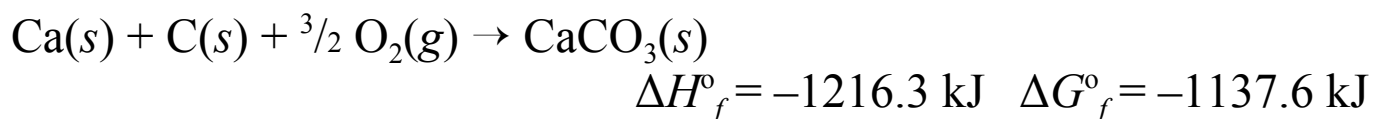
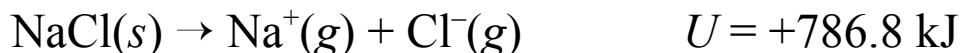


Thermodynamics of Crystal Formation

- All stable ionic crystals have negative standard enthalpies of formation, ΔH_f° , and negative standard free energies of formation, ΔG_f° .

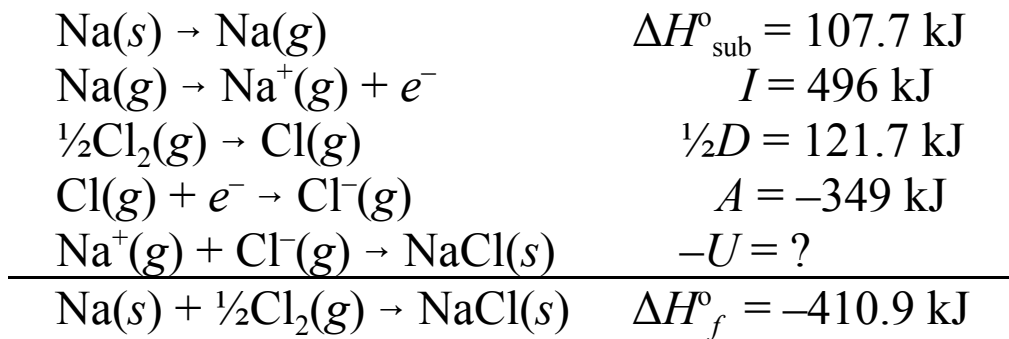
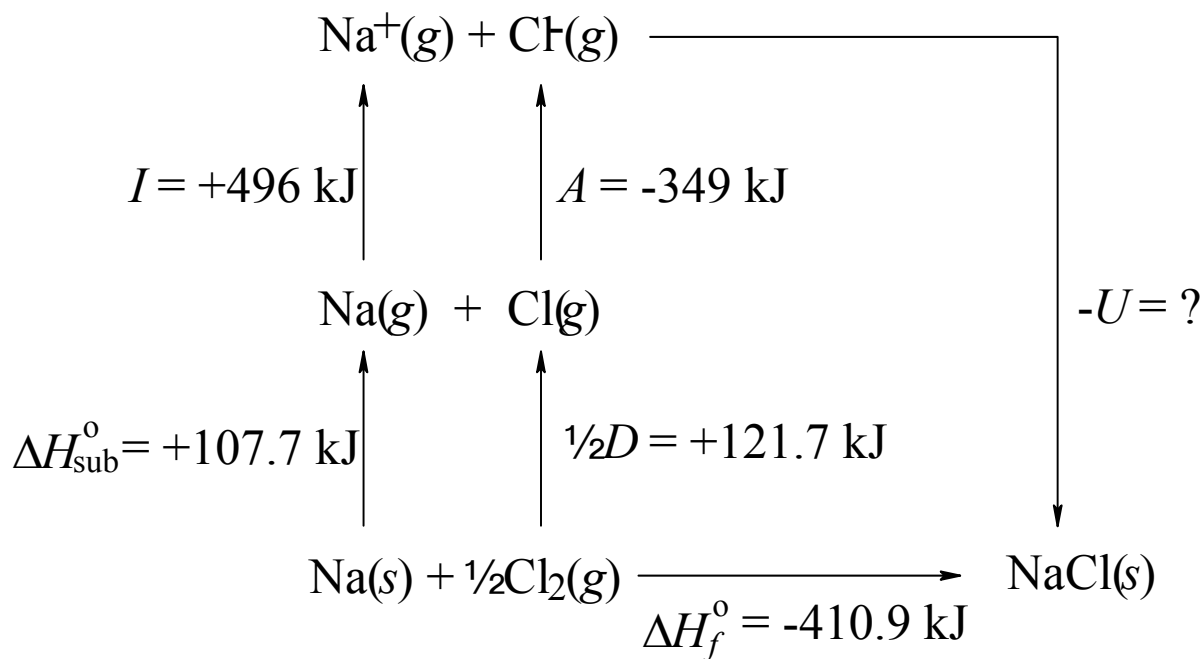


- The exothermic and spontaneous formation of ionic solids can be understood in terms of a Hess's Law cycle, called the Born-Haber cycle.
- The lattice energy is the most important factor in making the formation of ionic crystals exothermic and spontaneous.
- Lattice energy, U , is defined as the enthalpy required to dissociate one mole of crystalline solid in its standard state into the gaseous ions of which it is composed; e.g.,



- ✓ Defined in this way, lattice energy is a positive (endothermic) quantity.
- ✓ Sometimes lattice energy is defined by the reverse reaction, in which case the values are negative (exothermic).

Born-Haber Cycle for NaCl(s)



$$\Rightarrow \Delta H_f^0 = \Delta H_{\text{sub}}^0 + I + \frac{1}{2}D + A - U$$

$$\begin{aligned} \therefore U &= \Delta H_{\text{sub}}^0 + I + \frac{1}{2}D + A - \Delta H_f^0 \\ &= 107.7 \text{ kJ} + 496 \text{ kJ} + 121.7 \text{ kJ} + (-349 \text{ kJ}) - (-410.9 \text{ kJ}) \\ &= 787 \text{ kJ} \end{aligned}$$

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_0 (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⁺		2522			3795
Ca ²⁺		2253			3414
Sr ²⁺		2127			3217

Calculating Lattice Energy

- ✓ In principle, the lattice energy for a crystal of known structure can be calculated by summing all the attractive and repulsive contributions to the potential energy.
- For a pair of gaseous ions

$$U = \frac{Z^+Z^-}{r_0} \left(\frac{e^2}{4\pi\epsilon_0} \right)$$

where Z^+, Z^- = ionic charges

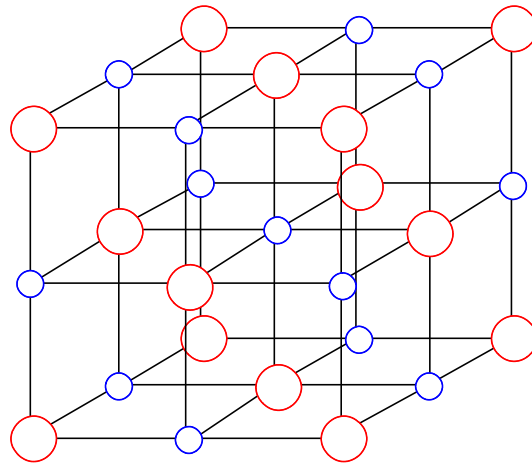
r_0 = distance between ions

e = electronic charge = 1.602×10^{-19} C

$4\pi\epsilon_0$ = vacuum permittivity = 1.11×10^{-10} C²·J⁻¹·m⁻¹

- Potential energy is negative for the attraction of oppositely charged ions and positive for repulsion of like-charged ions.
- The potential energy arising from repulsions and attractions acting on one reference ion can be calculated.
- Scaled up to a mole of ion pairs (and with a change of sign) this should equal the lattice energy of the crystal.

Calculating U for NaCl



Consider the potential energy arising from attractions and repulsions acting on a central Na⁺ ion of NaCl.

Neighbors	Distance
6 Cl ⁻	r_0
12 Na ⁺	$\sqrt{2}r_0$
8 Cl ⁻	$\sqrt{3}r_0$
6 Na ⁺	$\sqrt{4}r_0$
24 Cl ⁻	$\sqrt{5}r_0$
...	...

$$U = \frac{Z^+Z^-}{r_0} \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} + \dots \right)$$

☞ The series in parentheses converges at a value that defines the *Madelung constant*, M .

Calculating U for NaCl

- For a mole of ion pairs (N), using the Madelung constant (M), the expression for the potential energy of an NaCl-type lattice due to Coulombic interactions is

$$U = \frac{NMZ^+Z^-}{r_0} \left(\frac{e^2}{4\pi\epsilon_0} \right)$$

- ☞ For the NaCl-type lattice $M = 1.74756$, and for NaCl $r_0 = 280$ pm. Using these values, $U_{\text{NaCl}} = -867$ kJ/mol, which is too negative (cf., -786.8 kJ/mol from Born-Haber data).
 - Discrepancy arises from assuming ions are point charges.
 - Electron clouds of adjacent ions repel each other as they approach one another.

- Born proposed that the repulsive (positive) contribution to the potential energy is given by

$$U_{\text{rep}} = \frac{NB}{r^n}$$

where B is a constant specific to the ionic compound and n is a power in the range 6 - 12.

- Adding the Born repulsion correction to the Coloumbic term gives

$$U = \frac{NMZ^+Z^-}{r} \left(\frac{e^2}{4\pi\epsilon_0} \right) + \frac{NB}{r^n}$$

Born-Landé Equation

- ✓ At $r = r_0$ the potential energy must be a minimum, so

$$\left(\frac{dU}{dr} \right)_{r_0} = 0 = \frac{-NMZ^+Z^-e^2}{4\pi\epsilon_0 r_0^2} - \frac{nNB}{r_0^{n+1}}$$

- ✓ Solving for B gives

$$B = \frac{-MZ^+Z^-e^2 r_0^{n-1}}{4\pi\epsilon_0 n}$$

- ✓ Substituting for B in the equation for the Coulombic and Born contributions to potential energy gives the *Born-Landé equation*,

$$U_0 = \frac{NMZ^+Z^-e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n} \right)$$

- The value of n can be calculated from measurements of compressibility or estimated from theory.
- ☞ For NaCl, $n = 9.1$ from experiment, and the Born-Landé equation gives $U_0 = -771$ kJ/mol.
- In the absence of experimental data, Pauling's approximate values of n can be used.

Ion configuration	He	Ne	Ar, Cu ⁺	Kr, Ag ⁺	Xe, Au ⁺
n	5	7	9	10	12

Born-Mayer Equation

- Born-Landé values are approximate.
- Mayer showed that $e^{-r/\rho}$, where ρ is a constant dependant on the compressibility of the crystal, gives a better repulsion term than $1/r^n$.
- Using this improved repulsion term leads to the *Born-Mayer equation*:

$$U_0 = \frac{NMZ^+Z^-e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0} \right)$$

- $\rho = 30$ pm works well for all alkali metal halides and other simple cases when r_0 values are in pm.
- Further refinements involve terms for van der Waals (dispersion) energy and evaluation of the zero point energy.

Kapustinskii's Equation

- In the absence of detailed structural data, *Kapustinskii's equation*¹ can be used to estimate U :

$$U = \frac{1.202 \times 10^5 VZ^+Z^-}{r^+ + r^-} \left(1 - \frac{34.5}{r^+ + r^-} \right)$$

where r^+ and r^- are ionic radii (pm) and V is the number of ions per formula unit (e.g., 2 for NaCl, 3 for CaCl₂).

- Kapustinskii's equation has been used with ionic compounds containing polyatomic ions as a means of calculating their *thermochemical radii*, in which the ions are treated as spheres.²

Ion	r^- (pm)	Ion	r^- (pm)
NO ₃ ⁻	189	SO ₄ ²⁻	230
BrO ₃ ⁻	191	CrO ₄ ²⁻	240
IO ₄ ⁻	249	BeF ₄ ²⁻	245
BF ₄ ⁻	228	BO ₃ ³⁻	191
CO ₃ ²⁻	185	PO ₄ ³⁻	238

¹A. F. Kapustinskii, "Lattice energy of ionic crystals," *Quart. Rev. Chem. Soc.*, **1956**, *10*, 283–294.

²Data from R. B. Heslop and K. Jones, *Inorganic Chemistry: A Guide to Advanced Study*, Elsevier, Amsterdam, 1976, p. 123.