rh_2(CH_3COO)_4Cl]$ [22]

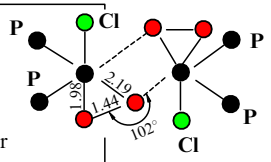
$Rh_2OCl_2(CO)_3$, red, m.p. 125

$RhCl_2$, cr., red, ΔH = −163, Ox in air, $CdCl_2$ str. type

$[RhCl_2(CO)(PR_3)]$, cr., yel. [5]

$[RhPy_6]Hal_2$, Hal = Cl–I, cr. yel.
$[RhPy_5Hal]Hal$, Hal = Cl–I, cr. yel.
$[RhDipy_2ClX]_2$, X = NO_3, ClO_4, cr. red.-vlt., diamagn.
$[Rh(AsR_3)_4Hal_2]$; **$[Rh(AsR_3)_3Hal_2]_2$**

Dioxygen compl.
$[RhCl(PPh_3)_2(O_2)]_2$, O_2 attached reversible
***trans*-$RhCl[P(C_6H_{11})_3]_2L$**, L = O_2 (bl.), N_2, P_4, H_2, CO, C_2H_4 (yel., diamagn.) [4]
$RhHal(PPh_3)_2(RNC)(O_2)$, diamagn., O_2 attached reversible (R = *n*-$CH_3C_6H_4$) or irreversible (R = *tert*-Bu) [10]
$\{Rh(O_2)[(Ph_2PCH_2—)_2]_2\}^+[PF_6]^-$, isostruct. to Ir complex, Rh—O 2.02, O—O 1.42; O_2 attached reversible



$M_2[HRh(CN)_4(H_2O)]$

$[Rh_3(CO)_n(PR_3)_3]$, n = 5, 7 [12]
$Rh_4(CO)_n(PR_3)_{12-n}$

$[Rh_2(PPh_3)_8]$, cr., light grn., diamagn.
$[Rh_2(PF_3)_8]$, cr., orange, m. p. 93

Na[Rh(CO)$_2$(PPh$_3$)$_2$] [1]
HRh(CO)(PR$_3$)$_3$

HRh(PR$_3$)$_4$; **H$_2$RhCl(PR$_3$)$_2$**
Rh(NO)$^+$(PPh$_3$)$_3$
[HRh(N$_2$)(PR$_3$)$_2$] [1]

HRh(PF$_3$)$_4$, liq. colrl., m.p. −40, b.p. 90 (dec.), tetrah., **· 0.5 C$_6$H$_6$**
K[Rh(PF$_3$)$_4$], cr., colrl.

Li_4RhH_4
Li_4RhH_5 [3]

$M_2[Rh_6C(CO)_n]$, n = 13, 15
$K[Rh_6N(CO)_{15}]$
$Cs_2[Rh_9P(CO)_{21}]$, C, N and P at. – clust a centres [21]

$[Rh(CO)(PR_3)_4]_2S$; **$[Rh(CO)SP_2]$**, oct. and square [25]
$(C_5H_5)Rh(C_5H_6)$; + H^+ ⟶ H_2↑ + $[Rh^{III}(C_5H_5)_2]^+$

$RhCl_3$

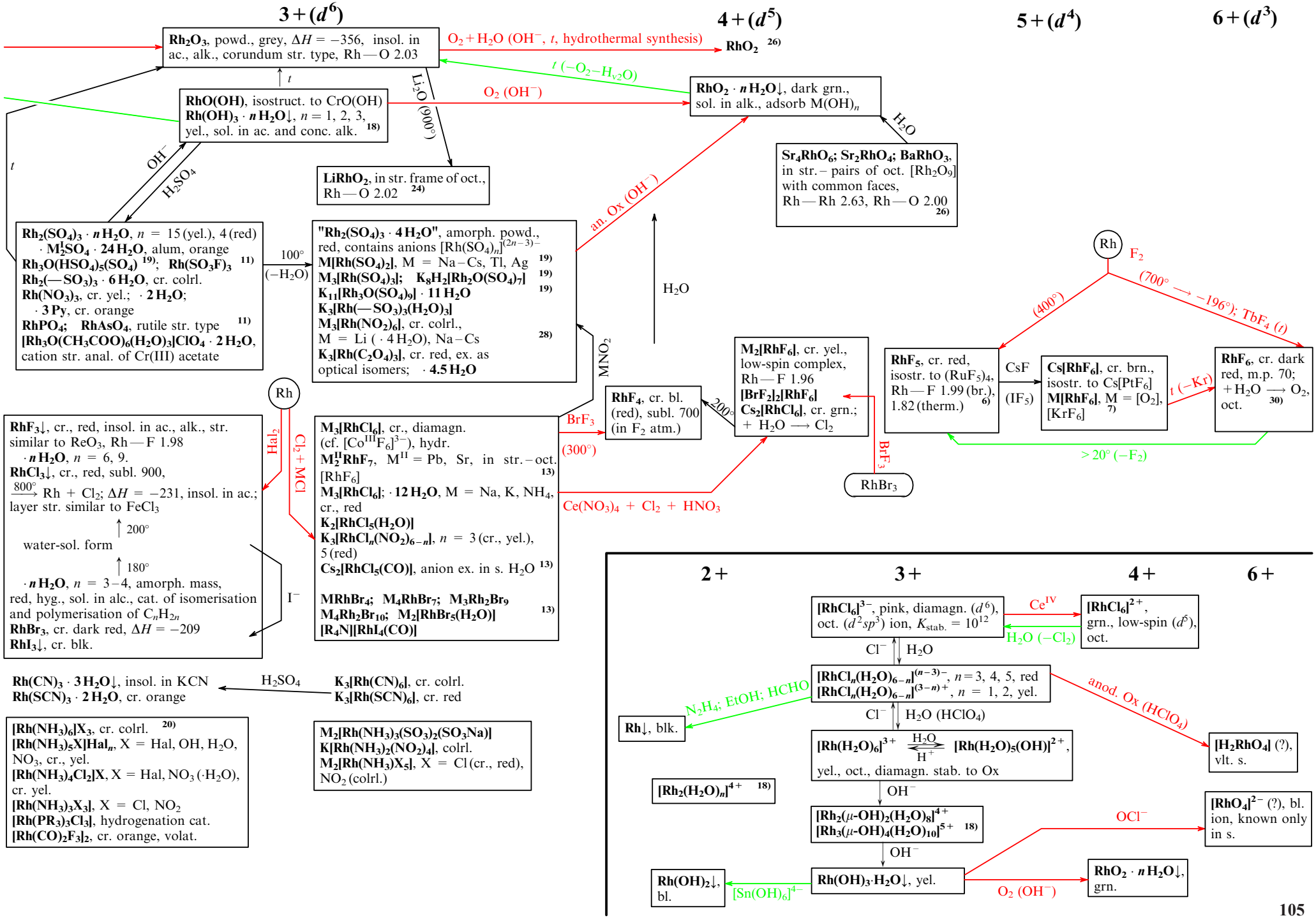
S (*t*)

$Rh(HS)_3$↓, brn. —*t*→ **Rh_2S_3**, cr., blk., insol. in aq. regia,
↓ t
Rh_3S_4, in str. frame of oct.

Rh_9S_8	**RhS_2** **$RhSe_2$** **$RhTe_2$** pyrite str. type	**Rh_2S_5** **Rh_2Se_5** **Rh_2Te_5**

Rh_2P, RhP_2, RhP_3

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_40, © Springer-Verlag Berlin Heidelberg 2011


3+(d6)
4+(d5)
5+(d4)
6+(d3)
Rh2O3, powd., grey, ΔH = −356, insol. in ac., alk., corundum str. type, Rh—O 2.03
O2 + H2O (OH−, t, hydrothermal synthesis)
RhO2 26)
t (−O2−Hv2O)
t
RhO(OH), isostruct. to CrO(OH)
Rh(OH)3 · n H2O↓, n = 1, 2, 3, yel., sol. in ac. and conc. alk. 18)
Li2O (900°)
O2 (OH−)
RhO2 · n H2O↓, dark grn., sol. in alk., adsorb M(OH)n
H2O
LiRhO2, in str. frame of oct., Rh—O 2.02 24)
Sr4RhO6; Sr2RhO4; BaRhO3, in str. – pairs of oct. [Rh2O9] with common faces, Rh—Rh 2.63, Rh—O 2.00 26)
OH−
H2SO4
an. Ox (OH−)
Rh2(SO4)3 · n H2O, n = 15 (yel.), 4 (red)
· M2ISO4 · 24 H2O, alum, orange
Rh3O(HSO4)5(SO4) 19); Rh(SO3F)3 11)
Rh2(—SO3)3 · 6 H2O, cr. colrl.
Rh(NO3)3, cr. yel.; · 2 H2O;
· 3 Py, cr. orange
RhPO4; RhAsO4, rutile str. type 11)
[Rh3O(CH3COO)6(H2O)3]ClO4 · 2 H2O, cation str. anal. of Cr(III) acetate
100° (−H2O)
"Rh2(SO4)3 · 4 H2O", amorph. powd., red, contains anions [Rh(SO4)n](2n−3)− 19)
M[Rh(SO4)2], M = Na–Cs, Tl, Ag 19)
M3[Rh(SO4)3]; K8H2[Rh2O(SO4)7] 19)
K11[Rh3O(SO4)9] · 11 H2O 19)
K3[Rh(—SO3)3(H2O)3]
M3[Rh(NO2)6], cr. colrl., M = Li (· 4 H2O), Na–Cs 28)
K3[Rh(C2O4)3], cr. red, ex. as optical isomers; · 4.5 H2O
H2O
MNO2
Rh
F2
(700° ⟶ −196°); TbF4 (t)
(400°)
RhF5, cr. red, isostr. to (RuF5)4, Rh—F 1.99 (br.), 1.82 (therm.) 6)
CsF
(IF5)
Cs[RhF6], cr. brn., isostr. to Cs[PtF6]
M[RhF6], M = [O2], [KrF6] 7)
t (−Kr)
RhF6, cr. dark red, m.p. 70; +H2O ⟶ O2, oct. 30)
> 20° (−F2)
M2[RhF6], cr. yel., low-spin complex, Rh—F 1.96
[BrF2]2[RhF6]
Cs2[RhCl6], cr. grn.; + H2O ⟶ Cl2
200°
RhF4, cr. bl. (red), subl. 700 (in F2 atm.)
BrF3
(300°)
BrF3
RhBr3
Rh
Hal2
Cl2 + MCl
RhF3↓, cr., red, insol. in ac., alk., str. similar to ReO3, Rh—F 1.98
· n H2O, n = 6, 9.
RhCl3↓, cr., red, subl. 900,
800° ⟶ Rh + Cl2; ΔH = −231, insol. in ac.; layer str. similar to FeCl3
200°
water-sol. form
180°
· n H2O, n = 3–4, amorph. mass, red, hyg., sol. in alc., cat. of isomerisation and polymerisation of CnH2n
RhBr3, cr. dark red, ΔH = −209
RhI3↓, cr. blk.
I−
M3[RhCl6], cr., diamagn. (cf. [Co^III F6]3−), hydr.
M2^II RhF7, M^II = Pb, Sr, in str.–oct. [RhF6] 13)
M3[RhCl6]; · 12 H2O, M = Na, K, NH4, cr., red
K2[RhCl5(H2O)]
K3[RhCln(NO2)6−n], n = 3 (cr., yel.), 5 (red)
Cs2[RhCl5(CO)], anion ex. in s. H2O 13)
MRhBr4; M4RhBr7; M3Rh2Br9
M4Rh2Br10; M2[RhBr5(H2O)] 13)
[R4N][RhI4(CO)]
Ce(NO3)4 + Cl2 + HNO3
Rh(CN)3 · 3 H2O↓, insol. in KCN
Rh(SCN)3 · 2 H2O, cr. orange
H2SO4
K3[Rh(CN)6], cr. colrl.
K3[Rh(SCN)6], cr. red
[Rh(NH3)6]X3, cr. colrl. 20)
[Rh(NH3)5X]Hal2, X = Hal, OH, H2O, NO3, cr., yel.
[Rh(NH3)4Cl2]X, X = Hal, NO3 (·H2O), cr. yel.
[Rh(NH3)3X3], X = Cl, NO2
[Rh(PR3)3Cl3], hydrogenation cat.
[Rh(CO)2F3]2, cr. orange, volat.
M2[Rh(NH3)3(SO3)2(SO3Na)]
K[Rh(NH3)2(NO2)4], colrl.
M2[Rh(NH3)X5], X = Cl (cr., red), NO2 (colrl.)
2+
3+
4+
6+
[RhCl6]3−, pink, diamagn. (d6), oct. (d2sp3) ion, Kstab. = 10^12
Ce^IV
H2O (−Cl2)
[RhCl6]2+, grn., low-spin (d5), oct.
Cl−
H2O
[RhCln(H2O)6−n](n−3)−, n = 3, 4, 5, red
[RhCln(H2O)6−n](3−n)+, n = 1, 2, yel.
N2H4; EtOH; HCHO
anod. Ox (HClO4)
Cl−
H2O (HClO4)
Rh↓, blk.
[H2RhO4] (?), vlt. s.
[Rh(H2O)6]3+ ⇌ [Rh(H2O)5(OH)]2+ (H2O / H+)
yel., oct., diamagn. stab. to Ox
[Rh2(H2O)n]4+ 18)
OH−
[Rh2(μ-OH)2(H2O)8]4+
[Rh3(μ-OH)4(H2O)10]5+ 18)
OCl−
[RhO4]2− (?), bl. ion, known only in s.
OH−
Rh(OH)2↓, bl.
[Sn(OH)6]4−
Rh(OH)3·H2O↓, yel.
O2 (OH−)
RhO2 · n H2O↓, grn.

IRIDIUM

Ir^0 5d ↓↑ ↓↑ ↓ ↓ ↓ | 6s ↓↑ | 6p | 6d

EN 1.5

1+ (d^8) **2+ (d^7)** **3+ (d^6)**

0 (d^9)

O_2 (1070°)

Ir, silver wh., v. hard, brittle met. d = 22.65, m.p. 2447, b.p. 4380, sol. in (HCl + O_2) at 125°, insol. in aq. regia; cub. cl. pack., a = 3.83, Ir—Ir 2.70

$(NH_4)_2[IrCl_6]$ —(Δ)→

HIr(CO)$_4$ MIr(CO)$_4$ [1]
H$_3$Ir(CO)$_2$
H$_3$Ir(CO)L$_3$
M[Ir(CO)$_3$L][*], M = Na, Hg, $[NiPhen_3]^{2+}$, $[AuL]^+$, $[SnCl_2]^{2+}$ [6]
HIr(CO)$_n$L$_{4-n}$, hydrogenation cat.$^{+}_{-}$, n = 2, mol. – trig. bipyr. [1]

H$_2$Ir$_2$(CO)$_4$L$_2$(SO$_2$)

[R$_4$N][HIr$_4$(CO$_2$)$_{11}$]
M[Ir$_4$(CO)$_{11}$X], X = Cl, CN, SCN, RCOO [8]

H_2 (20°); Na/Hg (THF)
CO + H_2 (p)

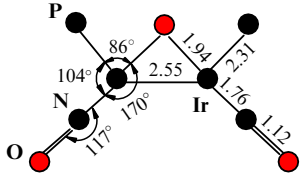
≥ 798°

[Ir(CO)(OH)L$_2$] $\overset{CO_2}{\underset{-CO}{\rightleftharpoons}}$ **Ir(CO)(OH)(CO$_2$)L$_2$**, more stab. than Rh anal. [11]

[Ir(S$_2$)L$_2$]IO$_4$ ⟶ [Ir(S$_2$O)L$_2$]IO$_3$ $\xrightarrow{IO_4^-}$ **[Ir(S$_2$O$_2$)L$_2$]IO$_3$** [2]
L = $(Ph_2PCH_2—)_2$

[Ir(CO)$_3$L$_2$]ClO$_4$ [6]

O[Ir(NO)L]$_2$ · C$_6$H$_6$



Ir$_2$(CO)$_8$, cr. yel.-grn., subl. 160, readily sol. in org. solv., dat. not reacts with H_2O [10]
Ir$_3$(CO)$_n$L$_{8-n}$ [6]
Ir$_2$(CO)$_4$L$_2$(SO$_2$)$_2$ [10]

IrCl$_3$ — CO (p, t, Cu)

Ir$_4$(CO)$_{12}$, cr., yel., dec. 210, dat. not react with ac. and alk., cluster [Ir$_4$] tetrah., Ir—Ir 2.68, all CO are therm., 170° ⟶ Ir
Ir$_4$(CO)$_8$L$_4$
↓ CO + H_2
Ir$_4$(CO)$_n$L$_{12-n}$ [8]

CO + NaOEt

[Ir(CO)$_3$Hal]$_n$, Hal = Cl–I, cr. brn. subl. 100, dec. with H_2O, Ir—Ir 2.85
***trans*-[Ir(CO)ClL$_2$]**, cr. yel. mol. square, "Vaska compl."
IrHal(CO)$_2$L$_2$, Hal = Cl–I [6], · **C$_6$H$_6$**, mol. trig. bipyr., Ir—P 2.34 (ax.), Ir—C 2.04 (equ.), Ir—Cl 2.37 (equ.)
Ir(CO)$_2$Cl(AsR$_3$)$_2$
[Ir(CO)Hal$_2$HL$_2$]; [Ir(CO)Hal$_2$HL]$_2$ [6]
[Ir(CO)Hal(NO)L$_2$]$^+$[BF$_4$]$^-$ · C$_6$H$_6$, Hal = Cl, I, cation – tetrag. pyram. with NO at the vertex

CO (t)
773°
EtOH + L
736°

IrCl$_2$↓, cr. brn., ΔH = −138, insol. in ac., alk., $CdCl_2$ type str.

IrF$_3$↓, cr. blk., not hydr.; 250° ⟶ Ir + F_2, ReO_3 str. type, Ir—F 2.01
IrCl$_3$↓, α-, β-, cr. olive grn., ΔH = −203, diamagn., insol. in ac., alk. [14]
· n **H$_2$O**, cr., yel.
IrBr$_3$, cr., brn., ΔH = −167
IrI$_3$, cr., blk.

[Ir(PR$_3$)$_3$Hal$_3$], cr. yel.

Br_2 → **Ir$_2$Br$_7$**

Ir(CO)$_2$Hal$_2$, Hal = Cl, Br, I, cr. colrl. or yel., hyd.
[Ir(CO)IL]$_2$I$_2$(SO$_2$) [9]

***trans*-[IrHal(NO)L$_2$]BF$_4$**, Hal = Cl–I [9]

[IrHal(CO)(SO$_4$)L$_2$]
[IrI$_3$(CO)$_3$]
[IrHal$_3$(CO)L$_2$], Hal = Cl (orange), I (red), μ = 4.3, oct., 2 L – *trans* [15]

[R$_4$N]$_2$Ir$_6$(CO)$_{16}$, cr., brn., anion oct. cluster, Ir—Ir ~ 2.75 [12]
[R$_4$N][Ir$_8$(CO)$_{22}$]
[R$_4$N][Ir$_8$(CO)$_{20}$] [1]

M[Ir(PF$_3$)$_4$], M = H, K
[H$_5$Ir(PF$_3$)$_2$], pentag. bipyr.
[H$_2$Ir(N$_3$)(PR$_3$)$_3$], octa.

I_2, (Et_2O, −80°)

[IrCl(PF$_3$)$_2$]$_2$, 2 squares with a common $[Cl_2]$ edge [6]
[IrI(PF$_3$)$_4$], cr. yel., dec. 25
[Ir(N$_3$)(PR$_3$)$_3$]

Ir$_6$(CO)$_{16}$, cr. red

[IrCl(X)^{0}L$_2$], X = P_4, N_2, cr., diamagn.; [2]
+ $CSCl_2$ ⟶ $[Ir^{III}Cl_3(CS)L_2]$ + N_2

[Ir(CO)ClL$_2$L$'_2$], L$'_2$ = Cl_2, HCl, SO_2, H_2; tetrag. pyram., at the base – $[IrClP_2]$-*trans*

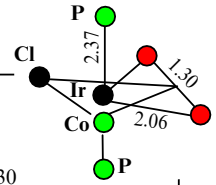
H$_3$IrL$_2$; H$_3$IrL$_3$ [13]
[HIr(NO)$^+$L$_3$]ClO$_4$, cation trig. bipyr., 2 isomers: (1) brn., 2L-ax., (2) blk., 3L-equ.

[Ir(NH$_3$)$_5$]$_2$, cr., yel., diamagn., cluster, 90° ⟶ Ir + NH_3

Ir$_2$S$_3$ $\overset{t}{\longleftarrow}$ **IrS$_2$; Ir$_2$S$_8$**, $\overset{t}{\longrightarrow}$ Ir + S
Ir$_2$P, *anti*-CaF_2 str. type

O_2 (bz.) / $-O_2$ (vac.)

Dioxygen compl.
[Ir(CO)HalL$_2$(O$_2$)$^-$], Hal = Cl, Br, cr., red; $h\nu$-vis ⟶ dec. [3]; O—O 1.30 and 1.36 (correspond to superoxides)
[Ir(CO)IL$_2$(O$_2$)$^{2-}$] · **CH$_2$Cl$_2$**, not evolv. O_2, isostr. to Cl- compl., but O—O 1.51 (correspond to peroxides), Ir—O ≈ 2.05
{Ir(O$_2$)$^{2-}$[(R$_2$PCH$_2$—)$_2$]$_2$}[PF$_6$], cation – trig. bipyr. [Ir(O_2)P_4], Ir—O 1.96, O—O 1.52, O_2 attached irreversible (see Tab. "Oxygen")
[IrCl(C$_2$H$_4$)L$_2$(O$_2$)$_2$], $\nu_{O=O}$ 825 cm^{-1} [7]

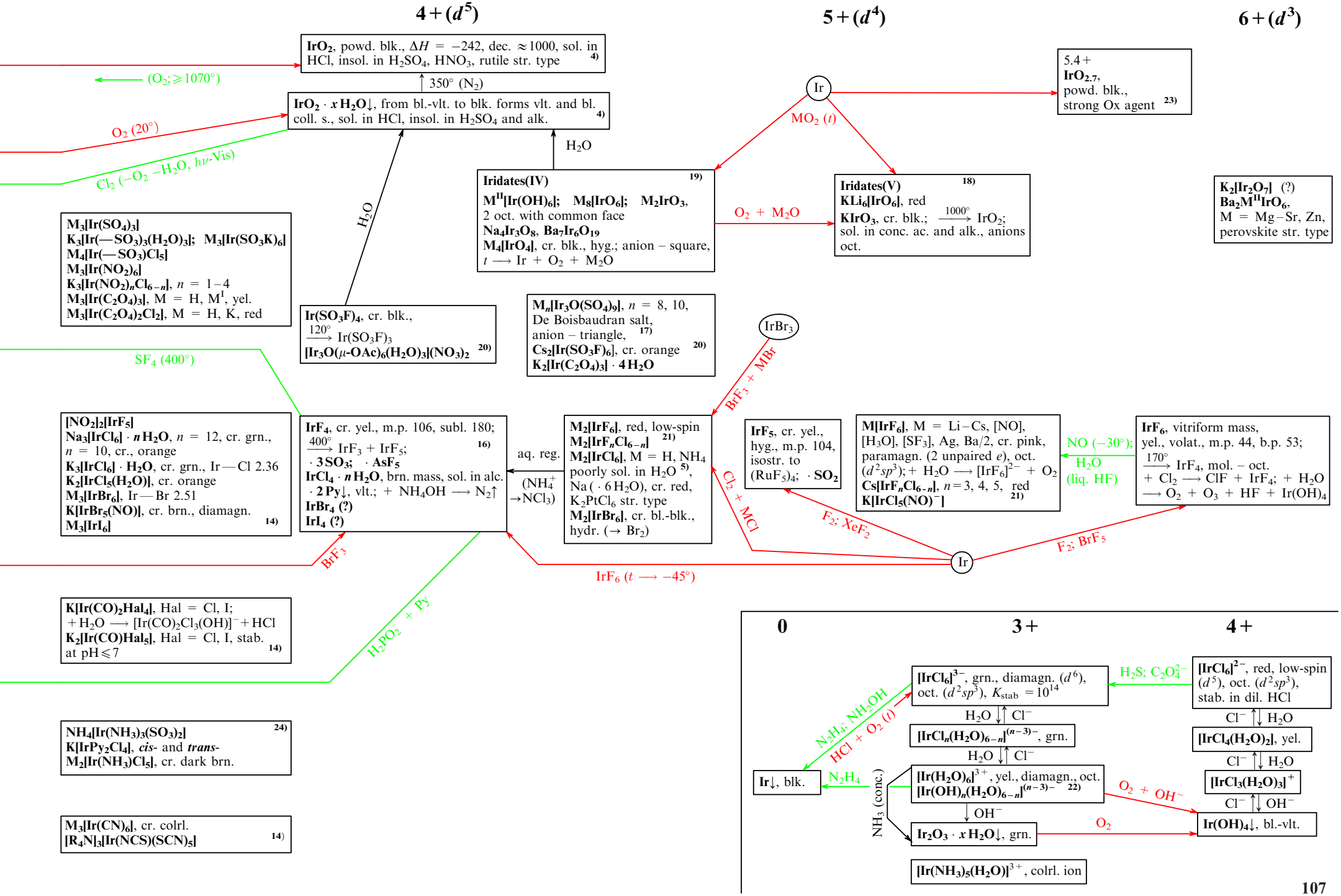


[Ir(NH$_3$)$_6$]X$_3$
[Ir(NH$_3$)$_5$X]Hal$_n$, X = Hal, H_2O, NO_2
[Ir(NH$_3$)$_4$X$_2$]X
***trans*-[IrPy$_4$Cl$_2$]Cl**
[IrPy$_3$Cl$_3$], 2 yel. isomers (*mer*- and *fac*-)

[Ir(C$_5$H$_5$)$_2$]$^+$X, dicyclopentadienyliridium(III) salts, v. stab., diamagn., cation – struct. anal. of $Fe(C_5H_5)_2$

[*] L = Her., Ph_3P.

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4 + (d5)
5 + (d4)
6 + (d3)
IrO2, powd. blk., ΔH = −242, dec. ≈1000, sol. in HCl, insol. in H2SO4, HNO3, rutile str. type 4)
(O2; ≥1070°)
350° (N2)
IrO2 · x H2O↓, from bl.-vlt. to blk. forms vlt. and bl. coll. s., sol. in HCl, insol. in H2SO4 and alk. 4)
O2 (20°)
Cl2 (−O2 −H2O, hν-Vis)
H2O
Ir
MO2 (t)
5.4 + IrO2.7, powd. blk., strong Ox agent 23)
Iridates(IV) 19)
MII[Ir(OH)6]; M8[IrO6]; M2IrO3, 2 oct. with common face
Na4Ir3O8, Ba7Ir6O19
M4[IrO4], cr. blk., hyg.; anion – square, t ⟶ Ir + O2 + M2O
O2 + M2O
Iridates(V) 18)
KLi6[IrO6], red
KIrO3, cr. blk.; 1000° ⟶ IrO2; sol. in conc. ac. and alk., anions oct.
K2[Ir2O7] (?)
Ba2MIIIrO6, M = Mg–Sr, Zn, perovskite str. type
M3[Ir(SO4)3]
K3[Ir(—SO3)3(H2O)3]; M3[Ir(SO3K)6]
M4[Ir(—SO3)Cl5]
M3[Ir(NO2)6]
K3[Ir(NO2)nCl6−n], n = 1–4
M3[Ir(C2O4)3], M = H, MI, yel.
M3[Ir(C2O4)2Cl2], M = H, K, red
H2O
Ir(SO3F)4, cr. blk., 120° ⟶ Ir(SO3F)3
[Ir3O(μ-OAc)6(H2O)3](NO3)2 20)
Mn[Ir3O(SO4)9], n = 8, 10, De Boisbaudran salt, anion – triangle, 17)
Cs2[Ir(SO3F)6], cr. orange 20)
K2[Ir(C2O4)3] · 4 H2O
IrBr3
BrF3 + MBr
SF4 (400°)
[NO2]2[IrF5]
Na3[IrCl6] · n H2O, n = 12, cr. grn., n = 10, cr., orange
K3[IrCl6] · H2O, cr. grn., Ir—Cl 2.36
K2[IrCl5(H2O)], cr. orange
M3[IrBr6], Ir—Br 2.51
K[IrBr5(NO)], cr. brn., diamagn.
M3[IrI6] 14)
IrF4, cr. yel., m.p. 106, subl. 180; 400° ⟶ IrF3 + IrF5; · 3 SO3; · AsF5
IrCl4 · n H2O, brn. mass, sol. in alc. · 2 Py↓, vlt.; + NH4OH ⟶ N2↑
IrBr4 (?)
IrI4 (?) 16)
aq. reg.
(NH4+ →NCl3)
M2[IrF6], red, low-spin
M2[IrFnCl6−n] 21)
M2[IrCl6], M = H, NH4 poorly sol. in H2O 5), Na(· 6 H2O), cr. red, K2PtCl6 str. type
M2[IrBr6], cr. bl.-blk., hydr. (→ Br2)
Cl2 + MCl
IrF5, cr. yel., hyg., m.p. 104, isostr. to (RuF5)4; · SO2
M[IrF6], M = Li–Cs, [NO], [H3O], [SF3], Ag, Ba/2, cr. pink, paramagn. (2 unpaired e), oct. (d2sp3); + H2O ⟶ [IrF6]2− + O2
Cs[IrFnCl6−n], n = 3, 4, 5, red 21)
K[IrCl5(NO)−]
NO (−30°); H2O (liq. HF)
IrF6, vitriform mass, yel., volat., m.p. 44, b.p. 53; 170° ⟶ IrF4, mol. – oct.
+ Cl2 ⟶ ClF + IrF4; + H2O ⟶ O2 + O3 + HF + Ir(OH)4
BrF3
IrF6 (t ⟶ −45°)
F2; XeF2
F2; BrF5
Ir
K[Ir(CO)2Hal4], Hal = Cl, I; + H2O ⟶ [Ir(CO)2Cl3(OH)]− + HCl
K2[Ir(CO)Hal5], Hal = Cl, I, stab. at pH ⩽ 7 14)
H2PO2− + Py
NH4[Ir(NH3)3(SO3)2] 24)
K[IrPy2Cl4], cis- and trans-
M2[Ir(NH3)Cl5], cr. dark brn.
M3[Ir(CN)6], cr. colrl.
[R4N]3[Ir(NCS)(SCN)5] 14)
0
3 +
4 +
[IrCl6]3−, grn., diamagn. (d6), oct. (d2sp3), Kstab = 10^14
H2S; C2O4 2−
[IrCl6]2−, red, low-spin (d5), oct. (d2sp3), stab. in dil. HCl
H2O ⇅ Cl−
Cl− ⇅ H2O
[IrCln(H2O)6−n](n−3)−, grn.
[IrCl4(H2O)2], yel.
Cl− ⇅ H2O
[IrCl3(H2O)3]+
N2H4; NH4OH
HCl + O2 (t)
Ir↓, blk.
N2H4
[Ir(H2O)6]3+, yel., diamagn., oct.
[Ir(OH)n(H2O)6−n](n−3)− 22)
O2 + OH−
NH3 (conc.)
OH−
Cl− ⇅ OH−
Ir2O3 · x H2O↓, grn.
O2
Ir(OH)4↓, bl.-vlt.
[Ir(NH3)5(H2O)]3+, colrl. ion

PALLADIUM

Pd⁰ 4*d* | 5*s* | 5*p* | 5*d* — EN 1.3

0(d^{10})

Pd, met. silver-wh., mild, d = 12.0, m. p. 1554, b. p. 2940, sol. in HNO_3 (*t*), aq. regia, paramagn., cub. cl. pack., a = 3.88, Pd—Pd 2.74; sol. ⩾ 1000 vol. H_2 (ut to **Pd_3H_4**);
[H] $\overset{Pd}{\rightleftarrows}$ $H^+ + e^-$

Spongy Pd, moist. sol. 12000 vol. H_2, act. hydro- and degidrogenation cat.

Pd-blk.↓, powd., sol. 870 vol. H_2/1 vol.

Pd-coll., gel $\overset{-H_2O}{\underset{H_2O}{\rightleftharpoons}}$ sol;
sol. H_2 in 3–8 time > cr. Pd

$[Pd(NH_3)_2Cl_2]$ —H_2 (900°)→ Pd
N_2H_4 (OH^-) → Pd
Na_2PdCl_4 —Protect. coll.→ Pd

$[Pd_2(CO)_2Dipy_2] \cdot 4H_2O$, red [9]
$[Pd_3(CO)_3(PPh_3)]$ $\xrightarrow{CO\,(p)}$ **$Pd(CO)_3(PPh_3)$**
$Pd_4(CO)_5(PR_3)_4$
$Pd_7(CO)_7(PR_3)_7$, single-cap. oct. [Pd_7]
$Pd_8(CO)_8(PR_3)_7$
$Pd_{10}(CO)_{18-n}(PR_3)_n$, n = 4, 6
$Pd_{23}(CO)_{20}(PR_3)_8$, mol. – clusters
trans-**{$PdPy_2[Mn(CO)_5]_2$}** [4]

$[Pd(PR_3)]_n$, n = 2, 3, 4, cr., yel., sol. in bz. [1]; + O_2 ⟶ **$[Pd(PPh_3)_2(O_2)]$**
$[Pd(PPh_3)_4]$, cross-coupling react. cat. (Nobel – Prize 2010) [1]

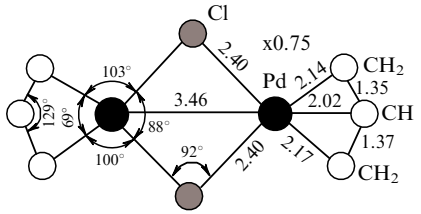
$Pd[P(OPh)_3]_4$, cr. colrl., dec. 125
$Pd(PF_3)_4$, liq. colrl., m. p. −41, dec. −20
$Pd(AsR_3)_4$, cr., colrl., Ox by air
$Pd(CNR)_n$, n = 2–4, cr. blk., insol. in org. solv. + Py ⟶ Pd↓;
+ O_2 ⟶ **$[Pd(O_2)(CNR)_2]$**

Pd(NO)Cl, cr. brn., diamagn.
$[Pd(NO)_2Cl_2]_n$

$K_2[Pd(CN)_2]$
$K_4[Pd(CN)_4]$, cr. yel.;
+ H_2O ⟶ H_2↑ + …
$[PR_4][Pd(CN)(CO)]$ [7]

$KPdH_3$ [21]

$Pd_2(CO)_2Cl$
$[Pd_2(CH_3COO)_2(CO)_2]_2 \cdot 2CH_3COOH$ [11]



2+(d^8)

PdO, powd. blk., dec. 200, ΔH = −121 [8], sol. in conc. HBr, insol. in aq. regia, PtS str. type, Pd—O 2,01; "palladit"
↑ 500°
$Pd(OH)_2 \cdot nH_2O$↓, brn., sol. in ac., alk., NH_4OH, weak Ox

O_2 (900°); Na_2O_2 ⟶ PdO
PdO —875°; H_2 (20°) + Q→ Pd
PdO —K_2O (600°, Ar)→ Palladates (II)
PdO ⇄ $Pd(OH)_2$: OH^- / H^+

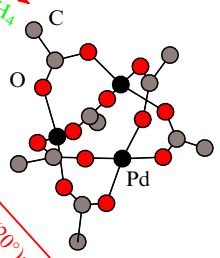
Palladates (II) [2]
$M_2[Pd(OH)_4]$, cr. yel., sol. in H_2O, M = Na, K, Ba/2 (· H_2O), anion – square, diamagn.
M_2PdO_2, in str. – chains of squares with common edges
$M^{II}Pd_3O_4$, M = Ca – Ba, Cd, blk., columns of squares
$Na_2Pd_3O_4$; **K_6PdO_4**, orange

H_2SO_4 (*t*); $KHSO_4$; $H_2SeO_4 + HNO_3$; $BrSO_3F$ → Pd

$Pd(ClO_4)_2 \cdot 4H_2O$, brn.
$PdSO_4 \cdot 2H_2O$, red-brn., hyg.
$Pd(SO_3F)_2$, purp., μ = 3.39 [12]
$PdSeO_4$, brn.; · **$(NH_4)_2SeO_4$**; **Pd[$Pt(SO_3F)_6$]**
$[Pd(NO_3)_2]_n$ $\xleftarrow{N_2O_5}$ **$\cdot 2H_2O$**, yel.
$[Pd(NO_2)_2(NH_3)_2]$, *cis*- and *trans*- [13]
$[Pd_4(NO_2)_8(PR_3)_4]$
$[Pd(CH_3COO)_2]_3$, brn., sol. in bz., **$\cdot 0.5C_6H_6$**,
Pd_2OCl_2, ribbon of squares *trans*-$[PdO_{2/2}Cl_2]$ [20]

$Na_6[Pd(SO_3)_4] \cdot 2H_2O$, in str. squares $[PdS_4]$, Pd—S ≈ 2.33
$M_2[Pd(SO_3)_2] \cdot nH_2O$, squares – *cis*-$[PdS_{2/2}O_{2/2}]$, Pd—S 2.41, [15]
$K_2[Pd(NO_3)_4]$, orange, hyd.
$M_2[Pd(NO_2)_4]$, yel., $K_{stab.}$ = 10^{20} [15]
$M_2[Pd(NO_2)_nCl_{4-n}]$, n = 1–3

$M_2[Pd(C_2O_4)_2] \cdot nH_2O$; $H_2[Pd(C_2O_4)_2] \cdot 6H_2O$, yel., in str. – columns of squares, Pd—O 2.00, Pd—Pd 3.69



Cl₂ (300°); HCl + Cl₂ (20°); HNO_3 + HBr; Br_2 + HBr → Pd

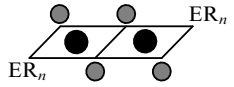
	ΔH
PdF_2, light vlt., TiO_2 str. type, + H_2O ⟶ $Pd(OH)_2$ + HF	−469
$PdCl_2$, red, hyg., m. p. 680, subl. 600, α-$PdCl_2$ – ribbon of squares $[PdCl_{4/2}]$ β-, str. anal. $PtCl_2$; · **$2H_2O$**, red	−163
$PdBr_2$↓, brn., sol. in HBr	−105
PdI_2↓, blk., dec. 350, (⟵$Pd^{2+} + I^-$, qualitat. react.). In str. $PdBr_2$ and β-PdI_2 – gauffer chains of squares, α-PdI_2 – plane chains	−63

CsF (SeF_4) → **$CsPd_2F_5$**, **Rb_3PdF_5**, orange; **K_2PdF_4** [5]
HCl → **$H_2[PdCl_4]$**, ex. only in s.

	$K_{stab.}$
$M_2[PdCl_4]$, grn.-brn. (K, gold-yel.), anion – square	10^{15}
$K_2[PdBr_4]$, red-brn.	10^{13}
$K_2[PdI_4]$, red	10^{25}
$[R_4N]_2[Pd_2Hal_6]$, Hal = Cl–I [3]	—

H_2; Pd; SO_2; I_2; SF_4 → Pd

$Pd(NH_3)_2Cl_2$↓, *cis*- yel.-brn., unstab.
trans- orange, $\xrightarrow{210°}$ Pd + …, square
$[PdCl_2(CO)]_n$, cr., yel.-brn.; + H_2O ⟶ Pd + Cl_2 + CO
$[PdCl_2(ER_n)]_2$, stab. E = P > As > S > Se > Te > Sb
$PdI_2(CNR)_2$, cr., orange.



$[PdCl_2(CH_2{=}CH_2)]_2$

$[PdCl(CH_2{\cdots}CH{\cdots}CH_2)]_2$,
(π-allyl – bidentate, donor of 4 el.)
$Pd(N_3)_2$, red-brn., exp.
$Pd_3(PS_4)_2$, in str. – oct. [PdS_6], [14]
Pd[MF_6], M = Ge, Pt, cr. orange
$Pd(CN)_2$↓, amorph., wh., dec. 210, ΔH = −348;
· **$2PR_3$** [13]
$Pd(SCN)_2$, cr., red, ΔH = −255

EtOH + PR_3 → Pd

HPdCl₃(CO); M[$PdCl_3(CO)$]

$[Pd^{II}(NH_3)_4][Pd^{II}Cl_4]$, "Vauquelin salt", cr., red, str. anal. of "Magnus salt", Pd—Pd 3.25

$K_2[Pd(N_3)_4]$; $K_2[PdCl_2(N_3)_2]$

$K_2[Pd(CN)_4] \cdot 3H_2O$, colrl. $\xrightarrow{200°}$ $-H_2O$, in str. – column of squares (dsp^2), Pd—C ≈ 2.0, Pd—Pd 3.74, $K_{stab.}$ = 10^{42}
$Ba[Pd(CN)_4] \cdot 4H_2O$, grn., Pd—Pd 2.73
$K_2[Pd(SCN)_4]$, needles, red, Pd—S 2.3 (in square)

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200° (−O_2, −H_2O)

$PdO_2 \cdot n H_2O$↓, dark-red., fresh prec. – sol. in ac., alk., strong Ox

NH_3

$[Pd(NH_3)_6](OH)_4$, cr. colrl., strong bas.

PdO

$M_2O + MO_2$

Palladates (IV) [2)]

$M_2Pd(OH)_6$; $\xrightarrow{-H_2O}$ M_2O + $PdO_{1.63}$

M_2PdO_3, M = Na–Rb, diamagn., isostr. to Li_2MnO_4

(2.33–2.66) + **$M_xPd_3O_4$**
M = Li–K, Tl
blk. [2)]

$Pd(NO_3)_2$

N_2O_5

$Pd(NO_3)_4$, cr. brn., diamagn., Ox,
+ I^- ⟶ I_2;
+ Fe^{2+} not react.

$Pd(SO_3F)_2$

$S_2O_6F_2$

"$Pd(SO_3F)_3$" = $Pd^{II}[Pd^{IV}(—OSO_2F)_6]$,
cr. red, hyg., dec. 180,
$\mu_{eff.}$ = 3.45; $\xrightarrow{130°}$ $Pd(SO_3F)_2$ [12)]

F_2(500°)

$M_2[Pd(SO_3)_2(OH)_2]$, M = Na, K, brn., unstab.
$M_2[Pd(SO_3F)_6]$, M = Cs, [NO], [ClO_2], Ba/2 [12)]
$K_2[PdO(C_2O_4)_2] \cdot 2H_2O$, red.
$M_2[Pd(C_2O_4)_2Cl_2]$, M = Na, K, yel. ;
+ H_2O ⟶ $PdO_2 \cdot 6H_2O$

PdF_3 = $Pd^{II}[Pd^{IV}F_6]$ (?), cr. blk., hyg., sol. in BrF_3, $\mu_{eff.}$ = 2.88 (high-spin. compl. Pd^{2+}, d^8), str. like ReO_3, all at. Pd equivalent, Pd — F 2.04;
+ H_2O ⟶ O_2 + ...; stab. > PdF_4
BrF_3 ↓↑ 180°
· **BrF_3**, cr., brn., paramagn., $\mu_{eff.}$ = 2.24

$Na[PdF_4]$; $M_2M'[PdF_6]$,
(M, M′) = (K, Li), (K, Na), (Cs, K),
isostr. to $K[BrF_4]$ and $K_2Na[AlF_6]$,
anions – oct. ($t_{2g}^6 e_g^1$) Pd^{3+} [17)]

Pd

$S_2O_6F_2$;
$MCl + HSO_3F$

$HCl + Cl_2$; aq. regia

$M_2[PdF_6]$, M = K–Cs, M^{II}/2, Xe/2 [6)],
$[SeF_3]_2[PdF_6]$; $\xrightarrow{155°}$ PdF_2 + SeF_4↑ + SeF_6↑
$[XeF]^+[Pd_2F_9]^-$; $\xrightarrow{280°}$ XeF_4 + PdF_3 [6)]
$H_2[PdCl_6]$, ex. in dil. s., blk.;
+ H_2O ⟶ Cl_2 + $PdCl_2$
$M_2[PdCl_6]$, cr. red, diamagn., K_2PtCl_6, str. type, Pd — Cl 2.30;
+ H_2O (*t*) ⟶ M_2PdCl_4 + Cl_2
$M_2[PdBr_6]$

$MPdF_6$,
M = Na, $[O_2]$ [19)]

F_2 (*t*, *p*)

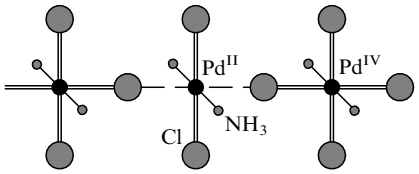
PdF_4, cr. red, dist. UCl_4 str. type (CN Pd 8),
+ H_2O ⟶ O_2 [16)]

***trans*-$[Pd(NH_3)_2Cl_4]$**, red-orange, oct., strong Ox

$Hg(CN)_2$

$Pd(CN)_4$,cr., pink.
$\xrightarrow{20°}$ $(CN)_2$

$[Pd^{II}(NH_3)_4][Pd^{IV}Cl_6]$
"$PdHal_3 \cdot 2NH_3$" = $[Pd^{II}(NH_3)_2Hal_2][Pd^{IV}(NH_3)_2Hal_4]$,
Hal = Cl, Br, in str. – chains of alternate oct. and squares



Cl_2

Hal_2
(HX)

$[PdEn_2]Hal_2$

$[Pd^{II}En_2][Pd^{IV}En_2Hal_2]X_4$, Hal = Cl, Br;
X = ClO_4, NO_3 [18)]

Pd_2S, PdS↓, blk.-brn., ΔH = −77, insol. in HCl, $(NH_4)_2S$; cr. insol. in aq. regia, str.-like PtS, "breggite" (+PtS +NiS)
PdS_2, cr. blk., sol. in aq. regia, FeS_2 dist. str. type
Pd_2Se, Pd_2Te, PdSe, PdTe, Pd_9Te_4 [10)]
Pd_3Sb, "stibiopalladinite" **PdSb, $PdSb_2$**
Pd_3As, "arsenopalladinite" **$PdAs_2$**, "sperrylite"

0 2+ 4+

Pd↓

aq. regia

N_2H_4 (protect. coll.)

PdO↓, coll.

$HClO_4$ HNO_3

$[Pd(H_2O)_4]^{2+}$,brn.

HCl

N_2H_4; HCOONa

$[PdCl_4]^{2-}$, red, square (dsp^2)

Cl_2; aq. regia

H_2O (*t*, $-Cl_2$); HCl (*t*)

$[PdCl_6]^{2-}$, red, diamagn. (d^6), oct. (d^2sp^3), strong Ox

HCl NH_3

$[Pd(NH_3)_4]^{2+}$, colr., $K_{stab.}$ = 10^{30}

Cl_2

***trans*-$[Pd(NH_3)_4Cl_2]^{2+}$**

Series of *trans*-act. of Pd(II) and Pd(IV) are similar to rows of Pt(II) and Pt(IV)

PLATINUM

Pt⁰ 5d ↑↓ ↑↓ ↑↓ ↑↓ ↓ | 6s ↓ | 6p | 6d | EN 1.4

2+ (d^8)

PtO, (?) powd., blk.-vlt., sol. in aq. regia, PtS str. type; s. O_2 in str. Pt [27]

Pt(OH)₂, $\xrightarrow{150°}$ H_2O + Pt + PtO_2 · *n* H_2O↓, red, sol. in conc. ac., alk., Red (dry-blk.) ↑ 140°

Platinates (II) [1]
Na_2PtO_2, powd. grey $\xrightarrow{550°}$ Pt + ...
$M^{II}Pt_3O_4$, cr. blk., dec. 800, in str. — chains or columns $[PtO_4]$ squares

Pt_3O_4, CaF_2 dist. str. type

Bronzes [2]
$M^I_xPt_3O_4$, x = 0.25
$TlPt_3O_4$, $K_3Pt_2O_4$

Pt_2O_3, powd. brn.

$Pt_2O_3 \cdot x\,H_2O$↓

Pt, met., silver-wh., not v. hard, ductile, d = 21.46, m.p. 1769 [22], b.p. ~ 3900, sol. in aq. regia, Br_2, $M_2O_2(t)$. Cub. cl. pack. a = 3.92, Pt—Pt 2.78

Spongy Pt, adsorb. ≈100 vol. H_2, O_2 (on Pt-electrodes)

Coll. Pt — hydrogenation, Ox dec. H_2O_2 cat.

Pt-blk.↓, H_2 sol. max at 0°

O_2(510°)
560°; H_2 (20°, +Q)
$M^I_2O_2$
$MNO_3 + O_2$
PtO_2
Pt
$M'O_2$

[Pt(NO₃)₂(PPh₃)₂]
[Pt(NO₂)₂(NH₃)₂]; [Pt(NH₃)₂(μ-NO₂)]$_n$X$_n$
[Pt₂(NH₃)₄(μ-HPO₄)₂]$_n$, "**blue**", in str. $[Pt]_\infty$ linear chains, Pt—Pt 2.65—2.80 [31]
[Pt(CO₃)(PR₃)₂], mol. — square
[Pt(CH₃COO)₂]₃
[Pt₄(OAc)₄En₄]Cl₄ · 4 H₂O; [Pt₄] — square [32]

$M_6[Pt(SO_3)_4] \cdot n\,H_2O$; $M_2[Pt(SO_3)_2] \cdot n\,H_2O$
$Na_6[Pt(S_2O_3)_4] \cdot 10\,H_2O$, yel.
$M_2[Pt(NO_2)_4] \cdot 2\,H_2O$
$K_2[Pt(NO_2)_nCl_{4-n}]$, n = 1–3; **$K_2[Pt(NO_3)_4] \cdot 0.5\,H_2O$** [28]
$K_2[Pt(C_2O_4)_2] \cdot 4\,H_2O$, vlt. [contain ~10 % — Pt (IV)] in str. — colomns of squares
$H_2[Pt(C_2O_4)_2] \cdot 2\,H_2O$, yel.

$K_5[Pt_4O_3(NO_2)_9]$ [28)]
$K_8[Pt_7O_6(NO_2)_{12}] \cdot 7\,H_2O$,

$Pt_2(CH_3COO)_6$, cr. brn., diamagn.
$Pt_4(CH_3COO)_{10}(OH)_2$ [13]

$H_2[PtCl_4]$
Zn; $C_2O_4^{2-}$; N_2H_4
HCOONa; $SnCl_2$
583°
Cl_2 (> 500°), HCl
t
H_2PtCl_6
HCl
(−H_2PtCl_6 −Pt)
Pt
Hal_2
400°

PtCl
PtBr₂

	ΔH
PtF_2 (?) ⇄ Pt + PtF_4	−372
$PtCl_2$↓, light-brn., oct. $[Pt_6]$ cluster in $[Cl_{12}]$ cubooct.	−140
$PtBr_2$↓, red-brn.	−79
PtI_2↓, blk., insol. in ac., dec. 400, layers of squares [8]	−17

$H_2[PtCl_4]$, s., dark-red, $K_{stab.}$ = 10^{17}; $\xrightarrow{20°}$ Pt↓ + H_2PtCl_6 + $PtCl_2$
$M_2[PtCl_4]$, M = Na(· 4 H_2O), K, red, anion — square (dsp^2)
$M_2[PtBr_4]$, brn., $K_{stab.}$ = 10^{21}
$M_2[PtI_4]$, $K_{stab.}$ = 10^{30}; **$[R_4N]_2[Pt_2Hal_6]$**
$M_2[PtHal_2(NO_2)_2]$, *cis*- and *trans*-
$M_2[PtClBrI(NO_2)]$, 3 isomers [6]
$[PtCl_4]^{2-}$
K_2PtCl_4 str.

PtF_3, yel., ΔH = −202, in str. — oct. $[Pt^{II,IV}F_6]$, high-spin Pt(II) comp., μ_{eff} = 3.05 [14]
$PtCl_3$, grn., ΔH = −129, + HCl⟶$[Pt^{II}Cl_4]^{2-}$ + $[Pt^{IV}Cl_6]^{2-}$; $\xrightarrow{435°}$ $PtCl_2$
$PtBr_3$, blk.-grn., ΔH = −125
PtI_3↓, powd. graphite-like $\xrightarrow{270°}$ I_2 + PtI_2, diamagn., in str. — chains of Pt(II) squares and Pt(IV) oct.

Pt_3I_8↓ $\xrightarrow{350°}$ PtI_2; Pt(II) frame squares and Pt (IV) oct.

0 (d^{10})

$[Pt(CO_2)]_n$, cr., brn.
$Pt_3(CO)_3(PPh_3)_4$ [8]
$Pt_3(CO)_4(PR_3)_4$ [5]
$Pt_4(CO)_5(PPhMe_2)_4$

[PtHal₂L₂], L = AsR_3, SbR_3, PF_3, PCl_3
[PtHal₂(PR₃)₂], *cis*- and *trans*-, Hal = Cl—I

cis-**[Pt(NH₃)₂Cl₂]**↓, "Peyrone salt", yel.
trans-**[Pt(NH₃)₂Cl₂]**↓, "Reise chloride of II base", yel.-grn., squares, Pt—N 2.0; Pt—Cl 2.3, K_{stab} = 10^{29}
[PtPy(NH₃)(NO₂)Cl]

290°

[Pt(NH₃)₄][PtCl₄], "Magnus salt", dark-grn, in str. — columns alternate squares anions and cations

$PtF_3(CO)_2$, yel., hyg., subl., *hv*-vis. — dec.
"$PtCl_3(NH_3)_2$" = *trans*-$[Pt^{II}(NH_3)_2Cl_2]$ × × *trans*-$[Pt^{IV}(NH_3)_2Cl_4]$, blk., diamagn.
"$PtCl_3(EtNH_2)_4 \cdot 2\,H_2O$" = = $[Pt^{II}L_4][Pt^{IV}L_4Cl_2]Cl_4 \cdot 2\,H_2O$, L = $EtNH_2$, "Wolfram salt"
$[PtEn_2][PtHal_2En_2](ClO_4)_4$ [15]
$[PtCl_3En]$, tetr. pyram. [13]

$Pt(PR_3)_n$, n = 2, 3, 4, cr., yel. (n = 3, mol — triangle)
[Pt(PPh₃)₃(SO₂)] · 0.7 SO_2, tetrah.
$Pt[P(OR)_3]_4$, cr., colrl.
***trans*-HPtHal(PR₃)₂**, Hal = Cl, Br, mol. — square, hydrogenation cat.
[Pt(PPh₃)₂(O₂)], O—O 1.45, 1.50; of oxydation cat.
[Pt(PPh₃)₂(π-C₂H₄)], C—C 1.43
$Pt(C_2H_4)_3$; $\xrightarrow[450°]{O_2(CHCl_3)}$ **$Pt(O_2)(C_2H_4)_2$** $\xrightarrow[-20°]{}$ Pt + PtO + ...
$Pt(Ph_2PCH_2—)_2]_2$, stab. to Ox [23]
$Pt(PF_3)_4$, liq., colrl., m.p. −15, dec. 90, diamagn., tetrah. [11]

PF_3 + Cu (p, t)

$[Pt_2(RCN)_6]X_2$ [26]
$M_2[Pt_n(CO)_{2n}]$, n = 3, 6, 9
$M_4[Pt_{19}(CO)_{22}]$ [4]
***trans*-$[H_2Pt(AsR_3)_2]$** [25]
$Na_2[PtH_4]$ [24]

[PtCl₂(CO)₂], yel., m.p. 142, diamagn., sol. in CCl_4, μ = 4.85; + H_2O ⟶ Pt + ...
$[Pt_2Cl_4(CO)_3]_n$, m.p. 130, sol. in CCl_4
[PtCl₂(CO)]₂, yel., m.p. 195, subl., hydr., $\xrightarrow{300°}$ Pt + $COCl_2$; mol — 2 squares with $[Cl_2]$ common edge
[PtCl₂(C₂H₄)]₂, orange, hyg., dec 200, sol. in alc., acet.
$\uparrow\downarrow$ C_2H_4
[PtCl₂(C₂H₄)₂], cr. yel., instab.

HCl (conc.)
H[Pt(CO)Cl₃], yel. s.
M[Pt(CO)Cl₃]

KH + H_2
Pt
$M_2[PtH_4]$, diamagn. (d^2), anion — square (M = Na) or oct. (K – Cs)
M_3PtH_5

HCl (−KCl)
$K[PtCl_3(C_2H_4)] \cdot H_2O$, "Zeise salt", cr. yel., sol. in H_2O, C—C 1.37, [9]
$K_2[Pt(C{\equiv}CR)_4]$

$K_4[Fe(CN)_6]$ (Gmelin)
Pt

EtOH
$PtCl_4$

$Pt(CN)_2$↓, amorph, yel., infl. in air
$Pt(SCN)_2$↓, brn.

200°

$H_2[Pt(CN)_4] \cdot 5\,H_2O$, red, strong, ac., $K_{stab.}$ = 10^{41}
$M_2[Pt(CN)_4]$, M = Na, K(· 3 H_2O, bl.-yel.), NH_4 M^{II}/2, Ag, Hg/2, in str. columns of squares, Pt—Pt 2.8—3.7
$M_2[Pt(SCN)_4]$, M = K, $[Pt(NH_3)_4]$/2, red

2.25+
$M_{1.75}[Pt(CN)_4] \cdot 1.5\,H_2O$, M = K – Cs [30]

K
Pt
Cl
NH_3

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_43, © Springer-Verlag Berlin Heidelberg 2011

PtI_2; Pt — O_2(150 · 10^5 Pa), $KClO_3$ — $O_2(-H_2O, t)$

PtO_2, blk.; $\xrightarrow{510^\circ}$ Pt + O_2; insol. in aq. regia; α-, hex., layered str.; $\xrightarrow{700^\circ}$ β-, rh., dist. TiO_2 str. type, hydrogenation of C = C and C = O act. cat. [17]

$PtO_2 \cdot n\,H_2O\downarrow$, n = 1 (blk.), 2 (brn.), 3 (yel.), 4 (wh.)
$H_2[Pt(OH)_6]$, yel., sol. in ac., alk., dec. 120, oct. [18]

H_2PtCl_6 — $NaNO_3$ (t); M_2CO_3; MOH

Platinates (IV)
$M_2[Pt(OH)_6] \cdot n\,H_2O$, yel., oct., diamagn.
Na_4PtO_4; M_8PtO_6; M_2PtO_3, M = Na (red) K – Rb (grn.); in str. — layers of oct.
$M_4Pt_3O_8$; $M^{II}PtO_3$; $Ba_3Pt_2O_7$; $M^{II}_2PtO_4$; $M^{II}_4PtO_6$; $\xrightarrow{t}$ Pt + O_2 + M_2O_n [3]

Sulphides
PtS↓, grey needles, ΔH = −50, insol. in aq. regia, in str. — $[SPt_4]$ — tetrah., $[PtS_4]$ — square (dsp^2), "cooperit"
PtS str.
M_2PtS_2, M = K, Rb, chains of rectangles
Pt_2S_3, grey powd., + O_2 ⟶ Pt + SO_2
$H_2Pt_4S_6$, **$M_2Pt_4S_6$**, grey-bl., **$M_4Pt_3S_6$**, red
in str. — chains of rectangles with common edges
$PtS_2\downarrow$, cr. grey-grn., leave touch, ΔH = −88, sol. in HNO_3, M_2S; CdI_2 str. type; $\xrightarrow{t}$ Pt + …
$(NH_4)_2[Pt(S_5)_3] \cdot 2\,H_2O$; **$Pt_5Se_4$** [29]

$PtO_3\downarrow$ (?), red-brn. + HCl ⟶ Cl_2 + + H_2PtCl_6; does not react. with H_2O_2 (0°); 20° ⟶ O_2
CH_3COOH
$K_2[Pt_3O_{10}]$ (?), golden film

OH⁻
$H[Pt(SO_4)_2] \cdot 5\,H_2O$, cr. orange
$K_2[Pt_2(SO_4)_4L_3]$, L = H_2O, NH_3, NR_3
$K_4[Pt_2(SO_4)_4X_2]$, X = OH, Hal, NO_2, SCN, anions — $Cu(CH_3COO)_2 \cdot H_2O$, str. anal., Pt — Pt 2.48
$M_6[Pt_2(PO_4)_4(H_2O)_2]$

$Pt(SO_3F)_4$ [19] — H_2O (slow); $HSO_3F + S_2O_6F_2$

Pt — Hal$_2$; HBr + HNO_3; aq. regia

$M_2[Pt(IO_3)_6]$, M = K – Cs, NH_4, dec. ≈300 [7]
$Cs[Pt(SO_3F)_5]$; **$Cs_2[Pt(SO_3F)_6]$** [7]
$M_2[Pt(SO_3F)_6]$, M = Cs, $[ClO_2]$, $[BF_2]$, Ba/2, yel.
$K_2[Pt(NO_2)_6]$, yel., resist. to Red

$PtOF_3$, cr. brn., nonvolat., slow. hydr.

PtF_5, cr., red, m.p. 80; $\xrightarrow{t}$ $PtF_4 + PtF_6\uparrow$; strong Ox, + $BrF_3 \rightarrow BrF_5$

PtF_4 — XeF_2 (−Xe)

Pt — F_2 + O_2 (450°); F_2 (1000° ⟶ −196°); XeF_4 (−PtF_4, −Xe)

$M^+[PtF_6]^-$, M = K – Cs (yel.-brn.) $[O_2]$ (orange, subl. 100, m.p. 219 (p), 2 unpair. el.) $[H_3O]$, $[IF_4]$, $[ClF_6]$, $[Xe_2F_3]$, Xe, Xe/2, XeF_5, KrF, paramagn. (d^5, 1 unpair. el.), anion — oct. (d^2sp^3), strongest Ox,
+ H_2O ⟶ PtO_2 + $[PtF_6]^{2-}$ + O_2
$M[Pt_2F_{11}]$, M = $[O_2]$, [KrF] [20]

Xe; O_2 / H_2O

PtF_6, cr. red, m.p. 61, b.p. 69, + H_2O ⟶ O_2 + + PtO_2 + $[PtF_6]^{2-}$, strongest Ox, ΔH = −714 [21]

375° / 400°
Cs_2PtCl_5, diamagn., Pt(II) squares and Pt(IV) oct.
K_2PtI_5, chains of $[PtI_4I_{2/2}]$ oct. [30]
$M_4[Pt_3I_{11}]$; **$M[PtI_4]$**

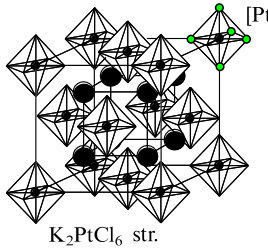
	ΔH
PtF_4, cr., brn., subl. 300, diamagn., dist. UCl_4 str. type (CN 8)	−740 [8]
$PtCl_4$, red-brn., hyg.,	−246
$\cdot 5\,H_2O$, light-yel., dec. 38	−142
$PtBr_4\downarrow$, blk.-brn., sol. in alc., Et_2O	
$PtI_4\downarrow$, blk.-brn., $\xrightarrow{300^\circ}$ **Pt_3I_8**;	−42
$\cdot 2\,H_2O$ = *trans*-$[PtI_4(H_2O)_2]$, blk.	
In str. $PtHal_4$ — chains of oct.	

$H_2[PtF_6] \cdot n\,H_2O$
$M_2[PtF_6]$, M = Na – Cs, $M^{II}/2$, Ln/3, $Pd^{II}/2$, $[BrF_2]^+$, $[SeF_3]^+$, yel., diamagn., oct.
$[XeF]^+[Pt_2F_9]^-$ [12]
$H_2[PtCl_6] \cdot 4\,H_2O$ = $[H_3O]_2[PtCl_6] \cdot 2\,H_2O$, (red — admix. of I_2), strong ac., sol. in alc., Et_2O [16]
$M_2[PtCl_6]$, cr. yel., cub., sol. Li(· 6 H_2O) > > Na(· 6 H_2O) ≫ K > NH_4 ≫ Rb > Cs > Ag↓; diamagn. (d^6), oct. (d^2sp^3), Pt — Cl 2.32
$H_2[PtBr_6] \cdot 9\,H_2O$, red
$M_2[PtBr_6]$, M = K, Na (· 6 H_2O), red
$H_2[PtI_6] \cdot 9\,H_2O$, blk.
$M_2[PtI_6]$, M = K, Na (· 6 H_2O), dark-red, unstab. light-sensitive, [qualitative react. on Pt(IV)] [16]

$[Pt(NH_3)_2Cl_2]$
trans- — Cl_2 / $C_2O_4^{2-}$ — ***trans*-$[Pt(NH_3)_2Cl_4]$**, "Gerhardt salt", yel.-grn., dec. 280
cis- — Cl_2 / $C_2O_4^{2-}$ — ***cis*-$[Pt(NH_3)_2Cl_4]\downarrow$**, "Cleve salt", yel., $\xrightarrow{160^\circ}$ grn., dec. 240
cis- — H_2O_2 — ***cis*-$[Pt(NH_3)_2Cl_2(OH)_2]$**, "oxo Pt" [33]
$[Pt(NH_3)Py(NO_2)ClBrI]$, ex. 15 isomers

In the *trans*-position to Cl — gr. NH_3 is more mobile than in the *cis*- position (the I.I. Chernyaev rule of ***trans*-effect**). Series of *trans*-effect:
Pt(II): NO_2, I, SCN > Br > Cl > NH_3, Py > H_2O
Pt(IV): I > Br > Cl > OH > NH_3, Py, NO_2, NO_3

$K_2[Pt(CN)_5] \cdot 3\,H_2O$, in str. $[Pt(CN)_4]$, columns of squares 1 gr. CN — among columns disordered


$[PtCl_6]^{2-}$
K_2PtCl_6 str.

$H_2[Pt(CN)_6] \cdot 2\,H_2O$, cr. colrl., strong ac.
$K_2[Pt(CN)_6]$, light-yel., dec. 395,
gr. [Pt — C — N] linear
$M_2[Pt(SCN)_6]$, M = H (· 2 H_2O), K – Cs, Pb/2
$M_2[Pt(SeCN)_6]$

Amminocomplexes of Pt (ions in s.)

2+ 4+

$[Pt(NH_3)Cl_3]^-$, orange, $K_{stab.} = 10^{24}$ — Cl_2 / $C_2O_4^{2-}$ — **$[Pt(NH_3)Cl_5]^-$**, yel. oct. ion

↑ HCl (t)

$[Pt(NH_3)_3Cl]^+$, light-yel., $K_{stab.} = 10^{33}$ — Cl_2 / $C_2O_4^{2-}$ — ***mer*-$[Pt(NH_3)_3Cl_3]^+$**, light-yel.

↑ HCl

$[Pt(NH_3)_4]^{2+}$, "colrl., I base Reise", $K_{stab.} = 10^{36}$ — Cl_2; H_2O_2 / $C_2O_4^{2-}$ — ***trans*-$[Pt(NH_3)_4X_2]^{2+}$**, X = Cl, OH, colrl. ***cis*-$[Pt(NH_3)_4X_2]^{2+}$**, light-yel.

***fas*-$[Pt(NH_3)_3Cl_3]^+$**, yel. ion

$[Pt(NH_3)_5Cl]^{3+}$; **$[Pt(NH_3)_6]^{4+}$**, colrl.

INERT GASES

		1s	2s	2p	3s	3p	4s	4p	4d	5s	5p	5d	6s	6p	6d	EN
Helium	He^0	↓↑														4.5
Neon	Ne^0	↓↑	↓↑	↓↑ ↓↑												4.0
Argon	Ar^0	↓↑	↓↑	↓↑ ↓↑	↓↑	↓↑ ↓↑										2.9
Krypton	Kr^0	↓↑	↓↑	↓↑ ↓↑	↓↑	↓↑ ↓↑	↓↑	↓↑ ↓↑								2.6
Xenon	Xe^0	↓↑	↓↑	↓↑ ↓↑	↓↑	↓↑ ↓↑	↓↑	↓↑ ↓↑		↓↑	↓↑ ↓↑					2.25
Radon	Rn^0	↓↑	↓↑	↓↑ ↓↑	↓↑	↓↑ ↓↑	↓↑	↓↑ ↓↑		↓↑	↓↑ ↓↑		↓↑	↓↑ ↓↑		2.0

Formation of Rn, He and Ar in the nuclear decay

$^{232}_{90}Th \xrightarrow{\alpha} \ldots \; ^{220}_{86}\mathbf{Rn}$; 54.5 s. $\quad ^{235}_{92}U \xrightarrow{\alpha} \ldots \; ^{219}_{86}\mathbf{Rn}$; 3.92 s.

$^{238}_{92}U \xrightarrow{\alpha} \ldots \; ^{222}_{86}\mathbf{Rn}$; 3.82 d. $\quad \ldots {}^{218}_{85}At \xrightarrow{\beta} {}^{218}_{86}\mathbf{Rn}$ 0.019 s.

$^{238}_{92}U \longrightarrow \cdots 8\alpha + 6\beta + {}^{206}_{82}Pb$; $+8e \longrightarrow 8\,{}^{4}_{2}\mathbf{He}$ – stab.

obtained from natural gas (containing > 0.1% He) by fractional distillation

$^{40}_{19}K + e \longrightarrow {}^{40}_{18}\mathbf{Ar}$ – stab.

	He	**Ne**	**Ar**	**Kr**	**Xe**	**Rn**
	gas colrl., in the discharge emit					
	yel.	orange	red	grn.-vlt.	vlt.	wh. light
Contain in atm. (% vol. · 10^4)	5.24	18.2	9340	11.4	0.087	$6 \cdot 10^{-14}$
m. p.	−269.7	−248.6	−189.4	−157.3	−111.9	−71.0
b. p.	**−268.9**	−245.9	−185.8	−153.2	−108.1	−61.9
d (at b. p.)	0.126	1.20	1.40	2.60	3.06	4.40
sol. in H_2O (% vol.) by 0°	0.008	0.010	0.034	—	30	51 readily sol. in org. solv.
	cub. cl. pack.					
a = 4.42 ($p = 125 \cdot 10^5$) ↓ −258°		4.52	5.43	5.69 ↓ −247°	6.24 ↓	—
	hex. pl. pack.					
a =	3.47	3.14	—	4.00	4.34	
c =	5.54	5.14	—	6.53	7.09 [13]	
($p = 130 \cdot 10^5$) ↑ −270° cub. (α-Fe str. type) a = 4.11 ($p = 30 \cdot 10^5$)						

H_2O; p-$C_6H_4(OH)_2$

Clathrate inclusion compounds

	p_E at synthesis (Pa · 10^{-6})	t. dec. ($p = 10^5$)
E · 5.75 H_2O (8: 46), E = Ne	300	—
Ar	150	−42.8
Kr	15	−28
Xe	~1	−4
Rn	~1	—
E · 3p-$C_6H_4(OH)_2$, E = Ar, Kr, Xe (hydroquinone)		

1+ 2+

$He(N_2)_{11}$ [16]

N_2 (770 Pa, 20°)

F_2 (−188°, disharge; $h\nu$-UV)

H_2O (−O_2)

$B(OTeF_5)_3$

$Kr[OTeF_5]_2$, unstab. [18]

KrF_2, cr. colrl., subl. < 0, exp., dec. ≈0, ΔH = + 22, Ox > XeF_n (+NF_3 → $[NF_4]^+$), donor act. in relation to F^-: XeF_6 > XeF_2 > $KrF_2 \gg XeF_4$; sol. in HF, BrF_5; in str. – layers of linear mol., Kr — F 1.89

· **XeF_6**, m. p. 40 (dec.).; sol. in BrF_5 [11]

EF_n

$[Kr_2F_3]^+[\exists F_6]^-$, E = As, Sb, Nb, Ta, U, Np, Pu, Am, cr., colrl. [1]

↓ 25° (−Kr −F_2)

$[KrF]^+[EF_6]_x$, E = As, Sb, Au, Rh, Ru, Pt, cr. stab.

$[FKrL]^+X^-$, L = MCN [14]

PtF_6

$Xe[Pt^VF_6]$ **$Xe[PtF_6]_{1.8}$** powd., red, subl. vac.; + $H_2O \longrightarrow Xe + HF + PtO_2 + O_2$

PdF_4; RuF_6

$Xe[MF_6]$, M = Pd, Ru, Rh, Sb

$Xe_2[SiF_6]$, dec. ≈20

165°

$Xe(ClO_4)_2$, **$Xe(IO_2F_4)_2$**
$Xe(SO_3F)_2$, **$Xe(SeOF_5)_2$**, **$Xe(TeOF_5)_2$**, **$Xe(NO_3)_2$** (dec. −70)
$Xe(PO_2F_2)_2$, **$Xe[N(SO_2F)_2]_2$**, **$Xe(CF_3COO)_2$**, stab. at 20; gr. [OXeO] – linear; Xe — O 2.12
$Xe[Pt^VF_6]_2$, **$Xe[Pt_2^{IV}F_{10}]$**, yel.
$Xe[EF_6]_2$, E = P – Sb, Ta, yel. [19]

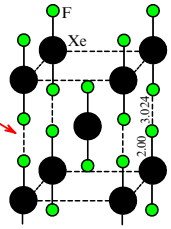
F_2(400°, p, hv); (120°, MgF_2)

H_2O (−O_2 −F^-) (slow.); OH^- (immed.)

$[Xe(OTeF_5)]^+X^-$, X = AsF_6, Sb_2F_{11} [12]
$[Xe(C_6F_5)]^+X^-$

F_2

$XeF_2 \cdot XeF_4$, m. p. 107 [11]



XeF_2, cr. colrl., m. p. 136, b. p. 338, ΔH = −176, 350° ⟶ Xe + XeF_4. Sol. in H_2O 0.15M (0°), readily sol. in HF (not dis.). In str. and gas – linear mol. (ψ-trig. bipyr.), Xe — F 2.00, v. strong Ox and F-agent; $+Ag^+ \longrightarrow Ag^{II}$; $Co^{II} \longrightarrow Co^{III}$; $Np^V \longrightarrow Np^{VII}$ [13]
H_2O (−O_2 −F^-) ⟶ F_2 (slow); + $OH^- \longrightarrow F_2$ (immed.); + $BrO_3^- \longrightarrow BrO_4^-$

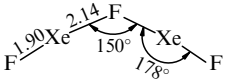
$M[SbF_6]$, $M^+ = [O_2]$; $[HalF_2]$; $[N_2F_3]$; $[IF_6]$ (25°)

F_2; BrF_5; XeF_n (NiF_2, NaF, cat., in sol. BrF_5)

$[O_2]X$ (−O_2;) (clean atm. from Xe*)

$[XeF]^+X^-$, X = ClO_4, SO_3F, $[N(SO_2F)_2]$, $OSeF_5$, $OTeF_5$, NO_3, VF_6, CF_3COO, SbF_6, Sb_2F_{11}, NbF_6, TaF_6, Ta_2F_{11}, MoF_7, WF_7, PdF_5, PtF_6, Pt_2F_{11}, gr. F — Xe — F linear, Xe — F 1.87 – 2.12 [2]

$[Xe_2F_3]^+[EF_6]^-$, E = As, Sb, Ta, Au, cation – angular [14]



CCl_4 ($h\nu$-UV)

$XeCl_2$, cr. colrl., subl., dec. 80

$[RnF]^+[SbF_6]^-$ (?)

Sld. products fluoration of Rn **RnF_n** (?), n = 4 or 6, + $H_2O \longrightarrow RnO_3$ (?) [3]

N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_44, © Springer-Verlag Berlin Heidelberg 2011

4+ 6+ 8+

XeF_6 — HPO_2F_2, $-195° \longrightarrow 22°$ → **XeO_3**, needles, colrl., exp., sol. in H_2O 2 *M*, $\Delta H = +402$, $+I^- \longrightarrow Xe$ (rapidly); mol. – ψ-tetrah. [:XeO_3] (sp^3), Xe—O 1.76, ∠OXeO 103 (cf IO_3^-) [20]

XeO_4, gas, light yel., subl. −196, m. p. −36, exp., $\Delta H = +640$, mol. – tetrah., Xe—O 1.74 [17]

$< 0° (-Xe-O_2)$

H_2O

$[H_4XeO_6]$, $K_1 = 10^{-2}$, $K_2 = 10^{-6}$, $K_3 = 10^{-11}$; **$[H_3XeO_6]^- \rightleftarrows [H_2XeO_6]^{2-} \rightleftarrows [HXeO_6]^{3-}$**
pH ≈6 ≈10 ≈12
colrl. oct. ions, strongest Ox;
$+ Mn^{2+} \longrightarrow HMnO_4$; $+ IO_3^- \longrightarrow IO_4^-$;
$+ Co^{II} \longrightarrow Co^{III}$

$Xe(OH)_4$, cr. colrl., m. p. 90, b. p. 115, exp.

$H_2O \rightleftarrows H^+$

$H_2XeO_4 \rightleftarrows H^+ + HXeO_4^-$, s. stab., v. strong Ox, $+ Fe^{2+} \longrightarrow Fe^{3+}$ (pH = 7); $+ Hg \longrightarrow Hg_2^{2+}$

$-O_2$ (immed.)

OH^- (Xe)

$MOH\ (-Xe-O_2)$; $O_3 + MOH$; XeF_2

$H_2O + MgO$ ($-MgF_2\downarrow$)

Xenates, $MHXeO_4$, M_2XeO_4, $Ba_3XeO_6\downarrow$, $M[XeO_3Hal]$, Hal = F–Br, colrl., stab. F > Cl > Br, anion – $[XeO_3F_{2/2}]$

$XeF_2\ (-Xe)$

Perxenates
$Na_3HXeO_6 \cdot H_2O$
$M_{4/n}[XeO_6]$, M = Li↓, Na ($\cdot n H_2O\downarrow$, n = 6; 8), K–Cs, Ba↓, Ag↓ (blk.), Zn↓, Pb↓, Th↓, UO_2^{2+}, Au^{3+} ($\cdot 40\,H_2O\downarrow$), (orange), La↓ (yel.)
$\xrightarrow{t}$ Xe + O_2 + M_2O_n,
anion – oct., Xe—O 1.86 [21]

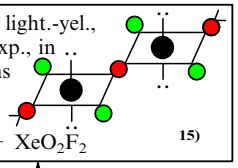
XeO_2F_2, cr. colrl., m. p. 31, mol. – ψ-trig. bipyr., $\Delta H = +235$; > 25° $\longrightarrow XeO_2 + O_2$ (slow.)

Xe — OF_2 → **$[XeO_2F]^+X^-$**, X = EF_6, wh., sld.
$XeO_2(OTeF_5)_2$, gr. [:XeO_4] – disphenoid

H_2O; N_2O_5 — **$Cs[XeO_2F_3]$**

$K_4XeO_6 \cdot 2\,XeO_3\downarrow$, cr., yel., exp.;
$+ Mn^{2+} \xrightarrow[H^+]{} HMnO_4$

$XeOF_2$, cr. light.-yel., m. p. 90, exp., in .. str. – chains of square; −15° $\longrightarrow$ $\longrightarrow XeF_2 + XeO_2F_2$ [15]



$(-Xe-O_2)$

$XeOF_4$, liq., $d = 3.17$, m. p. −41, dec. > 300, $\Delta H = -25$, volat. > XeF_6, mol. – tetr. pyram., O – ax.
$Cs[(XeOF_4)_3F]$ [6] · **$C_{7.8}$**, graphitide

$KOH\ (-Xe)$

XeO_3F_2

XeO_4

$KMnO_4 + XeO_3 + MOH$

$POF_3\ (-PF_5)$

$Xe(TeO_2F_4)_2$ [19]
$Xe(OTeF_5)_4$, cr. yel., m. p . 72 (dec.), squares [XeO_4]

$H_2O\ (-80°)$

$Cs[XeOF_3]$ yel. [15]

H_2O

$[XeOF_3]^+X^-$, X = SbF_6 (m. p. 104), Sb_2F_{11} (m. p. 61), cr. colrl., cation – disphenoid [6]
$XeO(OTeF_5)_4$
$Xe(OTeF_5)_6$, cr., red [18]

H_2O; SiO_2 — $NaNO_3$ (70° → −196°)

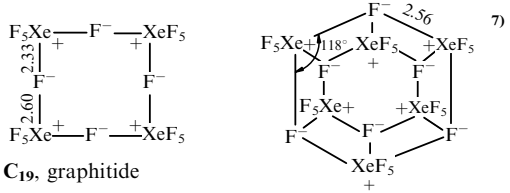
$M[XeOF_5]$, M = NO, R_4N, anion – ψ-pentag. bipyr. [23]

$[XeOF_5]^+[Sb_2F_{11}]^-$ [10]

XeF_4, cr. colrl., m. p. 135 [11], subl., $\Delta H = -251$, sol. in HF, strong Ox;
$+ Pt \longrightarrow PtF_4 + PtF_6$;
$+ NH_3 \longrightarrow N_2 + \ldots$; $+ Ag \longrightarrow Ag^{2+}$;
mol. – square (ψ-oct., sp^3d^2), Xe—F 1.95

F_2 [(*t*, *p*); (NiF_2)]

XeF_6, cr. colrl., subl., m. p. 49 (yel. liq.), b. p. 75, $\Delta H = -338$, exp.;
$+ HF$ (liq.) $\longrightarrow [XeF_5]^+ + [HF_2]^-$;
$h\nu \longrightarrow XeF_2 + XeF_4 + \ldots$; in gas – ψ-pentag. bipyr. (sp^3d^3), (cf IF_6^-). In str. – cycles tetra- and hexamers (3:1):



7)

· **C_{19}**, graphitide

F_2 (300° 10^7 Pa); $h\nu$

Xe — KrF_2 (20°) [4] / F_2 (−195°)

EF_5 MF EF_n MF

$[XeF_3]^+X^-$, X = AsF_6, SbF_6, $[Sb_2F_{11}]$, cr. yel.-grn., cation ψ-trig. bipyr. (T-shaped) (sp^3d) [5]

$M[XeF_5]$, M = Na–Cs, [NO], $[R_4N]$, anion – flat pentag. (ψ-pentag. bipyr., sp^3d^3),
$M_2[XeF_6]$, M = Na–Cs, cr. colrl., anion – oct.,
$\xrightarrow{t}$ XeF_n + MF + O_2 [22]

$[XeF_5]^+X^-$, $[Xe_2F_{11}]^+X^-$, X = BF_4, Al_2F_7, GaF_4, SO_3F, EF_6 (E = P–Sb, V–Ta, U, Ru, Pd, Pt, Au); [:XeF_5]$^+$ – ψ-oct., II coord. sphere Xe – single-cap antiprism (CN 9) [8, 13]

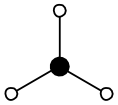
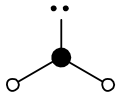
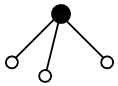
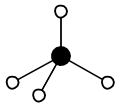
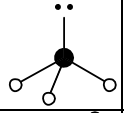
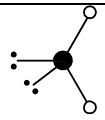
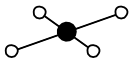
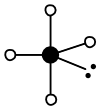
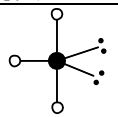
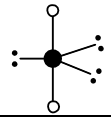
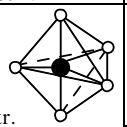
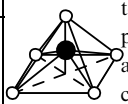
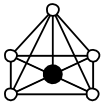
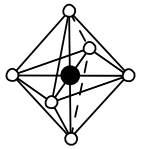
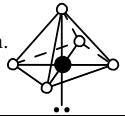
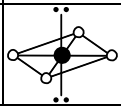
$MXeF_7$; 50° $\longrightarrow$ $M_2XeF_8 + XeF_6$
M_2XeF_8, M = Na–Cs, $[NO]^+$, cr. yel., anion – square antiprism, Xe—F 2.1–1.95 [9]

Acidity decreases in the series:
$XeF_6 > XeO_2F_4 > XeO_3F_2 > XeO_4 > XeOF_4 > XeF_4 > XeO_2F_2 > XeO_3 \sim XeF_2$

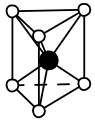
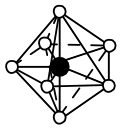
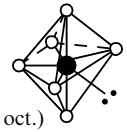
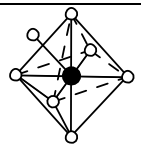
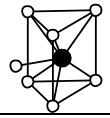
Xe
F
O

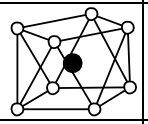
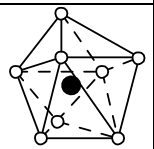
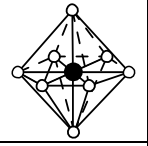
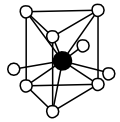
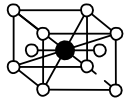
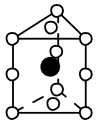
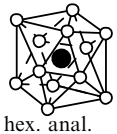
VALENCE STATE (HYBRIDIZATION TYPES) AND COORDINATION POLYHEDRA OF CENTRAL ATOMS

(E – localized el. pair)

Number of el. pairs	Valence state, val. angle	Type of mol. or ion	CN	Spatial configuration	Examples
2	***sp***, 180° ***7s5f***, 180°	AX_2	2 2	linear (dumb–bell) 	$BeHal_2$, Hal = F–I, CO_2, N_2O d^{10}: $ZnCl_2$ (gas), $HgCl_2$, $[Ag(NH_3)_2]^+$, d^0: $[UO_2]^{2+}$, $[NpO_2]^{2+}$, $[PuO_2]^{2+}$
2	p^2, 90°	AX_2	2	angular 	H_2S, H_2Se, $[TlCl_2]^-$
3	sp^2, 120° d^2s, 120°	AX_3	3	flat triangle 	$K[BeF_3]$ (gas), $[BO_3]^{3-}$, $[CO_3]^{2-}$, $[NO_3]^-$; d^{10}: $[HgI_3]^-$ d^6: $[FeO_3]^{4-}$ d^0: $ScHal_3$ (gas)
		AX_2E	2	angular (ψ-triangle) 	$SnHal_2$ (gas), $[NO_2]^-$, N_2F_2, O_3, SO_2
3	p^3, 90°	AX_3	3	trig. pyram. 	PH_3, AsF_3 (gas)
4	sp^3, ≈109° 28′	AX_4	4	tetrah. 	$[Be(H_2O)_4]^{2+}$, $[BF_4]^-$, CH_4, $[SiO_4]^{4-}$ d^{10}: $Ni(CO)_4$, $[Cu(CN)_4]^{3-}$, $GeCl_4$ d^9: $Co(CO)_3(NO)$, $Cs_2[CuCl_4]$ d^8: $[Fe(CO)_2(NO)_2]$, $[Co(CO)_4]^-$ d^7: $[Mn(CO)(NO)_3]$, $[CoCl_4]^{2-}$ d^6: $[FeCl_4]^{2-}$; d^5: $[MnCl_4]^{2-}$; d^3: $[FeO_4]^{3-}$
	sp^3, ≈ 103°	AX_3E	3	trig. pyram. (ψ-tetrah.) 	NH_3, NF_3, $[AsO_3]^{3-}$, $[H_3O]^+$, $[SO_3]^{2-}$, $[Se_n]$, $[SeO_3]^{2-}$,$[BrO_3]^-$, XeO_3
	sp^3, ≈ 103°	AX_2E_2	2	angular (ψ-tetrah.) 	H_2O, OF_2, $[S_n]$, SCl_2, $[ClF_2]^+$, $[ClO_2]^-$, XeO_2
	d^3s, 109° 28′	AX_4	4	tetrah.	d^2: $Cr(OC_4H_9\text{-}t)_4$, $[MnO_4]^{3-}$, $[FeO_4]^{2-}$ d^1: VCl_4, $[CrO_4]^{3-}$, $[MnO_4]^{2-}$, $[RuO_4]^-$ d^0: $TiCl_4$, $[VO_4]^{3-}$, $[CrO_4]^{2-}$, $[MnO_4]^-$
	dsp^2, 90°	AX_4	4	square 	d^8: $[Co(CN)_4]^{3-}$, $[PtCl_4]^{2-}$, CuO, $[Au(OH)_4]^-$
5	sp^3d, 120° (equ.), 90° (ax.)	AX_5	5	trig. bipyr.	$AlH_3 \cdot 2NR_3$, $[SnCl_5]^-$, SOF_4, $[IO_5]^{3-}$, ClO_2F_3
		AX_5	5	tetr. pyram.	$[InCl_5]^{2-}$
		AX_4E	4	disphenoid (ψ-trig. bipyr.) 	$[PBr_4]^-$, $[SbF_4]^-$, SF_4, $TeCl_4$, $[HalF_4]^+$, XeO_2F_2 (2F-ax.), XeO_3F
		AX_3E_2	3	T-shaped (ψ-trig. bipyr.) 	ClF_3, BrF_3, $[XeF_3]^+$, $XeOF_2$
		AX_2E_3	2	linear (ψ-trig. bipyr.) 	$[ICl_2]^-$, $[Hal_3]^-$, XeF_2
	dsp^3, 120° (equ.), 90° (ax.)	AX_5	5	trig. bipyr. ⇅ tetr. pyram. (central at. – over the center of square)  	d^8: $[Mn(CO)_5]^-$, $Fe(CO)_5$, $[CuCl_5]^{3-}$ ($3d^9 \longrightarrow 3d^8 4d^1$), $[Pt(SnCl_3)_5]^{3-}$, d^7: $Mn(CO)_4(NO)$ (r.), $[NiBr_3(PEt_3)_2]$
	d^2sp^2, 90°	AX_5	5		d^6: $[RuCl_2(PR_3)_3]$ d^4: $[Et_4N]_2[MnCl_5]$
	d^3sp	AX_5	5	trig. bipyr.	d^0: $NbCl_5$, $VHal_5$
	d^4s, 90°	AX_5	5	tetr. bipyr. 	d^2: $VCl_3(SMe_2)_2$, $[Mo(CN)_5]^-$, $[ReOHal_4]^-$
6	sp^3d^2, 90°	AX_6	6	oct. 	$[Mg(H_2O)_6]^{2+}$, $[AlF_6]^{3-}$, $[Pb(OH)_6]^{2-}$, $[PCl_6]^-$, d^{10}: AgCl, $[InF_6]^{3-}$, $[Sb(OH)_6]^-$, TeF_6, IOF_5 d^9: $K_2[CuCl_4]$; d^8: $[AuBr_6]^{3-}$ high-spin: d^7: $[Fe^I(NO)^+(H_2O)_5]^{2+}$; d^6: $[Fe(H_2O)_6]^{2+}$, $[CoF_6]^{3-}$; d^5: $[Mn(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$; d^4: $[Cr(H_2O)_6]^{2+}$, $Mn(C_2O_4)_3]^{3-}$
		AX_5E	5	tetr. pyram. (ψ-oct.) 	$[SbF_5]^{2-}$, $[SF_5]^-$, $HalF_5$, $[HalOF_4]^-$, $[XeF_5]^+$
		AX_4E_2	4	square (ψ-oct.) 	$[ICl_4]^-$, XeF_4

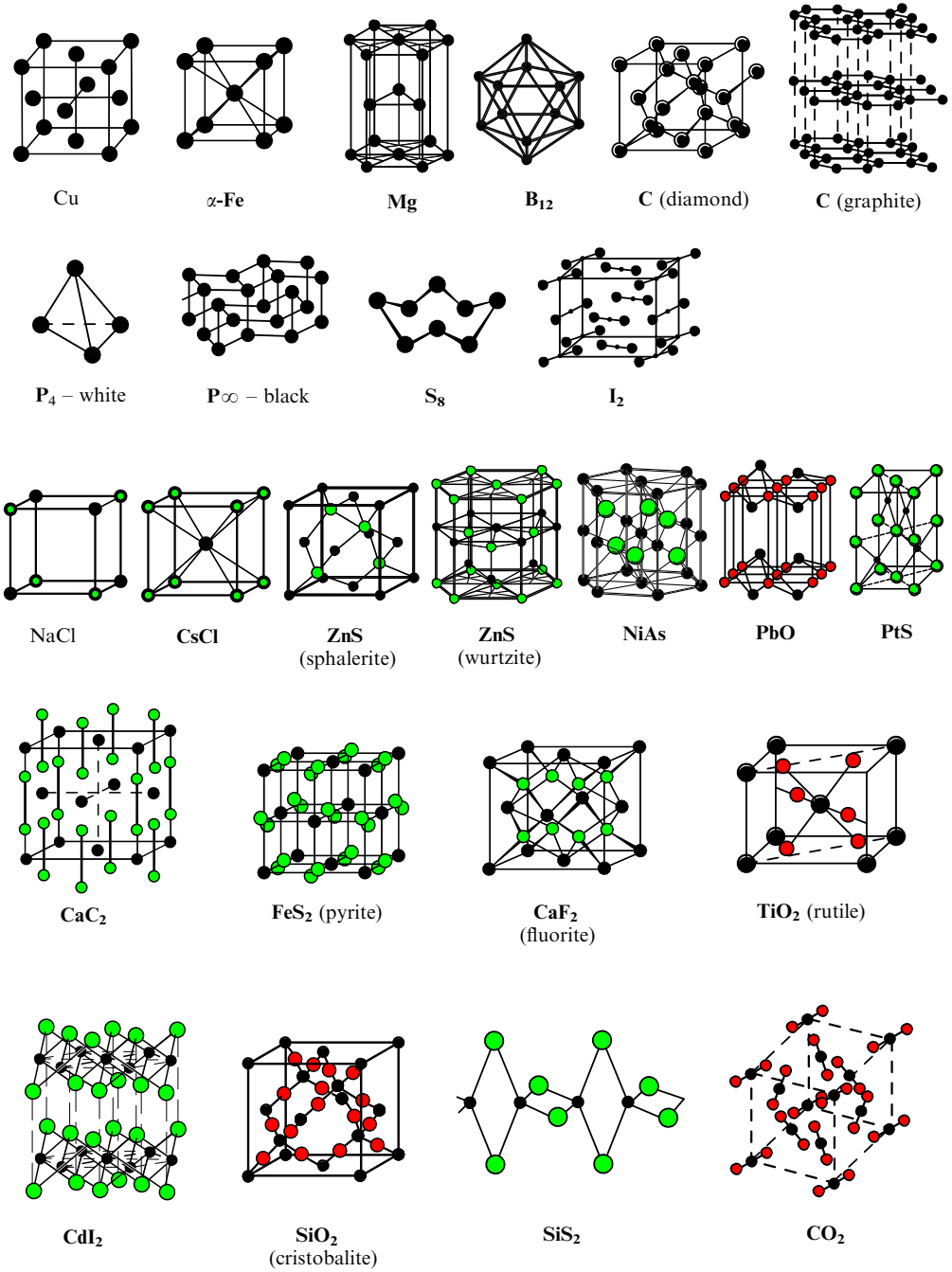
N. Turova, *Inorganic Chemistry in Tables*, DOI 10.1007/978-3-642-20487-6_45, © Springer-Verlag Berlin Heidelberg 2011

Number of el. pairs	Valence state, val. angle	Type of mol. or ion	CN	Spatial configuration	Examples
6	d^2sp^3, 90°	AX_6	6	oct.	low spin: d^7: $[Os(NH_3)_6]^+$, $[NiF_6]^{3-}$; d^6: $Cr(CO)_6$, $[Mn(CN)_6]^{5-}$; d^5: $[Mn(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, d^4: $[TiDipy_3]$, $[Mo(CN)_6]^{4-}$, d^3: $[V(H_2O)_6]^{2+}$, $[Cr(NH_3)_6]^{3+}$, PtF_6; d^2: $[V(H_2O)_6]^{3+}$, $[CrF_6]^{2-}$, RuF_6; d^1: $[Ti(H_2O)_6]^{3+}$, $[VF_6]^{2-}$, $[MoF_6]^-$, ReF_6, $OsOF_5$; d^0: $[Sc(OH)_6]^{3-}$, $[TiHal_6]^{2-}$, $[VF_6]^-$, $[ReO_3Cl_3]^{2-}$, $[OsO_4(OH)_2]^{2-}$
	d^4sp (?)	AX_5E	6	trig. prism 	d^2: MoS_2, WS_2
7	sp^3d^3, sp^3d^2f (?)	AX_7	7	pentag. bipyr. 	IF_7
		AX_6E	6	dist. oct. (ψ-pentag. . bipyr. or ψ-single-cap. oct.) 	$[IF_6]^-$, XeF_6 (gas), $[XeOF_5]^-$
		AX_5E_2	5	flat pentagon (ψ-pentag. bipyr.)	$[XeF_5]^-$
	d^5sp, d^4sp^2, d^3sp^3	AX_7	7	pentag. bipyr.	d^0: $(NH_4)_3[ZrF_7]$, OsF_7; d^1: OsF_7; d^2: $[V(CN)_7]^{4-}$; d^3: $[Mo(CN)_7]^{4-}$; d^4: $[Re(CN)_7]^{4-}$
			7	single-cap. oct. 	d^0: $[NbOF_6]^{3-}$
			7	single-cap. trig. prism 	d^0: $[NbF_7]^{2-}$, $[TaF_7]^{2-}$, LnO(OH), YO(OH)

Number of el. pairs	Valence state, val. angle	Type of mol. or ion	CN	Spatial configuration	Examples
8	sp^3d^4, d^4sp^3	AX_8	8	antiprism (∠ 45° – Archimedes antiprism) 	$[XeF_8]^{2-}$, $[Ba(H_2O)_8]^{2+}$, $Zr[IO_3]_4$, $[TaF_8]^{3-}$, $[W(CN)_8]^{2-}$, $[ReF_8]^{2-}$, $[Eu(H_2O)_6Cl_2]^+$
				cube	ThO_2, UO_2, $(NH_3)_4[U(C_2O_4)_4]$
			8	dodecah. 	$Ti(NO_3)_4$, $[ZrF_8]^{4-}$, $[Co(NO_3)_4]^{2-}$, $[Cr^V(O_2)_4]^{3-}$, $[Mo(CN)_8]^{2-}$, $[Fe(NO_3)_4]^-$, $[Re(CN)_8]^{3-}$
				hex. bipyr. 	$[UO_2(H_2O)_6]^{2+}$
9		AX_9	9	tetr. single-cap prism	Li_3ThI_7
				three-cap trig. prism 	$PbCl_2$, $EuCl_2$, $[Nd(H_2O)_9]^{3+}$, $[Th(SO_4)_4]^{4-}$, $K_2[PaF_7]$, UCl_3, $[ReH_9]^{2-}$, $Tl(NO_3)_3 \cdot 3H_2O$
	sp^3d^5	AX_8E	8	square antiprism	$[XeF_8]^{2-}$
10		AX_{10}	10	square prism with 2 centered facec 	$[Th(tropolonat)_5]^-$
				pentag. bipyr.	$[UO_2(C_2O_4)_2]^{2-}$
11		AX_{11}	11	trig. prism with a centred bases and edges 	LnF_3, UF_3, $Th(NO_3)_4 \cdot 5H_2O$
12		AX_{12}	12	icosah.  (cuboct. and hex. anal. occur in ionic cr.)	$La_2(SO_4)_3 \cdot 9H_2O$, $[Ce(NO_3)_6]^{3-}$, $[Th(NO_3)_6]^{2-}$, $[UO_2(C_2O_4)_3]^{4-}$

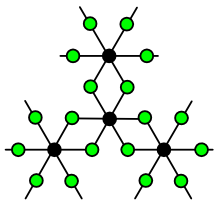
MAIN TYPES OF CRYSTAL STRUCTURES

Formula		Str. type	CN and polyhedron of central at.	CN and polyhedron of ligand
Simple subst.	**Cu**	cub. cl. pack	12, cubooct.	—
	α-Fe	cub. body-centred	8, cub.	—
	Mg	hex. cl. pack	12, hex. anal. of cubooct.	—
	B_{12}	tetr.	5(=8–3), pentag. pyram.	
	C (diamond)	cub.	4(= 8–4), tetrah.	—
	C (graphite)	hex.	3, triangle	—
	P_4 – white	cub.	3 (= 8–5), trig. pyram., ∠PPP 60	—
	P∞ – black	rh.	3, trig. pyram.	—
	S_8	rh.	2 (= 8–6), ∠SSS 108	—
	I_2	rh.	1 (= 8–7)	—
	CN = 8–№ gr. (Hume-Rothery principle)			
Comp. **AX** type	**NaCl**	cub.	6, oct.	6, oct.
	CsCl	cub.	8, cube	8, cube
	ZnS (sphalerite)	cub.	4, tetrah.	4, tetrah.
	ZnS (wurtzite)	hex.	4, tetrah.	4, tetrah.
	= ZnO	hex.	6, oct.	6, oct.
	NiAs			
	BN white (graphite str. type)	hex.	3, triangle	3, triangle
	PbO	tetr.	4, tetr. pyram.	4, tetrah.
	PtS	tetr.	4, square	4, tetrah.
Comp. **AX_2** type	**CaC_2**	tetr.	10 and 2, tetr. pyram,	5, tetr. pyram.
	FeS_2 (pyrite)	cub.	6, oct.	4, tetrah.
	CaF_2 (fluorite)	cub.	8, cub.	4, tetrah.
	$PbCl_2$	rh.	9, three-cap trig. prism	{ 4, tetrah. { 5, pentag. pyram.
	TiO_2 (rutile)	tetr.	6, oct.	3, triangle
	CdI_2	hex.	6, oct.	3, trig. pyram.
	$CdCl_2$	rhombohe-dral	6, oct.	3, trig. pyram.
	SiO_2 (cristobalite)	cub.	4, tetrah.	2, dumb-bell
	SiS_2	rh.	4, tetrah.	2, angular
	CO_2	cub.	2, dumb-bell	1

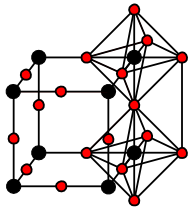


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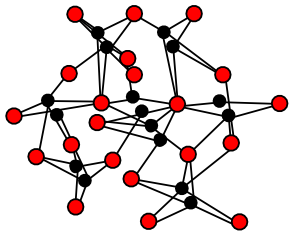
Formula		Str. type	CN and polyhedron of central at.	CN and polyhedron of ligand
Comp. AX_3 type	$FeCl_3$	rhombohe-dral	6, oct.	3, trig. pyram.
	ReO_3	cub.	6, oct.	2, dumb-bell
	$PuBr_3$	rh.	8, dist. [$PuBr_8$]	3, trig. pyram. 2, angular
	UCl_3	hex.	9, three-cap. trig. prism	3, trig. pyram.
	LaF_3	hex.	3(triangle) + 6(prism) + + 2(ax.) = 11	4, tetrah.
	YF_3	rh.	9 = 8 + 1	3, triangle —
Comp AX_4 type	UCl_4	tetr.	4 (dist. tetrah.) + + 4 (μ) = 8	2, angular
	ZrF_4	monocl.	8, antiprism	2, angular
Comp A_2O_3 type	α-Al_2O_3 (corundum)	rhombo-hedral	6, dist. oct.	4, dist. tetrah.
	Mn_2O_3	cube	6 (vertex of cube)	4, tetrah.
	La_2O_3	hex.	7, single-cap oct.	4 (= 3 + 1)
Triple comp.	$MgAl_2O_4$ (spinel)	cub.	Mg – 4, tetrah. Al – 6, oct.	4, tetrah. (= 3Al + 1Mg)
	$CaTiO_3$ (perovskite)	rh.(pseudo-cub.)	Ca – 12, cubooct. (cube from 4 gr. [TiO_3]) Ti – 6, oct.	2 Ti + 4 Ca (tetr. bipyr.)
	K_2PtCl_6	cub. (*anti*-CaF_2 type)	K – 12, cubooct. (tetrah. from 4 gr. [$PtCl_6$]) Pt – 6, oct.	2Pt + 4K (tetr. bipyr.)
	K_2NiF_4	tetr.	K – 9 Ni – 6, dist. oct.	2 Ni
Gas hydrates (clathrates) **8 X · 46 H_2O**, X = Cl_2, H_2S, CO_2, CH_4, Xe, N_2O, AsH_3, Ne–Rn **6 X · 46 H_2O**, X = Br_2, SO_2, inclusion comp. "guest" in the str. of ice		cub., a = 12	20 H_2O, pentagondodecah.	



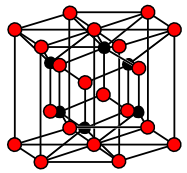
$FeCl_3$



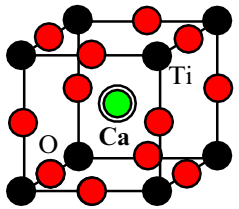
ReO_3



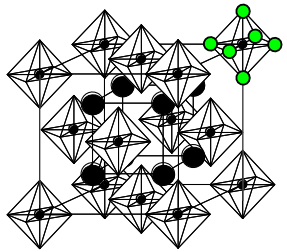
α-Al_2O_3 (corundum)



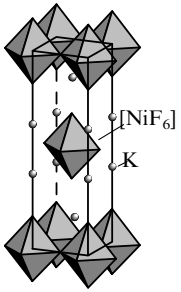
La_2O_3



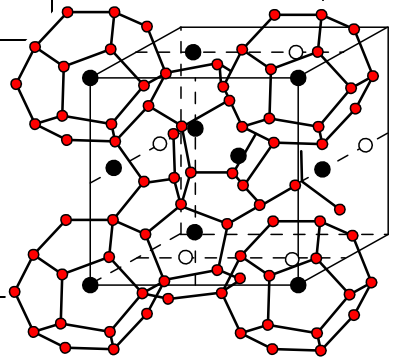
$CaTiO_3$ (perovskite)



K_2PtCl_6



K_2NiF_4



X · 5.75 H_2O (8:46)

central at.

Hal, S, C

O

EFFECTIVE IONIC RADII *(r)*

The listed data are based on r O^{2-} =1.40 Å (CN 6), e.g., in the $M^{II}O$ structures. However, in the solid state physics, the so-called crystal *r* are larger than ionic radii by 0.14 Å, exclusion the cases Ha^{l-}, H^{+}, N^{3-}, N^{5-}, E^{2-} (E=O, S, Se, Te) and OH^{-}, for which they are smaller by 0.14 Å (Shannon R.D., Acta Crystallogr., 1976, **A32,** 751).

Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*
Ac^{3+}	6	1.12	B^{3+}	3	0.01	Ca^{2+}	6	1.00	Cm^{3+}	6	0.97	Cu^{2+}	4	0.57	Fe^{2+}	4	0.63	Hg^{2+}	2	0.69	La^{3+}	6	1.03
Ag^{1+}	2	0.67		4	0.11		7	1.06	Cm^{4+}	6	0.85		5	0.65		6	0.78		4	0.96		7	1.10
	4	1.00		6	0.27		8	1.12		8	0.95		6	0.73		8	0.92		6	1.02		8	1.16
	5	1.09	Ba^{2+}	6	1.35		9	1.18	Co^{2+}	4	0.58	Cu^{3+}	6	0.54	Fe^{3+}	4	0.49		8	1.14		9	1.22
	6	1.15		7	1.38		10	1.23		5	0.67	Dy^{2+}	6	1.07		5	0.58	Ho^{3+}	6	0.90		10	1.27
	7	1.22		8	1.42		12	1.34		6	0.74		7	1.13		6	0.64		8	1.01		12	1.36
	8	1.28		9	1.47	Cd^{2+}	4	0.78		8	0.90		8	1.19		8	0.78		9	1.07	Li^{1+}	4	0.59
Ag^{2+}	4	0.79		10	1.52		5	0.87	Co^{3+}	6	0.61	Dy^{3+}	6	0.91	Fe^{4+}	6	0.58	Ho^{3+}	10	1.12		6	0.76
	6	0.94		11	1.57		6	0.95	Co^{4+}	4	0.40		7	0.97	Fe^{6+}	4	0.25	I^{1-}	6	2.20		8	0.92
Ag^{3+}	4	0.67		12	1.61		7	1.03		6	0.53		8	1.03	Fr^{1+}	6	1.80	I^{5+}	3	0.44	Lu^{3+}	6	0.86
	6	0.75	Be^{2+}	3	0.16		8	1.10	Cr^{2+}	6	0.73		9	1.08	Ga^{3+}	4	0.47		6	0.95		8	0.98
Al^{3+}	4	0.39		4	0.27		12	1.31	Cr^{3+}	6	0.61	Er^{3+}	6	0.89		5	0.55	I^{7+}	4	0.42		9	1.03
	5	0.48		6	0.45	Ce^{3+}	6	1.01	Cr^{4+}	4	0.41		7	0.94		6	0.62		6	0.53	Mg^{2+}	4	0.57
	6	0.53	Bi^{3+}	5	0.96		7	1.07		6	0.55		8	1.00	Gd^{3+}	6	0.94	In^{3+}	4	0.62		5	0.66
Am^{2+}	7	1.21		6	1.03		8	1.14	Cr^{5+}	4	0.34		9	1.06		7	1.00		6	0.80		6	0.72
	8	1.26		8	1.17		9	1.19		6	0.49	Eu^{2+}	6	1.17		8	1.05		8	0.92		8	0.89
	9	1.31	Bi^{5+}	6	0.76		10	1.25		8	0.57		7	1.20		9	1.11	Ir^{3+}	6	0.68	Mn^{2+}	4	0.66
Am^{3+}	6	0.97		8	0.96		12	1.34	Cr^{6+}	4	0.26		8	1.25	Ge^{2+}	6	0.73	Ir^{4+}	6	0.62		5	0.75
	8	1.09	Bk^{3+}	6	0.83	Ce^{4+}	6	0.87		6	0.44		9	1.30	Ge^{4+}	4	0.39	Ir^{5+}	6	0.57		6	0.83
Am^{4+}	6	0.85		8	0.93		8	0.97	Cs^{1+}	6	1.67		10	1.35		6	0.53	K^{1+}	4	1.37		7	0.90
	8	0.95	Br^{1-}	6	1.96		10	1.07		8	1.74	Eu^{3+}	6	0.95	H^{1+}	1	0.38		6	1.38		8	0.96
As^{3+}	6	0.58	Br^{3+}	4	0.59		12	1.14		9	1.78		7	1.01		2	0.18		7	1.46	Mn^{3+}	5	0.58
As^{5+}	4	0.33	Br^{5+}	3	0.31	Cf^{3+}	6	0.95		10	1.81		8	1.07	Hf^{4+}	4	0.58		8	1.51		6	0.58
	6	0.46	Br^{7+}	4	0.25	Cf^{4+}	6	0.82		11	1.85		9	1.12		6	0.71		9	1.55			0.64
At^{7+}	6	0.62		6	0.39		8	0.92		12	1.88	F^{1-}	2	1.28		7	0.76		10	1.59	Mn^{4+}	4	0.39
Au^{1+}	6	1.37	C^{4+}	3	0.08	Cl^{1-}	6	1.81	Cu^{1+}	2	0.46		3	1.30		8	0.83		12	1.64		6	0.53
Au^{3+}	4	0.68		4	0.15	Cl^{5+}	3	0.12		4	0.60		4	1.31	Hg^{1+}	3	0.97				Mn^{5+}	4	0.33
	6	0.85		6	0.16	Cl^{7+}	4	0.08		6	0.77		6	1.33		6	1.19				Mn^{6+}	4	0.25
Au^{5+}	6	0.57					6	0.27															

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Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*	Ion	C N	*r*
Mn^{7+}	4	0.25	Nd^{3+}	12	1.27	Pa^{3+}	6	1.04	Pr^{4+}	8	0.96	S^{2-}	6	1.84	Sr^{2+}	10	1.36	Ti^{4+}	6	0.60	V^{5+}	6	0.54
	6	0.46	Ni^{2+}	4	0.55	Pa^{4+}	6	0.90	Pt^{2+}	4	0.60	S^{4+}	6	0.37		12	1.44		8	0.74	W^{4+}	6	0.66
Mo^{3+}	6	0.69		5	0.63		8	1.01		6	0.80	S^{6+}	4	0.12	Ta^{3+}	6	0.72	Tl^{1+}	6	1.50	W^{5+}	6	0.62
Mo^{4+}	6	0.65		6	0.69	Pa^{5+}	6	0.78	Pt^{4+}	6	0.62		6	0.29	Ta^{4+}	6	0.68		8	1.59	W^{6+}	4	0.42
Mo^{5+}	4	0.46	Ni^{3+}	6	0.56		8	0.91	Pt^{5+}	6	0.57	Sb^{3+}	4	0.76	Ta^{5+}	6	0.64		12	1.70		5	0.51
	6	0.61	Ni^{4+}	6	0.48		9	0.95	Pu^{3+}	6	1.00		5	0.80		7	0.69	Tl^{3+}	4	0.75		6	0.60
Mo^{6+}	4	0.41	No^{2+}	6	1.1	Pb^{2+}	4	0.98	Pu^{4+}	6	0.86		6	0.76		8	0.74		6	0.88	Xe^{8+}	4	0.40
	5	0.50	Np^{2+}	6	1.10		6	1.19		8	0.96	Sb^{5+}	6	0.60	Tb^{3+}	6	0.92		8	0.98		6	0.48
	6	0.59	Np^{3+}	6	1.01		7	1.23	Pu^{5+}	6	0.74	Sc^{3+}	6	0.74		7	0.98	Tm^{2+}	6	1.03	Y^{3+}	6	0.90
	7	0.73	Np^{4+}	6	0.87		8	1.29	Pu^{6+}	6	0.71		8	0.87		8	1.04		7	1.09		7	0.96
N^{3-}	4	1.46		8	0.98		9	1.35	Ra^{2+}	8	1.48	Se^{2-}	6	1.98		9	1.09	Tm^{3+}	6	0.88		8	1.02
N^{3+}	6	0.16	Np^{5+}	6	0.75		10	1.40		12	1.70	Se^{4+}	6	0.50	Tb^{4+}	6	0.76		8	0.99		9	1.07
N^{5+}	3	0.10	Np^{6+}	6	0.72		11	1.45	Rb^{1+}	6	1.52	Se^{6+}	4	0.28		8	0.88		9	1.05	Yb^{2+}	6	1.02
	6	0.13	Np^{7+}	6	0.71		12	1.49		7	1.56		6	0.42	Tc^{4+}	6	0.64	U^{3+}	6	1.02		7	1.08
Na^{1+}	4	0.99	O^{2-}	2	1.35	Pb^{4+}	4	0.65		8	1.61	Si^{4+}	4	0.26	Tc^{5+}	6	0.60	U^{4+}	6	0.89		8	1.14
	5	1.00		3	1.36		5	0.73		9	1.63		6	0.40	Tc^{7+}	4	0.37		7	0.95	Yb^{3+}	6	0.87
	6	1.02		4	1.38		6	0.77		10	1.66	Sm^{2+}	7	1.22		6	0.56		8	1.00		7	0.92
	7	1.12		6	1.40		8	0.94		11	1.69		8	1.27	Te^{2-}	6	2.21		9	1.05		8	0.98
	8	1.18		8	1.42	Pd^{1+}	2	0.59		12	1.72		9	1.32	Te^{4+}	3	0.52		12	1.17		9	1.04
	9	1.24	OH^{1-}	2	1.32	Pd^{2+}	4	0.64		14	1.83	Sm^{3+}	6	0.96		4	0.66	U^{5+}	6	0.76	Zn^{2+}	4	0.60
	12	1.39		3	1.34		6	0.86	Re^{4+}	6	0.63		7	1.02		6	0.97		7	0.84		5	0.68
Nb^{3+}	6	0.72		4	1.35	Pd^{3+}	6	0.76	Re^{5+}	6	0.58		8	1.08	Te^{6+}	4	0.43	U^{6+}	2	0.45		6	0.74
Nb^{4+}	6	0.68		6	1.37	Pd^{4+}	6	0.61	Re^{6+}	6	0.55		9	1.13		6	0.56		4	0.52		8	0.90
	8	0.79	Os^{4+}	6	0.63	Pm^{3+}	6	0.97	Re^{7+}	4	0.38		12	1.24	Th^{4+}	6	0.94		6	0.73	Zr^{4+}	4	0.59
Nb^{5+}	4	0.48	Os^{5+}	6	0.57		8	1.09		6	0.53	Sn^{4+}	4	0.55		8	1.05		7	0.81		5	0.66
	6	0.64	Os^{6+}	5	0.49		9	1.14	Rh^{3+}	6	0.66		5	0.62		9	1.09		8	0.86		6	0.72
	7	0.69		6	0.54	Po^{4+}	6	0.94	Rh^{4+}	6	0.60		6	0.69		10	1.13	V^{2+}	6	0.79		7	0.78
	8	0.74	Os^{7+}	6	0.52		8	1.08	Rh^{5+}	6	0.55		7	0.75		11	1.18	V^{3+}	6	0.64		8	0.84
Nd^{2+}	8	1.29	Os^{8+}	4	0.39	Po^{6+}	6	0.67	Ru^{3+}	6	0.68		8	0.81		12	1.21	V^{4+}	5	0.53		9	0.89
	9	1.35	P^{3+}	6	0.44	Pr^{3+}	6	0.99	Ru^{4+}	6	0.62	Sr^{2+}	6	1.18	Ti^{2+}	6	0.86		6	0.58			
Nd^{3+}	6	0.98	P^{5+}	4	0.17		8	1.13	Ru^{5+}	6	0.56		7	1.21	Ti^{3+}	6	0.67		8	0.72			
	8	1.11		5	0.29		9	1.18	Ru^{7+}	4	0.38		8	1.26	Ti^{4+}	4	0.42	V^{5+}	4	0.35			
	9	1.16		6	0.38	Pr^{4+}	6	0.85	Ru^{8+}	4	0.36		9	1.31		5	0.51		5	0.46			

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