Appendices

A.1 Physical Constants

Angstrom unit	Å	10^{-10} m = 10^{-8} cm = 10^{-4} μm
Avogadro constant	$\mathcal{N}_A$	6.02204×10^{23} mol^{-1}
Bohr radius	a_0	0.52917 Å
Boltzmann constant	k_b	1.38066×10^{-23} J·K^{-1} ($= R/\mathcal{N}_A$)
		8.61738×10^{-5} eV·K^{-1}
Calorie	cal	4.184 J
Elementary charge	q	1.60218×10^{-19} C
Electron rest mass	m_0	0.91095×10^{-30} kg
Electron Volt	eV	1.60218×10^{-19} J
		23.053 kcal·mol^{-1}
Gravitational constant	g	9.81 m·s^{-2}
Gas constant	R	1.98719 cal·mol^{-1}·K^{-1}
		8.31440 J·mol^{-1}·K^{-1}
Permeability in vacuum	μ_0	$4\pi 10^{-9} = 1.25633 \times 10^{-6}$ H·m^{-1}
Permittivity in vacuum	ε_0	8.85418×10^{-12} F·m^{-1} ($=1/\mu_0 c^2$)
Planck's constant	h	6.62617×10^{-34} J·s
Reduced Planck's constant	$\hbar$	1.05458×10^{-34} J·s ($= h/2\pi$)
Proton rest mass	M_p	1.67264×10^{-27} kg
Standard atmosphere	atm	1.01325×10^{5} N·m^{-2}
Thermal voltage at 300 K	$k_b T/q$	0.0259 V
Velocity of light in vacuum	c	2.99792×10^{8} m·s^{-1}
Wavelength of 1-eV quantum	λ	1.23977 μm

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A.2 International System of Units (SI Units)

Base units

Quantity	*Unit name*	*Unit symbol*
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

Prefixes

Factor	*Prefix*	*Symbol*	*Factor*	*Prefix*	*Symbol*
10^{24}	yotta	Y	10^{-1}	deci	d
10^{21}	zetta	Z	10^{-2}	centi	c
10^{18}	exa	E	10^{-3}	milli	m
10^{15}	peta	P	10^{-6}	micro	μ
10^{12}	tera	T	10^{-9}	nano	n
10^{9}	giga	G	10^{-12}	pico	p
10^{6}	mega	M	10^{-15}	femto	f
10^{3}	kilo	k	10^{-18}	atto	a
10^{2}	hecto	h	10^{-21}	zepto	z
10^{1}	deka	da	10^{-24}	yocto	y

Derived units

Quantity	*Special name*	*Unit symbol*	*Dimension*
Angle	radian	–	rad
Solid angle	steradian	–	sr
Speed, velocity	–	–	$\mathrm{m{\cdot}s^{-1}}$
Acceleration	–	–	$\mathrm{m{\cdot}s^{-2}}$
Angular velocity, frequency	–	$\mathrm{rad{\cdot}s^{-1}}$	
Angular acceleration	–	–	$\mathrm{rad{\cdot}s^{-2}}$
Frequency	hertz	Hz	$\mathrm{s^{-1}}$
Force	newton	N	$\mathrm{kg{\cdot}m{\cdot}s^{-2}}$
Pressure, stress	pascal	Pa	$\mathrm{N{\cdot}m^{-2}}$
Work, energy, heat	joule	J	$\mathrm{N{\cdot}m}$, $\mathrm{kg{\cdot}m^{2}{\cdot}s^{-2}}$
Power	watt	W	$\mathrm{J{\cdot}s}$
Electric charge	coulomb	C	$\mathrm{A{\cdot}s}$

Electric potential	volt	V	$J \cdot C^{-1}$, $W \cdot A^{-1}$
Resistance	ohm	Ω	$V \cdot A^{-1}$
Conductance	siemens	S	$A \cdot V^{-1}$, Ω^{-1}
Magnetic flux	weber	Wb	$V \cdot s$
Inductance	henry	H	$Wb \cdot A^{-1}$
Capacitance	farad	F	$C \cdot V^{-1}$
Electric field strength	–	–	$V \cdot m^{-1}$, $N \cdot C^{-1}$
Magnetic induction	tesla	T	$Wb \cdot m^{-2}$, $N \cdot A^{-1} \cdot m^{-1}$
Electric displacement	–	–	$C \cdot m^{-2}$
Magnetic field strength	–	–	$A \cdot m^{-1}$
Celsius temperature	degrees Celsius	°C	K
Luminous flux	lumen	lm	$cd \cdot sr$
Illuminance	lux	lx	$lm \cdot m^{-2}$
Radioactivity	becquerel	Bq	s^{-1}
Catalytic activity	katal	kat	$mol \cdot s^{-1}$

A.3 Physical Properties of Elements in the Periodic Table

The following figures summarize the general physical properties of most elements in the periodic table. These include their natural forms (Fig. A.1) with the structure in which they crystallize, their density of mass (Fig. A.2), boiling point (Fig. A.3), melting point (Fig. A.4), thermal conductivity (Fig. A.5), molar volume (Fig. A.6), specific heat (Fig. A.7), atomic radius (Fig. A.8), oxidation states (Fig. A.9), ionic radius (Fig. A.10), electronegativity (Fig. A.11), and electron affinity (Fig. A.12).

A.3.1 Chapter 2: Atomic Orbital

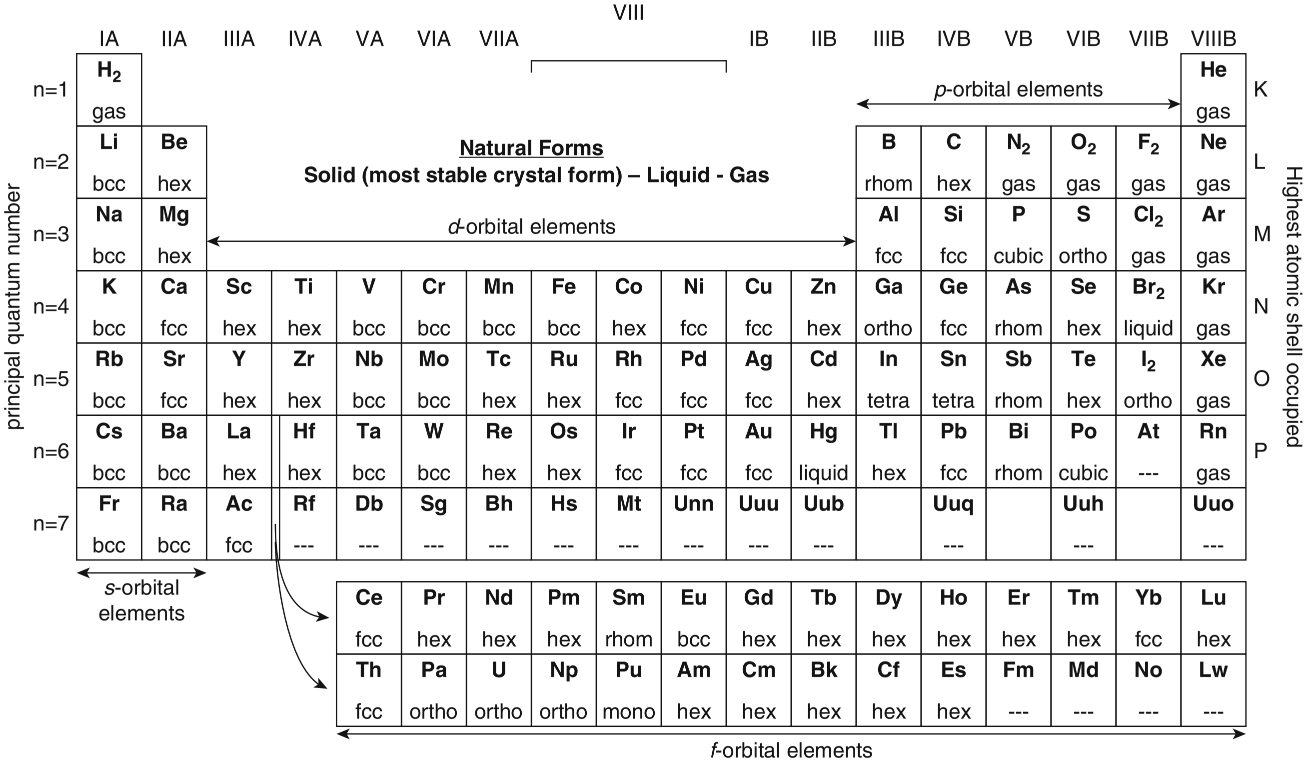
Generalities and Description

Since the discovery of the Schrödinger equation in 1925, it is well known that quantum particles such as electrons can be described as both particles (in the classical approach) and as *wave*. The wave description of an electron states implies that position cannot be fully known; instead, a wavefunction is required to describe the *probability* of finding any electron in a given region.

When electrons are linked to the nucleus of an atom, they cannot occupy all the available positions around the nucleus, and their position is quantified in *confined regions called atomic orbital*. An atomic orbital is a mathematical function describing the wave behavior of electrons in one of these confined regions (Fig. A.13).

Each atomic orbital is distinguished by three quantum numbers: n, l, and m.

n is a positive integer called the *principal quantum number*, l is an integer between 0 and $n - 1$ called the *azimuthal or angular quantum number*, and m is an integer between −l and l called the *magnetic quantum number*.

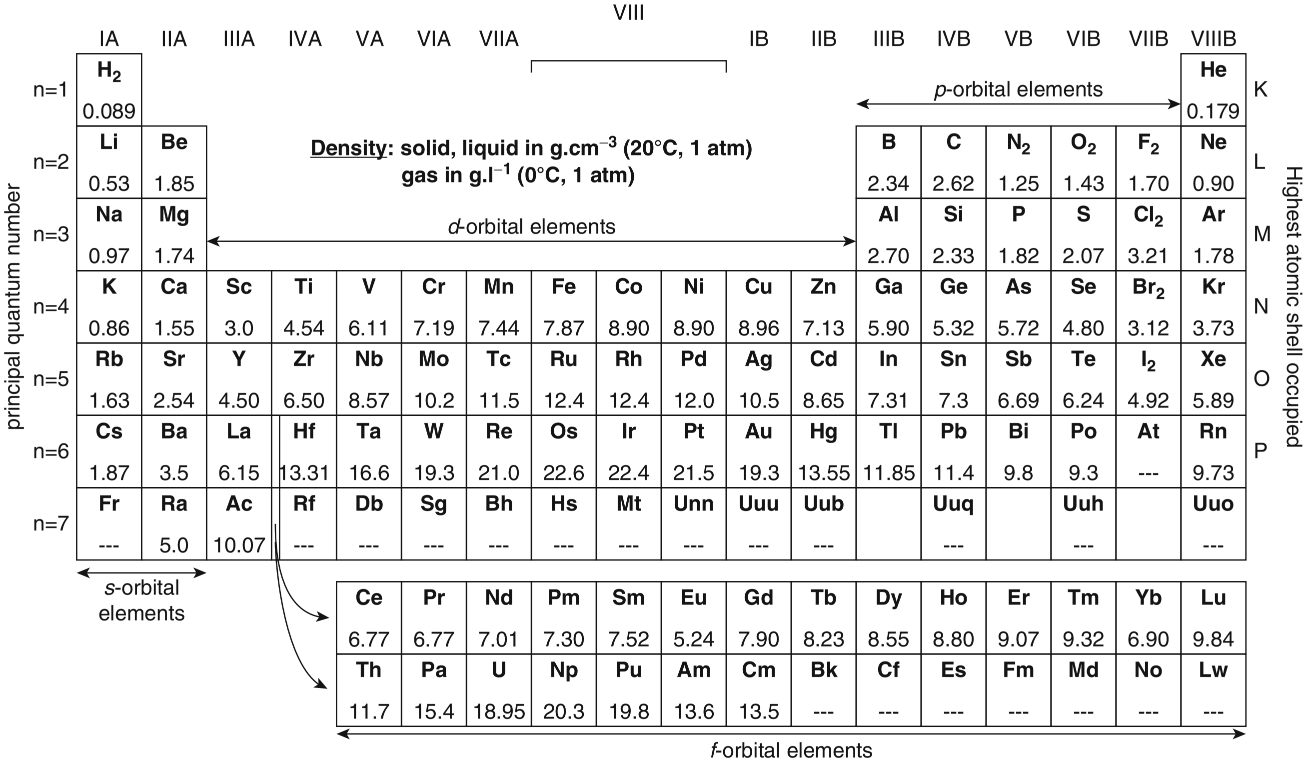


Natural Forms
Solid (most stable crystal form) – Liquid - Gas

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H_2** gas																	**He** gas	K
n=2	**Li** bcc	**Be** hex											**B** rhom	**C** hex	**N_2** gas	**O_2** gas	**F_2** gas	**Ne** gas	L
n=3	**Na** bcc	**Mg** hex											**Al** fcc	**Si** fcc	**P** cubic	**S** ortho	**Cl_2** gas	**Ar** gas	M
n=4	**K** bcc	**Ca** fcc	**Sc** hex	**Ti** hex	**V** bcc	**Cr** bcc	**Mn** bcc	**Fe** bcc	**Co** hex	**Ni** fcc	**Cu** fcc	**Zn** hex	**Ga** ortho	**Ge** fcc	**As** rhom	**Se** hex	**Br_2** liquid	**Kr** gas	N
n=5	**Rb** bcc	**Sr** fcc	**Y** hex	**Zr** hex	**Nb** bcc	**Mo** bcc	**Tc** hex	**Ru** hex	**Rh** fcc	**Pd** fcc	**Ag** fcc	**Cd** hex	**In** tetra	**Sn** tetra	**Sb** rhom	**Te** hex	**I_2** ortho	**Xe** gas	O
n=6	**Cs** bcc	**Ba** bcc	**La** hex	**Hf** hex	**Ta** bcc	**W** bcc	**Re** hex	**Os** hex	**Ir** fcc	**Pt** fcc	**Au** fcc	**Hg** liquid	**Tl** hex	**Pb** fcc	**Bi** rhom	**Po** cubic	**At** ---	**Rn** gas	P
n=7	**Fr** bcc	**Ra** bcc	**Ac** fcc	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce fcc	**Pr** hex	**Nd** hex	**Pm** hex	**Sm** rhom	**Eu** bcc	**Gd** hex	**Tb** hex	**Dy** hex	**Ho** hex	**Er** hex	**Tm** hex	**Yb** fcc	**Lu** hex
Th fcc	**Pa** ortho	**U** ortho	**Np** ortho	**Pu** mono	**Am** hex	**Cm** hex	**Bk** hex	**Cf** hex	**Es** hex	**Fm** ---	**Md** ---	**No** ---	**Lw** ---

Fig. A.1 Natural forms of elements in the periodic table

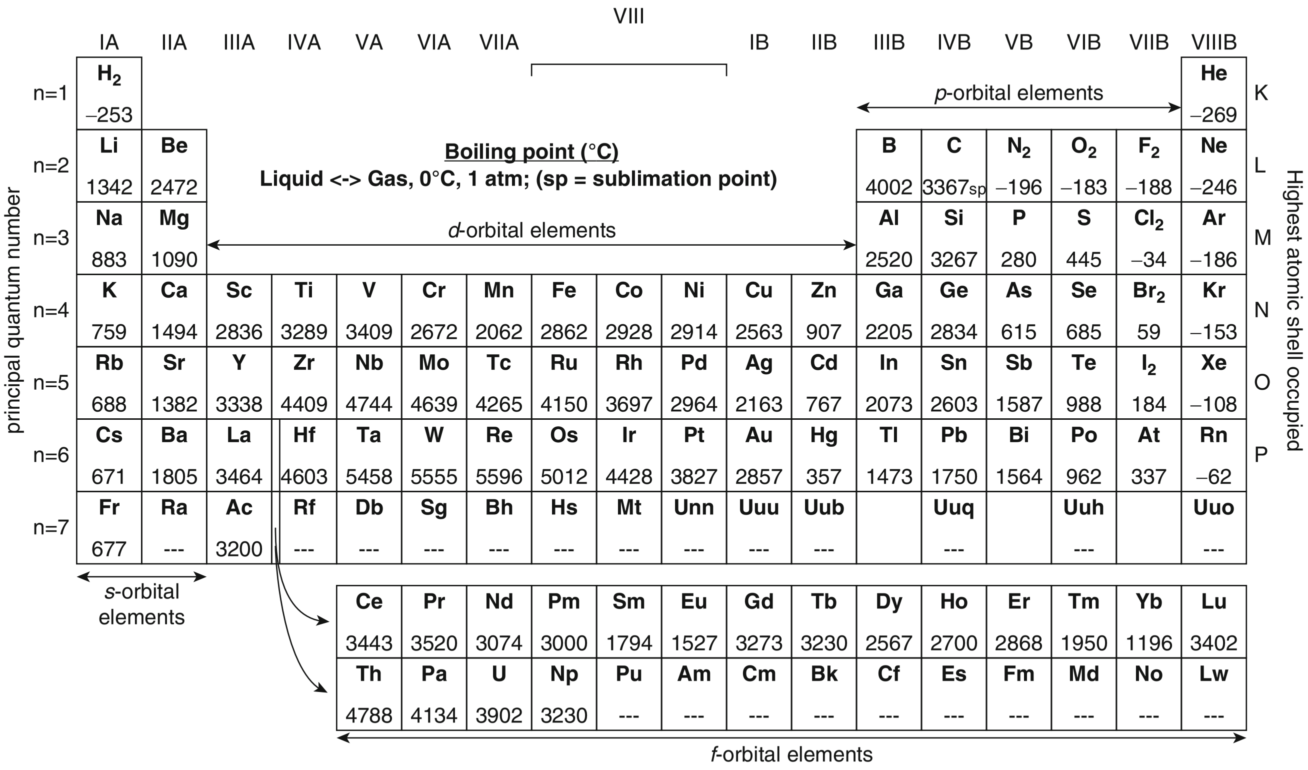


Density: solid, liquid in g.cm^{-3} (20°C, 1 atm)
gas in g.l^{-1} (0°C, 1 atm)

principal quantum number	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	Highest atomic shell occupied
n=1	**H_2** 0.089																	**He** 0.179	K
n=2	**Li** 0.53	**Be** 1.85											**B** 2.34	**C** 2.62	**N_2** 1.25	**O_2** 1.43	**F_2** 1.70	**Ne** 0.90	L
n=3	**Na** 0.97	**Mg** 1.74											**Al** 2.70	**Si** 2.33	**P** 1.82	**S** 2.07	**Cl_2** 3.21	**Ar** 1.78	M
n=4	**K** 0.86	**Ca** 1.55	**Sc** 3.0	**Ti** 4.54	**V** 6.11	**Cr** 7.19	**Mn** 7.44	**Fe** 7.87	**Co** 8.90	**Ni** 8.90	**Cu** 8.96	**Zn** 7.13	**Ga** 5.90	**Ge** 5.32	**As** 5.72	**Se** 4.80	**Br_2** 3.12	**Kr** 3.73	N
n=5	**Rb** 1.63	**Sr** 2.54	**Y** 4.50	**Zr** 6.50	**Nb** 8.57	**Mo** 10.2	**Tc** 11.5	**Ru** 12.4	**Rh** 12.4	**Pd** 12.0	**Ag** 10.5	**Cd** 8.65	**In** 7.31	**Sn** 7.3	**Sb** 6.69	**Te** 6.24	**I_2** 4.92	**Xe** 5.89	O
n=6	**Cs** 1.87	**Ba** 3.5	**La** 6.15	**Hf** 13.31	**Ta** 16.6	**W** 19.3	**Re** 21.0	**Os** 22.6	**Ir** 22.4	**Pt** 21.5	**Au** 19.3	**Hg** 13.55	**Tl** 11.85	**Pb** 11.4	**Bi** 9.8	**Po** 9.3	**At** ---	**Rn** 9.73	P
n=7	**Fr** ---	**Ra** 5.0	**Ac** 10.07	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce 6.77	**Pr** 6.77	**Nd** 7.01	**Pm** 7.30	**Sm** 7.52	**Eu** 5.24	**Gd** 7.90	**Tb** 8.23	**Dy** 8.55	**Ho** 8.80	**Er** 9.07	**Tm** 9.32	**Yb** 6.90	**Lu** 9.84
Th 11.7	**Pa** 15.4	**U** 18.95	**Np** 20.3	**Pu** 19.8	**Am** 13.6	**Cm** 13.5	**Bk** ---	**Cf** ---	**Es** ---	**Fm** ---	**Md** ---	**No** ---	**Lw** ---

Fig. A.2 Density of mass of elements in the periodic table

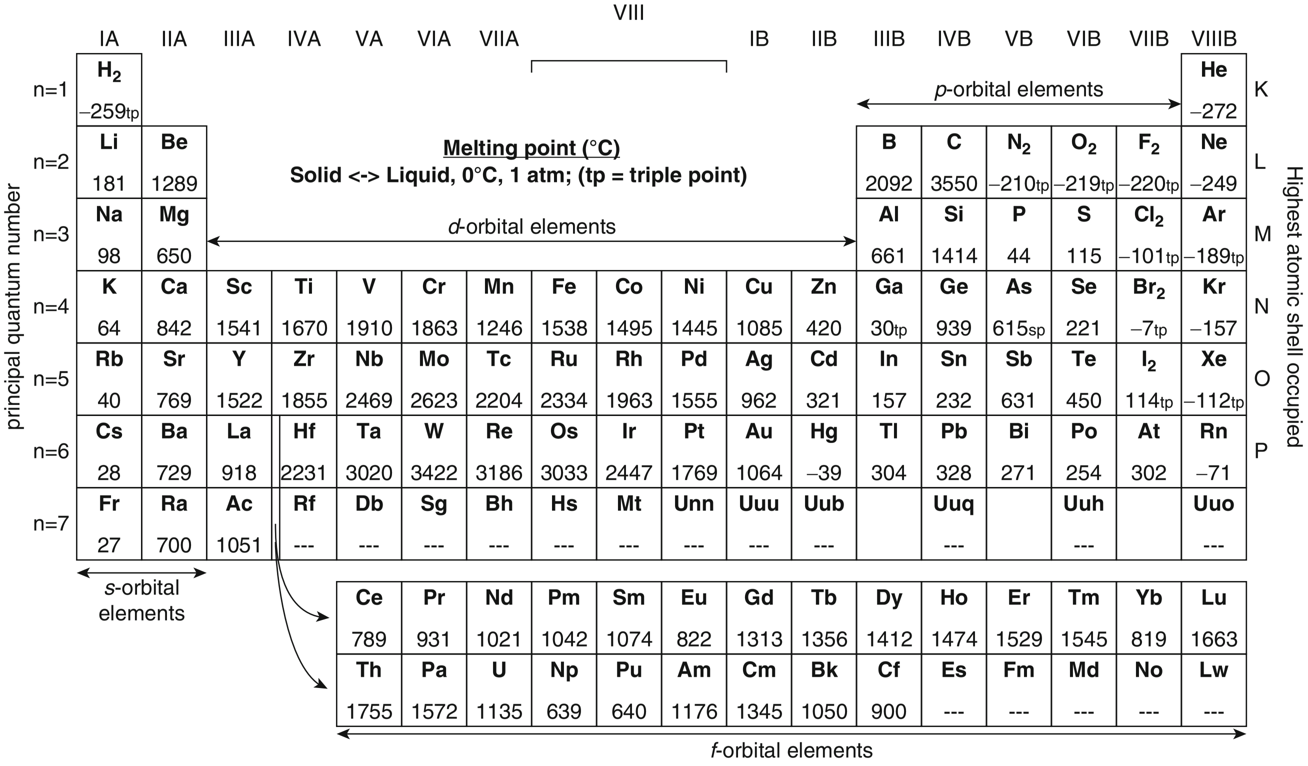


Boiling point (°C)
Liquid <-> Gas, 0°C, 1 atm; (sp = sublimation point)

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H_2** −253																	**He** −269	K
n=2	**Li** 1342	**Be** 2472											**B** 4002	**C** 3367sp	**N_2** −196	**O_2** −183	**F_2** −188	**Ne** −246	L
n=3	**Na** 883	**Mg** 1090											**Al** 2520	**Si** 3267	**P** 280	**S** 445	**Cl_2** −34	**Ar** −186	M
n=4	**K** 759	**Ca** 1494	**Sc** 2836	**Ti** 3289	**V** 3409	**Cr** 2672	**Mn** 2062	**Fe** 2862	**Co** 2928	**Ni** 2914	**Cu** 2563	**Zn** 907	**Ga** 2205	**Ge** 2834	**As** 615	**Se** 685	**Br_2** 59	**Kr** −153	N
n=5	**Rb** 688	**Sr** 1382	**Y** 3338	**Zr** 4409	**Nb** 4744	**Mo** 4639	**Tc** 4265	**Ru** 4150	**Rh** 3697	**Pd** 2964	**Ag** 2163	**Cd** 767	**In** 2073	**Sn** 2603	**Sb** 1587	**Te** 988	**I_2** 184	**Xe** −108	O
n=6	**Cs** 671	**Ba** 1805	**La** 3464	**Hf** 4603	**Ta** 5458	**W** 5555	**Re** 5596	**Os** 5012	**Ir** 4428	**Pt** 3827	**Au** 2857	**Hg** 357	**Tl** 1473	**Pb** 1750	**Bi** 1564	**Po** 962	**At** 337	**Rn** −62	P
n=7	**Fr** 677	**Ra** ---	**Ac** 3200	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce 3443	**Pr** 3520	**Nd** 3074	**Pm** 3000	**Sm** 1794	**Eu** 1527	**Gd** 3273	**Tb** 3230	**Dy** 2567	**Ho** 2700	**Er** 2868	**Tm** 1950	**Yb** 1196	**Lu** 3402
Th 4788	**Pa** 4134	**U** 3902	**Np** 3230	**Pu** ---	**Am** ---	**Cm** ---	**Bk** ---	**Cf** ---	**Es** ---	**Fm** ---	**Md** ---	**No** ---	**Lw** ---

Fig. A.3 Boiling point of elements in the periodic table



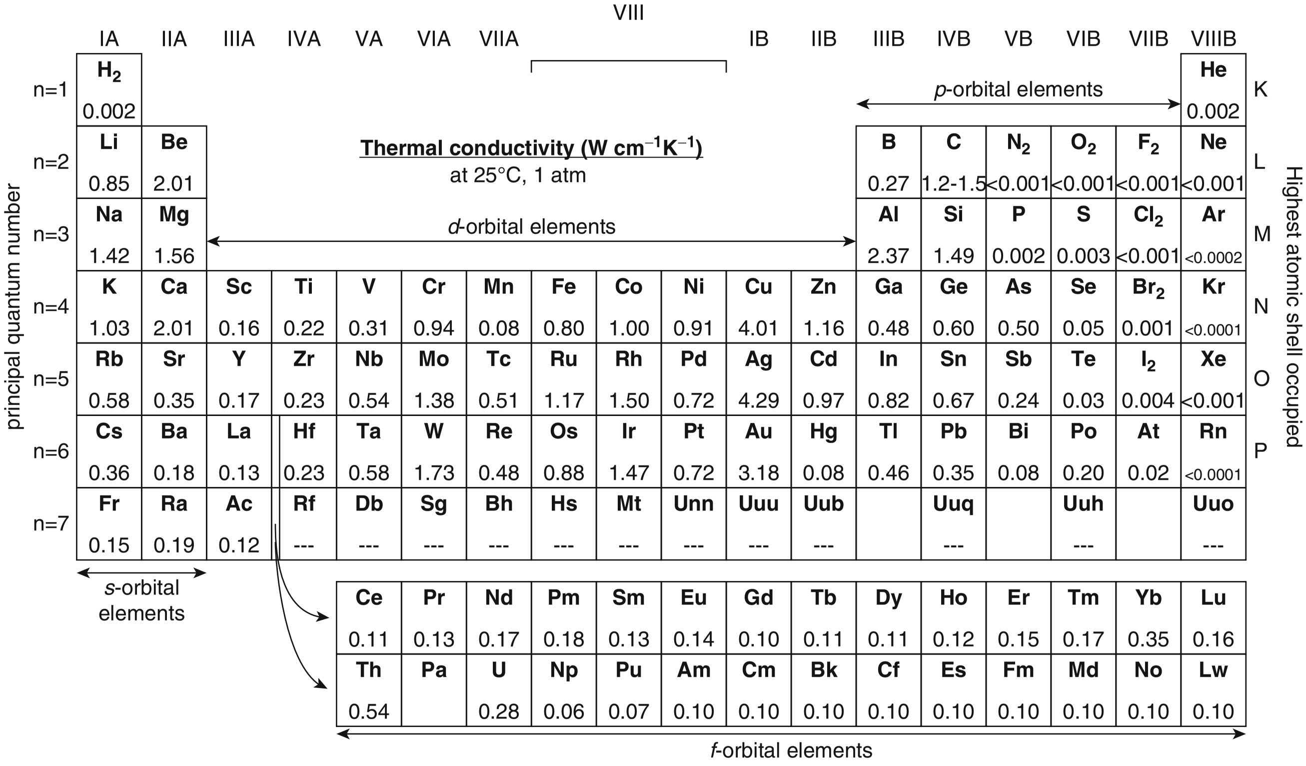
Melting point (°C)

Solid <-> Liquid, 0°C, 1 atm; (tp = triple point)

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H$_2$** −259tp																	**He** −272	K
n=2	**Li** 181	**Be** 1289											**B** 2092	**C** 3550	**N$_2$** −210tp	**O$_2$** −219tp	**F$_2$** −220tp	**Ne** −249	L
n=3	**Na** 98	**Mg** 650											**Al** 661	**Si** 1414	**P** 44	**S** 115	**Cl$_2$** −101tp	**Ar** −189tp	M
n=4	**K** 64	**Ca** 842	**Sc** 1541	**Ti** 1670	**V** 1910	**Cr** 1863	**Mn** 1246	**Fe** 1538	**Co** 1495	**Ni** 1445	**Cu** 1085	**Zn** 420	**Ga** 30tp	**Ge** 939	**As** 615sp	**Se** 221	**Br$_2$** −7tp	**Kr** −157	N
n=5	**Rb** 40	**Sr** 769	**Y** 1522	**Zr** 1855	**Nb** 2469	**Mo** 2623	**Tc** 2204	**Ru** 2334	**Rh** 1963	**Pd** 1555	**Ag** 962	**Cd** 321	**In** 157	**Sn** 232	**Sb** 631	**Te** 450	**I$_2$** 114tp	**Xe** −112tp	O
n=6	**Cs** 28	**Ba** 729	**La** 918	**Hf** 2231	**Ta** 3020	**W** 3422	**Re** 3186	**Os** 3033	**Ir** 2447	**Pt** 1769	**Au** 1064	**Hg** −39	**Tl** 304	**Pb** 328	**Bi** 271	**Po** 254	**At** 302	**Rn** −71	P
n=7	**Fr** 27	**Ra** 700	**Ac** 1051	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce 789	**Pr** 931	**Nd** 1021	**Pm** 1042	**Sm** 1074	**Eu** 822	**Gd** 1313	**Tb** 1356	**Dy** 1412	**Ho** 1474	**Er** 1529	**Tm** 1545	**Yb** 819	**Lu** 1663
Th 1755	**Pa** 1572	**U** 1135	**Np** 639	**Pu** 640	**Am** 1176	**Cm** 1345	**Bk** 1050	**Cf** 900	**Es** ---	**Fm** ---	**Md** ---	**No** ---	**Lw** ---

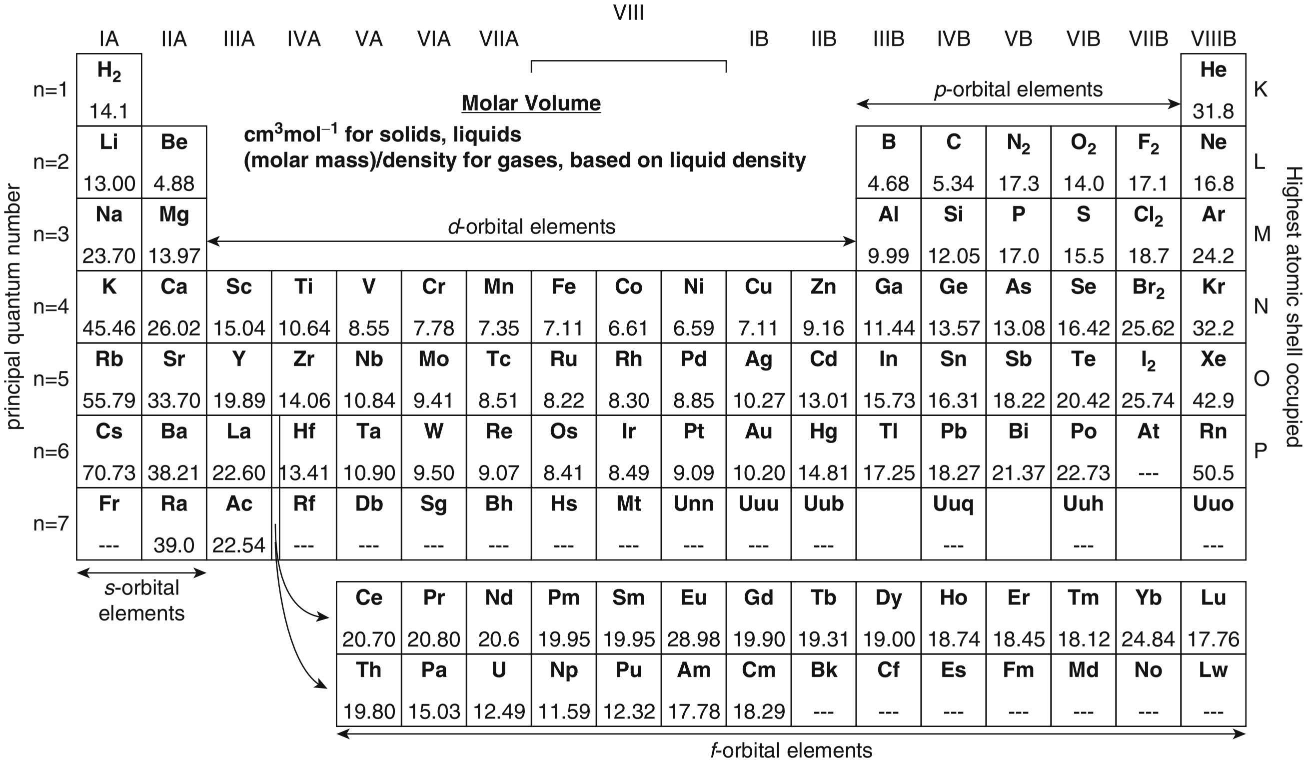
Fig. A.4 Melting point of elements in the periodic table



	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H$_2$** 0.002																	**He** 0.002	K
n=2	**Li** 0.85	**Be** 2.01											**B** 0.27	**C** 1.2-1.5	**N$_2$** <0.001	**O$_2$** <0.001	**F$_2$** <0.001	**Ne** <0.001	L
n=3	**Na** 1.42	**Mg** 1.56											**Al** 2.37	**Si** 1.49	**P** 0.002	**S** 0.003	**Cl$_2$** <0.001	**Ar** <0.0002	M
n=4	**K** 1.03	**Ca** 2.01	**Sc** 0.16	**Ti** 0.22	**V** 0.31	**Cr** 0.94	**Mn** 0.08	**Fe** 0.80	**Co** 1.00	**Ni** 0.91	**Cu** 4.01	**Zn** 1.16	**Ga** 0.48	**Ge** 0.60	**As** 0.50	**Se** 0.05	**Br$_2$** 0.001	**Kr** <0.0001	N
n=5	**Rb** 0.58	**Sr** 0.35	**Y** 0.17	**Zr** 0.23	**Nb** 0.54	**Mo** 1.38	**Tc** 0.51	**Ru** 1.17	**Rh** 1.50	**Pd** 0.72	**Ag** 4.29	**Cd** 0.97	**In** 0.82	**Sn** 0.67	**Sb** 0.24	**Te** 0.03	**I$_2$** 0.004	**Xe** <0.001	O
n=6	**Cs** 0.36	**Ba** 0.18	**La** 0.13	**Hf** 0.23	**Ta** 0.58	**W** 1.73	**Re** 0.48	**Os** 0.88	**Ir** 1.47	**Pt** 0.72	**Au** 3.18	**Hg** 0.08	**Tl** 0.46	**Pb** 0.35	**Bi** 0.08	**Po** 0.20	**At** 0.02	**Rn** <0.0001	P
n=7	**Fr** 0.15	**Ra** 0.19	**Ac** 0.12	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce 0.11	**Pr** 0.13	**Nd** 0.17	**Pm** 0.18	**Sm** 0.13	**Eu** 0.14	**Gd** 0.10	**Tb** 0.11	**Dy** 0.11	**Ho** 0.12	**Er** 0.15	**Tm** 0.17	**Yb** 0.35	**Lu** 0.16
Th 0.54	**Pa**	**U** 0.28	**Np** 0.06	**Pu** 0.07	**Am** 0.10	**Cm** 0.10	**Bk** 0.10	**Cf** 0.10	**Es** 0.10	**Fm** 0.10	**Md** 0.10	**No** 0.10	**Lw** 0.10

Fig. A.5 Thermal conductivity of elements in the periodic table



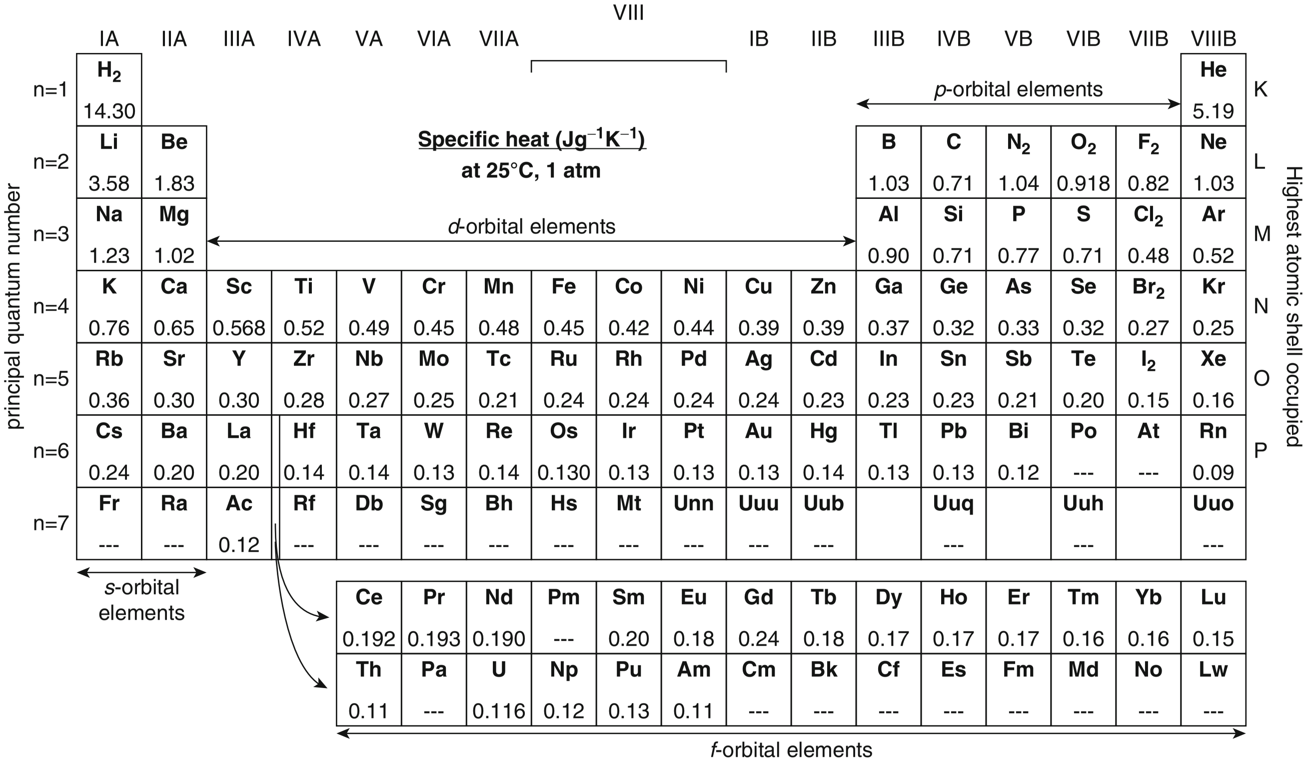
Molar Volume

cm^3mol^{-1} for solids, liquids
(molar mass)/density for gases, based on liquid density

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	H_2 14.1																	He 31.8	K
n=2	Li 13.00	Be 4.88											B 4.68	C 5.34	N_2 17.3	O_2 14.0	F_2 17.1	Ne 16.8	L
n=3	Na 23.70	Mg 13.97											Al 9.99	Si 12.05	P 17.0	S 15.5	Cl_2 18.7	Ar 24.2	M
n=4	K 45.46	Ca 26.02	Sc 15.04	Ti 10.64	V 8.55	Cr 7.78	Mn 7.35	Fe 7.11	Co 6.61	Ni 6.59	Cu 7.11	Zn 9.16	Ga 11.44	Ge 13.57	As 13.08	Se 16.42	Br_2 25.62	Kr 32.2	N
n=5	Rb 55.79	Sr 33.70	Y 19.89	Zr 14.06	Nb 10.84	Mo 9.41	Tc 8.51	Ru 8.22	Rh 8.30	Pd 8.85	Ag 10.27	Cd 13.01	In 15.73	Sn 16.31	Sb 18.22	Te 20.42	I_2 25.74	Xe 42.9	O
n=6	Cs 70.73	Ba 38.21	La 22.60	Hf 13.41	Ta 10.90	W 9.50	Re 9.07	Os 8.41	Ir 8.49	Pt 9.09	Au 10.20	Hg 14.81	Tl 17.25	Pb 18.27	Bi 21.37	Po 22.73	At ---	Rn 50.5	P
n=7	Fr ---	Ra 39.0	Ac 22.54	Rf ---	Db ---	Sg ---	Bh ---	Hs ---	Mt ---	Unn ---	Uuu ---	Uub ---		Uuq ---		Uuh ---		Uuo ---	

Ce 20.70	Pr 20.80	Nd 20.6	Pm 19.95	Sm 19.95	Eu 28.98	Gd 19.90	Tb 19.31	Dy 19.00	Ho 18.74	Er 18.45	Tm 18.12	Yb 24.84	Lu 17.76
Th 19.80	Pa 15.03	U 12.49	Np 11.59	Pu 12.32	Am 17.78	Cm 18.29	Bk ---	Cf ---	Es ---	Fm ---	Md ---	No ---	Lw ---

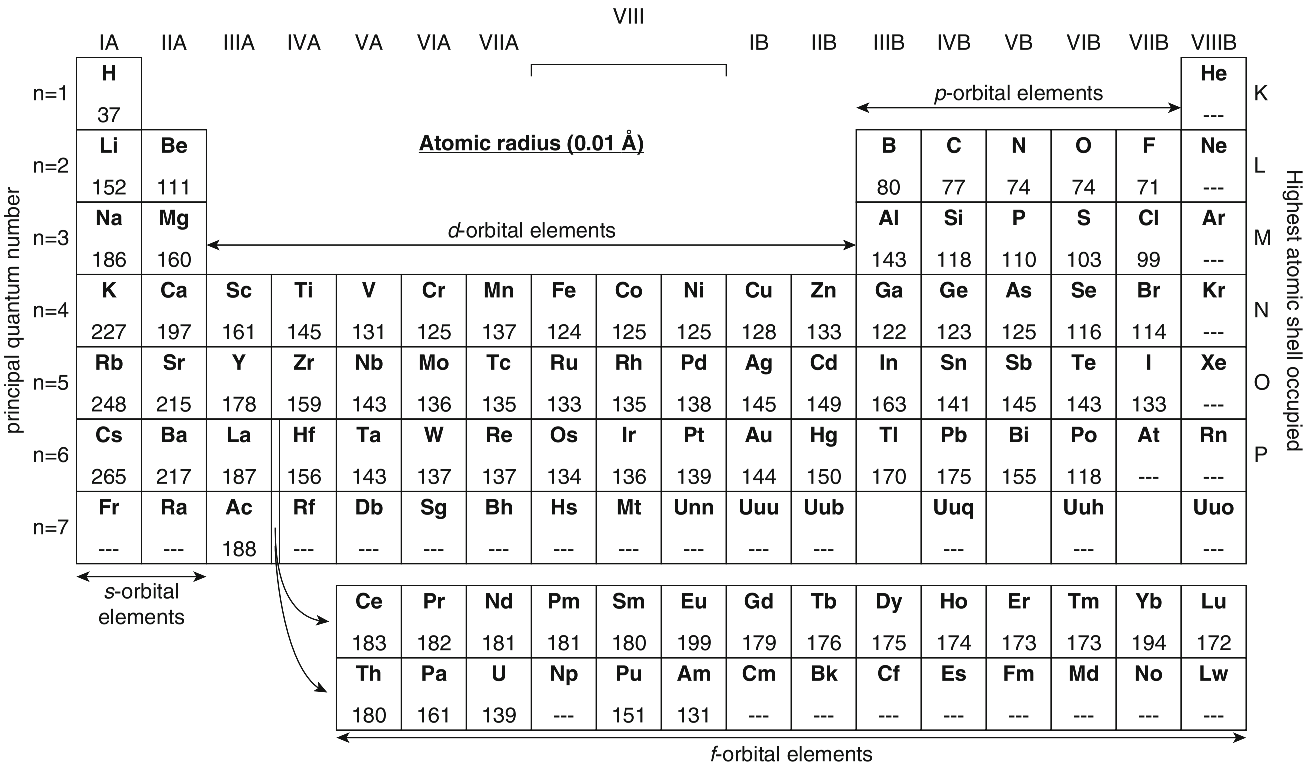
Fig. A.6 Molar volume of elements in the periodic table



Specific heat ($Jg^{-1}K^{-1}$)
at 25°C, 1 atm

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H_2** 14.30																	**He** 5.19	K
n=2	**Li** 3.58	**Be** 1.83											**B** 1.03	**C** 0.71	**N_2** 1.04	**O_2** 0.918	**F_2** 0.82	**Ne** 1.03	L
n=3	**Na** 1.23	**Mg** 1.02											**Al** 0.90	**Si** 0.71	**P** 0.77	**S** 0.71	**Cl_2** 0.48	**Ar** 0.52	M
n=4	**K** 0.76	**Ca** 0.65	**Sc** 0.568	**Ti** 0.52	**V** 0.49	**Cr** 0.45	**Mn** 0.48	**Fe** 0.45	**Co** 0.42	**Ni** 0.44	**Cu** 0.39	**Zn** 0.39	**Ga** 0.37	**Ge** 0.32	**As** 0.33	**Se** 0.32	**Br_2** 0.27	**Kr** 0.25	N
n=5	**Rb** 0.36	**Sr** 0.30	**Y** 0.30	**Zr** 0.28	**Nb** 0.27	**Mo** 0.25	**Tc** 0.21	**Ru** 0.24	**Rh** 0.24	**Pd** 0.24	**Ag** 0.24	**Cd** 0.23	**In** 0.23	**Sn** 0.23	**Sb** 0.21	**Te** 0.20	**I_2** 0.15	**Xe** 0.16	O
n=6	**Cs** 0.24	**Ba** 0.20	**La** 0.20	**Hf** 0.14	**Ta** 0.14	**W** 0.13	**Re** 0.14	**Os** 0.130	**Ir** 0.13	**Pt** 0.13	**Au** 0.13	**Hg** 0.14	**Tl** 0.13	**Pb** 0.13	**Bi** 0.12	**Po** ---	**At** ---	**Rn** 0.09	P
n=7	**Fr** ---	**Ra** ---	**Ac** 0.12	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	
					Ce 0.192	**Pr** 0.193	**Nd** 0.190	**Pm** ---	**Sm** 0.20	**Eu** 0.18	**Gd** 0.24	**Tb** 0.18	**Dy** 0.17	**Ho** 0.17	**Er** 0.17	**Tm** 0.16	**Yb** 0.16	**Lu** 0.15	
					Th 0.11	**Pa** ---	**U** 0.116	**Np** 0.12	**Pu** 0.13	**Am** 0.11	**Cm** ---	**Bk** ---	**Cf** ---	**Es** ---	**Fm** ---	**Md** ---	**No** ---	**Lw** ---	

Fig. A.7 Specific heat of elements in the periodic table

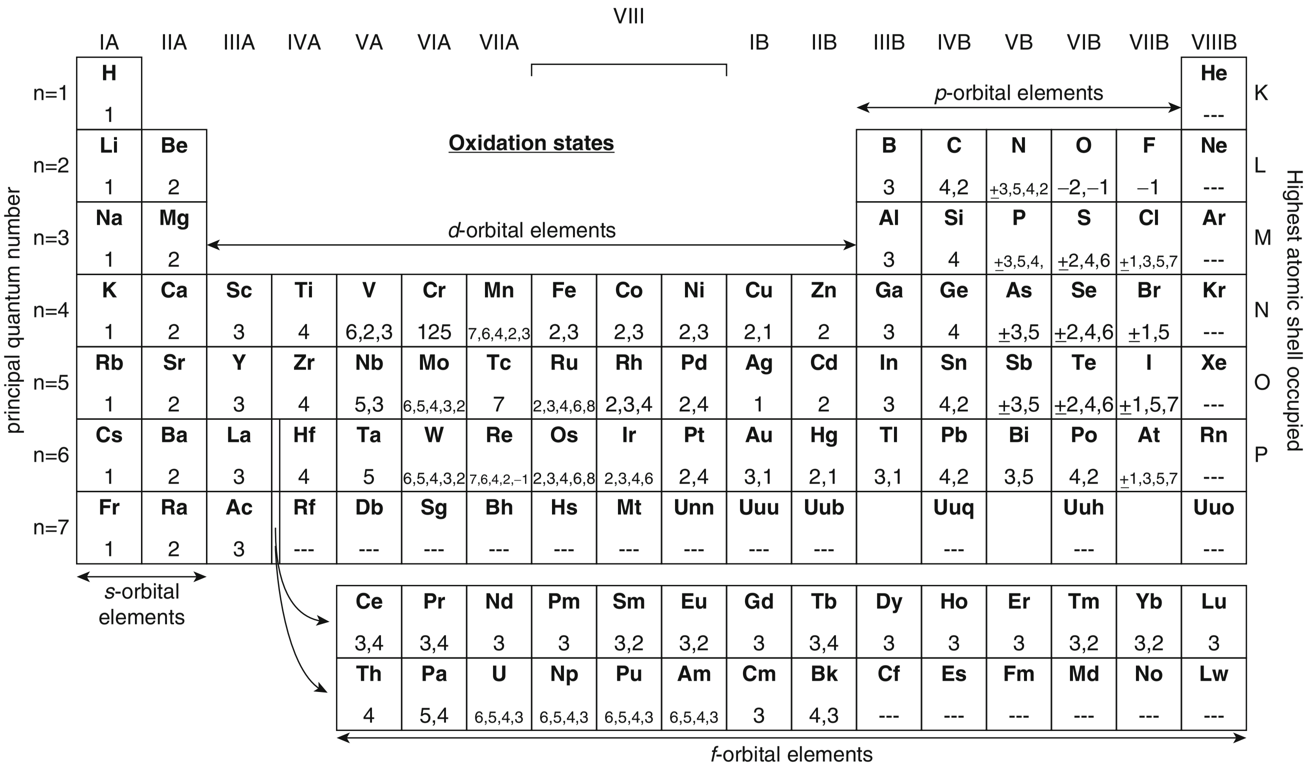


Atomic radius (0.01 Å)

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H** 37																	**He** ---	K
n=2	**Li** 152	**Be** 111											**B** 80	**C** 77	**N** 74	**O** 74	**F** 71	**Ne** ---	L
n=3	**Na** 186	**Mg** 160											**Al** 143	**Si** 118	**P** 110	**S** 103	**Cl** 99	**Ar** ---	M
n=4	**K** 227	**Ca** 197	**Sc** 161	**Ti** 145	**V** 131	**Cr** 125	**Mn** 137	**Fe** 124	**Co** 125	**Ni** 125	**Cu** 128	**Zn** 133	**Ga** 122	**Ge** 123	**As** 125	**Se** 116	**Br** 114	**Kr** ---	N
n=5	**Rb** 248	**Sr** 215	**Y** 178	**Zr** 159	**Nb** 143	**Mo** 136	**Tc** 135	**Ru** 133	**Rh** 135	**Pd** 138	**Ag** 145	**Cd** 149	**In** 163	**Sn** 141	**Sb** 145	**Te** 143	**I** 133	**Xe** ---	O
n=6	**Cs** 265	**Ba** 217	**La** 187	**Hf** 156	**Ta** 143	**W** 137	**Re** 137	**Os** 134	**Ir** 136	**Pt** 139	**Au** 144	**Hg** 150	**Tl** 170	**Pb** 175	**Bi** 155	**Po** 118	**At** ---	**Rn** ---	P
n=7	**Fr** ---	**Ra** ---	**Ac** 188	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce 183	**Pr** 182	**Nd** 181	**Pm** 181	**Sm** 180	**Eu** 199	**Gd** 179	**Tb** 176	**Dy** 175	**Ho** 174	**Er** 173	**Tm** 173	**Yb** 194	**Lu** 172
Th 180	**Pa** 161	**U** 139	**Np** ---	**Pu** 151	**Am** 131	**Cm** ---	**Bk** ---	**Cf** ---	**Es** ---	**Fm** ---	**Md** ---	**No** ---	**Lw** ---

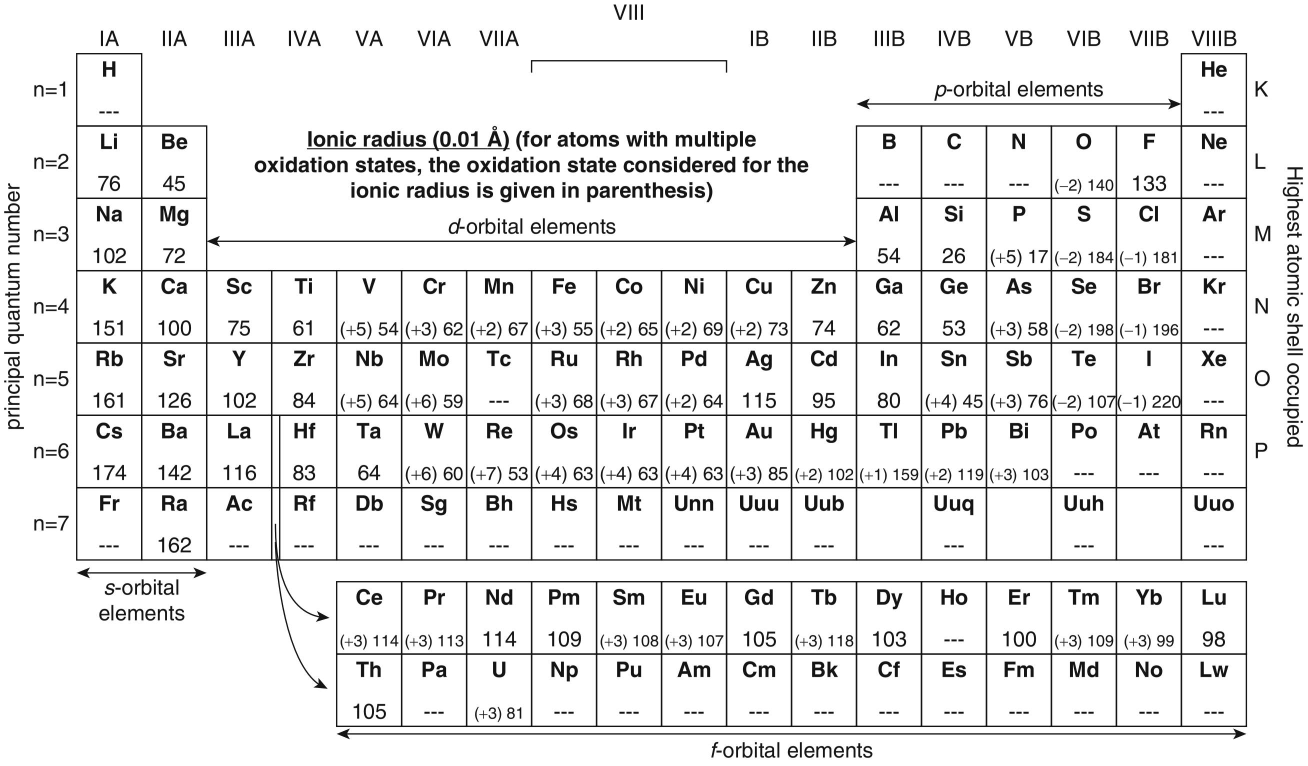
Fig. A.8 Atomic radius of elements in the periodic table



	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H** 1																	**He** ---	K
n=2	**Li** 1	**Be** 2											**B** 3	**C** 4,2	**N** ±3,5,4,2	**O** −2,−1	**F** −1	**Ne** ---	L
n=3	**Na** 1	**Mg** 2											**Al** 3	**Si** 4	**P** ±3,5,4,	**S** ±2,4,6	**Cl** ±1,3,5,7	**Ar** ---	M
n=4	**K** 1	**Ca** 2	**Sc** 3	**Ti** 4	**V** 6,2,3	**Cr** 125	**Mn** 7,6,4,2,3	**Fe** 2,3	**Co** 2,3	**Ni** 2,3	**Cu** 2,1	**Zn** 2	**Ga** 3	**Ge** 4	**As** ±3,5	**Se** ±2,4,6	**Br** ±1,5	**Kr** ---	N
n=5	**Rb** 1	**Sr** 2	**Y** 3	**Zr** 4	**Nb** 5,3	**Mo** 6,5,4,3,2	**Tc** 7	**Ru** 2,3,4,6,8	**Rh** 2,3,4	**Pd** 2,4	**Ag** 1	**Cd** 2	**In** 3	**Sn** 4,2	**Sb** ±3,5	**Te** ±2,4,6	**I** ±1,5,7	**Xe** ---	O
n=6	**Cs** 1	**Ba** 2	**La** 3	**Hf** 4	**Ta** 5	**W** 6,5,4,3,2	**Re** 7,6,4,2,−1	**Os** 2,3,4,6,8	**Ir** 2,3,4,6	**Pt** 2,4	**Au** 3,1	**Hg** 2,1	**Tl** 3,1	**Pb** 4,2	**Bi** 3,5	**Po** 4,2	**At** ±1,3,5,7	**Rn** ---	P
n=7	**Fr** 1	**Ra** 2	**Ac** 3	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce 3,4	**Pr** 3,4	**Nd** 3	**Pm** 3	**Sm** 3,2	**Eu** 3,2	**Gd** 3	**Tb** 3,4	**Dy** 3	**Ho** 3	**Er** 3	**Tm** 3,2	**Yb** 3,2	**Lu** 3
Th 4	**Pa** 5,4	**U** 6,5,4,3	**Np** 6,5,4,3	**Pu** 6,5,4,3	**Am** 6,5,4,3	**Cm** 3	**Bk** 4,3	**Cf** ---	**Es** ---	**Fm** ---	**Md** ---	**No** ---	**Lw** ---

Fig. A.9 Oxidation states of elements in the periodic table

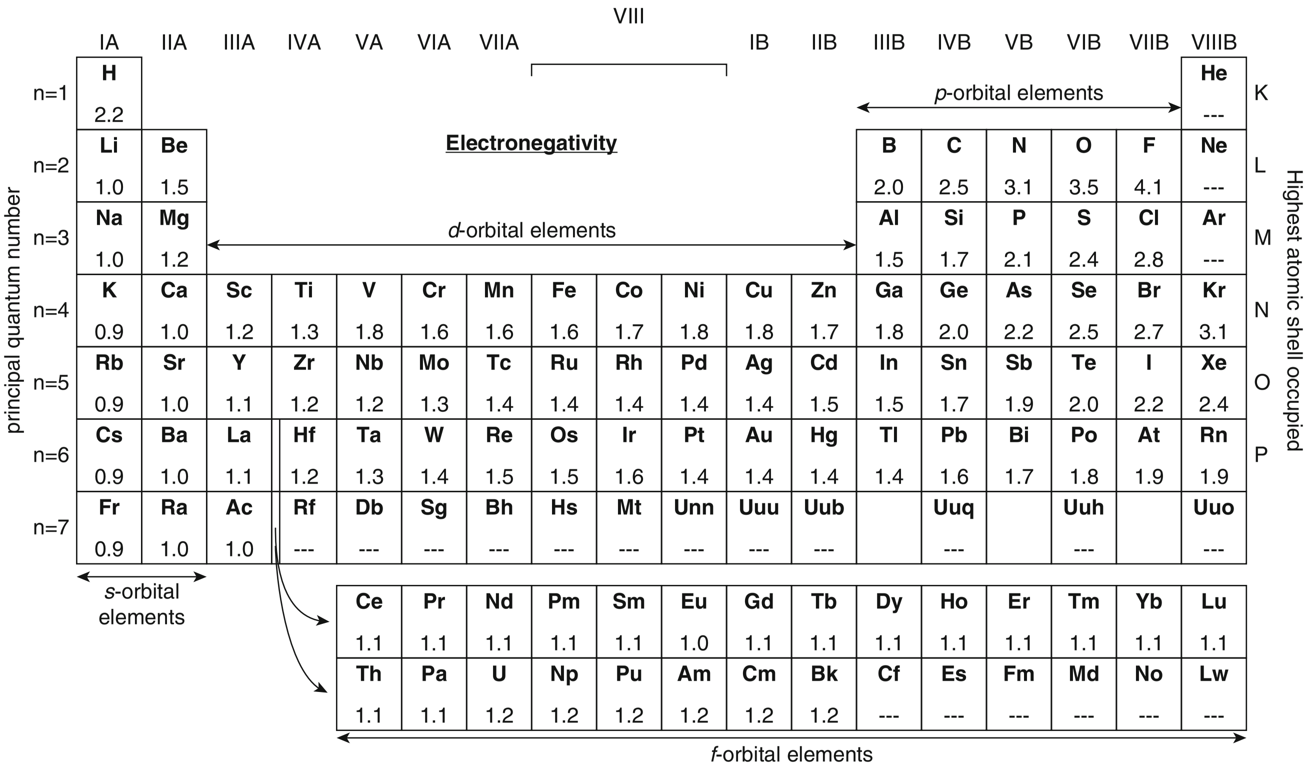


Ionic radius (0.01 Å) (for atoms with multiple oxidation states, the oxidation state considered for the ionic radius is given in parenthesis)

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H** ---																	**He** ---	K
n=2	**Li** 76	**Be** 45											**B** ---	**C** ---	**N** ---	**O** (−2) 140	**F** 133	**Ne** ---	L
n=3	**Na** 102	**Mg** 72											**Al** 54	**Si** 26	**P** (+5) 17	**S** (−2) 184	**Cl** (−1) 181	**Ar** ---	M
n=4	**K** 151	**Ca** 100	**Sc** 75	**Ti** 61	**V** (+5) 54	**Cr** (+3) 62	**Mn** (+2) 67	**Fe** (+3) 55	**Co** (+2) 65	**Ni** (+2) 69	**Cu** (+2) 73	**Zn** 74	**Ga** 62	**Ge** 53	**As** (+3) 58	**Se** (−2) 198	**Br** (−1) 196	**Kr** ---	N
n=5	**Rb** 161	**Sr** 126	**Y** 102	**Zr** 84	**Nb** (+5) 64	**Mo** (+6) 59	**Tc** ---	**Ru** (+3) 68	**Rh** (+3) 67	**Pd** (+2) 64	**Ag** 115	**Cd** 95	**In** 80	**Sn** (+4) 45	**Sb** (+3) 76	**Te** (−2) 107	**I** (−1) 220	**Xe** ---	O
n=6	**Cs** 174	**Ba** 142	**La** 116	**Hf** 83	**Ta** 64	**W** (+6) 60	**Re** (+7) 53	**Os** (+4) 63	**Ir** (+4) 63	**Pt** (+4) 63	**Au** (+3) 85	**Hg** (+2) 102	**Tl** (+1) 159	**Pb** (+2) 119	**Bi** (+3) 103	**Po** ---	**At** ---	**Rn** ---	P
n=7	**Fr** ---	**Ra** 162	**Ac** ---	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce (+3) 114	**Pr** (+3) 113	**Nd** 114	**Pm** 109	**Sm** (+3) 108	**Eu** (+3) 107	**Gd** 105	**Tb** (+3) 118	**Dy** 103	**Ho** ---	**Er** 100	**Tm** (+3) 109	**Yb** (+3) 99	**Lu** 98
Th 105	**Pa** ---	**U** (+3) 81	**Np** ---	**Pu** ---	**Am** ---	**Cm** ---	**Bk** ---	**Cf** ---	**Es** ---	**Fm** ---	**Md** ---	**No** ---	**Lw** ---

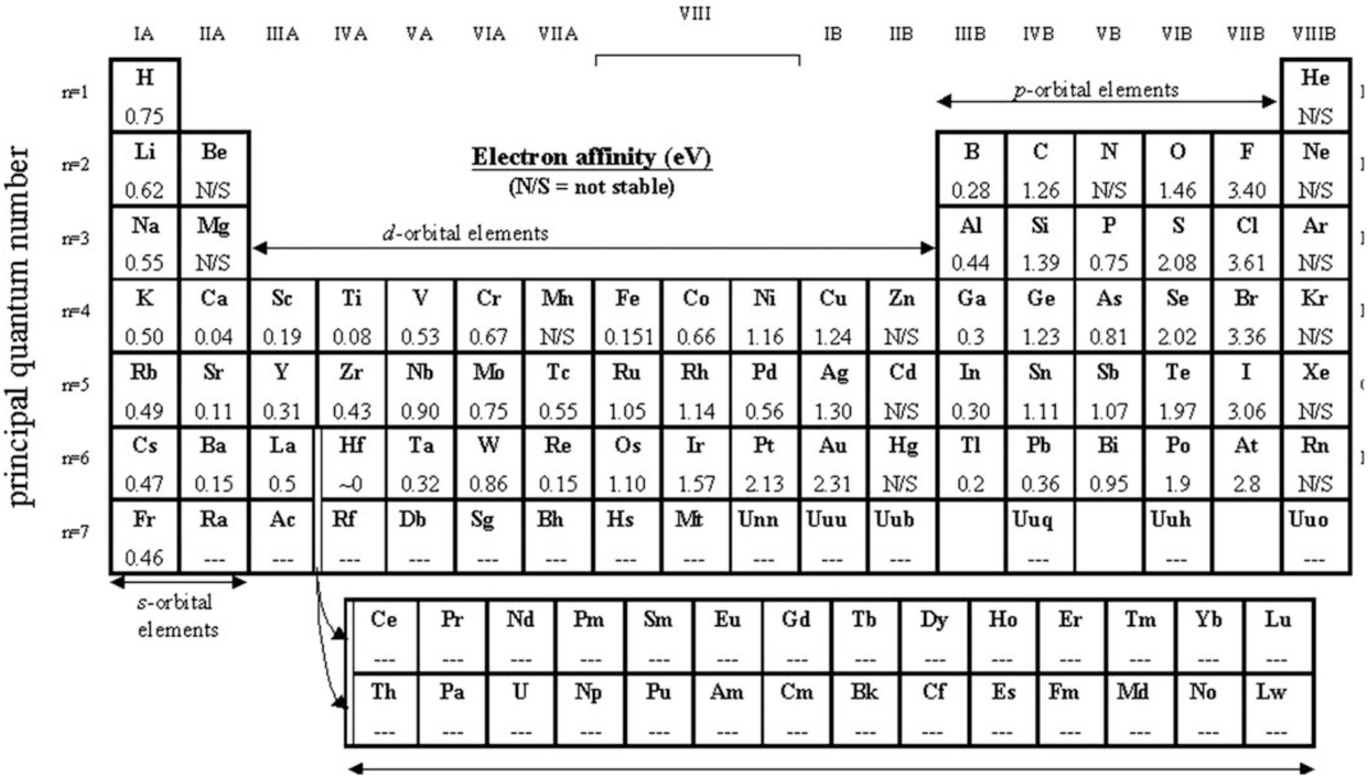
Fig. A.10 Ionic radius of elements in the periodic table



	IA	IIA	IIIA	IVA	VA	VIA	VIIA				IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB	
n=1	**H** 2.2																	**He** ---	K
n=2	**Li** 1.0	**Be** 1.5											**B** 2.0	**C** 2.5	**N** 3.1	**O** 3.5	**F** 4.1	**Ne** ---	L
n=3	**Na** 1.0	**Mg** 1.2											**Al** 1.5	**Si** 1.7	**P** 2.1	**S** 2.4	**Cl** 2.8	**Ar** ---	M
n=4	**K** 0.9	**Ca** 1.0	**Sc** 1.2	**Ti** 1.3	**V** 1.8	**Cr** 1.6	**Mn** 1.6	**Fe** 1.6	**Co** 1.7	**Ni** 1.8	**Cu** 1.8	**Zn** 1.7	**Ga** 1.8	**Ge** 2.0	**As** 2.2	**Se** 2.5	**Br** 2.7	**Kr** 3.1	N
n=5	**Rb** 0.9	**Sr** 1.0	**Y** 1.1	**Zr** 1.2	**Nb** 1.2	**Mo** 1.3	**Tc** 1.4	**Ru** 1.4	**Rh** 1.4	**Pd** 1.4	**Ag** 1.4	**Cd** 1.5	**In** 1.5	**Sn** 1.7	**Sb** 1.9	**Te** 2.0	**I** 2.2	**Xe** 2.4	O
n=6	**Cs** 0.9	**Ba** 1.0	**La** 1.1	**Hf** 1.2	**Ta** 1.3	**W** 1.4	**Re** 1.5	**Os** 1.5	**Ir** 1.6	**Pt** 1.4	**Au** 1.4	**Hg** 1.4	**Tl** 1.4	**Pb** 1.6	**Bi** 1.7	**Po** 1.8	**At** 1.9	**Rn** 1.9	P
n=7	**Fr** 0.9	**Ra** 1.0	**Ac** 1.0	**Rf** ---	**Db** ---	**Sg** ---	**Bh** ---	**Hs** ---	**Mt** ---	**Unn** ---	**Uuu** ---	**Uub** ---		**Uuq** ---		**Uuh** ---		**Uuo** ---	

Ce 1.1	**Pr** 1.1	**Nd** 1.1	**Pm** 1.1	**Sm** 1.1	**Eu** 1.0	**Gd** 1.1	**Tb** 1.1	**Dy** 1.1	**Ho** 1.1	**Er** 1.1	**Tm** 1.1	**Yb** 1.1	**Lu** 1.1
Th 1.1	**Pa** 1.1	**U** 1.2	**Np** 1.2	**Pu** 1.2	**Am** 1.2	**Cm** 1.2	**Bk** 1.2	**Cf** ---	**Es** ---	**Fm** ---	**Md** ---	**No** ---	**Lw** ---

Fig. A.11 Electronegativity of elements in the periodic table



Electron affinity (eV)
(N/S = not stable)

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB
n=1	H 0.75																	He N/S
n=2	Li 0.62	Be N/S											B 0.28	C 1.26	N N/S	O 1.46	F 3.40	Ne N/S
n=3	Na 0.55	Mg N/S											Al 0.44	Si 1.39	P 0.75	S 2.08	Cl 3.61	Ar N/S
n=4	K 0.50	Ca 0.04	Sc 0.19	Ti 0.08	V 0.53	Cr 0.67	Mn N/S	Fe 0.151	Co 0.66	Ni 1.16	Cu 1.24	Zn N/S	Ga 0.3	Ge 1.23	As 0.81	Se 2.02	Br 3.36	Kr N/S
n=5	Rb 0.49	Sr 0.11	Y 0.31	Zr 0.43	Nb 0.90	Mo 0.75	Tc 0.55	Ru 1.05	Rh 1.14	Pd 0.56	Ag 1.30	Cd N/S	In 0.30	Sn 1.11	Sb 1.07	Te 1.97	I 3.06	Xe N/S
n=6	Cs 0.47	Ba 0.15	La 0.5	Hf ~0	Ta 0.32	W 0.86	Re 0.15	Os 1.10	Ir 1.57	Pt 2.13	Au 2.31	Hg N/S	Tl 0.2	Pb 0.36	Bi 0.95	Po 1.9	At 2.8	Rn N/S
n=7	Fr 0.46	Ra ---	Ac ---	Rf ---	Db ---	Sg ---	Bh ---	Hs ---	Mt ---	Unn ---	Uuu ---	Uub ---		Uuq ---		Uuh ---		Uuo ---

Ce ---	Pr ---	Nd ---	Pm ---	Sm ---	Eu ---	Gd ---	Tb ---	Dy ---	Ho ---	Er ---	Tm ---	Yb ---	Lu ---
Th ---	Pa ---	U ---	Np ---	Pu ---	Am ---	Cm ---	Bk ---	Cf ---	Es ---	Fm ---	Md ---	No ---	Lw ---

Fig. A.12 Electron affinity of elements in the periodic table

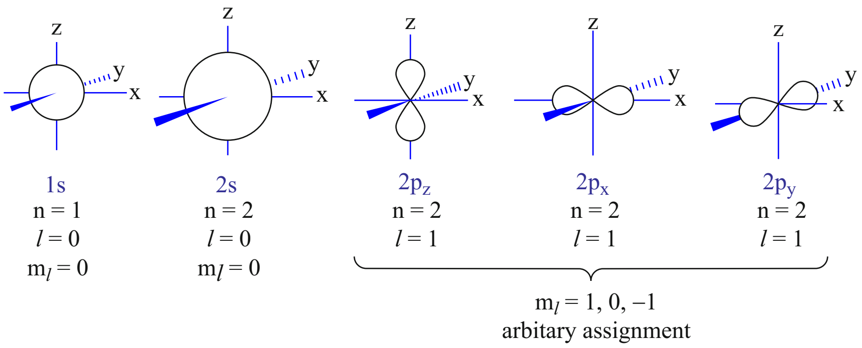


Fig. A.13 Sketch of 1s, 2s, and 2p atomic orbital wavefunctions

Any given (*n*, l, *m*) corresponds to one atomic orbital and can hold two electrons because of the Pauli principle. These two electrons thus have opposite spin.

The principal quantum number n refers to one shell of electrons around the nucleus and describes the size of orbitals. The higher this number, the farther is the shell from the nucleus. The completion of this layer with electrons describes the number of covalent bond which can be formed, and thus the n shell of an atom is primordial I the description of its properties.

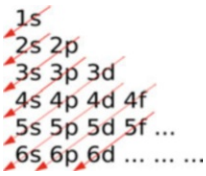
For a given *n*, the azimuthal number l refers to one particular orbital atomic in the n shell and describes the shape of the orbital.

l = 0 corresponds to an s orbital (sharp)
l = 1 corresponds to a p orbital (principal)
l = 2 corresponds to a d orbital (diffuse)
l = 3 corresponds to an f orbital (fundamental)

The magnetic quantum number m describes the orientation of orbitals in space.

For a given atom of known atomic number, the atomic electrons occupy orbitals from the lower shells with low-energy to the highest-energy shells.

The *Aufbau principle* (or Pauli rule) states which orbital are occupied by electrons for a given atom:



In this representation, the number corresponds to the principal quantum number *n*, while the letter (s, p, d, or f) gives the azimuthal quantum number l. The magnetic quantum number is not represented and is suggested by the value of l since m is between −l and l. The red arrow gives the order in which the atomic orbital is filled. This order is the same for all atoms.

Example 1 Helium (He), two electrons.

First, the 1s orbital is filled. This orbital corresponds to $n = 1$, $l = 0$. Since m is between −l and l, the only value possible for m is 0. Thus the 1s orbital corresponds to $(n, l, m) = (1, 0, 0)$. The Pauli principle states that this orbital can hold two electrons. Thus for helium, the electronic configuration is $1s^2$.

Example 2 Carbon (C), 6 electrons.

First the 1s orbital is filled and can hold two electrons, similarly to the helium atom.

Then the 2s orbital is filled. This orbital corresponds to $n = 2$, $l = 0$, which forces $m = 0$. Thus, the 2s orbital corresponds to the $(n, l, m) = (2, 0, 0)$ configuration and can hold two electrons.

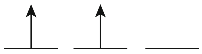
Then the 2p orbital is filled. This orbital corresponds to $n = 2$ and $l = 1$. Since $l = 1$, the values possible for m are −1, 0, and 1. Thus the 2p orbital contains the three configurations (2, 1, −1), (2, 1, 0), and (2, 1, 1) and can hold a total of six electrons. The last two electrons of carbon can thus be contained in the 2p orbital. This 2p is not completely filled for the carbon atom and can hold four more electrons.

This explains why the carbon atom can be involved in four covalent bonds.

The electronic configuration of carbon is written $1s^2\ 2s^2\ 2p^2$ or $[He]\ 2s^2\ 2p^2$.

A question remains unanswered: There are three p orbitals (p_x, p_y, p_z) in the 2p subshell, and these orbitals of same energy levels, called degenerate levels, are equivalent. Does the second electron go into the same orbital as the first, or does it go to another p orbital? To answer this question, we can use Hund's rule. This rule states that when filling the orbitals, one electron is added to each degenerate orbital before two electrons are added to the same orbital. Moreover, all the first electrons added to the degenerate orbitals have the same spin orientation.

As a result, the electrons in the 2p orbitals for carbon can be represented as follows:



A.3.2 Tight-Binding Method

For being one the most fundamental theoretical calculation tool in crystalline structure band energy modeling, multiple books concerning tight-binding method can be found in the literature, such as in Razeghi (1989). It is similar to the LCAO (linear combination of atomic orbital) used in chemistry: Both models are approximation and rely on the periodicity of crystalline structures in order to model the interactions between atoms.

Understanding the tight-binding method is primordial, and this textbook assumes that its basic concepts are known. Yet, this appendix offers an overview of the method based on the example of a one-dimensional periodic structure composed of one type of atom. The similarity between the results obtained here and the equations found in the chapter can be easily noticed.

Bloch's Theorem

Let's consider a crystalline structure in which the atoms are assumed to be perfectly arranged, so that they introduce a periodic, infinite potential. This potential V has the same periodicity as the crystalline structure.

Without loss of generalities, the Schrödinger equation for an electron inside the crystalline structure can be written:

$$\widehat{\mathrm{H}}\psi(\vec{r}) = \left(-\frac{\hbar^2}{2m}\Delta + V(\vec{r})\right)\psi(r) = E\psi(\vec{r}) \tag{1}$$

where E is the energy eigenvalue of the Hamiltonian operator.

The *Bloch's theorem* states that given a periodic potential V, the eigenstates ψ of the one-electron Hamiltonian (1) with periodic potential can be written as the product of a plane wave with a periodic function in the Bravais lattice of the solid. In other words:

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}u_{n\vec{k}}(\vec{r}) \tag{2}$$

where $u_{n\vec{k}}(\vec{r} + \vec{R}) = u_{n\vec{k}}(\vec{r} + \vec{R})$ for any $\vec{R}$ of the Bravais lattice.From Bloch's theorem (2), we get the following result: Any wavefunction which is eigenstate of a Hamiltonian with periodic potential verifies:

$$\psi_{n\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{R}}\psi_{n\vec{k}}(\vec{r}) \tag{3}$$

This means that when the physical space in real space is shifted of a vector from the Bravais lattice $\vec{R}$, only the phase of the wavefunction is affected.

The Tight-Binding Method: Generalities

Let's define the $\phi_n(\vec{r})$ atomic orbitals, which are eigenstates of the Hamiltonian H_{at} of a single atom. When this atom is placed inside a crystalline structure, the electrons inside the structure can no longer be considered as a collection of isolated electrons, since the low distance between atoms makes valence electrons interact with each other. In other words, the atomic orbitals overlap adjacent atomic sites and thus are no longer eigenstates of the new Hamiltonian of the crystal. One of the assumptions of the tight-binding model is that the Hamiltonian of the crystal can be still described as the sum of Hamiltonian of each single atom with a small perturbation:

$$\widehat{\mathrm{H}}\left(\vec{r}\right) = \sum_{\vec{R}_n} \widehat{\mathrm{H}}_{at}\left(\vec{r} - \underset{n}{\vec{R}}\right) + \Delta U\left(\vec{r}\right) \tag{4}$$

where $\underset{n}{\vec{R}}$ locates all the atomic sites inside the crystal and $\Delta U\left(\vec{r}\right)$ is the potential energy of interaction between atomic sites and is considered as a perturbation.

Since the effect of interaction between atoms is considered small, in the tight-binding method, one writes the solution of the Hamiltonian crystal as combination of atomic orbitals described above. In other words, we write any eigenstate of the Hamiltonian (3) in this form:

$$\psi_k\left(\vec{r}\right) = \sum_{\vec{R}_n} \sum_m c_m\left(\vec{R}_n\right)\phi_m\left(\vec{r} - \vec{R}_n\right) \tag{5}$$

where the first sum is over each atom of the crystalline structure and the second sum is over the different atomic orbitals of a single isolated atom. The $c_m\left(\vec{R}_n\right)$ are constants that need to be solved. The two following steps are dedicated to finding the value of these constants.

First of all, the Bloch's theorem states that $\psi_k\left(\vec{r}\right)$ has the same period as the crystalline structure, so that we can write:

$$\psi_k\left(\vec{r} + \vec{R}_n\right) = e^{i\vec{k}\vec{R}_n}\psi_k\left(\vec{r}\right) \tag{6}$$

The reader can easily verify that this equation leads to the following result:

$$b_m\left(\vec{R}_n\right) = e^{i\vec{k}\vec{R}_n} b_m\left(\vec{0}\right) \tag{7}$$

Then, the normalization of wavefunction to unity can be written:

$$\int \psi_k{}^*\left(\vec{r}\right)\psi_k\left(\vec{r}\right)d^3r = 1 \tag{8}$$

which after simplifications and neglecting atomic overlap integrals gives the following result:

$$b_m\left(\vec{0}\right) \simeq \frac{1}{\sqrt{N.}} \tag{9}$$

Using (4), (5), and (6) that the actual form of any eigenstate is:

$$\psi_k(\vec{r}) \simeq \frac{1}{\sqrt{N}} \sum_{\vec{R}_n} \sum_m e^{i\vec{k}\vec{R}_n} \phi_m(\vec{r} - \vec{R}_n) \tag{10}$$

In this equation, the first sum is labeled over the position $\vec{R}_n$ of every atom in the crystalline structure, and the second sum is labeled over the different valence orbitals of a given isolated atom.

Example

Let's give an example of use of the tight-binding method for a one-dimensional crystalline structure composed of one type of atom. Moreover, we assume that this atom only has one valence atomic orbital.

As seen in the previous section, any eigenstate of the Hamiltonian can be written $\psi_k(\vec{r}) \simeq \frac{1}{\sqrt{N}} \sum_{\vec{R}_n} \sum_m e^{i\vec{k}\vec{R}_n} \phi_m(\vec{r} - \vec{R}_n)$. For this example, $m = 1$, since the atom only has one valence orbital. Let N be the total number of atoms in the structure, and let's use a more condensed formalism where $| k >= \psi_k(\vec{r})$ and $| n >= \phi(\vec{r} - \vec{R}_n)$, so that:

$$| k >= \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{inka} | n >$$

where a is the distance between atoms.

We then assume that the orbital wavefunctions of only closest atoms overlap so that in the Hamiltonian matrix, all components $<i|H|j> = H_{i,j}$ are equal to zero, except the tridiagonal values.

In other words:

$$\begin{cases} < i|H|j >= 0 \quad if \quad | i - j |> 1 \\ < i|H|i >= E_0 \\ < i \pm 1|H|i >= -\Delta \end{cases}$$

where $-\Delta$ can be interpreted as the bonding energy between atoms. In addition, we write the normalization equation between atoms wavefunction as:

$$< i|i >= 1 \quad \text{and} \quad < i \pm 1|i >= S < 1$$

Since $|k>$ is eigenstate of the Hamiltonian, we can determine its corresponding eigenvalue by writing:

$$\hat{H}|k >= E|k >= \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{inka} \hat{H} \ | n >$$

which, after multiplying on the left by $<k|$, leads to:

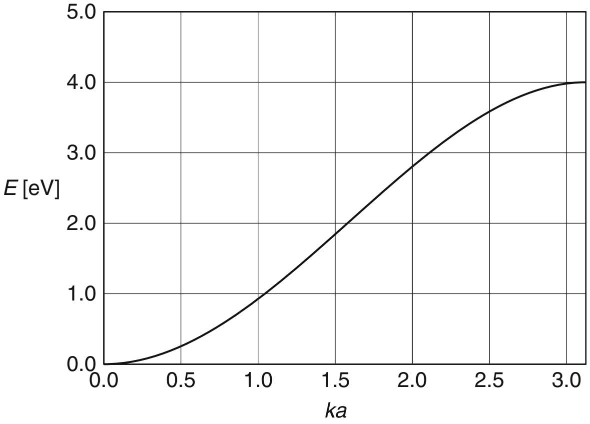
$$< k \mid \widehat{H}|k >=< k|E_k|k >= E_k = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} e^{i(n-m)\text{ka}} < m|H|n >$$

And:

$$E_k = \frac{1}{N}\sum_{n=1}^{N} < n|H|n > + \frac{1}{N}\sum_{n=1}^{N} < n-1|H|n > e^{+\text{ika}} + \frac{1}{N}\sum_{n=1}^{N} < n-1|H|n > e^{-\text{ika}}$$

Thus the dispersion relation inside the crystal can is:

$$E_k = E(k) = E_0 - 2\Delta\cos(ka)$$



The result obtained here can be reproduced for different crystal structures and atomic orbitals.

A.4 Physical Properties of Important Semiconductors

Semiconductor		Bandgap energy (eV)		Band	
		300 K	0 K		ε
Element	C	5.47	5.48	Indirect	5.7
	Si	1.12	1.17	Indirect	11.9
	Ge	0.66	0.74	Indirect	16.0
	Sn		0.082	Direct	
IV-IV	α-SiC	2.996	3.03	Indirect	10.0

(continued)

Semiconductor		Bandgap energy (eV)		Band	ε
		300 K	0 K		
III-V	BN	~7.5		Indirect	7.1
	GaN	3.36	3.50	Direct	12.2
	GaP	2.26	2.34	Indirect	11.1
	BP	2.0			
	AlSb	1.58	1.68	Indirect	14.4
	GaAs	1.42	1.52	Direct	13.1
	InP	1.35	1.42	Direct	12.4
	GaSb	0.72	0.81	Direct	15.7
	InAs	0.36	0.42	Direct	14.6
	InSb	0.17	0.23	Direct	17.7
II-VI	ZnS	3.68	3.84	Direct	5.2
	ZnO	3.35	3.42	Direct	9.0
	CdS	2.42	2.56	Direct	5.4
	CdSe	1.70	1.85	Direct	10.0
	CdTe	1.56		Direct	10.2
IV-VI	PbS	0.41	0.286	Indirect	17.0
	PbTe	0.31	0.19	Indirect	30.0

Semiconductor	Intrinsic carrier concentration at 300 K (cm^{-3})
Ge	2.4×10^{13}
Si	1.45×10^{10}
GaAs	2.15×10^{6}

Semiconductor		Mobility at 300 K ($\mathrm{cm}^2/\mathrm{Vs}$)		Effective masses (in units of m_0)	
		Electrons	Holes	Electrons m_e	Holes m_h
Element	C	1800	1200	0.2	0.25
	Si	1500	450	0.98[a] 0.19[b]	0.16[c] 0.49[d]
	Ge	3900	1900	1.64[a] 0.082[b]	0.04[c] 0.28[d]
	Sn	1400	1200		
IV-IV	α-SiC	400	50	0.60	1.00
III-V	BN				
	GaN	380		0.19	0.60
	GaP	100	75	0.82	0.60
	BP				
	AlSb	200	420	0.12	0.98
	GaAs	8500	400	0.067	0.082[c] 0.45[d]
	InP	4600	150	0.077	0.64

(continued)

Semiconductor		Mobility at 300 K (cm^2/Vs)		Effective masses (in units of m_0)	
		Electrons	Holes	Electrons m_e	Holes m_h
	GaSb	5000	850	0.42	0.04[c] 0.4[d]
	InAs	33,000	460	0.023	0.40
	InSb	80,000	1250	0.0145	0.40
II-VI	ZnS	165	5	0.40	
	ZnO	200	180	0.27	
	CdS	340	50	0.21	0.80
	CdSe	800		0.13	0.45
	CdTe	1050	100		
IV-VI	PbS	600	700	0.25	0.25
	PbTe	6000	4000	0.17	0.20

[a] Longitudinal effective mass
[b] Transverse effective mass
[c] Light-hole effective mass
[d] Heavy-hole effective mass

A.5 The Taylor Expansion

The Taylor expansion is a powerful mathematical method which yields a simple polynomial approximation for any mathematical function near a given point.

Let us consider a function f which can be differentiated at least $(n + 1)$ times at $x = x_0$. The Taylor expansion is such that the value of f at any point x can be determined from its value and that of its n consecutive derivatives at x_0 through:

$$\begin{aligned} f(x) &= f(x_0) + f'(x_0)(x - x_0) + \frac{f''(x_0)}{2!}(x - x_0)^2 + \ldots \\ &\ldots + \frac{f^{(n)}(x_0)}{n!}(x - x_0)^n + R_n \end{aligned} \tag{A.1}$$

where R_n is called the remainder and is equal to:

$$R_n = \frac{f^{(n+1)}(\xi)}{(n+1)!}(x - x_0)^{n+1} \tag{A.2}$$

for an appropriate value ξ such that $|\xi - x_0| \leq |x - x_0|$.

As a result of this expansion, an approximate value of the function f near the point $x = x_0$ is obtained by neglecting the remainder R_n in Eq. (A.2). In principle, the more terms one chooses to keep in the expansion, the more accurate result one will get. R_n is used to evaluate the magnitude of the calculation error. It is often useful to carry the Taylor expansion near an extremum of the function f because some of its derivatives are then equal to zero, and a simplified expression is obtained.

A few examples of Taylor expansion for commonly used functions are given below:

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots + \frac{x^n}{n!} + \cdots = \sum_{n=0}^{\infty} \frac{x^n}{n!} \tag{A.3}$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + - \cdots = \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)!} \tag{A.4}$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^3}{3!} - \frac{x^5}{5!} + - \cdots = \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n}}{(2n)!} \tag{A.5}$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - + \cdots = \sum_{n=0}^{\infty} \frac{(-1)^{n+1} x^n}{n} \tag{A.6}$$

There exist convergence ranges in evaluating the infinite sums inEq. (A.6) to Eq. (A.5). This means that the Taylor expansion will no longer be valid when trying to evaluate the sums for a value of x outside the convergence range. For example, the convergence range for e^x, $\sin(x)$, and $\cos(x)$ is $(-\infty, +\infty)$, whereas the convergence range for $Ln(1 - x)$ is $(-\infty, 1]$.

A.6 Fourier Series and the Fourier Transform

Fourier Series

A function $f(t)$ is periodic with a period T when it satisfies $f(t + T) = f(t)$ for any value of t. If such a periodic function is also piecewise continuous, then it can be written as the sum of trigonometric functions such that:

$$f(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left(a_n \cos(nwt) + b_n \sin(nwt)\right) \tag{A.7}$$

where we have denoted $w = \frac{2\pi}{T}$, and:

$$a_0 = \frac{2}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} f(t)dt \tag{A.8}$$

$$a_n = \frac{2}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} f(t) \cos(nwt)dt \tag{A.9}$$

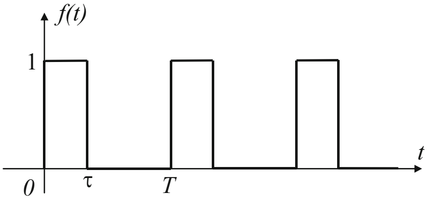


Fig. A.14 Example of periodic function used to illustrate the concept of Fourier series

$$b_n = \frac{2}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} f(t) \sin(nwt) dt \tag{A.10}$$

Such a sum of trigonometric functions is called the Fourier series of *f*(*t*), and the coefficients a_n and b_n are called its Fourier coefficients. The usefulness of such a mathematical expansion lies in its physical interpretation. Indeed, one can see that a periodic function of time can be decomposed into individual sine-like and cosine-like components, each periodic with a frequency *nw* where *n* is an integer. The magnitude of each component is given by the Fourier coefficients a_n and b_n. One can therefore obtain a "spectrum of frequencies" for the original function, which finds a number of applications in physics phenomena.

For example, the Fourier expansion of the function shown in Fig. A.14 is:

$$f(t) = \frac{\tau}{T} + \sum_{n=1}^{\infty} \frac{1}{n\pi} [\sin nw\tau \cos nwt + (1 - \cos nw\tau) \sin nwt] \tag{A.11}$$

Fourier Transformation

The Fourier transformation is a mathematical operation which consists of associating to a given function *f* a second function, called its Fourier transform *F*. The functions *f* and *F* do not operate on the same variables. The Fourier transform is similar to a Fourier series but can be applied to a general function *f*(*t*) as long as it is pulse-like and $\int_{-\infty}^{\infty} |f(t)| dt < \infty$. Its Fourier transform *F* is then defined by:

$$F(w) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-iwt} dt \tag{A.12}$$

Note that the Fourier transform *F* operates on frequencies *w*, whereas the original function *f* operates on time *t*. The Fourier transform plays the same role as the Fourier coefficients in Eq. (A.12), except that the summations on frequencies are now continuous rather than discrete. The original function *f* can be expressed in terms of its Fourier transform *F* through:

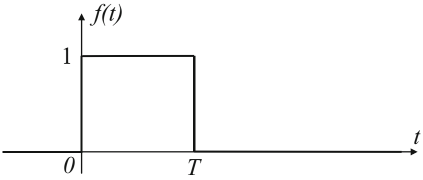


Fig. A.15 Example of an arbitrarily chosen function used to illustrate the concept of Fourier transform

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(w) e^{iwt} dw \tag{A.13}$$

For example, the Fourier transform of the function shown in Fig. A.15 is:

$$F(w) = \frac{1 - e^{-iwT}}{iw\sqrt{2\pi}} \tag{A.14}$$

A.7 The Pseudopotential Approach

When we want to calculate the band structure of a solid from first principles and write down the exact Hamiltonian of the system, we are confronted with a very difficult problem because not only do we have the Coulomb potential of the nuclear charges, but we also have the electron-electron interaction of the other electrons in the system to deal with. The way to avoid it is to make some simplifications, which keep the essence of the problem and make the solution tractable. We use the insight that we have and argue that, surely, it is possible to assume that the strongly bound full shells around the atom are not participating in the banding of the solid and they can be separated out, i.e., excluded from the banding electrons. The valence electrons can be treated separately and do not see the full potential of the nucleus. We know already from Chap. 4 that the outer shell electrons see a screened potential because the core electrons screen out the full nuclear attraction. But this is not all, we do not want to just take into account the screening, which is a many body effect, but go further and not allow the valence states to be mixed in the core states at all. So there are two effects to be considered. One is the screening, which can be considered to give rise to an effective nuclear charge and can be treated using the self-consistent "Hartree-Fock method". The other is projecting out the core eigenstates out of the solutions altogether. The latter is the pseudopotential method. In the pseudopotential method, one first decides which core states must be projected out. One does this by making the sought after Bloch wavefunctions orthogonal to these core states. Then one derives the effective potential for which these new Bloch states are the eigenfunction solution of the Schrödinger equation.

This procedure then makes the envelope wavefunction of the Bloch wave $u_{\vec{k}}$ in:

$$\Psi_{\vec{k}}\left(\vec{r}\right) = u_{\vec{k}}\left(\vec{r}\right)e^{i\vec{k}.\vec{r}} \tag{A.15}$$

a much more smooth function than it would be if it were subject to the full or even screened Coulomb potential of the lattice ions. How do we find an approximation for this effective potential? In a naïve way, we have done this already in the Kronig-Penney model in Chap. 5. The Kronig-Penney model is indeed a truncated pseudopotential approximation to the true potential, but it is constructed in an ad hoc manner, without a well-defined prescription. The pseudopotentials used to calculate the band structure of solids are however derived using well-defined prescriptions.

One of the assumptions is that the basis states of all the electrons in the solid are constituted by core electron wavefunctions ϕ_j and valence electron wavefunctions χ_k and that these can be made orthogonal to each other. One then constructs the eigenstates of interest, namely, for the higher valence energy level states. These are built to avoid the core regions occupied by the core electrons. An example is as follows. Assuming $b_{n\vec{k}} = \sum_{\vec{s}} e^{i\vec{k}.s} b_n\left(\vec{r} - \vec{s}\right)$ is a core function solution of the Schrödinger equation with energy E_n, we construct a more extended valence state which is made orthogonal to the core states and is of the form:

$$\Psi_{\vec{k}} = \sum_{\vec{g}} \alpha_{\vec{k}-\vec{g}}\chi_{\vec{k}-\vec{g}} \tag{A.16}$$

$$\chi_{\vec{k}} = e^{i\vec{k}.\vec{r}} - \sum_j a_j b_{j\vec{k}} \tag{A.17}$$

The a_j are selected to make the valence wavefunctions orthogonal to the core states. This new wavefunction has the core states projected out of it and is forced to also satisfy the Schrödinger equation. The projected states however introduce a new term in the SE which plays the role of a potential. The new term due to the core states, when combined with the old, gives us now an effective potential, which repels the valence electrons out of the core region, making the effective potential much more smooth than the original one. The pseudopotential method is a way of projecting out the core functions, out of what would normally be the total wavefunction, so that the more loosely bound valence functions avoid the region, which is normally filled by the core states. They do not see the strong Coulomb field anymore because they are forced to adopt a higher orbital or what is in effect a more loosely bound character near the core.

The two methods, Hartree-Fock self-consistent field or "HFT" method, which takes care of the potential of the other electrons and the Pauli principle, and the pseudopotential method, which forces the higher levels to avoid being core-like, can in principle be combined to produce an accurate band structure calculation. The HFT method assumes that the Coulomb potential of the other electrons can be treated as an average potential, which can be evaluated self-consistently. It also assumes that the many particle wavefunctions are Slater determinants of Bloch functions so that they automatically satisfy the Pauli principle. The details of the "Pseudopotential and HFT" are beyond the scope of this book, and the reader is referred to the specialized works in the books by Ziman (1998), Callaway (1964), and Harrison (1966).

Further Reading

Callaway J (1964) Energy Band Theory. Academic Press, New York

Chuang SL (1995) Physics of Optoelectronic Devices. Wiley, New York

Harrison WA (1966) Pseudopotentials in the Theory of Metals. W.A. Benjamin, New York

Ziman JM (1998) Principles of the Theory of Solids. Cambridge University Press, Cambridge

A.8 The Monte-Carlo Method

Scattering in a Crystal

Electrons in a crystal with a given band structure can be considered as a collection of free particles. In the six-dimensional phase space of momentum $\vec{k}$ and space $\vec{r}$, we can represent each electron by a point of coordinates $(\vec{r}, \vec{k})$. As we have seen in Sect. 5.2.6, the motion of the electron is described by:

$$\hbar \frac{d\vec{k}}{dt} = q\left(\vec{E} + \vec{v} \times \vec{B}\right) \tag{A.18}$$

where $\vec{k}$ is the wavevector of the electron, q the electric charge, $\vec{E}$ the electric field, $\vec{v}$ the velocity, and $\vec{B}$ the magnetic field. In this appendix, we are going to study only the action of an electric field on the electron, so we put $\vec{B} = \vec{0}$. Under these conditions, the electrons start their journey by following a ballistic trajectory (they are freely accelerated). However, this motion is interrupted by collisions with atoms, impurities, etc., which we will consider as scattering events. As a result, the movement of the particles is far more complex, and it is useful to describe the motion of the electrons by a distribution function $f(\vec{k}, \vec{r}, t)$, which is the average occupancy of a point in the above phase space.

The time evolution of this function is described by the Boltzmann equation:

$$\frac{\partial f}{\partial t}+\vec{v}\cdot\vec{\nabla}_{\vec{r}}f+\frac{d\vec{k}}{dt}\cdot\vec{\nabla}_{\vec{k}}f=\left(\frac{\partial f}{\partial t}\right)_{coll} \tag{A.19}$$

where, together with Eq. (A.18), the LHS describes all the ways the function evolves in phase space when subject to an electric and magnetic field.

If $\left(\frac{\partial f}{\partial t}\right)_{coll}dt$ describes the variation of the distribution during dt due to the collisions, the global variation can be written:

$$f\left(\vec{r}+d\vec{r},\vec{k}+d\vec{k},t+dt\right)=f\left(\vec{r},\vec{k},t\right)+\left(\frac{\partial f}{\partial t}\right)_{coll}dt \tag{A.20}$$

to first order:

$$f\left(\vec{r},\vec{k},t\right)+\frac{\partial f}{\partial t}dt+\vec{\nabla}_{\vec{r}}f\cdot d\vec{r}+\vec{\nabla}_{\vec{k}}f\cdot d\vec{k}=f\left(\vec{r},\vec{k},t\right)+\left(\frac{\partial f}{\partial t}\right)_{coll}dt \tag{A.21}$$

$$\frac{\partial f}{\partial t}+\vec{\nabla}_{\vec{r}}f\cdot\frac{d\vec{r}}{dt}+\vec{\nabla}_{\vec{k}}f\cdot\frac{d\vec{k}}{dt}=\left(\frac{\partial f}{\partial t}\right)_{coll} \tag{A.22}$$

Using $\vec{F}=\hbar\frac{d\vec{k}}{dt}=q\left(\vec{E}+\vec{v}\times\vec{B}\right)$, we get:

$$\frac{\partial f}{\partial t}+\vec{\nabla}_{\vec{r}}f\cdot\vec{v}+\vec{\nabla}_{\vec{k}}f\cdot\frac{\vec{F}}{\hbar}=\left(\frac{\partial f}{\partial t}\right)_{coll} \tag{A.23}$$

This equation states that the changes of the distribution function with time (represented by the first term on the LHS of this equation) are determined by the flow of electrons in real space (the second term in the LHS of the equation) and by the flow of electrons in $\vec{k}$-space (the last term in the LHS of the equation) and the collisions (right-hand side of the equation). The right-hand side describes the effects of the many different types of scattering mechanisms, which are active, including optical phonon scattering, acoustic scattering, impurity scattering, etc., so that it is often very difficult to solve for $f\left(\vec{k},\vec{r},t\right)$ analytically. However, given the scattering rates, a numerical solution or simulation of this equation, which is called the Monte-Carlo simulation, is always possible. This so-called Monte-Carlo method is a powerful tool and is becoming more and more popular.

Monte-Carlo Simulation

The idea of this method, introduced in the 1960s (see Shur 1990), is to simulate the motion of the particle in $\vec{k}$-space while keeping track of it in real space. In this model,

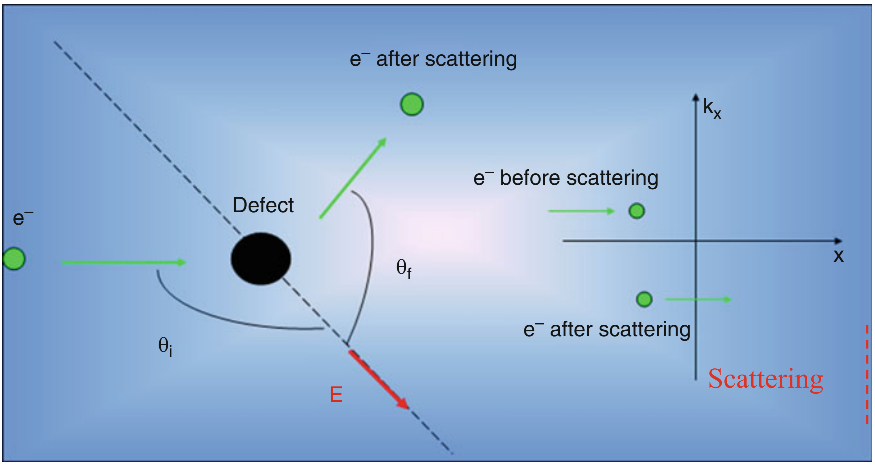


Fig. A.16 On the left, sketch of the scattering of an electron by an impurity. On the right, illustration of the disappearance and the appearance of the electron in the phase space

we consider that the motion of the electron is well described by Eq. (A.18) between two scattering events. But this free flight is interrupted by scattering processes that occur with a rate λ_i (i stands for the scattering process that we are considering). These processes are instantaneous events and change only the wavevector of the electron. They can be visualized as the particle disappearing and reappearing instantaneously at a different point of phase space (see Fig. A.16). If we observe a single electron for a sufficiently long time, the distribution of the times that the electron spends in the vicinity of different points in $\vec{k}$-space will reproduce the shape of $f(\vec{k}, \vec{r}, t)$.

The Monte-Carlo simulation can be divided into three different parts. First, we generate randomly with a computer the time remaining before the next scattering event. Then, between the two scattering events, we determine the motion of the electron using Eq. (A.22). Finally, we generate randomly the new direction of the wavevector.

- For the purpose of this simulation, we introduce a scattering rate $\Gamma = \sum_{i=1}^{n} \lambda_i(\vec{k}) + \lambda_0$ where we have introduced an artificial scattering mechanism, with a rate λ_0, so that Γ is a constant (finite). This self-scattering process interrupts the motion but does not change the momentum in any way. It can be described by the probability $W_0(\vec{k}, \vec{k}') = \lambda_\circ(\vec{k})\delta(\vec{k} - \vec{k}')$. This rate is simply a mathematical tool used to make the global rate of the scattering events constant. In order not to change the rate too much, we choose λ_0 as small as possible. Thus, the probability of a scattering event between t and $t + dt$ can be described by $P(t)dt = e^{-\Gamma t}dt$. We use this distribution of probabilities to generate random times t_s between one collision and the following one ($t_s = -1/\Gamma \ \ln(1 - r)$, with r a random number between 0 and 1, follows this distribution).

- During these times t_s, the motion of the electron is well described by Eq. (A.18) with $\vec{B} = \vec{0}$ so that $\vec{k}(t) = \vec{k}_0 + \frac{q\vec{E}}{\hbar}t$, where $\vec{k}_0$ is the wavevector just after the previous collision, and $\vec{r}(t) - \vec{r}_0 = \int_{t_0}^{t} \vec{v}_g(t')dt' = \int_{t_0}^{t} \frac{1}{\hbar} \nabla_{\vec{k}} E dt'$, where $\vec{r}_0$ is the position of the particle in real space after the previous collision.
- The next step is to generate randomly the wavevector after each scattering event. But, before that, we need to determine which mechanism is responsible for the scattering. In order to find out which law we have to apply to generate the new wavevector, we assume that the probability of occurrence of one given process is proportional to its rate. To choose a mechanism, we generate randomly a number A, distributed with equal probability between 0 and Γ, and we test the inequality $\sum_{i=0}^{m} \lambda_i\left(\vec{k}\right) > A$. The first value of m satisfying this inequality is the scattering process we are going to use. We use the distribution function of probabilities of this mechanism to generate randomly the wavevector after the scattering event.

We repeat these three steps as long as we need to get a good approximation of $f\left(\vec{k}, \vec{r}, t\right)$. A criterion to stop our stimulation is to repeat the scenario until the differences in the drift velocity, for example, converge to a small enough number.

Thanks to this procedure, we are able to simulate the movement of the electron in the crystal. Then, we represent in a histogram the time that the electron spent in each cell of the phase space. It has been demonstrated that this histogram is proportional to the distribution function $f\left(\vec{k}, \vec{r}, t\right)$ when t tends to infinity.

Applications

The Monte-Carlo simulation is a useful tool to calculate quantities like the time spent in the valleys of a semiconductor or the diffusion coefficients of a material. It shows a good agreement with experiment as you can see in Fig. A.17. It can also be used to investigate the electron transport in small semiconductor devices. But this method only allows us to study a relatively small number of free electrons in the semiconductor: Typically 1 million electrons. The idea is that, for example, 1 million is enough to reproduce the behavior of all the particles. An example of a real space trajectory is shown in Fig. A.18.

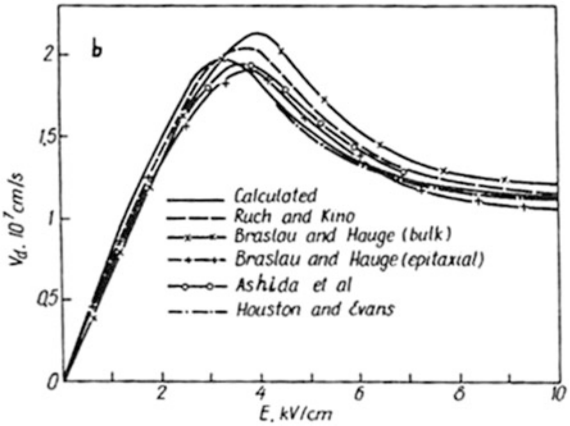


Fig. A.17 Measured and calculated drift velocity (Reprinted from Solid State Electronics Vol. 23, Pozhela, J., & Reklaitis, A., "Electron transport properties in GaAs at high electric fields," Fig. 7, p. 931, Copyright 2005, with permission from Elsevier)

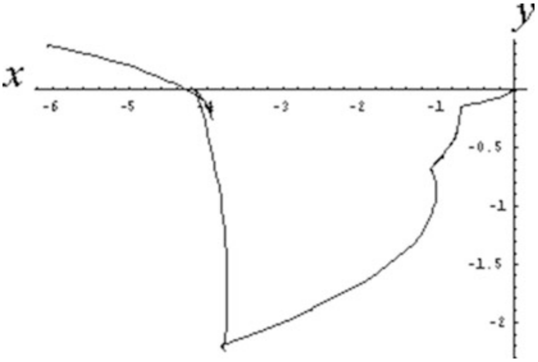


Fig. A.18 Simulation of the motion of an electron under an electric field E in the x-direction (ten collisions are simulated). The motion of the electron starts at the origin and evolves randomly. This figure represents the trajectory of the electron in real space

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Shur M (1990) Physics of Semiconductor Devices. Prentice-Hall, Englewoods Cliff

A.9 The Thermionic Emission

The thermionic emission theory is a semiclassical approach developed by Bethe (1942), which accurately describes the transport of electrons through a semiconductor-metal junction. The parameters taken into account are the temperature T, the energy barrier height $q\Phi_B$, and the bias voltage V between the far ends of the semiconductor and the metal. These quantities are illustrated in Fig. A.19.

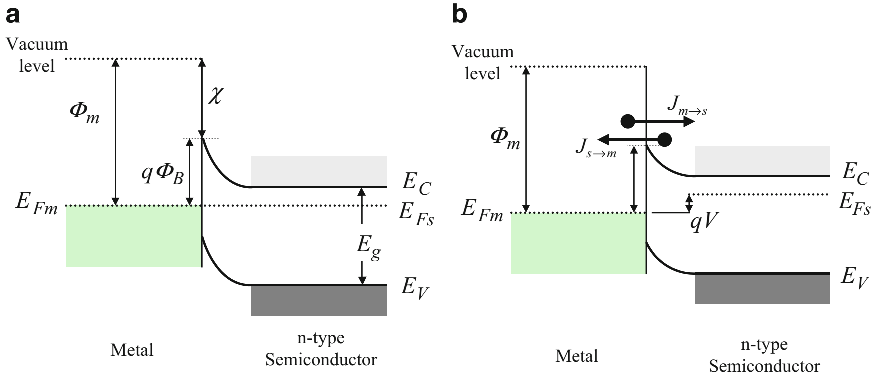

Fig. A.19 Energy band diagram of a Schottky metal-(n-type) semiconductor junction: (**a**) At equilibrium and (**b**) under forward bias ($V > 0$), showing the transport of electrons over the potential barrier as the main transport process under forward bias

The theory is based on the following three assumptions: (i) The energy barrier height $q\Phi_B$ at the interface is much higher than k_bT, (ii) the junction plane is at thermal equilibrium, and (iii) this equilibrium is not affected by the presence of an electrical current. By assuming these, the thermionic emission current only depends on the energy barrier height and not its spatial profile. Furthermore, the total current is therefore the sum of the current from the semiconductor into the metal, denoted $J_{s\to m}$, and that of the metal into the semiconductor, denoted $J_{m\to s}$.

To calculate the first current, $J_{s\to m}$, the theory assumes that the energy of the electrons in the conduction band is purely kinetic and that their velocity is distributed isotropically. The current density from the semiconductor into the metal can be calculated by summing the current contribution from all the electrons that have an energy higher than the barrier $q\Phi_B$ and that have a velocity component from the semiconductor toward the metal. This results in the following expression:

$$J_{s\to m} = \left(\frac{4\pi q m^* k_b^2}{h^3}\right) T^2 e^{-\frac{q\Phi_B}{k_b T}} e^{\frac{qV}{k_b T}} \tag{A.24}$$

or:

$$J_{s\to m} = A^* T^2 e^{-\frac{q\Phi_B}{k_b T}} e^{\frac{qV}{k_b T}} \tag{A.25}$$

where k_b is the Boltzmann constant, V is the bias voltage, Φ_B is the barrier height, T is the temperature in degrees Kelvin, h is Planck's constant, and m^* is the electron effective mass in the direction perpendicular to the junction plane, and $A^* = 4\pi q m^* k_b^2/h^3$ is called the effective Richardson constant for thermionic emission. This quantity can be related to the Richardson constant for free electrons, $A = 120\ \mathrm{A{\cdot}cm^{-2}{\cdot}K^{-2}}$, as discussed below.

Table A.1 Examples of values for A^*/A in a few semiconductors (Sze 1981)

Semiconductor	Si	Ge	GaAs
n-type <111>	2.2	1.11	0.068 (low field) 1.2 (high field)
n-type <100>	2.1	1.19	0.068 (low field) 1.2 (high field)
p-type	0.66	0.34	0.62

For n-type semiconductors with an isotropic electron effective mass m^* in the minimum of the conduction band, we have $A^*/A = m^*/m_0$, where m_0 is the electron rest mass.

For n-type semiconductors with a multiple-valley conduction band, the effective Richardson constant A^* associated with each local energy minimum is given by $A^*/A = \left(l_x^2 m_y^* m_z^* + l_y^2 m_z^* m_x^* + l_z^2 m_x^* m_y^*\right)^{1/2}/m_0$, where l_x, l_y, and l_z are the direction cosines corresponding to this energy minimum in the first Brillouin zone.

In the case of a p-type semiconductor, we need to consider the heavy-hole and the light-hole bands in the valence band, both of which have their maximum at the center of the Brillouin zone. The effective Richardson constant is then given by the following expression $A^*/A = \left(m_{lh}^* + m_{hh}^*\right)/m_0$, where m_{hh}^* and m_{lh}^* are the heavy-hole and light-hole effective masses, respectively. A few examples of values for A^*/A are given in Table A.1.

The second current contribution to the thermionic emission current is the current flowing from the metal into the semiconductor, $J_{m \to s}$. As the barrier height for the transport of electrons in this direction is independent of the applied bias voltage V (Fig. A.19b), $J_{m \to s}$ is also independent of the bias voltage. $J_{m \to s}$ is therefore equal to the opposite of $J_{s \to m}$ when $V = 0$, because no net current exists at equilibrium. Using Eq. (A.25), we obtain:

$$J_{m \to s} = -A^* T^2 e^{-\frac{q\Phi_B}{k_b T}} \tag{A.26}$$

The total current density is therefore:

$$\begin{aligned} J &= J_{s \to m} + J_{m \to s} = A^* T^2 e^{-\frac{q\Phi_B}{k_b T}} \left[e^{\frac{qV}{k_b T}} - 1\right] \\ &= J_{ST}\left[e^{\frac{qV}{k_b T}} - 1\right] \end{aligned} \tag{A.27}$$

This expression shows that the thermionic emission current resembles the diode equation obtained in Eq. 9.52. The difference lies in the saturation current density which is now given by:

$$J_{ST} = A^* T^2 e^{-\frac{q\Phi_B}{k_b T}} \tag{A.28}$$

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A.10 Physical Properties and Safety Information of Metalorganics

Table A.2 and Table A.3 summarize some of the basic thermodynamic properties of metalorganic sources commonly used in MOCVD, including their chemical formula and abbreviation, boiling point, melting point, and the expression of their vapor pressure as a function of temperature.

Additional information on their other important physical properties is also provided for a number of important metalorganic sources, including diethylzinc (Table A.4), trimethylindium (Table A.5), triethylindium(Table A.6), trimethylgallium (Table A.7), and triethylgallium (Table A.8).

In the rest of this Appendix, general information about the safety of metalorganic compounds will be given. This will be helpful in developing safety and health procedures during their handling.

Chemical Reactivity

Metalorganics catch fire if exposed to air, react violently with water and any compound containing active hydrogen, and may react vigorously with compounds containing oxygen or organic halide.

Stability

Metalorganics are stable when stored under a dry, inert atmosphere and away from heat.

Fire Hazard

Metalorganics are spontaneously flammable in air, and the products of combustion may be toxic. Metalorganics are pyrophoric by the paper char test used to gauge pyrophoricity for transportation classification purposes (Mudry 1975).

Firefighting Technique

Protect against fire by strict adherence to safe operating procedures and proper equipment design. In case of fire, immediate action should be taken to confine it. All lines and equipment which could contribute to the fire should be shut off. As in any fire, prevent human exposure to fire, smoke, or products of combustion. Evacuate nonessential personnel from the fire area.

The most effective fire extinguishing agent is dry chemical powder pressurized with nitrogen. Sand, vermiculite, or carbon dioxide may be used. *Caution:*

Table A.2 Physical properties of some organometallics used in MOCVD (Ludowise 1985 and http://electronicmaterials.rohmhaas.com)

Compound	Formula	Abbreviation	Melting point (°C)	Boiling point (°C)	Log$_{10}$ P(mmHg) (T in K)	Temperature range (°C)
Group II sources						
Dimethylberyllium	$(CH_3)_2Be$	DMBe				
Diethylberyllium	$(C_2H_5)_2Be$	DEBe	12	194	7.59–2200/T	
Bis-cyclopentadienyl magnesium	$(C_5H_5)_2Mg$	Cp_2Mg	176		25.14–2.18 ln T–4198/T	
Group IIB sources						
Dimethylzinc	$(CH_3)_2Zn$	DMZn	−42	46	7.802–1560/T	
Diethylzinc	$(C_2H_5)_2Zn$	DEZn	−28	118	8.280–2190/T	
Dimethylcadmium	$(CH_3)_2Cd$	DMCd	−4.5	105.5	7.764–1850/T	
Group III sources						
Trimethylaluminum	$(CH_3)_3Al$	TMAl	15.4	126	7.3147–1534.1/(T-53)	17–100
Triethylaluminum	$(C_2H_5)_3Al$	TEAl	−58	194	10.784–3625/T	110–140
Trimethylgallium	$(CH_3)_3Ga$	TMGa	−15.8	55.7	8.07–1703/T	
Triethylgallium	$(C_2H_5)_3Ga$	TEGa	−823	143	8.224–2222/T	50–80
Ethyldimethylindium	$(CH_3)_2(C_2H_5)In$	EDMIn	5.5			10–38
Trimethylindium	$(CH_3)_3In$	TMIn	88.4	133.8	10.520–3014/T	
Triethylindium	$(C_2H_5)_3In$	TEIn	−32	184	1.2	44
					3	53
					12	83

Table A.3 Physical properties of some organometallics used in MOCVD (Ludowise 1985 and http://electronicmaterials.rohmhaas.com)

Compound	Formula	Abbreviation	Melting point (°C)	Boiling point (°C)	Log_{10} P(mmHg) (T in K)	Temperature range (°C)
Group IV sources						
Tetramethylgermanium	$(CH_3)_4Ge$	TMGe	−88	43.6	139	0
Tetramethyltin	$(CH_3)_4Sn$	TMSn	−53	78	7.495–1620/*T*	
Tetraethyltin	$(C_2H_5)_4Ge$	TESn	−112	181		
Group V sources						
Diethylarsine hydride	$(C_2H_5)_2AsH$	DEAs			7.339–1680/*T*	
Tertiarybutylarsine	$(C_4H_9)AsH_2$	TBAs			7.5–1562.3/*T*	
Tertiarybutylphosphine	$(C_4H_9)PH_2$	TBP			7.586–1539/*T*	
Trimethylphosphorus	$(CH_3)_3P$	IMP	−85	37.8	7.7329–1512/*T*	
Triethylphosphorus	$(C_2H_5)_3P$	TEP	−88	127	7.86–2000/*T*	18–78.2
Trimethylarsenic	$(CH_3)_3As$	TMAs	−87.3	50–52	7.7119–1563/*T*	
Triethylarsenic	$(C_2H_5)_3As$	TEAs	−91	140	15.5	37
Trimethylantimony	$(CH_3)_3Sb$	TMSb	−86.7	80.6	7.7280–1709/*T*	
Triethylantimony	$(C_2H_5)_3Sb$	TESb	−98	116	17	75
Group VI sources						
Diethylselenide	$(C_2H_5)_2Se$	DESe	–	108		
Dimethyltellurium	$(CH_3)_2Te$	DMTe	10	82	7.97–1865/*T*	
Diethyltellurium	$(C_2H_6)_2Te$	DETe	–	137–138	7.99–2093/*T*	

Table A.4 Chemical properties of diethylzinc (Razeghi 1989)

Acronym	DEZn
Formula	$(C_2H_5)_2Zn$
Formula weight	123.49
Metallic purity	99.9999 wt% (min) zinc
Appearance	Clear, colorless liquid
Density	$1.198\ g{\cdot}ml^{-1}$ at 30 °C
Melting point	-30 °C
Vapor pressure	3.6 mmHg at 0 °C 16 mmHg at 25 °C 760 mmHg at 117.6 °C
Behavior toward organic solvents	Completely miscible, without reaction, with aromatic and saturated aliphatic and alicyclic hydrocarbons. Forms relatively unstable complexes with simple ethers, thioethers, phosphines, and arsines but more stable complexes with tertiary amines and cyclic ethers
Stability in air	Ignites on exposure (pyrophoric)
Stability in water	Reacts violently, evolving gaseous hydrocarbons, carbon dioxide, and water
Storage stability	Stable indefinitely at ambient temperatures when stored in an inert atmosphere

Table A.5 Chemical properties of trimethylindium (Razeghi 1989)

Acronym	TMIn
Formula	$(CH_3)_3In$
Formula weight	159.85
Metallic purity	99.999 wt% (min) indium
Appearance	White, crystalline solid
Density	$1.586\ g{\cdot}ml^{-1}$ at 19 °C
Melting point	89 °C
Boiling point	135.8 °C at 760 mmHg 67 °C at 12 mmHg
Vapor pressure	15 mmHg at 41.7 °C
Stability in air	Pyrophoric, ignites spontaneously in air
Solubility	Completely miscible with most common solvents
Storage stability	Stable indefinitely when stored in an inert atmosphere

Re-ignition may occur. *Do not use water, foam, carbon tetrachloride, or chlorobromomethane* extinguishing agents, as these materials react violently and/or liberate toxic fumes on contact with metalorganics.

When there is a potential for exposure to smoke, fumes, or products of combustion, firefighters should wear full-face positive-pressure self-contained breathing apparatus or a positive-pressure supplied-air respirator with escape pack and impervious clothing including gloves, hoods, aluminized suits, and rubber boots.

Table A.6 Chemical properties of triethylindium (Razeghi 1989)

Acronym	TEIn
Formula	$(C_2H_5)_3In$
Formula weight	202.01
Metallic purity	99.9999 wt% (min) indium
Appearance	Clear, colorless liquid
Density	1.260 g·ml^{-1} at 20 °C
Melting point	−32 °C
Vapor pressure	1.18 mmHg at 40 °C 4.05 mmHg at 60 °C 12.0 mmHg at 80 °C
Behavior toward organic solvents	Completely miscible, without reaction, with aromatic and saturated aliphatic and alicyclic hydrocarbons. Forms complexes with ethers, thioethers, tertiary amines, phosphines, arsines, and other Lewis bases
Stability in air	Ignites on exposure (pyrophoric)
Stability in water	Partially hydrolyzed, loses one ethyl group with cold water
Storage stability	Stable indefinitely at ambient temperatures when stored in an inert atmosphere

Table A.7 Chemical properties of trimethylgallium (Razeghi 1989)

Acronym	TMGa
Formula	$(CH_3)_3In$
Formula weight	114.82
Metallic purity	99.9999 wt% (min) gallium
Appearance	Clear, colorless liquid
Density	1.151 g·ml^{-1} at 15 °C
Melting point	−15.8 °C
Vapor pressure	64.5 mmHg at 0 °C 226.5 mmHg at 25 °C 760 mmHg at 55.8 °C
Behavior toward organic solvents	Completely miscible, without reaction, with aromatic and saturated aliphatic and alicyclic hydrocarbons. Forms complexes with ethers, thioethers, tertiary amines, tertiary phosphines, tertiary arsines, and other Lewis bases
Stability in air	Ignites on exposure (pyrophoric)
Stability in water	Reacts violently, forming methane and Me_2GaOH or $[(Me_2Ga)_2O]_x$
Storage stability	Stable indefinitely at ambient temperatures when stored in an inert atmosphere

Human Health

Metalorganics cause severe burns and should not get in the eyes and on the skin or clothing.

Ingestion and inhalation. Because of the highly reactive nature of metalorganics with air and moisture, ingestion is unlikely.

Skin and eye contact. Metalorganics react immediately with moisture on the skin or in the eye to produce severe thermal and chemical burns.

Table A.8 Chemical properties of triethylgallium (Razeghi 1989)

Acronym	TEGa
Formula	$(C_2H_5)_3Ga$
Formula weight	156.91
Metallic purity	99.9999 wt% (min) gallium
Appearance	Clear, colorless liquid
Density	$1.0586\ g{\cdot}ml^{-1}$ at 20 °C
Melting point	−82.3 °C
Vapor pressure	16 mmHg at 43 °C 62 mmHg at 72 °C 760 mmHg at 143 °C
Behavior toward organic solvents	Completely miscible, without reaction, with aromatic and saturated aliphatic and alicyclic hydrocarbons. Forms complexes with ethers, thioethers, tertiary amines, tertiary phosphines, tertiary arsines, and other Lewis bases
Stability in air	Ignites on exposure (pyrophoric)
Stability in water	Reacts vigorously, forming ethane and Et_2GaOH or $[(Et_2Ga)_2O]_x$
Storage stability	Stable indefinitely at room temperatures in an inert atmosphere

First Aid

If contact with metalorganics occurs, immediately initiate the recommended procedures below. Simultaneously contact a poison center, a physician, or the nearest hospital. Inform the person contacted of the type and extent of exposure, describe the victim's symptoms, and follow the advice given.

Ingestion. Should metalorganics be swallowed, immediately give several glasses of water but do not induce vomiting. If vomiting does occur, give fluids again. Have a physician determine if condition of patient will permit induction of vomiting or evacuation of the stomach. Do not give anything by the mouth to an unconscious or convulsing person.

Skin contact. Under a safety shower, immediately flush all affected areas with large amounts of running water for at least 15 min. Remove contaminated clothing and shoes. Do not attempt to neutralize with chemical agents. Get medical attention immediately. Wash clothing before reuse.

Eye contact. Immediately flush the eyes with large quantities of running water for a minimum of 15 min. Hold the eyelids apart during the flushing to ensure rinsing of the entire surface of the eyes and lids with water. Do not attempt to neutralize with chemical agents. Obtain medical attention as soon as possible. Oils or ointments should not be used at this time. Continue the flushing for an additional 15 min if a physician is not immediately available.

Inhalation. Exposure to combustion products of this material may cause respiratory irritation or difficulty with breathing. If inhaled, remove to fresh air. If not breathing, clear the victim's airway and start mouth-to-mouth artificial respiration which may be supplemented by the use of a bag-mask respirator or manually triggered oxygen supply capable of delivering 1 liter per second or more. If the victim is breathing, oxygen may be delivered from a demand-type or continuous-flow inhaler, preferably with a physician's advice. Get medical attention immediately.

Industrial Hygiene

Ingestion. As a matter of good industrial hygiene practice, food should be kept in a separate area away from the storage/use location. Smoking should be avoided in storage/use locations. Before eating, hands and face should be washed.

Skin contact. Skin contact must be prevented through the use of fire-retardant protective clothing during sampling or when disconnecting lines or opening connections. Recommended protection includes a full-face shield, impervious gloves, aluminized polyamide coat, hood, and rubber boots. Safety showers – with quick-opening valves which that stay open – should be readily available in all areas where the material is handled or stored. Water should be supplied through insulated and heat-traced lines to prevent freeze-ups in cold weather.

Eye contact. Eye contact with liquid or aerosol must be prevented through the use of a full-face shield selected with regard for use-condition exposure potential. Eyewash fountains, or other means of washing the eyes with a gentle flow of tap water, should be readily available in all areas where this material is handled or stored. Water should be supplied through insulated and heat-traced lines to prevent freeze-ups in cold weather.

Inhalation. Metalorganics should be used in a tightly closed system. Use in an open (e.g., outdoor) or well-ventilated area to minimize exposure to the products of combustion if a leak should occur. In the event of a leak, inhalation of fumes or reaction products must be prevented through the use of an approved organic vapor respirator with dust, mist, and fume filter. Where exposure potential necessitates a higher level of protection, use a positive-pressure, supplied-air respirator.

Spill Handling

Make sure all personnel involved in spill handling follow proper firefighting techniques and good industrial hygiene practices. Any person entering an area with either a significant spill or an unknown concentration of fumes or combustion products should wear a positive-pressure, supplied-air respirator with escape pack. Block off the source of spill, and extinguish fire with extinguishing agent. Re-ignition may occur. If the fire cannot be controlled with the extinguishing agent, keep a safe distance, protect adjacent property, and allow product to burn until consumed.

Corrosivity to Materials of Construction

This material is not corrosive to steel, aluminum, brass, nickel, or other common metals when blanketed with a dry inert gas. Some plastics and elastomers may be attacked.

Storage Requirements

Containers should be stored in a cool, dry, well-ventilated area. Store away from flammable materials and sources of heat and flame. Exercise due caution to prevent damage to or leakage from the container.

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