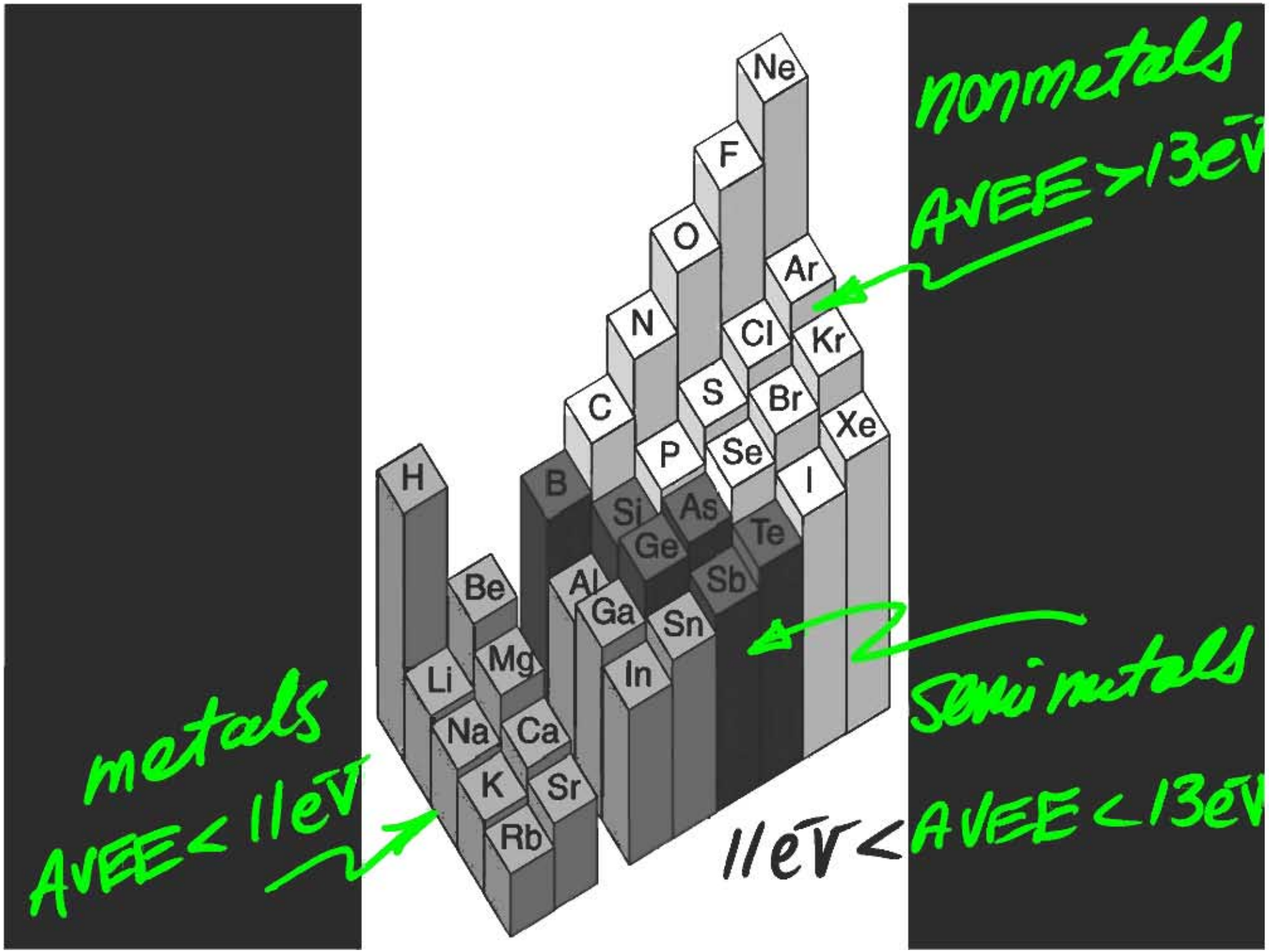
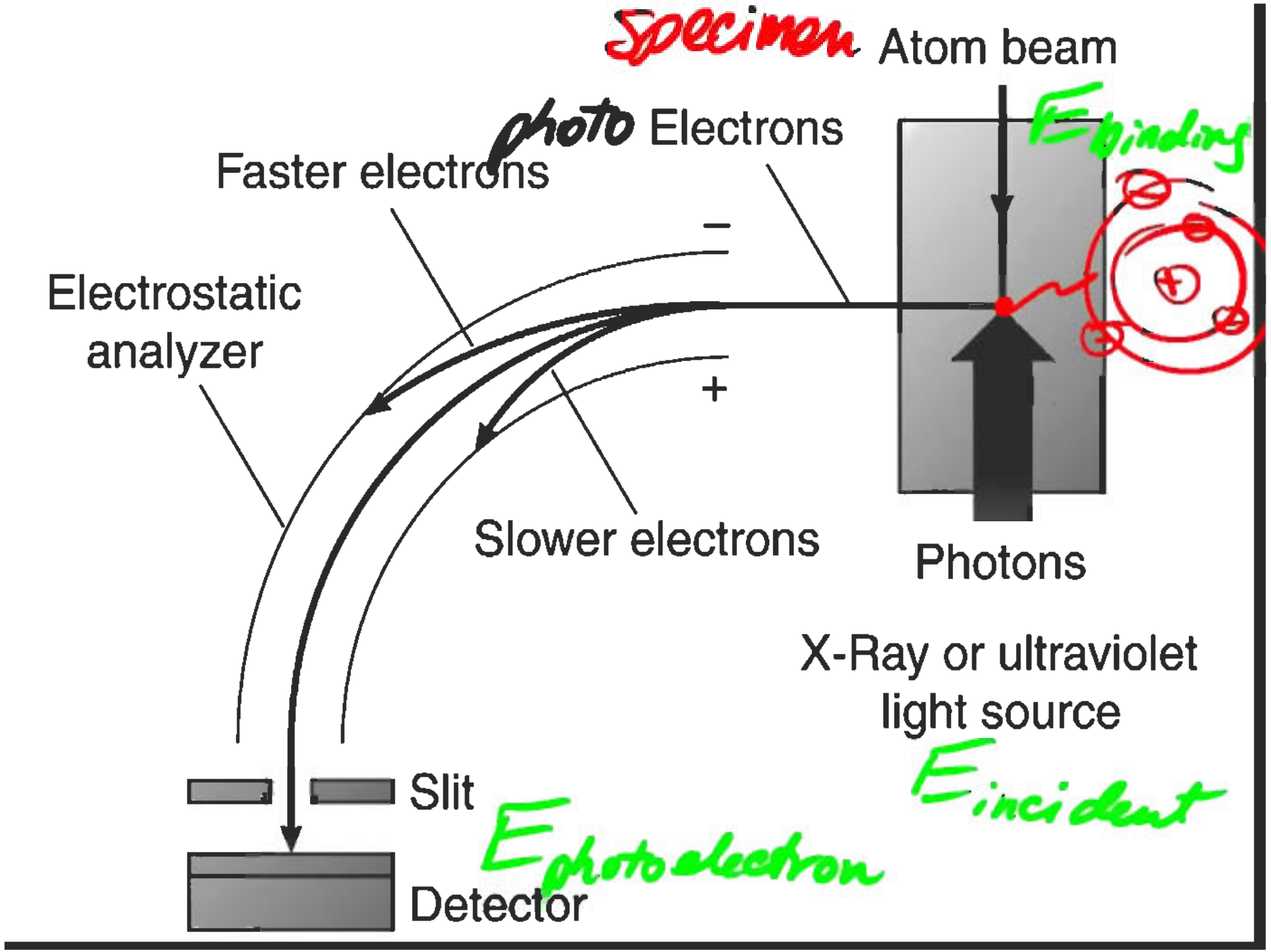
Welcome to 3.091

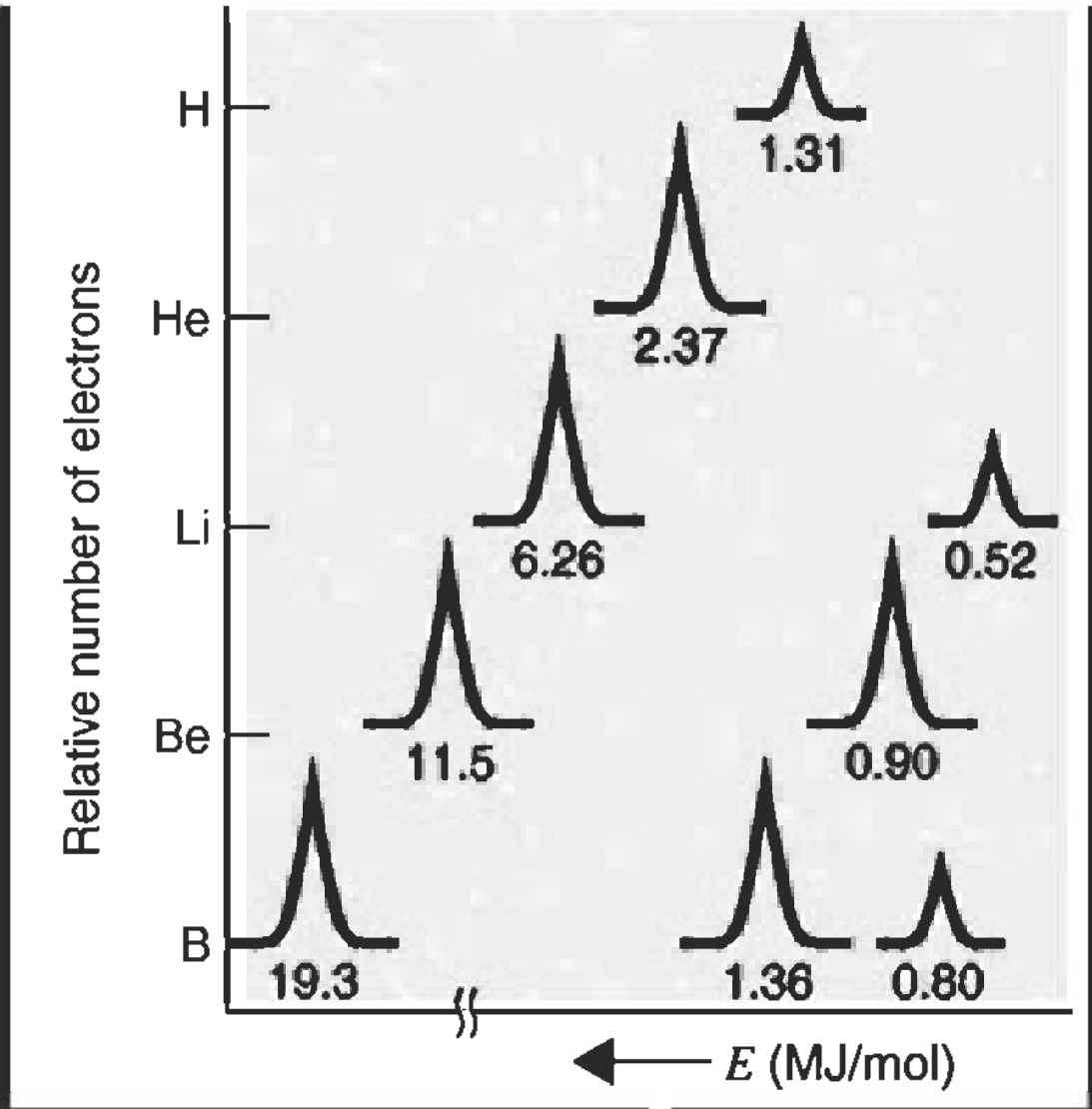
Lecture 8

September 24, 2004


Ne
F
O
Ar
N
Cl
Kr
C
S
Br
Xe
P
Se
I
H
B
Si
As
Te
Ge
Sb
Be
Al
Ga
Sn
Mg
In
Li
Na
Ca
K
Sr
Rb
nonmetals
AVEE > 13eV
metals
AVEE < 11eV
semimetals
11eV < AVEE < 13eV

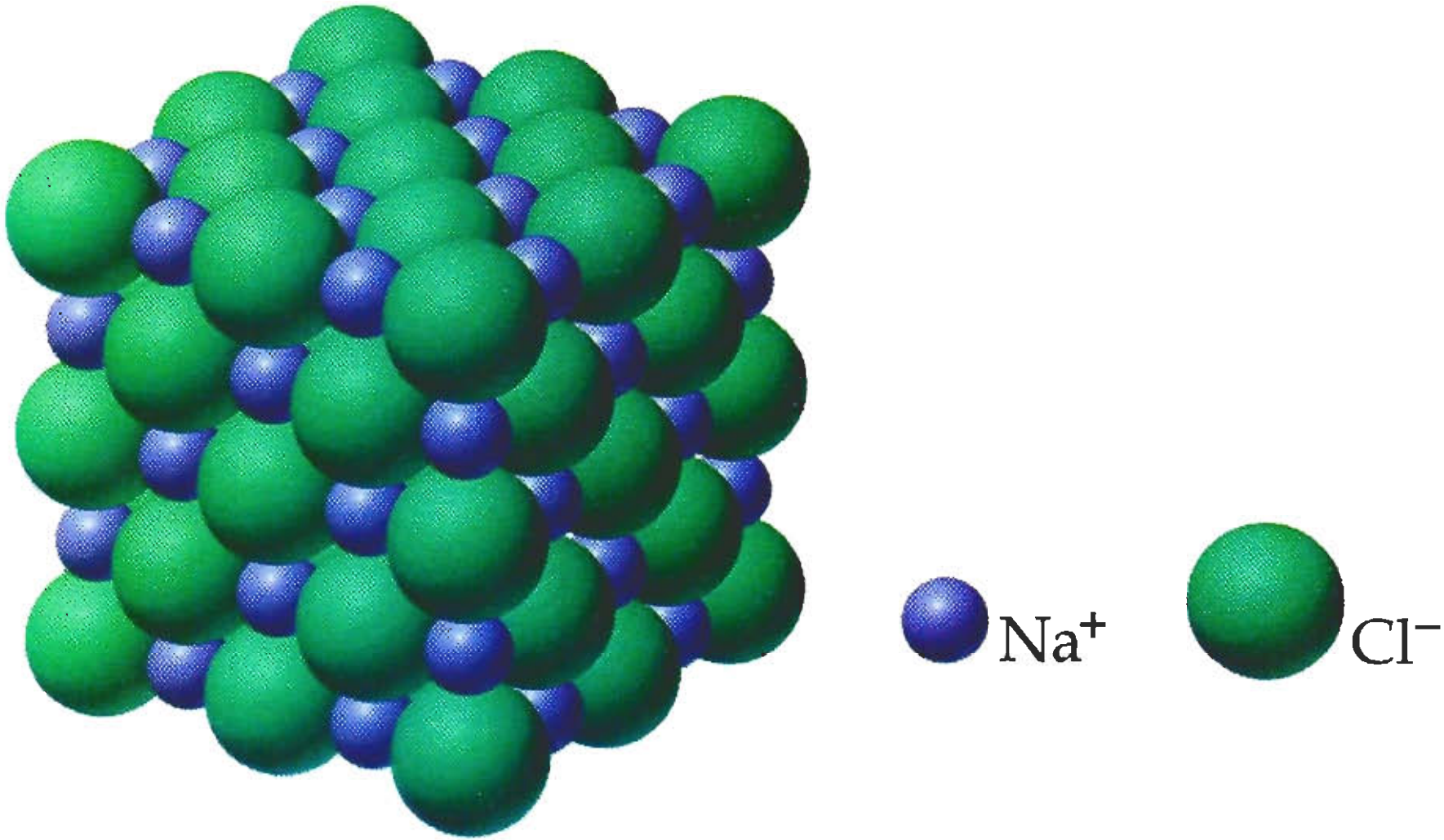

Specimen
Atom beam
photo Electrons
Faster electrons
E binding
−
Electrostatic analyzer
+
Slower electrons
Photons
X-Ray or ultraviolet light source
E incident
Slit
E photoelectron
Detector

intensity ⇒ population ↑



energy ⇒ identity

"characteristic"


Na^+
Cl^-

Properties of Ionic Crystals

- solid at room temperature
- high melting points & boiling points
- transparent to visible light
- electrical insulators
- hard & brittle
- soluble in water & other polar solvents
- melt to form ionic liquids (useful in electrolytic extraction of metals)

The search for ionicity => ?

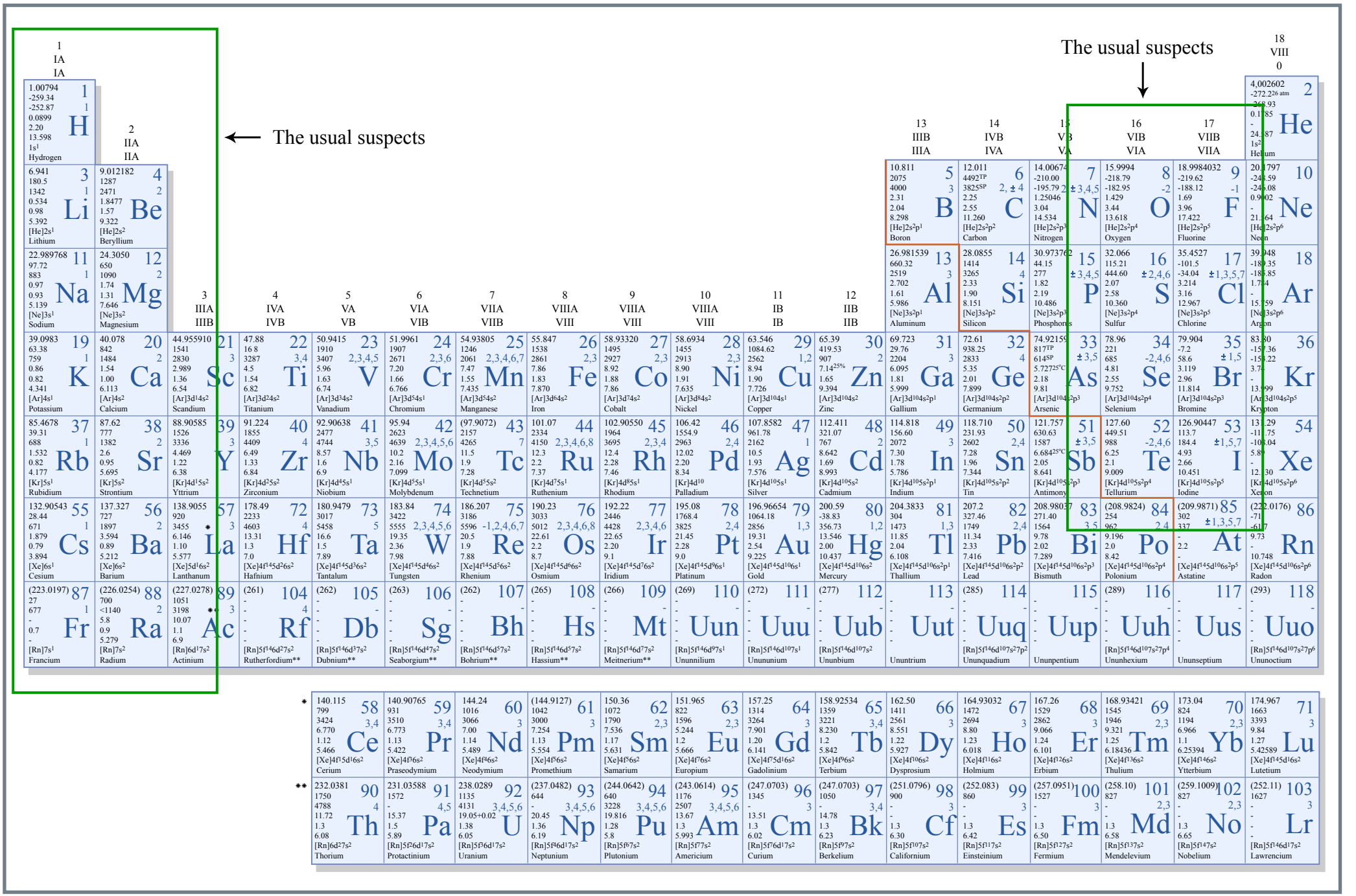
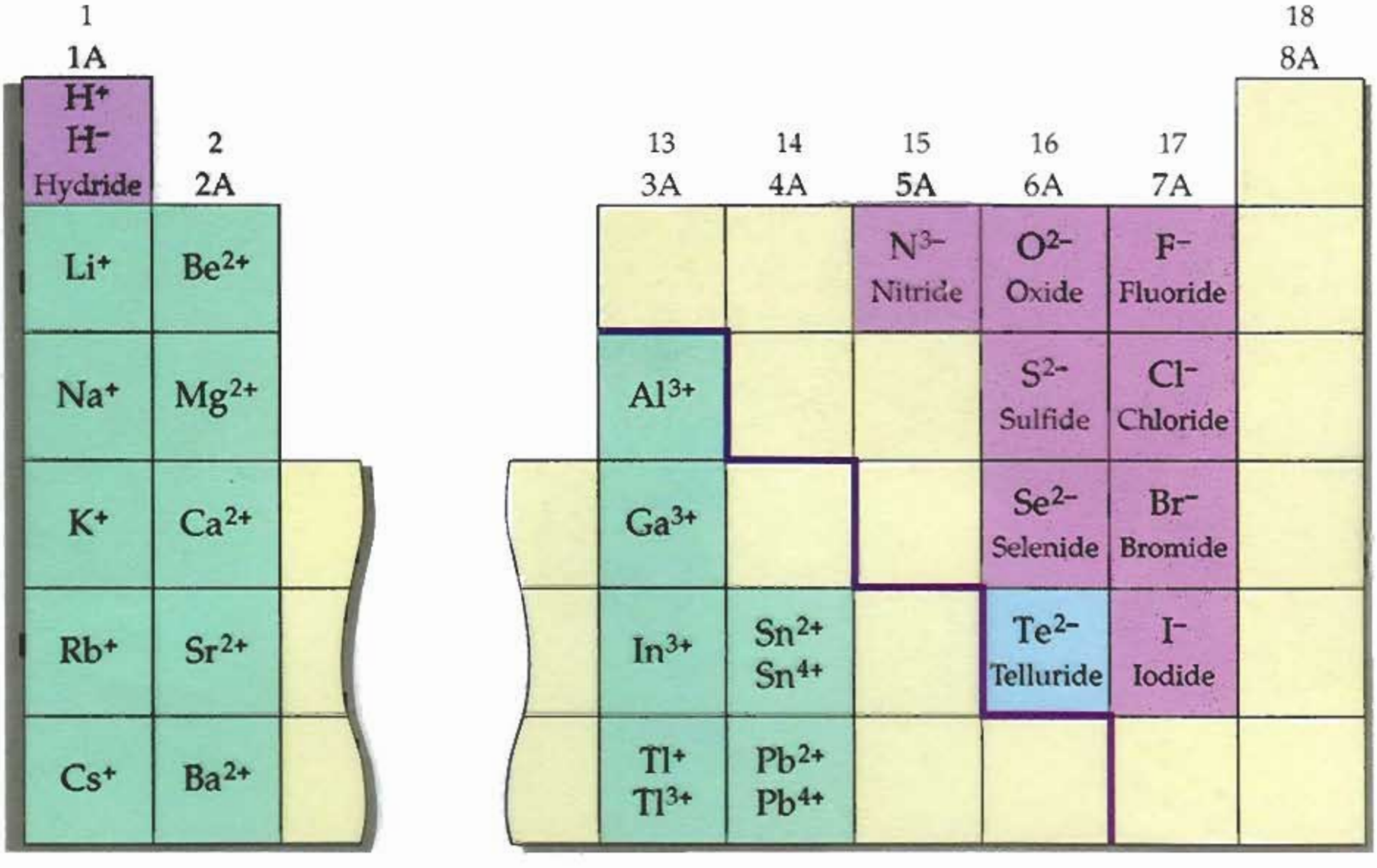
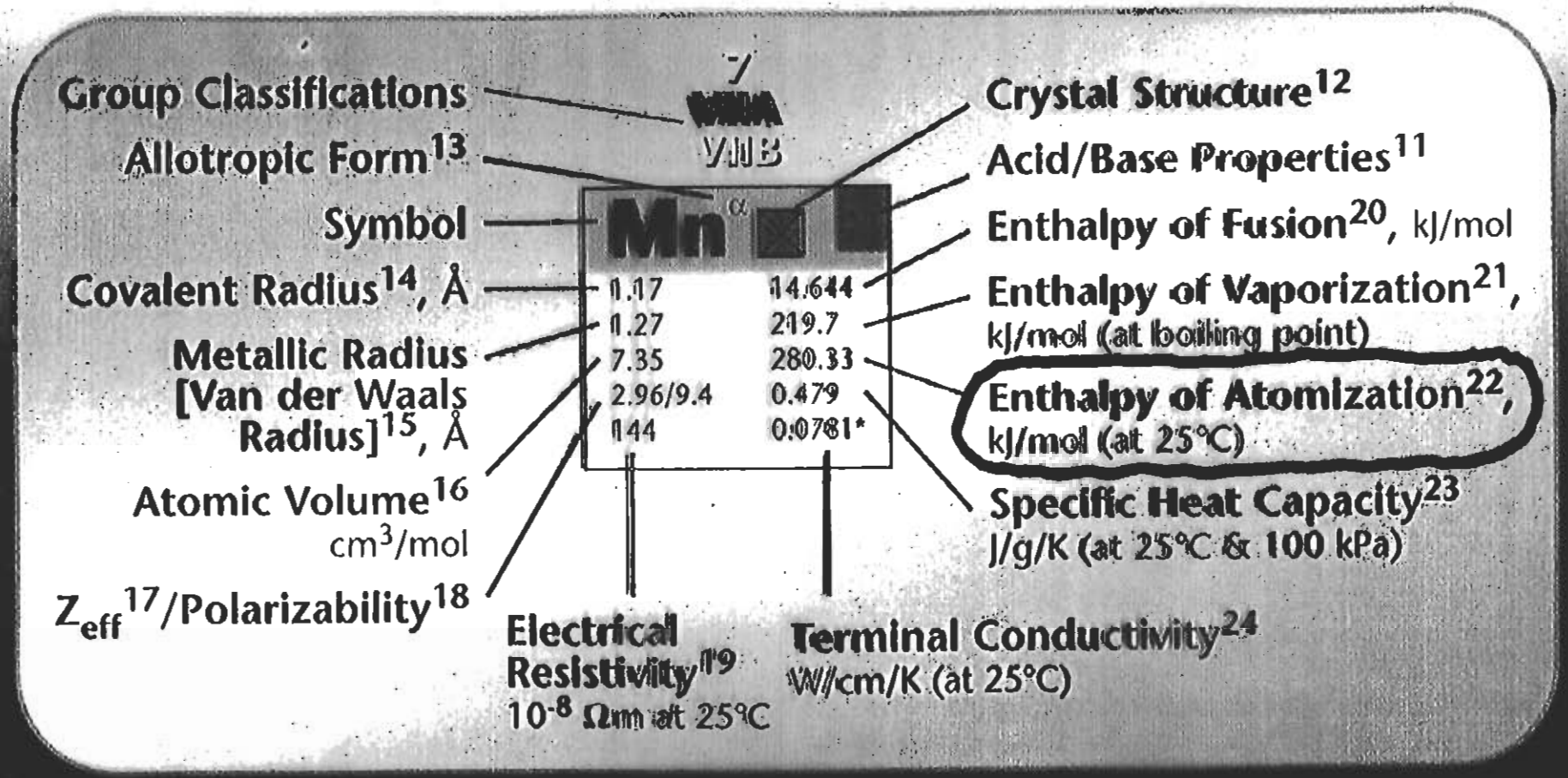


Figure by MIT OCW.


1
1A
2
2A
13
3A
14
4A
15
5A
16
6A
17
7A
18
8A
H+
H−
Hydride
Li+
Be2+
Na+
Mg2+
K+
Ca2+
Rb+
Sr2+
Cs+
Ba2+
Al3+
Ga3+
In3+
Tl+
Tl3+
Sn2+
Sn4+
Pb2+
Pb4+
N3−
Nitride
O2−
Oxide
F−
Fluoride
S2−
Sulfide
Cl−
Chloride
Se2−
Selenide
Br−
Bromide
Te2−
Telluride
I−
Iodide

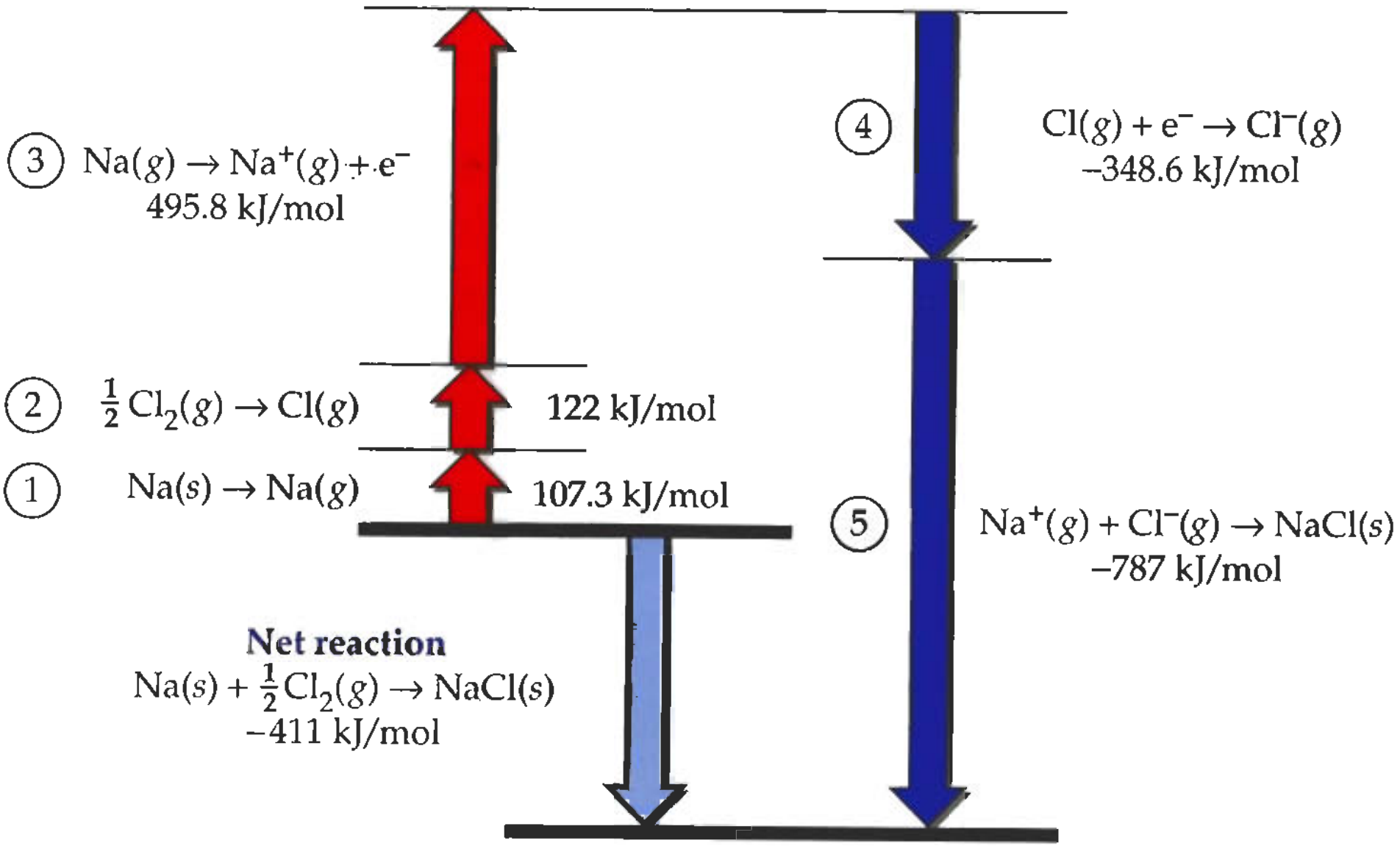

Group Classifications
Allotropic Form[13]
Symbol
Covalent Radius[14], Å
Metallic Radius
[Van der Waals Radius][15], Å
Atomic Volume[16]
cm³/mol
Z_eff[17]/Polarizability[18]
7
VIIA
VIIB
Mn α
1.17
1.27
7.35
2.96/9.4
144
14.644
219.7
280.33
0.479
0.0781*
Crystal Structure[12]
Acid/Base Properties[11]
Enthalpy of Fusion[20], kJ/mol
Enthalpy of Vaporization[21],
kJ/mol (at boiling point)
Enthalpy of Atomization[22],
kJ/mol (at 25°C)
Specific Heat Capacity[23]
J/g/K (at 25°C & 100 kPa)
Electrical Resistivity[19]
10⁻⁸ Ωm at 25°C
Terminal Conductivity[24]
W//cm/K (at 25°C)

1.23	3.00	0.89	11.72		
1.55	134.68	1.12	294.66		
13.00	160.67	4.88	326.35		
1.26/24.3	3.582	1.66/5.60	1.825		
9.47	0.848	3.70	2.01		
Na		**Mg**			
1.54	2.594	1.36	8.954		
1.90	89.04	1.60	128.66		
23.70	108.37	13.97	148.53		
1.84/23.6	1.228	2.25/10.6	1.023		
4.88	1.42	4.48	1.56		
K		**Ca**		**Sc** α	
2.03	2.32	1.74	8.54	1.44	14.10
2.35	77.5	1.97	150	1.65	314.20
45.46	89.54	26.02	184*	15.04	343*
2.26/43.4	0.757	2.68/22.8	0.647	2.77/17.8	0.568
7.39	1.025	3.42	2.01*	56.2	0.158
Rb		**Sr**		**Y**	
2.16	2.19	1.91	9.16	1.62	17.15
2.48	69.2	2.15	150	1.78	393
55.79	82.0	33.70	163.2	19.89	418*
2.77/47.3	0.363	3.24/27.6	0.301	3.42/22.7	0.298
13.1	0.582	13.4	0.354*	59.6	0.172*
Cs		**Ba**		**La** α	
2.35	2.10	1.98	7.66	1.69	6.20

3

IIIB

Figure 6.6 A Born-Haber cycle for NaCl



Lattice energies of some ionic solids (kJ/mol)

Cation	Anion				
	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1,036	853	807	757	2,925
Na^+	923	787	747	704	2,695
K^+	821	715	682	649	2,360
Be^{2+}	3,505	3,020	2,914	2,800	4,443
Mg^{2+}	2,957	2,524	2,440	2,327	3,791
Ca^{2+}	2,630	2,258	2,176	2,074	3,401
Al^{3+}	5,215	5,492	5,361	5,218	15,916

Figure by MIT OCW.

Ionic Radii (Å) for Ions with Noble-gas Electron Configurations

[He]

Li^+ 0.68 Be^{2+} 0.30

[Ne]

O^{2-} 1.45 F^- 1.33

Na^+ 0.98 Mg^{2+} 0.65 Al^{3+} 0.45

S^{2-} 1.90 Cl^- 1.81 [Ar]

K^+ 1.33 Ca^{2+} 0.94 Sc^{3+} 0.68

Se^{2-} 2.02 Br^- 1.96 [Kr]

Rb^+ 1.48 Sr^{2+} 1.10 Y^{3+} 0.90

Te^{2-} 2.22 I^- 2.19 [Xe]

Cs^+ 1.67 Ba^{2+} 1.31 La^{3+} 1.22

Selected Properties of Structural Metals

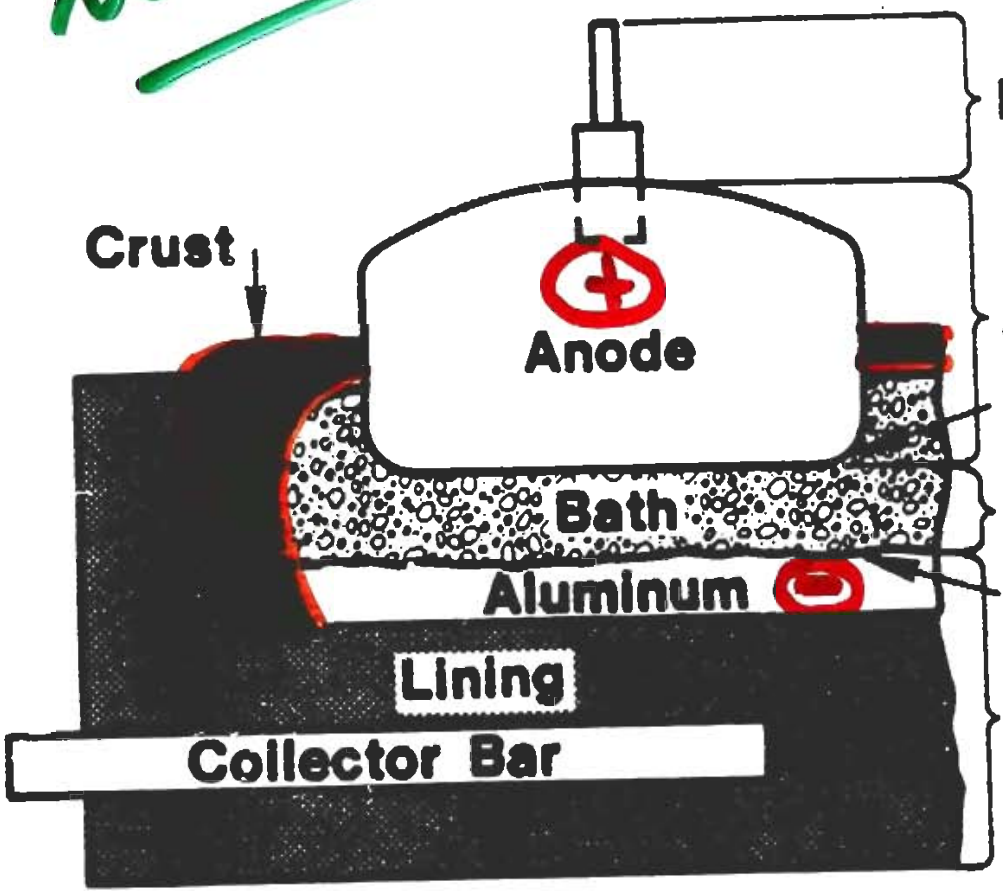
	Fe	Al	Mg	Ti
capacity (10^6 tpy)	800	25	0.60	0.10
price ($/kg)	0.40	1.85	3.40	10
sales (10^9 $)	320	46	2.0	1.0
abundance (%)	5.0	8.2	2.1	0.66
(rank)	4	3	8	9

Selected Properties of Structural Metals

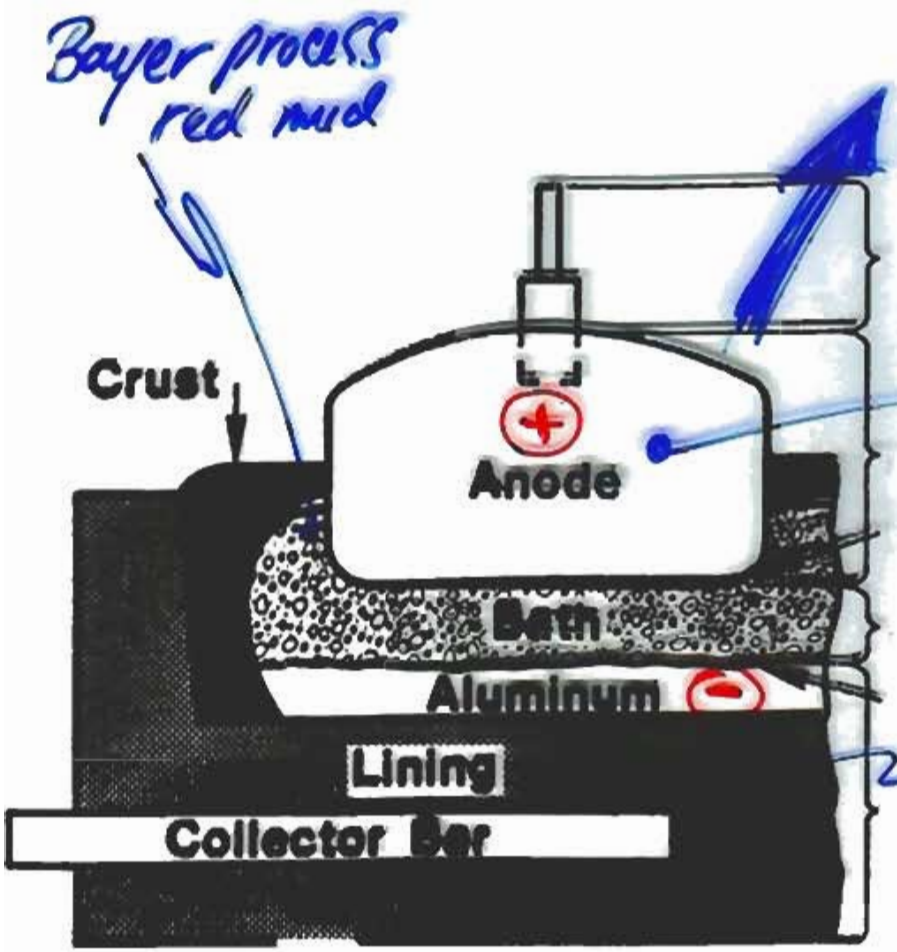
	Fe	Al	Mg	Ti
m.p. (°C)	1535	660	650	1675
b.p. (°C)	2860	2518	1093	3260
ρ (g/cm^3)	7.87	2.70	1.74	4.51
E (GPa)	211	71	45	116
E /ρ	27	26	26	26

NOT TO SCALE

GA 11994



Voltage Component	Volts	% Of Total
External	.16	3.4
Anode	.32	6.9
Polarizations	.60	12.9
Bath	1 76	38.0
Decomposition	1.20	25.9
Cathode	.47	10.1
Other	.13	2.8
Total	4.64	100.0



Bayer process red mud

fugitive emissions from the Hall cell: Carbon dioxide, fluorides, PFC's, particulates

anode prebake operation*: SO_2 + volatile organic compounds (VOCs) + particulates

spent potliner contains fluorides + cyanides ~ 150,000 TPY disposed in U.S.

* $\frac{1}{2}$ kg. C / kg. Al ⇒ Carbon intensive!