Fundamental processes: Atomic Physics

CERN Accelerator School: Ion Sources
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Outline and intro

- Electrons in an atom
- Electron configurations
- Periodic table of elements
- Ionization energies
- Negative ions – electron affinity
- Atomic processes in ion sources
- Ways to ionize atoms:
  - Hot surface
  - Particle impact
  - Photons

- Interest of atomic physics:
  - study of the atom as an isolated system of electrons and an atomic nucleus
  - Processes: atom ionization and excitation by photons or collisions with particles
- Atomic physics for ion sources:
  - Energy required for ionization
  - Efficiency of ionization

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Physical quantities and units

- Kinetic energy of charged particles is measured in *electron volts* (eV).
- 1 eV: energy acquired by singly charged particle moving through potential of 1 Volt.

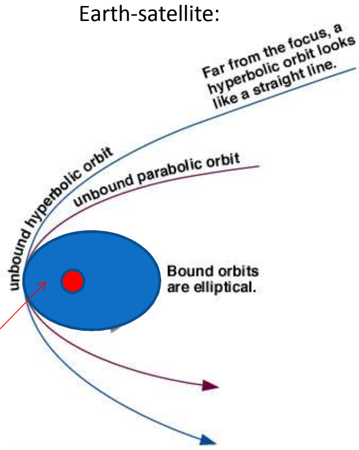
- 1 eV = e * (1 Volt) = 1.6022×10^{-19} J
- Mass of electron: m_e = 9.109×10^{-31} kg
- Mass of proton: m_p = 1.672×10^{-27} kg
- Atomic mass unit = 1/12 carbon-12 mass: 1 u = 1.6606×10^{-27} kg
- Elementary charge of particle is e = 1.6022×10^{-19} C (or A*s)

- Electron with 1 eV kinetic energy is moving with a velocity of about 594 km/s
- 1eV = thermal energy at 11 600 K

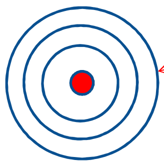
Electrons in an atom

- Analogy:
  - Satellite orbiting the Earth contains gravitational potential energy
  - Satellite can orbit the Earth at any height. Or, it can contain any amount of gravitation energy—its gravitational potential energy is continuous
- Similarly, electron orbiting nucleus possesses electric potential energy. But it can only stay in a finite number of discrete energy levels (or orbits)
- => **energy levels of atoms are 'quantized'**

Earth-satellite:



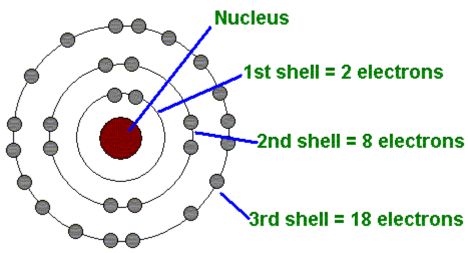
Nucleus-electrons



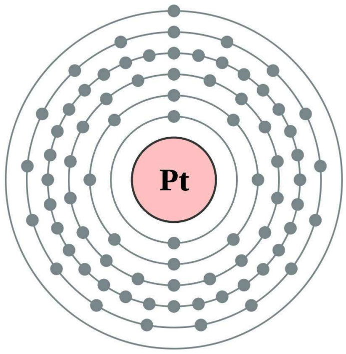
Allowed states

Electrons in an atom

- Electrons orbit the atomic nucleus on orbits of fixed energy
- Energy of each electron level/orbit shell is determined mostly by the attraction of the nucleus and to a smaller degree by the repulsion of other electrons
- **Factors influencing electron energy: nucleus, el-el interation, spin-orbit (energy scale:)**
- Quantum mechanics is behind the existence of shells and the number of electrons on each shell



78: Platinum **2,8,18,32,17,1**



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Atomic shell structure

Energy scale	Energy (eV)	Energy (cm^{-1})	Contributing effects
Gross structure	1 – 10	$10^4 - 10^5$	electron–nuclear attraction electron-electron repulsion electron kinetic energy
Fine structure	0.001 – 0.01	10 – 100	spin-orbit interaction relativistic corrections
Hyperfine structure	$10^{-6} - 10^{-5}$	0.01 – 0.1	nuclear interactions (hyperfine structure, isotope shift)

Spin-orbit interaction: interaction between electron’s spin and orbital angular momentum (i.e. magnetic field generated by the electron's orbit around nucleus)
Hyperfine structure: nuclear spin experiences magnetic field due to current loop of electron and dipolar interaction of the electronic and nuclear spins

Electron quantum numbers

- n Principal Quantum Number (QN)
  - Specifies shell (radial dependence)
- l Azimuthal QN
  - s, p, d, f, … correspond to $l = 0, 1, 2, 3, \ldots n\text{-}1$
  - Gives orbital angular momentum $L^2 = \hbar^2 l(l+1)$
- m_l Magnetic QN
  - Projection of azimuthal QN along an axis ($-l < m_l < l$)
  - Projected angular momentum is $L_z = m_l \hbar$
- m_s Spin projection QN
  - Electron spin = (-1/2, 1/2)
- j total orbital angular momentum
  - Spin-orbit coupling: $j = 1/2, 3/2 \ldots n{-}1/2$, total: $J^2 = \hbar^2 j(j+1)$
- m_j orbital angular momentum
  - $m_j = -j, -j+1 \ldots j$ and satisfies $m_j = m_l + m_s$

Quantum Numbers: describe the conserved quantities of the system: e.g. energy and angular momentum, spin

With spin-orbit interaction l, m, s no longer commute with Hamiltonian => change over time. Need new QN's

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Electron quantum numbers

- In an electronic configuration, electrons can't have the same quantum number
  - Pauli exclusion principle
  - Applying this can be a bit complicated at times
- Some states may be indistinguishable
  - Have degeneracy rather than new configuration
- Example: Configuration: $2p^2$ ($n = 2$ with 2p electrons)
  - Important since this represents the electronic configuration of many of the most abundant ions
  - Total Spin: $S = 0$ (Singlet) or 1 (Triplet)
  - Orbital Angular Momentum: $L = 0, 1, 2$
  - Thus J (= L + S) could range from 0 to 3

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Electron configuration

Quantum number	symbol	Value
principal	n	any integer > 0
orbital	l	integer up to $(n-1)$
magnetic	m_l	integer from $-l$ to $+l$
spin	m_s	$\pm 1/2$

$n = 1, 2, 3, ...$	$l = 0, 1, 2, ..., n-1$	$m = 0, \pm 1, \pm 2, ..., \pm l$	Orbital
1	0	0	$1s$
2	0	0	$2s$
2	1	0	$2p_z$
2	1	+	$2p_x$
2	1	-	$2p_y$

Orbital names: s, p, d, f, g, h ..:
sharp, principal, diffuse, fundamental, and then alphabetic

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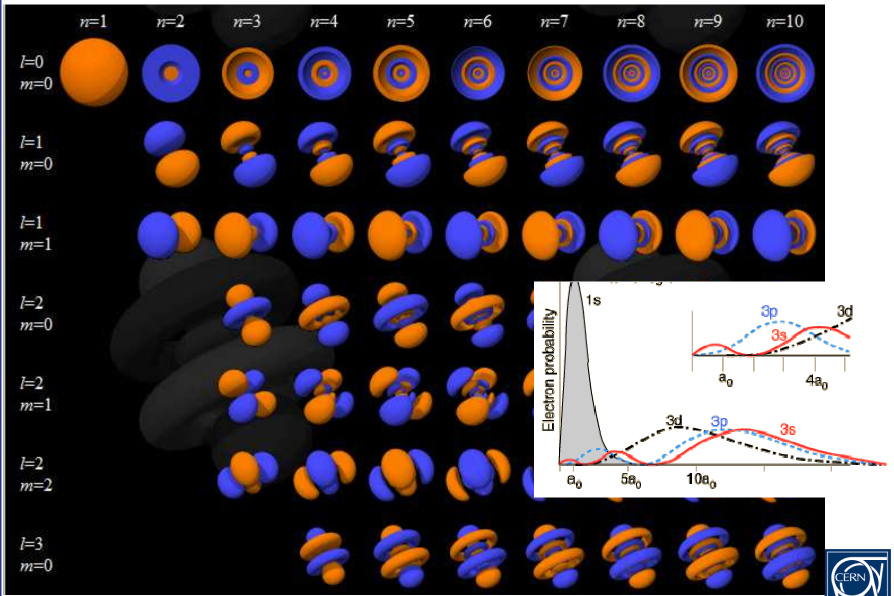
Electron orbitals



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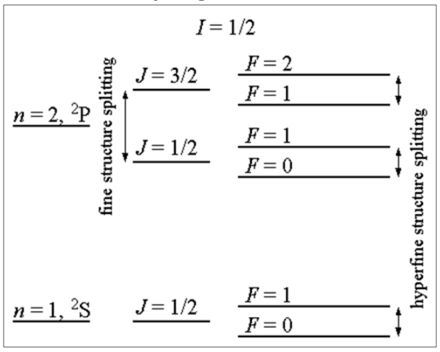
Electron terms

Hydrogen terms



F=|J-I| to J+I

Term symbols contain 3 pieces of information:

"Spin multiplicity" = 2*S*+1
(Where *S* is the total spin quantum number for the atom)

$^2P_{3/2}$

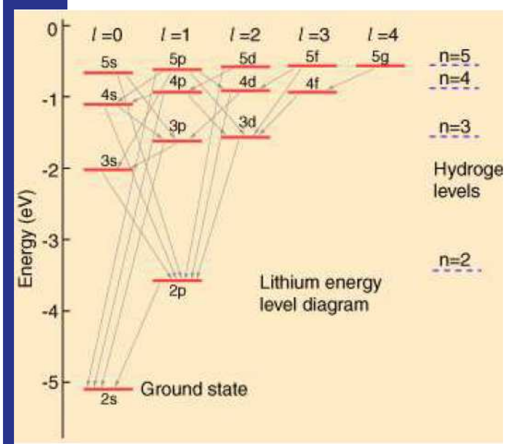
Gives *L*, the total orbital angular momentum quantum number for the atom:

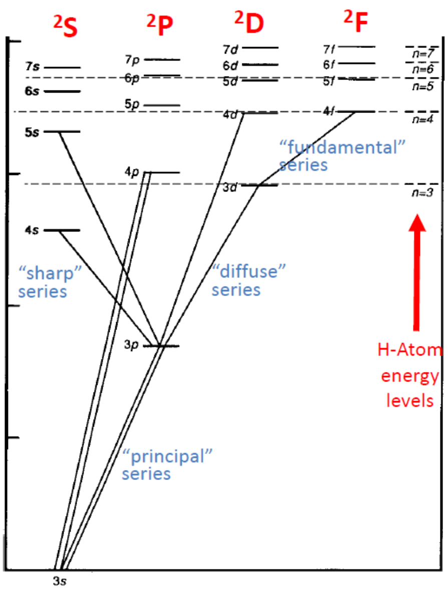
- S: *L = 0*
- P: *L = 1*
- D: *L = 2*
- F: *L = 3, etc.*

J, the total angular momentum quantum number for the atom. *i.e.*, how *L* and *S* are coupled

Electron configuration

- Examples:





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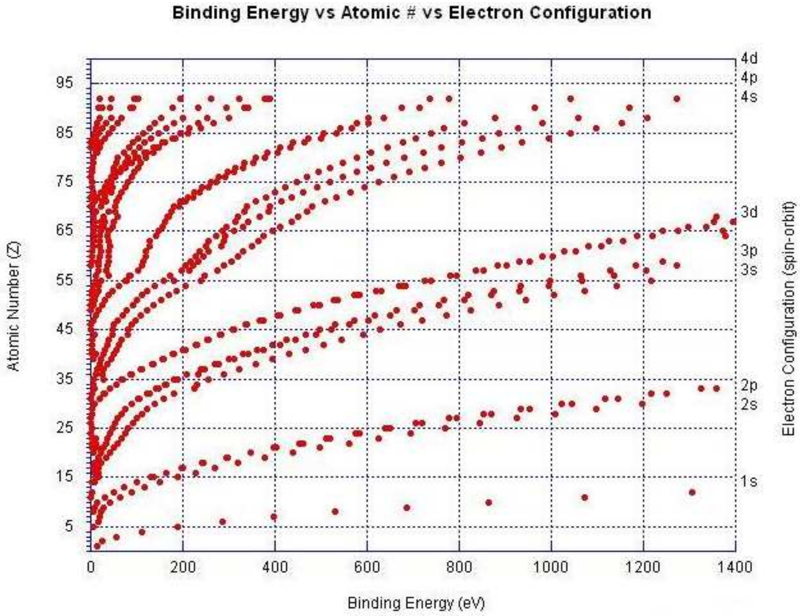
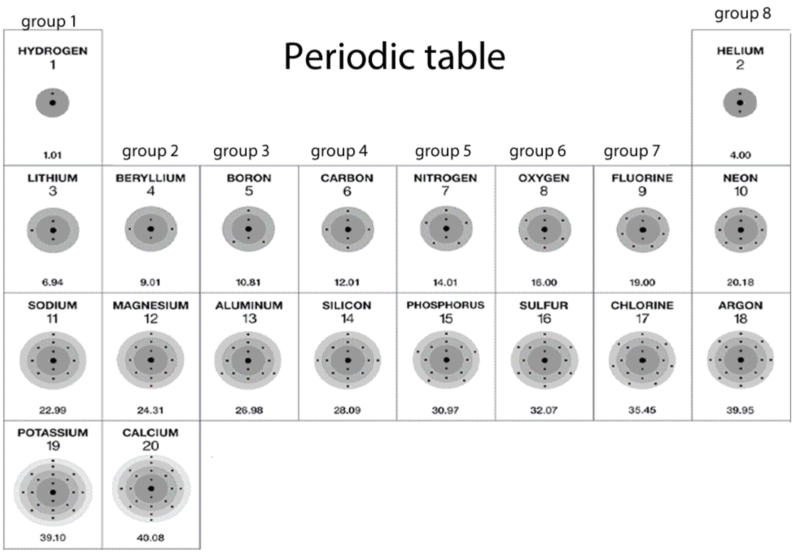
Electron binding energies

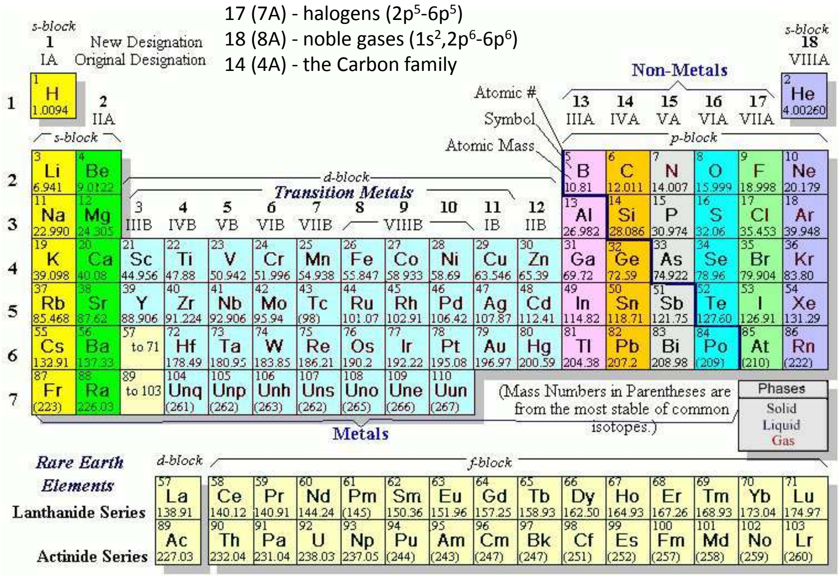


Periodic table of elements



Periodic table of elements

1 (1A) - alkali metals ($1s^1$-$7s^1$)
2 (2A) - alkaline earth metals ($1s^2$-$7s^2$)
17 (7A) - halogens ($2p^5$-$6p^5$)
18 (8A) - noble gases ($1s^2$,$2p^6$-$6p^6$)
14 (4A) - the Carbon family

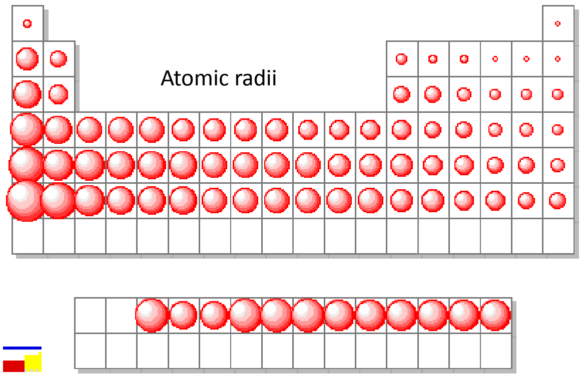


Ionization energy

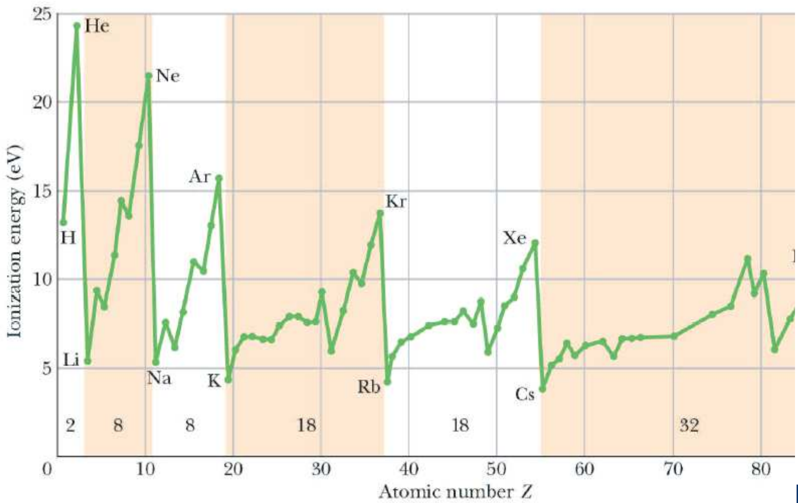
- **Ionization energy (IE)**: **minimum energy required to remove an electron from gaseous atom** or ion (not solid or liquid)
- First ionization energy: minimum energy needed to remove an electron from the highest occupied sub-shell (outermost electron) of gaseous atom
- Second ionization energy: minimum energy needed to remove the second electron from the highest occupied sub-shell of gaseous atom
- Third, fourth, … ionization energy – analogous
- “Total” ionization energy: minimum energy required to remove all electrons from gaseous atom
- Naming: known also as ionization potential
- Units: eV or kJ/mol in chemistry
- It governs chemical properties of atoms

Ionization energy and shell structure

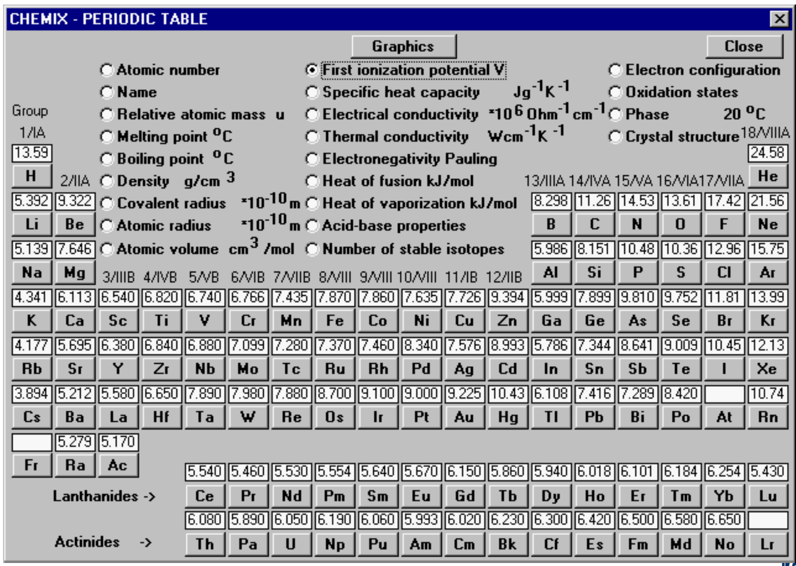
- **IE shows how easy it is to pull electron completely from atomic nucleus**
- IE is influenced by (in order of importance):
  - Nuclear charge – nucleus-electron attraction increases with nuclear charge
  - Number of shells – in presence of levels closer to nucleus outermost electrons are further from nucleus and are not so strongly attracted
  - Shielding – electrons on orbits closer to nucleus shied/protect outermost electron from attraction of nucleus
- Atomic radii and IE are connected
- What has lower 1st IE:
  - Mg or Ne
  - K or Ca
  - K or Rb
  - P or Ar
  - Etc …



First ionization energy

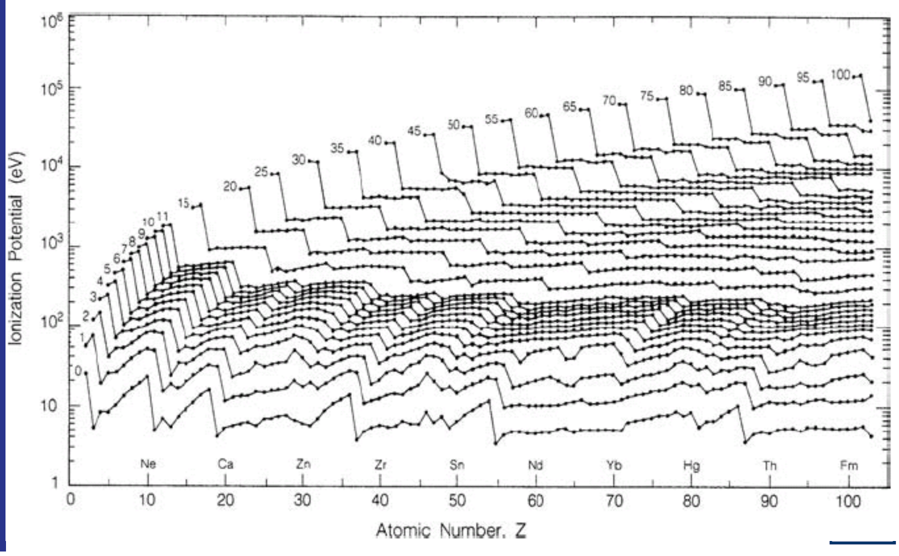


First ionization energy



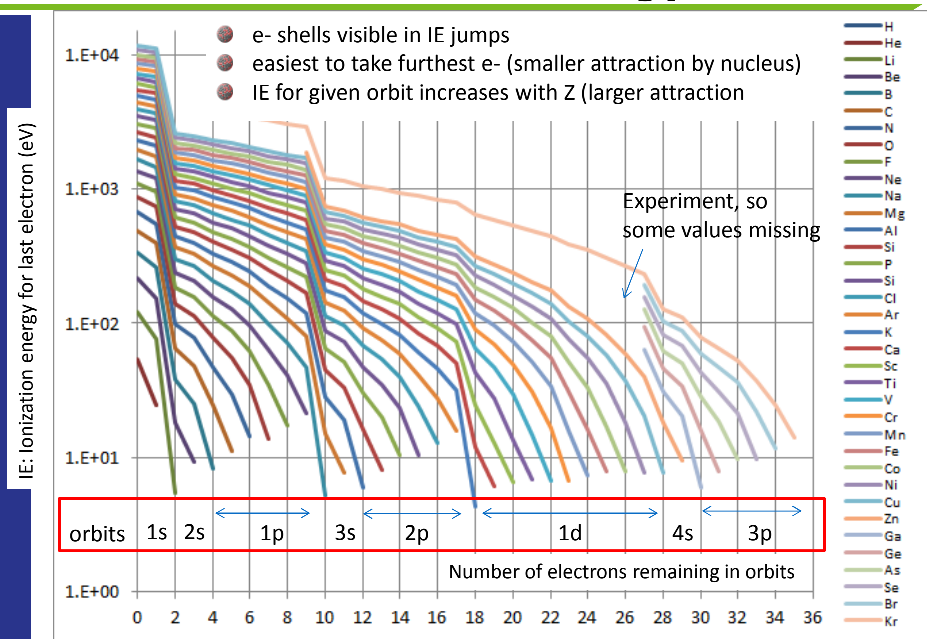
Ionization energy

- Ionization energy for multiply charged ions



Ionization energy

- e- shells visible in IE jumps
- easiest to take furthest e- (smaller attraction by nucleus)
- IE for given orbit increases with Z (larger attraction

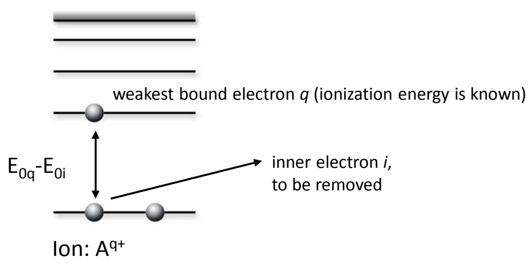


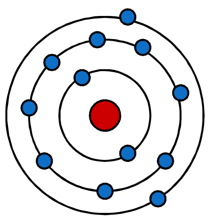
Ionization energy

- When ionization energies for more bound electrons are not known, Carlson-correction is used:
- Ionization energy $P_{q,i}$ is calculated from ionization energy $W_i(q)$ of ion with charge state *q* and the atomic binding energies of electrons (measured or calculated)

$$P_i = E_{0i} + W_i(q) - E_{0q}$$

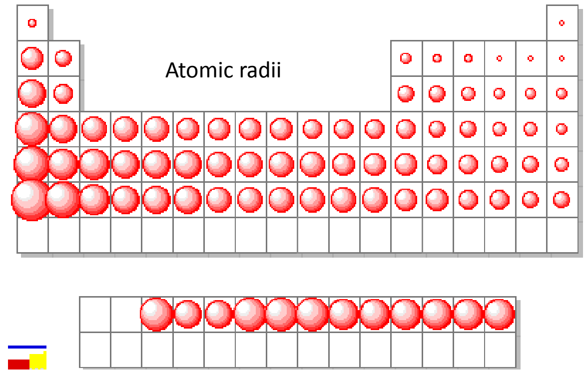
E_{0i} : binding energy of an electron in the i-th shell of an atom
E_{0q} : atomic binding energy of the electron, which is the weakest bound electron in the ion of the charge state q
$W_i(q)$: ionization energy of the ion (describes always the weakest bound electron)





Negative ions: electron affinity

- **Electron affinity (EA):** energy given off when neutral atom in gas phase gains extra electron to form *negatively charged ion*
- IE is influenced by the same effects as EI:
  - Nuclear charge
  - Number of shells
  - Shielding
- Atomic radii and IA are connected



Electron affinity

- Electron affinity <0 – negative ion is not stable

Electron affinities and ionization energies of elements

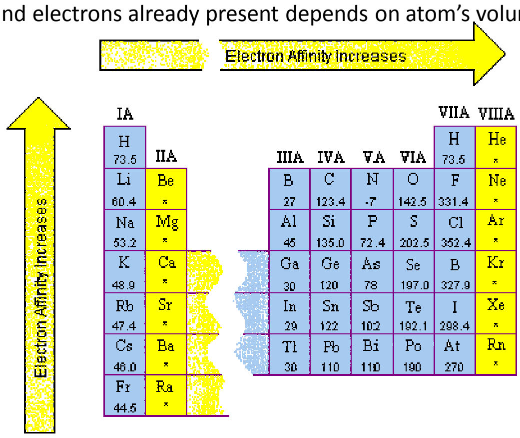
Group

Ionization potential (eV)
– Electron affinity (eV)

I A	II A	III A	IV A	V A	VI A	VII A	VIII A
1 H 13.59 0.75							2 He 24.58 0.078
3 Li 3.39 0.62	4 Be 9.32 < 0	5 B 8.30 0.28	6 C 11.26 1.26	7 N 14.54 ≤ 0	8 O 13.61 1.46	9 F 17.42 3.39	10 Ne 21.56 < 0
11 Na 5.14 0.54	12 Mg 7.64 < 0	13 Al 5.98 0.46	14 Si 8.15 1.38	15 P 10.55 0.74	16 S 10.36 2.07	17 Cl 13.01 3.61	18 Ar 15.76 < 0
19 K 4.34 0.50	20 Ca 6.11 ≈ 0	31 Ga 6.00 0.3	32 Ge 7.88 1.2	33 As 9.81 0.80	34 Se 9.75 2.02	35 Br 11.84 3.36	36 Kr 14.00 < 0
37 Rb 4.18 0.48	38 Sr 5.69 < 0	49 In 5.78 0.3	50 Sn 7.34 1.25	51 Sb 8.64 1.05	52 Te 9.01 1.97	53 I 10.45 3.06	54 Xe 12.13 < 0
55 Cs 3.89 0.47	56 Ba 5.21 < 0	81 Tl 6.11 0.3	82 Pb 7.41 1.1	83 Bi 7.29 1.1	84 Po 8.43 1.9	85 Ar 9.5 2.8	86 Rn 10.74 < 0

Electron affinity patterns

- Electron affinities get smaller when going down a column of periodic table:
  - electron added to atom is placed in larger orbitals, where it spends less time near nucleus
  - number of electrons on atom increases as we go down a column, so repulsion between electron being added and electrons already present on a neutral atom becomes larger
- Electron affinity data are complicated because repulsion between electron added to atom and electrons already present depends on atom's volume



Atomic processes in ion sources

In most ion sources, ions are produced in a plasma.
The basic atomic processes (selection) in plasmas are:

collisions with electrons

Impact Ionization — Three-Body-Recombination (TBR)

$$A^{Z+} + e \leftrightarrow A^{(Z+1)+} + e' + e''$$

Impact excitation — Impact disexcitation

$$A^{Z+} + e \leftrightarrow \left(A^{Z+}\right)^* + e' \Rightarrow$$ Non-radiative transition

A^{Z+}: Atom of species A with charge state Z
e': electron changed energy

collisions with photons

Photo ionization — Radiative Recombination (RR)

$$A^{Z+} + h\upsilon \leftrightarrow A^{(Z+1)+} + e \Rightarrow$$ Line spectrum

Excitation — Spontaneous emission

$$A^{Z+} + h\upsilon \leftrightarrow \left(A^{Z+}\right)^*$$

Photo absorption — Bremsstrahlung

$$A^{Z+} + h\upsilon + e \leftrightarrow A^{Z+} + e' \Rightarrow$$ Continuous spectrum

The electron changes from one free state to another free state with lower energy.

- O. Kester

Atomic processes in ion sources

From these multiple processes arise the dynamic balance quantities:

- Distribution of the abundance of all charge states Z (=0...Z_{max}), **Ionization equilibrium**
- Number of emitted and absorbed photons per time interval, **Radiative equilibrium**

The density of the particle species are determined from so-called **rate equations**:

$$\frac{dn}{dt} = \text{souces} - \text{sinks}$$

Example: impact ionization: $$\frac{dn_{z+1}}{dt} = n_e \cdot n_z \cdot v_e \sigma_{z \to z+1} - n_e \cdot n_{z+1} \cdot \beta_{z+1,TBR}$$

$\beta_{z+1,\,TBR}$: rate coefficient for Three-Body-Recombination (TBR)

The **rate coefficients** often not be calculated with sufficient precision; experimental data are only available to a limited extent. Therefore one tries to obtain data from thermo dynamical equilibrium.

With decreasing electron density the TBR drops, so that the impact ionization is not in equilibrium with the TBR anymore. The RR rate also decreases but not as strong. With decreasing n_e also the photo ionization becomes unlikely. As result the impact ionization and the RR-process dominate. The photons leave the plasma without being re-absorbed.

- O. Kester

Atomic processes in ion sources

$q^{n+} \to q^{(n+1)+}$ $q^{n+} \to q^{(n-1)+}$

- **Ionization**
  - single-ionization
  - double-ionization

  The production of higher charge states is a successive process

  The ionization has energy threshold
  → higher charge states need higher projectile energies (electron energies)

- **Charge exchange**
  (for low charge states)

- **Recombination**
  - radiative recombination
    The cross section is larger for lower electron temperatures
  - dielectronic recombination
    (resonant process)

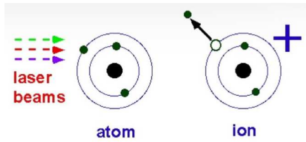
- **Charge exchange**
  (for high charge states)

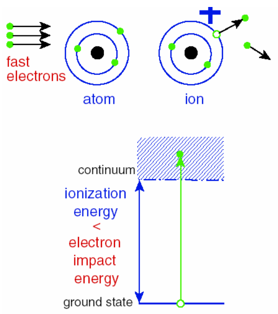
  depending on the neutral particle density residual gas)

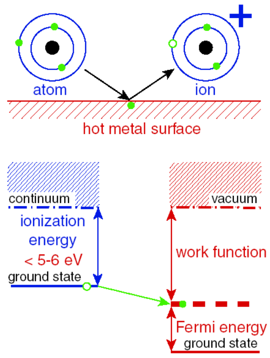
  cross section are larger for higher charge states

Ways to ionize atoms

- Positive ions:
  - Electron impact
  - Photons
  - Hot surfaces
- Negative ions:
  - Electron attachment
  - Charge exchange of a positive ion on a hot surface or in metal vapour
  - (Molecule dissociation)
  - (Molecule excitation)

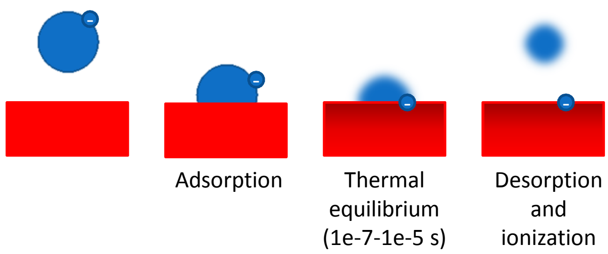






Surface ionization

- **Surface ionization: ionization by contact with a (metal) surface**
- Requirements:
  - Atom sticks (is adsorbed) to the surface long enough to reach thermodynamic equilibrium => atom valence electron is “broadened” and can move between atom and surface
  - Surface is hot enough to desorb particles: some are neutral atoms, or positive/negative ions
- Material work function (W) = minimal energy required for an electron to escape the material surface
- Boltzmann distribution?



Surface ionization

- Degree of positive surface ionization: **Saha-Langmuir equation**

$$Pi = \frac{ions}{atoms} = G\ \exp\left(\frac{W-Ei}{kT}\right)$$

Constant describing atom properties → G

Material **work function** → W

Atom **ionization energy** → Ei

Material **temperature** → T

Boltzman's constant → k

- Not important: Charge state before adsorbing on the surface (due to equilibrium)
- Important: material work function and state of particles before desorption (but after adsorption), i.e. atom ionization energy

$$G = \frac{g_i}{g_A}\frac{1-r}{1-r_0} = \frac{2Ji+1}{2JA+1}\frac{1-r}{1-r_0}$$

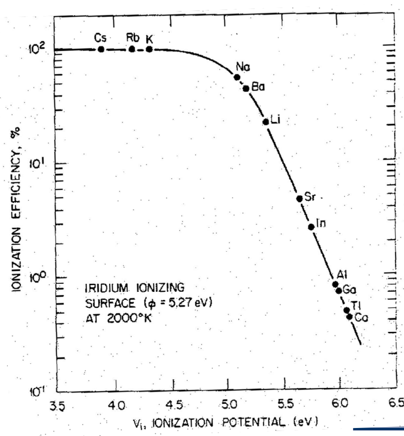
gi/gA=1/2 for group I and 2 for group II

J = 0, 1, … = quantum number (electron total angular momentum)
r = 0 to 1, reflection coefficient

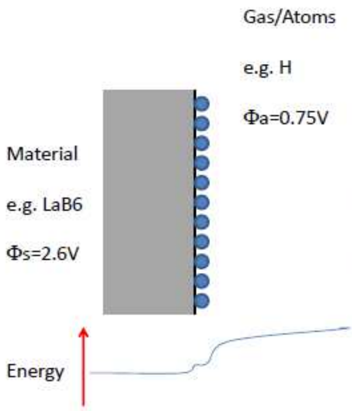
Surface ionization

particle	Ei (eV)	W-Ei (eV)	Pi(1000 K)	Pi(1500 K)	Pi(2000 K)	Pi(2000 K)
Cs	3.88	0.64	790	72	20	10
K	4.32	0.20	6.3	2.2	1.6	1.3
Na	5.12	-0.60	5e-4	5e-3	1.6e-2	3e-2
Li	5.40	-0.88	2e-5	6e-4	3e-3	8e-3

- Pi decreases with increasing T if *W-Ei* > 0
- T must be sufficiently high to evaporate given element (e.g. Li, Na).
- On the contrary, the diffusion of surface material must be low enough (< 10% of a mono-layer), to keep the ionization conditions as constant as possible
- **=> trade-off required**



Surface negative ionization



- If the base material has a low work-function, and the atoms a high electron affinity-
- The electrons have a finite probability of being present on the electron.
- Use plasma bombardment to liberate the atoms from the surface.
- Use a alkali metal coating deposited on the surfaces inside a plasma discharge source, to produce the ions.

Resonant ionization by photons

RILIS (Resonant ionization laser ion source)

absorption

$h\nu + E_l \rightarrow E_u$

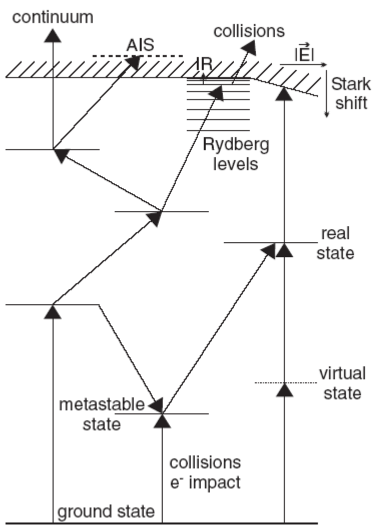
emission

spontaneous (isotropic) $E_u \rightarrow E_l + h\nu$

stimulated (direction of incoming photon) $h\nu + E_u \rightarrow E_l + 2h\nu$

Orders of magnitudes for the cross sections:

- non-resonant (direct ionization): $\sigma = 10^{-19} - 10^{-17}$ cm^2
- resonant: $\sigma = 10^{-10}$ cm^2
- AIS (auto-ionizing states): $\sigma = 1.6 \times 10^{-14}$ cm^2
- Rydberg states: $\sigma \sim 10^{-14}$ cm^2

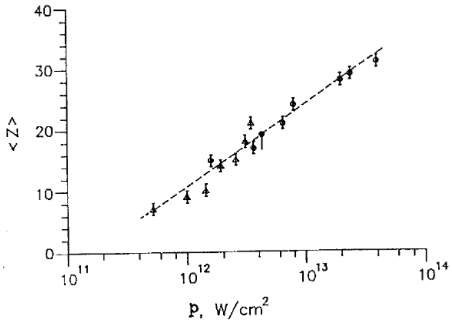


Excitation schemes used for resonant laser ionization

Non-resonant photo-ionization

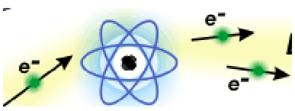
- In contrast to resonant ionization, ions/plasma within this source is generated via energy deposition
- Laser frequency couples to free electron plasma frequency (either in material, or formed plasma)
- The laser beam penetrates material
- Local heating of electrons by inverse Bremsstrahlung + excitation of atoms
- Material is ablated and an expanding plasma-plume develops
- If plasma density is lowered and cut-off frequency drops below laser-frequency, laser light can re-enter plasma.
- => Electrons inside plasma are accelerated up to 100 keV

Charge state vs laser power



Ionization by particle impact

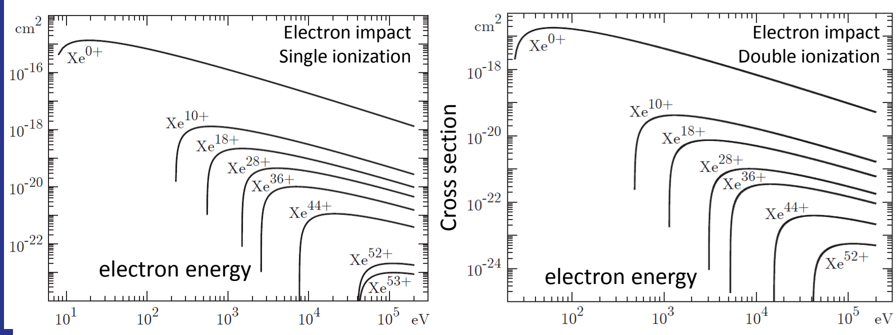
- Impact ionization is by orders of magnitudes higher than cross section for photo ionization
- Cross section depends on mass of colliding particle: energy transfer of a heavy particle is lower, proton needs for an identical ionization probability an ionization energy three orders of magnitudes higher than electron
- Thus, electrons are most common ionizing particles



- Processes involved:
  - Direct knockout ionization
  - Indirect processes (based on inner-shell excitation and subsequent autoionization); more important for heavier atoms

Ionization by electron impact

- Ionization cross section: electron energy has to be > ionization energy



- For energetic reasons most probable process is ionization releasing only one electron from atomic shell
- To produce highly charged ions, kinetic energy of projectile electrons has to be at least equivalent to *n*-th ionization potential

Ionization by electron impact

- Approximation of cross section and ionization time for production of bare ions from H-like ions using Mosley's law, for X-ray frequencies emitted in transitions from continuum to K-shell:

σ – single ionization cross-section cm²
j_e – electron current density A/cm²

$$E_{i\to k}(Z) = 13.6 \cdot Z^2\ [eV] \rightarrow$$

$$\sigma_{z-1\to z} = 4.5 \cdot 10^{-14} \cdot \frac{\ln e}{e \cdot 13.6^2 Z^4} = \frac{9 \cdot 10^{-17}}{Z^4}$$

with $E = e \cdot E_{i\to k}(Z)$

$$\nu_{z-1\to z} = \frac{j_e}{e}\sigma_{z-1\to z} = \frac{1}{\tau_{z-1\to z}}$$

$$\rightarrow\ j_e \tau_{z-1\to z} = \frac{e}{\sigma_{z-1\to z}} \approx \frac{eZ^4}{9 \cdot 10^{-17}} \approx \left(\frac{Z}{5}\right)^4$$

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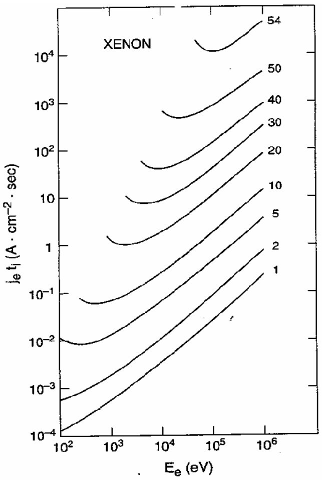
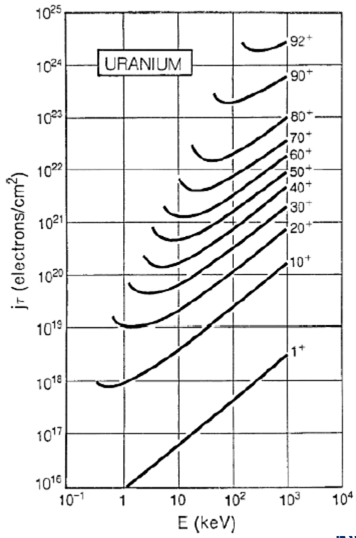
Ionization by electron impact

- Lotz formula: semi-empirical formula for cross-section of multiple ionization

$$\sigma_{q\to q+1} = 4.5\cdot 10^{-14}\cdot \sum_{nl} \frac{\ln\left(E_{kin}/P_i\right)}{E_{kin}\cdot P_i} \quad [\mathrm{cm}^2]$$

Ionization factor $j_e{}^*\tau$ for different charge states of Xe depending on electron energy





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Optimal electron energy

- Where σ(E) has maximum, ionization factor $j_e{}^*\tau$ has minimum there
- Cross section for the last electron, which is removed, determines ionization time

$$\frac{d\sigma_{z\to z+1}}{dE} = 4.5\cdot 10^{-14}\cdot \sum_{i=1}^{N} \frac{d}{dE}\left(\frac{\ln\left(E_{kin}/P_i\right)}{E_{kin}\cdot P_i}\right) = 0$$

$$\sum_{i=1}^{N} \frac{1}{P_i E^2}\left(1-\ln\left(\frac{E}{P_i}\right)\right) = 0 \quad \Rightarrow \quad E_{\max} = \exp\left(\frac{\sum_{i=1}^{N}\frac{1+\ln P_i}{P_i}}{\sum_{i=1}^{N} 1/P_i}\right) = e\cdot\exp\left(\frac{\sum_{i=1}^{N}\frac{\ln P_i}{P_i}}{\sum_{i=1}^{N} 1/P_i}\right)$$

- Optimal energy of last electron, which is removed:

$$E_{\max} \approx e\cdot\exp\left(\frac{\frac{\ln P_z}{P_z}}{1/P_z}\right) = e\cdot P_z$$

- => Optimal energy is nearly e-times ionization energy of last electron removed from ion with charge state z

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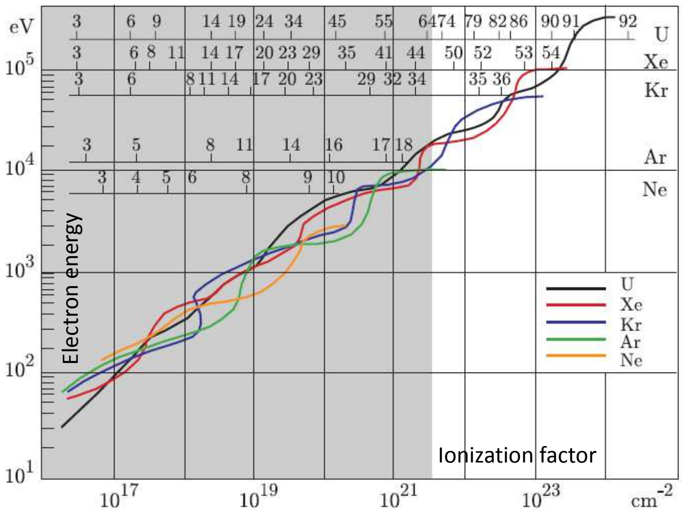
Ion. factor and optimal electron energy



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Summary

- Atomic physics governs many aspects of ion sources
- Electron shell structure determines energy required to excite electrons and even to eject them from atoms (ionization)
- These energies dictate chemical properties of elements
- There are different paths to atom ionization (surface, particle, photon impact)
- Their details depend on electron structure of ionized atoms and involve many atomic physics processes

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