

Thermodynamics

First Law of Thermodynamics (also called the **Law of Conservation of Energy**):

Energy may be exchanged between a system and its surroundings but **the total energy of the system and the surroundings remains constant**, that is, energy must be conserved. Any energy lost from the system must be gained by the surroundings and any energy gained by the system is lost from the surroundings.

[The system is that part of the environment that we are concerned with. The surroundings are everything outside of the system. For example, a chemical reaction is a system and the atmosphere outside of the reaction is the surroundings.]

Energy terms:

Endothermic – the **system absorbs energy/ heat** from the surroundings

Exothermic – the **system loses energy/ heat** to the surroundings

Enthalpy (H) – a thermodynamic function/ term used to describe the energy/ heat content of a system

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

For a chemical reaction: $\Delta H = H_{\text{products}} - H_{\text{reactants}}$

The enthalpy (heat) change that accompanies a reaction is called the **enthalpy of reaction** or **heat of reaction** (ΔH_{rxn})

If $\Delta H > 0$ (i.e. a **positive** value) the reaction is **endothermic**

That is, energy must be supplied in order for the rxn. to proceed.

If $\Delta H < 0$ (i.e. a **negative** value) the reaction is **exothermic**

That is, energy is released from the rxn. No energy is required for the rxn. to proceed.

This means that exothermic rxns. are quite **feasible/ favorable** as no additional energy is required. The reactants possess enough energy and the rxn. is thermodynamically spontaneous.

➤ Calorimetry

The value of ΔH can be determined experimentally by measuring the heat flow accompanying a chemical reaction. **Measurement of heat flow is called calorimetry.**

The device used to measure heat flow is called a **calorimeter** e.g. a Styrofoam cup

e.g. (1) How much heat is required to warm 250 g of water from 22°C to 98°C? The specific heat capacity of water is 4.18 J g⁻¹ K⁻¹.

Use $q = mC_s\Delta T$ where q = quantity of heat lost or gained (J)

m = mass (g)

C_s = specific heat capacity (J g⁻¹ K⁻¹)

ΔT = change in temperature (K)

For the above question: $\Delta T = 98 - 22 = 76$ K

$$\begin{aligned}\text{Therefore: } q &= (250 \text{ g})(4.18 \text{ J g}^{-1} \text{ K}^{-1})(76 \text{ K}) \\ &= 7.9 \times 10^4 \text{ J}\end{aligned}$$

e.g. (2) When 50 mL of 1.0M HCl and 50 mL of 1.0M NaOH are mixed in a Styrofoam cup, the temperature of the resulting solution increases from 21.0°C to 27.5°C. Calculate ΔH for the reaction in kJ mol⁻¹ of HCl.

Assuming: Total volume of solution = 100 mL

Density of the solution = 1.0 g mL⁻¹

C_s of the solution is 4.18 J g⁻¹ K⁻¹

Based on the first 2 assumptions, 1 mL = 1 g

Therefore: total mass of solution = 50 + 50 = 100 g

$\Delta T = 27.5 - 21.0 = 6.5$ K

$$\begin{aligned}\text{Therefore: } q &= mC_s\Delta T \\ &= (100 \text{ g})(4.18 \text{ J g}^{-1} \text{ K}^{-1})(6.5 \text{ K}) \\ &= 2.7 \times 10^3 \text{ J}\end{aligned}$$

Since the reaction was **exothermic** (because there was an increase in temperature):

$$\Delta H = -q = -2.7 \times 10^3 \text{ J or } -2.7 \text{ kJ}$$

No. of mols of HCl used = vol. x conc./ 1000

$$= 50 \times 1.0 / 1000$$

$$= 0.050 \text{ mols.}$$

Since 0.050 mols. produced 2.7 kJ of energy:

$$\Delta H \text{ in (kJ mol}^{-1}\text{)} = -2.7 / 0.050$$

[i.e. Find ΔH for 1 mol]

$$= -54 \text{ kJ mol}^{-1} \text{ of HCl}$$

➤ Energetics of covalent bond formation (Bond enthalpy)

Bonds:

Single bonds are longer than double bonds which are longer than triple bonds.

As bond length increases, bond strength decreases.

Bond length $\text{C}\equiv\text{C} < \text{C}=\text{C} < \text{C}-\text{C}$

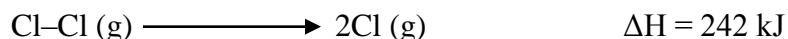
Bond strength $\text{C}-\text{C} < \text{C}=\text{C} < \text{C}\equiv\text{C}$

Also, as bond strength increases, bond enthalpy increases.

For covalent bonds to be formed, bonds in reactant molecules must be broken.

Bond enthalpy – enthalpy change/ energy required to break a chemical bond.

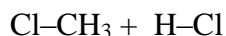
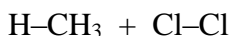
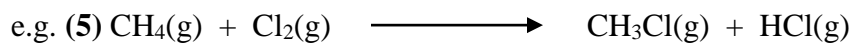
e.g. The bond enthalpy of Cl_2 is the enthalpy change when 1 mole of Cl_2 dissociates into Cl atoms:



The higher the bond enthalpy, the stronger the bond.

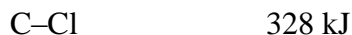
When considering bond enthalpy/ bond energy, the enthalpy change for a reaction (ΔH_{rxn}) would be equal to the total energy required to break all of the bonds in the reactants minus the total energy released when all of the bonds are formed in the products:

$$\Delta H_{\text{rxn}} = (\text{sum of bond enthalpies of bonds broken}) - (\text{sum of bond enthalpies of bonds formed})$$



Bonds broken:

Bonds formed:



$$\Delta H_{\text{rxn}} = \sum \text{of bond enthalpies of bonds broken} - \sum \text{of bond enthalpies of bonds formed}$$

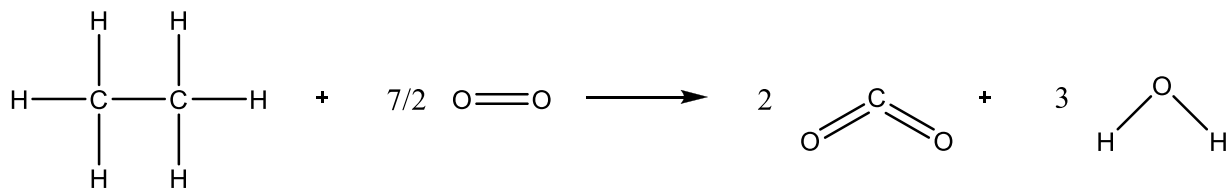
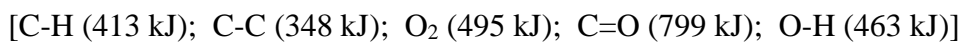
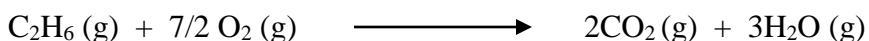
$$\Delta H_{\text{rxn}} = [\mathbf{D}(\text{C}-\text{H}) + \mathbf{D}(\text{Cl}-\text{Cl})] - [\mathbf{D}(\text{C}-\text{Cl}) + \mathbf{D}(\text{H}-\text{Cl})] \quad [\mathbf{D} = \text{symbol for Bond}$$

$$= [413 \text{ kJ} + 242 \text{ kJ}] - [328 \text{ kJ} + 431 \text{ kJ}]$$

Enthalpy]

$$= -104 \text{ kJ}$$

e.g. (6) Using bond enthalpies, calculate ΔH for the following reaction:



$$\Delta H = \sum \mathbf{D} (\text{bonds broken}) - \sum \mathbf{D} (\text{bonds formed})$$

$$= [\mathbf{D}(\text{C}-\text{C}) + 6 \mathbf{D}(\text{C}-\text{H}) + 7/2 \mathbf{D}(\text{O}=\text{O})] - [4 \mathbf{D}(\text{C}=\text{O}) + 6 \mathbf{D}(\text{O}-\text{H})]$$

$$= [348 \text{ kJ} + (6 \times 413 \text{ kJ}) + (7/2 \times 495 \text{ kJ})] - [(4 \times 799 \text{ kJ}) + (6 \times 463 \text{ kJ})]$$

$$= 4558.5 \text{ kJ} - 5974 \text{ kJ}$$

$$= -1415.5 \text{ kJ}$$

[Hint: It is often useful to draw out all of the bonds in the reactant and product molecules.]

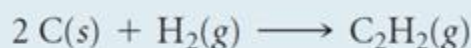
➤ Hess' Law

Hess' Law states that if a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps.

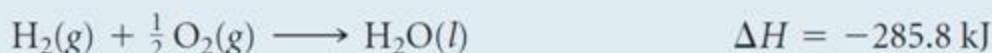
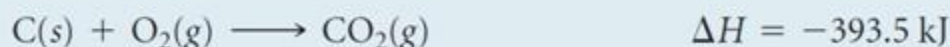
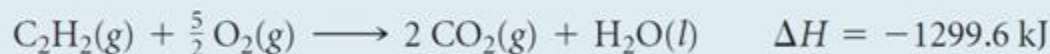
Hess' Law provides a useful means of calculating energy changes that are difficult to measure directly.

e.g. (3)

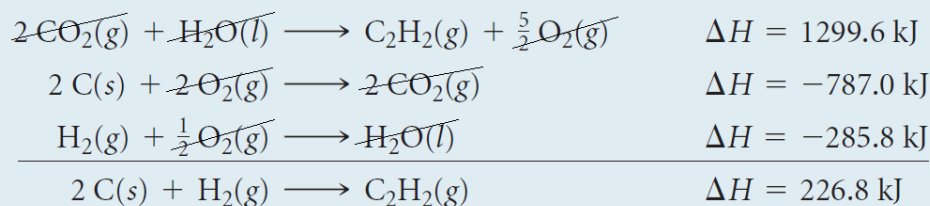
Calculate ΔH for the reaction



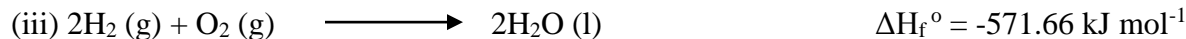
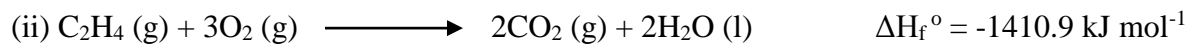
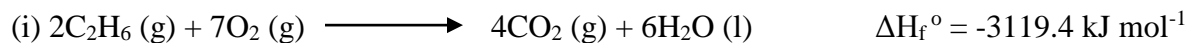
given the following chemical equations and their respective enthalpy changes:



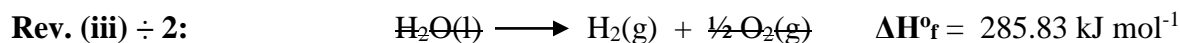
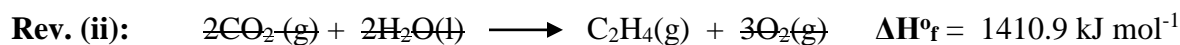
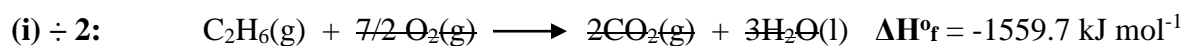
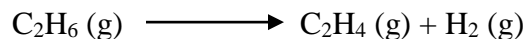
Because the target equation has C_2H_2 as a product, we turn the first equation around; the sign of ΔH is therefore changed. The desired equation has $2 \text{C}(s)$ as a reactant, so we multiply the second equation and its ΔH by 2. Because the target equation has H_2 as a reactant, we keep the third equation as it is. We then add the three equations and their enthalpy changes in accordance with Hess's law:



e.g. (4) Using the following thermochemical equations:



Find the value of ΔH_f° for the formation of ethene from ethane, i.e. ΔH_f° for the reaction:



Using Hess' Law:

$$\Delta H_f^\circ (\text{ethene}) = -1559.7 \text{ kJ mol}^{-1} + 1410 \text{ kJ mol}^{-1} + 285.83 \text{ kJ mol}^{-1} = 137.03 \text{ kJ mol}^{-1}$$

Born-Haber Cycle

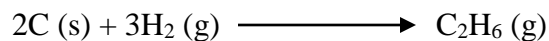
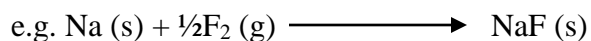
Ionic compounds result from the electrostatic force of attraction between positively-charged ions (cations) and negatively-charged ions (anions), creating a strong solid lattice structure.

The formation of ionic compounds can be envisioned as occurring via a series of distinct, defined steps each with its own energy change. The graphical representation of all of these steps is referred to as a **Born-Haber Cycle**.

Several energy transformations/ changes need to be defined:

Enthalpy of formation (ΔH_f)

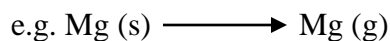
This refers to the energy change which occurs when one (1) mole of a compound in its standard state is formed from its constituent elements in their naturally occurring standard states.



[**Standard state** – the physical state of the element at **1 atm.**; **25°C (298 K)**]

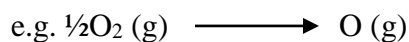
Enthalpy of vaporization (ΔH_{vap})

This refers to the energy change which occurs when a solid or liquid element is converted to one (1) mole of its gaseous atoms.



Enthalpy of atomization (ΔH_{atom})

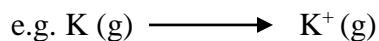
This refers to the energy change which occurs when a gaseous molecule is converted into one (1) mole of its constituent gaseous atoms.



Since energy needs to be supplied to cause vaporization and atomization, these processes are **endothermic**.

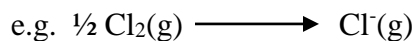
Ionization energy ($\Delta H_{\text{i.e.}}$)

This is the energy required to remove electrons from atoms or ions in their gaseous state to form one (1) mole of gaseous cations.



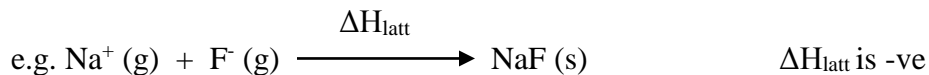
Electron affinity ($\Delta H_{\text{e.a.}}$)

This refers to the energy change which occurs when atoms in their gaseous state gain electrons to form one (1) mole of gaseous anions.



Lattice energy (ΔH_{latt})

This is the energy released when one (1) mole of an ionic compound is formed from its constituent ions in their gaseous state. Lattice energy is therefore **exothermic**.



Unlike the other energy changes (ΔH_{vap} , ΔH_{atom}) lattice energy cannot be measured directly; its value is determined by the construction of a **Born-Haber Cycle**.

Approach to the Born-Haber Cycle:

- Determine the **naturally occurring states** of all chemical species i.e. whether they are solid, liquid or gas.
- Convert all solid or liquid reactants to their gaseous state (ΔH_{vap}).
- Convert all molecular reactants (e.g. gases) to their atoms (ΔH_{atom}).
- Ionize all reactants appropriately (i.e. whether by ionization energy ($\Delta H_{\text{i.e.}}$) or electron affinity ($\Delta H_{\text{e.a.}}$)).
- Fill in the given **energy value** for each step/ energy change.
- Using **Hess' Law**, determine the missing value.

e.g. (7) Construct a Born-Haber cycle for the formation of lithium chloride and use this cycle to calculate the lattice energy of lithium chloride from the following data:

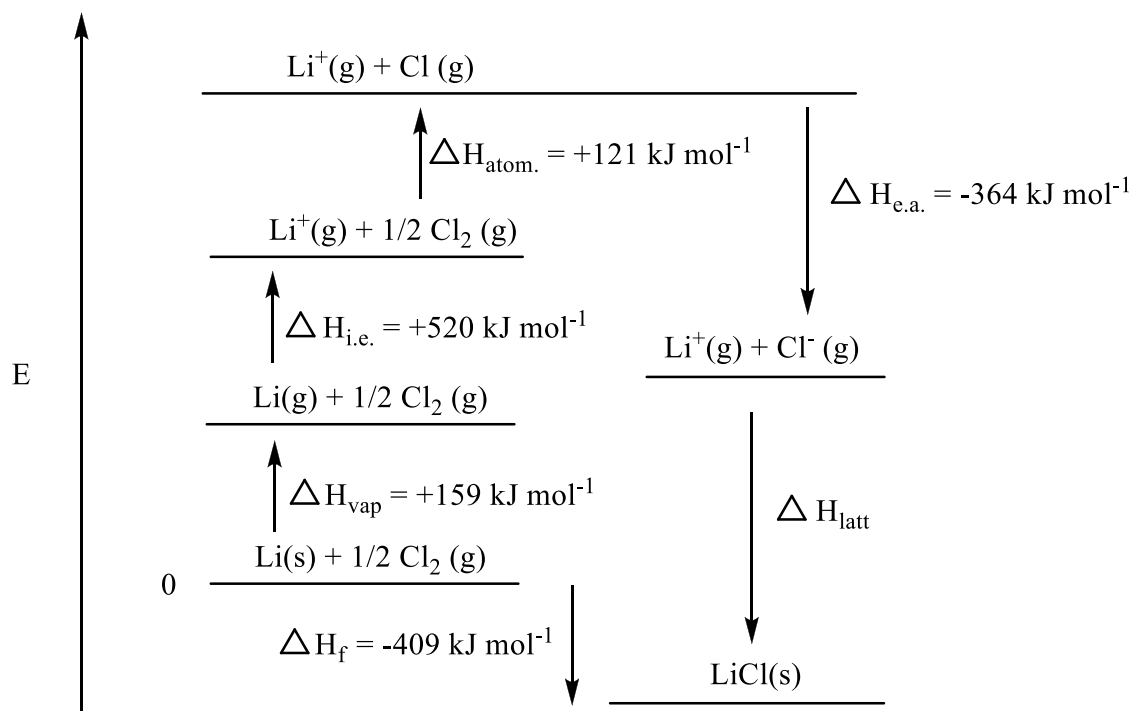
First ionization energy for lithium, $\Delta H = +520 \text{ kJ mol}^{-1}$

Enthalpy of vaporization of lithium, $\Delta H = +159 \text{ kJ mol}^{-1}$

Enthalpy of atomization of chlorine, $\Delta H = +121 \text{ kJ mol}^{-1}$

Electron affinity of chlorine atoms, $\Delta H = -364 \text{ kJ mol}^{-1}$

Enthalpy of formation of lithium chloride, $\Delta H = -409 \text{ kJ mol}^{-1}$



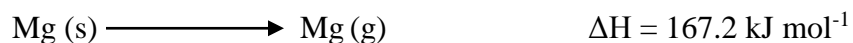
Using Hess' Law, ΔH for the overall change will be equal to the sum of all the ΔH values for the individual steps:-

$$\Delta H_f (\text{LiCl}) = \Delta H_{\text{vap}} (\text{Li}) + \Delta H_{\text{i.e.}} (\text{Li}) + \Delta H_{\text{atom}} (\text{Cl}) + \Delta H_{\text{e.a.}} (\text{Cl}) + \Delta H_{\text{latt}} (\text{LiCl})$$

$$-409 \text{ kJ mol}^{-1} = (+159 \text{ kJ mol}^{-1}) + (+520 \text{ kJ mol}^{-1}) + (+121 \text{ kJ mol}^{-1}) + (-328 \text{ kJ mol}^{-1}) + \Delta H_{\text{latt}}$$

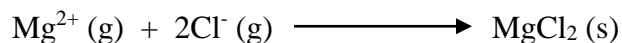
$$\Delta H_{\text{latt}} (\text{LiCl}) = -845 \text{ kJ mol}^{-1}$$

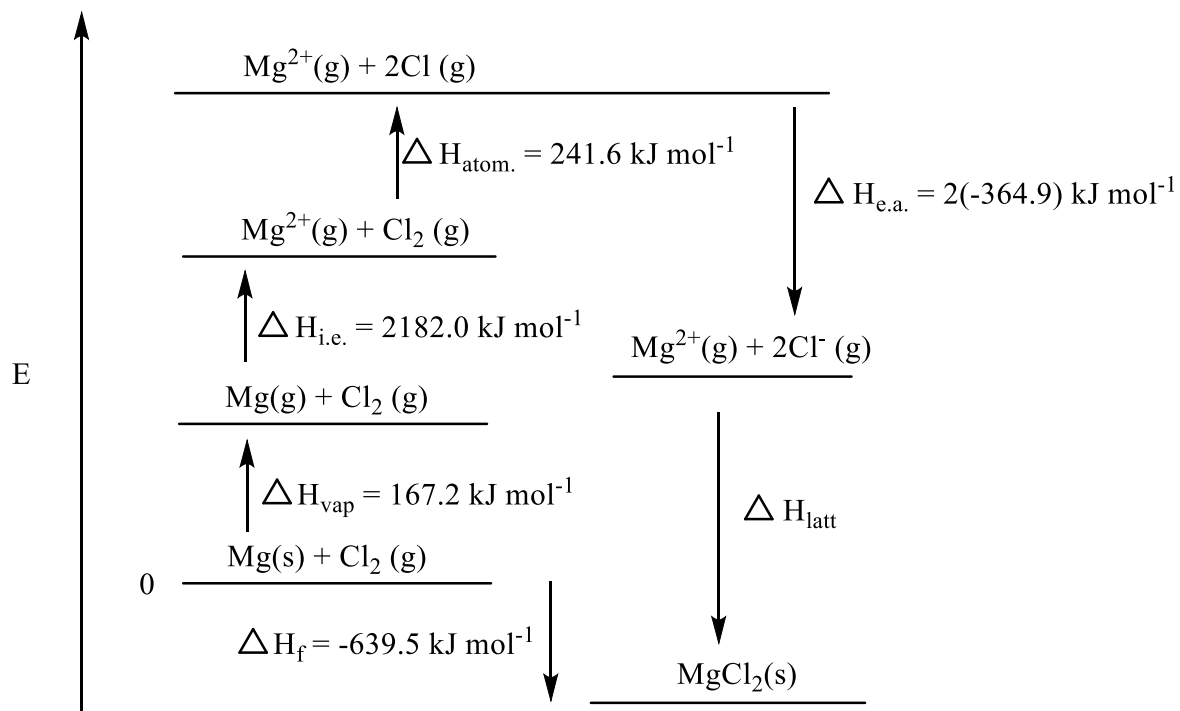
e.g. (8) Given the following data:



$$\Delta H \text{ formation of MgCl}_2 = -639.5 \text{ kJ mol}^{-1}$$

Calculate the lattice energy of MgCl_2 , i.e. for ΔH the process:





Using Hess' Law:

$\Delta H_f(\text{MgCl}_2) = \Sigma \Delta H$ values for all the individual steps

$$-639.5 \text{ kJ mol}^{-1} = 167.2 \text{ kJ mol}^{-1} + 2182.0 \text{ kJ mol}^{-1} + 241.6 \text{ kJ mol}^{-1} + 2(-364.9) \text{ kJ mol}^{-1} + \Delta H_{\text{latt}}$$

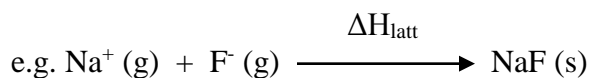
$$-639.5 \text{ kJ mol}^{-1} = 1861 \text{ kJ mol}^{-1} + \Delta H_{\text{latt}}$$

$$\Delta H_{\text{latt}}(\text{MgCl}_2) = -2500.5 \text{ kJ mol}^{-1}$$

Lattice Energy

Ionic compounds are extremely stable due to the attraction between ions of opposite charge. This attraction enables the ions to form a solid arrangement known as a **lattice**.

Lattice energy – This is the energy released when one (1) mole of an ionic compound is formed from its constituent ions in their gaseous state.



This process releases a large amount of energy, i.e. it is **highly exothermic**.

Therefore, lattice energy is a **measure of the stability** of an ionic compound and the force of attraction between its oppositely-charged ions.

Lattice energy increases as: (1) Ionic radius decreases

(2) Charges on the ions increase

e.g. Consider MgF_2 and CaF_2 . Which would have the higher lattice energy?

MgF_2 has the higher lattice energy. Due to the **smaller ionic radius** of Mg^{2+} , the force of attraction between Mg^{2+} and F^- is greater than that between Ca^{2+} and F^- . Mg^{2+} and F^- are **bonded more strongly in its lattice** and a larger amount of energy is therefore released when the lattice is formed.

e.g. Consider NaF and CaO . Which would have the higher lattice energy?

Recall: $\text{NaF} = \text{Na}^+ \text{F}^-$ $\text{CaO} = \text{Ca}^{2+} \text{O}^{2-}$

CaO has the higher lattice energy due to its **composite ions having higher charges** than those of NaF , therefore the force of attraction between Ca^{2+} and O^{2-} is greater and a larger amount of energy is therefore released when the lattice is formed.

In the above examples, since MgF_2 and CaO have the **higher lattice energies**, they are **more stable** ionic compounds than CaF_2 and NaF respectively.



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