

Thermochemistry is the study of the relationships between chemical reactions and energy changes involving heat.

- **Energy** is anything that has the capacity to do work.
- **Work** is a force acting over a distance.
 - Energy = work = force \times distance
- **Heat** is the flow of energy caused by a difference in temperature.
- Energy can be transferred between system and surrounding

Temperature: measure of the heat

Exo-

Endo-

In nature, there is a derive towards increases stability in terms of energy

Classification of Energy:

- **Kinetic energy** Due to motion
- **Thermal energy** is the energy associated with temperature (kinetic)
- **Potential energy**: Due to position and composition
 - ✓ Ball on top of a hill.
- **Chemical energy**: Associate with position of electrons and nucli
 - Potential energy due to the structure of the atoms, the attachment between atoms, the atoms' positions relative to each other in the molecule, or the molecules' relative positions in the structure

Units of Energy:

- The SI units: 1 Joule = 1 N \cdot m = 1 kg \cdot m²/s²
- 1 Cal = 1000 cal = 1Kcal = 4.184 KJ

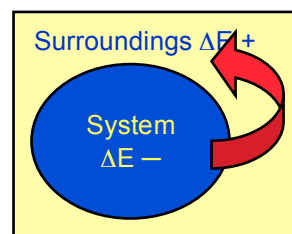
Law of conservation of energy: energy cannot be created or destroyed (only transferred)

System and Surroundings

★ The total energy of the universe is constant

$$\Delta \text{Energy}_{\text{universe}} = 0$$

$$= \Delta \text{Energy}_{\text{system}} + \Delta \text{Energy}_{\text{surroundings}}$$



The First Law of Thermodynamics: Law of Conservation of Energy

- Δ : is the symbol that is used to mean change (Δ = Final amount – initial amount)
- ΔE = The internal energy = the sum of the kinetic and potential energies of all of the particles that compose the system.
- $\Delta E = E_{\text{final}} - E_{\text{initial}}$

ΔE is a state function: A function or property whose value depends only on the present state (condition) of the system.

➤ So it independent on the path.

e.g cold water \Rightarrow Hot water

✚ It is also an extensive property

➤ $\Delta E = q + w$

– q = heat (thermal) energy

– w = work energy

★ q and w are NOT state functions; their value depends on the process.

+q

-q

+w

-w

+ ΔE

- ΔE



What is the change in the internal energy of the system that does 150 J work and gains 75 J of heat?

Quantity of Heat Energy Absorbed: Heat Capacity

$$q = C \times \Delta T$$

- The increase in temperature is directly proportional to the amount of heat absorbed.
 - ✓ When a system absorbs heat, its temperature increases.
- The proportionality constant is called the **heat capacity, C**.
 - Units of C are J/°C or J/K.
- The larger the heat capacity of the object being studied, the smaller the temperature rise will be for a given amount of heat.
- The heat capacity of an object depends on its amount of matter.
- ✓ 200 g of water requires twice as much heat to raise its temperature by one degree, as does 100 g of water.

- The **molar heat capacity** is the amount of heat energy required to raise the temperature of one mole of a substance by one degree. It is an intensive property
- The **specific heat capacity (C_s)** is the amount of heat energy required to raise the temperature of one gram of a substance one degree. Units $J/(g \cdot ^\circ C)$ or $J/(g \cdot K)$
 - ✓ The heat capacity of an object depends on the type of material.
- ★ **Specific Heat (C_s)** is an intensive property since it depends on the kind of substance being heated, not on the amount.
- ★ **Specific Heat** $q = m \cdot \Delta T \cdot C_s$

Elements		Compounds	
Substance	Specific Heat (J/g-K)	Substance	Specific Heat (J/g-K)
$N_2(g)$	1.04	$H_2O(l)$	4.18
$Al(s)$	0.90	$CH_4(g)$	2.20
$Fe(s)$	0.45	$CO_2(g)$	0.84
$Hg(l)$	0.14	$CaCO_3(s)$	0.82



What amount of heat has been absorbed by 1.000 kg of water if its temp. increased from $18.22^\circ C$ to $22.73^\circ C$?

18869.89 J



What is the specific heat of a metal if 24.8 g absorbs 65.7 J of energy and the temperature rises from $20.2^\circ C$ to $24.5^\circ C$?

0.616



Calculate the mass in grams for a pure silver sample that loses 3.22 kJ when its temperature drops from $145^\circ C$ to $24^\circ C$. *specific heat for silver is $0.233 J/g \cdot K$*

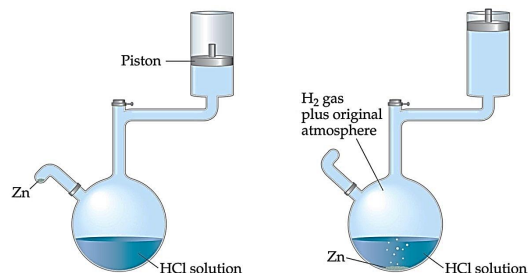
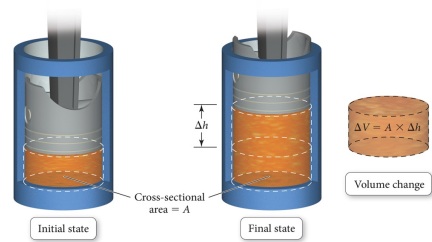
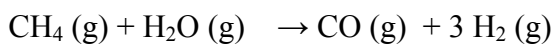
Pressure–Volume Work

- ✓ PV work is work caused by a volume change against an external pressure
- ✓ **Work:** In ordinary chemical reactions work generally arises as a result of pressure-volume changes (gas)

$$Work_{gas} = \text{External Pressure} \times \text{Change in } Volume_{gas}$$

$$w = -P\Delta V$$

$$\Delta_{\text{gas moles}} = \text{Gas moles in reactant side} - \text{Gas moles in product side}$$



What is the work done (J) by a reaction if the volume increases from 1.5 L to 1.9 L against external pressure equal to 2.3 atm? 101.3 J = 1 atm.L

0.92 atm.L

90

Remember $\Delta E = q + w$ and $w = -P\Delta V$

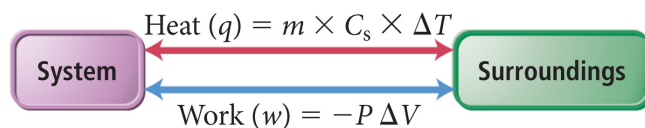
Two possibilities:

- ΔE at Constant Volume (Bomb Calorimeter):

- ΔE at Constant Pressure:

- What happens when two objects at different temperatures are placed in contact
- A block of metal at 55 °C is submerged in water initially at 25 °C

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



How to measure heat transferred during a reaction (using Calorimetry)

- We have to define some variables

- Enthalpy (ΔH): Heat transferred or evolved in a chemical reaction at constant pressure

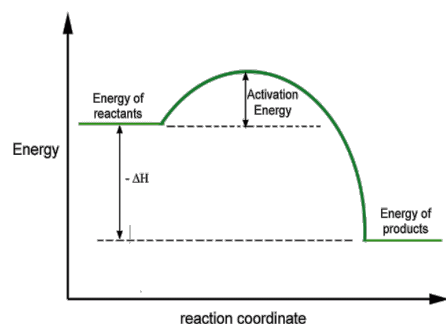
$$\mathbf{H = E + PV}$$

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

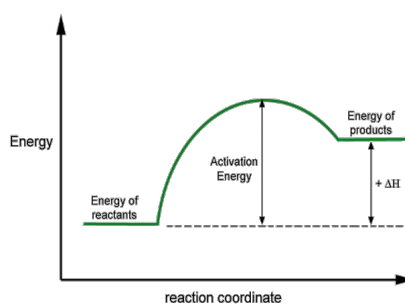
- Since ΔE , P and V are all state functions, So ΔH is a state function

- Differences in ΔH and ΔE are usually small

$\Delta H < 0$



$\Delta H > 0$

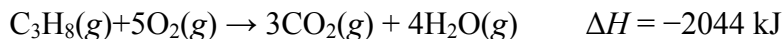


Molecular View of Exothermic Reactions:

- For an exothermic reaction, the surrounding's temperature rises due to a release of thermal energy by the reaction.
- This extra thermal energy comes from the conversion of some of the chemical potential energy in the reactants into kinetic energy in the form of heat.
- During the course of a reaction, existing bonds are broken and new bonds are made.
- The products of the reaction have *less* chemical potential energy than the reactants.
- The difference in energy is released as heat.

Enthalpy of Reaction:

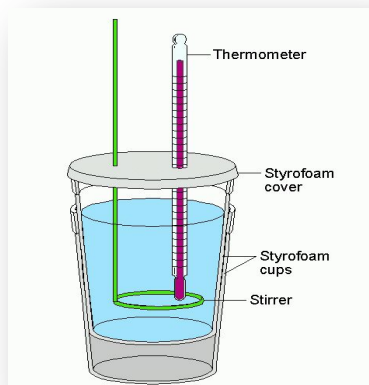
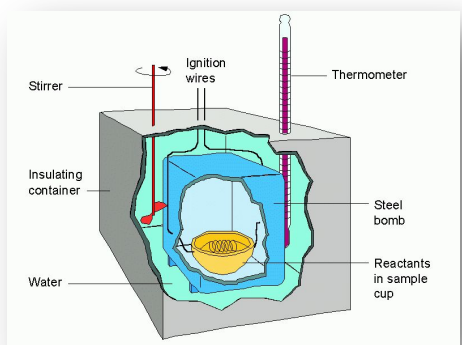
- The enthalpy change in a chemical reaction is an extensive property.
 - The more reactants you use, the larger the enthalpy change.



****Remember to pay attention for the states of each reactant and product as this affects the value of ΔH .**

Calorimetry

The amount of heat absorbed or released during a physical or chemical change can be measured, usually by the change in temperature of a known quantity of water in a calorimeter.



✚ Solving problems at Constant V (Bomb Calorimeter)

Recall:

$$\Delta E = q + w \quad \text{and } w = -P\Delta V$$

- $P\Delta V = 0$, Work = 0
- therefore $\Delta E = q_v$
- $\Delta H \approx \Delta E$

The heat capacity of the bomb calorimeter is known and tested

- The heat capacity of the calorimeter**
- is the amount of heat absorbed by the calorimeter for each degree rise in temperature and is called the **calorimeter constant** (C_{cal} , $\text{J}/^\circ\text{C}$)

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta T \quad (\text{q relates to } \Delta E)$$

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

✍️ A 1.994 g sample of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, is combusted in a **bomb calorimeter**. The temperature of the calorimeter increases by 10.91 K. If the heat capacity of the bomb is 615.5 J/K. **what is the heat of reaction of the combustion of 1 mol of ethanol?**

-6715.105

4.331 X10⁻²

-155.0

- ✓ Measuring ΔH using Calorimetry at Constant Pressure using a Coffee cup calorimeter.
 - Where $\Delta H = q_p = q_{\text{rxn}}$
 - **Reactions done in aqueous solution are at constant pressure.**
 - Open to the atmosphere
 - The calorimeter is often nested foam cups containing the solution.
 - *To get $\Delta H_{\text{reaction}}$ per mol, divide by the number of moles.*

There are three cases:


The first case: You add a known mass of an ionic compound to a known mass of water at T_i a solution form. The temperature of the solution is recorded as T_f . (Remember mass of the solution is the mass of the water plus the mass of the ionic compound)

Solute + Water → Solution

$$q_{\text{reaction}} = -q_{\text{solution}}$$

$$= -(\text{mass}_{\text{solution}} \times C_{s, \text{solution}} \times \Delta T)$$

- $\Delta H_{\text{reaction}} = q_{\text{constant pressure}} = q_{\text{reaction}}$
 - ✓ **To get $\Delta H_{\text{reaction}}$ per mol, divide by the number of moles.**

 MgO reacts with water to form Mg(OH)₂. If 5.00 g MgO is combined with 100.0 g H₂O in a coffee cup calorimeter, the temperature of the resulting **solution** increases from 22.3 °C to 32.9 °C. Calculate the enthalpy change for the reaction per mole of MgO. Assume that the specific heat capacity of the solution is 4.18 J/g·K.

-4.65


0.125 mol MgO

-37.4

The second Case: You add a hot metal of known mass at T_{im} to water at T_{iw}. After a while equilibrium established, at equilibrium the temperature of the water will equal the temperature of the metal so T_f will be the same for both the metal and the water.


$$q_{\text{water}} = -q_{\text{metal}}$$

$$(\text{mass} \times C_s \times \Delta T)_{\text{water}} = -(\text{mass} \times C_s \times \Delta T)_{\text{metal}}$$

 135 g of aluminum (initially at 400°C) are mixed with an unknown mass of water (initially at 25°C). When thermal equilibrium is reached, the system has a temperature of 80°C. Find the mass of the water. *specific heat for Aluminum is 0.90 J/g.K*

169 g

Practice

 A 50.6 g sample of iron metal is heated and put into 104.0 g of water at 19.7 °C in a calorimeter. If the final temperature of the iron sample and the water is 24.3 °C, what was the temperature of the iron sample when it was placed in the water?

-87.822

112.1

The third case is where a reaction takes place in a container. The heat evolved from the reaction used to raise the temperature of known mass of water at T_{iw} . At equilibrium the temperature of water will be T_{fw} .

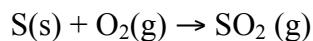
➤ **Not that the reaction is totally isolated from water so no solution formed**

$$q_{\text{reaction}} = -q_{\text{water}}$$

$$q_{\text{reaction}} = -(\text{mass} \times C_s \times \Delta T)_{\text{water}} \quad (\text{remember } \Delta H = q_p)$$



In a simple coffee cup calorimeter 0.80 g of sulfur is reacted with O_2 to form SO_2 according to the following eqn.



All of the heat evolved is used to raise the temperature of 100.0 g H_2O by 17.8 °C. What is the ΔH of reaction for 1 mol of sulfur?

-7.45KJ


0.25 mol S

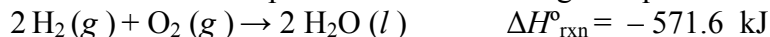
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➤ **There are different ways (paths) to calculate ΔH of the reaction**


1. **Using Stoichiometry**
2. **Using ΔH of many step reactions (Hess's Law)**
3. **Calculating Standard Enthalpy Change for a Reaction**

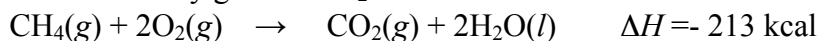
1. **Stoichiometry of the reaction:**

 The main engines of the space shuttle burn hydrogen to produce water. How much heat (in kJ) is associated with this process if 1.32×10^5 kg of liquid H_2 is burned?




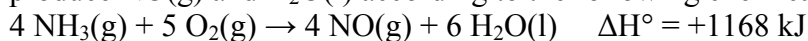
-1.87 X10¹⁰ KJ

 How many grams of O_2 react if 306 kcal are released in the following reaction?



91.9 g

 How much heat is absorbed/released when 20.00 g of $NH_3(g)$ reacts in the presence of excess $O_2(g)$ to produce $NO(g)$ and $H_2O(l)$ according to the following chemical equation?

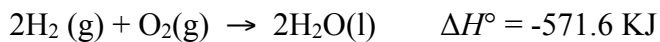
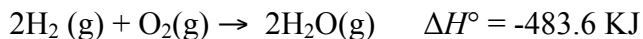



342.9 KJ

2. **Using Hess's Law:**

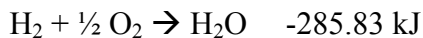
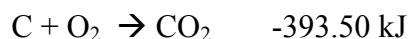
- When we reverse a reaction, we change the sign of ΔH
- When you multiply the reaction with factor ΔH is multiplied by the same factor
- All substances NOT appearing in desired eqn. MUST cancel
- ★ Change in enthalpy depends on state


Example: Calculate the ΔH in KJ for the reaction: $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$ Given the following :

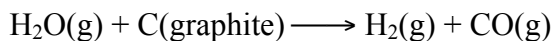


 Calculate ΔH for the combustion of methane, CH_4 :
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

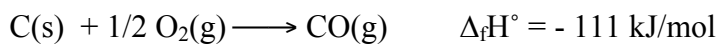
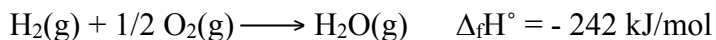
Reactions	ΔH°
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 Calculate ΔH rxn for :



From reference books we find



3. Calculating Standard Enthalpy Change for a Reaction

Standard Conditions:

- The **standard state** is the state of a material at a defined set of conditions.
 - Pure gas at exactly 1 atm pressure
 - Pure solid or liquid in its most stable form at exactly 1 atm pressure and temperature of interest
 - Usually 25 °C
 - Substance in a solution with concentration 1 M
 - The **standard enthalpy change, ΔH°** , is the enthalpy change when all reactants and products are in their standard states.
 - The **standard enthalpy of formation, ΔH_f°** , is the enthalpy change for the reaction forming 1 mole of a pure compound from its constituent elements.
 - The elements must be in their standard states.
 - **The ΔH_f° for a pure element in its standard state = 0 kJ/mol.**
-
- **Enthalpy of formation, $\Delta H_f^\circ = \Delta H$** for the rxn in which **1 mol** of compound is formed from its **constituent elements**, then with ALL substances in their standard states (in kJ/mol)
 - Standard conditions (standard state): 1 atm and 25 °C
 - **$\Delta H_f^\circ = 0$ for an element in its standard state**
 - ★ Because the definition requires **1 mole** of compound be made, the coefficients of the reactants **may be fractions**.

Examples:

- $1/2 \text{ N}_2(\text{g}) + 3/2 \text{ H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g}) \quad \Delta H_f^\circ = -46.2$
- $\text{Na}(\text{s}) + 1/2 \text{ Cl}_2(\text{g}) \rightarrow \text{NaCl}(\text{s}) \quad \Delta H_f^\circ = -411.0$
- $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond}) \quad \Delta H_f^\circ = +1.897$

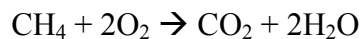
4. Calculating Standard Enthalpy Change for a Reaction

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

Σ means sum.

n is the coefficient of the reaction

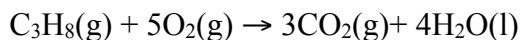
🧑🏻 Calculate ΔH for the combustion of methane, CH_4 :



Substance	ΔH_f°
CH_4	-74.80 kJ
O_2	0 kJ
CO_2	-393.50 kJ
H_2O	-285.83 kJ

-890.36 KJ

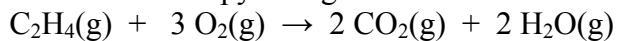
🧑🏻 Use ΔH_f° to find the heat of combustion of propane



Substance	ΔH_f°
C_3H_8	-103.85 kJ
CO_2	-393.50 kJ
H_2O	-285.83 kJ

-22219.97 KJ

🧑🏻 The standard enthalpy change for the combustion of 1 mole of ethene is -1323.1 kJ.



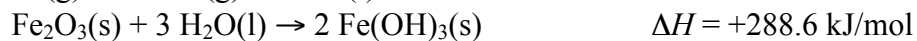
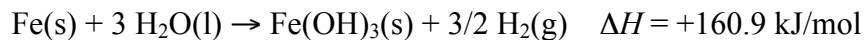
Calculate ΔH_f° for ethene based on the following standard molar enthalpies of formation.

molecule	ΔH_f° (kJ/mol)
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{g})$	-241.8
H_2O	-285.83

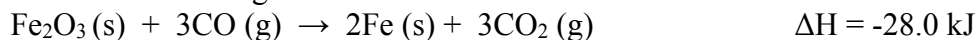
52.5 KJ/mol

Name _____ ID _____ ICE-4 Lab# _____

- Determine the standard enthalpy of formation of $\text{Fe}_2\text{O}_3(\text{s})$ given the thermochemical equations below.



- Given the following reactions



Calculate the enthalpy of the reaction of Fe_2O_3 with CO

