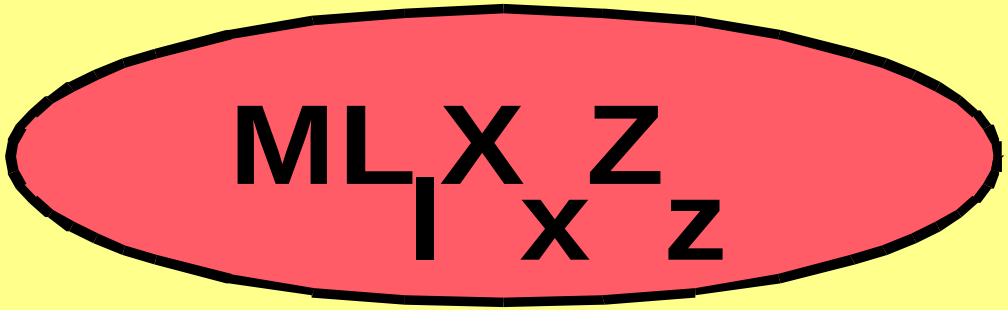
This presentation is 15 years old and without the spoken accompaniment it is difficult to follow. However, some of the slides might be useful.

Definition of the Class of a Covalent Compound

M= is the element whose compound is to be classified

The general class of ALL compunds of M is given by



Definitions of Ligand Class

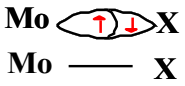
Monofunctional Ligands.
The functions are in class X, L, or Z.

1) The X-class.
An X ligand function donates one electron to the formation of the bond.

2) The L-class.
An L ligand funnction donates rwo electrons to the formation of the bond.

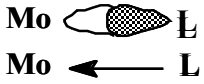
3) The Z-class
A Z ligand donates NO electrons to the formation of the bond BUT receives TWO electrons from the bond

σ-bond



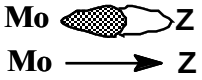
Class X

dative σ-bond



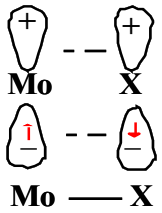
Class L

acceptor σ-bond



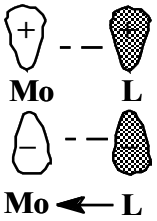
Class Z

π-bond



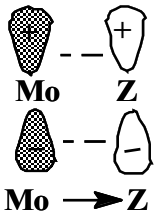
Class X

dative π-bond



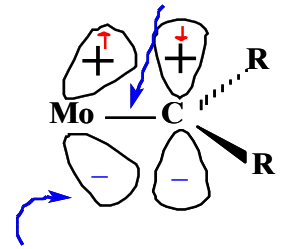
Class L

acceptor π-bond

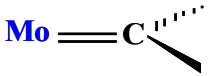


Class Z

a σ-bond, X-function



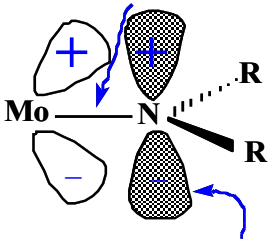
a π-bond, X - function



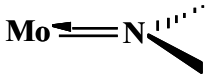
Class $\overline{X}_2$

(i)

a σ-bond, X-function



a π-bond, L-function

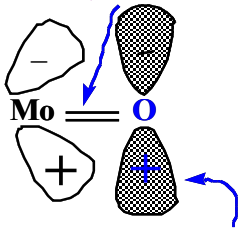


Class $\overline{LX}$

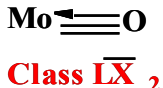
(ii)

a σ-bond, X-function

a π-bond, X-function



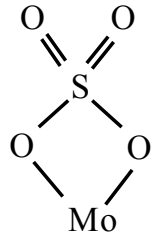
a π-bond, L-function



Class $\overline{LX}_2$

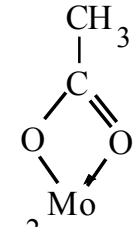
(iii)

Mono- and poly-functional Ligands



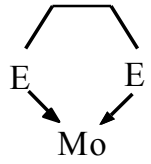
η^2-sulphato

Class X_2



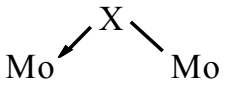
η^2-acetato

Class LX



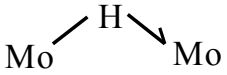
E = PR_2, NR_2 , SR, OR

Class L_2



X = Cl, Br, I, SR, NR_2

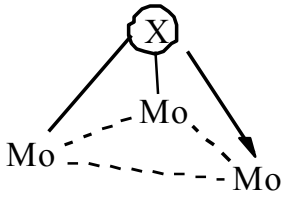
Class X-μ -L



μ-hydrido

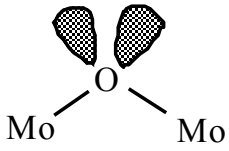
Class X -μ - L

(i)



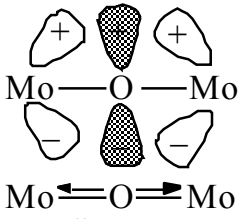
X = O, S, Se

Class X_2- μ^2- L



Class X-μ-X

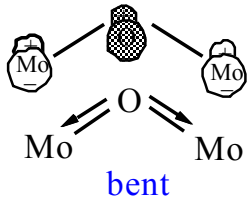
(ii)



linear

Class LX--μ-LX

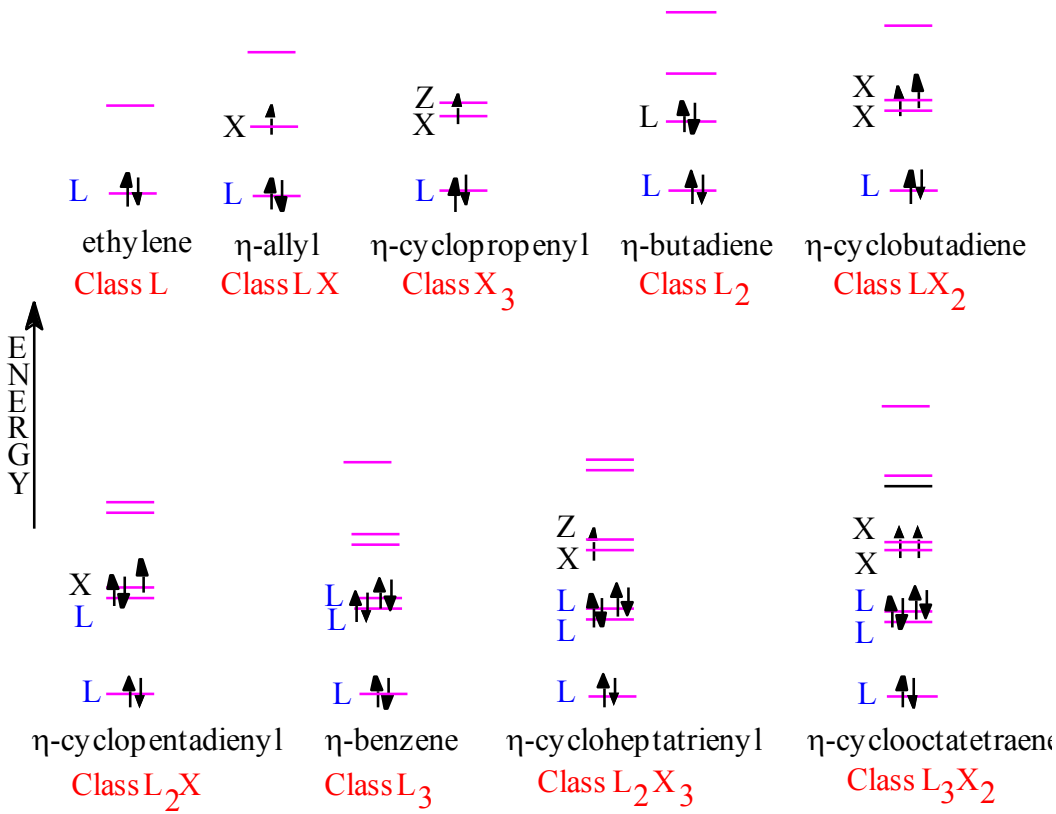
(iii)



bent

Class LX--μ-LX

Figure 3. Examples of polydentate and bridging ligands


ENERGY
L
ethylene
Class L
X
L
η-allyl
Class L X
Z
X
L
η-cyclopropenyl
Class X3
L
η-butadiene
Class L2
X
X
L
η-cyclobutadiene
Class LX2
X
L
L
η-cyclopentadienyl
Class L2X
L
L
L
η-benzene
Class L3
Z
X
L
L
L
η-cycloheptatrienyl
Class L2X3
X
X
L
L
L
η-cyclooctatetraene
Class L3X2

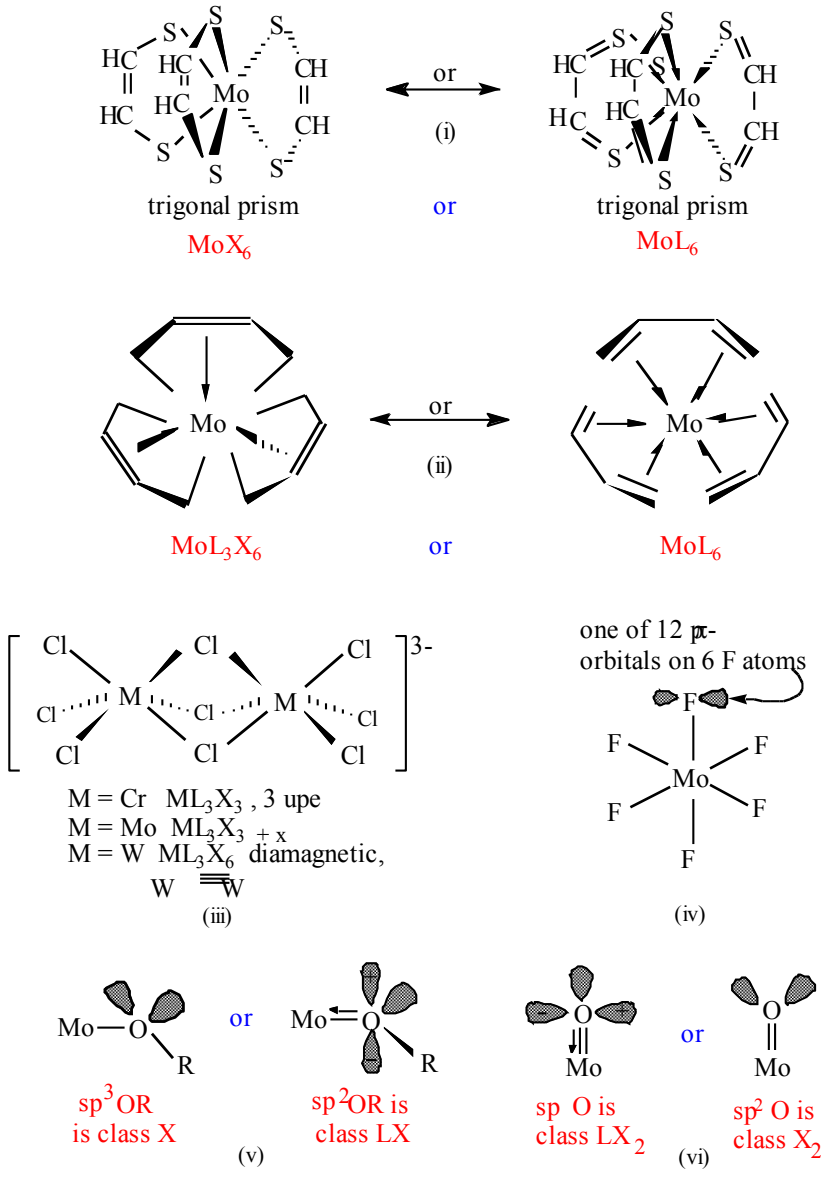


Figure 5. Non-innocent ligand systems.

Table 8. Examples of ligands with poly-functional ligating atoms.

Ligand	Class	Representation	Examples.
O	$\bar{X}_2$	M = O	
	$\bar{X}_2$	M = S	
	$\bar{X}_2$	M = NR	
	$\bar{X}_2$	M = CR_2	
	$\bar{X}_3$	M ≡ C	
	$\bar{X}_3$	M ≡ N	
	$\bar{X}L$ [b]		
	$\bar{X}_4$	M ≡ M	

[a] Re-N = 1.79Å [b] For reduction to E.Q.N. is $\bar{X}L \rightleftharpoons L_2$

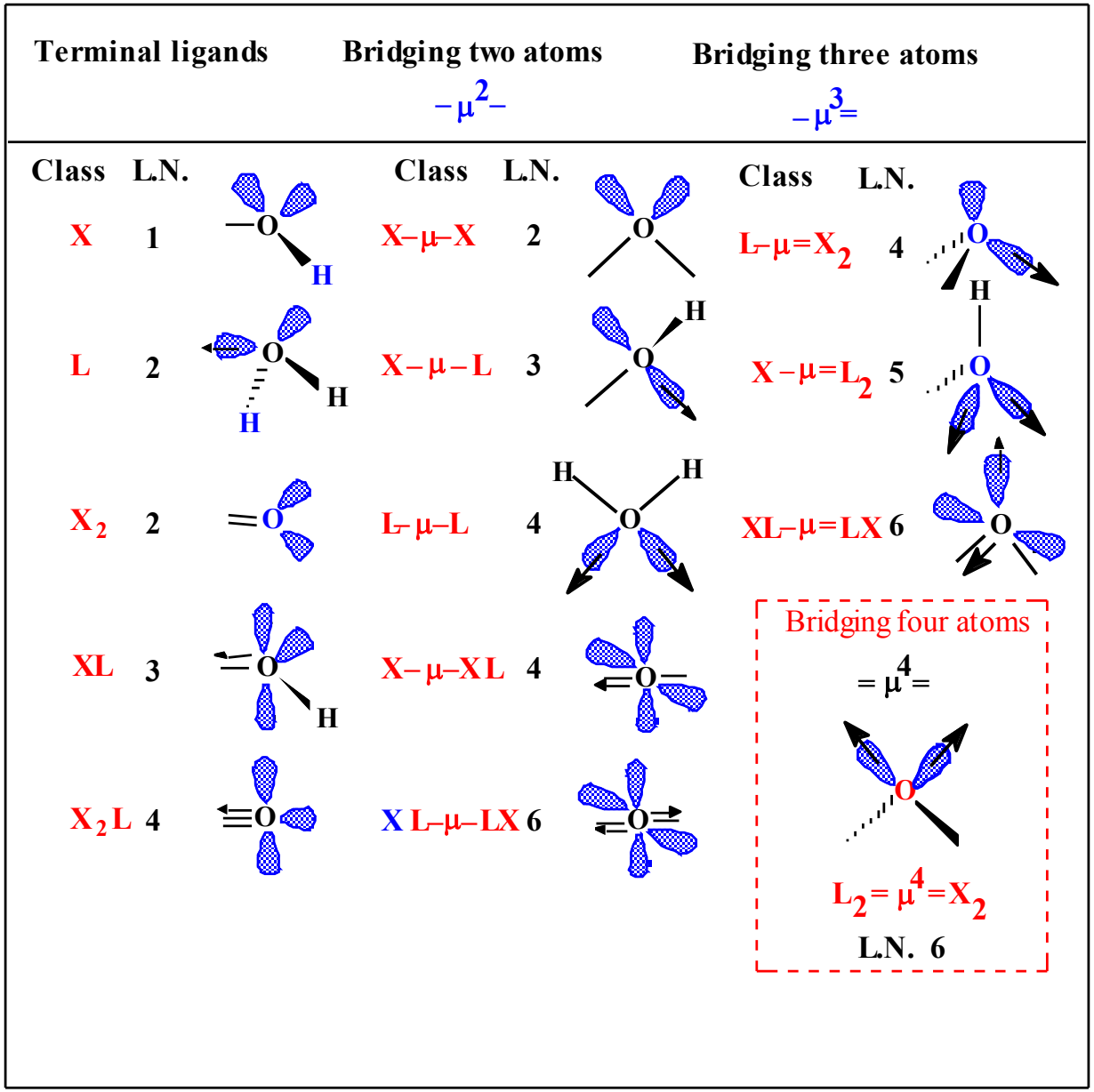


Figure 12. Classification of ligands found in aqueous systems

Table 1.Typical ligands found in molybdenum chemistry classified according to the number of electrons required for bonding (x), the number of electrons donated to the molybdenum (L.N.) and the $L_lX_XZ_Z$ class.‡

x Electrons required by ligand	L.N. Electrons donated to metal by the ligand	Class	Examples
2	0	Z	BH_3, BF_3, BCl_3, BR_3, $B(C_6F_5)_3$, $AlMe_3$, SiF_4, (generally, Lewis acids)
1	1	X	H
1	1		CR_3, -CR=CR_2, -C≡CR, -COR, -C_6H_5, η^1-CH_2CH=CH_2, η^1-C_5H_5, CF_3, C_6F_5, CH_2CMe_3, CH_2SiMe_3, CH_2CMe_2Ph
1	1		NR_2, OR, -OOR, F
1	1		SiR_3, -PR_2, SR, Cl
1	1		GeR_3, AsR_2, SeR, Br
1	1		SnR_3, I
1	1		CN, SCN, NCS, N_3, OCN, NCO, OSO_2R, ONO, ONO_2, $OClO_3$, $OSiR_3$
1	1		$Mn(CO)_5$, $Fe(\eta$-$C_5H_5)(CO)_2$, $Mo(\eta$-$C_5H_5)(CO)_3$, $Au(PPh_3)$, HgCl,

x Electrons required by ligand	L.N. Electrons donated to metal by the ligand	Class	Examples
2	2	X_2	bidentate with mono-functional ligating atoms, $-SCH_2CH_2S-$, oxalato, o-quinones, $-(S)_2-$, SO_4, CO_3, $-(O)_2-$, metallacycles $-(CH_2)_n-$,, where n = 2*, 3 or 4
2	2	$\boxed{\bar{X}}_2$	
0	2	L	NH_3, NR_3, OH_2, OR_2, PR_3, $P(OR)_3$, SR_2, SeR_2, AsR_3
0	2		CO, $H_2C=CH_2$, $R_2C=CR_2$, RC=CR, $S=CR_2$, N_2, PF_3
0	2		T.H.F., Et_2O, DMSO, RCN, RNC, py
0	2		L-function of X-μ-L-ligands, e.g. in bridging Cl. Also the half-arrow function of agostic hydrogen, see Figure 3 (i).

V.N. x	L.N. Electrons donated	Class	Examples
3	3	$\boxed{\bar{X}}_3$†	
1	3	XL	η-C_3H_5 (generally η-allylic systems,) acac, dmg, η^2-acetato, η-O_2CR, η-S_2CR, η-S_2CNR_2, η-S_2PR_2, $NH_2CH_2CO_2$- (amino acids), BF_4, BH_4,
1	3	$\boxed{\bar{X}}$L†	
4	4	X_4	≡MoX_2L_2, e.g. in $[Mo_2Cl_8]^{4-}$
2	4	X_2L	η-C_4H_4, (generally η-cyclobutadiene derivatives)
2	4	X_2L	NR (linear imido ligands)
0	4	L_2	η-C_4H_6, (dienes generally)*, bipyridyl, o-phenanthroline, ethylenediamine $RS(CH)_2SR$, diphosphines, e.g. diphos(dppe)

x Electrons required	L.N. Electrons donated	Class	Examples
1	**5**	**L_2X**	**η^5-C_5H_5, dienyls generally**
2	**6**	**L_2X_2**	**1,5,-diazacyclooctane-N,N'-diacetate (dacoda)**
0	**6**	**L_3**	**η^6-Benzene, (η^6-arenes generally), η^6-C_7H_8, η^6-COT, $RSi(CH_2PMe_2)_3$**
1	**7**	**L_3X**	**None known**
3	**7**	**L_2X_3**	**η-C_7H_7**
4	**8**	**L_2X_4**	**edta**
2	**8**	**L_3X_2**	**η^8-COT, η^5-$C_5H_4(CH_2)_3NR$**
3	**9**	**L_3X_3**	**η-$C_5H_4(CH_2)_3N$= (linear imido)**
0	**12**	**L_6**	**{$FB(ONCHC_5H_3)_3P$} , $P(bipy)_3$**

How to determine the class of compounds of M which are cations or anions

Rule 1.

X and 1e = X^- = L

1+ 1 2

Rule 2

Lless 1e = L^+ = X

2 - 1 1

Rule 3. when no X available

then L+ 1e = L^- = LX

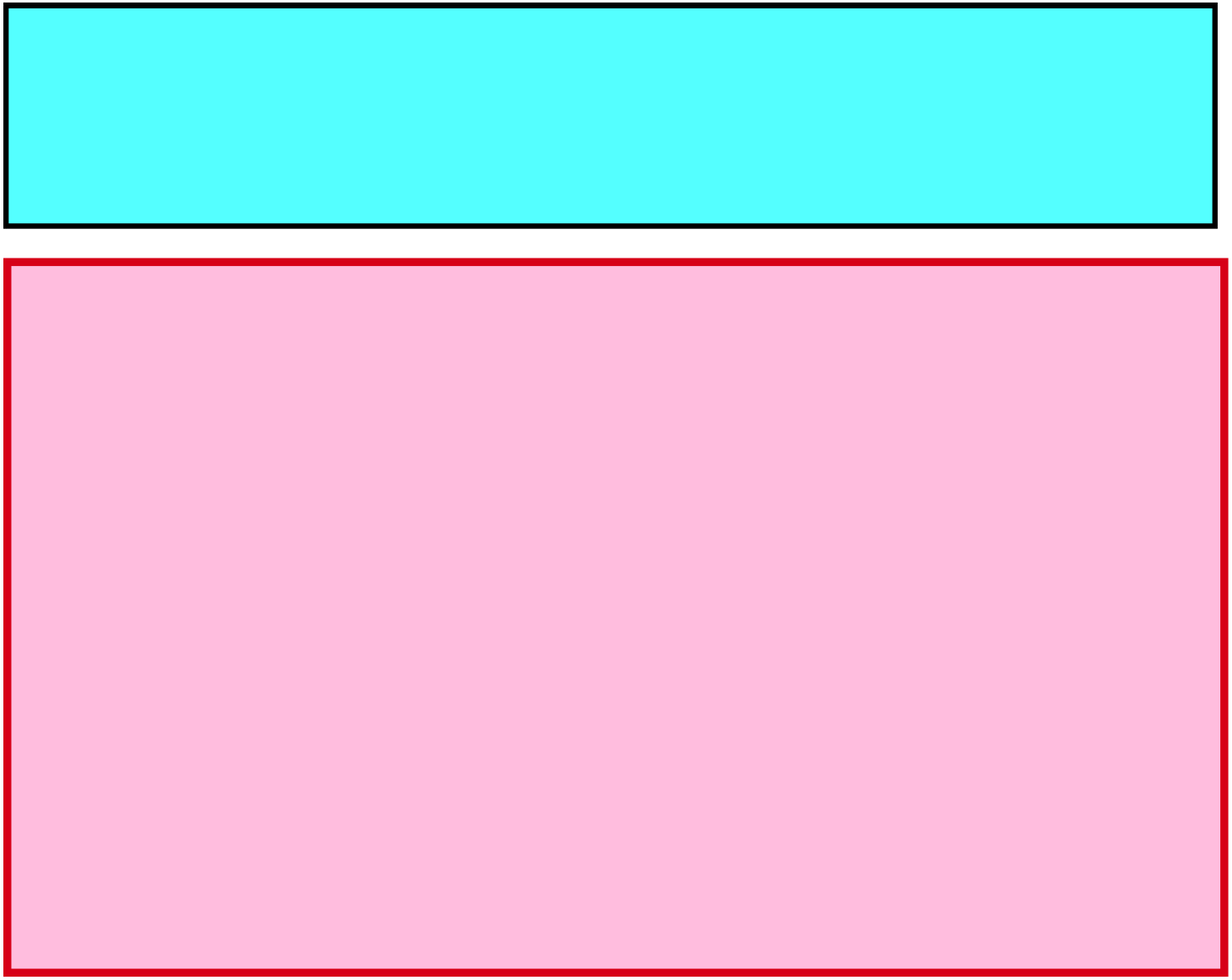
2 + 1 = 3

Rule 4. X^+ = Z

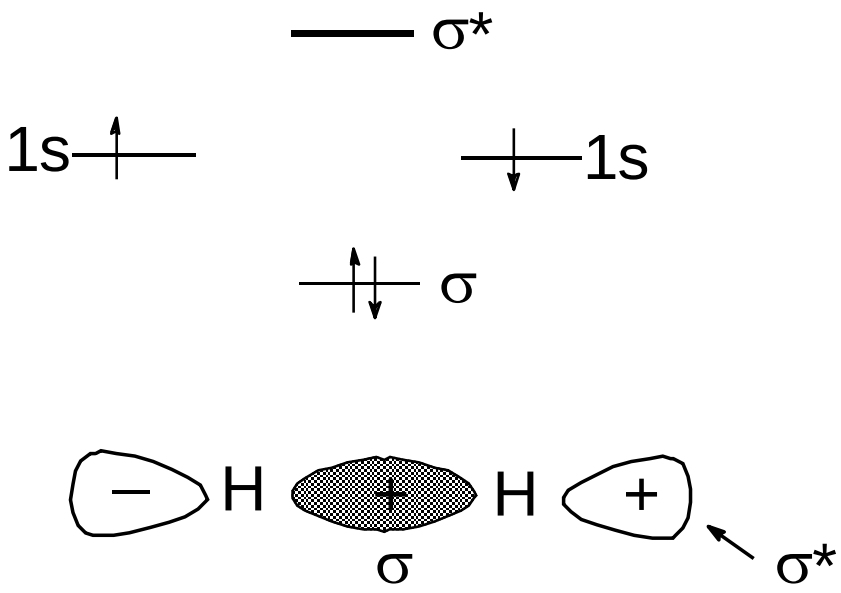
1-1= 0

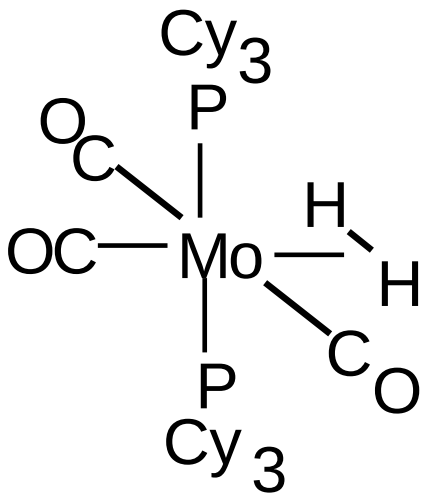
Table 7. Examples of conversion of the classes of ions to the Equivalent Neutral Class

Compound	Molecular ion	Rearrange	**Rule applied**	Equiv.Neutral Class E.N.C.
$[Co(NH_3)_6]^{3+}$	$[ML_6]^{3+}$	$[ML_3(L^+)_3]$	$L^+ = X$	ML_3X_3
$[CoF_6]^{3-}$	$[MX_6]^{3-}$	$[MX_3(X^-)_3]$	$X^- = L$	ML_3X_3
$[Co(NH_3)_4Cl_2]^+$	$[ML_4X_2]^+$	$[ML_3(L^+)X_2]$	$L^+ = X$	ML_3X_3
$[Mn(CO)_5]^-$	$[ML_5]^-$	$[ML_4(L^-)]$	$L^- = LX$	ML_5X
$[Mn(CO)_6]^+$	$[ML_6]^+$	$[ML_5(L^+)]$	$L^+ = X$	ML_5X
$[Co(\eta\text{-}C_5H_5)_2]^+$	$[ML_4X_2]^+$	$[ML_3(L^+)X_2]$	$L^+ = X$	ML_3X_3
$[NiCl_4]^{2-}$	$[MX_4]^{2-}$	$[MX_2(X^-)_2]$	$X^- = L$	ML_2X_2
$[Pt(NH_3)Cl_3]^-$	$[MLX_3]^-$	$[MLX_2(X^-)]$		
$[Cr(CO)_5]^{2-}$	$[ML_5]^{2-}$	$[ML_3(L^-)_2]$	$L^- = LX$	ML_5X_2
$[Ir(PR_3)_2H_6]^+$	$[ML_2X_6]^+$	$[ML(L^+)X_5$	$L^+ = X$	MLX_7
NH_4^+	$[ML_4]^+$	$[MX_3(X^+)]$	$X^+ = Z$	ML_3Z
PCl_4^+	$[ML_4]^+$	$[MX_3(X^+)]$	$X^+ = Z$	ML_3Z

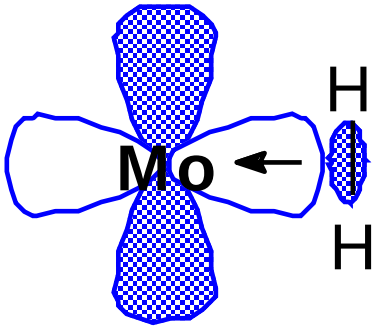


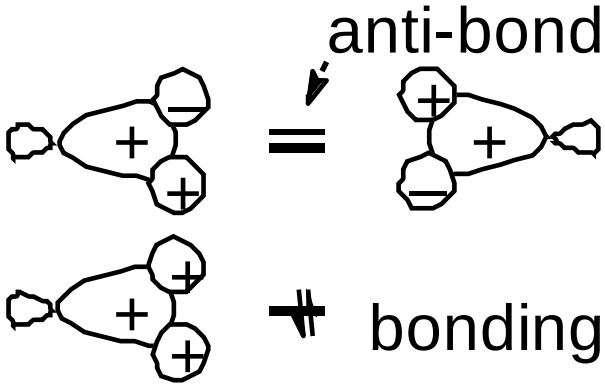
Bonding in H_2

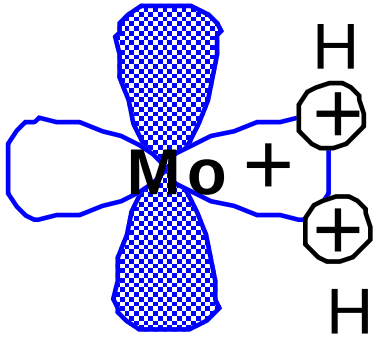




Kubas

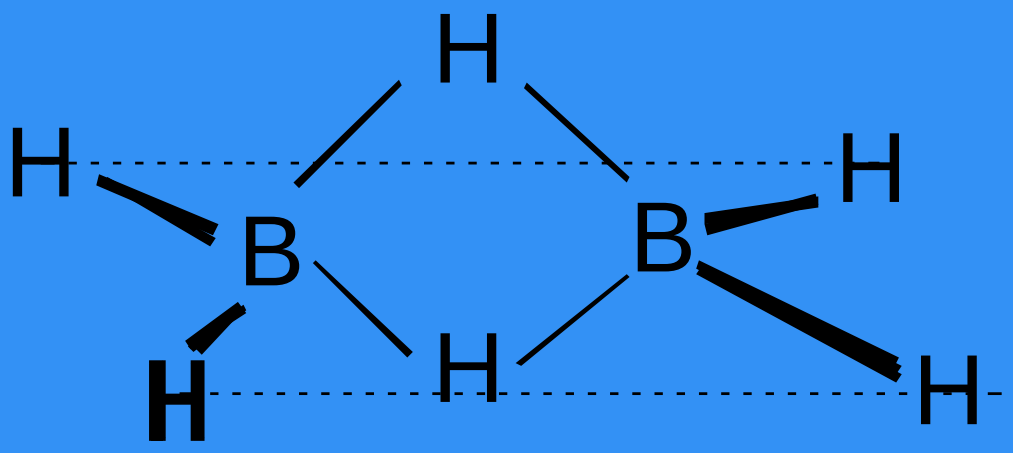






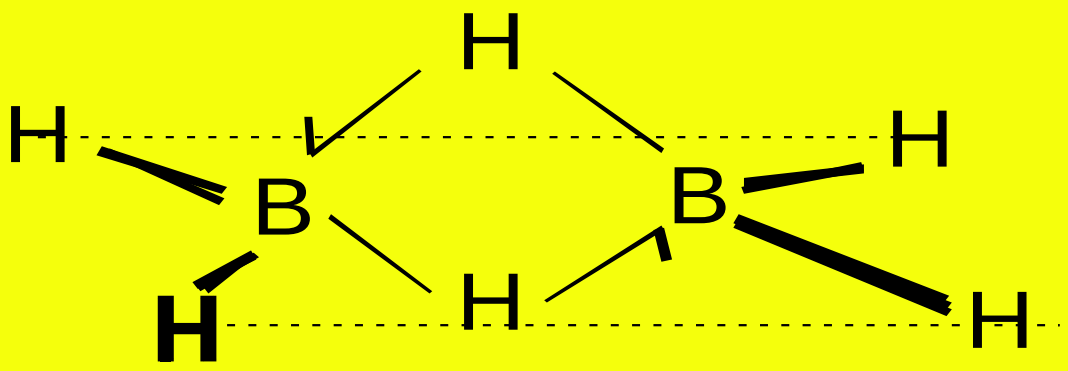
two-electron three-centred bond

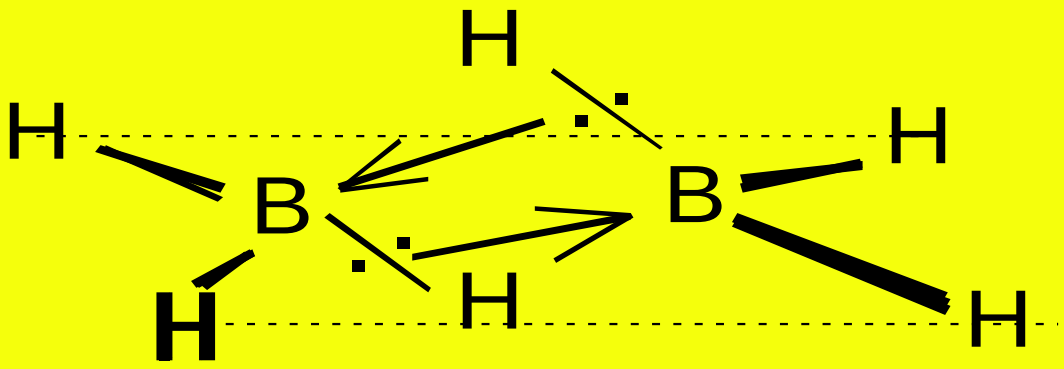
THE CLASSICAL EXAMPLE OF THE THREE-ELECTRON BOND



The Half-arrow convention

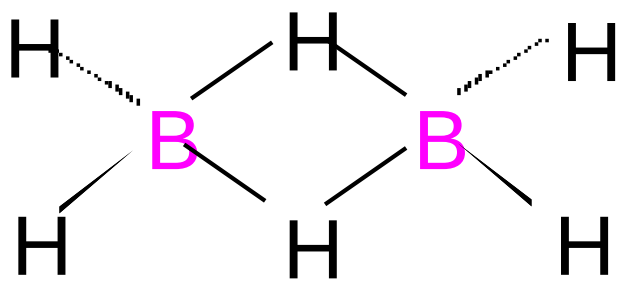
Hydrogen acting as a H- μ–L 3-electron ligand





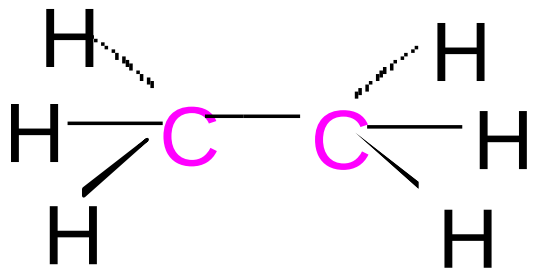
another way to raw it

How do you count electrons in diborane?



6H = 6
2B = 6
12

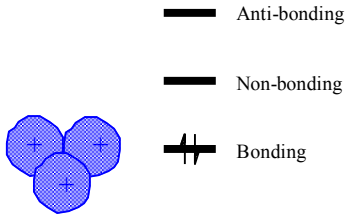
6 each?



6H = 6
2C = 8
14

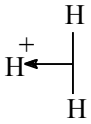
7 each?

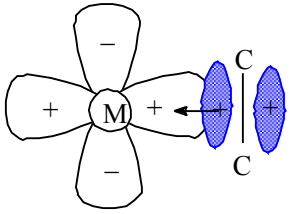
Two-electron Three-centre Bonds in Metal-ligand Systems



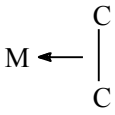
The 2-electron 3-centre bond (written as a 2e-3c bond) of the H_3^+ cation.

A VB representation

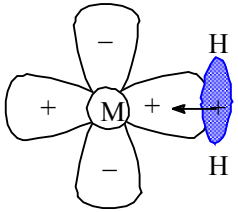




Showing the the L-function (donor) of the ethene ligand in the metal-ethene bond. Also known as "**forward donation** "



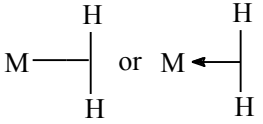
A common VB representation

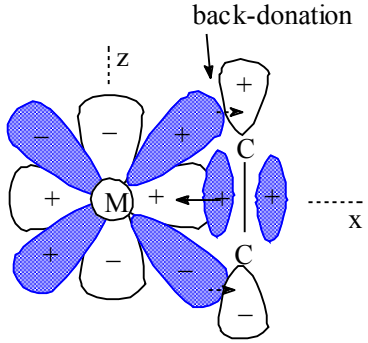


The 2e-3c bond of the transition metal-dihydrogen system.

Written as M(η^2-H_2)

Alternatve VB drawings



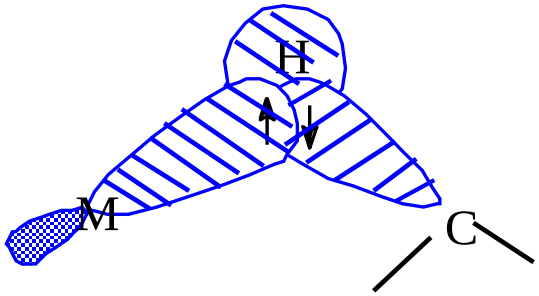


Showing both the forward donation AND the "**back-donation** ". The back-donation is from the electron pair in the filled d_{zx} metal orbital into the empty p*-orbital of the ethene/ Known as the Chatt-Dewar model. There is no simple black line VB representation for this bonding. The ethene is described as a **π-acid** - because it accepts an electron pair into an empty orbital of π-symmetry wrt to the M-ethene axis. This back-donation and is called a

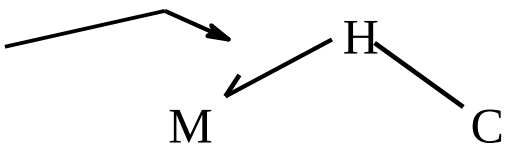
$d_\pi \rightarrow p_\pi$ bond .

Written as M(η^2-C_2H_4)

The agostic M-H-C bond



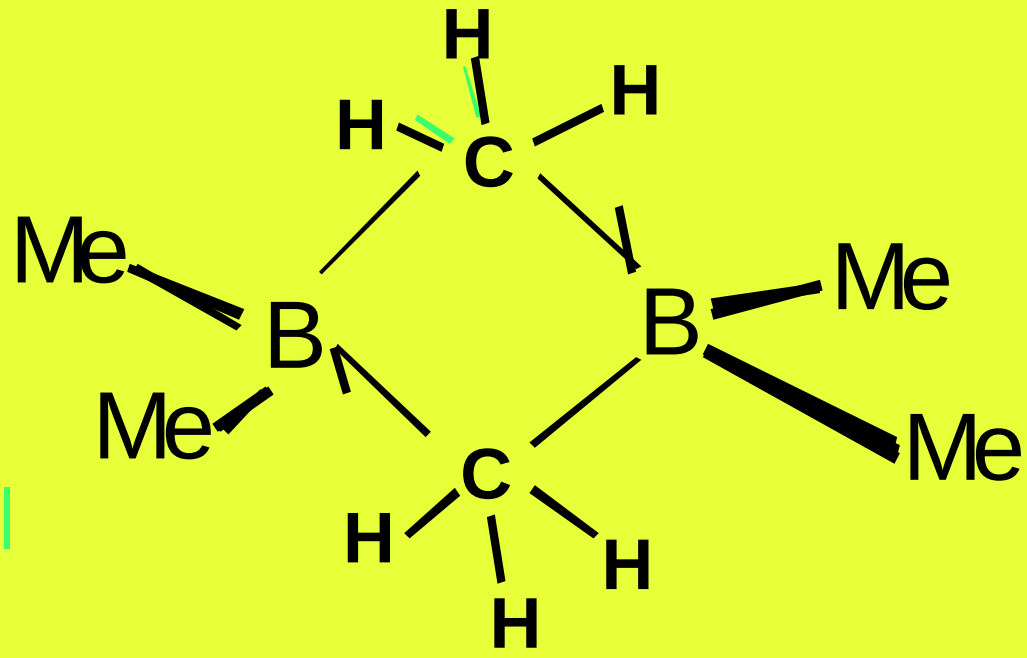
half arrow convention



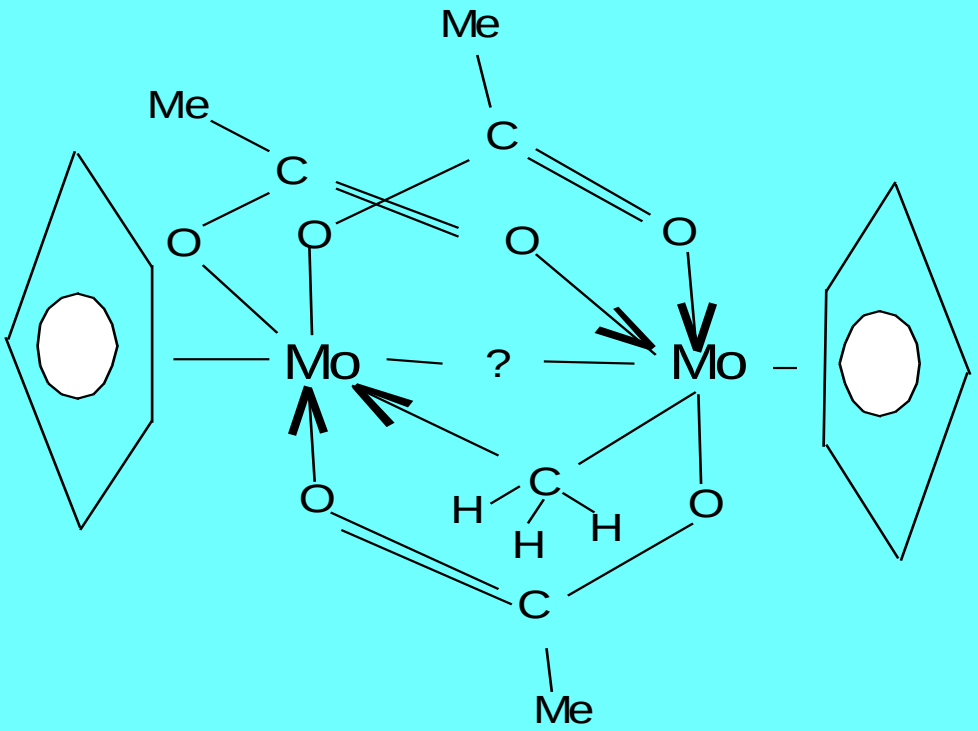
An unsymmetrical two-electron, three-centre bond

formed between a C-H bond and a metal

Classification of Al_2Me_6
using the half-arrow notation



Each Al has class MLX_3 so EN = 8



Mo	6	6
Cp	5	5
OAc	4	5
Me	2	1
	17	17

Therefore to achieve the 18 electrons a single bond is required.

Classification of Covalent Compounds of All the Elements

This requires the determination of

A. The Valency Number m denoted V.N.

B. The Ligand Bond Number, denoted L.B.N.

C. The Elecron Number, denoted E.N.

DEFIN I TIONS

I **Valency Number** (V.N.) = x

(where x is the number of X-functions on the ligands).

II **Ligand Bond Number** (L.B.N.) = l + x

(this is the sum of the number of L- and X-functions).

III **Electron Number** (E.N.) = **Me** + 2l + x

Me is the number of electrons in the valency shell of the element M.

The magnitude of the number n of d^n is given as,

n = **Me** - x (-2z, where appropriate).

ELECTRON NUMBER E.N.

VALENCY NUMBER V.N.

	12	13	14	15	16	17	18
0	ML_3		ML_4		ML_5		ML_6
1		ML_3X		ML_4X		ML_5X	
2	ML_2X_2		ML_3X_2		ML_4X_2		ML_5X_2
3		ML_2X_3		ML_3X_3		ML_4X_3	
4	MLX_4		ML_2X_4		ML_3X_4		ML_4X_4
5		MLX_5		ML_2X_5		ML_3X_5	
6	MX_6		MLX_6		ML_2X_6		ML_3X_6

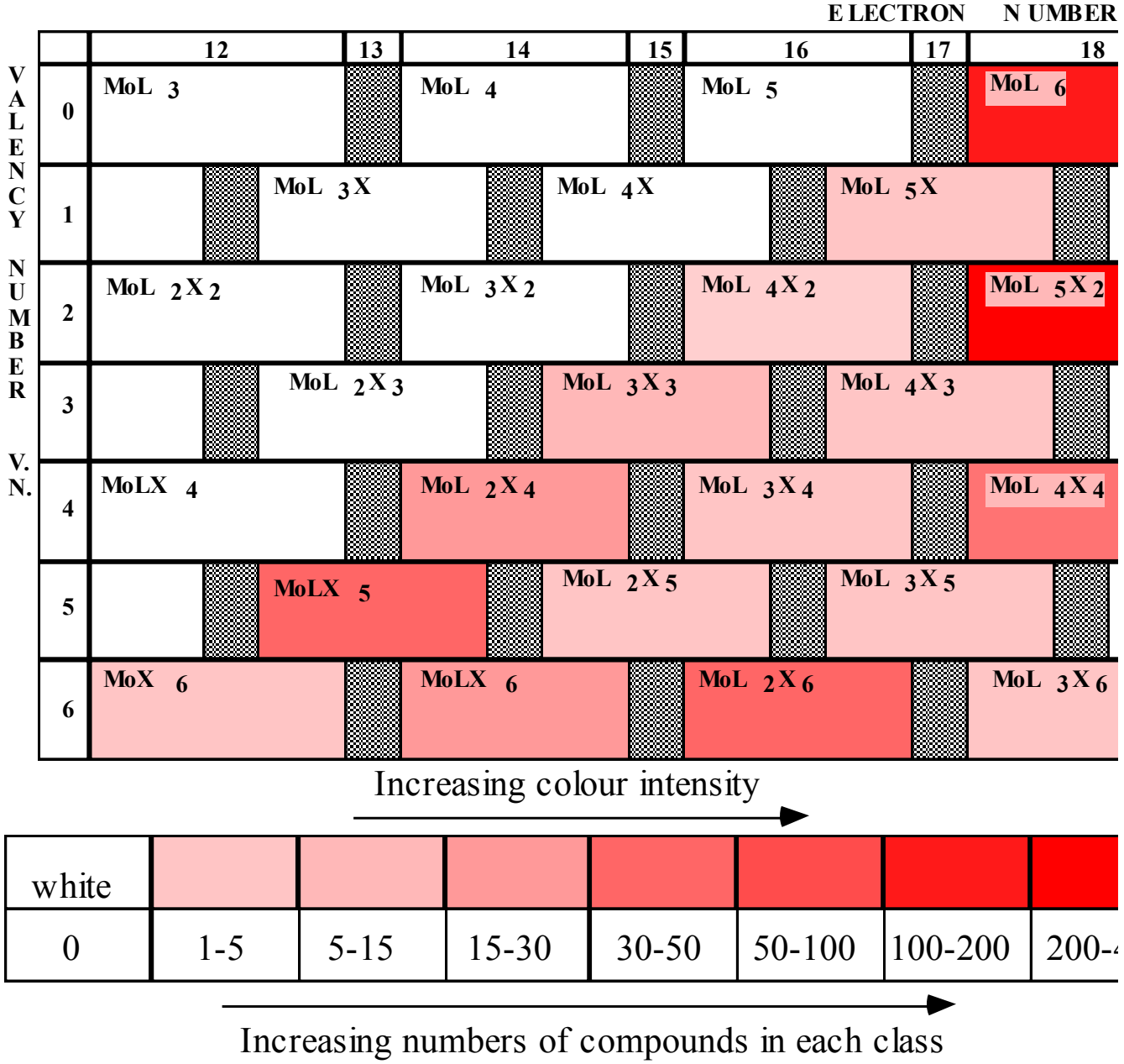


Figure 1. The MLX plot for molybdenum. The population density for each ML_lX_x class is shown by the colour intensity scale

Stability of a Compound towards isolation at room temperature

There are THREE RULES

Rule 1. Filled Valency Orbitals.
The octet rule, the 18-electron rule

Rule 2. Steric saturation.

d-block transition metal prefer
L.B.N. = 6 for normal size ligands
the 5f, lanthanide elements prefer
L.B.N. = 7,8 for normal size ,igands

Rule 3. Pauling ERlectronuetraliy principle.
Actual charge on an atom in a molecule must lie between +1e and -1e,

DO NOT CONFUSE

COORDINATION NUMBER C.N.

WITH LIGAND BOND NUMBER

FOR EXAMPLE

Ferrocene is class FeL_4X_2 so has L.B.N = 6

However the coordination number
C.N. of ferrocene is 10-- there are
10 carbons bonding to the iron center

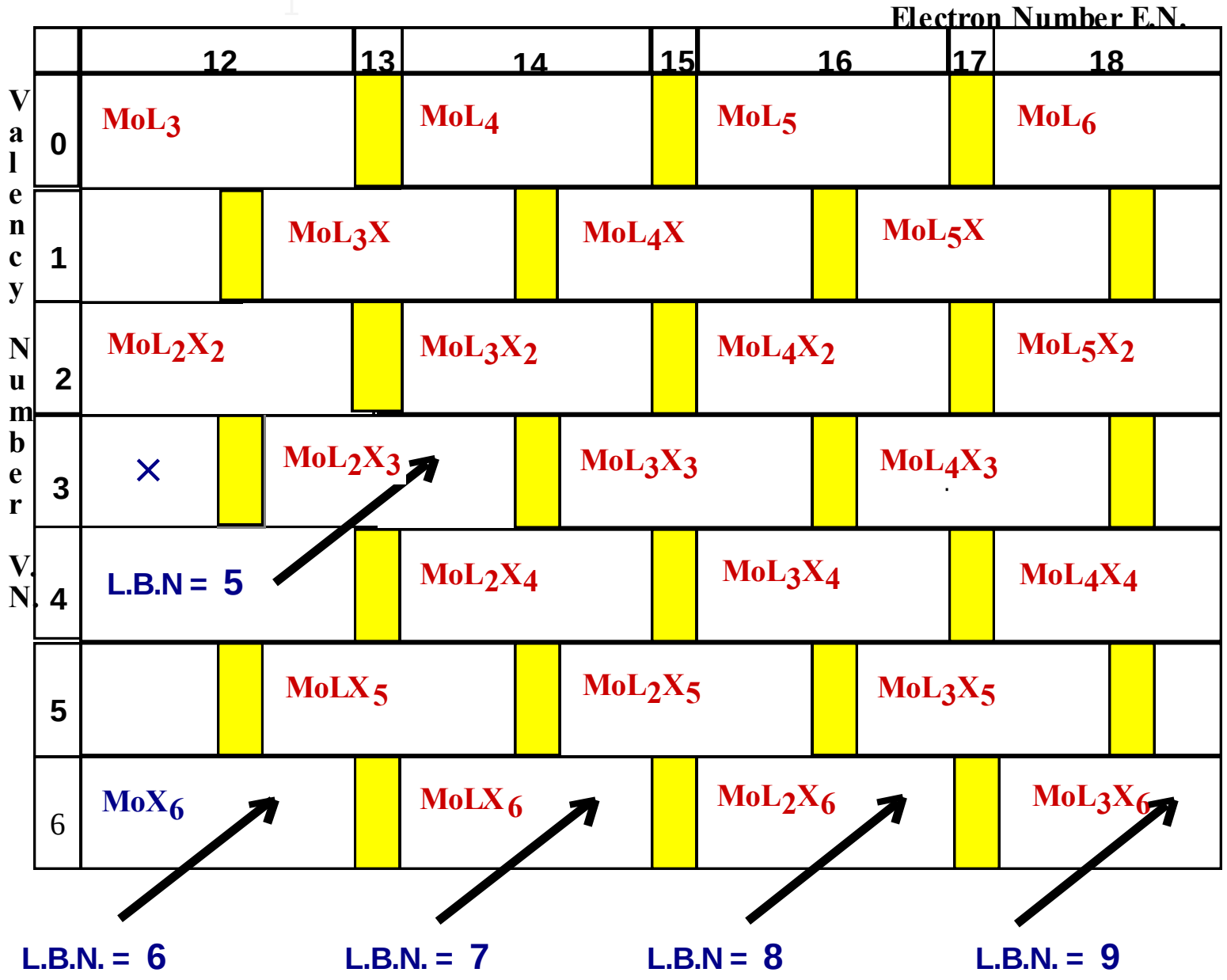
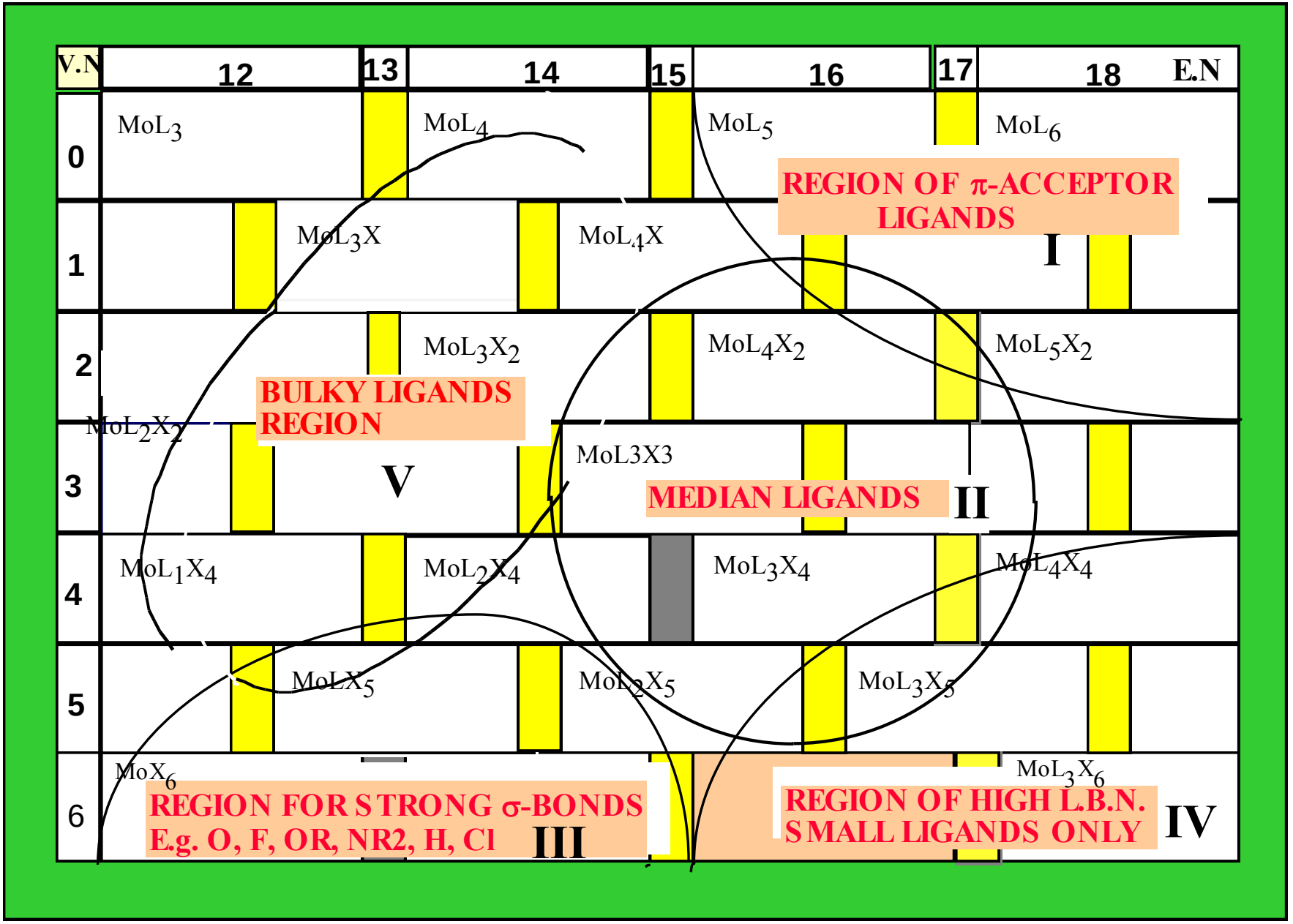

Electron Number E.N.
12
13
14
15
16
17
18
Valency Number V.N.
0
1
2
3
4
5
6
MoL3
MoL4
MoL5
MoL6
MoL3X
MoL4X
MoL5X
MoL2X2
MoL3X2
MoL4X2
MoL5X2
×
MoL2X3
MoL3X3
MoL4X3
L.B.N = 5
MoL2X4
MoL3X4
MoL4X4
MoLX5
MoL2X5
MoL3X5
MoX6
MoLX6
MoL2X6
MoL3X6
L.B.N. = 6
L.B.N. = 7
L.B.N = 8
L.B.N. = 9

Figure 6.


V.N
12
13
14
15
16
17
18
E.N
0
1
2
3
4
5
6
MoL3
MoL4
MoL5
MoL6
MoL3X
MoL4X
MoL3X2
MoL4X2
MoL5X2
MoL2X2
MoL3X3
MoL1X4
MoL2X4
MoL3X4
MoL4X4
MoLX5
MoL2X5
MoL3X5
MoX6
MoL3X6
REGION OF π-ACCEPTOR LIGANDS
I
BULKY LIGANDS REGION
V
MEDIAN LIGANDS
II
REGION FOR STRONG σ-BONDS
E.g. O, F, OR, NR2, H, Cl
III
REGION OF HIGH L.B.N.
SMALL LIGANDS ONLY
IV

MLX Classification of Reactions according to Products (no mechanism implied)

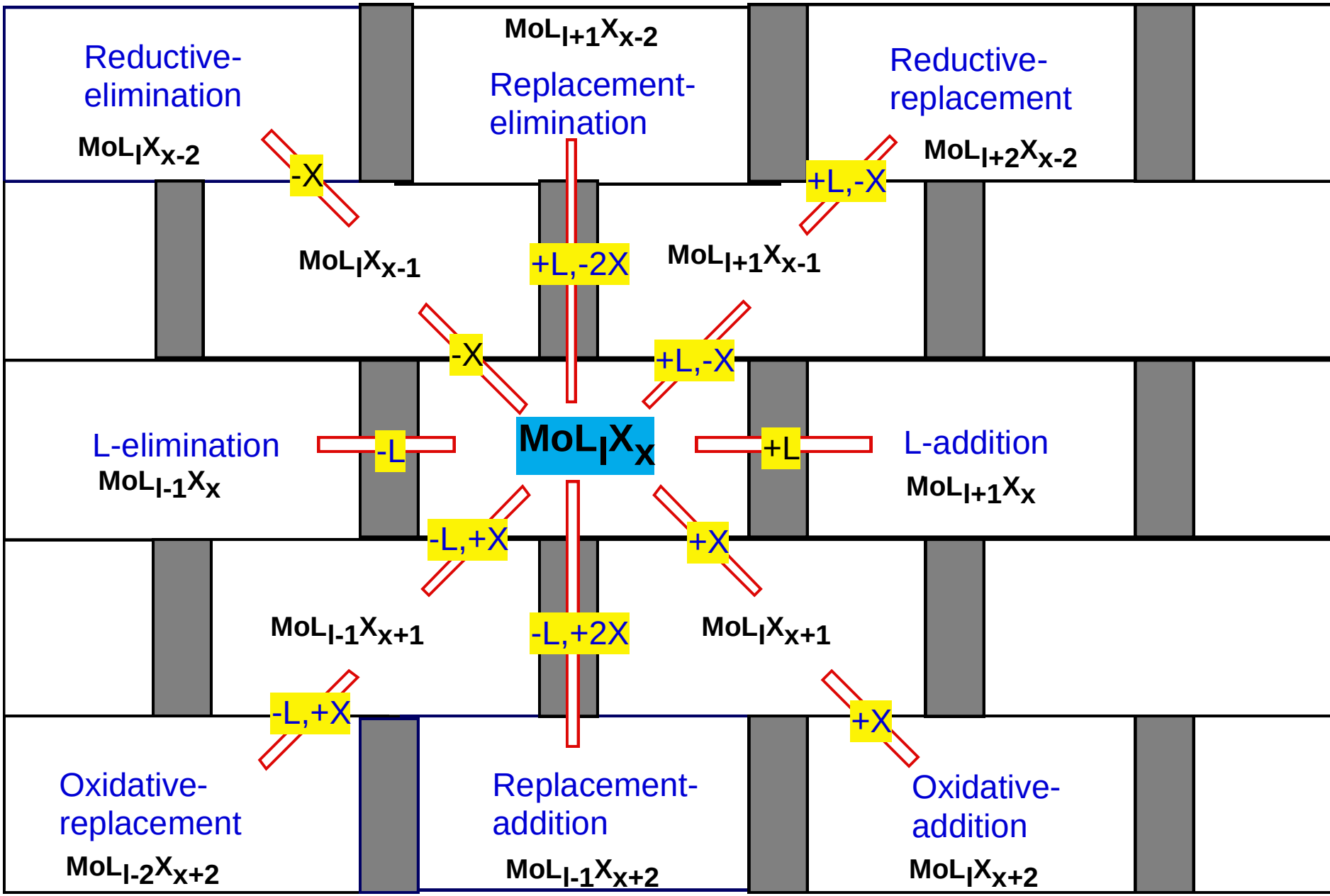


Table 4. Classification of reactions by the reaction products

Change in L_l and/or X_X	Change in E.N.	Change in V.N.	Name of reaction
$-L_l$ then $+L'_l$	0	0	L_l -substitution
$-X_X$ then $+X'_X$	0	0	X_X -substitution
$+L_l$	$+2l$	0	L_l-addition
$-L_l$	$-2l$	0	L_l-elimination
$+X_X$	$+x$	$+x$	X_X-oxidative-addition
$-X_X$	$-x$	$-x$	X_X-reductive-elimination
$+L$ then $-X$[a]	+1	-1	reductive-replacement[a]
$-L$ then $+X$[b]	-1	-1	oxidative-replacement[b]
$-L_n$ then $+X_{2n}$ (n=1)	0	+2	replacement-addition[c]
$+L_n$ then $-X_{2n}$ (n=1)	0	-2	replacement-elimination[d]
L goes to new L' or	0	0	L-substitution
X goes to new X'	0	0	X-substitution

[a] When the ligands are unchanged the reaction is a 1-electron reduction.
[b] When the ligands are unchanged the reaction is a 1-electron oxidation.
[c] Assuming n = 1. Generally called n-replacement-addition.
[d] Assuming n = 1. Generally called n-replacement-elimination.

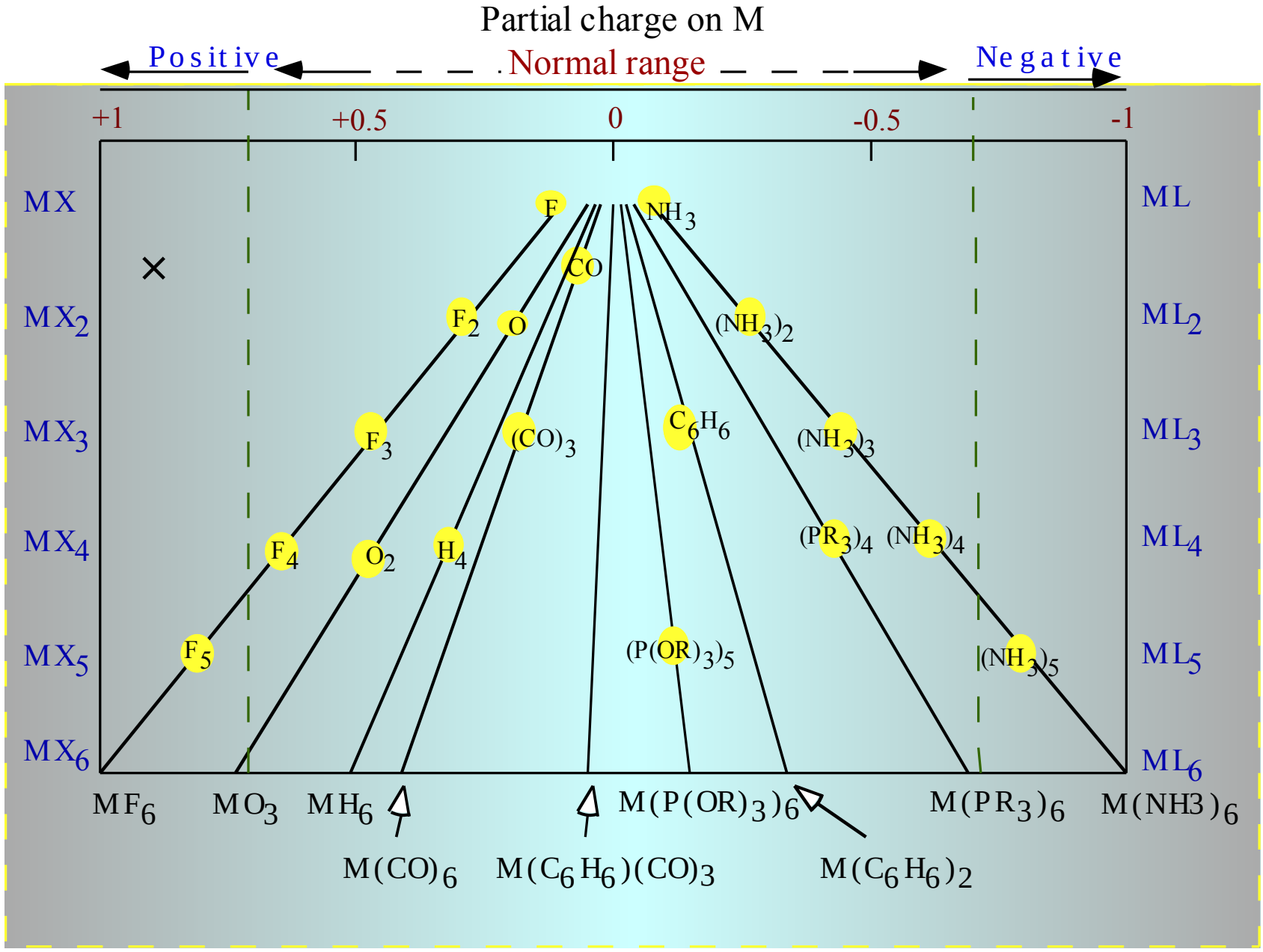
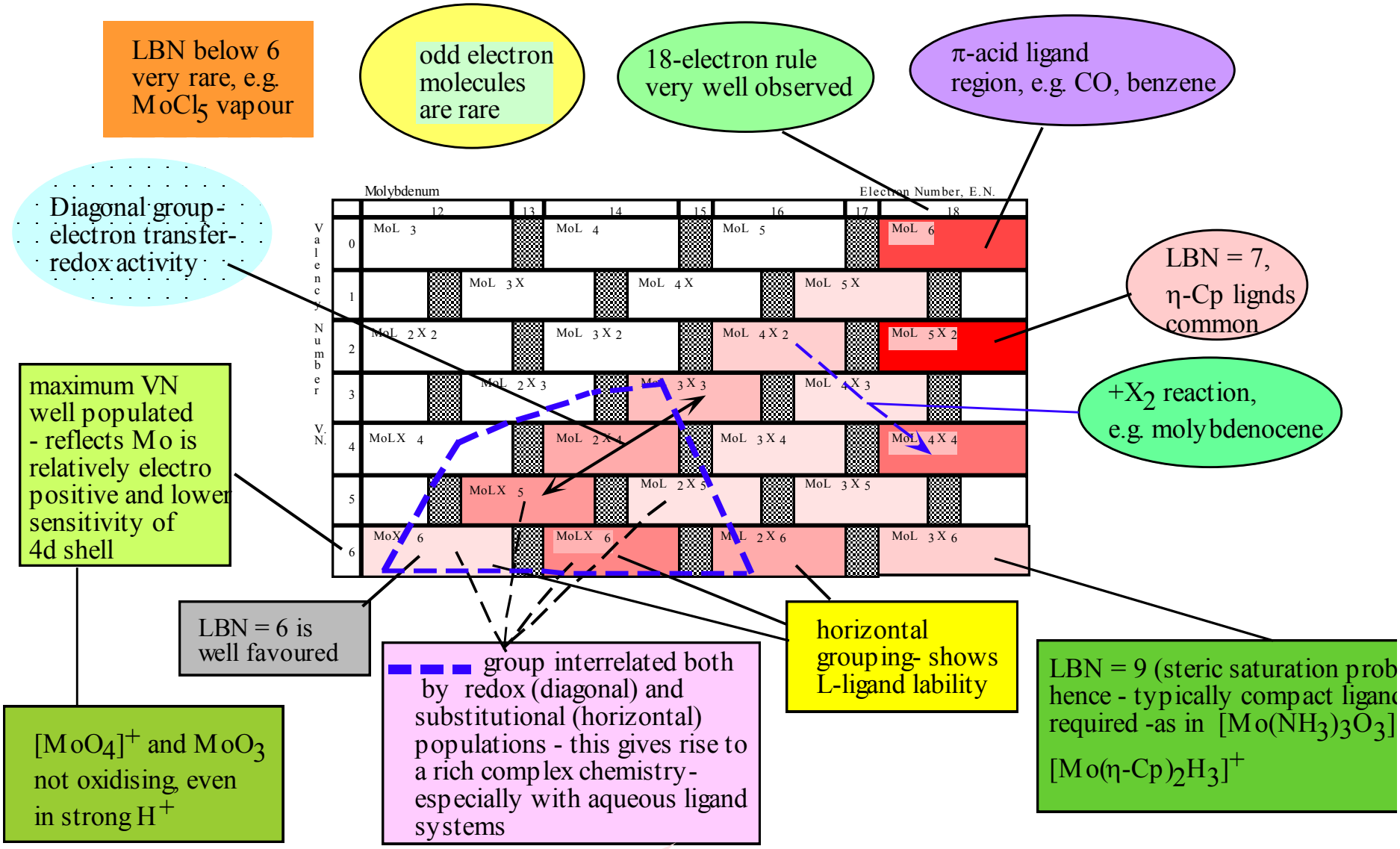

Partial charge on M
Positive
Normal range
Negative
+1
+0.5
0
-0.5
-1
MX
MX2
MX3
MX4
MX5
MX6
ML
ML2
ML3
ML4
ML5
ML6
F
NH3
CO
F2
O
(NH3)2
F3
(CO)3
C6H6
(NH3)3
F4
O2
H4
(PR3)4
(NH3)4
F5
(P(OR)3)5
(NH3)5
MF6
MO3
MH6
M(P(OR)3)6
M(PR3)6
M(NH3)6
M(CO)6
M(C6H6)(CO)3
M(C6H6)2

Figure 7

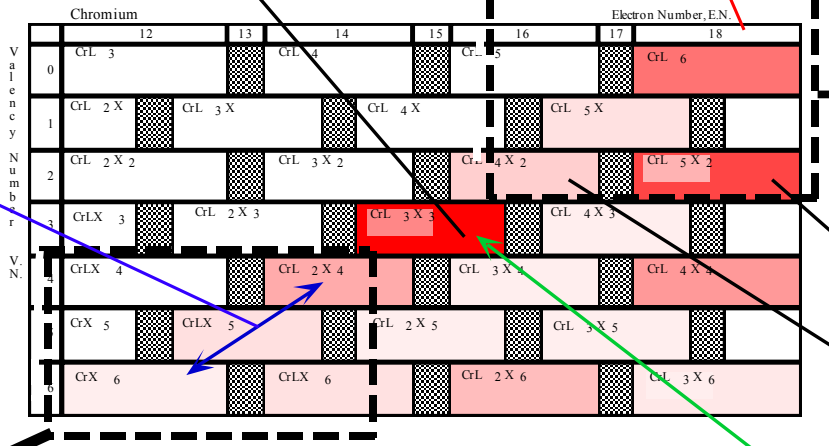

LBN below 6 very rare, e.g. $MoCl_5$ vapour
odd electron molecules are rare
18-electron rule very well observed
π-acid ligand region, e.g. CO, benzene
Diagonal group - electron transfer - redox activity
Molybdenum
Electron Number, E.N.
Valency Number V.N.
12
13
14
15
16
17
18
0
1
2
3
4
5
6
MoL 3
MoL 4
MoL 5
MoL 6
MoL 3 X
MoL 4 X
MoL 5 X
MoL 2 X 2
MoL 3 X 2
MoL 4 X 2
MoL 5 X 2
MoL 2 X 3
MoL 3 X 3
MoL 4 X 3
MoLX 4
MoL 2 X 4
MoL 3 X 4
MoL 4 X 4
MoLX 5
MoL 2 X 5
MoL 3 X 5
MoX 6
MoLX 6
MoL 2 X 6
MoL 3 X 6
LBN = 7, η-Cp lignds common
+X_2 reaction, e.g. molybdenocene
maximum VN well populated - reflects Mo is relatively electro positive and lower sensitivity of 4d shell
LBN = 6 is well favoured
group interrelated both by redox (diagonal) and substitutional (horizontal) populations - this gives rise to a rich complex chemistry - especially with aqueous ligand systems
horizontal grouping - shows L-ligand lability
LBN = 9 (steric saturation prob hence - typically compact ligand required -as in $[Mo(NH_3)_3O_3]$
$[Mo(\eta\text{-}Cp)_2H_3]^+$
$[MoO_4]^+$ and MoO_3 not oxidising, even in strong H^+

Comments on CHROMIUM

Cr, VN = 3, d^3
Remarkable non-lability, inert to substitution, but as diagonal relationship shows, s readily reduced

18-electron rule very well obeyed as the 3d , 4s and 4p orbitals all have "valency energy"

LBN = 6 very well represented. Higher values of LBN are most often found when EN = 18.



Compounds in this region are very similar to those of Mo and W

L-substitution by dissciative mechanism

L-substitution by associative mechanism

This region is very different from Mo and W: the higher VN region is much less populated for Cr- due to the sensitivity of 3d orbitals to induced charge AND the ligand orbitals required for desired strong σ-bonds are those (2p) of C,N,O and F, which are the relatively electronegatve.atoms. Electron energies in 3d orbitals are more sensitive to charge- compared to 4d and 5d

K_2CrO_4 and CrO_3 are strongly oxidising in H^+ acid.

The absence of both CrL_2X_3 and CrL_4X_3 - for which LBN = 5 and 7, respectively, clearly reflects of the L-substitutional inertness of CrL_3X_3

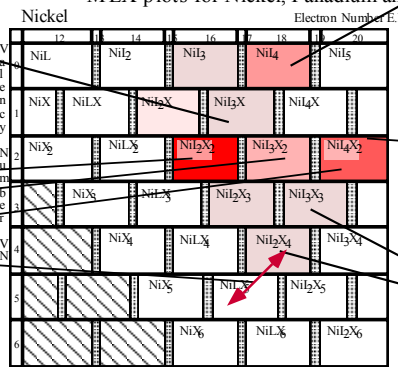
LBN = 4 common since already d^{10}, gives NiL_4. Also, 16-electron d^8 electronically favoured

18-electon rule quite well obeyed, except that NiL_2X_2 very common and 20e NiL_4X_2 also found

Tetrahedral, d^{10} NiL_4 has weakish M-L bonds although since the d-electrons are low in energy. Ligand dissociation (-L) a common reaction step.

A few examples of VN = 1, reflecting steric saturation, e.g. $[Ni(PPh_3)_3]^+$

MLX plots for Nickel, Palladium and Platinum



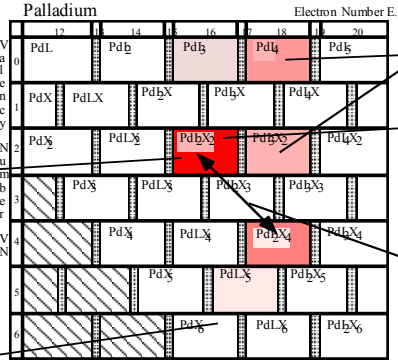
Rare examples of 20-electron compounds but note LBN = 6.

L-substitution by
(i) Associative mechanism
(ii) Both (i) and (iii)
(iii) Dissociative mechanism

Shows LBN = 6 favoured

Higher VN = 3 or 4 are very rare since Ni has 3d orbitals and high I.P's, as expected towards end of d-block.

Simple redox chemistry is rare for Ni and virtually unknown for Pd and Pt. This reflected by absence of diagonal groups. i.e. absence of odd-electron compounds.



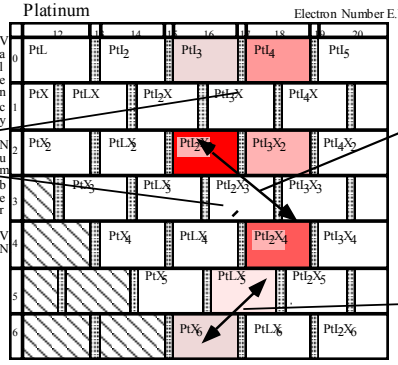
L-substitution by dissociative process

L-substitution by associative process

The special case of d^8 configuration. No Td structures as Δ_{Td} inceases

Related by +/-X_2. Oxidative-addition/ reductive elimination reactions are very common

Increasing stabilisation of higher VN



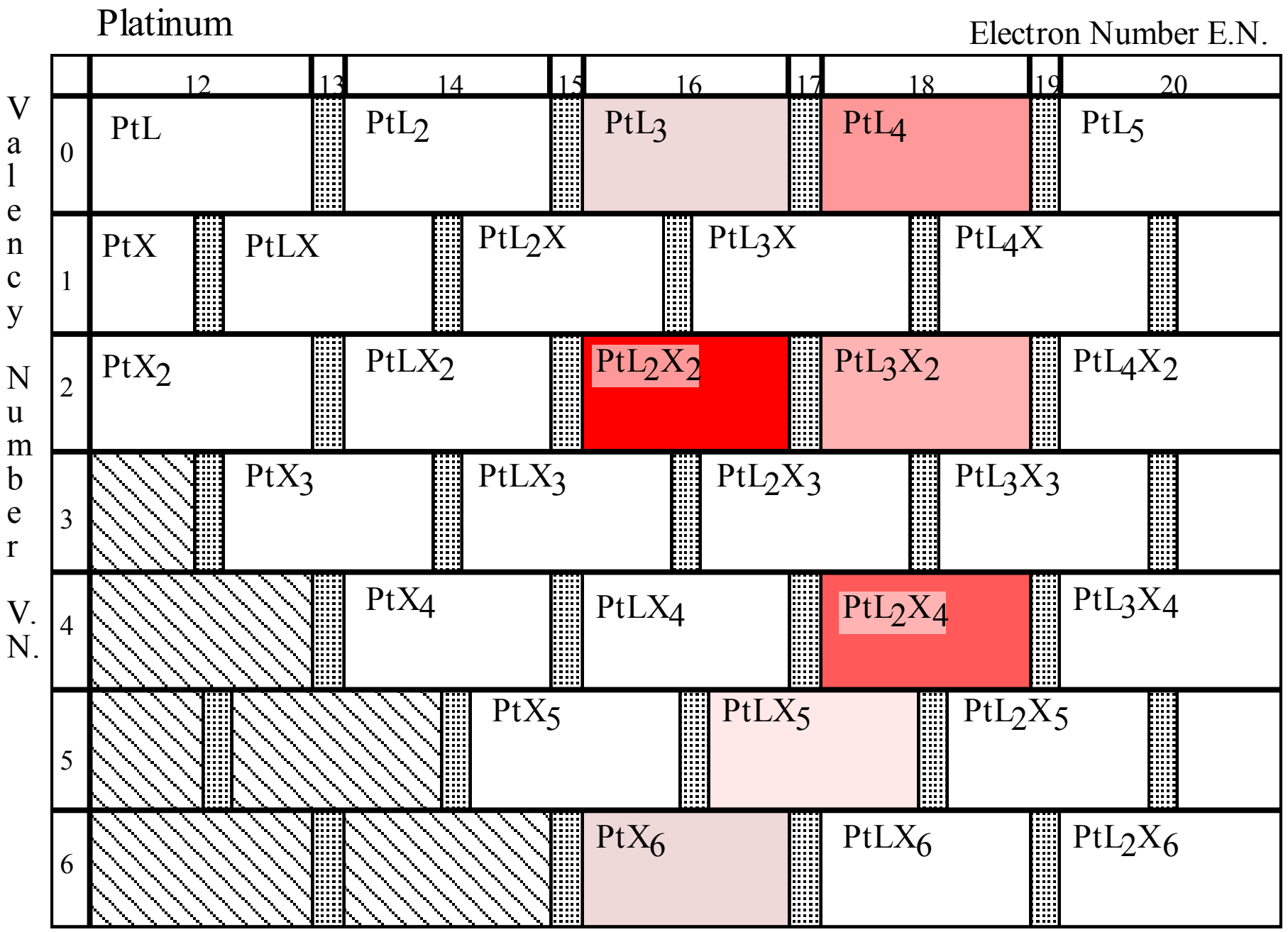
Related by +/-X_2. Oxidative-addition/ reductive elimination reactions are very common

NO odd electron compounds known

NO 20-electron compounds known, for Pd and Pt. This reflects increase in Δ_{Oh}

LBN = 6

Increasing stabilisation of higher VN. e.g. PtF_6


Platinum
Electron Number E.N.
12
13
14
15
16
17
18
19
20
Valency Number V.N.
0
1
2
3
4
5
6
PtL
PtL2
PtL3
PtL4
PtL5
PtX
PtLX
PtL2X
PtL3X
PtL4X
PtX2
PtLX2
PtL2X2
PtL3X2
PtL4X2
PtX3
PtLX3
PtL2X3
PtL3X3
PtX4
PtLX4
PtL2X4
PtL3X4
PtX5
PtLX5
PtL2X5
PtX6
PtLX6
PtL2X6

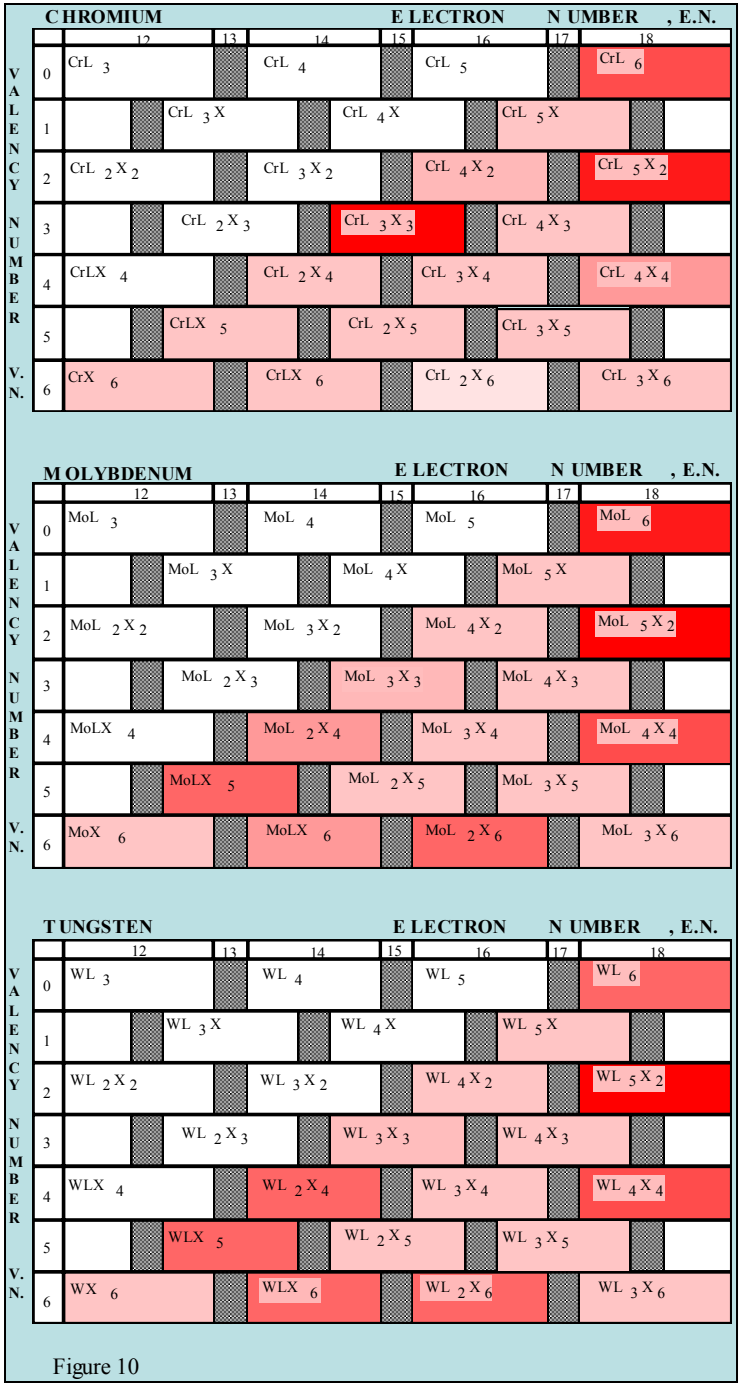
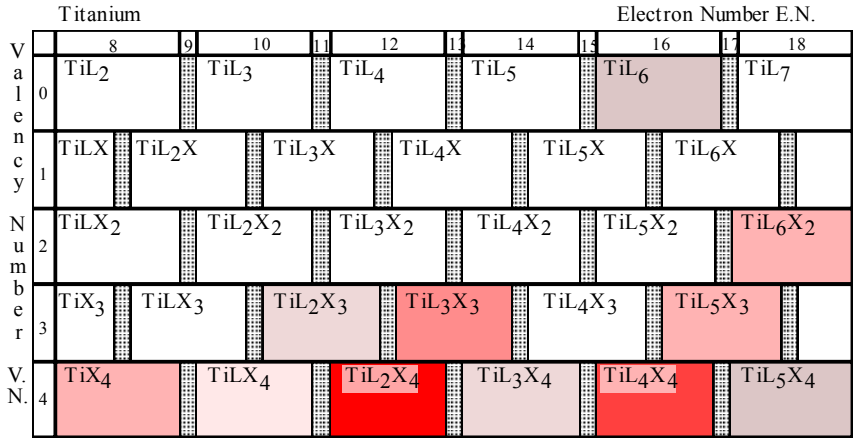
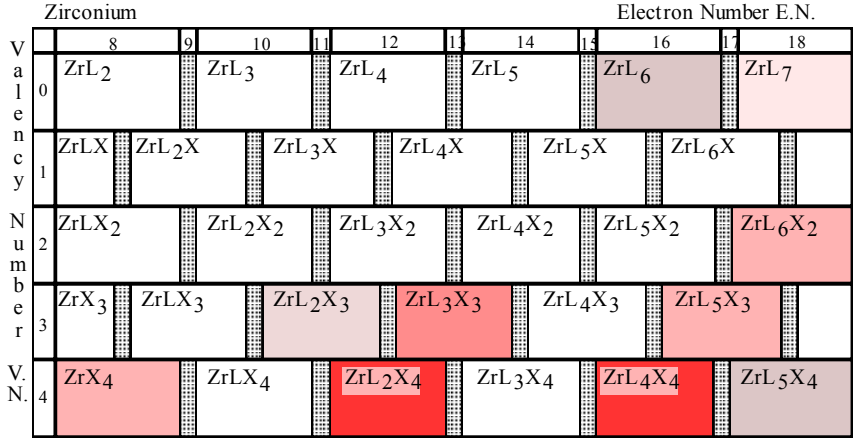
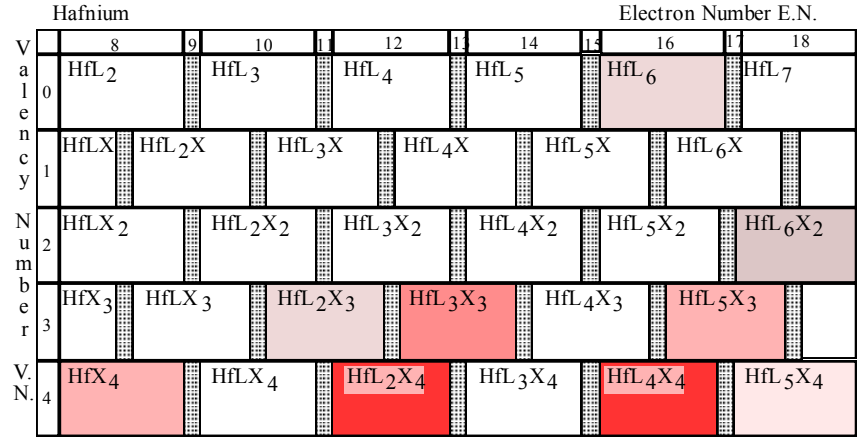

CHROMIUM ELECTRON NUMBER, E.N.
12 13 14 15 16 17 18
VALENCY NUMBER V.N.
0 CrL 3 CrL 4 CrL 5 CrL 6
1 CrL 3 X CrL 4 X CrL 5 X
2 CrL 2 X 2 CrL 3 X 2 CrL 4 X 2 CrL 5 X 2
3 CrL 2 X 3 CrL 3 X 3 CrL 4 X 3
4 CrLX 4 CrL 2 X 4 CrL 3 X 4 CrL 4 X 4
5 CrLX 5 CrL 2 X 5 CrL 3 X 5
6 CrX 6 CrLX 6 CrL 2 X 6 CrL 3 X 6
MOLYBDENUM ELECTRON NUMBER, E.N.
12 13 14 15 16 17 18
VALENCY NUMBER V.N.
0 MoL 3 MoL 4 MoL 5 MoL 6
1 MoL 3 X MoL 4 X MoL 5 X
2 MoL 2 X 2 MoL 3 X 2 MoL 4 X 2 MoL 5 X 2
3 MoL 2 X 3 MoL 3 X 3 MoL 4 X 3
4 MoLX 4 MoL 2 X 4 MoL 3 X 4 MoL 4 X 4
5 MoLX 5 MoL 2 X 5 MoL 3 X 5
6 MoX 6 MoLX 6 MoL 2 X 6 MoL 3 X 6
TUNGSTEN ELECTRON NUMBER, E.N.
12 13 14 15 16 17 18
VALENCY NUMBER V.N.
0 WL 3 WL 4 WL 5 WL 6
1 WL 3 X WL 4 X WL 5 X
2 WL 2 X 2 WL 3 X 2 WL 4 X 2 WL 5 X 2
3 WL 2 X 3 WL 3 X 3 WL 4 X 3
4 WLX 4 WL 2 X 4 WL 3 X 4 WL 4 X 4
5 WLX 5 WL 2 X 5 WL 3 X 5
6 WX 6 WLX 6 WL 2 X 6 WL 3 X 6

Figure 10

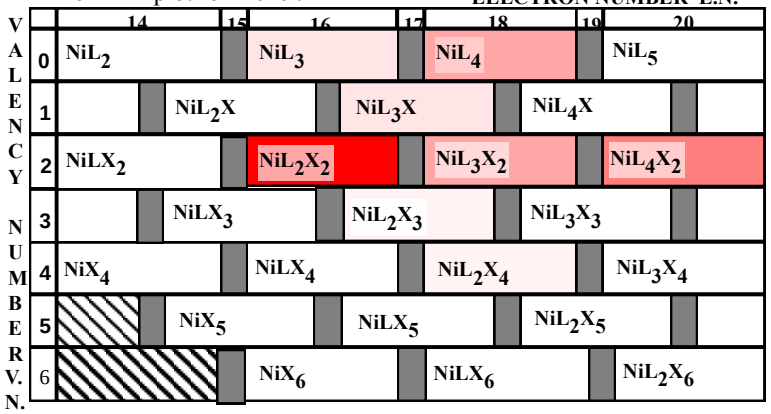
MLX plots for Titanium, Zirconium and Hafnium



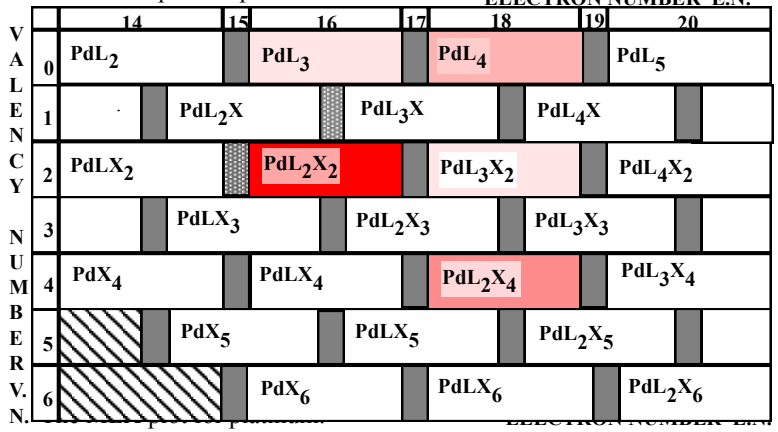




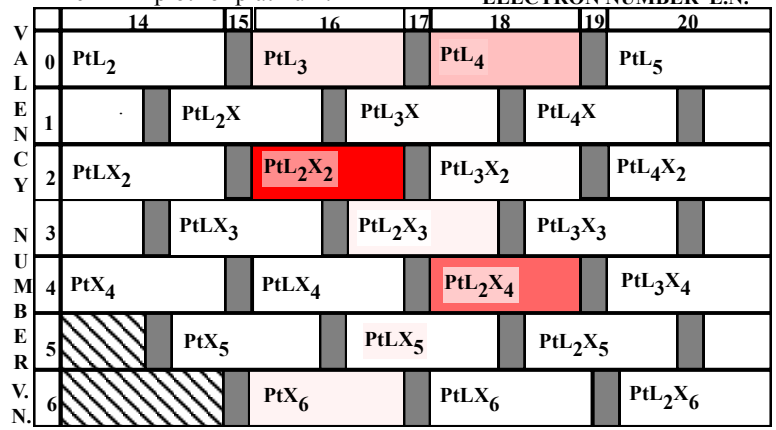
The MLX plot for nickel.



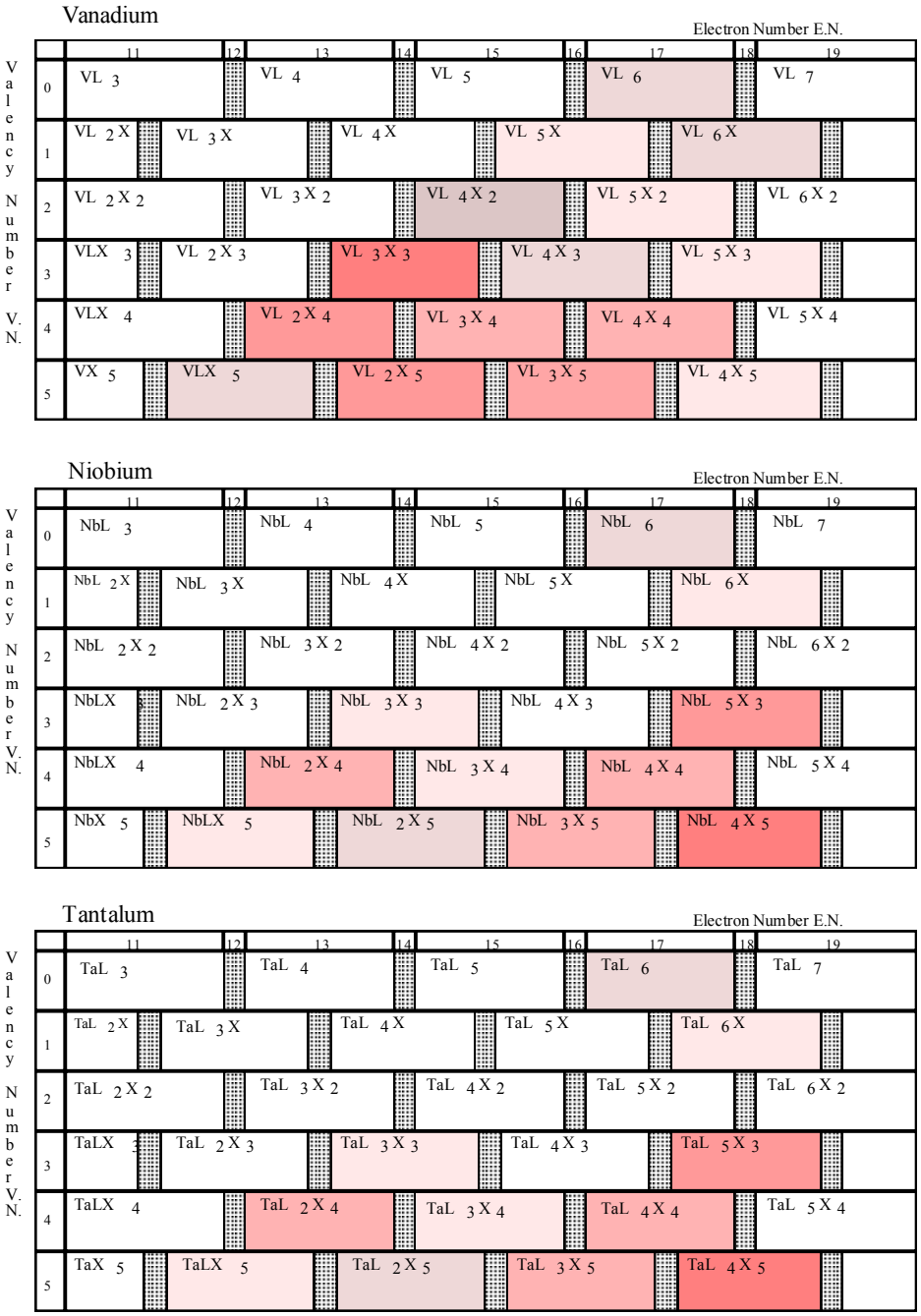
The MLX plot for palladium.



The MLX plot for platinum.

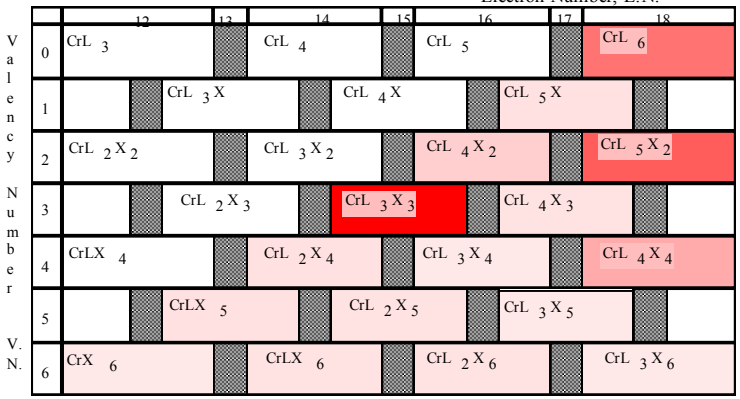


MLX plots for Vanadium, Niobium and Tantalum

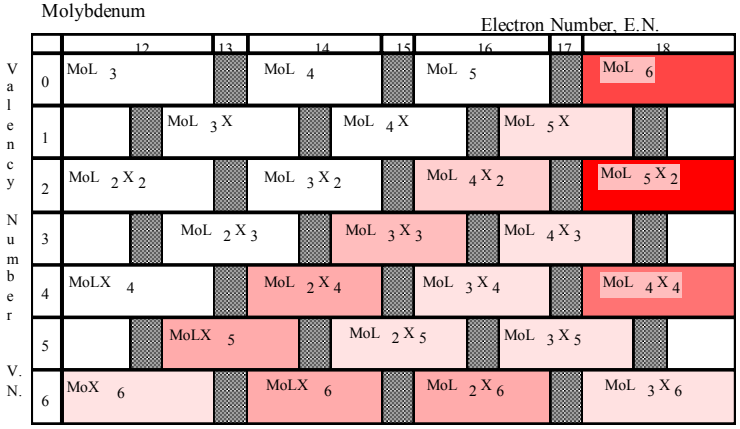


MLX Plots for Chromium, Molybdenum and Tungsten

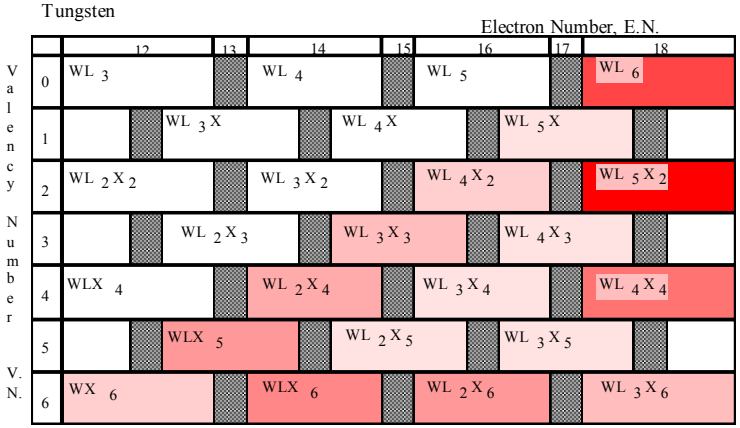
Chromium



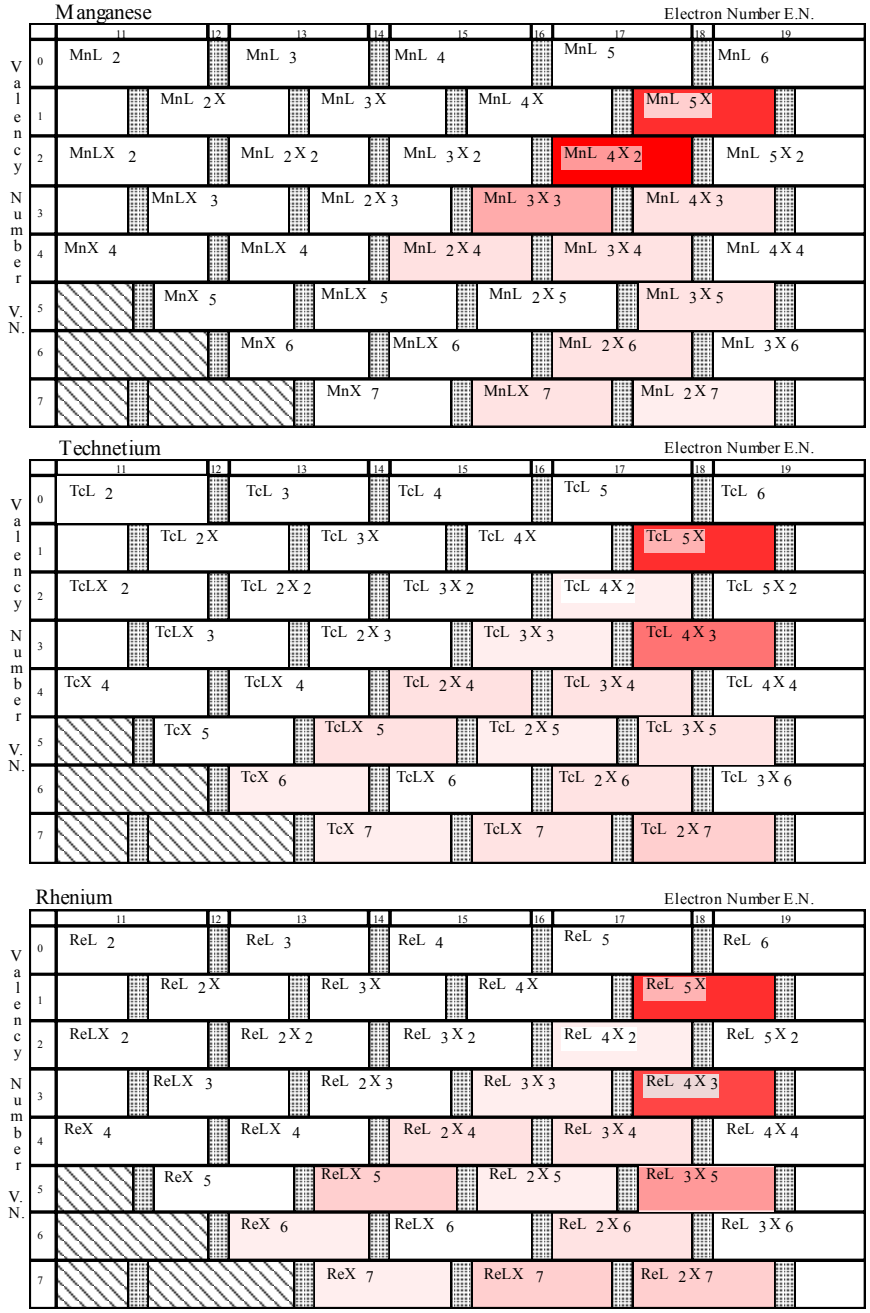
Molybdenum



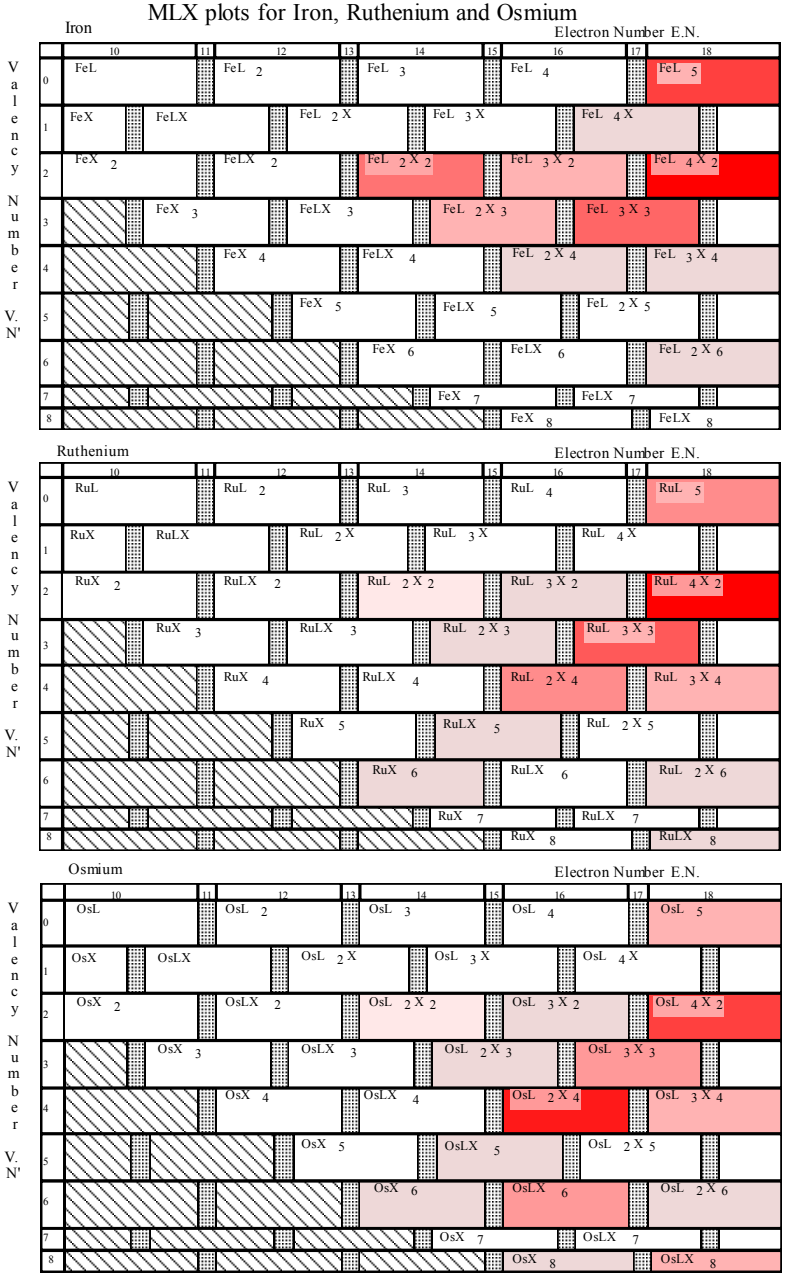
Tungsten



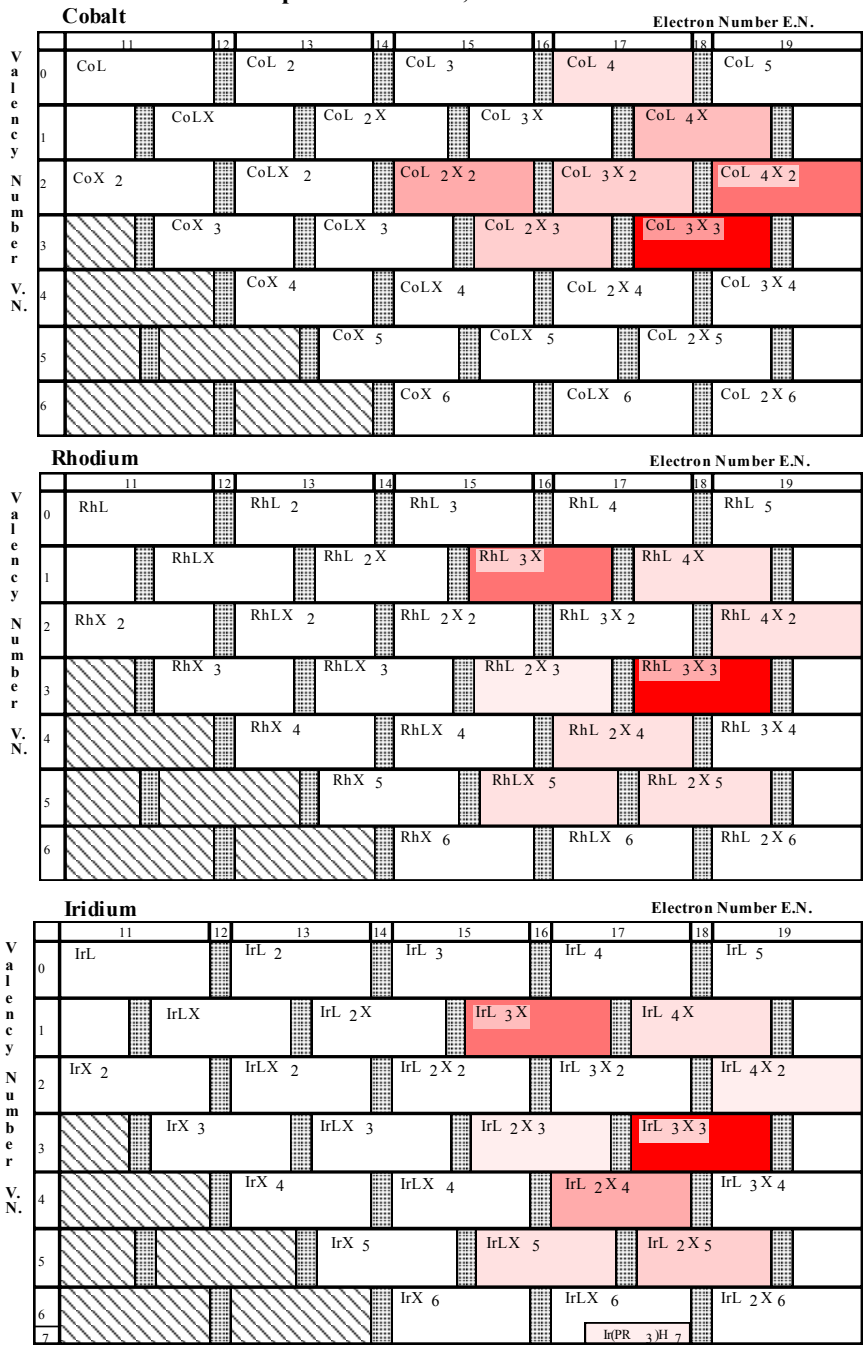
MLX plots for Manganese, Technetium and Rhenium



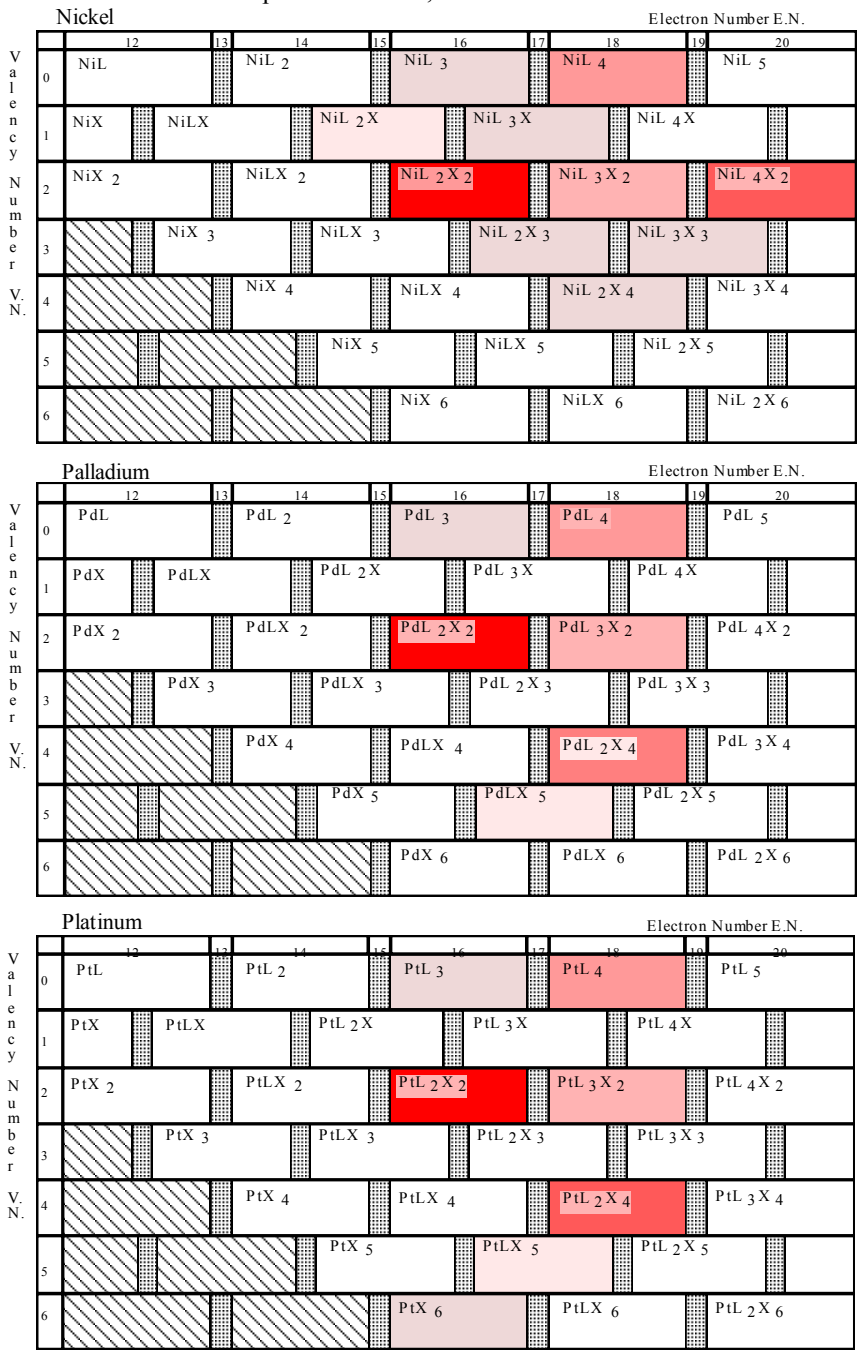
MLX plots for Iron, Ruthenium and Osmium



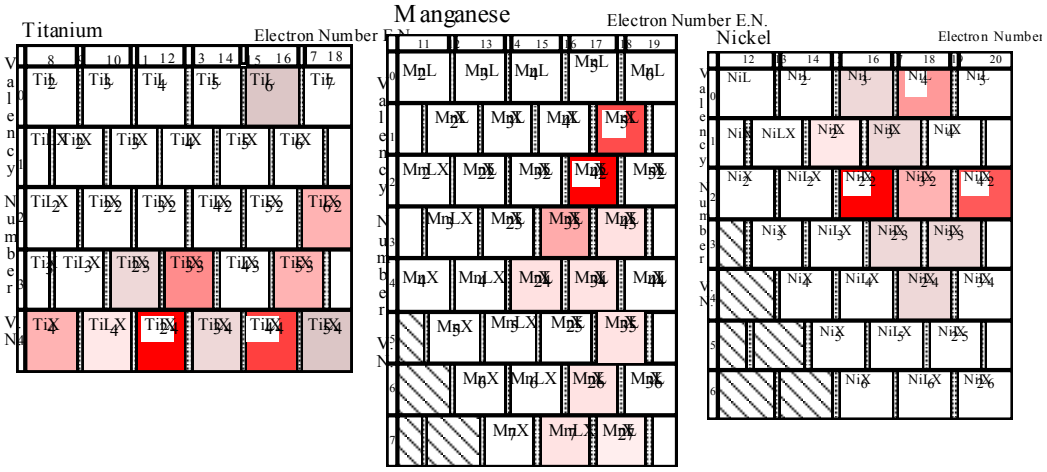
MLX plots for Cobalt, Rhodium and Iridium



MLX plots for Nickel, Palladium and Platinum



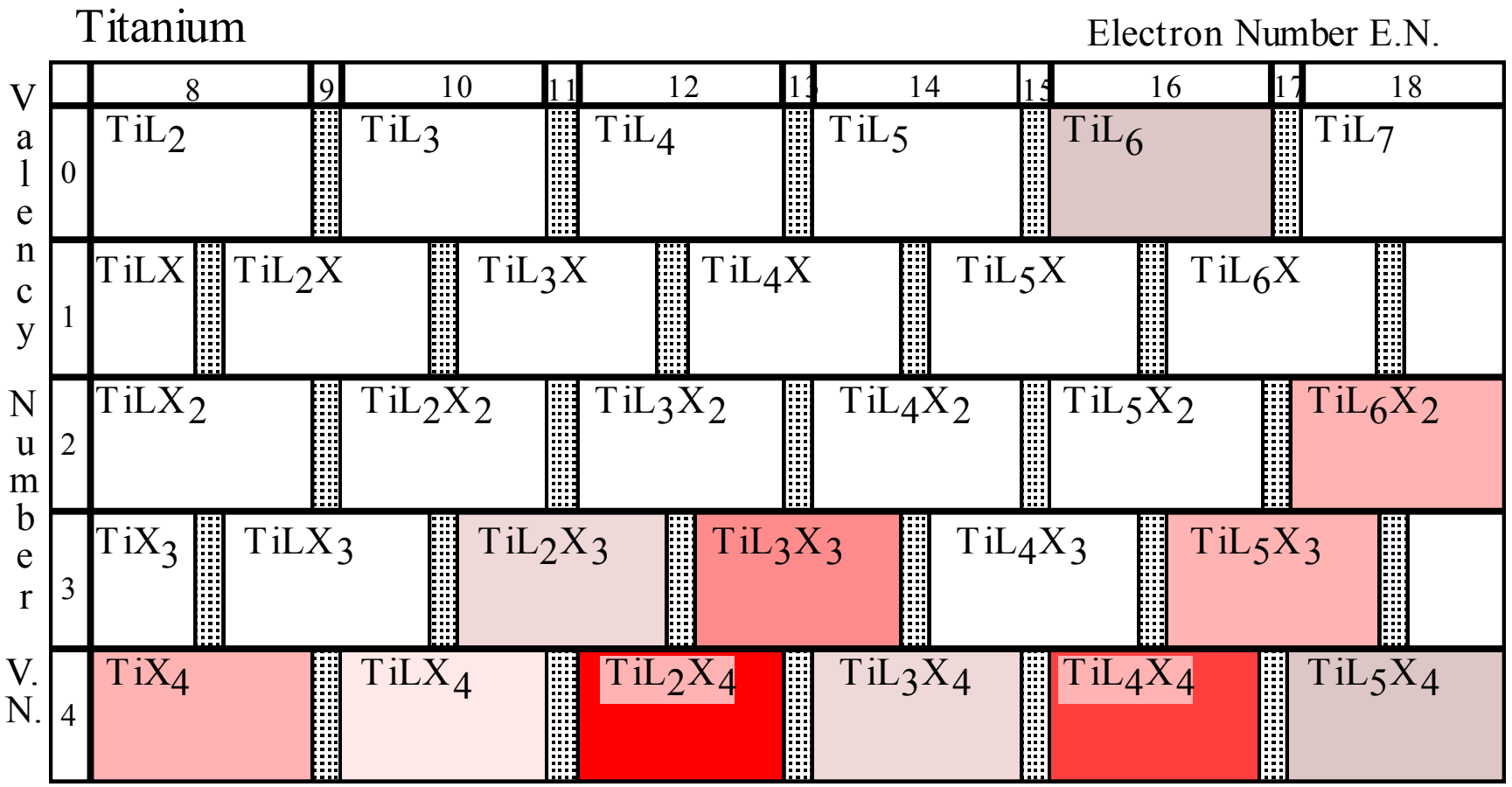
MLX plots for Titanium, Manganese and Nickel



Rule 1) Filled orbitals (18 electrons): Only possible for Ti when there are very small or compact ligands since a further 14-electrons are required. E.g. $[TiCp_2(CO)_2]$. $TiCl_4$ is apparently an 8-electron compound but if the *symmetry allowed contributions from the Cl p π-orbitals* are counted then there are an extra 10 electrons which gives the value for EN = 18-electrons!
For Mn, excellent for VN = 1 where also LBN = 6. but poor for VN = 3 and 5 since LNB = 7 or 8 respectively AND higher VN for Mn are rare since 3d orbitals are rapidly lowered in energy by the increasing patrial +ve change on the Mn centre.
For Ni, 18-electrons are found for NiL_4, NiL_3X_2 and (very rare) NiL_2X_4,. Higher VN's for Ni not found since increase effective nuclear charge at this end of the d-block TM's means the I.P.'s too high. The special stability of square-planer, 16-electron NiL_2X_2 is associated with the d^8 configuration.

Rule 2) Steric saturation: For Ti: unusually high LBN's (and high co-ordination nos) are commonly found, e.g. in 16-electron TiL_4X_4, LBN = 8. For Ni. low LBN's (3,4,5) are found since Ni already has 10 electrons and only requires 4 x L ligands to give 18e NiL_4, e.g. $Ni(CO)_4$.

Rule 3) Electroneutrality rule: For Ti: since I.P.'s are low all 4 valency electrons are accessible to most ligands, e.g TiI_4.
For Mn, the increase of effective nuclear charge with increasing atomic number across the d-block elements means that the higher VN's are only obtainable with the first row elements as ligand atoms (since these for the strongest σ-bonds). Hence VN = 4 is found with F, O, N, and C ligands, e.g. MnR_4, $R = CH_2SiMe_3$. VN = 7 is known only for $[Mn(=X)_4]^-$, where X = O or NR, the electron donation from the appropriate symmetry combination of the pπ=orbitals of the X ligands and the negative charge resulting from the anion helps reduce the induced positive charge on the Mn centre. Nonetheless, the $[MnO_4]^-$ and Mn_2O_7 compounds are amongst the most oxidising known (in aqueous acid). which shows these Mn centres have exceptionally high partial +ve charges.


Titanium
Electron Number E.N.
Valency Number V.N.
8
9
10
11
12
13
14
15
16
17
18
0
TiL2
TiL3
TiL4
TiL5
TiL6
TiL7
1
TiLX
TiL2X
TiL3X
TiL4X
TiL5X
TiL6X
2
TiLX2
TiL2X2
TiL3X2
TiL4X2
TiL5X2
TiL6X2
3
TiX3
TiLX3
TiL2X3
TiL3X3
TiL4X3
TiL5X3
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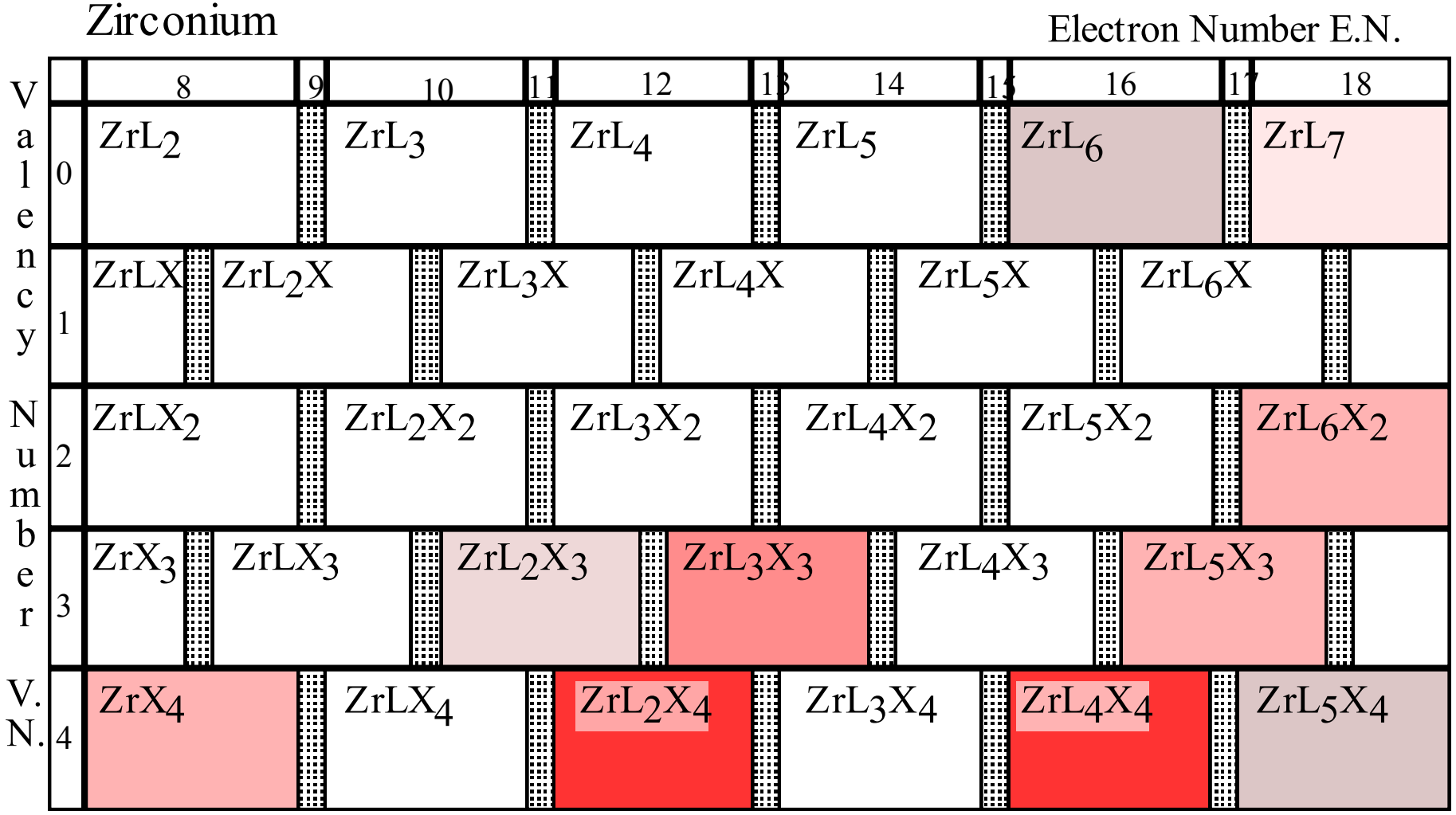
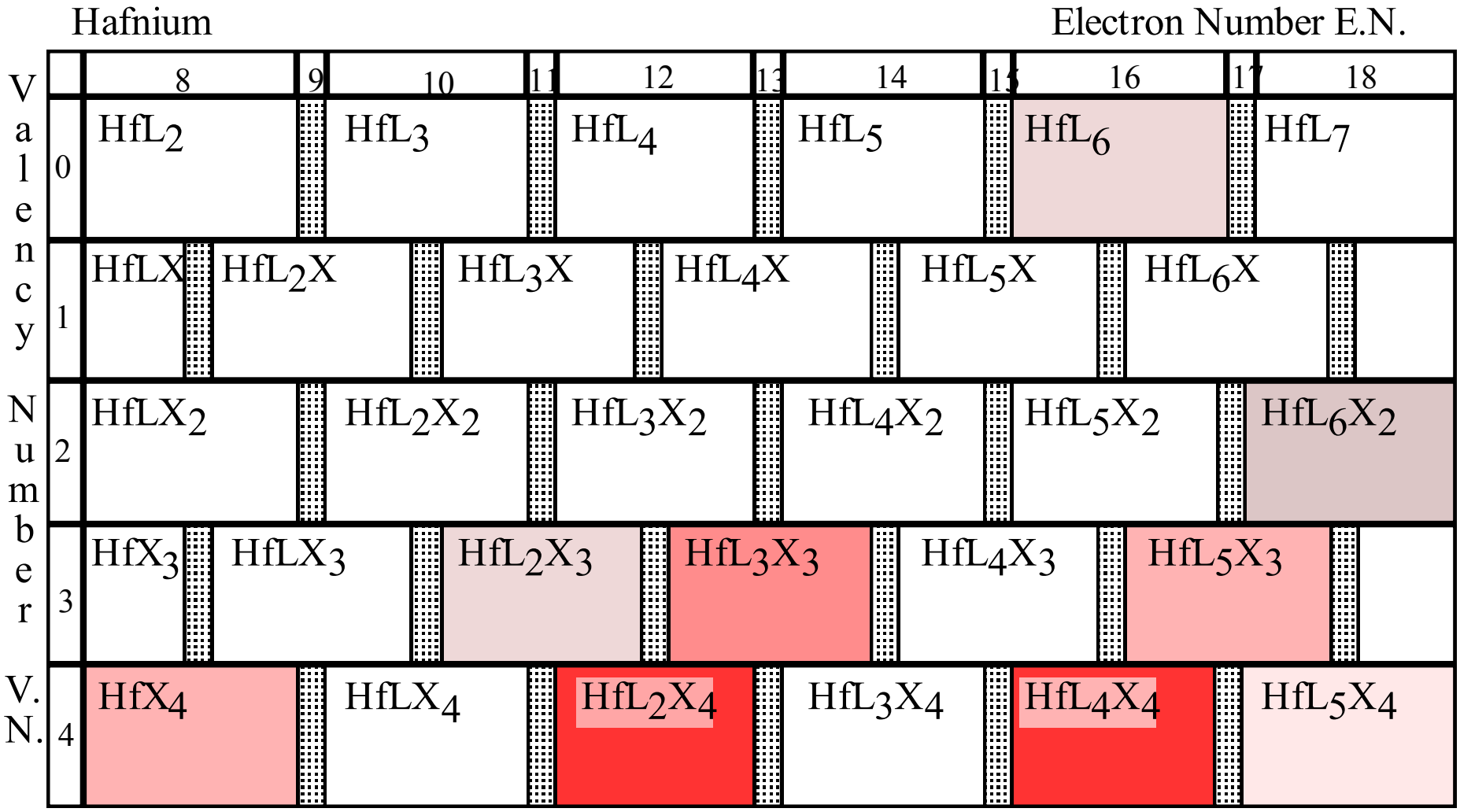
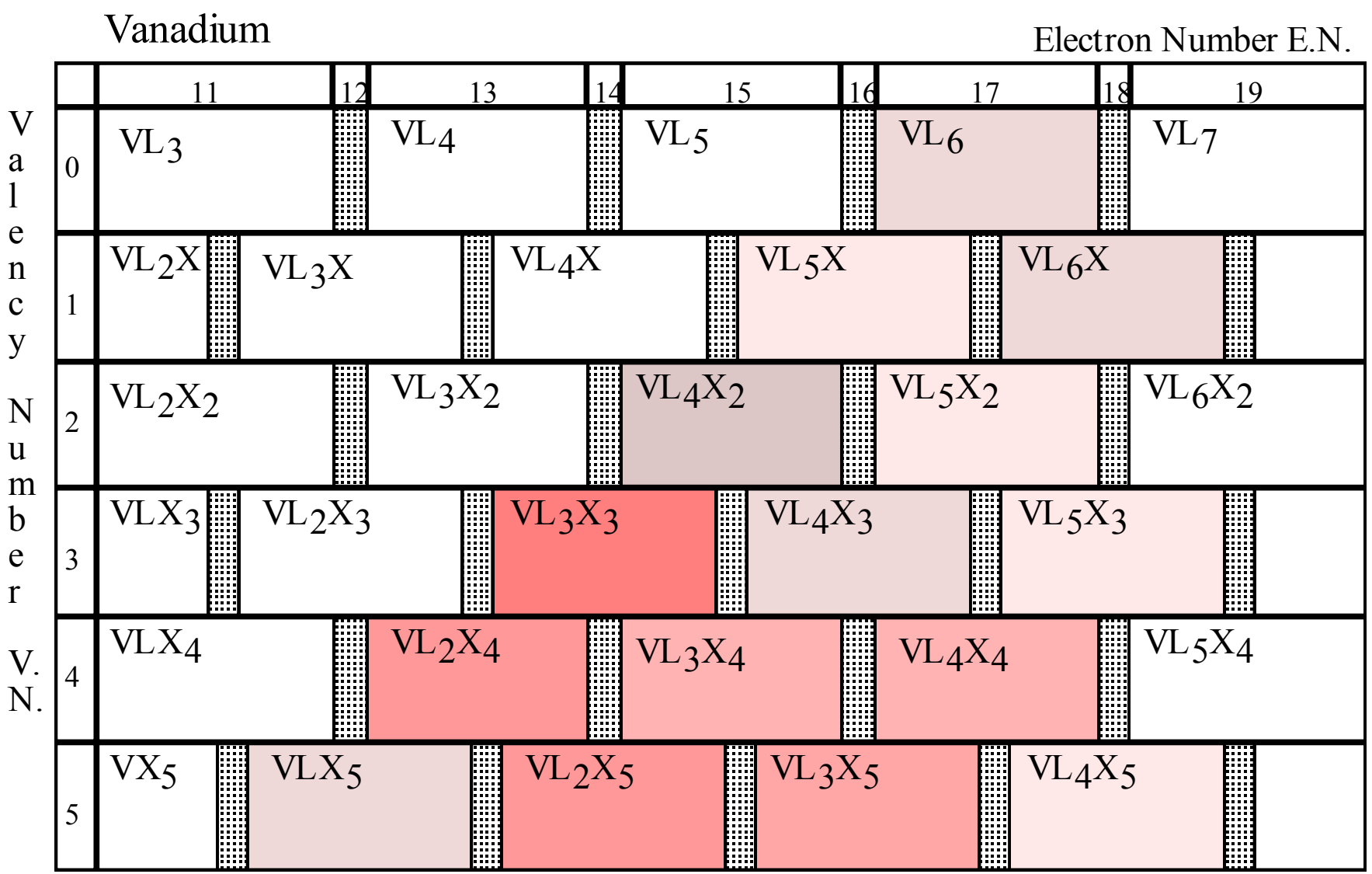
TiX4
TiLX4
TiL2X4
TiL3X4
TiL4X4
TiL5X4


Zirconium
Electron Number E.N.
Valency Number V. N.
8
9
10
11
12
13
14
15
16
17
18
0
ZrL2
ZrL3
ZrL4
ZrL5
ZrL6
ZrL7
1
ZrLX
ZrL2X
ZrL3X
ZrL4X
ZrL5X
ZrL6X
2
ZrLX2
ZrL2X2
ZrL3X2
ZrL4X2
ZrL5X2
ZrL6X2
3
ZrX3
ZrLX3
ZrL2X3
ZrL3X3
ZrL4X3
ZrL5X3
4
ZrX4
ZrLX4
ZrL2X4
ZrL3X4
ZrL4X4
ZrL5X4


Hafnium
Electron Number E.N.
Valency Number V.N.
8
9
10
11
12
13
14
15
16
17
18
0
HfL2
HfL3
HfL4
HfL5
HfL6
HfL7
1
HfLX
HfL2X
HfL3X
HfL4X
HfL5X
HfL6X
2
HfLX2
HfL2X2
HfL3X2
HfL4X2
HfL5X2
HfL6X2
3
HfX3
HfLX3
HfL2X3
HfL3X3
HfL4X3
HfL5X3
4
HfX4
HfLX4
HfL2X4
HfL3X4
HfL4X4
HfL5X4

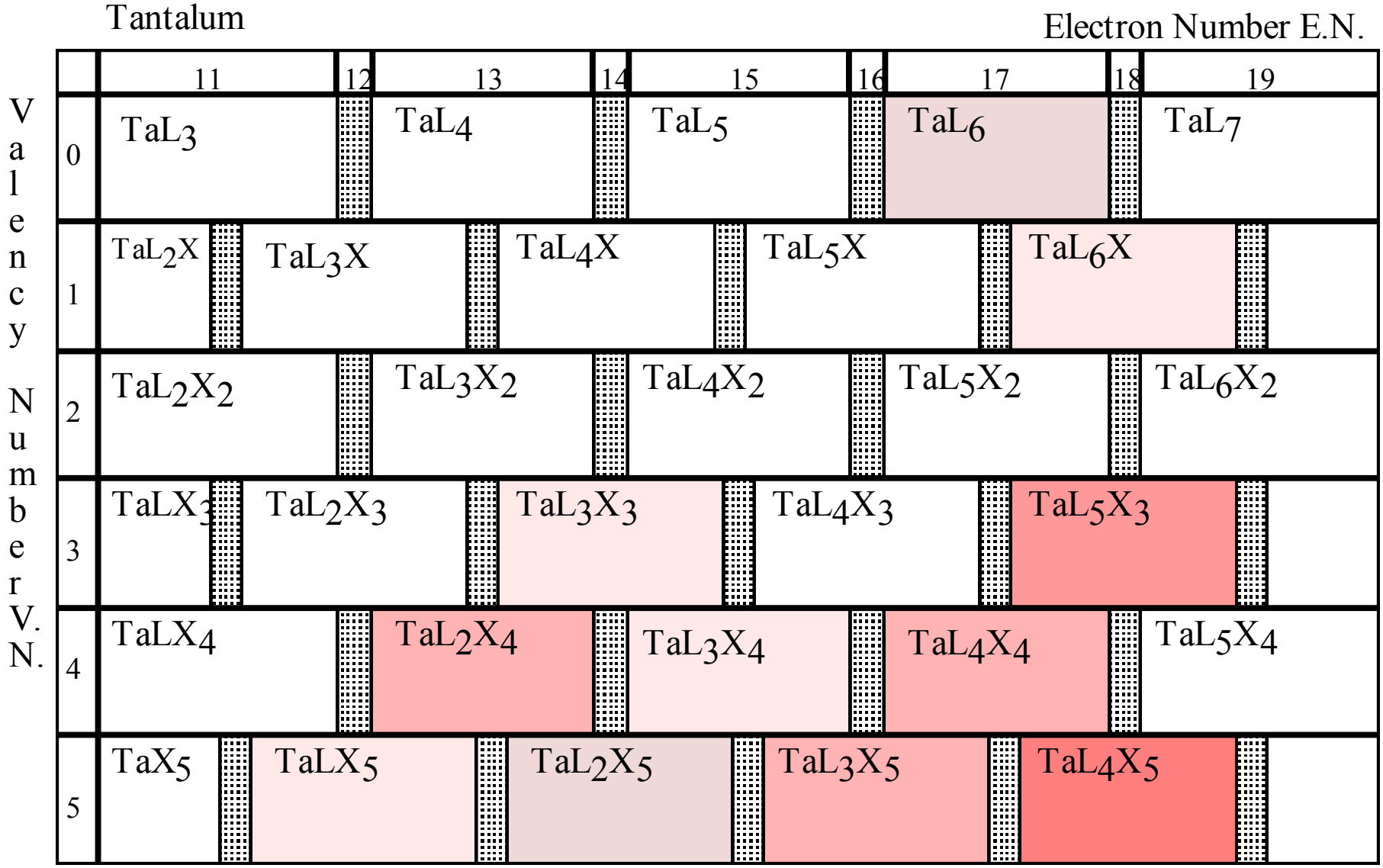

Vanadium
Electron Number E.N.
11
12
13
14
15
16
17
18
19
Valency Number V. N.
0
VL3
VL4
VL5
VL6
VL7
1
VL2X
VL3X
VL4X
VL5X
VL6X
2
VL2X2
VL3X2
VL4X2
VL5X2
VL6X2
3
VLX3
VL2X3
VL3X3
VL4X3
VL5X3
4
VLX4
VL2X4
VL3X4
VL4X4
VL5X4
5
VX5
VLX5
VL2X5
VL3X5
VL4X5

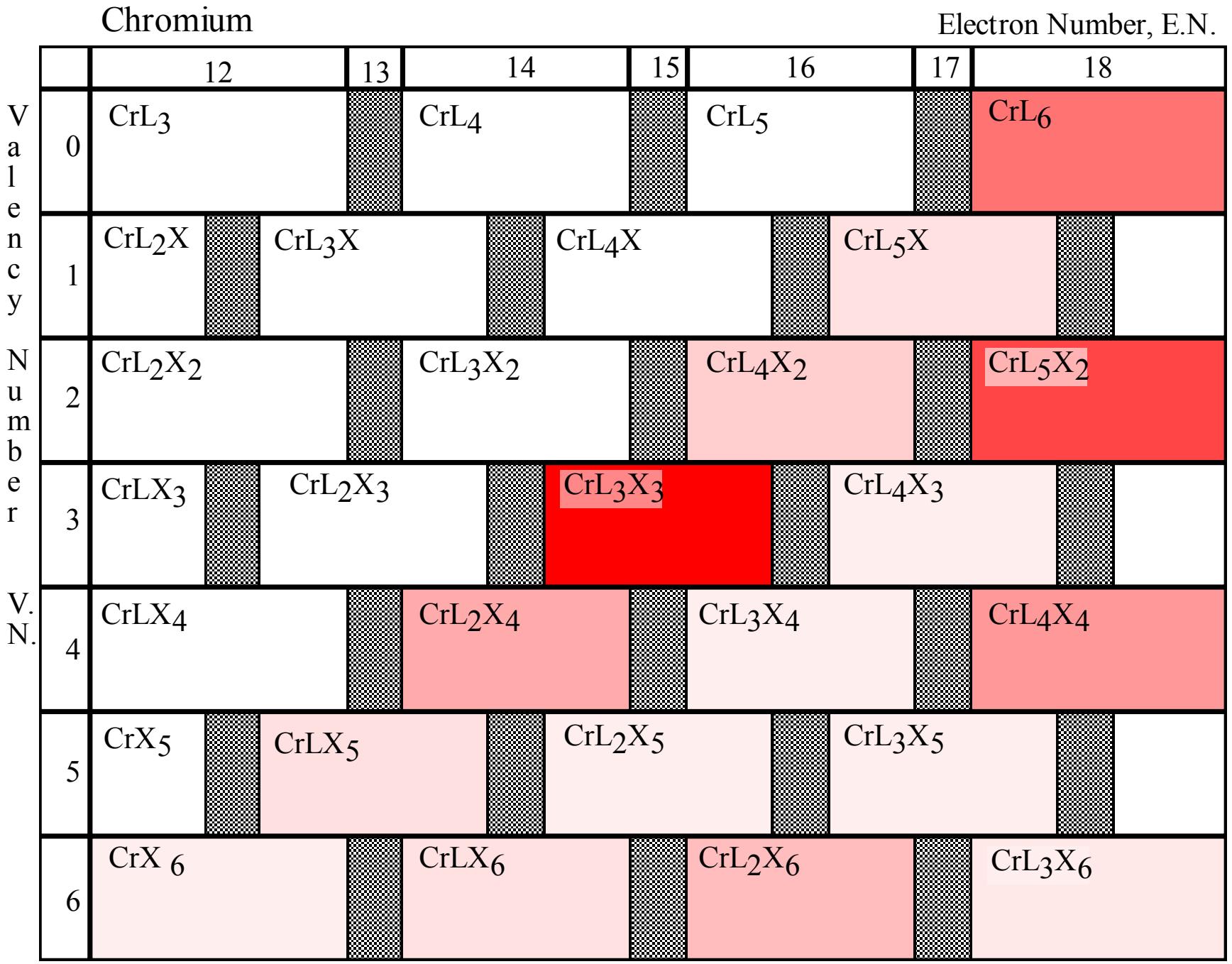
Niobium

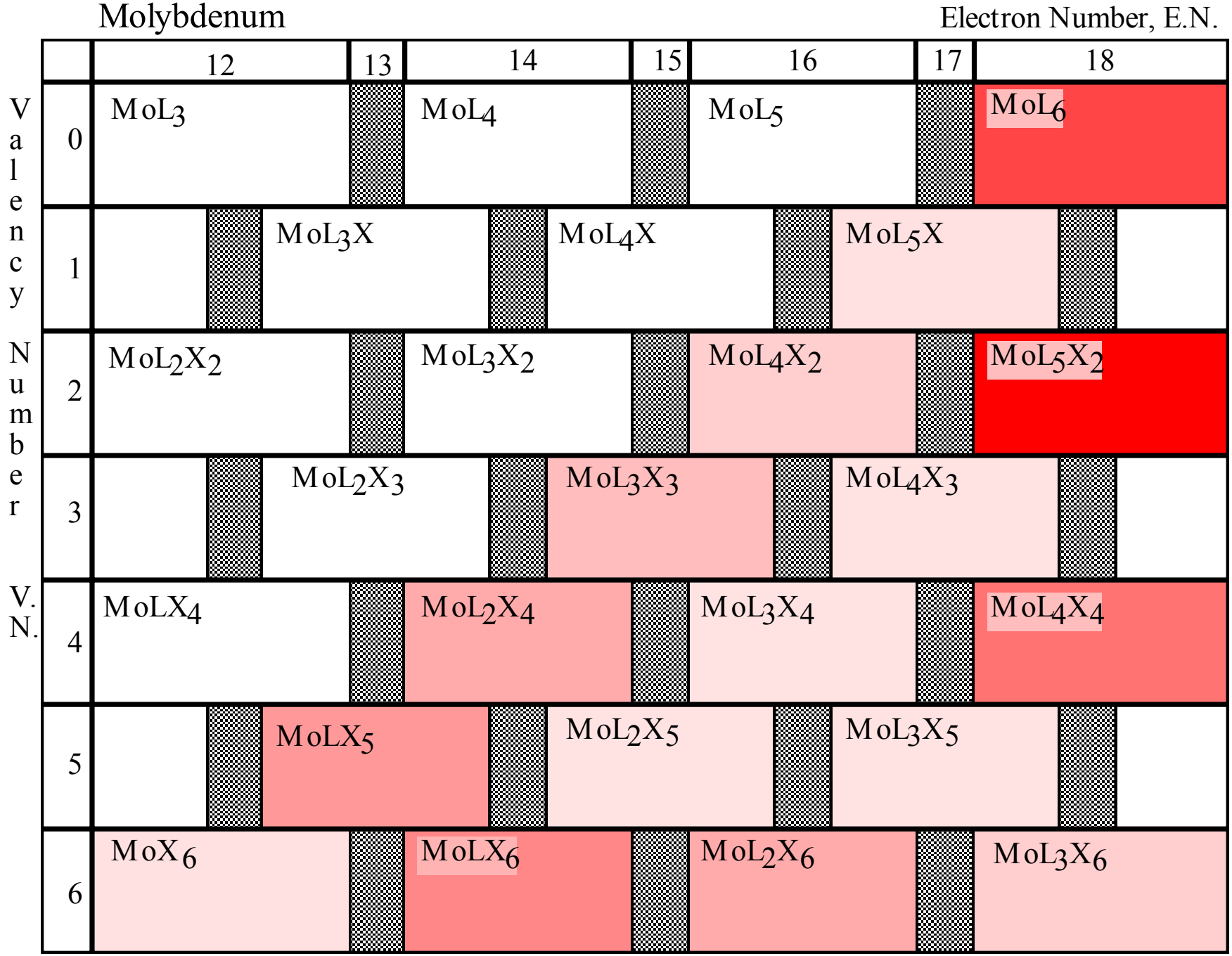
Electron Number E.N.

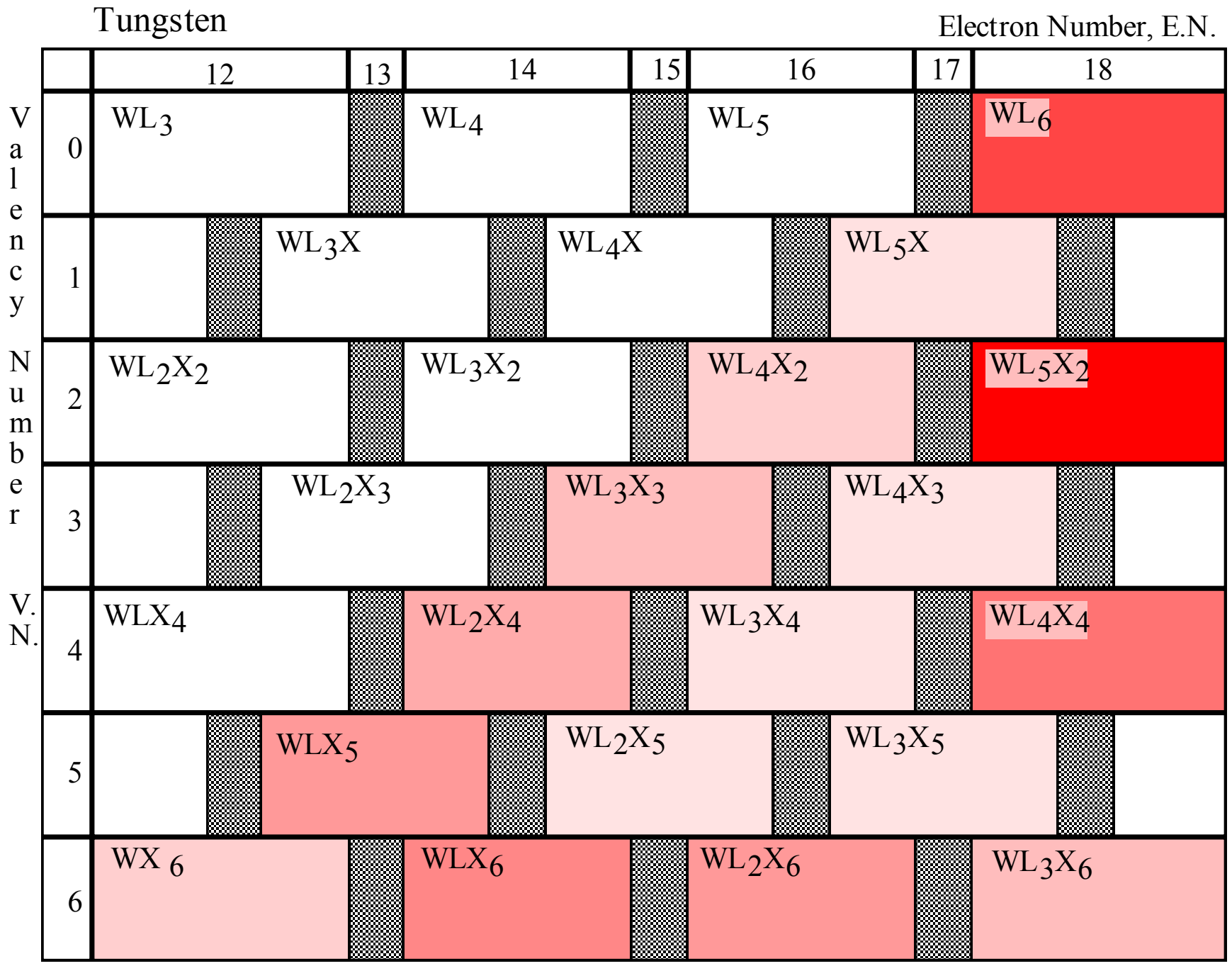
Valency Number V.N.

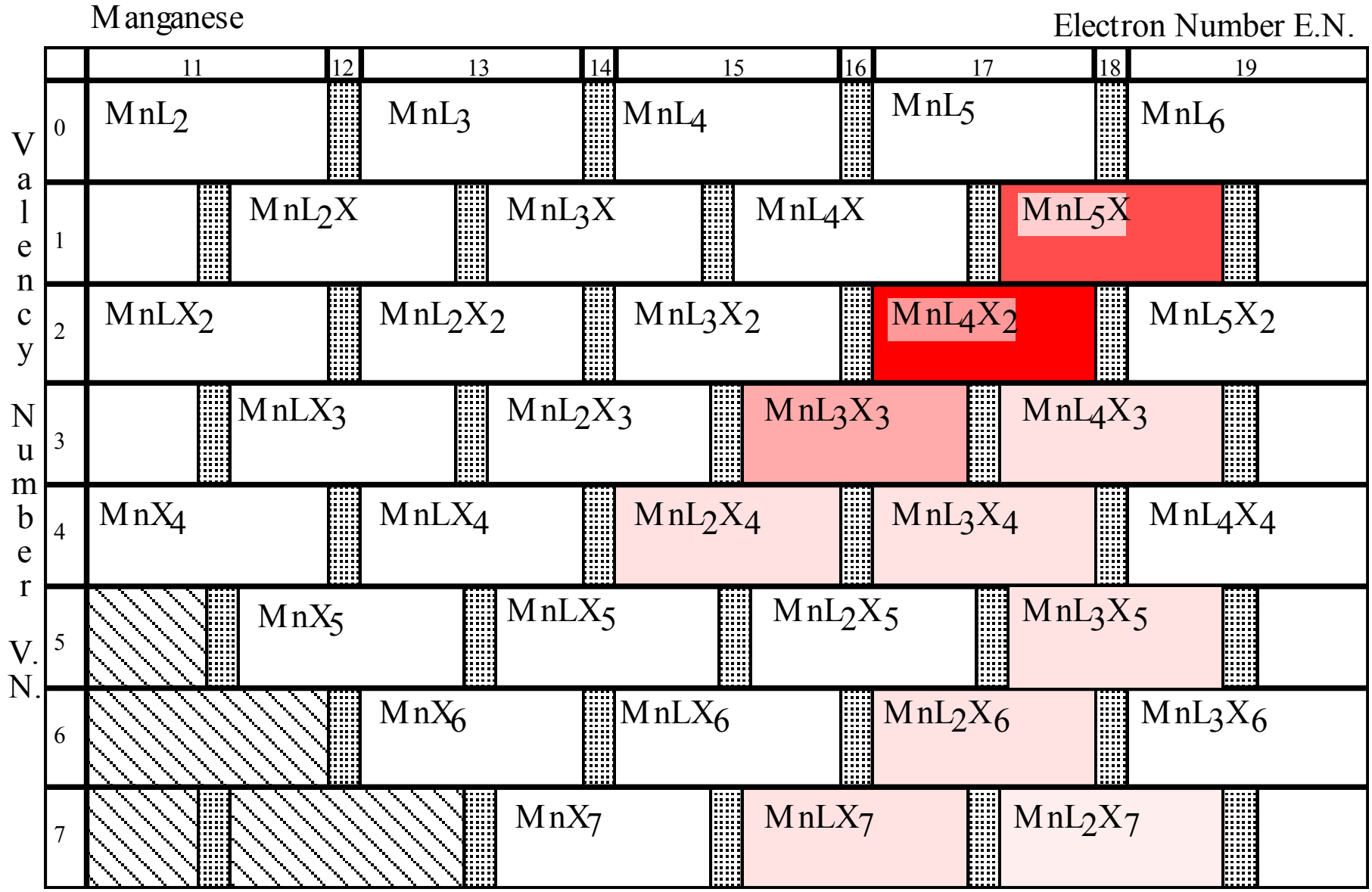
	11	12	13	14	15	16	17	18	19
0	NbL_3		NbL_4		NbL_5		NbL_6		NbL_7
1	NbL_2X		NbL_3X		NbL_4X		NbL_5X		NbL_6X
2	NbL_2X_2		NbL_3X_2		NbL_4X_2		NbL_5X_2		NbL_6X_2
3	$NbLX_3$		NbL_2X_3		NbL_3X_3		NbL_4X_3		NbL_5X_3
4	$NbLX_4$		NbL_2X_4		NbL_3X_4		NbL_4X_4		NbL_5X_4
5	NbX_5		$NbLX_5$		NbL_2X_5		NbL_3X_5		NbL_4X_5

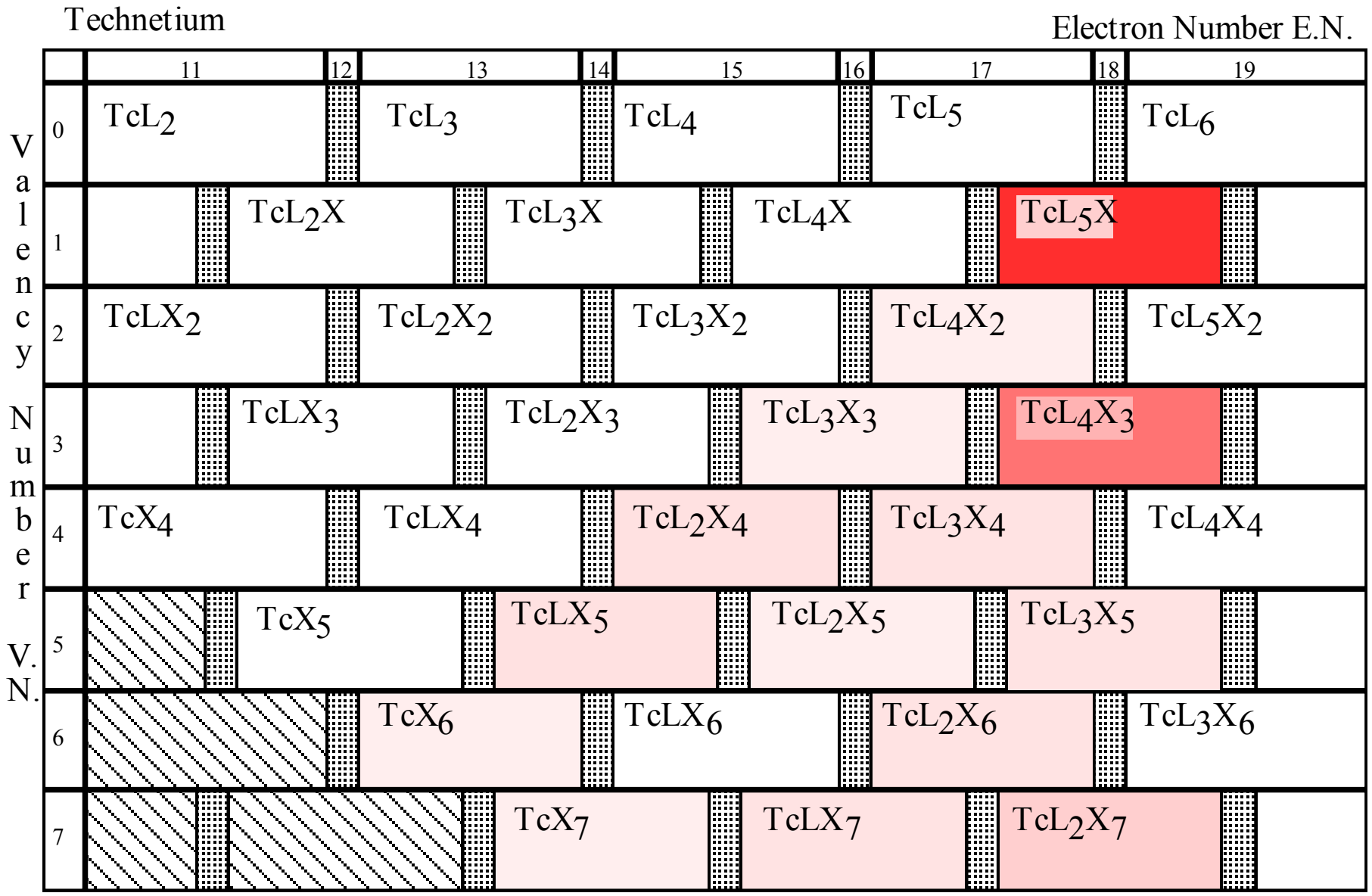

Tantalum
Electron Number E.N.
Valency Number V.N.
11
12
13
14
15
16
17
18
19
0
TaL3
TaL4
TaL5
TaL6
TaL7
1
TaL2X
TaL3X
TaL4X
TaL5X
TaL6X
2
TaL2X2
TaL3X2
TaL4X2
TaL5X2
TaL6X2
3
TaLX3
TaL2X3
TaL3X3
TaL4X3
TaL5X3
4
TaLX4
TaL2X4
TaL3X4
TaL4X4
TaL5X4
5
TaX5
TaLX5
TaL2X5
TaL3X5
TaL4X5


Chromium
Electron Number, E.N.
12
13
14
15
16
17
18
Valency Number V.N.
0
1
2
3
4
5
6
CrL3
CrL4
CrL5
CrL6
CrL2X
CrL3X
CrL4X
CrL5X
CrL2X2
CrL3X2
CrL4X2
CrL5X2
CrLX3
CrL2X3
CrL3X3
CrL4X3
CrLX4
CrL2X4
CrL3X4
CrL4X4
CrX5
CrLX5
CrL2X5
CrL3X5
CrX 6
CrLX6
CrL2X6
CrL3X6


Molybdenum
Electron Number, E.N.
12
13
14
15
16
17
18
Valency Number V.N.
0
1
2
3
4
5
6
MoL3
MoL4
MoL5
MoL6
MoL3X
MoL4X
MoL5X
MoL2X2
MoL3X2
MoL4X2
MoL5X2
MoL2X3
MoL3X3
MoL4X3
MoLX4
MoL2X4
MoL3X4
MoL4X4
MoLX5
MoL2X5
MoL3X5
MoX6
MoLX6
MoL2X6
MoL3X6


Tungsten
Electron Number, E.N.
12
13
14
15
16
17
18
Valency Number V.N.
0
1
2
3
4
5
6
WL3
WL4
WL5
WL6
WL3X
WL4X
WL5X
WL2X2
WL3X2
WL4X2
WL5X2
WL2X3
WL3X3
WL4X3
WLX4
WL2X4
WL3X4
WL4X4
WLX5
WL2X5
WL3X5
WX 6
WLX6
WL2X6
WL3X6


Manganese
Electron Number E.N.
Valency Number V.N.
11
12
13
14
15
16
17
18
19
0
1
2
3
4
5
6
7
MnL2
MnL3
MnL4
MnL5
MnL6
MnL2X
MnL3X
MnL4X
MnL5X
MnLX2
MnL2X2
MnL3X2
MnL4X2
MnL5X2
MnLX3
MnL2X3
MnL3X3
MnL4X3
MnX4
MnLX4
MnL2X4
MnL3X4
MnL4X4
MnX5
MnLX5
MnL2X5
MnL3X5
MnX6
MnLX6
MnL2X6
MnL3X6
MnX7
MnLX7
MnL2X7


Technetium
Electron Number E.N.
Valency Number V.N.
11
12
13
14
15
16
17
18
19
0
1
2
3
4
5
6
7
TcL2
TcL3
TcL4
TcL5
TcL6
TcL2X
TcL3X
TcL4X
TcL5X
TcLX2
TcL2X2
TcL3X2
TcL4X2
TcL5X2
TcLX3
TcL2X3
TcL3X3
TcL4X3
TcX4
TcLX4
TcL2X4
TcL3X4
TcL4X4
TcX5
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TcL3X6
TcX7
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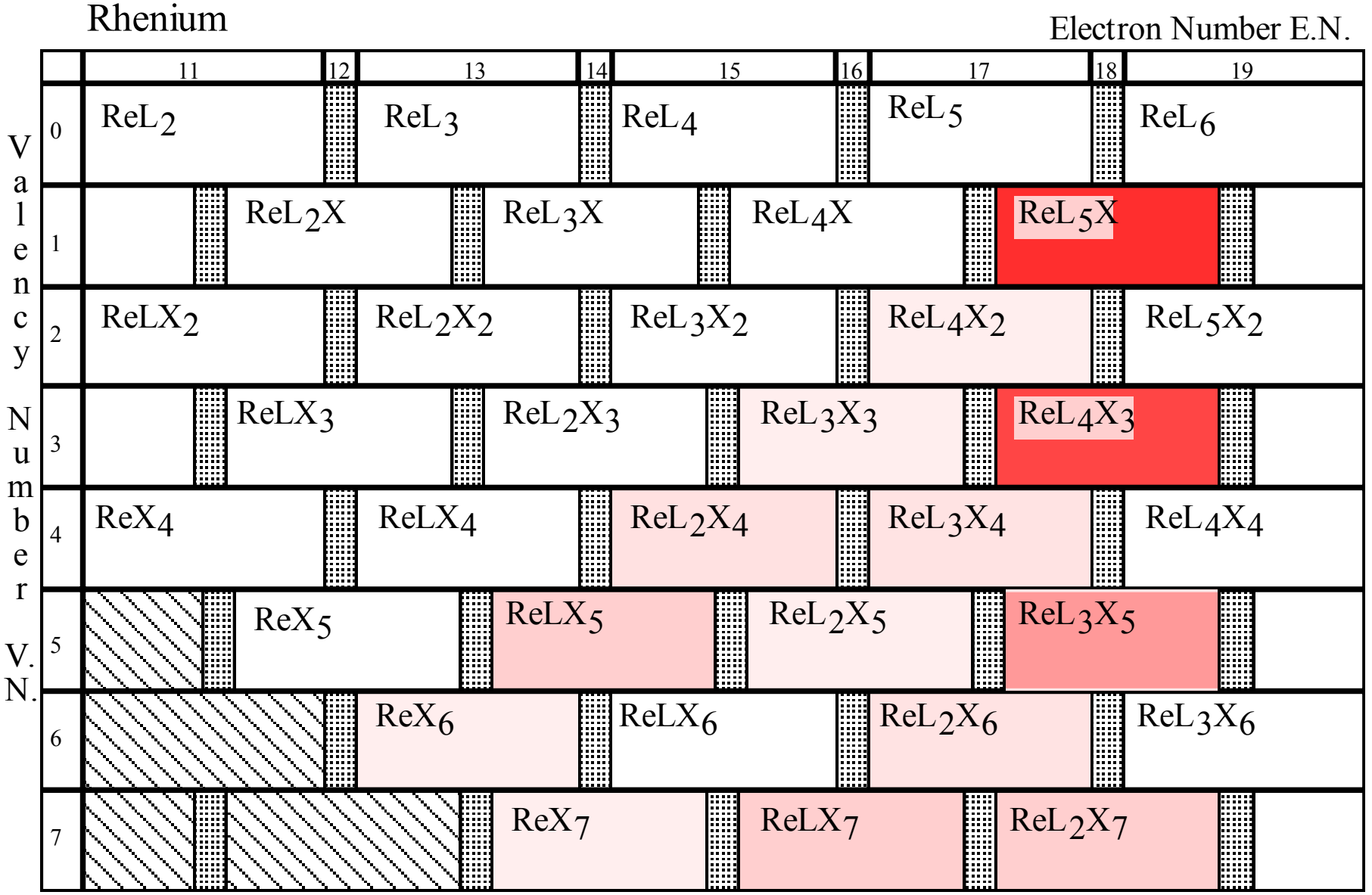
TcL2X7


Rhenium
Electron Number E.N.
11
12
13
14
15
16
17
18
19
Valency Number V. N.
0
1
2
3
4
5
6
7
ReL2
ReL3
ReL4
ReL5
ReL6
ReL2X
ReL3X
ReL4X
ReL5X
ReLX2
ReL2X2
ReL3X2
ReL4X2
ReL5X2
ReLX3
ReL2X3
ReL3X3
ReL4X3
ReX4
ReLX4
ReL2X4
ReL3X4
ReL4X4
ReX5
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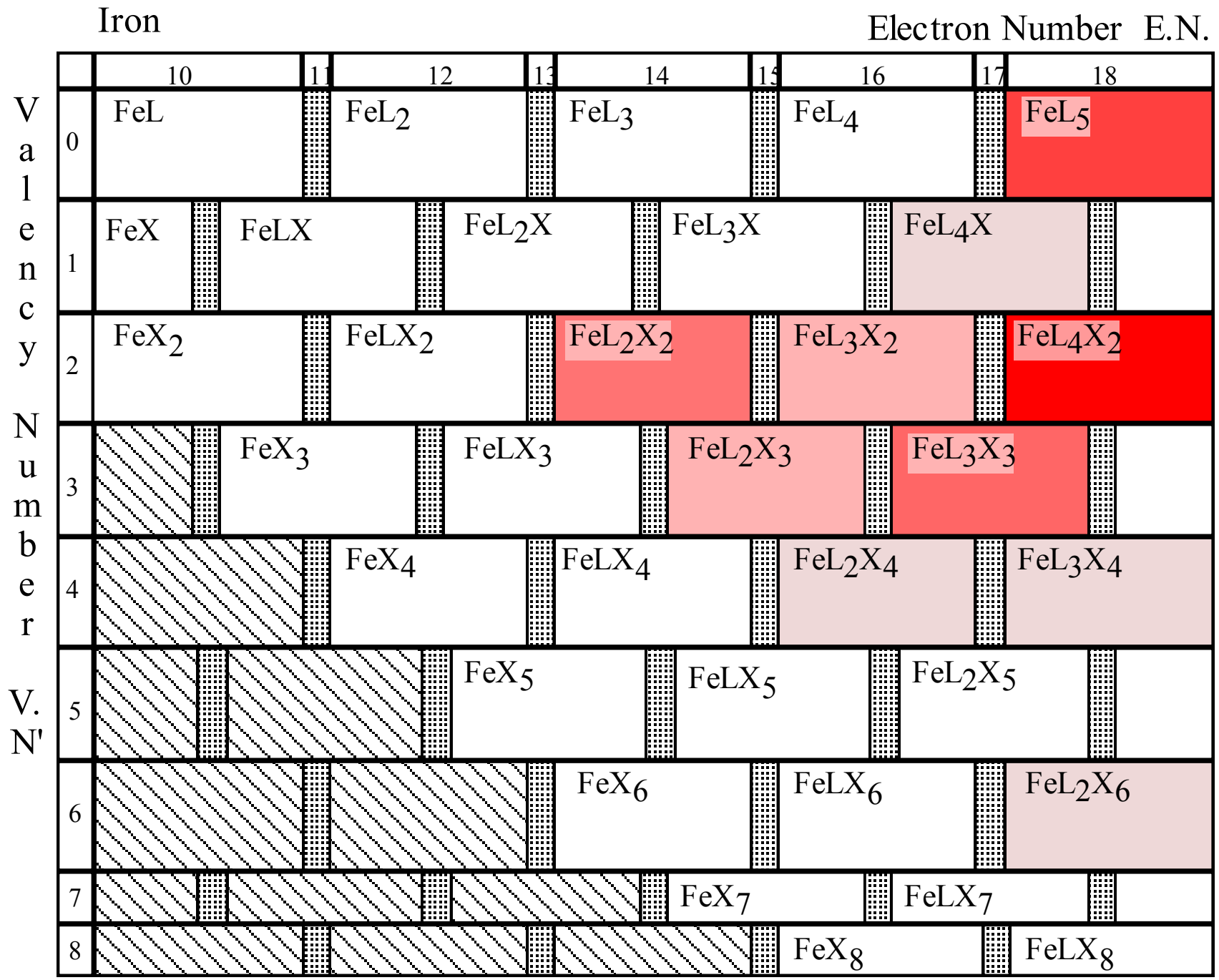
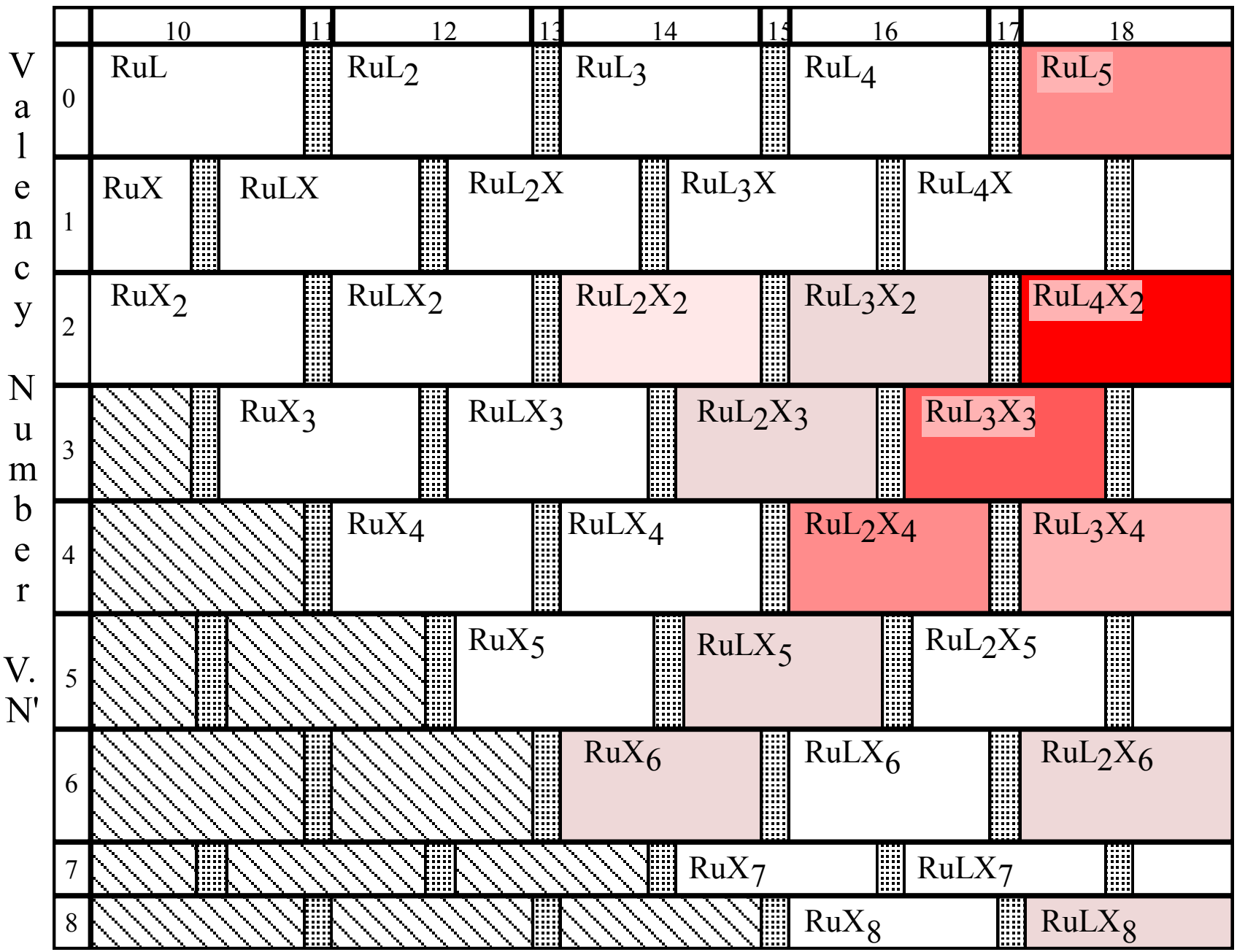
ReL3X6
ReX7
ReLX7
ReL2X7


Iron
Electron Number E.N.
Valency Number V. N'
10
11
12
13
14
15
16
17
18
0
1
2
3
4
5
6
7
8
FeL
FeL2
FeL3
FeL4
FeL5
FeX
FeLX
FeL2X
FeL3X
FeL4X
FeX2
FeLX2
FeL2X2
FeL3X2
FeL4X2
FeX3
FeLX3
FeL2X3
FeL3X3
FeX4
FeLX4
FeL2X4
FeL3X4
FeX5
FeLX5
FeL2X5
FeX6
FeLX6
FeL2X6
FeX7
FeLX7
FeX8
FeLX8


Ruthenium
Electron Number E.N.
Valency Number V. N'
10
11
12
13
14
15
16
17
18
0
1
2
3
4
5
6
7
8
RuL
RuL2
RuL3
RuL4
RuL5
RuX
RuLX
RuL2X
RuL3X
RuL4X
RuX2
RuLX2
RuL2X2
RuL3X2
RuL4X2
RuX3
RuLX3
RuL2X3
RuL3X3
RuX4
RuLX4
RuL2X4
RuL3X4
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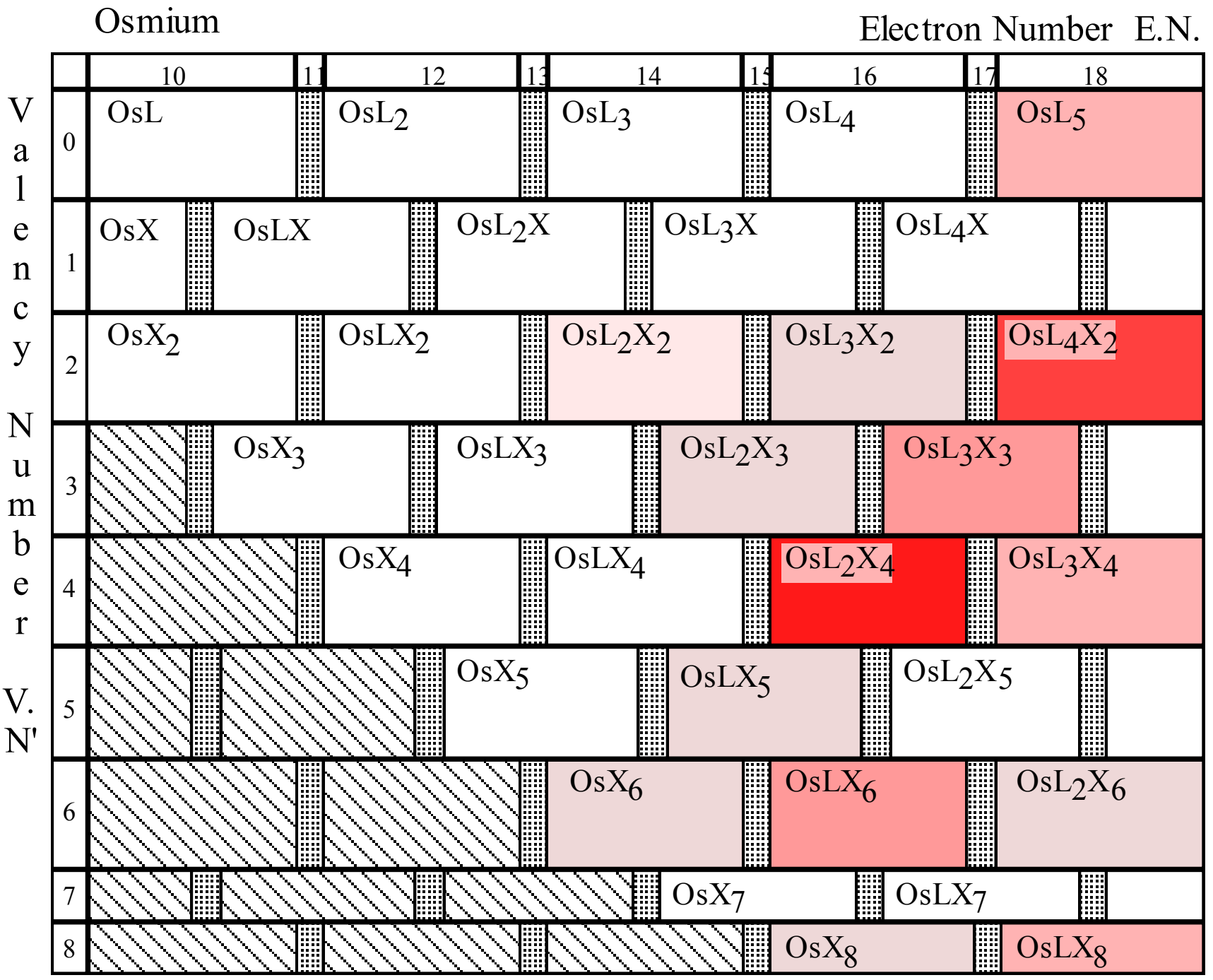
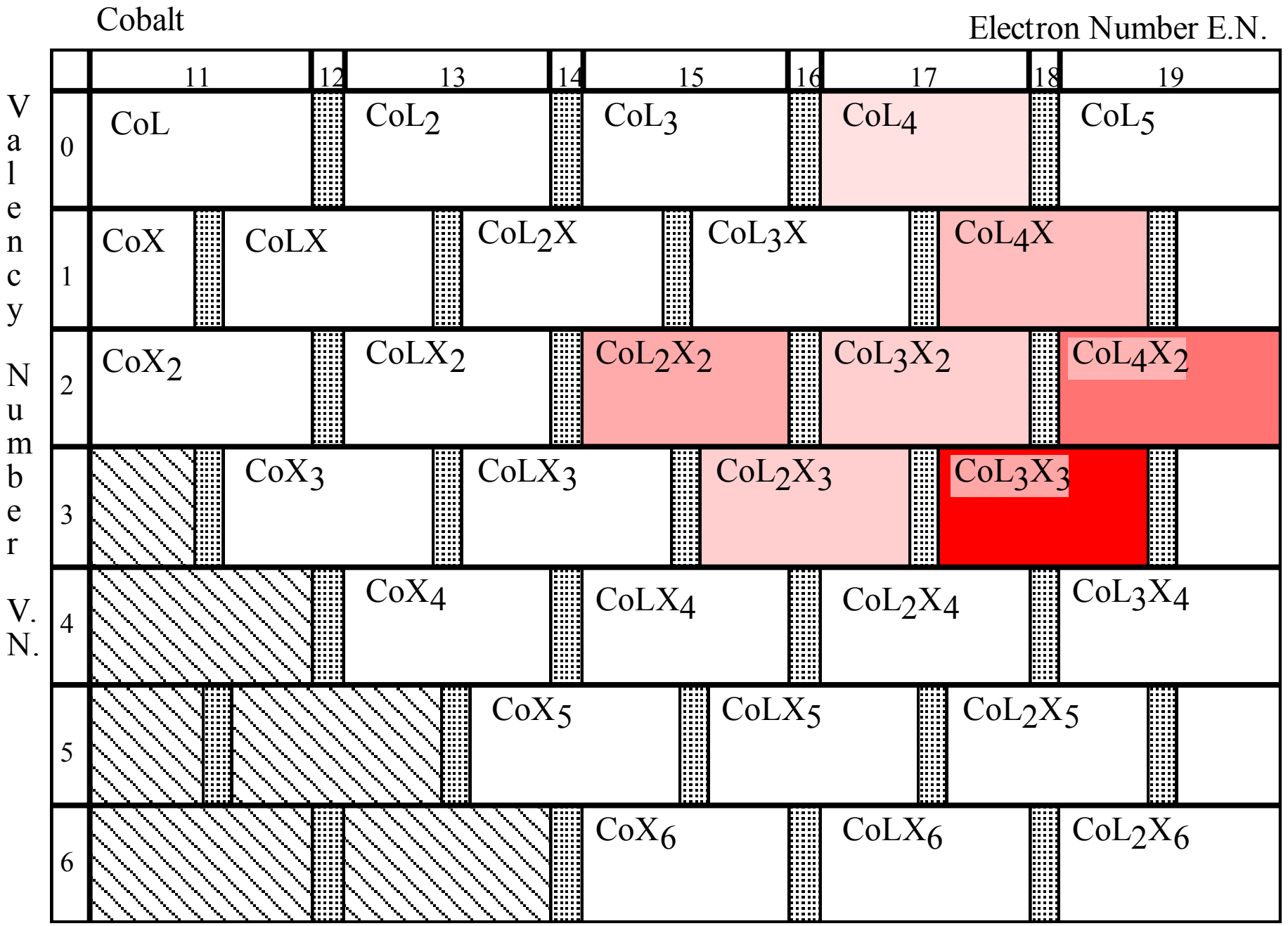
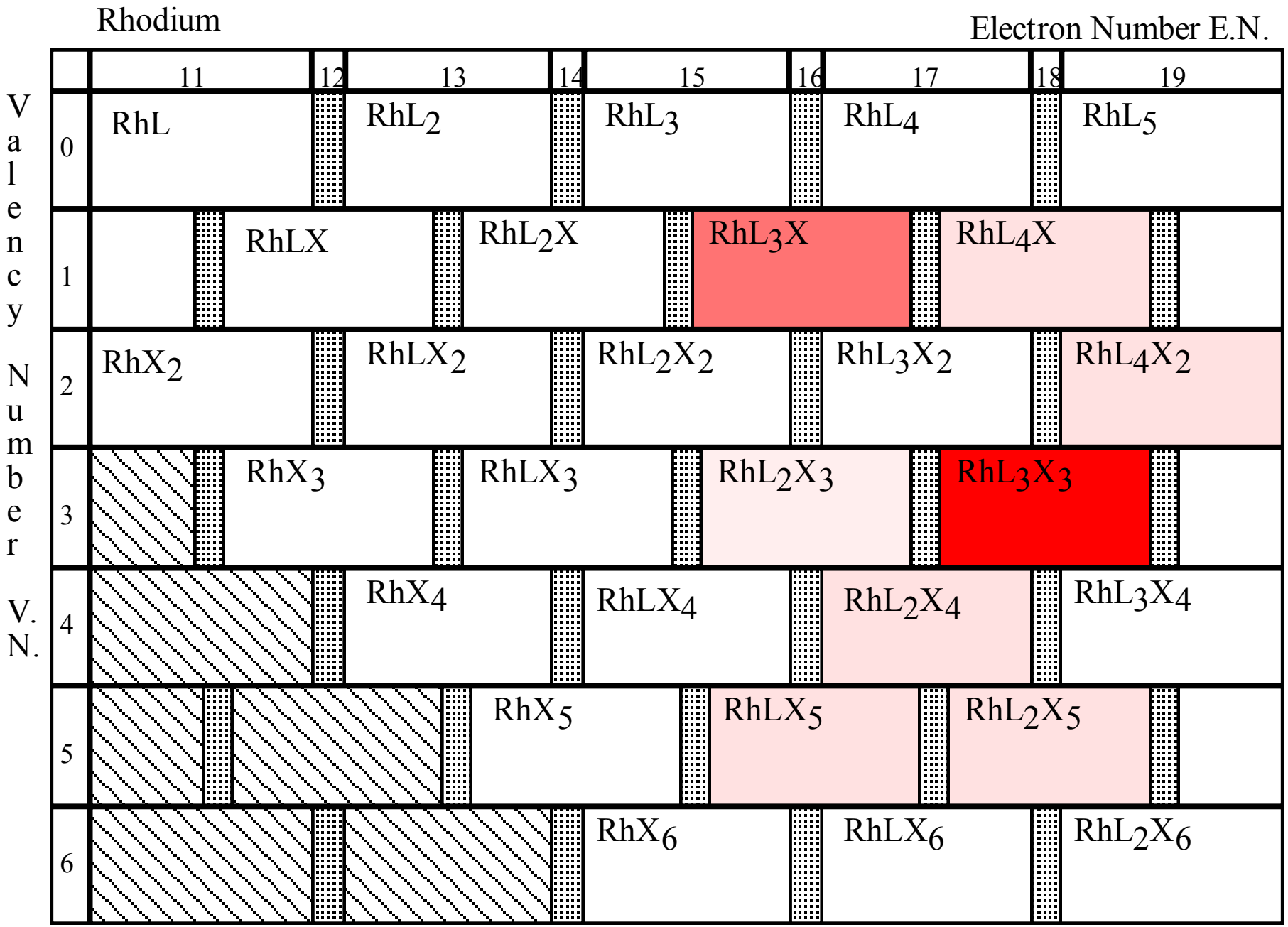
RuL2X6
RuX7
RuLX7
RuX8
RuLX8


Osmium
Electron Number E.N.
Valency Number V. N'
10
11
12
13
14
15
16
17
18
0
1
2
3
4
5
6
7
8
OsL
OsL2
OsL3
OsL4
OsL5
OsX
OsLX
OsL2X
OsL3X
OsL4X
OsX2
OsLX2
OsL2X2
OsL3X2
OsL4X2
OsX3
OsLX3
OsL2X3
OsL3X3
OsX4
OsLX4
OsL2X4
OsL3X4
OsX5
OsLX5
OsL2X5
OsX6
OsLX6
OsL2X6
OsX7
OsLX7
OsX8
OsLX8


Cobalt
Electron Number E.N.
Valency Number V. N.
11
12
13
14
15
16
17
18
19
0
CoL
CoL2
CoL3
CoL4
CoL5
1
CoX
CoLX
CoL2X
CoL3X
CoL4X
2
CoX2
CoLX2
CoL2X2
CoL3X2
CoL4X2
3
CoX3
CoLX3
CoL2X3
CoL3X3
4
CoX4
CoLX4
CoL2X4
CoL3X4
5
CoX5
CoLX5
CoL2X5
6
CoX6
CoLX6
CoL2X6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Valency Number V. N.
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18
19
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RhL3
RhL4
RhL5
1
RhLX
RhL2X
RhL3X
RhL4X
2
RhX2
RhLX2
RhL2X2
RhL3X2
RhL4X2
3
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RhLX3
RhL2X3
RhL3X3
4
RhX4
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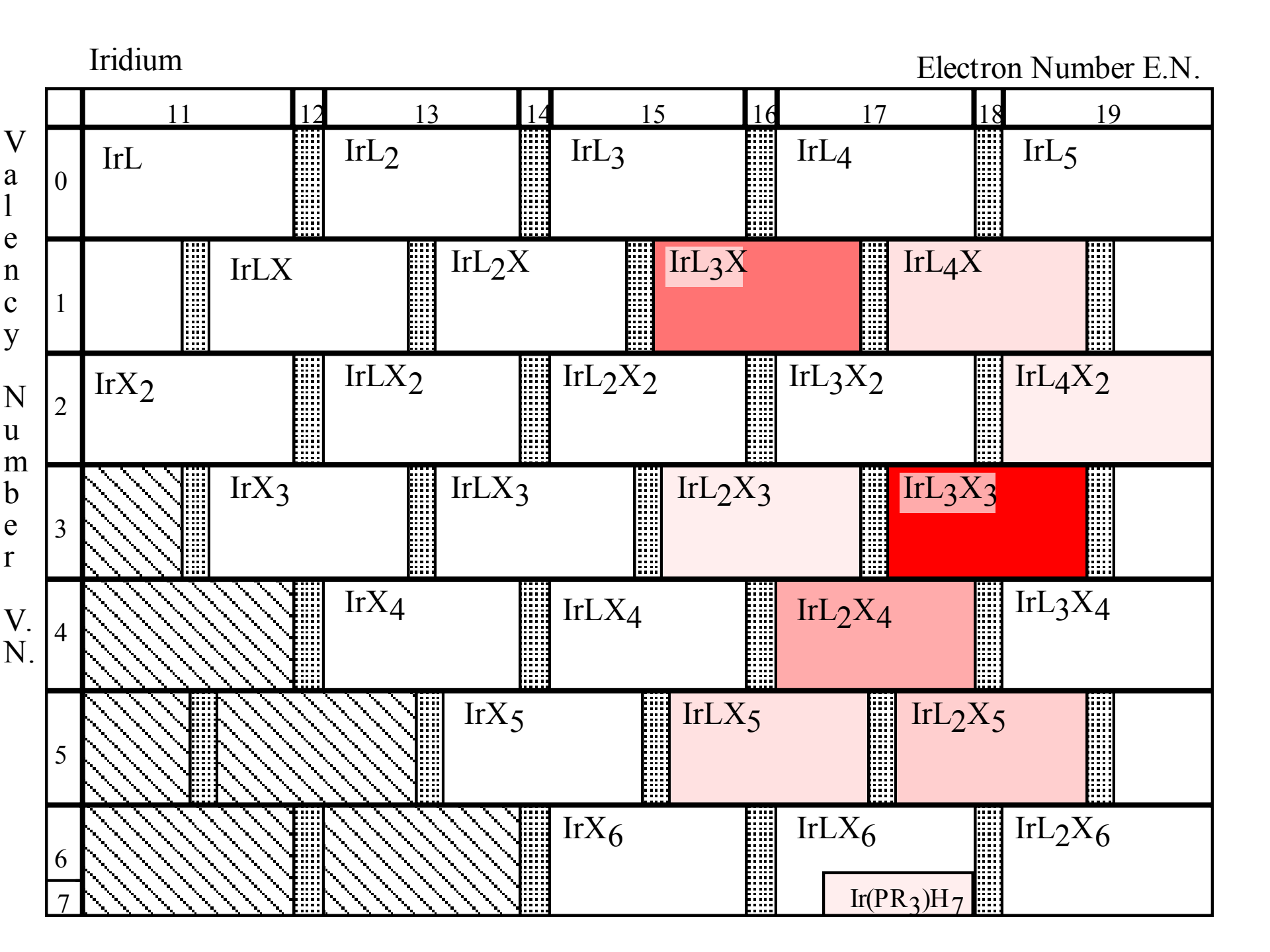
6
RhX6
RhLX6
RhL2X6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IrL5
IrLX
IrL2X
IrL3X
IrL4X
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IrX3
IrLX3
IrL2X3
IrL3X3
IrX4
IrLX4
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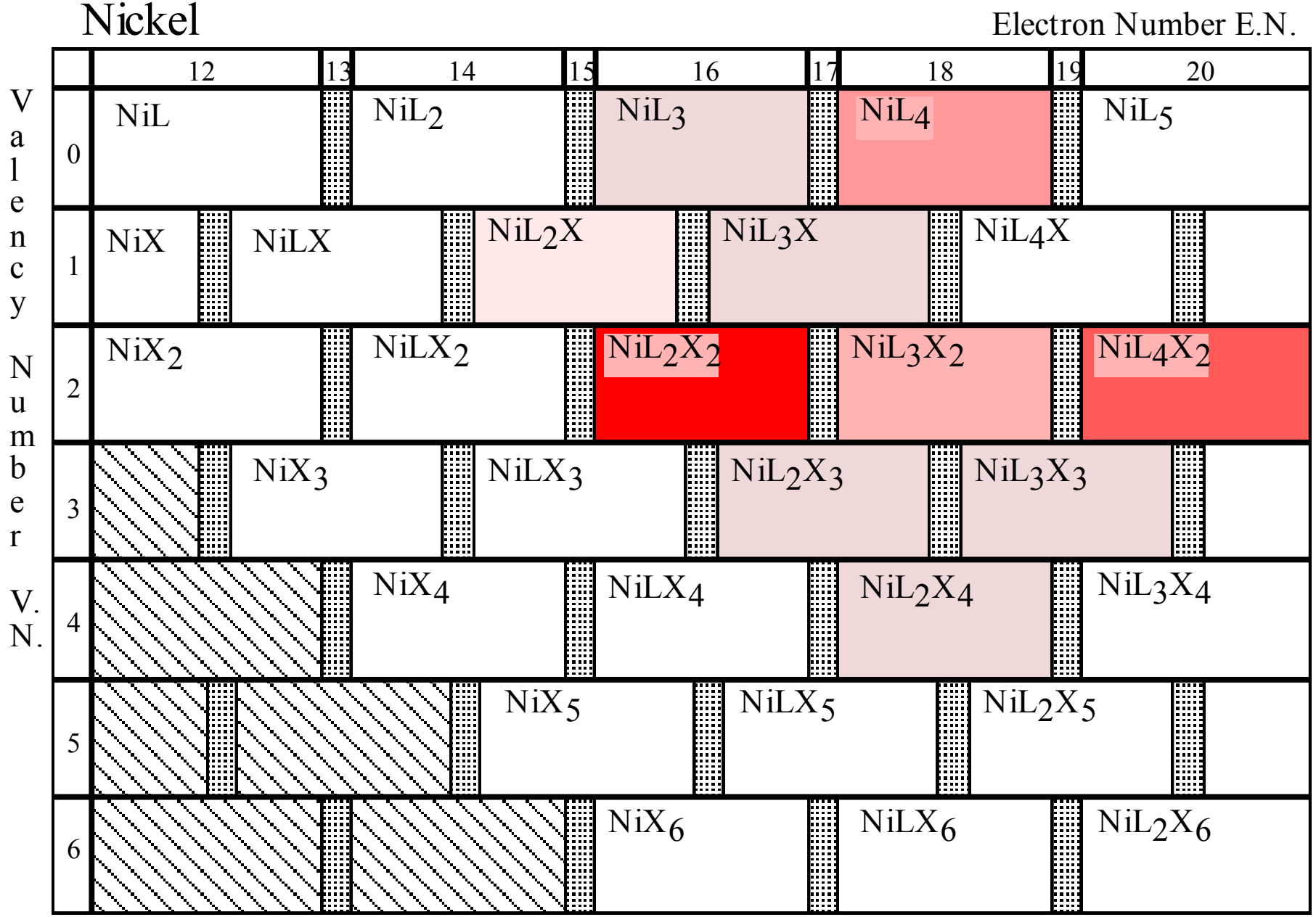
IrX5
IrLX5
IrL2X5
IrX6
IrLX6
IrL2X6
Ir(PR3)H7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Valency Number V.N.
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5
6
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NiL2
NiL3
NiL4
NiL5
NiX
NiLX
NiL2X
NiL3X
NiL4X
NiX2
NiLX2
NiL2X2
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NiL4X2
NiX3
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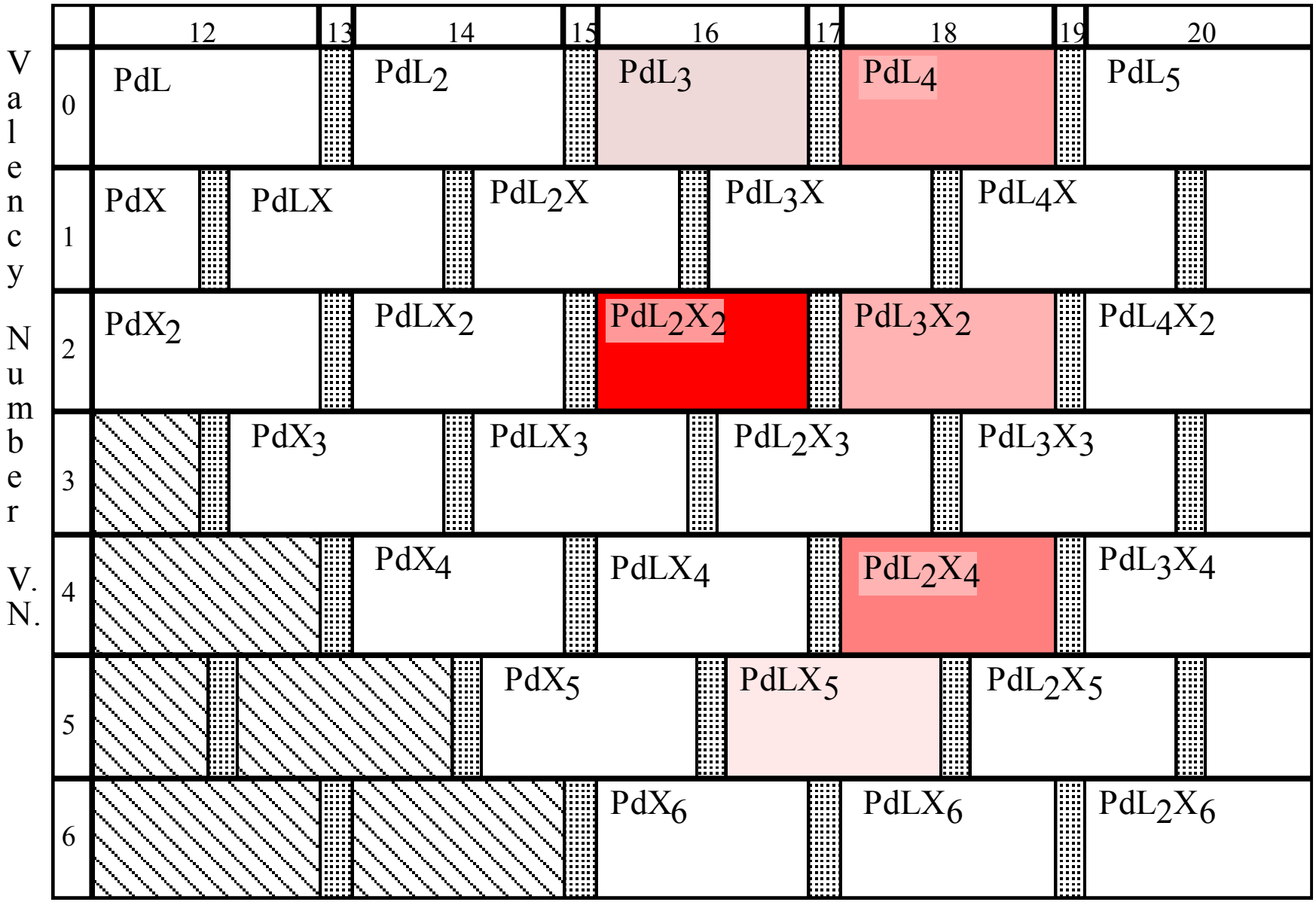
NiL2X6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19
20
Valency Number V.N.
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3
4
5
6
PdL
PdL2
PdL3
PdL4
PdL5
PdX
PdLX
PdL2X
PdL3X
PdL4X
PdX2
PdLX2
PdL2X2
PdL3X2
PdL4X2
PdX3
PdLX3
PdL2X3
PdL3X3
PdX4
PdLX4
PdL2X4
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PdX5
PdLX5
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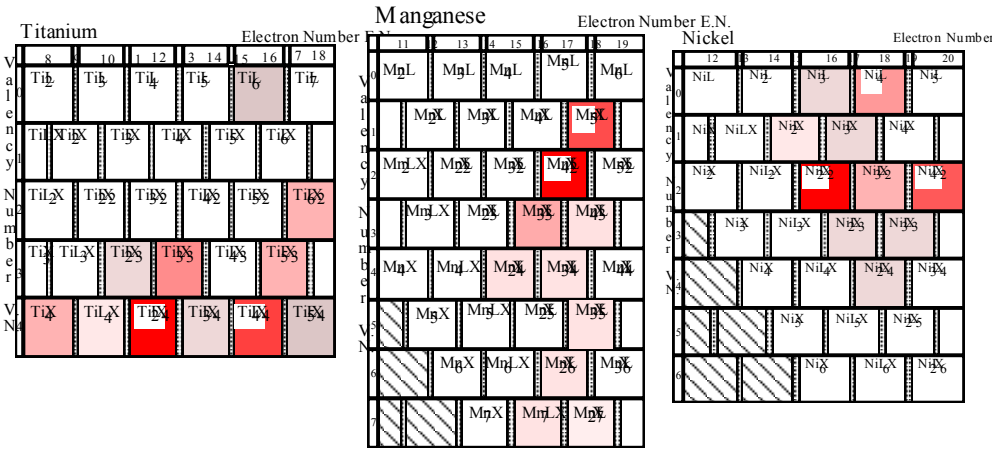
PdX6
PdLX6
PdL2X6

MLX plots for Titanium, Manganese and Nickel



Rule 1) Filled orbitals (18 electrons): Only possible for Ti when there are very small or compact ligands since a further 14-electrons are required. E.g. $[TiCp_2(CO)_2]$. $TiCl_4$ is apparently an 8-electron compound but if the *symmetry allowed contributions from the Cl p π-orbitals* are counted then there are an extra 10 electrons which gives the value for EN = 18-electrons!

For Mn, excellent for VN = 1 where also LBN = 6. but poor for VN = 3 and 5 since LNB = 7 or 8 respectively AND higher VN for Mn are rare since 3d orbitals are rapidly lowered in energy by the increasing patrial +ve change on the Mn centre.

For Ni, 18-electrons are found for NiL_4, NiL_3X_2 and (very rare) NiL_2X_4,. Higher VN's for Ni not found since increase effective nuclear charge at this end of the d-block TM's means the I.P.'s too high. The special stability of square-planer, 16-electron NiL_2X_2 is associated with the d^8 configuration.

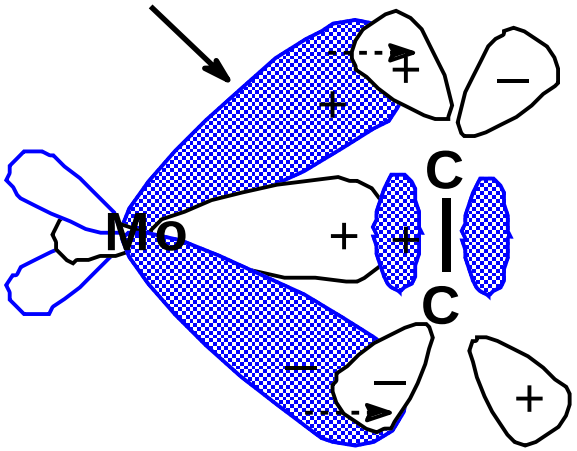
Rule 2) Steric saturation: For Ti: unusually high LBN's (and high co-ordination nos) are commonly found, e.g. in 16-electron TiL_4X_4, LBN = 8. For Ni. low LBN's (3,4,5) are found since Ni already has 10 electrons and only requires 4 x L ligands to give 18e NiL_4, e.g. $Ni(CO)_4$.

Rule 3) Electroneutrality rule: For Ti: since I.P.'s are low all 4 valency electrons are accessible to most ligands, e.g TiI_4.

For Mn, the increase of effective nuclear charge with increasing atomic number across the d-block elements means that the higher VN's are only obtainable with the first row elements as ligand atoms (since these for the strongest σ-bonds). Hence VN = 4 is found with F, O, N, and C ligands, e.g. MnR_4, R = CH_2SiMe_3. VN = 7 is known only for $[Mn(=X)_4]^-$, where X = O or NR, the electron donation from the appropriate symmetry combination of the pπ=orbitals of the X ligands and the negative charge resulting from the anion helps reduce the induced positive charge on the Mn centre. Nonetheless, the $[MnO_4]^-$ and Mn_2O_7 compounds are amongst the most oxidising known (in aqueous acid). which shows these Mn centres have exceptionally high partial +ve charges.

Back-donation--- but how much ?

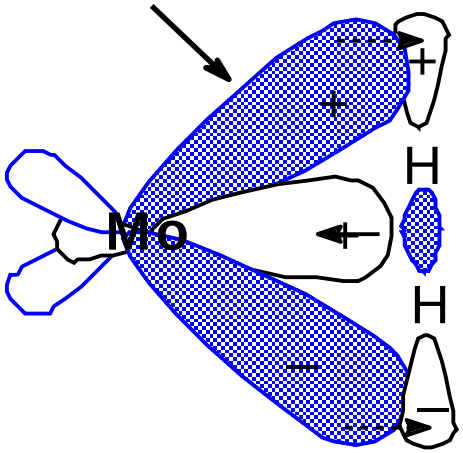
back donation



π^*

Chatt-Dewar

back donation



σ^*

H-H 0.84Å

(cf 0.74Å in H_2)

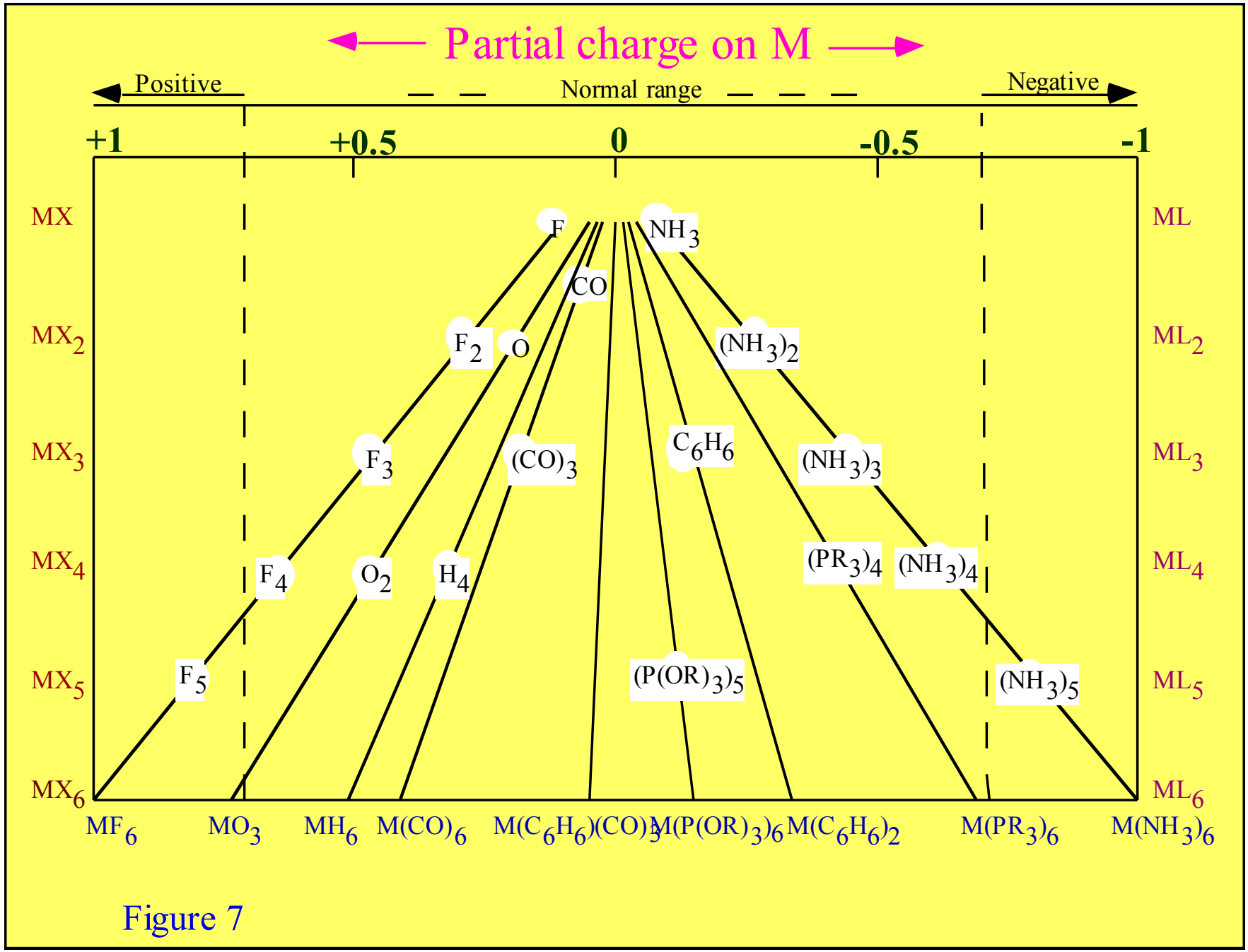

Partial charge on M
Positive
Normal range
Negative
+1
+0.5
0
-0.5
-1
MX
MX2
MX3
MX4
MX5
MX6
ML
ML2
ML3
ML4
ML5
ML6
F
NH3
CO
F2
O
(NH3)2
F3
(CO)3
C6H6
(NH3)3
F4
O2
H4
(PR3)4
(NH3)4
F5
(P(OR)3)5
(NH3)5
MF6
MO3
MH6
M(CO)6
M(C6H6)(CO)3
M(P(OR)3)6
M(C6H6)2
M(PR3)6
M(NH3)6

Figure 7

Table 5. Examples of ligand functionality and denticity.

Number of ligating atoms	Number of orbitals[a] used in bond formation	Description	Typical examples of ligands
1	1	mono-dentane, mono-functional	H, Me, NR_2 (bent), NH_3, CO, H_2
1	2	mono-dentate, bi-functional	NR_2 (planer), $=CR_2$, =O
1	3	mono-dentate, tri-functional	N, CR (carbyne)
1	4	mono-dentate, tetra-functional	quadruple bonds
2	1 and 1	bi-dentate, each mono-functional	oxolate, acetate, ethylene-diamine
2	2 and 1	bi-dentate, one bifunctional the other mono-functional	$R_2N(CH_2)_2NR$ with planer CNR
2	1(MO)	bidentate, monofunctional	η-ethene[b]
2	1 + 1(AO's)	bi-dentate, bifunctional	C_2H_4 in metallacyclopropane[b]
3	2(MO's)	tridentate, bi-functional	η-allyl
5	3(MO's)	penta-dentate, trifunctional	η-cyclopentadienyl
6	3 (MO's)	hexa-dentate, tri-functional	η-benzene

[a] Essentially atomic orbitals (AO) unless otherwise indicated. MO indicates a molecular orbital.

[b] These are alternative descriptions. for the bonding of ethene.

Table 6 Rules for classification of covalent molecules and molecular ions

Initial class	Rule for reduction to E.N.C.	V.N. given by	L.B.N. given by	Limits
MX_X neutral	-	x	x	x Š Me
$[MX_X]^{m-}$ anions	$X^- \otimes L$	x - m	x	m Š x
$[MX_X]^{m+}$ cations	$X^+ \otimes Z$	x - m	x	m Š x
ML_l neutral	-	x = 0	l	availability of M orbitals, 18e rule
$[ML_l]^{m-}$ anions	L^- ' LX	m	l + m	availability of ligand orbitals
$[ML_l]^{m+}$ cations	L^+ ' X	m	l	m Š n
ML_lX_X neutral	-	x	l + x	x Š Me, availability of M orbitals
$[M_lX_X]^{m-}$ anions	X^- ' L, then L^- ' LX	x-m (m Š x) m - x (l+x > m> x)	l + x l + m + x	As for $[ML]^{m-}$ and $[MX]^{m-}$ anions
$[ML_lX_X]^{m+}$ cations	L^+ ' X, then X^+' Z	x + m (m < l) 2l + x - m (m>l)	l + x l + x	As for $[ML]^{m+}$ and $[MX]^{m+}$ cations

Table 9. Determination of MLXZ class and reduction to the neutral class of oxygen derivatives; where O is a $(\bar{X})_2$ class ligand.

Molecule or Ion	Class	Rule	Equivalent Neutral Class
CO_2	$M(\bar{X}_2)$	--	MX_4
CO_3^{2-}	$M\bar{X}_2(\bar{X}_2^-)_2$	$\bar{X}_2^- \ll X$	MX_4
MoO_2Cl_2	$M(\bar{X}_2)_2X_2$	--	MX_6[b]
SO_3	$M(\bar{X}_2)_3$	--	MX_6
SO_2Cl_2	$M(\bar{X}_2)_2X_2$	--	MX_6
Me_2CO	$[M(\bar{X}_2)_2X_2]$	--	MX_4
MoO_4^{2-}	$[M(\bar{X}_2)_2(\bar{X}^-)$	$\bar{X}_2^- \ll X$	MX_6[b]
ReO_4^-	$[M(\bar{X}_2)_3(\bar{X}^-)$	$\bar{X}_2^-$, X	MX_7[b]
NO_2^-	$[M(\bar{X}_2)(\bar{X}_2^-)]$	$\bar{X}_2^-$, X	MX_3
PHO_3^{2-}	$[M(\bar{X}_2)(\bar{X}_2^-)_2X]$	$\bar{X}_2^-$, X	MX_5
$[VO(H_2O)_4]^{2+}$	$[M(\bar{X}_2)L_2(L^+)_2$	L^+, X	ML_2X_4[b]
$VO(acac)_2$	$[M\bar{X}_2(LX)_2]$	--	ML_2X_4[b]
$[VO(SCN)_4]^{2-}$[a]	$[M(\bar{X}_2)^-X_3X^-]$	$\bar{X}_2^-$, LX X^-, L	ML_2X_4[b]

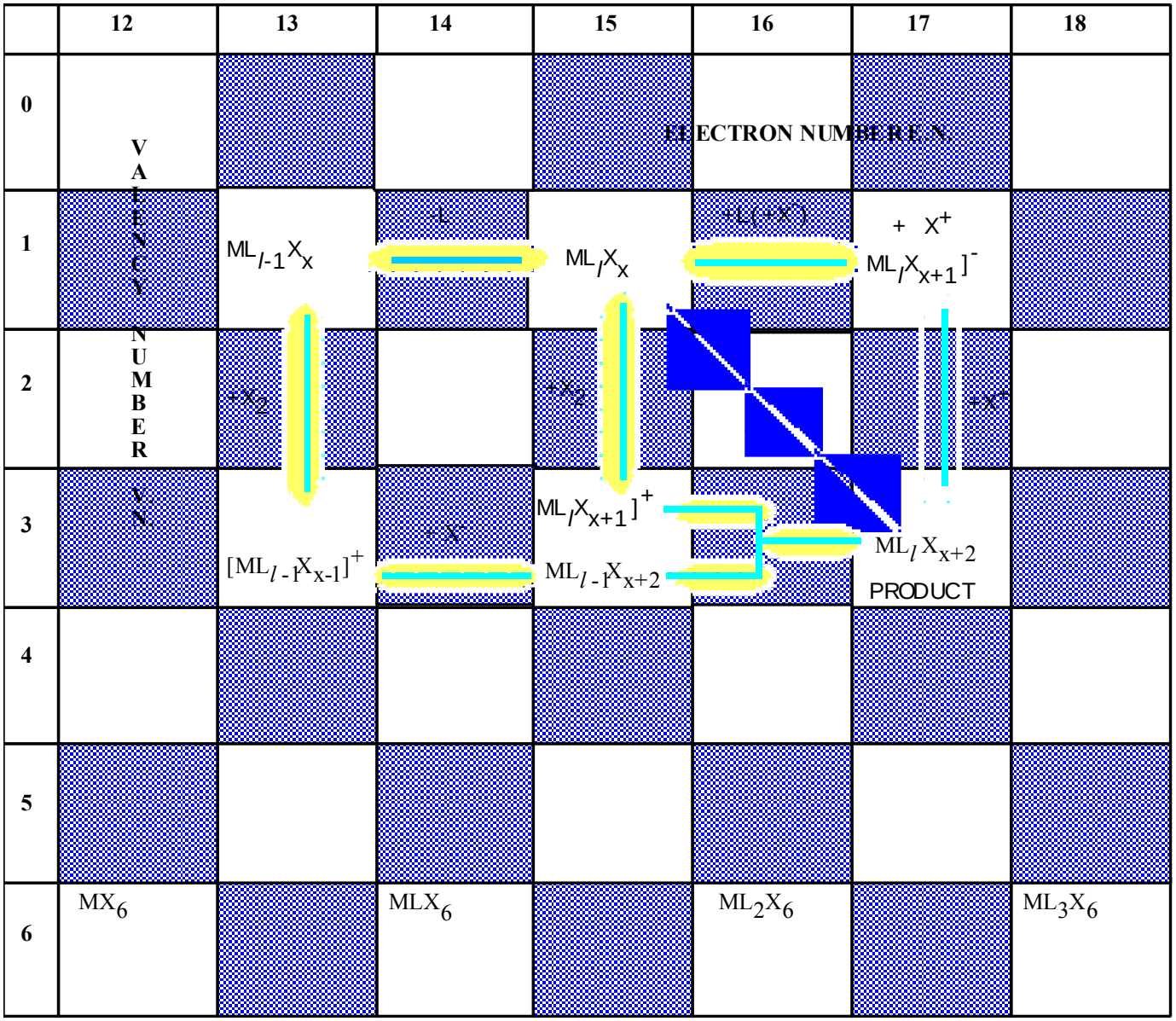
[a] The V = O distance = 1.62Å so O is dassified as $(\bar{X}_2)^-$. [b] The metal centre has empty d-orbitals, if p_π-lone pair electrons on the oxygen donate to the metal the number of L-functions increases by one or more according to symmetry considerations.

Table 3. **Summary of new definitions for the classification of covalent compounds**

Term	Short Symbol
A one-electron ligand function	X
Number of X ligands	x
A two-electron ligand function	L
Number of L ligands	l
Electron number of ligand of class L_lX_X	L.N. = $2l + x$
A mono-functional X_X -ligand-atom	$X_X = 1$
A poly-functional X_X -ligand atom	$X_X > 1$
General representation for the class of a covalent compound	ML_lX_X
Electron Number of Mo in MoL_lX_X	E.N. = 6 (for Mo) + $2l + x$
Valency Number	V.N. = x
Ligand Bond Number	L.B.N. = $l + x$
n of d^n	n = 6(for Mo) - x -(2z)
Number of electrons in the valency shell of the metal	Me
Equivalent Neutral Class	E.N.C.

Table 4. Classification of reactions by the reaction products

Change in L_l and/or X_X	Change in E.N.	Change in V.N.	Name of reaction
$-L_l$ then $+L'_l$	0	0	L_l -substitution
$-X_X$ then $+X'_X$	0	0	X_X -substitution
$+L_l$	$+2l$	0	L_l-addition
$-L_l$	$-2l$	0	L_l-elimination
$+X_X$	$+x$	$+x$	X_X-oxidative-addition
$-X_X$	$-x$	$-x$	X_X-reductive-elimination
$+L$ then $-X^a$	+1	-1	reductive-replacement[a]
$-L$ then $+X^b$	-1	-1	oxidative-replacement[b]
$-L_n$ then $+X_{2n}$ (n=1)	0	+2	replacement-addition[c]
$+L_n$ then $-X_{2n}$ (n=1)	0	-2	replacement-elimination[d]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5
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ELECTRON NUMBER E.N.
+L
+L(+X)
+ X+
ML/-1Xx
ML/Xx
ML/Xx+1]-
+X2
+X2
+X+
ML/Xx+1]+
+X
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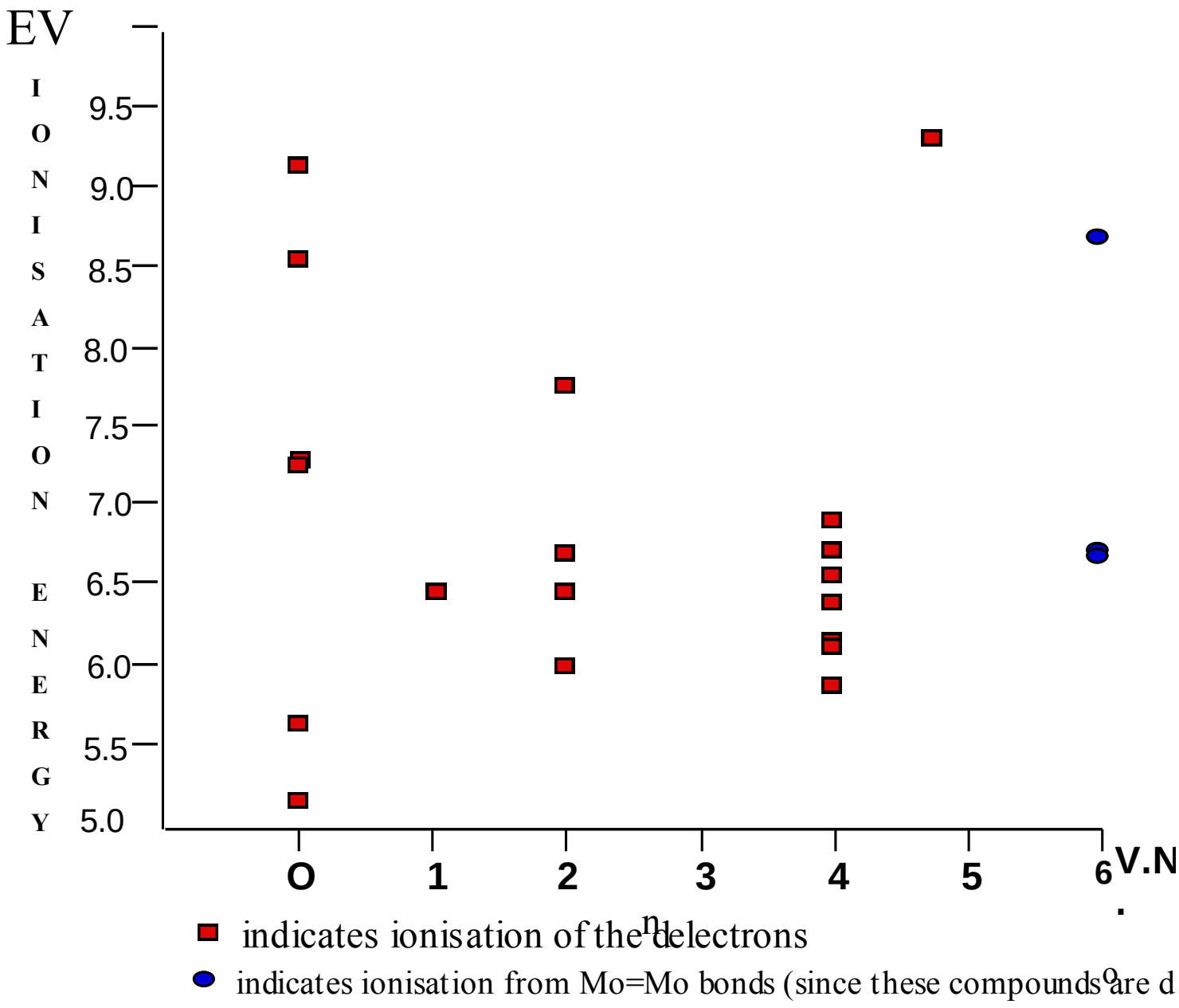
PRODUCT
MX6
MLX6
ML2X6
ML3X6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7.5
7.0
6.5
6.0
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5.0
O
1
2
3
4
5
6
V.N.
indicates ionisation of the d electrons
indicates ionisation from Mo=Mo bonds (since these compounds are d
Valency Number