

Hess's Law

Enthalpy (H)

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 (ΔH)

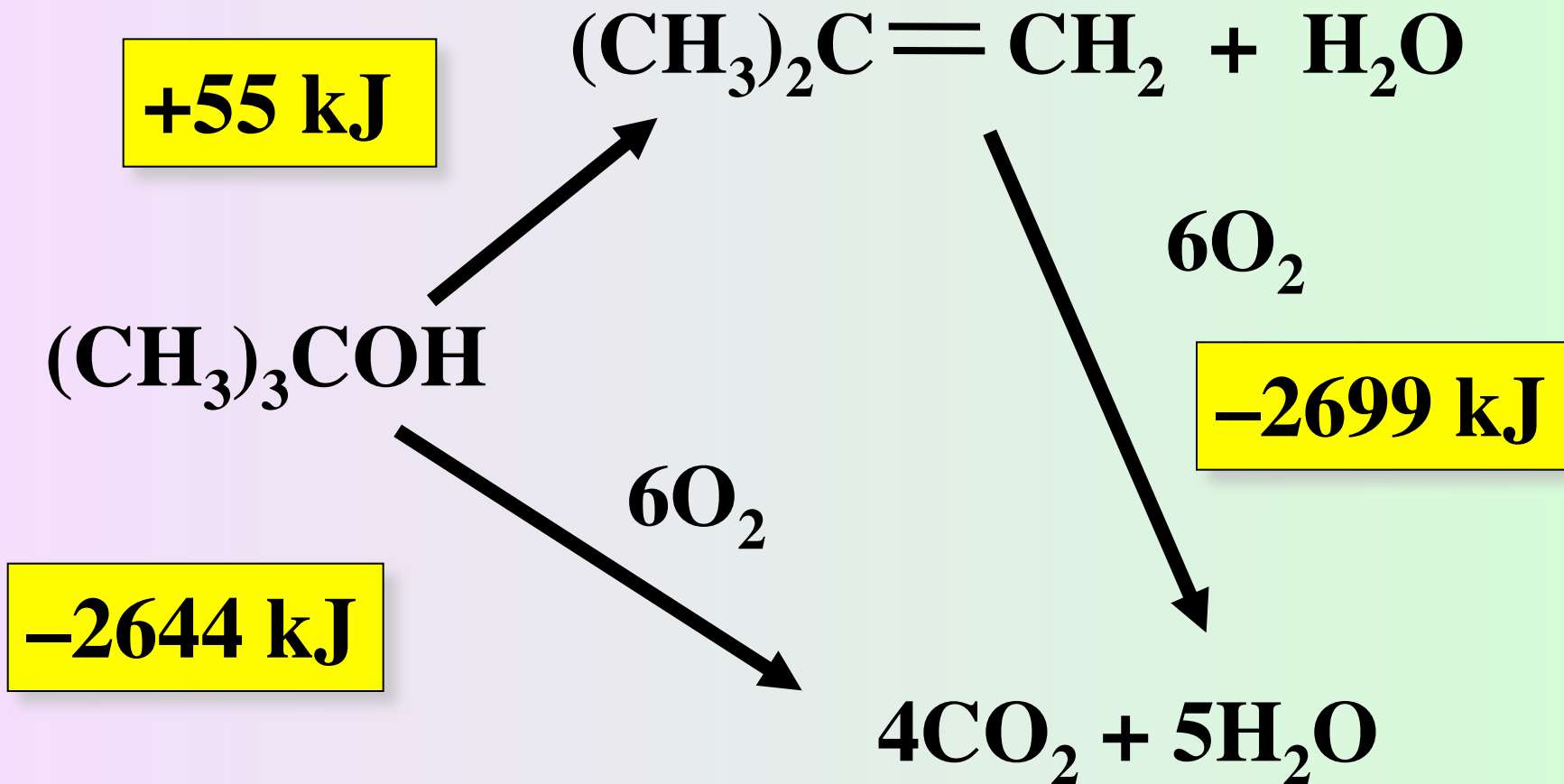
Enthalpy (ΔH)

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

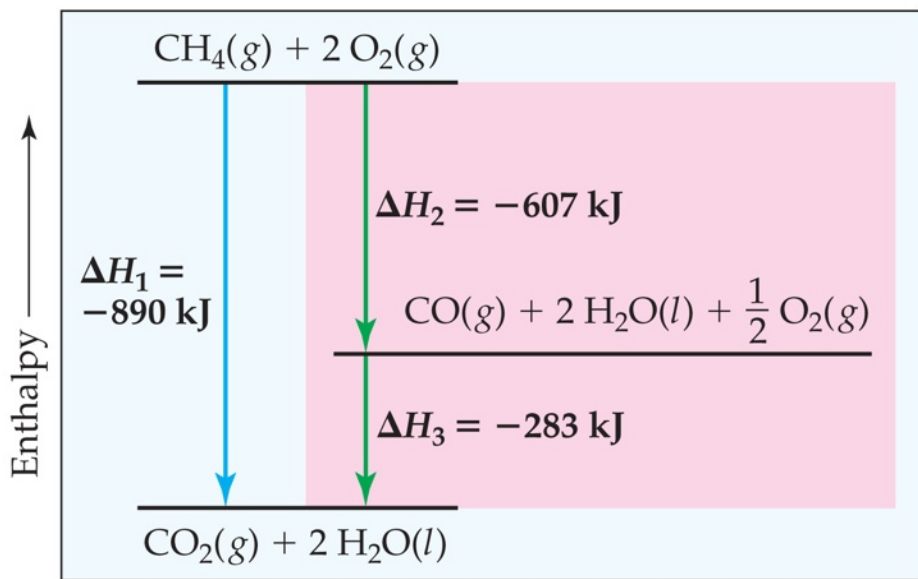
ie: the change in enthalpy is the same whether the reaction takes place in one step or a series of steps

Hess's Law

Measured values of ΔH°

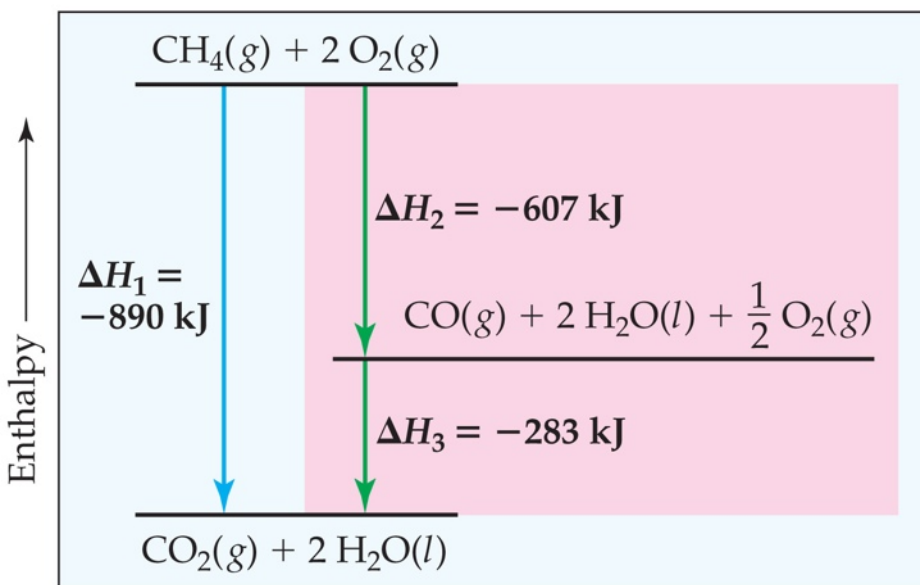


Hess's Law



Hess's law states that “[i]f 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's Law



Because ΔH is a state function, the total enthalpy change depends only on the initial state of the reactants and the final state of the products.

Hess's Law

ΔH for a reaction is equal to the difference in enthalpies of the products and the enthalpies of the reactants:

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

ΔH is equal to the heat given off or absorbed at constant pressure

An exothermic reaction

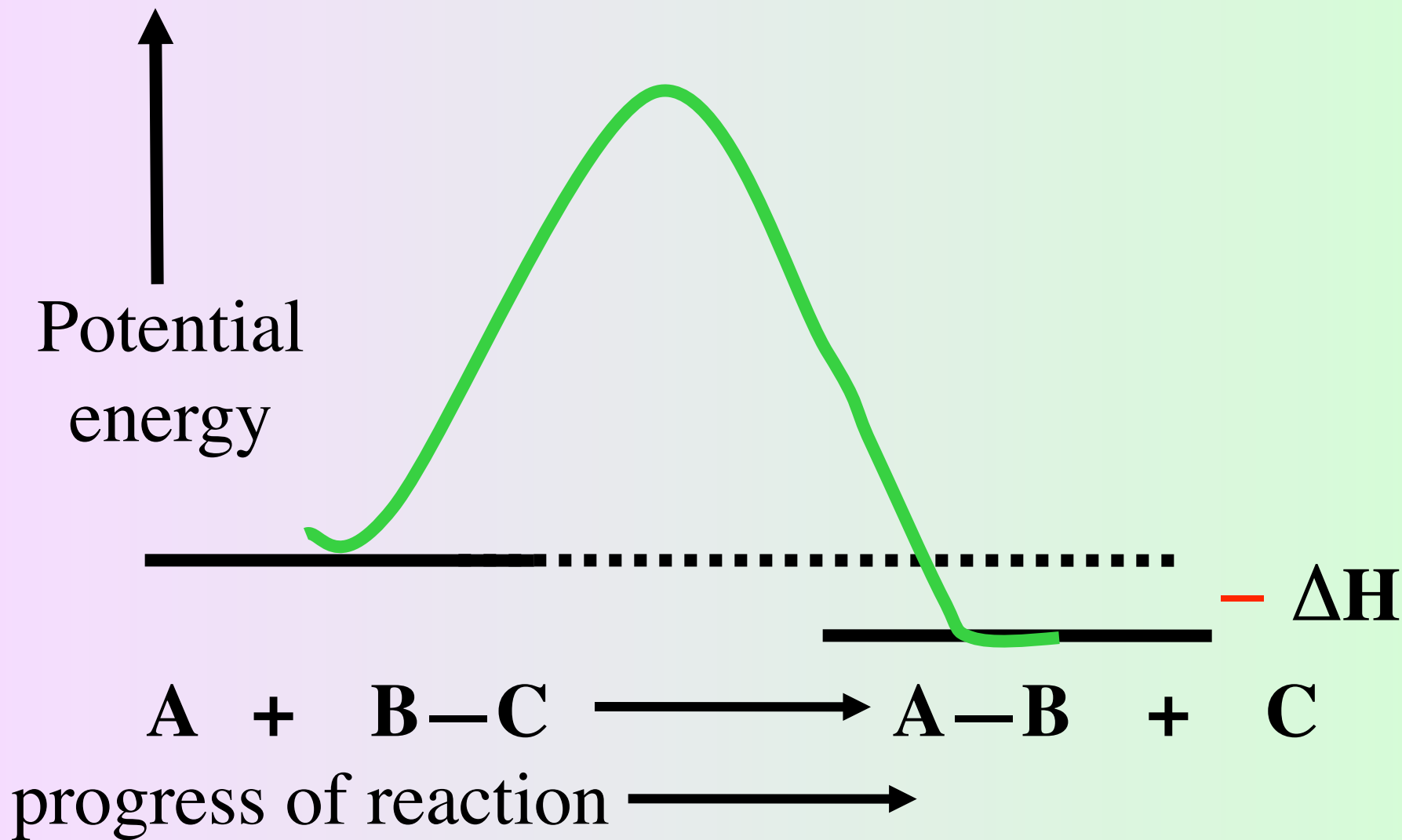


**stronger chemical bonds in products
than in reactants**

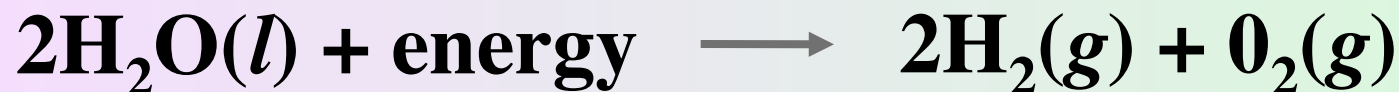
less potential energy in products

**The sign of ΔH is for $-$ for an exothermic
process**

Consider a hypothetical one-step reaction (exothermic)



An endothermic reaction

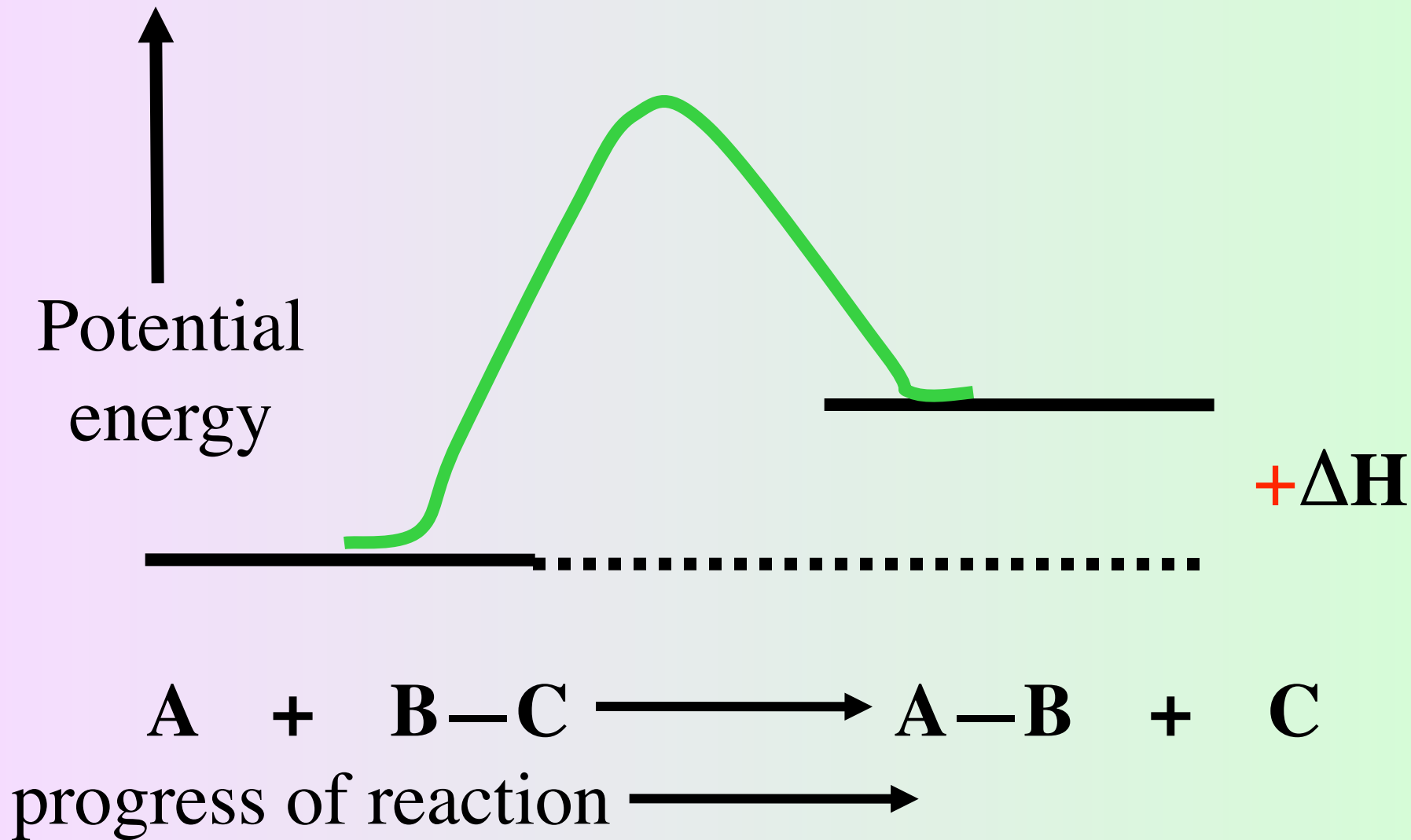


**weaker chemical bonds in products
in reactants**

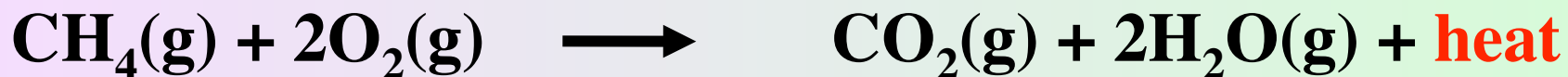
more potential energy in products

**The sign of ΔH is + for an endothermic
process**

Consider a hypothetical one-step reaction (endothermic)



ways to express combustion of methane



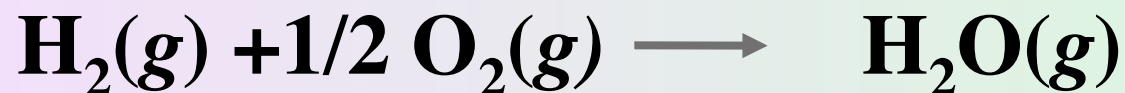
$$\Delta\text{H} = -890 \text{ kJ}$$

Thermochemical equations

- 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 ΔH .**
- 3. If a reaction is multiplied by some factor, its ΔH must be multiplied by the same factor.**

Thermochemical equations

2. Reverse the direction of a given reaction, reverse the sign of ΔH .



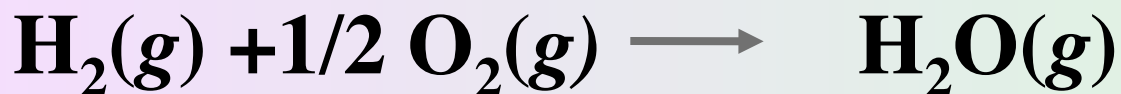
$$\Delta H^\circ = -241.8 \text{ kJ/mol}$$



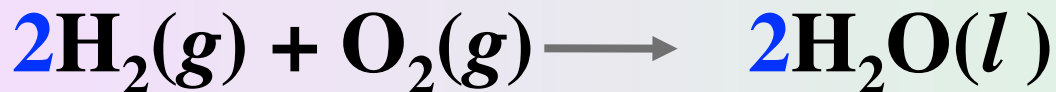
$$\Delta H^\circ = +241.8 \text{ kJ/mol}$$

Thermochemical equations

3. If a reaction is multiplied by some factor, its ΔH 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

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

5. ΔH depends on temperature

the temperature is the same for reactants and products.

Standard Enthalpy of Formation and Reaction

$$\Delta H^{\circ}_f$$

$$\Delta H^{\circ}_{rxn}$$

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** ΔH_f°

Standard enthalpy of formation

$$\Delta H_f^\circ$$

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

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

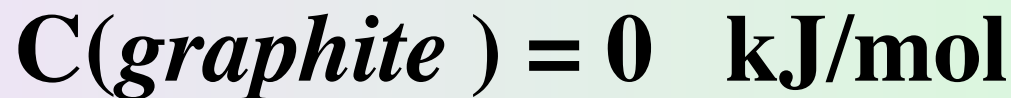
- for substances that exist as gases the pressure is 1 atm
- for a substance present in a solution, the standard state is a concentration is 1 molar

Standard Enthalpies of Formation

Compound	ΔH_f° (kJ/mol)
CO₂(g)	-393.5
NH₃(g)	-46.3
NO₂(g)	33.85
H₂O(liq)	-285.8
H₂O(g)	-241.8
Al₂O₃(s)	-1669.8

The Reference Point

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



Standard enthalpy of reaction

ΔH° 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?

directly

indirectly

The Direct Method

used for compounds that can be directly synthesized from their elements



Standard Enthalpies of Formation

Compound	ΔH_f° (kJ/mol)
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CO₂(g)	-393.5
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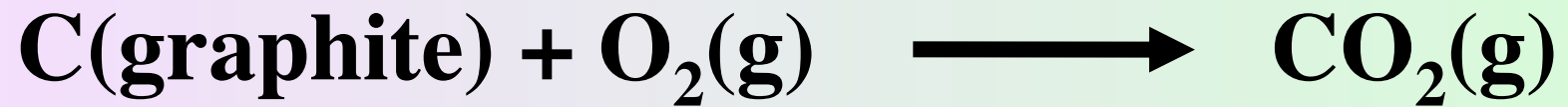
NH₃(g)	-46.3
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NO₂(g)	33.85
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H₂O(liq)	-285.8
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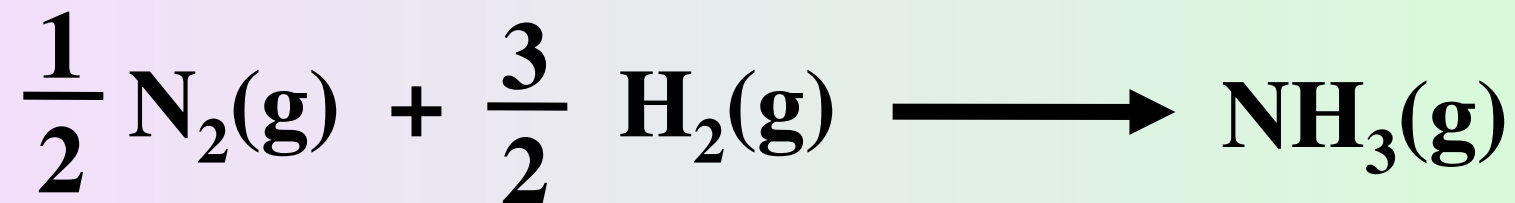
Al₂O₃(s)	-1669.8
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$$\Delta H^\circ = -393.5 \text{ kJ}$$

Standard Enthalpies of Formation

Compound	ΔH_f° (kJ/mol)
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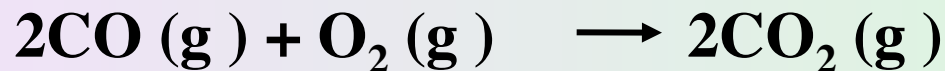
$$\Delta H^\circ = -46.3 \text{ kJ}$$

The Indirect Method

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 steps.

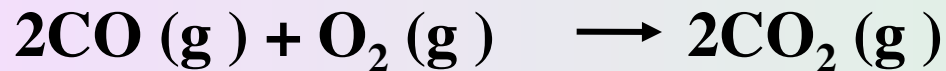
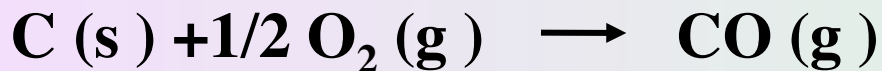
Use Hess's law to calculate the heat of reaction (ΔH_{rxn}) for the burning of carbon monoxide:



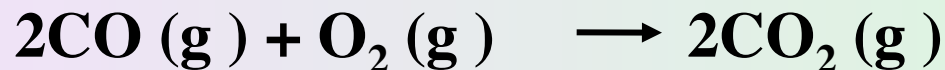
Standard enthalpies of formation: (ΔH°_f)

Carbon monoxide -110 kJ/mol

Carbon dioxide -394 kJ/mol



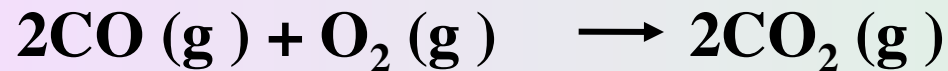
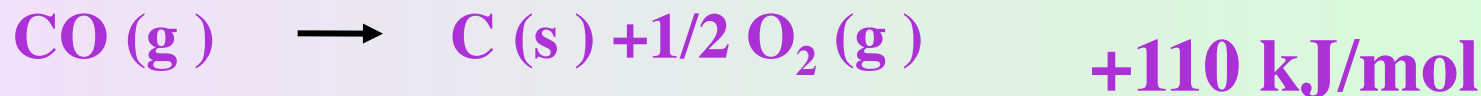
Use Hess's law to calculate the heat of reaction (ΔH) for the burning of carbon monoxide:



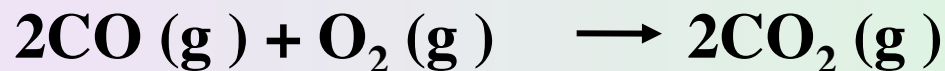
Standard enthalpies of formation: (ΔH°_f)

Carbon monoxide -110 kJ/mol

Carbon dioxide -394 kJ/mol



Use Hess's law to calculate the heat of reaction (ΔH) for the burning of carbon monoxide:



Standard enthalpies of formation: (ΔH°_f)

Carbon monoxide -110 kJ/mol

Carbon dioxide -394 kJ/mol



Given:

ΔH° 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: ΔH°_f for benzene

Given:

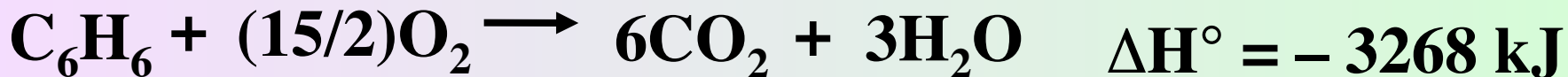
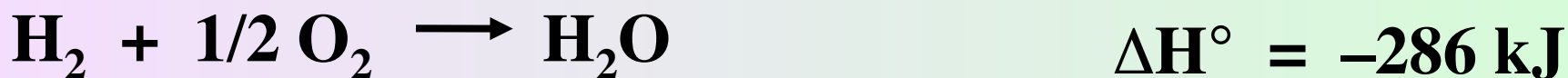
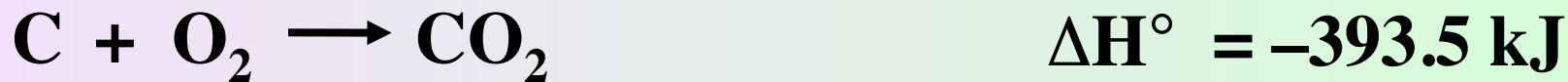
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and standard enthalpies of formation:

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carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



Given:

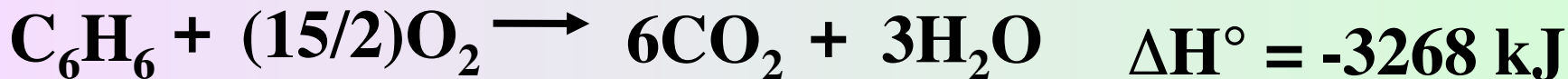
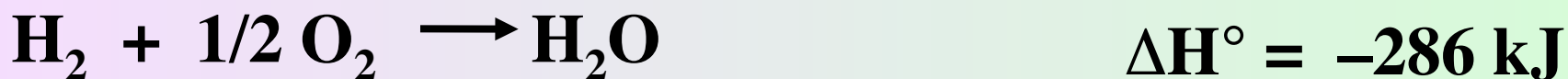
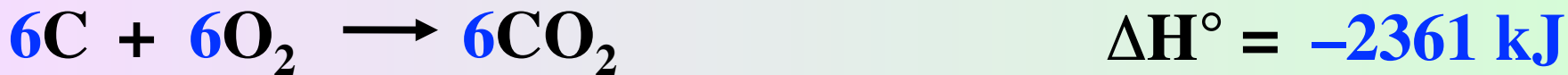
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Calculate: ΔH°_f for benzene



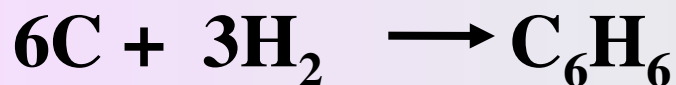
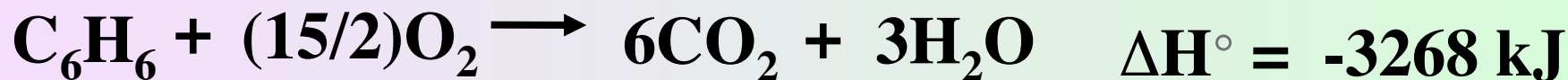
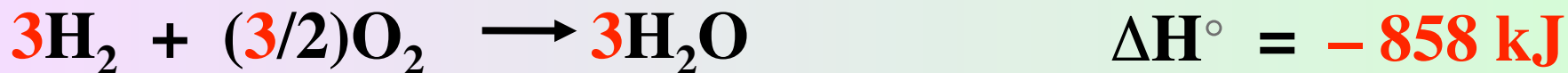
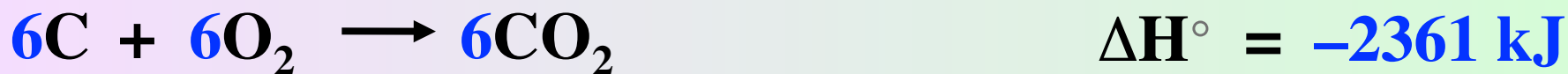
Given:

ΔH° for combustion of benzene = -3268 kJ/mol
and standard enthalpies of formation:

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carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



Given:

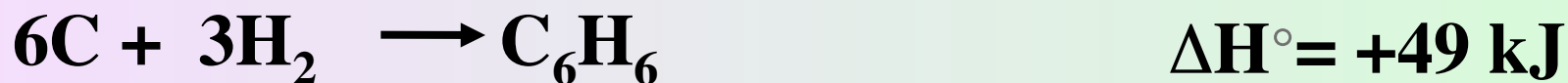
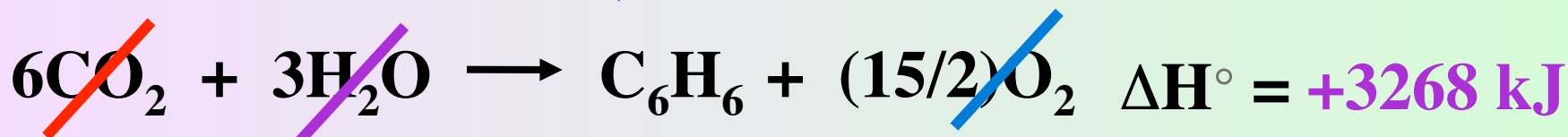
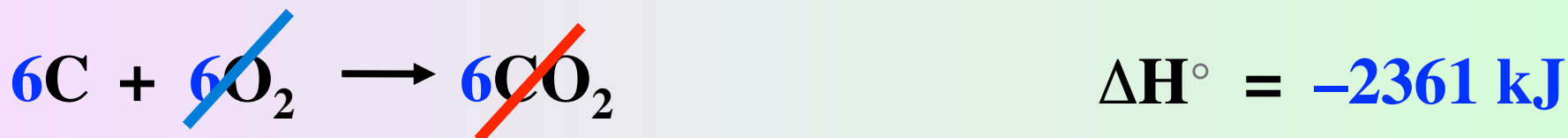
ΔH° for combustion of benzene = -3268 kJ/mol

and standard enthalpies of formation:

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



Alternative and easier method

$$\Delta H^\circ =$$

(sum of heats of formation of products)

minus

(sum of heats of formation of reactants)

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

Given:

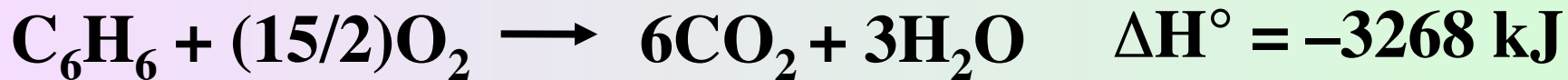
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and standard enthalpies of formation:

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carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



Given:

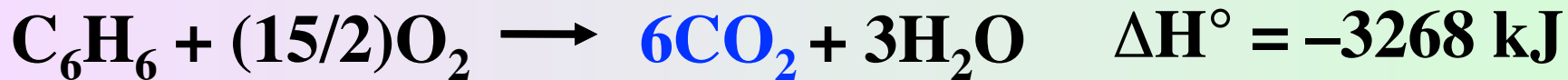
ΔH° for combustion of benzene = -3268 kJ/mol

and standard enthalpies of formation:

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



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

Given:

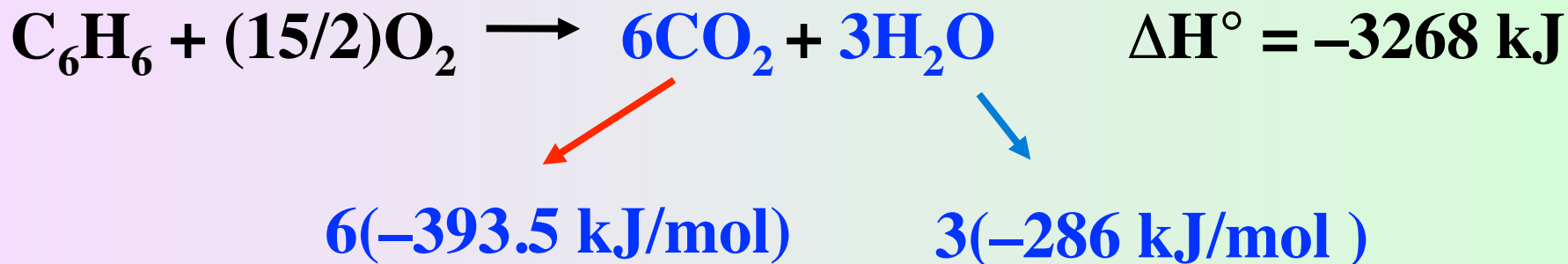
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Calculate: ΔH°_f for benzene



Given:

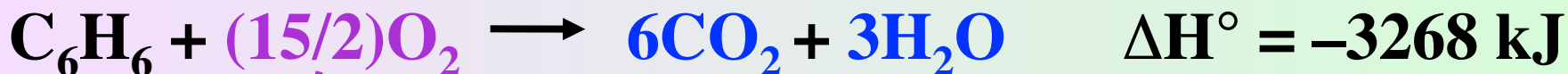
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Calculate: ΔH°_f for benzene



$15/2(0)$

Given:

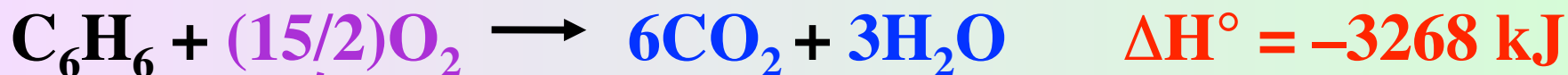
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and standard enthalpies of formation:

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



$15/2(0)$

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

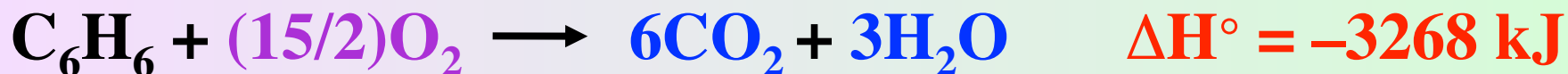
Given:

ΔH° for combustion of benzene = -3268 kJ/mol
and standard enthalpies of formation:

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



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

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

(-3219 kJ)

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

Given:

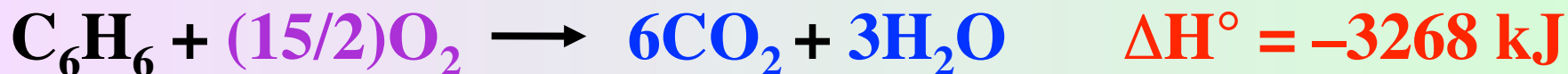
ΔH° for combustion of benzene = -3268 kJ/mol

and standard enthalpies of formation:

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



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

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

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

Given:

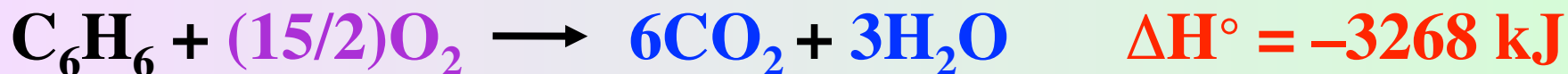
ΔH° for combustion of benzene = -3268 kJ/mol

and standard enthalpies of formation:

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



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

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

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

Given:

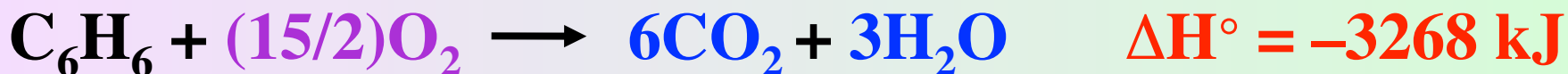
ΔH° for combustion of benzene = -3268 kJ/mol

and standard enthalpies of formation:

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate: ΔH°_f for benzene



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

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

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

Given the standard enthalpies of formation

propane C_3H_8 = -104 kJ/mol

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate ΔH° for combustion of propane.

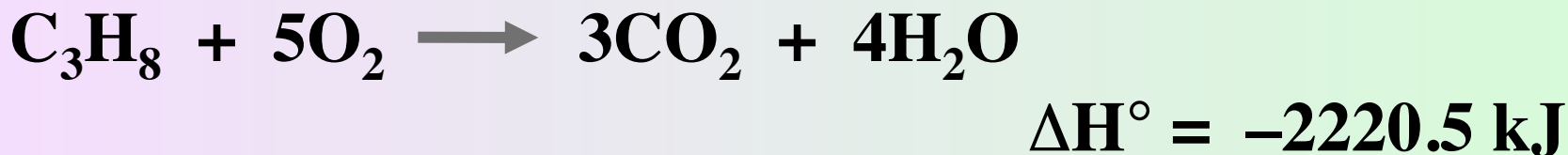
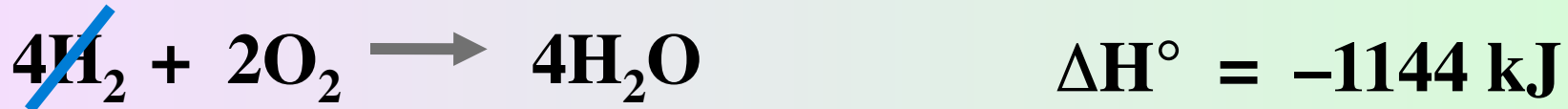
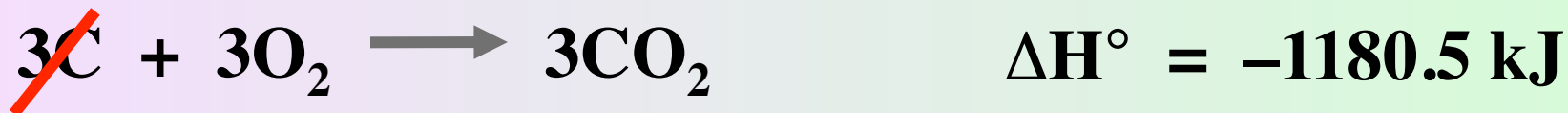
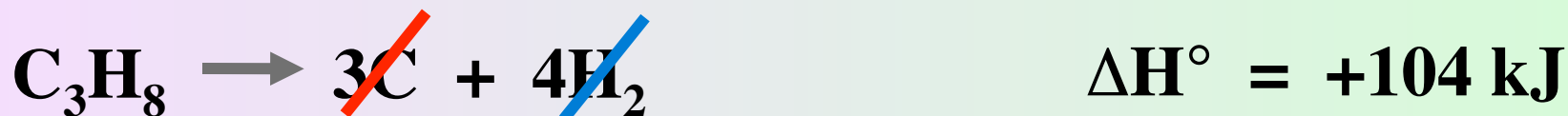
Given the standard enthalpies of formation

propane C_3H_8 = -104 kJ/mol

water = -286 kJ/mol

carbon dioxide = -393.5 kJ/mol

Calculate ΔH° for combustion of propane.

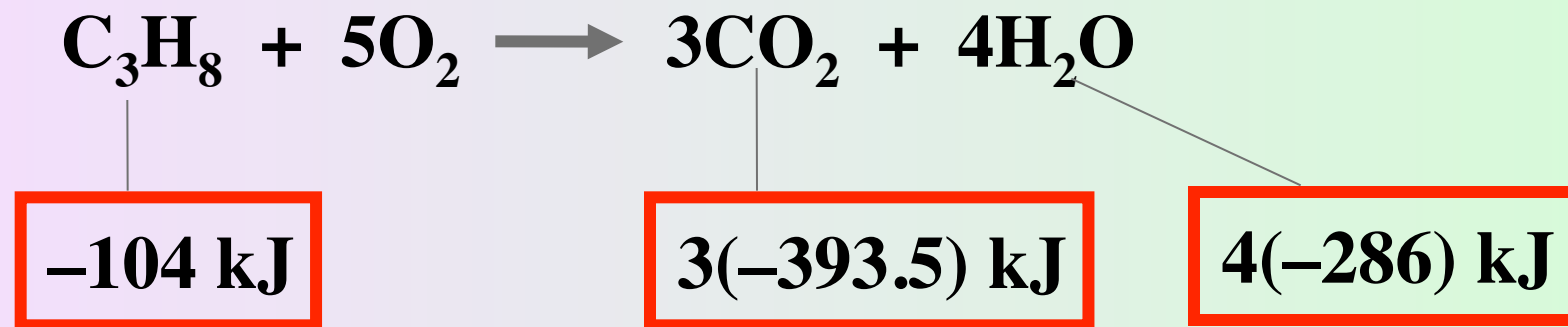


Alternative and easier method

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

Given the standard enthalpies of formation

Calculate ΔH° for combustion of propane.



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

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