



# Thermodynamics Guide

*Definitions, guides, and tips*



# Definitions

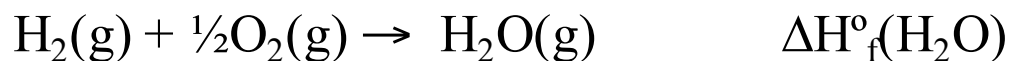
*What each thermodynamic value means*

# Enthalpy of Formation



## Definition

*The enthalpy required or released during formation of a molecule from its elements.*



**Sign:**  $\Delta\text{H}^\circ_{\text{f}}$  can be positive or negative.

**Direction:** From elements to product.

**Phase:** The phase of the product being formed can be anything, but the elemental starting materials must be in their elemental standard phase.

## Notes:

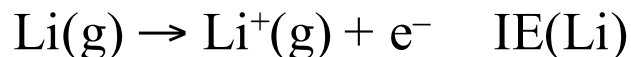
- RC&O Appendix 1 collects these values.
- Limited by what values are experimentally available.
- Knowing the elemental form of each atom is helpful.

# Ionization Enthalpy (IE)



## Definition

*The enthalpy required to remove one electron from an atom or ion.*



**Sign:** IE is always positive — removing electrons from proximity of nucleus requires enthalpy input

**Direction:** IE goes from atom to ion/electron pair.

**Phase:** IE is a gas phase property. Reactants and products must be gas phase.

## Notes:

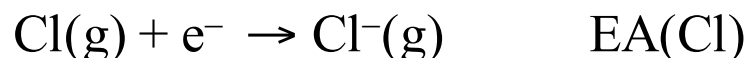
- Phase descriptors are not generally given to an electron.
- Ionization energy is taken to be identical to ionization enthalpy.
- The first IE of Li(g) is shown above. A second, third, or higher IE can also be determined. Removing each additional electron costs even more enthalpy.

# Electron Affinity (EA)



## Definition

*How much enthalpy is gained when an electron is added to an atom or ion.  
(How much an atom “wants” an electron).*



**Sign:** EA is always positive, but the **enthalpy is negative:**  $\Delta H^\circ_{\text{rxn}} < 0$ . This is because of how we describe the property as an “affinity”. Adding electrons is exothermic, so usually a negative sign needs to be added to the provided value!

**Direction:** EA goes from atom/electron pair to an anion.

**Phase:** EA is a gas phase property. Reactants and products must be gas phase.

## Notes:

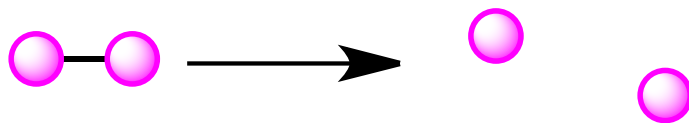
- Phase descriptors are not generally given to an electron.
- The first EA of Cl(g) is shown above. A second, third, or higher EA can also be determined.

# Bond Dissociation Enthalpy



## Definition

*The enthalpy required to break a bond homolytically.*



**Sign:** BDE is always positive — breaking bonds requires enthalpy input

**Direction:** BDE is the breaking of bonds.



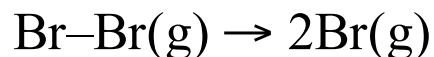
**Phase:** Not always explicitly given. Usually gas phase.

# BDE Cases with Multiple Bonds

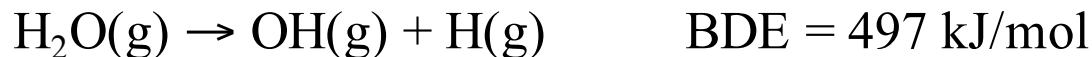


*Is each bond different?*

*Bromine has a single BDE:*



*Water has two bonds, each with different energy:*



**BDE(O–H) for water = 462 kJ/mol** (average of first and second BDE)

*Because the values are averages, can use as a good approximation for **any molecule**.*

*Methane, ethane, propane: all made of  $sp^3$  C–H bonds, all have:  
 $\text{BDE}(\text{C}–\text{H}) = 411 \text{ kJ/mol}$  (per C–H bond)*



## Definition

*Enthalpy released when gas phase ions come together to form a solid ionic lattice*



**Sign:**  $\Delta H^\circ_{\text{latt}}$  is always negative (exothermic to form a lattice). Gas phase ions are generally quite unstable.

**Direction:** From gas phase ions to solid lattice.

**Phase:** Gas phase ion reactants moving to solid phase salt product.

## Notes:

- Very often required when dealing with thermodynamics of salts.
- $\Delta H^\circ_{\text{lattice}}$  can be estimated using the Born-Landé equation.

$$\Delta H^\circ_{\text{lattice}} = -\frac{N_A \cdot A \cdot z^+ \cdot z^- \cdot e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$



# Enthalpy of Vaporization



## Definition

*Enthalpy change when a molecule moves from liquid phase to gas phase*



**Sign:** Can be positive or negative.

**Direction:** From liquid phase molecule to gas phase molecule.

**Phase:** Liquid phase reactants to gas phase product.

## Notes:

- Does not involve covalent bond breaking.

# Enthalpy of Sublimation



## *Definition*

*Enthalpy change when a molecule moves from solid phase to gas phase*



**Sign:** Can be positive or negative.

**Direction:** From solid phase molecule to gas phase molecule.

**Phase:** Solid phase reactants to gas phase product.

## **Notes:**

- No covalent bonds breaking.

# Enthalpy of Fusion



## *Definition*

*Enthalpy change when a molecule moves from solid phase to liquid phase*



**Sign:** Can be positive or negative.

**Direction:** From solid phase molecule to liquid phase molecule.

**Phase:** Solid phase reactants to liquid phase product.

## **Notes:**

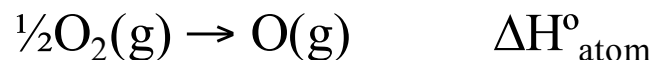
- No covalent bonds breaking.

# Enthalpy of Atomization



## Definition

*Enthalpy required to generate 1 mole of gas phase atoms from the elemental form*



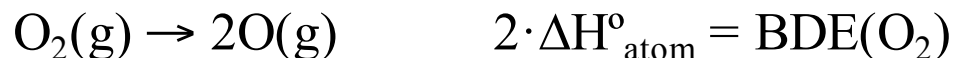
**Sign:**  $\Delta H^\circ_{\text{atom}}$  is almost always positive (endothermic to break bonds and form gas phase atoms).  $\Delta H^\circ_{\text{atom}} = 0$  for noble gases (they are already atoms!).

**Direction:** Atoms are the product.

**Phase:** Resulting atoms are gas phase, but starting material takes the phase of the subject elemental form.

## Notes:

- Involves bond breaking. Either metallic bonds or covalent bonds are broken.
- Often the same as other thermodynamic values:

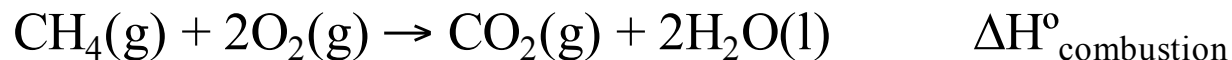


# Enthalpy of Combustion



## Definition

*Enthalpy change when a molecule reacts with O<sub>2</sub> to form CO<sub>2</sub> and H<sub>2</sub>O*



**Sign:** Positive or negative, but usually hydrocarbon combustion is exothermic.

**Direction:** With CO<sub>2</sub> and H<sub>2</sub>O as products.

**Phase:** Variable — depending on the conditions of measurement. Typically, standard phase species will be used (especially liquid water and gaseous CO<sub>2</sub>). Combustion reactant (methane in example above) is more often in gas phase, even if that is not the standard phase (i.e. octane gas).

## Notes:

- Enthalpy of combustion values are not always available. This reaction type is a common subject of predictive questions: i.e. “predict  $\Delta H^\circ_{\text{combustion}}$  based on enthalpy of formation values.”



# Guides

*How to use thermodynamic values to solve problems*

# Enthalpy of Formation

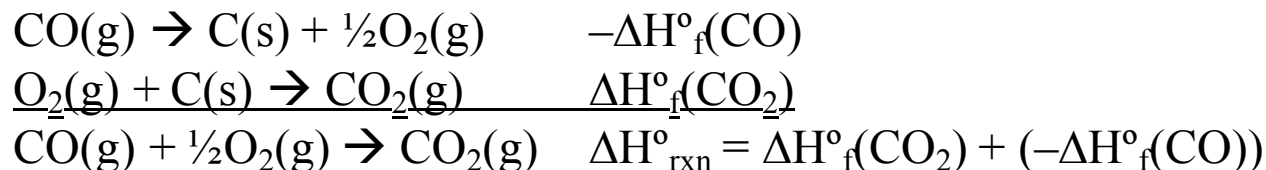


*Use enthalpy of formation to calculate enthalpy of a reaction:*



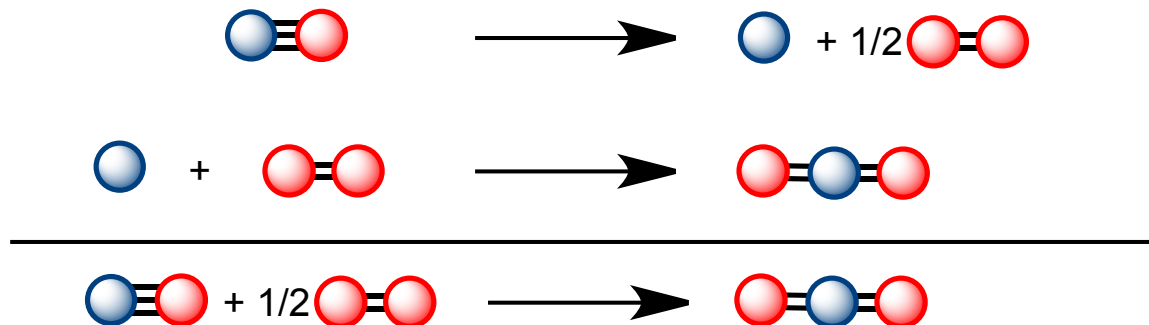
- 1. Is an enthalpy of formation value available for each reactant and product?*
- 2. Use the following expression, derived from a sum of  $\Delta H^\circ_{\text{f}}$  reactions.*

$$\Sigma(\text{Enthalpy of products}) - \Sigma(\text{enthalpy of reactants}) = \Delta H^\circ_{\text{rxn}}$$



*In cartoon form:*

*(1) Break up CO into elements ( $-\Delta H^\circ_{\text{f}}$ ). (2) combine elements to form  $\text{CO}_2$ .*

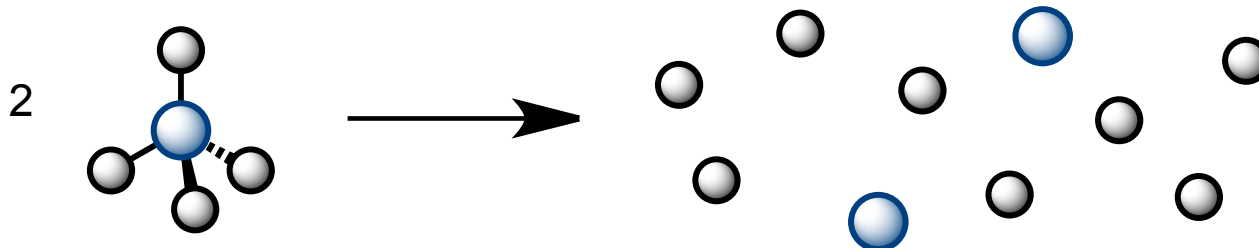


# Bond Dissociation Enthalpy

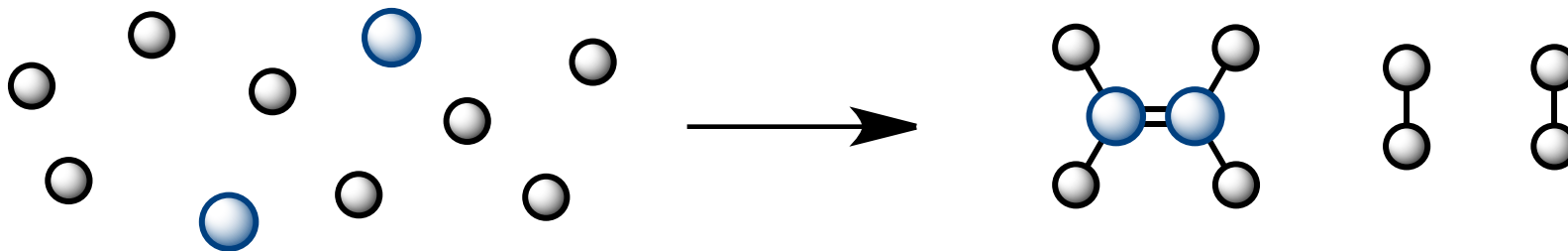


Using BDE to calculate enthalpy of reaction:

1. "Blow up" the reactants into individual atoms!



2. Assemble the free atoms into the product structure.



3. Net reaction:  $2\text{CH}_4(\text{g}) \rightarrow \text{H}_2\text{C}=\text{CH}_2 + 2\text{H}_2(\text{g})$

- Good for covalent molecules (bonds required).
- $\Delta H^\circ_{\text{rxn}} = \text{BDE}(\text{reactants}) - \text{BDE}(\text{products})$

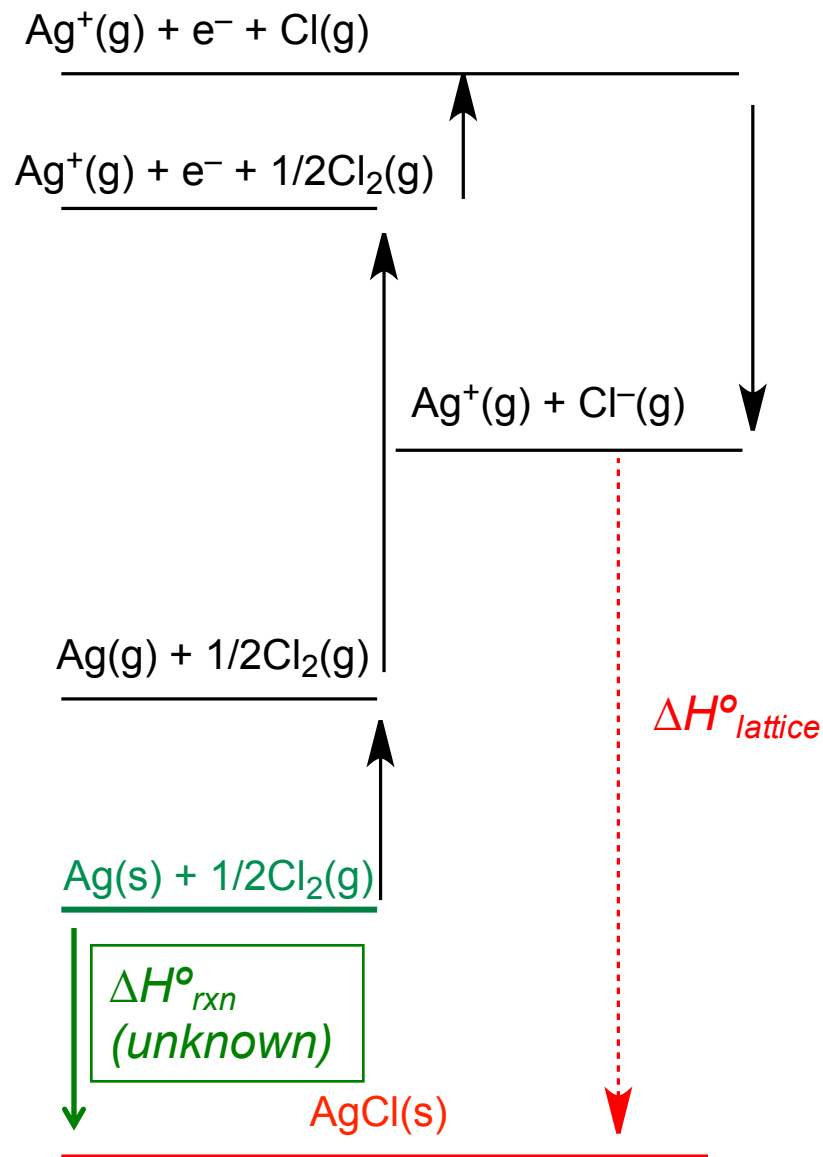


# Lattice Enthalpy



Use lattice enthalpy to calculate enthalpy of a reaction:  $\text{Ag(s)} + 1/2\text{Cl}_2(\text{g}) \rightarrow \text{AgCl(s)}$

- A thermochemical cycle involving a salt will often require lattice enthalpy.
- The lattice enthalpy generates gas phase ions, which are readily converted to gas phase atoms using **ionization enthalpy** or **electron affinity** values.
- Gas phase atoms can be related to almost anything using **enthalpy of atomization** or **bond dissociation enthalpy** values.
- Once a complete Born-Haber cycle is constructed, write an equation to solve for the unknown value.
- Note that  $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{f}}(\text{AgCl(s)})$  in this special case.

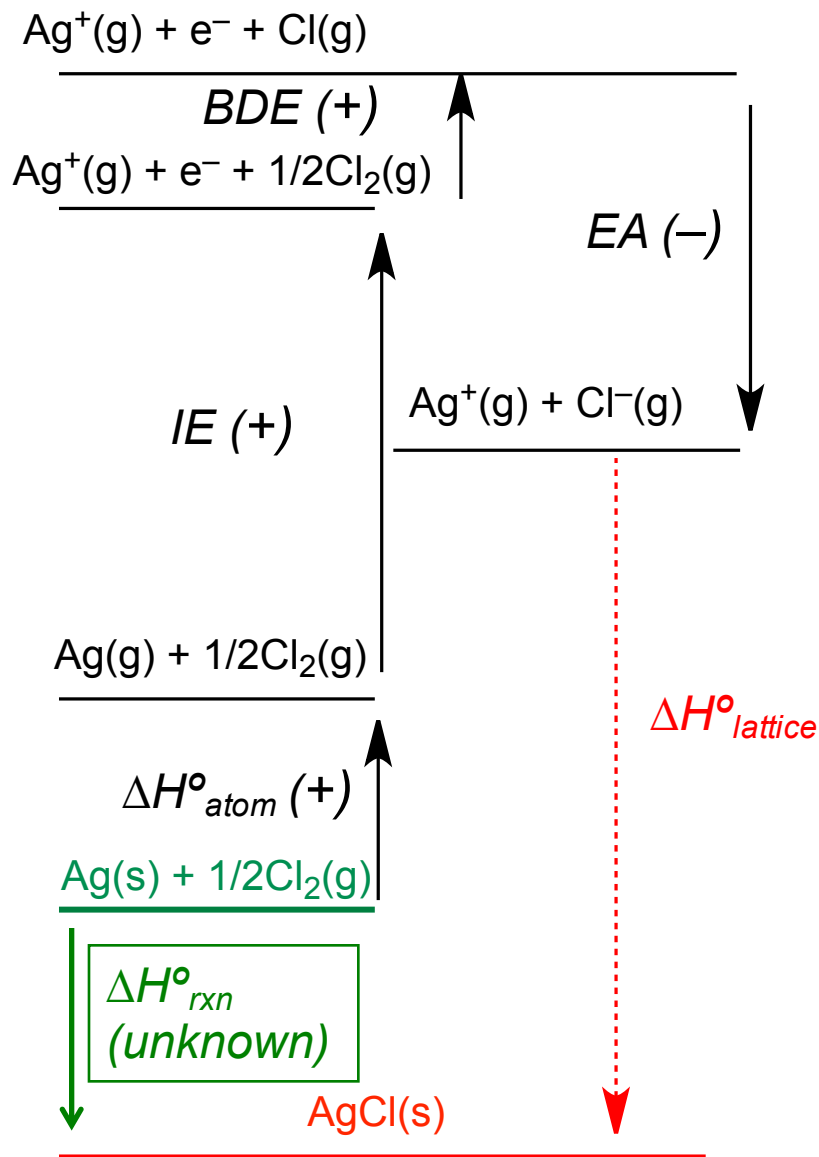


# Lattice Enthalpy



Use lattice enthalpy to calculate enthalpy of a reaction:  $\text{Ag(s)} + 1/2\text{Cl}_2(\text{g}) \rightarrow \text{AgCl(s)}$

- Signs: The Born-Haber diagram should be drawn such that moving from a lower energy level to a higher energy level will have a positive sign.
- Arrowheads indicate the direction of the reaction (which may be the opposite direction from thermodynamic value, leading to a sign change).
- An equation solving for  $\Delta H^\circ_{\text{rxn}}$  is shown below. The equation is a summation (all numbers added) but some of the values will have negative signs in front of them.



$$0 = -\Delta H^\circ_{\text{rxn}} + \Delta H^\circ_{\text{atom}} + \text{IE} + \text{BDE} + (\text{EA}) + \Delta H^\circ_{\text{latt}}$$

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{atom}} + \text{IE} + \text{BDE} + (\text{EA}) + \Delta H^\circ_{\text{latt}}$$