

CHEM 205 section 03

LECTURE #20

Tues. March 18, 2008

LECTURE TOPICS:

TODAY'S CLASS: finish Ch.8

NEXT CLASS: start Ch.9

(1)

Elements in same period/row have:

- 1.) SAME CORE e^- configuration
- 2.) VALENCE e^- s IN SAME "SHELL" (in orbitals of relatively similar E)

Compare: Ti vs. Co

Core: $[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$

Valence: $4s^2 3d^{\dots}$

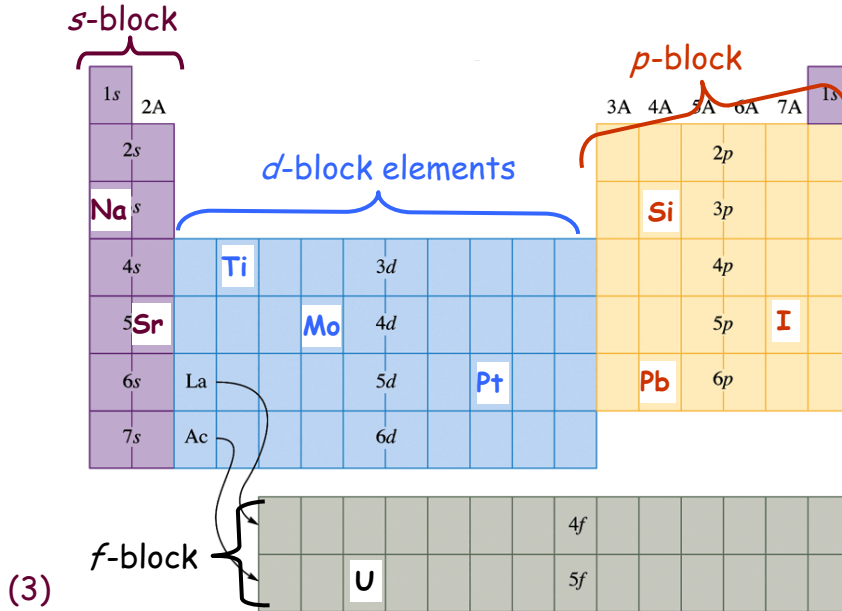
	1s	2A		3A	4A	5A	6A	7A	1s
1	1s								
2	2s					2p			
3	3s					3p			
4	4s		Ti			4p			
5	5s					5p			
6	6s	La				6p			
7	7s	Ac							

Labels in diagram:
- Ti: $4s^2 3d^2$
- Co: $4s^2 3d^7$
- Core: $[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$
- Valence: $4s^2 3d^{\dots}$

(2)

Elements in same "block" of periodic table have:

- 1.) VALENCE e^- s in same TYPE(S) of orbital



(3)

Some d- & f-block elements have unusual e^- configuration

- observed configurations for these elements (pink) not same as predicted
- note: some periodic tables show La & Ac as 1st members of d-block
 - matches their observed configurations, *BUT*...
 - makes more of the other f-block predictions incorrect

Suggestion: see Kotz Table 8.3 to see observed configurations for these elements (but don't memorize)

1 H	2 He																	10 Ne	
3 Li	4 Be											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
11 Na	12 Mg											29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr		
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe		
55 Cs	56 Ba	57-70 * Lu	71 Hf	72 Ta	73 W	74 Re	75 Os	76 Ir	77 Pt	78 Au	79 Hg	80 Tl	81 Pb	82 Bi	83 Po	84 At	86 Rn		
87 Fr	88 Ra	89-102 ** Lr	103 Rf	104 Db	105 Sg	106 Bh	107 Hs	108 Mt	109 Ds	110 Uuu	111 Uub	112 Uuq	114 Uuq						

*lanthanoids
**actinoids

(4)

Full *d*- and full *f*-subshells are part of the CORE

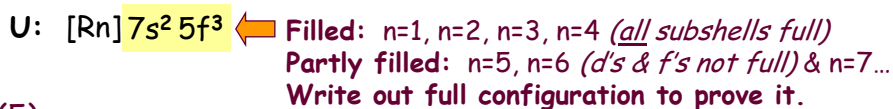
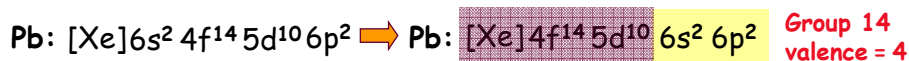
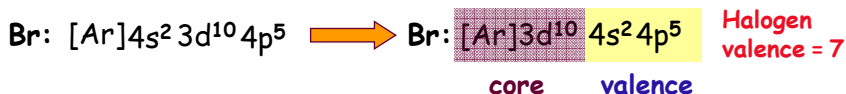
Once a set of *d*- or *f*- orbitals is FILLED,
it becomes lower in E than the closest-E s-orbital...

WHY?

- Recall: as \uparrow E, differences in orbital energies are smaller...
- Subtle changes in shielding result from filling *d* (& *f*) orbitals
 \Rightarrow subshell lower in E once occupied!

In order of orbital filling

Better (explains observed "valence"):
Reorder to match shifted energies



(5)

Electron spin, configuration & magnetism

- For atoms with many electrons:
most e^- 's are in same orbital as another e^- ...
 \therefore have opposite spins \Rightarrow e^- 's are "paired"
 \rightarrow substance repelled slightly by magnets
"diamagnetic"
- If atom has unpaired electron(s):
e.g., if odd # e^- 's, or due to Hund's rule...
 \rightarrow substance IS attracted to magnetic field!
"paramagnetic"

WHY?

- e^- 's each generate small magnetic field
- unpaired \Rightarrow not 'cancelled' by partner's field

RESULT:

- two possible orientations of unpaired e^- 's field
aligned with magnet's field ($m_s = +\frac{1}{2}$)
aligned against magnet's field ($m_s = -\frac{1}{2}$)

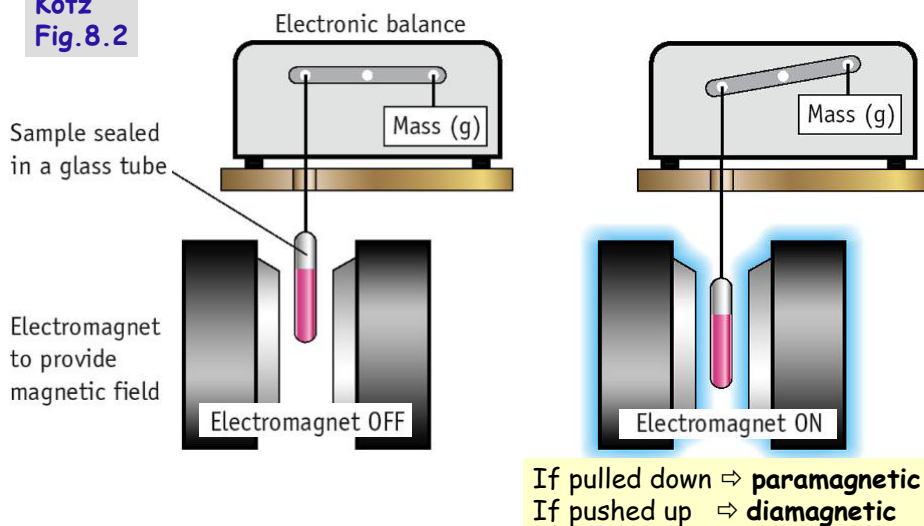
(6)



O_2 = paramagnetic
(liquid here, $<90\text{K}$)
Clings between
poles of a strong
magnet

Magnetism reveals unpaired e-s in substances' atoms

Kotz
Fig.8.2



Typically... (although it's a little more complex than just this...)

- (7)
- the larger the # of unpaired e-s in a substance's atoms or molecules, the stronger its interaction with a magnetic field

Which metal will be less strongly attracted to a magnet?

Magnetic resonance imaging (MRI) instruments in hospitals depend on precisely calibrated, strong electromagnets. To keep the instrument functioning properly and to keep the area around the instrument safe, all furniture, tools, custodial equipment *etc.* in the vicinity must be made out of non-magnetic materials.

Documented Accident Cases Involving Non-MRI Safe Equipment:

The nurse entered the magnet room with a pair of scissors. The metal scissors were pulled out of her hands into the magnet where they hit the patient causing a cut on the patient's head. Operator error appears to have contributed to the incident.

Source: http://www.magmedix.com/products/accessories/non_magnetic_tool_kits.html

Should the tools used in the vicinity of an MRI instrument be made of **stainless steel (mostly iron) OR aluminum?**
Explain, and include appropriate diagrams.

(8)

See Kotz p.337 for more on MRI

8.5 Electron configuration of ions

RECALL: achieving noble gas e^- configuration is "goal" of all atoms!

If a nonmetal and a representative group metal react:

- e^- s from valence orbitals of metal are lost
- e^- s enter valence of nonmetal
- "ionic" bonding results

When LOSING e^- s to make a cation:

- remove e^- s from shell with highest n value



Zumdahl's

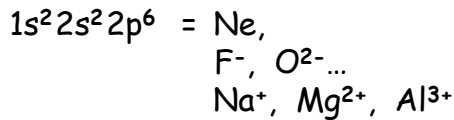
TABLE 8.3 Common Ions with Noble Gas Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^-, Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}		S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}		Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}		Te^{2-}	I^-	[Xe]

Same e^- configuration = "Isoelectronic" species

= atoms/ions containing the same # of e^- s

E.g.: species described by same noble gas configuration



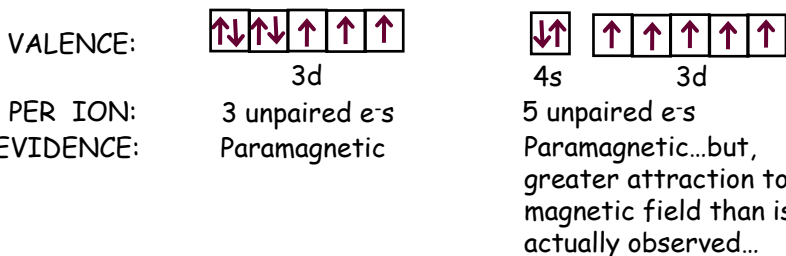
1 H	2 2A He											13 3A B	14 4A C	15 5A N	16 6A O	17 7A F	18 Ar
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac†	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub						

Configurations of d-block transition-metal ions

- For *d*-shells: emptying order is not same as filling order...
 \Rightarrow *s* subshell loses *e*-s before *d* subshell...
- To predict the *e*⁻ configuration of a transition-metal cation: remove valence *e*-s from subshell with highest *n* value 1st...

BASED ON EXPERIMENTAL EVIDENCE:

Chemical & physical properties of transition-metal cations are characteristic of having valence of d-electrons, not s...



(11)

8.6 Periodic trends in properties

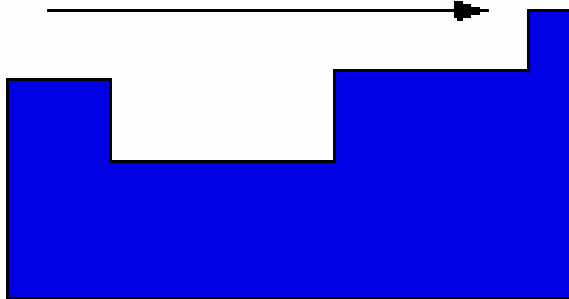
- Atomic & ionic size
- Ionization energy
- Electron affinity

EXPLAINED using effective nuclear charge, estimated by:

- calculating $Z_{\text{eff}}^{\text{min}}$ (how much + charge do the *e*-s feel?) **AND**
- considering orbital size (how far from this + charge are they?)

Higher effective nuclear charge
 ...electrons held more tightly

Larger orbitals
 ...*e*-s held
 less tightly
 farther away,
 so weaker
 electrostatic
 attraction to
 nucleus...



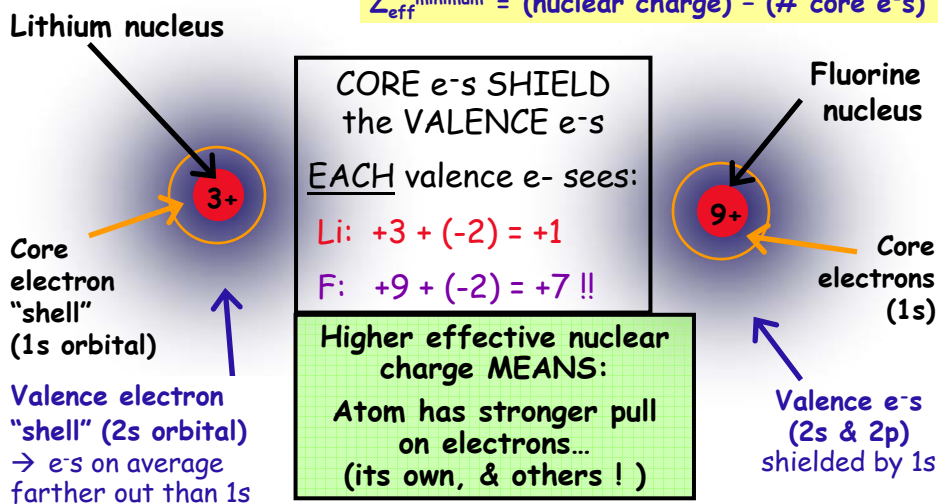
(12)

Effective nuclear charge: helps understand properties

"Highly-shielded extreme" of Z^* = useful tool for main gp elements:

- treat valence e^- s as: (1) all the same (even if have both s & p e^- s)
(2) shielded fully by core e^- s (& not each other)

$$Z_{\text{eff}}^{\text{minimum}} = (\text{nuclear charge}) - (\# \text{ core } e^-s)$$



Trends in size: atomic radii (pm) for main group elements

Fig. 8.11

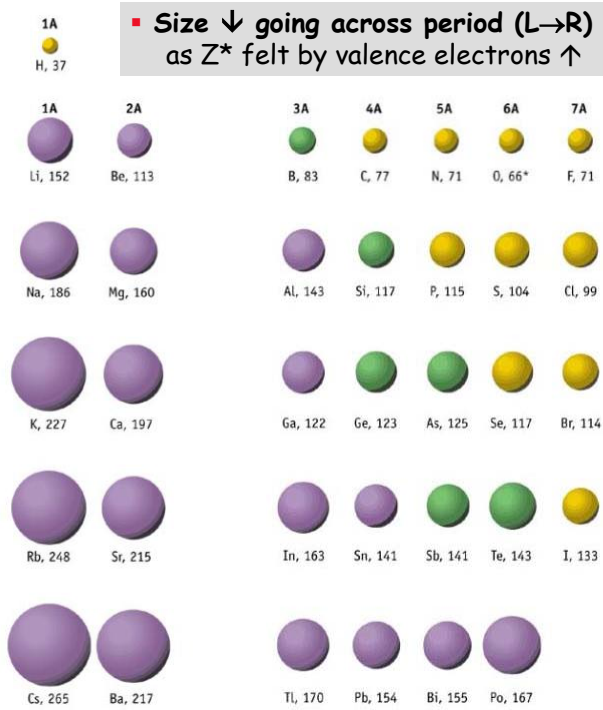
▪ Size ↓ going across period (L→R) as Z^* felt by valence electrons ↑

- Atom size ↑ going down a group as add more shells of core e^- s...

Note: below 5th row, changes in size are small, because E of high-E orbitals are very similar...

Transition metals?

- more complex trends
- whole courses devoted to them



Ion sizes: fewer or more electrons than parent atom?

CATIONS: fewer e⁻...
 ∴ smaller than parent atoms
less total shielding
 ⇒ e⁻s held more tightly

ANIONS: more e⁻...
 ∴ larger than parent atoms
more total shielding
 ⇒ e⁻s held more loosely

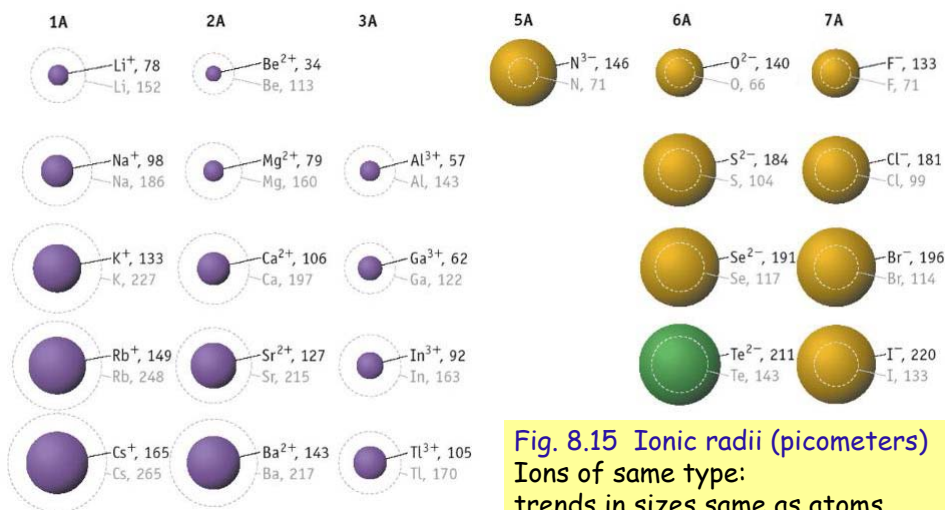


Fig. 8.15 Ionic radii (picometers)
 Ions of same type:
 trends in sizes same as atoms

Ionization energy



I.E. = quantity of energy required to remove an electron from a gaseous atom (1st I.E.) or ion (2nd I.E., 3rd...)



PERIODIC TREND:

First ionization energy (REMOVE 1e⁻ ONLY...FROM NEUTRAL ATOM)

- **Increases** from left to right in a period:
 - Harder to remove when feeling larger Z_{eff}
 - Recall reactivity: elements on right side tend to GAIN e⁻s !
- **Decreases** going down a group
 - Because e⁻s in BIGGER orbitals are held less tightly

It is much easier to remove valence e⁻s than core e⁻s ...

Z's **TABLE 7.5** Successive Ionization Energies in Kilojoules per Mole for the Elements in Period 3

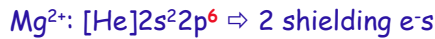
Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

*Note the large jump in ionization energy in going from removal of valence electrons to removal of core electrons.

↑
General decrease

General increase →

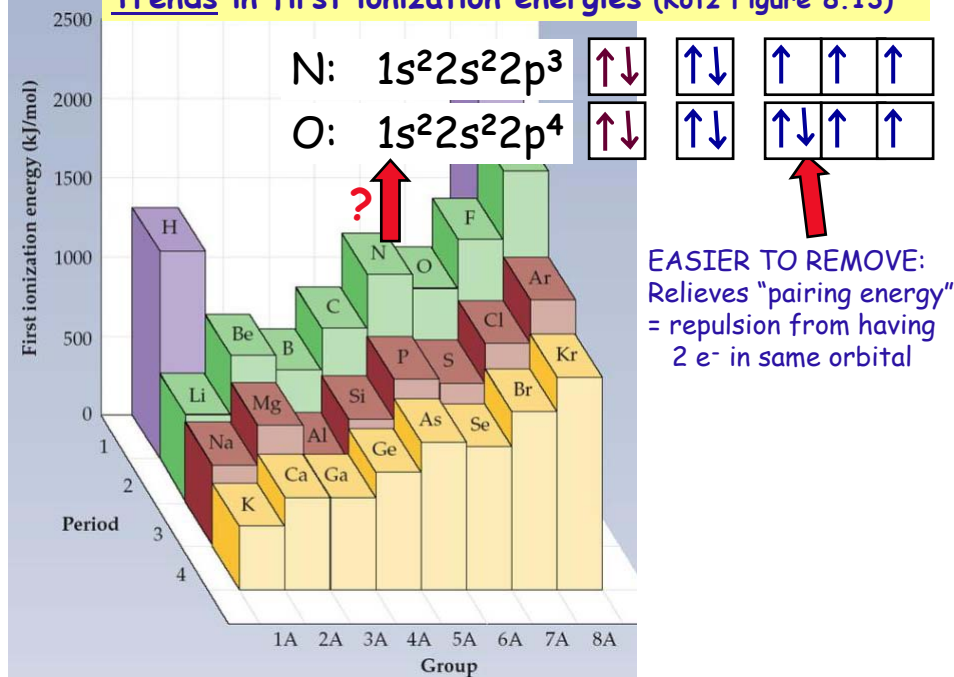
Consider magnesium's 2nd vs. 3rd ionization:



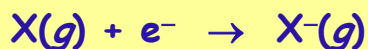
(17) $Z_{eff} \approx +12 - 10 = +2$

$Z_{eff} \approx +12 - 2 = +10!$

Trends in first ionization energies (Kotz Figure 8.13)



Electron Affinity



= energy change associated with addition of an electron to a gas-phase atom

energy is released...so it is negative (atom loses energy)

Not necessarily making element's most stable anion...



PERIODIC TREND: *many exceptions (focus on trend)*

- Amount of E \uparrow (larger -ve #) from left to right in a period:
 - Because Z_{eff} is larger \Rightarrow greater attraction for e^- !
- Amount of E \downarrow (smaller -ve #) going down a group
 - Because weaker attraction to nucleus when e^- is farther away!

(19)

Fig. 8.14

On your own: Consider H, C, F, Br, Na, Cu

Which of these element(s) has/have:

1. Electrons in d-orbitals?
2. A valence e^- in an orbital described by:
 $(n, \ell, m_\ell, m_s) = (2, 1, 0, +\frac{1}{2})$
3. Largest two atomic radii?
4. Smallest two atomic radii?
5. Highest effective nuclear charge (valence e^-)?
6. Highest electron affinity?
7. Lowest electron affinity?
8. Lowest 1st ionization energy?

(20)

8.7 Reactivity trends: Why do rxns tend to yield atoms with noble gas e⁻ configuration?

Once achieved, this configuration is DIFFICULT TO CHANGE.

1. To add another e⁻ to atom/ion with noble gas config'n...

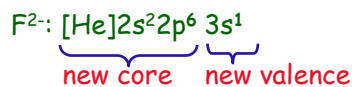
Energetically unfavourable because:

- Adding e⁻ to next (higher) energy level
- $Z_{\text{eff}}^{\text{min}}$ for this new valence shell is very LOW (actually negative!)
 - ⇒ insufficient attraction to keep extra e⁻ at this distance

Fluorine forms F⁻, but not F²⁻:



What do the n=2 e⁻s feel?
⇒ $Z_{\text{eff}}^{\text{min}} \approx +9 - 2 = +7$
⇒ strong attraction...



What would the 3s e⁻ feel?
⇒ $Z_{\text{eff}}^{\text{min}} \approx +9 - 10 = -1$
⇒ net repulsion...

Less unfavourable for heavier atoms (e.g., lower in group):

1. Higher energy levels closer together: easier to enter next energy level
2. Smaller repulsion: larger valence orbitals ⇒ weaker interaction with $Z_{\text{eff}}^{\text{min}}$

Once achieved, noble gas configuration DIFFICULT TO CHANGE...

2. To remove core e⁻s: requires a LOT of energy...

Main group metals: form cations with noble gas e⁻ config.

Higher charged ions unfavourable because:

- Need to remove e⁻ from full octet (was core, = new valence shell)
- $Z_{\text{eff}}^{\text{min}}$ for this lower E level is very HIGH
 - ⇒ strong attraction to nucleus, requires high E to remove e⁻

Potassium forms K⁺, not K²⁺:



To remove an n=3 e⁻:

⇒ $Z_{\text{eff}}^{\text{min}} \approx +19 - 10 = +9$ strong attraction b/w each e⁻ & nucleus
very difficult to break...

Transition metals: most-common ions arise from

- (a) emptying the s subshell
- (b) emptying or half-emptying the d subshell

ASSIGNED READINGS

BEFORE NEXT CLASS:

read all of Ch.8 + Ch.9 1st few sections

practice explaining trends in atomic properties
thinking about effective nuclear charge
identifying valence electrons (atoms & ions)

(23)