Chemistry 1B

Fall 2016

experience Lecture 9 (chapter 13; pp 596-614)

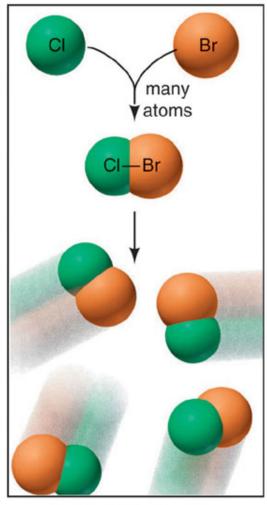
Chapter 13 (pp 596-614)– Overview of bonding and ionic bonding (lect 9)

• Chapter 13 (pp 621-650)- "Classical" picture of (pp 602-606) bonding and molecular geometry (lect 10-12)

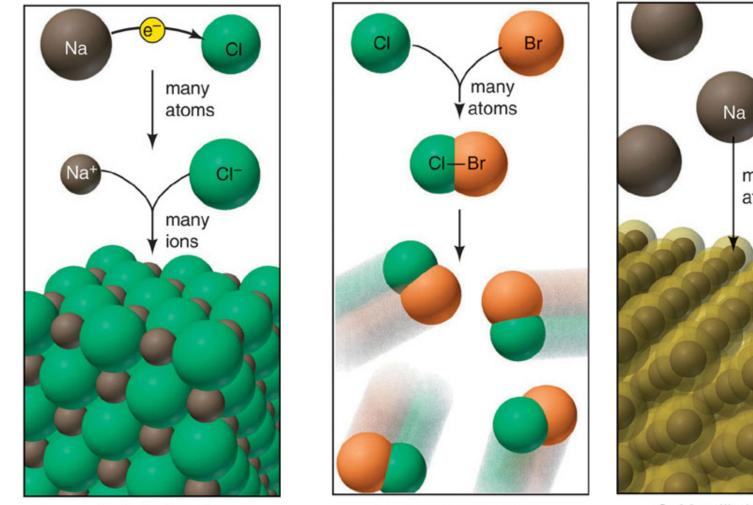
 Chapter 19 (pp 940-944;- Bonding in transition metal 952-954; complexes (lect 13-14) 963-970)

Chapter 14- Quantum mechanical description
 of bonding

- Ionic
- Covalent
- Metallic

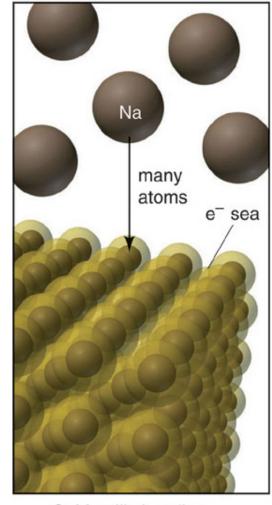


B Covalent bonding



A lonic bonding

B Covalent bonding



C Metallic bonding

hello Lewis electron-dot diagrams



G. N. Lewis- UC Berkeley



The Atom and the Molecule

by Gilbert N. Lewis Journal of the American Chemical Society Volume 38, 1916, pages 762-786 Received January 26, 1916

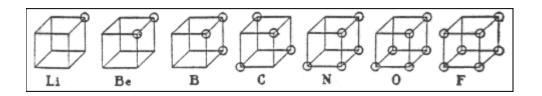
The Cubical Atom.

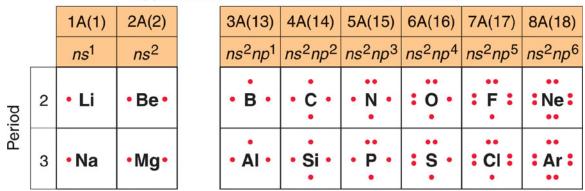
A number of years ago, to account for the striking fact which has become known as Abegg's law of valence and countervalence, and according to which the total difference between the maximum negative and positive valences or polar numbers of an element is frequently eight and is in no case more than eight, I designed what may be called the theory of the cubical atom. This theory, while it has become familiar to a number of my colleagues, has never been published, partly because it was in many respects incomplete. Although many of these elements of incompleteness remain, and although the theory lacks to-day much of the novelty which it originally possessed, it seems to me more probable intrinsically than some of the other theories of atomic structure which have been proposed, and I cannot discuss more fully the nature of the differences between polar and nonpolar compounds without a brief discussion of this theory.

The pictures of atomic structure which are reproduced in Fig. 2,1 and in which the circles represent the electrons in the outer shell of the

The Cubical Atom.

The pictures of atomic structure which are reproduced in Fig. 2,1 and in which the circles represent the electrons in the outer shell of the





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To form compounds, atoms will gain, lose, or share electrons to attain "complete outer shells".

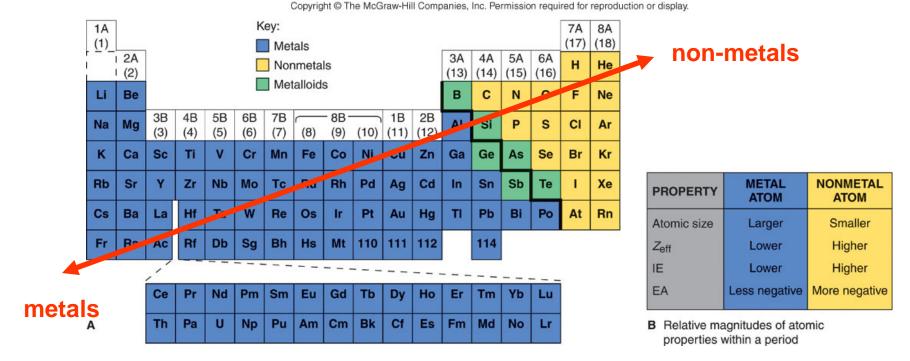
For hydrogen, a "complete shell" corresponds to 2 electrons (1s²).

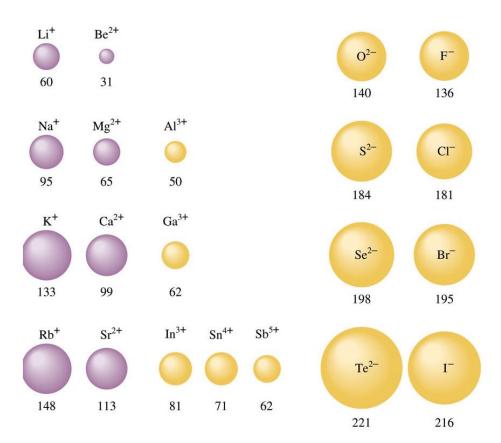
For atoms in period 'n', a "complete shell" often corresponds to 8 electrons ($ns^2 np^6$) octet structure.

• ionic bonding (pp. 606-614)

• covalent bonding (pp. 615-650; 602-606)

 metallic bonding (extra fun, but no extra tuition charge \$\$\$'s)





$$r \approx 52.9 \text{ pm} \frac{n^2}{Z_{eff}}$$

n and $\mathbf{Z}_{\scriptscriptstyle eff}$ of outermost electron

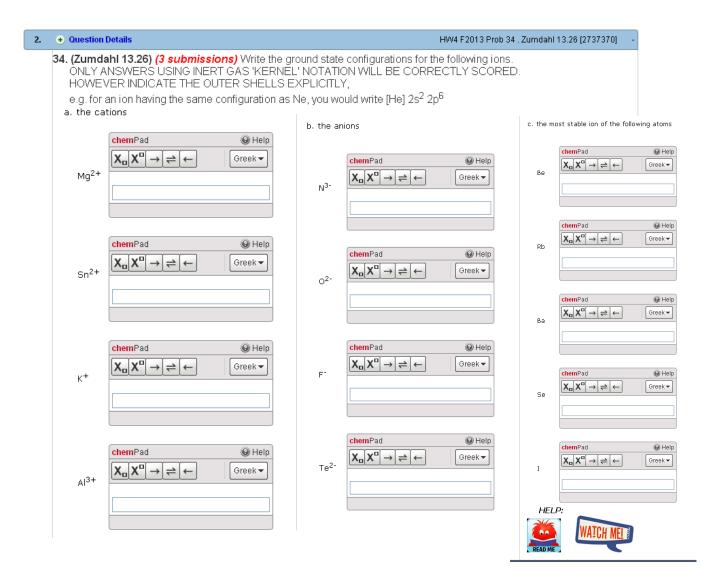
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- Electronegativity- the tendency of an atom to attract electrons and to 'hold on to' its own electrons
- Mulliken: (EN)_{MUL} = (IE EA)/2 (arbitrary units) (see ch13 prob 13.18)
- e.g. for Na (EN) _{MUL} = [(496) (-52.9)]/2=274 (kJ/mol) for Cl (EN) _{MUL} = [(1256) - (-349)]/2=802 (kJ/mol)
- High electronegativity- *wants to accept electrons* Low electronegativity- *will donate electrons* atoms with high electronegativity are *electronegative* atoms with low electronegativity are *electropositive*
- non-metals are electronegative metals are electropositive

- metallic atoms *lose* electrons to attain an 'octet' structure
- nonmetallic atoms gain electrons to attain an 'octet' structure

Na + Cl
[Ne]3s [Ne]3s²3p⁵
$$\rightarrow$$
 [Ne] [Ne]3s²3p⁶

HW#4 Prob. 30 (Zumdahl 13.26)



18

- In ionic compounds cations(+) are formed by metal atoms (lowish IE's) donating electrons to non-metals (largish EA's) to form anions(-)
- In many instances [e.g. Na(g) + Cl(g) → Na⁺(g) + Cl⁻ (g)] the process is energetically unfavorable (endothermic, needs to absorb energy)
- However ionic compounds do exist as crystalline solids due to the favorable (exothermic) LATTICE ENERGY associated with the process of gas phase ions going to solids
 [e.g. Na⁺(g) + Cl⁻(g) → Na⁺Cl⁻(s)]

• Coulombic forces stabilize ionic bonds in crystalline solids:

 $E = k \frac{Q_A Q_B}{R_{AB}}$ (opposite charges, large negative energies **STABILIZE**)

- The magnitude of the lattice energy depends on charges and sizes of ions:
 - the magnitude of the ionic charges (Q_AQ_B); the larger the greater stabilization [e.g. for Ca²⁺(SO₄)²⁻ (Q_AQ_B)= -4 and for Na⁺Cl⁻(s) (Q_AQ_B)= -1; thus lattice energy greater for Ca(SO₄)]
 - the interionic distance R_{AB} (sum of ionic radii); the smaller the greater stabilization
 [e.g. R_{AB} for Na⁺Cl⁻(s) smaller than R_{AB} K⁺Cl⁻(s); thus lattice energy greater for NaCl]

Ionic Bonding

and Lattice Energy

(Pp 609-613)

Learning Objectives V- section II.3

Learning Objectives and Worksheet V

Chemistry 1B-AL Fall 2016

Lecture 9 Types of Chemical Bonds- General Considerations

Read pp. 596-614

This class will be devoted to the general aspects of three types of chemical bonding-ionic, covalent, and metallic. The discussion will be based on our understanding of the quantum mechanics of atomic structure, but the interactions among atoms will focus on more 'classical' concepts. Later in the quarter we will revisit covalent bonding and fully understand the quantum mechanical basis of molecular bonding and structure.

I. Lewis hypothesis

- G.N. Lewis proposed that stable molecules would be formed if each atom attained a stable configuration of ______ electrons for H atoms and ______ electrons for other atoms. This would correspond to the ______ completely filled shell configuration for n=1 and the completely filled shell configuration for n=2, 3, ...
- In order to attain these stable electronic configurations in a molecule, the atoms could
 _____, ____, or ______ electrons by interacting with other atoms.

Tool to construct Lewis Structure: http://www.stolaf.edu/depts/chemistry/courses/toolkits/123/is/lewis/

Tutorial on how to draw dot structure: https://chemistry.boisestate.edu/richardbanks/inorganic/electron-dot.htm

II. Ionic bonding

HW#4: 34, 39

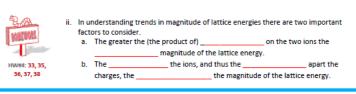
- In ionic bonds metallic atoms with _____ IE's tend to ______ electrons to form ______ negative EAs tend to ______ electrons to form ______.
- The electronegativity of an atom is a measure of its ability to _________
 its own electrons and ________ electrons from other atoms. In general ________ atoms are highly electronegative while _______ atoms are less electronegative (electropositive).
- 3. Strength of ionic bonding:

 Although Na has relatively low IE and Cl has a relatively large (negative) EA the electron transfer reaction:

 $Na(g) + Cl(g) \rightarrow Na^+(g) + Cl^-(g)$

is highly endothermic (+146 kJ/mol) (i.e. neutrals more stable than ions).So, in the ionic compound NaCl(s) what factor stabilizes the ions relative to Na and Cl atoms?

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet V



- 4. What are the general characteristics of ionic compounds with respect to:
 - i. deformability
 - ii. electrical conductivity _____
 - iii. boiling and melting points ______

More on lattice structures: http://intro.chem.okstate.edu/1314f97/chapter8/ionSize.html

Lattice energy calculator: https://scilearn.sydney.edu.au/fychemistry/calculators/lattice_energy.shtml

III. Covalent bonding (the most general considerations)

- 1. To form a complete octet an atom may
 - i. Share one pair of electrons to form a 'single' covalent bond
 - Share more (2 or 3) pairs of electrons with another atom to form a 'multiple' (double or triple) covalent bond
 - iii. Retain a pair of non-bonding electrons (a non-bonding or lone pair)
- 2. Covalent bonds occur between atoms of ______ electronegativity.
- In compounds with covalent bonding the intramolecular (bonding) forces are strong but
 often the intermolecular (among molecules) forces are weak (especially compared to ionic
 compounds). This leads to the following general characteristics of compounds with covalent
 bonding with respect to:

i. deformability vis a vis state of matter

- ii. electrical conductivity
- iii. boiling and melting points
- 4. Bonds between differing atoms are never 100% covalent or 100% ionic
 - i. a bond between atom of somewhat differing electronegativity will be a
 ______ covalent bond where the electron pairs are shared ______

Introduction to types of bonding

- ionic, covalent, metallic
- covalent- octets and much more soon
- metallic- added value topic soon
- ionic between

metals (low IE, gives up e^D relatively easily) + non-metal (large negative EA, wants to accept e^D relatively strongly)

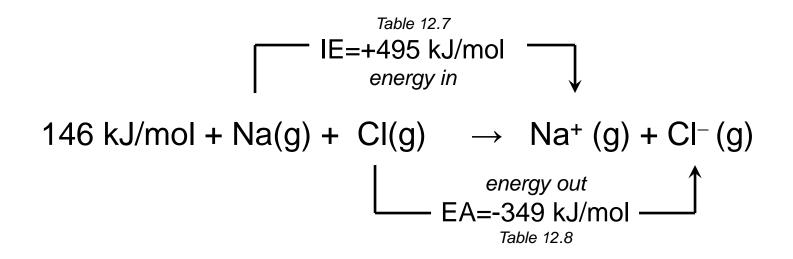
- metallic atoms *lose* electrons to attain an 'octet' structure
- nonmetallic atoms gain electrons to attain an 'octet' structure

Na + Cl
[Ne]3s [Ne]3s²3p⁵
$$\rightarrow$$
 [Ne] [Ne]3s²3p⁶

- △H, the change in enthalpy for a reaction, is the HEAT given off or absorbed by the reaction (for our purposes △H □ energy change)
- if heat is given off by the reaction [surroundings heat up], the reaction is EXOTHERMIC and ΔH < 0 [products MORE STABLE than reactants]
- if heat is absorbed by the reaction [surroundings cool], the reaction is ENDOTHERMIC and ΔH > 0 [reactants MORE STABLE than products; ionization is endothermic, IE > 0]
- Δ H for a complex process can be calculated by summing Δ H's for the individual steps of the process



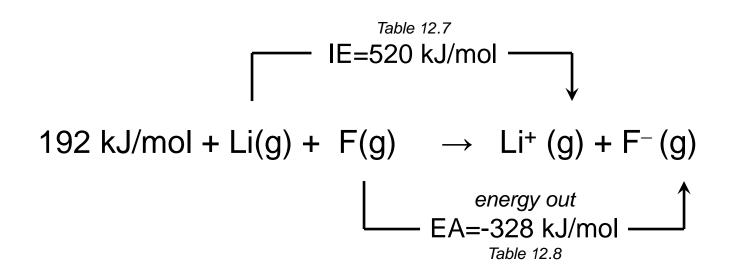




NET ENERGY CHANGE = + 146 kJ/mol (+495kJ-349kJ)

ENDOTHERMIC

gas phase ions unstable relative to atoms



NET ENERGY CHANGE = + 192 kJ/mol (520 – 328)

ENDOTHERMIC

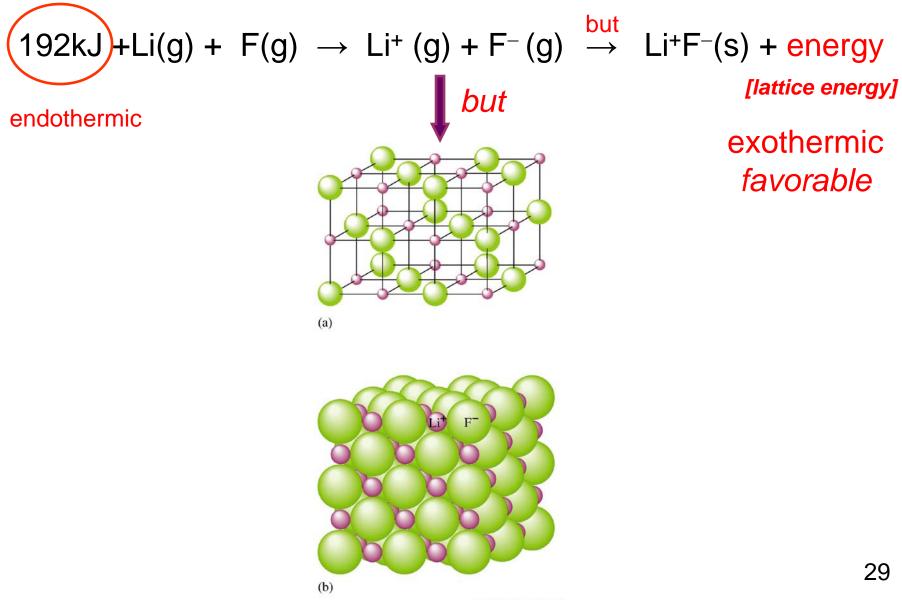
gas phase ions unstable relative to atoms



so if Li⁺+F¹ is unstable relative to Li + F why does one get stable crystals of lithium fluoride??

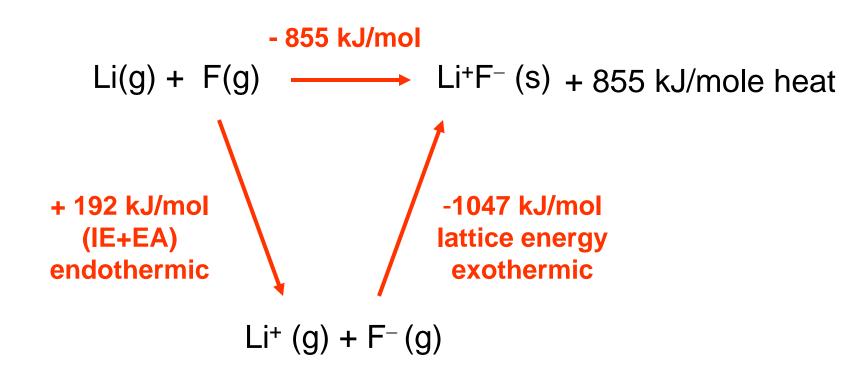


but Li⁺F⁻ is a salt (solid) figure 13.10



$Li^{+}(g) + F^{-}(g) \rightarrow Li^{+}F^{-}(s) + 1047 \text{ kJ/mole}$

lattice energy of LiF(s)= -1047 kJ/mole exothermic stabilizes ionic solids



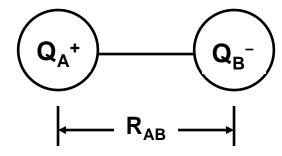
∆H= +192 kJ/mol – 1047 kJ/mol=-855 kJ/mole

exothermic Li⁺F⁻(s) STABLE relative to Li(g) + F(g) Born cycle: measuring lattice energies (fig. 13.9) (are not responsible for this concept)

heat given off by $Li^+(g) + F^-(g)$ Li⁺F⁻(s) difficult to measure directly

Born cycle: find an alternative set of reactions where heat of reaction CAN be measured for each step and the combinations of these reactions leads to Li⁺ (g) + F⁻ (g) Li⁺F⁻ (s)

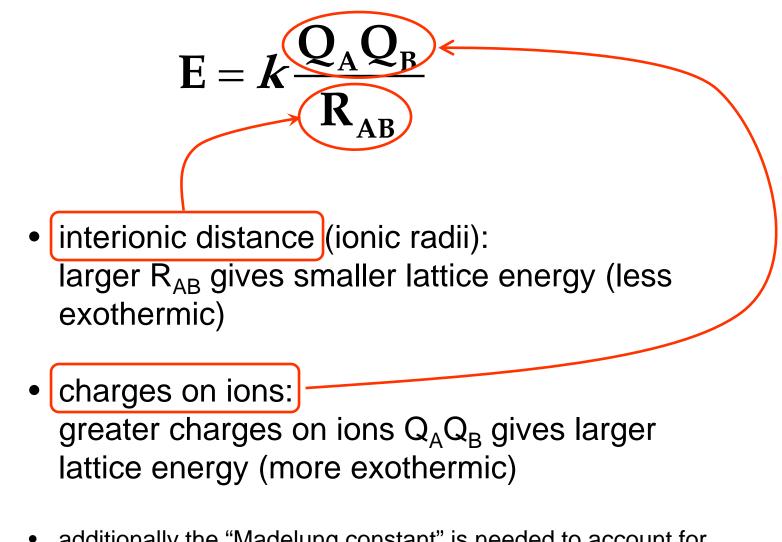
Use this cycle to compute Lattice Energy (LE)



$$E = \frac{Q_A Q_B}{4\pi\varepsilon_0 R_{AB}}$$

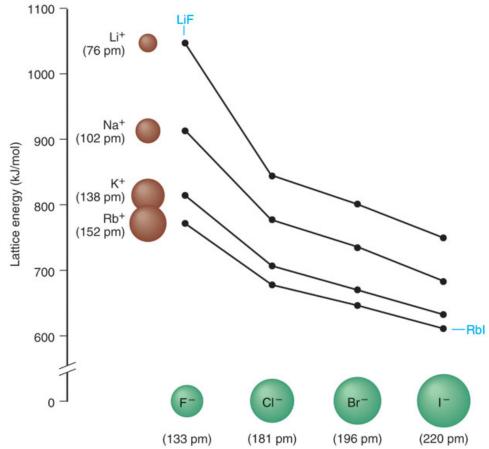
= 2.31 × 10⁻¹⁹ J nm $\frac{Q_A Q_B}{R_{AB}}$
= $k \frac{Q_A Q_B}{R_{AB}}$

two important factors in estimating LATTICE ENERGIES



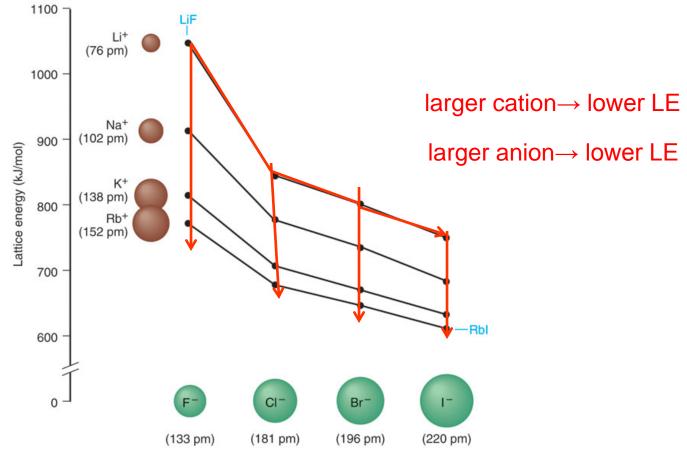
 additionally the "Madelung constant" is needed to account for the 3D ionic interactions in an actual crystal

Silberberg figure 9.7



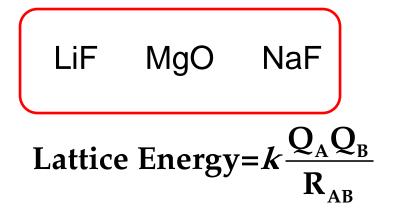
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Silberberg figure 9.7



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trends in lattice energy (you ARE responsible for this) (HW#4 prob 35 Z#13.32)

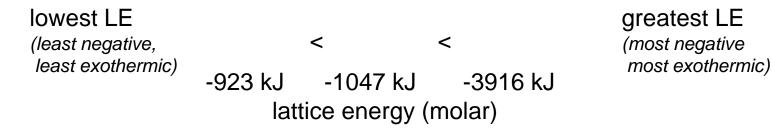


ionic size (R_{AB})

• ionic charge $Q_A Q_B$ (p. 612) (usually more important)

Mg^{2+,}Li⁺,Na⁺,O²,F

Li⁺ smaller than Na⁺



WebAssign HW#4 prob 31 (Zumdahl 13.32)

note will (irres	jive [almost always] M ²⁺ X pective of ion size (R _{AB})	have $M^{2+}X^{2-}$ vs $M^{2+}X_{2}$ the details of the ionic crystal interactions T^{2+} a greater (more exothermic) lattice energy than $M^{2+}X_{2+}$ and d; and the reason would be 'greater charge interaction'.
n	nost exothermic	justification (essay)
a.	LìF CsF	
ь.	🔍 NaBr 🔘 NaI	
с.	● BaCl ₂ ● BaO	
d.	 CaSO₄ Na₂SO₄ 	
е.	 KF K₂O 	
f.	 Na₂S Li₂O 	

a riddle: how are different bonding types like different styles of parenting ?

parenting and the three major types of bonding !!!

1. Which type of child rearing scenario is most analogous to ionic bonding?

a. hippie commune ; b. (very) old fashion parenting; c. modern (politically correct) parenting

2. Which type of child rearing scenario is most analogous to covalent bonding?

a. hippie commune ; b. (very) old fashion parenting; c. modern (politically correct) parenting

- 3. Which type of child rearing scenario is most analogous to metallic bonding?
 - a. hippie commune ; b. (very) old fashion parenting; c. modern (politically correct) parenting

(explain your answers)



• Bond energies, bond lengths, bond order (after Lewis structures chapter 13.10-13.12)

- 'strong' metals and 'strong' nonmetals are likely to form ionic compounds
- lattice energy stabilizes solids
- hydration of ions in aqueous solvents can contribute to solubility (Olmstead figure 2.2)
- ionic compounds 'crack' (fig Silb 9.8)
- ionic compounds have high boiling and melting points (table Silb 9.1) (fig. Silb 9.10)

 ionic compounds conduct electricity in molten (liquid) phase or in solution (Silb fig. 9.9)

- sharing of electrons leads to lower energy than two isolated atoms (figure 13.01)
- lone or non-bonding pairs
- more than one-pair of electrons may be shared to form stable 'octet' (single, double, triple bonds with bond orders 1, 2, 3 respectively)
- covalent bonding CANNOT be satisfactorily explained by classical electrostatics, but we need quantum mechanics chapter 14

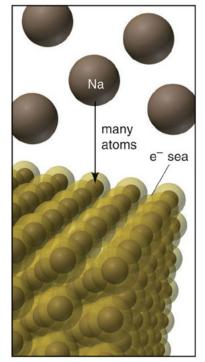
factoids about covalent bonding in molecules

- usually bonding between atoms of similar electronegativity (metallic bonding will be special case)
- many covalently bound molecules have strong intramolecular forces (the covalent bonds) but weak intermolecular forces; thus relatively low melting and boiling points (figure 9.14)
- poor conductors
- some atoms form extended networks of covalent bonds with high melting/ boiling points and hardness (figure 9.15)
 graphene

- electron transfer in ionic compounds may be incomplete
- two atoms may not equally share electrons in a covalent bond
- the greater the ΔEN the more ionic (figure S9.22)
- polar covalent bonds and covalency in ionic bonds (figure 13.11) (figure S9.21), (figure 13.12),
- continuum across period (more covalent as ΔEN decreases) (figure S9.25), (figure S9.24)

- the degree of 'attraction' of a given atom for electrons (its own and from other atoms)
- Mulliken scale: $(EN)_{MUL} = (IE EA)/2$ (arbitrary units)
- Pauling electronegativities (section 13.2)
 trends (figure Zumdahl 13.3, figure Silb 9.19) HW#4
- oxidation number and electronegativity (common valences) (table 13.5, figure Silb 9.3) HW#4

electron sea model



C Metallic bonding

- electrical and thermal conductivity
- moderate melting point; high boiling point (table S9.7) (figure S9.26)
- malleability (figure S9.27)

- Ionic
- Covalent
- Metallic

a riddle: how are different bonding types like different styles of parenting ?

parenting and the three major types of bonding !!!

sharing electrons ⇔ sharing child rearing responsibilities

1. Which type of child rearing scenario is most analogous to ionic bonding?

a. hippie commune ; **b.** (very) old fashion parenting; **c.** modern (politically correct) parenting

2. Which type of child rearing scenario is most analogous to covalent bonding?

a. hippie commune ; **b.** (very) old fashion parenting; **c.** modern (politically correct) parenting

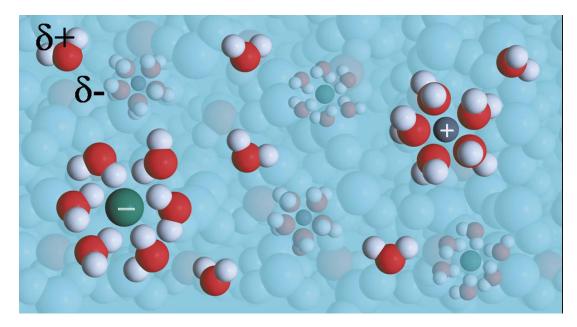
3. Which type of child rearing scenario is most analogous to metallic bonding?

a. hippie commune ; **b.** (very) old fashion parenting; **c.** modern (politically correct) parenting

(explain your answers)

END OF LECTURE

Olmstead figure 2.2: hydration of ions



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https://www.youtube.com/ watch?v=EBfGcTAJF40

Silberberg figure 9.8

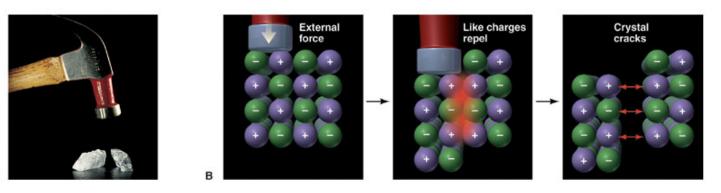
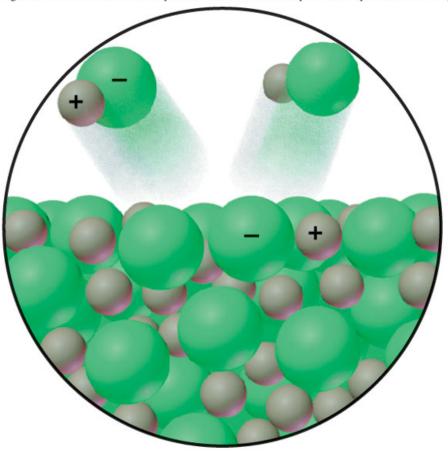
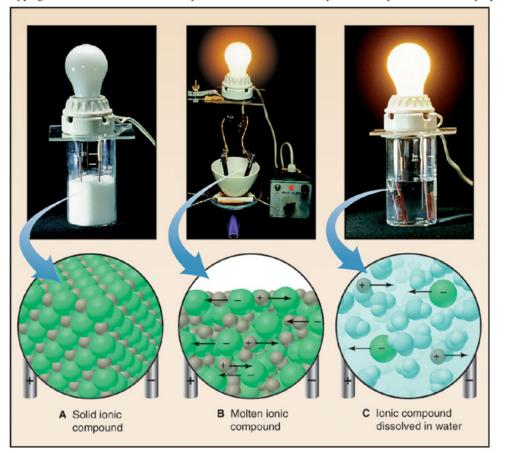


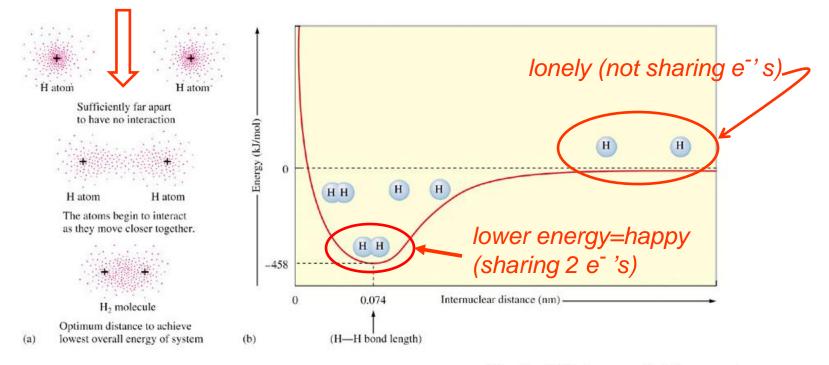
Table 9.1Melting and BoilingPoints of Some Ionic Compounds						
Compound	mp (°C)	bp (°C)				
CsBr	636	1300				
NaI	661	1304				
MgCl ₂	714	1412				
KBr	734	1435				
CaCl ₂	782	>1600				
NaCl	801	1413				
LiF	845	1676				
KF	858	1505				
MgO	2852	3600				



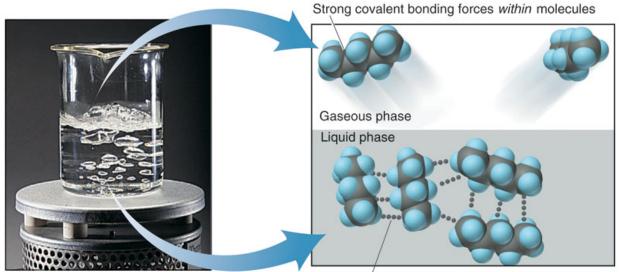
Silberberg figure 9.9



higher electron density in bonding region



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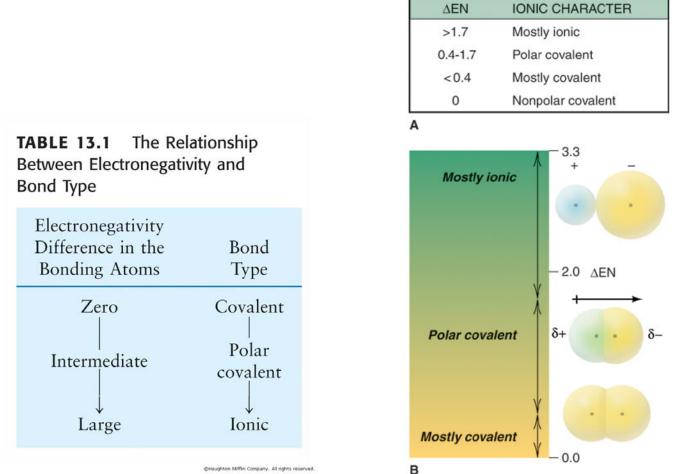


Weak intermolecular forces between molecules

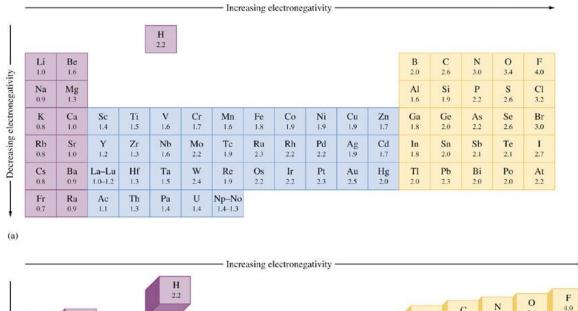
A Quartz Silicon Oxygen Carbon B Diamond



Zumdahl, Table 13.1; Silberberg figure 9.22



Pauling electronegativity (figure 13.3)

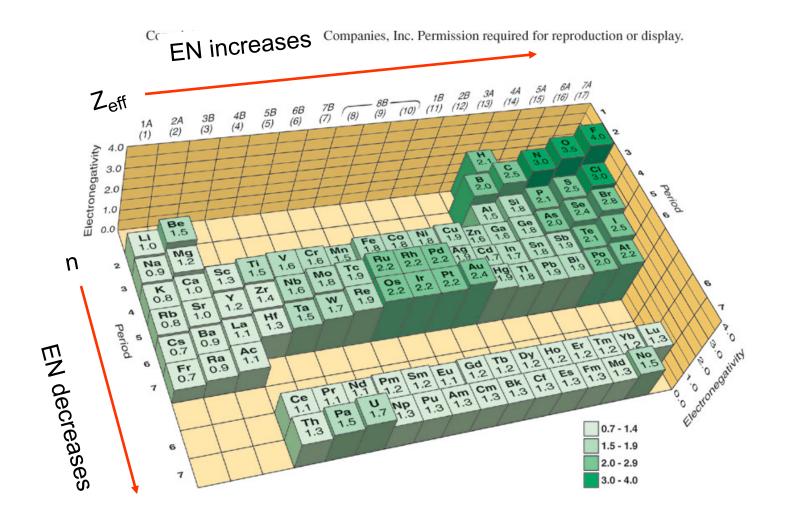


----- Decreasing electronegativity

(b)

Li	Be		1								1	B 2.0	C 2.6	3.0	3.4	
1.0	1.6	-											C ¹	р	S	C1 3.2
Na	Mg 1.3											A1 1.6	Si 1.9	Р 2.2	2.6	1.000
0.9 K		Sc	Ti	V 1.6	Cr 1.7	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	Se 2.6	Br 3.0
0.8	Ca 1.0	1.4	1.5	Nb	Mo) Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	1 2.7
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	1.6	2.2	1.9	2.3	2.2	2.2	1.9	1.7	1.8	2.0	2.1	2.1	2.1
Cs 0.8	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.3	Au 2.5	Hg 2.0	T1 2.0	Pb 2.3	Bi 2.0	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np-No 1.4-1.3			1	1		1		1		

Silberberg figure 9.19



Zumdahl 13.15) (3 submission lectronegativity n each of the following groups	of elements.		-	areasing
Use the appropriate = or < syn	nbol to separate	substances in the list.)		
(a) C, N, O		(b) S, Se, Cl		
chem Pad	Help	chem Pad	() Help	
$X_{\alpha}X^{\alpha} \rightarrow \rightleftharpoons \leftarrow$	Greek 🕶	$X_{n}X^{n} \to \rightleftharpoons \leftarrow$	Greek 🕶	
(c) Si, Ge, Sn		(d) TI, S, Ge		
$\begin{array}{c} \text{chemPad} \\ \hline X_{n} X^{n} \rightarrow \rightleftharpoons \leftarrow \end{array}$	€ Help Greek ▼	$\begin{array}{c} \text{ChemPad} \\ \hline X_{\square} X^{\square} \rightarrow \rightleftharpoons \leftarrow \end{array}$	© Help Greek ◄	

TABLE 13.5 Common lons with Noble Gas Electron Configurations in Ionic Compounds

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

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		1A(1)	2A(2)
		ns ¹	ns ²
iod	2	• Li	•Be•
Period	3	•Na	•Mg•

3A(13)	4A(14)	5A(15)	6A(16)	7A(17)	8A(18)
ns²np¹	ns²np²	ns²np³	ns²np4	ns²np⁵	ns²np ⁶
• B •	• • •	• N •	:0.	: F :	:Ne:
• AI •	• Si •	• • •	: :.	: ;;	: Ar :

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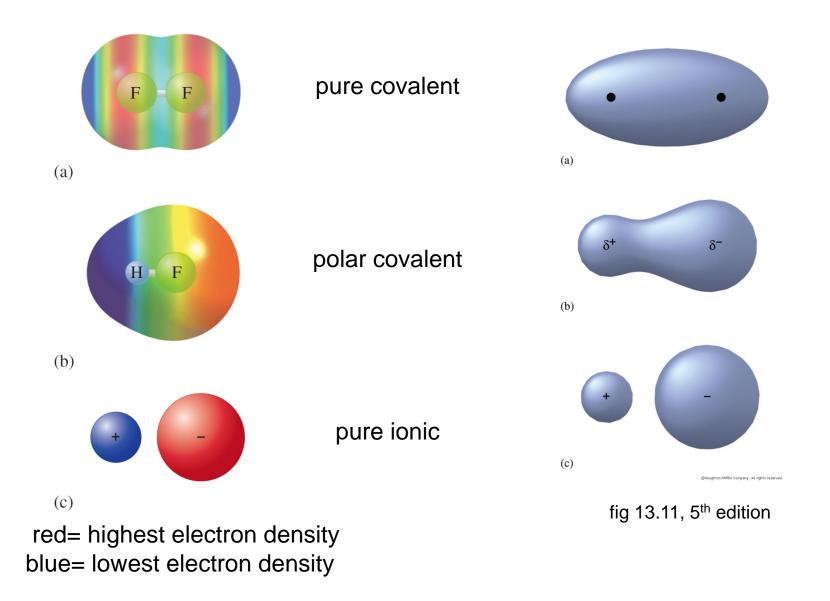
KNOW:

NH₄⁺, NO₃⁻, SO₄²⁻, HSO₄⁻, CN⁻, OH⁻, PO₄³⁻, CO₃²⁻, HCO₃⁻, C₂H₃O₂⁻, MnO₄⁻

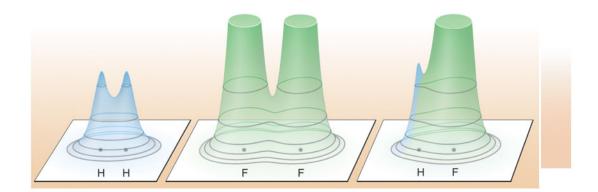
HW#4 *prob* 32

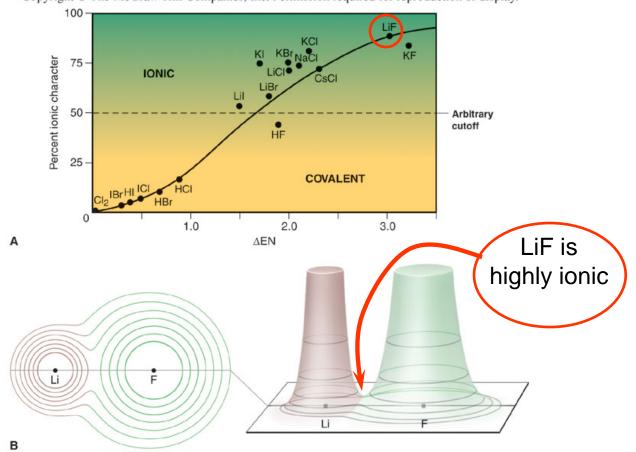
compound. In the chemPad e sure not to have a	-	from the following pairs of elements. Name each script pad button the to indicate subscripts and be
elements	empirical formula	name
. Al and S	$ \begin{array}{c} ChemPad \\ \hline \\ \hline $	
. Kand N	$ \begin{array}{c} ChemPad \\ \hline X_{\Box} X^{\Box} \rightarrow \rightleftharpoons \leftarrow \\ \hline Greek \bullet \end{array} $	

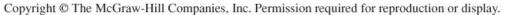
Bond polarity (figure 13.12 Zumdahl)



66

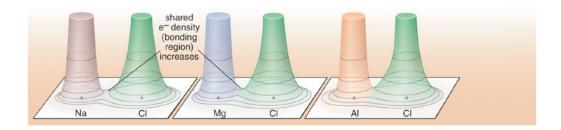






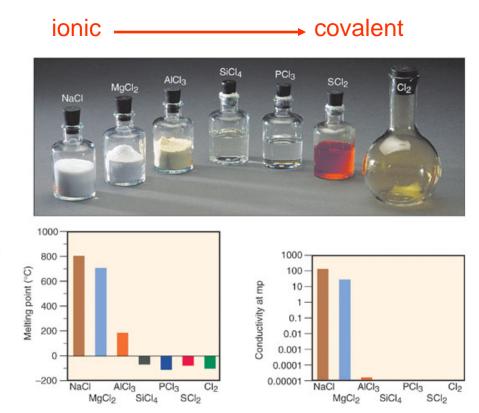
Silberberg figure 9.25

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more covalent as one goes across row

Silberberg figure 9.24 (X-CI) X: NaCl \Rightarrow Cl₂



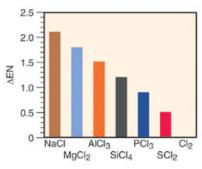
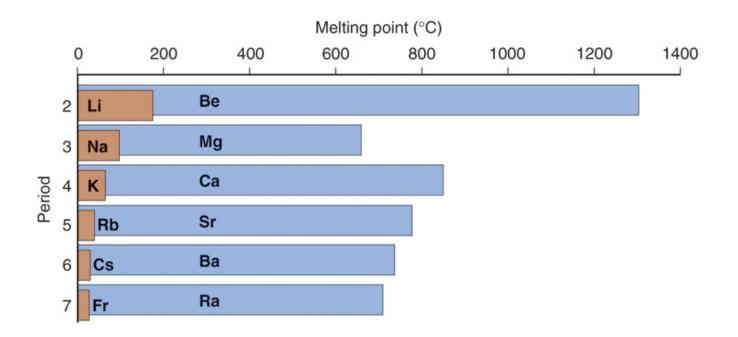




Table 9.7Melting and BoilingPoints of Some Metals								
Element	mp (°C)	bp (°C)						
Lithium (Li)	180	1347						
Tin (Sn)	232	2623						
Aluminum (Al)	660	2467						
Barium (Ba)	727	1850						
Silver (Ag)	961	2155						
Copper (Cu)	1083	2570						
Uranium (U)	1130	3930						

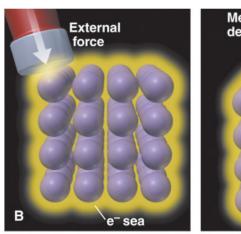
2nd period metals harder to melt

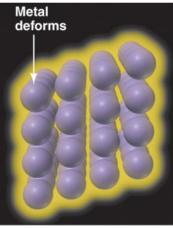


Silberberg figure 9.27

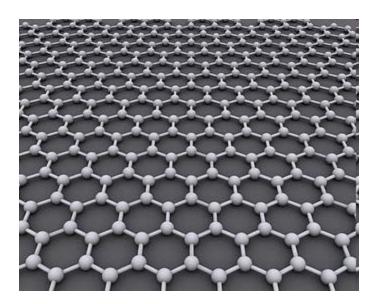


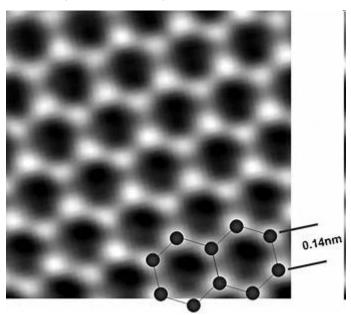






Graphene is a one-atom-thick planar sheet of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.





Potential applications

Graphene transistors Integrated circuits Anti-bacterial Single molecule gas detection

2010 Nobel Prize in physics



Nobel Prize in physics won by Russian duo working in Manchester

"for groundbreaking experiments regarding the two-dimensional material graphene",