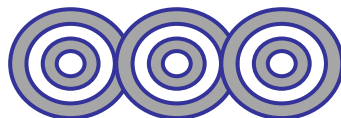




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Chapter 6

Thermochemistry

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6.4

Enthalpy of chemical reactions

Constant Volume Processes

If a chemical reaction is run at constant volume, then $\Delta V = 0$ and no P-V work will result from this change.

$$w = -P \Delta V$$

$$\Delta E = q + w$$

$$\Delta E = q - P \Delta V$$

at constant volume; $\Delta V=0$, so $w=0$

$$\Delta E = q_v$$

the subscript “ v ” means that this process carried out at constant-volume.

Constant Pressure Processes

In general, for a constant-pressure process we write

$$\begin{aligned}\Delta E &= q + w \\ &= q_p - P\Delta V\end{aligned}$$

or

$$q_p = \Delta E + P\Delta V$$

where the subscript “p” denotes constant-pressure condition.

This thermodynamic function of a system called ***enthalpy (H)***, which is defined by the equation;

$$H = E + PV$$

where E is the internal energy of the system and P and V are the pressure and volume of the system, respectively.

$$**H = E + PV**$$

Because E and PV have energy units, enthalpy also has energy units.

E , P , and V are all state functions, that is, the changes in $(E + PV)$ depend only on the initial and final states. It follows, therefore, that the change in H , or ΔH , also depends only on the initial and final states. Thus, H is a state function.

For any process, the change in enthalpy is given by;

$$**\Delta H = \Delta E + \Delta(PV)**$$

If the pressure is held constant, then

$$**\Delta H = \Delta E + P\Delta V**$$

Enthalpy of Reactions

Because most reactions are constant-pressure processes, we can equate the heat change in these cases to the change in enthalpy. For any reaction of the type

Reactants → Products

we define the change in enthalpy, called the enthalpy of reaction, ΔH , as the difference between the enthalpies of the products and the enthalpies of the reactants:

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

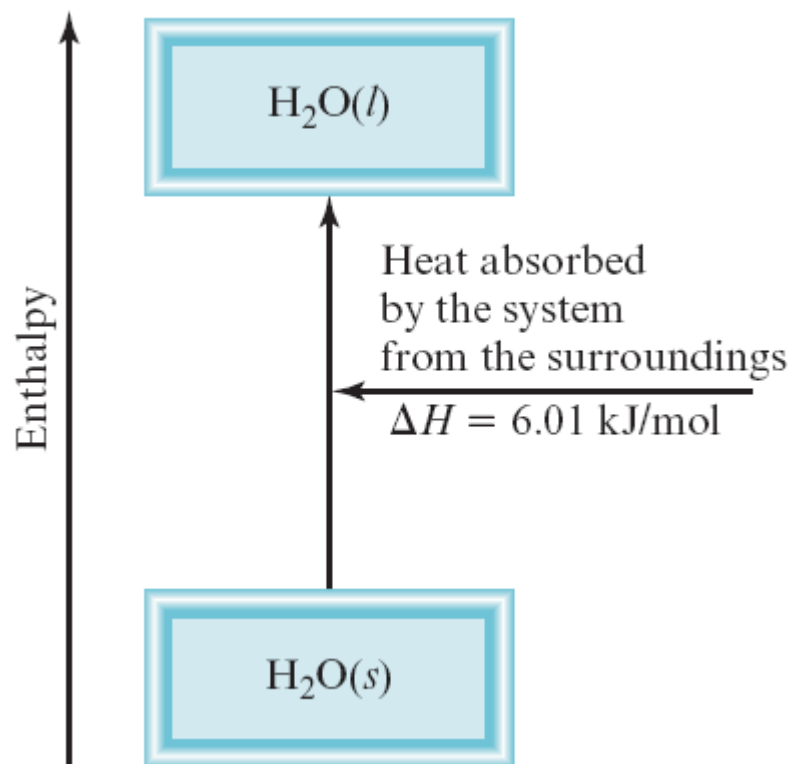
The enthalpy of reaction can be positive or negative, depending on the process.

-For an **endothermic** process (heat absorbed by the system from the surroundings), ΔH is positive (that is, $\Delta H > 0$).

-For an **exothermic** process (heat released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$).

Thermochemical Equations

Physical change ...

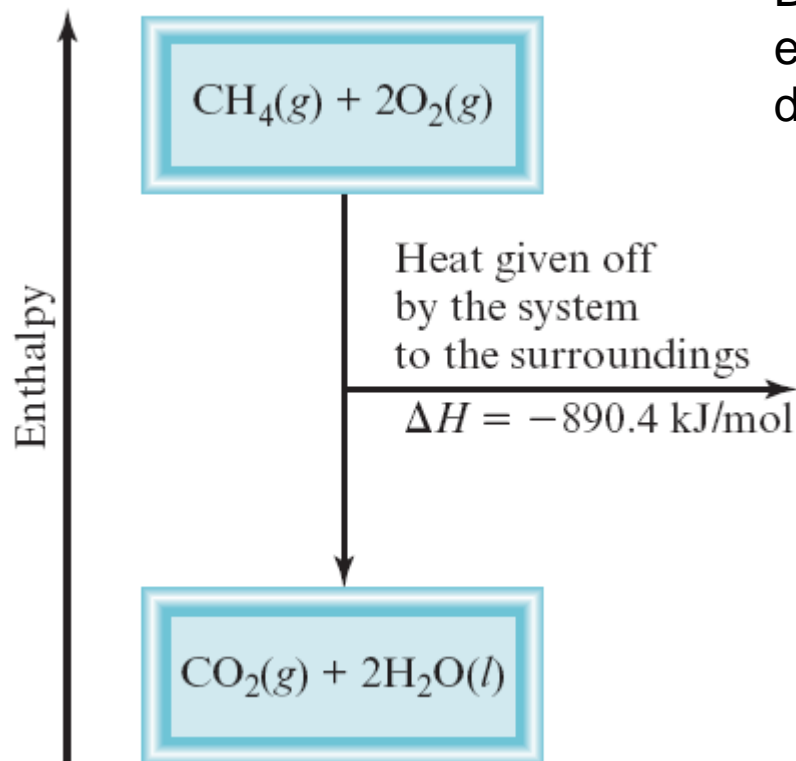


Melting 1 mole of ice at 0°C (an endothermic process) results in an enthalpy increase in the system of 6.01 kJ.



Thermochemical Equations

Chemical change ...

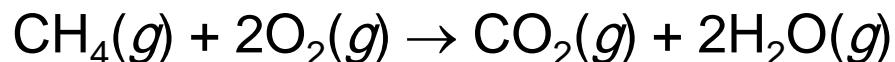


Burning 1 mole of methane in oxygen gas (an exothermic process) results in an enthalpy decrease in the system of 890.4 kJ.

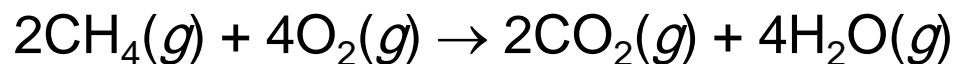


Enthalpy Guidelines

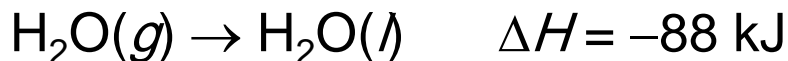
1. Enthalpy is an extensive property. The magnitude of ΔH , therefore, is directly proportional to the amount of reactant consumed in the process.
2. ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.
3. ΔH for a reaction depends on the state of the products and the state of the reactants.



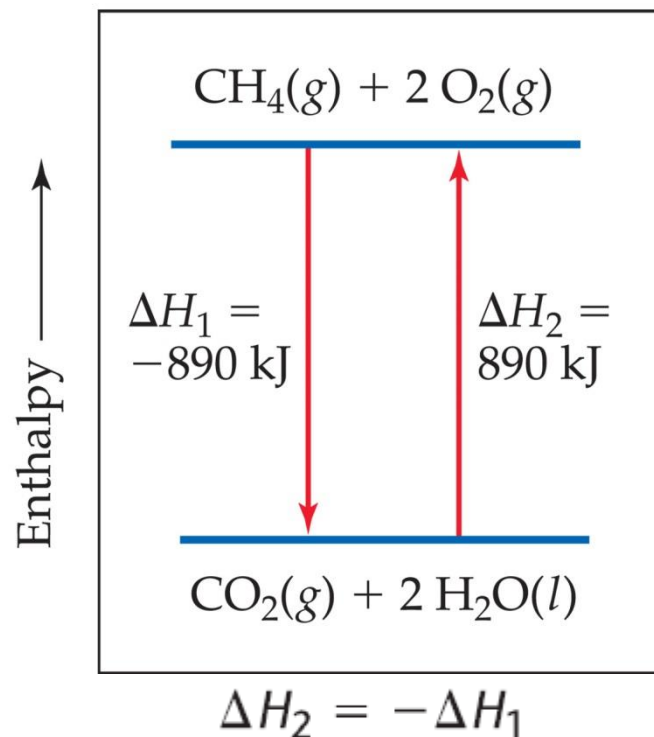
$$\Delta H = -890 \text{ kJ}$$



$$\Delta H = -1780 \text{ kJ}$$

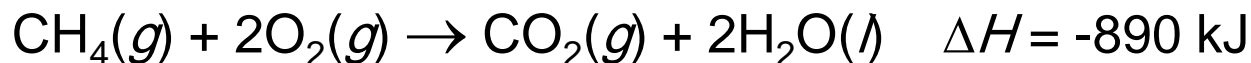


Condensation of gaseous water to form liquid water



Example

How much heat is released when 4.50 g of methane gas is burned in a constant pressure system?



Solution

By adding the atomic weights of C and 4 H, we have 1 mol CH₄ = 16.0 g CH₄. We can use the appropriate conversion factors to convert grams of CH₄ to moles of CH₄ to kilojoules:

$$\text{Heat} = (4.50 \text{ g CH}_4) \left(\frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \right) \left(\frac{-890 \text{ kJ}}{1 \text{ mol CH}_4} \right) = -250 \text{ kJ}$$

The negative sign indicates that the system released 250 kJ into the surroundings.

EXAMPLE

Given the thermochemical equation

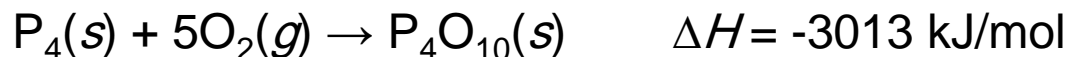


calculate the heat evolved when 87.9 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3 .

$$\Delta H = 87.9 \text{ g } \cancel{\text{SO}_2} \times \frac{1 \cancel{\text{ mol SO}_2}}{64.07 \text{ g } \cancel{\text{SO}_2}} \times \frac{-198.2 \text{ kJ}}{2 \cancel{\text{ mol SO}_2}} = -136 \text{ kJ}$$

Practice Exercise

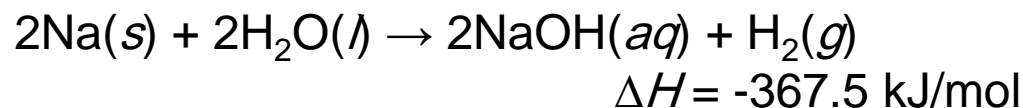
Calculate the heat evolved when 266 g of white phosphorus (P_4) burns in air according to the equation



A Comparison of ΔH and ΔE

What is the relationship between ΔH and ΔE for a process?

Let us consider the reaction between sodium metal and water:



$$\Delta E = \Delta H - P \Delta V$$

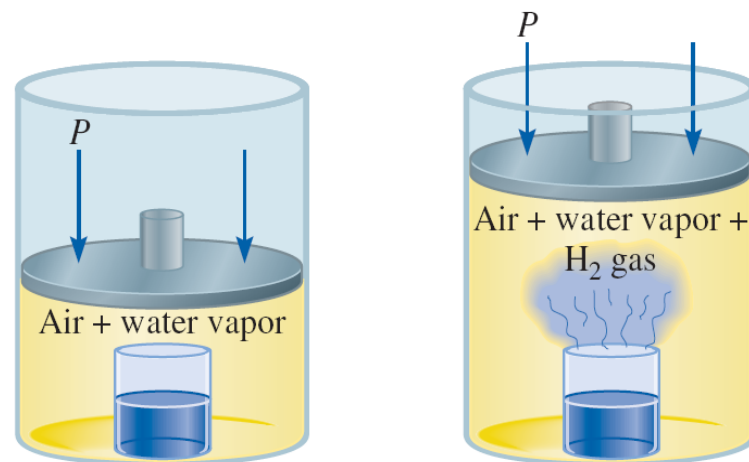
at 25°C (298 K) and 1 atm, 1 mole of H_2 has

$PV = 1 \times 0.0821 \times 298 = 24.5 \text{ L}\cdot\text{atm}$, so;

$-P \Delta V = -24.5 \text{ L}\cdot\text{atm} = -2.5 \text{ kJ}$. Finally;

$$\Delta E = -367.5 \text{ kJ/mol} - 2.5 \text{ kJ/mol}$$
$$= -370.0 \text{ kJ/mol}$$

This calculation shows that ΔE and ΔH are approximately the same.



A beaker of water inside a cylinder fitted with a movable piston. The pressure inside is equal to the atmospheric pressure. As the Na metal reacts with water, the H_2 gas generated pushes the piston upward (doing work on the surroundings) until the pressure inside is again equal to the pressure outside.

Recall that;

$$PV = nRT$$

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J} = 0.1013 \text{ kJ}$$

Another way to calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature. In this case,

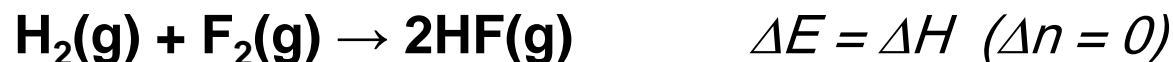
$$\begin{aligned}\Delta E &= \Delta H - \Delta(PV) \\ &= \Delta H - \Delta(nRT)\end{aligned}$$

$$\Delta E = \Delta H - RT \Delta n$$

where Δn is defined as

$\Delta n = (\text{number of moles of product gases} - \text{number of moles of reactant gases})$

For reactions that do not result in a change in the number of moles of gases from reactants to products,
e.g.,



EXAMPLE

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO₂ at 1 atm and 25°C:



$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases} \\ &= 2 - 3 = -1\end{aligned}$$

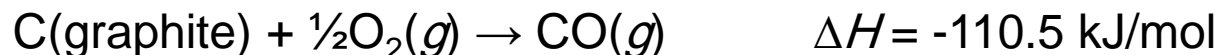
$$R = 8.314 \text{ J/K}\cdot\text{mol}, \quad T = 298 \text{ K}$$

$$\Delta E = \Delta H - RT \Delta n$$

$$= -566000 - (8.314 \times 298 \times -1) = -563522 \text{ J/mol} = -563.5 \text{ kJ/mol}$$

Practice Exercise

What is ΔE for the formation of 1 mole of CO at 1 atm and 25°C?



$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases} \\ &= 1 - \frac{1}{2} = \frac{1}{2}\end{aligned}$$

$$= -110500 - (8.314 \times 298 \times \frac{1}{2}) = -111739 \text{ J/mol} = -111.74 \text{ kJ/mol}$$

6.5

Calorimetry

In the laboratory, heat changes in physical and chemical processes are measured with a calorimeter; a closed container designed specifically for this purpose. Calorimetry; the measurement of **heat changes**.

- **Calorimetry**: the measurement of heat flow.
- **Calorimeter**: a device used measure heat flow.

Specific Heat and Heat Capacity

The **specific heat** (s) of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius. It has the units $\text{J/g}\cdot^{\circ}\text{C}$.

The **heat capacity** (C) of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius. Its units are $\text{J}/^{\circ}\text{C}$.

Specific heat is an intensive property whereas heat capacity is an extensive property.

The relationship between the heat capacity and specific heat of a substance is

$$C = m s$$

where m is the mass of the substance in grams. e.g., the specific heat of water is $4.184 \text{ J/g}\cdot^{\circ}\text{C}$, and the heat capacity of 60.0 g of water is
 $(60.0 \text{ g})(4.184 \text{ J/g}\cdot^{\circ}\text{C}) = 251 \text{ J}/^{\circ}\text{C}$

The equations for calculating the heat change are given by

$$q = m s \Delta t$$

$$q = C \Delta t$$

where:

q: the amount of heat that has been absorbed or released in a particular process.

Δt: is the temperature change; $\Delta t = t_{final} - t_{initial}$

The sign convention for *q* is the same as that for enthalpy change;

q is - positive for endothermic processes, and

- negative for exothermic processes.

The specific heats of some common substances

Substance	Specific Heat (J/g °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H ₂ O	4.184
CH ₃ CH ₂ OH	2.460

Notice that the specific heat of liquid water is higher than those of the other substances listed. The high specific heat of water affects Earth's climate because it makes the temperatures of the oceans relatively resistant to change. It also is very important in maintaining a constant temperature in our bodies.

EXAMPLE

A 466-g sample of water is heated from 8.50°C to 74.60°C. Calculate the amount of heat absorbed (in kilojoules) by the water.

$$\begin{aligned} q &= m s \Delta t \\ &= (466 \text{ g}) (4.184 \text{ J/g } ^\circ\text{C}) (74.60^\circ\text{C} - 8.50^\circ\text{C}) \\ &= 1.29 \times 10^5 \text{ J} = 129 \text{ kJ.} \end{aligned}$$

Practice Exercise

An iron bar of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

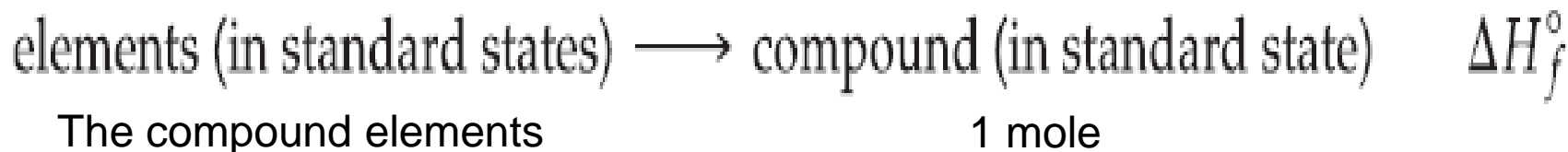
6.6

Standard enthalpy of formation and reaction

The reference point for all enthalpy expressions is called the standard enthalpy of formation (ΔH_f°).

Substances are said to be in the standard state at 1 atm and 25°C, hence the term “standard enthalpy”. The superscript ° represents standard-state conditions (1 atm), and the subscript “f” stands for formation.

The **standard enthalpy of formation** of a compound is the heat change that results when **1 mole** of the compound is formed from its elements at **1 atm** and **25°C**.



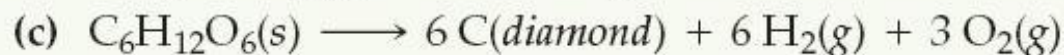
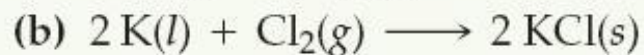
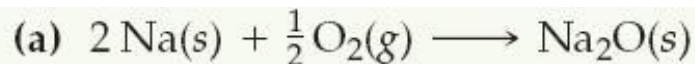
Example



- The elemental source of oxygen is O_2 , not O or O_3 , because O_2 is the stable form of oxygen at standard conditions.
- Similarly, the elemental source of carbon is graphite and not diamond, because graphite is the more stable (lower energy).
- Likewise, the most stable form of hydrogen under standard conditions is $\text{H}_2(\text{g})$.

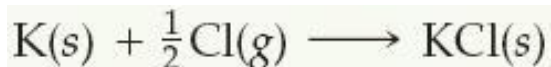
Example

For which of the following reactions at 25 °C would the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of formation?

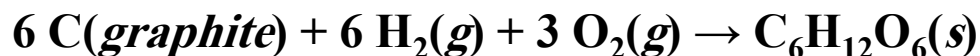


(a) 1 mol Na_2O is formed from the elements sodium and oxygen in their proper states, solid Na and O_2 gas, respectively. Therefore, the enthalpy change for reaction (a) corresponds to a standard enthalpy of formation.

(b) Potassium is given as a liquid. It must be changed to the solid form, its standard state at 25°C. Furthermore, two moles of product are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of $\text{KCl}(s)$. The equation for the formation reaction of 1 mol of $\text{KCl}(s)$ is



(c) The reaction does not form a substance from its elements. Instead, a substance decomposes to its elements, so this reaction must be reversed. Next, the element carbon is given as diamond, whereas graphite is the standard state of carbon at 25°C and 1 atm. The correct equation should be



The standard enthalpy of formation of any **element** in its most stable form is **zero**.

-e.g., Molecular oxygen (O_2) is more stable than the other allotropic form of oxygen, ozone (O_3), at 1 atm and 25°C . Thus, we can write $\Delta H^\circ_f (\text{O}_2) = 0$, but $\Delta H^\circ_f (\text{O}_3) = 142.2 \text{ kJ/mol}$.

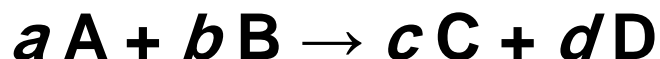
-e.g., graphite is a more stable allotropic form of carbon than diamond at 1 atm and 25°C , so we have $\Delta H^\circ_f (\text{C, graphite}) = 0$ and $\Delta H^\circ_f (\text{C, diamond}) = 1.90 \text{ kJ/mol}$.

Standard enthalpies of formation of some substances at 25°C

Substance	$\Delta H^\circ_f (\text{kJ/mol})$	Substance	$\Delta H^\circ_f (\text{kJ/mol})$
O(g)	249.4	$\text{C}_2\text{H}_2(\text{g})$ acetylene	226.7
$\text{O}_2(\text{g})$	0	$\text{C}_6\text{H}_6(\text{l})$ benzene	49.0
$\text{O}_3(\text{g})$	142.2	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ glucose	-1273
$\text{Cl}_2(\text{g})$	0	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$ sucrose	-2221
$\text{H}_2\text{O}_2(\text{l})$	-187.6	NH_3 ammonia	-46.19
$\text{H}_2\text{O(g)}$	-241.8	HF(g)	-268.6
$\text{H}_2\text{O(l)}$	-285.8	HCl(g)	-92.3
CO(g)	-110.5	HBr(g)	-36.23
$\text{CO}_2(\text{g})$	-393.5	HI(g)	25.9
$\text{CH}_4(\text{g})$ methane	-74.8	NaCl(s)	-410.9
$\text{C}_2\text{H}_6(\text{g})$ ethane	-84.68	AgCl(s)	-127
$\text{C}_3\text{H}_8(\text{g})$ propane	-103.85	$\text{NaHCO}_3(\text{s})$ sodium bicarbonate	-947.7
$\text{CH}_3\text{OH(l)}$ methanol	-238.6	$\text{Na}_2\text{CO}_3(\text{s})$ sodium carbonate	-1130.9
$\text{C}_2\text{H}_5\text{OH(l)}$ ethanol	-277.7	$\text{CaCO}_3(\text{s})$ calcium carbonate	-1207.1

The importance of the standard enthalpies of formation is that once we know their values, we can readily calculate the **standard enthalpy of reaction**, $\Delta H^\circ_{\text{rxn}}$, defined as the enthalpy of a reaction carried out at 1 atm.

e.g., consider the hypothetical reaction



where a , b , c , and d are stoichiometric coefficients. For this reaction

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

We can generalize this Equation as

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

where m and n denote the stoichiometric coefficients for the reactants and products,

To use the Equation to calculate $\Delta H^\circ_{\text{rxn}}$, we must know the ΔH°_f values of the compounds that take part in the reaction. These values can be determined by applying direct method or indirect method.

The Direct Method

This method of measuring ΔH_f° works for compounds that can be readily synthesized from their elements.

Example,,,

Calculate the enthalpy of formation of carbon dioxide $\text{CO}_2(\text{g})$.



$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \Delta H_f^\circ(\text{CO}_2, \text{g}) - [\Delta H_f^\circ(\text{C, graphite}) + \Delta H_f^\circ(\text{O}_2, \text{g})] \\ &= -393.5 \text{ kJ/mol}\end{aligned}$$

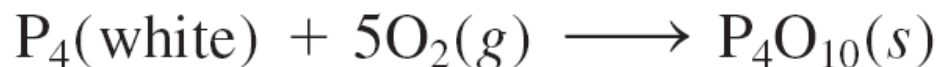
Because both graphite and O_2 are stable allotropic forms of the elements,

$\Delta H_f^\circ(\text{C, graphite})$ and $\Delta H_f^\circ(\text{O}_2, \text{g}) = \text{zero}$

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$$

Other compounds that can be studied by the direct method are; **SF₆**, **P₄O₁₀** and **CS₂**. The equations representing their syntheses are



Note that S(rhombic), P(white), C(graphite) are the most stable allotropes of sulfur, phosphorus and carbon, respectively, at 1 atm and 25°C, so their ΔH°_f values = 0.

Substance	ΔH°_f (kJ/mol)
S(rhombic)	0
S(monoclinic)	0.30
C(graphite)	0
C(diamond)	1.9
P(white)	0
O ₂ (g)	0
F ₂ (g)	0

The Indirect Method

Many compounds cannot be directly synthesized from their elements. In these cases, ΔH_f° can be determined by Hess's law.

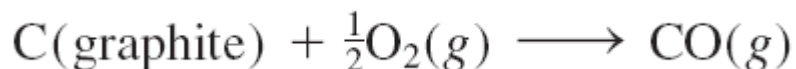
***Hess's law** stated that: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.*

In other words, if a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of ΔH for each individual step.

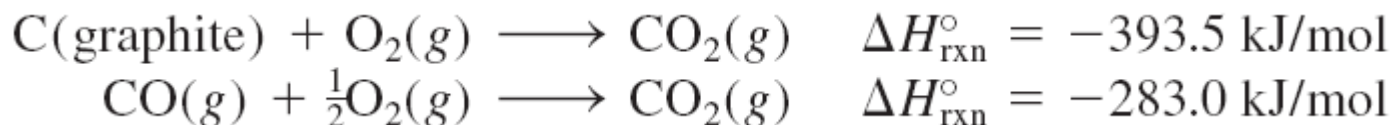
Enthalpy change is a state function, its independent on the number of steps or the nature of the path by which the reaction is carried out.

Example

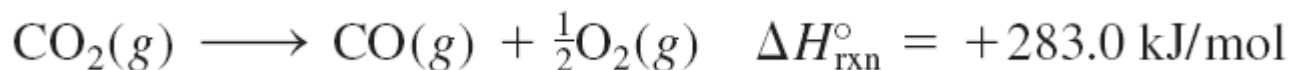
Let's say we are interested in the standard enthalpy of formation of carbon monoxide (CO). We might represent the reaction as



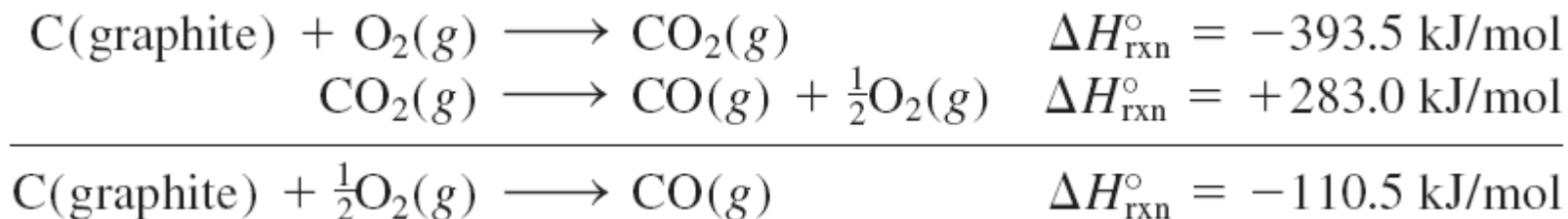
However, burning graphite also produces some CO_2 , so we cannot measure the enthalpy change for CO directly as shown. Instead, we must employ an indirect route, based on Hess's law. It is possible to carry out the following two separate reactions, which do go to completion:



First, we reverse the second Equation

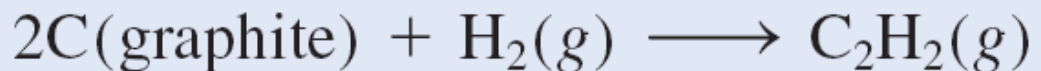


Because chemical equations can be added and subtracted just like algebraic equations,

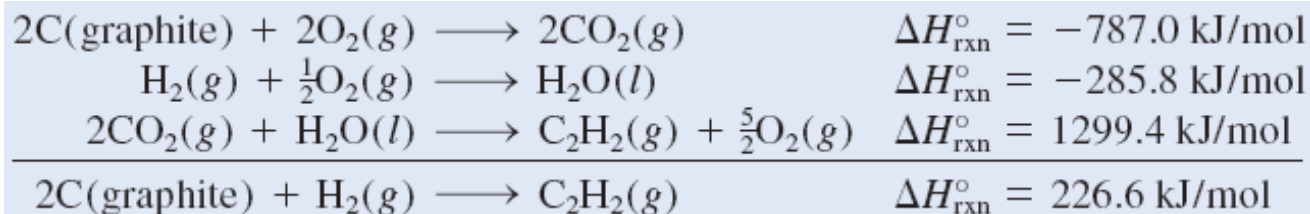
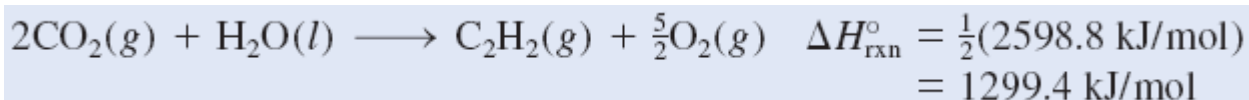
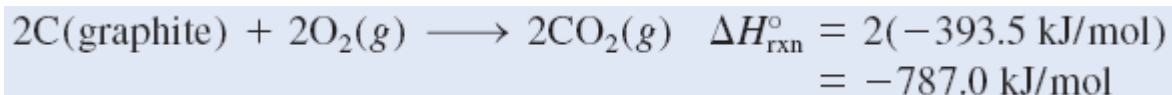
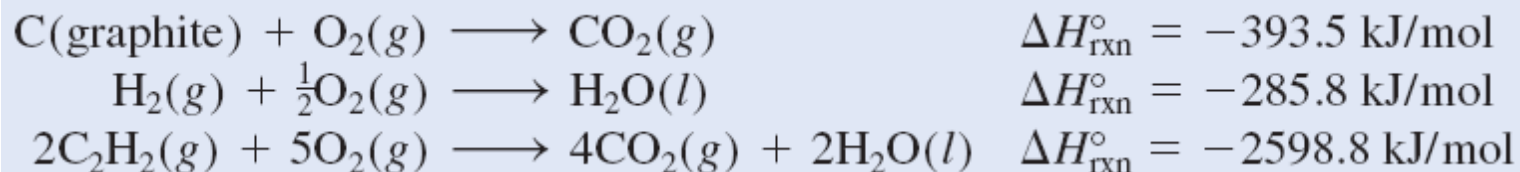


EXAMPLE

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:



The equations for each step and the corresponding enthalpy changes are



EXAMPLE

The thermite reaction involves aluminum and iron(III) oxide



This reaction is highly exothermic and the liquid iron formed is used to weld metals. Calculate the heat released in kJ/g of Al reacted with Fe_2O_3 .

$\Delta H_f^\circ(\text{Fe}(l)) = 12.40 \text{ kJ/mol}$, $\Delta H_f^\circ(\text{Al}_2\text{O}_3(s)) = -1669.8 \text{ kJ/mol}$, $\Delta H_f^\circ(\text{Fe}_2\text{O}_3(s)) = -822.2 \text{ kJ/mol}$.

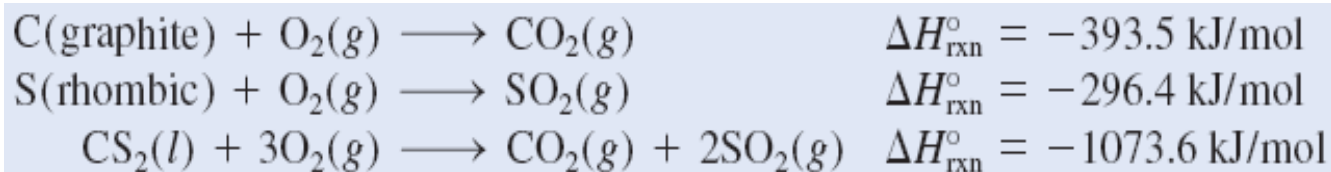
$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= [\Delta H_f^\circ(\text{Al}_2\text{O}_3) + 2\Delta H_f^\circ(\text{Fe})] - [2\Delta H_f^\circ(\text{Al}) + \Delta H_f^\circ(\text{Fe}_2\text{O}_3)] \\ &= [(-1669.8 \text{ kJ/mol}) + 2(12.40 \text{ kJ/mol})] - [2(0) + (-822.2 \text{ kJ/mol})] \\ &= -822.8 \text{ kJ/mol}\end{aligned}$$

This is the amount of heat released for two moles of Al reacted. to convert to kJ/g Al. The molar mass of Al is 26.98 g, so

$$\begin{aligned}\text{heat released per gram of Al} &= \frac{-822.8 \text{ kJ}}{2 \text{ mol Al}} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \\ &= -15.25 \text{ kJ/g}\end{aligned}$$

Practice Exercise

Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that



Practice Exercise

Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. The standard enthalpy of formation of benzene is 49.04 kJ/mol.

