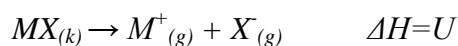


SOLIDS

LATTICE ENERGY

It is the energy released during the formation of 1 mole of crystal from its gaseous ions (exothermic) or the energy required to decompose 1 mole of crystal into gaseous ions (endothermic).



The lattice energy of a crystal is given by the electrostatic energy equation between oppositely charged ions.

$$E = - \frac{Z^+ \cdot Z^- \cdot e^2}{r}$$

Z⁺ and Z⁻: absolute charge of positive and negative ions

e⁻: electron charge

r: intercenter distance of ions

Electrostatic energy also depends on the number of ions and their arrangement (A) in space.

The pulling energy of 1 mole of crystal is

$$E = - \frac{N \cdot A \cdot Z^+ \cdot Z^- \cdot e^2}{r}$$

N: Avagadro number.

A: A constant which is related to the geometry of the crystal and is called Madelung constant.

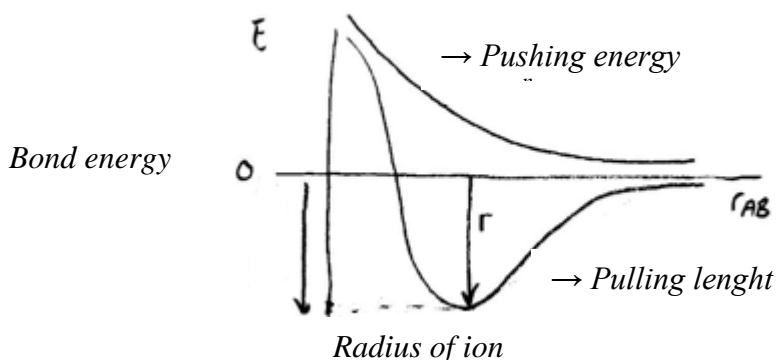
Madelung constants were calculated by considering the contributions of all ions for their crystal structure. The Madelung constants of crystals similar to each other are considered the same. For example, because the structure of AgCl is similar to that of NaCl, A value is taken as 1.74756. A values of MX₂ structures in calculations are approximately 50% larger than MX structures.

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The smaller the r value, the greater the lattice energy will be. Because the closer the ions are to each other, the stronger the attraction and the more stable the crystal will be. Mathematically, if r is 0, an infinite amount of energy will be emitted. But r cannot be 0 because when the ions are close enough to touch each other, the electron clouds of the ions push each other. The power of this pushing increases with the decrease of r value. The pushing force is given by B/r^n (B is the Born constant, n is the Born pushing term). The mean Born pushing term of some ions was determined. The n value of a crystal is found from the values of the Born pushing term of the ions as follows. For example, for LiCl, the Born pushing term for Li^+ is 5 and the Born pushing term for Cl^- is 9. The value of 7, which is the average of the two, is n value of the crystal. Chemists generally use $n=9$ for all crystals, but it is more accurate to find n by using the values of certain ions.

together is the total crystal energy (U) and this energy equation is the sum of the pulling forces in the crystal. The n value increases as the number of electrons increases.

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



The n values of ions matching the noble gas structure is the same as the n values of noble gases.

U = The lattice energy of 1 mole crystal

$$U = E_{\text{pulling}} + E_{\text{pushing}}$$

$$U = - \frac{N \cdot A \cdot z^+ \cdot z^- \cdot e^2}{r} + \frac{NB}{r^n}$$

In equilibrium (minimum point) $dU/dr = 0$ and $r = r_0$

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$$\frac{dU}{dr} = \frac{N A z^+ z^- e^2}{r_0^2} - \frac{n N B}{r_0^{n+1}} = 0 \Rightarrow \text{Born Constant } B = \frac{A \cdot z^+ z^- \cdot e^2 \cdot r_0^{n-1}}{n}$$

$$U = - \frac{N \cdot A \cdot z^+ z^- \cdot e^2}{r_0} + \frac{N \cdot B}{r_0^n} \Rightarrow U = - \frac{N \cdot A \cdot z^+ z^- \cdot e^2}{r_0} + \frac{N \cdot A \cdot z^+ z^- \cdot e^2 \cdot r_0^{n-1}}{r_0^n}$$

$$U = - \frac{N \cdot A \cdot z^+ z^- \cdot e^2}{r_0} \left(1 - \frac{1}{n} \right) \quad \text{Born-Lande Equation}$$

*ionic model
calculation method*

In SI unit this
equation

$$U = - \frac{N \cdot A \cdot z^+ z^- \cdot e^2}{4 \pi \epsilon_0 r_0} \left(1 - \frac{1}{n} \right) \quad \begin{array}{l} \epsilon_0 = \text{dielectric const.} \\ \text{free space} \\ \epsilon_0 = 8,854 \cdot 10^{-12} \text{ C}^2 \text{ J}^{-1} \end{array}$$

Theoretically, the lattice energy found in this way corresponding to the experimental values within the 3% error range.

The Born-Lande equation was slightly modified by Born-Mayer and is given as follows.

$$U = - \frac{N \cdot A \cdot z^+ z^- \cdot e^2}{4 \pi \epsilon_0 r_0} \left(1 - \frac{p}{r_0} \right)$$

$$U = - \frac{A \cdot z^+ z^- \cdot e^2 \cdot 1,39 \cdot 10^{-4}}{r_0} \left(1 - \frac{p}{r_0} \right)$$

p : compressibility constant or repulsion between electron shells of ions

p : $3.45 \times 10^{-11} \text{ m}$ (34.5 pm)

The Russian chemist Kapustinskii (1956), proposed the following relation for a crystalline lattice energy by designing a rock salt structure where all ionic structures are energy equivalent.

$$U = - \frac{n z^+ z^- \cdot K}{r_0} \left(1 - \frac{0,345 \text{ \AA}}{r_0} \right) \quad U = - \frac{n z^+ z^- \cdot K}{r_0} \left(1 - \frac{p}{r_0} \right)$$

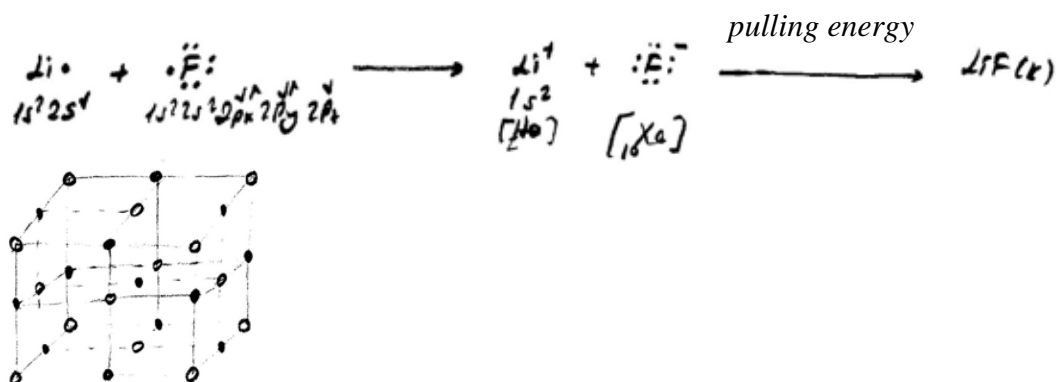
n : Total ions number in crystal structure, for example KCl: $1+1=2$

K : $1.21 \times 10^3 \text{ kJ} \cdot \text{\AA} \cdot \text{mole}^{-1}$

The Kapustinskii equation is applied to all ionic crystals and independent of the crystal structure (independent of Madelung constant). Thus the lattice energies of crystals containing non-spherical ions such as CO_3^{2-} , NO_3^- and SO_4^{2-} can be calculated.

IONIC BOND

It is called chemical bonds that are formed between the atoms of an element with high electronegativity and the atoms of an element with low electronegativity and which are based on the exchange of electrons. As a result, (+) and (-) charged ions are formed and they pull each other. Since the area around the electrically charged particles has the same effect everywhere, the ion bonds are not oriented in the direction. This is the most important feature that separates ionic bonds from covalent bonds. The strongest ionic compound is CsF.



The Na^+ ion in the middle is under the pulling effect of 6 Cl^- ions at the closest distance.

$$F_{\text{pulling}} = \frac{6(e^+ \cdot e^-)}{r} = -\frac{6e^2}{r}$$

The Na^+ ion is under the pulling effect of 8 Cl^- ions from the distance $r\sqrt{3}$ (cube diagonal)

$$F_{\text{pulling}} = \frac{8(e^+ \cdot e^-)}{r\sqrt{3}} = -\frac{8e^2}{r\sqrt{3}}$$

The central Na^+ ion is pushed by the total 12 Na^+ ions. 4 in the top, 4 in the bottom and 4 in the middle.

$$F_{\text{pushing}} = \frac{12(e^+ \cdot e^-)}{r\sqrt{2}} = +\frac{12e^2}{r\sqrt{2}}$$

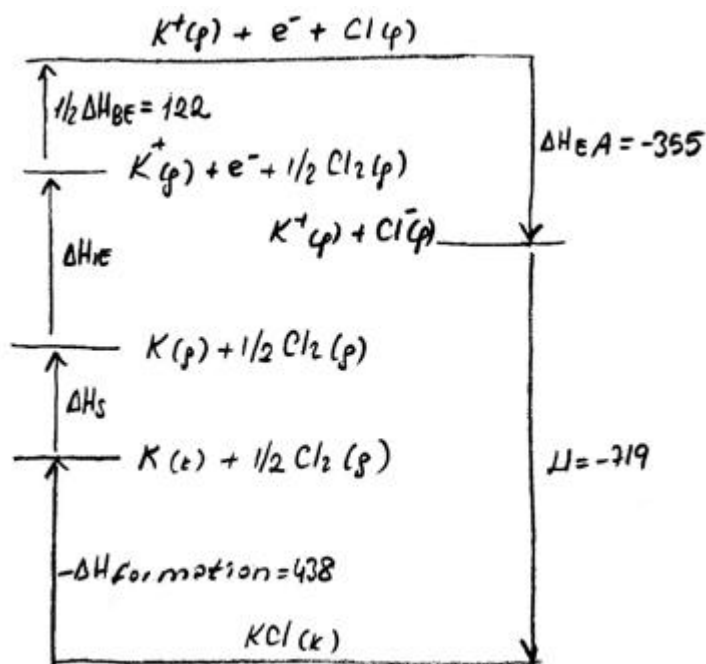
$$\Sigma = -\frac{6e^2}{r} - \frac{8e^2}{r\sqrt{3}} + \frac{12e^2}{r\sqrt{2}} = \frac{e^2}{r} \left(-6 - \frac{8}{\sqrt{3}} + \frac{12}{\sqrt{2}} \right)$$

These numbers are represented by a constant. It is called A or Madelung constant. It varies from crystal to crystal. A includes pulling and pushing forces. A varies because the distances from crystal to crystal vary.

BORN-HABER CYCLE

The lattice energy of a crystal cannot be measured directly, but can be found indirectly with the help of experimental lattice energy values, thermodynamic data and Hess's law. In 1919, for the first time Born and Haber in this way have determined the lattice energy of NaCl. In Born-Haber cycle

1. Atomization energy or sublimation energy of the metal forming the crystal= ΔH_s
2. Total ionization energy to form the cation in the crystal= $\sum \Delta H_{IE}$
3. Bond energy of the anion-forming gas molecule= ΔH_{BE} , dissociation energy
4. Electron affinity= ΔH_{EA}
5. The standard formation energy of the crystal= $\Delta H^\circ_{\text{formation}}$ is the energy released during the formation of an ionic compound from its elements under standard conditions.
6. Lattice energy = U



Because the energy received and given in this cycle balances each other or the sum of all the energy changes in the cycle from a thermodynamic point of view is 0, an ionic crystal lattice energy is

$$\Delta H_s + \frac{1}{2} \Delta H_{BE} + \sum \Delta H_{IE} + n \Delta H_{EA} + U + \Delta H^\circ_{\text{formation}} = 0$$

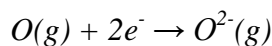
n : number of electrons required to form an anion

Since $\frac{1}{2} X_2(g) \rightarrow X(g)$, half of the total dissociation energy ($\frac{1}{2} \Delta H_{BE}$) given for molecule X_2 is used in the calculation. $\Delta H_{\text{atomization}} = \frac{1}{2} [BE + RT]$ (R is too small, R negligible)

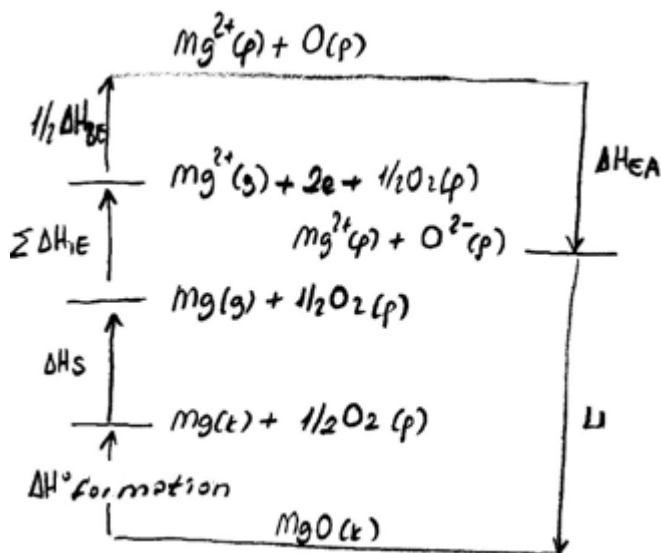
APPLICATIONS OF LATTICE ENERGY

Determination of Electron Affinity and Ion Affinity

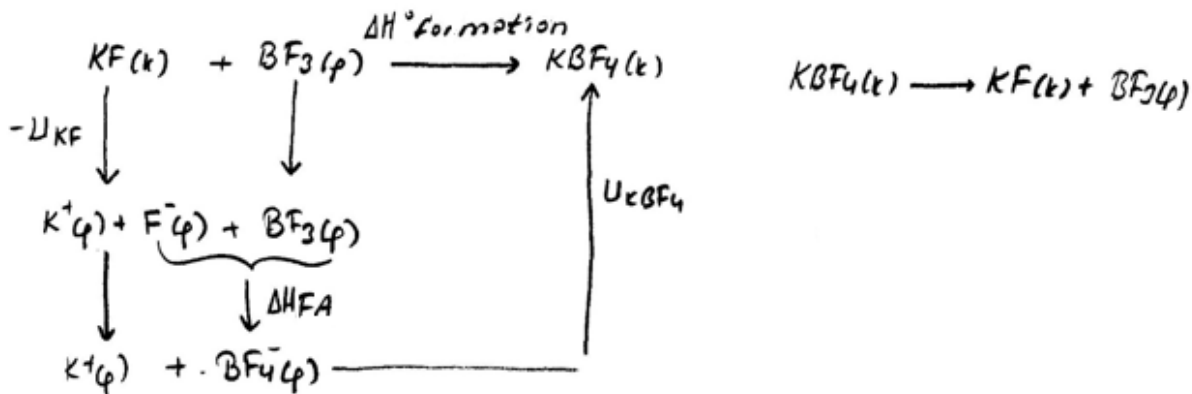
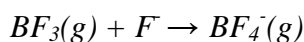
Electron affinity can be measured in atoms capable of being converted to negatively charged ions.



For this calculation Madelung constant and lattice energy can be taken from a known oxide compound, such as MgO, and the compound can be considered to be 100% ionic. $\sum \Delta H_{IE}$ is the sum of the first and second ionization energies of Mg.



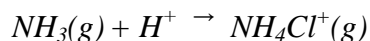
Similarly the fluoride ion affinity (ΔH_{FA}) of BF_3 can be calculated.



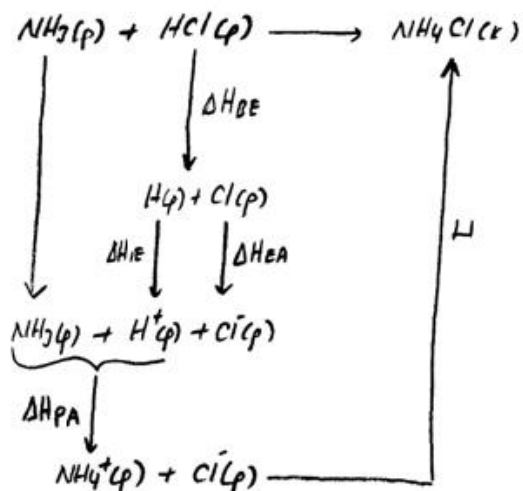
Using the lattice energy of KF and the enthalpy of the $KBF_4(k) \rightarrow KF(k) + BF_3(g)$ reaction, the F^- ion affinity of the BF_3 molecule can be calculated.

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Determination of Proton Affinity

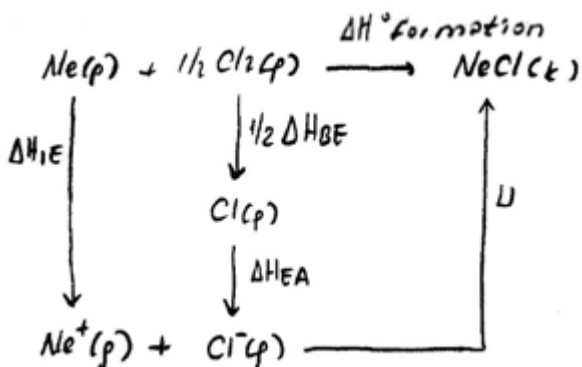


The proton affinity (PA) of this reaction is the reaction enthalpy for a proton breaking-off and it can find the Born-Haber cycle.



Determination of Disproportionation and Formation Enthalpies

One of the first applications of this method is to determine whether the neon forms a salt in the form of Ne^+Cl^- . However, it was concluded that the compound cannot be formed because it gives $\Delta H^\circ_{\text{formation}} = (+)$ value. Similarly, it was investigated whether $\text{Xe}^+\text{PtF}_6^-$ can form or not and the compound was synthesized according to the results.

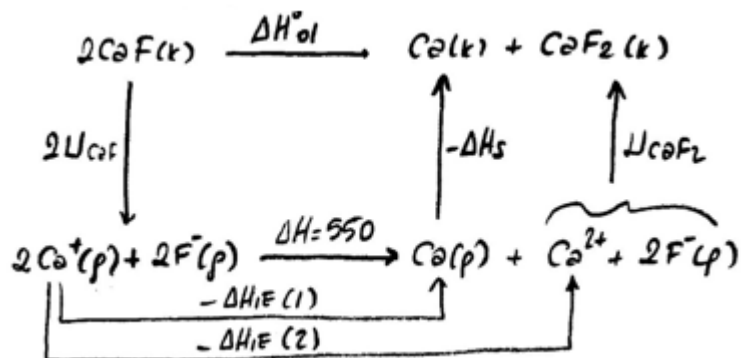


ΔH_{IE} : this value is too high, so $\Delta H^\circ_{\text{formation}}$ is endothermic.

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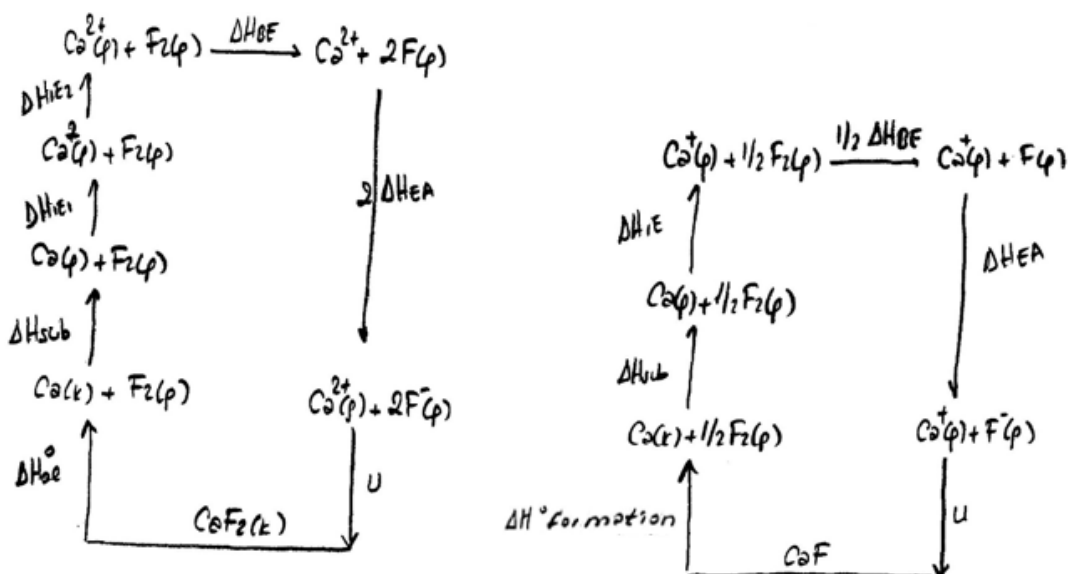
Formation probability of CaF: $2\text{CaF}(k) \rightarrow \text{CaF}_2 + \text{Ca}(k)$

Born-Haber cycle about disproportionation of CaF



CaF is unstable due to disproportionation. Enthalpy change (ΔH) was found to be +550. Therefore, Ca^+ will not make up disproportionation and the probability of obtaining Ca^+ in a solid fluoride will depend mainly on the magnitude of the lattice energies of CaF and CaF_2 .

It is expected that the lattice energy of CaF_2 will be greater than CaF for three reasons: Z^{2+} is twice as large as Z^+ . The radius of Ca^{2+} is smaller than Ca^+ . The Madelung constant of the MX_2 salt is about 1.5 times greater than that of the MX salt. Thus, the lattice energy of CaF is less than that of CaF_2 . So CaF is more unstable.



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An ionic compound is composed of gaseous ions while adopting the most stable structure, giving the lowest Gibbs energy. Therefore, the stability of a crystal depends on the value of the free energy exchange (ΔG°). The negatively smaller the value, the more stable it is. Two terms contribute to the free energy change according to the $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ correlation. The first one is the enthalpy change in crystalline formation (ΔH°) and the other is the entropy change (ΔS°). Since the transition from an irregular structure to a regular structure in the transition from the gas phase to the solid phase, entropy in crystal formation is reduced, so the entropy change is (-). In this aspect, entropy change is not in favor of crystal formation. Since crystal formation is an exothermic reaction, the enthalpy change is always (-) and makes crystal formation voluntary. The formation of solids from gaseous ions is a reaction that gives so much exothermic that the contribution of entropy to Gibbs free energy remains very small at very high temperatures. Therefore, it can be ignored alongside ΔH° . Therefore, the discussion of thermodynamic properties of solids focuses on enthalpy changes, and it is expected that the structure giving the most energy during its formation will be the most stable. The enthalpy change is related to the crystal lattice energy. Lattice energy (ΔH°_2) is defined as the standard molar enthalpy change for the formation of a crystal from gaseous ions. In order to break down a crystal into gaseous ions, energy as much as lattice energy is needed. $\Delta H_{\text{lattice}}$ is always marked (+) because the degradation of the crystal lattice is always endothermic.

$$\Delta H_{\text{atomization}} = \frac{1}{2} [BE + RT] \quad RT \text{ is not important so } \Delta H_{\text{atomization}} = \frac{1}{2} BE$$

Electron affinity may be exothermic or endothermic according to the type of nonmetal.

$$\Delta H_{\text{formation}}: \Delta H_{\text{sub}} + \frac{1}{2} BE + IE + EA - \Delta H_{\text{lattice}}$$