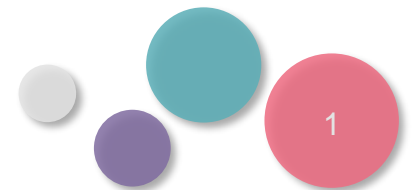


Chapter 9: Thermochemistry

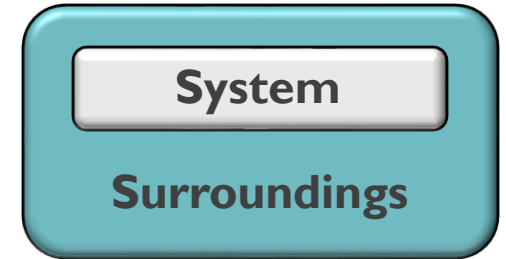


Energy and Energy Changes

Thermochemistry is the study of heat (the transfer of thermal energy) in chemical reactions.

The **system** is a part of the universe that is of specific interest.

The **surroundings** constitute the rest of the universe outside the system. The system is usually defined as the substances involved in chemical and physical changes.



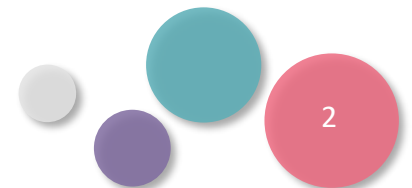
Universe = System + Surroundings

Heat is the transfer of thermal energy.

Heat is either absorbed or released during a process.

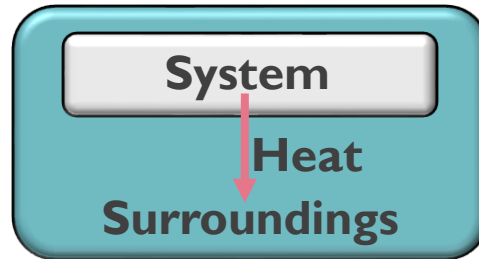
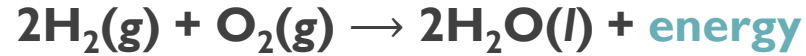
The SI energy unit is a Joule, J. Often calories are used, and 1 calorie is the amount of heat required to raise 1 g of water by 1°C.

- 1 cal = 4.184 J
- calorie is not the same as a nutritional calorie (Cal)
- 1 Cal = 1000 cal

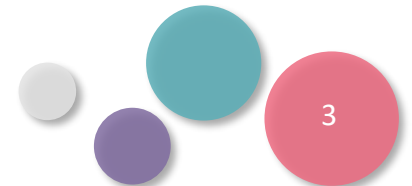
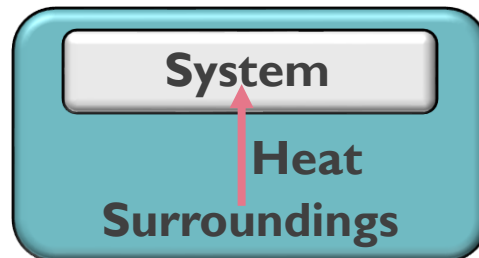
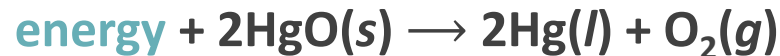


Energy and Energy Changes

An **exothermic process** occurs when heat is transferred from the system to the surroundings. “Feels hot!”



An **endothermic process** occurs when heat is transferred from the surroundings to the system. “Feels cold”



Calorimetry: Specific Heat and Heat Capacity

Calorimetry is the measurement of heat changes. Heat changes are measured in a device called a calorimeter.

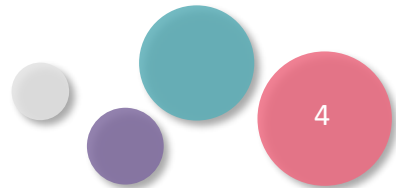
The **specific heat capacity** (*c*) of a substance is the amount of heat required to raise the temperature of 1 g of the substance by 1°C. (**J/(g °C)**)

The **heat capacity** (*C*) is the amount of heat required to raise the temperature of an object by 1°C. (**J/°C**). The “object” may be a given quantity of a substance.

Substance	Specific Heat (J/g · °C)
Al(s)	0.900
Au(s)	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu(s)	0.385
Fe(s)	0.444
Hg(l)	0.139
H ₂ O(l)	4.184
C ₂ H ₅ OH(l) Ethanol	2.46

$$\text{Heat capacity of 1 kg of water} = \frac{4.184 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} \times 1000 \text{ g} = \frac{4184 \text{ J}}{^\circ\text{C}}$$

↑ Specific heat capacity of water
 ↑ Heat Capacity of 1 kg water



Specific Heat and Heat Capacity

The heat associated with a temperature change may be calculated:

$$q = cm\Delta T$$

$$q = C\Delta T$$

m is the mass.

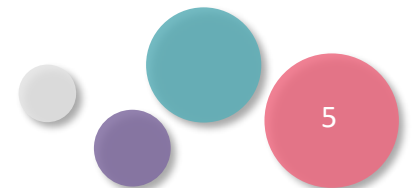
c is the specific heat capacity.

ΔT is the change in temperature ($\Delta T = T_{\text{final}} - T_{\text{initial}}$)

C is the heat capacity ($C = cm$)

q : transfer of thermal energy between two bodies at different temperatures

Calculate the amount of heat required to heat 1.01 kg of water from 0.05°C to 35.81°C.



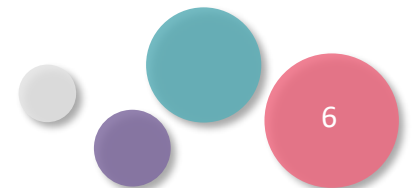
Practice

Calculate the amount of heat (in kJ) required to heat 255 g of water from 25.2°C to 90.5°C.

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.

If 1.45 kJ of heat are added to a 200. g sample of aluminum metal and the temperature of the metal increases by 7.98 °C, what is the specific heat of aluminum?

If a 352 g piece of glass is heated from 22°C to 162°C, how much heat is required?
The specific heat of glass is 0.739 J/g ·°C.



Constant Pressure Calorimetry

A coffee-cup calorimeter may be used to measure the heat exchange for a variety of reactions at constant pressure (allows heat to equal ΔH):

Reaction Type	Example	ΔH (kJ/mol)
Heat of Neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{NaCl}(aq)$	-56.2
Heat of Ionization	$\text{H}_2\text{O}(l) \rightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	+56.2
Heat of Fusion	$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$	+6.01
Heat of Vaporization	$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$	+44.0

Concepts to consider for coffee-cup calorimetry:

$$q_p = \Delta H$$

[Calorimetry Video 1](#)

[Calorimetry Video 2](#)

System: reactants and products

Surroundings: water in the calorimeter

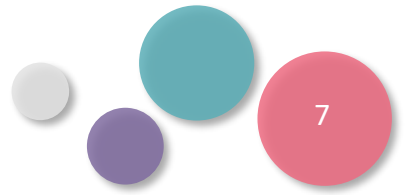
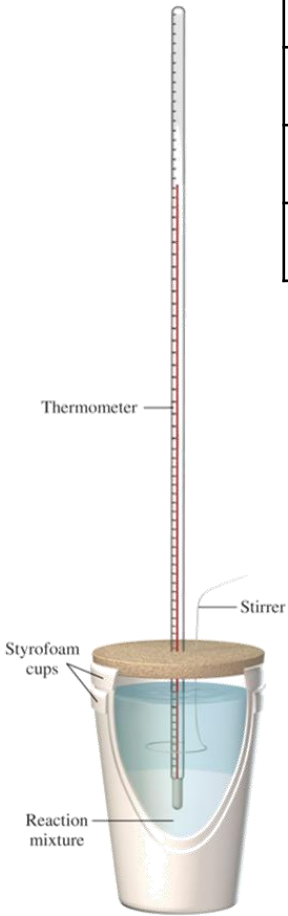
For an **exothermic** reaction: the **system loses heat** (indicated with a negative sign)

For an **endothermic** reaction: the **system gains heat** (the system absorbs heat)

$$q_{\text{sys}} = -mc\Delta T$$

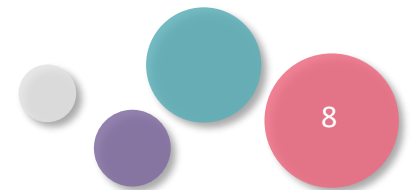
$$q_{\text{surr}} = mc\Delta T$$

$$q_{\text{sys}} = -q_{\text{surr}}$$



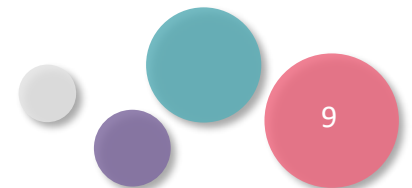
Practice

A metal pellet with a mass of 100.0 g, originally at 88.4°C, is dropped into 125 g of water originally at 25.1°C. The final temperature of both pellet and the water is 31.3°C. Calculate the heat capacity C (in J/°C) of the pellet.



Practice

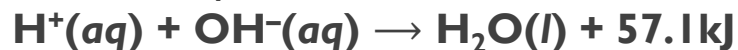
A 50.0 g sample of iron (specific heat capacity = $0.444 \text{ J/g}^\circ\text{C}$) is heated to 75.2°C and placed into a calorimeter holding 70.0 g of water (specific heat capacity = $4.184 \text{ J/g}^\circ\text{C}$) at a temperature of 25.0°C . Assuming no heat loss to the calorimeter, what will be the final temperature reached in the calorimeter.



Practice

50.00 mL of aqueous copper(II) sulfate reacts with 50.00 mL of aqueous sodium hydroxide in a calorimeter. The initial temperature of both solutions is 21.40 °C and the highest temperature reached in the calorimeter is 24.60 °C. Determine the quantity of thermal energy transferred by the reaction to the water, and state whether the reaction was endothermic or exothermic.

Whenever an acid is neutralized by a base, the net reaction is:

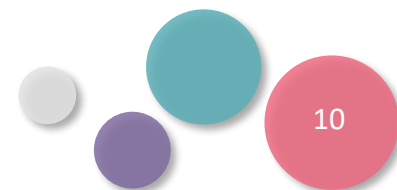


Calculate the heat evolved for the following experiments:

(a) 0.60 mol of HNO₃ solution is mixed with 0.30 mol of KOH solution.

(b) 400 cm³ of 0.2 M H₂SO₄ is mixed with 600 cm³ of 0.1 M NaOH solution.

Is this reaction endothermic or exothermic?



Constant Volume Calorimetry

Constant volume calorimetry is carried out in a device known as a constant-volume bomb. A constant-volume calorimeter is an isolated system. Bomb calorimeters are typically used to determine heats of combustion.

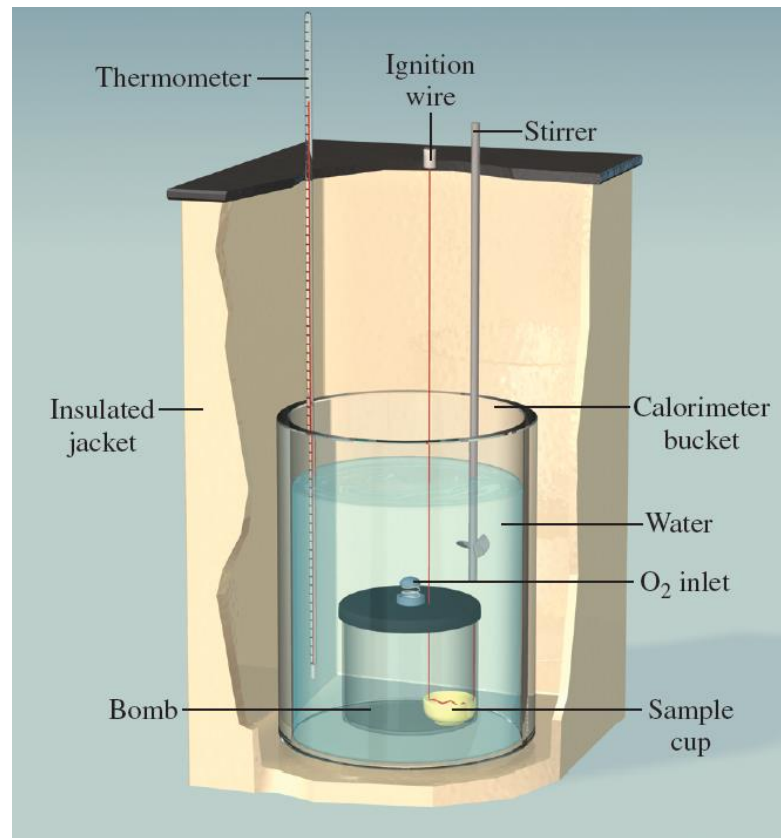
$$q_{\text{cal}} = -q_{\text{rxn}}$$

To calculate q_{cal} , the heat capacity of the calorimeter must be known.

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

$$q_{\text{rxn}} = -q_{\text{cal}}$$

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T$$



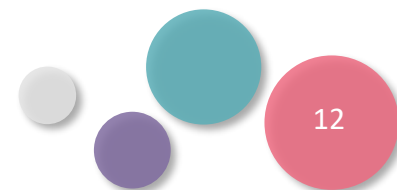
Practice

A 1.0 g sample of propane, C_3H_8 , was burned in a calorimeter. The temperature rose from $28.5\text{ }^\circ\text{C}$ to $32.0\text{ }^\circ\text{C}$ and heat of combustion 10.5 kJ/g . Calculate the heat capacity of the apparatus in $\text{kJ}/^\circ\text{C}$.

Methylhydrazine (CH_6N_2) is used as a liquid rocket fuel. The combustion of methylhydrazine with oxygen produces $\text{N}_2(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.



When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from $25.0\text{ }^\circ\text{C}$ to $39.5\text{ }^\circ\text{C}$. The heat capacity of the calorimeter is $7.794\text{ kJ}/^\circ\text{C}$. Calculate the heat of combustion for one mole of methylhydrazine.



Introduction to Thermodynamics

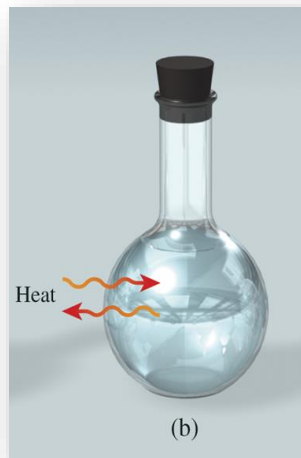
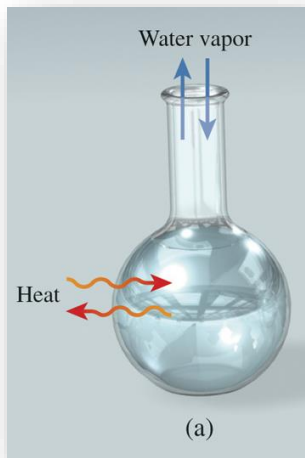
Thermodynamics is the study of the interconversion of heat and other kinds of energy.

In thermodynamics, there are three types of systems:

An **open system** can exchange mass and energy with the surroundings.

A **closed system** allows the transfer of energy but not mass.

An **isolated system** does not exchange either mass or energy with its surroundings.

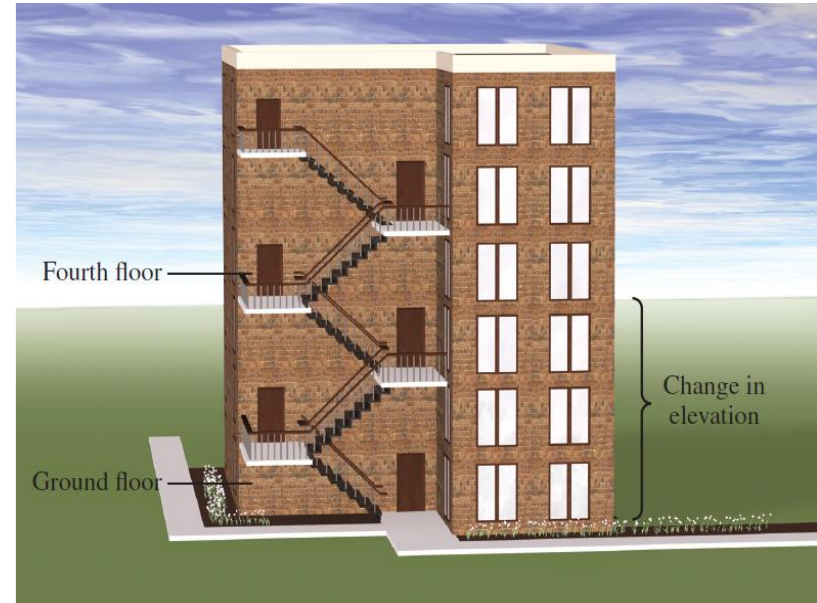


Introduction to Thermodynamics

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

The magnitude of change depends only on the initial and final states of the system.

Energy
Pressure
Volume
Temperature

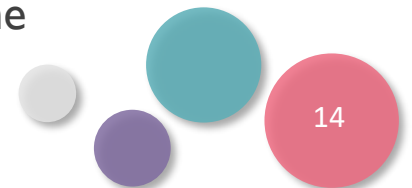


The **first law of thermodynamics** states that energy can be converted from one form to another but cannot be created or destroyed.

$$\Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0$$

ΔU is the change in the internal energy. “sys” and “surr” denote system and surroundings, respectively. $\Delta U = U_f - U_i$; the difference in the energies of the initial and final states.

$$\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$$



Work and Heat

The overall change in the system's internal energy is given by:

$$\Delta U = q + w$$

q is heat

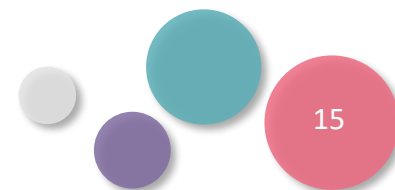
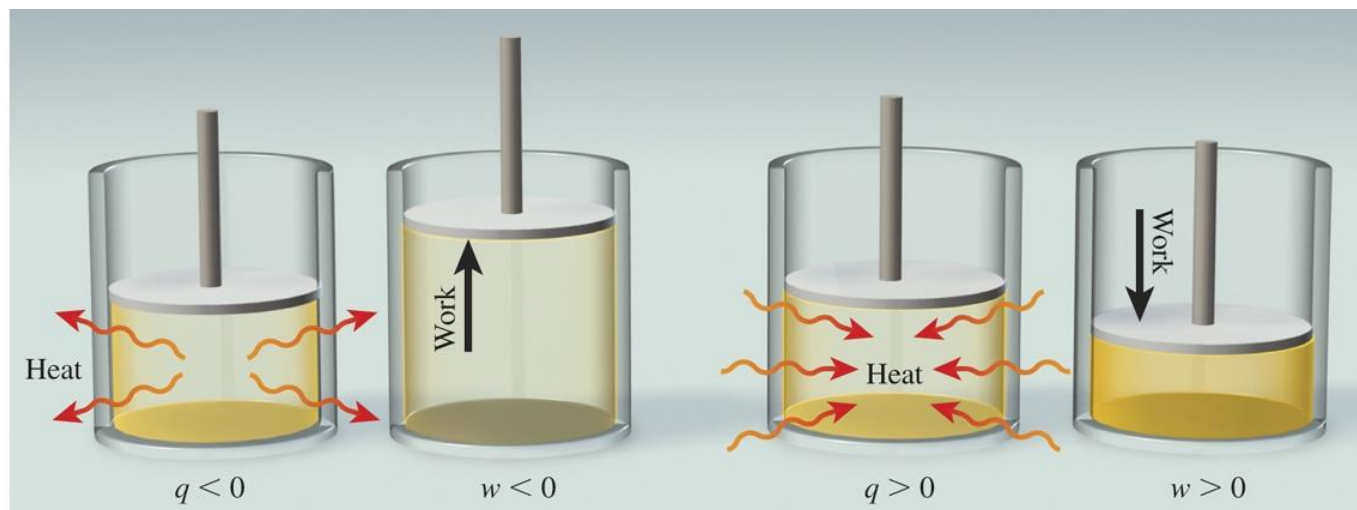
q is **positive** for an endothermic process (heat **absorbed** by the system)

q is **negative** for an exothermic process (heat **released** by the system)

w is work

w is **positive** for work done **on** the system

w is **negative** for work done **by** the system

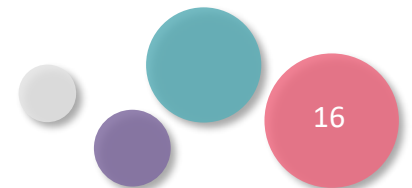


Practice

Calculate the overall change in internal energy, ΔU , (in joules) for a system that absorbs 188 J of heat and does 141 J of work on its surroundings.

Calculate the total change in internal energy, ΔE , of a system when 400 J heat is applied to expanding $\text{O}_2(\text{g})$ and the gas does 350 J of work on its surroundings.

A reaction occurs in a closed container that releases 1150 J of heat into the surroundings. As the reaction proceeds, the product falls out as a solid and causes the container to contract. This results in the surroundings performing 480 J of work on the system. What is ΔE for the system?

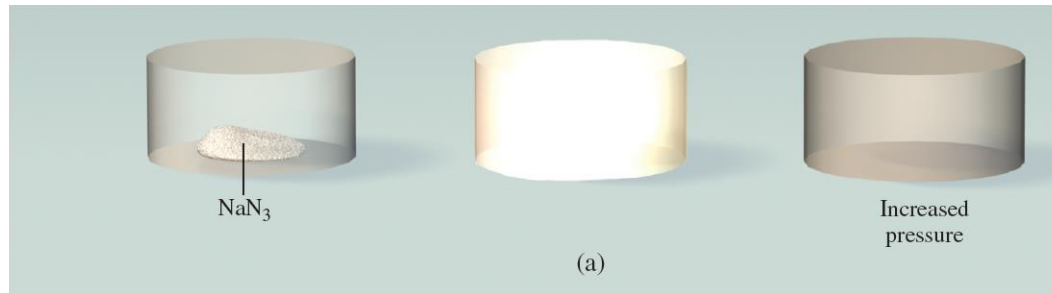


Enthalpy: Constant Volume or Constant Pressure

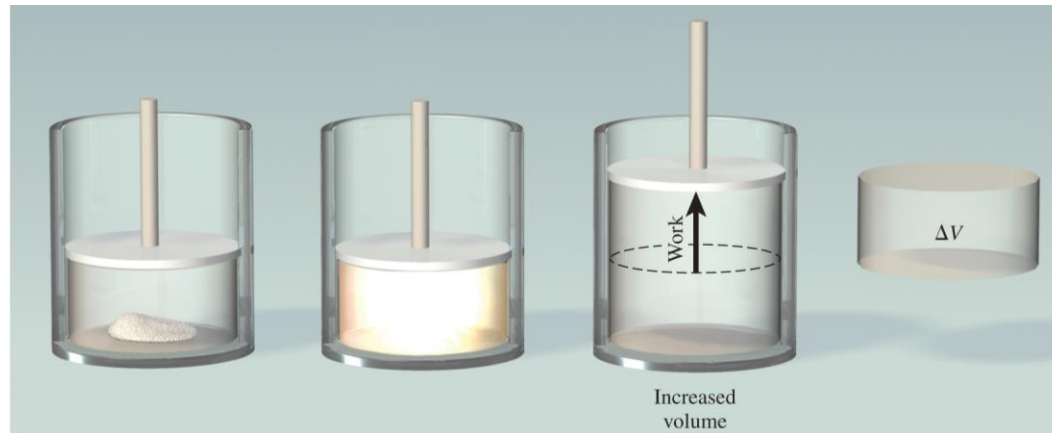
Sodium azide detonates to give a large quantity of nitrogen gas.



Under **constant volume** conditions, pressure increases:



Under **constant pressure** conditions, volume increases:



Enthalpy: Constant Volume or Constant Pressure

Pressure-volume, or PV work, is done when there is a volume change under constant pressure.

$$w = -P\Delta V$$

P is the external opposing pressure. ΔV is the change in the volume of the container.

Pressure-volume, or PV work, is done when there is a volume change under constant pressure.

$$w = -P\Delta V$$

$$\Delta U = q + w$$

substitute

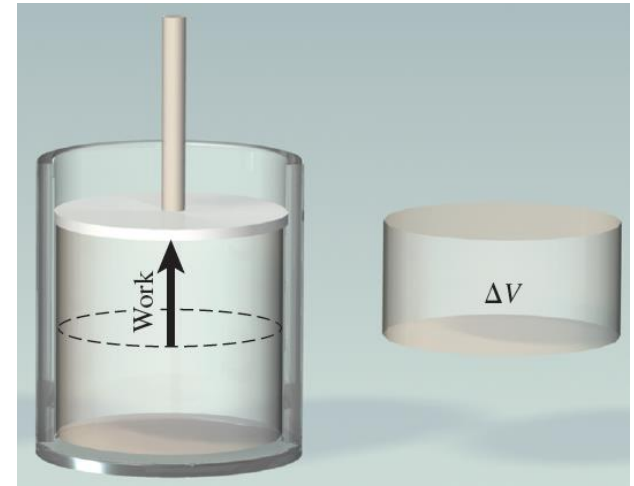
$$\Delta U = q - P\Delta V$$

When a change occurs at constant volume, $\Delta V = 0$ and no work is done.

$$q_v = \Delta U$$

Under conditions of constant pressure:

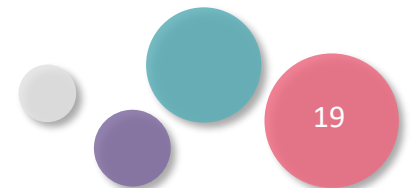
$$q_p = \Delta U + P\Delta V$$



Practice

A fuel combusts at 3.00 atm constant pressure. The reaction releases 75.0 kJ of heat and causes the system to expand from 7.50 L to 20.0 L. What is the change in the internal energy?

(NOTE: $0.1013 \text{ kJ} = 1 \text{ L}\cdot\text{atm}$ and $101.3 \text{ J} = 1 \text{ L}\cdot\text{atm}$)



Enthalpy and Enthalpy Changes

The thermodynamic function of a system called **enthalpy** (H) is defined by the equation:

$$H = U + PV$$

A note about SI units:

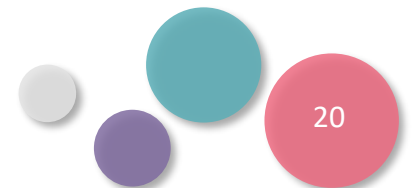
Pressure: pascal; $1 \text{ Pa} = \frac{1 \text{ kg}}{(\text{m} \cdot \text{s}^2)}$

Volume: cubic meters: m^3

PV (pressure \cdot volume): $\frac{1 \text{ kg}}{(\text{m} \cdot \text{s}^2)} (\text{m}^3) = \frac{1 \text{ kg} \cdot \text{m}^2}{(\text{s}^2)} = 1 \text{ J}$

Enthalpy: joules

U , P , V , and H are all state functions.



Enthalpy and Enthalpy Changes

For any process, the *change* in enthalpy is:

$$\Delta H = \Delta U + \Delta(PV) \quad (1)$$

If pressure is constant:

$$\Delta H = \Delta U + P\Delta V \quad (2)$$

Rearrange to solve for ΔU :

$$\Delta U = \Delta H - P\Delta V \quad (3)$$

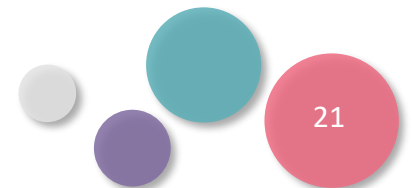
Remember, q_p :

$$q_p = \Delta U + P\Delta V \quad (4)$$

Substitute equation (3) into equation (4) and solve for q_p :

$$q_p = (\Delta H - P\Delta V) + P\Delta V \quad (5)$$

$$q_p = \Delta H \quad \text{for a constant-pressure process}$$



Enthalpy and Enthalpy Changes

The **enthalpy of reaction** (ΔH) is the difference between the enthalpies of the products and the enthalpies of the reactants:

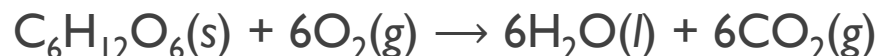
$$\Delta H = H_{(\text{products})} - H_{(\text{reactants})}$$

Assumes reactions in the lab occur at constant pressure

$\Delta H > 0$ (+) **endothermic process**

$\Delta H < 0$ (-) **exothermic process (sometimes called spontaneous reaction)**

Calculate the standard enthalpy for the following reaction:

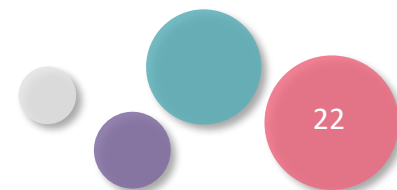


$$\Delta H_f \text{ for } \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) = -1275 \text{ kJ}$$

$$\Delta H_f \text{ for } \text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ}$$

$$\Delta H_f \text{ for } \text{O}_2(\text{g}) = 0 \text{ kJ}$$

$$\Delta H_f \text{ for } \text{CO}_2(\text{g}) = -393.5 \text{ kJ}$$

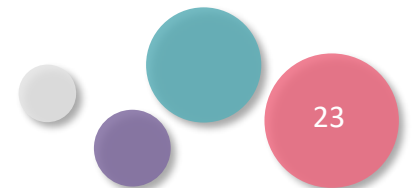


Practice

Given the thermochemical equation for photosynthesis,



calculate the solar energy required to produce 75.0 g of $\text{C}_6\text{H}_{12}\text{O}_6$.



Practice

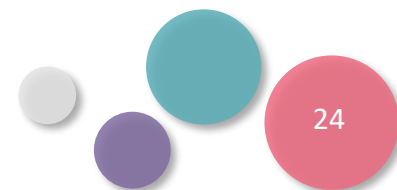
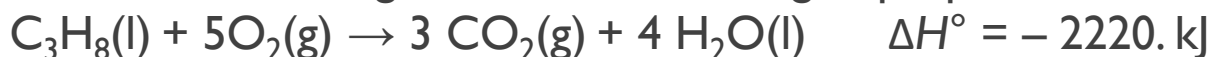
How much energy will be produced when 5.23 g of C_8H_{18} reacts with excess oxygen for the reaction:



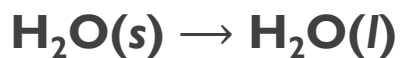
Consider the following reaction: $2Mg(s) + O_2(g) \rightarrow 2MgO(s) \quad \Delta H = -1204 \text{ kJ}$

a) Is this reaction endothermic or exothermic? b) Calculate the amount of heat transferred when 2.4g of $Mg(s)$ reacts at constant pressure.

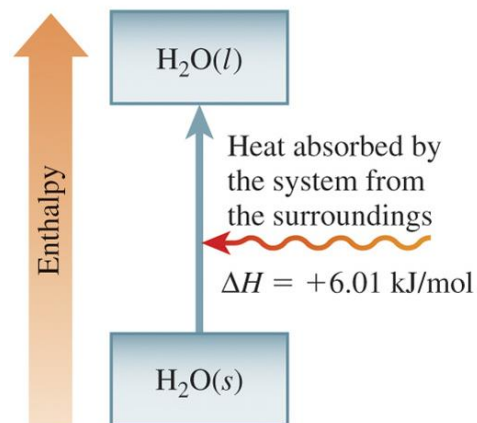
Calculate the heat generated when 500. g of propane burns in excess O_2 .



Thermochemical Equations



$$\Delta H = +6.01 \text{ kJ/mol}$$



Concepts to consider:

Is this a constant pressure process?

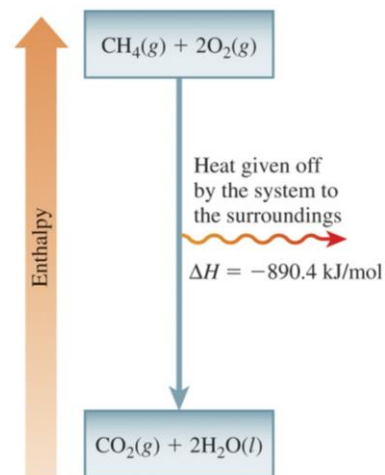
What is the system?

What are the surroundings?

$\Delta H > 0$ endothermic



$$\Delta H = -890.4 \text{ kJ/mol}$$



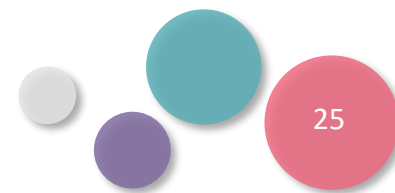
Concepts to consider:

Is this a constant pressure process?

What is the system?

What are the surroundings?

$\Delta H < 0$ exothermic



Standard Enthalpies of Formation

The **standard enthalpy of formation** (ΔH_f°) is defined as the heat change that results when 1 mole of a compound is formed from its constituent elements in their standard states.



The superscripted degree sign denotes standard conditions and “f” stands for formation
1 atm pressure for gases and 1 M concentration for solutions.

ΔH_f° for an element in its most stable form is zero. ΔH_f° for many substances are tabulated in **Appendix G** of the textbook.

The **standard enthalpy of reaction** ($\Delta H_{\text{Rxn}}^\circ$) is defined as the enthalpy of a reaction carried out under standard conditions.



$$\Delta H_{\text{Rxn}}^\circ = [c\Delta H_f^\circ(\text{C}) + d\Delta H_f^\circ(\text{D})] - [a\Delta H_f^\circ(\text{A}) + b\Delta H_f^\circ(\text{B})]$$

$$\Delta H_{\text{Rxn}}^\circ = \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants})$$

n and m are the stoichiometric coefficients for the reactants and products.

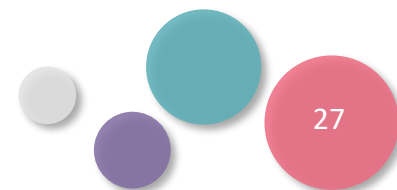
Practice

Using data from Appendix G ([textbook link here](#)), calculate $\Delta H_{\text{Rxn}}^{\circ}$ for $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$.

The combustion of thiophene, $\text{C}_4\text{H}_4\text{S}(\text{l})$, a compound used in the manufacture of pharmaceuticals, produces carbon dioxide and sulfur dioxide gases and liquid water. The enthalpy change in the combustion of one mole of $\text{C}_4\text{H}_4\text{S}(\text{l})$ is -2523kJ . Use this information and data below to establish ΔH_f° for $\text{C}_4\text{H}_4\text{S}(\text{l})$.



$\text{CO}_2(\text{g})$	-393.5kJ mol^{-1}
$\text{SO}_2(\text{g})$	-296.8kJ mol^{-1}
$\text{O}_2(\text{g})$	0kJ mol^{-1}
$\text{H}_2\text{O}(\text{l})$	-285.8kJ mol^{-1}



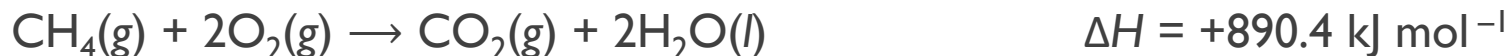
Thermochemical Equations

Enthalpy is an extensive property; these are properties dependent on the amount of matter involved.



Double the amount of matter, double the enthalpy

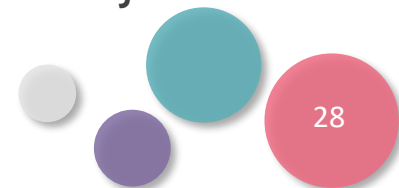
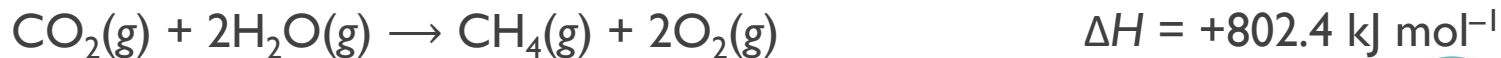
- 1) Always specify the physical states of reactants and products because they help determine the actual enthalpy changes.



- 2) When multiplying an equation by a factor (n), multiply the ΔH value by same factor.

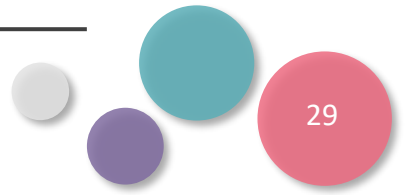
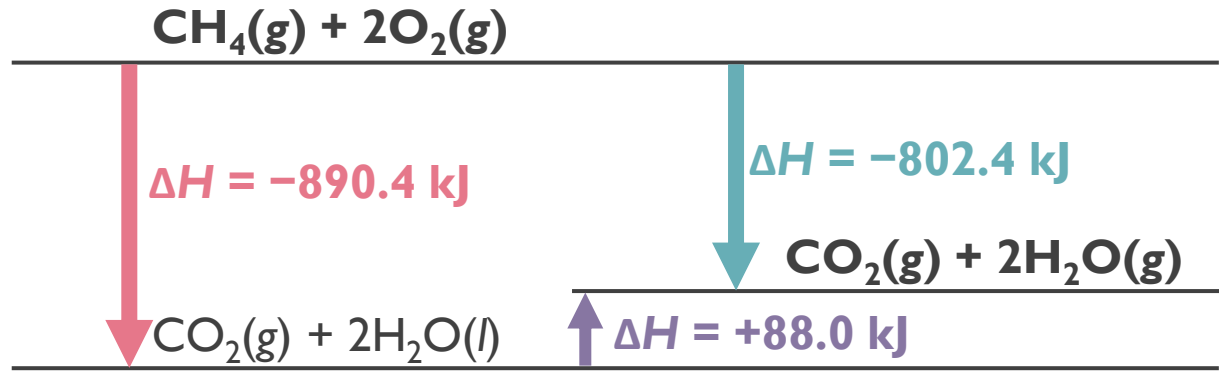
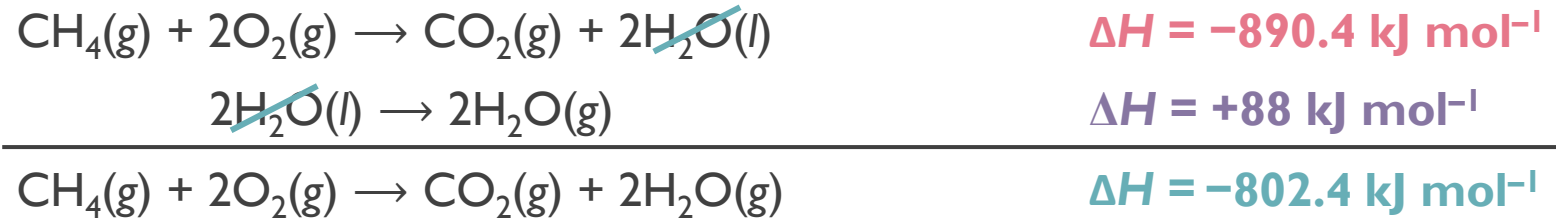


- 3) Reversing an equation changes the sign but not the magnitude of ΔH .



Hess's Law

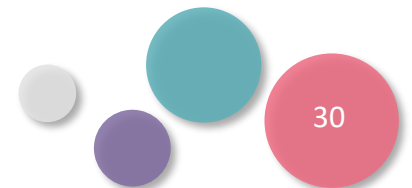
Hess's law states that the change in enthalpy for a stepwise process is the sum of the enthalpy changes for each of the steps.



Hess's Law

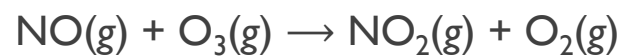
When applying Hess's Law:

- 1) Manipulate thermochemical equations in a manner that gives the overall desired equation:
 - Reactants on reactant side/products on product side
 - Cancel out what is not found in overall reaction
- 2) Remember the rules for manipulating thermochemical equations:
 - Always specify the physical states of reactants and products
 - When multiplying an equation by a factor (n), multiply ΔH by the same factor
 - Reversing an equation changes the sign but not the magnitude of ΔH
- 3) Add the ΔH for each step after proper manipulation.
- 4) Process is useful for calculating enthalpies that cannot be found directly.

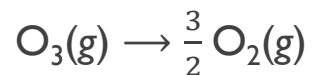


Hess's Law

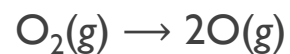
Given these thermochemical equations:



$$\Delta H = -198.9 \text{ kJ mol}^{-1}$$

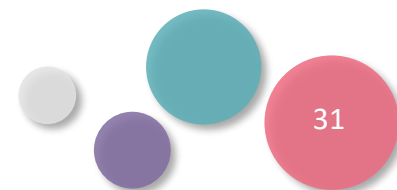


$$\Delta H = -142.3 \text{ kJ mol}^{-1}$$



$$\Delta H = +495 \text{ kJ mol}^{-1}$$

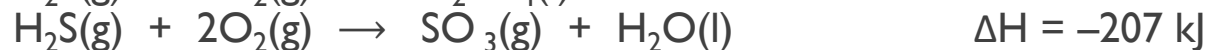
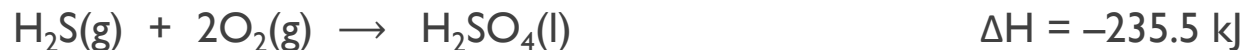
determine the enthalpy change for the following reaction: $\text{NO}(g) + \text{O}(g) \rightarrow \text{NO}_2(g)$



Practice

Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values:

$$\Delta H = +72.5 \text{ kJ}$$

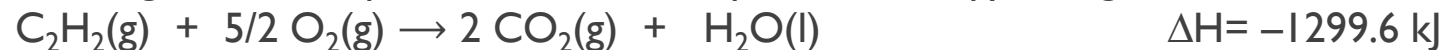


Calculate ΔH for the reaction

$$\Delta H = +226.8 \text{ kJ}$$



Given the following chemical equations and their respective enthalpy changes.



Calculate ΔH for the reaction

$$\Delta H = -2486.3 \text{ kJ}$$



Given the following chemical equations and their respective enthalpy changes.

