

THERMOCHEMISTRY

Lecture 14



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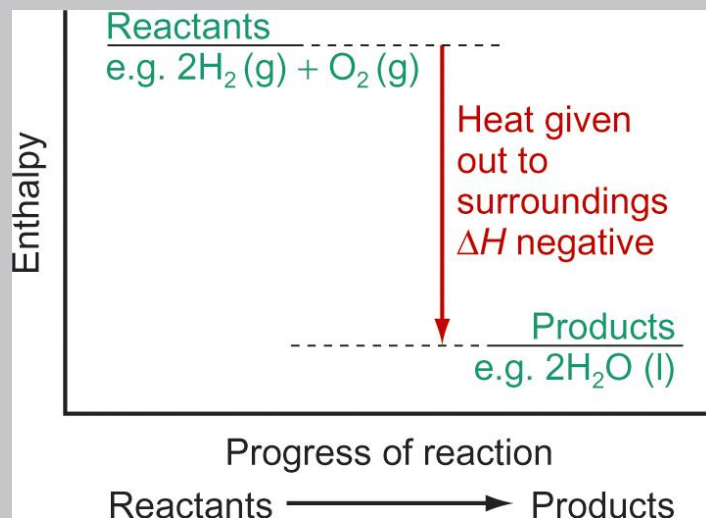
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HEAT OF REACTION - ΔH

thermochemistry – studies heat changes that occur during reactions

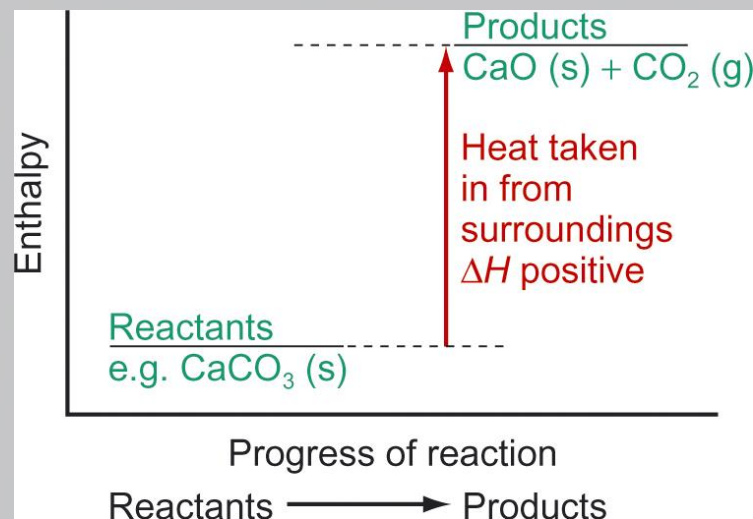
heat (q) – energy that is transferred as a result of temperature differences

enthalpy change, ΔH or $\Delta_{\text{rxn}}H$ - heat transferred at constant pressure by a chemical reaction or process



Reaction can **give off heat** and warm the 'outside'

$\Delta_{\text{rxn}}H$ becomes **negative**
EXOTHERMIC reaction (e.g. combustion)



Reaction can 'give off cold' and cool down the 'outside' (**absorbs heat**)

$\Delta_{\text{rxn}}H$ becomes **positive**
ENDOTHERMIC reaction (e.g. cold pack)

unit of heat: Joule, $1 \text{ J} = 1 \text{ Nm} = 1 (\text{kgms}^{-1})\text{m} = 1 \text{ kgm}^2\text{s}^{-2}$



ΔH – MOLAR QUANTITY



$$\Delta_{\text{rxn}} H = +178 \text{ kJ}$$

endothermic

1 mole of $\text{CaCO}_3 (\text{s})$ reacts
1 mole of $\text{CaO} (\text{s})$ produced
1 mole of $\text{CO}_2 (\text{g})$ produced

needs 178 kJ
needs 178 kJ
needs 178 kJ



2 moles of $\text{CaCO}_3 (\text{s})$ react
2 moles of $\text{CaO} (\text{s})$ produced
2 moles of $\text{CO}_2 (\text{g})$ produced

needs 356 kJ
needs 356 kJ
needs 356 kJ



ΔH – MOLAR QUANTITY



$$\Delta_{\text{rxn}} H = -1267 \text{ kJ}$$

exothermic

4 moles of $\text{NH}_3 (\text{g})$ react

-1267 kJ

gives off 1267 kJ

1 mole of $\text{NH}_3 (\text{g})$ reacts

-1267/4 = -317 kJ

gives off 317 kJ

3 moles of $\text{O}_2 (\text{g})$ react

-1267 kJ

gives off 1267 kJ

1 mole of $\text{O}_2 (\text{g})$ reacts

-1267/3 = -422 kJ

gives off 422 kJ

2 moles of $\text{N}_2 (\text{g})$ form

-1267 kJ

gives off 1267 kJ

1 mole of $\text{N}_2 (\text{g})$ forms

-1267/2 = -633 kJ

gives off 633 kJ

6 moles of $\text{H}_2\text{O} (\text{g})$ form

-1267 kJ

gives off 1267 kJ

1 mole of $\text{H}_2\text{O} (\text{g})$ forms

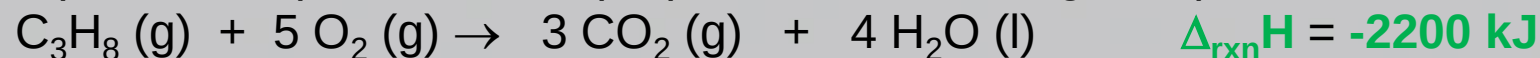
-1267/6 = -211 kJ

gives off 211 kJ



SAMPLE PROBLEM

A portable cap stove burns propane fuel according to equation:



How much heat will be released when 500g of propane combusts completely in oxygen?

When 1 mol of C_3H_8 reacts with oxygen, 2200 kJ of energy is released.

How many moles of C_3H_8 in 500 g? molar mass = 44.1 g/mol

Heat supplied by burning 500 g C_3H_8

$$500 \text{ g C}_3\text{H}_8 \times \frac{1 \text{ mol}}{44.1 \text{ g}} = 11.3 \text{ mol C}_3\text{H}_8$$

$$2220 \frac{\text{kJ}}{\text{mol}} \times 11.3 \text{ mol} = 25200 \text{ kJ}$$

ALTERNATIVELY use **proportions**:

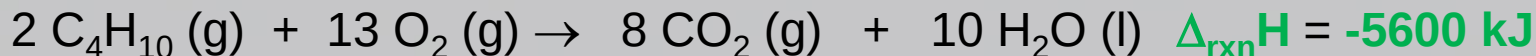
$$\frac{500 \text{ g}}{44.1 \text{ g}} = \frac{\text{heat released}}{2220 \text{ kJ}}$$

$$\text{heat released} = \frac{500 \text{ g} \times 2220 \text{ kJ}}{44.1 \text{ g}} = 25200 \text{ kJ}$$



SAMPLE PROBLEM

How much heat will be released when 2.9 g of butane (molar mass 58.0 g/mol) combusts completely in oxygen according to:



2 moles of C₄H₁₀ (2 × 58.0 = 116 g) can release 5600 kJ of heat

$$2.9 \text{ g} \times \frac{2 \text{ mol}}{116 \text{ g}} \times \frac{5600 \text{ kJ}}{2 \text{ mol}} = \frac{2.9 \text{ g} \times 5600 \text{ kJ}}{116 \text{ g}} = 140 \text{ kJ of released heat}$$

Proportions:

$$\frac{2.9 \text{ g}}{116 \text{ g}} = \frac{\text{heat released}}{5600 \text{ kJ}}$$

$$\text{heat released} = \frac{2.9 \text{ g} \times 5600 \text{ kJ}}{116 \text{ g}} = 140 \text{ kJ of released heat}$$



PRACTICE PROBLEMS

PROBLEM 1: Although the process also requires water, a simplified equation for rusting (with rust shown as Fe_2O_3) is: $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \Rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$ $\Delta_{\text{rxn}}H = -1.65 \times 10^3 \text{ kJ}$
How much rust forms when $4.93 \times 10^3 \text{ kJ}$ of heat is released?

$1.57 \times 10^6 \text{ g}$

238 g

477 g

954 g

107 g

PROBLEM 2: The combustion of 1.00 mole of methane, CH_4 , produces carbon dioxide and water and releases 802 kJ/mol. When 3.00 mol of oxygen react with a stoichiometric quantity of methane, what is the heat change for the reaction?

$-8.02 \times 10^2 \text{ kJ}$

$-2.41 \times 10^3 \text{ kJ}$

$8.02 \times 10^2 \text{ kJ}$

$1.20 \times 10^3 \text{ kJ}$

$-1.20 \times 10^3 \text{ kJ}$



STANDARD CONDITIONS

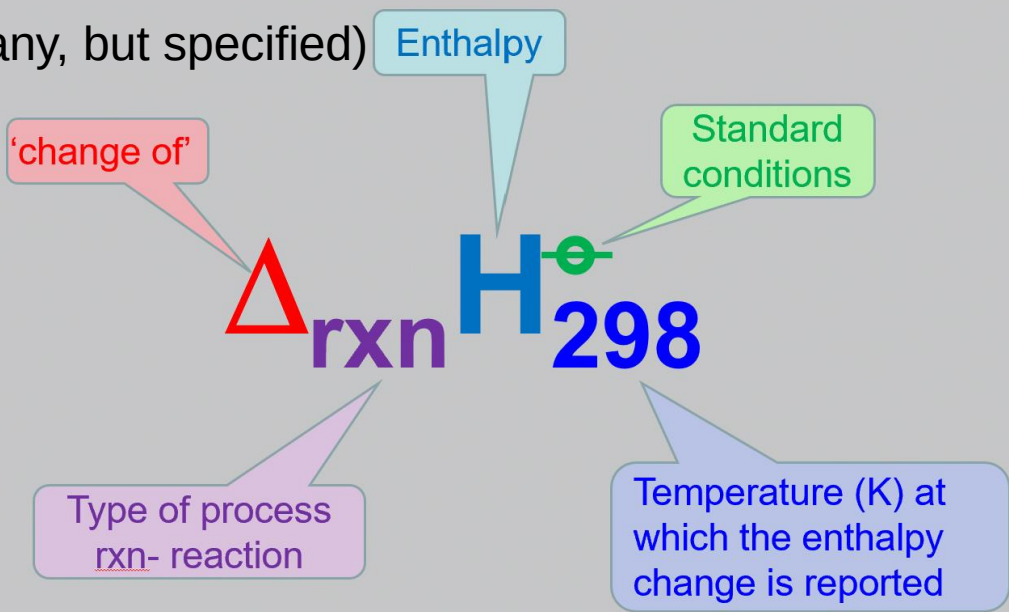
Any chemical equation that describes a reaction has a value of ΔH ($\Delta_{\text{rxn}}H$)

$\Delta_{\text{rxn}}H$ depends on T , P and the physical state of the components (H_2O : liquid or steam)

Standard conditions – allow comparison between values:

- Solids and liquids must be pure solids and liquids
- Solutions at 1 mol/L
- Gases at the pressure of 1 bar
- Temperature usually 298 K (can be any, but specified)
- Always have a sign

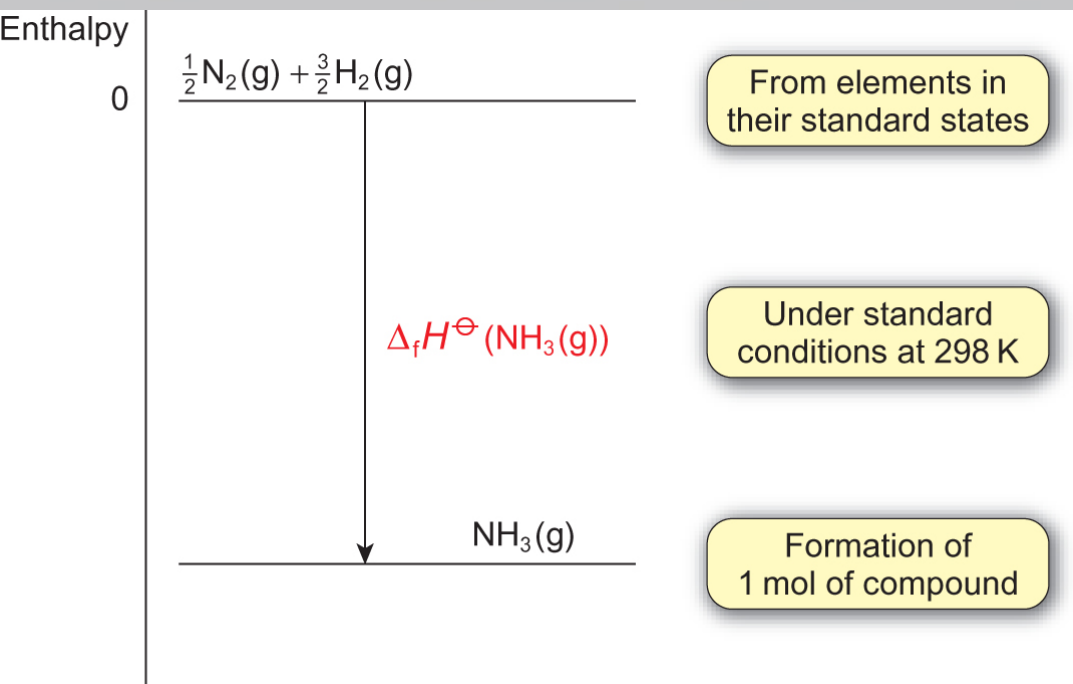
NOT STP or SATP !



STANDARD HEAT OF FORMATION - $\Delta_f H^\circ$ (X)

standard enthalpy change of the formation $\Delta_f H^\circ$ (X) = **heat of formation** - heat transferred when 1 mole of substance X is formed from its elements at standard conditions (kJ/mol)

enthalpy of formation for an element in its standard state is ZERO



$$\Delta_f H^\circ_{298} (\text{N}_2 (\text{g})) = 0 \text{ kJ/mol}$$

$$\Delta_f H^\circ_{298} (\text{H}_2 (\text{g})) = 0 \text{ kJ/mol}$$

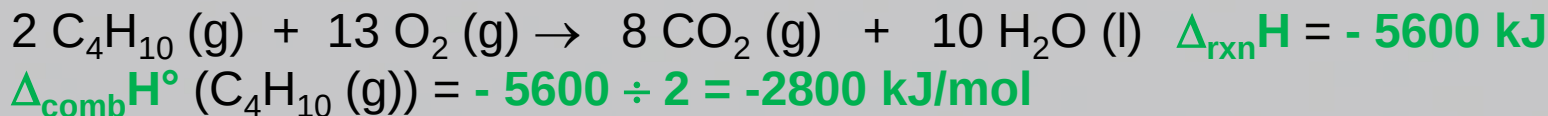
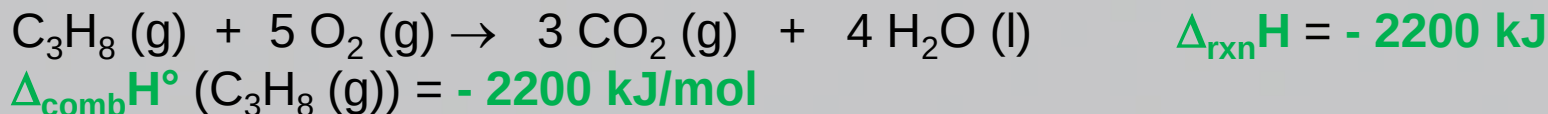
$\text{H}_2 (\text{g}), \text{N}_2 (\text{g}), \text{O}_2 (\text{g})$
 $\text{F}_2 (\text{g}), \text{Cl}_2 (\text{g}), \text{Br}_2 (\text{l}), \text{I}_2 (\text{s})$
Noble gases (g)
 $\text{P}_4 (\text{s}), \text{As}_4 (\text{s}), \text{S}_8 (\text{s}), \text{C} (\text{s, graphite})$
Metals (s) except Hg (l), [Cs and Ga]



STANDARD HEAT OF COMBUSTION - $\Delta_{\text{comb}}H^\circ$

standard enthalpy change of combustion $\Delta_{\text{comb}}H^\circ$ (X) – heat of combustion-released when 1 mole of substance X burns completely in oxygen gas at 1 bar pressure

always negative – always exothermic - - $\Delta_{\text{comb}}H^\circ$ (X)



Thermochemical equation can have fractional coefficients



OTHER STANDARD HEATS

$\Delta_{\text{fus}}H^\circ$ (X) heat of fusion of X, $X(s) \rightarrow X(l)$ **always ENDO**

$\Delta_{\text{vap}}H^\circ$ (X) heat of vaporisation of X, $X(l) \rightarrow X(g)$ **always ENDO**

$\Delta_{\text{sub}}H^\circ$ (X) heat of sublimation of X, $X(s) \rightarrow X(g)$ **always ENDO**

per 1 mole of substance !!!



HESS'S LAW

The total enthalpy change for a chemical reaction is independent of the path by which the reaction occurs, provided the starting and finishing states are the same for each reaction path

ΔH – state function – change independent of path,
change is reversible



$$\Delta H_1$$



$$\Delta H_2$$



$$\Delta H_1 + \Delta H_2$$

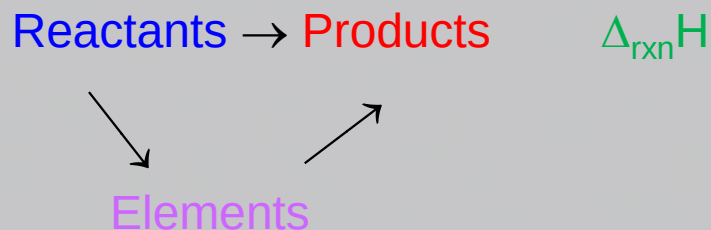


$$-\Delta H_1$$

$$\Delta_{\text{rxn}} H \text{ (forward reaction)} = - \Delta_{\text{rxn}} H \text{ (backward reaction)}$$



HESS'S LAW, cnt.



Reactants $\rightarrow$ Elements $-\Delta_f H^\circ$ (reactant 1) $-\Delta_f H^\circ$ (reactant 2) etc $-\sum \Delta_f H^\circ$ (reactants)

Elements $\rightarrow$ Products $-\Delta_f H^\circ$ (product 1) $-\Delta_f H^\circ$ (product 2) etc $\sum \Delta_f H^\circ$ (products)

$$\Delta_{\text{rxn}}H = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$



SAMPLE PROBLEMS

Calculate $\Delta_r H$ for the reaction $C_4H_4(g) + 2H_2(g) \Rightarrow C_4H_8(g)$, using the following information:

$\Delta_{\text{combustion}} H$ for $C_4H_4(g) = -2341 \text{ kJ/mol}$

$\Delta_{\text{combustion}} H$ for $C_4H_8(g) = -2755 \text{ kJ/mol}$

$\Delta_{\text{combustion}} H$ for $H_2(g) = -286 \text{ kJ/mol}$

Group of answer choices

-700 kJ

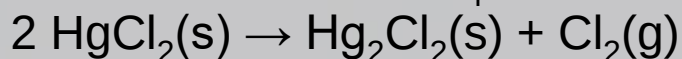
-128 kJ

-158 kJ

-316 kJ

-4810 kJ

What is the value of $\Delta_r H^\circ$ in kJ for:



given the $\Delta_f H^\circ$ values (in kJ/mol) for $\text{HgCl}_2 = -230$ and $\text{Hg}_2\text{Cl}_2 = -265$?

Group of answer choices

-195

-495

-35

+195

+35



PRACTICE PROBLEMS

Given the thermochemical equation: $2 \text{NO(g)} + \text{O}_2\text{(g)} \Rightarrow 2 \text{NO}_2\text{(g)}$ $\Delta H = 1140 \text{ kJ}$

Calculate ΔH for the reaction $\text{NO}_2\text{(g)} \Rightarrow \text{NO(g)} + 1/2 \text{O}_2\text{(g)}$

Group of answer choices

-114 kJ

+114.0 kJ

-570 kJ

+570 kJ

+128 kJ

What is the standard enthalpy of formation of propene, C_3H_6 , in kJ/mol, if its standard enthalpy of combustion is -2059 kJ/mol ?

The heats of formation of H_2O and CO_2 are -286 kJ/mol and -394 kJ/mol , respectively.

Group of answer choices

-1379

-19

-2059

-699

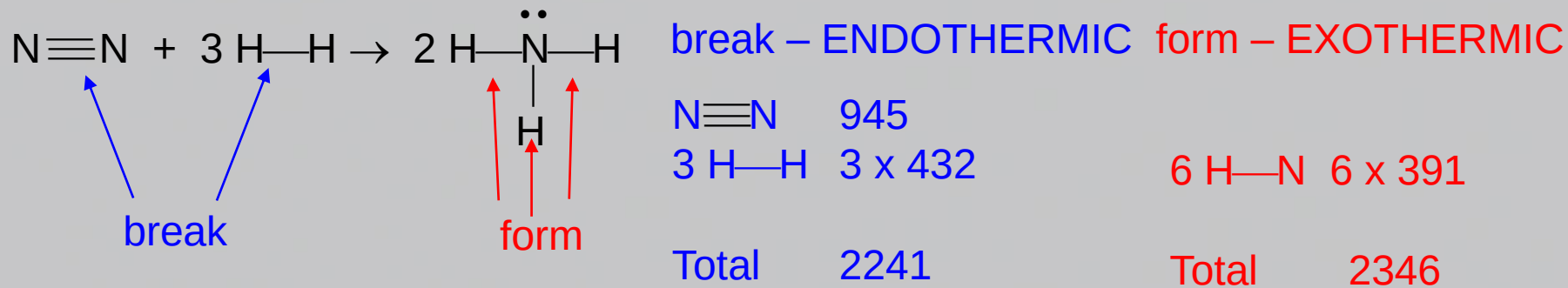
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BOND ENTHALPY

Bond dissociation enthalpy, $D(A-B)$, is the enthalpy change per mole when a particular chemical bond, $A-B$, is broken under standard conditions in the gas phase

Reactants	→	Products	The overall result is an approximation of ΔH
break bonds	→	form bonds	
ENDOTHERMIC	→	EXOTHERMIC	



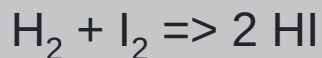
$N \equiv N$	945 kJ/mol
$H-H$	432 kJ/mol
$H-N$	391 kJ/mol

$$\Delta_{\text{rxn}}H = 2241 - 2346$$

$$\Delta_{\text{rxn}}H = -105 \text{ kJ}$$

SAMPLE PROBLEMS:

Estimate the delta H in kJ, for the following reaction from the bond energies given.



Bond energy (kJ/mol); H-H, 436; H-I, 297; I-I, 151.

Group of answer choices

884

-7

-290

+7

+290

Which of the following statements concerning estimating delta H from bond energies is incorrect?

Group of answer choices

The sum of the bond energies of the reactants is subtracted from the sum of the bond energies of the products.

Bond breaking is endothermic (pos).

Bond making is exothermic (neg).

Bond energies must be multiplied by the number of each bond and the number of moles of the species in the balanced equation.

Bond energies are average values.



LATTICE ENERGY



Reflects ‘strength’ of ionic bond

QUALITATIVE TRENDS:

a) Charge

Charge increases,
 $\Delta_{\text{latt}}H^\circ$ increases (more negative)

compound	$\Delta_{\text{latt}}H^\circ$ kJ/mol
NaCl	-787
MgCl ₂	-2524
AlCl ₃	-5492
NaO ₂	-2695
MgO	-3791

b) Size

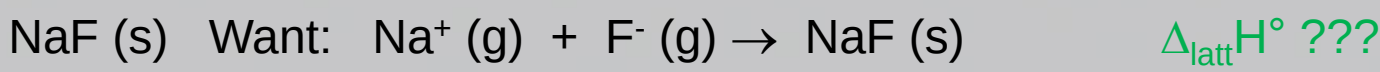
Size increases,
 $\Delta_{\text{latt}}H^\circ$ decreases (less negative)

compound	$\Delta_{\text{latt}}H^\circ$ kJ/mol
LiCl	-853
NaCl	-787
KCl	-715
LiBr	-807
NaBr	-747
KBr	-682



HESS'S LAW

Cannot measure directly



- | | | |
|---|---------------------------|---|
| 1 | Δ _f H° (NaF) | Na (s) + ½ F ₂ (g) → NaF (s) |
| 2 | Δ _{subl} H° (Na) | Na (s) → Na (g) |
| 3 | IE (Na) | Na (g) → Na ⁺ (g) + e |
| 4 | EA (F) | F (g) + e → F ⁻ (g) |
| 5 | Bond energy F-F | F ₂ (g) → 2 F (g) |

- | | | | | |
|---|------|-------------------------------|------------------------|-----------------------------|
| 3 | Flip | Na ⁺ (g) + e | → Na (g) | - IE (Na) |
| 2 | Flip | Na (g) | → Na (s) | - Δ _{subl} H° (Na) |
| 1 | | Na (s) + ½ F ₂ (g) | → NaF (s) | Δ _f H° (NaF) |
| 5 | Flip | F (g) | → ½ F ₂ (g) | -½ Bond energy F-F |
| | x ½ | | | |
| 4 | Flip | F ⁻ (g) | → F (g) + e | - EA (F) |

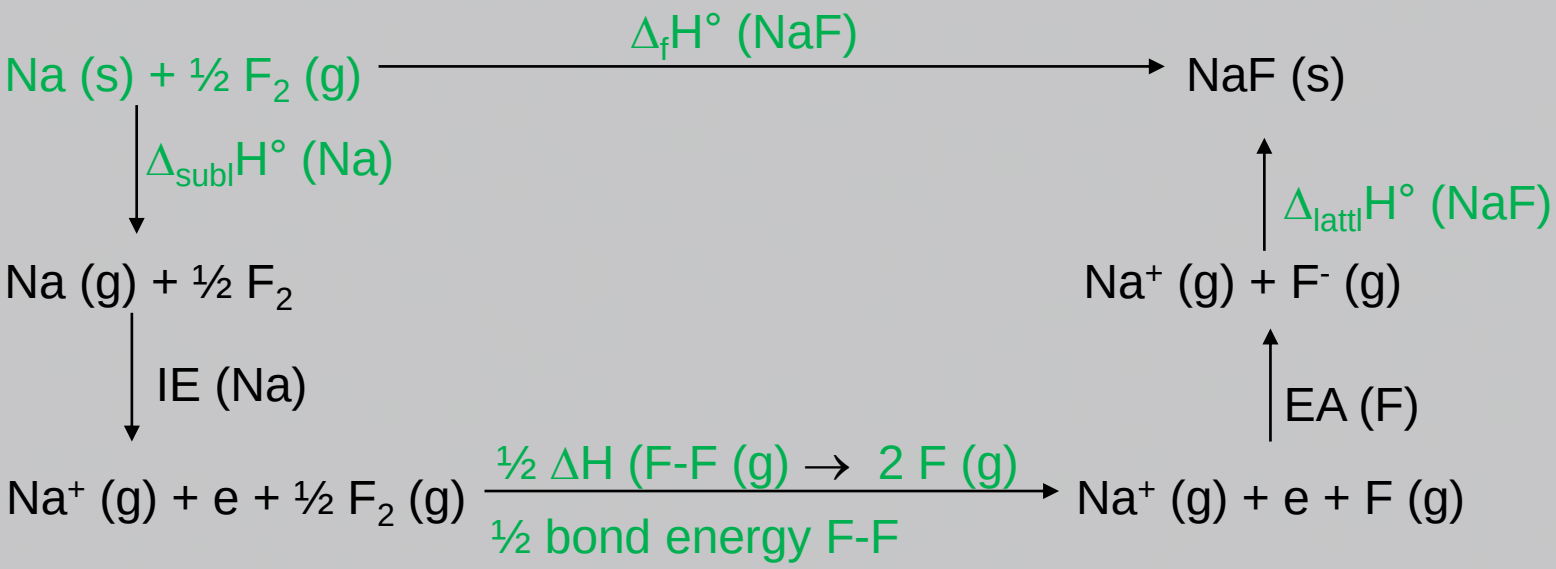
Na⁺ (g) + F (g) → NaF (s)

Δ_{latt}H° (NaF)

Δ_{latt}H° (NaF) = Δ_fH° (NaF) - Δ_{subl}H° (Na) - IE (Na) - ½ Bond energy F-F - EA



BORN – HABER CYCLE



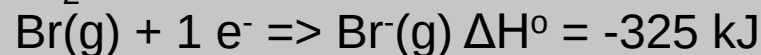
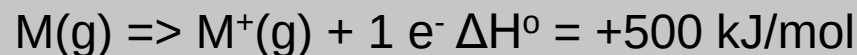
$$\Delta_f H^\circ (\text{NaF}) = \Delta_{\text{subl}} H^\circ (\text{Na}) + \text{IE (Na)} + \frac{1}{2} \text{ Bond energy F-F} + \text{EA (F)} + \Delta_{\text{latt}} H^\circ (\text{NaF})$$

$$\Delta_{\text{latt}} H^\circ (\text{NaF}) = \Delta_f H^\circ (\text{NaF}) - \Delta_{\text{subl}} H^\circ (\text{Na}) - \text{IE (Na)} - \frac{1}{2} \text{ Bond energy F-F} - \text{EA (F)}$$



SAMPLE PROBLEM

An ionic compound, MBr, has $\Delta H^\circ_f = -500 \text{ kJ/mol}$. Given the information below, calculate its lattice energy.



Group of answer choices

-515 kJ/mol

-1015 kJ/mol

-15 kJ/mol

+515 kJ/mol

-915 kJ/mol



BALANCING EQUATIONS



BALANCING EQUATIONS



BALANCING EQUATIONS



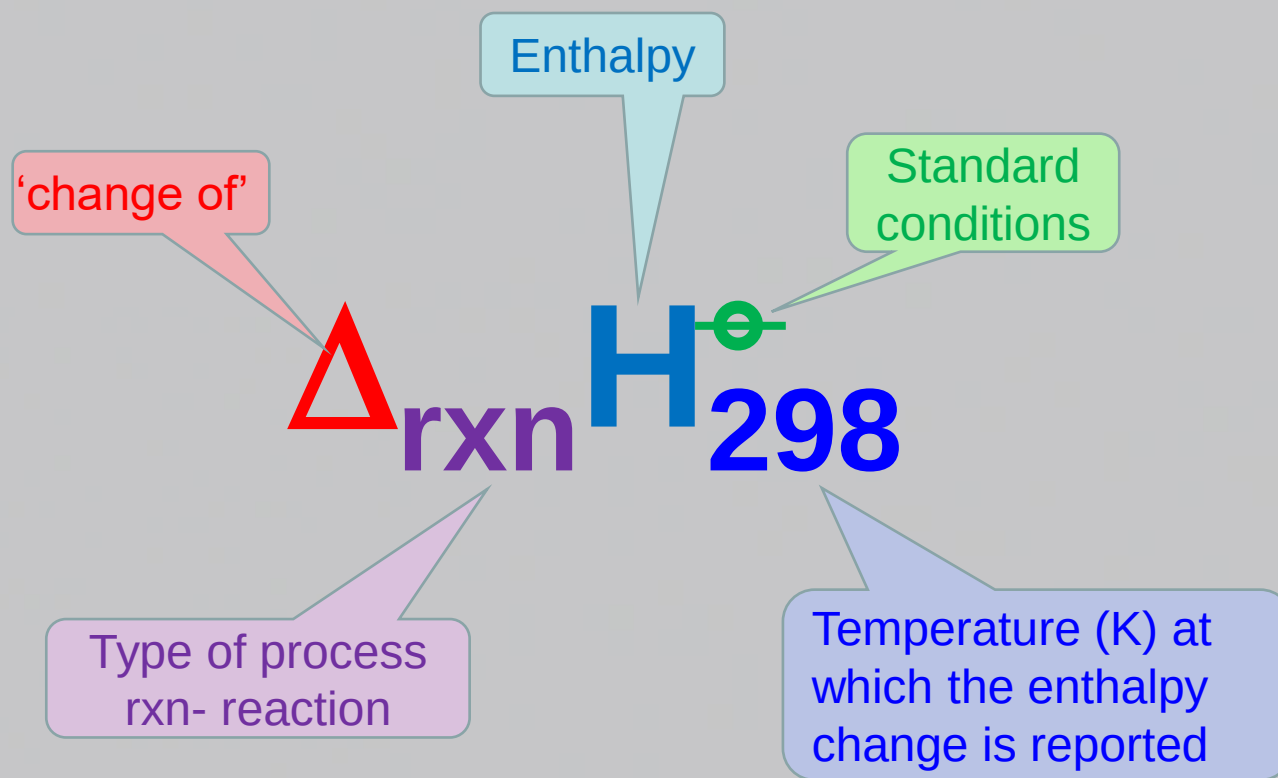
BALANCING EQUATIONS



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