

# Enthalpy

heat changes taking place at a constant  
pressure  $\Delta H$

# Enthalpy ( $H$ )

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**Every system (sample of matter) has stored energy.**

**total enthalpy ( $H$ ) of a system can not be measured**

**only heat exchanges with the surroundings can be ascertained ( $\Delta H$ )**

# Hess's Law

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$\Delta H$  for a reaction is equal to the difference in enthalpies of the products and the enthalpies of the reactants:

$$\Delta H = \Delta H(\text{products}) - \Delta H(\text{reactants})$$

$\Delta H$  is equal to the heat given off or absorbed at constant pressure

# A State Function

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**Does not depend on how the system arrived at its present state; only on the characteristics of the present state.**

**Volume, Pressure, Temperature, ,  $\Delta H$**

# Enthalpy ( $\Delta H$ )

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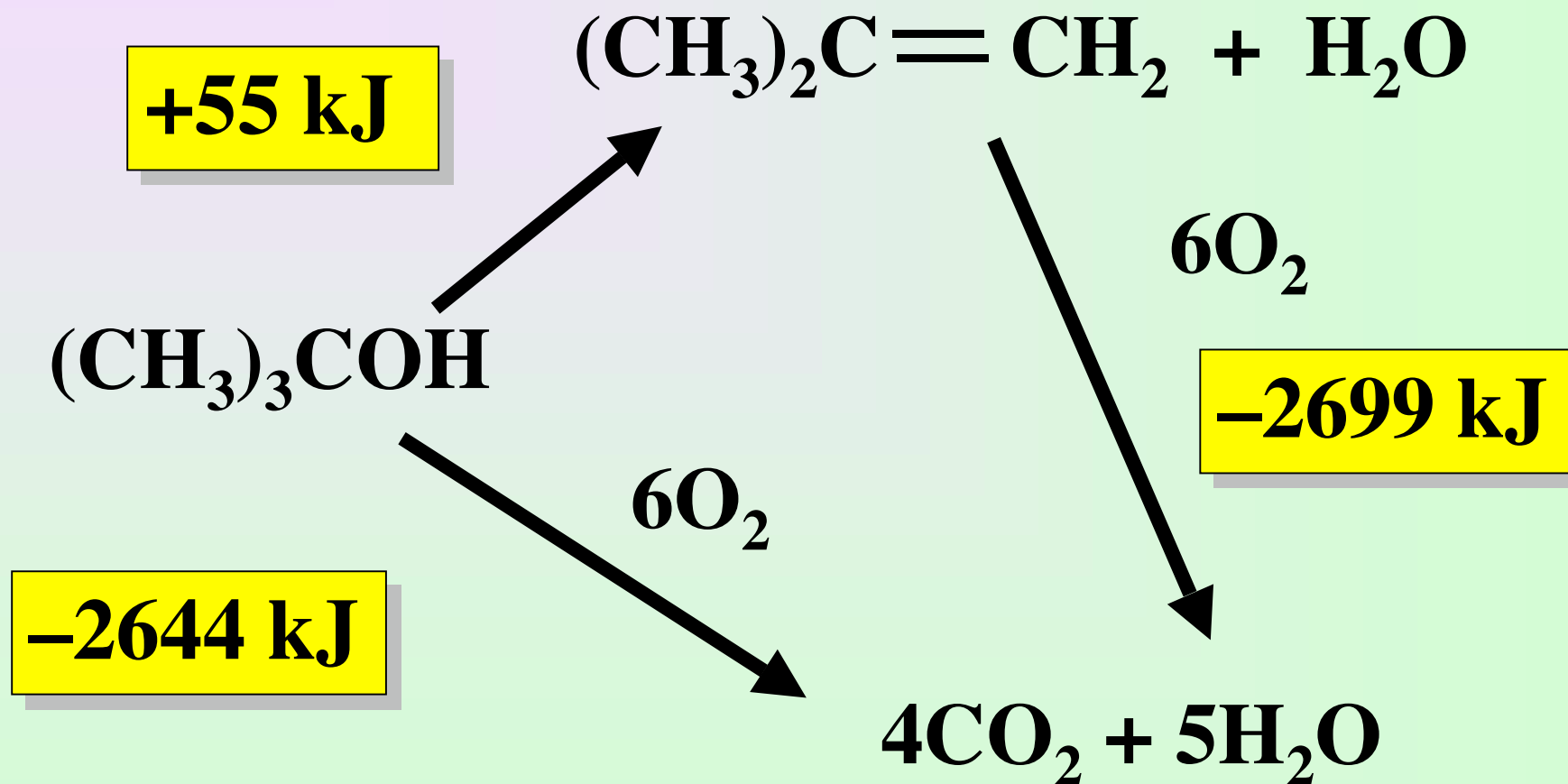
since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is pathway independent

*ie: the change in enthalpy is the same whether the reaction takes place in one step or a series of steps*

**Hess's Law**

## Measured values of $\Delta H^\circ$

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## An exothermic reaction

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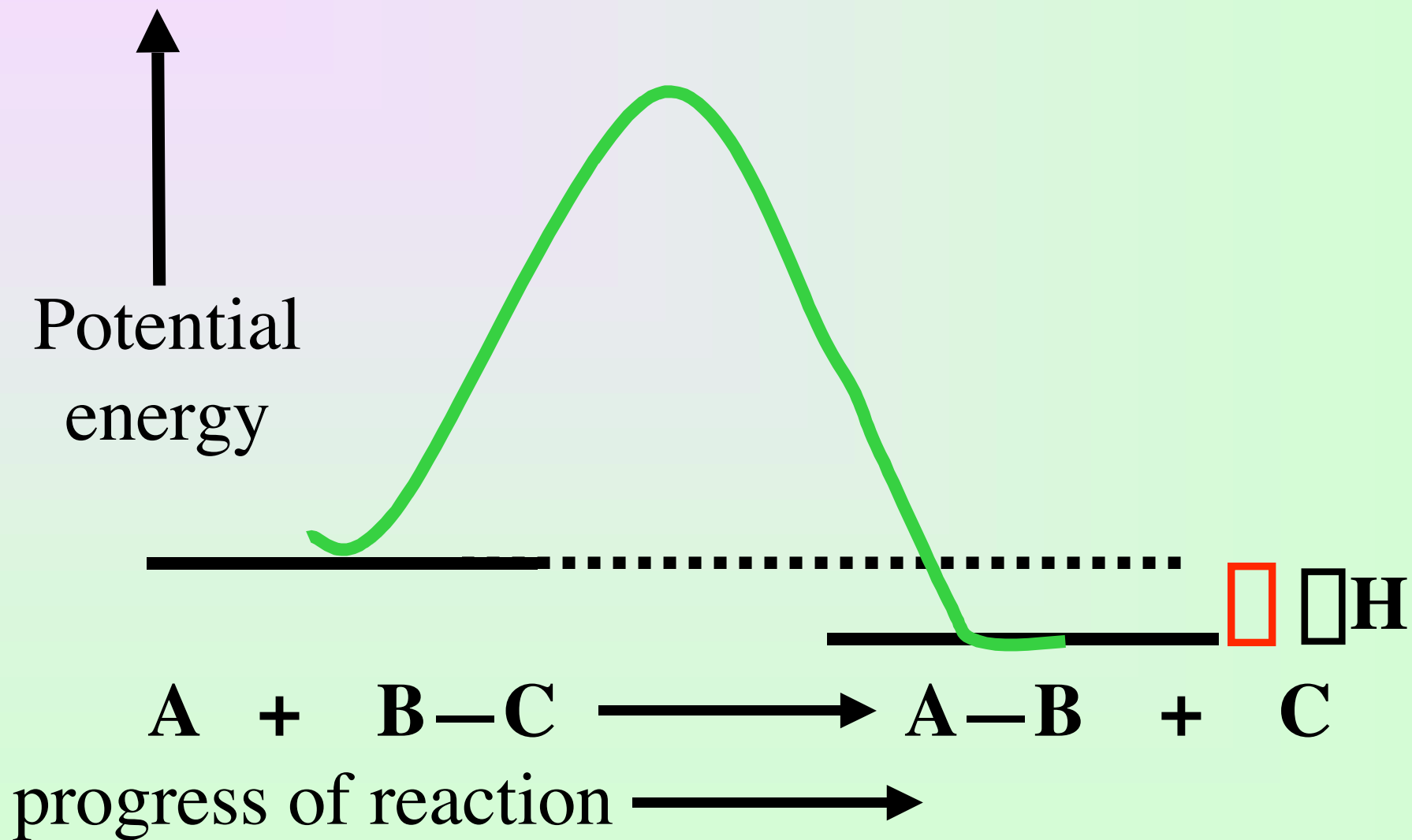


**stronger chemical bonds in products  
than in reactants**

**less potential energy in products**

**The sign of  $\Delta H$  is for **—** for an exothermic  
process**

**Consider a hypothetical one-step reaction (exothermic)**



# An endothermic reaction

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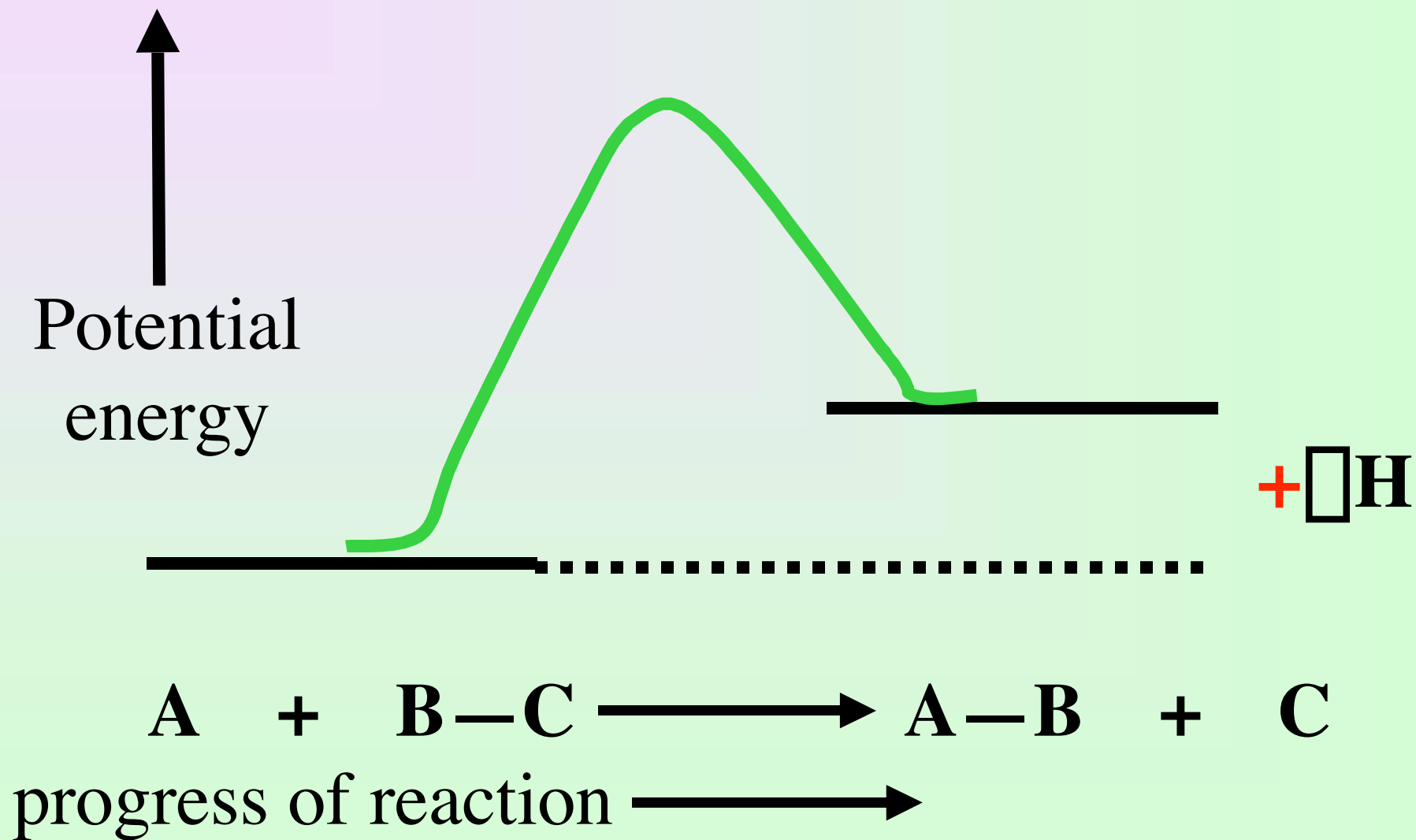


**weaker chemical bonds in products  
in reactants**

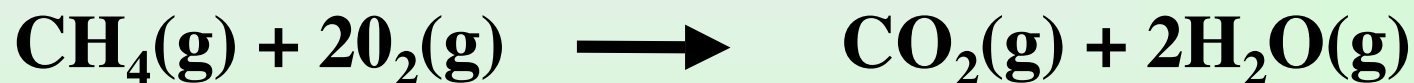
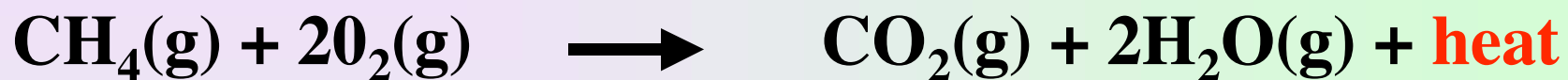
**more potential energy in products**

**The sign of  $\Delta H$  is + for an endothermic  
process**

**Consider a hypothetical one-step reaction (endothermic)**



## ways to express combustion of methane



$$\Delta H = -890 \text{ kJ}$$

# Thermochemical equations

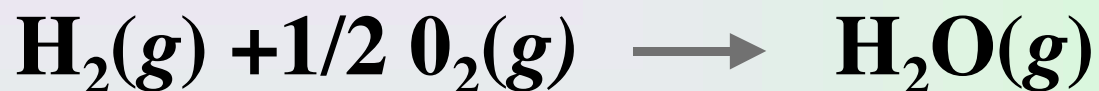
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- 1. Stoichiometric coefficients always refer to the number of moles of each substance.**
- 2. Reversing the direction of a given reaction, reverses the sign of  $\Delta H$ .**
- 3. If a reaction is multiplied by some factor, its  $\Delta H$  must be multiplied by the same factor.**

# Thermochemical equations

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2. Reverse the direction of a given reaction, reverse the sign of  $\Delta H$ .



$$\Delta H^\circ = -241.8 \text{ kJ/mol}$$

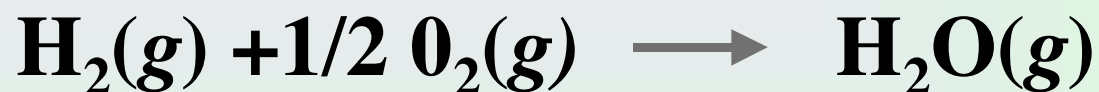


$$\Delta H^\circ = +241.8 \text{ kJ/mol}$$

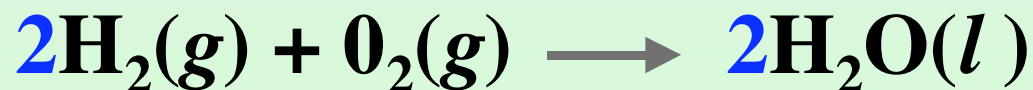
# Thermochemical equations

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3. If a reaction is multiplied by some factor, its  $\Delta H$  must be multiplied by the same factor.



$$\Delta H^\circ = -241.8 \text{ kJ/mol}$$



$$\Delta H^\circ = -483.6 \text{ kJ/2mol}$$

# Thermochemical equations

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**4. Physical state of all reactants and products is important.**

**5.  $\Delta H$  depends on temperature**

**the temperature is the same for reactants and products.**

# Standard Enthalpy of Formation and Reaction



Sometimes using calorimetry to measure the heat generated by a chemical reaction is impossible.

Example:



we can calculate an enthalpy change by using **standard enthalpies of formation**



# Standard enthalpy of formation

$$\Delta H_f^\circ$$

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**the change in enthalpy that accompanies the formation of 1 mole of a compound from its elements with all substances in standard state**

# Standard State

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**the state at which a substance exists ( **in its most stable form** ) under conditions of 1atm and 25°C**

- for substances that exist as gases the pressure is 1 atm**
- for a substance present in a solution, the standard state is a concentration is 1 molar**

# Standard Enthalpies of Formation

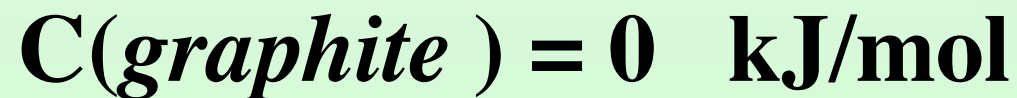
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Compound	$\Delta H_f^\circ$ (kJ/mol)
$\text{CO}_2(\text{g})$	-393.5
$\text{NH}_3(\text{g})$	-46.3
$\text{NO}_2(\text{g})$	33.85
$\text{H}_2\text{O}(\text{liq})$	-285.8
$\text{H}_2\text{O}(\text{g})$	-241.8
$\text{Al}_2\text{O}_3(\text{s})$	-1669.8

# The Reference Point

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**Standard enthalpy of formation of any element in its standard state = 0.**

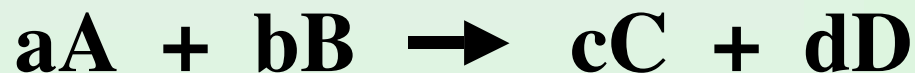


# Standard enthalpy of reaction

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$\Delta H^\circ$  for a reaction can be calculated for a reaction by subtracting the sum of the standard enthalpies of formation of the reactants from the sum of the standard enthalpies of formation of the products

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f (\text{products}) - \sum m \Delta H^\circ_f (\text{reactants})$$



$$\Delta H^\circ_{\text{rxn}} = [c \Delta H^\circ_f (\text{C}) + d \Delta H^\circ_f (\text{D})] - [a \Delta H^\circ_f (\text{A}) + b \Delta H^\circ_f (\text{B})]$$

# How are heats of formation and reaction determined?

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**directly**

**indirectly**

# The Direct Method

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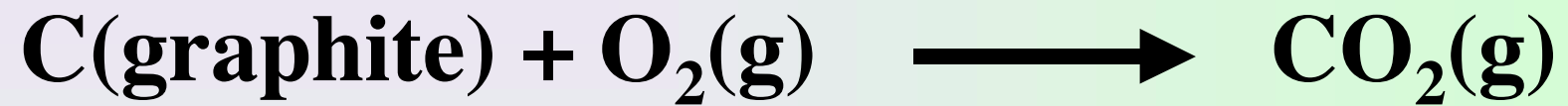
used for compounds that can be directly synthesized from their elements


$$\Delta H_f = 0$$

# Standard Enthalpies of Formation

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Compound	$\Delta H_f^\circ$ (kJ/mol)
CO <sub>2</sub> (g)	-393.5
NH <sub>3</sub> (g)	-46.3
NO <sub>2</sub> (g)	33.85
H <sub>2</sub> O(liq)	-285.8
H <sub>2</sub> O(g)	-241.8
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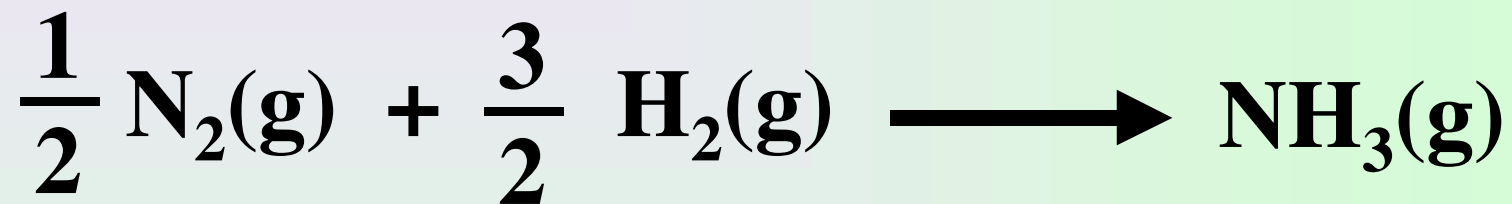


$$\Delta H^\circ = -393.5 \text{ kJ}$$

# Standard Enthalpies of Formation

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Compound	$\Delta H_f^\circ$ (kJ/mol)
CO <sub>2</sub> (g)	-393.5
NH <sub>3</sub> (g)	-46.3
NO <sub>2</sub> (g)	33.85
H <sub>2</sub> O(liq)	-285.8
H <sub>2</sub> O(g)	-241.8
Al <sub>2</sub> O <sub>3</sub> (s)	-1669.8



$$\Delta H^\circ = -46.3 \text{ kJ}$$

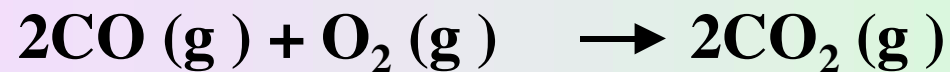
# The Indirect Method

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## Hess's Law

**When reactants are converted to products, the change in enthalpy is the same whether the reaction occurs in one step or in a series of step.**

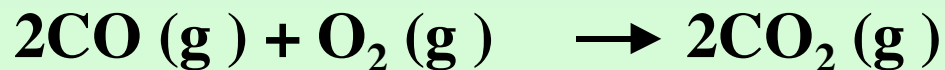
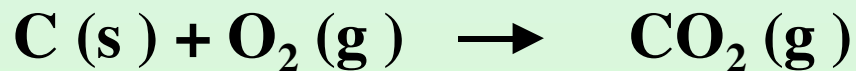
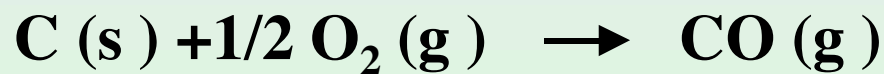
Use Hess's law to calculate the heat of reaction ( $\Delta H_{\text{rxn}}$ ) for the burning of carbon monoxide:



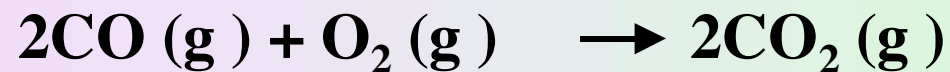
Standard enthalpies of formation: ( $\Delta H^\circ_f$ )

Carbon monoxide	<u>-110 kJ/mol</u>
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Carbon dioxide	-394 kJ/mol
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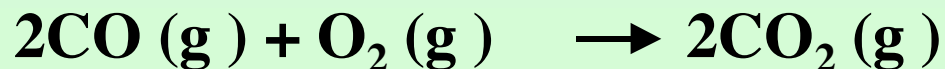
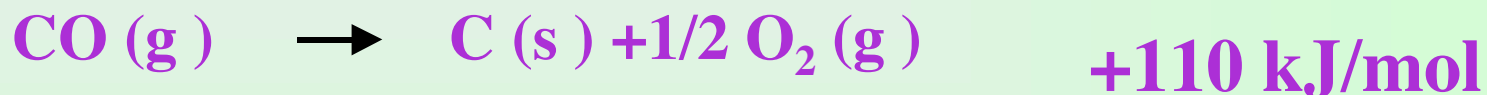


Use Hess's law to calculate the heat of reaction ( $\Delta H$ ) for the burning of carbon monoxide:

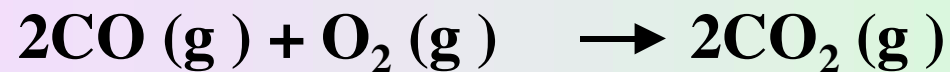


Standard enthalpies of formation: ( $\Delta H^\circ_f$ )

Carbon monoxide	<b>-110 kJ/mol</b>
Carbon dioxide	<b>-394 kJ/mol</b>



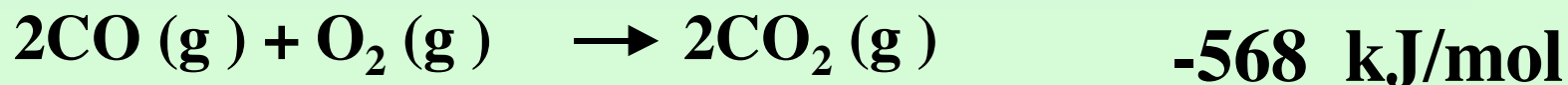
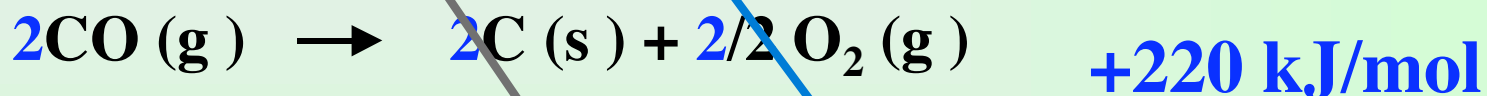
Use Hess's law to calculate the heat of reaction ( $\Delta H$ ) for the burning of carbon monoxide:



Standard enthalpies of formation: ( $\Delta H^\circ_f$ )

Carbon monoxide -110 kJ/mol

Carbon dioxide -394 kJ/mol



**Given:**

**$\Delta H^\circ$  for combustion of benzene**

$$= -3268 \text{ kJ/mol}$$

**and standard enthalpies of formation:**

**water**  $= -286 \text{ kJ/mol}$

**carbon dioxide**  $= -393.5 \text{ kJ/mol}$

**Calculate:  $\Delta H^\circ_f$  for benzene**

**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

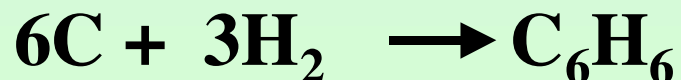
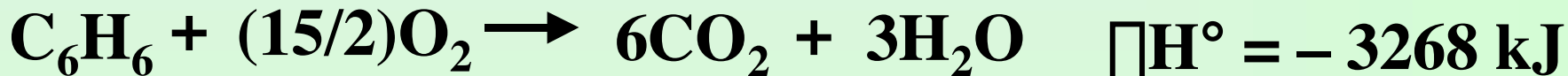
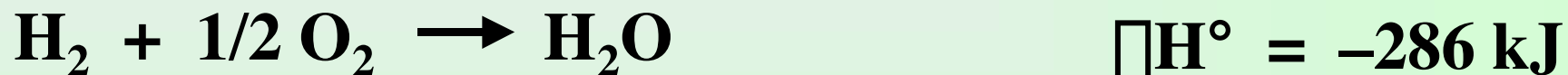
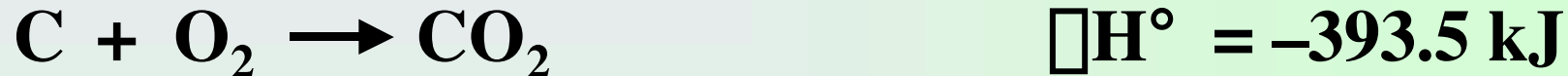
and standard enthalpies of formation:

water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---



**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

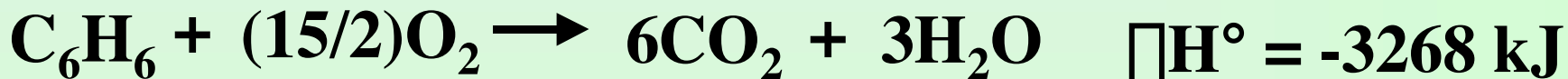
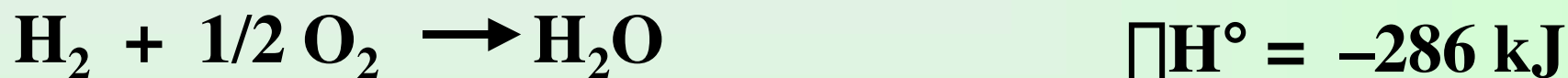
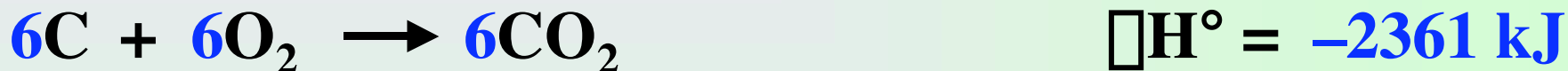
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Calculate:  $\Delta H^\circ_f$  for benzene

---



**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

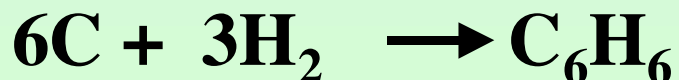
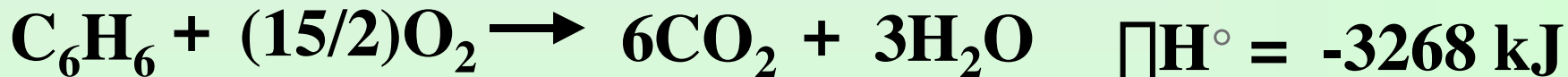
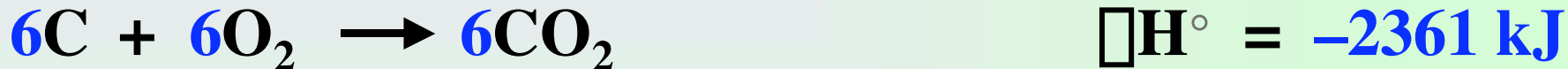
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Calculate:  $\Delta H^\circ_f$  for benzene

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**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

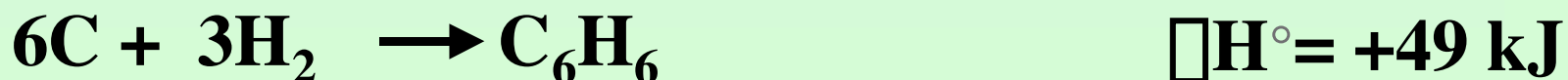
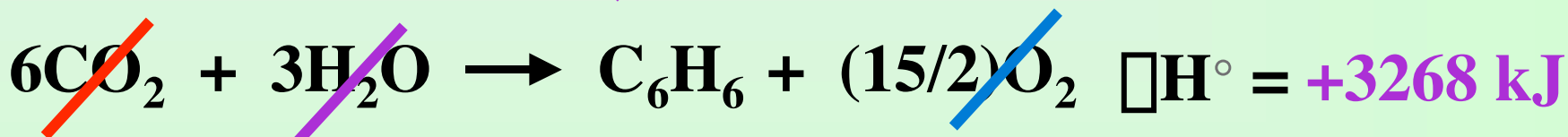
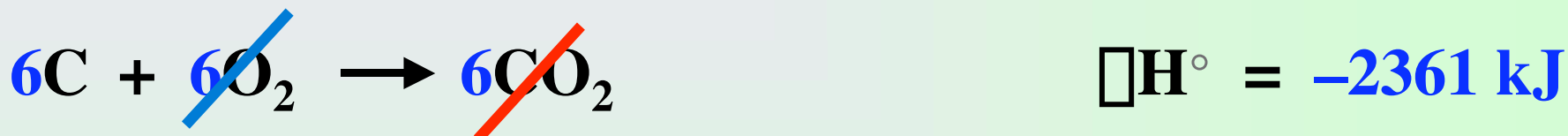
and standard enthalpies of formation:

water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

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## Alternative and easier method

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$$\Delta H^\circ =$$

(sum of heats of formation of products)

minus

(sum of heats of formation of reactants)

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f (\text{products}) - \sum m \Delta H^\circ_f (\text{reactants})$$

**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

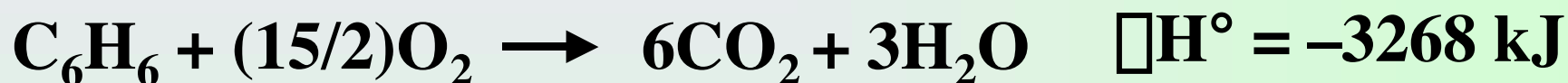
and standard enthalpies of formation:

water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---



**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

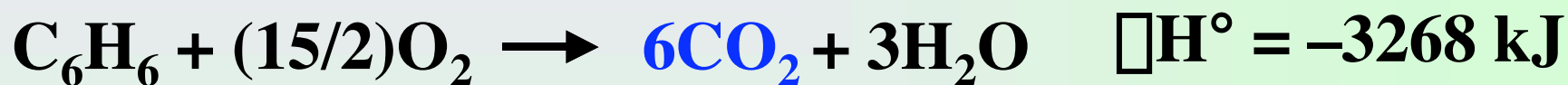
and standard enthalpies of formation:

water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

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 $6(-393.5 \text{ kJ/mol})$

**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

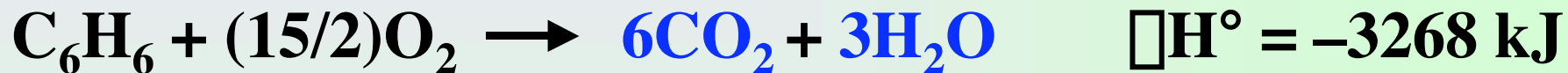
and standard enthalpies of formation:

water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---



$6(-393.5 \text{ kJ/mol})$

$3(-286 \text{ kJ/mol})$

**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

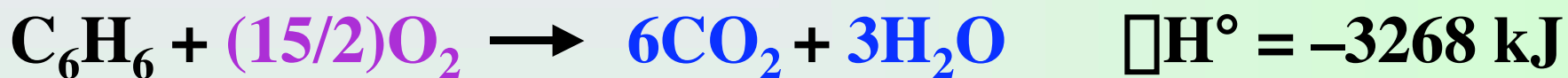
and standard enthalpies of formation:

water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---



$\Delta H^\circ_f$  (benzene)

$6(-393.5 \text{ kJ/mol})$

$3(-286 \text{ kJ/mol})$

$15/2(0)$

**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

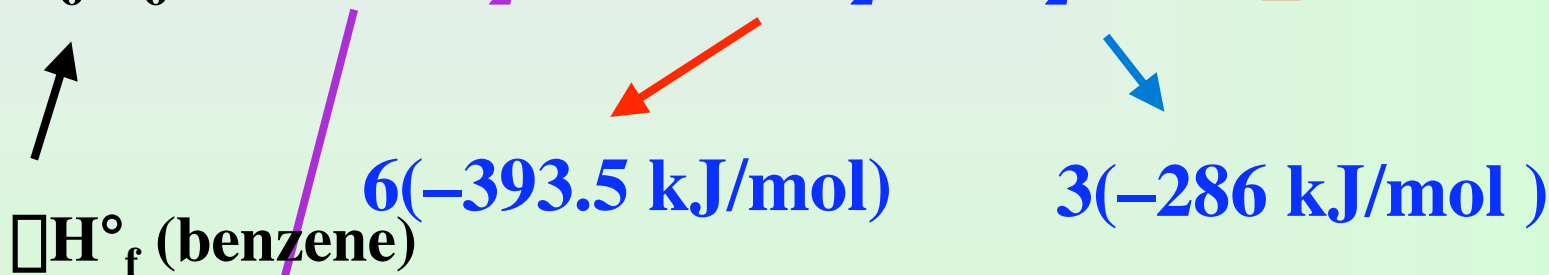
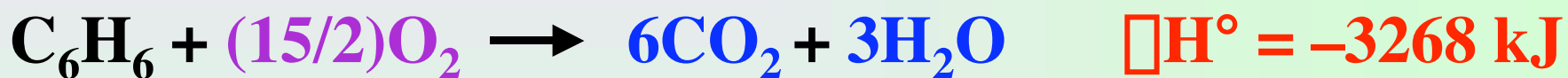
and standard enthalpies of formation:

water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---



$15/2(0)$

$$\Delta H^\circ = H(\text{products}) - H(\text{reactants})$$

**Given:**

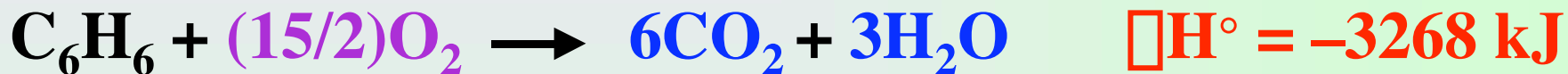
$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol  
and standard enthalpies of formation:

water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---



$$6(-393.5 \text{ kJ/mol}) + 3(-286 \text{ kJ/mol})$$

$(\Delta H^\circ_f \text{ (benzene)})$

$(-3219 \text{ kJ})$

$$\Delta H^\circ = \text{H(products)} - \text{H(reactants)}$$

**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

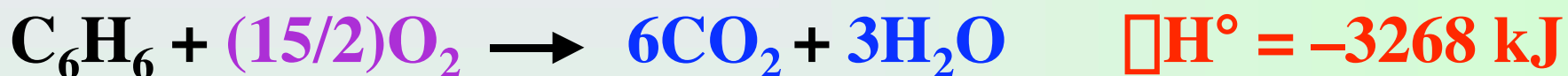
and standard enthalpies of formation:

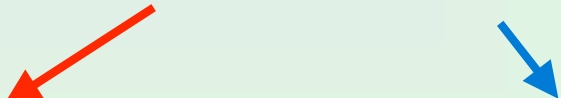
water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---





$6(-393.5 \text{ kJ/mol}) + 3(-286 \text{ kJ/mol})$

$$-3268 \text{ kJ} = (-3219 \text{ kJ}) - (\Delta H^\circ_f (\text{benzene}))$$

$$\Delta H^\circ = H(\text{products}) - H(\text{reactants})$$

**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

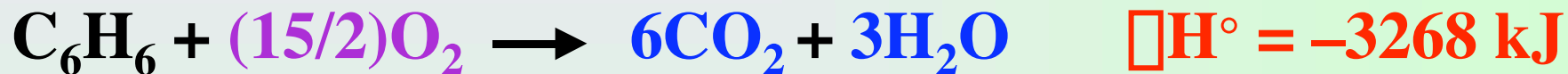
and standard enthalpies of formation:

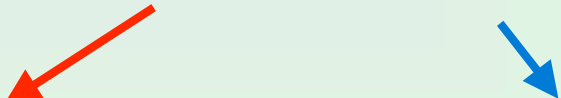
water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---





$6(-393.5 \text{ kJ/mol}) + 3(-286 \text{ kJ/mol})$

$$(-3219 \text{ kJ}) + 3268 \text{ kJ} = (\Delta H^\circ_f (\text{benzene}))$$

$$\Delta H^\circ = H(\text{products}) - H(\text{reactants})$$

**Given:**

$\Delta H^\circ$  for combustion of benzene =  $-3268$  kJ/mol

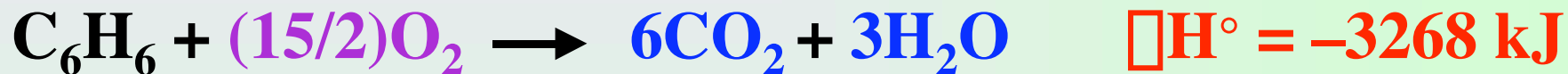
and standard enthalpies of formation:

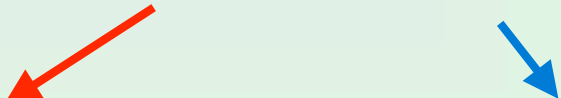
water =  $-286$  kJ/mol

carbon dioxide =  $-393.5$  kJ/mol

Calculate:  $\Delta H^\circ_f$  for benzene

---




$$6(-393.5 \text{ kJ/mol}) + 3(-286 \text{ kJ/mol})$$

$$\mathbf{+49 \text{ kJ}} = (\Delta H^\circ_f (\text{benzene}))$$

$$\Delta H^\circ = \mathbf{H(\text{products})} - \mathbf{H(\text{reactants})}$$

## Given the standard enthalpies of formation

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propane  $\text{C}_3\text{H}_8$  =  $-104 \text{ kJ/mol}$

water =  $-286 \text{ kJ/mol}$

carbon dioxide =  $-393.5 \text{ kJ/mol}$

Calculate  $\Delta H^\circ$  for combustion of propane.

## Given the standard enthalpies of formation

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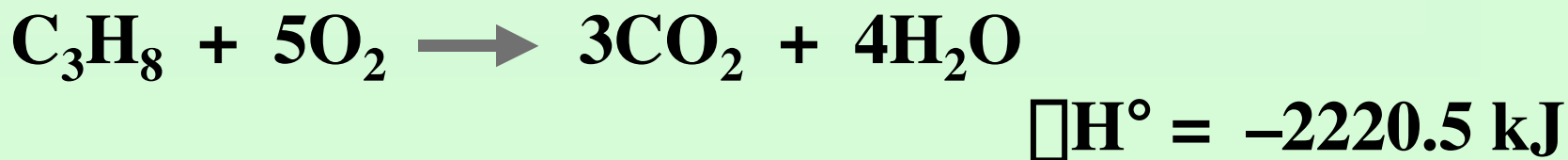
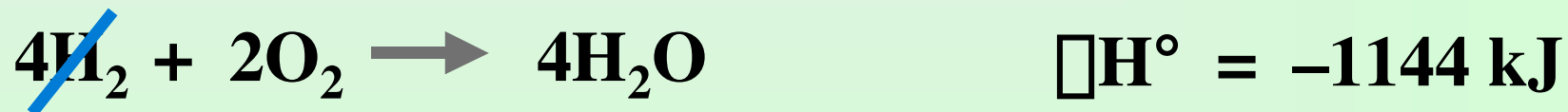
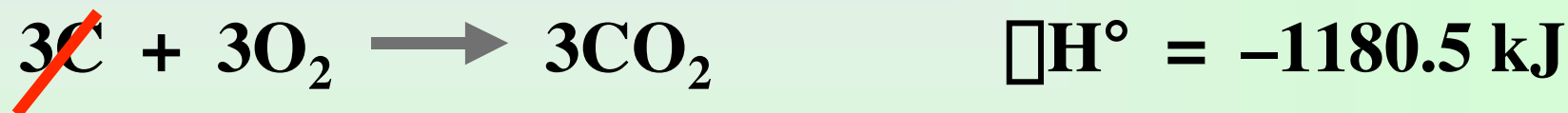
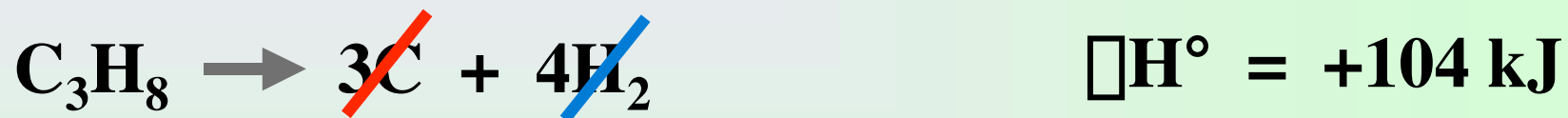
propane  $\text{C}_3\text{H}_8$  =  $-104 \text{ kJ/mol}$

water =  $-286 \text{ kJ/mol}$

carbon dioxide =  $-393.5 \text{ kJ/mol}$

Calculate  $\Delta H^\circ$  for combustion of propane.

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## Alternative and easier method

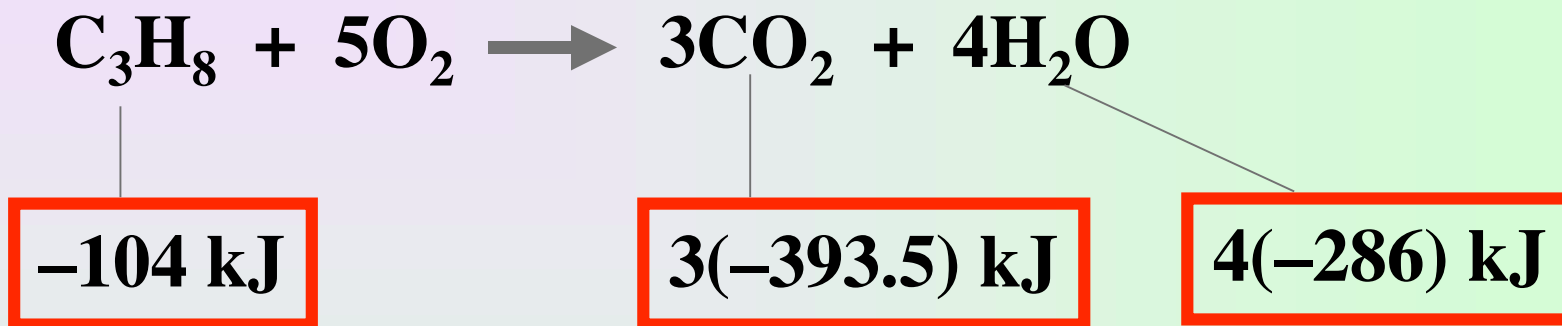
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$$\Delta H^\circ = H(\text{products}) - H(\text{reactants})$$

Given the standard enthalpies of formation

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Calculate  $\Delta H^\circ$  for combustion of propane.



$$\Delta H^\circ = [ 3(-393.5 \text{ kJ}) + 4(-286\text{kJ}) ] - [ -104 \text{ kJ} ]$$

$$\Delta H^\circ = -2220.5 \text{ kJ}$$