The Concept of the Chemical Bond

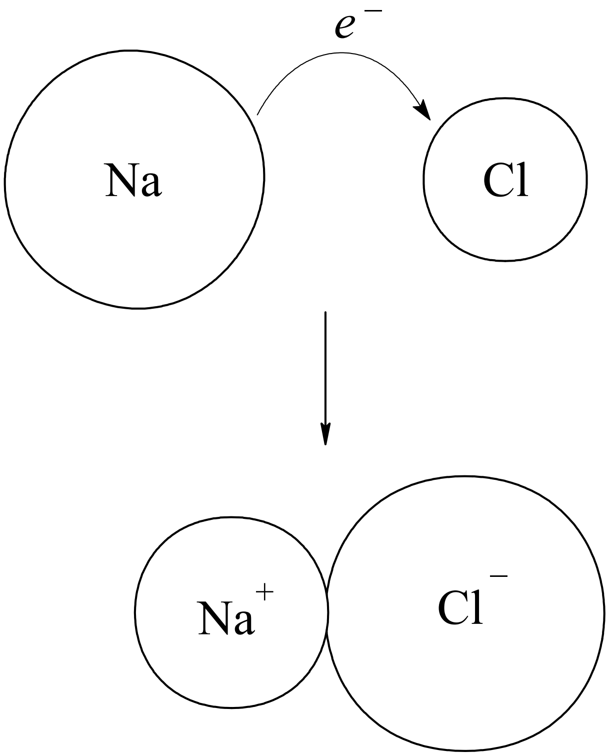
L A **chemical bond** exists between any two atoms that are strongly attracted to one another in a compound or element.

L There are three extreme models commonly used to classify bonds:
ionic
covalent
metallic

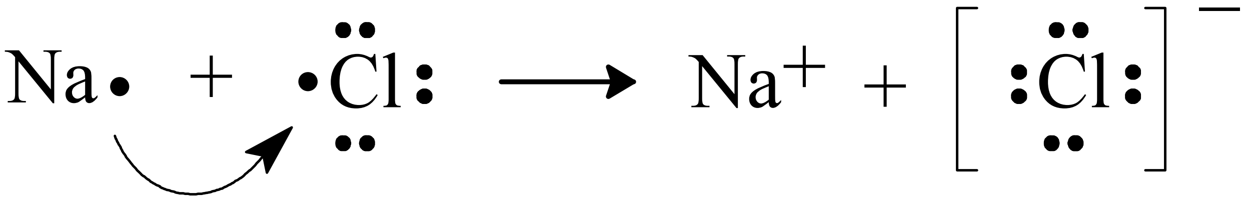
U We will concentrate on ionic and covalent bonds in this course.

Idealized Formation of an Ionic Bond

- An **ionic bond** is formed by electrostatic forces of attraction between ions.



Electron Dot (Lewis Dot) Representation of Idealized Formation of an Ionic Bond



The Covalent Bond

L A **covalent bond** is formed by sharing electrons between atoms.

L A **pure covalent bond** exists when the electron sharing is perfectly equal.

U A pure covalent bond only exists if the two bonded atoms are identical (homonuclear bond).

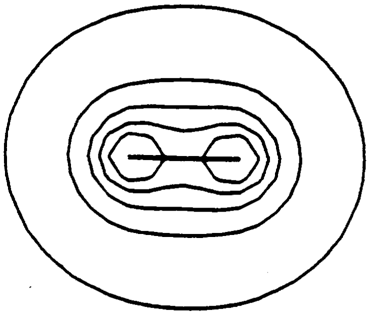
L A **polar covalent bond** exists when the electron sharing is unequal.

U When two different atoms are bonded together, their different abilities to attract electrons result in unequal sharing.

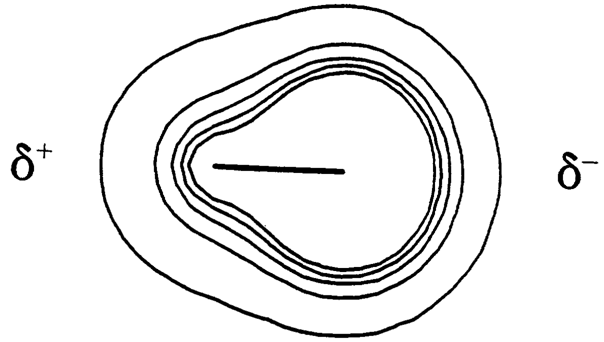
U The atom that attracts electrons more strongly becomes partially negative ($\delta-$) and the other atom becomes partially positive ($\delta+$), giving the bond an electrical polarity.

U All bonds between atoms of different elements (heteronuclear bonds) are polar to some extent.

Electron Density Distributions
Pure Covalent Bond (H_2)
vs.
Polar Covalent Bond (HF)

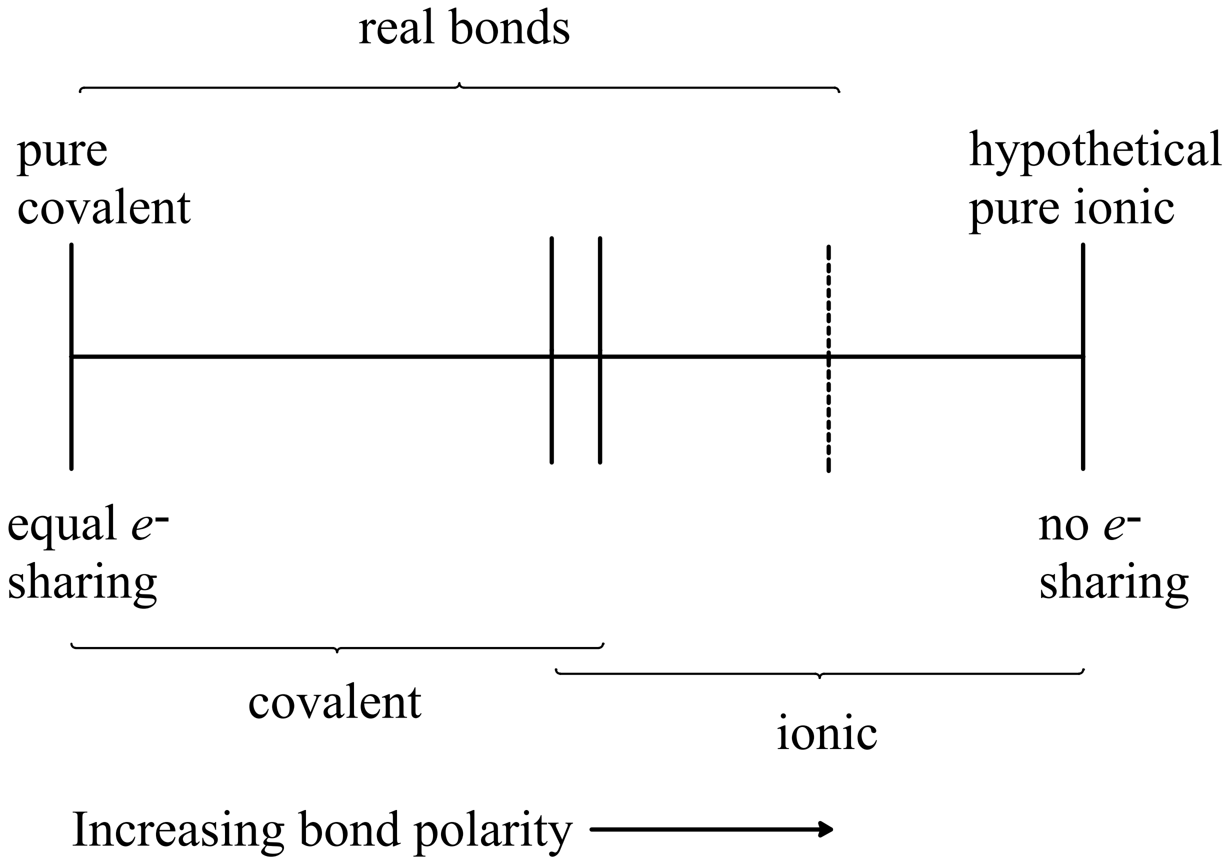


H—H



H—F

Bond Types


real bonds
pure covalent
hypothetical pure ionic
equal e^- sharing
no e^- sharing
covalent
ionic
Increasing bond polarity

Electronegativity

- The attraction an atom has for electrons *in a chemical bond* is called its **electronegativity**.

Robert S. Mulliken (1934): Electronegativity calculated as the average of ionization energy and electron affinity.

$$\chi = \frac{I + A}{2}$$

Problems:

  - Electron affinity data are not reliably known for many elements.
  - Both A and I refer to gaseous atoms, not atoms in a chemical bond.

Pauling Electronegativities

Linus Pauling - 1930's

- Pauling's scale is based on the increase in *bond energy*, *D*, for a heteronuclear bond compared to the average of the homonuclear bond energies of two bonded atoms.

$H_2(g) \rightarrow 2H(g) \qquad \Delta H^\circ = +435 \text{ kJ/mol} \equiv D(H_2)$

$F_2(g) \rightarrow 2F(g) \qquad \Delta H^\circ = +155 \text{ kJ/mol} \equiv D(F_2)$

$HF(g) \rightarrow H(g) + F(g) \qquad \Delta H^\circ = +565 \text{ kJ/mol} \equiv D(HF)$

$$\frac{D(H_2) + D(F_2)}{2} = \frac{435 \text{ kJ} + 155 \text{ kJ}}{2} = 295 \text{ kJ}$$

- Pauling attributed the extra bond strength to coulombic attraction between the partial ionic charges on the atoms created by unequal sharing; i.e., *partial ionic character*.

- The Pauling scale sets $\chi = 4.0$ as the maximum electronegativity, given to fluorine.

Electronegativities

(Pauling Scale)

	1A	2A	3B	4B	5B	6B	7B	+)	8B	),	1B	2B	3A	4A	5A	6A	7A
1	H 2.1																
2	Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
5	Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
7	Fr 0.7	Ra 0.9	Ac-No 1.1-1.7														

Periodic Trends in Electronegativity

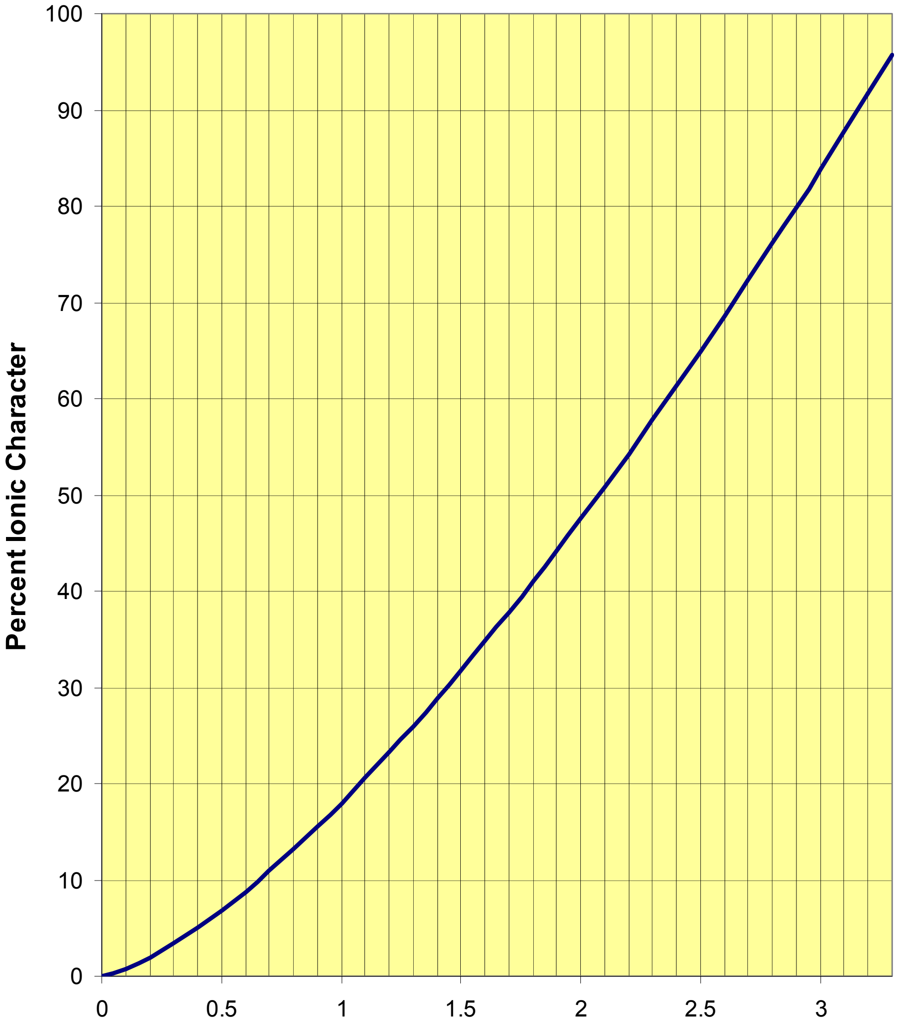
1. Electronegativity increases across a period.

2. Electronegativity decreases down a group.

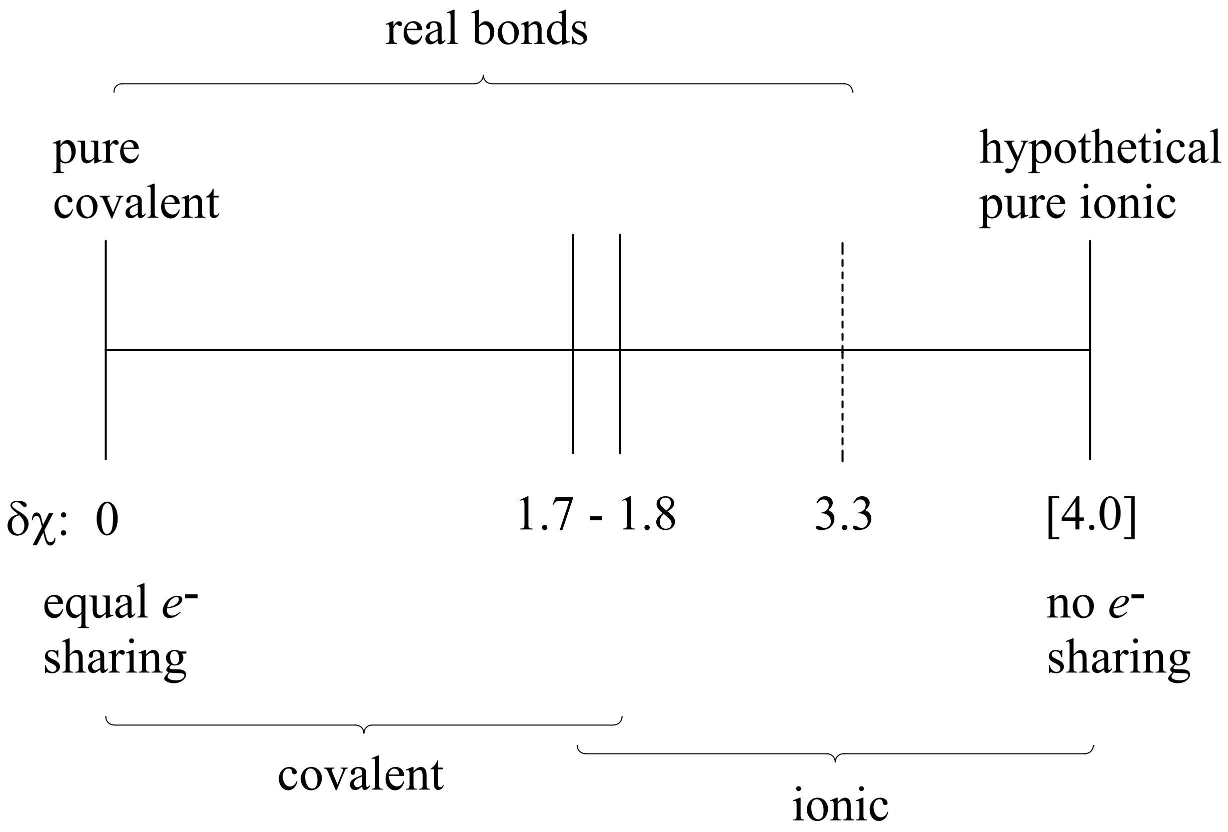
3. Metals have low electronegativities.

4. Nonmetals have high electronegativities.

Pauling's Estimatation of Ionic Character



Bond Type and Electronegativity Difference (δχ)



Increasing bond polarity ⟶

Energetics of Ionic Bond Formation[*]

- Force of attraction between an ion pair:

$$F = \frac{-q^{+}q^{-}}{r^{2}}$$

- Energy of attraction between an ion pair:

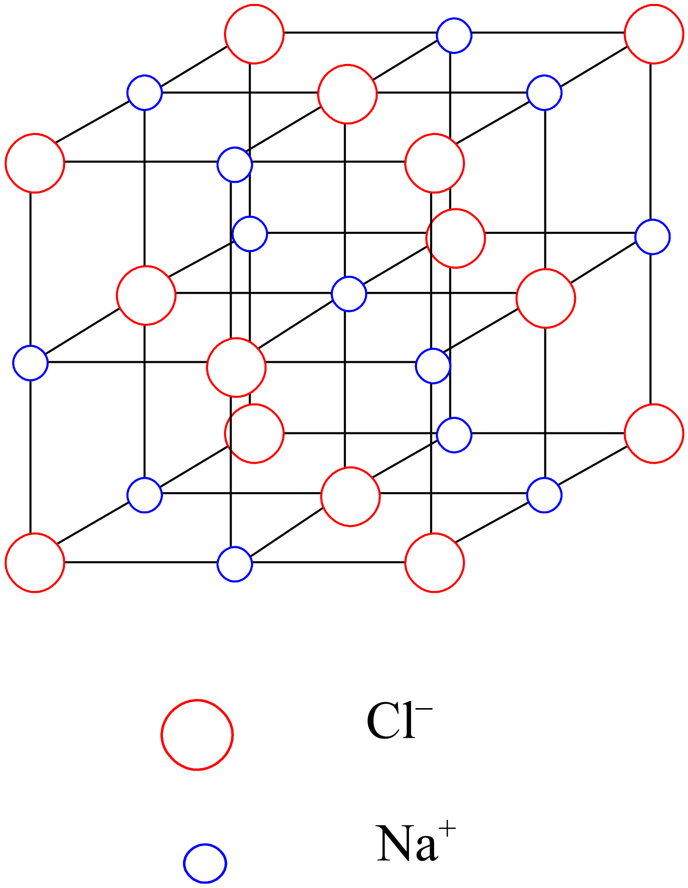
$$E = \frac{-kq^{+}q^{-}}{r}$$

where k is a proportionality constant.

---

[*] The forms of these equations depend upon the units chosen. We are only interested in the relationships they express.

The NaCl Lattice



Energetics of Ionic Crystals

- The formation of a binary ionic compound from its elements is generally an exothermic process.

$$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl_2}(g) \rightarrow \mathrm{NaCl}(s) \qquad \Delta H_f^\circ = -410.9\ \mathrm{kJ}$$

- Formation of the ions is often endothermic or weakly exothermic.

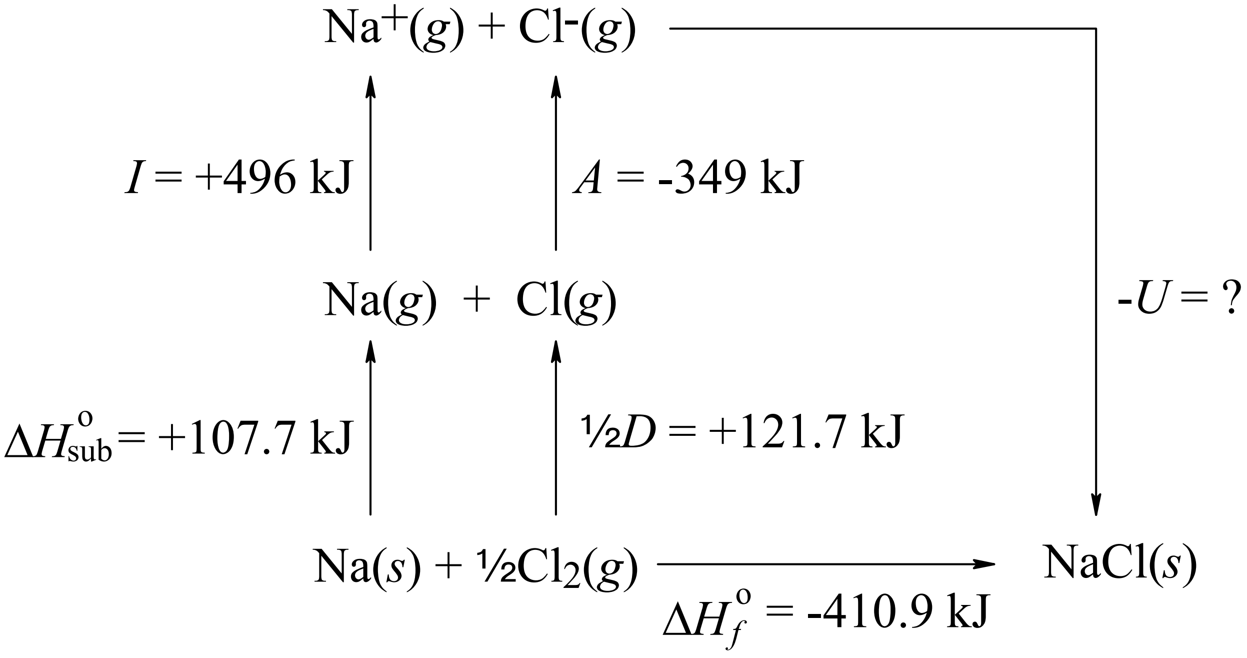
$$\begin{array}{ll}
\mathrm{Na}(s) \rightarrow \mathrm{Na}(g) & \Delta H^\circ = +107.7\ \mathrm{kJ} \\
\mathrm{Na}(g) \rightarrow \mathrm{Na}^+(g) + e^- & \Delta H^\circ = I_1(\mathrm{Na}) = +496\ \mathrm{kJ} \\
\hline
\mathrm{Na}(s) \rightarrow \mathrm{Na}^+(g) + e^- & \Delta H_f^\circ = +603.7\ \mathrm{kJ} = +604\ \mathrm{kJ}
\end{array}$$

$$\begin{array}{ll}
\tfrac{1}{2}\mathrm{Cl_2}(g) \rightarrow \mathrm{Cl}(g) & \Delta H^\circ = \tfrac{1}{2}D(\mathrm{Cl_2}) = +121.7\ \mathrm{kJ} \\
\mathrm{Cl}(g) + e^- \rightarrow \mathrm{Cl}^-(g) & \Delta H^\circ = A(\mathrm{Cl}) = -349\ \mathrm{kJ} \\
\hline
\tfrac{1}{2}\mathrm{Cl_2}(g) + e^- \rightarrow \mathrm{Cl}^-(g) & \Delta H_f^\circ = -227.3\ \mathrm{kJ} = -227\ \mathrm{kJ}
\end{array}$$

- The most favorable contribution to ΔH_f° is the energy released in bringing the ions together in the crystal lattice, the negative of the **lattice energy**, *U*, the enthalpy to dissociate one mole of ionic solid into its component gaseous ions.

$$\begin{array}{ll}
\mathrm{NaCl}(s) \rightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) & \Delta H^\circ \equiv U = +788\ \mathrm{kJ} \\
\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \rightarrow \mathrm{NaCl}(s) & \Delta H^\circ \equiv -U = -788\ \mathrm{kJ}
\end{array}$$

Born-Haber Cycle for NaCl(*s*)



$\mathrm{Na}(s)\ 6\ \mathrm{Na}(g)$	$\Delta H^o{}_{\mathrm{sub}} = 107.7$ kJ
$\mathrm{Na}(g)\ 6\ \mathrm{Na}^+(g) + e^-$	$I = 496$ kJ
$½\mathrm{Cl}_2(g)\ 6\ \mathrm{Cl}(g)$	$½D = 121.7$ kJ
$\mathrm{Cl}(g) + e^-\ 6\ \mathrm{Cl}^-(g)$	$A = –349$ kJ
$\mathrm{Na}^+(g) + \mathrm{Cl}^-(g)\ 6\ \mathrm{NaCl}(s)$	$–U = ?$
$\mathrm{Na}(s) + ½\mathrm{Cl}_2(g)\ 6\ \mathrm{NaCl}(s)$	$\Delta H^o{}_f = –410.9$ kJ

Y $\Delta H^o{}_f = \Delta H^o{}_{\mathrm{sub}} + I + ½D + A – U$

ˆ $U = \Delta H^o{}_{\mathrm{sub}} + I + ½D + A – \Delta H^o{}_f$

$= 107.7\text{ kJ} + 496\text{ kJ} + 121.7\text{ kJ} + (–349\text{ kJ}) – (–410.9\text{ kJ})$

$= 787$ kJ

Factors Favoring a More Stable Crystal Lattice

Large values of lattice energy, *U*, are favored by

1. Higher ionic charges
2. Smaller ions
3. Shorter distances between ions

Selected Lattice Energies, U^o (kJ/mol)
(Born-Haber Cycle Data)

	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1049.0	862.0	818.6	762.7	2830
Na^+	927.7	786.8	751.8	703	2650
K^+	825.9	716.8	688.6	646.9	2250
Rb^+	788.9	687.9	612	625	2170
Cs^+	758.5	668.2	635	602	2090
Mg^{2+}		2326			3795
Ca^{2+}					3414
Sr^{2+}		2127			3217