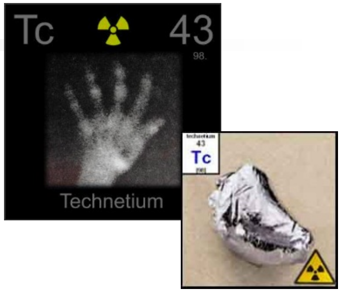
CHEMISTRY 1000



Topic #1: Atomic Structure and Nuclear Chemistry

Fall 2020

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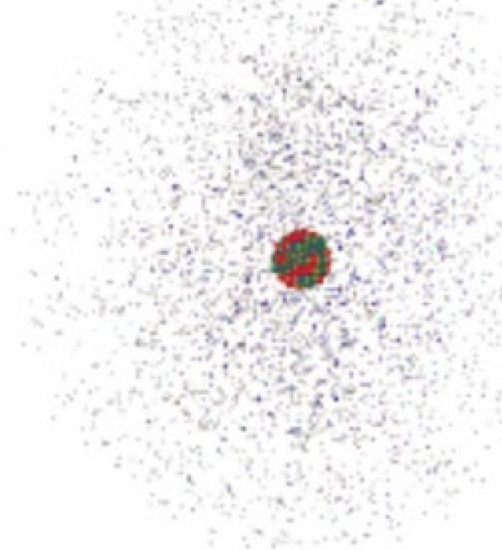
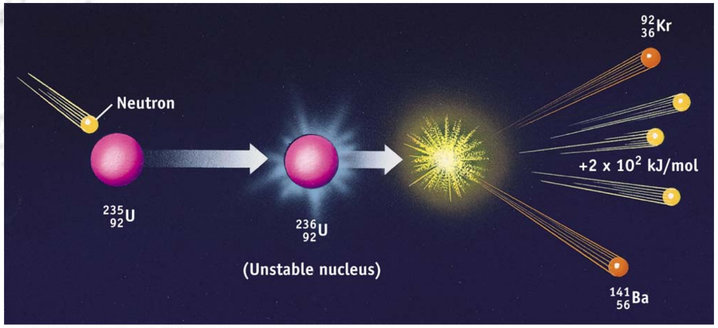
See Exercise 5.3





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Periodic Trends and Effective Nuclear Charge

- Imagine four atoms/ions:
  - One has a nucleus with charge +1 and a single electron
  - One has a nucleus with charge +1 and two electrons
  - One has a nucleus with charge +2 and a single electron
  - One has a nucleus with charge +2 and two electrons.

Which is biggest? Which could lose an electron most easily? Which would acquire an extra electron most easily?

Periodic Trends and Effective Nuclear Charge

- Most electrons do not 'feel' the full positive charge of the nucleus. Other electrons in the atom (particularly those in lower energy orbitals) 'shield' some of this charge. The amount of positive charge 'felt' by an electron in a given orbital is called the **effective nuclear charge (Z_{eff}).**
- The following table lists the atomic number (Z) and effective nuclear charges (Z_{eff}) for electrons in the 2*s* and 2*p* orbitals of neutral atoms of the elements in the second period:

Element	***Z***	**Z_{eff} (2*s*)**	**Z_{eff} (2*p*)**
Li	3	1.28	
B	5	2.58	2.42
C	6	3.22	3.14
N	7	3.85	3.83
O	8	4.49	4.45
F	9	5.13	5.10

Periodic Trends and Effective Nuclear Charge

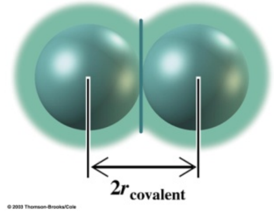
- Note that the effective nuclear charge on an *s* orbital is slightly higher than on a *p* orbital in the same shell. Why?

- Also, note that Z_{eff} does not increase by 1 when Z increases by 1. Why not?

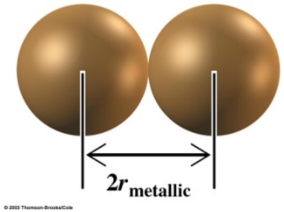
- Effective nuclear charge explains several of the **periodic trends** (atomic properties that can be predicted using the periodic table) including atomic size, ionization energy and electron affinity.

Atomic Size

- There are different ways of estimating the size of an atom:
  - The **covalent radius** is half the distance between the nuclei of two identical atoms joined by a single covalent bond. It is typically used when discussing molecules (like chlorine gas) or network solids (like diamond):



  - The **metallic radius** is half the distance between the nuclei of two adjacent atoms in the crystalline solid metal:



  - The **van der Waals radius** is half the distance between the nuclei of two adjacent atoms in a solid sample of noble gas. These radii are difficult to measure and noble gases are typically left out of discussions of atomic radius.

Atomic Size

- As a general rule, atomic radius
  - __________________ from left to right across a period. As the effective nuclear charge on the valence electrons increases, they are attracted more strongly to the nucleus.
  - __________________ from top to bottom down a group as more shells of electrons are added.

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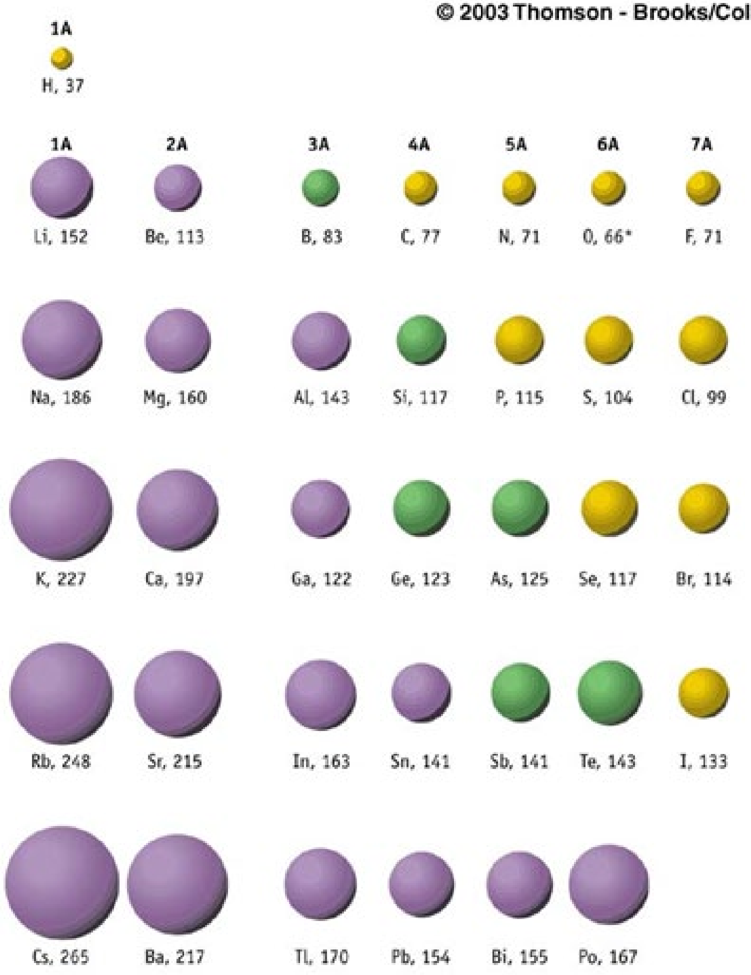


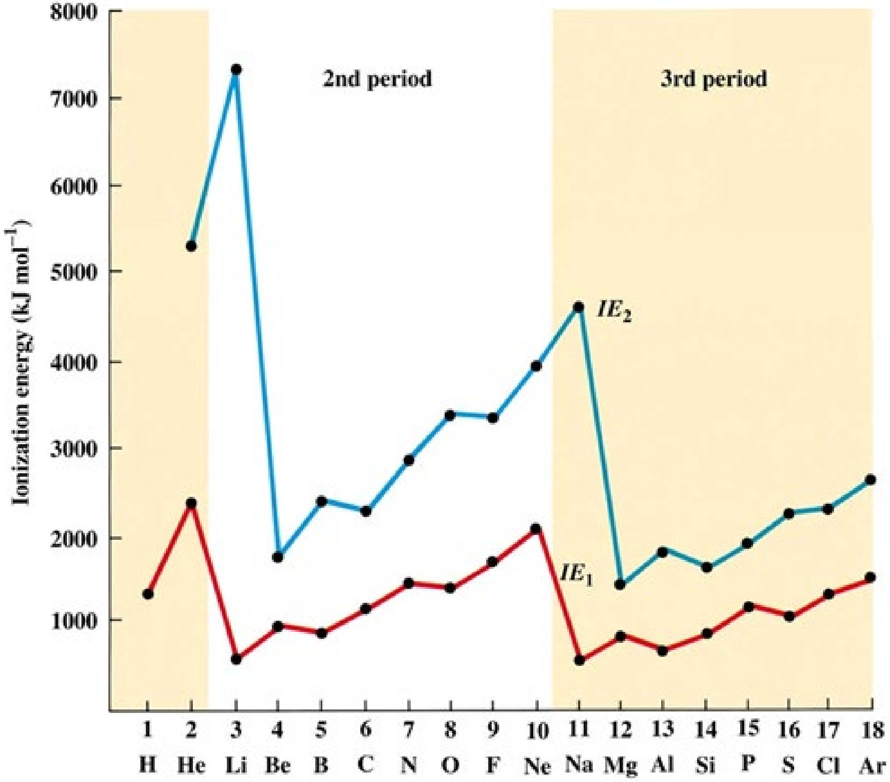
Ionization Energy

- An element’s **first ionization energy** (E_i) is the energy that must be absorbed in order to **remove** a valence electron from a neutral atom in the gas phase:

- As a general rule, first ionization energy
  - ____________________ from left to right across a period. As the effective nuclear charge on the valence electrons increases, they are attracted more strongly to the nucleus.
  - ____________________ from top to bottom down a group as more shells of electrons are added, and the valence electrons are farther from the nucleus.

- An element’s **second ionization energy** (E_{i2}) is the energy to that must be absorbed to remove a valence electron from a cation (with charge of +1) in the gas phase:

Ionization Energy



- Exceptions:
  - There is a slight decrease from group 2 to group 13 because the average distance from the nucleus to a *p* electron is slightly larger than the average distance to an *s* electron in the same shell.
  - There is a slight decrease from group 15 to group 16 due to electron-electron repulsion of electrons in the same orbital.

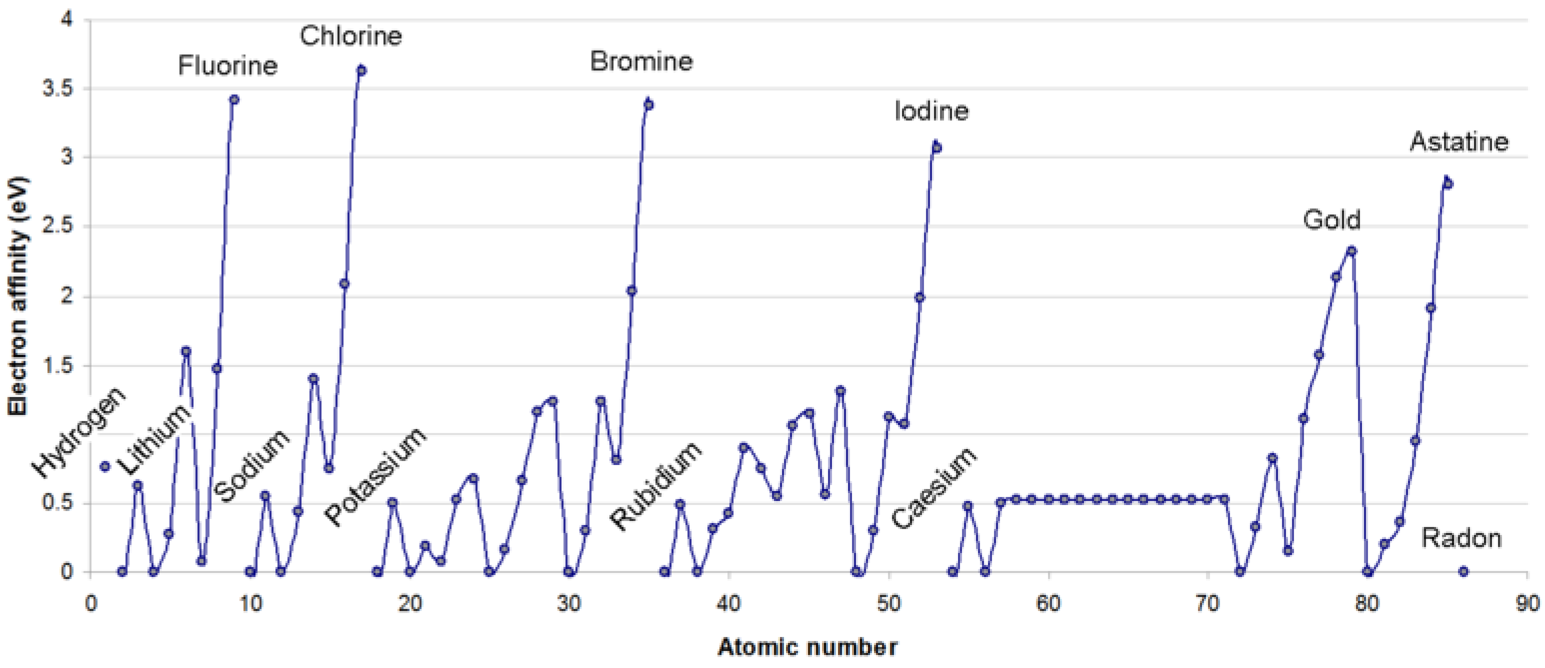
Electron Affinity

- An element's **electron affinity** (E_{ea}) is the energy released when a neutral atom in the gas phase **acquires** an extra electron in the lowest energy orbital available:

  The energy change for this reaction is negative (energy is released), but the electron affinity is positive (energy is released).

- As a general rule, electron affinity
  - ____________________ from left to right across a period. As the effective nuclear charge on the new valence electron increases, it is attracted more strongly to the nucleus.
  - ____________________ from top to bottom down a group as more shells of electrons are added, and the new valence electron is farther from the nucleus.
  - Elements whose valence electrons are all in filled subshells do not have a measurable electron affinity and are omitted from most data tables:

Electron Affinity



- As you can see, exceptions to the trend are common!
  - For example, the electron affinity for an element in group 15 is slightly less negative than that for the element to its left.

    This is due to increased electron-electron repulsion when adding electrons into a half-full orbital.

Image from http://commons.wikimedia.org/wiki/File:Electron_affinities_of_the_elements.png

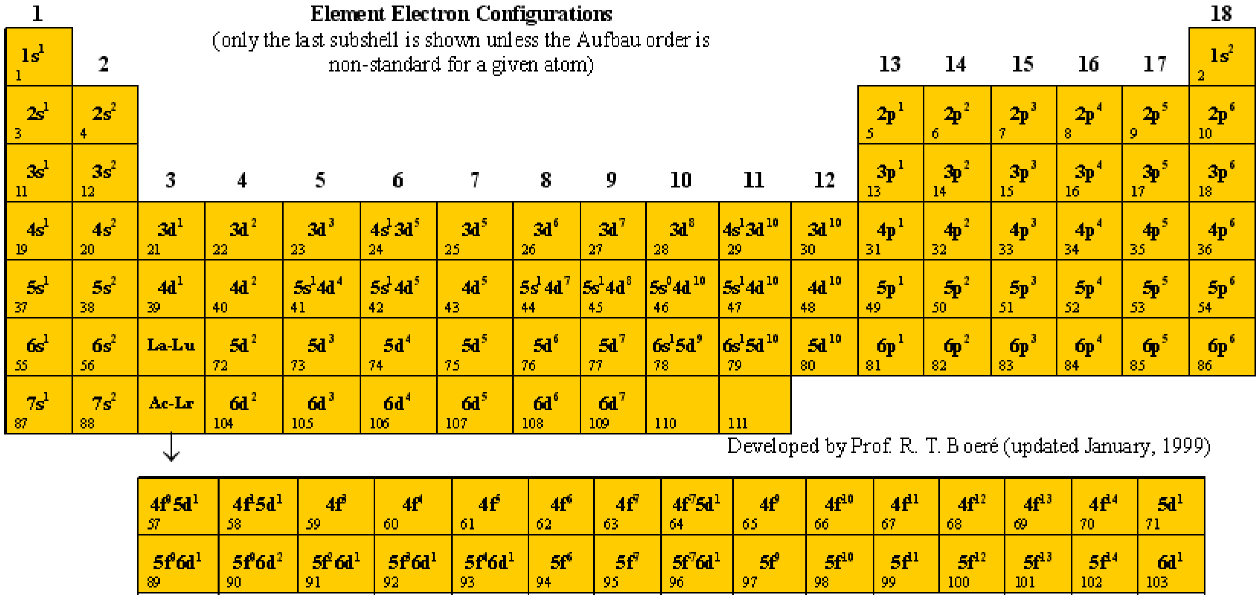
Electronegativity

- Electronegativity (χ) is a term that is often used to describe the overall ability of an element to both hold onto its own electrons and attract electrons from other elements. Conceptually, it is therefore a combination of ionization energy and electron affinity.

- Given this definition,
  - Which element(s) should have the highest electronegativity?
  - Which element(s) should have the lowest electronegativity?

Summary of Periodic Trends

- All of the periodic trends can be accounted for by considering electron configuration and effective nuclear charge. They can be predicted from the periodic table:



Element Electron Configurations
(only the last subshell is shown unless the Aufbau order is non-standard for a given atom)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
$1s^1$ 1																	$1s^2$ 2
$2s^1$ 3	$2s^2$ 4											$2p^1$ 5	$2p^2$ 6	$2p^3$ 7	$2p^4$ 8	$2p^5$ 9	$2p^6$ 10
$3s^1$ 11	$3s^2$ 12											$3p^1$ 13	$3p^2$ 14	$3p^3$ 15	$3p^4$ 16	$3p^5$ 17	$3p^6$ 18
$4s^1$ 19	$4s^2$ 20	$3d^1$ 21	$3d^2$ 22	$3d^3$ 23	$4s^1 3d^5$ 24	$3d^5$ 25	$3d^6$ 26	$3d^7$ 27	$3d^8$ 28	$4s^1 3d^{10}$ 29	$3d^{10}$ 30	$4p^1$ 31	$4p^2$ 32	$4p^3$ 33	$4p^4$ 34	$4p^5$ 35	$4p^6$ 36
$5s^1$ 37	$5s^2$ 38	$4d^1$ 39	$4d^2$ 40	$5s^1 4d^4$ 41	$5s^1 4d^5$ 42	$4d^5$ 43	$5s^1 4d^7$ 44	$5s^1 4d^8$ 45	$5s^0 4d^{10}$ 46	$5s^1 4d^{10}$ 47	$4d^{10}$ 48	$5p^1$ 49	$5p^2$ 50	$5p^3$ 51	$5p^4$ 52	$5p^5$ 53	$5p^6$ 54
$6s^1$ 55	$6s^2$ 56	La-Lu	$5d^2$ 72	$5d^3$ 73	$5d^4$ 74	$5d^5$ 75	$5d^6$ 76	$5d^7$ 77	$6s^1 5d^9$ 78	$6s^1 5d^{10}$ 79	$5d^{10}$ 80	$6p^1$ 81	$6p^2$ 82	$6p^3$ 83	$6p^4$ 84	$6p^5$ 85	$6p^6$ 86
$7s^1$ 87	$7s^2$ 88	Ac-Lr	$6d^2$ 104	$6d^3$ 105	$6d^4$ 106	$6d^5$ 107	$6d^6$ 108	$6d^7$ 109	110	111							

Developed by Prof. R. T. Boeré (updated January, 1999)

$4f^0 5d^1$ 57	$4f^1 5d^1$ 58	$4f^3$ 59	$4f^4$ 60	$4f^5$ 61	$4f^6$ 62	$4f^7$ 63	$4f^7 5d^1$ 64	$4f^9$ 65	$4f^{10}$ 66	$4f^{11}$ 67	$4f^{12}$ 68	$4f^{13}$ 69	$4f^{14}$ 70	$5d^1$ 71
$5f^0 6d^1$ 89	$5f^0 6d^2$ 90	$5f^2 6d^1$ 91	$5f^3 6d^1$ 92	$5f^4 6d^1$ 93	$5f^6$ 94	$5f^7$ 95	$5f^7 6d^1$ 96	$5f^9$ 97	$5f^{10}$ 98	$5f^{11}$ 99	$5f^{12}$ 100	$5f^{13}$ 101	$5f^{14}$ 102	$6d^1$ 103

On tests, “element A is to the right of element B” will **NOT** be accepted as an explanation of why element A has a higher ionization energy than element B. That’s a predictive tool (aka ‘memory trick’).
An explanation relies upon fundamental properties of the two elements – numbers of protons and electrons, effective nuclear charge, distance from nucleus to electron(s), etc.